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A W–Ag–Se cluster compound: (μ_3-bromo)(μ_3-tetraselenidotungstide)tris(triphenylphosphinesilver) ethanol solvate, [(μ_3-Br)(μ_3-WSe$_4$)(AgPPh$_3$)$_3$]·EtOH

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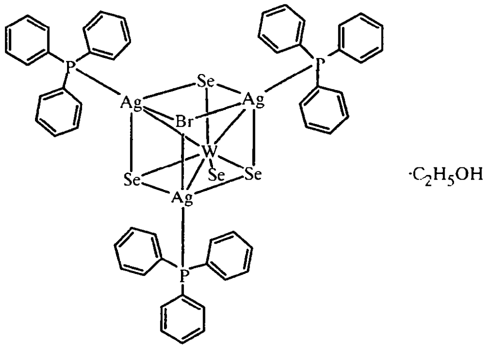
Abstract

The title compound, μ_3-bromo-2:3:4κ^3*Br*-tri-μ_3-selenido-1:2:3κ^3*Se*;1:2:4κ^3*Se*;1:3:4κ^3*Se*-selenido-1κ*Se*-tris(triphenylphosphine)-2κ*P*,3κ*P*,4κ*P*-trisilvertungsten ethanol solvate, [Ag$_3$WBrSe$_4$(C$_{18}$H$_{15}$P)$_3$]·C$_2$H$_5$OH, is composed of discrete [(μ_3-Br)(μ_3-WSe$_4$)(AgPPh$_3$)$_3$] neutral clusters and EtOH molecules. The structure can be described either as (i) a cubane-like [WAg$_3$Se$_3$Br]$^{2+}$ cluster core with another Se^{2-} ligand bound to the W atom and three PPh$_3$ ligands attached to the three Ag atoms, or as (ii) three Ag(PPh$_3$)$^+$ fragments linked by one μ_3-WSe$_4^{2-}$ and one μ_3-Br ligand. The average W—Ag bond distance is 3.01 (1) Å, which is too long to be considered a metal–metal interaction.

Comment

The coordination chemistry of *M*S$_4^{2-}$ (*M* = Mo, W) has been widely investigated, primarily because of its relevance in modeling certain molybdo-enzymes (Holm & Berg, 1986; Coucouvanis, 1991) and hydrodesulfurization catalysts (Harris & Chianelli, 1984; Müller, 1986), especially certain Mo(W)–Cu(Ag)–S clusters, which have been found to have non-linear optical properties (Shi *et al.*, 1994). However, research on the corresponding chemistry of *M*Se$_4^{2-}$ (*M* = Mo, W) has only been carried out recently (Ansari & Ibers, 1990; Roof & Kolis, 1993). Up to now, only a few mixed-metal selenide compounds containing *M*Se$_4^{2-}$ (*M* = Mo, W) units have been structurally characterized; examples include [(μ_3-Cl)(μ_3-WSe$_4$)(CuPPh$_3$)$_3$] (Christuk *et al.*, 1992), [(NC)Cu(μ-Se)$_2$*M*Se$_2$Cu(CN)]$^{2-}$ and [(Me$_2$PhP)Au(μ-Se)$_2$*M*(μ-Se)$_2$]$^{2-}$ (*M* = Mo, W; Salm & Ibers, 1994; Salm *et al.*, 1995), [(μ_3-I)(μ_3-*M*Se$_4$)(Ag*L*)$_3$] (*M* = Mo, W; *L* = PMe$_2$Ph, PPh$_3$; Ansari *et al.*, 1994; Du *et al.*, 1994; Zhang *et al.*, 1997) and [MoSe$_4$(Cu*R*$_2$-NCS$_2$)$_x$]$^{2-}$ (*R* = Et, Me; *x* = 3, 4; Hong *et al.*, 1997). We report herein the crystal structure of [(μ_3-Br)(μ_3-W-Se$_4$)(AgPPh$_3$)$_3$]·EtOH, (I).



