Acta Cryst E STRUCTURE REPORTS

ISSN 1600-5368

# Crystal structures of $ZnCl_2·2.5H_2O$, $ZnCl_2·3H_2O$ and $ZnCl_2·4.5H_2O$

**Erik Hennings, Horst Schmidt* and Wolfgang Voigt**

TU Bergakademie Freiberg, Institute of Inorganic Chemistry, Leipziger Strasse 29, D-09596 Freiberg, Germany. *Correspondence e-mail: horst.schmidt@chemie.tu-freiberg.de

Received 15 October 2014
Accepted 11 November 2014

Edited by M. Weil, Vienna University of Technology, Austria

**Keywords**: crystal structure; low-temperature salt hydrates; chloride hydrates; zinc salts

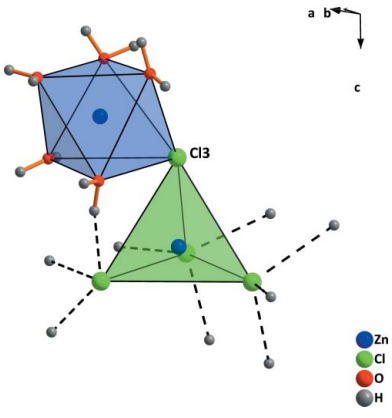
**CCDC references**: 1033587; 1033586; 1033585

**Supporting information**: this article has supporting information at journals.iucr.org/e

The formation of different complexes in aqueous solutions is an important step in understanding the behavior of zinc chloride in water. The structure of concentrated $ZnCl_2$ solutions is governed by coordination competition of $Cl^-$ and $H_2O$ around $Zn^{2+}$. According to the solid–liquid phase diagram, the title compounds were crystallized below room temperature. The structure of $ZnCl_2·2.5H_2O$ contains $Zn^{2+}$ both in a tetrahedral coordination with $Cl^-$ and in an octahedral environment defined by five water molecules and one $Cl^-$ shared with the $[ZnCl_4]^{2-}$ unit. Thus, these two different types of $Zn^{2+}$ cations form isolated units with composition $[Zn_2Cl_4(H_2O)_5]$ (pentaaqua-$\mu$-chlorido-trichloridodizinc). The trihydrate {hexaaquazinc tetrachloridozinc, $[Zn(H_2O)_6][ZnCl_4]$}, consists of three different $Zn^{2+}$ cations, one of which is tetrahedrally coordinated by four $Cl^-$ anions. The two other $Zn^{2+}$ cations are each located on an inversion centre and are octahedrally surrounded by water molecules. The $[ZnCl_4]$ tetrahedra and $[Zn(H_2O)_6]$ octahedra are arranged in alternating rows parallel to [001]. The structure of the 4.5-hydrate {hexaaquazinc tetrachloridozinc trihydrate, $[Zn(H_2O)_6][ZnCl_4]·3H_2O$}, consists of isolated octahedral $[Zn(H_2O)_6]$ and tetrahedral $[ZnCl_4]$ units, as well as additional lattice water molecules. O—H···O hydrogen bonds between the water molecules as donor and $ZnCl_4$ tetrahedra and water molecules as acceptor groups leads to the formation of a three-dimensional network in each of the three structures.

## 1. Chemical context

Zinc chloride solutions, especially at lower temperatures, are helpful in the understanding of the formation of different complex ion species in solution. The solubility of zinc chloride in water has been investigated by several authors in different concentration areas and at different temperatures (Haghighi *et al.*, 2008; Mylius & Dietz, 1905; Jones & Getman, 1904; Chambers & Frazer, 1900; Biltz, 1902; Dietz, 1899; Etard, 1894). In the literature (Mylius & Dietz, 1905), the 4-, 3-, and 2.5-hydrates have been reported at lower temperatures. We have also found the 2.5-hydrate, the trihydrate and the 4.5-hydrate as stable phases along the equilibrium crystallization curves. The 4.5-hydrate crystallizes below 240 K. The crystal structure of the trihydrate reported herein has also been determined by Wilcox (2009) in his thesis, but was never published. While writing the formula of the trihydrate in a more detailed formula as $[Zn(H_2O)_6][ZnCl_4]$, the analogy to other structures like that of $[Mg(H_2O)_6][SO_4]$ (Zalkin *et al.*, 1964) and $[Zn(H_2O)_6][SO_4]$ (Spiess & Gruehn, 1979) becomes obvious. These structures are very similar in the arrangement of octahedral units and anions in the unit cell.



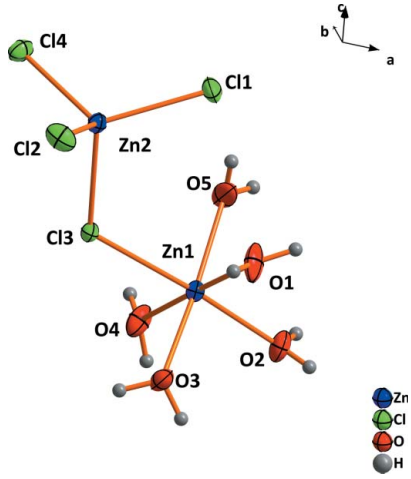



**Figure 1**
The asymmetric unit of $ZnCl_2·2.5H_2O$. Displacement ellipsoids are drawn at the 50% probability level.

## 2. Structural commentary

Within the crystal structure of the 2.5-hydrate, there are two crystallographic different $Zn^{2+}$ cations, as shown in Fig. 1. The Zn1 cation is octahedrally coordinated by five water molecules and one chloride anion. The Zn2 cation is coordinated by four chloride anions, one shared with the Zn1 cation, leading to the formation of isolated $[Zn_2Cl_4(H_2O)_5]$ units. Since the bond lengths of the bridging Cl atom of the tetrahedron are shorter than to that of the octahedron, the latter becomes more distorted. The crystal structure of zinc chloride trihydrate consists of three crystallographically different $Zn^{2+}$ cations (Fig. 2*a*). Two (Zn2 and Zn3) are located about an inversion centre and are coordinated octahedrally by six water molecules, forming $[Zn(H_2O)_6]^{2+}$ cations. The third one (Zn1) is tetrahedrally coordinated by chlorine anions, $[ZnCl_4]^{2-}$. The polyhedra are not connected by sharing a single atom like in the 2.5-hydrate, but they are linked by hydrogen bonds (Fig. 2*b*). The octahedra and tetrahedra are arranged in a CsCl-like arrangement with eight tetrahedra located around

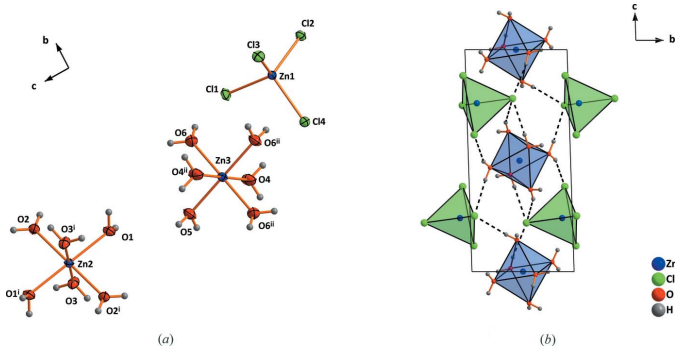



**Figure 2**
(*a*) The molecular units and (*b*) the unit cell in the structure of $ZnCl_2·3H_2O$. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $1-x, 1-y, 2-z$; (ii) $1-x, 1-y, 1-z$.]

