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Crystal and Molecular Structure of Sodium Aquo(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetato)europate(III) Tetrahydrate, $Na^+(EuDOTA\cdot H_2O)^-\cdot 4H_2O$, and Its Relevance to NMR Studies of the Conformational Behavior of the Lanthanide Complexes Formed by the Macrocyclic Ligand DOTA

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$Na^+(EuDOTA\cdot H_2O)^-\cdot 4H_2O$ crystallizes in space group $P\bar{1}$ with cell dimensions a = 8.710 (2) Å, b = 9.120 (2) Å, c = 15.742 (1) Å, α = 92.87 (1)°, β = 85.43 (1)°, and γ = 86.31 (1)°. d(calcd) = 1.797 g cm^{-3} for Z = 2. The crystal structure was solved by direct methods. Full-matrix least-squares refinement with all non-hydrogen atoms treated anisotropically gave an agreement factor R of 0.032 for 3142 unique reflections. The europium ion is nine-coordinate, being linked to the four nitrogen atoms of DOTA and to four carboxyl oxygen atoms of this ligand as well as to one hydration water molecule. The coordination polyhedron can be described as a distorted capped square antiprism. The crystal packing consists of parallel EuDOTA chains that are linked, alternatively, through six-membered water rings, hydrogen bonded to carboxyl oxygens, and through Na^+ ions and water molecules that form a pattern of Na–O and O–O short contacts with carboxyl oxygens. The overall conformation of the macrocyclic ring, in spite of its partially asymmetric nature, is very close to a {3333} "square" in keeping with the stereochemical arrangement deduced from previous NMR studies. The relative NMR dipolar shifts computed from the solid-state structure of $EuDOTA^-$ and induced in solution by Yb^{3+} are in very good agreement, thus suggesting that the lanthanide DOTA complexes are unusually rigid.

Introduction

Macrocyclic ligands substituted with functional groups are particularly advantageous in that they form complexes with a variety of metal cations in water,[2–5] some of these complexes being exceedingly stable over a large pH range. For instance, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate, designated here as DOTA, forms the most stable complexes known to date with calcium[2,3] and with the lanthanide ions.[5]

No less remarkable is the fact that the lanthanide DOTA complexes exhibit two rare features in lanthanide chemistry: they are axially symmetric and they are rigid on the NMR time scale. It has indeed been reported[5] that the ethylenic groups of DOTA undergo a slow inversion of conformation around 0 °C. The NMR spectra of lanthanide DOTA complexes are thus strongly temperature dependent, and the activation parameters of the conformational process taking place along the tetraaza ring have been measured. Furthermore, the proton NMR shifts induced by the paramagnetic ions can be very large (for instance, up to 150 ppm in the case of YbDOTA) and reflect directly the solution structure of the complexes.[5] Recently, multinuclear NMR studies[6] have indicated that the lanthanide DOTA complexes act as axially symmetric shift reagents for small inorganic substrates such as the sodium or chloride ions or the water molecule. It was also found that the DOTA complexes are monohydrated. Some of the conclusions drawn from these NMR investigations have been confirmed by luminescence spectroscopy and by luminescence lifetime measurements,[7,8] but no crystal structure of a lanthanide polyaza polycarboxylic macrocyclic complex has yet been reported. In view of the many interesting properties of the lanthanide DOTA compounds and in view of their potential application as water-soluble axially symmetric shift reagents, we have determined the crystallographic structure of $Na^+(EuDOTA\cdot H_2O)^-\cdot 4H_2O$. This crystal structure is described below and is in excellent agreement with the solution structure established by NMR spectroscopy.

Experimental Section

Colorless crystals of $Na^+(EuDOTA\cdot H_2O)^-\cdot 4H_2O$ were obtained by slow evaporation at 293 K of a 0.1 M solution of the complex, which was prepared as described elsewhere.[5] Elemental analyses of the crystals were consistent with the composition found by X-ray diffraction.

Crystal Data: Triclinic, space group $P\bar{1}$, a = 8.710 (2) Å, b = 9.120 (2) Å, c = 15.742 (1) Å, α = 92.87 (1)°, β = 85.43 (1)°, γ = 81.36 (1)°, V = 1230.0 (5) Å^3, d(calcd) = 1.797 g cm^{-3}, Z = 2, μ(Mo K$\bar{\alpha}$) = 26.364 cm^{-1}.

