tion is readily understood. Of course, in the absence of compelling evidence, translation of such large blocks *in toto* must be considered unlikely. The conservative view is to postulate the reorganization of the structure to be brought about by the diffusion of much smaller blocks, consisting of from one to perhaps three atoms each, which then reassemble in a pattern that recreates many of the features of the original structure.

A stereoscopic drawing of the structure of the *M′* phase is shown in Fig. 4.

The Patterson, Fourier, and least-squares calculations were performed at the California Institute of Technology under the CRYRM crystallographic computing system (Duchamp, 1964) through the generosity of Prof. R. E. Marsh, to whom the author is also greatly indebted for his expert advice on data handling. Dr W. R. Busing, Oak Ridge National Laboratory, was kind enough to furnish the computer program ORABS. Thanks are also due Mr W. Gehrer who patiently, over a period of many months, measured the intensities and backgrounds one by one.

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The Crystal Structure of a Double Oxalate of Yttrium and Ammonium, $NH_4Y(C_2O_4)_2.H_2O$

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A three-dimensional X-ray analysis of $NH_4Y(C_2O_4)_2.H_2O$ has yielded the positions of all the atoms except hydrogen with standard deviations of 0·0012 Å for Y, and less than 0·02 Å for the other atoms. The crystals are monoclinic with $a = 9·18 \pm 0·01$, $b = 6·09 \pm 0·01$, $c = 7·89 \pm 0·01$ Å, $\beta = 90·2° \pm 0·1°$; space group $P2/n$; $Z = 2$. There is ninefold coordination; eight oxygen atoms and the H_2O form a slightly distorted trigonal prism arrangement around the yttrium, at distances ranging from 2·343 Å (for the H_2O) to 2·412 Å. The two independent oxalate ions are planar and have crystallographic centres of symmetry. Their dimensions are in agreement with the results of previous work on oxalates.

Introduction

Hydrated oxalates of the rare earths having the composition $Ln_2(C_2O_4)_3.10H_2O$ (Ln = lanthanide) have been known for some time, and are thought to be interstitial hydrates though their detailed structures are not known (Gilpin & McCrone, 1952). Recently, Barrett, McDonald & Topp (1964) made a study of the precipitation of the rare earth oxalates from oxalic acid solution, in the course of which a new series of double salts was discovered with the composition $NH_4Ln(C_2O_4)_2.nH_2O$. Yttrium and the elements in the group Sm–Tm formed monohydrates which appeared to be isomorphous, while the remaining rare earths formed trihydrates exhibiting a number of different X-ray powder diffraction patterns. The monohydrated yttrium salt was obtained as single crystals and the present paper describes an X-ray analysis of the structure. The other members of the monohydrate series presumably also have this structure.

Experimental

$NH_4Y(C_2O_4)_2.H_2O$ is precipitated from strongly acidic solutions containing an excess of oxalate ion by the addition of ammonia. Prepared in this way, it is a fine powder. Crystals for the present work were grown hydrothermally. The prisms so obtained showed development of the forms {010} and {101} and were invariably twinned.

The intensity data were collected from three sets of equi-inclination Weissenberg photographs: (0–5,*k*,*l*), (*h*,*k*,0–6), and (*h*,0–4,*l*). Nickel-filtered Cu *Kα* radia-

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tion was used throughout. The crystal used for the *a*- and *c*-axis photographs measured 0·1 × 0·2 × 0·3 mm, and the oscillation directions were approximately along the diagonals of the largest face. A fragment of the same crystal was used for the *b*-axis setting. This crystal, like all the others, was twinned, but one component was much stronger than the other and no difficulty was experienced in indexing the photographs. Intensities were measured visually and brought to the same scale by direct comparison of reflexions common to the different sets of photographs, after correction for Lorentz and polarization factors. Absorption corrections were not applied. The relative F^2 values so obtained were used directly to compute the Patterson function in three dimensions. In all, 938 independent non-zero reflexion intensities were measured.

