Zn(1)—O(4)—C(10)	115.8 (3)	C(1)—C(2)—C(3)	117.3 (5)
Zn(1)—O(2)—C(8)	116.2 (4)	C(1)—C(2)—C(21)	124.8 (5)
Zn(1)—N(1)—C(1)	115.1 (3)	C(3)—C(2)—C(21)	117.9 (5)
Zn(1)—N(1)—C(9)	99.7 (3)	C(6)—C(5)—C(4)	118.8 (7)
C(1)—N(1)—C(9)	111.1 (4)	C(2)—C(3)—C(4)	122.8 (5)
Zn(1)—N(1)—C(7)	100.0 (2)	C(1)—C(6)—C(5)	121.7 (5)
C(1)—N(1)—C(7)	113.3 (4)	C(2)—C(21)—C(22)	113.2 (6)
C(9)—N(1)—C(7)	116.4 (4)	C(5)—C(4)—C(3)	119.9 (6)
O(4)—C(10)—O(3)	123.7 (5)		

Data collection: *DIF4* (Stoe & Cie, 1991*a*). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXTL-Plus*88 (Sheldrick, 1988). Program(s) used to refine structure: *SHELXTL-Plus*88. Molecular graphics: *SHELXTL-Plus*88.

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Acta Cryst. (1996). C52, 812–817

Trimethyloxosulfonium Salts. IX. Study of some Mixed Compounds, $(CH_3)_3SOCdCl_{3-x}Br_x$

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Abstract

Crystal structures of six $(CH_3)_3SOCdCl_{3-x}Br_x$ mixed compounds [(1) $x = 2.116$, (2) $x = 1.787$, (3) $x = 1.183$, (4) $x = 0.962$, (5) $x = 0.607$, (6) $x = 0.286$]

have been determined. Each has space group *Pnma* and is a structural analogue of $(CH_3)_3SOCdCl_3$ and $(CH_3)_3SOCdBr_3$, reported previously. The distribution of Br and Cl atoms among the two anionic sites was especially studied. We have shown that the occupation probabilities are related to the x value but do not vary with it linearly: the Cl atoms showed a preference for the most symmetric site (*m* symmetry), while the Br atoms were better located on a general position more distant from the Cd ion. It is therefore not possible to describe these mixed compounds in terms of continuous solid-solution series.

Comment

In a previous paper (Puget, Jannin, de Brauer & Perret, 1991) we described the structures of the isostructural *catena*-trichlorocadmate and *catena*-tribromocadmate salts of $(CH_3)_3SO$. As a continuation, the crystal structures of six compositional analogues $(CH_3)_3SOCdCl_{3-x}Br_x$ are reported here. The precision of the results is very good and the crystal growth process leads to homogeneous bromine and chlorine composition in the whole crystal. Therefore, this study allows us to examine the influence of the site type on the kind of anionic substitution and the modifications resulting from it. No papers in the literature seem to deal with this subject for the Cl–Br couple. We have only found some reports about cationic substitution (Nord, 1983; Thomas, Mayo & Watts, 1992).

$$Me \longrightarrow SO^+Cd^{2+}[Cl_{3-x}Br_x]^{3-}$$

(with Me substituents above and below)
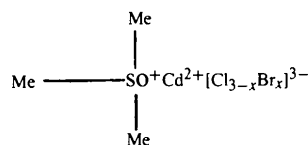
As found for the isostructural *catena*-tribromocadmate salt, the structure of each of the $(CH_3)_3SOCdCl_{3-x}Br_x$ compounds exhibits two crystallographically non-equivalent anionic sites where Br^- and Cl^- ions may both be located. The first shared (Br,Cl) site, labelled $(Br,Cl)_{(1)}$, is situated on the mirror $y = 0.25$. Its multiplicity is 4 and its occupation factor is 0.5. The second site, named $(Br,Cl)_{(2)}$, is in a general position. Its multiplicity is 8 and its total occupancy is 1. The occupation rates of Br and Cl atoms in each of the two available sites were refined with the only constraint that the total occupancy should be 0.5 on site $(Br,Cl)_{(1)}$ and 1 on site $(Br,Cl)_{(2)}$. The resulting values for each of the six compounds are listed in Table 3. Figs. 1 and 2, respectively, show the variations of the occupancies of the sites $(Br,Cl)_{(1)}$ and $(Br,Cl)_{(2)}$ *versus* the composition (x). These figures clearly show that these variations are effectively related to the composition but are not proportional to it: Br and Cl atoms are not equally

