Ethylenediaminium tetrachlorozincate

William T. A. Harrison

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

The title compound, $(C_2H_{10}N_2)[ZnCl_4]$, contains a network of ethylenediaminium cations and tetrahedral tetrachlorozincate anions. A three-dimensional network of N—H···Cl hydrogen bonds, some of which are bifurcated, helps to establish the crystal packing.

Comment

The title compound, (I), (Fig. 1), contains a network of ethylenediaminium cations and tetrahedral tetrachlorozincate anions. The $ZnCl_4^{2-}$ anion has been seen in many crystal structures and possesses (Table 1) typical Zn—Cl bond lengths (Deeth *et al.*, 1984), with a mean value of 2.268 (4) Å. The Cl—Zn—Cl bond angles in (I) indicate relatively little distortion from a regular tetrahedron [spread of values 104.78 (10)–115.57 (13)°].

$$H_3N^+ \diagup\diagdown NH_3^+ \cdot [ZnCl_4]^{2-}$$

(I)
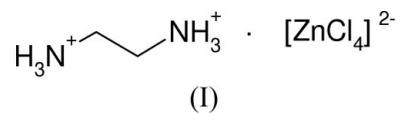
To ensure charge balance for (I), the organic species must be doubly protonated. Each –NH$_3$ group participates in N—H···Cl hydrogen bonds (Table 2), three of which are bifurcated. These interactions help to establish a three-dimensional hydrogen-bond network (Fig. 2) in (I). Such N—H···Cl and N—H···(Cl,Cl) interactions have been discussed in the context of crystal engineering (Brammer *et al.*, 2002).

Compound (I) is clearly different from the phase described as $(C_2H_{10}N_2)_2 \cdot ZnCl_6$ (Deeth *et al.*, 1984), which is probably better formulated as $(C_2H_{10}N_2)_2 \cdot ZnCl_4 \cdot Cl_2$, *i.e.* it contains tetrachlorozincate anions, as does (I), as well as two 'free' Cl$^-$ ions, and not $ZnCl_6^{4-}$ moieties. Deeth *et al.* (1984) reported some basic geometric information for $(C_2H_{10}N_2)_2 \cdot ZnCl_6$ and
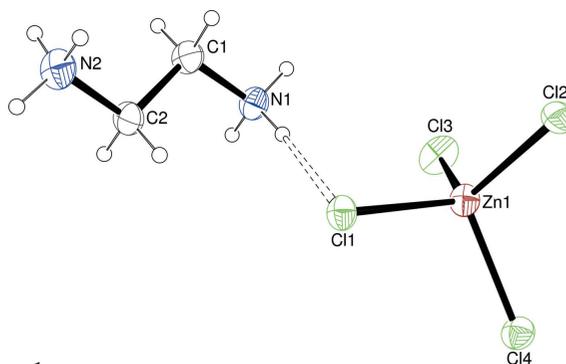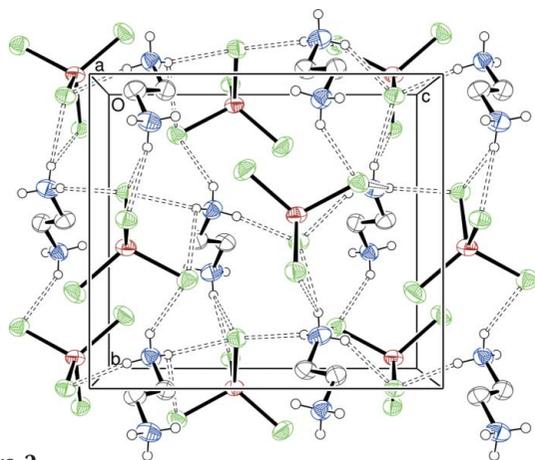

Figure 1
A view of (I), showing 30% probability displacement ellipsoids and arbitrary spheres for the H atoms. The hydrogen bond is indicated by dashed lines.

