Asian Journal of Chemistry Vol. 4, No. 1 (1992), 184–187

NOTES

Co-ordination Complexes of Tetradentate N_2O_2 Donor Macrocyclic Ligand (b, i) Dibenzo-*m*-(dinitrobenzo)5,8-diaza, 1,12-dioxocyclotetradeca 4,8-diene with Cu(II), Ni(II) and Co(II)

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Twelve new tetracoordinated macrocyclic complexes of Cu(II), Ni(II) and Co(II) possessing the general formulae $\{M(L)\}X_2$ and $\{Co(L)(H_2O)_2\}X_2$ where L = title macrocyclic ligand, M = Cu(II) and Ni(II) and $X = Cl^-$, SCN^-, BF_4^- and ClO_4^- have been prepared. The complexes have been characterised using elemental analysis, molar conductance, IR spectra, magnetic measurements and electronic spectral studies. The complexes of Cu(II) and Ni(II) were assigned to have square planar structures whereas the Co(II) complexes are octahedral by the axial coordination of two water molecules.

In continuation of our earlier work on the macrocyclic complexes of first row transition metals[1-4], the present communication deals with the synthesis and characterisation of the complexes of Cu(II), Ni(II) and Co(II) with the title ligand. The present ligand is a N_2O_2 donor type coordinating through its two nitrogen and two oxygen atoms to the central metal atom, which, in the present case, are Cu(II), Ni(II) and CO(II). All the complexes were found to be electrolytic in nature, the anions being outside the coordination sphere. The Cu(II) and Ni(II) complexes were square planar whereas the Co(II) complexes obtain an octahedral structure by the coordination of two water molecules

The complexes have been prepared in two steps as follows:

Step A: To a solution of 1,2-dichloro-4,5-dinitrobenzene (2.37 g; 0.01 mole) in methanol, was added a measured amount of salicylaldehyde (2.44 g; 0.02 mole) slowly with constant stirring. This solution was refluxed for 8 hrs and left overnight. The product A which crystallised out next morning was filtered, washed with methanol and used in step B.

Step B: Product A (4.08 g; 0.01 mole) was suspended in methanol and 0.01 mole of metal salt and ethylenediamine (0.60 ml; 0.01 mole) also in methanol was added with constant stirring and refluxing. The refluxing was continued for 4 hrs at the end of which the solvent was distilled off and the complexes were crystallised out using petroleum ether-ethanol mixture and analysed (Table 1).

The free macrocyclic ligand was obtained by extricating out Ni from $[Ni(L)]Cl_2$ complex with KCN using standard method.

On the basis of elemental analysis (Table 1), the molecular formulae of the complexes were found to be $[Ni(L)]X_2$ and $[Co(L)(H_2O)_2]X_2$ where $X=Cl^-$, SCN^-, BF_4^-, ClO_4^- and L = (b, j) dibenzo-m-(dinitrobenzo)-5,8-diaza-1,12-dioxocyclotetradeca 4.8-diene (DIMOT)($C_{22}H_{16}N_4O_6$).

TABLE 1

ANALYTICAL, MOLAR CONDUCTANCE DATA AND μ_{eff} VALUES

Compound	% Found/(Calcd.)				Λ_M* (ohm^{-1} cm^2 mole^{-1})	μ_{eff} (B.M.)
	M	C	H	N		
$[Cu(DIMOT)]Cl_2$	10.69 (11.10)	46.13 (46.64)	2.52 (2.82)	9.05 (9.89)	54.3	2.09
$[Cu(DIMOT)](SCN)_2$	9.63 (10.31)	46.69 (47.13)	2.98 (2.61)	12.98 (13.74)	52.31	2.13
$[Cu(DIMOT)](ClO_4)_2$	8 65 (9.06)	37.05 (37.98)	1.98 (2.30)	7.83 (8.05)	59.32	2.14
$[Cu(DIMOT)](BF_4)_2$	8.92 (9.41)	38.85 (39.46)	1.91 (2.39)	7.93 (8.37)	51.32	2.10
$[Ni(DIMOT)]Cl_2$	9.88 (10.33)	46.81 (47.05)	2.52 (2.85)	9.06 (9.98)	56.31	1.13
$[Ni(DIMOT)](SCN)_2$	8.92 (9.57)	46.98 (47.52)	1.83 (2.64)	12.90 (13.86)	55.15	1.02
$[Ni(DIMOT)](ClO_4)_2$	8.03 (8.40)	37.80 (38.26)	1.98 (2.31)	7.99 (8.11)	57.31	1.05
$[Ni(DIMOT)](BF_4)_2$	8.05 (8.73)	39.18 (39.75)	1.89 (2.40)	7.93 (8.43)	53.32	0.92
$[Co(DIMOT)]Cl_2$	9.75 (10.33)	46.80 (47.05)	1.92 (2.85)	9.08 (9.98)	56.31	5.06
$[Co(DIMOT)](SCN)_2$	8.92 (9.57)	46.90 (47.52)	1.94 (2.64)	13.18 (13.86)	56.31	4.99
$[Co(DIMOT)]ClO_4)_2$	8.80 (8.40)	37.62 (38.26)	1.94 (2.31)	7.85 (8.11)	50.12	5.07
$[Co(DIMOT)](BF_4)_2$	8.31 (8.78)	38.95 (39.75)	1.95 (2.40)	7.63 (8.43)	60.12	5.14

