1,4,10,13-Tetrathia-7,16-diazacyclo-octadecane, a Macrocyclic Sexadentate Ligand

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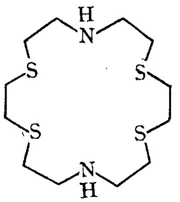
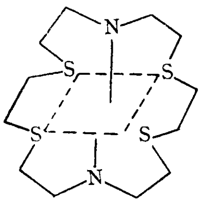
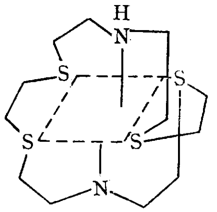
WE report the preparation of the title compound (I), an 18-membered macrocycle, which behaves as a sexadentate chelating agent. This macrocycle (I) has been prepared as white crystalline needles, m.p. 125°, (8%), by the reaction of the disodium salt of ethane-1,2-dithiol and di-(2-bromoethyl)amine[1] in ethanol at high dilution. The desired product can be separated from polymeric material by recrystallisation from ethanol. The proposed structure (I) is supported by the following evidence. Elemental analysis is compatible with the empirical formula $C_{12}H_{26}N_2S_4$, which is confirmed by molecular weight measurement [Found: M(osmometric in benzene), 323, 326. Calc.: M, 327]. The n.m.r. spectrum is also compatible with structure (I) but does not rule out alternative cyclic structures. The mass spectrum does not show a molecular ion, and the parent peak at m/e 267 corresponds to $[M - CH_2{\cdot}SCH_2]^{+\cdot}$. Further breakdown occurs with loss of fragments caused by cleavage of carbon–carbon bonds.



(I)



(IIa)



(IIb)

Compound (I) reacted readily with nickel(II) and cobalt(II) picrate to form a yellow [Ni(ligand)]-(picrate)$_2$ and olive-green [Co(ligand)](picrate)$_2$, which were characterised by elemental analysis. The nickel(II) complex has a magnetic moment of 2·9 B.M., consistent with an octahedral configuration, whereas the value for the cobalt(II) complex is 2·3 B.M. Although this is in the range for square-planar configuration, this is thought to be unlikely and an interpretation involving a spin-free/spin-paired equilibrium is tentatively preferred. This point is being clarified by a variable temperature study.

The ligand (I) can co-ordinate as a sexadentate in two possible octahedral configurations, (IIa and IIb). In both, the four sulphur atoms lie in the equatorial plane and the two nitrogen donors occupy *trans*-positions. In (IIa) the macrocycle is bent about each donor atom, while in (IIb) the two pairs of S–N–S donors are planar. The ligand is a little more crowded in configuration (IIb) but this allows a more perfect fit of the six donor atoms around an octahedral metal than configuration (IIa).

Pedersen[2] has prepared the analogous 18-membered poly-ether heterocycle in 1·8% yield by cyclisation of a linear chloro-alcohol, together with many similar poly-ethers using various techniques. One of these planar poly-ethers has been shown[3] to act as a bistridentate ligand.

Curry and Busch[4] have described the only other macrocyclic sexadentate chelating agent, produced by a template synthesis as its iron(III) complex, but this ligand cannot be isolated free of the metal.

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[1] B. Bobranski, T. Jakobiec, and D. Prelicz, *Acta Polon. Pharm.*, 1955, **12**, 195.
[2] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.
[3] A. C. L. Su and J. F. Weiher, *Inorg. Chem.*, 1968, **7**, 176.
[4] J. D. Curry and D. H. Busch, *J. Amer. Chem. Soc.*, 1964, **86**, 592.