S2	0.0669 (1)	−0.0341 (1)	0.1316 (2)	0.0290 (6)
N1	−0.0069 (5)	0.0452 (5)	0.2719 (5)	0.039 (2)
C1	−0.0030 (6)	0.0336 (5)	0.1846 (6)	0.028 (2)
C2	0.0443 (7)	−0.0070 (8)	0.3324 (7)	0.053 (4)
C3	−0.0117 (10)	−0.0844 (9)	0.364 (1)	0.089 (5)
C4	−0.0692 (6)	0.1062 (8)	0.3105 (7)	0.048 (3)
C5†	−0.050 (1)	0.137 (1)	0.404 (1)	0.065 (7)
C6†	−0.022 (2)	0.182 (2)	0.338 (2)	0.07 (1)

† Disordered site (see below).

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

Pt1—S1	2.314 (2)	Cu1—Cl1	2.297 (3)
Pt1—S1^{i}	2.314 (2)	Cu1—Cl1^{ii}	2.349 (3)
Pt1—S2	2.309 (2)	Cu1—S1^{iii}	2.336 (3)
Pt1—S2^{i}	2.309 (2)	Cu1—S2	2.426 (3)
S1—Pt1—S1^{i}	180	S1^{iii}—Cu1—S2	106.30 (9)
S1—Pt1—S2	75.60 (8)	Cu1—Cl1—Cu1^{iv}	120.6 (1)
S2—Pt1—S2^{i}	180	Pt1—S1—Cu1^{v}	111.6 (1)
Cl1—Cu1—Cl1^{ii}	110.18 (8)	Pt1—S1—C1	87.3 (3)
Cl1—Cu1—S1^{iii}	113.2 (1)	Cu1^{v}—S1—C1	111.9 (3)
Cl1—Cu1—S2	111.19 (9)	Pt1—S2—Cu1	105.5 (1)
Cl1^{ii}—Cu1—S1^{iii}	117.0 (1)	Pt1—S2—C1	87.5 (3)
Cl1^{ii}—Cu1—S2	97.75 (9)	Cu1—S2—C1	104.7 (3)

Symmetry codes: (i) $-x, -y, -z$; (ii) $\frac{1}{4}+y, \frac{1}{4}-x, \frac{1}{4}+z$; (iii) $\frac{1}{4}-y, \frac{1}{4}+x, \frac{1}{4}-z$; (iv) $\frac{1}{4}-y, x-\frac{1}{4}, z-\frac{1}{4}$; (v) $y-\frac{1}{4}, \frac{1}{4}-x, \frac{1}{4}-z$.

One of the two crystallographically independent methyl C atoms was disordered in two sites (C5 and C6). The occupancy of the C5 site was refined as 0.66 (7) and the sum of occupancies of the C5 and C6 sites was made equal to 1.00. Atoms C5 and C6 were refined with isotropic displacement parameters. H atoms were not included in the refinement.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993); program(s) used to solve structures: *SAPI*91 (Fan, 1991); program(s) used to refine structures: *TEXSAN LS*; software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: MU1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrabutylammonium Di-μ-iodo-bis(iodoargentate) Hexatungstate, $[^{n}Bu_4N]_4[Ag_2I_4][W_6O_{19}]$

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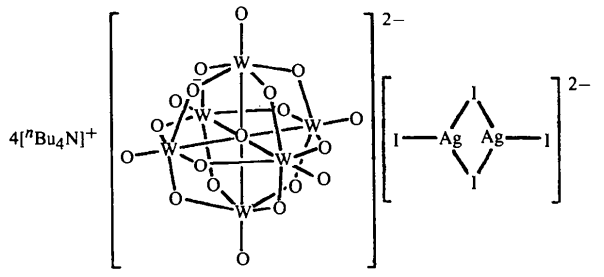
Abstract

The title compound, $4C_{16}H_{36}N^{+}.Ag_2I_4^{2-}.W_6O_{19}^{2-}$, prepared from $(NH_4)_2WO_2S_2$, $^{n}Bu_4NBr$ and AgI, is a new type of complex. The compound contains the hexatungstate cage anion $[W_6O_{19}]$ and the planar disilver anion $[Ag_2I_4]$, the charge of these two species being balanced by four tetrabutylammonium cations, $^{n}Bu_4N$.

