ported before for the complexes with the N_4 ligands (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy. The $[M_2(N_4)_2]^{2+}$ dications have a twofold axial symmetry. The two metal 1B centers have pseudotetrahedral geometries with similar configurations (ΔΔ or ΛΛ). The ligands, acting as bis-bidentates, contain two inequivalent pyridine–imine moieties, of which the protons may be denoted H(A) and H(B).

In solutions of the complexes having the 1,2-ethanediyl bridges H(A)–H(B) exchange is observed (on the basis of ^{1}H and ^{15}N NMR spectra), a process which is caused by a conformational movement between two identical structures. Furthermore, only for the silver(I) complexes could it be deduced (from loss of $^3J(^1H-^{107,109}Ag)$) that these complexes are prone to intermolecular Ag^+ exchange (above 241 K for 6-R = H and 324 K for 6-R = Me).

When chiral C atoms are introduced in the 1,2-alkanediyl bridges (N_4 = (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$Cy), the conformational movement, now between diastereomeric structures, does not take place, because of a slightly higher stability of one of the isomers. Only in the silver(I) complex with 6-R = H could the occurrence of Ag^+ exchange be observed. This process induced a configurational (ΔΔ ⇄ ΛΛ) interconversion, which was observed as H(A)–H(B) exchange. The copper(I) complexes (6-R = H, Me) and the silver(I) complex (6-R = Me) are kinetically much more stable. From dynamic ^{1}H NMR experiments mechanisms are proposed for the intermolecular Ag^+ exchange and the induced H(A)–H(B) exchange in the silver(I) complex with 6-R = H. It appeared that in the pure complex these processes follow both an associative and a dissociative path, while in samples of this complex and added $[Ag(O_3SCF_3)]$ the associative mechanism is dominating.

The bulkiness of the 6-R substituents and of the 1,2-alkanediyl bridges has a large influence, by a shielding effect, on the rate of intermolecular Ag^+ exchange and therefore on the rate of the configurational, ΔΔ–ΛΛ, exchange process. These rates are much lower when 6-R = Me instead of 6-R = H and when the bridging groups are (*R*,*S*)-1,2-cyclohexanediyl instead of 1,2-ethanediyl.

Intermolecular Ag^+ exchange observed in the silver(I) complexes having the ethanediyl (R = H or Me) or (*R*,*S*)-1,2-cyclohexanediyl (R = H) groups and added $[Ag(O_3SCF_3)]$ is much faster than intermolecular ligand exchange between the $[Ag_2(N_4)_2]^{2+}$ dications and free added ligand.

This study gives a view of all inter- and intramolecular processes in these binuclear $[M_2(N_4)_2]^{2+}$ dications and shows that these depend on the metal 1B center (M = Ag(I), Cu(I)) and the various substituents in the N_4 ligand system. These results may have importance in understanding the occurrence of such processes not only in coordination complexes but also in biological systems that contain metal ions in the active sites.

Acknowledgment. The FD mass spectral data were kindly collected by Prof. N. M. M. Nibbering and his co-workers. J. M. Ernsting is thanked for recording the 250-MHz ^{1}H NMR spectra and Dr. A. Pagelot for recording the 400-MHz ^{1}H NMR spectra.

Registry No. 2a, 76317-71-0; **2b**, 76317-73-2; **3a**, 76317-75-4; **3b**, 90605-91-7; **5a**, 92346-69-5; **5b**, 92346-71-9; **6a**, 92346-73-1; **6b**, 92365-89-4.

Supplementary Material Available: Tables of IR data (Table SI) and FD mass spectral data (Table SII) of $[M_2(\mathbf{4})_2](O_3SCF_3)_2$ (M = Ag(I) or Cu(I)) (2 pages). Ordering information is given on any current masthead page.

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Commission of the European Communities, European Institute for Transuranium Elements, D-7500 Karlsruhe, West Germany,
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Structural Characterization of a Terbium(III) Complex with 1,4,8,11-Tetraazacyclotetradecane-1,4,8,11-tetraacetic Acid. Lanthanide Ions and the Conformation of the 14-Membered Macrocycles

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The molecular and crystal structure of $Na^+[TbTETA]^-\cdot 6H_2O\cdot {}^1/_2NaCl$ (TETA = 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid) has been determined from three-dimensional X-ray intensity data. The space group is $P2/c$, and the lattice parameters are a = 17.980 (3) Å, b = 9.081 (2) Å, c = 17.713 (3) Å, β = 106.00 (1)°, and d = 1.775 g cm^{-3} for Z = 4. The structure was solved by direct methods. Full-matrix least-squares refinement with all non-hydrogen atoms treated anisotropically gave an agreement factor R of 0.036 for 4111 unique reflections. The Tb^{3+} ion is eight-coordinated, being linked to the four nitrogen atoms and the four carboxylic oxygen atoms of the ligand. The coordination polyhedron of the terbium ion is a strongly distorted dodecahedron, but although no symmetry is imposed by the space group, the TETA ligand approximates the C_2 symmetry fairly well. The conformation of the 14-membered macrocyclic ring is compared with the various conformations adopted by other macrocycles with the same cavity size. The TETA ligand exhibits a biangular {77} structure, which is the most suited for the complexation of a 4f metal ion located out of the mean plane of the macrocyclic ring. In the crystal, the $[TbTETA]^-$ complex units are associated through sodium ions and water molecules into layers that alternate with aqueous layers containing the chloride ions.

