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Bis(tetra-*n*-butylammonium) (a redetermination at 150 K) and bis(tetraphenylarsonium) bis(1,3-dithiole-2-thione-4,5-dithiolato)zinc(II) (at 300 K)

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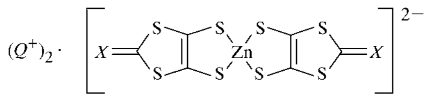
The title compounds are salts of the general form $(Q^+)_2[\mathrm{Zn(dmit)_2}]^{2-}$, where dmit corresponds to the ligand $(\mathrm{C_3S_5})^-$ present in both and Q^+ to the counter-cations $(^n\mathrm{Bu_4N})^+$ [or $\mathrm{C_{16}H_{36}N^+}$] and $(\mathrm{Ph_4As})^+$ [or $\mathrm{C_{24}H_{20}As^+}$], respectively. In the first case, Zn is in the 4*e* special positions of space group *C*2/*c* and hence the $[\mathrm{Zn(dmit)_2}]^{2-}$ dianion possesses twofold axial crystallographic symmetry. Including these, there are now 11 known examples of $[\mathrm{Zn(dmit)_2}]^{2-}$ or its analogues, with O replacing the exocyclic thione S, and $[\mathrm{Zn(dmio)_2}]^{2-}$ dianions in nine structures with various *Q*. Comparison of these reveals a remarkable variation in details of the conformation which the dianion may adopt in terms of Zn coordination, equivalence of the Zn—S bond lengths, displacement of Zn from the plane of the ligand and overall dianion shape.

Comment

Chohan *et al.* (1997) and Harrison *et al.* (2000, and references therein) have already pointed out the importance of onium salts of the $[\mathrm{Zn(dmit)_2}]^{2-}$ dianion, where dmit is the 1,3-dithiole-2-thione-4,5-dithiolate ligand, as stable and convenient precursors for the formation of complexes with other transition and main group metal elements and the synthesis of heterocyclic compounds. Müller *et al.* (1998) concur with this view and show that it is equally applicable to the analogous $[\mathrm{Zn(dmio)_2}]^{2-}$ dianion, where dmio is the 1,3-dithiole-2-one-4,5-dithiolate ligand, *i.e.* with O now replacing the thione S of dmit. Müller *et al.* (1998), however, use the acronym 'dmid' rather than 'dmio' used here.

The $[\mathrm{Zn(dmit)_2}]^{2-}$ dianions of the title compounds, $Q = {}^n\mathrm{Bu_4N}$ at 150 K (IV-150) (Fig. 1 and Table 1) and $Q = \mathrm{Ph_4As}$ (IX) (Fig. 2 and Table 2), are as anticipated for this type of species although the twofold axial crystallographic symmetry of the dianion in (IV-150) is a notable but not unusual feature. As a result, whereas the asymmetric unit of (IX) consists of a complete dianion and two distinct $\mathrm{Ph_4As}$ counter-cations, that of (IV-150) contains Zn, one complete dmit ligand and only a single cation. Aside from a degree of disorder affecting two of the ^{n}Bu groups in (IV-150), the counter-cations are unremarkable and are not discussed further.



(IV-150): $Q^+ = {}^n\mathrm{Bu_4N^+}$; X=S
IX: $Q^+ = \mathrm{Ph_4As^+}$; X=S
dmit: X=S; dmio: X=O

The results for (IV-150) and (IX) can be compared (Table 3), with a series of previously known related structures, as Chohan *et al.* (1997) and Harrison *et al.* (2000) have already but now focused upon the shape of the dianions rather than details of their internal geometry and the sometime presence of S···S inter-anion contacts. Certain conventions are noted here which have been adopted in the creation of Table 3. First, in the calculation of out-of-plane Zn and exocyclic thione S for dmit and O for dmio distances, $\mathrm{Zn_{op}}$ and $\mathrm{one_{op}}$, respectively, the reference ligand plane has been defined by the C═C bond and the four S attached to it, *e.g.* S1, S2, C1, C2, S3 and S4 in Figs. 1 and 2 or their equivalent. Second, the angle IP, defined as the angle between the plane defined by Zn1, S1 and S2 and that defined by Zn1, S6 and S7 (Fig. 2), is used as a measure of the flattening of the tetrahedral coordination of Zn. This usage avoids complications which would be induced by Zn out-of-plane distances if the ligand planes as defined first above were used for this purpose. The angle *L*, calculated as X—Zn—X', where X and X' are exocyclic thione S or, for dmio O, *e.g.* S5—Zn1—S10 in Fig. 2, is used as a measure of the non-linear or V-shaped nature of the dianions. The entries in the table are in order of decreasing *L*, which is also wholly compatible with the dianions ordered in categories according to their crystallographic symmetry, which decreases down the list.

