Metal Complexes of the Macrocycle derived from Heptane-2,4,6-trione and 1,2-Diaminoethane

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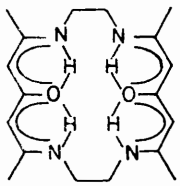
Summary Copper(II) and nickel(II) derivatives of the macrocyclic Schiff base derived from heptane-2,4,6-trione and 1,2-diaminoethane are reported.

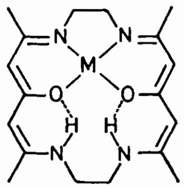
HEPTANE-2,4,6-TRIONE (H_2daa) reacts with 1,2-diaminoethane(en) in ethanol to give yellow crystals of 5,9,14,18-tetramethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (daen) (**1**).[1] The formulation of (I) is supported by spectral data. [^{1}H n.m.r. ($CDCl_3$) 1·84 (12H, s, Me), 3·30 (8H, m, CH_2), 4·73 (4H, s, CH), and 10·20 p.p.m. (4H, br, N · · H · · O). Irradiation at the NH resonance reduced the CH_2 multiplet to a single peak. ^{13}C N.m.r. ($CDCl_3$) 18·9 (Me), 43·2 (CH_2), 96·7 (CH), 157·5 (CN) and 189·7 p.p.m. (CO); i.r., no bands ascribable to free $>$NH stretching vibrations or carbonyl stretching modes, but bands at 1620 (w, sh) and 1580 cm^{-1} (s, br)]. We now report the isolation of mononuclear metal(II) complexes of this ligand representative of a class of compounds in which the metal ion has the choice of two 'compartments' for interaction.

The reaction of a chloroform solution of (**1**) with an ethanolic solution of copper(II) acetate gave on dilution with ethanol a greenish-brown precipitate, i.r. 3160 (NH, H-bonded), 1630 (CN, co-ordinated),[2] and 1590 cm^{-1}.

Chemical analysis and m.s. (parent ion m/e = 393), support the formulation Cu(daen). Ni(daen) can be prepared by a similar method (i.r. 3220, 1640, and 1590 cm^{-1}; m.s. parent ion m/e = 388). The diffuse reflectance spectra show bands at 623 nm [Cu(daen)] and 585 nm [Ni (daen)] suggesting that the complexes have square planar configuration (**2**).[2] The complexes have also been prepared by a template synthesis.



(1)



(2)

If a chloroform solution of (**1**) was added to an aqueous solution of copper(II) acetate and stirred for 1·5 h, a green precipitate of $Cu_2(daa)_2$[3] was recovered from the aqueous layer leaving a deep violet chloroform layer.[1] This layer was not chromatographed (as in ref. 1) and removal of the solvent gave a purple oil and a green-brown solid. Subsequent recrystallisation of the oil from $CHCl_3$–hexane gave purple crystals of the copper(II) complex of the acyclic Schiff base, 6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraone.[1] The green-brown solid analysed as 2 Cu : 3 daen and only after several chloroform washings was Cu(daen) recovered. The reaction of nickel(II) acetate with (**1**) in $CHCl_3$–H_2O gave a compound analysing as 2 Ni : 3 daen as a suspension in the aqueous layer and no acyclic product was recovered from this reaction. Ni(daen) was obtained from the product after several chloroform washings.

The reactions of 1,2-diaminopropane (pn) and 1,3-diaminopropane (pd) with H_2daa in ethanol gave the corresponding macrocyclic Schiff bases, dapn and dapd. The reaction of dapn with $M(II)(OAc)_2$, (M = Cu, Ni), gave M(dapn), but we have been unable to isolate complexes with dapd using the procedures described.

We thank the S.R.C. for a Studentship (to S.E.G.).

(*Received, 2nd September* 1974; *Com.* 1119.)

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