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Synthesis and Characterization of Some Novel Complexes of Iron(III) with Ketoanil Schiff Base

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The present communication is related to investigate structure of newly developed molecular models prepared by the interaction of a typical ketoanil Schiff's base, *p*-phenyldianil of 2-thiophene glyoxal (PDATG) with Fe(III) salts. Stoichiometries of the complexes have been established from the data of their analysis. For the identification of modes of coordination and to investigate structural change in ligand during interaction with metal ions, infrared data of ligand have been compared with those of complexes. Absorption spectra falling in the visible range have been studied in conjugation with ligand field theory. Different values of g, $g_{\parallel}$ and $g_{\perp}$ have been calculated at room temperature and liquid nitrogen temperature from ESR spectrum of each sample.

Key Words: Ketoanil schiff base, Fe(III) salts.

INTRODUCTION

Schiff bases derived from aniline and its derivatives and aromatic aldehyde derivatives have a wide variety of applications in many fields, *e.g.*, biological[1,2] and analytical chemistry[3]. It is well known from the literature that much work have been done on the synthesis and characterization of these compounds[4,5]. The present work deals with the synthesis and characterization of complexes of Fe(III) salts with *para*-phenyldianil of 2-thiophene glyoxal (PDATG).

EXPERIMENTAL

Chemicals used in the synthesis were laboratory grade B.D.H. or S.M. products. Infrared spectra of ketoanil *para*-phenyldianil of 2-thiophene glyoxal (PDATG) and its complexes were recorded in the range 4000-250 cm^{-1} in Nujol mull medium on Perkin Elmer-580 spectrophotometer using CsBr optics at micro analytical laboratories, University of Roorkee, Roorkee. The electronic spectra of the complexes were recorded at room temperature (24 ºC) on Bausch and Lomb Spectronic-20 spectrophotometer. For each sample ESR measurements were performed at room temperature and at liquid nitrogen temperature in Regional Sophisticated Instrumentation Centre Indian Institute of Technology, Madras. The magnetic field and microwave frequency calibrations were made using powered DPPH calibrant. Instrument used was EPR E-4 spectrometer operating at 9.5 GHz-10.0 GHz, modulation and phase sensitive detections.

Synthesis of *p*-phenyldianil of 2-thiophene glyoxal (PDATG)

Preparation of 2-thiophene glyoxal: It was obtained by the oxidation of 2-acetyl thiophene with an equimolar amount of selenium dioxide in acetic acid-alcohol (3:2, v/v) by refluxing for 2 h. The resultant solution was poured into hot water and the solution was then boiled under reflux for 0.5 h. On cooling dark brown viscous glyoxal settled in the bottom of the flask. It was dissolved in alcohol and crystallized.

Synthesis of Schiff base: Solutions of *p*-phenyldiamine and 2-thiophene glyoxal containing equimolar quantities (glyoxal in slight excess) in chloroform, when mixed together showed a sharp and deep colour change from light orange to dark brown indicating the formation of a new compound. The reaction mixture was then concentrated on water bath and dried in air at 45 ºC. Solid obtained was repeatedly washed with ether to remove unreacted glyoxal, if any. The product was purified by recrystallization from acetone. Elemental analysis (%): Calcd. (Found): C 61.01 (61.36); H 3.46 (3.41); N 8.12 (7.96).

Synthesis of complexes: *p*-Phenyldianil of 2-thiophene glyoxal (PDATG) was dissolved in acetone whereas metal salt solutions were prepared in acetone or in its mixture with alcohol or water. On mixing the reactant solutions in appropriate proportions (PDATG in excess), complexes of Fe(III) were precipitated from the reaction mixture and the precipitates were washed with acetone and ether, respectively till free from unreacted ligand. Final products were dried in hot air oven at *ca.* 50 ºC and collected in air tight tubes.

