

# Structure of Tetramethylammonium Tribromocadmate at Room Temperature

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**Abstract.**  $[\text{N}(\text{CH}_3)_4][\text{CdBr}_3]$ ,  $M_r = 426.2$ , hexagonal,  $P6_3/m$ ,  $a = 9.404$  (3),  $c = 6.990$  (1) Å,  $V = 535.4$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.644$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 130.64$  cm<sup>-1</sup>,  $F(000) = 392$ ,  $T = 295$  K, final  $R = 0.035$  for 401 independent reflections. The structure consists of infinite linear chains made up of face-shared  $\text{CdBr}_6$  octahedra and disordered  $\text{N}(\text{CH}_3)_4$  groups. C atom thermal parameters are very large.

**Experimental.** Single crystals were grown by evaporation from aqueous solution. A spherical specimen with radius 0.11 mm, data collected on a Rigaku AFC-5 diffractometer, graphite-monochromated  $\text{Mo } K\alpha$  radiation; scan mode  $\theta-2\theta$ , scan speed  $10^\circ \text{ min}^{-1}$  in  $\theta$ , scan width  $1.5^\circ + 0.5^\circ \tan \theta$ ; cell dimensions from 24 reflections,  $15.4 < \theta < 17.7^\circ$ ; Lorentz and polarization corrections; absorption corrections, minimum and maximum transmission coefficients 0.144 and 0.196;  $\sin \theta / \lambda < 0.904$  Å<sup>-1</sup> ( $0 \leq h \leq 14$ ,  $0 \leq k \leq 14$ ,  $-12 \leq l \leq 12$ ); three standard reflections (212, 022 and 004) monitored every 150

reflections showed no significant variation in intensity; 2512 reflections measured, 1182 unique reflections [ $R_{\text{int}} = 0.029$  based on  $F$  for 461 unique reflections with  $F > \sigma(F)$ ], of which 402, with  $F > 3\sigma(F)$ , were used in the refinement. The positional parameters of non-H atoms of the isomorphous crystal  $[\text{N}(\text{CH}_3)_4][\text{CdCl}_3]$  (Morosin, 1972) were used as starting parameters; atomic scattering factors for

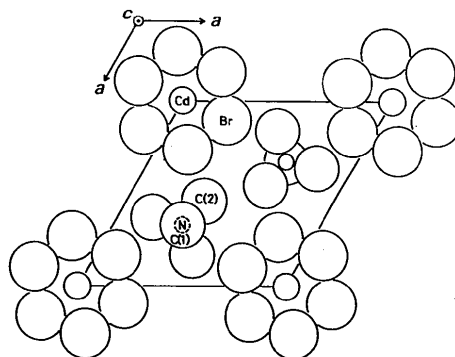


Fig. 1.  $c$ -axis projection of the structure of  $[\text{N}(\text{CH}_3)_4][\text{CdBr}_3]$ . For simplicity, one of the two configurations related by mirror symmetry at  $z = \frac{1}{4}$  or  $\frac{3}{4}$  is shown for each  $\text{N}(\text{CH}_3)_4$  group.

Table 1. Positional parameters and equivalent isotropic temperature factors (Å<sup>2</sup>) with e.s.d.'s in parentheses

$$B_{\text{eq}} = (4/3) \sum_i \sum_j B_{ij} a_i \cdot a_j$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Cd	0.0000	0.0000	0.0000	2.96
Br	0.1072 (1)	0.2651 (1)	0.2500	3.29
N	0.6667	0.3333	0.2500	3.15
C(1)	0.6667	0.3333	0.4550 (59)	20.8
C(2)	0.5390 (26)	0.3688 (25)	0.1906 (68)	17.4

Table 2. Bond lengths (Å) and angles (°) at 295 K with e.s.d.'s in parentheses

Cd—Br	2.788 (1)	N—C(1)	1.43 (4)	N—C(2)	1.46 (3)
Br—Cd—Br <sup>i</sup>	84.87 (3)	Br—Cd—Br <sup>ii</sup>	95.13 (3)		
C(1)—N—C(2)	107 (2)	C(2)—N—C(2)	112 (2)		

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

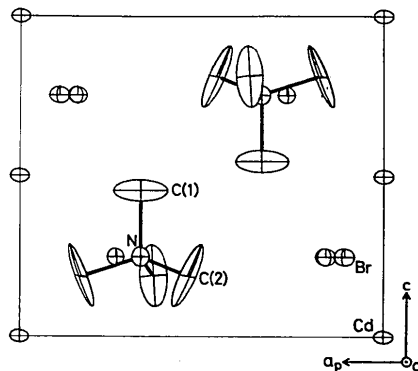


Fig. 2.  $a$ -axis projection of the structure of  $[\text{N}(\text{CH}_3)_4][\text{CdBr}_3]$ . For simplicity, one of the two configurations related by mirror symmetry at  $z = \frac{1}{4}$  or  $\frac{3}{4}$  is shown for each  $\text{N}(\text{CH}_3)_4$  group.

