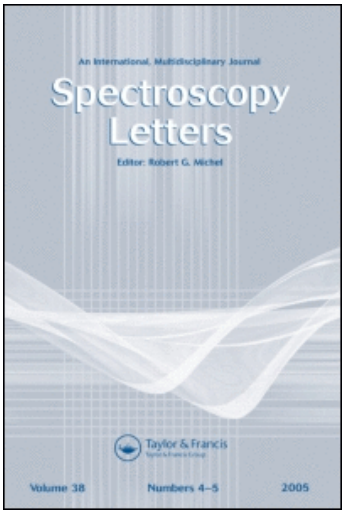

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Stereochemistry of New Nitrogen Containing Heterocyclic Aldehydes. II. Novel Bis-Bidentate Azodye Compounds

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To cite this Article El-bindary, Ashraf A. and El-sonbati, Adel Z.(1999) 'Stereochemistry of New Nitrogen Containing Heterocyclic Aldehydes. II. Novel Bis-Bidentate Azodye Compounds', Spectroscopy Letters, 32: 4, 581 — 600
To link to this Article: DOI: 10.1080/00387019909350008
URL: http://dx.doi.org/10.1080/00387019909350008

SPECTROSCOPY LETTERS, 32(4), 581–600 (1999)

Stereochemistry of New Nitrogen Containing Heterocyclic Aldehydes. II. Novel Bis-Bidentate Azodye Compounds

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ABSTRACT

A novel family of chelating bis-bidentate azodye compounds[1] with Cu(II), Co(II), Ni(II), Fe(II), Hg(II), Pd(II), UO_2(II), Fe(III), Cr(III), La(III), Ru(III) and Zr(IV) has been prepared and characterized on the basis of analytical, magnetic, ^1H and ^{13}C NMR, EPR and electronic spectral studies. Tentative structures for the polymeric complexes are proposed. The important IR bands and the main ^1H and ^{13}C signals are assigned and discussed relative to the molecular structure. Various EPR parameters for Cu(II), have been calculated. The ligand acts as a dibasic bis-bidentate chelating agent coordinating through CO, N=N, COOH and OH groups by replacement of a proton from the two latter groups. Considerable interest has also been focused on the synthesis of the azo compound and its polymeric metal complex due to its wide potential applications. The thermal decomposition behavior of the complexes is also discussed.

[1] System name: [5-(2-Carboxyphenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde]

INTRODUCTION

In continuation of our theoretical and practical interest in the synthesis and study of new families of complexes with quinoline derivatives, much interest has been given to the synthesis of novel chelating bis-bidentate azodye models.

Because there is a limited number of reports concerning the reaction of bis-bidentate azo compounds with d-and/or f-block elements. Only El-Sonbati has investigated the complexes of 8-hydroxy-7-quinolinecarboxaldehyde (oxine) and its Schiff bases[1-4].

El-Sonbati and El-Bindary were the first who prepared 5-(2-carboxyphenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde (LH_2) and isolated its solid polymeric complexes with metal halides in various oxidation states.

The synthesized complexes of this type of ligand which has many potential donor sites, exhibit biological activity and industrial importance. Hence, the reaction of the above ligand with several metal ions may lead to the preparation of binuclear complexes with interesting chemical and physical properties. Ultimately these studies are related to the rational design and synthesis of new metal-containing agents with anticancer activity[1]. In certain instances the complexing product with Pd(II) has an agent with more activity than that of the ligand only.

EXPERIMENTAL

All metal salts and organic materials were reagent grade products. 8-hydroxy-7-quinolinecarboxaldehyde (oxine) was prepared according to the method of El-Sonbati[1-4].

Preparation of the Novel Azo Compound

2-carboxyaniline (1.4 g, 10 mmoles) dissolved in hydrochloric acid (20 mmoles/25 mL distilled H_2O). The hydrochloric compound was diazotized below -5 °C with a solution of sodium nitrite (0.8 g, 10 mmoles/30 mL distilled H_2O). The diazonium chloride was coupled with an alkaline solution of oxine (1.7 g, 10 mmoles).

The crude dye was collected by filtration and was crystallized from dimethylformamide, then dried in a vacuum desiccator over P_2O_5. Yield (≅ 1.6 g) 65 %; m.p. 290 °C; pink (MW. 321). (Found: C, 63.6, H, 3.4, N, 13.1. Calcd. for $C_{17}H_{11}N_3O_4$: C, 63.8; H, 3.3; N, 12.9 %). The purity was checked by elemental analysis and IR spectra. The ^1H NMR spectrum shows characteristic bands at δ = 3.4, 7.1 and 8.9 ppm for carboxy group, phenyl protons and two hydroxy protons, respectively.

