

A sulfur(II) complex of a dithioimido-  
diphosphinate

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Received 13 January 2011

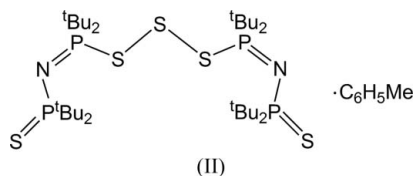
Accepted 24 January 2011

Online 4 February 2011

The structure of bis[*P,P*-di-*tert*-butyl-*N*-(di-*tert*-butylphosphorothioyl)phosphinimidothioato- $\kappa$ S]sulfur(II) toluene solvate (systematic name: 5,13-dibutyl-7,7,11,11-tetramethyl-8,9,10-trithia-6,12-diaza-5 $\lambda^5$ ,7 $\lambda^5$ ,11 $\lambda^5$ ,13 $\lambda^5$ -tetraphosphaheptadeca-6,11-diene-5,13-dithione toluene solvate), C<sub>32</sub>H<sub>72</sub>N<sub>2</sub>P<sub>4</sub>S<sub>5</sub>·C<sub>7</sub>H<sub>8</sub>, at 173 K has monoclinic (*C*2/*c*) symmetry. The S<sup>II</sup> centre of (SP<sup>*t*</sup>Bu<sub>2</sub>NP<sup>*t*</sup>Bu<sub>2</sub>PS<sup>-</sup>)<sub>2</sub>S is coordinated in an *S*-monodentate fashion to two [(SP<sup>*t*</sup>Bu<sub>2</sub>)<sub>2</sub>N]<sup>-</sup> monoanions. The molecule resides on a twofold axis which bisects the central S atom. The internal P—S distance is *ca* 0.19 Å longer than the terminal P=S bond and there is a compensating alternation in P—N bond distances. The central S—S—S angle is 106.79 (8)°. The toluene solvent molecule is disordered about a twofold axis.

## Comment

Recently, we described the synthesis and structure of the dimer (SP<sup>*t*</sup>Bu<sub>2</sub>NP<sup>*t*</sup>Bu<sub>2</sub>PS<sup>-</sup>)<sub>2</sub>, (I), which is formed by one-electron oxidation of the corresponding monoanion, [(SP<sup>*t*</sup>Bu<sub>2</sub>)<sub>2</sub>N]<sup>-</sup>, with iodine (Fig. 1; Ritch *et al.*, 2007). Compound (I) was obtained upon recrystallization of a concentrated solution of the crude product from tetrahydrofuran (THF). We now report the isolation of the minor product of that oxidation, (SP<sup>*t*</sup>Bu<sub>2</sub>NP<sup>*t*</sup>Bu<sub>2</sub>PS<sup>-</sup>)<sub>2</sub>S, (II), as colourless block-shaped crystals when toluene is used as the recrystallization solvent. The identity of complex (II) as the toluene solvate was established by a single-crystal X-ray diffraction study.



Complexes (III) (Fig. 1), in which a central divalent chalcogen  $E^{II}$  ( $E = \text{Se or Te}$ ) is coordinated to two dichalcogenoimidodiphosphinate ligands, [( $E'PR_2$ )<sub>2</sub>N]<sup>-</sup> ( $E' =$

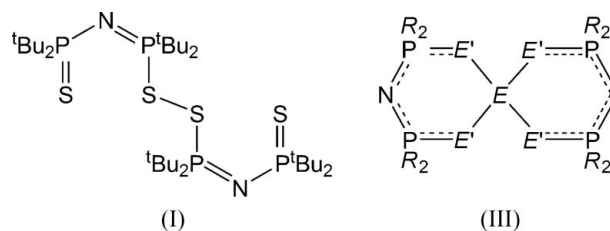
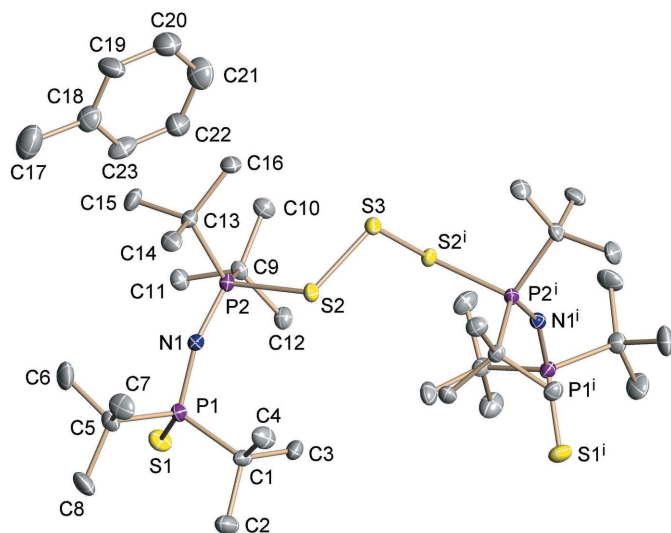


Figure 1

Schematic representations of compounds (I) and (III) ( $E = \text{Se or Te}$ ;  $E' = \text{S or Se}$ ).

