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Structural characterization of two tetrachloridozincate salts of 4-carboxy-1*H*-imidazol-3-ium: a salt hydrate and a co-crystal salt hydrate

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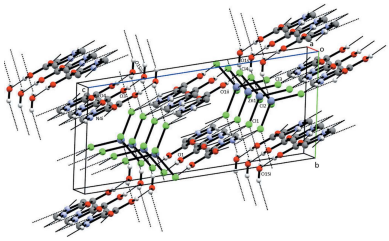
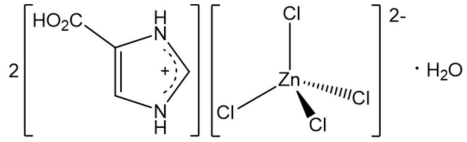
Imidazole-containing compounds exhibit a myriad of pharmacological activities. Two tetrachloridozincate salts of 4-carboxy-1*H*-imidazol-3-ium, $ImHCO_2H^+$, are reported. Bis(4-carboxy-1*H*-imidazol-3-ium) tetrachloridozincate monohydrate, $(C_4H_5N_2O_2)_2[ZnCl_4]\cdot H_2O$, (I), crystallizes as a monohydrate salt, while bis(4-carboxy-1*H*-imidazol-3-ium) tetrachloridozincate bis(1*H*-imidazol-3-ium-4-carboxylato) monohydrate, $(C_4H_5N_2O_2)_2[ZnCl_4]\cdot 2C_4H_4N_2O_2\cdot H_2O$, (II), is a co-crystal salt with six residues: two $ImHCO_2H^+$ cations, two formula units of the zwitterionic 1*H*-imidazol-3-ium-4-carboxylate, $ImHCO_2$, one tetrachloridozincate anion and one water molecule disordered over two sites in a 0.60 (4):0.40 (4) ratio. The geometric parameters of the $ImHCO_2H^+$ and the $ImHCO_2$ moieties are the same within the standard uncertainties of the measurements. Both compounds exhibit extensive hydrogen bonding, including involvement of the tetrachloridozincate anion, resulting in interconnected chains of anions joined by water molecules.

1. Chemical context

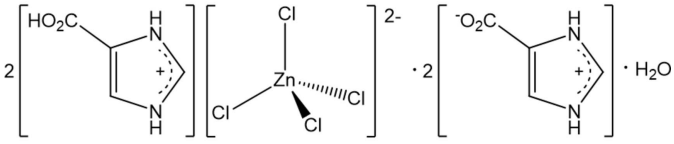
Imidazole-containing compounds find use in numerous pharmaceuticals including fungicides, antiviral agents, anti-arrhythmics, antihistamines, and anthelmintics (Varala *et al.*, 2007; Horton *et al.*, 2003; López-Rodríguez *et al.*, 1999). Recent studies have shown that imidazole and benzimidazole derivatives exhibit pharmacological activity in histamine signaling (Tichenor *et al.*, 2015; Marson, 2011), and act as tau aggregation inhibitors for Alzheimer's disease (Bulic *et al.*, 2013), and in the central nervous system (Robichaud *et al.*, 2011; Sheffler *et al.*, 2011). Further, derivatized imidazole-5-carboxylic acids have been shown to be angiotensin-converting enzyme (ACE) inhibitors (Jallapally *et al.*, 2015; Li *et al.*, 1998; Yanagisawa *et al.*, 1996).

As a result of the myriad binding modes available to imidazole ligands that bear carboxylic acid substituents, they have found use in the preparation of several metal organic frameworks, MOFs (Starosta & Leciejewicz, 2006; Yin *et al.*, 2009, 2012; Sun & Yang, 2007; Sun *et al.*, 2006). The synthesis and characterization of novel MOFs is an area of active research because of their potential use in such diverse areas as gas storage, catalysis, chemical sensors and molecular separation (Dey *et al.*, 2014; Kreno *et al.*, 2012; Farha & Hupp, 2010). Neutral carboxyimidazoles exist in their zwitterionic form and none of the reported compounds have the carboxyimidazole ligand in the fully protonated form. However, there are examples of MOFs with anionic repeating units and imidazolium cations (Shao & Yu, 2014; Wang *et al.*, 2013).

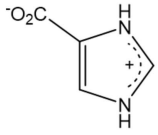




(I)



(II)



(III)

Although the structures of the zwitterionic 1*H*-imidazol-3-ium-4-carboxylate, (III), (Cao *et al.*, 2012) and the corresponding 2-isopropyl (Du *et al.*, 2011) and 2-methyl (Guo, 2009) derivatives have been reported, to our knowledge, fully protonated imidazolecarboxylic acid species have not been structurally characterized. Compounds (I) and (II) possess the carboxyimidazole in its fully protonated form and so contribute to the knowledge base of this class of compounds.

2. Structural commentary

Fig. 1 shows the atom-labeling scheme employed for (I). The asymmetric unit consists of two 4-carboxy-1*H*-imidazol-3-ium cations ($ImHCO_2H^+$), one tetrachloridozincate anion, and one water molecule. Thus, compound (I) is classified as a salt solvate (Grothe *et al.*, 2016) with four residues.

Compound (II) is an example of a rare co-crystal salt solvate with six residues (Grothe *et al.*, 2016). The asymmetric unit consists of two $ImHCO_2H^+$ cations, one tetrachloridozincate anion, two 1*H*-imidazol-3-ium-4-carboxylate zwitterions ($ImHCO_2$), and one water molecule. The atom-labeling scheme employed is shown in Fig. 2.

The geometric parameters determined for the tetrachloridozincate anions in (I) and (II) are found in Tables 1 and 2, respectively. The average Zn—Cl bond length is 2.273 (3) and 2.272 (15) Å, respectively, for (I) and (II), which are within the range 2.2409 (3)–2.3085 (7) Å found in other

Table 1
Selected geometric parameters (Å, °) for (I).

Zn1—Cl2	2.2690 (7)	O1—C1	1.313 (2)
Zn1—Cl3	2.2704 (6)	O2—C1	1.200 (2)
Zn1—Cl4	2.2737 (6)	O3—C5	1.305 (2)
Zn1—Cl1	2.2794 (6)	O4—C5	1.201 (3)
Cl2—Zn1—Cl3	107.93 (2)	Cl3—Zn1—Cl1	112.84 (2)
Cl2—Zn1—Cl4	111.11 (2)	Cl4—Zn1—Cl1	107.92 (2)
Cl3—Zn1—Cl4	109.21 (3)	O2—C1—O1	124.9 (2)
Cl2—Zn1—Cl1	107.85 (2)	O4—C5—O3	125.4 (2)
O2—C1—C2—N1	4.6 (3)	O4—C5—C6—N3	−1.8 (3)

Table 2
Selected geometric parameters (Å, °) for (II).

Zn1—Cl3	2.2577 (12)	O3—C8	1.220 (5)
Zn1—Cl4	2.2589 (11)	O4—C8	1.277 (5)
Zn1—Cl1	2.2758 (12)	O5—C12	1.274 (5)
Zn1—Cl2	2.2948 (12)	O6—C12	1.222 (5)
O1—C4	1.271 (4)	O7—C16	1.224 (5)
O2—C4	1.229 (4)	O8—C16	1.267 (5)
Cl3—Zn1—Cl4	111.21 (4)	Cl1—Zn1—Cl2	108.62 (5)
Cl3—Zn1—Cl1	112.42 (5)	O2—C4—O1	126.3 (4)
Cl4—Zn1—Cl1	109.31 (5)	O3—C8—O4	125.6 (4)
Cl3—Zn1—Cl2	104.23 (5)	O6—C12—O5	126.3 (4)
Cl4—Zn1—Cl2	110.95 (4)	O7—C16—O8	126.3 (4)
N2—C1—C4—O2	5.7 (6)	N5—C9—C12—O6	3.2 (6)
N3—C5—C8—O3	−2.3 (6)	N7—C13—C16—O7	6.3 (6)

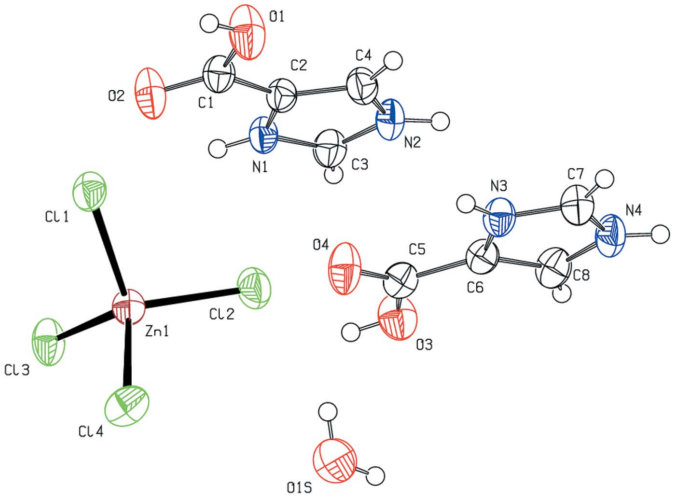


Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Non-hydrogen anisotropic displacement parameters are drawn at the 50% probability level.

