

QM/MM Based Study of Electronic Structure of Platinum Dihalides

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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 , $i = 1 - 17$, 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 PtCl₂.

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 ($\chi_2, \chi_3, \chi_4, \chi_8, \chi_9, \chi_{13}, \chi_{17}$) have no contribution in the formation of 1st MO (ϕ_1) as these have zero coefficient values. And the rest ten AOs ($\chi_1, \chi_5, \chi_6, \chi_7, \chi_{10}, \chi_{11}, \chi_{12}, \chi_{14}, \chi_{15}, \chi_{16}$) 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 PtBr₂.

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 PtCl₂; (b) Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ) of PtBr₂; (c) Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ) of PtI₂; (d) Eigenvector values of atomic orbitals (χ) in molecular orbitals (ϕ) of PtF₂.

		(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	0.0000	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	0.0000	-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	-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	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	0.0003
	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	-0.0002
	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	0.0000
	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	-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	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	0.0000	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	0.5819
	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	0.0289
	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	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	0.0000	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	0.5811
	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	0.0289
	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	-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	0.0000	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	0.0000	-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	-0.0000	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	0.1256
	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	0.0009
	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	-0.0005
	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	0.0000
	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	-0.0002
	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	0.0000
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	0.0000	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	-0.5245
	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	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	0.0530
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	0.0000	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	-0.5272
	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	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	0.0533

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	0.4042	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	-0.0990	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	0.1418	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	-0.9918	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
	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
I-2	χ_{10}	-0.6655	-0.6925	0.1701	0.0000	-0.0000	-0.0501	0.0000	0.0000	0.0000	0.0000	0.0000	0.0247	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
	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
I-3	χ_{14}	-0.6654	0.6927	0.1701	0.0000	0.0000	0.0501	0.0000	0.0000	0.0000	0.0000	0.0000	0.0247	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	0.3609	-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	0.0000	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
	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
F-2	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	
	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	
F-3	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	-0.0000	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_{13} , 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 PtI₂.

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_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 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 combing 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 4dxy, 4dxz, $4dx^2 - y^2$, 5s, 5px, 5py, 5pz AOs of PtCl₂; (b) Coefficient values of 4dxy, 4dxz, $4dx^2 - y^2$, 5s, 5px, 5py, 5pz AOs of PtBr₂; (c) Coefficient values of 4dxy, 4dxz, $4dx^2 - y^2$, 5s, 5px, 5py, 5pz AOs of PtI₂; (d) Coefficient values of 4dxy, 4dxz, $4dx^2 - y^2$, 5s, 5px, 5py, 5pz AOs of PtF₂; (e) Summation values of various AOs of halides of Pt(II).

(a)							
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	0.0360	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 _{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	0.0445	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			
$\Sigma 5d_{z2}$	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: $F^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{ox} < \text{SCN} < \text{Cl}^- < \text{CN}^- < \text{Br}^- < \text{I}^-$. 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