Comment

Polyoxometallates are unique in their topological and electronic versatility and are important in analytical and clinical chemistry (Semenovskaya, 1986), catalysis (Neumann & Lissel, 1989), biochemistry, medicine and solid-state devices (Triki, Ouahab, Padiou & Grandjean, 1989). The coordination compounds of Ag also have many important properties, *e.g.* the superionic conductivity of M_2AgI_3, MAg_4I_5 (M = NH^{+}, K^{+}, Na^{+}) and $C_8H_{22}N_2Ag_2I_4$ (Thackeray & Coetzer, 1975). Thus, these compounds have attracted much interest (Pope &

Müller, 1991). We have synthesized the title compound $[^nBu_4N]_4[Ag_2I_4][W_6O_{19}]$, (I), containing hexatungstate $[W_6O_{19}]$ (Fuchs, Freivald & Hartl, 1978) and the disilver anion Ag_2I_4 (Helgesson & Jagner, 1990), by solid-state reaction at low temperature.



(I)

In the W_6O_{19} unit, which has a cage structure, each W atom is octahedrally surrounded by one central O, one terminal O and four bridging O atoms. The six W atoms form an octahedron whose centre is occupied by O4. The structure of the W_6O_{19} unit can be regarded as the condensation of six WO_6 octahedra sharing a common vertex at O4.

The six atoms of the Ag_2I_4 anion are arranged in a planar configuration and possess a centre of symmetry.

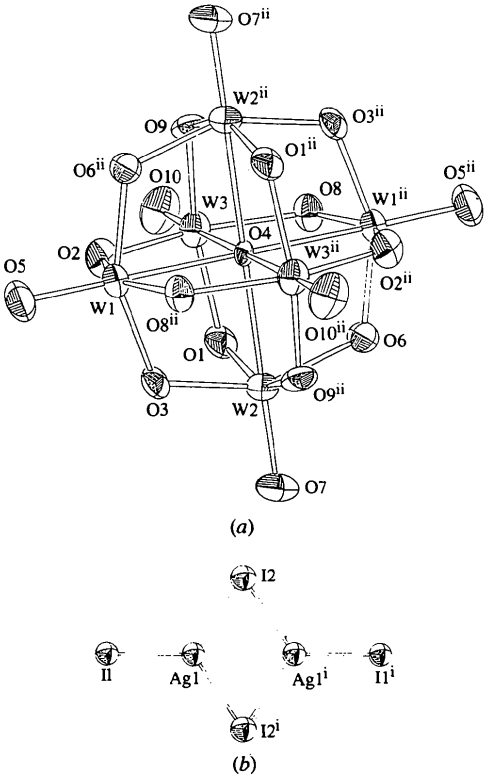


Fig. 1. The structure of (*a*) $[W_6O_{19}]^{2-}$ and (*b*) $[Ag_2I_4]^{2-}$. Symmetry codes: (i) $-x, -y, 2-z$; (ii) $1-x, -y, 1-z$.

The two Ag atoms are connected to each other through two I-atom bridges and each exhibits planar triangular geometry. The other two I atoms bond to two Ag atoms as terminal groups. In the similar compound $C_8H_{22}N_2Ag_2I_4$, containing the $Ag_2I_4^{2-}$ ion, I ions form tetrahedra, each containing an Ag^+ ion at its centre and sharing two of its edges to form a chain.

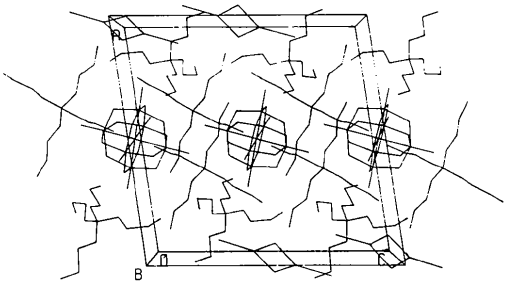


Fig. 2. The packing of $[^nBu_4N]_4[W_6O_{19}][Ag_2I_4]$ in the unit cell.

Experimental

A well ground mixture of $(NH_4)_2WO_2S_2$, AgI and $^nBu_4NBr$ (molar ratio 1:2:2) was heated for 10 h at 368 K. After extracting the product with thf (30 ml) and filtering the yellow solution, yellow rod-shaped crystals were obtained 15 days later.