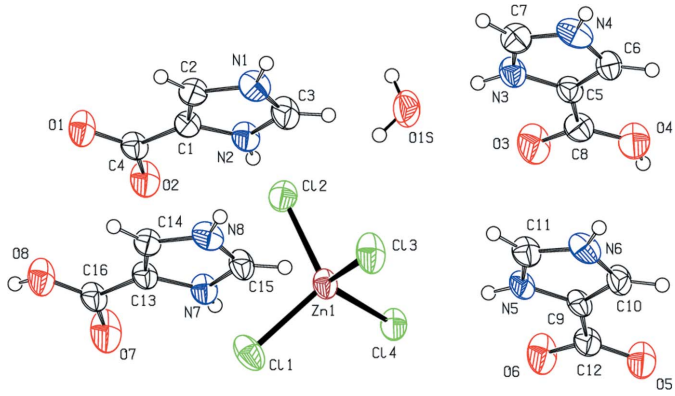


Figure 2
The molecular structure of (II), showing the atom-labeling scheme. Non-hydrogen anisotropic displacement parameters are drawn at the 50% probability level.

Table 3
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*S*—H1*SA*···Cl2	0.83 (2)	2.42 (2)	3.192 (3)	155 (4)
O1*S*—H1*SB*···Cl4^{i}	0.81 (2)	2.94 (4)	3.392 (2)	118 (3)
O1*S*—H1*SB*···Cl1^{ii}	0.81 (2)	3.05 (4)	3.540 (3)	122 (4)
O1—H1*A*···Cl4^{iii}	0.83 (2)	2.25 (2)	3.0723 (19)	171 (3)
O3—H3*A*···O1*S*^{iv}	0.83 (2)	1.77 (2)	2.576 (3)	163 (3)
N1—H1*N*···Cl1	0.84 (2)	2.37 (2)	3.2105 (17)	178 (2)
N2—H2*N*···Cl1^{i}	0.86 (2)	2.85 (2)	3.3787 (19)	122 (2)
N2—H2*N*···O2^{i}	0.86 (2)	1.99 (2)	2.745 (2)	146 (2)
N3—H3*N*···Cl3^{v}	0.83 (2)	2.37 (2)	3.1941 (18)	177 (2)
N4—H4*N*···Cl3^{vi}	0.86 (2)	2.83 (2)	3.3586 (19)	121 (2)
N4—H4*N*···O4^{i}	0.86 (2)	2.00 (2)	2.753 (2)	146 (2)

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

examples of tetrachloridozincate salts (Govindan *et al.*, 2014*a*,*b*; Leesakul *et al.*, 2012; Goh *et al.*, 2012; Kefi *et al.*, 2011). The same example structures exhibit Cl—Zn—Cl angles in the range 102.256 (10) to 112.72 (3)°. The average angles found in (I) and (II) are 109 (2)° and 109 (3)°, respectively, and the individual values exhibit comparable ranges (Tables 1 and 2).

There are no noteworthy differences in the C—C and C—N bond lengths between the $ImHCO_2H^+$ cations and $ImHCO_2$ zwitterions found in (I) and (II). The N—C′ bond length, where C′ is the carbon atom bonded to both nitrogen atoms in a given ring (formally, the 2 position in the ring), is consistently shorter than the N—C″ bond length, where C″ represents the carbon in the formal 4 or 5 position in the ring, for all of the $ImHCO_2H^+$ and $ImHCO_2$ residues. This observation is consistent with other reported imidazoles and imidazolium salts (*e.g.*, Mohamed *et al.*, 2014; Trifa *et al.*, 2013; Chérif *et al.*, 2013; Yu, 2012; Zhu, 2012).

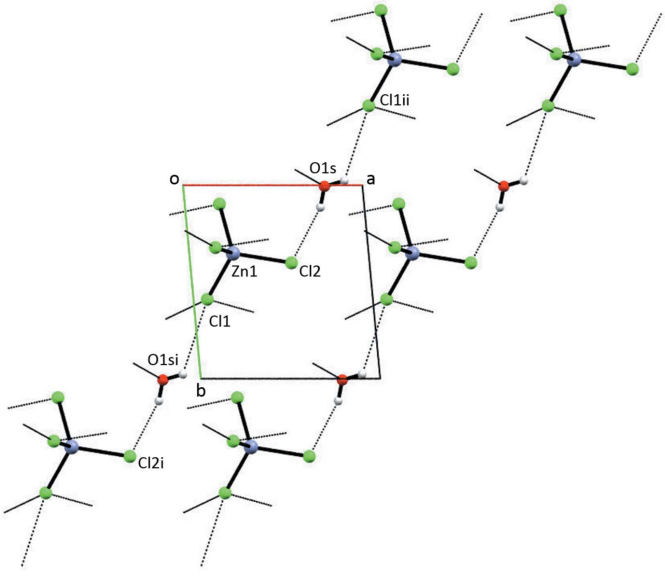


Figure 3
Partial packing diagram of (I), showing the water–tetrachloridozincate chains. Only the tetrachloridozincate anion and the water of hydration are shown.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O5^{i}	0.87 (2)	1.63 (2)	2.476 (4)	163 (5)
O4—H4*A*···O6^{i}	0.87 (2)	2.52 (4)	3.205 (4)	136 (4)
O8—H8*A*···O1^{ii}	0.85 (2)	1.65 (2)	2.484 (4)	166 (5)
O8—H8*A*···O2^{ii}	0.85 (2)	2.63 (4)	3.162 (4)	122 (4)
O1*S*—H1*A*···Cl2	0.85 (2)	2.52 (5)	3.330 (9)	159 (10)
O1*S*—H1*B*···Cl1^{iii}	0.84 (2)	2.97 (9)	3.546 (15)	128 (10)
O1*S*—H1*B*···Cl4^{iii}	0.84 (2)	2.93 (7)	3.499 (11)	127 (8)
O2*S*—H2*A*···Cl2	0.85 (2)	2.61 (12)	3.382 (17)	150.20
O2*S*—H2*B*···Cl1^{iii}	0.85 (2)	2.36 (10)	3.13 (2)	150 (17)
N1—H1*N*···O2^{iv}	0.88 (2)	1.86 (2)	2.712 (4)	160 (4)
N2—H2*N*···Cl2	0.87 (2)	2.44 (2)	3.297 (3)	167 (4)
N3—H3*N*···O1*S*	0.87 (2)	2.01 (2)	2.860 (10)	168 (4)
N3—H3*N*···O2*S*	0.87 (2)	1.89 (2)	2.739 (12)	165 (4)
N4—H4*N*···O3^{iv}	0.85 (2)	1.92 (3)	2.677 (5)	148 (4)
N5—H5*N*···Cl4	0.86 (2)	2.39 (2)	3.247 (3)	173 (4)
N6—H6*N*···O6^{iv}	0.87 (2)	1.85 (3)	2.661 (4)	156 (4)
N7—H7*N*···Cl1	0.89 (2)	2.32 (2)	3.205 (3)	175 (4)
N8—H8*N*···O7^{iv}	0.87 (2)	1.78 (2)	2.628 (4)	164 (4)

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

The carboxy and carboxylate groups are tilted slightly from the imidazole plane in all cases. The N—C—C—O torsion angles are reported in Tables 1 and 2. In both (I) and (II), the carboxy and carboxylate groups are unsymmetrical. For the carboxy groups, the C—OH bond is longer than the C=O bond. These observations are consistent with the geometric parameters found in similar imidazolecarboxylic acids (Cao *et al.*, 2012; Du *et al.*, 2011; Guo, 2009). The observed O—C—O bond angles of the fully protonated form in (I) and (II) and the zwitterionic form in (II) are the same within the standard uncertainties of the refinement.

