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The Heterobimetallic Polymeric Zigzag Chain $[(W_4S_{16}Ag_4)^{4-}]_n$ Derived from the Linear Chain $[(WS_4Ag)^-]_n$: Synthesis, Characterization, and Structure of $[W_4S_{16}Ag_4{\cdot}2Ca(DMSO)_6]_n$ (DMSO = Dimethyl Sulfoxide)

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Introduction

The thiometalates, such as tetrathiotungstate and tetrathiomolybdate, have been extensively used in the synthesis of transition metal sulfides.[1] For the tungsten(molybdenum)−silver−sulfur system, many discrete complexes have been obtained, such as $[(PPh_3)_2AgS_2MS_2Ag(PPh_3){\cdot}0.8CH_2Cl_2]$ (linear),[2] $[Et_4N][(PPh_3)_2AgS_3MOCu(CN)]$(butterfly-type),[3] $[\{Ag(Ph_3P)\}_3MS_4\{S_2P(OEt)_2\}]$(cubane-like),[4] $[(PPh_3)_4Ag_4W_2S_8]$(cage),[5] $[Bu_4N]_2[M_2Ag_3(\mu_3\text{-}S)_2(\mu\text{-}S)_4S_2Et_2dtc]$,[6] and $[Ag_6S_6M_2(SCMe_3)_2(O)_2(PPh_3)_4]$ (double-cubane-like)[7] (M = Mo, W), but polymeric complexes of this kind are fewer, with their general polymeric configuration being linear chain, e.g. $[PPh_4{\cdot}AgMoS_4]_n$,[8] $[AgMS_4{\cdot}4\text{-}MePyH]_n$,[9] and $[tmenH_2{\cdot}W_2Ag_2S_8{\cdot}tmen{\cdot}H_2O]_n$[10] (M = Mo, W; tmen = *N,N,N′,N′*-tetramethylethylenediamine). Recently, the assembly of WS_4^{2-} and Ag^+ has been found to be flexible in our laboratory; through nonbonding interactions with the complementary small molecules (or cations) and the solvent, they can assemble into polymeric complexes with different configurations. For example, novel polymeric complexes $[WS_4Ag{\cdot}NH_3C(CH_2OH)_3{\cdot}H_2O]_n$[11] and $[W_4S_{16}Ag_5{\cdot}Nd(DMF)_8]_n$[12] were isolated by addition of a little water in the solution of the linear chain complex $[WS_4Ag{\cdot}NH_3C(CH_2OH)_3{\cdot}2DMF]_n$ in EtOH and $Nd(NO_3)_3{\cdot}6H_2O$ in the reaction of ammonium tetrathiotungstate and silver nitrate in DMF, respectively. Herein, the synthesis, characterization, and structure of another novel polymeric tungsten−silver−sulfur complex, $[W_4S_{16}Ag_4{\cdot}2Ca(DMSO)_6]_n$, are reported. This complex is obtained by addition of bivalent cations Ca(II) in the solution of the linear chain complex $[WS_4Ag{\cdot}HNEt_3{\cdot}DMF]_n$[13] in DMSO (DMSO = dimethyl sulfoxide).

Table 1. Crystal Data and Refinement Details for the Structure of $[W_4S_{16}Ag_4{\cdot}2Ca(DMSO)_6]_n$ (**2**)

compound	$[W_4Ag_4S_{16}{\cdot}2Ca(DMSO)_6]_n$
formula	$C_{24}H_{72}O_{12}Ca_2S_{28}Ag_4W_4$
M_f	2697.67
a, Å	15.388(9)
b, Å	16.882(5)
c, Å	17.784(4)
α, deg	115.02(2)
β, deg	102.98(3)
γ, deg	77.41(4)
V, Å^3	4039.7
Z	2
space group	$P\bar{1}$
T, °C	23
Λ(Mo Kα), Å	0.710 73
ρ_{calcd}, g/cm^3	2.22
μ(Mo−Kα), cm^{-1}	75.9
R^a	0.067
$R_w{}^b$	0.080

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F_o|^2) + (0.010|F_o|)^2 + 1.00]^{-1}$.

