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*Acta Cryst.* (1999). C**55**, 1275–1278

# Tetrachlorotetrakis(propan-2-ol)uranium(IV) and tetrachlorotetrakis(propan-2-ol)thorium(IV)

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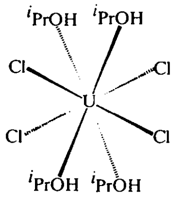
(*Received 1 December 1998; accepted 6 April 1999*)

## Abstract

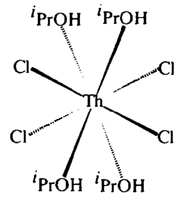
The title complexes, [$UCl_4(C_3H_8O)_4$] and [$ThCl_4(C_3H_8O)_4$], are isomorphous and crystallize in the tetragonal space group $I4_1/a$. The molecules have approximate dodecahedral symmetry and occupy sites of $\bar{4}$ symmetry. Principal bond lengths include U—Cl = 2.6478 (10), U—O = 2.478 (3), Th—Cl = 2.7066 (8) and Th—O = 2.515 (2) Å.

## Comment

In previous publications, we have examined the direct reaction between lanthanide and actinide metals and elemental iodine, employing either tetrahydrofuran (THF) or alcohols as solvent (Barnhart *et al.*, 1995; Van der Sluys *et al.*, 1992). We have now extended these studies to include the reaction of thorium and uranium metal turnings with chlorine gas, which may be conveniently bubbled through a flask containing isopropanol solvent and the appropriate actinide metal. Subsequent work-up provides crystals of uranium or thorium tetrachloride which contain four coordinated molecules of isopropanol. $UCl_4(^iPrOH)_4$ (Smith *et al.*, 1969) and $ThCl_4(^iPrOH)_4$ (El Aggan, 1973) have been described previously but they have not been structurally characterized. We report here the structural characterization of tetrachlorotetrakis(isopropanol)uranium(IV), (I), and tetrachlorotetrakis(isopropanol)thorium(IV), (II).



(I)



(II)

Complexes (I) and (II) are isostructural and crystallize in the tetragonal space group $I4_1/a$. The complexes occupy sites of $\bar{4}$ symmetry (Figs. 1 and 2). The ligands define a somewhat distorted dodecahedral structure about the metal center, with the chloride ligands occupying '*B*' sites and the isopropanol ligands occupying '*A*' sites (Kepert, 1978).

The U—Cl distance of 2.6478 (10) Å is slightly longer than the mean value of 2.595 (2) Å observed in seven-coordinate $UCl_4(thf)_3$ (Van der Sluys *et al.*, 1993),

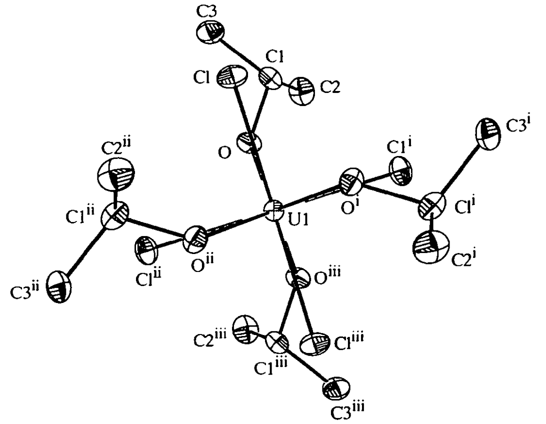


Fig. 1. The molecular structure of (I), showing the atom-numbering scheme and with 50% probability displacement ellipsoids. H atoms have been omitted for clarity. The view is down the fourfold axis of the $\bar{4}$ symmetry element [symmetry codes: (i) $y - \frac{1}{4}, \frac{5}{4} - x, \frac{1}{4} - z$; (ii) $\frac{5}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$; (iii) $1 - x, \frac{3}{2} - y, z$].

*Acta Crystallographica Section C*
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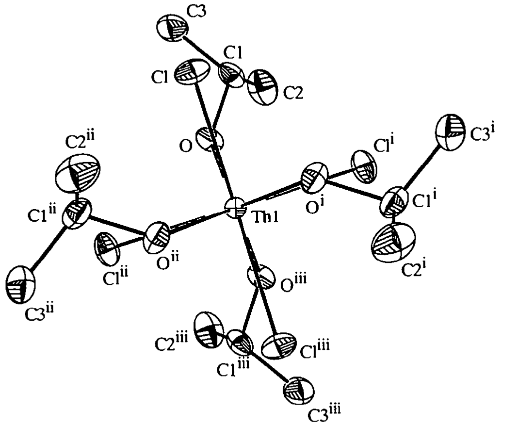

