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Preparation, Crystal and Molecular Structure of $GdCl_3$(18-crown-6)·EtOH

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Abstract

The structure of the title compound has been determined from single-crystal X-ray analysis. The triclinic cell has dimensions a = 13.225(3), b = 10.246(2), c = 8.283(2) Å, α = 112.1(1), β = 101.9(1) and γ = 85.0(1)°, space group $P\bar{1}$, Z = 2. The structure was refined by least square methods to the conventional R value 0.032 for 2791 observed reflections. The molecule is formed by $[GdCl_2EtOH(18\text{-crown-}6)]^+$ cations and Cl^- anions. In the cation the crown ether ligand, which includes the Gd ion, is folded away from the side where a chlorine and the ethanolic oxygen are coordinated to the metal ion; a second chloride ion is coordinated on the opposite side.

Introduction

The coordination chemistry of hydrated lanthanide(III) chlorides with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was investigated in methanolic solution [1].

The most relevant results of this thermodynamic study are: (a) the stabilities of the complexes formed in solution decrease with increasing atomic number from La^{3+} to Gd^{3+}, (b) no heat of reaction was detected with the post-Gd^{3+} lanthanide cations. The trend in the stability sequence was related to the relative sizes of cation and ligand cavity: the lanthanide(III) cations are too small for a facile arrangement in the cavity of the crown ether due to important factors governing the interaction like solvation, conformation of the ligand in solution and ligand–cation binding. In the sequence of the thermodynamic data, the gadolinium(III) complex is the least stable in solution. This fact prompted us to isolate this compound in the crystalline form and solve its structure.

Experimental

Preparation of the Complex

The complex was prepared by mixing ethanolic solutions of $GdCl_3$ and 18-crown-6 in the stoichiometric ratio 1:1. The crude white material was recrystallized from ethanol. *Anal.* Calcd. for $GdCl_3(C_{12}H_{24}O_6)C_2H_5OH$: C, 29.28; Cl, 18.54; H, 4.36; Found: C, 28.98; Cl, 19.00; H, 4.90.

X-ray Measurements and Structure Determination

The crystal and refinement data are summarized in Table I $[Gd(18\text{-crown-}6)ClEtOH]Cl^-$ is in the

TABLE I. Crystal Data.

Compound	$[Gd(18\text{-crown-}6)Cl_2EtOH][Cl]$
Formula	$C_{14}Cl_3H_{30}O_7Gd$
M	574
Space group	$P\bar{1}$
Crystal system	triclinic
a (Å)	13.225(3)
b (Å)	10.246(3)
c (Å)	8.283(2)
α (°)	112.1(1)
β (°)	101.9(1)
γ (°)	85.0(1)
U (Å^3)	1017.7
Z	2
D_c (g cm^{-3})	1.87
F(000)	570
Radiation (λ/Å)	MoKα (0.7107)
μ (cm^{-1})	34.4
Reflections measured	3873
Scan method	$\vartheta/2\vartheta$
Scan speed (min^{-1})	1.8
Scan width (°)	1.20
Background counts (s)	10
$2\vartheta_{max}$ (°)	50
σ limit $\lvert I > n\sigma(I)\rvert$	n = 3
Unique observed reflections	2791
R ($R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$)	0.032

0020-1693/85/$3.30

form of colourless transparent prisms. They are sensitive to atmospheric moisture and were therefore mounted in thin-walled Lindemann glass capillaries in an inert atmosphere glove box. The X-ray intensity data were collected on a four-circles Philips PW 1100 automated diffractometer with graphite monochromated MoKα radiation. The unit cell parameters were determined on the basis of 25 strong reflections found by mounting the crystal at random, varying the orientation angles ϕ and χ in the range of 120° each with the detector position varying between $\vartheta = 5°$ and $\vartheta = 10°$. For the determination of precise lattice parameters 20 strong reflections with $10° \leqslant \vartheta \leqslant 14°$ were considered. The intensities of the two standard reflections 0 –2 1 and 1 3 –1, monitored at 180 reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects, and for absorption following the method of North *et al.* [2]. The structure was solved using three-dimensional Patterson and Fourier techniques and refined by full matrix least-squares, with anisotropic thermal parameters for Gd and Cl, and isotropic for the remaining non hydrogen atoms. In the refinements $w = 1$ showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect both to F_o and to λ^{-1} sin ϑ. Hydrogen atoms were observed and included in the refinement with unique fixed isotropic thermal parameters ($U = 0.06$ Å^2). The anomalous dispersion terms [3] for Gd were taken into account in the refinement.