Solution and Refinement of the Structure. The triclinic space group symmetry was established by Weissenberg photographs. Three-dimensional intensity data were collected at 293 ± 1 K with an Enraf-Nonius CAD 4 X-ray diffractometer using monochromatic Mo K$\bar{\alpha}$ radiation. Cell dimensions were refined by the least-squares method from angle data recorded for 25 reflections. A total of 7283 observed reflections were then measured in the θ–2θ scan mode. As a check on the stability of the diffractometer and of the crystal, two reflections were measured at 30-min intervals during data collection. The intensities were corrected for Lorentz, polarization, and absorption effects. The calculated transmission factors range from 71.4% to 99.9%.

The structure was solved by direct methods, which also established unequivocally the space group $P\bar{1}$. Full-matrix least-squares refinement was carried out on 3142 independent reflections for which $F^2 \geq 3\sigma(F^2)$. The calculations included both f' and f'' for anomalous dispersion effects of the Eu and Na atoms. All non-hydrogen atoms were treated anisotropically. The H atoms were given the same isotropic temperature factor B = 5.0 Å^2. Since the water hydrogen atoms could not be located, they were omitted from calculations. The final agreement factors

$$R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$$

and

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$$

(weighted R factor) are 0.032 and 0.054, respectively. The programs used for this study were part of the Enraf-Nonius SDP programs.[9] Atomic scattering factors were taken from ref 10.

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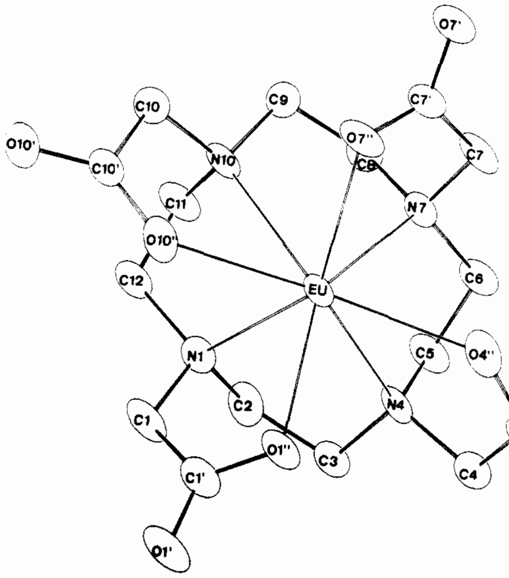

Figure 1. Perspective view of the (EuDOTA)$^-$ complex.

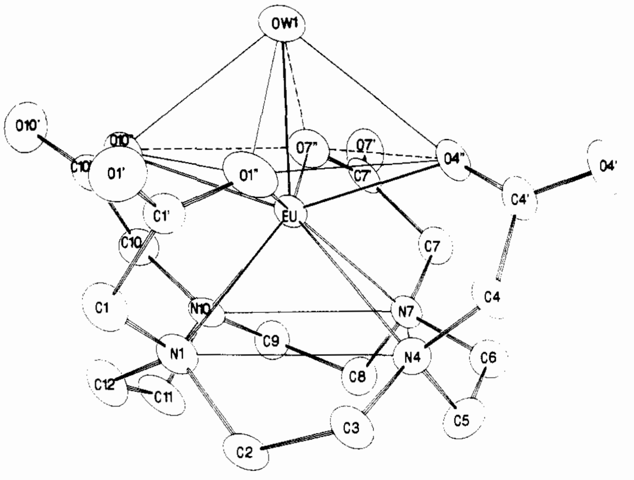

Figure 2. The coordination polyhedron in (EuDOTA·H_2O)$^-$.