Crystal data

The crystals are monoclinic with:
$a = 9{\cdot}18 \pm 0{\cdot}01$, $b = 6{\cdot}09 \pm 0{\cdot}01$, $c = 7{\cdot}89 \pm 0{\cdot}01$ Å, $\beta = 90{\cdot}2 \pm 0{\cdot}1°$. Systematic absences: $h0l$ for $(h+l)$ odd; space group $P2/n$ (no. 13); $Z = 2$; linear absorption coefficient for Cu $K\alpha$: 58 cm^{-1}; density calculated for two formula weights per unit cell: 2·27 g.cm^{-3}; density measured by flotation: 2·26 g.cm^{-3}.

Structure analysis and refinement

The coordinates of all the atoms except those in NH_4 and H_2O were readily found from the three-dimensional Patterson sections. A projection of the structure along the *b* axis is shown in Fig. 1. The carbon and oxygen atoms are in general positions of $P2/n$:

$$\pm(x\,y\,z;\ \tfrac{1}{2}-x\ y\ \tfrac{1}{2}-z);$$

the yttrium atoms and the NH_4 and H_2O are situated on the twofold axes, while the two pairs of oxalate ions (which are not equivalent) are located on crystallographic centres of symmetry. The asymmetric unit thus consists of one Y atom, NH_4 and H_2O together with two half oxalate ions, making nine atoms in all, excluding the hydrogen atoms.

Sections of the three-dimensional electron density function, calculated from signs determined by the coordinates of the yttrium atoms and oxalate ions, were used to locate the NH_4 and H_2O. One extra peak, of about the same height as a carbon atom, was found within the sphere of attraction of the yttrium at $x = \frac{1}{4}$, $y = 0{\cdot}51$, $z = \frac{1}{4}$, and a second appeared on the other twofold axis at $x = \frac{1}{4}$, $y = 0{\cdot}48$, $z = \frac{3}{4}$. The R index at this stage was 31%. Of the two extra peaks, that closer to the yttrium was the larger and was believed to be the H_2O, but initially both were put in as oxygen atoms for the least-squares refinement.

The scale factor, atomic coordinates and anisotropic thermal parameters were refined on DEUCE with the structure factor least-squares program of J. S. Rollett. The program calculates thermal parameters B_{ij} for each atom according to:

$$f = f_0 \exp\{-0{\cdot}693(h^2B_{11} + k^2B_{22} + l^2B_{33} + klB_{23} + hlB_{31} + hkB_{12})\}\ .$$

Initially, weighting scheme no. 2 was used:

$$\text{for } |F_o| \le |F^*|,\ \sqrt{w_2} = |F_o|/|F^*|$$
$$\text{for } |F_o| > |F^*|,\ \sqrt{w_2} = |F^*|/|F_o|$$

where F^* is some fixed value near the middle of the range. The atomic scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and carbon, while that of Thomas & Umeda (1957) was used for yttrium. After six rounds of refinement using this scheme, R was reduced to 11·7%.

At this stage, new electron density sections were calculated through the centres of the atoms, and it was now evident that the H_2O was associated with the yttrium. This peak was higher than the other in the ratio of 8:7, and it made contacts of 2·7–2·8 Å with the neighboring atoms, appropriate to O–H···O bonds, while the second peak had contacts of 2·9–3·0 Å which would be expected for N–H···O bonds. Another two rounds of refinement were now carried out, making eight in all, with the appropriate scattering factors. The effect of this was to change R to 11·6%, scarcely a significant improvement.

The effect of altering the weighting scheme to no. 1 was now tried:

$$\text{for } |F_o| \le |F^*|,\ \sqrt{w_1} = 1$$
$$\text{for } |F_o| > |F^*|,\ \sqrt{w_1} = |F^*|/|F_o|$$

When the refinement was continued with this scheme, the R value fluctuated at first, and it was found necessary to apply half-shifts. However, after another eight rounds, satisfactory convergence was achieved with R now equal to 10·5% and no shift greater than 0·0001. The changes in the atomic coordinates brought about by changing the weighting scheme are shown in Table 2. These are the differences between the results of the 8th and the 16th rounds of refinement. In the case of the x and z coordinates, it will be seen that the shifts are all less than the s.d.'s based on round 16 (*cf.* Table 1), but some of the y shifts are considerably greater than the corresponding s.d.'s. Whether these changes represent a real gain in accuracy is questionable. In any case, the final coordinates listed in Table 1 are taken from the 16th round, as are the individual values of the anisotropic temperature factors listed in Table 3.