Experimental Section

All experiments were carried out in the air. $(NH_4)_2WS_4$ was obtained by published procedures.[14] Other chemicals were used as purchased. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer using KBr pellets. Elemental analyses were performed by the Elemental Analysis Laboratories in our Institute.

$[WS_4Ag{\cdot}HNEt_3{\cdot}DMF]_n$ (1). To a solution of $(NH_4)_2WS_4$ (0.70 g, 2 mmol) in 5 mL of DMF was added a solution of $AgNO_3$ (0.68 g, 4 mmol) and triethylamine (0.28 mL, 2 mmol) in 10 mL of CH_3CN with stirring, and then a dark precipitate of AgS was formed and removed by filtration. A 0.58 g yield of orange crystals was obtained from allowing the orange filtrate to stand at ambient temperature in air for 1 week. Anal. Calcd (found): C, 18.16 (18.32); H, 3.89 (3.81); N, 4.71 (4.79). IR (KBr pellet, cm^{-1}): W−μ_2-S, 451.8 (vs) and 437.8 (vs); C=O, 1660.6 (vs) and 1647.1 (vs).

$[W_4S_{16}Ag_4{\cdot}2Ca(DMSO)_6]_n$ (2). To a solution of complex **1** (0.30 g, 0.5 mmol) in 10 mL of DMSO was added a solution of $Ca(NO_3)_2{\cdot}4H_2O$ (0.24 g, 1 mmol) in 5 mL of DMSO with stirring; no precipitate was formed. A 0.25 g yield of orange-yellow crystals was obtained by allowing the mixed solution to stand for several days at ambient temperature in air. Anal. Calcd (found): C, 10.69 (10.59); H, 2.69 (2.71); S, 33.28 (33.47); W, 27.26 (27.11). IR (KBr pellet, cm^{-1}): W−S_t, W−μ_2-S, and W−μ_3-S, 487.9 (m), 447.4 (vs), and 412.7 (shoulder); S=O, 1020.2 (vs), 1010.5 (vs), and 995.1 (vs).

Crystal Structure Determination. The X-ray single crystal structure of complex **1** has been determined before.[13] Crystals of complex **2** were selected and mounted on glass fibers for the X-ray single-crystal diffraction experiment. The crystallographic and machine data are given in Table 1 and the Supporting Table S1. Diffraction data were collected on a CAD-4 κ-geometry diffractometer by use of Mo Kα radiation. Cell constants and orientation matrixes were obtained from least-squares methods by using setting angles of 25 reflections in the range 12° < 2θ < 50°. Intensities were corrected for polarization and Lorentz factors and for absorption by using empirical psi-scan data and the method of Walker and Stuart (DIFABS).[15]

The structure was solved by direct method using MULTAN, and the positions of three heavy atoms were obtained from *E*-map. The remaining non-hydrogen atoms were located from difference Fourier map. No attempt was made to locate hydrogen atoms for the structural determination. The sulfur atoms of five DMSO groups, of which three are bonded to the Ca1 atom and other two to the Ca2 atom, were disordered; the populations of the disordered sulfur atoms were fixed at 0.5. One of the six DMSO groups around the Ca2 atom was refined

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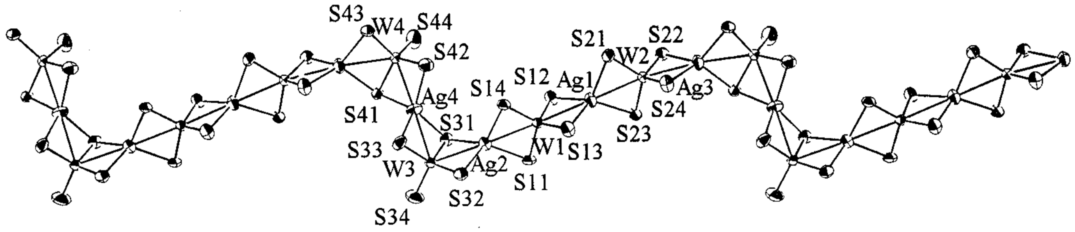


Figure 1. ORTEP drawing of a portion of the polymeric anion of **2** (thermal ellipsoids at 50% probability level).