Fig. 2. The molecular structure of (II), showing the atom-numbering scheme and with 50% probability displacement ellipsoids. H atoms have been omitted for clarity. The view is down the fourfold axis of the $\bar{4}$ symmetry element [symmetry codes: (i) $y - \frac{1}{4}, \frac{5}{4} - x, \frac{1}{4} - z$; (ii) $\frac{5}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$; (iii) $1 - x, \frac{3}{2} - y, z$].

but is directly comparable to the distances of 2.627 (4) and 2.620 (4) Å found in $UCl_4(MeCN)_4$ (Cotton *et al.*, 1984). The U—O distance of 2.478 (3) Å is longer than the value of 2.40 (1) Å found for the isopropanol ligands in $U_2I_4(O^iPr)_4(^iPrOH)_2$ (Van der Sluys *et al.*, 1992), but is comparable with the U—O distance of 2.50 (1) Å to the methanol ligand in $UO_2(thd)_2(MeOH)$, where thd is tetramethylheptane-3,5-dionate (Mackinnon & Taylor, 1983).

The Th—Cl distance of 2.7066 (8) Å may be compared with that of 2.710 (7) Å in $ThCl_4(MeOH)_2$-$(H_2O)_2$·15-crown-5·$CH_3CN$ (Rogers & Benning, 1988), 2.688 (2)–2.692 (2) Å in $ThCl_4(Me_2NCH_2CH_2NMe_2)_2$ (Rabinovich *et al.*, 1997) and 2.7038 (10)–2.7198 (10) Å in [$ThCl_4(thf)_3(H_2O)$]·thf (Spry *et al.*, 1997). The Th—O bond length to the isopropanol ligands [2.515 (2) Å] is intermediate between the Th—O distances to the methanol ligands in $ThCl_4(MeOH)_2$-$(H_2O)_2$·15-crown-5·$CH_3CN$, which have a mean value of 2.562 (3) Å (Rogers & Benning, 1988), and the Th—O distance to the isopropanol ligands in $Th_2I_4(O^iPr)_4$-$(^iPrOH)_2$ of 2.437 (6) Å (Barnhart *et al.*, 1995).

There are two types of Cl—*M*—Cl angles in each complex, namely 95.713 (13) and 143.22 (4)° in (I), and 95.838 (10) and 142.80 (3)° for (II). Similarly, O—*M*—O angles are also of two types, namely 69.79 (14) and 132.28 (9)° for (I), and 70.30 (10) and 131.96 (7)° for (II).

## Experimental

Approximately 5 g of cleaned metal turnings of the appropriate metal were placed in a Schlenk flask and 30 ml of dried degassed isopropanol was added. Chlorine gas, diluted with nitrogen, was bubbled through the solution at the rate of 0.02–0.06 l min$^{-1}$ for 30 min. The resulting solution was filtered, and the filtrate was allowed to evaporate slowly under an inert atmosphere to produce colorless (thorium) or pale-green (uranium) crystals of the title compounds.

### Compound (I)

*Crystal data*

[$UCl_4(C_3H_8O)_4$]
$M_r = 620.21$
Tetragonal
$I4_1/a$
$a = 10.330 (1)$ Å
$c = 20.222 (4)$ Å
$V = 2157.9 (5)$ Å$^3$
$Z = 4$
$D_x = 1.909$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.6$–$14.0°$
$\mu = 8.03$ mm$^{-1}$
$T = 203$ K
Block
0.25 × 0.23 × 0.21 mm
Green

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$2\theta/\theta$ scans
Absorption correction: empirical (Siemens, 1994*a*)
$T_{min} = 0.16$, $T_{max} = 0.18$
2122 measured reflections
948 independent reflections
853 reflections with $I > 2\sigma(I)$

$R_{int} = 0.047$
$\theta_{max} = 24.95°$
$h = -12 \rightarrow 0$
$k = -12 \rightarrow 0$
$l = -24 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: <2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.051$
$S = 1.07$
948 reflections
48 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.54$ e Å$^{-3}$ (1.13 Å from U1)
$\Delta\rho_{min} = -1.18$ e Å$^{-3}$ (1.02 Å from U1)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| U1 | 1/2 | 3/4 | 1/8 | 0.01369 (12) |
| Cl | 0.26774 (10) | 0.67779 (11) | 0.16631 (5) | 0.0224 (2) |
| O | 0.3711 (3) | 0.7027 (3) | 0.02448 (13) | 0.0199 (6) |
| C1 | 0.2429 (4) | 0.7429 (4) | 0.0007 (2) | 0.0220 (9) |
| C2 | 0.2582 (5) | 0.8061 (5) | −0.0667 (2) | 0.0298 (11) |
| C3 | 0.1525 (4) | 0.6271 (5) | 0.0002 (2) | 0.0269 (10) |

