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NATURAL BOND ORBITAL (NBO) POPULATION ANALYSIS OF OS_3 (CO) $_{10}${M-PH_2PC (ME) $_{2PPH2}$}

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ABSTRACT

The molecular structure of $Os_3(CO)_{10}$\{m-$Ph_2PC(Me)_2PPh_2$\} (1-me2) was calculated by the b3lyp density functional model using LANL2DZ basis set for os and 6-31g(p, d) for other atoms. Stability of the molecule arising from hyper conjugative interaction and charge delocalization has been analyzed using natural bond orbital (NBO) analysis. The second order perturbation energies of the most interaction NBOs and the population of electrons in core, valance and rydberg sub-shell have been predicted by density functional theory (DFT) computation Gaussian 09w software package. The natural atomic orbital occupancies showed the presence of charge delocalization within the molecule .the natural hybrid atomic orbital studies to Know about the type of orbital's and its percentage of s-type and p-type character.

KEYWORDS: Density Functional Theory Natural Atomic Orbital, Natural Bond Orbital

INTRODUCTION

Density functional theory (DFT) is useful and reliable method for studying the physical and chemical properties of molecules [1]. DFT recovers electron correlation in the self-consistent kohn-sham procedure through the functions of electron density .DFT is commonly used to examine the electronic structure of transition metal complexes [2, 3]. It meets the requirements of being accurate, easy to use and sufficiently rapid to allow the study of relatively a technique for studying hybridization and covalence effects in polyatomic wave functions,. Geometric optimization and electronic structure of [4] has been determined on the basis of the density functional theory (DFT) calculations and additional information about binding has been obtained by NBO analysis. Becker's hybrid exchange functional called "b3," combined with the lyp correlation functional, is the most widely applied of the many possible choices of exchange and correlation functional this is called the b3lyp method [5, 6]. The objective of the present work is to investigate the nature of bonding in an Os_3 (CO) $_{10}${m-Ph_2PC (Me) $_{2PPh2}$} [7]. The NBOs in terms of their constituent hybrids, polarization coefficients occupancies each NBO is labeled as being of core (cr), bond (bd), valence lone pair (lp), or extra-valence rydberg (ry) type, with affixed asterisk (*) for non-lewis orbital's [8]. NBO analysis stresses the role of intermolecular orbital interaction in the complex, particularly charge transfer. This is carried out by considering all possible interactions between filled donor and empty acceptor NBO_S and estimating their energetic importance by second-order perturbation theory [9]. For each donor NBO (i) and acceptor NBO (j) the stabilization energy E (2) associated with electron delocalization between donor and acceptor is estimated as [10]

$$E\,(2) = \Delta Eij = qi\,\frac{f(i,j)^2}{\varepsilon j - \varepsilon i}$$

Where qi is the orbital occupancy, εi and εj are diagonal elements

And F (i, j) is the off-diagonal NBO Fock matrix [11, 12] element.

Computational Details

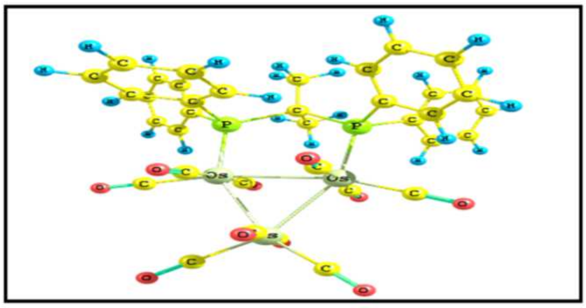
The All the calculations were carried out with the Gaussian 09 software package [13]. Calculations of systems contain C, H, and O is described by the standard 6-31G (d,p) basis set[14] function of the density functional theory (DFT). The LANL2DZ [15] effective core potential (ECP) basis set (Los Alamos National Laboratory basis sets, developed by (Hay and Wadt) [16] was used for Os atom. Geometry optimization was performed utilizing Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP). NBO calculations were performed with the NBO code in Gaussian.

RESULTS AND DISCUSSIONS

All the results presented in this work were obtained at the DFT-B3lyp level, and LANL2DZ basis set was used Os atoms, 6-31G (p, d) for H, C, O, p atoms. Geometry parameters of Os_3 (CO) $_{10}${m-ph$_2$PC (me) $_{2pph2}$} are close to the experimental values. Performed at the DFT-b3lyp method and LANL2DZ basis set for metal atoms, the structural parameters of title compound are in good agreement with the crystal structures[]. The optimized structure of compound is shown in Fig.1, and the important bond lengths and bond angles are listed in Table 1.

