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Bis(tetraphenylphosphonium) bis(tetraselenomolybdato)palladate(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.013 Å
R factor = 0.053
wR factor = 0.152
Data-to-parameter ratio = 20.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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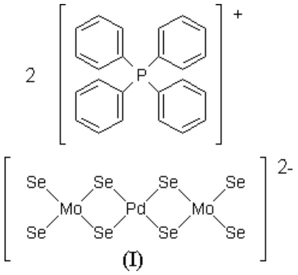
In the title compound, $(C_{24}H_{20}P)_2[Pd(MoSe_4)_2]$, the $[Pd(MoSe_4)_2]^{2-}$ anion has the Pd^{II} atom on a crystallographic inversion center with distorted square-planar geometry, coordinated by two nearly tetrahedral bidentate $MoSe_4{}^{2-}$ ligands. It is the first complex of palladium and tetraselenomolybdate to be structurally characterized.

Comment

The tetrathiometallates $MS_4{}^{2-}$ and tetraselenometallates $MSe_4{}^{2-}$ (M = Mo, W) chelate metal ions. These compounds are of interest as models of active centers in both enzymes (nitrogenase) and catalysts (hydrodesulfurization), as well as for their potential non-linear optical properties. The thiometallate chemistry has been known longer and is more extensive than that of the corresponding selenometallate compounds, and both the thio and seleno complexes of tungsten are more stable and numerous than those of molybdenum (Müller *et al.*, 1981; Ansari & Ibers, 1990; Zhang, Leung & Xin, 2002). While the chemistry of mixed-metal selenide complexes often parallels that of the soluble mixed-metal sulfides, at least one selenide complex has been synthesized for which there is no known sulfur analog, *viz.* $[Ni(Se_2)(WSe_4)]^{2-}$ (Ansari *et al.*, 1989). We present here the product of a reaction between the tetraphenylphosphonium salt of the tetraselenomolybdate ion and Pd^{2+} to yield crystals of $[PPh_4]_2[Pd(MoSe_4)_2]$, (I) (Ph is phenyl).


(I)

The $[Pd(MoSe_4)_2]^{2-}$ ion is located at a crystallographic inversion center. The geometry about the Pd^{II} atom is distorted square planar and the bidentate $MoSe_4{}^{2-}$ ligands are nearly tetrahedral. The Se1—Pd—Se2 angle formed by one $MoSe_4{}^{2-}$ moiety is 101.53 (3)°, while the Se1—Pd—Se2^{i} [symmetry code: (i) $1 - x, 2 - y, 1 - z$] angle formed between two ligands is 78.47 (3)°. The Pd—Se bond lengths are 2.448 (2) Å, which is near the middle of the range of ten different Pd—Se distances found in $[N(C_2H_5)_4]_5$-$[2Pd(Se_4)_2{\cdot}0.5Pd(Se_5)_2]$ [these Pd—Se distances vary from 2.358 (13) to 2.489 (12) Å; McConnachie *et al.*, 1993]. These Pd—Se bonds are shorter than all Pd—Se bonds in three

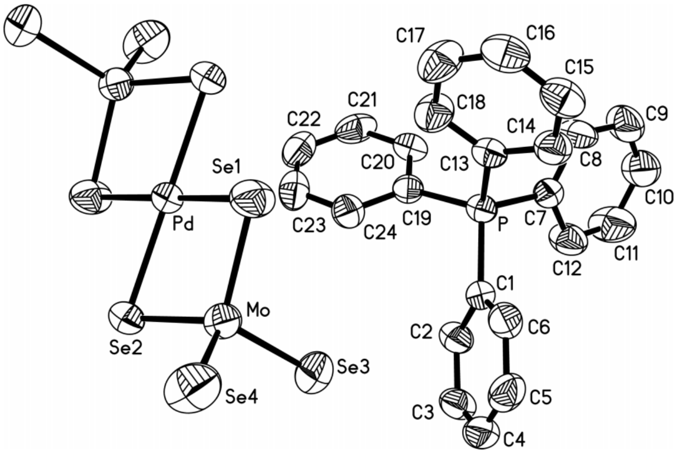


Figure 1

View of the title compound, with displacement ellipsoids drawn at the 50% probability level. Only the unique PPh_4^+ cation is drawn, and the unlabeled atoms of the anion are related by the symmetry code (1 − *x*, 2 − *y*, 1 − *z*). H atoms have been omitted.

different neutral WSe_4 complexes of Pd^{2+} with bidentate phosphine ligands [these distances range from 2.465 (1) to 2.490 (1) Å; Zhang, Song *et al.*, 2002].

