A Template Synthesis of Metal Complexes of Macrocyclic Ligands

By P. CHAVE and C. L. HONEYBOURNE*
(*School of Chemistry, University of Bristol, Bristol,* BS8 1TS)

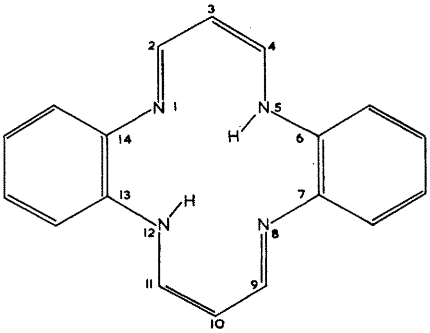
Summary Metal complexes of a conjugated macrocyclic ligand have been prepared by a template synthesis.

1,1,3,3-TETRAMETHOXYPROPANE has been used to synthesise 1,3-bidentate Schiff's bases.[1,2] Attempts to extend this method to the synthesis of tetra-azacyclotetradecenes from an *ortho*-diamine and 1,1,3,3-tetramethoxypropane were unsuccessful. Since bis-(*NN'*-dibenzyl-1-amino-3-iminopropenenickel(II) dichloride was synthesised from benzylamine and bis(malondialdehyde)nickel(II) dichloride,[3] the use of template reactions in the synthesis of macrocyclic ligands was investigated. The reactants were *o*-diamine (A) (2 mol.), 1,1,3,3-tetramethoxypropane (B) (2 mol.), metal dichloride hydrate (C) (1 mol.), and sufficient 2N-hydrochloric acid for the hydrolysis of the methoxy-compound (D).

Simultaneous reaction of (A), (B), (C), and (D) in ethanol solution proved unsatisfactory. However, when (A) and (C) were treated under reflux for 1 hr. in ethanol, and then (B) and (D) were added, and the mixture heated for a further 5 hr., deep-red solutions were obtained; from the cool solutions red solids separated. For (A; 4,5-dimethyl-*o*-phenylenediamine) and (B; $NiCl_2,6H_2O$ or $CoCl_2,6H_2O$) metal chloride complexes with the tetradentate, non-cyclic *NN'*-di-(*o*-aminophenyl)-1-amino-3-iminopropene were obtained.

(B) and (D) were heated for ½ hr. (ethanol) and then (C) was added; after a further 8 hr. under reflux, an insoluble yellow-green solid (E) was obtained. This was suspended in an ethanolic solution of (A) and after 4 hr. under reflux, an intensely coloured solution was obtained; a coloured solid separated from the cool solution. For (A; *o*-phenylenediamine) and (C; $CuCl_2,2H_2O$) elemental analyses indicate that the yellow-brown solid is the copper chloride complex of the macrocyclic ligand (I) (tdct). The i.r. spectrum of the above compound is consistent with the presence of N–H and C=N bonds, being similar to those of copper halide complexes of malondianil and methyl-substituted malondianils.[3,4]

The copper compound was first isolated as the yellow-brown trichloride ($C_{18}H_{17}CuCl_3N_4$) which slowly liberated carbon dioxide from aqueous sodium hydrogen carbonate solution. The chocolate brown, more soluble, dichloride was obtained by heating the trichloride in an ethanolic solution of either potassium t-butoxide or tetrabutylammonium hydroxide. This brown compound is stable to attack by 10N-aqueous sodium hydroxide solution at 60° for 15 hr.



The highest mass peaks in the mass spectrum of the above copper compound have been mass-matched to tdct-ato-Cu^{II} [m/e found: 349·0518, 351·0494; required: 349·0514, 351·0496], the intensities and peak height ratio of the peaks at m/e = 36 and 38 being consistent with our proposed immediate loss of HCl. Apart from the two peaks mentioned above, the intensities of the peaks corresponding to copper-containing fragments are extremely low. The low relative intensity of the peak corresponding to the free ligand (m/e found: 288·1370; required: 288·1375) indicates that this ligand is less stable, under the experimental conditions, than the porphyrins.[5]

We are extending our synthetic method to include a wide range of metal and metal halide complexes of conjugated, macrocyclic ligands, and intend to make a comparative study between the spectroscopic and magnetic properties of these substances and those of their porphyrin and phthalocyanin analogues.

(*Received, January 23rd,* 1969; *Com.* 098.)

---

[1] C. L. Honeybourne and G. A. Webb, *Chem. Comm.*, 1968, 739.
[2] C. L. Honeybourne and G. A. Webb, *Spectrochim. Acta*, 1969, *A*, **25**, in the press.
[3] C. L. Honeybourne, Ph.D. Thesis, University of Surrey (1968).
[4] C. P. Richards, M.Sc. Thesis, University of Surrey (1968).
[5] A. H. Jackson, G. W. Kenner, K. H. Smith, R. T. Aplin, H. Budzikiewicz, and C. Djerassi, *Tetrahedron*, 1965, **21**, 2913.