Le passage de la sous-structure à la surstructure s'effectue par la mise en ordre des sites de cuivre comme le montre la Fig. 3.

Nous tenons à remercier M. A. Mazurier qui nous a apporté son aimable collaboration lors des mesures expérimentales et Mme R. Ollitrault-Fichet pour la préparation des cristaux.

Références

BECKER, P. J. & COPPENS, P. (1975). Acta Cryst. A31, 417–425.
BUSING, W. R. (1971). Acta Cryst. A27, 683–684.

CARCALY, C., CHÉZEAU, N., RIVET, J. & FLAHAUT, J. (1973). Bull. Soc. Chim. Fr. pp. 1191–1195.
COLLIN, G. & LARUELLE, P. (1971). Bull. Soc. Fr. Minéral. Cristallogr. 94, 175–176.
DONNAY, G., DONNAY, J. D. H. & KULLERUD, G. (1958). Am. Mineral. 43, 228–242.
FRUEH, A. J. (1955). Z. Kristallogr. 106, 299–307.
JAULMES, S., RIVET, J. & LARUELLE, P. (1977). Acta Cryst. B33, 540–542.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univ. de York, Angleterre, et de Louvain, Belgique.
MEULENAER, J. DE & TOMPA, H. (1965). Acta Cryst. 19, 1014–1018.

Structures of Trimethyloxosulfonium Salts. V. The catena-Tri-μ-chloro-cadmate and the catena-Tri-μ-bromo-cadmate

BY RENÉ PUGET, MICHEL JANNIN, CHRISTINE DE BRAUER AND RENÉ PERRET

Laboratoire de Physique du Solide, associé au CNRS (URA 785), Université de Bourgogne, BP 138, 21004 Dijon CEDEX, France

Abstract. $[(CH_3)_3SO][CdCl_3]$, $M_r = 311\cdot93$, orthorhombic, $Pnma$, $a = 6\cdot688$ (1), $b = 10\cdot147$ (2), $c = 13\cdot446$ (2) Å, $V = 912\cdot5$ (5) Å^3, $Z = 4$, $D_x = 2\cdot270$, $D_m = 2\cdot25$ (8) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 3·424 mm^{-1}, $F(000) = 600$, $T = 293$ K, final $R = 0\cdot015$, $wR = 0\cdot017$ for 1256 independent observed reflections. $[(CH_3)_3SO][CdBr_3]$, $M_r = 445\cdot3$, orthorhombic, $Pnma$, $a = 6\cdot946$ (1), $b = 10\cdot543$ (2), $c = 13\cdot782$ (2) Å, $V = 1009\cdot3$ (6) Å^3, $Z = 4$, $D_x = 2\cdot928$, $D_m = 2\cdot90$ (8) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 14·053 mm^{-1}, $F(000) = 816$, $T = 293$ K, final $R = 0\cdot014$, $wR = 0\cdot016$ for 808 independent observed reflections. These two compounds are isotypic. Each Cd atom is coordinated by six halogen atoms, giving a quasi-regular octahedron; the octahedra, linked by sharing two opposite faces, form linear anionic chains parallel to the a axis. The pyramidal thiocations $(CH_3)_3SO^+$, located between the anionic chains, have only one symmetry plane. The H atoms were located.

Introduction. In previous papers, we have described the structures of trimethyloxosulfonium iodide, bromide, chloride, nitrate and chromate (Jannin, Puget, de Brauer & Perret, 1991a,b,c; de Brauer, Jannin, Puget & Perret, 1991). In this paper, we describe the structures of the isostructural catena-trichlorocadmate and catena-tribromocadmate salts.

Experimental. The crystals were obtained by slow evaporation of aqueous solutions in which $(CH_3)_3SOX$ and CdX_2 ($X = Cl$ or Br) were dissolved in stoichiometric proportions.