Introduction

It has long been recognized that lanthanide ions form essentially electrostatic, nondirectional coordination bonds. The lanthanide complexes are thus highly labile and exhibit a variety of structures in solution. The resulting intramolecular conformational processes are usually too fast to be observed by NMR.[4] One obvious way to find exceptions to this general rule involves the synthesis of complexes with rigid and sterically demanding ligands. The macrocyclic 1,4,7,10-tetraazacyclo-

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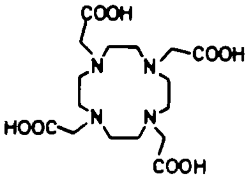
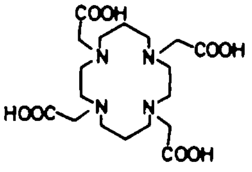
tetradecane-1,4,7,10-tetraacetic acid, DOTA, proved to be an



DOTA



TETA

excellent choice along this line of reasoning. In the solid, EuDOTA keeps the C_4 symmetry of the free ligand,[5] and its structure is identical with the solution conformation deduced from an NMR investigation.[6] Even the acetate groups are rigid in solution although lanthanide–oxygen bonds are usually short-lived on the NMR time scale.[7] Maybe still more surprising is the fact that the hydration water molecule of EuDOTA is located near the main symmetry axis both in the crystal[5] and in solution.[8] Furthermore, the conformational process taking place in the DOTA ring is readily observed by NMR at room temperature.[6] Very few other examples of stereochemical rigidity in lanthanide complexes have been reported so far.[9,10] We were thus prompted to investigate the crystal structure of the Tb(III) complex of another macrocycle with carboxylic pendant arms: 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid, TETA. Although DOTA and TETA have similar structures, it will be shown that they wrap themselves around lanthanide ions in a different manner.

Another impetus behind the present study is correlating the conformation of different macrocyclic compounds that exhibit internal cavities of the same size. Cycloalkanes and their polyoxa analogues have been popular objects for conformational analyses and strain energy calculations.[11-13] Moreover, the crystal structures of several polyethers have been reported recently.[14-16] A wealth of data is thus available for answering the question of whether we could predict the structure of lanthanide polyaza polyacetic acid complexes by simply relying on data already obtained for other macrocyclic compounds. In other words, do the lanthanide ions have any influence on the conformation of macrocyclic ligands such as DOTA or TETA?

Solving this problem was straightforward in the case of DOTA[6] because cyclododecane and 12-crown-4 (in its complexes with alkali ions) exhibit a "square" {3333} conformation.[11,14] By calculation, it was also found that this conformation exhibits the lowest strain energy.[11] These {3333} structures contain four equivalent coplanar methylene groups or ether oxygens that point to one side of the ring. Binding sites are thus readily available for coordination, and it was anticipated that the lanthanide DOTA complexes would adopt a square-antiprismatic geometry.[6] A similar attempt to propose a structural model for a TETA complex is thwarted by the higher mobility of the 14-membered macrocycles. Cyclotetradecane crystallizes in the quadrangular {3434} conformation.[15] On the other hand, 1,4,8,11-tetraoxacyclotetradecane when dissolved in $CHCl_2F$ has been reported to be involved in an equilibrium between two forms, a {3434} and a {77} conformation, the latter also being the solid-state structure of this crown ether.[16] Force field calculations[13] have shown that the strain enthalpies of these two conformations are not very different. It is against this background that an analysis of the crystal structure of a lanthanide TETA complex appeared warranted.

Table I. Crystallographic Data and Data Collection Procedures

formula	$NaTb[C_{18}N_4O_8]\cdot 6H_2O\cdot 0.5NaCl$
mol wt	719.45
space group	$P2/c$
a, Å	17.980 (3)
b, Å	9.081 (2)
c, Å	17.713 (3)
β, deg	106.00 (1)
V, Å^3	2780 (2)
Z	4
d(calcd), g/cm^3	1.775
μ(Mo K$\bar{\alpha}$), cm^{-1}	27.493
cryst dimen, mm	0.2 × 0.2 × 0.4
temp, °C	20
diffractometer	Enraf-Nonius CAD4
radiation (λ, Å)	graphite monochromated Mo K$\bar{\alpha}$ (0.710 73)
scan mode	$\theta/2\theta$
collecn range	$+h,+k,\pm l$ ($2 < 2\theta < 50°$)
no. of intens measmnts	4843
no. of indep obsd reflecns	4356
no. of data used in refinement $[I > 3\sigma(I)]$	4114
no. of variables	363
largest Δ/σ	0.01
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.036
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2]^{1/2}$	0.060
esd $= [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)]^{1/2}$	2.295

Experimental Section

Colorless prismatic crystals of the title compound, $NaTbTETA\cdot 6H_2O\cdot {}^1/_2NaCl$, suitable for X-ray analysis, were obtained by letting ethanol slowly diffuse into a concentrated aqueous solution of the terbium complex at pH 6.8.

