Ten-co-ordinate Thorium: the Crystal Structure of Potassium Thorium Tetroxalate Tetrahydrate

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Summary The thorium atoms in $K_4Th(C_2O_4)_4,4H_2O$ are each surrounded by ten oxygens at the vertices of a bicapped square antiprism; this co-ordination number is achieved by oxalate bridging, the resulting chains being cross-linked by hydrogen bonding.

VERY few instances of complexes with ten-co-ordinate metal atoms have yet been described. In a review of high co-ordination numbers, Muetterties and Wright[1] suggested the bicapped square antiprism of D_{4d} symmetry as a likely shape for such complexes. But none of the ten-co-ordinate complexes yet reported[2] seems to be well described by this arrangement, with the possible exception of uranium(IV) acetate.[3] Here, however, two of the ten oxygens are much more distant from the uranium than the other eight, and the structure is much distorted by the short 'bite' of the acetate ligand.

We investigated the crystal structure of potassium thorium tetroxalate, which was prepared essentially by Cleve's[4] method. Found K 19·7 (by flame emission), Th 28·2, C 11·83, H 1·18%. Calculated for $K_4Th(C_2O_4)_4,4H_2O$ K 19·2, Th 28·5, C 11·82, H 0·98%.

Crystal data $C_8H_8O_{20}K_4Th$: $M = 812{\cdot}65$; triclinic, $a = 9{\cdot}562$, $b = 13{\cdot}087$, $c = 10{\cdot}387$ Å, $\alpha = 115{\cdot}75°$, $\beta = 80{\cdot}90°$, $\gamma = 112{\cdot}66°$, $U = 1079$ Å^3; $D_m = 2{\cdot}48$ (by flotation), $Z = 2$, $D_c = 2{\cdot}49$ g.cm.$^{-3}$; space group $P\bar{1}$ (C_i^1, No. 2); monochromatised Mo-K_α radiation ($\mu = 86{\cdot}7$ cm.$^{-1}$), 4493 unique non-zero reflections were collected from a small crystal (maximum length 0·18 mm.) on a Philips Pailred automatic diffractometer.

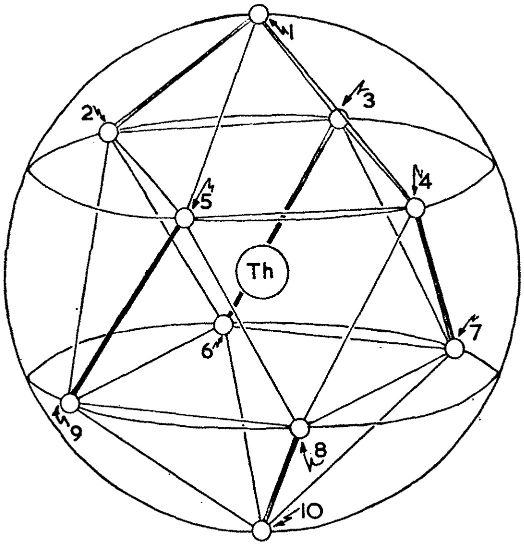

FIGURE. Bicapped square antiprismatic co-ordination of thorium. Only the ligand oxygen atoms in the co-ordination sphere are shown; the polyhedron edges spanned by oxalate groups are indicated by heavy lines.

The structure was solved by conventional Patterson and difference Fourier techniques and refined by block-diagonal least-squares. To reduce the computational work in the early cycles, all reflections with $\theta < 30°$ and a random one-sixth of the remainder—some 1076 in total—were used. Anisotropic vibration parameters have been used for the metal atoms only and no correction has yet been made for absorption or extinction, nor has the imaginary part of the anomalous dispersion been allowed for. Nevertheless the convergence of the refinement to the present R value of 0·082 indicates that the salient features of the structure are well determined.

Each thorium is surrounded by ten oxygens at the vertices of a slightly irregular bicapped square antiprism (Figure; the numbering follows Muetterties and Wright[1]). The Th–O distances are 2·60 ± 0·03 Å (axial) and 2·46 ± 0·02 Å (others). None of the five oxalate groups spans any of the eight square edges of the antiprism, which are longer (3·11 ± 0·20 Å) than the eight pyramid edges (2·67 ± 0·06 Å) or the eight equatorial ones (2·76 ± 0·17 Å). As the oxalate groups span positions 1–2, 3–6, 4–7, 5–9, and 8–10 of the polyhedron, a chiral structure results, but equal numbers of right- and left-handed polyhedra occur in the crystal. The oxalates at 1–2 and 8–10 (*i.e.* those containing the apical oxygens) are quadridentate,[5] lying across centres of symmetry at 0,0,0 and $\frac{1}{2},\frac{1}{2}$,0 and so bridging adjacent polyhedra and producing chains parallel to [110]. The water molecules link the chains together by hydrogen-bonding in the [100], [111], and [$1\bar{1}0$] directions.

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