

Jung-eun Kwak,<sup>a</sup> Danielle L. Gray,<sup>a</sup> Hoseop Yun<sup>b</sup> and James A. Ibers<sup>a\*</sup><sup>a</sup>Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA, and <sup>b</sup>Department of Chemistry, Ajou University, Suwon 441-749, South KoreaCorrespondence e-mail:  
ibers@chem.northwestern.edu

## Key indicators

Single-crystal X-ray study  
 $T = 153$  K  
Mean  $\sigma(S-S) = 0.004$  Å  
 $R$  factor = 0.031  
 $wR$  factor = 0.085  
Data-to-parameter ratio = 20.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Uranium trisulfide,  $US_3$ Uranium trisulfide,  $US_3$ , is isostructural with  $USe_3$ , which has the  $ZrSe_3$  structure type. In the asymmetric unit, the site symmetries of the U atom and the three S atoms are  $m$ . The structure consists of two-dimensional layers that stack perpendicular to the  $[001]$  direction. Each layer comprises  $US_8$  bicapped trigonal prisms that edge share in the  $[100]$  direction and face share in the  $[010]$  direction. The compound may be described as  $U^{4+}(S^{2-})(S_2^{2-})$ .Received 23 February 2006  
Accepted 1 March 2006

## Comment

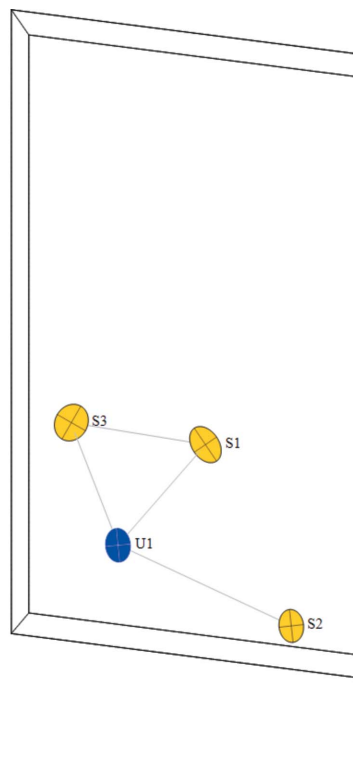
The  $UQ_3$  ( $Q = S, Se$  or  $Te$ ) compounds have been extensively studied for their magnetic properties. The crystal structures of  $USe_3$  (Ben Salem *et al.*, 1984) and  $UTe_3$  (Stöwe, 1996) have been determined from single crystals. However, we can find no report of a corresponding determination of the crystal structure of  $US_3$ . Powder diffraction studies indicate that  $US_3$  has the  $ZrSe_3$  structure type with  $a = 5.39$  Å,  $b = 3.89$  Å,  $c = 18.22$  Å and  $\beta = 80.30^\circ$  (Flahaut & Picon, 1958) or  $\beta = 99.30^\circ$  (Ellert *et al.*, 1974).Fig. 1 shows the asymmetric unit and Fig. 2 shows the crystal structure of  $US_3$ , as derived here from single-crystal data. The

Figure 1

A view of the asymmetric unit of  $US_3$ , with displacement ellipsoids at the 95% probability level. Color code: U blue and S yellow.

US<sub>8</sub> bicapped trigonal prisms edge share in the [100] direction and face share in the [010] direction to form layers that stack perpendicular to [001]. The U—S bond distances of 2.753 (2)–2.825 (2) Å are comparable to those of 2.73–2.99 Å in CrU<sub>8</sub>S<sub>17</sub> (Noel *et al.*, 1975). The average S—S single-bond distance in  $\gamma$ -S<sub>8</sub> is 2.045 (2) Å (Gallacher & Pinkerton, 1993). In US<sub>3</sub> there is an S—S distance of 2.086 (4) Å. Thus the compound may be described as U<sup>4+</sup>(S<sup>2-</sup>)(S<sub>2</sub><sup>2-</sup>).

## Experimental

US<sub>3</sub> was obtained as black plates from a solid-state reaction of Cs<sub>2</sub>S<sub>3</sub> (0.25 mmol), UCl<sub>4</sub> (0.15 mmol) and AgCl (Aldrich, 99.5%, 0.1 mmol). The Cs<sub>2</sub>S<sub>3</sub> reactive flux was prepared by the stoichiometric reaction of Cs (Alfa Aesar, 99.8%), and S (Mallinkrodt, 99.6%) in liquid NH<sub>3</sub> at 194 K. UCl<sub>4</sub> was prepared by a modified literature synthesis (Hermann & Suttle, 1957) in which UO<sub>3</sub> and hexachloropropene (Aldrich, 96%) were reacted and allowed to reflux at 431 K for 3.5 h. The resulting green precipitate was filtered, washed with CCl<sub>4</sub> and dried under vacuum. The reactants were loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was evacuated to 10<sup>-4</sup> Torr, sealed and then placed in a computer-controlled furnace. The sample was heated to 523 K, kept at 523 K for 72 h, then heated to 923 K, kept at 923 K for 24 h and then cooled at 5 K h<sup>-1</sup> to 298 K. The resulting crystals were washed with *N,N*-dimethylformamide. The yield was about 10% based on U.

