Acta Cryst. (1987). C**43**, 1056–1058

Structure of Thorium Nitrate–1,4,7,10,13,16-Hexaoxacyclooctadecane–Water (1/1/3), $[Th(OH_2)_3(NO_3)_4]$.18-Crown-6 at 123 K*

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(*Received* 4 *November* 1986; *accepted* 23 *December* 1986)

Abstract. Triaquatetranitratothorium(IV)–18-crown-6, $[Th(OH_2)_3(NO_3)_4].C_{12}H_{24}O_6$, $M_r = 798{\cdot}4$, monoclinic, $C2/c$, $a = 14{\cdot}189\,(6)$, $b = 11{\cdot}729\,(3)$, $c = 15{\cdot}252\,(7)$ Å, $\beta = 90{\cdot}66\,(3)^\circ$, $V = 2538{\cdot}2$ Å^3, $Z = 4$, $D_x = 2{\cdot}09$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 61{\cdot}9$ cm^{-1}, $F(000) = 1552$, $T = 123$ K, final $R = 0{\cdot}045$ for 2125 observed $[F_o \geq 5\sigma(F_o)]$ reflections. The $Th(NO_3)_4(OH_2)_3$ moiety resides on a crystallographic twofold axis containing the Th atom and one water molecule. The crown ether resides around a center of inversion and is hydrogen bonded to four water molecules coordinated to two different Th centers resulting in polymeric zigzag chains. The eleven-coordinate Th atom has approximate decahexahedral geometry with average Th—O(nitrate) and Th—O(water) distances of 2·56 (4) and 2·463 (3) Å, respectively. The crown ether adopts neither the elliptical conformation found in the free crown ether nor the symmetric D_{3d} form found for most 18-crown-6 complexes.

Introduction. 18-Crown-6 is flexible towards conformational change and various conformations have been found to be stabilized by fairly weak hydrogen bonds from neutral molecules (Vogtle & Weber, 1985; Izatt & Christensen, 1979, 1981). These interactions include NH···O(crown) hydrogen bonds, OH···O hydrogen bonds, and even weak CH acidic CH···O interactions. Most of these solvent complexes exhibit the symmetric D_{3d} crown-ether conformation found in many 18-crown-6 complexes with rare-earth, alkali and alkaline-earth salts. This is probably due to a compensation for otherwise unfavorable electrostatic interactions between the O atoms in this conformation (Uiterwijk, Harkema, van de Waal, Gobel & Nibbeling, 1983). In our efforts to compare the structural chemistry of *f*-element complexed *versus* hydrogen-bonded crown ethers we have carried out a complete single-crystal X-ray diffraction study of the title compound. The synthesis has been reported by Klimes, Knochel & Rudolph (1977).

Experimental. Clear parallelepipeds grown from CH_3CN at 278 K. D_m not determined. Crystal 0·28 × 0·33 × 0·33 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Cell constants from setting angles of 25 reflections ($\theta > 19^\circ$). Correction for Lorentz–polarization effect and for absorption (empirical), min., max. transmission coefficients 0·13, 0·18. $\theta_{\max} = 25^\circ$; h 0 to 16, k 0 to 13, l −18 to 18. 2455 reflections measured, 2125 independent observed reflections $[F_o \geq 5\sigma(F_o)]$, $R_{\text{int}} = 0{\cdot}03$. Structure solved *via* Patterson function and subsequent difference Fourier techniques. Crown-ether H atoms placed 0·95 Å from the bonded C atom with a fixed isotropic thermal parameter $B = 3{\cdot}2$ Å^2 and allowed to ride on that atom. Water-molecule H atoms observed in a difference Fourier map and fixed with $B = 3{\cdot}2$ Å^2. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); structure refined with *SHELX*76 (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized, weights $= [\sigma(F_o)^2 + 0{\cdot}0004F_o^2]^{-1}$, 173 parameters varied. $R = 0{\cdot}045$, $wR = 0{\cdot}059$, $S = 1{\cdot}5$. Δ/σ in final least-squares refinement cycle $< 0{\cdot}01$, $\Delta\rho < 1{\cdot}5$ e Å^{-3} in final difference map.

Discussion. Fractional coordinates and U_{eq} values are given in Table 1,‡ distances and angles in Table 2, and an *ORTEP* drawing (Johnson, 1965) indicating the polymeric nature of the title complex in Fig. 1.