The values given in Table 3 give rise to some general observations. First, the ligand bite angles show little variation and fall in the comparatively narrow range 93.44 (10)–95.22 (4)° and have, therefore, virtually no effect on the

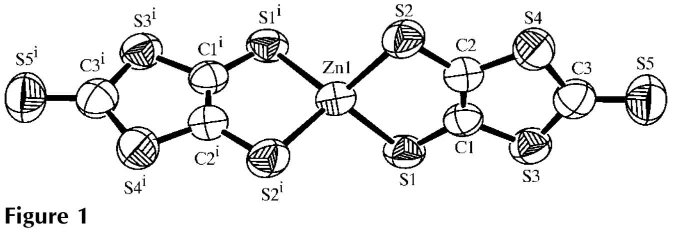


Figure 1
The dianion of (IV-150) showing the atom labels. Atoms are shown as 50% probability ellipsoids. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

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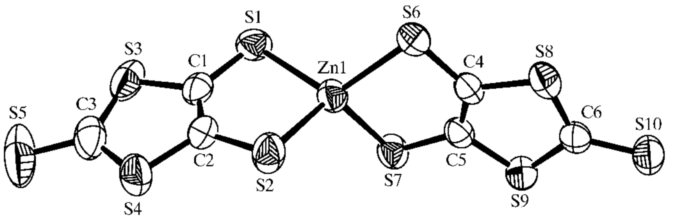

Figure 2
The dianion of (IX). The representation is the same as in Fig. 1.

variation in the shape of the dianions. In all but two cases, both ligands of (I) by symmetry and fortuitously the second ligand of (IX), the bidentate ligands coordinate in an asymmetric manner contributing therefore to the variation in *L*. Angle *L* is clearly affected primarily by variation of $\mathrm{Zn_{op}}$ and to a lesser extent by $\mathrm{one_{op}}$, in which the variation is less and essentially random in nature. The primary significance of $\mathrm{one_{op}}$ is its relationship to $\mathrm{Zn_{op}}$. If these have the same or different signs, the chelate formed by the ligand is overall boat- or Z-shaped, respectively, with displacement of Zn and thione S or, for dmio, O, from the chelate mean plane in both cases.

In terms of crystallographic symmetry, the dianions of the compounds presented in Table 3 occur in three groups. Group 1 has (I) as the only representative. This is the most constrained situation and here the dianion is subject to the operation of a crystallographic twofold axis running along its length and passing through Zn, and C and S of the thione groups. As a consequence, the ligands coordinate in a symmetric manner, Zn and thione S are rigorously confined to the ligand planes and the dianion is strictly linear from one thione S to the other. Here, however, is found by far the lowest value of IP, 69.29 (12)°, corresponding to the most flattened form of tetrahedral coordination of Zn in the series.

In group 2, with compounds (II)–(V) providing five cases, the dianions are again subject to the operation of a crystallographic twofold axis but now perpendicular to the length of the ligand. Now, as for group 3, excepting the second ligand of (IX), the ligands coordinate in an asymmetric manner and contribute to the non-linearity of the dianions with *L* now in the range 171.05 (8)–177.86 (3)°. Within the group, the values of *L* indicate the existence of two subgroups as (II) and (III) together with the smallest $\mathrm{Zn_{op}}$ and *L* values of 177.86 (3) and 177.04 (4)°, respectively, and (III)–(V) with greater $\mathrm{Zn_{op}}$ and smaller *L*. An IP now in the range 81.18 (6)–83.58 (9)° indicates a much less flattened coordination of Zn than before.

The dianions of group 3, (VI)–(IX) and again five cases, are totally free from constraint by symmetry. These display the least linearity, with *L* in the range 158.51 (2)–169.49 (1)° and still less flattened Zn coordination, with IP in the range 82.47 (4)–89.25 (18)°, which last is close to the ideal of 90°. Noticeable here is the special situation of (IX) with the smallest value of *L* where Zn is similarly greatly displaced from the planes of both ligands, whereas in (VI)–(VIII), the Zn displacement is much greater for one ligand than the other.