Table 1. *Fractional atomic coordinates with standard deviations*

	x	y	z
Y	0·7500 (0)	0·1045 (2)	0·7500 (0)
C(1)	0·4556 (14)	0·0967 (20)	0·5347 (18)
C(2)	0·5140 (15)	0·1071 (22)	0·0473 (17)
O(1)	0·3256 (12)	0·1104 (18)	0·4913 (13)
O(2)	0·5227 (11)	0·2283 (16)	0·6323 (13)
O(3)	0·4356 (10)	0·1551 (14)	0·1704 (11)
O(4)	0·8840 (10)	0·2286 (14)	0·5104 (12)
H_2O	0·2500 (0)	0·5108 (21)	0·2500 (0)
NH_4	0·2500 (0)	0·4853 (33)	0·7500 (0)

Observed and calculated structure factors are compared in Table 4.

Table 2. *Changes in fractional coordinates produced by altering the weighting scheme*

	x	y	z
Y	0	0·0002	0
C(1)	0·0005	0·0036	0·0009
C(2)	0·0001	0·0007	0·0001
O(1)	0·0009	0·0024	0·0002
O(2)	0·0005	0·0010	0·0005
O(3)	0·0006	0·0027	0·0003
O(4)	0·0000	0·0038	0·0003
H_2O	0	0·0020	0
NH_4	0	0·0009	0

Description of the structure

The most interesting feature of the structure is the coordination around the yttrium atom. There are nine oxygen atoms within 2·42 Å of the yttrium, as shown in Fig. 1. Looking down the twofold axis, there appears to be a distorted anti-prism arrangement of eight oxygen atoms with the ninth on the axis. However, if the nine atoms are projected normally onto a plane containing the twofold axis and the bond O(1)–Y–O(1′), the true symmetry of the coordination polyhedron is revealed. The projection is shown in Fig. 2, and it will be seen that there is substantially threefold symmetry

