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Synthesis and Characterization of Iron Complexes with Bidentate Ketoanils

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ABSTRACT: Nine complexes of iron (III) chloride, bromide, iodide, nitrate, and acetate with two bidentate ligands, 3-hyroxyanil of 2-hydroxyphenylglyoxal and 2-pyridine anil of acetylglyoxal, have been synthesized and characterized by their elemental analysis, magnetic measurements, and infrared, electronic and electronic spin resonance spectroscopy. Based on magneto- spectral studies all the complexes were assigned octahedral geometry.

Key words: Ketoanils, magnetic moment, electronic spin resonance, ligand field parameters

I. INTRODUCTION

Schiff's bases obtained by condensation of aldehydes , ketones or glyoxals with primary amines , are preponderant over variety of other organics owing to their multifarious roles in diverse disciplines, viz. in chemistry as starting materials in the synthesis of heterocycles [1-4], as novel ligands in forming complexes of unusual stereochemistries [5-6] and isomeric structures [5,6] and as analytical reagents [8,9], in industries as dyes [10], in medical science as bacterecide, fungicide, anticancer, antimalarial, antitubercolosis, analgesic etc. agents [11-13] and in agriculture as herbicides [14].

The enhanced biological properties of metal-based organic compounds [14-16] observed generally and novel ligation properties of Schiff's bases aroused our interest to synthesize and characterize coordination complexes of chloride ,bromide , iodide , nitrate and acetate salts of iron (III) with 3-hydroxy anil of 2-hydroxyphenylglyoxal (HAHPG) and 2-pyridine anil of acetylglyoxal (PAAG) bidentate (ON) ligands by elemental analysis, magnetic measurements, and IR, ESR and electronic spectra and report in the present communication.

II. EXPERIMENTAL

Synthesis of ligands: Both ligands, HAHPG and PAAG, were synthesized by the common method in two steps (Scheme1). 2- Hydroxy phenyl glyoxal and acetyl glyoxal prepared by oxidation of 2-hydroxy acetophenone and diacetyl with selenium dioxide respectively in alcohol by reported methods [18,19] were mixed in equimolar quantities with 2-aminophenol and 2-aminopyridine respectively in alcohol and reaction mixtures were evaporated on water bath. The residue of HAHPG was washed with ice cold alcohol and benzene successively whereas residue of PAAG was washed with ether. Both the products were dried in hot air oven at 60˚C.

$$\text{RCOCH}_3 \xrightarrow{[O]} \text{RCOCHO} + \text{H}_2\text{O}$$

SeO_2/EtOH
I

$$\text{RCOCHO}+\text{H}_2\text{N-R}' \xrightarrow[\text{II}]{\text{EtOH}} \text{RCOCH=N-R}' + \text{H}_2\text{O}$$

Where, $R=C_6H_4(OH)$-or CH_3CO- and $R' = C_6H_4(OH)$-or C_5H_4N

Synthesis of complexes: All the complexes of HAHPG with Fe (III) salts were prepared by mixing warm saturated solution of ligand with saturated solution of each of the metal salts in stoichiometric quantities in acetone or acetone- H_2O-HCl (9:1.5**:** 0.5,v/v) and the reaction mixtures were evaporated to dryness on water bath after refluxing for 1h. Residues were washed with water and filtered. Water insoluble residues of bromo, iodo, and nitro complexes were finally washed with alcohol and alcohol –carbontetrachloride (5:2, v/v) successively and dried in oven at -65˚C. Filtrates containing chloro and acetato complexes were evaporated to dryness on water bath and residues were washed with acetone-benzene-methanol(4:3:4,v/v) and ether solvents successively as identified by TLC to recover the products; the Fe(III)-PAAG complex precipitated while mixing the reactants in acetone was washed with acetone and dried in oven. All the complexes are non-hygroscopic and fairly stable in air. All chemicals used in the synthetic work were BDH/E. Mark laboratory reagents whereas in TLC work BDH solvents were used after their distillation.

