metal-organic compounds

Bis(phenylammonium) tetrachlorido-zincate(II) monohydrate

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In the crystal structure of the title compound, $(C_6H_8N)[ZnCl_4]\cdot H_2O$, the Zn atom has a tetrahedral geometry and is coordinated by four Cl atoms. The water molecule and phenylammonium cations interact with two $[ZnCl_4]^{2-}$ anions, forming discrete structural motifs via O—H$\cdots$Cl and N—H$\cdots$Cl/O interactions. Intermolecular π–π stacking is present between adjacent phenylammonium cations (centroid–centroid distance = 3.672 Å).

Related literature

Analogous complexes have been reported by Rademeyer (2005) and Bringley & Rajeswaran (2006).
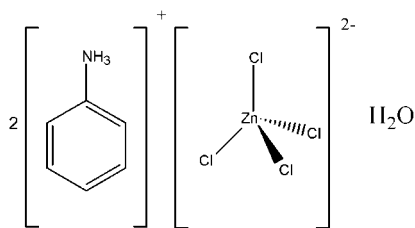
Experimental

Crystal data

$(C_6H_8N)[ZnCl_4]\cdot H_2O$
$M_r = 413.45$
Triclinic, $P\bar{1}$
$a = 7.5594$ (3) Å
$b = 9.8406$ (3) Å
$c = 13.0494$ (4) Å
$\alpha = 95.559$ (2)°
$\beta = 102.980$ (2)°
$\gamma = 111.7002$ (17)°
$V = 861.36$ (5) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.04$ mm^{-1}
$T = 173$ (2) K
$0.2 \times 0.2 \times 0.15$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.662$, $T_{max} = 0.731$
6199 measured reflections
3525 independent reflections
2964 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.074$
$S = 1.06$
3525 reflections
207 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$Cl4^i	0.92 (6)	2.30 (6)	3.172 (3)	159 (6)
O1—H2$\cdots$Cl2	0.82 (5)	2.43 (5)	3.215 (4)	162 (5)
N1—H1A$\cdots$O1^{ii}	0.85 (4)	2.04 (4)	2.889 (4)	173 (4)
N1—H1B$\cdots$O1	0.90 (4)	2.37 (4)	3.022 (3)	130 (3)
N1—H1B$\cdots$Cl3	0.90 (4)	2.64 (4)	3.343 (3)	135 (3)
N1—H1C$\cdots$Cl1^{iii}	0.91 (4)	2.57 (4)	3.426 (3)	156 (3)
N2—H2B$\cdots$Cl2^i	0.85 (4)	2.45 (4)	3.276 (3)	167 (4)
N2—H2C$\cdots$Cl1^{iii}	0.85 (5)	2.47 (4)	3.246 (3)	153 (4)
N2—H2D$\cdots$Cl3	0.97 (4)	2.35 (4)	3.262 (3)	156 (3)

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1994); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Siemens, 1994); software used to prepare material for publication: SHELXTL.

References

Bringley, J. F. & Rajeswaran, M. (2006). Acta Cryst. E**62**, m1304–m1305.
Rademeyer, M. (2005). Acta Cryst. E**61**, m304–m306.
Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
Siemens (1994). SAINT and SHELXTL. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). SMART. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supplementary materials

Bis(phenylammonium) tetrachloridozincate(II) monohydrate

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Comment

Organic-inorganic hybrid materials are interesting for their potential application in photography and drug delivery (Bringley & Rajeswaran, 2006). In these complexes, the frameworks of the organoammonium cation and the counter inorganic anionic species are stabilized by the hydrogen bonds and coulombic attractions. The analogous complexes bis(*p*-toluidinium) tetrachlorozincate(II) (Rademeyer, 2005) and *p*-phenylenediammonium tetrachlorozincate(II) (Bringley & Rajeswaran, 2006) had been reported with different supramolecular structural motifs. Here, a new member of this family, the title compound is presented, which is obtained during our studies of the preparation of new zinc phosphates. As shown in Fig 1, the crystal structure of the title compound contains a $[ZnCl_4]^{2-}$ tetrahedral anion unit, two phenylammonium cations and a water molecule. The Zn atom has a tetrahedral coordination sphere surrounded by four Cl atoms. The bond angles Cl—Zn—Cl vary from 104.38 (4) to 114.11 (4)°, and the bond length of Zn—Cl lie in the range from 2.2498 (10) Å to 2.2880 (9) Å. These values indicate that the anionic $[ZnCl_4]^{2-}$ tetrahedra is slightly distorted. The inorganic species are isolated by the organic phenylammonium cations (Fig 2). Two water molecules hydrogen bond to two $[ZnCl_4]^{2-}$ anions *via* O—H···Cl interactions, forming a ring with chair conformation and the N atom of the phenylammonium cation participates in two hydrogen bonds with two Cl acceptors in two neighboring $[ZnCl_4]^{2-}$ anions *via* N—H···Cl interactions. These connections results a discrete cluster supramolecular structural feature, different with the layer motifs in its analogous complexes. The intermolecular π-π stacking is evident between the adjacent phenylammonium cations.

