Molecular Simulation of Tricarbonyl (1-4-η-5-exo-N-X,X-dimethylpyridino-cyclohexa-1,3-diene) Iron Complexes:- A Semi Empirical PM6 Approach

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Authors' contributions

This work was carried out in collaboration between all authors. Author OFA designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript under the supervision of authors TIO and IAA. Author TIO managed the analyses of the study. Author IAA managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

We report herein the simulation of Tricarbonyl (1-4-η-5-exo-N-X,X-dimethyl pyridino-cyclohexa-1,3-diene) iron complexes that were carried out on the theoretical ground state geometries, electronic, thermodynamic properties and vibrational frequencies using semi empirical PM6 method. The geometries, electronic states, thermodynamic properties and vibrational frequencies were discussed. The calculated infra red vibrational frequency of all optimized geometries reveal imaginary frequency values indicating that they are dynamically unstable.

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1. INTRODUCTION

Molecular simulation has bacome a powerful tool to aid the experimental scientist in understanding the structure and property relationship of existing materials and predicting the properties of new ones [1-3]. Its advent and popularity have improved the the studies of new molecular systems. Theoretical experiments by computer simulations [4-6] have succeeded in determining the properties of compounds within limits of accuracy of the experimental values [7,8]. The James Stewart Semi-empirical parameterization method three, PM 3, ab initio and density functional theory (DFT) have been reported to produce suitable calculations concerning Transition metal complexes and organometallic compounds [8-17] and in particular the PM3 has made tremedous progress in computing a wide variety of ground state properties of similar complexes of irontricarbonyl [18-23]. Therefore, it is interesting extending the parameterization method six, PM6 approach to the study of Tricarbonyl (1-4-η-5-exo-N-X,X-dimethylpyridino-cyclohexa-1,3-diene) iron complexes. The PM6 method combines the simplicity and general applicability of the ab initio method without necessarily increasing the computation cost of PM3 [24]. The complexes reported in this paper were modeled using Spartan' 14.V1.1.2 [25], and the theoretical investigations carried out on optimized geometries. The electronic structures, dipole moments, thermodynamic stabilities and vibrational frequencies were calculated using Semi-empirical PM6 parameterization method. The PM6 offers great advantage over PM3 with Molecular mechanics' correction terms for a number of difficult cases, improved parameters and adjustment of the core repulsion functions, development of new methods for computing one-center, two-electron integrals for Transition metals and introduction of recent experimental data. The use of ab initio and density functional theoretical results to complement experimental data and careful study and pruning of experimental data to achieve quality and consistency of results [24]. Hence, the use of PM6 method for the calculation and determination of the molecular properties of Tricarbonyl (1-4-η-5-exo-N-X,X-dimethylyridino-cyclohexa-1,3-diene) iron complexes. The structure is shown in Fig. 1, while the optimized structures are shown in Fig. 2.

2. COMPUTATIONAL METHODOLOGY

All the complexes were modeled using Spartan' 14 series of programms [25]. The quantum calculations were performed on the geometries of the resulting conformers. Semi-empirical molecular orbital calculations were carried out on a number of species involved. All structures were fully optimized. The theoretical ground state geometries, electronic structure, thermodynamic parameters and vibrational frequencies of these modeled compounds were all investigated at the Semi-empirical PM6 method and the results are discussed. We have also examined HOMO and LUMO levels; the energy band gap is evaluated as the difference between the HOMO and LUMO energies. The optimized geometries of these Tricarbonyl(1-4-η-5-exo-N-X,X-imethylyridino-cyclohexa-1,3-diene) iron complexes are shown in Fig. 2.
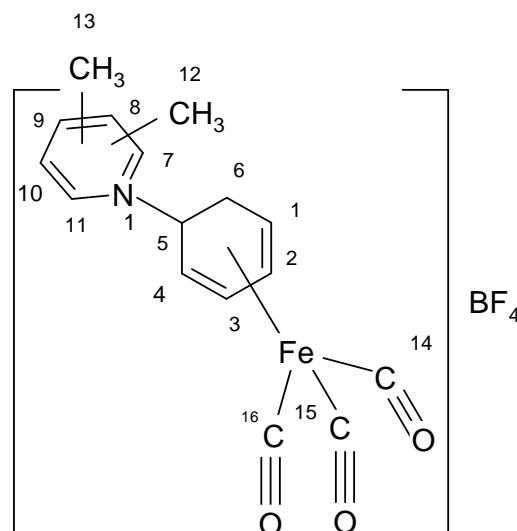