It is clear that the linearity of the dianions, *L*, correlates not only with their classification in terms of crystallographic symmetry but also, because of the manner in which it is calculated, with the values of $\mathrm{Zn_{op}}$. The flattening of the tetrahedral Zn coordination, IP, on the other hand, relates to the crystallographic dianion symmetry solely in terms of ranges of values and correlates with no other entries in the table. *L* and IP are in any case crude measures of completely different aspects of the shape of the dianions and no relationship between them is therefore expected. Any relationship between the nature of the counter-cations and the shape of the dianions is at best superficial and supported by nothing more than (I), methanol solvate with $Q = \mathrm{Et_4N}$, at one extreme, (IX) with bulky $Q = \mathrm{Ph_4As}$ at the other and species such as (IV) with $Q = {}^n\mathrm{Bu_4N}$ in between. However, (VI), $Q = \mathrm{Ph_4P}$ and DMSO solvate, and particularly (VIII), $Q = \mathrm{Et_4N}$, are anomolous in terms of the predicated series. This implies that the size of the counter-cations probably determines the shape of the dianions only in combination with several other factors, such as counter-cation shape, the presence of solvent molecules and the presence of short inter-anion S···S contacts, less than the sum of the van der Waals radii, which do not in fact occur in either (IV) or (IX).

Experimental

The salt, (IV) or (IX), was prepared following a general procedure (Valade *et al.*, 1985) from $\mathrm{Na_2dmit}$, $\mathrm{ZnSO_4}$ and ${}^n\mathrm{Bu_4NBr}$ or $\mathrm{Ph_4AsCl}$. Red crystals of (IV) were obtained from $\mathrm{Me_2CO}$/2-propanol (m.p. 436–438 K). IR (KBr): 1411 (C=C), 1055 (C=S), 889 (C—S) $\mathrm{cm^{-1}}$. UV–vis (MeCN): 499 and 308 nm. Red crystals of (IX) were obtained from DMSO (m.p. 478–481 K). IR (KBr): 1437 (C=C), 1056 (C=S), 888 (C—S) $\mathrm{cm^{-1}}$. UV–vis (MeCN): 497 and 311 nm.

Compound (IV150)

Crystal data

$(\mathrm{C_{16}H_{36}N})_2[\mathrm{Zn(C_3S_5)_2}]$
$M_r = 942.95$
Monoclinic, $C2/c$
$a = 19.2564$ (3) Å
$b = 8.9478$ (2) Å
$c = 29.2379$ (5) Å
$\beta = 92.9544$ (7)°
$V = 5031.06$ (16) Å^3
$Z = 4$
$D_x = 1.245$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22 851 reflections
$\theta = 3.2$–28.6°
$\mu = 0.93$ mm^{-1}
$T = 150$ (2) K
Block, red
0.25 × 0.22 × 0.10 mm

Table 1
Selected geometric parameters (Å, °) for (IV-150).

Zn1—S1	2.3308 (9)	C1—S3	1.747 (3)
Zn1—S2	2.3401 (10)	C2—S4	1.749 (3)
S1—C1	1.733 (3)	S3—C3	1.719 (4)
S2—C2	1.726 (3)	S4—C3	1.720 (4)
C1—C2	1.351 (4)	C3—S5	1.642 (4)
S1—Zn1—S1^{i}	122.45 (5)	C1—C2—S2	127.5 (3)
S1—Zn1—S2^{i}	112.12 (3)	C1—C2—S4	114.8 (2)
S1—Zn1—S2	95.15 (3)	S2—C2—S4	117.71 (19)
S2^{i}—Zn1—S2	122.06 (6)	C3—S3—C1	99.30 (16)
C1—S1—Zn1	95.11 (11)	C3—S4—C2	99.48 (17)
C2—S2—Zn1	94.97 (11)	S5—C3—S3	124.5 (2)
C2—C1—S1	127.1 (2)	S5—C3—S4	124.5 (2)
C2—C1—S3	115.4 (3)	S3—C3—S4	111.0 (2)
S1—C1—S3	117.58 (19)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill the Ewald sphere
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.770$, $T_{\max} = 0.859$
22 851 measured reflections
5525 independent reflections
2563 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 28.6°$
$h = -25 \rightarrow 23$
$k = -9 \rightarrow 11$
$l = -37 \rightarrow 39$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.132$
$S = 0.98$
5525 reflections
269 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

Compound (IX)