Analysis and physical measurements: Carbon, hydrogen and nitrogen contents of the samples were estimated microanalytically at RSIC, Punjab University , Chandigarh. Infrared spectra were recorded in 4000-400cm^{-1} range on Bruker IFS-66 VFT-IR spectrometer in KBR discs. Magnetic susceptibility measurements were performed on the vibrating sample magnetometer model-155 at RSIC, I.I.T Madras in magnetic field 6 KGauss at room temperature. Electron spin resonance spectra were recorded on EPR, E-4 spectrometer operating at 9.410 GH_z -9.475 GH_z frequency at room temperature at R.S.I.C, I.I.T Madras; value of Lande's splitting factors, $g_{av,}$ g_{11} and $g_{1,}$ have been calculated from known equations .Reflectance spectra of the complexes were recorded at R.S.I.C, Punjab University, Chandigarh.

III. RESULTS AND DISCUSSION

Proposed molecular formulae of the complexes are consistent with their elemental analysis data. In order to identify coordinating sites of the ligands in their corresponding complexes IR spectra of free ligands were compared with that of complexes. Selected vibrational bands of the ligands and their complexes are listed in table 1. A sharp band at 1660cm^{-1} in the spectrum of HAHPG of CH=N stretch appeared at 1596-1616 cm^{-1} in its complexes .The lowering in frequency of CH=N group of ligand on complexation and appearance of a new weak band in 420-480 cm^{-1} region in complex spectra assigned to ν Fe-N vibration [20,21] clearly shows coordination of azomethine nitrogen with the metal .The displacement of aromatic ν C=C band(s) of ligand from 1585 cm^{-1} to 1440-1510 cm^{-1}in the complexes could be attributed [22] to the change of benzenoid (orthophenolic) to quinonoid (enolic) structure. The presence of phenolic group peak of ligand (3650cm^{-1}) in the complexes in 3360-3650cm^{-1}region is the strong evidence of non-participation of meta substituted phenolic group of other benzene ring . A strong band at 1230cm^{-1} in free ligand has been assigned [23] to enolic C-O stretch. Upon complexation this band displaced to higher frequency (1300-1390cm^{-1}) indicating coordination of enolic oxygen of quinonoid structure. A new band at 475-565 cm^{-1} attributed to ν Fe-O supports the coordination of enolic oxygen.

In the spectrum of PAAG two bands occurring at 1618 cm^{-1}and 1682 cm^{-1} corresponding to acyclic CH=N stretching and cyclic CH=N stretching respectively observed at 1575 cm^{-1}and 1666 cm^{-1}in the complex. The shifting of both these peaks to lower frequencies obviously indicates coordination of azomethine and pyridine nitrogen with Fe(III). A new broad band at 475 cm^{-1} in complex spectrum attributable to ν Fe-N supports the coordination of azomethine and pyridine nitrogen; the broad peak structure could be due to mixing of two closely spaced peaks of Fe-N bonds of both donor nitrogens.

Lattice water [24] displayed symmetric and antisymmetric stretching vibrations in 3200-3399cm^{-1} region in all the complexes whereas symmetric and antisymmetric bending vibrations seemed to be mixed with CH=N (azomethine) and C=C (aromatic) stretching bands. Coordinated water exhibited twisting, wagging or rocking vibrations in 800-990cm^{-1} range; ν Fe-OH$_2$ are generally mixed with ν Fe-N peaks as revealed by their broad peak structures.

The infrared spectra of nitrato complexes generally display six bands due to ν (NO$_2$) symmetric, ν (N-O), δ(NO$_2$) symmetric, ν (NO$_2$) asymmetric, δ(NO$_2$) asymmetric and ρ_r(NO$_2$) asymmetric out –of-plane vibrations; two pairs of bands resulting by combination of ν (NO$_2$) symmetric and δ(NO$_2$) symmetric, and by ν (NO$_2$) symmetric and ν (NO$_2$) asymmetric are also observed. Absorption spectrum of nitrato complex displayed four bands at 1280cm^{-1} 1060cm^{-1}, 1470cm^{1} and 850cm^{-1}corresponding to ν (NO$_2$) symmetric, ν (NO), ν (NO$_2$) asymmetric and ρr(NO$_{2)}$ asymmetric out-of-plane, respectively, only out of the expected six bands. But spectrum exhibited two pairs of combination bands at 1700cm^{-1} and 1725cm^{-1} and 2330cm^{-1} and 2426cm^{-1}; the energy separation of the first two and last two of these bands is 25cm^{-1}and 96cm^{-1}. These results lead us to propose [24] monoligancy of nitrate ion through nitrogen. The peak of Fe-N stretch seem to be mixed with azomethine nitrogen - iron stretching band as this band has broad doublet structure.

