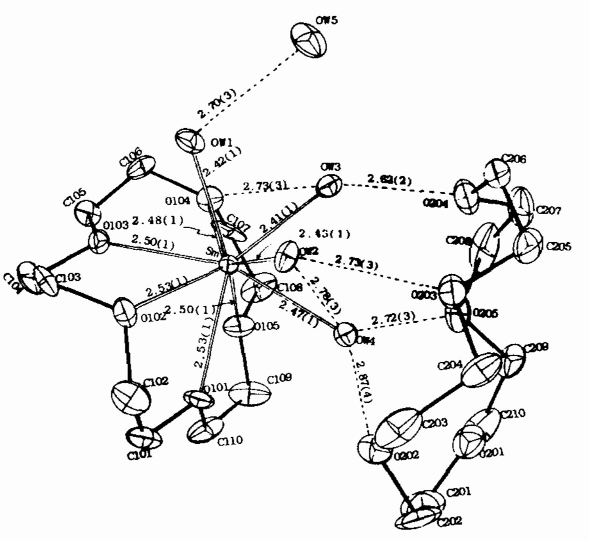

Fig. 1. ORTEP drawing of the molecule with numbering scheme. The coordination bonds are indicated by open lines, interatomic bonds by heavy lines, hydrogen bonds by dashed lines. OWs are oxygen of water molecules.

rium(III) ion is found to be coordinated with nine oxygen atoms, five are from one of the ether molecules and the remaining four are from water molecules. The second ether molecule does not take part in coordination. Three of the water molecules link to the second ether ring by forming hydrogen bonds with the oxygen atoms in it. The other coordinated oxygen atom of a water molecule forms a hydrogen bond with a perchlorate ion and the fifth water molecule.

A structure determination on the lanthanum complex of the same ligand was also performed, which gave rise to an identical structure except for the replacement of the samarium by the lanthanum atom.

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The Crystal and Molecular Structure of Ammonium Thorium Hexasulphate Dihydrate

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Various sulphato complexes of thorium have been prepared but the co-ordination number of thorium in such complexes has not been characterised. To establish the maximum co-ordination number of thorium we prepared $(NH_4)_8Th(SO_4)_6 \cdot 2H_2O$. It has been discussed and suggested by V. A. Golovnya and G. T. Boltova [1] that in the sulphate compounds of Ce(IV) and U(VI) the co-ordination number 8 is retained. In the lower sulphato complexes some of the water molecules cannot be removed easily; these water molecules are directly bonded to the central atom. The X-ray diffraction study of potassium thorium tetrasulphate tetrahydrate has shown that the coordination number of thorium is nine and a chain-like structure is observed. The structure is complex, and although the water molecules can be readily removed yet two water molecules are directly bonded to the thorium. All modes of bonding for sulphato groups are observed, that is, bidentate chelate, bidentate bridging, and monodentate.

E. L. Muetterties and C. M. Wright [2] suggested that hexasulphato thorium ion, $Th(SO_4)_6^{8-}$, isolated in the form of salts might be analogous to lanthanum case, since in $La_2(SO_4)_3 \cdot 9H_2O$ [3] the eicosahedron is established for the co-ordination of lanthanum ion. Twelve oxygen atoms are within 2.60–2.74 Å.

It was decided to undertake a three dimensional single crystal structure analysis to determine the nature of the thorium co-ordination.

Experimental

An irregular shaped crystal of 0.38 mm in diameter was mounted along the real *c* axis. Preliminary optical and X-ray examination indicated the crystals to be triclinic. The unit cell parameters, from the high angle precession data and Weissenberg data with Mo-K_α radiation were determined as:

Ammonium thorium hexasulphate dihydrate:

$N_8H_{32}Th/S_6O_{24} \cdot 2H_2O$
M = 988
Triclinic
a = 9.82 Å α = 57.95°
b = 9.76 Å β = 89.7°
c = 10.40 Å γ = 115.416°
U = 729.58 Å^3 Z = 1
μ(for MoK_α) = 63.74 cm^{-1}.

The space group $P\bar{1}$ has been used so far for refinement. Zirconium filtered Mo-K_α radiation was used to collect equi-inclination Weissenberg data for the layers [kh0–hk10] and precession data for the layers h0l and 0kl by the multiple film technique.