distributed on the two anionic sites. Cl atoms exhibit a higher affinity for the most symmetric site while Br atoms preferably occupy the other site, which is more distant from the Cd atom. In each $(CH_3)_3SOCdCl_{3-x}Br_x$ compound, the Cd atoms are coordinated to six halogen atoms defining quasi-regular octahedra, as shown in Fig. 3. Two of the halogen atoms are located on opposed apexes in $(Br,Cl)_{(1)}$ sites while the other four halogens are in $(Br,Cl)_{(2)}$ sites at general positions.

The Cd—X bond lengths become progressively longer when the bromine rate increases, and are intermediate between those found for $(CH_3)_3SOCdCl_3$ and $(CH_3)_3SOCdBr_3$. Fig. 4 shows the variation with x for each kind of Cd—X bond length, where X is the Br,Cl site: Cd—$X(1)$ bond lengths range from 2.6065 (3) or 2.6279 (3) Å for (6), and 2.6824 (3) or 2.7009 (3) Å for
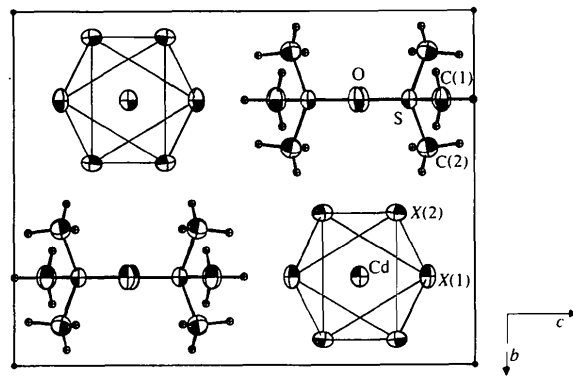

Fig. 3. Projection of the $(CH_3)_3SOCdCl_{3-x}Br_x$ structure along the a axis. Ellipsoids are shown at the 50% probability level.

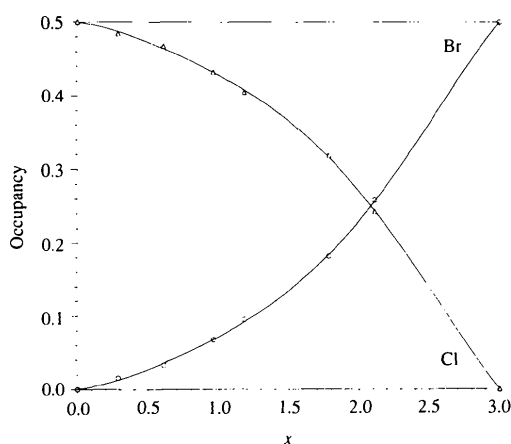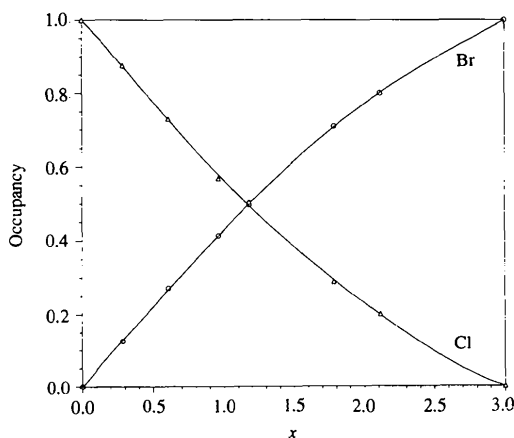Fig. 1. Cl and Br atom occupancy in the site $(Cl,Br)_{(1)}$ *versus* the composition x.

Fig. 4. Cd—X bond lengths *versus* the composition x. (Symmetry code: as given in Table 2.)

Fig. 2. Cl and Br atom occupancy in the site $(Cl,Br)_{(2)}$ *versus* the composition x.

