

**Bis[2,2'-(phenylphosphinediyl)-
dibenzenethiolato- κ^3 S,P,S']-
germanium(IV)**

Michael Y. Chiang,^{a,b*} Jing-Wei Lin^{a,b} and Wen-Feng Zeng^c

^aDepartment of Chemistry, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, ^bCentre for Nanoscience and Technology, National Sun Yat-Sen University, 70 Lein-Hai Road, Kaohsiung 804, Taiwan, and ^cDepartment of Food Science and Technology, Tajen Institute of Technology, Pingtung 90703, Taiwan
Correspondence e-mail: michael@mail.nsysu.edu.tw

Received 6 September 2004

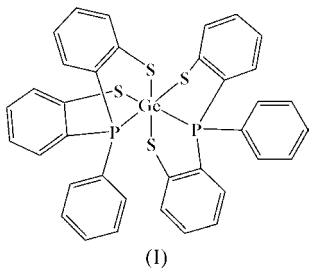
Accepted 15 December 2004

Online 15 January 2005

Two tridentate phosphinethiolate ligands, $[\text{PhP}(\text{C}_6\text{H}_4\text{S}-2)_2]^{2-}$, coordinate to the Ge^{IV} centre in a facial manner yielding the title compound, $[\text{Ge}(\text{C}_{18}\text{H}_{13}\text{PS}_2)_2]$, which exhibits a pseudo-twofold symmetry with the two P-atom donors in a *cis* configuration. The Ge centre has a distorted octahedral environment. Two phenyl rings, one from each of the phosphinethiolate ligands, are parallel to one another, indicating π - π interactions. The molecules are linked by weak $\text{C}-\text{H}\cdots\pi$ and $\text{C}-\text{H}\cdots\text{S}$ interactions.

Comment

Thiolates and phosphines are common ligands in coordination chemistry. Bidentate ligands using a combination of both donor sites have attracted much attention in recent decades (Stephan, 1984; Dilworth *et al.*, 1992). Metal complexes bearing polydentate ligands with both donor sites, *e.g.* $[\text{PhP}(\text{C}_6\text{H}_4\text{S}-2)_2]^{2-}$ are used in frontier research areas, such as biomimetic (Nguyen *et al.*, 1996), metal-organic chemical



vapour deposition (Pérez-Lourido *et al.*, 1999) and catalytic (Clark *et al.*, 2000) studies. In the course of studying the different ³¹P NMR behaviour of metal complexes with phosphinethiolate, we found that metal complexes containing the heavier congener of group 14 (*i.e.* Ge, Sn or Pb) have seldom been studied. Only one relevant structure with Sn, *viz.* $\{\text{PhP}[\text{C}_6\text{H}_3(\text{S}-2)(\text{SiMe}_3-3)]_2\}_2\text{Sn}_2$ (Froelich *et al.*, 1996), has

been reported to date. We report here the first crystal structure of a Ge complex obtained by the reaction of a phosphinethiolate ligand and germanium chloride in tetrahydrofuran. *n*-BuLi was used to remove H atoms from the proligands (phenylphosphinethiol), yielding the tridentate ligand $[\text{PhP}(\text{C}_6\text{H}_4\text{S}-2)_2]^{2-}$ (*L*), which coordinates to the Ge centre to give the title complex, GeL_2 , (I).

Complex (I) contains a Ge centre with two $[\text{PhP}(\text{C}_6\text{H}_4\text{S}-2)_2]^{2-}$ ligands (Fig. 1). Each tridentate ligand uses one P- and two S-atom donor sites to coordinate to the Ge centre in a facial manner. Molecular models strongly suggest that the ligand favours facial over meridional coordination in an octahedral complex, mainly due to the pyramidal coordination of P (Dilworth *et al.*, 1996). The octahedron formed by the two ligands around the Ge centre is slightly distorted due to the bite angles of the ligands (*ca* 81–85°) and the steric repulsion between the phosphine groups, which leads to a P1–Ge–P2 angle of 100.34 (3)°.

