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The Crystal Structure of Tetrapotassium Tetraoxalatothorium(IV) Tetrahydrate, $K_4Th(C_2O_4)_4.4H_2O$

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The title compound is triclinic, space group $P\bar{1}$, with $a=9{\cdot}562$ (18), $b=13{\cdot}087$ (25), $c=10{\cdot}387$ (20) Å, $\alpha=115{\cdot}75$ (3), $\beta=80{\cdot}90$ (3), $\gamma=112{\cdot}66$ (3)°, and $Z=2$. 3825 unique X-ray data more than 3σ above background were collected on a Pailred diffractometer. The structure was solved by conventional heavy-atom methods and refined by block-diagonal least-squares calculations to a final R (based on F) of 0·084. The thorium is ten-coordinate. One quarter of the oxalate groups are tetradentate and bridging, and link the thorium atoms into infinite chains parallel to [110]. The other oxalates are bidentate and non-bridging. The thorium–oxalate chains are cross-linked in several directions into a three-dimensional framework by the hydrogen bonds formed by the four water molecules. The coordination polyhedron of the thorium is a bicapped square antiprism with only very small deviations from the ideal D_{4d} symmetry. Apart from uranium(IV) acetate, which shows large distortions, the present compound seems to be the only reported example of this coordination geometry. The oxalate geometry shows no abnormal features and the four potassium ions are coordinated rather irregularly by six, seven, eight, and nine oxygens respectively.

Introduction

Potassium thorium oxalate was first prepared, but not analysed, by Berzelius (1829); its formula was determined much later by Cleve (1874). Johnson & Larson (1962), having demonstrated the isomorphism of $K_4Zr(C_2O_4)_4.5H_2O$ with $K_4Hf(C_2O_4)_4.5H_2O$, supposed that this isomorphism extended also to the uranium and thorium complexes, though they recognized the last to be a tetrahydrate. Their hypothesis is disproved by the present study.

We undertook the structure analysis of single crystals of the thorium and the uranium compounds to determine whether the metal coordination was dodecahedral or antiprismatic. The thorium compound is triclinic, $P\bar{1}$, and the uranium compound orthorhombic, $Fdd2$; neither has any similarity to the zirconium or the hafnium complex. In the case of the thorium compound, as already reported (Akhtar & Smith, 1969), bridging oxalates were found, bringing the metal coordination number up to ten. We now present full details of this structure; the study of the uranium complex is in progress.

Experimental

The compound was prepared by a modification of Cleve's (1874) procedure. A potassium oxalate solution was added to a thorium nitrate solution until the precipitate which was formed initially had almost completely redissolved. The solution was filtered and ethanol was added drop by drop to the filtrate until colourless crystals of the complex started to form. On standing the solution deposited further crystals, chemical analysis of which gave the results in Table 1. Potassium was determined by flame emission spectroscopy, thorium gravimetrically by precipitation as oxalate and ignition to the dioxide, and carbon and hydrogen by standard microanalytical techniques.

Table 1. *Elemental analysis of* $K_4Th(C_2O_4)_4.4H_2O$

	K	Th	C	H
Calculated for $K_4ThC_8H_8O_{20}$ (%)	19·2	28·5	11·83	0·98
Found (%)	19·7	28·2	11·83	1·18

Data from a small (approximately 0·17 × 0·09 × 0·15 mm) crystal were collected on a Pailred two-circle X-ray diffractometer. The unit-cell parameters given above were used for structure solution and refinement but it was observed at a late stage that this cell may be reduced by the Delaunay method *via* the transformation matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

to $a=9{\cdot}652$ (18), $b=12{\cdot}690$ (24), $c=10{\cdot}387$ (20) Å, $\alpha=111{\cdot}74$ (3), $\beta=99{\cdot}10$ (3), and $\gamma=105{\cdot}54$ (3)°. All the results in this paper are reported in terms of the former cell. Molybdenum $K\alpha$ radiation from a Philips 1010 fully stabilized generator and a silicon (111) crystal monochromator was used to obtain 3825 independent reflexion intensities more than three times $\sqrt{(I_o-I_b)}$ above background, measured by a NaI(Tl) crystal scintillator with pulse-height discrimination. The ω-scan technique (stationary counter, moving crystal) was employed with a scanning rate of 2·5° $\min^{-1}$, and background counting for 12 s at each end of the scan. The diffractometer employs Weissenberg geometry; layers $hk\bar{13}$ to $hk13$ were explored up to $\theta=30°$. The calculated density of 2·49 g cm^{-3} for

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$Z=2$ agreed well with the value of 2·48 g cm^{-3} measured by flotation in a mixture of benzene and 1,1,2,2-tetrabromoethane. No symmetry except that due to the Friedel law, nor any systematic absences were observed. The cell content suggests the space group $P\overline{1}$, which was chosen and was confirmed by the successful refinements.