Atomic scattering factors were from ref. 3. Data processing and computation were carried out using the SHELX-76 program package [4]. Final positional parameters are presented in Table II. Selected distances and angles in the gadolinium coordination sphere are shown in Table III, while Table IV shows distances, angles and torsion angles in the crown ether ligand*.

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*Thermal parameters, observed and calculated structure factors have been deposited with the Editor-in-Chief.

TABLE II. Fractional Coordinates (×10^4) (for Hydrogen Atoms ×10^3) with e.s.d.s in Parentheses.

Atom	x	y	z	Atom	x	y	z
Gd	2739.3(3)	2874.7(3)	660.1(5)				
O(1)	1593(4)	3850(5)	2898(6)				
C(2)	531(7)	4218(9)	2382(12)	H(21)	23(6)	403(9)	323(12)
				H(22)	52(6)	505(9)	210(11)
C(3)	110(6)	3128(9)	629(11)	H(31)	–61(7)	334(9)	14(11)
O(4)	769(4)	3032(5)	–561(6)	H(32)	10(6)	233(9)	88(11)
C(5)	367(6)	2076(8)	–2333(10)	H(51)	–29(7)	248(9)	–283(11)
				H(52)	25(6)	120(9)	–218(11)
C(6)	1138(6)	1921(9)	–3451(11)	H(61)	131(6)	279(9)	–364(11)
				H(62)	96(6)	119(9)	–448(12)
O(7)	2094(3)	1523(5)	–2557(6)				
C(8)	2761(7)	683(9)	–3714(12)	H(81)	307(6)	133(9)	–403(11)
				H(82)	239(6)	–15(9)	–462(11)
C(9)	3521(6)	52(8)	–2631(11)	H(91)	327(6)	–54(9)	–227(11)
				H(92)	410(6)	–50(9)	–342(11)
O(10)	3979(4)	1131(5)	–1025(7)				
C(11)	4931(6)	1603(9)	–1146(11)	H(111)	474(6)	193(9)	–208(12)
				H(112)	544(6)	73(9)	–130(11)
C(12)	5345(6)	2696(8)	587(11)	H(121)	551(6)	230(9)	154(11)
				H(122)	600(7)	318(9)	64(11)
O(13)	4565(4)	3761(5)	1005(6)				
C(14)	4956(6)	4971(8)	2514(11)	H(141)	529(6)	474(9)	354(11)
				H(142)	547(6)	541(9)	200(11)
C(15)	4086(6)	5958(8)	3046(11)	H(151)	378(6)	635(9)	220(12)
				H(152)	426(6)	665(9)	424(12)
O(16)	3336(4)	5134(5)	3237(6)				
C(17)	2622(6)	5922(8)	4320(11)	H(171)	224(7)	640(9)	374(11)
				H(172)	302(6)	652(9)	565(11)
C(18)	2064(6)	4843(8)	4603(10)	H(181)	250(6)	434(9)	530(11)
				H(182)	142(6)	529(9)	539(11)
Cl(1)	3878(1)	2068(2)	3289(2)				
Cl(2)	2497(1)	4844(2)	–820(3)				
Cl(3)	1047(2)	–1630(2)	–3210(3)				

(continued on facing page)

TABLE II *(continued)*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(17)	1961(4)	686(5)	197(6)				
C(19)	1673(6)	205(8)	1473(10)	H(191)	181(6)	100(9)	261(12)
				H(192)	95(7)	4(9)	109(11)
C(20)	2253(7)	−1111(9)	1507(12)	H(201)	203(6)	−140(9)	247(11)
				H(202)	216(6)	−181(9)	39(12)
				H(203)	297(7)	−95(9)	191(11)

TABLE III. Selected Distances (Å) and Angles (°) with e.s.d.s in Parentheses Involving Gadolinium and Coordinated Ligands.

