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Metal Complexes of Polycyclic Tertiary Amines. III. Crystal Structure of 1,4-Diazabicyclo[2.2.2]-octan-1,4-diium Tetrachloromercurate(II) Monohydrate, $[(CH_2)_6N_2H_2]HgCl_4 \cdot H_2O$

LANGFORD BOOK* and THOMAS C. W. MAK**

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Halomercurate(II) salts of various $MX{:}HgX_2$ ratios are well known and have been frequently reviewed [1–4]. Many of the reported complexes exist as hydrates, and the available X-ray structural data on halomercurates(II) show that there is no simple relationship between stoichiometry and structure. In the case of the chloro complexes, the mercury(II) atom is often surrounded by chloride ligands to form distorted octahedral $HgCl_6$ units [2], which may be linked into chains as in $K_2HgCl_4 \cdot H_2O$ [5], layers as in α-NH_4HgCl_3 [6], or two-fold ribbons of $[Hg_2Cl_6]_n^{2-}$ as in $NaHgCl_3 \cdot H_2O$ [7]. The occurrence of discrete $HgCl_4^{2-}$ anions in crystalline compounds is uncommon, the first instance being reported two decades ago for a complex of composition $(C_{20}H_{17}N_2O_3)_2HgCl_4 \cdot 2H_2O$ formed by the alkaloid peroline [8, 9]. More examples became known in recent years, and invariably a bulky counter cation is present in each case (Table II). The present work reports the preparation and X-ray analysis of a complex of this type, which contains the fully protonated form of the $(CH_2)_6N_2$ cage system.

Experimental

Preparation

1,4-Diazabicyclo[2.2.2]octane, commonly known as triethylenediamine and commercially as DABCO, $(CH_2)_6N_2$, was dissolved in water and mixed with a suspension of a half molar equivalent of Hg_2Cl_2 in water. The resulting mixture was heated to around 80 °C with stirring for 30 minutes. Hydrochloric acid (6 *M*) was added in an attempt to dissolve the white precipitate. After cooling to room temperature the precipitate was filtered off. Slow evaporation of the clear solution yielded colourless crystals which turned out to be $[(CH_2)_6N_2H_2]HgCl_4 \cdot H_2O$, rather than the desired mercury(I) complex with triethylenediamine.

Crystal Data

$[(CH_2)_6N_2H_2]HgCl_4 \cdot H_2O$, m = 474.58, orthorhombic, a = 8.567(2), b = 11.573(4), c = 13.119(3) Å, U = 1300.8(6) Å^3, D_c = 2.422, D_m = 2.48(1) g cm^{-3} (flotation in s-$C_2H_2Br_4/CCl_4$), Z = 4, space

TABLE I. Fractional Coordinates and Thermal Parameters (Å^2 × 10^3) of All Non-hydrogen Atoms.

Atom	x	y	z	U_{eq}*
Hg	0.25094(14)	0.46853(7)	0.00080(5)	63.1(3)
Cl(1)	0.2396(9)	0.4696(4)	0.1934(3)	64(2)
Cl(2)	0.0066(8)	0.5668(6)	−0.0395(5)	72(2)
Cl(3)	0.4825(7)	0.5965(5)	−0.0392(5)	55(2)
Cl(4)	0.3196(7)	0.2858(6)	−0.0806(4)	71(2)
O	0.663(2)	0.237(2)	0.325(1)	112(8)
N(1)	0.110(2)	0.087(2)	0.220(1)	54(6)
N(2)	0.372(2)	0.133(1)	0.301(1)	60(6)
C(1)	0.222(3)	0.129(2)	0.142(1)	80(11)
C(2)	0.371(2)	0.165(2)	0.190(2)	76(9)
C(3)	0.090(2)	0.181(2)	0.294(1)	51(7)
C(4)	0.245(3)	0.197(2)	0.351(1)	75(8)
C(5)	0.175(3)	−0.016(1)	0.270(1)	51(7)
C(6)	0.342(3)	0.009(2)	0.310(2)	71(9)

*Equivalent isotropic temperature factor calculated as one-third of the trace of the orthogonalized U_{ij} matrix.

