Inorganica Chimica Acta, 215 (1994) 209-213

Note

Synthesis and crystal structure of $[GdCl_2(\text{dibenzo-18-crown-6})(MeCN)][SbCl_6]\cdot 2MeCN$, dibenzo-18-crown-6 = 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene

Gerald R. Willey*, Paul R. Meehan,
Martin D. Rudd, Howard J. Clase
and Nathaniel W. Alcock
*Department of Chemistry, University of Warwick,
Coventry CV4 7AL (UK)*

(Received June 17, 1993; revised August 27, 1993)

Abstract

Treatment of $GdCl_3(THF)_2$ with an acetonitrile solution of antimony(V) chloride (as halide abstractor) in the presence of dibenzo-18-crown-6 provides the yellow crystalline salt $[GdCl_2(\text{dibenzo-18-crown-6})(MeCN)][SbCl_6]\cdot 2MeCN$ whose structure has been determined by single-crystal X-ray diffraction. The gadolinium atom is situated within the ring cavity, bonded to all six oxygen atoms of the oxacrown, Gd–O 2 545(4)–2.683(4) Å. Further bonding to two chlorine atoms, located on opposite sides of the ring plane, Gd–Cl 2 632(2), 2.679(2) Å, and one acetonitrile molecule, Gd–N 2.579(5) Å, gives a nine-coordinate cation geometry approximating a planar hexagon with two capping atoms above and one below the plane.

Key words: Crystal structures; Crown ether complexes; Gadolinium complexes

Introduction

Lanthanide(III) ions form complexes with crown ethers that show diverse structural features [1]. In terms of metal binding, two contrasting types have been recognised, viz. *encapsulation* where the metal fits inside the crown cavity and is bound by direct $(M\cdots O_{crown})$ interactions and *second sphere coordination* in which the metal is held in a peripheral location via $(O_{crown}\cdots H_2O\cdots M)$ hydrogen bonding. As part of a study of dibenzo-18-crown-6/f-block metal ion complexation, we were particularly interested in obtaining structural parameters of an anhydrous encapsulated Gd(III)(f^7) compound. The synthesis of the title compound exploits halide abstraction by $SbCl_5$ from the bis-adduct $GdCl_3(THF)_2$ in the presence of the oxacrown ligand. This route was used successfully in the preparation of threaded $[ScCl_2(\text{18-crown-6}][SbCl_6]$ [2] where the metal dichloride cation generated *in situ* was stabilised by pentacoordinate crown complexation. A search of the Cambridge Data base files reveals six Gd(III)–crown ether structures of which two feature second sphere attachment, i.e. $Gd(H_2O)_3(NO_3)_3$-(18-crown-6) [3] and $GdCl_3(H_2O)_8$(15-crown-5) [4], and four involve encapsulation, i.e. $[Gd(\text{18-crown-6})(NO_3)_2]_3[Gd(NO_3)_6]$ [5], $[Gd(\text{dibenzo-30-crown-10})(NCS)_3(H_2O)_2]$ [6], $[GdCl(\text{18-crown-6})(H_2O)_2]Cl_2\cdot H_2O$ [7] and $[GdCl_2(\text{18-crown-6})(EtOH)]Cl$ [8].

Experimental

Standard Schlenk techniques were used in conjunction with a conventional dinitrogen atmosphere glove-box for all manipulations of materials. IR spectra were obtained using a Perkin-Elmer 580 B spectrometer with samples as nujol mulls placed between CsI discs. Elemental analyses were carried out by Medac Ltd., Brunel University, Uxbridge, Middlesex. $GdCl_3\cdot 6H_2O$, $SbCl_5$ and dibenzo-18-crown-6 were purchased from Aldrich Chemical Co., and used as supplied. All solvents were dried over CaH_2 and subsequently Na/benzophenone and distilled under a dinitrogen atmosphere prior to use.

