

POLYMETALLIC COMPLEXES

Part XLIV. Complexes of Cobalt (II), Nickel (II), Copper (II), Zinc (II), Cadmium (II) and Mercury II with Doubly-Bidentate O N Z N O Donor Chelating Azo Dye Ligands, 4,4'-Bis (2'-Hydroxy-1'-Naphthyl-Azo)-Diphenyl and 1,4-Bis (2'-Hydroxy-1'-Naphthyl-Azo)-Benzene

BIPIN B. MAHAPATRA, J. NANDA AND S.P. PRADHAN

P.G. Department of Chemistry, G.M. College, Sambalpur-768004, Orissa, India

(Received January 27, 1994; revised May 16, 1995)

The title doubly-bidentate bis-azo dye ligands form dimeric complexes of the type $[M_2L_2/L'_2(H_2O)_4]$, $[M'_2L_2/L'_2]$ where $M=Co(II)$, $Ni(II)$, $Cu(II)$, $M'=Zn(II)$, $Cd(II)$, $Hg(II)$. The complexes of the former category are found to be six coordinated, either octahedral or distorted octahedral and the complexes of the later type are four-coordinated with a tetrahedral geometry around the metal ions. The complexes have been characterized basing upon analytical, conductance, magnetic susceptibility, i.r., electronic, T.G.A., D.T.A., E.S.R. and N.M.R. data.

Key words: Polymetallic complexes, Chelating ligands.

Introduction

The pharmacological activity of azo dyes is well-recognized [1-3]. Analytical application [4] of azo dyes in the chemical and food processing laboratories have been studied in details [5]. Potentiometric and spectrophotometric application of azo dyes have also been reported [6]. Our literature survey reveals that no systematic approach has been made as yet by any scientist to study the complexation property of multi-donor chelating mono-azo and bis-azo dyes with transition and main-group metal ions. Earlier, we had reported [7-12] the preparation and characterization of some new azo dyes and their metal complexes. The present paper describes the synthesis of two new chelating bis-azo dyes having O N Z N O potential donor atoms (Fig. 1) and their twelve metal complexes with $Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$, $Cd(II)$, and $Hg(II)$ ions.

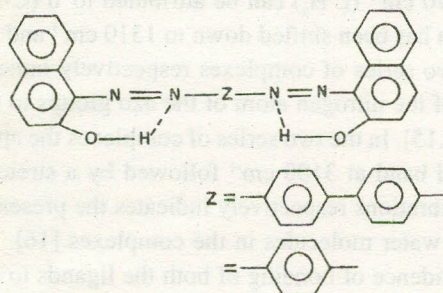


Fig. 1.

Materials and Methods

All the chemicals were of AR grade.

Preparation of the ligands. The biz-azo dye (LH_2) was prepared by the coupling reaction of diazonium chloride obtained from benzidine with alkaline solution of β -naphthol at $0^\circ C$ when coffee coloured compound separated out. The

other biz-azo dye was synthesized in an analogous method from *p*-phenylenediamine and β -naphthol when a dark-brown coloured compound was formed. Both the azo dyes were then washed with water and recrystallized from ethanol (95%).

Preparation of metal complexes. The metal complexes were prepared by reacting ethanolic solution of the metal (II) Chlorides with the ligands in 2:1 molar ratio. The pH of the resulting solution was then raised to ~ 7 by adding sodium acetate solution drop by drop with constant stirring when the metal chelates separated out. These were then filtered, washed with ethanol followed by ether and dried in vacuo.

