

Crystallographic Studies of Tetramethylammonium Tetrahalogenomercurates. The Crystal Structure of Tetramethylammonium Tetrabromomercurate(II)

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The crystals of $[(\text{CH}_3)_4\text{N}]_2[\text{HgBr}_4]$ are orthorhombic, space group $Pnma$ (D_{2h}^{16}), with $a = 12.801$, $b = 9.309$, $c = 16.148$ Å. The structure has been refined to $R = 0.053$ for 925 Cu data. The Hg atom is located in the mirror plane and has slightly distorted tetrahedral coordination. The Hg-Br mean bond length is 2.587 Å, and the bond angles range from 108.2 to 113.7°. $[(\text{CH}_3)_4\text{N}]_2[\text{HgCl}_4]$ and $[(\text{CH}_3)_4\text{N}]_2[\text{HgI}_4]$ are isomorphous with the title compound.

Introduction

The coordination of Hg in the halogenomercurates of general formulae $\text{M}[\text{HgX}_3]$ and $\text{M}_2[\text{HgX}_4]$ seems to depend upon the complexity of the cation and the nature of the halogen. Where M is a simple cation, e.g. an alkali metal or ammonium ion and $\text{X} = \text{Cl}$, the characteristic coordination of mercury is digonal and the structure consists of Cl-Hg-Cl quasi-molecules as in the structure of HgCl_2 itself. The digonal coordination is usually extended to the octahedral effective coordination, Cl atoms from the neighbouring molecules complete the $[2+4]$ coordination sphere. Two Hg-Cl bond lengths are short and always close to the sum of the covalent radii, the additional four Cl atoms are significantly further away but at a distance which is less than the sum of the van der Waals radii. In the crystal structure, HgCl_6 octahedra form columns (Grdenić, 1965; Sagisawa, Kitahama, Kiriya & Kiriya, 1974).

Where the cation is more complex, e.g. tetramethylammonium, tetramethylsulphonium (Fenn, 1966) or even the bis-(3,5-diphenyl-1,2-dithiolium) ion (Mason, Robertson & Rusholme, 1974) and $\text{X} = \text{Cl}$, Br or I, isolated HgX_3 or HgX_4 anions occur in the crystal structure and the effective coordination around Hg is based upon the trigonal or tetrahedral characteristic coordination (Grdenić, 1965). In addition to these examples, in the crystal structure of thallium(I) hexabromomercurate(II) isolated HgBr_6 octahedra, again containing HgBr_2 quasi-molecules, occur (Brodersen, Thiele & Görz, 1973); and in the structure of 3,5-bis(*N,N*-diethylimmonium)-1,2,4-trithiolane-tetraiodo- μ -iodomercurate(II), discrete $[\text{Hg}_2\text{I}_6]^{2-}$ anions in the form of edge-condensed bitetrahedrons have been found (Beurskens, Bosman & Cras, 1972).

The structure of $[(\text{CH}_3)_4\text{N}]_2[\text{Hg}^{\text{II}}\text{Br}_4]$, as reported in this paper, contains fairly regular $[\text{HgBr}_4]^{2-}$ tetrahedral anions. $[(\text{CH}_3)_4\text{N}]_2[\text{Hg}^{\text{II}}\text{Br}_4]$ as well as the $[\text{Hg}^{\text{II}}\text{Cl}_4]$ and $[\text{Hg}^{\text{II}}\text{I}_4]$ compounds are isomorphous with the analogous $[\text{Co}^{\text{II}}\text{Cl}_4]$, $[\text{Ni}^{\text{II}}\text{Cl}_4]$, $[\text{Zn}^{\text{II}}\text{Cl}_4]$ (Morosin &

Lingafelter, 1959; Wiesner, Srivastava, Kennard, Divaira & Lingafelter, 1967), $[\text{Cu}^{\text{II}}\text{Cl}_4]$ (Morosin & Lingafelter, 1961; Clay, Murray-Rust & Murray-Rust, 1975), $[\text{Fe}^{\text{II}}\text{Cl}_4]$ (Lauher & Ibers, 1975) and very probably also with $[\text{Mn}^{\text{II}}\text{Cl}_4]$ (Morosin, 1967) compounds.

