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Synthesis and Magneto-Spectral Properties of Co(II), Ni(II), Cu(II) Complexes with 4-Methyl Isonitrosoacetophenone

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Studies of the complexes of transition metal ions with 4-methyl isonitrosoacetophenone (HIMAP) have been carried out on the basis of elemental analysis, molar conductance electronic spectra etc. The complexes have been assigned the formula $M(IMAP)_2$ (M = Co, Ni or Cu).

Key words: Spectral, Co(II), Ni(II), Cu(II), Complexes, 4-Methyl isonitrosoacetophenone

INTRODUCTION

The ligand 4-methyl isonitrosoacetophenone (HIMAP) having structure (Fig. 1) has been used for few analytical applications[1–3]. However, strucural studies of the complexes of transition metal ions with HIMAP have not been reported so far. Present paper describes the isolation and characterisation of the complexes of Co(II), Ni(II) and Cu(II) on the basis elemental analysis, magnetic measurement and spectral analysis.

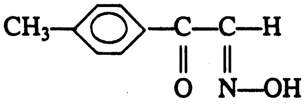

Fig. 1

EXPERIMENTAL

The chemicals used were of A.R. grade. The, ligand 4-methyl isonitrosoacetophenone were prepared by the method described in the literature[4]. The metal complexes were prepared as follows:

$Co(IMAP)_2$: Aqueous solution of cobalt nitrate and HIMAP was mixed in the molar ratio of 1 : 2 and pH of the solution was maintained 6.0–6.5 by HCl/NH_4OH. On refluxing on a steam bath for 1/2 h, a yellow coloured complex was found. It was filtered, washed, dried in air, recrystallsed from chloroform.

$Ni(IMAP)_2$: 0.652 g of HIMAP was dissolved in minimum volume of alcohol and equal volume of water was added. Similarly 0.497 g of nickel acetate hydrate was dissolved in alcohol and water mixture (1 : 1). The nickel solution was added to the reagent solution dropwise with constant stirring. The pH was adjusted to 5.0–5.6 with HCl/NH_4OH. A green coloured solid complex formed was seperated by filtration, washed with 1 : 1 aqueous alcohol, recrystallised from chloroform.

$Cu(IMAP)_2$: 0.369 g of copper acetate was dissolved in minimum quantity of alcohol and equal volume of water. Similarly 0.326 g of HIMAP was dissolved in minimum quantity of alcohol and equal volume of water. The copper solution was added to the reagent solution dropwise with constant stirring in a conical flask. The solid colnplex fonned was diggested on waterbath at 60°C. On cooling, it was filtered through filter paper, washed with 50% alcohol and dried.

Magnetic measurements of solid complexes were carried out from room temperature to liquid nitrogen temperature with Gouy balance using mercury tetra-thiocyanato cobalt(II) as standard. Diamagnetic corrections were calculated by the method given in the literature. Visible and ultraviolet spectra of the ligand and the complexes were recorded on a Schimadzu UV-2000 spectrophotometer. Infrared spectra of the ligand and the complexes were obtained on SPECORD 75 IR in potassium bromide pellets. The conductance measurements were made in nitrobenzene solution.

RESULTS AND DISCUSSION

Analytical and magnetic data of the complexes are reported in Table-1. All the complexes are quite soluble in chloroform, nitrobenzene and benzene and sparingly soluble in ethanol. Molar conductance values in nitrobenzene are also reported.

TABLE-1

ANALYTICAL DATA, MOLAR CONDUCTANCE IN NITROBENZENE AND $\mu_{eff.}$ AT ROOM TEMPERATURE*

Complex (colour)	% Analysis, found (calcd.)				μ_{eff} (B.M.)
	C	H	N	M	
$Co(IMAP)_2$	56.00	4.02	7.13	14.98	5.08
(Yellow)	(56.11)	(4.20)	(7.30)	(15.37)	
$Ni(IMAP)_2$	56.32	14.12	7.29	15.18	3.37
(Green)	(56.45)	(4.21)	(7.31)	(15.82)	
$Cu(IMAP)_2$	55.45	4.21	7.11	16.12	2.05
(Light Green)	(55.74)	(4.15)	(7.22)	(16.39)	

The results of magnetic susceptibility mesurements in a temperature range 80 K to 300 K are given in Table-2. The magnetic moments of $Cu(IMAP)_2$ is 2.05 BM at 300 K which is much less than the spin only value for one unpaired electron. It is reduced to 1.49 BM at 80 K. The low value of the magnetic moment is probably due to the antiferromagnetic nature. The high spin Ni(II) species is feebly ferromagnetic nature. The magnetic behaviour of Co(II) are inconsistent with pseudo-octahedral geometries[5].

The electronic spectral data for ligand field transition are summarised in Table-3. All the complexes show a group of three or more bands in the 47.84 kK range which can be assigned as π–π^*or ligand-metal transitions.

