

The crystal was kindly provided by Professors K. N. Houk and P. Deslongschamps

References

- Brillon, D. & Deslongchamps, P. (1987). *Can. J. Chem.* **65**, 56–68.
 Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution*. In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.
 Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P., & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

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[12]aneS₄PdCl₂

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Abstract

The title compound, dichloro(1,4,7,10-tetrathia-cyclododecane-*S*¹,*S*⁴)palladium(II), has the metal coordinated in a square plane by the chloride ligands and by two of the four sulfur donors of the macrocycle. The conformation adopted by the macrocycle is unsymmetrical with one of the uncoordinated thia donors *endo* and the other *exo* with respect to the ring (these donors lie along an edge and at a corner respectively). The species may be regarded as an intermediate in the reaction between PdCl₂ and [12]aneS₄ which leads to the formation of [Pd([12]aneS₄)]²⁺.

Comment

The conformation of the ring seen in this structure is different from that in the free ligand where all four sulfur donors are *exo* and lie at the corners of a square (Robinson & Sangokoya, 1988; Cooper, Foxman, Hartman, Storey & Wolf, 1987). It also differs from that in [Pd([12]aneS₄)]²⁺ where the metal is displaced by 0.31 Å from the S₄ square plane, on the other side of which lie all the C atoms of the macrocycle (Blake & Schröder, 1990).

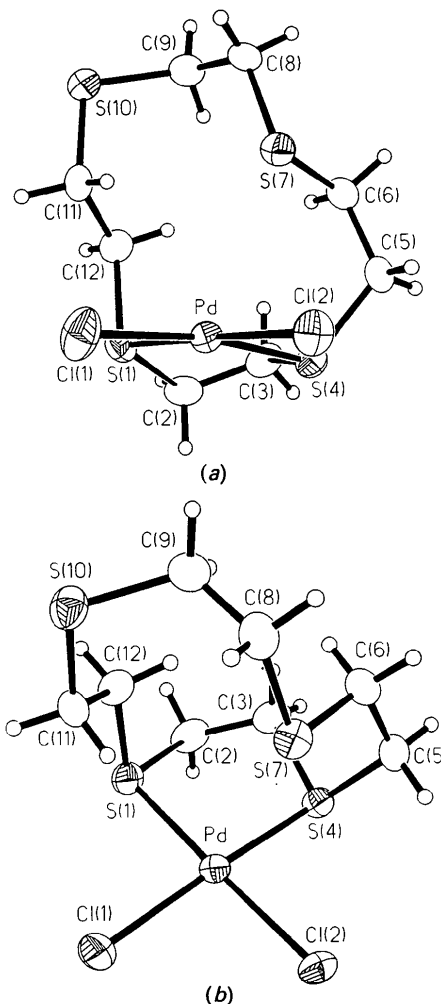


Fig. 1. Two views of the molecule: (a) and (b) are projections parallel and perpendicular to the square plane respectively. Thermal ellipsoids are drawn at the 30% probability level, except for those of H atoms which have been assigned arbitrary radii.

Experimental

Crystal data

C₈H₁₆Cl₂PdS₄
M_r = 417.7
 Orthorhombic
*Pbc*2₁
a = 7.5289 (8) Å
b = 14.5526 (16) Å
c = 12.8578 (11) Å
V = 1408.8 Å³
Z = 4
D_x = 1.970 Mg m⁻³

Mo Kα radiation
 λ = 0.71073 Å
 Cell parameters from 57 reflections
 θ = 9–11.5°
 μ = 2.256 mm⁻¹
T = 277 K
 Column
 1.28 × 0.39 × 0.39 mm
 Orange

Data collection

Stoe Stadi-4 four-circle diffractometer
 ω–2θ scans
R_{int} = 0.007
 θ_{max} = 22.5°
h = –8 → 8

Absorption correction: $k = -15 \rightarrow 0$
 semi-empirical $l = -13 \rightarrow 13$
 $T_{\min} = 0.126$, $T_{\max} = 0.147$
 2468 measured reflections 3 standard reflections
 1835 independent reflections frequency: 120 min
 1809 observed reflections intensity variation: 1%
 $[F \geq 4.0\sigma(F)]$

Refinement

Refinement on F $(\Delta/\sigma)_{\max} = 0.16$
 Final $R = 0.0161$ $\Delta\rho_{\max} = 0.75 \text{ e } \text{\AA}^{-3}$
 $wR = 0.0229$ $\Delta\rho_{\min} = -0.44 \text{ e } \text{\AA}^{-3}$
 $S = 1.170$ Extinction correction: isotropic
 1809 reflections Extinction coefficient: $\chi = 0.00111(7)$
 137 parameters Atomic scattering factors from *SHELXTL/PC*
 H atoms in fixed calculated positions
 $w = 1/[\sigma^2(F) + 0.0003F^2]$

