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Key indicators

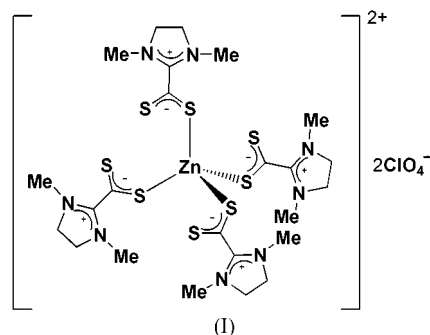
Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$
 R factor = 0.083
 wR factor = 0.173
Data-to-parameter ratio = 21.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetrakis(1,3-dimethylimidazolidinium-2-dithiocarboxylate- κS)zinc(II) diperchlorate

The title compound, $[\text{Zn}(\text{C}_6\text{H}_{10}\text{N}_2\text{S}_2)_4](\text{ClO}_4)_2$, containing four inner-salt ligands, is considered to retain an inner-salt structure in the crystal structure, where the planes of the carbenium and the dithiocarboxylate moieties are nearly perpendicular to each other [$85(2)^\circ$]. The asymmetric unit consists of one-half of the complex molecule, as the complex has twofold crystallographic symmetry. The backbone $\text{C}-\text{C}$ bond length [$\text{N}_2\text{C}-\text{CS}_2 = 1.488(7)\text{ \AA}$] is significantly shorter than that of a normal $\text{C}-\text{C}$ single bond.

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Comment

Bis(N,N -disubstituted amino)carbenium dithiocarboxylates are a structurally interesting unique class of inner salts. They have been investigated with regard to their syntheses, structures, and reactivities (Nakayama, 1993, 2000, 2002). Their thermodynamic stability is apparently due to delocalization of the positive and the negative charges on the $\text{N}-\text{C}-\text{N}$ and the $\text{S}-\text{C}-\text{S}$ moieties, respectively. The most remarkable structural characteristic of these compounds is that the CS_2 and CN_2 groups are almost perpendicular (Sheldrick *et al.*, 1980; Ziegler *et al.*, 1987; Borer *et al.*, 1989; Kuhn *et al.*, 1987; Nagasawa *et al.*, 1995; Nakayama *et al.*, 2000; Fujihara *et al.*, 2002). We report here the structure of the title complex, (I) (Fig. 1).



The coordination geometry of the Zn atom can be described as distorted tetrahedral (Table 1). The Zn atom lies on a crystallographic site of twofold symmetry. The $\text{Zn}-\text{S}$ bond lengths [$\text{Zn}-\text{S}1 = 2.3811(13)\text{ \AA}$ and $\text{Zn}-\text{S}3 = 2.3747(13)\text{ \AA}$] are in the range found for related compounds (Cox & Tiekink, 1997), while the non-bonded $\text{Zn}\cdots\text{S}$ distance is about 3.39 \AA [$\text{Zn}\cdots\text{S}2 = 3.4358(15)\text{ \AA}$ and $\text{Zn}\cdots\text{S}4 = 3.3361(15)\text{ \AA}$]. 1,3-Dimethylimidazolidinium-2-dithiocarboxylate acts as a monodentate ligand in the crystal structure. The dihedral angle [$85(2)^\circ$] between the plane of the carbenium moiety and that of the dithiocarboxylate moiety is close to 90° as a result of the above-mentioned delocalization of the charges. The reduced length of the $\text{N}_2\text{C}-\text{CS}_2$ bond [$1.488(7)\text{ \AA}$] is attributable to the Coulombic interaction, as revealed in the free

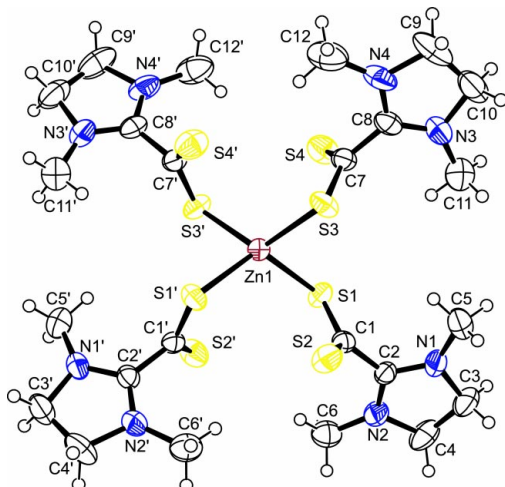


Figure 1
The structure of the cation of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. [Symmetry code: (') $-x, y, \frac{3}{2} - z$.]

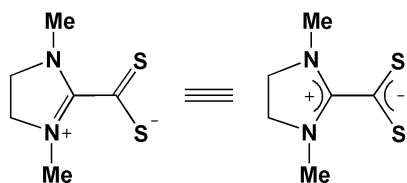


Figure 2
The canonical structure of 1,3-dimethylimidazolidinium-2-dithiocarboxylate.

ligand (Nakayama, 2000). The negative charge spreads equally over these two S atoms since the two C—S bond lengths are not significantly different. The average C—N bond length is 1.31 Å, slightly shorter than a normal Csp^3-Nsp^3 bond length (1.36 Å; Allen *et al.*, 1987), indicating the contribution of the canonical structure shown in Fig. 2. The overall structure of the ligands in (I) is very similar to that of the free ligand. According to these results, the ligand in (I) is considered to retain the inner-salt structure even in the metal complex. The layered structure of the Zn atom, S atoms, organic moieties, and perchlorate anions along the *ab* plane is shown in Fig. 3.

