Synthesis of a Heterobimetallic Ladder Polymer $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br]_n$

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Introduction

The molecular construction of extended structures from discrete transition metal complexes has been the subject of numerous studies in recent years.[1] Typical convenient precursors for extended heterobimetallic arrays are tetrathiometalates $[MS_n]^{2-}$ (M = Mo, W) and $[ReS_4]^-$, which may react with various metal complexes, resulting in a wide variety of cluster frameworks.[2,3] One such example is a series of polymeric M/Ag/S systems. Müller *et al.* characterized the first polymeric Mo/Ag/S cluster $[PPh_4]_n[MoS_4Ag]_n$, which was characterized by resonance Raman spectroscopy.[4] One of us determined interesting one-dimensional extended structures of the Mo(W)/Ag/S compounds $[RPyH]_n[MS_4Ag]_n$ (R = α-Me, γ-Me; M = Mo, W), which were synthesized by the reactions of $[NH_4]_2[MS_4]$ with AgX (X = Br, I) in methyl-substituted pyridine.[5a] Later the analogous polymers, $[H_3NC(CH_2OH)_3{\bullet}2DMF]_n[WS_4Ag]_n$ (single chain), $[H_3NC(CH_2OH)_3{\bullet}H_2O]_n[WS_4Ag]_n$ (double chain),[5b] $[Ln(DMF)_8]_n[W_4Ag_5S_{16}]_n$ (Ln = Nd, La) (single chain),[5c] and$\{[Ca(DMSO)_6]_2\}_n[W_4Ag_4S_{16}]_n$ (single chain)[5d] were reported.

On the other hand, we recently found an intriguing route to an organometallic tris(sulfido) complex anion $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3]$, which was prepared in a large scale from the reaction of $[(\eta^5\text{-}C_5Me_5)WCl_4]$ and $Li_2(SCH_2CH_2S)$ followed by cation exchange with PPh_4Br.[6] Having noted that $[(\eta^5\text{-}C_5Me_5)WS_3]^-$ may serve as a potential building block for heterometallic sulfide clusters, we have examined construction of new types of clusters by treating $[(\eta^5\text{-}C_5Me_5)WS_3]^-$ with Cu^I and Ag^I complexes.[7] We herein report the synthesis and characterization of a novel polymeric cluster $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br]_n$ (**1**) and its reaction with PPh_3 to give $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br(PPh_3)_2]$ (**2**).

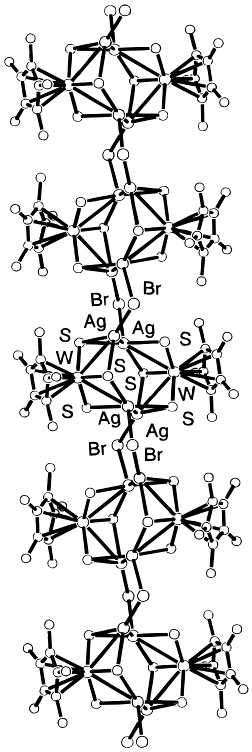

Figure 1. Ladder-shaped one-dimensional structure of $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br]_n$ (**1**).

Results and Discussion

When AgBr was added to an acetonitrile solution of $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3]$ (molar ratio = 3:1), the red color of the solution darkened immediately, and the mixture was stirred for 5 min. After an insoluble residue was filtered off, diethyl ether was layered onto the filtrate, from which dark red prismatic crystals of **1** were formed in 31% yield.

The X-ray study revealed that compound **1** possesses an unusual ladder-shaped one-dimensional structure. As shown in Figure 1, it consists of $[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_4$ clusters linked by two Br bridges. This unprecedented one-dimensional array runs parallel to the crystallographic *c* axis. An asymmetric unit of the crystal contains two halves of the $[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_4Br_2$ fragments, and adjacent $[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_4$ clusters twist by 46.7°. There is no short contact between the ladder-shaped chains.

