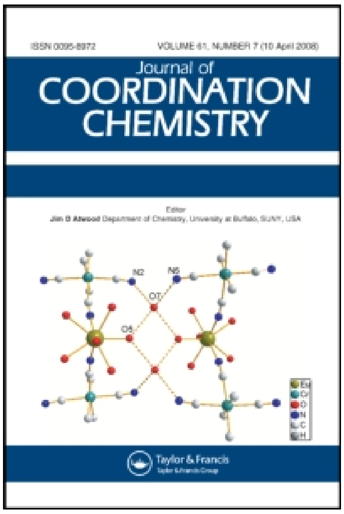

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

f-ELEMENT/CROWN ETHER COMPLEXES 12. SYNTHESIS AND CRYSTAL STRUCTURE OF $[Y(NO_3)_3(OH_2)_2(NCMe)][Y(NO_3)_3(OH_2)_2(OHME)]\cdot 2(BENZO\text{-}15\text{-}CROWN\text{-}5)\cdot OHMe$

Robin D. Rogers[a]; Eric J. Voss[a]
[a] Department of Chemistry, Northern Illinois University, DeKalb, IL, U.S.A.

To cite this Article Rogers, Robin D. and Voss, Eric J.(1988) 'f-ELEMENT/CROWN ETHER COMPLEXES 12. SYNTHESIS AND CRYSTAL STRUCTURE OF $[Y(NO_3)_3(OH_2)_2(NCMe)][Y(NO_3)_3(OH_2)_2(OHME)]\cdot 2(BENZO\text{-}15\text{-}CROWN\text{-}5)\cdot OHMe$', Journal of Coordination Chemistry, 16: 4, 405 — 414

To link to this Article: DOI: 10.1080/00958978808081667

URL: http://dx.doi.org/10.1080/00958978808081667

J. Coord. Chem. 1988, Vol. 16, p. 405-414
Reprints available directly from the publisher
Photocopying permitted by license only

f-ELEMENT/CROWN ETHER COMPLEXES 12.† SYNTHESIS AND CRYSTAL STRUCTURE OF $[Y(NO_3)_3(OH_2)_2(NCMe)][Y(NO_3)_3(OH_2)_2(OHME)]\cdot 2(BENZO\text{-}15\text{-}CROWN\text{-}5)\cdot OHMe$

ROBIN D. ROGERS‡ and ERIC J. VOSS

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, U.S.A.

(Received February 2, 1987; in final form June 11, 1987)

The title complex has been synthesized *via* reaction of hydrated yttrium(III) nitrate with benzo-15-crown-5 in a 3:1 solvent mixture of acetonitrile and methanol. Its crystal and molecular structure have been determined by single crystal X-ray diffraction. This complex is monoclinic, $P2_1/c$, with $a = 16.180(3)$, $b = 18.955(3)$, $c = 16.660(3)$Å, $\beta = 91.01(2)°$ and $D_{calc} = 1.64$ g cm^{-3} for $Z = 4$ formula units. Least-squares refinement utilizing 5234 independent observed $[F_o \geq 3\sigma(F_o)]$ reflections led to the final R value of 0.055. There are two independent yttrium(III) cations in the asymmetric unit. Each is nine-coordinate with three bidentate nitrate groups, two water molecules, and a coordinated solvent molecule. The geometry approximates a tricapped trigonal prism, with the nitrate chelate bites occupying '*c*' edges. The Y—O(nitrate) and Y—O(water) separations average 2.42(3) and 2.33(3)Å, respectively. Each water molecule is hydrogen bonded to two oxygens of a benzo-15-crown-5 molecule resulting in polymeric chains along *a* of cation 1/crown 1/cation 2/crown 2/cation 1 ···. These chains are hydrogen bonded together *via* the Y(III) cations containing the OHMe group and the uncoordinated OHMe solvent molecule. The coordinated methanol is a hydrogen bond donor to the oxygen of the uncoordinated methanol group, which in turn is hydrogen bonded to a terminal nitrate oxygen atom of a symmetry related cation. The crown ethers adopt a fairly symmetrical conformation, not found for the free ether nor normally found in its metal complexes.

Keywords: yttrium, crown ether, structure, x-ray, hydrogen bonding

INTRODUCTION

In our research into the interaction of crown ethers with hydrated lanthanide and actinide salts, the metal : crown stoichiometry and overall structure have been related directly to the number of possible hydrogen bonds between coordinated water molecules and the crown ether. We are continuing to investigate such complexes in order to determine not only how the various hydrogen bonding patterns influence crown conformation, but also to find out how this same hydrogen bonding controls the metal ion coordination number, coordination polyhedron, and the number of tight ion pairs present.

