

**QM/MM Based Study of Platinum halides and Their
Selective Complexes of diverse applications**

Final Report

of

Project

(Letter No./Regional Office Lucknow/ 5496-99/2021-22)

(Dated: 15-03-2022)

(G.O. No.-107/2021/2584/70-4-2021-4(28)/2021)

(Dated: 28-12-2021)

Submitted

By

Dr. ANIL KUMAR SONI

(Associate Professor)

Department of Chemistry

Shia Post Graduate College

Sitapur Road, Lucknow-226020

To

Department of Higher Education

Prayagraj, Uttar Pradesh

o/c

Prof. Syed Shabihe Raza Baqri

Principal

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Accredited with Grade 'A' by NAAC

SHIA P.G. COLLEGE

Sitapur Road, Lucknow-226020
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Tel: 0522-2743777

Ref. No.: SDC/6.7.89/25-26

Date: 16/12/2025

सेवा में,

शिक्षा निदेशक (उ0शि0) उत्तर प्रदेश

शिक्षा डिग्री विकास अनुभाग

प्रयागराज - 211001

द्वारा- क्षेत्रीय उच्च शिक्षा अधिकारी, सेक्टर-एम आशियाना, निकट स्मृति उपवन, लखनऊ-226012

विषय: रिसर्च एण्ड डेवलपमेन्ट योजना के अंतर्गत शोध कार्यों के लिए पृथक पृथक वर्षों में आवंटित धनराशि का उपयोगिता प्रमाण पत्र उपलब्ध कराये जाने के संबंध में।

महोदय,

उपर्युक्त विषयक आपके कार्यालय के पत्रांक: डिग्री विकास/2460/2025-26 दिनांक 11.12.2025 का संदर्भ ग्रहण करते हुए रिसर्च एण्ड डेवलपमेन्ट योजना के अंतर्गत शोध कार्यों हेतु वित्तीय वर्ष 2021-22 में आवंटित धनराशि का उपयोगिता प्रमाण पत्र व वार्षिक रिपोर्ट पूर्व में प्रमुख शोधकर्ता (डॉ० अनिल कुमार सोनी एसोसिएट प्रोफेसर, रसायन विज्ञान विभाग, शिया पी.जी. कालेज लखनऊ) द्वारा श्रीमान जी के कार्यालय में दिनांक 20.10.2023 को उपलब्ध कराया जा चुका है।

रिसर्च एण्ड डेवलपमेन्ट योजना के अंतर्गत शोध कार्यों के लिए वित्तीय वर्ष 2021-22 में प्राप्त धनराशि 3,50,000/- (रुपया तीन लाख पचास हजार) का उपयोग प्रमाण पत्र प्रमुख शोधकर्ता द्वारा किये गये शोध कार्यों की अंतिम रिपोर्ट के साथ पुनः एक बार शासन द्वारा उपलब्ध कराये गये प्रारूप पर बिन्दुवार प्रेषित की जा रही है।

(डॉ० अनिल कुमार सोनी)

प्रमुख शोधकर्ता, रसायन विज्ञान विभाग

शिया पी०जी० कालेज,

लखनऊ

(प्रो० सै० शबीहे रज़ा बाकरी)

प्राचार्य,

शिया पी०जी० कालेज,

लखनऊ

शिया पी.जी. कालेज,

लखनऊ (उ०प्र०) 226020



शिया पी.जी. कालेज

(नैक प्रत्यायन 'ए')

लखनऊ विश्वविद्यालय से सहयुक्त मुस्लिम (शिया) अल्पसंख्यक संस्था,
कला, विज्ञान, वाणिज्य और विधि संकायों में छात्र एवं छात्राओं के शिक्षण हेतु।
सीतापुर रोड, लखनऊ २२६०२० (उ० प्र०) भारत।

वेबसाइट : www.shiacollege.org
www.shiapgcollege.ac.in

ई-मेल : principal@shiapgcollege.ac.in
मोबा०: 9919716121, 7007817525

तो 0 सै 0 शबीहे रजा बाकरी
प्राचार्य

पत्रांक: SDC/5634/23
दिनांक : 13/10/2023

सेवा में,

क्षेत्रीय उच्च शिक्षा अधिकारी,
सेक्टर-एम आशियाना,
निकट स्मृति उपवन,
लखनऊ-226012

विषय: शोध कार्यो "रिसर्च एण्ड डेवलपमेन्ट" योजनान्तर्गत स्वीकृत प्रोजेक्ट की
धनराशि का उपभोग प्रमाण पत्र प्रस्तुत करने के संबंध में।

महोदय,

उपर्युक्त विषयक आपके कार्यालय के पत्रांक क्षे.काल./5496-99/2021-22 दिनांक 15.03.2022 व शिक्षा निदेशक उच्च शिक्षा उ०प्र० प्रयागराज के पत्रांक/ डिग्री विकास/155223/2021-22 दिनांक 25.02.2022 का संदर्भ ग्रहण करते हुए शोध कार्यो हेतु "रिसर्च एण्ड डेवलपमेन्ट" योजनान्तर्गत डॉ० अनिल कुमार सोनी, सहायक प्रोफेसर, रसायन विज्ञान विभाग, शिया पी.जी. कालेज लखनऊ को स्वीकृत अनुदान धनराशि के क्रम में व्यय किये गये धनराशि का उपभोग प्रमाण पत्र चार्टर्ड एकाउन्टेन्ट से बिन्दुवार प्रमाणित कराकर प्रमाणित बिलों की मूल प्रति आपकी सेवा में सत्यापन हेतु प्रेषित हैं।

संलग्नक: उक्तवत

प्राचार्य
शिया पी.जी. कालेज,
लखनऊ
Principal
Shia Post Graduate College
Lucknow (U.P.) India-20

प्रमुख शोधकर्ता रसायन शास्त्र विभाग,
शिया पी.जी. कालेज लखनऊ- 226020
अनिल कुमार सोनी
रसायन विज्ञान विभाग
शिया पी.जी. कालेज लखनऊ-226020

20/10/23
क्षेत्रीय उच्च शिक्षा अधिकारी
लखनऊ



शिया पी.जी. कालेज

(नैक प्रत्यायन 'ए')

लखनऊ विश्वविद्यालय से सहयुक्त मुस्लिम (शिया) अल्पसंख्यक संस्था,
कला, विज्ञान, वाणिज्य और विधि संकायों में छात्र एवं छात्राओं के शिक्षण हेतु।
सीतापुर रोड, लखनऊ २२६०२० (उ० प्र०) भारत।

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www.shiapgcollege.ac.in

ई-मेल : principal@shiapgcollege.ac.in
मोबा०: 9919716121, 7007817525

प्रो० सै० शबीहे रजा बाकरी
प्राचार्य

पत्रांक: SDC/6528/25
दिनांक : 26/05/2025

सेवा में,

क्षेत्रीय उच्च शिक्षा अधिकारी,
सेक्टर-एम आशियाना,
निकट स्मृति उपवन,
लखनऊ-226012

विषय: शोध कार्यो "रिसर्च एण्ड डेवलपमेन्ट" योजनान्तर्गत स्वीकृत प्रोजेक्ट की धनराशि का उपभोग प्रमाण पत्र प्रस्तुत करने के संबंध में।

महोदय,

उपर्युक्त विषयक आपके कार्यालय के पत्रांक क्षे.का.ल./5496-99/2021-22 दिनांक 15.03.2022 व शिक्षा निदेशक उच्च शिक्षा उ०प्र० प्रयागराज के पत्रांक/ डिग्री विकास/155223/2021-22 दिनांक 25.02.2022 का संदर्भ ग्रहण करते हुए शोध कार्यो हेतु "रिसर्च एण्ड डेवलपमेन्ट" योजनान्तर्गत डॉ० अनिल कुमार सोनी, सहायक प्रोफेसर, रसायन विज्ञान विभाग, शिया पी.जी. कालेज लखनऊ को स्वीकृत अनुदान धनराशि के क्रम में व्यय किये गये धनराशि का उपभोग प्रमाण पत्र चार्टर्ड एकाउन्टेन्ट से बिन्दुवार प्रमाणित कराकर प्रमाणित बिलों की मूल प्रति आपकी सेवा में सत्यापन हेतु प्रेषित हैं।

संलग्नक: उक्तवत

प्राचार्य

शिया पी.जी. कालेज,
Principal
Shia Post Graduate College
Lucknow (U.P.) India-20

प्रमुख शोधकरी स्थापन शास्त्र विभाग,
शिया पी.जी. कालेज लखनऊ- 226020

प्रारूप- II

रिसर्च एण्ड डेवलपमेन्ट योजना में किए गए कार्य की अंतिम रिपोर्ट

विश्वविद्यालय/महाविद्यालय का नाम: शिया पी.जी. कालेज, लखनऊ
परियोजना प्रगति की वार्षिक रिपोर्ट : अंतिम रिपोर्ट
संदर्भ संख्या: शासनादेश संख्या 5496 / 2021-22 दिनांक 15.03.2022
रिपोर्ट की अवधि: (Third Year)
शोध परियोजना का शीर्षक: "QM/MM based study of Platinum halides and their selective complexes of diverse application."

(क) प्रमुख शोधकर्ता/सह प्रमुख शोधकर्ता का नाम : डॉ० अनिल कुमार सोनी

(ख) सम्बन्धित विभाग/संस्थान का नाम: रसायन शास्त्र विभाग, शिया पी.जी. कालेज, लखनऊ

(ग) परियोजना प्रारम्भ करने की तिथि : 12.04.2022

स्वीकृत अनुदान के सापेक्ष किया गया व्यय विवरण

(क) कुल स्वीकृत धनराशि (रूपये) : 350000

(ख) कुल व्यय की धनराशि (रूपये) : 350000 + 1653

(ग) परियोजना का प्रगति विवरण :

I परियोजना का संक्षिप्त उद्देश्य : Page no. (i - ii)

II कार्य का पूर्ण विवरण : Page no. (iii - xvii)

III क्या प्रगति मूल कार्य योजना के अनुसार तथा उद्देश्य प्राप्त करने की दिशा में की गई है? : हाँ

IV अध्ययन के निष्कर्षों का एक सारांश : Page no. (xviii) to (xxvi)

V अन्य कोई विवरण (यदि आवश्यक हो) : Published Research Paper (Annexure-A, B, C, D, E)

III शोध परियोजना के संबंध में किए गए व्यय का विवरण
रिसर्च एण्ड डेवलपमेंट योजना में किए गए कार्य की वार्षिक रिपोर्ट/अंतिम रिपोर्ट

1. विश्वविद्यालय/महाविद्यालय का नाम: शिया पी.जी. कालेज, लखनऊ
2. प्रमुख शोधकर्ता (P.I.)/सह प्रमुख शोधकर्ता (Co.P.I.) का नाम : डॉ० अनिल कुमार सोनी
3. विभाग/ संस्थान का नाम: रसायन शास्त्र विभाग, शिया पी.जी. कालेज, लखनऊ
4. अनुमोदन पत्र संख्या एवं तारीख : ६००५-ल०/५५१६-११/२०२१-२२ दिनांक १५/३/२०२२ व ३०/३/२०२२
5. शोध परियोजना का शीर्षक: *QM/MM Based study of Platinum Halides and their selective complexation of diverse applications.*
6. परियोजना प्रारम्भ करने की तिथि: ०१.०५.२०२२
7. (क) व्यय की अवधि : ०१.०५.२०२२ से ०१.०४.२०२५ तक
(ख) व्यय का विवरण

क्रमांक	मद	प्रथम वर्ष	द्वितीय वर्ष	तृतीय वर्ष
1	अनावर्ती व्यय का विवरण (उपकरण आदि)	350000	00	00
2	अवर्ती व्यय का विवरण			
	(i) प्रोजेक्ट स्टाफ			
	(ii) आकस्मिकता (Contingency)			
	(iii) उपभोज्य सामग्री (Consumables)	1653	00	00
	(iv) यात्रा/फील्ड वर्क			
	(v) Over head charges (10%)			
	महायोग	351653	00	00



प्रमुख शोधकर्ता

रसायन विज्ञान विभाग

शिया पी.जी. कालेज, लखनऊ
अनिल कुमार सोनी

शिया पी.जी. कालेज, लखनऊ-226020

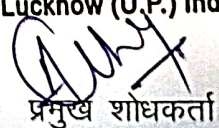
सह प्रमुख शोधकर्ता
प्रमुख शोधकर्ता

अनिल कुमार सोनी
शिया पी.जी. कालेज, लखनऊ-226020



प्राचार्य

शिया पी.जी. कालेज, लखनऊ
Shia Post Graduate College
Lucknow (U.P.) India-20



प्रमुख शोधकर्ता

शिया पी.जी. कालेज, लखनऊ

प्रमुख शोधकर्ता

अनिल कुमार सोनी

शिया पी.जी. कालेज, लखनऊ-226020

K A Z & ASSOCIATES

CHARTERED ACCOUNTANTS

UTILISATION CERTIFICATE FOR "RESEARCH & DEVELOPMENT" HEAD FOR DR. ANIL KUMAR SONI, ASSISTANT PROFESSOR

This is to certify that Dr. Anil Kumar Soni, Assistant professor, Chemistry Department, Shia P.G. College, Lucknow-226020(PAN- FCDPS8567Q) have received Rs. 3,50,000.00 as grant in aid in the Scheme "Research & Development Scheme" from Department of Higher Education, Government of Uttar Pradesh in May-22.

After cross verification of records and books of account we have reached to the conclusion that Dr. Anil Kumar Soni, Assistant professor has utilized Rs. 351653.00 against different research expenses and Equipment used in work.

FOR K A Z & ASSOCIATES
(Chartered Accountants)



CA QAZI ZEESHAN
Partner
MNO-435346
Date-10-10-2023
Place-Lucknow
UDIN- 23435346BGVVSH5075

© 645A/1224, Behind Atal Chauraha, Saraswati Puram, Jankipuram Extn., Lko.- 226 031
✉ caqazizeeshanalam@gmail.com
☎ : 7844022859 ☎ : 7318204492

प्रेषक,

क्षेत्रीय उच्च शिक्षा अधिकारी,
सेक्टर-एम, आशियाना,
लखनऊ।

सेवा में,

प्राचार्य/प्राचार्या,

1. कमला नेहरु भौतिक एवं सामाजिक विज्ञान संस्थान, सुलतानपुर।
2. ए०एन०डी० टीचर्स ट्रेनिंग कालेज, सीतापुर।
3. आई०टी० कालेज, लखनऊ।
4. शिया पी०जी० कालेज, लखनऊ।

पत्रांक/क्ष०का०ल०/ 54 96 - 99 /2021-22,

दिनांक 15.03.2022

विषय: अनुदानित महाविद्यालयों के शिक्षकों को शोध कार्यों हेतु "रिसर्च एण्ड डेवलपमेण्ट" योजनान्तर्गत आवंटित धनराशि के सम्बन्ध में।

महोदय/महोदया,

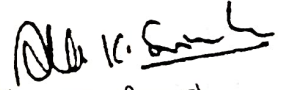
उपर्युक्त विषयक कृपया शिक्षा निदेशक, उच्च शिक्षा, उ०प्र०, प्रयागराज के पत्रांक/डिग्री विकास/155223/2021-22, दिनांक 25.02.2022 का संदर्भ ग्रहण करने का कष्ट करें, जिसके द्वारा निर्देशित किया गया है कि संलग्न सूची के अनुसार सम्बन्धित क्षेत्रीय उच्च शिक्षा अधिकारी के खाते में स्थानांतरित की गयी धनराशि अशासकीय अनुदानित महाविद्यालयों के सम्बन्धित शिक्षक/शोधकर्ता को उपलब्ध कराये जाने हेतु महाविद्यालय को धनराशि स्थानांतरित करते हुए निर्धारित प्रारूप पर सूचना तत्काल उपलब्ध कराना सुनिश्चित करें।

अतः शिक्षा निदेशक, उच्च शिक्षा, उ०प्र०, प्रयागराज के उक्त पत्र दिनांक 25.02.2022 की छायाप्रति संलग्न कर प्रेषित करते हुए तत्काल अपेक्षित है कि संलग्न सूची के अनुसार धनराशि स्थानांतरित किये जाने हेतु निम्नानुसार सूचना उपलब्ध कराने का कष्ट करें -

1. जिस नाम से बैंक खाता संचालित है का नाम,
2. बैंक खाता संख्या(संयुक्त खाता संख्या)
3. खाता का प्रकार(बचत/चालू) खाता,
4. बैंक का आई०एफ०एस०सी० कोड नम्बर,
5. बैंक शाखा का नाम,
6. बैंक पास-बुक की छायाप्रति,

संलग्नक-उक्तवत्।

भवदीय,



डॉ०(आलोक कुमार श्रीवास्तव),
क्षेत्रीय उच्च शिक्षा अधिकारी,
लखनऊ।



प्रेषक .

शिक्षा निदेशक (उच्च शिक्षा), उ० प्र०,
शिक्षा डिप्टी निगारा अनुभाग,
प्रयागराज।

रोचा में,

क्षेत्रीय उच्च शिक्षा अधिकारी,

लखनऊ / गोरखपुर / झाँसी / ग्वालियर / मेरठ / कागपुर

पत्रांक: डिप्टी विकास / 155 2 23

/ 2021-22 दिनांक : 05/02/2022

विषय:- प्रदेश के राजकीय/अनुदानित महाविद्यालयों के शिक्षकों को शोध कार्य हेतु "रिसर्च एण्ड डेवलपमेंट" योजनान्तर्गत अनुमान महाविद्यालय के खाते में स्थानान्तरण किये जाने के सम्बन्ध में।

महोदय,

उपर्युक्त विषयक शासन के पत्र सं०- 93/2021/1401/सत्तर-4-2021-4(28)/2021 दिनांक 22.10.2021 एवं शासनादेश संख्या-107/2021/2584/सत्तर-4-2021-4 (28)/2021 दिनांक 28 दिसम्बर 2021 का संदर्भ ग्रहण करने का कष्ट करें, जो प्रदेश के राजकीय/अनुदानित महाविद्यालयों के शिक्षकों को शोध कार्य हेतु "रिसर्च एण्ड डेवलपमेंट" योजनान्तर्गत अनुदान के सम्बन्ध में है।

उक्त के संबंध में संबंधित क्षेत्रीय उच्च शिक्षा अधिकारी को निर्देशित किया जाता है कि अशासकीय महाविद्यालयों में संलग्न विवरण एवं शासनादेश के अनुसार धनराशि तत्काल स्थानान्तरित कर स्थानान्तरण का विवरण निम्न प्रारूप में इस कार्यालय को उपलब्ध कराना सुनिश्चित करें।

प्रारूप	
क्षेत्रीय उच्च शिक्षा अधिकारी कार्यालय का नाम	
शोधकर्ता का नाम	
महाविद्यालय का नाम	
स्थानान्तरित की गई धनराशि	
संलग्नक:- यथोक्त	

भवदीय

[Signature]

डॉ० (कृष्ण चन्द्र वर्मा)

संयुक्त निदेशक (उच्च शिक्षा)

कृते-शिक्षा निदेशक (उ० शि०)

उत्तर प्रदेश, प्रयागराज।

पृष्ठांकन संख्या: डिप्टी विकास/155 2 23 - 224 / उसी तिथि को।

प्रतिलिपि:- संबंधित प्राचार्य/प्राचार्या अशासकीय महाविद्यालय उत्तर प्रदेश को सूचनार्थ एवं आवश्यक कार्यवाही हेतु प्रेषित।

[Signature]

डॉ० (कृष्ण चन्द्र वर्मा)

संयुक्त निदेशक (उच्च शिक्षा)

कृते-शिक्षा निदेशक (उ० शि०)

उत्तर प्रदेश, प्रयागराज।

Scanned with CamSc

राजसनादेश संख्या-93/2021/1401/संस्त-4-2021-4(26)/2021 दिनांक 22 अक्टूबर 2021 द्वारा
क राजकीय एवं अनुदानित महाविद्यालयों के शिक्षकों की सेवा कागरी हेतु शिक्षा एवं उच्च शिक्षा
विभाग द्वारा धनराशि रु 2567800/- (रुपये पाँच लाख, सत्तर हजार आठ सौ मात्र) की राशि को क्रम में
असासकीय महाविद्यालयों में स्थानान्तरित की जाने वाली धनराशि का विवरण

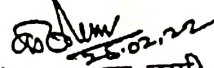
क्रम सं०	विशेष एण्ड डेवेलपमेंट योजना हेतु धनराशि के आहरण का विवरण	प्रमुख सेवा कागरी का नाम एवं संस्थान का नाम	आवृत्ति धनराशि	निदेशक द्वारा दी गई धनराशि
1.	क्षेत्रीय उच्च शिक्षा अधिकारी बरेली	डॉ० सुनील कुमार जोशी, वर्द्धमान पी०जी० कालेज बिजनौर	69500	357500
		डॉ० अन्जु बसल, वर्द्धमान पी०जी० कालेज बिजनौर	119000	
		डॉ० चन्द्रमोहन, वर्द्धमान पी०जी० कालेज बिजनौर	119000	
		डॉ० मनु प्रताप, बरेली कालेज बरेली	50000	
2.	क्षेत्रीय उच्च शिक्षा अधिकारी मेरठ	डॉ० सचिन कुमार शर्मा, मेरठ कालेज मेरठ	190000	557800
		डॉ० सीमा, मेरठ कालेज मेरठ	187800	
		डॉ० योगेश कुमार, डी०एच० कालेज मुजफ्फरनगर	180000	
3.	क्षेत्रीय उच्च शिक्षा अधिकारी कानपुर	डॉ० सरिका दुबे, प्रयाग महिला विद्यापीठ डिग्री कालेज, प्रयागराज।	85000	85000
4	क्षेत्रीय उच्च शिक्षा अधिकारी गोरखपुर	डॉ० वृजेश कुमार पाण्डेय सन्त विनोबा स्नातकोत्तर महाविद्यालय देवरिया	242500	242500
5	क्षेत्रीय उच्च शिक्षा अधिकारी, लखनऊ	डॉ० सुनील कुमार, ए०एन०डी० टीचर्स ट्रेनिंग कालेज, सीतापुर	296000	296000
		योग	1538800	

25.10.22
डॉ० (कृष्ण चन्द्र वर्मा)
संयुक्त निदेशक (उ०शि०)
कृते शिक्षा निदेशक (उ०शि०)
उ०प्र०, प्रयागराज।

शासनादेश संख्या-107/2021/2504/सत्तर-4-2021-4(20)/2021 दिनांक 28 दिसम्बर 2021 द्वारा
 के राजकीय एवं अनुदानित महाविद्यालयों के शिक्षकों को शोध कार्यों हेतु रिसर्च एण्ड डेवलपमेंट
 योजनान्तर्गत धनराशि रू० 5036650/- (रुपये पचास लाख, छत्तीस हजार छः सौ पचास मात्र) की स्वीकृति
 के क्रम में अशासकीय महाविद्यालयों में स्थानान्तरित की जाने वाली धनराशि का विवरण

क्रमसं०	रिसर्च एण्ड डेवलपमेंट योजना हेतु धनराशि के आवरण का विवरण	प्रमुख शोध कर्ता का नाम एवं संस्थान का नाम	अभिष्टा धनराशि	निदेशालय द्वारा डॉ. का० के खाते में स्थानान्तरित की गई धनराशि
01	क्षेत्रीय उच्च शिक्षा अधिकारी मेरठ	डॉ० राजवीर सिंह गोघर महाविद्यालय रामपुर, मनिहारन, साहारनपुर	122750	1610750
		डॉ० नीरज तोमर मेरठ कालेज मेरठ	285000	
		डॉ० अमित तोमर मेरठ कालेज मेरठ	133000	
		डॉ० आशीष तोमर मेरठ कालेज मेरठ	197000	
		डॉ० अर्चना मेरठ कालेज मेरठ	63500	
		डॉ० अनीता मलिक मेरठ कालेज मेरठ	235000	
		डॉ० युद्वीर सिंह मेरठ कालेज मेरठ	157000	
		डॉ० हृदयेश आर्य एन०आर०ई०सी०कालेज, खुर्जा, बुलन्दशहर	307500	
		डॉ० अमिता शर्मा रघुनाथ गर्ल्स पोस्ट ग्रेजुएट कालेज मेरठ	110000	
02	क्षेत्रीय उच्च शिक्षा अधिकारी, कानपुर	डॉ० प्रीती पाण्डेय एस०एन०सेन बी०बी०पी०जी०कालेज कानपुर	172500	763400
		डॉ० राजीव कुमार डी०बी०एस०कालेज कानपुर	257000	
		डॉ० अनुराग त्रिपाठी कुलभाष्कर आश्रम पी०जी०कालेज प्रयागराज	75500	
		डॉ० पवन कुमार पचौरी कुलभाष्कर आश्रम पी०जी०कालेज प्रयागराज	129200	
		डॉ० जितेन्द्र सिंह भदौरिया कुलभाष्कर आश्रम पी०जी०कालेज प्रयागराज	129200	

	क्षेत्रीय उच्च शिक्षा अधिकारी, गोरखपुर	डॉ० गुरेश गणेश त्रिपाठी एत विद्यापीठ पीठ कालेज गोरखपुर	137000	
		डॉ० मोहजीत तिमारी पीठआर०पीठगोरखपुर महाविद्यालय गोरखपुर	182800	318600
	क्षेत्रीय उच्च शिक्षा अधिकारी, लखनऊ	डॉ० सुरेश प्रताप सिंह कमला मेहरन नीतिम एवं सामाजिक विज्ञान संस्थान गुल्शनपुर	140000	844000
		डॉ० प्रवीण कुमार सिंह कमला मेहरन नीतिम एवं सामाजिक विज्ञान संस्थान गुल्शनपुर	74000	
		डॉ० सुनीता शर्मा कमला मेहरन नीतिम एवं सामाजिक विज्ञान संस्थान गुल्शनपुर	77000	
		डॉ० राजकुमार मिश्रा कमला मेहरन नीतिम एवं सामाजिक विज्ञान संस्थान गुल्शनपुर	60000	
		डॉ० अनिल कुमार सोनी शिया पीठपीठ कालेज लखनऊ	350000	
		डॉ० अल्फ्रेड लॉरिन्स इशाबेला धारन कालेज लखनऊ	235000	
05	क्षेत्रीय उच्च शिक्षा अधिकारी, झाँसी	डॉ० अभिलाष कुमार श्रीवास्तव अतर्रा पोस्ट ग्रेजुएट कालेज अतर्रा बौदा	103000	172000
		डॉ० बृजेंद्र सिंह बौदा बुन्देलखण्ड महाविद्यालय झाँसी	69000	


 डॉ० (कृष्ण चन्द्र वर्मा)
 संयुक्त निदेशक (उ०शि०)
 कृते शिक्षा निदेशक (उ०शि०)
 उ०प्र०, प्रयागराज।

➤ **PROPOSED OBJECTIVE OF THE RESEARCH WORK:**

Day-to-day expanding in the chemistry of platinum and its complexes is due to their applications directly or indirectly pre-requisite for many of today's problems related to anticancer drugs, photochemistry, biological system, materials science and nanoscience. This is due to its versatile electron-transfer pathways. Survey of literature shows that platinum and its compounds now used as sensors and switches, as catalyst, as antimicrobial agents, as biomarkers, as metallopharmaceuticals in treatment of cancer. Platinum based complex compounds have also been used as drugs to activate or help to generate redox reactions. A survey of literature shows that designing of new ligands that can complexed with platinum in different oxidation states can lead to develop new materials. For new materials of diverse applications there is and will be a continuous step-by-step study to discover new ligands and their new platinum complex. These complex compounds can formed either from their simple compounds or by substitution reactions from pre-synthesized complex compounds. The development of new platinum-based materials is and will be an ongoing need for various fields of science and technology, and thus for society. It is difficult to synthesize new molecule and test their various properties in laboratory, because, it involves huge expenditure and consumes enormous time. Now, chemistry together with physics and computer science has shifted from, how to make a molecule to what molecule to make, in other words molecule design. The emergence of computational chemistry and various software have given a quantitative nature to the relationship between molecule, its property, its synthesis and thus its various applications. To achieve the above goal the basic requirement is "to study the atomic and sub-atomic i.e., electronic structure of platinum halides and their complexes by evaluating eigenvalues, eigenvector and overlap matrix of molecular orbitals".

During this course, three objectives arose: (i) to draw the 3D structure of all the compounds and to optimize their geometry using semiempirical, ab-initio and or density functional theory based methods (ii) to calculate or evaluate the eigenvector, overlap matrix and eigenvalues of the compounds and (iii) build up molecular orbital diagram of compounds that at a glance provides clear cut electronic picture of the molecule, which more precisely can explain or help to explain the various properties

of the molecule. For geometry optimization the three dimensional (3D) modeling of the above mentioned species will be made on CAChe pro software and or Gaussian software. After that a quantitative atomic orbital (AO) and molecular orbital (MO) treatment will be made on platinum halides and their complexes to study (i) involvement of metal (n-1)d-, ns-and np-orbitals in hybridizations and its type that will be used to get information related to shape (bond angle) and size (bond length); (ii) contribution of various AOs in the construction of MOs through LCAO approximation using values of eigenvector and overlap matrix; (iii) nature of MOs by distinguishing them in to bonding, nonbonding and antibonding MO through population analysis; (iv) molecular orbital energy diagram and its construction using eigenvalues and overlap-population contribution; and (v) splitting of metal (n-1)d-orbitals and its magnitude.

1.DETAIL DESCRIPTION OF PROPOSAL (INTRODUCTION):

Mathematical treatment of various laws of physics and chemistry were too complex to be solved [1]. But, it is only possible by Walter Kohn, that has developed the mathematics and John Pople that has made its quantum mechanical forms. Both the scientists were jointly awarded Noble Prize in chemistry in 1998. Kohn for simplifying the mathematics in descriptions of bonding of atoms, which is a pre-requisite for many of today's calculations, and Pople for development of the computational quantum chemistry, which is used and will be used in various fields of science[2-4]. Day-to-day developments in theoretical and computational works make it possible to have a deeper insight in the sub-atomic nature of atoms, ions and molecules [5-7]. In this research work, atomic and molecular orbitals based analysis will be made to see electronic structure of platinum halides and their selective complexes of diverse use. Platinum forms compounds in 0, +2, +3, +4, +5 and +6 oxidation states. Main oxidation states of platinum are 0, +2 and +4, while +5 and +6 are shown by fluorides or fluoro complexes, and +3 usually in binuclear compounds with M—M bonds [8, 9]. The ability of platinum to exist in many oxidation states is an important property of this element, which plays an important role in its applications. Platinum readily forms coordinate complexes and these complexes have their applications in diverse fields [10-37].

2. SCIENTIFIC UTILITY OF THE WORK (AIM OF THE WORK):

Day-to-day expanding in the chemistry of platinum and its complexes is due to their applications directly or indirectly pre-requisite for many of today's problems related to anticancer drugs [10-18], photochemistry[19-22], biological system [23-25], materials science [26, 27] and nanoscience[28]. This is due to its versatile electron-transfer pathways. Survey of literature shows that platinum and its compounds now used as sensors and switches[27, 29], as catalyst[30-33], as antimicrobial agents[25], as biomarkers[24], as metallopharmaceuticals in treatment of cancer[18]. Platinum based complex

compounds have also been used as drugs to activate or help to generate redox reactions [35-37]. A survey of literature shows that designing of new ligands that can complexed with platinum in different oxidation states can lead to develop new materials [8-37]. For new materials of diverse applications there is and will be a continuous step-by-step study to discover new ligands and their new platinum complex. These complex compounds can formed either from their simple compounds or by substitution reactions from pre-synthesized complex compounds. The development of new platinum-based materials is and will be an ongoing need for various fields of science and technology, and thus for society. It is difficult to synthesize new molecule and test their various properties in laboratory, because, it involves huge expenditure and consumes enormous time. Now, chemistry together with physics and computer science has shifted from, how to make a molecule to what molecule to make, in other words molecule design. The emergence of computational chemistry and various software have given a quantitative nature to the relationship between molecule, its property, its synthesis and thus its various applications.

3. OBJECTIVE:

To achieve the above goal the basic requirement is “to study the atomic and sub-atomic i.e., electronic structure of platinum halides and their complexes by evaluating eigenvalues, eigenvector and overlap matrix of molecular orbitals”. During this course, three objectives arose: (i) to draw the 3D structure of all the compounds and to optimize their geometry using semiempirical [38], ab-initio [39] and or density functional theory based methods [40] (ii) to calculate or evaluate the eigenvector, overlap matrix and eigenvalues of the compounds and (iii) build up molecular orbital diagram of compounds that at a glance provides clear cut electronic picture of the molecule, which more precisely can explain or help to explain the various properties of the molecule. For geometry optimization the three dimensional (3D) modeling of the above mentioned species will be made on CAChe pro software and or Gaussian

software. After that a quantitative atomic orbital (AO) and molecular orbital (MO) treatment will be made on platinum halides and their complexes to study (i) involvement of metal (n-1)d-, ns- and np-orbitals in hybridizations and its type that will be used to get information related to shape (bond angle) and size (bond length); (ii) contribution of various AOs in the construction of MOs through LCAO approximation using values of eigenvector and overlap matrix; (iii) nature of MOs by distinguishing them into bonding, nonbonding and antibonding MO through population analysis; (iv) molecular orbital energy diagram and its construction using eigenvalues and overlap-population contribution; and (v) splitting of metal (n-1)d-orbitals and its magnitude.

4. METHODOLOGY:

A survey of literatures show that the nature and formation of chemical bond in molecules have been explained quantum mechanically by various theories. Among them much attention has been given to valence bond (V.B.) theory and molecular orbital (M.O.) theory. V. B. theory, as introduced by Heitler and London (1927) [41] and modified by Pauling and Slater (1931) [42, 43], is based on atomic orbitals (AOs); electronic configuration of elements; overlap of AOs; the hybridization of AOs and its wave function and superposition. While, M.O. theory, as developed by F. Hund and R. S. Mulliken (1932) based on concept of MOs in molecule [44, 45]. MOs in molecule are formed by AOs of atoms that constitute the molecule. The wave functions of these AOs are represented by their wave functions. Which when linearly combined by adopting LCAOs (linear combination of atomic orbitals) methods form MOs. In mathematical point of view this can take place by addition and subtraction of wave functions (AOs). (Wave mechanics expressed AOs as wave functions which is the amplitude of electron waves) of individual AO. The combining AOs having equal ($\Delta\varepsilon = 0$) or nearly equal energy ($\Delta\varepsilon \approx 0$) must be in same phase during overlapping. The solution of Schrödinger's wave equation gives wave function for the electron wave. However, since it cannot

be solved for any system containing more than one electron, MOs which are more than one electron wave functions for molecules are difficult to obtain directly from Schrödinger's wave equation. To overcome this problem, an approximation method known as LCAOs has been adopted. Mulliken and Hund developed MO theory to understand the role of quantum mechanics in the study of molecules and its spectra qualitatively. Hartree, Fock and Slater developed and put forward the mathematics of this qualitative form and their solutions, too [46-48]. Mulliken and Hund have proposed MO theory. But, its practical form was developed by Roothaan and Hall to solve the Hartree-Fock equations for polyatomic molecule by expanding the MOs in term of atomic-like functions [49, 50].

V.B. Theory and M.O. theory on their refinements they give same wave function for the molecule but they differ in their approximations only. Roothaan made a rigorous mathematical framework for the MO method. He concerned only with the electronic part of the molecular wave functions. The main aim of his work was to find approximate electronic wave functions for a molecule by assigning to each electron wave function that has their effect on the whole molecular system.

Roothaan gave each electron a wave function depending on the space coordinates of that electron only, called molecular orbital (MO):

$$\varphi_i^\mu = \varphi_i(x^\mu, y^\mu, z^\mu) \quad \text{Eq.1}$$

where x^μ, y^μ, z^μ or simply the superscript μ , stand for the coordinates of the μ^{th} electron; the subscript i labels the different MOs. The total N-electron wave function was then built up by him as a product of such MOs. Further he proposed that a particular MO φ_i may occur not more than twice in the product wave function (Pauli principle).

Roothaan gave each electron a wave function which in addition to the space coordinates also contains the spin coordinates of that electron, and which

are called as molecular spin orbital (MSO). Since he would neglect magnetic effects, each MSO factors into a MO and a spin function:

$$\begin{aligned}\psi_{\kappa}^{\mu} &= \psi_{\kappa}(x^{\mu}, y^{\mu}, z^{\mu}, s^{\mu}) \\ \psi_{i(\kappa)} &= \psi_{\kappa}(x^{\mu}, y^{\mu}, z^{\mu}) \eta_{\kappa}(s^{\mu}) \\ \psi_{\kappa}^{\mu} &= \psi_{i(\kappa)}^{\mu} \eta_{\kappa}^{\mu}\end{aligned}\quad \text{Eq.2}$$

where the superscript μ again stand for the (in this case space and spin) coordinates of the μ^{th} electron; the subscript κ and i label the different MSOs and MOs, respectively.

The total N-electron wave function was then built up by Roothaan as an antisymmetrized product of MSOs (AP).

$$\phi = (N!)^{1/2} \psi_1^1 \psi_2^2 \dots \psi_N^N = (N!)^{-1/2} \begin{pmatrix} \psi_1^1 \psi_2^1 & \dots & \psi_N^1 \\ \psi_1^2 \psi_2^2 & \dots & \psi_N^2 \\ \dots & \dots & \dots \\ \psi_1^N \psi_2^N & \dots & \psi_N^N \end{pmatrix} \quad \text{Eq.3}$$

Hartree–Fock–Roothaan theory (MOT) make quantitative predictions and these can also be compared with results that were obtained or can be obtained from experiments. All details of the equations described above were made by Roothaan [49]. In order to obtain much new insight into bonding and antibonding characteristics and the polarities of the MOs of the electron in a molecule, Mulliken (in 1955) refined Roothaan's SCF-LCAO-MO method [51]. Mulliken defined ϕ_i as MOs of polyatomic molecule

$$\phi_i = \sum_{rk} c_{irk} \chi_{rk} \quad \text{Eq.4}$$

$$N(i) = N(i) \sum_{rk} c_{rk}^2 + 2N(i) \sum_{l>k} c_{l,ik} c_{l,il} S_{r_k s_l} \quad \text{Eq.5}$$

where χ_r is the AOs on atom k , χ_s is the AOs on atom l , c_r is the coefficient of χ_r , c_s is the coefficient of χ_s , r represent an atomic orbital of atom (k) and s represent an atomic orbital of atom (l), and $S_{r_k s_l}$ represent overlap integral of

overlap between one atomic orbital (r) on atom (k) and other atomic orbital (s) on atom (l).

For subsequent application of equation 5 Mulliken obtained following equations

$$N(k) = N(c_r^2 + c_r c_s S_{rs}) \quad \text{Eq.6}$$

$$N(l) = N(c_r c_s S_{rs} + c_s^2) \quad \text{Eq.7}$$

The sum of $N(k)$ and $N(l)$ is just N (see Eq. 5). All details of the equations described above were made by Mulliken [91].

Mulliken analyzed, in his seminal publications (i) described bonding molecular orbital and non-bonding molecular orbitals using overlap populations [51], (ii) correlated non-Coulombic bond energies with LCAO bond orders [52], (iii) described in the MO the % character of overlapping orbital in term of gross population and (iv) finally he correlated the bonded interaction of V.B.T. with positive overlap population and non-bonded repulsion of V.B.T. with negative population analysis. A survey of literature also indicated that there are several ways to deal with overlap populations, but Mulliken population analysis (MPA) is widely used. Stout and Politzer [55] modified Mulliken overlap population by splitting it between two non-equivalent atoms k and l . $c_{ik}^2 / (c_{ik}^2 + c_{il}^2)$ for the atom k and $c_{il}^2 / (c_{ik}^2 + c_{il}^2)$ for the atom l . That result in unequal distribution of electrons between k and l . This method is called a modified Mulliken population analysis (MMPA). Ros and Schuit [56] proposed r_k^{th} AO to the i^{th} MO is $c_{ir_k}^2 / \sum_{(l)} c_{il}^2$.

Appendix:

Input Control Parameters

EHT option	: Normal EHT
Basis Contraction	: ST0-6G
Parameter K	: 1.7500
Request MOs	: All molecular orbitals
Calculate dipole moment	

Net molecular charge = 0.0000 a.u.

Standard parameters are from file: Procedure Editor database: Procedure EHT_Scf.

