

**Cu(II), Ni(II) AND Co(II) COMPLEXES OF DISALICYLALDIMINE OXAMIDE AND N, N'-Di (O-HYDROXYACETOPHENONE IMINE) OXAMIDE, THE SCHIFF BASES DERIVED FROM OXALDIHYDRAZIDE AND SALICYLALDEHYDE AND O-HYDROXYACETOPHENONE**

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**ABSTRACT**

Cu(II), Ni(II) and Co(II) complexes of the title ligands have been synthesized and characterized by analytical, spectroscopic and magnetic moment data. The complexes are coloured and insoluble in common organic solvents and decompose above 250° C. Cu(II) complexes are planar or pseudo-octahedral while Ni(II) and Co(II) complexes have octahedral stereochemistry. Some of them show subnormal magnetic moments. The ligands coordinate to Cu(II) in enol form and Ni(II) and Co(II) in the keto form.

**INTRODUCTION**

RECENTLY, a number of publications have appeared on the transition metal complexes of Schiff bases derived from monoacylhydrazines<sup>1-5</sup>. These bases act either as a bidentate or tridentate ligands and some of their compounds show subnormal magnetic moments. The dihydrazides having two-CONHNH<sub>2</sub> groups have been reported to coordinate through  $\text{>NH}^6$ . Since no previous work on the Schiff bases derived from the organic acid dihydrazides has been reported, the present paper, therefore, describes Cu(II), Ni(II) and Co(II) complexes of the title ligands.

**MATERIALS AND METHODS**

*Preparation of the ligands.*—Oxalldihydrazide<sup>7</sup>, m.p. 234° (Lit. 232°), was prepared by the reaction of diethyloxalate diluted with ethanol and hydrazine hydrate in 1 : 2 molar ratio. The product was filtered and washed with alcohol. The ligands H<sub>2</sub>L and H<sub>2</sub>J were prepared by mixing dilute ethanolic solution of oxalldihydrazide and salicylaldehyde and O-hydroxyacetophenone in 1 : 2 molar ratio. The products were filtered, washed with hot water to free from oxalldihydrazide and finally with ethanol and dried at 110°.

H<sub>2</sub>L, m.p. >250° Found (Calcd. %) C = 58.30 (58.99); H = 4.20 (4.29); N = 16.03 (16.50).

H<sub>2</sub>J, m.p. >250° Found (Calcd. %) C = 60.27 (61.02); H = 5.06 (5.10); N = 15.50 (15.82)

*Preparation of the complexes.*—Since both the ligands are insoluble in water and very slightly soluble in ethanol, the complexes were prepared by taking metal : ligand (8 : 1) mixture in water or ethanol and stirring at room temperature (30°) or above (70°) for 24–36 hr. The products were filtered, washed with water or alcohol and dried at room temperature over anhydrous calcium chloride.

Analytical procedures and instruments used were same as reported earlier<sup>5</sup>. The data are summarized in Tables I and II.

**RESULTS AND DISCUSSION**

Cu(II) reacts with H<sub>2</sub>L both in alcoholic and aqueous media while Ni(II) and Co(II) fail to react with it. H<sub>2</sub>J, however, reacts with Cu(II), Ni(II) and Co(II) chloride in alcoholic medium but only Cu(II) complex could be isolated from aqueous medium.

All the complexes have 1 : 1 stoichiometry. The complexes prepared in alcoholic medium have one chloride ion present while the complexes prepared in aqueous medium are free from the anion. All the complexes are coloured and insoluble in common organic solvents and decompose or melt with decomposition above 250° C. Loss of weight at 110° corresponds to number of water molecules in the lattice structure or weakly coordinated water molecules. The solubility and high decomposition temperature indicate the polymeric nature of complexes in solid state<sup>8</sup>.

*Electronic Spectra*

The chromophores  $\text{>C=O}$ ,  $\text{>C=N-}$  in conjugation with benzene nucleus, shift the primary and secondary bands of benzene at 204 and 256 nm respectively to longer wavelength<sup>9</sup>. In H<sub>2</sub>L, the 204 nm band appears at 200 nm and the other band at 256 nm shifts to 295 nm. A band characteristics of the salicylaldehydato group<sup>10</sup> appears at 365 nm. In H<sub>2</sub>J, the two bands appear at 225 and 310 nm respectively.