(1). Cd—$X(2)$ bond lengths vary from 2.6780 (2) or 2.6878 (2) Å in (6) to 2.7712 (2) or 2.7748 (2) Å in (1) (see Table 2).

X-atom angles change little across the range of compounds considered. In all compounds, X—Cd—X angles between two opposite X atoms are equal to 180° when the halogens are in $(Br,Cl)_{(1)}$ sites. If X atoms are in $(Br,Cl)_{(2)}$ sites, these angles are 180° only for (1) and (2) but are very near for the others. The angles between adjacent halogens reflect the weak distortion of the octahedron: some of them range between 83.5 and 86° and the others between 93.5 and 97.5°. Fig. 5 clearly shows that the differences between the largest and the smallest $X(1)$—Cd—$X(2)$ and $X(2)$—Cd—$X(2)$ for adjacent X atoms are more important in (6) than in (1). The deformations of the octahedra are therefore more marked for the compounds rich in chlorine.
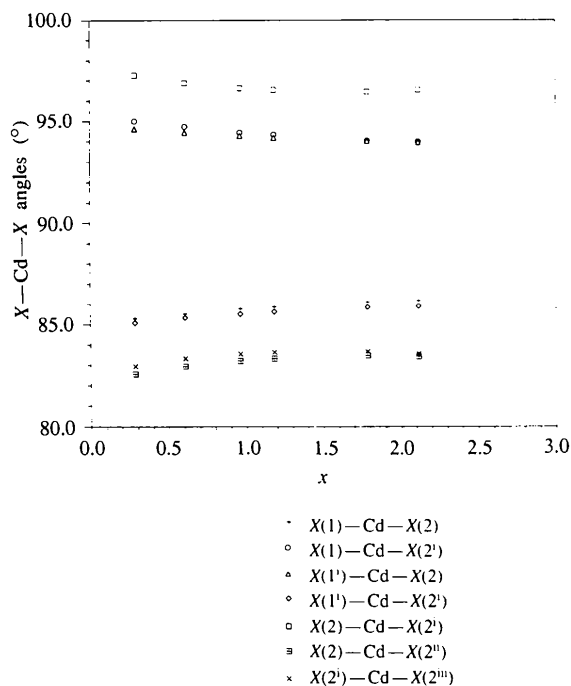
$$C_3H_9OS^+.Cd^{2+}.(Br_xCl_{3-x})^{3-}$$

Fig. 5. *X*—Cd—*X* angle values *versus* the composition *x*. (Symmetry codes: as given in Table 2.)

Legend:
- *X*(1)—Cd—*X*(2)
- *X*(1)—Cd—*X*(2')
- *X*(1')—Cd—*X*(2)
- *X*(1')—Cd—*X*(2')
- *X*(2)—Cd—*X*(2')
- *X*(2)—Cd—*X*(2'')
- *X*(2')—Cd—*X*(2''')

The distribution of the halogen atoms on the two sites is the consequence of the properties of the Br^- and Cl^- ions relating to bulkiness and polarizability. The Cl^- ion radius is smaller (Shannon & Prewitt, 1969) and it is less polarizable than the Br^- ion ($\alpha_{Cl} = 2.96$ and $\alpha_{Br} = 4.16$; Gready, Backskay & Huch, 1970).

It is therefore not possible to describe all these mixed compounds in terms of continuous solid solution series in spite of the fact that the substitution of Cl by Br leads to smooth linear expansions of the *a*, *b* and *c* lattice parameters. As in an ideal solution, the existence of a continuous series of solid solutions imposes the equal distribution of the substituted atoms in the host sites. This condition can only be realised in particular cases. The crystal-field influence and the individual properties of the substituted atoms modify the occupancies of sites of different types. To have the chance to lead to continuous solid solution series, the substitution must involve only one site and ions showing very similar properties. For example, the mixed compounds $[(CH_3)_4N]M_{1-x}M'_xCl_4$ (*M* = Mn, Co, Zn), studied in our laboratory by Perret, Godefroy & Arend (1985), exhibit the particular properties of solid solutions.