Hydrated yttrium(III) nitrate reacts with 12-crown-4 in CH_3CN or in a 3/1 CH_3CN : OHMe mixture to form the anhydrous product, $Y(NO_3)_3$(12-crown-4).[2] This same reaction with 15-crown-5 yields $[Y(NO_3)_2(OH_2)_5][NO_3]\cdot 2$(15-crown-5)[3] which exhibits only two tight ion pairs (Y^{3+}/NO_3^-), with five coordinated water molecules for a coordination number of nine. When hydrated YCl_3 and 15-crown-5 react under similar conditions an eight coordinate $[Y(OH_2)_8]^{3+}$ ion results and no tight ion

---

† For part 11, see reference 1. ‡ Author for correspondence.

pairs.[4,5] A similar synthesis utilizing 18-crown-6 gives intermediate results with 9-coordinate and 8-coordinate Y(III) cations and only one tight ion pair in $[Y(OH_2)_7(OHMe)][YCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7 \cdot 2H_2O$.[6] In King's study of the reaction of hydrated lanthanide nitrates with benzo-15-crown-5, the heavier lanthanides tended toward solvent complexes of the type $Ln(NO_3)_3(OH_2)_3 \cdot$benzo-15-crown-5$\cdot(CH_3)_2CO$.[7] The benzo substituent reduces the flexibility of the crown ether and creates oxygens in the crown ring of different basicity (the aryl oxygen atoms being less basic). The crystallographic study presented here was undertaken to assess the effect on structure and hydrogen bonding of this crown ether's size, restricted flexibility, and electronic environment. As it turned out, it also allows us to study structural effects of our solvent system, initially chosen for its utility in dissolving all of our starting materials and excellent crystallization properties.

EXPERIMENTAL

Synthesis and Crystallization of $[Y(NO_3)_3(OH_2)_2(NCMe)][Y(NO_3)_3(OH_2)_2(OHMe)] \cdot 2(\text{benzo-15-crown-5}) \cdot OHMe$

1 mmol of benzo-15-crown-5 in 5 cm^3 of a 3 : 1 mixture of CH_3CN and CH_3OH was added to a stirring solution of 1 mmol of $Y(NO_3)_3 \cdot nH_2O$ in 5 cm^3 of the same solvent mixture. The reaction mixture was heated to 60°C for 1 h then cooled to 22°C. The reaction mixture was allowed to slowly evaporate to 1/8 of its original volume, placed in a round bottom flask, and stored at 22°C. Over a period of several weeks crystals deposited along the walls of the flask. The crystals are sensitive to solvent loss when removed from the solvent vapour saturated flask and will completely decompose over a period of 8 to 10 days, going opaque. A melting point range of 95–105°C was observed for a freshly prepared crystal; however, no analytical data were obtained. Eight crystals were mounted and cell parameters determined. All were identical.

X-ray Data Collection, Structure Determination, and Refinement for $[Y(NO_3)_3(OH_2)_2(NCMe)][Y(NO_3)_3(OH_2)_2(OHMe)] \cdot 2(\text{benzo-15-crown-5}) \cdot OHMe$

A clear single crystal of the title complex was mounted on a pin and transferred to the goniometer. The crystal was cooled to -150°C during data collection using a stream of cold nitrogen gas to prevent decomposition. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 19°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be $P2_1/c$ from systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization effects, and for absorption.

Calculations were carried out with the SHELX system of computer programs.[8] Neutral atom scattering factors for Y, O, N, C, and H were taken from reference 9 and the scattering was corrected for the real and imaginary components of anomalous dispersion.[9]

The positions of the yttrium atoms were revealed using the direct methods program MULTAN.[10] A difference Fourier map phased on the yttrium atoms readily revealed the positions of the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma \| F_o \| - | F_c \| / \Sigma | F_o | = 0.076$. The crown hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl, methanol, and

TABLE I
Crystal Data and Summary of Intensity Data Collection and Structure Refinement

Cmpd	$[Y(NO_3)_3(OH_2)_2(NCMe)][Y(NO_3)_3(OH_2)_2-(OHMe)]\cdot 2$(benzo-15-crown-5)$\cdot$OHMe
Colour/Shape	clear/plate
Mol. wt.	1263.6
Space group	$P2_1/c$
Temp., °C	-150
Cell Constants	
a, Å	16.180(3)
b, Å	18.955(3)
c, Å	16.660(3)
β, deg	91.01(2)
Cell vol, Å	5108.8
Formula units/unit cell	4
ρ(calc), g cm^{-3}	1.64
μ(calc), cm^{-1}	23.0
Range of relative transm. factors	70/100%
Radiation, graphite monochromator	Mo$K\alpha$ ($\lambda = 0.71073$)
Max crystal dimensions, mm	$0.08 \times 0.22 \times 0.50$
Scan width	$0.80 + 0.35\tan\theta$
Standard reflections	080; 800; 008
Decay of standards	$\pm 2\%$
Reflections measured	9587
2θ range, deg	$2 < 2\theta < 50$
Range of h, k, l	$+19$, $+22$, ± 19
Reflections observed [$F_o \geq 3\sigma(F_o)$]	5234
No. of parameters varied	676
Weights	$[\sigma(F_o)^2 + 0.0001F_o^2]^{-1}$
GOF	1.07
R	0.055
R_w	0.055

water hydrogen atoms were not located. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.055$ and $R_w = 0.055$. A final difference Fourier showed no feature greater than 1.0 e$^-$/Å^3. The weighting scheme was based on $[\sigma(F_o)^2 + pF_o^2]^{-1}$ where $p = 0.0001$; no systematic variation of $w(|F_o| - |F_c|)$ *vs* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

