

5958 measured reflections
4849 independent reflections

2 standard reflections
every 98 reflections
intensity decay: <2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.147$
 $S = 1.077$
4849 reflections
408 parameters
H atoms treated by a
mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 1.148P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.01$
 $\Delta\rho_{\max} = 0.66 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected bond lengths (Å)

Ni1—N1B	2.113 (3)	Ni1—N1A	2.129 (3)
Ni1—N1E	2.118 (3)	Ni1—N1C	2.134 (3)
Ni1—N1F	2.121 (3)	Ni1—N1D	2.139 (4)

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

D—H...A	D—H	H...A	D...A	D—H...A
N2A—H2AA...O5 ⁱ	0.88 (5)	1.82 (5)	2.690 (6)	172 (4)
N2B—H2BA...O1 ⁱⁱ	0.85 (5)	1.93 (6)	2.749 (6)	163 (4)
N2C—H2CA...O4 ⁱⁱⁱ	0.87 (4)	1.87 (3)	2.723 (5)	168 (3)
N2D—H2DA...O1 ^{iv}	0.83 (4)	1.99 (4)	2.812 (5)	169 (4)
N2E—H2EA...O4 ^v	0.88 (5)	1.93 (5)	2.768 (6)	160 (4)
N2F—H2FA...O2	0.86 (4)	1.98 (5)	2.801 (5)	163 (4)

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

H atoms were initially idealized and those relevant for the description of the hydrogen bonding were subsequently refined with a unique refinable N—H distance [final value 0.85 (2) Å], while those attached to carbon were allowed to ride. The ethanol solvate molecule could only be worked out with restrained C—O and C—C distances, and a fractional occupation factor which refined to a final value of 0.52 (4). Only the five H atoms attached to carbon were included; the hydroxy H atom was not found and was thus disregarded. During refinement, the terminal methyl group was allowed to rotate. The rather large displacement parameters exhibited by the solvate and the concentration of the largest residual electron-density peaks around it (range 0.67–0.35 e Å⁻³) suggested some kind of disorder. Outside this zone, the final ΔF map showed no relevant features, with extreme values below 0.35 e Å⁻³.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL97*, *PARST* (Nardelli, 1983) and *CSD* (Allen & Kennard, 1993).

This work was supported by the Universidad de Buenos Aires and by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), grant PMT-PICT0051. MP is a member of CONICET.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1429). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 860–863

μ_3 -Iodo-2:3:4 κ^3 I-tri- μ_3 -sulfido-1:2:3 κ^3 S; 1:2:4 κ^3 S;1:3:4 κ^3 S-sulfido-1 κ S-tris- (triphenylphosphine)-2 κ P,3 κ P,4 κ P- trisilvertungsten-triphenylphosphine sulfide (1/1)

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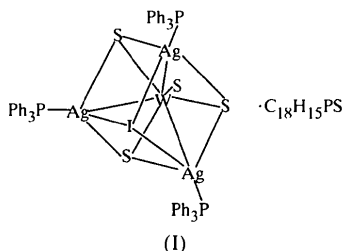
(Received 21 July 1998; accepted 18 February 1999)

Abstract

The crystal structure of [Ag₃WS₄I{P(C₆H₅)₃}₃]₃·SP(C₆H₅)₃ comprises discrete neutral [Ag₃WS₄I{P(C₆H₅)₃}₃] and SP(C₆H₅)₃ molecules. The [Ag₃WS₄I{P(C₆H₅)₃}₃] skeleton is cubane-like and the phosphorus environment of the SP(C₆H₅)₃ molecule is a distorted tetrahedron.

Comment

Mo(W)—Cu(Ag)—S clusters have been studied intensively and extensively because of their biological functions (McLendon & Martell, 1976), and have been found recently to exhibit a strong non-linear optical (NLO) effect (Hou *et al.*, 1994; Chen *et al.*, 1995; Shi & Xin, 1995). Some W—Ag—S clusters are comparable with or even superior to C_{60} , one of the best NLO materials (Hou *et al.*, 1996). In this paper, we report the structure of a new W—Ag—S cluster, *i.e.* $[Ag_3WS_4I\{P(C_6H_5)_3\}_3] \cdot SP(C_6H_5)_3$ (I).



