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A First Comparison of Solid State and Solution Structure of a Complex between Lanthanum Nitrate and 1,9-Diaza-18-crown-6

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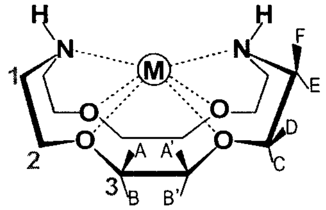
ABSTRACT



The structure of the complex between lanthanum(III)nitrate and 1,9-diaza-18-crown-6 is analyzed with three independent methods. The conformation observed by analysis of vicinal NMR coupling constants in solution agrees with both the one found by a single crystal Xray study and with simulations by molecular orbital and force field calculations. In the acetonitrile solution, the NMR data show a bent crown conformation with nearly C_{2v} symmetry, which is stable on the NMR time scale.

The application of lanthanides in many fields is closely related to their unusually high coordination number and large charge density.[1] Many uses require complexation of the lanthanide with suitable organic ligands,[2,3] which then allow, for example, introduction of other functions into systems like chemical nucleases.[4] Despite this, there are not many structural investigations with such systems.[2,3,5] In particular there has been to the best of our knowledge no attempt to compare solid state structures with those in solution.[5e] We report here such an endeavor by the analysis of the complex

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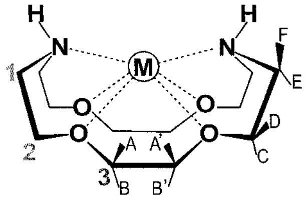
between lanthanum nitrate and the 1,9-diaza-18-crown-6 (**I**, see Scheme 1) by Xray diffraction and NMR measurements of vicinal coupling constants. The results not only provide evidence for a coordination number as large as 12 but also show clear de-symmetrization of the azacrown ligand as stable species on the NMR time scale, with a rather good coincidence between solid state and solution structure which moreover is supported by some preliminary SCF MO calculations.

Scheme 1. Complex **1** (Shown without the Nitrate Counterions) with Hydrogen Atom Numbering



The bond lengths and angles in the crystal structure of **1** (Figure 1, Table 1 and Table 2) show the lanthanum atom coordinated by four oxygens and two nitrogens of the ligand and with six oxygens of three bidentate nitrate groups, with the total coordination number equal to 12. The resulting polyhedron around the lanthanum atom can be described as a distorted icosahedron. The macrocyclic ligand is characterized by a slightly distorted C_2 symmetry; its bond distances and bond angles deviate little from normal, unstrained parameters. The geometry is in line with nearly optimal contacts between donor atoms and the metal ion; opposite torsional angles, which would be identical with perfect C_{2v} symmetry, vary only by up to 4.2° for angles C4−O3−C5−C6 and C10−O6−C11−C12 (see Table 2). The shape of the cycle can be characterized as a sequence of B−C−B- -C−B conformations, where B is a boatlike connection and C a chairlike connection. The bonds lengths La- -O vary in the interval 2.644(3)−2.781(3) Å, with the La- -ONO$_2$ bonds being systematically shorter. In contrast to earlier data[6] for a 222-cryptate complex of lanthanum nitrate, La- -N distances for complex **1** (2.720(3)−2.742(3) Å) are in, or slightly below, the range of La−O (O of the diazacrown), with 2.742(3)−2.781(3) Å. Analysis of the crystal packing has revealed that the molecules are assembled into dimers by means of weak interatomic contacts formed by nitrogen hydrogen with the NO_3 group (N(1)−N(1H)···O(11a) (−*x*, 1 − *y*, −1 − *z*).