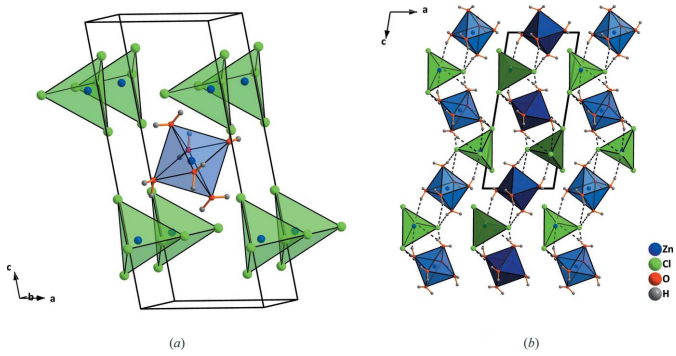



**Figure 3**
(*a*) Arrangement of $[ZnCl_4]^{2-}$-anions and $[Zn(H_2O)_6]^{2+}$ cations in a CsCl-like structure and (*b*) formation of chains by alternation of different coordination polyhedra in $ZnCl_2·3H_2O$. Dashed lines indicate hydrogen bonds. Only hydrogen bonds in one chain are shown.

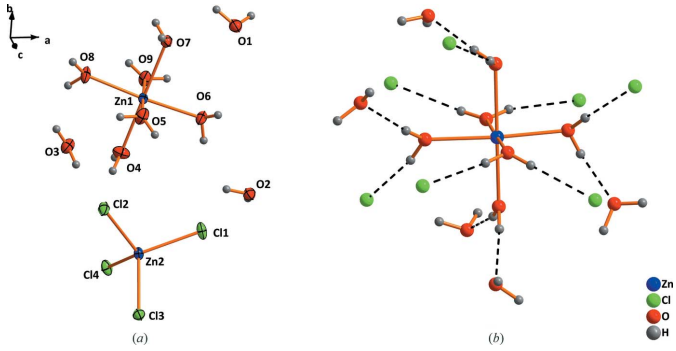



**Figure 4**
(*a*) The molecular units in the structure of $ZnCl_2·4.5H_2O$ and (*b*) formation of a second coordination shell. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

one octahedron (Fig. 3*a*). As shown in Fig. 4*a*, in the asymmetric unit of $ZnCl_2·4.5H_2O$, two different $Zn^{2+}$ cations are present. The Zn1 cation is coordinated octahedrally by six water molecules and the Zn2 cation tetrahedrally by four chloride anions. The three remaining water molecules are hydrogen-bonded to a $[Zn1(H_2O)]^{2+}$ octahedron (Fig. 4*b*).

**Table 1**
Hydrogen-bond geometry (Å, °) for $ZnCl_2·2.5H_2O$.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1*A*···Cl2$^{i}$ | 0.83 (1) | 2.43 (1) | 3.243 (2) | 167 (3) |
| O1—H1*B*···O5$^{ii}$ | 0.84 (1) | 2.02 (1) | 2.853 (3) | 178 (4) |
| O2—H2*A*···Cl2$^{iii}$ | 0.83 (1) | 2.51 (2) | 3.299 (2) | 158 (3) |
| O2—H2*B*···Cl4$^{ii}$ | 0.84 (1) | 2.41 (1) | 3.2212 (19) | 162 (3) |
| O3—H3*B*···Cl1$^{iv}$ | 0.83 (1) | 2.42 (1) | 3.225 (2) | 164 (3) |
| O3—H3*A*···Cl4$^{v}$ | 0.83 (1) | 2.38 (1) | 3.205 (2) | 171 (3) |
| O4—H4*B*···Cl2$^{v}$ | 0.83 (1) | 2.35 (1) | 3.181 (2) | 177 (3) |
| O4—H4*A*···Cl1$^{iii}$ | 0.83 (1) | 2.45 (2) | 3.2349 (19) | 157 (3) |
| O5—H5*A*···Cl4$^{i}$ | 0.83 (1) | 2.55 (2) | 3.233 (2) | 141 (3) |
| O5—H5*B*···Cl1 | 0.83 (1) | 2.56 (1) | 3.359 (3) | 163 (3) |

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (v) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

**Table 2**
Hydrogen-bond geometry (Å, °) for $ZnCl_2·3H_2O$.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1$B$···Cl3$^{i}$ | 0.84 (1) | 2.42 (1) | 3.2520 (14) | 168 (4) |
| O1—H1$A$···Cl4$^{ii}$ | 0.84 (1) | 2.43 (1) | 3.2431 (14) | 166 (3) |
| O2—H2$A$···Cl2$^{iii}$ | 0.84 (1) | 2.41 (2) | 3.2260 (14) | 163 (4) |
| O2—H2$B$···Cl3$^{iv}$ | 0.84 (1) | 2.54 (2) | 3.3264 (15) | 157 (3) |
| O3—H3$B$···Cl2$^{ii}$ | 0.84 (1) | 2.42 (2) | 3.1715 (14) | 149 (3) |
| O3—H3$B$···Cl2$^{v}$ | 0.84 (1) | 2.81 (3) | 3.3159 (14) | 120 (2) |
| O3—H3$A$···Cl4$^{iv}$ | 0.83 (1) | 2.45 (1) | 3.2552 (15) | 162 (3) |
| O4—H4$A$···Cl4 | 0.84 (1) | 2.43 (2) | 3.2307 (18) | 159 (4) |
| O4—H4$B$···Cl1$^{vi}$ | 0.84 (1) | 2.39 (1) | 3.2114 (17) | 167 (4) |
| O5—H5$B$···Cl3$^{vii}$ | 0.84 (1) | 2.91 (5) | 3.4565 (17) | 125 (5) |
| O5—H5$B$···Cl4$^{vii}$ | 0.84 (1) | 2.59 (3) | 3.3527 (18) | 151 (6) |
| O5—H5$A$···Cl1$^{ii}$ | 0.84 (1) | 2.48 (1) | 3.3159 (18) | 170 (5) |
| O6—H6$A$···Cl1 | 0.84 (1) | 2.52 (2) | 3.3142 (18) | 158 (4) |
| O6—H6$B$···Cl3$^{i}$ | 0.84 (1) | 2.41 (1) | 3.2405 (17) | 169 (3) |

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $-x, -y+2, -z+1$; (iv) $x, y, z+1$; (v) $x, y-1, z+1$; (vi) $x, y-1, z$; (vii) $-x+1, -y+1, -z+1$.