Coordination sphere			
Distances from 18-crown-6		Distances from other ligands	
Gd−O(1)	2.497(6)	Gd−Cl(1)	2.734(3)
Gd−O(4)	2.608(5)	Gd−Cl(2)	2.695(3)
Gd−O(7)	2.498(5)	Gd−O(17)	2.414(6)
Gd−O(10)	2.527(6)		
Gd−O(13)	2.576(6)		
Gd−O(16)	2.538(5)		
Angles		Angles	
O(1)−Gd−O(4)	63.2(2)	Cl(1)−Gd−Cl(2)	145.1(1)
O(4)−Gd−O(7)	62.4(2)	Cl(1)−Gd−O(17)	76.4(2)
O(7)−Gd−O(10)	63.0(2)	Cl(2)−Gd−O(17)	138.5(2)
O(10)−Gd−O(13)	63.0(2)		
O(13)−Gd−O(16)	61.9(2)		
O(16)−Gd−O(1)	63.9(2)		

TABLE IV. 18-Crown-6 Geometry (Distances Å, Angles (°)).

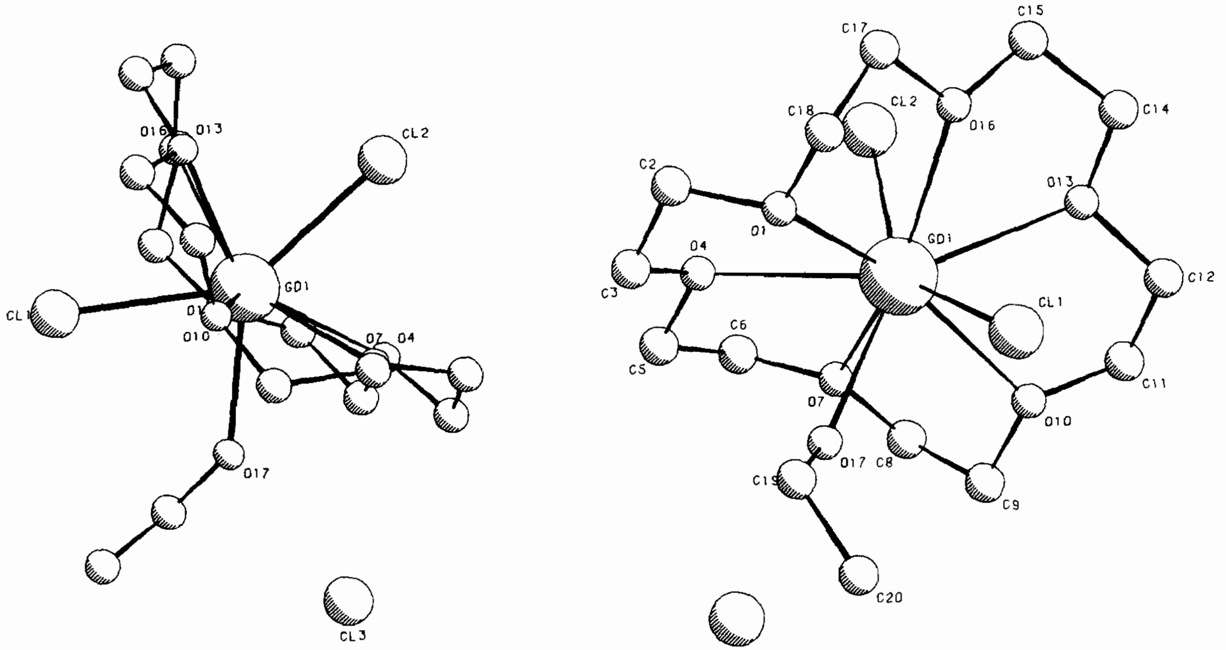
Atoms	Distances 2−3	Angles 1−2−3	Torsion angles 1−2−3−4
C(18)−O(1)−C(2)−C(3)	1.44(1)	111.8(7)	−179.2(7)
O(1)−C(2)−C(3)−O(4)	1.49(1)	107.8(8)	−54.3(9)
C(2)−C(3)−O(4)−C(5)	1.42(1)	108.1(7)	−175.4(7)
C(3)−O(4)−C(5)−C(6)	1.44(1)	111.5(7)	−174.4(7)
O(4)−C(5)−C(6)−O(7)	1.47(1)	108.4(7)	53.5(9)
C(5)−C(6)−O(7)−C(8)	1.44(1)	106.5(7)	150.7(7)
C(6)−O(7)−C(8)−C(9)	1.43(1)	114.2(6)	−163.7(7)
O(7)−C(8)−C(9)−O(10)	1.48(1)	105.2(7)	−52.5(9)
C(8)−C(9)−O(10)−C(11)	1.43(1)	109.8(7)	−95.1(9)
C(9)−O(10)−C(11)−C(12)	1.42(1)	112.5(6)	−179.1(7)
O(10)−C(11)−C(12)−O(13)	1.48(1)	108.1(7)	−55.2(9)
C(11)−C(12)−O(13)−C(14)	1.43(1)	107.5(7)	−170.5(7)
C(12)−O(13)−C(14)−C(15)	1.43(1)	111.4(7)	−172.2(7)
O(13)−C(14)−C(15)−O(16)	1.49(1)	109.2(7)	52.8(9)
C(14)−C(15)−O(16)−C(17)	1.43(1)	105.4(7)	158.6(7)
C(15)−O(16)−C(17)−C(18)	1.42(1)	114.7(7)	−169.4(7)
O(16)−C(17)−C(18)−O(1)	1.49(1)	104.7(7)	−57.3(8)
C(2)−O(1)−C(18)−C(17)	1.44(1)	111.8(7)	−95.0(8)