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

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Eu	0.59075 (2)	0.25268 (2)	0.30724 (1)	1.614 (6)
Na	0.3710 (3)	−0.1792 (3)	0.4009 (2)	3.45 (5)
N(1)	0.8490 (5)	0.0568 (5)	0.3034 (3)	2.15 (9)
N(4)	0.8430 (5)	0.3800 (5)	0.3199 (3)	2.08 (9)
N(7)	0.6373 (5)	0.4563 (5)	0.1753 (3)	2.18 (9)
N(10)	0.6457 (5)	0.1353 (5)	0.1575 (3)	2.08 (9)
C(2)	0.9883 (6)	0.1332 (7)	0.2888 (4)	2.7 (1)
C(3)	0.9791 (6)	0.2664 (6)	0.3423 (4)	2.7 (1)
C(5)	0.8826 (7)	0.4748 (7)	0.2406 (4)	2.7 (1)
C(6)	0.7400 (6)	0.5615 (6)	0.1982 (4)	2.5 (1)
C(8)	0.7048 (7)	0.3860 (7)	0.0980 (4)	3.0 (1)
C(9)	0.6284 (7)	0.2546 (7)	0.0828 (3)	2.7 (1)
C(11)	0.8035 (7)	0.0436 (7)	0.1505 (4)	3.1 (1)
C(12)	0.8508 (7)	−0.0426 (6)	0.2346 (4)	2.7 (1)
C(1)	0.8525 (7)	−0.0392 (7)	0.3874 (4)	2.5 (1)
C(1′)	0.7760 (6)	0.0425 (6)	0.4625 (4)	2.0 (1)
O(1′)	0.8018 (4)	−0.0154 (5)	0.5365 (2)	2.56 (8)
O(1″)	0.6847 (4)	0.1635 (5)	0.4452 (2)	2.71 (8)
C(4)	0.8044 (6)	0.4736 (7)	0.3927 (4)	2.7 (1)
C(4′)	0.6334 (7)	0.5509 (6)	0.3938 (3)	2.3 (1)
O(4′)	0.6037 (5)	0.6693 (5)	0.4273 (3)	3.16 (9)
O(4″)	0.5369 (4)	0.4879 (4)	0.3635 (3)	2.67 (8)
C(7)	0.4800 (7)	0.5427 (7)	0.1562 (4)	2.6 (1)
C(7′)	0.3522 (6)	0.4406 (8)	0.1683 (3)	2.3 (1)
O(7′)	0.2436 (5)	0.4728 (5)	0.1222 (3)	3.53 (9)
O(7″)	0.3702 (4)	0.3307 (5)	0.2262 (3)	2.73 (8)
C(10)	0.5236 (7)	0.0371 (7)	0.1557 (4)	2.8 (1)
C(10′)	0.4703 (6)	−0.0339 (6)	0.2421 (4)	2.4 (1)
O(10′)	0.3880 (5)	−0.1323 (5)	0.2453 (3)	3.69 (9)
O(10″)	0.5068 (4)	0.0154 (4)	0.3102 (2)	2.51 (8)
O(W1)	0.3595 (4)	0.2586 (5)	0.4107 (2)	2.75 (8)
O(W2)	0.2217 (6)	0.6247 (6)	0.3773 (4)	6.4 (1)
O(W3)	0.2024 (6)	−0.0673 (6)	0.1005 (3)	4.8 (1)
O(W4)	−0.0314 (6)	0.2815 (5)	−0.0754 (3)	4.2 (1)
O(W5)	0.1392 (8)	0.2341 (7)	0.0681 (4)	7.3 (2)

[a] $B_{eq} = {}^1/_3 \text{ trace } \tilde{B}$.

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

Eu-N(1)	2.649 (3)	Eu-O(4″)	2.247 (3)
Eu-N(4)	2.651 (3)	Eu-O(7″)	2.428 (3)
Eu-N(7)	2.900 (3)	Eu-O(10″)	2.387 (3)
Eu-N(10)	2.519 (3)	Eu-O(W1)	2.480 (3)
Eu-O(1″)	2.511 (3)		

N(1)-Eu-N(4)	67.35 (9)	N(10)-Eu-O(1″)	130.36 (9)
N(1)-Eu-N(10)	72.5 (1)	N(10)-Eu-O(4″)	134.4 (1)
N(4)-Eu-N(7)	66.52 (9)	N(10)-Eu-O(7″)	70.78 (9)
N(7)-Eu-N(10)	64.69 (9)	N(10)-Eu-O(10″)	73.5 (1)
N(1)-Eu-N(7)	107.56 (9)	N(1)-Eu-O(W1)	124.5 (1)
N(4)-Eu-N(10)	100.3 (1)	N(4)-Eu-O(W1)	129.86 (9)
N(1)-Eu-O(1″)	60.79 (9)	N(7)-Eu-O(W1)	127.93 (9)
N(1)-Eu-O(4″)	130.24 (9)	N(10)-Eu-O(W1)	129.81 (9)
N(1)-Eu-O(7″)	142.35 (9)	O(1″)-Eu-O(4″)	91.1 (1)
N(1)-Eu-O(10″)	74.46 (9)	O(1″)-Eu-O(10″)	78.46 (9)
N(4)-Eu-O(1″)	77.6 (1)	O(4″)-Eu-O(7″)	83.2 (1)
N(4)-Eu-O(4″)	66.89 (9)	O(7″)-Eu-O(10″)	87.2 (1)
N(4)-Eu-O(7″)	127.7 (1)	O(1″)-Eu-O(7″)	147.51 (9)
N(4)-Eu-O(10″)	141.3 (1)	O(4″)-Eu-O(10″)	143.4 (1)
N(7)-Eu-O(1″)	143.63 (9)	O(1″)-Eu-O(W1)	72.07 (9)
N(7)-Eu-O(4″)	70.25 (9)	O(4″)-Eu-O(W1)	74.71 (9)
N(7)-Eu-O(7″)	63.25 (9)	O(7″)-Eu-O(W1)	75.58 (9)
N(7)-Eu-O(10″)	134.52 (0)	O(10″)-Eu-O(W1)	68.67 (9)

The positional parameters from the final least-squares cycle and their associated standard deviations are listed in Table I.