Table 2. *Selected geometric parameters (Å, °) for (I)*

| | | | |
|---|---|---|---|
| U1—O | 2.478 (3) | C1—C3 | 1.518 (6) |
| U1—Cl | 2.6478 (10) | C1—C2 | 1.519 (6) |
| O—C1 | 1.469 (5) | | |
| O$^{i}$—U1—O$^{ii}$ | 69.79 (14) | Cl—U1—Cl$^{ii}$ | 95.713 (13) |
| O$^{i}$—U1—O | 132.28 (9) | O—U1—Cl$^{i}$ | 76.61 (7) |
| O—U1—Cl$^{iii}$ | 143.22 (7) | Cl—U1—Cl$^{i}$ | 95.713 (13) |
| O$^{i}$—U1—Cl | 73.38 (7) | C1—O—U1 | 134.2 (2) |

| | | | |
|---|---|---|---|
| $O^{ii}$—U1—Cl | 76.62 (7) | O—C1—C3 | 109.5 (3) |
| O—U1—Cl | 73.54 (7) | O—C1—C2 | 108.8 (4) |
| $Cl^{iii}$—U1—Cl | 143.22 (4) | C3—C1—C2 | 113.4 (4) |

Symmetry codes: (i) $y - \frac{1}{4}, \frac{5}{4} - x, \frac{1}{4} - z$; (ii) $\frac{5}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$; (iii) $1 - x, \frac{3}{2} - y, z$.

## Compound (II)

### *Crystal data*

$[ThCl_4(C_3H_8O)_4]$
$M_r = 614.22$
Tetragonal
$I4_1/a$
$a = 10.447$ (1) Å
$c = 20.395$ (1) Å
$V = 2225.9$ (3) Å$^3$
$Z = 4$
$D_x = 1.833$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.8$–$14.0°$
$\mu = 7.19$ mm$^{-1}$
$T = 203$ K
Block
0.6 × 0.4 × 0.2 mm
Colorless

### *Data collection*

Siemens $R3m/V$ diffractometer
$\omega$ scans
Absorption correction: empirical (Siemens, 1994*a*)
$T_{min} = 0.06$, $T_{max} = 0.24$
2232 measured reflections
1622 independent reflections
1405 reflections with $I > 2\sigma(I)$

$R_{int} = 0.023$
$\theta_{max} = 30°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 14$
$l = -1 \rightarrow 28$
3 standard reflections every 97 reflections intensity decay: none

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.045$
$S = 1.18$
1622 reflections
51 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.22$ e Å$^{-3}$ (0.79 Å from Th1)
$\Delta\rho_{min} = -0.77$ e Å$^{-3}$ (1.11 Å from Th1)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Th1 | 1/2 | 3/4 | 1/8 | 0.01541 (6) |
| Cl | 0.26561 (7) | 0.67680 (8) | 0.16733 (4) | 0.02942 (16) |
| O | 0.3701 (2) | 0.7018 (2) | 0.02418 (10) | 0.0248 (4) |
| HO1 | 0.399 (5) | 0.645 (6) | 0.000 (3) | 0.080 |
| C1 | 0.2443 (3) | 0.7430 (3) | 0.00090 (14) | 0.0276 (7) |
| C2 | 0.2587 (4) | 0.8050 (4) | −0.06572 (17) | 0.0428 (9) |
| C3 | 0.1529 (3) | 0.6302 (4) | 0.00036 (19) | 0.0389 (8) |

Table 4. *Selected geometric parameters (Å, °) for (II)*

| | | | |
|---|---|---|---|
| Th1—O | 2.515 (2) | O—C1 | 1.462 (3) |
| Th1—Cl | 2.7066 (8) | C1—C2 | 1.513 (5) |
| O—HO1 | 0.83 (6) | C1—C3 | 1.517 (5) |
| $O^{i}$—Th1—$O^{ii}$ | 70.30 (10) | Cl—Th1—$Cl^{i}$ | 95.838 (10) |
| $O^{i}$—Th1—O | 131.96 (7) | HO1—O—C1 | 110 (4) |
| O—Th1—$Cl^{iii}$ | 143.67 (5) | HO1—O—Th1 | 116 (4) |
| $O^{i}$—Th1—Cl | 73.18 (5) | C1—O—Th1 | 133.78 (16) |
| O—Th1—Cl | 73.50 (5) | O—C1—C2 | 109.1 (3) |
| $Cl^{iii}$—Th1—Cl | 142.80 (3) | O—C1—C3 | 109.8 (2) |
| O—Th1—$Cl^{i}$ | 76.57 (5) | C2—C1—C3 | 112.9 (3) |

Symmetry codes: (i) $y - \frac{1}{4}, \frac{5}{4} - x, \frac{1}{4} - z$; (ii) $\frac{5}{4} - y, \frac{1}{4} + x, \frac{1}{4} - z$; (iii) $1 - x, \frac{3}{2} - y, z$.

