

2.65 (1) Å. With one Mg and one Sr(1) they provide the molecule with a tetrahedral coordination. The molecule  $W(2)$  forms a bridge between one Sr(1) and two Sr(2),  $W(3)$  a bridge between two Sr(2) and  $W(4)$  and  $W(5)$  are terminal to Na(2). The molecule  $W(6)$  is enclosed in a cavity formed by three O(10), three O(11) and one  $W(5)$ .

The connections between polyhedra in the title compound follow closely those observed in other uranyl carbonates containing Mg, Ca and/or Sr. Typical in this respect are the edge-sharing links between the  $UO_2O_6$  hexagonal bipyramid and the three surrounding  $Sr(O,W)_8$  polyhedra (Fig. 1), which correspond to the situation for Ca in schröckingerite,  $NaCa_3[UO_2(CO_3)_3](SO_4)F \cdot 10H_2O$ , or the presence of Mg in the form of  $MgW_6$  octahedra as found for instance in  $SrMg[UO_2(CO_3)_3] \cdot 12H_2O$  (Mereiter, 1986a,c). Three-dimensional interconnections and the arrangement of  $[UO_2(CO_3)_3]$  units in the title compound resemble the

trigonal-rhombohedral framework structure of andersonite,  $Na_2Ca[UO_2(CO_3)_3] \cdot 5-6H_2O$  (Coda *et al.*, 1981).

#### References

- CODA, A., DELLA GIUSTA, A. & TAZZOLI, V. (1981). *Acta Cryst.* B37, 1496–1500.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
MEREITER, K. (1986a). *Neues Jahrb. Mineral. Monatsh.* pp. 481–492.  
MEREITER, K. (1986b). *Acta Cryst.* C42, 1678–1681.  
MEREITER, K. (1986c). *Tschermaks Mineral. Petrogr. Mitt.* 35, 1–18.  
NARDELLI, M. (1982). *PARST. A System of Computer Routines for Calculating Molecular Parameters from the Results of Crystal Structure Analysis.* Univ. of Parma, Italy.  
SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1988). C44, 1175–1178

## Structure of Caesium Tricarbonatodioxouranate(VI) Hexahydrate

BY K. MEREITER

*Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Vienna, Austria*

(Received 15 January 1988; accepted 29 February 1988)

**Abstract.**  $Cs_4[UO_2(CO_3)_3] \cdot 6H_2O$ ,  $M_r = 1089.8$ , monoclinic,  $P2_1/n$ ,  $a = 18.723$  (3),  $b = 9.647$  (2),  $c = 11.297$  (2) Å,  $\beta = 96.84$  (1)°,  $V = 2026$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.573$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 147$  cm<sup>-1</sup>,  $F(000) = 1912$ ,  $T = 295$  K, final  $R = 0.041$  for 2267 observed reflections. The asymmetric unit contains four independent Cs ions with coordination numbers 9 and 11 ( $Cs-O < 3.75$  Å), one  $[UO_2(CO_3)_3]$  unit and six Cs-bonded water molecules. Cs ions and  $[UO_2(CO_3)_3]$  units show a layer-like arrangement parallel to (101), but on the whole the structure is framework-like with dominating links parallel to (100).

**Introduction.** The uranyl carbonates  $M_4[UO_2(CO_3)_3]$  with  $M = Tl, NH_4, K, Rb$  and  $Cs$  form a series of isostructural anhydrous salts, the water solubility of which increases considerably in the given order. During attempts to grow the anhydrous Cs salt, analogous to the K and Rb compounds, by room-temperature evaporation of aqueous solutions, the title compound was obtained, recognized to be a hydrate and subjected to a structural study. The existence of this hydrate has not been mentioned in previous works (Bachelet,

Cheyilan, Douis & Goulette, 1954; *Gmelin Handbook of Inorganic Chemistry*, 1983). The intended anhydrous caesium uranyl carbonate could be obtained, however, by evaporation crystallization at elevated temperatures. With the Rb compound it will be the subject of a forthcoming publication (Mereiter, Preisinger & Mikenda, 1988).

