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Spectral Studies of Co(II), Ni(II) and Cu(II) Complexes with *o*-(bis-Acetylacetonato) Phenylene Diamine

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A series of the complexes of the type MLB_2 [M = Co(II), Ni(II) and Cu(II) ions, B = H_2O, pyridine and α-picoline] have been synthesised with Schiff base as nitrogen and oxygen donor ligands. Characterisation of the ligand and the complexes has been done on the basis of elemental analysis, spectral studies, magnetic susceptibility and electrical conductivity measurements. The ligand has been found to coordinate through two nitrogen and two oxygen atoms. Since the complexes are found to be octahedral in nature the remaining two coordination sites of the metal are satisfied by oxygen of H_2O and nitrogen of nitrogen donor molecules such as pyridine and α-picoline.

Key words: Spectral, cobalt, nickel, copper complexes, *o*-(bis-acetylacetonato) phenylene diamine

INTRODUCTION

Much work on metal complexes has been carried out with Schiff base as nitrogen and oxygen donor ligands[1–5]. Therefore, in the present investigation we report a series of complexes of Co(II), Ni(II) and Cu(II) ions of the type MLB_2 with Schiff base as ligand H_2L.

EXPERIMENTAL

All the chemicals used in the present work were from BDH of the reagent grade. Acetylacetone and *o*-phenylene diamine obtained from Aldrich (USA) were used without further purification. For the preparation of the ligand, the procedure as reported in literature was followed[1–5]. *o*-Phenylene diamine was dissolved in dry and cold methanol and allowed to react with the methanolic solution of acetylacetone in 1 : 2 ratio under reflux on a water bath for several hours at room temperature. The resulting solution thus obtained on crystallisation produced a cream coloured solid which was then separated by filtration, washed and finally dried over KOH in a desiccator. The compound was further analysed and found to contain C = 70.59, H = 7.05 and N = 10.29% which corresponds with the m.f. $C_{16}H_{20}N_2O_2$ (Fig. 1).

The solution of the ligand in methanol was allowed to react with ethanolic solution of metal acetate in equimolar proportion under reflux on water bath for several hours at room temperature. The resulting solution on crystallisation gave

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solids of different colour for different metals. The solid was then separated by filtration, washed and finally dried over KOH in a desiccator. Acetates of Co(II), Ni(II) and Cu(II) were used separately and the complexes with each metal were prepared with the ligand H_2L in the presence of bases like H_2O, pyridine and α-picoline.

Copper was estimated iodometrically, Nickel and cobalt were estimated gravimetrically as bisdimethyl glyoximato Ni(II) and $CoSO_4$ respectively. C, H and N were estimated by semimicro-combustion method. Magnetic susceptibility of the complexes was determined by Gouy's method by using $Hg[Co(NCS)_4]$ as a calibrant. Electrical conductivity of solutions of complexes was measured by conductivity meter bridge manufactured by Wiss-Techeu Stathen type-LBR at room temperature in DMF (solvent). The cell constant was measured at room temperature 30°C using N/10 and N/100 KCl solution. The infrared spectra of the complexes were recorded on Perkin-Elmer-577 spectrophotometer using KBr pellets in the range of 4000–400 cm^{-1} at CDRI, Lucknow. The electronic absorption spectra of the complexes were recorded with Hitachi-320 spectrophotometer at CDRI, Lucknow.

RESULTS AND DISCUSSION

On the basis of analytical data (Table-1), the complexes were found to possess the m.f. of the type MLB_2 where M = Co(II), Ni(II) and Cu(II) ions and B = H_2O, pyridine and α-picoline (Fig. 2).

The reactions taking place in the preparation of the ligand and its metal complexes involving *o*-phenylene diamine, acetylacetone (enolic) and metal acetates can be represented as:

