

orthorhombic crystal with $P2_12_12_1$ symmetry, which is the space group of NaAlCl_4 (Rubbens, Barbier, Mairesse, Wallart & Wignacourt, 1977). All these results show the important position of the K^+ salt in this family. The structural evolution of the different salts will be discussed later.

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A Refinement of Zinc Dichloride–Hydrochloric Acid–Water (2:1:2)*

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Abstract. $\text{HCl} \cdot 2\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, orthorhombic, $Fdd2$, $Z = 8$, $a = 9.243$ (1), $b = 22.885$ (1), $c = 8.886$ (1) Å, $V = 1879.7$ Å³ at 279 K. The structure contains symmetrical, staggered H_3O_2^+ ions [$\text{O} \cdots \text{O}$ 2.377 (9) Å]. Each ion is hydrogen bonded to four equivalent Cl atoms [$\text{O} \cdots \text{Cl}$ 3.151 (5) and 3.156 (4) Å]. Each Zn atom is tetrahedrally surrounded by four Cl atoms. These tetrahedra are joined at their corners to form a three-dimensional network with composition Zn_2Cl_5^- .

Introduction. The crystal structure of $\text{HCl} \cdot 2\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ was determined by Follner (1970). This study indicated the presence of H_3O_2^+ ions in the structure. A neutron diffraction study of the structure has been planned in order to obtain more detailed information on the geometry of this ion and the hydrogen-bond system. As a preliminary to this study, a new refinement of X-ray data has been made.

Crystals of the compound were found to be stable only when in contact with their mother liquor or dry HCl gas, which made it difficult to obtain crystals

ideally mounted for intensity data collection. Soda-glass capillary tubes were filled with a concentrated aqueous solution of ZnCl_2 supersaturated with HCl gas, and carefully sealed. Crystallization was induced by cooling this liquid with dry ice. Crystals were grown using a zone-melting technique. Cell dimensions and intensity data were measured at 279 K using a semi-automatic Stoe–Philips Weissenberg diffractometer (Ni-filtered $\text{Cu } K\alpha$ radiation), modified for low-temperature work. The cell dimensions were determined from 38 θ values measured using two crystals rotated about [010] and [101] respectively. Intensity data out to $\sin \theta/\lambda = 0.63$ Å⁻¹ were collected using a cylindrical crystal (diameter 0.22 mm, length 0.27 mm) rotating about [101]. One end of the crystal was in contact with its mother liquor, the other end with a gas bubble. Six layers of data were collected using an ω -2 θ scan technique. Three test reflections were monitored periodically within each layer. The zero-layer test reflections were remeasured before each new layer. The intensities of the test reflections showed an approximately linear decline with respect to elapsed time. An appropriate correction was subsequently applied to all intensities. The total decrease in intensity was about 11%. The intensities were corrected for Lorentz,

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polarization and absorption effects ($\mu = 191 \text{ cm}^{-1}$ for Cu $K\alpha$ radiation). The resulting structure factors were assigned variances using the expression: $\sigma^2(F^2) = \sigma_c^2(F^2) + [\sigma^2(\mu)/\mu^2 + \sigma^2(t)/t^2](\mu t F^2)^2$, where σ_c^2 is based on counting statistics, and the second term takes account of errors in the applied absorption correction brought about by errors in μ and t , the mean path length through the crystal. The value of the quantity $[\sigma^2(\mu)/\mu^2 + \sigma^2(t)/t^2]$ was estimated as 0.03.

Interlayer scale factors were calculated by a least-squares procedure using equivalent reflections in different layers. A normal probability plot was computed of $\delta m = (F_1^2 - kF_2^2)/[\sigma^2(F_1^2) + k^2\sigma^2(F_2^2)]^{1/2}$, where k is the scale factor determined in this way between the squares of the observed structure factors F_1 and F_2 of two equivalent reflections (Abrahams & Keve, 1971). The plot had a reasonably linear appearance with slope 0.81 and intercept 0.04. This suggests a satisfactory scaling procedure and assignment of variances. 458 reflections were measured within one octant of the Cu $K\alpha$ sphere (88.5% of the accessible reflections), together with 260 Friedel pairs. Twenty reflections had $F^2 < 2\sigma_c(F^2)$ and were later given zero weight in the refinements.