Figure 2 presents an ORTEP view of the repeating unit, with the numbering scheme adopted. Selected bond distances and angles are given in Table 1. The geometries of two crystallographically independent $[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_4$ clusters in the chain are practically identical, and an inversion center resides in the middle of each cluster core. Within the cluster, two $(\eta^5\text{-}C_5Me_5)WS_3$ moieties are interconnected by four Ag atoms in a somewhat complicated way. The Ag(1) atom (or Ag(3)) bridges two sulfurs of one $(\eta^5\text{-}C_5Me_5)WS_3$ moiety, and it is also bound

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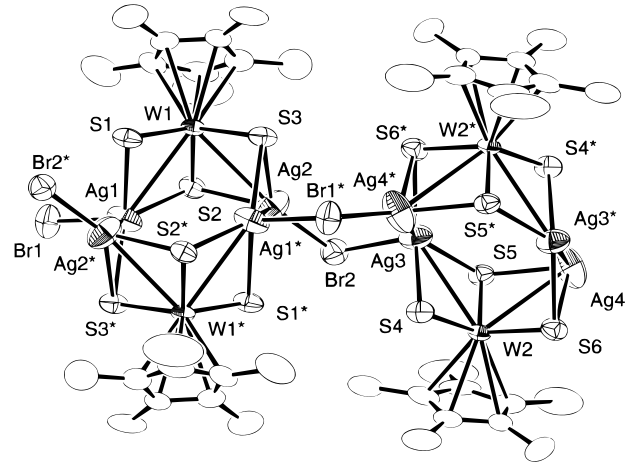

Figure 2. ORTEP drawing of a repeating unit of **1** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

to a sulfur atom of the other $(\eta^5\text{-}C_5Me_5)WS_3$ moiety, resulting in a distorted tetrahedral AgS_3Br coordination geometry. On the other hand, Ag(2) (or Ag(4)) assumes an approximately trigonal planar geometry with two S atoms of a $(\eta^5\text{-}C_5Me_5)WS_3$ group and a Br bridge. Due to the different coordination numbers of Ag atoms, their Ag−Br bond distances are different. The Ag(1)−Br(1) (or Ag(3)−Br(2)) length of 2.674(2) Å (2.691(2) Å) is 0.17 Å (0.19 Å) substantially longer than that of Ag(2)−Br(2*) (or Ag(4)−Br(1*)), and the mean Ag(1)(Ag(3))−S distance is also 0.02 Å longer than the mean Ag(2)(Ag(4))−S distance. The Ag(1)−Ag(2*) and Ag(3)−Ag(4*) distances of 2.916(2) and 2.895(2) Å indicate the presence of weak interactions between the Ag atoms. They are shorter than those in $[(PPh_3)_4Ag_4(mt)_4]$ (3.089(2)−3.110(1) Å) (mt = 2-mercaptothiazoline)[8a] and $[\{Ag(2\text{-}Me_3SiC_6H_4S)\}_4]_2$ (3.065(4)−3.320(5) Å)[8b] and are close to the one in $[Ag(tu)_3]_2[ClO_4]_2$ (2.845(1) Å) (tu = thiourea).[8c] Likewise, weak dative bonding may exist between d^{10} Ag^I and d^0 W^{VI}, judging from the observed mean W−Ag length of 3.005(2) Å, which is comparable to those found in $[\gamma\text{-}MePyH]_n[WS_4Ag]_n$ (2.971(2) Å)[5a] and $[Nd(DMF)_8]_n[W_4Ag_5S_{16}]_n$ (2.964(2) Å).[5c] Three S atoms of each $(\eta^5\text{-}C_5Me_5)WS_3$ fragment are inequivalent, and W−S distances vary from 2.210(4) to 2.281(4) Å. However they all fall in-between the W−S single bond and W═S double bond distances observed for $[(\eta^5\text{-}C_5Me_5)W(S)_2(SCH_2Ph)]$ (2.328(4) Å *vs* 2.149(3) Å) and $[(\eta^5\text{-}C_5Me_5)W(S)\{SC(Ph){=}C(Ph)S\}]^-$ (2.326(2) Å *vs* 2.186(2) Å).[6] It is of interest to compare the repeating core geometry of the $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_2Ag_4Br_2]$ unit in **1** with the geometry of the closely related cluster compounds $[(MS_4)_2Ag_4(PPh_3)_4]$ (M = Mo, W).[9] The $M_2S_6Ag_4$ skeleton of the latter clusters is hexagonal prismatic, while in the former cluster unit two Ag−S bonds, namely, Ag(1)−S(1) and Ag(1*)−S(1*) (or Ag(4)−S(4) and Ag(4*)−S(4*)), are broken. The difference may arise from the steric hindrance occurring between adjacent $\eta^5\text{-}C_5Me_5$ rings and bromides in the polymeric structure of **1**.

