

COPPER(II), NICKEL(II) AND COBALT(II) COMPLEXES OF DISALICYLALDIMINE PHTHALAMIDE AND Di(*o*-HYDROXYACETOPHENONEIMINE) PHTHALAMIDE

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ABSTRACT

Copper(II), nickel(II) and cobalt(II) complexes of the disalicylaldimine phthalamide (H_4J) and di (*o*-hydroxyacetophenoneimine) phthalamide (H_4K) of the composition $Ni(H_3J)Cl$, $Cu(H_2J)$ and $M_2L \cdot nH_2O$ (where $M = Cu^{II}$, Ni^{II} and Co^{II} , $H_4L = H_4J$ and H_4K) were prepared and characterized by analysis, infrared and electronic spectra and magnetic data. The complexes are insoluble, decompose above 250° and show anomalous magnetic moments. Copper(II) and nickel(II) complexes are pseudo-octahedral. The ligands bind the metal ions through phenolic, carbonyl and imino groups.

INTRODUCTION

IN continuation of our study on acylhydrazine-Schiff base complexes¹ copper(II), nickel(II) and cobalt(II) complexes of two new Schiff bases derived from phthalic acid dihydrazide and salicylaldehyde or *o*-hydroxyacetophenone are reported in the present paper.

EXPERIMENTAL

Phthalic acid dihydrazide, mp $> 250^\circ$, was prepared by reacting diethylphthalate and hydrazine hydrate. The ligands (H_4J) and (H_4K) were prepared by condensing the dihydrazide with salicylaldehyde or *o*-hydroxyacetophenone in 1 : 2 molar ratio in ethanol, recrystallized from ethanol and dried at 110° . (H_4J , $C_{22}H_{18}N_4O_4$, m.p. $213-215^\circ$, Found: C, 65.38; H, 4.40; N, 13.61. Req'd.: C, 65.77; H, 4.48; N, 13.93%. H_4K , $C_{24}H_{22}N_4O_4$, m.p. 199° , Found: C, 66.27; H, 5.02; N, 12.84. Req'd.: C, 67.00; H, 5.12; N, 13.02%).

The metal(II) complexes were prepared by reacting the metal(II) chlorides or acetates in 1:1 or 4:1 (M:L) ratios in aqueous or ethanolic medium. The complexes were not obtained in all the cases. The composition of the complexes was established by elemental analysis and ligand estimations. The instruments used for physico-chemical measurements were the same as described earlier¹. Analytical, electronic and magnetic data of the complexes are summarized in Table I and some important i.r. bands are given in Table II.

RESULTS AND DISCUSSION

The complexes obtained with copper(II), nickel(II) and cobalt(II) chlorides have 1:1 (M:L) stoichiometry while those with copper(II), nickel(II) and cobalt(II) acetates have 2:1 (M:L) ratio (Table I). Copper(II) complexes are either reddish brown or green and nickel(II) complexes are either green or yellowish green while the cobalt(II) complexes are reddish brown or dark red.

The complexes are insoluble in water or common organic solvents and decompose, in general, above 250° . The nickel(II) and cobalt(II) complexes are hydrated when freshly prepared but on drying in the

oven, the water molecules are lost between $110-130^\circ$ signifying their presence in lattice. The solubility and decomposition temperature of the complexes indicate the predominantly ionic character of M-L bonds in otherwise polymeric molecules.

Electronic Spectra

In copper(II), nickel(II) and cobalt(II) complexes, ligand bands at 225, 245, 300, 365 nm in H_4J and 242, 295, 375 nm in H_4K are considerably red shifted and offer good evidence of ligand bonding. Copper(II) complexes show $L \rightarrow M$ charge transfer bands between 440-500 nm responsible for their dark colour. In addition to these absorption bands, the copper(II) complexes show a broad band between 750-800 nm due to ${}^2T_{2g} \leftarrow {}^2E_g$ transition². The broadness and the position of the bands favour distorted octahedral stereochemistry due to Jahn-Teller effect.