The title compound is composed of discrete $[Ag_3WS_4I\{P(C_6H_5)_3\}_3]$ and $SP(C_6H_5)_3$ molecules (Fig. 1). The skeleton of the cubane-like tetranuclear cluster consists of one W, one μ_3 -I, three μ_3 -S and three Ag atoms. The cluster has crystallographically imposed C_{3v} symmetry, the W, I and S1 atoms being located on the

C_3 axis. Three rhombic WS_2Ag planes, together with SAg_2I , form the cubane-like core. The W atom is bound to three μ_3 -S atoms and one terminal S atom, basically retaining the tetrahedral geometry of the $[WS_4]^{2-}$ anion. Each Ag atom is bound to three μ_3 -S atoms, one μ_3 -I atom and one P atom of $P(C_6H_5)_3$. The $SP(C_6H_5)_3$ moiety, in which the P atom is positioned at the center of the distorted tetrahedral $SP(C_6H_5)_3$ array, has the same symmetry as the neutral cluster, with the C_3 axis passing through the P2 and S3 atoms.

In the three WS_2Ag planes, the sets of μ_3 -S—W— μ_3 -S [$110.02(5)^\circ$] and S—Ag—S [$89.62(9)^\circ$] angles are necessarily equal, while the W—S—Ag angles range from $77.19(5)$ to $78.62(5)^\circ$. In the three SAg_2I planes, the sets of three Ag—I—Ag [$70.56(3)^\circ$] and Ag—S—Ag [$82.97(6)^\circ$] angles are also necessarily equal, while the S—Ag—I angles vary in the range of about 1.6° [$101.75(5)$ – $103.39(5)^\circ$]. Likewise, the lengths of the three W— μ_3 -S bonds and the Ag—I bonds are necessarily identical, while the lengths of six Ag—S bonds are divided into two sets, 2.638(2) and 2.571(2) Å. The W—S_t (S_t represents terminal S) distance of 2.112(4) Å, which is significantly shorter than those of three μ_3 -S—W bonds [2.241(2) Å], reflects the obvious double bond between the S_t and W atoms.

It is interesting that the $SP(C_6H_5)_3$ molecule exists between W—Ag—S molecules in the title compound, which is similar to the arrangement in $[Ag_3WS_4Br-$