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*Present address: Department of Chemistry, Nankai University, Tianjin, China

**Author to whom correspondence should be addressed.

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TABLE II. Comparison of Discrete $HgCl_4^{2-}$ Ions in Known Crystal Structures.[a]

Compound	Hg–Cl (Å)	Cl–Hg–Cl (°)	No. of interactions (range in Å)		Reference
			electrostatic	H-bonding	
$(C_{20}H_{17}N_2O_3)_2HgCl_4 \cdot 2H_2O$[b]	2.48(×2), 2.51(×2)	98–119		2(3.27)	9
$(C_{15}H_{11}S_2)_2HgCl_4$[c]	2.441, 2.462, 2.476, 2.523	100.9–122.1	4(3.15–3.40)		12
	2.448, 2.465, 2.474, 2.535	102.5–115.8	4(3.20–3.30)		
$Cs_3(Cl)HgCl_4$	2.438(×2), 2.441, 2.540	100.8–123.1	8(3.36–3.65)		13
$(C_6H_{18}N_3)(Cl)HgCl_4$[d]	2.434, 2.445, 2.535, 2.577	92.0–121.0	1(3.28)	2(3.23–3.29)	14
$[(CH_3)_2NH_2]_2HgCl_4$	2.424, 2.457, 2.479, 2.530	101.7–114.7		5[e](3.24–3.35)	15
$(CH_3NH_3)_2HgCl_4$	2.464, 2.467, 2.470, 2.478	103.9–114.2		9[f](3.20–3.37)	16
$[(CH_2)_6N_2H_2]HgCl_4 \cdot H_2O$	2.438, 2.444, 2.529, 2.531	100.5–121.1	2(3.36–3.39)	2(3.22–3.23)	This work

[a] $[(CH_3)_4N]_2HgCl_4$, which has not been subjected to X-ray analysis, is isomorphous with the corresponding bromo complex containing discrete monomeric $HgBr_4^{2-}$ units [11]. [b] $C_{20}H_{17}N_2O_3$ represents the protonated form of the alkaloid peroline. [c] $C_{15}H_{11}S_2$ represents the 3,5-diphenyl-1,2-dithiolium cation. The asymmetric unit contains two $HgCl_4^{2-}$ ions, and the Cl···S anion–cation contacts were referred to as charge transfer interactions. [d] $C_6H_{18}N_3$ stands for the N-(2-ammoniumethyl)-piperazinium trication. [e] Including one bifurcated hydrogen bond. [f] It is not possible to predict which of these N···Cl contacts correspond to actual hydrogen bonds.

group $P2_12_12_1$ (D_2^4, No. 19), MoKα radiation (graphite monochromatized), $\bar{\lambda}$ = 0.71069 Å, μ = 126.3 cm^{-1}.

Structure Determination and Refinement

An approximately spherical crystal of radius *ca.* 0.3 mm was used for data collection on a microprocessor-controlled Nicolet R3m four-circle diffractometer. Of the 1225 unique reflections with $|F_o| > 3\sigma(|F_o|)$, 980 were considered observed ($2\theta < 50°$) and used in subsequent calculations. Data were collected in the $\omega/2\theta$ mode with variable scan speeds (2.55 to 9.77° min^{-1}) and monitored with three standard reflections, which showed only 2% fluctuation in intensity. In addition to Lorentz and polarization factors, empirical absorption correction based on ψ-scans of selected reflections was applied. Other structure determination and refinement details are similar to those previously reported [10]. The conventional R index converged to 0.052, and R_w to 0.057 with the weighting scheme $w = [\sigma^2(|F_o|) + 0.0008|F_o|^2]^{-1}$. No hydrogen atoms were located, but those belonging to the six methylene groups were generated with C–H bonds fixed at 0.96 Å in a tetrahedral arrangement. A final difference Fourier map showed no significant features other than diffraction ripples around the Hg atom in the range 2.0 to −1.5 eÅ^{-3}, presumably caused by series termination effects. Atomic coordinates

