

Manganese(II), Cobalt(II), Nickel(II), Copper(II) & Mercury(II) Complexes with 5-(2-Hydroxyphenyldiazo)salicylaldehyde

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Received 18 February 1986; revised and
accepted 3 June 1986

5-(2-Hydroxyphenyldiazo)salicylaldehyde, a chelating bis-bidentate azodye, forms polymeric complexes with manganese(II), cobalt(II), nickel(II), copper(II) and mercury(II) ions. These compounds have been characterised on the basis of elemental analysis, conductance, magnetic susceptibility, IR and electronic spectral and molecular weight data. Cobalt(II) and manganese(II) complexes are octahedral, nickel(II) and copper(II) complexes are square-planar and the mercury(II) complex possess tetrahedral geometry. All the complexes are polymeric in nature.

Although many complex compounds with azodyes as ligands have been reported¹, little work has been done on the complexes of chelating bis-bidentate azodyes. The present note reports the preparation and characterisation of a new dibasic bis-bidentate chelating azodye, 5-(2-hydroxyphenyldiazo)salicylaldehyde, and its complexes with divalent metal ions manganese, cobalt(II), nickel(II), copper(II) and mercury(II).

All the chemicals used were of AR grade. The azodye ligand was prepared by the usual method². The metal chelates were isolated by reacting ethanolic so-

lutions of the metal chloride and the ligand in stoichiometric proportion and refluxing for 0.5 h. The products were filtered, washed with EtOH, Et₂O and dried *in vacuo*.

Metal, nitrogen, carbon and hydrogen contents of the complexes were estimated by standard procedures. Conductances were measured using 10⁻³M dimethylformamide solutions of the complexes. Magnetic susceptibility measurements were made on solid samples by the Gouy method at room temperature. The IR spectra were recorded in KBr phase on a Perkin-Elmer 398 spectrophotometer. The electronic spectra were recorded using 10⁻³MDMF solutions of the polymeric complexes on a Hilger and Watt Uvispek spectrophotometer. Molecular weights of the complexes were determined by the Rast method. Analysis, magnetic susceptibility and molecular weight data are recorded in Table 1.

All the complexes have high melting points (> 280°C) and are insoluble in common organic solvents but sparingly soluble in dimethylformamide. Non-electrolytic nature of the complexes is indicated by their low conductance values (5-9 ohm⁻¹cm²mol⁻¹).

The structurally important IR bands like $\nu(\text{C-O})$, $\nu(\text{C=O})$, $\nu(-\text{N}=\text{N}-)$, $\nu(\text{M-O})$ and $\nu(\text{M-N})$ have been assigned which throw light on the structural features of the new azodye ligand and its mode of bonding to the metal ions. A broad band at 3450 cm⁻¹ in the free ligand is ascribed to $\nu(\text{OH})$ vibration, lowered due to intramolecular O—H...O and O—H...N hydrogen bonding. The disappearance of this band in metal chelates is indicative of deprotonation of phenolic hy-

Table 1—Analytical, Colour, Magnetic Moment and
Molecular Weight Data

Compound (Colour)	Found (Calc.) %				$\mu_{\text{eff. (B.M.)}}$	Molec. weight Found (Calc.)
	M	N	C	H		
LH ₂ (Deep brown)	—	11.3 (11.57)	64.3 (64.46)	3.98 (4.13)	—	238 (240)
[CoL ₂ .2H ₂ O] _n (Reddish brown)	17.2 (17.5)	8.1 (8.36)	46.4 (46.58)	3.5 (3.58)	4.8	638.00 (665.86)
[NiL] _n (Red)	19.3 (19.5)	9.2 (9.44)	52.1 (52.22)	2.5 (2.67)	—	545.00 (593.42)
[CuL] _n (Coffee colour)	20.8 (20.9)	9.1 (9.22)	51.3 (51.40)	2.4 (2.63)	1.7	578.00 (603.00)
[MnL ₂ .2H ₂ O] _n (Deep brown)	16.2 (16.5)	8.2 (8.44)	46.9 (47.14)	3.5 (3.62)	5.5	622.00 (657.86)
[HgL] _n (Dark grey)	45.35 (45.47)	6.2 (6.37)	35.3 (35.41)	1.7 (1.81)	—	835.00 (877.08)