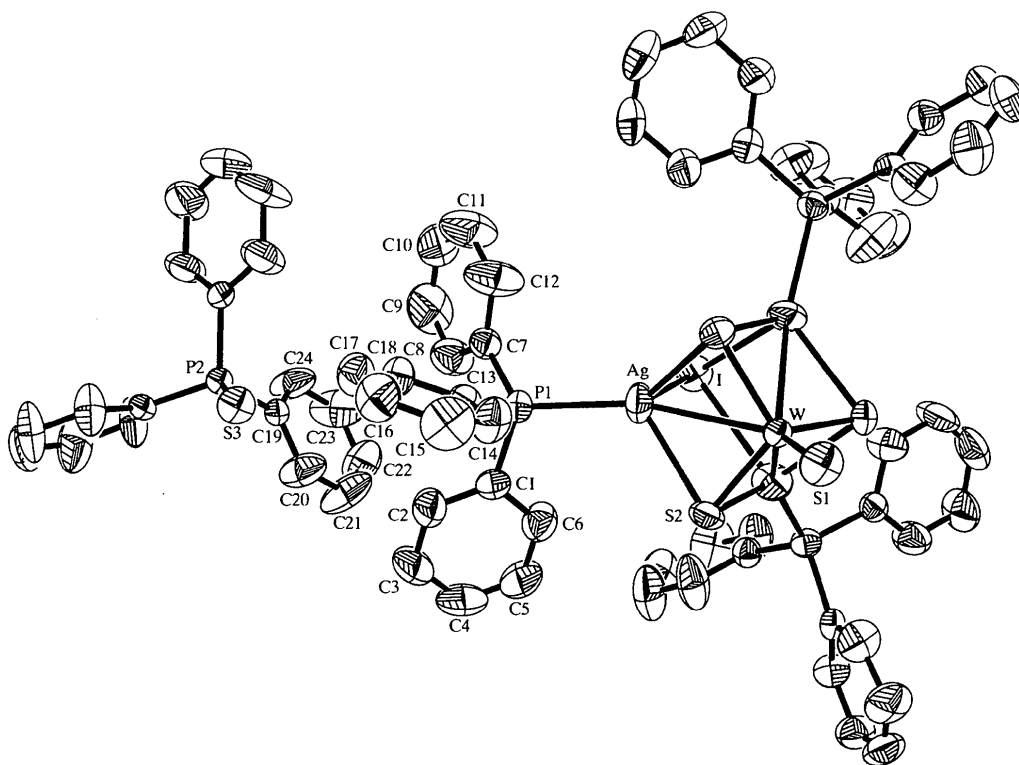


Fig. 1. View of the title complex, with displacement ellipsoids shown at the 30% probability level.

{P(C₆H₅)₃]₃·SP(C₆H₅)₃ (Lang *et al.*, 1993). SP(C₆H₅)₃ may be produced by the reaction of P(C₆H₅)₃ with S of (NH₄)₂WS₄ in the presence of oxidizer AgI, while Ag¹ is reduced to Ag⁰.

Experimental

AgI, (NH₄)₂WS₄ and P(C₆H₅)₃ in a molar ratio of 2:1:2 were ground well and heated together at 373 K for 10 h. The product mixture was extracted with DMF, and ¹PrOH was added to the upper layer of the solution. Orange columnar crystals were obtained after several days.

Crystal data

[Ag ₃ WS ₄ I(C ₁₈ H ₁₅ P) ₃]. C ₁₈ H ₁₅ PS	Mo K α radiation
$M_r = 1843.74$	$\lambda = 0.71073 \text{ \AA}$
Trigonal	Cell parameters from 32 reflections
$R3c$	$\theta = 2.48\text{--}17.49^\circ$
$a = 16.4555(9) \text{ \AA}$	$\mu = 3.230 \text{ mm}^{-1}$
$c = 44.178(5) \text{ \AA}$	$T = 296(2) \text{ K}$
$V = 10360.0(13) \text{ \AA}^3$	Irregular
$Z = 6$	$0.55 \times 0.50 \times 0.33 \text{ mm}$
$D_x = 1.773 \text{ Mg m}^{-3}$	Orange
D_m not measured	

Data collection

Siemens P4 diffractometer	$R_{\text{int}} = 0.025$
ω scans	$\theta_{\text{max}} = 28.21^\circ$
Absorption correction:	$h = -18 \rightarrow 0$
empirical (Kopfmann & Huber, 1968)	$k = 0 \rightarrow 21$
$T_{\text{min}} = 0.192$, $T_{\text{max}} = 0.275$	$l = -1 \rightarrow 57$
5757 measured reflections	3 standard reflections
2755 independent reflections	every 97 reflections
2032 reflections with $I > 2\sigma(I)$	intensity decay: 2.49%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.003$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$\Delta\rho_{\text{max}} = 1.606 \text{ e \AA}^{-3}$
$wR(F^2) = 0.071$	$\Delta\rho_{\text{min}} = -1.542 \text{ e \AA}^{-3}$
$S = 1.007$	Extinction correction: none
2755 reflections	Scattering factors from
259 parameters	<i>International Tables for Crystallography</i> (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

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

$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \cdot a_j$				
	x	y	z	U_{eq}
W	1/3	2/3	0.170990(7)	0.03170(11)
I	1/3	2/3	0.27393(2)	0.0539(2)
Ag	0.27196(4)	0.52718(4)	0.22354(2)	0.0614(2)
S1	1/3	2/3	0.12317(9)	0.0608(10)
S2	0.18473(11)	0.58652(12)	0.18743(5)	0.0459(4)
S3	0	0	0.28879(8)	0.0526(8)
P1	0.18616(13)	0.37474(12)	0.24712(4)	0.0392(4)
P2	0	0	0.33312(7)	0.0341(6)