Preparation of the complexes

$GdCl_3(THF)_2$

$SOCl_2$ (25 cm^3, 343 mmol) was added dropwise to a stirred solution of $GdCl_3\cdot 6H_2O$ (5.01 g, 13.5 mmol) in THF (50 cm^3) and the resulting mixture was heated at reflux for 6 h. Removal of solvent from the resulting light yellow solution provided an off-white solid which was washed with ether and then recrystallised from THF/CH_2Cl_2 in the presence of charcoal to give the product as white needle crystals. Yield (based on $GdCl_3\cdot 6H_2O$) 4.34 g, 79%. *Anal.* Calc. for $C_8H_{16}O_2$-$GdCl_3$: C, 23.56; H, 3.95; Cl, 26.08. Found: C, 23.23; H, 3.94; Cl, 26.00%. $\bar{\nu}_{max}$ (cm^{-1}): ν(C–O–C) 862, 1019, ν(GdCl) 273 (Nujol).

---

*Author to whom correspondence should be addressed.

SSDI 0020-1693(93)03687-6

[$GdCl_2$(dibenzo-18-crown-6)(MeCN)][$SbCl_6$] 2MeCN

Direct addition of an acetonitrile solution of $SbCl_5$ (0.10 g, 0.334 mmol) to a chilled and stirred solution of $GdCl_3(THF)_2$ (0.16 g, 0.392 mmol) in acetonitrile (25 cm^3) provided a clear solution. Addition of dibenzo-18-crown-6 (0.12 g, 0.333 mmol) in acetonitrile (25 cm^3) to this solution was followed by warming (40 °C) and stirring for 6 h. Removal of solvent from the resulting yellow solution gave a yellow micro-crystalline solid which was washed with toluene and dried *in vacuo*. Recrystallisation from $MeCN/CH_2Cl_2$ provided yellow needle crystals of an adduct containing three molecules of acetonitrile per Gd. Yield (based on $GdCl_3(THF)_2$) 0.30 g, 74%; m.p. 270–272 °C (decomp.). *Anal.* Calc. for $C_{26}H_{33}N_3O_6GdCl_8Sb$: C, 29.85; H, 3.18; N, 4.02; Cl, 27.11. Found: C, 29.44; H, 3.09; N, 3.99; Cl, 27.03%. $\bar{\nu}_{max}$ (cm^{-1}): (C–C)/(C–O–C) 1324, 1250, 1192, 1123, 1083, 1061, 1051, 1026, 951, 857, 840, (CN) 2304, 2275, 2249, (SbCl) 345, (GdCl) 278 (Nujol).

X-ray structural analysis

$C_{22}H_{27}NO_6Cl_8GdSb \cdot 2C_2H_3N$, $M = 964.1 + 82.1$, triclinic, space group $P\bar{1}$, $a = 8.024(3)$, $b = 15.024(7)$, $c = 17.371(8)$ Å, $\alpha = 76.10(4)$, $\beta = 86.87(3)$, $\gamma = 75.53(3)°$, U = 1968.3 Å^3, Z = 2, $D_c = 1.77$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 2.94 mm^{-1}, $T = 290$ K, $R = 0.035$ for 6121 unique observed ($I/\sigma(I) \geq 2.0$) reflections.

The air-sensitive crystal was mounted in a Lindemann tube. Data were collected with a Siemens R3m four circle diffractometer in ω–2θ mode. Maximum 2θ was 50° with scan range $\pm 0.75°(\omega)$ around the Kα_1–Kα_2 angles, scan speed 3.6–15°(ω) min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Ranges of *hkl* were: 0/9; −15/17; −20/20. Three standard reflections were monitored every 200 reflections, and showed no change during data collection. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($26 < 2\theta < 28°$). The 6964 reflections were processed using profile analysis to give 6923 unique reflections ($R_{int} = 0.018$), of which 6121 were considered observed ($I/\sigma(I) \geq 2.0$). These were corrected for Lorentz, polarisation and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.44 and 0.58. Crystal dimensions were 0.23×0.30×1.10 mm.

No systematic reflection conditions; space group $P\bar{1}$ was selected and shown to be correct by the successful refinement. Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found by E-map expansion and successive Fourier syntheses, including one molecule of acetonitrile solvent and a second molecule distributed over two sites (estimated occupancies 0.5 each). Anisotropic temperature factors were used for all non-H atoms, apart from the part-occupied solvent. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.08$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; the methyl group of the ordered solvent was treated as a rigid CH_3 unit; those on the other solvent molecules were not included. Final refinement was on F by least-squares methods refining 398 parameters, including an extinction parameter (final value 0.00175(12)). Largest positive and negative peaks on a final difference Fourier synthesis were of height 1.0 and −1.8 e Å^{-3} (all near the heavy atoms).