Crystal data

$(C_{24}H_{20}As)_2[Zn(C_3S_5)_2]$
$M_r = 1224.67$
Triclinic, $P\overline{1}$
$a = 10.3451$ (5) Å
$b = 15.0563$ (7) Å
$c = 18.8083$ (8) Å
$\alpha = 73.072$ (1)°
$\beta = 85.867$ (1)°
$\gamma = 72.259$ (1)°
$V = 2668.9$ (2) Å^3
$Z = 2$
$D_x = 1.524$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4866 reflections
$\theta = 2.3$–$24.9°$
$\mu = 2.12$ mm^{-1}
$T = 300$ (2) K
Block, red
$0.33 \times 0.21 \times 0.15$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.738$, $T_{\max} = 0.862$
16 003 measured reflections
9377 independent reflections
6069 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 25.0°$
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 17$
$l = -22 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.067$
$S = 0.86$
9377 reflections
604 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (IX).

Zn1—S1	2.3360 (10)	S5—C3	1.646 (4)
Zn1—S6	2.3458 (10)	C1—C2	1.347 (4)
Zn1—S7	2.3458 (10)	S6—C4	1.747 (3)
Zn1—S2	2.3674 (10)	S7—C5	1.743 (3)
S1—C1	1.740 (4)	S8—C6	1.725 (4)
S2—C2	1.733 (4)	S8—C4	1.754 (3)
S3—C3	1.728 (4)	S9—C6	1.719 (4)
S3—C1	1.745 (3)	S9—C5	1.751 (3)
S4—C3	1.711 (5)	S10—C6	1.660 (3)
S4—C2	1.755 (3)	C4—C5	1.349 (4)
S1—Zn1—S6	118.44 (4)	S5—C3—S4	125.2 (3)
S1—Zn1—S7	117.89 (4)	S5—C3—S3	123.4 (3)
S6—Zn1—S7	94.02 (3)	S4—C3—S3	111.4 (2)
S1—Zn1—S2	94.36 (3)	C4—S6—Zn1	94.86 (12)
S6—Zn1—S2	118.53 (4)	C5—S7—Zn1	94.65 (12)
S7—Zn1—S2	115.56 (4)	C6—S8—C4	98.36 (17)
C1—S1—Zn1	94.92 (12)	C6—S9—C5	98.44 (16)
C2—S2—Zn1	94.10 (12)	C5—C4—S6	126.3 (3)
C3—S3—C1	98.84 (19)	C5—C4—S8	115.3 (3)
C3—S4—C2	99.15 (18)	S6—C4—S8	118.3 (2)
C2—C1—S1	127.1 (3)	C4—C5—S7	126.9 (3)
C2—C1—S3	115.5 (3)	C4—C5—S9	115.7 (3)
S1—C1—S3	117.2 (2)	S7—C5—S9	117.4 (2)
C1—C2—S2	127.3 (3)	S10—C6—S9	123.4 (2)
C1—C2—S4	115.0 (3)	S10—C6—S8	124.4 (2)
S2—C2—S4	117.7 (2)	S9—C6—S8	112.18 (18)

Table 3
Selected distances and angles (Å, °) for the dianions in Q_2ZnX_2 (X = dmit or, where indicated, dmio, and Q = various counter-cations).

Room-temperature data except where indicated.

