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Article

Double-Stranded W/Ag/S Chain Structure Generated from $[syn\text{-}\{WO(NCS)_2\}_2(\mu\text{-}S)_2]$ Building Blocks

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The dimeric W^V complex $[Et_4N]_4[syn\text{-}\{O{=}W(NCS)_3\}_2(\mu\text{-}S)_2]$, **1**, prepared from $[Et_4N]_2[WS_4]$, SCN^-, and Cd^{2+}, shows interesting reactivity patterns in that the thiocyanate *trans* to the oxo group can in part be replaced, initiated by Mn^{2+}, by dimethylformamide (DMF) to form $[Et_4N]_{2.5}[\{O{=}W(NCS)_{2.25}(DMF)_{1.25}\}_2(\mu\text{-}S)_2]$, **2**. With Ag^+, **1** undergoes partial replacement of SCN^- by DMF and coordinates to the silver ions to generate $\{[Et_4N]_{2.5}[\{W_2O_2(NCS)_2(\mu\text{-}S)_2\}(\mu\text{-}NCS)_2(DMF)\{Ag_{0.5}(SCN)\}]\}_n$, **3**. Compound **3** constitutes a polymeric double-stranded chain, with normal bonding interactions [via W–(μ-NCS)–Ag] between the two strands, and moderate intrastrand [W–(μ-NCS)···Ag] bonding. The crystal and molecular structures of the three compounds are described.

Introduction

The thiometalate family containing the early transition metals vanadium, molybdenum, or tungsten has been of continuous interest in the context of the biological significance (molybdenum- and vanadium-based nitrogenases,[1,2] molybdo- and tungstopterin cofactors in oxygenases[3,4]), industrial applications (hydrodesulfurization in petrochemistry[5,6]), and potential in material science such as nonlinear optics.[7] Starting from the anions $[MO_xS_{4-x}]^{2/3-}$ (M = Mo, W, V) with the metal in the d^0 configuration, dinuclear and trinuclear oxo−thiometal compounds containing the $\{E{=}M^{IV}(M^{VI}S_4)_2\}$ (M = Mo, W; E = O or S) core have been studied with respect to, inter alia, redox models of biological systems.[8,9] Common synthetic methods to generate these mixed d^2/d^0 systems are thermal decomposition[10] or acidification[11] of aqueous solutions of tetrathiometalates under aerobic conditions. A dinuclear compound containing d^1 Mo^V centers, viz. $[Mo_2(\eta^2\text{-}CS_3)_4(\mu{-}S_2)_2]^{2-}$, has been synthesized from $[MoS_4]^{2-}$ and CS_2.[12]

As has been pointed out previously,[13a] the thiomolybdenyl moiety can serve either as a nucleophilic entity, or as a source of sulfide ions. Thus, on one hand, various heterometallic cluster compounds have been synthesized with $[MoO_xS_{4-x}]^{2-}$

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as a multidentate ligand, including polymeric S=Mo(μ-S)Ag systems.[13b] On the other hand, removal of sulfide ions from $[MoS_4]^{2-}$ by transition metal ions forming insoluble sulfides allows for the introduction of non-sulfur terminal ligands to the residual thiomolybdate in a metathetical reaction. Exploiting this latter synthetic approach, we report on the preparation of new systems containing the [*syn*-$\{W^V{}_2O_2(\mu\text{-}S)_2\}]^{2+}$ core, generated from tetrathiotungstate(VI) and the sulfide scavenger Cd^{2+} in the presence of the compensating ligands SCN^- and DMF (dimethylformamide), and on successive reactions in the presence of Mn^{2+} or Ag^+.