RESULTS AND DISCUSSION

$[Y(NO_3)_3(OH_2)_2(NCMe)][Y(NO_3)_3(OH_2)_2(OHMe)]\cdot 2$(benzo-15-crown-5)$\cdot$OHMe (now referred to as YNB15) crystallizes as a hydrogen bonded polymeric chain along *a* consisting of crown ether/Y(III) cation containing NCMe/crown ether/Y(III) cation containing OHME/crown ether ···. A portion of this chain is depicted in Figure 1. The hydrogen bonding in the chain consist of Y—O—H ··· O(crown) interactions. The chains are linked *via* hydrogen bonds from the coordinated methanol group to the uncoordinated methanol and from the uncoordinated solvent molecule to a terminal nitrate oxygen atom of a symmetry related cation. There are no hydrogen bond acceptor atoms in the Y(III) cation containing the acetonitrile molecule. A packing diagram is given in Figure 2.

TABLE II
Final Fractional Coordinates

Atom	*x/a*	*y/b*	*z/c*
Y(1)	−0.06341(4)	0.21468(4)	0.49709(4)
Y(2)	0.43390(4)	0.15675(4)	0.64582(4)
O(1)	−0.0034(3)	0.1608(3)	0.3792(3)
O(2)	−0.1350(3)	0.1498(3)	0.3906(3)
O(3)	−0.0752(3)	0.1082(3)	0.2840(3)
O(4)	0.0120(3)	0.3062(3)	0.4274(3)
O(5)	−0.1197(3)	0.3020(3)	0.4073(3)
O(6)	−0.0477(4)	0.3857(3)	0.3516(3)
O(7)	−0.0652(3)	0.0942(3)	0.5383(3)
O(8)	−0.0614(3)	0.1708(3)	0.6342(3)
O(9)	−0.0615(3)	0.0586(3)	0.6634(3)
O(10)	0.0730(3)	0.2041(3)	0.5372(3)
O(11)	−0.2005(3)	0.2078(3)	0.5368(3)
O(12)	0.3678(3)	0.0419(3)	0.6701(3)
O(13)	0.4939(3)	0.0554(3)	0.7109(3)
O(14)	0.4314(3)	−0.0459(3)	0.7285(3)
O(15)	0.3656(3)	0.1628(3)	0.7720(3)
O(16)	0.4938(3)	0.1950(3)	0.7737(3)
O(17)	0.4307(3)	0.1780(3)	0.8866(3)
O(18)	0.4600(3)	0.0769(3)	0.5368(3)
O(19)	0.4472(3)	0.1858(3)	0.5020(3)
O(20)	0.4621(3)	0.1042(3)	0.4101(3)
O(21)	0.2968(3)	0.1676(3)	0.5999(3)
O(22)	0.5716(3)	0.1923(3)	0.6248(3)
O(23)	0.4115(3)	0.2789(3)	0.6449(3)
O(24)	0.6750(3)	0.2902(3)	0.4731(3)
O(25)	0.6342(3)	0.1485(3)	0.4837(3)
O(26)	0.7248(3)	0.0943(3)	0.6155(3)
O(27)	0.7179(3)	0.2102(3)	0.7173(3)
O(28)	0.7240(4)	0.3291(3)	0.6143(3)
O(29)	0.2345(3)	0.3027(3)	0.5426(3)
O(30)	0.2003(3)	0.1938(2)	0.4344(3)
O(31)	0.1915(3)	0.0715(3)	0.5330(3)
O(32)	0.1209(3)	0.1286(3)	0.6693(3)
O(33)	0.1727(3)	0.2666(3)	0.6785(3)
O(34)	0.3855(4)	0.3497(3)	0.7702(4)
N(1)	−0.0716(4)	0.1386(3)	0.3488(3)
N(2)	−0.0518(4)	0.3339(4)	0.3929(4)
N(3)	−0.0625(4)	0.1061(4)	0.6143(4)
N(4)	0.4302(4)	0.0145(3)	0.7040(3)
N(5)	0.4301(4)	0.1785(3)	0.8140(3)
N(6)	0.4573(4)	0.1222(4)	0.4809(4)
N(7)	−0.0745(4)	0.3211(3)	0.5775(4)
C(1)	0.6239(5)	0.2569(5)	0.4133(4)
C(2)	0.6475(5)	0.1821(5)	0.4079(4)
C(3)	0.6652(5)	0.0771(4)	0.4847(4)
C(4)	0.6668(5)	0.0525(4)	0.5705(4)
C(5)	0.7171(5)	0.0858(5)	0.7007(4)
C(6)	0.7590(5)	0.1474(5)	0.7408(4)
C(7)	0.7679(5)	0.2710(5)	0.7317(4)
C(8)	0.7254(5)	0.3355(5)	0.6989(5)
C(9)	0.6805(6)	0.3801(4)	0.5690(6)
C(10)	0.6564(5)	0.3568(5)	0.4931(6)
C(11)	0.6138(6)	0.4050(5)	0.4426(7)
C(12)	0.5966(6)	0.4716(6)	0.4708(9)
C(13)	0.6231(6)	0.4937(5)	0.5477(8)

