Journal of Inclusion Phenomena and Molecular Recognition in Chemistry 7: 277–287, 1989.

f-Element/Crown Ether Complexes: 21.* Conformational Changes in Metal Complexed versus Hydrogen Bonded Benzo-15-crown-5 in the Structure of $[Y(OH_2)_3(NCMe)(benzo\text{-}15\text{-}crown\text{-}5)][ClO_4]_3\cdot benzo\text{-}15\text{-}crown\text{-}5\cdot CH_3CN$

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(Received: 10 November 1987)

Abstract. Crystalline $[Y(OH_2)_3(NCMe)(benzo\text{-}15\text{-}crown\text{-}5)][ClO_4]_3\cdot benzo\text{-}15\text{-}crown\text{-}5\cdot CH_3CN$ can be obtained by slowly cooling a reaction mixture of $Y(ClO_4)_3\cdot n\ H_2O$ with benzo-15-crown-5 in a solution of acetonitrile and methanol (3 : 1) from 60°C to room temperature. The crystal structure of this complex has been determined at −150 and 20°C. The complex is triclinic, $P\bar{1}$. At −150°C the cell parameters are $a = 11.986(4)$, $b = 12.071(7)$, $c = 16.364(5)$ Å, $\alpha = 93.56(3)$, $\beta = 98.68(3)$, $\gamma = 109.68(4)°$, vol = 2187 Å^3, and $D_{calc} = 1.61$ g cm^{-3} for $Z = 2$ formula units. 3633 independently observed $[F_o \geqslant 5\sigma(F_o)]$ reflections were used in the final least-squares refinement leading to an agreement index of $R = 0.048$. The Y(III) ion coordination geometry approximates a tricapped trigonal prism with three water molecules and three benzo-15-crown-5 oxygen atoms forming the prism, with the two remaining benzo-15-crown-5 oxygen atoms and the acetonitrile molecule completing the coordination as capping atoms. The three water molecules hydrogen bond a second crown ether molecule and two of the perchlorate anions. The two acetonitrile molecules have contacts with perchlorate oxygen atoms close enough for some weak interaction. One perchlorate is ordered, one is partially disordered as is the coordinated solvent molecule, and the third anion is totally disordered. The two unique crown ether molecules have distinctively different conformations.

Key words. Benzo-15-crown-5, yttrium perchlorate, low temperature crystal structure, hydrogen bonding, complexation.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82073 (30 pages).

1. Introduction

18-crown-6 has a cavity size suited for in-cavity complexation of early lanthanide(III) ions and the crystal structures of $[M(NO_3)_3(18\text{-}crown\text{-}6)]$ (M = La [2], Nd [3]) and $[Nd(NO_3)_2(18\text{-}crown\text{-}6)]_3[Nd(NO_3)_6]$ [4] have been reported. As the lanthanide ion gets smaller (and heavier) the structurally characterized complexes reveal more distortion in the crown ether as it wraps the metal ion as in $[MCl(OH_2)_2(18\text{-}crown\text{-}6)]Cl_2\cdot 2\,H_2O$ (M = Sm, Gd, Tb) [5], $[GdCl_2(OHEt)(18\text{-}crown\text{-}6)]Cl$ [6], and in $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-}crown\text{-}6)]_2Cl_7\cdot 2\,H_2O$ (M = Dy, Y) [7]. In the last example rearrangement can occur, totally excluding the crown ether, and the resulting $[Dy(OH_2)_8]Cl_3\cdot 18\text{-}crown\text{-}6\cdot 4\,H_2O$ [8] has been characterized.

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* For Part 20, see reference [1].

We and others have begun exploring the use of smaller crown ethers, 15-crown-5 and the partially constrained benzo-15-crown-5, as complexing agents for the mid to late lanthanides. Our work has focused on reaction of these with hydrated lanthanide salts (and the similar Y^{3+}). Very few complexes of these crown ethers directly coordinated to a lanthanide element have been structurally characterized. Lee *et al.*, have characterized $[M(OH_2)_4(15\text{-crown-}5)][ClO_4]_3\cdot 15\text{-crown-}5\cdot H_2O$ (M = La, Sm) [9] and $Eu(NO_3)_3(15\text{-crown-}5)$ [10], $[Pr_2(CF_3CO_2)_3(OH)(15\text{-crown-}5)_2][Pr_2(CF_3CO_2)_8]$ [11], and $[YbCl_2(15\text{-crown-}5)][AlCl_2Me_2]$ [12] have also been reported. We have for the most part been unsuccessful in this regard, crystallizing only second sphere, hydrogen bonded complexes: $[M(OH_2)_8]Cl_3\cdot 15\text{-crown-}5$ (M = Gd [7], Y [14, 15], Lu [13]), $[Y(NO_3)_2(OH_2)_5][NO_3]\cdot 2(15\text{-crown-}5)$ [16], $[Y(NO_3)_2(OH_2)_3]\cdot 1.5(15\text{-crown-}5)\cdot Me_2CO$ [1], and $[Y(NO_3)_3(OH_2)_2(NCMe)]$-$[Y(NO_3)_3(OH_2)_2(OHMe)]\cdot 2(\text{benzo-}15\text{-crown-}5)\cdot OHMe$ [17]. In addition King has reported the synthesis of $Ln(NO_3)_3(OH_2)_3\cdot \text{benzo-}15\text{-crown-}5\cdot Me_2CO$ [18].

