

# Coordination Chain Polymers of Schiff Base Derived from Ortho-Aminobenzoic Acid and Terephthalaldehyde

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The Schiff base synthesised by condensing *o*-aminobenzoic acid and terephthalaldehyde in ethanolic medium, forms complexes  $[ML_2H_2O]_n$  with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). These were obtained by refluxing the metal : ligand :: 1 : 1 in dimethylformamide. The polymeric octahedral structures of the insoluble complexes have been arrived at on the basis of elemental, ir and rs studies, magnetic measurements and thermal analysis.

THIS paper is in continuation of earlier publications<sup>1, 2</sup> from these laboratories, on the syntheses of new coordination polymers. The present communication describes the synthesis of Schiff base by the condensation of *o*-aminobenzoic acid and terephthalaldehyde, and the syntheses of metal chelates with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The structures of the polymeric metal-chelates were established from data on elemental analyses, infra-red spectra, electronic spectra, magnetic susceptibility and thermogravimetric measurements.

## Experimental

Chemicals employed were of analytical reagent grade and used without further purification.

Ethanolic solutions of *o*-aminobenzoic acid (13.7 gms) and terephthalaldehyde (6.7 gms) were mixed and a yellow crystalline solid Schiff base was obtained immediately. The mixture was heated on water bath for 1 hr and the solid filtered, washed successively with water and ethanol, and dried. It is insoluble in common organic solvents like benzene, chloroform, acetone, but highly soluble in dimethylformamide. Calculated for  $C_{22}H_{15}N_2O_2$ : C, 70.96; H, 4.30; N, 7.52. Found: C, 70.80; H, 4.54; N, 7.28%.

The metal acetate in dimethylformamide (DMF) was slowly added to a DMF solution of the ligand. In all the cases precipitation occurred almost immediately upon mixing the two reactants, but the mixtures were refluxed for 4 hr at 120° to ensure complete precipitation and allowed to cool overnight at room temperature. The metal chelates were filtered, washed with DMF and dried. The polymeric chelates are insoluble in all common organic solvents like acetone, ethanol, chloroform, methanol, benzene, DMF and DMSO.

Results of C, H, N and M analyses are given in Table 1.

TABLE I—ANALYTICAL DATA

Complex	Colour	Decomposition Temperature (°C)	Elemental analysis: Found (Calc) %			
			C	H	N	M
(MnL <sub>2</sub> H <sub>2</sub> O) <sub>n</sub>	Yellowish brown	360	58.23 (58.62)	2.76 (3.10)	5.89 (6.10)	12.83 (12.19)
(CoL <sub>2</sub> H <sub>2</sub> O) <sub>n</sub>	Greenish brown	400	56.51 (56.78)	3.66 (3.87)	5.73 (6.02)	12.08 (12.66)
(NiL <sub>2</sub> H <sub>2</sub> O) <sub>n</sub>	Yellow	400	56.54 (56.81)	3.47 (3.87)	5.58 (6.02)	12.25 (12.63)
(CuL <sub>2</sub> H <sub>2</sub> O) <sub>n</sub>	Green	300	56.00 (56.23)	3.26 (3.83)	5.25 (5.96)	13.38 (13.52)
(ZnL <sub>2</sub> H <sub>2</sub> O) <sub>n</sub>	Bright yellow	420	56.63 (56.00)	3.69 (3.81)	5.27 (5.93)	14.13 (13.87)
(CdL <sub>2</sub> H <sub>2</sub> O) <sub>n</sub>	Yellow	460	50.62 (50.92)	3.28 (3.47)	6.04 (5.40)	21.47 (21.68)

Infra-red spectra were recorded in KBr pellets in the range of 4000-400 cm<sup>-1</sup> using a Perkin-Elmer-577 Grating Infra-red Spectrophotometer.

Electronic reflectance spectra were obtained on a manual reading spectrophotometer using MgO.

Magnetic susceptibility measurements were made at room temperature by the Faraday method.

Thermal decomposition was studied by heating the samples at the rate of 10°/min and heated up to 800°.

