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The Synthesis and Characterization of *uns-cis* Dicyano 1,10-diamino-4,7-diazadecane Cobalt(III) Chloride

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As part of our investigation of complexes of the type Co(tetramine)L_2^{n+}, we report the synthesis and characterization of *uns-cis* Co(3,2,3-tet)$(CN)_2^+$ (3,2,3-tet is the flexible tetramine ligand 1,10-diamino-4,7-diazadecane). This is the first reported diacido cobalt(III) complex with this polyamine which adopts the *uns-cis* stereochemistry. Other *uns-cis* cobalt complexes of 3,2,3-tet are known only when a bidentate chelating ligand occupies two coordination sites on the cobalt ion [1].

Uns-cis Co(3,2,3-tet)$(CN)_2^+$ is formed when hot aqueous solutions of sodium cyanide and *trans* (Co(3,2,3-tet)Cl_2)Cl are mixed. The solution changes from green to yellow orange immediately upon mixing. The product crystallizes upon reduction of the volume and can be recrystallized from ethanol–water (1-1: v/v). When the same reaction is carried out in dimethyl sulfoxide and the resulting solution is chromatographed on Sephadex SP-C25 ion exchange resin with 0.001 *M* aqueous perchloric acid as the eluent, two bands appear initially, with the dominant band being the *uns-cis* isomer. When the reaction mixture is allowed to stand at room temperature for several days only one band is observed.

The stereochemistry of the isolated complex was identified by spectroscopic methods including electronic and vibrational spectroscopy and proton and ^{13}C nuclear magnetic resonance spectroscopy. All of the evidence is consistent only with the *uns-cis* stereochemistry.

The electronic spectrum of the complex shows two distinct bands which can be assigned to the $^1A_{1g} > {}^1T_{1g}$ (24,500 cm^{-1}) and $^1A_{1g} > {}^1T_{2g}$ (31,200 cm^{-1}) transitions in the octahedral approximation. This assignment is consistent with any stereochemistry, however most *trans* diacidotetramine cobalt(III) complexes show an additional band resulting from the splitting of the $^1T_{1g}$ state upon lowering the symmetry to approximately D_{4h}.

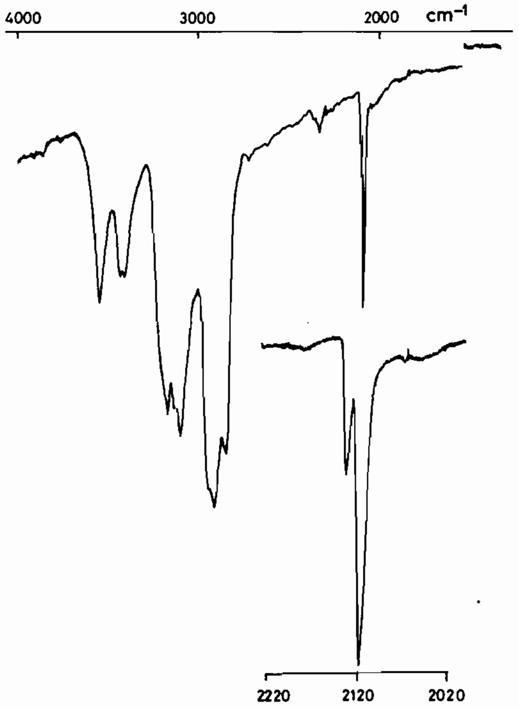

Fig. 1. Infrared spectrum of Co(3,2,3-tet)$(CN)_2$Cl in Nujol.

The vibrational spectrum shows a large number of bands in the NH stretching region and two distinct bands in the cyanide region (Fig. 1). The presence of two distinct cyanide bands indicate an *uns-cis* stereochemistry, since two cyanides should be equivalent in either the *trans* or *s-cis* stereochemistry because of the twofold symmetry of these complexes. These two bands are a further indication of *uns-cis* stereochemistry.

The conclusive proof for our assignment of the stereochemistry comes from the NMR spectra of the complex. The proton NMR spectrum of the complex shows four broad signals in the region where the amine protons are generally found [2]. These signals appear at 3.9(2), 4.8(1), 5.8(2) and 7.1(1) ppm from TMS. *Trans* diacido 3,2,3-tet cobalt(III) complexes show only three features in this region of the spectrum. Other *uns-cis* cobalt(III) complexes with 3,2,3-tet show four resonances in the amine region of the spectrum. The other regions of the proton NMR show a series of complex multiplets which are not germane to the assignment of stereochemistry. All of the bands in the proton spectrum are broad due to coupling with the metal and with the amine nitrogens.

The carbon-13 NMR spectrum gives the final proof of the stereochemistry. The spectrum has

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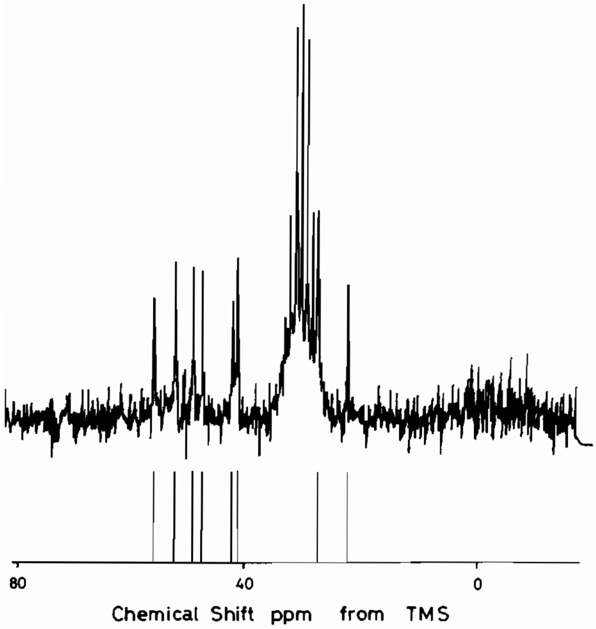

Fig. 2. ^{13}C NMR of $Co(3,2,3\text{-tet})(CN)_2B(C_6H_5)_4$ in acetone d_6 (99.5 atom% d).

eight well resolved features, all well above the noise. The spectrum is represented schematically in Fig. 2. The carbons at the lowest chemical shift can be assigned to the polyamine carbon atoms which are not attached to the amine nitrogens [3]; all of the other carbon atoms are attached to the nitrogens. The carbons of the cyanides do not appear in the ^{13}C NMR spectrum. These carbon atoms, with no protons bonded to them, are expected to decay slowly. The cyanide carbon signal should be near 145 ppm from TMS [4] and should appear as an octet (due to coupling with cobalt spin 7/2).

This evidence combines to prove the stereochemistry of the complex, the first reported example of a *cis*-diacido(3,2,3-tet)cobalt(III) complex. The other compound detected in ion exchange experiments may be the *trans* isomer. We were, however, unable to isolate this complex. The synthesis of the *uns-cis*-dicyano(3,2,3-tet)cobalt(III) cation demonstrates the electronic demands of the cyanide ligand. In all other diacido 3,2,3-tet cobalt(III) complexes, the *trans* isomer is more stable than the *cis* isomers by 12 to 21 kJ/mol because of the reduced strain energy of the *trans* complexes [5]. Thus, the *trans* directing influence of CN^- must be greater than the *trans-cis* strain energy difference.

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