

Bis(tetraphenylphosphonium) (hexa-sulfido- $2\kappa^2S^1, S^6$)di- μ -sulfido-disulfido- $1\kappa^2S$ -tungsten(VI)zinc(II) acetone solvate

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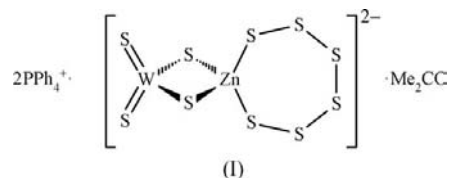
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The title complex, $(C_{24}H_{20}P)_2[WZnS_4(S_6)] \cdot C_3H_6O$ or $(Ph_4P)_2-[WS_2(\mu-S)_2\{Zn(S_6)\}] \cdot Me_2CO$, was unexpectedly obtained on attempted recrystallization of a mixed tungsten–zinc complex of a tris(pyrazolato)borate ligand. The two metal centres of the anion have distorted tetrahedral coordination and the two tetrahedra share one $S \cdots S$ edge; tungsten is additionally coordinated by two terminal sulfide ligands and zinc by a chelating S_6^{2-} ligand, which has one central S—S bond significantly longer than the other four, a pattern found to be consistent for this ligand. This is the first reported example of a tetrahedral zinc centre bridging an edge of a single tetrathio-tungstate(VI) or tetrathiomolybdate(VI) anion, although there are many previous examples with other metals.

Comment

We have recently reported the structure of (acetato- κO)-[tris(3,5-dimethylpyrazolyl)hydroborato]zinc(II), $Zn[HB(3,5-Me_2Pz)_3(OAc)]$ (Beheshti *et al.*, 2009). In an attempt to prepare a complex in which the acetate ligand is replaced by the sulfur-donating metalloligand $[WS_4]^{2-}$, we treated the zinc complex with ammonium tetrathio-tungstate(VI). IR spectroscopy indicates a successful reaction, but attempted recrystallization from acetone by vapour diffusion of diethyl ether as precipitant leads to decomposition and the unexpected isolation of the title mixed-metal complex (I), in which all the ligands are composed exclusively of S atoms, $[S_2W(\mu-S)_2Zn(S_6)]^{2-}$, as an acetone solvate of the tetraphenylphosphonium salt. The product was identified through crystal structure determination. The structure of the anion is shown in Fig. 1, with selected bond lengths, angles and torsion angles given in Table 1. The well known cations and solvent molecule have unremarkable structures.

Mixed-metal complexes in which one or more ML_n units (M is any metal and L_n are terminal or chelating ligands bonded only to M) are attached to tetrathiometalate(VI) centres $[M'S_4]^{2-}$ ($M' = Mo$ or W) or their mixed oxo–thio analogues $[M'S_3O]^{2-}$ and $[M'S_2O_2]^{2-}$ are very common. The ML_n units bridge one or more of the $S \cdots S$ edges of the M' coordination tetrahedron. Only one of these complexes (Wang *et al.*, 2001) has $M = Zn$ and $M' = W$, apart from polymorphs of $(Ph_4P)_2-[Zn(WS_4)_2]$, in which two tetrathio-tungstate anions are coordinated to a central Zn^{2+} ion in a linear trinuclear array (Paulat-Böschen *et al.*, 1978; Crossland *et al.*, 2008).



In the title complex, both metal centres have distorted tetrahedral coordination, the two tetrahedra sharing an $S \cdots S$ edge. In the case of atom W1, the minor distortion consists mainly of an elongation of the bonds to the bridging S atoms relative to the terminal S atoms, which is expected; angular distortions from the regular tetrahedral geometry are very small. By contrast, both distance and angle distortions are found for atom Zn1. The bonds to the bridging sulfide ligands are significantly longer than those to the chelating hexasulfide ligand, and the angle between the bridging ligands is markedly reduced from the ideal tetrahedral value, while the opposite bite angle of the chelate ligand is enlarged; furthermore, the dihedral angle between the $S3/Zn1/S4$ and $S5/Zn1/S10$ planes, which would be 90° for an ideal tetrahedron, is only $78.97(7)^\circ$. The bridging ligands display very acute $W-S-Zn$ angles. The