Complex (I) exhibits a pseudo-twofold symmetry on the P1/P2/S1/S3 plane through the Ge centre. In a rare Re^{IV} analogue, ReL_2 (Dilworth *et al.*, 1996), the pseudo-twofold symmetry becomes crystallographically real. The overall geometry of these two complexes is strikingly similar, except that the P1–Re–P2 angle of 108.8 (1)° is somewhat larger than the P1–Ge–P2 angle in (I).

The Ge–P bond lengths [2.4131 (10) and 2.4173 (12) Å] in (I) are almost identical to those observed in $\text{Ge}[\text{Me}_3\text{SiC}(\text{PMe}_2)_2]_2\text{Cl}_2$ (2.410–2.413 Å; Karsch *et al.*, 1996), the only six-coordinated Ge complex reported to date containing Ge–P bonds. Most of the Ge–S distances in (I) are around 2.4 Å (Table 1). These values are comparable with those cited for the six-coordinate complex $[\text{Ge}(L^1\text{Fe}_2)_2]\text{BPh}_4$ [2.422, 2.433 and 2.438 Å; *L*¹ is 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane; Glaser *et al.*, 1999]. The reported Ge–S bond lengths in Ge complexes involving the mercaptophenyl

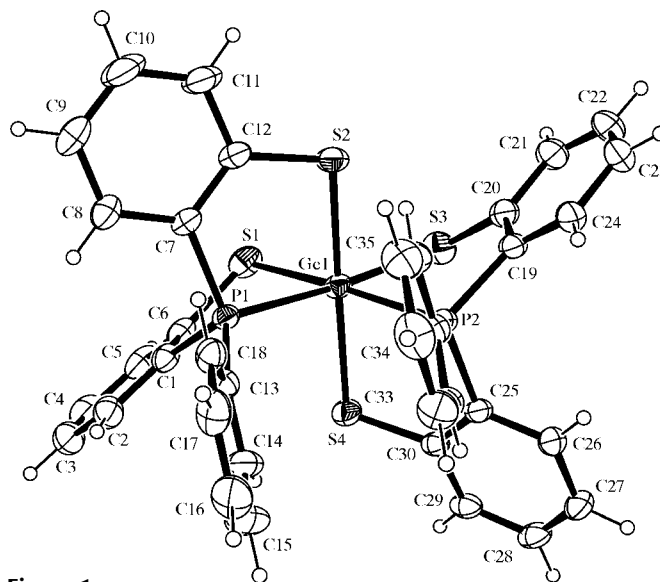
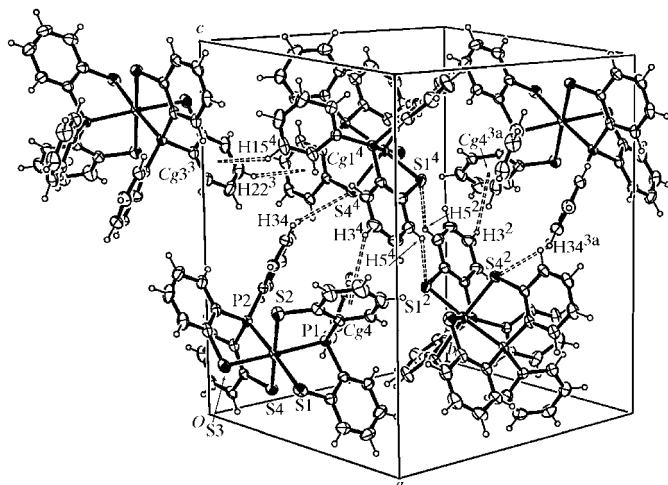


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.


Figure 2

The molecular packing of (I), showing the intermolecular C—H...S and most of the C—H... π interactions (Table 2). [Symmetry codes: (2) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (3) $-x, -y, 1 - z$; (3a) $1 - x, 1 - y, 1 - z$; (4) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

group range from 2.195 Å in tris(benzene-1,2-dithiolato- κ^2S,S')germanium(IV) (Pfeiffer *et al.*, 1989) to 2.477 Å in $\text{Ge}(L^2)_2$ [L^2 is 2,2'-thiobis(4,6-di-*tert*-butylphenolate); Pastor *et al.*, 1997]. Of all the Ge—S distances in (I), only the Ge—S1 distance of 2.343 (1) Å is significantly shorter than the others (Table 1).

