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Crystal structure of non-centrosymmetric bis(4-methoxybenzylammonium) tetrachloridozincate

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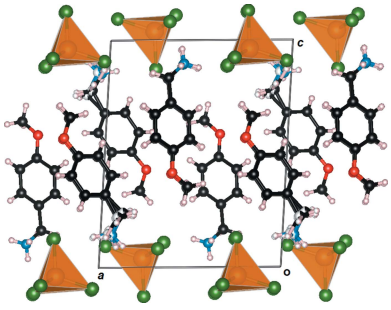
The structure of the title non-centrosymmetric organic–inorganic hybrid salt, $(C_8H_{12}NO)_2[ZnCl_4]$, consists of two 4-methoxybenzylammonium cations sandwiched between anionic layers, formed by isolated tetrachloridozincate tetrahedra. The double layers extend parallel to the *ac* plane. The crystal packing is assured by Coulombic interactions and by a complex N—H···Cl and C—H···Cl hydrogen-bonding system mostly involving the positively charged ammonium groups and the chloride ligands of the isolated tetrahedral $[ZnCl_4]^{2-}$ units. One of the methyleneammonium groups is disordered over two sets of sites in a 0.48 (2):0.52 (2) ratio. The crystal investigated was twinned by non-merohedry with a twin component ratio of 0.738 (2):0.262 (2).

1. Chemical context

Non-linear optical (NLO) materials have received much attention in different research areas due to their potential applications in high-density optical data storage, electro-optical shutters, optical communication and signal processing (Maury & Le Bozec, 2005; Green *et al.*, 2011; Evans & Lin, 2002). Mostly connected in the past to a few families of inorganic materials, the research was then extended to organic materials, generally salts of amino acids with organic acids, which are expected to have relatively strong NLO properties due to delocalized electrons at π–π^* orbitals. More recently, organic–inorganic hybrid materials showing non-centrosymmetric structures started gaining attention in the field, since they are expected to offer enhanced properties, such as second harmonic generation efficiency, by combining the characteristic features of both organic and inorganic moieties. These materials are usually constituted by the crystal packing of inorganic anions (typically halogenidometalates) and organic ammonium cations ensured by hydrogen bonds and Coulombic interactions (Brammer *et al.*, 2002). Herein we report the synthesis and crystal structure of a new organic–inorganic hybrid compound, bis(4-methoxybenzylammonium) tetrachloridozincate. This salt crystallizes in a non-centrosymmetric space group and hence could be a potential candidate for second order non-linear optical properties.



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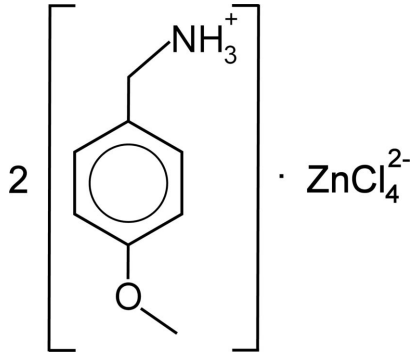

2. Structural commentary

The asymmetric unit of the crystal structure consists of an isolated tetrachloridozincate anion, $[ZnCl_4]^{2-}$ and two 4-methoxybenzylammonium cations, $(C_8H_{12}NO)^+$, as shown in Fig. 1. One of the cations shows positional disorder of the methyleneammonium moiety. The lengths of the C—C, C—N and C—O bonds in the two independent 4-methoxybenzylammonium cations are in accordance with corresponding distances found in the literature (Groom *et al.*, 2016). The Zn^{II} atom is tetrahedrally coordinated by four chloride ligands with Zn—Cl bond lengths ranging from 2.249 (2) to 2.289 (2) Å and Cl—Zn—Cl bond angles varying between 107.25 (8) and 112.41 (10)°.

3. Supramolecular features

The crystal structure consist of 4-methoxybenzylammonium cations sandwiched between tetrachloridozincate layers extending parallel to the *ac* plane, as shown in Fig. 2. The cationic units are linked into a two-dimensional network by weak C—H···π interactions (Table 1). The crystal packing is assured by a complex hydrogen-bonding system, mostly involving the positively charged ammonium groups and the chloride ligands of the isolated tetrahedral $[ZnCl_4]^{2-}$ units (Table 1), which reinforce the Coulombic interactions, as depicted in Fig. 3. Whereas the N2 atom is blocked by a very efficient hydrogen-bonding system involving five donor···acceptor distances ranging from 3.279 (8) to 3.452 (7) Å, the N1 ammonium group is disordered over two sets of sites as a consequence of a less efficient hydrogen bonding.

