the temperature factors of nitrate group III and of the water molecule; these parameters are extensively coupled with the coordinates. The final shifts were all less than 0·4σ. The final R index is 0·076 for 357 observed reflections of non-zero weight; the goodness of fit, $[\Sigma w(F_o^2-F_c^2)^2/(m-s)]^{\frac{1}{2}}$, is 4·0.

The structure we find is almost identical – except for the changes in dimensions in the cation associated with replacing an O_2 bridge with an NH_2 bridge – with that of the μ-peroxo compound $(NH_3)_5Co(O_2)Co(NH_3)_5(NO_3)_5$ (Marsh & Schaefer, 1968). As in that compound, the structure we have derived is based on the space group $P4_2/mnm$ – the highest symmetry space group consistent with the systematic absences. There seems to be no advantage in assuming a lower symmetry, as the disorder (which affects every atom in the structure except for the cobalt) would remain while the number of parameters would increase.

Discussion

The largest difference between the structure we have found and that derived by Vannerberg (1963) is in the orientation of the $(NH_3)_5Co(NH_2)Co(NH_3)_5^{5+}$ cation. Vannerberg assumed the polar space group $P4_2nm$ with the cation positioned on a twofold axis parallel to **c** and on a mirror plane parallel to $(1\bar{1}0)$; we find it to be rotated 90° from this orientation, lying on a mirror plane parallel to (001). The disorder allows the cation to accomodate the diagonal mirror plane (Fig. 1).

The cation is shown in Fig. 2. It is obviously highly strained, as manifested by the extreme length of the Co–N(1) bond (about 0·1 Å longer than the normal value for a Co–N distance) and the almost ridiculous valency angle at N(1). The strain is caused by interactions between ammonia groups N(3) in the two halves of the cation; it is partly relieved by an enlargement of the N(1)–Co–N(3) angles to 93°.

Nitrate group I (Fig. 1) is satisfactorily represented by two sets of isotropic, half-weight atoms, suggesting that the group is disordered between two positions related by a mirror plane parallel to (110) and separated by about 0·45 Å; the N–O distances are 1·23 Å (twice) and 1·24 Å and the O–N–O angles 121 and 119° (twice). Nitrate group II is somewhat less satisfactory: the distances are 1·20 (twice) and 1·22 Å and all three angles are 120°, but even assuming twofold disorder we find it necessary to introduce anisotropic temperature factors for the oxygen atoms, implying very large in-plane displacements and, perhaps, additional disorder. The same situation obtains in the μ-O_2 compound (Marsh & Schaefer, 1968), although there nitrate group II was found to have one N–O bond parallel to the c axis rather than parallel to [110].

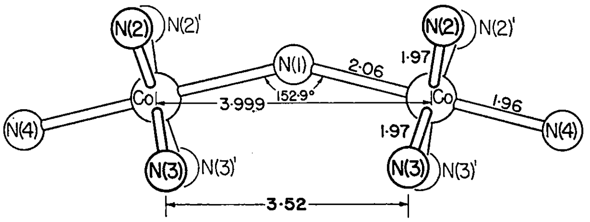

Fig. 2. A drawing of the cation, showing the more important dimensions. Standard deviations in the bond distances are about 0·02 – 0·03 Å.

We have represented nitrate group III by fourfold disorder of isotropic atoms, plus an additional atom (perhaps a water molecule) in one-eighth of the available sites. This is a slightly simpler representation than was proposed for the μ-O_2 compound, where this nitrate group was found to have at least eightfold disorder. It is possible that the model we propose here would not have been as satisfactory had the data been of as high quality as they were for the μ-O_2 compound; crystals of it did not show signs of decomposition, and three complete sets of intensity data were collected.

No analysis for water was made, since its presence was not suspected until the refinement was nearly complete. We did not have enough material to make such an analysis, and its preparation is difficult. Our results suggest that there is approximately one-quarter molecule of water per formula unit in the crystal we used; it is likely that the water content is variable, and is related to the differences in intensity and cell dimensions we find in going from one crystal to another.

We are very grateful to Professor C. Brubaker for providing the crystals.

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An X-ray study of gel-grown strontium tartrate tetrahydrate

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The space group ($P2_12_12_1$) and unit-cell dimensions ($a=9{\cdot}48\pm0{\cdot}04$, $b=10{\cdot}96\pm0{\cdot}04$, $c=9{\cdot}46\pm0{\cdot}04$ Å) of gel-grown strontium tartrate have been determined by the precession method.

Recently, there has been renewed interest in the growth of crystals in silica gel (Dennis & Henisch, 1967; Henisch, Dennis & Hanoka, 1965). Using this technique, we have grown a large variety of single crystals such as the alkaline earth tartrates and various sulfite, formate, and borate salts. Briefly, the method consists of adding an acid (tartaric acid, for example) to a sodium metasilicate solution. After the mixture has set, an appropriate solution is placed on top of the gel (in this case, strontium chloride). Diffusion into the gel takes place and under the proper conditions of *p*H, concentration of the active ingredients, density of the gel, and temperature, crystals grow in the gel (strontium tartrate in this example). We report here the results of an X-ray study of gel-grown strontium tartrate tetrahydrate ($SrC_4H_4O_6.4H_2O$).