The bromide: prismatic colorless crystals, density measured by pycnometry in xylene, $D_m = 2\cdot90$ (8) Mg m^{-3}, crystal size 0·18 × 0·19 × 0·20 mm. Enraf–Nonius CAD-4 diffractometer. Unit-cell dimensions from least-squares refinement of 25 reflections with $5 < \theta < 13°$. Systematic absences $0kl$ ($k + l = 2n$) and $hk0$ ($h = 2n$). Space group $Pn2_1a$ (No. 33) or $Pnma$ (No. 62). $\omega/2\theta$ scan, scan width 1·2°. $1 < \theta < 30°$. $-9 < h < 9$, $-12 < k < 12$, $0 < l < 16$. Four orientation reference reflections (020, $\bar{1}22$, $1\bar{2}2$, $2\bar{3}2$) every 200 scans showed no significant variation. Four intensity reference reflections ($0\bar{5}1$, $\bar{1}22$, $\bar{1}31$, $0\bar{4}6$) recorded every 2 h showed fading of 11·5% during 232 h; decay corrections. 8788 measured reflections, 4480 with $I > 3\sigma(I)$. Lorentz and polarization corrections. Absorption corrections from ψ scans: relative transmission factor between 0·830 and 0·999. 816 reflections after averaging: $R_{int} = 0\cdot027$. Patterson function used for structure determination in $Pnma$. H atoms from difference Fourier synthesis. Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. Extinction coefficient refined: $g = 1\cdot9730 \times 10^{-7}$ (Stout & Jensen, 1968). Unit weights. 69 vari-

ables. Final refinement with 808 reflections (three rejected as unobserved, five as bad) gave $R = 0.014$, $wR = 0.016$ and $S = 1.226$. Maximum and minimum peak heights in final difference Fourier synthesis 0.389 and -0.294 e Å^{-3}. $\Delta/\sigma_{max} = 0.01$.

The chloride: prismatic colorless crystals, density measured by pycnometry in xylene, $D_m = 2.25$ Mg m^{-3}, crystal size $0.21 \times 0.21 \times 0.24$ mm. Enraf–Nonius CAD-4 diffractometer. Unit-cell constants from least-squares refinement of 25 reflections with $5 < \theta < 15°$. Same systematic absences. Space group $Pn2_1a$ (No. 33) or $Pnma$ (No. 62). $\omega/2\theta$ scan, scan width $1.2°$. $1 < \theta < 28$. $-9 < h < 9$, $-14 < k < 14$, $-5 < l < 18$. Four orientation reference reflections ($\overline{4}4\overline{5}$, $\overline{2}31$, $3\overline{6}5$, $1\overline{2}3$) every 200 scans showed no significant variations; the same intensity reference reflections recorded every 2 h showed fading of -1% during 126 h; decay corrections. 7554 measured reflections, 6160 with $I > 3\sigma(I)$. Lorentz and polarization corrections. Absorption corrections from ψ scans: relative transmission factor between 0.919 and 0.999. 1256 reflections after averaging: $R_{int} = 0.017$. Heavy-atom coordinates from assumed isostructural bromide used as initial model in $Pnma$. H atoms located by difference Fourier synthesis. Anisotropic least-squares full-matrix refinement (on F) for non-H atoms; isotropic for H atoms. Extinction coefficient refined $g = 1.3224 \times 10^{-6}$ (Stout & Jensen, 1968). Unit weights. 69 variables. Final refinement with 1256 reflections gave $R = 0.015$, $wR = 0.017$ and $S = 0.765$. Maximum and minimum peak heights in final Fourier synthesis 0.266 and -0.728 e Å^{-3}. $\Delta/\sigma_{max} = 0.00$.

Scattering factors for neutral atoms and f', f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: VAX 730.

Discussion. The final atomic coordinates are reported in Table 1 for the bromide and Table 3 for the chloride. The main interatomic distances and bond angles are listed in Table 2 for the bromide and Table 4 for the chloride.*

In these two compounds, each Cd atom is coordinated by six halogen atoms giving a quasi-regular octahedron. The octahedra are linked by two opposite shared faces to form complex anionic chains $(CdX_3)_\infty$ parallel to the a axis. This anionic columnar arrangement is found frequently in ABX_3 compounds, for instance in $(CH_3)_4NCdCl_3$ (TMCC)