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the C11–C16 and C1–C6 rings, respectively

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*1···Cl3	0.89	2.32	3.19 (2)	164
N1*A*—H1*A*2···Cl2^{i}	0.89	2.75	3.26 (2)	118
N1*A*—H1*A*3···Cl4^{i}	0.89	2.64	3.34 (2)	137
C8*A*—H8*A*2···Cl4^{ii}	0.97	2.77	3.72 (2)	168
N1*B*—H1*B*1···Cl4^{ii}	0.89	2.78	3.61 (3)	154
N1*B*—H1*B*2···Cl2^{i}	0.89	2.66	3.33 (2)	133
N1*B*—H1*B*3···Cl3	0.89	2.80	3.45 (2)	131
C8*B*—H8*B*2···Cl1^{ii}	0.97	2.82	3.60 (2)	138
N2—H1*N*···Cl1^{iii}	0.89	2.65	3.364 (7)	138
N2—H1*N*···Cl2^{iii}	0.89	2.75	3.336 (7)	125
N2—H2*N*···Cl3^{iv}	0.89	2.45	3.279 (8)	156
N2—H3*N*···Cl1^{iv}	0.89	2.72	3.331 (7)	127
N2—H3*N*···Cl2	0.89	2.71	3.452 (7)	141
C2—H2···*Cg*1	0.93	2.62	3.432 (8)	146
C6—H6···*Cg*2^{i}	0.93	2.86	3.579 (8)	135

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

4. Database survey

A search of the Cambridge Structural Database (Version 5.37; last update February 2016; Groom *et al.*, 2016) for related compounds showed the occurrence of the cadmium analogue

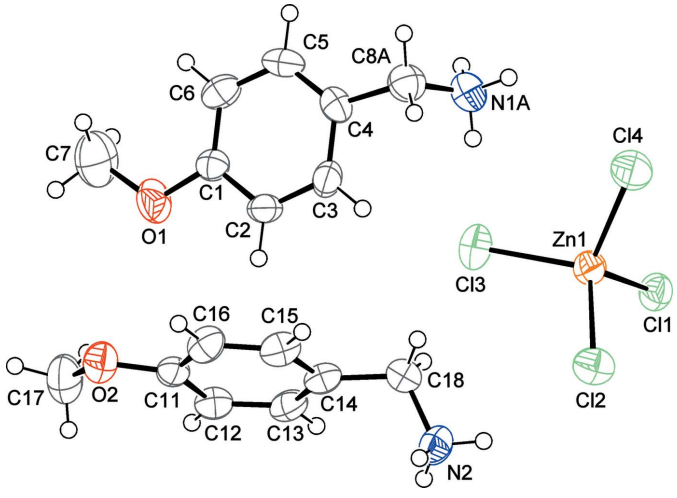

Figure 1
The asymmetric unit of the title compound with displacement ellipsoids drawn at the 50% probability level. Only the major component of the disordered methyleneammonium group is shown for clarity.

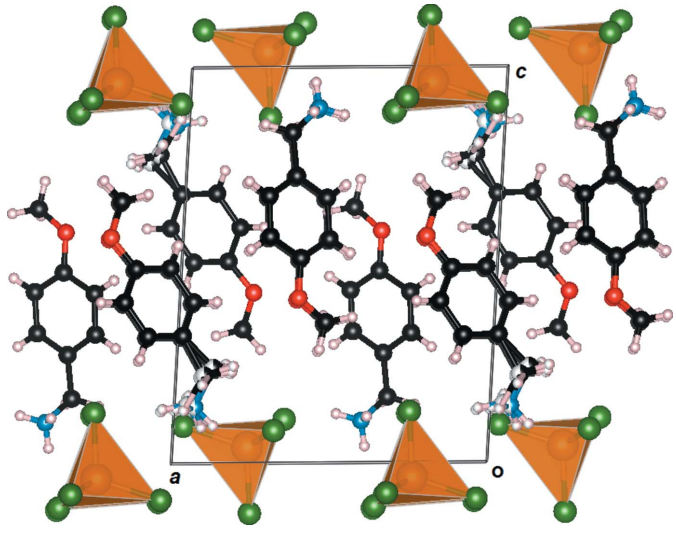

Figure 2
Packing diagram of the title compound viewed along the *b* axis, showing the alternate stacking, along the *c* axis, of organic and inorganic layers.