Discussion of the Structure

Figure 1 shows views of the molecular structure down *c* with the numbering scheme and on to the O(17), Cl(1) and Cl(2) plane. The molecule is formed by $[GdCl_2(18\text{-crown-}6)EtOH]^+$ cations and Cl^- anions. The Gd ion is linked to the six oxygen atoms of the crown ether ring, to two chlorine atoms, and to the oxygen of the ethanol ligand; one chlorine is on the more hindered side of the ring and the second chlorine and the ethanolic oxygen on the opposite side. In fact the crown ether ring is folded away from the pair of singly coordinated ligands. The best mean plane passing through the ether oxygens leaves two diametrically opposed atoms O(1) and O(10) −0.79 and −0.80 Å respectively out of the plane in the direction of the chlorine Cl(1) and ethanol ligands; the other four oxygens are O(4) 0.46, O(7) 0.34, O(13) 0.47 and O(16) 0.32 Å, all displaced in the direction of the second chlorine atom Cl(2) coordinated to the metal ion; the gadolinium atom is at −0.27 Å. The conformation of the ether oxygens is close to that adopted in the cationic moiety $[UCl_3(18\text{-crown-}6)]^+$ [5]. However, in the title compound the crown ether ligand is non symmetrical, while in the uranium(IV) derivative a C_2 symmetry was found. This could be related to the guest ion shape $[GdCl_2EtOH]^+$, less symmetrical than $[UCl_3]^+$, which induces a reduction in the symmetry of the coordinated crown ether. (The alkali metal−crown ether complexes with a spherical guest display D_{3d} symmetry).