Experimental

$[(\text{CH}_3)_4\text{N}]_2[\text{Hg}^{\text{II}}\text{Cl}_4]$ was prepared from a mixture of tetramethylammonium chloride and mercury(II) chloride in ethanol. $[(\text{CH}_3)_4\text{N}]_2[\text{Hg}^{\text{II}}\text{I}_4]$ was similarly prepared from acetone. The crystals of $[(\text{CH}_3)_4\text{N}]_2[\text{Hg}^{\text{II}}\text{Br}_4]$ were obtained by cooling a solution of mixed tetramethylammonium bromide and mercury(II) bromide in concentrated hydrobromic acid (Topsøe, 1884; Deacon & West, 1961). Weissenberg and oscillation photographs showed that $[(\text{CH}_3)_4\text{N}]_2[\text{Hg}^{\text{II}}\text{Br}_4]$ was orthorhombic. From the systematic absences ($0kl$ when $k+l$ odd and $hk0$ when h odd) possible space groups were $Pnma$ or $Pna2_1$. The density determined pycnometrically was 2.27 g cm^{-3} and the value calculated for $Z = 4$ is 2.307 g cm^{-3} . The centrosymmetric space group was established by the structure solution.

Cell parameters for $[(\text{CH}_3)_4\text{N}]_2[\text{HgBr}_4]$ were obtained from oscillation and Weissenberg photographs and then refined by least-squares methods from the 2θ values for 18 reflexions measured on a Philips PW 1100 automatic diffractometer. The unit-cell parameters for $[(\text{CH}_3)_4\text{N}]_2[\text{HgCl}_4]$ and $[(\text{CH}_3)_4\text{N}]_2[\text{HgI}_4]$ were calculated from powder diffraction data obtained with the General Electric XRD-5 powder diffractometer. These cell data are summarized in Table 1 along with the cell parameters of the related Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) salts for comparison.

A prismatic crystal $0.12 \times 0.10 \times 0.07$ mm was chosen for data collection. The intensities were measured by the ω scan technique at room temperature on a Philips PW 1100 diffractometer with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418$). Three standard reflexions were measured every two hours

Table 1. Cell parameters (Å) for some tetramethylammonium (TMA) tetrahalogenometallates

	TMAMnCl ₄ ^(a)	TMAFeCl ₄ ^(a)	TMACoCl ₄ ^(a)	TMANiCl ₄ ^(a)	TMACuCl ₄ ^(a)	TMAZnCl ₄ ^(a)	TMAHgCl ₄ ^(a)	TMAHgBr ₄ ^(a)	TMAHgI ₄ ^(a)
<i>a</i>	12.33	12.312	12.276	12.2639	12.30	12.276	12.42 (2)	12.801 (3)	13.39 (3)
<i>b</i>	9.06	8.998	9.001	8.9819	9.03	8.998	9.06 (2)	9.309 (2)	9.69 (1)
<i>c</i>	15.64	15.580	15.539	15.4861	15.59	15.541	15.68 (3)	16.148 (7)	16.80 (3)

(a) Morosin (1967). (b) Lauher & Ibers (1975). (c) Wiesner, Srivastava, Kennard, Di Vaira & Lingafelter (1967). (d) Clay, Murray-Rust & Murray-Rust (1975). (e) This paper.

and there was no indication of crystal decomposition during the data collection period. The integration speed was $0.04^\circ \text{ s}^{-1}$ and the integration interval $2.0^\circ \theta$. The 931 reflexions with intensity greater than $3\sigma(I)$ were measured from $\theta=3$ to 70° . The data were corrected for Lorentz and polarization effects, but not for absorption [$\mu(\text{Cu } K\alpha) = 262 \text{ cm}^{-1}$].

Structure determination and refinement

Hg and Br atom positions were determined from a three-dimensional Patterson synthesis. Six cycles of isotropic least-squares refinement gave an R of 0.126. The N and C atoms of the $[(\text{CH}_3)_4\text{N}]^+$ ions were located by the subsequent series of Fourier syntheses and least-squares refinement. Refinement of positional and isotropic thermal parameters reduced R to 0.105. At this stage the C atoms of the cations displayed high B values. The six cycles of anisotropic temperature refinement executed on all atoms reduced the R value finally to 0.053. The six low-angle reflexions were excluded from the final cycles of refinement, the large difference in the observed and calculated structure-factor amplitudes being attributed to an extinction effect. The shifts in atomic parameters at the final cycle were smaller than 0.2σ . Unit weight was assumed for all observations. The atomic scattering factors were taken as those of the neutral atoms given in *International Tables for X-ray Crystallography* (1962). Anomalous dispersion effects were included for all atoms and the values for $\Delta f'$ and $\Delta f''$ were those of Cromer & Liberman (1970). The final positional and thermal parameters are given in Table 2.*

The calculations were carried out on the UNIVAC 1110 computer of Zagreb University Computing Centre with the system of programs developed by Domenicano, Spagna & Vaciago (1969).