Calculated Number of valence electrons = 24

Overlap Matrix

	1	2	3	4	5	6	7	8	
1	1.0000								
2	-0.0000	1.0000							
3	-0.0000	0.0000	1.0000						
4	0.0000	0.0000	0.0000	1.0000					
5	0.0000	0.0000	-0.0000	0.0000	1.0000				
6	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	1.0000			
7	0.0000	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	1.0000		
8	0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	1.0000	
9	0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	
10	0.1923	0.2789	0.0139	0.0000	0.0825	-0.0479	0.0082	0.0000	
11	-0.3085	-0.3783	-0.0257	0.0000	-0.1183	0.0688	-0.0156	0.0000	
12	-0.0153	-0.0257	0.1367	0.0000	-0.0134	0.0034	0.0750	0.0000	
13	0.0000	0.0000	0.0000	0.1380	0.0000	0.0000	0.0000	0.0760	
14	0.1922	-0.2788	-0.0139	0.0000	0.0825	-0.0479	0.0082	0.0000	
15	0.3085	-0.3783	-0.0257	0.0000	0.1182	-0.0688	0.0156	0.0000	
16	0.0153	-0.0257	0.1367	0.0000	0.0134	-0.0034	-0.0750	0.0000	
17	0.0000	0.0000	0.0000	0.1380	0.0000	0.0000	0.0000	-0.0760	
	9	10	11	12	13	14	15	16	17
9	1.0000								
10	0.0000	1.0000							
11	0.0000	-0.0000	1.0000						
12	0.0000	0.0000	0.0000	1.0000					
13	0.0038	0.0000	0.0000	0.0000	1.0000				
14	0.0000	0.0003	-0.0021	-0.0001	0.0000	1.0000			
15	0.0000	0.0021	-0.0088	-0.0005	0.0000	0.0000	1.0000		
16	0.0000	0.0001	-0.0005	0.0009	0.0000	-0.0000	0.0000	1.0000	
17	-0.0038	0.0000	0.0000	0.0000	0.0009	0.0000	0.0000	0.0000	1.0000

Total Energy = -13.9101 au

Eigenvalues

	1	2	3	4	5	6	7	8	
	-0.9727	-0.9670	-0.5654	-0.5377	-0.5377	-0.5265	-0.5236	-0.5236	
	9	10	11	12	13	14	15	16	17
	-0.4627	-0.4627	-0.4378	-0.4378	-0.4358	-0.1784	-0.1784	0.0366	0.3443

Eigenvectors

			1	2	3	4	5	6	7	8
1	1 Pt	6s	-0.0704	-0.0000	0.1786	-0.0000	-0.0000	0.0000	-0.0000	-0.0000
2	1 Pt	6px	-0.0000	0.0312	-0.0000	0.0000	0.0000	-0.1299	0.0032	0.0000
3	1 Pt	6py	-0.0000	0.0015	-0.0000	-0.0000	-0.0000	-0.0065	-0.0649	-0.0000
4	1 Pt	6pz	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	0.0000	-0.0000	0.0650
5	1 Pt	5dx2-y2	-0.0621	-0.0000	0.2745	0.0402	0.0000	0.0000	-0.0000	-0.0000
6	1 Pt	5dz2	0.0360	0.0000	-0.1593	0.0000	0.0000	-0.0000	0.0000	0.0000
7	1 Pt	5dxy	-0.0062	0.0000	0.0274	-0.4030	-0.0001	0.0000	0.0000	0.0000
8	1 Pt	5dxz	-0.0000	-0.0000	0.0000	0.0001	-0.4045	-0.0000	0.0000	-0.0000
9	1 Pt	5dyz	0.0000	0.0000	-0.0000	0.0000	-0.0201	-0.0000	0.0000	-0.0000
10	2 Cl	3s	-0.6839	0.6981	-0.1032	0.0000	0.0000	0.0385	0.0000	0.0000
11	2 Cl	3px	-0.0122	0.0100	-0.5661	0.0306	0.0000	0.6562	0.0346	0.0000
12	2 Cl	3py	-0.0006	0.0005	-0.0281	-0.6161	-0.0001	0.0326	-0.6953	-0.0000
13	2 Cl	3pz	0.0000	0.0000	-0.0000	0.0001	-0.6169	0.0000	-0.0000	0.6962
14	3 Cl	3s	-0.6836	-0.6984	-0.1032	-0.0000	-0.0000	-0.0385	0.0000	0.0000
15	3 Cl	3px	0.0122	0.0100	0.5660	-0.0306	-0.0000	0.6563	0.0346	0.0000
16	3 Cl	3py	0.0006	0.0005	0.0281	0.6157	0.0001	0.0326	-0.6957	-0.0000
17	3 Cl	3pz	0.0000	0.0000	-0.0000	-0.0001	0.6165	0.0000	-0.0000	0.6966

9 10 11 12 13 14 15 16

ix

1	1	Pt	6S	0.0000	0.0000	-0.0000	-0.0000	0.3897	-0.0000	-0.0000	-1.0938
2	1	Pt	6Px	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0505	-0.0000	0.0007
3	1	Pt	6Py	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	1.0163	0.0000	0.0000
4	1	Pt	6Pz	-0.0000	-0.0000	-0.0000	0.0000	0.0000	-0.0000	1.0175	-0.0000
5	1	Pt	5Dx2-y2	-0.0000	-0.4975	-0.0000	-0.0913	-0.7688	-0.0000	-0.0000	-0.3649
6	1	Pt	5Dz2	-0.0000	-0.8660	-0.0000	-0.0000	0.4461	0.0000	0.0000	0.2117
7	1	Pt	5Dxy	-0.0000	-0.0496	0.0001	0.9161	-0.0766	0.0000	0.0000	-0.0364
8	1	Pt	5Dxz	-0.0497	0.0000	0.9195	-0.0001	0.0000	-0.0000	0.0000	-0.0000
9	1	Pt	5Dyz	0.9988	-0.0000	0.0457	-0.0000	-0.0000	-0.0000	0.0000	0.0000
10	2	Cl	3S	0.0000	0.0000	-0.0000	-0.0000	0.0315	0.0000	0.0000	0.2963
11	2	Cl	3Px	0.0000	0.0000	0.0000	0.0176	-0.1621	0.0092	0.0000	-0.5579
12	2	Cl	3Py	-0.0000	-0.0000	-0.0000	-0.3546	-0.0081	-0.1852	-0.0000	-0.0277
13	2	Cl	3Pz	-0.0000	0.0000	-0.3551	0.0000	-0.0000	0.0000	-0.1854	0.0000
14	3	Cl	3S	0.0000	0.0000	0.0000	0.0000	0.0315	0.0000	0.0000	0.2966
15	3	Cl	3Px	0.0000	0.0000	-0.0000	-0.0176	0.1621	0.0092	0.0000	0.5585
16	3	Cl	3Py	-0.0000	-0.0000	0.0000	0.3545	0.0081	-0.1851	-0.0000	0.0278
17	3	Cl	3Pz	-0.0000	0.0000	0.3549	-0.0000	-0.0000	0.0000	-0.1853	0.0000

17

1	1	Pt	6S	0.0008
2	1	Pt	6Px	1.3371
3	1	Pt	6Py	0.0665
4	1	Pt	6Pz	0.0000
5	1	Pt	5Dx2-y2	0.0003
6	1	Pt	5Dz2	-0.0002
7	1	Pt	5Dxy	0.0000
8	1	Pt	5Dxz	0.0000
9	1	Pt	5Dyz	-0.0000
10	2	Cl	3S	-0.3916
11	2	Cl	3Px	0.5819
12	2	Cl	3Py	0.0289
13	2	Cl	3Pz	0.0000
14	3	Cl	3S	0.3910
15	3	Cl	3Px	0.5811
16	3	Cl	3Py	0.0289
17	3	Cl	3Pz	-0.0000

Wyberg Bond Index and Mulliken Atomic Population Array

	1	2	3
1	8.7898		
2	0.8536	7.6050	
3	0.8534	0.0174	7.6051

Net Atomic Charges (au)

1	Pt	1.2102
2	Cl	-0.6050
3	Cl	-0.6051

Dipole Moment 0.001859 Debye

5. TECHNICAL PROGRAMME AND YEAR WISE PLAN OF WORK:

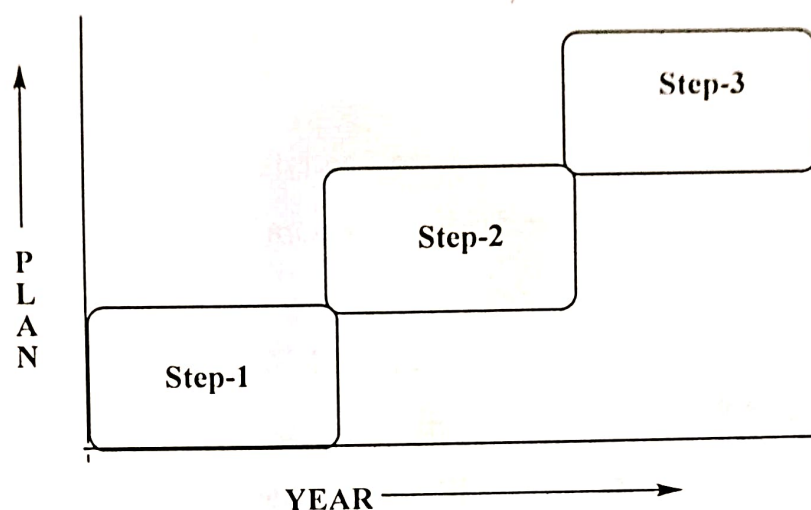


Figure 1. Year wise plan of work

Step-1. Electronic structure related study will be carried out for Platinum and their halides.

Step-2. Study of Platinum complexes of diverse application based on spectroscopic and thermodynamic properties will be carried out

Step-3. In the third years, once the nature and type of interaction are understood then it will be applied to other interesting molecules, where the type of interaction is still not well understood.

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➤ SHORT SUMMARY OF THE RESEARCH WORK DONE:

In the final report of above project five type of research works have been performed:

1. Firstly, we have studied super halogen PtF_6 and its interaction with serotonin molecule. This work is collaborated with Pandey's Research Group (PGR). This was due to lack of some laboratory facilities. Where the works were performed on gauss view 6.0 program package in the Molecular Modelling Laboratory of the K.S. Saket P.G. College, Ayodhya. The works were performed by opting DFT/B3LYP method with 6-311G(dp) basis set without symmetry constrain. The properties that have been calculated are HOMO, LUMO, MSSP, UV-Vis, etc. Further HOMO and LUMO have been used to calculate other electronic properties (ESR) based on them. Topological data (bond length, Å) as calculated were correlated with X-ray crystal data available in literature. Further, molecular electronic surface plot (MESP) used to describe physiochemical properties qualitatively in term of colour coding that is red signify (-)ve ESP, blue signify most (+)ve ESP and green showed zero (0) ESP. The optical transition in SER was based on TDDFT by opting same level of geometry. The work on UV-Vis spectra showed most intense peak at 147nm (UV region) and $f = 0.8805$ in between two electronic transitions $S_0 \rightarrow S_3$. Two other back to back absorption peaks appear at 139nm and 133nm with transition scale $S_0 \rightarrow S_4$, $S_0 \rightarrow S_5$. All possible orientations with SER of super-halogen PtF_6 have also been studied. All these possible orientations were obtained by opting minimum energy structures. The most stable conformer of $\text{PtF}_6@SER$ is optimized by using combination DFT/B3LYP method and SDD basis set Pt and 6-31G(d,p) for rest atom. The optimized geometry of $\text{PtF}_6@SER$ having no negative frequencies along with corresponding bond length (Pt—F) lies in between 1.902Å-2.326Å, however in free PtF_6 the bond length in between Pt—F falls some shorter bond length range 1.901Å-1.952Å. The change in bond length is due to attraction of charge from SER molecule by super-halogen species PtF_6 . To gain stability some bond length which are directly involve in interaction with SER molecule are elongated and other bonds are contracted 1.398Å-1.4443Å. The bond length in between C—C of R1 nearly unchanged however groups attached with ring R1 are involving interaction with super-halogen are significantly changed. The other bond length of SER remains nearly unchanged however change appears in bond length in SER molecules due to change of computational method only. The interaction

showed increase in chemical softness (S) and simultaneously decrease in chemical hardness (η). The nonlinear optical parameters were increased after interaction of PtF_6 with SER due to increase in the moment of π -electron. This clearly indicates with interaction of any super-halogen species increase moment of π -electron in SER play significant role to design new non-linear optical materials.

- Secondly, we have studied non-existence of platinum difluoride. As we know that platinum on reaction with halogen forms three halides viz., platinum(II) chloride, platinum(II) bromide and platinum(II) iodide, except platinum(II) fluoride. In this work the not existence of PtF_2 has been studied theoretically. For this thermodynamic, valence bond theory and molecular orbital theory based study have also been performed on this molecule. In order to obtain minimum energy structure we optimized the geometry of this halide by opting AM1 for thermodynamic work and EHT for population analysis. All the calculations were performed on CAChe software. The thermodynamic study supported the presumption of disproportionation reaction: $2\text{PtF}_2 \rightarrow \text{Pt} + \text{PtF}_4$. To check the validity of this disproportionation concept thermodynamics works have also been performed. The enthalpy (H°), entropy (S) and free energy (G) of platinum metal are zero, zero and 1.3432 (kcal/mol), respectively. And that of PtF_2 are 30.176 (kcal/mol), 62.008 (cal/mol) and 11.692 (kcal/mol), respectively. And of PtF_4 are 4140.219 (kcal/mol), 4139.767 (cal/mol) and +57.193 (kcal/mol), respectively. The change in enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) are (kcal/mol) for the reaction is given below:

$\Delta H_{\text{Reaction}} = \Sigma(H_{\text{Product}}) - \Sigma(H_{\text{Reactant}})$ $= 4140.219 - 60.352$ $= 4089.867$	$\Delta S_{\text{Reaction}} = \Sigma(S_{\text{Product}}) - \Sigma(S_{\text{Reactant}})$ $= 4139.767 - 124.016$ $= 4015.751$	$\Delta G_{\text{Reaction}} = \Sigma(G_{\text{Product}}) - \Sigma(G_{\text{Reactant}})$ $= -55.850 - 23.384$ $= -78.234$
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V.B.T showed sd-hybridization rather than sp-hybridization. This was supported by our data as evaluated theoretically by adopting Landis concept, which showed negligible contribution of 5s-orbital of platinum.

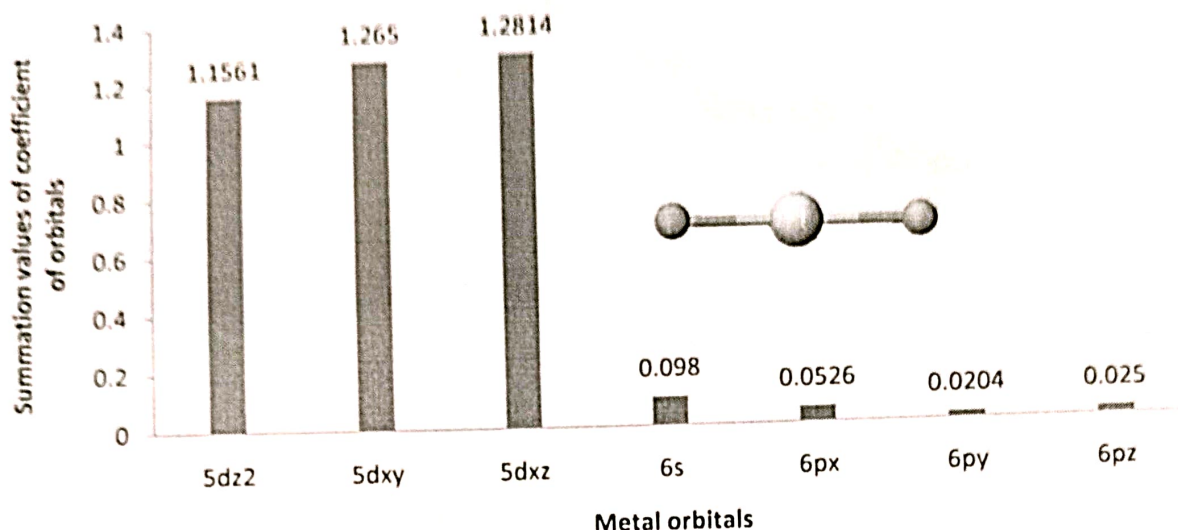


Figure 1. Extent of involvement of metal orbital in the formation of MOs of PtF_2

Table 1. Energy gap between overlapping orbitals of Pt and halogen (F, Cl, Br, I) in platinum halides

PtF₂	$\Delta_{5d-2s} = 1.007$	$\Delta_{5d-2p} = 0.202$	$\Delta_{6s-2s} = 1.136$	$\Delta_{6s-2p} = 0.332$	$\Delta_{6p-2s} = 1.269$	$\Delta_{6p-2p} = 0.464$
PtCl₂	$\Delta_{5d-3s} = 0.504$	$\Delta_{5d-3p} = 0.059$	$\Delta_{6s-3s} = 0.633$	$\Delta_{6s-3p} = 0.188$	$\Delta_{6p-3s} = 0.765$	$\Delta_{6p-3p} = 0.321$
PtBr₂	$\Delta_{5d-4s} = 0.348$	$\Delta_{5d-4p} = 0.019$	$\Delta_{6s-4s} = 0.477$	$\Delta_{6s-4p} = 0.148$	$\Delta_{6p-4s} = 0.610$	$\Delta_{6p-4p} = 0.280$
PtI₂	$\Delta_{5d-5s} = 0.199$	$\Delta_{5d-5p} = 0.016$	$\Delta_{6s-5s} = 0.328$	$\Delta_{6s-5p} = 0.113$	$\Delta_{6p-5s} = 0.460$	$\Delta_{6p-5p} = 0.246$

Mulliken's population based studies have pointed that the overlap is very poor due to dis-similarity of energies of combining orbitals of Pt and F atom. In Table 1 given above the energy gap between overlapping orbitals of Pt and halogen (F, Cl, Br, I) atoms in platinum halides was tabulated that also proved the unstability of PtF_2 molecule. As orbital of the metal, Pt and halogen, F of this molecule has maximum instability i.e., having different energy. The possible overlaps between the various AOs of ruthenium (Pt-1) and halogens (F-2 and F-2) in each MO will be 88, as describes. The $\Sigma\phi$ is very much low that is 0.2. This also proved that PtF_2 failed to match the criteria of overlapping and thus MOT too. Using eigenvalues and population analysis MO diagram has also been drawn, which clearly supported non-existence of PtF_2 in nature but its existence insitu and thus also supported presumption of disproportionation reaction.

3. Thirdly, we have modelled protonated PtF_n ($n = 1-6$), a new series of superacids of platinum. Various applications of superhalogens are in chemical and health industries as air purifying agents, electrolytic salts for lithium-ion batteries, and efficient materials for hydrogen storage. In the last three decades, researchers have paid close attention to the discovery of new classes of superhalogens in order to design new superacids. The initial geometry of protonated PtF_n ($n = 1-6$) and corresponding anions of superhalogens are formed by using GaussView 6.0. The modeled geometries are optimized by using a selfconsistent field with a linear combination of atomic orbital molecular molecular by using the *Gaussian 16W* software package. All calculations are performed using DFT with the B3LYP method. In the present work, we have employed the SDD basis set for Pt and 6-31++G (d, p) for F and H atoms. All geometries are optimized along with normal mode frequencies. The geometries corresponding to minima on potential energy surface (PES) are employed for further calculations.

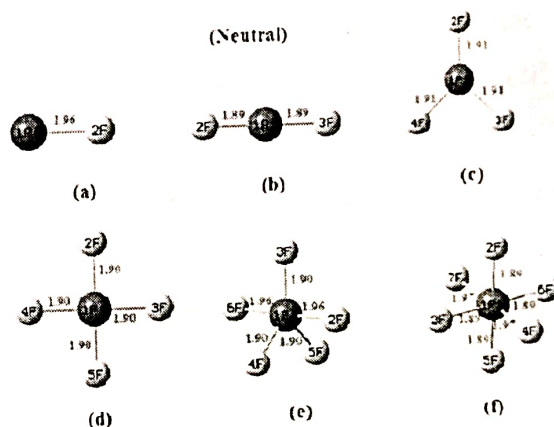


Figure 1. Equilibrium geometries of PtF_n ($n = 1-6$) neutral. The central blue sphere represents (Pt) atoms, and peripheral light-blue spheres represent (F) atoms with bond lengths (in Å).

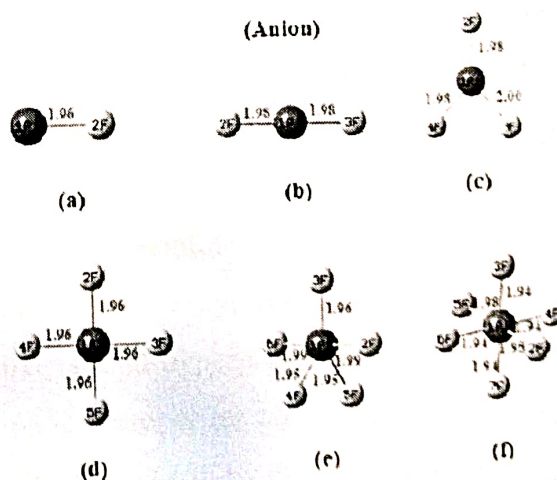


Figure 2. Equilibrium geometries of PtF_n ($n = 1-6$) anion. The central blue sphere represents (Pt) atoms, and peripheral pale light blue spheres represent (F) atoms with bond lengths (in Å).

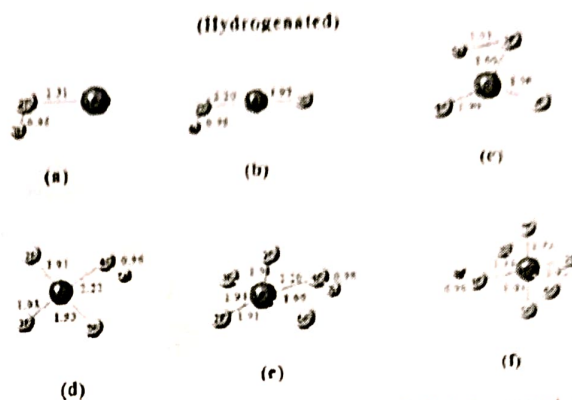
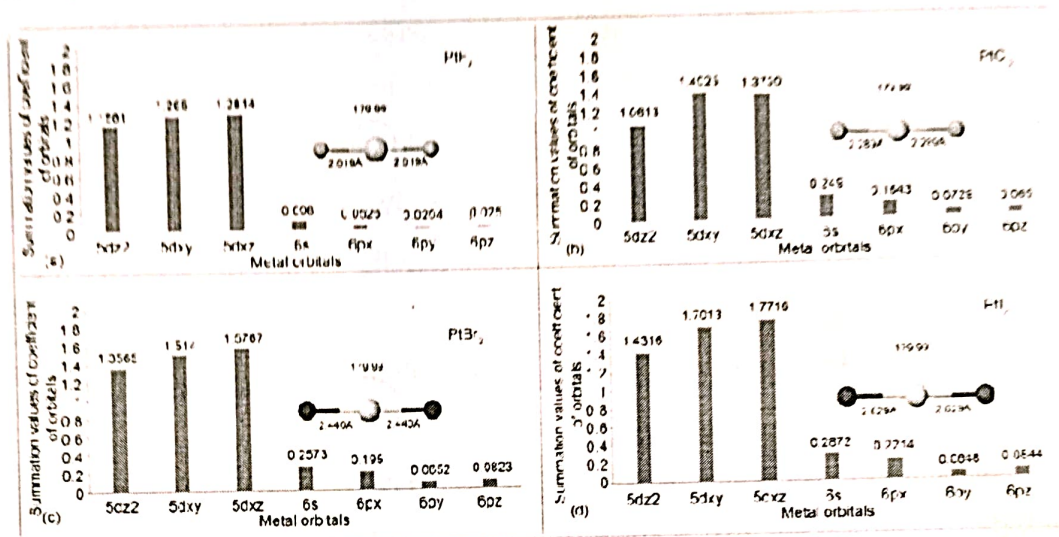


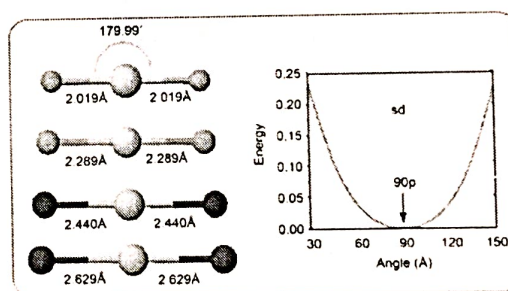
Figure 3. Equilibrium geometries of PtF_n ($n = 1-6$) hydrogenated. The central blue sphere represents (Pt) atoms, and peripheral light-blue spheres represent (F) atoms with bond lengths (in Å).

The calculated vertical de-attachment energy (VDE) of PtF_n ($n = 1-6$) reestablishes the superhalogenic behavior. The vibrational frequency, dissociation energy through the HF channel, and optimized geometries are utilized to discuss the stability of HPtF_n ($n = 1-6$). The deprotonation energy of HPtF_n is used to calculate the acidic strength of HPtF_n ($n = 1-6$). The acidity of protonated PtF_n ($n = 1-6$) is directly related to its counterpart superhalogen anions. The computed correlation factor ($R^2 = 0.9754$) shows that VDE is directly associated with acidity. The mechanism of acidity of HPtF_n ($n = 1-6$) is described by using natural bond orbital analysis charges on atoms. The electronic properties of HPtF_n ($n = 1-6$) are calculated using the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy. The nature of chemical reactivity is also determined by the HOMO–LUMO plot of HPtF_n ($n = 1-6$). It has formed the supersalts using superacids HPtF_n ($n = 1-6$) and superbase (OLi_3OH), and the nature of supersalts is compared with traditional salt LiF . The most stable conformers of supersalts PtF_nOLi_3 ($n = 2-6$) are analyzed for optoelectronic properties. It has computed the dissociation of supersalts through neutral and anions through superhalogens and superalkalis. The computed results show that PtF_4OLi_3 favors dissociation through anions as in traditional salts. The nonlinear optical parameters are calculated using dipole moment, mean polarizability, anisotropic polarizability, molar reflectivity (MR), order parameters, and hyperpolarizability of PtF_nOLi_3 ($n = 2-4$). The estimated nonlinear optical properties parameters are compared with corresponding parameters of traditional salt LiF by the same level theory.

4. Fourthly, atomic and molecular orbitals-based analysis has been made to see electronic structure of platinum halides. Since their summation values are significantly lower than those of the s orbital and much lower than those of the d orbital, the involvement of the 3 p atomic orbitals is negligible.



It is apparent from figure (given above) that the ns & (n-1)d orbitals perform an essential function in the Pt—X bond, with the 5p orbital contributing a negligible role.



Above figure reflected that bond angle has two minima one below 90° and one above 90°. Since bond angle and contributions of s-orbital & d-orbital of Pt(II) are maximum with a negligible contribution of p-orbitals, study strongly supports Landis concepts of sdⁿ-hybridization (here, n=1). These halides follow nephelauxetic effect and experimental data also support cloud-expanding effect. It is also evident from result obtained that summation values are lowest for chloride (fluoride) & highest for iodide. This is attributable to cloud expansion of halides. Consequently, iodide induces a more significant cloud expansion effect than bromide, which in fact exceeds chloride in platinum diiodide, platinum dibromide, & platinum dichloride (platinum difluoride), correspondingly. Effective positive charge on Pt(II) is diminished more significantly by iodide than by chloride (or

fluoride). The result aligns well with the nephelauxetic series of ligands. This effect could be further associated with differences in energy levels amongst ns & np orbitals. These two orbitals exhibit a substantial difference in energy. Iodide has a stronger nephelauxetic effect & a higher covalent bond character since its s & p orbitals are substantially closer. The result is consistent with the results of the study, which indicate that covalent character increases in the following order: $\text{PtI}_2 > \text{PtBr}_2 > \text{PtCl}_2 > \text{PtF}_2$. This will assist in addressing challenges of synthesizing various complexes that have yet to be synthesized, as well as refining the existing complexes for diverse applications.

5. Fifthly, atomic orbital and molecular orbital analysis along with spectroscopic studies have been made to see electronic structure of cisplatin ($\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$). It was Rosenberg, who accidentally finds out the biological activity of cisplatin, ie. $\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ in 1965. Actually it was synthesized by Peyrone in 1844. The anti-tumor activity of square planar complexes ($\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ and $[\text{Pt(en)Cl}_2]$) and octahedral complexes ($\text{cis-[Pt(NH}_3)_2\text{Cl}_4]$ and $[\text{Pt(en)Cl}_4]$) against sarcoma-180 (in mice) and against murine leukemia (L-1210) cells were also discovered by Rosenberg. Harder and Rosenberg reported selective inhibition of DNA synthesis in vitro by $\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ below $5\mu\text{M}$. Cisplatin was launched in 1978 as anticancer drug but it is still used for treatment of testicular, ovarian, bladder and neck cancers in humans. Prediction of atomic, molecular, electronic structure along with spectroscopic characteristic of metal complexes have always been challenging for computational chemists. CAChe Pro software of Fujitsu and Gaussian-03 software have been used to obtain minimum energy structure. For this cisplatin has opted with EHT (for population analysis) and DFT (for spectroscopic analysis).

Following points have been reflected from the study: (i) AOs analysis shows sd^3 -hybridization and thus supported Landis concept of sd^n -hybridization, where $n = 3$. The result showed involvement of three p orbitals are negligible as their summation values are very low in comparison to d orbital and considerably low with respect to s orbital. (ii) In total thirty one AOs are involved in the formation of thirty one MOs of cisplatin. As, there is only $28e^-$ to be filled, hence, we considered only fourteen MOs (ϕ_1 - ϕ_{14}) and rest vacant MOs (ϕ_{15} - ϕ_{31})

have been exempted. Among fourteen MOs, twelve are bonding, one is antibonding (ϕ_2) and one is non-bonding (ϕ_6). (iii) Cisplatin showed one absorption band at 3.9845eV with peak corresponded to 311.16nm of low oscillator strength (0.0014). (iv) Cisplatin molecule showed 27 normal vibrations, which distributed in $9A_1 + 5A_2 + 8B_1 + 5B_2$.

➤ **PAPER PUBLICATIONS:**

1. The first paper entitled, **"The docking study of 3-(2-aminoethyl)-1Hindol-5-ol and effect of nonlinear optoelectronic properties after its interaction with super-halogen PtF_{6n} "** has been published in REVELATION, A Peer Reviewed & Refereed Annual Journal of Popular Science Vol.7, No.1 (2022). ISSN: 2456-7698 RNI: UPBIL 04909. (Annexure-A).
2. The second paper entitled, **"Platinum difluoride: A Theoretical and Computational Based Study"** has been published in Advances in Biological Chemistry (Scientific Research Publishing Inc.: A peer reviewed scopus journal), Vol.13 (2023). (Annexure-B).
3. The third paper entitled, **"Superacidic Properties of Protonated PtF_n ($n = 1-6$) and Their Ability to Form Supersalts: DFT Study"** has been published in Macromolecular Symposia (Wiley-VCH GmbH: A peer reviewed scopus journal), Vol.413 (2024). (Annexure-C).
4. The fourth paper entitled, **"QM/MM Based Study of Electronic Structure of Platinum Dihalides"** has been published in Open Journal of Applied Sciences (Scientific Research Publishing Inc.: A peer reviewed scopus journal), Vol.15 (2025). (Annexure-D).
5. The fifth paper entitled, **"Cisplatin at atomic, molecular and electronic level: A DFT based study"** has been ^{published} ~~accepted/inpress~~ in Open Journal of Applied Sciences (Scientific Research Publishing Inc.: A peer reviewed scopus journal) ^{vol.15(5)} (2025). (Annexure-E).

Annexure-A

The docking study of 3-(2-aminoethyl)-1Hindol-5-ol and effect of nonlinear optoelectronic properties after it's interaction with super-halogen PtF₆.

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Publication Info Received : 02/01/2023 Revised & Accepted : 24/01/2023 Keywords: SER, HOMO LUMO, TDDFT, NLO Corresponding Author: *Email : asinghkssaket@gmail.com	Abstract In present communication geometry optimization of 3-(2-aminoethyl)-1Hindol-5-ol(SER) has been done by using combination of DFT/B3LYP method and 6-311G(dp) basis set without any symmetry constrain. The electronic properties of SER are calculated by using HOMO,LUMO,MESP plot. The UV spectra of SER calculated by using Time dependent density funtional theory (TDDFT) by suing same level theory. The electrophonic index Log S and Log P are used to discuss transport properties through cell membrane of SER molecule. The biological activity of SER is calculated by using PASS online server. The calculated docking parameters of SER molecule to 4ib4 protein show that nitrogen in –NH₂ group bind well targeted protein. The interaction of superhalogen PtF₆ calculated by placing PtF₆ at top of ring R1 and stability of optimized geometry calculated by using thermodynamical parameters of reaction. The calculated electronic reactivity parameters and non linear optical parameters of SER molecule with SER@PtF₆ are compared. The NLO parameters enhance due to increase moment of π electron after interaction PtF₆ with SER molecule provides new path way to design new liquid crystal materials.
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Introduction

In human body molecule Serotonin,(SER) with chemical formula C₁₀H₁₂N₂O, systematic name 3-(2-aminoethyl)-1Hindol-5-ol, is responsible for the primary neurotransmitter adaptable humor, anxiety and happiness [1]. The role of Serotonin in the central nervous system, is very important and originate during the human body and forces a extensive display of physical functions. Approximately 95% of body's serotonin is really originated in the gastrointestinal region, somewhere it controls intestinal association [2]. By using biosynthesis process from the necessary amino acid tryptophan [3] and kaput behind by

monoamine oxidase to produce 5-hydroxyindoleacetic acid by using Serotonin. while such, monoamine oxidase inhibitors and other complexes that add to serotonin absorption have been worn to delight misery [4]. In a neurotransmitter like humans life's on earth all bilateral etc. Serotonin plays important role [5]. In emissions of seed this is important to originate in plants, particularly in seeds; anywhere serotonin inspires the digestive zone of animals [6]. In fungi numerous study on Serotonin is connected tryptamines[7-8]. One of important monoamine (5-hydroxytryptamine, 5-HT) is neurotransmitter, substitute as a chemical envoy that transmits nerve signals among nerve cells and that root

blood container to thin. Serotonin has been concerned a lot of vital nervous system-mediated functions included sleep, feeding etc [8-10]. In academia and the pharmaceutical industry title molecule shows important application in delighting equivalent diseases, due to long-standing target shows greater interest to researcher [11-14]. The Yue Yang et.al. reported crystal structure of serotonin[15]. The geometrical parameters and IR vibrational frequencies of serotonin are calculated and reported by using various quantum chemical methods [16]. In present communication geometry opto electronic and docking study of title molecule is calculated by combination of DFT/B3LYP method and 6-311G(d,p) basis set. The biochemical activity of SER molecule has been reported in this communication. The docking of SER molecule with suitable protein has been performed by using AUTO dock software. The development of polarity and enhancement of optoelectronic properties of title molecule after interaction of superhalogen species PtF₆ having EA 8.64eV[17] are also discussed in this communication. The present study explores optoelectronics and pharmaceutical properties of title molecule.

Computational method

The entire calculations have been carried out by using G16 program package[18] on personal laptop. The initial geometry of title molecule is design by using gauss view 6.0 program package [19]. The geometry of title molecule is optimized by using combination of B3LYP/DFT method[20-21] and 6-311G (d, p) basis set [22-23] without any symmetry constrains. To study interaction of superhalogen PtF₆ with title molecule at various possible orientation full geometry optimization have been done by using DFT method and SDD basis set. The most stable geometry is further optimized by using DFT/B3LYP method. To gain better accuracy in method SDD basis set employed for Pt however 6-311G (d,p) basis set for rest atoms. The HOMO LUMO MESP plot of title molecule is drawn by using Gassview 6.0. The calculated electron affinities (EA) of PtF₆ by using this method are well matched with previous reported [17].

Result and discussion

The geometry of title molecule is optimized by using combination of DFT/B3LYP method and 6-311G (d, p) basis set. The optimized geometry of title molecule along with corresponding bond length (Å) is shown in fig-1. The calculated bond length are well matched with previous reported bond length by using various method [15] and also reported by X-ray crystal data method. The reported crystal structure of title molecule is Orthorhombic, type P212121 with $a=8.2248\text{Å}$, $b=8.7542\text{Å}$, $c=13.0712\text{Å}$. The calculated bond length in between C-C lies in between 1.399-1.422 for ring R1 however C-C bond length of ring R2 lies in between 1.362 Å-1.422 Å are well matched with corresponding observed bond length[15]. The N-H bond of NH₂ are lies with in range 1.019 Å-1.020 Å are well matched with corresponding observed bond length 0.90 Å. The bond length of O-H adjacent of ring R1 are 0.90 Å are also well matched with observed bond length 0.86 Å. The other calculated optimized bond length are well matched with computed [16] and observed bond length [15].

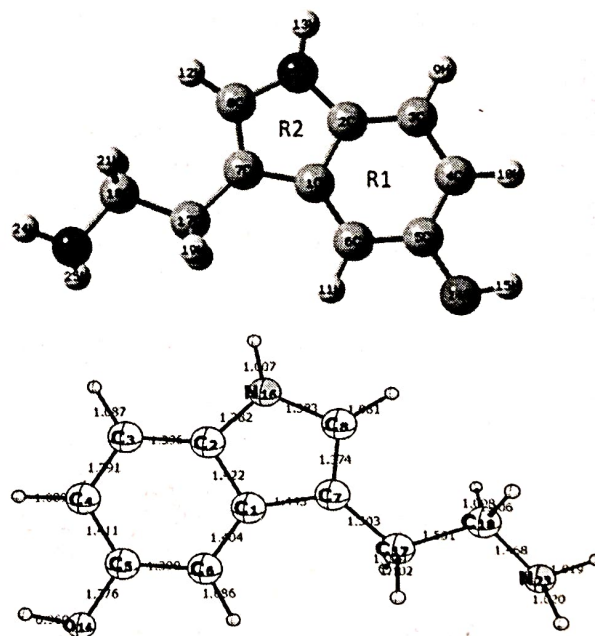


Figure-1 Optimized geometry of SER(upper) with bond length(lower)

Electronic properties of SER

Two frontiers molecular orbitals are highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital's (LUMO) plays significant role to describe nature reactivity. The energy gap in between HOMO and LUMO orbitals are known and band gap. The band gap is inversely proportional to chemical reactivity and directly related with chemical stability. The lower band gap means more polarity appears on atoms and hence more chemical reactive less kinetic stability[24]. The HOMO LUMO plot of SER are shown in fig-2 . The both HOMO LUMO molecular orbital's are P-type molecular and HOMO is distributed over whole molecule except NH₂ group presented on pentene ring however LUMO is distributed over whole molecule. The charge transfer from HOMO → LUMO means charge transfer from whole molecule to NH₂ group to stabilize molecule.

Molecular electrostatic surface plot (MESP) of SER

The physiochemical property with chemical system is described by using MESP plot [25-26]. The nature of electropotential surface is described by using color coding e.g., red-signify negative electrostatic potential; blue signifies the most positive electrostatic potential and green colour shows zero potential. The intensity of electrostatic potential are computed as blue>green>yellow>orange>red. The MESP plot of SER is also shown in fig-2. The oxygen of hydroxyl group encircled by red color so oxygen of -OH group behaves as electronegative charge center however nitrogen of -NH₂ group encircles by blue color so behaves as most electropositive charge center.

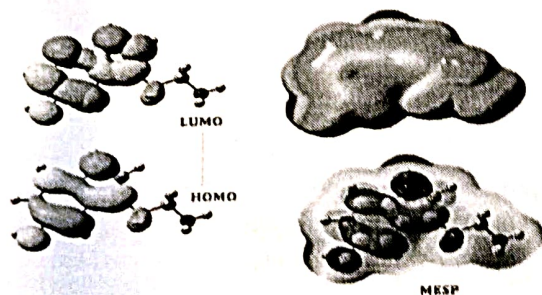


Fig-2 HOMO LUMO MESP (Solid, Transparent) plot of SER molecule

TDDFT calculation of SER molecule: The optical transition in SER molecule has been calculated by using TDDFT on optimized geometry by using same level theory. In present study we have calculated transition state up to twenty states. The calculated UV-Vis spectra is shown in fig-3 The computed Transition states transition energy (eV) transition orbital's Oscillatory strength, wave length (nm) of Title molecule. The most intense absorption peak appears at 147nm falls in ultraviolet region. This transition peaks appears($f=0.8805$) in between two electron transition from S0 S3 however corresponding transition orbitals with % contribution H-2 LUMO(13%), H-1 LUMO(14%), HOMO L+1 (49%) having transition energy 8.420eV. The other two back to back absorption peak appears at 139nm,133nm with transition states S0 S4, S0 S5 however corresponding transition orbitals with % contribution H-1 L+1 (64%), HOMO LUMO (10%) and H-1 L+1 (74%), HOMO LUMO (8%) respectively. The other significant absorption peaks with contributing orbital's are listed in table-1

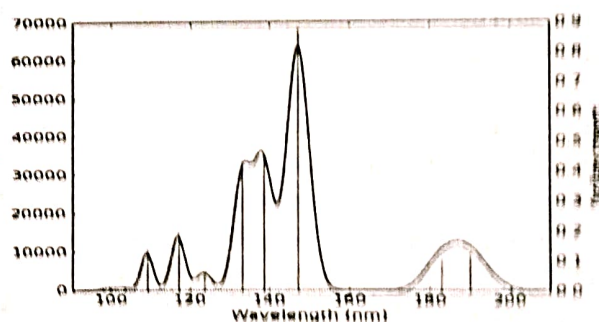


Fig-3 UV-Vis plot of SER by using TDDFT method

Table-1 Calculated Transition rates transition energy (eV) transition orbital's
Oscillatory strength(f) Calculated) max) of Title molecule

Excited State	E (eV)	Oscillatory Strength (f)	Calculated (λmax)	Transition Orbital's
$S_0 \rightarrow S_1$	6.522	0.1268	190	H-1→LUMO (18%), H-1→L+1 (16%), H→L (68%)
$S_0 \rightarrow S_2$	6.778	0.1138	183	H-1→LUMO (18%), HOMO→LUMO (14%), HOMO→L+1 (22%)
$S_0 \rightarrow S_3$	8.420	0.8805	147	H-2→LUMO (13%), H-1→LUMO (14%), HOMO→L+1 (49%)
$S_0 \rightarrow S_4$	8.944	0.4576	139	H-1→L+1 (64%), HOMO→LUMO (10%)
$S_0 \rightarrow S_5$	9.303	0.4139	133	H-1→L+1 (74%), HOMO→LUMO (8%)
$S_0 \rightarrow S_{11}$	10.595	0.1916	117	H-2→LUMO (25%), HOMO→L+2 (56%)
$S_0 \rightarrow S_{12}$	11.361	0.1337	109	H-4→LUMO (20%), H-2→L+1 (39%), H-1→L+2 (18%)

Biological activity and Docking of SER molecule with suitable protein: The ALOGPS 2.1 program based on electron topological indices is introduced by Tetko et al [27-29] which is very useful to calculate Log P and Log S parameters. Firstly we have calculated value of LogP and LogS by using ALOGPS 2.1 program. The calculated value of LogP (4.12) implies that SER could easily transport through cell membranes so SER is very important for pharmacological industries. The value Log S (-2.87) computed by ALOGPS 2.1 program falls in medium range of membrane permeability because for more than 85% of drug value of LogS falls in between -1 to -6. More than 900 pharmacological effects are calculated by PASS online program. The mutagenicity, carcinogenicity, teratogenicity, and embryotoxicity are example of biological activity calculated by PASS online server. The calculated biological activity for Pa>60% are listed in Table-3. The calculated results of PASS online server based on analysis of structure activity relationships (SAR) analysis. The calculated biological activity by PASS online servers of sample of 46000 drugs whose biological activities are experimentally verified are nearly 85% matched with corresponding experimentally activity of drugs [30]

The SER molecule shows anticancer (0.813), Catalase stimulant(0.798) Phobic disorders treatment(0.811), 5-Hydroxytryptamine release stimulant(0.658), Antimitotic(0.623), Imidazoline receptor agonist(0.622), Apoptosis agonist(0.638) activities. The antineoplastic drug or anticancer drug, is

successful in the handling of mean, or cancerous, disease or to stop abnormal growth of body cells. The extreme individual experiences crazy fear concerning a condition, alive being, place is known as phobia which is type of anxiety disorder, or object. The 5-hydroxytryptamine (5-HT) is a stirring moderator recognized to be released in lung. Capsaicin-sensitive lung vagal (CSLV) afferents function as a main sensor for noticing chemical stimuli and construct following impulses during lung swelling.

