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## Bis{2-[1-(thiosemicarbazono)ethyl]-pyridinium} hexakis(nitrato-*O,O'*)-thorate(IV) tetramethanol solvate

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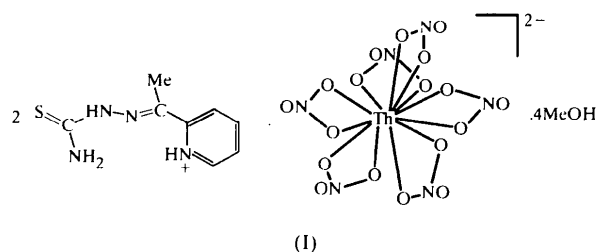
## Abstract

Pale yellow crystals of the title compound, (C<sub>8</sub>H<sub>11</sub>N<sub>4</sub>S)<sub>2</sub>·[Th(NO<sub>3</sub>)<sub>6</sub>]·4CH<sub>4</sub>O, are formed when thorium nitrate and acetylpyridine thiosemicarbazone are refluxed in methanol. Thorium is 12-coordinate. The complex anion possesses inversion symmetry. The almost planar 2-[1-(thiosemicarbazono)ethyl]pyridinium cations show bond lengths which indicate a considerable delocalization of electron density.

## Comment

Heterocyclic thiosemicarbazones, as well as their metal complexes, are currently under discussion because of their biological activity (West *et al.*, 1990, and references therein). Although a number of studies dealing with complex-formation properties exists (West *et al.*, 1990, and references therein; Garg *et al.*, 1988, and references therein), comparatively few structural reports have been published (Abram *et al.*, 1998). Studies on reactions of heterocyclic thiosemicarbazones with actinides have not yet been reported. As part of our systematic studies on the complex-formation properties of tri- and pentadentate thiosemicarbazones, we investigated the reaction of 2-acetylpyridine thiosemicarbazone (HAPTSC) with thorium(IV) nitrate.

Heating of Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O with excess HAPTSC in methanol results in the formation of (H<sub>2</sub>ATPSC)<sub>2</sub>·[Th(NO<sub>3</sub>)<sub>6</sub>], which crystallizes upon concentration of the reaction mixture. In this compound, thorium does not form any bonds to the thiosemicarbazone. In the remaining filtrate, however, a thorium thiosemicarbazonato complex of the tentative composition [Th(APTSC)(OH<sub>2</sub>)(NO<sub>3</sub>)<sub>2</sub>]<sup>−</sup> could be detected by a fast-atom bombardment (FAB<sup>−</sup>) mass spectrometry peak of reasonable intensity at *m/z* = 583. All attempts to isolate and crystallize this complex have failed up to now. The structure of (H<sub>2</sub>APTSC)<sub>2</sub>[Th(NO<sub>3</sub>)<sub>6</sub>]·4MeOH, (I) (Fig. 1), consists of a discrete complex anion and two acetylpyridinium thiosemicarbazone cations. Reasonable hydrogen bonds are only formed between the cations and the cocrystallized solvent, and between the two methanol molecules. Only one very weak hydrogen bond may be attributed between N12 and O33<sup>i</sup> of the complex anion [N12—H12 0.82 (5), H12···O33<sup>i</sup> 2.32 (5), N12···O33<sup>i</sup> 3.095 (4) Å and N12—H12—O33 158 (4)<sup>o</sup>; symmetry code: (i) *x*, *y* + 1, *z*] (see Fig. 2).



The metal atom is 12-coordinate with a coordination sphere which can be described as a distorted icosahedron with 12 isosceles and eight equilateral triangles forming the surface of the coordination polyhedron (Fig. 1). The metal is located on a centre of inversion. With this, the structure of the anion comes close to the [Th(NO<sub>3</sub>)<sub>6</sub>]<sup>2−</sup> anion (without inversion, but with approximate C<sub>2</sub> symmetry) in tris-2,2′-bipyridinium nitrate hexanitrothorate(IV) (Khan *et al.*, 1984) and in