Preparation of the Metal Complexes

All the metal complexes in this work were prepared using a 1 : 1 metal salts : ligand molar ratio following a general method. Hot solutions of anhydrous metal salts (10 mmoles), in EtOH (30 mL) and a solutions of the required amount of 5-(2-carboxyphenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde (LH_2) (0.8 g, 2.5 mmoles) in EtOH (30 mL), were stirred at room temperature and then maintained at reflux temperature on a water bath for 3 h. The products were filtered, washed with EtOH, Et_2O and dried in vacuo to give the polymeric complexes as powder. Yield in Table 1.

C, H, and N were determined by the standard micromethods in the microanalytical unit of Mansoura University, Egypt and the metal contents of the complexes were estimated by standard methods[5,6]. The other measurements were carried out as reported earlier[7,8].

RESULTS AND DISCUSSION

The compounds prepared are listed in Table 1, together with the analytical data. The presence of coordinated water was confirmed by TG data where loss in weight corresponding to one water molecule for compound (3), and two water molecules for compound (1), (2) and (7) occurs at 280 °C. No coordinated water molecules were found in compounds (4) - (6) and (8) - (13).

Infrared Spectra

A partial assignment of the absorption bands observed for LH_2 and the metal complexes is given in Table 2. 5-(2-Carboxyphenyldiazo)-8-hydroxy-7-

Table 1. Analytical and Magnetic Moment Data for Complexes Derived from LH_2

	Complexes[a]	Found (Calcd.) (%)					μeff.[b]	Yield
		C	H	N	Metal	H_2O/Cl	(B.M.)	(%)
(1)	$[CuL.{}_2OH_2]_n^c$ $C_{16}H_{13}N_3O_6Cu$	50.0 (49.7)	3.0 (3.1)	10.3 (10.0)	15.0 (15.2)	9.0 (8.6)	1.92	58
(2)	$[CoL.2OH_2]_n^c$ $C_{16}H_{13}N_3O_6Co$	49.1 (49.3)	3.2 (3.1)	10.3 (10.2)	14.4 (14.2)	9.0 (8.7)	4.82	62
(3)	$[FeL.2OH_2]_n^c$ $C_{16}H_{13}N_3O_6Fe$	50.0 (49.7)	3.0 (3.2)	10.0 (10.2)	14.0 (13.6)	9.1 (8.8)	5.10	65
(4)	$[NiL]_n$ $C_{16}H_9N_3O_4Ni$	54.2 (54.0)	2.6 (2.4)	11.0 (11.1)	15.5 (15.6)	-	1.87	55
(5)	$[FeL.Cl]_n^d.OH_2$ $C_{16}H_{11}N_3O_5ClFe$	50.0 (49.7)	2.2 (2.2)	10.4 (10.2)	14.0 (14.3)	8.9 (8.7)	2.62	67
(6)	$[CrL.Cl]_n.OH_2$ $C_{16}H_{11}N_3O_5ClCr$	50.1 (50.2)	2.1 (2.2)	10.0 (10.3)	13.0 (12.8)	9.0 (8.7)	3.89	53
(7)	$[ZnL.2OH_2]_n^c$ $C_{16}H_{13}N_3O_6Zn$	48.3 (48.5)	3.0 (3.1)	10.2 (10.0)	16.0 (15.6)	8.9 (8.6)	dia.	68
(8)	$[PdL]_n$ $C_{16}H_9N_3O_4Pd$	49.8 (50.0)	2.0 (2.1)	10.0 (9.9)	24.8 (25.1)	-	dia.	60
(9)	$[UO_2L]_n$ $C_{16}H_9N_3O_6U$	34.7 (34.6)	1.5 (1.5)	7.0 (7.1)	41.0 (40.4)	-	dia.	55
(10)	$[HgL]_n$ $C_{16}H_9N_3O_4Hg$	39.1 (39.2)	2.2 (2.1)	7.9 (8.1)	-	-	dia.	64
(11)	$[ZrL.Cl_2]_n.OH_2.EtOH$ $C_{18}H_{17}N_3O_6Cl_2Zr$	37.5 (37.5)	1.9 (1.8)	7.6 (7.7)	16.4 (16.7)	13.2 (13.0)	dia.	54
(12)	$[RuL.Cl.EtOH]_n.EtOH$ $C_{20}H_{21}N_3O_5ClRu$	41.6 (41.6)	3.2 (2.9)	7.8 (7.7)	18.8 (18.5)	6.7 (6.5)	1.13	50
(13)	$[LaL.(O_2NO)]_n.OH_2$ $C_{16}H_{11}N_4O_8La$	37.9 (37.8)	2.0 (1.9)	10.2 (10.4)	26.2 (25.9)	-	dia.	45

(Cont. Table 1.)