$Th(NO_3)_4(OH_2)_3$.18-crown-6 consists of zigzag polymeric chains of $Th(NO_3)_4(OH_2)_3$ moieties hydrogen bonded on either side of 18-crown-6 molecules. The Th and O(7) atoms reside on a crystallographic twofold axis. The eleven-coordinate Th atom has decahexahedral geometry (Gopal, Rutherford & Robertson, 1980) and is almost identical to the parent complex for the pentahydrate, $Th(NO_3)_4(OH_2)_3.2(H_2O)$ (Ueki, Zalkin & Templeton, 1966). The average Th—O(nitrate) and Th—O(water) separations are 2·56 (4) and

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* *f*-Element/Crown Ether Complexes. 8. Part 7: Rogers & Kurihara (1987).

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‡ Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43720 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/87/061056-03$01.50

2·463 (3) Å. The corresponding values in the room-temperature X-ray diffraction determination of $Th(NO_3)_4(OH_2)_3.2(H_2O)$ are 2·57 and 2·46 Å.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters for* $Th(NO_3)_4(OH_2)_3$.-18-*crown*-6

	x	y	z	U_{eq}*(Å^2)
Th	0·0000	0·31050 (3)	0·2500	0·012
O(1)	0·1656 (5)	0·3283 (5)	0·3142 (4)	0·029
O(2)	0·1530 (5)	0·3996 (5)	0·1848 (4)	0·029
O(3)	0·2869 (4)	0·4060 (6)	0·2527 (4)	0·034
O(4)	0·1005 (5)	0·1751 (5)	0·1608 (5)	0·032
O(5)	−0·0472 (5)	0·1323 (5)	0·1639 (4)	0·031
O(6)	0·0509 (6)	0·0205 (5)	0·0970 (5)	0·048
O(7)	0·0000	0·5203 (7)	0·2500	0·026
O(8)	0·0042 (4)	0·3715 (5)	0·4046 (4)	0·022
O(9)	−0·0142 (5)	0·6833 (4)	0·3678 (4)	0·029
O(10)	0·1416 (4)	0·6568 (5)	0·4826 (4)	0·023
O(11)	0·1494 (4)	0·4140 (5)	0·5173 (4)	0·024
N(1)	0·2055 (5)	0·3786 (6)	0·2510 (4)	0·019
N(2)	0·0361 (6)	0·1071 (6)	0·1401 (5)	0·031
C(1)	0·0683 (7)	0·7505 (8)	0·3540 (6)	0·030
C(2)	0·1255 (8)	0·7633 (8)	0·4366 (6)	0·033
C(3)	0·1960 (7)	0·5782 (7)	0·4337 (6)	0·025
C(4)	0·2301 (6)	0·4831 (7)	0·4946 (6)	0·024
C(5)	0·1718 (7)	0·3360 (7)	0·5842 (6)	0·025
C(6)	0·0922 (7)	0·2535 (7)	0·5962 (6)	0·025

* $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table 2. *Bond distances* (Å) *and angles* (°) *for* $Th(NO_3)_4(OH_2)_3$.18-*crown*-6

Th—O(1)	2·544 (7)	Th—O(2)	2·617 (6)
Th—O(4)	2·540 (6)	Th—O(5)	2·554 (6)
Th—O(7)	2·461 (8)	Th—O(8)	2·465 (6)
O(1)—N(1)	1·268 (9)	O(2)—N(1)	1·272 (9)
O(3)—N(1)	1·199 (9)	O(4)—N(2)	1·25 (1)
O(5)—N(2)	1·28 (1)	O(6)—N(2)	1·23 (1)
O(9)—C(1)	1·43 (1)	O(9)—C(6^{ii})	1·45 (1)
O(10)—C(2)	1·45 (1)	O(10)—C(3)	1·42 (1)
O(11)—C(4)	1·45 (1)	O(11)—C(5)	1·40 (1)
C(1)—C(2)	1·50 (1)	C(3)—C(4)	1·53 (1)
C(5)—C(6)	1·50 (1)		

