Geometric Isomers of Chloroammine[tris-(2-aminoethyl)amine]cobalt(III) Chloride

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Summary Two geometric isomers of $[CoCl(NH_3)(tren)]Cl_2$ have been isolated in pure form after careful decomposition of $[NH_3(tren)CoO{\cdot}OCo(tren)NH_3]Cl_4$ in concentrated aqueous ammonium chloride solution.

IT has long been recognized that the structure of the quadridentate ligand tris-(2-aminoethyl)amine $[N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$, tren] limits its bis(unidentate ligand) six-co-ordinate complexes to the *cis* configuration. A recent study[1] presents kinetic evidence for the existence, in the same preparation, of two isomers of $[CoCl(H_2O)(tren)]SO_4$, in that two different rates of acid hydrolysis were observed. The two possible structures were designated arbitrarily as α, in which the chloride is *cis* to tertiary nitrogen, and *β*, in which the chloride is *trans*. That system of designation has been retained.

$[NH_3(tren)CoO{\cdot}OCo(tren)NH_3]Cl_4$ was allowed to decompose in warm, concentrated ammonium chloride solution. Two compounds were obtained, each of which, by analysis and conductance measurements, has the formula $[CoCl(NH_3)(tren)]Cl_2$. The less soluble isomer, which crystallized when the solution was cooled, is light purple (typical *purpureo* colour). Fractional crystallization of the filtrate by addition of ethanol and cooling yielded, as the last fraction, a carmine red monohydrate, which became anhydrous and oxblood red after being heated at 105° for 3 h.

The red isomer is thermodynamically less stable; it changes spontaneously but slowly into the *purpureo* form in hot solution, but it is stable in the dry state.

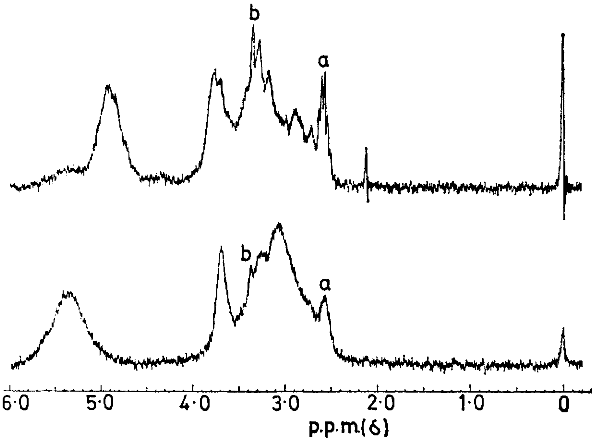

FIGURE. 60 *MHz* ^{1}H *n.m.r. Spectra of* purpureo (*lower*) *and red* (*upper*) *isomers of* [CoCl(NH_3)(tren)]I_2 *in* $(CD_3)_2SO$ *with* Me_4Si *reference. Solvent impurities are* (*a*) Me_2SO *and* (*b*) H_2O.

The *purpureo* complex shows a sharp i.r. band at 1257cm^{-1} with a profile similar to that of the NH_3 symmetrical deformation band of [Co$(NH_3)_6$]Cl_3 which shifts to lower frequency upon deuteriation and has been identified as $\delta_S(NH_3)$. This frequency is significantly lower than the median value (1310 cm^{-1}) reported for cobalt(III) ammine complexes,[2] and is consistent with a longer (M–NH_3) bond.[2,3] Unfortunately, the red compound isomerized during deuteriation, but by comparison with the spectra of other compounds, it seems reasonable to assign the band in its spectrum at 1298 cm^{-1} to $\delta_S(NH_3)$. Spectra taken in KBr discs show sharp, moderately strong absorptions at 342 cm^{-1} for the *purpureo* isomer and at 336 cm^{-1} for the red, which are assigned tentatively to ν(Co–Cl). The lower frequency is consistent with a longer (Co–Cl) bond in the red complex.

^{1}H N.m.r. spectra (60 and 100 MHz) of the iodide salts of the isomeric cations were taken in $(CD_3)_2SO$. In freshly prepared solutions the NH_2 resonances were symmetrical and very broad, at 5·25 and 4·9 p.p.m. downfield from Me_4Si for the *purpureo* and red cations, respectively. The NH_3 resonance of the *purpureo* ion at 3·65 p.p.m. was broad, symmetrical, and nearly separate from the CH resonances, which appeared as two large and one small, overlapping, very broad bands between 2·6 and 3·4 p.p.m. For the red cation the CH and NH_3 resonances overlap strongly between 2·4 and 3·9 p.p.m., and there is some fine structure. In 6M-HCl this region shows an array of some fifteen overlapping bands in which NH_3 and CH contributions cannot be differentiated. Because of low solubility a spectrum of comparable quality cannot be obtained for the *purpureo* cation in the same medium.

Space-filling models show a remarkable difference in the environments of the co-ordinated ammonia molecules in the two structures. In the α structure Co, Cl, 3N, and 6H atoms of the primary amino-groups are all approximately coplanar. The ammonia molecule is free to rotate about the (Co–N) axis in the model and is expected to have little non-bonding interaction with adjacent atoms. In the β-structure, on the other hand, where the ammonia is *cis* to the tertiary amino-nitrogen atom, its hydrogen atoms touch adjacent hydrogen atoms of methylene groups bonded to tertiary nitrogen, and it is not free to rotate in the model. It is postulated that the NH_3 protons in the α-structure are in equivalent environments and give rise to the singlet absorption of the *purpureo* isomer, whereas the NH_3 protons in the β-structure are differentiated by non-equivalent environments to give the more complex spectrum.

A preliminary determination of the rates of acid hydrolysis of the isomeric cations (in 0·1M-$HClO_4$ at *ca.* 26°) revealed that the red cation undergoes aquation about twice as fast as the *purpureo*-isomer. The pseudo-first-order rate constants, determined over four half lives, were roughly 15×10^{-5} and $7{\cdot}4 \times 10^{-5}$ min^{-1}, respectively.

X-Ray structure determinations have shown that the chelate rings of tris-(2-aminoethyl)amine are severely strained in the distorted octahedral complex [Ni$(NCS)_2$(tren)].[4] The strain causes displacement of the primary amino-groups towards the tertiary nitrogen atom as well as lengthening of the tertiary-N–C bond in one chelate ring and of the (C–C) bond in another. It is reasonable that intramolecular strain sufficient to produce these effects also would compress the tertiary-N–Co bond and that an electronic effect would be transmitted to the position *trans* to tertiary nitrogen.[5] On the basis of three such effects described above, the α-structure is assigned to the *purpureo* compound and the β-structure to the red.

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