Recently, we were successful in the synthesis and structural characterization of the title complex. This complex bears a striking similarity to the $[M(OH_2)_4(15\text{-crown-}5)][ClO_4]_3\cdot 15\text{-crown-}5\cdot H_2O$ structures studied by Lee and is the subject of this report.

2. Experimental

2.1. SYNTHESIS AND CRYSTALLIZATION OF $[Y(OH_2)_3(NCMe)(\text{BENZO-}15\text{-CROWN-}5)]$-$[ClO_4]_3\cdot \text{BENZO-}15\text{-CROWN-}5\cdot CH_3CN$

1 mmol of benzo-15-crown-5 in 5 mL of a 3 : 1 mixture of acetonitrile and methanol was added to a stirred solution of 1 mmol of $Y(ClO_4)_3\cdot n\ H_2O$ in 5 mL of the same solvent mixture. The reaction mixture was heated to 60°C for 1 h, cooled to 22°C, concentrated to 2/3 of its original volume, and stored in a covered flask at 5°C. Crystals formed over a period of several weeks at this temperature. The transparent crystals lose solvent slowly when removed from the solvent mixture and turn opaque over a period of approximately three days. One crystal coated in epoxy prior to data collection at room temperature experienced a linear 10% decay in intensity over a period of seven days. Analysis: Calcd. for $[Y(OH_2)_3(NCMe)(\text{benzo-}15\text{-crown-}5)][ClO_4]_3\cdot \text{benzo-}15\text{-crown-}5\cdot CH_3CN$: C, 36.26; H, 4.94; N, 2.64; Found: C, 36.72; H, 5.47; N, 1.87. Variations in calculated and experimental values may have resulted from loss of CH_3CN during analysis.

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT FOR $[Y(OH_2)_3(NCMe)(\text{BENZO-}15\text{-CROWN-}5)][ClO_4]_3\cdot \text{BENZO-}15\text{-CROWN-}5\cdot CH_3CN$

Transparent single crystals of the title complex were mounted on pins and transferred to the goniomenter. For one data set the crystal was cooled to −150°C during data collection using a stream of cold nitrogen gas, a second was collected at 20°C. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Statistical tests indicated that the space group was centric and the subsequent solution and successful refinement of the structure in the space group $P\bar{1}$ confirmed this despite the presence of disorder. A summary of data collection is given in Table I.

Table I. Crystal data and summary of intensity data collection and structure refinement

Cmpd.	$[Y(OH_2)_3(NCMe)(\text{benzo-15-crown-5})][ClO_4]_3 \cdot \text{benzo-15-crown-5} \cdot CH_3CN$	
Color/Shape	clear/parallelepiped	clear/fragment
Mol wt.	1060	1060
Space group	$P\bar{1}$	$P\bar{1}$
Temp., °C	−150	20
Cell Constants[a]		
a, Å	11.986(4)	12.121(1)
b, Å	12.071(7)	12.269(1)
c, Å	16.364(5)	16.467(2)
α, deg	93.56(3)	92.910(8)
β, deg	98.68(3)	99.264(8)
γ, deg	109.68(4)	109.846(8)
Cell vol, Å^3	2187	2259
Formula units/unit cell	2	2
D_{calc}, g cm^{-3}	1.61	1.56
μ(calc), cm^{-1}	15.4	14.9
Diffractometer/Scan	Enraf-Nonius CAD4/$\theta - 2\theta$	Enraf-Nonius CAD4/$\theta - 2\theta$
Range of relative transm. factors, %	77/100	85/100
Radiation, graphite monochromator	MoK_α ($\lambda = 0.71073$)	MoK_α ($\lambda = 0.71073$)
Max crystal dimensions, mm	0.25 × 0.32 × 0.40	0.23 × 0.25 × 0.40
Scan width	$0.80 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$
Standard reflections	600, 040, (0, 0, 12)	600, 040, 009
Decay of standards	±2%	−10%
Reflections measured	6436	7938
2θ range, deg	$2 \leqslant 2\theta \leqslant 47$	$2 \leqslant 2\theta \leqslant 50$
Range of h, k, l	+13, ±13, ±18	+14, ±14, ±19
Reflections observed $[F_o \geqslant 5\sigma(F_o)]$[b]	3633	4376
Computer Programs[c]	SHELX [19]	SHELX [19]
Structure Solution	Heavy atom techniques	Coordinates from $T = -150$
No. of parameters varied	572	572
Weights	$[\sigma(F_o)^2 + 0.00004F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00009F_o^2]^{-1}$
GOF	1.24	1.40
$R = \Sigma\lVert F_o\rvert \cdot \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.048	0.065
R_w	0.050	0.067
Largest feature final diff. map	0.8e^-/Å	0.7e^-/Å

