metal-organic papers

Bis(N-methylpyridinium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate(II)

Yan-Ling Wang, Wen-Tao Yu, Dong Xu,* Xin-Qiang Wang, Wen-Feng Guo and Guang-Hui Zhang

State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China

Correspondence e-mail: wangyl@icm.sdu.edu.cn

In the title complex, $(C_6H_8N)_2[Zn(dmit)_2]$ (dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate, C_3S_5), each Zn atom is coordinated by four dmit S atoms that define a distorted tetrahedral arrangement. The crystal structure is stabilized by C—H$\cdots$S hydrogen bonding and S$\cdots$S contacts.

Comment

Since 1979 (Steimeck & Kirmse, 1979), metal bis(2-thioxo-1,3-dithiole-4,5-dithiolate) (dmit) complexes have attracted increasing attention owing to their potential applications as precursors for electrical conductors and superconductors (Cassoux, 1999; Robertson & Cronin, 2002) and for their optical and photoelectrical properties (Winter *et al.*, 1992; Zuo *et al.*, 1996; Wang *et al.*, 1999; Bai *et al.*, 1999; Zhai *et al.*, 1999; Dai *et al.*, 2000; Liu *et al.*, 2002). Of these complexes, $[Zn(dmit)_2]^{2-}$ salts have received much attention for their use as stable dmit precursors in the syntheses of other metal–dmit salts (Svenstrup & Becher, 1995; Pullen & Olk, 1999). Furthermore, Zn complexes of dmit show promise as organic optical materials. The Zn complex anion effectively promotes photoelectric properties and second harmonic generation by replacing the iodide in hemicyanine (Li *et al.*, 1996; Xia *et al.*, 1997). An unsymmetric zinc complex of dmit has been reported to possess reverse saturable absorption characteristics, an optical limiting response (Sun *et al.*, 2001) and third-order nonlinearity (Dai *et al.*, 2000).

(I)
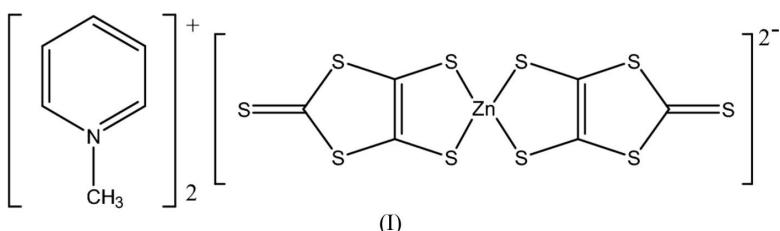
In terms of their solid-state chemistry, these dmit complexes often display intermolecular S$\cdots$S contacts, at distances less than the sum of the van der Waals radii, *i.e.* 3.70 Å (Bondi, 1964). It is well known that the cation in the complexes influences the nature and extent of the S$\cdots$S intermolecular contacts and therefore the overall packing. For example, the S$\cdots$S connectivity in $[Q]_2[Sn(dmit)_3]$ varies with the size of cation, *i.e.* from a three-dimensional arrangement to a chain, and may even be absent (Assis *et al.*, 1999). Such an impact on crystal structure has also been found in some Zn–dmit complexes (Chohan *et al.*, 1997; Harrison *et al.*, 2000).

The title compound, (I), belongs to the class of salts of the general formula $[Q]_2[Zn(dmit)_2]$. Although (I) has not
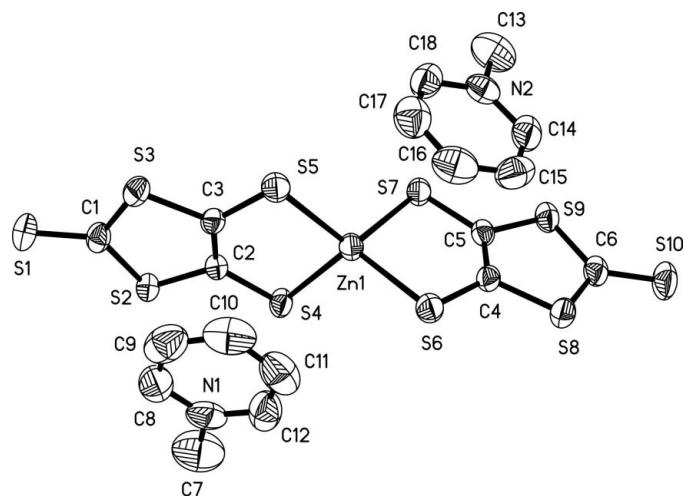
Figure 1
Perspective view of the asymmetric unit, with the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

Figure 2
Packing diagram of (I), showing the S···S contacts (dashed lines). H atoms have been omitted.

