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Synthesis of bis[(ferrocenylmethyl)trimethylammonium] [bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate] and [bis(1,3-dithiole-2-one-4,5-dithiolato)zincate] salts, ([$FcCH_2NMe_3$]$_2$[Zn(dmit)$_2$] and [$FcCH_2NMe_3$]$_2$[Zn(dmio)$_2$]) : crystal structures of [$FcCH_2NMe_3$]$_2$[Zn(dmit)$_2$] and [NEt_4]$_2$[Zn(dmit)$_2$]·MeOH

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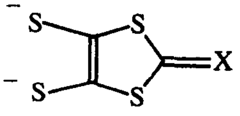
Abstract—The crystal structures of [(ferrocenylmethyl)trimethyl-ammonium]$_2$[Zn(dmit)$_2$], {[$FcCH_2NMe_3$]$_2$[Zn(dmit)$_2$]}, (**4**), and {[NEt_4]$_2$[Zn(dmit)$_2$]·MeOH} (**5**) are reported (dmit = 1,3-dithiole-2-thione-4,5-dithiolato). The dihedral angle between the C_5 planes in the [$FcCH_2NMe_3$]$^+$ cation of **4** is 1.66°; the C_5 rings are within 1.6(4)° of an eclipsed conformation. The zinc atoms in both the ionic complexes have distorted tetrahedral geometries. The bite angles of the dmit ligands are 93.67(4)° in **4** and 93.43(8) and 94.01(9)° in **5**, with the remaining S—Zn—S bond angles having distinct values in the two complexes. The Zn—S bond lengths are similar in the two complexes being in the range 2.3311(12) to 2.350(2) Å. Different interanionic S···S contacts in the two complexes, at distances less than twice the van der Waals radius of S, lead to different packing arrangements. Spectral details (NMR, IR and UV-visible) of **4** and [$FcCH_2NMe_3$]$_2$[Zn(dmio)$_2$] (**6**, dmio = 1,3-dithiole-2-one-4,5-dithiolato) have also been obtained. © 1997 Elsevier Science Ltd

Keywords: crystallography; 1,3-dithiole-2-thione-4,5-dithiolato (dmit) complexes; 1,3-dithiole-2-one-4,5-dithiolato (dmio) complexes; zinc complexes; ferrocene derivatives.

Complexes of the 1,3-dithiole-2-thione-4,5-dithiolato ligand, (**1**, dmit), have attracted much attention in recent years [1]. Of particular interest has been the conducting properties of transition metal dmit complexes, such as those of nickel and palladium [2]. Determination of the solid state structures of the metal



(**1**; X = S)

(**2**; X = O)

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complexes, in general has also attracted much attention [3].

While the dmit ligand is readily available from reaction of CS_2 and sodium in DMF solution [4], convenient and stable storage forms of dmit are necessary. Particularly useful, in this respect, are zinc-bis(dmit) salts, $[Q]_2[Zn(dmit)_2]$, and thioesters, $(ArCO)_2(dmit)$ [5]. The former can transfer the dmit moiety directly on reaction with metal halides, while the latter readily provides the dmit dianion on base hydrolysis.

Related to dmit is the 1,3-dithiole-2-one-4,5-dithiolate unit, (**2**, dmio); this is readily obtained [6] on reaction of a dmit source, usually a thioester, with $Hg(OAc)_2$. Again suitable storages of this dithiolato ligand are necessary: thioesters, $(ArCO)_2(dmio)$, and zinc salts, $[Q]_2[Zn(dmio)_2]$, have proved to be satisfactory here as well.

Various zinc-bis(dmit) salts have been reported: particularly well-used have been onium salts, in particular quaternary ammonium salts. Despite their great use as precursors of other metal–dmit complexes, little attention has been paid to the structures of $[Q]_2[Zn(dmit)_2]$ compounds, with the crystal structure of $[NBu_4]_2[Zn(dmit)_2]$ (**3**) being currently the only one [7] in the Cambridge Crystallographic Data Base. As the anion–anion interactions and packing can be influenced by the cation, $[Q]^+$, as shown for example by $[Q][Sb(dmit)_2]$ complexes [8], we have determined the crystal structures of [(ferrocenylmethyl)trimethylammonium]$_2$[Zn(dmit)$_2$], $\{[FcCH_2NMe_3]_2[Zn(dmit)_2]$, **4**$\}$, and $\{[NEt_4]_2[Zn(dmit)_2]\cdot MeOH\}$ (**5**). We now report our findings and in addition, we also describe the synthesis of $[FcCH_2NMe_3]_2[Zn(dmio)_2]$ (**6**).