C1	0.0669(5)	0.3449(5)	0.2562(2)	0.042(2)
C2	-0.0046(7)	0.2553(6)	0.2611(3)	0.071(3)
C3	-0.0950(6)	0.2347(7)	0.2680(3)	0.086(4)
C4	-0.1132(7)	0.3081(9)	0.2703(3)	0.082(3)
C5	-0.0470(7)	0.3939(8)	0.2659(3)	0.080(3)
C6	0.0446(6)	0.4152(6)	0.2585(2)	0.065(2)
C7	0.2350(5)	0.3587(5)	0.2825(2)	0.042(2)
C8	0.1878(7)	0.3309(9)	0.3091(3)	0.073(3)
C9	0.2287(9)	0.3195(9)	0.3349(3)	0.099(4)
C10	0.3184(8)	0.3327(8)	0.3336(3)	0.087(3)
C11	0.3642(8)	0.3565(10)	0.3066(3)	0.105(4)
C12	0.3230(7)	0.3716(9)	0.2815(3)	0.092(4)
C13	0.1728(5)	0.2791(5)	0.2236(2)	0.0367(15)
C14	0.1738(8)	0.2881(7)	0.1927(2)	0.065(2)
C15	0.1527(8)	0.2133(8)	0.1739(2)	0.082(3)
C16	0.1395(7)	0.1309(7)	0.1857(2)	0.070(3)
C17	0.1422(6)	0.1222(6)	0.2154(2)	0.065(2)
C18	0.1564(6)	0.1943(5)	0.2347(2)	0.053(2)
C19	-0.0158(5)	0.0916(5)	0.3493(2)	0.0376(15)
C20	-0.0708(8)	0.1186(8)	0.3336(3)	0.079(3)
C21	-0.0817(10)	0.1905(9)	0.3448(3)	0.099(4)
C22	-0.0427(8)	0.2339(7)	0.3706(3)	0.083(3)
C23	0.0101(8)	0.2078(8)	0.3863(3)	0.105(4)
C24	0.0220(7)	0.1332(8)	0.3760(3)	0.080(3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

W—S1	2.112(4)	Ag—P1	2.414(2)
W—S2	2.241(2)	Ag—S2 ¹	2.571(2)
W—Ag	3.0595(7)	Ag—S2	2.638(2)
I—Ag	2.9876(11)		
S2 ¹¹ —W—S2	110.02(5)	S2—Ag—W	45.58(4)
Ag ¹¹ —I—Ag	70.56(3)	I—Ag—W	97.53(2)
S2 ¹¹ —Ag—S2	89.62(9)	W—S2—Ag ¹¹	78.62(5)
S2 ¹¹ —Ag—I	103.39(5)	W—S2—Ag	77.19(5)
S2—Ag—I	101.75(5)	Ag ¹¹ —S2—Ag	82.97(6)
P1—Ag—W	155.37(6)	C19 ¹¹¹ —P2—C19 ¹¹	105.3(3)
S2 ¹¹ —Ag—W	45.89(4)	C19 ¹¹¹ —P2—S3	113.4(3)

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

H atoms were placed at calculated positions with a C—H distance of 0.93 \AA . The maximum ($\frac{1}{3}, \frac{2}{3}, 0.1490$) and minimum (0, 0, 0.0223) residual peaks in the final difference map were 0.97 and 0.79 \AA , respectively, from the W atom.

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: SHELXTL (Sheldrick, 1995). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP in SHELXTL. Software used to prepare material for publication: SHELXL93.

This research was supported by grants from the Beijing Municipal Bureau of Scientific & Technological Cadre, and the Beijing Science and Technology Commission of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1221). Services for accessing these data are described at the back of the journal.