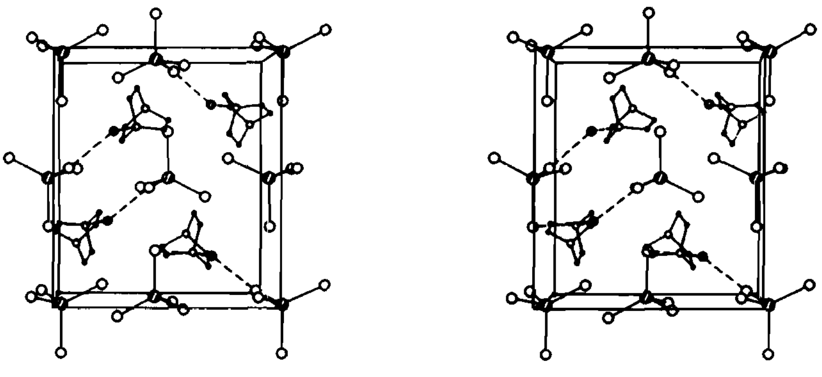

Fig. 1. Stereo drawing of the crystal structure of $[(CH_2)_6N_2H_2]HgCl_4 \cdot H_2O$. The origin of the unit cell lies at the lower left corner, with *a* pointing towards the reader, *b* from left to right, and *c* upwards. The large and small shaded spheres indicate Hg and O respectively, and hydrogen bonds are represented by broken lines.

and equivalent isotropic thermal parameters of the non-hydrogen atoms are listed in Table I. Anisotropic thermal parameters, calculated positions of methylene hydrogen atoms, selected bond distances and angles, as well as observed and calculated structure factors, are available upon request.

Results and Discussion

The structure of the title compound features a discrete HgCl$_4^{2-}$ species which departs considerably from regular tetrahedral geometry. Generally speaking an isolated HgCl$_4^{2-}$ anion has short Hg–Cl bonds in the range 2.43–2.46 Å and longer ones at 2.48–2.54 Å, the latter often associated with strong electrostatic interactions or hydrogen bonding involving the corresponding Cl and neighboring atoms*. In the present complex, Cl(1) and Cl(2) are each hydrogen-bonded to a neighboring water molecule, at O–H···Cl distances of 3.22(2) and 3.23(2) Å respectively, and Cl(3) has two short electrostatic interactions under 3.4 Å (Table II) with the formally positive N(1) and N(2) atoms in two neighboring $[(CH_2)_6N_4H_2]^{2+}$ cations. The closest intermolecular contact involving Cl(4) is with a neighboring N(1) atom at 3.42 Å. The environment around the HgCl$_4^{2-}$ anion thus correlates fairly well with the observed pattern of two short [Hg–Cl(2) = 2.438(6), Hg–Cl(4) = 2.444(6) Å] and two long [Hg–Cl(1) = 2.531(4), Hg–Cl(3) = 2.529(6) Å] bonds. The geometry, distortion, and environment of discrete HgCl$_4^{2-}$ anions in known crystal structures are listed for comparison in Table II.

To our knowledge the structure of the globular 1,4-diazabicyclo]2.2.2[octan-1,4-diium dication (fully protonated triethylenediamine) has been determined for the first time. Although the pesence of the heavy Hg atom precludes the attainment of high precision, the averaged molecular dimensions [C–N = 1.48(1), C–C = 1.52(2) Å; C–N–C = 109(1), C–C–N = 110(1)°] are in excellent agreement with the corresponding values [1.470(7), 1.513(5) Å; 108.4(2), 110.5(4)°] for the room temperature phase II of triethylenediamine [17].

The water molecule plays an important role in the crystal packing (Fig. 1), forming an acceptor hydrogen bond of 2.78(3) Å with the protonated N(2) atom and, as noted previously, donor hydrogen bonds with the Cl(1) and Cl(2) atoms of two different HgCl$_4^{2-}$ anions.

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*An interaction may be considered strong if the interatomic distance is significantly shorter than the sum of appropriate van der Waals radii, *e.g.* 1.90 Å for Cl, 1.55 Å for N, 1.50 Å for O, 1.80 Å for S, and 1.70 Å for Cs.