

A Neutron Diffraction Study of $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$

KARIN AURIVILLIUS and CLAES STÅLHANDSKE

Chemical Center, Divisions of Inorganic Chemistry 1, 2, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden

The crystal structure of $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ has been refined from neutron diffraction single-crystal data (2181 reflections) to $R=0.047$ and $R_w=0.040$. The crystals are orthorhombic, space group $Pbam$ with $a=8.258(2)\text{Å}$, $b=11.663(2)\text{Å}$, $c=8.926(2)\text{Å}$ and $Z=4$.

The structure is built up of HgCl_2 molecules, K^+ and Cl^- ions and water molecules, which *via* weak hydrogen bonds are joined to half the chloride ions. The mercury atom is thus two-coordinated, bonded to two chlorine atoms at the distances $2.383(1)\text{Å}$ in a nearly linear way [$\angle\text{Cl}(3)-\text{Hg}-\text{Cl}(3) 169.96(4)^\circ$]. The distances to next-nearest chlorine atoms indicate that they are mainly ionic in character. In the water molecule the distances $\text{O}-\text{H}$ and $\text{H}-\text{H}$ are $0.948(2)$ and $1.533(3)\text{Å}$, respectively, with an angle $\text{H}-\text{O}-\text{H}$ of $107.9(3)^\circ$. In the hydrogen bond the distance $\text{O}-\text{H}\cdots\text{Cl}(2)$ is $3.249(1)\text{Å}$ with $\text{H}\cdots\text{Cl}(2)$ $2.329(2)\text{Å}$ and the angle $\text{O}-\text{H}\cdots\text{Cl}(2)$ $163.6(2)^\circ$. The water molecules are joined two and two *via* the hydrogen bonds to the chloride ions $\text{Cl}(2)$.

The crystal structure of " $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ " has been the object of several X-ray diffraction studies.¹⁻³ In Ref. 3 the compound was carefully studied by modern X-ray technique and computation methods. The positions of all non-hydrogen atoms were found and it turned out that the best way to write the formula of the compound is $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ as no ions HgCl_4^{2-} exist.

In connection with recent NMR and IR studies performed by other authors it seemed advantageous to perform a neutron diffraction investigation to elucidate the hydrogen bonding system and to compare the determined proton-proton distances with those obtained by other methods.

EXPERIMENTAL

Large single crystals of $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ can be obtained from an aqueous solution of HgCl_2 and KCl in the molar ratio 1:2. The single crystal used in this neutron diffraction study was kindly placed at our disposal by Dr. Svan-son, University of Gothenburg, Sweden. As the crystal was too large for neutron diffraction measurements it was diminished in size by washing with a saturated solution of the compound. Some crystal data are given in Table 1.

Intensity data were collected at room temperature on a Hilger-Ferranti four-circle diffractometer, located at the DR3 reactor at The Danish Atomic Energy Commission Research Establishment, Risø, Denmark. The wavelength of the monochromatized neutron beam was 1.025Å and the flux at the specimen about 0.9×10^6 neutrons $\text{cm}^{-2}\text{s}^{-1}$. The reflections were measured by the ω -scan method using the step-scan technique. In the range $0.06 < \sin \theta/\lambda < 0.79$ a total of 2384 reflections were measured. Half the reflection sphere was measured in the $\sin \theta/\lambda$ interval $0.06-0.20$, a quadrant in the interval $0.20-0.50$ and an octant above 0.50 . One standard reflection was measured after every 15th reflection. Background corrections were made using a method described by Lehmann and Larsen.⁴ In this program the peak is separated from the background so that $\sigma(I)/I$ is minimized, where $\sigma(I)$ is the estimated standard deviation based on counting statistics. Squared structure amplitudes were calculated as $F_o^2 = I \sin^2 2\theta$. An absorption correction

Table 1. Crystal data.

$\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$; F.W. 438.6 g mol^{-1} Orthorhombic, $Pbam$ (No. 55)
$a=8.258(2)\text{Å}$, $b=11.663(2)\text{Å}$, $c=8.926(2)\text{Å}$, $V=859.6\text{Å}^3$, $Z=4$.
$D_x=3.39\text{ g cm}^{-3}$
Neutrons, $\lambda=1.025\text{Å}$; $\mu=1.67\text{ cm}^{-1}$.

Table 2. Crystal dimensions. Boundary planes and their distances from an internal origin.

