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Bis(tetraphenylphosphonium) bis(2-oxo-1,3-dithiole-4,5-dithiolato)zincate(II)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.005 Å
R factor = 0.051
wR factor = 0.168
Data-to-parameter ratio = 18.9

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

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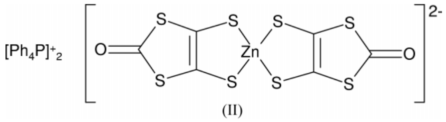
The asymmetric unit of the title compound, (Ph_4P)-$[Zn(C_3OS_4)_2]$, comprises six crystallographically independent entities, *viz*. two zincate anions and four counter-cations. Only the complex anions are of interest, noting in particular the tetrahedral coordination of the Zn atoms distorted primarily by the bite angles and asymmetric chelation of the ligands, and the non-linear nature of and departures from planarity in the anions themselves.

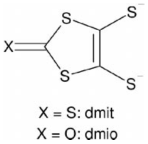
Comment

Compounds (I) of the general form $[Q]_2[Zn(dmit)_2]$, where Q is an onium counter-cation and dmit represents the 2-thioxo-1,3-dithiole-4,5-dithiolate dianion, are commonly employed as stable and convenient precursors in the synthesis of other dmit complexes and heterocyclic compounds and have been quite widely studied (Harrison *et al.*, 2000, and references therein). Replacement of the ligand 2-thione S atom by an O atom yields the otherwise very similar dmio species encountered in compounds (II) of the form $[Q]_2[Zn(dmio)_2]$, which have been much less frequently studied. It is in this context that the structure of the title compound, (II) (Q = Ph_4P), is presented here.



(II)

The asymmetric unit of (II) ($Q = Ph_4P$) comprises six crystallographically independent species, *viz*. two $[Zn(dmio)_2]$ dianions and four Ph_4P counter-cations. Aside from noting C—P and phenyl C—C distances in the ranges 1.789 (4)–1.815 (4) and 1.361 (6)–1.407 (6) Å, respectively, the cations are unremarkable and are not discussed further. The dianions, on the other hand, are depicted in Fig. 1 in order to indicate their connectivities and labelling scheme.



The labelling scheme is such that, not only can each anion be specifically identified by the number associated with the Zn atom that it contains, but so can the individual dmio ligands be identified in terms of the number associated with the oxo O atom. Thus, the geometric data given in Table 1 are to be considered in terms of anion 1, comprising ligands 1 and 2, and anion 2, comprising ligands 3 and 4. Moreover, the C atoms,

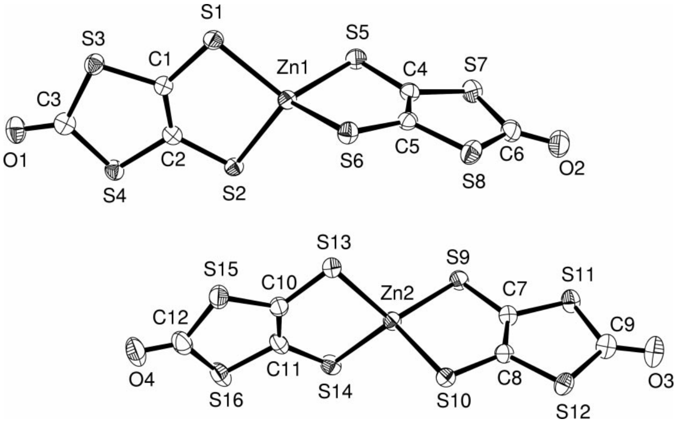


Figure 1

The anions of (II) (Q = Ph_4P) showing the labelling scheme. Atoms are shown as 50% probability displacement ellipsoids. The relative position of the anions is artificial, having been adjusted for convenience in the preparation of the drawing.

and especially the S atoms, have been labelled in such a manner that for the series of m ligands (m = 1–4) all S atoms identified in sets by numbers of the form $n + 4(m - 1)$ (n = 1–4) and all C atoms identified in sets as $n' + 3(m - 1)$ (n' = 1–3) have the same functionality. Thus, for example, S atoms in the set S1, S5, S9 and S13 all form shorter bonds to Zn atoms than do atoms S2, S6, S10 and S14 and these assignments determine the numbering of the remaining atoms as shown in Fig. 1, although the C atoms bonded to the oxo O atom, C3, C6, C9 and C12, are readily identifiable in their own right. Thus, the bond and angle designations in Table 1, which are those for ligand 1, are equally applicable to all four ligands.