Table 2. Atomic Coordinates and Thermal Parameters for the Anion of $[W_4Ag_4S_{16}{\cdot}2Ca(DMSO)_6]_n$ (**2**)

atom	*x*	*y*	*z*	B_{eq}[a] (Å^2)
W1	0.2920(1)	0.13801(9)	−0.10298(8)	2.64(4)
W2	0.1383(1)	0.42257(8)	0.19103(8)	2.44(4)
W3	0.4263(1)	−0.15566(9)	−0.40022(8)	2.94(4)
W4	0.0636(1)	−0.26861(9)	−0.49902(9)	3.09(4)
Ag1	0.2122(2)	0.2831(2)	0.0405(2)	4.30(9)
Ag2	0.3566(2)	−0.0010(2)	−0.2568(2)	4.09(9)
Ag3	0.0985(2)	0.5654(2)	0.3530(2)	4.45(9)
Ag4	0.2449(2)	−0.2108(2)	−0.4435(2)	4.54(9)
S11	0.3788(7)	0.1590(6)	−0.1742(6)	4.0(3)
S12	0.1607(7)	0.2178(6)	−0.1151(5)	4.0(3)
S13	0.3581(8)	0.1745(7)	0.0287(6)	4.8(3)
S14	0.2690(7)	−0.0006(6)	−0.1507(6)	4.0(3)
S21	0.0942(7)	0.2914(5)	0.1263(6)	4.2(3)
S22	0.0170(7)	0.5185(6)	0.2015(6)	4.0(3)
S23	0.2251(7)	0.4480(5)	0.1240(6)	4.0(3)
S24	0.2159(8)	0.4304(6)	0.3138(6)	4.5(3)
S31	0.2977(7)	−0.0650(6)	−0.4144(5)	3.7(3)
S32	0.5021(7)	−0.1087(7)	−0.2724(6)	4.3(3)
S33	0.4029(8)	−0.2900(6)	−0.4327(7)	4.8(3)
S34	0.5102(9)	−0.1629(9)	−0.4854(7)	7.6(4)
S41	0.1523(7)	−0.2821(5)	−0.5891(5)	3.3(3)
S42	0.1310(8)	−0.2213(7)	−0.3666(6)	4.8(3)
S43	0.0146(8)	−0.3925(7)	−0.5263(6)	5.6(3)
S44	−0.0513(9)	−0.1730(8)	−0.5065(9)	7.6(5)

[a] $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

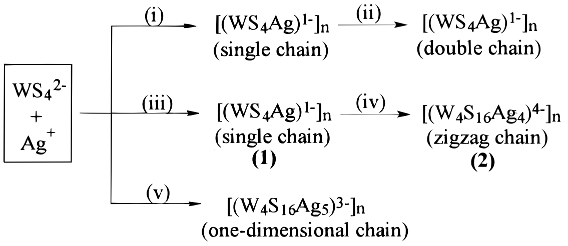
Table 3. Selected Bond Distances (Å) for $[W_4Ag_4S_{16}{\cdot}2Ca(DMSO)_6]_n$ (**2**)

W1−Ag1	2.971(3)	W4−S41	2.240(11)
W1−Ag2	2.959(3)	W4−S42	2.221(9)
W1−S11	2.203(13)	W4−S43	2.201(12)
W1−S12	2.193(10)	W4−S44	2.140(12)
W1−S13	2.210(9)	Ag1−S12	2.514(9)
W1−S14	2.207(9)	Ag1−S13	2.557(11)
W2−Ag1	2.978(3)	Ag1−S21	2.567(12)
W2−Ag3	2.960(3)	Ag1−S23	2.572(8)
W2−S21	2.199(9)	Ag2−S11	2.528(9)
W2−S33	2.174(9)	Ag2−S14	2.553(12)
W2−S23	2.188(12)	Ag2−S31	2.562(8)
W2−S24	2.207(10)	Ag2−S32	2.544(10)
W3−Ag2	2.974(3)	Ag3−S22	2.563(9)
W3−Ag4	2.969(4)	Ag3−S24	2.525(10)
W3−S31	2.259(9)	Ag3−S41[b]	2.583(10)
W2−S32	2.201(9)	Ag3−S43[b]	2.517(13)
W3−S33	2.182(10)	Ag4−S31	2.567(11)
W3−S34	2.151(16)	Ag4−S33	2.515(11)
W4−Ag3[a]	2.968(3)	Ag4−S41	2.576(8)
W4−Ag4	2.975(4)	Ag4−S42	2.528(14)