**Table 3**
Hydrogen-bond geometry (Å, °) for $ZnCl_2·4.5H_2O$.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1$B$···Cl3$^{i}$ | 0.84 (1) | 2.50 (2) | 3.300 (3) | 161 (6) |
| O1—H1$A$···O3$^{ii}$ | 0.84 (1) | 2.00 (2) | 2.823 (4) | 167 (5) |
| O2—H2$B$···O7$^{iii}$ | 0.84 (1) | 2.02 (2) | 2.853 (3) | 176 (6) |
| O2—H2$A$···Cl2$^{iv}$ | 0.83 (1) | 2.75 (5) | 3.347 (2) | 130 (5) |
| O2—H2$A$···Cl1 | 0.83 (1) | 2.68 (4) | 3.386 (2) | 143 (6) |
| O2—H2$A$···Cl2$^{iv}$ | 0.83 (1) | 2.75 (5) | 3.347 (2) | 130 (5) |
| O2—H2$B$···O7$^{iii}$ | 0.84 (1) | 2.02 (2) | 2.853 (3) | 176 (6) |
| O3—H3$A$···Cl2 | 0.84 (1) | 2.41 (2) | 3.237 (3) | 171 (5) |
| O3—H3$B$···Cl3$^{v}$ | 0.84 (1) | 2.71 (5) | 3.312 (3) | 130 (5) |
| O3—H3$B$···Cl4$^{v}$ | 0.84 (1) | 2.79 (4) | 3.512 (3) | 146 (6) |
| O4—H4$B$···O1$^{vi}$ | 0.84 (1) | 2.01 (2) | 2.831 (4) | 167 (5) |
| O4—H4$A$···O3$^{vii}$ | 0.84 (1) | 1.99 (2) | 2.821 (4) | 175 (6) |
| O5—H5$A$···Cl1$^{viii}$ | 0.84 (1) | 2.32 (1) | 3.157 (2) | 180 (6) |
| O5—H5$B$···Cl4$^{vii}$ | 0.84 (1) | 2.33 (2) | 3.165 (3) | 175 (5) |
| O6—H6$A$···Cl4$^{viii}$ | 0.84 (1) | 2.32 (1) | 3.159 (2) | 177 (4) |
| O6—H6$B$···O1$^{ix}$ | 0.84 (1) | 1.92 (2) | 2.754 (3) | 175 (6) |
| O7—H7$A$···O2$^{x}$ | 0.84 (1) | 1.90 (1) | 2.739 (3) | 176 (5) |
| O7—H7$B$···Cl2$^{ix}$ | 0.84 (1) | 2.38 (3) | 3.181 (2) | 160 (6) |
| O8—H8$A$···Cl3$^{x}$ | 0.84 (1) | 2.34 (2) | 3.155 (3) | 164 (5) |
| O8—H8$B$···O2$^{iii}$ | 0.84 (1) | 1.91 (2) | 2.738 (3) | 170 (5) |
| O9—H9$A$···Cl1$^{x}$ | 0.84 (1) | 2.39 (1) | 3.230 (2) | 176 (4) |
| O9—H9$B$···Cl3$^{xi}$ | 0.84 (1) | 2.42 (2) | 3.236 (2) | 167 (5) |

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iv) $x+1, y, z$; (v) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (vi) $x, y-1, z-1$; (vii) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$; (viii) $-x+\frac{3}{2}, -y, z-\frac{1}{2}$; (ix) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (x) $x, y, z-1$; (xi) $x+1, y, z-1$.

## 3. Supramolecular features

In the structure of $ZnCl_2·2.5H_2O$, all terminal $Cl^-$ anions are connected to the octahedral parts of neighbouring $[Zn_2Cl_4(H_2O)_5]$ units by three O—H···Cl hydrogen bonds per anion (Table 1, Fig. 5). The coordination polyhedra in the trihydrate are arranged in zigzag chains parallel to [001] in the crystal structure. The chains are highlighted in different shades of colors in Fig. 3*b*. Hydrogen bonds (Table 2) are established within one chain and between neighbouring chains (not shown in the Figure). As can be seen from Fig. 4*b*, five water molecules in the crystal structure of $ZnCl_2·4.5H_2O$ are connected *via* hydrogen bonds to the $[Zn1(H_2O]^{2+}$ octahedron, three of them at the axial coordination sites and two of them at the

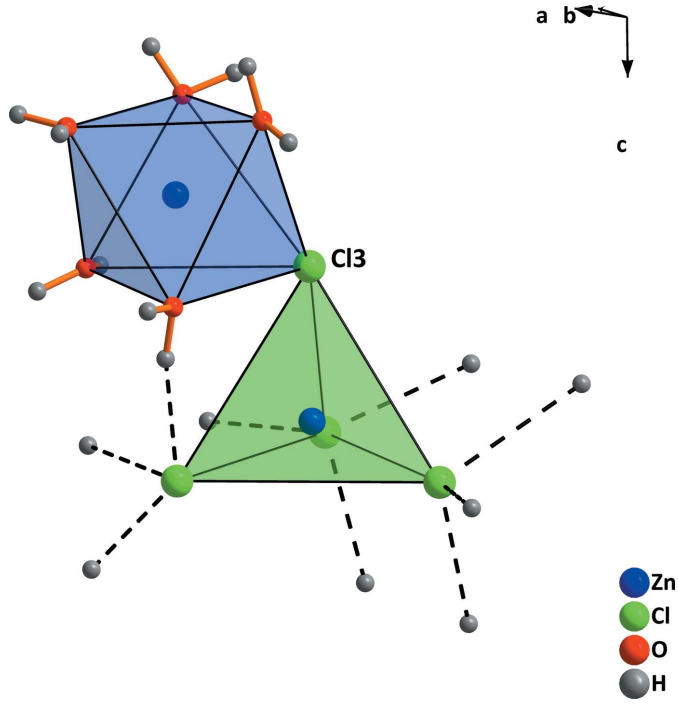



**Figure 5**
The connection of individual $[Zn_2Cl_4(H_2O)_5]$ units through hydrogen bonds (dashed lines) in the structure of $ZnCl_2·2.5H_2O$.

equatorial coordination sites. Seven chloride anions from $[Zn2Cl_4]^{2-}$ tetrahedra contribute to the second coordination sphere of Zn1. Thus, every coordinating water molecule forms two hydrogen bonds. The structural situation in this salt can be compared with the second coordination shells around magnesium in magnesium halide nonahydrates like $MgBr_2·9H_2O$ or $MgI_2·9H_2O$ (Hennings *et al.*, 2013). Each water molecule of the $[Mg(H_2O)_6]^{2+}$ octahedra forms two hydrogen bonds, thus six water molecules and six halide atoms are involved in the second shell. However, in case of the magnesium halides each water molecule donates a hydrogen bond towards a halide anion and towards another water molecule. The hydrogen-bond geometry in $ZnCl_2·4.5H_2O$ is given inTable 3.

## 4. Database survey

For crystal structures of other zinc chloride hydrates ($ZnCl_2·RH_2O$), see: Follner & Brehler (1970; $R$ = 1.33); Wilcox (2009; $R$ = 3). For crystal structures of anhydrous zinc chloride, see: Brehler (1961); Yakel & Brynestad (1978). For similar structural set-ups in comparison with the 3-hydrate, $[Zn(H_2O)_6][ZnCl_4]$, see: Zalkin *et al.* (1964; $[Mg(H_2O)_6][SO_4]$); Spiess & Gruehn (1979; $[Zn(H_2O)_6][SO_4]$); Agron & Busing (1985; $[Mg(H_2O)_6][Cl_2]$); Ferrari *et al.* (1967; $[Zn(H_2O)_6][NO_3]_2$).

## 5. Synthesis and crystallization

Zinc chloride 2.5 hydrate was crystallized from an aqueous solution of 73.41 wt% $ZnCl_2$ at 280 K after 2 d, zinc chloride

**Table 4**
Experimental details.

| | $ZnCl_2·2.5H_2O$ | $ZnCl_2·3H_2O$ | $ZnCl_2·4.5H_2O$ |
|---|---|---|---|
| Crystal data | | | |
| $M_r$ | 362.66 | 380.68 | 434.72 |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Triclinic, $P\overline{1}$ | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 150 | 150 | 120 |
| $a, b, c$ (Å) | 7.2909 (5), 9.7971 (5), 15.0912 (10) | 6.4339 (5), 6.5202 (5), 14.2769 (11) | 6.9795 (3), 12.5421 (6), 18.1849 (11) |
| $\alpha, \beta, \gamma$ (°) | 90, 103.375 (5), 90 | 90.910 (6), 99.146 (6), 95.574 (6) | 90, 90, 90 |
| $V$ (Å$^3$) | 1048.72 (12) | 588.21 (8) | 1591.86 (14) |
| $Z$ | 4 | 2 | 4 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 5.57 | 4.98 | 3.70 |
| Crystal size (mm) | 0.27 × 0.19 × 0.11 | 0.60 × 0.42 × 0.16 | 1.00 × 0.75 × 0.09 |
| Data collection | | | |
| Diffractometer | Stoe IPDS 2 | Stoe IPDS 2T | Stoe IPDS 2T |
| Absorption correction | Integration (Coppens, 1970) | Integration (Coppens, 1970) | Integration (Coppens, 1970) |
| $T_{min}$, $T_{max}$ | 0.287, 0.534 | 0.093, 0.441 | 0.050, 0.708 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 9997, 2923, 2222 | 13092, 3239, 3120 | 40776, 4414, 3955 |
| $R_{int}$ | 0.043 | 0.091 | 0.140 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.628 | 0.693 | 0.694 |
| Refinement | | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.018, 0.035, 1.01 | 0.029, 0.089, 1.02 | 0.021, 0.053, 0.99 |
| No. of reflections | 2171 | 3239 | 4414 |
| No. of parameters | 130 | 161 | 208 |
| No. of restraints | 15 | 18 | 27 |
| H-atom treatment | Only H-atom coordinates refined | All H-atom parameters refined | All H-atom parameters refined |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.44, −0.36 | 0.95, −0.95 | 0.77, −0.64 |
| Absolute structure | – | – | Flack $x$ determined using 1730 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons & Flack, 2004) |
| Absolute structure parameter | – | – | 0.089 (8) |