Investigation on a selected crystal was made with an Enraf-Nonius CAD-4 X-ray diffractometer. Unit cell dimensions were obtained by least-squares analysis of setting angles of 25 diffraction maxima. A systematic search of a limited hemisphere of reciprocal space revealed systematic absences consistent with space groups Pc and $P2/c$, but the space group Pc was considered as doubtful since Z was likely to be equal to 4. Intensity data were measured with an aperture of $(0.80 + 0.35 \tan \theta)°$ and a maximum scan time of 60 s. Two reflections monitored periodically showed no crystal decomposition. Intensities were corrected for Lorentz–polarization effects. Absorption corrections were applied by an empirical method based on a set of scans of reflections having values near 90°.[17] The transmission factors ranged from 92.0 to 100%. The structure was solved by direct methods using the computer program MULTAN 78.[18] The distribution of normalized structure factors was clearly centric, and hence space group $P2/c$ was definitively selected for structure solution and refinement. The E-map calculated with the set of phases presenting the highest combined figure of merit given by MULTAN 78 revealed the position of the terbium atom. Six subsequent difference Fourier maps, in alternance with isotropic full-matrix least-squares refinements (minimizing $\sum w\ [|F_o| - |F_c|]^2$), were necessary to locate all other

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Table II. Atomic Positional and Equivalent Isotropic Thermal Parameters with Standard Deviations in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
Tb	0.30012 (1)	0.20268 (2)	0.55967 (1)	1.693 (5)
N(1)	0.1838 (2)	0.1128 (5)	0.4488 (2)	2.51 (9)
N(4)	0.1993 (2)	0.0848 (5)	0.6226 (2)	2.35 (9)
N(8)	0.2586 (2)	0.4459 (5)	0.6134 (3)	2.40 (9)
N(11)	0.3023 (2)	0.4181 (5)	0.4619 (2)	2.31 (9)
C(2)	0.1197 (3)	0.0648 (7)	0.4833 (3)	3.1 (1)
C(3)	0.1512 (3)	−0.0135 (6)	0.5598 (3)	2.9 (1)
C(5)	0.1449 (3)	0.1755 (7)	0.6546 (4)	3.0 (1)
C(6)	0.1786 (4)	0.3189 (7)	0.6944 (4)	3.4 (1)
C(7)	0.1859 (3)	0.4426 (7)	0.6367 (4)	3.4 (1)
C(9)	0.2486 (3)	0.5650 (6)	0.5522 (3)	3.2 (1)
C(10)	0.3103 (3)	0.5576 (6)	0.5092 (3)	3.1 (1)
C(12)	0.2385 (3)	0.4410 (7)	0.3868 (3)	3.2 (1)
C(13)	0.2062 (4)	0.3001 (7)	0.3479 (4)	3.3 (1)
C(14)	0.1493 (3)	0.2251 (7)	0.3868 (4)	3.3 (1)
C(1)	0.2099 (3)	−0.0190 (7)	0.4129 (4)	3.4 (1)
C(1′)	0.2965 (3)	−0.0186 (7)	0.4189 (3)	3.1 (1)
C(4)	0.2465 (3)	−0.0080 (6)	0.6876 (3)	2.9 (1)
C(4′)	0.3182 (3)	−0.0713 (6)	0.6704 (3)	3.0 (1)
C(8)	0.3232 (3)	0.4898 (6)	0.6819 (3)	2.9 (1)
C(8′)	0.3652 (3)	0.3564 (7)	0.7281 (3)	2.6 (1)
C(11)	0.3755 (3)	0.3943 (7)	0.4404 (3)	3.0 (1)
C(11′)	0.4392 (3)	0.3293 (6)	0.5067 (3)	2.5 (1)
O(1′)	0.3208 (3)	−0.1176 (5)	0.3835 (3)	4.5 (1)
O(1″)	0.3371 (2)	0.0796 (4)	0.4609 (2)	2.84 (8)
O(4′)	0.3593 (3)	−0.1548 (5)	0.7195 (3)	4.3 (1)
O(4″)	0.3331 (2)	−0.0319 (4)	0.6063 (2)	2.78 (8)
O(8′)	0.4072 (3)	0.3787 (5)	0.7955 (2)	3.7 (1)
O(8″)	0.3576 (2)	0.2343 (4)	0.6936 (2)	2.37 (7)
O(11′)	0.5041 (2)	0.3141 (5)	0.4965 (3)	3.28 (9)
O(11″)	0.4227 (2)	0.2902 (4)	0.5693 (2)	2.41 (8)
Na(1)	0.4447 (2)	0.1757 (3)	0.8776 (2)	4.31 (6)
Na(2)	0.5000	0.1794 (5)	0.2500	7.6 (2)
Cl	0.0000	0.9776 (3)	0.2500	4.68 (6)
O(w1)	0.5000	0.9153 (8)	0.2500	5.6 (2)
O(w2)	0.5136 (5)	0.0527 (8)	0.4088 (6)	11.8 (3)
O(w3)	0.4928 (3)	0.3771 (5)	0.1600 (3)	4.2 (1)
O(w4)	0.9756 (3)	0.6574 (5)	−0.0032 (2)	3.7 (1)
O(w5)	0.0613 (3)	0.2578 (7)	0.1680 (3)	5.3 (1)
O(w6)	0.0000	0.4758 (8)	0.2500	5.8 (2)
O(w7)	0.0682 (4)	0.6988 (6)	0.3614 (5)	7.0 (2)

[a] $B_{eq} = {}^1/_3(\text{trace}\,\widetilde{B})$.

