

Complexing Behaviour of Some Schiff Bases with Co(II), Ni(II) and Cu(II)

B.K. RAI

Department of Chemistry L.N.T. College, Muzaffarpur-842 001, India

A series of homobinuclear metal complexes of the type $[M(HL^{1-2})_2X_2]$ where $M = Co(II), Ni(II)$ and $Cu(II)$; $HL^1 = 2-(3',4'-dimethyl)$ phenyl imino-3-hydroxy butane; $HL^2 = 2-(3',5'-dimethyl)$ phenyl-imino-3-hydroxy butane; $X = Cl^-, Br^-, I^-, NO_3^-$ and ClO_4^- have been synthesized and characterised on the basis of elemental analysis, magnetic susceptibility, conductivity measurements, infrared and electronic spectral data.

Key Words: Cobalt, Nickel, Copper, 2-(3',4'-Dimethyl)/(3',5'-dimethyl) phenyl imino-3-hydroxy butane.

INTRODUCTION

The coordination compounds with Schiff base ligands have gained importance in recent past¹⁻⁵, due to their industrial⁶, antimicrobial⁷, fungicidal⁸, anti-cancer⁹ and anti-inflammatory¹⁰ activities. This prompted me to synthesize metal complexes with Schiff bases derived from diacetyl monoxime with 3,4/3,5-dimethyl aniline. These are of considerable importance in the preparation of a series of homobinuclear metal complexes. The Schiff base ligands HL^1 and HL^2 act in a bidentate manner to form the series of complexes having the formula $[M(HL^{1-2})_2X_2]$ where $M = Co(II), Ni(II)$ and $Cu(II)$; $X = Cl^-, Br^-, I^-, NO_3^-$ and ClO_4^- when the ligand is allowed to react with metal salts in molar ratio 2 : 1 in ethanolic and aqueous media respectively.

EXPERIMENTAL

Chemicals used were either of BDH or E. Merck quality. Metal salts and solvents were used without further purification.

Preparation of Ligand HL^{1-2}

The ligands HL^1 and HL^2 were synthesized by condensing equimolecular quantities of diacetyl monoxime and aromatic amines in an ethanolic medium. The complex compounds were prepared by refluxing together Schiff bases HL^1 and HL^2 with appropriate metal solution in molar ratio 2 : 1.

[†]This paper was presented in Seminar on Recent Trends in Chemistry, organised by Indian Council of Chemists (Muzaffarpur chapter) at L.S. College, Muzaffarpur, India on 21-22 Dec., 2000.

The metal contents in the complexes have been determined by standard methods¹¹. Carbon, hydrogen and nitrogen contents of the complexes were estimated using a MLW-CHN microanalyser. The infrared spectra of the ligands and complexes were recorded on a Perkin-Elmer spectrophotometer. Reflectance spectra were recorded on a Cary-2390 spectrophotometer. Room temperature magnetic susceptibilities were measured by Gouy method using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as the calibrant. The conductivity measurements are made on a systronics conductometer model 303 using DMSO as a solvent. Analytical data, colour, electronic spectra, conductivity measurements and magnetic moments are recorded in Table-1.

TABLE-1
COLOUR, ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND
CONDUCTIVITY MEASUREMENT DATA FOR METAL COMPLEXES WITH
LIGANDS HL^1 AND HL^2

