Chloropentaminecobalt(III) Complexes Containing Monodentate Propylenediamine

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USING a modification of established methods for preparing cis-chloro(amine)bisethylenediaminecobalt(III) complexes,¹ we have prepared an isomeric mixture of complexes formulated as $[Co(en)_{a}(pnH)Cl]Cl_{3}*$ (reaction 1). The complexes

$$trans-[Co(en)_2Cl_2]Cl + pn \cdot HCl \xrightarrow{MeOH} [Co(en)_2(pnH)Cl]Cl_3 \qquad (1)$$

are unique in two ways. Firstly, each contains propylenediamine functioning as a monodentate ligand; and secondly, each has a cationic charge of 3+ rather than 2+ which is the normal charge for chloropentaminecobalt(III) complexes.

Elemental analysis of the mixture is in accord with the above formulation, and an aqueous molar conductivity of 401 ст.² ohm⁻¹ (0.001 м, 25°) substantiates that the complexes are tri-univalent electrolytes. The presence of a single uncoordinated amine was verified using the method of Phillips and Royer.²

For complexes of the formulation [Co(en)₂-(pnH)Cl]Cl₃, three types of isomerism are possible: geometric, optical (both antipodic and diastereomeric), and linkage. A kinetic study of the

mercury(II) ion-induced aquation of [Co(en)2-(pnH)Cl]Cl₃ has substantiated that the material is an isomeric mixture. The method of preparation together with a very close visible spectral similarity between the mixture and cis-[Co(en)₂NH₃Cl]Cl₂ indicates that isomers having the cis-configuration predominate.† The mixture prepared using laevopropylenediamine, $[Co(en)_2(-)pnHCl]Cl_3,$ exhibits little optical rotation at the sodium D-line $([\alpha]_{\rm p} = 0 \pm 11^{\circ})$. This indicates the presence of nearly equal amounts of cis-diastereomers since one antipode of the ammonia analogue, D-cis-[Co-(en)₂NH₃Cl]Cl₂, has a large rotation at this wavelength ($[\alpha]_{D} = +190^{\circ}$) and *laevo*-propylenediamine dihydrochloride exhibits a very small rotation $([\alpha]_{\mathbf{D}} = -4.0^{\circ})$. Co-ordination of propylenediamine primarily through the 1-amino-group is suggested by the observation that 1-aminoalkanes react more readily according to reaction (2) than do 2-aminoalkanes.1b,3

$$trans-[Co(en)_2Cl_2]Cl + NH_2R \rightarrow [Co(en)_2(NH_2R)Cl]Cl_2$$
(2)

Work is presently under way to separate and characterize the individual isomers.

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* en is ethylenediamine; pnH is monoprotonated propylenediamine.

[†] For [Co(en)₂(pnH)Cl]Cl₂, λ_{max} 527 mμ (ε 74) and 367 mμ (ε 82); for cis-[Co(en)₂NH₃Cl]Cl₂, λ_{max} 525 mμ (ε 73) and $367 \text{ m}\mu \ (\epsilon \ 77).$

¹ (a) J. Meisenheimer and H. Kiderlen, Annalen, 1924, 438, 212; (b) J. C. Bailar, Jr., and L. B. Clapp, J. Amer. Chem. Soc., 1945, 67, 171; (c) S. C. Chan and F. Leh, J. Chem. Soc. (A), 1966, 129; (d) M. D. Alexander and D. H. Busch, ³ I. F. Phillips and D. J. Royer, *Inorg. Chem.*, 1965, 4, 616.
³ M. D. Alexander and D. H. Busch, unpublished results.