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.

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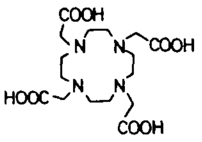
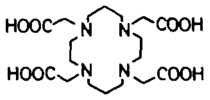
Lanthanide complexes are known to form exceedingly labile species. Two rare exceptions to this rule are reported in the present paper.



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 $Na^+(EuDOTA \cdot H_2O)^- 4H_2O$ 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.

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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), μ = 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-