EXPERIMENTAL

NMR spectra were obtained on a Bruker 250 MHz instrument; IR spectra were recorded on Philips Analytical PU9800 and Nicolet 205 Fourier-transform spectrometers. X-ray data for **5** were collected on a Nicolet instrument, while that for **4** by the EPSRC data collection service, based at the University of Wales, Cardiff.

Published procedures were used to prepare (ferrocenylmethyl)trimethylammonium iodide, from ferrocene and $Me_2NCH_2NMe_2$, followed by reaction with MeI [9]; $[NEt_4]_2[Zn(dmit)_2]$, from CS_2, Na, $ZnSO_4\cdot 7H_2O$ and $[NEt_4]Br$ [10]; $(PhCO)_2dmit$, from $[NEt_4]_2[Zn(dmit)_2]$ and PhCOCl [3]; $(PhCO)_2dmio$, from $(PhCO)_2dmit$, and $Hg(OAc)_2$ [5]; and Na_2dmio, from $(PhCO)_2dmio$ and NaOEt [5].

Preparation of $[NEt_4]_2[Zn(dmio)_2]$

This was prepared by a similar method to that used for $[NMe_4]_2[Zn(dmio)_2]$ [5]. To a stirred solution containing $Na_2(dmio)$ (2 mmol) was added a solution of $ZnSO_4\cdot 7H_2O$ (0.029 g, 0.67 mmol) in aqueous ammonia solution (5 cm^3) [5]. The mixture was stirred for 15 min and then air was bubbled through for 30 min. After filtering, to the filtrate was added a solution of $[NEt_4]Br$ (0.355 g, 1.1 mmol) and the reaction was stirred for 4 h at room temperature. The precipitate was collected and recrystallized from Me_2CO/propan-2-ol; m.p. 230–232°C (dec), yield 0.25 g, 64%.

Preparation of $[FcCH_2NMe_3]_2Zn(dmit)_2]$ (**4**)

Sodium metal (5.9 g, 0.257 mole) was reacted with carbon disulphide (100 cm^3) in DMF solution (200 cm^3) at -5°C, under nitrogen. After 5 h, more sodium (5.9 g) and carbon disulphide (30 cm^3) were added to the reaction mixture. The reaction was left overnight. Excess sodium was filtered off, using dry glass wool, and methanol (50 cm^3) added to the filtrate to destroy any sodium. All volatiles were removed, using a rotary evaporator at 45°C. Solutions of zinc sulphate$\cdot 7H_2O$ (14.4 g, 0.05 mole) in ammonia (200 cm^3) and ferrocenylmethyl(trimethyl)ammonium iodide (38.7 g, 0.1 mole) in water (100 cm^3) were added and the reaction mixture left overnight. The purple precipitate was collected, washed with propanol-2-ol and diethyl ether, and recrystallised from acetone : propan-2-ol (7 : 3); yield 29.8 g, 73%, m.p. 163–165°C (dec). Found: C, 41.6; H, 4.1; N, 2.9. $C_{34}H_{40}Fe_2N_2S_{10}Zn$ requires: C, 41.9; H, 4.1; N, 2.9%. ^1H NMR (DMSO-d_6, 250 MHz): δ: 2.90 [s, 9H, NMe_3], 4.24 [s, 5H, unsubstituted cp-H], 4.37 [m, 4H, substituted cp-H], 4.47[t, 2H, $J = 1.7$ Hz, CH_2N]. ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ: 53.1 [t, $J = 3.9$ Hz, Me], 67.2 [CH_2], 70.7 [unsubstituted cp-C], 71.7, 73.6, 74.7 [substituted cp-C], 136.7 [C=C], 208.5 [C=S]. IR(KBr, cm^{-1}) 1477, 1466, 1422, 1052, 1033, 996, 890, 869, 521, 485, 461. UV-visible (λ_{max}, nm): 490 (CH_2Cl_2); 510 (Me_2CO).