After correcting for Lorentz, polarization, and absorption effects [the last by a procedure based on Busing & Levy (1957) using $8\times8\times8$ Gaussian points and a μ of 86·74 cm^{-1} from the thorium absorption coefficient measured by Roof (1959) and other coefficients from *International Tables for X-ray Crystallography*], we found the positions of the 33 non-hydrogen atoms from Patterson and difference Fourier syntheses. Least-squares refinement, minimizing $\sum(|kF_o|-|F_c|)^2$ and using unit weights was performed on the SRC Atlas computer by the Sheffield crystallographic programs. Block-diagonal approximations were used; initially one block for each atom; later cycles had one block for each oxalate group, one for each of the water oxygens and the metal atoms, and one for the scale factor with an overall temperature factor which was not applied. Scattering factors were taken from *International Tables for X-ray Crystallography*. Anomalous dispersion corrections for thorium, $\Delta f'=-12·0$ and $\Delta f''=14·4$, were taken from Roof (1961). The final R value, defined as $\sum(|kF_o|-|F_c|)/\sum(|kF_o|)$, based on observed reflexions only, was 0·084. All parameter shifts on the final cycle of refinement were less than 0·1 of the corresponding estimated standard deviations; analysis of the residual errors with respect to F_o and to

Table 2. *Atomic positional and vibrational parameters with estimated standard deviations, referring to the last significant figure, in parentheses*

The positional parameters are multiplied by 10^5 (Th) or 10^4 (other atoms). The expressions used for the vibration factor were $\exp\,[-10^{-4}(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+kl\beta_{23}+lh\beta_{31}+hk\beta_{12})]$ and $\exp\,[-(B\sin^2\theta)/\lambda^2]$: B is in Å^2.

