

Space group *P2₁/c* for (1) was determined by the unique systematic absences (*h0l* absent if *l* = 2*n* + 1, *0k0* absent if *k* = 2*n* + 1). The shape of the anisotropic displacement ellipsoids of the phosphite O atoms suggested the presence of disorder. A difference map showed maxima in positions consistent with an equal disordering of the phosphite atoms O4, O5 and O6, associated with a slight rotation of the ligand O atoms around the P—Co vector. A view of the phosphite ligand down the P—Co vector showing the positions of the six half O atoms has been deposited as supplementary material. The 'Pr groups of the phosphite ligand are ordered. The unit cell was also found to contain two CH₂Cl₂ solvent molecules disordered around inversion centres. A disorder model was used to account for the electron density in these regions of the unit cell. An electron density map showing the positions of the atoms of the solvent molecule, C13 (multiplicity 0.5), C11 (0.667), C12 (0.667) and C13 (0.667), has also been deposited as supplementary material.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

This research was supported by NSERC, Canada, and the University of Toronto.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a view of the phosphite ligand down the P—Co vector and an electron density map showing the positions of the atoms of the solvent molecule, have been deposited with the IUCr (Reference: FG1073). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(CuX)_n Helical Chains in [Pt(S₂CNEt₂)₂-Cu₂X₂] (X = Br, Cl)

KENJI TOKORO, MASAHIRO EBIHARA AND
TAKASHI KAWAMURA

*Department of Chemistry, Faculty of Engineering,
Gifu University, Yanagido, Gifu 501-11, Japan*

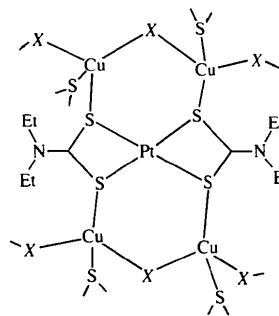
(Received 19 September 1994; accepted 7 February 1995)

Abstract

In poly[di- μ -bromo-bis(μ_3 -*N,N*-diethyldithiocarbamato)-dicopper(I)platinum(II)], [Pt(S₂CNEt₂)₂Cu₂Br₂], and poly[di- μ -chloro-bis(μ_3 -*N,N*-diethyldithiocarbamato)-dicopper(I)platinum(II)], [Pt(S₂CNEt₂)₂Cu₂Cl₂], a helical chain of (CuX)_n (X = Br, Cl) extends around a 4₁ axis and each Pt(S₂CNEt₂)₂ group links two of the helical chains with its four S atoms. Each Cu atom is surrounded by two S and two halogen atoms and has slightly distorted tetrahedral coordination geometry.

Comment

Dithiocarbamato complexes form various types of adducts with copper(I) halides because the bonding capacities of the S atoms are not otherwise fully saturated. Co(S₂CNR₂)₃ has three possible interligand S–S chelating sites and reacts with CuBr or CuI utilizing these three chelating sites to give heterobimetallic adducts of 1:1, 1:2 and 1:3 stoichiometries: e.g. [Co{S₂CN(CH₂)₄}₃(CuBr)] (Engelhardt, Healy, Papasergio & White, 1985), [Co(S₂CNPr₂)₃(CuI)] (Engelhardt, Healy, Skelton & White, 1988), [Co(S₂CNEt₂)₃(CuBr)₂].2CH₃CN and [Co{S₂CN(CH₂)₄}₃(CuI)₃] (Engelhardt, Healy, Shephard, Skelton & White, 1988). These mixed-metal complexes have either discrete or one- or three-dimensional polymeric structures in the solid state. We report here the interesting structures of [Pt(S₂CNEt₂)₂Cu₂Br₂]_n, (1), and [Pt(S₂CNEt₂)₂Cu₂Cl₂]_n, (2), constructed from planar



(1) X = Br
(2) X = Cl

dithiocarbamato platinum(II) units and $(\text{CuX})_n$ helical chains.