In both iron(III) acetato complexes the separation of asymmetric and symmetric ν C-O bands observed at 1600cm^{-1} and 1452cm^{-1}, and 1600cm^{-1} and 1470cm^{-1} either similar (148cm^{-1}) or higher (170cm^{-1}) than that exits in the free acetate ion (153cm^{-1}) [24] indicates monoligancy of acetate ion. The characteristic ν Fe-O band occurs at 480cm^{-1}or mixed with enolic ν Fe-O doublet band at 565cm^{-1}.

The diamagnetism exhibited by nitrato and isomeric aquo complexes of HAHPG characteristic of low-spin d^6 configuration , owes to the reduction of Fe(III) to Fe(II) by transfer of electron from deprotonated enolic group of ligand whereas pairing of electrons is subjected to strong field of ligand around Fe (II).In chloro, bromo, iodo and acetato complexes the reducing effect of the ligand is completely neutralized by oxidising character of the anionic ligands and magnetic moments of these complexes in between 0.96-1.84 BM are characteristic of spin-paired d^{5}configuration of metal in them. However lower values of μ_{eff} in these complexes than spin-only value (1.73BM) could be attributed to antiferro magnetic interaction in them. The magnetic moment of 1.92BM of PAAG complex is consistent with spin-paired d^5 configuration.

In the e.s.r spectra of nitrato and aquo isomeric HAHPG complexes absence of any signal, indicating their diamagnetic nature, coroborates magnetic results. The μ_{eff} values calculated from g_{av} values, revealing low-spin d^{5}configuration of Fe(III) in chloro, bromo, iodo and acetato complexes of HAHPG are in conformity with the inference derived from magnetic measurements. The small difference in g_{11} and g_1 values reveals negligible distortion in the octahedral geometry of bromo, iodo, and acetato complexes whereas considerable difference in the Lande’s splitting parameters indicate tetragonal or trigonal ligand field component either less than or comparable to the spin-orbit constant and symmetry of ligand field must be as low as rhombic in chloro complexes of HAHPG and PAAG.

Table 1:

				Analysis% Calc.(found)			I.R bands (cm^{-1})									
S no.	**Compound**	**Colour**	**M.P ˚C**	C	H	N	**νCH=N Acyclic**	**νCH=N Cyclic**	**νC=C Aromatic**	**νOH Phenolic**	**νC-O phenolic enolic**	**νM-O**	**νM-N**	**νH_2 O symetric+asymetric**	**ρ_r $H_2O\rho_w$ $H_2O\rho_tH_2O$**	**Frequency of Anionic ligands**
1	HAHPG	-	0	-	-	-	1660sh	-	1585	3650	1230	-	-	-	-	-
2	$[Fe_2(HAHPG)Cl_5(H_2O)_3]2H_2O$	Black Brown	>300	27.13(27.46)	3.23(2.89)	2.26(2.18)	1616	-	1490	-	1330,1415	475sh	420br	3330br	8,40,970	-
3	$[Fe(HAHPG)_2Br(H_2O)]H_2O$	Brown	>300	51.14(51.19)	3.68(3.46)	4.30(4.29)	1596	-	1470,1440	3360	1300	530	450br	3350d	808	-
4	$[Fe(HAHPG)_2I(H_2O)]H_2O$	yellow Brown	>300	48.08(47.62)	3.43(3.59)	4.01(4.34)	1600	-	1485d	3660	1330,1290	530	480br	3285br	8,35,990	-
5	$[Fe(HAHPG)(NO_3)(H_2O)_3]$	Black Brown	>300	40.79(40.87)	3.89(3.66)	6.79(6.65)	1600	-	1495,1470	3375br,d	1378	520	450br,’d	-	850br,980sh	1280,850br,1060sh,1470,1725 1700,2330,2426(NO_3)
6	$[Fe((HAHPG)_2(H_2O)_2]2H_2O$	Black	>300	55.27(55.55)	4.61(4.53)	4.61(4.92)	1600	-	1470	3460br	1325	520	475br	3200	850	-
7	$[Fe((HAHPG)_2(H_2O)_2]2H_2O$	Light Brown	>300	55.27(55.26)	4.61(4.32)	4.61(4.73)	1610	-	1482,1454	3371br	1384,1328	555	474br	3371br	8,77,834	-
8	$[Fe_2(HAHPG)Ac_5(H_2O)_5]$	Chocolate	>300	39.07(40.21)	4.75(4.33)	1.89(2.07)	1600	-	1452	3375br	1330	565d	474br	3375br	830	1600,1452(vc=o)
9	$[Fe_2(HAHPG)_3Ac_3(H_2O)_3]$	Brown	>300	54.19(55.42)	4.23(3.92)	3.95(4.30)	1600	-	1510,1455	3650	1390d,1295	480,515	430, 467	3365	850	16001470(vc=o)
10	PAAG	-	-	-	-	-	1618br	1682	1496	-	-	-	-	-	-	-
11	$[Fe_2(PAAG)Cl_6(H_2o)_2]$	Brown	~260	20.12(20.29)	2.23(1.82)	5.22(5.21)	1575	1666	1487	-	-	-	475br	-	900	-