Description of the Structure and Discussion

The Coordination Polyhedron. The structure is illustrated in Figures 1 and 2, which show the molecular geometry around the europium atom. The thermal motions of the atoms are depicted as 50% probability ellipsoids. DOTA forms a shell around the europium ion, which is linked to the four nitrogen atoms and to four carboxyl oxygen atoms of the ligand. The europium ion is also associated with one water oxygen atom, reaching in this way a coordination number of 9.

Table II lists selected interatomic distances and angles involving the europium ion and the atoms of the coordination sphere. The variation among Eu–N and Eu–O(carboxyl) distances are statistically significant. These distances range respectively from 2.519 (3) to 2.900 (3) Å and from 2.247 (3) to 2.511 (3) Å. As expected, the Eu–N are much longer than the Eu–O distances. The Eu–N mean distance, 2.680 (3) Å, compares favorably with the values (2.64, 2.70 Å) observed in $Eu(ClO_4)_3$·crypt(2.2.2)·CH_3CN[11] and the Eu–O(carboxyl) mean distance, 2.393 (3) Å, is quite close to the average Eu–O(carboxyl) distance of 2.45 Å found in tris(hydroxyacetato)europium.[12] Also, the Eu–O(water) bond length of 2.480 (3) Å is in good agreement with the Eu–O(water) distance reported in the complex $Eu_2(OOC{-}CH_2{-}COO)_3$·$8H_2O$.[13] The angles subtended at europium between pairs of atoms range from 60.79 (9) to 91.1 (1)°.

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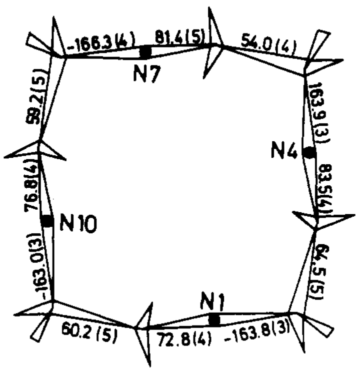

Figure 3. Torsional angles in the {3333} "square" conformation of the DOTA ring. Standard deviations are given in parentheses.

The coordination polyhedron about europium is best described in terms of a distorted capped square antiprism:[14] the eight-coordinated donor atoms of the DOTA macrocycle are at the vertices of the two square bases and one water oxygen atom is in the axial position (Figure 2). The least-squares equations of the two square planes, [N(1), N(4), N(7), N(10)] (plane I) and [O(1″), O(4″), O(7″), O(10″)] (plane II), are $0.8173x + 0.0404y - 0.5748z - 2.9569 = 0$ and $0.8157x + 0.0373y - 0.5772z - 0.5819 = 0$, respectively.

The displacements of the atoms from their respective least-squares plane are <0.008 Å for plane I and <0.03 Å for plane II. These two planes are parallel within 0.25°, and the Eu atom is displaced by 0.7 Å from plane II toward the inside of the DOTA shell.

Conformation of the Ligand. Bond lengths and bond angles in the DOTA ligand are given in Table III. Torsional angles are reported in Figure 3. The macrocyclic ring of DOTA exhibits the characteristic "square" conformation of the 12-membered cycles. This conformation, label {3333} by Dale,[15] has been observed by X-ray diffraction or by dynamic NMR spectroscopy in the following compounds: cyclododecane,[16] azacyclododecane,[17] tetraoxacyclododecane or 12-crown-4,[18] and a substituted tetraaza derivative of cyclododecane.[19] The {3333} conformation of tetraoxa or tetraaza derivatives of cyclododecane is particularly suitable for the complexation of metal ions since all the methylenic hydrogens are fully staggered and since the four oxygen or nitrogen atoms are pointing toward the same side of the ring. Indeed, it has also been observed in sandwich 1:2 complexes of 12-crown-4 with alkali-metal ions.[20,21]