*Values in nitrobenzene.

The I.R. spectra of the complexes show bands in the region 2900–2700 cm^{-1}, 1590–1450 cm^{-1} which corresponds to νCH and aromatic ring vibrations[5]. The azomethine stretch is identified at 1600±30 cm^{-1} as a sharp band and its negative shift as compared to the free ligand value confirm the coordination of azomethine nitrogen to the metal ions[6]. The C—O stretching frequency, observed at 1230 cm^{-1} in free ligand also show a considerable negative shift indicating the coordination through O- atoms[7]. In the IR spectra of metal complexes, the chloride ion shows mainly one absorption at 505 ± 5 cm^{-1} which along with conductance values show its ionic nature[8]. The bands corresponding to thiocyanate ions appear at 2040–2080 cm^{-1} and at 950 cm^{-1}. These values suggest the presence of uninegative uncoordinated thiocyanate[9]. The bands observed at 1060 cm^{-1} and 930 cm^{-1} are due to the ionic uninegative perchlorate whereas the bands at 1540 cm^{-1} are because of ionic uninegative tetrafluoroborate[10]. The coordination of water molecules in the case of Co(II) complexes is evidenced by the lower shifting of H—O—H bending and O—H stretching vibrations appearing at 1600 cm^{-1} and 3400 cm^{-1} respectively[11].

The magnetic moments (Table 1) of Cu(II) complexes lie in the range of 2.05–2.15 B.M. These higher values are probably due to the orbital contribution[12,13]. The μ_{eff} values for Ni(II) complexes lie in the range of 0.85–1.05 B.M. which are much lower than the spin only value of two electrons and higher than zero, this is because of the partial paramagnetism which arises due to the spin-crossover phenomenon between the diamagnetic singlet and paramagnetic triplet states of the ion. This suggests a planar structure for the complexes as a result of dsp^2 hybridisation[14]. The magnetic moment values for Co(II) complexes lie in the range 4.70–5.20 B.M. These values are well within the reported range of octahedral complexes. The slightly higher values in this case are also due to the orbital contribution[15].

In the reflectance spectra of the Cu(II) complexes, bands seen at around 15.00 kK, 20.00 kK and 12.00 kK are assigned to the transitions, ${}^2B_{1g} \rightarrow {}^2E_{1g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^1B_{1g} \rightarrow {}^2B_{2g}$ respectively. These suggest a planar geometry for the complexes[16]. The Ni(II) complexes show one main band at 18.50 kK assigned to ${}^1A_{1g} \rightarrow {}^2A_{2g}$ transition. In addition, weak bands at 10.00 kK–12.50 kK and 22.00–25.00 kK were also seen. These bands also correspond to the planar geometry for the complexes[17]. In the complexes of Co(II), three bands corresponding to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)\nu_1$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)\nu_2$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)\nu_3$ are seen at 8.50 kK, 15.50 kK and 22.50 kK respectively. In some of the complexes the band was splitted into two bands. These bands along with the ν_2/ν_1 ratio which lie in the range 1.90–2.10 confirm pseudo-octrahedral structures for these complexes[18].

Thus on the basis of above discussion, the macrocyclic ligand was found to possess a planar structure which gives a square planar geometry to the Cu(II) and Ni(II) complexes and octahedral structures to the

Co(II) complexes. The octahedral structure in this case is obtained by the axial coordination of two water molecules to the square planar structure.

ACKNOWLEDGEMENTS

Two of us (S.S and N.A) are grateful to the C.S.I.R., New Delhi for the award of research fellowships for this work. The services of R.S.I.C., C.D.R.I., Lucknow are gratefully acknowledged.

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(*Received*: 18 June 1990; *Accepted*: 1 December 1990) AJC–249