TABLE II
Final Fractional Coordinates

Atom	x/a	y/b	z/c
C(14)	0.6640(6)	0.4463(5)	0.5971(7)
C(15)	0.2367(4)	0.3146(4)	0.4571(4)
C(16)	0.2620(4)	0.2458(4)	0.4190(4)
C(17)	0.2230(4)	0.1248(4)	0.4086(4)
C(18)	0.1692(4)	0.0712(4)	0.4495(4)
C(19)	0.1372(4)	0.0307(4)	0.5819(4)
C(20)	0.1465(4)	0.0563(4)	0.6670(4)
C(21)	0.1366(4)	0.1620(4)	0.7451(4)
C(22)	0.1169(4)	0.2384(4)	0.7377(4)
C(23)	0.1644(4)	0.3364(4)	0.6590(4)
C(24)	0.2009(4)	0.3570(4)	0.5863(4)
C(25)	0.1998(4)	0.4266(4)	0.5635(4)
C(26)	0.1629(5)	0.4774(4)	0.6120(4)
C(27)	0.1250(5)	0.4573(4)	0.6820(4)
C(28)	0.1258(4)	0.3880(4)	0.7059(4)
C(29)	0.4445(6)	0.3308(5)	0.5860(5)
C(30)	0.3624(6)	0.4200(4)	0.7437(6)
C(31)	−0.0705(5)	0.3840(5)	0.5915(5)
C(32)	−0.0812(7)	0.4643(6)	0.6090(6)

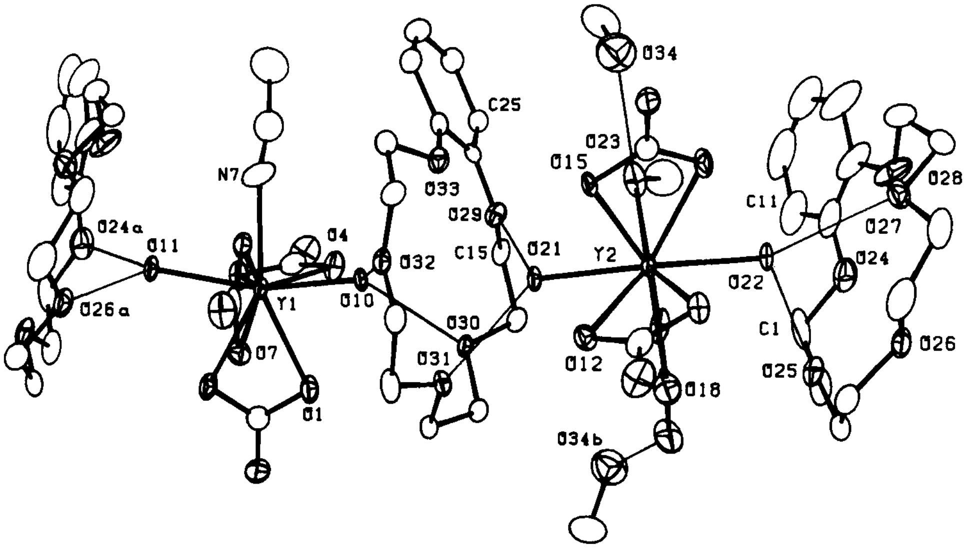

FIGURE 1 Portion of the polymeric chain along *a*. The atoms are represented by their 50% probability ellipsoids for thermal motion.