Experimental

Homogeneous composition in the whole crystal is the essential condition that allows a study of halogenide-ion distribution in our mixed compounds. The monocrystals we have used were therefore grown by the procedure described by Arend, Perret, Wüest & Kerkoc (1986) based on a temperature-difference growth with thermally enforced convection and the use of saturated solutions in equilibrium with precipitated solid phase. This method enables a constant concentration of the solution to be maintained just around the crystal during its growth process. Monocrystals were all grown under the same conditions of temperature: $T = 294$ K, $\Delta T = 3$ K. The supersaturated solutions were obtained by dissolution of weighted amounts of $(CH_3)_3SOCl$, $CdCl_2$, $(CH_3)_3SOBr$ and $CdBr_2$ in a constant volume of warm water [molar ratio $(3 - x'):(3 - x'):x':x'$]. The composition of the mother solution near the growing crystal is different from that of the solid mixture initially solved. Chemical analysis was therefore necessary for each composition. It shows that the bromine ratio value (*x*) of the mixed compounds strongly depends on the composition of the starting mixture of solids and is always a little higher. The analysis results have been systematically verified at the end of each structure refinement by comparison with the *x* value calculated from the occupation probabilities of Cl and Br in the two anionic sites.

Compound (1)

Crystal data

$C_3H_9OS^+.Cd^{2+}.$
$(Br_{2.116}Cl_{0.884})^{3-}$
$M_r = 405.79$
Orthorhombic
Pnma
$a = 6.847\,(1)$ Å
$b = 10.429\,(2)$ Å
$c = 13.655\,(2)$ Å
$V = 975.1$ Å^3
$Z = 4$
$D_x = 2.767$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5\text{--}15°$
$\mu = 11.24$ mm^{-1}
$T = 293$ K
Prismatic
$0.2 \times 0.2 \times 0.2$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans (*MolEN*; Fair, 1990)
$T_{min} = 0.9409$, $T_{max} = 0.9995$
8949 measured reflections
2057 independent reflections
1087 observed reflections
$[I > 3\sigma(I)]$

$R_{int} = 0.016$
$\theta_{max} = 30°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -5 \rightarrow 19$
4 standard reflections
frequency: 120 min
intensity decay: 3.1%

Refinement

Refinement on *F*
$R = 0.0113$
$wR = 0.0133$
$S = 1.05$
1087 reflections
71 parameters
Only H-atom *U*'s refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.201$ e Å^{-3}
$\Delta\rho_{min} = -0.196$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient:
7.144×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

$C_3H_9OS^+.Cd^{2+}.-$
$(Br_{1.787}Cl_{1.213})^{3-}$
$M_r = 391.1$
Orthorhombic
$Pnma$
$a = 6.825\ (1)$ Å
$b = 10.415\ (2)$ Å
$c = 13.630\ (2)$ Å
$V = 968.9$ Å^3
$Z = 4$
$D_x = 2.684$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5-15°$
$\mu = 10.03$ mm^{-1}
$T = 293$ K
Prismatic
$0.2 \times 0.2 \times 0.2$ mm
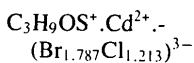Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans (*MolEN*; Fair, 1990)
$T_{min} = 0.8789$, $T_{max} = 0.9997$
5228 measured reflections
1481 independent reflections
939 observed reflections
$[I > 3\sigma(I)]$

$R_{int} = 0.014$
$\theta_{max} = 30°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -5 \rightarrow 20$
4 standard reflections
frequency: 120 min
intensity decay: 3.0%

Refinement

Refinement on F
$R = 0.015$
$wR = 0.017$
$S = 1.29$
939 reflections
71 parameters
Only H-atom U's refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.913$ e Å^{-3}
$\Delta\rho_{min} = -0.521$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient:
9.613×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (3)

Crystal data

$C_3H_9OS^+.Cd^{2+}.-$
$(Br_{1.183}Cl_{1.817})^{3-}$
$M_r = 364.5$
Orthorhombic
$Pnma$
$a = 6.782\ (1)$ Å
$b = 10.335\ (2)$ Å
$c = 13.572\ (2)$ Å
$V = 951.3$ Å^3
$Z = 4$
$D_x = 2.546$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5-15°$
$\mu = 7.88$ mm^{-1}
$T = 293$ K
Prismatic
$0.2 \times 0.2 \times 0.2$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{int} = 0.018$
$\theta_{max} = 30°$