	x/a	y/b	z/c	β_{11} or B	β_{22}	β_{33}	β_{23}	β_{31}	β_{12}
Th	22478 (9)	27945 (7)	5313 (9)	22·4 (6)	7·6 (3)	37·3 (6)	20·5 (8)	1·6 (10)	−6·9 (7)
K(1)	2668 (8)	7980 (6)	851 (8)	93 (8)	75 (6)	99 (9)	62 (12)	−34 (13)	−23 (11)
K(2)	9068 (6)	6941 (5)	2872 (6)	72 (6)	52 (4)	62 (6)	58 (9)	18 (10)	39 (8)
K(3)	6366 (8)	3973 (6)	3040 (8)	96 (8)	90 (7)	105 (9)	99 (13)	26 (13)	75 (12)
K(4)	6699 (9)	1617 (6)	5032 (8)	167 (12)	55 (5)	103 (9)	16 (11)	38 (17)	55 (13)
Oxalate(1)									
O(1)	1885 (18)	806 (13)	551 (22)	60 (20)	19 (11)	146 (28)	81 (29)	−30 (37)	13 (24)
O(2)	−420 (19)	1077 (14)	−229 (26)	75 (23)	30 (13)	223 (39)	157 (38)	−33 (46)	3 (27)
C(1)	629 (26)	−104 (20)	207 (29)	72 (29)	28 (16)	102 (33)	91 (39)	17 (49)	−40 (34)
Oxalate(2)									
O(3)	3271 (19)	4009 (13)	−930 (18)	100 (23)	16 (10)	63 (20)	42 (24)	−23 (34)	−32 (25)
O(4)	4970 (17)	4336 (14)	1110 (18)	53 (19)	42 (13)	76 (20)	81 (27)	−18 (31)	−19 (24)
C(2)	4497 (27)	4904 (19)	−628 (22)	108 (33)	34 (16)	35 (22)	16 (31)	36 (42)	110 (38)
Oxalate(3)									
O(5)	383 (23)	2613 (21)	2431 (22)	112 (29)	108 (23)	79 (25)	107 (40)	53 (42)	92 (42)
O(6)	3295 (21)	3171 (15)	2791 (19)	99 (25)	45 (14)	69 (22)	55 (29)	6 (37)	7 (30)
O(7)	−182 (31)	2553 (41)	4565 (32)	131 (40)	404 (74)	151 (42)	407 (98)	84 (66)	150 (89)
O(8)	2927 (24)	3554 (21)	5104 (21)	120 (30)	125 (25)	59 (23)	113 (40)	26 (41)	62 (44)
C(3)	773 (38)	2761 (36)	3630 (32)	118 (45)	142 (42)	83 (38)	108 (66)	−28 (65)	76 (70)
C(4)	2491 (28)	3176 (25)	3886 (32)	70 (30)	72 (24)	112 (37)	114 (50)	3 (52)	67 (43)
Oxalate(4)									
O(9)	283 (17)	3381 (14)	188 (19)	48 (19)	31 (12)	92 (23)	17 (27)	−4 (32)	15 (24)
O(10)	2410 (19)	4915 (15)	2059 (20)	64 (21)	40 (13)	94 (24)	12 (29)	−34 (35)	32 (27)
O(11)	−1107 (19)	4544 (16)	1245 (21)	59 (21)	53 (15)	100 (25)	22 (31)	−15 (35)	58 (29)
O(12)	1667 (21)	6432 (14)	2470 (21)	105 (26)	19 (11)	102 (25)	36 (28)	−29 (39)	10 (27)
C(5)	81 (27)	4356 (24)	1036 (31)	63 (28)	71 (23)	112 (36)	142 (50)	21 (50)	43 (41)
C(6)	1475 (24)	5324 (22)	1987 (24)	46 (25)	61 (20)	46 (24)	20 (36)	−28 (39)	51 (36)
Oxalate(5)									
O(13)	1763 (21)	1564 (15)	−2085 (20)	99 (25)	37 (13)	74 (22)	−25 (28)	−92 (37)	43 (29)
O(14)	4241 (17)	2004 (15)	−855 (19)	49 (19)	50 (14)	70 (21)	45 (29)	75 (32)	21 (26)
O(15)	2631 (38)	597 (34)	−4196 (27)	286 (63)	238 (48)	68 (30)	−123 (62)	−107 (68)	369 (96)
O(16)	5005 (22)	832 (18)	−2898 (23)	91 (27)	69 (18)	110 (29)	−12 (36)	−18 (43)	86 (37)
C(7)	2805 (42)	1184 (32)	−2867 (33)	215 (61)	119 (36)	81 (36)	83 (59)	88 (74)	274 (84)
C(8)	4084 (31)	1317 (24)	−2127 (34)	97 (36)	47 (20)	118 (40)	65 (48)	−91 (60)	17 (43)
O(17)	1291 (27)	9257 (22)	3222 (26)	4·5 (5)					
O(18)	7251 (33)	2041 (27)	2177 (33)	6·2 (6)					
O(19)	4275 (27)	6529 (21)	4535 (26)	4·5 (5)					
O(20)	4057 (81)	713 (64)	1935 (80)	16·4 (15)					

$(\sin\theta)/\lambda$ showed no anomalous features, and a final difference Fourier synthesis showed no peaks higher than 3 e Å^{-3}. None of the four peaks observed at 1 e Å^{-3} or higher could be interpreted as an atom, even at a fractional population.

The atomic positional and vibrational parameters together with their estimated standard deviations (which are the values derived from the matrix described above) are listed in Table 2. The principal interatomic distances and angles are in Table 3. The observed and calculated structure factors are given in Table 4.*

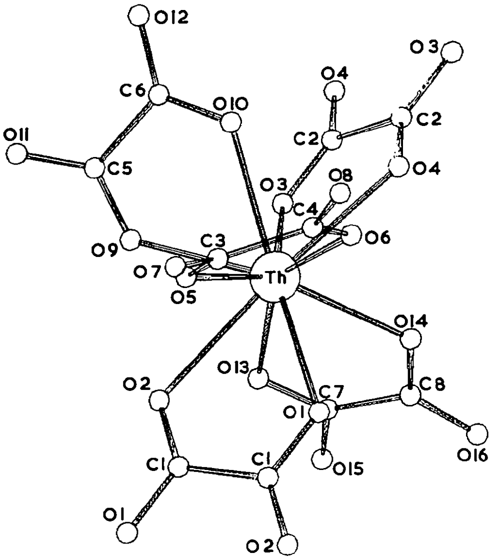

Fig. 1. The five oxalate groups coordinated to one thorium atom.