(I)

The crystal structure of (I) consists of two neutral molecules. The structure is similar to the Mo–Ag–S cubane [(μ_3-Cl)(μ_3-MoS$_4$)(AgPPh$_3$)$_3$] (Zhu *et al.*, 1992) and the W–Cu–Se cubane [(μ_3-Cl)(μ_3-WSe$_4$)(CuPPh$_3$)$_3$] (Christuk *et al.*, 1992). The [WAg$_3$Se$_3$Br]$^{2+}$ cluster core is cubane-like and is completed by three Ag atoms, one Br atom and a tridentate WSe$_4^{2-}$ ligand. One PPh$_3$ ligand is also attached to each of the three Ag atoms. The coordination geometry of the W atom is a distorted tricapped tetrahedron. The W—Se$_t$ (*t* = terminal) bond length is 0.10–0.12 Å shorter than the W—Se$_b$ (*b* = bridging) bond lengths. However, the angles between the terminal and bridging Se atoms are less obtuse than those between the bridging Se atoms themselves, and this is probably caused by some hindrance exerted by

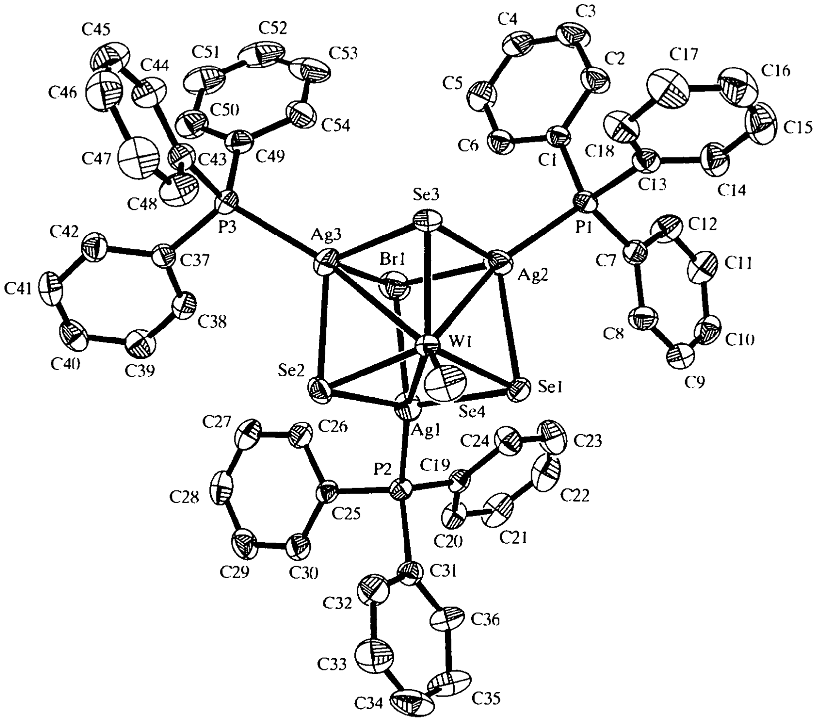


Fig. 1. The molecular structure of the $[(\mu_3\text{-Br})(\mu_3\text{-WSe}_4)(\text{AgPPh}_3)_3]$ cluster showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

the three Ag atoms capping the Se1/Se2/Se3 face of the tetrahedron. The average W—Ag distance of 3.01 (1) Å in (I) is too long to be considered a metal–metal bond. The average Ag—Se bond length of 2.65 (2) Å in (I) agrees well with that of 2.638 (2) Å in $[(\mu_3\text{-I})(\mu_3\text{-WSe}_4)(\text{AgPPh}_3)_3]$ (Du *et al.*, 1994) and 2.622 (1) Å in $[(\mu_3\text{-I})(\mu_3\text{-WSe}_4)(\text{AgPMe}_2\text{Ph})_3]$ (Ansari *et al.*, 1994). It is interesting to note that the title compound has three long Ag—Br bonds, which suggests that the presence of halide atoms is necessary for the formation of cubane-like clusters because the weak interaction between the Br and three Ag atoms stabilizes it. The average Ag—Br distance [2.95 (3) Å] in (I) is longer than the Ag—Cl distance [2.842 (2) Å] in $[(\mu_3\text{-Cl})(\mu_3\text{-WSe}_4)(\text{AgPPh}_3)_3]$ (Zhang *et al.*, 1997) and is shorter than the Ag—I distance [3.064 (2) Å] in $[(\mu_3\text{-I})(\mu_3\text{-WSe}_4)(\text{AgPPh}_3)_3]$ (Du *et al.*, 1994). The Br atom is at one vertex of the $[\text{WAg}_3\text{Se}_3\text{Br}]^{2+}$ cube. However, the average Ag—Br—Ag angle of 72.1 (9)° deviates greatly from the standard cubane angle of 90°. An *ORTEP*II plot (Johnson, 1976) of (I) with the atomic numbering scheme is presented in Fig. 1. The ethanol solvent molecule is encapsulated in a hole formed by the phenyl rings of the P1 and P2 phosphines. The short contacts observed between the C31–C36 phenyl ring of P1 and the ethanol molecule are: $\text{C32}\cdots\text{C56}^{\text{i}}$ 3.85 (5), $\text{C33}\cdots\text{C56}^{\text{i}}$ 3.63 (6) and $\text{C34}\cdots\text{C56}^{\text{i}}$ 3.74 (7) Å [symmetry code: (i) $2-x$, $1-y$, $-z$].

