Pak. j. sci. ind. res., vol. 37, nos. 1-2, Jan.-Feb. 1994

POLYMETALLIC COMPLEXES
Part-XLV. Complexes of Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II) with Bis-Bidentate Chelating Diazo Dye Ligands

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(Received December 16, 1992; revised October 13, 1993)

Bis-bidentate ligands 1-(2-carboxyphenyl-azo)-2,4-dihydroxy-benzene and 4,4'-*bis* (2,4-dihydroxyphenyl-1-azo-3,3'-dimethyl)-diphenyl having ON–NO and ON⌒NO potential donor atoms respectively form polynulear complexes with some divalent transitional and non-transitional metal ions. The nickel (II) complex with former ligand is found to be square-planar whereas the other cobalt (II), nickel (II) and copper (II) complexes are either octahedral or distorted octahedral. The complexes with zinc (II), cadmium (II) and mercury (II) are assigned to have tetrahedral stereochemistry around the metal ions. The characterisation of the complex compounds has been made basing upon analytical, conductance, magnetic susceptibility measurement, thermal i.r., electronic spectra, n.m.r and e.s.r spectral data.

Key words: Polymetallic complexes, Azodye complexes, *Bis*-bidentate chelating ligand complexes.

Introduction

The azo dyes possess strong pharmacological properties [1]. The azo dyes are also used as food preservants [2] and for dyeing food grains. Some of the azo dyes are used in the laboratory as an indicator [3] in acid-base titrations. Spectrophotometric and potentiometric studies of Co (II), Ni(II) and Cu(II) chelates with azo dyes have been reported. The azo dyes are also used for spectrophotometric determination of vanadium in steel [4]. The pharmacological, analytical and chelating properties of azo dyes made us interested to synthesize new azo dyes and their metal chelates with some divalent metal ions [5]. The present study reports the synthesis and characterisation of two new *bis*-bidentate diazo dyes (Figs. 1-2) having ON – NO and ON ⌒ NO donor atoms and their metal chelates with Co(II), Ni(II), Cu(II), Zn(II); Cd(II) and Hg(II) ions.

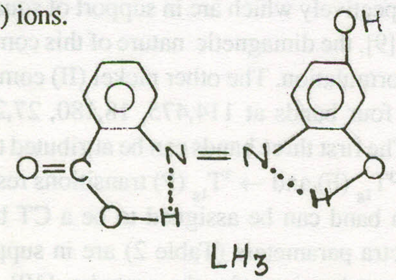

Fig. 1.

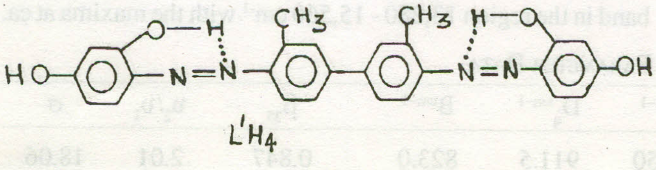

Fig. 2.

Experimental

All the chemicals were of E. Merck grade. The ligands were prepared by diazonium chlorides obtained from the coupling reaction of anthranilic acid and *o*-toludine respectively with the alkaline solution of resorcinol at 0 - 5°.

Preparation of complexes. The metal complexes were prepared by reacting the ethanolic solution of metal (II) chlorides in 2 : 1 molar ratio. On raising the pH of the resulting solution to around 7 by adding ammonium hydroxide dropwise, the metal complexes separated out. The complexes were filtered, washed with ethanol followed by ether and dried under reduced pressure.

Metal, carbon, hydrogen and nitrogen contents were estimated by standard procedures. Conductance measurement of the complexes were made in DMF solution (10^{-2} M). The magnetic susceptibility measurements were made at room temperature by Gouy method. I.R. spectra were recorded in KBr disc using a Perkin-Elmer 398 spectrophotometer, electronic spectra (10^{-2} M in DMF) using a Hilger and Watt Uvispeck spectrophotometer, n.m.r. spectra in acetone d_6 on a Em-390 (90 HMz) n.m.r. spectrophotometer at room temperature and e.s.r spectra on a E-4 spectrometer. Molecular weight of the ligands and the complexes were determined by Rast method using camphor as solid solvent. The analytical data are compiled in Table 1.