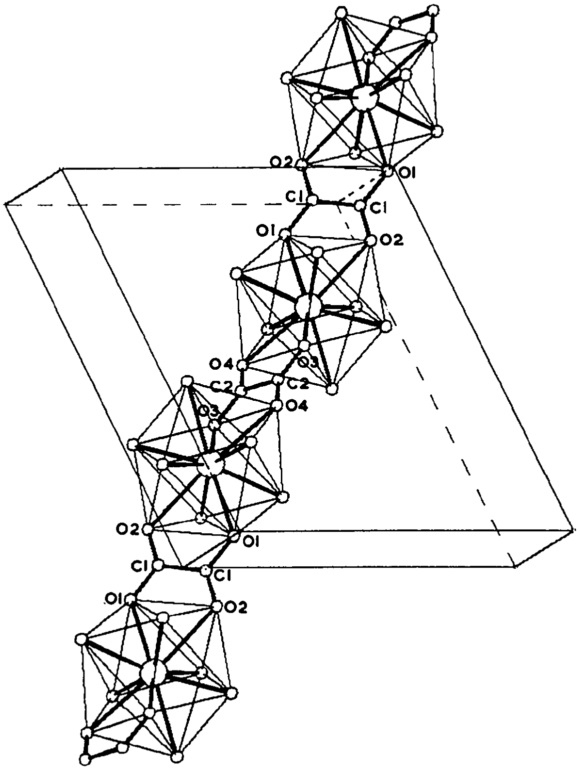

Fig. 2. The oxalate-bridged chain parallel to [110].

Table 3. *Bond lengths* (Å) *and principal angles* (°)

Thorium coordination polyhedron			
Th—O(1)	2·44 (2)	Square edges	
Th—O(2)	2·62 (2)	O(1)—Th—O(5)	75·1 (7)
Th—O(3)	2·49 (2)	O(5)—Th—O(9)	74·0 (7)
Th—O(4)	2·57 (2)	O(9)—Th—O(13)	79·8 (6)
Th—O(5)	2·47 (2)	O(13)–Th—O(1)	83·5 (6)
Th—O(6)	2·47 (2)	O(3)—Th—O(14)	78·2 (6)
Th—O(9)	2·41 (2)	O(14)–Th—O(6)	91·0 (6)
Th—O(10)	2·48 (2)	O(6)—Th—O(10)	77·9 (6)
Th—O(13)	2·48 (2)	O(10)–Th—O(3)	71·6 (6)
Th—O(14)	2·49 (2)	Mean	78·87
Means			
Th—O(axial)	2·595	Equatorial edges	
Th—O(other)	2·467	O(1)—Th—O(6)	71·1 (6)
Pyramid edges		O(6)—Th—O(5)	64·5 (7)
		O(5)—Th—O(10)	75·8 (7)
O(2)—Th—O(1)	62·3 (7)	O(10)–Th—O(9)	63·7 (6)
O(2)—Th—O(5)	62·2 (7)	O(9)—Th—O(3)	71·2 (6)
O(2)—Th—O(9)	64·0 (6)	O(3)—Th—O(13)	66·2 (6)
O(2)—Th—O(13)	63·5 (7)	O(13)–Th—O(14)	63·6 (6)
O(4)—Th—O(3)	63·4 (6)	O(14)–Th—O(1)	68·9 (6)
O(4)—Th—O(14)	65·0 (6)	Mean	68·12
O(4)—Th—O(6)	65·7 (6)	Chelate edges	
O(4)—Th—O(10)	65·9 (6)	Mean	63·48
Mean	64·00	All polyhedron edges	
O(2)—Th—O(4)	174·7 (6)	Mean	70·33
Mean dimensions of the oxalate groups			
C—C	1·532	C—C—O(*l*)	115·6
C—O(*l*)*	1·255	C—C—O(*t*)	119·3
C—O(*t*)†	1·247	O(*l*)—C—O(*l*)	128·4
		O(*l*)—C—O(*t*)	124·9
Hydrogen bonds			
O(17)-H····O(13)	2·94 (3)	O(19)-H····O(8)	2·81 (4)
O(17)-H····O(15)	2·68 (5)	O(19)-H····O(10)	2·84 (3)
O(18)-H····O(5)	2·82 (4)	O(20)-H····O(1)	2·81 (8)
O(18)-H····O(20)	2·86 (8)	{ O(20)-H····O(16)	3·05 (8)
		{ O(20)-H····O(17)	3·10 (8)
Potassium coordination			
K(1)—O(17)	2·77 (3)	K(2)—O(8)	2·73 (3)
K(1)—O(9)	2·78 (2)	K(2)—O(7)	2·74 (4)
K(1)—O(16)	2·80 (2)	K(2)—O(12)	2·74 (2)
K(1)—O(14)	2·95 (2)	K(2)—O(3)	2·78 (2)
K(1)—O(12)	2·97 (2)	K(2)—O(11)	2·79 (2)
K(1)—O(11)	2·98 (2)	K(2)—O(13)	2·81 (2)
K(1)—O(20)	3·03 (8)	K(2)—O(17)	2·86 (3)
K(1)—O(2)	3·12 (2)	K(2)—O(9)	3·01 (2)
K(1)—O(18)	3·12 (3)	K(4)—O(19)	2·76 (3)
K(3)—O(18)	2·71 (3)	K(4)—O(16)	2·80 (3)
K(3)—O(6)	2·72 (2)	K(4)—O(7)	2·81 (4)
K(3)—O(19)	2·79 (3)	K(4)—O(12)	2·85 (2)
K(3)—O(8)	2·82 (3)	K(4)—O(15)	2·94 (4)
K(3)—O(4)	2·86 (2)	K(4)—O(16)	2·96 (3)
K(3)—O(11)	2·88 (2)	K(4)—O(18)	3·18 (4)