3. Supramolecular features

An extensive hydrogen-bonding network in (I) involving the tetrachloridozincate anion and the water of hydration results in chains parallel to [2$\bar{2}$0], as seen in Fig. 3 and Table 3. Additional Cl···H—O—H···Cl interactions along [100] join

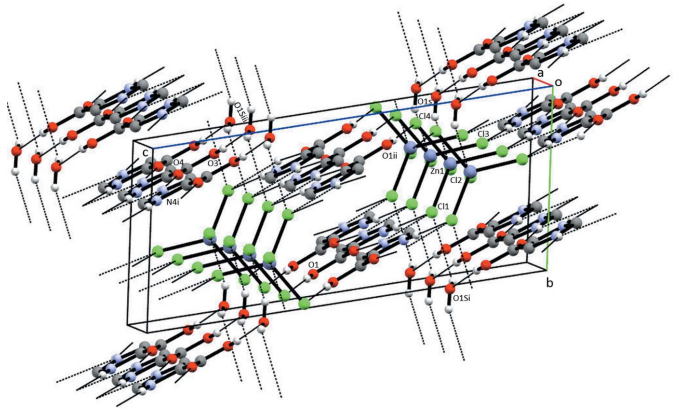


Figure 4
Packing diagram of (I), showing the hydrogen-bonding scheme. Only H atoms involved in the interactions are shown.

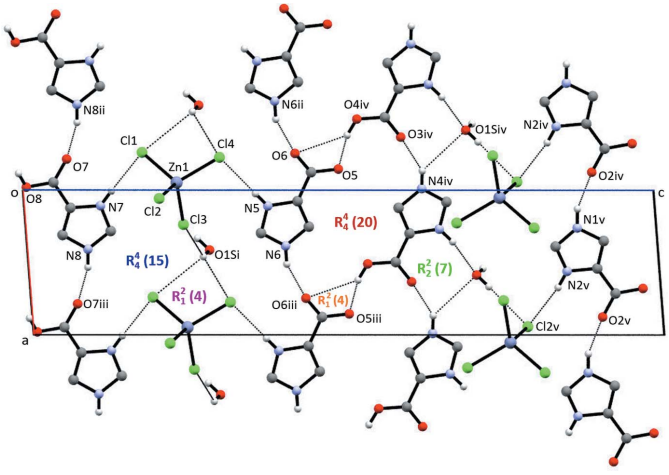


Figure 5
A view of the hydrogen bonding in (II), showing the ring motifs. Only H atoms involved in the interactions are shown. Only the major contributor to the disorder model of the water molecule is shown.

the chains (Fig. 4). N—H···O(water), N—H···Cl, and O—H···O hydrogen bonds incorporate the $ImHCO_2H^+$ cations into the three-dimensional extended structure. Using graph-set analysis to describe the hydrogen bonding (Etter *et al.*, 1990), an $R_4^4(20)$ ring is observed with four oxygen acceptors, two oxygen donors and two nitrogen donors. One oxygen donor, two oxygen acceptor rings, $R_1^2(4)$, involving a carboxy group are also present.

Figs. 5 and 6 show two views of the crystal packing observed in (II). Hydrogen-bonding parameters are found in Table 4. As seen in Fig. 5, there are several hydrogen-bonding ring motifs that are common to (I) and (II). An $R_4^4(20)$ ring is observed with four oxygen acceptors, two oxygen donors and two nitrogen donors, and there is a one oxygen donor, two oxygen acceptor ring, $R_1^2(4)$, involving a carboxy group. $R_2^2(7)$ rings involving two nitrogen donors and two oxygen acceptors are also observed. There are two rings containing chlorine acceptor atoms: an $R_4^4(15)$ system with one oxygen donor, three nitrogen donors, one oxygen acceptor and three chlorine acceptors; and an $R_1^2(4)$ ring with a single oxygen donor and two chlorine acceptors. Similarly to (I), chains of hydrogen-bonded tetrachloridozincate anions and water molecules of hydration are found parallel to $[2\bar{2}0]$.

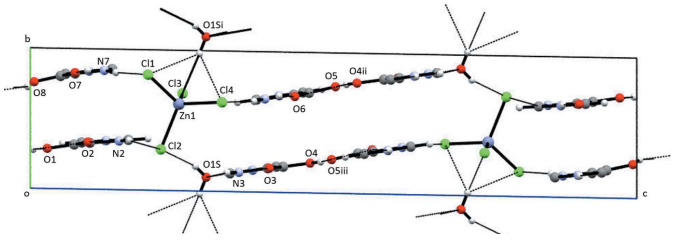


Figure 6
A second view of the hydrogen bonding in (II). Only H atoms involved in the hydrogen bonds are shown. Only the major contributor to the disorder model of the water molecule is shown.

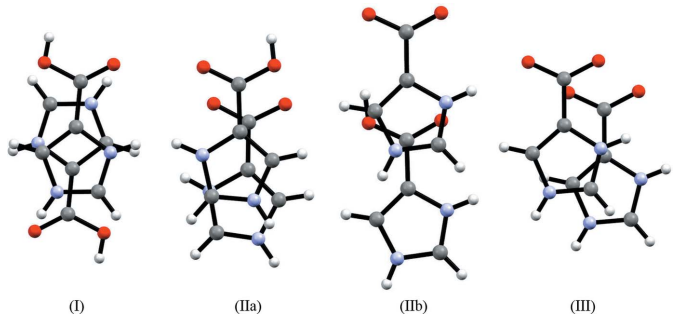


Figure 7
Projections of π-stacked molecules. The molecules are related by the symmetry transformations (I) $-x+1, -y+1, -z+1$; (IIa) x, y, z; (IIb) $x+1, y-1, z$; (III) $x, y, z+1$.

In (I), a weak π–π interaction between $ImHCO_2H^+$ cations related by a crystallographically imposed center of symmetry is observed with a centroid-to-centroid distance of 3.5781 (15) Å and an interplanar distance of 3.4406 (9) Å, corresponding to 0.983 Å slippage (Spek, 2009). Two independent weak π–π interactions between $ImHCO_2H^+$ cations and $ImHCO_2$ zwitterions are observed in (II). The principal one involves the rings containing N1 and N7 with a centroid-to-centroid distance of 3.5871 (3) Å, an interplanar distance of 3.3591 (18) Å and a dihedral angle of 2.6 (2)° between rings (Spek, 2009). The weaker π–π interaction involves the rings containing N3 and N5 and has a centroid-to-centroid distance of 3.740 (3) Å, an interplanar distance of 3.3140 (17) Å and a dihedral angle of 1.2 (2) Å between planes.

Fig. 7 shows representations of the observed π stacking in which members of interacting pairs of molecules are projected into the same plane. A π–π interaction is also observed in the solid-state structure of the $ImHCO_2$ zwitterion, labeled (III) (Cao *et al.*, 2012). In (III), the centroid–centroid distance is longer [3.674 (4) Å] than that observed between the fully protonated form in (I) and the principal interaction between the zwitterion and the protonated form in (II). In all of the pairs except in (I), the members of the pairs are arranged in a head-to-head configuration.

