Stereoselective Chelation in Diacidocobalt(III) Complexes of the Asymmetric Quadridentate Ligand 4-Methyl-1,8-diamino-3,6-dithiaoctane

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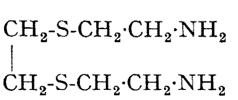
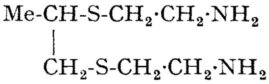
1,8-Diamino-3,6-dithiaoctane (I) can function as a quadridentate ligand in the synthesis of cobalt(III) complexes,[1] and is totally geometrically selective, giving only



$$\begin{array}{l}CH_2\text{-}S\text{-}CH_2\cdot CH_2\cdot NH_2\\ |\\ CH_2\text{-}S\text{-}CH_2\cdot CH_2\cdot NH_2\end{array}$$

(I)

the symmetrical *cis* isomer (II). We now describe cobalt(III) complexes of the asymmetric ligand ($\pm$)-4-methyl-1,8-diamino-3,6-dithiaoctane (III) (epe) and report



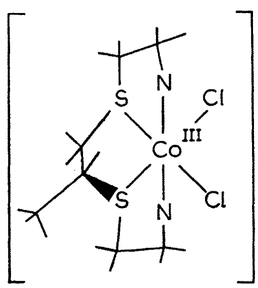
$$\begin{array}{l}Me\text{-}CH\text{-}S\text{-}CH_2\cdot CH_2\cdot NH_2\\ |\\ CH_2\text{-}S\text{-}CH_2\cdot CH_2\cdot NH_2\end{array}$$

(III)

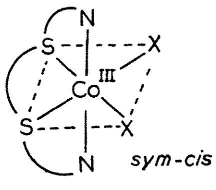
that in such complexes it exhibits total geometric and optical stereoselectivity. The ligand was synthesized by a known method[2] and a series of complexes prepared following closely the analogous work[1] with (I).

The four key complexes [Co epe Cl_2]Cl, [Co epe Br_2]Br, [Co epe $(NO_2)_2$]Cl and [Co epe CO_3]Cl were prepared by air oxidation of an appropriate cobalt(II) salt in the presence of ligand monohydrohalide in methanol. All complexes were characterized by elemental analyses, i.r. and electronic absorption spectra, and chemical reactions. All data are completely consistent with an octahedral geometry in which the axially co-ordinated amine groups are *trans* to each other while the in-plane monodentate groups are mutually *cis*. This geometry is designated as symmetrical *cis*-(II).

The racemic complex (Co epe Cl_2)Cl was resolved into its optical isomers using antimonyl-(+)-tartrate as the resolving agent.† In numerous syntheses and interconversions using optically active materials, no geometric isomerization was observed. Complete retention of configuration was always achieved: the starting material could be regenerated *via* any number of different steps (o.r.d. and c.d.)



(IV)



(II)

Finally, we have demonstrated by decomposing both enantiomers of (Co epe Cl_2)Cl with cyanide ion, that $(+)_{546}$-*sym-cis*-(Co epe Cl_2)Cl contains only $(+)_{589}$-epe and that $(-)_{546}$-*sym-cis*-(Co epe Cl_2)Cl contains exclusively

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† The (+) complex exhibits a specific rotation $[\alpha]_{546}$ of + 1885 ± 10° and the (−) complex has $[\alpha]_{546}$ of − 1885 ± 10°.

$(-)_{589}$-epe. Bosnich and Phillip[3] assign the absolute configuration of $(+)_{589}$-epe as D and, from similar arguments and c.d. spectra, we conclude that $(+)_{546}$-*sym-cis*-[Co epe Cl_2]$^+$ ion has the absolute configuration shown in (IV) while $(-)_{546}$-*sym-cis*-[Co epe Cl_2]$^+$ is the mirror image form.

In comparing the stereochemistries of cobalt(III) complexes having ligands with a donor-atom sequence of N N N N, with ligands of the type N S S N, two unique and important contrasts become apparent. First, *sym-cis*-[Co epe Cl_2]$^+$ does not isomerize to the unsymmetrical *cis*‡ or *trans* geometries in basic solution or in the presence of basic Li_2CO_3 solution as do the corresponding complexes derived from triethylenetetramine.[4] Second, the relative stabilities of the possible geometric isomers are determined by somewhat different effects. Goto *et al.* recently studied a number of methyl substituted triethylenetetramine ligands and demonstrated that substitution of a methyl group on one of the carbon atoms of the central chelate ring causes the exclusive production of the unsymmetrical *cis* isomer.[5] The chelate ring size, as controlled by varying the number of CH_2 groups between adjacent nitrogens, greatly affects the relative stabilities of the geometric isomers.[6] As ring size increases *trans* isomers increase in stability. Our work with nitrogen–sulphur–sulphur–nitrogen ligands shows exclusive formation of the symmetrical *cis* geometry in the 2,2,2-case. This almost certainly is a ring-size effect deriving from the relatively long Co–S distance.

The significance of the absolute stereospecificity of this new ligand (epe) upon co-ordination to cobalt(III) extends well beyond its fundamental stereochemical importance. Cobalt(III) complexes containing four inert donors and two reactive sites have been instrumental in revealing the detailed mechanisms of the metal ion promotion of those crucial nucleophilic processes that involve the organic carbonyl function; i.e., amino acid esters and amides and peptides.[7] To date, the studies have involved such familiar inert ligands as ethylenediamine and triethylenetetra-amine. Two limitations of these systems are the absence of stereospecificity and the fact that the manner of chelation of the so-called inert ligands may change during the course of the reaction of interest. Ligands such as epe therefore hold much promise for future studies in this important area.

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‡ The unsymmetrical *cis* geometry is analogous to the *β-cis* designation adopted by Sargeson for triethylenetetramine complexes.

[1] J. H. Worrell and D. H. Busch, *Inorg. Chem.*, in the press.
[2] F. P. Dwyer and T. E. MacDermott, *J. Amer. Chem. Soc.*, 1963, **84**, 2916.
[3] B. Bosnich and A. T. Phillip, *J. Amer. Chem. Soc.*, 1968, **90**, 6352.
[4] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 1965, **4**, 45; E. Kyuno, L. Boucher, and J. C. Bailar, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 1120, 1125, 5447.
[5] M. Goto, M. Saburi and S. Yoshikawa, *Inorg. Chem.*, 1969, **8**, 358.
[6] H. G. Hamilton, jun., and M. D. Alexander, *Inorg. Chem.*, 1966, **5**, 2060; *J. Amer. Chem. Soc.*, 1967, **89**, 5065; B. Bosnich, *et al.*, *J. Chem. Soc.* (*A*), 1966, 1331.
[7] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1968, **90**, 6032, and references therein.