The results obtained are given in Table II. From the ΔH° and ΔS° values it can be seen that the observed stability is entropic in origin.

1 Zhou Jingzhong and Wang Dexi, *J. Nucl. Radiochem., Beijing, 4,* 174 (1982).
2 R. M. Izatt *et al., J. Am. Chem. Soc., 99,* 8344 (1977).

A15

Solution and Solid State Structures of Lanthanide Complexes with Polyaza Polyacetic Macrocyclic Ligands: A Comparison of NMR and X-Ray Studies

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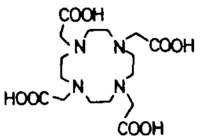
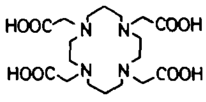
Lanthanide complexes are known to form exceedingly labile species. Two rare exceptions to this rule are reported in the present paper.



DOTA



TETA

The ligand DOTA was found [1, 2] to form rigid lanthanide complexes in solution: the configuration of the ethylenediamine groups undergoes a very slow inversion as shown by NMR. Furthermore, the activation energy for this process is unusually large. An analysis of the solid state structure of $Na^+(Eu\text{-}DOTA\cdot H_2O)^- 4H_2O$ has now been carried out, The metal ions lie between two planes made up respectively by the four nitrogens of the macrocycle and by the four carboxylate groups. The metal ion is also coordinated to one water molecule and its coordination polyhedron is a slightly distorted capped square antiprism. This structure exhibits an axial symmetry (C_4 axis) and the induced paramagnetic shifts can thus be reliably computed by the simple dipolar equation $\Delta\nu = 3\cos^2\theta - 1/r^3$. The calculated dipolar shifts of $(YbDOTA)^-$ are in excellent agreement with the experimental shifts, thus indicating that the DOTA complexes are highly symmetrical and have exactly the same structure in the solid and in solution.

The conformational properties of the paramagnetic lanthanide TETA complexes are no less surprising. Adding two $-CH_2-$ units to the DOTA structure brings about drastic changes in both the conformation and the structure of the macrocyclic complexes. As shown by a crystallographic investigation of $Na^+(TbTETA)^-\cdot 5H_2O(NaCl)_{1/2}$, the metal ion lies in a distorted dodecahedral environment of nitrogen atoms and carboxylate groups. This structure has an approximate C_2 axis and the induced paramagnetic shifts can no longer be calculated by the simpler form of the dipolar equation but have to be computed by the complete two-term dipolar equation. In this case, the calculated shifts are once again in excellent agreement with the experimental shifts. Moreover, the TETA complexes exhibit a quite unusual conformational behavior: the two orthogonal trapezoids in the dodecahedron are slowly moving up and down and are exchanging their position. This leads to profound alterations of the NMR spectra with temperature except for the two protons of the two propylenediamine carbon atoms in β positions. These protons lie on both sides of a near-plane of symmetry, the values of their dipolar geometric factors are not altered by the conformational changes and accordingly, their NMR peaks are not involved in exchange processes.

The DOTA and TETA complexes thus exhibit several intriguing features which have not been observed so far for other lanthanide complexes.

1 J. F. Desreux, *Inorg. Chem., 19,* 1319 (1980).
2 C. C. Bryden, C. N. Reilley and J. F. Desreux, *Anal. Chem., 54,* 610 (1982).

A16

Structure of the Pentahydrate of the Samarium(III) Perchlorate Complex with the Crown Polyether 1,4,7,10,13-Pentaoxacyclopentadecane, $[Sm(C_{10}H_{20}O_5)_2(H_2O)_4]^{3+}\cdot 3ClO_4^-\cdot H_2O$

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The structure of samarium(III) perchlorate complex with the title ligand has been determined. This compound crystallizes in space group $P2_1/c$, a = 16.150(5), b = 14.898(5), c = 21.055(5) Å, β = 129.37(3)°, $Z = 4$, $V = 3916.27$ Å^3, $D_c = 1.66$, $D_m = 1.62$ g cm^{-3} (by floatation), $\mu = 18.30$ cm^{-1} for MoKα radiation. The structure was mainly solved by heavy atom and Fourier method, and refined by full-matrix least squares techniques to a reliability index, R(F) of 0.061, based on 3540 reflections. The sama-

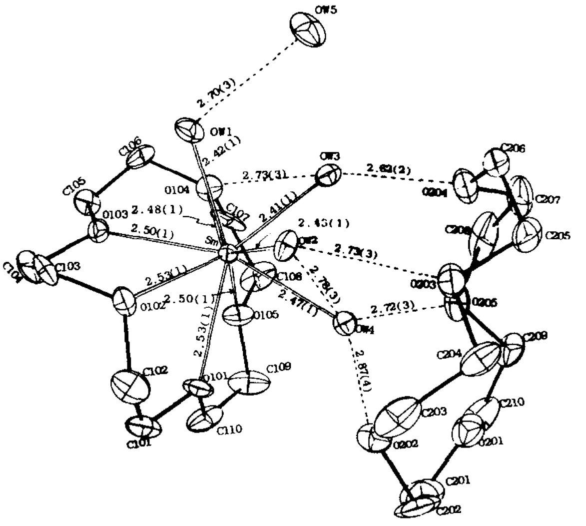

Fig. 1. ORTEP drawing of the molecule with numbering scheme. The coordination bonds are indicated by open lines, interatomic bonds by heavy lines, hydrogen bonds by dashed lines. OWs are oxygen of water molecules.

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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A17

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 scale-factor were refined for four cycles by block-diagonal