Asian Journal of Chemistry Vol. 2, No. 3 (1990), 286–289

Novel Schiff Base Complexes of 2-hydroxy-1-naphthalidene Oxalyldihydrazone

D. K. DWIVEDI*, R. K. SHUKLA and B. K. SHUKLA
Chemical Laboratories, Atarra College, Atarra–210 201, India

Polymerization reactions involving the formation of Schiff base metal complexes have been described. Schiff base acts as hexadentate and oxobridged binuclear 2 : 1 polymeric structure is proposed with the help of analytical, magnetic, thermal and spectral studies. The metal ion is the bridging unit between the donor sites of the ligand and the polymeric chain grows through consecutive ligand-metal linkages.

INTRODUCTION

Search for inorganic polymeric complexes continues to be important due to limitation of organic polymers in respect of their thermal stability. Metal complexes of Schiff bases of hydrazides with aldehydes or ketones have been of special interest in recent years,[1–3] particularly in the context of therapeutic value of hydrazide and hydrazone. Coordination occurs both in keto[3], as well as in enolic[4,5] form. Formation of oxygen bridged bi- and trinuclear complexes have also been described in a review by Sin and Hariss[6]. Mixed ligand complexes of oxotitanium(IV) and tin(IV) with dihydrazones are also reported.[7] The present paper describes the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with di-2-hydroxy-1-naphthalidene oxalyldihydrazone (OXN) by elemental, magnetic, thermal, infrared and electronic spectra.

EXPERIMENTAL

Oxalyldihydrazide (Fluka, AG), 2-hydroxy-1-naphthaldehyde (Fluka AG), metal acetates (BDH) and DMF (Sisco) were used as received.

Preparation of the Ligand

A mixture of oxalyldihydrazide (0.01 mole) and 2-hydroxy-1-naphthaldehyde (0.02 mole) both in ethanolic, DMF solution was refluxed on water bath for *ca* 2h. The mixture was allowed to cool, when a bright yellow product was obtained. The product thus obtained was filtered, washed several times with hot ethanol and dried. The purity of the compound was checked by T.L.C. M.pt. above 200°C.

Synthesis of the Metal Complexes

To a suspension of the ligand (0.02 mole) in hot DMF, 5 cm^3 aqueous ammonia was added and the mixture was refluxed on a sand both until a yellow solution was obtained. The metal salt solutions (DMF + water) was added to the ligand solution and the mixture was refluxed for *ca* 3–4h on a sand bath. After refluxing, the mixture was concentrated to a small volume and then referigerated overnight. The solid product which settled down was filtered washed with hot DMF and dried. The complexes are coloured, air stable and insoluble in common organic solvents such as ethanol, carbon tetrachloride, DMF and DMSO.

RESULTS AND DISCUSSION

The following analytical data (Table 1) of the complexes agree with the general formula $(M_2L{\cdot}4H_2O)_n$ where M = Co(II), Ni(II) or Cu(II) and $L = C_{24}H_{14}N_4O_4 = OXN$.

TABLE 1

COLOUR AND COMPOSITION OF THE COMPLEXES

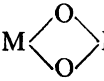
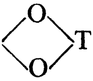
Compound	Colour	Elemental analysis found (Calcd.) %			
		Metal	C	H	N
H_4L	Yellow	—	66.10 (67.28)	4.06 (4.22)	13.21 (13.15)
$(Co_2L{\cdot}4H_2O)_n$	Reddish Brown	19.05 (19.28)	46.20 (47.57)	3.03 (3.57)	8.42 (9.12)
$(Ni_2L{\cdot}4H_2O)_n$	Reddish Brown	18.52 (19.27)	46.89 (47.58)	3.23 (3.58)	8.76 (9.13)
$(Cu_2L{\cdot}4H_2O)_n$	Reddish	20.42 (20.32)	45.15 (46.45)	3.65 (3.55)	8.24 (9.03)

$H_4L = C_{24}H_{18}N_4O_4$

The spectra of the ligand show the following important bands.

(i) νNH at 3180 cm^{-1}, (ii) νC=O at 1680 cm^{-1}, (iii) νO–H at 2800 cm^{-1} (Intramolecularly Hydrogen bonded), (iv) νC=N at 1625 cm^{-1} and νC=C at 1610 cm^{-1}, (v) CNH stretching and NH deformation at 1575 cm^{-1}, (vi) νC–O of phenol at 1530 cm^{-1}, (vii) OH deformation at 1325 cm^{-1} due to phenol, (viii) C–O deformation at 1245 cm^{-1}, (ix) >N–N< stretching at 1035 cm^{-1}.

It is evident that the ligand exists in ketonic form in solid state, while in solution, it changes into enolic form through tautomerism because NH, and CNH stretching frequencies alongwith NH deformation at 1575 cm^{-1} disappear in all the complexes. The new bands appearing in the region 1660–50, 1595–85 and 1310–1300 cm^{-1} are due to O–C=N (conversion of O–C–NH into O–C=N), >C=N–N=C< and C–O stretching vibrations respectively. These new bands are diagnostic of the presence of enolic form of the ligand in the complexes.

