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

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Abstract

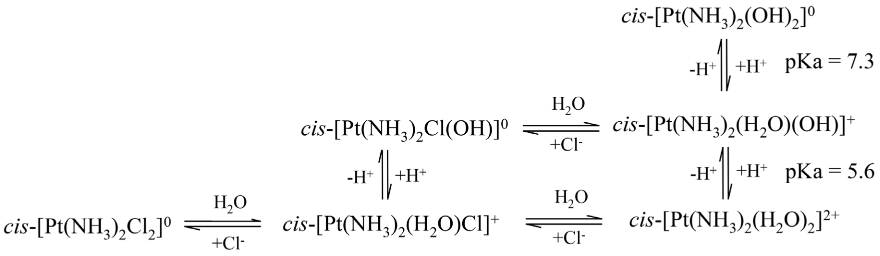
Recently, we have studied electronic structure of platinum dihalides ($Pt(II)X_2$). Here, atomic orbital and molecular orbital analysis along with spectroscopic studies have been made to see electronic structure of cisplatin (cis-$[Pt(NH_3)_2Cl_2]$). CAChe Pro software of Fujitsu and Gaussian-03 software 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 coeffient of AOs reflected sd^3-hybridization and thus supported Landis concept of sd^n-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, sd^3-Hybridization, UV-Spectrum and IR-Spectrum

1. Introduction

It was Rosenberg, who accidentally found out the biological activity of cisplatin, *i.e.*, cis-$[Pt(NH_3)_2Cl_2]$ in 1965 [1]. Actually it was synthesized by Peyrone in 1844 [2]. The anti-tumor activity of square planar complexes (cis-$[Pt(NH_3)_2Cl_2]$ and $[Pt(en)Cl_2]$) and octahedral complexes (cis-$[Pt(NH_3)_2Cl_4]$ and $[Pt(en)Cl_4]$) 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 cis-$[Pt(NH_3)_2Cl_2]$ 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 cis-$[Pt(NH_3)_2Cl_2]$ 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, 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]. 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:

$$\mathrm{Pt}-1=6\mathrm{s},6\mathrm{px},6\mathrm{py},6\mathrm{p}z,5\mathrm{dx}2-\mathrm{y}2,5\mathrm{dz}2,5\mathrm{dxy},5\mathrm{dxz},5\mathrm{dyz}=9$$

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

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

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

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

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

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

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

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

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

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

$$\mathrm{Total}=31$$

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 (5dx2-y2), χ_6 (5dz2), 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 $\phi_1-\phi_{17}$ as described below.