RESULTS AND DISCUSSION

The molecular formulae deduced from analytical data are recorded in Table-1. The comparison of infrared data of ligand with those of complexes was made in order to investigate structural change in ligand, if any, during complexation with ions and to identify coordination seats. Although all infrared frequencies of PDATG have been subjected to shifted, those corresponding to carbonyl and azomethine groups of ligand are subjected to highest perturbation on complexation; medium

TABLE-1
ANALYTICAL RESULTS OF COMPLEXES

Complex	m.w.	Elemental analysis (%)					
		Carbon		Hydrogen		Nitrogen	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
$Fe_2(PDATG)Cl_4\cdot 4H_2O$	678.0	31.85	32.25	2.95	3.00	4.13	4.39
$Fe_2(PDATG)Br_4\cdot 4H_2O$	856.0	25.23	25.39	2.34	2.76	3.27	3.60
$Fe(PDATG)I\cdot 8H_2O$	680.0	31.76	31.55	4.12	3.86	4.12	3.68
$Fe_2(PDATG)(SO_4)_2\cdot 11H_2O$	854.0	25.29	25.39	3.98	3.99	3.28	3.20
$Fe_2(PDATG)_2(CNS)_2$	932.0	48.93	48.65	2.58	2.68	9.01	9.01
$Fe_2(PDATG)_2(NO_3)_2$	940.0	45.96	46.18	2.55	2.60	8.94	9.14
$Fe_2(PDATG)(CH_3COO)\cdot 2H_2O$	503.0	47.71	48.00	3.18	3.19	5.57	5.43

PDATG = *p*-Phenyldianil of 2-thiophene glyoxal intensity doublet band corresponding to 1:4 disubstitution observed at 830 cm^{-1} in ligand, is little disturbed in its frequency value but peak structure is changed from doublet to singlet invariably in all the iron(III) complexes. Lowering in the carbonyl and azomethine group frequencies may be accounted for considering their participation in complexation. However, shifting in frequency corresponding to 1:4 disubstitution could be attributed to some structural change in ligand during complexation possibly benzenoid to quinonoid and this may be substantiated by change in frequency of benzene ring breathing. Participation of carbonyl and azomethine groups in coordination is confirmed by the new bands appeared in the regions 600-400 cm^{-1} and 430-310 cm^{-1} corresponding to metal-oxygen and metal-nitrogen bonds, respectively (Table-2).

TABLE-2
ANALYTICAL AND SPECTRAL DATA

Compound	Key IR bands (cm^{-1})			1:4 Di-substitution	ν(Fe-O)	ν(Fe-N)
	Carbonyl	Azomethine	Thienyl			
$Fe_2(PDATG)Cl_4·4H_2O$	1610	1610	660	830	545,530	400
$Fe_2(PDATG)Br_4·4H_2O$	1640	1620	660	830	500	400
$Fe(PDATG)(SO_4)_2·11H_2O$	1620	1620	660	820	490	310
$Fe_2(PDATG)_2(CNS)_2$	1700	1625	660,520	825	400	390
$Fe_2(PDATG)_2(NO_3)_2$	1630	1630	–	820	505	430
$Fe_2(PDATG)(CH_3COO)·2H_2O$	1620	1570	650	–	600,490	320

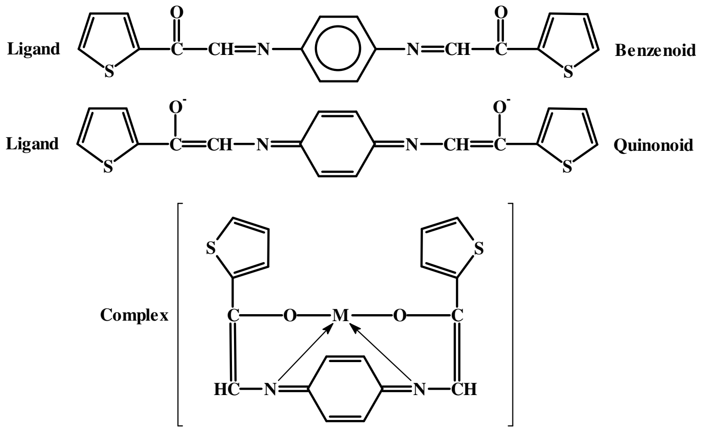
PDATG = *p*-Phenyldianil of 2-thiophene glyoxal

In halogeno complexes bridging metal-halogen bands could not be identified except that of Fe-Cl-Fe as frequencies of such vibrations is below 250 cm^{-1} whereas terminal metal-halogen vibrations except Fe-I occuring above 250 cm^{-1} have been identified with certainty.