Table 1: Optimized Geometrical Parameters of Complexes

Length(Nm) or Angle(O)	Exp.	B3lyp
Os(1)- Os(2)	2.8717	2.9618
Os(2)- Os(3)	2.8978	2.96722
Os(1)- Os(3)	2.8801	2.95583
Os(1)- P(1)	2.3396	2.38996
Os(2)- P(2)	2.359	2.42131
Os(1)- Os(2)- Os(3)	59.892	59.806
Os(3)- Os(1)- Os(2)	60.50	60.188
Os(1)- Os(3)- Os(2)	59.61	60.006
P(1)- Os(1)- Os(2)	89.98	90.295
P(1)- Os(1)- Os(3)	149.87	149.934
P(2)- Os(2)- Os(1)	96.00	96.219
P(2)- Os(2)- Os(3)	155.62	156.024



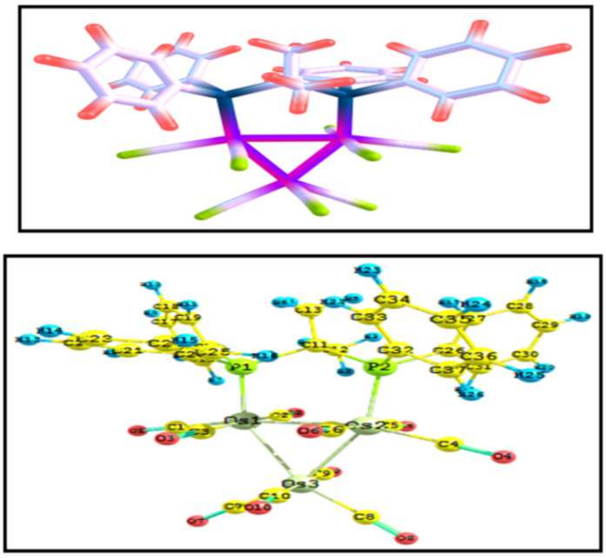


Figure 1: DFT-Optimized Structures for Complex

NBO Analysis

The natural population analysis describes the distribution of electrons in various sub-shells of their atomic orbital’s [17] . The accumulation of charges on the individual atom and the accumulation of electrons in the core, valence and Rydberg sub-shell are also presented in table 2.In this case of compound,the most electronegative charge of -1.40121, -1.39844 and -1.30347 are accumulation on Os$_1$,Os$_2$ and Os$_3$ respectively. These on electronegative atoms have a tendency to donate an electron. Whereas the most electropositive charge of 1.34819 and 1.31192 are accumulation on p$_4$ and p$_5$ respectively. These on electronegative atoms have a tendency to accept an electron [18]. NBO analysis of complex is performed to estimate the delocalization pattems of electron density from the principal occupied Lewis type (bond or lone pair) orbitals to un occoupied non –lewis (anti-bonding or Rydberg) orbitals[19]. Table3. Lists the occupancies and energies of most σ interaction NBOs along with their percentage of hybrid atomic orbital contribution

Table 2: Accumulation of Natural Population of Electron in Core, Valence and Rydberg Orbitals

Atom	No	Charge	Core	Valence	Rydberg	Total
Os	1	-1.40121	67.95453	9.39913	0.04755	77.40121
Os	2	-1.39844	67.95511	9.39616	0.04717	77.39844
Os	3	-1.30347	67.95037	9.31391	0.03918	77.30347
Os	4	1.34819	9.99623	3.59198	0.06360	13.65181
Os	5	1.31192	9.99638	3.63037	0.06134	13.68808
P	6	-0.45842	1.99965	6.43717	0.02160	8.45842
P	7	-0.44837	1.99963	6.42560	0.02314	8.44837
O	8	-0.43328	1.99962	6.41037	0.02329	8.43328
O	9	-0.46109	1.99965	6.43996	0.02148	8.46109
O	10	-0.45175	1.99963	6.42900	0.02313	8.45175
O	11	-0.44160	1.99962	6.41876	0.02322	8.44160