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Pd	-0.05429 (3)	-0.06461 (1)	0*	0.0238 (1)
Cl(1)	-0.19669 (10)	-0.20113 (5)	0.04311 (9)	0.0455 (2)
Cl(2)	-0.29969 (9)	-0.00235 (5)	-0.08551 (7)	0.0364 (2)
S(1)	0.18716 (9)	-0.11671 (5)	0.08628 (6)	0.0296 (2)
C(2)	0.30259 (34)	-0.01051 (22)	0.11925 (22)	0.0347 (3)
C(3)	0.30130 (34)	0.05968 (20)	0.03418 (27)	0.0332 (3)
S(4)	0.07538 (10)	0.07422 (5)	-0.01601 (8)	0.0268 (2)
C(5)	0.11814 (35)	0.10379 (21)	-0.15151 (22)	0.0332 (3)
C(6)	0.22475 (36)	0.03587 (21)	-0.21746 (22)	0.0322 (3)
S(7)	0.10553 (14)	-0.07130 (5)	-0.23429 (7)	0.0337 (2)
C(8)	0.26360 (36)	-0.13620 (21)	-0.31258 (23)	0.0374 (3)
C(9)	0.42448 (34)	-0.17397 (22)	-0.25808 (27)	0.0376 (3)
S(10)	0.39670 (12)	-0.27670 (5)	-0.18021 (7)	0.0359 (2)
C(11)	0.25769 (34)	-0.24026 (18)	-0.07290 (25)	0.0310 (3)
C(12)	0.33818 (33)	-0.16084 (19)	-0.01272 (24)	0.0326 (3)

*Coordinate fixed to define origin.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Pd—Cl(1)	2.325 (1)	Pd—Cl(2)	2.333 (1)
Pd—S(1)	2.261 (1)	Pd—S(4)	2.253 (1)
S(1)—C(2)	1.823 (3)	S(1)—C(12)	1.824 (3)
C(2)—C(3)	1.497 (4)	C(3)—S(4)	1.832 (3)
S(4)—C(5)	1.823 (3)	C(5)—C(6)	1.530 (4)
C(6)—S(7)	1.813 (3)	S(7)—C(8)	1.823 (3)
C(8)—C(9)	1.503 (4)	C(9)—S(10)	1.811 (3)
S(10)—C(11)	1.811 (3)	C(11)—C(12)	1.517 (4)
Cl(1)—Pd—Cl(2)	94.5 (1)	Cl(1)—Pd—S(1)	88.1 (1)
Cl(2)—Pd—S(1)	176.7 (1)	Cl(1)—Pd—S(4)	171.1 (1)
Cl(2)—Pd—S(4)	87.2 (1)	S(1)—Pd—S(4)	89.8 (1)
Pd—S(1)—C(2)	102.3 (1)	Pd—S(1)—C(12)	106.1 (1)
C(2)—S(1)—C(12)	99.4 (1)	S(1)—C(2)—C(3)	113.9 (2)
C(2)—C(3)—S(4)	110.0 (2)	Pd—S(4)—C(3)	105.5 (1)
Pd—S(4)—C(5)	112.0 (1)	C(3)—S(4)—C(5)	101.5 (1)
S(4)—C(5)—C(6)	118.0 (2)	C(5)—C(6)—S(7)	111.2 (2)
C(6)—S(7)—C(8)	100.9 (1)	S(7)—C(8)—C(9)	117.3 (2)
C(8)—C(9)—S(10)	117.8 (2)	C(9)—S(10)—C(11)	104.3 (1)
S(10)—C(11)—C(12)	112.4 (2)	S(1)—C(12)—C(11)	112.0 (2)

The title compound was prepared by refluxing PdCl_2 and $[\text{12}]janeS_4$ in MeCN under N_2 for 4 h; the crystals were grown in MeCN. The data were collected with the crystal held in the cold stream of an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986) using ω - 2θ scans and the learnt-profile

method (Clegg, 1981). The structure was solved by interpretation of a Patterson synthesis which yielded the positions of the metal and one S atom. Refinement was by full-matrix least squares with all non-H atoms allowed anisotropic thermal motion. A determination of the polarity of the structure clearly favoured that adopted [$\eta = 1.02(4)$]. *SHELXTL/PC* (Sheldrick, 1990) was used to solve and refine the structure and to generate the figures and tables.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55465 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1010]

References

- Blake, A. J. & Schröder, M. (1990). *Adv. Inorg. Chem.* **35**, 1–80.
 Clegg, W. (1981). *Acta Cryst.* **A37**, 22–28.
 Cooper, S. R., Foxman, B. M., Hartman, J. R., Storey, J. M. E. & Wolf, R. E. (1987). *J. Am. Chem. Soc.* **109**, 4328–4335.
 Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
 Robinson, G. H. & Sangokoya, S. A. (1988). *J. Am. Chem. Soc.* **110**, 1494–1497.
 Sheldrick, G. M. (1990). Univ. of Göttingen, Germany.

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Structure of the Organic Radical Cation Salt 2,3,6,7-Tetrakis(methylthio)naphthalene Hexafluoroarsenate

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Abstract

Dimers of planar TMTN molecules [TMTN = 2,3,6,7-tetrakis(methylthio)naphthalene] form stacks along the *c* direction, surrounded by disordered AsF_6^- ions. The interplanar distances between the TMTN molecules are 3.275 (4) \AA (within the dimer) and 3.645 (4) \AA (between the dimers). The TMTN molecules within the dimer are related by a centre of symmetry.

Comment

This work is part of a series of studies into the structures and physical properties of electro-