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

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

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

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

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

$$\begin{aligned}\phi_6 = &-0.0001\chi_1 - 0.0001\chi_2 - 0.0005\chi_3 - 0.0004\chi_4 + 0.0025\chi_5 + 0.0004\chi_6 \\ &- 0.0116\chi_7 - 0.0439\chi_8 - 0.0003\chi_9 - 0.0021\chi_{24} + 0.0090\chi_{25} + 0.0000\chi_{26} \\ &- 0.0078\chi_{27} + 0.0030\chi_{28} - 0.0146\chi_{29} + 0.0035\chi_{30} - 0.0082\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_7 = &+0.0006\chi_1 + 0.0006\chi_2 + 0.0002\chi_3 + 0.0000\chi_4 + 0.0065\chi_5 + 0.0150\chi_6 \\ &+ 0.0022\chi_7 - 0.0007\chi_8 - 0.0485\chi_9 - 0.0013\chi_{24} + 0.0071\chi_{25} - 0.0001\chi_{26} \\ &- 0.0135\chi_{27} - 0.0049\chi_{28} + 0.0246\chi_{29} - 0.0037\chi_{30} + 0.0189\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_8 = &-0.0000\chi_1 - 0.0001\chi_2 + 0.0022\chi_3 - 0.0005\chi_4 + 0.0008\chi_5 - 0.0003\chi_6 \\ &+ 0.0125\chi_7 - 0.0062\chi_8 + 0.0047\chi_9 + 0.0151\chi_{24} - 0.0809\chi_{25} - 0.0037\chi_{26} \\ &+ 0.0043\chi_{27} - 0.0130\chi_{28} + 0.0700\chi_{29} - 0.0103\chi_{30} + 0.0049\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_9 = &-0.2285\chi_1 0.0095\chi_2 - 0.0007\chi_3 + 0.0001\chi_4 - 0.0129\chi_5 + 0.1983\chi_6 \\ &+ 0.0002\chi_7 + 0.0004\chi_8 + 0.0830\chi_9 + 0.0582\chi_{24} - 0.2540\chi_{25} + 0.4471\chi_{26} \\ &- 0.1179\chi_{27} + 0.0584\chi_{28} - 0.3201\chi_{29} - 0.4053\chi_{30} + 0.1102\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_{10} = &-0.0002\chi_1 + 0.0004\chi_2 + 0.0072\chi_3 - 0.0032\chi_4 - 0.0667\chi_5 + 0.0035\chi_6 \\ &- 0.4884\chi_7 + 0.1179\chi_8 - 0.0154\chi_9 - 0.0315\chi_{24} + 0.3166\chi_{25} - 0.3364\chi_{26} \\ &+ 0.0861\chi_{27} + 0.0314\chi_{28} - 0.3733\chi_{29} - 0.2774\chi_{30} + 0.0751\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_{11} = &-0.0499\chi_1 - 0.0503\chi_2 + 0.0045\chi_3 - 0.0008\chi_4 + 0.2047\chi_5 + 0.0568\chi_6 \\ &- 0.0235\chi_7 + 0.0039\chi_8 + 0.0673\chi_9 - 0.0049\chi_{24} - 0.4321\chi_{25} - 0.4140\chi_{26} \\ &+ 0.0943\chi_{27} - 0.0050\chi_{28} - 0.3716\chi_{29} + 0.4838\chi_{30} - 0.1036\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_{12} = &+0.0003\chi_1 + 0.0003\chi_2 + 0.0088\chi_3 + 0.0337\chi_4 - 0.0047\chi_5 - 0.0057\chi_6 \\ &- 0.0475\chi_7 - 0.1928\chi_8 + 0.0136\chi_9 + 0.0001\chi_{24} + 0.0042\chi_{25} + 0.1744\chi_{26} \\ &+ 0.6619\chi_{27} - 0.0001\chi_{28} + 0.0047\chi_{29} + 0.1704\chi_{30} + 0.6587\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_{13} = &+0.0007\chi_1 + 0.0091\chi_2 + 0.1143\chi_3 - 0.0264\chi_4 + 0.0127\chi_5 - 0.0007\chi_6 \\ &+ 0.1100\chi_7 - 0.0106\chi_8 + 0.0007\chi_9 - 0.0092\chi_{24} + 0.4776\chi_{25} - 0.0380\chi_{26} \\ &+ 0.0059\chi_{27} + 0.0096\chi_{28} - 0.4750\chi_{29} + 0.0234\chi_{30} + 0.0038\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_{14} = &+0.0023\chi_1 - 0.0026\chi_2 - 0.0006\chi_3 + 0.0002\chi_4 + 0.0460\chi_5 + 0.0929\chi_6 \\ &- 0.0040\chi_7 - 0.0164\chi_8 - 0.1961\chi_9 - 0.0003\chi_{24} + 0.0225\chi_{25} - 0.1648\chi_{26} \\ &- 0.6613\chi_{27} - 0.0004\chi_{28} + 0.0327\chi_{29} + 0.1642\chi_{30} + 0.6653\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_{15} = &+0.0389\chi_1 + 0.1216\chi_2 - 0.0097\chi_3 + 0.0023\chi_4 + 0.0880\chi_5 - 0.1168\chi_6 \\ &- 0.0104\chi_7 + 0.0042\chi_8 - 0.0156\chi_9 + 0.0022\chi_{24} - 0.4134\chi_{25} + 0.1078\chi_{26} \\ &- 0.0565\chi_{27} + 0.0022\chi_{28} - 0.4273\chi_{29} - 0.0288\chi_{30} + 0.0401\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_{16} = &0.0001\chi_1 + 0.0062\chi_2 + 0.0621\chi_3 - 0.0141\chi_4 + 0.0019\chi_5 - 0.0013\chi_6 \\ &+ 0.0199\chi_7 + 0.0055\chi_8 + 0.0005\chi_9 + 0.0024\chi_{24} - 0.3509\chi_{25} - 0.5485\chi_{26} \\ &+ 0.1439\chi_{27} - 0.0025\chi_{28} + 0.2486\chi_{29} - 0.5891\chi_{30} + 0.1558\chi_{31}\end{aligned}$$

$$\begin{aligned}\phi_{17} = &+0.0011\chi_1 - 0.0007\chi_2 - 0.0022\chi_3 + 0.0152\chi_4 + 0.0128\chi_5 + 0.0317\chi_6 \\ &+ 0.2237\chi_7 + 0.9513\chi_8 - 0.0622\chi_9 - 0.0009\chi_{24} - 0.0044\chi_{25} + 0.0487\chi_{26} \\ &+ 0.1590\chi_{27} + 0.0011\chi_{28} + 0.0071\chi_{29} + 0.0501\chi_{30} + 0.1586\chi_{31}\end{aligned}$$