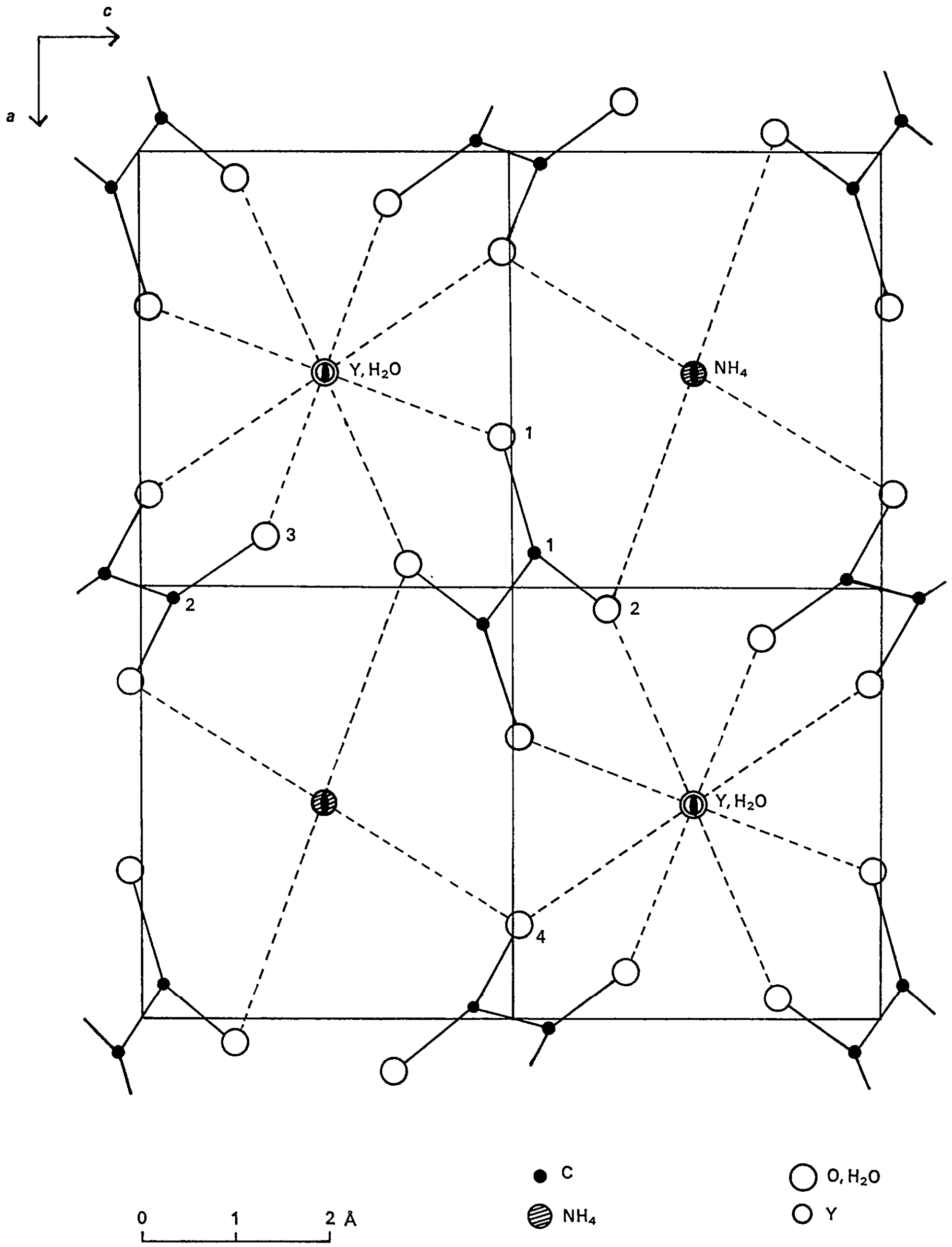

Fig. 1. Projection of the structure along the *b* axis, with the atoms numbered to correspond to Table 1.

in this direction. The coordination group of the yttrium is thus a distorted trigonal prism with three extra atoms opposite the rectangular faces. The prism is outlined in Fig. 3 (a redrawing of part of Fig. 1), where its configuration with respect to the twofold axis is clearly shown. The bonds Y–O(1), Y–O(1′) and Y–H_2O must be imagined as perpendicularly intersecting the sides of the prism. The triangular ends, formed by the atoms O(2), O(3) and O(4), are not quite parallel to the plane of the three central bonds, but the deviations from trigonal symmetry are small. The five independent Y–O distances, listed in Table 5, range from 2·412 to 2·343 Å (for Y–H_2O). The closest approach of two oxygen atoms not belonging to the same oxalate ion

Table 3. *Anisotropic thermal parameters*

	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Y	0·0036	0·0039	0·0088	0	0·0068	0
C(1)	0·0069	0·0081	0·0175	−0·0067	0·0064	0·0041
C(2)	0·0091	0·0137	0·0134	0·0017	0·0059	0·0036
O(1)	0·0107	0·0220	0·0143	−0·0084	0·0017	0·0039
O(2)	0·0088	0·0141	0·0183	−0·0147	−0·0020	0·0068
O(3)	0·0078	0·0077	0·0131	−0·0018	0·0119	0·0017
O(4)	0·0091	0·0083	0·0149	0·0016	0·0168	0·0084
H_2O	0·0094	0·0063	0·0207	0	0·0102	0
NH_4	0·0147	0·0212	0·0223	0	0·0130	0

Table 4. *Observed and calculated structure factors*

The columns give respectively *l*, F_c and KF_o for each pair of values *h*, *k*.

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  6 -083 091
  8  179 184
 10 -104 091
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  2  038 076
  3 -120 116
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```

is 2·732 Å [O(1)–O(3)]. The Y–C distances are very uniform, falling within the narrow range 3·18–3·20 Å.