The Swiss dock online server which predicts targeted protein for docking. The simli code of optimized geometry SER uploaded on server provides number of protein for docking. The Swiss dock predicts 4ib4 protein for docking. The Pdb file of crystal structure of 4ib4 protein has been downloaded from protein data bank. The 4ib4 protein or chimeric protein of 5-HT_{2B}-BRIL in complex with ergotamine. The 4ib4 protein is responsible for cholesterol homeostasis motivate together a numeral of unusual genetic disorders and give to common irregular and complex disorders counting heart disease, stroke, second type diabetes, as well as Alzheimer's disease. The docking of title molecule is performed by Autodock 4.2 tools by using energy-minimized molecules for dock. The macromolecules are created by combining polar hydrogens, Kollman charges. In present calculation a grid box having dimensions of 60x60x60 was positioned about the area of concern. The Lamarckian Genetic Algorithm was employed to choose best ten conformers

for stability on basis of least binding energy. In docking operation we have selected Cygwin terminal. The SER is binds guanine in the DNA because SER is alkylating compound which interact with minor groove, and utilized in anticancer drug. The docking picture of Auto Dock obtained by using Chimera10.1 shown in fig-4(a) and (b). In interaction two hydrogen bonding appears in between targeted protein and SER molecule. The Serine amino acids facilitates in advancing muscle increase and in the production of immune system however Methionine(MET) is utilizes in management of kidney stones, preserving well skin as well as controlling attack of pathogenic bacteria. The amino acids methionine (met), Sulphur-containing nature and serine (ser) Hydroxylic are grouped based on characteristics of the side chains. The met amino acids having hydrophobic chain reaction however ser having polar neutral chain so they interact with hydrpphilic and polar site of SER molecule. The serine(ser) amino acids connected with neutral polar atom of H in $-NH_2$ group . The nitrogen pulls electron from hydrogen and create more polarity so hydrogen of $-NH_2$ the nitrogen methionine (met) with bond length 2.305Å. According to MESP plot discussion nitrogen of $-NH_2$ group shows most electropositive charge center means hydrophilic charge center so nitrogen of SER molecule bind with hydrophobic chain center Met with bond length 2.752Å. The ser amino acids with SER molecule bind strongly as compared binding with met amino acids. The full fitness score – 1172.82 and binding affinity -6.8 kJ/mol shows that targeted protein bind well with targeted protein.

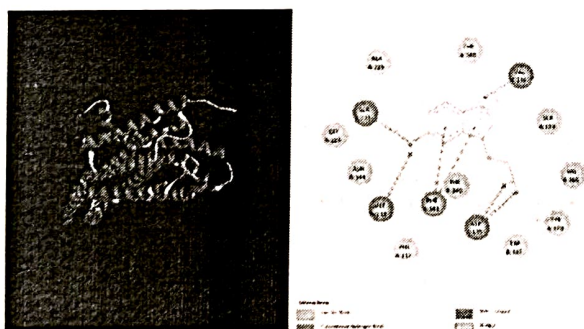


Fig- 4 (a) Hydrogen Bonding of SER with targeted protein 4ib4

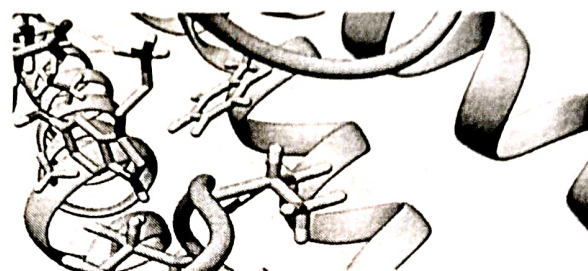


Fig- 4(b) Docking picture of targeted protein with SER (Ribbon type)

S. No.	Activity	Pa	Pi
1	Catalase Stimulant	0,798	0,001
2	Phobic disorders treatment	0,811	0,029
3	5 Hydroxytryptamine release stimulant	0,658	0,031
4	Antimitotic	0,623	0,005
5	Imidazoline receptro agonist	0,622	0,005
6	Apoptosis agonist	0,638	0,022
7	MAP kinase stimulant	0,624	0,013

Table-2 Calculated Biological activity by using PASS online server for Pa>60%

Geometry and thermodynamical stability of PtF₆@ SER molecule

Parameters	Gibbs Free energy (au)	Electronic energy (au)	Enthalpy (au)	Entropy (Kcal/mol-K)
Reaction	0.32501	0.40214	0.42154	-30.4180

Table-3 Calculated thermodynamical parameters of reaction

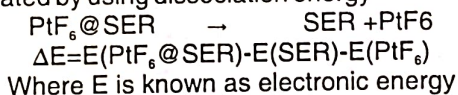


Figure-5 Optimized geometry of PtF6@SER (Upper) and corresponding bond length (lower)

In this section we have computed how nonlinear opto-electronic properties of SER are changed after interaction of SER with superhalogen PtF_6 . To study interaction of SER with superhalogen PtF_6 we have placed PtF_6 at all possible orientation with SER and after optimization minimum energy obtained are shown in fig-5. The most stable conformer of $\text{PtF}_6@SER$ is further optimized by using combination DFT/B3LYP method and SDD basis set for Pt and 6-311G (d, p) for rest atom. The optimized geometry of $\text{PtF}_6@SER$ having no negative frequencies along with corresponding bond length is presented in fig-5(lower). The Pt-F lies in between 1.902 Å-2.326 Å however in free PtF_6 the

bond length in between Pt-F falls some shorter bond length range 1.901 Å-1.952 Å. The change in bond length due to attraction of charge from SER molecule by superhalogen species PtF_6 . To gain stability some bond length which are directly involve in interaction with SER molecule are elongated and other bonds are contracted. 1.398 Å-1.443 Å. The bond length in between C-C of ring R1 nearly unchanged however groups attached with ring R1 are involving interaction with superhalogen are significantly changed. The other bond length of SER remains nearly unchanged however change appears in bond length in SER molecule due to change of computational method only.

The stability of $\text{PtF}_6@SER$ is calculated by using dissociation energy



The calculated dissociation energy $\Delta E_{\text{diss}} > 0$ is positive means $\text{PtF}_6@SER$ is stable against dissociation through PtF_6 . The calculated absorption energy easily indicates adsorption of PtF_6 with SER favors spontaneous reaction on forward direction. The calculated Gibbs free energy, Enthalpy(H), entropy(S) are calculated and listed in table- at T=300K

Comparison of Non linear optical and electronic properties of SER compound with $SER@PtF_6$. The nonlinear optical parameters are described by several parameters like dipole moment mean polarizability hyperpolarizability molar refractivity as well as order parameters. The dipole moment mean polarizability hyperpolarizability are calculated in Cartesian coordinate system[31] in three dimension x,y,z are given by

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \text{-----(6)}$$

The response of any system under application of applied field is describe by polarizability as well The response of any system under application of applied field is describe by polarizability as well hyperpolarizability

$$\langle \alpha \rangle = 1/3 [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \text{-----(7)}$$

$$\beta_{\text{Total}} = [(\beta_{xxx}^2 + \beta_{xyy}^2 + \beta_{xzz}^2) + (\beta_{yyy}^2 + \beta_{yxx}^2 + \beta_{yzz}^2) + (\beta_{zzz}^2 + \beta_{zxx}^2 + \beta_{zyy}^2)]^{1/2} \text{-----(8)}$$

$$MR = \left[\frac{n^2 - 1}{n^2 + 2} \right] \left(\frac{MR}{\rho} \right) = 1.33 \pi N \text{-----(10)}$$

The MR index for any system is computed [32-34]
(For ϵ : 1 a.u. = 0.1482 $\times 10^{-24}$ esu; for β_0 : 1 a.u. = 8.639 $\times 10^{-33}$ esu)

The NLO parameters of SER and SER@PTF₆ are calculated and listed in table-5. The dipole moment is signature of distribution charge in molecule. The interaction of well known superhalogen species with SER extract electron from SER compound produce polarity on SER@PTF₆ so charge distribution changed and hence enhancement of dipole moment after interaction of PtF₆ with SER. The calculated molar refractivity mean polarizability lies within range of NLO active materials however corresponding parameters enhance after doping PtF₆ with SER due to much change torsional angle. The calculated hyperpolarizability ($\chi^{(3)}$) is higher than NLO reference agent urea (0.1947×10^{-30} esu) however corresponding value increase nearly 2.5 times after interaction PtF₆. The moment of π electron in molecule increase after interaction of SER with PtF₆. The ionization potential and electron affinity of any system are calculated by using negative of Eigen value of HOMO and LUMO [35]

$$IP = -\text{HOMO} \text{ and } EA = -\text{LUMO} \text{ -----(13)}$$

The ionization potential decreases due to

interaction of superhalogen PtF₆ with SER however electron affinity increases after interaction of PtF₆ with SER. The electronegativity and chemical hardness of any system are computed by [36-37]

$$\mu = - (IP + EA) / 2, \text{ -----(14)}$$

$$\eta = (IP - EA) / 2, \text{ -----(15)}$$

The absolute electronegativity as well as chemical hardness are computed by using finite-difference methods [38-39]. The inverse of hardness is termed as global softness, $S = 1 / 2\eta$. The global electrophilicity index $\omega = \mu^2 / 2\eta$ [40]. The calculated energy gap decreases after interaction PtF₆ with SER however chemical softness increases and chemical hardness decreases after interaction PtF₆ with SER. One of important conclusion draw from this interaction study is that terminal doping of superhalogen PtF₆ may large enhance nonlinear optical behaviors of PtF₆@SER. The interaction of superhalogen with any chemical system provides a path way for researchers to design new liquid crystal in future.

Table-4 Calculated Nonlinear optical (NLO) electronic parameters of SER and SER@PtF₆

IP(eV)	EA(eV)	$\alpha_0 - \alpha_{\infty}$ (eV)	χ (eV)	η (eV)	ζ (eV)	S (eV) ⁻¹	μ (eV)	ΔN_{max}	$\langle \hat{A}_0 \rangle$ (a.u)	MR (e.s.u.)	$\hat{\alpha}_{total}$ (esu $\times 10^{-30}$) (e.s.u.)	Die.M om. (D)
SER												
5.066	0.078	4.989	2.572	-2.572	2.494	0.2004	16.500	1.031	118.625	52.215	192.369	3.541
SER@PtF₆												
3.165	1.957	1.209	2.561	-2.561	0.604	0.827	5.424	3.095	162.570	60.151	486.327	10.582

Conclusion

In present communication geometry optimization of SER has been done by using combination of DFT/B3LYP method and 6-311G(d,p) basis set and optimized geometry well matched with observed and previously computed result. The calculated HOMO-LUMO gap shows SER is chemically less reactive. The MESP plot shows that Nitrogen of -NH₂ group is most electropositive charge center however oxygen of -OH group shows most electronegative charge center. The TDDFT calculation shows that most prominent peak appears in ultraviolet (UV) region (147 nm) with significant oscillatory strength.

The docking of SER with targeted protein 4ib4 shows that nitrogen of SER connected with MET and Gly residue of target protein having bond length 2.142Å and 2.234Å respectively. The binding affinity -6.8 kJ/mol shows that targeted protein bind well with targeted protein 4ib4. The interaction of PtF₆ superhalogen with SER are studied by placing PtF₆ at front of ring R1. The geometry of PtF₆ slightly distorted (distorted octahedron) after optimization. The ionization of SER increases after interaction PtF₆. The dissociation energy and thermodynamical parameters of reaction shows interaction PtF₆ with SER moves spontaneously forward direction. The band gap of SER decreases after

interaction PtF6 however chemical softness increase and simultaneously chemical hardness decreases. The nonlinear optical parameters are increase after interaction of PtF6 with SER due to increase moment of π electron. This clearly indicate that interaction of any superhalogen species increase moment of π electron in SER play significant role to design new non linear optical materials.

Acknowledgment

One of the authors, Anil kumar soni, is grateful and thanks to the Uttar Pradesh government (India) [Patrank/degree/vikas/155223/2021-22 dated 25.02.2022] for proviing him funding.

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Annexure-B

Platinum Difluoride: A Theoretical and Computational Based Study

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How to cite this paper: Soni, A.K. and Sahu, V.K. (2023) Platinum Difluoride: A Theoretical and Computational Based Study. *Advances in Biological Chemistry*, 13, 236-246.

<https://doi.org/10.4236/abc.2023.136017>

Received: October 13, 2023

Accepted: December 3, 2023

Published: December 6, 2023

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Abstract

Platinum on reaction with halogen forms three halides viz., platinum (II) chloride, platinum (II) bromide and platinum (II) iodide, except platinum (II) fluoride. In this research work, the not existence of PtF₂ has been studied theoretically. For this thermodynamic, valence bond theory and molecular orbital theory based study have also been performed on this molecule. In order to obtain minimum energy structure we optimized the geometry of this halide by opting AM1 for thermodynamic work and EHT for population analysis. All the calculations were performed on CAChe software. The thermodynamic study supported the presumption of disproportion reaction: 2PtF₂ → Pt + PtF₄. V.B.T showed sd-hybridization rather than sp-hybridization. This was supported by our data as evaluated theoretically by adopting Landis concept, which showed negligible contribution of 5s-orbital of platinum. Mulliken's population analysis based studies have pointed that the overlap is very poor due to the dis-similarity of energy of combining orbitals of Pt and F atom. The Σφ is very small that is 0.2. This also proved that PtF₂ failed to match the criteria of overlapping and thus MOT too. Using eigenvalues and population analysis MO diagram has also been drawn, which clearly supported non-existence of PtF₂ in nature but its existence *in situ* and thus also supported the presumption of disproportionation reaction.

Keywords

PtF₂, Molccecual Mechanics, Quantum Mechanism, VBT and MOT

1. Introduction

Platinum occurs naturally as the elements, generally with small amounts of the other platinum metals [1]. The ability of platinum to exist in many oxidation

states is an important property of this element (0, +2, +3, +4, +5 and +6), which plays an important role in its applications [2] [3]. A number of complexes are formed by the platinum metal in +2 oxidation state. Pt^{2+} is soft acid so stable complexes are formed with S or P as donor atoms but few with O-donors, though there are important amines. +4 oxidation state is more stable for platinum fluoride: " $2PtF_2 \rightarrow Pt + PtF_4$ ", that is why PtF_2 is unknown, presumably unstable with respect to disproportionation: This would occur as a consequence of the stability of low spin d^6 platinum (IV) state and of the oxidizing power of fluorine. The terms "stable" and "unstable" are used to refer to the thermodynamic properties of the complex species considered. Low-spin complexes generally undergo rapid one-electron oxidation or reduction. Due to lower ionization energies (Scheme 1), platinum forms large number of compounds in higher states.

Platinum readily form coordinate complexes and these complexes have their applications in diverse fields: sensors and switches, as catalysts, antimicrobial agents, as biomarkers, as metallopharmaceuticals in treatment of cancer, activate or help to generate redox reactions in photochemistry [4] [5], in biological system [6] [7] [8], materials science [9] [10] [11] and nanoscience [12]. Generally, the compounds formed by platinum are less liable. A survey of literature shows that designing of new ligands that can complexes with platinum in different oxidation states can lead to the develop of new materials [13]. For new materials of diverse applications, there are and will be a continuous step-by-step study to discover new ligands and their new platinum complex.

2. Materials and Methods

In this study platinum (II) fluoride is the study material, which does not exist. That is why it is selected for study rather than other platinum dihalides. The adopted methods for various calculations of platinum difluoride are based on Mulliken's population analysis [14]. Mulliken defined ϕ_i (molecular orbital), $n_{r,i}$ (the contributions of electrons in each occupied MO) and $n_{r-s,i}$ (overlap population that explain bonding, antibonding and nonbonding nature of bond), as below:

$$\phi_i = \sum_{rk} c_{irk} \chi_{rk} \quad (1)$$

$$n_{r,i} = n_i c_{ri}^2 \quad (2)$$

$$n_{r-s,i} = n_i (2c_{ri} c_{si} S_{rs}) \quad (3)$$

here n_i is the number of electron in ϕ_i , $i = 1 - 17$, c_{ri} is the coefficient of atomic orbitals for Pt-atom, c_{si} is the coefficient of AOs for other (X-2 or X-3) and S_{rs} is the overlap integral between the two AOs (one of an atom Pt-1

Pt	IE ₁	IE ₂	IE ₃	IE ₄
KJmol ⁻¹	870	1791	(2800)	(3900)

Values in parentheses are estimated

Scheme 1. Ionization energy/enthalpy of platinum.

or X-2 and one of another atom X-2 or X-3). In order to obtain minimum energy structure we optimized the geometry of each halide by using Extended Hückel Theory (EHT). All the calculations were performed on CAChe software as described in our recent work [14]. From minimum energy structure, we have extracted values of eigenvectors, overlap matrix and eigenvalues. By submitting the values of eigenvector (Table 1) and overlap matrix (Table 2) in Equation (3), we have derived the values of overlap population and tabulated in Table 3. And the summation of values of overlap population was obtained to describe bonding, nonbonding and antibonding molecular orbitals have also been incorporated in this Table. After that using all above along with eigenvalues molecular orbital diagram has been drawn. Before this, we have also examined the nature and contribution of atomic orbitals and then their mixing (valence bond theory) or overlapping (molecular orbital theory). V.B. Theory and M.O. theory on their refinements gave same wave function for the molecule but they differ in their approximations only. Mulliken (1955) [15] [16] [17] [18] also correlated the bonded interaction of V.B.T. with positive overlap population and non-bonded repulsion of V.B.T. with negative population analysis.

3. Results and Discussion

To check the validity of the disproportionation concept that is " $2\text{PtF}_2 \rightarrow \text{Pt} + \text{PtF}_4$ " [1], thermodynamics works have also been performed. The enthalpy (H), entropy (S) and free energy (G) of platinum metal are zero, zero and 1.3432 (kcal/mol), respectively. And that of PtF_2 are 30.176 (kcal/mol), 62.008 (cal/mol) and 11.692 (kcal/mol), respectively. And of PtF_4 are 4140.219 (kcal/mol), 4139.767 (cal/mol) and +57.193 (kcal/mol), respectively. The change in enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) are (kcal/mol) for the reaction is 4089.867, 4015.751 and -1,192,603, respectively. And after that of bonding nature in platinum difluoride has been studied. The optimized geometry as obtained from molecular mechanics method of platinum (II) fluoride is shown in Figure 1.

The MOs of this molecule as formed by linear combination of nine orbitals (five 4d-orbitals, one 5s orbital and three 5p orbitals) from ruthenium and four orbitals (three 2p orbitals and one 2s orbital) from each bromine are shown below

$$\text{Pt-1} = 5dx^2-y^2, 5dz^2, 5dxy, 5dxz, 5dyz, 6s, 6px, 6py, 6pz = 9$$

$$\text{F-2} = 2s, 2px, 2py, 2pz = 4$$

$$\text{F-3} = 2s, 2px, 2py, 2pz = 4$$

$$\text{Total} = 17$$

In order to examine the contribution of various atomic orbitals in the formation of molecular orbitals the LCAO has been studied. The 17 AOs on LCAO approximations give 17 MOs. Thus, $\chi_1 - \chi_9$ are AOs of platinum ($\chi_1 = 6s$, $\chi_2 = 6px$, $\chi_3 = 6py$, $\chi_4 = 6pz$, $\chi_5 = 5dx^2 - y^2$, $\chi_6 = 5dz^2$, $\chi_7 = 5dxy$, $\chi_8 = 5dxz$, $\chi_9 = 5dyz$)

Table 1. Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ) of PtF_2 .

Atom	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}	ϕ_{13}	ϕ_{14}	ϕ_{15}	ϕ_{16}	ϕ_{17}
Pt-1	χ_1	-0.0229	-0.0000	0.0751	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.3609	-0.0005	0.0000	0.9884	0.0000
	χ_2	0.0000	-0.0024	0.0000	0.0000	0.0000	0.0470	0.0032	-0.0000	0.0000	0.0000	0.0000	0.0000	0.1013	-0.0020	0.0000	1.1344
	χ_3	0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0004	-0.0012	0.0188	0.0000	-0.0000	-0.0000	-0.0000	0.0631	-1.0023	-0.0000	-0.0095
	χ_4	0.0000	0.0002	0.0000	0.0000	-0.0000	-0.0048	-0.0188	-0.0012	-0.0000	-0.0000	-0.0000	0.0000	0.9972	0.0636	0.0005	-0.1146
	χ_5	-0.0270	-0.0000	0.1456	-0.0098	-0.0010	-0.0000	-0.0000	-0.0017	-0.5050	0.0103	-0.1006	-0.7948	-0.0002	0.0000	0.3438	0.0000
F-2	χ_6	0.0153	-0.0000	-0.0824	0.0168	-0.0011	-0.0000	0.0000	-0.0000	-0.8573	0.0108	0.1724	0.4496	0.0001	-0.0000	-0.1945	-0.0000
	χ_7	0.0005	0.0000	-0.0024	-0.0060	-0.0965	-0.0000	0.0000	0.0000	0.0085	0.9902	-0.0604	0.0133	-0.0000	0.0000	-0.0058	0.0000
	χ_8	0.0055	0.0000	-0.0294	-0.0950	0.0061	0.0000	0.0000	-0.0000	-0.1000	-0.0620	-0.9751	0.1606	-0.0000	-0.0000	-0.0695	-0.0000
	χ_9	0.0000	0.0000	0.0002	0.0014	0.0097	-0.0000	-0.0000	-0.9949	0.0008	-0.0996	0.0144	-0.0013	0.0000	0.0000	0.0006	0.0000
	χ_{10}	-0.6995	0.7077	-0.0367	0.0000	0.0000	-0.0124	0.0000	0.0000	0.0000	0.0000	0.0000	0.0471	0.0001	-0.0000	-0.2300	-0.3013
F-3	χ_{11}	-0.0044	-0.0044	-0.6640	-0.0701	-0.0014	-0.6929	-0.0711	0.0014	-0.0000	-0.0002	0.0114	-0.1374	-0.0082	0.0002	0.2663	0.2713
	χ_{12}	0.0000	-0.0004	0.0056	-0.0440	-0.6981	0.0058	-0.0443	0.7043	0.0000	-0.0000	0.0070	0.0011	-0.0051	0.0804	-0.0022	-0.0023
	χ_{13}	0.0004	0.0000	0.0670	-0.6946	0.0443	0.0695	-0.7007	-0.0447	-0.0000	0.0070	0.1121	0.0139	-0.0800	-0.0051	-0.0269	-0.0274
	χ_{14}	-0.6995	0.0000	-0.0367	-0.0000	-0.0000	0.0124	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0471	0.0001	0.0000	-0.2300	0.3013
	χ_{15}	0.0044	-0.7078	0.6640	0.0711	0.0014	-0.6928	-0.0713	0.0014	-0.0000	0.0002	-0.0114	0.1374	-0.0080	0.0002	-0.2663	0.2713
	χ_{16}	-0.0000	0.0000	-0.0056	0.0440	0.6980	0.0058	-0.0443	0.7043	0.0000	0.1126	-0.0070	-0.0012	-0.0051	0.0804	0.0022	-0.0023
	χ_{17}	-0.0004	0.0000	-0.0672	0.6944	-0.0443	0.0705	-0.7007	-0.0447	0.0000	-0.0070	-0.1121	-0.0139	-0.0800	-0.0051	0.0269	-0.0274

Table 2. Overlap matrix or overlap integrals values (S_{ij}) of various overlaps of atomic orbitals of constituent atoms in PtF_2 .

AOs	6s	6px	6py	6pz	5d x^2-y^2	5dz 2	5dxy	5dxz	5dyz	2s	2px	2py	2pz	3s	2px	2py	2pz
6s (Pt-1)	1.0000									(F-2)	(F-2)	(F-2)	(F-2)	(F-3)	(F-3)	(F-3)	(F-3)
6px (Pt-1)	0.0000	1.0000															
6py (Pt-1)	0.0000	0.0000	1.0000														
6pz (Pt-1)	0.0000	0.0000	0.0000	1.0000													
5d x^2-y^2 (Pt-1)	0.0000	0.0000	0.0000	0.0000	1.0000												
5dz 2 (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000											
5dxy (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000										
5dxz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
5dyz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000								
2s (F-2)	0.1701	0.2642	-0.0022	-0.0267	0.0876	-0.0495	-0.0015	-0.0177	0.0001	1.0000							
2px (F-2)	-0.1400	-0.2106	0.0023	0.0280	-0.0901	0.0505	0.0019	0.0227	-0.0002	0.0000	1.0000						
2py (F-2)	0.0012	0.0023	0.0669	-0.0002	0.0015	-0.0004	0.0442	-0.0002	-0.0045	0.0000	0.0000	1.0000					
2pz (F-2)	0.0141	0.0280	-0.0002	0.0641	0.0136	-0.0128	-0.0002	0.0414	-0.0003	0.0000	0.0000	0.0000	1.0000				
2s (F-3)	0.1701	-0.2641	0.0022	0.0267	0.0876	-0.0495	-0.0015	-0.0177	0.0001	0.0000	0.0000	0.0000	1.0000				
2px (F-3)	0.1400	-0.2106	0.0023	0.0281	0.0901	-0.0505	-0.0019	-0.0227	0.0002	0.0000	-0.0001	0.0000	0.0000	1.0000			
2py (F-3)	-0.0012	0.0023	0.0669	-0.0002	-0.0015	0.0004	-0.0442	0.0002	0.0045	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000		
2pz (F-3)	-0.0142	0.0281	-0.0002	0.0641	-0.0136	0.0128	0.0002	-0.0414	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	

Table 3. Coefficient values of $4d_{xy}$, $4d_{xz}$, $4d_{x^2-y^2}$, $5s$, $5p_x$, $5p_y$, $5p_z$ AOs of PtF_2 .

MOs	$5d_{z^2}$ (Pt-1)	$5d_{xy}$ (Pt-1)	$5d_{xz}$ (Pt-1)	$6s$ (Pt-1)	$6p_x$ (Pt-1)	$6p_y$ (Pt-1)	$6p_z$ (Pt-1)
ϕ_1	0.0153	0.0005	0.0055	0.0229	0.0000	0.0000	0.0000
ϕ_2	0.0000	0.0000	0.0000	0.0000	0.0024	0.0000	0.0002
ϕ_3	0.0824	0.0024	0.0294	0.0751	0.0000	0.0000	0.0000
ϕ_4	0.0168	0.0060	0.0950	0.0000	0.0000	0.0000	0.0000
ϕ_5	0.0011	0.0965	0.0061	0.0000	0.0000	0.0000	0.0000
ϕ_6	0.0000	0.0000	0.0000	0.0000	0.0470	0.0004	0.0048
ϕ_7	0.0000	0.0000	0.0000	0.0000	0.0032	0.0012	0.0188
ϕ_8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0188	0.0012
ϕ_9	0.0000	0.1005	0.0083	0.0000	0.0000	0.0000	0.0000
ϕ_{10}	0.8573	0.0085	0.1000	0.0000	0.0000	0.0000	0.0000
ϕ_{11}	0.0108	0.9902	0.0620	0.0000	0.0000	0.0000	0.0000
ϕ_{12}	0.1724	0.0604	0.9751	0.0000	0.0000	0.0000	0.0000
$\Sigma =$	1.1561	1.2650	1.2814	0.0980	0.0526	0.0204	0.0250



Bond Length=2.019Å

Bond Angle=179.99°

Figure 1. Structure of PtF_2 .

Table 4. Quantitative and qualitative nature of occupied molecular orbitals of platinum difluoride.

MO No.	$\Sigma n_{r,s,l}$	sign	MOs	MO No.	$\Sigma n_{r,s,l}$	sign	MOs
ϕ_1	0.0198	+	BMO	ϕ_7	0.0035	+	BMO
ϕ_2	-0.0016	+	ABMO	ϕ_8	0.0036	+	BMO
ϕ_3	0.0720	+	BMO	ϕ_9	0.0000	0	NBO
ϕ_4	0.0121	+	BMO	ϕ_{10}	0.0000	0	NBO
ϕ_5	0.0121	+	BMO	ϕ_{11}	-0.0200	-	ABMO
ϕ_6	0.0275	+	BMO	ϕ_{12}	-0.0200	-	ABMO

and χ_{10} - χ_{17} are AOs of chlorine ($\chi_{10} = 3s$, $\chi_{11} = 3p_x$, $\chi_{12} = 3p_y$, $\chi_{13} = 3p_z$ for F-2 and $\chi_{14} = 3s$, $\chi_{15} = 3p_x$, $\chi_{16} = 3p_y$, $\chi_{17} = 3p_z$ for F-3). The magnitude of contribution of various AOs (χ) in the formation of 17 MOs (ϕ_1 to ϕ_{17}) is demonstrated in Table 4 reflected that nine AOs (χ_2 , χ_3 , χ_4 , χ_7 , χ_9 , χ_{12} , χ_{13} , χ_{16} , χ_{17}) have no contribution in the formation of 1st MO (ϕ_1) as these have zero or near zero coefficient values. And the rest eight AOs (χ_1 , χ_5 , χ_6 , χ_8 , χ_{10} , χ_{11} , χ_{14} , χ_{15}) have their contribution in ϕ_1 . By adopting same view the contributions AOs in ϕ_2 to ϕ_{17} MOs can also be described. The characteristics of transition metal (TM) elements are due to their d orbitals of (n - 1) shell and s and p

orbitals of n shell. As the atom of TM elements form compound they adopt either concept of bonded attraction and non-bonded repulsion of VB (Valence Bond) theory and or positive and negative overlap populations of MO (Molecular Orbital) theory [17] [18] [19] [20]. In the first case, they may undergo various type of hybridization that depends upon the oxidation state of TM and number and nature of combining atoms or ions, and in the second case formation of molecular orbital by LCAO approximation [19]. At first we have to examine the extent of involvement of 4d, 5s and 5p AOs of Pt-1 in the formation of MOs in platinum dihalides. For this, values of coefficient " χ " of $5d_z^2$, $5d_{xy}$, $5d_{xz}$, 6s, $6p_x$, $6p_y$ and $6p_z$ have presented in Table 3. The " χ " of non-bonding orbitals $5d_{x^2-y^2}(\chi_5)$ and $5d_{yz}(\chi_9)$ are excluded. It was Landis, who discovered sd^n -hybridization ($n = 1$ to 5) along with molecular shape and bond angles in his seminal publications [20] [21] [22]. Further, he also explained co-relationship between sd^n -hybridization and its bond angle by plotting a graph between energy and bond angle. In order to explore atomic orbitals detail with respect to hybridization, we have examined the contribution of 5d, 6s and 6p AOs of Pt-1 in PtF_2 . For this only occupied MO ($\phi_1 - \phi_{12}$) were considered. And values of c_i of each χ of $5d_z^2$, $5d_{xy}$, $5d_{xz}$, 6s, $6p_x$, $6p_y$ and $6p_z$ of above twelve molecular orbitals were added and the results were tabulated in Table 3. Analysis of this table reflected that major contributions are from orbitals of 5d and 6s. The negligible contribution of 5s-orbital has disclosed sd -hybridization. The involvement of three p-orbitals is negligible as their summation values are very low in comparison to d-orbital and considerably also low with respect to s-orbital. The graphical point of view of the same is reflected from Figure 2.

The shape of each MO ($\phi_1 - \phi_{17}$) has been determined by the relative magnitudes and signs of the different coefficients. For this the $Pt(II)X_2$ has been decomposed into three parts: Pt-1, F-1 and F-2, and the MO of the complete system has been obtained by allowing the orbitals of Pt-1 (5d, 6s, 6p), F-1 (ns and np) and F-2 (ns and np) to overlap. The combining atomic orbital must have 1)

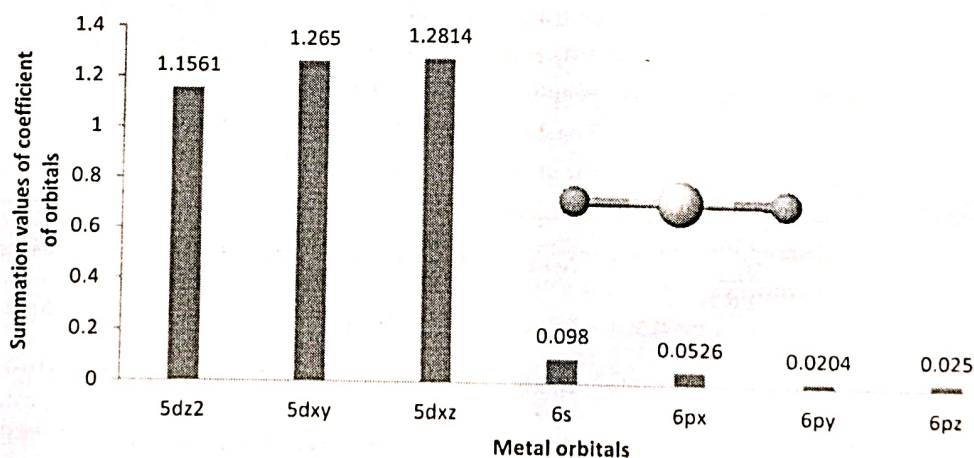


Figure 2. Extent of involvement of metal orbital in the formation of MOs of PtF_2 .

same or nearly same energy *i.e.*, comparable energy, 2) proper orientation *i.e.*, same symmetry about the molecular axis and 3) extent of overlapping of orbitals should be maximum *i.e.*, not less than 40%.

The energy gap between overlapping orbitals of Pt and halogen (F, Cl, Br, I) atoms in platinum halides as demonstrated in Scheme 2 also proved the not existence of PtF₂ molecule. As orbital of the metal, Pt and halogen, F of this molecule has maximum instability *i.e.*, having different energy. The possible overlaps between the various AOs of ruthenium (Pt-1) and halogens (F-2 and F-2) in each MO will be 88. To solve Equation (3) for these 88 overlaps in MOs of platinum difluoride, we need eigenvector values (C_r and C_s), values of overlap matrix (S_{rs}) and number of electrons (n_i) in each MO. The eigenvector and overlap integral values for platinum difluoride have been taken from Table 1 and Table 2, respectively. The number of electrons is taken as two for ϕ_1 to ϕ_{12} and zero for ϕ_{13} to ϕ_{17} . Finally, Equation (3) has been solved for twelve MOs. The summation values of overlap population of these twelve MOs have been presented in Table 4.

In order to get a precise description, the sum of overlap population for the twelve MOs of PtF₂ has also been worked out and results are presented in Table 4. As can be seen from the table among the twelve molecular orbitals, seven are bonding, two are nonbonding and three are antibonding. The bonding molecular orbitals are ϕ_1 and $\phi_3 - \phi_8$. The nonbonding molecular orbitals are ϕ_9 and ϕ_{10} , which are purely two d atomic orbitals of platinum namely dx^2-y^2 and dyz . The three antibonding molecular orbitals are ϕ_2 and $\phi_{11} - \phi_{12}$. All these have also been clearly shown by Figure 3.

4. Conclusions

1) The thermodynamic study supported the presumption of disproportionation reaction: $2PtF_2 \rightarrow Pt + PtF_4$.

2) V.B.T showed sd-hybridization rather than sp-hybridization. This was supported by our data as evaluated theoretically by adopting Landis concept, which showed negligible contribution of 5s-orbital of platinum.

3) Mulliken's population-based studies have pointed that the overlap is very poor due to dissimilarity of energy of combining orbitals of Pt and F atom. The $\Sigma\phi$ is very much low that is 0.2. This also proved that PtF₂ failed to match the criteria of overlapping and thus MOT, too.

PtF ₂					
$\Delta_{5d-2s} = 1.007$	$\Delta_{5d-2p} = 0.202$	$\Delta_{6s-2s} = 1.136$	$\Delta_{6s-2p} = 0.332$	$\Delta_{6p-2s} = 1.269$	$\Delta_{6p-2p} = 0.464$
PtCl ₂					
$\Delta_{5d-3s} = 0.504$	$\Delta_{5d-3p} = 0.059$	$\Delta_{6s-3s} = 0.633$	$\Delta_{6s-3p} = 0.188$	$\Delta_{6p-3s} = 0.765$	$\Delta_{6p-3p} = 0.321$
PtBr ₂					
$\Delta_{5d-4s} = 0.348$	$\Delta_{5d-4p} = 0.019$	$\Delta_{6s-4s} = 0.477$	$\Delta_{6s-4p} = 0.148$	$\Delta_{6p-4s} = 0.610$	$\Delta_{6p-4p} = 0.280$
PtI ₂					
$\Delta_{5d-5s} = 0.199$	$\Delta_{5d-5p} = 0.016$	$\Delta_{6s-5s} = 0.328$	$\Delta_{6s-5p} = 0.113$	$\Delta_{6p-5s} = 0.460$	$\Delta_{6p-5p} = 0.246$

Scheme 2. Energy gap between overlapping orbitals of Pt and halogen (F, Cl, Br, I) in platinum halides.

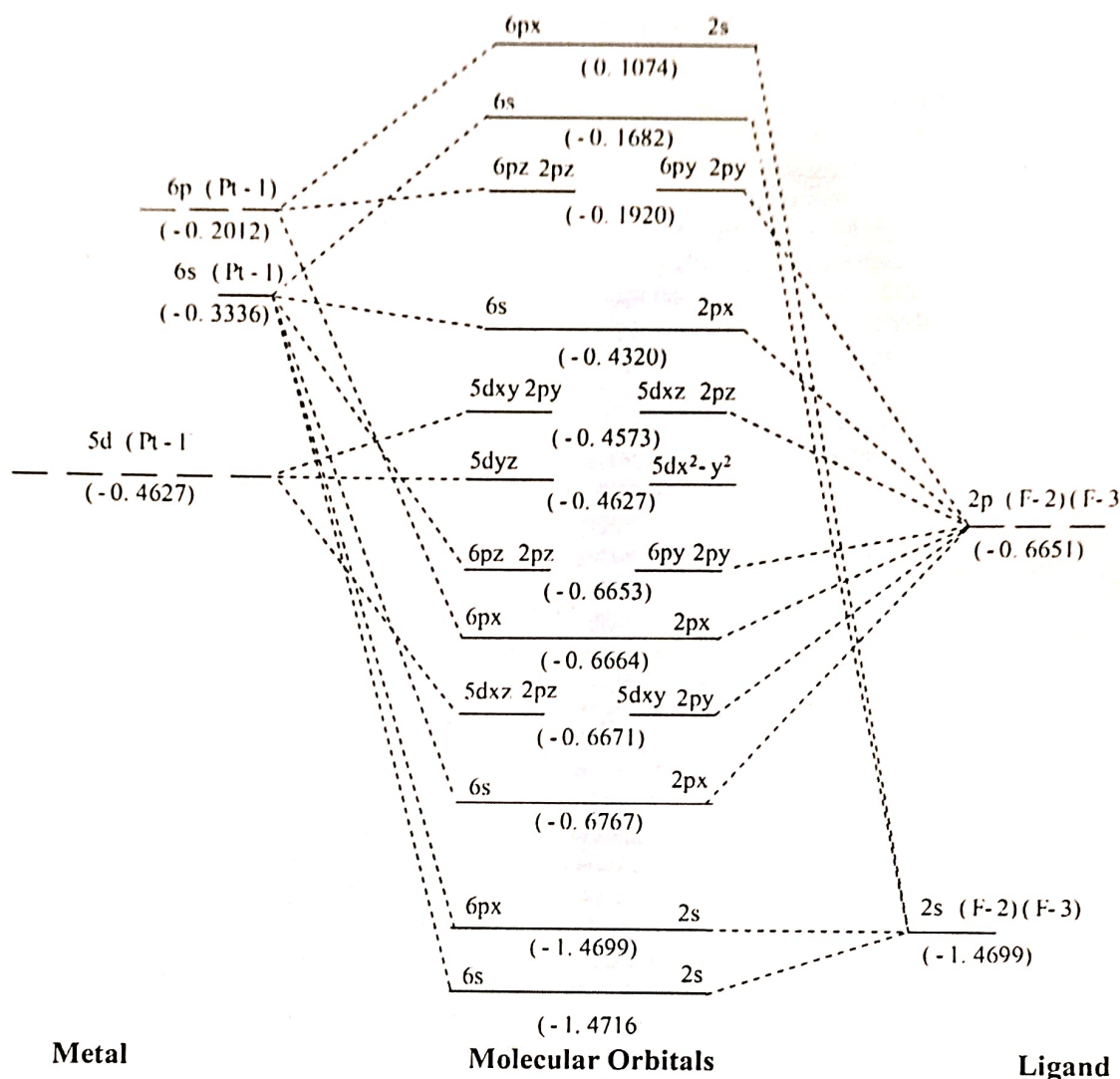


Figure 3. MO diagram of PtF₂ along with the energy of AOs and MOs in eV as shown in parenthesis.

4) Using eigenvalues and population analysis MO diagram has also been drawn, which clearly supported non-existence of PtF₂ in nature but its existence *in situ* and thus also supported presumption of the disproportionation reaction.

Acknowledgements

Authors are thankful to the Principal, Shia P.G. College, Sitapur Road, Lucknow for laboratory facilities and support. Anil Kumar Soni also gratefully acknowledges the financial support (Letter No./Reginal office Lucknow/5496-99/2021-22, Dated; 15-03-2022) given by Research & Development, Lucknow (U.P.).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Annexure-C



Superacidic Properties of Protonated PtF_n ($n = 1-6$) and Their Ability to Form Supersalts: DFT Study

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In the present communication, this study has modeled protonated PtF_n ($n = 1-6$), a new series of superacids. The calculated vertical de-attachment energy (VDE) of PtF_n ($n = 1-6$) reestablishes the superhalogenic behavior. The vibrational frequency, dissociation energy through the HF channel, and optimized geometries are utilized to discuss the stability of HPTF_n ($n = 1-6$). The deprotonation energy of HPTF_n is used to calculate the acidic strength of HPTF_n ($n = 1-6$). The acidity of protonated PtF_n ($n = 1-6$) is directly related to its counterpart superhalogen anions. The computed correlation factor ($R^2 = 0.9754$) shows that VDE is directly associated with acidity. The mechanism of acidity of HPTF_n ($n = 1-6$) is described by using natural bond orbital analysis charges on atoms. The electronic properties of HPTF_n ($n = 1-6$) are calculated using the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy. The nature of chemical reactivity is also determined by the HOMO–LUMO plot of HPTF_n ($n = 1-6$). It has formed the supersalts using superacids HPTF_n ($n = 1-6$) and superbase (OLi_3OH), and the nature of supersalts is compared with traditional salt LiF . The most stable conformers of supersalts PtF_nOLi_3 ($n = 2-6$) are analyzed for optoelectronic properties. It has computed the dissociation of supersalts through neutral and anions through superhalogens and superalkalis. The computed results show that PtF_4OLi_3 favors dissociation through anions as in traditional salts. The nonlinear optical parameters are calculated using dipole moment, mean polarizability, anisotropic polarizability, molar reflectivity (MR), order parameters, and hyperpolarizability of PtF_nOLi_3 ($n = 2-4$). The estimated nonlinear optical properties parameters are compared with corresponding parameters of traditional salt LiF by the same level theory.

