Tabelle 2. *Punktlagen und Atomkoordinaten des Sodaliths*

Raumgruppe $P\bar{4}3n$

	Punktlagenbezeichnung	Punktlagen	Paulingsche Parameter	Verfeinerte Parameter	Isotrope Temperaturfaktorkoeffizienten
2 Cl	2 (*a*)	000			$1{\cdot}90 \pm 0{\cdot}04$
8 Na	8 (*e*)	*xxx*	$x=0{\cdot}175$	$x=0{\cdot}1777$ $\pm 0{\cdot}0004$	$1{\cdot}49 \pm 0{\cdot}04$
6 Si	6 (*d*)	$\frac{1}{4}0\frac{1}{2}$			$0{\cdot}35 \pm 0{\cdot}04$
6 Al	6 (*c*)	$\frac{1}{4}\ \frac{1}{2}0$			$0{\cdot}80 \pm 0{\cdot}07$
24 O	24 (*i*)	*xyz*	$x=0{\cdot}135$	$x=0{\cdot}1401$ $\pm 0{\cdot}0004$	$0{\cdot}89 \pm 0{\cdot}02$
			$y=0{\cdot}440$	$y=0{\cdot}4385$ $\pm 0{\cdot}0003$	
			$z=0{\cdot}150$	$z=0{\cdot}1487$ $\pm 0{\cdot}0004$	

der spektralchemischen Analyse. Der Deutschen Forschungsgemeinschaft gilt unser Dank für die Bereitstellung von Röntgengeräten und dem Deutschen Rechenzentrum Darmstadt für die Benutzung der IBM 7090.

Tabelle 3. *Atomabstände und Bindungswinkel*

SiO_4-Tetraeder	
Si–O-Abstand:	$1{\cdot}628 \pm 0{\cdot}004$ Å
O–O-Abstände:	$2{\cdot}629 \pm 0{\cdot}008$
	$2{\cdot}714 \pm 0{\cdot}008$
O–Si–O-Winkel:	107·7°
	113·0
AlO -Tetraeder	
Al–O-Abstand:	$1{\cdot}728 \pm 0{\cdot}004$ Å
O–O-Abstände:	$2{\cdot}806 \pm 0{\cdot}008$
	$2{\cdot}855 \pm 0{\cdot}008$
O–Al–O-Winkel:	108·5°
	111·3
Si–O–Al-Winkel:	138·3
Na–Cl-Abstand:	$2{\cdot}730 \pm 0{\cdot}004$ Å
Na–O-Abstand:	$2{\cdot}351 \pm 0{\cdot}008$

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Rotation of the Complex Ion in, and Dimorphism of, Aquopentamminecobalt(III) Perchlorate

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(*Received* 3 *January* 1967)

The crystals of aquopentamminecobalt(III) perchlorate have been reported as being cubic with $a = 11{\cdot}32$ (units presumably kX). They are now shown to exhibit dimorphism, some being orthorhombic ($Pmn2_1$; $a = 11{\cdot}37$, $b = 16{\cdot}74$, $c = 7{\cdot}79 \pm 0{\cdot}05$ Å) and the others cubic ($Pn3n$; $a = 22{\cdot}68 \pm 0{\cdot}02$ Å). There is no temperature-dependent displacive phase transition. The cubic crystals are shown to be pseudo-face-centred ($Fm3m$; $a = 11{\cdot}34 \pm 0{\cdot}01$ Å), and it is suggested that the diffraction effects of this pseudo-symmetry are indeed indicative of ellipsoidal rotation of the complex cation.

Introduction

The crystals of the more common inorganic salts of the hexammine complexes of cobalt and related metals are cubic. So too are many of their mono-substituted derivatives (Hassel & Bödtker Naess, 1928, 1929; Hassel & Kringstad, 1932). In the case of the hexammine compounds this symmetry is understandable since the hexammine cobalt complex ion has the configuration of a regular octahedron. However, in the mono-substituted ions the octahedron is no longer regular.

