Containment of Two Metal Ions in the Ring of One Cyclic Ligand: Metal Complexes of an Octadentate Macrocycle with only Sulphur Donor Atoms

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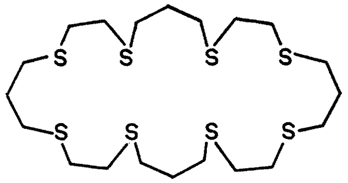
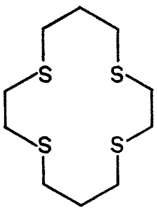
Summary The isolation of an octadentate thioether macrocycle and its metal-ion complexes is described. Physical measurements on these complexes indicate that the ligand is able to circumscribe completely two metal ions.

METAL chelates of several macrocyclic ligands containing only sulphur donors have been prepared recently.[1,2] The tetradentate and hexadentate ligands are reported to form metal complexes in which all donor atoms are co-ordinated to a single metal ion resulting in square-planar, tetragonal, and octahedral geometries. We report here the synthesis of an octadentate thioether macrocyclic ligand and its metal-ion complexes. We believe this to be the first example of a macrocyclic ligand which is able to circumscribe completely two metal ions.

The ligand 1,4,8,11,15,18,22,25-octathiacyclo-octacosane (oto) (I) is obtained from the reaction of the dianion of 1,4,8,11-tetrathioundecane with 1,3-dibromopropane. This reaction has been reported to give the tetradentate 1,4,8,11-tetrathiacyclotetradecane (ttp) (II) in low yield (7·5%) due to formation of polymeric materials. Extraction of the polymeric residue, which remains after complete sublimation of (II), with hot absolute ethanol yielded a white solid (I) (*ca.* 25% yield) which has been characterized as the dimer of (II), m.p. (66—67°), $m/e = 536$ (M), $M(\mathrm{CHCl_3})$ 523, 546, elemental analysis correct for (I), and n.m.r. τ7·25 (overlapping s and t, area 32) and 8·02 (quint., area 8).†



(I)



(II)

Thus, under the conditions originally employed, there is a greater tendency for 1,3-dibromopropane to fuse two dianions together than to close the tetrafunctional ring. Further investigation has shown that by dilution of reactants prior

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† The n.m.r. spectra of (I) and (II) are essentially identical and are similar to the patterns reported for 1,4,8,11-tetra-azacyclotetradecane (B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102, 1109.)

to mixing, the yield of (II) is greatly increased (50—60%) while the yield of (I) is lowered substantially.

TABLE

	Colour	μ_{eff}(B.M.)	(mho-cm^2) Λ_M mol	λ_{max} (MeNO$_2$) (cm^{-1})	λ_{max} (solid) (cm^{-1})
[Ni$_2$(oto)](BF$_4$)$_4$,2MeNO$_2$	Red	[a]	310[b]	19,900 (ϵ 210) 22,700	19,600 22,700
[Ni$_2$(oto)(NCS)$_4$],2H$_2$O (V)	Blue-green	3·08	47[b]	9900 (ϵ 44) 11,000 (ϵ 57) 16,956 (ϵ 47)	9800 10,980 16,700

[a] Low spin. [b] 10^{-4} M in MeNO$_2$.

Reaction of (I) with an excess of the hexa-acetic acid derivative of nickel(II) tetrafluoroborate (III) in nitromethane yielded the deep-red complex [Ni$_2$(oto)](BF$_4$)$_4$, 2MeNO$_2$ (IV) (see Table). The nitromethane in (IV) can be removed *in vacuo* at 110°, to give the red–orange [Ni$_2$(oto)]-(BF$_4$)$_4$. Addition of an excess of potassium thiocyanate to the red solution of (IV) in nitromethane still containing a slight excess of (III) yielded a blue solution from which the complex [Ni$_2$(oto)(NCS)$_4$],2H$_2$O (V) was isolated. Elemental analysis shows that in these complexes the metal to ligand ratio is 2 : 1.

Physical measurements indicate that the octadentate ligand yields complexes in which four donor atoms are co-ordinated to each of the two nickel atoms. The tetrafluoroborate salt is a low-spin, 4 : 1 electolyte in nitromethane with a visible spectrum characteristic of nickel(II) in a square-planar environment. The thiocyanate derivative is a high-spin, nonelectrolyte in nitromethane with a near i.r.–visible spectrum typical of six-co-ordinate tetragonal nickel(II). The visible spectra of both complexes are almost identical to those of the corresponding Ni(ttp)X$_2$ complex.[1]

The complexes react readily with water giving free ligand and solvated nickel(II) ion. The tetragonal complex seems to be more stable toward dissociation than square-planar [Ni$_2$(oto)](BF$_4$)$_4$,2MeNO$_2$, which, in turn, is more stable than the desolvated BF$_4^-$ salt. The latter is readily dissociated by moist air.

The octadentate ligand reacts with PdCl$_4^{2-}$ and PtCl$_4^{2-}$ to give complexes in which the metal to ligand ratio is 4:1, [Pd$_4$(oto)Cl$_8$] and [Pt$_4$(oto)Cl$_8$]. These complexes are very stable, and only the palladium complex is soluble in dimethylformamide. Physical measurements indicate that the ligand acts in a bidentate fashion toward each of the four metal ions resulting in four square-planar metal ions per molecule.

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[1] W. Rosen and D. H. Busch, *Chem. Comm.*, 1969, 148; *J. Amer. Chem. Soc.*, 1969, **91**, 4694; *Inorg. Chem.*, 1970, 9, 262.

[2] D. St. C. Black and I. A. McLean, *Tetrahedron Letters*, 1969, 3961.