Compound/ Colour	Found (Calculated) %				λ_{max} electronic (cm^{-1})	μ_{eff} (B.M.)	Ω_{max} (ohm^{-1} $\text{cm}^2 \text{mol}^{-1}$)
	Metal	C	H	N			
$\text{Co}(\text{HL}^1)_2\text{Cl}_2$ (Yellowish red)	10.85 (10.90)	53.55 (53.73)	5.53 (5.50)	10.27 (10.40)	16600	5.16	15.8
$\text{Co}(\text{HL}^2)_2\text{Cl}_2$ (Orange)	10.90 (10.99)	53.67 (53.73)	5.41 (5.59)	10.38 (10.44)	16910	5.17	17.2
$\text{Co}(\text{HL}^1)_2\text{Br}_2$ (Reddish brown)	9.31 (9.43)	45.98 (46.09)	4.69 (4.80)	8.35 (8.96)	16700	5.20	15.7
$\text{Co}(\text{HL}^2)_2\text{Br}_2$ (Light green)	9.34 (9.43)	45.98 (46.09)	4.58 (4.80)	8.43 (8.96)	16710	5.24	17.6
$\text{Co}(\text{HL}^1)_2\text{I}_2$ (Brownish red)	8.01 (8.19)	39.98 (40.07)	4.11 (4.17)	7.70 (7.79)	17200	5.10	15.7
$\text{Co}(\text{HL}^2)_2\text{I}_2$ (Brown)	8.12 (8.19)	39.97 (40.07)	4.09 (4.17)	7.59 (7.79)	17100	5.12	17.3
$\text{Co}(\text{HL}^1)_2(\text{NO}_3)_2$ (Yellowish red)	9.92 (10.00)	48.85 (48.90)	5.01 (5.09)	14.21 (14.26)	17300	5.26	14.2
$\text{Co}(\text{HL}^2)_2(\text{NO}_3)_2$ (Brown)	9.84 (10.00)	48.79 (48.90)	4.91 (5.09)	14.17 (14.26)	17310	5.28	15.6
$\text{Co}(\text{HL}^1)_2(\text{ClO}_4)_2$ (Yellowish red)	8.80 (8.87)	43.19 (43.37)	4.48 (4.51)	8.28 (8.43)	17400	5.19	16.1
$\text{Co}(\text{HL}^2)_2(\text{ClO}_4)_2$ (Yellowish red)	8.72 (8.87)	43.28 (43.37)	4.43 (4.51)	8.36 (8.43)	17410	5.21	18.4
$\text{Ni}(\text{HL}^1)_2\text{Cl}_2$ (Yellowish red)	10.88 (10.95)	53.55 (53.76)	5.52 (5.61)	10.39 (10.45)	13700 17300 25650	2.71	19.2
$\text{Ni}(\text{HL}^2)_2\text{Cl}_2$ (Yellowish red)	10.87 (10.95)	53.68 (53.76)	5.49 (5.61)	10.28 (10.45)	13710 17320 25670	2.73	17.1
$\text{Ni}(\text{HL}^1)_2\text{Br}_2$ (Reddish brown)	9.33 (9.39)	46.91 (46.09)	4.74 (4.80)	8.91 (8.96)	13000 17460 25600	3.09	14.3

