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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1066). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Chen, X.-M., Shi, K.-L., Mak, T. C. W. & Luo, B.-S. (1995). *Acta Cryst.* **C51**, 358–361.
- González-Platas, J. & Ruiz-Pérez, C. (1997). *NEWCORR. A Program for Absorption Correction*. University of La Laguna, Spain.
- Lumme, P. O. & Lindell, E. (1988). *Acta Cryst.* **C44**, 463–465.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Stoe & Cie (1992a). *DIF4. Diffractometer Control Program*. Version 6.2D. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1992b). *REDU4. Data Reduction Program*. Version 6.2D. Stoe & Cie, Darmstadt, Germany.
- Veidis, M. V., Dockum, B., Charron, F. F. Jr, Reiff, W. M. & Brennan, T. F. (1981). *Inorg. Chim. Acta*, **53**, L197–199.
- Wieghardt, K. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1153–1172.

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## A dichloropalladium(II) complex with a mixed donor bidentate ligand: dichloro[2-(diphenylphosphino)-1-(methylthio)ethane-P,S]palladium(II)

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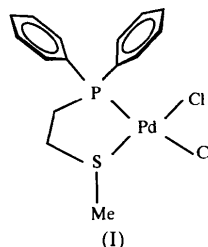
### Abstract

The title compound, [PdCl<sub>2</sub>(C<sub>15</sub>H<sub>17</sub>PS)], was prepared by the reaction of *cis*-dichlorobis(benzonitrile)-palladium(II) with the ligand 1-(thiomethyl)-2-(diphenylphosphino)ethane in acetone. The crystal structure of the resulting palladium(II) complex has been determined. The length of the Pd—Cl bonds is consistent with the *trans*-influence order: P > S.

### Comment

The synthesis of symmetrical Pd<sup>II</sup> complexes bearing bidentate P- or N-donor ligands, and their activity as catalyst precursors in homogeneous catalysis, have been extensively investigated (Abu-Surrah & Rieger, 1996). However, little research effort has been directed towards asymmetrical complexes with chelates that consist of mixed donor atoms, such as P and S or N.

In previous reports we described the use of symmetrical and unsymmetrical donor ligands (Abu-Surrah & Hodali, 1991), in complexes with late transition metals, in the preparation of potential catalyst precursors (Abu-Surrah & Rieger, 1998). A general feature of the coordination chemistry of complexes that carry mixed donor ligands is that a strong donor group at one end, such as an aryl phosphine, can stabilize the metal ion in low oxidation states, while a weakly coordinating site having an S or N atom can be substituted by a π-acceptor ligand (Abu-Surrah & Hodali, 1990; Kittaneh & Hodali, 1982). The presence of a vacant coordinating site is a fundamental property in homogeneous catalysis, since it permits organic substrates to enter the coordination sphere of the metal ion (Collman *et al.*, 1980), thereby generating catalytically active systems. The title compound, [Pd(S-P)Cl<sub>2</sub>], (I), where (S-P) is 1-(thiomethyl)-2-(diphenylphosphino)ethane, was used successfully as a catalyst for homopolymerization of norbornene to poly(2,3-bicyclo[2.2.1]hept-2-ene) after activation with methylaluminumoxane (MAO). However, it showed a lower activity compared with the symmetrical Pd<sup>II</sup> complex, [Pd(P-P)Cl<sub>2</sub>], where (P-P) is 1,2-bis(diphenylphosphino)ethane (Abu-Surrah *et al.*, 1999).



The crystals of the title complex are monoclinic and belong to the space group  $P2_1/n$ . The Pd atom is at the center of a square-planar arrangement. The length of the Pd—Cl1 [2.3115(12) Å] and Pd—Cl2 [2.3719(13) Å] bonds are shorter in (I) than in the corresponding symmetrical biphosphine complex [Pd-(P-P)Cl<sub>2</sub>] [2.415(3) and 2.394(3) Å, respectively; Singh *et al.*, 1995]. Furthermore, the metal–halide bond *trans* to the S atom [Pd—Cl1; 2.3115(12) Å] is shorter than that *trans* to the P atom [Pd—Cl2; 2.3719(13) Å]. This could be due to the stronger *trans* influence (Atwood, 1997) of the P donor atom compared to the S atom.

The increased length of the Pd—Cl bond when P is the *trans* group is in agreement with previous NMR

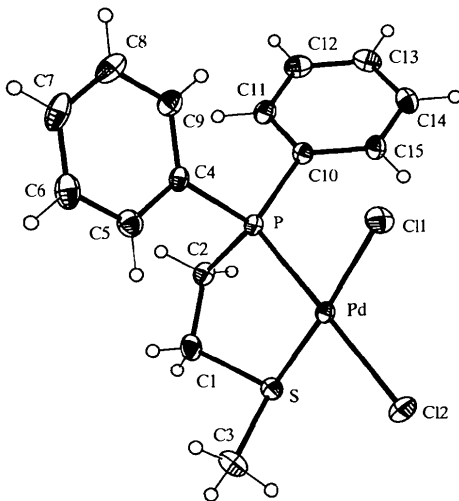


Fig. 1. The molecular view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

investigations carried out on the corresponding mono- and dialkyl complexes (the methyl signals are shifted upfield with increasing *trans* influence; Abu-Surrah & Hodali, 1991). This was explained in terms of a weakening effect caused by the P-donor atom on the Pd—CH<sub>3</sub> bond *trans* to it.

