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Synthesis and Structure of [(μ_3-I)(μ_3-WSe$_4$){Ag(PMe$_2$Ph)}$_3$]

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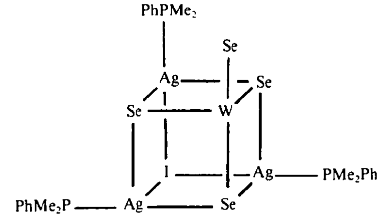
Abstract

Reaction of $[NPr_4]_2[WSe_4]$ with $[Ag(PMe_3)I]_4$ in CH_3CN followed by addition of PMe_2Ph affords the title compound, (μ_3-iodo)(μ_3-tetraselenidotungstide)tris(dimethylphenylphosphinesilver), [(μ_3-I)(μ_3-WSe$_4$){Ag-$C_8H_{11}P$)}$_3$] [systematic name: tris(dimethylphenylphosphine)-2κP,3κP,4κP-μ_3-iodo-2:3:4$\kappa^3 I$-tri-μ_3-selenido-1:2:3$\kappa^3 Se$;1:2:4$\kappa^3 Se$;1:3:4$\kappa^3 Se$-selenido-1κSe-trisilvertungsten], a neutral cubane cluster. The compound was characterized by a single-crystal X-ray structure determination. The molecule has crystallographically imposed symmetry 3, with the W, the I and one Se atom located on the threefold axis. The structure can be described either as three $Ag(PMe_2Ph)^+$ fragments bridged by one μ_3-WSe_4^{2-} ligand and one μ_3-I^- ligand, or as a WAg_3Se_3I cubane cluster core with an Se^{2-} ligand bound to W and a PMe_2Ph ligand bound to each Ag.

Comment

The coordination chemistry of MS_4^{2-} (M = Mo, W) has been the subject of intense investigation, primarily because of its relevance in modeling certain molybdoenzymes (Coucouvanis, 1991; Holm & Berg, 1986) and in copper-molybdenum antagonism (Sarkar & Mishra, 1984). However, the related chemistry of MSe_4^{2-} (M = Mo, W) had not been investigated until recently (Ansari & Ibers, 1990). Among the few mixed-metal selenides that have been structurally characterized are $[Ni(WSe_4)_2^{2-}]$ and $[Ni(Se_2)(WSe_4)]^{2-}$ (Ansari, Chau, Mahler & Ibers, 1989), $[(PPh_3)_3Ag_2(WSe_4)]$ (Müller *et al.*, 1989), and the cubanes (μ_3-Cl)(μ_3-WSe$_4$)[CuL]$_3$ and (μ_3-Cl)(μ_3-MoOSe$_3$)[CuL]$_3$ (Christuk, Ansari & Ibers, 1992; Müller, Wienböker & Penk, 1989). Here we summarize the synthesis and report the structural details of [(μ_3-I)(μ_3-WSe$_4$){Ag(PMe$_2$Ph)}$_3$], (I).



(I)

The title compound (I) is similar to the Ag/Mo/S cubane [(μ_3-Cl)(μ_3-WS$_4$){Ag(PPh$_3$)}$_3$] (Zhu, Wu, Du, Wu & Lu, 1992) and the Cu/W/Se cubane [(μ_3-Cl)(μ_3-WSe$_4$){Cu(PPh$_3$)}$_3$] (Christuk, Ansari & Ibers, 1992). In each structure the Mo or W atom is tetrahedrally coordinated by one apical and three bridging chalcogenides and the Ag or Cu atom is tetrahedrally coordinated by two bridging chalcogenides, one halide and one phosphine. Although these structures may be discussed in terms of cubanes, they may also be viewed as comprising three $Ag(PMe_2Ph)^+$ units bridged by a (μ_3-I)$^-$ ligand and a (μ_3-WSe$_4$)$^{2-}$ ligand.

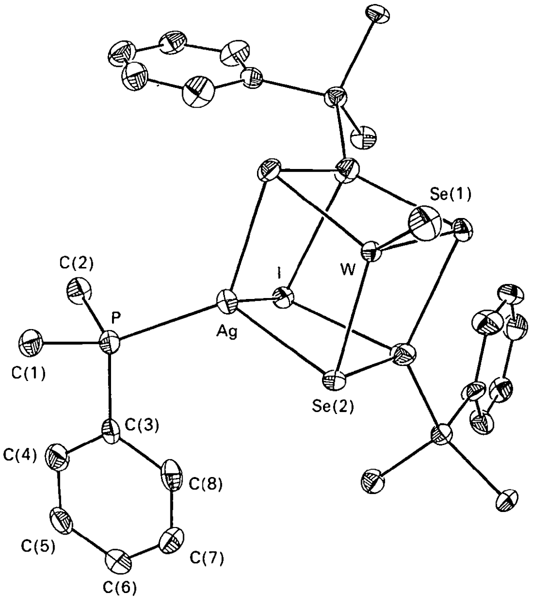


Fig. 1. A view of the title compound with 50% probability displacement ellipsoids shown. H atoms have been omitted.

