

Data collection: CAD-4 (Enraf-Nonius, 1977). Cell refinement: CAD-4 (Enraf-Nonius, 1977). Data reduction: *MolEN* (Fair, 1990). Program(s) used to refine structure: *LSFM MolEN* (Fair, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF MolEN* (Fair, 1990).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
S1	0.6485 (2)	0.3457 (1)	0.3247 (2)	0.0671 (7)
S2	0.8110 (1)	0.5792 (1)	0.4708 (1)	0.0522 (6)
S3	0.7446 (2)	0.4430 (1)	0.5319 (1)	0.0534 (6)
S4	0.5836 (2)	0.6768 (1)	0.3840 (1)	0.0511 (5)
S5	0.0799 (2)	0.7979 (1)	0.1993 (2)	0.0614 (6)
S6	0.2427 (2)	1.0310 (1)	0.2201 (2)	0.0787 (7)
S7	0.3074 (2)	0.8938 (1)	0.3501 (2)	0.0640 (7)
S8	0.1483 (2)	1.1271 (1)	0.3294 (2)	0.0744 (7)

Table 2. Anisotropic thermal parameters (\AA^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0797 (6)	0.0562 (8)	0.0675 (6)	0.0211 (6)	0.0413 (4)	0.0063 (6)
S2	0.0365 (4)	0.0697 (8)	0.0559 (5)	-0.0037 (5)	0.0239 (3)	0.0058 (6)
S3	0.0530 (5)	0.0669 (9)	0.0430 (4)	0.0066 (6)	0.0249 (3)	0.0133 (5)
S4	0.0536 (4)	0.0487 (7)	0.0511 (5)	-0.0067 (5)	0.0317 (3)	-0.0092 (5)
S5	0.0754 (6)	0.0472 (7)	0.0651 (5)	0.0031 (6)	0.0438 (4)	-0.0095 (5)
S6	0.0760 (5)	0.088 (1)	0.0731 (5)	-0.0369 (6)	0.0533 (3)	-0.0208 (6)
S7	0.0421 (5)	0.093 (1)	0.0674 (7)	0.0069 (7)	0.0246 (4)	-0.0128 (7)
S8	0.1215 (8)	0.0496 (8)	0.0682 (6)	-0.0331 (7)	0.0571 (5)	-0.0219 (6)

Table 3. Geometric parameters (\AA , $^\circ$)

S1—S1	2.060 (2)	S5—S5	2.039 (3)
S1—S3	2.043 (2)	S5—S7	2.035 (2)
S2—S3	2.040 (2)	S6—S7	2.051 (2)
S2—S4	2.049 (2)	S6—S8	2.040 (3)
S4—S4	2.037 (1)	S8—S8	2.058 (2)
S1—S1—S3	107.9 (1)	S5—S5—S7	107.38 (9)
S3—S2—S4	107.78 (9)	S7—S6—S8	107.1 (1)
S1—S3—S2	107.75 (9)	S5—S7—S6	107.71 (7)
S2—S4—S4	108.62 (9)	S6—S8—S8	107.95 (8)
S1'—S1—S3—S2	-99.1 (1)	S5'—S5—S7—S6	-99.9 (1)
S3—S1—S1'—S3'	98.5 (1)	S7—S5—S5'—S7'	99.8 (1)
S4—S2—S3—S1	99.2 (1)	S8—S6—S7—S5	99.2 (1)
S3—S2—S4—S4'	-98.4 (1)	S7—S6—S8—S8'	-98.6 (1)
S2—S4—S4'—S2'	98.0 (1)	S6—S8—S8'—S6'	99.5 (1)

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). Starting coordinates and atom numbering were taken from Watanabe (1974).

We thank the College of Arts and Sciences of the University of Toledo for support of the X-ray facility.

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55547 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1021]

References

- Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.
 Enraf-Nonius (1977). *CAD-4 Operations Manual*. Enraf-Nonius, Delft, The Netherlands.