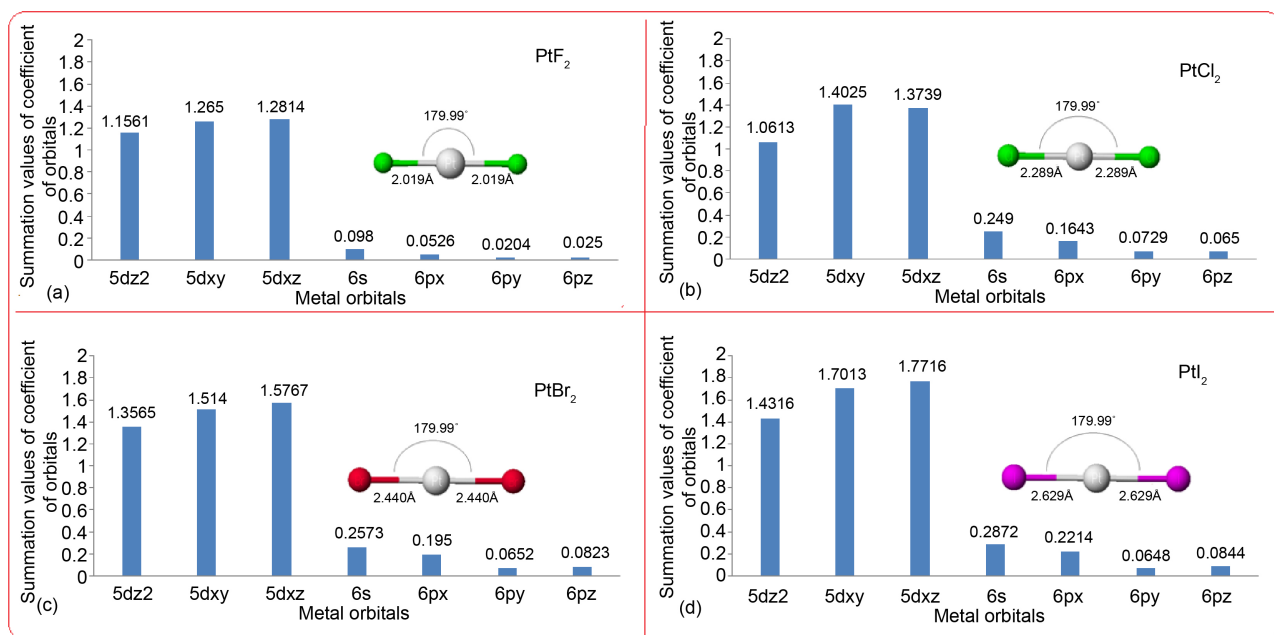


Figure 5. (a) Extent of involvement of metal orbitals in the formation of MOs of PtCl₂, (b) Extent of involvement of metal orbitals in the formation of MOs of PtCl₂, (c) Extent of involvement of metal orbitals in the formation of MOs of PtBr₂ and (d) Extent of involvement of metal orbitals in the formation of MOs of PtI₂.

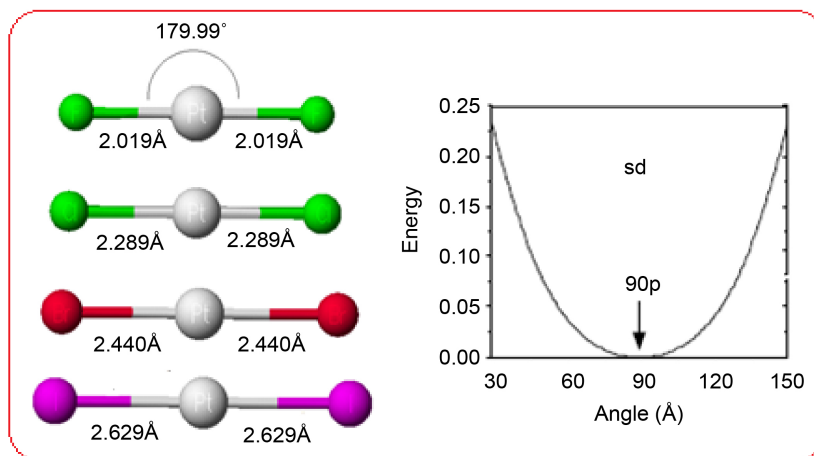


Figure 6. Plot between energy and bond angle(Å) for sd-hybridization.

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_{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 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_{rs}) of various overlaps of atomic orbitals of constituent atoms in PtCl_2 ; (b) Overlap matrix or overlap integrals values (S_{rs}) of various overlaps of atomic orbitals of constituent atoms in PtBr_2 ; (c) Overlap matrix or overlap integrals values (S_{rs}) of various overlaps of atomic orbitals of constituent atoms in PtI_2 ; (d) Overlap matrix or overlap integrals values (S_{rs}) 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

(b)																	
AOs	6s	6px	6py	6pz	5dx ² - y ²	5dz ²	5dxy	5dxz	5dyz	4s	4px	4py	4pz	4s	4px	4py	4pz
	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Br-2)	(Br-2)	(Br-2)	(Br-2)	(Br-3)	(Br-3)	(Br-3)	(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

(c)																	
AOs	6s	6px	6py	6pz	5dx ² - y ²	5dz ²	5dxy	5dxz	5dyz	5s	5px	5py	5pz	5s	5px	5py	5pz
	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(Pt-1)	(I-2)	(I-2)	(I-2)	(I-2)	(I-3)	(I-3)	(I-3)	(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.