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The title compound possesses crystallographically imposed symmetry 3. The W—Se(bridging) distance, 2.364 (1) Å, is greater than the W—Se(apical) distance, 2.262 (2) Å. The Ag—I distance of 3.109 (1) Å is normal and the Ag···W distance of 2.976 (1) Å is too long to be considered a metal-metal bond. The W—Se(apical) distance of 2.262 (2) Å is slightly longer than the analogous distance in the copper cubane [2.201(3) Å; Christuk, Ansari & Ibers, 1992], but shorter than those observed for the free WSe_4^{2-} anion [2.307 (3)-2.310 (10) Å] (Müller, Wienböker & Penk, 1989). A view of the structure is presented in Fig. 1.

Experimental

Equimolar amounts of $[NPr_4]_2[WSe_4]$ and $[Ag(PMe_3)I]_4$ were warmed in anhydrous CH_3CN at 343 K for 10 min. PMe_2Ph and fresh CH_3CN were added to the resultant precipitate to afford a clear orange solution of the title compound. Crystals were grown as red blocks by storing the solution in a refrigerator overnight. These crystals were washed with 1-propanol and diethyl ether.

Crystal data

$[Ag_3WSe_4I(C_8H_{11}P)_3]$
$M_r = 1364.61$
Trigonal
$R\bar{3}c$
$a = 13.488\ (6)$ Å
$c = 65.499\ (26)$ Å
$V = 10319.5\ (77)$ Å^3
$Z = 12$
$D_x = 2.635$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 18.58$-$22.93°$
$\mu = 10.3$ mm^{-1}
$T = 108\ (2)$ K
Rectangular block
0.48 × 0.37 × 0.23 mm
Red

Data collection

Picker diffractometer
θ-2θ scans
Absorption correction: analytical
$T_{min} = 0.027$, $T_{max} = 0.149$
6479 measured reflections
3298 independent reflections
2493 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.093$
$\theta_{max} = 30.07°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = -92 \rightarrow 92$
6 standard reflections monitored every 100 reflections
intensity variation: 7%

Refinement

Refinement on F^2
$R(F) = 0.050$
$wR(F^2) = 0.121$
$S = 1.47$
3296 reflections
111 parameters
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = -0.033$

$\Delta\rho_{max} = 1.90$ e Å^{-3}
$\Delta\rho_{min} = -2.58$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
W	1/3	2/3	0.353965 (8)	0.01500 (13)
Se1	1/3	2/3	0.38850 (3)	0.0300 (3)
Se2	0.27453 (7)	0.47749 (6)	0.343452 (13)	0.0195 (2)
I	1/3	2/3	0.286546 (14)	0.0197 (2)
Ag	0.45515 (5)	0.61388 (6)	0.321658 (11)	0.0236 (2)
P	0.5654 (2)	0.5628 (2)	0.30002 (3)	0.0202 (4)
C1	0.6799 (7)	0.5448 (7)	0.31083 (14)	0.023 (2)
C2	0.6342 (7)	0.6654 (7)	0.28007 (13)	0.024 (2)
C3	0.4788 (7)	0.4319 (7)	0.28633 (15)	0.023 (2)
C4	0.3625 (8)	0.3599 (9)	0.2921 (2)	0.034 (2)
C5	0.2979 (7)	0.2610 (8)	0.2821 (2)	0.031 (2)
C6	0.3376 (8)	0.2321 (8)	0.2652 (2)	0.032 (2)
C7	0.4489 (7)	0.3015 (7)	0.25880 (15)	0.027 (2)
C8	0.5181 (8)	0.3987 (8)	0.2697 (2)	0.030 (2)

Table 2. *Selected geometric parameters* (Å, °)

W—Se1	2.262 (2)	Se2—Ag	2.622 (1)
W—Se2	2.364 (1)	I—Ag	3.109 (1)
W···Ag	2.976 (1)	Ag—P	2.391 (2)
Se2—Ag^{i}	2.593 (1)		
Se1—W—Se2	106.93 (3)	P—Ag—Se2^{ii}	128.95 (6)
Se2^{ii}—W—Se2	111.89 (2)	P—Ag—Se2	127.89 (6)
W—Se2—Ag^{i}	73.62 (3)	Se2^{ii}—Ag—Se2	97.40 (5)
W—Se2—Ag	73.07 (3)	P—Ag—I	95.92 (7)
Ag^{i}—Se2—Ag	88.03 (4)	Se2^{ii}—Ag—I	99.36 (4)
Ag^{i}—I—Ag	71.29 (4)	Se2—Ag—I	98.71 (4)