Fig. 1. Structure of Tricarbonyl(1-4-η-5-exo-N-X,X-dimethylpyridino-cyclohexa-1,3-diene)iron tetrafluoroborate complexes

3. RESULTS AND DISCUSSION

3.1 Geometrical Parameters

Geometric parameters (bond length/Å, bond angles and dihedral angles in degrees) of the studied Tricarbonyl(1-4-η-5-exo-N-X,X-dimethyl pyridino-cyclohexa-1,3-diene iron complexes [26, 27] in their global minimum obtained by Semi-empirical PM6 are shown Table 1. The ground state geometrical parameters showed the bond length C_5-N, C_7-N, C_7-C_8, C_8-C_9, C_7-C_{12} and C_{11}-N with values 1.581, 1.388, 1.419, 1.402, 1.489 and 1.378 Å for 2,3-dimethylpyridino organometallic complex. The corresponding values of C_7-N and C_{11}-N increased to 1.405 and 1.390 Å

respectively, this increase is attributed to the electron donor methyl substituents [28-30] in 2 and 6 position of the pyridine ring. The metal - carbon bond distances range from 1.756 - 1.799 Å, while the metal-ligand bond distance ranges between 1.743 Å and 1.760 Å. The variations observed for the bond length C_7-C_8 is as a result of electron donating ability of the methyl group on the ortho and meta and para positions. This observation also reflected in the bond angle C_{12}-C_7-C_8 which displayed a progressive increase in value as a result of electron donating ability of the second methyl substituent which changes from the meta to para position thus increasing the bond angle C_{12}-C_7-N from 120.12° to 120.63°. The H_6-C_5-N-C_{11} and H_6-C_5-N-C_7 dihedral angles also increased progressively as the position of the methyl group are varied except for the 3,4-Me_2 and 3,5-Me_2 which displayed a radical departure from others due to the donor ability of the methyl substituents [31]. The results are collected in Table 1.

3.2 Electronic Property

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry and play vital role in electrical, optical and chemical properties of a molecule. These orbitals determine the polarizability, kinetic stability and a number of properties. Spectroscopic data for a number of π-systems are usually determined either in solution or in the solid state (crystals or thin film). Our calculations are for isolated molecules in the gas phase. Experimentally, the HOMO and the LUMO energies can be obtained from an empirical data based on the onset of the oxidation and reduction of peaks measured by cyclic voltametry, in gas-phase chemistry, the HOMO and the LUMO energies are calculated using quantum mechanical calculations [32,33,34]. However, solid state packing effects are not included in our calculations as this tends to affect the
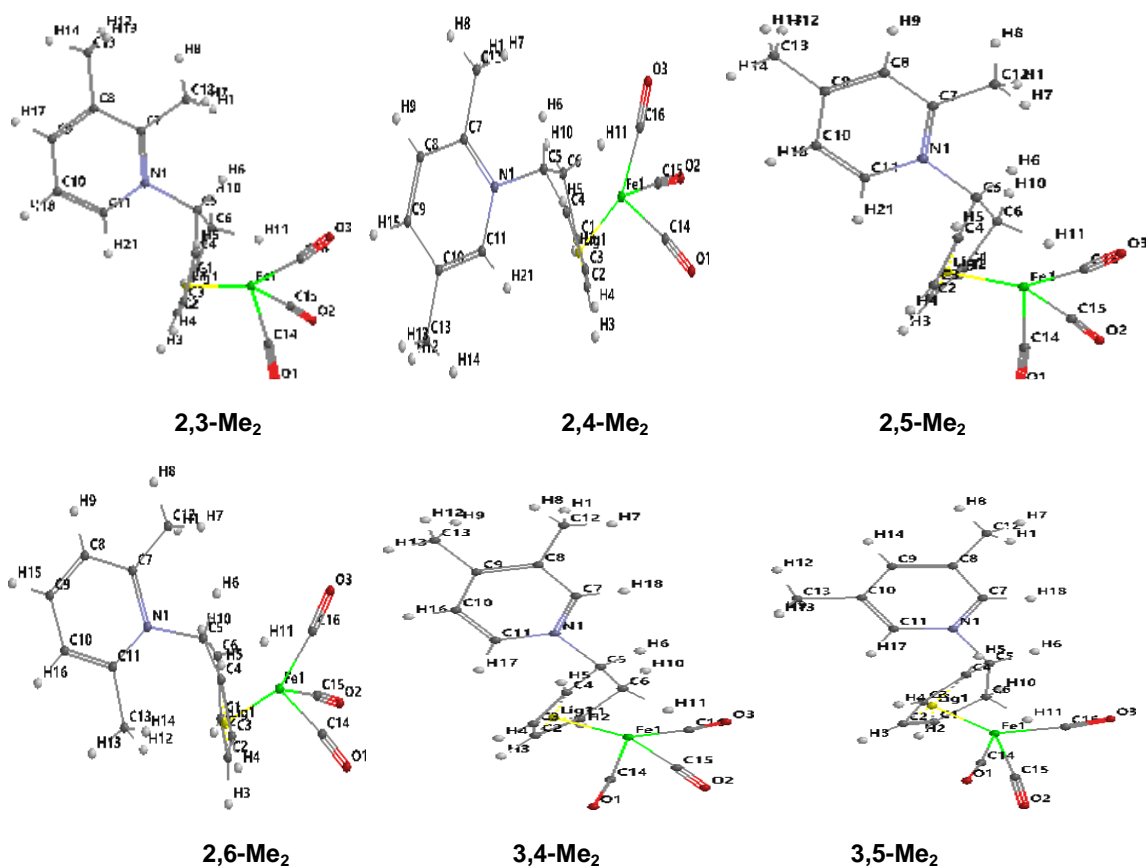

