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Research Article

STUDY OF QUANTUM MECHNICAL PARAMETERS OF 1, 1′ BIS (THIOCYNATO MERCURIO) FERROCENE WITH THE HELP OF DENSITY FUNCTION THEORY

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ABSTRACT

Recently density function theory attained great prominence in quantum chemistry research. Calculation of quantum mechanical parameters viz. energies of binding orbitals, heat of formation, total energy, electronic energy, core-core repulsion etc. have been done with the help of density function theory using CAChe software for the complex 1,1′ bis (thiocyanatomercurio) ferrocene. Bonding orbital energies and core-core repulsion values indicate the comparative stability of the complexes.

Keywords: Density function theory (DFT), Core-core repulsion, Electronic energy, Bonding molecular orbitals.

1. INTRODUCTION

The sandwich structure of ferrocene was established by crystallographic studies and valence bond structure was proposed by Dunitz and Orgel [1, 2]. But the calculation of the relative energy levels and involvement of various atomic orbital in the formation of molecular orbital was a subject of uncertainty and complexity. Application of molecular mechanics and quantum chemistry to organometallic and transition metal compounds made it possible to study the quantum mechanical parameters like eigenvalues, eigenvectors, core-core repulsion, Ionization potential (IP), etc. in order to examine the extent of involvement different orbitals of iron in the complex formation [3-10].

The complexes of ferrocene prepared by reaction of 1,1′ bis (thiocyanatomercurio) ferrocene with $M(NCS)_2$[M=Fe (II), Co (II), Ni (II), Cu (II), Zn (II)] are further reacted with pyridine, nicotinamide, bipyridine and phenanthroline. The structure and reactivity have been established by elemental analysis, conductance measurement and electronic spectral studies [11]. The density functional theory (DFT) has recently been used for study of molecular electronic structure [12-14]. In DFT a Gaussian type orbital is a function of the form $e^{-\alpha r^2}$. However, in the semi empirical calculations, the atomic orbitals have been used as slater-type orbitals as basis sets. In the case of diatomic molecules, the hydrogenic orbitals form the basis set. For 1s orbitals of the two atoms constitute the basis for the MO and for polyatomic molecules the first basis set used in large scale computational studies consisted of Slater-type orbitals.

$$S_{nlm}(r,\theta,\varphi) = N_n r^{n-1} e^{-\xi r} Y_{l,m}(\theta,\varphi)$$

Where $N_n$is the normalization constant defined as

$$N_n = \frac{2\ (\xi)^{n+\frac{1}{2}}}{[(2n)!\ ]^{\frac{1}{2}}}$$

Where $\xi$is the orbital exponent, n and l are the principal and azimuthal quantum numbers and $Y_{l,m}(\theta,\varphi)$ are the angular dependent spherical harmonics.

2. METHODOLOGY

The LCAO approximation from Hartree-Fock calculations to Roothaan equation provided a theoretical basis for approximate molecular orbital theories [15-17]. Later on, the successful employment of gradient correlated DFT played a historic role in calculating, particularly of heavier atoms [18-21], the different quantum mechanical parameters and in the use of small core relativistic effect core potentials (ECP) [22] which forms a basis for the calculation of energy, bond energies, vibrational spectra, NMR shifts,

activation energies of chemical reaction and other properties with good accuracy [23]. The coefficients in linear combination for each molecular orbital being formed by solution of the Roothaan equation [24]. The most efficient way to solve the Roothaan equation is to use matrix algebra method. In Matrix algebra methods, the matrix elements are computed and the secular equations are solved to give the set of orbital energies. These eigen values are used to solve Roothaan equations for eigen vectors. In this method we assumed a reasonable approximation for the exchange correlation energy function $E_{xc}(r)$ and then with an initial guess for the molecule's electron density r (x,y,z) found by superimposing calculated electron densities of the individual atoms at the nuclear geometry chosen for the calculation. From the initial r, we calculate $E_{xc}(r)$ and then find its functional derivative to obtain an initial estimate of the exchange correlation potential [25-27]. The 3D modelling and geometry optimization of all the compounds given in table 1 have been performed with PC model software using semi-empirical PM3 and the quantum mechanical parameters like heat of formation, total energy, electronic energy, core-core repulsion, IP, bond distribution angle are calculated with the help of CAChe software.

3. RESULTS AND DISCUSSION

The values of different mechanical parameters are given in the tables 2 to 7 by displaying specific parameters and their values.