Plane	<i>d</i> (mm)
$(\bar{1}\bar{2}0)$	2.5
$(\bar{1}10)$	3.4
(130)	3.2
$(\bar{1}30)$	3.6
(100)	2.1
$(\bar{1}00)$	2.1
(001)	5.0
$(00\bar{1})$	5.0

Crystal volume 253 mm.³

was applied using Gaussian numerical integration where the crystal shape was described by 8 boundary planes (Table 2). The linear absorption coefficient was calculated to 1.67 cm⁻¹ assuming the incoherent scattering cross-section for hydrogen to be 40 barns and using the values of μ/ρ for Hg, Cl, K, O, and H tabulated in the International Tables for X-Ray Crystallography.⁵ The resulting transmission factors fall in the range 0.34–0.56. The symmetry-related reflections were not averaged as the mean-path lengths varied considerably. 203 reflections with $F_o^2 < 2\sigma_c(F^2)$, where $\sigma_c(F^2)$ is based on counting statistics, were considered as unobserved and were excluded in the refinements.

STRUCTURE REFINEMENT

The starting parameters were those from the X-ray study.³ A subsequent difference Fourier synthesis revealed the positions of the hydrogen atoms. Finally the parameters were refined using full-matrix least-squares with anisotropic temperature factors for all atoms, a scale factor and an extinction parameter.⁶ The function to be minimized was $\sum w_i(|F_o| - |F_c|)^2$. Each reflection was assigned a weight w_i , according to

$$w_i^{-1} = \sigma^2(|F_o|) = \sigma_c^2(|F_o|^2) / 4|F_o|^2 + a|F_o|^2$$

where $\sigma_c^2(|F_o|^2)$ is based on counting statistics. In the final refinement the constant a was 0.004. In the positional parameters the last shifts were less than 1% of their standard deviations. The agreement factors were

$$R = \sum(|F_o| - |F_c|) / \sum |F_o| = 0.047 \text{ and}$$

$$R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2} = 0.040.$$

The standard deviation of an observation of unit weight S , defined by

$$S = [\sum w_i(|F_o| - |F_c|)^2 / (m - n)]^{1/2}, \text{ was } 0.92,$$

where m and n are the number of observations and parameters varied. The final isotropic extinction parameter was $1.31(3) \times 10^4$. Calculations with anisotropic extinction correction gave no further improvements.

The coherent scattering factors used were $\bar{b}_{\text{Hg}} = 1.27$, $\bar{b}_{\text{Cl}} = 0.96$, $\bar{b}_{\text{O}} = 0.580$ and $\bar{b}_{\text{H}} = -0.374$ (all $\times 10^{-12}$) cm.⁷ Final positional and thermal parameters are given in Tables 3 and 4. A list of observed and calculated structure factors is available from the authors on request. The calculations were carried out on the UNIVAC 1108 computer in Lund using programs briefly described by Stålhandske.⁸

DISCUSSION

Comparison of the present neutron diffraction results with those obtained from X-ray diffraction (diffractometer data, 843 independent reflections³) show no essential differences in the positional parameters or in the bond lengths of the non-hydrogen atoms. The standard deviations in positional parameters of the

Table 3. Final fractional atomic coordinates with estimated standard deviations in parentheses. In brackets are given values according to an X-ray study by Aurivillius and Stålhandske.³

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Hg	0	0	0.22921(8) [0.22925(8)]
K(1)	0.0823(2) [0.0819(3)]	0.3405(2) [0.3410(2)]	0
K(2)	0.1054(2) [0.1047(3)]	0.3052(1) [0.3047(2)]	$\frac{1}{2}$
Cl(1)	0.20454(8) [0.2042(3)]	0.07605(6) [0.0763(2)]	0
Cl(2)	0.24905(9) [0.2489(4)]	0.06027(5) [0.0601(2)]	$\frac{1}{2}$
Cl(3)	-0.11661(6) [-0.1169(2)]	0.18606(4) [0.1860(2)]	0.25257(6) [0.2520(3)]
O	0	$\frac{1}{2}$	0.2310(2) [0.231(1)]
H	-0.0869(2)	0.4769(2)	0.2934(2)

Table 4. Final anisotropic thermal parameters, β_{ij} , with standard deviations in parentheses. The expression used is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ with $\beta_{13} = \beta_{23} = 0$ for the fourfold positions. The β_{ij} values are multiplied by 10^6 .