Results and Discussion

All the complexes are amorphous in nature, have high melting points and are insoluble in common organic solvents but sparingly soluble in dimethyl formamide. Analysis and conductance data show the composition of the complexes $[M_2(LH)_2(H_2O)_4]$, $[M'_2(LH)_2]$, where M = Co(II), Cu(II), M' =

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Ni(II), Zn(II), Cd(II), Hg(II); LH_3 = 1(C2'-carboxyphenylazo)-2,4-dihydroxy benzene, $[M_2L'H_2Cl_2(H_2O)_6]$ and $M_2L'H_2Cl_2(H_2O)_2]$ where M = Co(II), Ni(II), Cu(II), M' = Zn(II), Cd(II), Hg(II); $L'H_4$ = 4,4'-*bis* (2,4-dihydroxyphenyl-1-azo-3,3'-dimethyl) diphenyl. The non-electrolytic nature of the complexes is indicated by the low Δ_M values in DMF (4.8 - 6.9) mhos cm² mole $^{-1}$.

In the i.r. spectra of the ligands the broad band appearing at ca. 2900 - 3600 cm^{-1} may be attributed to O-H...N intramolecular hydrogen bonding. Disappearance of this band in the metal complexes indicates bonding of phenolic OH groups to the metal ions. In the ligands the band appearing at 1512 cm^{-1} (LH_3) and at 1505 cm^{-1} ($L'H_4$) can be assigned to phenolic C-O vibration and in the metal chelates a new band appears at ca. 1500 cm^{-1} in addition to the previous one which shows the bonding of one of the phenolic oxygen atoms of the resorcinol moiety to the metal ions. The sharp bands observed at 1620 cm^{-1} in both the ligands suffer bathochromic shift of ca. 20 cm^{-1} in the complexes, indicating bonding of one of the azonitrogen atoms to the metal ions [6].

TABLE 1. ANALYTICAL AND MOLECULAR WEIGHT DATA OF THE LIGANDS AND THE COMPLEXES.

Compound and colour	% (Found/Calculated) M	C	H	N	Mol-wt22 found
LH_3	-	11.7	3.6	10.2	234
Brown	-	(12.09)	(3.87)	(10.85)	
$L'H_4$	-	68.4	4.5	12.1	418
Purple	-	(68.72)	(4.85)	(12.33)	
$[Co_2(LH)_24H_2O]$	16.4	43.9	3.2	7.5	655
Black	(16.78)	(44.45)	(3.41)	(7.97)	
$[Co_2L'H_2Cl_2(H_2O)_6]$	15.4	41.2	2.2	7.3	672
Brown	(15.73)	(41.66)	(2.67)	(7.47)	
$[Ni_2 (LH)_2]$	18.1	49.2	2.2	8.5	565
Red	(18.65)	(49.57)	(2.54)	(8.89)	
$[Ni_2L'H_2Cl_2(H_2O)_6]$	15.4	41.3	2.5	7.1	668
Reddish brown	(15.68)	(41.68)	(2.67)	(7.48)	
$[Cu_2 (LH)_24H_2O]$	17.8	43.4	3.1	7.6	675
Black	(17.86)	(43.68)	(2.67)	(7.48)	
$[Cu_2L'H_2Cl_2(H_2O)_6]$	16.7	40.8	2.5	7.2	684
Reddish brown	(16.79)	(41.26)	(2.64)	(7.40	
$[Zn_2(LH)_2]$	20.1	48.2	2.2	8.4	598
Reddish brown	(20.34)	(48.54)	(2.48)	(8.71)	
$[Cd_2(LH)_2]$	30.1	42.2	1.9	7.2	660
Reddish brown	(30.51)	(42.34)	(2.18)	(7.60)	
$[Cd_2L'H_2Cl_2(H_2O)_2]$	28.4	39.5	2.2	6.8	725
Brown	(28.68)	(39.80)	(2.55)	(7.14)	
$[Hg_2(LH)_2]$	43.2	33.8	1.6	5.8	835
Reddish brown	(43.93)	(34.16)	(1.75)	(6.13)	
$[Hg_2L'HCl_2(H_2O)_2]$	41.2	32.1	1.8	5.2	886
Reddish brown	(41.78)	(32.49)	(2.08)	(5.83)	