$\omega/2\theta$ scans
Absorption correction:
ψ scans (*MolEN*; Fair, 1990)
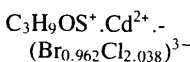$T_{min} = 0.9206$, $T_{max} = 0.9997$
8657 measured reflections
1738 independent reflections
957 observed reflections
$[I > 3\sigma(I)]$

$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -5 \rightarrow 20$
4 standard reflections
frequency: 120 min
intensity decay: 11.7%

Refinement

Refinement on F
$R = 0.0109$
$wR = 0.0126$
$S = 0.82$
957 reflections
71 parameters
Only H-atom U's refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.246$ e Å^{-3}
$\Delta\rho_{min} = -0.297$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient:
5.269×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (4)

Crystal data

$C_3H_9OS^+.Cd^{2+}.-$
$(Br_{0.962}Cl_{2.038})^{3-}$
$M_r = 354.7$
Orthorhombic
$Pnma$
$a = 6.765\ (1)$ Å
$b = 10.304\ (2)$ Å
$c = 13.544\ (2)$ Å
$V = 944.1$ Å^3
$Z = 4$
$D_x = 2.496$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5-15°$
$\mu = 7.07$ mm^{-1}
$T = 293$ K
Prismatic
$0.2 \times 0.2 \times 0.2$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans (*MolEN*; Fair, 1990)
$T_{min} = 0.8573$, $T_{max} = 0.9987$
7311 measured reflections
1444 independent reflections
899 observed reflections
$[I > 3\sigma(I)]$

$R_{int} = 0.015$
$\theta_{max} = 30°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -5 \rightarrow 19$
4 standard reflections
frequency: 120 min
intensity decay: 0.9%

Refinement

Refinement on F
$R = 0.0107$
$wR = 0.0120$
$S = 0.88$
899 reflections
71 parameters
Only H-atom U's refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.330$ e Å^{-3}
$\Delta\rho_{min} = -0.202$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient:
9.247×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (5)

Crystal data
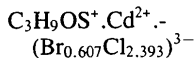
$C_3H_9OS^+.Cd^{2+}.$
  $(Br_{0.607}Cl_{2.393})^{3-}$
$M_r = 339.2$
Orthorhombic
Pnma
$a = 6.744\,(1)$ Å
$b = 10.253\,(2)$ Å
$c = 13.517\,(2)$ Å
$V = 934.6$ Å^3
$Z = 4$
$D_x = 2.409$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
  reflections
$\theta = 5$–15°
$\mu = 5.74$ mm^{-1}
$T = 293$ K
Prismatic
$0.2 \times 0.2 \times 0.2$ mm
Colourless

Data collection

Enraf–Nonius CAD-4
  diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scans (*MolEN*; Fair,
  1990)
  $T_{min} = 0.9311$, $T_{max} =$
  0.9997
8466 measured reflections
1696 independent reflections
1045 observed reflections
  $[I > 3\sigma(I)]$

$R_{int} = 0.015$
$\theta_{max} = 30°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -5 \rightarrow 20$
4 standard reflections
  frequency: 120 min
  intensity decay: 6.8%

Refinement

Refinement on F
$R = 0.0100$
$wR = 0.0113$
$S = 0.84$
1045 reflections
71 parameters
Only H-atom U's refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.270$ e Å^{-3}
$\Delta\rho_{min} = -0.229$ e Å^{-3}
Extinction correction: Stout
  & Jensen (1968)
Extinction coefficient:
  4.610×10^{-6}
Atomic scattering factors
  from *International Tables
  for X-ray Crystallography*
  (1974, Vol. IV)

Compound (6)

Crystal data

$C_3H_9OS^+.Cd^{2+}.$
  $(Br_{0.286}Cl_{2.714})^{3-}$
$M_r = 324.5$
Orthorhombic
Pnma
$a = 6.716\,(1)$ Å
$b = 10.192\,(2)$ Å
$c = 13.476\,(2)$ Å
$V = 922.4$ Å^3
$Z = 4$
$D_x = 2.339$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
  reflections
$\theta = 5$–15°
$\mu = 4.53$ mm^{-1}
$T = 293$ K
Prismatic
$0.2 \times 0.2 \times 0.2$ mm
Colourless