Preparation of $[FcCH_2NMe_3]_2[Zn(dmio)_2]$ (**6**)

To a stirred solution of sodium dmio (2 mmol) was added a solution of $ZnSO_4\cdot 7H_2O$ (0.29 g, 0.67 mmol) in aqueous ammonia (5 cm^3). The mixture was stirred for 16 min and aerated for 15 min, filtered and to the filtrate was added a solution of (ferrocenylmethyl)trimethylammonium iodide (1.1 mmol) in water. The reaction mixture was stirred for 4 h at room temperature, and the precipitate was collected, washed with propan-2-ol and recrystallised from Me_2CO : propan-2-ol (7 : 3) to give green-brown crystals of the title product, yield 0.25 g, 64%, m.p. 243–245°C. Found: C, 44.2; H, 4.5; N, 2.9. $C_{34}H_{40}Fe_2N_2O_2S_8Zn$ requires: C, 43.4; H, 4.2; N, 3.0%. ^1H NMR (DMSO-d_6, 250 MHz); δ: 2.91 [s, 9H, NMe_3], 4.25 [s, 5H, unsubstituted cp-H], 4.37 [m, 4H, substituted cp-H], 4.49 [t, 2H, $J = 1.7$ Hz, CH_2N]. ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ: 53.1 [t, $J = 3.9$ Hz, Me], 67.2 [CH_2], 70.7 [unsubstituted cp-C], 71.7, 73.6, 74.7 [substituted cp-C], 121.1 [C=C], 193.9

[C=O]. IR (cm^{-1}) 877, 1452, 1608, 1660. UV-visible (λ_{max}, nm); 378, 465(sh) (Me_2CO).

Crystal structure determination of **4**

The orange crystal, used in the analysis, was grown from acetone/propan-2-ol. Data were collected on a Delft Instruments FAST diffractometer with monochromated Mo-K_α radiation. Corrections were made for Lorentz and polarization effects only. Crystal data and structure refinement details are listed in Table 1.

The positions of the zinc and iron were located from a Patterson vector map using SHELXS86 [11]. The positions of the remaining non-hydrogen atoms were located on successive difference Fourier maps using SHELXL93 [12]. The positions of the hydrogen atoms were calculated from geometrical calculations. During refinement the aromatic hydrogens were allowed to ride on their attached carbon atoms. Full-matrix least-squares refinements with anisotropic temperature factors for the Zn, Fe, S, C and N atoms and common isotropic temperature factors according to type (methyl, aromatic, etc.) for the H atoms were carried out. Molecular diagrams were obtained by the programs PLOTAID [13] and ORTEX [14].

Crystal structure determination of **5**

The dark-red crystal of **5** used in the X-ray determination was grown from a solution of $[NEt_4]_2[Zn(dmit)_2]$ in MeOH. Data collection and cell refinement: Nicolet P3 software [15]. Data collection used ω scan rates of 1.0 ($I_p < 150$) to 29.3 ($I_p > 2500$)° min^{-1}, where I_p was the prescan intensity. Scan width was 0.6° ω. Background counts were taken at $\pm 1.0°$ m ω from the Bragg angle of each reflection. Data reduction used the program RDNIC [16]. In the course of data collection, the standard reflections decreased in intensity by about 27%. A linear correction was applied to compensate for this. Absorption correction involved an empirical method based on psi scans [17]. The Patterson (heavy atom) method

Table 1. Crystal data and structure refinement

	4	**5**
Empirical Formula	$C_{34}H_{40}Fe_2N_2S_{10}Zn$	$C_{23}H_{44}N_2OS_{10}Zn$
Formula Weight	974.35	750.63
Temperature (K)	293	293
Wavelength (Å)	0.71069	0.71069
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*Pbcn*
a (Å)	14.723(4)	9.584(4)
b (Å)	15.3238(11)	23.043(10)
c (Å)	18.122(2)	15.721(11)
β (°)	95.60(2)	90
V ($Å^3$)	4069.1(12)	3472(3)
Z	4	4
D_x ($Mg\ m^{-3}$)	1.590	1.436
Absorption coefficient (mm^{-1})	1.830	1.323
F(000)	2000	1584
Crystal size (mm)	0.145 × 0.180 × 0.290	0.4 × 0.4 × 0.1
Colour	Orange	Dark red
θ range (°)	1.92 to 24.96	25 max
Index range	$-15 \leqslant h \leqslant 16$	$0 \leqslant h \leqslant 11$
	$-17 \leqslant k \leqslant 18$	$0 \leqslant k \leqslant 27$
	$-18 \leqslant l \leqslant 20$	$0 \leqslant l \leqslant 18$
Reflections collected	8653	3480
Independent reflections	3135 [*R*(int) = 0.0711]	2602 [*R*(int) = 0.013]
Obs. reflections	2531 ($I > 2\sigma(I)$)	1637 ($F > 4\sigma(F)$)
Refinement method	Full-matrix l.s. on F^2	Full-matrix l.s. on *F*
Number of parameters	225	120
Goodness-of-fit (S)	1.009 (based on F^2)	1.034 (based on *F*)
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0543$	$R = 0.066$
	$wR2 = 0.1315$	$wR = 0.0587$
R indices (all data)	$R1 = 0.0614$	
	$wR2 = 0.1339$	
Final weighing scheme	*a*	*b*
Residual diffraction (e/$Å^3$) max (min)	1.443 (−0.433)	0.59 (−0.51)