- Fair, C. K. (1990). *MolEN*. An interactive intelligent system for crystal structure analysis. Enraf-Nonius, Delft, The Netherlands.
 Goldsmith, L. M. & Strouse, C. E. (1977). *J. Am. Chem. Soc.* **99**, 7580–7589.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Rettig, S. J. & Trotter, J. (1987). *Acta Cryst.* **C43**, 2260–2262.
 Templeton, L. K., Templeton, D. H. & Zalkin, A. (1976). *Inorg. Chem.* **15**, 1999–2001.
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
 Watanabe, Y. (1974). *Acta Cryst.* **B30**, 1396–1401.
 Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1993). **C49**, 126–129

Synthesis and Structures of the Quaternary Sulfides $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$ and $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$

PING WU AND JAMES A. IBERS

Department of Chemistry, Northwestern University,
 Evanston, Illinois 60208-3113, USA

(Received 8 May 1992; accepted 3 August 1992)

Abstract

The new quaternary compounds $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$ and $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$ have been synthesized. $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$ has a hexagonal structure and $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$ has both hexagonal and trigonal phases. The two compounds have similar structures to that of CdI_2 , with double close-packed sulfur layers and transition-metal and main-group atoms disordered over the octahedral sites inside the double layers. These layers are separated by potassium ions that occupy trigonal prismatic sites.

Comment

Two new quaternary sulfides, $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$ and $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$, have been synthesized as part of a continuing effort to explore the synthesis and properties of new complex chalcogenides (Lu & Ibers, 1991a,b; Mansuetto, Keane & Ibers, 1992; Wu & Ibers, 1992). Trichet & Rouxel (1977) studied the analogous system $\text{Na}_x\text{Zr}_{1-x}\text{In}_x\text{S}_2$ with X-ray powder diffraction techniques and complex impedance measurements. Three different phases, all good ionic conductors, were found in the composition range $0 < x < 1$. The intercalated compounds A_xZrS_2 (Cousseau, Trichet & Rouxel, 1973; Rouxel, Cousseau & Trichet, 1971) and A_xSnS_2 (Le Blanc, Danot & Rouxel, 1969) ($A = \text{Li, Na, K}$) show similar structural features. Their structures have generally been postulated from cell constants obtained from powder samples.

The present samples were prepared by the reaction of K_2S_5 [prepared from elemental K (AESAR, 99%) and S (Alfa, 99.9995%)] with Zr (Johnson Matthey, 99.9%) and In powder (Johnson Matthey, 99.999%) or Cr and Sn powder (both Johnson Matthey, 99.999%) and elemental S in quartz tubes. Each reaction was carried out at 1273 K for 6 days; the tubes were then cooled at a rate of 4 K h^{-1} . Semiquantitative EDAX analysis revealed the presence of all four elements in a ratio of approximately 1:1:1:4. X-ray diffraction powder patterns of ground bulk samples were obtained with a Philips X-ray diffractometer. These showed that $K_{0.5}Zr_{0.5}In_{0.5}S_2$ has only a hexagonal phase, whereas both hexagonal and trigonal phases were present in the $K_{0.5}Cr_{0.5}Sn_{0.5}S_2$ samples as prepared. Complex impedance measurements were made on pressed pellets of these compounds. $K_{0.5}Zr_{0.5}In_{0.5}S_2$ has an ionic conductivity of $0.5(2) \text{ M}\Omega^{-1} \text{ cm}^{-1}$ at room temperature. [Trichet & Rouxel (1977) reported a higher conductivity ($10^2 \text{ M}\Omega^{-1} \text{ cm}^{-1}$ at 300 K) for the $x = 0.50$ phase of the $Na_xZr_{1-x}In_xS_2$ system, but lower conductivities (10^{-2} to $10^{-1} \text{ M}\Omega^{-1} \text{ cm}^{-1}$) for the $x = 0.35$ and $x = 0.80$ phases.] The conductivity of the bulk $K_{0.5}Cr_{0.5}Sn_{0.5}S_2$ samples containing both phases was below the instrumental limit (estimated at $0.01 \text{ M}\Omega^{-1} \text{ cm}^{-1}$).