Data collection

Enraf–Nonius CAD-4
  diffractometer

$R_{int} = 0.012$
$\theta_{max} = 30°$

$\omega/2\theta$ scans
Absorption correction:
  ψ scans (*MolEN*; Fair,
  1990)
  $T_{min} = 0.8440$, $T_{max} =$
  0.9999
7157 measured reflections
1415 independent reflections
1103 observed reflections
  $[I > 3\sigma(I)]$

Refinement

Refinement on F
$R = 0.0106$
$wR = 0.0130$
$S = 1.13$
1103 reflections
71 parameters
Only H-atom U's refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.003$

$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -5 \rightarrow 20$
4 standard reflections
  frequency: 120 min
  intensity decay: 1.4%

$\Delta\rho_{max} = 0.189$ e Å^{-3}
$\Delta\rho_{min} = -0.172$ e Å^{-3}
Extinction correction: Stout
  & Jensen (1968)
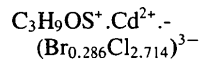Extinction coefficient:
  0.229×10^{-5}
Atomic scattering factors
  from *International Tables
  for X-ray Crystallography*
  (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)–(6)*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(1)				
Cd	0.40357 (2)	1/4	0.25034 (1)	2.139 (4)
S	0.2236 (1)	1/4	0.64161 (4)	2.14 (1)
O	0.1850 (3)	1/4	0.7451 (1)	3.18 (4)
C(1)	0.0108 (4)	1/4	0.5715 (2)	2.91 (5)
C(2)	0.3545 (3)	0.1152 (2)	0.6037 (1)	2.95 (4)
Cl,Br(1)	0.65227 (5)	1/4	0.40212 (2)	2.405 (8)
Cl,Br(2)	0.65354 (3)	0.42701 (2)	0.16486 (1)	2.304 (4)
(2)				
Cd	0.40236 (4)	1/4	0.25037 (2)	2.174 (5)
S	0.2232 (1)	1/4	0.64099 (6)	2.19 (2)
O	0.1835 (4)	1/4	0.7449 (2)	3.15 (6)
C(1)	0.0094 (7)	1/4	0.5711 (4)	2.96 (9)
C(2)	0.3545 (5)	0.1145 (3)	0.6027 (2)	3.00 (6)
Cl,Br(1)	0.65103 (9)	1/4	0.40139 (4)	2.51 (1)
Cl,Br(2)	0.65248 (5)	0.42697 (3)	0.16493 (2)	2.397 (7)
(3)				
Cd	0.40003 (2)	1/4	0.25054 (1)	2.077 (3)
S	0.2220 (1)	1/4	0.64047 (4)	2.132 (9)
O	0.1848 (3)	1/4	0.7448 (1)	3.08 (4)
C(1)	0.0048 (4)	1/4	0.5703 (2)	3.00 (6)
C(2)	0.3555 (4)	0.1140 (2)	0.6021 (1)	2.98 (4)
Cl,Br(1)	0.64893 (1)	1/4	0.40013 (3)	2.410 (9)
Cl,Br(2)	0.65030 (4)	0.42666 (2)	0.16556 (2)	2.364 (4)
(4)				
Cd	0.39917 (2)	1/4	0.25056 (1)	2.106 (4)
S	0.2215 (1)	1/4	0.64025 (4)	2.14 (1)
O	0.1833 (3)	1/4	0.7446 (1)	3.04 (4)
C(1)	0.0052 (4)	1/4	0.5697 (2)	3.11 (6)
C(2)	0.3552 (4)	0.1136 (2)	0.6014 (1)	3.04 (4)
Cl,Br(1)	0.64803 (8)	1/4	0.39975 (3)	2.44 (1)
Cl,Br(2)	0.64944 (4)	0.42628 (3)	0.16582 (2)	2.409 (5)
(5)				
Cd	0.39755 (2)	1/4	0.25064 (1)	2.015 (3)
S	0.22055 (8)	1/4	0.64010 (3)	2.061 (8)
O	0.1830 (2)	1/4	0.7450 (1)	2.94 (3)
C(1)	0.0023 (3)	1/4	0.5698 (2)	2.95 (5)
C(2)	0.3535 (3)	0.1127 (2)	0.6012 (1)	2.92 (3)
Cl,Br(1)	0.64674 (7)	1/4	0.39908 (3)	2.350 (4)
Cl,Br(2)	0.64787 (4)	0.42545 (2)	0.16652 (2)	2.317 (9)