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	1171(9)	346(3)	1605(12)	195(4)	0	0
K(1)	902(24)	422(11)	761(24)	-1(13)	0	0
K(2)	837(23)	418(12)	978(26)	-1(14)	0	0
Cl(1)	663(8)	400(4)	853(9)	-13(5)	0	0
Cl(2)	996(10)	357(4)	1010(10)	71(5)	0	0
Cl(3)	880(6)	345(3)	779(6)	81(3)	56(5)	-19(3)
O	939(18)	863(12)	826(18)	-198(12)	0	0
H	1208(23)	855(14)	1455(29)	-94(15)	188(22)	104(17)

Table 5. Selected interatomic distances (Å) and angles ($^\circ$). Estimated standard deviations are given in parentheses. Notations of the atoms, cf. Table 3.

Mercury to chlorine			
Hg-2Cl(3)	2.383(1)	$\angle \text{Cl}(3) - \text{Hg} - \text{Cl}(3)$	169.96(4)
-2Cl(1)	2.797(1)		
-2Cl(2)	3.251(1)		
Potassium to oxygen or chlorine			
K(1)-2O	2.859(2)	K(2)-Cl(2)	3.093(2)
-Cl(1)	3.245(2)	-2Cl(3)	3.187(1)
-Cl(1)	3.263(2)	2Cl(3)	3.189(1)
-Cl(1)	3.268(2)	-Cl(2)	3.209(2)
-2Cl(3)	3.320(1)	-Cl(2)	3.335(2)
-2Cl(3)	3.371(1)	-2O	3.419(2)
Oxygen to chlorine < 3.70 Å			
O-2Cl(2)	3.249(1)	$\angle \text{Cl}(2) - \text{O} - \text{Cl}(2)$	84.68(4)
-2Cl(1)	3.315(1)	$\angle \text{Cl}(1) - \text{O} - \text{Cl}(1)$	103.10(4)
		$\angle \text{Cl}(1) - \text{O} - \text{Cl}(2)$	86.12(2)
Distances and angles involving the hydrogen atoms			
O-2H	0.948(2)	$\angle \text{H} - \text{O} - \text{H}$	107.9(3)
H-H	1.533(3)		
H-Cl(2)	2.329(2)	$\angle \text{Cl}(2) - \text{H} - \text{O}$	163.6(2)
H-Cl(1)	3.195(2)	$\angle \text{Cl}(1) - \text{H} - \text{O}$	88.9(1)

chlorine and oxygen atoms are about one fourth those found in the X-ray work, cf. Table 3. The interatomic distances (Table 5), uncorrected for thermal motion, are now determined with a higher degree of accuracy; *e.s.d.*'s in the actual distances being 0.001-0.002 Å. Moreover, the positions of the hydrogen atoms are determined accurately.

As stated in the previous paper our opinion is that the best way to describe the compound is that the structure is built up of HgCl_2 mole-

cules, K^+ and Cl^- ions and water molecules. The formula should thus be written $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ instead of $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$. Half the chloride ions are joined to the water molecules by hydrogen bonds. A projection of the structure on the *xy*-plane is given in Fig. 1. The distances mercury to two chlorine atoms, forming the nearly linear HgCl_2 molecule [$\angle \text{Cl}(3) - \text{Hg} - \text{Cl}(3)$ 169.96(4) $^\circ$] are 2.383(1) Å. The next nearest chlorine neighbours are then located about 0.4 and 0.9 Å further away at

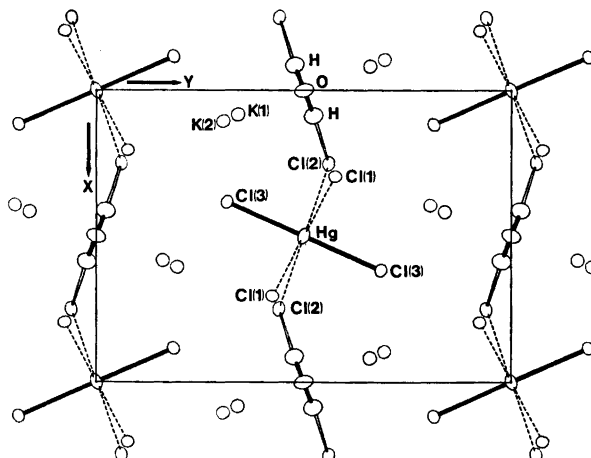


Fig. 1. Projection of the structure of $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ on the xy -plane. The HgCl_2 molecule is indicated by heavy lines, weak mercury-chlorine interactions by dashed lines and hydrogen bonds by open lines.

distances indicating that they are most probably ionic in character. The polyhedron around mercury is a distorted octahedron with two mercury-chlorine distances much shorter than the others. The structure can be described as being built up of "chains" of these octahedra, which run along $[001]$, with the polyhedra sharing edges. The "chains" are joined by weak hydrogen bonds to sheets parallel to the xz -plane (Fig. 1).