It is clear from Table 1 that the internal geometry remains essentially constant for all four dmio ligands in (II) (Q = Ph_4P) and, with the exception of bonds of the type C3—O1, is indistinguishable from that observed for dmit in (I) as summarized by Harrison *et al.* (2000). All four dmio ligands in (II) (Q = Ph_4P) chelate Zn in an asymmetric manner, with one Zn—S distance significantly shorter than the other but with bite angles in the narrow range 94.14 (3)–95.71 (3)°. The interligand S—Zn—S angles, on the other hand, fall in a much wider range, 113.00 (4)–122.24 (4)°. Thus, the coordination of Zn, although tetrahedral in nature, is clearly distorted, as is found in (I).

It is of particular interest in (II) (Q = Ph_4P) to consider the disposition of the atoms in the anions relative to ligand planes defined in terms of the C═C bond and the S atoms associated with it, for example, C1, C2 and S1 to S4 for ligand 1. Within the ligands, the displacements of the oxo O atom and the C atom to which it is attached, *e.g.* O1 and C3, range from −0.007 (3) to −0.136 (3) Å and −0.009 (4) to −0.082 (4) Å, respectively, are all negative, and follow the same sequence in terms of relative magnitude through the series. More notable, however, are the displacements of Zn, which are much greater for ligands 2 and 4 than for ligands 1 and 3. These displacements can be considered as a measure of the tilt of the ligands about the vector joining the thiol S atoms, *e.g.* S1 and S2 of ligand 1, whose overall effect, along with the oxo O-atom displacements and the asymmetry of ligand chelation, is to render the anions non-linear as measured, crudely, by the O—Zn—O angles of 164.06 (4) and 161.93 (4)° (Table 1). The dihedral angles between the ligand planes, 83.78 (3) and 87.27 (4)°, for the anions are not too dissimilar.

Within the unit cell, the anions are found loosely associated in layers parallel to ($\overline{1}01$) and passing through 0,0,0, with their long axes more or less parallel to [101] (Fig. 2). The P atoms of the counter-cations lie between these layers but the phenyl groups, to some extent, penetrate into them. As a consequence, by no means uniquely but unlike many other cases, there are virtually no S···S contacts between anions either within or between the anion layers. Thus there is in this case no possibility of the existence of the significant and potentially useful physical properties often ascribed to such intermolecular interactions.

Experimental

Compound (II) (Q = Ph_4P) was prepared by a general route (Chohan *et al.*, 1997) from $ZnSO_4{\cdot}7H_2O$, Na_2(dmio) and Ph_4PCl, and recrystallized from acetone to yield crystals (m.p. 436–438 K) suitable for analysis. IR (KBr, cm^{-1}) 1660 (C═O), 1441 (C═C). ^{13}C NMR (DMSO-d_6, 63.3 MHz): δ 118.6 [J(P—C) = 88.6 Hz, C_{ipso}], 120.0 [J(P—C) = 12.5 Hz, C_{meta}], 121.1 (C═C), 132.0 [J(P—C) = 11.0 Hz, C_{ortho}], 136.1 [J(P—C) = 2.2 Hz, C_{para}], 193.9 (C═O).

Crystal data

$(C_{24}H_{20}P)_2[Zn(C_3S_4O)_2]$
M_r = 1104.65
Triclinic, $P\overline{1}$
a = 16.5321 (2) Å
b = 17.3265 (2) Å
c = 17.9862 (2) Å
α = 88.5668 (7)°
β = 74.5401 (7)°
γ = 87.3795 (5)°
V = 4959.98 (10) Å^3
Z = 4
D_x = 1.479 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 63366 reflections
θ = 2.9–27.5°
μ = 0.94 mm^{-1}
T = 120 (2) K
Plate, red
0.14 × 0.12 × 0.04 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.783, T_{max} = 0.969
43 340 measured reflections
22 769 independent reflections
17 597 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.6°
$h = -21 \rightarrow 21$
$k = -22 \rightarrow 22$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.168
S = 1.10
22 769 reflections
1207 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0836P)^2 + 4.0139P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

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Table 1
Selected geometric parameters (Å, °) for the anions of (II) (Q = Ph_4P).

