

Tricaesium Tetrachloromercurate(II) Chloride

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Abstract. Cs_3HgCl_5 , orthorhombic, $Pnma$; $a=8.916(1)$, $b=10.772(1)$, $c=13.505(1)$ Å; $Z=4$, $D_c=3.98$, D_m unknown, but >3.25 g cm $^{-3}$. The compound was prepared in the course of a study of simple pentacoordination. The structure consists of Cs^+ , Cl^- and distorted tetrahedral $[\text{HgCl}_4]^{2-}$ ions.

Introduction. Initial cell dimensions were determined from precession photographs (Mo $K\alpha$ radiation). Systematic absences ($0kl$ for $k+l$ odd, $hk0$ for h odd) indicated space group $Pnma$ (No. 62) or $Pn2_1a$ (alternative orientation of $Pna2_1$, No. 33). The centrosymmetric $Pnma$ was subsequently confirmed by successful refinement.

A colourless prismatic needle with six faces, $\pm(100)$, $\pm(011)$, $\pm(01\bar{1})$, was mounted in a sealed Lindemann glass tube on a Hilger & Watts Y290 diffractometer, with

a misaligned about 10° from the φ axis. Unit-cell parameters and the orientation matrix were refined by least squares from 12 reflexions ($38 < 2\theta < 52^\circ$, Mo $K\alpha$ radiation, Zr filter, $\lambda=0.71069$ Å) (Busing & Levy, 1967). Intensities were collected for all unique reflexions with $2\theta \leq 55^\circ$ ($\theta-2\theta$ scan mode, 3s count at each of 80 steps of 0.01° in θ , background counts of 60s at each end of the scan). Three standard reflexions monitored at regular intervals showed $<1.5\%$ total intensity decay; linear decay functions were calculated and applied. The crystal was measured with a travelling microscope, and absorption corrections were applied by a Gaussian integration method ($\mu=214$ cm $^{-1}$, 1600 grid points, minimum and maximum transmission factors are 0.044 and 0.107). The absorption correction was subsequently 'refined', as was a crude isotropic extinction parameter g , such that F_c is reduced by a factor $(1-0.0001 g F_c^2/\sin \theta)$ (Sheldrick, 1975). All 1440 independent reflexions with positive net recorded intensity were used for structure solution and refinement. The structure was solved by Patterson and Fourier techniques, and refined by full-matrix least squares to a minimum value of $\sum w\Delta^2$ [$\Delta=|F_o|-|F_c|$, $w=1/\sigma^2(F_o)$, based on counting statistics]. Scattering factors for Cs^+ , Hg^{2+} and Cl^- were those of Cromer & Waber (1974) and Cromer & Ibers (1974). Three cycles with individual isotropic thermal parameters gave values for R and R_w [$=(\sum w\Delta^2/\sum wF_o^2)^{1/2}$] of 10.4 and 10.1%. With anisotropic thermal parameters for all atoms, the final values were $R=5.56$ and $R_w=4.67\%$. g refined to 0.00092 (3). The number of parameters refined was 51. A final difference map showed no significant features. Atomic parameters are shown in Table 1 and bond lengths and angles in Table 2.*

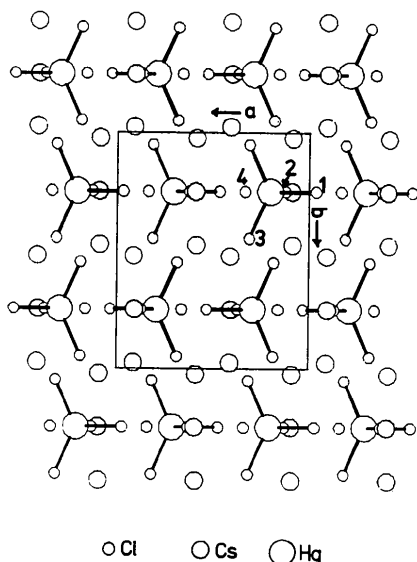


Fig. 1. Projection along z , showing the labelling of the Cl atoms.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31845 (10 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	2060 (1)	2500	3828 (1)	439 (4)	291 (3)	371 (4)	0	-24 (3)	0
Cs(1)	927 (1)	2500	-485 (1)	364 (5)	287 (5)	329 (5)	0	-16 (4)	0
Cs(2)	885 (1)	243 (1)	6661 (1)	509 (4)	393 (4)	421 (4)	-54 (3)	-36 (4)	-40 (3)
Cl(1)	-332 (5)	2500	4850 (3)	354 (21)	481 (23)	389 (20)	0	49 (17)	0
Cl(2)	1258 (7)	2500	2100 (3)	765 (38)	1156 (50)	291 (22)	0	-111 (23)	0
Cl(3)	3142 (4)	4490 (3)	4307 (3)	631 (20)	273 (13)	683 (19)	-21 (14)	-30 (17)	-94 (14)
Cl(4)	3380 (4)	2500	7371 (3)	350 (20)	415 (20)	398 (21)	0	29 (17)	0