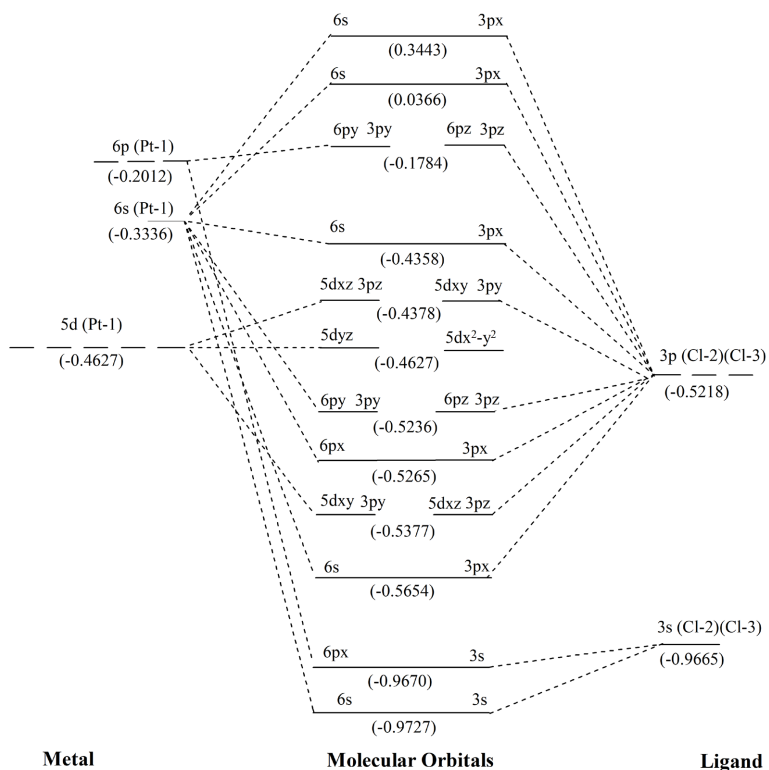


Figure 7. MO diagram of PtCl₂ along with energy of AOs and MOs in eV as show in parenthesis.

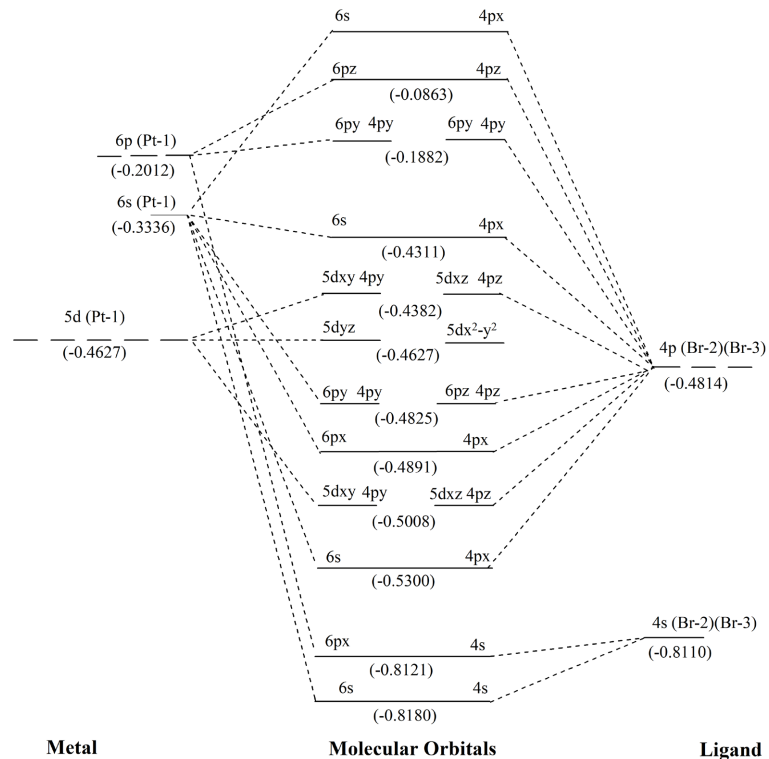


Figure 8. MO diagram of PtBr₂ along with energy of AOs and MOs in eV as show in parenthesis.