* O(ligand).
† O(terminal).

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30860 (37 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Although the use of anisotropic vibrational parameters gave a significant improvement in R, there are few obvious correlations between the shapes of the thermal ellipsoids and the expected directions of atomic motion. The β_{ij}'s probably contain some systematic errors due to incomplete removal of X-ray absorption effects from the data. One atom, O(20), representing one of the water molecules, showed an unrealistically high isotropic B factor, and at first we thought the site was only fractionally populated. Failure to find the remaining fraction of an oxygen led to the following explanation. Four other oxygen atoms, O(1), O(16), O(17), and O(18) lie within hydrogen-bonding distance of O(20), though O(16) and O(17) are barely close enough. A count of hydrogen atoms shows that O(20) can be involved in only three hydrogen bonds. We conclude that some (say, half) of the O(20) atoms are bonded to O(1), O(16), and O(18), whilst the rest are bonded to O(1), O(17), and O(18). The equilibrium position of O(20) is slightly different for the two cases, our observed position being a mean and the high B value reflecting the spatial separation of the two positions.

Discussion of the structure

The structure is illustrated in Figs. 1 to 5.

The thorium coordination

The thorium coordination polyhedron approximates rather closely to the bicapped square antiprism predicted for ten-coordination by Muetterties & Wright (1967). There is some necessary loss of the ideal D_{4d} symmetry owing to the fixed bite of the oxalate ligands and there is no crystallographically imposed symmetry. As this polyhedron seems to be quite rare among coordination compounds, we thought it worth while to analyse it rather carefully, to determine its shape parameters, and to assess the aptness of the idealized polyhedron we have chosen to describe the distorted one we have measured. The literature abounds with 'somewhat distorted' and 'approximate' coordination polyhedra, but there seems to be no accepted method of quantifying the distortions. We conceived the method of fitting an idealized polyhedron by the least-squares method to the experimental points, and using the root-mean-square deviation of the actual from the ideal as a measure of the distortion. As the method appears to be of some general applicability, we will outline the steps involved.

In describing coordination polyhedra in general, the angles subtended at the central metal atom are likely to be of much greater interest than the metal–ligand bond distances, for the latter, though not readily distorted, may show wide variation in an anisoleptic compound. We therefore limited our consideration to these angles by replacing all the ligand atoms by the points of intersection of the metal–ligand bonds with a sphere of 1 Å radius centred on the thorium atom, which was also the origin of a Cartesian coordinate system. The ideal D_{4d} polyhedron of the present structure has a unique axis, along which the ligands occur in sets of 1, 4, 4, and 1. So we next determined the 'best' orientation for this axis by finding (*a*) the normal to the least-squares plane through each set of four equivalent ligand atoms and (*b*) the vectors defining the positions of the two axial ligands, and then taking a weighted mean of these four approximations to the direction required. The axial system was then rotated