1. Introduction

Various applications of superhalogens are in chemical and health industries as air purifying agents,^[1,2] electrolytic salts for lithium-ion batteries,^[3,4] and efficient materials for hydrogen storage.^[5] In the last three decades, researchers have paid close attention to the discovery of new classes of superhalogens in order to design new superacids. Hall and Constant coined the term superacids in 1927,^[6] but Gillespie^[7,8] was the first to publish a scientific idea about superacids. Superacids are any species more acidic than 100% H_2SO_4 or with a Hammett acidity function less than -12 . The chemistry of superacids is first introduced by Olah and Hogeveen.^[9,10] The Gibbs' free energy change for deprotonation^[11,12] is an important parameter for calculating species' acidity strength. For superacid, the calculated Gibbs deprotonation energy is less than the corresponding value of pure sulfuric acid ($302.2 \text{ kcal mol}^{-1}$). The protonated superhalogens are the building blocks of superacids. The superacids have a wide range of applications in petrochemistry, e.g., catalysts for alkylations.^[6] One of the important applications of superacids is in alkane isomerization and hence superacids are a useful material in the field of the catalyst industry.^[7] The superacids have wide

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DOI: 10.1002/masy.202300084

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industrial applications, e.g., triflic acid, which is already employed in fine chemical synthesis, batteries, and ionic liquids anions.^[8] The superacids are used as catalysts to synthesize new materials which are useful in the medical field.^[9,10]

The combination of antimony pentafluoride (SbF_5) and fluoro-sulfuric acid (HSO_3F) in the molar ratio of 1:1 is known as magic acid, which was first synthesized by Olah and Schlosberg.^[11] This magic acid fulfills the criteria of superacids that can cooperate with hydrocarbons. The superacids are of three types; Bronsted, Lewis, and conjugate of Bronsted/Lewis acids. Currently, work is being done to discover a new class of superacids through conjugate Bronsted/Lewis combinations.^[14,15] The most acidic superacid HSbF_6 reported till now is also incorporated with Lewis acid (SbF_5) and Bronsted acid (HF).^[16,17] In HSbF_6 , HF is Bronsted acid that relies on H^+ ; however, F^- combined with Lewis acid SbF_5 forms SbF_6^- and behaves as a superhalogen. The calculated deprotonation energy of $\text{F}(\text{SO}_3)_2\text{H}$, $\text{FSO}_3\text{SbF}_5\text{H}$, and HAlCl_4 species belongs to the superacid family,^[16,18] but the acidity strength of these species is greater than that of the strongest superacid, HSbF_6 (255.5 kcal mol⁻¹).^[17] The reported species $\text{HAL}_n\text{F}_{3n+1}$ ($n = 1-4$) are more acidic than HSbF_6 for $n > 4$.^[19] As an extension of this work, protonation of anions of superhalogens $\text{In}_n\text{F}_{3n+1}$, $\text{Sn}_n\text{F}_{4n+1}$, and $\text{Sb}_n\text{F}_{5n+1}$ ($n = 1-3$) are also reported.^[20] Ambrish et al. reported protonated hypervalent superhalogen anions $\text{B}(\text{BF}_4)_4^-$, $\text{B}(\text{AlF}_4)_4^-$, $\text{Al}(\text{BF}_4)_4^-$, and $\text{Al}(\text{AlF}_4)_4^-$ showing more acidity than the strongest superacid HSbF_6 .^[21] The researchers^[22-27] are trying to explore new superacids using the combination of Bronsted/Lewis acids, which can react to very weak bases. The acidity of any superacid is determined by the electronic stability of its anionic superhalogen component. The VDE is an important parameter to determine the electronic stability of the anionic part of the superhalogen. In the present communication, we have examined the superacidic properties of protonated superhalogens of PtF_n ($n = 1-6$), which is already examined using the DFT/SDD method.^[28] Several electronic properties of protonated superhalogens are discussed using the electronic properties of these superacids described by highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) orbitals. The whole study is divided into four segments. In the first segment, we discussed the stability of protonated superhalogen dissociation through the HF channel and the deprotonation energy of HPtF_n ($n = 1-6$). In the second segment, using NBO charge, we discussed the mechanism of acidity of HPtF_n ($n = 1-6$) and the relation between their acidity and vertical de-attachment energy (VDE). In the third segment, we examined several electronic properties of HPtF_n ($n = 1-6$) by using HOMO and LUMO energies.

In the last segment, we explored the formation and stability of supersalts by using superacids and superbase (OLiOH). Due to numerous applications of supersalts in the field of various photonic technologies, including optical switching and data processing,^[29,30] a number of inorganic, organic nonlinear optical properties (NLO) materials, and organometallic have been studied.^[31] The NLO materials have excess electron donor and electron acceptor units in such a way that the movement of electron cloud from donor to acceptor creates high polarizability as compared with traditional salt LiF . In the present communication, we have also discussed the electro-optical behavior of supersalts.

2. Computational Method

The initial geometry of protonated PtF_n ($n = 1-6$) and corresponding anions of superhalogens are formed by using GaussView 6.0.^[32] The modeled geometries are optimized by using a self-consistent field with a linear combination of atomic orbital-molecular molecular by using the Gaussian 16W software package.^[33] All calculations are performed using DFT^[34,35] with the B3LYP method.^[36,37] In the present work, we have employed the SDD basis set^[38,39] for Pt and 6-31++G (d, p) for F and H atoms.^[40-42] Several researchers have already employed this method for geometry optimization.^[43,44] All geometries are optimized along with normal mode frequencies. The geometries corresponding to minima on potential energy surface (PES) are employed for further calculations.

The HOMO and LUMO electronic orbitals are plotted with the help of Gauss View 6.0.^[32] The VDE of anions PtF_n is calculated by

$$\text{VDE} = E(\text{PtF}_n^-)_{\text{optimized}} - E(\text{PtF}_n)_{\text{single point}} \quad (1)$$

The energy required to move an anion from its ground vibronic state to its neutral ground vibronic state is transition energy. Adiabatic detachment energy (ADE) of a system is the energy needed to optimize the geometry of any system from the ground state anions geometry.

Adiabatic electron affinity of any species calculated by

$$\text{ADE} = E(\text{PtF}_n^-)_{\text{Opt}} - E(\text{PtF}_n)_{\text{Opt}} \quad (2)$$

The vertical detachment energy (VDE) is defined as the energy difference between the optimized geometry of the anionic species of PtF_n and the corresponding energy of its neutral state. The ADE basically measures the change in geometry of the optimized anionic state after removing the charge. The VDE measures the energy difference without changing the geometry of anionic PtF_n to correspond to its neutral stage.

3. Result and Discussion

3.1. Geometry of Anions of PtF_n ($n = 1-6$)

First, we have modeled all possible structures of anions of PtF_n ($n = 1-6$), and after geometries optimization, the most stable geometries of neutral molecules (Figure 1) and anions (Figure 2) of PtF_n ($n = 1-6$) are plotted. The bond length in between PtF^- is 1.96 Å with $C_{\infty v}$ symmetry. The average bond length between $\text{Pt}-\text{F}$ is 1.98 Å in PtF_2^- with $D_{\infty h}$ symmetry. The FeF_3^- shows trigonal type geometry with D_{3h} symmetry showing trigonal structure. The bond length $\text{Pt}-\text{F}$ at the top is 2.04 Å, which is 0.06 Å greater than other PtF bonds. In anions of PtF_4 , two geometries are stable; however, the square plane of anion PtF_4^- is more stable than the tetrahedral geometry of anion PtF_4^- , so we have discussed only the square planer geometry of anionic PtF_4^- . The PtF_4^- shows a square planer with all four bonds between $\text{Pt}-\text{F}$ nearly equal to 1.96 Å. For $n = 5$, PtF_5^- , five F atoms attached with the central Pt atom show distorted trigonal bipyridyl structure. In this structure, two F atoms lie in an axial plane and are slightly enlarged to

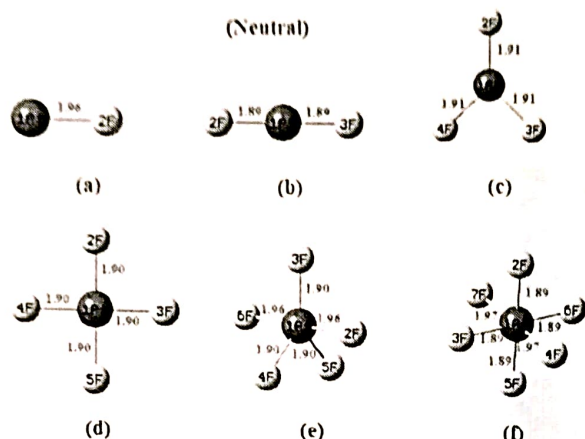


Figure 1. Equilibrium geometries of PtF_n ($n = 1-6$) neutral. The central blue sphere represents (Pt) atoms, and peripheral light-blue spheres represent (F) atoms with bond lengths (in Å).

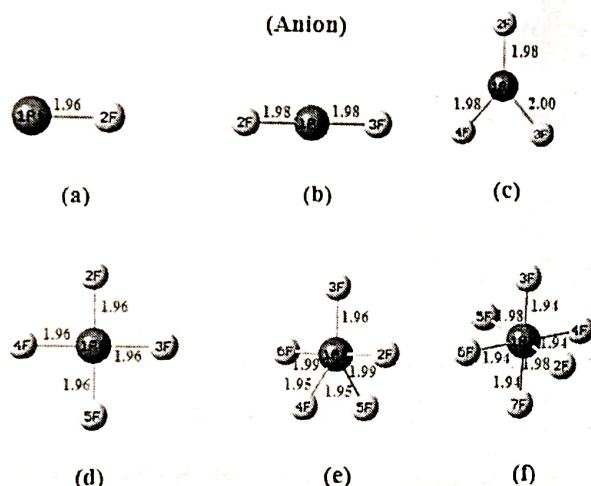


Figure 2. Equilibrium geometries of PtF_n ($n = 1-6$) anion. The central blue sphere represents (Pt) atoms, and peripheral pale light-blue spheres represent (F) atoms with bond lengths (in Å).

1.99 Å; however, the other three F atoms form tetrahedral geometry with bond lengths between 1.95 and 1.96 Å. Initially modeled PtF_6^- geometry is octahedral; however, after geometry optimization due to Jahn-Teller distortion geometry of PtF_6^- changes O_h to D_{4h} symmetry. The axial bond length between Pt-F is elongated to 1.98 Å compared to all four-bond lengths Pt-F in the tetrahedral plane (1.94 Å). The calculated geometry parameters of PtF_n ($n = 1-6$) are well-matched with the reported geometries.^[28] The calculated VDE and adiabatic de-attachment energy (ADE) (Table 1) of PtF_n ($n = 1-6$) reestablishes their superhalogenic behavior for $n > 1$.

3.2. Geometry and Stability of HPtF_n ($n = 1-6$)

We have calculated several geometries of protonated anions of PtF_n ($n = 1-6$) or HPtF_n ($n = 1-6$). The geometry of all structures is optimized. After optimization of all possible geometry of

Table 1. Calculated vertical detachment energies (VDEs) and adiabatic electronic affinities (AEAs) of optimized PtF_n ($n = 1-6$) complexes.

Species	VDE [eV]	AEA [eV]
PtF	2.64	2.64
PtF_2	4.84	4.85
PtF_3	4.85	4.49
PtF_4	5.51	6.50
PtF_5	6.70	6.74
PtF_6	8.40	8.41

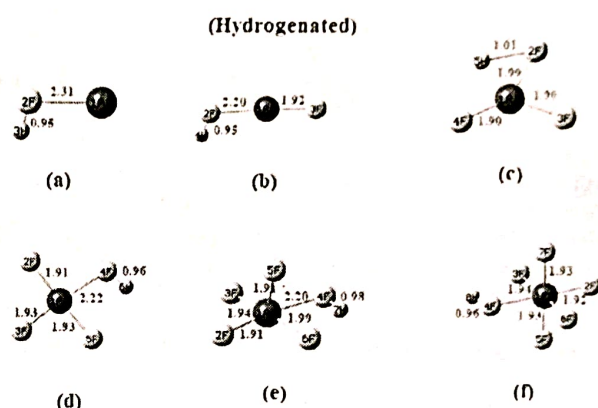


Figure 3. Equilibrium geometries of PtF_n ($n = 1-6$) hydrogenated. The central blue sphere represents (Pt) atoms, and peripheral light-blue spheres represent (F) atoms with bond lengths (in Å).

HPtF_n , the most stable conformers are collected in Figure 3. The bond length between Pt-F is underestimated in hydrogenated as compared with the respective bond length in anions of PtF_n . The most stable geometry of HPtF_n ($n = 1-6$) shows that the bond length between Pt-FH is elongated as compared with the rest of Pt-F. The calculated bond lengths of Pt-FH lie between 2.31 and 1.99 Å; however, the bond lengths of HF lie between 0.96 and 1.01 Å in HPtF_n . The calculated bond length Pt-FH attains the highest value for $n = 1$ and lowest for $n = 3$. The bond length H-F falls to the highest value for $n = 3$ in HPtF_n .

The optimized geometry of HPtF_n (Figure 3) can be represented as $\text{PtF}_{n-1}/\text{HF}$. We have further optimized all geometries of $\text{PtF}_{n-1}/\text{HF}$; the most optimized geometry and respective bond lengths are presented in Figure 3. In HPtF_1 , the bond length between Pt-FH becomes slightly larger, 1.99 Å, as compared with other Pt-F, which are 1.90 Å. However, hydrogen in HF nearly behaves as a free entity, but hydrogen shows nonbonding interaction with the F_4 atom, and the whole geometry of HPtF_1 is slightly distorted from symmetry. In the next HPtF_4 ($n = 4-6$), bond lengths between Pt-HF are overestimated than other bonds between Pt-F; however, the bond length between H-F is equivalent to the corresponding bond length HF in the free state. This way, we write HPtF_n to be composed of two entities, $\text{HF}/\text{PtF}_{n-1}$. Let us calculate the dissociation of HPtF_n through the HF channel. For This, we have designed various components of Pt_{n-1} and HF using the Gauss view and most stable optimized geometries of $\text{PtF}_{n-1}/\text{HF}$ are shown in Figure 1. The calculated bond HF (0.96 Å) is nearly comparable with the observed HIF bond length

Table 2. Calculated values of highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy band gap (ΔE_{gap}), free energy change for deprotonation (ΔG_{depro}), and deprotonation energy (ΔE_{depro}) for H-PtF_n ($n = 1-6$).

Species	Symmetry	ΔE_{depro} [eV]	G_{depro} [kcal mol ⁻¹]
H-PtF	C _s	0.44	307.48
H-PtF ₂	C _s	1.39	285.58
H-PtF ₃	C _s	1.26	287.59
H-PtF ₄	C _i	1.71	278.11
H-PtF ₅	C _i	1.97	270.77
HPtF ₆	C _i	1.90	264.75

in a free state. The calculated bond length Pt–F lies between 1.89 and 1.97 Å. The linear geometry PtF shows C_{infv} symmetry. The PtF₂ shows nearly linear geometry with D_{infh} shorter PtF bond length than the corresponding bond length in PtF complexes. The trigonal geometry of PtF₃ has C_{2v} symmetry. The initial geometry of PtF₄ is tetrahedral, and after optimization, the geometry changes to distorted planer geometry with C_s with slightly lower negative energy than square planer geometry with D_{4h} symmetry. In the present communication, we have only considered the square planer geometry of PtF₄. The PtF₅ has planer geometry C_s. The initial O_h geometry of PtF₆ changes to D_{4h} geometry due to the Jahn–Teller distortion.

The calculated bond length for PtF_n ($n = 1-6$) in neutral and anionic complexes is well-matched with previously calculated results.^[28]

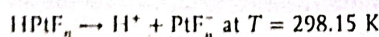
In the next section, let us check the stability of HPtF_n ($n = 1-6$) dissociation through the HF channel by using the following equation

$$\Delta E_n = -\{E[\text{HPtF}_n] - E[\text{PtF}_{n-1}] - E[\text{HF}]\} \quad n = 1-6 \quad (3)$$

The dissociation energy of HPtF_n ($n = 1-6$) through the HF channel is calculated and listed in Table 2. The calculated dissociation energy $\Delta E_{\text{diss}} > 0$ implies that HPtF_n ($n = 1-6$) is stable through the HF channel. This way, the HPtF_n superacid can be represented by the combination of PtF_{n-1} (Lewis acids) and HF (Bronsted acid). Except for HPtF₃, where the hydrogen of Pt–FH interacts with the F₄ atom, the calculated dissociation energy increases continuously from $n = 1-6$, indicating a discontinuity in deprotonation energy in HPtF₃.

3.3. Deprotonation Energy of HPtF_n

The acidity of any species is defined by deprotonation energy. The deprotonation energy of any species can be computed by



$$\Delta G_{\text{acid}} = \Delta G[\text{PtF}_n^-] + \Delta G[\text{H}^+] - \Delta G[\text{HPtF}_n] \quad (n = 1-6) \quad (4)$$

where the value $\Delta G[\text{H}^+] = -6.28 \text{ kcal mol}^{-1}$ is taken from the literature.^[49]

The deprotonation energy of HPtF_n ($n = 1-6$) is calculated and listed in Table 2. According to this table, the calculated deprotonation energy of HPtF is greater than the indicated deprotonation

Table 3. Calculated NBO charges on HF/PtF_{n-1} ($n = 1-6$).

Species	PtF _{n-1}	H	F	HF
HPtF	-0.148	0.492	-0.344	0.148
HPtF ₂	-0.163	0.515	-0.352	0.163
HPtF ₃	-0.163	0.501	-0.336	0.165
HPtF ₄	-0.181	0.518	-0.337	0.181
HPtF ₅	-0.194	0.519	-0.325	0.194
HPtF ₆	-0.244	0.575	-0.330	0.345

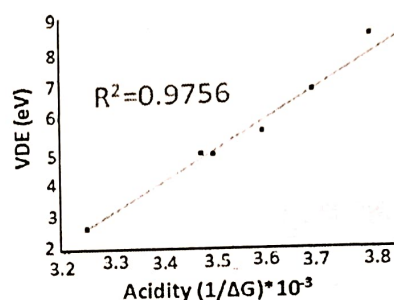


Figure 4. Graph plotted in between acidity of HPtF_n ($n = 1-6$) V s⁻¹ vertical de-attachment energy of corresponding anionic superhalogen.

energy of H₂SO₄, and the calculated deprotonation energy for $n > 1$ is less than the indicated deprotonation energy of H₂SO₄. As a result, all species with $n > 1$ belong to the superacid family. The calculated deprotonation energy of HPtF₆ is comparable to the deprotonation energy of the strongest superacid, HSBF₆, and less than the deprotonation energy of H₂SO₄.^[46,47] The calculated deprotonation energy of HPtF₆ is well-matched with the previously reported value.^[48] The calculated deprotonation energy of HPtF₄ is comparable to the corresponding reported value of HTaF₅; however, HPtF₅ is more acidic than HTaF₅.^[11] The calculated deprotonation energy of HPtF₆ is the same as that of H₂SO₄ by Czapla and Skurski.^[49]

Let us look further into the mechanism of HPtF_n superacidity using NBO charge analysis. The NBO charge (Table 3) shows that the charge on PtF_{n-1} is nearly the same at HF units. Again, HPtF_n can be written as PtF_{n-1}/HF Bronsted/Lewis acids. Except for HPtF₆, the NBO charge analysis reveals that charges on the HF unit are nearly equal to charges on the PtF_{n-1} unit. Except for HPtF₆, binding between HF and PtF_{n-1} is completely electrovalent. The NBO charge on PtF₅ in HPtF₆ is -0.244e, but the NBO charge on HF is 0.345e, indicating non-electrovalent interaction when compared to other HPtF_n ($n = 1-5$). The HF entity in HPtF₆ back-donates 0.101e charge to PtF₅. HPtF_n dissociates with HF and PtF_{n-1} entities, but HF atom F atom extracts charge from H and releases a proton (H⁺), and this F⁻ interacts with PtF_{n-1} to produce PtF_n ($n = 1-6$). As a result, the stability of PtF_n ($n = 1-6$) is directly related to the acidity of HPtF_n ($n = 1-6$). Figure 4 shows a graph connecting VDE and the acidity corresponding to protonated species. The acidity of any species is defined as

$$\text{Acidity} = \frac{1}{\Delta G \cdot 10^{-1}} \quad (5)$$

Table 4. Calculated electronic reactivity parameters of HPtF_n ($n = 1-6$) complexes.

Species	E_h [eV]	IP [eV]	ΔE_{gap} [eV]	χ [eV]	μ [eV]	η [eV]	S [eV] ⁻¹	$\bar{\mu}$ [eV]	ΔH_{max}	ECT
HPtF_1	5.0064	3.4035	1.6030	4.2050	4.2050	0.8014	0.6238	11.0307	5.2471	13.24548
HPtF_2	7.0236	2.7587	4.2650	4.8911	4.8911	2.1325	0.2345	5.6092	2.2936	3.752467
HPtF_3	7.6930	4.7090	2.9839	6.2010	6.2010	1.4920	0.3351	12.8867	4.1562	14.43096
HPtF_4	9.2067	4.6375	4.5692	6.9221	6.9221	2.2846	0.2189	10.48666	3.0299	7.109378
HPtF_5	9.9499	7.7395	2.2103	8.8447	8.8447	1.1051	0.4524	35.3924	8.0035	125.6182
HPtF_6	10.7019	6.3191	4.3828	8.5106	8.5106	2.1914	0.2282	16.5258	3.8836	13.24548

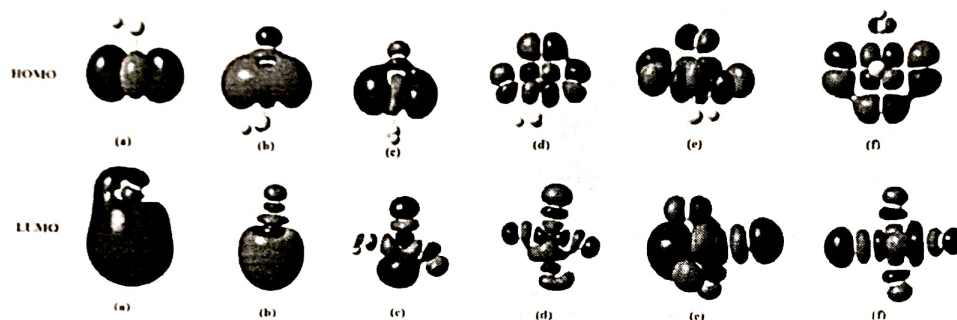


Figure 5. Highest occupied molecular orbital (HOMO, upper) and lowest unoccupied molecular orbital (LUMO, lower) surfaces of hydrogenated HPtF_n ($n = 1-6$) clusters.

The acidity of any system is reverse of deprotonation energy as deprotonation energy of any species is increased species become less acidic.

The calculated correlation equation between VDE and acidity for linear fitting is

$$Y = -31.19143 + 10.33421x \quad (R^2 = 0.9752) \quad (6)$$

The calculated correlation factor ($R^2 = 0.9756$) indicates a good correlation between VDE and the acidity of superacids reported in the literature.^[50,51]

From this discussion, we can say that superhalogen anions are the building block of superacids.

3.4. Electronic Properties of HPtF_n

Several electronic properties of HPtF_n ($n = 1-6$) have also been calculated. The most occupied molecular orbitals HOMO and the least occupied molecular orbitals LUMO are the main frontier molecules that determine electronic properties. Table 4 shows the calculated band gap of HPtF_n ($n = 1-6$). The energy gap of HPtF_n ($n = 1-6$) is between 1.6030 and 4.5692 eV. HPtF_1 has the smallest energy gap, indicating that it is highly reactive, whereas HPtF_4 has the largest gap, indicating that it is less chemically reactive. Figure 5 depicts the HOMO and LUMO plots of HPtF_n ($n = 1-6$). HOMO is distributed over PtF_{n-1} , whereas LUMO is distributed over the entire molecule. The transfer HOMO $\rightarrow$ LUMO shows that charge transfers from PtF_{n-1} to HF units. This can be explained by the ECT of HPtF_n , considering its constituents PtF_{n-1} and HF units approaching each other. The ECT is calculated by

following equation^[52]

$$\text{ECT} = (\Delta N_{\text{max}}) \text{PtF}_{n-1} - (\Delta N_{\text{max}}) \text{HF}$$

$$(\Delta N_{\text{max}}) = -\frac{\mu_x}{\eta_x} \quad (7)$$

The calculated value $\text{ECT} > 0$ for HPtF_n (Table 4). In the formation of HPtF_n the charge transfers from PtF_{n-1} to HF and thus PtF_{n-1} behave as electron donor and thus nucleophilic with high chemical potential; however, HF shows electrophilic behavior with low chemical potential.

The difference in energy between HOMO and LUMO is an energy gap and is directly related to the electronic reactivity of the system. The band gap is directly related to chemical stability. The chemical system with a low band gap means a more polarized system and less chemically stable.

3.5. Formation of Supersalts

As we know, strong acids and strong bases react to form salts. Similarly, we modeled supersalts using superacids HPtF_n ($n = 1-6$) and superbase OLi_3OH .

The optimized geometry with no imaginary frequencies of OLi_3OH using the DFT/6-311++G(d,p) method is shown in Figure 6. In a protonation reaction, the basicity of proton affinity (PA) OLi_3OH is calculated by a change in enthalpy of its gas phase. The superbasic nature established by calculated PA for OLi_3OH is 244.5 kcal mol⁻¹, more than the PA value of LiOH (239.42 kcal mol⁻¹).^[53]

After the formation of ionic salt and water from the acids and bases reaction, let us examine the possibility obtained from the

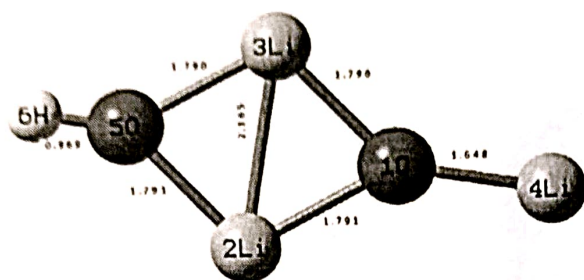
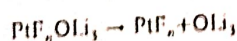


Figure 6. Optimized geometry of OLi_3OH by using DFT/6-311++G(d,p) method.

reaction of superacids and superbase. By using superacid HPtF_n ($n = 2-6$) and superbase OLi_3OH , we have modeled various possible geometry of PtF_nOLi_3 , and after optimization by same level theory, most optimized geometries of supersalts are presented in Figure 7.

The optimized geometry of PtF_2OLi_3 shows a distorted hexagon with one Li atom outward connected with O at 1.87 Å. In PtF_3OLi_3 , the PtF_3 axial was placed with OLi_3 , and after optimization optimized geometry of supersalt PtF_3OLi_3 shown in Figure 7b, which is just similar to PtF_2OLi_3 with additional F_2 with $\angle \text{F}_2\text{-Pt-F}_2$ angle 101.240 rather than 180° and is more stable than optimized geometry PtF_3OLi_3 presented in Figure 7f in trigonal OLi_3 placed parallel with PtF_3 and after geometry optimization one of F atom in trigonal PtF_3 attach with Li_4 atom. In the following calculation, we only considered the geometry of PtF_3OLi_3 shown in Figure. Figure 7c shows two stable geometries in PtF_4OLi_3 (d). In the first geometry, PtF_4 's square planer geometry interacts with axial trigonal OLi_3 , causing the trigonal geometry of OLi_3 to be slightly distorted. The second geometry is a tetrahedral geometry of PtF_4 placed axially with OLi_3 and optimized geometry shown in Figure 7d in which one Li is displaced out of the plane in OLi_3 . Because the minimum energy of optimized geometry corresponds to Figure 7c, we focused on Figure 7c supersalts in the following section. For $n = 5$, PtF_5OLi_3 , we OLi_3 placed parallel and axial positions of PtF_5 , and after optimization, two optimized PtF_5OLi_3 geometry are shown in Figure 7g and h. Because the minimum energy of the optimized geometry of OLi_3PtF_5 is shown Figure 7g, we have only discussed them. In PtF_6OLi_3 , we have considered three initial geometry in which PtF_6 placed parallel axial and perpendicular positions with OLi_3 . After optimization, only one geometry corresponding to axial orientation having stable geometry with no imaginary frequencies is shown in Figure 7e. The stable geometry of PtF_6OLi_3 with two F atoms is slightly displaced with PtF_6 and connected between two Li of OLi_3 with bond length Li-F between 1.77–1.79 Å and 1.72–1.73 Å, respectively. Although the stable geometry of PtF_6OLi_3 is completely unsymmetrical, we have considered this for further calculation.

The stability of the most stable conformer of supersalts PtF_nOLi_3 is checked by dissociation through neutral and ionic modes. The dissociation of supersalts by neutral the ionic modes of dissociation is calculated by the following equation



$$\Delta E_A = E(\text{PtF}_n) + E(\text{OLi}_3) - E(\text{PtF}_n\text{OLi}_3) \quad (9)$$



$$\Delta E_B = E(\text{OLi}_3^+) + E(\text{PtF}_n^-) - E(\text{PtF}_n\text{OLi}_3) \quad (11)$$

The calculated binding energy of OLi_3PtF_n from both modes neutral (ΔE_A) and ionic modes (ΔE_B) is shown in Table 5. For PtF_4OLi_3 calculated value of $\Delta E_A > \Delta E_B$, so this complex favors the neutral dissociation rather than ionic dissociation; however, for the rest of the supersalts $\Delta E_A < \Delta E_B$ and favors ionic dissociation just as in traditional salt LiF . In $n = 6$ PtF_6OLi_3 , dissociation through neutral modes becomes unstable; however, dissociation through ionic mode also has low dissociation energy due to its unsymmetrical geometry.

3.6. Electronic Properties of Supersalts

After releasing a water molecule, superacids and superbases interact to form supersalts. Superalkali (OLi_3) acts as an electron donor in supersalts, while superhalogen (PtF_n) acts as an electron acceptor. Because supersalts have electrovalent or ionic interactions, they are easily polarized. We discussed the optoelectronic properties of supersalts in this section. Previously, researchers reported that supersalt families exhibit extraordinary optoelectronic behaviors.^[54,55] Several global reactivity indices are calculated using HOMO and LUMO energy. Ionization potential and electron affinity are the negative eigenvalues of HOMO and LUMO energies, respectively. Any system's electronegativity equals the negative half of the sum of its HOMO and LUMO energies, but the electronegative potential is the inverse of global electronegativity. The chemical softness of any system is defined as how easily it reacts with specific species, and the inverse is defined as chemical hardness. The chemical harness is equal to half of the HOMO LUMO energy difference. The global softness is the inverse of the energy difference between HOMO and LUMO energies. All calculated parameters for global reactivity are calculated and listed in Table 5. The energy gap of supersalts OLi_3PtF_n ranges from 1.818 to 4.021 eV. The lowest energy gap was obtained for OLi_3PtF_5 , making it the most reactive species; however, the highest energy gap was obtained for OLi_3PtF_2 , making it the least reactive. The chemical hardness and chemical softness values support this conclusion.

3.7. Nonlinear Optical Properties (NLO) of Supersalts

Due to low ionization potential, superalkalies have potential dipping ability and can be utilized to synthesize a variety of charge transfer salts. For example, new species of supersalts^[54–58] are formed superalkalies interacting with their counterpart superhalogen. These supersalts can be illustrious from traditional salts on the foundation of their chosen detachment to the ionic superalkali and superhalogen fragments.^[55] The interaction of superalkali Bli_6 with different superhalogen has been reported.^[53] The interaction of BF_4 superhalogen with Fli_2 , Oli_3 , and Nli_4 superalkalies^[58] has been reported. A system's mean polarizability and hyperpolarizability are defined by its response to an

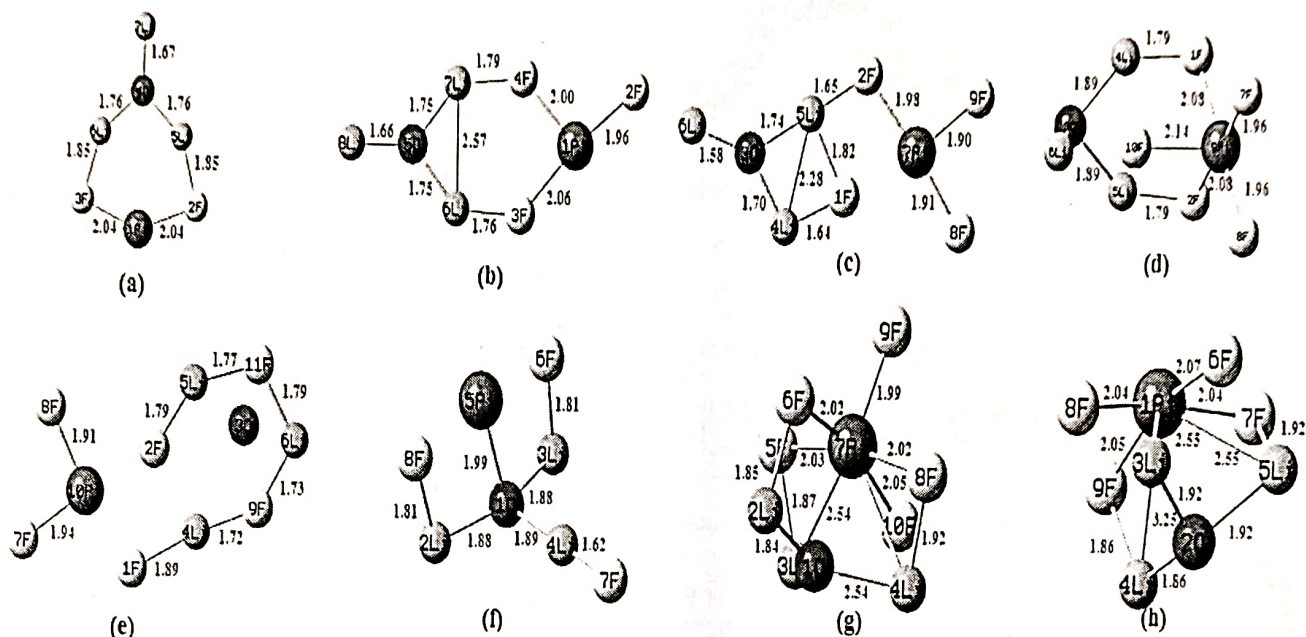


Figure 7. Optimized geometry of $OLi_3 PtF_n$ ($n = 2-6$).

Table 5. Calculated electronic reactivity and nonlinear optical properties (NLO) parameters of $OLi_3 PtF_n$ ($n = 2-6$) complexes.

Salt	IP [eV]	E_A [eV]	E_{gao} [eV]	X [eV]	μ [eV]	η [eV]	S [eV] ⁻¹	Ω [eV]	ΔE_B [eV]	ΔE_A [eV]	μ [D]	$\langle \alpha \rangle$ [a.u.]	B [a.u.]	MR [e.s.u.]	α_{anis} [a.u.]	Order para.
$OLi_3 PtF_2$	5.752	1.731	4.021	3.742	-3.742	2.011	0.249	3.481	3.761	5.936	8.604	65.491	227.274	24.435	15.741	0.093
$OLi_3 PtF_3$	5.813	3.931	1.882	4.872	-4.872	0.941	0.531	12.612	3.075	6.045	10.959	63.898	384.091	23.840	24.203	0.132
$OLi_3 PtF_4$	6.798	3.189	3.609	4.994	-4.994	1.805	0.277	6.909	6.567	7.708	4.971	55.471	503.047	20.696	64.371	0.012
$OLi_3 PtF_5$	7.379	5.561	1.818	6.470	-6.470	0.909	0.550	23.026	4.873	3.610	10.612	80.923	610.529	30.192	101.370	0.441
$OLi_3 PtF_6$	8.691	6.644	2.047	7.668	-7.668	1.024	0.489	28.720	-5.127	2.610	3.731	90.141	585.355	33.632	46.713	0.189

applied electric field. Using an electric field of 0.001 a.u., the mean polarizability and hyperpolarizability of supersalts are calculated and listed in Table 3. The superalkali OLi_3 -based supersalts got much attention due to their enormously high NLO properties.^[59,60] In the present communication, we have selected OLi_3 as superalkali and PtF_n ($n > 1$) as superhalogen. The dipole moment is a signature of charge magnitude and distribution. Because of their symmetric distribution, $OLi_3 PtF_3$ has the greatest dipole moment, resulting in uniform polarity. Except for $n = 4, 6$, the calculated dipole moment increases as the number of atoms increases in $OLi_3 PtF_n$. Because of its highly asymmetrical geometry and unusual charge distribution, $OLi_3 PtF_6$ has a lower dipole moment. Since $PtF_4 OLi_3$ prefers neutral dissociation over ionic dissociation, the interaction between PtF_4 and OLi_3 is partially covalent, and the dipole moment for $n = 4$ deviates from normal variation. In Table 5, several NLO parameters, i.e., dipole moment μ , mean polarizability $\langle \alpha \rangle$, anisotropy polarizability ($\Delta \alpha$), order parameters, and first static hyperpolarizability β in a Cartesian frame, are calculated by using the following equations

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (12)$$

$$\langle \alpha \rangle = 1/3 [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \quad (13)$$

The first-order hyperpolarizability of the system is defined by a $3 \times 3 \times 3$ matrix of a third-rank tensor. By utilizing Kleinman's third rank matrix with 27 components can be reduced to 10 components of symmetry.^[61] After applying a homogeneous external electric field, all components of β are coefficients in the Taylor series expansion of the energy expansion becomes:

$$E = E^0 - \mu_a F_a - 1/2 \alpha_{ab} F_a F_b - 1/6 \beta_{abc} F_a F_b F_c \quad (14)$$

where E^0 is the energy of the unperturbed molecules, F_a the field at the origin, and μ_a , α_{ab} , and β_{abc} are the components of dipole moment, polarizability, and the first hyperpolarizabilities, respectively.

The total hyperpolarizability β_{TOTAL} is calculated by

$$\begin{aligned} \beta_{TOTAL} &= [\beta_x^2 + \beta_y^2 + \beta_z^2]^{1/2}; \text{ where } \beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}, \beta_y \\ &= \beta_{yyy} + \beta_{yzz} + \beta_{yxx}, \beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy} \end{aligned} \quad (15)$$



The anisotropic polarizability is calculated by

$$\Delta\alpha = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{2} \right]^{1/2} \quad (16)$$

The molar refractive index is calculated by the Lorenz–Lorentz formula^[62,63]

$$MR = \left[\frac{n^2 - 1}{n^2 + 2} \right] \left(\frac{MW}{P} \right) = 1.33\alpha\pi \quad (17)$$

In this formula, N is the Avogadro number; α is the mean polarizability.

The ordered parameter is defined in terms of molecular polarizability (α_e) along the x-axis and polarizability (α_o) along the y-axis and calculated as^[64–66]

$$S = \frac{\alpha_e - \alpha_o}{\alpha_e + \alpha_o} \quad (18)$$

The OLi_3PtF_6 and OLi_3PtF_5 have the highest calculated mean polarizability values, while OLi_3PtF_4 has the lowest. The mean polarizability decreases as n increases, but when $n = 3$, this parameter suddenly increases and reaches its maximum value for OLi_3PtF_6 (90.141 a.u.) and is comparable to other studies reported. The calculated hyperpolarizability of OLi_3PtF_6 is almost ten times and for OLi_3PtF_4 six times greater than for LiF (9.17 a.u.). Supersalts' hyperpolarizability ranges from 227.274 to 610.529 a.u. The calculated hyperpolarizability value for OLi_3PtF_3 is 27 times to that of the reference material urea (0.1947*10^{–30} e.s.u.) but ten times for OLi_3PtF_2 , which has the lowest hyperpolarizability value. Except for OLi_3PtF_6 , the value of hyperpolarizability of OLi_3PtF_n increases with increasing n due to their asymmetrical geometry. The calculated hyperpolarizability of OLi_3PtF_5 is seven times and for OLi_3PtF_2 , almost three times greater than the hyperpolarizability (90.20 a.u.) value of LiF.^[53] The ICT of π electron polarizes supersalts and is responsible for nonlinear optical behavior.^[53,55]

4. Conclusion

The superacidic properties of protonated PtF_n ($n = 1–6$) are investigated in this paper using the DFT/SDD/6-31++G(d,p) method. The protonated HPTF_n can be represented by Lewis and Brønsted acids ($\text{HF}/\text{PtF}_{n-1}$). The calculated deprotonation energies of HPTF_n show that all species for $n > 1$ belong to the superacid family. The calculated deprotonation energy of HPTF_6 is equal to the deprotonation energy of the most acidic species, HSbF_6 . The calculated correlation factor ($R^2 = 0.9752$) shows that the acidity of HPTF_n is directly related to the anionic superhalogen part's VDE. The interaction of superacids and superbases (OLi_3) to form supersalts demonstrates that the dissociation of PtF_nOLi_3 through the ionic channel is the same as in traditional salt LiF except for PtF_4OLi_3 . The mean polarizability decreases as the number of n increases. When $n = 3$, this parameter suddenly increases and reaches its maximum value for OLi_3PtF_6 (90.141 a.u.). The calculated hyperpolarizability of OLi_3PtF_5 is almost seven times that of OLi_3PtF_2 and nearly three times that of LiF (90.20 a.u.). As a

result, these supersalts may be capable of producing new NLO-active materials in the future. We hope that our research will lead to the development of new commercial superacids and supersalts that are both beneficial and environmentally friendly.