Table 1: Complexes of study

Compound No	1,1' bis (thiocyanatomercurio) ferrocene complexes
1	$Fe(C_5H_4)_2$ - $(Hg\ SCN)_2$.2Fe $(NCS)_2$. nL
2	$Fe(C_5H_4)_2$ - $(Hg\ SCN)_2$.2Co $(NCS)_2$. nL
3	$Fe(C_5H_4)_2$ - $(Hg\ SCN)_2$.2Ni $(NCS)_2$. nL
4	$Fe(C_5H_4)_2$ - $(Hg\ SCN)_2$.2Cu $(NCS)_2$. nL
5	$Fe(C_5H_4)_2$ - $(Hg\ SCN)_2$.2Zn $(NCS)_2$. nL
	1,1' bis (selenocyanatomercurio) ferrocene complexes
	$Fe(C_5H_4)_2$ - $(Hg\ SeCN)_2$.2Fe $(NCS)_2$. nL
1A	$Fe(C_5H_4)_2$ - $(Hg\ SeCN)_2$.2Co $(NCS)_2$. nL
2A	$Fe(C_5H_4)_2$ - $(Hg\ SeCN)_2$.2Ni $(NCS)_2$. nL
3A	$Fe(C_5H_4)_2$ - $(Hg\ SeCN)_2$.2Cu $(NCS)_2$. nL
4A	$Fe(C_5H_4)_2$ - $(Hg\ SeCN)_2$.2Zn $(NCS)_2$. nL
5A	For n =1, L = bipyridyl or phenanthroline; n = 2, L = nicotinamide

Table 2: Bonding orbitals and their energies in nicotinamide complexes

Compound No	Metal Ion	No. of Binding orbitals	Energy HBO	Energy LBO	Energy LABO
1	Fe	125	-0.16050	-41.5437	0.00507
1A	Fe	120	-0.16853	-42.4109	0.04997
2	Co	125	-0.25030	-43.231	0.11838
2A	Co	126	-0.05424	-42.7539	0.02422
3	Ni	132	-0.11754	-42.8811	0.13332
3A	Ni	125	-0.12588	-43.2882	0.19133
4	Cu	130	-0.36245	-42.4579	0.05144
4A	Cu	123	-0.01000	-43.0707	0.05944
5	Zn	122	-0.00112	-43.0155	0.24099
5A	Zn	120	-0.06982	-43.0294	0.10460

For the sake of study and discussion the complexes are divided into three groups viz. Nicotinamide, Bipyridyl and Phenanthroline. Each group has two sets, one of selenocyanato and the other of thiocyanatomercurio ferrocene. The point group of all the complexes irrespective of the group belongs to which L is C_1. This shows a similarity in their structure. The number of filled levels in Fe(II) thiocyanato and selenocynato group of complexes in 110. Whereas in case of Co(II) analog, one additional singly occupied level appears in both thio and selanocynato sets of complexes. In the case of complexes Fe(II), Ni(II),Cu(II) and Zn(II), the

thiocyanato derivatives are more stable than their selenocynato counterparts whereas in case of Co(II) complexes, the selenocynato derivative is more stable. The energy of lowest antibonding orbital is higher in case of thiocyanato derivatives in the complexes of iron, nickel and copper whereas in cobalt and zinc the selenocynato derivatives show higher values.

Table 3: Bonding orbitals and their energies in bipyridyl complexes

Compound No	Metal Ion	No. of Binding orbitals	Energy HBO	Energy LBO	Energy LABO
6	Fe	108	-0.1295	-41.7338	0.09114
6A	Fe	105	-0.1522	-42.2522	0.03517
7	Co	107	-0.0123	-41.7372	0.02150
7A	Co	104	-0.0503	-41.7716	0.02597
8	Ni	112	-0.2111	-42.0182	0.01099
8A	Ni	109	-0.1686	-42.0731	0.04270
9	Cu	106	-0.0034	-41.6779	0.32030
9A	Cu	106	-0.0257	-41.6599	0.15030
10	Zn	104	-0.0505	-41.7323	0.07470

Table 4: Bonding orbitals and their energies in phenanthroline complexes

Compound No	Metal Ion	No. of Binding orbitals	Energy HBO	Energy LBO	Energy LABO
11	Fe	110	-0.1614	-42.5020	0.0617
11A	Fe	110	-0.0603	-42.2454	0.0442
12	Co	104	-0.1358	-42.8288	0.0203
12A	Co	110	-0.0728	-42.4009	0.0144
13	Ni	119	-0.0474	-45.5673	0.1209
13A	Ni	112	-0.0457	-45.1792	0.0094
14	Cu	111	-0.0586	-43.1735	0.0633
14A	Cu	113	-0.0285	-43.3096	0.1815
15	Zn	110	-0.0098	-42.4037	0.2457
15A	Zn	108	-0.1770	-42.4007	0.0399