A weighting scheme of the form $w = 1/(\sigma^2(F) + gF^2)$ with $g = 0.007$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.035$, $R_w = 0.061$, $S = 0.69$; R for all reflections = 0.040. Maximum shift/error in final cycle was 0.014. Computing was with SHELXTL PLUS [9] on a DEC Microvax-II. Scattering factors in the analytical form and anomalous dispersion factors were taken from International Tables [10] (stored in the program). The final atomic positional parameters are listed in Table 1.

Results and discussion

The use of $GdX_3 \cdot 6H_2O$ ($X = Cl^-$, NO_3^-) as starting materials in the preparation of gadolinium(III)–crown ether compounds is bedevilled by the strong retention of water molecule(s) and/or nitrate anions coordinated to the metal. As an alternative anhydrous halide source, and one conveniently soluble in organic solvents, we decided to seek a suitable THF adduct. Removal of water from commercial gadolinium(III) chloride hexahydrate was effected by the conventional treatment with thionyl chloride [11]. Recrystallisation of the crude product from boiling THF in the presence of charcoal provided white crystals of the analytically pure bis-adduct $GdCl_3(THF)_2$ [12]. Interestingly only two such adducts have been reported in the literature; both involve an O-donor ligand and a seven-coordinate metal geometry, i.e. $GdCl_3$(dimethoxyethane)$_2$ [13] and $GdCl_2Ph(THF)_4$ [14].

Treatment of $GdCl_3(THF)_2$ with $SbCl_5$ and dibenzo-18-crown-6 (1:1.1) in acetonitrile provided the title compound in good yield (74%) as bright yellow needle crystals. These rapidly lose CH_3CN and break down to an amorphous solid on exposure to air and need to be handled under a dinitrogen atmosphere. The IR spectrum shows typical coordinated ligand bands at 1250, 1192, 1026, 951, 840 ν(C–C)/ν(C–O–C) (oxacrown) and 2304, 2275, 2249 ν(C≡N) (acetonitrile) cm^{-1} and, in the low frequency region, characteristic broad intense bands at 345 ν(Sb–Cl) and 278 ν(GdCl) cm^{-1}.

TABLE 1. Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U^a
Gd(1)	1571.1(2)	895.9(1)	2135.0(1)	39(1)*
Cl(1)	4404.5(17)	−302.3(10)	2779.9(9)	63(1)*
Cl(2)	−1092.6(15)	1253.2(9)	1148.3(8)	54(1)*
O(1)	3159(5)	1782(3)	1022(2)	52(1)*
O(4)	3386(4)	1953(2)	2467(2)	53(1)*
O(7)	1167(5)	1327(3)	3519(2)	58(1)*
O(14)	−224(5)	102(2)	3233(2)	52(1)*
O(17)	1191(4)	−737(2)	2080(2)	49(1)*
O(20)	2754(4)	203(2)	869(2)	48(1)*
C(2)	4192(8)	2402(5)	1150(4)	67(2)*
C(3)	4851(7)	2024(4)	1974(4)	64(2)*
C(5)	3750(8)	1824(4)	3297(3)	67(2)*
C(6)	2077(9)	1966(4)	3724(3)	68(2)*
C(8)	−289(7)	1228(4)	3965(4)	57(2)*
C(9)	−1005(9)	1741(5)	4529(3)	79(3)
C(10)	−2454(9)	1528(5)	4952(4)	83(3)*
C(11)	−3126(8)	813(6)	4836(4)	80(3)*
C(12)	−2421(7)	314(4)	4268(3)	64(2)*
C(13)	−1040(6)	540(4)	3830(3)	51(2)*
C(15)	−637(8)	−768(4)	3194(4)	67(2)*
C(16)	856(8)	−1327(4)	2824(3)	62(2)*
C(18)	2429(7)	−1279(3)	1612(3)	59(2)*
C(19)	2375(7)	−670(3)	792(3)	55(2)*
C(21)	2811(6)	854(3)	148(3)	47(2)*
C(22)	2672(7)	706(5)	−593(3)	64(2)*
C(23)	2778(7)	1448(5)	−1262(3)	70(2)*
C(24)	3013(7)	2293(5)	−1171(3)	71(2)*
C(25)	3132(7)	2437(4)	−425(3)	61(2)*
C(26)	3034(6)	1721(4)	232(3)	51(2)*
N(101)	−222(6)	2597(3)	2069(3)	67(2)*
C(101)	−982(7)	3358(4)	2041(4)	66(2)*
C(102)	−1905(10)	4326(5)	1994(5)	94(3)*
Sb(1)	2549.0(5)	5261.7(2)	3179.8(2)	57(1)*
Cl(3)	4354.1(22)	6173.0(11)	2400.0(11)	77(1)*
Cl(4)	141.2(21)	6338.7(11)	2459.0(11)	79(1)*
Cl(5)	2828.9(27)	4354.0(11)	2208.6(11)	86(1)*
Cl(6)	698.1(27)	4371.2(12)	3934.7(12)	88(1)*
Cl(7)	4984.5(25)	4183.4(13)	3855.5(11)	92(1)*
Cl(8)	2199.5(25)	6184.4(12)	4133.2(11)	83(1)*
N(001)	2760(11)	2133(5)	5565(4)	107(4)*
C(001)	2945(8)	2793(5)	5717(3)	70(3)*
C(002)	3166(11)	3671(7)	5861(6)	108(4)*
N(201)^b	8046(51)	3514(32)	9631(34)	348(37)
C(201)^b	7007(51)	4086(32)	9822(34)	166(10)
C(202)^b	5677(51)	4817(32)	10066(34)	400(39)
N(301)^b	8231(19)	3565(10)	9636(9)	93(4)
C(301)^b	8821(19)	4133(10)	9753(9)	162(9)
C(302)^b	9578(19)	4860(10)	9903(9)	229(16)