As one would expect, the polymeric compound **1** is insoluble in common organic solvents. However, when PPh_3 was added to a $CHCl_3$ suspension of **1** (molar ratio = 3:1), **1** was found to dissolve gradually. After a standard workup, an incomplete cubane cluster $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br(PPh_3)_2]$, **2**, was isolated in 83% yield. Thus strong donor ligands such as PPh_3 facilitate fragmentation of the polymeric structure of **1** into its components.

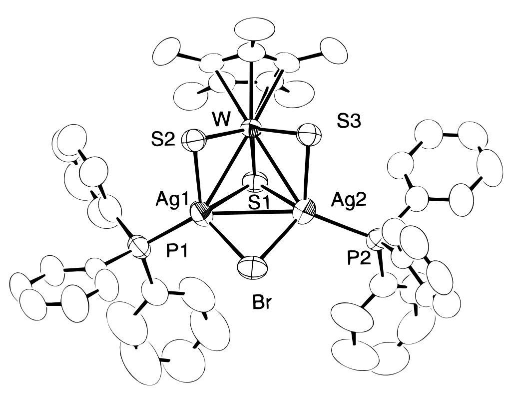

Figure 3. Molecular structure of $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br(PPh_3)_2]$ (**2**), with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **1**

W(1)−Ag(1)	3.021(1)	W(1)−Ag(2)	2.967(2)
W(2)−Ag(3)	3.030(2)	W(2)−Ag(4)	3.000(2)
Ag(1)−Ag(2)	2.916(2)	Ag(3)−Ag(4)	2.895(2)
W(1)−S(1)	2.210(4)	W(1)−S(2)	2.257(4)
W(1)−S(3)	2.274(4)	W(2)−S(4)	2.215(4)
W(2)−S(5)	2.262(4)	W(2)−S(6)	2.281(4)
Ag(1)−Br(1)	2.674(2)	Ag(2)−Br(2)	2.509(2)
Ag(3)−Br(2)	2.691(2)	Ag(4)−Br(1)	2.500(2)
Ag(1)−S(1)	2.566(4)	Ag(1)−S(2)	2.505(4)
Ag(1)−S(3)	2.533(4)	Ag(2)−S(2)	2.498(4)
Ag(2)−S(3)	2.497(4)	Ag(3)−S(4)	2.583(4)
Ag(3)−S(5)	2.490(4)	Ag(3)−S(6)	2.496(4)
Ag(4)−S(5)	2.513(4)	Ag(4)−S(6)	2.529(4)
S(1)−W(1)−S(2)	109.8(1)	S(1)−W(1)−S(3)	103.8(2)
S(2)−W(1)−S(3)	110.1(1)	S(4)−W(2)−S(5)	110.2(1)
S(4)−W(2)−S(6)	103.6(2)	S(5)−W(2)−S(6)	110.0(1)
Ag(1)−W(1)−Ag(2)	80.78(5)	Ag(3)−W(2)−Ag(4)	86.28(5)
W(1)−S(1)−Ag(1)	78.1(1)	W(1)−S(2)−Ag(1)	78.6(1)
W(1)−S(2)−Ag(2)	77.0(1)	W(1)−S(3)−Ag(2)	76.8(1)
W(2)−S(4)−Ag(3)	77.9(1)	W(2)−S(5)−Ag(3)	79.1(1)
W(2)−S(5)−Ag(4)	77.7(1)	W(2)−S(6)−Ag(4)	77.0(1)
W(1)−S(3)−Ag(1*)	106.6(2)	W(2)−S(6)−Ag(3*)	102.3(2)
S(1)−Ag(1)−S(2)	92.3(1)	S(2)−Ag(2)−S(3)	96.1(1)
S(4)−Ag(3)−S(5)	97.1(1)	S(5)−Ag(4)−S(6)	95.1(1)
S(1)−Ag(1)−S(3*)	118.8(1)	S(4)−Ag(3)−S(6*)	118.2(1)
Ag(1)−S(2)−Ag(2)	101.7(1)	Ag(3)−S(5)−S(4)	110.0(2)
Ag(1)−S(3*)−Ag(2*)	70.9(1)	Ag(3)−S(6*)−Ag(4*)	102.3(2)
Ag(1)−Br(1)−Ag(4)	96.15(8)	Ag(2)−Br(2)−Ag(3)	94.93(8)