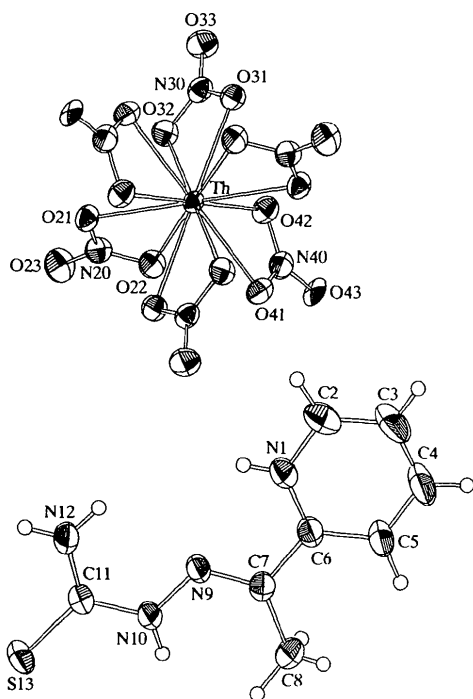


Fig. 1. An ellipsoid representation (Zsolnai, 1995; 50% probability) of (I).

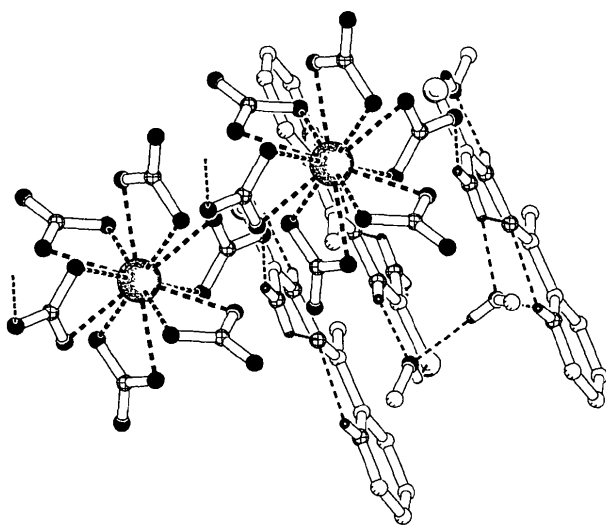


Fig. 2. The hydrogen-bonding scheme in (I) (Spek, 1998a).

$[Th(NO_3)_3(Me_3PO)_4][Th(NO_3)_6]$  (Alcock *et al.*, 1977), and is in contrast to the asymmetric complex anions in  $[Mg(H_2O)_6][Th(NO_3)_6] \cdot 2H_2O$  (Šćavničar & Prodić, 1965) and  $[Th(NO_3)_3(tdpo)_4]_2[Th(NO_3)_6]$  [tdpo is tris(dimethylamido)phosphine oxide] (English *et al.*, 1979). In two more recent papers, the  $[Th(NO_3)_6]^{2-}$  anion is described as nearly regular icosahedral (Ming *et al.*, 1988; Aparna *et al.*, 1995) and comparable with  $[Ce$

$(NO_3)_6]^{2-}$  in  $(NH_4)_2[Ce(NO_3)_6]$  (Beineke & Delgandio, 1968).

The distortions in the  $ThO_{12}$  icosahedron in the title compound are mainly established by the O—Th—O angles, which deviate significantly from the situation in a regular icosahedron where O—Th—O angles of 63.5 (five such), 116.5 (five such) and 180° (one such) for each specific O atom are expected. The experimental results show O—Th—O angles in the ranges 49.5–49.9 (one such), 67.1–68.3 (four such), 111.7–112.9 (four such) and 130.1–130.5° (one such), and an angle of 180° (one such, by symmetry) for any individual O atom. All Th—O bond lengths lie randomly in the range 2.553 (3)–2.580 (3) Å. The second coordination sphere of thorium is an almost regular octahedron, with Th—N distances between 2.996 (5) and 3.007 (5) Å, and a maximum deviation of the N—Th—N angles from 90° of 1.58°.