Table III. Interatomic Distances (Å) and Angles (deg) in the DOTA Ligand

N(1)–C(1)	1.622 (5)	C(8)–C(9)	1.475 (6)
N(1)–C(2)	1.495 (5)	C(11)–C(12)	1.623 (6)
N(1)–C(12)	1.375 (4)	C(1)–C(1′)	1.426 (5)
N(4)–C(3)	1.529 (5)	C(4)–C(4′)	1.547 (5)
N(4)–C(4)	1.382 (5)	C(7)–C(7′)	1.560 (6)
N(4)–C(5)	1.598 (6)	C(10)–C(10′)	1.602 (7)
N(7)–C(6)	1.458 (5)	C(1′)–O(1′)	1.325 (5)
N(7)–C(7)	1.534 (5)	C(1′)–O(1″)	1.313 (5)
N(7)–C(8)	1.390 (5)	C(4′)–O(4′)	1.161 (5)
N(10)–C(9)	1.643 (6)	C(4′)–O(4″)	1.202 (5)
N(10)–C(10)	1.490 (5)	C(7′)–O(7′)	1.247 (5)
N(10)–C(11)	1.491 (5)	C(7′)–O(7″)	1.390 (6)
C(2)–C(3)	1.431 (5)	C(10′)–O(10′)	1.230 (5)
C(5)–C(6)	1.582 (6)	C(10′)–O(10″)	1.224 (5)
C(1)–N(1)–C(2)	113.4 (3)	N(10)–C(11)–C(12)	115.8 (3)
C(1)–N(1)–C(12)	106.5 (3)	N(1)–C(12)–C(11)	110.8 (3)
C(2)–N(1)–C(12)	107.1 (3)	N(1)–C(1)–C(1′)	113.3 (3)
C(3)–N(4)–C(4)	104.6 (3)	C(1)–C(1′)–O(1′)	117.0 (3)
C(3)–N(4)–C(5)	114.6 (3)	C(1)–C(1′)–O(1″)	112.5 (4)
C(4)–N(4)–C(5)	109.5 (3)	O(1′)–C(1′)–O(1″)	130.5 (3)
C(6)–N(7)–C(7)	109.1 (3)	N(4)–C(4)–C(4′)	109.6 (3)
C(6)–N(7)–C(8)	105.1 (3)	C(4)–C(4′)–O(4′)	116.6 (4)
C(7)–N(7)–C(8)	106.0 (3)	C(4)–C(4′)–O(4″)	120.8 (3)
C(9)–N(10)–C(10)	111.2 (3)	O(4′)–C(4′)–O(4″)	122.6 (4)
C(9)–N(10)–C(11)	111.9 (3)	N(7)–O(7)–C(7′)	109.0 (3)
C(10)–N(10)–C(11)	110.0 (3)	C(7)–C(7′)–O(7′)	112.4 (4)
N(1)–C(2)–C(3)	113.0 (3)	C(7)–C(7′)–O(7″)	119.0 (3)
N(4)–C(3)–C(2)	109.4 (3)	O(7′)–C(7′)–O(7″)	128.6 (4)
N(4)–C(5)–C(6)	117.1 (3)	N(10)–C(10)–C(10′)	118.7 (3)
N(7)–C(6)–C(5)	108.5 (3)	C(10)–C(10′)–O(10′)	123.8 (4)
N(7)–C(8)–C(9)	107.0 (3)	C(10)–C(10′)–O(10″)	119.2 (4)
N(10)–C(9)–C(8)	114.3 (3)	O(10′)–C(10′)–O(10″)	116.9 (4)

Examination of the data reported in Table III and Figure 3 reveals that the DOTA ring, in its complex with europium(III), is partially asymmetric. Significant differences are observed between N–C and C–C distances as well as between internal angles at nitrogen and carbon atoms. These differences do not appear to be spurious effects arising from inadequate treatment of molecular thermal motions in the crystallographic analysis. The EuDOTA complex adopts a very crowded conformation and appears to be highly strained as evidenced by marked deviations from the expected values of several valency angles and of the length of some of the bonds forming these angles. No such effects have been observed in the case of a substituted tetraazacyclododecane derivative[19] or of a terbium complex with TETA,[22] a ligand which is similar to DOTA but which exhibits a larger internal cavity.[3] However, shortenings of C–C bonds in macrocyclic polyethers have been reported for all the structures investigated so far. No satisfactory explanation of this phenomenon has yet been put forward.[23] Irregular bond distances have also been observed in the complex formed between $Sm(NO_3)_3$ and cryptand (2.2.2).[24] Finally, it is noteworthy that the torsional angles in the DOTA ring do not always have exactly the expected values. A few of them differ by several degrees from the average values found for coordinated 12-crown-4, which are −165, 59, and 80°[20] on going counterclockwise along the ring from one heteroatom to the next. The corresponding torsion angles in cyclododecane are −165, 70, and 70°,[16] and values of −165, 64, and 76° have been obtained in the case of uncoordinated tetraazacyclododecane.[19,25]