non-hydrogen atoms. In the last cycles of refinement (with weights $w = 1/\sigma(F_o)^2$ and $\sigma(F_o^2) = [\sigma(I)^2 + (0.05I)^2]^{1/2}/Lp$), all non-hydrogen atoms were treated anisotropically. A secondary extinction coefficient was refined to a value of $g = 9.3 \times 10^{-8}$ (with $F_c = F_c/[1 + g(F_c)^2Lp]$). The scattering factors and anomalous dispersion corrections were taken from ref 19. The contributions of the scattering amplitudes of all non-water hydrogen atoms, in their expected positions, were included in a final structure factor calculation with an assigned isotropic thermal parameter of 5.00 Å. The maximum and minimum heights in a final Fourier synthesis were 0.7 and −0.5 e Å^{-3}, respectively. All calculations were performed on a PDP 11/34 using the Enraf-Nonius structure determination package.[20] Relevant crystal and experimental data are provided in Table I. The atomic positional parameters from the final least-squares cycle are listed in Table II. Structure factors anisotropic thermal parameters, and hydrogen coordinates are available as supplementary material.

Results and Discussion

The Coordination Polyhedron. Figure 1 illustrates the molecular geometry and the atom-labeling scheme for the non-hydrogen atoms of TbTETA. The thermal motions of the atoms are depicted as 50% probability ellipsoids. As expected, the terbium ion has the smallest vibrational amplitudes (maximum rms value 0.152 Å) and is fairly isotropic. Moreover, the ring nitrogens exhibit less anisotropy than the ring carbons. Significant differences in thermal amplitudes are also observed between carboxyl oxygens, depending on whether they are bonded to the terbium ion or not.

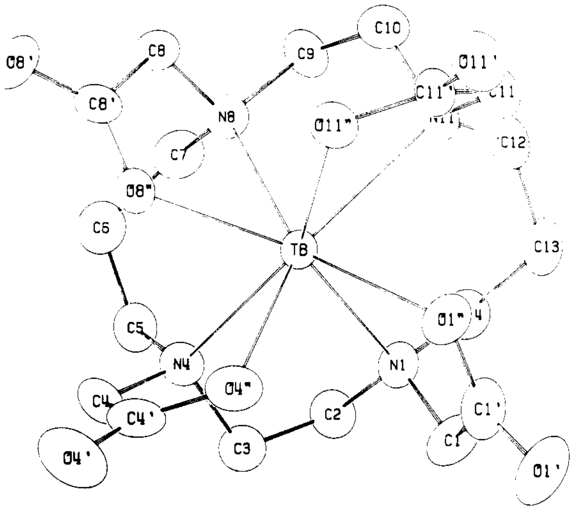

Figure 1. Perspective view of the TbTETA complex.

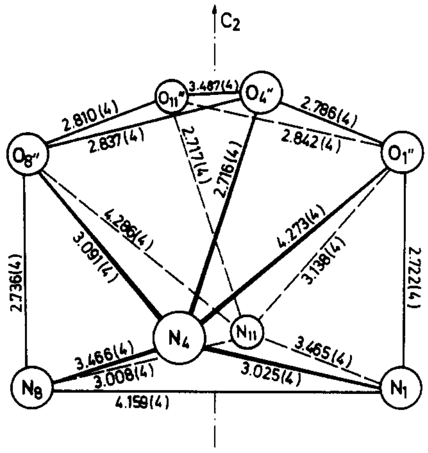

Figure 2. Coordination polyhedron about the terbium ion.

Table III. Selected Interatomic Distances (Å) and Angles (deg) Involving Terbium and Atoms from the Coordination Sphere

(a) Bond Lengths

Tb–N(1)	2.575 (3)	Tb–O(1″)	2.322 (2)
Tb–N(4)	2.606 (3)	Tb–O(4″)	2.302 (3)
Tb–N(8)	2.595 (3)	Tb–O(8″)	2.330 (3)
Tb–N(11)	2.620 (3)	Tb–O(11″)	2.304 (3)

(b) Bond Angles

N(1)–Tb–N(4)	71.4 (1)	N(8)–Tb–O(1″)	149.0 (1)
N(1)–Tb–N(8)	107.1 (1)	N(8)–Tb–O(4″)	136.67 (9)
N(1)–Tb–N(11)	83.65 (9)	N(8)–Tb–O(8″)	67.25 (9)
N(4)–Tb–N(8)	83.6 (1)	N(8)–Tb–O(11″)	92.61 (9)
N(4)–Tb–N(11)	136.74 (9)	N(11)–Tb–O(1″)	78.58 (9)
N(8)–Tb–N(11)	70.4 (1)	N(11)–Tb–O(4″)	151.50 (9)
N(1)–Tb–O(1″)	67.29 (9)	N(11)–Tb–O(8″)	119.86 (9)
N(1)–Tb–O(4″)	93.2 (1)	N(11)–Tb–O(11″)	66.63 (9)
N(1)–Tb–O(8″)	148.7 (1)	O(1″)–Tb–O(4″)	74.1 (1)
N(1)–Tb–O(11″)	136.4 (1)	O(1″)–Tb–O(8″)	133.46 (9)
N(4)–Tb–O(1″)	120.13 (9)	O(1″)–Tb–O(11″)	75.82 (9)
N(4)–Tb–O(4″)	66.86 (9)	O(4″)–Tb–O(8″)	75.56 (9)
N(4)–Tb–O(8″)	77.32 (9)	O(4″)–Tb–O(11″)	98.42 (9)
N(4)–Tb–O(11″)	150.94 (9)	O(8″)–Tb–O(11″)	74.68 (9)

The terbium ion is completely encapsulated by the macrocycle and is linked to the four nitrogen atoms and the four carboxylic groups of the ligand. In this respect, the structure is similar to the molecular geometry already reported for EuDOTA.[5] However, no metal-coordinated water molecule is found in the case of TbTETA, and, furthermore, the co-

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(19) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England 1974; Vol. IV, Table 2.2B.