Structure Determination and Refinement

Using 4051 unique reflections as the criterion a three dimensional Patterson synthesis was computed and there was no big peak except the origin peak. Thorium was put at the origin and to start the temperature factor for thorium was put as 2. The parameters for thorium only along with the scalefactor were refined for four cycles by block-diagonal least square refinement, which reduced the discrepancy index to 0.21. Twenty-one atoms were then put successfully and all were refined isotropically and the R factor was 18.4%. The oxygen atoms of sulphato groups were much distorted from tetrahedral configuration. Throughout the analysis the structure factors for neutral thorium, sulphur, oxygen and nitrogen were used. The R factor was not going down than 18%, indicating that either the space group is not P1 or while calculating the absorption correction the crystal should not be assumed as a sphere, rather all the faces of the crystal should be measured correctly.

In conclusion, there are some prospects for refining this structure to a low R value.

Discussion

Although the structure is not finished completely, nevertheless, the salient features of the structure have been solved. The structure of sulphato complexes of thorium are suggested as isolated unit complexes, in which the sulphato groups are bonding to the central atom as unidentate or bidentate ligands and it was proposed that the maximum co-ordination number for thorium is retained as eight. On the other hand they may also be chain compounds in which some of the sulphato groups are acting as bridges. Bridging sulphates are present in $K_4(Th(SO_4)_4 \cdot 2H_2O) \cdot 2H_2O$ [4].

X-ray diffraction study of $(NH_4)_8Th(SO_4)_6 \cdot 2H_2O$ has confirmed that isolated unit structures are present and the sulphato groups have either the co-ordinating capacity of two or one. No bridging sulphates are present in the structure under discussion.

The thorium–oxygen distances vary over a wide range (2.32 to 2.69 Å). From the geometry of the interatomic distances it appears that thorium is ten co-ordinate. The co-ordination polyhedron is a distorted bicapped square antiprism. Bicapped square antiprism is observed in protactinium metal [5]. Out of the six sulphato groups four are bidentate, and two are mono-dentate. The oxygens of the water molecules are not taking part in the co-ordination. This proves that in hexa sulphato complexes all the molecules of water of crystallisation are removed easily.

As the structure has not yet been refined to a high degree of accuracy there is some uncertainty about the precise details of the thorium co-ordination polyhedron. As there are only 6 Th–S vectors in the Patterson the thorium and sulphur atoms must form a centrosymmetric arrangement. But the oxygens may show small differences from C_1 symmetry and thus cause the difficulties of refinement which were observed. The determination of the actual distortions from this arrangement may take much further study.

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Apparent Molal Volumes and the Hydration of the Lanthanide(III)–Ethylenediaminetetraacetate Complexes

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The ethylenediamine-tetraacetate (edta) complexes of the lanthanide(III) ions (Ln^{3+}) have been studied very thoroughly owing to their importance in the ion exchange separation and in the analytical chemistry of the lanthanides. In spite of the detailed studies, the structure of the $Lnedta^-$ complexes in solution – the number of the coordinated donor atoms of the ligand as well as the number of the water molecules coordinated in the inner sphere – is not clear-cut and the interpretation of the different indirect experimental data is disputed. As a consequence of the relatively high coordination number (CN) of the Ln^{3+} ions, the edta ligand does not occupy all the coordination sites. According to the X-ray studies of the solid complexes $KLnedta(H_2O)_x$ the number of water molecules found in the first coordination sphere is 3 for the lighter and 2 for the heavier elements while the CN decreases from 9 to 8 [1]. Similar conclusions were drawn from the trend of the stability constants of the Ln(edta)X (X = iminodiacetate or nitrilotriacetate) mixed ligand as well as the $Ln(edta)_2^{5-}$ complexes [2, 3]. The heat capacity changes for the formation of the Lnedta complexes have been explained by the same assumption [4]. In the case of the Euedta and Gdedta complexes hydration equilibria have been observed by electron spectroscopic [5, 6] and ^{17}O-NMR spectroscopic methods [7]. However from the study of the relaxation times of the H_2O protons in the presence of the Lnedta complexes it was concluded that the CN is 9 for the whole series and hydration isomers do not form [8].

Recently we have determined the apparent molal volumes (ϕ_v) of the KLnedta complexes. The apparent molal volumes obtained at infinite dilution