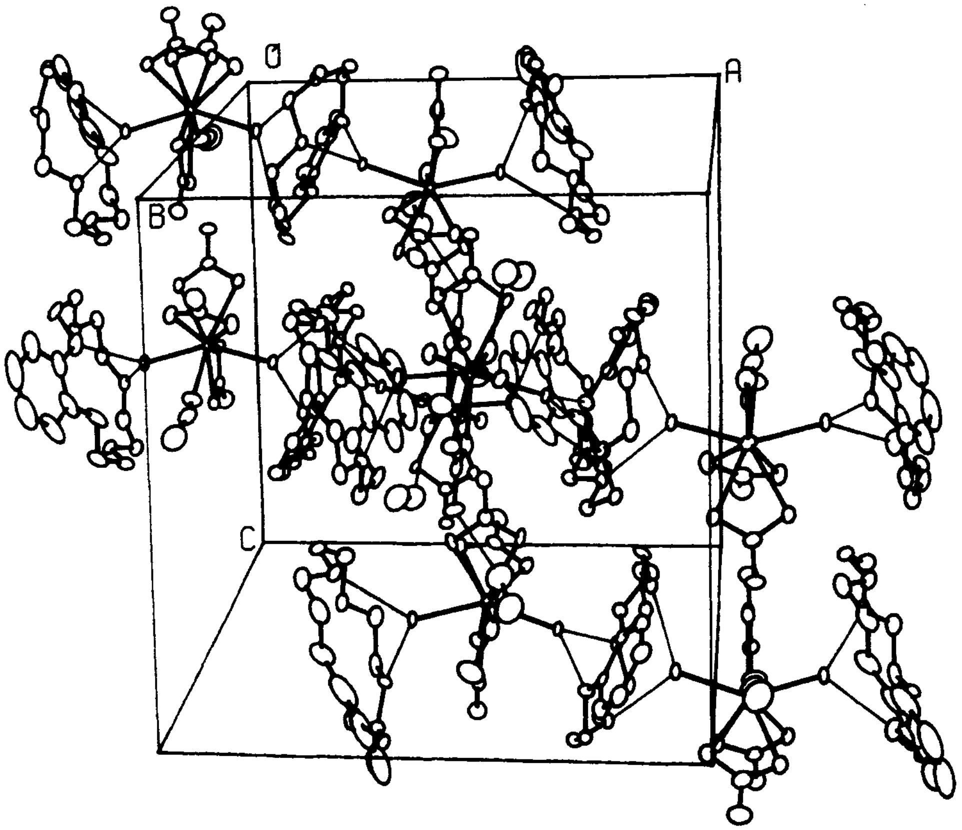

FIGURE 2 Cell packing.

Y(III) Coordination

Each yttrium(III) cation is nine-coordinate with three bidentate nitrates, two water molecules, and a solvent molecule in the primary coordination sphere. Acetonitrile is coordinated to Y(1) with an Y(1)–N(7) separation of 2.430(6)Å (Table III). The Y(2) coordination is completed by O(23) of a methanol molecule (Y(2)–O(23) = 2.343(6)Å). The Y–O(nitrate) and Y–OH_2 distances average 2.42(3) and 2.33(3)Å, respectively. These are in good agreement with other Y(III) complexes of similar geometry; $[Y(NO_3)_2(OH_2)_5][NO_3]\cdot 2(15\text{-crown-}5)$:[3] Y–O(nitrate) = 2.44(6)Å, Y–OH_2 = 2.36(3)Å and $Y(NO_3)_3(OH_2)_3\cdot 2(C_{10}H_8N_2)$:[11] Y–O(nitrate) = 2.45(3)Å, Y–OH_2 = 2.32(1)Å. After a correction[12] of 0.008Å for the difference in the CN = 9 ionic radius of Dy(III) and Y(III) and 0.032Å for Gd(III)–Y(III), these values are comparable to those found in $Dy(NO_3)_3(OH_2)_3\cdot$(2-methoxy-1,3-xylyl)-15-crown-4:[13] Dy–O(nitrate) = 2.45(3)Å, Dy–OH_2 = 2.35(2)Å and $Gd(NO_3)_3(OH_2)_3\cdot$18-crown-6:[14] Gd–O(nitrate) = 2.45(4)Å, Gd–OH_2 = 2.39(6)Å.

The exact nature of the coordination polyhedra for both Y(III) cations can be obtained following the discussions of Drew.[15] Each cation is a tricapped trigonal prism with nitrate oxygen atoms capping each quadrilateral face: O(2), O(4), and O(8) for Y(1) and O(12), O(16), and O(19) for Y(2). The nitrate chelate bites thus occupy '*c*' edges (as defined by Drew) in the tricapped trigonal prism, as do all nitrate ligands in structurally characterized $Ln(NO_3)_3L_3$, where L is a unidentate ligand.[13–15] It is

TABLE III
Selected Bond Distances (Å) and Angles (deg)

Atoms	Distance	Atoms	Distance
Y(1) -- O(1)	2.431(5)	Y(1) -- O(2)	2.434(5)
Y(1) -- O(4)	2.428(5)	Y(1) -- O(5)	2.400(5)
Y(1) -- O(7)	2.385(5)	Y(1) -- O(8)	2.431(5)
Y(1) -- O(10)	2.303(4)	Y(1) -- O(11)	2.329(4)
Y(1) -- N(7)	2.430(6)	Y(2) -- O(12)	2.462(5)
Y(2) -- O(13)	2.403(5)	Y(2) -- O(15)	2.395(5)
Y(2) -- O(16)	2.434(5)	Y(2) -- O(18)	2.408(5)
Y(2) -- O(19)	2.471(5)	Y(2) -- O(21)	2.342(4)
Y(2) -- O(22)	2.360(4)	Y(2) -- O(23)	2.343(6)