Metal, carbon, hydrogen and nitrogen contents in the complexes were estimated by standard methods. Conductance was measured in $10^{-3}M$ dimethyl formide solution of the complex. Magnetic susceptibility measurements were made on the solid samples by the Gouy method. The I.R. spectra were recorded on Perkin-Elmer 398 spectrophotometer. The electronic spectra were recorded on a Hilger and Watt Uvispeck spectrophotometer using $10^{-2}M$ DMF solution of the complexes. The DTG and TGA studies of the complexes are made using a derivatograph supplied by Hungarican optical works with a heating rate of $10^\circ C$ per minute. The 1H nmr spectra of the ligands are scanned on a EM-390 NMR spectrophotometer using acetone d_6 as the solvent and TMS as an internal standard. The E.S.R. spectra of copper (II) complexes were recorded in polycrystalline at room temperature with a Varian E-4 E.S.R. spectrometer.

Results and Discussion

The elemental analysis (Table 1) shows that the compositions of complexes were $[M_2L_2/L'_2(H_2O)_4]$ and $[M'L_2/L'_2]$ where $M=Co(II)$, $Ni(II)$, $Cu(II)$; $M'=Zn(II)$, $Cd(II)$, $Hg(II)$;

TABLE I. ANALYTICAL AND IR SPECTRAL DATA OF THE LIGANDS AND COMPLEXES

Compounds	Colour	Found/Calcd		ν (C-O)		ν (M-O)	
		M	C	H	N	ν (-N=N-)	ν (M-N)
LH ₂	Coffee	-	77.2	10.8	4.3	<u>1490</u>	-
			77.73	11.33	4.35	1610	-
L'H ₂	Dark-Brown	-	74.5	12.7	4.1	<u>1460</u>	-
			74.64	13.39	4.30	1640	-
[Co ₂ L ₂ (H ₂ O) ₄]	Buff	9.9	65.5	3.3	9.4	<u>1455</u>	<u>510</u>
		10.1	65.87	3.43	9.60	1580	410
[Co ₂ L' ₂ (H ₂ O) ₄]	Dark-brown	11.2	60.6	3.7	10.5	<u>1425</u>	<u>510</u>
		11.52	61.06	3.91	10.96	1610	410
[Ni ₂ L ₂ (H ₂ O) ₄]	Brown	9.8	65.2	3.2	9.3	<u>1450</u>	<u>505</u>
		10.07	65.89	3.43	9.60	1570	410
[Ni ₂ L' ₂ (H ₂ O) ₄]	Light Brown	11.2	60.7	3.7	10.5	<u>1420</u>	<u>510</u>
		11.49	61.09	3.91	10.96	1600	415
[Cu ₂ L ₂ (H ₂ O) ₄]	Light green	10.5	64.8	3.2	9.2	<u>1450</u>	<u>500</u>
		10.8	65.36	3.40	9.53	1575	415
[Cu ₂ L' ₂ (H ₂ O) ₄]	Light brown	12.1	60.2	3.6	10.5	<u>1420</u>	<u>500</u>
		12.31	60.52	3.87	10.86	1610	405
[Zn ₂ L ₂]	Buff	11.5	68.8	2.6	10.0	<u>1445</u>	<u>510</u>
		11.81	69.39	2.89	10.11	1580	415
[Zn ₂ L' ₂]	Light pink	13.2	64.3	3.1	11.2	<u>1425</u>	<u>500</u>
		13.57	64.81	3.27	11.46	1605	405
[Cd ₂ L ₂]	Light Violet	18.5	63.6	2.5	9.1	<u>1450</u>	<u>510</u>
		18.72	63.95	2.66	9.32	1585	410
Cd ₂ L'2	Pink	21.1	58.7	2.9	10.4	<u>1420</u>	<u>505</u>
		21.27	59.04	3.02	10.59	1610	410
[Hg ₂ L ₂]	Light pink	21.5	55.3	2.1	8.1	<u>1450</u>	<u>500</u>
		21.92	55.76	2.32	8.13	1570	415
[Hg ₂ L' ₂]	Pink	32.2	50.4	2.4	8.8	<u>1425</u>	<u>510</u>
		32.52	50.60	2.59	9.08	1605	415

LH₂ = 4,4'-bis(2'-hydroxy-1'-naphthyl-azo) diphenyl, L'H₂ = 1,4'-bis(2'-hydroxy-1'-naphthyl-azo)-benzene

LH₂ = 4,4'-bis(2'-hydroxy-1'-naphthyl-azo)-diphenyl and L'H₂ = 1,4'-bis(2'-hydroxy-1'-naphthyl-azo)-benzene. All the complexes are amorphous in nature, have high melting points and are insoluble in common organic solvents but sparingly soluble in DMF. The low conductance values (3.2-4.7 mhos cm² mol⁻¹) of the complexes in dioxane indicate their non-electrolytic nature.