O(1)—Th—O(2)	49·2 (2)	O(1)—Th—O(4)	74·7 (2)
O(2)—Th—O(4)	64·7 (2)	O(1)—Th—O(5)	120·0 (2)
O(2)—Th—O(5)	110·2 (2)	O(4)—Th—O(5)	50·1 (2)
O(1)—Th—O(7)	85·3 (1)	O(2)—Th—O(7)	66·5 (1)
O(4)—Th—O(7)	128·7 (1)	O(5)—Th—O(7)	144·9 (2)
O(1)—Th—O(8)	66·2 (2)	O(2)—Th—O(8)	103·7 (2)
O(4)—Th—O(8)	133·3 (2)	O(5)—Th—O(8)	137·1 (2)
O(7)—Th—O(8)	73·1 (1)	O(1)—Th—O(1^{i})	170·6 (3)
O(2)—Th—O(1^{i})	126·0 (2)	O(4)—Th—O(1^{i})	111·6 (2)
O(5)—Th—O(1^{i})	68·5 (2)	O(8)—Th—O(1^{i})	110·9 (2)
O(2)—Th—O(2^{i})	132·9 (3)	O(4)—Th—O(2^{i})	158·0 (2)
O(5)—Th—O(2^{i})	108·0 (2)	O(8)—Th—O(2^{i})	62·1 (2)
O(4)—Th—O(4^{i})	102·6 (3)	O(5)—Th—O(4^{i})	67·5 (2)
O(8)—Th—O(4^{i})	71·1 (2)	O(5)—Th—O(5^{i})	70·1 (3)
O(8)—Th—O(5^{i})	75·1 (2)	O(8)—Th—O(8^{i})	146·3 (3)
Th—O(1)—N(1)	99·5 (5)	Th—O(2)—N(1)	95·8 (4)
Th—O(4)—N(2)	96·9 (5)	Th—O(5)—N(2)	95·6 (5)
C(1)—O(9)—C(6^{ii})	113·8 (6)	C(2)—O(10)—C(3)	112·9 (7)
C(4)—O(11)—C(5)	111·5 (7)	O(1)—N(1)—O(2)	115·5 (7)
O(1)—N(1)—O(3)	123·1 (7)	O(2)—N(1)—O(3)	121·3 (7)
O(4)—N(2)—O(5)	117·2 (7)	O(4)—N(2)—O(6)	122·3 (8)
O(5)—N(2)—O(6)	120·5 (9)	O(9)—C(1)—C(2)	111·6 (7)
O(10)—C(2)—C(1)	113·7 (7)	O(10)—C(3)—C(4)	109·0 (7)
O(11)—C(4)—C(3)	108·0 (7)	O(11)—C(5)—C(6)	110·1 (8)
C(5)—C(6)—O(9^{ii})	107·2 (7)		

Symmetry code: atoms related to those in Table 1 by (i) $-x, y, 0·5-z$; (ii) $-x, 1-y, 1-z$.

The 18-crown-6 molecule resides around a center of inversion. The six O atoms participate in hydrogen bonds to three H atoms from two water molecules on one side of the inversion center and three H atoms from a different $Th(NO_3)_4(OH_2)_3$ unit on the other. The three independent H···O(crown) separations are 1·70[O(7)], 1·90 and 1·91 Å with an average O···O distance of 2·69 (5) Å. The average O—H···O angle is 164°.

The bond distances and angles in the crown ring are nearly identical with those found for the free crown at 100 K given below in square brackets (Maverick, Seiler, Schweizer & Dunitz, 1980): C—O = 1·43 (2) [1·423], C—C = 1·51 (2) Å [1·512 Å], C—O—C = 113 (1) [112·8 (2)], C—C—O = 110 (2)° [109 (3)°]. The crown-ether conformation as defined by the O—C—C—O and C—C—O—C torsion angles is unusual. The torsion-angle sequence [starting with O(9)—C(1)—C(2)—O(10), unique angles given] for the crown ether in the title complex is g^+(48°), g^+(64°), a(166°), g^+(71°), a(−170°), a(−171°), g^-(−67°), a(179°), g^-(−83°), g^-, g^-, a, g^-, a, a, g, a, g. Calculations by Uiterwijk *et al.* (1983) revealed 27 ideal conformations for 18-crown-6 of which 14 had a conformational energy ≤ 21 kJ mol^{-1}. Of the latter 14 the conformation observed here was of highest conformational energy and in fact has been observed in the literature only once in $[Co(OH_2)_6][CoCl_4]$.18-crown-6.acetone (Vance, Holt, Pierpont & Holt, 1980). The most commonly observed crown-ether conformation in its complexes with ions and hydrogen-bond donors is the symmetrical D_{3d} ($ag^+aag^-aag^+aa$) form (Uiterwijk *et al.*, 1983). The free crown ether has a more elliptical form ($g^-aag^+aaaag^-g^+aag^-aaaag^+$) (Maverick *et al.*, 1980).