(6)				
Cd	0.39586 (2)	1/4	0.25073 (1)	1.938 (3)
S	0.21934 (7)	1/4	0.63998 (3)	1.950 (7)
O	0.1822 (2)	1/4	0.74516 (9)	2.84 (2)
C(1)	0.0002 (3)	1/4	0.5698 (1)	2.80 (4)
C(2)	0.3524 (2)	0.1120 (1)	0.6011 (1)	2.81 (3)
Cl,Br(1)	0.64513 (6)	1/4	0.39899 (3)	2.240 (9)
Cl,Br(2)	0.64605 (4)	0.42399 (3)	0.16755 (2)	2.290 (4)

Table 2. Selected geometric parameters (Å, °) for (1)–(6)

(1)

Cd—X(1)	2.6824 (3)	S—O	1.437 (1)
Cd—X(1')	2.7009 (3)	S—C(1)	1.743 (3)
Cd—X(2)	2.7748 (2)	S—C(2)	1.746 (1)
Cd—X(2')	2.7712 (2)		
X(1)—Cd—X(1')	180.0	X(2')—Cd—X(2")	180.0
X(1)—Cd—X(2)	86.18 (1)	X(2')—Cd—X(2"')	83.53 (1)
X(1)—Cd—X(2')	93.98 (1)	O—S—C(1)	112.7 (1)
X(1')—Cd—X(2)	93.94 (1)	O—S—C(2)	112.70 (7)
X(1')—Cd—X(2')	85.90 (1)	C(1)—S—C(2)	105.44 (8)
X(2)—Cd—X(2')	96.53 (1)	C(2)—S—C(2")	107.27 (8)
X(2)—Cd—X(2")	83.41 (1)		

(2)

Cd—X(1)	2.6677 (6)	S—O	1.442 (3)
Cd—X(1')	2.6871 (6)	S—C(1)	1.742 (5)
Cd—X(2)	2.7689 (3)	S—C(2)	1.751 (2)
Cd—X(2')	2.7637 (3)		
X(1)—Cd—X(1')	180.0	X(2')—Cd—X(2")	180.0
X(1)—Cd—X(2)	86.12 (1)	X(2')—Cd—X(2"')	83.66 (1)
X(1)—Cd—X(2')	94.03 (1)	O—S—C(1)	112.3 (2)
X(1')—Cd—X(2)	94.00 (1)	O—S—C(2)	112.8 (1)
X(1')—Cd—X(2')	85.85 (1)	C(1)—S—C(2)	105.4 (1)
X(2)—Cd—X(2')	96.44 (1)	C(2)—S—C(2")	107.3 (1)
X(2)—Cd—X(2")	83.46 (1)		

(3)

Cd—X(1)	2.6403 (5)	S—O	1.438 (1)
Cd—X(1')	2.6611 (5)	S—C(1)	1.754 (3)
Cd—X(2)	2.7467 (2)	S—C(2)	1.751 (1)
Cd—X(2')	2.7383 (2)		
X(1)—Cd—X(1')	180.0	X(2')—Cd—X(2")	179.74 (1)
X(1)—Cd—X(2)	85.86 (1)	X(2')—Cd—X(2"')	83.63 (1)
X(1)—Cd—X(2')	94.34 (1)	O—S—C(1)	112.78 (5)
X(1')—Cd—X(2)	94.17 (1)	O—S—C(2)	112.55 (6)
X(1')—Cd—X(2')	85.63 (1)	C(1)—S—C(2)	105.83 (9)
X(2)—Cd—X(2')	96.53 (1)	C(2)—S—C(2")	106.77 (9)
X(2)—Cd—X(2")	83.32 (1)		

(4)