^{a}Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. ^{b}Occupancy 0.5

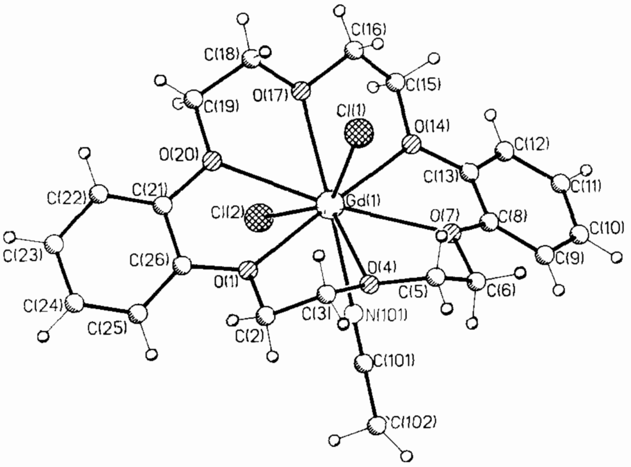

Fig. 1. Perspective view of the [GdCl$_2$(dibenzo-18-crown-6)-(MeCN)]$^+$ cation showing the atom labelling scheme

The structure of the title compound consists of discrete [GdCl$_2$(dibenzo-18-crown-6)(MeCN)]$^+$ cations and SbCl$_6$$^-$ anions with two further acetonitrile (solvate) molecules trapped in the lattice. The cation is shown in Fig. 1 together with the atom labelling used. Selected bond lengths and angles are listed in Table 2. The gadolinium atoms sits in the crown cavity and is bonded to the six oxygen atoms of the oxacrown, one solvent (MeCN) molecule and two chlorine atoms located on opposite sides of the ring plane, Cl(1)–Gd–Cl(2) 147.4(1)°; it is essentially coplanar (+0.03(66) Å) with the three coordinated ligand atoms Cl(1), Cl(2), N(101). The Gd–O bond distances lie in the range 2.545(4)–2.683(4) Å and are similar to those in other nine-coordinate crown species, e.g. [GdCl$_2$(18-crown-6)-(EtOH)]$^+$ [8] (Gd–O 2.497(6)–2.608(5) Å) and [GdCl(18-crown-6)(H$_2$O)$_2$]$^{2+}$ [7] (Gd–O 2.472(6)–2.565(7) Å). These are almost as long as the Gd–Cl bonds indicating relatively weak interactions with the ether oxygen atoms. The overall geometry (Fig. 2) can best be described as capped hexagonal planar, bent slightly about the O(1)–O(14) axis away from the doubly-capped side; the largest deviations from the mean plane through the six oxygen atoms of the ring are ±0.4 Å. This arrangement leaves the two benzene ring segments of the crown folded over towards the two single ligands and into what is clearly the more sterically occupied side of the ring. The angle between the benzene ring planes is 50.3°. The non-equivalence of the metal–chlorine bond distances Gd–Cl(2) > Gd–Cl(1) is seen as a direct result of this steric crowding. The gadolinium atom in the analogous [GdCl$_2$(18-crown-6)(EtOH)]$^+$ cation [8] enjoys a somewhat similar ligand environment but with one subtle difference. Once more two diametrically opposite ring oxygen atoms are displaced much further from the least-squares plane ($O_{crown} \times 6$) than the other four but, in this instance, these now lie on the *same* side as the Cl/EtOH pair of ligands with the ring folded in the reverse direction and towards the single chlorine atom on the opposite side; again the two Gd–Cl bond distances are non-equivalent.