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**

W−Ag(1)	3.0505(5)	W−Ag(2)	3.0461(5)
Ag(1)−Ag(2)	3.1179(9)	W−S(1)	2.275(1)
W−S(2)	2.224(1)	W−S(3)	2.202(1)
Ag(1)−S(1)	2.640(2)	Ag(1)−S(2)	2.506(2)
Ag(2)−S(1)	2.582(1)	Ag(2)−S(3)	2.562(2)
Ag(1)−Br	2.7098(9)	Ag(2)−Br	2.7378(8)
Ag(1)−P(1)	2.399(2)	Ag(2)−P(2)	2.407(2)
S(1)−W−S(2)	109.11(5)	S(1)−W−S(3)	107.75(5)
Ag(1)−W−Ag(2)	61.52(2)	S(1)−Ag(1)−S(2)	90.78(5)
S(1)−Ag(2)−S(3)	89.33(4)	W−S(1)−Ag(1)	76.32(4)
W−S(1)−Ag(2)	77.40(4)	W−S(2)−Ag(1)	80.07(5)
W−S(3)−Ag(2)	79.09(4)	Ag(1)−S(1)−Ag(2)	73.30(4)
Ag(1)−Br−Ag(2)	69.83(2)	Br−Ag(1)−S(1)	104.78(4)
Br−Ag(1)−S(2)	112.70(4)	Br−Ag(2)−S(3)	115.28(4)
Br−Ag(2)−S(1)	105.60(4)		

The molecular structure of **2** is shown in Figure 3, and selected bond lengths and angles are given in Table 2. The structure of **2** has virtual but not crystallographically imposed mirror symmetry. The seven-atom $[WS_3Ag_2Br]$ cluster geometry in **2** may be regarded as an intermediate between the six-atom $[WS_3Ag_2]$ skeleton in $[WOS_3Ag_2(PPh_3)_3]$[10a] and the eight-atom cubane structure of $[WS_3Ag_3X]$ in $[WOS_3Ag_3(PPh_3)_3X]$.[10b]

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Each Ag atom is bound to two sulfides, one bromide, and one PPh_3 ligand, forming a distorted tetrahedral coordination geometry. The mean Ag−Br (2.723(8) Å) and Ag−S lengths (2.572(2) Å) are slightly longer than the corresponding distances in **1**. The mean W−Ag bond of 3.0483(5) Å is slightly elongated compared with **1** (3.005(2) Å) and $[\gamma\text{-MePyH}]_n[AgWS_4]_n$ (2.971(2) Å).[5a] The Ag−Ag distance (3.1179(9) Å) is also 0.21 Å longer than those in **1**, suggesting that there is only weak interaction between the Ag atoms if any.

Experimental Section

General Information. All manipulations were carried out under argon using standard Schlenk techniques. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon and collected by distillation. CD_2Cl_2 was vacuum-transferred from calcium hydride. ^1H NMR spectrum for **2** was recorded on a Varian UNITYplus-500 spectrometer, and chemical shifts were quoted in δ (ppm) relative to CH_2Cl_2 in CD_2Cl_2. IR spectra were recorded on a Perkin Elmer 2000FT-IR spectrophotometer using either KBr pellets or Nujol mulls between CsI plates. The UV−vis spectrum for **2** was measured on Jasco V-560 spectrophotometer. C, H, and S analyses were performed on a Leco-CHNS microanalyzer.

Synthesis of $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br]_n$ (1). AgBr (0.09 g, 0.48 mmol) was added to a red solution of $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3]$ (0.12 g, 0.16 mmol) in CH_3CN (20 mL). The color of solution turned to dark red within seconds. The mixture was stirred for 5 min at room temperature. The red insoluble residue was filtered off, and 0.035 g (31%) of dark red prismatic crystals of **1** were obtained by layering diethyl ether (20 mL) onto the dark-red filtrate. Anal. Calcd for $C_{10}H_{15}Ag_2BrS_3W$: C, 16.89; H, 2.13; S, 13.53. Found: C, 16.74; H, 2.11; S, 13.17. IR (KBr pellets): 435 (m), υ(W−S) cm^{-1}.

Synthesis of $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br(PPh_3)_2]$ (2). PPh_3 (0.055 g, 0.21 mmol) was added to a slurry of **1** (0.05 g, 0.07 mmol) in $CHCl_3$ (20 mL). The resulting suspension was stirred for 8 h at room temperature. After filtration, the solution was concentrated to *ca.* 4 mL under reduced pressure, and Et_2O (4 mL) was added. Allowing the solution to stand for 2 days resulted in formation of dark-red crystals of **2**•$CHCl_3$, which were collected and washed with diethyl ether and dried under vacuum. Yield: 0.079 g (83%). Anal. Calcd for $C_{46}H_{45}Ag_2BrP_2S_3W$: C, 44.72; H, 3.68; S, 7.78. Found: C, 44.83; H, 3.70; S, 7.43. IR (Nujol mull, CsI): 504 (s), 450 (m), 424 (w), υ(W−S) cm^{-1}. UV−vis ($CHCl_3$) (λ_{max}/nm (ϵ /M^{-1} cm^{-1})): 380 (8900). ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 7.40−7.60 (30H, m, PPh_3); 2.14 (15H, s, $\eta^5\text{-}C_5Me_5$).