**Experimental.** Rectangular plates flattened on (100) and stretched along  $z$ , typical dimensions  $6 \times 4 \times 0.5$  mm, colour yellow, fluorescence bright yellow-green, stable in humid air, in dry air dehydrating to a whitish matter, readily dissolving in water, grown by room-temperature evaporation of solutions obtained by digesting 10 g  $Ag_4[UO_2(CO_3)_3]$  in a solution of 6.7 g  $CsCl$  in 60 g  $H_2O$  and subsequent removal of the insoluble residue ( $AgCl$ ) by filtration. X-ray data collection with a lacquer-coated sphere of 0.20 mm diameter on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized  $Mo K\alpha$  radiation. Unit-cell dimensions from 72 reflections,  $7 < \theta < 23^\circ$ . 3585 independent reflections measured with  $\theta-2\theta$  scans, scan width  $1 + 0.35 \tan \theta$ ,  $\theta$  range 2 to 25°,

Table 1. Atomic coordinates and isotropic or equivalent isotropic thermal parameters

	x	y	z	B(Å <sup>2</sup> )
Cs(1)	0.5535 (1)	0.2154 (1)	0.5773 (1)	2.99 (3)*
Cs(2)	0.2678 (1)	0.3570 (1)	0.3085 (1)	3.44 (3)*
Cs(3)	0.4293 (1)	0.2408 (1)	-0.0721 (1)	3.24 (3)*
Cs(4)	0.7051 (1)	0.2876 (1)	0.2026 (1)	3.53 (3)*
U	0.50003 (3)	0.41711 (6)	0.25402 (6)	1.56 (2)*
O(1)	0.5460 (5)	0.4215 (10)	0.1246 (9)	2.3 (2)
O(2)	0.4536 (5)	0.4138 (11)	0.3819 (9)	2.5 (2)
C(1)	0.5103 (8)	0.1208 (15)	0.2519 (15)	2.1 (3)
O(3)	0.5606 (5)	0.1991 (11)	0.3035 (9)	2.6 (2)
O(4)	0.4539 (5)	0.1849 (11)	0.2016 (9)	2.6 (2)
O(5)	0.5177 (6)	-0.0103 (12)	0.2481 (10)	3.2 (2)
C(2)	0.3808 (8)	0.5576 (16)	0.1260 (14)	2.2 (3)
O(6)	0.3852 (5)	0.4260 (10)	0.1326 (9)	2.2 (2)
O(7)	0.4349 (5)	0.6243 (11)	0.1853 (9)	2.7 (2)
O(8)	0.3275 (6)	0.6205 (12)	0.0706 (10)	3.5 (2)
C(3)	0.6161 (7)	0.5761 (15)	0.3744 (13)	1.8 (3)
O(9)	0.5618 (5)	0.6325 (10)	0.3162 (9)	2.2 (2)
O(10)	0.6162 (5)	0.4404 (11)	0.3801 (9)	2.5 (2)
O(11)	0.6717 (6)	0.6446 (11)	0.4225 (10)	3.0 (2)
W(1)	0.3489 (6)	0.0553 (13)	0.3211 (11)	4.4 (3)
W(2)	0.2881 (7)	0.6720 (14)	0.4362 (12)	5.1 (3)
W(3)	0.3724 (6)	0.0840 (13)	0.5741 (11)	4.4 (3)
W(4)	0.6975 (7)	-0.0198 (15)	0.1002 (12)	5.4 (3)
W(5)	0.7475 (6)	0.5899 (13)	0.0623 (11)	4.6 (3)
W(6)	0.5978 (7)	0.1021 (15)	-0.0661 (12)	5.5 (3)

$$* B_{eq} = \frac{2}{3} \pi^2 (U_{11} + U_{22} + U_{33}).$$

index range  $h-22$  to  $22$ ,  $k 0$  to  $11$ ,  $l 0$  to  $13$ . Three standard reflections monitored every hour revealed continuous loss in intensity due to slow crystal dehydration (total loss 12%), time-dependent linear correction applied. Absorption correction for a sphere,  $\mu R = 1.5$ , transmission factors 0.13–0.15.