The Se—Mo—Se angle for the chelating tetraselenomolybdate ligands is 106.95 (4)°, while the remaining Se—Mo—Se angles range from 109.11 (4) to 110.63 (5)°. The angle between the terminal Se_2Mo plane and that of the bridging $MoSe_2Pd$ plane is 90.37 (4)°. The bridging Mo—Se bond distances are 2.359 (2) Å, within the range of bridging Mo—Se distances in a series of three Au, two Ag, and nine Cu complexes with $MoSe_4$ ligands [these distances vary from 2.184 (6) to 2.388 (4) Å; Zhang, Leung & Xin, 2002]. Although the Pd—Se bond distances in the four-membered ring of the $[Pd(MoSe_4)_2]^{2-}$ anion are near the average found in five- and six-membered rings in $[2Pd(Se_4)_2{\cdot}0.5Pd(Se_5)_2]^{5-}$ (McConnachie *et al.*, 1993), the bridging Mo—Se distances in the four-membered rings of the $[Pd(MoSe_4)_2]^{2-}$ anion are shorter than any of the Mo—Se distances in the five-membered $MoSe_4$ rings of either $[MoSe(Se_4)_2]^{2-}$ [2.432 (4)–2.505 (4) Å; O'Neal & Kolis, 1988] or $[MoO(Se_4)_2]^{2-}$ [2.479 (1)–2.512 (1) Å; Wardle *et al.*, 1988]. The terminal Mo—Se bond distances in $[Pd(MoSe_4)_2]^{2-}$ average 2.269 (6) Å, which is nearly identical to the terminal Mo—Se distance in the $[MoSe(Se_4)_2]^{2-}$ ion of 2.270 (4) Å, and slightly shorter than the Mo—Se distances in a free $[MoSe_4]^{2-}$ ion of 2.293 (1) Å (O'Neal & Kolis, 1988).

$[PPh_4]_2[Pd(MoSe_4)_2]$ has the first complex anion containing only Pd and $MoSe_4{}^{2-}$ to be structurally characterized. While the analogous complex anions $[Pd(MoS_4)_2]^{2-}$, $[Pd(WS_4)_2]^{2-}$ and $[Pd(WSe_4)_2]^{2-}$ are already known (Müller *et al.*, 1981; Ansari *et al.*, 1989), only the single-crystal structures of salts of $[Pd(WS_4)_2]^{2-}$ have been determined (twice, with different cations; Potvin & Manoli, 1990; Long *et al.*, 1997). In addition, $[PPh_4]_2[Pd(WSe_4)_2]$ is found to be isostructural with $[PPh_4]_2[Ni(WSe_4)_2]$ by X-ray powder diffraction (Ansari *et al.*, 1989).

The Mo···Pd distance [2.9212 (9) Å] is 0.16 Å longer than the sum of the metallic radii for Mo and Pd. The metallic radii for Mo and W are identical, but the W···Pd distances in $[(WSe_4)_2Pd_4(dppm)_2]$ [2.944 (1) Å], $[(WSe_4)Pd(dppe)]$ [2.9628 (4) Å] and $[(WSe_4)Pd(dppp)]$ [3.0302 (8) Å] are all longer [dppm is bis(diphenylphosphino)methane, dppe is 1,2-bis(diphenylphosphino)ethane and dppp is 1,3-bis(diphenylphosphino)propane] (Zhang, Song *et al.*, 2002). The W···Pd distances in both $[Pd(WS_4)_2]^{2-}$ ions [2.893 (2) Å] are slightly shorter, perhaps due to the smaller size of S *versus* Se atoms.

A planar MQ_2M' rhomboid (M = Mo, W; Q = S, Se; M' = Ni, Pd) with tetrahedral coordination at M and square-planar coordination at M' has ideal $M{-}Q{-}M'$ bridge angles of 80.23°, but the actual bridge angles are significantly less in each of these structures of complexes with only MQ_4 ligands. This structure has the smallest $M{-}Q{-}M'$ angle [74.82 (4)°], compared to 75.0 (1)° in $[Ni(WSe_4)_2]^{2-}$ and 78.4 (1)° in the $[Pd(WS_4)_2]^{2-}$ ions.