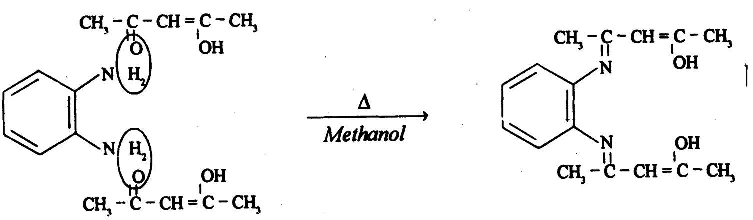

Fig. 1

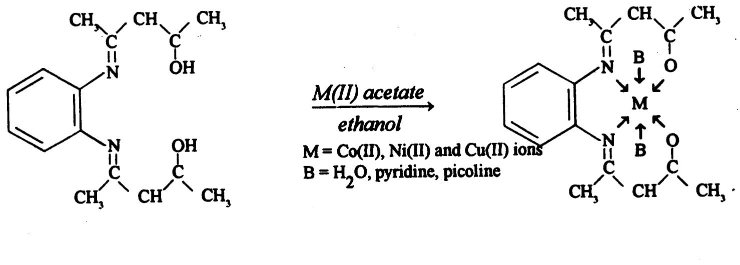

Fig. 2

All the complexes having different colour are stable at room temperature. The molar conductance values in the range of 25 to 35 for the complexes using 10^{-3} molar solution in DMF (Table-1) shows that these complexes can be represented as $[M(C_{16}H_{18}N_2O_2)(B)_2]$. Molecular weights of these complexes indicate the monomeric nature of the complexes.

TABLE-1
ANALYTICAL, MAGNETIC MOMENT AND ELECTRICAL CONDUCTANCE DATA OF THE METAL COMPLEXES

Compound (colour)	μ_{eff} (B.M.)	Λ_m (Ω^{-1} cm^2 mol^{-1})	Analysis %, found (calcd.)			
			M	C	H	N
$[Co(C_{16}H_{18}N_2O_2)(H_2O)_2]$ (Golden brown)	4.85	30	16.04 (16.14)	52.50 (52.61)	6.10 (6.02)	7.78 (7.67)
$[Co(C_{16}H_{18}N_2O_2)(C_5H_5N)_2]$ (Yellowish brown)	4.75	35	12.01 (12.09)	63.95 (64.07)	5.82 (5.75)	11.61 (11.50)
$[Co(C_{16}H_{18}N_2O_2)(C_5H_4NCH_3)_2]$ (Yellowish brown)	4.80	25	11.35 (11.43)	62.15 (62.25)	6.27 (6.21)	10.96 (10.87)
$[Ni(C_{16}H_{18}N_2O_2)(H_2O)_2]$ (Greenish brown)	2.90	25	16.02 (16.10)	52.52 (52.64)	6.10 (6.02)	7.78 (7.68)
$[Ni(C_{16}H_{18}N_2O_2)(C_5H_5N)_2]$ (Greenish brown)	2.80	30	12.42 (12.50)	63.95 (64.10)	5.80 (5.74)	11.62 (11.50)
$[Ni(C_{16}H_{18}N_2O_2)(C_5H_4NCH_3)_2]$ (Greenish brown)	2.85	35	11.20 (11.28)	65.20 (65.28)	6.28 (6.22)	10.96 (10.88)
$[Cu(C_{16}H_{18}N_2O_2)(H_2O)_2]$ (Parrot green)	1.96	35	17.10 (17.18)	51.84 (51.95)	6.03 (5.95)	7.65 (7.56)
$[Cu(C_{16}H_{18}N_2O_2)(C_5H_5N)_2]$ (Faint green)	1.92	30	12.84 (12.92)	63.40 (63.48)	5.76 (5.70)	11.48 (11.39)
$[Cu(C_{16}H_{18}N_2O_2)(C_5H_4NCH_3)_2]$ (Faint green)	1.95	35	12.12 (12.20)	64.60 (64.68)	6.24 (6.16)	10.86 (10.75)

Infrared Spectra: In case of ligand, a strong band is obtained at 3550 cm^{-1} indicating the presence of a —OH group in the ligand. Disappearance of this band in all the metal chelates indicates the bonding of the phenolic —OH group to the metal ions. Further, it is confined by obtaining a band around 540 cm^{-1} due ν(M—O) vibrations (Table-2). The presence of $—C—CH_3$ and —CH— groups present in the ligand is indicated by bands around 1850 and 2970 cm^{-1} respectively. A number of specific bands indicates the presence of phenyl group in the ligand as well as complexes. A strong band due to the chelated acetylacetone ligand appears at 1560–1510 cm^{-1} indicating the presence of ν(C═C) vibration in the ligand.