Compound/ Colour	Found (Calculated) %				λ_{\max} electronic (cm^{-1})	μ_{eff} (B.M.)	Ω_{max} (ohm^{-1} $\text{cm}^2 \text{mol}^{-1}$)
	Metal	C	H	N			
Ni(HL ²) ₂ Br ₂ (Reddish brown)	9.22 (9.39)	46.03 (46.09)	4.62 (4.80)	8.89 (8.96)	13910 17480 25710	3.10	15.3
Ni(HL ¹) ₂ I ₂ (Brownish red)	8.11 (8.16)	39.88 (40.08)	4.12 (4.17)	7.71 (7.79)	13880 17620 25740	2.82	21.4
Ni(HL ²) ₂ I ₂ (Brownish)	8.10 (8.16)	39.96 (40.08)	4.01 (4.17)	7.69 (7.79)	13890 17640 25760	2.84	16.3
Ni(HL ¹) ₂ (NO ₃) ₂ (Greenish red)	9.91 (9.97)	48.85 (48.92)	4.99 (5.09)	14.20 (14.26)	14010 17910 26300	2.85	19.7
Ni(HL ²) ₂ (NO ₃) ₂ (Greenish red)	9.09 (9.97)	48.81 (48.97)	4.97 (5.09)	14.19 (14.26)	14020 17930 26320	2.42	10.2
Ni(HL ¹) ₂ (ClO ₄) ₂ (Yellowish red)	8.78 (8.84)	43.31 (43.39)	4.46 (4.52)	8.39 (8.43)	14030 18000 26330	2.91	19.4
Ni(HL ²) ₂ (ClO ₄) ₂ (Yellowish red)	8.67 (8.84)	43.22 (43.39)	4.42 (4.52)	8.36 (8.43)	14040 18020 12350	2.95	21.2
Cu(HL ¹) ₂ Cl ₂ (Dark green)	11.69 (11.75)	53.19 (53.28)	5.47 (5.55)	10.29 (10.36)	11200 14500	1.70	18.9
Cu(HL ²) ₂ Cl ₂ (Dark green)	11.67 (11.75)	53.07 (53.28)	5.49 (5.55)	10.18 (10.36)	11300 14600	1.71	16.3
Cu(HL ¹) ₂ Br ₂ (Greenish brown)	9.89 (10.01)	45.67 (45.76)	4.69 (4.76)	8.73 (8.89)	11400 14700	1.74	15.9
Cu(HL ²) ₂ Br ₂ (Greenish brown)	9.79 (10.01)	45.59 (45.76)	4.72 (4.76)	8.81 (8.89)	11500 14900	1.76	21.7
Cu(HL ¹) ₂ (NO ₃) ₂ (Greenish red)	10.59 (10.70)	48.30 (48.52)	4.98 (5.05)	14.03 (14.15)	11900 15300	1.85	16.2
Cu(HL ²) ₂ (NO ₃) ₂ (Greenish red)	10.59 (10.70)	48.41 (48.52)	4.91 (5.05)	14.09 (14.15)	11600 15500	1.87	15.6
Cu(HL ¹) ₂ (ClO ₄) ₂ (Yellowish red)	9.38 (9.50)	42.83 (43.07)	4.29 (4.48)	8.91 (8.37)	11700 15400	1.89	15.3
Cu(HL ²) ₂ (ClO ₄) ₂ (Yellowish red)	9.42 (9.50)	42.95 (43.07)	4.42 (4.48)	8.28 (8.37)	12000 15200	1.90	20.4

RESULTS AND DISCUSSION

The molecular formulae of the complexes have been assigned on the basis of their analytical data. The Co(II), Ni(II) and Cu(II) complexes are thus assigned the formulae $M(\text{HL}^{1-2})\text{X}_2$.

Infrared Spectra

The vibrational spectra of the ligands as well as complexes have been recorded in the frequency range $4000\text{--}400\text{ cm}^{-1}$ (Table-2) and structurally important vibrational bands for O—H stretch C=N stretch (oxime and azomethine) and N—O stretch provide unequivocal evidence relating to the structure of the complexes. The infrared spectra of the ligands HL¹ and HL² show a broad and strong band at $3400\text{--}3420\text{ cm}^{-1}$ which is assigned to $\nu(\text{O—H})$ of the N—O—H groups. The width of this band manifests intramolecular as well as intermolecular hydrogen bonding. In the spectra of the complexes this band remains almost unaffected indicating non-involvement of the alcoholic group of the N—OH group. The infrared spectrum of the ligands HL¹ and HL² exhibits two sharp and strong bands at $1625\text{--}1615\text{ cm}^{-1}$ and $1480\text{--}1465\text{ cm}^{-1}$ which have been attributed to (C=N) stretching vibrations of azomethine and oxime groups respectively. The characteristic behaviour of these bands, *i.e.*, the shift of the azomethine and oxime (C=N) bands respectively towards red and blue region of the spectra as compared with free ligands HL¹ and HL² can be attributed to the variation in electronic environment due to coordination with metal ions. The next IR spectral bands of the ligand are in the region $1100\text{--}1000\text{ cm}^{-1}$ and one of them is the strongest which has been assigned to the $\nu(\text{N—O})$. In the spectra of the complexes this band remains unperturbed which suggests that oxygen atom of the (N—O) group is not involved in coordination. The appearance of a few additional sharp and intense bands in comparison to ligands in the vicinity of 700 cm^{-1} indicates the presence of metal-halogen or metal-oxygen bonds¹².