[a] $w = 1/[\sigma^2(F_o^2 + (0.0826P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.
[b] $w = 1/(\sigma^2 F + 0.000355F^2)$

was used to locate the non-H atoms of the anion. The non-H atoms of the cation and the solvent molecule were determined from subsequent difference maps. Refinement was by full matrix least squares. Of the non-H atoms, only Zn and S were refined anisotropically. H-atoms of the cation were placed in calculated positions with C—H = 0.95 Å and refined riding upon the C atom to which they were attached with separate group Uiso's for methylene and methyl H atoms [refined values were 0.066(9) and 0.095(9) $Å^2$, respectively]. Methyl groups were treated as rigid bodies. All computations were performed on the SUN SPARC server (UNIX operating system) of the Computing Centre of the University of Aberdeen. Structure solution [10] and refinement software [18]. SHELXS86 and SHELX76. Molecular graphics: PLOTAID [13] and ORTEX [14]. Software used to prepare data for publication XPUB. [19].

Crystal data and structure refinement details are listed in Table 1.

RESULTS AND DISCUSSION

The syntheses of $[FcCH_2NMe_3]_2[Zn(dmio)_2]$ (**6**) and $[FcCH_2NMe_3]_2[Zn(dmit)_2]$ (**4**) were achieved by similar reactions as used for other zinc-bis(dmio) and -(dmit) salts. In the visible region, these salts had λ_{max} values in the visible region in acetone solution at 465(sh) and 510 nm, respectively. In the IR spectra, $\nu(CO)$ value in **6** is 1660 and the $\nu(CS)$ values in **4** are 1061 and 996 cm^{-1}. In the ^{13}C NMR spectra, the values of $\delta(C{=}C)$ and $\delta(C{=}O)$ in **6** are 121.1 and 193.9, respectively, while the values of $\delta(C{=}C)$ and $\delta(C{=}S)$ in **4** are 136.7 and 208.5 ppm, respectively.

Recrystallisation of $[NEt_4]_2[Zn(dmit)_2]$ from methanol led to the isolation of the methanol solvate, **5**.

Crystal structure of 4

This structure consists of $[CpFeC_5H_4CH_2NMe_3]^+$ cations and $[Zn(dmit)_2]^{2-}$ anions in the 8*f* and 4*e* positions, respectively, of the space group *C*2/*c*. Thus, while the cations occupy the general positions, the anions are in special positions subject to the constraints imposed by a 2-fold crystallographic axis. The asymmetric unit consists of a representative cation, one dmit ligand and Zn. The atom numbering system for the cation and the anion is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. There are no cation–anion interactions.

In the cation, the Fe—C bond lengths are in the range 2.020(4) to 2.050(4) Å, with Fe—$Cp_{centroid}$ distances of 1.653(4) Å, for the unsubstituted ring, and 1.641(4) Å, for the substituted ring: similar values have been reported [20] for $[CpFeC_5H_4CH_2NMe_3]I$. The angle between the C_5 planes is 1.66°. The C_5 planes are within 1.6(4)° of an eclipsed conformation: corresponding values for $[CpFeC_5H_4CH_2NMe_3]I$ were reported [10] to be 2.7(1) and 4.6(1)° while for $[CpFeC_5H_4CH_2NMe_3]_2[M_6O_{19}]$, the values [21] are 3.5(1) and *ca* 11°. The Me_3N group is directed away from the Fe centre with a C(9)—C(4)—N bond angle of 114.3(3)° (the same value obtained [20] in the $[Mo_6O_{19}]^{2-}$ salt).

The crystallographic 2-fold axis to which the anion is subject is perpendicular to the S(5)—Zn—S(5′) vector (Fig. 1: symmetry operation: i, $-x, y, 1/2-z$) i.e. the long axis of the anion. The coordination of zinc is tetrahedral with Zn—S bond lengths of 2.3311(12) and 2.3445(12) Å and dmit bite angles of 93.67(4)°. Each of the dmit ligands is essentially planar [$\Sigma\Delta^2 = 0.0014$] and the perpendicular distance of Zn from the best ligand plane is 0.0827(5) Å. The angle between the perpendiculars to the mean planes of the dmit ligands is 83.2(5)°.