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[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 18°$ (for both).

[b] Corrections: Lorentz, polarization and absorption (empirical, psi scan).

[c] Neutral atom scattering factors and anomalous dispersion corrections from ref. [20].

The room temperature data was used first after a correction for the linear 10% decay in reflection intensity. The perchlorate anions and the coordinated solvent molecule were found to be disordered. In an attempt to better resolve the disorder a low temperature data set was collected. The disorder was still present and was presumed to be static in nature. In the final disorder model, one $[ClO_4]^-$ anion is completely ordered (Cl(1), O(14)—O(17)), anchored by solvent coordinated water molecule hydrogen bonding. In the second anion (Cl(2), O(18)—O(21)), one oxygen atom is ordered, again anchored by hydrogen bonds, however, three

Table II. Final fractional coordinates for YPCB15 (−150°C)

Atom	x/a	y/b	z/c
Y	0.24822(6)	0.19753(6)	0.78133(4)
O(1)	0.0875(4)	0.2260(4)	0.8510(2)
O(2)	0.0445(4)	0.0971(4)	0.7075(3)
O(3)	0.2370(4)	0.1131(4)	0.6404(3)
O(4)	0.2565(4)	−0.0049(4)	0.7668(3)
O(5)	0.1792(4)	0.0681(4)	0.8901(3)
O(6)	0.3183(4)	0.3741(4)	0.8715(3)
O(7)	0.4198(4)	0.3056(4)	0.7323(3)
O(8)	0.1918(4)	0.3288(4)	0.6997(3)
O(9)	0.4250(4)	0.4114(4)	0.5826(3)
O(10)	0.3568(4)	0.5428(4)	0.6975(3)
O(11)	0.5219(4)	0.5369(4)	0.8492(3)
O(12)	0.6553(4)	0.3971(4)	0.7998(3)
O(13)	0.6043(4)	0.3454(4)	0.6243(3)
N(1)	0.4229(4)	0.1971(4)	0.8733(3)
N(2)	−0.1007(7)	0.7356(6)	0.7061(4)
C(1)	−0.0333(6)	0.1962(6)	0.7999(4)
C(2)	−0.0595(6)	0.0834(6)	0.7465(4)
C(3)	0.0232(6)	0.0098(6)	0.6365(4)
C(4)	0.1200(6)	0.0668(6)	0.5869(4)
C(5)	0.3087(6)	0.0395(6)	0.6373(4)
C(6)	0.2672(6)	−0.0609(6)	0.6895(4)
C(7)	0.2115(6)	−0.0918(6)	0.8215(4)
C(8)	0.2239(6)	−0.0267(6)	0.9052(4)
C(9)	0.1448(6)	0.1199(6)	0.9552(4)
C(10)	0.0904(6)	0.2006(6)	0.9335(4)
C(11)	0.0490(6)	0.2570(6)	0.9902(4)
C(12)	0.0652(6)	0.2326(6)	1.0730(4)
C(13)	0.1248(6)	0.1566(6)	1.0957(4)
C(14)	0.1643(6)	0.0980(6)	1.0377(4)
C(15)	0.3411(6)	0.4691(6)	0.5564(4)
C(16)	0.3752(7)	0.5786(6)	0.6169(4)
C(17)	0.4197(7)	0.6388(6)	0.7649(5)
C(18)	0.5409(7)	0.6352(6)	0.8025(5)
C(19)	0.6284(6)	0.5330(7)	0.9000(5)
C(20)	0.7156(6)	0.5068(6)	0.8517(5)
C(21)	0.7351(6)	0.3684(7)	0.7532(5)
C(22)	0.6661(7)	0.2831(7)	0.6765(5)
C(23)	0.5214(6)	0.2782(7)	0.5552(4)
C(24)	0.4258(6)	0.3177(6)	0.5310(4)
C(25)	0.3412(7)	0.2607(7)	0.4592(5)
C(26)	0.3515(8)	0.1656(7)	0.4144(5)
C(27)	0.4456(8)	0.1274(7)	0.4399(5)
C(28)	0.5326(7)	0.1829(7)	0.5116(5)
C(29)	0.504(1)	0.213(1)	0.9314(7)
C(30)[a]	0.612(1)	0.224(1)	0.9953(8)
C(30)′	0.547(1)	0.253(1)	1.0268(9)
C(31)	−0.0760(8)	0.6608(8)	0.6747(5)
C(32)	−0.0429(9)	0.5669(7)	0.6361(5)
Cl(1)	−0.0991(2)	0.2481(2)	0.5364(1)
Cl(2)	0.1210(2)	0.5515(2)	0.8793(1)
Cl(3)	0.6115(2)	−0.0009(2)	0.8225(1)