Structure solved with direct and Fourier methods, H atoms not located. Refinement on  $F$  with anisotropic temperature factors only for Cs and U. Final  $R = 0.041$ ,  $wR = 0.039$ ,  $w = [\sigma^2(F_o) + 0.0001F_o^2]^{-1}$ ,  $S = 1.29$  on 2267 reflections with  $F_o \geq 6\sigma(F_o)$ ; 127 parameters varied,  $(\Delta/\sigma)_{max} < 0.01$ ;  $\Delta\rho$  in final difference Fourier map within  $-1.3$  and  $1.3 e \text{ \AA}^{-3}$ . Isotropic extinction parameter  $X = 0.00011$  according to the definition of program *SHELX76* (Sheldrick, 1976) with which the calculations were carried out. Neutral-atom scattering functions and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Final atomic parameters are given in Table 1, bond lengths and angles in Table 2.\* The structure is built up from four independent Cs ions, one  $[\text{UO}_2(\text{CO}_3)_3]$  unit and six Cs-bonded water molecules.

The  $[\text{UO}_2(\text{CO}_3)_3]$  unit (Fig. 1), which consists of an almost linear uranyl group  $\text{O}(1)-\text{U}-\text{O}(2)$  and three

Table 2. Bond lengths (Å) and angles (°)