Here, the coefficient of χ is the eigenvector (taken from **Table 1**). The remaining fourteen MOs, ϕ_{18}-ϕ_{31}, 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 cisplain is formed. Hence, only seventeen MOs have been considered here.

$$\mathrm{Pt}^{2+} + 2\mathrm{Cl}^- \rightarrow \mathrm{PtCl}_2 \tag{1}$$

$$\mathrm{PtCl}_2 + 2\mathrm{NH}_3 \rightarrow \text{cis-}\left[\mathrm{Pt}\left(\mathrm{NH}_3\right)_2\mathrm{Cl}_2\right] \tag{2}$$

Table 1. Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ_i) of cis-$Pt(NH_3)Cl_2$.

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_{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

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 combing 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 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-$[Pt(NH_3)_2Cl_2]$. 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$(NH_3)_2Cl_2$] 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].

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

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	5dx2-y2	0.4306	**Cl-11**	**AO**	**$\Sigma\phi_{1-14}$**	**N-3**	**AO**	**$\Sigma\phi_{1-14}$**
χ_6	5dz2	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

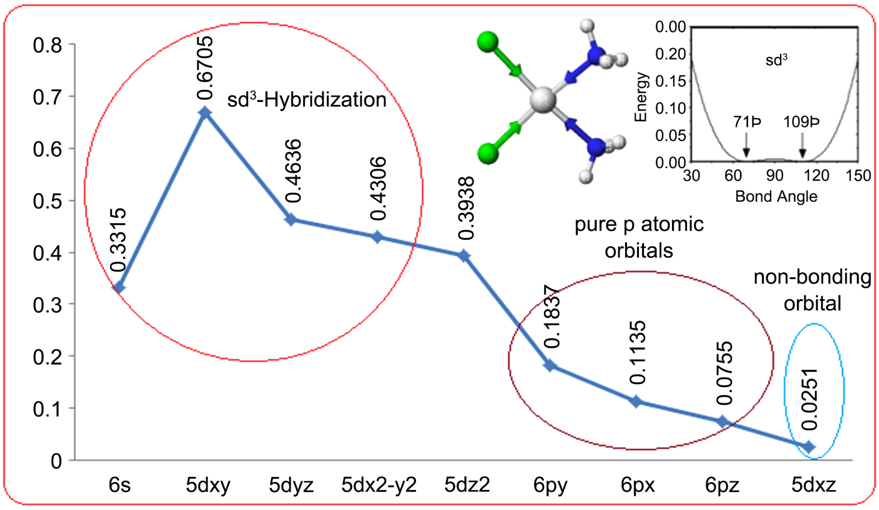


Figure 1. Contribution of atomic orbital in sd^3 hybridization [21].

The shape of each MO (ϕ_1-ϕ_{17}) has been determined by the relative magnitudes and signs of the different coefficients. For this cis-[Pt(NH$_3$)$_2$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: $n_{r-s,i} = n_i\left(2c_{ri}c_{si}S_{rs}\right)$. To calculate overlap populations for 88 overlaps (overlap of 2NH$_3$ ligands have been excluded) in MOs of cis-[Pt(NH$_3$)$_2$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 cis-[Pt(NH$_3$)$_2$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 cis-[Pt(NH$_3$)$_2$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 cis-Pt(NH$_3$)Cl$_2$.