L is the anion of LH_2

[a] Air-stable, insoluble in H_2O and common organic solvents, were confirmed by spot test technique, its characteristic odour and fumes with NH_4OH solution.

[b] Per metal ion and measured at room temperature.

[c] The stoichiometry of the complexes obtained after drying at 110°C shows the presence of water molecules. On heating the complexes at 160°C, the mass loss corresponding to the loss of the water molecules present. The anhydrous residual mass in each case, which was subjected to elemental analysis, corresponded to the stoichiometry $(ML)_n$, which confirmed that the water molecules were present in the coordinated form; the presence of coordinated water was confirmed by TG data where the loss in weight corresponded to one or two water molecules.

[d] The magnetic moment is 2.62 B.M. which may seem anomalous; the $\mu_{eff.}$ value is too small for high-spin (S = 5/2) or too large for low-spin (S= 1/2) iron(III) complexes. For iron(III) compounds of intermediate spin (S = 3/2), the expected $\mu_{eff.}$ value is ca. 4.00 B.M. The intermediate value observed here can result from; (i) anti-ferromagnetic types of interactions assuming a trimeric structure, (ii) a spin equilibrium between low and high-spin stated and (iii) a quantum mechanical mixing of spin states[5]. A trinuclear structure does not fit with the analytical data and hence must be discarded. There is, then, the possibility of the second and third alternatives. But for the third, the spin-admixed system usually occurs between quarter and sextet states. The moment 2.62 B.M. is low for such a system. The second alternative, that a spin equilibrium exists between low and high-spin states, is more appropriate. Equilibria of the type (S = 1/2) (S = 5/2) are well characterized for several iron(III) compounds[24].

[e] Lower than the value expected for one unpaired electron. This might be either due to the high values of spin-orbit coupling constraints in the heavier transition elements which often lead to very low magnetic moments or metal-metal interaction or extensive electron delocalisation[25].

Table 2. Characterstic IR Bands (cm^{-1}) and Thermal Data of LH_2 and its Complexes

Species[a]	ν(C-O) phenolic	ν(C=O) carbonyl	ν(N=N) azo	Coordinated H_2O molecule	Stab. range TG °C	Temp. Peaks °C DTA	DTG
LH_2[b]	1340	1710	1540				
(1)	1350	1695	1530	3460, 825, 700	235	150 exo, 250 endo	270
						265 exo, 450 exo	462
(2)	1353	1690	1525	3390, 830, 705	245	160 exo, 270 endo	290
						280 exo, 470 exo	481
(3)	1360	1693	1530	3355, 835, 715	250	155 exo, 280 endo	269
						301 exo, 530 exo	540
(4)	1358	1696	1520		240	245 endo, 250 exo	267
						500 exo	510
(5)	1365	1700	1535		260	230 endo, 255 exo	256
						520 exo	530
(6)	1367	1685	1525		225	225 endo, 245 exo	266
						510 exo	520
(7)	1355	1705	1532	3320, 832, 708	255	205 exo, 240 endo	255
						250 exo, 540 exo	562
(8)	1365	1690	1528		270	270 endo, 290 exo	640
						630 exo	
(9)[c]	1368	1700	1530		280	260 endo, 285 exo	240
						610 exo	615
(10)	1365	1698	1532		230	236 endo, 258 exo	240
						410 exo	395
(11)	1364	1695	1534		225	225 endo, 245 exo	236
						400 exo	395
(12)[d]	1360	1690	1530		225	150 exo, 200 exo	305
						320 endo, 670 exo	660
(13)	1378	1680	1480		230	170 exo, 290 exo	280
						230 exo, 570 exo	550

(Cont. Table 2).

[a] See Table 1.

[b] νOH phenolic 3400, νOH stretching 3030, νOH deformation 930, νC=O stretching 1660, νCOO symmetric stretching 1395 cm^{-1}.

[c] $F_{UO} = 6.912$ (mdyn/A°), $r_{UO} = 1.736$ (A°).

[d] The peaks at 885, 1055, 1105, 1270 and 1930 cm^{-1} are due to ethanol since they all appear in the spectrum of neat ethanol[26].

for the complexes : (1) 230; (3) 245; (4) 260; (5) 250;
(6) 280; (7) 310; (8) 340; (9) 330; (10) 290;
(11) 300; (12) 350 and (13) 210 cm^{-1}.

quinolinecarboxaldehyde (Fig.1) possesses five potential donor sites: (i) carboxylate oxygen; (ii) azo nitrogen atom; (iii) carbonyl oxygen atom; (iv) phenolic oxygen and (v) nitrogen pyridine. Due to the 1,2-position of these donor groups in the molecule, six-membered chelate ring formation is possible on complexing (Fig. 2).