[a] $x, y - 1, z - 1$. [b] $x, y + 1, z + 1$.

using a rigid model, in which the positions of sulfur and carbon atoms changed with that of the corresponding oxygen atom. The refinement of structure was performed by full-matrix least-squares techniques using the MolEN program package.[16] All calculations were carried out on a COMPAQ PROLINEA 4/50 computer. Atomic scattering factors were taken from ref 17. Atomic coordinates and thermal parameters for the anion are listed in Table 2, and those for the cations in Supporting Table S2.

Scheme 1



(i) $NH_3C(CH_2OH)_3^+$/DMF; (ii) $H_2O/NH_3C(CH_2OH)_3^+$; (iii) $HNEt_3^+$/DMF; (iv) Ca^{2+}/DMSO; (v) Ln^{3+}/DMF

Results and Discussion

Synthesis of $[W_4S_{16}Ag_4{\cdot}2Ca(DMSO)_6]_n$ (2). The linear chain complex **1** was employed as a starting material to synthesize the zigzag chain complex **2**. In principle, Ca^{2+} cations, which as complementary ions were added in the solution of complex **1** in DMSO, are oxygenphilic and not sulfurphilic; they don't readily react with the cluster anions containing only metallic W and Ag and non-metallic S atoms in the solution, but tend to be coordinated by oxygen atoms of DMSO molecules to form larger complex bivalent cations $Ca(DMSO)_6^{2+}$. These complex cations can induce the cluster anions in the solution to assemble into the anionic zigzag chains of **2** with tetravalent anionic cluster fragments $(W_4S_{16}Ag_4)^{4-}$ as cyclic units through charge-charge interaction and other nonbonding interactions; furthermore, they have an appropriate size, and can crystallize from the solution with the zigzag chain anions.

Along with **2**, two other novel polymeric W/Ag/S complexes, $[WS_4Ag{\cdot}NH_3C(CH_2OH)_3{\cdot}H_2O]_n$[11] and $[W_4S_{16}Ag_5{\cdot}Ln(DMF)_8]_n$,[12] were also derived from the system of ammonium tetrathiotungstate and silver nitrate (see Scheme 1). Hydrogen bonding played a crucial role in the formation of the former double chain complex which was achieved only through addition of a little water in a solution of the linear chain complex $[WS_4Ag{\cdot}NH_3C(CH_2OH)_3{\cdot}2DMF]_n$ in EtOH. The latter was obtained through addition of $Ln(NO_3)_3{\cdot}xH_2O$ into the reaction of WS_4^{2-} and Ag^+; therein, trivalent complex cations $Ln(DMF)_8^{3+}$, also an inductor like $Ca(DMSO)_6^{2+}$, induced the assembly of WS_4^{2-} and Ag^+ into $[(W_4S_{16}Ag_5)^{3-}]_n$ with trivalent anionic cluster fragments as cyclic units.

Structure of $[W_4S_{16}Ag_4{\cdot}2Ca(DMSO)_6]_n$ (2). Complex **2** crystallized in the triclinic system with space group $P\bar{1}$. The X-ray single-crystal structural analysis showed that the cyclic unit $(W_4S_{16}Ag_4)^{4-}$ of the polymeric anion is related with two bivalent cations $Ca(DMSO)_6^{2+}$. The ORTEP drawing of a portion of the anion is shown in Figure 1, and selected bond distances (Å) and angles (deg) are listed in Tables 3 and 4, respectively. The configuration of polymeric anions can be viewed as a zigzag chain which is propagated by cell transition along the *b* + *c* axis. The edges formed by (W3, Ag4, W4) and (W3, Ag2, W1, Ag1, W2, Ag3, W4[b]) are approximately alternately perpendicular to each other; the average angle of Ag−W−Ag at corners is 93.7°, and the average values of