Experimental

The 1,3-dimethylimidazolidinium-2-dithiocarboxylate ligand was synthesized according to a published procedure (Akimoto & Nakayama, 1997). To a solution of $[Zn(H_2O)_6](ClO_4)_2$ (0.0539 g, 0.145 mmol) in ethanol (25 ml) was slowly added a solution of 1,3-dimethylimidazolidinium-2-dithiocarboxylate (0.1 g, 0.573 mmol) in CH_2Cl_2 (25 ml). The resulting mixture was stirred for 3 h. The solvent was removed by evaporation to obtain a pale-red powder of (I). Red crystals suitable for X-ray diffraction were obtained from acetonitrile/diethyl ether. Spectroscopic analysis, IR (KBr, ν cm^{-1}): 2927, 1615, 1020; 1H NMR (CD_3CN , δ): 3.86 (*s*_b, 4H), 2.99 (*s*_b, 6H); ^{13}C NMR (CD_3CN , δ): 221, 166, 49, 32; analysis calculated for $C_{40}H_{80}Cl_2N_8O_8S_8Zn$: C 40.27, H 6.76, N 9.26%; found: C 40.24, H 6.75, N 9.38%.

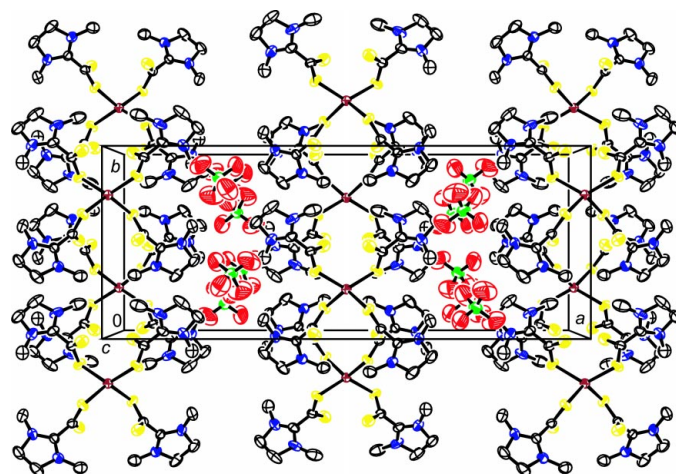


Figure 3
The packing of (I), projected along *c*. H atoms have been omitted for clarity.

Crystal data

$[Zn(C_6H_{10}N_2S_2)_4](ClO_4)_2$
 $M_r = 961.39$
Orthorhombic, *Pbcn*
 $a = 28.6778$ (10) Å
 $b = 11.3532$ (4) Å
 $c = 12.6453$ (5) Å
 $V = 4117.1$ (3) Å³
 $Z = 4$
 $D_x = 1.551$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 8876 reflections
 $\theta = 2.3$ – 27.8°
 $\mu = 1.18$ mm⁻¹
 $T = 298$ (2) K
Block, red
 $0.42 \times 0.25 \times 0.22$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{min} = 0.636$, $T_{max} = 0.781$
27 560 measured reflections

4933 independent reflections
4577 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.036$
 $\theta_{max} = 27.9^\circ$
 $h = -37 \rightarrow 37$
 $k = -14 \rightarrow 14$
 $l = -7 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.083$
 $wR(F^2) = 0.173$
 $S = 1.31$
4933 reflections
235 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 12.633P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.68$ e Å⁻³
 $\Delta\rho_{min} = -0.42$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1—Zn1	2.3811 (13)	C2—N2	1.313 (6)
S3—Zn1	2.3747 (13)	C7—C8	1.494 (7)
C1—C2	1.481 (6)	C7—S4	1.635 (5)
C1—S2	1.636 (5)	C7—S3	1.685 (5)
C1—S1	1.698 (5)	C8—N4	1.309 (7)
C2—N1	1.310 (6)	C8—N3	1.315 (7)
S3—Zn1—S3 ⁱ	124.10 (7)	S1—Zn1—S1 ⁱ	120.55 (7)
S3—Zn1—S1	95.41 (5)	S2—C1—S1	130.9 (3)
S3—Zn1—S1 ⁱ	111.75 (4)	S4—C7—S3	130.7 (3)

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

H atoms were placed in calculated positions, with C—H = 0.96 Å (for CH₃) and 0.97 Å (for CH₂), and were included in the final cycles of refinement in a riding model, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms.

Data collection: *SMART-W2K/NT* (Bruker, 2003); cell refinement: *SMART-W2K/NT*; data reduction: *SAINT-W2K/NT* (Bruker, 2003); program(s) used to solve structure: *SHELXTL-NT* (Bruker, 2003); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-NT*.

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