The structural model was refined by full-matrix least-squares techniques starting from the atomic coordinates given by Follner (1970). The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F^2)/4F^2$. It was not possible to locate the H atoms in the difference maps, so they were placed at the centre of the short O...O bond and in the O...Cl bonds at 0.9 Å from the O atoms. The positional and thermal parameters ($B = 6 \text{ Å}^2$) for the H atoms were not refined. 42 parameters were allowed to vary in the final cycles of refinement. These comprised one overall scale factor, one isotropic extinction parameter, and positional and individual anisotropic thermal parameters for the non-hydrogen atoms.

Anomalous-dispersion effects were used to determine the absolute atomic arrangement. A refinement with opposite signs on all z coordinates produced an increase in the R value from 0.031 to 0.039, and in estimated standard deviations of more than 25% for most of the parameters. It also gave a slope in the δR plot of 0.63 compared with 0.80 for the earlier refine-

ment. The configuration obtained first was thus assumed to be correct.

The final refinements converged to $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.031$ (0.032 including zero-weight data), $R_w = |\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2|^{1/2} = 0.040$. The scattering factors for the non-hydrogen atoms were those given by Hanson, Herman, Lea & Skillman (1964), and for H those given by Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections were taken from Cromer & Liberman (1970). The programs used for all computations with IBM 370/155 and IBM 1800 computers have been described by Lundgren (1975). Final positional parameters are given in Table 1.* The value of the extinction parameter g , as defined by Coppens & Hamilton (1970), was $3.8 (2) \times 10^3$.

Discussion. The atomic arrangement is illustrated in Fig. 1. Interatomic distances and angles of interest are given in Fig. 2. All atom positions reported by Follner (1970) agree within the error limits with those obtained in this paper. The structure comprises a three-dimensional network of Zn and Cl ions. Each Zn ion is tetrahedrally surrounded by four Cl ions, three of which also participate in a similar coordination to other Zn ions; the distances from these to the Zn ion are 2.292 (1), 2.293 (1) and 2.302 (1) Å. The fourth Cl ion, which is only 2.219 (2) Å from the Zn ion, has two short O contacts of 3.151 (5) and 3.156 (4) Å. Although the H atoms cannot be localized, it may be inferred that each O atom forms part of an H_5O_2^+ complex which donates protons to four Cl ions. These hydrogen bonds from the H_5O_2^+ ion to its surroundings are longer than those found in earlier studies. In the di- and trihydrates of hydrogen chloride, which also contain H_5O_2^+ ions hydrogen-bonded to Cl ions, the five O...Cl bonds are all between 3.01 and 3.10 Å (Lundgren, 1974). In these cases the Cl ions are bonded to no positive ion other than H_5O_2^+ , and can thus be expected to be stronger hydrogen-bond acceptors.

It can also be deduced that at least one O-H...Cl bond is far from linear, since the angle subtended at the O by the two Cl acceptors is $77.1 (1)^\circ$. This is much less than the expected H-O-H angle. In the fifteen H_5O_2^+ ions reviewed by Lundgren (1974) the X...O...X angles are between 90.8 and 119.1° .

The H_5O_2^+ ion has a staggered conformation: the angle between the two planes defined by the O...O bond and the bisectors of each Cl...O...Cl angle is 67.9° . The O...O distance is $2.377 (9) \text{ Å}$ [$2.388 (9) \text{ Å}$ when no H atoms were included in the structure factor calculation]. This implies a very short hydrogen bond.