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Comment

Titanium tetrahalides are strong Lewis acids and form Lewis acid–Lewis base adducts with electron-pair donors (Emeléus & Rao, 1958; Rao, 1960; Mazo *et al.*, 1987; Hensen, Lemke & Näther, 1997; Hensen, Pickel *et al.*, 1997). Thus, titanium tetrachloride forms complexes with 3,4-dimethylpyridine (3,4-dimepy), 4-methylpyridine (4-mepy) and *N*-methylimidazole (NMI) in a 1:2 ratio. The structures of (I), (II) and (III) have been determined as part of our studies on the structures and properties of adducts of titanium tetrahalides and tertiary amines.

Acta Cryst. (1999). **C55**, 863–867

Addition compounds of titanium tetrachloride with aromatic nitrogen bases

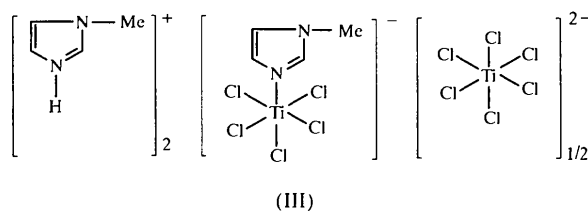
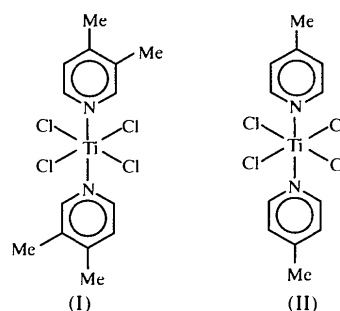
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(Received 8 October 1998; accepted 11 January 1999)

Abstract

Three reaction products of an addition reaction of titanium tetrachloride with aromatic nitrogen bases are presented. *trans*-Tetrachlorobis(3,4-dimethylpyridine)-titanium, [TiCl₄(C₇H₉N)₂], (I), and *trans*-tetrachlorobis(4-methylpyridine)titanium, [TiCl₄(C₆H₇N)₂], (II), are both neutral complexes in which the central Ti atom is bonded to four Cl and two N atoms of two 3,4-dimethylpyridine and 4-methylpyridine ligands, respectively, resulting in a slightly distorted octahedral environment around the Ti atom. The methylpyridine ligands occupy axial positions, with the four chloro ligands in the equatorial plane. The ionic structure of bis(1-methylimidazolium) hexachlorotitanate(IV) pentachloro(*N*-methylimidazole-*N*³)-titanate(IV), (C₄H₇N₂)₂[TiCl₅(C₄H₆N₂)] [TiCl₆]_{0.5}, (III), consists of a pentachloro(*N*-methylimidazole-*N*³)titanate anion and half a [TiCl₆]²⁻ complex anion, in both of which the Ti atom appears in a nearly perfect octahedral coordination sphere with two *N*-methylimidazolium cations as counter-ions.



Compounds (I) and (II) belong to the symmetry point group C_{2h} , with the Ti atom on a special position of site symmetry $2/m$ and the pyridine moiety located on a crystallographic mirror plane. Only the Cl atoms and two H atoms of each methyl group occupy a general position. The Ti centre appears in a nearly ideal octahedral environment, where the two methylpyridine ligands occupy axial positions and the four chloro ligands lie in the equatorial plane. There are only minor deviations from perfect octahedral coordination. The planes of the methylpyridine rings almost exactly bisect the Cl–Ti–Cl angle. A least-squares fit of (I) and (II), fitting all non-H atoms excluding the methyl groups (r.m.s. deviation of 0.014 Å), shows that these two structures do not show any significant difference. The only comparable structure to (I) and (II) retrieved from the Cambridge Structural Database (Version 5.12 of April 1998; Allen & Kennard, 1993), is TiCl₄(py)₂ (Mazo *et al.*, 1987). The geometrical parameters of all three structures are in excellent agreement. Thus, the conclusion can be drawn that the methyl groups in (I) and (II) have no influence on the geometry of the rest of the molecule.