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Polymetallic Complexes, Part LXXIII: Complex of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Mn(II) and Fe(II) with $\overset{\frown\frown\frown}{\mathrm{NOON}}$ donor Bis-bidentate Chelating Azodye Ligands

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Sixteen dinuclear metal complexes of compositions $[M_2L/L'Cl_2(H_2O)_6]$ and $[M'_2L/L'Cl_2(H_2O)_2]$ have been synthesised, where LH_2 = 3, 3'-di-(phenylazo)-di-β-naphthol, $L'H_2$ = 3,3'-di-(*p*-sulphonic phenyl azo)-di-β-naphthol, M = Mn(II) Fe(II), Co(II), Cu(II), Zn(II) and M' = Ni(II), Cd(II), Hg(II). The complexes of the former category are either octahedral or distorted octahedral. The Ni(II) complexes are square planar whereas Cd(II) and Hg(II) complexes possess a tetrahedral geometry around the metal ions. The characterisation of ligands and the complexes is made basing upon analytical, conductance, magnetic susceptibility, infrared, electronic spectra apart from NMR, ESR and X-ray data. Both the azo dyes behave as bis-bidentate ligands and coordinated to two metal ions favouring the formation of dinuclear complexes.

INTRODUCTION

Azo and bis azo dyes are well known for their chemotherapeutic properties[1]. They are also used as food preservants and for dyenig food grains[2]. Some of the azo dyes find application in the laboratory as indicators in acid-base titrations[3]. Azo dyes are also used for spectrophotometric determination of vanadium in steel. The pharmacological, analytical and complexing character of these compounds prompted us to synthesize new multidentate azo and bis-azo dyes and their polymeric metal complexes with some divalent metal ions[4]. The present study reports the preparation of two new bis-bidentate azo dyes having $\overset{\frown\frown\frown}{\mathrm{NOON}}$ potential donor atoms and their chelates with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

EXPERIMENTAL

All the chemicals were of AR grade. The azo dyes were prepared by the coupling reaction of diazonium chlorides obtained from aniline and sulphanilic acid separately with alkaline solution of di-β-naphthol in 2 : 1 molar ratio at 0–5°C.

Preparation of Complexes: The metal complexes were prepared by reacting the ethanolic solution of metal (II) chlorides with the ligands in ethanol in 2 : 1

ratio. On raising the pH of the solution to around 7 by adding NH_4OH dropwise and constant stirring, the metal chelates separated out. Then the complexes were filtered, washed with ethanol followed by ether and dried in vacuum.

Metal, carbon, hydrogen, and nitrogen contents were estimated by standard method. Conductance measurements of the complexes were made in dimethyl formamide solution (10^{-2} M). The magnetic susceptibility measurements were made at room temperature by Gouy method. IR spectra were recorded in KBr discs using Perkin-Elmer 398 spectrophotometer, electronic spectra (10^{-2} M in DMF) using a Hilger and Watt Uvispeck spectrophotometer, NMR spectra in acetone-d_6 on a EM-390 (90 MHz) NMR spectrophotometer at room temperature and ESR spectra on a E-4 spectrometer. X-ray diffraction study (power pattern) of the complex $[Co_2LCl_2(H_2O)_6]$ has been recorded in a PW 1130/00 model X-ray diffractometer supplied by M/S Phillips Holland.

RESULTS AND DISCUSSION

All complexes are amorphous in nature, have high melting point and are insoluble in common organic solvents but sparingly soluble in DMF. Analysis and conductance data show the composition of the complexes $[M_2(L/L')Cl_2(H_2O)_6]$ and $[M'_2(L/L')Cl_2(H_2O)_2]$ where M = Mn(II), Fe(II), Co(II), Cu(II), Zn(II); M′ = Ni(II), Cd(II), Hg(II); LH_2 = 3, 3′-di(phenylazo)-di-β-naphthol; $L'H_2$ = 3,3′-di(*p*-sulphonic phenyl azo)-di-β-naphthol. The complexes are non-electrolytic in nature as indicated by their low Λ_m values of DMF (4.5 – 7.2 mhos cm^2 $mole^{-1}$).

In the IR spectrum of the ligand LH_2, one broad band is appearing at *ca.* 3450 $cm^{-1}$and in $L'H_2$ a double hump is appearing at 3480–3400 cm^{-1} which may be attributed to O—H—N intramolecular hydrogen bonding. Disappearance of these bands in the metal complexes indicates the bonding of the phenolic OH groups to the metal ions. In the ligand LH_2 the band observed at 1495 cm^{-1} and in $L'H_2$ the band appeared at 1510 cm^{-1} can be assigned to phenolic C—O vibration and a decrease of *ca.* 10 cm^{-1} is observed in the metal chelates indicating the coordination of the azo dyes to the metal ions through phenolic oxygen atoms. The sharp bands observed at 1610 cm^{-1} (LH_2) and 1620 cm^{-1} ($L'H_2$) can be assigned to —N=N— band and it undergoes bathochromic shift of *ca.* 20 cm^{-1} in the complexes showing bonding of one of the azo nitrogen atoms to the metal ions[6]. In case of complexes, broad bands are observed at *ca.* 3450–3350 cm^{-1} and sharp peaks at *ca.* 840–810 cm^{-1} assignable to OH stretching, rocking and wagging vibrations respectively, thus indicating the presence of coordinated water molecules in these complexes[7]. The evidence of bonding of these ligands to the metal ions is obtained by the appearance of bands at *ca.* 420 cm^{-1} and *ca.* 530 cm^{-1} assignable to ν(M—N) and ν(M—O) respectively in the far infrared spectra of the complexes[8].