Fig. 1 shows the coordination around a $\text{Pt}(\text{S}_2\text{CNET}_2)_2$ residue in (1). Each $\text{Pt}(\text{S}_2\text{CNET}_2)_2$ unit has a normal planar structure and links two $(\text{CuBr})_n$ helical chains by using its four S atoms. Each Cu atom has a slightly distorted tetrahedral environment. Bond angles around the Cu atom are $98.1(1)$ – $118.5(1)^\circ$. The lengths of the Cu—S bonds are $2.342(3)$ and $2.434(3)$ Å and those of the Cu—Br bonds are $2.418(2)$ and $2.467(2)$ Å. Polymeric structures of $[\text{Cu}\{\text{S}_2\text{CN}(\text{CH}_2)_5\}_2(\text{CuBr})_n]$ ($n = 4$ or 6) comprising planar $\text{Cu}\{\text{S}_2\text{CN}(\text{CH}_2)_5\}_2$ residues and polymeric chains of $(\text{CuBr})_n$ have also been reported (Golding, Rae, Ralph & Sulligoi, 1974). In these complexes the Cu—S distances are $2.269(1)$ – $2.476(3)$ Å and the Cu—Br distances are in a rather wide range of $2.357(3)$ – $2.863(7)$ Å.

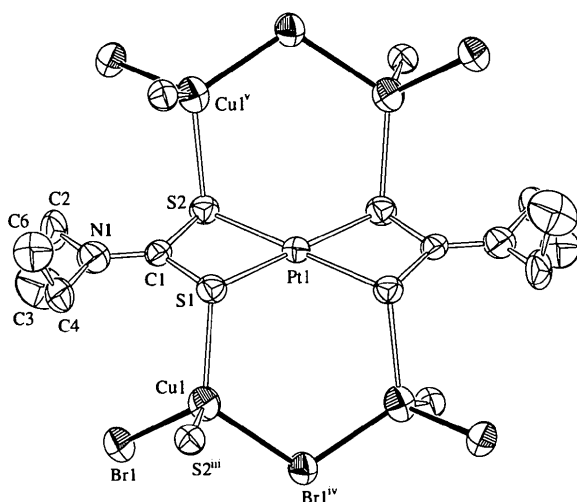


Fig. 1. ORTEP (Johnson, 1976) diagram of a $\text{Pt}(\text{S}_2\text{CNET}_2)_2$ residue in $[\text{Pt}(\text{S}_2\text{CNET}_2)_2\text{Cu}_2\text{Br}_2]_n$, (1). Displacement ellipsoids are drawn at the 50% probability level. Only one of the two disordered C-atom sites, C6, is shown for clarity. Solid bonds represent the $(\text{CuBr})_n$ helix.

The unit cell of (2) viewed along the b axis is shown in Fig. 2. Each Pt atom lies on an inversion centre. Each $(\text{CuCl})_n$ helical chain extends around a 4_1 axis. The coordination in (2) is similar to that in (1) and the complexes are isostructural. The Cu—S distances [$2.336(3)$ and $2.426(3)$ Å] are longer and the Cu—Cl distances [$2.297(3)$ and $2.349(3)$ Å] are shorter than those in similar complexes with tetrahedral CuS_2Cl_2 moieties, such as $[\text{Cu}_3(\text{S}_2\text{CNET}_2)_2\text{Cl}_3]$ [Cu—S $2.268(1)$ and $2.281(1)$ Å, Cu—Cl $2.388(1)$ and $2.394(1)$ Å (Hendrickson, Martin & Taylor, 1975)]. In the $(\text{CuX})_n$ helical chains of (1) and (2), the Cl—Cu—Cl angle [$110.18(8)^\circ$] is a little larger than the Br—Cu—Br angle [$106.70(6)^\circ$]. The difference between the Cu—Br

and Cu—Cl distances is approximately 0.12 Å, which is comparable to the difference in the covalent radii of Cl and Br (0.15 Å; Cotton & Wilkinson, 1988).