(20) "Enraf-Nonius Structure Determination Package", Version 18; Enraf-Nonius: Delft, 1981.

ordination polyhedron is no longer a square antiprism but may be best described in terms of a severely distorted dodecahedron with a C_2 symmetry axis passing through the midpoints of the nitrogen atoms and of the coordinated oxygen atoms. A schematic view of the TbTETA polyhedron together with the interatomic distances is shown in Figure 2. Selected distances and angles in the coordination polyhedron are listed in Table III.

It is well-known,[21] that the two most common geometries of the eight-coordinate complexes are the square antiprism and the dodecahedron. Folding by equal amounts the two square faces of a square antiprism leads to a dodecahedron with a fourfold rotatory inverter axis perpendicular to the D_4 axis of the original square polyhedron. A D_2 symmetry is maintained during this process. As suggested by Porai-Koshits and Aslanov,[22] the shape of the eight-coordinate polyhedra can best be assessed by computing four angles δ_n between pairs of adjacent faces. For the ideal dodecahedron, all angles δ_n are equal (29.5°) while in the case of a square antiprism, two equivalent small ($\delta_{1,2} = 0°$) and two equivalent large angles ($\delta_{3,4} = 52.4°$) are found. A score of monomeric complexes adopt geometries that are intermediate between the two idealized forms:[21] they can be classified according to the values of their δ_n angles, $\delta_{1,2}$ increasing regularly from 0 to 29.5° and $\delta_{3,4}$ decreasing simultaneously from 52.4 to 29.5°. The δ_n angles of the TbTETA compound are 28.30, 28.60, 48.56, and 49.14°, respectively. This compound is not on the D_2 pathway between the square antiprism and the dodecahedron since it exhibits δ_n angles that are not intermediate between the ideal values. So far, such highly distorted structures have been found only in the case of polymeric complexes.[21] For instance, the δ_n values of polymeric erbium bis(isonicotinate) dihydrate[23] are respectively $\delta_{1,2} = 25.2°$ and $\delta_{3,4} = 49.8°$. In these polymeric structures, the ligands are bound to several metal ions, a feature that might bring about severe distortion of the coordination polyhedra. TbTETA appears to be unique in this respect among the monomeric complexes;[21] its unusual structure is tentatively ascribed to the steric requirements of the ligand.

Another set of angles, ϕ_1 and ϕ_2, have been used in comparisions between an experimentally determined structure and one of the idealized eight-coordinate polyhedra: these angles represent the twist that distortion brings about in the two trapezoidal planes of a dodecahedron.[21,22] They are of course equal to zero for a perfect dodecahedron, and they reach a value of 24.5° in the case of a square antiprism. The values of ϕ_1 and ϕ_2 for the two trapezoids of TbTETA that are defined by the atoms N(8)N(1)O(8″)O(1″) and N(4)N(11)O(4″)O(11″) are 25.44 and 32.79°, respectively, a further indication of the strongly distorted nature of this complex.

The least-squares equations of the mean planes of the nitrogen atoms and of the carboxyl oxygens are $0.8385x - 0.4437y + 0.3163z - 3.1808 = 0$ and $0.8365x - 0.4448y + 0.3200z - 5.6697 = 0$, respectively. As expected for a dodecahedron, two nitrogen atoms (N(4) and N(11)) are displaced by 0.286 (5) Å from their mean plane toward the metal ion and the two other nitrogen atoms are displaced in the opposite direction by the same amount. Likewise, atoms O(8″) and O(1″) are located 0.293 (4) Å below the mean oxygen plane while atoms O(4″) and O(11″) are displaced by the same amount above this plane. The Tb(III) ion is found 1.249 (1) Å above the mean plane of the nitrogen atoms and 1.212 (1) Å below the mean plane of the oxygen atoms. Moreover, as shown in Table III, the Tb–N distances range from 2.575 (3) to 2.620 (3) Å and the Tb–O distances range from 2.302 (3) to 2.330 (3) Å. The maximum deviations from the mean Tb–N (2.599 (3) Å) and Tb–O (2.315 (3) Å) interatomic distances are 0.024 (3) and 0.015 (3) Å, respectively, i.e. much smaller than reported for EuDOTA.[5] However, it is noteworthy that the exact values of the mean Tb–N and Tb–O distances could have been computed simply by using the corresponding distances reported for EuDOTA[5] and the effective ionic radii listed by Shannon,[24] the difference in coordination number being taken into account. Thus, the larger size of the internal cavity of the macrocycle TETA brings about no significant changes in the metal-donor atom distances. However, the TETA cycle is more flexible and can wrap itself around the terbium ion in a more effective way. Accordingly, the hydration numbers of EuDOTA and TbTETA are different. The DOTA complexes were found to be monohydrated both in the crystal[5] and in solution;[8,25] their square-antiprismatic structures leave enough room for a water molecule on the C_4 axis. On the contrary, in the dodecahedral configuration of TbTETA, the oxygen atoms are in close contact (from 2.786 (4) to 2.842 (4) Å); they are not separated by more than two van der Waals radii and there is no space left for a water molecule. The same behavior can be expected in solution since a water coordination number of 0.6 was deduced from Eu(III) luminescence lifetime measurements by Bryden and Reilley.[25]