Experimental

The title compound (I) was obtained unintentionally in the synthesis of zinc phosphate with $ZnCl_2$, phenyltrichloroiminophosphorane and toluene as started materials under hydrothermal reaction conditions.

Refinement

The H atoms bonded to the O atoms of the water molecules were located in a difference map and refined with distance restraints of O—H = 0.82 (5) Å, and with $U_{iso}(H) = 1.2Ueq(O)$. The remaining H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å and with $U_{iso}(H) = 1.2$ (1.5 for methyl groups) times $U_{eq}(C)$.
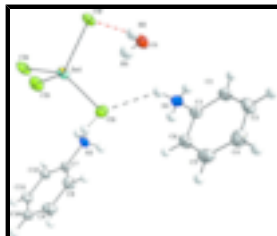
supplementary materials

Figures

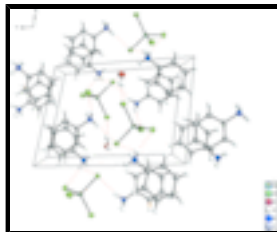Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.

Fig. 2. The packing of (I), viewed down the *a* axis, showing the N—H···Cl and O—H···Cl hydrogen bonds between the phenylammonium cations, water molecule and $[ZnCl_4]^{2-}$ anions.

Bis(phenylammonium) tetrachloridozincate(II) monohydrate

Crystal data

$(C_6H_8N)[ZnCl_4]\cdot H_2O$	$Z = 2$
$M_r = 413.45$	$F_{000} = 420$
Triclinic, $P\overline{1}$	$D_x = 1.594$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.5594$ (3) Å	Cell parameters from 10379 reflections
$b = 9.8406$ (3) Å	$\theta = 1.0$–27.9º
$c = 13.0494$ (4) Å	$\mu = 2.04$ mm^{-1}
$\alpha = 95.559$ (2)º	$T = 173$ (2) K
$\beta = 102.980$ (2)º	Block, colorless
$\gamma = 111.7002$ (17)º	$0.2 \times 0.2 \times 0.15$ mm
$V = 861.36$ (5) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	3525 independent reflections
Radiation source: fine-focus sealed tube	2964 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.029$
$T = 173(2)$ K	$\theta_{max} = 26.4$º
ω scans	$\theta_{min} = 3.0$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{min} = 0.662, T_{max} = 0.731$	$k = -12 \rightarrow 10$
6199 measured reflections	$l = -15 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.033$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.074$	$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 0.7185P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
3525 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
207 parameters	$\Delta\rho_{min} = -0.51$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Zn1	0.39838 (5)	0.66322 (3)	0.65645 (2)	0.02118 (10)
Cl1	0.25725 (10)	0.70110 (7)	0.78706 (5)	0.02594 (15)
Cl2	0.37065 (10)	0.83134 (7)	0.55119 (5)	0.02404 (15)
Cl3	0.72039 (10)	0.70842 (8)	0.72409 (6)	0.03091 (16)
Cl4	0.21253 (12)	0.43307 (7)	0.55340 (5)	0.03313 (18)
O1	0.7752 (4)	0.8859 (3)	0.48763 (18)	0.0356 (5)
H1A	1.161 (6)	1.009 (4)	0.635 (3)	0.053*
H1B	0.990 (6)	0.912 (4)	0.658 (3)	0.053*
H1C	1.177 (6)	0.900 (4)	0.696 (3)	0.053*
H2B	0.797 (6)	0.369 (4)	0.608 (3)	0.053*
H2C	0.957 (6)	0.480 (4)	0.685 (3)	0.053*
H2D	0.770 (6)	0.495 (4)	0.665 (3)	0.053*
N1	1.1214 (4)	0.9670 (3)	0.68468 (19)	0.0276 (5)
C1	1.1729 (4)	1.0783 (3)	0.7830 (2)	0.0225 (6)
C2	1.2276 (4)	1.2263 (3)	0.7763 (2)	0.0304 (6)
H2A	1.2312	1.2559	0.7110	0.037*
C3	1.2775 (5)	1.3303 (3)	0.8690 (3)	0.0370 (7)