The spectrum of the ligand shows a broad band centered to ν(OH)(1400 cm^{-1})[8] (intramolecular hydrogen bonded). There are other bands ν(N=N)(1540), ν(C=O)(carbonyl group)(1710) and ν(C=N)(quinoline ring)(1540 cm^{-1})[1-4,9]. The broadness of the OH stretching band at 3030 cm^{-1} and the out-of-plane OH deformation band at 930 cm^{-1} in the ligand is indicative of a hydrogen bonded carboxylic acid group.

The strong band observed at 1660 cm^{-1} in the free ligand is assigned to the carbonyl stretch of the carboxylic acid group[2,10]. Ionization of the carboxylic acid results in equilibration of the two C-O bands of the carboxylate group and disappearance of the characteristic carbonyl absorption. Two new bands are generated in the ranges (symmetric) 1620 -1555 and (asymmetric) 1440 - 1310 cm^{-1} due to vibrations of the COO^- structure[11]. This points to the probable existence of a Zwitter ion as in the structure of Fig. 3.

Further proof to the azo moity is the appearance of two bands 1405(C-N) and 1260(C-O) cm^{-1}. In all the complexes the strong carbonyl band disappears and is replaced by a

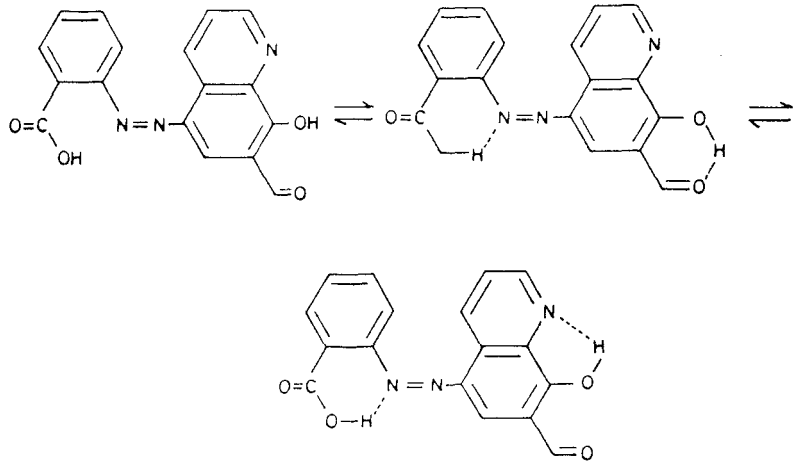

Fig. 1: Structure of the ligand

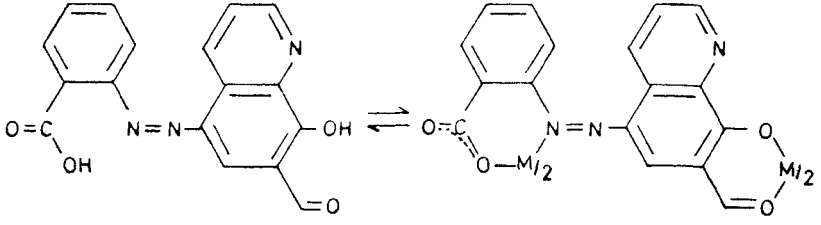

Fig. 2: Structure of Metalchelates

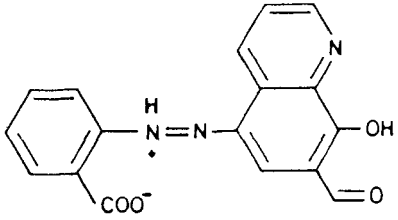

Fig. 3: Ionization of the Carboxylic acid and existance of a Zwitter Ion

strong and broad absorption at 1395 ±± 5 cm^{-1} which is assigned to the symmetric vibration of the carboxylate group[12].

The difference between ν_{asym} COO and ν_{sym} COO (ν) can be regarded as a measure of the type of M-COO bond. If $\Delta\nu > 225$ cm^{-1} it is mainly ionic. The ν value for LH_2 is 265 cm^{-1}, confirming the covalent character of the -COOH group. $\Delta\nu$ Values are larger than 225 cm^{-1} for all the complexes, indicating a covalent bond, except for compound (13) (see footnote, Table 2).

The absence of both the O-H stretch and deformation absorption bands and the replacement of the C=O vibration by a band assigned to the carboxylate group in the spectra of the metal complexes is indicative of the metal attachment as an anionic ligand via the carboxylate oxygen atom.

