

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Piperazinediium tetrachloridozincate(II)

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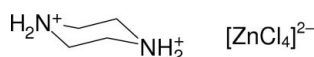
Received 13 April 2009; accepted 14 April 2009

 Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.042; wR factor = 0.094; data-to-parameter ratio = 23.6.

In the title compound, $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{ZnCl}_4]$, the Zn atom adopts a slightly distorted tetrahedral geometry. In the crystal, the dication and dianion interact by way of $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{N}-\text{H}\cdots(\text{Cl},\text{Cl})$ hydrogen bonds to result in a layered network propagating in (010). The hydrogen-bonding network is unbalanced, with three Cl atoms accepting two hydrogen bonds each and one Cl atom not accepting any hydrogen bonds: the latter shows the shortest Zn–Cl bond length. The crystal studied was found to be an inversion twin.

Related literature

For related structures, see: Bremner & Harrison (2003); Kefi & Nasr (2005); Wilkinson & Harrison (2007). For reference structural data, see: Allen *et al.* (1995). For details of graph-set theory, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$(\text{C}_4\text{H}_{12}\text{N}_2)[\text{ZnCl}_4]$
 $M_r = 295.33$
 Orthorhombic, $P2_12_12_1$
 $a = 8.2309$ (3) Å
 $b = 11.0845$ (3) Å
 $c = 11.8443$ (4) Å
 $V = 1080.62$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.21$ mm⁻¹
 $T = 120$ K
 $0.13 \times 0.09 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2003)
 $T_{\min} = 0.681$, $T_{\max} = 0.882$
 8838 measured reflections
 2388 independent reflections
 2194 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.094$
 $S = 1.08$
 2388 reflections
 101 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.92$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.77$ e Å⁻³
 Absolute structure: Flack (1983),
 946 Friedel pairs
 Flack parameter: 0.44 (2)

Table 1

Selected bond lengths (Å).

| | | | |
|---------|-------------|---------|-------------|
| Zn1–Cl1 | 2.2768 (12) | Zn1–Cl3 | 2.2532 (12) |
| Zn1–Cl2 | 2.3119 (12) | Zn1–Cl4 | 2.2634 (12) |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| N1–H1 \cdots Cl2 | 0.92 | 2.33 | 3.239 (5) | 171 |
| N1–H2 \cdots Cl4 | 0.92 | 2.77 | 3.168 (4) | 107 |
| N1–H2 \cdots Cl1 ⁱ | 0.92 | 2.49 | 3.206 (4) | 135 |
| N2–H3 \cdots Cl2 ⁱⁱ | 0.92 | 2.28 | 3.174 (4) | 164 |
| N2–H4 \cdots Cl4 ⁱⁱⁱ | 0.92 | 2.50 | 3.194 (5) | 133 |
| N2–H4 \cdots Cl1 ⁱⁱⁱ | 0.92 | 2.70 | 3.346 (4) | 128 |

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

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK, and SORTAV (Blessing, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

We thank the EPSRC UK National Crystallography Service (University of Southampton) for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2253).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1995). *International Tables for Crystallography*, Vol. C, Section 9.5, pp. 685–706. Dordrecht: Kluwer Academic Publishers.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Bremner, C. A. & Harrison, W. T. A. (2003). *Acta Cryst.* **E59**, m425–m426.
- Bruker (2003). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Kefi, R. & Nasr, C. B. (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 241.
- Nonius (1998). COLLECT. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Wilkinson, H. S. & Harrison, W. T. A. (2007). *Acta Cryst.* **E63**, m1610–m1612.

supplementary materials

Acta Cryst. (2009). E65, m565 [doi:10.1107/S1600536809013981]

Piperazinediium tetrachloridozincate(II)

P. A. Sutherland and W. T. A. Harrison

Comment

As part of our ongoing investigations of hydrogen bonding networks in molecular salts containing metal-chlorido complexes, (Bremner & Harrison, 2003), we now report the structure of the title compound, (I). The structure of a monohydrate containing the same cation and anion was reported previously (Kefi & Nasr, 2005).

The Zn atom in (I) adopts a slightly distorted tetrahedral coordination arising from four chloride ions (Table 1, Fig. 1) and the organic dication adopts a typical chair geometry with normal bond lengths and angles (Allen *et al.*, 1995), the two nitrogen atoms being displaced from the mean plane of the four carbon atoms by $-0.654(7)\text{\AA}$ and $0.685(6)\text{\AA}$ for N1 and N2, respectively.

