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The complex salt benzodiimidazolium tetrachlorozincate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.026
wR factor = 0.072
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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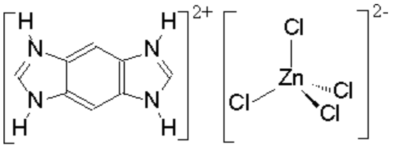
The title compound, $(C_8H_8N_4)[ZnCl_4]$, consists of the benzodiimidazolium cation and tetrachlorozincate anion. As expected, the benzodiimidazolium is essentially planar, while the $[ZnCl_4]^{2-}$ unit has a regular tetrahedral geometry; they have approximate C_{2h} and T_d symmetry, respectively. The hydrogen bonding formed by the chloride ligand with the HN moiety leads to an extended two-dimensional structure.

Comment

Crystal engineering of inorganic/organic hybrid materials is based on a modular approach, where discrete building blocks are constructed into extended networks. In the search for reliable strategies for crystal synthesis by design, a key goal is the identification and exploitation of robust synthons to control the relative orientation of the molecular components of the solid. Among the usual interactions found to assemble the molecular crystal, hydrogen-bonding interactions have attracted more attention. Recently, Aullon *et al.* (1998) have shown that, in the case of transition metal chloride complexes, M—Cl moieties are much better hydrogen-bond acceptors than are their organic analogues (organochlorine species, C—Cl). Gillon *et al.* (2000) have exploited the $MX\cdots HN^+$ hydrogen-bond synthon in synthesizing a series of complex salts [4,4′-H_2bipy][MX_4] (X = Cl, M = Pd, Pt, Co, Zn, Hg, Mn, Cd, and Pb). In these salts they observed three structural forms for the halometallate species: mononuclear square planar (M = Pd, Pt), tetrahedral (M = Co, Zn, Hg), and polymeric *cis* edge-sharing octahedral (M = Mn, Cd, Pb). In the first form, there are interactions of $MCl_2\cdots HN$ yielding four-membered ring $R^1_2(4)$ hydrogen bonding. However, they did not observe the same pattern of hydrogen bond in the structure of the tetrahedral metal centre. Here we report a complex salt composed of a tetrahedral tetrachlorometalate anion and a protonated planar nitrogen heterocycle. In the crystal structure, four-membered ring hydrogen bonding was observed. Moreover, such hydrogen bonding leads to a two-dimensional sheet structure.



(I)

As shown in Fig. 1, the complex salt, (I), is composed of a benzodiimidazolium cation and a tetrachlorozincate anion. Selected bond lengths and angles are listed in Table 1. The cation is planar, as expected. The $[ZnCl_4]^{2-}$ unit has a regular

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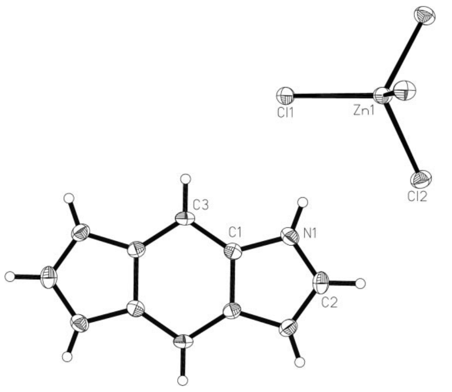

Figure 1
The structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

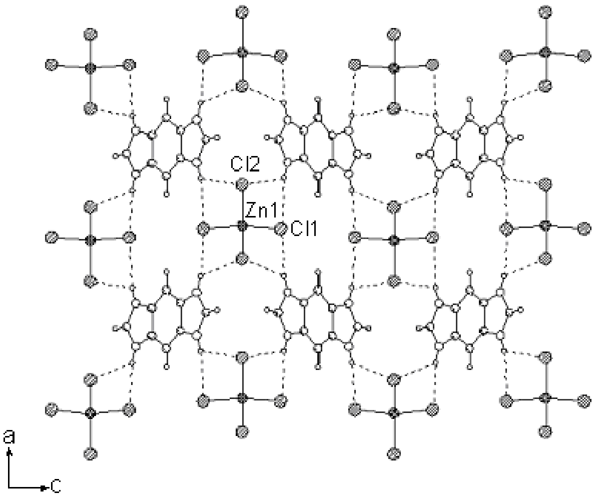

Figure 2
The crystal packing diagram for the title compound, viewed along the *b* axis, showing the hydrogen bonding.