Table II. (*Continued*)

Atom	*x/a*	*y/b*	*z/c*
O(14)	−0.0310(4)	0.3138(4)	0.6157(3)
O(15)	−0.0183(4)	0.2278(4)	0.4858(3)
O(16)	−0.1802(4)	0.1358(4)	0.5505(3)
O(17)	−0.1654(4)	0.3148(4)	0.4960(3)
O(18)	0.2033(4)	0.5100(4)	0.9319(3)
O(191)	0.003(1)	0.5073(9)	0.8896(6)
O(201)	0.139(1)	0.670(1)	0.8993(7)
O(211)	0.134(1)	0.5208(9)	0.7945(7)
O(221)	0.6704(8)	−0.0815(8)	0.7857(6)
O(231)	0.7105(9)	0.0947(9)	0.8687(6)
O(241)	0.545(1)	0.036(1)	0.7572(7)
O(251)	0.531(1)	−0.052(1)	0.8795(7)
O(192)	0.011(2)	0.510(2)	0.921(1)
O(202)	0.154(1)	0.665(1)	0.8673(9)
O(212)	0.086(2)	0.470(2)	0.796(1)
O(222)	0.532(2)	−0.007(2)	0.742(1)
O(232)	0.566(2)	−0.060(1)	0.886(1)
O(242)	0.640(2)	−0.099(2)	0.791(2)
O(252)	0.696(2)	0.116(2)	0.839(1)
O(193)	−0.002(2)	0.469(2)	0.878(1)
O(203)	0.187(2)	0.690(2)	0.923(1)
O(213)	0.165(2)	0.588(2)	0.804(1)
O(223)	0.689(2)	−0.028(2)	0.790(1)
O(233)	0.680(2)	0.092(2)	0.908(2)
O(243)	0.543(2)	0.079(2)	0.790(1)
O(253)	0.517(2)	−0.092(2)	0.846(1)

[a] C(30) and C(30)′ are disordered 50%/50%; disorder of the anions is discussed in the text; the major form of each anion is designated as 1.

orientations for the remaining three atoms of this group were observed. One orientation is a major one with occupancies of 0.5 for the three disordered atoms. Two minor orientations were observed with occupancies of 0.25 each. A similar disorder was observed for the third perchlorate anion except that all four oxygen atoms are disordered. Again, however, one orientation predominates (occupancy 0.5, O(22)1—O(25)1) with two minor orientations of 0.25 occupancy each.

The coordinated solvent molecule was also observed to be disordered. Two orientations for the terminal carbon atom C(30) were found and given occupancies of 0.5 each. Two orientations of C(29) could not be resolved due to their close proximity, and as a result the thermal parameter for this atom refined to a fairly large isotropic value ($B = 6.8$ Å^2).

Once the low temperature determination was complete, the coordinates and disorder model developed were used in the refinement of the room temperature data.

The crown hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The remaining hydrogen atoms were not included in the final refinement. Refinement of the nonhydrogen atoms with anisotropic temperature factors (except for N(1) and the disordered atoms) led to the final values of *R* given in Table I. The final values of the positional parameters are given in Table II for the low temperature structure and deposited in Supplementary Material for the room temperature determination.

3. Results and Discussion

Reaction of $Y(ClO_4)\cdot n\ H_2O$ with benzo-15-crown-5 in a 3 : 1 mixture of acetonitrile and methanol produces a complex containing both metal coordinated and hydrogen bonded ethers: $[Y(OH_2)_3(NCMe)$(benzo-15-crown-5)]$[ClO_4]_3$·benzo-15-crown-5·CH_3CN (now referred to as YPCB15). The overall structure is similar to that observed by Lee for 15-crown-5 in $[M(OH_2)_4$(15-crown-5)]$[ClO_4]_3$·15-crown-5·H_2O [9] (M = Sm, La). An ORTEP illustration of the Y(III) ion environment without the perchlorate ions and the noncoordinated CH_3CN molecule is presented in Figure 1 for the low temperature determination. Average distances and angles are reported in Table III. The more accurate low temperature determination will be discussed with parameters for the 20°C study provided in tabular form for comparison.