Fig. 2. Optimized structures of Tricarbonyl (1-4-η-5-exo-N-X, X-dimethyl pyridino-cyclohexa1,3-diene) iron tetrafluoroborate complexes. (BF₄ is excluded for clarity)

HOMO and the LUMO energy levels in a thin film compared to an isolated molecule [27-29]. The calculated electronic parameters (energy band gaps, i.e. HOMO- LUMO) of the X, X-substituted pyridino-organometallic complexes are 7.23, 7.36, 7.23, 7.34, 7.26 and 7.21 eV respectively for X = 2,3-Me$_2$, 2,4- Me$_2$, 2,5-Me$_2$, 2,6-Me$_2$, 3,4-Me$_2$ and 3,5-Me$_2$. They LUMO level suffers destabilization from the electron donor methyl substituents on the pyridine ring. There are no significant changes in band gap even though the position of the substituent changes. The HOMO energy is concentrated on the cyclohexa-1,3-diene irontricarbonyl unit while the LUMO energy is found on the dimethylpyridine moiety. The HOMO and LUMO energies and energy band gaps are shown in Table 2. The HOMO and LUMO diagrams are presented in Fig. 3 while the orbital energy diagrams are displayed in Fig. 4.

Table 1. Geometric parameters (bond length/Å,bond angles and dihedral angles in degrees) of the studied Tricarbonyl (1-4-η-5-exo-N-X,X-dimethyl pyridino-cyclohexa-1,3-diene iron complexes

| Bond length in angstroms units						
Bond/Å	2,3-diMe	2,4-diMe	2,5-diMe	2,6-diMe	3,4-diMe	3,5-diMe
C$_5$-N	1.581	1.577	1.579	1.595	1.575	1.756
C$_7$-N	1.388	1.392	1.382	1.405	1.382	1.372
C$_7$-C$_8$	1.419	1.399	1.410	1.395	1.396	1.408
C$_8$-C$_9$	1.402	1.404	1.387	1.398	1.425	1.404
C$_7$-C$_{12}$	1.489	1.487	1.487	1.490	-	-
C$_{11}$-N	1.378	1.384	1.380	1.390	1.368	1.364
Bond angles in degrees						
Bond Angle / °	2,3-diMe	2,4-diMe	2,5-diMe	2,6-diMe	3,4-diMe	3,5-diMe
C$_5$-N-C$_7$	121.76	121.30	120.76	116.27	119.07	118.66
C$_5$-N-C$_{11}$	118.60	119.86	119.85	125.51	122.82	121.58
C$_{12}$-C$_7$-N	95.40	120.12	120.63	120.73	-	-
C$_{12}$-C$_7$-C$_8$	120.98	119.17	119.74	118.15	-	-
C$_8$-C$_9$-C$_{13}$	119.42	121.08	-	-	121.25	-
Dihedral angles in degrees						
Bond/°	2,3-diMe	2,4-diMe	2,5-diMe	2,6-diMe	3,4-diMe	3,5-diMe
C$_5$-N-C$_7$-C$_{12}$	3.38	0.31	0.09	1.50	-	-
H$_6$-C$_5$-N-C$_7$	15.47	23.90	27.60	29.76	10.62	12.84
H$_6$-C$_5$-N-C$_{11}$	-158.64	-156.49	-152.81	-150.26	-164.63	-167.36
C$_{12}$-C$_7$-C$_8$-C$_9$	177.03	179.35	179.51	179.60	-	-