Acknowledgements

The author Anil Kumar Soni is grateful and thanks the Uttar Pradesh government (India) [Patrank/degree/vikas/155223/2021-22 dated 25.02.2022] for providing him funding.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

Keywords

deprotonation energy, HOMO, LUMO, nonlinear optical properties (NLO), VDE

Received: April 4, 2023
Revised: May 21, 2023

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Annexure-D

QM/MM Based Study of Electronic Structure of Platinum Dihalides

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How to cite this paper: Soni, A.K., Swati and Sahu, V.K. (2025) QM/MM Based Study of Electronic Structure of Platinum Dihalides. *Open Journal of Applied Sciences*, 15, 305-328.

<https://doi.org/10.4236/ojapps.2025.151020>

Received: December 6, 2024

Accepted: January 27, 2025

Published: January 30, 2025

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Abstract

In this research work, atomic and molecular orbitals based analysis has been made to see electronic structure of platinum halides (platinum dichloride, platinum dibromide, platinum diiodide and platinum difluoride). The geometry optimization and three dimensional (3D) modeling of the above mentioned species have been made on CAChe pro software. The results show: (i) The involvement of three p atomic orbitals is negligible as their summation values are very low in comparison to d orbital and considerably low with respect to s orbital. (ii) The study well support the Landis concepts of sd^n -hybridization (here $n = 1$) as bond angle and contributions of s-orbital and d-orbital of Pt(II) are maximum with negligible contribution of p-orbitals. (iii) These halides also support the cloud-expanding effect with experimental data and also follow the nephelauxetic effect. The result is in good agreement with experiment results that covalent character increases in the order: $PtI_2 > PtBr_2 > PtCl_2 > PtF_2$. (iv) And thus the study will help to fine tune the existing complexes of these halides.

Keywords

Platinum Dhalides, Mulliken Population Analysis, sd-Hybridization, Molecular Orbital Diagram

1. Introduction

Mathematical treatment of various laws of physics and chemistry were too complex to be solved [1]. However, it is only possible by Walter Kohn, who has developed the mathematics and John Pople, who has made its quantum mechanical forms. Both scientists were jointly awarded Noble Prize in chemistry in 1998:

Kohn for simplifying the mathematics in descriptions of bonding of atoms, and Pople for development of the computational quantum chemistry [2]-[4]. Day-to-day developments in theoretical and computational works make it possible to have a deeper insight in the sub-atomic nature of atoms, ions and molecules [5]-[7]. In this research work, atomic and molecular orbitals based analysis will be made to see electronic structure of platinum halides. Platinum forms compounds in 0, +2, +3, +4, +5 and +6 oxidation states. Main oxidation states of platinum are 0, +2 and +4, while +5 and +6 are shown by fluorides or fluoro-complexes, and +3 is usually in binuclear compounds with M-M bonds [8] [9]. The ability of platinum to exist in many oxidation states is an important property of this element, which plays an important role in its applications. Platinum readily forms coordinate complexes and these complexes have their applications in diverse fields [10]-[18]. Day-to-day expansion in the chemistry of platinum and its complexes is due to their applications directly or indirectly pre-requisite for many of today's problems related to anticancer drugs, photochemistry [19]-[22], biological system [23]-[25], materials science [26] [27] and nanoscience [28]. This is due to its versatile electron-transfer pathways. Survey of literature shows that platinum and its compounds are now used as sensors and switches [29], as catalyst [30]-[33], as antimicrobial agents [25], as biomarkers [24], as metallopharmaceuticals in treatment of cancer [18]. Platinum based complex compounds have also been used as drugs to activate or help to generate redox reactions [34]-[36]. A survey of literature shows that designing new ligands that can complexes with platinum in different oxidation states can lead to the development of new materials [36]. For new materials of diverse applications, there is and will be a continuous step-by-step study to discover new ligands and their new platinum complex. These complex compounds can formed either from their simple compounds or by substitution reactions from pre-synthesized complex compounds. The development of new platinum-based materials is and will be an ongoing need for various fields of science and technology, and thus for society. It is difficult to synthesize new molecule and test their various properties in laboratory, because it involves huge expenditure and consumes enormous time. Now, chemistry together with physics and computer science has shifted from, how to make a molecule to what molecule to make, in other words, molecule design. The emergence of computational chemistry and various software, have given a quantitative nature to the relationship between molecule, its property, its synthesis and thus its various applications [37].

2. Materials and Methods

The study material are platinum (II) halides. Three simple platinum dihalides exist. These are platinum (II) chloride, platinum (II) bromide and platinum (II) iodide, except platinum(II) fluoride which does not exist. The adopted methods for various calculations of platinum dihalides are based on Mulliken's population analysis [38]-[41]. Mulliken defined ϕ_i (molecular orbital), $n_{r,i}$ (the contributions of electrons in each occupied MO) and $n_{r,s,i}$ (overlap population that explain

bonding, antibonding and nonbonding nature of bond), as below:

$$\phi_i = \sum_{rk} c_{irk} \chi_{rk} \quad (1)$$

$$n_{r,i} = n_i c_{ri}^2 \quad (2)$$

$$n_{r-s,i} = n_i (2c_{ri} c_{si} S_{rs}) \quad (3)$$

here n_i is the number of electron in ϕ_i , $i = 1 - 17$, c_{ri} is the coefficient of atomic orbitals for Pt-atom, c_{si} is the coefficient of AOs for other atom (X – 2 or X – 3) and S_{rs} is the overlap integral between the two AOs (one of an atom Pt – 1 or X – 2 and one of another atom X – 2 or X – 3). In order to obtain minimum energy structure we optimized the geometry of each halide by opting Extended Hückel Theory (EHT) [42]. All the calculations were performed on CAChe software. From minimum energy structure we have extracted values of eigenvectors, overlap matrix and eigenvalues. By submitting the values of eigenvector and overlap matrix in Equation (3), we have derived the values of overlap population. And the summation of values of overlap population was obtained to describe bonding, nonbonding and antibonding molecular orbitals. After that using all above along with eigenvalues molecular orbital diagram has been drawn. Before all these we have also examine the nature and contribution of atomic orbitals and then their mixing (valence bond theory) or overlapping (molecular orbital theory). V.B. Theory and M.O. theory on their refinements gave same wave function for the molecule but they differ in their approximations only. Mulliken (1955) also correlated the bonded interaction of V.B.T. with positive overlap population and non-bonded repulsion of V.B.T. with negative population analysis [38]-[41].

3. Results and Discussion

A systematic molecular mechanics based investigation of bonding nature in platinum dihalides has been studied. Platinum dihalides, which are under investigation, are dichloride, dibromide, diiodide and difluoride (which do not exist but also studied to explain its unstability). After gaining minimum energy structures a quantitative atomic orbital (AO) and molecular orbital (MO) treatment have also been made on platinum halides to study (i) involvement of metal (n – 1)d-, ns- and np-orbitals in hybridizations and its type that has been used to get information related to shape (bond angle) and size (bond length); (ii) contribution of various AOs in the construction of MOs through LCAO approximation using values of eigenvector and overlap matrix; (iii) nature of MOs by distinguishing them in to bonding, nonbonding and antibonding MO through population analysis and (iv) molecular orbital energy diagram and its construction using eigenvalues and overlap-population contribution.

3.1. Platinum Dichloride

The optimized geometry as obtained from molecular mechanics method of

platinum(II) chloride is given below (Figure 1).



Figure 1. Structure of PtCl_2 .

The MOs of this molecule are formed by linear combination of nine orbitals (five 4d-orbitals, one 5s orbital and three 5p orbitals) from platinum and four orbitals (three 3p orbitals and one 3s orbital) from each chlorine atom as shown below

Pt-1 = $5dx^2 - y^2$, $5dz^2$, $5dxy$, $5dxz$, $5dyz$, $6s$, $6px$, $6py$, $6pz$	= 9AOs
Cl-2 = $3s$, $3px$, $3py$, $3pz$	= 4AOs
Cl-3 = $3s$, $3px$, $3py$, $3pz$	= 4AOs
Total	= 17AOs

In order to examine the contribution of various AOs in the formation of MOs the LCAO has been made. The 17 AOs on LCAO approximations give 17 MOs. The various AOs are represented by ' χ ' and MOs by ' ϕ '. Thus, $\chi_1 - \chi_9$ are AOs of platinum ($\chi_1 = 6s$, $\chi_2 = 6px$, $\chi_3 = 6py$, $\chi_4 = 6pz$, $\chi_5 = 5dx^2 - y^2$, $\chi_6 = 5dz^2$, $\chi_7 = 5dxy$, $\chi_8 = 5dxz$, $\chi_9 = 5dyz$) and $\chi_{10} - \chi_{17}$ are AOs of chlorine ($\chi_{10} = 3s$, $\chi_{11} = 3px$, $\chi_{12} = 3py$, $\chi_{13} = 3pz$ for Cl-2 and $\chi_{14} = 3s$, $\chi_{15} = 3px$, $\chi_{16} = 3py$, $\chi_{17} = 3pz$ for Cl-3). The magnitude of contribution of various AOs (χ) in the formation of 17 MOs (ϕ_1 to ϕ_{17}) is demonstrated in Table 1(a). A close look at this table reflected that seven AOs (χ_2 , χ_3 , χ_4 , χ_8 , χ_9 , χ_{13} , χ_{17}) have no contribution in the formation of 1st MO (ϕ_1) as these have zero coefficient values. And the rest ten AOs (χ_1 , χ_5 , χ_6 , χ_7 , χ_{10} , χ_{11} , χ_{12} , χ_{14} , χ_{15} , χ_{16}) have their contribution in ϕ_1 . By adopting same view the contributions AOs in ϕ_2 to ϕ_{17} MOs can be describe.

3.2. Platinum Dibromide

The optimized geometry (Figure 2) as obtained from molecular mechanics method of platinum (II) bromide is given below.



Figure 2. Structure of PtBr_2 .

The MOs of this molecule as formed by linear combination of nine orbitals (five 4d-orbitals, one 5s orbital and three 5p orbitals) from platinum and four orbitals (three 3p orbitals and one 3s orbital) from each bromine are shown below:

Pt-1 = $5dx^2 - y^2$, $5dz^2$, $5dxy$, $5dxz$, $5dyz$, $6s$, $6px$, $6py$, $6pz$,	= 9
Br-2 = $4s$, $4px$, $4py$, $4pz$	= 4
Br-3 = $4s$, $4px$, $4py$, $4pz$	= 4
Total	= 17

Table 1. (a) Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ) of PtCl_2 ; (b) Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ) of PtBr_2 ; (c) Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ) of PtI_2 ; (d) Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ) of PtF_2 .

(a)																	
Atom	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}	ϕ_{13}	ϕ_{14}	ϕ_{15}	ϕ_{16}	ϕ_{17}
Pt-1	χ_1	-0.0704	-0.0000	0.1786	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.3897	0.0000	0.0000	-1.0938	0.0008
	χ_2	-0.0000	0.0312	-0.0000	0.0000	0.0000	-0.1299	0.0032	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0505	0.0000	0.0007	1.3371
	χ_3	0.0000	0.0015	-0.0000	-0.0000	-0.0000	-0.0065	-0.0649	0.0000	0.0000	-0.0000	-0.0000	-0.0000	1.0163	0.0000	-0.0000	0.0665
	χ_4	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	0.0000	-0.0000	0.0650	-0.0000	0.0000	-0.0000	0.0000	0.0000	1.0175	-0.0000	0.0000
	χ_5	-0.0621	-0.0000	0.2745	0.0402	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	-0.4975	0.0000	-0.0913	-0.7688	-0.0000	0.0000	-0.3649
	χ_6	0.0360	-0.0000	-0.1593	-0.0000	-0.0000	-0.0000	0.0000	-0.0000	0.0000	-0.8660	0.0000	0.0000	0.4461	0.0000	-0.0000	0.2117
	χ_7	-0.0062	0.0000	0.0274	-0.4030	-0.0001	-0.0000	0.0000	0.0000	0.0000	-0.0496	0.0001	0.9161	-0.0766	-0.0000	0.0000	-0.0364
	χ_8	-0.0000	0.0000	-0.0000	0.0001	-0.4045	0.0000	0.0000	-0.0000	-0.0497	0.0000	0.9195	-0.0001	0.0000	-0.0000	-0.0000	-0.0000
	χ_9	0.0000	0.0000	-0.0000	0.0000	-0.0201	-0.0000	-0.0000	-0.0000	0.9988	-0.0000	0.0457	0.0000	0.0000	0.0000	0.0000	0.0000
Cl-2	χ_{10}	-0.6839	0.6981	-0.1032	0.0000	0.0000	0.0385	0.0000	0.0000	0.0000	0.0000	0.0000	0.0315	0.0000	-0.0000	0.2963	-0.3916
	χ_{11}	-0.0122	0.0100	-0.5661	0.0306	0.0000	0.6562	0.0346	0.0000	-0.0000	-0.0000	0.0000	0.0176	-0.1621	0.0092	0.0000	-0.5579
	χ_{12}	-0.0006	0.0005	-0.0281	-0.6161	-0.0001	0.0326	-0.6953	0.0000	0.0000	-0.0000	-0.0000	-0.3546	-0.0081	-0.1852	-0.0000	-0.0277
	χ_{13}	0.0000	0.0000	-0.0000	0.0001	-0.6169	0.0000	0.0000	0.6962	-0.0000	0.0000	-0.3551	0.0000	-0.0000	0.0000	-0.1854	0.0000
Cl-3	χ_{14}	-0.6836	-0.6984	-0.1032	0.0000	-0.0000	-0.0385	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0315	0.0000	0.0000	0.2966	0.3910
	χ_{15}	0.0122	0.0100	0.5660	-0.0306	-0.0000	0.6563	0.0346	0.0000	0.0000	-0.0000	0.0000	-0.0176	0.1621	0.0092	0.0000	0.5585
	χ_{16}	0.0006	0.0005	0.0281	0.6157	0.0001	0.0326	-0.6957	0.0000	0.0000	-0.0000	0.0000	0.3545	0.0081	-0.1851	0.0000	0.0278
	χ_{17}	0.0000	0.0000	0.0000	-0.0001	0.6165	0.0000	0.0000	0.6966	0.0000	0.0000	0.3549	-0.0000	0.0000	0.0000	-0.1853	-0.0000
(b)																	
Atom	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}	ϕ_{13}	ϕ_{14}	ϕ_{15}	ϕ_{16}	ϕ_{17}
Pt-1	χ_1	0.0841	0.0000	-0.1732	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.4114	0.0000	0.0000	1.0271	0.0025
	χ_2	-0.0001	-0.0425	-0.0000	0.0000	0.0000	-0.1455	-0.0008	0.0061	-0.0000	0.0000	0.0000	-0.0001	-0.0127	-0.1011	0.0023	-1.2428
	χ_3	0.0000	0.0004	-0.0000	-0.0001	0.0000	0.0012	-0.0608	-0.0026	0.0000	0.0000	0.0001	-0.0000	-0.0000	-1.0088	0.0433	-0.0104
	χ_4	0.0000	0.0043	-0.0000	0.0000	-0.0001	0.0147	-0.0026	0.0605	-0.0000	0.0000	-0.0000	0.0001	0.0000	-0.0423	-1.0037	-0.0002
	χ_5	0.0786	0.0000	-0.3736	0.0099	0.0559	-0.0001	-0.0000	0.0000	0.0017	-0.5050	0.0132	0.0834	-0.7260	-0.0000	0.0000	0.3274
	χ_6	-0.0445	0.0000	0.2113	-0.0010	-0.0970	0.0000	0.0000	-0.0000	0.0000	-0.8573	0.0011	-0.1443	0.4107	0.0000	-0.0000	-0.1852
	χ_7	-0.0013	0.0000	0.0063	0.5567	-0.0069	0.0000	-0.0001	0.0000	0.1005	0.0085	0.8286	0.0051	0.0122	0.0001	0.0000	-0.0055
	χ_8	-0.0159	0.0000	0.0755	0.0054	0.5483	0.0000	0.0000	0.0001	0.0083	-0.1000	-0.0071	0.8161	0.1468	-0.0000	0.0001	-0.0662
	χ_9	0.0001	0.0000	-0.0006	-0.0563	-0.0040	0.0000	-0.0000	-0.0000	0.9949	0.0008	-0.0837	-0.0075	-0.0012	0.0000	0.0000	0.0006
Br-2	χ_{10}	0.6804	-0.6973	0.1205	0.0000	0.0000	0.0423	0.0000	0.0000	0.0000	0.0000	0.0000	0.0230	0.0000	-0.0000	-0.2529	0.3213
	χ_{11}	0.0064	-0.0102	0.5266	0.0052	0.0556	0.6480	-0.0089	0.0701	-0.0000	-0.0000	-0.0034	-0.0446	-0.2344	0.0019	0.0150	0.5279
	χ_{12}	-0.0001	0.0001	-0.0044	0.5531	-0.0063	-0.0054	-0.6994	-0.0304	0.0000	-0.0000	-0.4433	-0.0031	0.0020	0.1499	-0.0064	-0.0044
	χ_{13}	-0.0006	0.0010	-0.0532	0.0058	0.5503	-0.0655	-0.0297	0.6959	-0.0000	0.0000	0.0035	-0.4411	0.0237	0.0063	0.1492	-0.0533
Br-3	χ_{14}	0.6820	0.6956	0.1207	0.0000	0.0000	-0.0424	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0230	0.0000	0.0000	-0.2521	-0.3230
	χ_{15}	-0.0064	-0.0102	-0.5271	-0.0052	-0.0557	0.6474	-0.0088	0.0699	0.0000	-0.0000	0.0034	0.0447	0.2345	0.0019	0.0151	-0.5263
	χ_{16}	0.0001	0.0001	0.0044	-0.5544	0.0064	-0.0054	-0.6977	-0.0304	0.0000	-0.0000	0.4442	0.0031	-0.0020	0.1503	-0.0065	0.0044
	χ_{17}	0.0006	0.0010	0.0533	-0.0059	-0.5516	-0.0654	-0.0296	0.6943	0.0000	0.0000	-0.0035	0.4420	-0.0237	0.0063	0.1495	0.0532

Continued

Continued

		(c)																
Atom	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}	ϕ_{13}	ϕ_{14}	ϕ_{15}	ϕ_{16}	ϕ_{17}	
Pt-1	χ_1	-0.1194	0.0000	-0.1678	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.4042	0.0000	0.0000	-1.0097	0.0002
	χ_2	0.0000	-0.0612	0.0000	0.0000	0.0000	0.1535	0.0055	-0.0012	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0990	0.0225	0.0002	1.2035
	χ_3	0.0000	0.0005	0.0000	0.0000	0.0000	-0.0013	-0.0078	-0.0552	0.0000	0.0000	0.0000	0.0000	0.0000	0.1418	0.9967	0.0000	-0.0101
	χ_4	0.0000	0.0062	0.0000	0.0000	0.0000	-0.0155	0.0549	-0.0078	0.0000	0.0000	0.0000	0.0000	0.0000	-0.9918	0.1402	0.0000	-0.1216
	χ_5	-0.1235	0.0000	-0.4048	-0.0627	-0.0213	0.0000	0.0000	0.0000	-0.0017	-0.5050	0.0209	0.0742	-0.7114	0.0000	0.0000	-0.2913	0.0001
	χ_6	0.0699	0.0000	0.2289	0.1116	0.0184	0.0000	0.0000	0.0000	0.0000	-0.8573	-0.0145	-0.1310	0.4024	0.0000	0.0000	0.1648	0.0000
	χ_7	0.0021	0.0000	0.0068	0.1065	-0.6408	0.0000	0.0000	0.0000	-0.1005	0.0085	0.7518	-0.0843	0.0119	0.0000	0.0000	0.0049	0.0000
I-2	χ_8	0.0250	0.0000	0.0818	-0.6314	-0.1033	0.0000	0.0000	0.0000	-0.0083	-0.1000	0.0811	0.7407	0.1438	0.0000	0.0000	0.0589	0.0000
	χ_9	-0.0002	0.0000	-0.0007	-0.0054	0.0657	0.0000	0.0000	0.0001	-0.9949	0.0008	-0.0767	0.0022	-0.0012	0.0000	0.0000	-0.0005	0.0000
	χ_{10}	-0.6655	-0.6925	0.1701	0.0000	-0.0000	-0.0501	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0247	0.0000	0.0000	0.2514	-0.3004
	χ_{11}	0.0164	-0.0089	0.5111	-0.0494	-0.0124	-0.6459	0.0690	-0.0157	0.0000	0.0000	-0.0096	-0.0493	-0.2631	0.0128	-0.0029	-0.5128	0.5004
I-3	χ_{12}	-0.0001	0.0001	-0.0043	0.0823	-0.4980	0.0054	-0.0987	-0.6939	0.0000	0.0000	-0.4946	0.0550	0.0022	-0.0184	-0.1290	0.0043	-0.0042
	χ_{13}	-0.0017	0.0009	-0.0517	-0.4956	-0.0815	0.0653	0.6905	-0.0976	0.0000	0.0000	-0.0544	-0.4922	0.0266	0.1284	-0.0182	0.0518	-0.0506
	χ_{14}	-0.6654	0.6927	0.1701	0.0000	0.0000	0.0501	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0247	0.0000	0.0000	0.2514	0.3002
	χ_{15}	-0.0164	-0.0089	-0.5111	0.0493	0.0124	-0.6460	0.0689	-0.0157	0.0000	0.0000	0.0096	0.0493	0.2631	0.0128	-0.0029	0.5129	0.5002
	χ_{16}	0.0001	0.0001	0.0043	-0.0823	0.4979	0.0054	-0.0987	-0.6940	0.0000	0.0000	0.4946	-0.0550	-0.0022	-0.0184	-0.1290	-0.0043	-0.0042
	χ_{17}	0.0017	0.0009	0.0516	0.4955	0.0815	0.0652	0.6906	-0.0976	0.0000	0.0000	0.0543	0.4921	-0.0266	0.1284	-0.0182	-0.0518	-0.0505
	(d)																	
Atom	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}	ϕ_{13}	ϕ_{14}	ϕ_{15}	ϕ_{16}	ϕ_{17}	
Pt-1	χ_1	-0.0229	-0.0000	0.0751	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.3609	-0.0005	0.0000	0.9884	0.0000
	χ_2	0.0000	-0.0024	0.0000	0.0000	0.0000	0.0470	0.0032	-0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.1013	-0.0020	0.0000	1.1344
	χ_3	0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0004	-0.0012	0.0188	0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.0631	-1.0023	-0.0000	-0.0095
	χ_4	0.0000	0.0002	0.0000	0.0000	-0.0000	-0.0048	-0.0188	-0.0012	-0.0000	0.0000	-0.0000	-0.0000	0.0000	0.9972	0.0636	0.0005	-0.1146
	χ_5	-0.0270	-0.0000	0.1456	-0.0098	-0.0010	-0.0000	-0.0000	0.0000	-0.0017	-0.5050	0.0103	-0.1006	-0.7948	-0.0002	0.0000	0.3438	0.0000
	χ_6	0.0153	-0.0000	-0.0824	0.0168	-0.0011	-0.0000	0.0000	-0.0000	0.0000	-0.8573	0.0108	0.1724	0.4496	0.0001	-0.0000	-0.1945	-0.0000
	χ_7	0.0005	0.0000	-0.0024	-0.0060	-0.0965	-0.0000	0.0000	0.0000	-0.1005	0.0085	0.9902	-0.0604	0.0133	-0.0000	0.0000	-0.0058	0.0000
F-2	χ_8	0.0055	0.0000	-0.0294	-0.0950	0.0061	0.0000	0.0000	-0.0000	-0.0083	-0.1000	-0.0620	-0.9751	0.1606	-0.0000	-0.0000	-0.0695	-0.0000
	χ_9	0.0000	0.0000	0.0002	0.0014	0.0097	-0.0000	-0.0000	-0.0000	-0.9949	0.0008	-0.0996	0.0144	-0.0013	0.0000	0.0000	0.0006	0.0000
	χ_{10}	-0.6995	0.7077	-0.0367	0.0000	0.0000	-0.0124	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0471	0.0001	-0.0000	-0.2300	-0.3013
	χ_{11}	-0.0044	-0.0044	-0.6640	-0.0701	-0.0014	-0.6929	-0.0711	0.0014	-0.0000	-0.0000	-0.0002	0.0114	-0.1374	-0.0082	0.0002	0.2663	0.2713
	χ_{12}	0.0000	-0.0004	0.0056	-0.0440	-0.6981	0.0058	-0.0443	0.7043	0.0000	-0.0000	-0.1126	0.0070	0.0011	-0.0051	0.0804	-0.0022	-0.0023
	χ_{13}	0.0004	0.0000	0.0670	-0.6946	0.0443	0.0695	-0.7007	-0.0447	-0.0000	0.0000	0.0070	0.1121	0.0139	-0.0800	-0.0051	-0.0269	-0.0274
	χ_{14}	-0.6995	0.0000	-0.0367	-0.0000	-0.0000	0.0124	0.0000	0.0000	-0.0000	0.0000	0.0000	-0.0000	0.0471	0.0001	0.0000	-0.2300	0.3013
F-3	χ_{15}	0.0044	-0.7078	0.6640	0.0711	0.0014	-0.6928	-0.0713	0.0014	0.0000	-0.0000	0.0002	-0.0114	0.1374	-0.0080	0.0002	-0.2663	0.2713
	χ_{16}	-0.0000	0.0000	-0.0056	0.0440	0.6980	0.0058	-0.0443	0.7043	0.0000	-0.0000	0.1126	-0.0070	-0.0012	-0.0051	0.0804	0.0022	-0.0023
	χ_{17}	-0.0004	0.0000	-0.0672	0.6944	-0.0443	0.0705	-0.7007	-0.0447	0.0000	0.0000	-0.0070	-0.1121	-0.0139	-0.0800	-0.0051	0.0269	-0.0274

In order to examine the contribution of various atomic orbitals in the formation of molecular orbitals the LCAO has been studied. The 17 AOs on LCAO approximations give 17 MOs. Thus, χ_1 – χ_9 are AOs of platinum ($\chi_1 = 6s$, $\chi_2 = 6px$, $\chi_3 = 6py$, $\chi_4 = 6pz$, $\chi_5 = 5dx^2 - y^2$, $\chi_6 = 5dz^2$, $\chi_7 = 5dxy$, $\chi_8 = 5dxz$, $\chi_9 = 5dyz$) and χ_{10} – χ_{17} are AOs of chlorine ($\chi_{10} = 3s$, $\chi_{11} = 3px$, $\chi_{12} = 3py$, $\chi_{13} = 3pz$ for Br-2 and $\chi_{14} = 3s$, $\chi_{15} = 3px$, $\chi_{16} = 3py$, $\chi_{17} = 3pz$ for Br-3). The magnitude of contribution of various AOs (χ) in the formation of 17 MOs (ϕ_1 to ϕ_{17}) is demonstrated in Table 1(b). A close look at this table reflected that six AOs (χ_2 , χ_3 , χ_4 , χ_9 , χ_{13} , χ_{16}) have no contribution in the formation of 1st MO (ϕ_1) as these have zero or near zero coefficient values. And the rest eleven AOs (χ_1 , χ_5 , χ_6 , χ_7 , χ_8 , χ_{10} , χ_{11} , χ_{12} , χ_{14} , χ_{15} , χ_{17}) have their contribution in ϕ_1 . By adopting same view the contributions AOs in ϕ_2 to ϕ_{17} MOs can be describe.

3.3. Platinum Diiodide

The optimized geometry (Figure 3) as obtained from molecular mechanics method of platinum(II) bromide is given below.



Figure 3. Structure of PtI_2 .

The MOs of this molecule as formed by linear combination of nine orbitals (five 4d-orbitals, one 5s orbital and three 5p orbitals) from platinum and four orbitals (three 3p orbitals and one 3s orbital) from each bromine are shown below

Pt-1 = $5dx^2 - y^2$, $5dz^2$, $5dxy$, $5dxz$, $5dyz$, $6s$, $6px$, $6py$, $6pz$,	=	9
I-2 = $4s$, $4px$, $4py$, $4pz$	=	4
I-3 = $4s$, $4px$, $4py$, $4pz$	=	4
Total	=	17

In order to examine the contribution of various atomic orbitals in the formation of molecular orbitals, the LCAO has been studied. The 17 AOs on LCAO approximations give 17 MOs. Thus, χ_1 – χ_9 are AOs of platinum ($\chi_1 = 6s$, $\chi_2 = 6px$, $\chi_3 = 6py$, $\chi_4 = 6pz$, $\chi_5 = 5dx^2 - y^2$, $\chi_6 = 5dz^2$, $\chi_7 = 5dxy$, $\chi_8 = 5dxz$, $\chi_9 = 5dyz$) and χ_{10} – χ_{17} are AOs of chlorine ($\chi_{10} = 3s$, $\chi_{11} = 3px$, $\chi_{12} = 3py$, $\chi_{13} = 3pz$ for I-2 and $\chi_{14} = 3s$, $\chi_{15} = 3px$, $\chi_{16} = 3py$, $\chi_{17} = 3pz$ for I-3). The magnitude of contribution of various AOs (χ) in the formation of 17 MOs (ϕ_1 to ϕ_{17}) is demonstrated in Table 1(c). A close look at this table reflected that seven AOs (χ_2 , χ_3 , χ_4 , χ_9 , χ_{12} , χ_{13} , χ_{16}) have no contribution in the formation of 1st MO (ϕ_1) as these have zero or near zero coefficient values. And the rest ten AOs (χ_1 , χ_5 , χ_6 , χ_7 , χ_8 , χ_{10} , χ_{11} , χ_{14} , χ_{15} , χ_{17}) have their contribution in ϕ_1 . By adopting same view the contributions AOs in ϕ_2 to ϕ_{17} MOs can be describe.

3.4. Platinum Difluoride

The optimized geometry (Figure 4) as obtained from molecular mechanics

method of platinum(II) fluoride is given below.



Figure 4. Structure of PtF₂.

The MOs of this molecule as formed by linear combination of nine orbitals (five 4d-orbitals, one 5s orbital and three 5p orbitals) from platinum and four orbitals (three 2p orbitals and one 2s orbital) from each bromine are shown below

Pt-1 = 5d _{x² - y²} , 5d _{z²} , 5d _{xy} , 5d _{xz} , 5d _{yz} , 6s, 6p _x , 6p _y , 6p _z ,	=	9
F-2 = 2s, 2p _x , 2p _y , 2p _z	=	4
F-3 = 2s, 2p _x , 2p _y , 2p _z	=	4
Total	=	17

In order to examine the contribution of various atomic orbitals in the formation of molecular orbitals the LCAO has been studied. The 17 AOs on LCAO approximations give 17 MOs. Thus, χ_1 - χ_9 are AOs of platinum ($\chi_1 = 6s$, $\chi_2 = 6p_x$, $\chi_3 = 6p_y$, $\chi_4 = 6p_z$, $\chi_5 = 5d_{x^2 - y^2}$, $\chi_6 = 5d_{z^2}$, $\chi_7 = 5d_{xy}$, $\chi_8 = 5d_{xz}$, $\chi_9 = 5d_{yz}$) and χ_{10} - χ_{17} are AOs of chlorine ($\chi_{10} = 3s$, $\chi_{11} = 3p_x$, $\chi_{12} = 3p_y$, $\chi_{13} = 3p_z$ for F-2 and $\chi_{14} = 3s$, $\chi_{15} = 3p_x$, $\chi_{16} = 3p_y$, $\chi_{17} = 3p_z$ for F-3). The magnitude of contribution of various AOs (χ) in the formation of 17 MOs (ϕ_1 to ϕ_{17}) is demonstrated in Table 1(d). A close look at this Table 1(d) reflected that nine AOs (χ_2 , χ_3 , χ_4 , χ_7 , χ_8 , χ_{12} , χ_{13} , χ_{16} , χ_{17}) have no contribution in the formation of 1st MO (ϕ_1) as these have zero or near zero coefficient values. And the rest eight AOs (χ_1 , χ_5 , χ_6 , χ_9 , χ_{10} , χ_{11} , χ_{14} , χ_{15}) have their contribution in ϕ_1 . By adopting same view the contributions AOs in ϕ_2 to ϕ_{17} MOs can be describe.

3.5. Role of Metal Orbital

The characteristics of transition metal (TM) elements are due to their d orbitals of (n - 1) shell and s and p orbitals of n shell. When atom of TM elements form compound they adopted either concept of bonded attraction and non-bonded repulsion of VB (Valence Bond) theory, and or positive and negative overlap populations of MO (Molecular Orbital) theory. In the first case they may undergo various type of hybridization that depends upon the oxidation state of TM and number and nature of combining atoms or ions, and in the second case formation of molecular orbital by LCAO approximation. At first we have to examine the extent of involvement of 4d, 5s and 5p AOs of Pt-1 in the formation of MOs in platinum dihalides. For this, values of coefficient ' χ ' of 5d_{z²}, 5d_{xy}, 5d_{xz}, 6s, 6p_x, 6p_y and 6p_z have been separately tabulated for each MO for each platinum halides and are given in Table 2(a)-(d), respectively. The ' χ ' of non-bonding orbitals 5d_{x²-y²}(χ_5) and 5d_{yz}(χ_9) are excluded. To see the total involvement of seven AOs of Pt-1 in twelve MOs (ϕ_1 - ϕ_{12}), the coefficient value of each orbital has been added. The five vacant MOs (ϕ_{13} - ϕ_{17}) are exempted here, as there is only 24e⁻ to be filled by Aufbau principle, Hund's rule and Pauli's exclusion principle and thus we

Table 2. (a) Coefficient values of $4d_{xy}$, $4d_{xz}$, $4d_{x^2-y^2}$, $5s$, $5p_x$, $5p_y$, $5p_z$ AOs of $PtCl_2$; (b) Coefficient values of $4d_{xy}$, $4d_{xz}$, $4d_{x^2-y^2}$, $5s$, $5p_x$, $5p_y$, $5p_z$ AOs of $PtBr_2$; (c) Coefficient values of $4d_{xy}$, $4d_{xz}$, $4d_{x^2-y^2}$, $5s$, $5p_x$, $5p_y$, $5p_z$ AOs of PtI_2 ; (d) Coefficient values of $4d_{xy}$, $4d_{xz}$, $4d_{x^2-y^2}$, $5s$, $5p_x$, $5p_y$, $5p_z$ AOs of PtF_2 ; (e) Summation values of various AOs of halides of Pt(II).

(a)							
MOs	$5d_{z^2}$ (Pt-1)	$5d_{xy}$ (Pt-1)	$5d_{xz}$ (Pt-1)	$6s$ (Pt-1)	$6p_x$ (Pt-1)	$6p_y$ (Pt-1)	$6p_z$ (Pt-1)
ϕ_1	0.0360	0.0062	0.0000	0.0704	0.0000	0.0000	0.0000
ϕ_2	0.0000	0.0000	0.0000	0.0000	0.0312	0.0015	0.0000
ϕ_3	0.1593	0.0274	0.0000	0.1786	0.0000	0.0000	0.0000
ϕ_4	0.0000	0.4030	0.0001	0.0000	0.0000	0.0000	0.0000
ϕ_5	0.0000	0.0001	0.4045	0.0000	0.0000	0.0000	0.0000
ϕ_6	0.0000	0.0000	0.0000	0.0000	0.1299	0.0065	0.0000
ϕ_7	0.0000	0.0000	0.0000	0.0000	0.0032	0.0649	0.0000
ϕ_8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0650
ϕ_9	0.0000	0.0000	0.0497	0.0000	0.0000	0.0000	0.0000
ϕ_{10}	0.8660	0.0496	0.0000	0.0000	0.0000	0.0000	0.0000
ϕ_{11}	0.0000	0.0001	0.9195	0.0000	0.0000	0.0000	0.0000
ϕ_{12}	0.0000	0.9161	0.0001	0.0000	0.0000	0.0000	0.0000
$\Sigma =$	1.0613	1.4025	1.3739	0.2490	0.1643	0.0729	0.0650
(b)							
MOs	$5d_{z^2}$ (Pt-1)	$5d_{xy}$ (Pt-1)	$5d_{xz}$ (Pt-1)	$6s$ (Pt-1)	$6p_x$ (Pt-1)	$6p_y$ (Pt-1)	$6p_z$ (Pt-1)
ϕ_1	0.0445	0.0013	0.0159	0.0841	0.0001	0.0000	0.0000
ϕ_2	0.0000	0.0000	0.0000	0.0000	0.0425	0.0004	0.0043
ϕ_3	0.2113	0.0063	0.0755	0.1732	0.0000	0.0000	0.0000
ϕ_4	0.0010	0.5567	0.0054	0.0000	0.0000	0.0001	0.0000
ϕ_5	0.0970	0.0069	0.5483	0.0000	0.0000	0.0000	0.0001
ϕ_6	0.0000	0.0000	0.0000	0.0000	0.1455	0.0012	0.0147
ϕ_7	0.0000	0.0001	0.0000	0.0000	0.0008	0.0608	0.0026
ϕ_8	0.0000	0.0000	0.0001	0.0000	0.0061	0.0026	0.0605
ϕ_9	0.0000	0.1005	0.0083	0.0000	0.0000	0.0000	0.0000
ϕ_{10}	0.8573	0.0085	0.1000	0.0000	0.0000	0.0000	0.0000
ϕ_{11}	0.0011	0.8286	0.0071	0.0000	0.0000	0.0001	0.0000
ϕ_{12}	0.1443	0.0051	0.8161	0.0000	0.0000	0.0000	0.0001
$\Sigma =$	1.3565	1.5140	1.5767	0.2573	0.1950	0.0652	0.0823

Continued

(c)							
MOs	5d _{z²} (Pt-1)	5d _{xy} (Pt-1)	5d _{xz} (Pt-1)	6s (Pt-1)	6p _x (Pt-1)	6p _y (Pt-1)	6p _z (Pt-1)
ϕ_1	0.0699	0.0021	0.0250	0.1194	0.0000	0.0000	0.0000
ϕ_2	0.0000	0.0000	0.0000	0.0000	0.0612	0.0005	0.0062
ϕ_3	0.2289	0.0068	0.0818	0.1678	0.0000	0.0000	0.0000
ϕ_4	0.1116	0.1065	0.6314	0.0000	0.0000	0.0000	0.0000
ϕ_5	0.0184	0.6408	0.1033	0.0000	0.0000	0.0000	0.0000
ϕ_6	0.0000	0.0000	0.0000	0.0000	0.1535	0.0013	0.0155
ϕ_7	0.0000	0.0000	0.0000	0.0000	0.0055	0.0078	0.0549
ϕ_8	0.0000	0.0000	0.0000	0.0000	0.0012	0.0552	0.0078
ϕ_9	0.0000	0.1005	0.0083	0.0000	0.0000	0.0000	0.0000
ϕ_{10}	0.8573	0.0085	0.1000	0.0000	0.0000	0.0000	0.0000
ϕ_{11}	0.0145	0.7518	0.0811	0.0000	0.0000	0.0000	0.0000
ϕ_{12}	0.1310	0.0843	0.7407	0.0000	0.0000	0.0000	0.0000
$\Sigma =$	1.4316	1.7013	1.7716	0.2872	0.2214	0.0648	0.0844
(d)							
MOs	5d _{z²} (Pt-1)	5d _{xy} (Pt-1)	5d _{xz} (Pt-1)	6s (Pt-1)	6p _x (Pt-1)	6p _y (Pt-1)	6p _z (Pt-1)
ϕ_1	0.0153	0.0005	0.0055	0.0229	0.0000	0.0000	0.0000
ϕ_2	0.0000	0.0000	0.0000	0.0000	0.0024	0.0000	0.0002
ϕ_3	0.0824	0.0024	0.0294	0.0751	0.0000	0.0000	0.0000
ϕ_4	0.0168	0.0060	0.0950	0.0000	0.0000	0.0000	0.0000
ϕ_5	0.0011	0.0965	0.0061	0.0000	0.0000	0.0000	0.0000
ϕ_6	0.0000	0.0000	0.0000	0.0000	0.0470	0.0004	0.0048
ϕ_7	0.0000	0.0000	0.0000	0.0000	0.0032	0.0012	0.0188
ϕ_8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0188	0.0012
ϕ_9	0.0000	0.1005	0.0083	0.0000	0.0000	0.0000	0.0000
ϕ_{10}	0.8573	0.0085	0.1000	0.0000	0.0000	0.0000	0.0000
ϕ_{11}	0.0108	0.9902	0.0620	0.0000	0.0000	0.0000	0.0000
ϕ_{12}	0.1724	0.0604	0.9751	0.0000	0.0000	0.0000	0.0000
$\Sigma =$	1.1561	1.2650	1.2814	0.0980	0.0526	0.0204	0.0250
(e)							
AO	Pt(II)Cl ₂	Pt(II)Br ₂	Pt(II)I ₂	Pt(II)F ₂			
$\Sigma 5d_{z^2}$	1.0613	1.3565	1.4316	1.1561			
$\Sigma 5d_{xy}$	1.4025	1.5140	1.7013	1.2650			
$\Sigma 5d_{xz}$	1.3739	1.5767	1.7716	1.2814			
$\Sigma 6s$	0.2490	0.2573	0.2872	0.0980			
$\Sigma 6p_x$	0.1643	0.1950	0.2214	0.0526			
$\Sigma 6p_y$	0.0729	0.0652	0.0648	0.0204			
$\Sigma 6p_z$	0.0650	0.0823	0.0844	0.0250			

considered only twelve MOs among seventeen MOs. The summation values of AOs in these twelve MOs have been placed at the bottom of each table (Table 2(a)-(d)), which clearly reflects maximum involvement is of 5d orbital. Next to this is 5s orbital. It is also predicted from the summation values of d orbital. The non-bonding orbitals must have lowest summation values ($\Sigma dx^2 - y^2 = 0.9656$ and $\Sigma dyz = 1.0646$ in PtCl_2 , $\Sigma dx^2 - y^2 = 1.2117$ and $\Sigma dyz = 1.1479$ in PtBr_2 , $\Sigma dx^2 - y^2 = 1.2141$ and $\Sigma dyz = 1.1467$ in PtI_2 and $\Sigma dx^2 - y^2 = 0.8010$ and $\Sigma dyz = 1.1210$ in PtF_2). The involvement of three p orbitals are negligible as their summation values are very low in comparison to d orbital and considerably low with respect to s orbital.