For (I), all H atoms were refined using geometry constraints and a riding model. Isotropic displacement parameters were set at 0.05 Å$^2$. For (II), all H atoms, except for the alcohol H atom, were refined using geometry constraints and a riding model. These idealized H atoms were refined with isotropic displacement parameters set to 1.5 (methyl) or 1.2 (methine) times the equivalent isotropic $U$ value of the parent atom. The alcohol H-atom coordinates were refined with the isotropic displacement parameter fixed at 0.08 Å$^2$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989) for (I); *XSCANS* (Siemens, 1994*b*) for (II). Cell refinement: *CAD*-4 *Software* for (I); *XSCANS* for (II). Data reduction: *XCAD*4 (Harms & Wocadlo, 1996) for (I); *XSCANS* for (II). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXTL* (Siemens, 1994*a*).

We acknowledge the Nuclear Materials Stockpile Management Program for funding.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1458). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). C55, 1278-1280

# Poly[[aqua(2,2'-bipyridine-*N*,*N'*)cadmium(II)]-$\mu_3$-sulfito-*O*:*O*:*O'*] hydrate]

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(*Received 15 December 1998; accepted 14 April 1999*)

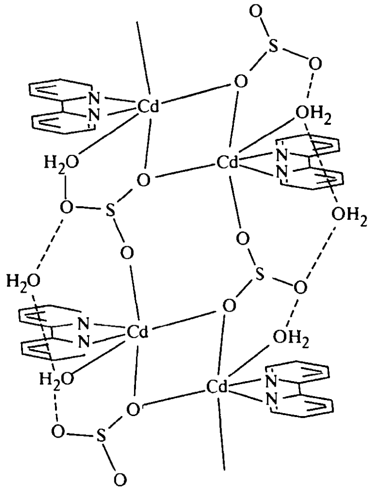
## Abstract

The title compound, $\{[Cd(SO_3)(C_{10}H_8N_2)(H_2O)]\cdot H_2O\}_n$, consists of ladder-type chains formed by distorted $CdN_2O_4$ octahedra replicated by two different types of embedded symmetry centres. The sulfite anion displays a regular geometry and coordinates through two O atoms, the third O atom only being involved in hydrogen bonding.

## Comment

The sulfite ion has been extensively studied as a component of many coordination compounds [34 entries in the 1998 version of the Cambridge Structural Database (CSD; Allen & Kennard, 1993)]. As demonstrated therein, the anion is able to adopt different modes of coordination depending on the characteristics of the metal present, due to its being composed both of soft (S) and hard (O) bases, according to Pearson's classification (Pearson, 1973).

However, and in spite of the great number of sulfite-containing organometallic compounds described in the literature, not a single crystallographic study has been reported on sulfite–cadmium complexes, the only structurally related studies being those performed on cadmium sulfite salts by Kiers & Vos (1978) and Engelen *et al.* (1987). Pursuant of our interest in cadmium sulfur oxoanion complexes, we report herein the crystal structure of the title compound, (I).



(I)

The cadmium ion interacts with the bidentate bipyridine, three symmetry-related sulfite groups and a coordination water molecule, all of which provide a heavily distorted octahedral environment, with N1, N2, O3$^{ii}$ and O1*W* occupying the equatorial positions, and O3 and O1$^{i}$ occupying the apical sites [symmetry codes: (i) $x, y, z-1$; (ii) $1-x, -y, 1-z$] (Fig. 1). The degree of deformation achieved by the polyhedron can be assessed by the maximum deviations from ideal geometry: N1 deviates by 0.111 (2) Å from the equatorial plane and Cd—O1$^{i}$ is 17.6 (1)° from the normal to the plane. Even the (in principle equivalent) Cd—N bonds display a striking difference of *ca* 5% in length as a result of the overall strain developed. A search in the CSD showed this difference to be in the upper 20% of the distribution for *ca* 3000 cases explored.

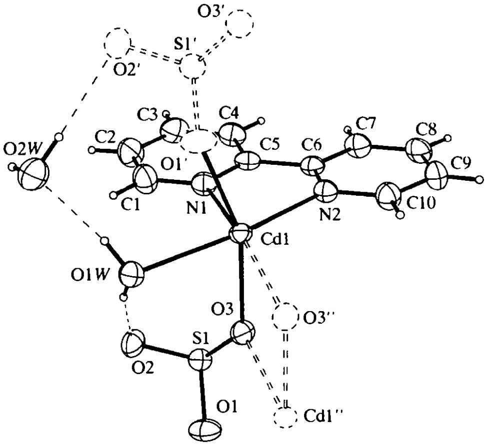


Fig. 1. Molecular diagram showing the numbering scheme used, as well as details of the cation coordination environment and some interchain hydrogen-bonding interactions. Displacement ellipsoids are drawn at the 50% probability level.