Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Tris[diphenyl(2-pyridyl)phosphine]-μ_3-iodo-tri-μ_3-sulfido-sulfidotrisilver-tungsten dichloromethane hemisolvate

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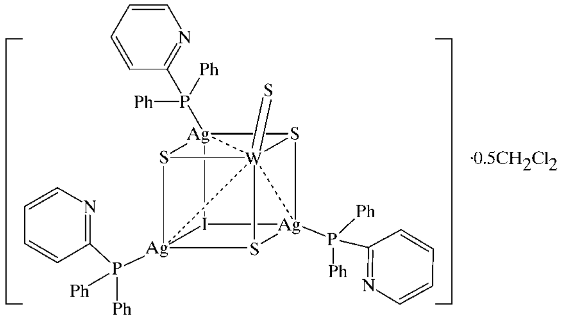
Received 7 July 2003
Accepted 8 August 2003
Online 16 September 2003

The title compound, $[Ag_3WIS_4(C_{17}H_{14}NP)_3]\cdot 0.5CH_2Cl_2$, is a cubane-type heterometallic cluster containing diphenyl(2-pyridyl)phosphine (Ph_2PPy). The pyridyl group of Ph_2PPy remains uncoordinated, so the Ph_2PPy ligand is monodentate and coordinates to one Ag atom. The W atom and three Ag atoms form a distorted tetrahedral geometry, capped by one I atom and three S atoms.

Comment

During the past two decades, many surprising results have been generated in the course of investigations of cluster complexes. Transition metal clusters, in particular, are appealing in coordination chemistry because of their intriguing structural diversity (Gade, 2000; Johnson & Raymond, 2001) and their relevance as industrial catalysts (Chandler *et al.*, 2001), non-linear optical materials (Zhang *et al.*, 2000) and models for cluster sites in proteins (Davies *et al.*, 2001). There are many kinds of sulfur-bridged heterometallic cluster compounds containing simple ligands, such as halogen, CO and PPh_3, with intact or altered $[MS_4]^{2-}$ (M = Mo or W) units as essential structures. However, a cubane-type heterometallic cluster containing diphenyl(2-pyridyl)phosphine (Ph_2PPy) has not been reported. We have synthesized the title compound, $WS_4IAg_3(Ph_2PPy)_3\cdot 0.5CH_2Cl_2$, (I), and its structure is presented here.

In the cubane-type cluster moiety of (I), one W atom and three Ag atoms form a slightly distorted tetrahedral geometry, with W—Ag bond lengths of 2.9718 (7)–3.0324 (9) Å and Ag—W—Ag angles of 68.08 (2)–74.00 (2)° (Fig. 1 and Table 1). Three faces of this tetrahedron are capped by three μ_3-S ligands and the fourth face is capped by one μ_3-I ligand. Disregarding the metal–metal interactions, the W atom has an essentially tetrahedral geometry, with three μ_3-S ligands and one terminal S ligand, the S—W—S bond angles being 107.26 (7)–111.19 (6)°. The bond distances between the μ_3-S atoms and the W atom are 2.2314 (14)–2.2419 (15) Å. The S1═W1 bond distance is similar to reported values, *e.g.* 2.102 (2) Å in $WS_4BrCu_3(PPh_3)_3$ (Lang *et al.*, 1993) and 2.15 (1) Å in $WS_4IAg_3(AsPh_3)_3$ (Sakane *et al.*, 1996). Each Ag atom also has a slightly distorted tetrahedral geometry, being surrounded by two μ_3-S ligands, one μ_3-I ligand and one P atom. The Ph_2PPy ligand is monodentate and the pyridyl moiety of Ph_2PPy remains uncoordinated. The P—Ag—S, P—Ag—I and S—Ag—I bond angles are in the ranges 122.29 (6)–128.42 (5), 103.24 (5)–108.87 (5) and 98.45 (4)–105.05 (4)°, respectively. The Ag—I bond lengths [3.0160 (10)–3.0870 (11) Å] are longer than the Ag—S bond lengths [2.5272 (17)–2.6450 (17) Å], whereas the Ag—I—Ag angles



(I)

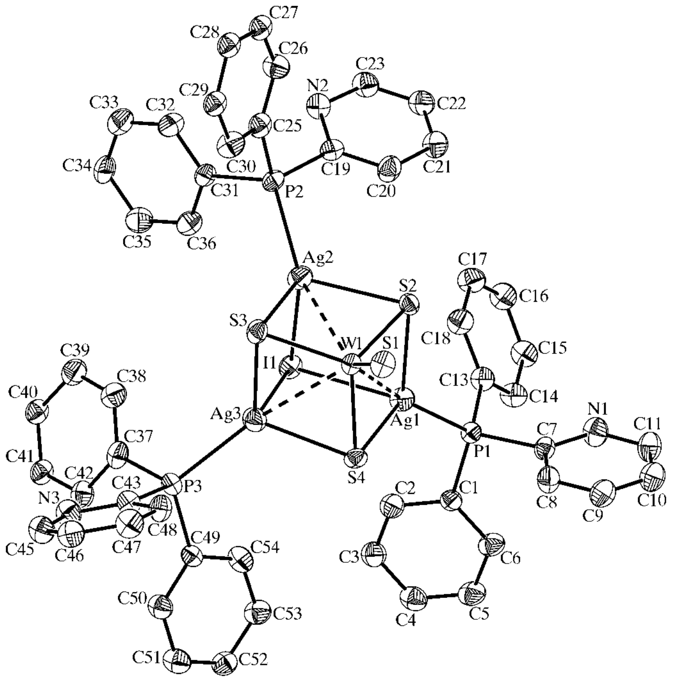


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. The H atoms and the solvent molecule have been omitted for clarity.