Cpd/gp	Q^+/sol.	Zn—S1/6[a]	Zn—S2/7[a]	Bite	Zn_{op}[b]	one_{op}[b]	IP[b]	L[b]	CSD ref.
(I)/1	Et_4N/MeOH	2.346 (3)	2.346 (3)	94.00 (9)	0	0	69.29 (12)	180	NEYSOZ
		2.350 (3)	2.350 (3)	93.44 (10)	0	0			
(II)/2	DMPy[c]	2.3372 (12)	2.3419 (12)	95.22 (4)	−0.0171 (4)	0.0687 (17)	81.18 (6)	177.86 (3)	DOQXIQ
(III)/2	$FcCH_2NMe_3$[d]	2.3311 (19)	2.345 (2)	93.65 (6)	−0.074 (1)	−0.025 (2)	83.58 (9)	177.04 (4)	NEYSIT
(IV-150)/2	$^nBu_4N$	2.3308 (9)	2.3401 (10)	95.15 (3)	0.1078 (14)	−0.005 (2)	81.71 (3)	175.14 (2)	this work
(IV)/2	$^nBu_4N$	2.330 (3)	2.345 (3)	94.99 (12)	−0.0995 (14)	−0.001 (4)	81.78 (16)	175.02 (9)	DOZPUD
(V)/2	Et_4N	2.308 (2)	2.313 (2)	93.81 (8)	−0.2119 (8)	0.036 (7)	82.08 (13)	171.05 (8)	JAFXET (dmio)
(VI-150)/3	Ph_4P/DMSO	2.3284 (9)	2.3376 (8)	95.06 (3)	0.098 (1)	0.045 (1)	82.47 (4)	169.49 (1)	DOQXUC
		2.3355 (8)	2.3473 (9)	95.05 (3)	−0.263 (1)	−0.138 (1)			
(VII)/3	$^nBu_4N$	2.324 (4)	2.346 (3)	95.06 (13)	0.055 (1)	0.075 (10)	89.25 (18)	169.19 (13)	JAFXIX (dmio)
		2.338 (4)	2.344 (4)	93.61 (13)	−0.368 (1)	−0.061 (11)			
(VIII-150)/3	Et_4N	2.3355 (19)	2.3478 (10)	95.27 (3)	−0.014 (1)	0.064 (1)	86.20 (5)	168.07 (1)	DOQXOW
		2.3447 (10)	2.3519 (8)	94.49 (3)	0.342 (1)	0.096 (1)			‘anion 1’
(VIII-150)/3	Et_4N	2.3383 (9)	2.3405 (11)	95.12 (4)	−0.005 (1)	−0.055 (1)	84.67 (5)	166.24 (1)	DOQXOW
		2.3484 (9)	2.3521 (10)	94.77 (3)	−0.369 (1)	−0.132 (1)			‘anion 2’
(IX)/3	Ph_4As	2.3360 (10)	2.3675 (12)	94.36 (3)	−0.4651 (15)	−0.159 (2)	88.97 (4)	158.51 (2)	‘this work’
		2.3458 (10)	2.3458 (10)	94.02 (3)	−0.5158 (13)	0.0289 (17)			

Notes: (*a*) S1 and S2 as in Fig. 2 are implied in the first or only line of entries for each compound and S6 and S7 in the second; (*b*) these quantities are defined in the text; (*c*) 1,4-dimethylpyridinium; (*d*) (ferrocenylmethyl)trimethylammonium. For all except (IV-150) and (IX), the tabulated values have been obtained by means of *PLATON* (Spek, 1990) from CIF data extracted from the Cambridge Structural Database (CSD; Allen & Kennard, 1993) at the Chemical Database Service of the EPSRC at Daresbury (Fletcher *et al.*, 1996). Full references for the CSD codes are as follows: DOQXIQ, DOQXOW and DOQXUC (Harrison *et al.*, 2000); DOZPUD (Wang *et al.*, 1986); NEYSIT and NEYSOZ (Chohan *et al.*, 1997) and JAFXET and JAFXIX (Müller *et al.*, 1998).

In the course of the refinement of (IV-150), severe disorder of the terminal methylene, C10 and C14, and methyl groups, C11 and C15, of two of the ^{n}Bu groups of the ^{n}Bu$_4$N counter-cation became apparent necessitating the splitting of each of these atoms over two sites of equal occupancy distinguished by suffix *A* or *B*. In addition, constraints of 1.52 (1) and 2.48 (1) Å for direct C—C bonds and C—C—C angles defining C···C contacts, respectively, were applied to the refinement of the disordered species, 16 constraints in all. Even then, the need for further splitting of C14*B* and C15*A* was indicated but was not implemented. In the final stages of refinement, H atoms were introduced in calculated positions and refined with a riding model, with C—H = 0.99 and 0.98 Å, and $U_{\rm iso}$ = 1.2 and 1.5$U_{\rm eq}$ of the C atom to which they were attached for the methylene and methyl-H atoms, respectively, of (IV-150), and with C—H = 0.93 Å and $U_{\rm iso}$ = 1.2$U_{\rm eq}$ for the phenyl-H atoms of (IX). Rotation parameters were refined for the methyl groups as rigid bodies of ordered C8 and C19 of (IX) but not for the remainder.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998) for (IV-150), and *SMART* (Bruker, 1999) for (IX); cell refinement: *DENZO* and *COLLECT* for (IV-150), and *SAINT* (Bruker, 1999) for (IX); data reduction: *DENZO* and *COLLECT* for (IV-150), and *SAINT* for (IX). For both compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1005). Services for accessing these data are described at the back of the journal.

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