Table 5. *Yttrium–oxygen distances in the coordination group with standard deviations*

Sum of Goldschmidt radii for Y^{3+} and O^{2-} is 2·38 Å.

Y–O(1)	2·412 (0·011) Å
Y–O(2)	2·405 (0·010)
Y–O(3)	2·408 (0·009)
Y–O(4)	2·379 (0·009)
Y–H_2O	2·343 (0·013)

Ninefold coordination is not uncommon in rare-earth compounds. A number of solid salts are known which have been shown to contain the group $Ln(H_2O)_9^{3+}$ with the same trigonal prismatic geometry as has been found in the present study (Moeller, Martin, Thompson, Ferrus, Feistel & Randall, 1965). This configuration is also found in the rare-earth hydroxides, though its presence in $Y(OH)_3$ has not been established (Roy & McKinstry, 1953). In YF_3, the ninth fluorine atom is only slightly farther from the central atom than are the other eight (Zalkin & Templeton, 1953). It seems probable that the bonding in coordination compounds of yttrium and the rare earths is largely electrostatic in character, in view of the preponderance of high coordination numbers.

Oxalate ions

The oxalate ions in the present structure are planar; both have a centre of symmetry. The dimensions shown in Table 6 agree with those found in other oxalate structures, including ammonium oxalate monohydrate in which the ions are non-planar (Jeffrey & Parry, 1952, 1954; Sterling, 1964, 1965; Padmanabhan, Srikantha & Medhi Ali, 1965). The differences exhibited by the individual C–O bonds and O–C–C angles in Table 6 are probably not significant.

Table 6. *Bond lengths and angles in the two independent oxalate ions, with standard deviations*

C(1)–C(1′)	1·534 (0·026) Å
C(1)–O(1)	1·244 (0·017)
C(1)–O(2)	1·270 (0·016)
C(2)–C(2′)	1·524 (0·026)
C(2)–O(3)	1·244 (0·016)
C(2)–O(4)	1·277 (0·016)
O(1)–C(1)–O(2)	126·2 (1·3)°
O(1)–C(1)–C(1′)	117·6 (1·2)
O(2)–C(1)–C(1′)	116·3 (1·1)
O(3)–C(2)–O(4)	124·5 (1·2)
O(3)–C(2)–C(2′)	119·1 (1·1)
O(4)–C(2)–C(2′)	116·4 (1·1)

Environments of H_2O *and* NH_4 (*Table* 7)

The ammonium ion is at the centre of a distorted tetrahedron formed by the pairs O(2) and O(4) which are at a suitable distance for hydrogen bond formation, but the angles are not favorable. The angle O(4)–N–O(4′) is 107·9°, not too far removed from the tetrahedral value, but O(2)–N–O(2′) is 119·2° and the traces of the planes containing these angles are at only 79° to one another (Fig. 1). This bonding arrangement would thus be associated with considerable strain, but no other is possible.

On energetic grounds one would expect the hydrogen atoms of the water molecule to point away from the yttrium ions, and this condition would be fulfilled by bonding to the pair O(3), O(3′), but unfortunately the angle O(3)–H_2O–O(3′) is only 80°, which seems al-

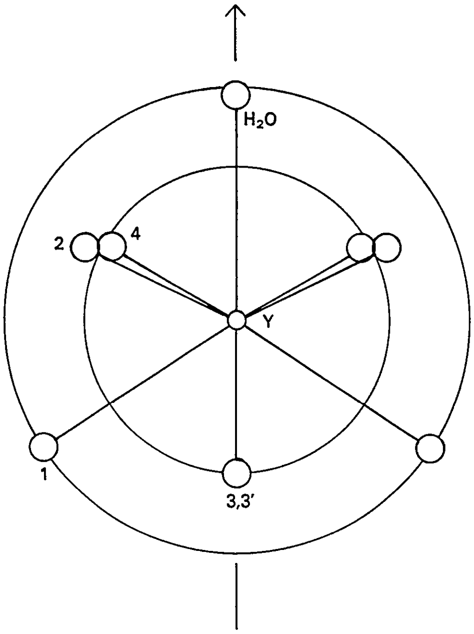

Fig. 2. Projection of the coordination group onto the plane containing the twofold axis and the bond Y–O(1), showing the threefold symmetry. Y at ¾, 0·1045, ¾.

