SHORT COMMUNICATIONS

The Structure of the *trans*-Dichlorobistrimethylenediaminecobalt(III) Ion, *trans*-$[CoCl_2tn_2]^+$ *1

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(Received March 4, 1970)

Ethylenediamine, $H_2N-CH_2-CH_2-NH_2$ (=en), can form a stable five-membered chelate ring in combination with many transition metals; the geometry of the ring has been well established. On the other hand, trimethylenediamine, $H_2N-CH_2-CH_2-CH_2-NH_2$ (=tn), possesses one more CH_2-group than does ethylenediamine and forms a six-membered ring in chelation with several metals. The metal chelates of the trimethylenediamine are, however, less stable and less easily prepared than the corresponding ethylenediamine chelates.[1] The instability of the tn-compounds may be due to the distortion which is presumably existent in the six-membered chelate ring. In order to elucidate the conformation of the tn-chelate ring, we have attempted a crystal structure analysis of *trans*-[Co Cl_2 tn_2]Cl·HCl·$2H_2O$.

The crystal is green and monoclinic, with cell dimensions of $a=10.68$, $b=8.55$, $c=9.46$ Å, and $\beta=112.2°$. The space group is $P2_1/c$, and the unit cell contains two formula units ($\rho_{obsd}=1.59$ and $\rho_{calcd}=1.60$ g·cm^{-3}). The $h0l$ and $hk0$ intensity data were recorded on Weissenberg photographs (Ni$K\alpha$ radiation, $\lambda=1.6591$ Å). The intensities were measured visually, and no absorption corrections were applied. The positions of the heavy atoms could be obtained from Patterson projections, $P(UW)$ and $P(UV)$, and those of the light atoms, from Fourier maps. The R-value was reduced to 0.14 by means of the usual refinements. Refinement on the basis of the three-dimensional data is now going on.

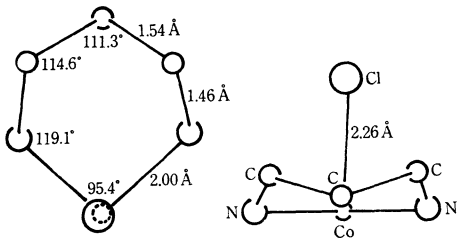

Fig. 1. The elevation and projection of *trans*-[Co Cl_2 tn_2]$^+$. Asymmetric half of the cation is drawn.

The crystal structure is similar to that of *trans*-[Co Cl_2 en_2]Cl·HCl·$2H_2O$;[2] the crystal consists of *trans*-[Co Cl_2 tn_2]$^+$, Cl^- and $[H_2O\cdots H\cdots OH_2]^+$. In Fig. 1 the structure of the complex ion is illustrated. Since the cobalt is located on a special position, the symmetry of the complex ion is $\bar{1}$.

The chelate ring takes a chair form.[3] The ring has an approximate mirror plane which is normal to the ring plane and which passes through the cobalt atom and the middle carbon atom. The bond lengths of Co–N, N–C, and C–C are in good agreement with those in *trans*-[Co X_2 en_2]$^+$.[4,5] In Table 1 the average values of the two bond angles which are related by the pseudo mirror plane are compared with the corresponding values in the en-complexes. The deviation of the N–Co–N angle from 90° in the tn-complex is almost equal to that in the en-complexes. However, the values of the Co–N–C and N–C–C angles in the former are appreciably larger than 109.5°, while they are quite close to the tetrahedral angle in the latter. The lower stability in the tn-complexes may be attributable, at least in part, to these bond-angle strains. Recently a tn-ring which takes a twisted form and the N-Co-N angle of which is less than 90° was found in [Cu(*o*-haph:tn:*o*-haph)].[6]

TABLE 1

	trans-[Co Cl_2 tn_2]$^+$	*trans*-[Co X_2 en_2]$^+$	
		X=Cl	X=Br
∠N-Co-N	95°	86°	87°
∠Co-N-C	119	109	109
∠N-C-C	115	107	109

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