## Experimental

The title compound was prepared as previously described (Abu-Surrah & Hodali, 1991). Recrystallization from acetone afforded yellow crystals suitable for X-ray analysis.

### Crystal data

[PdCl<sub>2</sub>(C<sub>15</sub>H<sub>17</sub>PS)]

*M<sub>r</sub>* = 437.68

Monoclinic

*P*2<sub>1</sub>/*n*

*a* = 11.360 (3) Å

*b* = 12.237 (2) Å

*c* = 11.717 (2) Å

β = 93.63 (3)°

*V* = 1625.5 (6) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.788 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 24 reflections

θ = 3.0–9.8°

μ = 1.683 mm<sup>-1</sup>

*T* = 193 (2) K

Prismatic

0.21 × 0.18 × 0.15 mm

Yellow

### Data collection

Rigaku AFC-7S diffractometer

ω/2θ scans

Absorption correction:

ψ scan (North *et al.*, 1968)

*T<sub>min</sub>* = 0.745, *T<sub>max</sub>* = 0.777

3252 measured reflections

3100 independent reflections

2623 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.023

θ<sub>max</sub> = 26.48°

*h* = -14 → 14

*k* = 0 → 15

*l* = 0 → 14

3 standard reflections

every 200 reflections

intensity decay: < 2%

### Refinement

Refinement on *F*<sup>2</sup>

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.037

*wR* (*F*<sup>2</sup>) = 0.077

*S* = 1.030

3093 reflections

199 parameters

H atoms refined isotropically

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + *P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.437 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.578 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Pd—P	2.2213 (13)	Pd—Cl1	2.3115 (12)
Pd—S	2.2764 (12)	Pd—Cl2	2.3719 (13)
P—Pd—S	87.74 (5)	P—Pd—Cl2	177.64 (4)
P—Pd—Cl1	89.04 (5)	S—Pd—Cl2	90.01 (5)
S—Pd—Cl1	176.61 (4)	Cl1—Pd—Cl2	93.21 (5)

The intensity data were corrected for Lorentz and polarization effects. All non-H atoms were refined anisotropically and the H atoms were refined isotropically. An empirical ψ-scan absorption correction was carried out.

Data collection: *TEXSAN* (Molecular Structure Corporation, 1993). Cell refinement: *TEXSAN*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1039). Services for accessing these data are described at the back of the journal.

## References

- Abu-Surrah, A. S. & Hodali, H. A. (1990). *Inorg. Chim. Acta*, **174**, 223–229.
- Abu-Surrah, A. S. & Hodali, H. A. (1991). *Transition Met. Chem.* **16**, 458–461.
- Abu-Surrah, A. S., Lappalainen, K., Klinga, M., Leskelä, M., Hodali, H. A. & Rieger, B. (1999). In preparation.
- Abu-Surrah, A. S. & Rieger, B. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 2475–2477.
- Abu-Surrah, A. S. & Rieger, B. (1998). *J. Mol. Catal. A: Chem.* **35**, 2475–2477.
- Atwood, J. D. (1997). *Inorganic and Organometallic Reaction Mechanisms*, 2nd ed., pp. 48–51. New York: VCH.
- Collman, J. P., Hegedus, L. S., Norton, J. R. & Finke, R. G. (1980). *Principles and Applications of Organotransition Metal Chemistry*, edited by A. Kelly, pp. 54–59. Mill Valley: University Science Books.
- Kittaneh, I. M. & Hodali, H. A. (1982). *Inorg. Chim. Acta*, **60**, 223–226.
- Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1990). *SHELXTL/PC*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Singh, S., Jha, N. K., Narula, P. & Singh, T. P. (1995). *Acta Cryst. C51*, 593–595.

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### Bis(tetramethylammonium) tetra- $\mu_3$ -sulfido-tetrakis[(2,2-dimethylpropanethiolato-S)iron]: a heterocubane complex anion with crystallographically imposed $\bar{4}2m$ symmetry

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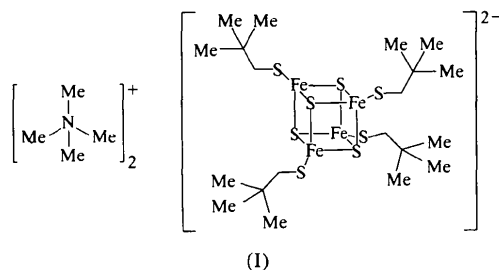
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#### Abstract

The title compound, (C<sub>4</sub>H<sub>12</sub>N)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(C<sub>5</sub>H<sub>11</sub>S)<sub>4</sub>], was prepared from iron(III) chloride by reaction with sodium 2,2-dimethylpropanethiolate, lithium sulfide and tetramethylammonium chloride in methanol. The anion has crystallographically imposed  $\bar{4}2m$  symmetry, giving rise to a compressed tetragonal arrangement of the Fe<sub>4</sub>S<sub>4</sub> core, with four short [2.246(2) Å] and eight long [2.289(2) Å] Fe—S distances.