The sulphato complex of Fe(III) shows bands at 1130, 1120, 1055, 985, 660 and 600 cm^{-1}. These bands are assigned[6,7] to coordinated sulphate group. The free sulphate ion has a regular tetrahedral structure belonging to the point group T_d. When it functions as a unidentate ligand the coordinated oxygen is no longer symmetrically equivalent to the other three and the effective symmetry is lowered to C_{3v}. In the complexes where sulphate ion functions as a bidentate bridge[4], its effective symmetry is reduced to C_{2v} and has at least two characteristic vibrations at 1055 and 995 cm^{-1}. In the present complex these vibrations are occurring at 1055 and 985 cm^{-1} indicating bidentate bridging coordination of sulphate ion with Fe(III).

The thiocynato complex has bands at 2045, 520 and 825 cm^{-1} which may be assigned[5] to C-N stretching (ν_1), N-C-S bending (ν_2) and C-S stretching (ν_3), respectively. Metal-sulphur stretching frequency is observed at 260 cm^{-1}. Perusal of these characteristic bands of thiocyanato group in this complex leads to the inference that thiocyanato group coordinates[8] with the metal through its nitrogen as well as sulphur atoms. The infrared spectrum of nitrato complex has bands at 1380, 1015 and 820 cm^{-1} which could be assigned[4] to NO_2 asymmetric stretching, N-O stretching and out-of-plane N-O rocking, respectively. All the three bands are resembling to those exhibited by nitro group functioning as bidentate bridging ligand. In the acetato Fe(III) complex, two bands observed were at 1620 and 1430 cm^{-1} which can be assigned[4,6,9] to ν(COO) asymmetric and ν(COO) symmetric vibrations, respectively. The separation of two stretching frequencies (190 cm^{-1}) is characteristic[8] of the bidentate bridging coordination of acetate ion.

These studies reveal that PDATG has offered its carbonyl oxygen and azomethine nitrogen atoms for coordination with metal ions and thienyl sulphur atom has been prevented from complexation. Prevention of sulphur from coordination may be attributed to its lower electron donating ability than carbonyl oxygen and azomethine nitrogen atoms and its greater distance from carbonyl oxygen than that between oxygen and nitrogen which, most probably, is due to the free rotation of thiophen ring attached with chain carbon through a single bond. Higher frequencies of metal-oxygen bond than metal-nitrogen bond in the complexes confirm the quinonoid form of ligand in complexes. On the basis of infrared spectral studies, the mechanism of complex formation may be shown as under:



(where M is bivalent metal having 4 coordination number)

Absorption spectral bands of Fe(III) complexes could be best fitted in accordance with Tanabe-Sugano predictions[10] to different spin allowed transitions from the ground state $^6A_{1g}$. These spin allowed transitions are consistent with the fact that in high spin d^5 octahedral configuration spin forbidden transitions are never possible. Various ligand field parameters, *viz*., 10 Dq, B and C, β and LFSE for each of the complexes have been calculated (Table-3). In all the Fe (III) complexes ligand field of PDATG is constant and the variation in the values of ligand field parameters could be attributed to the varying fields of anionic ligands, *viz*., Cl^-, Br^-, I^-, SO_4^{2-} and CNS^-. Perusal of 10 Dq and β values leads to an inference that strengths of the anionic ligands and covalent character of the complexes are in the following order of the ligands present in the coordination sphere.