H3A	1.3147	1.4309	0.8663	0.044*
C4	1.2716 (5)	1.2844 (3)	0.9656 (2)	0.0348 (7)
H4A	1.3056	1.3544	1.0277	0.042*
C5	1.2156 (4)	1.1353 (3)	0.9701 (2)	0.0316 (7)
H5A	1.2128	1.1054	1.0353	0.038*
C6	1.1637 (4)	1.0302 (3)	0.8782 (2)	0.0272 (6)
H6A	1.1235	0.9293	0.8806	0.033*
C7	0.7857 (4)	0.3408 (3)	0.7537 (2)	0.0218 (5)
C8	0.8080 (4)	0.4193 (3)	0.8526 (2)	0.0286 (6)
H8A	0.8530	0.5227	0.8656	0.034*
C9	0.7616 (5)	0.3402 (3)	0.9319 (2)	0.0329 (7)
H9A	0.7745	0.3910	0.9989	0.039*
C10	0.6963 (4)	0.1864 (3)	0.9124 (2)	0.0313 (7)
H10A	0.6646	0.1342	0.9660	0.038*
C11	0.6783 (5)	0.1108 (3)	0.8134 (2)	0.0336 (7)
H11A	0.6358	0.0075	0.8005	0.040*
C12	0.7234 (4)	0.1884 (3)	0.7330 (2)	0.0283 (6)
H12A	0.7116	0.1380	0.6660	0.034*
N2	0.8335 (4)	0.4257 (3)	0.66876 (19)	0.0269 (5)
H1	0.747 (8)	0.786 (6)	0.479 (4)	0.100 (18)*
H2	0.678 (7)	0.892 (5)	0.502 (4)	0.073 (15)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02679 (18)	0.01853 (16)	0.02121 (16)	0.01000 (13)	0.01001 (13)	0.00611 (12)
Cl1	0.0323 (4)	0.0261 (3)	0.0229 (3)	0.0118 (3)	0.0140 (3)	0.0057 (3)
Cl2	0.0348 (4)	0.0179 (3)	0.0217 (3)	0.0111 (3)	0.0101 (3)	0.0071 (2)
Cl3	0.0276 (4)	0.0347 (4)	0.0344 (4)	0.0161 (3)	0.0094 (3)	0.0089 (3)
Cl4	0.0506 (5)	0.0172 (3)	0.0283 (3)	0.0108 (3)	0.0101 (3)	0.0038 (3)
O1	0.0429 (14)	0.0299 (12)	0.0435 (13)	0.0189 (11)	0.0216 (11)	0.0108 (10)
N1	0.0323 (14)	0.0290 (13)	0.0236 (12)	0.0136 (12)	0.0099 (11)	0.0048 (10)
C1	0.0246 (14)	0.0250 (14)	0.0223 (13)	0.0138 (12)	0.0086 (11)	0.0046 (11)
C2	0.0347 (17)	0.0310 (16)	0.0282 (15)	0.0151 (13)	0.0088 (12)	0.0103 (12)
C3	0.0443 (19)	0.0228 (15)	0.0450 (18)	0.0151 (14)	0.0121 (15)	0.0073 (13)
C4	0.0395 (18)	0.0325 (17)	0.0321 (16)	0.0164 (14)	0.0100 (14)	−0.0018 (13)
C5	0.0361 (17)	0.0385 (17)	0.0252 (14)	0.0182 (14)	0.0126 (13)	0.0065 (12)
C6	0.0315 (16)	0.0245 (14)	0.0293 (14)	0.0125 (12)	0.0122 (12)	0.0081 (11)
C7	0.0213 (14)	0.0230 (13)	0.0206 (13)	0.0079 (11)	0.0061 (10)	0.0065 (10)
C8	0.0366 (17)	0.0241 (14)	0.0272 (14)	0.0131 (13)	0.0121 (12)	0.0038 (11)
C9	0.0416 (18)	0.0383 (17)	0.0239 (14)	0.0204 (15)	0.0117 (13)	0.0058 (12)
C10	0.0316 (16)	0.0399 (17)	0.0251 (14)	0.0143 (14)	0.0081 (12)	0.0181 (13)
C11	0.0387 (18)	0.0213 (15)	0.0330 (16)	0.0064 (13)	0.0033 (13)	0.0095 (12)
C12	0.0358 (17)	0.0218 (14)	0.0207 (13)	0.0069 (12)	0.0042 (12)	0.0032 (11)
N2	0.0351 (15)	0.0195 (12)	0.0225 (12)	0.0054 (11)	0.0112 (11)	0.0037 (10)

