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Aggregation of the Half-Sandwich Trisulfido Complex of Tungsten with Silver Ions: Synthesis of a Cyanide-Bridged Helical Polymer $\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}_\infty$ and a Cyclic Cluster $[(\eta^5\text{-}C_5Me_5)WS_3Ag]_4$

Jian-Ping Lang and Kazuyuki Tatsumi*

Research Center for Materials Science, and Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

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Introduction

In our laboratory, a series of heterometallic sulfido clusters and polymers have been synthesized using the half-sandwich trisulfido complex anions $[(\eta^5\text{-}C_5Me_5)MS_3]^{n-}$ [M = Nb, Ta (n = 2),[1] M = W, Mo (n = 1)[2]] as building components.[3] For instance, the tungsten trisulfido complex was assembled with coinage metal ions by the reactions of $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ with CuX (X = Br, NCS) and AgBr, which resulted in the formation of double-cubane clusters $(PPh_4)_2\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Cu_6X_6\}$[3b,e] and a ladder polymer $[(\eta^5\text{-}C_5Me_5)WS_3Ag_2Br]_\infty$, respectively.[3c]

In this context, we were interested in introducing metal cyanide into our cluster syntheses, because of the ability of cyanide to bridge various metal atoms.[4−6] Thus we carried out the reaction of $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ with AgCN, and here report the isolation and structures of an unusual helical polymer $\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}_\infty$ (**1**) and an octanuclear cluster $[(\eta^5\text{-}C_5Me_5)WS_3Ag]_4$ (**2**). The latter cluster was also obtained in high yield from the reaction of $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ with $[Ag(CH_3CN)_4](PF_6)$.

Table 1. Bond Lengths (Å) and Angles (deg) for $\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}_\infty$ (**1**)

W(1)−Ag(1)	2.976(1)	W(1)−Ag(2)	2.921(1)
W(2)−Ag(1)	2.980(1)	W(2)−Ag(3)	2.932(1)
W(1)−S(1)	2.321(4)	W(1)−S(2)	2.212(4)
W(1)−S(3)	2.185(4)	W(2)−S(4)	2.231(4)
W(2)−S(5)	2.260(4)	W(2)−S(6)	2.222(4)
Ag(1)−S(1)	2.472(4)	Ag(1)−S(2)	2.571(2)
Ag(1)−S(4)	2.451(2)	Ag(1)···S(5)	2.81
Ag(2)−S(1)	2.483(5)	Ag(2)−S(3)	2.479(4)
Ag(3)−S(5)	2.492(4)	Ag(3)−S(6)	2.483(4)
Ag(2)−C(21)	2.08(1)	Ag(3*)−N(1)	2.11(2)
N(1)−C(21)	1.14(2)		
Ag(1)−W(1)−Ag(2)	64.32(5)	Ag(1)−W(2)−Ag(3)	65.79(4)
S(1)−W(1)−S(2)	108.7(1)	S(1)−W(1)−S(3)	109.6(2)
S(2)−W(1)−S(3)	102.9(2)	S(4)−W(2)−S(5)	106.6(2)
S(4)−W(2)−S(6)	104.5(2)	S(5)−W(2)−S(6)	111.1(2)
S(1)−Ag(1)−S(2)	93.9(1)	S(1)−Ag(1)−S(4)	131.0(2)
S(2)−Ag(1)−S(4)	122.2(1)	S(1)−Ag(2)−S(3)	95.8(1)
S(5)−Ag(3)−S(6)	95.9(1)	S(5)−Ag(3)−N(1*)	126.4(4)
S(6)−Ag(3)−N(1*)	133.8(4)	W(1)−S(1)−Ag(1)	76.7(1)
W(1)−S(1)−Ag(2)	74.8(1)	W(1)−S(3)−Ag(2)	77.3(1)
W(2)−S(4)−Ag(1)	78.9(1)	W(2)−S(5)−Ag(3)	76.0(1)
W(2)−S(6)−Ag(3)	76.9(1)	Ag(1)−S(1)−Ag(2)	78.6(1)
Ag(2)−C(21)−N(1)	173(1)	Ag(3*)−N(1)−C(21)	179(1)

Results and Discussion

When 3 equiv of AgCN was added to a red solution of $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ in CH_3CN, the color of the solution darkened immediately. The solution was allowed to stir for 1 min, and unreacted AgCN and dark red powder were immediately filtered off. Diethyl ether was carefully layered on the filtrate, from which dark red plates (**1**, 35% yield) and large black plates (**2**, <1% yield) were formed. Compound **1** is practically insoluble in common organic solvents, whereas **2** dissolves readily in $CHCl_3$ and DMF, and slightly in CH_3CN. Both compounds are stable toward oxygen and moisture. The X-ray fluorescence microanalysis of **1** and **2** indicated that they contain tungsten, silver, and sulfur in the ratios of 2.0:2.8:5.8 and 1.0:1.0:3.1, respectively. The formula and structures of **1** and **2** were established by the single-crystal X-ray analysis, and the results of their elemental analyses were consistent with the formulation.