Table 2. Bond lengths (Å) and angles (°)

Hg—Cl(1)	2.540 (1)	Cl(1)—Hg—Cl(2)	105.9 (1)
Hg—Cl(2)	2.441 (1)	Cl(1)—Hg—Cl(3)	100.8 (1)
Hg—Cl(3)	2.438 (1)	Cl(2)—Hg—Cl(3)	111.7 (1)
Hg...Cl(4)	4.927 (1)	Cl(3)—Hg—Cl(3')	123.1 (1)

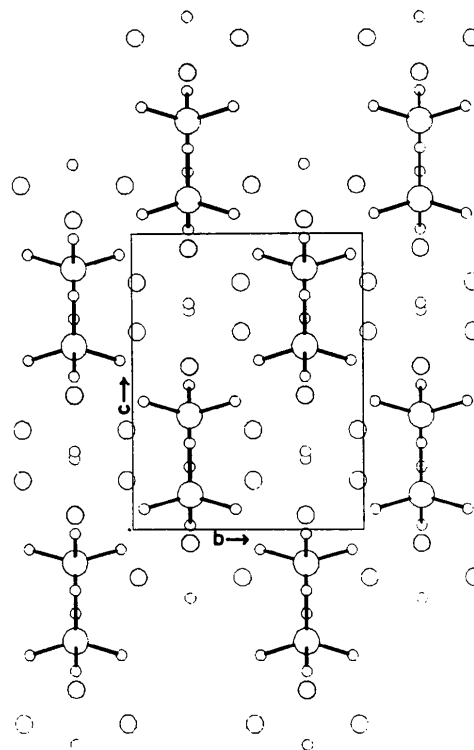
Discussion. The $[\text{HgCl}_5]^{3-}$ ion can be crystallized as the $[\text{Cr}(\text{NH}_3)_6]^{3+}$ salt (Clegg, Greenhalgh & Straughan, 1975), and has a regular trigonal-bipyramidal geometry. All previously reported Cs_3MCl_5 structures form an isomorphous series in space group $I4/mcm$ (Dunsmuir & Lane, 1971) with distorted $[\text{MCl}_4]^{2-}$ ions and separate Cl^- ions [M=Co (Powell & Wells, 1935; Figgis, Gerloch & Mason, 1964), Mn (Goodyear & Kennedy, 1976), Ni (Iberson, Gut & Gruen, 1962)], and Cs_3HgI_5 contains $[\text{HgI}_4]^{2-}$ and separate I^- ions (Federov, Pakhomov & Ivanova-Korfini, 1975). We investigated the structure of Cs_3HgCl_5 in order to determine whether it contained discrete $[\text{HgCl}_5]^{3-}$ or $[\text{HgCl}_4]^{2-}$ anions.

The structure consists of Cs^+ , $[\text{HgCl}_4]^{2-}$ and Cl^- ions. One-third of the Cs^+ ions and all the anions lie on crystallographic mirror planes at $y = \pm \frac{1}{4}$ (Figs. 1 and 2). The $[\text{HgCl}_4]^{2-}$ anion is considerably distorted from a regular tetrahedral geometry, as is usual in tetrahedral Hg^{II} complexes. The Cl^- ion is almost 5 Å from the nearest Hg atom. Closest interionic distances of various types are $\text{Cs}^+ \cdots \text{Cl}-\text{Hg}$ 3.359, $\text{Cs}^+ \cdots \text{Cl}^-$ 3.412, $\text{Hg}-\text{Cl} \cdots \text{Cl}-\text{Hg}$ 3.960, $\text{Hg}-\text{Cl} \cdots \text{Cl}^-$ 3.925, all others > 4 Å, indicating no unusual interactions.

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Fig. 2. Projection along x .