We thank the donors to the Petroleum Research Fund administered by the American Chemical Society for support of this work and the NSF Chemical Instrumentation Program for funds used to purchase the diffractometer.

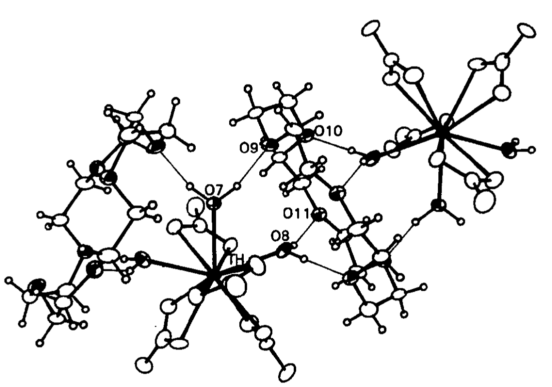

Fig. 1. $Th(NO_3)_4(OH_2)_3$.18-crown-6. 50% probability ellipsoids for thermal motion. H atoms arbitrarily reduced.

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Acta Cryst. (1987). C**43**, 1058–1061

Structure of *catena*-Aqua(2,2′-bipyridine)(2-imidazolidinethione-*S*)-*μ*-[sulfato(2−)-*O*:*O*′]-cadmium(II) Monohydrate and its Solid-State ^{113}Cd NMR Spectrum

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(*Received* 4 *August* 1986; *accepted* 13 *January* 1987)

Abstract. [Cd(SO$_4$)(C$_3$H$_6$N$_2$S)(C$_{10}$H$_8$N$_2$)(H$_2$O)].H$_2$O, $M_r = 502{\cdot}84$, monoclinic, $P2_1/n$, $a = 6{\cdot}736$ (1), $b = 25{\cdot}728$ (3), $c = 10{\cdot}011$ (2) Å, $\beta = 90{\cdot}72$ (2)°, $V = 1734$ (1) Å^3, $Z = 4$, $D_m = 1{\cdot}91$ (2), $D_x = 1{\cdot}93$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 15{\cdot}2$ cm^{-1}, $F(000) = 1008$, $T \simeq 298$ K, $R(F) = 0{\cdot}044$ for 3285 reflections. The structure may be described as six-coordinate Cd^{II} species which are bridged by two different O atoms of sulfate ions to form an infinite chain of the type: –OSO$_2$O–Cd–OSO$_2$O–. The remaining intermolecular distances are normal van der Waals distances. The coordination polyhedron of Cd^{II} may be described in terms of an approximate octahedron with a water O atom, an S atom and two N atoms from the bipyridine in the equatorial plane and sulfate O atoms in the axial positions. The water of hydration is hydrogen bonded to the coordinated water. The Cd–O(SO$_4$) distances are 2·273 (4) and 2·298 (4) Å, whereas the Cd–O(H$_2$O) distance is 2·315 (4) Å. The Cd–S and Cd–N distances are 2·628 (1) and 2·373 (5), 2·393 (5) Å, respectively. The cross-polarization magic-angle spinning ^{113}Cd NMR signal is observed at 137 p.p.m., deshielded relative to the solid Cd(ClO$_4$)$_2$ in Al$_2$O$_3$ standard. The principal components of the chemical shift tensor were calculated from the spinning side bands and were found to be +285, +137 and −10 p.p.m. No solution ^{113}Cd NMR was observed.

Introduction. In recent years there has been considerable research effort expended in the application of ^{113}Cd NMR to the solution of problems dealing with metal sites in a wide variety of chemical and biological compounds (Rodesiler, Turner, Charles, Griffith & Amma, 1984; Armitage & Boulanger, 1983; Ellis, 1983). The development of solid-state cross-polarization magic-angle spinning (CP/MAS) ^{113}Cd NMR has even further enhanced the potential utility of this metal-ion probe (Ackermann, Orr, Bartuska & Maciel, 1979; Mennitt, Shatlock, Bartuska & Maciel, 1981; Maciel, 1984; Marchetti, Ellis & Bryant, 1985). The combination of X-ray crystallography and (CP/MAS) NMR offers an excellent opportunity to study and attempt to correlate metal-ion geometry with ^{113}Cd NMR chemical shifts, and perhaps by this means to convert ^{113}Cd NMR into a much more useful chemical tool. The ultimate goal of such studies is to be

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0108-2701/87/061058-04$01.50