Figure 3
Packing diagram of (I), showing the C—H···S hydrogen bonds as dashed lines.

displayed interesting optical properties to date, it was synthesized to study further the impact of the cation on the intermolecular interactions in $[Zn(dmit)_2]^{2-}$ salts. The study reveals that, besides S···S contacts, there are C—H···S non-classical hydrogen bonds operating in the crystal structure of (I).

In the molecular structure of (I) (Fig. 1 and Table 1), there are no features that differ from those of the other known structures of $[Zn(dmit)_2]^{2-}$ in terms of ligand behaviour and coordination characteristics of the Zn^{2+} ion (Wang *et al.*, 1985; Chohan *et al.*, 1997; Harrison *et al.*, 2000; Comerlato *et al.*, 2002). The Zn—S bond lengths range from 2.3245 (16) Å to 2.3447 (15) Å, and the S—Zn—S bond angles range from 94.89 (5) Å to 122.58 (6) Å, so that the ZnS_4 core adopts a distorted tetrahedral geometry. The dihedral angle between the two dmit rings is 87.8 (2)°, *i.e.* the two dmit rings are nearly perpendicular. The Zn ion deviates from the dmit rings by 0.296 (1) and −0.160 (1) Å. As expected, the *N*-methyl-pyridinium ring is planar.

There are two types of intermolecular interactions in the crystal structure of (I), *viz.* S···S contacts and non-classical C—H···S hydrogen bonds. Fig. 2 highlights the short S···S contacts, the shortest such contact being 3.492 (2) Å for S2···S10[ii] [symmetry code: (ii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$]. As a comparison, there are no S···S contacts less than the sum of their van der Waals radii in the analogous structure with $Q = $ 1,4-dimethylpyridinium. On the other hand, the shortest S···S contact previously reported in Zn–dmit complexes, of 3.5792 (13) Å, occurs in the structure with $Q = NEt_4$, *i.e.* where Q is small (Harrison *et al.*, 2000). Additionally, there are three types of C—H···S hydrogen bonds in the structure, as illustrated in Fig. 3 and listed in Table 2.

Experimental

The title complex was prepared according to the procedure described by Steimeck & Kirmse (1979). The high optical-quality single crystals used for X-ray structure analysis were obtained by evaporation of an acetone solution of (I) held at room temperature.
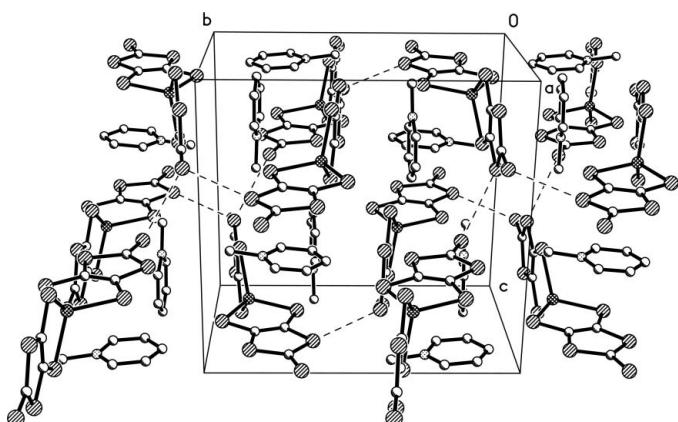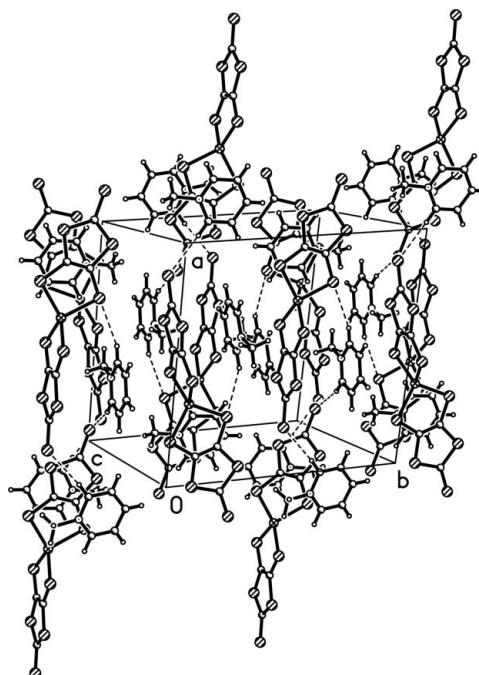
Crystal data

