

SHORT STRUCTURAL PAPERS

Papers intended for publication under this heading must be in the format prescribed in Notes for Authors, *Acta Cryst.* (1973), **B29**, 154.

Acta Cryst. (1974), **B30**, 1603

Ammonium Mercury(II) Trichloride Monohydrate

BY KENSHÔ SAGISAWA, KATSUKI KITAHAMA, HIDEKO KIRIYAMA AND RYÔITI KIRIYAMA

The Institute of Scientific and Industrial Research, Osaka University, Yamadakami, Suita, 565 Japan

(Received 11 January 1974; accepted 11 February 1974)

Abstract. $\text{NH}_4\text{HgCl}_3 \cdot \text{H}_2\text{O}$, orthorhombic, $Pnma$ (or $Pn2_1a$), $a=8.727$ (4), $b=4.344$ (3), $c=17.73$ (1) Å, $V=672.3$ Å³, F.W. 343.0, $Z=4$, $D_x=3.388$, $D_m=3.366$ g cm⁻³, $\lambda(\text{Mo } K\alpha_1)=0.7093$ Å. Mercury and chlorine atoms form double chains running along the b axis, among which water molecules and ammonium ions are located to form weak hydrogen bonds. The structure holds fairly well to a molecular form [HgCl_2], as in HgCl_2 crystals.

Introduction. Crystals were prepared from aqueous solution. The single crystal used measured 0.16 mm along its needle axis (b axis) and had a cross section of 0.035×0.055 mm. It was sealed in a Lindemann-glass capillary to protect it from atmospheric moisture. In total, 872 independent reflexions were collected on a Rigaku automatic four-circle diffractometer with Mo $K\alpha$ radiation using the $2\theta-\omega$ scan technique. Corrections were made for Lorentz and polarization effects, but not for absorption ($\mu_r=0.76$). The systematic absences are $k+l \neq 2n$ for $0kl$ and $h \neq 2n$ for $hk0$; the space group is therefore $Pnma$ or $Pn2_1a$: the former was chosen for the structure determination.

The position of the mercury atom was uniquely determined from a three-dimensional Patterson synthesis, and the other atoms except for hydrogen were located by three-dimensional Fourier syntheses starting with the mercury atom phases and the observed structure amplitudes. It was difficult to distinguish between oxygen and nitrogen atoms from the heights of peaks in the electron-density map, so their assignment was made on the basis of chemical considerations.

The positional parameters thus obtained were refined by the block-diagonal least-squares method, omitting 267 reflexions with $F_o^2 < 3\sigma(F_o^2)_{\text{count}}$ and 101, 020, and 024 which suffered from heavy extinction effects. Thermal factors were treated anisotropically for mercury and chlorine atoms, and isotropically for the others. The residual for 602 reflexions used in this refinement was 0.081 and that for all reflexions was 0.13. The three-dimensional ($F_o - F_c$) synthesis showed no ripple larger than $8.0 \text{ e } \text{Å}^{-3}$. The atomic scattering factors for Cl^- , O, N, and Hg^{2+} with anomalous dispersion corrections were taken from *International*

Tables for X-ray Crystallography (1962). All calculations were performed on the NEAC 2200/700 in the Computer Center, Osaka University, using UNICS programs *RSSFR-5*, *HBL5-V* and *RSDA-4*.†

The atomic coordinates and the thermal parameters with their standard deviations are listed in Table 1. The large thermal factors of all atoms are consistent with the efflorescent nature of this crystal.

Table 1. Final positional and thermal parameters of $\text{NH}_4\text{HgCl}_3 \cdot \text{H}_2\text{O}$

Positional parameters are listed as fractions of cell edges. Anisotropic temperature factors are expressed as $\exp[-(\frac{1}{4})(B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots)]$, and isotropic temperature factors as $\exp(-B \sin^2 \theta/\lambda^2)$. Estimated standard deviations are indicated in parentheses with respect to the last decimal place given.

	x	y	z	B		
Hg	0.57543 (20)	0.25	0.40332 (08)			
Cl(1)	0.4159 (13)	0.25	0.29513 (49)			
Cl(2)	0.7513 (12)	0.75	0.36403 (55)			
Cl(3)	0.6605 (13)	0.25	0.53000 (52)			
O	0.0493 (47)	0.25	0.4258 (22)			6.4 (9)
N	0.1173 (49)	0.75	0.3152 (24)			5.0 (9)
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	3.42 (06)	3.71 (07)	1.94 (05)	0	-0.96 (06)	0
Cl(1)	3.22 (41)	4.10 (46)	2.32 (32)	0	-0.72 (35)	0
Cl(2)	3.15 (44)	3.66 (47)	3.28 (40)	0	+0.99 (36)	0
Cl(3)	4.10 (51)	4.02 (50)	2.26 (35)	0	-0.68 (35)	0

Discussion. This work was undertaken in order to provide the structural basis for our nuclear-magnetic-resonance studies. The structure projected along the b axis is shown in Fig. 1. The bond lengths and angles are listed in Table 2 with those for the sodium salt, $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$ (Malčić, 1959), for comparison. Mercury and chlorine atoms form double chains along the b axis, among which ammonium ions and water molecules are placed to bind them with weak hydrogen

† A table of calculated and observed structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30374 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

bonds. In these chains, six chlorine atoms form a distorted octahedron around each mercury atom, but two of them are much closer to the centre atom than the remaining four, as shown in Table 2. In other words, it is clear that a molecular form of $[\text{HgCl}_2]$ is held fairly well in this structure. Such a quasi-molecule of $[\text{HgCl}_2]$ is often found in mercury(II) chloride complexes, for example NH_4HgCl_3 (Harmsen, 1938), $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ (MacGillavry, de Wilde & Bijvoet, 1938) and $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$, as well as HgCl_2 itself (Brökken & Scholten, 1934; Grdenić, 1950).