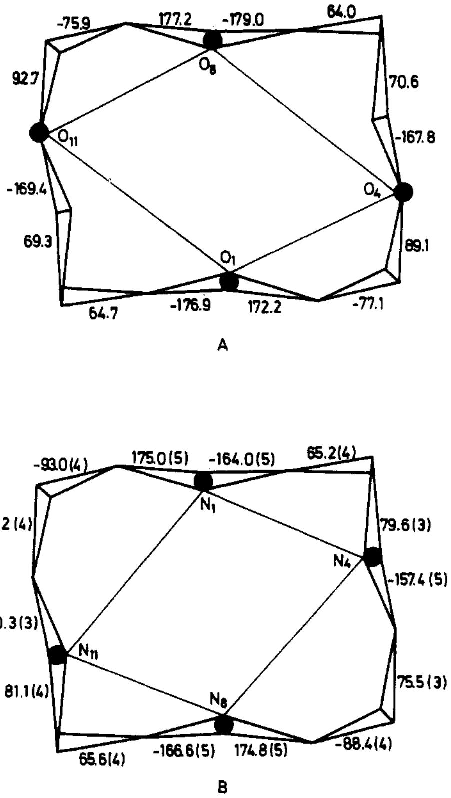

Figure 3. (A) Conformation of 1,4,8,11-tetraoxacyclotetradecane with corresponding torsion angles (taken from ref 12). (B) Conformation of the TETA ring with corresponding torsion angles. Standard deviations are given in parentheses.

Conformation of the Ligand. Bond angles and distances within the TETA ligand (see Table IV) are in agreement with values found for noncyclic polyaza polyacetic acid complexes except for some C–C bonds that are shorter than expected. This phenomenon has been observed for most macrocyclic ligands and has received no satisfactory explanation so far.[26]

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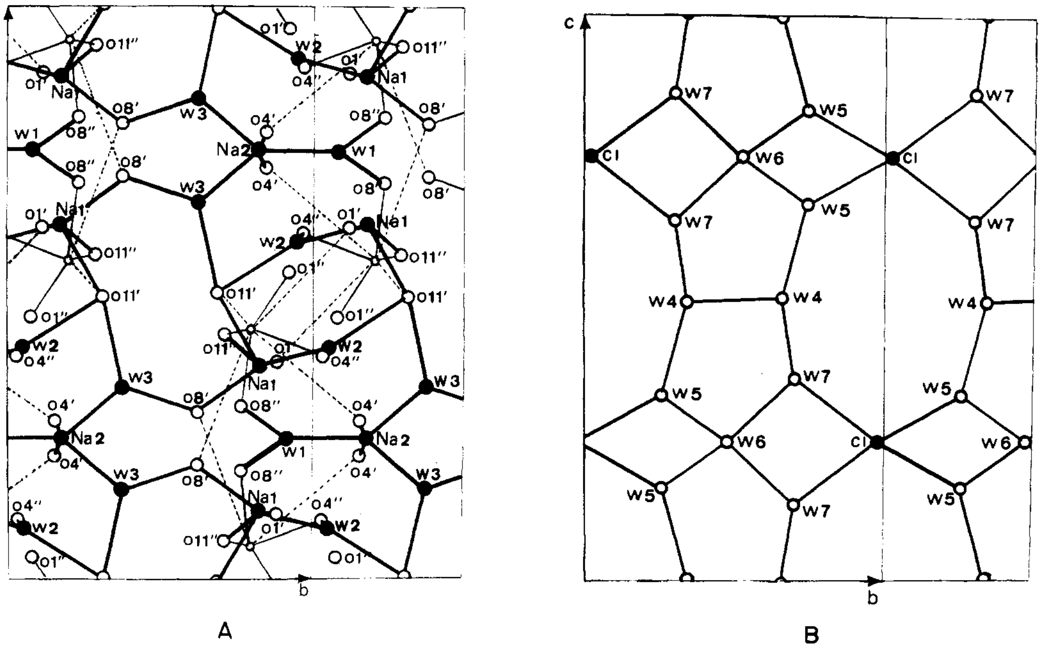

Figure 4. Packing patterns in $Na^+[TbTETA]^-\cdot 6H_2O\cdot {}^1/_2NaCl$ as projections in the *b,c* plane: (A) at around $x = 0.5$ (small circles denote Tb(III) ions and the symbols ω designate water oxygen atoms; the dotted lines join the carboxyl oxygens O(1′), O(4′), O(8′), and O(11′) to the Tb ion of the TbTETA unit to which they belong); (B) at around $x = 0$.

In any case, all deviations from average values are much smaller than those reported for EuDOTA, a compound for which strain was alluded to in order to account for the large deviations observed.