S or Se), have been prepared and structurally characterized for the following combinations of chalcogens: Se(S<sub>4</sub>) (Husebye & Maartmann-Moe, 1983), Te(S<sub>4</sub>) (Bjørnevåg *et al.*, 1982; Birdsall *et al.*, 2000), Se(Se<sub>4</sub>) (Cea-Olivares *et al.*, 1998, 2005), Te(Se<sub>4</sub>) (Novosad *et al.*, 1998; Birdsall *et al.*, 2000) and Te(S<sub>2</sub>Se<sub>2</sub>) (Sekar & Ibers, 2003). All these examples exhibit a central four-coordinate chalcogen(II) atom which is chelated by two bidentate dichalcogenoimidodiphosphinate ligands. The geometry of the complexes is regular square-planar in the cases of Se(Se<sub>4</sub>) and Te(Se<sub>4</sub>), but distortions arising from the different sizes of the chalcogen donors are observed for Te(S<sub>2</sub>Se<sub>2</sub>). The majority of the Te(S<sub>4</sub>) complexes are also square-planar, even for nonsymmetrical dichalcogenoimidodiphosphinate ligands, [( $E'PR_2$ )( $E'PR'_2$ )N]<sup>-</sup> ( $R \neq R'$ ). However, in one example, Te[(SP(OPh)<sub>2</sub>)(SPEt<sub>2</sub>)N]<sub>2</sub>, the different electronic effects of the substituents result in Te—S bond lengths that differ by *ca* 0.4 Å (Birdsall *et al.*, 2000). In contrast with the Te(S<sub>4</sub>) complexes, the only known Se(S<sub>4</sub>) complex adopts an approximately trapezoidal planar arrangement, with a disparity of 0.7–0.8 Å in the Se—S distances (Husebye & Maartmann-Moe, 1983).

The title complex, (II), is the first example of a bis-(dichalcogenoimidodiphosphinate) in which the central chalcogen is sulfur(II). In contrast with the congeneric Se(S<sub>4</sub>) and Te(S<sub>4</sub>) complexes (see above), (II) adopts an acyclic rather than a spirocyclic (or pseudo-spirocyclic) structure; a two-coordinate S<sup>II</sup> atom is bonded in an *S*-monodentate fashion to two [(SP<sup>*t*</sup>Bu<sub>2</sub>)<sub>2</sub>N]<sup>-</sup> monoanions, each of which carries a non-bonding (terminal) P=S functionality. The molecules of (II) reside on a twofold axis that bisects the S—S—S angle of 106.79 (8)°, which is consistent with two stereochemically active lone pairs on sulfur. A view of the structure of (II) is shown in Fig. 2, with selected bond distances and angles listed in Table 1. As expected, the terminal P=S distance [1.9745 (15) Å] reflects a typical double-bond value [*cf.* 1.974 (1) Å for the related disulfide, (I)], while the internal P—S distance is significantly longer (by *ca* 0.19 Å) and close to the distance of 2.135 (1) Å reported for (I) (Ritch *et al.*, 2007). Bond-order alternation in the P—N linkages is indicated by a difference of *ca* 0.07 Å in the bond lengths. The S—S distances are close to the single-bond value of 2.05 Å (Steudel *et al.*, 2005) and the S—S—S bond angle is similar to reported values for trisulfides (Chivers *et al.*, 1998). The S—P—N—P torsion angles within each [(SP<sup>*t*</sup>Bu<sub>2</sub>)<sub>2</sub>N]<sup>-</sup> ligand indicate the non-planarity of this framework, and the virtual torsion angle S1—P1—P2—S2 of *ca* 125° demonstrates the *anti* configuration of



**Figure 2**

A view of complex (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms and the solvent molecule have been omitted for clarity. [Symmetry code: (i)  $-x, y, -z + \frac{3}{2}$ .]

the two S atoms. The two ligands also coordinate to the central S atom in an *anti* fashion.

Consistent with the solid-state structure, the solution  $^{31}\text{P}$  NMR spectrum of (II) in  $d_8$ -THF at 233 K consists of two mutually coupled doublets. However, upon warming the solution to room temperature a (reversible) collapse of these signals to give one broad resonance is observed, suggesting the occurrence of a dynamic exchange process that renders the two P-atom environments equivalent at higher temperatures. A four-coordinate complex of the type (III) is a possible intermediate in this interchange. In a related observation, two broad resonances were reported for the distorted square-planar complex  $\text{Te}[(\text{SP}(\text{OPh})_2)(\text{SP}(\text{Et})_2\text{N})]_2$  (see above) at room temperature, indicative of fluxional behaviour, but decomposition occurred at higher temperatures (Birdsall *et al.*, 2000).

