

**Computational and Analytical
Studies of Metal Complexes of the Schiff Base
(1R,2E)-1,2-di(furan-2-yl)-2-[(2-sulfanylphenyl)imino]ethanol**

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We report a combined experimental and computational study of metal complexes of the Schiff base of (1R,2E)-1,2-di(furan-2-yl)-2-[(2-sulfanylphenyl)imino]ethanol. The molecular structures and infrared spectra of Co, Ni, Cu and Zn complexes of schiff base ligand (1R,2E)-1,2-di(furan-2-yl)-2-[(2-sulfanylphenyl)imino]ethanol are studied in detail by molecular mechanics (MM+) and PM3 method. It has been shown that the proposed structures for the compounds derived from micro analytical, magnetic and various spectral data were consistent with the energy environment calculated by molecular mechanics (MM+) and semi empirical PM3 method. IR spectra simulated by PM3 method is also in accordance with experimental data. Coordination effects on $\nu(\text{C}=\text{N})$ modes in the Schiff base ligands are in close agreement with the observed results.

Key Words: Schiff bases, Metal complexes, IR Simulations, Molecular mechanics, Hyperchem.

INTRODUCTION

There is a general agreement that the theory of transition metal chemistry has lagged behind the quantum theory of organic chemistry because quantitative wave functions are more complicated¹. Although last decade witnessed the establishment of computational chemistry methods as a standard tool for the quantitative calculations of transition metal complexes. A good computational chemistry model is only as good as the parameters or theory upon which it is based².

Higher tendency for chelation, stability and diversity of the structure and specialty in applications in biological systems are the reasons for our interest in the Schiff base complexes of a ligand (1R,2E)-1,2-di(furan-2-yl)-2-[(2-sulfanylphenyl)imino]ethanol (FATP) (Fig. 1) (Schiff base obtained by the condensation of furoin with 2-amino thio phenol). Literature survey shows that Schiff base complexes derived from aminothiophenol are widely studied³⁻⁶, but no study have been reported towards the particular ligand and its complexes. It is known that the metal complexes are much more bioactive than the ligands⁷⁻¹⁰.

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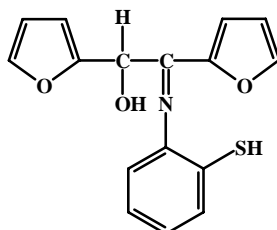


Fig. 1. Structure of (1R,2E)-1,2-di(furan-2-yl)-2-[(2-sulfanylphenyl)imino]ethanol (FATP)

A combined experimental and computational study of Schiff base complexes of FATP by molecular mechanics and semi-empirical methods are reported. The purpose of the present paper is to prove that MM+ and semi empirical calculations (PM3) are reliable methods to investigate the stability and structure as a confirmative approach to the experimental studies. Additional aim of this report results out semi-empirical calculations using the PM3 method to simulate infrared spectra of the title compounds.

EXPERIMENTAL

Preparation of furoin-2-aminothiophenol: An ethanolic solution of furoin (2.88 g, 0.015 mol) was mixed with a solution of 2-aminothiophenol (1.87 g, 0.015 mol) in hot ethanol and refluxed for 4 h on a water bath. The resulting solution was concentrated and cooled in an ice bath. The precipitate formed was collected through filtration using a vacuum pump and washed with ethanol and dried over anhydrous CaCl_2 (m.p. 115 °C).

Synthesis of complexes: Co(II), Ni(II), Cu(II) and Zn(II) complexes of FATP were prepared by mixing ethanolic solutions of metal acetate (0.005 mol), 2-amino thiophenol (0.005 mol) and furoin (0.005 mol) in the presence of sodium acetate (1 g). The resulting solution was refluxed for *ca.* 3-4 h, concentrated and kept overnight in an ice bath. The complex formed was filtered using a vacuum pump and washed with ethanol, chloroform and ether, dried in a desiccators over anhydrous calcium chloride. In the preparation of Cu(II) complex, sodium acetate was not added.

The molecular mechanics studies were carried out by (MM+) and semi-empirical calculations used to predict the stability of the complexes in different environments. We simulated IR spectra by PM3 methods. The simulation and computational methods we adopted was hyperchem 8.0¹¹. All the calculations refer to isolated molecules in vacuum.

RESULTS AND DISCUSSION

The ligand FATP and its complexes were characterized on the basis of elemental analysis and spectral data. The UV and IR spectra showed the characteristic bands. Molar conductivity and magnetic susceptibility value also support octahedral geometry. Based on the above results, the structure of the ligand FATP and its complexes were confirmed (Fig. 2).