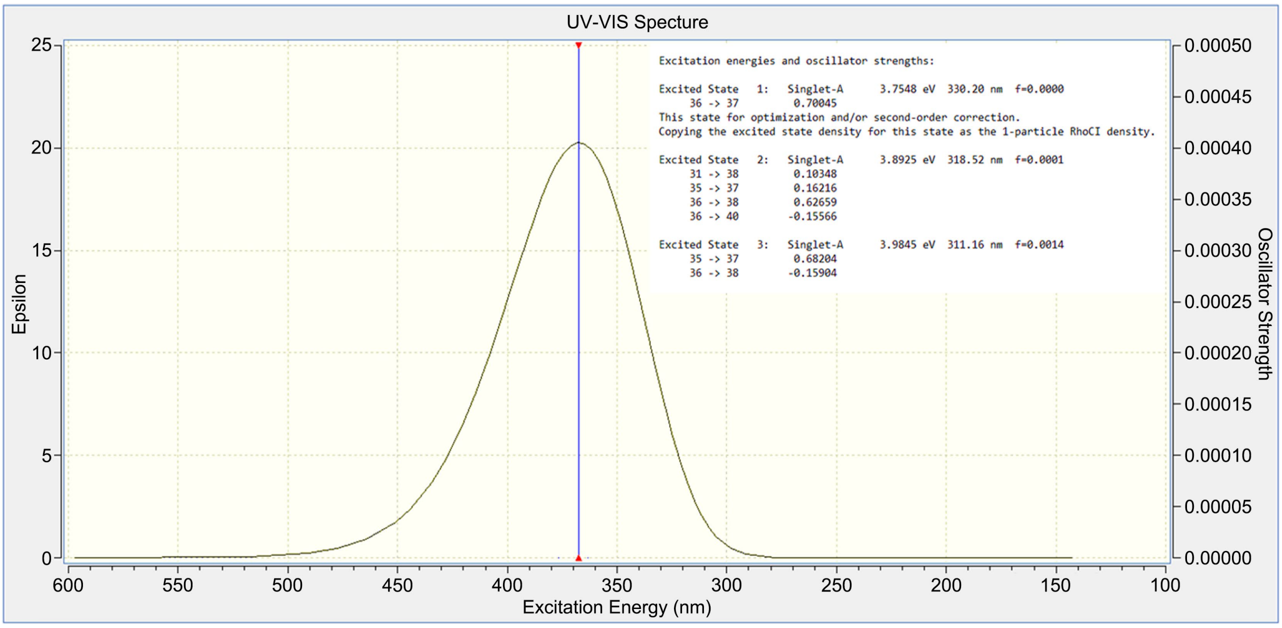
AOs	6s	6px	6py	6pz	5dx^2-y^2	5dz^2	5dxy	5dxz	5dyz	3s	3px	3py	3pz	3s	3px	3py	3pz
	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Cl-2)	(Cl-2)	(Cl-2)	(Cl-2)	(Cl-3)	(Cl-3)	(Cl-3)	(Cl-3)
6s (Pt-1)	1.0000																
6px (Pt-1)	0.0000	1.0000															
6py (Pt-1)	0.0000	0.0000	1.0000														
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-$Pt(NH_3)Cl_2$.

MO No.	$\Sigma n_{r\text{-}s,i}$	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.

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 tans-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. 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) 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 computationally 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**.



```
Excitation energies and oscillator strengths:

Excited State   1:   Singlet-A      3.7548 eV  330.20 nm  f=0.0000
     36 -> 37         0.70045
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   2:   Singlet-A      3.8925 eV  318.52 nm  f=0.0001
     31 -> 38         0.10348
     35 -> 37         0.16216
     36 -> 38         0.62659
     36 -> 40        -0.15566

Excited State   3:   Singlet-A      3.9845 eV  311.16 nm  f=0.0014
     35 -> 37         0.68204
     36 -> 38        -0.15904
```

