Synthesis, characterization and quantum chemical investigation of iron(II) tris(1,10-phenanthroline complexes)

B.Semire, M.A.Olandipo*, I.O.Adeoye

Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Oyo State, (NIGERIA)
E-mail : semireban@yahoo.com, oladipomary@yahoo.com, adeoyeid@yahoo.com

ABSTRACT

Iron (II) complex of 1,10-Phananthroline was synthesized and isolated. The compound was characterized by microanalysis, magnetic susceptibility, Infrared and electronic spectra measurements. The room temperature magnetic moment of the complex suggests that it is a diamagnetic compound. Quantum chemical calculations at MM3 and PM3 of semi-empirical method show that bond lengths and bond angles are in good agreement with experimental results. However, there are some deviations, the largest deviations observed in bond lengths is 0.075(Å) while that of the bond angles is 4.99(Å) for PM3 calculations.
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KEYWORDS

INTRODUCTION

Metal complexes of 1,10-Phenanthroline has found wide application in coordination chemistry, industries and medicine, especially in DNA recognition and interaction[1-4]. Although many complexes of 1,10-Phenanthroline have been prepared and characterized[5], in this paper, we report the results of our investigation on the iron(II) complexes of 1,10-Phenanthroline using quantum chemical methods as compared with the experimental.

EXPERIMENTAL

The 1,10 phenanthroline monohydrate, solvents and other reagents were commercially available (B.D.H and Aldrich chemical Co.Inc), solvents were purified according to literature procedures[6].

Synthesis of the complex

3.00g (0.015moles) of 1,10-Phenanthroline monohydrate and 1.95g(0.005moles) ferrous ammonium sulphate hexahydrate were dissolved in $200cm^3$ distilled water. 5.00g of potassium cyanide in $5cm^3$ distilled water was added, the mixture was stirred for about 5 minutes and cooled to room temperature. The solution was aged for a few hours and isolated by suction filtration, washed in distilled water and dried over silica gel in a dessicator.

Physical measurements

The percentage iron of the complex was determined using complexometric titration. The melting point and decomposition temperatures of the compound were determined using the Gallenkamp melting point apparatus. The electronic spectra of the complex in methanol were measured on the Lamda 3B UV/Visible spectrophotometer between 190-900nm. The infrared spectra of the compound was recorded on a Pye-Unicam SP3-300 spectrophotometer using pressed KBr discs.

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The room temperature magnetic moment of the compound was taken using the Guoy method[7].

The computational methods

All calculations were performed utilizing MOPAC 2002 version 2.02[8] and Spartan 2.0.1 essential[9] at Molecular Mechanics(MM3) and Semi empirical(PM3) methods[10,11]. The molecular geometry resulting from MM3 optimization was used as starting points for full optimization at PM3, level of semi empirical method. The infrared intensities, atomic and molecular properties were also calculated at PM3 level.

RESULTS AND DISCUSSION

The compound displayed a shade of grey colour with melting point between 232-235°C. It is moderately soluble in ethanol and water but was sparingly soluble in chloroform (TABLE 1). The solubility appears to be related to the ability of the solvent to either associate through weak hydrogen bonding with the complex or to produce charged species of the complex by hydrogen ions donations[12].

Magnetic property

The effective magnetic moment (μeff) are expected to be in excess of the spin-only value due to spin orbit coupling and the mixing of excited T terms into the ground terms. The magnetic moment for the complex is 0.26BM(TABLE 1), factors such as impurities and uncertainties in diamagnetic corrections could account for this. Therefore, the magnetic moment of the complex is considered essentially equal to zero[12,13].

The visible absorption spectra of the complex consist of two main bands as studied in methanol(34,900 cm^{-1} and 17,970cm^{-1}). It suggests that the intense absorption bands in the visible region of the complex arise from excitation of a 3d electron to a level of the ligand. However, this is in agreement that charge transfer transition also occur in the same region as π-π*.