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

A crystal was mounted on a glass fiber and transferred to the cold stream of a CAD-4 diffractometer for unit-cell determination, then to a Picker diffractometer for data collection. Cell refinement and data reduction were performed by the local programs *CELREF* and *NUPICK*, respectively. Intensity data were processed and corrected for absorption and crystal decay with the use of the local programs *NUPICK* and *AGNOST*. The structure was solved using *SHELXTL/PC* (Sheldrick, 1990) and refined using *SHELXL92* (Sheldrick, 1993). The positions of all non-H atoms were determined by direct methods with the *SHELXTL/PC* software package. Phenyl H atoms were placed in calculated positions and were refined using a riding model. Positions for the methyl H atoms were determined by assuming tetrahedral geometry and selecting a torsion angle corresponding to the maximum difference electron density in the appropriate region; the torsion angles were then refined as additional least-squares parameters. All non-H atoms were refined anisotropically and H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameters of the parent C atoms. No unusual features were observed in the final difference electron-density map. Molecular graphics were produced using *SHELXTL/PC* and the material for publication was prepared using *SHELXL92*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71809 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1076]

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Lithium Bis(tetramethylammonium) Hexanitrocobaltate(III) at 113 and 293 K

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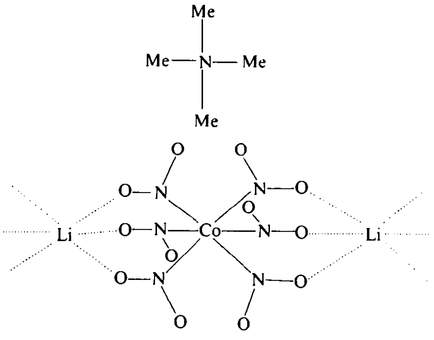
Abstract

The crystal structure of $Li[N(CH_3)_4]_2[Co(NO_2)_6]$ has been determined at 113 and 293 K. The crystals belong to the $P\bar{3}m1$ space group. They are built up of $[Co(NO_2)_6]^{3-}$ octahedra piled along the $\bar{3}$ axes, with the Li^+ ions sandwiched between them at $\frac{1}{2}c$ in an octahedral first coordination sphere involving six symmetry-related O atoms from the nitro groups. Both $[Co(NO_2)_6]^{3-}$ and LiO_6 octahedra exhibit D_{3d} symmetry. On cooling, the unit cell contracts: a 3.21% reduction in volume results from a 1.37% contraction of the *a* edge and a 0.51% contraction of the *c* edge. Bond distances and angles from the two analyses are not significantly different. The two N—O distances of the nitro group differ significantly [1.2421 (5) and 1.2265 (4) Å at 113 K, 1.242 (2) and 1.224 (2) Å at 293 K]. The Co—N bond length of 1.966 (1) Å at 293 K is significantly longer ($\Delta/\sigma = 11.8$) than the corresponding value [1.9516 (7) Å] in $K_{2-0.36}Na_{1+0.36}[Co(NO_2)_6]$, in which the NO_2^- ion shows C_{2v} symmetry, as a consequence of the differing environments of this anion in the two compounds.

Comment

Fig. 1 shows the interaction of the ions in the crystal, (I), while Fig. 2 shows their packing in the unit cell. The octahedral $[Co(NO_2)_6]^{3-}$ anions lie in columns parallel to the $\bar{3}$ axis with the Co atom at the (0,0,0) symmetry centre; adjacent anions are linked by the Li^+ cation at the $(0,0,\frac{1}{2})$ symmetry centre which is thereby surrounded by an octahedron of O1 atoms. The symmetry of these two octahedra is D_{3d}, and the N1···N1 $(y-x, -x, z)$ and O1···O1 $(y-x, -x, z)$ edges have lengths which differ from those of the N1···N1 $(y, y-x, -z)$ and O1···O1 $(x-y, x, 1-z)$ edges, respectively (see Fig. 2 and Table 2).



(I)

Considering the data of Table 2, it appears that there are no significant differences (*i.e.* $>3\sigma$) between corresponding bond lengths and angles at the different temperatures but the Li···O1, O1···O1^{iv} and O2···N2^{i} contacts are significantly shorter at 113 K. The contraction is more pronounced for O2···N2^{i}, in agreement with the fact that the contraction of the *a* unit-cell edge is about 3.4 times larger than that of the *c* edge.

The NO_2^- ion is unsymmetrical (the two N—O distances being significantly different) and lies in a mirror plane which is parallel to the *c* unit-cell edge.

It is interesting to compare the geometry of the complex anion with that of the same anion determined very accurately by Ohba, Toriumi, Sato & Saito (1978) in $K_{2-0.36}Na_{1+0.36}[Co(NO_2)_6]$ at 297 K. In this compound the geometry of the complex anion is T_h (that of the CoN_6 group is O_h). The Co—N distance of 1.9516 (7) Å

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