LH_3 = 1-(2'-Carboxyphenylazo)-2,4-dihydroxy-benzene, $L'H_4$ = dihydroxyphenylazo-3,3'-dimethyl)-diphenyl.

In the ligand LH_3, the υ as (COO^-) and υ_s (COO^-) bands appear at 1650 cm^{-1} and 1420 cm^{-1} respectively and in the metal chelates these bands are observed at ca. 1560 cm^{-1} and ca. 1355 cm^{-1} with a difference of ca. 205 cm^{-1}, suggestive of monodentate nature of the carboxylate group [7]. In case of complexes of cobalt (II) and copper (II) with the ligand LH and in case of all complexes with $L'H_3$ broad bands are observed at ca. 3350 - 3450 cm^{-1} followed by sharp peaks at ca. 840 cm^{-1} and ca. 760 cm^{-1} assignable to OH stretching, rocking and wagging vibrations respectively, thus indicating the presence of co-ordinated water molecules in these complexes. The evidence of bonding of the ligand of the metal ions is obtained by appearance of bands at ca. 440 cm^{-1} υ (M-N) and ca. 505 cm^{-1} (M-O) in the far i.r. spectra of the complexes.

The nickel (II) complex with ligand LH_3 is found to be diamagnetic whereas the cobalt (II) and copper (II) complexes of this series possess lower than usual, μ_{eff} values (2.8 BM) and 1.4 BM respectively). These results are indicative of metal - metal interactions supporting their dimeric structures. The cobalt (II), nickel (II) and copper (II) complexes with the latter ligand exhibit normal magnetic moments (5.1 BM, 3.2 BM and 1.8 BM respectively) indicating the presence of 3, 2 and 1 unpaired electrons respectively.

The electronic spectra of the cobalt (II) complexes show four ligand field bands at ca. 9010, 18125, 21250 and 32180 cm^{-1} assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), \rightarrow {}^4A_{2g}(F), \rightarrow {}^4T_{1g}(P)$ and CT band respectively. The values of spectra parameters like D_q, B, β_{35}, υ_2 and υ_1 of the cobalt (II) complexes are suggestive of an octahedral stereo-chemistry around the metal ions [8]. The nickel (II) complex with LH_3 exhibits two bands at 16,540 and 17,450 cm^{-1} assignable to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_{1g}$ transitions respectively which are in support of square planar configuration [9]. the dimagnetic nature of this complex also support this formulation. The other nickel (II) complex with $L'H_4$ exhibits four bands at 114,475, 18,180, 27,215 and 33,560 cm^{-1}. The first three bands can be attributed to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), \rightarrow {}^3T_{1g}(F)$ and $\rightarrow {}^3T_{1g}(P)$ transitions respectively and the fourth band can be assigned to be a CT band. The values of spectra parameters (Table 2) are in support of an octahedral stereochemistry for the complex [10]. Both the copper (II) complexes show the broad assymetric ligand field band in the region 13,280 - 15,560 cm^{-1} with the maxima at ca.

TABLE 2. LIGAND FIELD PARAMETER DATA.

Compound	$\upsilon_1^{cm^{-1}}$	$\upsilon_2^{cm^{-1}}$	$\upsilon_3^{cm^{-1}}$	$D_q^{cm^{-1}}$	$B^{cm^{-1}}$	β_{35}	υ_2/υ_1	σ
$[Co_2(LH)_2(H_2O)_4]$	9,010	18,125	21,250	911.5	823.0	0.847	2.01	18.06
$[Co_2L'H_2Cl_2(H_2O)_6]$	8,870	17,465	21.135	859.5	799.3	0.823	1.98	21.5
$[Ni_2L'H_2Cl_2(H_2O)_6]$	11,475	18,180	27.215	1147.5	664.6	0.638	1.58	56.73

14,275 cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$ transition in a distorted octahedral geometry [11].