Atoms	Angle	Atoms	Angle
O(1) -- Y(1) -- O(2)	52.5(2)	O(1) -- Y(1) -- O(4)	72.7(2)
O(2) -- Y(1) -- O(4)	104.4(2)	O(1) -- Y(1) -- O(5)	86.5(2)
O(2) -- Y(1) -- O(5)	74.0(2)	O(4) -- Y(1) -- O(5)	52.9(2)
O(1) -- Y(1) -- O(7)	80.6(2)	O(2) -- Y(1) -- O(7)	73.6(2)
O(4) -- Y(1) -- O(7)	146.2(2)	O(5) -- Y(1) -- O(7)	146.5(2)
O(1) -- Y(1) -- O(8)	128.1(2)	O(2) -- Y(1) -- O(8)	120.7(2)
O(4) -- Y(1) -- O(8)	134.0(2)	O(5) -- Y(1) -- O(8)	145.1(2)
O(7) -- Y(1) -- O(8)	53.3(2)	O(1) -- Y(1) -- O(10)	78.6(2)
O(2) -- Y(1) -- O(10)	127.5(2)	O(4) -- Y(1) -- O(10)	73.4(2)
O(5) -- Y(1) -- O(10)	126.3(2)	O(7) -- Y(1) -- O(10)	81.3(2)
O(8) -- Y(1) -- O(10)	72.6(2)	O(1) -- Y(1) -- O(11)	127.0(2)
O(2) -- Y(1) -- O(11)	74.7(2)	O(4) -- Y(1) -- O(11)	131.6(2)
O(5) -- Y(1) -- O(11)	82.1(2)	O(7) -- Y(1) -- O(11)	81.3(2)
O(8) -- Y(1) -- O(11)	73.2(2)	O(10) -- Y(1) -- O(11)	145.6(2)
O(1) -- Y(1) -- N(7)	145.9(2)	O(2) -- Y(1) -- N(7)	141.5(2)
O(4) -- Y(1) -- N(7)	73.3(2)	O(5) -- Y(1) -- N(7)	75.0(2)
O(7) -- Y(1) -- N(7)	129.4(2)	O(8) -- Y(1) -- N(7)	76.4(2)
O(10) -- Y(1) -- N(7)	89.5(2)	O(11) -- Y(1) -- N(7)	79.1(2)
O(12) -- Y(2) -- O(13)	52.6(2)	O(12) -- Y(2) -- O(15)	71.9(2)
O(13) -- Y(2) -- O(15)	80.2(2)	O(12) -- Y(2) -- O(16)	106.7(2)
O(13) -- Y(2) -- O(16)	72.0(2)	O(15) -- Y(2) -- O(16)	53.2(2)
O(12) -- Y(2) -- O(18)	69.5(2)	O(13) -- Y(2) -- O(18)	76.3(2)
O(15) -- Y(2) -- O(18)	141.5(2)	O(16) -- Y(2) -- O(18)	140.8(2)
O(12) -- Y(2) -- O(19)	113.7(2)	O(13) -- Y(2) -- O(19)	125.1(2)
O(15) -- Y(2) -- O(19)	152.8(2)	O(16) -- Y(2) -- O(19)	137.9(2)
O(18) -- Y(2) -- O(19)	52.4(2)	O(12) -- Y(2) -- O(21)	73.7(2)
O(13) -- Y(2) -- O(21)	126.1(2)	O(15) -- Y(2) -- O(21)	80.4(2)
O(16) -- Y(2) -- O(21)	128.3(2)	O(18) -- Y(2) -- O(21)	89.2(2)
O(19) -- Y(2) -- O(21)	76.2(2)	O(12) -- Y(2) -- O(22)	133.7(2)
O(13) -- Y(2) -- O(22)	85.4(2)	O(15) -- Y(2) -- O(22)	124.6(2)
O(16) -- Y(2) -- O(22)	71.5(2)	O(18) -- Y(2) -- O(22)	83.6(2)
O(19) -- Y(2) -- O(22)	72.2(2)	O(21) -- Y(2) -- O(22)	144.9(2)
O(12) -- Y(2) -- O(23)	143.8(2)	O(13) -- Y(2) -- O(23)	148.7(2)
O(15) -- Y(2) -- O(23)	83.4(2)	O(16) -- Y(2) -- O(23)	76.7(2)
O(18) -- Y(2) -- O(23)	130.2(2)	O(19) -- Y(2) -- O(23)	77.9(2)
O(21) -- Y(2) -- O(23)	76.5(2)	O(22) -- Y(2) -- O(23)	82.1(2)
Y(1) -- O(1) -- N(1)	96.0(4)	Y(1) -- O(2) -- N(1)	96.1(4)
Y(1) -- O(4) -- N(2)	95.7(4)	Y(1) -- O(5) -- N(2)	97.2(4)
Y(1) -- O(7) -- N(3)	96.6(4)	Y(1) -- O(8) -- N(3)	94.9(4)
Y(2) -- O(12) -- N(4)	95.2(4)	Y(2) -- O(13) -- N(4)	97.2(4)
Y(2) -- O(15) -- N(5)	96.1(4)	Y(2) -- O(16) -- N(5)	94.3(4)
Y(2) -- O(18) -- N(6)	97.1(4)	Y(2) -- O(19) -- N(6)	94.1(4)
Y(2) -- O(23) -- C(29)	126.7(5)		

interesting to note that in most complexes of this type the unidentate ligands occupy a triangular face as for example in $Dy(NO_3)_3$·(2-methoxy-1,3-xylyl)-15-crown-4. If this were true of the title complex, however, the polymeric structure observed, which maximizes hydrogen bonds to the crown ether, could not be obtained. Instead, the two water molecules are related diagonally across a quadrilateral face with the solvent molecule occupying a third corner of this face. This same geometry has been observed for $Eu(NO_3)_3(\text{tetramethylurea})_3$[15] and $Gd(NO_3)_3(OH_2)_3$·18-crown-6.

