Template Synthesis and X-Ray Structure Determination of a Nickel(II) Complex of a Novel Monoanionic Macrocyclic Ligand

By N. W. Alcock

(*The Department of Molecular Sciences, The University of Warwick, Coventry* CV4 7AL)

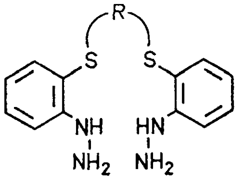
and P. A. Tasker*

(*The Department of Chemistry, The Polytechnic of North London, Holloway, London* N7 8DB)

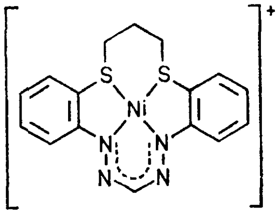
Summary Extension of the 'template effect' of metal ions to the reaction of co-ordinated dihydrazines has resulted in the synthesis of a novel monoanionic macrocyclic ligand complex of nickel(II), shown by an X-ray structure determination to have a planar N_2S_2 donor set.

Many of the syntheses of macrocyclic ligands which employ the 'template effect' of metal ions involve the formation of imine groups by reaction of primary amines with carbonyl containing compounds.[1] A severe limitation[2] in the use of metal ions to direct the stereochemistry of such reactions is that primary amines cannot be co-ordinated to the metal ion at the stage where nucleophilic attack at the carbonyl is required. This restriction does not apply to hydrazines because two lone pairs of electrons are present in the functional group. Consequently we have chosen to study applications of dihydrazines such as (I) and (II) to template syntheses of complexes of macrocyclic ligands.

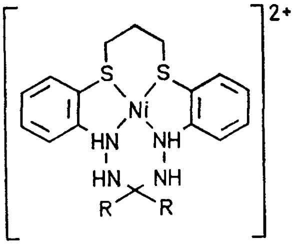
We report here an unusual cyclisation reaction which occurs when a tetrahydrofuran solution of (II) is treated in air with formaldehyde and nickel(II) salts. The deep red-purple complex resulting from the reaction in the presence of nickel(II) perchlorate is diamagnetic and has been shown to be structure (III). I.r. spectra confirm the absence of NH groups in the complex and show a single broad band



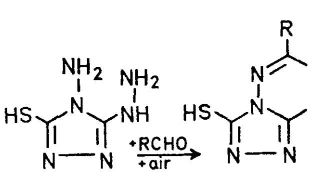
(I), R = $(CH_2)_2$
(II), R = $(CH_2)_3$



(III)



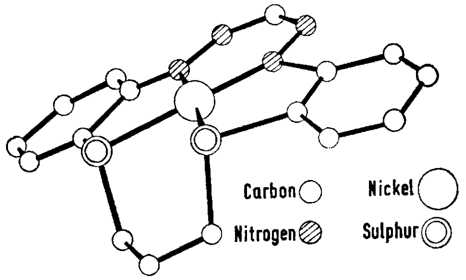
(IV)



(V) (VI)

at 1100 cm^{-1} characteristic of unco-ordinated perchlorate.[3]

A single-crystal X-ray diffraction study was undertaken to confirm the presence of the proposed monoanionic ligand. The compound crystallizes as monohydrate in the triclinc space group $P\bar{1}$ with $a = 11{\cdot}382$ Å, $b = 14{\cdot}272$ Å, $c = 7{\cdot}572$ Å, $\alpha = 106{\cdot}3°$, $\beta = 83{\cdot}08°$, $\gamma = 114{\cdot}3°$, $D_m = 1{\cdot}56$, $D_c = 1{\cdot}55$ and $Z = 2$. The structure was solved by the heavy-atom method using 1096 observed reflections ($I/\sigma(I) > 3{\cdot}0$) which were collected with a Stoe 2-circle automatic diffractometer. The positions of all non-hydrogen atoms have been assigned and refinement using isotropic temperature factors for all atoms has given a current R factor of 11·0%.



FIGURE

The configuration of the cation is shown in the Figure. The complex shows planar co-ordination geometry for the nickel ion, with the conjugated anionic chelate ring lying close to this plane. The saturated -$(CH_2)_3$- bridge between the two sulphur donors is puckered to give a conventional chair-form six-membered ring.

Using cyclohexanone instead of formaldehyde in the above reaction has allowed isolation of a complex [IV; R = -$(CH_2)_5$-]. A similar species (IV; R = H) is possibly an intermediate in the reaction giving (III). The formation of these 14-membered heterocycles is clearly facilitated by correct orientation of the two hydrazino-groups by co-ordination of (II) in an equatorial-octahedral or square-planar manner to the nickel. The subsequent cyclisation reactions are then probably analogous to those giving[4] the six-membered ring of (VI) by treating (V) in the absence of metal ions with aldehydes in air.

We thank Mr. L. Carr for technical assistance.

(*Received, 28th September* 1972; *Com.* 1665.)

---

[1] D. H. Busch, *Helv. Chim. Acta, Fasciculus, Extraordinarius Alfred Werner*, 1967, 174; D. H. Busch, *Adv. Chem., Series* No 100, 1971, 44.

[2] M. Green, J. Smith, and P. A. Tasker, *Inorg. Chim. Acta*, 1971, **5**, 17.

[3] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

[4] R. G. Dickinson and N. W. Jacobsen, *Chem. Comm.*, 1970, 1719.