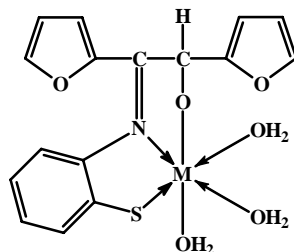


Fig. 2. Structure of metal complexes of (1R,2E)-1,2-di(furan-2-yl)-2-[(2-sulfanylphenyl)imino]ethanol; M = Co(II), Ni(II), Cu(II), Zn(II)

Stability of complexes by MM+ calculations: The energy environment in molecule can be predicted well in advance by computational chemistry tools. This prediction tool will become a great advantage for synthetic scientists. Generally transition metal complexes existing in tetrahedral, square planar or octahedral geometry. It is decided to simulate this three conventional structure to predict the synthetic feasibility of the coordination compounds in MM2 force field. The different stoichiometric ratios (6 coordinated and 4 coordinated were modelled by using hyperchem 8 GUI). All the molecular mechanics calculations were carried on Pentium IV 2.46 GHz with the MM+ force field. The search of the lowest energy conformations are performed by Monte Carlo methods. This method generated new confirmations with randomly varied torsion angle. Monte Carlo search used the temperature $T = 300$ to 400 K. The molecule obtained is minimized by using Polak-Ribiere optimizer. Energy minimization was terminated when the gradient root mean square was below 0.01 kcal/mol. After the minimization acceptance was determined by the following criteria 1) Execution of a conformational search by the simulated annealing method heat time - 0.1 ps, run time - 0.5 ps, cool time - 0.1 ps, starting temperature 100 K, simulation temperature 300 K, with a temperature step 30 K, which is described by Choe *et al.*⁹. The structure obtained was minimized with a semi-empirical method (PM3) and it is verified that there were no negative frequencies in the vibration spectrum. The data is given in Table-1.

First column of the table corresponds to the energy components obtained after energy minimization of 6 coordinated system. In the middle of the table, the single point energy value of a tetrahedrally coordinated complex modelled in GUI are reported. Table-1 clearly shows that octahedral geometry is energetically favoured over tetrahedral geometry in all cases. Structure obtained after MM+ minimization is given in Fig. 3 (Co complex) and Fig. 4 (Ni complex). This data strongly confirms the analytical results.

Stability of complexes by semi-empirical calculations: Semi-empirical method is another tool for the determination of stability of molecule by incorporating quantum mechanical parameters into the calculation. We used PM3 method for the semi-empirical calculation. The molecule constructed in the hyperchem GUI initially optimized by using MM+ force field and Polak-Ribiere optimizer¹², then PM3

TABLE-1
 VARIOUS COMPONENTS OF ENERGY AFTER MM+ MINIMIZATION

MM+ (kcal/mol)			
	Co six coordinate system (converged)	Co tetrahedral geometry (single point)	Co four coordinate system (converged)
Energy	67.93110	287.174000	98.618850
Bond	3.51599	120.082000	3.201910
Angle	49.65480	153.679000	91.108600
Dihedral	-6.21116	4.279810	0.127940
Vdw	18.14190	6.444690	3.341860
Stretch-bend	-0.24490	0.464145	-0.749599
Electrostatic	3.07457	2.223800	1.588170
	Ni six coordinate system (converged)	Ni tetrahedral geometry (single point)	Ni four coordinate system (converged)
Energy	55.330498	272.92720	81.179466
Bond	2.131900	108.26500	3.423260
Angle	37.251000	151.35700	67.806700
Dihedral	-3.371770	8.68938	2.616270
Vdw	14.468300	-0.91886	4.942420
Stretch-bend	-0.451447	2.07631	-0.257724
Electrostatic	5.302510	3.45840	2.648520
	Cu six coordinate system (converged)	Cu tetrahedral geometry (single point)	Cu four coordinate system (converged)
Energy	50.803123	269.207390	82.449661
Bond	1.911410	110.628000	3.573600
Angle	36.868100	145.501000	68.826000
Dihedral	-4.597500	5.505710	2.721660
Vdw	13.880500	5.586900	4.931190
Stretch-bend	-0.445664	-0.184451	-0.248667
Electrostatic	3.186320	2.169680	2.645880
	Zn six coordinate system (converged)	Zn tetrahedral geometry (single point)	Zn four coordinate system (converged)
Energy	46.73159	289.74520	88.11412
Bond	1.34338	106.20500	4.16389
Angle	36.10640	170.03000	73.54900
Dihedral	-3.57938	4.63397	2.08451
Vdw	10.21140	6.18490	5.82331
Stretch-bend	-0.32602	-0.27872	-0.22570
Electrostatic	2.97581	-	2.71915

method is applied on the molecule. We developed three set of compounds for the semi empirical study. One set is with an assumption that the molecular ratio is in octahedral geometry. Second set is the tetrahedrally coordinated molecule. Third set is for the optimization of 4 coordinated system to optimize by using PM3 method of calculation. The result of PM3 calculation is summarized in the Table-2. It is highly intriguing that all the factors which contribute to the total energy of the system is always in favour of octahedral geometry as expected in the analytical result and proved by MM+ calculations.