Table IV. Interatomic Distances (Å) and Angles (deg) in the TETA Ligand

(a) Bond Lengths

N(1)–C(1)	1.491 (5)	C(9)–C(10)	1.510 (6)
N(1)–C(2)	1.509 (5)	C(12)–C(13)	1.494 (6)
N(1)–C(14)	1.502 (5)	C(13)–C(14)	1.541 (6)
N(4)–C(3)	1.500 (5)	C(1)–C(1′)	1.531 (6)
N(4)–C(4)	1.489 (5)	C(4)–C(4′)	1.516 (6)
N(4)–C(5)	1.504 (5)	C(8)–C(8′)	1.539 (6)
N(8)–C(7)	1.474 (5)	C(11)–C(11′)	1.516 (5)
N(8)–C(8)	1.485 (5)	C(1′)–O(1′)	1.242 (5)
N(8)–C(9)	1.507 (5)	C(1′)–O(1″)	1.259 (5)
N(11)–C(10)	1.503 (5)	C(4′)–O(4′)	1.234 (5)
N(11)–C(11)	1.483 (5)	C(4′)–O(4″)	1.287 (5)
N(11)–C(12)	1.512 (4)	C(8′)–O(8′)	1.241 (4)
C(2)–C(3)	1.497 (5)	C(8′)–O(8″)	1.254 (5)
C(5)–C(6)	1.525 (6)	C(11′)–O(11′)	1.236 (5)
C(6)–C(7)	1.548 (6)	C(11′)–O(11″)	1.275 (5)

(b) Bond Angles

C(1)–N(1)–C(2)	107.8 (3)	N(11)–C(10)–C(9)	110.3 (3)
C(1)–N(1)–C(14)	110.4 (3)	N(11)–C(12)–C(13)	113.1 (3)
C(2)–N(1)–C(14)	106.5 (3)	C(12)–C(13)–C(14)	113.2 (4)
C(3)–N(4)–C(4)	109.0 (3)	N(1)–C(14)–C(13)	115.8 (3)
C(3)–N(4)–C(5)	107.7 (3)	N(1)–C(1)–C(1′)	113.7 (3)
C(4)–N(4)–C(5)	108.1 (3)	C(1)–C(1′)–O(1′)	117.1 (4)
C(7)–N(8)–C(8)	109.3 (3)	C(1)–C(1′)–O(1″)	117.1 (3)
C(7)–N(8)–C(9)	106.1 (3)	O(1′)–C(1′)–O(1″)	125.8 (4)
C(8)–N(8)–C(9)	107.8 (3)	N(4)–C(4)–C(4′)	113.3 (3)
C(10)–N(11)–C(11)	108.1 (3)	C(4)–C(4′)–O(4′)	118.0 (4)
C(10)–N(11)–C(12)	107.9 (3)	C(4)–C(4′)–O(4″)	117.8 (3)
C(11)–N(11)–C(12)	107.8 (3)	O(4′)–C(4′)–O(4″)	124.2 (4)
N(1)–C(2)–C(3)	111.3 (3)	N(8)–C(8)–C(8′)	112.4 (3)
N(4)–C(3)–C(2)	112.7 (3)	C(8)–C(8′)–O(8′)	117.5 (4)
N(4)–C(5)–C(6)	115.2 (3)	C(8)–C(8′)–O(8″)	117.8 (3)
C(5)–C(6)–C(7)	114.2 (4)	O(8′)–C(8′)–O(8″)	124.7 (4)
N(8)–C(7)–C(6)	116.2 (3)	N(11)–C(11)–C(11′)	113.1 (3)
N(8)–C(9)–C(10)	111.9 (3)	C(11)–C(11′)–O(11′)	118.2 (4)
		C(11)–C(11′)–O(11″)	118.3 (3)
		O(11′)–C(11′)–O(11″)	123.5 (4)

The overall conformation of the TETA cycle is shown in Figure 3 together with the torsion angles. The wedge representation[12] of the {77} conformation of uncomplexed 1,4,8,11-tetraoxacyclotetradecane is also shown in Figure 3. As already mentioned, 14-membered cycles can adopt two conformations of similar strain energies. In the rectangular {3434} "diamond lattice" conformation, the adjoining bonds of the four corners of the rectangle exhibit torsion angles of the same sign. If this conformation is to be selected as a geometric model for TbTETA, one has to find four atoms with their substituents pointing toward the same side of the mean plane of the ring; furthermore, these atoms must be separated alternatively by ethylene and propylene units. An inspection of the crystal structure of cyclotetradecane[15] clearly shows that selecting four such atoms is impossible. In the less regular biangular {77} conformation of 1,4,8,11-tetraoxacyclotetradecane,[16] two of the four corner atoms are "pseudocorners"; the torsion angles of their adjoining ring bonds do not have the same sign (see Figure 3). In this conformation, the free electron pairs of two oxygen atoms (O(1) and O(8)) are pointing upward while the electron pairs of the two other oxygen atoms (O(4) and O(11)) are pointing downward. Simply replacing oxygen atoms by nitrogen atoms would obviously not lead to a structure appropriate for the complexation of a lanthanide. However, as shown in Figure 3, changing the position of two of the heteroatoms leads to a new structure in which all the coordination sites are conveniently located for the complexation of a metal ion. In this process, the cycle keeps its {77} conformation and it remains divided into propylene and ethylene groups although the position of these groups has been modified. Apart from the location of the heteroatoms, there are only minor differences between the conformations of TETA and of its polyether analogue. All the torsion angles are similar except at the "pseudocorners". These positions are characterized by the large torsion angles of the adjoining bonds;[12] displacing two heteroatoms apparently leads to an inversion of the absolute values of these angles. Thus, the complexation of a lanthanide ion by TETA does not prevent the 14-membered heterocycle from adopting one of its most stable conformations; the major role of the metal ion

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is simply to bring the four carboxylic pendant arms on the same side of the ring.

