A New Sulphur-containing Macrocyclic Sexadentate Ligand: 12,13,26,27-Tetrahydrotetrabenzo[*e,i,o,s,*][1,4,11,14,7,18]-tetrathiadiazacycloeicosine

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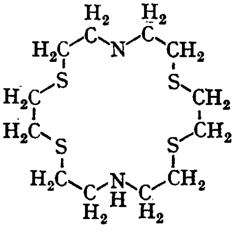
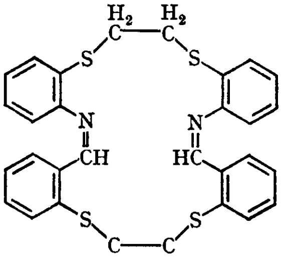
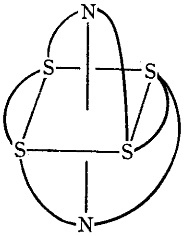
THE initial report of the preparation of a sexadentate macrocyclic chelate containing six nitrogen donors[1] has been followed recently by a report of the syntheses of the nickel(II) and cobalt(II) complexes of the new sexadentate ligand (I).[2] As a consequence of its flexibility, (I) might co-ordinate in two possible configurations around an octahedral metal ion and hence no absolute assignment of its configuration after complexation has been made.[2] We report the syntheses of complexes of the highly conjugated macrocyclic sexadentate ligand (II) (ms) which, because of the planarity of each S–N–S portion of the structure, can only co-ordinate octahedrally as in (III).

Reaction *in situ* of the appropriate metal salt with 1,2-bis-(2-aminophenylthio)ethane[3] and 1,4-bis-(2-formylphenyl)-1,4-dithiabutane (stoicheiometric ratios in solution) yields the compounds (M ms)X_2 (M = Ni, X = ClO_4, I and M = Co, X = ClO_4). The complexes all yield satisfactory analytical data and their i.r. spectra give no evidence for the presence of uncondensed amine or aldehyde. Conductivity studies in nitromethane reveal that the complexes are bi-univalent electrolytes and the i.r. spectra of the perchlorate salts show single broad absorptions at about 1100 cm.$^{-1}$ [γ(Cl–O)], typical of ionic perchlorate groups.[4]


(I)


(II)

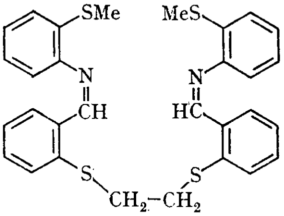
The mid-brown complexes (Ni ms)X_2 (X = ClO_4,I) have room-temperature magnetic moments of 3·07 and 3·12 B.M., respectively, which are in accord with the assigned six-co-ordinate structures.



(III)

For comparison, the nickel perchlorate complex of the closely related linear sexidentate ligand (IV), *NN'*-[ethylenebis(thio-*o*-phenylenemethylene)]bis-[2-(methylthio)aniline], has also been prepared. This yellow-brown paramagnetic (μ 3·08 B.M.) complex has an i.r. spectrum very similar to the analogous macrocyclic sexadentate complex. This complex is also considered to be six-co-ordinate.

If (Ni ms)$(ClO_4)_2$ is heated in dimethylformamide, ligand displacement occurs and the free macrocycle (II) can be isolated from the solution as yellow crystals, *m/e* 543, which corresponds to the parent ion for the macrocyclic ligand. By reaction of the free macrocycle with nickel perchlorate in acetone, (Ni ms)$(ClO_4)_2$ can be recovered.



(IV)

The dark brown (Co ms)$(ClO_4)_2$ has a magnetic moment of 1·86 B.M., which is in the expected range (1·7—2·0 B.M.)[5] for six-co-ordinate low-spin cobalt(II) complexes. In contrast the similar complex of (I) has a moment of 2·3 B.M.

This investigation was supported by the U.S. Public Health Service. Correct nomenclature has been provided by Dr. Kurt Loening.

(*Received, September 30th, 1968; Com.* 1336.)

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