The bonding in the bidentate nitrate ligands is normal with the average terminal N–O distance (1.22(1)Å significantly shorter than the average of the remaining N–O separations (1.276(9)Å). The longest terminal N–O bond length (1.233(8)Å) involves O(20), a hydrogen bond acceptor. It should also be noted that in each case the Y–O separation to a capping NO_3^- oxygen atom is longer (2.44(2)Å average) than the remaining Y–O(nitrate) distances (2.40(1)Å).

We assume that a similar geometry is obtained in the heavier lanthanide complexes of formulation $Ln(NO_3)_3(OH_2)_3$·benzo-15-crown-5·$(CH_3)_2CO$ prepared by King.[7] The differences observed in the coordination geometry of the cations in the title complex probably reflect the use of coordinating solvents in the present study.

Hydrogen Bonding

Although the hydrogen atoms associated with the water and solvent molecules were not located, the hydrogen bonding is readily apparent from the donor contact geometries presented in Table IV. Each crown ether has four hydrogen bonding contacts, two on one side of the crown from one water molecule coordinated to Y(1) and two on the other side of the crown ether from one water molecule coordinated to Y(2). The HO–H···O contacts range from 2.706(6) to 2.908(7)Å and average 2.77(7)Å. Only one oxygen atom of each crown ether does not participate in a hydrogen bond and in each case this atom is one of the less basic aryl ethers. In dibenzo-18-crown-6·$2(CH_3CN)$[16] and dibenzo-18-crown-6·$2(CH_3NO_2)$[16] the conformational rigidity imposed by two benzo substituents results in weak hydrogen bonds almost exclusively to aryl oxygen atoms.

TABLE IV
Hydrogen Bonding Contacts

Atoms	Distance	Atoms	Distance
O(10) - - O(30)	2.708(6)	O(10) - - O(32)	2.726(6)
O(11) - - O(24)^a	2.748(7)	O(11) - - O(26)^a	2.805(7)
O(21) - - O(29)	2.908(7)	O(21) - - O(31)	2.719(6)
O(22) - - O(25)	2.706(6)	O(22) - - O(27)	2.821(6)
O(23) - - O(34)	2.524(8)		
O(34)^b - - O(20)	2.762(8)		
Atoms	**Angle**	**Atoms**	**Angle**
O(30) - - O(10) - - O(32)	105.3(2)	O(24)^a - - O(11) - - O(26)^a	107.3(2)
O(29) - - O(21) - - O(31)	104.1(2)	O(25) - - O(22) - - O(27)	100.8(2)

[a] Atoms are related to those in Table II by $x-1, y, z$. [b] $x, 0.5-y, z-0.5$.

TABLE V
Torsion Angles

Atoms	Angle
O(24) -- C(1) -- C(2) -- O(25)	61.3
C(1) -- C(2) -- O(25) -- C(3)	−173.4
C(2) -- O(25) -- C(3) -- C(4)	167.0
O(25) -- C(3) -- C(4) -- O(26)	−64.5
C(3) -- C(4) -- O(26) -- C(5)	166.7
C(4) -- O(26) -- C(5) -- C(6)	−161.6
O(26) -- C(5) -- C(6) -- O(27)	62.3
C(5) -- C(6) -- O(27) -- C(7)	−161.6
C(6) -- O(27) -- C(7) -- C(8)	174.6
O(27) -- C(7) -- C(8) -- O(28)	−68.1
C(7) -- C(8) -- O(28) -- C(9)	174.3
C(8) -- O(28) -- C(9) -- C(10)	−157.2
O(28) -- C(9) -- C(10) -- O(24)	1.4
C(9) -- C(10) -- O(24) -- C(1)	154.6
C(10) -- O(24) -- C(1) -- C(2)	−172.6
O(29) -- C(15) -- C(16) -- O(30)	63.1
C(15) -- C(16) -- O(30) -- C(17)	−173.4
C(16) -- O(30) -- C(17) -- C(18)	162.3
O(30) -- C(17) -- C(18) -- O(31)	−68.3
C(17) -- C(18) -- O(31) -- C(19)	171.2
C(18) -- O(31) -- C(19) -- C(20)	−159.0
O(31) -- C(19) -- C(20) -- O(32)	62.6
C(19) -- C(20) -- O(32) -- C(21)	−172.5
C(20) -- O(32) -- C(21) -- C(22)	173.5
O(32) -- C(21) -- C(22) -- O(33)	−62.1
C(21) -- C(22) -- O(33) -- C(23)	177.8
C(22) -- O(33) -- C(23) -- C(24)	−161.9
O(33) -- C(23) -- C(24) -- O(29)	4.4
C(23) -- C(24) -- O(29) -- C(15)	152.6
C(24) -- O(29) -- C(15) -- C(16)	−171.0

O(23) of the coordinated methanol group donates a hydrogen to form an O(23)–H···O(34) interaction and is 2.524(8)Å from O(34). The uncoordinated methanol group donates a hydrogen to O(20), a terminal nitrate oxygen atom of a symmetry related Y(2) cation (O(34)····O(20) = 2.762(8)Å). It is interesting that this interaction is favoured over further hydrogen bonding with the remaining available crown oxygen atoms.