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2009), *SHELXS97* and *SHELXL2012* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

trihydrate from an aqueous solution of 69.14 wt% $ZnCl_2$ at 263 K after 2 d and zinc chloride 4.5 hydrate from an aqueous solution of 53.98 wt% $ZnCl_2$ at 223K after 2 d. For preparing these solutions, zinc chloride (Merck, 99%) was used. The content of $Zn^{2+}$ was analysed by complexometric titration with EDTA. The crystals are stable in their saturated solutions over a period of at least four weeks. The samples were stored in a freezer or a cryostat at low temperatures. The crystals were separated and embedded in perfluorinated ether for X-ray diffraction analysis.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The H atoms of each structure were placed in the positions indicated by difference Fourier maps. For all three structures, distance restraints were applied for all water molecules, with O—H and H—H distance restraints of 0.84 (1) and 1.4 (1) Å, respectively. For $ZnCl_2·2.5H_2O$ $U_{iso}$ values were set at $1.2U_{eq}$(O) using a riding-model approximation.

## References


Agron, P. A. & Busing, W. R. (1985). *Acta Cryst.* C**41**, 8–10.
Biltz, W. (1902). *Z. Phys. Chem.* **40**, 185–221.
Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Brehler, B. (1961). *Z. Kristallogr.* **115**, 373–402.
Chambers, V. J. & Frazer, F. C. J. (1900). *Am. Chem. J.* **23**, 512–520.
Coppens, P. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 255–270. Copenhagen: Munksgaard.
Dietz, R. (1899). *Z. Anorg. Chem.* **20**, 240–263.
Etard, A. (1894). *Ann. Chim. Phys.* **7**, 503–574.
Ferrari, A., Braibanti, A., Lanfredi, A. M. M. & Tiripicchio, A. (1967). *Acta Cryst.* **22**, 240–246.
Follner, H. & Brehler, B. (1970). *Acta Cryst.* B**26**, 1679–1682.
Haghighi, H., Chapoy, A. & Tohidi, B. (2008). *Ind. Eng. Chem. Res.* **47**, 3983–3989.
Hennings, E., Schmidt, H. & Voigt, W. (2013). *Acta Cryst.* C**69**, 1292–1300.
Jones, H. C. & Getman, F. H. (1904). *Z. Phys. Chem.* **49**, 385–455.
Mylius, F. & Dietz, R. (1905). *Z. Anorg. Chem.* **44**, 209–220.
Parsons, S. & Flack, H. (2004). *Acta Cryst.* A**60**, s61.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spiess, M. & Gruehn, R. (1979). *Z. Anorg. Allg. Chem.* **456**, 222–240.
Stoe & Cie (2009). *X-AREA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wilcox, R. J. (2009). PhD thesis, North Carolina State University, Raleigh, USA.
Yakel, H. L. & Brynestad, J. (1978). *Inorg. Chem.* **17**, 3294–3296.
Zalkin, A., Ruben, H. & Templeton, D. H. (1964). *Acta Cryst.* **17**, 235–240.

# supporting information

*Acta Cryst.* (2014). E**70**, 515-518 [doi:10.1107/S1600536814024738]

# Crystal structures of $ZnCl_2·2.5H_2O$, $ZnCl_2·3H_2O$ and $ZnCl_2·4.5H_2O$

**Erik Hennings, Horst Schmidt and Wolfgang Voigt**

## Computing details

For all compounds, data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-RED* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### (ZnCl2_2halbH2O_150K) Pentaaqua-$\mu$-chlorido-trichloridodizinc

*Crystal data*

$[Zn_2Cl_4(H_2O)_5]$
$M_r$ = 362.66
Monoclinic, $P2_1/n$
$a$ = 7.2909 (5) Å
$b$ = 9.7971 (5) Å
$c$ = 15.0912 (10) Å
$\beta$ = 103.375 (5)°
$V$ = 1048.72 (12) Å$^3$
$Z$ = 4
$F(000)$ = 712
$D_x$ = 2.297 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 245 reflections
$\theta$ = 3.6–29.1°
$\mu$ = 5.57 mm$^{-1}$
$T$ = 150 K
Prism, colourless
0.27 × 0.19 × 0.11 mm

*Data collection*

Stoe IPDS 2 diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method scans
Absorption correction: integration (Coppens, 1970)
$T_{min}$ = 0.287, $T_{max}$ = 0.534
9997 measured reflections
2923 independent reflections
2222 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.043
$\theta_{max}$ = 26.5°, $\theta_{min}$ = 2.5°
$h$ = −10→10
$k$ = −13→13
$l$ = −19→20