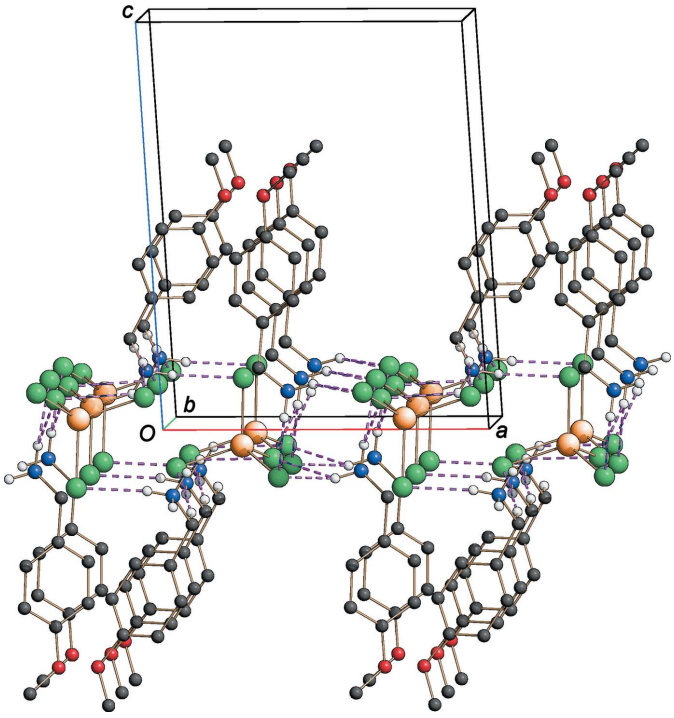

Figure 3
Partial packing diagram of the title compound approximately viewed along the *b* axis, showing the hydrogen-bonding network (dashed lines).

of formula $(C_8H_{12}NO)_2[CdCl_4]$ (Kefi *et al.*, 2011), in which the coordination sphere of the metal is octahedral, giving rise to the formation of perovskite-like edge-sharing units that built up two-dimensional anionic layers parallel to the *bc* plane.

5. Synthesis and crystallization

Single crystals of $(C_8H_{12}NO)_2[ZnCl_4]$ were synthesized starting from 4-methoxybenzylamine (Sigma–Aldrich, 98%), zinc chloride (Sigma–Aldrich, 98%) and HCl (37%), which were weighted in the stoichiometric proportion conforming to the equation reaction:

$$2\ C_8H_{11}NO + 2\ HCl + ZnCl_2 \rightarrow (C_8H_{12}NO)_2[ZnCl_4]$$

After mixing the reagents in 50 ml of water and stirring at room temperature for more 3 h, the resulting solution was placed in a Petri dish and allowed to evaporate slowly. Single crystals suitable for X-ray diffraction were obtained within a week (yield: 75%).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystals of bis(4-methoxybenzylammonium) tetrachloridozincate were systematically affected by non-merohedral polar twinning. The ratio of the twin components of the crystal selected for X-ray analysis was refined to 0.738 (2):0.262 (2). One methyleneammonium group was found to be disordered over two sets of sites with a refined occupancy ratio of 0.52 (2):0.48 (2). During the refinement of the disordered group, the C—C and C—N bond lengths were constrained to be 1.50 (2) and 1.47 (1) Å, respectively. EADP and ISOR restraints (Sheldrick, 2015*b*) were also applied. All H atoms were placed geometrically and refined using a riding-model approximation, with C—H = 0.93–0.97 Å, N—H = 0.89 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C, N)$ for methyl and ammonium H atoms, for which a rotating model was applied.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_8H_{12}NO)_2[ZnCl_4]$
M_r	483.54
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	294
a, *b*, *c* (Å)	10.6849 (10), 7.4540 (7), 13.3961 (12)
β (°)	93.482 (2)
V (Å^3)	1064.97 (17)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.67
Crystal size (mm)	0.31 × 0.29 × 0.11
Data collection	
Diffractometer	Bruker SMART CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.604, 0.827
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2132, 2132, 1932
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.108, 1.08
No. of reflections	2132
No. of parameters	239
No. of restraints	29
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.42, −0.44
Absolute structure	No quotients, so Flack parameter determined by classical intensity fit
Absolute structure parameter	0.09 (2)

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012), *VESTA* (Momma & Izumi, 2011) and *SCHAKAL* (Keller, 1999).