The  $H_2APTSC$  counter-ions are protonated at the N atoms of the pyridine ring, as could be derived from the structure determination. The bonding situation in the organic molecule comes close to that in the hydrochloride of the thiosemicarbazone despite the latter being aggregated to form dimers in the solid-state structure *via* hydrogen bonds (Abram & Abram, 1997). The molecule is almost planar, with a maximum deviation from a least-squares plane including all non-H atoms of 0.034 (4) Å (r.m.s. deviation of the fitted atoms: 0.0212 Å). The C11—S13 distance of 1.681 (3) Å is intermediate between typical C—S single- and double-bond lengths. This agrees well with the C11—N10 and C11—N12 bond lengths of 1.361 (4) and 1.316 (5) Å which indicate partial double-bond character. The C7—N9 bond [1.283 (4) Å] is significantly shorter than a C—N single bond, as can be expected for a thiosemicarbazone.

## Experimental

$Th(NO_3)_4 \cdot 4H_2O$  (55 mg, 0.1 mmol) was suspended in MeOH (approximately 20 ml) and a solution of HAPTSC (48 mg, 0.25 mmol) in MeOH (10 ml) was added. The mixture was refluxed for 30 min. During this time,  $Th(NO_3)_4$  dissolved and a clear yellow solution was obtained. Upon concentrating and cooling, pale yellow crystals of  $(H_2APTSC)_2[Th(NO_3)_6]$  deposited [yield 45 mg (40% based on Th)]. IR: (NH) 3452, 3293, 3107  $cm^{-1}$ , (C=N) 1615, 1565  $cm^{-1}$ ,  $(NO_3^-)$  1505, 1293, 1035, 805  $cm^{-1}$ . FAB<sup>+</sup> MS:  $m/z$  194  $[(H_2APTSC)]^+$ . Elemental analysis found: C 21.30, H 2.95, N 17.78, S 5.51%; calculated for  $C_{20}H_{38}N_{14}O_{22}S_2Th$ : C 21.45, H 3.04, N 17.52, S 5.72%.

## Crystal data

$(C_8H_{11}N_4S)_2[Th(NO_3)_6] \cdot 4CH_4O$   
 $M_r = 1122.80$   
 Triclinic  
 P1

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 3 reflections  
 $\theta = 9.83$ – $14.90^\circ$

$a = 9.070 (3) \text{ \AA}$   
 $b = 10.974 (5) \text{ \AA}$   
 $c = 12.102 (4) \text{ \AA}$   
 $\alpha = 64.85 (3)^\circ$   
 $\beta = 71.36 (3)^\circ$   
 $\gamma = 76.37 (3)^\circ$   
 $V = 1026.2 (6) \text{ \AA}^3$   
 $Z = 1$   
 $D_x = 1.817 \text{ Mg m}^{-3}$   
 $D_m$  not measured

$\mu = 3.830 \text{ mm}^{-1}$   
 $T = 208 (2) \text{ K}$   
 Plate  
 $0.30 \times 0.30 \times 0.10 \text{ mm}$   
 Yellow

#### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega$  scans  
 Absorption correction:  
 $\psi$  scan (PLATON; Spek,  
 1998a)  
 $T_{\min} = 0.437$ ,  $T_{\max} = 0.978$   
 5315 measured reflections  
 4460 independent reflections

4435 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$   
 $\theta_{\text{max}} = 26.98^\circ$   
 $h = -1 \rightarrow 11$   
 $k = -13 \rightarrow 13$   
 $l = -14 \rightarrow 15$   
 3 standard reflections  
 every 300 reflections  
 intensity decay: none