From single-crystal data, it was found that the hexagonal and trigonal phases have closely related layered structures that can be derived from that of CdI_2 . There are double close-packed layers of S atoms. The metal atoms (Zr/In or Cr/Sn) are disordered and occupy all the octahedral sites between the double sulfur layers. Bond lengths compare well with literature values: for example, the (Zr/In)—S bond length is $2.591(1) \text{ \AA}$ compared with average lengths of $2.58(1) \text{ \AA}$ for Zr—S in $KCuZrS_3$ (Mansuetto, Keane & Ibers, 1992) and 2.65 \AA for In—S in $KInS_2$ -III (Range & Mahlberg, 1975), and the (Cr/Sn)—S bond length is $2.481(1) \text{ \AA}$ compared with average lengths of $2.42(4) \text{ \AA}$ for Cr—S in $CuCrS_2$ (Le Nagard, Collin

& Gorochoy, 1979) and $2.56(3) \text{ \AA}$ for Sn—S (tetravalent Sn) in Sn_2S_3 (Kniep, Mootz, Severin & Wunderlich, 1982). In both structures, the S—M—S bond angles are $\sim 92^\circ$ and the K sites are coordinated by six S atoms in a trigonal prismatic arrangement. In $K_{0.5}Zr_{0.5}In_{0.5}S_2$, the K cations are disordered over two sites and in both structures the K cations exhibit large thermal motion in the ab plane, consistent with the high ionic conductivity in $K_{0.5}Zr_{0.5}In_{0.5}S_2$. The two structures differ in how the layers stack; in the hexagonal $K_{0.5}Zr_{0.5}In_{0.5}S_2$ structure the close-packed sulfur double layers stack with an $ABAB\dots$ sequence (Fig. 1) while in the trigonal $K_{0.5}Cr_{0.5}Sn_{0.5}S_2$ they stack with an $ABCABC\dots$ sequence (Fig. 2).

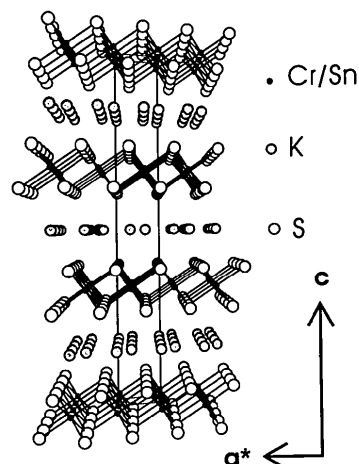


Fig. 2. View of the $K_{0.5}Cr_{0.5}Sn_{0.5}S_2$ structure down the b axis.

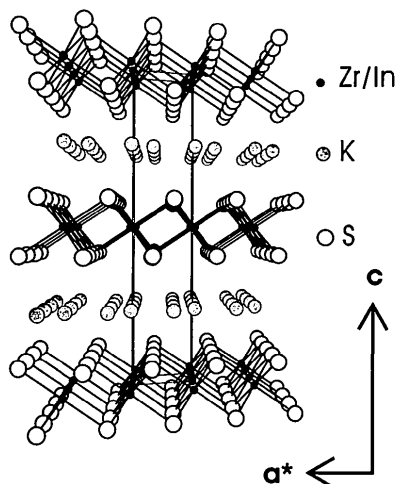


Fig. 1. View of the $K_{0.5}Zr_{0.5}In_{0.5}S_2$ structure down the b axis.

