

Coordination Template Reactions: Part I—Complexes of Macrocyclic Ligand Tetrabenzo[*b,f,j,n*] [1,5,9,13]tetraazacyclohexadecine with Copper (II) & Nickel (II)

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Six new four coordinate macrocyclic complexes of Cu(II) and Ni(II) possessing the general formulae $[M(L)] X$ or Y_2 , where $M = Cu(II)$ or $Ni(II)$, $L = \text{tetrabenzo}[b,f,j,n][1,5,9,13]\text{tetraazacyclohexadecine}$, $X = \text{succinate}$, phthalate and $Y = \text{anthranilate ion}$, have been prepared. The complexes have been characterised using molar conductance, infrared, magnetic and electronic spectral data and have been assigned planar geometries.

Some cationic complexes of a macrocyclic ligand formed by self condensation of four molecules of *o*-aminobenzaldehyde have been prepared using a variety of organic salts of Cu(II) and Ni(II). Earlier work on similar complexes containing inorganic salts of these metals¹⁻³ has been reported. Formation of the macrocycle and the mechanism of self condensation depend upon the nature of anion as well, and hence organic anions such as succinate, phthalate or anthranilate, which normally give non-electrolytic complexes, were used in the present study to determine

their relative donor strengths with respect to the macrocyclic ligand prepared⁴⁻⁷.

The complexes have been prepared by refluxing the corresponding metal (II) salt with *o*-aminobenzaldehyde which was freshly prepared by standard methods. The complexes were crystallised from the solution using petroleum ether-ethanol mixture. The complexes have been characterised on the basis of elemental analysis, molar conductance, infrared, magnetic moment and electronic spectral data.

The analytical results (Table I) show that in case of both the metals, only one molecule of the ligand, obtained by the self condensation of four molecules of aldehyde, is coordinated. The molar conductance values ($30-37 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in nitrobenzene) show that the complexes are electrolytes and thus the anion is not coordinated in any case. The structure of the cationic part of the complex may be represented by (I).

It is thus clear that the ligand is capable of functioning as a tetradentate ligand; in doing so it completely encircles the metal ion in a planar manner. Since this type of close packed ring structure will confer extensive stability on complexes, the anions

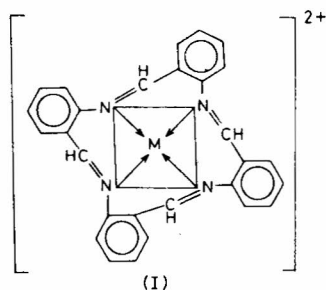


Table I—Analytical and Magnetic Moment Data of the Complexes

Formula (colour)	Found (calc.), %				$\mu_{\text{eff.}}$ (B.M.)
	M	C	H	N	
$[Cu(C_{28}H_{20}N_4)] (CH_3COO)_2$ (Dark green)	10.00 (10.73)	64.05 (64.91)	4.58 (4.06)	10.28 (9.46)	1.904
$[Cu(C_{28}H_{20}N_4)] (C_8H_4O_4)$ (Brown)	9.08 (9.92)	67.00 (67.55)	3.28 (3.75)	9.51 (8.76)	1.899
$[Cu(C_{28}H_{20}N_4)] (C_7H_6O_2N)_2$ (Dark green)	8.01 (8.48)	67.90 (67.42)	4.00 (4.28)	10.65 (11.23)	1.864
$[Ni(C_{28}H_{20}N_4)] (CH_3COO)_2$ (Brown)	8.78 (9.98)	64.95 (65.40)	3.62 (4.09)	9.90 (9.54)	0.573
$[Ni(C_{28}H_{20}N_4)] (C_8H_4O_4)$ (Reddish brown)	8.28 (9.23)	68.75 (68.07)	3.20 (3.78)	9.55 (8.82)	0.299
$[Ni(C_{28}H_{20}N_4)] (C_7H_6O_2N)_2$ (Dark brown)	7.21 (7.84)	67.02 (67.85)	4.92 (4.30)	11.62 (11.31)	0.570

$(CH_3COO)_2 = \text{succinate}$; $C_8H_4O_4 = \text{phthalate}$ and $(C_7H_6O_2N)_2 = \text{anthranilate ions}$.

which are otherwise coordinating in nature are not found to do so in the present case. Their coordination will cause ring opening with the consequent formation of octahedral structures which are expected to be less stable.

The coordination mode of ligand is established by the infrared spectra; the stretching and deformation frequencies expected for the NH_2 group and the usual $\text{C}=\text{O}$ stretch of the aldehyde are absent, and in their place is present a strong band at 1570 cm^{-1} assignable to the stretching mode of the coordinated and conjugated $\text{C}=\text{N}$ group. The IR spectra provide strong evidence for the presence of a closed cyclic system containing schiff base type linkages. The infrared spectra of anions show that these are not coordinated as indicated by conductance values² also.

The magnetic moments lie in the usual range for one and zero unpaired electrons for Cu(II) and Ni(II) complexes respectively. The reflectance spectra of Cu(II) complexes exhibit a single band at 16.50 kK assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition. In the case of Ni(II) complexes, the main band is seen at 19.00 kK, which

may be assigned to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition. A few more bands are observed in the range 8.00-10.50 kK or 22.00-25.00 kK.

These compounds are remarkably stable in nature suffering no decomposition even in boiling acids. Their stability is probably due to the cyclic nature of the ligand and the protective effect of coordination. As an outcome of this stability, the complexes also do not undergo addition or substitution reactions with strong coordinating ligands such as di-, tri-, or tetra-amines, mainly due to the absence of terminal groups which are capable of stepwise dissociation and substitution.

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