A New Series of Macrocyclic Planar Chelate Complexes

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ALTHOUGH several syntheses have been reported in which cyclization occurs around a metal ion,[1–4] none seems to have been recorded in which cobalt(II) can be used as well as nickel(II) and copper(II), or in which the resulting ligand is both of "N_4 type" and anionic.

Complexes of the type (I)—(V) have been obtained in 60—90% yields by the condensation of (VI) (1 mole) with the appropriate diamine (2 moles) in the presence of the hydrated metal acetate in methanol. (If no metal ions were present, a high-melting material was obtained which did not react with cobalt, nickel, or copper ions.)

The complexes are highly coloured, crystalline solids, soluble in chloroform and benzene. Analysis for C, N, and H established the empirical formula of (I), (II), (IV), and (V), and molecular weight determination showed (I), (II), and (V) to be monomeric in benzene solution.

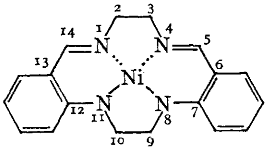
The magnetic moments of 6,7:12,13-dibenzo-1,4,8,11-tetra-azacyclotetradecane-4,14-dieneato-nickel(II) and the corresponding copper(II) and cobalt(II) compounds are 0·00 ± 0·05, 1·87 ± 0·05,

$2{\cdot}15 \pm 0{\cdot}05$ B.M. respectively, values which are consistent with planar configurations.

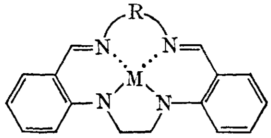
The visible/ultraviolet spectra in benzene were not affected by pyridine, which suggests a reluctance by the metals in the complexes to change co-ordination numbers. The spectra are very similar to those of the analogous acyclic chelate compounds, (VII)—(IX) (which were prepared from the metal acetates and ligands, the latter having been synthesized by condensation of *o*-aminobenzaldehyde and the appropriate diamine).

The ^{1}H n.m.r. spectrum of (I) in $CDCl_3$ showed peaks in the ratio of 1 : 2 : 2 at τ values of 1·96, 6·42, and 6·53 which are ascribed to methine, methylene, and methylene hydrogen atoms respectively. No indications were found of hydrogen atoms bonded to nitrogen, particularly 8- and 11-N. Presumably considerable delocalization of electrons occurs. The infrared spectra in Nujol mulls and potassium bromide discs showed the presence of C=N groups by absorption at 1609 ± 5 cm.$^{-1}$, and the absence of N–H groups in all the complexes.

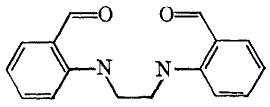
The production of a neutral complex in these reactions shows a much greater similarity to the formation of metal salen complexes from metal ion, salicylaldehyde, and ethylenediamine,[5] than to related systems in which tetra-aza-metal(II) cations are formed which contain secondary amine groups.[2,4]



(I)



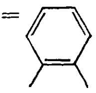
	M	R
(II)	Co	S
(III)	Co	T
(IV)	Ni	T
(V)	Cu	S

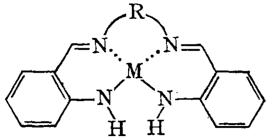


(VI)

S= $-CH_2{\cdot}CH_2-$

T=





(VII) M=Ni, R=S and T
(VIII) M=Co, R=S
(IX) M=Cu, R=S

(*Received, March 4th*, 1968; *Com.* 256.)

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