The electronic spectra of HIMAP in methanol shows an intense band at 47.84 kK. It splits into two strong bands 43.10 kK aud 42.79 kK. These can be explained by presuming that the symmetric π electron system cloud of HIMAP. They may be assinged to π–π* transitions.

TABLE-2
MAGNETIC SUSCEPTIBILITY OF COMPLEXES AT DIFFERENT TEMPERATURE
DIMAGNETIC CORRECTION FOR LIGAND 16.44 C.I.S. 10^{-3} kg ATOM

Absolute Temp(K)	$Co(IMAP)_2$		$Ni(IMAP)_2$		$Cu(IMAP)_2$	
	χA	μ_{eff} BM	χA	μ_{eff} BM	χA	μ_{eff} BM
80	24333	3.90	8998	2.30	3565	1.49
100	23456	4.28	7723	2.46	3220	1.58
120	22425	4.37	7202	2.60	3057	1.69
150	21340	5.00	6597	2.78	2700	1.78
215	15944	5.18	6309	3.26	2138	1.89
300	10977	5.08	5742	3.67	1792	2.05

TABLE-3
ELECTRONIC SPECTRAL DATA OF THE METAL COMPLEXES

Complex	Absorption spectra in methanol (nm)	Wave No. (kK)
$Co(IMAP)_2$	225	44.37
	290	34.38
	352	28.40
	388	25.77
$Ni(IMAP)_2$	211	47.34
	228	43.73
	335	29.80
$Cu(IMAP)_2$	206	47.84
	232	43.10
	233	42.79

The electronic spectrum of Co(II) complex (Table-4) shows very broad intense band in the 44.27 kK region and two bands in the 25–28 kK range. A shoulder also appears in the 34.38 kK region. This region screened by the intense charge transfer band exhibited a broad maxima at 25.77 kK. The electronic spectrum resembles with those of Co(II) complexes in octahedral environment[6].

The electronic spectra of nickel(II) complex (Table-4) resemble to those of tetrahedral or planar nickel(II) complexes[7].

A broad band for Cu(II) at 29.67 kK in $Cu(IMAP)_2$ suggest distorted octrahedral geometry. Distorted octrahedral species of Cu(II) complexes are also characterised by the presence of two main absorption bands[8, 9].

IR spectra of the complexes are practically identical. The frequency of some significant bands of the free ligand and of the metal complexes are reported in Table-4. The assignments for the frequencies of different groups in the metal complexes corresponding to those considered for ligands have been proposed and have been arrived at on the basis of literature data.

TABLE-4
INFRARED SPECTRAL DATA (cm^{-1}) OF HIMAP AND ITS METAL COMPLEXES

HIMAP	Co(IMAP)$_2$	Ni(IMAP)$_2$	Cu(IMAP)$_2$	Assignments
3289	—	—	—	ν(OH), Ar—H
—	3422	3424	3424	ν(Ar—H)
2923	—	—	—	aromatic (C—H)
1640	—	—	—	ν(C═O)
—	1607	1595	1589	ν(C═O), ν(C═N)
1448	1445	1452	1456	CH$_3$
1398	—	—	—	
—	1235	1200	1205	ν(N—O)
1176	1184	1175	1180	N-Oxide ν(N → O)
1005	1044	1018	1039	ν(C—O), Str
—	900	891	891	ν(N → O)
763	793	768	768	Para substitution
658	625	689	628	

The ν(O—H) of the oxime group observed at 3234 cm^{-1} in HIMAP absent in the spectra of the complexes suggesting replacement of the oxime proton by the metal ion during complexation[10]. The peak observed near 1607 cm^{-1} in spectrum of Co(IMAP)$_2$, may be assigned to the perturbed ν(C═O) and/or ν(C═N) stretching vibration involving bonding through oxygen and nitrogen donor atoms. Ni(IMAP)$_2$ and Cu(IMAP)$_2$ exibit perturbed ν(C═O) and/or ν(C═N) bands at 1595–1589 cm^{-1}. The N → O stretching vibration in the metal complexes is observed in the range 1240–1200 cm^{-1}. The N—O vibration is known to occur at lower range than of N → O and it is generally observed between 1040–1020 cm^{-1}. In Co(IMAP)$_2$, Ni(IMAP)$_2$ and Cu(IMAP)$_2$ N → O stretching frequency appears around 1235, 1200, 1205 cm^{-1} respectively. Sharp peaks which appear in the range 1300–1200 cm^{-1} are characteristics of N-oxide stretching mode in aromatic ring[11]. The complexes of Co(II), Pd(II) and Pt(II) with dimethyl glyoxime which have N-oxide linkage in their structures shows two N-oxide bands in the range 1300–1050 cm^{-1}. It may be noted that the bands at 1183, 1018 cm^{-1} in Co(IMAP)$_2$, 1175, 1044 cm^{-1} in Ni(IMAP)$_2$, and 1180–1039 cm^{-1} in Cu(IMAP)$_2$ which are atributed to the N—O stretching in the ligand[12]. The bonding modes of CH$_3$ appeared at 1447–1434 cm^{-1}.

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