4. Database survey

The structure of 1-*H*-imidazol-3-ium-4-carboxylate has been reported (Cao *et al.*, 2012) and the structures of the 2-methyl and 2-isopropyl derivatives of the zwitterion 5-carboxy-1*H*-3-ium-4-carboxylate monohydrate have been reported (Guo, 2009; Du *et al.*, 2011). Several polymeric compounds with bridging 1*H*-imidazole-4-carboxylato ligands have been reported, including one with Ca^{II} (Starosta & Leciejewicz, 2006) and two with Cd^{II} (Yin *et al.*, 2009, 2012). The structures of monomeric compounds with 1*H*-imidazole-4-carboxylato-κ^2N,O ligands and Mg^{II} (Gryz *et al.*, 2007), Mn^{II} (Xiong *et al.*, 2013), Co^{II} (Chen, 2012; Artetxe *et al.*, 2013), Ni^{II} (Zheng *et al.*, 2011), Cu^{II} (Reinoso *et al.*, 2015), and Zn^{II} (Gryz *et al.*, 2007; He, 2006; Shuai *et al.*, 2011) have been determined. Tetranuclear Mn^{II} complexes with 1*H*-imidazole-4-carboxylato-κ^2N,O and the structurally similar 4-imidazoleacetate ligand

Table 5
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$(C_4H_5N_2O_2)_2[ZnCl_4]\cdot H_2O$	$(C_4H_4N_2O_2)_2[ZnCl_4]\cdot 2C_4H_5N_2O_2H_2O$
M_r	451.39	675.57
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	200	200
a, b, c (Å)	6.9094 (10), 7.5828 (12), 16.468 (3)	6.9369 (19), 6.9624 (15), 28.483 (8)
α, β, γ (°)	79.455 (4), 84.489 (4), 83.833 (4)	89.524 (9), 85.622 (9), 71.202 (8)
V (Å^3)	840.7 (2)	1298.3 (6)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.12	1.42
Crystal size (mm)	0.60 × 0.50 × 0.20	0.50 × 0.25 × 0.20
Data collection		
Diffractometer	Bruker SMART X2S benchtop	Bruker SMART X2S benchtop
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.41, 0.68	0.50, 0.76
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10429, 3375, 2995	10560, 4855, 3619
R_{int}	0.032	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.616
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.064, 1.03	0.050, 0.135, 1.03
No. of reflections	3375	4855
No. of parameters	227	395
No. of restraints	8	16
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, −0.28	0.63, −0.71

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

have also been characterized (Boskovic *et al.*, 2000). The structures of numerous imidazolium salts are known (*e.g.*, Mohamed *et al.*,, 2014; Trifa *et al.*, 2013; Chérif *et al.*, 2013; Yu, 2012; Zhu, 2012; Ishida & Kashino, 2001; Gili *et al.*, 2000; Pavan Kumar & Kumara Swamy, 2005; Hashizume *et al.*, 2001; Moreno-Fuquen *et al.*, 2009*a*,*b*, 2011; Zhang *et al.*, 2011; Sun *et al.*, 2002; Fukunaga & Ishida, 2003). There are many examples of reported structures of tetrachloridozincate salts (*e.g.*, Govindan *et al.*, 2014*a*,*b*; Leesakul *et al.*, 2012; Goh *et al.*, 2012; Kefi *et al.*, 2011).

5. Synthesis and crystallization

Compounds (I) and (II) were obtained during the attempted syntheses of Zn^{II} coordination polymers. (I) was obtained by dissolving 113 mg (0.829 mmol) $ZnCl_2$ and 194 mg (1.73 mmol) 1*H*-imidazole-4-carboxylic acid in ethanol. Six drops of 6 *M* HCl were added and the mixture was heated to reflux with stirring. The warm solution was filtered and the filtrate was allowed to cool. After a few days, crystalline clumps of the product were obtained. ^{1}H NMR (400 MHz, dmso-d_6, p.p.m.): 7.97 (*s*, 2H), 8.51 (*s*, 2H). ^{13}C NMR (100 MHz, dmso-d_6, p.p.m.): 126.1, 127.4, 137.7, 161.3. A crystal cut from a larger mass of crystals was used for X-ray analysis.

Compound (II) was prepared similarly to (I) except that methanol was the solvent and no HCl was added to the reaction mixture. Single crystals for X-ray analysis were obtained by slow evaporation of a methanol solution.^{1}H NMR (400 MHz, dmso-d_6, p.p.m.): 8.15 (*s*, 4H), 8.95 (*s*, 4H). ^{13}C NMR (100 MHz, dmso-d_6, p.p.m.): 125.4, 126.1, 137.6, 160.3.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. For (I), data completeness was 97.9% and for (II) it was 95.2%. For both (I) and (II), all hydrogen atoms were located in difference Fourier maps. The hydrogen atoms bonded to carbon were refined using a riding model with a C—H distance of 0.95 Å and hydrogen-atom isotropic displacement parameters were set using the approximation U_{iso}(H) = 1.2U_{eq}(C). The O—H and N—H distances were restrained to 0.84 and 0.88 Å, respectively. The isotropic displacement parameters of the hydrogen atoms bonded to nitrogen were set using the approximation U_{iso}(H) = 1.2U_{eq}(N). In (I), isotropic displacement parameters of the hydrogen atoms bonded to oxygen were refined freely, but for (II) they were set using the approximation U_{iso}(H) = 1.5U_{eq}(O). For (II), the water molecule is disordered over two positions. In addition to the aforementioned distance restraint,

an H—O—H angle restraint of 105° was employed. The occupancies refined to 0.60 (4):0.40 (4).

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Structural characterization of two tetrachloridozincate salts of 4-carboxy-1*H*-imidazol-3-ium: a salt hydrate and a co-crystal salt hydrate

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Computing details

For both compounds, data collection: *APEX2* (Bruker, 2013); cell refinement: *APEX2* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(I) Bis(4-carboxy-1*H*-imidazol-3-ium) tetrachloridozincate monohydrate

Crystal data

$(C_4H_5N_2O_2)_2[ZnCl_4]\cdot H_2O$
M_r = 451.39
Triclinic, $P\overline{1}$
a = 6.9094 (10) Å
b = 7.5828 (12) Å
c = 16.468 (3) Å
α = 79.455 (4)°
β = 84.489 (4)°
γ = 83.833 (4)°
V = 840.7 (2) Å^3
Z = 2
$F(000)$ = 452
D_x = 1.783 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6894 reflections
θ = 2.5–27.5°
μ = 2.12 mm^{-1}
T = 200 K
Plate, clear colourless
0.60 × 0.50 × 0.20 mm