Acknowledgements

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supporting information

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: SHELXT (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *ORTEP-3* (Farrugia, 2012), *VESTA* (Momma & Izumi, 2011) and *SCHAKAL* (Keller, 1999); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015*b*).

Bis(4-methoxybenzylammonium) tetrachloridozincate

Crystal data

$(C_8H_{12}NO)_2[ZnCl_4]$
M_r = 483.54
Monoclinic, $P2_1$
a = 10.6849 (10) Å
b = 7.4540 (7) Å
c = 13.3961 (12) Å
β = 93.482 (2)°
V = 1064.97 (17) Å^3
Z = 2
$F(000)$ = 496
D_x = 1.508 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 196 reflections
θ = 7.3–17.5°
μ = 1.67 mm^{-1}
T = 294 K
Prism, colourless
0.31 × 0.29 × 0.11 mm

Data collection

Bruker SMART CCD diffractometer
ω scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.604, T_{max} = 0.827
2132 measured reflections
2132 independent reflections
1932 reflections with $I > 2\sigma(I)$
θ_{max} = 25.5°, θ_{min} = 1.5°
h = −12→12
k = 0→9
l = 0→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.108
S = 1.08
2132 reflections
239 parameters
29 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.2617P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Absolute structure: No quotients, so Flack parameter determined by classical intensity fit
Absolute structure parameter: 0.09 (2)

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.

Refinement. Refined as a 2-component twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Zn1	0.23731 (7)	0.06114 (12)	−0.04066 (6)	0.0413 (2)	
Cl1	0.35118 (19)	−0.1525 (3)	−0.11156 (13)	0.0464 (5)	
Cl2	0.3173 (2)	0.3349 (3)	−0.08077 (16)	0.0515 (5)	
Cl3	0.2564 (2)	0.0169 (3)	0.12644 (14)	0.0541 (5)	
Cl4	0.03137 (18)	0.0515 (5)	−0.09460 (17)	0.0714 (7)	
O1	0.2318 (5)	0.1370 (9)	0.5695 (4)	0.0585 (16)	
O2	0.3732 (5)	0.6144 (8)	0.5857 (4)	0.0541 (15)	
N1A	−0.039 (2)	−0.010 (3)	0.1458 (15)	0.060 (4)	0.52 (2)
H1A1	0.0398	0.0184	0.1345	0.090*	0.52 (2)
H1A2	−0.0863	−0.0023	0.0889	0.090*	0.52 (2)
H1A3	−0.0418	−0.1214	0.1693	0.090*	0.52 (2)
C8A	−0.087 (2)	0.115 (3)	0.2197 (13)	0.051 (4)	0.52 (2)
H8A1	−0.1741	0.0889	0.2288	0.062*	0.52 (2)
H8A2	−0.0816	0.2370	0.1945	0.062*	0.52 (2)
N1B	−0.062 (2)	0.077 (4)	0.1398 (13)	0.060 (4)	0.48 (2)
H1B1	−0.0269	0.1835	0.1303	0.090*	0.48 (2)
H1B2	−0.1227	0.0581	0.0926	0.090*	0.48 (2)
H1B3	−0.0039	−0.0084	0.1365	0.090*	0.48 (2)
C8B	−0.1142 (17)	0.073 (4)	0.2386 (12)	0.051 (4)	0.48 (2)
H8B1	−0.1541	−0.0422	0.2483	0.062*	0.48 (2)
H8B2	−0.1775	0.1656	0.2421	0.062*	0.48 (2)
N2	0.4066 (6)	0.6363 (10)	0.1058 (5)	0.0491 (16)	
H1N	0.4869	0.6150	0.1236	0.074*	
H2N	0.3897	0.7516	0.1158	0.074*	
H3N	0.3916	0.6099	0.0414	0.074*	
C1	0.1468 (6)	0.1175 (9)	0.4901 (5)	0.0369 (16)	
C2	0.1783 (7)	0.2035 (10)	0.4051 (5)	0.0424 (18)	
H2	0.2535	0.2663	0.4048	0.051*	
C3	0.0987 (8)	0.1978 (11)	0.3188 (6)	0.0456 (18)	
H3	0.1199	0.2572	0.2612	0.055*	
C4	−0.0124 (7)	0.1024 (10)	0.3201 (5)	0.0409 (18)	
C5	−0.0412 (7)	0.0166 (11)	0.4056 (6)	0.049 (2)	
H5	−0.1157	−0.0477	0.4061	0.059*	
C6	0.0374 (7)	0.0223 (10)	0.4917 (6)	0.047 (2)	
H6	0.0162	−0.0372	0.5493	0.057*	
C7	0.2037 (11)	0.0551 (19)	0.6615 (7)	0.085 (3)	
H7A	0.1208	0.0892	0.6781	0.128*	
H7B	0.2634	0.0939	0.7135	0.128*	