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.035
$S$ = 1.01
2171 reflections
130 parameters
15 restraints
Hydrogen site location: difference Fourier map
Only H-atom coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.0151P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.44 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.36 e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.78704 (3) | 0.77180 (3) | 0.15458 (2) | 0.01517 (6) |
| Zn2 | 0.47584 (3) | 0.76881 (3) | 0.35389 (2) | 0.01443 (6) |
| Cl3 | 0.48529 (7) | 0.77940 (6) | 0.20228 (3) | 0.01632 (11) |
| Cl4 | 0.31569 (9) | 0.95388 (6) | 0.38493 (4) | 0.02143 (13) |
| Cl1 | 0.77848 (8) | 0.75449 (6) | 0.43488 (4) | 0.02454 (13) |
| Cl2 | 0.30975 (10) | 0.57892 (6) | 0.37038 (4) | 0.02560 (14) |
| O3 | 0.6623 (3) | 0.62440 (18) | 0.06100 (13) | 0.0239 (4) |
| H3A | 0.715 (4) | 0.602 (3) | 0.0197 (16) | 0.029* |
| H3B | 0.553 (2) | 0.644 (3) | 0.0340 (19) | 0.029* |
| O2 | 1.0303 (2) | 0.76289 (19) | 0.10641 (13) | 0.0269 (4) |
| H2A | 1.101 (4) | 0.831 (2) | 0.114 (2) | 0.032* |
| H2B | 1.094 (4) | 0.691 (2) | 0.108 (2) | 0.032* |
| O4 | 0.6948 (3) | 0.92487 (18) | 0.06129 (14) | 0.0276 (4) |
| H4A | 0.690 (5) | 1.0064 (14) | 0.076 (2) | 0.033* |
| H4B | 0.724 (5) | 0.921 (3) | 0.0111 (13) | 0.033* |
| O1 | 0.8850 (3) | 0.6172 (2) | 0.24737 (16) | 0.0332 (5) |
| H1A | 0.997 (2) | 0.600 (3) | 0.272 (2) | 0.040* |
| H1B | 0.801 (4) | 0.558 (3) | 0.245 (2) | 0.040* |
| O5 | 0.8963 (3) | 0.9128 (2) | 0.25850 (17) | 0.0381 (5) |
| H5A | 1.002 (3) | 0.948 (3) | 0.268 (3) | 0.046* |
| H5B | 0.874 (5) | 0.891 (4) | 0.3079 (14) | 0.046* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.01214 (12) | 0.01726 (12) | 0.01619 (12) | 0.00135 (11) | 0.00343 (9) | −0.00051 (10) |
| Zn2 | 0.01283 (11) | 0.01446 (12) | 0.01622 (12) | −0.00030 (10) | 0.00379 (9) | −0.00026 (10) |
| Cl3 | 0.0111 (2) | 0.0235 (3) | 0.0147 (2) | 0.0010 (2) | 0.00364 (18) | −0.0011 (2) |
| Cl4 | 0.0257 (3) | 0.0181 (3) | 0.0218 (3) | 0.0061 (2) | 0.0080 (2) | −0.0005 (2) |
| Cl1 | 0.0151 (2) | 0.0355 (3) | 0.0205 (3) | 0.0024 (2) | −0.0011 (2) | 0.0020 (2) |
| Cl2 | 0.0296 (4) | 0.0200 (3) | 0.0255 (3) | −0.0110 (2) | 0.0030 (3) | 0.0015 (2) |
| O3 | 0.0209 (10) | 0.0246 (9) | 0.0287 (10) | −0.0020 (8) | 0.0110 (8) | −0.0088 (7) |
| O2 | 0.0163 (8) | 0.0275 (10) | 0.0393 (10) | 0.0031 (8) | 0.0111 (7) | 0.0025 (9) |
| O4 | 0.0307 (11) | 0.0200 (9) | 0.0369 (11) | 0.0082 (8) | 0.0173 (9) | 0.0101 (8) |
| O1 | 0.0187 (11) | 0.0389 (11) | 0.0425 (12) | 0.0123 (9) | 0.0084 (9) | 0.0253 (10) |
| O5 | 0.0176 (11) | 0.0506 (13) | 0.0470 (14) | −0.0106 (9) | 0.0095 (10) | −0.0309 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn1—O4 | 2.0604 (18) | Zn1—Cl3 | 2.4691 (6) |
| Zn1—O2 | 2.0681 (17) | Zn2—Cl4 | 2.2635 (6) |
| Zn1—O1 | 2.0742 (19) | Zn2—Cl2 | 2.2647 (6) |
| Zn1—O3 | 2.0767 (18) | Zn2—Cl1 | 2.2659 (6) |
| Zn1—O5 | 2.103 (2) | Zn2—Cl3 | 2.3073 (6) |
| | | | |
| O4—Zn1—O2 | 87.79 (8) | O2—Zn1—Cl3 | 176.40 (6) |
| O4—Zn1—O1 | 178.76 (8) | O1—Zn1—Cl3 | 90.93 (6) |
| O2—Zn1—O1 | 90.97 (8) | O3—Zn1—Cl3 | 86.54 (5) |
| O4—Zn1—O3 | 91.09 (8) | O5—Zn1—Cl3 | 88.40 (6) |
| O2—Zn1—O3 | 90.45 (8) | Cl4—Zn2—Cl2 | 108.71 (2) |
| O1—Zn1—O3 | 88.83 (9) | Cl4—Zn2—Cl1 | 115.00 (3) |
| O4—Zn1—O5 | 92.24 (10) | Cl2—Zn2—Cl1 | 111.63 (3) |
| O2—Zn1—O5 | 94.72 (8) | Cl4—Zn2—Cl3 | 107.72 (2) |
| O1—Zn1—O5 | 87.95 (9) | Cl2—Zn2—Cl3 | 106.58 (2) |
| O3—Zn1—O5 | 173.95 (8) | Cl1—Zn2—Cl3 | 106.80 (2) |
| O4—Zn1—Cl3 | 90.30 (6) | Zn2—Cl3—Zn1 | 121.38 (2) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*A*···Cl2$^{i}$ | 0.83 (1) | 2.43 (1) | 3.243 (2) | 167 (3) |
| O1—H1*B*···O5$^{ii}$ | 0.84 (1) | 2.02 (1) | 2.853 (3) | 178 (4) |
| O2—H2*A*···Cl2$^{iii}$ | 0.83 (1) | 2.51 (2) | 3.299 (2) | 158 (3) |
| O2—H2*B*···Cl4$^{ii}$ | 0.84 (1) | 2.41 (1) | 3.2212 (19) | 162 (3) |
| O3—H3*B*···Cl1$^{iv}$ | 0.83 (1) | 2.42 (1) | 3.225 (2) | 164 (3) |
| O3—H3*A*···Cl4$^{v}$ | 0.83 (1) | 2.38 (1) | 3.205 (2) | 171 (3) |
| O4—H4*B*···Cl2$^{v}$ | 0.83 (1) | 2.35 (1) | 3.181 (2) | 177 (3) |
| O4—H4*A*···Cl1$^{iii}$ | 0.83 (1) | 2.45 (2) | 3.2349 (19) | 157 (3) |
| O5—H5*A*···Cl4$^{i}$ | 0.83 (1) | 2.55 (2) | 3.233 (2) | 141 (3) |
| O5—H5*B*···Cl1 | 0.83 (1) | 2.56 (1) | 3.359 (3) | 163 (3) |

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+3/2, *y*−1/2, −*z*+1/2; (iii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iv) *x*−1/2, −*y*+3/2, *z*−1/2; (v) *x*+1/2, −*y*+3/2, *z*−1/2.

### (zncl2_3H2O_150K) Dexaaquazinc tetrachloridozinc

*Crystal data*

$[Zn(H_2O)_6][ZnCl_4]$
$M_r$ = 380.68
Triclinic, $P\overline{1}$
*a* = 6.4339 (5) Å
*b* = 6.5202 (5) Å
*c* = 14.2769 (11) Å
*α* = 90.910 (6)°
*β* = 99.146 (6)°
*γ* = 95.574 (6)°
*V* = 588.21 (8) Å$^3$
*Z* = 2
*F*(000) = 376
$D_x$ = 2.149 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 16445 reflections
*θ* = 2.9–29.7°
*μ* = 4.98 mm$^{-1}$
*T* = 150 K
Prism, colourless
0.60 × 0.42 × 0.16 mm

*Data collection*

Stoe IPDS 2T diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method scans
Absorption correction: integration (Coppens, 1970)
$T_{min}$ = 0.093, $T_{max}$ = 0.441
13092 measured reflections
3239 independent reflections
3120 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.091
$\theta_{max}$ = 29.5°, $\theta_{min}$ = 2.9°
$h$ = −8→8
$k$ = −8→8
$l$ = 0→19

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.089
$S$ = 1.02
3239 reflections
161 parameters
18 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0816P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.95 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.95 e Å$^{-3}$
Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.027 (3)