Nickel(II) complexes (nos. 2 and 4) show bands at 1062 (ν_1), 663 (ν_2), 365 (ν_3) and 1025 (ν_1), 625 (ν_2) 420 (ν_3) nm respectively which are characteristic of octahedral complexes². The ligand field parameters (Δ , B , β , β° , ν_2/ν_1 and L.F.S.E.) for the complex $Ni(H_3J)Cl$ are 9420, 910, 0.862, 13.8, 1.603, 32.2 and for $Ni_2(J) \cdot 4H_2O$ are 9756, 937, 0.887, 11.3, 1.640 and 33.4 respectively. It is evident from these parameters that the octahedral symmetry is more perfect in neutral nickel(II) complex than in the chloro complex which in turn suggests that the chloride ion is coordinated to the metal ion. The interaction between ${}^3T_{1g}$ (P) and ${}^3T_{1g}$ (F) states³ gradually lowers the ratio ν_2/ν_1 from the theoretical value of 1.80 to 1.50-1.70 and values in the 1.60-1.70 range are common for octahedral nickel(II) complexes. The values 1.603 and 1.64 for the present nickel(II) complexes confirm the octahedral stereochemistry.

The spectra of the cobalt(II)- H_4J and $-H_4J$ complexes are quite different from those of tetrahedral, octahedral or square planar cobalt(II) complexes, but, show similarity with trigonal-bipyramidal⁴ and square-pyramidal⁵ complexes. Due to the lower symmetry of the ligand fields offered by the ligands, the bands

TABLE I

Analytical, electronic and magnetic moment data of copper(II), nickel(II) and cobalt(II) complexes of disulcylal-
aldimine phthalimide (H_4J) and di-(o-hydroxyacetophenoneimine) phthalimide (H_4K)

Sl. No.	Complex	Colour	Melting dec. point °C	Analysis (Found/Calcd. %)			Magnetic moment μ_{eff} B.M.	Electronic spectral bands, λ_{max} nm
				Metal	Nitrogen	Ligand		
1.	$Cu(H_2J)$	Reddish brown	>250 d	13.5 (13.7)	12.8 (12.8)	87.8 (86.9)	1.9	240, 290, 370, 500, 800
2.	$Ni(H_3J) Cl^*$	Green	>250 d	12.2 (11.9)	11.0 (11.3)	80.2 (80.9)	3.2	255, 300, 365, 663, 1062
3.	$Cu_2(J)$	Reddish brown	>250 m, d	23.7 (24.2)	11.0 (10.7)	73.8 (75.8)	1.2	300, 390, 440, 755
4.	$Ni_2(J) \cdot 4H_2O$	Yellowish green	>250 d	20.5 (20.1)	10.1 (9.7)	68.2 (67.7)	2.5	250, 300, 420, 625, 1025
5.	$Co_2(J) \cdot 2H_2O$	Reddish brown	>250 d	20.9 (21.3)	10.0 (10.1)	72.9 (72.1)	3.7	223, 277, 395 550
6.	$Cu_2(K) \cdot 2H_2O$	Dark green	>250 m, d	22.1 (21.6)	9.3 (9.5)	73.0 (72.3)	1.6	238, 270, 330, 475, 750
7.	$Co_2(K) \cdot 4H_2O$	Dark red	-250 d	19.5 (19.2)	9.5 (9.1)	70.1 (69.2)	4.1	240, 325, 470, 520

* % Chloride = 6.7 (7.2).

TABLE II

Some important infrared bands of ligands and their metal(II) complexes

Sl. No.	Complex	$\nu OH + \nu NH$	$\nu C=O$	$\nu C=N$	Amide II + $\nu C-O$ phenyl	νNCO	$\nu C-O$	$\nu M-O$ (phenolic)	$\nu M-O$ (carbonyl)	$\nu M-N$
1.	$Cu(H_2J)$	3250s	1640s	1620s	1570s 1562s	..	1326s 1278m 1250m	585m	445m	380vw 355w
2.	$Ni(H_3J) Cl^*$	3340m 3220m	1635msh	1620s	1560s	..	1315m 1270s	560m 535m	420w	350w
3.	$Cu_2(J)$	1610s	..	1530s	1315m	555msh	460s	350m
4.	$Ni_2(J) \cdot 4H_2O$	3600- 3100sbr	..	1620s 1608ssh	1535s	1525ssh	1305m	550m	..	317w
5.	$Co_2(J) \cdot 2H_2O$	3620m	..	1615m	1540m	1525m	1302m	..	420w	325w
6.	$Cu_2(K) \cdot 2H_2O$	3620s 3540s	..	1600ssh	1545s	1505s	..	550m	435m	355w
7.	$Co_2(K) \cdot 4H_2O$	3620m	..	1645m 1630m 1585ssh	1525s	1520s 1510s	..	550w	425msh	335ssh
H_4J		3170m	1660s	1625s	1573w 1560ssh	..	1280s 1270s 1265s
H_4K		3180s	1660s	1608	1560s	..	1264m 1255ssh 1240sh

s = strong, ssh = strong shoulder, sbr = strong broad, m = medium, msh = medium shoulder, w = weak.

are split and overlapped with one another and hence broad, suggesting a stereochemistry intermediate to that of the trigonal-bipyramidal and square-pyramidal cobalt(II) complexes.