Data collection

Bruker SMART X2S benchtop diffractometer
Radiation source: sealed microfocus tube
Doubly curved silicon crystal monochromator
Detector resolution: 8.3330 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.41, T_{max} = 0.68
10429 measured reflections
3375 independent reflections
2995 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 26.4°, θ_{min} = 2.5°
h = −8→8
k = −9→9
l = −20→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.064
S = 1.03
3375 reflections
227 parameters
8 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.2531P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ 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	0.24426 (3)	0.35245 (3)	0.23892 (2)	0.03225 (8)
Cl1	0.07702 (7)	0.58951 (7)	0.29003 (3)	0.04037 (13)
Cl2	0.56514 (8)	0.40109 (8)	0.22143 (4)	0.04596 (14)
Cl3	0.14855 (8)	0.32216 (8)	0.11448 (3)	0.04391 (14)
Cl4	0.19391 (9)	0.09768 (8)	0.33224 (3)	0.04754 (14)
O1S	0.7881 (4)	0.0065 (3)	0.25272 (16)	0.0744 (6)
H1SA	0.755 (6)	0.114 (3)	0.256 (2)	0.113 (16)*
H1SB	0.902 (3)	−0.023 (6)	0.241 (3)	0.112 (17)*
O1	0.2088 (3)	0.8341 (3)	0.57654 (11)	0.0583 (5)
H1A	0.096 (3)	0.846 (4)	0.5976 (19)	0.080 (11)*
O2	0.0547 (2)	0.7334 (2)	0.48378 (10)	0.0499 (4)
O3	0.4700 (2)	0.1089 (2)	0.82247 (10)	0.0488 (4)
H3A	0.371 (3)	0.082 (4)	0.8047 (18)	0.068 (9)*
O4	0.2491 (2)	0.1786 (3)	0.92209 (10)	0.0509 (4)
N1	0.4180 (2)	0.6761 (2)	0.39214 (10)	0.0328 (4)
H1N	0.328 (3)	0.656 (3)	0.3653 (13)	0.039*
N2	0.7041 (3)	0.6977 (3)	0.42572 (12)	0.0398 (4)
H2N	0.830 (2)	0.694 (3)	0.4249 (15)	0.048*
N3	0.5549 (2)	0.2595 (2)	1.00903 (11)	0.0354 (4)
H3N	0.448 (3)	0.280 (3)	1.0351 (14)	0.042*
N4	0.8615 (3)	0.2308 (3)	0.97687 (12)	0.0414 (4)
H4N	0.985 (2)	0.234 (3)	0.9774 (16)	0.05*
C1	0.2014 (3)	0.7670 (3)	0.50896 (12)	0.0340 (4)
C2	0.3956 (3)	0.7354 (3)	0.46709 (12)	0.0304 (4)
C3	0.6053 (3)	0.6554 (3)	0.36821 (13)	0.0374 (5)
H3	0.6597	0.6168	0.3185	0.045*
C4	0.5780 (3)	0.7487 (3)	0.48777 (13)	0.0365 (4)
H4	0.6113	0.7864	0.5362	0.044*
C5	0.4145 (3)	0.1639 (3)	0.89239 (12)	0.0352 (4)
C6	0.5806 (3)	0.2008 (3)	0.93398 (12)	0.0320 (4)
C7	0.7275 (3)	0.2773 (3)	1.03332 (14)	0.0404 (5)
H7	0.7507	0.3166	1.0828	0.048*
C8	0.7758 (3)	0.1833 (3)	0.91435 (13)	0.0395 (5)
H8	0.8402	0.1452	0.8661	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03082 (14)	0.03910 (14)	0.02828 (13)	−0.00235 (10)	−0.00091 (9)	−0.01089 (10)
Cl1	0.0302 (3)	0.0506 (3)	0.0444 (3)	0.0027 (2)	−0.0016 (2)	−0.0234 (2)
Cl2	0.0303 (3)	0.0544 (3)	0.0579 (3)	−0.0051 (2)	−0.0010 (2)	−0.0226 (3)
Cl3	0.0329 (3)	0.0699 (4)	0.0337 (3)	−0.0025 (2)	−0.0048 (2)	−0.0219 (2)
Cl4	0.0491 (3)	0.0446 (3)	0.0421 (3)	0.0028 (2)	0.0056 (2)	0.0016 (2)
O1S	0.0736 (16)	0.0632 (14)	0.0966 (17)	0.0020 (12)	−0.0382 (14)	−0.0293 (12)
O1	0.0376 (10)	0.0984 (14)	0.0484 (10)	−0.0049 (9)	−0.0019 (8)	−0.0392 (10)
O2	0.0282 (8)	0.0812 (12)	0.0462 (9)	−0.0099 (8)	−0.0035 (7)	−0.0234 (8)
O3	0.0444 (10)	0.0668 (11)	0.0403 (9)	−0.0072 (8)	−0.0005 (7)	−0.0231 (8)
O4	0.0276 (8)	0.0815 (12)	0.0447 (9)	−0.0031 (8)	−0.0002 (7)	−0.0164 (8)
N1	0.0264 (9)	0.0406 (9)	0.0332 (9)	−0.0024 (7)	−0.0075 (7)	−0.0089 (7)
N2	0.0227 (9)	0.0491 (10)	0.0480 (10)	−0.0037 (8)	−0.0042 (8)	−0.0081 (8)
N3	0.0266 (9)	0.0453 (10)	0.0340 (9)	−0.0015 (8)	0.0024 (7)	−0.0098 (8)
N4	0.0235 (9)	0.0515 (11)	0.0478 (11)	−0.0049 (8)	−0.0014 (8)	−0.0046 (9)
C1	0.0316 (11)	0.0408 (11)	0.0299 (10)	−0.0025 (9)	−0.0045 (8)	−0.0064 (8)
C2	0.0286 (10)	0.0335 (10)	0.0297 (9)	−0.0016 (8)	−0.0055 (8)	−0.0060 (8)
C3	0.0308 (11)	0.0429 (11)	0.0383 (11)	−0.0020 (9)	−0.0016 (9)	−0.0080 (9)
C4	0.0323 (11)	0.0411 (11)	0.0381 (11)	−0.0051 (9)	−0.0085 (9)	−0.0082 (9)
C5	0.0343 (12)	0.0373 (11)	0.0324 (10)	−0.0011 (9)	−0.0016 (8)	−0.0034 (8)
C6	0.0295 (11)	0.0351 (10)	0.0298 (9)	−0.0017 (8)	0.0008 (8)	−0.0043 (8)
C7	0.0330 (12)	0.0484 (12)	0.0410 (11)	−0.0048 (9)	−0.0045 (9)	−0.0094 (10)
C8	0.0310 (11)	0.0479 (12)	0.0369 (11)	−0.0013 (9)	0.0063 (9)	−0.0062 (9)

Geometric parameters (Å, º)

Zn1—Cl2	2.2690 (7)	N2—C4	1.362 (3)
Zn1—Cl3	2.2704 (6)	N2—H2N	0.864 (16)
Zn1—Cl4	2.2737 (6)	N3—C7	1.321 (3)
Zn1—Cl1	2.2794 (6)	N3—C6	1.378 (2)
O1S—H1SA	0.829 (19)	N3—H3N	0.830 (16)
O1S—H1SB	0.806 (18)	N4—C7	1.316 (3)
O1—C1	1.313 (2)	N4—C8	1.356 (3)
O1—H1A	0.828 (18)	N4—H4N	0.858 (16)
O2—C1	1.200 (2)	C1—C2	1.465 (3)
O3—C5	1.305 (2)	C2—C4	1.355 (3)
O3—H3A	0.827 (17)	C3—H3	0.95
O4—C5	1.201 (3)	C4—H4	0.95
N1—C3	1.317 (3)	C5—C6	1.468 (3)
N1—C2	1.379 (2)	C6—C8	1.354 (3)
N1—H1N	0.838 (16)	C7—H7	0.95
N2—C3	1.323 (3)	C8—H8	0.95
Cl2—Zn1—Cl3	107.93 (2)	O1—C1—C2	112.04 (17)
Cl2—Zn1—Cl4	111.11 (2)	C4—C2—N1	106.33 (17)
Cl3—Zn1—Cl4	109.21 (3)	C4—C2—C1	132.70 (18)

Cl2—Zn1—Cl1	107.85 (2)	N1—C2—C1	120.95 (17)
Cl3—Zn1—Cl1	112.84 (2)	N1—C3—N2	107.86 (18)
Cl4—Zn1—Cl1	107.92 (2)	N1—C3—H3	126.1
H1SA—O1S—H1SB	119 (4)	N2—C3—H3	126.1
C1—O1—H1A	107 (2)	C2—C4—N2	106.69 (18)
C5—O3—H3A	107 (2)	C2—C4—H4	126.7
C3—N1—C2	109.33 (16)	N2—C4—H4	126.7
C3—N1—H1N	124.5 (16)	O4—C5—O3	125.4 (2)
C2—N1—H1N	126.2 (16)	O4—C5—C6	122.53 (18)
C3—N2—C4	109.79 (17)	O3—C5—C6	112.00 (18)
C3—N2—H2N	125.9 (17)	C8—C6—N3	106.23 (18)
C4—N2—H2N	124.3 (17)	C8—C6—C5	132.12 (18)
C7—N3—C6	109.06 (17)	N3—C6—C5	121.61 (17)
C7—N3—H3N	125.3 (17)	N4—C7—N3	107.89 (19)
C6—N3—H3N	125.6 (17)	N4—C7—H7	126.1
C7—N4—C8	110.01 (18)	N3—C7—H7	126.1
C7—N4—H4N	126.0 (17)	C6—C8—N4	106.81 (18)
C8—N4—H4N	123.9 (17)	C6—C8—H8	126.6
O2—C1—O1	124.9 (2)	N4—C8—H8	126.6
O2—C1—C2	123.11 (18)		