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.11523 (3) | 0.89978 (3) | 0.24118 (2) | 0.01505 (10) |
| Zn2 | 0.5000 | 0.5000 | 1.0000 | 0.01412 (10) |
| Zn3 | 0.5000 | 0.5000 | 0.5000 | 0.01952 (10) |
| Cl4 | 0.11763 (7) | 0.54937 (6) | 0.21964 (3) | 0.01909 (11) |
| Cl1 | 0.00446 (7) | 0.93575 (7) | 0.38328 (3) | 0.02259 (12) |
| Cl2 | −0.08727 (7) | 1.02596 (6) | 0.11685 (3) | 0.01956 (11) |
| Cl3 | 0.45614 (6) | 1.04172 (7) | 0.25090 (3) | 0.02155 (12) |
| O1 | 0.3849 (2) | 0.5508 (2) | 0.85688 (10) | 0.0202 (3) |
| O3 | 0.2012 (2) | 0.3787 (2) | 1.01476 (10) | 0.0220 (3) |
| O2 | 0.4233 (2) | 0.7893 (2) | 1.04390 (10) | 0.0218 (3) |
| O4 | 0.1902 (3) | 0.4054 (2) | 0.43689 (13) | 0.0338 (4) |
| O5 | 0.4216 (3) | 0.4000 (3) | 0.63059 (11) | 0.0316 (3) |
| O6 | 0.4103 (3) | 0.7891 (2) | 0.53108 (12) | 0.0330 (4) |
| H3A | 0.153 (4) | 0.406 (4) | 1.0635 (14) | 0.027 (7)* |
| H1A | 0.2554 (19) | 0.549 (5) | 0.837 (2) | 0.031 (7)* |
| H5A | 0.324 (6) | 0.304 (6) | 0.631 (5) | 0.099 (19)* |
| H5B | 0.523 (6) | 0.365 (9) | 0.670 (3) | 0.11 (2)* |
| H3B | 0.158 (4) | 0.255 (2) | 1.001 (2) | 0.028 (7)* |
| H4B | 0.150 (6) | 0.2781 (19) | 0.433 (3) | 0.046 (9)* |
| H1B | 0.444 (5) | 0.656 (4) | 0.835 (3) | 0.052 (10)* |
| H6B | 0.430 (6) | 0.842 (5) | 0.5863 (12) | 0.043 (9)* |

| | | | | |
|---|---|---|---|---|
| H2B | 0.469 (5) | 0.846 (5) | 1.0973 (12) | 0.033 (8)* |
| H4A | 0.138 (7) | 0.443 (7) | 0.3831 (16) | 0.068 (13)* |
| H2A | 0.326 (5) | 0.848 (6) | 1.012 (3) | 0.067 (12)* |
| H6A | 0.312 (5) | 0.856 (6) | 0.505 (3) | 0.068 (13)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.01631 (13) | 0.01664 (13) | 0.01182 (13) | 0.00047 (8) | 0.00172 (8) | 0.00148 (8) |
| Zn2 | 0.01421 (15) | 0.01364 (15) | 0.01422 (15) | 0.00026 (10) | 0.00197 (10) | 0.00211 (10) |
| Zn3 | 0.02499 (17) | 0.01508 (16) | 0.01623 (16) | 0.00053 (11) | −0.00294 (12) | 0.00295 (11) |
| Cl4 | 0.0226 (2) | 0.01568 (19) | 0.0180 (2) | 0.00149 (13) | 0.00074 (14) | 0.00044 (14) |
| Cl1 | 0.0276 (2) | 0.0269 (2) | 0.0138 (2) | −0.00023 (16) | 0.00716 (15) | −0.00085 (15) |
| Cl2 | 0.0214 (2) | 0.01837 (19) | 0.0172 (2) | 0.00167 (14) | −0.00233 (15) | 0.00332 (14) |
| Cl3 | 0.01682 (19) | 0.0240 (2) | 0.0227 (2) | −0.00282 (15) | 0.00277 (15) | 0.00254 (15) |
| O1 | 0.0181 (5) | 0.0231 (6) | 0.0185 (6) | 0.0001 (4) | 0.0003 (5) | 0.0057 (5) |
| O3 | 0.0204 (6) | 0.0212 (6) | 0.0243 (7) | −0.0047 (5) | 0.0081 (5) | −0.0033 (5) |
| O2 | 0.0246 (6) | 0.0193 (6) | 0.0205 (6) | 0.0071 (5) | −0.0021 (5) | −0.0003 (5) |
| O4 | 0.0339 (8) | 0.0262 (7) | 0.0336 (8) | −0.0064 (6) | −0.0133 (7) | 0.0092 (6) |
| O5 | 0.0396 (8) | 0.0325 (8) | 0.0208 (7) | −0.0004 (6) | 0.0011 (6) | 0.0091 (6) |
| O6 | 0.0504 (10) | 0.0230 (7) | 0.0246 (8) | 0.0105 (6) | −0.0011 (7) | 0.0001 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn1—Cl2 | 2.2460 (5) | Zn2—O2 | 2.1066 (13) |
| Zn1—Cl1 | 2.2706 (5) | Zn2—O2$^{i}$ | 2.1066 (13) |
| Zn1—Cl3 | 2.2785 (5) | Zn3—O4 | 2.0829 (16) |
| Zn1—Cl4 | 2.3024 (5) | Zn3—O4$^{ii}$ | 2.0829 (16) |
| Zn2—O3 | 2.0506 (13) | Zn3—O6 | 2.0852 (16) |
| Zn2—O3$^{i}$ | 2.0506 (13) | Zn3—O6$^{ii}$ | 2.0852 (16) |
| Zn2—O1 | 2.1027 (13) | Zn3—O5$^{ii}$ | 2.1045 (16) |
| Zn2—O1$^{i}$ | 2.1027 (13) | Zn3—O5 | 2.1045 (16) |
| | | | |
| Cl2—Zn1—Cl1 | 115.478 (19) | O1—Zn2—O2$^{i}$ | 87.84 (5) |
| Cl2—Zn1—Cl3 | 109.745 (18) | O1$^{i}$—Zn2—O2$^{i}$ | 92.16 (5) |
| Cl1—Zn1—Cl3 | 110.036 (19) | O2—Zn2—O2$^{i}$ | 180.0 |
| Cl2—Zn1—Cl4 | 109.947 (18) | O4—Zn3—O4$^{ii}$ | 180.0 |
| Cl1—Zn1—Cl4 | 104.334 (18) | O4—Zn3—O6 | 89.91 (7) |
| Cl3—Zn1—Cl4 | 106.860 (18) | O4$^{ii}$—Zn3—O6 | 90.09 (7) |
| O3—Zn2—O3$^{i}$ | 180.0 | O4—Zn3—O6$^{ii}$ | 90.09 (7) |
| O3—Zn2—O1 | 88.54 (5) | O4$^{ii}$—Zn3—O6$^{ii}$ | 89.91 (7) |
| O3$^{i}$—Zn2—O1 | 91.46 (5) | O6—Zn3—O6$^{ii}$ | 180.0 |
| O3—Zn2—O1$^{i}$ | 91.46 (5) | O4—Zn3—O5$^{ii}$ | 91.29 (7) |
| O3$^{i}$—Zn2—O1$^{i}$ | 88.54 (5) | O4$^{ii}$—Zn3—O5$^{ii}$ | 88.71 (7) |
| O1—Zn2—O1$^{i}$ | 180.00 (3) | O6—Zn3—O5$^{ii}$ | 91.31 (7) |
| O3—Zn2—O2 | 88.50 (6) | O6$^{ii}$—Zn3—O5$^{ii}$ | 88.69 (7) |
| O3$^{i}$—Zn2—O2 | 91.50 (6) | O4—Zn3—O5 | 88.71 (7) |
| O1—Zn2—O2 | 92.17 (5) | O4$^{ii}$—Zn3—O5 | 91.29 (7) |

| | | | |
|---|---|---|---|
| O1$^{i}$—Zn2—O2 | 87.83 (5) | O6—Zn3—O5 | 88.69 (7) |
| O3—Zn2—O2$^{i}$ | 91.50 (6) | O6$^{ii}$—Zn3—O5 | 91.31 (7) |
| O3$^{i}$—Zn2—O2$^{i}$ | 88.50 (6) | O5$^{ii}$—Zn3—O5 | 180.00 (9) |

