Asian Journal of Chemistry Vol. 20, No. 5 (2008), 3828-3832

Synthesis and Characterization of Co(II), Ni(II) and Cu(II) Complexes of Bidentate Schiff Base

S.N. VIDYARTHI*, DUSHYANT KUMAR, RAKESH SINGH and SHASHIKIRAN TIWARI
Department of Chemistry, J.P. University, Chapra-841 301, India

In present studies, Co(II), Ni(II) and Cu(II) complexes with bidentate Schiff base have been prepared and characterized. The complexes were coloured, amorphous in nature and are soluble in DMSO and DMF. The conductance measurement shows the complexes are non-electrolytes in DMF. Elemental analysis confirmed to the 1:2 stoichiometry. Magnetic, electronic and IR spectral information suggest the octahedral structure for Co(II), Ni(II) and Cu(II) complexes.

Key Words: Co(II), Ni(II) and Cu(II) complexes, Schiff base, Octahedral, Stoichiometry.

INTRODUCTION

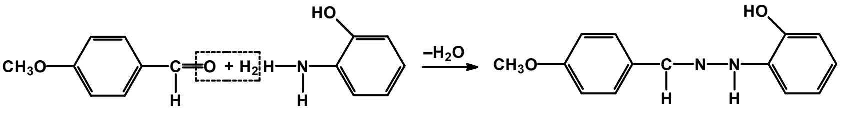
Schiff bases and related complexes have been extensively studied because of their applications in analytical[1], medicinal[2] and biological[3] system. Literature survey reveals that although metal complexes of Schiff bases derived from various amines have been studied extensively[4], but no report is available in literature on the complexes of Co(II), Ni(II) and Cu(II) with *p*-methoxy benzylidine-*o*-hydroxy phenyl hydrazone. Herein, the synthesis of Schiff base by the condensation of *o*-hydroxy phenyl hydrazine and *p*-methoxy benzaldehyde is reported. This ligand molecule has both nitrogen and oxygen donor sites. It coordinates with the metal ion in a bidentate manner through the aldimino nitrogen and phenolic oxygen atoms of the ligand molecule.

EXPERIMENTAL

Electronic spectra of the complexes were recorded on a Shimadzu UV-160 spectrophotometer. IR spectra of the samples were recorded on a Perkin-Elmer 783 spectrophotometer as KBr discs. Magnetic susceptibility measurements of the complexes were determined using a Guoy balance at room temperature by using $Hg[Co(SCN)_4]$ as a calibrant. Molar conductance of the complexes was measured in ethanol-water at room temperature using a systronics conductivity bridge type 305. All the chemicals used were of AR grade.

Synthesis of ligand: The mixture of *o*-hydroxy phenyl hydrazine (0.01 mol) and *p*-methoxy benzaldehyde (0.01 mol) in ethanol was refluxed for 7 h in water bath. The reaction mixture was cooled and treated with cold water. The pale yellow mass, thus separated, was washed with slightly acidic water to remove unreacted amine. It was recrystallized from ethanol, yield 65 %.

The compound was further analyzed and found to contain C 69.42 %, H 5.78 % and N 11.57 % which corresponds to the molecular formula $C_{14}H_{14}N_2O_2$. The expected chemical reaction during the condensation is given below:



p-methoxy benzylidine
o-hydroxy phenyl hydrazone

Preparation of the complexes: The solution of the corresponding metal(II) acetate/chloride was mixed with alcoholic solution of the Schiff base and the resulting solution was refluxed with occassional shaking in presence of water, ammonia and α-picoline. The molar ratio of the metal and the ligand solutions was always kept 1:2, respectively and the complexes of Co(II), Ni(II) and Cu(II) were prepared separately in presence of the bases. The refluxing of solution was continued for 1 h till the complex separated out. The precipitate thus obtained was dried over fused $CaCl_2$ kept in a desiccator. On the basis of elemental analysis, the complexes were found to be monomeric and to possess the general m.f. $[M(L_2)(B)_2]$ where M = Co(II), Ni(II) and Cu(II)]' $L^- = C_{14}H_{13}N_2O_2$ and B = water, ammonia and α-picoline.