H7C	0.2078	−0.0729	0.6549	0.128*
C11	0.3734 (7)	0.5951 (10)	0.4849 (5)	0.0393 (16)
C12	0.4613 (7)	0.4999 (11)	0.4364 (6)	0.0423 (18)
H12	0.5296	0.4487	0.4721	0.051*
C13	0.4466 (7)	0.4808 (12)	0.3325 (6)	0.0450 (19)
H13	0.5050	0.4138	0.2997	0.054*
C14	0.3470 (6)	0.5594 (13)	0.2768 (5)	0.0440 (16)
C15	0.2628 (7)	0.6580 (10)	0.3274 (6)	0.0472 (18)
H15	0.1967	0.7140	0.2912	0.057*
C16	0.2727 (8)	0.6769 (10)	0.4303 (6)	0.0468 (18)
H16	0.2134	0.7427	0.4629	0.056*
C17	0.4625 (10)	0.5122 (14)	0.6466 (6)	0.070 (3)
H17A	0.4541	0.3873	0.6299	0.105*
H17B	0.4473	0.5292	0.7158	0.105*
H17C	0.5458	0.5517	0.6346	0.105*
C18	0.3266 (7)	0.5243 (12)	0.1665 (6)	0.054 (2)
H18A	0.3437	0.3989	0.1535	0.065*
H18B	0.2394	0.5470	0.1461	0.065*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0397 (4)	0.0455 (4)	0.0384 (4)	−0.0002 (5)	0.0005 (4)	0.0012 (4)
Cl1	0.0524 (11)	0.0456 (9)	0.0416 (9)	0.0014 (9)	0.0070 (9)	−0.0042 (9)
Cl2	0.0516 (11)	0.0415 (10)	0.0607 (11)	0.0008 (10)	−0.0015 (10)	0.0091 (9)
Cl3	0.0695 (12)	0.0560 (13)	0.0369 (9)	0.0119 (11)	0.0042 (10)	0.0018 (8)
Cl4	0.0364 (9)	0.115 (2)	0.0623 (12)	−0.0014 (15)	−0.0031 (9)	−0.0049 (16)
O1	0.056 (3)	0.076 (4)	0.042 (3)	0.006 (3)	−0.014 (3)	0.001 (3)
O2	0.063 (3)	0.056 (4)	0.044 (3)	0.002 (3)	0.007 (3)	−0.004 (3)
N1A	0.056 (7)	0.077 (12)	0.047 (4)	−0.011 (9)	−0.007 (5)	−0.003 (8)
C8A	0.047 (6)	0.055 (7)	0.052 (6)	0.001 (5)	−0.002 (5)	0.004 (5)
N1B	0.056 (7)	0.077 (12)	0.047 (4)	−0.011 (9)	−0.007 (5)	−0.003 (8)
C8B	0.047 (6)	0.055 (7)	0.052 (6)	0.001 (5)	−0.002 (5)	0.004 (5)
N2	0.051 (4)	0.058 (4)	0.038 (3)	0.006 (3)	0.006 (3)	0.007 (3)
C1	0.033 (4)	0.037 (4)	0.041 (4)	0.003 (3)	0.004 (3)	−0.001 (3)
C2	0.037 (4)	0.043 (4)	0.048 (4)	−0.010 (3)	0.010 (3)	−0.006 (3)
C3	0.058 (5)	0.048 (4)	0.031 (4)	−0.005 (4)	0.008 (3)	−0.001 (3)
C4	0.041 (4)	0.040 (5)	0.041 (4)	0.003 (3)	−0.004 (3)	−0.008 (3)
C5	0.034 (4)	0.044 (5)	0.069 (5)	−0.010 (3)	0.005 (4)	−0.002 (4)
C6	0.052 (5)	0.038 (4)	0.053 (4)	0.000 (4)	0.014 (4)	0.010 (3)
C7	0.105 (8)	0.086 (7)	0.062 (5)	0.012 (9)	−0.016 (6)	0.013 (7)
C11	0.044 (4)	0.034 (4)	0.041 (4)	−0.010 (4)	0.007 (3)	−0.002 (3)
C12	0.036 (4)	0.038 (4)	0.052 (5)	0.002 (3)	0.004 (4)	0.005 (4)
C13	0.038 (4)	0.047 (4)	0.052 (5)	0.000 (4)	0.016 (4)	0.000 (4)
C14	0.043 (4)	0.042 (4)	0.048 (4)	−0.006 (5)	0.010 (3)	0.007 (4)
C15	0.042 (4)	0.043 (4)	0.057 (4)	0.004 (4)	0.007 (4)	0.010 (4)
C16	0.051 (4)	0.039 (4)	0.052 (4)	0.006 (4)	0.015 (4)	−0.002 (3)
C17	0.093 (7)	0.071 (7)	0.045 (5)	0.000 (6)	−0.004 (5)	0.001 (5)