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) −*x*+1, −*y*+1, −*z*+1.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*B*···Cl3$^{iii}$ | 0.84 (1) | 2.42 (1) | 3.2520 (14) | 168 (4) |
| O1—H1*A*···Cl4$^{iv}$ | 0.84 (1) | 2.43 (1) | 3.2431 (14) | 166 (3) |
| O2—H2*A*···Cl2$^{v}$ | 0.84 (1) | 2.41 (2) | 3.2260 (14) | 163 (4) |
| O2—H2*B*···Cl3$^{vi}$ | 0.84 (1) | 2.54 (2) | 3.3264 (15) | 157 (3) |
| O3—H3*B*···Cl2$^{iv}$ | 0.84 (1) | 2.42 (2) | 3.1715 (14) | 149 (3) |
| O3—H3*B*···Cl2$^{vii}$ | 0.84 (1) | 2.81 (3) | 3.3159 (14) | 120 (2) |
| O3—H3*A*···Cl4$^{vi}$ | 0.83 (1) | 2.45 (1) | 3.2552 (15) | 162 (3) |
| O4—H4*A*···Cl4 | 0.84 (1) | 2.43 (2) | 3.2307 (18) | 159 (4) |
| O4—H4*B*···Cl1$^{viii}$ | 0.84 (1) | 2.38 (1) | 3.2114 (17) | 167 (4) |
| O5—H5*B*···Cl3$^{ii}$ | 0.84 (1) | 2.91 (5) | 3.4565 (17) | 125 (5) |
| O5—H5*B*···Cl4$^{ii}$ | 0.84 (1) | 2.59 (3) | 3.3527 (18) | 151 (6) |
| O5—H5*A*···Cl1$^{iv}$ | 0.84 (1) | 2.48 (1) | 3.3159 (18) | 170 (5) |
| O6—H6*A*···Cl1 | 0.84 (1) | 2.52 (2) | 3.3142 (18) | 158 (4) |
| O6—H6*B*···Cl3$^{iii}$ | 0.84 (1) | 2.41 (1) | 3.2405 (17) | 169 (3) |

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+2, −*z*+1; (iv) −*x*, −*y*+1, −*z*+1; (v) −*x*, −*y*+2, −*z*+1; (vi) *x*, *y*, *z*+1; (vii) *x*, *y*−1, *z*+1; (viii) *x*, *y*−1, *z*.

### (ZnCl2_4halbH2O_120K) Hexaaquazinc tetrachloridozinc trihydrate

*Crystal data*

$[Zn(H_2O)_6][ZnCl_4]\cdot 3H_2O$
$M_r$ = 434.72
Orthorhombic, $P2_12_12_1$
*a* = 6.9795 (3) Å
*b* = 12.5421 (6) Å
*c* = 18.1849 (11) Å
*V* = 1591.86 (14) Å$^3$
*Z* = 4
*F*(000) = 872
$D_x$ = 1.814 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 33650 reflections
*θ* = 1.8–29.6°
*μ* = 3.70 mm$^{-1}$
*T* = 120 K
Prism, colourless
1 × 0.75 × 0.09 mm

*Data collection*

Stoe IPDS 2T diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 6.67 pixels mm$^{-1}$
rotation method scans
Absorption correction: integration (Coppens, 1970)
$T_{min}$ = 0.050, $T_{max}$ = 0.708
40776 measured reflections
4414 independent reflections
3955 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.140
$\theta_{max}$ = 29.6°, $\theta_{min}$ = 2.8°
*h* = −9→9
*k* = −17→17
*l* = −25→25

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.053
*S* = 0.99
4414 reflections

208 parameters
27 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.77$ e Å$^{-3}$
$\Delta\rho_{min} = -0.64$ e Å$^{-3}$
Absolute structure: Flack *x* determined using 1730 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons & Flack, 2004)
Absolute structure parameter: 0.089 (8)

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.77065 (5) | 0.00714 (2) | 0.06201 (2) | 0.01250 (7) |
| Zn2 | 0.31706 (5) | 0.03464 (3) | 0.81771 (2) | 0.01309 (7) |
| Cl3 | 0.27768 (11) | −0.08062 (5) | 0.91458 (4) | 0.01637 (13) |
| Cl4 | 0.22957 (11) | −0.06620 (6) | 0.71906 (4) | 0.01873 (14) |
| Cl1 | 0.62302 (10) | 0.09178 (6) | 0.80989 (4) | 0.01949 (14) |
| Cl2 | 0.11859 (11) | 0.17633 (6) | 0.83407 (4) | 0.01869 (14) |
| O5 | 0.7005 (4) | 0.0248 (2) | 0.17173 (12) | 0.0221 (4) |
| O6 | 1.0486 (3) | −0.03761 (19) | 0.08567 (14) | 0.0194 (4) |
| O4 | 0.6863 (4) | −0.15048 (17) | 0.05792 (14) | 0.0230 (5) |
| O7 | 0.8639 (3) | 0.17112 (16) | 0.06267 (13) | 0.0155 (4) |
| O2 | 0.7609 (3) | 0.27476 (16) | 0.93613 (13) | 0.0180 (4) |
| O3 | 0.0251 (4) | 0.25556 (19) | 0.66850 (15) | 0.0233 (5) |
| O1 | 0.6408 (4) | 0.75102 (19) | 0.91896 (15) | 0.0216 (5) |
| O8 | 0.5001 (3) | 0.05893 (19) | 0.03098 (15) | 0.0216 (5) |
| O9 | 0.8442 (3) | −0.00564 (19) | −0.04927 (12) | 0.0193 (4) |
| H6A | 1.106 (7) | −0.008 (3) | 0.1205 (18) | 0.027 (12)* |
| H1A | 0.732 (5) | 0.761 (4) | 0.890 (2) | 0.030 (12)* |
| H4B | 0.681 (8) | −0.188 (3) | 0.0199 (16) | 0.031 (12)* |
| H7A | 0.829 (8) | 0.201 (4) | 0.0235 (16) | 0.033 (13)* |
| H9A | 0.784 (6) | 0.017 (4) | −0.0860 (17) | 0.029 (12)* |
| H5A | 0.747 (7) | −0.006 (4) | 0.2084 (19) | 0.043 (15)* |
| H5B | 0.586 (3) | 0.032 (4) | 0.184 (3) | 0.041 (14)* |
| H8A | 0.433 (6) | 0.015 (3) | 0.008 (2) | 0.031 (13)* |
| H7B | 0.816 (9) | 0.204 (4) | 0.099 (2) | 0.054 (18)* |
| H8B | 0.423 (6) | 0.106 (3) | 0.045 (3) | 0.028 (12)* |
| H6B | 1.069 (8) | −0.1034 (13) | 0.084 (3) | 0.038 (15)* |
| H9B | 0.959 (3) | −0.014 (5) | −0.061 (3) | 0.050 (16)* |
| H4A | 0.629 (7) | −0.181 (4) | 0.092 (2) | 0.035 (14)* |
| H2A | 0.780 (9) | 0.239 (4) | 0.8979 (19) | 0.049 (17)* |
| H3A | 0.046 (8) | 0.228 (4) | 0.7098 (15) | 0.040 (15)* |
| H1B | 0.550 (6) | 0.791 (4) | 0.906 (3) | 0.047 (17)* |
| H2B | 0.645 (3) | 0.292 (4) | 0.939 (4) | 0.050 (17)* |