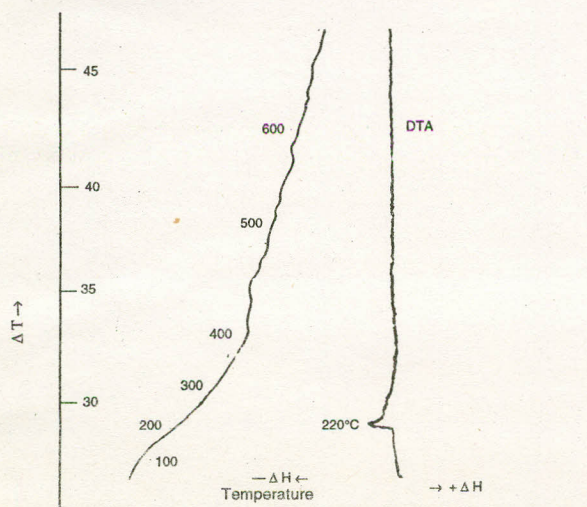
In the I.R. spectra of the ligands the broad bands appearing at 2900-3050 cm⁻¹ (LH₂) and 2880-2980 cm⁻¹ (L'H₂) can be ascribed due to O-H...N intramolecular hydrogen bonding. Absence of these bands in the metal complexes indicates the deprotonation of phenolic OH group there by confirming the bonding of Oxygen atom to the metal atoms. The appearance of the bands at 1490 cm⁻¹ in the ligand (LH₂) and at 1460 cm⁻¹ (L'H₂) can be assigned to ν (C-O) vibration. The negative shift of this band by ~ 40 cm⁻¹ in the metal chelates indicates the bonding of phenolic oxygen atom to the metal ions. The sharp bands at 1610 cm⁻¹ (LH₂) and 1640 cm⁻¹ (L'H₂) due to ν (-N=N-) suffer a bathochromic shift of ~ 30-40

cm⁻¹ in the metal complexes showing [8] the coordination of one of the azo nitrogen atoms on either side of the bis-azo dyes to the metal ions. The band appearing at 1390 cm⁻¹ (LH₂) and at 1370 cm⁻¹ (L'H₂) can be attributed to ν (C-N) vibration which has been shifted down to 1310 cm⁻¹ and 1260 cm⁻¹ in the two series of complexes respectively indicating the bonding of the nitrogen atom of the azo groups to the metal atoms [14,15]. In the two series of complexes the appearance of a broad band at 3100 cm⁻¹ followed by a stretching and rocking vibrations respectively indicates the presence of coordinated water molecules in the complexes [16]. The conclusive evidence of bonding of both the ligands to the metal ions is indicated by the appearance of bands at ~ 410-415 cm⁻¹ and ~ 500-510 cm⁻¹ assignable to ~ (M-N) and ~ (M-O) vibrations respectively [17].