Cs coordination polyhedra (Cs—O, $W \leq 3.75 \text{ \AA}$ )			
Cs(1)—O(1)	3.32 (1)	Cs(2)—O(1)	3.52 (1)
—O(1 <sup>b</sup> )	3.61 (1)	—O(6)	3.20 (1)
—O(3)	3.12 (1)	—O(8 <sup>iii</sup> )	3.29 (1)
—O(5 <sup>ii</sup> )	3.20 (1)	—O(11 <sup>i</sup> )	3.11 (1)
—O(7 <sup>i</sup> )	3.08 (1)	—W(1)	3.28 (1)
—O(9)	2.98 (1)	—W(1 <sup>iv</sup> )	3.13 (1)
—O(10)	3.42 (1)	—W(2)	3.37 (1)
—W(1 <sup>ii</sup> )	3.32 (1)	—W(2 <sup>iii</sup> )	3.35 (1)
—W(2)	3.18 (1)	—W(6 <sup>v</sup> )	3.66 (1)
—W(3)	3.62 (1)	Mean	3.324
—W(3 <sup>ii</sup> )	3.71 (1)		
Mean	3.322		
Cs(3)—O(2)	3.41 (1)	Cs(4)—O(2)	3.27 (1)
—O(2 <sup>ii</sup> )	3.35 (1)	—O(3)	3.18 (1)
—O(4)	3.12 (1)	—O(8 <sup>iv</sup> )	3.20 (1)
—O(5 <sup>iii</sup> )	3.22 (1)	—O(10)	3.12 (1)
—O(6)	3.11 (1)	—O(11 <sup>viii</sup> )	3.16 (1)
—O(7 <sup>vii</sup> )	3.25 (1)	—W(4)	3.18 (1)
—O(9 <sup>vi</sup> )	3.04 (1)	—W(4 <sup>ix</sup> )	3.28 (1)
—W(4 <sup>iii</sup> )	3.18 (1)	—W(5)	3.46 (1)
—W(5 <sup>vi</sup> )	3.71 (1)	—W(5 <sup>viii</sup> )	3.30 (1)
—W(6)	3.42 (1)	Mean	3.239
—W(6 <sup>vii</sup> )	3.72 (1)		
Mean	3.320		
UO <sub>2</sub> O <sub>6</sub> polyhedron			
U—O(1)	1.77 (1)	O(1)—U—O(2)	179.4 (5)
—O(2)	1.78 (1)	O(1)—U—[O(3)—O(10)]	88.5–93.3 (5)
—O(3)	2.42 (1)	O(2)—U—[O(3)—O(10)]	87.2–91.0 (5)
—O(4)	2.45 (1)	O(3)—U—O(4)	53.4 (4)
—O(6)	2.41 (1)	O(4)—U—O(6)	68.3 (4)
—O(7)	2.42 (1)	O(6)—U—O(7)	53.6 (4)
—O(9)	2.44 (1)	O(7)—U—O(9)	66.0 (4)
—O(10)	2.46 (1)	O(9)—U—O(10)	53.2 (4)
Mean U—[O(3)—O(10)]	2.434	O(10)—U—O(3)	65.7 (4)
CO <sub>3</sub> groups			
C(1)—O(3)	1.29 (2)	O(3)—C(1)—O(4)	115.6 (13)
—O(4)	1.30 (2)	O(3)—C(1)—O(5)	121.3 (14)
—O(5)	1.27 (2)	O(4)—C(1)—O(5)	123.1 (14)
C(2)—O(6)	1.27 (2)	O(6)—C(2)—O(7)	114.7 (13)
—O(7)	1.31 (2)	O(6)—C(2)—O(8)	123.2 (14)
—O(8)	1.27 (2)	O(7)—C(2)—O(8)	122.1 (14)
C(3)—O(9)	1.27 (2)	O(9)—C(3)—O(10)	116.8 (14)
—O(10)	1.31 (2)	O(9)—C(3)—O(11)	123.6 (14)
—O(11)	1.30 (2)	O(10)—C(3)—O(11)	119.5 (14)
Mean C—O	1.288		
Probable hydrogen bonds			
W(1)—O(4)	2.81 (2)	O(4)—W(1)—W(3)	113.9 (5)
—W(3)	2.85 (2)	O(10 <sup>i</sup> )—W(2)—W(5 <sup>v</sup> )	97.3 (5)
W(2)—O(10 <sup>i</sup> )	2.79 (2)	O(5 <sup>ii</sup> )—W(3)—O(11 <sup>i</sup> )	115.5 (5)
—W(5 <sup>v</sup> )	2.85 (2)	O(11 <sup>viii</sup> )—W(4)—W(6)	102.3 (6)
W(3)—O(5 <sup>ii</sup> )	2.79 (2)	O(8 <sup>iii</sup> )—W(5)—W(3 <sup>iii</sup> )	87.4 (5)
—O(11 <sup>i</sup> )	2.75 (2)	O(5 <sup>vii</sup> )—W(6)—O(7 <sup>ii</sup> )	81.8 (5)
W(4)—O(11 <sup>viii</sup> )	2.95 (2)		
—W(6)	2.75 (2)		
W(5)—O(8 <sup>iii</sup> )	2.80 (2)		
—W(3 <sup>iii</sup> )	2.87 (2)		
W(6)—O(5 <sup>vii</sup> )	2.94 (2)		
—O(7 <sup>ii</sup> )	2.99 (2)		

Symmetry code: none  $x, y, z$ ; (i)  $1-x, 1-y, 1-z$ ; (ii)  $1-x, -y, 1-z$ ; (iii)  $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ; (iv)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (v)  $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ ; (vi)  $1-x, 1-y, -z$ ; (vii)  $1-x, -y, -z$ ; (viii)  $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ; (ix)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (x)  $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (xi)  $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$ .

chelating bidentate  $\text{CO}_3$  groups in equatorial positions, closely resembles, in bond lengths, bond angles and conformation, corresponding units in previously studied uranyl carbonates (Mereiter, 1986*a,b*, and references therein). The  $\text{U}(\text{CO}_3)_3$  entity of the unit is comparatively flat and shows an r.m.s. deviation from planarity of  $0.05 \text{ \AA}$ .\* The interactions between the unit and the surrounding Cs ions (Fig. 1) allow us to distinguish six

\* See deposition footnote.