HOMO   **LUMO**
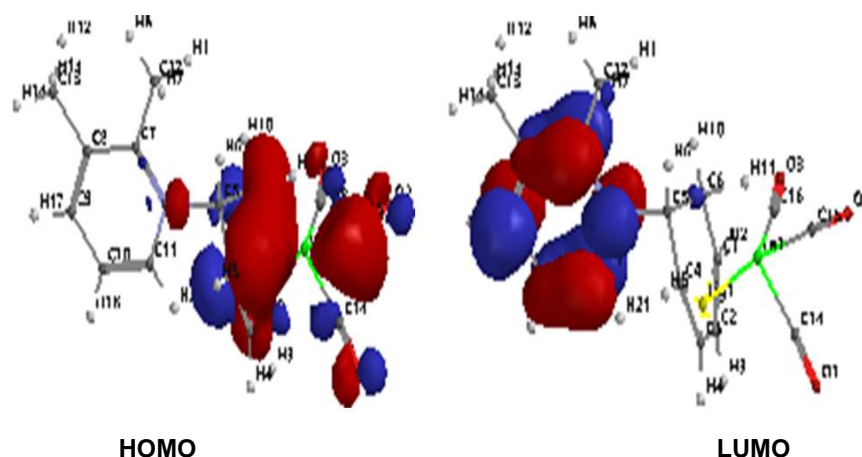
Fig. 3. HOMO and LUMO energy diagrams of X, X-dimethylpyridino derivatives of 1-4-η-cyclohexa-1,3-diene iron tricarbonyl complexes

Table 2. Electronic parameters for Tricarbonyl(1-4-η-5-exo-N-X,X dimethyl pyridino-cyclohexa-1,3-diene) iron complexes

Dimethyl group	Dipole moment/Debye	E_{HOMO}/eV	E_{LUMO}/eV	Band gap Eg/eV
2,3-	5.31	-11.79	-4.56	7.23
2,4-	5.61	-11.76	-4.40	7.36
2,5-	5.60	-11.78	-4.55	7.23
2,6-	5.36	-11.80	-4.46	7.34
3,4-	5.22	-11.76	-4.50	7.26
3,5-	5.20	-11.78	-4.57	7.21