From Table 2(e) and Figure 5, it is evident that the involvement of 5p orbital in Pt-X bond is insignificant and the main role is played by 'ns' and $(n-1)d$ orbital. It was Landis, who discovered sd^n -hybridization ($n = 1$ to 5) along with molecular shape and bond angles in his seminal publications. Further, he also explained co-relationship between sd^n -hybridization and its bond angle by plotting a graph between energy and bond angle as shown in Figure 6. This figure reflected that bond angle has two minima one below 90° and one above 90° . This is because the energy curves are function of the bond angles. The bond angles as presented in Figure 1 that also hold up Landis concept sd^n hybridization when $n = 1$. Landis recommended that transition metals in their valency shell can accommodate only $12e^-$ ($10e^-$ in five $(n-1)d$ orbitals and $2e^-$ in one ns-orbital). The $18e^-$ can be in their valency shell ($10e^-$ in five $(n-1)d$ orbitals, $2e^-$ in one ns-orbital and $6e^-$ in three np orbitals). Further, a close look at the Table 2(e) and right side of the curves of Figure 1 clearly demonstrated that the summation values are highest in case of iodide and lowest in chloride. This is due to cloud expanding of halides. For a given metal ion, the ability of ligands to induce this cloud expanding increases according to nephelauxetic series: $\text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{ox} < \text{SCN}^- < \text{Cl}^- < \text{CN}^- < \text{Br}^- < \text{I}^-$. Thus, iodide produces greater cloud expanding effect than bromide, which in turn produces higher than chloride in platinum diiodide, platinum dibromide and platinum dichloride, respectively. In other words the effective positive charge on Pt(II) is reduced greater by iodide and lesser by chloride. This result is in good agreement with nephelauxetic series of ligands [43]. This effect can further be related with difference in energy level of ns and np orbitals. These two orbitals differ in energy significantly. The energy difference $\Delta\epsilon$ in s and p orbitals of chloride, bromide and iodide are not same. The s and p orbitals in iodide are close as compared to s and p orbitals of bromide and chloride, as shown below.

Energy (eV)	F	Cl	Br	I
ϵ_s	-1.4699	-0.9665	-0.8110	-0.6615
ϵ_p	-0.6651	-0.5218	-0.4814	-0.4867
$\Delta\epsilon_{s,p}$	-0.8048	-0.4447	-0.3296	-0.1748

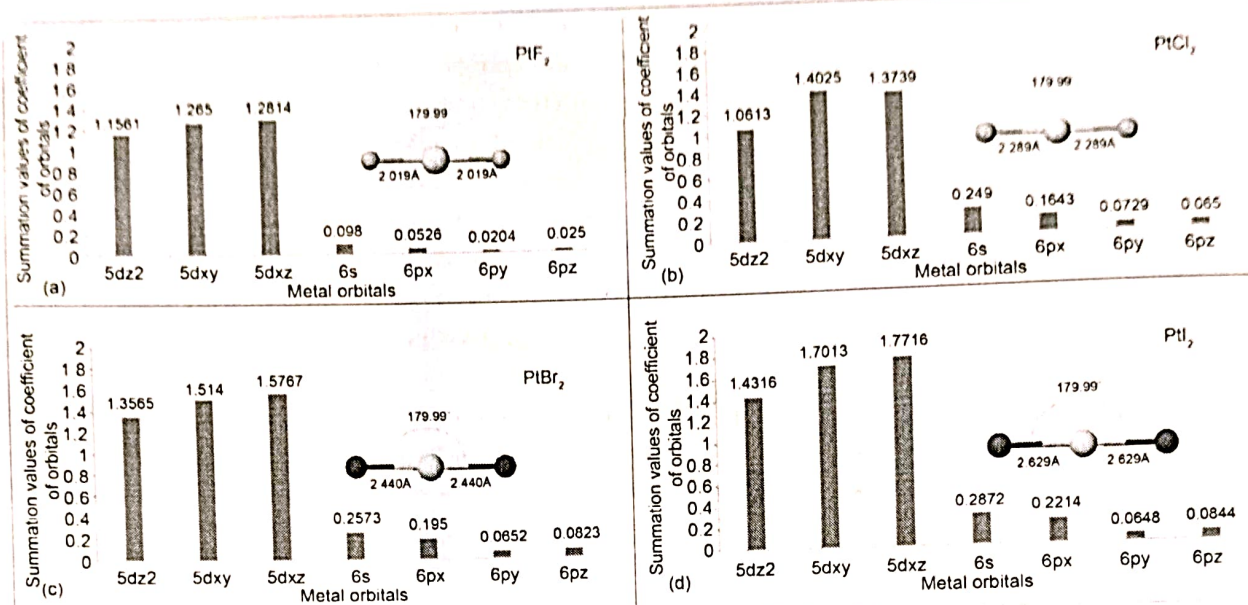


Figure 5. (a) Extent of involvement of metal orbitals in the formation of MOs of PtCl₂, (b) Extent of involvement of metal orbitals in the formation of MOs of PtCl₂, (c) Extent of involvement of metal orbitals in the formation of MOs of PtCl₂ and (d) Extent of involvement of metal orbitals in the formation of MOs of PtCl₂.

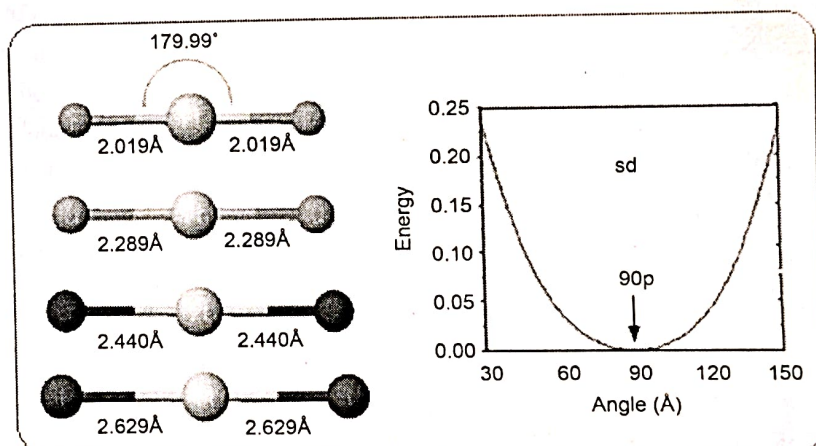


Figure 6. Plot between energy and bond angle(Å) for sd-hybridization.

Iodide, in which s and p orbitals are much close causes greater nephelauxetic effect and thus increases the covalent bond character in the molecule. Percentage of ionic and covalent bond character of PtCl₂, PtBr₂ and PtI₂ has been calculated by solving equation "% ionic character = $16 \times \Delta\chi + 3.5 \times (\Delta\chi)^2$ ", and results are shown below:

Compound	PtF ₂	PtCl ₂	PtBr ₂	PtI ₂
% Ionic Character	37.32	16.79	12.50	6.59
% Covalent Character	62.69	83.21	87.50	93.41

The result is in good agreement with experiment results that covalent character increases in the order: $\text{PtI}_2 > \text{PtBr}_2 > \text{PtCl}_2 > \text{PtF}_2$.

3.6. Overlap Population Analysis

The shape of each MO ($\phi_1 - \phi_{17}$) has been determined by the relative magnitudes and signs of the different coefficients [38]. For this the Pt(II)X_2 has been decomposed into three parts: Pt-1, X-1 and X-2, and the MO of the complete system has been obtained by allowing the orbitals of Pt-1 (5d, 6s, 6p), X-1 (ns and np) and X-2 (ns and np) to overlap. The possible overlaps between the various AOs of platinum (Pt-1) and halogens (X-2 and X-2) in each MO will be 88, as describes. To solve Equation (3) for these 88 overlaps in MOs of platinum dihalides, we need eigenvector values (c_n and $c_{n'}$), values of overlap matrix (S_n) and number of electrons (n_i) in each MO. The eigenvector and overlap integral values for platinum dihalides have been taken from Table 1(a)-(d) and Table 3(a)-(d), respectively. The number of electrons is taken as two for ϕ_1 to ϕ_{12} and zero for ϕ_{13}

Table 3. (a) Overlap matrix or overlap integrals values (S_n) of various overlaps of atomic orbitals of constituent atoms in PtCl_2 ; (b) Overlap matrix or overlap integrals values (S_n) of various overlaps of atomic orbitals of constituent atoms in PtBr_2 ; (c) Overlap matrix or overlap integrals values (S_n) of various overlaps of atomic orbitals of constituent atoms in PtI_2 ; (d) Overlap matrix or overlap integrals values (S_n) of various overlaps of atomic orbitals of constituent atoms in PtF_2 .

(a)																	
AOs	6s	6px	6py	6pz	5dx ² - y ²	5dz ²	5dxy	5dxz	5dyz	3s	3px	3py	3pz	3s	3px	3py	3pz
	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Cl-2)	(Cl-2)	(Cl-2)	(Cl-2)	(Cl-3)	(Cl-3)	(Cl-3)	(Cl-3)
6s (Pt-1)	1.0000																
6px (Pt-1)	0.0000	1.0000															
6py (Pt-1)	0.0000	0.0000	1.0000														
6pz (Pt-1)	0.0000	0.0000	0.0000	1.0000													
5dx ² - y ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	1.0000												
5dz ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000											
5dxy (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000										
5dxz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
5dyz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000								
3s (Cl-2)	0.1923	0.2789	0.0139	0.0000	0.0825	-0.0479	0.0082	0.0000	0.0000	1.0000							
3px (Cl-2)	-0.3085	-0.3783	-0.0257	0.0000	-0.1183	0.0688	-0.0156	0.0000	0.0000	0.0000	1.0000						
3py (Cl-2)	-0.0153	-0.0257	0.1367	0.0000	-0.0134	0.0034	0.0750	0.0000	0.0000	0.0000	0.0000	1.0000					
3pz (Cl-2)	0.0000	0.0000	0.0000	0.1380	0.0000	0.0000	0.0000	0.0760	0.0038	0.0000	0.0000	0.0000	1.0000				
3s (Cl-3)	0.1922	-0.2788	-0.0139	0.0000	0.0825	-0.0479	0.0082	0.0000	0.0000	0.0003	-0.0021	-0.0001	0.0000	1.0000			
3px (Cl-3)	0.3085	-0.3783	-0.0257	0.0000	0.1182	-0.0688	0.0156	0.0000	0.0000	0.0021	-0.0088	-0.0005	0.0000	0.0000	1.0000		
3py (Cl-3)	0.0153	-0.0257	0.1367	0.0000	0.0134	-0.0034	-0.0750	0.0000	0.0000	0.0001	-0.0005	0.0009	0.0000	0.0000	0.0000	1.0000	
3pz (Cl-3)	0.0000	0.0000	0.0000	0.1380	0.0000	0.0000	0.0000	-0.0760	-0.0038	0.0000	0.0000	0.0000	0.0009	0.0000	0.0000	0.0000	1.0000

Continued

AOs	(b)																
	6s (Pt-1)	6px (Pt-1)	6py (Pt-1)	6pz (Pt-1)	5dx ² - y ² (Pt-1)	5dz ² (Pt-1)	5dxy (Pt-1)	5dxz (Pt-1)	5dyz (Pt-1)	4s (Br-2)	4px (Br-2)	4py (Br-2)	4pz (Br-2)	4s (Br-3)	4px (Br-3)	4py (Br-3)	4pz (Br-3)
6s (Pt-1)	1.0000																
6px (Pt-1)	0.0000	1.0000															
6py (Pt-1)	0.0000	0.0000	1.0000														
6pz (Pt-1)	0.0000	0.0000	0.0000	1.0000													
5dx ² - y ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	1.0000												
5dz ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000											
5dxy (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000										
5dxz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
5dyz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000								
4s (Br-2)	0.1612	0.2376	-0.0020	-0.0240	0.0691	-0.0391	-0.0012	-0.0140	0.0001	1.0000							
4px (Br-2)	-0.2686	-0.3511	0.0038	0.0463	-0.1101	0.0616	0.0023	0.0282	-0.0003	0.0000	1.0000						
4py (Br-2)	0.0022	0.0038	0.1066	-0.0004	0.0019	-0.0005	0.0589	-0.0003	-0.0059	0.0000	0.0000	1.0000					
4pz (Br-2)	0.0271	0.0463	-0.0004	0.1019	0.0171	-0.0165	-0.0003	0.0554	-0.0005	0.0000	0.0000	0.0000	1.0000				
4s (Br-3)	0.1615	-0.2380	0.0020	0.0241	0.0692	-0.0392	-0.0012	-0.0140	0.0001	0.0001	-0.0006	0.0000	0.0001	1.0000			
4px (Br-3)	0.2689	-0.3514	0.0038	0.0463	0.1103	-0.0617	-0.0023	-0.0283	0.0003	0.0006	-0.0028	0.0000	0.0003	0.0000	1.0000		
4py (Br-3)	-0.0023	0.0038	0.1068	-0.0004	-0.0019	0.0005	-0.0590	0.0003	0.0060	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	1.0000	
4pz (Br-3)	-0.0272	0.0463	-0.0004	0.1021	-0.0171	0.0166	0.0003	-0.0556	0.0005	-0.0001	0.0003	0.0000	0.0002	0.0000	0.0000	0.0000	1.0000

AOs	(c)																
	6s (Pt-1)	6px (Pt-1)	6py (Pt-1)	6pz (Pt-1)	5dx ² - y ² (Pt-1)	5dz ² (Pt-1)	5dxy (Pt-1)	5dxz (Pt-1)	5dyz (Pt-1)	5s (I-2)	5px (I-2)	5py (I-2)	5pz (I-2)	5s (I-3)	5px (I-3)	5py (I-3)	5pz (I-3)
6s (Pt-1)	1.0000																
6px (Pt-1)	0.0000	1.0000															
6py (Pt-1)	0.0000	0.0000	1.0000														
6pz (Pt-1)	0.0000	0.0000	0.0000	1.0000													
5dx ² - y ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	1.0000												
5dz ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000											
5dxy (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000										
5dxz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
5dyz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000								
5s (I-2)	0.1516	0.2190	-0.0018	-0.0221	0.0611	-0.0346	-0.0010	-0.0123	0.0001	1.0000							
5px (I-2)	-0.2549	-0.3361	0.0036	0.0431	-0.0999	0.0559	0.0021	0.0251	-0.0003	0.0000	1.0000						
5py (I-2)	0.0021	0.0036	0.0906	-0.0004	0.0016	-0.0005	0.0484	-0.0003	-0.0049	0.0000	0.0000	1.0000					
5pz (I-2)	0.0258	0.0431	-0.0004	0.0863	0.0150	-0.0141	-0.0003	0.0454	-0.0004	0.0000	0.0000	0.0000	1.0000				
5s (I-3)	0.1515	-0.2190	0.0018	0.0221	0.0611	-0.0345	-0.0010	-0.0123	0.0001	0.0001	-0.0005	0.0000	0.0000	1.0000			
5px (I-3)	0.2549	-0.3360	0.0036	0.0431	0.0999	-0.0559	-0.0021	-0.0251	0.0003	0.0005	-0.0019	0.0000	0.0002	0.0000	1.0000		
5py (I-3)	-0.0021	0.0036	0.0906	-0.0004	-0.0016	0.0005	-0.0484	0.0003	0.0049	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	1.0000	
5pz (I-3)	-0.0258	0.0431	-0.0004	0.0863	-0.0150	0.0141	0.0003	-0.0454	0.0004	0.0000	0.0002	0.0000	0.0001	0.0000	0.0000	0.0000	1.0000

Continued

(d)																	
AOs	6s	6px	6py	6pz	5dx ² - y ²	5dz ²	5dxy	5dxz	5dyz	2s	2px	2py	2pz	3s	2px	2py	2pz
	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(F-2)	(F-2)	(F-2)	(F-2)	(F-3)	(F-3)	(F-3)	(F-3)
6s (Pt-1)	1.0000																
6px (Pt-1)	0.0000	1.0000															
6py (Pt-1)	0.0000	0.0000	1.0000														
6pz (Pt-1)	0.0000	0.0000	0.0000	1.0000													
5dx ² - y ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	1.0000												
5dz ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000											
5dxy (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000										
5dxz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
5dyz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000								
2s (F-2)	0.1701	0.2642	-0.0022	-0.0267	0.0876	-0.0495	-0.0015	-0.0177	0.0001	1.0000							
2px (F-2)	-0.1400	-0.2106	0.0023	0.0280	-0.0901	0.0505	0.0019	0.0227	-0.0002	0.0000	1.0000						
2py (F-2)	0.0012	0.0023	0.0669	-0.0002	0.0015	-0.0004	0.0442	-0.0002	-0.0045	0.0000	0.0000	1.0000					
2pz (F-2)	0.0141	0.0280	-0.0002	0.0641	0.0136	-0.0128	-0.0002	0.0414	-0.0003	0.0000	0.0000	0.0000	1.0000				
2s (F-3)	0.1701	-0.2641	0.0022	0.0267	0.0876	-0.0495	-0.0015	-0.0177	0.0001	0.0000	0.0000	0.0000	0.0000	1.0000			
2px (F-3)	0.1400	-0.2106	0.0023	0.0281	0.0901	-0.0505	-0.0019	-0.0227	0.0002	0.0000	-0.0001	0.0000	0.0000	0.0000	1.0000		
2py (F-3)	-0.0012	0.0023	0.0669	-0.0002	-0.0015	0.0004	-0.0442	0.0002	0.0045	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	
2pz (F-3)	-0.0142	0.0281	-0.0002	0.0641	-0.0136	0.0128	0.0002	-0.0414	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000

to ϕ_{17} . Finally, Equation (3) has been solved for twelve MOs with respect to each halide. In order to get a precise description, the sums of overlap population for the eleven MOs of platinum halides have also been worked out and results are presented in Table 4(a)-(d). As can be seen from the table that among the twelve molecular orbital, eight are bonding, two are nonbonding and two are antibonding. The bonding molecular orbitals are $\phi_1 - \phi_8$. The nonbonding molecular orbital are ϕ_9 and ϕ_{10} , which are purely two d atomic orbitals of platinum namely $dx^2 - y^2$ and dyz . The antibonding molecular orbital are $\phi_{11} - \phi_{12}$. A comparative study of Table 4(a)-(d) reflected that in all cases the non-bonding electrons are present in 9th and 10th molecular orbitals. Further, similarity in positions of nonbonding molecular orbitals prompted us to examine the eigenvalues of Pt⁺² ion and to compare them with the eigenvalues of the halides. The eigenvalues of the molecular orbitals of all the halides are included in Table 5, which shows that nonbonding orbitals are degenerate in all the cases.

Table 4. (a) Quantitative and qualitative nature of occupied molecular orbitals of platinum dichloride; (b) Quantitative and qualitative nature of occupied molecular orbitals of platinum dibromide; (c) Quantitative and qualitative nature of occupied molecular orbitals of platinum diiodide; (d) Quantitative and qualitative nature of occupied molecular orbitals of platinum difluoride.

(a)			
MO No.	$\Sigma n_{r,s,i}$	Sign	MOs
ϕ_1	0.0545	+	BMO
ϕ_2	0.0236	+	BMO
ϕ_3	0.0022	+	BMO
ϕ_4	0.0753	+	BMO
ϕ_5	0.0753	+	BMO
ϕ_6	0.1168	+	BMO
ϕ_7	0.0259	+	BMO
ϕ_8	0.0259	+	BMO
ϕ_9	0.0000	0	NBO
ϕ_{10}	0.0000	0	NBO
ϕ_{11}	-0.0997	-	ABMO
ϕ_{12}	-0.0992	-	ABMO

(b)			
MO No.	$\Sigma n_{r,s,i}$	Sign	MOs
ϕ_1	0.0563	+	BMO
ϕ_2	0.0277	+	BMO
ϕ_3	0.1901	+	BMO
ϕ_4	0.0734	+	BMO
ϕ_5	0.0733	+	BMO
ϕ_6	0.1273	+	BMO
ϕ_7	0.0184	+	BMO
ϕ_8	0.0184	+	BMO
ϕ_9	0.0000	0	NBO
ϕ_{10}	0.0000	0	NBO
ϕ_{11}	-0.0877	-	ABMO
ϕ_{12}	-0.0877	-	ABMO

Continued

(c)			
MO No.	$\Sigma n_{r-s,i}$	Sign	MOs
ϕ_1	0.0788	+	BMO
ϕ_2	0.0367	+	BMO
ϕ_3	0.1632	+	BMO
ϕ_4	0.0641	+	BMO
ϕ_5	0.0641	+	BMO
ϕ_6	0.1280	+	BMO
ϕ_7	0.0143	+	BMO
ϕ_8	0.0143	+	BMO
ϕ_9	0.0000	0	NBO
ϕ_{10}	0.0000	0	NBO
ϕ_{11}	-0.0737	-	ABMO
ϕ_{12}	-0.0738	-	ABMO

(d)			
MO No.	$\Sigma n_{r-s,i}$	Sign	MOs
ϕ_1	0.0198	+	BMO
ϕ_2	-0.0016	+	ABMO
ϕ_3	0.0720	+	BMO
ϕ_4	0.0121	+	BMO
ϕ_5	0.0121	+	BMO
ϕ_6	0.0275	+	BMO
ϕ_7	0.0035	+	BMO
ϕ_8	0.0036	+	BMO
ϕ_9	0.0000	0	NBO
ϕ_{10}	0.0000	0	NBO
ϕ_{11}	-0.0200	-	ABMO
ϕ_{12}	-0.0200	-	ABMO

MOs is molecular orbitals, BMO is bonding molecular orbital, ABMO is antibonding molecular orbital and NBO is nonbonding molecular orbitals.

Table 5. Energy (eV) of all the seventeen molecular orbitals of PtX₂.

MO No.	PtCl ₂	PtBr ₂	PtI ₂	PtF ₂
1	-0.9727	-0.8180	-0.6717	-1.4716
2	-0.9670	-0.8121	-0.6632	-1.4699
3	-0.5654	-0.5300	-0.5150	-0.6767
4	-0.5377	-0.5008	-0.4872	-0.6671
5	-0.5377	-0.5008	-0.4872	-0.6671
6	-0.5265	-0.4891	-0.4749	-0.6664
7	-0.5236	-0.4825	-0.4676	-0.6653
8	-0.5236	-0.4825	-0.4676	-0.6653
9 ^a	-0.4627	-0.4627	-0.4627	-0.4627
10 ^a	-0.4627	-0.4627	-0.4627	-0.4627
11	-0.4378	-0.4382	-0.4388	-0.4573
12	-0.4378	-0.4382	-0.4388	-0.4573
13	-0.4358	-0.4311	-0.4317	-0.4320
14	-0.1784	-0.1882	-0.1920	-0.1952
15	-0.1784	-0.1882	-0.1920	-0.1952
16	0.0366	-0.0863	-0.1277	-0.1682
17	0.3443	0.1528	0.0768	0.1074

^aThe energy nonbonding molecular orbitals are -0.4627, which is equivalent to the energy of degenerate d atomic orbitals (-0.4627 eV).

3.7. Molecular Orbital Diagram of Pt(II) Halides

In order to demonstrate the energy levels of different molecular orbitals, the position of nonbonding molecular orbitals and the magnitude of splitting of d orbitals, more precisely the molecular orbital diagram has been drawn separately for the four halides as Figures 7-10, respectively. The molecular orbital diagram is important in the sense that energy of each molecular orbital is shown which at a glance provides information about the difference in energies of various molecular orbitals and explains various properties of the molecule.

4. Conclusions

(i) The involvement of three p atomic orbitals is negligible as their summation values are very low in comparison to d orbital and considerably low with respect to s orbital. From Table 2(e) and Figure 5, it is evident that the involvement of 5p orbital in Pt-X bond is insignificant and the main role is played by "ns" and (n - 1)d orbital. Figure 6 reflected that bond angle has two minima one below 90° and one above 90°. The study well supported the Landis concepts of sdⁿ-hybridation (here n = 1) as bond angle and contributions of s-orbital and d-orbital of Pt(II) are maximum with negligible contribution of p-orbitals.

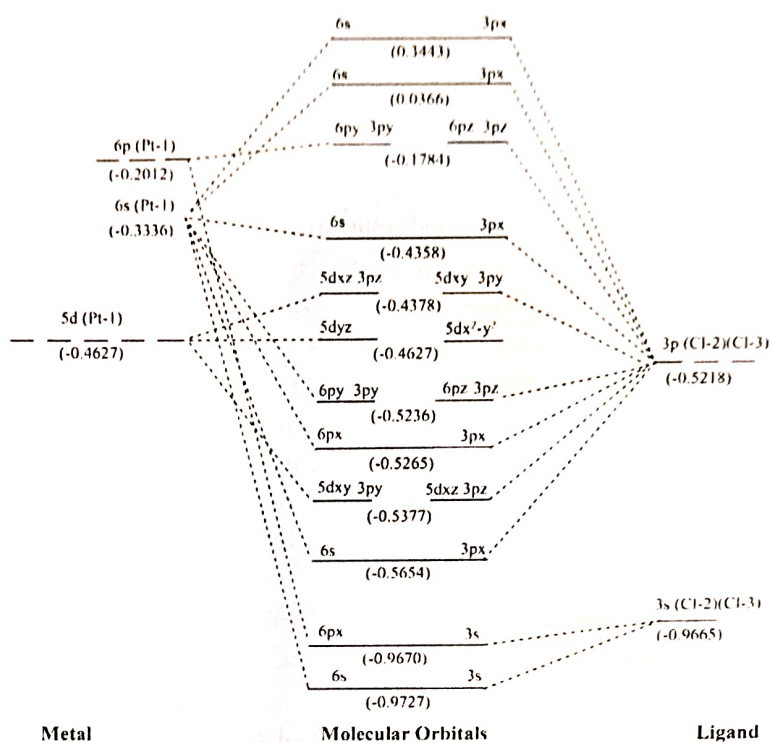


Figure 7. MO diagram of PtCl₂ along with energy of AOs and MOs in eV as show in parenthesis.

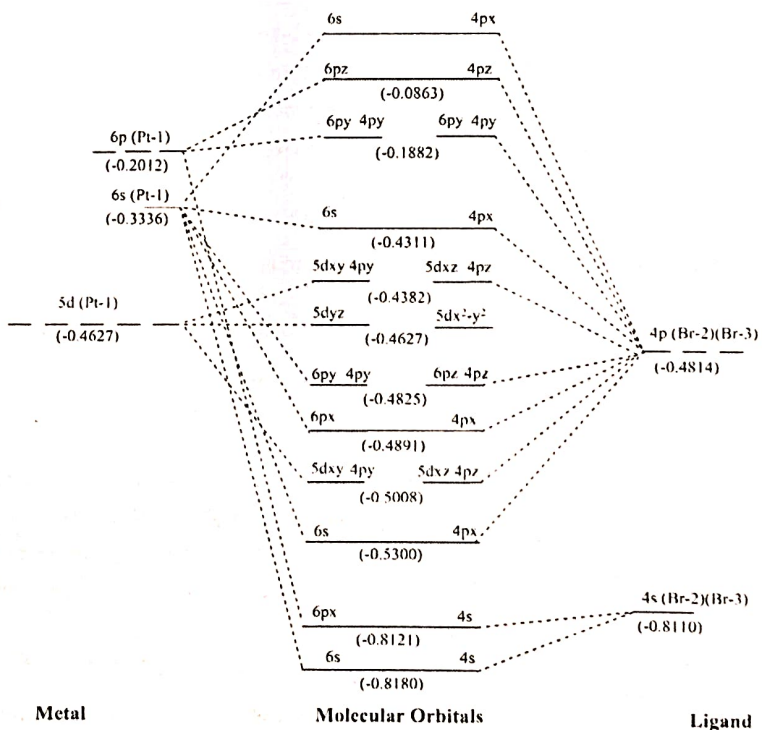


Figure 8. MO diagram of PtBr₂ along with energy of AOs and MOs in eV as show in parenthesis.

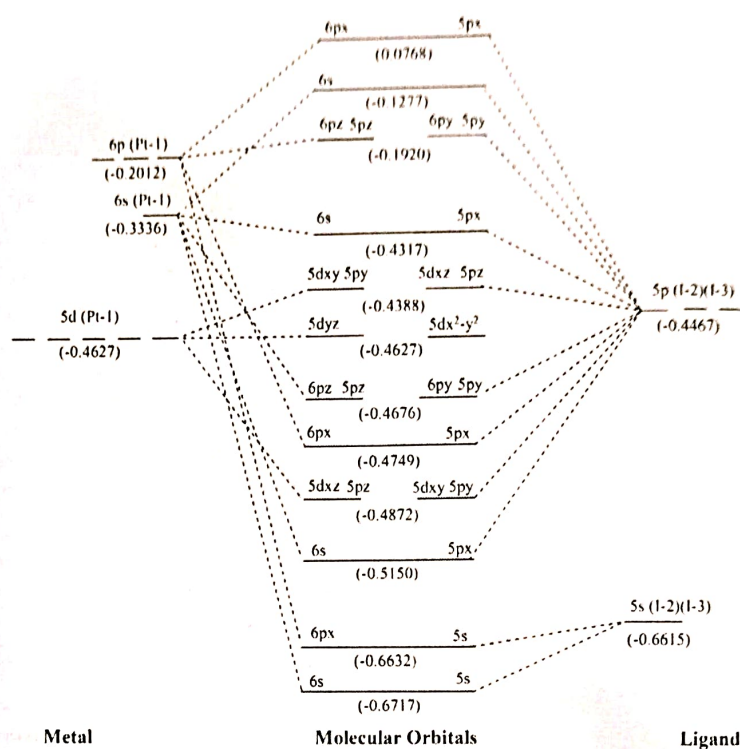


Figure 9. MO diagram of PtI₂ along with energy of AOs and MOs in eV as show in parenthesis.

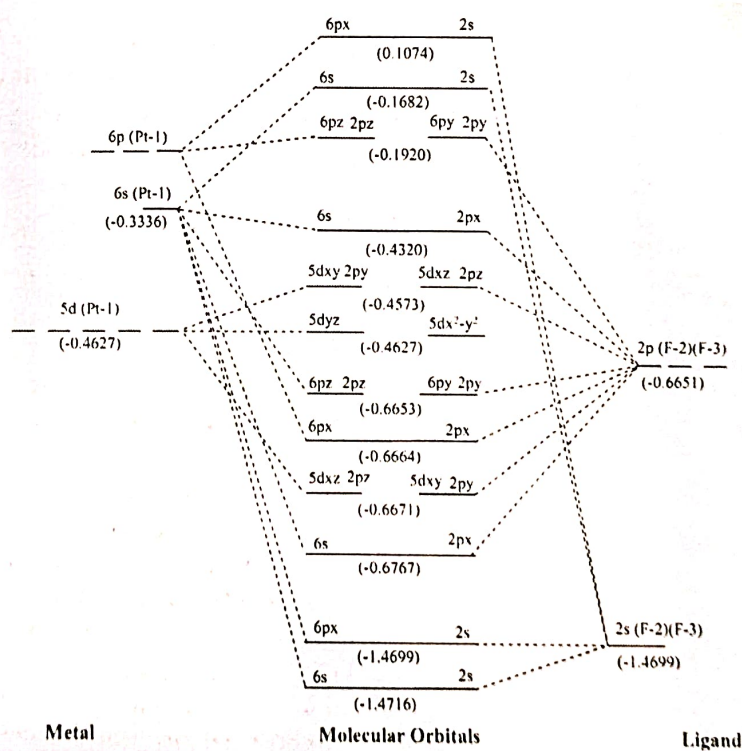


Figure 10. MO diagram of PtF₂ along with energy of AOs and MOs in eV as show in parenthesis.

(ii) These halides also support the cloud-expanding effect with experimental data and also follow the nephelauxetic effect. Table 2(e) and right side of the curves of Figure 5 clearly demonstrate that the summation values are highest in case of iodide and lowest in chloride (fluoride). This is due to cloud expanding of halides. Thus, iodide produces greater cloud expanding effect than bromide, which in turn produces higher than chloride in platinum diiodide, platinum dibromide and platinum dichloride (platinum difluoride), respectively. In other words, the effective positive charge on Pt(II) is reduced greater by iodide and lesser by chloride (fluoride). This result is in good agreement with nephelauxetic series of ligands. This effect can further be related with difference in energy level of ns and np orbitals. These two orbitals differ in energy significantly. Iodide, in which s and p orbitals are much closer, causes greater nephelauxetic effect and thus increases the covalent bond character in the molecule. The result is in good agreement with experiment results that covalent character increases in the order: $\text{PtI}_2 > \text{PtBr}_2 > \text{PtCl}_2 > \text{PtF}_2$.

(iii) This study of atomistic details of halides of Pt(II) compounds and construction of molecular orbital diagram (Figures 6-10) that at a glance provide an insight of electronic behavior.

(iv) The study will help to fine tune the existing complexes of these halides.

Acknowledgements

I am very thankful to Principal and Head of Department of Chemistry, Shia P. G. College, Sitapur Road, Lucknow-226020 (U.P.) for laboratory facilities and also to Department of Higher Education, Prayagraj, Uttar Pradesh for financial assistance (Letter No./Reginal Office Lucknow/5496-99/2021-22; Dated: 15-03-2022 and G.O. No.-107/2021/2584/70-4-2021-4(28)/2021; Dated: 28-12-2021).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Annexure-E

Cisplatin at atomic, molecular and electronic level: A DFT based studyAnil Kumar Soni¹¹Department of Chemistry, Shia Post Graduate College Sitapur Road, Lucknow-226020 (U.P.) India.e-mail: anilsony82@gmail.comIffat Azim²

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Swati³³AcademyofScientificandInnovativeResearchNPL,ChemicalandFoodBNDDivision, CSIR-National Physical Laboratory, Dr K. S. Krishnan Marg, New Delhi-110012, India.e -mail: swati.amv1987@gmail.com,Vishnu Kumar Sahu^{4*}⁴Department of Chemistry, Maharani LalKunwari, Post Graduate College, Tulsipur Road, Balrampur-271201(U.P.), India.e-mail: vishnukr_sahu@rediffmail.com**Abstract**

Recently, we have studied electronic structure of platinum dihalides (Pt(II)X₂). Here, atomic orbital and molecular orbital analysis along with spectroscopic studies have been made to see electronic structure of cisplatin (cis-[Pt(NH₃)₂Cl₂]). CAChe Pro software of Fujitsu and Gaussian-03 software have been used to obtain minimum energy structure. For this cisplatin has opted with EHT (for population analysis) and DFT (for spectroscopic analysis). Summation values of coefficient of AOs reflected sd³-hybridization and thus supported Landis concept of sdⁿ-hybridization, where n = 3. Sum of overlap population used to characterize the fourteen MOs (as there are 28e⁻) into BMOs, ABMO and NBMOs. UV-spectrum of cisplatin shows one absorption band at 3.9845eV with peak corresponded to 311.16nm of oscillator strength (0.0014). IR-spectrum analysis shows 27 normal vibrations.

Key words: Cisplatin, Mulliken population analysis, sd³-hybridization, UV-spectrum and IR-spectrum

1. Introduction:

It was Rosenberg, who accidentally finds out the biological activity of cisplatin, i.e. $\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ in 1965 [1]. Actually it was synthesized by Peyrone in 1844 [2]. The anti-tumor activity of square planar complexes ($\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ and $[\text{Pt(en)Cl}_2]$) and octahedral complexes ($\text{cis-[Pt(NH}_3)_2\text{Cl}_4]$ and $[\text{Pt(en)Cl}_4]$) against sarcoma-180 (in mice) and against murine leukemia (L-1210) cells were also discovered by Rosenberg [3]. Harder and Rosenberg reported selective inhibition of DNA synthesis in vitro by $\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ below $5\mu\text{M}$ [4]. Cisplatin was launched in 1978 as anticancer drug but it is still used for treatment of testicular [5], ovarian [6], bladder [7] and neck cancers [8] in humans. The activity of $\text{cis-[Pt(NH}_3)_2\text{Cl}_2]$ against tumor is associated with reactions replacing the halides. The effective anti-tumor compounds have features in common that may aid us in understanding their interaction with biological systems [9]. These agents usually have two exchangeable ligands in cis positions. These complexes are bifunctional reagents that may undergo nucleophilic substitution at two cis positions (scheme 1), which assumes monomeric species and preservation of the cis configuration thermodynamically [10]. Prediction of atomic, molecular, electronic structure along with spectroscopic characteristic of metal complexes have always been challenging for computational chemists.

2. Materials and Methods:

In this research work, atomic, molecular orbitals and spectroscopic analysis has been made to see electronic structure of cisplatin. Firstly a quantitative atomic orbital (AO) and molecular orbital (MO) treatment have also been made on above species to study (i) involvement of metal (n-1)d-, ns- and np-orbitals in hybridizations and its type that has been used to get information related to shape (bond angle) and size (bond length) [11]; (ii) contribution of various AOs in the construction of MOs through LCAO approximation using values of eigenvector and overlap matrix [12] and (iii) nature of MOs by distinguishing them into bonding, nonbonding and antibonding MO through population analysis [13]. The adopted methods for various calculations of above species are based on Mulliken's population analysis, which has been well described in our recent publications [14]. After that UV-Vis and IR spectroscopic analysis have also been made [15]. CAChePro software of Fujitsu [16] and Gaussian-03 software [17] have been used to obtain minimum energy structure. For this cisplatin has opted with EHT [18] and DFT methods [19].