TABLE-2
VARIOUS COMPONENTS OF ENERGY AFTER PM3 MINIMIZATION

	Semi-empirical minimization (kcal/mol)		
	Co six coordinate system (converged)	Co tetrahedral geometry (single point)	Co four coordinate system (converged)
Total energy	-116736.0641	-101797.3409	-102028.7433
Binding energy	-4737.158273	-4047.896131	-4279.29853
Isolated atomic energy	-111998.9059	-97749.44477	-97749.44477
Electronic energy	-888453.9096	-729954.3718	-720669.8157
Core-core interaction	771717.8455	628157.0309	618641.0724
Gradient	0.0074437	84.561937	0.0070732
	Ni six coordinate system (converged)	Ni tetrahedral geometry (single point)	Ni four coordinate system (converged)
Total energy	-122516.4887	-107577.7245	-107828.155
Binding energy	-4652.132843	-3962.829706	-4213.260209
Isolated atomic energy	-117864.3559	-103614.8948	-103614.8948
Electronic energy	-894118.4088	-746386.7753	-722868.8199
Core-core interaction	771601.92	638809.0508	615040.6649
Gradient	0.010001	84.5094588	0.005975
	Cu six coordinate system (converged)	Cu tetrahedral geometry (single point)	Cu four coordinate system (converged)
Total energy	-125794.2973	-110916.1081	-111145.6504
Binding energy	-4519.56546	-3890.837314	-4120.379584
Isolated atomic energy	-121274.7319	-107025.2708	-107025.2708
Electronic energy	-913280.0895	-759640.4355	-736789.8227
Core-core interaction	787485.7921	648724.3273	625644.1723
Gradient	0.0094272	83.4601369	0.0097097
	Zn six coordinate system (converged)	Zn tetrahedral geometry (single point)	Zn four coordinate system (converged)
Total energy	-99010	-84188	-84376
Binding energy	-4311.8	-3739	-3927
Isolated atomic energy	-94698	-80449	-80449
Electronic energy	-742190	-633619	-606327
Core-core interaction	643180	549431	521951
Gradient	0.00708	81.0878	0.00538

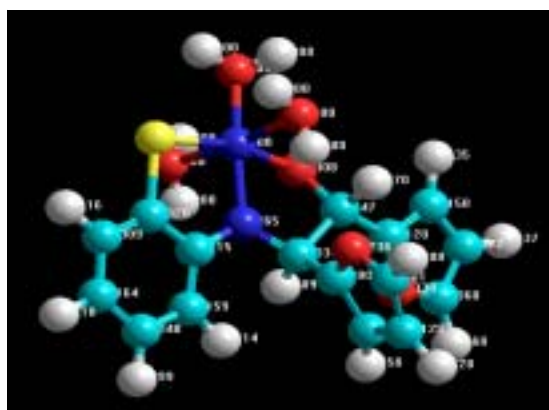


Fig. 3. Co complexes with octahedral geometry

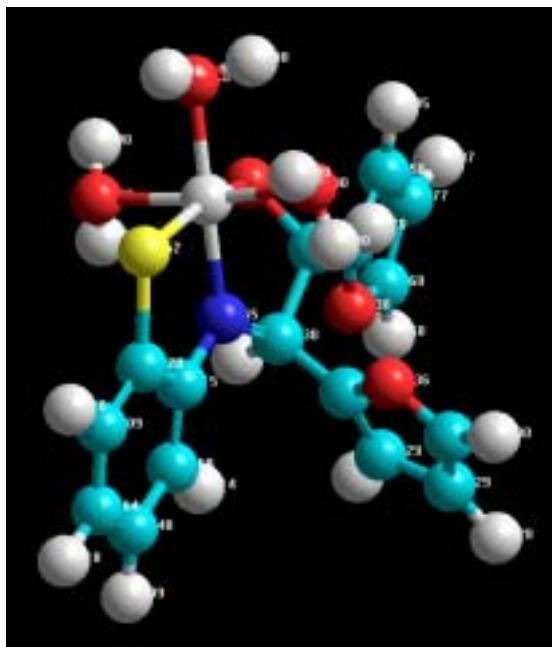


Fig. 4. Ni complexes with octahedral geometry

Correlation of chemical descriptors of ligands and complexes: We further studied the gradation of various components of energy of both ligand and complexes from Co to Zn. It is highly noticeable that there is high resemblance between gradations of properties of ligand and complexes and the data is given in Table-3.