C18	0.048 (4)	0.067 (6)	0.047 (4)	−0.016 (4)	0.002 (4)	−0.006 (4)

Geometric parameters (Å, º)

Zn1—Cl1	2.249 (2)	C2—C3	1.393 (11)
Zn1—Cl3	2.2595 (19)	C2—H2	0.9300
Zn1—Cl4	2.275 (2)	C3—C4	1.385 (11)
Zn1—Cl2	2.289 (2)	C3—H3	0.9300
O1—C1	1.363 (8)	C4—C5	1.363 (11)
O1—C7	1.424 (11)	C5—C6	1.385 (11)
O2—C11	1.359 (9)	C5—H5	0.9300
O2—C17	1.435 (11)	C6—H6	0.9300
N1A—C8A	1.473 (10)	C7—H7A	0.9600
N1A—H1A1	0.8900	C7—H7B	0.9600
N1A—H1A2	0.8900	C7—H7C	0.9600
N1A—H1A3	0.8900	C11—C12	1.371 (11)
C8A—C4	1.523 (15)	C11—C16	1.403 (11)
C8A—H8A1	0.9700	C12—C13	1.398 (11)
C8A—H8A2	0.9700	C12—H12	0.9300
N1B—C8B	1.469 (10)	C13—C14	1.392 (11)
N1B—H1B1	0.8900	C13—H13	0.9300
N1B—H1B2	0.8900	C14—C15	1.372 (11)
N1B—H1B3	0.8900	C14—C18	1.504 (10)
C8B—C4	1.510 (15)	C15—C16	1.384 (11)
C8B—H8B1	0.9700	C15—H15	0.9300
C8B—H8B2	0.9700	C16—H16	0.9300
N2—C18	1.474 (10)	C17—H17A	0.9600
N2—H1N	0.8900	C17—H17B	0.9600
N2—H2N	0.8900	C17—H17C	0.9600
N2—H3N	0.8900	C18—H18A	0.9700
C1—C2	1.366 (10)	C18—H18B	0.9700
C1—C6	1.369 (10)		
Cl1—Zn1—Cl3	107.25 (8)	C5—C4—C3	119.2 (7)
Cl1—Zn1—Cl4	112.41 (10)	C5—C4—C8B	110.5 (11)
Cl3—Zn1—Cl4	109.72 (9)	C3—C4—C8B	130.3 (11)
Cl1—Zn1—Cl2	108.22 (8)	C5—C4—C8A	129.8 (11)
Cl3—Zn1—Cl2	110.50 (9)	C3—C4—C8A	110.9 (11)
Cl4—Zn1—Cl2	108.73 (11)	C4—C5—C6	122.0 (7)
C1—O1—C7	117.6 (7)	C4—C5—H5	119.0
C11—O2—C17	117.9 (6)	C6—C5—H5	119.0
C8A—N1A—H1A1	109.5	C1—C6—C5	118.5 (7)
C8A—N1A—H1A2	109.5	C1—C6—H6	120.7
H1A1—N1A—H1A2	109.5	C5—C6—H6	120.7
C8A—N1A—H1A3	109.5	O1—C7—H7A	109.5
H1A1—N1A—H1A3	109.5	O1—C7—H7B	109.5
H1A2—N1A—H1A3	109.5	H7A—C7—H7B	109.5
N1A—C8A—C4	111.8 (14)	O1—C7—H7C	109.5