The structural characterization of (II) reveals an interesting trend in the bonding arrangements for bis(imidodithiodiphosphinates) with a central  $E(\text{S}_4)$  core. As the size of the central chalcogen decreases from Te to S, the structure changes from square-planar ( $E = \text{Te}$ ) to trapezoidal planar ( $E = \text{Se}$ ) and, finally, to an acyclic two-coordinate complex ( $E = \text{S}$ ), despite the large bite of the ligand. This sequence manifests the decreasing ability of the central chalcogen(II) along the series  $\text{Te} > \text{Se} > \text{S}$  to accept ligand electron density from imidodithiodiphosphinates, which are relatively weak ligands (Husebye & Maartmann-Moe, 1983).

## Experimental

The oxidation of  $(\text{TMEDA})\text{Na}[(\text{SP}^t\text{Bu}_2)_2\text{N}]$  (TMEDA is tetramethylethylenediamine) with one half-equivalent of  $\text{I}_2$  in tetrahydrofuran (THF) was carried out according to the literature method of Ritch *et al.* (2007). Recrystallization of the crude yellow product from toluene (268 K, several days) gave a small crop of colourless

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

S1—P1	1.9745 (15)	P2—S2	2.1612 (14)
P1—N1	1.626 (3)	S2—S3	2.0642 (13)
N1—P2	1.553 (3)		
N1—P1—S1	117.34 (11)	S3—S2—P2	115.50 (5)
P2—N1—P1	155.41 (19)	S2—S3—S2 <sup>i</sup>	106.79 (8)
N1—P2—S2	101.01 (12)		
P2—S2—S3—S2 <sup>i</sup>	−96.81 (6)	S2—P2—N1—P1	−87.9 (5)
S1—P1—N1—P2	−43.0 (5)	N1—P2—S2—S3	174.00 (12)

Symmetry code: (i)  $-x, y, -z + \frac{3}{2}$ .

crystals of the title complex, (II).  $^{31}\text{P}$  NMR ( $d_8$ -THF, 233 K):  $\delta$  79.2 ( $d$ ,  $^2J_{\text{PP}} = 50$  Hz), 59.5 ( $d$ ,  $^2J_{\text{PP}} = 50$  Hz). The THF solvent was dried with Na/benzophenone and distilled onto 4  $\text{\AA}$  molecular sieves before use. The reaction, and the manipulation of the air- and moisture-sensitive  $(\text{TMEDA})\text{Na}[(\text{SP}^t\text{Bu}_2)_2\text{N}]$  reagent, were carried out under an atmosphere of argon or under vacuum. All glassware was carefully dried prior to use. Complex (II) can be handled in air for short periods of time without significant decomposition.

## Crystal data

$\text{C}_{32}\text{H}_{72}\text{N}_2\text{P}_4\text{S}_5\text{-C}_7\text{H}_8$	$V = 4840 (3) \text{\AA}^3$
$M_r = 861.23$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 22.271 (5) \text{\AA}$	$\mu = 0.40 \text{ mm}^{-1}$
$b = 18.970 (4) \text{\AA}$	$T = 173 \text{ K}$
$c = 15.610 (3) \text{\AA}$	$0.10 \times 0.03 \times 0.03 \text{ mm}$
$\beta = 132.79 (3)^\circ$	

## Data collection

Nonius KappaCCD area-detector diffractometer	19034 measured reflections
Absorption correction: integration ( <i>SCALEPACK</i> ; Otwinowski & Minor, 1997)	4274 independent reflections
$T_{\min} = 0.961$ , $T_{\max} = 0.988$	2612 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.070$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	11 restraints
$wR(F^2) = 0.122$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
4274 reflections	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$
271 parameters	

The central S atom lies on a crystallographic twofold axis, so only one half of the molecule is present in the asymmetric unit. The molecule is well ordered and no special considerations were necessary for the refinement. A toluene solvent molecule is also present in the asymmetric unit and was disordered over a crystallographic twofold axis, hence it was modelled at 0.50 occupancy. Several restraints were applied to obtain a well behaved toluene molecule: all seven atoms were fitted to coplanarity within 0.005  $\text{\AA}$ , the aromatic C—C bond lengths were restrained to 1.390 (5)  $\text{\AA}$  and the methyl group C atom was restrained to be equidistant from the *ortho*-C atoms within the aromatic ring ( $\pm 0.005 \text{\AA}$ ). H atoms were calculated geometrically, with C—H = 0.95 (aromatic) or 0.98  $\text{\AA}$  (methyl), and treated as riding on their respective C atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ .

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008);

program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *pubCIF* (Westrip, 2010).

The authors thank NSERC, Canada, for financial support, and Alberta Ingenuity and the Izaak Walton Killam Memorial Fund (University of Calgary) for scholarships.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3147). Services for accessing these data are described at the back of the journal.

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