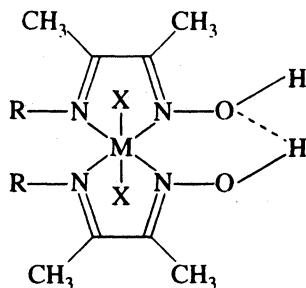
Electronic spectra and magnetic moment data

The Co(II) complexes of the type $[\text{Co}(\text{HL}^{1-2})_2\text{X}_2]$ possess magnetic moment values in the range 5.10–5.28 B.M. at 25°C and exhibit a multiple band structure in the region $16000\text{--}18000\text{ cm}^{-1}$ ($16600\text{--}17410\text{ cm}^{-1}$), the nature and width of which spreading over 3000 cm^{-1} suggests octahedral environment around cobalt(II) ion in these complexes. The Ni(II) complexes of the type $[\text{Ni}(\text{HL}^{1-2})_2\text{X}_2]$ have magnetic moment values in the region 2.7–3.1 B.M. at room temperature, which suggests octahedral arrangement of the ligand atoms around it. The electronic spectra of these complexes consist of three bands, in the regions $13500\text{--}14500\text{ cm}^{-1}$ ($13700\text{--}14040\text{ cm}^{-1}$), the next one in the vicinity of 18000 cm^{-1} ($17300\text{--}18020\text{ cm}^{-1}$) followed by a strong intense band near 26000 cm^{-1} ($25650\text{--}26350\text{ cm}^{-1}$). The Cu(II)-complexes of the type $[\text{Cu}(\text{HL}^{1-2})_2\text{X}_2]$ have magnetic moments in the range 1.7–1.9 B.M. which corresponds to one unpaired electron. The electronic spectra of all the complexes of Cu(II) of the type $[\text{Cu}(\text{HL}^{1-2})_2\text{X}_2]$ have shown two broad bands, one in the region $10000\text{--}12000\text{ cm}^{-1}$ and the other in the region $14000\text{--}16000\text{ cm}^{-1}$ which indicate that the geometries of all Cu(II) complexes are octahedral. Molar conductance values for the complexes are found in the range $15.22\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ which support non-electrolytic nature of the complexes.

TABLE-2
KEY IR BANDS (cm^{-1}) OF THE LIGANDS AND THEIR METAL COMPLEXES OF
THE TYPE $[\text{M}(\text{HL}^{1-2})_2\text{X}_2]$

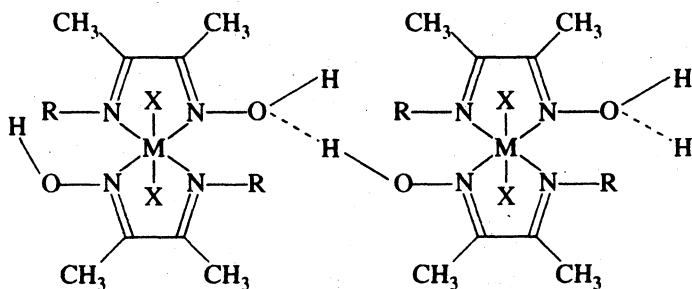
Compounds	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{N})$ azomethine	$\nu(\text{C}=\text{N})$ oxime	$\nu(\text{N}-\text{O})$
HL ¹	3420 m,b	1615 s	1465 s	1090 s
HL ²	3425 m,b	1625 s	1480 s	1095 s
Ni(HL ¹) ₂ Cl ₂	3415 m,b	1590 s	1500 s	1090 s
Ni(HL ²) ₂ Cl ₂	3420 m,b	1595 s	1510 s	1090 s
Ni(HL ¹) ₂ Br ₂	3415 m,b	1585 s	1495 s	1085 s
Ni(HL ²) ₂ Br ₂	3420 m,b	1585 s	1505 s	1090 s
Ni(HL ¹) ₂ I ₂	3425 m,b	1590 s	1490 s	1090 s
Ni(HL ²) ₂ I ₂	3425 m,b	1595 s	1515 s	1100 s
Ni(HL ¹) ₂ (NO ₃) ₂	3420 m,b	1585 s	1495 s	1095 s
Ni(HL ²) ₂ (NO ₃) ₂	3420 m,b	1590 s	1510 s	1095 s
Ni(HL ¹) ₂ (ClO ₄) ₂	3425 m,b	1590 s	1500 s	1090 s
Ni(HL ²) ₂ (ClO ₄) ₂	3425 m,b	1595 s	1505 s	1100 s
Co(HL ¹) ₂ Cl ₂	3420 m,b	1580 s	1490 s	1090 s
Co(HL ²) ₂ Cl ₂	3425 m,b	1595 s	1510 s	1095 s
Co(HL ¹) ₂ Br ₂	3420 m,b	1590 s	1495 s	1095 s
Co(HL ²) ₂ Br ₂	3420 m,b	1595 s	1515 s	1100 s
Co(HL ¹) ₂ I ₂	3420 m,b	1585 s	1490 s	1090 s
Co(HL ²) ₂ I ₂	3425 m,b	1600 s	1505 s	1095 s
Co(HL ¹) ₂ (NO ₃) ₂	3425 m,b	1580 s	1500 s	1090 s
Co(HL ²) ₂ (NO ₃) ₂	3420 m,b	1600 s	1510 s	1100 s
Co(HL ¹) ₂ (ClO ₄) ₂	3420 m,b	1590 s	1490 s	1090 s
Co(HL ²) ₂ (ClO ₄) ₂	3420 m,b	1595 s	1515 s	1095 s
Cu(HL ¹) ₂ Cl ₂	3425 m,b	1585 s	1495 s	1090 s
Cu(HL ²) ₂ Cl ₂	3425 m,b	1590 s	1505 s	1095 s
Cu(HL ¹) ₂ Br ₂	3420 m,b	1580 s	1495 s	1090 s
Cu(HL ²) ₂ Br ₂	3425 m,b	1595 s	1510 s	1095 s
Cu(HL ¹) ₂ (NO ₃) ₂	3420 m,b	1580 s	1500 s	1090 s
Cu(HL ²) ₂ (NO ₃) ₂	3425 m,b	1600 s	1515 s	1095 s
Cu(HL ¹) ₂ (ClO ₄) ₂	3420 m,b	1585 s	1495 s	1090 s
Cu(HL ²) ₂ (ClO ₄) ₂	3425 m,b	1600 s	1505 s	1095 s