The nickel(II) complexes are found to be diamagnetic whereas the Co(II), Cu(II), Mn(II) and Fe(II) complexes possess lower μ_{eff} values. The subnormal magnetic moment values are indicative of metal-metal interactions supporting dimeric structures[9].

The electronic spectra of the Co(II) complexes exhibit four bands at *ca.* 8550, 17155, 14895 and 33500 cm^{-1}, the last band being a CT band and the first three bands may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $\rightarrow {}^4A_{2g}(F)$ and $\rightarrow {}^4T_{1g}(P)$ transitions respectively in conformity with an octahedral configuration[10]. Distorted octahedral stereochemistry is assigned to the Cu(II) complexes with a broad band at 15455-13265 cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$ transition[11]. The Ni(II) complexes exhibit two bands at 16,520 and 17,560 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[12]. The diamagnetic nature of the complexes also supports this formulation. The electronic spectra of Mn(II) complexes consist of three bands at *ca.* 13,540 cm^{-1}, *ca.* 22,760 cm^{-1} and *ca.* 27,550 cm^{-1} assignable to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $\rightarrow {}^4A_{1g}(G)$ and $\rightarrow {}^4E_g(D)$ transitions respectively which are in agreement with an octahedral geometry[13]. The Fe(II) complexes show bands at *ca.* 18,480 cm^{-1} and a shoulder at *ca.* 20,550 cm^{-1} which may be ascribed to the transition $^5T_{2g} \rightarrow {}^5E_g$ suggesting an octahedral stereochemistry around the metal ions[14].

The ^1H NMR spectrum of the ligand LH_2 displays a complex pattern between 7.0–8.0 δ which corresponds to twenty phenyl protons.

The ESR spectrum of the complex $[Cu_2L'Cl_2(H_2O)_6]$ has been recorded at X-band at room temperature. The computation made by Piesach and Blumberg's method[15] suggests the presence of two g-values, $g_{\parallel} = 2.2071$ and $g_{\perp} = 2.0808$ for the Cu(II) ions. It has been observed that $g_{\perp} < 2.1$ and $g_{\parallel} < 2.3$ which indicates that the complexes are largely covalent and a mixed Cu—N and Cu—O bonding in the complex[16]. The axial symmetry parameter (G) has been found to be 2.56 by using the relation $G = \frac{g_{\parallel} - 2}{g_{\perp} - 2}$. This value indicates strong exchange interaction among magnetically equivalent Cu(II) ions in the unit cell. The ESR spectrum of $[Cu_2LCl_2(H_2O)_6]$ is recorded at X-band at room temperature. The g_{av} value is found to be 2.1222 using Kneubuhl's method[17]. This type of spectrum appears due to extensive coupling operating between two copper ions in a dinuclear structure[18].

The X-ray diffraction study (powder method) of the compound $[Co_2LCl_2(H_2O)_6]$ has been indexed in the X-ray diffractometer and the unit cell parameters have been calculated with the help of computer from the indexed data. The unit cell parameters like $A = 14.896$, $B = 8.420$, $C = 13.305$, $\alpha = 90.0$, $\beta = 107.45$, $\gamma = 90.0$ and volume of unit cell = 1591.98 suggest the monoclinic nature of the complex. In addition to the above information we can infer the number of formula units per cell which is compatible with the monoclinic system. The number of formula units (n) per unit cell is calculated from the relation