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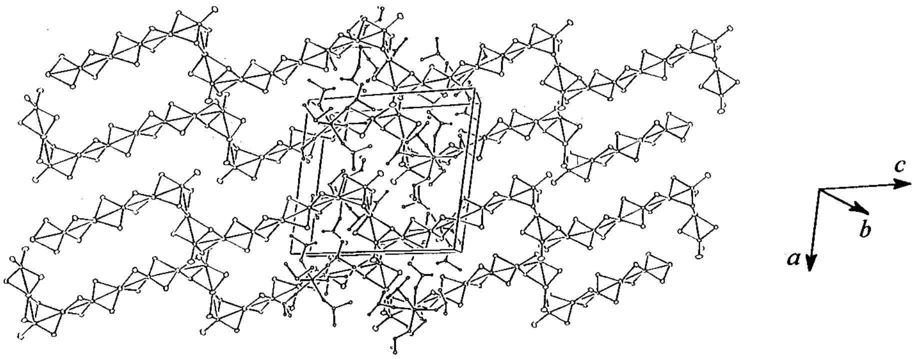

Figure 2. Packing drawing of **2**.

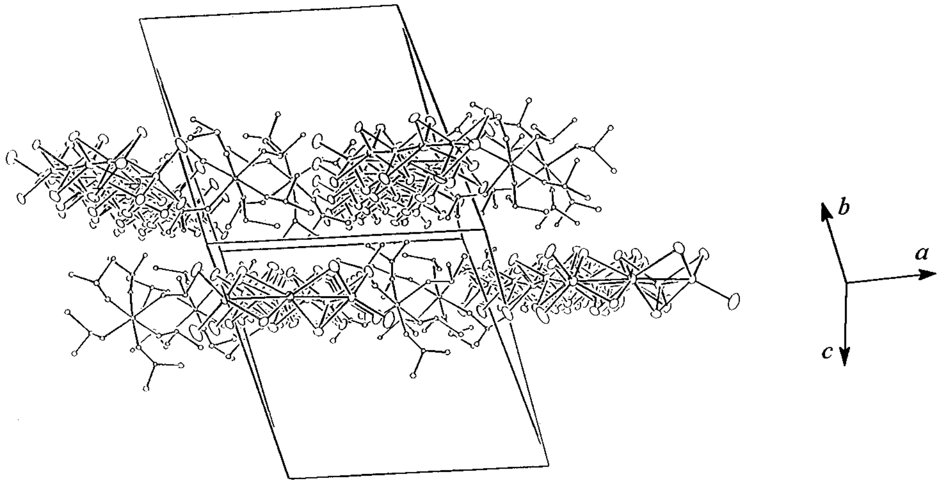

Figure 3. Packing drawing of **2**.

Table 4. Selected Bond Angles (deg) for $[W_4Ag_4S_{16}\cdot 2Ca(DMSO)_6]_n$ (**2**)