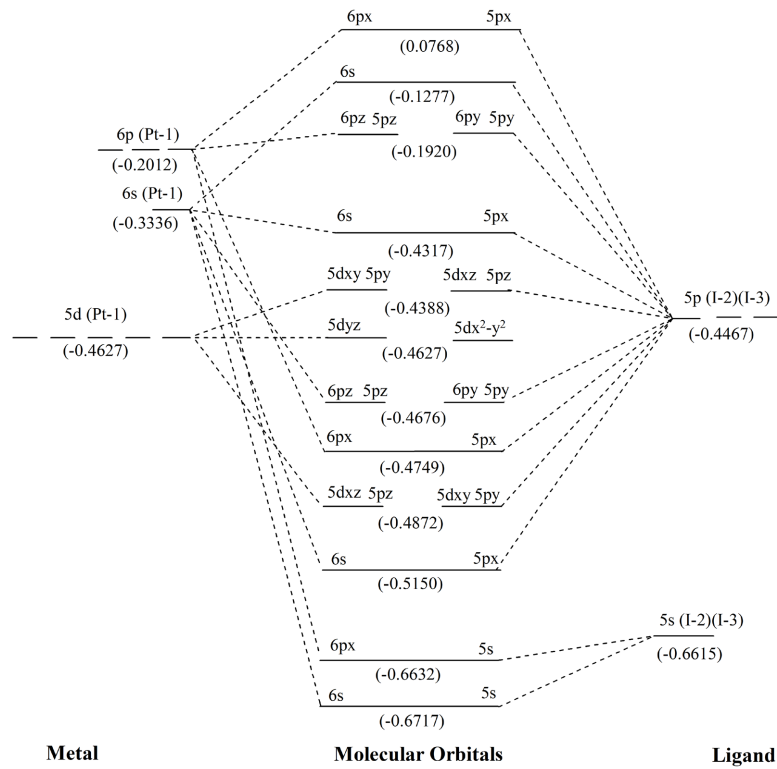


Figure 9. MO diagram of PtI₂ along with energy of AOs and MOs in eV as show in parenthesis.

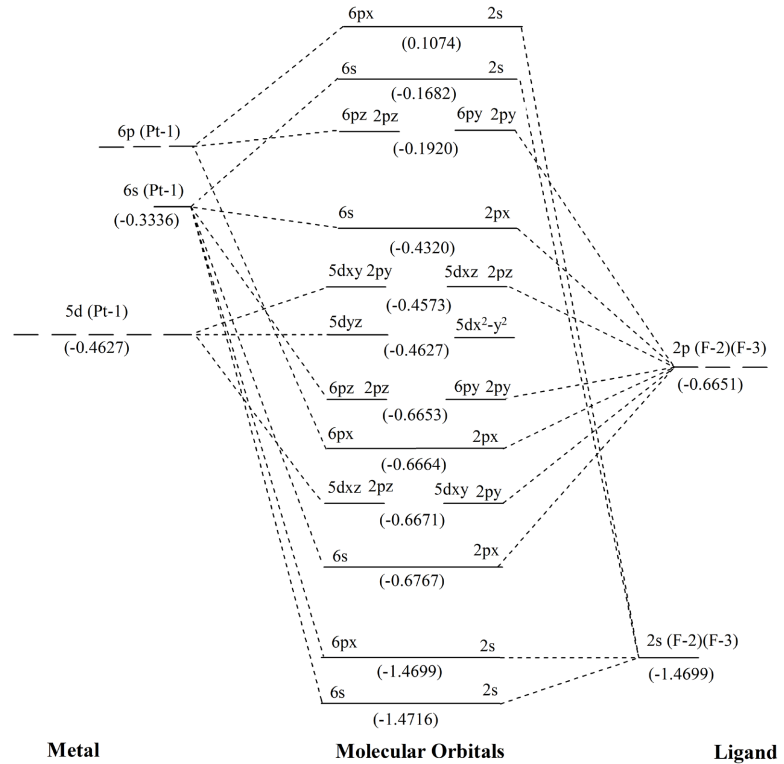


Figure 10. MO diagram of PtF₂ along with energy of AOs and MOs in eV as show in parenthesis.

(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.

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Conflicts of Interest

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

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