RESULTS AND DISCUSSION

Elemental analysis, electrical conductivity and magnetic susceptibility data of the complexes are given in Table-1. The analytical data of all the complexes corresponds to the general formula $[M(L_2)(B_2)]$. Magnetic susceptibility value of Co(II), Ni(II) and Cu(II) complexes at room temperature are consistent with regular octahedral geometry for Co(II), Ni(II) and distorted octahedral geometry for Cu(II) metal ions.

The elemental analysis of the complexes shows monomeric nature of the complexes and the values of electrical conductance support their neutral nature.

The values of magnetic moment for Co(II) complexes (Table-1) obtained in the range of 4.75-4.85 BM due to orbital contribution 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 $^4T_{1g} \rightarrow {}^4T_{2g}(P)$ in the region of 23000-25500 cm^{-1} have been obtained, respectively[9] 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 BM indicate octahedral nature of the complexes. The complexes of Ni(II) ion show three bands due to the spin allowed transition from the $^3A_{2g}$, the ground term to the three excited triplet terms ($^4A_{2g} \rightarrow {}^3T_{2g}$ = 8400 cm^{-1}; $^3A_{2g} \rightarrow {}^3T_{1g}$ = 16200 cm^{-1} and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ = 22500 cm^{-1}) indicating the octahedral nature of the complexes.

The values of magnetic moment for Cu(II) complexes obtained in the range of 1.85-1.95 BM 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 Jahn Teller distortion in the range of 9600-14500 cm^{-1} due to $^2E_g \rightarrow {}^2T_{2g}$ transition supporting octahedral or tetragonal field for the complexes.

TABLE-1
CHARACTERISTICS DATA OF METAL(II) COMPLEXES BASED ON BIDENTATE SCHIFF BASE

Complexes	Elemental analysis: Calcd. (Found) %				ohm^{-1} cm^2 mol^{-1}	Magnetic moment (BM)
	M	C	H	N		
$[Co(C_{14}H_{13}N_2O_2)_2(H_2O)_2]$	9.96	58.04	5.24	9.80	16	4.96
	(10.20)	(58.24)	(5.20)	(9.70)		
$[Co(C_{14}H_{13}N_2O_2)_2(NH_3)_2]$	10.02	58.30	5.62	14.70	22	4.92
	(10.24)	(58.40)	(5.56)	(14.61)		
$[Co(C_{14}H_{13}N_2O_2)_2(C_6H_7N)_2]$	7.87	65.85	5.56	11.60	28	4.98
	(8.10)	(66.03)	(5.50)	(11.55)		
$[Ni(C_{14}H_{13}N_2O_2)_2(H_2O)_2]$	9.95	58.02	5.25	9.80	12	2.98
	(10.17)	(58.26)	(5.20)	(9.71)		
$[Ni(C_{14}H_{13}N_2O_2)_2(NH_3)_2]$	10.04	58.28	5.60	14.68	18	2.90
	(10.21)	(58.46)	(5.56)	(14.61)		
$[Ni(C_{14}H_{13}N_2O_2)_2(C_6H_7N)_2]$	7.84	65.80	5.56	11.62	20	2.94
	(8.07)	(66.05)	(5.50)	(11.55)		
$[Cu(C_{14}H_{13}N_2O_2)_2(H_2O)_2]$	10.60	57.58	5.20	9.70	24	1.96
	(10.92)	(57.78)	(5.15)	(9.63)		
$[Cu(C_{14}H_{13}N_2O_2)_2(NH_3)_2]$	10.78	57.76	5.60	14.56	12	1.90
	(10.95)	(56.98)	(5.52)	(14.49)		
$[Cu(C_{14}H_{13}N_2O_2)_2(C_6H_7N)_2]$	8.52	65.48	5.51	11.55	14	1.92
	(8.68)	(65.61)	(5.46)	(11.48)		