DOI: 10.1107/S0108270103017645

[67.845 (18)–72.55 (2)°] are much smaller than the Ag—S—Ag angles [81.61 (5)–87.91 (5)°]. These geometric properties around the Ag atoms correspond well to those in $WS_4IAg_3(PPh_3)_3$ (Jin *et al.*, 1999).

The dichloromethane solvent molecule shows orientational disorder. The C atom has two possible positions, *viz*. C55 and C55^i [symmetry code: (i) $1 - x, -y, 2 - z$], each having an occupancy of 50%, and atoms Cl1 and Cl1^i are shared by the two orientations. Evidently, there are weak interactions between the S atoms and the phenyl rings (Table 2).

Experimental

The synthesis of (I) was performed in dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. $(NH_4)_2WS_4$ was prepared in our laboratory, and the other reagents were commercially available and were used without further purification. $(NH_4)_2WS_4$ (0.035 g, 0.1 mmol) and AgI (0.070 g, 0.3 mmol) were mixed and ground for 30 min. The mixture was then placed in a tinfoil-wrapped reaction tube with Ph_2PPy (0.079 g, 0.3 mmol), and CH_2Cl_2 (20 ml) was added. The resulting mixture was stirred for 24 h at room temperature under a purified nitrogen atmosphere. After filtration, the clear yellow solution obtained was layered with ^{i}PrOH (50 ml), and yellow crystals of (I) were obtained at room temperature after several days. Analysis calculated for $C_{51.5}H_{43}Ag_3ClIN_3P_3S_4W$: C 38.85, H 2.72, N 2.64%; found: C 38.79, H 2.68, N 2.66%.

Crystal data

$[Ag_3WIS_4(C_{17}H_{14}NP)_3]\cdot 0.5CH_2Cl_2$
$M_r = 1594.85$
Triclinic, $P\overline{1}$
$a = 12.045$ (3) Å
$b = 13.367$ (4) Å
$c = 19.886$ (5) Å
$\alpha = 74.86$ (1)°
$\beta = 87.99$ (1)°
$\gamma = 64.23$ (1)°
$V = 2771.9$ (13) Å^3

$Z = 2$
$D_x = 1.911$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6969 reflections
$\theta = 2.3$–27.2°
$\mu = 3.99$ mm^{-1}
$T = 293$ (2) K
Brick, yellow
0.3 × 0.2 × 0.2 mm

Data collection

Bruker SMART Apex CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.411$, $T_{max} = 0.452$
13 773 measured reflections

9582 independent reflections
8034 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 25.0°$
$h = -14 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -23 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.091$
$S = 1.04$
9582 reflections
613 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 1.55P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.67$ e Å^{-3}
$\Delta\rho_{min} = -1.63$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Ag1—P1	2.3856 (15)	Ag2—Ag3	3.3685 (10)
Ag1—S4	2.5274 (15)	Ag3—P3	2.3885 (15)
Ag1—S2	2.5609 (16)	Ag3—S3	2.5777 (17)
Ag1—W1	2.9718 (7)	Ag3—S4	2.5839 (18)
Ag1—I1	3.0870 (11)	Ag3—W1	2.9846 (9)
Ag2—P2	2.4072 (17)	Ag3—I1	3.0160 (10)
Ag2—S3	2.5772 (17)	S1—W1	2.1102 (17)
Ag2—S2	2.6450 (17)	S2—W1	2.2314 (14)
Ag2—I1	3.0201 (10)	S3—W1	2.2380 (17)
Ag2—W1	3.0324 (9)	S4—W1	2.2419 (15)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···S4^{ii}	0.93	2.78	3.706 (7)	172
C52—H52···S4^{iii}	0.93	2.92	3.810 (7)	160
C41—H41···I1^{iv}	0.93	3.15	4.010 (6)	155
C36—H36···I1	0.93	3.04	3.962 (7)	174

Symmetry codes: (ii) $1 + x, y, z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $2 - x, -y, 1 - z$.

All H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and allowed for as riding, with isotropic displacement parameters of $1.2U_{eq}$(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China (grant Nos. 20171020, 10104007 and 90101028) and the Nanjing University Talent Development Foundation (grant No. 0205005122). The authors thank Professor Yong-Jiang Liu for the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1133). Services for accessing these data are described at the back of the journal.

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