SHORT-FORMAT PAPERS

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Reinvestigation of the Structure of PdS

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Abstract. $M_r = 138{\cdot}46$, tetragonal, $P4_2/m$, $a = 6{\cdot}429\,(2)$, $c = 6{\cdot}611\,(2)$ Å, $V = 273{\cdot}3$ Å^3, $Z = 8$, $D_x = 6{\cdot}728$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}7093$ Å, $\mu = 141{\cdot}3$ cm^{-1}, $F(000) = 496$, $T = 106$ K, R (on F_o^2) = 0·0354 for 694 averaged reflections (including those having $F_o^2 < 0$). Atom Pd(1) sits in a slightly ruffled square of S atoms, while a rectangular plane coordinates atom Pd(2), and atom Pd(3) is both bent out of the plane and coordinated rectangularly. Four Pd atoms in a distorted tetrahedron coordinate each S atom. The square-planar coordination about the three independent Pd atoms is more regular than reported by Gaskell [*Z. Kristallogr.* (1937), **96**, 203–213].

Experimental. Single crystals of PdS were isolated from a reaction of $EuPd_3S_4$ (Keszler, Ibers & Mueller, 1985) with ~ 1 at. % Br_2 heated in a sealed, evacuated silica tube at 900 K for 12 d. The crystal used for data collection was elongated about the a axis, and formed a thick plate parallel to the $(2\bar{3}0)$ face; crystal volume $2{\cdot}4 \times 10^{-5}$ mm^3. Unit-cell parameters were derived from a least-squares analysis of 25 reflections, in the range $10° < \theta < 18°$, automatically centered on an Enraf–Nonius CAD-4 X-ray diffractometer. As opposed to the limitations of the usual CAD-4 software, we imposed the conditions $a = b$ and $\alpha = \beta = \gamma = 90°$. Intensity data were collected with the $\omega/2\theta$ scan technique; intensities of six standards monitored throughout data collection were constant within intensity statistics. A total of 3809 X-ray diffraction intensities, measured to $(\sin\theta_{\max})/\lambda = 0{\cdot}8287$ Å^{-1} in the index range $-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-10 \leq l \leq 10$, were corrected for absorption with use of the analytical method (de Meulenaer & Tompa, 1965); min. and max. transmission factors were 0·51 and 0·89. The F_o^2 values were averaged to yield 694 unique data $[R_{\rm int}(F^2) = 0{\cdot}061]$. The structure was refined from the previous model (Gaskell, 1937). Scattering factors and anomalous-dispersion terms were taken from the usual sources (Cromer & Waber, 1974; Cromer, 1974). All calculations were performed on a Harris 1000 computer with methods and programs standard for this laboratory (Waters & Ibers, 1977). The final refinement on F_o^2, based on 23 variables and 694 observations, resulted in an R index on F^2 of 0·035 and an isotropic-extinction parameter (Zachariasen, 1968) of $1{\cdot}3\,(1) \times 10^{-6}$, with Δ/σ not exceeding 0·008.* Other residuals are $wR(F^2) = 0{\cdot}061$, where the weights are derived from counting statistics and a value of p of 0·04, and $R(F)$ $[F_o^2 > 3\sigma(F_o^2)] = 0{\cdot}028$. Error in an observation of unit weight is 0·87. A final difference electron density map exhibited no features with height greater than 0·7% of a Pd atom.

Table 1 lists fractional coordinates and equivalent isotropic thermal parameters. A list of selected bond distances and angles may be found in Table 2. Fig. 1 displays the unit cell and the coordination about the Pd atoms.

Related literature. The square-planar coordination geometries about the Pd atoms are more regular than those reported in the classic structure of Gaskell (1937). The geometry about atom Pd(2) is similar to that proposed by Childs & Hall (1973) for the Pd site in Braggite (Pt,Pd,Ni)S, although the Pd(2)—S distance at 2·318 (1) Å is significantly longer than that of 2·26 (1) Å in Braggite.

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* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42414 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters and equivalent isotropic thermal parameters for* PdS

	Site symmetry	x	y	z	B_{eq}(Å^2)
Pd(1)	$\bar{4}$	0	0	$\frac{1}{4}$	0·35 (1)
Pd(2)	$2/m$	$\frac{1}{2}$	0	0	0·33 (1)
Pd(3)	m	0·257132 (59)	0·467792 (55)	0	0·33 (1)
S(1)	1	0·30754 (13)	0·19361 (14)	0·22904 (13)	0·37 (1)

Gaskell (1937) obtained: Pd(3) 0·25 (1), 0·48 (1), 0; S(1) 0·32 (1), 0·19 (1), 0·23 (1), for x, y, z respectively.