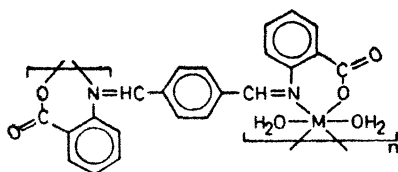
## Results and Discussion

The ir spectrum of the Schiff base shows a weak band at 2640-2500 cm<sup>-1</sup>, which is assigned to hydrogen bonded O-H stretching of carboxylic groups<sup>3</sup>. This band vanishes in the spectra of

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complexes, indicating the involvement of carboxylic OH in complexation. The strong band at 1680 and 1350  $\text{cm}^{-1}$  due to C=O and C-OH stretchings in the ligand<sup>4</sup>, disappear on complexation, and are replaced by two equivalent C-O bonds intermediate in force constant between C=O and C-OH<sup>5</sup>. Asymmetric and symmetric COO stretchings appear at 1540 and 1385, 1550 and 1380, 1555 and 1390, 1545 and 1400, 1540 and 1390, and 1540 and 1380  $\text{cm}^{-1}$  in Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes respectively. Nakamoto has pointed out that the separation may be taken as covalence in M-O bond. The O-H in-plane and out-of-plane deformations at 1285 and 950  $\text{cm}^{-1}$  in the Schiff base vanishes in the complexes supporting coordination through COOH. Ligand shows C=N stretching at 1625  $\text{cm}^{-1}$  which shifts to 1620-1615  $\text{cm}^{-1}$  on complexes indicating the involvement of azomethine N in coordination<sup>7</sup>. The bands at 3500-3400, 1695-1690 and 840-820  $\text{cm}^{-1}$  are attributed to O-H stretching, HOH bonding and M-OH<sub>2</sub> stretching<sup>6</sup>.

The complexes of bivalent metals with the Schiff base are extremely insoluble. The elemental analyses are in reasonably good agreement with a ligand to metal ratio 1 : 1, which is approached as polymerization is achieved. The following structure may be suggested.



This ligand : metal ratio does not permit a monomeric complex to exist since the four coordinating groups of one ligand molecule cannot attach to a single metal ion and attachment of the two groups at one end of the molecule would not satisfy the charge requirement of the metal(II) ions.

The positions of *d-d* bands and their assignments<sup>8</sup> are given in Table 2. A magnetic moment

TABLE 2—ELECTRONIC SPECTRA AND MAGNETIC MOMENT

Complex	$\mu_{\text{eff}}$ (BM)	Band Position (nm)	Assignment
Mn(II)	5.52	580	${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$
		500	${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$
		455	${}^6A_{1g} \rightarrow {}^4E_g(G)$
		360	${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$
		340	${}^6A_{1g} \rightarrow {}^4E_g(D)$
Co(II)	5.20	820	${}^4T_{1g}(F) \rightarrow {}^4E_g$
		475	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
Ni(II)	3.19	900	${}^3A_{2g} \rightarrow {}^3T_{2g}$
		650	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
Cu(II)	1.80	400	${}^2A_{1g} \rightarrow {}^2T_{1g}(P)$
		500	${}^2E_g \rightarrow {}^2T_{2g}$

value of 5.52 BM for Mn(II) is less than that generally observed for octahedral complexes. This may be explained by the assumption of antiferromagnetic interaction between the Mn(II) ions in solid state<sup>9</sup>. Co(II) exhibits a magnetic moment of 5.20 BM as expected for octahedral complexes<sup>10</sup>. In the drs, the bands at 475 and 820 nm have been assigned for octahedral Co(II) but the transition  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$  is not seen due to limited spectral range. Ni(II) complex is octahedral as evidenced by drs and magnetic moment of 3.19 BM<sup>10</sup>. Cu(II) shows a broad band at 500 nm, assigned to  ${}^2E_g \rightarrow {}^2T_{2g}$  for distorted octahedral complex; the broadening of band may be due to Jahn-Teller effect<sup>11</sup>.

The complexes lose ligand water at 220-240°; the loss corresponds to calculated amount for dihydrates. These decompose at high temperatures, the order of thermal stability being Cd(460°) > Zn(420°) > Co(400°) ≈ Ni(400°) > Mn(360°) > Cu(300°). This is in good agreement with the assumption that half-filled *d*<sup>5</sup> and completely-filled *d*<sup>10</sup> metal complexes are more stable<sup>12</sup>, however, Mn(II) does not follow this rule. The residues do not conform to the metal oxide alone indicating that the organic part does not volatilize completely even at 800°.

The molecular weights of these metal chelates could not be ascertained for lack of their solubility in common organic solvents. The extreme insolubility and the high thermal stability of the complexes suggest their polymeric nature.

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