Cd—X(1)	2.6300 (5)	S—O	1.437 (1)
Cd—X(1')	2.6516 (5)	S—C(1)	1.748 (3)
Cd—X(2)	2.7355 (2)	S—C(2)	1.752 (1)
Cd—X(2')	2.7269 (2)		
X(1)—Cd—X(1')	180.0	X(2')—Cd—X(2")	179.73 (1)
X(1)—Cd—X(2)	85.77 (1)	X(2')—Cd—X(2"')	83.54 (1)
X(1)—Cd—X(2')	94.44 (1)	O—S—C(1)	112.7 (1)
X(1')—Cd—X(2)	94.27 (1)	O—S—C(2)	112.84 (6)
X(1')—Cd—X(2')	85.52 (1)	C(1)—S—C(2)	105.54 (9)
X(2)—Cd—X(2')	96.63 (1)	C(2)—S—C(2")	106.6 (1)
X(2)—Cd—X(2")	83.21 (1)		

(5)

Cd—X(1)	2.6172 (2)	S—O	1.440 (1)
Cd—X(1')	2.6375 (2)	S—C(1)	1.752 (2)
Cd—X(2)	2.7164 (4)	S—C(2)	1.750 (1)
Cd—X(2')	2.7065 (4)		
X(1)—Cd—X(1')	180.0	X(2')—Cd—X(2")	179.69 (1)
X(1)—Cd—X(2)	85.52 (1)	X(2')—Cd—X(2"')	83.31 (1)
X(1)—Cd—X(2')	94.72 (1)	O—S—C(1)	112.72 (9)
X(1')—Cd—X(2)	94.44 (1)	O—S—C(2)	112.70 (5)
X(1')—Cd—X(2')	85.32 (1)	C(1)—S—C(2)	105.51 (7)
X(2)—Cd—X(2')	96.87 (1)	C(2)—S—C(2")	107.12 (7)
X(2)—Cd—X(2")	82.94 (1)		

(6)

Cd—X(1)	2.6065 (3)	S—O	1.439 (1)
Cd—X(1')	2.6279 (3)	S—C(1)	1.749 (2)

Cd—X(2)	2.6878 (2)	S—C(2)	1.7468 (8)
Cd—X(2')	2.6780 (2)		
X(1)—Cd—X(1')	180.0	X(2')—Cd—X(2")	179.63 (1)
X(1)—Cd—X(2)	85.30 (1)	X(2')—Cd—X(2"')	82.93 (1)
X(1)—Cd—X(2')	95.00 (1)	O—S—C(1)	112.74 (8)
X(1)—Cd—X(2)	94.61 (1)	O—S—C(2)	112.59 (5)
X(1')—Cd—X(2')	85.08 (1)	C(1)—S—C(2)	105.56 (5)
X(2')—Cd—X(2')	97.25 (1)	C(2)—S—C(2")	107.26 (6)
X(2)—Cd—X(2")	82.56 (2)		

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

Table 3. Occupation rates in the two different sites of the $(CH_3)_3SOCdCl_{3-x}Br_x$ mixed crystals

	Site (Cl,Br)$_{(1)}$		Site (Cl,Br)$_{(2)}$		
	Cl(1)	Br(1)	Cl(2)	Br(2)	
	$(1 - a)$	a	$(1 - b)$	b	$x = 2(a + b)$
(1)	0.484	0.516	0.200	0.800	2.116
(2)	0.635	0.365	0.289	0.711	1.787
(3)	0.809	0.191	0.504	0.496	1.183
(4)	0.864	0.136	0.586	0.413	0.962
(5)	0.935	0.065	0.729	0.271	0.607
(6)	0.966	0.034	0.874	0.126	0.286

Heavy-atom coordinates from the assumed isostructural tri-bromocadmate (Puget, Jannin, de Brauer & Perret, 1991) were used in an initial model to solve the structure of (1). Then, the structure of each other compound was solved using the heavy-atom coordinates found for the compound with the next highest Br concentration. The occupancies of the shared (Cl, Br) sites were refined using the *PROMETHEUS* programs (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983).

For all compounds, data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *MolEN*; program(s) used to refine structure: *PROMETHEUS*; molecular graphics: *ORTEP*II (Johnson, 1976).

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