Geometric parameters (Å, °)

Zn1—Cl3	2.2497 (10)	C5—C6	1.381 (4)

Zn1—Cl4	2.2626 (13)	C5—H5A	0.9300
Zn1—Cl1	2.2737 (9)	C6—H6A	0.9300
Zn1—Cl2	2.2880 (9)	C7—C12	1.373 (4)
O1—H1	0.91 (6)	C7—C8	1.379 (4)
O1—H2	0.82 (5)	C7—N2	1.481 (3)
N1—C1	1.478 (3)	C8—C9	1.385 (4)
N1—H1A	0.85 (4)	C8—H8A	0.9300
N1—H1B	0.90 (4)	C9—C10	1.384 (4)
N1—H1C	0.91 (4)	C9—H9A	0.9300
C1—C2	1.377 (4)	C10—C11	1.379 (4)
C1—C6	1.380 (4)	C10—H10A	0.9300
C2—C3	1.388 (4)	C11—C12	1.387 (4)
C2—H2A	0.9300	C11—H11A	0.9300
C3—C4	1.384 (4)	C12—H12A	0.9300
C3—H3A	0.9300	N2—H2B	0.85 (4)
C4—C5	1.380 (4)	N2—H2C	0.85 (4)
C4—H4A	0.9300	N2—H2D	0.97 (4)
Cl3—Zn1—Cl4	114.11 (4)	C1—C6—C5	118.4 (3)
Cl3—Zn1—Cl1	111.96 (4)	C1—C6—H6A	120.8
Cl4—Zn1—Cl1	109.28 (4)	C5—C6—H6A	120.8
Cl3—Zn1—Cl2	109.65 (4)	C12—C7—C8	122.0 (3)
Cl4—Zn1—Cl2	106.88 (4)	C12—C7—N2	119.8 (2)
Cl1—Zn1—Cl2	104.38 (3)	C8—C7—N2	118.1 (2)
H1—O1—H2	104 (4)	C7—C8—C9	118.3 (3)
C1—N1—H1A	111 (3)	C7—C8—H8A	120.8
C1—N1—H1B	113 (2)	C9—C8—H8A	120.8
H1A—N1—H1B	107 (3)	C10—C9—C8	120.7 (3)
C1—N1—H1C	112 (2)	C10—C9—H9A	119.7
H1A—N1—H1C	108 (3)	C8—C9—H9A	119.7
H1B—N1—H1C	105 (3)	C11—C10—C9	119.9 (3)
C2—C1—C6	122.2 (3)	C11—C10—H10A	120.1
C2—C1—N1	118.9 (2)	C9—C10—H10A	120.1
C6—C1—N1	118.9 (2)	C10—C11—C12	120.2 (3)
C1—C2—C3	118.6 (3)	C10—C11—H11A	119.9
C1—C2—H2A	120.7	C12—C11—H11A	119.9
C3—C2—H2A	120.7	C7—C12—C11	118.9 (3)
C4—C3—C2	120.0 (3)	C7—C12—H12A	120.5
C4—C3—H3A	120.0	C11—C12—H12A	120.5
C2—C3—H3A	120.0	C7—N2—H2B	112 (3)
C5—C4—C3	120.3 (3)	C7—N2—H2C	110 (3)
C5—C4—H4A	119.9	H2B—N2—H2C	110 (3)
C3—C4—H4A	119.9	C7—N2—H2D	109 (2)
C4—C5—C6	120.5 (3)	H2B—N2—H2D	110 (3)
C4—C5—H5A	119.8	H2C—N2—H2D	105 (3)
C6—C5—H5A	119.8		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