This $MoSe_4$ ligand has the bridging $Q{-}M{-}Q$ angle closest to tetrahedral in the ionic complexes [106.95 (4)°, compared to 103.62 (3)° in $[Ni(WSe_4)_2]^{2-}$ and 105.0 (2)° in both $[Pd(WS_4)_2]^{2-}$ ions]. Another sign of the near tetrahedral nature of these $MoSe_4$ ligands is the non-bonding Se1···Se2 distance of 3.792 (1) Å, compared to an average of 3.776 (3) Å for the other five Se···Se non-bonding distances in the same $MoSe_4$ ligands, and the comparable distance in $[Ni(WSe_4)_2]^{2-}$ [3.691 (1) Å]. Interestingly, the Se1···Se2^{i} non-bonding distance (between $MoSe_4$ ligands) is much shorter [3.096 (1) Å] and approaches the sum of the van der Waals radii for Se atoms.

In each of the complexes with only MQ_4 ligands, the largest absolute deviation from the expected coordination geometries occurs for the $Q{-}M'{-}Q$ angles, expected to be 90° (if square planar). This bridging Se—Ni—Se angle [101.53 (3)°] is larger than that in both $[Pd(WS_4)_2]^{2-}$ ions [98.1 (2)°], but smaller than that in $[Ni(WSe_4)_2]^{2-}$ [111.01 (3)°]. For all metal complexes with MQ_4 ligands, the ligands stay nearly tetrahedral despite a variety of chelation and bridging modes, while the geometry at M' is most variable.

Experimental

All reactions were carried out in an inert atmosphere of dry prepurified nitrogen using standard Schlenk-line techniques. All solvents were dried and distilled before use. Reaction of one equivalent of palladium(II) acetate (Aldrich) with two equivalents of $[PPh_4]_2[MoSe_4]$ (synthesized according to a literature method; O'Neal & Kolis, 1988), produced $[PPh_4]_2[Pd(MoSe_4)_2]$ in low yield. Either *N*,*N*-dimethylformamide (DMF) or *N*,*N*-dimethylacetamide (DMA) could be used as the reaction solvent. Slow diffusion of tetrahydrofuran (THF) into either solvent system resulted in precipitation of small black crystals. While $[Ni(WSe_4)_2]^{2-}$ reacts to form the unique and more stable $[Ni(Se_2)(WSe_4)]^{2-}$, no such reaction is observed here (as is also the case for the analogous $[Pd(WSe_4)_2]^{2-}$) (Ansari *et al.*, 1989). IR and UV–Vis spectra were used to characterize the product; IR: 1836, 1442, 1107, 530 cm^{-1}; UV–Vis: 350, 570 nm.

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Crystal data

$(C_{24}H_{20}P)_2[PdMo_2Se_8]$
$M_r = 1608.70$
Triclinic, $P\overline{1}$
$a = 9.4976\ (9)$ Å
$b = 12.5798\ (16)$ Å
$c = 12.622\ (3)$ Å
$\alpha = 66.096\ (13)°$
$\beta = 84.511\ (13)°$
$\gamma = 70.047\ (9)°$
$V = 1294.3\ (4)$ Å^3

$Z = 1$
$D_x = 2.064$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26 reflections
$\theta = 6.5$–$40.9°$
$\mu = 6.54$ mm^{-1}
$T = 293\ (2)$ K
Flake/arrowhead, black
$0.48 \times 0.42 \times 0.36$ mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (*SHELXTL*; Bruker, 2002)
$T_{min} = 0.058$, $T_{max} = 0.095$
6737 measured reflections
5698 independent reflections
3974 reflections with $I > 2\sigma(I)$

$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 1$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.152$
$S = 1.02$
5698 reflections
277 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0733P)^2 + 3.8281P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.63$ e Å^{-3}
$\Delta\rho_{min} = -1.09$ e Å^{-3}

H atoms were included in calculated positions, with C—H = 0.93 Å, and treated as riding, with $U_{iso} = 1.2U_{eq}$ of the parent atom. The maximum and minimum density peaks in the final difference Fourier map were 1.29 and 0.52 Å, respectively, from atom Se4.

Data collection: *XSCANS* (Siemens, 1991–1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 2002); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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