N1A—C8A—H8A1	109.3	H7A—C7—H7C	109.5
C4—C8A—H8A1	109.3	H7B—C7—H7C	109.5
N1A—C8A—H8A2	109.3	O2—C11—C12	124.6 (7)
C4—C8A—H8A2	109.3	O2—C11—C16	115.1 (6)
H8A1—C8A—H8A2	107.9	C12—C11—C16	120.3 (6)
C8B—N1B—H1B1	109.5	C11—C12—C13	119.0 (7)
C8B—N1B—H1B2	109.5	C11—C12—H12	120.5
H1B1—N1B—H1B2	109.5	C13—C12—H12	120.5
C8B—N1B—H1B3	109.5	C14—C13—C12	121.7 (7)
H1B1—N1B—H1B3	109.5	C14—C13—H13	119.1
H1B2—N1B—H1B3	109.5	C12—C13—H13	119.1
N1B—C8B—C4	110.6 (15)	C15—C14—C13	117.7 (7)
N1B—C8B—H8B1	109.5	C15—C14—C18	121.2 (7)
C4—C8B—H8B1	109.5	C13—C14—C18	120.9 (7)
N1B—C8B—H8B2	109.5	C14—C15—C16	122.3 (8)
C4—C8B—H8B2	109.5	C14—C15—H15	118.9
H8B1—C8B—H8B2	108.1	C16—C15—H15	118.9
C18—N2—H1N	109.5	C15—C16—C11	119.0 (7)
C18—N2—H2N	109.5	C15—C16—H16	120.5
H1N—N2—H2N	109.5	C11—C16—H16	120.5
C18—N2—H3N	109.5	O2—C17—H17A	109.5
H1N—N2—H3N	109.5	O2—C17—H17B	109.5
H2N—N2—H3N	109.5	H17A—C17—H17B	109.5
O1—C1—C2	114.5 (6)	O2—C17—H17C	109.5
O1—C1—C6	124.9 (7)	H17A—C17—H17C	109.5
C2—C1—C6	120.6 (7)	H17B—C17—H17C	109.5
C1—C2—C3	120.6 (7)	N2—C18—C14	112.9 (7)
C1—C2—H2	119.7	N2—C18—H18A	109.0
C3—C2—H2	119.7	C14—C18—H18A	109.0
C4—C3—C2	119.1 (7)	N2—C18—H18B	109.0
C4—C3—H3	120.5	C14—C18—H18B	109.0
C2—C3—H3	120.5	H18A—C18—H18B	107.8

Hydrogen-bond geometry (Å, º)

*Cg*1 and *Cg*2 are the centroids of the C11–C16 and C1–C6 rings, respectively

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*1···Cl3	0.89	2.32	3.19 (2)	164
N1*A*—H1*A*2···Cl2^{i}	0.89	2.75	3.26 (2)	118
N1*A*—H1*A*3···Cl4^{i}	0.89	2.64	3.34 (2)	137
C8*A*—H8*A*2···Cl4^{ii}	0.97	2.77	3.72 (2)	168
N1*B*—H1*B*1···Cl4^{ii}	0.89	2.78	3.61 (3)	154
N1*B*—H1*B*2···Cl2^{i}	0.89	2.66	3.33 (2)	133
N1*B*—H1*B*3···Cl3	0.89	2.80	3.45 (2)	131
C8*B*—H8*B*2···Cl1^{ii}	0.97	2.82	3.60 (2)	138
N2—H1*N*···Cl1^{iii}	0.89	2.65	3.364 (7)	138
N2—H1*N*···Cl2^{iii}	0.89	2.75	3.336 (7)	125
N2—H2*N*···Cl3^{iv}	0.89	2.45	3.279 (8)	156

N2—H3*N*···Cl1^{iv}	0.89	2.72	3.331 (7)	127
N2—H3*N*···Cl2	0.89	2.71	3.452 (7)	141
C2—H2···*Cg*1	0.93	2.62	3.432 (8)	146
C6—H6···*Cg*2^{i}	0.93	2.86	3.579 (8)	135

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