2,3-Me$_2$ **2,4-Me$_2$**   **2,5-Me$_2$**   **2,6-Me$_2$**
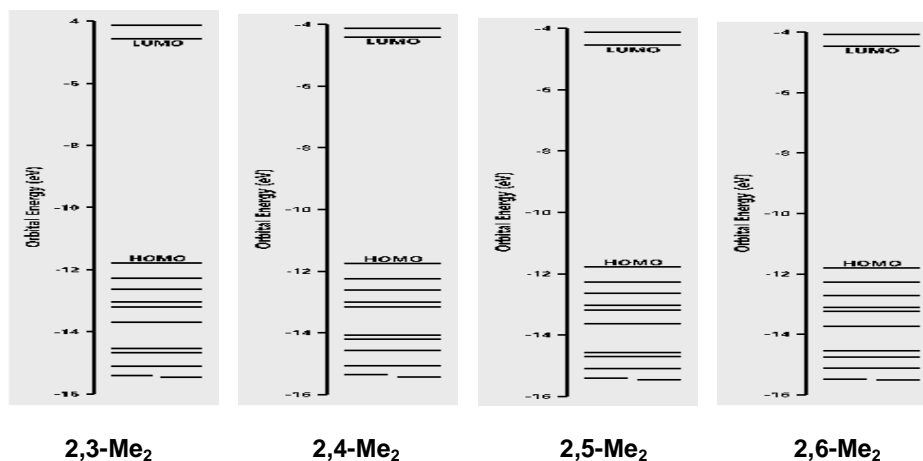
Fig. 4. Orbital energy diagrams of X, X-dimethylpyridino derivatives of 1,4-η-cyclohexa-1,3-diene iron tricarbonyl complexes
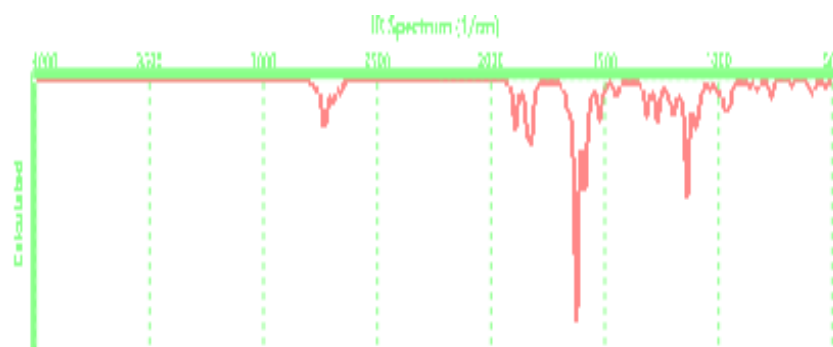
Fig. 5. Infra-red spectrum showing vibrational frequencies and intensities for Tricarbonyl(1-4-η 5-exo-N-X,X-dimethylyridino-cyclohexa-1,3-diene) iron complexes

3.3 Thermodynamics Parameters and Stabilities

The calculated thermodynamic parameters include the standard heat of formation, absolute enthalpy, free energy and absolute entropy for these complexes. Thermodynamic stabilities are expected when ΔH and ΔG values are negative thus indicating the spontaneity of the formation of the complexes. The more negative these values are and the more positive ΔS, the more stable would be the pyridino complexes. The free energy, heat of reaction and entropy are all positive. This implies that the formation of these complexes is not spontaneous hence their formation is accompanied by external effects. The thermodynamic parameters are displayed in Table 3.

Table 3. Thermodynamic parameters for Tricarbonyl(1-4-η-5-exo-N-X,X- dimethylyridino-cyclohexa-1,3-diene) iron complexes.at 298.15K

$X,X-Me_2$	Heat of formation H_f /kJmol^{-1}	Free energy G/ kJmol^{-1}	Entropy S/ Jmol^{-1}K^{-1}	Enthalpy H/ kJmol^{-1}
2,3-	160.81	734.86	545.99	897.62
2,4-	140.29	714.29	546.56	877.22
2,5-	151.71	726.05	546.33	888.91
2,6-	177.38	753.44	542.22	915.07
3,4-	146.09	720.08	548.14	883.47
3,5-	146.74	720.15	549.68	884.00

3.4 Vibrational Frequencies

The calculated vibrational frequencies for the Tricarbonyl(1-4-η-5-exo-N-X,X-dimethyl pyridine-cyclohexa-1,3-diene) iron complexes are shown in Fig. 5. According to group representation theory in chemistry, we are able to deduce that, there are 105 kinds of vibrational modes. The calculated Hessian matrices reveal that all optimized geometries are local minima with Modifying values for 37 low frequency terms for 2,3-Me$_2$, 2,4-Me$_2$, 2,5-Me$_2$ and 2,6-Me$_2$ while 3,4-Me$_2$ and 3,5-Me$_2$ show 36 and 38 low frequency values respectively, while the remaining frequency values correspond to normal vibrational mode thus indicating they are dynamically unstable.

4. CONCLUSION

The C1 symmetry point group Tricarbonyl (1-4-η-5-exo-N-X,X-dimethylyridino-cyclohexa-1,3-diene) iron complexes were calculated using Semi-empirical PM6. The properties investigated include optimized geometries, dipole moments, electronic structure, thermodynamic properties and vibrational frequencies. The PM6 method reveal that the formation of these complexes is not spontaneous and all the optimized geometries present modifying values of low frequency terms indicating that they are dynamically unstable.

The calculated energy band gaps Eg (HOMO-LUMO) present no appreciable change, in value however, the dipole moments changes. We have been able to take critical look at these complexes at the molecular level which may rather be difficult to accomplish under experimental conditions. Our results may therefore form the basis for reference for further experimental and theoretical work.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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