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and interatomic contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53818 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates for* (CH$_3$)$_3$SOCdBr$_3$ *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq} (Å^2)
Cd	0.40615 (6)	0.250	0.25021 (3)	2.305 (6)
Br(1)	0.15459 (8)	0.250	0.09638 (3)	2.48 (0)
Br(2)	0.65589 (5)	0.42659 (3)	0.16503 (3)	2.436 (6)
S	0.2233 (2)	0.250	0.64321 (9)	2.24 (2)
O	0.1846 (6)	0.250	0.7459 (3)	3.36 (8)
C(1)	0.0124 (9)	0.250	0.5730 (4)	2.8 (1)
C(2)	0.3525 (6)	0.3835 (4)	0.6067 (3)	3.21 (8)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* (CH$_3$)$_3$SOCdBr$_3$

Pyramidal trimethyloxosulfonium

S—O	1.440 (4)	O—S—C(1)	112.7 (3)
S—C(1)	1.755 (6)	O—S—C(2)	112.4 (2)
S—C(2)	1.744 (5)	C(1)—S—C(2)	105.7 (2)
		C(2)—S—C(2)	107.8 (3)

CdBr$_6$ octahedron

Cd—Br(1)		2.729 (1)	Br(1)—Cd—Br(1)	179.7 (1)
Cd—Br(1)		2.748 (1)	Br(1)—Cd—Br(2)	94.0 (1)
Cd—Br(2)	(×4)	2.802 (1)	Br(1)—Cd—Br(2)	96.8 (2)
			Br(2)—Cd—Br(2)	180.0 (1)
			Br(2)—Cd—Br(2)	83.3 (1)

Table 3. *Final atomic coordinates for* (CH$_3$)$_3$SOCdCl$_3$ *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq} (Å^2)
Cd	0.39436 (5)	0.250	0.25083 (2)	1.835 (3)
Cl(1)	0.1436 (1)	0.250	0.10127 (5)	2.12 (1)
Cl(2)	0.64429 (7)	0.42200 (5)	0.16873 (4)	2.182 (7)
S	0.2183 (1)	0.250	0.63993 (5)	1.84 (1)
O	0.1805 (3)	0.250	0.7453 (2)	2.86 (4)
C(1)	−0.0020 (5)	0.250	0.5689 (2)	2.64 (5)
C(2)	0.3522 (4)	0.3884 (2)	0.6007 (2)	2.70 (4)

Table 4. *Main interatomic distances* (Å) *and bond angles* (°) *for* (CH$_3$)$_3$SOCdCl$_3$

Pyramidal trimethyloxosulfonium

S—O	1.439 (2)	O—S—C(1)	112.9 (1)
S—C(1)	1.756 (3)	O—S—C(2)	112.8 (1)
S—C(2)	1.747 (2)	C(1)—S—C(2)	105.5 (1)
		C(2)—S—C(2)	107.0 (2)

CdCl$_6$ octahedron

Cd—Cl(1)		2.595 (1)	Cl(1)—Cd—Cl(1)	181.0 (2)
Cd—Cl(1)		2.618 (1)	Cl(1)—Cd—Cl(2)	94.8 (1)
Cd—Cl(2)	(×2)	2.648 (1)	Cl(1)—Cd—Cl(2)	95.3 (1)
Cd—Cl(2)	(×2)	2.657 (1)	Cl(2)—Cd—Cl(2)	179.6 (1)
			Cl(2)—Cd—Cl(2)	82.1 (1)

described by Morosin (1972). In each octahedron, two opposite X-atom angles X—Cd—X are very near to 180 (1)°; the same angles with adjacent X atoms are between 82 and 86° or 98 and 94°, respectively, showing a weak distortion of the octahedra, as found
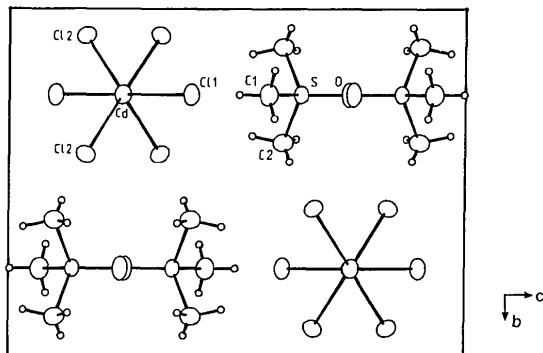
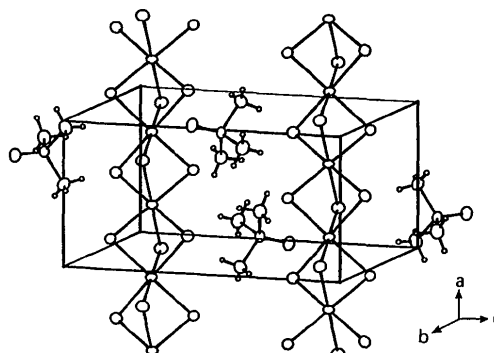Fig. 1. Projection along the *a* axis of the atomic arrangement of (CH₃)₃SOCdCl₃.