#### Comment

Iron–sulfide–thiolate complexes of the general formula [Fe<sub>4</sub>S<sub>4</sub>(RS)<sub>4</sub>]<sup>n-</sup> (*n* = 1, 2 or 3) have been studied extensively due to their importance as model compounds for enzyme centres (Holm *et al.*, 1990) and in view of their interesting properties (Harris, 1989; Hoveyda & Holm, 1997; Noodleman *et al.*, 1995; Segal *et al.*, 1998; Zhou & Holm, 1997). The first structurally characterized example was described by Averill *et al.* (1972). Mixed iron–chalcogenide–chalcogenolate complexes of the general composition [Fe<sub>4</sub>X<sub>4</sub>(RY)<sub>4</sub>]<sup>n-</sup> (*X* = S, Se or Te; *Y* = S, Se or Te; *n* = 2 or 3) are also known (Bobrik *et al.*, 1978; Carney *et al.*, 1988; Henkel *et al.*, 1989). During our investigations of the iron–sulfide–thiolate reaction system, the title compound, [Me<sub>4</sub>N]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(C<sub>5</sub>H<sub>11</sub>S)<sub>4</sub>], (I), was synthesized.



The structure of (I) consists of discrete [Fe<sub>4</sub>S<sub>4</sub>(C<sub>5</sub>H<sub>11</sub>S)<sub>4</sub>]<sup>2-</sup> anions and [Me<sub>4</sub>N]<sup>+</sup> counter-cations. The cations have their expected geometries, with N—C distances of 1.456(12) Å. The anion exhibits a cubane-type geometry, with a slightly compressed tetragonal [Fe<sub>4</sub>S<sub>4</sub>]<sup>2+</sup> core containing two sets of Fe—S distances: four are short [2.246(2)] and eight long [2.289(2)], giving an average of 2.275 Å. Compressed Fe<sub>4</sub>S<sub>4</sub> cubane cores have been observed in virtually all complexes containing iron in the mean oxidation state +2.5. For instance, in the chemically related anions [Fe<sub>4</sub>S<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>S)<sub>4</sub>]<sup>2-</sup> (Que *et al.*, 1974) and [Fe<sub>4</sub>S<sub>4</sub>(AdS)<sub>4</sub>]<sup>2-</sup> (AdS<sup>-</sup> = adamantanethiolate; Kambayashi *et al.*, 1992), the mean values of the Fe—S bond lengths are 2.267(5) and 2.252(16) Å, respectively, for the set of shorter ones, while the mean values of the longer ones are 2.296(4) and 2.315(10) Å, respectively. Compared with these values, the Fe—S distances observed here appear to be shortened. This shortening can most probably be traced back to a pronounced librational motion of the Fe<sub>4</sub>S<sub>8</sub> frame. A bond-length correction assuming rigid-body behaviour resulted in corrected values of 2.256 and 2.303 Å for the sets of shorter and longer bonds, respectively, and these values are in good agreement with the literature. The S—Fe—S angles occur as sets of four smaller [104.02(9)°] and eight larger [104.57(5)°] ones. The Fe—S—Fe angles are

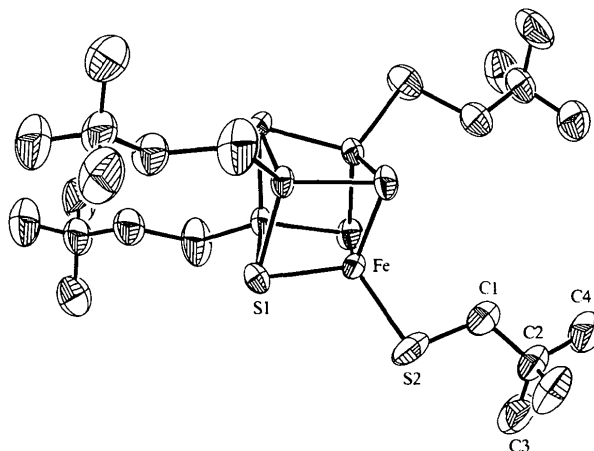


Fig. 1. The structure of the title complex anion, [Fe<sub>4</sub>S<sub>4</sub>(C<sub>5</sub>H<sub>11</sub>S)<sub>4</sub>]<sup>2-</sup>, shown with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.