Table 2

			ESR spectral parameters				Ligand field bands and parameters				
									Racah's Parameter		
S.NO	Compound	μ_{eff} (BM) 6 KH_z	g_{11}	g_1	g_{av}	μ_{eff} Calc From ESR	Ligand field bands (cm^{-1})	10 Dq cm^{-1}	B	C	Nephlauxetric Ratio β
1	$[Fe_2(HAHPG)Cl_5(H_2O)_3]2H_2O$	1.47	1.84	1.52	1.74	1.50	21053 $^2T_{2g} \rightarrow {}^2A_{1g}$	21053	752	3384	0.58
2	$[Fe(HAHPG)_2BrH_2O]H_2O$	1.58	1.71	1.76	1.73	1.49	20833 $^2T_{2g} \rightarrow {}^2A_{1g}$	20833	744	3348	0.57
3	$[Fe(HAHPG)_2I\ H_2O]H_2O$	1.02	1.8	1.74	1.78	1.54	19608 $^2T_{2g} \rightarrow {}^2A_{1g}$	19608	700	3150	0.54
4	$[Fe(HAHPG)NO_3(H_2O)_3]$	Dia	—	—	—	No Singal	20833(ν_1) $^1A_{1g} \rightarrow {}^1T_{1g}$ 31746(ν_2) $^1A_{1g} \rightarrow {}^1T_{2g}$	21920	548	2247	0.52
5	$[Fe(HAHPG)_2(H_2O)_2]2H_2O$	Dia	—	—	—	No Singal	20833(ν_1) $^1A_{1g} \rightarrow {}^1T_{1g}$ 31250(ν_2) $^1A_{1g} \rightarrow {}^1T_{2g}$	21920	548	2247	0.52
6	$[Fe(HAHPG)_2(H_2O)_2]2H_2O$	Dia	—	—	—	No Singal	21053(ν_1) $^1A_{1g} \rightarrow {}^1T_{1g}$ 29411(ν_2) $^1A_{1g} \rightarrow {}^1T_{2g}$	22160	554	2271	0.52
7	$[Fe_2(HAHPG)Ac_5(H_2O)_5]$	1.87	1.7	1.74	1.71	1.48	21277 $^2T_{2g} \rightarrow {}^2A_{1g}$	21277	760	3420	0.58
8	$[Fe_2(HAHPG)_3Ac_3(H_2O)_3]$	1.19	1.78	1.74	1.76	1.52	21277 $^2T_{2g} \rightarrow {}^2A_{1g}$	21277	760	3420	0.58
9	$[Fe_2(PAAG)Cl_6(H_20)_2]$	1.84	1.84	1.74	1.76	1.52	21053 $^2T_{2g} \rightarrow {}^2A_{1g}$	21053	752	3384	0.58

Two ligand field bands displayed in the electronic spectra of nitrato and aquo complexes of HAHPG in 2083-21053cm^{-1} and 29411-31746cm^{-1} regions, characteristic of spin paired d^6 Fe(II) octahedral stereochemistry, are attributed to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions respectively [25] whereas other complexes displayed only one ligand field band in 19608 - 21277cm^{-1} range corresponding to $^2T_{2g} \rightarrow {}^2A_{1g}$ transition of d^5 spin paired Fe(III) octahedral geometry. Ligand field parameters calculated using reported eqations [25] are noted in Table 2. Besides ligand field bands several ligand to metal charge transfer bands have also been identified in 34965-47170cm^{-1} region of spectra of all the complexes.

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