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Crystal Structure of [Yb $(NO_3)_3$ (phen) (H_2O)] · (12-crown-4)

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Abstract. The title complex was prepared by reacting $Yb(NO_3)_3$ (12-crown-4) with 1,10-phenanthroline (hereafter phen) in acetone. It crystallized in the triclinic space group $P\bar{1}$ with $a = 10.095(5)$, $b = 17.415(4)$, $c = 8.710(2)$ Å; $\alpha = 92.45(2)$, $\beta = 115.83(3)$, $\gamma = 74.08(3)°$ and $D_c = 1.85$ g cm^{-3}; $Z = 2$. The metal ion in this complex is nine-coordinated to three bidentate nitrate ions, two nitrogen atoms of a phen and a water molecule. The crown ligand is hydrogen bonded to the coordination water molecule. The symmetry change of the crown ether is also discussed.

Key words: Crown ether, ytterbium nitrate, phen, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. 82158 (27 pages).

1. Introduction

Crystal structures of rare earth crown ether complexes have been studied extensively [1], but research on mixed ligand complexes are rare and only three crystal structures have been reported, $[MCl_3$ (EO3)] · (18-crown-6) (EO3=triethyleneglycol, M=Dy, Y) [2] and [La $(NO_3)_3$ (bipy) $(H_2O)_2$] · (benzo-15-crown-5) [3], all of which have a crown molecule hydrogen-bonded with the metal ions. The La-bipy-benzo-15-crown-5 complex has a structure very different from the previously reported La $(NO_3)_3$ (benzo-15-crown-5) [4]. To explore the interaction between rare earth crown ether complexes and a second ligand, we synthesized ytterbium 12-crown-4 complexes and used phen as the second ligand. Three types of 12-crown-4 complexes have been isolated: [Ce $(NO_3)_3$ (12-crown-4) (H_2O)] · (12-crown-4) [5], La $(NO_3)_3$ (H_2O) (12-crown-4) [6] and RE $(NO_3)_3$ (12-crown-4) (RE=Pr-Sm,Eu,Y,Yb) [6–9]. Crystals of [La $(NO_3)_3$ (12-crown-4) (H_2O)] · (12-crown-4) [6], which is isostructural with the Ce complex [5], were obtained when an equimolar ratio of [La $(NO_3)_3$ (H_2O) (12-crown-4)] and phen were mixed together. By the same procedure, we have successfully prepared crystals of [Yb $(NO_3)_3$ (phen) (H_2O)] · (12-crown-4). X-ray structure analysis confirmed that the crown ligand was replaced by phen and was in the second coordination sphere.

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TABLE I. Crystal data and summary of data collection and refinement.

Formula	$YbC_{20}H_{26}O_{14}N_5$
Mol. wt.	733.6
Space group	$P\bar{1}$
a(Å)	10.095(5)
b(Å)	17.415(4)
c(Å)	8.710(2)
α(°)	92.45(2)
β(°)	115.83(3)
γ(°)	74.08(3)
Cell vol. (Å^3)	1320
Z	2
D_c (g cm^{-3})	1.85
μ(MoK_α), cm^{-1}	38.1
Crystal size (mm)	0.32 × 0.28 × 0.46
Scan mode	$\omega/2\theta$
scan range (°)	3–54
scan width (°)	1.6
scan speed (°/min)	6.0
hkl range	13, ±23, ±12
Reflections measured	6033
Reflections observed, $I > 3\sigma(I)$	5213
No. parameters varied	358
R	0.088
R_w	0.094
$(\Delta/\sigma)_{max}$	0.003
$\Delta\rho_{max}$, e Å^{-3}	1.0

2. Experimental

The Yb $(NO_3)_3$ (12-crown-4) complex was prepared by the reaction of Yb $(NO_3)_3 \cdot 6$ (H_2O) with 12-crown-4 in an equimolar ratio. The structure is reported elsewhere [6].