In the crystal of (I), the components interact by way of simple N—H \cdots Cl and bifurcated N—H \cdots (Cl,Cl) hydrogen bonds (Table 2), such that each NH₂ group forms one simple and one bifurcated bond. Some of the bifurcated H \cdots Cl contacts are relatively long, but still significantly shorter than the H \cdots Cl van der Waals' contact distance of 2.95\AA .

This hydrogen-bond connectivity results in a layered network propagating in (010) (Fig. 2). It is notable that this H bonding arrangement is unbalanced (Wilkinson & Harrison, 2007), with Cl1, Cl2 and Cl4 accepting two hydrogen bonds each, whereas Cl3 does not accept any H bonds. This may correlate with the fact that the Zn1—Cl3 bond length in (I) is the shortest of the four zinc–chloride links. Within the layers, various graph-set motifs (Bernstein *et al.*, 1995) are apparent, including $R^2_2(6)$ and $R^4_4(14)$ loops.

In (C₄H₁₂N₂).[ZnCl₄].H₂O (Kefi & Nasr, 2005), a combination of N—H \cdots Cl, N—H \cdots O and O—H \cdots Cl hydrogen bonds results in a three-dimensional network.

Experimental

In an attempt to prepare a zinc–arsenite open-framework compound, ZnO, As₂O₃ and piperazine hexahydrate were dissolved in a 1:1:1 molar ratio in dilute HCl solution. Colourless slabs of (I) grew as the water slowly evaporated, accompanied by octahedra of As₂O₃.

Refinement

The H atoms were placed in idealized locations (C—H = 0.99\AA , N—H = 0.92\AA) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$.

Figures



Fig. 1. View of the molecular structure of (I) showing 50% displacement ellipsoids (arbitrary spheres for the H atoms) with the hydrogen bonds indicated by double dashed lines.

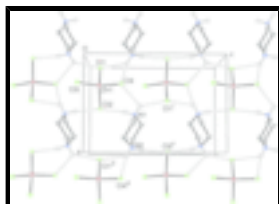


Fig. 2. Part of an (010) hydrogen bonded sheet in the structure of (I) with the hydrogen bonds shown as double dashed lines. All the carbon-bound H atoms are omitted for clarity. Symmetry codes as in Table 2.

Piperazinediium tetrachloridozincate(II)

Crystal data

(C₄H₁₂N₂)[ZnCl₄]

M_r = 295.33

Orthorhombic, *P*2₁2₁2₁

Hall symbol: P 2ac 2ab

a = 8.2309 (3) Å

b = 11.0845 (3) Å

c = 11.8443 (4) Å

V = 1080.62 (6) Å³

Z = 4

*F*₀₀₀ = 592

D_x = 1.815 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 8676 reflections

θ = 2.9–27.5°

μ = 3.21 mm⁻¹

T = 120 K

Slab, colourless

0.13 × 0.09 × 0.04 mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 120 K

ω and *φ* scans

Absorption correction: multi-scan
(SADABS; Bruker, 2003)

T_{min} = 0.681, *T_{max}* = 0.882

8838 measured reflections

2388 independent reflections

2194 reflections with *I* > 2σ(*I*)

R_{int} = 0.058

θ_{max} = 27.5°

θ_{min} = 3.0°

h = -9→10

k = -12→14

l = -15→15

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.042

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0219*P*)² + 3.2663*P*]

| | |
|--|--|
| $wR(F^2) = 0.094$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.08$ | $(\Delta/\sigma)_{\max} < 0.001$ |
| 2388 reflections | $\Delta\rho_{\max} = 0.92 \text{ e } \text{\AA}^{-3}$ |
| 101 parameters | $\Delta\rho_{\min} = -0.77 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |
| Secondary atom site location: difference Fourier map | Absolute structure: Flack (1983), 946 Friedel pairs |
| | Flack parameter: 0.44 (2) |