Magnetic Measurement

Copper(II) complex (no. 1) is normal paramagnetic but nos. 3 and 6 show anomalous magnetic moments indicating either partial reduction of copper(II) to copper (I) or strong spin-spin coupling between unpaired electrons in the structural unit in the solid state. Decrease in μ_{eff} values are also indicative of M-M interactions for geometric reasons with one, two, three or even four bridging atoms⁶ due to super-exchange *via* overlap of the metal d-orbitals with the orbitals of the bridging oxygen atom.

The nickel(II) complexes (nos. 2 and 4) show μ_{eff} values 3.2 and 2.5 B.M. per nickel atom respectively. The 3.2 B.M. value is normal for octahedral complexes with no appreciable intermolecular interaction. Nickel(II) is diamagnetic in the square planar complexes. Subnormal magnetic moments in the solid state have been explained on the basis of absorption spectra⁷ by proposing mixed stereochemistries but the electronic absorption bands for the second nickel(II) complex are characteristic of nickel(II) in octahedral environment; hence the anomalous μ_{eff} values may be due to the presence of oxo-bridges.

The μ_{eff} values for the cobalt(II) complexes are 3.7 and 4.1 B.M. per cobalt atom. There is no demarcation in μ_{eff} values for trigonal-bipyramidal and square-pyramidal complexes⁸. In view of the electronic absorption bands as discussed earlier which do not favour a tetrahedral structure, pentacoordinate cobalt(II), which has μ_{eff} values usually lying in the range reported for tetrahedral complexes, may be proposed in the present complexes. M-M interactions in the solid state as a result of oxo-bridges may be the cause of lowering in μ_{eff} values.

Infrared spectra

H₄J and H₄K show a medium intensity broad band at 3170 and 3180 cm⁻¹ respectively which can be assigned to νOH and νNH vibrations. The 3250 cm⁻¹ band in copper(II) complex (no. 1) and 3220 cm⁻¹ band in nickel(II) complex (no. 2) are due to νNH only because in the neutral copper(II) complex both the -OH groups get deprotonated while only one -OH group gets deprotonated in nickel(II) complex with the second -OH group appearing at 3340 cm⁻¹. The increase in νOH frequency may be due to the release of -OH group as a result of coordination of $\geq \text{C}=\text{N}-$ to nickel(II). The positive shift of the 3μ bands by 80 and 50 cm⁻¹ in copper(II) and nickel(II) complexes as compared to the corresponding band in ligand is an indirect evidence of the coordination of $\geq \text{C}=\text{O}$ group⁹.

The strong bands present at 1660 cm⁻¹ in the two ligands are due to amide I ($\geq \text{C}-\text{O}$ group)⁹. This

group suffers a negative shift by 20-25 cm⁻¹ in the keto complexes and appears as a strong shoulder to the strong absorption band at 1620 cm⁻¹ due to $\geq \text{C}=\text{N}-$ group. Such a weakening of the $\nu\text{C}=\text{O}$ band is due to electron drain from oxygen which in consequence indicates bonding of oxygen to the metal ion. But in other complexes the strong band at 1660 cm⁻¹ in the ligands is replaced by a strong band in the 1620-1590 cm⁻¹ region with medium to weak bands on the two sides of main band. Such a strong band is due to conjugated $\geq \text{C}=\text{N}-\text{N}=\text{C} <$ group. The bands due to $\geq \text{C}=\text{N}-$ group occur at 1625 and 1605 cm⁻¹ in H₄J and H₄K respectively. The coordinated $\geq \text{C}=\text{N}-$ group absorbs in the 1620-1585 cm⁻¹ region while the uncoordinated $\geq \text{C}=\text{N}-$ group absorbs as a weak to medium band around 1645 cm⁻¹ (ref. 10).

In the complexes (nos. 3, 4, 5, 6 and 7) containing enolized ligands new bands between 1520-1500 cm⁻¹ are assigned to νNCO^{11} . A strong band present in these complexes between 1550-1530 cm⁻¹ may suggest the presence of bridged $\geq \text{C}-\text{O}$ (phenolic) group.

$\nu\text{M}-\text{O}$ (phenolic), $\nu\text{M}-\text{O}$ (carbonyl) and $\nu\text{M}-\text{N}$ may be tentatively assigned in the 570-500, 460-410 and 380-315 cm⁻¹ regions respectively.

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