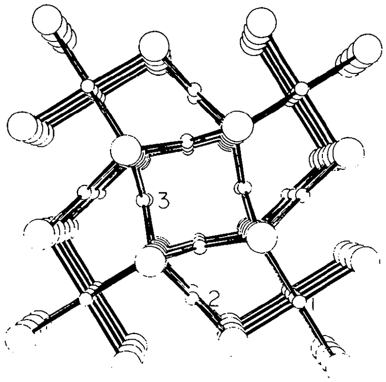

Fig. 1. Perspective view of PdS along [001]. Pd atoms are small open circles; S atoms are large open circles.

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* PdS

Pd(1)–4S(1)	2·341 (1)	S(1)–Pd(1)–S(1)	173·21 (4)
Pd(2)–4S(1)	2·318 (1)	S(1)–Pd(1)–S(1)	90·20 (1)
Pd(3)–2S(1)	2·337 (1)	S(1)–Pd(2)–S(1)	81·57 (5)
Pd(3)–2S(1)	2·346 (1)	S(1)–Pd(3)–S(1)	89·65 (3)
Pd(3)–Pd(3)	3·150 (1)	S(1)–Pd(3)–S(1)	100·08 (5)
Pd(1)–2Pd(1)	3·306 (1)	S(1)–Pd(3)–S(1)	169·46 (4)
Pd(1)–4Pd(2)	3·615 (1)	Pd(2)–S(1)–Pd(3)	93·19 (4)
Pd(1)–4Pd(3)	3·809 (1)	Pd(2)–S(1)–Pd(1)	101·77 (3)
Pd(2)–2Pd(3)	3·389 (1)	Pd(2)–S(1)–Pd(3)	105·34 (4)
Pd(2)–4Pd(3)	3·702 (1)	Pd(1)–S(1)–Pd(3)	108·73 (3)
Pd(3)–4Pd(3)	3·986 (1)	Pd(3)–S(1)–Pd(3)	116·66 (4)
Pd(1)–4Pd(3)	4·144 (1)	Pd(3)–S(1)–Pd(1)	124·73 (4)
S(1)–S(1)	3·029 (2)		
S(1)–2S(1)	3·302 (2)		
S(1)–2S(1)	3·316 (2)		
S(1)–S(1)	3·510 (2)		

References

Childs, J. D. & Hall, S. R. (1973). *Acta Cryst.* **B29**, 1446–1451.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Gaskell, T. F. (1937). *Z. Kristallogr.* **96**, 203–213.

Keszler, D. A., Ibers, J. A. & Mueller, M. H. (1985). *J. Chem. Soc.* In the press.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Waters, J. M. & Ibers, J. A. (1977). *Inorg. Chem.* **16**, 3273–3277.

Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

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Structure of a Methoxo-Bridged Dichromium Complex

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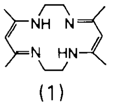
Abstract. Di-μ-methoxo-bis[(7-amino-4-methyl-5-azahept-3-en-2-onato-*O*,*N*,*N'*)aquachromium(III)] diperchlorate, $[Cr_2(CH_3O)_2(C_7H_{13}N_2O)_2(H_2O)_2]-(ClO_4)_2$, $M_r = 683{\cdot}4$, $P\bar{1}$, $a = 8{\cdot}087$ (2), $b = 8{\cdot}950$ (2), $c = 11{\cdot}018$ (3) Å, $\alpha = 68{\cdot}92$ (2), $\beta = 73{\cdot}59$ (2), $\gamma = 83{\cdot}61$ (2)°, $V = 713{\cdot}75$ Å^3, $Z = 1$, $D_x = 1{\cdot}590$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}00$ mm^{-1}, $F(000) = 354$, $T = 291$ K, $R = 0{\cdot}045$ for 1533 unique observed reflections. The cation has crystallographic $\bar{1}$ symmetry, with a strictly planar central Cr_2O_2 ring and rather unsymmetrical bridging geometry [Cr—O = 1·976 (3) and 1·940 (3) Å, Cr—O—Cr = 100·8 (1)°]. Coordination of Cr is essentially octahedral. The six-membered chelate ring is almost planar [Cr 0·329 (1) Å from the mean plane of the other atoms, r.m.s. $\Delta = 0{\cdot}015$ (6) Å]; the five-membered chelate ring is strongly non-planar to allow for staggering of the H atom substituents.

Experimental. Compound obtained by reaction of $CrCl_2$ with the macrocyclic base 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (1) in aqueous methanol, followed by air oxidation and perchlorate ion-exchange (Ramasami, 1984). The macrocyclic ligand is hydrolyzed under the reaction conditions.



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