Crystal data

$(C_{16}H_{36}N)_4[Ag_2I_4][W_6O_{19}]$
$M_r = 3100.31$
Monoclinic
$P2_1/c$
$a = 16.636\ (3)$ Å
$b = 16.733\ (3)$ Å
$c = 17.190\ (3)$ Å
$\beta = 98.25\ (1)°$
$V = 4736\ (1)$ Å^3
$Z = 2$
$D_x = 2.17$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13–15°$
$\mu = 9.158$ mm^{-1}
$T = 296$ K
Rod
0.50 × 0.15 × 0.15 mm
Yellow

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.802$, $T_{max} = 0.912$
13 820 measured reflections
6917 independent reflections
3240 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.02$
$\theta_{max} = 23.05°$
$h = 0 \rightarrow 18$
$k = -17 \rightarrow 18$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 150 reflections
intensity decay: 2.8%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.047$
$S = 1.08$
$(\Delta/\sigma)_{max} = 0.12$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -1.00$ e Å^{-3}
Extinction correction: none

3240 reflections
369 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso}
W1	0.37525 (5)	0.05983 (5)	0.45982 (5)	3.70 (4)
W2	0.53598 (5)	0.01970 (5)	0.37639 (5)	4.11 (4)
W3	0.55481 (5)	0.12340 (5)	0.53920 (5)	3.96 (4)
I1	0.0729 (1)	0.0336 (1)	0.7762 (1)	6.75 (9)
I2	−0.0632 (1)	0.1242 (1)	0.9903 (1)	8.4 (1)
Ag1	0.0272 (1)	0.0119 (1)	0.9179 (1)	6.9 (1)
O1	0.5736 (7)	0.1139 (7)	0.4308 (7)	4.5 (6)
O2	0.4445 (8)	0.1475 (6)	0.4977 (7)	4.5 (6)
O3	0.4286 (7)	0.0638 (7)	0.3686 (6)	4.1 (6)
O4	1/2	0.0	1/2	0.0
O5	0.2826 (8)	0.1040 (8)	0.4300 (8)	5.9 (7)
O6	0.6284 (7)	−0.0333 (7)	0.4331 (6)	4.2 (6)
O7	0.562 (1)	0.0326 (9)	0.2830 (7)	6.6 (8)
O8	0.6434 (7)	0.0499 (7)	0.5629 (7)	4.0 (6)
O9	0.5141 (8)	0.0834 (7)	0.6297 (6)	4.4 (6)
O10	0.597 (1)	0.2142 (8)	0.5696 (9)	6.6 (8)
N1	0.369 (1)	0.216 (1)	0.7619 (8)	4.2 (8)
N2	0.841 (1)	0.193 (1)	0.689 (1)	4.8 (9)
C1	0.315 (1)	0.164 (1)	0.702 (2)	5 (1)
C2	0.235 (1)	0.200 (1)	0.672 (1)	6 (1)
C3	0.191 (1)	0.148 (1)	0.610 (1)	6.0 (5)†
C4	0.108 (2)	0.177 (2)	0.580 (1)	8.2 (7)†
C5	0.386 (1)	0.298 (1)	0.728 (1)	5 (1)
C6	0.429 (1)	0.297 (1)	0.656 (1)	6 (1)
C7	0.434 (1)	0.380 (2)	0.627 (1)	7.0 (6)†
C8	0.470 (2)	0.385 (1)	0.554 (1)	7.6 (6)†
C9	0.444 (1)	0.169 (1)	0.782 (1)	5 (1)
C10	0.512 (1)	0.206 (1)	0.841 (1)	6 (1)
C11	0.586 (2)	0.151 (2)	0.857 (2)	8.6 (7)†
C12	0.659 (2)	0.184 (2)	0.907 (2)	11 (1)†
C13	0.327 (1)	0.231 (1)	0.833 (1)	5 (1)
C14	0.296 (1)	0.160 (1)	0.870 (1)	5 (1)
C15	0.256 (1)	0.186 (1)	0.942 (1)	7.1 (6)†
C16	0.224 (2)	0.121 (2)	0.983 (2)	8.7 (7)†
C17	0.840 (2)	0.123 (1)	0.745 (1)	8 (1)
C18	0.772 (2)	0.071 (2)	0.736 (2)	9 (2)
C19	0.767 (2)	0.006 (2)	0.796 (2)	10.7 (9)†
C20	0.813 (2)	−0.058 (2)	0.792 (2)	13 (1)†
C21	0.924 (1)	0.227 (1)	0.704 (1)	7 (1)
C22	0.946 (2)	0.266 (2)	0.777 (1)	8 (2)
C23	1.036 (2)	0.296 (2)	0.784 (2)	9.7 (8)†
C24	1.062 (2)	0.338 (2)	0.860 (2)	10.7 (9)†
C25	0.778 (2)	0.248 (2)	0.704 (1)	8 (2)
C26	0.773 (1)	0.322 (2)	0.657 (2)	8 (2)
C27	0.703 (2)	0.375 (2)	0.685 (2)	8.9 (7)†
C28	0.689 (2)	0.445 (2)	0.634 (2)	12 (1)†
C29	0.825 (2)	0.165 (2)	0.604 (1)	9 (2)
C30	0.874 (2)	0.104 (2)	0.581 (2)	12 (2)
C31	0.865 (3)	0.076 (3)	0.492 (3)	17 (2)†
C32	0.833 (4)	0.110 (4)	0.437 (4)	22 (2)†

† B_{iso}.