Experimental

$[\text{Et}_4\text{N}]_2[\text{WSe}_4]$ and $\text{Ag(PPh}_3)_3\text{Br}$ in a 1:2.5 molar ratio were slowly stirred in CH_2Cl_2 solvent for 30 min at room temperature. The red filtrate was covered with a layer of EtOH and left in a refrigerator for a period of one week. Red crystals of the title compound were thus obtained and washed with ethanol and diethyl ether.

Crystal data

$[\text{Ag}_3\text{WBrSe}_4(\text{C}_{18}\text{H}_{15}\text{P})_3]\cdot\text{C}_2\text{H}_6\text{O}$
$M_r = 1736.09$
Triclinic
$P\bar{1}$
$a = 12.336\,(1)$ Å
$b = 13.447\,(1)$ Å
$c = 20.024\,(1)$ Å
$\alpha = 75.44\,(1)°$
$\beta = 88.71\,(1)°$
$\gamma = 63.80\,(1)°$
$V = 2869.7\,(2)$ Å^3
$Z = 2$
$D_x = 2.009$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7012 reflections
$\theta = 2.95$–$33.23°$
$\mu = 6.360$ mm^{-1}
$T = 293\,(2)$ K
Block
0.52 × 0.36 × 0.32 mm
Red

Data collection

Siemens SMART CCD area-detector diffractometer

10 443 reflections with $I > 2\sigma(I)$

ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.064$, $T_{max} = 0.131$
18 940 measured reflections
12 806 independent reflections

$R_{int} = 0.025$
$\theta_{max} = 27.5°$
$h = -15 \rightarrow 16$
$k = -16 \rightarrow 17$
$l = 0 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.107$
$S = 1.038$
12 806 reflections
622 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0410P)^2 + 8.4051P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.346$ e Å^{-3}
$\Delta\rho_{min} = -2.128$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

W1—Se4	2.263 (1)	Ag1—Se1	2.640 (1)
W1—Se1	2.370 (1)	Ag1—Br1	2.901 (1)
W1—Se3	2.382 (1)	Ag2—Se3	2.658 (1)
W1—Se2	2.383 (1)	Ag2—Se1	2.679 (1)
W1—Ag3	3.001 (1)	Ag2—Br1	2.979 (1)
W1—Ag1	3.007 (1)	Ag3—Se3	2.638 (1)
W1—Ag2	3.033 (1)	Ag3—Se2	2.647 (1)
Ag1—Se2	2.625 (1)	Ag3—Br1	2.963 (1)
Se4—W1—Se1	107.20 (3)	Se2—Ag1—Br1	101.59 (3)
Se4—W1—Se3	106.95 (3)	Se1—Ag1—Br1	103.34 (3)
Se1—W1—Se3	111.66 (2)	Se3—Ag2—Br1	102.80 (3)
Se4—W1—Se2	107.70 (3)	Sc1—Ag2—Br1	100.38 (3)
Se1—W1—Se2	111.20 (2)	Se3—Ag3—Br1	103.72 (3)
Se3—W1—Se2	111.84 (2)	Sc2—Ag3—Br1	99.49 (3)

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Coverage of the unique set was over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analyzing the duplicate reflections; it was found to be negligible.

Data collection: *SMART* (Siemens, 1996*a*). Cell refinement: *SAINT* (Siemens, 1996*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1390). Services for accessing these data are described at the back of the journal.

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Dichloro{2-[(η^5-cyclopentadienyl)phenylmethyl]phenolato-*O*}titanium

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Abstract

The title compound, $[TiCl_2(C_{18}H_{14}O)]$, with a chiral C atom, crystallizes as a racemate. The Ti—O bond length is 1.794 (3) Å. The plane of the cyclopentadienyl ring forms dihedral angles of 68.8 (7) and 79.2 (6)° with the two phenyl rings.