It is worth noting that with gadolinium two types of complex exist, the derivative with the metal ion inserted into the macrocycle (present compound) or the complex $Gd(NO_3)_3(H_2O)_3L$ [6] where the crown ether (L) is bound only to the coordinated water molecules by O(crown) O−H(water) hydrogen bonds, and according to the authors this is 'the driving force for the formation of stable 1:1 adduct'.

The similarity in the ionic radii of U^{4+} (0.93 Å) [7] and Gd^{3+} (0.938 Å) [7] makes possible a comparison of the two compounds. The $M-O_{ether}$ dis-



(a) (b)

Fig. 1. View of the molecule. (a) onto the O(7), Cl(1), Cl(2) plane. (b) View down *c*.

tances show a close agreement (Gd–O range from 2.497(6) to 2.608(5) Å) and U–O range from 2.48(5) to 2.61(5) Å). A more accurate comparison is impossible due to the difference in accuracy in the structure determination for the two compounds, the uranium derivative being partially disordered. The Gd–Cl bond distances are not equivalent, the Gd–Cl(2) distance (2.695(3) Å) being significantly shorther with respect to the Gd–Cl(1) (2.734(3) Å) probably due to the different hindering around the two metal atoms. The difference cannot be detected in the uranium derivative, because of the higher e.s.d.s but on average, the U–Cl bond distances are shorther (2.66(5) Å) with respect to those of the Gd derivative (2.714(3) Å) indicating a more ionic character in the lanthanoid derivative.

There is a short contact between the anion Cl(3) and the coordinated oxygen of the ethanol ligand 3.018(6) Å which suggests a Cl(3)···H–O$_{(\mathrm{ethanol})}$ hydrogen bond. (The O(17)···Cl(1) contact is 3.196(6) Å but with unfavourable orientation). The Gd–O (ethanol distance) of 2.414(6) compares with the average of the Gd–O(H_2O) distances in the Gd(NO_3)$_3$(H_2O)$_3$·L [6] derivative (2.40(1) Å) where Gd is again 9 coordinated. The conformation of the crown ether is defined by the torsion angles about the C–C bonds all close (±7°) to synclinal staggered conformation (±60°) and those about the C–O bonds close within ±30° to anticlinal conformation (±120°) or within ±10° to antiplanar conformation (180°). The regularity of the bond lengths and angles in the crown ether (the C–O distances are all in the range 1.42–1.44(1) Å; C–C within 1.47–1.49(1) Å with C–O–C within 111.4–114.7(5)° and O–C–C within 104.7–109.3(1)° indicates that no particular strain exists in the [GdCl$_2$·EtOH(18-crown-6)]$^+$ cation due to particular intramolecular contacts as is shown in Fig. 2 which represents the molecular packing.

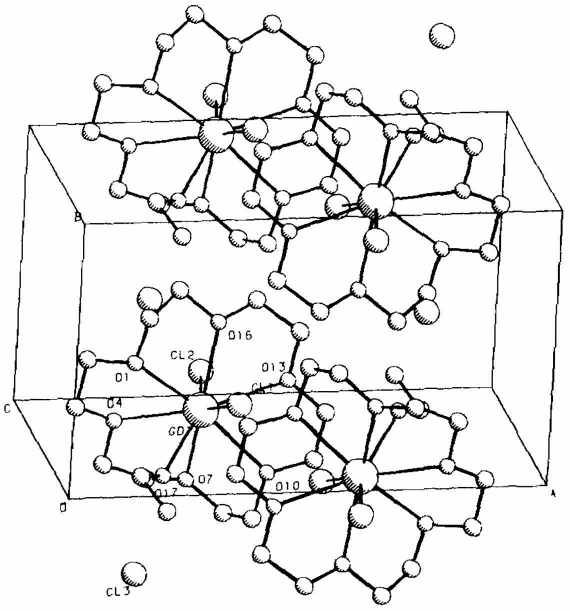


Fig. 2. Unit cell content.

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