3. Results and Discussion:

The molecular orbitals of cisplatin are formed by linear combination of 9 orbitals from platinum, 4 orbitals of each nitrogen, 4 orbitals of each halogen and 1 orbital from each hydrogen as given below:

Pt-1	= 6s, 6px, 6py, 6pz, 5dx ² -y ² , 5dz ² , 5dxy, 5dxz, 5dyz	= 9
N-2	= 2s, 2px, 2py, 2pz	= 4
N-3	= 2s, 2px, 2py, 2pz	= 4
H-4	= 1s	= 1
H-5	= 1s	= 1
H-6	= 1s	= 1
H-7	= 1s	= 1
H-8	= 1s	= 1
H-9	= 1s	= 1
Cl-10	= 3s, 3px, 3py, 3pz	= 4
Cl-11	= 3s, 3px, 3py, 3pz	= 4

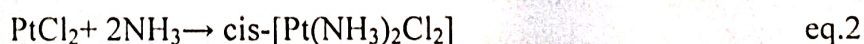
Total = 31

In total thirty one atomic orbital (AOs) are involved in the formation of thirty one molecular orbitals (MOs). But here we discuss only seventeen MOs of one Pt²⁺ (9MOs) and 2Cl⁻ (2×4MOs), because we have to see the effect of cisplatin (eq. 1 and 2) formation on these orbitals. The fourteen MOs of ligands 2NH₃ (2×7) are kept out of discussion (eq. 2). The AOs are represented by 'χ' and MOs by 'φ'. Here χ₁ to χ₉ are AOs of Pt and remaining eight AOs of two Cl by χ₂₄ to χ₃₁ viz. , χ₁ (6s), χ₂ (6px), χ₃ (6py), χ₄ (6pz), χ₅ (5dx²-y²), χ₆ (5dz²), χ₇ (5dxy), χ₈ (5dxz), χ₉ (5dyz), χ₂₄ (3s), χ₂₅ (3px), χ₂₆ (3py), χ₂₇ (3pz), χ₂₈ (3s), χ₂₉ (3px), χ₃₀ (3py), and χ₃₁ (3pz). The form of the seventeen MOs i.e., the magnitude of contribution of various thirty one AOs in the formation of seventeen MOs is demonstrated by φ₁ - φ₁₇ as described below.

$$\begin{aligned}
 \phi_1 &= -0.0031 \chi_1 + 0.0247 \chi_2 - 0.0014 \chi_3 + 0.0004 \chi_4 + 0.0013 \chi_5 + 0.0113 \chi_6 - 0.0003 \chi_7 + 0.0000 \chi_8 + 0.0048 \chi_9 - 0.0408 \chi_{24} - 0.0023 \chi_{25} - 0.0028 \chi_{26} + 0.0006 \chi_{27} - 0.0386 \chi_{28} - 0.0017 \chi_{29} + 0.0032 \chi_{30} - 0.0006 \chi_{31} \\
 \phi_2 &= +0.0000 \chi_1 + 0.0018 \chi_2 + 0.0282 \chi_3 - 0.0061 \chi_4 - 0.0025 \chi_5 + 0.0001 \chi_6 - 0.0185 \chi_7 + 0.0039 \chi_8 - 0.0006 \chi_9 - 0.0353 \chi_{24} - 0.0086 \chi_{25} + 0.0040 \chi_{26} - 0.0012 \chi_{27} + 0.0339 \chi_{28} + 0.0090 \chi_{29} + 0.0026 \chi_{30} - 0.0010 \chi_{31} \\
 \phi_3 &= -0.0414 \chi_1 + 0.0102 \chi_2 - 0.0007 \chi_3 + 0.0001 \chi_4 + 0.0009 \chi_5 + 0.0178 \chi_6 - 0.0002 \chi_7 + 0.0002 \chi_8 + 0.0089 \chi_9 - 0.6966 \chi_{24} + 0.0047 \chi_{25} + 0.0010 \chi_{26} - 0.0003 \chi_{27} - 0.6987 \chi_{28} + 0.0045 \chi_{29} - 0.0016 \chi_{30} + 0.0004 \chi_{31} \\
 \phi_4 &= 0.0000 \chi_1 + 0.0010 \chi_2 + 0.0139 \chi_3 - 0.0035 \chi_4 - 0.0055 \chi_5 + 0.0002 \chi_6 - 0.0377 \chi_7 + 0.0097 \chi_8 - 0.0012 \chi_9 + 0.7038 \chi_{24} - 0.0024 \chi_{25} + 0.0084 \chi_{26} - 0.0022 \chi_{27} - 0.7020 \chi_{28} + 0.0035 \chi_{29} + 0.0080 \chi_{30} - 0.0021 \chi_{31}
 \end{aligned}$$

$$\begin{aligned}
\phi_5 &= -0.0044 \chi_1 - 0.0028 \chi_2 + 0.0005 \chi_3 - 0.0001 \chi_4 + 0.0723 \chi_5 + 0.0022 \chi_6 - 0.0089 \chi_7 + 0.0041 \chi_8 + 0.0185 \chi_9 + 0.0148 \chi_{24} - 0.0879 \chi_{25} - 0.0144 \chi_{26} + 0.0053 \chi_{27} + 0.0120 \chi_{28} - 0.0732 \chi_{29} + 0.0226 \chi_{30} - 0.0082 \chi_{31} \\
\phi_6 &= -0.0001 \chi_1 - 0.0001 \chi_2 - 0.0005 \chi_3 - 0.0004 \chi_4 + 0.0025 \chi_5 + 0.0004 \chi_6 - 0.0116 \chi_7 - 0.0439 \chi_8 - 0.0003 \chi_9 - 0.0021 \chi_{24} + 0.0090 \chi_{25} + 0.0000 \chi_{26} - 0.0078 \chi_{27} + 0.0030 \chi_{28} - 0.0146 \chi_{29} + 0.0035 \chi_{30} - 0.0082 \chi_{31} \\
\phi_7 &= +0.0006 \chi_1 + 0.0006 \chi_2 + 0.0002 \chi_3 + 0.0000 \chi_4 + 0.0065 \chi_5 + 0.0150 \chi_6 + 0.0022 \chi_7 - 0.0007 \chi_8 - 0.0485 \chi_9 - 0.0013 \chi_{24} + 0.0071 \chi_{25} - 0.0001 \chi_{26} - 0.0135 \chi_{27} - 0.0049 \chi_{28} + 0.0246 \chi_{29} - 0.0037 \chi_{30} + 0.0189 \chi_{31} \\
\phi_8 &= -0.0000 \chi_1 - 0.0001 \chi_2 + 0.0022 \chi_3 - 0.0005 \chi_4 + 0.0008 \chi_5 - 0.0003 \chi_6 + 0.0125 \chi_7 - 0.0062 \chi_8 + 0.0047 \chi_9 + 0.0151 \chi_{24} - 0.0809 \chi_{25} - 0.0037 \chi_{26} + 0.0043 \chi_{27} - 0.0130 \chi_{28} + 0.0700 \chi_{29} - 0.0103 \chi_{30} + 0.0049 \chi_{31} \\
\phi_9 &= -0.2285 \chi_1 + 0.0095 \chi_2 - 0.0007 \chi_3 + 0.0001 \chi_4 - 0.0129 \chi_5 + 0.1983 \chi_6 + 0.0002 \chi_7 + 0.0004 \chi_8 + 0.0830 \chi_9 + 0.0582 \chi_{24} - 0.2540 \chi_{25} + 0.4471 \chi_{26} - 0.1179 \chi_{27} + 0.0584 \chi_{28} - 0.3201 \chi_{29} - 0.4053 \chi_{30} + 0.1102 \chi_{31} \\
\phi_{10} &= -0.0002 \chi_1 + 0.0004 \chi_2 + 0.0072 \chi_3 - 0.0032 \chi_4 - 0.0667 \chi_5 + 0.0035 \chi_6 - 0.4884 \chi_7 + 0.1179 \chi_8 - 0.0154 \chi_9 - 0.0315 \chi_{24} + 0.3166 \chi_{25} - 0.3364 \chi_{26} + 0.0861 \chi_{27} + 0.0314 \chi_{28} - 0.3733 \chi_{29} - 0.2774 \chi_{30} + 0.0751 \chi_{31} \\
\phi_{11} &= -0.0499 \chi_1 - 0.0503 \chi_2 + 0.0045 \chi_3 - 0.0008 \chi_4 + 0.2047 \chi_5 + 0.0568 \chi_6 - 0.0235 \chi_7 + 0.0039 \chi_8 + 0.0673 \chi_9 - 0.0049 \chi_{24} - 0.4321 \chi_{25} - 0.4140 \chi_{26} + 0.0943 \chi_{27} - 0.0050 \chi_{28} - 0.3716 \chi_{29} + 0.4838 \chi_{30} - 0.1036 \chi_{31} \\
\phi_{12} &= +0.0003 \chi_1 + 0.0003 \chi_2 + 0.0088 \chi_3 + 0.0337 \chi_4 - 0.0047 \chi_5 - 0.0057 \chi_6 - 0.0475 \chi_7 - 0.1928 \chi_8 + 0.0136 \chi_9 + 0.0001 \chi_{24} + 0.0042 \chi_{25} + 0.1744 \chi_{26} + 0.6619 \chi_{27} - 0.0001 \chi_{28} + 0.0047 \chi_{29} + 0.1704 \chi_{30} + 0.6587 \chi_{31} \\
\phi_{13} &= +0.0007 \chi_1 + 0.0091 \chi_2 + 0.1143 \chi_3 - 0.0264 \chi_4 + 0.0127 \chi_5 - 0.0007 \chi_6 + 0.1100 \chi_7 - 0.0106 \chi_8 + 0.0007 \chi_9 - 0.0092 \chi_{24} + 0.4776 \chi_{25} - 0.0380 \chi_{26} + 0.0059 \chi_{27} + 0.0096 \chi_{28} - 0.4750 \chi_{29} + 0.0234 \chi_{30} + 0.0038 \chi_{31} \\
\phi_{14} &= +0.0023 \chi_1 - 0.0026 \chi_2 - 0.0006 \chi_3 + 0.0002 \chi_4 + 0.0460 \chi_5 + 0.0929 \chi_6 - 0.0040 \chi_7 - 0.0164 \chi_8 - 0.1961 \chi_9 - 0.0003 \chi_{24} + 0.0225 \chi_{25} - 0.1648 \chi_{26} - 0.6613 \chi_{27} - 0.0004 \chi_{28} + 0.0327 \chi_{29} + 0.1642 \chi_{30} + 0.6653 \chi_{31} \\
\phi_{15} &= +0.0389 \chi_1 + 0.1216 \chi_2 - 0.0097 \chi_3 + 0.0023 \chi_4 + 0.0880 \chi_5 - 0.1168 \chi_6 - 0.0104 \chi_7 + 0.0042 \chi_8 - 0.0156 \chi_9 + 0.0022 \chi_{24} - 0.4134 \chi_{25} + 0.1078 \chi_{26} - 0.0565 \chi_{27} + 0.0022 \chi_{28} - 0.4273 \chi_{29} - 0.0288 \chi_{30} + 0.0401 \chi_{31} \\
\phi_{16} &= 0.0001 \chi_1 + 0.0062 \chi_2 + 0.0621 \chi_3 - 0.0141 \chi_4 + 0.0019 \chi_5 - 0.0013 \chi_6 + 0.0199 \chi_7 + 0.0055 \chi_8 + 0.0005 \chi_9 + 0.0024 \chi_{24} - 0.3509 \chi_{25} - 0.5485 \chi_{26} + 0.1439 \chi_{27} - 0.0025 \chi_{28} + 0.2486 \chi_{29} - 0.5891 \chi_{30} + 0.1558 \chi_{31} \\
\phi_{17} &= +0.0011 \chi_1 - 0.0007 \chi_2 - 0.0022 \chi_3 + 0.0152 \chi_4 + 0.0128 \chi_5 + 0.0317 \chi_6 + 0.2237 \chi_7 + 0.9513 \chi_8 - 0.0622 \chi_9 - 0.0009 \chi_{24} - 0.0044 \chi_{25} + 0.0487 \chi_{26} + 0.1590 \chi_{27} + 0.0011 \chi_{28} + 0.0071 \chi_{29} + 0.0501 \chi_{30} + 0.1586 \chi_{31}
\end{aligned}$$

Here the coefficient of χ is the eigenvector (taken from Table-1). The remaining fourteen MOs, ϕ_{18} - ϕ_{31} , kept out of discussion as these remaining MOs have been formed by fourteen AOs of two NH_3 molecules as neutral ligands following eq. 1 and eq. 2, respectively. Eq. 1 represents formation of molecular compound PtCl_2 , which in eq. 2 complexes with 2NH_3 ligands and thus cisplatin is formed. Hence only seventeen MOs have been considered here.



When platinum forms compounds it adopted either concept of bonded attraction and non-bonded repulsion of VB (Valence Bond) theory, and or positive and negative overlap populations of MO (Molecular Orbital) theory [13]. In the first case platinum may undergoes various type of hybridization that depends upon its oxidation state, and number and nature of combining atoms or ions [11], and in the second case platinum forms molecular orbital by LCAO approximation [20]. In cisplatin, platinum acquires +2 oxidation state that may be neutralized by two chloride ion (2Cl^-), while two neutral ammine ligands (2NH_3) complex through coordinate bonds by donating two pairs of its lone pair of electrons. At first we have to examine the extent of involvement of 5d, 6s and 6p AOs of Pt-1 in the formation of MOs in cis-[Pt(NH₃)₂Cl₂]. For this, values of coefficient ' χ ' of 5d, 6s and 6p of platinum metal have been tabulated in Table 2. To see the total involvement of seven AOs of Pt-1 in fourteen MOs (ϕ_1 - ϕ_{14}), the coefficient value of each orbital has been added. The rest vacant MOs are exempted here, as there is only $28e^-$ to be filled by Aufbau principle, Hund's rule and Pauli's exclusion principle as described in our previous publication [14] and thus we considered only these MOs among seventeen MOs. The summation values of AOs in these fourteen MOs have been placed same table, which clearly reflects maximum involvement is of 5d orbital. Next to this is 6s orbital. It is also predicted from the summation values of d orbital. The non-bonding orbital i.e. $5d_{xz}$ must have lowest summation value which is 0.0251. The involvement of three p orbitals are negligible as their summation values are very low in comparison to d orbital and considerably low with respect to s orbital (0.3315). From Table 2 and figure 1, it is evident that the involvement of 6p orbital in Pt—L bond in cis-[Pt(NH₃)₂Cl₂] is insignificant and the main role is played by ' ns ' and ' $(n-1)d$ ' orbital. It was Landis, who discovered sd^n -hybridization (here $n = 3$) along with molecular shape and bond angles in his seminal publications [21].

The shape of each MO (ϕ_1 - ϕ_{17}) has been determined by the relative magnitudes and signs of the different coefficients. For this cis-[Pt(NH₃)₂Cl₂] has been decomposed into three parts: Pt-1, X-1 and X-2, and the MO of the complete system has been obtained by allowing the orbitals of Pt-1 (5d, 6s, 6p), X-1 (ns and np) and X-2 (ns and np) to overlap. The possible overlaps between the various AOs of ruthenium (Pt-1) and halogens (X-2 and X-2) in each MO will be 88. After that overlap populations have been calculated by solving equation: $n_{r-s,i} = n_i(2c_{ri}c_{si}S_{rs})$. To calculate overlap populations for 88 overlaps (overlap of 2NH_3 ligands have been excluded) in MOs of cis-[Pt(NH₃)₂Cl₂], we need eigenvector values (c_{ri} and c_{si}), values of overlap matrix (S_{rs}) and number of electrons (n_i) in each MO. The eigenvector and overlap integral values for cis-[Pt(NH₃)₂Cl₂] have been taken from Table 1 and Table 3, respectively. The number of electrons is taken as two for ϕ_1 to ϕ_{14} and zero for

ϕ_{15} to ϕ_{17} . In order to get a precise description, the sums of overlap population for the fourteen MOs of $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ have also been worked out and results are presented in Table 4. As can be seen from this table that among the fourteen molecular orbital, twelve are bonding, one is nonbonding and one is antibonding. The bonding molecular orbitals are ϕ_1 , ϕ_3 – ϕ_5 , ϕ_7 – ϕ_{14} . The nonbonding molecular orbital is ϕ_6 , which is purely dxz atomic orbital of platinum. The antibonding molecular orbital is ϕ_2 .

Metallic complexes have generally two selective absorption bands [22]. The first lies in the visible region. First band is attributed to electron transitions in the unsaturated transition shell of the central ion. The complexes which co-ordinate only one kind of ligand should naturally have narrower, symmetrical first bands than those which have ligands of different kinds, and among the latter, those which have ligands situated far apart in the spectrochemical series should have broader and less symmetrical first bands and sometimes these bands may be analyzed into two or more components. The second lies in the near ultraviolet region. The second band may be attributed to the co-ordination electrons, and is, therefore, the most general characteristic which a co-ordination compound should possess. Some complexes however, give the third band in the region of shorter wavelength. All the co-ordination compounds which have or seem to have at least a pair of negative ligands in trans-position showed the third bands (Table 5), but none of those deficient of the condition. Some of the co-ordinated compounds lack the first bands and most of them the third, they never fail to give the second bands. Cisplatin shows one absorption band (Figure 2) as opted by Gaussian-03 [17]. The PBE1PBE functional is a hybrid density functional theory (DFT) method, and SDD (Stuttgart-Dresden) pseudo-potentials are a type of pseudopotential used in DFT calculations to represent the interaction between the core and valence electrons. Using PBE1PBE functional with SDD pseudopotentials can be a computationally efficient and accurate way to model the electronic structure and properties of materials [23]. By RTD-PBE1PBE-FC method with SDD basis set were used to calculate the UV-Vis spectrum of cisplatin. Figure 2 reflects excitation energies and oscillator strengths. The band of absorption was recorded at 3.9845 eV with peak corresponded to 311.16 nm and shows oscillator strength 0.0014, as shown in Table 6.

By default, the PBE1PBE functional and SDD pseudo-potentials were used to calculate IR-spectrum by Gaussian-03 (Figure 3). The number of the normal vibrations of a single cisplatin molecule is 27, distributed in $9A_1 + 5A_2 + 8B_1 + 5B_2$, as shown in Table 7. The notations for modes used are σ -stretching, δ -bending, ρ -rocking, π -out of plane bending and τ -torsion; the 's' and 'as' stands for symmetric and asymmetric, respectively, and the index 'op' denotes out-of-plane, and TED for total energy distribution.

4. Conclusion:

Following points have been reflected from the above study: (i) AOs analysis shows sd^3 -hybridization and thus supported Landis concept of sd^n -hybridization, where $n = 3$. The result showed involvement of three p orbitals are negligible as their summation values are very low in comparison to d orbital and considerably low with respect to s orbital. (ii) In total thirty one AOs are involved in the formation of thirty one MOs of cisplatin. As, there is only $28e^-$ to be filled, hence, we considered only fourteen MOs (ϕ_1 - ϕ_{14}) and rest vacant MOs (ϕ_{15} - ϕ_{31}) have been exempted. Among fourteen MOs, twelve are bonding, one is antibonding (ϕ_2) and one is non-bonding (ϕ_6). (iii) Cisplatin showed one absorption band at 3.9845eV with peak corresponded to 311.16nm of low oscillator strength (0.0014). (iv) Cisplatin molecule showed 27 normal vibrations, which distributed in $9A_1 + 5A_2 + 8B_1 + 5B_2$.

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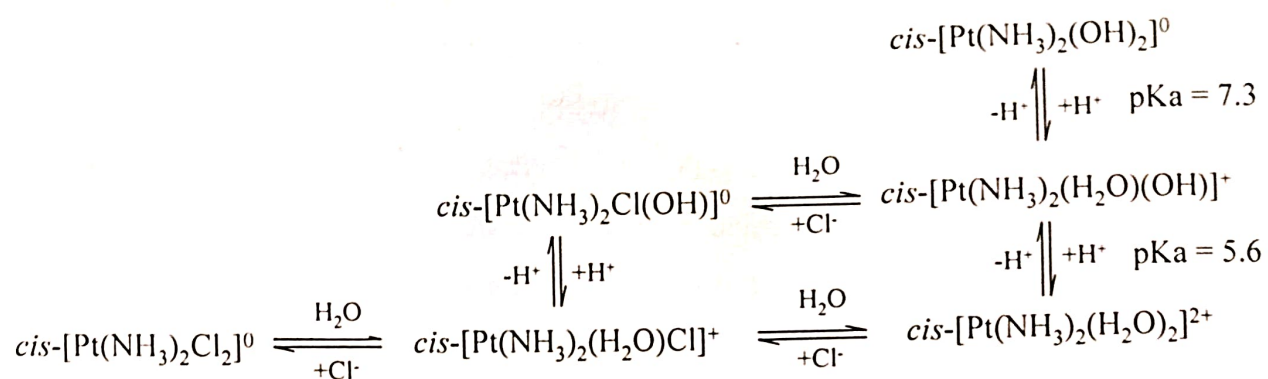
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Acknowledgements

I am very thankful to Principal and Head of Department of Chemistry, Shia P. G. College, Sitapur Road, Lucknow-226020(U.P.) for laboratory facilities and also to Department of Higher Education, Prayagraj, Uttar Pradesh for financial assistance (Letter No./Reginal Office Lucknow/ 5496-99/2021-22; Dated: 15-03-2022 and G.O. No.-107/2021/2584/70-4-2021-4(28)/2021; Dated: 28-12-2021).



Scheme -1. Hydrolysis of cis-platin in the stepwise reaction [10].

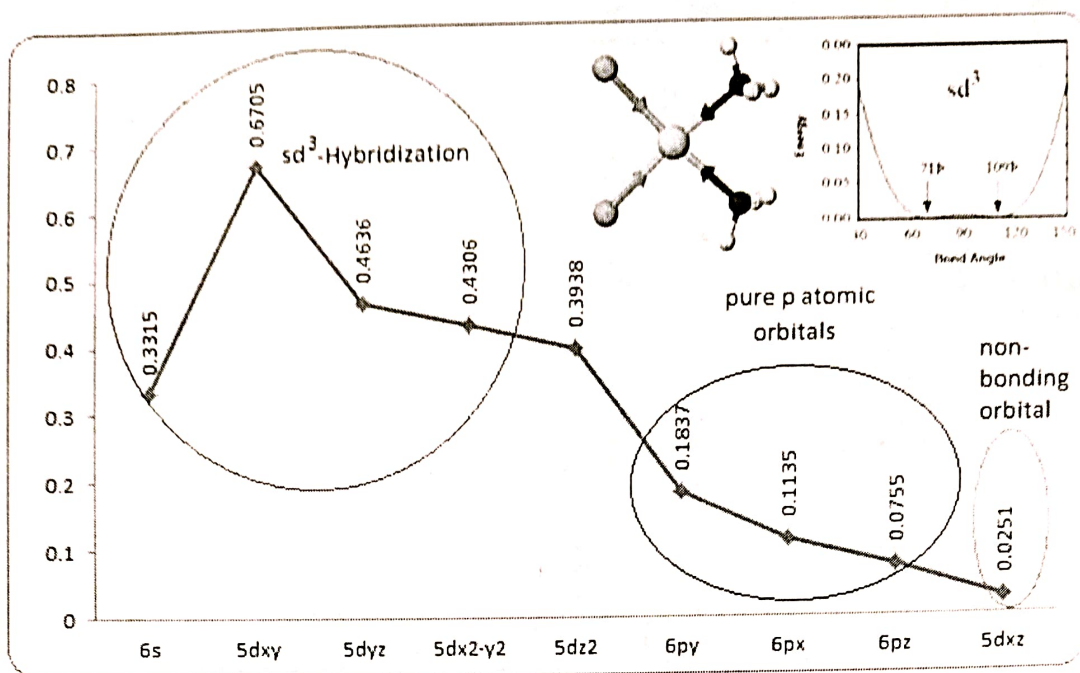


Figure 1. Contribution of atomic orbital in sd^3 hybridization [21]

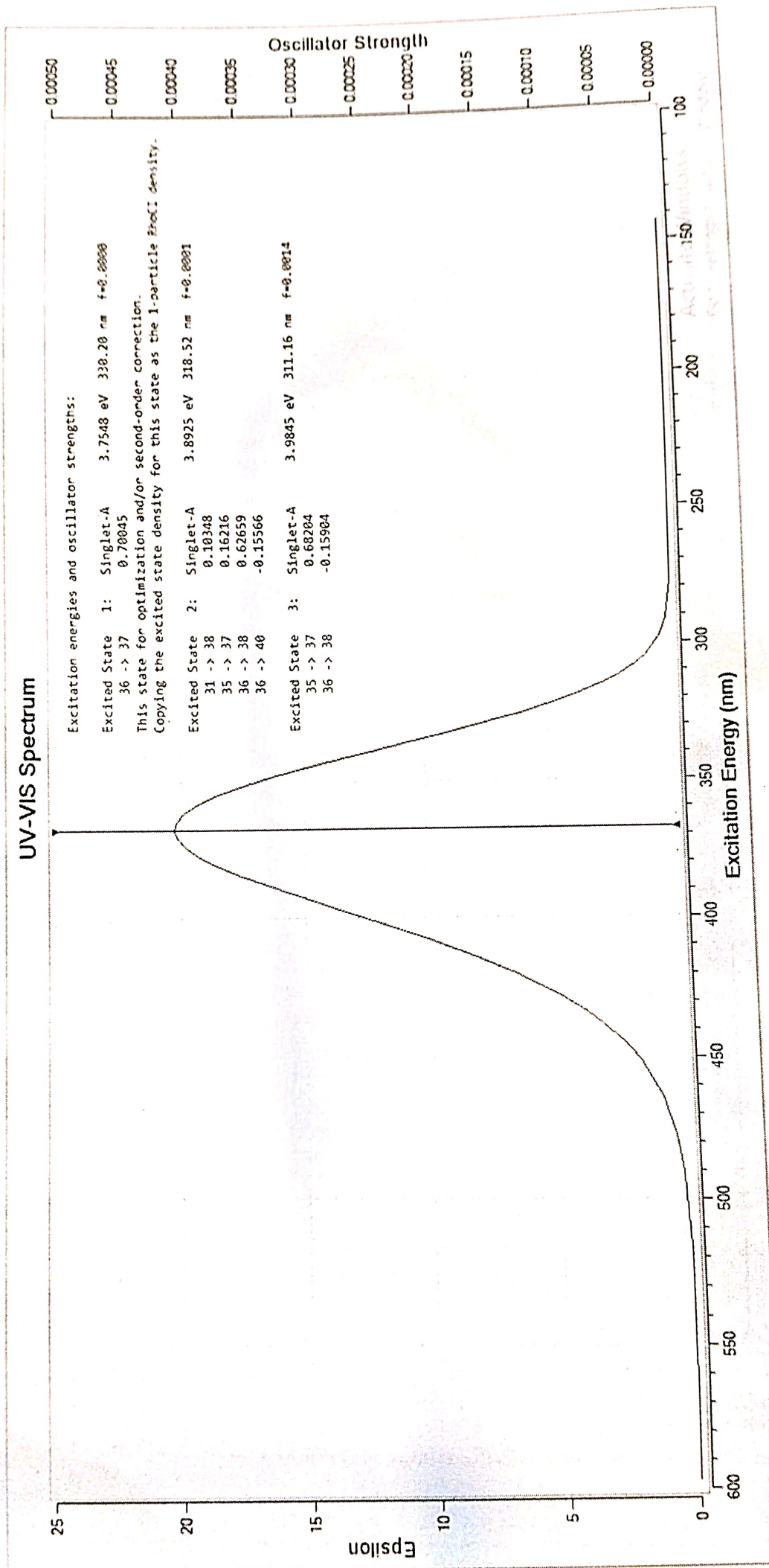


Figure 2. UV-Vis Spectrum of cisplatinopted by RTD-PBE1PBE-FC/SDD

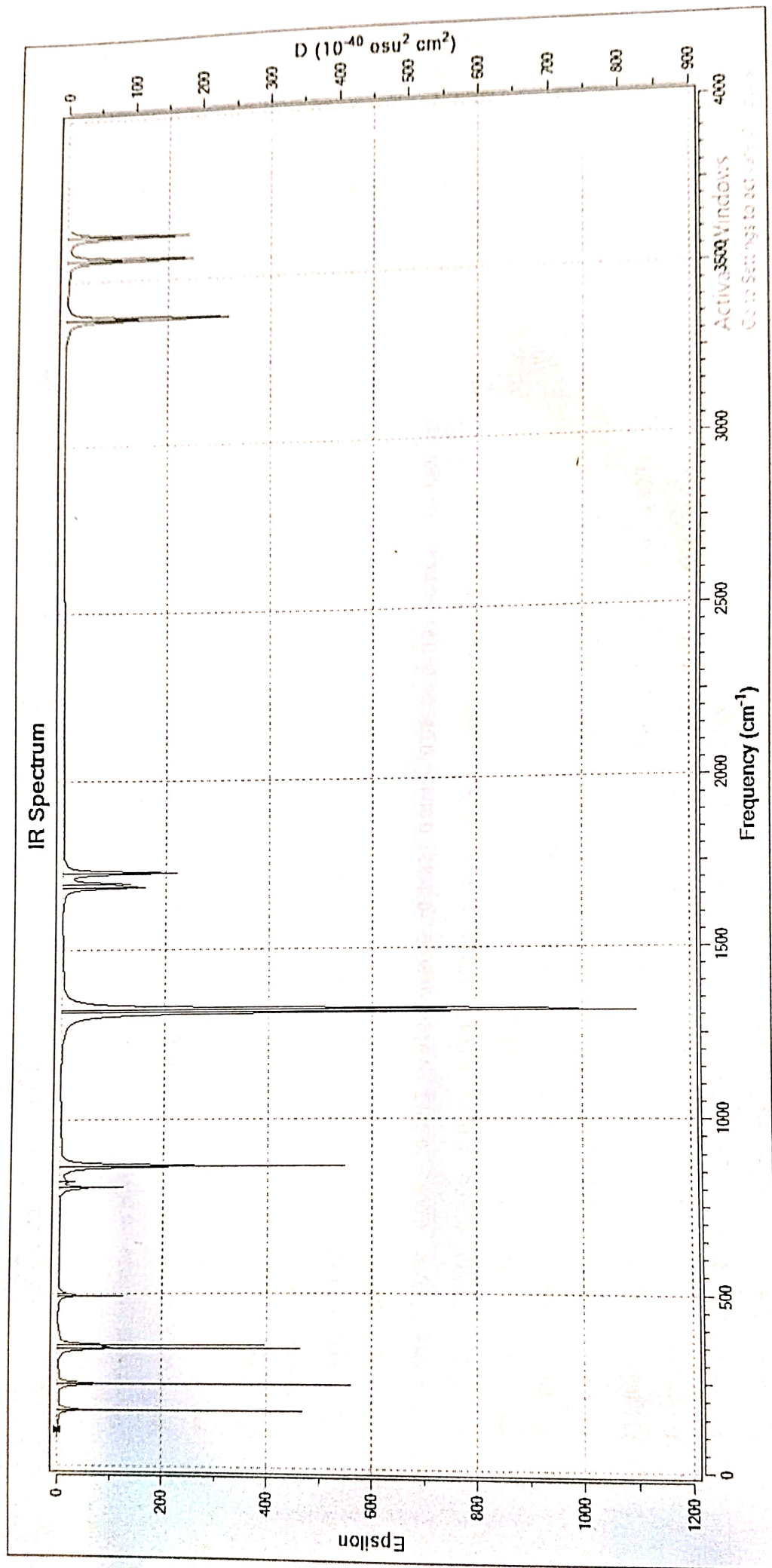


Figure 3. IR- Spectrum of cisplatin opted by PBE1PBE/SDD

Table 1. Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ_i) of cis-Pt(NH₃)Cl₂

Atom	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}	ϕ_{13}	ϕ_{14}	ϕ_{15}	ϕ_{16}	ϕ_{17}
Pt-1																	
χ_1	-0.0031	0.0000	-0.0414	0.0000	-0.0044	-0.0001	0.0006	-0.0000	-0.2285	-0.0002	-0.0499	0.0003	0.0007	0.0023	0.0389	0.0001	0.0011
χ_2	0.0247	0.0018	0.0102	0.0010	-0.0028	-0.0001	0.0006	-0.0001	0.0095	0.0004	-0.0503	0.0003	0.0091	-0.0026	0.1216	0.0062	-0.0007
χ_3	-0.0014	0.0282	-0.0007	0.0139	0.0005	-0.0005	0.0002	0.0022	-0.0007	0.0072	0.0045	0.0088	0.1143	-0.0006	-0.0097	0.0621	-0.0022
χ_4	0.0004	-0.0061	0.0001	-0.0035	-0.0001	-0.0004	0.0000	-0.0005	0.0001	-0.0032	-0.0008	0.0337	-0.0264	0.0002	0.0023	-0.0141	0.0152
χ_5	0.0013	-0.0025	0.0009	-0.0055	0.0723	0.0025	0.0065	0.0008	-0.0129	-0.0667	0.2047	-0.0047	0.0127	0.0460	0.0880	0.0019	0.0128
χ_6	0.0113	0.0001	0.0178	0.0002	0.0022	0.0004	0.0150	-0.0003	0.1983	0.0035	0.0568	-0.0057	-0.0007	0.0929	-0.1168	-0.0013	0.0317
χ_7	-0.0003	-0.0185	-0.0002	-0.0377	-0.0089	-0.0116	0.0022	0.0125	0.0002	-0.4884	-0.0235	-0.0475	0.1100	-0.0040	-0.0104	0.0199	0.2237
χ_8	0.0000	0.0039	0.0002	0.0097	0.0041	-0.0439	-0.0007	-0.0062	0.0004	0.1179	0.0039	-0.1928	-0.0106	-0.0164	0.0042	0.0055	0.9513
χ_9	0.0048	-0.0006	0.0089	-0.0012	0.0185	-0.0003	-0.0485	0.0047	0.0830	-0.0154	0.0673	0.0136	0.0007	-0.1961	-0.0156	0.0005	-0.0622
Cl-10																	
χ_{24}	-0.0408	-0.0353	-0.6966	0.7038	0.0148	-0.0021	-0.0013	0.0151	0.0582	-0.0315	-0.0049	0.0001	-0.0092	-0.0003	0.0022	0.0024	-0.0009
χ_{25}	-0.0023	-0.0086	0.0047	-0.0024	-0.0879	0.0090	0.0071	-0.0809	-0.2540	0.3166	-0.4321	0.0042	0.4776	0.0225	-0.4134	-0.3509	-0.0044
χ_{26}	-0.0028	0.0040	0.0010	0.0084	-0.0144	0.0000	-0.0001	-0.0037	0.4471	-0.3364	-0.4140	0.1744	-0.0380	-0.1648	0.1078	-0.5485	0.0487
χ_{27}	0.0006	-0.0012	-0.0003	-0.0022	0.0053	-0.0078	-0.0135	0.0043	-0.1179	0.0861	0.0943	0.6619	0.0059	-0.6613	-0.0565	0.1439	0.1590
Cl-11																	
χ_{28}	-0.0386	0.0339	-0.6987	-0.7020	0.0120	0.0030	-0.0049	-0.0130	0.0584	0.0314	-0.0050	-0.0001	0.0096	-0.0004	0.0022	-0.0025	0.0011
χ_{29}	-0.0017	0.0090	0.0045	0.0035	-0.0732	-0.0146	0.0246	0.0700	-0.3201	-0.3733	-0.3716	0.0047	-0.4750	0.0327	-0.4273	0.2486	0.0071
χ_{30}	0.0032	0.0026	-0.0016	0.0080	0.0226	0.0035	-0.0037	-0.0103	-0.4053	-0.2774	0.4838	0.1704	0.0234	0.1642	-0.0288	-0.5891	0.0501
χ_{31}	-0.0006	-0.0010	0.0004	-0.0021	-0.0082	-0.0082	0.0189	0.0049	0.1102	0.0751	-0.1036	0.6587	0.0038	0.6653	0.0401	0.1558	0.1586

Table 2. Contribution of atomic orbitals (AOs) of platinum atom in hybridization (sd^3)

AO	Pt-1	$\sum\phi_{1-14}$	Cl-10	AO	$\sum\phi_{1-14}$	N-2	AO	$\sum\phi_{1-14}$
χ_1	6s	0.3315	χ_{24}	3s	1.6140	χ_{10}	2s	1.3091
χ_2	6px	0.1135	χ_{25}	3px	1.7099	χ_{11}	2px	1.4675
χ_3	6py	0.1837	χ_{26}	3py	1.6091	χ_{12}	2py	1.7562
χ_4	6pz	0.0755	χ_{27}	3pz	1.6626	χ_{13}	2pz	1.2671
χ_5	5dx ² -y ²	0.4306	Cl-11	AO	$\sum\phi_{1-14}$	N-3	AO	$\sum\phi_{1-14}$
χ_6	5dz ²	0.3938	χ_{28}	3s	1.6108	χ_{14}	2s	1.3076
χ_7	5dxy	0.6705	χ_{29}	3px	1.7785	χ_{15}	2px	1.4605
χ_8	5dxz	0.0251	χ_{30}	3py	1.5800	χ_{16}	2py	1.7106
χ_9	5dyz	0.4636	χ_{31}	3pz	1.6610	χ_{17}	2pz	1.1874

Table 3. Overlap matrix or overlap integrals values (S_{rs}) of various overlaps of atomic orbitals of constituent atoms in *cis*-Pt(NH₃)Cl₂

AOs	6s (Pt-1)	6px (Pt-1)	6py (Pt-1)	6pz (Pt-1)	5dx ² -y ² (Pt-1)	5dz ² (Pt-1)	5dxy (Pt-1)	5dxz (Pt-1)	5dyz (Pt-1)	3s (Cl-2)	3px (Cl-2)	3py (Cl-2)	3pz (Cl-2)	3s (Cl-3)	3px (Cl-3)	3py (Cl-3)	3pz (Cl-3)
6s (Pt-1)	1.0000																
6px (Pt-1)	0.0000	1.0000															
6py (Pt-1)	0.0000	0.0000	1.0000														
6pz (Pt-1)	0.0000	0.0000	0.0000	1.0000													
5dx ² -y ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	1.0000												
5dz ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000											
5dxy (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000										
5dxz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
5dyz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000								
3s (Cl-2)	0.1149	-0.1084	0.1295	-0.0330	-0.0080	-0.0242	-0.0446	0.0114	-0.0136	1.0000							
3px (Cl-2)	0.1408	-0.0698	0.1774	-0.0452	-0.0394	-0.0264	-0.0454	0.0116	-0.0232	0.0226	1.0000						
3py (Cl-2)	-0.1682	0.1774	-0.1331	0.0540	-0.0146	0.0315	0.0652	-0.0232	0.0198	-0.0026	0.0037	1.0000					
3pz (Cl-2)	0.0428	-0.0452	0.0540	0.0650	-0.0041	-0.0216	-0.0232	-0.0199	0.0238	0.0011	-0.0016	0.0002	1.0000				
3s (Cl-3)	0.1148	-0.1264	-0.1128	0.0296	0.0052	-0.0248	0.0454	-0.0119	-0.0106	0.0001	-0.0001	-0.0001	0.0000	1.0000			
3px (Cl-3)	0.1642	-0.1232	-0.1803	0.0472	-0.0198	-0.0319	0.0634	-0.0166	-0.0211	0.0004	-0.0004	-0.0004	0.0001	0.0222	1.0000		
3py (Cl-3)	0.1466	-0.1803	-0.0823	0.0422	0.0360	-0.0285	0.0505	-0.0211	-0.0118	0.0004	-0.0004	-0.0003	0.0001	-0.0005	0.0007	1.0000	
3pz (Cl-3)	-0.0384	0.0472	0.0422	0.0676	-0.0024	0.0197	-0.0211	-0.0246	-0.0219	-0.0001	0.0001	0.0001	0.0001	-0.0004	0.0006	-0.0000	1.0000

Table 4. Quantitative and qualitative nature of occupied molecular orbitals of *cis*-Pt(NH₃)Cl₂

MO No.	$\Sigma n_{r-s,i}$	sign	MOs
ϕ_1	0.0004	+	BMO
ϕ_2	-0.0009	-	ABMO
ϕ_3	0.0181	+	BMO
ϕ_4	0.0100	+	BMO
ϕ_5	0.0011	+	BMO
ϕ_6	0.0000	0	NBO
ϕ_7	0.0001	+	BMO
ϕ_8	0.0001	+	BMO
ϕ_9	0.1250	+	BMO
ϕ_{10}	0.0821	+	BMO
ϕ_{11}	0.0271	+	BMO
ϕ_{12}	0.0228	+	BMO
ϕ_{13}	0.0599	+	BMO
ϕ_{14}	0.0364	+	BMO

MOs is molecular orbitals, BMO is bonding molecular orbital, ABMO is antibonding molecular orbital and NBO is nonbonding molecular orbitals

Table 5. First, second and third absorption band of transplatin

Complex Compound	First band		Second band		Third band		$\epsilon_2 - \epsilon_1$	$\epsilon_3 - \epsilon_2$
	$\epsilon_1(10^{13})$	$\log \epsilon$	$\epsilon_2(10^{13})$	$\log \epsilon$	$\epsilon_3(10^{13})$	$\log \epsilon$		
trans-[Pt(NH ₃) ₂ Cl ₂]	80.0	1.23	95.8	1.88	110.2	2.02	15.8	1.4

Table 6. UV-Vis data of cisplatin as calculated by RTD-PBE1PBE-FC/SDD

cis-[Pt(NH ₃) ₂ Cl ₂]	Absorption energy	Wave length	Oscillator strength
Excitation State: 1	3.7548eV	330.20 nm	0.0000
Excitation State: 2	3.8925 eV	318.52 nm	0.0001
Excitation State: 3	3.9845 eV	311.16 nm	0.0014

Table 7. Calculated (PBE1PBE/SDD)normal vibrational mode of Cisplatin

S.No.	Freq.	Assignment, TED, %
27	3635.83	$\nu_{\text{a}}(\text{NH}_3) B_2, A_2$ 100 $\nu(\text{NH})$
26	3635.07	
25	3565.31	$\nu_{\text{a}}(\text{NH}_3) A_1, B_1$ 100 $\nu(\text{NH})$
24	3564.65	
23	3383.72	$\nu_{\text{s}}(\text{NH}_3) B_1, A_1$ 100 $\nu(\text{NH})$
22	3383.38	
21	1728.13	$\delta_{\text{a}}(\text{NH}_3) B_2, 59\delta(\text{HNPt} + \text{HNH}) + 40\tau(\text{NPt})$
20	1721.95	$\delta_{\text{a}}(\text{NH}_3) A_2, 58\delta(\text{HNPt} + \text{HNH}) + 41\tau(\text{NPt})$
19	1695.36	$\delta_{\text{a}}(\text{NH}_3) A_1, 65\delta(\text{HNPt} + \text{HNH}) + 35\tau(\text{NPt})$
18	1685.27	$\delta_{\text{a}}(\text{NH}_3) B_1, 65\delta(\text{HNPt} + \text{HNH}) + 35\tau(\text{NPt})$
17	1322.68	$\delta_{\text{s}}(\text{NH}_3) A_1, 100\delta(\text{HNPt} + \text{HNH})$
16	1315.71	$\delta_{\text{s}}(\text{NH}_3) B_1, 100\delta(\text{HNPt} + \text{HNH})$
15	866.61	$\rho(\text{NH}_3) A_1, 75\delta(\text{HNPt}) + 24\tau(\text{NPt})$
14	823.83	$\rho(\text{NH}_3) B_1, 75\delta(\text{HNPt}) + 24\tau(\text{NPt})$
13	804.39	$\rho(\text{NH}_3) B_2, 88\delta(\text{HNPt}) + 10\tau(\text{NPt})$
12	781.16	$\rho(\text{NH}_3) A_2, 88\delta(\text{HNPt}) + 11\tau(\text{NPt})$
11	499.31	$\nu_{\text{s}}(\text{PtN}) A_1, 100\nu(\text{PtN})$
10	493.01	$\nu_{\text{a}}(\text{PtN}) B_1, 99\nu(\text{PtN})$
09	349.96	$\nu_{\text{s}}(\text{PtCl}) A_1, 96\nu(\text{PtCl})$
08	340.43	$\nu_{\text{a}}(\text{PtCl}) B_1, 99\nu(\text{PtCl})$
07	239.10	$\delta(\text{NPtCl}) B_1, 97\delta(\text{NPtCl})$
06	237.93	$\delta(\text{NPtN}) A_1, 60\delta(\text{NPtN}) + 35\delta(\text{NPtCl})$
05	162.75	$\tau_{\text{a}}(\text{PtN}) A_2, 92\tau(\text{PtN})$
04	145.72	$\tau_{\text{s}}(\text{PtN}) B_2, 99\tau(\text{PtN})$
03	141.90	$\pi_{\text{s}}(\text{NPtCl}) B_2, 70\delta_{\text{op}}(\text{NPtCl}) + 28\tau(\text{PtN})$
02	131.54	$\delta(\text{ClPtCl}) A_1, 72\delta(\text{ClPtCl}) + 13\delta(\text{NPtCl}) + 12\delta(\text{NPtN})$
01	106.20	$\pi_{\text{a}}(\text{NPtCl}) A_2, 63\delta_{\text{op}}(\text{NPtCl}) + 35\tau(\text{PtN})$

Cisplatin at Atomic, Molecular and Electronic Level: A DFT Based Study

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How to cite this paper: Soni, A.K., Azim, I., Swati and Sahu, V.K. (2025) Cisplatin at Atomic, Molecular and Electronic Level: A DFT Based Study. *Open Journal of Applied Sciences*, 15, 1429-1441.
<https://doi.org/10.4236/ojapps.2025.155100>

Received: April 17, 2025

Accepted: May 25, 2025

Published: May 28, 2025

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Abstract

Recently, we have studied electronic structure of platinum dihalides (Pt(II)X₂). Here, atomic orbital and molecular orbital analysis along with spectroscopic studies have been made to see electronic structure of cisplatin (cis-[Pt(NH₃)₂Cl₂]). CAChe Pro software of Fujitsu and Gaussian-03 software have been used to obtain minimum energy structure. For this, cisplatin has been opted with EHT (for population analysis) and DFT (for spectroscopic analysis). Summation values of coefficient of AOs reflected sd³-hybridization and thus supported Landis concept of sdⁿ-hybridization, where n = 3. Sum of overlap population used to characterize the fourteen MOs (as there are 28e⁻) into BMOs, ABMO and NBMOs. UV-spectrum of cisplatin shows one absorption band at 3.9845 eV with peak corresponded to 311.16 nm of oscillator strength (0.0014). IR-spectrum analysis shows 27 normal vibrations.