YPCB15 exists in a hydrogen bonded network. The major hydrogen bond contacts (Table IV) are between the three water molecules and the noncomplexed benzo-15-crown-5 ether. One water molecule (O(7)) donates hydrogen bonds exclusively to the crown ether, the other two donate one to the ether and one each to perchlorate anions. The contact between O(7) and the less basic aryl ether oxygen atom (O(7)···O(9) = 2.831(6) Å) is the longest of all the water donated hydrogen bond contacts. The other aryl ether, O(13), has no hydrogen bonding interactions. The

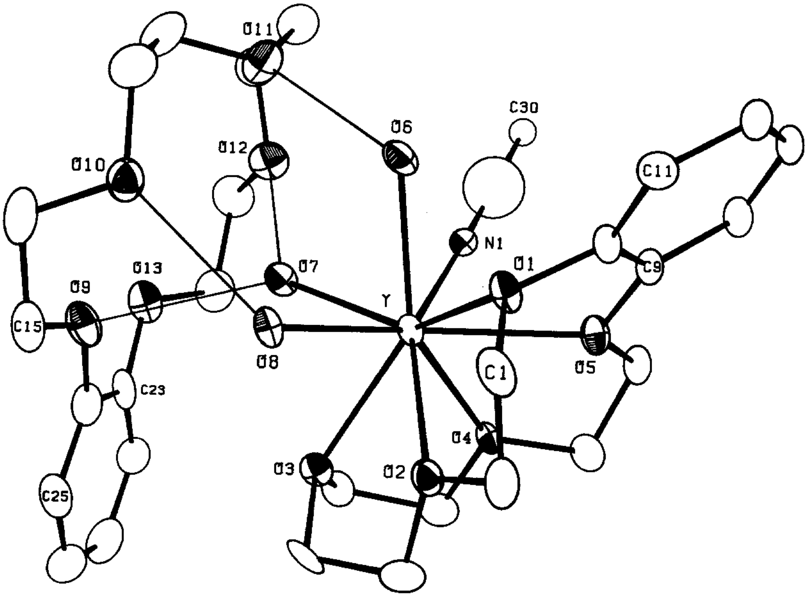

Fig. 1. Y(III) ion environment: 50% probability thermal ellipsoids, H atoms, ClO_4^- anions, and uncoordinated CH_3CN molecule omitted.

Table III. Bond distances (Å) and angles (deg) for YPCB15 (−150° and 20°C)

Atoms	Distance (−150°C)	Distance (20°C)
Y—O(1)	2.487(5)	2.489(6)
Y—O(2)	2.414(4)	2.429(4)
Y—O(3)	2.428(4)	2.427(5)
Y—O(4)	2.477(5)	2.487(5)
Y—O(5)	2.493(4)	2.500(5)
Y—O(6)	2.335(4)	2.355(5)
Y—O(7)	2.323(4)	2.318(5)
Y—O(8)	2.338(5)	2.353(6)
Y—N(1)	2.388(5)	2.408(6)
N(1)—C(29)	1.21(1)	1.16(1)
N(2)—C(31)	1.16(1)	1.14(2)
C(29)—C(30)	1.50(2)	1.54(2)
C(29)—C(30)′	1.56(2)	1.58(2)
C(31)—C(32)	1.46(1)	1.47(2)
O—C(ar)1[a]	1.394(8)	1.378(8)
O—C(ak)1	1.45(1)	1.437(7)
C(ar)—C(ar)1	1.38(1)	1.387(7)
C(ak)—C(ak)1	1.50(1)	1.49(1)
O—C(ar)2	1.380(8)	1.366(5)
O—C(ak)2	1.43(1)	1.43(1)
C(ar)—C(ar)2	1.39(2)	1.38(2)
C(ak)—C(ak)2	1.504(5)	1.48(2)