It seems that the crystal symmetry of these complex salts depends on (i) the effective symmetry of the complex cation, and (ii) the nature and symmetry of the anion or anionic components. With regard to the former, it is clear that the requirements of cubic symmetry of the crystal are satisfied by the unsymmetrical monosubstituted hexammine complex ion by either (i) random distribution of its orientation or (ii) its rotation.

In this connection it must be observed that the possibility of rotation of polyatomic groups was established by Pauling (1930).

Dimorphism in aquopentammine cobalt(III) perchlorate and the orthorhombic dimorph

Preliminary investigations on the polarizing microscope indicated that this salt forms two sets of crystals, one being of octahedral habit, the other of long prismatic habit. The former is optically isotropic while the latter is optically anisotropic and optically biaxial. Further both straight and oblique extinctions were obtained for the anisotropic crystals when viewed along the '*c*' axis. These directions were inclined to each other at about 56°.

Both dimorphs were examined optically to see whether they were related by a temperature-dependent displacive phase transition, the isotropic one being cooled to liquid air temperature and the anisotropic one being heated until it decomposed. No phase transition was observed. Ultraviolet spectroscopy in conjunction with volumetric analysis confirmed the existence of dimorphism, the former being used to identify the complex cation and the latter to establish the lack of water of crystallization.

The densities of the anisotropic and isotropic crystals were found to be $1{\cdot}96 \pm 0{\cdot}01$ and $2{\cdot}09 \pm 0{\cdot}01$ g.cm^{-3} respectively. X-ray investigation showed the anisotropic dimorph to be orthorhombic in symmetry and to contain four molecules per unit cell. From Weissenberg photographs using Cu $K\alpha$ radiation the cell dimensions were found to be $a = 11{\cdot}37$, $b = 16{\cdot}74$, $c = 7{\cdot}79 \pm 0{\cdot}05$ Å. The space group symmetry is $Pmn2_1$, revealed by the diffraction data as well as non-centrosymmetry revealed by both anomalous scatter and a pyroelectric test.

These cell dimensions indicate that the [110] direction is inclined to the [100] direction at an angle of 55°49′. It is therefore now seen that the orthorhombic crystals exist in two habits, one in which the crystal faces are defined by the forms {100}, {010}, and {001}, and the other having the crystal faces defined by the {001}, {110} and {1$\bar{2}$0} forms.

The cubic dimorph

Hassel & Bödtker Naess (1928) reported the cubic crystals as having a lattice parameter of 11·32*. The results obtained from powder photography seemed at first to corroborate this, suggesting a face-centred Bravais lattice with $a = 11{\cdot}34$ Å. However, further examination of the powder data prompted by the evidence from a single-crystal rotation photograph showed that the Bravais lattice is not face-centred but primitive. The single-crystal rotation photograph showed strong layer lines corresponding to a cell dimension of 11·34 Å, but revealed also the existence of weak intermediate layer lines indicative of a true cell dimension of 22·68 Å. Further, the reflexions of the 4th, 8th and 12th layers are strong – stronger than those of the other even-numbered layers, and much stronger than those of the odd-numbered layers. No diffuseness was observed in the reflexions. Thus, there was no suggestion of disorder.

From Weissenberg photographs the conditions for reflexions (on the basis that $a = 22{\cdot}68$ Å) were found to be:

hkl	none
hhl	$l = 2n \circlearrowright$
$0kl$	$k + l = 2n \circlearrowright$

The space group symmetry is thus $Pn3n$.

Fig. 1 shows how the orthorhombic cell is related to the cubic cell; the face diagonal of the latter is 16·03 Å, which is approximately equal to b and $2c$ for the orthorhombic cell.

Suggested ellipsoidal rotation of the $[Co(NH_3)_5H_2O]^{3+}$ ion

Diffraction methods cannot in general distinguish rotating from static and randomly oriented polyatomic groups, since on the macroscopic scale the latter simulate spherical symmetry of the group. It must be observed, though, that this difficulty arises when the rotations are spherical or effectively so – for example, random orientations of ellipsoidal rotations. However, where ellipsoidal rotations are associated with an ordered arrangement, there need be no ambiguity in their revelation by diffraction methods.