There are two types of S···S contacts between the anions in **4**, somewhat less than twice the van der Waals radius of sulfur [1.85 Å], see Fig. 2. The shortest of these (type A) is $S(3^{ii})\cdots S(3^{iii})$ at 3.519(2) Å [symmetry operations: ii, x, $1-y$, $1/2+z$; iii, $1/2-x$, $1/2+y$, $1/2-z$]. The other S···S contact is $S(4^{i})\cdots S(4^{ii}) = 3.696(2)$ Å (type B). The next shortest contacts, but outside the van der Waals radii sum, are $S(5^{ii})\cdots S(3^{iii})$ and $S(5^{iii})\cdots S(3^{ii})$] at 3.799(2) Å. The type A contacts connect the anions into zigzag chains parallel to [−101]. The slightly longer contact of type B interconnect the zigzag chains creating secondary chains in the form of "flights of stairs" whose directions are perpendicular either to 110, for the chain at $z = 1/2$, or to −110 for the chain at $z = 0$ (for the choice of origin used in this structure determination).

Crystal structure of 5

The orthorhombic unitcell of **5** with space group *Pbcn* contains four formula units. Whereas the NEt_4 cations occupy the general 8*d* positions the anions are in the special positions (4c) with a 2-fold axis passing through Zn, S(3), S(6), C(2) and C(4) (see Fig. 3). The asymmetric unit, therefore, contains, in addition to Zn and a complete cation, somewhat more than half of each of the two dmit ligands. There is in addition a feature, also associated with a crystallographic 2-fold axis, which has been interpreted as a molecule of MeOH. The C-atom (Csol) of this molecule lies upon the 2-fold axis while O is distributed over a pair of half occupied symmetry related sites.

In the anion Zn is in a rather distorted tetrahedral environment. While the Zn—S bonds [2.346(2) and 2.350(2) Å] are, within error, equal, the S—Zn—S angles show considerable variation. Thus the bite angles of the dmit ligands [94.01(8) and 93.43(9)°] are very much less than the remaining S—Zn—S angles [106.22(8) and 130.98(9)°] both of which occur twice. A significant feature of the geometry of the anion, directly related to the inequality of the "non-bite" angles at Zn, is the angle between the essentially planar ligands which varies slightly depending upon the man-