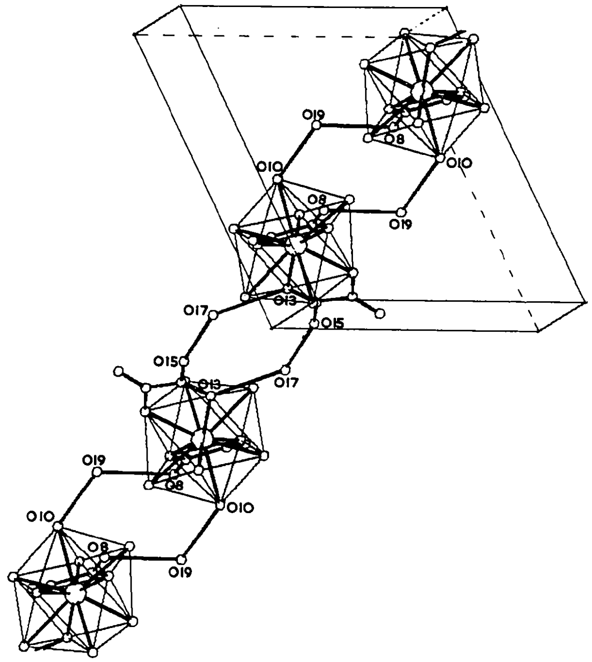

Fig. 3. The hydrogen-bonded chain produced by O(17) and O(19).

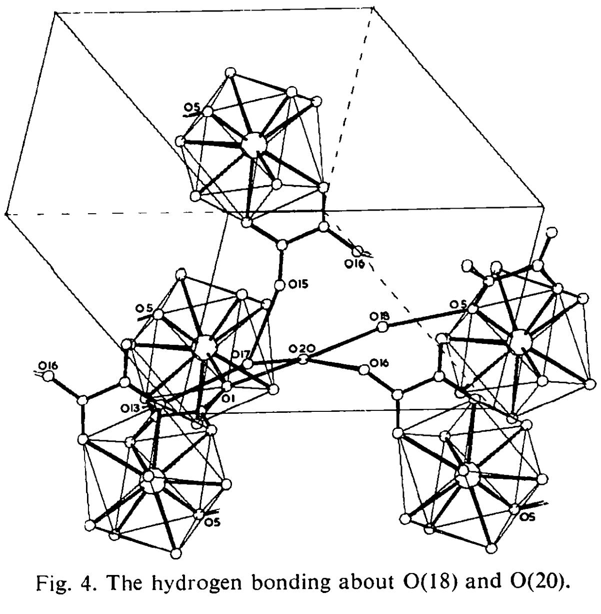

Fig. 4. The hydrogen bonding about O(18) and O(20).

to make this direction the z axis (with arbitrary choice of x) and the ligand positions were reduced to spherical polar coordinates. It was then a simple matter to obtain the mean θ values for each set of vertices of the polyhedron, to obtain a 'best' orientation for the x axis (now the prime meridian of the coordinate system) defined by reference to any corner of the ideal polyhedron, and to calculate the angular deviations of the real atoms from the ideal positions, in latitude, in longitude, and overall.

This method may be applied to any polyhedron having a unique axis (though a small modification is required if any non-axial set contains fewer than three ligands); for non-polar polyhedra, such as the present, it is necessary to take a mean θ from separate θ and $180-\theta$ values.

The bicapped square antiprism, of D_{4d} symmetry, has two independent shape parameters. They are conveniently chosen as θ (the angle unique axis–metal–non-axial ligand) and the ratio of metal–ligand bond distances for axial and antiprism ligands. Our best values for these parameters in the present structure, the former determined by the above procedure, are 63·9° and 1·045, with a root-mean-square angular deviation of actual positions from ideal ones (σ) of 4·23°. Bearing in mind the fixed bite of the oxalate group and the fact that the angles subtended by the polyhedron edges are about 60°, we think that this small deviation fully justifies the description of this structure as 'only slightly' distorted from D_{4d} symmetry. An attempt to describe the present structure in terms of a pentagonal antiprism led to a minimum σ of over 20°.