Also, in all the complexes the 3400 cm^{-1} band disappeared. However, a broad band characteristic band of νOH of coordinated water is observed in the 3500 - 3200 cm^{-1} region in the spectra of the complexes[13] (1) - (3) and (7). The presence of coordinated water is further confirmed by the appearance of a non-ligand band in the 830 - 740 cm^{-1} region assignable to a rocking mode of water[9]. Also, the complex does not lose weight on heating at 110 °C for one hour, so water or ethanol is coordinated. In compound (12) the presence of a new band at 970 - 1010 cm^{-1} due to ν(C-O) stretch indicates ethanol coordination, the ν(C-O) in ethanol occurs[1,14] at 1034 cm^{-1}. The absence of νOH(phenolic) at 3400 cm^{-1} in the spectra of the metal complexes support the cleavage of intramolecularly hydrogen bonded[1-4] OH and subsequent deprotonation of the phenolic group and confirmed by shifts to higher frequency in ν (C-O)(phenolic) by 20 - 30 cm^{-1}. A shift to lower frequency of ν(C=O) and ν(-N=N-) in the spectra of the complexes reveals their involvement in complex formation. A bathochromic shift of the -N=N- band located at 1540 cm^{-1} in the free ligand, is observed on complexation (1535 - 1520 cm^{-1}). As the strength the metal-carboxy bond decreases that of the metal-azo link increases, leading to lower ν(-N=N-). The spectrum of compound (11) does not show any bands due to Zr=O or Zr-O-Zr stretch indicating the absence of these groups. Two bands due to ν(Zr-N) in the complex suggests that the azo compound occu-position.

The medium intensity band around 440 cm^{-1} is due to the (Zr-O) vibration. The observed constancy in the frequencies of these bands shows that the coordination number six has been maintained in the complex. The azo compound favors the cis-position in the complex whereas the chlorine atoms occupy trans-position.

The IR spectrum of complex (13) shows two strong absorptions at ~ 1475 (ν_4) and 1290 cm^{-1} (ν_1) due to the coordinated C_2v nitrate group. The magnitude of $\nu_4 - \nu_1$ is 180 cm^{-1} indicating that the nitrate group is coordinated in a bidentate position[4]. No change is observed in νC=N of the quinoline ring, indicating non-involvement in coordination.

Magnetochemical and Ligand Field Spectral Studies

The experimental magnetic moments of the complexes are listed in Table 1. The values obtained for the complexes (1) - (6) and (12) are paramagnetic while the rest are diamagnetic. The values for (1), (6) and (12) are 1.92, 2.89 and 1.31 B.M., respectively; the value for complex (5) indicates a low-spin complex while complexes (2) and (3) are high-spin. The observed value for complex (4) lies between those expected for low-spin and high-spin[14], which may be due to an equilibrium between these states.

The electronic spectra of the complexes are summarized in Table 3 together with the proposed assignment and suggested geometries. The results obtained are in good agreement with other spectra and the literature.

The electronic spectrum of the ligand showed two absorption bands in the visible region at ~ 25000 and ~ 21750 - 20830 cm^{-1} due to azohydrazone tautomerism (Fig.4), well-known in such systems[15]. The lower wave length band must be assigned to the $\Pi - \Pi^*$ transition of the azo form since all compounds in which the -OH group is methylated or complexed exist only in the azo form and show a single intense absorption at ~25000 cm^{-1}. The ~21750 - 20830 cm^{-1} band must, therefore, be attributed to the hydrazone form in agreement with the earlier observation that the hydrazone form generally absorbs at a longer wave length[16].

In the o-carboxy compound, intramolecular H-bonding as shown in Fig. 4 is possible. Esterification of the -COOH group is then expected to result in a large hypsochromic

shift of the absorption maximum because the Π^*-level will certainly be lower in energy in the H-bonded form due to a shift of the electron density from the N-atom towards the H-atom[17]. Thus, the observed hypsochromic shifts are consistent with intramolecular H-bonding. Such bonding is not favored in the corresponding hydrazone which, consequently, is much less stable in the free acid. Because of this the free acid shows only a single absorption peak corresponding to the azo form.

EPR Studies of the Copper(II) Complex

The EPR spectrum of compound (1) with $g_{\parallel} > g_{\perp} > 2.0023$ (free electron spin) characteristic of a tetragonally distorted octahedral geometry with $d_{x^2-y^2}$ orbital lowest in energy. Various parameters have been calculated by the method of approximation suggested by Knebuhl[18] and Garmen[19] and the values are given in Table 4. The $g_{\parallel}$ and $g_{\perp}$ values obtained in this compound suggest that the principal axes of the octahedral are parallel to each other and all the sites are equivalent in every orientation in the static magnetic field. The $g_{\parallel}$ obtained for compound (1) is less than 2.3 indicating covalent character of the metal-ligand band[3]. Further, the value is consistent with the mixed Cu-N and Cu-O bonded copper complex. The axial symmetry parameter (G) for the compound (1) is found to be greater than 4 (Table 4). The calculated g_{av}. is in agreement with an orbitally non-degenerate state[5,6]. The trend $g_{\parallel} > g_{\perp} > g_e$ (free ion spin value) indicates the presence of an unpaired electron in d_{x2-y2} orbital.