Results and discussion

The structure of $[(\text{CH}_3)_4\text{N}]_2[\text{HgBr}_4]$ is shown in Fig. 1. The two cations and the anion have crystallographically imposed mirror plane symmetry. From the interatomic distances and angles given in Table 3 it is evident that $[(\text{CH}_3)_4\text{N}]^+$ and $[\text{HgBr}_4]^{2-}$ tetrahedra deviate slightly from the ideal tetrahedral geometry. The closest intermolecular approach of 3.45 \AA is $\text{Br}(3) \cdots \text{H}_3\text{C}(21)$, the rest are normal intermolecular interactions.

The structural data are influenced by large thermal parameters, particularly those of the atoms in the $[(\text{CH}_3)_4\text{N}]^+$ ions. The large temperature factors of the atoms in the cations most likely result from the

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31381 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Positional and anisotropic thermal parameters ($\times 10^4$) with their standard deviations in parentheses

Temperature factor has the form $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	0.2495 (1)	$\frac{1}{4}$	0.4069 (1)	36 (1)	50 (1)	21 (0)	—	1 (2)	—
Br(1)	0.0476 (2)	$\frac{1}{4}$	0.4000 (3)	23 (2)	166 (6)	50 (2)	—	7 (3)	—
Br(2)	0.3169 (3)	0.0213 (3)	0.3329 (3)	100 (3)	116 (5)	98 (2)	78 (6)	40 (4)	-103 (6)
Br(3)	0.3226 (4)	$\frac{1}{4}$	0.5561 (3)	91 (4)	372 (12)	24 (2)	—	-32 (4)	—
N(1)	0.139 (3)	$\frac{1}{4}$	0.102 (2)	190 (43)	46 (35)	50 (17)	—	46 (50)	—
N(2)	0.483 (2)	$\frac{1}{4}$	0.836 (1)	49 (16)	2 (23)	22 (9)	—	-9 (21)	—
C(11)	0.257 (3)	$\frac{1}{4}$	0.093 (2)	12 (15)	343 (84)	44 (14)	—	-8 (40)	—
C(12)	0.097 (7)	$\frac{1}{4}$	0.017 (4)	253 (102)	1507 (502)	37 (29)	—	-82 (93)	—
C(13)	0.102 (6)	0.375 (10)	0.144 (5)	334 (92)	1482 (404)	335 (90)	398 (293)	99 (147)	-1206 (333)
C(21)	0.443 (5)	$\frac{1}{4}$	0.747 (3)	186 (61)	284 (99)	49 (21)	—	-104 (64)	—
C(22)	0.395 (4)	$\frac{1}{4}$	0.889 (3)	52 (34)	1688 (470)	54 (30)	—	87 (53)	—
C(23)	0.536 (5)	0.381 (5)	0.854 (3)	574 (108)	300 (83)	104 (28)	-871 (176)	-181 (94)	185 (81)

Table 3. Bond lengths (\AA) and angles ($^\circ$) with standard deviations in parentheses

Hg—Br(1)	2.587 (3)	Br(1)—Hg—Br(2)	108.2 (1)
Hg—Br(2)	2.589 (3)	Br(1)—Hg—Br(3)	113.7 (1)
Hg—Br(3)	2.585 (4)	Br(2)—Hg—Br(2) ^(a)	110.6 (2)
		Br(2)—Hg—Br(3)	108.0 (1)
N(1)—C(11)	1.51 (6)	C(11)—N(1)—C(12)	106 (4)
N(1)—C(12)	1.47 (7)	C(11)—N(1)—C(13)	112 (4)
N(1)—C(13)	1.43 (9)	C(12)—N(1)—C(13)	109 (4)
		C(13)—N(1)—C(13)'	109 (8)
N(2)—C(21)	1.53 (6)	C(21)—N(2)—C(22)	108 (3)
N(2)—C(22)	1.41 (6)	C(21)—N(2)—C(23)	110 (2)
N(2)—C(23)	1.43 (5)	C(22)—N(2)—C(23)	105 (3)
		C(23)—N(2)—C(23)'	118 (4)