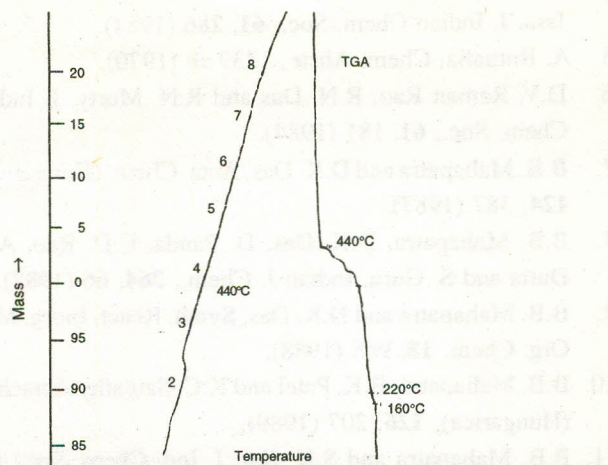
The cobalt (II), nickel (II) and copper (II) complexes exhibit magnetic moments ca 5.1 B.M., 3.1 B.M. and 1.9 B.M. respectively indicating the presence of three, two and one unpaired electrons respectively.

In the electronic spectra of cobalt (II) complexes four bands are noticed at Ca 9,110(12), 18,340(23), 21,520(32) and 31,270 cm^{-1} assignable to ${}^4T_{1g} \rightarrow {}^4T_{2g}(\text{F})$, $\rightarrow {}^4A_{2g}(\text{F})$, $\rightarrow {}^4T_{1g}(\text{P})$ and CT transitions respectively. The values of spectral parameters $Dq(911, 907.5) \text{ cm}^{-1}$, $B(835.33, 833.33) \text{ cm}^{-1}$, $\beta(0.8602, 0.8582)$; $V_2/V_1(2.013, 2.009)$ and $\delta(16.25, 16.52)$ of the complexes $[\text{Co}_2\text{L}_2(\text{H}_2\text{O})_4]$ and $[\text{Co}_2\text{L}'_2(\text{H}_2\text{O})_4]$ respectively are suggestive of an octahedral stereo chemistry around the metal [18] atoms. Both the copper (II) complexes show one broad assymmetric ligand field band in the region $\sim 13,350\text{-}14,970 \text{ cm}^{-1}$ with the maxima at $14,190 \text{ cm}^{-1}$ assignable to $2E_g \rightarrow 2T_{2g}$ transition in a distorted octahedral geometry [19]. The electronic spectra of Ni(II) complexes show four bands around 9,480 (5.5), 15,650 (10.5), 27,355 (17.5) and $35,550 \text{ cm}^{-1}$. The former three bands can be inferred to $3A_{2g}(\text{F}) \rightarrow 3T_{1g}(\text{F})$, $\rightarrow 3T_{2g}(\text{F})$ and $\rightarrow 3T_{1g}(\text{P})$ transitions respectively, whereas the fourth can be suggested for a CT band. The ligand field parameters $Dq(617, 587.5) \text{ cm}^{-1}$; $B(971, 958.33) \text{ cm}^{-1}$, $\beta(0.9327, 0.9205)$; $\delta(7.21, 8.63)$ and $V_2/V_1(1.65, 1.62)$ suggest pseudo-octahedral structure with D_{4h} symmetry [20-22].

The complex $[\text{Zn}_2\text{L}_2(\text{H}_2\text{O})_4]$ is stable upto 160°C indicating coordinated nature of all the four water molecules. Thereafter the complex starts losing its mass gradually and at 220°C loses two water molecules (2.94% experimental and 3.03% theoretical), evident from the sharp endothermic peak on the DTA (Graph 1). At 360°C the compound further registers a mass loss of 3.1% (theoretical) corresponding to the loss of two water molecules against a mass loss of 3.34% (experimental). Thereafter the complex loses its mass slowly upto 440°C and after that the thermogram becomes a straight line indicating no further loss of mass up to 1000°C (Graph 2).



Graph 1: DTA graph of $[\text{Zn}_2\text{L}_2(\text{H}_2\text{O})_4]$



Graph 2: TGA graph of $[\text{Zn}_2\text{L}_2(\text{H}_2\text{O})_4]$

The ${}^1\text{H}$ nmr spectra of the ligands (LH_2) and ($\text{L}'\text{H}_2$) display unsymmetric complex patterns between $\delta 7.1\text{-}8.5$ and $\delta 6.6\text{-}8.0$ due to twenty and sixteen phenyl protons respectively.