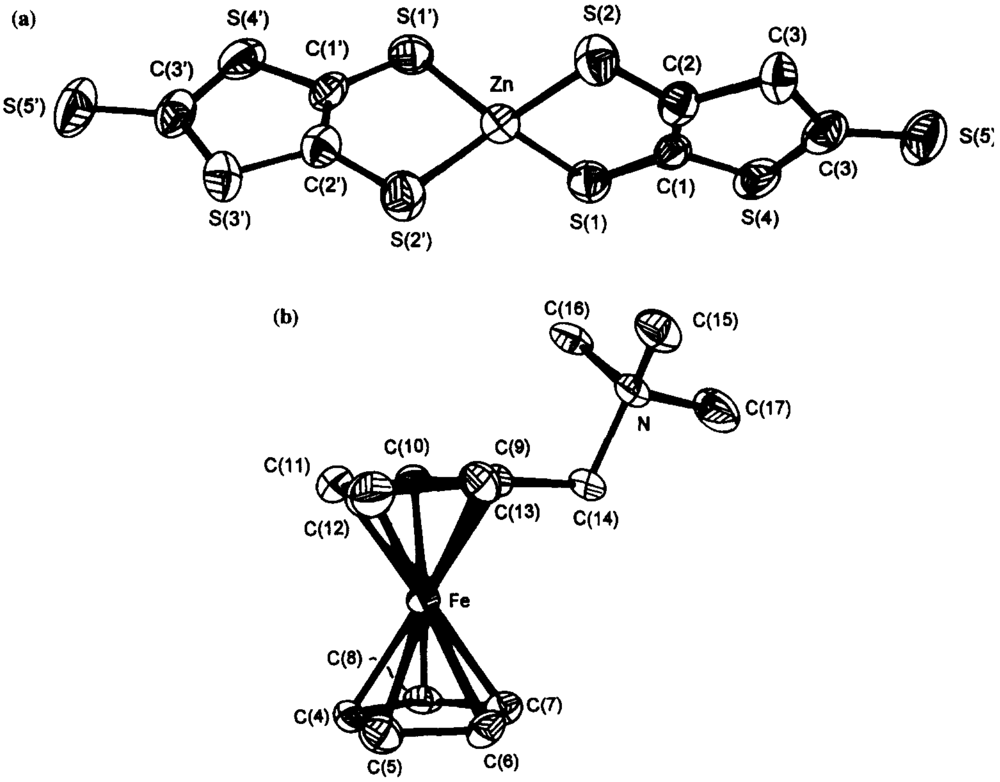


Fig. 1. Perspective views of the cation (20% ellipsoids) and dianion (40% ellipsoids) in **4** showing the numbering scheme: H-atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **4**

Zn—S(2)	2.3311(12)	Zn—S(1^{i})	2.3445(12)
Zn—S(2^{i})	2.3311(12)	Zn—S(1)	2.3445(12)
S(1)—C(1)	1.739(4)	S(2)—C(2)	1.735(4)
S(3)—C(3)	1.710(5)	S(3)—C(2)	1.743(4)
S(4)—C(3)	1.732(5)	S(4)—C(1)	1.756(4)
S(5)—C(3)	1.652(4)		
C(1)—C(2)	1.343(6)	C(4)—C(5)	1.373(7)
C(4)—C(8)	1.408(7)	C(5)—C(6)	1.409(6)
C(6)—C(7)	1.385(7)	C(7)—C(8)	1.399(6)
C(9)—C(10)	1.427(6)	C(9)—C(13)	1.441(6)
C(9)—C(14)	1.487(6)	C(10)—C(11)	1.417(6)
C(11)—C(12)	1.399(7)	C(12)—C(13)	1.416(6)
Fe—C(9)	2.020(4)	Fe—C(4)	2.031(4)
Fe—C(7)	2.032(4)	Fe—C(10)	2.034(4)
Fe—C(5)	2.032(4)	Fe—C(6)	2.035(4)
Fe—C(8)	2.040(4)	Fe—C(12)	2.046(4)
Fe—C(13)	2.036(4)	Fe—C(11)	2.050(4)
S(2)—Zn—S(2^{i})	114.89(7)	S(2)—Zn—S(1^{i})	121.85(5)
S(2^{i})—Zn—S(1^{i})	93.67(4)	S(2)—Zn—S(1)	93.67(4)
S(2^{i})—Zn—S(1)	121.85(5)	S(1^{i})—Zn—S(1)	113.30(7)
C(1)—S(1)—Zn	96.10(13)	C(2)—S(2)—Zn	97.02(14)
C(3)—S(3)—C(2)	98.8(2)	C(3)—S(4)—C(1)	98.3(2)
C(2)—C(1)—S(1)	127.2(3)	C(2)—C(1)—S(4)	115.0(3)
S(1)—C(1)—S(4)	117.8(2)	C(1)—C(2)—S(2)	125.9(3)
C(1)—C(2)—S(3)	116.0(3)	S(2)—C(2)—S(3)	118.1(2)
S(5)—C(3)—S(3)	124.3(3)	S(5)—C(3)—S(4)	123.9(3)
S(3)—C(3)—S(4)	111.8(2)	C(10)—C(9)—C(14)	126.8(4)
C(13)—C(9)—C(14)	126.0(4)		

Table 3. Selected bond lengths (Å) and angles (°) for **5**

Zn—S(1)	2.346(2)	Zn—S(4)	2.350(2)
C(1)—S(1)	1.738(7)	C(1)—S(2)	1.745(7)
C(2)—S(2)	1.720(6)	C(2)—S(3)	1.660(11)
C(3)—S(4)	1.736(7)	C(3)—S(5)	1.762(8)
C(4)—S(5)	1.732(7)	C(4)—S(6)	1.633(11)
C(1)—C(1^i)	1.363(13)	C(3)—C(3^i)	1.337(14)
S(4)—Zn—S(1)	106.22(8)	S(4^i)—Zn—S(1)	130.98(9)
S(1^i)—Zn—S(1)	94.01(8)	S(4^i)—Zn—S(4)	93.43(9)
C(1)—S(1)—Zn	96.5(2)	C(3)—S(4)—Zn	96.4(3)
C(2)—S(2)—C(1)	98.4(4)	C(4)—S(5)—C(3)	99.1(4)
S(2)—C(1)—S(1)	118.1(4)	S(5)—C(3)—S(4)	117.7(4)
S(3)—C(2)—S(2)	123.8(3)	S(6)—C(4)—S(5)	124.6(3)
C(1^i)—C(1)—S(1)	126.5(6)	C(3^i)—C(3)—S(4)	126.9(6)
C(1^i)—C(1)—S(2)	115.4(5)	C(3^i)—C(3)—S(5)	115.4(5)
S(2^i)—C(2)—S(2)	112.5(4)	S(5^i)—C(4)—S(5)	110.8(4)

Symmetry operation: i, $-x, y, 1/2-z$.