Figure 2
The unit-cell packing in (I), viewed down [100], with hydrogen bonds indicated a dashed bond.

noted that other workers would report its full single-crystal structure in due course, but we have not been able to locate this paper. Based on similarities in cell parameters and space group, $(C_2H_{10}N_2)_2 \cdot HgCl_6$ (Spengler *et al.*, 1998) probably has a close structural relationship to $(C_2H_{10}N_2)_2 \cdot ZnCl_6$. However, the detailed coordination about the metal atom is likely to be different in the two phases. As noted above, the zinc compound probably contains relatively regular tetrahedral complex ions, whereas in the mercury compound, the metal coordination could be described as grossly distorted tetrahedral or possibly five-coordinate.

Experimental

Acidified aqueous zinc chloride and ethylenediamine were mixed in a 1:1 ratio in a Petri dish, resulting in a clear solution. Rod and block-like crystals of (I) grew as the water evaporated over a few days at 298 K.

Crystal data

$(C_2H_{10}N_2)[ZnCl_4]$
$M_r = 269.29$
Orthorhombic, $P2_12_12_1$
$a = 8.832 (4)$ Å
$b = 9.811 (4)$ Å
$c = 11.089 (5)$ Å
$V = 960.9 (7)$ Å^3
$Z = 4$
$D_x = 1.862$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25
    reflections
$\theta = 10.0–15.0°$
$\mu = 3.60$ mm^{-1}
$T = 298 (2)$ K
Rod, colourless
$0.40 \times 0.10 \times 0.10$ mm

Data collection

Siemens $P4$ diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan
    (*XEMP*; Siemens, 1990)
    $T_{min} = 0.327$, $T_{max} = 0.715$
1744 measured reflections
1616 independent reflections
1383 reflections with $I > 2\sigma(I)$

$R_{int} = 0.114$
$\theta_{max} = 26.0°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -6 \rightarrow 13$
3 standard reflections
    every 97 reflections
    intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.084$
$wR(F^2) = 0.209$
$S = 1.05$
1616 reflections
84 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1645P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -1.09$ e Å^{-3}
Absolute structure: Flack (1983),
    with 507 Friedel pairs
Flack parameter: $-0.01 (5)$

Table 1
Selected bond lengths (Å).

Zn1—Cl3	2.240 (3)	Zn1—Cl4	2.275 (3)
Zn1—Cl2	2.262 (3)	Zn1—Cl1	2.296 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$Cl2^i	0.89	2.48	3.240 (10)	144
N1—H1$A\cdots$Cl4^i	0.89	2.94	3.472 (9)	120
N1—H1$B\cdots$Cl4^{ii}	0.89	2.40	3.185 (10)	147
N1—H1$C\cdots$Cl1	0.89	2.29	3.173 (10)	169
N2—H2$C\cdots$Cl2^{iii}	0.89	2.47	3.239 (11)	146
N2—H2$C\cdots$Cl4^{iv}	0.89	2.83	3.381 (10)	121
N2—H2$D\cdots$Cl1^{iv}	0.89	2.46	3.242 (11)	148
N2—H2$E\cdots$Cl1^v	0.89	2.65	3.260 (9)	127
N2—H2$E\cdots$Cl2^v	0.89	2.85	3.618 (11)	146

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

The H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.97 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}$(carrier), allowing for free rotation of the rigid –NH$_3$ groups about their C—N bonds.

Data collection: *XSCANS* (Siemens, 1990); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

References

Brammer, L., Swearingen, J. K., Bruton, E. A. & Sherwood, P. (2002). *Proc. Natl Acad. Sci. USA*, **99**, 4956–4961.
Deeth, R. J., Hitchman, M. A., Lehmann, G. & Sachs, H. (1984). *Inorg. Chem.* **23**, 1310–1320.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Siemens (1990). *XSCANS* and *XEMP*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spengler, R., Zouari, R., Ben Salah, A., Zimmermann, H. & Burzlaff, H. (1998). *Acta Cryst.* C**54**, IUC98000034.