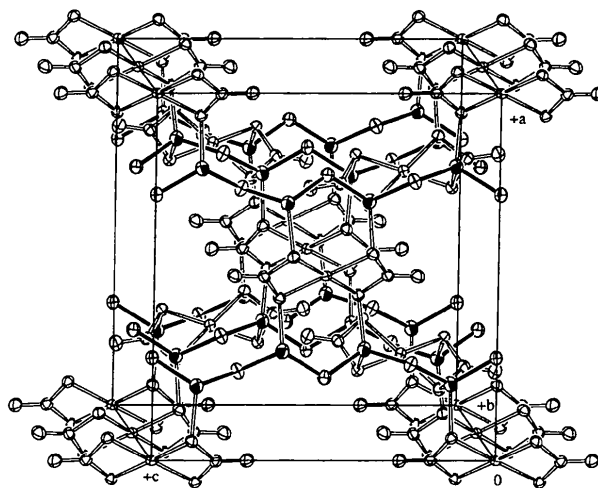


Fig. 2. Unit cell of $[\text{Pt}(\text{S}_2\text{CNET}_2)_2\text{Cu}_2\text{Cl}_2]_n$, (2), viewed along the b axis. Displacement ellipsoids are drawn at the 50% probability level. The alkyl groups of the $\text{Pt}(\text{S}_2\text{CNET}_2)_2$ residues are omitted for clarity. Solid bonds represent the $(\text{CuCl})_n$ helix. Hatched ellipsoids represent Cu atoms.

Experimental

Complex (1): To 12.5 ml of a dichloromethane solution of $\text{Pt}(\text{S}_2\text{CNET}_2)_2$ (63 mg, 0.13 mmol) and $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ (82 mg, 0.26 mmol), Bu_4NBr (84 mg, 0.25 mmol) in 7.5 ml of dichloromethane was added. All the reactants dissolved; the resultant yellow solution was stirred for 1 h and then settled for 16 h to give yellow prismatic crystals suitable for X-ray study (72%). Elemental analysis: calculated for $\text{C}_{10}\text{H}_{20}\text{Br}_2\text{Cu}_2\text{N}_2\text{PtS}_4$ C 15.43, H 2.59%; found C 15.19, H 2.42%.

Complex (2): The synthesis of complex (2) was carried out analogously to that described for (1) by using Bu_4NCl instead of Bu_4NBr . A yellow powder precipitated after several minutes (64%), but it did not dissolve in any common organic solvent. The elemental analysis of the powder was consistent with $[\text{Pt}(\text{S}_2\text{CNET}_2)_2\text{Cu}_2\text{Cl}_2]_n$: calculated for $\text{C}_{10}\text{H}_{20}\text{Cl}_2\text{Cu}_2\text{N}_2\text{PtS}_4$ C 17.42, H 2.93, N 4.06%; found C 17.27, H 2.95, N 4.06%. The single crystal of (2) was obtained incidentally in the preparation of $[\text{Pt}_3(\text{S}_2\text{CNET}_2)_6\text{Cu}_2](\text{BF}_4)_2$ by reaction of $\text{Pt}(\text{S}_2\text{CNET}_2)_2$ and $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ in CH_2Cl_2 (Ebihara *et al.*, 1994). $\text{Pt}(\text{S}_2\text{CNET}_2)_2$ (200 mg, 0.41 mmol) and $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ (89 mg, 0.28 mmol) were dissolved in 15 ml of CH_2Cl_2 under Ar and stirred for 6 h at 293 K. After filtration of the orange–yellow reaction solution, n -hexane was layered onto the filtrate to give $[\text{Pt}_3(\text{S}_2\text{CNET}_2)_6\text{Cu}_2](\text{BF}_4)_2$ as a yellow powder. The powder was dissolved in CH_2Cl_2 – $(\text{CH}_3)_2\text{CO}$ (1:1 v/v) mixed solvent and n -hexane was layered to give pale yellow prismatic crystals of (2) suitable for X-ray study. Attempts to reproduce this synthesis of (2) have been unsuccessful.

Compound (1)*Crystal data*[Cu₂PtBr₂(C₅H₁₀NS₂)₂] $M_r = 778.51$

Tetragonal

 $I4_1/a$ $a = 15.967 (1) \text{ \AA}$ $c = 15.348 (4) \text{ \AA}$ $V = 3912.9 (8) \text{ \AA}^3$ $Z = 8$ $D_x = 2.643 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation $\lambda = 0.7107 \text{ \AA}$

Cell parameters from 23 reflections

 $\theta = 12.51\text{--}14.62^\circ$ $\mu = 13.78 \text{ mm}^{-1}$ $T = 296 \text{ K}$

Prismatic

 $0.3 \times 0.2 \times 0.07 \text{ mm}$

Yellow

Data collection

AFC-7R diffractometer

 $\omega/2\theta$ scans

Absorption correction:

refined from ΔF

(DIFABS; Walker & Stuart, 1983)