Packing Pattern. The packing of $Na^+(EuDOTA{\cdot}H_2O)^-{\cdot}4H_2O$ is illustrated in Figure 4. Four unit cells are shown as projections in the *bc* plane. The crystal consists of parallel chains of EuDOTA complex units, cross-linked through a remarkable network of $Na^+{\cdots}O$ and O···O (possible hydrogen bonds) close contacts, involving the Na^+ ion, carboxylate oxygen atoms, and five independent water molecules. $Na^+{\cdots}O$ and O···O close contacts, shown by dotted lines in Figure 4, range respectively from 2.274 (3) to 2.684 (3) Å and from 2.612 (5) to 2.936 (4) Å. On one side of each EuDOTA chain, the network consists of hydrogen bonds between water (O(W3), O(W4), and O(W5)) and carboxylate oxygen atoms

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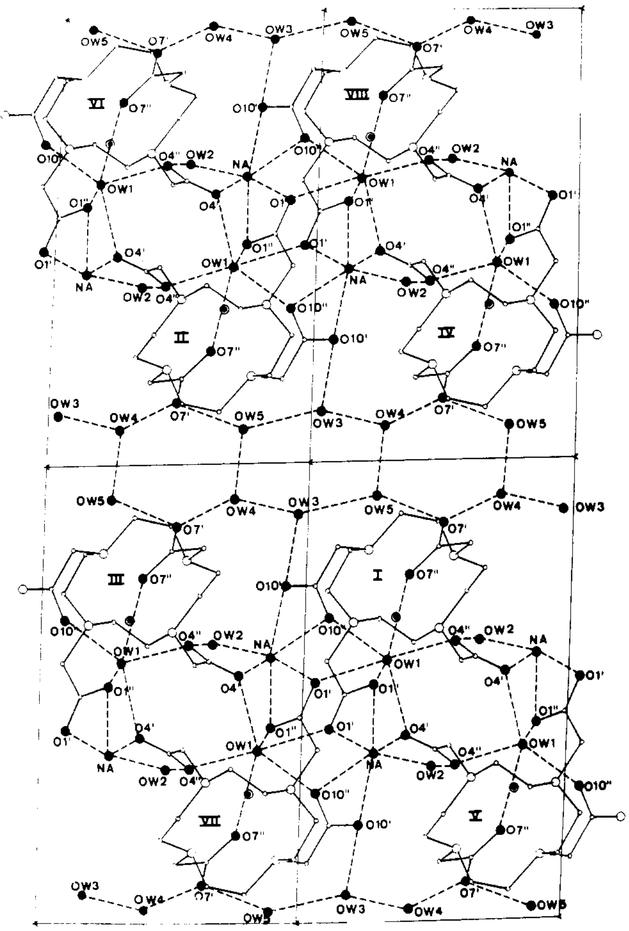

Figure 4. Packing pattern of $Na^+(EuDOTA{\cdot}H_2O)^-{\cdot}4H_2O$ as a projection in the *bc* plane. Axis *b* is horizontal from left to right. ⊙ represents the Eu positions. Symmetry codes relating different (EuDOTA) units are as follows: (I) *x*, *y*, *z*; (II) −*x*, −*y*, −*z*; (III) *x*, *y* − 1, *z*; (IV) −*x*, −*y* + 1, −*z*; (V) −*x* + 1, −*y* + 1, −*z* + 1; (VI) *x* − 1, *y* − 1, *z* − 1; (VII) −*x* + 1, −*y*, −*z* + 1; (VIII) *x* − 1, *y*, *z* − 1.

(O(10′) and O(7′)) forming infinite chains of six-membered rings, parallel to the *b* axis. In this hydrogen-bonding scheme, each water has two possible orientations presumably because of statistical disorder among the protons. On the opposite side of each of EuDOTA chain, the bridging between the carboxylate oxygens is assumed, on the one hand, by the Na^+ ion and one water oxygen (O(W2)) and, on the other hand, by the water oxygen (O(W1)) coordinated to the europium. Moreover, the Na^+ ions are irregularly surrounded by five carboxylate oxygens (O(10″), O(10′), O(1″), O(1′), O(4′)) from three diffrerent EuDOTA units and by the water oxygen O(W2), which is hydrogen bonded to the carboxylate oxygen O(4″).

