

SHORT STRUCTURAL PAPERS

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Caesium Dioxopentakis(thiocyanato)uranate(VI)

BY NATHANIEL W. ALCOCK AND MICHAEL M. ROBERTS

Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL, England

AND DAVID BROWN

Chemistry Division, AERE Harwell, Oxfordshire OX11 0RA, England

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Abstract. $\text{Cs}_3[\text{UO}_2(\text{NCS})_5]$, orthorhombic, *Pnma*, $a = 13.673$ (5), $b = 13.283$ (4), $c = 11.588$ (5) Å, $U = 2104.6$ Å³, $Z = 4$, $D_x = 3.03$ Mg m⁻³; $\mu(\text{Mo } K\alpha) = 12.877$ mm⁻¹, $R = 0.062$ ($R_w = 0.062$) for 1099 reflections. The complex contains $[\text{UO}_2(\text{NCS})_5]^{3-}$ ions with distorted pentagonal bipyramidal geometry around the uranium atom. The U–O distances in the linear UO_2^{2+} group are 1.76 (3) and 1.78 (2) Å. The linear thiocyanate groups are nitrogen bonded to the uranium atom with U–N distances of 2.41 (3), 2.42 (4) and 2.45 (3) Å.

Introduction. Structural data reported for $\text{Cs}_3[\text{UO}_2(\text{NCS})_5]$, final R value 0.155, indicated surprisingly that the UO_2^{2+} group was non-linear (Arutyunyan & Porai-Koshits, 1964). As part of an investigation of the structural chemistry of actinide(V) and (VI) compounds, and because accurate data were required to supplement a spectroscopic study (Denning & Softley, 1981), the structure of this compound has been redetermined.

Suitable crystals were obtained using the method described for the preparation of $(\text{NH}_4)_3[\text{UO}_2(\text{NCS})_5]$ (Markov, Trageim & Shul'gina, 1964). The crystal used had the dimensions $0.55 \times 0.34 \times 0.19$ mm, giving transmission factors between 0.086 and 0.199.

Reflection data were collected using a Syntex P2₁ automatic four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Accurate lattice parameters were obtained from least-squares calculations based on the positions of 15 reflections. The scan range used (2θ) about the $K\alpha_1$ and $K\alpha_2$ positions was $\pm 1.45^\circ$. The θ – 2θ scan technique was used, at rates varying from 1.0 to 29.3° min⁻¹, depending on the intensity of a 2 s pre-scan. During the data collection, the three check reflections monitored every 100

reflections showed a gradual decrease in intensity. In addition, after the first 575 reflections were collected, X-ray generator problems caused the level of intensity of the X-ray beam to be slightly diminished. For the 1649 reflections collected afterwards, a fixed scaling factor of 1.098 was therefore used. The first and second data sets were also rescaled to allow for the crystal decomposition, using equations (1) and (2), respectively:

$$F = F_o(1 + 0.000160T) \quad (1)$$

$$F = F_o(1 + 0.000067T) \quad (2)$$

[$T =$ time (h) from start of data collection].

2224 reflections were collected in the range $0 \leq 2\theta \leq 50^\circ$. Of these, 1099 were considered observed [$I/\sigma(I) \geq 3.0$] and used in the refinement.

With the previously published atomic positions (Arutyunyan & Porai-Koshits, 1964) in space group *Pnma* as the starting point, the structure was refined by least-squares methods with anisotropic temperature factors for all atoms. An isotropic extinction correction gave no improvement, and this was therefore not finally applied. The weighting scheme $W = XY$ was applied, where $X = 1.0$ or $\sin \theta/0.25$ for $\sin \theta \leq 0.25$ and $Y = 1.0$ or $100.0/F_o$ for $F_o \geq 100.0$. The final and weighted R values were 0.062.

Absorption corrections were applied using the program *ABSCOR* (Alcock, 1970). The scattering factors used were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). Computing was performed using the XRAY76 system (Stewart, 1976) on a Burroughs B6700 computer. The final difference Fourier map showed ripples $\leq 2.9 \text{ e } \text{Å}^{-3}$ around the uranium atom and $\leq 1.9 \text{ e } \text{Å}^{-3}$ near the caesium atoms.