\* Lists of structure factors, anisotropic thermal parameters, coordination geometry of the water molecules, and least-squares planes, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44817 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

inner and six outer cations. Five of the six inner Cs ions share triangle faces with the coordination polyhedron of uranium, a  $\text{UO}_2\text{O}_6$  hexagonal bipyramid, and show corresponding Cs—O bond lengths of 2.98–3.61 (1) Å and distances to the central uranium of 4.13–4.20 Å. Only Cs(2) (lower left in Fig. 1) has an outlying position relative to the  $\text{UO}_2\text{O}_6$  polyhedron with the result that the distance Cs(2)—O(4) = 4.17 (1) Å cannot be regarded as a bond and Cs(2)—U = 4.50 Å clearly exceeds the corresponding values for the first five Cs.

The four different Cs ions exhibit irregular coordination by O and  $W$  ligands ( $W = \text{H}_2\text{O}$ ). Their coordination numbers are not well defined because Cs—O,  $W$  bond lengths, which start at 2.98 (1) Å and are most frequent in the range 3.1–3.4 Å, do not show a clear-cut gap to non-bonding distances. The Cs—O,  $W$  bond-distance limit of 3.75 Å, which was adopted for this work and used in Table 2, represents a compromise which is slightly larger than the shortest Cs—C separation of 3.68 (1) Å between Cs(2) and C(2). With this limit the coordination number is 11 for Cs(1) and Cs(3), and 9 for Cs(2) and Cs(4). However, each of the latter Cs has two further O/ $W$  neighbours at distances between 3.81 and 4.01 (1) Å.

Considering Cs—O,  $W$  distances  $\leq 3.75$  Å, five of the six different water molecules exhibit pyramidal coordination by three Cs, while the sixth molecule,  $W(3)$ , is coordinated by two Cs. By using 3.4 Å as an arbitrary border between strong and weak Cs— $W$  bonds, the water molecules may be subdivided into two groups. The members of the first group —  $W(1)$ ,  $W(2)$  and  $W(4)$  — each have three strong Cs— $W$  bonds while the members of the second group —  $W(3)$ ,  $W(5)$  and  $W(6)$  — exhibit two or three weak Cs— $W$  bonds. Stereochemical considerations indicate that all molecules donate pairs of hydrogen bonds with  $W$ -acceptor distances of 2.75–2.99 (2) Å and acceptor— $W$ -acceptor angles of 82–116 (0.5)° (Table 2). In accordance with the subdivision the molecules of the first

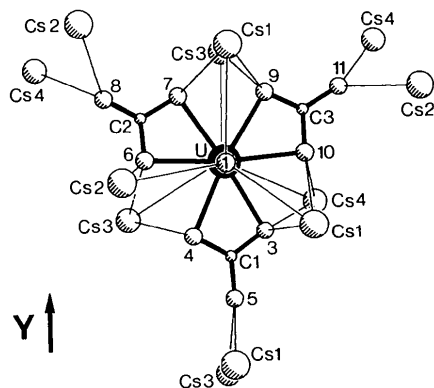


Fig. 1.  $[\text{UO}_2(\text{CO}_3)_3]$  unit with surrounding Cs ions in a view approximately parallel to the uranyl group O(1)—U—O(2).

group do not accept hydrogen bonds, while those of the second group show one [ $W(5)$ ,  $W(6)$ ] or two [ $W(3)$ ] accepted hydrogen bonds.