LH₂ = 5-(2-Hydroxyphenyldiazo)salicylaldehyde)

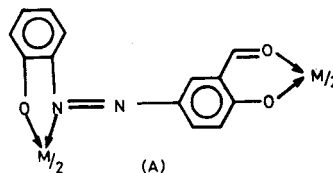
droxyl groups and consequent dibasic nature of the ligand. The band occurring at 1340 cm^{-1} in the ligand may be assigned to $\nu(\text{C-O})$ vibration which shifts to higher frequency region ($\sim 1350\text{ cm}^{-1}$) on complexation indicating bonding through both the phenolic oxygen atoms. The ligand shows a band at 1540 cm^{-1} due to the $\nu(-\text{N}=\text{N}-)$ mode. In the metal chelates this frequency is lowered to $\sim 1530\text{ cm}^{-1}$ indicating the bonding of the azo nitrogen to the metal atom. The $\nu(\text{C-N})$ vibration appearing at 1490 cm^{-1} in the ligand suffers a downward shift of $\sim 10\text{ cm}^{-1}$ thereby supporting the coordination of one of the azo nitrogen atoms to the metal ion. The observation of a band at 1640 cm^{-1} in the azodye is due to the $\nu(\text{C=O})$, and on complexation it shifts to $\sim 1620\text{ cm}^{-1}$ showing the bonding of the carbonyl oxygen atom to the metal atoms. In the case of cobalt(II) and manganese(II) complexes, presence of coordinated water molecule is shown³ by the occurrence of a broad band near 3400 cm^{-1} followed by two weak bands at ~ 860 and $\sim 760\text{ cm}^{-1}$ assigned to the OH stretching, rocking and wagging vibrations, respectively. The conclusive evidence of bonding is provided by the occurrence⁴ of $\nu(\text{M-O})$ and $\nu(\text{M-N})$ bands at ~ 450 and 510 cm^{-1} respectively in the far IR spectra of the complexes.

The cobalt(II), copper(II) and manganese(II) complexes exhibit magnetic moment values expected for an octahedral stereochemistry. The degree of polymerization of the metal complexes was found to be 2.

The electronic spectrum of cobalt(II) complex shows bands at 9010 , 18350 and 21250 cm^{-1} assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $\rightarrow {}^4A_{2g}(F)$ and $\rightarrow {}^4T_{1g}(P)$ transitions respectively. The calculation of spectral parameters like $B(832)\text{ cm}^{-1}$, $10 Dq(9340)\text{ cm}^{-1}$, $\beta_{35}(0.85)$ and $\nu_2/\nu_1(2.01)$ suggests an octahedral structure⁵. The nickel(II) complex exhibits two bands at 16500 and 17600 cm^{-1} attributable to the transitions ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and $\rightarrow {}^1E_g$ respectively which are consistent with a square-planar configuration^{6,7}. The diamagnetic nature of the complex also supports this formulation. Mn(II) complex shows four electronic absorption bands at 18400 , 22500 , 24350 and 27600

cm^{-1} assignable to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $\rightarrow {}^4T_{2g}(G)$, 4E_g and ${}^4T_{2g}(D)$ transitions, respectively, suggesting⁸ a high-spin octahedral configuration for the complex. Copper(II) complex exhibits a broad absorption band at 14100 cm^{-1} indicating a square planar geometry⁹⁻¹².

On the basis of above considerations, it is suggested that the azodye ligand behaves as a bisbidentate dibasic (LH_2) anion bonding to the metal ions through two phenolic oxygen, diazo nitrogen and carbonyl oxygen atoms. The following tentative structure (A) can be proposed for the repeating unit of the polymeric metal chelates.



The authors are thankful to Dr. B. Pradhan, Assistant Professor, R.E.C., Rourkela for supplying magnetic data and Prof. G.B. Behera for the IR spectra of the compounds.

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