Yb $(NO_3)_3$ (12-crown-4) (0.5 mmol) dissolved in 10 mL acetone which contained a very small amount of water was mixed with phen (0.5 mmol) under stirring. The precipitate of powdered [Yb $(NO_3)_3$ (phen) (H_2O)] · (12-crown-4) was filtered off and the filtrate was allowed to evaporate slowly over P_2O_5 in a dessiccator. Crystals of the title compound suitable for X-ray analysis were obtained in a week.

Data collection was performed on a Nicolet R3m/E four-circle diffractometer equipped with a graphite monochromater, using $\omega/2\theta$ scan technique. A total of 6033 reflections were collected, of which 5213 reflections with $I > 3\sigma(I)$ were

TABLE II. Final fractional coordinates for [Yb $(NO_3)_3$ (phen) (H_2O)] · (12-crown-4).

Atom	x/a	y/b	z/c
Yb	0.0978(1)	0.2155(1)	0.3869(1)
N(1)	0.300(2)	0.0659(9)	0.561(2)
N(2)	–0.118(2)	0.358(1)	0.180(2)
N(3)	0.077(2)	0.244(1)	0.703(2)
N(4)	0.133(2)	0.1403(8)	0.157(2)
N(5)	–0.131(2)	0.1764(8)	0.196(2)
O(11)	0.158(2)	0.0795(8)	0.499(2)
O(12)	0.350(2)	0.123(1)	0.537(2)
O(13)	0.398(2)	0.002(1)	0.640(3)
O(21)	–0.081(2)	0.3430(8)	0.336(2)
O(22)	–0.043(2)	0.3054(8)	0.122(2)
O(23)	–0.216(2)	0.4167(9)	0.094(2)
O(31)	–0.025(1)	0.2206(8)	0.572(2)
O(32)	0.191(2)	0.252(1)	0.675(2)
O(33)	0.058(2)	0.2648(9)	0.826(2)
Ow(1)	0.260(2)	0.2823(9)	0.386(2)
O(1)	0.513(2)	0.3357(8)	0.348(2)
O(2)	0.187(2)	0.4192(8)	0.176(2)
O(3)	0.310(2)	0.4549(8)	0.521(2)
O(4)	0.514(2)	0.2995(9)	0.664(2)
C(1)	0.266(2)	0.120(1)	0.146(2)
C(2)	0.284(2)	0.079(1)	0.010(2)
C(3)	0.150(2)	0.062(1)	–0.121(2)
C(4)	0.013(2)	0.084(1)	–0.110(2)
C(5)	–0.126(2)	0.068(1)	–0.237(2)
C(6)	–0.255(3)	0.087(1)	–0.223(2)
C(7)	–0.266(2)	0.127(1)	–0.077(2)
C(8)	–0.405(2)	0.150(1)	–0.054(2)
C(9)	–0.399(2)	0.186(2)	0.087(3)
C(10)	–0.265(2)	0.196(1)	0.215(3)
C(11)	–0.133(2)	0.1406(9)	0.056(2)
C(12)	0.008(2)	0.1210(9)	0.038(2)
C(21)	0.450(2)	0.400(1)	0.221(3)
C(22)	0.288(3)	0.406(2)	0.094(3)
C(23)	0.150(3)	0.497(1)	0.238(3)
C(24)	0.153(2)	0.491(1)	0.408(3)
C(25)	0.322(3)	0.419(2)	0.671(3)
C(26)	0.491(3)	0.364(1)	0.767(3)
C(27)	0.650(3)	0.291(2)	0.635(4)
C(28)	0.623(2)	0.350(2)	0.505(3)

TABLE III. Selected bond lengths (Å) and angles (°).