There may be two C=N stretching frequencies; one is coordinated at 1625 and other one noncoordinated at 1660–50 cm^{-1} due to difference in environment. N—N stretching occurs at 1035 cm^{-1}, shows a positive shift less than 50 cm^{-1} suggesting monodentate nature of N–N. The negative shift of C=N stretching at 1625 cm^{-1} indicates the involvement of azomethine nitrogen in chelation. The disappearance of O–H stretching at 2800 and O–H deformation at 1335 cm^{-1} in all the complexes suggest the involvement of phenolic oxygen in coordination. The association of water molecules in the complexes is confirmed by the presence of new bands in the region 3500–3350, 1640–35 and at 980–70 cm^{-1} due to -OH stretching. HOH deformation and rocking mode of coordinated water respectively. The percentage weight-loss observed between 180–230° by T. G. analysis corresponds to $4H_2O$ for basic unit supporting the above assumption. The new ligand bands are observed in the region 620–10, 560–55, 480–90 and 885–80 cm^{-1}, which may be attributed to νM–O, Phenolic, νM–O enolic and νM–N stretching and νM  M type stretching vibrations respectively. Similar range is reported in dihydrazone complexes around 830–20 cm^{-1} suggesting the presence of polymeric (O–Ti–O–Ti–) or Ti  Ti grouping.[7, 12]

Thus the ligand behaves as hexadentate and tetrabasic in which two phenolic oxygen, two azomethine nitrogen and two enolic oxygen are involved in complex formation. The decomposition temperature of the complexes fall in the range 320–400°. The order of thermal stability is Ni(II) >Co(II)=Cu(II).

All the complexes are paramagnetic. The lower value of magnetic moment than the normal range may be due to binuclear polymeric structure of the complexes. The binuclear compounds show subnormal magnetic moments due to super exchange interaction through *s* or *p* orbitals of the bridging hydroxylic oxygen atoms. At room temperature,

TABLE 2

MAGNETIC MOMENT AND VARIOUS LIGAND FIELD PARAMETERS

Complex	Magnetic moment, B.M.	band cm^{-1}	Assignment	ν_2/ν_1	10 Dq	β'	β	$\beta°$
Co(II)	3.52	10638	$4T_{1g} \rightarrow 4T_{2g}(F)$	2.12	11970	896	.922	7.82
		22608	$\rightarrow 4A_{2g}(F)$					
		22727	$\rightarrow 4T_{2g}(P)$					
Ni(II)	2.54	10638	$3T_{2g} \rightarrow 3T_{2g}(F)$					
		17094	$\rightarrow 3T_{1g}(F)$	1.59	10638	861	.815	18.46
		27778	$\rightarrow 3T_{1g}(P)$					
Cu(II)	1.39	11111	$2B_{2g} \rightarrow 2A_{1g}$					
		14285	$\rightarrow 2B_{1g}$	1.13	11997	—	—	—
		16129	$\rightarrow 2E_g$					

the diamagnetic singlet groundstate is more populated than paramagnetic triplet state and hence there is lowering of magnetic moment. Cryomagnetic studies are essential to determine the type of interaction and hence the structures of the compounds. The magnetic moment values and various ligand field parameters[12] viz. ν_2/ν_1, 10Dq, B′, β, β° have been calculated (Table 2). Both these data show octahedral geometry of the complexes[13]. The structure of present polynuclear complexes cannot be ascertained without X-ray analysis. However enolic oxygen bridge structures have been tentatively assigned on the bases of present physicochemical properties.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. Arun K. Dey University of Allahabad and Prof. B. V. Agarwala, University of Jabalpur for taking keen interest in the work. Thanks are also due to U.G.C. and C.S.I.R for financial support.

REFERENCES

1. H. D. Juneja and K. N. Munshi, *Indian J. Chem.*, **26A**, 257, 708 (1987); **27A**, 451 (1985).
2. P. L. Maurya, B. V. Agarwala and A. K. Dey, *Polymer Bull.*, **1**, 631 (1979); **3**, 253 (1980).
3. K. K. Khalikov, A. A. Shabilalov and M. A. Azizov, *Russ. J. Inorg. Chem.*, **15**, 1022 (1970).
4. A. P. Narimanidze, A. M. Mamulashvili and T. K. Dzhashiashvili, *Tr. Gruz. Politelh Inst.*, **4**, 34 (1975).
5. H. K. Duggal and B. V. Agarwala, *Synth. React. Inorg. Met. Org. Chem.*, **18**, 871 (1988).
6. E. Sinn and C. M. Harris, *Coord. Chem. Revs.*, **4**, 391 (1969).
7. G. H. Havanur, V. K. Revankar and V. B. Mahale, *Indian J. Chem.*, **27A**, 803 (1988).
8. M. A. M. Ali and S. G. Beoh, *J. Inorg. Nucl. Chem.*, **41**, 809 (1979).
9. M. A. M. Ali, S. E. Livingstone and D. J. Phillips, *Inorg. Chim. Acta*, **1**, 531 (1973).
10. C. N. R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York (1963).
11. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compound, John Wiley and Sons, New York (1978).
12. N. S. Biradar, V. B. Mahale and V. H. Kulkarni, *J. Inorg. Nucl. Chem.*, **35**, 2565 (1973).
13. A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier Amsterdam (1965).

[*Received*: 25 July 1989; *Accepted*: 10 November 1989] AJC–108