TABLE 2. Selected bond lengths (A) and angles (°)

Gd(1)–Cl(1)	2.632(2)	Gd(1)–Cl(2)	2.679(2)
Gd(1)–O(1)	2.545(4)	Gd(1)–O(4)	2.582(4)
Gd(1)–O(7)	2.620(4)	Gd(1)–O(14)	2.569(4)
Gd(1)–O(17)	2.570(4)	Gd(1)–O(20)	2.683(4)
Gd(1)–N(101)	2.579(5)	O(1)–C(2)	1.452(9)
O(1)–C(26)	1.409(6)	O(4)–C(3)	1.426(7)
O(4)–C(5)	1.444(7)	O(7)–C(6)	1.457(9)
O(7)–C(8)	1.386(6)	O(14)–C(13)	1.405(6)
O(14)–C(15)	1.445(8)	O(17)–C(16)	1.436(6)
O(17)–C(18)	1.462(6)	O(20)–C(19)	1.455(7)
O(20)–C(21)	1.399(5)	C(2)–C(3)	1.481(9)
C(5)–C(6)	1.490(9)	C(8)–C(9)	1.401(9)
C(8)–C(13)	1.388(9)	C(9)–C(10)	1.405(10)
C(10)–C(11)	1.375(12)	C(11)–C(12)	1.390(10)
C(12)–C(13)	1.377(8)	C(15)–C(16)	1.492(8)
C(18)–C(19)	1.493(7)	C(21)–C(22)	1.373(8)
C(21)–C(26)	1.399(8)	C(22)–C(23)	1.420(8)
C(23)–C(24)	1.374(11)	C(24)–C(25)	1.376(9)
C(25)–C(26)	1.381(7)	N(101)–C(101)	1.145(7)
C(101)–C(102)	1.443(9)	Sb(1)–Cl(3)	2.386(2)
Sb(1)–Cl(4)	2.376(2)	Sb(1)–Cl(5)	2.381(2)
Sb(1)–Cl(6)	2.377(2)	Sb(1)–Cl(7)	2.361(2)
Sb(1)–Cl(8)	2.367(2)		
Cl(1)–Gd(1)–Cl(2)	147.4(1)	Cl(1)–Gd(1)–O(1)	93.9(1)
Cl(2)–Gd(1)–O(1)	89.4(1)	Cl(1)–Gd(1)–O(4)	75.7(1)
Cl(2)–Gd(1)–O(4)	132.6(1)	O(1)–Gd(1)–O(4)	61.1(1)
Cl(1)–Gd(1)–O(7)	84.0(1)	Cl(2)–Gd(1)–O(7)	121.6(1)
O(1)–Gd(1)–O(7)	121.0(1)	O(4)–Gd(1)–O(7)	61.4(1)
Cl(1)–Gd(1)–O(14)	90.2(1)	Cl(2)–Gd(1)–O(14)	87.8(1)
O(1)–Gd(1)–O(14)	175.8(1)	O(4)–Gd(1)–O(14)	119.1(1)
O(7)–Gd(1)–O(14)	58.4(1)	Cl(1)–Gd(1)–O(17)	75.4(1)
Cl(2)–Gd(1)–O(17)	74.8(1)	O(1)–Gd(1)–O(17)	119.5(1)
O(4)–Gd(1)–O(17)	151.0(1)	O(7)–Gd(1)–O(17)	116.9(1)
O(14)–Gd(1)–O(17)	62.7(1)	Cl(1)–Gd(1)–O(20)	81.8(1)
Cl(2)–Gd(1)–O(20)	72.4(1)	O(1)–Gd(1)–O(20)	58.3(1)
O(4)–Gd(1)–O(20)	112.7(1)	O(7)–Gd(1)–O(20)	165.7(1)
O(14)–Gd(1)–O(20)	123.5(1)	O(17)–Gd(1)–O(20)	61.2(1)
Cl(1)–Gd(1)–N(101)	140.9(1)	Cl(2)–Gd(1)–N(101)	71.7(1)
O(1)–Gd(1)–N(101)	80.8(1)	O(4)–Gd(1)–N(101)	67.8(1)
O(7)–Gd(1)–N(101)	66.7(1)	O(14)–Gd(1)–N(101)	95.4(1)
O(17)–Gd(1)–N(101)	140.5(1)	O(20)–Gd(1)–N(101)	124.8(1)
C(2)–O(1)–C(26)	115.8(4)	C(3)–O(4)–C(5)	113.0(4)
C(6)–O(7)–C(8)	115.0(5)	C(13)–O(14)–C(15)	116.6(4)
C(16)–O(17)–C(18)	111.2(3)	C(19)–O(20)–C(21)	114.3(4)
O(1)–C(2)–C(3)	106.1(5)	O(4)–C(3)–C(2)	106.4(4)
O(4)–C(5)–C(6)	107.9(5)	O(7)–C(6)–C(5)	106.1(5)
O(7)–C(8)–C(9)	125.7(6)	O(7)–C(8)–C(13)	114.8(5)
O(14)–C(13)–C(8)	113.5(4)	O(14)–C(15)–C(16)	107.4(5)
O(17)–C(16)–C(15)	107.6(4)	O(17)–C(18)–C(19)	106.8(4)
O(20)–C(19)–C(18)	106.3(5)	O(1)–C(26)–C(21)	114.6(4)
Gd(1)–N(101)–C(101)	178.4(5)	N(101)–C(101)–C(102)	178.5(7)