Yb–N(4)	2.45(2)	Yb–N(5)	2.44(1)	Yb–O(11)	2.41(1)
Yb–O(12)	2.42(1)	Yb–O(21)	2.36(1)	Yb–O(22)	2.46(1)
Yb–O(31)	2.41(2)	Yb–O(32)	2.39(2)	Yb–Ow(1)	2.26(2)
N(4)–Yb–N(5)		67.8(5)	N(4)–Yb–O(11)		78.9(5)
N(5)–Yb–O(11)		77.7(4)	N(4)–Yb–O(12)		77.4(5)
N(5)–Yb–O(12)		124.2(5)	O(11)–Yb–O(12)		53.1(6)
N(4)–Yb–O(21)		122.9(4)	N(5)–Yb–O(21)		82.9(5)
O(11)–Yb–O(21)		142.1(6)	O(12)–Yb–O(21)		152.4(5)
N(4)–Yb–O(22)		72.0(4)	N(5)–Yb–O(22)		70.3(5)
O(11)–Yb–O(22)		142.9(4)	O(12)–Yb–O(22)		136.7(6)
O(21)–Yb–O(22)		51.8(5)	N(4)–Yb–O(31)		140.6(5)
N(5)–Yb–O(31)		79.6(5)	O(11)–Yb–O(31)		73.1(5)
O(12)–Yb–O(31)		105.6(5)	O(21)–Yb–O(31)		71.5(5)
O(22)–Yb–O(31)		117.5(5)	N(4)–Yb–O(32)		152.2(5)
N(5)–Yb–O(32)		133.6(6)	O(11)–Yb–O(32)		88.3(5)
O(12)–Yb–O(32)		75.2(6)	O(21)–Yb–O(32)		81.8(5)
O(22)–Yb–O(32)		127.5(5)	O(31)–Yb–O(32)		54.0(6)
N(4)–Yb–Ow(1)		88.7(6)	N(5)–Yb–Ow(1)		141.8(5)
O(11)–Yb–Ow(1)		128.4(5)	O(12)–Yb–Ow(1)		75.3(6)
O(21)–Yb–Ow(1)		85.9(6)	O(22)–Yb–Ow(1)		74.1(5)
O(31)–Yb–Ow(1)		130.4(5)	O(32)–Yb–Ow(1)		80.0(6)

TABLE IV. Selected torsion angles (°) for the title complex.

C(21)–C(22)–O(2)–C(23)	72.0	C(22)–O(2)–C(23)–C(24)	–137.8
C(23)–C(24)–O(3)–C(25)	–157.9	C(24)–O(3)–C(25)–C(26)	166.5
C(25)–C(26)–O(4)–C(27)	127.9	C(26)–O(4)–C(27)–C(28)	–78.6
C(27)–C(28)–O(1)–C(21)	165.6	C(28)–O(1)–C(21)–C(22)	–150.0
O(1)–C(21)–C(22)–O(2)	60.6	O(2)–C(23)–C(24)–O(3)	67.3
O(3)–C(25)–C(26)–O(4)	–66.0	O(4)–C(27)–C(28)–O(1)	–64.9

considered observed. Corrections for LP factors and absorption based on the Ψ scan technique were applied.

The position of the Yb(III) ion was established from the Patterson map. The remaining non-hydrogen atoms were found in succeeding Fourier synthesis. The coordinates and anisotropic thermal parameters were refined by the block-matrix least squares technique. The positions of hydrogen atoms were fixed by theoretical models and refined with isotropic thermal parameters. The final R and R_w are 0.088 and 0.094, respectively, due to the low quality of the crystals. Crystal data and a summary of the data collection and refinement are listed in Table I.

