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Polymetallic Complexes Part-LXIX: Preparation and Characterisation of Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) and Mercury(II) Complexes with Bis-Bidentate $\widehat{NO}$—$\widehat{ON}$ Donor Azodye Ligands

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Bis-3,3′-(*p*-tolylazo)-2,2′-dihydroxydinaphathalene and bis 3, 3′-(*p*-anisylazo)-2,2′-dihydroxydinaphthalene act as a bis-bidentate $\widehat{NO}$—$\widehat{ON}$ donor chelating ligands co-ordinating to the metal atoms through azo nitrogen and phenolic oxygen atoms. The complexes formed by Co(II) ions are octahedral, Cu(II) distorted-octahedral, Ni(II) square-planar and tetrahedral stereochemistry has been suggested for the rest Zn(II), Cd(II) and Hg(II) complexes basing upon elemental analysis, magnetic moment, conductivity measurement, IR, electronic spectra, NMR and ESR spectral data. All the twelve complexes are dimeric in nature.

INTRODUCTION

In our attempt[1] to synthesize and characterise polymetallic complexes through polydentate azodye chelates, the present work reports the preparation of two new $\widehat{NO}$—$\widehat{ON}$ donor ligands and their twelve complexes.

RESULTS AND DISCUSSION

The complexes have the compositions $[M_2(L/L')Cl_2(H_2O)_6]$ and $[M_2(L/L')Cl_2(H_2O)_2]$ where M = Co(II), Cu(II), M′ = Ni(II), Zn(II), Cd(II), Hg(II), LH_2 = bis-3,3′-(*p*-tolylazo)-2,2′-dihydroxy dinaphthalene]; $L'H_2$ = bis [3,3′-(*p*-anisylazo)-2,2′-dihydroxydinaphthalene] (Table-1). The twelve complexes are quite stable at room temperature as well as up to 100°C indicating coordinating nature of the water molecules present in the complexes. The complexes are amorphous in nature, have high melting points and are slightly soluble in DMF. Non-electrolytic nature of the complexes is shown by the low conductance values in DMF (2.8–7.2 Ω^{-1} cm^2 mol^{-1})

In the IR spectra of the ligands, broad bands appear at *ca.* 3000 cm^{-1} (LH_2) and 3475–3380 cm^{-1} ($L'H_2$) assignable to O—H---N intramolecular hydrogen bonding. The absence of this band in the metal chelates suggests coordination of the deprotonated dianionic ligands to the metal ions. The sharp band observed at *ca.* 1585 cm^{-1} and *ca.* 1500 cm^{-1} can be attributed to ν(—N=N—) and ν(C—O) vibrations respectively and a negative shift of these bands 10–30 cm^{-1} in the metal complexes indicate the bonding of the ligands through azo nitrogen and phenolic oxygen atoms respectively[2]. The presence of coordinated water molecules in case of Co(II) and Cu(II) complexes is shown by the appearance of broad bands and double humps at *ca.* 3500 cm^{-1} followed by sharp peak at *ca.* 830 cm^{-1} assignable to OH stretching and rocking vibrations respectively[3]. The medium intensity bands found at *ca.* 505 cm^{-1} and *ca.* 410 cm^{-1} in the far IR spectra of the complexes can be ascribed to ν(M—O) and ν(M—N) vibrations respectively[4].

The Ni(II) complexes are found to be diamagnetic in nature. Sub-normal magnetic moments of Co(II) and Cu(II) complexes indicate metal-metal interactions in a polynuclear stereochemistry[5].

TABLE-1
ANALYTICAL AND IR SPECTRAL DATA (cm^{-1}).

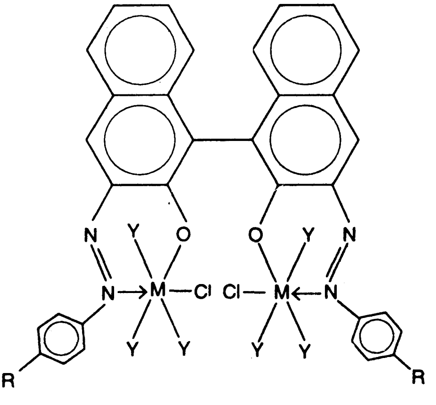
Compounds (Colour)	% Analysis, Found/(Calcd)				ν(—N=N—)	ν(C—O)
	M	C	H	N		
LH_2	—	78.16	4.98	10.72	1585	1500
(Reddish brown)		(77.60)	(4.60)	(10.50)		
$L'H_2$	—	73.64	4.69	10.10	1580	1505
(Coffee)		(73.20)	(4.30)	(9.80)		
$[Co_2LCl_2(H_2O)_6]$	14.42	49.94	4.40	6.85	1560	1480
(Brown)	(14.10)	(49.50)	(4.20)	(6.70)		
$[Co_2L'Cl_2(H_2O)_6]$	13.88	48.06	4.24	6.59	1570	1490
(Brown)	(13.50)	(47.70)	(4.20)	(6.20)		
$[Ni_2LCl_2(H_2O)_2]$	15.77	5480	3.76	7.52	1565	1485
(Orange red)	(15.50)	(54.50)	(3.60)	(7.30)		
$[Ni_2L'Cl_2(H_2O)_2]$	15.12	52.54	3.60	7.21	1565	1495
(Red)	(14.80)	(52.10)	(3.40)	(7.10)		
$[Cu_2LCl_2(H_2O)_6]$	15.38	49.38	4.35	6.77	1570	1490
(Greyish black)	(15.10)	(49.10)	(4.10)	(6.50)		
$[Cu_2L'Cl_2(H_2O)_6]$	14.80	47.54	4.19	6.52	1570	1480
(Brown)	(14.60)	(47.20)	(4.00)	(6.40)		
$[Zn_2LCl_2(H_2O)_2]$	17.25	53.84	3.69	7.39	1565	1480
(Grey)	(17.10)	(53.20)	(3.40)	(7.10)		
$[Zn_2L'Cl_2(H_2O)_2]$	16.55	51.66	3.54	7.09	1560	1490
(Brown)	(16.20)	(51.20)	(3.30)	(6.90)		
$[Cd_2LCl_2(H_2O)_2]$	26.39	47.89	3.28	6.57	1575	1485
(Red)	(26.10)	(47.50)	(3.10)	(6.40)		
$[Cd_2L'Cl_2(H_2O)_2]$	25.43	46.16	3.16	6.33	1565	1480
(Red)	(25.20)	(45.80)	(3.00)	(6.10)		
$[Hg_2LCl_2(H_2O)_2]$	39.01	39.68	2.72	5.44	1570	1480
(White)	(38.70)	(39.20)	(2.50)	(5.20)		
$[Hg_2L'Cl_2(H_2O)_2]$	37.84	38.48	2.64	5.28	1560	1485
(Greyish white)	(37.60)	(38.20)	(2.40)	(5.10)		