Fig. 2. Atom packing of the unit cell of (CH₃)₃SOCdCl₃.

in TMCC. The Cd—X bond lengths range between 2·731 and 2·803 Å (average 2·767 Å) for the bromide and 2·595 and 2·657 Å (average 2·637 Å) for the chloride (*N.B.* for hexagonal TMCC Cd—Cl = 2·644 Å). These bond lengths are always lower than the ionic radii sums (Shannon & Prewitt, 1969). Cd and $X(1)$ atoms are located in the mirror plane (y = 0·25 or 0·75), as S, O and C(1) atoms of (CH₃)₃SO⁺. The pyramidal thiocation has only this symmetry element, as found in almost all the other salts studied but it closely approximates to 3*m* symmetry. In the two title compounds, this cation has exactly the same geometrical features.

The projection along the *a* axis of the atomic arrangement of (CH₃)₃SOCdCl₃ is shown in Fig. 1 and Fig. 2 shows the atom packing of the unit cell.

This work was carried out at the Centre de Diffractométrie de l'Université de Bourgogne.

References

BRAUER, C. DE, JANNIN, M., PUGET, R. & PERRET, R. (1991). *Acta Cryst.* C47. In the press.

Enraf–Nonius (1977). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

JANNIN, M., PUGET, R., DE BRAUER, C. & PERRET, R. (1991*a*). *Acta Cryst.* C47, 1687–1689.

JANNIN, M., PUGET, R., DE BRAUER, C. & PERRET, R. (1991*b*). *Acta Cryst.* C47. In the press.

JANNIN, M., PUGET, R., DE BRAUER, C. & PERRET, R. (1991*c*). *Acta Cryst.* C47. In the press.

MOROSIN, B. (1972). *Acta Cryst.* B28, 2303–2305.

SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B25, 925–936.

STOUT, G. H. & JENSEN, L. M. (1968). In *X-ray Structure Determination.* New York: Macmillan.

Structures of 1,1,1,1,1,2,2,2,2,2-Decaammine-3,3-diaqua-1,3;2,3-di-(μ-pyrazinato-N,N')-dicobalt(III)silver(I) Nitrate Tetrahydrate and 1,1,1,1,1-Pentaammine-2-(diethylenetriamine-N,N',N")-1,2-(μ-pyrazinato-N,N')-cobalt(III)copper(II) Perchlorate

BY XU BING, CHEN DONG AND TANG WENXIA

Coordination Chemistry Institute, Nanjing University, Nanjing, People's Republic of China

AND YU KAIBEI AND ZHOU ZHONGYUANG

Research Center of Analysis and Measurement, Acadamia Sinica, Chengdu, People's Republic of China

Abstract. Complex (I): [(NH₃)₅Co(μ-C₄H₄N₂)Ag(H₂O)₂(μ-C₄H₄N₂)Co(NH₃)₅](NO₃)₇.4H₂O, M_r = 1098·3, monoclinic, *C2/c*, *a* = 9·431 (2), *b* = 12·374 (2), *c* = 33·716 (6) Å, β = 92·42 (1)°, V = 3922·6 Å³, Z = 4, D_x = 1·860 g cm⁻³, μ(Mo *K*α, λ = 0·71070 Å) = 18·40 cm⁻¹, $F(000)$ = 2248, T = 298 K, R = 0·038 and wR = 0·038 for 2272 significant reflections. The cation has point group symmetry