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.061$   
 $S = 1.057$   
 4460 reflections  
 344 parameters  
 All H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.0391P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 1.020 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.015 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{eq}}$
Th	0	0	0	0.02360 (6)
N20	0.1656 (4)	0.0742 (3)	0.1373 (3)	0.0354 (6)
O21	0.2398 (3)	0.0354 (3)	0.0457 (2)	0.0339 (5)
O22	0.0175 (3)	0.0898 (3)	0.1587 (2)	0.0377 (5)
O23	0.2346 (4)	0.0940 (3)	0.1976 (3)	0.0536 (8)
N30	0.0160 (3)	-0.2851 (3)	0.1926 (3)	0.0324 (6)
O31	-0.0479 (3)	-0.2497 (2)	0.1024 (2)	0.0348 (5)
O32	0.0704 (3)	-0.1922 (3)	0.1982 (2)	0.0358 (5)
O33	0.0246 (4)	-0.4011 (3)	0.2679 (3)	0.0483 (7)
N40	-0.3055 (3)	0.0731 (3)	0.1620 (3)	0.0358 (6)
O41	-0.2430 (3)	0.1582 (3)	0.0541 (2)	0.0373 (5)
O42	-0.2334 (3)	-0.0460 (3)	0.1926 (2)	0.0368 (5)
O43	-0.4251 (3)	0.1043 (3)	0.2297 (3)	0.0561 (8)
N1	0.2631 (4)	0.4791 (3)	0.8229 (3)	0.0338 (6)
C2	0.2090 (5)	0.5394 (5)	0.9060 (4)	0.0477 (10)
C3	0.2595 (7)	0.4872 (5)	1.0141 (4)	0.0625 (13)
C4	0.3660 (7)	0.3734 (6)	1.0338 (4)	0.0621 (13)
C5	0.4229 (6)	0.3136 (4)	0.9462 (4)	0.0456 (9)
C6	0.3696 (4)	0.3692 (3)	0.8379 (3)	0.0312 (7)
C7	0.4253 (4)	0.3153 (3)	0.7368 (3)	0.0283 (6)
C8	0.5462 (5)	0.1945 (4)	0.7489 (4)	0.0417 (9)
N9	0.3631 (3)	0.3836 (3)	0.6433 (2)	0.0283 (5)
N10	0.4083 (4)	0.3437 (3)	0.5440 (3)	0.0307 (6)
C11	0.3404 (4)	0.4116 (3)	0.4456 (3)	0.0284 (6)
N12	0.2350 (4)	0.5155 (3)	0.4515 (3)	0.0392 (7)
S13	0.39680 (11)	0.36056 (10)	0.32408 (8)	0.0382 (2)
O50	0.8471 (3)	0.3330 (3)	0.3817 (3)	0.0429 (6)

C51	0.9980 (6)	0.2673 (6)	0.3956 (9)	0.0757 (18)
O60	0.6503 (3)	0.1458 (3)	0.4584 (3)	0.0413 (6)
C61	0.7193 (7)	0.0093 (5)	0.4840 (5)	0.0535 (11)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Th—O42	2.553 (3)	C6—C7	1.477 (4)
Th—O21	2.556 (2)	C7—N9	1.283 (4)
Th—O41	2.558 (3)	N9—N10	1.361 (4)
Th—O31	2.562 (3)	N10—C11	1.361 (4)
Th—O32	2.580 (3)	C11—N12	1.316 (5)
N1—C6	1.341 (5)	C11—S13	1.681 (3)
N1—C6—C7	118.2 (3)	C11—N10—N9	119.4 (3)
N9—C7—C6	113.5 (3)	N12—C11—N10	117.1 (3)
C7—N9—N10	118.3 (3)	N10—C11—S13	118.8 (3)

Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O50 <sup>i</sup>	0.80 (4)	2.00 (4)	2.767 (4)	162 (4)
N10—H10...O60	0.83 (5)	2.20 (5)	2.970 (4)	153 (4)
N12—H12A...O33 <sup>ii</sup>	0.82 (5)	2.32 (5)	3.095 (4)	158 (4)
N12—H12B...O50 <sup>i</sup>	0.87 (5)	2.11 (5)	2.950 (4)	163 (4)
O50—H50...O60	0.79 (5)	1.92 (5)	2.705 (4)	180 (6)
O60—H60...S13	0.76 (5)	2.54 (5)	3.172 (3)	143 (5)

Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $x, 1 + y, z$ .

C—H distances are in the range 0.77 (7)–1.08 (9)  $\text{\AA}$ .

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *SET4* in *CAD-4 Software*. Data reduction: *PLATON* (Spek, 1998a) and *HELENA* (Spek, 1998b). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1328). Services for accessing these data are described at the back of the journal.