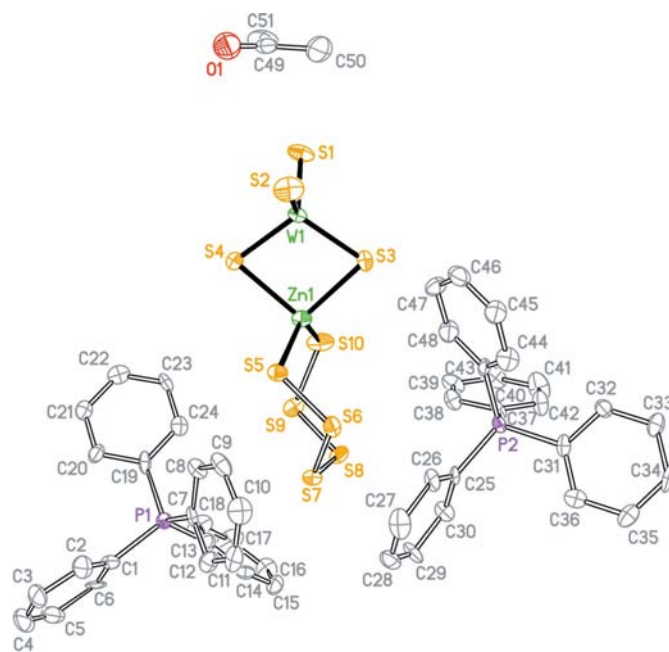


Figure 1
The structure of the asymmetric unit of (I), showing atom labels and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

four-membered WS₂Zn ring is approximately planar [the 'hinge' dihedral angle between the WS₂ and ZnS₂ planes is 172.19 (15)°; this angle adopts a wide range of values in other complexes with two sulfide bridges].

The S₆²⁻ ligand, together with the Zn centre, has a crown-like conformation, with torsion angles around the S—S bonds slightly exceeding the range 80–100% with alternating positive and negative signs (Table 1). A search of the Cambridge Structural Database (CSD; Version 5.30 with updates to February 2009; Allen, 2002) gives 30 entries with this ligand as a chelating ligand to a single metal centre, as well as five entries in which it is a bridging ligand bonded to two metal ions, and 11 cases of an uncoordinated dianion. For each of these situations, the central S—S bond of the S₆ chain (taken as the mean value within each of the three distinct groups) is significantly longer than the four other S—S bonds. This pattern is found for the title complex also, with a central bond length of 2.072 (3) Å and other S—S bond lengths essentially identical at 2.046 Å. The Zn—S bonds to this ligand have lengths of 2.268 (2) and 2.286 (3) Å in the title complex, similar to those of other zinc complexes of this ligand (mean = 2.296 Å and range = 2.261–2.341 Å for eight entries in the CSD).

Experimental

(NH₄)₂[WS₄] (0.032 g, 0.05 mmol; McDonald *et al.*, 1983) and PPh₄Cl (0.032 g, 0.05 mmol) were dissolved in acetone (30 ml) and solid Zn[HB(3,5-Me₂Pz)₃(OAc)] (0.011 g, 0.05 mmol; Beheshti *et al.*, 2009) was added. The mixture was stirred for *ca* 4 h. The white solid that precipitated was filtered off, the filtrate was evaporated to dryness *in vacuo* and the residue was washed with diethyl ether (2 × 5 ml) and dried *in vacuo* to give a yellow powder. The IR spectrum [$\nu(\text{B—H}) = 2541 \text{ cm}^{-1}$ and $\nu(\text{W—S}) = 454$ and 463 cm^{-1}] confirms the presence of [HB(3,5-Me₂Pz)₃][−] and WS₄^{2−} ligands in the complex. This product decomposed during an attempted recrystallization by slow diffusion of diethyl ether into a saturated solution in acetone; on leaving the solution to stand in a refrigerator for two months, air-stable pale-yellow crystals of (PPh₄)₂[WS₄ZnS₆]·Me₂CO were obtained.