| | | | | |
|---|---|---|---|---|
| H3B | −0.041 (7) | 0.310 (3) | 0.676 (4) | 0.047 (16)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.01058 (15) | 0.01326 (13) | 0.01365 (14) | 0.00118 (11) | −0.00037 (11) | 0.00004 (10) |
| Zn2 | 0.00971 (15) | 0.01571 (13) | 0.01386 (14) | −0.00083 (11) | −0.00053 (11) | −0.00135 (11) |
| Cl3 | 0.0161 (3) | 0.0176 (3) | 0.0154 (3) | −0.0007 (2) | −0.0006 (2) | 0.0012 (2) |
| Cl4 | 0.0175 (3) | 0.0241 (3) | 0.0146 (3) | −0.0049 (3) | −0.0008 (3) | −0.0039 (2) |
| Cl1 | 0.0108 (3) | 0.0288 (3) | 0.0189 (3) | −0.0047 (2) | 0.0008 (3) | −0.0050 (3) |
| Cl2 | 0.0137 (3) | 0.0185 (3) | 0.0239 (4) | 0.0027 (2) | −0.0013 (3) | −0.0032 (2) |
| O5 | 0.0198 (11) | 0.0340 (11) | 0.0126 (9) | 0.0063 (10) | 0.0007 (8) | 0.0015 (8) |
| O6 | 0.0161 (10) | 0.0193 (10) | 0.0227 (11) | 0.0046 (9) | −0.0063 (8) | −0.0035 (9) |
| O4 | 0.0319 (13) | 0.0176 (10) | 0.0195 (11) | −0.0053 (9) | 0.0026 (11) | −0.0007 (8) |
| O7 | 0.0147 (10) | 0.0154 (9) | 0.0164 (10) | 0.0004 (7) | 0.0007 (8) | −0.0009 (8) |
| O2 | 0.0170 (11) | 0.0175 (9) | 0.0194 (10) | −0.0004 (8) | 0.0005 (9) | −0.0012 (8) |
| O3 | 0.0220 (12) | 0.0236 (11) | 0.0245 (13) | 0.0060 (9) | −0.0043 (10) | −0.0005 (9) |
| O1 | 0.0189 (12) | 0.0199 (10) | 0.0260 (12) | −0.0012 (9) | 0.0012 (9) | −0.0014 (9) |
| O8 | 0.0122 (10) | 0.0244 (11) | 0.0281 (13) | 0.0056 (8) | −0.0062 (9) | −0.0088 (9) |
| O9 | 0.0157 (10) | 0.0294 (11) | 0.0127 (9) | 0.0038 (9) | 0.0025 (8) | 0.0012 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn1—O4 | 2.064 (2) | Zn1—O7 | 2.157 (2) |
| Zn1—O6 | 2.065 (2) | Zn2—Cl1 | 2.2570 (8) |
| Zn1—O5 | 2.066 (2) | Zn2—Cl2 | 2.2728 (8) |
| Zn1—O8 | 2.075 (2) | Zn2—Cl4 | 2.2783 (8) |
| Zn1—O9 | 2.094 (2) | Zn2—Cl3 | 2.2953 (8) |
| | | | |
| O4—Zn1—O6 | 90.86 (10) | O6—Zn1—O7 | 88.54 (9) |
| O4—Zn1—O5 | 94.02 (10) | O5—Zn1—O7 | 87.92 (10) |
| O6—Zn1—O5 | 92.91 (10) | O8—Zn1—O7 | 88.72 (9) |
| O4—Zn1—O8 | 91.75 (10) | O9—Zn1—O7 | 90.25 (9) |
| O6—Zn1—O8 | 175.34 (10) | Cl1—Zn2—Cl2 | 109.67 (3) |
| O5—Zn1—O8 | 90.76 (10) | Cl1—Zn2—Cl4 | 112.35 (3) |
| O4—Zn1—O9 | 87.81 (10) | Cl2—Zn2—Cl4 | 111.95 (3) |
| O6—Zn1—O9 | 87.15 (9) | Cl1—Zn2—Cl3 | 111.20 (3) |
| O5—Zn1—O9 | 178.17 (10) | Cl2—Zn2—Cl3 | 108.60 (3) |
| O8—Zn1—O9 | 89.09 (10) | Cl4—Zn2—Cl3 | 102.86 (3) |
| O4—Zn1—O7 | 178.00 (10) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*B*···Cl3$^{i}$ | 0.84 (1) | 2.50 (2) | 3.300 (3) | 161 (6) |
| O1—H1*A*···O3$^{ii}$ | 0.84 (1) | 2.00 (2) | 2.823 (4) | 167 (5) |
| O2—H2*B*···O7$^{iii}$ | 0.84 (1) | 2.02 (2) | 2.853 (3) | 176 (6) |
| O2—H2*A*···Cl2$^{iv}$ | 0.83 (1) | 2.75 (5) | 3.347 (2) | 130 (5) |

| | | | | |
|---|---|---|---|---|
| O2—H2*A*···Cl1 | 0.83 (1) | 2.68 (4) | 3.386 (2) | 143 (6) |
| O2—H2*A*···Cl2$^{iv}$ | 0.83 (1) | 2.75 (5) | 3.347 (2) | 130 (5) |
| O2—H2*B*···O7$^{iii}$ | 0.84 (1) | 2.02 (2) | 2.853 (3) | 176 (6) |
| O3—H3*A*···Cl2 | 0.84 (1) | 2.41 (2) | 3.237 (3) | 171 (5) |
| O3—H3*B*···Cl3$^{v}$ | 0.84 (1) | 2.71 (5) | 3.312 (3) | 130 (5) |
| O3—H3*B*···Cl4$^{v}$ | 0.84 (1) | 2.79 (4) | 3.512 (3) | 146 (6) |
| O4—H4*B*···O1$^{vi}$ | 0.84 (1) | 2.01 (2) | 2.831 (4) | 167 (5) |
| O4—H4*A*···O3$^{vii}$ | 0.84 (1) | 1.99 (2) | 2.821 (4) | 175 (6) |
| O5—H5*A*···Cl1$^{viii}$ | 0.84 (1) | 2.32 (1) | 3.157 (2) | 180 (6) |
| O5—H5*B*···Cl4$^{vii}$ | 0.84 (1) | 2.33 (2) | 3.165 (3) | 175 (5) |
| O6—H6*A*···Cl4$^{viii}$ | 0.84 (1) | 2.32 (1) | 3.159 (2) | 177 (4) |
| O6—H6*B*···O1$^{ix}$ | 0.84 (1) | 1.92 (2) | 2.754 (3) | 175 (6) |
| O7—H7*A*···O2$^{x}$ | 0.84 (1) | 1.90 (1) | 2.739 (3) | 176 (5) |
| O7—H7*B*···Cl2$^{ix}$ | 0.84 (1) | 2.38 (3) | 3.181 (2) | 160 (6) |
| O8—H8*A*···Cl3$^{x}$ | 0.84 (1) | 2.34 (2) | 3.155 (3) | 164 (5) |
| O8—H8*B*···O2$^{iii}$ | 0.84 (1) | 1.91 (2) | 2.738 (3) | 170 (5) |
| O9—H9*A*···Cl1$^{x}$ | 0.84 (1) | 2.39 (1) | 3.230 (2) | 176 (4) |
| O9—H9*B*···Cl3$^{xi}$ | 0.84 (1) | 2.42 (2) | 3.236 (2) | 167 (5) |

Symmetry codes: (i) $x$, $y$+1, $z$; (ii) −$x$+1, $y$+1/2, −$z$+3/2; (iii) $x$−1/2, −$y$+1/2, −$z$+1; (iv) $x$+1, $y$, $z$; (v) −$x$, $y$+1/2, −$z$+3/2; (vi) $x$, $y$−1, $z$−1; (vii) −$x$+1/2, −$y$, $z$−1/2; (viii) −$x$+3/2, −$y$, $z$−1/2; (ix) $x$+1/2, −$y$+1/2, −$z$+1; (x) $x$, $y$, $z$−1; (xi) $x$+1, $y$, $z$−1.