C3—N1—C2—C4	−0.3 (2)	C7—N3—C6—C8	0.2 (2)
C3—N1—C2—C1	−178.98 (18)	C7—N3—C6—C5	178.29 (19)
O2—C1—C2—C4	−173.6 (2)	O4—C5—C6—C8	175.7 (2)
O1—C1—C2—C4	6.0 (3)	O3—C5—C6—C8	−2.2 (3)
O2—C1—C2—N1	4.6 (3)	O4—C5—C6—N3	−1.8 (3)
O1—C1—C2—N1	−175.81 (19)	O3—C5—C6—N3	−179.68 (18)
C2—N1—C3—N2	0.6 (2)	C8—N4—C7—N3	0.5 (3)
C4—N2—C3—N1	−0.6 (2)	C6—N3—C7—N4	−0.5 (3)
N1—C2—C4—N2	−0.1 (2)	N3—C6—C8—N4	0.1 (2)
C1—C2—C4—N2	178.4 (2)	C5—C6—C8—N4	−177.7 (2)
C3—N2—C4—C2	0.4 (2)	C7—N4—C8—C6	−0.4 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*S*—H1*SA*···Cl2	0.83 (2)	2.42 (2)	3.192 (3)	155 (4)
O1*S*—H1*SB*···Cl4^{i}	0.81 (2)	2.94 (4)	3.392 (2)	118 (3)
O1*S*—H1*SB*···Cl1^{ii}	0.81 (2)	3.05 (4)	3.540 (3)	122 (4)
O1—H1*A*···Cl4^{iii}	0.83 (2)	2.25 (2)	3.0723 (19)	171 (3)
O3—H3*A*···O1*S*^{iv}	0.83 (2)	1.77 (2)	2.576 (3)	163 (3)
N1—H1*N*···Cl1	0.84 (2)	2.37 (2)	3.2105 (17)	178 (2)
N2—H2*N*···Cl1^{i}	0.86 (2)	2.85 (2)	3.3787 (19)	122 (2)
N2—H2*N*···O2^{i}	0.86 (2)	1.99 (2)	2.745 (2)	146 (2)
N3—H3*N*···Cl3^{v}	0.83 (2)	2.37 (2)	3.1941 (18)	177 (2)

N4—H4*N*···Cl3^{vi}	0.86 (2)	2.83 (2)	3.3586 (19)	121 (2)
N4—H4*N*···O4^{i}	0.86 (2)	2.00 (2)	2.753 (2)	146 (2)

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

(II) bis(4-carboxy-1*H*-imidazol-3-ium) tetrachloridozincate bis(1*H*-imidazol-3-ium-4-carboxylato) monohydrate

Crystal data

$(C_4H_4N_2O_2)_2[ZnCl_4]\cdot 2C_4H_5N_2O_2H_2O$
M_r = 675.57
Triclinic, $P\overline{1}$
a = 6.9369 (19) Å
b = 6.9624 (15) Å
c = 28.483 (8) Å
α = 89.524 (9)°
β = 85.622 (9)°
γ = 71.202 (8)°
V = 1298.3 (6) Å^3
Z = 2
F(000) = 684
D_x = 1.728 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3388 reflections
θ = 3.1–23.6°
μ = 1.42 mm^{-1}
T = 200 K
Block, clear colourless
0.50 × 0.25 × 0.20 mm

Data collection

Bruker SMART X2S benchtop diffractometer
Radiation source: sealed microfocus tube
Detector resolution: 8.3330 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.50, T_{max} = 0.76
10560 measured reflections
4855 independent reflections
3619 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 26.0°, θ_{min} = 2.9°
h = −8→8
k = −8→7
l = −35→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.135
S = 1.03
4855 reflections
395 parameters
16 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 0.0203P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Zn1	−0.05225 (7)	0.61778 (7)	0.24502 (2)	0.03731 (17)	
Cl1	−0.26017 (17)	0.82285 (19)	0.19411 (4)	0.0531 (3)	
Cl2	0.05785 (16)	0.29226 (16)	0.21504 (3)	0.0436 (3)	
Cl3	0.23787 (18)	0.6937 (2)	0.25097 (4)	0.0560 (3)	

Cl4	−0.22620 (16)	0.63506 (17)	0.31606 (3)	0.0408 (3)	
O1	0.3219 (4)	0.2856 (5)	0.02796 (9)	0.0471 (8)	
O2	0.1247 (4)	0.3358 (5)	0.09533 (10)	0.0517 (8)	
O3	0.3667 (5)	0.1705 (6)	0.39393 (12)	0.0661 (10)	
O4	0.4907 (5)	0.2123 (5)	0.46135 (10)	0.0559 (9)	
H4A	0.379 (5)	0.223 (8)	0.4788 (16)	0.084*	
O5	−0.1453 (5)	0.7598 (5)	0.50318 (10)	0.0537 (8)	
O6	−0.2533 (5)	0.6845 (6)	0.43625 (10)	0.0615 (9)	
O7	−0.2136 (5)	0.8281 (6)	0.07375 (11)	0.0685 (10)	
O8	−0.0196 (5)	0.7583 (5)	0.00627 (10)	0.0508 (8)	
H8A	−0.114 (6)	0.723 (8)	−0.0045 (16)	0.076*	
O1S	0.414 (2)	0.099 (2)	0.2899 (6)	0.070 (4)	0.60 (4)
H1A	0.334 (16)	0.176 (12)	0.272 (3)	0.105*	0.60 (4)
H1B	0.459 (16)	−0.021 (6)	0.279 (3)	0.105*	0.60 (4)
O2S	0.495 (5)	0.150 (4)	0.2703 (12)	0.093 (10)	0.40 (4)
H2A	0.381 (15)	0.15 (3)	0.262 (8)	0.14*	0.40 (4)
H2B	0.59 (2)	0.08 (3)	0.251 (5)	0.14*	0.40 (4)
N1	0.7400 (5)	0.3481 (6)	0.12509 (13)	0.0451 (9)	
H1N	0.870 (3)	0.342 (7)	0.1225 (15)	0.054*	
N2	0.4407 (5)	0.3466 (6)	0.14633 (11)	0.0392 (8)	
H2N	0.328 (4)	0.352 (6)	0.1626 (12)	0.047*	
N3	0.7314 (6)	0.1382 (5)	0.34378 (11)	0.0405 (8)	
H3N	0.644 (5)	0.134 (6)	0.3241 (12)	0.049*	
N4	1.0110 (6)	0.1551 (6)	0.36673 (14)	0.0460 (9)	
H4N	1.133 (4)	0.158 (7)	0.3638 (15)	0.055*	
N5	0.1092 (5)	0.6640 (5)	0.38684 (11)	0.0370 (8)	
H5N	0.024 (5)	0.646 (6)	0.3686 (12)	0.044*	
N6	0.3850 (5)	0.6882 (6)	0.41028 (12)	0.0437 (9)	
H6N	0.511 (4)	0.687 (7)	0.4100 (15)	0.052*	
N7	0.1081 (5)	0.8476 (5)	0.12179 (11)	0.0370 (8)	
H7N	0.006 (5)	0.834 (6)	0.1409 (12)	0.044*	
N8	0.4083 (5)	0.8406 (5)	0.09664 (12)	0.0392 (8)	
H8N	0.533 (4)	0.846 (6)	0.0945 (14)	0.047*	
C1	0.4601 (6)	0.3304 (6)	0.09817 (12)	0.0317 (9)	
C2	0.6497 (6)	0.3318 (6)	0.08465 (14)	0.0403 (10)	
H2	0.7095	0.3232	0.0533	0.048*	
C3	0.6112 (6)	0.3560 (7)	0.16165 (15)	0.0463 (11)	
H3	0.6366	0.3667	0.1937	0.056*	
C4	0.2872 (6)	0.3160 (6)	0.07221 (13)	0.0352 (9)	
C5	0.7016 (6)	0.1709 (6)	0.39137 (13)	0.0349 (9)	
C6	0.8780 (6)	0.1832 (6)	0.40570 (13)	0.0385 (9)	
H6	0.9044	0.207	0.437	0.046*	
C7	0.9189 (7)	0.1297 (6)	0.32923 (14)	0.0443 (10)	
H7	0.9775	0.1092	0.2977	0.053*	
C8	0.5038 (7)	0.1835 (6)	0.41683 (14)	0.0412 (10)	
C9	0.0765 (6)	0.6982 (6)	0.43471 (12)	0.0332 (9)	
C10	0.2521 (6)	0.7147 (6)	0.44949 (13)	0.0411 (10)	
H10	0.2774	0.7396	0.4808	0.049*	