TABLE-3
CORRELATION IN BEHAVIOUR OF CHEMICAL
DESCRIPTORS OF LIGANDS AND METAL COMPLEXES

Parameters	FATP	CoFATP	NiFATP	CuFATP	ZnFATP
Various chemical descriptors at 0 K					
Energy (kcal/mol)	-76605.21	-116736	-122516	-125794	-99010
Binding energies (kcal/mol)	-3761	-4736	-4652.13	-4529	-4311
Heat of formation (kcal/mol)	7.734	-477.2	-392.6	-282.1	-123.8
Electronic energy (kcal/mol)	-538337	-888487.4	-894118.43	-913286	-742238
Nuclear energy (kcal/mol)	461731	771751	771601	787492	643228
Dipole moment (debyes)	3.261	5.708	1.274	2.286	3.591
rms gradient (kcal/mol/ang)	0.0934	0.1954	0.091	0.081	0.089
Zero point vibration energies (kcal/mol)	158.2	201.33	203.14	202.95	202.95
Various energy chemical descriptors at 300 K					
Energies (kcal/mol)	-76435	-116520	-122298	-125577	-98796
Free energy (kcal/mol)	-76479	-116567	-122347	-125624	-98852
Entropy (kcal/mol/deg)	0.1483	0.158	0.1631	0.158	0.1841
Heat capacity (kcal/mol/deg)	0.07	0.089	0.091	0.089	0.097

PM3 IR simulation: The proposed structures of the samples were optimized and their IR spectra generated based on PM3 semi-empirical calculations using hyperchem 8.00. The assignment of the calculated wave numbers is aided by the animation option of same program, which gives a visual presentation of the shape of the vibrational modes.

Infrared spectra of ligand *viz.*, (1R,2E)-1,2-di(furan-2-yl)-2-[(2-sulfanylphenyl)imino]ethanol and complexes of Ni, Co, Cu and Zn are analyzed by FT IR. This experimental data is compared with computational values obtained by PM3 method and subsequent force matrix generation. The data summarized in the Table-4. We gave assignment of the most important infrared bands with the aim of detecting the coordination effects. The ligand FATP has some possible donor sites. According to the experimental study the $\nu(\text{C}=\text{N})$ is in the range of 1676 cm^{-1} , computational value is found to be 1859 cm^{-1} . This bands moved to lower wave numbers on coordination both in computational and experimental study. This conclusion was based on the fact that the coordination in the complex occurred through the azomethine nitrogen¹³. Computational frequency range of $\nu(\text{H}_2\text{O})$ was also compared. This values are analytically $3405, 3410, 3443, 3430\text{ cm}^{-1}$ and computationally $3627, 3731, 3691, 3728\text{ cm}^{-1}$ for Co, Ni, Cu, Zn, respectively. The correlation effect is in the range of 0.91 to 0.93. In addition, to that we compared the bands observed for $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{O})$ ^{14,15}. These values are also in good correlation.

TABLE-4
COMPARISON OF IR DATA (cm^{-1})

Substances	$\nu(\text{H}_2\text{O})$		$\nu(\text{C}=\text{N})$		$\nu(\text{M}-\text{N})$		$\nu(\text{M}-\text{O})$	
	PM3	Exp.	PM3	Exp.	PM3	Exp.	PM3	Exp.
Ligand FATP	–	–	1859	1676	–	–	–	–
Co(FATP) (H_2O) ₃	3627	3405	1381	1646	586	586	480	481
Ni(FATP) (H_2O) ₃	3731	3410	1760	1646	586	586	478	481
Cu(FATP) (H_2O) ₃	3691	3443	1714	1647	563	586	477	483
Zn(FATP) (H_2O) ₃	3728	3430	1735	1645	–	579	483	478

Conclusion

In support to analytical data the computational data confirms the octahedral geometry from MM+, semi empirical and IR analysis of metal complexes of (1R,2E)-1,2-di(furan-2-yl)-2-[(2-sulfanylphenyl)imino]ethanol.

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