With a density of $2{\cdot}09 \pm 0{\cdot}01$ g.cm^{-3} the crystal contains 32 $[Co(NH_3)_5H_2O(ClO_4)_3]$ molecules per unit cell ($a = 22{\cdot}68$ Å). The space group symmetry $Pn3n$ requires 48 general equivalent positions in the unit cell, the nature and distribution of the symmetry elements in which are shown in Fig. 2. Thus, the $[Co(NH_3)_5H_2O]^{3+}$

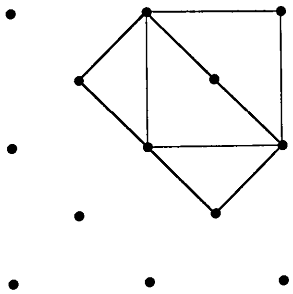

Fig. 1. Dimensions of the orthorhombic cell relative to those of the cubic cell.

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* Presumably kX.

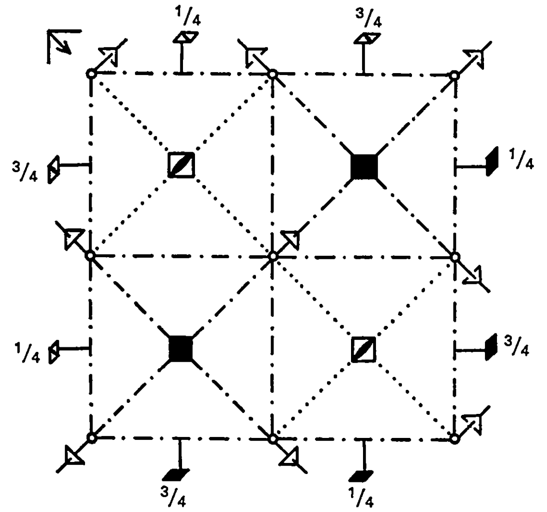

Fig. 2. Symmetry elements of the space group *Pn*3*n*.

ions, which are shown by diffraction data to be located on the (400) planes, must be distributed as follows:

(i) 8 on the positions of $\bar{3}$ symmetry
(ii) 12 on axes of $\bar{4}$ symmetry
(iii) 12 on axes of 4-fold symmetry

In order to satisfy these symmetry requirements the complex ion must have the symmetry of either an ellipsoid of revolution or a sphere. Spherical symmetry is, however, precluded by the diffraction data, since the observed systematic variation in the intensities of the *h*00 reflexions indicates that the ion possesses different orientations in the various members of the (400) planes. Thus the symmetry of the ion must be ellipsoidal; and the positions and orientations of the ellipsoidal ions are shown in Fig. 3.

Such ellipsoidal symmetry may be explained in terms of a statistical distribution about a particular direction. However, in the case of this structure – and others with the symmetry of the space group *Pn*3*n* which requires symmetrically related orientations of ellipsoidal components – such distribution would have to be associated separately with each of the body diagonals of the unit cell, as well as the cube axes. These distributions would require curiously ordered restrictions on randomness.

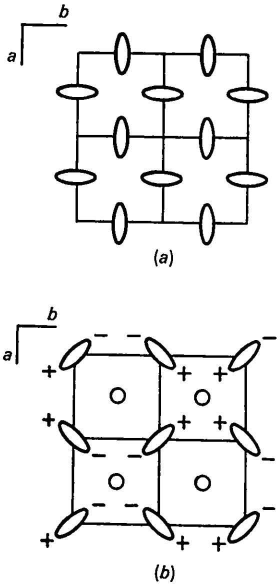

Fig. 3. Position and orientation of $[Co(NH_3)_5H_2O]^{3+}$ ellipsoids at (*a*) $z=\frac{1}{4}$ and (*b*) $z=0$. Circles indicate ellipsoids with their axes parallel to z. At $z=\frac{1}{2}$ each ellipsoid on {020} planes is similarly positioned but rotated through 90° in a plane defined by the z direction and the axis of the ellipsoid.

Thus, ordered orientations of the ellipsoids seem to support the dynamic model of rotating ions.

We are indebted to Dr G. C. Lalor[†] for his assistance in supplying the crystals and performing the ultraviolet spectroscopy, and to Mr T. Carrington[†] for performing the volumetric analysis.

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