Crystal data

(C ₂₄ H ₂₀ P) ₂ [WZnS ₄ (S ₆)]·C ₃ H ₆ O	$V = 5340.6 (8) \text{ \AA}^3$
$M_r = 1306.64$	$Z = 4$
Orthorhombic, <i>Pna</i> 2 ₁	Mo $K\alpha$ radiation
$a = 31.212 (3) \text{ \AA}$	$\mu = 3.09 \text{ mm}^{-1}$
$b = 11.3211 (9) \text{ \AA}$	$T = 150 \text{ K}$
$c = 15.1140 (13) \text{ \AA}$	$0.28 \times 0.24 \times 0.08 \text{ mm}$

Data collection

Bruker SMART 1K CCD diffractometer	40633 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	10420 independent reflections
$T_{\min} = 0.478$, $T_{\max} = 0.790$	9214 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.059$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	H-atom parameters constrained
$wR(F^2) = 0.100$	$\Delta\rho_{\text{max}} = 1.29 \text{ e \AA}^{-3}$
$S = 1.25$	$\Delta\rho_{\text{min}} = -3.27 \text{ e \AA}^{-3}$
10420 reflections	Absolute structure: Flack (1983),
597 parameters	4973 Friedel pairs
16 restraints	Flack parameter: 0.058 (7)

Table 1

Selected geometric parameters (Å, °).

W1—S1	2.152 (2)	Zn1—S10	2.286 (3)
W1—S2	2.153 (3)	S5—S6	2.045 (3)
W1—S3	2.232 (2)	S6—S7	2.045 (3)
W1—S4	2.223 (2)	S7—S8	2.072 (3)
Zn1—S3	2.403 (3)	S8—S9	2.046 (3)
Zn1—S4	2.436 (2)	S9—S10	2.047 (4)
Zn1—S5	2.268 (2)		
S1—W1—S2	109.58 (10)	S4—Zn1—S10	115.80 (9)
S1—W1—S3	110.44 (10)	S5—Zn1—S10	123.33 (9)
S1—W1—S4	108.67 (9)	W1—S3—Zn1	78.52 (7)
S2—W1—S3	110.13 (10)	W1—S4—Zn1	77.99 (7)
S2—W1—S4	110.69 (10)	Zn1—S5—S6	106.30 (11)
S3—W1—S4	107.31 (8)	S5—S6—S7	106.88 (13)
S3—Zn1—S4	95.76 (8)	S6—S7—S8	108.73 (13)
S3—Zn1—S5	116.45 (9)	S7—S8—S9	108.71 (14)
S3—Zn1—S10	104.32 (10)	S8—S9—S10	107.19 (15)
S4—Zn1—S5	98.08 (9)	Zn1—S10—S9	107.01 (13)
S10—Zn1—S5—S6	53.54 (16)	S7—S8—S9—S10	99.67 (16)
Zn1—S5—S6—S7	−88.56 (14)	S8—S9—S10—Zn1	−79.30 (16)
S5—S6—S7—S8	87.21 (15)	S5—Zn1—S10—S9	17.36 (19)
S6—S7—S8—S9	−83.01 (17)		

H atoms were positioned geometrically and refined with a riding model (including free rotation about C—C bonds), with the $U_{\text{iso}}(\text{H})$ values constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Similarity and rigid-bond restraints were applied to the displacement parameters of three C atoms in one phenyl ring, which otherwise had extreme anisotropic behaviour with large standard uncertainties. The largest difference peak and deepest hole lie 0.05 and 1.13 Å, respectively, from W1.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3117). Services for accessing these data are described at the back of the journal.

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