

Coordination Template Reactions, Part III: Complexes of Tetradentate 1,3,7,9 and 1,3,8,10 Tetraenes with Cu(II) & Ni(II)

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Eight macrocyclic complexes have been prepared using the template condensation reactions between glyoxal, ethylenediamine and propylenediamine. The complexes which possess the general formula $M(L' \text{ or } L'')X_2$ where $M = \text{Cu(II)}$ and Ni(II) ; $X = \text{Cl}^-$, SCN^- and L' or $L'' =$ macrocyclic ligand, have been assigned octahedral structures on the basis of analytical, magnetic and spectral measurements.

INTRODUCTION

A number of coordination complexes of a variety of N_4 and N_6 donor macrocycles have been reported from this laboratory¹⁻³. The present work deals with the template condensation reactions between ethylenediamine or propylenediamine and glyoxal trihydrate in presence of metal salts resulting in hexacoordinated complexes which have been assigned octahedral structures on the basis of analytical, conductance, magnetic and spectroscopic data.

EXPERIMENTAL

The complexes have been prepared by adding glyoxal trihydrate (0.02 mole) to a refluxing solution of amine (0.02 mole) in methanol containing corresponding metal(II) chlorides (0.01 mole). The refluxing was continued for 4 hrs. and then methanol was distilled off and the complexes were crystallised out from the viscous liquid using petroleum ether, purified by running over TLC plates, dried and analysed. The thiocyanate complexes were prepared by adding NH_4SCN to the solution prior to refluxing and removing NH_4Cl so formed by filtration. The extrication of Ni(II) chloride complexes with KCN, using standard procedure has resulted in free macrocycles characterised as follows:

Ligand L' $\text{C}_8\text{H}_{12}\text{N}_4$, Found: C = 58.10%, H = 7.60%, N = 33.80% (mol. wt = 154). Calcd: C = 58.50%, H = 7.31%, N = 34.10% (mol. wt = 164)

Ligand $L'' = C_{10}H_{16}N_4$, Found: C = 64.10%, H = 8.72%, N = 29.41% (mol. wt = 202). Calcd: C = 65.50%, H = 8.31%, N = 29.22% (mol. wt. = 192).

The reactions of these isolated ligands with $NiCl_2$ give the original complex thus supporting the *in situ* synthesis used in the investigation. The conductivity of complexes was measured in methanol by direct reading conductivity bridge. Analytical data and IR studies were obtained from CDRI, Lucknow.

RESULTS AND DISCUSSION

The analytical data of the complexes correspond to 1 : 1 metal-ligand stoichiometry (Table 1). The molar conductance values in methanol of the complexes are in the range (8.80–59.15 $ohm^{-1} cm^2 mole^{-1}$) suggesting the non-electrolytic nature of the complexes. The μ_{eff} value of all the complexes (Table 1) show that these are all high spin with a pseudooctahedral environment around the metal ion⁴.

TABLE I
ANALYTICAL AND MAGNETIC DATA OF Cu(II) AND Ni(II) COMPLEXES

Formulae	% Found (Calcd)				μ_{eff} (B.M.)
	M	C	H	N	
Cu(L')Cl ₂	20.86 (21.77)	32.48 (32.16)	3.86 (4.02)	18.62 (18.76)	1.80
Cu(L')(NCS) ₂	19.14 (18.48)	35.35 (34.93)	3.82 (3.49)	25.02 (24.40)	2.05
Ni(L')Cl ₂	19.01 (19.95)	32.65 (32.69)	5.06 (5.08)	18.36 (19.07)	3.15
Ni(L')(NCS) ₂	16.44 (17.30)	36.02 (35.44)	4.09 (3.54)	25.25 (24.80)	3.03
Cu(L'')Cl ₂	18.85 (19.44)	36.60 (36.75)	5.01 (4.90)	17.95 (17.15)	1.98
Cu(L'')(SCN) ₂	16.82 (17.09)	38.25 (38.76)	4.60 (4.30)	23.00 (22.61)	1.85
Ni(L'')Cl ₂	17.69 (18.22)	37.85 (37.31)	5.28 (4.97)	17.92 (17.41)	2.98
Ni(L'')(SCN) ₂	15.31 (15.48)	39.81 (39.27)	4.82 (4.36)	23.40 (22.91)	3.20

The coordination mode of ligand is established by the IR spectra of the complexes. The stretching and deformation frequencies expected for the NH_2 group and the usual $C=O$ stretch is absent and in their place a strong band is present at $1590 cm^{-1}$ assigned as the stretching mode of

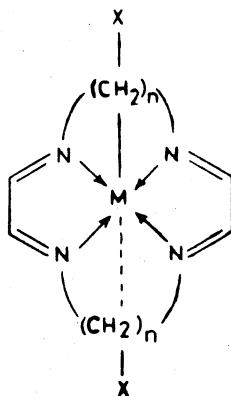
coordinated and conjugated azomethine group and provides strong evidence for a closed cyclic system containing Schiff base linkage⁵⁻⁷.

The coordination of chloride is predicted by the presence of M-Cl stretching around 310 cm^{-1} , while the thiocyanate complexes exhibit bands at 2100 cm^{-1} and 810 cm^{-1} corresponding to N-bonded thiocyanate ion. The bands around $430 \pm 10\text{ cm}^{-1}$ in the complexes originate from Cu-N or Ni-N vibration and confirm the coordination of ligands through their azomethine nitrogens^{8,9}.

The electronic spectra of Cu(II) complexes show one or two broad maxima lying between $20,000\text{--}18,000\text{ cm}^{-1}$ corresponding to the two transitions. ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g(A_{2g})$ coupled together in one broad envelope and thus correspond to distorted octahedral geometry¹⁰.

The Ni(II) complexes show three bands around $11,000$, $15,000$ and $26,500\text{ cm}^{-1}$ corresponding to the three octahedral transitions as ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$; out of these ν_3 transition is somewhat obscured by strong charge transfer band at $30,000\text{ cm}^{-1}$. The ν_1 band in all the complexes shows pronounced splitting with the well defined components at $10,500$ and $11,500\text{ cm}^{-1}$ and thus these spectra correspond better to D_{4h} symmetry rather than O_h ¹¹⁻¹³.

On the basis of above evidence the following structures are suggested for the complexes.



For L' , $n = 2$

L'' , $n = 3$

$X = \text{Cl}^-, \text{SCN}^-$

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