Approximate metal-ligand σ-bond coefficients (α^2), which are defined as the fraction of unpaired electron density located on the copper ion, for this sample under study was calculated, neglecting the Π-bonding, with the help of the optical absorption data in the solid state using the relation

$$g_{av} = 2.0023 - \lambda\alpha^2/\Delta E,$$

where $\lambda = -828$ cm^{-1}. The α^2 value (Table 4) for compound (1) indicate considerable covalency in the bonding between Cu(II) ion and the ligand, comparable to that obtained

Table 3. Electronic Spectral Data of the Complexes Together with the Assignments and the Proposed Geometries.

Species[ab]	Band Position (cm^{-1})	Assignments	Geometry	Ref.
(1)	15385	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral	9
	25100	CT		
(2)[c]	9000	$^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1)	Octahedral	7
	18000	$^4T_{1g} \rightarrow {}^4T_{1g}$ (P) (ν_2)		
(3)	11220	$^5A_{2g} \rightarrow {}^5E_g$	Octahedral	9
(4)	14650	$^3A_{2g} \rightarrow {}^1E_g$	Distorted-	7
	16830	$^3A_{2g} \rightarrow {}^3T_{1g}$	octahedral	
	20988	$^3A_{2g} \rightarrow {}^1T_{1g}$		
	25870	$^3A_{2g} \rightarrow {}^1T_{1g}$ (P)		
	31700	CT		
	33900			
(5)[d]	14952	$^6A_{1g} \rightarrow {}^4T_{1g}$	Pseudo- octahedral	5
	25560	$^6A_{1g} \rightarrow {}^4E_g$		
	31280	CT		
(6)	15140	$^4A_{2g} \rightarrow {}^2T_{2g}$	Pseudo- octahedral	24
	21880	$^4A_{2g} \rightarrow {}^4T_{2g}$		
	25150	$^4A_{2g} \rightarrow {}^4T_{1g}$		
	33380	CT		
(8)	16999	$^1A_{1g} \rightarrow {}^1A_{2g}$	Square-Planer	7
	28100	$^1A_{1g} \rightarrow {}^1B_{1g}$		
	30800	$^1A_{1g} \rightarrow {}^1E_g$		
(9)	23700	$^1E_g^* \rightarrow {}^3\pi_u$		
(12)	17510	$^2T_{2g} \rightarrow {}^2A_{2g}$	Octahedral	25
	20000	CT		
	25590			

[a] See Table 1, [b] The electronic spectra of the new complexes are characterized by small shifts and splitting of the ligand bands and intense metal-to-ligand charge-transfer bands, originating in the UV and trailing off into the visible region. Metal-to-ligand charge-transfer bands are common in aromatic azo and aromatic amine compounds.

(Cont. Table 3).

[c] Dq = 1011 cm^{-1}, B = 676 cm^{-1}, b = 0.69.

[d] The iron(III) complex reported herein is dark red, as is common for iron(III) compounds. This colour is usually ascribed to the presence in the spectra of such compounds. This unfortunate situation is found in the present iron (III) complex and the positions and intensities of the spectral bands are affected little by the anion. A low-intensity band is however observed at 14952 cm^{-1} and can be assigned to low spin and at 25560 cm^{-1}, to high spin. A similar absorption has also been observed in the electronic spectrum of other five-coordinate iron(III) complexes[27].

CT = charge transfer.

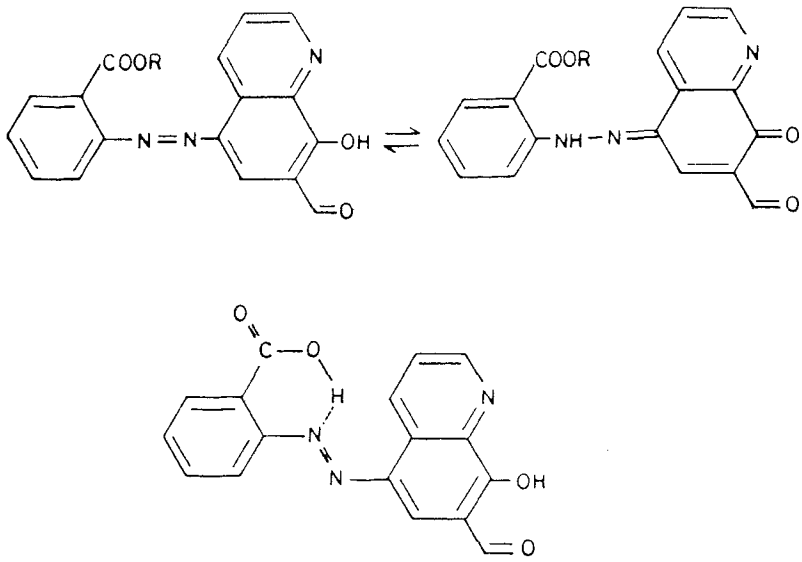

Fig. 4 : Azohydrazone tautomerism and intramolecular H-bonding of the O-Carboxy Compound

Table 4. Electron Paramagnetic Resonance Spectrum of Compound (1)

Species*	$g_{\|\|}$	$g_{\perp}$	g_{av}	G	α	$A_{\|\|}$ (cm^{-1})
1	2.2533	2.0262	2.1019	>4	.46	84.6×10^{-4}

*Number as given in Table 1.