Comparison with NMR Data. The environment of the lanthanide cation is probably identical in solution and in the solid state since there is a nearly quantitative fit between the crystal structure reported in the present paper and the conformation previously established by NMR spectroscopy.[5] It is well-known[26] that the paramagnetic lanthanide ions induce large NMR shifts that are essentially dipolar in origin and that are thus dependent upon the mean solution structure of the metal complexes. Provided these complexes are axially symmetric, a condition that is met with $EuDOTA^-$ in solution, each induced shift is directly dependent upon a mean geometric factor $\langle 3\cos^2\theta - 1/r^3\rangle$, where *r* is the distance between the metal cation and the nucleus under consideration and θ is the angle between the vector **r** and the main axis of symmetry. Lanthanide ions are also involved in contact interactions with ligands, but the resulting shifts are no longer simple functions of the solution geometry of the complexes. Since it has been amply demonstrated[26] that ytterbium(III) is the metal ion least susceptible to induce contact shifts, a comparison of the solid-state and solution structure of the DOTA complexes was carried out for this metal ion. The mean values of the geometric factors were calculated from the crystal structure of $EuDOTA^-$ and scaled to the experimental shifts recorded for the ytterbium(III) complex. Examination of the data collected in Table IV reveals that there is an excellent agreement between the calculated and experimental shifts not only in the case of the rigid 12-membered cycle but also for the acetate groups. The agreement would probably be even better if the contact contributions could be subtracted from the experimental shifts induced by ytterbium(III). The lanthanide DOTA complexes thus seem to be exceedingly rigid, axially symmetrical compounds with identical structure in solution and in the solid state, a feature rarely found in the coordination chemistry of lanthanides since these metals usually form highly labile complexes.

Table IV. Calculated and Experimental NMR Shifts of $YbDOTA^-$

	calcd[b]	exptl[c]		calcd[b]	exptl[c]
Hax1[a]	+144.2	+145.8	Heq2	+24.2	+27.2
Hax2	−52.8	−51.0	Hac1	−45.1	−40.2
Heq1	+19.2	+22.3	Hac2	−95.0	−94.0

[a] ax1 and ax2: ring protons in the axial position. eq1 and eq2: ring protons in the equatorial position. ac1 and ac2: acetate protons. [b] Dipolar geometric factors calculated from the crystal structure of $EuDOTA^-$ and scaled to the experimental shifts of $YbDOTA^-$. [c] Taken from ref 5; positive NMR shifts are shifts toward low fields.

Other structural details obtained by NMR are entirely borne out by the X-ray analysis reported in the present paper. An investigation of the ^{17}O and ^2H NMR shifts induced in the spectrum of water by the complete series of lanthanide DOTA complexes yielded a hydration number of 1 ± 0.3. Furthermore, the molecule of water of hydration was shown to be located near the main symmetry axis on the same side of the complexes as the carboxylate groups. Also, it was shown by ^{23}Na NMR that an interaction takes place between the lanthanide DOTA anions and the sodium cations, the latter being preferentially coordinated to the negatively charged carboxylate groups.[6] These findings are corroborated by our crystal structure analysis: in its complex with DOTA, the europium(III) ion is indeed coordinated to one molecule of water that is very nearly on the main symmetry axis (the mean value of the dipolar θ angle of the oxygen atom of this molecule is $-2.82°$). Moreover, the sodium ion is associated with carboxylate groups.

To our knowledge, the present structural analysis is one of the sole examples of a nearly perfect agreement between NMR spectroscopy and X-ray diffraction when these techniques are used for the determination of the conformation of paramagnetic lanthanide complexes.[26,27]

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(27) Three other examples are known: (a) The lanthanide tris(pyridine-2,6-dicarboxylates) investigated by: Albertsson, J. *Acta Chem. Scand.* **1970**, *24*, 1213. Desreux, J. F.; Reilley, C. N. *J. Am. Chem. Soc.* **1976**, *98*, 2105. (b) The complexes with dicyclo-18-crown-6 studied by: Harman, M. E.; Hart, F. A.; Hursthouse, M. B.; Moss, G. P.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1976**, 396. Catton, G. A.; Harman, M. E.; Hart, F. A.; Hawkes, G. E.; Moss, G. P. *J. Chem. Soc., Dalton Trans.* **1978**, 181. (c) The lanthanide tris[hydriodtris(pyrazol-1-yl)borates] very recently investigated by: Stainer, M. V. R.; Takats, J. *Inorg. Chem.* **1982**, *21*, 4050; *J. Am. Chem. Soc.* **1983**, *105*, 410. In all these cases, the crystallographic structures were known prior to the NMR analyses.

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Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters, hydrogen atom coordinates, polyhedral edge lengths and polyhedral angles, and packing bond distances and corresponding angles (Tables SI–SV) (18 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6, and Nicolet Instrument Corporation, Fremont, California 94539

Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes. X-ray Structure of $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(CH_3)C_6H_4CH_3][BF_4]$ and ^1H NMR Study of Stereoisomerism of the Organohydrazido(1–) Ligand in Complexes of This Type