Atoms	Angle	Angle	Atoms	Angle	Angle
O(1)—Y—O(2)	64.5(1)	64.0(2)	Y—O(1)—C(1)	117.6(4)	118.2(4)
O(1)—Y—O(3)	130.1(1)	129.3(2)	Y—O(1)—C(10)	116.3(4)	116.1(5)
O(2)—Y—O(3)	66.6(1)	66.3(2)	Y—O(2)—C(2)	122.3(3)	122.8(4)
O(1)—Y—O(4)	117.1(1)	116.7(2)	Y—O(2)—C(3)	118.9(4)	119.2(5)
O(2)—Y—O(4)	82.7(2)	82.0(2)	Y—O(3)—C(4)	117.7(4)	118.4(5)
O(3)—Y—O(4)	64.3(1)	64.2(2)	Y—O(3)—C(5)	112.5(3)	112.3(4)
O(1)—Y—O(5)	62.1(2)	62.0(2)	Y—O(4)—C(6)	122.4(4)	122.1(4)
O(2)—Y—O(5)	83.7(1)	82.9(2)	Y—O(4)—C(7)	123.7(4)	123.1(5)
O(3)—Y—O(5)	121.0(1)	120.7(2)	Y—O(5)—C(8)	119.9(4)	120.0(5)
O(4)—Y—O(5)	62.3(2)	62.2(2)	Y—O(5)—C(9)	115.7(4)	115.5(5)
O(1)—Y—O(6)	67.9(1)	68.5(2)	Y—N(1)—C(29)	165.5(7)	163(1)
O(2)—Y—O(6)	126.5(2)	126.9(2)			
O(3)—Y—O(6)	143.9(1)	143.9(2)	N(1)—C(29)—C(30)	172(1)	166(2)
O(4)—Y—O(6)	142.5(1)	142.7(2)	N(1)—C(29)—C(30)′	145(1)	145(2)
O(5)—Y—O(6)	94.9(1)	95.3(2)	N(2)—C(31)—C(32)	179.0(8)	179(1)
O(1)—Y—O(7)	140.9(2)	141.5(2)	C(ar)—O—C(ak)1	117(1)	117(2)
O(2)—Y—O(7)	130.0(1)	130.6(2)	C(ak)—O—C(ak)1	113(2)	114(2)
O(3)—Y—O(7)	70.9(1)	71.2(2)	O—C(ak)—C(ak)1	107(2)	108(2)
O(4)—Y—O(7)	101.6(2)	101.5(2)	C(ar)—C(ar)—C(ar)1	120(1)	120(1)
O(5)—Y—O(7)	142.6(2)	142.5(2)			
O(6)—Y—O(7)	78.2(2)	78.2(2)	O(5)—C(9)—C(10)	114.9(6)	114.8(7)
O(1)—Y—O(8)	79.4(2)	78.5(2)	O(5)—C(9)—C(14)	124.9(7)	126.3(8)
O(2)—Y—O(8)	71.7(1)	72.3(2)	O(1)—C(10)—C(9)	115.5(6)	115.7(7)
O(3)—Y—O(8)	77.0(2)	77.8(2)	O(1)—C(10)—C(11)	122.5(7)	122.5(8)
O(4)—Y—O(8)	139.7(1)	140.3(2)	C(ar)—O—C(ak)2	118(1)	119(1)
O(5)—Y—O(8)	140.5(2)	139.6(2)	C(ak)—O—C(ak)2	113(2)	113(2)
O(6)—Y—O(8)	77.0(1)	76.3(2)	O—C(ak)—C(ak)2	109(3)	110(3)
O(7)—Y—O(8)	74.3(2)	75.2(2)	C(ar)—C(ar)—C(ar)2	120(1)	120(1)
O(1)—Y—N(1)	115.1(2)	115.1(2)			
O(2)—Y—N(1)	150.7(2)	150.3(2)	O(13)—C(23)—C(24)	114.5(7)	115.0(9)
O(3)—Y—N(1)	112.0(2)	112.7(2)	O(13)—C(23)—C(28)	123.7(7)	125(1)
O(4)—Y—N(1)	71.6(2)	72.2(2)	O(9)—C(24)—C(23)	114.7(6)	115.3(7)
O(5)—Y—N(1)	72.1(2)	72.4(2)	O(9)—C(24)—C(25)	126.1(8)	124(1)
O(6)—Y—N(1)	73.2(2)	72.7(2)			
O(7)—Y—N(1)	70.6(2)	70.4(2)			
O(8)—Y—N(1)	137.6(1)	137.4(2)			

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[a] ar = aryl; ak = alkyl; 1 designates the complexed ether, 2 the hydrogen bonded ether.