$g_{av} = 1/3[g_{\|\|} + 2g_{\perp}]$, $G = g_{\|\|} - 2/ g_{\perp} - 2 = 9.7$ (this value is higher than 4 in compound (1); exchange interaction is considered to be absent).

by El-Sonbati et al[3,5,7,13]. The super-exchange splitting constant $A_{\|\|}$ was obtained (Table 4) semi-empirically, according to Pryce[20], form

$$\alpha^2 = A_{\|}/P + (g_{\|} - 2.0023) + 3/7 (g_{\perp} - 2.0023) + 0.04,$$

Where $P = 0.036$ cm^{-1}. The small super-exchange splitting constant $A_{\|\|}$ value and the shape of the spectrum exhibit similarities with comparable data for the blue copper proteins , characterized by small values of the parallel electron spin-nuclear spin hyperfine coupling constants ($A_{\|\|} \leq 100 \times 10^{-4}$ cm^{-1}).

Thermal Decomposition Studies

The thermal decomposition data (Table 2) of the complexes exhibit wide ranges of stability from ambient to ~ 235 °C. Two main decomposition steps characterize the thermal behaviour as represented by two TG peaks around 240 - 320 and 400 - 600 °C. DTA curve shows a similar behaviour for all the compounds[2,5,8]. The first peak resolved into two steps[5,6,13]. One is a weak sharp endothermic peak and the other is a medium exothermic peak, in the case for all complexes. The endothermic peaks refer to the decomposition of the polymeric complexes before they melt. The ultimate decomposition residue on heating in air is found to be the oxides of the general formula MO for all the metal complexes investigated, except those of Co(II) and Hg(II). The final residue was

found to be Co_3O_4 for the Co(II) complex. For Hg there is no a residue because of the sublimation.

The thermal behaviour of the metal complexes was investigated by differential thermal analysis (DTA). A different pattern was observed in the DTA curve of compound (11); the endothermic peak at 108 °C is due to the removal of uncoordinated water and ethanol, while the exothermic peak at 398 °C is due to the removal of hydrogen chloride[5,7]. An exothermic peak corresponding to formation of ZrO_2 appears at 690 °C.

For compounds (5), (6), (13), (1) - (3) and (7) DTA curves show;(i) the elimination of uncoordinated and coordinated water molecules at ca. 102 and 480 °C, respectively; (ii) the removal of HCl at 248 and 250 °C;(iii) the removal of nitrate at 446 and 456 °C and (iv) the formation of different oxides[5,7] at 450, 540, 630, 670, 530 and 610 °C.

The thermal weight loss curve (TG) for compound (12) shows an inflection at about 152 °C which corresponds to a 8.4 %. The first weight loss probably corresponds to a weight loss of 8.4 %. The first weight loss probably corresponds to the loss of coordinated ethanol while the second is apparently due to the loss of lattice ethanol.

Wrobeski and Brown[18,19] have postulated that hydrogen bonding between squarate and lattice solvent may be so strong that solvent coordinated to the metal is more easily lost from the complex. The calculated weight losses of 7.1 % are lower than those observed at 152 and 200 °C. It appears that the ruthenium compound loses the coordinated and lattice ethanol simultaneously. This may be due to a weaker binding of the lattice ethanol in this complex. The disparity between the theoretical and experimental weight losses again may be attributed to solvent contamination which can be used to explain the difference between the calculated (7.1 %) and found (8.4) values.

Subsequent steps in the decomposition of compound (12) seem to follow a complicated mechanism as observed for other complexes[8].

Finally, the thermal curves of all compounds (Table 2) show an exothermic effect in the temperature range 175 - 333 °C followed by an endothermic effect characterized

partially by overlapping. In the same temperature range, TG curves show a weight loss that corresponds to the elimination of the chlorine/nitrate and also at relatively higher temperature[7] (80 - 320 °C) a loss in weight is equivalent to one or two moles of coordinated water. To verify these processes, the IR spectra of the heated samples have been registered. These spectra show that the ν(M-X) (X = Cl, OH_2 or ONO_2) bands have disappeared, while the bands corresponding to the ligand remain. This suggest that in the temperature range 175 - 255 °C only the dehalogenation processes occur (endothermic effect). Therefore, the former exothermic effect is probably due to a structural change. The exothermic effect begins at about 500 °C and must be attributed to combustion of organic matter. As residues at the end of pyrolysis metallic oxides remain.