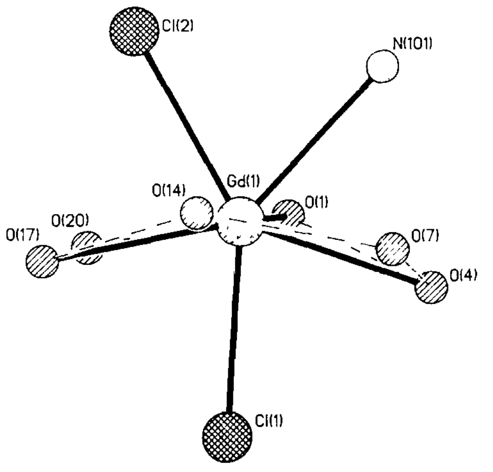

Fig 2 Environment of the central Gd atom in the $[GdCl_2(dibenzo\text{-}18\text{-}crown\text{-}6)(MeCN)]^+$ cation

TABLE 3 Torsion angles (°)

	This work[a]	Uncomplexed ligand	Na^+ complex
C(26)–O(1)–C(2)–C(3)	−152.8	−158.7	−166.6
O(1)–C(2)–C(3)–O(4)	−53.7	164.3	−61.7
C(2)–C(3)–O(4)–C(5)	−165.4	176.0	−179.6
C(3)–O(4)–C(5)–C(6)	168.1	103.4	174.7
O(4)–C(5)–C(6)–O(7)	53.9	−77.3	65.5
C(5)–C(6)–O(7)–C(8)	169.1	−74.1	179.3
C(6)–O(7)–C(8)–C(13)	−173.1	155.0	177.7
O(7)–C(8)–C(13)–O(14)	−2.9	−5.0	−1.3
C(8)–C(13)–O(14)–C(15)	164.9	−174.1	−178.5
C(13)–O(14)–C(15)–C(16)	−154.0	158.7	−176.7
O(14)–C(15)–C(16)–O(17)	−54.5	−164.3	−69.9
C(15)–C(16)–O(17)–C(18)	−169.8	−176.0	−179.0
C(16)–O(17)–C(18)–C(19)	167.0	−103.4	176.5
O(17)–C(18)–C(19)–O(20)	56.7	77.3	61.1
C(18)–C(19)–O(20)–C(21)	178.1	74.1	174.2
C(19)–O(20)–C(21)–C(26)	175.0	−155.0	180.0
O(20)–C(21)–C(26)–O(1)	−0.1	5.0	−1.0
C(21)–C(26)–O(1)–C(2)	150.4	174.1	172.5

[a] e.s.d.s = 0.2°.