$\text{Cd}^{2+}$ ,  $\text{Br}^-$ , N and C, and dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV); full-matrix least-squares refinement with anisotropic thermal parameters (a total of 23 parameters varied). At the final stage of refinement, reflection 100 was removed because of the possibility of extinction effects.  $R = 0.035$ ,  $wR = 0.029$ ,  $S = 1.07$ ,  $w = [\sigma^2(F_o)]^{-1}$ ,  $(\Delta/\sigma)_{\text{max}} = 0.006$ ;  $(\Delta\rho)_{\text{max}} = 0.8$ ,  $(\Delta\rho)_{\text{min}} = -0.7 \text{ e } \text{\AA}^{-3}$ . H atoms could not be found. Computer programs: *UNICS3* (Sakurai & Kobayashi, 1979). Final atomic parameters are given in Table 1.\* Bond lengths and angles are listed in Table 2. The crystal structure is shown in Figs. 1 and 2.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53048 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Related literature.** The intensities and spacings of 28 reflections for this compound, obtained using powder crystallography, have been reported by Daoud (1976). In the structure analysis of  $[\text{N}(\text{CH}_3)_4][\text{CdCl}_3]$  (Morosin, 1972), disorder of the  $\text{N}(\text{CH}_3)_4$  groups was concluded from a difference Fourier synthesis which excluded C atoms; each  $\text{N}(\text{CH}_3)_4$  group takes on two configurations with equal probability, related to each other by mirror symmetry. Such disorder of  $\text{N}(\text{CH}_3)_4$  groups was also confirmed in the present study. The  $[\text{N}(\text{CH}_3)_4][\text{MnCl}_3]$  crystal structure (Morosin & Graeber, 1967) is also isomorphous.

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## Structure of Bis( $\mu$ -methylenediphenylthiophosphinato)-gold(I)mercury(II) Bis(1,1-dicyanoethylene-2,2-dithiolato-*S,S'*)aurate

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**Abstract.**  $[\text{AuHg}(\text{C}_{13}\text{H}_{12}\text{PS})_2][\text{Au}(\text{C}_4\text{N}_2\text{S}_2)_2]$ ,  $M_r = 1337.26$ , triclinic,  $P\bar{1}$ ,  $a = 12.816$  (6),  $b = 12.837$  (7),  $c = 14.507$  (7)  $\text{\AA}$ ,  $\alpha = 92.93$  (4),  $\beta = 108.96$  (4),  $\gamma = 116.23$  (4) $^\circ$ ,  $V = 1971$  (2)  $\text{\AA}^3$ ,  $Z = 2$ ,  $D_x = 2.25 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 120.0 \text{ cm}^{-1}$ ,  $F(000) = 1240$ ,  $T = 298 \text{ K}$ , final  $R = 0.042$ ,  $wR = 0.0574$  for 3919 unique observed reflections. The molecule consists of an  $\text{Hg}^{\text{II}}\text{—Au}^{\text{I}}$  bimetallic cation with two methylenediphenylthiophosphinate ligands and an  $\text{Au}^{\text{III}}$  anion with two 1,1-dicyanoethylene-2,2-dithiolato ligands. The  $\text{Hg}^{\text{II}}$  and  $\text{Au}^{\text{I}}$  centers are linearly coordinated by two methylene groups and two S atoms, respectively. The  $\text{Au}^{\text{III}}$  is coordinated by four S atoms in a square-planar fashion.

**Experimental.** The bimetallic compound,  $[\text{Au}^{\text{I}}\text{Hg}^{\text{II}}(\text{C}_{13}\text{H}_{12}\text{PS})_2][\text{Au}^{\text{III}}(\text{C}_4\text{N}_2\text{S}_2)_2]$ , was obtained quantitatively by the reaction of  $[\text{Au}^{\text{I}}\text{Hg}^{\text{II}}(\text{C}_{13}\text{H}_{12}\text{PS})_2]\text{PF}_6$  (Wang & Fackler, 1988) with  $[\text{N}(n\text{-C}_4\text{H}_9)_4]$

$[\text{Au}(\text{C}_4\text{N}_2\text{S}_2)_2]$  (Khan, Wang & Fackler, 1989) in a 1:1 ratio in  $\text{CH}_2\text{Cl}_2$  solution. Crystals suitable for X-ray analysis were obtained by recrystallization from a dichloromethane–methanol solution. An orange rectangular crystal of dimensions  $0.20 \times 0.20 \times 0.40 \text{ mm}$  was selected and mounted in a random orientation on a glass fiber. Axial dimensions and triclinic symmetry were verified by axial rotation photographs. Unit-cell parameters were obtained from 25 reflections with  $8.30 < 2\theta < 23.0^\circ$ . Data collection was carried out at room temperature using Wyckoff ( $\omega$  scan) technique in bisecting geometry (Nicolet *R3m/E* diffractometer, graphite-monochromated  $\text{Mo } K\alpha$  radiation). 5420 reflections ( $-11 \leq h \leq 0$ ,  $|k| \leq 11$ ,  $|l| \leq 13$ ) measured with  $4 < 2\theta < 45^\circ$ . Scan rate variable,  $2.80\text{--}29.0^\circ \text{ min}^{-1}$ ; scan range  $-1.0^\circ$  in  $\omega$  from  $K\alpha_1$  to  $+1.0^\circ$  from  $K\alpha_2$ . Background intensities were estimated from a 96-step peak profile. Three standard reflections ( $355$ ,  $412$ ,  $322$ ) were measured every 97 reflections. The data were corrected for absorption, standard variation ( $< 3\%$ ), Lorentz and polarization effects. Absorp-

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