

The Crystal Structure of a Bifurcated Quinquedentate Cobalt(III) Complex

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Summary The crystal structure of a novel bifurcated quinquedentate cobalt(III) complex, 4-(2-aminoethyl)-1,4,7,10-tetra-azadecane-azidocobalt(III) nitrate hydrate is described.

In the course of a study on quinquedentate tetraethylene-pentaminecobalt(III) complexes an azido-complex containing branched form of the ligand was isolated.¹ The structure of the complex has been determined by X-ray methods and is shown (I) in the Figure.

$N_3]$ (NO₃)₂·H₂O, are monoclinic, $a = 8.26$, $b = 7.59$, $c = 27.48$ Å, $\beta = 95.91^\circ$, $D_m = 1.66 \pm 0.02$, $Z = 4$, $D_c = 1.68$ g.cm.⁻³; space group $P2_1/c$; 2739 X-ray reflections (709 unobservably weak) were recorded with Cu-K α radiation using a Supper equi-inclination diffractometer. After two cycles of full-matrix least-squares refinement with isotropic thermal parameters and two cycles with anisotropic thermal parameters, R is 0.08.

The other possible isomeric forms involving co-ordination of the bifurcated ligand are (II), (III), and (IV), all of which

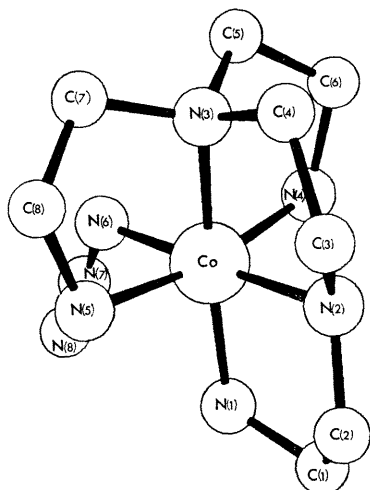
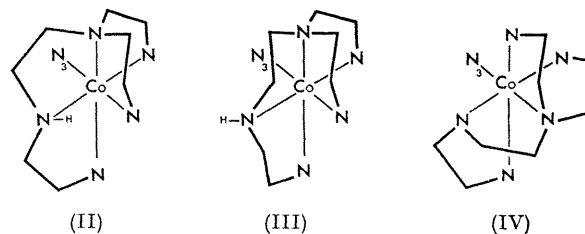


FIGURE. Structure of (I)

Crystals of racemic, 4-(2-aminoethyl)-1,4,7,10-tetra-azadecane-azidocobalt(III) nitrate hydrate, [Co trenen



are asymmetric. Isomers (II) and (III) are diastereoisomeric by virtue of the asymmetric configuration about one nitrogen atom. There is evidence for the existence of two additional azido-complexes other than (I), but it is not yet known whether they are (II) and (III) or the two diastereoisomeric forms of (II). A consideration of the effect of nonbonded atom interactions suggests that isomer (I) is the most stable followed by (II) and then (III). The preponderance of (I) in the preparative mixture from which the present crystals were isolated, is consistent with this, but it is not yet certain whether the preparation is equilibrium-controlled. Apart from the chelate conformations the only source of asymmetry in (I) is the configuration about the nitrogen atom *trans* to the substituent.

Compounds with this property are interesting in a mechanistic context where a proton is removed from the asymmetric centre by hydroxide ion and the complex is thereby allowed to racemise and hydrolyse. Racemisation of the azido-complex was observed around pH 7, but the azido-group remained intact.¹ However, the chloro- and nitrate-complexes do undergo base hydrolysis under these conditions and these reactions and their significance will be discussed elsewhere.¹

Dreiding scale models require the conformations of the

coupled chelate rings in the same plane to be catoptric in nature whether they have gauche or envelope forms. This is due to the tetrahedral stereochemistry about the nitrogen centres and the short length of the chelate skeleton. The present structure supports this analysis and the chelate rings are substantially gauche although individual rings are distorted from C_2 symmetry.

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¹ P. A. Marzilli, to be published.