Fig. 2 shows that the constituents of the title compound adopt layer-like arrangements parallel to (10 $\bar{1}$ ). Layers of  $[\text{UO}_2(\text{CO}_3)_3]$  units alternate with two different layers of Cs ions, one formed by Cs(1) and Cs(2), the other one by Cs(3) and Cs(4). The water molecules  $W(1)$ ,  $W(2)$  and  $W(3)$  can be assigned to the Cs(1) + Cs(2) layer,  $W(4)$ ,  $W(5)$  and  $W(6)$  to the Cs(3) + Cs(4) layer. Surprisingly, in view of this, the crystals are tabular with principal (100) faces which indicates that the cohesive forces are strongest parallel to this plane. Closer inspection of the structure reveals that this is attributable to the number of direct links parallel to (100) between the oppositely charged  $[\text{UO}_2(\text{CO}_3)_3]$  units and the Cs ions {the sandwich-like arrangement of Cs between  $[\text{UO}_2(\text{CO}_3)_3]$  units near  $x \sim 0$  and  $x \sim \frac{1}{2}$ }. Perpendicular to (100) the coherence of the structure may be weaker because in the regions of  $x \sim \frac{1}{4}$  and  $x \sim \frac{3}{4}$  the formally neutral water molecules are mainly responsible for connections (Fig. 3).

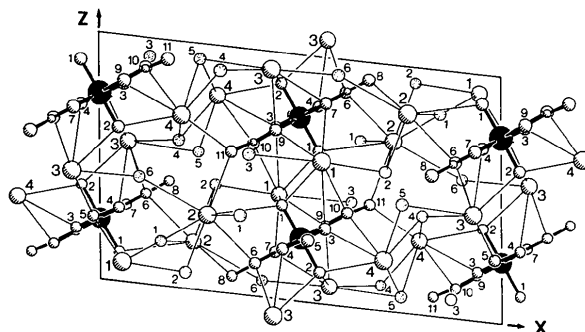


Fig. 2. Projection of the structure down the  $b$  axis. Water molecules are dotted.

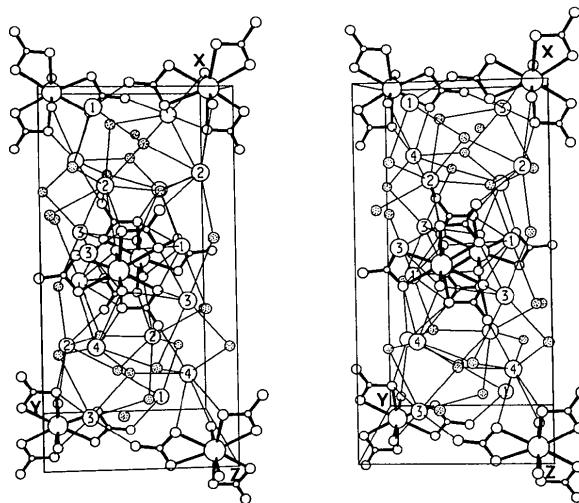


Fig. 3. Stereoscopic view of the structure approximately down  $c^*$ . Water molecules are dotted.

Support by Professor Dr A. Preisinger and the Austrian FWF (project 2178) is gratefully acknowledged.

#### References

BACHELET, M., CHEYLAN, E., DOUIS, M. & GOULETTE, J. C. (1954). *Bull. Soc. Chim. Fr.* pp. 173–179.

*Gmelin Handbook of Inorganic Chemistry* (1983). Uranium. Suppl. Vol. C13, 8th ed., pp. 12–22. Berlin: Springer.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 MEREITER, K. (1986a). *Acta Cryst.* C42, 1678–1681.  
 MEREITER, K. (1986b). *Acta Cryst.* C42, 1682–1684.  
 MEREITER, K., PREISINGER, A. & MIKENDA, W. (1988). In preparation.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1988). C44, 1178–1181

## Structure of Barium Tetraisothiocyanatocobaltate(II) Heptahydrate

BY K. MEREITER AND A. PREISINGER

*Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Vienna, Austria*

(Received 29 December 1987; accepted 2 March 1988)