Experimental

$K_{0.5}Zr_{0.5}In_{0.5}S_2$

Crystal data

$M_r = 186.70$

Hexagonal

$P6_3/mmc$

$a = 3.721(1) \text{ \AA}$

$c = 16.639(7) \text{ \AA}$

$V = 199.5(1) \text{ \AA}^3$

$Z = 2$

$D_x = 3.11 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.7093 \text{ \AA}$

Cell parameters from 54 reflections

$\theta = 18.5\text{--}19.5^\circ$

$\mu = 5.56 \text{ mm}^{-1}$

$T = 115 \text{ K}$

Plate

$0.16 \times 0.09 \times 0.03 \text{ mm}$

Red

Data collection

Picker diffractometer

θ - 2θ scans

Absorption correction:

analytical

$T_{\min} = 0.601$, $T_{\max} =$

0.842

3438 measured reflections

194 independent reflections

194 observed reflections

$R_{\text{int}} = 0.095$

$\theta_{\max} = 35.0^\circ$

$h = -6 \rightarrow 6$

$k = -6 \rightarrow 6$

$l = -26 \rightarrow 26$

6 standard reflections

monitored every 100

reflections

intensity variation: none

Refinement**Refinement on F^2**

$wR = 0.111$
 $S = 2.30$
 194 reflections
 12 parameters
 $w = 1/[\sigma^2(F^2) + (0.04F^2)^2]$
 $(\Delta/\sigma)_{\max} = 0.119$
 $\Delta\rho_{\max} = 7.7 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -3.0 \text{ e } \text{\AA}^{-3}$

Extinction correction:
 Zachariasen [1968, equations (3) and (4)]
 Extinction coefficient: $C = 0.77 (22) \times 10^{-6}$
 Atomic scattering factors
 from Cromer (1974) and
 Cromer & Waber (1974)
 (In, K, S); Cromer &
 Liberman (1981) (Zr)

Data collection: *PCPS/Picker*. Cell refinement: *CELREF*, local program. Data reduction: *NUPICK*, local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *NUCLS*, local program. Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *DATBL*, local program.

The stoichiometry of the material was constrained to be $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$ on the basis of the EDAX analysis and the homogeneity of the sample.

 $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$ **Crystal data**

$M_r = 169.02$
 Trigonal
 $R\bar{3}m$
 $a = 3.5786 (5) \text{ \AA}$
 $c = 24.832 (5) \text{ \AA}$
 $V = 275.4 (1) \text{ \AA}^3$
 $Z = 3$
 $D_x = 3.06 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\lambda = 0.7093 \text{ \AA}$

Cell parameters from 24
 reflections
 $\theta = 15.5\text{--}20^\circ$
 $\mu = 6.41 \text{ mm}^{-1}$
 $T = 115 \text{ K}$
 Plate
 $0.13 \times 0.12 \times 0.006 \text{ mm}$
 Black

Data collection

Enraf-Nonius CAD-4
 diffractometer
 ω - 2θ scans
 Absorption correction:
 analytical
 $T_{\min} = 0.645$, $T_{\max} = 0.962$
 2191 measured reflections
 259 independent reflections

259 observed reflections
 $R_{\text{int}} = 0.091$
 $\theta_{\max} = 39.5^\circ$
 $h = -6 \rightarrow 6$
 $k = -6 \rightarrow 6$
 $l = -43 \rightarrow 43$
 6 standard reflections
 frequency: 180 min
 intensity variation: none

Refinement

Refinement on F^2
 $wR = 0.100$
 $S = 1.91$
 259 reflections
 9 parameters
 $w = 1/[\sigma^2(F^2) + (0.04F^2)^2]$

$(\Delta/\sigma)_{\max} = 0.088$
 $\Delta\rho_{\max} = 2.4 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = 0.7 \text{ e } \text{\AA}^{-3}$
 Atomic scattering factors
 from Cromer (1974) and
 Cromer & Waber (1974)

Data collection: Enraf-Nonius CAD-4. Cell refinement: Enraf-Nonius CAD-4. Data reduction: *CADPROC*, local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *NUCLS*, local program. Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *DATBL*, local program.

The stoichiometry of the material was constrained to be $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$ on the basis of the EDAX analysis and the homogeneity of the sample.