O	12	-0.42836	1.99964	6.40664	0.02207	8.42836
O	13	-0.42917	1.99964	6.40745	0.02207	8.42917
O	14	-0.41396	1.99963	6.39088	0.02345	8.41396
O	15	-0.41481	1.99963	6.39174	0.02345	8.41481
O	16	0.73916	1.99843	3.20527	0.05714	5.26084
O	17	0.68745	1.99873	3.25716	0.05666	5.31255
C	18	0.72491	1.99875	3.21936	0.05698	5.27509
C	19	0.73413	1.99844	3.21085	0.05658	5.26587
C	20	0.69118	1.99873	3.25452	0.05558	5.30882
C	21	0.70441	1.99874	3.23992	0.05693	5.29559
C	22	0.76411	1.99857	3.17851	0.05881	5.23589
C	23	0.76053	1.99858	3.18213	0.05876	5.23947
C	24	0.73327	1.99882	3.21103	0.05688	5.26673
C	25	0.73294	1.99882	3.21134	0.05690	5.26706
C	26	-0.59349	1.99904	4.57503	0.01942	6.59349
C	27	-0.70069	1.99918	4.69000	0.01151	6.70069

Table 3: Calculated Natural Hybrid Orbital's (Nhos) and the Polarization Coefficient for Each Hybrid in the Corresponding NBO for the Selected σ Bonding Using the DFT Method

σ bond		%	% s	%p	%d	H.O
σ $(Os)_1$-$(Os)_2$	Os_1	44.37	8.66	54.09	37.25	$sp^{6.25}d^{4.30}$
	Os_2	55.63	1.60	49.92	48.47	$s\,p^{31.13}d^{30.23}$
σ $(Os)_3$-$(Os)_1$	Os_1	42.77	16.06	47.01	36.92	$sp^{2.93}d^{2.30}$
	Os_3	57.23	2.70	50.88	46.42	$sp^{18.84}d^{17.19}$
σ $(Os)_1$- P_4	Os_1	32.81	20.57	54.43	24.99	$sp^{2.65}d^{1.22}$
	P_4	67.19	34.74	65.09	0.17	$sp^{1.87}$
σ $(Os)_1$- C_{16}	Os_1	34.17	22.39	42.11	35.47	$sp^{1.88}d^{1.58}$
	C_{16}	65.83	65.24	34.76	0.01	$sp^{0.53}$
σ $(Os)_1$– C_{17}	Os_1	32.07	16.51	49.77	33.66	$sp^{3.01}d^{2.04}$
	C_{17}	67.93	67.48	32.51	0.01	$sp^{0.48}$
σ $(Os)_1$ - C_{18}	Os_1	32.09	15.94	50.02	33.99	$sp^{3.14}d^{2.13}$
	C_{18}	67.91	67.09	32.91	0.01	$sp^{0.49}$
σ $(Os)_1$ - P_5	Os_2	35.86	32.70	28.28	39.01	$sp^{0.86}d^{1.19}$
	P_5	64.14	34.59	65.26	0.14	$sp^{1.89}$
σ $(Os)_1$ - C_{19}	Os_2	34.09	21.69	42.31	35.97	$sp^{1.95}d^{1.66}$
	C_{19}	65.91	65.39	34.61	0.01	$sp^{0.53}$
σ $(Os)_2$ - C_{20}	Os_2	32.57	12.34	50.27	37.34	$sp^{4.08d}d^{3.03}$
	C_{20}	67.43	67.41	32.58	0.01	$sp^{0.48}$
σ $(Os)_2$ - C_{21}	Os_2	32.58	12.27	50.44	37.24	$sp^{4.11}d^{3.04}$
	C_{21}	67.42	67.26	32.73	0.01	$sp^{0.49}$
σ $(Os)_3$ - C_{22}	Os_3	36.16	30.33	24.31	45.33	$sp^{0.80}d^{1.49}$
	C_{22}	63.84	65.15	34.84	0.01	$sp^{0.53}$
σ $(Os)_3$ –C_{23}	Os_3	33.81	20.78	44.13	35.05	$sp^{2.12}d^{1.69}$
	C_{23}	66.19	65.22	34.77	0.01	$sp^{0.53}$
σ $(Os)_3$ -C_{24}	Os_3	32.64	13.35	50.91	35.69	$sp^{3.81}d^{2.67}$
	C_{24}	67.36	66.66	33.33	0.01	$sp^{0.50}$
σ $(Os)_3$-C_{25}	Os_3	32.71	13.18	50.68	36.08	$sp^{3.84}d^{2.74}$
	C_{25}	67.29	66.66	33.33	0.01	$sp^{0.50}$
σ P_4 - C_{26}	P_4	37.80	21.98	77.35	0.67	$sp^{3.52}$
	C_{26}	62.20	22.83	77.11	0.05	$sp^{3.38}$

