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 coordinating 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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A18

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

TABLE I. The ϕ_V and ϕ_V° Values of the KLnedta Complexes (cm^3/mol).

Ln	ϕ_V°	ϕ_V (0.04 *M*)	ϕ_V (0.09 *M*)
La	166.2	169.3	171.1
Pr	164.8	168.5	170.5
Nd	167.7	168.3	169.5
Sm	170.1	170.9	171.4
Eu	170.9	171.7	172.3
Gd	175.1	175.2	175.4
Dy	174.8	176.8	177.7
Er	170.8	171.0	171.5
Yb	170.5	171.1	171.5

(ϕ_V°) reflect the measure of the interaction between the ions and the solvent molecules [9]. For the KLnedta complexes the contribution of the K^+ ions to the measured apparent molal volumes is constant, thus the observed changes express the changes in the ϕ_V values of the $Lnedta^-$ ions.

The complexes KLnedta·$(H_2O)_x$ have been prepared by slow evaporation of the solutions containing equivalent amounts of $LnCl_3$ and K_4edta. The compounds obtained have been recrystallized from water. The concentration of the stock solutions KLnedta was determined gravimetrically precipitating the Ln-oxalates in acidic solution and weighing as oxides after ignition. The apparent molal volumes have been determined at 25 ± 0.01 °C by density measurement using a Hereaus/Paar DMA 02C instrument. The dilutions of the stock solutions have been carried out by weighing.

The apparent molal volumes of the KLnedta complexes show a linear dependency on the $\sqrt{c}$ values (c is the molar concentration) that is the Masson equation can be applied:

$$\phi_V = \phi_V^\circ + S_V\sqrt{c}$$

where the constant S_V is different for the various lanthanides. The ϕ_V° values are not exactly equal to the partial volumes of the complexes since the measurements have been carried out at $c > 0.01$ *M*. For the calculation of the ϕ_V° and S_V values the least squares method was applied. The ϕ_V° values and the ϕ_V values calculated at 0.04 and 0.09 *M* concentrations are summarized in Table I. The average reproducibility of the ϕ_V values is ±0.5 cm^3/mol.

The ϕ_V values of the KLnedta complexes alter with increasing atomic number but their change is not monotonic. The ϕ_V value of an ion is made up of several contributions, such as the intrinsic volume of the ion, the decrease of the volume of the water molecules coordinated in the inner sphere (due to the high electrostatic field of the ion) as well as the change of the structure of the solvent. It can be assumed that the intrinsic volume of the Lnedta complexes slightly decreases with decreasing ionic sizes and in the non-monotonic change of the ϕ_V values the other factors play the predominant role. The trend in the ϕ_V values can be interpreted assuming a decrease in the CN between Nd and Tb from 9 to 8 with the loss of a H_2O molecule from the inner sphere. In the complexes of the first elements (La–Ce) as a result of the fast break and re-formation of the Ln–O bonds there is probably nearly one free carboxylate group in average, which results in a stronger hydration of these complexes and the coordination of 3 or 4 water molecules in the inner sphere. With the decrease of the ionic sizes the average number of the free carboxylates gradually drops and between Tb and Lu practically all the functional groups of the edta are coordinated. This interpretation can be supported by other experimental data.

TABLE II. Protonation Constants of the Lnedta Complexes (I = 1 *M* KCl, t = 25 °C).

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho
100	54	42	35	31	27	20	8	5	3

The gradual decrease of the average number of the free carboxylates with growing atomic number is also reflected in the values of the protonation constants of the Lnedta complexes, which significantly decrease with decreasing ionic sizes (Table II). The protonation constant of the $Laedta^-$ is practically the same as that of the inert $Cr(H_2O)edta^-$ (k = 89 [10]) which has a free carboxylate group. However the protonation constants of the complexes $Eredta^-$–$Luedta^-$ are too low to determine by pH-metry.

The protonation constants have been determined by pH-potentiometry in the presence of Ln^{3+} ion excess to hinder the dissociation of the complexes. The possible formation of the dinuclear complexes was taken into account in the calculations.

