the temperature was allowed to reach 0° and the reaction mixture was worked up as above.

Diethyl citramalate (II) was obtained from crude I by treatment with ethanol and conc. sulphuric acid (reflux for 3 weeks), followed by preparative GLC. Another method, giving similar results, was also used. The crude reaction product was hydrolysed by treatment with potassium hydroxide (2 M) in ethanol (reflux overnight). Water was added, and the mixture was washed several times with ether. The aqueous layer was acidified, the solvent evaporated, and the residue was treated with ethanol and conc. sulphuric acid (reflux 3 days).

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An X-Ray Single Crystal Study of $K_2HgCl_4.H_2O$

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In connection with studies on the crystal chemistry of inorganic compounds of mercury(II) in different environments, the present X-ray single crystal investigation of $K_2HgCl_4.H_2O$ was performed. The compound has earlier been the object of X-ray diffraction studies.[1,2] The position of all non-hydrogen atoms were derived from intensity data and geometrical considerations in the study in 1938.[1] In the next work on the structure in 1955,[2] the positions of the mercury, potassium, and chlorine atoms were determined from two-dimensional Fourier projections.[2] The positions of the oxygen and hydrogen atoms were not found, however.

Considering the state of the experimental X-ray technique and of the numerical calculation methods at the time for the earlier investigations, the accuracy in the determination of the positions of the light atoms could not be particularly high because of the presence of the heavy mercury atoms. Our aim was to redetermine the positions of the light atoms in order to discuss the coordination of the mercury atoms. The compound $K_2HgCl_4.H_2O$ crystallizes in the orthorhombic space group *Pbam* (No. 55) with four formula units in a unit cell with the dimensions $a = 8.258$ Å, $b = 11.662$ Å, $c = 8.925$ Å, and $V = 860$ Å^3. X-Ray single crystal diffractometer data (PAILRED) were collected using MoK-radiation and a graphite monochromator. A suitable needle-shaped crystal was rotated along [001] and the recorded data resulted in 843 independent reflections with intensities larger than $3\sigma_I$. The intensities were corrected for absorption; the linear absorption coefficient was 203 cm^{-1}. The positions of the mercury atoms were obtained from three-dimensional Patterson functions and the positions of the chlorine, potassium and oxygen atoms from difference Fourier syntheses. A least-squares refinement of the positional parameters of all non-hydrogen atoms including one scale factor was at first performed with isotropic tem-

'able 1. Final positional and thermal parameters with standard deviations for the non-hydrogen atoms in $K_2HgCl_4.H_2O$ 'he point positions of the atoms are: 4 Hg in 4(*e*), 4 K1, 4 Cl1 in 4(*g*), 4 K2, 4 Cl2 in 4(*h*), 8 Cl3 in 8(*i*), 4 O in 4(*f* *bam*). The expression for the anisotropic temperature factors is exp $-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$ where $\beta_{13}=\beta_{23}=0$ for the fourfold point positions.

tom	*x*	*y*	*z*	β_{11}/B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
g	0	0	0.22925(8)	0.01204(10)	0.00302(4)	0.01636(10)	0.00203(4)	0	0
1	0.0819(3)	0.3410(2)	0	0.00833(39)	0.00297(17)	0.00787(29)	0.00048(20)	0	0
2	0.1047(3)	0.3047(2)	½	0.00759(35)	0.00339(17)	0.01036(35)	0.00024(21)	0	0
l1	0.2042(3)	0.0763(2)	0	0.00617(35)	0.00338(18)	0.00803(31)	0.00030(21)	0	0
l2	0.2489(4)	0.0601(2)	½	0.00882(40)	0.00268(18)	0.01018(36)	0.00077(22)	0	0
l3	−0.1169(2)	0.1860(2)	0.2520(3)	0.00827(27)	0.00290(12)	0.00823(22)	0.00072(15)	0.00070(22)	−0.00022(13
	0	½	0.2312(12)	3.6(2)					

perature factors introduced for the atoms. The resulting *R*-factor was 12.5 %. Anisotropic temperature factors were then inserted for the mercury, chlorine, and potassium atoms and a new refinement ended in an *R*-value of 4.5 % (818 reflections). Out of the 843 reflections, 25 at low angles ($\sin\theta/\lambda < 0.30$) had much too low observed intensities, probably depending on extinction effects, and they were omitted in the last refinement.

The final atomic parameters of all non-hydrogen atoms with standard deviations are presented in Table 1 and the *R.M.S.* components of the mercury, chlorine, and potassium atoms in Table 2.

Table 2. The R.M.S.-components, R_i (Å), of thermal vibrations of the atoms.

Atom	*R*1	*R*2	*R*3
Hg	0.257(1)	0.130(1)	0.214(1)
K1	0.178(3)	0.141(4)	0.171(4)
K2	0.204(4)	0.151(4)	0.163(4)
Cl1	0.180(4)	0.143(4)	0.155(4)
Cl2	0.203(4)	0.132(5)	0.178(4)
Cl3	0.185(3)	0.136(3)	0.170(3)

The parameters of all atoms are in good agreement with the values given by Mac Gillavry *et al.*,[1] including also the then geometrically derived value for the oxygen atom. The position of this atom has shifted only 0.17 Å. In connection with a nuclear magnetic resonance experiment on a single crystal of $K_2HgCl_4.H_2O$, performed by Itoh *et al.*,[3] the *z* parameter of the oxygen atom was calculated. The obtained value of $z=0.23$ is in excellent agreement with the value 0.231 found in the present X-ray diffraction study.