**Abstract.**  $\text{Ba}[\text{Co}(\text{NCS})_4] \cdot 1.7\text{H}_2\text{O}$ ,  $M_r = 554.7$ , tetragonal,  $I\bar{4}$ ,  $a = 18.950(4)$ ,  $c = 10.361(3)$  Å,  $V = 3721(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.980$  g cm<sup>-3</sup>,  $\text{Mo K}\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 34.6$  cm<sup>-1</sup>,  $F(000) = 2152$ ,  $T = 295$  K, final  $R = 0.040$  for 1257 observed reflections. Isostructural with  $\text{Ba}[\text{Zn}(\text{NCS})_4] \cdot 7\text{H}_2\text{O}$ . Two independent tetrahedral  $[\text{Co}(\text{NCS})_4]^{2-}$  anions are packed in chains parallel to  $c$ , and are linked *via* O–H...S-type hydrogen bonds with chains of edge-sharing  $\text{BaS}(\text{H}_2\text{O})_6$  polyhedra.

**Introduction.** During an investigation of  $\text{Na}_2[\text{Co}(\text{NCS})_4] \cdot 8\text{H}_2\text{O}$  (Mereiter & Preisinger, 1982) the title compound became of interest because symmetry, unit-cell dimensions and crystal habit indicated closely related structure-building principles. This was briefly mentioned in the cited work. Based on earlier work (Cuvelier, 1933; *Gmelins Handbuch der anorganischen Chemie*, 1961) the title compound was at that time considered as an octahydrate. The present investigation, however, showed it to be a heptahydrate which is isostructural with  $\text{Ba}[\text{Zn}(\text{NCS})_4] \cdot 7\text{H}_2\text{O}$  (Brodersen, Hummel, Böhm & Procher, 1985).

**Experimental.** Deep-blue needles, elongated parallel to  $c$ , obtained by room-temperature evaporation of a filtered solution made from 6.1 g  $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ , 2.8 g  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and 60 g  $\text{H}_2\text{O}$ . Preliminary information from precession photographs, further work on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized  $\text{Mo K}\alpha$  radiation. Unit-cell dimensions from 32 reflections,  $8 \leq \theta \leq 17^\circ$ . Data collection with a prism  $0.04 \times 0.04 \times 0.36$  mm

mounted with its long axis  $c$  parallel to the  $\phi$  axis,  $\omega$  scans, scan width  $1^\circ$ , scan rate  $0.6^\circ \text{min}^{-1}$ ; three standard reflections,  $\pm 1\%$  variation. 1750 independent reflections measured, corrected for  $L_p$ , absorption effects small (transmission factors in the range 0.86–0.88) and therefore neglected; range  $\theta$ :  $2 \rightarrow 25^\circ$ ;  $h, k$ :  $0 \rightarrow 22$ ;  $l$ :  $0 \rightarrow 12$ . 1257 reflections with  $F_o \geq 6\sigma(F_o)$  used. Structure determined by Patterson and Fourier methods in space group  $I\bar{4}$ ; alternative space groups  $I4$  and  $I\bar{4}/m$  rejected by stereochemical considerations. Refinement on  $F$  with anisotropic temperature factors for Ba, Co, S and O, and isotropic ones for C and N; 147 parameters varied. Final  $R = 0.040$ ,  $wR = 0.039$ ,  $w = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$ ,  $(\Delta/\sigma)_{\text{max}} = 0.01$ ,  $|\Delta\rho|_{\text{max}} = -0.6$  and  $0.6$  e Å<sup>-3</sup>. Calculations with program *SHELX76* (Sheldrick, 1976). Atomic scattering functions and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Final atomic parameters are given in Table 1, bond lengths and angles in Table 2.\* The structure contains two independent  $[\text{Co}(\text{NCS})_4]^{2-}$  anions of approximately tetrahedral configuration, both with symmetry 2, similar bond lengths but different degrees of distortion (Fig. 1). Both kinds of anions are packed rather efficiently in separate chains extending parallel to  $c$  (Fig. 2). Each chain is in contact with four others *via*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44824 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.