The Crystal and Molecular Structure of Trinitro(diethylenetriamine)cobalt(III)

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A diethylenetriamine molecule (=dien; H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2) can be linked to the metal atom by means of its three nitrogen atoms, thus forming the tridentate chelate rings. Therefore, when considered from the standpoint of the octahedral coordination, trinitro(diethylenetriamine)cobalt(III), [$Co(NO_2)_3$dien], may be existent in two geometric isomers, *i. e.*, cis-cis and cis-trans forms. An attempt has been made to elucidate the crystal and molecular structure of this complex compound.

Preparations of the compound were made in three different ways,[1] following the descriptions in "Inorganic Syntheses"; however, every specimen of the crystals obtained showed all the same X-ray diffraction patterns. The crystal is orthorhombic with cell dimensions of $a=13.03$, $b=12.70$ and $c=13.19$ Å. The space group is $Pbca$-D_{2h}^{15} from the systematic absences. The observed density is 1.80 g·cm^{-3} and there are eight formula units in a unit cell, the calculated density being 1.83 g·cm^{-3}.

The three-dimensional data of $h0l$—$h7l$, $hk0$ and $0kl$ were collected from the equi-inclination Weissenberg photographs taken with Ni$K\alpha$ radiation. The intensities of reflections were measured visually and corrected for the Lorentz-polarization factor and also for the spot extension. Approximate coordinates of the cobalt atom were obtained from the Patterson projections along the three principal axes, and, then, the minimum function maps were calculated by making use of the Co-Co interatomic vectors; the positions of the light atoms were deduced from these maps. The successive refinements of the Fourier projection and least-squares method were applied. The structure thus obtained was refined by the least-squares method with the three-dimensional data. A discrepancy index R is 0.19 at the present stage.

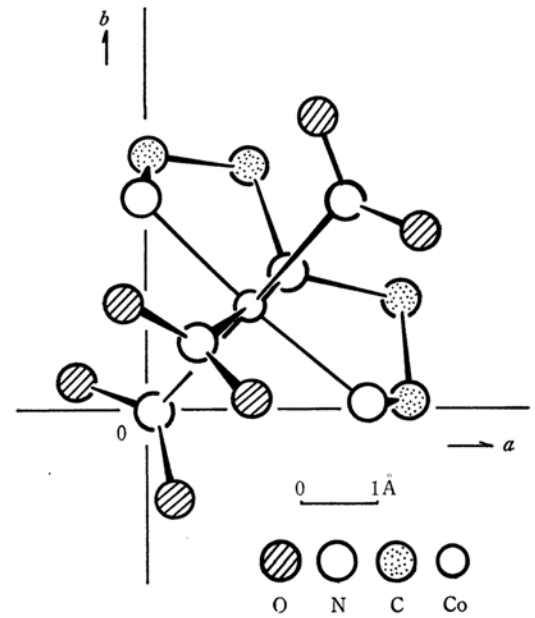

Fig. 1. The atomic arrangement projected along the c-axis.

The atomic arrangement projected along the c-axis is shown in Fig. 1. There is an approximate mirror plane in the complex molecule, which has the slightly distorted octahedral environment around the central cobalt atom, being bonded to six nitrogen atoms (three $N(NO_2)$ and three N(dien)). It is to be noted that the dien molecule is coordinated to the cobalt atom in the cis-trans (*mer*) positions. This makes a remarkable contrast to the case of [MoO_3(dien)] in which the dien molecule is known to be in the cis-cis (*fac*) form.[2] The cobalt-nitrogen bond lengths are 1.98—2.06 Å.

A full paper will be soon published.

1) "Inorganic Syntheses," Vol. VII, McGraw-Hill, Inc., New York (1963), pp. 209, 210.

2) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964).