The conformational preference of the 14-membered macrocycles also has a direct influence on the choice of the coordination polyhedron of the lanthanide ion. Indeed, the four heteroatoms of the conformations reproduced in Figure 3 are not coplanar, two of them being higher and two of them being lower than their mean plane. Only a dodecahedal structure could fit such an arrangement. Prior to the present crystallographic analysis, we could thus have proposed a geometrical model of TbTETA in the solid just as the structures of the DOTA complexes were easily foreseen because their was only one reasonable expectation.[5,6]

Packing Pattern. The packing pattern of Na^+ $[TbTETA]^- \cdot 6H_2O \cdot {}^1/_2NaCl$ is rather unusual (see Figure 4; packing interatomic distances and corresponding angles are available as supplementary material). The crystal consists of layers parallel to the *b*,*c* plane. These layers succeed each other at intervals of half the length of the unit cell along *a*; in addition to water molecules, they contain alternatively $Na^+[TbTETA]^-$ units or chloride ions. Within the layers located at around $x = 0.5$ (Figure 4A), TbTETA complex units are held together via water molecules and sodium ions that form with the TETA carboxylate oxygens a mixed network of O···O and Na···O close contacts. The Na···O and O···O contacts (probable hydrogen bonds) range from 2.320 (4) to 2.533 (3) Å and from 2.826 (4) to 2.869 (6) Å, respectively. It should be noted that particularly large amplitudes of thermal vibration are observed for the sodium ions Na(2) (rms values varying between 0.195 and 0.446 Å) and for the two water oxygens O(w7) (rms amplitudes between 0.255 and 0.346 Å) and O(w2) (rms amplitudes between 0.205 and 0.508 Å). Within the aqueous layers, which are located at around $x = 0$, the chloride ions and four symmetrically independant water molecules form an interesting network of hydrogen bonds, based on four- and five-membered rings. The corresponding pattern is shown in Figure 4B. The five-membered puckered rings of water molecules extend in infinite chains, parallel to the *c* axis, by sharing either one oxygen atom or one ring edge (the O···O contacts range from 2.851 (6) to 2.984 (6) Å). Moreover, the chains are cross-linked via hydrogen bonds to chloride ions so that parallel chains of four-membered planar rings are generated along the *b* axis. The dihedral angle between two successive four-membered rings has a value of 66.9 (1)°. Finally, the coordination polyhedron of the chloride ions is a distorted tetrahedron (see supplementary material).

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Registry No. $Na^+[TbTETA]^- \cdot 6H_2O \cdot {}^1/_2NaCl$, 92671-58-4.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters, hydrogen atom coordinates, and packing bond distances and corresponding angles (Tables SI-SIV) (22 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Physikalische und Theoretische Chemie der Universität Tübingen, 7400 Tübingen, West Germany, and Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91304

Gas-Phase Structure of Azidotrifluoromethane. An Electron Diffraction, Microwave Spectroscopy, and Normal-Coordinate Analysis

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The geometric structure of azidotrifluoromethane has been obtained by a combined analysis of electron diffraction intensities and ground-state rotational constants derived from the microwave spectrum. The following parameters were obtained (r_{av} values in Å and deg with 2σ uncertainties in units of the last decimal): $C-F = 1.328$ (2), $C-N_\alpha = 1.425$ (5), $N_\alpha-N_\beta = 1.252$ (5), $N_\beta-N_\omega = 1.118$ (3), $\angle CN_\alpha N_\beta = 112.4$ (2), $\angle N_\alpha N_\beta N_\omega = 169.6$ (3.4), $\angle FCF = 108.7$ (2). The CF_3 group is in the staggered position with respect to the N_3 group and tilted away from it by 5.8 (4)°.

Introduction

Structural data on covalent azides are rare due to the explosive nature[2,3] and handling difficulties encountered with these compounds. One of the more stable covalent azides is CF_3N_3, a compound originally prepared by Makarov and co-workers[4,5] and recently studied in more detail by two of us.[6] Although the closely related CH_3N_3 molecule has previously been studied by both electron diffraction[7] and microwave spectroscopy,[8] the available data were insufficient to determine whether the N_3 group is linear and to obtain a reliable value for the tilt angle of the methyl group. Furthermore, a comparison of the structures of CH_3N_3 and CF_3N_3 was expected to contribute to our knowledge of how the substitution of a CH_3 group by a CF_3 group influences the structure of the rest of the molecule.[9]

Experimental Section

Synthesis and Handling of CF_3N_3. The sample of CF_3N_3 was prepared as previously described.[6] Prior to the electron diffraction experiments, a small amount of N_2 formed by decomposition of some CF_3N_3 was pumped off at −196 °C. The only other decomposition

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