In metal complexes, the absorption bands are so much red shifted that the characteristic bands of salicylaldehyde group appears as high as 400 nm. Such a large red shift may be due to metal-ligand bonds. The Cu(II) complexes (nos. a, b, c and f), in addition to the ligand bands, show bands around 705, 685, 625 and 570 nm respectively. The octahedral complexes of Cu(II) show bands around 800 nm<sup>11</sup> in some olive green square planar Cu(II) chelates<sup>12</sup>. The appearance of a high energy band around 400 nm or 450 nm

TABLE I

Analytical, electronic and magnetic moment data of disalicylaldimine oxamide ( $H_2L$ ) and  $N, N'$ -di(O-hydroxyacetophenone imine) oxamide ( $H_2J$ ) complexes of Cu(II), Ni(II) and Co(II)

Sl. No.	Complex and Colour	Melting point/decomposition point	Analysis (%)				Magnetic moment/ $\mu_{\text{eff}}$ B.M.	Electronic bands/ $\lambda_{\text{max}}$ nm
			Metal	Nitrogen	Ligand	Acid		
(a)	Cu (HL) Cl.2H <sub>2</sub> O Darkgreen	>250 m	14.2 (13.8)	12.7 (12.2)	70.2 (70.8)	8.0 (7.7)	1.9	255, 345, 463, 705
(b)	CuL.2H <sub>2</sub> O Darkgreen	>250 m	14.7 (15.0)	13.2 (13.2)	77.0 (76.5)	..	1.8	220, 255, 340, 450, 475, 685
(c)	Cu (HJ) Cl.2H <sub>2</sub> O Darkgreen	>250 m	13.0 (13.5)	11. (11.9)	75.8 (75.1)	7.7 (7.6)	2.0	245, 305, 400, 625
(d)	Ni (HJ) Cl.2H <sub>2</sub> O Green	>250 m, d	13.5 (13.1)	12.0 (11.6)	73.8 (73.0)	6.9 (7.3)	3.0	225, 290, 610, 1000
(e)	CO (HJ) Cl.2H <sub>2</sub> O Purple	>250 m, d	12.8 (13.1)	11.3 (11.6)	73.2 (73.0)	7.2 (7.3)	5.1	230, 310, 525, 660, 687
(f)	CuJ.2H <sub>2</sub> O Darkgreen	>250 m	13.8 (14.1)	12.0 (12.4)	77.0 (77.9)	..	1.73	245, 325, 390, 570

m = melts.

m, d = melts with decomposition.

TABLE II

Some important infrared frequencies of  $H_2L$  and  $H_2J$  and their metal complexes (Frequencies in  $\text{cm}^{-1}$ )

Sl. No.	Complexes	$\nu(\text{OH})$ + $\nu(\text{NH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{NCO})$	Amide III	$\nu(\text{C-O})$	$\nu(\text{N-N})$
(a)	$H_2L$	3285 3210	1665	1600	..	1372	1255	1033
(a)	Cu (HL) Cl.2H <sub>2</sub> O	3670 3373	..	1598	1546	1380	1275 1250	1050
(b)	CuL.2H <sub>2</sub> O	3416	..	1608	1542 1533 1525	1375	1250	1037
	$H_2J$	3300	1684 1646	1604	..	1372	1242 1233	1020
(c)	Cu (HJ) Cl.2H <sub>2</sub> O	3526 3450 3350	..	1595 1580	1540 1512	1370	1260 1235	1020
(d)	Ni (HJ) Cl.2H <sub>2</sub> O	3516 3416 3296 3150	1675 1644	1600	..	1375	1258 1242 1220	1020
(e)	CO (HJ) Cl.2H <sub>2</sub> O	3440 3275	1650	1605	..	1375	1245 1235	1030
(f)	CuJ.2H <sub>2</sub> O	3605 3365 3300	..	1590	1540 1520	1360	1275 1242	1010

in some Cu(II) complexes has been a subject-matter of considerable discussion and it has been related to the presence of binuclear structures of Cu(II) complexes. Keeping the above facts and the observed magnetic moments in view, it is plausible to assign a molecularly associated or oxo-



bridged structures for the Cu(II) complexes (nos. *b*, *c*, and *f*) while in the complex (no. *a*) the band observed at 705 nm indicates it to have a pseudo-octahedral structure. The octahedral Ni(II) complexes<sup>13</sup> show three bands due to  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  (F),  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P) transitions. In the Ni(II) complex (no. *d*), the first two bands are observed at 1000, 610 nm respectively confirming its octahedral structure. In octahedral Co(II) complexes several transitions are expected but all of them are seldom observed<sup>11</sup>. The colour and absorption bands of Co(II) complex (no. *e*) indicate an octahedral stereochemistry.

#### Magnetic Moment

Cu(II) complexes (nos. *a* and *c*) synthesized in alcoholic medium are normal paramagnetic corresponding to one unpaired electron. The Cu(II) complexes (nos. *b* and *f*) prepared in aqueous medium have magnetic moment value slightly less than the value for one unpaired electron. The low magnetic moments may be due to some M-M interactions *via* oxo-bridges. The magnetic moment values of Ni(II) and Co(II) complexes correspond to two and three electrons respectively in octahedral environment.