C11	0.2965 (6)	0.6581 (7)	0.37284 (14)	0.0415 (10)
H11	0.357	0.6361	0.3415	0.05*
C12	−0.1239 (6)	0.7129 (6)	0.45951 (13)	0.0387 (9)
C13	0.1228 (6)	0.8218 (6)	0.07366 (12)	0.0327 (9)
C14	0.3108 (6)	0.8187 (6)	0.05808 (13)	0.0359 (9)
H14	0.3661	0.804	0.0262	0.043*
C15	0.2828 (6)	0.8583 (6)	0.13502 (13)	0.0395 (10)
H15	0.313	0.8756	0.1664	0.047*
C16	−0.0527 (6)	0.8025 (6)	0.04986 (13)	0.0371 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0263 (3)	0.0572 (3)	0.0303 (2)	−0.0159 (2)	−0.00276 (18)	0.0010 (2)
Cl1	0.0298 (6)	0.0833 (8)	0.0449 (6)	−0.0162 (6)	−0.0066 (4)	0.0210 (5)
Cl2	0.0350 (6)	0.0569 (7)	0.0396 (5)	−0.0163 (5)	0.0002 (4)	−0.0053 (4)
Cl3	0.0384 (7)	0.0955 (9)	0.0465 (6)	−0.0383 (7)	−0.0061 (5)	0.0008 (6)
Cl4	0.0300 (6)	0.0627 (7)	0.0325 (5)	−0.0195 (5)	0.0005 (4)	−0.0008 (4)
O1	0.0278 (17)	0.083 (2)	0.0384 (15)	−0.0286 (17)	−0.0010 (12)	−0.0070 (14)
O2	0.0223 (16)	0.092 (2)	0.0451 (16)	−0.0247 (17)	0.0012 (12)	−0.0051 (15)
O3	0.034 (2)	0.106 (3)	0.067 (2)	−0.032 (2)	−0.0113 (16)	−0.0099 (19)
O4	0.0332 (19)	0.089 (2)	0.0449 (18)	−0.0209 (19)	0.0054 (13)	−0.0038 (16)
O5	0.0321 (18)	0.090 (2)	0.0411 (16)	−0.0239 (18)	0.0005 (13)	−0.0055 (15)
O6	0.0292 (18)	0.112 (3)	0.0530 (18)	−0.035 (2)	−0.0055 (14)	−0.0124 (18)
O7	0.0241 (18)	0.138 (3)	0.0505 (18)	−0.036 (2)	0.0012 (14)	−0.0083 (19)
O8	0.0326 (18)	0.086 (2)	0.0427 (16)	−0.0312 (18)	−0.0062 (13)	−0.0057 (15)
O1S	0.042 (6)	0.110 (6)	0.048 (6)	−0.008 (5)	−0.014 (5)	−0.020 (4)
O2S	0.060 (14)	0.130 (12)	0.068 (13)	0.008 (11)	−0.035 (11)	−0.019 (11)
N1	0.0172 (19)	0.063 (2)	0.060 (2)	−0.0188 (19)	−0.0057 (16)	−0.0067 (18)
N2	0.0176 (18)	0.060 (2)	0.0417 (18)	−0.0154 (18)	−0.0014 (14)	−0.0019 (16)
N3	0.032 (2)	0.052 (2)	0.0397 (18)	−0.0163 (18)	−0.0075 (15)	0.0016 (16)
N4	0.023 (2)	0.050 (2)	0.069 (2)	−0.0163 (18)	−0.0057 (17)	0.0118 (18)
N5	0.0210 (18)	0.052 (2)	0.0406 (18)	−0.0135 (17)	−0.0100 (14)	−0.0015 (15)
N6	0.0174 (18)	0.060 (2)	0.058 (2)	−0.0166 (18)	−0.0085 (16)	0.0067 (17)
N7	0.0236 (19)	0.056 (2)	0.0353 (17)	−0.0183 (17)	−0.0008 (13)	0.0015 (15)
N8	0.0171 (18)	0.050 (2)	0.056 (2)	−0.0168 (17)	−0.0054 (15)	0.0018 (16)
C1	0.020 (2)	0.040 (2)	0.0378 (19)	−0.0145 (18)	−0.0013 (15)	−0.0030 (16)
C2	0.020 (2)	0.055 (3)	0.044 (2)	−0.011 (2)	0.0009 (16)	−0.0067 (19)
C3	0.028 (2)	0.068 (3)	0.047 (2)	−0.020 (2)	−0.0079 (19)	−0.002 (2)
C4	0.023 (2)	0.045 (2)	0.041 (2)	−0.0149 (19)	−0.0041 (16)	0.0011 (17)
C5	0.031 (2)	0.036 (2)	0.040 (2)	−0.0118 (19)	−0.0084 (17)	0.0009 (17)
C6	0.036 (2)	0.043 (2)	0.040 (2)	−0.015 (2)	−0.0093 (18)	−0.0013 (17)
C7	0.039 (3)	0.050 (3)	0.044 (2)	−0.015 (2)	0.0016 (19)	0.0033 (19)
C8	0.027 (2)	0.049 (3)	0.050 (2)	−0.015 (2)	−0.0047 (18)	−0.0028 (19)
C9	0.020 (2)	0.044 (2)	0.0370 (19)	−0.0120 (19)	−0.0081 (15)	0.0046 (17)
C10	0.031 (2)	0.056 (3)	0.038 (2)	−0.014 (2)	−0.0110 (17)	−0.0017 (18)
C11	0.026 (2)	0.058 (3)	0.042 (2)	−0.015 (2)	−0.0014 (17)	0.0025 (19)
C12	0.025 (2)	0.052 (3)	0.041 (2)	−0.014 (2)	−0.0040 (17)	−0.0012 (18)

C13	0.022 (2)	0.044 (2)	0.0352 (19)	−0.0141 (19)	−0.0042 (15)	0.0015 (16)
C14	0.023 (2)	0.047 (2)	0.038 (2)	−0.013 (2)	−0.0007 (16)	−0.0019 (17)
C15	0.032 (2)	0.052 (3)	0.039 (2)	−0.017 (2)	−0.0118 (17)	0.0020 (18)
C16	0.020 (2)	0.055 (3)	0.039 (2)	−0.015 (2)	−0.0053 (16)	0.0019 (18)

Geometric parameters (Å, º)

Zn1—Cl3	2.2577 (12)	N4—H4N	0.849 (19)
Zn1—Cl4	2.2589 (11)	N5—C11	1.317 (5)
Zn1—Cl1	2.2758 (12)	N5—C9	1.375 (5)
Zn1—Cl2	2.2948 (12)	N5—H5N	0.858 (19)
O1—C4	1.271 (4)	N6—C11	1.321 (5)
O2—C4	1.229 (4)	N6—C10	1.367 (5)
O3—C8	1.220 (5)	N6—H6N	0.868 (19)
O4—C8	1.277 (5)	N7—C15	1.321 (5)
O4—H4A	0.87 (2)	N7—C13	1.376 (4)
O5—C12	1.274 (5)	N7—H7N	0.889 (19)
O6—C12	1.222 (5)	N8—C15	1.325 (5)
O7—C16	1.224 (5)	N8—C14	1.367 (5)
O8—C16	1.267 (5)	N8—H8N	0.872 (19)
O8—H8A	0.851 (19)	C1—C2	1.345 (5)
O1S—H1A	0.85 (2)	C1—C4	1.487 (5)
O1S—H1B	0.84 (2)	C2—H2	0.95
O2S—H2A	0.85 (2)	C3—H3	0.95
O2S—H2B	0.85 (2)	C5—C6	1.347 (5)
N1—C3	1.309 (5)	C5—C8	1.479 (5)
N1—C2	1.375 (5)	C6—H6	0.95
N1—H1N	0.884 (19)	C7—H7	0.95
N2—C3	1.312 (5)	C9—C10	1.357 (5)
N2—C1	1.370 (5)	C9—C12	1.484 (5)
N2—H2N	0.871 (19)	C10—H10	0.95
N3—C7	1.318 (5)	C11—H11	0.95
N3—C5	1.365 (5)	C13—C14	1.339 (5)
N3—H3N	0.866 (19)	C13—C16	1.481 (5)
N4—C7	1.327 (6)	C14—H14	0.95
N4—C6	1.361 (5)	C15—H15	0.95