Table 1. *Fractional atomic coordinates, occupancies and equivalent isotropic thermal parameters (\AA^2) for $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$*

$$B_{\text{eq}} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	Occupancy	x	y	z	B_{eq}
Zr/In	1.0	0	0	0	0.90 (2)
K1	0.35 (2)	1/3	2/3	0.25	6.7 (5)
K2	0.15	0	0	0.25	2.8 (4)
S	1.0	2/3	1/3	0.4130 (1)	0.96 (2)

Table 2. *Geometric parameters (\AA , $^\circ$) for $\text{K}_{0.5}\text{Zr}_{0.5}\text{In}_{0.5}\text{S}_2$*

Zr/In—S ⁱ	2.591 (1)	K2—S	3.459 (2)
K1—S	3.459 (2)		
S ⁱ —Zr/In—S ⁱⁱ	91.79 (5)		

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

Table 3. *Fractional atomic coordinates, occupancies and equivalent isotropic thermal parameters (\AA^2) for $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$*

$$B_{\text{eq}} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	Occupancy	x	y	z	B_{eq}
Cr/Sn	1.0	0	0	0	0.51 (1)
K	0.25	0	0	0.16696 (34)	7.4 (4)
S	1.0	0	0	0.388637 (47)	0.73 (2)

Table 4. *Geometric parameters (\AA , $^\circ$) for $\text{K}_{0.5}\text{Cr}_{0.5}\text{Sn}_{0.5}\text{S}_2$*

Cr/Sn—S ⁱ	2.481 (1)	K—S ⁱⁱⁱ	3.458 (7)
K—S ⁱⁱ	3.446 (7)		
S ⁱ —Cr/Sn—S ⁱⁱ	92.31 (3)		

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

Use was made of the X-ray and scanning electron microscope facilities supported by the National Science Foundation through the Northwestern University Materials Research Center, Grant No. DMR 88-21571. This research was supported by the National Science Foundation through Grant DMR-8809854 (Science and Technology Center for Superconductivity).

Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55394 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1015]

References

- Cousseau, J., Trichet, L. & Rouxel, J. (1973). *Bull. Soc. Chim. Fr.* pp. 872-878.
 Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1, pp. 149-150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 Cromer, D. T. & Liberman, D. A. (1981). *Acta Cryst.* A37, 267-268.
 Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 149-150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

- Kniep, R., Mootz, D., Severin, U. & Wunderlich, H. (1982). *Acta Cryst.* B38, 2022–2023.
- Le Blanc, A., Danot, M. & Rouxel, J. (1969). *Bull. Soc. Chim. Fr.* pp. 87–90.
- Le Nagard, N., Collin, G. & Gorochov, O. (1979). *Mater. Res. Bull.* 14, 1411–1417.
- Lu, Y.-J. & Ibers, J. A. (1991a). *Inorg. Chem.* 30, 3317–3320.
- Lu, Y.-J. & Ibers, J. A. (1991b). *J. Solid State Chem.* 94, 381–385.
- Mansuetto, M. F., Keane, P. M. & Ibers, J. A. (1992). In preparation.
- Range, K.-J. & Mahlberg, G. (1975). *Z. Naturforsch. Teil B*, 30, 81–87.
- Rouxel, J., Cousseau, J. & Trichet, L. (1971). *C. R. Acad. Sci. Sér. C*, 273, 243–246.
- Sheldrick, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.
- Sheldrick, G. M. (1990). *SHELXTL/PC*. Version 4.1. An integrated system for solving, refining and displaying crystal structures from diffraction data. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
- Trichet, L. & Rouxel, J. (1977). *Mater. Res. Bull.* 12, 345–354.
- Wu, P. & Ibers, J. A. (1992). In preparation.
- Zachariasen, W. H. (1968). *Acta Cryst.* A24, 212–216.