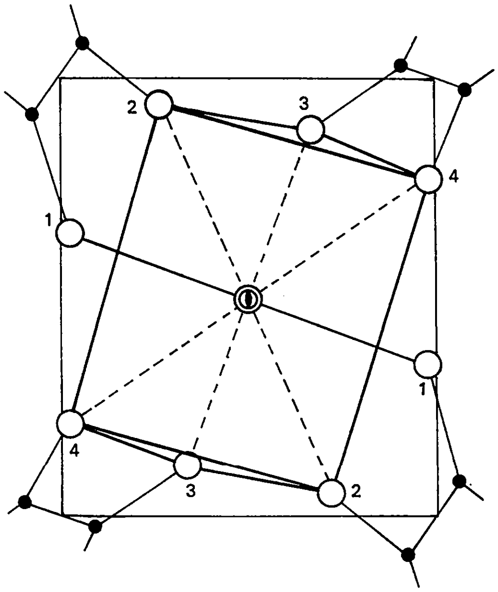

Fig. 3. A redrawing of part of Fig. 1, with the trigonal prism outlined.

Table 7. *Environments of* H_2O *and* NH_4: *distances from neighboring oxygen atoms, with angles of interest*

H_2O–O(1)	3·170 Å
H_2O–O(2)	2·783
H_2O–O(3)	2·827
H_2O–O(4)	2·758
NH_4–O(1)	3·140
NH_4–O(2)	3·095
NH_4–O(3)	3·677
NH_4–O(4)	2·962
O(2)–H_2O–O(2′)	110·3°
O(4)–H_2O–O(4′)	109·7
O(3)–H_2O–O(3′)	80·0
O(2)–NH_4–O(2′)	119·2
O(4)–NH_4–O(4′)	107·9

together too small. The angles O(2)–H_2O–O(2′) and O(4)–H_2O–O(4′) are close to the tetrahedral value, but bonding to either O(2) or O(4) would bring the hydrogen atoms in towards the yttrium. The question of the bonding of the water molecule must therefore remain open.

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An Accurate Correction Procedure for Equi-inclination Weissenberg Diagrams

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A method is presented by which the inclination error and the goniometer setting error can be derived from the deviations from linearity of lines of reciprocal-lattice points in upper-layer equi-inclination Weissenberg patterns. The method is most suitable for crystals having large unit cells and for rotation axes close to reciprocal-lattice directions.

Introduction

For crystals having large unit cells, the low-order reflexions in upper-layer equi-inclination Weissenberg patterns are quite close to the trace of the undeviated beam, or central axis. Even though the crystal alignment and inclination angle seem to be correct, these reflexions are often displaced from their proper positions. These displacements may serve as particularly sensitive diagnostic tools for improving these adjustments.

We shall here treat only the situation when the rotation axis is intended to coincide with a reciprocal-lattice axis. If this is not the case, the lack of coincidence could be treated as a known error, and we would be only interested in deviations from this. If this lack of coincidence were large, the reflexions involved would not be near the central axis of the Weissenberg diagram where all the sensitivity of this technique resides, so this method would not be recommended.

In the case treated here, the upper-layer zone is intended to rotate about a central reciprocal-lattice point which should remain stationary on the Ewald sphere. If all adjustments are correct, all straight lines of reciprocal-lattice points in the upper-layer zone that pass through the central stationary point become parallel straight lines on the Weissenberg pattern. If there is only an inclination error, the upper-layer zone rotates about the central stationary reciprocal-lattice point which is displaced from the surface of the Ewald sphere. If there is only a goniometer-setting error, the central reciprocal-lattice point rotates about the point on the Ewald sphere where it would be had there been no error. When each type of error occurs, the straight lines of reciprocal-lattice points that pass through the central point are no longer straight lines on the Weissenberg pattern. The resultant curves approach the undeviated straight lines far from the central axis of the pattern. The more closely the points on each curve approach the central axis, the more they deviate from