X-ray Diffraction Crystallography. X-ray-quality crystals of **1** and **2**•$CHCl_3$ were obtained directly from the preparation as described above. Diffraction data were collected on a Rigaku AFC7R diffractometer at ambient temperature by using graphite-monochromatized Mo Kα radiation (0.710 79 Å). A dark red single crystal of **1** with dimensions 0.15 × 0.20 × 0.20 mm was mounted on the top of a glass fiber, while a dark red single crystal of **2**•$CHCl_3$ with dimensions 0.90 × 0.35 × 0.20 mm was sealed in a capillary under argon. Cell constants and an orientation matrix for data collection were obtained from least-squares refinements using the setting angles of 25 carefully centered reflections in the range $29.7° < 2\theta < 30.0°$ for **1** and $22.0° < 2\theta < 24.7°$ for **2**•$CHCl_3$. The intensities of three representative reflections monitored every 150 reflections showed no sign of significant decay. An empirical absorption correction using the ψ scan technique was applied, which resulted in transmission factors ranging from 0.74 to 1.00 for **1** and from 0.41 to 1.00 for **2**•$CHCl_3$. The data were also corrected for Lorentz and polarization effects.

Table 3. Crystallographic Data for **1** and **2**•$CHCl_3$

formula	$C_{10}H_{15}Ag_2BrS_3W$	$C_{47}H_{46}Ag_2BrCl_3P_2S_3W$
fw	710.90	1354.86
cryst system	monoclinic	triclinic
space group	$P2_1/a$	$P1$
a, Å	13.676(2)	15.958(3)
b, Å	14.951(2)	16.373(7)
c, Å	15.509(2)	10.17(1)
α, deg		102.10(7)
β, deg	92.570(9)	93.29(4)
γ, deg		96.28(2)
V, Å^3	3168.1(6)	2574(3)
Z	8	2
D_{calcd}, g·cm^{-3}	2.981	1.748
μ, cm^{-1}	125.95	41.31
λ(Mo Kα), Å	0.710 69	0.710 69
R^a	0.048	0.031
$R_w{}^b$	0.054	0.042
GOF^c	1.93	1.79

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. [c] $GOF = \{\sum w(|F_o| - |F_c|)^2/(M - N)\}^{1/2}$, where M = number of reflections and N = number of parameters.

The structure of **1** was solved by direct methods[11] and expanded using Fourier techniques.[12] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were put at calculated positions without refinement. The final R and R_w factors were 0.048 and 0.054, respectively, for 4828 unique reflections with $I > 3.00\sigma(I)$. The maximum and minimum residual peaks on the final difference Fourier map are 2.24 and −2.53 e/Å^3, respectively, which appear in the vicinity of the W atoms.

The structure of **2**•$CHCl_3$ was also solved by direct methods[11] and expanded using Fourier techniques.[12] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions without refinement. Some carbon atoms from the phenyl groups were refined with relatively higher anisotropic temperature factors. The crystal contains one $CHCl_3$ solvent molecule in an asymmetric unit, which was refined isotropically without including the hydrogen atom. The final R and R_w factors were 0.031 and 0.042, respectively, for 7743 unique reflections with $I > 3.00\sigma(I)$. The maximum and minimum residual peaks on the final difference Fourier map are 0.94 and −0.72 e/Å^3, respectively.

Neutral atom scattering factors were taken from the Cromer and Waber.[13] Crystallographic calculations were carried out with a teXsan crystallographic software package of the Molecular Structure Corp. (1985 and 1992). Crystallographic data for **1** and **2**•$CHCl_3$ are summarized in Table 3.

Acknowledgment. J.-P.L. thanks the Japan Society for the Promotion of Science (JSPS) for a postdoctoral fellowship.

Supporting Information Available: Packing diagrams of **1** and **2**•$CHCl_3$ (2 pages). X-ray crystallographic files, in CIF format, for the two structures are available on the Internet only. Ordering and access information is given on any current masthead page.

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