Table IV. Hydrogen bonding contact geometries (Å, deg) for YPCB15 (−150° and 20°C)

Atoms	Distance (−150°C)	Distance (20°C)
O(6)—O(11)	2.659(6)	2.685(7)
O(6)—O(18)	2.702(8)	2.71(1)
O(7)—O(9)	2.831(6)	2.854(8)
O(7)—O(12)	2.686(6)	2.707(7)
O(8)—O(10)	2.678(6)	2.694(7)
O(8)—O(14)	2.755(6)	2.76(1)
C(32)—O(14)	3.11(1)	3.18(2)
C(32)—O(15)[a]	3.24(1)	3.27(1)
C(30)—O(20)1[b]	3.01(1)	3.08(2)
C(30)—O(23)1	3.11(2)	3.24(3)
C(30)—O(25)1[b]	3.27(2)	3.26(2)
C(30)—O(18)[c]	3.25(1)	3.26(2)
C(30)′—O(25)1	2.92(2)	2.90(2)
C(30)′—O(18)[c]	3.31(1)	3.36(2)
Atoms	**Angle**	**Angle**
O(11)—O(6)—O(18)	101.7(2)	100.9(3)
O(9)—O(7)—O(12)	99.4(2)	99.0(2)
O(10)—O(8)—O(14)	111.0(2)	111.0(3)

[a] Atoms related to those in Table II by $-x, 1-y, 1-z$.
[b] $1-x, 1-y, 2-z$.
[c] $1-x, -y, 2-z$.

relative positioning of the anions and uncoordinated solvent molecule are presented in Figure 2. The perchlorate anion containing Cl(1) is anchored by hydrogen bonds from O(8) and close contacts from C(32) and is thus ordered. O(18) of a second perchlorate (Cl(2)) is hydrogen bonded to O(6) and is the only ordered atom of this group. The third perchlorate has no hydrogen bonds from water molecules and is completely disordered. It is interesting to note that a major form of 50% occupancy is found for each of the disordered anions and two minor forms of 25% occupancy each are also observed. It appears that interactions between both solvent methyl groups and the anions (suggested by close C···O contacts) are too weak to provide an ordered anion environment.

The Y(III) ion coordination in the title complex is best described as a tricapped trigonal prism. The three water molecules all with hydrogen bond contacts to one side, form one triangular face. The other is formed by crown ether oxygen atoms O(2), O(4), and O(5). The quadrilateral faces are capped by N(1), O(1), and O(3).

O(7) has a weak hydrogen bond to O(9) (the longest of all such contacts) and exhibits the shortest Y—OH$_2$ separation of 2.323(4) Å. The remaining Y—OH$_2$ separations are 2.335(5) (O(6)) and 2.338(4) Å (O(8)). The Y—N(1) distance 2.388(5) Å is shorter than observed in $[Y(NO_3)_3(OH_2)_2(NCMe)][Y(NO_3)_3(OH_2)_2(OHMe)]\cdot 2$(benzo-15-crown-5)·OHMe [17] (YNB15, Y—NCMe = 2.430(6) Å) despite its capping position in the title complex. Initially, this was taken as possible

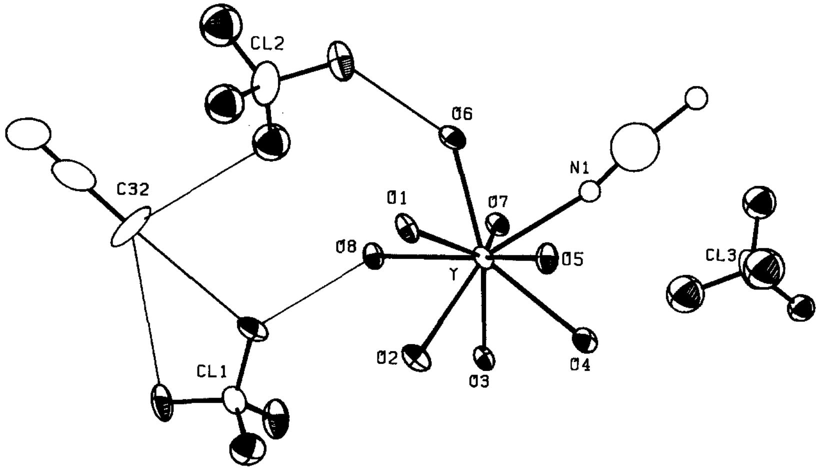

Fig. 2. Hydrogen bonding involving the ClO_4^- anions and uncoordinated solvent molecule.

evidence of a methanol contribution to this coordination site, however, examination of all geometries about the disordered atoms in this group precluded this possibility.