The oxacrown dimensions, e.g.

C–C (carbon(sp^3)atoms)	mean 1.489(5) Å
C–O (carbon(sp^3)atoms)	mean 1.447(5) Å
C–O (carbon(sp^2)atoms)	mean 1.399(5) Å
C–C (carbon(sp^2)atoms)	mean 1.386(15) Å
Subtended OGdO, (via C(sp^3))	mean 61.6(5)°
(via C(sp^2))	mean 58.3(1)°
OCC (carbon(sp^3)atoms)	mean 106.8(5)°
COC (carbon(sp^3)atoms)	mean 114.3(5)°

are indicative of an unstrained ring arrangement and are closely similar to those observed in both the 'free' ligand [15] and in a typical metal complex, i.e. [Na(dibenzo-18-crown-6)]Br·$6H_2O$ [16]. But there is a conspicuous change in ring conformation associated with insertion of the gadolinium atom in the cavity. For means of comparison the torsion angles around the oxacrown ring for the title compound, uncomplexed ligand and [Na(dibenzo-18-crown-6)]Br·$2H_2O$ are listed in Table 3. The $SbCl_6^-$ anions have a regular octahedral geometry with Sb–Cl bonds in the range 2.361(2)–2.386(2), mean 2.375(5) Å.

Supplementary material

Full tables of bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors are available from the authors on request.

Acknowledgement

We wish to thank the SERC for financial support of this work.

References

1 J.-C G Bunzli, *Coord Chem Rev, 60* (1984) 191; J.-C.G. Bunzli, B Klein, D. Wessner and N.W Alcock, *Inorg Chim Acta, 59* (1982) 269, R.D. Rogers and L K. Kurihara, *J Inclusion Phenom , 4* (1986) 351; R D Rogers, L K. Kurihara and E J. Voss, *Inorg Chem, 26* (1987) 2360, R.D Rogers and L K Kurihara, *Inorg Chim Acta, 129* (1987) 277; D.A Atwood, S G Bott and J.L. Atwood, *J. Coord Chem, 17* (1987) 93; R D Rogers, A N Rollins and M.M. Benning, *Inorg Chem , 27* (1988) 3826, and refs. therein

2 G R Willey, M.T Lakin and N W Alcock, *J Chem Soc , Chem. Commun ,* (1992) 1619.

3 J D.J. Backer-Dirks, J E Cooke, A.M R Galas, J S Ghotra, C J Gray, F A Hart and M B. Hursthouse, *J Chem Soc., Dalton Trans,* (1980) 2191

4 R.D Rogers and L.K Kurihara, *Inorg Chim Acta, 130* (1987) 131.

5 F Nicolo, J -C G. Bunzli and G. Chapius, *Acta Crystallogr., Sect C, 44* (1988) 1733

6 Y. Shiping, W Genglin, W. Honggen and Y. Xinkan, *Polyhedron, 10* (1991) 1889

7 R D Rogers and L.K. Kurihara, *Inorg Chem , 26* (1987) 1498

8 E Forsellini, F Benetollo, G. Bombieri, A Cassol and G De Paoli, *Inorg Chim Acta, 109* (1985) 167

9 G.M Sheldrick, *SHELXTL PLUS User's Manual,* Nicolet Instrument Co., Madison, WI, USA, 1986.

10 *International Tables for X-Ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974 (present distributor Kluwer, Dordrecht, Netherlands)

11 A R Pray, *Inorg Synth , 5* (1957) 153; J. Shamir, *Inorg Chim Acta, 156* (1989) 163.

12 G R Willey and M D Rudd, X-ray crystal structure determination in progress.

13 G. Wei, H Gao, Z. Jin and Q Shen, *J Struct Chem (Engl Transl), 8* (1989) 61

14 G Lin, Z. Jin, Y Zhang and W. Chen, *J Organomet. Chem , 396* (1990) 307

15 D Bright and M R Truter, *J Chem Soc B,* (1970) 1544.

16 M A. Bush and M.R. Truter, *J Chem Soc B,* (1971) 1440