Two phenyl rings, one from each of the two phosphinethiolate ligands, are parallel to each other, with a separation (ring centroid to phenyl plane) of 3.5 (1) Å. This usually indicates the existence of a π – π interaction. Although similar distances between phenyl planes are found in the $\text{Re}L_2$ analogue [3.1 (1) and 3.5 (1) Å for two independent molecules], the phenyl pairs are positioned differently in these two complexes. In $\text{Re}L_2$, the two phenyl rings are twisted away from each other, while those in (I) are arranged almost face-to-face (Fig. 1). Compared with the $\text{Re}L_2$ analogue, the smaller P—M—P angle (*ca* 8° smaller) in (I), together with the larger S—M—S angle (*ca* 10° larger) across it, provides evidence for a stronger π – π interaction in (I). These angular differences are consistent with the twist of the coordination planes around the metal centre. In (I), the twist between the P2/Ge1/S3 and P1/Ge1/S1 planes is 6.2 (1)°, while the twist between similar planes in $\text{Re}L_2$ is 17.1 (1)°. The smaller twist in (I) brings the two phenyl rings closer and hence produces a smaller P—M—P angle.

The molecules of (I) pack *via* weak C—H... π and C—H...S hydrogen-bond interactions (Table 2). The C—H...S interatomic distances and angles are comparable with those reported for $\text{Zn}_2(\mu\text{-C}_6\text{H}_4\text{S}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2$ [H...S = 2.84 Å, C...S = 3.637 (2) Å and C—H...S = 143°], where a possible C—H...S hydrogen bond was proposed (Hatch *et al.*, 2003).

Experimental

The title complex was obtained *via* a two-step reaction. First, the phosphinethiolate ligand was generated by mixing a tetrahydrofuran (THF) solution of the proligand $\text{PhP}(\text{C}_6\text{H}_4\text{SH-2})_2$ with *n*-BuLi in a 1:2 molar ratio at 273 K. An equimolar quantity (with respect to the

ligand) of GeCl_4 was added to this solution and the mixture stirred for 4 h. The yellow precipitate was extracted using CH_2Cl_2 and gave suitable crystals of (I) on recrystallization from THF. The melting point was determined to be 542 (1) K. The ^1H NMR spectrum gave a multiplet around 6.85–7.10 p.p.m. and ^{31}P NMR gave a singlet at –17.82 p.p.m.

Crystal data

$[\text{Ge}(\text{C}_{18}\text{H}_{13}\text{PS}_2)_2]$
 $M_r = 721.34$
 Monoclinic, $P2_1/c$
 $a = 11.537$ (4) Å
 $b = 16.729$ (3) Å
 $c = 16.882$ (4) Å
 $\beta = 95.96$ (2)°
 $V = 3240.7$ (14) Å³
 $Z = 4$

$D_x = 1.478$ Mg m^{–3}
 Mo $K\alpha$ radiation
 Cell parameters from 20 reflections
 $\theta = 4.9$ – 7.4 °
 $\mu = 1.33$ mm^{–1}
 $T = 298$ (2) K
 Prism, yellow
 $0.55 \times 0.35 \times 0.25$ mm

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.635$, $T_{\max} = 0.720$
 6696 measured reflections
 6369 independent reflections
 3913 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$
 $\theta_{\max} = 26$ °
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 20$
 $l = -20 \rightarrow 20$
 3 standard reflections
 every 150 reflections
 intensity decay: –0.4%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.094$
 $S = 1.01$
 6369 reflections
 389 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 0.8999P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.34$ e Å^{–3}
 $\Delta\rho_{\min} = -0.30$ e Å^{–3}
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.00152 (17)

Table 1

Selected geometric parameters (Å, °).