Table 1. Atomic coordinates ($\times 10^4$; $\times 10^5$ for U) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} ($\text{\AA}^2 \times 10^4$)
U	38540 (9)	25000	26017 (16)	456
Cs(1)	4619 (2)	7500	1168 (2)	628
Cs(2)	1499 (1)	4658 (2)	1681 (2)	657
S(1)	1492 (7)	4646 (7)	4740 (8)	822
S(2)	4221 (8)	6193 (6)	3871 (8)	829
S(3)	3071 (9)	2500	6980 (11)	766
N(1)	3945 (20)	3607 (21)	908 (24)	791
N(2)	3803 (25)	4245 (19)	3156 (28)	900
N(3)	3612 (31)	2500	4672 (37)	776
C(1)	3777 (21)	4333 (23)	399 (26)	621
C(2)	3960 (18)	5069 (19)	3467 (22)	464
C(3)	3396 (38)	2500	5643 (47)	674
O(1)	2560 (16)	2500	2419 (22)	606
O(2)	5138 (20)	2500	2726 (32)	858

$$U_{eq} = \frac{1}{3} \text{trace } \bar{U}$$

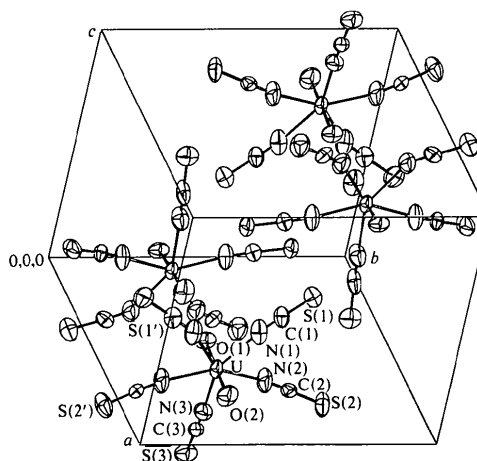


Fig. 1. Angled view of one unit cell (Cs omitted), showing the atomic numbering (thermal ellipsoids at 50% probability).

Table 2. Bond lengths (\AA) and angles ($^\circ$) for $\text{Cs}_3[\text{UO}_2(\text{NCS})_5]$ with e.s.d.'s in parentheses

Bond lengths

(i) Around uranium

U—N(1)	2.45 (3)	U—O(1)	1.78 (2)
U—N(2)	2.41 (3)	U—O(2)	1.76 (3)
U—N(3)	2.42 (4)		

(ii) Thiocyanate groups

S(1)—C(1)	1.60 (3)	N(1)—C(1)	1.15 (4)
S(2)—C(2)	1.60 (3)	N(2)—C(2)	1.17 (4)
S(3)—C(3)	1.61 (6)	N(3)—C(3)	1.16 (7)

Bond angles

(i) Around uranium

N(1)—U—N(1)	73.6 (9)	O(1)—U—O(2)	177.9 (15)
N(1)—U—N(2)	68.8 (10)		
N(2)—U—N(3)	74.4 (8)		
O(1)—U—N(1)	87.4 (9)	O(2)—U—N(1)	90.9 (12)
O(1)—U—N(2)	90.2 (8)	O(2)—U—N(2)	90.4 (9)
O(1)—U—N(3)	89.0 (13)	O(2)—U—N(3)	93.2 (16)

(ii) Thiocyanate groups

N(1)—C(1)—S(1)	177 (3)
N(2)—C(2)—S(2)	178 (3)
N(3)—C(3)—S(3)	179 (5)

(iii) Subtended by nitrogen

U—N(1)—C(1)	154 (2)
U—N(2)—C(2)	168 (2)
U—N(3)—C(3)	173 (4)

The final atomic coordinates are listed in Table 1; bond lengths and angles are given in Table 2.*

Discussion. The structure consists of caesium cations and $[\text{UO}_2(\text{NCS})_5]^{3-}$ anions with distorted pentagonal

bipyramidal geometry. The packing diagram, Fig. 1 (with caesium ions omitted), shows the $[\text{UO}_2(\text{NCS})_5]^{3-}$ units to lie in a staggered arrangement relative to each other down the *a* axis. One half of the $[\text{UO}_2(\text{NCS})_5]^{3-}$ ion is related to the other through a mirror plane that bisects the uranyl group and thiocyanate group 3. The thiocyanate groups are linear within experimental error, whilst the U—N—C angles lie in the range 154 (2)–173 (4) $^\circ$ (Table 2). The ring of coordinating N atoms is slightly puckered. Thus, for the mean plane defined by the U and N atoms, the two N(2) atoms are situated 0.02 (3) \AA above and the two N(1) atoms and the N(3) atoms are 0.04 (3) \AA below the plane. The extent of this puckering, however, is much less marked than suggested previously (Arutyunyan & Porai-Koshits, 1964).

The uranyl(VI) group is linear within experimental error [177.9 (15) $^\circ$], not bent as reported earlier (Arutyunyan & Porai-Koshits, 1964).

The N—N contacts in the uranium equatorial plane range from 2.75 (5) to 2.94 (4) \AA and the Cs—N, Cs—S and Cs—O contact distances fall in the ranges 3.44 (3) to 3.73 (4) \AA , 3.55 (2) to 3.84 (2) \AA and 3.32 (2) to 3.49 (2) \AA , respectively.