The infrared and electronic spectral data, magnetic moment and conductivity measurements strongly support the proposed structures of the complexes as shown in Figs. 1 and 2.



R = 3',4 dimethyl aniline or 3'-5'-dimethyl aniline
 M = Co(II), Ni(II) and Cu(II); X = Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻

Fig. 1



R = 3,4 dimethyl aniline or 3',5'-dimethyl aniline
 M = Co(II), Ni(II) and Cu(II); X = Cl⁻, Br⁻, I⁻, NO₃⁻ or ClO₄⁻

Fig. 2

REFERENCES

1. R.K. Choudhary, R.N. Pathak and L.K. Mishra, *J. Indian Chem. Soc.*, **77**, 32 (2000).
2. K.C. Satpathy, A.K. Panda, R. Mishra, A. Mahapatra and A. Patel, *Synth. React. Inorg. Met-Org. Chem.*, **22**, 201 (1992).
3. P.A. Vigato, S. Tampurini and D.E. Fenton, *Coord. Chem. Rev.*, **10**, 25 (1974).
4. P. Guerriero, P.A. Vigato, D.E. Fenton and P.C. Hellier, *Acta Chem. Scand*, **46**, 1025 (1992).
5. F.S. Watanabe and S.R. Olsen, *Soil Sci. Soc., Am. Proc.*, **29**, 672 (1995).
6. A.K. Dey, *J. Indian Chem. Soc.*, **63**, 339 (1966).
7. R.D. Jones, D.A. Summerville and F. Basolo, *Chem. Rev.*, **79**, 130 (1979).
8. Sudha Goyal and Keemati Lal, *J. Indian Chem. Soc.*, **66**, 477 (1989).
9. Wu Zishen, Gui Ziqui and Yen Zhenhuan, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 335 (1990).
10. R.K. Parashar, R.C. Sharma, Anil Kumar and Govind Mohan, *Inorg. Chim. Acta*, **151**, 201 (1988).
11. Vogel's Textbook of Quantitative Chemical Analysis, 5th Edn., ELBS (1997).
12. K. Nakamoto, *Infrared Spectroscopy of Inorganic and Co-ordination Compounds*, J. Wiley & Sons, New York (1978).