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Zn1 | 0.27149 (6) | 0.46334 (5) | 0.09228 (5) | 0.01746 (15) |
| Cl1 | 0.06341 (13) | 0.59864 (10) | 0.09534 (11) | 0.0192 (2) |
| Cl2 | 0.51483 (13) | 0.56726 (10) | 0.09893 (11) | 0.0193 (2) |
| Cl3 | 0.24980 (15) | 0.34993 (10) | -0.06487 (9) | 0.0212 (3) |
| Cl4 | 0.26367 (15) | 0.35675 (9) | 0.25519 (9) | 0.0182 (3) |
| C1 | 0.6765 (6) | 0.3608 (4) | 0.3437 (5) | 0.0211 (11) |
| H1A | 0.6095 | 0.2999 | 0.3040 | 0.025* |
| H1B | 0.7022 | 0.3292 | 0.4198 | 0.025* |
| C2 | 0.8319 (6) | 0.3817 (4) | 0.2790 (4) | 0.0189 (10) |
| H2A | 0.8947 | 0.3057 | 0.2747 | 0.023* |
| H2B | 0.8062 | 0.4078 | 0.2010 | 0.023* |
| C3 | 0.8383 (6) | 0.5925 (5) | 0.3449 (4) | 0.0196 (10) |
| H3A | 0.8136 | 0.6227 | 0.2681 | 0.024* |
| H3B | 0.9052 | 0.6539 | 0.3839 | 0.024* |
| C4 | 0.6815 (6) | 0.5734 (4) | 0.4092 (5) | 0.0189 (9) |
| H4A | 0.7063 | 0.5505 | 0.4881 | 0.023* |
| H4B | 0.6185 | 0.6495 | 0.4106 | 0.023* |
| N1 | 0.5828 (5) | 0.4761 (4) | 0.3544 (4) | 0.0180 (9) |
| H1 | 0.5509 | 0.5014 | 0.2839 | 0.022* |
| H2 | 0.4907 | 0.4625 | 0.3966 | 0.022* |
| N2 | 0.9310 (5) | 0.4768 (4) | 0.3369 (4) | 0.0189 (9) |
| H3 | 0.9583 | 0.4509 | 0.4082 | 0.023* |
| H4 | 1.0256 | 0.4894 | 0.2972 | 0.023* |

supplementary materials

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|------------|------------|--------------|-------------|--------------|
| Zn1 | 0.0130 (3) | 0.0212 (3) | 0.0182 (3) | -0.0007 (2) | -0.0003 (3) | -0.0015 (2) |
| C11 | 0.0164 (5) | 0.0221 (5) | 0.0191 (5) | 0.0024 (4) | -0.0007 (5) | -0.0019 (5) |
| C12 | 0.0142 (5) | 0.0253 (5) | 0.0183 (5) | -0.0030 (4) | 0.0008 (5) | 0.0002 (5) |
| C13 | 0.0181 (6) | 0.0240 (6) | 0.0214 (6) | -0.0006 (5) | -0.0002 (5) | -0.0045 (4) |
| C14 | 0.0151 (6) | 0.0188 (5) | 0.0205 (5) | -0.0014 (5) | -0.0001 (5) | -0.0003 (4) |
| C1 | 0.016 (3) | 0.017 (2) | 0.030 (3) | -0.001 (2) | 0.002 (2) | 0.000 (2) |
| C2 | 0.019 (2) | 0.019 (2) | 0.019 (2) | 0.0003 (19) | -0.001 (2) | -0.002 (2) |
| C3 | 0.013 (2) | 0.021 (2) | 0.024 (3) | 0.001 (2) | 0.000 (2) | 0.001 (2) |
| C4 | 0.013 (2) | 0.023 (2) | 0.021 (2) | -0.0004 (17) | 0.002 (2) | -0.002 (2) |
| N1 | 0.0091 (19) | 0.025 (2) | 0.020 (2) | -0.0019 (18) | 0.0000 (16) | 0.0001 (18) |
| N2 | 0.013 (2) | 0.024 (2) | 0.020 (2) | 0.0030 (19) | 0.0031 (17) | -0.0008 (18) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-------------|-------------|------------|-----------|
| Zn1—C11 | 2.2768 (12) | C3—N2 | 1.496 (6) |
| Zn1—C12 | 2.3119 (12) | C3—C4 | 1.513 (7) |
| Zn1—C13 | 2.2532 (12) | C3—H3A | 0.9900 |
| Zn1—C14 | 2.2634 (12) | C3—H3B | 0.9900 |
| C1—N1 | 1.499 (7) | C4—N1 | 1.498 (6) |
| C1—C2 | 1.510 (7) | C4—H4A | 0.9900 |
| C1—H1A | 0.9900 | C4—H4B | 0.9900 |
| C1—H1B | 0.9900 | N1—H1 | 0.9200 |
| C2—N2 | 1.498 (6) | N1—H2 | 0.9200 |
| C2—H2A | 0.9900 | N2—H3 | 0.9200 |
| C2—H2B | 0.9900 | N2—H4 | 0.9200 |
| C13—Zn1—C14 | 114.25 (4) | N2—C3—H3B | 109.6 |
| C13—Zn1—C11 | 108.73 (5) | C4—C3—H3B | 109.6 |
| C14—Zn1—C11 | 107.99 (5) | H3A—C3—H3B | 108.1 |
| C13—Zn1—C12 | 112.01 (5) | N1—C4—C3 | 110.2 (4) |
| C14—Zn1—C12 | 104.82 (5) | N1—C4—H4A | 109.6 |
| C11—Zn1—C12 | 108.84 (5) | C3—C4—H4A | 109.6 |
| N1—C1—C2 | 110.4 (4) | N1—C4—H4B | 109.6 |
| N1—C1—H1A | 109.6 | C3—C4—H4B | 109.6 |
| C2—C1—H1A | 109.6 | H4A—C4—H4B | 108.1 |
| N1—C1—H1B | 109.6 | C4—N1—C1 | 111.8 (4) |
| C2—C1—H1B | 109.6 | C4—N1—H1 | 109.2 |
| H1A—C1—H1B | 108.1 | C1—N1—H1 | 109.2 |
| N2—C2—C1 | 109.7 (4) | C4—N1—H2 | 109.2 |
| N2—C2—H2A | 109.7 | C1—N1—H2 | 109.2 |
| C1—C2—H2A | 109.7 | H1—N1—H2 | 107.9 |
| N2—C2—H2B | 109.7 | C3—N2—C2 | 110.8 (4) |
| C1—C2—H2B | 109.7 | C3—N2—H3 | 109.5 |
| H2A—C2—H2B | 108.2 | C2—N2—H3 | 109.5 |
| N2—C3—C4 | 110.3 (4) | C3—N2—H4 | 109.5 |