The one-dimensional polymer structure of **1** is shown in Figure 1a, and the bond distances and angles are given in Table 1. The polymer backbone is made of the pentanuclear $\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3\}$ fragments and μ-cyanide anions. Each cyanide links two cluster fragments through interactions with Ag(2) of one cluster and Ag(3*) of another, forming an intriguing helical array of the repeating $\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}$ units. Because compound **1** crystallizes in a centrosymmetric space group $P2_1/c$, there are two helical strands with opposite chirality in a unit cell. The Ag−CN−Ag portion is practically linear, with the Ag(2)−C(21)−N(1) and C(21)−N(1)−Ag(3*) angles being 173(1)° and 179(1)°, respectively. We assigned the atom coordinated at Ag(2) to carbon and that bound to Ag(3*) to nitrogen, on the basis of the peak heights on the Fourier map and the bond lengths. The resulting Ag(2)−C(21) distance of 2.08(1) Å and the Ag(3*)−N(1) distance of 2.11(2) Å are close to those found in $(^nPr_4N)[WS_4Ag(CN)]$

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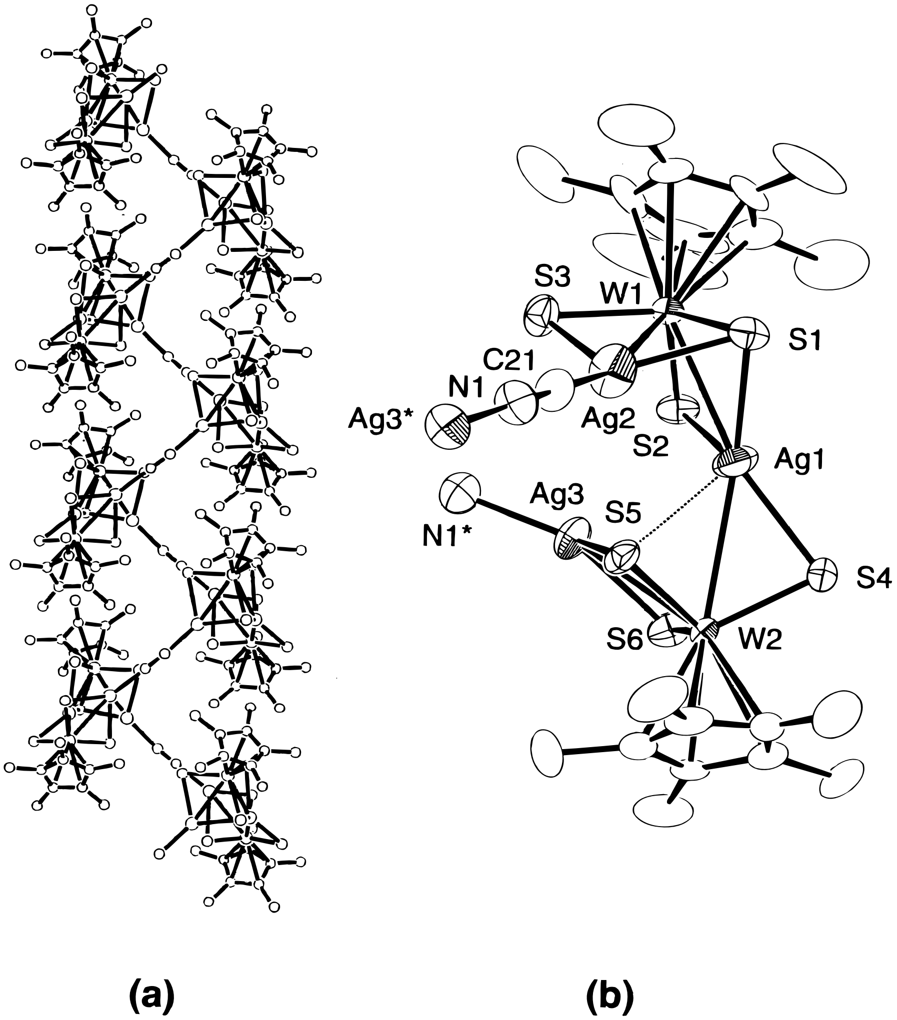

Figure 1. (a) Extended structure of $\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}_\infty$ (**1**) looking down the *c* axis. (b) The structure of the repeating unit of **1**, drawn with labeling scheme and 50% thermal ellipsoids.