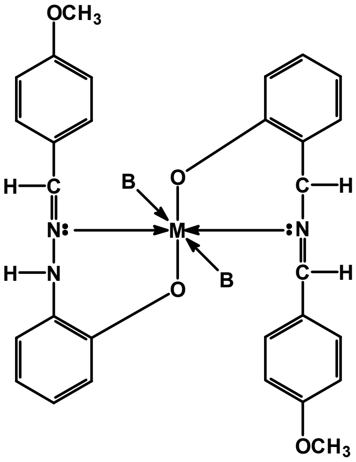
The key infrared frequencies are given in Table-2. The infrared spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation. The band at 1630 cm^{-1} is characteristics of the azomethine nitrogen atom present in the free ligand. The lowering in this frequency region (1590-1570 cm^{-1}), observed in all the complexes, indicates the involvement of the azomethine nitrogen atom in coordination[5]. It has been established that the formation of inter-molecular hydrogen bonding results in weakening and broadening of the band attributable to –OH vibration and also shifts to lower frequency[6]. In view of this, broad band with fine structure observed in the 3200-3150 cm^{-1} range is attributed to the intramolecular H-bonded –OH stretch[6]. This band is absent in the complexes showing that the ligands have reacted with the metal ion *via* deprotonation. Also the ligand and the complexes show an intense peak at 3260 cm^{-1}, which is characteristic of –NH stretching, indicating the existence of a free –NH group.

TABLE-2
KEY IR (cm^{-1}) FREQUENCIES OF THE SCHIFF BASES AND THEIR COMPLEXES

Assignments	L	$[Co(L_2)(B_2)]$	$[Ni(L_2)(B_2)]$	$[Cu(L_2)(B_2)]$
ν(C=N)	1650	1598	1591	1587
ν(C–O)	1280	1372	1371	1370
ν(M–N)	–	440	445	440
ν(M–O)	–	560	555	565

The band due to phenolic ν(C-O)[7] around 1280 cm^{-1} in ligands shows considerably high frequency shift and observed in the complexes around 1370 cm^{-1}. this suggests that oxygen atom of the phenolic –OH group has participated in coordination. The C=N stretch[8] for the ligands observed in the region 1630-1620 cm^{-1} which apeared at 1600-1550 cm^{-1} in the complexes suggesting the coordination[5] between nitrogen of the azomethine group and metal ion. The participation of azomethine nitrogen and phenolic oxygen is further confirmed by the presence of sharp and intense bands in the complexes obtained around 440 and 560 cm^{-1} due to ν(M–N) and ν(M–O) vibration, respectively.

Thus on the basis of elemental analysis, measurement of electrical conductivity, magnetic susceptibility and studies of electronic and IR spectral data, the structure of Co(II), Ni(II) and Cu(II) metal complexes has been suggested to be octahedral in nature as shown below:



M = Co(II), Ni(II) and Cu(II) metal
B = Water, ammonia and α-picoline

ACKNOWLEDGEMENT

The authors are cordially thankful to Dr. S.N. Dubey, the Principal of Rajendra College, Chapra for providing financial as well as research facilities.

REFERENCES

1. P.R. Palet, B.T. Thaker and S. Zele, *Indian J. Chem.*, **38A**, 563 (1999).
2. A. Mohindru, J.M. Fisher and M. Rabinovitz, *Nature*, **303**, 64 (1983).
3. P. Singh, R.L. Goel and B.P. Singh, *J. Indian Chem. Soc.*, **52**, 958 (1975).
4. R.H. Holm and M.J. O'Conner, in ed.: S.J. Lippard, The Stereochemistry of Bis-chelate Metal(II) Complexes, Progress in Inorganic Chemistry, Wiley-Interscience, New York, p. 14, 241 (1971).
5. B.B. Mahapatra and D.K. Das, *Indian J. Chem.*, **26A**, 173 (1987).
6. N.S. Biradar and B.R. Havinale, *Inorg. Chem. Acta*, **17**, 157 (1976).
7. K.M. Ibrahim, T.H. Racha, A.M. Abdullah and M.M. Hassanian, *Indian J. Chem.*, **32A**, 361 (1993).
8. N.S. Biradar and V.H. Kulkarni, *J. Inorg. Nucl. Chem.*, **33**, 2451 (1971).
9. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, p. 18, 498, 535, 587 (1968).

(*Received*: 26 September 2007; *Accepted*: 8 February 2008) AJC-6318