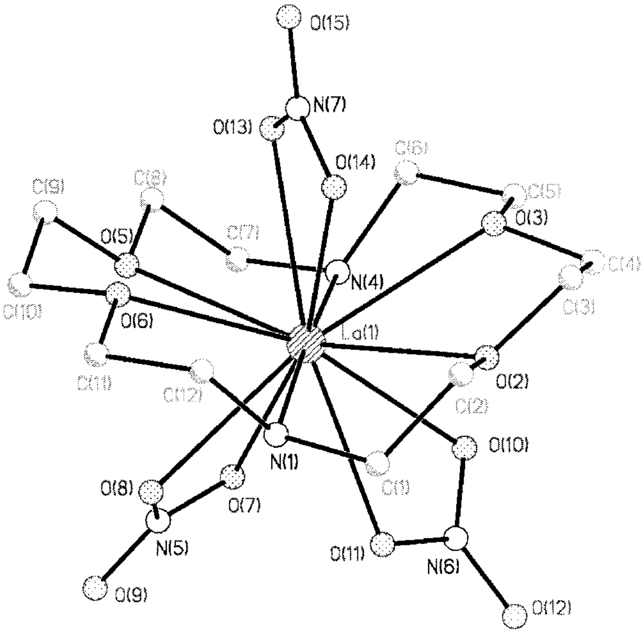


Figure 1. X-ray derived structure of complex **1** with atom numbering; hydrogen atoms omitted.

Ⓦ A 3D rotatable image of the packing structure in PDB format is available.

Table 1. Selected Bond Distances [Å] for Complex **1** (see Figure 1 for Numbering)

La(1)−N(1)	2.720(3)	N(1)−C(1)	1.472(5)	C(5)−C(6)	1.504(5)
La(1)−O(2)	2.774(3)	N(1)−C(12)	1.467(5)	O(6)−C(10)	1.427(4)
La(1)−O(3)	2.779(3)	C(1)−C(2)	1.508(5)	O(6)−C(11)	1.443(4)
La(1)−N(4)	2.742(3)	O(2)−C(2)	1.442(4)	C(7)−C(8)	1.507(5)
La(1)−O(5)	2.781(3)	O(2)−C(3)	1.425(4)	C(9)−C(10)	1.507(6)
La(1)−O(6)	2.742(3)	O(3)−C(4)	1.433(4)	C(11)−C(12)	1.497(5)
La(1)−O(7)	2.661(3)	O(3)−C(5)	1.439(4)		
La(1)−O(8)	2.644(3)	C(3)−C(4)	1.497(5)		
La(1)−O(10)	2.652(3)	N(4)−C(6)	1.476(5)		
La(1)−O(11)	2.659(3)	N(4)−C(7)	1.470(5)		
La(1)−O(13)	2.664(3)	O(5)−C(8)	1.451(4)		
La(1)−O(14)	2.681(3)	O(5)−C(9)	1.426(4)		

Table 2. Comparison of the Torsion Angles (deg) of the Structure of Complex **1** from X-ray Data (X-ray) and from ab Initio SCF MO Calculations (MO)

	X-ray	MO
C4−O3−C5−C6	171.5(3)	174
C5−O3−C4−C3	173.9(3)	175
O2−C3−C4−O3	61.1(4)	54
C2−O2−C3−C4	−179.0(3)	177
C3−O2−C2−C1	−176.6(3)	179
N1−C1−C2−O2	−60.9(4)	−56
C12−N1−C1−C2	−85.1(4)	−85
C1−N1−C12−C11	−174.2(3)	−176
O6−C11−C12−N1	−61.5(4)	−56
C10−O6−C11−C12	175.7(3)	174
C11−O6−C10−C9	174.9(3)	175
O5−C9−C10−O6	61.4(4)	54
C8−O5−C9−C10	178.7(3)	177
C9−O5−C8−C7	−179.5(3)	179
N4−C7−C8−O5	−61.3(4)	−56
C6−N4−C7−C8	−82.3(4)	−85
C7−N4−C6−C5	−173.1(3)	−176
O3−C5−C6−N4	−61.3(4)	−56

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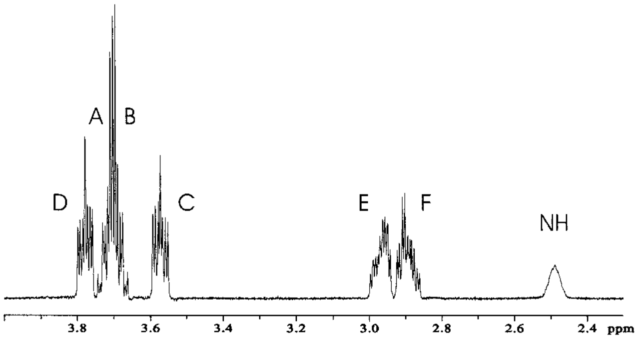

Figure 2. ^{1}H NMR spectrum of complex **1** (in CD_3CN, 303 K). For hydrogen numbering, see Scheme 1.