supporting information

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S3. Refinement

The H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.97 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}$(carrier), allowing for free rotation of the rigid –NH₃ groups about their C—N bonds.
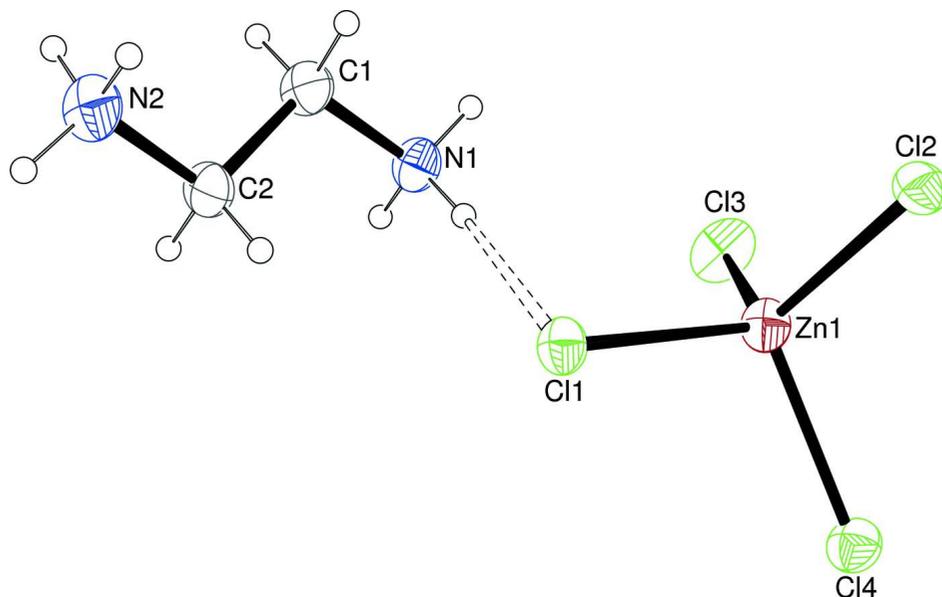
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Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 25 reflections
$a = 8.832$ (4) Å	$\theta = 10.0–15.0°$
$b = 9.811$ (4) Å	$\mu = 3.60$ mm^{-1}
$c = 11.089$ (5) Å	$T = 298$ K
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$Z = 4$	$0.40 \times 0.10 \times 0.10$ mm

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Radiation source: fine-focus sealed tube	1383 reflections with $I > 2\sigma(I)$
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$\omega/2\theta$ scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.8°$
Absorption correction: ψ scan	$h = 0\rightarrow10$
(*XEMP*; Siemens, 1990)	$k = 0\rightarrow12$
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1744 measured reflections	3 standard reflections every 97 reflections
	intensity decay: none

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.084$	$w = 1/[\sigma^2(F_o^2) + (0.1645P)^2]$
$wR(F^2) = 0.209$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
1616 reflections	$\Delta\rho_{max} = 0.71$ e Å^{-3}
84 parameters	$\Delta\rho_{min} = -1.09$ e Å^{-3}
0 restraints	Absolute structure: Flack (1983), with 507 Friedel pairs
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: −0.01 (5)
Secondary atom site location: difference Fourier map	

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 $F^2 > \sigma(F^2)$ 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	0.74608 (12)	0.44688 (10)	0.59176 (11)	0.0401 (4)
Cl1	0.5065 (3)	0.5365 (2)	0.6046 (2)	0.0414 (6)