tetrahedral geometry. The remarkable feature in the complex salt is the hydrogen bonding, which connects the cations and anions to form a two-dimensional sheet structure. As shown in Fig. 2, there are three types of ring hydrogen bonding in the structure: $R^1_2(4)$, $R^4_2(12)$, and $R^4_2(16)$ (Bernstein *et al.*, 1995). Table 2 presents the parameters of the hydrogen bonding. As with the observation of Lewis & Orpen (1998) for $[H_2bipy][MCl_4]$ (M = Pt, Pd), a pair of chloride ligands at a metal form a chelate hydrogen bond with a single H—N moiety. Due to the larger Cl—M—Cl angle in the tetrahedral geometry than that in square-planar geometry, the M—HN distance is shorter (3.177 Å) and the M—Cl···HN angles (78.2 and 82.9°) are smaller in our study than the corresponding values for the square-planar metal centre. Furthermore, each chloride ligand bridges two H atoms of HN moieties to form the other two types of hydrogen-bonded ring: $R^4_2(12)$ and $R^4_2(16)$. The NH···Cl···HN angles in the two different rings are 93.6 and 148.8°, respectively. The benzodiimidazolium ions bridged through hydrogen bonding along the *a* axis are in the same plane, while along the *c* axis they are arranged with a dihedral angle of 76.0°, in a zigzag pattern. Along the *b* axis, such sheets stack in an *ABAB* sequence. Therefore, no face-to-face π–π interactions exist. Non-classical Cl···H—C hydrogen-bonding [Cl1···H2$A^{\rm i}$ 2.876 Å and Cl1···H2$A^{\rm i}$—C2$^{\rm i}$ 139.1°; symmetry code: (i) $\frac{1}{2}-x, -\frac{1}{2}+y, z$] contributes to this type of stacking.

Experimental

Benzodiimidazole (DMBDIZ) was synthesized from 1,2,4,5-benzentetramine, according to the literature procedure of Ariant *et al.* (1960). The free ligand DMBDIZ and $ZnCl_2$ in 1 *M* hydrochloric acid were mixed and the resulting solution was allowed to stand at room temperature. Large plates formed slowly over a period of several days.

Crystal data

$C_8H_8N_4^+\cdot ZnCl_4^-$
M_r = 367.35
Orthorhombic, *Cmcm*
a = 8.719 (2) Å
b = 9.276 (2) Å
c = 15.226 (3) Å
V = 1231.4 (5) Å^3
Z = 4
D_x = 1.981 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 1–25°
μ = 2.84 mm^{-1}
T = 293 (2) K
Plate, colourless
0.4 × 0.4 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\min}$ = 0.33, $T_{\max}$ = 0.75
1169 measured reflections
607 independent reflections
539 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 25.0°
$h = -10 \rightarrow 0$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.073
S = 1.07
607 reflections
50 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.71 e Å^{-3}
$\Delta\rho_{\min}$ = −0.41 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0081 (10)

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.392 (3)	Zn1—Cl1	2.2980 (9)
N1—C2	1.321 (3)	Zn1—Cl2	2.2517 (9)
C1—C3	1.378 (3)		
C2—N1—C1	108.8 (2)	Cl1—Zn1—Cl1$^{\rm i}$	115.95 (5)
C3—C1—N1	130.6 (2)	Cl2—Zn1—Cl1	107.188 (16)

Symmetry code: (i) $x, y, \frac{3}{2}-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl1	0.93	2.50	3.323 (2)	148
N1—H1A···Cl2	0.93	2.75	3.344 (2)	123

H-atom coordinates were obtained from difference Fourier syntheses; their positions were constrained with a riding model and their individual isotropic displacement parameters were refined.

Data collection: *CAD*-4 *VAX*/*PC Diffractometer Control Software* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *VAX*/*PC Diffractometer Control Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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