Acta Cryst. (1993). C49, 129–130

catena-[Cd{ μ -S(CH₂)₃NHMe₂}Br₂]

WILLIAM CLEGG

Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, England

ISIDRE CASALS AND PILAR GONZÁLEZ-DUARTE

Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

(Received 18 June 1992; accepted 14 July 1992)

Abstract

The title complex, *catena*-poly[dibromocadmium- μ -3-dimethylamino-1-propanethiolato], contains polymeric chains of alternating Cd and S atoms with Cd—S bond lengths of 2.515(3) and 2.520(3) Å. Distorted tetrahedral coordination of Cd [with a wide S—Cd—S angle of 126.95(5)°] is completed by two Br ligands [Cd—Br 2.5834(15) and 2.6400(14) Å]. The longer Cd—Br bond is to a Br atom involved in inter-chain hydrogen bonding with the ammonium group of a mercaptoamine ligand of an adjacent chain, to give two-dimensional sheets.

Comment

Interest in cadmium-thiolate coordination chemistry centres mainly on structural and bioinorganic objectives (Dance, 1986; Blower & Dilworth, 1987). Cadmium-cysteine coordination in several metallothioneins has

been established by solution ¹¹³Cd NMR studies and by X-ray diffraction measurements (Robbins, McRee, Williamson, Collett, Xuong, Furey, Wang & Stout, 1991). As part of our extensive studies of the coordination chemistry of mercaptoamine ligands (Capdevila, Clegg, González-Duarte, Harris, Mira, Sola & Taylor, 1992, and references therein), and with the specific aim of correlating ¹¹³Cd solid-state NMR data with the coordination of Cd in different environments, we have determined the structure of *catena*-[Cd{ μ -S(CH₂)₃NHMe₂}Br₂].

The complex (Fig. 1) is isostructural with the corresponding chloride (Casals, González-Duarte, Sola, Font-Bardía, Solans & Solans, 1987) and with the analogous mercury chloride complex (Casals, González-Duarte, Sola, Miravittles & Molins, 1988). It consists of polymeric chains of alternating Cd and S atoms. The mercaptoamine ligands are doubly bridging through the S atom only, the protonated amine group playing no part in the metal coordination. The tetrahedral coordination of Cd by two thiolate and two Br ligands shows slightly more distortion than in the corresponding chloride, but less than in the analogous Hg complex; the correlation between such geometrical variations and solid-state ¹¹³Cd NMR parameters will be the subject of a separate publication.

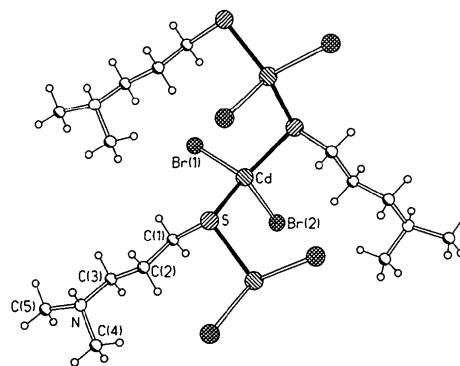


Fig. 1. Part of the polymeric chain structure, showing the labelling of the independent atoms.

The chains are held together in extended two-dimensional sheets by hydrogen bonding between ammonium groups and Br ligands. The H...Br and N...Br distances are 2.52(2) and 3.35(2) Å respectively, with an angle of 148(2)° at the H atom (these values are calculated from the refinement results, whereby the H atom was made to ride on its N atom with a fixed bond length of 0.93 Å). The Br ligand involved in hydrogen bonding forms a longer bond to the Cd atom.

Previous attempts to synthesize this complex gave no pure product, but a mixture containing also the salt [Me₂NH(CH₂)₃S]₂[CdBr₄] (Casals *et al.*, 1987). Comparable synthetic procedures with halides of Zn, Cd and Hg, and with the 4-mercapto-1-methylpiperidine ligand (a cyclic instead of linear γ -mercaptoamine) give dimeric [M₂(μ -SR)₂X₄] (Bayón, Casals, Gaete, González-Duarte