The TGA and DTA studies of the complex $[Cu_2(LH)_2(H_2O)_4]$ and the TGA study of the complexes $[Co_2L'H_2Cl_2(H_2O)_6]$ and $[Ni_2L'H_2Cl_2(H_2O)_6]$ have been reported. No mass loss is observed for all these three complexes upto 100° indicating co-ordinating nature of the water molecules, with the rise of temperature the three complexes suffer a mass loss of 30.8% between the range 100 - 950^0, 36.2% between 100 - 880^0 and 66.01% (100-420^0)respectively. There after the thermograms become a straight line indicating the stable nature of the products on heating.

The 'H n.m.r spectra of the ligands LH_3 and $L'H_4$ display complex patterns at σ 6.9 - 8.0 and σ 6.3 - 7.5 due to seven and twelve phenyl protons respectively. The sharp peak observed at σ 3.1 in $L'H_4$ can be assinged to six methyl protons. The phenolic protons are not observed as these fall out of the range measured.

The e.s.r spectra of the complexes $[Cu_2(LH)_2(H_2O)_4]$ and $[Cu_2(L'H_2)Cl_2(H_2O)_6]$ are recorded at x-band at room temperature. The g_{av} values for the two complexes have been calculated to be 2.1061 and 2.0637 respectively by applying Kneubuh's method [11]. This type of spectrum may result either from the regular octahedral stereochemistry undergoing a dynamic or pseudorotational type of Jahn-Teller distortion or to the extensive exchange coupling operating between the Cu(II) - Cu(II) ions [12].

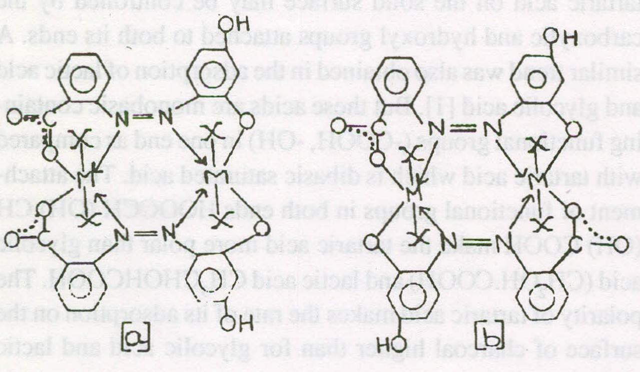

Fig. 3. (a, b)

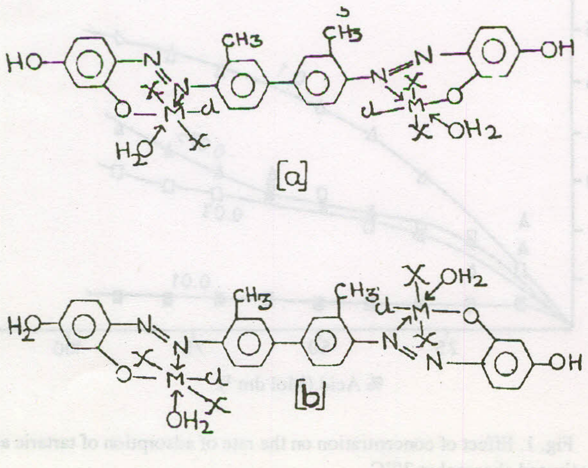

Fig. 4. (a, b)

The molecular weights of the complex compounds further support their dinuclear nature.

Basing upon above experimental evidence, it is concluded that both the azo dyes behave as bis-bidentate chelating ligands having $\overset{\frown}{O N}$ - $\overset{\frown}{N O}$ and $\overset{\frown}{O N}$$\frown$$\overset{\frown}{N O}$ donor atoms which are capable of holding two metal ions on either side thus forming dimeric complexes Fig. 3a, b and Fig. 4a, b respectively.

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