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## Chloro(*p*-chloroanilido-*N*)bis( $\eta^5$ -pentamethylcyclopentadienyl)uranium(IV)

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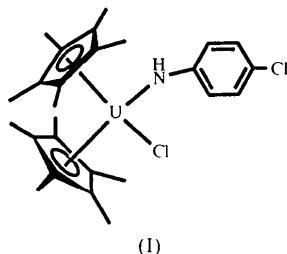
(Received 5 January 1999; accepted 21 May 1999)

### Abstract

The title complex,  $[UCl(C_{10}H_{15})_2(C_6H_4ClN)]$ , adopts the pseudo-tetrahedral geometry typical for bis(pentamethylcyclopentadienyl)uranium complexes, with a chloride and a *para*-substituted amide ligand occupying the plane bisecting the metallocene unit. Some important bond lengths include U—N 2.237 (3) and U—Cl 2.613 (1) Å.

### Comment

We have been examining the chemistry of uranium mono- and dialkyls with substituted anilines as a synthetic tool to yield mono and bis amide and imide complexes of actinides. Treatment of  $(C_5Me_5)_2U(CH_3)Cl$  with an excess of *p*-chloroaniline in hexane solution gave the title compound, (I), in modest yield.



In the solid state, the title molecule adopts a typical metallocene geometry, with an average  $M-C_{ring}$  bond length of 2.736 Å. This value is well within

the range typically found in bis(pentamethylcyclopentadienyl)uranium(IV) complexes (Arney *et al.*, 1992; Hall *et al.*, 1993; Arney & Burns, 1995). The  $C_p-M-C_p$  angle of  $135.1^\circ$  ( $C_p$  is the ring centroid) falls within the range of  $132-141^\circ$  reported for similar uranium(IV) structures (Arney & Burns, 1995; Arney *et al.*, 1992). The U—Cl bond length of 2.613 (1) Å is about 0.04 Å shorter than the U—Cl distance of 2.658 (2) Å reported for  $(C_5Me_5)_2U[(CH_2)(CH_2)P(Me)(Ph)]Cl$  (Cramer *et al.*, 1989), possibly reflecting the increased electron density in the title compound. However, the U—Cl bond length of the title compound is longer than the U—Cl distance of 2.583 (6) Å reported for the dichloride  $(C_5Me_5)_2UCl_2$  (Spirlet *et al.*, 1992). The U—N distance of 2.237 (3) Å is shorter than the U—N bond distance of 2.267 (6) Å reported for  $(C_5Me_5)_2U[NH(2,6-Me_2C_6H_3)]_2$  (Straub *et al.*, 1996). These differences in bond-length data qualitatively indicate that uranium(IV) complexes are structurally sensitive to the electronic and steric influences of the ancillary ligands.

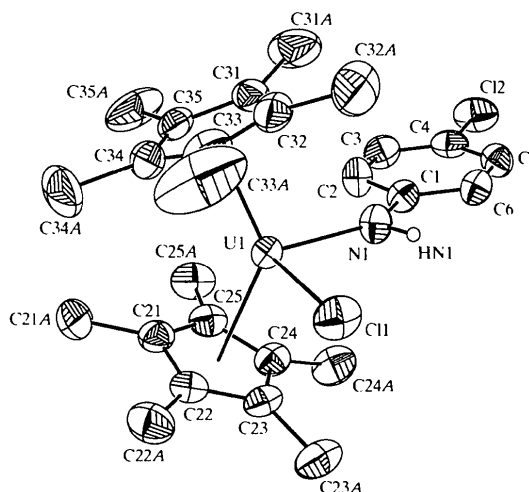


Fig. 1. View of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. H atoms, except for the amide H atom, have been omitted for clarity. The  $C_5Me_5$  ring (C31–C35A) is disordered over two positions and only the major component is shown.

### Experimental

The title compound was prepared by treatment of  $(C_5Me_5)_2U(CH_3)Cl$  with *p*-chloroaniline in hexane. The crude product was isolated by filtration of the reaction mixture, and recrystallization from a saturated hexane solution at 238 K yielded the pure product as dark-red blocks.

### Crystal data

$[UCl(C_{10}H_{15})_2(C_6H_4ClN)]$   
 $M_r = 670.48$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å