LH_2 = Bis-[3,3′-*p*-tolylazo-2,2′-dihydroxydinaphthalene]
$L'H_2$ = Bis-[3,3′-*p*-anisylazo-2,2′-dihydroxydinaphthalene]

In the electronic spectra of Co(II) complexes, four bands appear at *ca.* 8875, 17735, 20650 and 31450 cm^{-1}. The first three bands can be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, $\rightarrow {}^4A_{2g}(F)(\nu_2)$ and $\rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions respectively and the last is a charge transfer band. The ligand field parameters like $D_q = -(886, 899)$ cm^{-1}, B = (784, 790) cm^{-1}, β_{35} = (0,807, 0.813), ν_2/ν_1 = (1.998, 2.008) and σ = (23.91, 23.00) suggest an octahedral geometry for both the Co(II) complexes[6]. In the electronic spectra of the Cu(II) complexes, one broad asymmetric band appears at 14750–13520 cm^{-1} with maxima at *ca.* 14370 cm^{-1} attributable to $^2E_g \rightarrow {}^2T_{2g}$ transitions, suggestive of a distorted octahedral configuration[7]. In the Ni(II) complexes, two bands appear at *ca.* 16510 and *ca.* 17350 cm^{-1} assignable to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions respectively in support of a square planar configuration. This formulation is further supported by the diamagnetic nature of the complexes.

The ^1H NMR spectra of the ligand LH_2 display sharp peaks at δ 2.1 and a complex pattern at δ 6.8–8.0 due to six methyl (—CH_3) and eighteen phenyl protons respectively. In the ligand $L'H_2$ one sharp peak is observed at δ 3.8 due to six methoxy (—OCH_3) and one complex patterns at δ 6.87–7.8 due to eighteen phenyl protons.

The ESR spectrum of the complex $[Cu_2LCl_2(H_2O)_6]$ was recorded at X-band. It shows that the geometry around Cu(II) ion in the unit cell is tetragonal (elongated octahedral) with $g_\perp = 2.0506$ and $g_\parallel = 2.1885$. The axial symmetry parameter 'G' can be calculated to be 3.837 using the relation $G = \frac{g_\parallel - 2.002}{g_\perp - 2.002}$. It identifies the ligand as a strong field ligand and also indicates a strong exchange interaction among the magnetically equivalent Cu(II) ions in the dinuclear structure[9]. The $g_\parallel$ value is normally < 2.3 for covalent environment and ≥ 2.3 for ionic environment[10]. The $g_\parallel$ value of the present Cu(II) complex is < 2.3 indicating covalent nature of the complex. In the complex $[Cu_2L'Cl_2(H_2O)_6]$ the 'g_{av}' is found to be 2.1222 by applying Kneubuhl's method[11]. This type of spectrum may result either due to dynamic or pseudo-rotational type of Jahn-Teller distortion or



R = —CH3, —OCH_3, Y = H_2O

Fig. 1

due to extensive exchange coupling operating between the Cu(II)–Cu(II) ions in a dinuclear structure.

The Zn(II), Cd(II) and Hg(II) complexes can be suggested to possess tetrahedral geometry, based on the analytical and IR spectral data.

Hence both the azo dyes act as a doubly bidentate ligand coordinated to two metal atoms through two phenolic oxygen and two azo nitrogen atoms. The probable structure of the complexes is represented in Fig. 1.

EXPERIMENTAL

All the chemicals were of B.D.H. grade. Metal, carbon, hydrogen and nitrogen contents were estimated by standard procedures. Conductivity measurements in DMF were made using Toshniwal conductivity bridge. The magnetic moments were made at room temperature by Gouy method. IR spectra were recorded in KBr disc using Perkin-Elmer 998 spectrophotometer, electronic spectra (10^{-2} M in DMF) using a Hilger and Watt Uvispeck spectrophotometer, NMR spectra in acetone d_6 on an E_m–390 (90 MHz) NMR spectrophotometer and ESR spectra on a E–4 spectrometer.

The bis-azodye ligands were synthesized by following the coupling reaction between the diazonium chlorides obtained from *p*-toluidine and *p*-anisidine with alkaline solution of di-β-naphthol at 0–5°C.

Synthesis of complexes

The ethanolic solutions of metal(II) chlorides are reacted with ligand solution in EtOH and heating the reaction mixture over a heating mantle at 50–60°C for *ca.* $\frac{1}{2}$ h. On cooling pH of the solution was raised by the addition of conc. ammonia drop by drop slowly with constant stirring. The complexes thus isolated are then filtered, washed with ethyl alcohol followed by diethyl-ether and dried in vacuum.

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