[Ag−C = 2.09(1) Å][7a] and {Ag[N(CN)$_2$]} [Ag−N = 2.11(1) Å].[7b] However, the possibility of a partial disorder of atoms arising from the opposite orientation of cyanide cannot be ruled out in the X-ray structure of **1**.

The structure of the repeating pentanuclear cluster unit is shown in Figure 1b. This cluster is made of two $(\eta^5\text{-}C_5Me_5)WS_3$-Ag subunits that are connected by Ag(1). Coordination of sulfur atoms at Ag(1) occurs in an unsymmetric way. Bonding with the three sulfur atoms, namely S(1), S(2), and S(4), is relatively strong, forming a slightly pyramidalized Y-shape coordination geometry. In addition, we noticed a weak interaction between Ag(1) and S(5). The coordination of Ag(1) by sulfur is unsymmetrical. Because of the unsymmetrical coordination environment at Ag, W−S bond distances also vary substantially from 2.185(4) Å to 2.321(4) Å. The shortest W−S distance is comparable with the known W═S double bond lengths in $(\eta^5\text{-}C_5Me_5)W(S)_2(SCH_2Ph)$ (2.149(3) Å] and $(PPh_4)\{(\eta^5\text{-}C_5Me_5)W(S)[SC(Ph){=}C(Ph)S]\}$ [2.186(2) Å).[2a] On the other hand, two Ag(1)−W distances are nearly the same, with the average being 2.978 Å, which is slightly longer than Ag(2)−W(1) and Ag(3)−W(2). These Ag−W distances are not unusual as compared with the structures of $[Ag_4W_2S_8(PPh_3)_4]$ [2.997(3) Å],[8] $[\gamma\text{-MePyH}]_\infty[AgWS_4]_\infty$ [2.948(2) Å],[9a] and $[NH_3C(CH_2OH)_3]_\infty$-$[AgWS_4]_\infty\cdot(DMF)_\infty$ [2.931(2) Å],[9b] and suggest that dative interactions exist between the d^{10} Ag(I) and d^0 W(VI) centers.

Although cyanide-bridged metal polymers are ubiquitous, those having helical chain structures are very rare. An example is K[Cu(μ-CN)(CN)],[10] the structure of which consists of a spiral chain arrangement of Cu and μ-CN, and each Cu atom assumes a trigonal coordination geometry with the C atom of one μ-CN group, the N atom of another, and the C atom of one terminal CN group. The cluster structure of $[(OC)Pd(\mu\text{-}CN)Mn(\eta\text{-}C_5H_4\text{-}Me)(CO)_2]_4$ was reported to contain an orthogonal arrangement of helical units.[11] On the other hand, the CuCN adduct of thiomolybdate $(Me_4N)_2[MoS_4(CuCN)_2]$, which is closely related to **1**, has a polymer structure that consists of an infinite zigzag chain of $(CuCN)_\infty$.[12]

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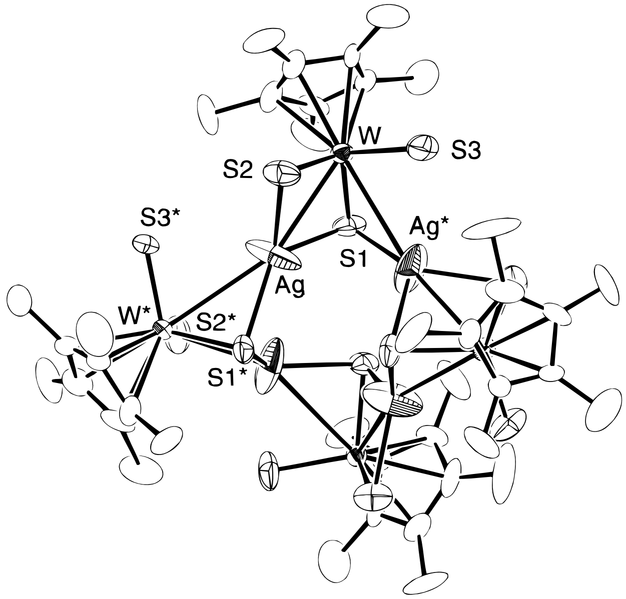