Table 2. *Interatomic distances and angles with standard deviations in parentheses*

Ammonium salt		Sodium salt	
Hg—Cl(1)	2.370 (10) Å	Hg—Cl(1)	2.35 Å
Hg—Cl(2)	2.749 (07)	Hg—Cl(2)	2.81
Hg—Cl(3)	2.366 (10)	Hg—Cl(3)	2.40
Hg—Cl(3')	3.218 (08)	Hg—Cl(3')	3.27
N—Cl(1)	3.41 (3)	O(1)—Cl(1)	3.30
N—Cl(1 ⁱⁱ)	3.41 (3)	O(1)—Cl(1 ⁱⁱ)	3.64
N—Cl(2 ⁱⁱ)	3.39 (4)	O(1)—Cl(2 ⁱⁱ)	3.32
N—Cl(2 ⁱⁱⁱ)	3.31 (4)	O(1)—Cl(2 ⁱⁱⁱ)	3.67
N—Cl(3')	3.36 (4)	O(1)—Cl(3')	3.64
N—O	2.99 (4)	O(1)—O(2)	3.36
O—Cl(2 ⁱⁱⁱ)	3.56 (3)	O(2)—Cl(2 ⁱⁱⁱ)	3.66
O—Cl(3')	3.43 (3)	O(2)—Cl(3')	3.51
O—O ^{iv}	3.52 (4)	O(2)—O(2 ^{iv})	2.99
Cl(1)—Hg—Cl(3)	162.3 (4)°	Na—Cl(1 ⁱⁱ)	2.72
Hg—Cl(2)—Hg ^v	104.4 (4)	Na—Cl(2 ⁱⁱⁱ)	2.99
Hg—Cl(3')—Hg ^v	84.9 (3)	Na—O(1)	2.50
O—N—O ^v	93.3 (14)	Na—O(2)	2.12
O—O ^{iv} —O ^v	76.2 (10)		

Symmetry relations

i	1-x	1-y	1-z
ii	-0.5+x	y	0.5-z
iii	-1+x	y	z
iv	-x	1-y	1-z
v	x	1+y	z

Of Cl(1) and Cl(3) forming the quasi-molecule $[\text{HgCl}_2]$, Cl(3) seems to contribute to the interaction with the adjacent quasi-molecules with its lone-pair electrons. This presumption, based on the crystal structure, has been actually confirmed by our recent study of the chlorine quadrupole resonance. Though the intermolecular interaction suggests disproportionation in the intramolecular bondings, the two Hg—Cl distances in the quasi-molecule were almost the same within the experimental errors.

It is interesting to compare the crystal structure of this complex with that of the sodium salt. There is a close resemblance between the double-chain structures of both salts. The distances Hg—Cl(2) and Hg—Cl(3') in the ammonium salt, however, are slightly shorter than those in the sodium salt, where Cl(3') belongs to the

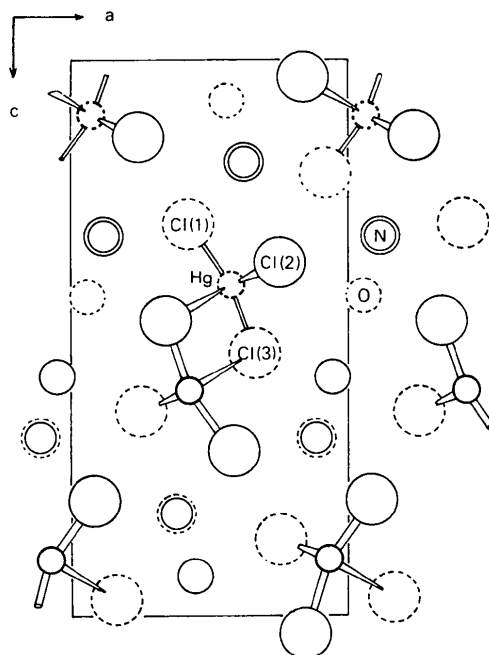


Fig. 1. The crystal structure projected along the b axis. Stippled circles represent atoms at $y = \frac{1}{4}$, and open circles atoms at $y = \frac{3}{4}$.

adjacent quasi-molecule, indicating a stronger intermolecular interaction in the ammonium salt. On the other hand, there is, between the two structures, a considerable difference in the location of cations. The ammonium ion is located at the position corresponding to that of water molecule (1) in the sodium salt, surrounded by seven nearest chlorine atoms and two water molecules, while the sodium ion is octahedrally surrounded by three chlorine atoms and three water molecules.

The hydrogen atoms of the water molecule were located by means of proton magnetic resonance. The results of the proton and chlorine magnetic resonances will be reported elsewhere.

References

- BRÖKKEN, H. & SCHOLTEN, W. (1934). *Z. Kristallogr.* **89**, 448–455.
 GRDENIĆ, D. (1950). *Arhiv za Kemiju*, **22**, 14–23; *Chem. Abs.* **46**, 9926h.
 HARMSEN, E. J. (1938). *Z. Kristallogr.* **100**, 208–211.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–207, 216. Birmingham: Kynoch Press.
 MACGILLAVRY, C. H., DE WILDE, J. H. & BIJVOET, J. M. (1938). *Z. Kristallogr.* **100**, 212–220.
 MALČIĆ, S. S. (1959). *Bull. Inst. Nucl. Sci. 'Boris Kidrič'*, **9**, 115–122.