σ P_4 - C_{35}	P_4	37.38	21.07	78.14	0.80	$sp^{3.71}$
	C_{35}	62.62	29.49	70.46	0.05	$sp^{2.39}$
σ P_4 - C_{46}	P_4	37.49	22.24	76.94	0.83	$sp^{3.46}$
	C_{46}	62.51	29.48	70.46	0.06	$sp^{2.39}$
σ P_5 - C_{26}	P_5	38.12	21.93	77.40	0.67	$sp^{3.53}$
	C_{26}	61.88	22.77	77.18	0.06	$sp^{3.39}$
σ P_5 - C_{57}	P_5	37.79	21.77	77.47	0.76	$sp^{3.56}$
	C_{57}	62.21	29.07	70.88	0.05	$sp^{2.44}$
σ P_5 - C_{68}	P_5	37.61	21.75	77.47	0.79	$sp^{3.56}$
	C_{68}	62.39	29.15	70.80	0.05	$sp^{2.43}$

As a result, in the NBO analysis, the donor–acceptor (bond–anti bond) interactions are taken into consideration by examining all possible interactions between ‘filled’ (donor) Lewis-type NBO and ‘empty’ (acceptor) non-Lewis NBO and then estimating their energies by second-order perturbation theory. These interactions (or energetic stabilizations) are referred to as ‘delocalization’ corrections to the zeroth-order natural Lewis structure. Therefore, the interaction having strongest stablsation takes place between effective donors and effective acceptors [20]. This bonding-anti bonding interactions can be quantitatively described in terms of the NBO approach that is expressed by means of second-order perturbation interaction energy E(2) Table 4. Lists the calculated second order interaction energies (E (2)) above 2.0 kJ.mol–1 between the donor–acceptor orbital’s of Os_3 $(CO)_{10}$\{m-ph$_2$pC (me)$_2$pph$_2$\}. In this compound, the bond pair donor orbital, □ □□□* interaction between the bond pair (Os) $_2$- P_5 bonding and the (Os) $_2$- P_5 anti bonding orbital give more stabilization of 174.07 kJ. Mol–1 while the interaction□□□*-□□* between (Os) $_1$ - C_{17} Donor and the (Os) $_1$ - C_{16} Acceptor orbital gives a very strong stabilization of 1723.03 kJ. Mol–1

Table 4: Second Order Perturbation Theory Analysis of the Fock Matrix in NBO Basis of Complex