The U—N bond lengths (2.40, 2.46 and 2.48 \AA) reported for the $[\text{UO}_2(\text{NCS})_5]^{3-}$ ion in $[\text{dpsH}]_3[\text{UO}_2(\text{NCS})_5]$ [dpsH = 2-(2-pyridylthio)pyridinium ion; Bombieri, Forsellini, Graziani & Pappalardo, 1979] and the associated U—O distances [1.72 (2) and 1.74 (2) \AA] are close to those now reported (Table 2). The thiocyanate groups are also linear in the former complex.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36939 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- ALCOCK, N. W. (1970). In *Crystallographic Computing*, edited by F. R. AHMED, pp. 271–278. Copenhagen: Munksgaard.
- ARUTYUNYAN, E. G. & PORAI-KOSHITS, M. A. (1964). *J. Struct. Chem. (USSR)*, **9**, 305–309.
- BOMBIERI, G., FORSELLINI, E., GRAZIANI, R. & PAPPALARDO, G. (1979). *Trans. Met. Chem.* **4**, 70–72.
- DENNING, R. G. & SOFTLEY, T. R. (1981). Private communication.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MARKOV, V. P., TRAGGEIM, E. N. & SHUL'GINA, I. M. (1964). *Russ. J. Inorg. Chem.* **9**, 305–308.
- STEWART, J. M. (1976). The XRAY76 system. Tech. Rep. TR-466. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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Samarium Pyrosilicate Sulfide, $\text{Sm}_4\text{S}_3\text{Si}_2\text{O}_7$

BY T. SIEGRIST

Laboratorium für Festkörperphysik ETH, CH-8093 Zürich, Switzerland

W. PETTER

Institut für Kristallographie und Petrographie ETH, CH-8092 Zürich, Switzerland

AND F. HULLIGER

Laboratorium für Festkörperphysik ETH, CH-8093 Zürich, Switzerland

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Abstract. $\text{Sm}_4\text{S}_3\text{Si}_2\text{O}_7$, space group $I4_1/amd$, $a = 11.839$ (5), $c = 13.928$ (5) Å, $Z = 8$, $D_x = 5.89$ g cm⁻³. The final R value was 0.054 for 937 observed reflections. $\text{Sm}_4\text{S}_3\text{Si}_2\text{O}_7$ has been found to crystallize in a new tetragonal structure type. The structure contains two kinds of Sm atoms. Sm(1) is coordinated to three O and three S atoms and Sm(2) to six O and three S atoms. The $[\text{Si}_2\text{O}_7]$ double tetrahedra are in the eclipsed configuration.

Introduction. In an attempt to grow SmS_2 single crystals by an iodine-transport reaction in a closed silica tube at 1073 to 1173 K we obtained transparent crystals the largest of which had dimensions of about $1 \times 1 \times 0.5$ mm. Thin plates have a yellowish color whereas bulky crystals look greenish. The crystals are stable in air. An electron-beam microprobe analysis yielded within the experimental accuracy the composition $\text{Sm}_4\text{S}_3\text{Si}_2\text{O}_7$. Obviously this silicate sulfide decomposes peritectically since all attempts to reproduce this phase, as well as other rare-earth analogs, by melting or sintering failed.

The shape of the single crystal was approximated by 11 faces, dimensions about $0.4 \times 0.3 \times 0.2$ mm. Precession patterns revealed tetragonal symmetry with the unambiguous systematic extinctions of space group $I4_1/amd$ (No. 141). For the structure determination we used a Syntex $P2_1$ four-circle diffractometer, mono-

chromatized Mo $K\alpha$ radiation, 2θ - θ scan to $\sin \theta/\lambda = 0.76$ Å⁻¹ ($2\theta_{\text{max}} = 65^\circ$), Lehmann-Larsen algorithm (Blessing, Coppens & Becker, 1972), absorption correction by *ORABS* program of the XRAY system 72 (1972) ($\mu_{\text{Mo}K\alpha} = 250$ cm⁻¹), 2405 reflections, 1053 unique reflections, 1017 observed $I > 3\sigma(I)$, Patterson and Fourier methods, and the XRAY system 72 (1972). The Patterson map was analyzed with a program written by Walpen (Walpen & Niggli, 1979). Scattering factors were taken from Cromer & Mann (1968) and the anomalous-dispersion factors for Sm from *International Tables for X-ray Crystallography* (1974). The structure was refined by the full-matrix least-squares method. An isotropic refinement with an extinction correction applied led to an R value of 0.064, all reflections included. An anisotropic refinement with 937 reflections in the range of $\sin \theta/\lambda$ from 0.3 to 0.8 Å⁻¹ lowered the R value to 0.054. A difference Fourier map showed only weak peaks in the vicinity of the Sm atoms. The final positional and thermal parameters are listed in Table 1.* Interatomic distances up to 3.3 Å are given in Table 2.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36958 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.