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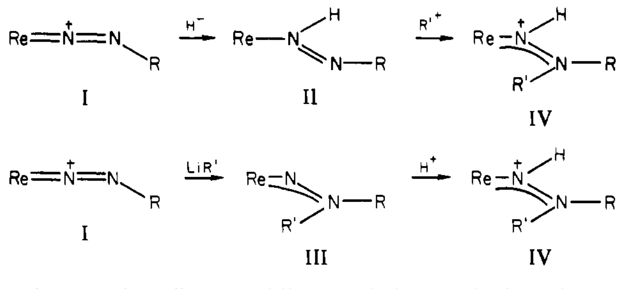
The organohydrazido(1–) complexes $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NHNRR')][BF_4]$ (where R = C_6H_4X; X = *p*-Me, *p*-OMe, or *p*-NEt_2; R′ = Me, *n*-Bu, or Ph) have been synthesized either by protonation of the corresponding organohydrazido(2–) complex $(\eta^5\text{-}C_5H_5)Re(CO)_2(NNRR')$ or by action of LiR′ on the corresponding aryldiazene complex $(\eta^5\text{-}C_5H_5)Re(CO)_2(NHNR)$. The complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(Me)C_6H_4Me]][BF_4]$ crystallizes in the space group $P2_1/c$ of the monoclinic system, with a = 10.060 (5) Å, b = 9.549 (3) Å, c = 18.193 (4) Å, β = 93.32 (3)°, and Z = 4. The calculated and measured densities are 2.015 and 2.02 (2) g cm^{-3}, respectively. On the basis of 1850 observed, three-dimensional, X-ray-counter measured intensities, with $F \geq 3\sigma(F)$ in the range $3° \leq 2\theta \leq 45°$ (Mo Kα), the structure was solved and refined by full-matrix, least-squares methods to R = 0.043 and R_w = 0.050, with anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms, including that of the NH group, were located and refined. Selected dimensions are Re–N(1) = 1.949 (9) Å, N(1)–N(2) = 1.32 (1) Å, Re–N(1)–N(2) = 139.1 (7)°, N(1)–N(2)–C(Me) = 115.7 (9)°, N(1)–N(2)–C(tol) = 121.6 (8)° and C(Me)–N(2)–C(tol) = 121.9 (9)°. In $CDCl_3$ solution, the ^1H NMR spectra of these organohydrazido(1–) complex cations exhibit resonances attributable to two stereoisomers in equilibrium. An analysis of the nuclear Overhauser effect (NOE), saturation transfer, and variable-temperature ^1H NMR spectra for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(Me)C_6H_4OMe]][BF_4]$ indicates that the stereoisomers interconvert by rotation about the N–N bond with an activation energy of 17.4 ± 0.5 kcal mol^{-1} and differ in ground-state energy by 0.39 ± 0.03 kcal mol^{-1} at 294 K. The more stable stereoisomer has essentially the same orientation of the organohydrazido(1–) ligand that is observed in the crystal structure.

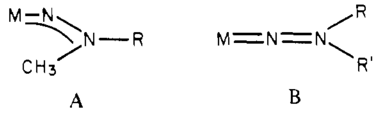
Introduction

Work described in a previous publication[2] and extended in this paper has shown that the aryldiazenido ligand (N_2R; R = aryl) in rhenium complex cations of composition $[CpRe(CO)_2(N_2R)]^+$ (I) (Cp = $\eta^5\text{-}C_5H_5$) is capable of transformation to give, first, aryldiazene (II) or substituted arylhydrazido(2–) (III) intermediates and, then, the substituted arylhydrazido(1–) derivatives (IV). This transformation is notable since it models a possible sequence of steps $M\text{-}N_2H \rightarrow M\text{-}N_2H_2 \rightarrow M\text{-}N_2H_3$ for the reduction and protonation of dinitrogen on a transition metal, M, though this sequence may not necessarily be followed in biological nitrogen fixation.[3]



Characterization of the structures and dynamics of such model intermediates as I–IV can potentially provide information about the electron distribution and bonding in the metal–diazo complex at each stage and help to establish the salient features that must exist in a given intermediate for it to undergo the next step in the transformation sequence.

In the previous paper,[2] we demonstrated that the arylmethylhydrazido(2–)-N^1 ligand in $CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]$ exhibited an unusual *bent* metal–ligand skeleton (A), rather than the linear skeleton (B) that has been commonly encountered in previously determined metal–hydrazido(2–) structures.[4] We attributed this to a difference in the electronic requirements of the metal in the two types.



As a consequence of this bent geometry, the hydrazido(2–) ligand of type A in these rhenium complexes is capable of protonation at the inner nitrogen atom N^1 to generate cations $[CpRe(CO)_2[NHN(CH_3)R]]^+$ that contain organohydrazido(1–) ligands. This paper deals with the structural characterization of examples of these rhenium hydrazido(1–) complexes, by using X-ray analysis to provide a comparison with the present hydrazido(2–) complexes[2] and ^1H NMR

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