^{1}H NMR Spectra

The proton magnetic resonance spectra of the ligand and of ($ZnL_2.OH_2$) have been recorded in DMSO-d_6 using TMS as the internal standard. The chemical shift values (δ, ppm) of the different protons have been recorded in Table 5. The broad signal exhibited by the ligand due to the OH(phenolic and carboxylic) protons at 8.9 ppm disappears in the zinc complex indicating the coordination of oxygen atoms with the metal ion[1-4]. The appearance of signals due to HC=N protons of the same positions in the ligand and its complex shows the non-involvement of this group in coordination.

^{13}C NMR Spectra

The ^{13}C NMR spectra of the ligand and the zinc complex have also been recorded. A considerable shift (Table 6) in the positions of the carbons attached to the different partcipation groups clearly indicates the bonding of the carbonyl oxygen atom of the phenolic and carboxylic groups to the zinc atom(Figure 5).

Taking into accounts all the above data, LH_2 contain five atoms capable of coordination, but due to steric condition, the nitrogen of the heterocyclic ring remains inert and LH_2 behaves as dibasic bis-bidentate ligand.

Table 5. ^{1}H NMR Spectra Data[a](δ ppm)[b] of Ligand and its Corresponding Zinc Complex.

Compound	OH (phenolic & carboxyl)	Ar-H	$HC=N_{py}$
LH_2	9.74	8.35-7.34	7.50
$[ZnL_2.2OH_2]$[d]	-	8.15-7.21	7.45

[a] Solvent DMSO-d_6 [b] Relative to TMS

[c] The aromatic proton resonances are not shifted indicating that the quinoline nitrogen does not participate in bonding.

[d] A signal at 3.06 ppm is assignable to water.

Table 6. ^{13}C NMR Spectra (δ ppm) of Ligand and its Corresponding Zinc Complex.

Compound	1	2	3	4	5	6	7
LH_2	156.20	117.80	182.00	123.00	142.50	126.00	131.20
$[ZnL_2.2OH_2]$[d]	150.42	176.31	176.31	124.80	141.21	125.22	130.21
	8	9	10	11	12	13	14
	151.80	138.50	119.10	115.90	129.00	118.52	158.20
	148.90	135.30	117.90	115.02	130.50	119.10	153.40

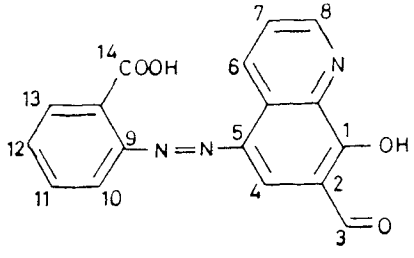

Fig. 5: ^{13}C NMR spectra of ligand and its Zinc complex.

Conclusion Remarks

From the overall studies presented, it is concluded that in the polymeric complexes (1) - (13) LH_2 behaves as a chelating bis-bidentate dibasic ligand, bonding through both the hydroxy group of quinoline and the carboxy group atom, and the aldehydic group oxygen atom and nitrogen atom of the azo group. The pyridine ring breathing mode of the ligand is observed[1-14] at ~ 996 cm^{-1}. It remains unaltered in the polymeric complexes commensurate with the absence of coordination through the nitrogen atom of the pyridine ring. In the complex (13) the absence of a band in the 1350 - 1400 cm^{-1} region in the spectrum of the nitrate complex confirms that ionic nitrates are absent[4] but covalently bonded in the lanthanide azo complex.

The decomposition of these polymeric complexes undergo two steps. The first step is due to the loss of ligand yielding the corresponding metal halides. In the second step the halogen/nitrate and the remaining part of the ligand are lost and conversion to metal oxide is absent. In the case of the mercury complex it is observed that the loss of ligand and the formation of oxide are simultaneous and a single step of decomposition is observed. At higher temperatures(500 °C) the sublimation of mercuric oxide takes place. The intermediate and end product is characterized by elemental analysis.

Finally, the thermal data of the complexes obtained from the corresponding TG and DTA curves confirm the anhydrous character of all the complexes except for (5), (6), (11) and (13) who lost water molecules in the temperature range 40 - 150 °C. The lower energy calculated from the corresponding area of the endothermic effect has the value 21.4 kJ/mol for compound (13); this value is indicative of a weak interaction of the water molecule in this compound.

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Date Received: February 15, 1999
Date Accepted: April 30, 1999