 $T_{\min} = 0.076$, $T_{\max} = 0.41$

2506 measured reflections

2344 independent reflections

1521 observed reflections

 $[I > 2\sigma(I)]$ $R_{\text{int}} = 0.041$ $\theta_{\text{max}} = 27.5^\circ$ $h = 0 \rightarrow 20$ $k = 0 \rightarrow 20$ $l = 0 \rightarrow 19$

3 standard reflections

monitored every 150 reflections

intensity decay: 1.56%

*Refinement*Refinement on F $R = 0.045$ $wR = 0.041$ $S = 1.56$

1521 reflections

97 parameters

H atoms not located

 $w = 1/[\sigma^2(F) + (0.08F)^2/4]$ $(\Delta/\sigma)_{\text{max}} < 0.0001$ $\Delta\rho_{\text{max}} = 0.97 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -1.29 \text{ e \AA}^{-3}$

Extinction correction: none

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 (\AA^2) for (1)
$$U_{\text{iso}} \text{ for C5 and C6; } U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \text{ for others.}$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$
Pt1	0	0	0	0.0330 (2)
Br1	0.23285 (7)	-0.03110 (7)	0.2502 (1)	0.0462 (4)
Cu1	0.20619 (9)	0.05168 (9)	0.1212 (1)	0.0486 (5)
S1	0.0642 (2)	0.0840 (2)	0.1031 (2)	0.0387 (8)
S2	-0.0665 (2)	-0.0327 (2)	0.1289 (2)	0.0376 (8)
N1	0.0054 (6)	0.0463 (7)	0.2666 (8)	0.050 (3)
C1	0.0023 (6)	0.0358 (7)	0.1813 (8)	0.034 (3)
C2	-0.0451 (8)	-0.006 (1)	0.3268 (9)	0.060 (5)
C3	0.0099 (9)	-0.080 (1)	0.359 (1)	0.086 (6)
C4	0.0669 (8)	0.1088 (9)	0.3031 (9)	0.056 (4)
C5†	0.042 (1)	0.141 (1)	0.393 (2)	0.072 (9)
C6†	0.025 (3)	0.178 (3)	0.326 (4)	0.07 (1)

† Disordered site (see below).

Table 2. Selected geometric parameters (\AA , $^\circ$) for (1)

Pt1—S1	2.313 (3)	S2—C1	1.74 (1)
Pt1—S1 ⁱ	2.313 (3)	N1—C1	1.32 (2)
Pt1—S2	2.305 (3)	N1—C2	1.48 (2)
Pt1—S2 ⁱ	2.305 (3)	N1—C4	1.51 (1)
Br1—Cu1	2.418 (2)	C2—C3	1.56 (2)
Br1—Cu1 ⁱⁱ	2.467 (2)	C4—C5	1.52 (3)
Cu1—S1	2.342 (3)	C4—C6	1.34 (4)
Cu1—S2 ⁱⁱⁱ	2.434 (3)	C5—C6	1.21 (5)
S1—C1	1.73 (1)		

S1—Pt1—S1 ⁱ	180	Pt1—S2—C1	87.9 (4)
S1—Pt1—S2	75.4 (1)	Cu1 ^v —S2—C1	103.3 (4)
S2—Pt1—S2 ⁱ	180	C1—N1—C2	121 (1)
Cu1—Br1—Cu1 ⁱⁱ	115.45 (5)	C1—N1—C4	118 (1)
Br1—Cu1—Br1 ^{iv}	106.70 (6)	C2—N1—C4	119 (1)
Br1—Cu1—S1	112.8 (1)	S1—C1—S2	108.5 (7)
Br1—Cu1—S2 ⁱⁱⁱ	112.7 (1)	S1—C1—N1	127.4 (9)
Br1 ^{iv} —Cu1—S1	118.5 (1)	S2—C1—N1	124.0 (9)
Br1 ^{iv} —Cu1—S2 ⁱⁱⁱ	98.12 (10)	N1—C2—C3	108 (1)
S1—Cu1—S2 ⁱⁱⁱ	107.2 (1)	N1—C4—C5	112 (1)
Pt1—S1—Cu1	112.5 (1)	N1—C4—C6	108 (2)
Pt1—S1—C1	87.9 (4)	C5—C4—C6	49 (2)
Cu1—S1—C1	111.8 (4)	C4—C5—C6	57 (2)
Pt1—S2—Cu1 ^v	106.5 (1)	C4—C6—C5	73 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z$; (iii) $\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z$; (iv) $\frac{1}{2} - y, x - \frac{1}{2}, z - \frac{1}{2}$; (v) $y - \frac{1}{2}, \frac{1}{4} - x, \frac{1}{4} - z$.