Figure 2. Molecular structure of $[(\eta^5\text{-}C_5Me_5)WS_3Ag]_4$ (**2**), with labeling scheme and 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W−Ag 2.948(2), W−Ag* 3.266(3), W−S(1) 2.273(4), W−S(2) 2.213(6), W−S(3) 2.165(5), Ag−S(1) 2.495(6), Ag−S(1*) 2.463(6), Ag−S(2) 2.489(6); Ag−W−Ag* 63.3(1), W−Ag−W* 154.6(1), S(1)−Ag−S(1*) 127.8(2), S(1)−Ag−S(2) 95.4(2), S(1)−Ag−S(2*) 129.4(2).

The X-ray-derived molecular structure of **2** is shown in Figure 2, with the selected bond distances and angles in the caption. The molecule may be viewed as a cyclic tetramer of $[(\eta^5\text{-}C_5Me_5)WS_3Ag]$, assuming a crystallographic $\bar{4}$ symmetry. Thus, four W atoms are coplanar, whereas Ag atoms are situated alternatively above and below the W_4 plane, forming a "four-flier pinwheel" structure. Interestingly, each Ag atom moves toward one W atom, so that the W−Ag distance is substantially shorter than W−Ag*. The coordination geometry at Ag is again a slightly pyramidalized Y-shape, and there is no other short contact with S atoms. Each $[(\eta^5\text{-}C_5Me_5)WS_3]^-$ unit carries three distinctively different S atoms, that is, terminal S, μ_2−S, and μ_3−S, which results in a large variation of W−S bond lengths. It is worth noting that several M/M′/S (M = Mo, W; M′ = Cu, Ag) clusters are known to contain $M_4M'_4$ cores that may be relevant to **2**. Examples are $[M_4Cu_4S_{12}O_4]^{4-}$ [13a] and $[W_4Ag_5S_{16}]_\infty[Nd(DMF)_8]_\infty$,[13b] where either Cu or Ag atom is coordinated by four S atoms with a distorted tetrahedral geometry.

Because the minor product **2** does not contain cyanide ligands, we searched for a better synthetic route to **2**. Thus $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ was reacted with 1 equiv of $[Ag(CH_3CN)_4](PF_6)$ in CH_3CN, and a subsequent standard workup gave rise to **2** in 85% yield. Even if the ratio of the reactants was varied from 2:1 to 1:3, the isolable product was only the octanuclear cluster. The IR spectrum of **2** is featured by the W=S stretching band at 480 cm^{-1} and W−S$_{br}$ bands at 457/429/407 cm^{-1}. The ^{1}H NMR spectrum shows a sharp singlet resonance at 2.27 ppm for the η^5-C_5Me_5 protons, and the UV−Vis spectrum shows a characteristic band at 405 nm.

Experimental Section

Table 2. Crystallographic Data for $\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}_\infty$ (**1**) and $[(\eta^5\text{-}C_5Me_5)WS_3Ag]_4$ (**2**)

	1	2
formula	$C_{21}H_{30}Ag_3NS_6W_2$	$C_{40}H_{60}Ag_4S_{12}W_4$
M	1180.14	2092.52
crystal system	monoclinic	tetragonal
space group	$P2_1/c$	$P\bar{4}2_1c$
a, Å	15.415(5)	17.824(4)
b, Å	9.616(6)	
c, Å	21.659(4)	8.558(3)
β, deg	109.91(2)	
V, Å^3	3018(1)	2719.0(9)
Z	4	2 (tetramer)
ρ_{calcd}, g/cm^3	2.60	2.56
λ(Mo−Kα), Å	0.71069	0.71069
μ, cm^{-1}	99.4	103.3
R[a]	0.046	0.064
R_w[b]	0.054	0.073

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

General Procedures. 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. $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ was prepared as described previously,[2a] and $[Ag(CH_3CN)_4](PF_6)$ was prepared according to the literature method.[14] Other chemicals were used as purchased. ^{1}H NMR spectrum for **2** was recorded on a Varian UNITYplus-500 spectrometer at ambient temperature, and chemical shifts are relative to undeutetated impurity of $CDCl_3$. IR spectra were recorded on a Perkin-Elmer 2000FT-IR spectrophotometer using KBr pellets. UV−Vis spectrum for **2** was measured on JASCO V-560 spectrophotometer. C, H, N, and S analyses were performed on a LECO−CHNS microanalyzer.