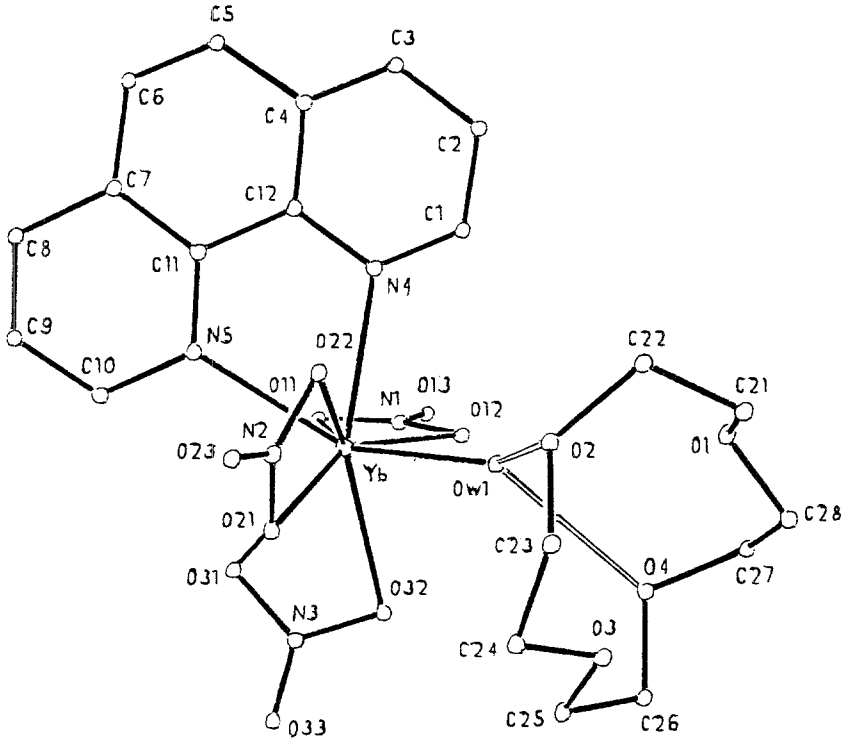

Fig. 1. Molecular structure of the title complex.

Results and Discussion

The atomic coordinates of the non-hydrogen atoms, selected bond lengths and angles are presented in Tables II and III, respectively. The molecular structure of the title complex is shown in Figure 1.

The coordination number of the metal ion in [Yb $(NO_3)_3$ (phen) (H_2O)] · (12-crown-4) is nine, with the metal ion bonding to three bidentate nitrate ions, two nitrogen atoms of a phen and a water molecule, but in Yb $(NO_3)_3$ (12-crown-4) it bonds with three bidentate nitrate ions and four oxygen atoms of a crown ether with a Yb–O (ether) separation of 2.51(1) Å. The Yb–O (nitrate) bond lengths in the title complex average 2.41(1) Å, shorter than that in Yb $(NO_3)_3$ (12-crown-4) by 0.06 Å. The mean Yb–N (phen) distance is 2.45(2) Å.

The water molecule is 2.26(2) Å from the metal ion. It forms two hydrogen bonds with the uncomplexed crown ether. The Ow(1)...O(2) and Ow(1)...O(4) separations are 2.793 and 2.734 Å, respectively.

The hydrogen-bonded crown ether in the title complex exhibits C_s symmetry, which is quite different from that of the directly coordinated molecule in Yb $(NO_3)_3$ (12-crown-4). The C_s symmetry is characterized by *gauche* (60°) O–C–C–O torsion angles (Table IV), two consecutively of the same sign, the next two of the opposite sign, and all but two of the C–O–C–C torsion angles are *anti* (180 or 120°) which occured between O–C–C–O angles of the same sign [10]. The 12-crown-4 molecule in Yb $(NO_3)_3$ (12-crown-4) adopts a conformation similar to C_4, which directs all the oxygen atoms toward the metal ion [6, 10].

From the above discussion we conclude that a number of structural changes occured as Yb $(NO_3)_3$ (12-crown-4) reacted with phen. The coordination number of the metal ion decreases from 10 to 9 and the phen replaces the crown ligand into the first coordination sphere. The crown ligand contacts with the Yb(III) ion through hydrogen bonds from the coordination water, consequently its symmetry changes from C_4 to C_s.

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