The conformational space for the complex **1** contains many conformers; eight of the reasonable looking conformers were simulated with force field calculations (gas phase simulations with CHARMm[7]). Final refinements of these structures were performed at the ab initio SCF MO level using an effective core potential (ECP) approach using the Gaussian program package.[8] A series of test calculations showed the LANL2MB basis set[8,9a] (STO-3G[9b,c] on first-row elements and Los Alamos ECP plus MBS on La[9d−f]) to be a good compromise between computational effort and the quality of results for the macrocyclic complexes studied. Surprisingly, only one conformer had a distinct minimum energy, with an energy at least 5 kcal/mol lower when compared to that of the other conformers studied. The corresponding geometry has a C_2-symmetrical structure quite close to the one observed by the solid state X-ray results (maximal deviation is about 7° for torsion angle O2−C3−C4−O3, see Table 2).

The solution structure of the complex was studied by analyzing the vicinal coupling constants in the NMR spectra of the complex in acetonitrile, which shows three carbon and seven proton signals, in accordance with an effective C_{2v} symmetry. This and the observed sharp signals (line width of methylene protons are in the range 1.0−1.2 Hz, see Figure 2) indicate that inversion of the structure (Scheme 1), for example, by decomplexation and reassociation is quite slow on the NMR time scale. The vicinal coupling constants $J_{H-C-C-H}$ and $J_{H-N-C-H}$, which characterize the conformation of the ligand, could all be analyzed to high accuracy by observation of many transitions (see Figure 2) in terms of the AA′BB′ spin system with fixed values of geminal couplings of 10.0 Hz for the - -OCH_2-CH_2O- moiety and the CDEF part of a $[CDFE]_2X$ spin system (where X denotes the NH protons, see Scheme 1) for the - -NCH_2-CH_2O- moiety, using the LAOCN-type program PAREMUS.[10] Assignment of proton signals was based on comparison with ^{13}C NMR and 2D COSY and on HSQC experiments. The final best values of vicinal coupling constants (Table 3) are accurate to 0.01−0.02 Hz. The vicinal couplings were then calculated using a generalized Karplus equation[11] based on both the X-ray-derived and the MO-calculated geometry (see Table 3). Comparison of experimental and calculated *J* values reveal good agreement for both calculated sets, which is remarkably good in view of the problems involved with the parametrization of the Karplus equation.[11] The observed vicinal coupling constants suggest slightly larger dihedral angles of the cis and trans protons protons which might be due to solvation effects in acetonitrile. Further investigations will shed light on the dependence of coordination numbers and of ligand conformations on the anions and the nature of other cations in such complexes.

Table 3. Comparison of Experimental and Calculated Vicinal Proton−Proton Couplings (Hz) for the X-ray Structure and for the ab Initio SCF MO Optimized Structure of Complex **1**[a]

	experimental NMR[b]	from X-ray	from MO calc.
H(A)−H(A′)[c]	2.75 (0.02)	2.4	3.3
H(A)−H(B′)/H(A′)−H(B)	6.70 (0.01)	5.7	5.6
H(B)−H(B′)[c]	2.75 (0.02)	2.4	3.4
H(C)−H(E)	6.82 (0.01)	6.4	6.2
H(C)−H(F)	3.08 (0.01)	2.5	3.0
H(D)−H(E)	3.25 (0.01)	2.6	3.1
H(D)−H(F)	7.47 (0.01)	6.4	6.2
H(E)−NH	4.19 (0.01)	4.6	4.7
H(F)−NH	7.49 (0.01)	7.1	6.8

[a] See Scheme 1 for numbering. [b] From measurements in CD_3CN at 30 K; spin system analysis see text. [c] Alternative assignment possible of protons A and B.

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Supporting Information Available: Experimental details for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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