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		υ_2-υ_1	υ_3-υ_2
	$\upsilon_1(10^{13})$	log ε	$\upsilon_2(10^{13})$	log ε	$\upsilon_3(10^{13})$	log ε		
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 υ-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	υ_a (NH_3) B_2, A_2 100υ (NH)
26	3635.07	
25	3565.31	υ_a (NH_3) A_1, B_1 100υ (NH)
24	3564.65	
23	3383.72	υ_s (NH_3) B_1, A_1 100υ (NH)
22	3383.38	
21	1728.13	δ_a (NH_3) B_2, 59δ(HNPt + HNH) + 40τ(NPt)
20	1721.95	δ_a (NH_3) A_2, 58δ(HNPt + HNH) + 41τ(NPt)
19	1695.36	δ_a (NH_3) A_1, 65δ(HNPt + HNH) + 35τ(NPt)
18	1685.27	δ_a (NH_3) B_1, 65δ(HNPt + HNH) + 35τ(NPt)
17	1322.68	δ_s (NH_3) A_1, 100δ(HNPt + HNH)
16	1315.71	δ_s (NH_3) B_1, 100δ(HNPt + HNH)
15	866.61	ρ(NH_3) A_1, 75δ(HNPt) + 24τ(NPt)
14	823.83	ρ(NH_3) B_1, 75δ(HNPt) + 24τ(NPt)
13	804.39	ρ(NH_3) B_2, 88δ(HNPt) + 10τ(NPt)
12	781.16	ρ(NH_3) A_2, 88δ(HNPt) + 11τ(NPt)
11	499.31	υ_s (PtN) A_1, 100υ (PtN)
10	493.01	υ_a (PtN) B_1, 99υ (PtN)
09	349.96	υ_s (PtCl) A_1, 96υ (PtCl)
08	340.43	υ_a (PtCl) B_1, 99υ (PtCl)
07	239.10	δ(NPtCl) B_1, 97δ(NPtCl)
06	237.93	δ(NPtN) A_1, 60δ(NPtN) + 35δ(NPtCl)
05	162.75	τ_a (PtN) A_2, 92τ(PtN)
04	145.72	τ_s (PtN) B_2, 99τ(PtN)
03	141.90	π_s (NPtCl) B_2, 70δ_{op} (NPtCl) + 28τ(PtN)
02	131.54	δ(ClPtCl) A_1, 72δ(ClPtCl) + 13δ(NPtCl) + 12δ(NPtN)
01	106.20	π_a (NPtCl) A_2, 63δ_{op} (NPtCl) + 35τ(PtN)

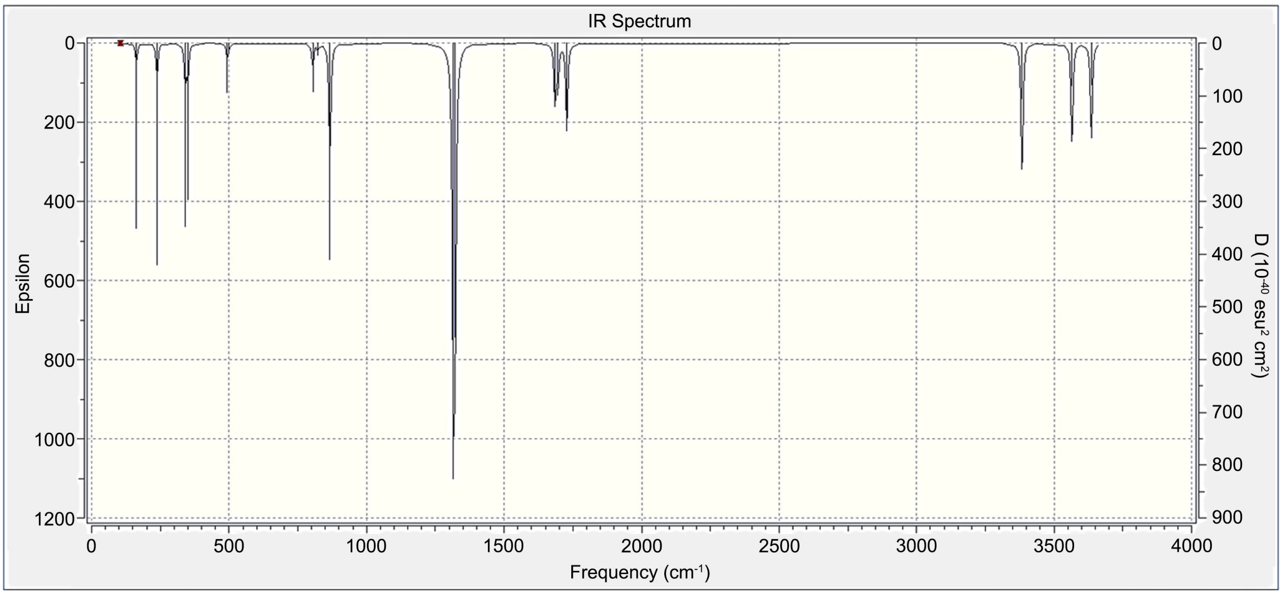


Figure 3. IR- Spectrum of cisplatin opted by PBE1PBE/SDD.

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 $9A_1 + 5A_2 + 8B_1 + 5B_2$.

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Conflicts of Interest

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

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