Table 5: Values of various parameters of complexes of nicotinamide

Compound No.	Metal Ion	Molecular Weight	Heat of Formation	Total Energy	Electronic Energy	Core-core Repulsion	Ionization Potential
1	Fe	1305.21	274.419	-6915.166	-66570.892	59655.725	8.055
1A	Fe	1117.61	220.948	-6882.300	-68558.492	61676.192	8.274
2	Co	1308.297	78.044	-7003.79	-65389.01	563855.215	7.313
2A	Co	1120.69	81.2188	-6968.47	-70952.730	63984.2569	6.948
3	Ni	1308.07	154.375	-6916.408	-68587.285	61670.8766	8.461
3A	Ni	1120.47	183.545	-6879.958	-65600.221	58720.263	7.992
4	Cu	1312.909	1057.36	-7478.579	-70399.378	629920.799	8.990
4A	Cu	1125.309	349.954	-7474.70	-60171.733	52697.663	11.36
5	Zn	1314.743	199.91	-6541.031	-62469.173	55928.141	7.896
5A	ZN	1127.14	268.369	-6502.87	-60011.362	53508.485	7.68

Table 6: Values of various parameters of complexes of bipyridyl

Compound No.	Metal Ion	Molecular Weight	Heat of Formation	Total Energy	Electronic Energy	Core-core Repulsion	Ionization Potential
7A	Co	1032.631	246.09	-5753.83	-48365.21	12611.379	9.16
7	Co	1220.231	209.99	-5790.585	-52393.02	46602.44	9.51
9A	Cu	1037.244	473.72	-6261.21	-49339.91	43078.699	10.877
9	Cu	1224.844	455.88	-6297.172	-50304.286	44007.113	12.055
6A	Fe	1029.54	402.028	-5666.95	-48627.831	42960.872	7.69
6	Fe	1217.14	414.056	-5701.623	-50360.906	44659.284	7.53
8A	Ni	1032.40	304.31	-5667.23	-49307.341	43640.109	8.86
8	Ni	1220.008	286.380	-5703.19	-51259.046	4555.851	8.59
10	Zn	1236.67	338.80	-5327.519	-43507.963	38180.443	8.57

Table 7: Values of various parameters of complexes of phenanthroline

Compound No.	Metal Ion	Molecular Weight	Heat of Formation	Total Energy	Electronic Energy	Core-core Repulsion	Ionization Potential
12	Co	1244.25	206.52	-6028.016	-57008.383	50980.366	9.49
12A	Co	1056.753	284.047	-5989.469	-53229.092	47239.622	8.71
14	Cu	1248.866	462.46	-6534.168	-50632.883	44098.715	10.047
14A	Cu	1061.26	439.735	-6499.968	-49824.068	43324.100	11.46
11	Fe	1241.16	307.03	-5943.543	-60527.557	54584.01	7.85
11A	Fe	1053.56	384.707	-5904.99	-52381.349	46476.359	8.261
13	Ni	1244.03	247.129	-5942.178	55015.546	4907.368	8.53
13A	Ni	1056.43	248.51	-5906.93	-57294.285	51387.352	8.594
15	Zn	1250.70	258.655	-5566.27	-50063.559	44495.283	7.67
15A	Zn	1063.10	319.66	-5530.444	-48216.666	42686.332	8.32

4. CONCLUSION

The study and analysis of the various parameters of the three classes of complexes reveals that the energy of highest bonding orbital (HBO) is highest in Nickel complexes, which is more in selenocyanato derivative as compared to thiocyanato counterpart. The energy of lowest bonding orbitals (LBO) in both selenocyanato and thiocyanato derivatives of Nickel are highest being -42.0182 and -42.0731. In case of Phenanthroline complexes, the energy of LBO is minimum in Nickel Complex for selenocyanato and thiocyanato derivative. The total energy of nicotinamide complexes of copper thio and selenocyanato are -7474.770 and -7478.5799 respectively. The heats of formation of these two copper complexes are at a higher end. The higher heats of formation indicate low stability. The similar trend is shown in thio and selenocyanato complexes of bipyrydyl and phenanthroline. DFT based studies of different complexes of Ferrocene have provided an idea of the comparable reactivity of the complexes towards different ligands. In future it will be helpful in QSAR study of theoretical drug designing with the help of software which is much economical than actual lab experiments and will support the green chemistry also.

Conflict of interest

Authors declare no conflict of interest.

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