The two crown ethers in YPCB15 have bonding parameters consistent with each other (Table III) and the literature, despite the drastically different environments and different conformations. The hydrogen bonded crown ether has contacts on one side of the molecule only. Starting with the O(9)—C(15)—C(16)—O(10) torsion angle (Table V), there are three consecutive O—C—C—O angles of

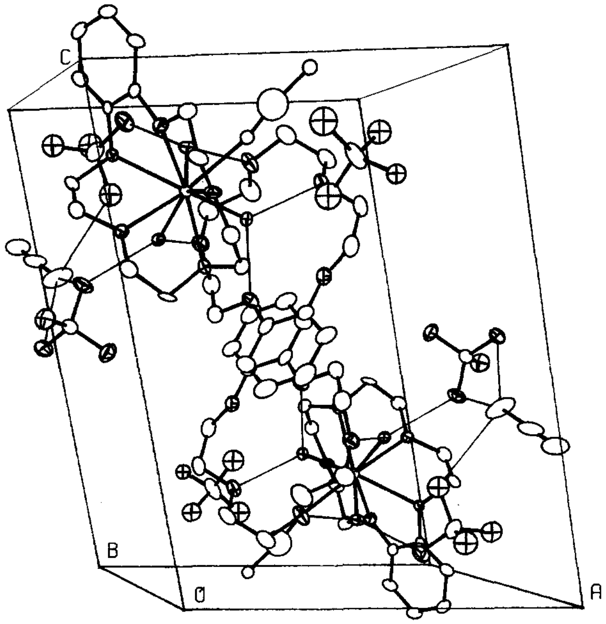

Fig. 3. Cell packing diagram.

Table V. Torsion angles (deg) for YPCB15 (−150°C)

Atoms	Angle
O(1)—C(1)—C(2)—O(2)	−49.5
C(1)—C(2)—O(2)—C(3)	−164.1
C(2)—O(2)—C(3)—C(4)	158.0
O(2)—C(3)—C(4)—O(3)	49.6
C(3)—C(4)—O(3)—C(5)	100.3
C(4)—O(3)—C(5)—C(6)	−79.2
O(3)—C(5)—C(6)—O(4)	−47.0
C(5)—C(6)—O(4)—C(7)	177.2
C(6)—O(4)—C(7)—C(8)	170.0
O(4)—C(7)—C(8)—O(5)	46.0
C(7)—C(8)—O(5)—C(9)	160.3
C(8)—O(5)—C(9)—C(10)	−173.0
O(5)—C(9)—C(10)—O(1)	−5.4
C(9)—C(10)—O(1)—C(1)	118.6
C(10)—O(1)—C(1)—C(2)	−101.4
O(9)—C(15)—C(16)—O(10)	−64.7
C(15)—C(16)—O(10)—C(17)	162.7
C(16)—O(10)—C(17)—C(18)	−95.1
O(10)—C(17)—C(18)—O(11)	−71.6
C(17)—C(18)—O(11)—C(19)	−170.1
C(18)—O(11)—C(19)—C(20)	−69.2
O(11)—C(19)—C(20)—O(12)	−57.0
C(19)—C(20)—O(12)—C(21)	−179.6
C(20)—O(12)—C(21)—C(22)	−157.8
O(12)—C(21)—C(22)—O(13)	64.4
C(21)—C(22)—O(13)—C(23)	−171.2
C(22)—O(13)—C(23)—C(24)	150.0
O(13)—C(23)—C(24)—O(9)	−4.1
C(23)—C(24)—O(9)—C(15)	170.9
C(24)—O(9)—C(15)—C(16)	−170.5

g^- (−60°) and one of g^+. (Note it is the O(12)—C(21)—C(22)—O(13) angle which is g^+ and it is O(13) which does not accept a hydrogen bond.) The O(13)—C(23)—C(24)—O(9) angle is *syn* (−4.1°) as expected. One of each pair of C—O—C—C angles between C—C torsion angles of like sign deviates significantly towards a *gauche* configuration. In YNB15 the hydrogen bonded crown ether has contacts on both sides and a much more symmetrical conformation results: alkyl O—C—C—O angles alternating $\pm g$ (the one aryl torsion angle was *syn*) and all C—O—C—C angles *anti* (180°). This conformation, which is not unlike the D_{3d} form of 18-crown-6, is that observed for the coordinated benzo-15-crown-5 ether in the title complex with distortions occurring around the capping atoms. The C—O—C—C angles involving O(1) and O(3) average 100°.

The variation in Y—O(ether) distances is quite large. The longest distance is to the aryl ether O(5) (2.493(4) Å) despite the fact that the other aryl ether, O(1) is in a capping position. The Y—O(1) separation of 2.487(5) Å is second largest and may reflect the distortion around O(1) requiring a closer metal contact. Similarly, despite its capping position the Y—O(3) distance, 2.428(4) Å, is shorter than the

Y—O(4) separation of 2.477(5) Å and longer than the Y—O(2) distance, 2.414(4) Å. The average of all five Y—O(ether) separations is 2.46(3) Å.

Acknowledgement

We are grateful to the donors to the Petroleum Research Fund administered by the American Chemical Society for support of this work and to the U.S. National Science Foundation Chemical Instrumentation Program for funds used to purchase the diffractometer.

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