In case of all the complexes, a strong band around 1640 cm^{-1} is obtained indicating the presence of ν(C═N) vibration. Lowering of this band in all the complexes [ν(C═N) = 1580 cm^{-1}] indicates participation of imine nitrogen atom in the coordination. At the same time no band is obtained around 1740–1630 cm^{-1} indicating the complete condensation of the amine and ketonic groups.

TABLE-2
ELECTRONIC AND IR SPECTRAL DATA OF THE METAL COMPLEXES

Compound	IR Spectral data (cm^{-1})			Electronic spectral data (cm^{-1})
	ν(C=N)	ν(M—N)	ν(M—O)	
$[Co(C_{16}H_{18}N_2O_2)(H_2O)_2]$	1610	440	545	17,500–23,000
$[Co(C_{16}H_{18}N_2O_2)(C_5H_5N)_2]$	1600	455	540	17,600–22,400
$[Co(C_{16}H_{18}N_2O_2)(C_5H_4NCH_3)_2]$	1590	450	535	17,800–22,600
$[Ni(C_{16}H_{18}N_2O_2)(H_2O)_2]$	1600	450	540	8,500–19,500
$[Ni(C_{16}H_{18}N_2O_2)(C_5H_5N)_2]$	1590	440	545	8,700–19,400
$[Ni(C_{16}H_{18}N_2O_2)(C_5H_4NCH_3)_2]$	1580	455	540	8,600–20,000
$[Cu(C_{16}H_{18}N_2O_2)(H_2O)_2]$	1610	450	535	9,700–14,300
$[Cu(C_{16}H_{18}N_2O_2)(C_5H_5N)_2]$	1580	455	530	9,600–14,200
$[Cu(C_{16}H_{18}N_2O_2)(C_5H_4NCH_3)_2]$	1590	440	540	9,400–14,000

The band around 450 cm^{-1} in all the metal chelates suggests ν(M—N) vibration which further confirms the coordination of nitrogen atoms of these groups with the metals. No separate band for coordinated H_2O is obtained as it is overlapped by ν(O—H) vibration. A strong band obtained around 1080–940 cm^{-1} in the complexes indicates the coordination of pyridine and picoline molecules.

Electronic Spectra and Magnetic Moment: The values of magnetic moment for Co(II) complexes (Table-1) obtained in the range of 4.75–4.85 B.M. due to orbital contributions indicate that Co(II) complexes should be octahedral in nature. In case of Co(II) complexes a weak band due to $^4T_{1g} \rightarrow {}^4T_{2g}$ at 8300 cm^{-1} and another broad and unsymmetrical band due to $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ in the region of 23,000–17,500 cm^{-1} have been obtained indicating the octahedral arrangement of the ligands around the central metal ion. In case of Ni(II) complexes the values of magnetic moment obtained in the range of 2.85–3.00 B.M. indicate octahedral nature of the complexes. The complexes of Ni(II) ion show three bands due to the spin allowed transitions from the $^3A_{2g}$ the ground term to the three excited triplet terms ($^3A_{2g} \rightarrow {}^3T_{2g}$ = 84,500 cm^{-1}; $^3A_{2g} \rightarrow {}^3T_{1g}$ = 15,200 cm^{-1} and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ = 20,400 cm^{-1}) indicating the octahedral nature of the complexes.

The values of magnetic moment for Cu(II) complexes obtained in the range of 1.85 B.M.–1.95 B.M. indicate the octahedral arrangement of the ligands around the central metal ion.

In case of Cu(II) complexes, a broad and unsymmetrical band is obtained due to J.T. distortion in the range of 9,400 cm^{-1} to 14,400 cm^{-1} due to $^2E_g \rightarrow {}^2T_{2g}$ transition supporting octahedral or tetragonal field for the complexes.

PMR spectra: In case of both, ligand and the metal complexes, one gets five PMR peaks and hence two cannot be distinguished on the basis of PMR spectroscopy. The enolic H-atom of the ligand cannot be detected in the PMR spectrum as its range falls beyond δ value 10 ppm and hence it is beyond the accessible range of the common PMR spectrometer. Involvement of the enolic O-atom in chelation is expected by the fact that the signal due to $\rangle$CH proton is shifted towards downfield.

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