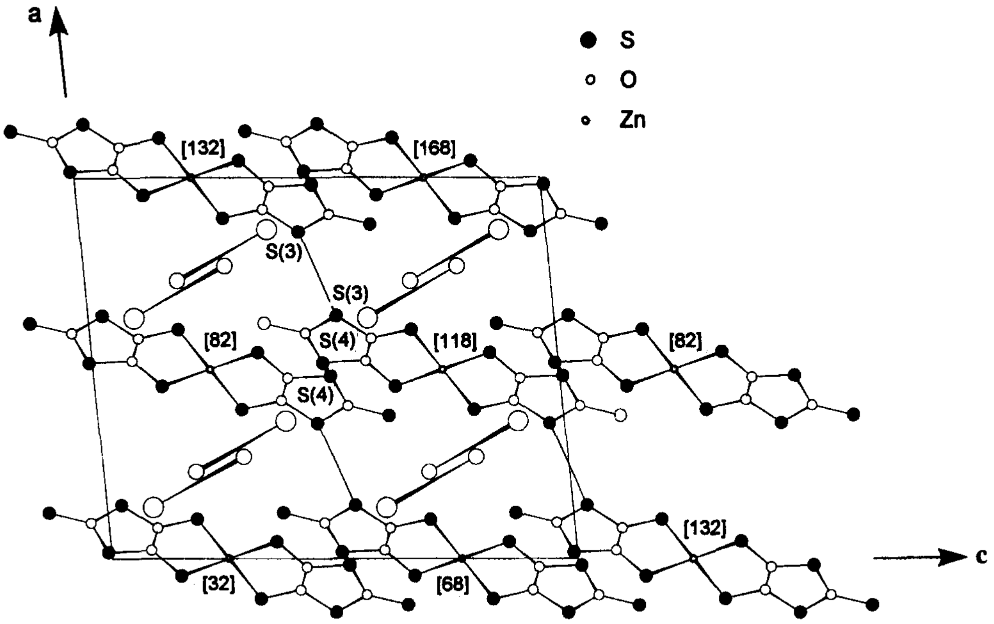


Fig. 2. The cell of **4** viewed down *b*. The outline of the cell and the direction of *a* and *c* are indicated. Selected S···S interanionic contacts (3.7 Å) are shown and numbers in parentheses indicate the heights of Zn and therefore of the individual ions in units of 100*y*/*b*. For clarity the $[FcCH_2NMe_3]^+$ cations are shown in highly schematic form as large circles centred on N and smaller circles centred on Fe with a bond joining them.

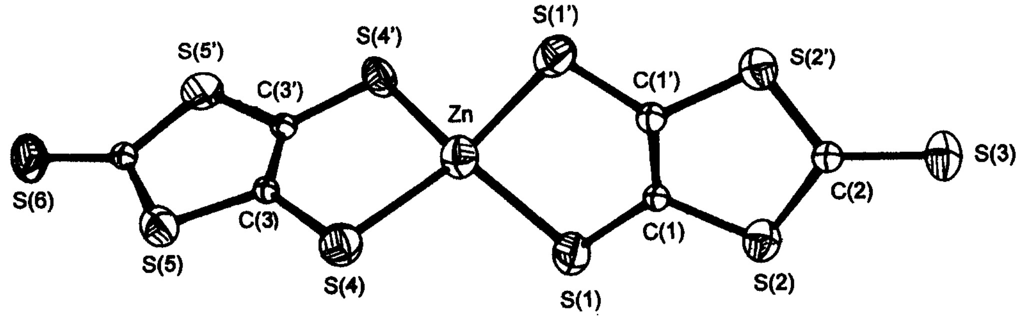


Fig. 3. Perspective view of the $[Zn(dmit)_2]^{2-}$ dianion in **5** showing the atom numbering scheme and 40% probability ellipsoids.