No available X-ray data on this crystal were known to us, but a similar material, calcium tartrate, is reported to be orthorhombic (Donnay & Nowacki, 1954), having the space group $P2_12_12_1$ with four molecules per unit cell and lattice constants (a,b,c) equal to 9·62, 10·54, and 9·20 Å, respectively. Electron spin resonance (e.s.r.) data (Murphy & Bohandy, 1967) of Cu^{2+} in strontium tartrate indicated that this crystal was probably isomorphous with calcium tartrate with four molecules per unit cell as expected. However, for the purpose of further e.s.r., optical, and piezoelectric measurements on this material, we needed to know the space group and lattice constants with certainty.

Zero, first, and second level X-ray precession pictures were taken with Mo $K\alpha$ radiation. Interpretation of these photographs showed that the strontium tartrate lattice is orthorhombic with the lattice constants:

$$\begin{aligned} a &= 9{\cdot}48 \pm 0{\cdot}04\ \text{Å} \\ b &= 10{\cdot}96 \pm 0{\cdot}04 \\ c &= 9{\cdot}46 \pm 0{\cdot}04 \end{aligned}$$

The diffraction symbol was determined to be $mmmP2_12_12_1$. This diffraction symbol unambiguously implies the space group $P2_12_12_1$ for strontium tartrate. Although a and c are nearly equal, the intensity of zero level reflections indicates that the crystal is not tetragonal. The crystals are elongated in the **c** direction and the principal faces are the prismatic ones (110) and ($\bar{1}10$), with their symmetry equivalents. (101) and ($\bar{1}01$), with their symmetry equivalents, are present as the principal, if not the only, end faces. The density of the crystal was measured and found to be 2·05 with the use of standard techniques. A computation of the density of $SrC_4H_4O_6.4H_2O$ with the measured lattice constants gave the value 2·08, in good agreement with the measured value.

Powder photographs of calcium tartrate and strontium tartrate were taken. Complete isomorphism to calcium tartrate is highly probable but cannot be claimed as certain without further intensity comparisons.

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Reinvestigation of the reaction of trimethylplatinum(IV) iodide with methylsodium.

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The product from the reaction of trimethylplatinum(IV) iodide and methylsodium is shown to be identical with that previously obtained from this reaction and subsequently characterized as tetramethylplatinum. However, the supposed tetramethylplatinum is now shown to be trimethylplatinum(IV) hydroxide.

Gilman & Lichtenwalter (1938, 1953) have reported the synthesis of tetramethylplatinum in 46% yield by reacting trimethylplatinum(IV) iodide with methylsodium in benzene-free hexanes. They based their identification of the compound primarily upon combustion analysis. The true composition of this substance could be questioned since the compound explodes when heated. The authors reported that tetramethylplatinum did not react with iodine in chloroform when refluxed for 24 hours nor did it react with benzoyl chloride in benzene when refluxed for 100 hours, but it did react with dry hydrogen chloride gas when the gas was bubbled through a refluxing solution of tetramethylplatinum in light petroleum (b.p. 60–68°) producing white crystals of trimethylplatinum(IV) chloride. Tetramethylplatinum was reported to be readily soluble in organic solvents and was said to crystallize from light petroleum in large hexagonal plates.

Rundle & Sturdivant (1947) described the crystals of tetramethylplatinum supplied by Gilman as rhomb-dodecahedra. They found the cell edge to be 10·165 Å (10·145 kX) long. They determined the density of the crystals to be 3·16 g.cm^{-3}, from which they deduced that the cell contains eight molecules giving a calculated density of 3·23 g.cm^{-3}. Qualitative intensity considerations combined with symmetry information obtained from the known Laue class, $4/m\ \bar{3}\ 2/m$, led to a structure with 2 tetramers per cell.

Tetramethylplatinum is unique not only in that it is the first molecule reported in which a platinum(IV) atom is bonded only to four organic ligands, but also in that the tetramer bonding requires the application of the concept of four-center two-electron bonds (Rundle & Sturdivant, 1947).

We have repeated the Gilman–Lichtenwalter synthesis of tetramethylplatinum. A suspension of methylsodium was prepared from sodium and dimethylmercury in benzene-free 2,3-dimethylbutane under a nitrogen atmosphere after the method of Schlenk & Holtz (1917). To the resulting black suspension were added trimethylplatinum(IV) iodide crystals which had either been recrystallized from benzene and vacuum dried to remove all the solvent molecules or had been recrystallized from chloroform and then air dried. The methylsodium–trimethylplatinum(IV) iodide mixture was stirred for 24 hours at room temperature and then

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