A less symmetrical polyhedron will, of course, lead to a better fit. Relaxation of the symmetry from D_{4d} to D_4 (a twisted prism rather than an antiprism) leads to a best fit at $\varphi = 41{\cdot}0°$ (instead of 45°) but σ drops only to 3·92°. Further relaxation to the polar C_4 (separate θ values for the two squares) leads to $\Delta\theta = 1{\cdot}9°$ and $\sigma = 3{\cdot}82°$. We conclude that these small improvements in agreement do not reveal any significant departure from D_{4d} symmetry, though it may be significant that the deviations in latitude are smaller ($\sigma = 2{\cdot}33°$) than those in longitude ($\sigma = 4{\cdot}07°$), and certainly the edges spanned by the oxalate groups are distinctly shorter than the other polyhedron edges.*

Our θ value, 63·9°, is significantly larger than the θ values reported for square antiprismatic eight-co-

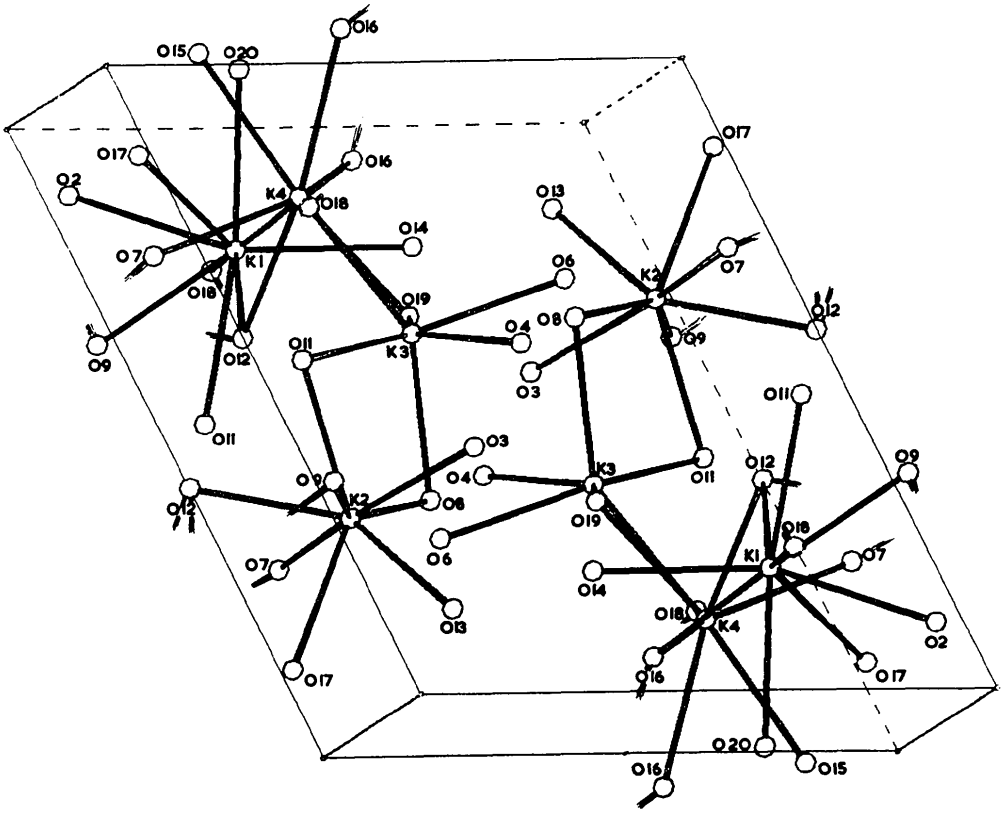

Fig. 5. The potassium ions in one unit cell and their nearest neighbours.

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* Since the above was written, Dollase (1974) has described a quite differently based method of determining the distortion of coordination polyhedra by carrying out a least-squares fit of an ideal polyhedron to the actual one. His method is undoubtedly a useful tool for the coordination chemist, but we feel that insofar as covalent bonding is under consideration the angular distortions are best considered separately from the radial ones, as we have done, and that our approach is essential in the case of anisoleptic compounds.

ordination [Lippard (1967) quotes values ranging from 54 to 59°] as might be expected, and is near 65·5° calculated for the hard sphere model of ten-coordination. The mean Th–O bond length, 2·493 Å, is normal.