(a) Primed atoms are related to the corresponding atoms by the mirror plane.

spherical disorder about the N atoms, as is observed in the Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) isomorphs. The mean C—N bond length in $[(\text{CH}_3)_4\text{N}]^+$ ions of 1.46 \AA is comparable with the mean values for this bond length (1.39, 1.49, 1.47, 1.49 and 1.43 \AA , respectively) in the five isomorphs. The same applies to the C—N—C bond angles which vary in this structure from 105 to 118 $^\circ$.

The $[\text{HgBr}_4]^{2-}$ anion is a slightly flattened tetrahedron with bond angles from 108.2 to 113.7 $^\circ$. In the Fe(II) compound these angles range from 107.96 to 113.63 $^\circ$, in Co(II) from 108.3 to 112.8 $^\circ$, in Ni(II) from 107.8 to 114.4 $^\circ$, in Cu(II) from 101.1 to 132.1 $^\circ$ and in Zn(II) from 109.1 to 112.1 $^\circ$. Angular deviations in all these isomorphs flatten the ideal tetrahedral shape. Apart from the anticipated exception of the Cu(II) salt, these distortions do not differ significantly and are independent of the electronic structure of the metal atom. This is once again confirmation that in all but the Cu compound, the distortion is the result of crystal packing conditions and not of the Jahn-Teller effect. The three Hg—Br bond lengths of 2.587, 2.589 and 2.585 \AA are equal to within experimental error and are slightly longer than those found in the structure of $[(\text{CH}_3)_4\text{N}][\text{Hg}^{11}\text{Br}_3]$ (mean value 2.52 \AA ; White, 1963) and in thallium hexabromomercurate(II) (2.54 \AA ; Brodersen, Thiele & Görz, 1973).

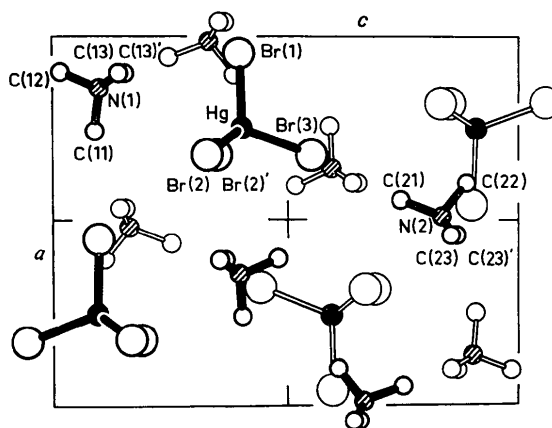


Fig. 1. The structure of tetramethylammonium tetrabromomercurate(II) viewed at an angle of about 6 $^\circ$ to the *b* axis so as to avoid overlapping the atoms. The coordinates of the labelled atoms are given in Table 2. Primed atoms are related to the corresponding unprimed atoms by reflexion in the mirror plane at $y = \frac{1}{4}$.

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References

- BEURSKENS, P. T., BOSMAN, W. P. J. H. & CRAS, J. A. (1972). *J. Cryst. Mol. Struct.* **2**, 183–188.
- BRODERSEN, K., THIELE, G. & GÖRZ, G. (1973). *Z. anorg. allgem. Chem.* **401**, 217–226.
- CLAY, R., MURRAY-RUST, J. & MURRAY-RUST, P. (1975). *Acta Cryst.* **B31**, 289–290.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- DEACON, G. B. & WEST, B. O. (1961). *J. Chem. Soc.* pp. 3929–3935.
- DOMENICANO, A., SPAGNA, R., VACIAGO, A. (1969). *Rend. Accad. Lincei*, **VIII**, **47**, 331–336.
- FENN, R. H. (1966). *Acta Cryst.* **20**, 24–27.
- GRDENIĆ, D. (1965). *Quart. Rev.* **19**, 303–328.

- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
- LAUHER, J. W. & IBERS, J. A. (1975). *Inorg. Chem.* **14**, 348–351.
- MASON, R., ROBERTSON, G. B. & RUSHOLME, G. A. (1974). *Acta Cryst.* **B30**, 894–904.
- MOROSIN, B. (1967). Private communication, quoted by WIESNER *et al.*
- MOROSIN, B. & LINGAFELTER, E. C. (1959). *Acta Cryst.* **12**, 611–612.
- MOROSIN, B. & LINGAFELTER, E. C. (1961). *J. Phys. Chem.* **65**, 50–51.
- SAGISAWA, K., KITAHAMA, K., KIRIYAMA, H. & KIRIYAMA, R. (1974). *Acta Cryst.* **B30**, 1603–1604.
- TOPSØE, H. (1884). *Z. Kristallogr.* **8**, 246–296.
- WHITE, J. C. (1963). *Acta Cryst.* **16**, 397–403.
- WIESNER, J. R., SRIVASTAVA, R. C., KENNARD, C. H. L., DIVAIRA, M. & LINGAFELTER, E. C. (1967). *Acta Cryst.* **23**, 565–574.

Acta Cryst. (1976). **B32**, 1417

Structure Cristalline de l'Oxyde Mixte de Molybdène–Tellure: MoTe_2O_7

PAR Y. ARNAUD

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Molybdenum–tellurium oxide, MoTe_2O_7 , is monoclinic with $a = 4.286$ (2), $b = 8.618$ (3), $c = 15.945$ (5) Å, $\beta = 95.68$ (1)°. $Z = 4$. Space group $P2_1/c$. The structure has been solved from 2349 independent reflexions. The final R value is 0.037. Double chains of distorted molybdenum octahedra along the a direction are linked by tetrahedral oxotellurium, Te^{IV} , units in a three-dimensional arrangement.

Introduction

On a reconnu aux oxydes mixtes de tellure et de molybdène d'intéressantes propriétés catalytiques en oxydation du propène, en acroléine (Shell, 1963–66) et en ammoxydation associés à l'oxyde de fer (SNPA, 1969, 1970). Leur étude radiocristallographique (Robin, Arnaud, Guidot & Germain, 1975; Bart, Petrini & Giordano, 1975) a permis de caractériser un nouveau composé défini MoTe_2O_7 qui paraît être la phase active de ces catalyseurs d'oxydation très sélectifs (95% en acroléine). La préparation de MoTe_2O_7 a déjà été décrite (Robin *et al.*, 1975) de même que les conditions d'obtention des cristaux. Le composé MoTe_2O_7 cristallisé (α MoTe_2O_7) est monoclinique avec une maille: $a = 4,286$ (2), $b = 8,618$ (3), $c = 15,945$ (5) Å, $\beta = 95,68$ (1)°, renfermant quatre unités formulaires. Le groupe d'espace est $P2_1/c$.

L'étude structurale de ce composé montrera quel est le mode d'association du tellure et du molybdène par rapport aux oxydes de départ.

Données expérimentales

Le cristal utilisé de forme presque sphérique mesurait 0,18 mm de diamètre. Les conditions expérimentales

pour la mesure des données de diffraction étaient: diffractomètre Philips PW 1100; longueur d'onde: molybdène avec monochromateur, 50 kV, 20 mA; θ maximum 35°, θ minimum 4°; mode de mesure: balayage ω ; largeur de balayage: 1,40°; vitesse de balayage 0,05° s⁻¹; nombre de réflexions mesurées: 2349; réflexions de référence 060 et 060. Aucune correction d'absorption n'a été effectuée.

Ces mesures ont été réalisées au Laboratoire des rayons X du CNRS à Grenoble.

Détermination de la structure

Une étude préliminaire par la méthode de Weissenberg conduisait au groupe d'espace $P2_1/c$. La détermination de l'arrangement atomique par des méthodes classiques confirme cette symétrie. Une synthèse de Patterson tridimensionnelle révèle les atomes de molybdène et de tellure. Une synthèse de Fourier effectuée à partir des coordonnées de ces atomes conduit à la localisation des atomes d'oxygène. Quelques cycles d'affinement amènent la facteur R (2349 réflexions) à la valeur 0,049. Après rejet de réflexions de faible intensité, pour 2012 réflexions il prend la valeur 0,037. Les calculs cristallographiques ont été réalisés à l'aide des programmes de Prewitt (1966).