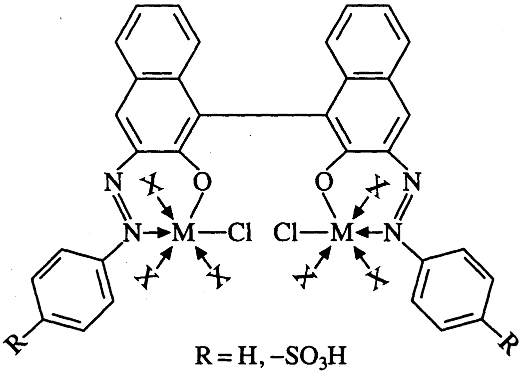
TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Compound	Colour	Analysis % found (calcd)					μ_{eff} B.M.
		C	N	H	M	Cl	
LH_2	Reddish brown	77.20 (77.73)	10.90 (11.33)	4.30 (4.45)	–	–	–
$L'H_2$	Brown	58.30 (58.71)	8.10 (8.56)	3.20 (3.36)	–	–	–
$[Cu_2LCl_2(H_2O)_6]$	Brown	47.70 (48.11)	6.70 (7.01)	3.60 (4.00)	15.70 (15.92)	8.50 (8.89)	1.51
$[Cu_2L'Cl_2(H_2O)_6]$	Coffee red	39.80 (40.08)	5.60 (5.84)	3.00 (3.34)	13.00 (13.25)	7.10 (7.41)	1.52
$[Co_2LCl_2(H_2O)_6]$	Brown	48.40 (48.67)	7.00 (7.09)	3.70 (4.05)	14.50 (14.94)	9.20 (9.00)	2.61
$[Co_2L'Cl_2(H_2O)_6]$	Reddish brown	40.00 (40.46)	5.60 (5.90)	3.10 (3.37)	12.10 (12.42)	7.20 (7.48)	2.58
$[Zn_2LCl_2(H_2O)_6]$	Chocolate brown	47.60 (47.89)	6.60 (6.89)	3.80 (3.99)	16.10 (16.30)	8.50 (8.85)	–
$[Zn_2L'Cl_2(H_2O)_6]$	Brown	39.40 (39.92)	5.40 (5.82)	2.90 (3.32)	13.20 (13.50)	7.00 (7.38)	–
$[Mn_2LCl_2(H_2O)_6]$	Coffee red	48.60 (49.17)	7.00 (7.17)	3.60 (4.09)	13.50 (14.06)	9.20 (9.09)	3.85
$[Mn_2L'Cl_2(H_2O)_6]$	Coffee	40.30 (40.81)	5.50 (5.95)	3.00 (3.40)	11.30 (11.67)	7.10 (7.54)	3.89
$[Fe_2LCl_2(H_2O)_6]$	Reddish brown	48.50 (49.06)	6.90 (7.15)	3.70 (4.08)	14.40 (14.26)	8.60 (9.07)	3.62
$[Fe_2L'Cl_2(H_2O)_6]$	Brown	40.50 (40.73)	5.60 (5.94)	3.00 (3.39)	11.70 (11.84)	7.70 (7.53)	3.59
$[Ni_2LCl_2(H_2O)_2]$	Red	52.00 (53.59)	7.50 (7.81)	2.90 (3.34)	16.00 (16.38)	9.60 (9.91)	–
$[Ni_2L'Cl_2(H_2O)_2]$	Red	43.40 (43.81)	6.10 (6.38)	2.60 (2.73)	12.90 (13.39)	7.80 (8.10)	–
$[Cd_2LCl_2(H_2O)_2]$	Grey	46.10 (46.61)	6.50 (6.79)	2.60 (2.91)	26.80 (27.28)	8.30 (8.61)	–
$[Cd_2L'Cl_2(H_2O)_2]$	Grey	38.80 (39.03)	5.30 (5.69)	2.00 (2.43)	22.60 (22.85)	7.30 (7.21)	–
$[Hg_2LCl_2(H_2O)_2]$	Grey	37.90 (38.39)	5.20 (5.59)	1.90 (2.39)	39.70 (40.11)	7.20 (7.09)	–
$[Hg_2L'Cl_2(H_2O)_2]$	Grey	32.60 (33.09)	4.50 (4.82)	1.60 (2.06)	33.90 (34.57)	6.00 (6.11)	–

$n = \frac{dNV}{M}$, where d = density of the compound, N = Avogadro's number, V = volume of the monoclinic unit cell, M = molecular weight of the compound. For this purpose we measure the density of the compound by floatation method in a saturated solution of KBr, NaCl and with CCl_4 separately. We found the observed density of the compound to be 1.64 approximately. The calculated molecular weight of the compound is 788.86 g. The volume of the monoclinic unit cell is found to be 1591.98 $Å^3$ which is equal to 1591.98×10^{-24} cm^3. We also know that one gram mole contains Avogadro number of molecules ($N = 6.023 \times 10^{23}$). This calculation gives the approximate number of formula units per unit cell to be 1.94. Hence, it is concluded that the exact number of formula units is 2. We observed that there is a centre of symmetry in the molecule. Hence, there are four positions of the units inside the monoclinic unit cell which is compatible with the monoclinic system.

All the Zn(II), Cd(II) and Hg(II) complexes are suggested to be four coordinated with a tetrahedral stereochemistry around the metal ions basing upon the analytical and IR spectral data.

Hence, the azo dyes act as bis-bidentate ligands bonded to the metal ions through two phenolic and two azo nitrogen atoms favouring the formation of dinuclear complexes. The tentative structure of the metal complexes can be represented in Fig 1.



R = H, $-SO_3H$
X = H_2O

Fig. 1.

TABLE-2
X-RAY DIFFRACTION DATA OF THE COMPLEX $[Co_2LCl_2(H_2O)_6]$

A	B	C	α	β	γ	Volume in Å
9.698	14.783	7.999	94.471	95.924	82.077	1127.41
14.896	8.420	13.305	90.000	107.457	90.000	1591.98

2-θ values:	10.4	12.2	16.2	17.1	19.2	22.5	23.5	27.7
	29.5	32.5	35.5	37.8	40.5	42.3	45.7	46.7
	48.0	49.6	51.4	53.0				

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