The observed $\text{Hg}-\text{Cl}$ distances of $2.383(1) \text{ \AA}$ are close to the values reported for HgCl_2 (Hg-2Cl 2.25 \AA , $\angle \text{Cl}-\text{Hg}-\text{Cl} 180^\circ$), Hg_3OCl_4 ¹⁰ [Hg-Cl $2.31(2) \text{ \AA}$, $\angle \text{Cl}-\text{Hg}-\text{O} 175.7(8)^\circ$] and for the two quasi-molecules HgCl_2 in $(\text{C}_6\text{H}_6\text{N}_6)_3\text{HgCl}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$ ¹¹ [Hg-2Cl $2.35(2)$; $2.37(2) \text{ \AA}$; $\angle \text{Cl}-\text{Hg}-\text{Cl} \sim 165^\circ$]. The $\text{Hg} \cdots \text{Cl}^-$ distances $2.797(1)$ and $3.251(1) \text{ \AA}$ can be compared to the values $2.99(2)$ and $3.08(2) \text{ \AA}$ reported for Hg_3OCl_4 .¹⁰ Both potassium atoms K(1) and K(2) are irregularly surrounded by two oxygen and seven chlorine atoms at distances varying from 2.86 to 3.37 \AA and from 3.09 to 3.42 \AA , respectively. These distances are in agreement with data on the coordination K-O and K-Cl reported in literature.¹²

In the water molecule the uncorrected O-H distance is $0.948(2) \text{ \AA}$ and the angle H-O-H is $107.9(3)^\circ$. The values can be compared to the average values of 0.956 \AA and 107.8° given by Ferraris and Franchini-Angela¹³ for the water

molecule in crystalline hydrates; all structure studies are based on neutron diffraction single-crystal data.

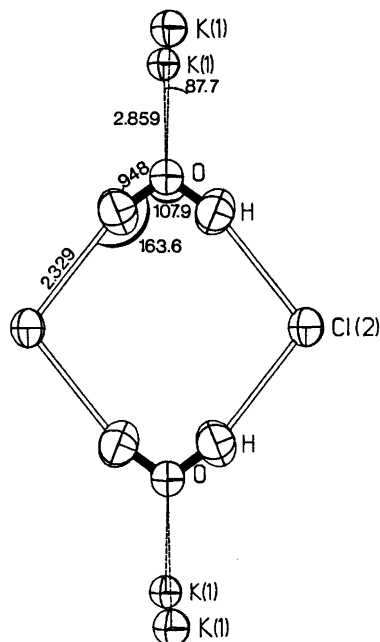


Fig. 2. The tetrahedral environment of the water molecule. The thermal ellipsoids are drawn to enclose 50% probability.

The O–Cl(2) and O–Cl(1) distances, 3.249(1) and 3.315(1) Å are both possible donor acceptor distances for hydrogen bonds, the distances nearly equal to the sum of the van der Waals radii, 3.20 Å.¹⁴ The H–Cl(2) and H–Cl(1) distances are 2.329(2) and 3.195(2) Å, compared to the value of the van der Waals radii sum 2.8 Å.¹⁵ The corresponding angles O–H–Cl(2) and O–H–Cl(1) are 163.6(2) and 88.9(1)°. The angle 163.6° and the distance 2.329 Å indicate that the chloride ions Cl(2) are joined to the water molecules by weak hydrogen bonds. The water molecules are linked two by two *via* the hydrogen bonds to the chloride ions Cl(2) (Fig. 2). As each water molecule has a tetrahedral environment, including the two hydrogen-bonded chloride ions Cl(2) and the two potassium ions K(1), situated along the two lone-pair orbitals of the water molecule, the compound belongs to the classification 2A of hydrates according to Ferraris and Franchini-Angela.¹³ The angle Cl(2)–O–Cl(2) of 84.7(2)° is smaller than the acceptor angles in most other hydrates. A very small angle of this type, 55.1°, was found for the hydrogen bonding system in $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$,¹⁶ however.

$\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ has been the object of NMR- and IR-studies by several authors.^{17–19} The proton-proton distance found within the molecule, 1.534(3) Å, is as expected²⁰ shorter than the values derived by NMR measurements, 1.607(3) Å.^{17,18}

The O–Cl(2) distance 3.25(3) Å, estimated from IR measurements of the partially deuterated compound,¹⁹ is in excellent agreement with the distance 3.249(1) Å obtained in the present study.

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