The results of the ^1H-NMR studies of the Lnedta–iminodiacetate and –methyl-iminodiacetate mixed ligand complexes have also shown that in the inner sphere of the Laedta there is enough free site for the coordination of the tridentate second ligand. However, by the formation of the respective Y- and Lu-mixed ligand complexes the coordinated edta and iminodiacetate or methyl-iminodiacetate ligands significantly repel each other.

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A19

The Relative Acidity of Th(IV) and U(IV) towards Chloride in Acetone

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A measure of Lewis acidity of a metal ion towards an anion like chloride, for instance, could be given in terms of the chloride ion concentrations at which the various metal–chloride complexes dominate. Since some analogies and differences between U(IV), Th(IV) and Ce(IV) have been studied in our laboratories, it was of interest to see whether such a strategy could be used in acetone to confirm the notion that their relative Lewis acidity towards chloride in acetone follows the order Ce(IV) > U(IV) > Th(IV).

In order to see whether different complexes can be distinguished, the uranium system was studied spectrophotometrically by titrating UCl_4 with But_4NCl. The results could not be satisfactorily explained in terms of the species UCl_4, UCl_5^- and UCl_6^{2-} unless UCl_3^+ is considered as well. The corresponding stepwise formation constants and distribution of the species are given in Fig. 1.

From this it follows that when UCl_4 is dissolved in acetone the $[Cl^-]$ is buffered at about 10^{-8} mol dm^{-3} which is small compared to the concentration of the other species. ($\pm 0.5 \times 10^{-3}$ mol dm^{-3}). Similarly the species UCl_6^{2-} can be ignored provided the $[Cl^-]$ is not increased beyond say 10^{-6} mol dm^{-3}. This justifies the description of the system in terms of three species which are in equilibrium as depicted below by the autoionization-equilibrium and constant.

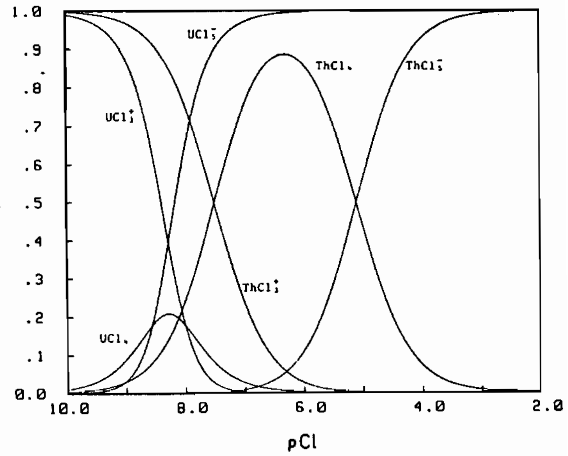

Fig. 1. Distribution diagram for the UCl_4–Chloride–System in acetone.

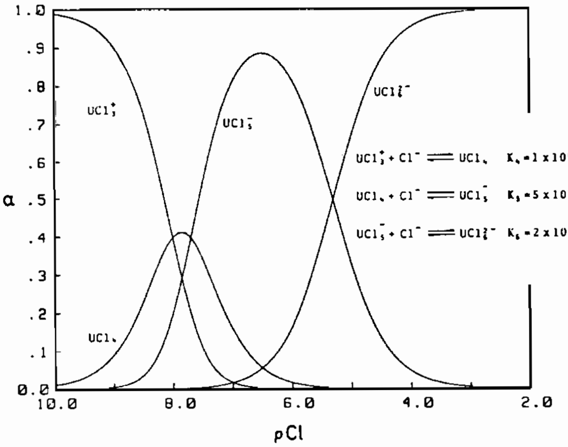

Fig. 2. Distribution diagram for the combined $ThCl_4$ and UCl_4 system in acetone.

Extent of autoionization:

$$2UCl_4 \rightleftharpoons UCl_3^+ + UCl_5^-$$

$$K_n = \frac{[UCl^+][UCl_5^-]}{[UCl_4]^2} = \frac{K_5}{K_4} = 0.5$$

Location of system on pCl Scale:

$$[Cl^-] = \frac{1}{\sqrt{K_5K_4}} = 1.4 \times 10^{-8}$$

If the same information could be got from the corresponding thorium system, it would similarly enable one to see where the system lies on the $[Cl^-]$-scale. From this one could then give a measure for the difference in Lewis acidity between U(IV) and

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