The e.s.r. spectrum of the complex $[\text{Cu}_2\text{L}_2(\text{H}_2\text{O})_4]$ was recorded at X-band. The "g" value (2.08467) was evaluated using Kneubuhl's method [23]. Since the 'g' value is less than 2.3, it can be suggested that the complex is largely covalent [24]. Further this value is consistent with the mixed Cu-O and Cu-N bonded copper complex.

Basing upon the above experimental evidence it can be suggested that both the azo dyes behave as bis-bidentate chelating ligands having O N-Z-N O potential donor atoms which can bind two metal atoms on either side to form dinuclear complexes (Fig. 2).

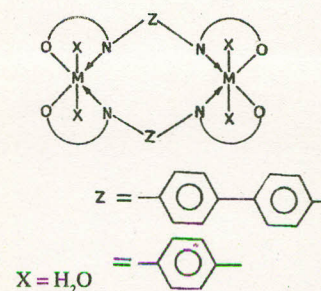


Fig. 2.

References

1. K.N. Gaind and J.K. Khanna, *Indian J. Pharm.*, **26**, (1964), 34.
2. K.N. Gaind and S.K. Gulati, *Indian J. Pharm.*, **28**, 272 (1966).
3. L.S. Goodman and A. Gilman, *The Pharmacological Basis of Therapeutics*, (Mc Milani; New York, 1970), 4th ed., pp.111.
4. M.M. Mustafa, H.A. Dessouki, A.K. Ghoneium and R.M.

- Issa, J. Indian Chem. Soc., **61**, 286 (1984).
5. A. Butualia, Chem. Abstr., 1339 ab (1970).
 6. D.V. Raman Rao, R.N. Das and R.N. Murty, J. Indian Chem. Soc., **61**, 181 (1984).
 7. B.B. Mahapatra and D.K. Das, Acta. Chem. (Hungarica), **124**, 387 (1987).
 8. B.B. Mahapatra, D.K. Das, D. Panda, C.D. Rao, A.L. Dutta and S. Guru, Indian J. Chem., **264**, 66 (1987).
 9. B.B. Mahapatra and D.K. Das, Synth. React. Inorg. Met. Org. Chem. **18**, 965 (1988).
 10. B.B. Mahapatra, B.K. Patel and K.C. Satpathy Actachim (Hungarica), **126**, 207 (1989).
 11. B.B. Mahapatra and S.K. Kar, J. Ind. Chem. Soc., **68**, 542 (1991).
 12. B.B. Mahapatra, A.K. Behera and P.K. Bhoi, Asian J. Chem., **4**, 873 (1992).
 13. R.B. King, Inorg. Chem., **5**, 300 (1966).
 14. R.K. Bajaj, G.S. Sodhi and N.K. Kaushik, Polyhedron, **3**, 3845 (1984).
 15. G.S. Sodhi, A.K. Sharma and N.K. Kaushik, J. Organomet. Chem., **238**, 177 (1982).
 16. Gamo, Bull. Chem. Soc., **34**, 760 (1961).
 17. J.K. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds*, (Plenum Press, New York, 1971).
 18. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, (Elsevier Amsterdam, 1968).
 19. C.K. Jorgensen, Acta. Chem. Scand., **10**, 887 (1966).
 20. A.B.P. Lever, Coord. Chem. Rev., **3**, 119, (1968).
 21. P.M. Borrmann, T. Chiners and K.N. Mahadev, J. Chem. Soc. Chem. Commun., 503 (1972).
 22. C.R. Hare and C.J. Ballhausen, J. Chem. Phys., **40**, 788 (1984).
 23. F.K. Kneulbuhl, J. Chem. Phys., **33**, 1074 (1960).
 24. D. Kivelson and R. Neiman, J. Chem. Phys., **35**, 149 (1961).