Crown Ether Conformation

Both benzo-15-crown-5 molecules in YNB15 have an identical conformation which is different from that observed in the free ether[17] or in many of its metal coordinated complexes.[18–20] From the torsion angles given in Table V a rather symmetrical conformation is revealed with the alkyl O–C–C–O angles alternating $\pm g$ ($\pm 60°$). The C–C–O–C angles are all approximately 180°. The overall conformation is not dissimilar to the symmetric D_{3d} conformation commonly observed for 18-crown-6.[21,22] (As further evidence of this the oxygen atoms of the crown ether deviate alternately an average of ±0.27Å from the mean plane defined by all five.) A similar conformation was observed in $[\mathrm{Na(OH_2)(benzo\text{-}15\text{-}crown\text{-}5)}]\mathrm{I}$,[23] $\mathrm{Mg(NCS)_2}$(benzo-15-crown-5)[24] and $\mathrm{Na(ClO_4)}$(benzo-15-crown-5).[25] The hydrogen bonding in the title complex is apparently enough to also stabilize this conformation.

The rest of the bonding in the crown ether molecules is normal.[26] The average distances and angles include: C(alkyl)–O = 1.43(1)Å, C(aryl)–O = 1.37(3)Å, C–C(alkyl) = 1.50(1)Å, C–C(aryl crown only) = 1.40(1)Å, O–C–C(alkyl) = 108(1)°, O–C–C(aryl) = 115(2)°, C(alkyl)–O–C(alkyl) = 113(1)°, and C(alkyl)–O–C(aryl) = 117(1)°.

ACKNOWLEDGEMENTS

The diffractometer was purchased with funds from the U.S. National Science Foundation Chemical Instrumentation Program.

SUPPLEMENTARY MATERIAL

Tables of fractional coordinates for calculated hydrogen atoms, thermal parameters, least-squares planes results, and observed and calculated structure factors are available from the Editor upon request.

REFERENCES

1. R.D. Rogers, L.K. Kurihara and M.M. Benning, *J. Inclusion Phenom.*, in press.
2. R.D. Rogers and L.K. Kurihara, *J. Inclusion Phenom.*, **4**, 351 (1986).
3. R.D. Rogers and L.K. Kurihara, *J. Less-Common Metals*, **127**, 199 (1987).
4. R.D. Rogers and L.K. Kurihara, *Inorg. Chim. Acta*, **116**, 171 (1986).
5. R.D. Rogers and L.K. Kurihara, *Inorg. Chim. Acta*, **129**, 277 (1987).
6. R.D. Rogers and L.K. Kurihara, *Inorg. Chem.*, **26**, 2360 (1987).
7. R.B. King and P.R. Heckley, *J. Am. Chem. Soc.*, **96**, 3118 (1974).
8. G.M. Sheldrick, SHELX, a system of computer programs for X-ray structure determination as locally modified (1976).
9. "International Tables for X-ray Crystallography" (Kynoch Press, Birmingham, England), Vol. IV, pp. 72, 99, 149 (1972).
10. G. Germain, P. Main and M.M. Woolfson, *Acta Cryst.*, **A27**, 368 (1971).
11. T.J.R. Weakley, *Inorg. Chim. Acta*, **63**, 161 (1982).
12. R.D. Shannon, *Acta Cryst.*, **A32**, 751 (1976).
13. G. Tomat, G. Valle, P. di Bernardo and P.L. Zanonato, *Inorg. Chim. Acta*, **110**, 113 (1985).
14. 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.*, 2191 (1980).
15. M.G.B. Drew, *Coord. Chem. Rev.*, **24**, 179 (1977).
16. R.D. Rogers, L.K. Kurihara and P.D. Richards, *J. Chem. Soc., Chem. Commun.*, 604 (1987).
17. I.R. Hanson, *Acta Cryst.*, **B34**, 1026 (1978).
18. J.-C. G. Bunzli in "Handbook on the Physics and Chemistry of Rare Earths," Vol. 9, K.A. Gschneidner Jr. and L. Eyring, Eds. (Elsevier, Amsterdam, in press, 1986).
19. S.G. Bott, H. Elgamal and J.L. Atwood, *J. Am. Chem. Soc.*, **107**, 1796 (1985).
20. N.S. Poonia, P. Bagdi and K.S. Sidhu, *J. Inclusion Phenom.*, **4**, 43 (1986).
21. M.J. Bovill, D.J. Chadwick, I.O. Sutherland and D. Watkins, *J. Chem. Soc., Perkin II*, 1529 (1980).
22. J.W.H.M. Uiterwijk, S. Harkema, B.W. van de Waal, F. Gobel and H.T.M. Nibbeling, *J. Chem. Soc., Perkin II*, 1843 (1983).
23. M.A. Bush and M.R. Truter, *J. Chem. Soc., Perkin II*, 341 (1972).
24. J.D. Owen, *J. Chem. Soc., Dalton Trans.*, 1418 (1978).
25. J.D. Owen, *J. Chem. Soc., Dalton Trans.*, 1066 (1980).
26. J-C.G. Bunzli and D. Wessner, *Coord. Chem. Rev.*, **60**, 191 (1984).