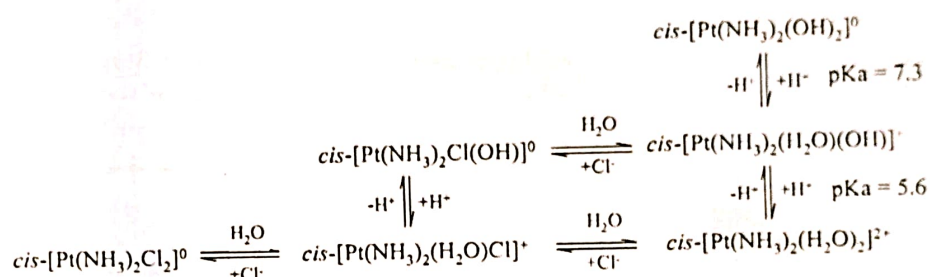
Keywords

Cisplatin, Mulliken Population Analysis, sd³-Hybridization, UV-Spectrum and IR-Spectrum

1. Introduction

It was Rosenberg, who accidentally found out the biological activity of cisplatin, *i.e.*, cis-[Pt(NH₃)₂Cl₂] in 1965 [1]. Actually it was synthesized by Peyrone in 1844 [2]. The anti-tumor activity of square planar complexes (cis-[Pt(NH₃)₂Cl₂] and [Pt(en)Cl₂]) and octahedral complexes (cis-[Pt(NH₃)₂Cl₄] and [Pt(en)Cl₄]) against sarcoma-180 (in mice) and against murine leukemia (L-1210) cells were also dis-

covered by Rosenberg [3]. Harder and Rosenberg reported selective inhibition of DNA synthesis in vitro by $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ below 5 μM [4]. Cisplatin was launched in 1978 as anticancer drug but it is still used for treatment of testicular [5], ovarian [6], bladder [7] and neck cancers [8] in humans. The activity of $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ against tumor is associated with reactions replacing the halides. The effective antitumor compounds have features in common that may aid us in understanding their interaction with biological systems [9]. These agents usually have two exchangeable ligands in cis positions. These complexes are bifunctional reagents that may undergo nucleophilic substitution at two cis positions (Scheme 1), which assumes monomeric species and preservation of the cis configuration thermodynamically [10]. Prediction of atomic, molecular, electronic structure along with spectroscopic characteristic of metal complexes have always been challenging for computational chemists.



Scheme 1. Hydrolysis of cis-platin in the stepwise reaction [10].

2. Materials and Methods

In this research work, atomic, molecular orbitals and spectroscopic analysis have been made to see electronic structure of cisplatin. Firstly a quantitative atomic orbital (AO) and molecular orbital (MO) treatment have also been made on above species to study 1) involvement of metal (n-1)d-, ns- and np-orbitals in hybridizations and its type that has been used to get information related to shape (bond angle) and size (bond length) [11]; 2) contribution of various AOs in the construction of MOs through LCAO approximation using values of eigenvector and overlap matrix [12] and 3) nature of MOs by distinguishing them into bonding, non-bonding and antibonding MO through population analysis [13]. The adopted methods for various calculations of above species are based on Mulliken's population analysis, which has been well described in our recent publications [14]. After that UV-Vis and IR spectroscopic analysis have also been made [15]. CAChe Pro software of Fujitsu [16] and Gaussian-03 software [17] have been used to obtain minimum energy structure. For this, cisplatin was opted by using EHT [18] and DFT methods [19].

3. Results and Discussion

The molecular orbitals of cisplatin are formed by linear combination of 9 orbitals from platinum, 4 orbitals of each nitrogen, 4 orbitals of each halogen and 1 orbital

from each hydrogen as given below:

$$\text{Pt} - 1 = 6s, 6px, 6py, 6pz, 5dx^2 - y^2, 5dz^2, 5dxy, 5dxz, 5dyz = 9$$

$$\text{N} - 2 = 2s, 2px, 2py, 2pz = 4$$

$$\text{N} - 3 = 2s, 2px, 2py, 2pz = 4$$

$$\text{H} - 4 = 1s = 1$$

$$\text{H} - 5 = 1s = 1$$

$$\text{H} - 6 = 1s = 1$$

$$\text{H} - 7 = 1s = 1$$

$$\text{H} - 8 = 1s = 1$$

$$\text{H} - 9 = 1s = 1$$

$$\text{Cl} - 10 = 3s, 3px, 3py, 3pz = 4$$

$$\text{Cl} - 11 = 3s, 3px, 3py, 3pz = 4$$

$$\text{Total} = 31$$

In total thirty-one atomic orbital (AOs) are involved in the formation of thirty-one molecular orbitals (MOs). But here we discuss only seventeen MOs of one Pt^{2+} (9 MOs) and 2Cl^- (2×4 MOs), because we have to see the effect of cisplatin (Equation (1) and (2)) formation on these orbitals. The fourteen MOs of ligands 2NH_3 (2×7) are kept out of discussion (Equation (2)). The AOs are represented by " χ " and MOs by " ϕ ". Here χ_1 to χ_9 are AOs of Pt and remaining eight AOs of two Cl by χ_{24} to χ_{31} viz., χ_1 (6s), χ_2 (6px), χ_3 (6py), χ_4 (6pz), χ_5 ($5dx^2 - y^2$), χ_6 ($5dz^2$), χ_7 (5dxy), χ_8 (5dxz), χ_9 (5dyz), χ_{24} (3s), χ_{25} (3px), χ_{26} (3py), χ_{27} (3pz), χ_{28} (3s), χ_{29} (3px), χ_{30} (3py), and χ_{31} (3pz). The form of the seventeen MOs i.e., the magnitude of contribution of various thirty-one AOs in the formation of seventeen MOs is demonstrated by $\phi_1 - \phi_7$ as described below.

$$\begin{aligned}\phi_1 = & -0.0031\chi_1 + 0.0247\chi_2 - 0.0014\chi_3 + 0.0004\chi_4 + 0.0013\chi_5 + 0.0113\chi_6 \\ & - 0.0003\chi_7 + 0.0000\chi_8 + 0.0048\chi_9 - 0.0408\chi_{24} - 0.0023\chi_{25} - 0.0028\chi_{26} \\ & + 0.0006\chi_{27} - 0.0386\chi_{28} - 0.0017\chi_{29} + 0.0032\chi_{30} - 0.0006\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_2 = & +0.0000\chi_1 + 0.0018\chi_2 + 0.0282\chi_3 - 0.0061\chi_4 - 0.0025\chi_5 + 0.0001\chi_6 \\ & - 0.0185\chi_7 + 0.0039\chi_8 - 0.0006\chi_9 - 0.0353\chi_{24} - 0.0086\chi_{25} + 0.0040\chi_{26} \\ & - 0.0012\chi_{27} + 0.0339\chi_{28} + 0.0090\chi_{29} + 0.0026\chi_{30} - 0.0010\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_3 = & -0.0414\chi_1 + 0.0102\chi_2 - 0.0007\chi_3 + 0.0001\chi_4 + 0.0009\chi_5 + 0.0178\chi_6 \\ & - 0.0002\chi_7 + 0.0002\chi_8 + 0.0089\chi_9 - 0.6966\chi_{24} + 0.0047\chi_{25} + 0.0010\chi_{26} \\ & - 0.0003\chi_{27} - 0.6987\chi_{28} + 0.0045\chi_{29} - 0.0016\chi_{30} - 0.0004\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_4 = & 0.0000\chi_1 + 0.0010\chi_2 + 0.0139\chi_3 - 0.0035\chi_4 - 0.0055\chi_5 + 0.0002\chi_6 \\ & - 0.0377\chi_7 + 0.0097\chi_8 - 0.0012\chi_9 + 0.7038\chi_{24} - 0.0024\chi_{25} + 0.0084\chi_{26} \\ & - 0.0022\chi_{27} - 0.7020\chi_{28} + 0.0035\chi_{29} + 0.0080\chi_{30} - 0.0021\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_5 = & -0.0044\chi_1 - 0.0028\chi_2 + 0.0005\chi_3 - 0.0001\chi_4 + 0.0723\chi_5 + 0.0022\chi_6 \\ & - 0.0089\chi_7 + 0.0041\chi_8 + 0.0185\chi_9 + 0.0148\chi_{24} - 0.0879\chi_{25} - 0.0144\chi_{26} \\ & + 0.0053\chi_{27} + 0.0120\chi_{28} - 0.0732\chi_{29} + 0.0226\chi_{30} - 0.0082\chi_{31}\end{aligned}$$

$$\begin{aligned}
\phi_6 &= -0.0001\chi_1 - 0.0001\chi_2 - 0.0005\chi_3 - 0.0004\chi_4 + 0.0025\chi_5 + 0.0004\chi_6 \\
&\quad - 0.0116\chi_7 - 0.0439\chi_8 - 0.0003\chi_9 - 0.0021\chi_{24} + 0.0090\chi_{25} + 0.0000\chi_{26} \\
&\quad - 0.0078\chi_{27} + 0.0030\chi_{28} - 0.0146\chi_{29} + 0.0035\chi_{30} - 0.0082\chi_{31} \\
\phi_7 &= +0.0006\chi_1 + 0.0006\chi_2 + 0.0002\chi_3 + 0.0000\chi_4 + 0.0065\chi_5 + 0.0150\chi_6 \\
&\quad + 0.0022\chi_7 - 0.0007\chi_8 - 0.0485\chi_9 - 0.0013\chi_{24} + 0.0071\chi_{25} - 0.0001\chi_{26} \\
&\quad - 0.0135\chi_{27} - 0.0049\chi_{28} + 0.0246\chi_{29} - 0.0037\chi_{30} + 0.0189\chi_{31} \\
\phi_8 &= -0.0000\chi_1 - 0.0001\chi_2 + 0.0022\chi_3 - 0.0005\chi_4 + 0.0008\chi_5 - 0.0003\chi_6 \\
&\quad + 0.0125\chi_7 - 0.0062\chi_8 + 0.0047\chi_9 + 0.0151\chi_{24} - 0.0809\chi_{25} - 0.0037\chi_{26} \\
&\quad + 0.0043\chi_{27} - 0.0130\chi_{28} + 0.0700\chi_{29} - 0.0103\chi_{30} + 0.0049\chi_{31} \\
\phi_9 &= -0.2285\chi_1 - 0.0095\chi_2 - 0.0007\chi_3 + 0.0001\chi_4 - 0.0129\chi_5 + 0.1983\chi_6 \\
&\quad + 0.0002\chi_7 + 0.0004\chi_8 + 0.0830\chi_9 + 0.0582\chi_{24} - 0.2540\chi_{25} + 0.4471\chi_{26} \\
&\quad - 0.1179\chi_{27} + 0.0584\chi_{28} - 0.3201\chi_{29} - 0.4053\chi_{30} + 0.1102\chi_{31} \\
\phi_{10} &= -0.0002\chi_1 + 0.0004\chi_2 + 0.0072\chi_3 - 0.0032\chi_4 - 0.0667\chi_5 + 0.0035\chi_6 \\
&\quad - 0.4884\chi_7 + 0.1179\chi_8 - 0.0154\chi_9 - 0.0315\chi_{24} + 0.3166\chi_{25} - 0.3364\chi_{26} \\
&\quad + 0.0861\chi_{27} + 0.0314\chi_{28} - 0.3733\chi_{29} - 0.2774\chi_{30} + 0.0751\chi_{31} \\
\phi_{11} &= -0.0499\chi_1 - 0.0503\chi_2 + 0.0045\chi_3 - 0.0008\chi_4 + 0.2047\chi_5 + 0.0568\chi_6 \\
&\quad - 0.0235\chi_7 + 0.0039\chi_8 + 0.0673\chi_9 - 0.0049\chi_{24} - 0.4321\chi_{25} - 0.4140\chi_{26} \\
&\quad + 0.0943\chi_{27} - 0.0050\chi_{28} - 0.3716\chi_{29} + 0.4838\chi_{30} - 0.1036\chi_{31} \\
\phi_{12} &= +0.0003\chi_1 + 0.0003\chi_2 + 0.0088\chi_3 + 0.0337\chi_4 - 0.0047\chi_5 - 0.0057\chi_6 \\
&\quad - 0.0475\chi_7 - 0.1928\chi_8 + 0.0136\chi_9 + 0.0001\chi_{24} + 0.0042\chi_{25} + 0.1744\chi_{26} \\
&\quad + 0.6619\chi_{27} - 0.0001\chi_{28} + 0.0047\chi_{29} + 0.1704\chi_{30} + 0.6587\chi_{31} \\
\phi_{13} &= +0.0007\chi_1 + 0.0091\chi_2 + 0.1143\chi_3 - 0.0264\chi_4 + 0.0127\chi_5 - 0.0007\chi_6 \\
&\quad + 0.1100\chi_7 - 0.0106\chi_8 + 0.0007\chi_9 - 0.0092\chi_{24} + 0.4776\chi_{25} - 0.0380\chi_{26} \\
&\quad + 0.0059\chi_{27} + 0.0096\chi_{28} - 0.4750\chi_{29} + 0.0234\chi_{30} + 0.0038\chi_{31} \\
\phi_{14} &= +0.0023\chi_1 - 0.0026\chi_2 - 0.0006\chi_3 + 0.0002\chi_4 + 0.0460\chi_5 + 0.0929\chi_6 \\
&\quad - 0.0040\chi_7 - 0.0164\chi_8 - 0.1961\chi_9 - 0.0003\chi_{24} + 0.0225\chi_{25} - 0.1648\chi_{26} \\
&\quad - 0.6613\chi_{27} - 0.0004\chi_{28} + 0.0327\chi_{29} + 0.1642\chi_{30} + 0.6653\chi_{31} \\
\phi_{15} &= +0.0389\chi_1 + 0.1216\chi_2 - 0.0097\chi_3 + 0.0023\chi_4 + 0.0880\chi_5 - 0.1168\chi_6 \\
&\quad - 0.0104\chi_7 + 0.0042\chi_8 - 0.0156\chi_9 + 0.0022\chi_{24} - 0.4134\chi_{25} + 0.1078\chi_{26} \\
&\quad - 0.0565\chi_{27} + 0.0022\chi_{28} - 0.4273\chi_{29} - 0.0288\chi_{30} + 0.0401\chi_{31} \\
\phi_{16} &= 0.0001\chi_1 + 0.0062\chi_2 + 0.0621\chi_3 - 0.0141\chi_4 + 0.0019\chi_5 - 0.0013\chi_6 \\
&\quad + 0.0199\chi_7 + 0.0055\chi_8 + 0.0005\chi_9 + 0.0024\chi_{24} - 0.3509\chi_{25} - 0.5485\chi_{26} \\
&\quad + 0.1439\chi_{27} - 0.0025\chi_{28} + 0.2486\chi_{29} - 0.5891\chi_{30} + 0.1558\chi_{31} \\
\phi_{17} &= +0.0011\chi_1 - 0.0007\chi_2 - 0.0022\chi_3 + 0.0152\chi_4 + 0.0128\chi_5 + 0.0317\chi_6 \\
&\quad + 0.2237\chi_7 + 0.9513\chi_8 - 0.0622\chi_9 - 0.0009\chi_{24} - 0.0044\chi_{25} + 0.0487\chi_{26} \\
&\quad + 0.1590\chi_{27} + 0.0011\chi_{28} + 0.0071\chi_{29} + 0.0501\chi_{30} + 0.1586\chi_{31}
\end{aligned}$$

Here, the coefficient of χ is the eigenvector (taken from Table 1). The remaining fourteen MOs, ϕ_{18} - ϕ_{31} , were kept out of discussion as these remaining MOs have been formed by fourteen AOs of two NH_3 molecules as neutral ligands following

Equation (1) and Equation (2), respectively. Equation (1) represents formation of molecular compound PtCl_2 , which in Equation (2) complexes with 2NH_3 ligands and thus cisplatin is formed. Hence, only seventeen MOs have been considered here.

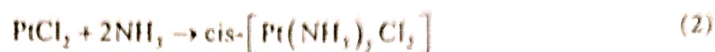


Table 1. Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ) of cis- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.

Atom	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}	ϕ_{13}	ϕ_{14}	ϕ_{15}	ϕ_{16}	ϕ_{17}	
Pt-1	χ_1	-0.0031	0.0000	-0.0414	0.0000	-0.0044	-0.0001	0.0006	-0.0000	-0.2285	-0.0002	-0.0499	0.0003	0.0007	0.0023	0.0389	0.0001	0.0011
	χ_2	0.0247	0.0018	0.0102	0.0010	-0.0028	-0.0001	0.0006	-0.0001	0.0095	0.0004	-0.0503	0.0003	0.0091	-0.0026	0.1216	0.0062	-0.0007
	χ_3	-0.0014	0.0282	-0.0007	0.0139	0.0005	-0.0005	0.0002	0.0022	-0.0007	0.0072	0.0045	0.0088	0.1143	-0.0006	-0.0097	0.0621	-0.0022
	χ_4	0.0004	-0.0061	0.0001	-0.0035	-0.0001	-0.0004	0.0000	-0.0005	0.0001	-0.0032	-0.0008	0.0337	-0.0264	0.0002	0.0023	-0.0141	0.0152
	χ_5	0.0013	-0.0025	0.0009	-0.0055	0.0723	0.0025	0.0065	0.0008	-0.0129	-0.0667	0.2047	-0.0047	0.0127	0.0460	0.0880	0.0019	0.0128
	χ_6	0.0113	0.0001	0.0178	0.0002	0.0022	0.0004	0.0150	-0.0003	0.1983	0.0035	0.0568	-0.0057	-0.0007	0.0929	-0.1168	-0.0013	0.0317
	χ_7	-0.0003	-0.0185	-0.0002	-0.0377	-0.0089	-0.0116	0.0022	0.0125	0.0002	-0.4884	-0.0235	-0.0475	0.1100	-0.0040	-0.0104	0.0199	0.2237
	χ_8	0.0000	0.0039	0.0002	0.0097	0.0041	-0.0439	-0.0007	-0.0062	0.0004	0.1179	0.0039	-0.1928	-0.0106	-0.0164	0.0042	0.0055	0.9513
	χ_9	0.0048	-0.0006	0.0089	-0.0012	0.0185	-0.0003	-0.0485	0.0047	0.0830	-0.0154	0.0673	0.0136	0.0007	-0.1961	-0.0156	0.0005	-0.0622
Cl-10	χ_{10}	-0.0408	-0.0353	-0.6966	0.7038	0.0148	-0.0021	-0.0013	0.0151	0.0582	-0.0315	-0.0049	0.0001	-0.0092	-0.0003	0.0022	0.0024	-0.0009
	χ_{11}	-0.0023	-0.0086	0.0047	-0.0024	-0.0879	0.0090	0.0071	-0.0809	-0.2540	0.3166	-0.4321	0.0042	0.4776	0.0225	-0.4134	-0.3509	-0.0044
	χ_{12}	-0.0028	0.0040	0.0010	0.0084	-0.0144	0.0000	-0.0001	-0.0037	0.4471	-0.3364	-0.4140	0.1744	-0.0380	-0.1648	0.1078	-0.5485	0.0487
	χ_{13}	0.0006	-0.0012	-0.0003	-0.0022	0.0053	-0.0078	-0.0135	0.0043	-0.1179	0.0861	0.0943	0.6619	0.0059	-0.6613	-0.0565	0.1439	0.1590
Cl-11	χ_{14}	-0.0386	0.0339	-0.6987	-0.7020	0.0120	0.0030	-0.0049	-0.0130	0.0584	0.0314	-0.0050	-0.0001	0.0096	-0.0004	0.0022	-0.0025	0.0011
	χ_{15}	-0.0017	0.0090	0.0045	0.0035	-0.0732	-0.0146	0.0246	0.0700	-0.3201	-0.3733	-0.3716	0.0047	-0.4750	0.0327	-0.4273	0.2486	0.0071
	χ_{16}	0.0032	0.0026	-0.0016	0.0080	0.0226	0.0035	-0.0037	-0.0103	-0.4053	-0.2774	0.4838	0.1704	0.0234	0.1642	-0.0288	-0.5891	0.0501
	χ_{17}	-0.0006	-0.0010	0.0004	-0.0021	-0.0082	-0.0082	0.0189	0.0049	0.1102	0.0751	-0.1036	0.6587	0.0038	0.6653	0.0401	0.1558	0.1586

When platinum forms compound it adopts either concept of bonded attraction and non-bonded repulsion of VB (Valence Bond) theory, and or positive and negative overlap populations of MO (Molecular Orbital) theory [13]. In the first case platinum may undergo various types of hybridization that depend upon its oxidation state, and number and nature of combining atoms or ions [11], and in the second case platinum forms molecular orbital by LCAO approximation [20]. In cisplatin, platinum acquires + 2 oxidation state that may be neutralized by two chloride ion (2Cl^-), while two neutral ammine ligands (2NH_3) complex through coordinate bonds by donating two pairs of its lone pair of electrons. At first, we have to examine the extent of involvement of 5d, 6s and 6p AOs of Pt-1 in the formation of MOs in cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. For this, values of coefficient " χ " of 5d, 6s and 6p of platinum metal have been tabulated in Table 2. To see the total involvement of seven AOs of Pt-1 in fourteen MOs (ϕ_1 - ϕ_{14}), the coefficient value of each orbital has been added. The rest vacant MOs are exempted here, as there is only $28e^-$ to

be filled by Aufbau principle, Hund's rule and Pauli's exclusion principle as described in our previous publication [14] and thus we considered only these MOs among seventeen MOs. The summation values of AOs in these fourteen MOs have been placed same table, which clearly reflects maximum involvement of 5d orbital. Next to this is 6s orbital. It is also predicted from the summation values of d orbital. The non-bonding orbital i.e., 5dxz must have the lowest summation value which is 0.0251. The involvement of three p orbitals is negligible as their summation values are very low in comparison to d orbital and considerably low with respect to s orbital (0.3315). From Table 2 and Figure 1, it is evident that the involvement of 6p orbital in Pt—L bond in *cis*-[Pt(NH₃)₂Cl₂] is insignificant and the main role is played by "ns" and (n-1)d orbital. It was Landis, who discovered *sdⁿ*-hybridization (here *n* = 3) along with molecular shape and bond angles in his seminal publications [21].

Table 2. Contribution of atomic orbitals (AOs) of platinum atom in hybridization (*sd³*).

AO	Pt-1	$\Sigma\phi_{1-14}$	Cl-10	AO	$\Sigma\phi_{1-14}$	N-2	AO	$\Sigma\phi_{1-14}$
χ_1	6s	0.3315	χ_{24}	3s	1.6140	χ_{10}	2s	1.3091
χ_2	6px	0.1135	χ_{25}	3px	1.7099	χ_{11}	2px	1.4675
χ_3	6py	0.1837	χ_{26}	3py	1.6091	χ_{12}	2py	1.7562
χ_4	6pz	0.0755	χ_{27}	3pz	1.6626	χ_{13}	2pz	1.2671
χ_5	5dx ² -y ²	0.4306	Cl-11	AO	$\Sigma\phi_{1-14}$	N-3	AO	$\Sigma\phi_{1-14}$
χ_6	5dz ²	0.3938	χ_{28}	3s	1.6108	χ_{14}	2s	1.3076
χ_7	5dxy	0.6705	χ_{29}	3px	1.7785	χ_{15}	2px	1.4605
χ_8	5dxz	0.0251	χ_{30}	3py	1.5800	χ_{16}	2py	1.7106
χ_9	5dyz	0.4636	χ_{31}	3pz	1.6610	χ_{17}	2pz	1.1874

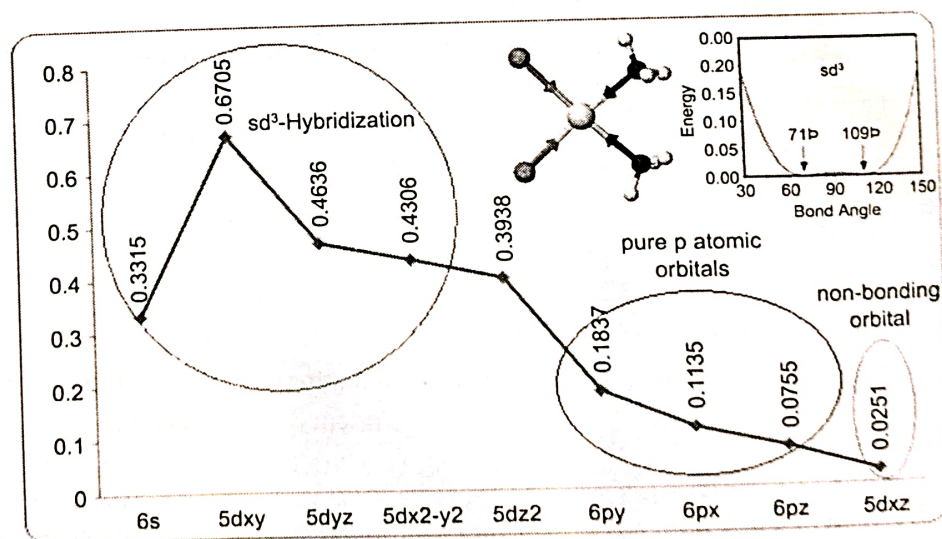


Figure 1. Contribution of atomic orbital in *sd³* hybridization [21].

The shape of each MO (ϕ_1 - ϕ_{17}) has been determined by the relative magnitudes and signs of the different coefficients. For this $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has been decomposed into three parts: Pt-1, X-1 and X-2, and the MO of the complete system has been obtained by allowing the orbitals of Pt-1 (5d, 6s, 6p), X-1 (ns and np) and X-2 (ns and np) to overlap. The possible overlaps between the various AOs of ruthenium (Pt-1) and halogens (X-2 and X-2) in each MO will be 88. After that overlap populations have been calculated by solving equation: $n_{r-s,i} = n_i (2c_{ri}c_{si}S_{rs})$. To calculate overlap populations for 88 overlaps (overlap of 2NH_3 ligands have been excluded) in MOs of $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, we need eigenvector values (c_{ri} and c_{si}), values of overlap matrix (S_{rs}) and number of electrons (n_i) in each MO. The eigenvector and overlap integral values for $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ have been taken from Table 1 and Table 3, respectively. The number of electrons is taken as two for ϕ_1 to ϕ_{14} and zero for ϕ_{15} to ϕ_{17} . In order to get a precise description, the sums of overlap population for the fourteen MOs of $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ have also been worked out and results are presented in Table 4. As can be seen from this table that among the fourteen molecular orbital, twelve are bonding, one is nonbonding and one is antibonding. The bonding molecular orbitals are ϕ_1 , ϕ_3 - ϕ_5 , ϕ_7 - ϕ_{14} . The nonbonding molecular orbital is ϕ_6 , which is purely dxz atomic orbital of platinum. The antibonding molecular orbital is ϕ_2 .

Table 3. Overlap matrix or overlap integrals values (S_{rs}) of various overlaps of atomic orbitals of constituent atoms in $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$.

AOs	6s	6px	6py	6pz	5dx ² -y ²	5dz ²	5dxy	5dxz	5dyz	3s	3px	3py	3pz	3s	3px	3py	3pz
	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Cl-2)	(Cl-2)	(Cl-2)	(Cl-2)	(Cl-3)	(Cl-3)	(Cl-3)	(Cl-3)
6s (Pt-1)	1.0000																
6px (Pt-1)	0.0000	1.0000															
6py (Pt-1)	0.0000	0.0000	1.0000														
6pz (Pt-1)	0.0000	0.0000	0.0000	1.0000													
5dx ² -y ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	1.0000												
5dz ² (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000											
5dxy (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000										
5dxz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
5dyz (Pt-1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000								
3s (Cl-2)	0.1149	-0.1084	0.1295	-0.0330	-0.0080	-0.0242	-0.0446	0.0114	-0.0136	1.0000							
3px (Cl-2)	0.1408	-0.0698	0.1774	-0.0452	-0.0394	-0.0264	-0.0454	0.0116	-0.0232	0.0226	1.0000						
3py (Cl-2)	-0.1682	0.1774	-0.1331	0.0540	-0.0146	0.0315	0.0652	-0.0232	0.0198	-0.0026	0.0037	1.0000					
3pz (Cl-2)	0.0428	-0.0452	0.0540	0.0650	-0.0041	-0.0216	-0.0232	-0.0199	0.0238	0.0011	-0.0016	0.0002	1.0000				
3s (Cl-3)	0.1148	-0.1264	-0.1128	0.0296	0.0052	-0.0248	0.0454	-0.0119	-0.0106	0.0001	-0.0001	-0.0001	0.0000	1.0000			
3px (Cl-3)	0.1642	-0.1232	-0.1803	0.0472	-0.0198	-0.0319	0.0634	-0.0166	-0.0211	0.0004	-0.0004	-0.0004	0.0001	0.0222	1.0000		
3py (Cl-3)	0.1466	-0.1803	-0.0823	0.0422	0.0360	-0.0285	0.0505	-0.0211	-0.0118	0.0004	-0.0004	-0.0003	0.0001	-0.0005	0.0007	1.0000	
3pz (Cl-3)	-0.0384	0.0472	0.0422	0.0676	-0.0024	0.0197	-0.0211	-0.0246	-0.0219	-0.0001	0.0001	0.0001	0.0000	-0.0004	0.0006	-0.0000	1.0000

Table 4. Quantitative and qualitative nature of occupied molecular orbitals of cis-Pt(NH₃)Cl₂.

MO No.	$\Sigma n_{r,i}$	sign	MOs
ϕ_1	0.0004	+	BMO
ϕ_2	-0.0009	-	ABMO
ϕ_3	0.0181	+	BMO
ϕ_4	0.0100	+	BMO
ϕ_5	0.0011	+	BMO
ϕ_6	0.0000	0	NBO
ϕ_7	0.0001	+	BMO
ϕ_8	0.0001	+	BMO
ϕ_9	0.1250	+	BMO
ϕ_{10}	0.0821	+	BMO
ϕ_{11}	0.0271	+	BMO
ϕ_{12}	0.0228	+	BMO
ϕ_{13}	0.0599	+	BMO
ϕ_{14}	0.0364	+	BMO

MOs is molecular orbitals, BMO is bonding molecular orbital, ABMO is antibonding molecular orbital and NBO is nonbonding molecular orbitals.

Metallic complexes generally have two selective absorption bands [22]. The first lies in the visible region. First band is attributed to electron transitions in the unsaturated transition shell of the central ion. The complexes which co-ordinate only one kind of ligand should naturally have narrower, symmetrical first bands than those that have ligands of different kinds, and among the latter, those that have ligands situated far apart in the spectrochemical series should have broader and less symmetrical first bands and sometimes these bands may analyzed into two or more component. The second lies in the near ultra-violet region. The second band may be attributed to the co-ordination electrons, and is, therefore, the most general characteristic which a co-ordination compound should possess. Some complexes however, give the third band in the region of shorter wave-length. All the co-ordination compounds that have or seem to have at least a pair of negative ligands in trans-position showed the third bands (Table 5), but none of those were deficient in the condition. Some of the co-ordinated compounds lack the first bands and most of them the third, they never fail to give the second bands. Cis-platin shows one absorption band (Figure 2) as opted by Gaussian-03 [17]. The PBE1PBE functional is a hybrid density functional theory (DFT) method, and SDD (Stuttgart-Dresden) pseudopotentials are a type of pseudopotential used in DFT calculations to represent the interaction between the core and valence electrons. Using PBE1PBE functional with SDD pseudopotentials can be a computa-

tionally efficient and accurate way to model the electronic structure and properties of materials [23]. By RTD-pbe1pbe-FC method with sdd basis set was used to calculate the UV-Vis spectrum of cisplatin. Figure 2 reflects excitation energies and oscillator strengths. The band of absorption was recorded at 3.9845 eV with peak corresponded to 311.16 nm and shows oscillator strength 0.0014, as shown in Table 6.

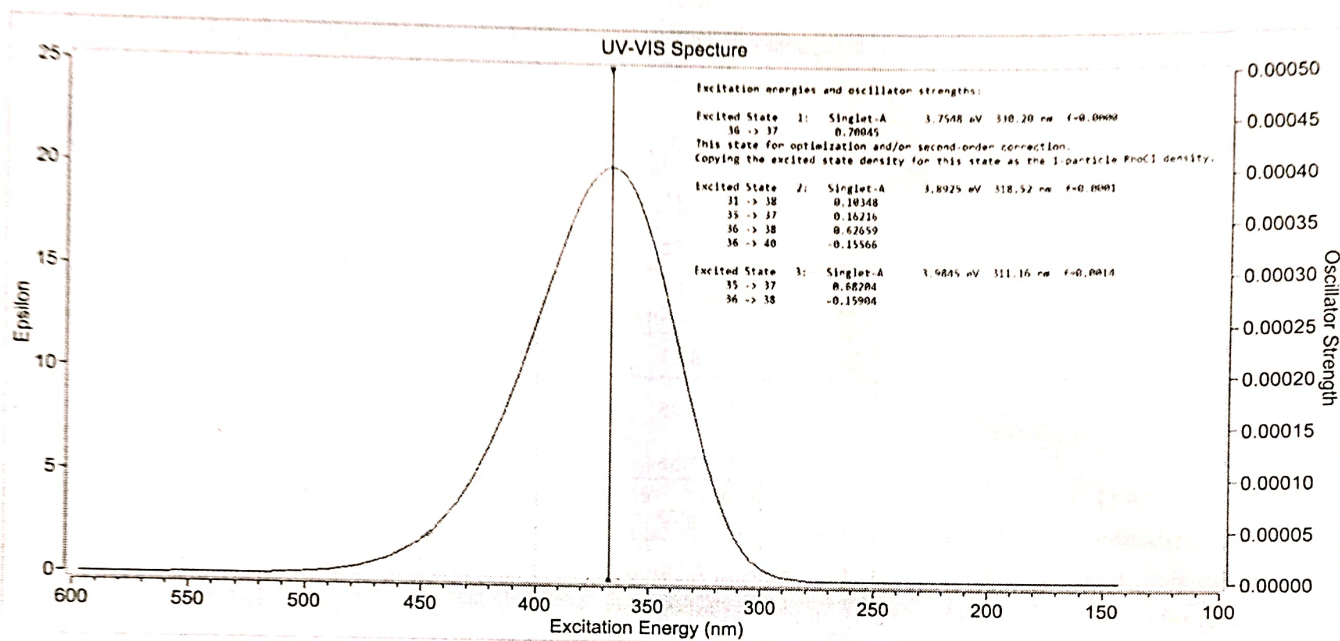


Figure 2. UV-Vis Spectrum of cisplatin opted by RTD-PBE1PBE-FC/SDD.

Table 5. First, second and third absorption band of transplatin.

Complex Compound	First band		Second band		Third band		$\nu_2-\nu_1$	$\nu_3-\nu_2$
	$\nu_1(10^{13})$	$\log \epsilon$	$\nu_2(10^{13})$	$\log \epsilon$	$\nu_3(10^{13})$	$\log \epsilon$		
trans-[Pt(NH ₃) ₂ Cl ₂]	80.0	1.23	95.8	1.88	110.2	2.02	15.8	1.4

Table 6. UV-Vis data of cisplatin as calculated by RTD-PBE1PBE-FC/SDD.

cis-[Pt(NH ₃) ₂ Cl ₂]	Absorption energy	Wave length	Oscillator strength
Excitation State: 1	3.7548 eV	330.20 nm	0.0000
Excitation State: 2	3.8925 eV	318.52 nm	0.0001
Excitation State: 3	3.9845 eV	311.16 nm	0.0014

By default, the pbe1pbe functional and sdd pseudo-potentials were used to calculate IR-spectrum by Gaussian-03 (Figure 3). The number of the normal vibrations of a single cisplatin molecule is 27, distributed in $9A_1 + 5A_2 + 8B_1 + 5B_2$, as shown in Table 7. The notations for modes used are ν -stretching, δ -bending, ρ -

rocking, π -out of plane bending and τ -torsion; the "s" and "as" stands for symmetric and asymmetric, respectively, and the index "op" denotes out-of-plane, and TED for total energy distribution.

Table 7. Calculated (PBE1PBE/SDD) normal vibrational mode of Cisplatin.

S.No.	Freq.	Assignment, TED, %
27	3635.83	ν_a (NH ₃) B ₂ , A ₂ 100 ν (NH)
26	3635.07	
25	3565.31	ν_a (NH ₃) A ₁ , B ₁ 100 ν (NH)
24	3564.65	
23	3383.72	ν_s (NH ₃) B ₁ , A ₁ 100 ν (NH)
22	3383.38	
21	1728.13	δ_a (NH ₃) B ₂ , 59 δ (HNPt + HNH) + 40 τ (NPt)
20	1721.95	δ_a (NH ₃) A ₂ , 58 δ (HNPt + HNH) + 41 τ (NPt)
19	1695.36	δ_a (NH ₃) A ₁ , 65 δ (HNPt + HNH) + 35 τ (NPt)
18	1685.27	δ_a (NH ₃) B ₁ , 65 δ (HNPt + HNH) + 35 τ (NPt)
17	1322.68	δ_s (NH ₃) A ₁ , 100 δ (HNPt + HNH)
16	1315.71	δ_s (NH ₃) B ₁ , 100 δ (HNPt + HNH)
15	866.61	ρ (NH ₃) A ₁ , 75 δ (HNPt) + 24 τ (NPt)
14	823.83	ρ (NH ₃) B ₁ , 75 δ (HNPt) + 24 τ (NPt)
13	804.39	ρ (NH ₃) B ₂ , 88 δ (HNPt) + 10 τ (NPt)
12	781.16	ρ (NH ₃) A ₂ , 88 δ (HNPt) + 11 τ (NPt)
11	499.31	ν_s (PtN) A ₁ , 100 ν (PtN)
10	493.01	ν_a (PtN) B ₁ , 99 ν (PtN)
09	349.96	ν_s (PtCl) A ₁ , 96 ν (PtCl)
08	340.43	ν_a (PtCl) B ₁ , 99 ν (PtCl)
07	239.10	δ (NPtCl) B ₁ , 97 δ (NPtCl)
06	237.93	δ (NPtN) A ₁ , 60 δ (NPtN) + 35 δ (NPtCl)
05	162.75	τ_a (PtN) A ₂ , 92 τ (PtN)
04	145.72	τ_s (PtN) B ₂ , 99 τ (PtN)
03	141.90	π_s (NPtCl) B ₂ , 70 δ_{op} (NPtCl) + 28 τ (PtN)
02	131.54	δ (ClPtCl) A ₁ , 72 δ (ClPtCl) + 13 δ (NPtCl) + 12 δ (NPtN)
01	106.20	π_a (NPtCl) A ₂ , 63 δ_{op} (NPtCl) + 35 τ (PtN)

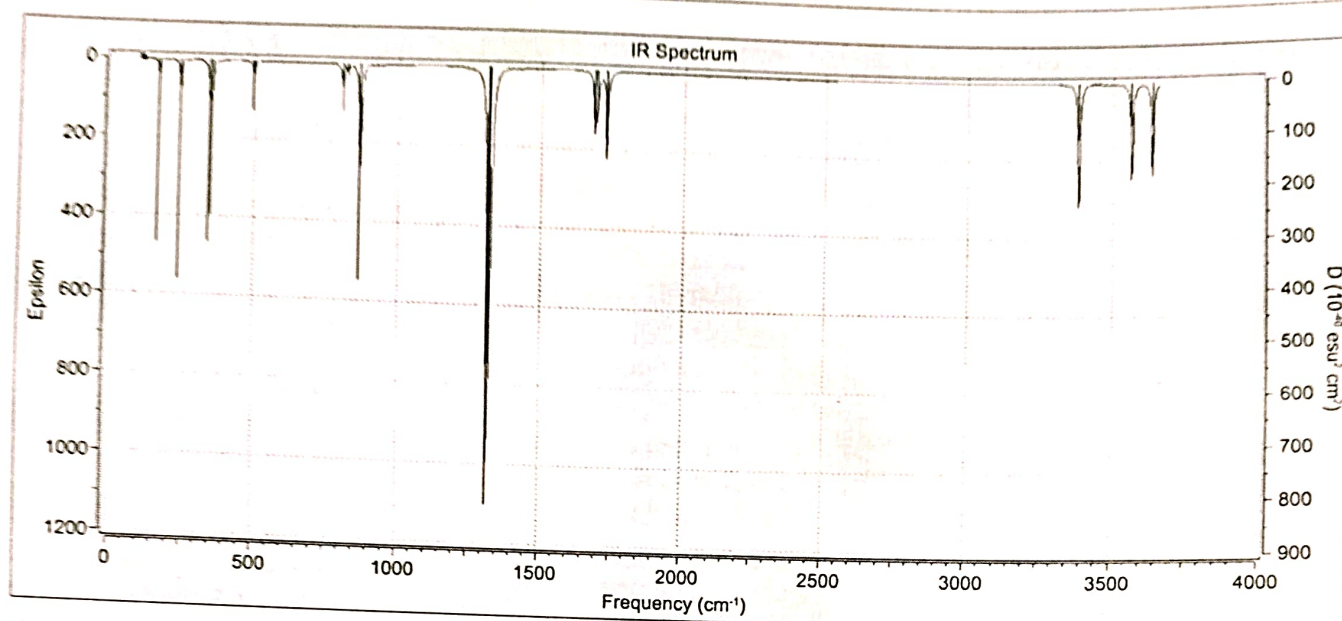


Figure 3. IR- Spectrum of cisplatin opted by PBE1PBE/SDD.

4. Conclusion

Following points have been reflected from the above study: 1) AOs analysis shows sd^3 -hybridization and thus supports Landis concept of sd^n -hybridization, where $n = 3$. The result showed involvement of three p orbitals is negligible as their summation values are very low in comparison to d orbital and considerably low with respect to s orbital. 2) In total thirty-one AOs are involved in the formation of thirty one MOs of cisplatin. As, there are only $28e^-$ to be filled, hence, we considered only fourteen MOs (ϕ_1 - ϕ_{14}) and rest vacant MOs (ϕ_{15} - ϕ_{31}) have been exempted. Among fourteen MOs, twelve are bonding, one is antibonding (ϕ_2) and one is non-bonding (ϕ_6). 3) Cisplatin showed one absorption band at 3.9845 eV with peak corresponded to 311.16 nm of low oscillator strength (0.0014). 4) Cisplatin molecule showed 27 normal vibrations, which distributed in $9A_1 + 5A_2 + 8B_1 + 5B_2$.

Acknowledgements

I am very thankful to Principal and Head of Department of Chemistry, Shia P. G. College, Sitapur Road, Lucknow-226020 (U.P.) for laboratory facilities and also to Department of Higher Education, Prayagraj, Uttar Pradesh for financial assistance (Letter No./Reginal Office Lucknow/5496-99/2021-22; Dated: 15-03-2022 and G.O. No.-107/2021/2584/70-4-2021-4(28)/2021; Dated: 28-12-2021).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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उपभोग प्रमाण-पत्र

प्रमाणित किया जाता है कि "QM/MM based study of Platinum halides and their selective complexes of diverse application." विषयक शोध परियोजना के अंतर्गत शासनादेश संख्या 5496/2021-22 दिनांक 15.03.2022 द्वारा स्वीकृत एवं भुगतान की गयी धनराशि रुपये 350000/- (तीन लाख पचास हजार रुपये मात्र) का उपयोग उसी उद्देश्य की पूर्ति हेतु किया गया है जिसके लिए वह वास्तव में स्वीकृत की गयी है।

प्राचार्य

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प्रमुख शोधकर्ता

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LUCKNOW