P1—Ge1	2.4131 (10)	S2—Ge1	2.3979 (11)
P2—Ge1	2.4173 (12)	S3—Ge1	2.3848 (10)
S1—Ge1	2.3429 (12)	S4—Ge1	2.4000 (10)
S1—Ge1—S3	97.23 (4)	S2—Ge1—P1	85.73 (3)
S1—Ge1—S2	94.46 (4)	S4—Ge1—P1	91.62 (3)
S3—Ge1—S2	90.35 (4)	S1—Ge1—P2	175.83 (3)
S1—Ge1—S4	90.57 (4)	S3—Ge1—P2	81.59 (3)
S3—Ge1—S4	92.46 (4)	S2—Ge1—P2	89.55 (4)
S2—Ge1—S4	173.88 (4)	S4—Ge1—P2	85.50 (4)
S1—Ge1—P1	81.12 (3)	P1—Ge1—P2	100.34 (3)
S3—Ge1—P1	175.61 (3)		

Table 2

Hydrogen-bond geometry (Å, °).

Cg1, Cg2, Cg3 and Cg4 represent the centroids of rings C25–C30, C1–C6, C19–C24 and C7–C12, respectively.

D—H...A	D—H	H...A	D...A	D—H...A
C5—H5...S1 ⁱ	0.93	2.88	3.671 (3)	143
C34—H34...S4 ⁱⁱ	0.93	2.99	3.808 (3)	147
C22—H22...Cg1 ⁱⁱⁱ	0.93	2.92	3.798 (4)	157
C27—H27...Cg2 ^{iv}	0.93	3.12	3.861 (4)	138
C15—H15...Cg3 ^v	0.93	3.27	3.987 (5)	136
C3—H3...Cg4 ^{vi}	0.93	3.28	4.032 (5)	139

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x, \frac{1}{2} - y, z + \frac{1}{2}$; (iii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $x - 1, y, z$; (v) $-x, y + \frac{1}{2}, \frac{1}{2} - z$; (vi) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

All H atoms were placed in calculated positions with C—H distances of 0.93 Å. They were included using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by the National Science Council of Taiwan (grant No. NSC92-2113-M-110-013)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1085). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Clark, K. A., George, T. A., Brett, T. J., Ross, C. R. & Shoemaker, R. K. (2000). *Inorg. Chem.* **39**, 2252–2253.
- Dilworth, J. R., Hutson, A. J., Lewis, J. S., Miller, J. R., Zheng, Y., Chen, Q. & Zubieta, J. (1996). *J. Chem. Soc. Dalton Trans.* pp. 1093–1104.
- Dilworth, J. R., Zheng, Y., Lu, S. & Wu, Q. (1992). *Transition Met. Chem.* **17**, 364–368.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Froelich, N., Hitchcock, P. B., Hu, J., Lappert, M. F. & Dilworth, J. R. (1996). *J. Chem. Soc. Dalton Trans.* pp. 1941–1946.
- Glaser, T., Bill, E., Weyhermüller, T., Meyer-Klaucke, W. & Wieghardt, K. (1999). *Inorg. Chem.* **38**, 2632–2642.
- Hatch, D. M., Wacholtz, W. F. & Mague, J. T. (2003). *Acta Cryst.* **C59**, m452–m453.
- Karsch, H. H., Deabelly, D., Keller, U., Steigelmann, O., Lachmann, J. & Müller, G. (1996). *Chem. Ber.* **129**, 671–676.
- Molecular Structure Corporation (1985). *TEXSAN*. Version 1.10. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. Version 5.32. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Nguyen, D. H., Hsu, H.-F., Millar, M. & Koch, S. A. (1996). *J. Am. Chem. Soc.* **118**, 8963–8964.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Pastor, S. D., Huang, V., NabiRahni, D., Kock, S. A. & Hsu, H.-F. (1997). *Inorg. Chem.* **36**, 5966–5968.
- Pérez-Lourido, P., Romero, J., Garcia-Vázquez, J. A. & Sousa, A. (1999). *Inorg. Chem.* **38**, 1293–1298.
- Pfeiffer, J., Noltemeyer, M. & Muler, A. (1989). *Z. Anorg. Allg. Chem.* **572**, 145–150.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stephan, D. W. (1984). *Inorg. Chem.* **23**, 2207–2210.