The Crystal Structure of Cobalt(III) Nitrate

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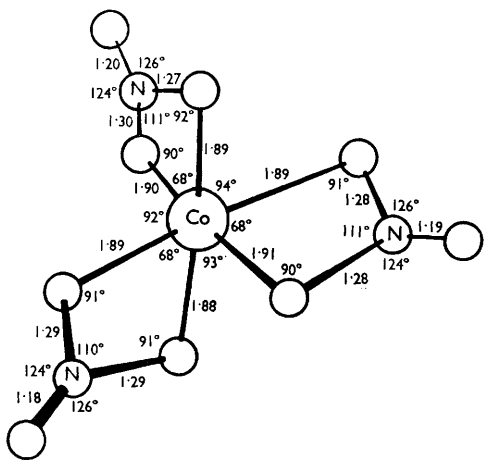
ANHYDROUS cobalt(III) nitrate has been reported[1] to have properties and spectra consistent with a covalent octahedral structure in which the cobalt atom is co-ordinated by three bidentate nitrato-groups. In view of the paucity of simple salts of cobalt(III) and the lack of structural work on anhydrous metal trinitrates in general it was felt that an *X*-ray structure determination of this compound would be valuable.

Crystals prepared by the method reported[1] and grown by slow vacuum sublimation at 40° were sealed into glass capillaries for *X*-ray photography and diffractometry. Weissenberg photographs showed the crystals to be triclinic, $a = 5{\cdot}67$, $b = 7{\cdot}44$, $c = 8{\cdot}83$ Å, $\alpha = 103{\cdot}7°$, $\beta = 102{\cdot}1°$, $\gamma = 106{\cdot}7°$, $Z = 2$. 1248 independent *X*-ray reflections were measured with the aid of a linear diffractometer and converted into structure factors in the usual way. The structure was solved by Patterson methods, followed by structure-factor calculations and Fourier syntheses. Three cycles of full-matrix, least-squares refinement of the atomic parameters have led to the present agreement factor, *R*, of 0·092 and further refinement is in progress. The present molecular dimensions are shown in the Figure. Standard deviations are about 0·01 and 0·02 Å for Co–O and N–O bonds and 1 and 0·5° for angles between bonds to light atoms and cobalt respectively.

The co-ordination of the cobalt atom is basically octahedral, the main deviation from an ideal octahedral arrangement being caused by the fact that the O–Co–O angle for each bidentate ligand is 68°. However, the three other O–Co–O angles shown in the Figure are close to 90°, while the remaining six are about 100°. The dihedral angles between the nitro-groups are, at this stage, indistinguishable from the regular octahedral value, 90°.

The three nitrato-groups are all equivalent, within experimental error, and have dimensions very similar to those found[2] in $Ti(NO_3)_4$ and $Sn(NO_3)_4$. This structural resemblance is reflected in the correspondingly high chemical reactivity exhibited by the anhydrous nitrates of titanium, tin, and cobalt. The equality of all six Co–O bonds is consistent with the spherical A_{1g} symmetry of the low-spin, d^6, electron configuration of octahedral Co^{III} and forms an interesting contrast with the observation[3] of unsymmetrical bidentate NO_3 bonding in the high-spin, d^7, dodecahedral Co^{II} ion $[Co(NO_3)_4]^{2-}$. The four different Co–O bond lengths reported for this ion ($2{\cdot}03 \pm 0{\cdot}02$, $2{\cdot}11 \pm 0{\cdot}01$, $2{\cdot}36 \pm 0{\cdot}02$ and $2{\cdot}54 \pm 0{\cdot}02$ Å) are all longer than the Co–O bonds in $Co(NO_3)_3$, presumably because of the greater electron repulsion and the diminished polarising power of Co^{II}, due to the extra electron.



FIGURE

Dimensions of the $Co(NO_3)_3$ *molecule (bond lengths in* Å).

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