Compound (2)*Crystal data*[Cu₂PtCl₂(C₅H₁₀NS₂)₂] $M_r = 689.62$

Tetragonal

 $I4_1/a$ $a = 15.835 (2) \text{ \AA}$ $c = 15.037 (3) \text{ \AA}$ $V = 3770.5 (9) \text{ \AA}^3$ $Z = 8$ $D_x = 2.429 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation $\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25

reflections

 $\theta = 12.63\text{--}14.88^\circ$ $\mu = 9.084 \text{ mm}^{-1}$ $T = 296 \text{ K}$

Prismatic

 $0.33 \times 0.15 \times 0.12 \text{ mm}$

Yellow

Data collection

AFC-7R diffractometer

 $\omega/2\theta$ scans

Absorption correction:

refined from ΔF

(DIFABS; Walker &

Stuart, 1983)

 $T_{\min} = 0.124$, $T_{\max} = 0.27$

2413 measured reflections

2255 independent reflections

1650 observed reflections

 $[I > 2\sigma(I)]$ $R_{\text{int}} = 0.021$ $\theta_{\text{max}} = 27.5^\circ$ $h = 0 \rightarrow 20$ $k = 0 \rightarrow 20$ $l = 0 \rightarrow 19$

3 standard reflections

monitored every 150 reflections

intensity decay: 2.29%

*Refinement*Refinement on F $R = 0.038$ $wR = 0.037$ $S = 1.73$

1650 reflections

98 parameters

H atoms not located

 $w = 1/[\sigma^2(F) + (0.09F)^2/4]$ $(\Delta/\sigma)_{\text{max}} = 0.002$ $\Delta\rho_{\text{max}} = 1.15 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -1.07 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1968) type

2 Gaussian isotropic

Extinction coefficient:

 $1.11 (6) \times 10^{-7}$

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV)

Table 3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for (2)
$$U_{\text{iso}} \text{ for C5 and C6; } U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \text{ for others.}$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$
Pt1	0	0	0	0.0247 (1)
Cu1	0.19980 (8)	0.04217 (8)	0.12879 (9)	0.0398 (4)
Cl1	0.2744 (1)	0.0134 (2)	0.0013 (2)	0.0389 (7)
S1	-0.0651 (1)	0.0841 (1)	0.1055 (2)	0.0296 (6)

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 (\AA , $^\circ$) 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 ⁱⁱⁱ —Cu1—S1 ⁱⁱⁱ	117.0 (1)	Pt1—S2—C1	87.5 (3)
Cl1 ⁱⁱⁱ —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: *SAPI91* (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, $[\text{Bu}_4\text{N}]_4[\text{Ag}_2\text{I}_4][\text{W}_6\text{O}_{19}]$

HONG-WEI HOU, XIANGRONG YE AND XINQUAN XIN*

State Key Laboratory of Coordination Chemistry,
Department of Chemistry, Nanjing University,
Nanjing 210093, People's Republic of China

ZHEMIN WANG, SHIXIONG LIU AND JINLING HUANG

Department of Chemistry, Fuzhou University,
Fuzhou 350002, People's Republic of China

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Abstract

The title compound, $4\text{C}_{16}\text{H}_{36}\text{N}^+ \cdot \text{Ag}_2\text{I}_4^{2-} \cdot \text{W}_6\text{O}_{19}^{2-}$, prepared from $(\text{NH}_4)_2\text{WO}_2\text{S}_2$, ${}^n\text{Bu}_4\text{NBr}$ and AgI , is a new type of complex. The compound contains the hexatungstate cage anion $[\text{W}_6\text{O}_{19}]$ and the planar disilver anion $[\text{Ag}_2\text{I}_4]$, the charge of these two species being balanced by four tetrabutylammonium cations, ${}^n\text{Bu}_4\text{N}$.

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 $M_2\text{AgI}_3$, $M\text{Ag}_4\text{I}_5$ ($M = \text{NH}^+, \text{K}^+, \text{Na}^+$) and $\text{C}_8\text{H}_{22}\text{N}_2\text{Ag}_2\text{I}_4$ (Thackeray & Coetzer, 1975). Thus, these compounds have attracted much interest (Pope &