Three complexes of Iron(II) 1,10-Phenanthroline (A=Iron(II) tris(1,10-phenanthroline), B=3-Chloro-tris(1,10-phenanthroline), and C=3-Bromo-tris(1,10-phenanthroline)) were modeled. Infrared spectra calculated for the complexes at PM3 were compared to the Iron(II) tris(1,10-Phenanthroline complex synthe-

bands observed in the ultraviolet region of the complex was 32206cm^{-1} for π-π* transition. Upon chelation the

TABLE 1 : Magnetic moment, melting point and solubility in selected solvents

Solvent	Solubility
Ethanol	S
Methanol	S
Water	VS
Chloroform	SS
Magnetic moment (BM)	0.26
Melting point (^{0}C)	232-235

S =Soluble, VS = Very soluble, and SS = Sparingly soluble

TABLE 2: 1R infrared spectral of iron (II) Tris(1,10-Phenanthroline) complexes

Observed (cm^{-1})	Intensities	Calculated (PM3) (cm^{-1}) A B C			Assignment
3403.09vw	1.792	3130 3128-3089 2214	3130 3128-3056	3130 3128-3070	
2067.71s	1.086	3x 18082-1875	1885-1872	1885-1873	C = N
		1744	-	1747	C = C
		1665	1668, 1665	1665	
1632.70b	7.959	1606	1605	1606	
		1545	1553, 1545	1560, 1553, 1545	
1452.86	18.361	1482-1466	1484-1466	1484-1466	
1427.57	3.038	1424	-	-	
1408.11	6.423	1401	1400	1400, 1378	
1342.20	20.869	1322	1322	1335-1322,1303	
1297.82	20.316	1292	1292	1292,1265	βC=CH
1214.54	22.834	1233 1221	1229 1221	1230,1230 1222	βC=CH
1137.95	23.126	1135	-	-	βC=CH
-		1076, 1060	1073	1073	Ring breathe
912.33	38.613	901	933	1060	
-		893	899	899, 893	
845.07	2.142	858	879	878	γC – CH
800.00w	34.520	800	812, 800	812, 800	γC – CH
778.95	20.397	782	782	786, 783	
723.28vs	5.610	739	744	744	Ring stretch
639.97	14.534	642	640	641	
-		562	560	562	
-		460	466	466	
-		292	292	291	

A=Iron (II) tris(1,10-phenanthroline), B=3-Chloro-tris(1,10-phenanthroline, and C= -Bromo-tris(1,10-phenanthroline)

TABLE 3: Selected bond lengths and angles calculated by molecular mechanics(MM3) and semi-empirical methods (PM3) for Iron(II) phenanthroline complexes

Bond	Bond lengths (A°) and bond angles in degree		
	MM3 A,B,C	PM3	Exp[a]
C-C	1.395[a]	1.374[Aa,b,c]	1.37[a]
C=N	1.346[a]	1.345[a,b,c]	1.34[a]
Cl -C	1.602	- 1.660[B]	-
Br -C	1.781	- 1.85C	1.854
Fe-N₁	1.925	1.962[*A,B,C], 1.964[B]	1.960
Fe-N₂	1.925	1.981[A,B,C]	`1.982
Fe-N₃	1.925	1.981, 1.980[B,C]	1.982
Fe-N₄	1.926	1.960[A,C], 1.961[C]	1.940
Fe-N₅	1.925	1.972[A,B,C]	2.007
Fe-N₆	1.925	1.971[A,C], 1.970[B]	2.000
CL-C = C	121.674[B]	120.632[B]	-
Br-C = C	199.92[C]	119.85[C]	120.26
N₂-Fe-N₁	86.595	84.610[A,B,C]	83.74
N₂-Fe-N₃	173.908	175.461[A,C], 175.780[B]	175.60
N₂⁻ Fe-N₄	92.762	93.634[A,B,C]	95.90
N₂-Fe-N₄	87.756	84.972[A,B,C]	94.50
N₂-Fe-N₆	92.378	93.534[A], 93.681[B], 93.221[C]	92.10
N₁- Fe-N₃	92.545	90.661[A,C], 92.550[B]	93.71
N₁- Fe-N₄	87.995	95.451[A,B,C]	94.50
N₁- Fe-N₅	92.599	90.327[A,B,C]	91.60
N₁- Fe-N₆	178.695	177.211[A,B,C]	175.10
N₃- Fe-N₄	86.534	86.628[A], 86.501[B], 86.384[C]	86.90
N₃-Fe-N₅	92.957	92.603[A,B,C]	92.10
N₃-Fe-N₆	88.496	81.776[A,B,C]	82.30
N₄-Fe-N₅	179.235	178.29[A], 176.956[B], 176.232[C]	176.80
N₄-Fe-N₆	92.854	92.019[A,B,C]	91.40
N₅-Fe-N₆	86.560	87.226[A], 86.711[B], 87.794[C]	91.84

*J.C.Lyeong et al.[13] Ball Korean Chem. 80C; 233,399; a=average bond lengths; A=Iron(II) tris(1,10-phenanthroline), B=3-Chloro-tris(1,10-phenanthroline, and C=3Bromo-tris(1,10-phenanthroline)

sized in the present work. However, the geometries results at MM3 and PM3 were compared to Iron(II) 3-Bromo-tris(1,10-Phenanthroline complex synthesized and characterized by X-ray diffractometer[14].