$(C_7H_8N)_2[Zn(C_3S_5)_2]$	$D_x = 1.657$ Mg m^{-3}
$M_r = 646.30$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 30
$a = 14.1687$ (19) Å	reflections
$b = 13.6246$ (16) Å	$\theta = 5.3–12.3°$
$c = 14.024$ (2) Å	$\mu = 1.77$ mm^{-1}
$\beta = 106.865$ (11)°	$T = 296$ (2) K
$V = 2590.8$ (6) Å^3	Block, red
$Z = 4$	$0.40 \times 0.36 \times 0.31$ mm

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Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.030$
ω scans	$\theta_{max} = 26.5°$
Absorption correction: ψ scan	$h = -17 \rightarrow 17$
($XSCANS$; Bruker, 1996)	$k = -17 \rightarrow 1$
$T_{min} = 0.552$, $T_{max} = 0.587$	$l = -1 \rightarrow 17$
6564 measured reflections	3 standard reflections
5378 independent reflections	every 97 reflections
3269 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.053$	$+ 1.3186P]$
$wR(F^2) = 0.138$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
5378 reflections	$\Delta\rho_{max} = 0.66$ e Å^{-3}
281 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}
H-atom parameters constrained	Extinction correction: $SHELXL97$
	Extinction coefficient: 0.0039 (4)

Table 1
Selected geometric parameters (Å, °).

Zn1—S4	2.3401 (15)	S5—C3	1.737 (5)
Zn1—S5	2.3245 (16)	S3—C3	1.746 (5)
Zn1—S6	2.3315 (16)	S6—C4	1.734 (5)
Zn1—S7	2.3447 (15)	S8—C4	1.749 (5)
S1—C1	1.639 (5)	S7—C5	1.737 (5)
S2—C1	1.714 (5)	S9—C5	1.746 (5)
S3—C1	1.731 (6)	S10—C6	1.635 (5)
S4—C2	1.737 (5)	S8—C6	1.714 (6)
S2—C2	1.753 (5)	S9—C6	1.732 (6)
S4—Zn1—S5	95.42 (5)	S5—Zn1—S6	122.58 (6)
S4—Zn1—S6	114.14 (6)	S5—Zn1—S7	115.94 (6)
S4—Zn1—S7	115.42 (6)	S6—Zn1—S7	94.89 (5)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C8—H8$A\cdots$S10^i	0.93	2.71	3.632 (8)	174
C14—H14$A\cdots$S4^{ii}	0.93	2.77	3.644 (7)	157
C18—H18$A\cdots$S1^{iii}	0.93	2.74	3.655 (8)	168

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

In the refinement, atoms C7–C11, and atoms C13, C15 and C16, were split into two positions each and this disorder model was tested, but no suitable model was found. Therefore, for these atoms, their displacement parameters and interatomic distances were restrained. The H atoms were included in the riding-model approximation, with C—H(phenyl) = 0.93 Å, C—H(methyl) = 0.96 Å, and U_{iso}(H) = $1.2U_{eq}$(C phenyl) and $1.5U_{eq}$ (C methyl).

Data collection: $XSCANS$ (Bruker, 1996); cell refinement: $XSCANS$; data reduction: $SHELXTL$ (Bruker, 1997); program(s) used to solve structure: $SIR97$ (Altomare *et al.*, 1999); program(s) used to refine structure: $SHELXTL$; molecular graphics: $SHELXTL$; software used to prepare material for publication: $WinGX$ (Farrugia, 1999).

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