The bicapped square antiprism, when substituted by five bidentate ligands, gives rise to five possible geometrical isomers, each of which exists in two enantiomeric forms. The edges of the polyhedron are of three kinds, which may be designated pyramid edges (*p*), square edges (*s*), and equatorial (*i.e.* crossing the equator) ones (*e*). Two pyramid edges, at opposite ends of the polyhedron, must be spanned by bidentate ligands, and two square edges, also at opposite ends, may be. Thus we obtain two distributions of the bidentate groups, p^2s^2e and p^2e^3, which give rise to three and two geometrical isomers respectively. As the bite of the oxalate group is on the short side for the thorium ten-coordination polyhedron, and the square edges are the longest (for all $\theta > 59°$), we are not surprised that the present complex exhibits one of the p^2e^3 forms. All five geometric isomers are illustrated schematically in Fig. 6. The principal bond lengths and angles in the thorium coordination polyhedron are listed in Table 3.

The oxalate groups

The oxalate groups show little variation one from another. The mean bond lengths and angles are given in Table 3 and are normal for metal oxalates. The least-squares planes through the oxalate atoms, together with deviations therefrom, are given in Table 5.

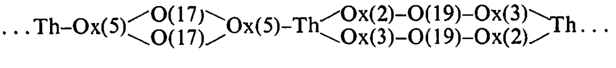
Table 5. *Least-squares planes of oxalate groups* ($pX+qY+rZ=s$) *referred to orthogonal axes a, b*, and c′, and mean deviations in* Å *of the oxalate* (D_{Ox}) *and thorium* (D_{Th}) *atoms from these planes*

Oxalate	p	q	r	s (Å)	D_{Ox}	D_{Th}
1	0·9305	−0·1100	0·3494	0·0000	0·004	0·025
2	0·6870	0·1698	0·7065	−0·4170	0·005	0·373
3	0·9491	0·3149	0·0092	−2·6522	0·096	0·081
4	0·6331	0·7226	0·2776	1·8109	0·195	0·168
5	0·8958	0·1284	0·4255	−3·1481	0·062	0·019

The water molecules and the hydrogen bonding

The water molecules represented by O(17) to O(20) form hydrogen bonds to oxalate oxygens and among themselves as listed in Table 3. As already noted, each O(20) atom is bonded to either O(16) or O(17) but not to both.

The O(17) atoms occur in pairs (related by a centre of symmetry in the crystal); both members of a pair link the oxalate (5) on one thorium to the oxalate (5) on another, each O(17) joining a ligand atom to a terminal one. The O(19)'s form a similar pair of bridges between a ligand atom of oxalate (2) and a terminal oxygen of oxalate (3), and also spanning a centre of symmetry. The two sets taken together alternate to form infinite chains of the form



$$\ldots\mathrm{Th{-}Ox(5)}\begin{matrix}\diagup\mathrm{O(17)}\diagdown\\ \diagdown\mathrm{O(17)}\diagup\end{matrix}\mathrm{Ox(5){-}Th}\begin{matrix}\diagup\mathrm{Ox(2){-}O(19){-}Ox(3)}\diagdown\\ \diagdown\mathrm{Ox(3){-}O(19){-}Ox(2)}\diagup\end{matrix}\mathrm{Th}\ldots$$

in the [112] direction. Another chain of hydrogen bonding through O(18) and O(20) runs

$$\ldots\mathrm{Th{-}Ox(1){-}O(20){-}O(18){-}Ox(3){-}Th}\ldots$$

parallel to [100].

O(20), however, is a junction point in the hydrogen bonding, doubly so because of the disorder. It is bonded either to an O(17), linking the second chains to the first, or to the O(16) of an Ox(5). Only half of these hydrogen bonds are present, but they may be seen to link the thorium atoms in several directions, and even to form closed loops. The hydrogen bonding is illustrated in Figs. 3 and 4.

The potassium ions

The potassium ions are surrounded by six, seven, eight, and nine oxygens at distances of 2·7 to 3·2 Å. The K–O distances are listed in Table 3; the coordination polyhedra are all, as expected, irregular.

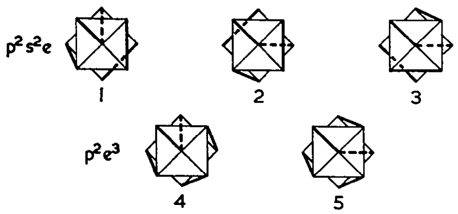


Fig. 6. The five possible geometric isomers of a pentakis-bidentate complex having bicapped square antiprismatic geometry. The heavy lines indicate those edges of the polyhedron which are spanned by ligands.

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