The relevant IR bands are compared with calculated values as shown in TABLE 2. The differences in calculated IR form observed are as a result of calculations of level of calculation performed in gas phase. The

TABLE 5 : Selected calculated atomic charges for iron(II) phenanthroline complexes at PM3 of semi empirical method

Complex A								
Atom	N1	N2	N3	N4	N5	N6	Fe	Cl	Br
Electrostatic	0.472	0.459	0.468	0.444	0.479	0.466	-0.739	_	_
Mullikan	0.448	0.448	0.448	0.448	0.448	0.448	-0.748	_	_

Complex B								
Atom	N1	N2	N3	N4	N5	N6	Fe	Cl	Br
Electrostatic	0.475	0.449	0.402	0.405	0.463	0.509	-0.688	0.062	_
Mullikan	0.433	0.453	0.450	0.450	0.450	0.450	-0.747	0.219	_

Complex C								
Atom	N1	N2	N3	N4	N5	N6	Fe	Cl	Br
Electrostatic	0.743	0.632	0.581	0.564	0.659	0.570	-1.262	_	0.167
Mullikan	0.454	0.449	0.448	0.448	0.449	0.449	-0.748	_	0.148

A=Iron(II) tris(1,10-phenanthroline), B=3-Chloro-tris(1,10-phenanthroline, and C=3-Bromo-tris(1,10-phenanthroline)

ligand experienced a bathochromic shift and a single broad band of 34904cm⁻¹(3129cm⁻¹ as calculated) was observed for the complex.

The experimentally determined bond lengths and bond angles[14] of C are compared with the values obtained from MM3 and PM3 calculations as presented in TABLE 3. There are good agreement between the experimental and calculated values; especially PM3 results are closer to the experimental result than that of MM3[14]. Largest derivations from experimental results in bond lengths and bond angles are 0.064(Å) and 2.66(Å) respectively for PM3 calculations. That of MM3 deviated by 0.075(Å) and 4.98(Å for bond lengths and bond angles respectively. The Molecular Mechanics calculated bond lengths and angles for the three complexes(i.e. complex A, complex B and complex C) were the same, however at PM3 level of calculations, bond lengths and angles for complex A and C were in agreement. Complex B showed a considerable deviation (TABLE 3). The calculated energies band gaps for the complex A, B and C are 7.64, 7.37 and 7.54 respectively, as reflected in the value of dipole moments for the three complexes(TABLE 4). The symmetry point group for the complex A is C3 and C1 for both complex B and C.

The Millikan and electrostatic charges calculated revealed that halides substitutents affect charges on Iron

TABLE 4 : Energies calculated for Iron(II) phenanthroline complexes at PM3 of semi empirical method (298.15⁰k and 1atm)

Molecules	E_TOTAL (Kcal/mol)	E_HOMO(eV)	E_LUMO(eV)	Ethalpy (ΔH,J/mol)	ΔS (J/mol)	ΔG (J/mol)	Piont group	Dipole (Debye)
A	111.60	-14.27	-6.63	1494.16	722.13	1278.86	C3	0.007
B	107.09	-14.04	-6.67	1472.53	759.18	1246.18	C1	0.18
C	122.94	-14.22	-6.68	1471.75	770.26	1242.10	C1	0.17
Phenanthroline	71.60	-9.15	-0.84	473.32	392.72	356.23	C2v	2.99

A=Iron(II) tris(1,10-phenanthroline), B=3-Chloro-tris(1,10-phenanthroline, and C=3-Bromo-tris(1,10-phenanthroline)

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(TABLE 5). The unique properties of complex B could be due to electronegative nature of the Chlorine atom as it affected the complex B through bonded electrons[15]. The dipole moment and atomic charges distribution in the complexes especially on Iron also agreed with dia-magnetic nature of the complexes.

CONCLUSION

The infrared and electronic spectra data of the complex synthesized indicate excitation of the 3d electron to the ligand, therefore $d\pi$ - $p\pi$ back bonding is suspected in the complex moiety. The solubility of the complex in ethanol and water show that there is formation of Hydrogen bonding with polar solvents. The calculated parameters are in good agreement with the experimental, which can serve as complementary, or supplementary data. The unique properties of complex B show the effect of electro negativity of Chlorine atom as it affected molecular properties through bonded electrons. The dipole moment and atomic charges distribution in the complexes especially on Iron also agreed with diamagnetic nature of the complexes

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