Donor (i)	Occupancies	Acceptor (j)	Occupancies	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
σ (Os)$_1$-(Os)$_2$	1.39568	LP*(4)(Os)$_2$	0.47452	13.88	1.96	0.152
σ(Os)$_1$- (Os)$_2$	1.39568	LP (4)(Os)$_3$	0.47520	52.67	1.72	0.277
σ (Os)$_1$- (Os)$_2$	1.39568	σ* (Os)$_1$ -(Os)$_2$	0.36751	71.87	1.17	0.276
σ (Os)$_1$- (Os)$_2$	1.39568	σ* (Os)$_1$ -(Os)$_3$	0.35548	136.94	1.28	0.400
σ (Os)$_1$- (Os)$_2$	1.39568	σ* (Os)$_1$ - P_4	0.09775	59.65	1.07	0.261
σ (Os)$_1$-(Os)$_2$	1.39568	σ* (Os)$_1$ - C_{17}	0.10396	84.16	1.00	0.299
σ (Os)$_1$- (Os)$_2$	1.39568	σ* (Os)$_1$ - C_{18}	0.10541	88.60	0.98	0.303
σ (Os)$_1$- (Os)$_3$	1.39146	LP*(4)Os$_2$	0.47452	87.49	1.97	0.384
σ (Os)$_1$- (Os)$_3$	1.39146	σ* (Os)$_1$ -(Os)$_2$	0.36751	162.98	1.18	0.418
σ (Os)$_1$- (Os)$_3$	1.39146	σ* (Os)$_1$ -(Os)$_3$	0.35548	68.64	1.29	0.284
σ (Os)$_1$- (Os)$_3$	1.39146	σ* (Os)$_1$ - C_{17}	0.10396	97.12	1.01	0.324
σ (Os)$_1$-(Os)$_3$	1.39146	σ* (Os)$_1$ - C_{18}	0.10541	90.89	0.99	0.309
σ (Os)$_1$- (Os)$_3$	1.39146	σ*O_6 - C_{16}	0.15323	76.02	0.07	0.074
σ (Os)$_1$- P_4	1.81629	σ* (Os)$_1$ -(Os)$_2$	0.36751	85.14	1.55	0.341
σ (Os)$_1$- P_4	1.81629	σ* (Os)$_1$ - P_4	0.09775	80.38	1.45	0.311
σ (Os)$_1$- P_4	1.81629	σ* (Os)$_1$- C_{16}	0.08049	60.47	1.41	0.268
σ (Os)$_1$- P_4	1.81629	σ* (Os)$_1$- C_{17}	0.10396	76.69	1.38	0.297
σ (Os)$_1$- P_4	1.81629	σ* (Os)$_1$- C_{18}	0.10541	68.14	1.36	0.277
σ (Os)$_2$- P_5	1.87347	σ* (Os)$_1$-(Os)$_2$	0.36751	148.14	1.46	0.442
σ (Os)$_2$- P_5	1.87347	σ* (Os)$_2$ - P_5	0.20889	174.07	1.40	0.449
σ(Os)$_2$ - P_5	1.87347	σ* (Os)$_2$ - C_{19}	0.08477	146.43	1.30	0.394
σ (Os)$_2$- P_5	1.87347	σ* (Os)$_2$ - C_{20}	0.13277	167.35	1.10	0.383
σ (Os)$_2$- P_5	1.87347	σ* (Os)$_2$ - C_{21}	0.13140	159.78	1.07	0.369
σ (Os)$_3$- C_{22}	1.92746	σ* (Os)$_1$- (Os)$_3$	0.35548	119.12	1.71	0.435
σ (Os)$_3$ - C_{22}	1.92746	σ* (Os)$_3$- C_{22}	0.15074	154.66	2.05	0.512
σ (Os)$_3$ - C_{22}	1.92746	σ * (Os)$_3$ - C_{24}	0.11764	142.57	1.34	0.395
σ* (Os)$_1$ -(Os)$_2$	0.36751	LP*(4)Os$_2$	0.47452	642.52	0.79	0.980

σ^* $(Os)_1$ -$(Os)_3$	0.35548	σ^* $(Os)_3$- C_{22}	0.15074	929.02	0.34	0.994
σ^* $(Os)_1$ - C_{17}	0.10396	LP*(4)Os_2	0.47452	115.21	0.96	0.552
σ^* $(Os)_1$ - C_{17}	0.10396	σ^* $(Os)_1$-$(Os)_3$	0.35548	590.85	0.28	0.756
σ^* $(Os)_1$ - C_{17}	0.10396	σ^* $(Os)_1$ - P_4	0.09775	921.46	0.07	0.697
σ^* $(Os)_1$ - C_{17}	0.10396	σ^* $(Os)_1$ - C_{16}	0.08049	1723.03	0.03	0.668
σ^* $(Os)_1$ - C_{18}	0.10541	$\sigma^*$$(Os)_1$- C_{17}	0.10396	1623.04	0.02	0.553

CONCLUSIONS

According to our results, following conclusions are derived for the $Os_3(CO)_{10}\{m\text{-}ph_2pC\ (me)_2pph_2\}$

- The potential energy surface analysis by the density functional theory B3LYP results seemed to be in a good agreement with experimental data.
- The natural population analysis of charge explains the most electronegative charge are accumulation on Os_1, Os2 and Os_3 respectively. Whereas the most electropositive charge are accumulation on p_4 and p_5 respectively
- The Natural Bond Orbital (NBO) analysis has provided the detailed insight into the type of hybridization and the nature of bonding in title compound.
- The molecular stabilization energy E2 Calculated by NBO method show the the strongest electron donation occurs from the □*-□□* interaction□ between $(Os)_1$ - C_{17} Donor and the $(Os)_1$ - C_{16} Acceptor orbital

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