$$I^- < Br^- < Cl^- < CNS^- < SO_4^{2-}$$

TABLE-3
d-d BANDS AND LIGAND FIELD PARAMETERS

Complex	Band frequency (cm^{-1})	Assignment	10 Dq (cm^{-1})	Racah's parameters (cm^{-1})	Naphelauxetic ratio (β)
Fe(III)-Cl-PDATG	16667 d	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$	7639	B = 694.5	0.5340
	19231				
	20408	$^4T_{2g}$ (G) $\leftarrow$			
	21978	^4E_g (G) $\leftarrow$			
	22472	$^4A_{1g}$ (G) $\leftarrow$			
	23256	$^4T_{2g}$ (D) $\leftarrow$			
	25316 sh	^4E_g (D) $\leftarrow$			
	27778 sh	$^4T_{1g}$ (P) $\leftarrow$			
Fe(III)-Br-PDATG	16393 t	$^4T_{1g}$ (G) $\leftarrow {}^6A_{1g}$	7514	B = 683.0	0.525
	17241 d				
	19417 d	$^4T_{2g}$ (G) $\leftarrow$			
	21055	^4E_g (G) $\leftarrow$			
	21505	$^4T_{1g}$ (G) $\leftarrow$			
	22472	$^4T_{2g}$ (D) $\leftarrow$			
	22988	^4T_g (D) $\leftarrow$			
	26774	$^4T_{1g}$ (P) $\leftarrow$			
Fe(III)-I-PDATG	16129 d	$^4T_{1g}$ (G) $\leftarrow {}^6A_{1g}$	7393	B = 672.0	0.5171
	18182				
	18692	$^4T_{2g}$ (G) $\leftarrow$			
	21053	^4E_g (G) $\leftarrow$			
	21739	$^4A_{1g}$ (G) $\leftarrow$			
	22988				
	23810	$^4T_{2g}$ (D) $\leftarrow$			
	26316	^4E_g (D) $\leftarrow$			
Fe(III)-(SO$_4$)-PDATG	18182 d	$^4T_{1g}$ (G) $\leftarrow {}^6A_{1g}$	8333	B = 757.6	0.582
	19417 d	$^4T_{2g}$ (G) $\leftarrow$			
	22727 d	^4T_g (G) $\leftarrow$			
	23256	$^4T_{1g}$ (G) $\leftarrow$			
	24691	$^4T_{2g}$ (D) $\leftarrow$			
	25641 sh				
	26667	^4E_g (D) $\leftarrow$			
	27778 sh				
Fe(III)-(CNS)-PDATG	16667 t	$^4T_{1g}$ (G) $\leftarrow {}^6A_{1g}$	7639	B = 694.5	0.534
	17699 d	$^4T_{2g}$ (G) $\leftarrow$			
	20619	^4E_g (G) $\leftarrow$			
	21277	$^4A_{1g}$ (G) $\leftarrow$			
	22988	$^4T_{2g}$ (D) $\leftarrow$			
	25316	^4E_g (D) $\leftarrow$			
	27397	$^4T_{1g}$ (P) $\leftarrow$			
	28169	$^4A_{2g}$ (F) $\leftarrow$			

Perusal of g, $g_{||}$ and $g_{\perp}$ values calculated at different temperatures from the ESR spectra recorded at room temperature and liquid air temperature reveals octahedral geometries (Table-4).

TABLE-4
VALUES OF g, $g_{||}$ AND $g_{\perp}$ FROM ESR SPECTRA AT RT AND LNT

Complex	g		$g_{\parallel}$		$g_{\perp}$	
	RT	LNT	RT	LNT	RT	LNT
Fe(III)-Cl-PDATG	2.023	1.993	1.821	–	2.360	–
Fe(III)-Br-PDATG	2.089	2.017	1.885	1.990	2.581	2.014
Fe(III)-I-PDATG	1.862	2.016	1.913	1.992	2.227	2.008
Fe(III)-SO_4-PDATG	1.815	1.979	1.892	2.023	2.178	1.989
Fe(III)-CNS-PDATG	1.999	1.979	2.061	2.023	2.974	1.993
Fe(III)-NO_3-PDATG	1.920	2.017	1.886	2.005	1.897	2.001
Fe(III)-CH_3COO-PDATG	1.853	1.983	1.819	1.931	2.510	2.002

RT = Room temperature, LNT = Liquid nitrogen temperature.

Considerable difference in room temperature data of $g_{||}$ and $g_{\perp}$ indicates the possibility of resonance at low temperature in all Fe(III) complexes. These results also indicate a tetragonal or trigonal ligand field component of magnitude either less than or comparable to the spin orbit coupling constant. The symmetry of the ligand field component must be as low as rhombic in all the compounds. These inferences are confirmed by the fact that all liquid nitrogen temperature $g_{||}$ and $g_{\perp}$ values are almost the same and g value is approximately isotropic in each sample. It is most likely to arrange all the Fe(III) complexes with respect to the difference in $g_{||}$ and $g_{\perp}$ values at room temperature to know the relative distortions in their cubic symmetry, Fe(III)-CNS-PDATG has the highest stereochemical distortion.

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