#### Infrared Spectra

Coordination of monoacylhydrazones to metal ions through  $\text{>C=O}$  and  $\text{>C=N}$  lowers  $\nu(\text{C=O})$  and  $\nu(\text{C=N})$ <sup>13</sup>. When these ligands undergo enolization, the  $\text{>C=O}$  and  $\text{>NH}$  groups are destroyed giving rise to  $-\text{C(OH):N}-$  group in which  $\nu(\text{OH})$ ,  $\nu(\text{C-O})$ , and  $\nu(\text{C=N-})$  should appear. Reaction with metal ions in enol form results in  $-\text{N=C-O}^{14}$  and  $\text{>C=N-N=C(1-3)}$  group vibrations.

In  $\text{H}_2\text{L}$  and  $\text{H}_2\text{J}$ , the bands in region 3000–3300  $\text{cm}^{-1}$  [ $\nu(\text{OH}) + \nu(\text{NH})$ ] and 1700–1650  $\text{cm}^{-1}$  [ $\nu(\text{C=O})$ ] indicate that the ligands exist primarily in the keto form. These spectra indicate the presence of strong intramolecular H-bonding in the molecule. In Cu(II) complexes broad band appears in the region 3300–3600  $\text{cm}^{-1}$  indicating the presence of free  $-\text{OH}$  group of either phenolic  $-\text{OH}$  or lattice water molecules. The  $\nu(\text{C=O})$  stretching frequency originally present in the ligands has disappeared in these complexes ruling out the possibility of coordination through  $\text{C=O}$  group. A very sharp and intense band at 1600  $\text{cm}^{-1}$  is observed indicating the presence of coordinated azine group  $\text{>C=N-N=C(}$  while the  $\text{NC(}$  group vibrations observed at about 1540  $\text{cm}^{-1}$  confirm the enolization process. The bands at 1255  $\text{cm}^{-1}$  in  $\text{H}_2\text{L}$  and 1242 and 1233  $\text{cm}^{-1}$  in  $\text{H}_2\text{J}$ ,

assigned to  $\nu(\text{C-O})$ , shift to higher frequencies on chelation. It appears the ligand chelates with Cu(II) in enol form.

The i.r. spectra of Ni(II) and Co(II) complexes (nos. *d* and *e*) show a broad band in the region 3500–3300  $\text{cm}^{-1}$  and a sharp and strong peak around 3300  $\text{cm}^{-1}$  which may be assigned to free  $\nu(\text{OH})$  of ligand or lattice water and  $\nu(\text{NH})$  respectively. The  $\nu(\text{C=O})$  stretching frequency originally present at 1684, 1646  $\text{cm}^{-1}$  shifts to lower frequency by 10–30  $\text{cm}^{-1}$  indicating coordination of the  $\text{>C=O}$  group. Amide II band in  $\text{H}_2\text{J}$  appears at 1560  $\text{cm}^{-1}$  but splits up in complexes and shows positive as well as negative shift. The decrease in frequency of amide II may be related to coordination of  $\text{>C=O}$  group. Amide (III) band at 1372  $\text{cm}^{-1}$  and  $\nu(\text{C-O})$  at 1242 and 1233  $\text{cm}^{-1}$  in  $\text{H}_2\text{J}$  shift to higher frequencies in metal complexes.

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1. Narang, K. K. and Aggarwal, A., *Inorg. Chim. Acta*, 1974, 9, 137; *Indian J. Chem.*, 1975, 13, 1072.
2. Iskander, M. F., El-Aggan, A. M., Refaat, L. S. and Elsayed, L., *Inorg. Chim. Acta*, 1975, 14, 167.
3. —, Elsayed, L. and Lasheen, M. A., *Ibid.*, 1976, 16, 147.
4. Biradar, N. S. and Havinale, B. R., *Ibid.*, 1976, 17, 157.
5. Narang, K. K. and Lal, R. A., *Indian J. Chem.*, 1976, 14 A, 442.
6. Dutta Ahmad, A., Mandal, P. K. and Roy Chaudhary, N., *J. Inorg. Nucl. Chem.*, 1966, 28, 2951.
7. Prager, B. and Jacobson, P., *Beilstein Handbuch Der Organischen Chemie*, 1920, 2, 559.
8. Ginsberg, A. P., Martin, R. L. and Sherwood, R. C., *Inorg. Chem.*, 1968, 7, 932.
9. Jaffé, H. H. and Orchin Milton, *Theory and Applications of Ultraviolet Spectroscopy*, John Wiley, New York, 1967, p. 164.
10. Rohatpi, K. K. and Sengupta, S. K., *J. Inorg. Nucl. Chem.*, 1972, 34, 3061.
11. Dunn, T. M., "The visible and ultraviolet spectra of complex compounds," In: *Modern Coordination Chemistry*, Eds. J. Lewis and R. G. Wilkins, Interscience, New York, N.Y., 1960.
12. Sacconi, L. and Ciampolini, M., *J. Chem. Soc.*, 1964, 276.
13. Issa, R. M., El-Shazly, M. F. and Iskander, M. F., *Z. Anorg. Allg. Chem.*, 1967, 98, 354.
14. Mashima, M., *Bull. Chem. Soc. Japan*, 1962, 35, 338.