Selected interatomic distances and angles in the structure are given in Table 3 and a projection of the structure on the *xy*-plane is presented in Fig. 1.

The nearest neighbours of the divalent mercury atom are only chlorine atoms. The shortest distances Hg−2 Cl are 2.383(2) Å and the corresponding angle Cl−Hg−Cl 170.2(2)°, indicating the presence of nearly linear molecules $HgCl_2$ as

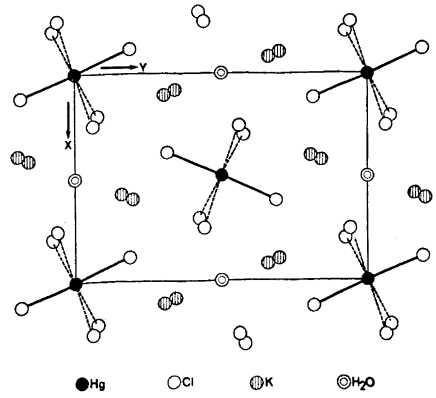

Fig. 1. Projection of the structure of $K_2HgCl_4.H_2O$ on the *xy*-plane, showing the octahedral environments of the mercury atoms. The heavy lines show the shortest mercury to chlorine contacts and the dotted lines the longer distances between mercury and chlorine. One unit cell is marked in the drawing.

Table 3. Selected interatomic distances (Å) and angles (°) in the structure of $K_2HgCl_4.H_2O$.

Hg – 2 Cl3	2.383(2)	∠Cl3 – Hg – Cl3	170.2(2)		
– 2 Cl1	2.797(2)	∠Cl1 – Hg – Cl1	86.0(1)		
– 2 Cl2	3.249(2)	∠Cl2 – Hg – Cl2	83.9(1)		
K1 – 2 O	2.856(8)			K2 – 2 O	3.419(8)
– 3 Cl1	3.249(4), 3.263(4), 3.265(4)			– Cl2	3.091(4)
– 4 Cl3	3.320(3), 3.369(3)			– 4 Cl3	3.187(4), 3.193(3)
				– 2 Cl2	3.215(4), 3.334(4)
O – 2 Cl2	3.247(8)	∠Cl2 – O – Cl2	84.8(3)		
– 2 Cl1	3.319(7)	∠Cl1 – O – Cl1	103.1(3)		

compared to the values reported for $HgCl_2$ [4] (Hg – 2 Cl 2.25 Å, ∠Cl – Hg – Cl 180°). Similar values are also given for the distances Hg – Cl in, *e.g.*, the structures of $CsHgCl_3$ [2] and NH_4HgCl_3 [5] (Hg – 2 Cl 2.29 Å, 2.34 Å, respectively). In the compound Hg_3OCl_4 [6] the mercury atom forms two nearly collinear bonds to one oxygen and one chlorine atom. The distance Hg – Cl is 2.32(2) Å and the angle O – Hg – Cl 175.8(8)°. In the present compound, the next nearest distances mercury to chlorine are considerably longer (Hg – 2 Cl 2.797(2) Å, 3.249(2) Å) indicating that these chlorine atoms probably occur as chloride ions. The distances mercury to chloride ions in NH_4HgCl_3 (2.99 Å) and in Hg_3OCl_4 (2.99(2) Å) are given as a comparison.

From a *geometrical* point of view, the coordination polyhedron around mercury is a distorted octahedron with two distances mercury to chlorine much shorter than the others. Fundamental building elements of the structure are then chains of deformed octahedra, sharing edges; a description that is in accordance with that given in Ref. 1.

The potassium atoms K1 and K2 (notations of the atoms, *cf.* Table 1) are each surrounded in an irregular way by seven chlorine and two oxygen atoms at distances varying from 2.86 to 3.37 Å and from 3.09 to 3.42 Å, respectively. These distances are in agreement with data available in the literature [7] on the coordination K – Cl and K – O.

Each water molecule has four neighbouring chloride ions at distances O – 2 Cl2 3.247(8) Å and O – 2 Cl1 3.319(8) Å with corresponding angles Cl – O – Cl of 84.8(3)° and 103.1(3)°. The distances and angles seem to indicate hydrogen bonds between the water molecules and the chloride ions. No effort has been made to determine the positions of the hydrogen atoms from the X-ray data available.

According to our opinion, the best way to describe $K_2HgCl_4.H_2O$ is that the structure is built up of molecules $HgCl_2$, ions K^+ and Cl^- and water molecules.

Neutron single crystal diffractometer data have been collected for the compound in order to determine the positions of the hydrogen atoms. The results of this investigation will be published elsewhere. Lists of observed and calculated structure factors are available by request to the authors.

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