### Crystal data

US <sub>3</sub>	$D_x = 5.822 \text{ Mg m}^{-3}$
$M_r = 334.21$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 2131 reflections
$a = 5.3738 (14) \text{ \AA}$	$\theta = 2.3\text{--}28.8^\circ$
$b = 3.9598 (10) \text{ \AA}$	$\mu = 43.95 \text{ mm}^{-1}$
$c = 9.032 (2) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\beta = 97.258 (3)^\circ$	Flat needle, black
$V = 190.66 (8) \text{ \AA}^3$	$0.346 \times 0.058 \times 0.014 \text{ mm}$
$Z = 2$	

### Data collection

Bruker SMART 1000 CCD diffractometer	521 independent reflections
$\omega$ scans	510 reflections with $I > 2\sigma(I)$
Absorption correction: numerical face indexed ( <i>SHELXTL</i> ; Sheldrick, 2003)	$R_{\text{int}} = 0.035$
$T_{\text{min}} = 0.049$ , $T_{\text{max}} = 0.542$	$\theta_{\text{max}} = 28.8^\circ$
2232 measured reflections	$h = -6 \rightarrow 7$
	$k = -5 \rightarrow 5$
	$l = -11 \rightarrow 11$

### Refinement

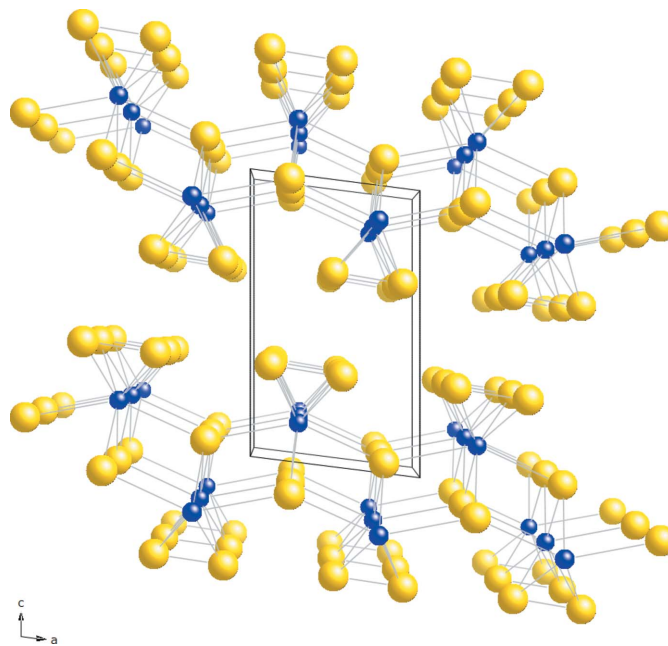
Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.16$	$\Delta\rho_{\text{max}} = 7.92 \text{ e \AA}^{-3}$
521 reflections	$\Delta\rho_{\text{min}} = -2.09 \text{ e \AA}^{-3}$
25 parameters	

**Table 1**

Selected bond lengths (Å).

U1—S1 <sup>i</sup>	2.7530 (18)	U1—S2 <sup>iii</sup>	2.7787 (18)
U1—S3 <sup>i</sup>	2.7716 (19)	U1—S2	2.825 (2)
U1—S2 <sup>ii</sup>	2.817 (2)	S1—S3	2.086 (4)

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



**Figure 2**

The structure of US<sub>3</sub>, viewed down [010].

The structure was standardized by means of the program *STRUCTURE TIDY* (Gelato & Parthé, 1987). The highest peak is 0.99 Å from atom S2 and the deepest hole is 0.78 Å from atom U.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *CRYSTALMAKER* (CrystalMaker Software, 2005); software used to prepare material for publication: *SHELXTL*.

Funding for this work was kindly provided by US Department of Energy grant ER-15522.

## References

- Ben Salem, A., Meerschaut, A. & Rouxel, J. (1984). *C. R. Acad. Sci. Sér. II*, **299**, 617–619.
- Bruker (2003). *SMART* (Version 5.054) and *SAINT-Plus* (Version 6.45a). Bruker AXS Inc., Madison, Wisconsin, USA.
- CrystalMaker Software (2005). *CRYSTALMAKER*. CrystalMaker Software Ltd, Yarnton, Oxfordshire OX5 1PF, England.
- Ellert, G. V., Kuz'micheva, G. M., Eliseev, A. A., Slovyanskikh, V. K. & Morozov, S. P. (1974). *Russ. J. Inorg. Chem.* (Translation of *Zh. Neorg. Khim.*), **19**, 1548–1551.
- Flahaut, J. & Picon, M. (1958). *Bull. Soc. Chim. Fr.* **6**, 772–780.
- Gallacher, A. C. & Pinkerton, A. A. (1993). *Acta Cryst.* **C49**, 125–126.
- Gelato, J. M. & Parthé, J. (1987). *J. Appl. Cryst.* **20**, 139–143.
- Hermann, J. A. & Suttle, J. F. (1957). *Inorganic Synthesis*, edited by T. Moeller, Vol. 5, *Uranium(IV) Chloride*, pp. 143–145. New York: McGraw-Hill Book Company.
- Noel, H., Potel, M. & Padiou, J. (1975). *Acta Cryst.* **B31**, 2634–2637.
- Sheldrick, G. M. (2003). *SHELXTL*. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
- Stöwe, K. (1996). *Z. Anorg. Allg. Chem.* **622**, 1419–1422.