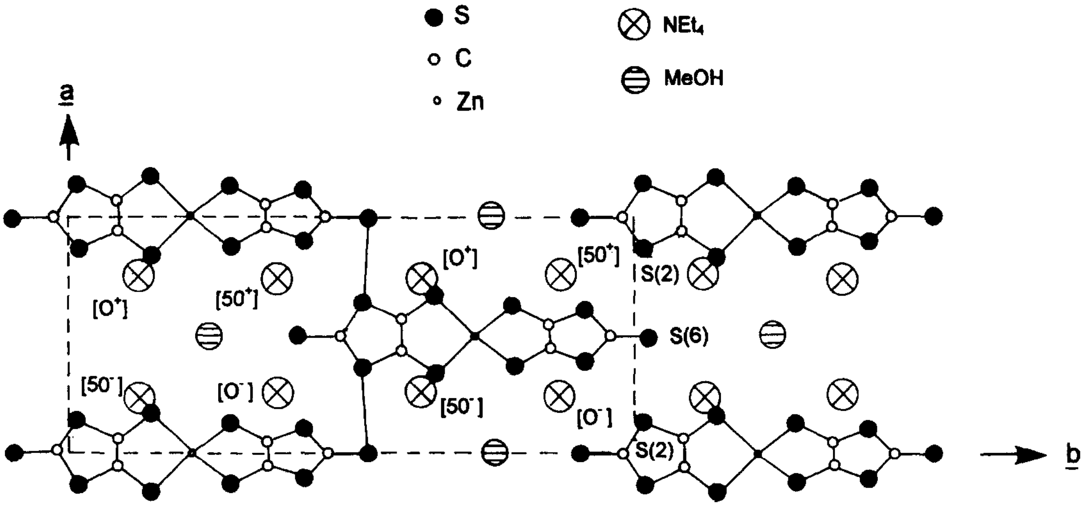


Fig. 4. The cell of **5** viewed down c. The outline of the cell and the directions of a and b are indicated. Slightly more than half of the cell in terms of height is shown centred on $z/c = 1/4$. The largest circles, centred on the N positions, are a crude representation of the cations and their heights are given in units of $100z/c$ accompanied by positive or negative signs indicating small (0.0021) departures from $z/c = 0$ or $1/2$. The disordered methanol molecules are sited at $z/c = 1/4$.

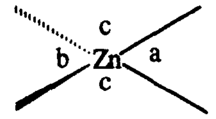
ner in which it is determined but is of the order of 69.5(5)°.

There are S···S interanionic contacts, much less than twice the van der Waals radius, involving S(6)···S(2) at 3.534(2) Å. These contacts connect the anions to form layers perpendicular to c at $z/c = 1/4$ and 3/4 (see Fig. 4). Adjacent layers are related by a crystallographic centre of symmetry. While the solvent molecules lie within the layers the cations are distributed between them.

Comparison of the structures of **1, 4** *and* **5**

The planar dmit ligands differ only very slightly in their bond lengths in the three complexes, **1, 4, 5**; the S—Zn—S angles do however show some differences, Table 4.

Table 4. Comparison of bond lengths (Å) and bond angles (°) in $[Q]_2[Zn(dmit)_2]$



[Q]	$[FcCH_2NMe_3]^a$	$[NEt_4]^a$	$[NBu_4]^b$
Zn—S (Å)	2.3445(12)	2.350(2)	2.345(3)
	2.3311(12)	2.346(2)	2.330(3)
S—Zn—S			
a (°)	93.67(4)	94.01(8)	95.0(1)
b (°)	93.67(4)	93.43(9)	95.0(1)
c (°)	114.89(7)	106.22(8)	112.3(1)

[a] This study.
[b] [7].

A significant difference between the dianions in **4** and **5** is the different orientation of the 2-fold symmetry axes. In **4**, the crystallographic 2-fold axis is perpendicular to the long axis of the dianion; in contrast in the dianions in **5**, the crystallographic 2-fold axis passes through Zn, S(3), S(6), C(2) and C(4), see Fig. 3. There are also differences in the angles between the mean planes of the dmit ligands in **4** [83.2(5)°] and in **5** [69.5(5)°].

The two types of S···S interanionic contacts between the dianions in **4**, 3.519(2) and 3.696(2) Å [$S(3^{ii})\cdots S(3^{iii})$ and $S(4^{i})\cdots S(4^{ii})$, respectively] result in a quite different packing arrangement in **4** compared to that in **5**, where the interanionic contacts involve S(6)···S(2) [with separations of 3.543(2) Å], see Figs 2 and 4.

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