Cl3—Zn1—Cl4	111.21 (4)	N1—C3—H3	126.0
Cl3—Zn1—Cl1	112.42 (5)	N2—C3—H3	126.0
Cl4—Zn1—Cl1	109.31 (5)	O2—C4—O1	126.3 (4)
Cl3—Zn1—Cl2	104.23 (5)	O2—C4—C1	117.2 (3)
Cl4—Zn1—Cl2	110.95 (4)	O1—C4—C1	116.5 (3)
Cl1—Zn1—Cl2	108.62 (5)	C6—C5—N3	106.6 (3)
C8—O4—H4A	122 (4)	C6—C5—C8	132.8 (4)
C16—O8—H8A	113 (3)	N3—C5—C8	120.6 (3)
H1A—O1S—H1B	111 (5)	C5—C6—N4	106.8 (3)
H2A—O2S—H2B	113 (6)	C5—C6—H6	126.6
C3—N1—C2	109.4 (3)	N4—C6—H6	126.6

C3—N1—H1N	132 (3)	N3—C7—N4	107.5 (4)
C2—N1—H1N	118 (3)	N3—C7—H7	126.3
C3—N2—C1	109.7 (3)	N4—C7—H7	126.3
C3—N2—H2N	128 (3)	O3—C8—O4	125.6 (4)
C1—N2—H2N	122 (3)	O3—C8—C5	118.2 (4)
C7—N3—C5	109.6 (3)	O4—C8—C5	116.2 (4)
C7—N3—H3N	121 (3)	C10—C9—N5	106.6 (3)
C5—N3—H3N	129 (3)	C10—C9—C12	133.0 (3)
C7—N4—C6	109.4 (4)	N5—C9—C12	120.4 (3)
C7—N4—H4N	120 (3)	C9—C10—N6	106.2 (3)
C6—N4—H4N	130 (3)	C9—C10—H10	126.9
C11—N5—C9	109.5 (3)	N6—C10—H10	126.9
C11—N5—H5N	124 (3)	N5—C11—N6	107.7 (3)
C9—N5—H5N	126 (3)	N5—C11—H11	126.1
C11—N6—C10	110.0 (3)	N6—C11—H11	126.1
C11—N6—H6N	125 (3)	O6—C12—O5	126.3 (4)
C10—N6—H6N	125 (3)	O6—C12—C9	117.6 (3)
C15—N7—C13	109.3 (3)	O5—C12—C9	116.1 (3)
C15—N7—H7N	126 (3)	C14—C13—N7	106.7 (3)
C13—N7—H7N	124 (3)	C14—C13—C16	133.2 (3)
C15—N8—C14	109.4 (3)	N7—C13—C16	120.1 (3)
C15—N8—H8N	128 (3)	C13—C14—N8	107.0 (3)
C14—N8—H8N	122 (3)	C13—C14—H14	126.5
C2—C1—N2	106.3 (3)	N8—C14—H14	126.5
C2—C1—C4	133.6 (3)	N7—C15—N8	107.6 (3)
N2—C1—C4	120.2 (3)	N7—C15—H15	126.2
C1—C2—N1	106.6 (3)	N8—C15—H15	126.2
C1—C2—H2	126.7	O7—C16—O8	126.3 (4)
N1—C2—H2	126.7	O7—C16—C13	117.8 (3)
N1—C3—N2	108.0 (4)	O8—C16—C13	115.9 (3)

C3—N2—C1—C2	−0.4 (5)	C11—N5—C9—C10	0.5 (5)
C3—N2—C1—C4	179.6 (4)	C11—N5—C9—C12	179.7 (4)
N2—C1—C2—N1	0.2 (5)	N5—C9—C10—N6	−0.5 (5)
C4—C1—C2—N1	−179.9 (4)	C12—C9—C10—N6	−179.6 (4)
C3—N1—C2—C1	0.1 (5)	C11—N6—C10—C9	0.4 (5)
C2—N1—C3—N2	−0.4 (5)	C9—N5—C11—N6	−0.2 (5)
C1—N2—C3—N1	0.5 (5)	C10—N6—C11—N5	−0.1 (5)
C2—C1—C4—O2	−174.2 (5)	C10—C9—C12—O6	−177.8 (5)
N2—C1—C4—O2	5.7 (6)	N5—C9—C12—O6	3.2 (6)
C2—C1—C4—O1	5.4 (7)	C10—C9—C12—O5	4.0 (7)
N2—C1—C4—O1	−174.7 (4)	N5—C9—C12—O5	−175.0 (4)
C7—N3—C5—C6	0.3 (5)	C15—N7—C13—C14	−0.4 (5)
C7—N3—C5—C8	−179.0 (4)	C15—N7—C13—C16	179.2 (4)
N3—C5—C6—N4	−0.8 (5)	N7—C13—C14—N8	0.5 (5)
C8—C5—C6—N4	178.4 (4)	C16—C13—C14—N8	−179.0 (4)
C7—N4—C6—C5	1.1 (5)	C15—N8—C14—C13	−0.4 (5)
C5—N3—C7—N4	0.4 (5)	C13—N7—C15—N8	0.1 (5)

C6—N4—C7—N3	−0.9 (5)	C14—N8—C15—N7	0.2 (5)
C6—C5—C8—O3	178.6 (5)	C14—C13—C16—O7	−174.2 (5)
N3—C5—C8—O3	−2.3 (6)	N7—C13—C16—O7	6.3 (6)
C6—C5—C8—O4	0.2 (7)	C14—C13—C16—O8	6.5 (7)
N3—C5—C8—O4	179.3 (4)	N7—C13—C16—O8	−173.0 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O5^{i}	0.87 (2)	1.63 (2)	2.476 (4)	163 (5)
O4—H4*A*···O6^{i}	0.87 (2)	2.52 (4)	3.205 (4)	136 (4)
O8—H8*A*···O1^{ii}	0.85 (2)	1.65 (2)	2.484 (4)	166 (5)
O8—H8*A*···O2^{ii}	0.85 (2)	2.63 (4)	3.162 (4)	122 (4)
O1*S*—H1*A*···Cl2	0.85 (2)	2.52 (5)	3.330 (9)	159 (10)
O1*S*—H1*B*···Cl1^{iii}	0.84 (2)	2.97 (9)	3.546 (15)	128 (10)
O1*S*—H1*B*···Cl4^{iii}	0.84 (2)	2.93 (7)	3.499 (11)	127 (8)
O2*S*—H2*A*···Cl2	0.85 (2)	2.61 (12)	3.382 (17)	150.20
O2*S*—H2*B*···Cl1^{iii}	0.85 (2)	2.36 (10)	3.13 (2)	150 (17)
N1—H1*N*···O2^{iv}	0.88 (2)	1.86 (2)	2.712 (4)	160 (4)
N2—H2*N*···Cl2	0.87 (2)	2.44 (2)	3.297 (3)	167 (4)
N3—H3*N*···O1*S*	0.87 (2)	2.01 (2)	2.860 (10)	168 (4)
N3—H3*N*···O2*S*	0.87 (2)	1.89 (2)	2.739 (12)	165 (4)
N4—H4*N*···O3^{iv}	0.85 (2)	1.92 (3)	2.677 (5)	148 (4)
N5—H5*N*···Cl4	0.86 (2)	2.39 (2)	3.247 (3)	173 (4)
N6—H6*N*···O6^{iv}	0.87 (2)	1.85 (3)	2.661 (4)	156 (4)
N7—H7*N*···Cl1	0.89 (2)	2.32 (2)	3.205 (3)	175 (4)
N8—H8*N*···O7^{iv}	0.87 (2)	1.78 (2)	2.628 (4)	164 (4)
C2—H2···O8^{v}	0.95	2.55	3.414 (5)	152
C3—H3···Cl2^{iv}	0.95	2.91	3.454 (4)	118
C6—H6···O5^{vi}	0.95	2.54	3.400 (5)	151
C7—H7···Cl2^{iv}	0.95	2.77	3.599 (4)	146
C10—H10···O4^{vi}	0.95	2.49	3.345 (5)	151
C11—H11···Cl3	0.95	2.75	3.523 (4)	139
C11—H11···Cl4^{iv}	0.95	2.92	3.528 (4)	123
C14—H14···O1^{v}	0.95	2.47	3.303 (5)	147
C15—H15···Cl3	0.95	2.8	3.511 (4)	132

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