Cl2	0.9010 (3)	0.6303 (3)	0.5849 (3)	0.0470 (7)
Cl3	0.7716 (4)	0.2983 (3)	0.4398 (3)	0.0622 (9)
Cl4	0.7838 (3)	0.3397 (3)	0.7712 (3)	0.0475 (7)
N1	0.4356 (10)	0.4257 (9)	0.3418 (8)	0.044 (2)
H1A	0.5159	0.4221	0.2935	0.052*
H1B	0.3905	0.3446	0.3435	0.052*
H1C	0.4650	0.4483	0.4159	0.052*
C1	0.3275 (12)	0.5296 (11)	0.2959 (11)	0.046 (3)
H1D	0.2940	0.5045	0.2156	0.055*
H1E	0.3774	0.6175	0.2910	0.055*
C2	0.1931 (11)	0.5392 (11)	0.3790 (11)	0.045 (3)
H2A	0.1402	0.4526	0.3811	0.054*
H2B	0.2268	0.5604	0.4601	0.054*
N2	0.0903 (11)	0.6472 (9)	0.3351 (10)	0.053 (3)
H2C	0.0063	0.6475	0.3795	0.064*
H2D	0.0666	0.6313	0.2584	0.064*
H2E	0.1360	0.7277	0.3411	0.064*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0411 (6)	0.0309 (6)	0.0483 (8)	0.0031 (5)	−0.0030 (6)	−0.0023 (5)
Cl1	0.0379 (11)	0.0363 (12)	0.0499 (14)	0.0040 (9)	−0.0024 (11)	−0.0030 (11)
Cl2	0.0501 (12)	0.0436 (14)	0.0471 (14)	−0.0111 (11)	−0.0013 (13)	0.0031 (12)
Cl3	0.082 (2)	0.0500 (15)	0.0543 (17)	0.0218 (14)	−0.0053 (15)	−0.0167 (13)
Cl4	0.0486 (14)	0.0435 (13)	0.0504 (16)	0.0083 (11)	−0.0019 (12)	0.0055 (12)
N1	0.043 (5)	0.042 (5)	0.046 (5)	0.007 (4)	−0.003 (4)	−0.004 (4)
C1	0.046 (6)	0.045 (6)	0.047 (6)	0.013 (5)	0.005 (5)	−0.001 (5)
C2	0.039 (5)	0.041 (5)	0.056 (7)	0.012 (4)	0.006 (5)	0.004 (5)
N2	0.052 (5)	0.042 (5)	0.065 (7)	0.016 (5)	0.005 (5)	−0.008 (5)

Geometric parameters (Å, º)

Zn1—Cl3	2.240 (3)	C1—H1D	0.9700
Zn1—Cl2	2.262 (3)	C1—H1E	0.9700
Zn1—Cl4	2.275 (3)	C2—N2	1.478 (12)
Zn1—Cl1	2.296 (3)	C2—H2A	0.9700
N1—C1	1.486 (12)	C2—H2B	0.9700
N1—H1A	0.8900	N2—H2C	0.8900
N1—H1B	0.8900	N2—H2D	0.8900
N1—H1C	0.8900	N2—H2E	0.8900
C1—C2	1.506 (15)		
Cl3—Zn1—Cl2	115.57 (13)	N1—C1—H1E	109.7
Cl3—Zn1—Cl4	110.01 (12)	C2—C1—H1E	109.7
Cl2—Zn1—Cl4	107.97 (11)	H1D—C1—H1E	108.2
Cl3—Zn1—Cl1	112.89 (12)	N2—C2—C1	109.1 (9)
Cl2—Zn1—Cl1	104.78 (10)	N2—C2—H2A	109.9

Cl4—Zn1—Cl1	104.93 (11)	C1—C2—H2A	109.9
C1—N1—H1A	109.5	N2—C2—H2B	109.9
C1—N1—H1B	109.5	C1—C2—H2B	109.9
H1A—N1—H1B	109.5	H2A—C2—H2B	108.3
C1—N1—H1C	109.5	C2—N2—H2C	109.5
H1A—N1—H1C	109.5	C2—N2—H2D	109.5
H1B—N1—H1C	109.5	H2C—N2—H2D	109.5
N1—C1—C2	109.8 (9)	C2—N2—H2E	109.5
N1—C1—H1D	109.7	H2C—N2—H2E	109.5
C2—C1—H1D	109.7	H2D—N2—H2E	109.5
N1—C1—C2—N2	177.4 (8)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl2[i]	0.89	2.48	3.240 (10)	144
N1—H1A···Cl4[i]	0.89	2.94	3.472 (9)	120
N1—H1B···Cl4[ii]	0.89	2.40	3.185 (10)	147
N1—H1C···Cl1	0.89	2.29	3.173 (10)	169
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Symmetry codes: (i) $-x+3/2$, $-y+1$, $z-1/2$; (ii) $x-1/2$, $-y+1/2$, $-z+1$; (iii) $x-1$, y, z; (iv) $-x+1/2$, $-y+1$, $z-1/2$; (v) $x-1/2$, $-y+3/2$, $-z+1$.