Reaction of $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ with AgCN. AgCN (0.053 g, 0.39 mmol) was added to a red solution of $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ (0.10 g, 0.13 mmol) in CH_3CN (20 mL). The solution immediately turned dark red and the mixture was stirred for 1 min at room temperature and then filtered. The two products were obtained from the dark red filtrate by layering diethyl ether (20 mL) onto it. Dark red plates of $\{[(\eta^5\text{-}C_5Me_5)WS_3]_2Ag_3(CN)\}_\infty$ (**1**) were isolated in 35% yield, and the trace amount of $[(\eta^5\text{-}C_5Me_5)WS_3Ag]_4$ (**2**) was isolated as large black plates. **1**: Anal. Calcd for $C_{21}H_{30}Ag_3NS_6W_2$: C, 21.37; H, 2.57; N, 1.19; S, 16.30. Found: C, 21.43; H, 2.59; N, 1.30; S, 16.61. IR (KBr disk): 2158 (m), 1487 (m), 1431 (m), 1374 (s), 1019 (s), 805 (m), 441 (s), 424 (w), 409 (s) cm^{-1}.

Reaction of $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ with $[Ag(CH_3CN)_4](PF_6)$. $[Ag(CH_3CN)_4](PF_6)$ (0.06 g, 0.15 mmol) in CH_3CN (10 mL) was added to a solution of $(PPh_4)[(\eta^5\text{-}C_5Me_5)WS_3]$ (0.11 g, 0.15 mmol) in CH_3CN (15 mL). Black microcrystals of $[(\eta^5\text{-}C_5Me_5)WS_3Ag]_4$ (**2**) gradually formed and the mixture was allowed to stir for 3 h at room temperature. After filtration, the resulting black microcrystals were washed with CH_3CN:Et_2O (1:5) and dried in vacuo. Yield: 0.067 g (85%). **2**: Anal.Calcd for $C_{10}H_{15}AgS_3W$: C, 22.96; H, 2.90; S, 18.39. Found: C, 23.09; H, 2.95; S, 18.76. UV−Vis ($CHCl_3$, λ_{max}/nm, ϵ/M^{-1}cm^{-1}): 405 (17700). IR (KBr disk): 1486 (m), 1455 (w), 1429 (m), 1373 (s), 1020 (s), 804 (m), 482 (m), 457 (w), 429 (s), 407 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.27 (60H, s, η^5-C_5Me_5).

X-ray Diffraction Crystallography. Single crystals of **1** and **2** 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 (0.71079 Å). A dark red plate of **1** with dimensions 0.35 × 0.20 × 0.15 mm and a black plate of **2** with dimensions 0.70 × 0.30 × 0.10 mm were put on glass fibers. 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 $25.0° < 2\theta < 30.0°$ for **1**, and $6.5° < 2\theta < 30.0°$ for **2**. Three standard reflections were monitored at regular intervals, and there was no sign of significant decay throughout the data collection. An empirical absorption correction using the ψ scan technique was applied to each data set, which resulted in transmission factors ranging from 0.36 to 0.98 for **1**, and from 0.55 to 1.00 for **2**. Each data set was also corrected

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for Lorentz and polarization effects. The summary of the crystal data are given in Table 2.

The structures were solved by direct methods [15a] and expanded using Fourier techniques,[15b] using 3579 observed reflections for **1** and 1696 observed reflections for **2** with $I > 3.00\sigma(I)$. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were put at calculated positions without refinement. The maximum and minimum residual peaks on the final difference Fourier map are 3.31 and −2.01 e/Å^3 for **1**, and 4.14 and −3.14 e/Å^3 for **2**, which appear in the vicinity of the W and Ag atoms.

Neutral atom scattering factors were taken from Cromer and Waber,[16a] and anomalous dispersion effects were included in F_c.[16b] Crystallographic calculations were carried out with a teXsan crystallographic software package of the Molecular Structure Corp. (1985 and 1992).

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **1** and **2** are available on the Internet only. This material is available free of charge at http://pubs.acs.org.

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