Table 1. Fractional coordinates ($\times 10^5$)

	<i>x</i>	<i>y</i>	<i>z</i>
Zn	1409 (7)	8062 (2)	0*
Cl(1)	24375 (12)	8933 (5)	9456 (16)
Cl(2)	-15208 (15)	7527 (5)	17973 (19)
Cl(3)	0	0	-15251 (19)
O	8801 (54)	3786 (19)	47145 (59)

* The z coordinate of the Zn atom has been fixed arbitrarily at the origin.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33258 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

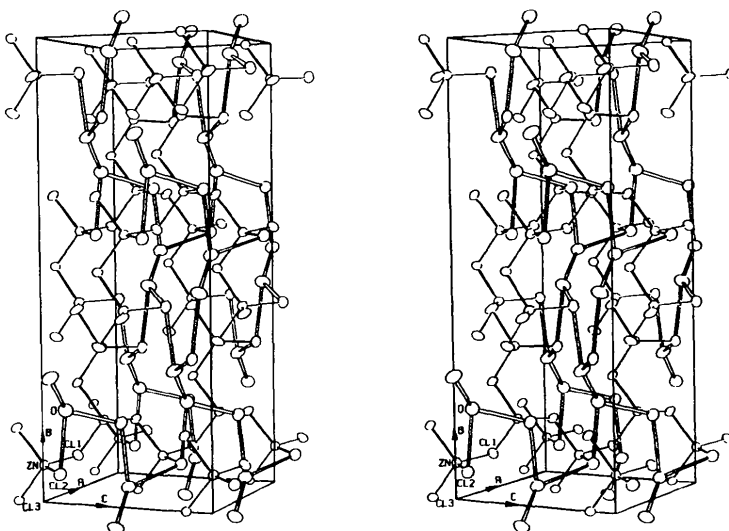


Fig. 1. Stereoscopic drawing of the crystal structure. The labelled atoms represent the chosen asymmetric unit. Zn-Cl contacts are shown as single lines, hydrogen bonds as double lines. The thermal ellipsoids include 50% probability.

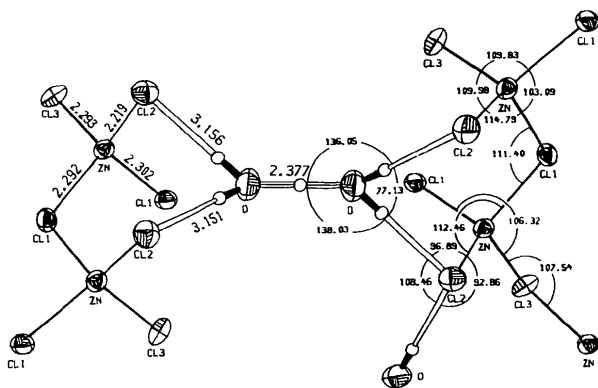


Fig. 2. Bond distances (Å) and angles (°). The average standard deviations are: Zn-Cl 0.001 Å, Cl...O 0.005 Å, O...O 0.009 Å, >Cl-Zn-Cl 0.05°, >Zn-Cl-Zn 0.06°, >Cl...O...O 0.2°, other denoted angles 0.1°. The H atoms are placed on the lines O...Cl and O...O (see text). There is a twofold rotation axis perpendicular to the plane of the paper at the centre of the O...O bond.

None of the fifteen ions studied earlier have O...O distances shorter than 2.41 Å. Their mean value is 2.44 Å. Newton & Ehrenson (1971) have obtained, from *ab initio* calculations on the H_5O_2^+ ion, an O...O distance of 2.36 Å, which is much shorter than observed distances in crystalline hydrates. The authors suggest that the O...O distance is shorter in a free ion than in an H_5O_2^+ ion hydrogen bonded in a crystal. This is in agreement with the situation in $\text{HCl} \cdot 2\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, where the H_5O_2^+ ion is bonded only by means of long

bent hydrogen bonds to atoms expected to be poor acceptors. We see that the O...O distance is unusually short in this case. However, since the O positions are extremely sensitive to the removal of the H atoms from the refinement, it is questionable whether the differences are as significant as the estimated standard deviations suggest.

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