Ag1−W1−Ag2	174.4(1)	S22−Ag3−S24	91.8(3)
S11−W1−S12	107.7(4)	S24−Ag3−S43^b	121.5(5)
S12−W1−S14	107.6(4)	S41^b−Ag3−S43^b	93.3(3)
S13−W1−S14	107.1(4)	W3−Ag4−W4	176.1(1)
Ag1−W2−Ag3	169.9(2)	S31−Ag4−S33	93.3(4)
S21−W2−S22	106.6(4)	S33−Ag4−S42	120.5(4)
S22−W2−S24	113.1(4)	S41−Ag4−S42	93.4(3)
S23−W2−S24	107.7(4)	W1−S11−Ag2	77.1(4)
Ag2−W3−Ag4	86.77(9)	W1−S12−Ag1	78.0(4)
S31−W3−S32	112.8(3)	W1−S13−Ag1	76.7(3)
S32−W3−S34	108.2(5)	W1−S14−Ag2	76.5(4)
S33−W3−S34	107.1(6)	W2−S21−Ag1	76.9(4)
Ag3^a−W4−Ag4	100.7(1)	W2−S22−Ag3	76.9(4)
S41−W4−S42	112.8(5)	W2−S23−Ag1	77.0(3)
S42−W4−S44	107.1(4)	W2−S24−Ag3	77.1(3)
S43−W4−S44	107.8(6)	W3−S31−Ag2	75.9(3)
W1−Ag1−W2	176.5(1)	W3−S31−Ag4	75.6(3)
S12−Ag1−S13	92.6(4)	Ag2−S31−Ag4	105.5(4)
S13−Ag1−S23	117.4(4)	W3−S32−Ag2	77.2(3)
S21−Ag1−S23	91.3(3)	W3−S33−Ag4	78.1(4)
W1−Ag2−W3	172.9(1)	W4−S41−Ag3^a	75.6(3)
S11−Ag2−S14	92.9(3)	W4−S41−Ag4	75.9(3)
S14−Ag2−S32	113.6(4)	Ag3^a−S41−Ag4	124.9(4)
S31−Ag2−S32	93.4(4)	W4−S42−Ag4	77.3(4)
W2−Ag3−W4^b	169.0(2)	W4−S43−Ag3^a	77.6(4)

^{a} $x, y - 1, z - 1$. ^{b} $x, y + 1, z + 1$.

W−Ag−W and other Ag−W−Ag angles are 173.6 and 172.2°, respectively. W1 and W2 atoms are tetrahedrally coordinated by four μ_2-S atoms, and the other two W atoms are coordinated by one terminal S, two μ_2-S, and one μ_3-S. The coordination tetrahedral geometry around Ag atoms is largely distorted with the coordination angles ranging from 91.3 to 123.5°. Four Ag atoms display three different coordination environments, the Ag1 atom is coordinated by four μ_2-S atoms, the Ag2 and Ag3 atoms by one μ_3-S and three μ_2-S atoms, and the Ag4 atom by two μ_2-S and two μ_3-S atoms. The bond lengths of W-S$_t$, W-μ_2-S, and W-μ_3-S are apparently different, and their average values are 2.146, 2.199, and 2.250 Å, respectively. In comparison, the W−S$_t$, W−μ_2-S and W−μ_3-S bond lengths are 2.128, 2.190, and 2.248 Å in $[W_4Ag_5S_{16}\cdot Nd(DMF)_8]_n$[12] and 2.144, 2.217, and 2.242 Å in $[\{Ag(Ph_3P)\}_3WS_4\{S_2P(OEt)_2\}]$,[4a] respectively. The average Ag−S length of 2.548 Å is comparable to the values observed in other polymeric complexes, e.g., 2.55 Å in $[AgWS_4\cdot HNEt_3\cdot DMF]_n$[13] and 2.543 Å in $[W_4Ag_5S_{16}\cdot Nd(DMF)_8]_n$.[12] However, the average W−Ag length of 2.969 Å is shorter than those found in $[AgWS_4\cdot HNEt_3\cdot DMF]_n$[13] (2.983 Å) and in $[WS_4Ag\cdot NH_3C(CH_2OH)_3\cdot H_2O]_n$[11] (2.980 Å), but comparable to that in $[W_4Ag_5S_{16}\cdot Nd(DMF)_8]_n$[12] (2.964 Å).

Packing drawings viewed along two different orientations are shown in Figures 2 and 3. The larger bivalent cations $Ca(DMSO)_6^{2+}$ are arrayed among the anionic chains. Each Ca(II) cation is coordinated by six DMSO molecules with an approximately octahedral geometry, and the average Ca−O bond length is 2.31 Å. These simple complex cations $Ca(DMSO)_6^{2+}$ are well separated from each other and from the anionic chains. The shortest distance between two Ca atoms is 7.97 Å.

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Supporting Information Available: Complete listing of crystallographic data, atomic positional parameters and their estimated standard deviations, bond distances and angles, and anisotropic displacement parameters (8 pages). Ordering information is given on any current masthead page.

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