O1—H1···Cl4[i]	0.92 (6)	2.30 (6)	3.172 (3)	159 (6)
O1—H2···Cl2	0.82 (5)	2.43 (5)	3.215 (4)	162 (5)
N1—H1A···O1[ii]	0.85 (4)	2.04 (4)	2.889 (4)	173 (4)
N1—H1B···O1	0.90 (4)	2.37 (4)	3.022 (4)	130 (3)
N1—H1B···Cl3	0.90 (4)	2.64 (4)	3.343 (3)	135 (3)
N1—H1C···Cl1[iii]	0.91 (4)	2.57 (4)	3.426 (3)	156 (3)
N2—H2B···Cl2[i]	0.85 (4)	2.45 (4)	3.276 (3)	167 (4)
N2—H2C···Cl1[iii]	0.85 (5)	2.47 (4)	3.246 (3)	153 (4)
N2—H2D···Cl3	0.97 (4)	2.35 (4)	3.262 (3)	156 (3)

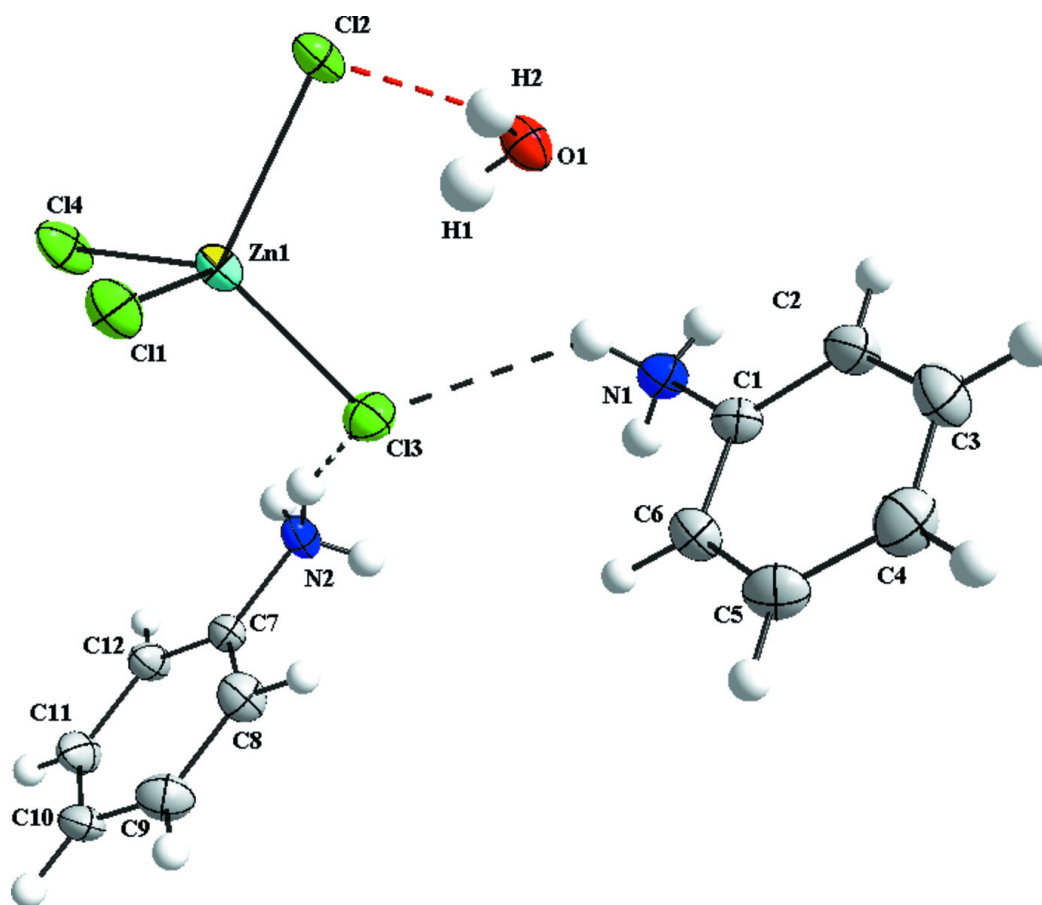Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+2, -z+1$; (iii) $x+1, y, z$.

Fig. 1

Fig. 2