	Anion 1		Anion 2	
	Ligand 1	Ligand 2	Ligand 3	Ligand 4
Zn1—S1	2.3315 (10)	2.3343 (10)	2.3233 (10)	2.3224 (10)
Zn1—S2	2.3625 (9)	2.3559 (10)	2.3621 (10)	2.3648 (10)
S1—C1	1.742 (3)	1.749 (4)	1.743 (4)	1.747 (4)
C1—S3	1.761 (4)	1.759 (4)	1.765 (4)	1.771 (4)
S3—C3	1.762 (4)	1.761 (4)	1.767 (4)	1.759 (5)
C3—S4	1.766 (4)	1.771 (4)	1.766 (4)	1.772 (5)
S4—C2	1.759 (3)	1.766 (4)	1.757 (4)	1.764 (4)
C2—S2	1.746 (4)	1.744 (4)	1.754 (4)	1.747 (4)
C1—C2	1.358 (5)	1.355 (5)	1.345 (5)	1.344 (6)
C3—O1	1.217 (4)	1.223 (5)	1.218 (5)	1.213 (5)
S1—Zn1—S5	113.00 (4)		116.39 (4)	
S1—Zn1—S6	122.24 (4)		120.49 (4)	
S2—Zn1—S5	119.41 (4)		118.00 (4)	
S2—Zn1—S6	115.03 (3)		113.19 (4)	
S1—Zn1—S2	95.05 (3)	94.14 (3)	95.71 (3)	94.80 (4)
Zn1—S1—C1	95.57 (12)	94.97 (12)	95.06 (12)	94.19 (14)
Zn1—S2—C2	94.71 (12)	94.54 (12)	94.19 (12)	93.30 (13)
S1—C1—S3	115.9 (2)	117.3 (2)	115.7 (2)	116.4 (2)
S1—C1—C2	127.0 (3)	126.2 (3)	127.8 (3)	126.7 (3)
S3—C1—C2	117.1 (3)	116.5 (3)	116.5 (3)	116.8 (3)
C1—S3—C3	97.45 (17)	98.04 (18)	97.51 (18)	97.6 (2)
S3—C3—S4	111.7 (2)	111.5 (2)	111.6 (2)	111.5 (2)
S3—C3—O1	123.8 (3)	124.3 (3)	123.3 (3)	124.8 (4)
S4—C3—O1	124.5 (3)	124.2 (3)	125.0 (3)	123.7 (4)
C3—S4—C2	98.13 (17)	97.68 (18)	97.70 (18)	98.0 (2)
S4—C2—S2	117.1 (2)	116.9 (2)	116.1 (2)	116.6 (2)
S4—C2—C1	115.6 (3)	116.3 (3)	116.7 (3)	116.0 (3)
S2—C2—C1	127.2 (3)	126.8 (3)	127.2 (3)	127.4 (3)
Zn_{oop}[a]	−0.2291 (14)	−0.5439 (14)	0.0576 (14)	−0.5703 (14)
$C3_{oop}$	−0.082 (4)	−0.045 (4)	−0.009 (4)	−0.017 (4)
$O1_{oop}$	−0.136 (3)	−0.117 (3)	−0.007 (3)	−0.033 (4)
IP[b]	83.78 (3)		87.27 (4)	
O1···Zn1···O2	164.06 (4)		161.93 (4)	

Notes: (*a*) oop denotes values corresponding to the displacements of the atoms so designated from the ligand planes as defined in the text. (*b*) IP is the angle between the ligand planes.

In the final stages of refinement, H atoms were introduced in calculated positions, with C—H = 0.95 Å, and refined with a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

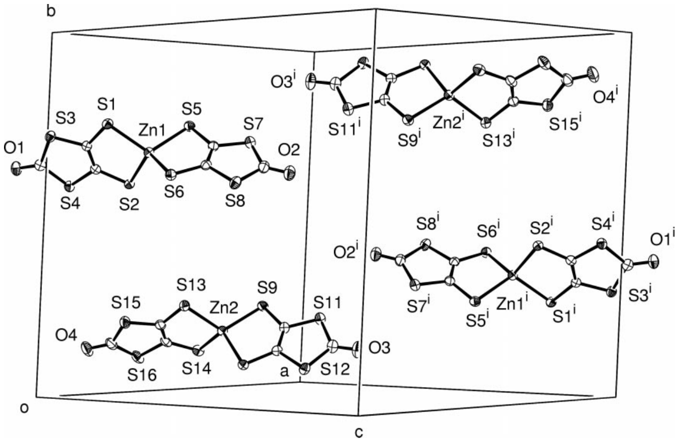

Figure 2
Part of a layer of anions in (II) (Q = Ph_4P). Atoms are shown as 50% probability displacement ellipsoids. Selected atoms are labelled. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

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