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

W1—O5	1.72 (1)	W2—O3	1.92 (1)
W1—O3	1.91 (1)	W3—O9	1.91 (1)
W2—O7	1.74 (1)	W3—O1	1.94 (1)
W2—O6	1.91 (1)	I2—Ag1^{i}	2.787 (3)
W3—O10	1.72 (1)	W1—O6^{ii}	1.90 (1)
W3—O8	1.92 (1)	W1—O4	2.3183 (8)
I1—Ag1	2.679 (2)	W2—O9^{ii}	1.91 (1)
Ag1···Ag1^{i}	3.112 (4)	W2—O4	2.3125 (8)
W1—O8^{ii}	1.89 (1)	W3—O2	1.91 (1)
W1—O2	1.92 (1)	W3—O4	2.3179 (8)
W2—O1	1.89 (1)	I2—Ag1	2.807 (3)
O5—W1—O8^{ii}	104.0 (6)	O5—W1—O6^{ii}	103.7 (6)
O5—W1—O4	179.9 (5)	O8^{ii}—W1—O6^{ii}	86.9 (5)
O8^{ii}—W1—O4	75.9 (3)	O6^{ii}—W1—O3	152.2 (5)
O6^{ii}—W1—O2	87.2 (5)	O3—W1—O2	85.7 (5)
O2—W1—O4	76.2 (4)	O4—W1—O6^{ii}	76.2 (3)
O2—W1—O5	104.0 (6)	O3—W1—O4	76.0 (3)
O3—W1—O5	104.0 (5)	O7—W2—O1	104.2 (6)
O7—W2—O3	104.0 (6)	O7—W2—O4	178.8 (6)
O1—W2—O9^{ii}	152.7 (4)	O1—W2—O6	87.1 (5)
O1—W2—O4	77.0 (3)	O9^{ii}—W2—O6	85.5 (5)
O9^{ii}—W2—O4	75.7 (3)	O1—W2—O3	87.3 (5)
O3—W2—O4	76.0 (3)	O3—W2—O6	152.1 (4)
O3—W2—O9^{ii}	87.1 (5)	O6—W2—O7	103.8 (6)
O7—W2—O9^{ii}	103.1 (6)	W2—O4—W2^{ii}	180.00
W2—O4—W3	89.85 (3)	W2—O4—W3^{ii}	90.15 (3)
W3—O4—W3^{ii}	180.00	W3—O4—W1	89.99 (3)
W3—O4—W1^{ii}	90.01 (3)	W1—O4—W1^{ii}	180 (3)
W2^{ii}—O6—W2	117.8 (6)	O6—W2—O4	76.2 (3)
O10—W3—O9	103.8 (6)	O10—W3—O2	104.6 (6)
O10—W3—O4	179.0 (5)	O9—W3—O2	86.8 (5)
O9—W3—O4	75.7 (3)	O2—W3—O8	151.7 (4)
O1—W3—O2	86.4 (5)	O1—W3—O4	76.0 (4)
O1—W3—O8	85.8 (5)	O1—W3—O9	151.7 (5)
O1—W3—O10	104.5 (6)	O2—W3—O4	76.3 (3)
O4—W3—O8	75.5 (3)	O8—W3—O9	87.3 (5)
O8—W3—O10	103.6 (6)	Ag1^{i}—I2—Ag1	67.60 (8)
I1—Ag1—I2^{i}	124.04 (9)	I1—Ag1—I2	123.56 (9)
I1—Ag1—I1^{i}	179.4 (2)	I2^{i}—Ag1—I2	112.40 (8)
I2^{i}—Ag1···Ag1^{i}	56.51 (7)	I2—Ag1···Ag1^{i}	55.89 (7)

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

The structure was solved by direct methods and refined using a full-matrix least-squares program. Half of the C atoms of the $[^nBu_4N]^+$ ions were refined isotropically; the remaining non-H atoms were refined anisotropically. All H atoms were determined by difference Fourier synthesis and by using the *HYDROGEN* program (B. A. Frenz & Associates, Inc., 1985). H-atom coordinates and isotropic displacement parameters were used in structure-factor calculations but not in the structure refinement. Calculations were carried out on a MicroVAX II with the *TEXSAN* program package (Molecular Structure Corporation, 1985).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: OH1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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