| | | | |
|-------------|-----------|-------------|-----------|
| N2—C3—H3A | 109.6 | C2—N2—H4 | 109.5 |
| C4—C3—H3A | 109.6 | H3—N2—H4 | 108.1 |
| N1—C1—C2—N2 | 57.4 (5) | C2—C1—N1—C4 | -56.6 (5) |
| N2—C3—C4—N1 | -56.4 (5) | C4—C3—N2—C2 | 58.8 (5) |
| C3—C4—N1—C1 | 55.8 (5) | C1—C2—N2—C3 | -59.1 (5) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1 \cdots Cl2 | 0.92 | 2.33 | 3.239 (5) | 171 |
| N1—H2 \cdots Cl4 | 0.92 | 2.77 | 3.168 (4) | 107 |
| N1—H2 \cdots Cl1 ⁱ | 0.92 | 2.49 | 3.206 (4) | 135 |
| N2—H3 \cdots Cl2 ⁱⁱ | 0.92 | 2.28 | 3.174 (4) | 164 |
| N2—H4 \cdots Cl4 ⁱⁱⁱ | 0.92 | 2.50 | 3.194 (5) | 133 |
| N2—H4 \cdots Cl1 ⁱⁱⁱ | 0.92 | 2.70 | 3.346 (4) | 128 |

Symmetry codes: (i) $-x+1/2, -y+1, z+1/2$; (ii) $-x+3/2, -y+1, z+1/2$; (iii) $x+1, y, z$.

Fig. 1

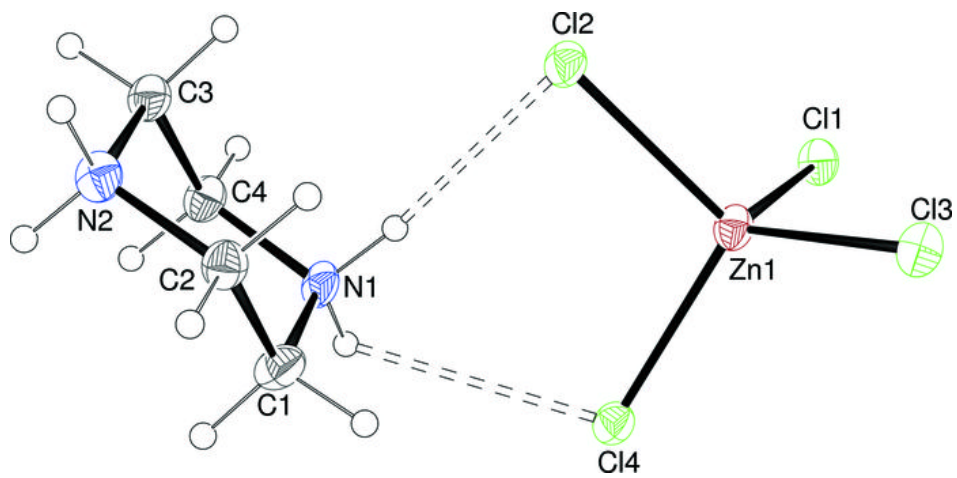


Fig. 2