Experimental Section

Materials and Methods. Starting compounds were obtained from commercial sources or prepared according to literature procedures ($[Et_4N]_2[WS_4]$ and $[Et_4N]_2[WOS_3]$[14]). IR spectra were obtained as KBr pellets with a Perkin-Elmer 1720 FT spectrometer. NMR spectra were recorded on a Varian Gemini 200 BB spectrometer with the normal spectrometer settings. Elemental analyses were carried out by combustion methods (C, H, N, S), flame AAS (Cd), and (Ag in compound **3**) ICP-MS (laser evaporation), employing silver metal for calibration.

Preparation of Complexes. $[Et_4N]_4[\{O{=}W(NCS)_3\}_2(\mu\text{-}S)_2]$, 1. To a solution of $[Et_4N]_2[WS_4]$ (0.28 g, 0.50 mmol) in 50 mL of acetonitrile and 5 mL of DMF were added $CdCl_2 \cdot 2H_2O$ (0.15 g, 0.65 mmol) and KSCN (0.20 g, 1.54 mmol). The mixture was stirred for ca. 5 h, during which time the color changed from yellow to red, and a yellow precipitate containing 29% Cd and 9.5% S formed. After filtration, red crystalline **1** was obtained by gas diffusion of diethyl ether into the filtrate. The same product has also been obtained by using $[Et_4N]_2[WOS_3]$ as precursor compound. Yield 0.10 g (30% based on W). Anal. Calcd for $C_{38}H_{80}N_{10}O_2S_8W_2$ ($M = 1332.3$ g mol^{-1}): C, 34.23; H, 6.05; N, 10.50; S, 19.24. Found: C, 34.17; H, 6.14; N, 10.71; S, 19.24.

$[Et_4N]_{2.5}[\{O{=}W(NCS)_{2.25}(DMF)_{1.25}\}_2(\mu\text{-}S)_2]$, 2. To a solution of **1** (0.10 g, 0.075 mmol) in 10 mL of acetonitrile was added $Mn[ClO_4]_2 \cdot 6H_2O$ (0.05 g, 0.14 mmol). A red sediment formed instantaneously, which was redissolved by addition of 1 mL of DMF. Brick red crystals of **2** were obtained by slow gas diffusion of diethyl ether into the solution. The identity of **2** is based on X-ray crystallography, elemental analysis, and spectral properties (IR and ^1H NMR); cf. Discussion section. Compound **2** is easily soluble in CH_3CN. Yield 0.045 g (52%). Anal. Calcd for $C_{29}H_{60.5}N_{8.5}O_{3.5}S_{6.5}W_2$ ($M = 1159.70$ g mol^{-1}): C, 30.01; H, 5.26; N, 10.26; S, 17.92. Found: C, 29.84; H, 5.13; N, 9.98; S, 18.12.

$\{[Et_4N]_{2.5}[\{W_2O_2(NCS)_2(\mu\text{-}S)_2\}\{Ag_{0.5}(SCN)\}(\mu\text{-}SCN)_2(DMF)]\}_n$, 3. To a solution of **1** (0.10 g, 0.075 mmol) in 10 mL of acetonitrile plus 1 mL of DMF was added $Ag[ClO_4]$ (0.05 g, 0.24 mmol). After shaking for 30 s, the solution was filtered. Orange-red crystals were obtained from the filtrate by slow gas diffusion of diethyl ether. Compound **3** is insoluble in CH_3CN and DMF. As shown by elemental analyses, the bulk material contained varying amounts of NCS^-/DMF, averaging to the described formulation. Yield 0.026 g (29% based on the av formulation). Semiquantitative ICP-MS analysis of the silver contents provided 4.8% of Ag; calcd for $C_{28}H_{57}Ag_{0.5}N_{8.5}O_3W_2$ ($M = 1205.62$ g mol^{-1}) 4.43. *Caution*: Perchlorates bear the risk of uncontrolled explosions when heated in contact with inflammable materials.

Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
chemical formula	$C_{38}H_{80}N_{10}O_2S_8W_2$	$C_{29}H_{60.5}N_{8.5}O_{3.5}S_{6.5}W_2$	$C_{28}H_{57}Ag_{0.5}N_{8.5}O_3W_2$
fw	1332.3	1159.70	1205.62
space group	*Pna*2$_1$	*C*2/*c*	*Fddd*
T, °C	−120	−120	−120
λ, Å	0.71073	0.71073	0.71073
a, Å	15.2671(11)	25.0926(18)	12.2321(10)
b, Å	18.9237(14)	12.1882(8)	24.965(2)
c, Å	19.2443(14)	28.914(2)	57.688(5)
V, Å^3	5559.9(7)	8803.3(11)	17616(2)
Z	4	8	16
D_{calcd}, g cm^{-3}	1.593	1.751	1.820
R1[a]	0.0433	0.0461	0.0604
wR2[a]	0.0985	0.1294	0.1584

[a] $R1 = \sum_h||F_o(h)| - |F_c(h)||/\sum_h|F_o(h)|$; $wR2 = \{\sum_h w[F_o(h)^2 - F_c(h)^2]^2/\sum_h w[F_o(h)^2]^2\}^{1/2}$.

X-ray Crystallography. Data collection was carried out on a Bruker SMART Apex CCD diffractometer at −120 °C with Mo Kα irradiation (graphite monochromator). Empirical absorption corrections were performed using equivalent reflections. For the solution and refinement of the structures, the program package SHELXL 97 was employed. H atoms of compound **1** were placed into calculated positions and included in the last cycles of refinement. No attempts were made to locate the protons in compounds **2** and **3**. Disorder and refinement information follows: For compound **2**, the final occupancies of N23 (SCN^-) and O02 (DMF) on one hand and C23 (SCN^-) and C05 (DMF) on the other hand in the axial position of one of the tungsten centers were refined jointly with the same temperature factor and a fixed occupancy of 0.5 for DMF and SCN^-, while S23 of SCN^- in this disordered position was allowed to float free, ending up with an occupancy factor of 0.3. All of the atoms of DMF and SCN^-, except of O01 from the nondisordered DMF, were refined isotropically. The disordered methyl groups C03/C04 and C07/C08 have been dealt with by a 1:1 model. Four of the carbon atoms of the 2.5 tetraethylammonium counterions were treated with a 1:1 disorder model; the carbon atoms C311−341 and 312−342 were refined isotropically. The same treatment was applied to C311−C314 and C321−C342 of the $[Et_4N]^+$ of compound **3**. In **3**, site occupancy of DMF and SCN^- in the axial position of W1 was considered by a 1:1 model. For further discussion, see the text. For crystal data, see Table 1.

Results and Discussion

Dinuclear compound **1** was obtained from tetrathiotungstate(VI) under aerobic conditions [or from oxo-trithiotungstate(VI)] in the presence of thiocyanate dissolved in a 10/1 mixture of CH_3CN/DMF by addition of cadmium chloride. The reaction is thermodynamically driven by abstraction of sulfido ligands from the thiotungstate by the Cd^{2+} ions, which forms CdS. The reaction does not occur in the absence of Cd^{2+}. Concomitantly, W^{VI} is reduced to W^V, presumably by sulfide. Whether this is a one-electron reduction ($W^{VI} \rightarrow W^V$), or a two-electron reduction ($W^{VI} \rightarrow W^{IV}$), followed by a symproportionation ($W^{IV} + W^{VI} \rightarrow W^V$), as proposed for the induced internal electron transfer in the system $[MoS_4]^{2-}/R_2S_2 \rightarrow [\{SMo^V(S_2)\}_2(\mu\text{-}S)_2]^{2-}$,[15a] has not been revealed. Mixed valence oligomeric species, such as $[O{=}Mo^{IV}(Mo^{VI}S_4)_2]^{2-}$ [15b] or $[S{=}W^{IV}(W^{VI}S_4)_2]^{2-}$,[15c] are known. On a formal basis, formation of the dinuclear complex occurs

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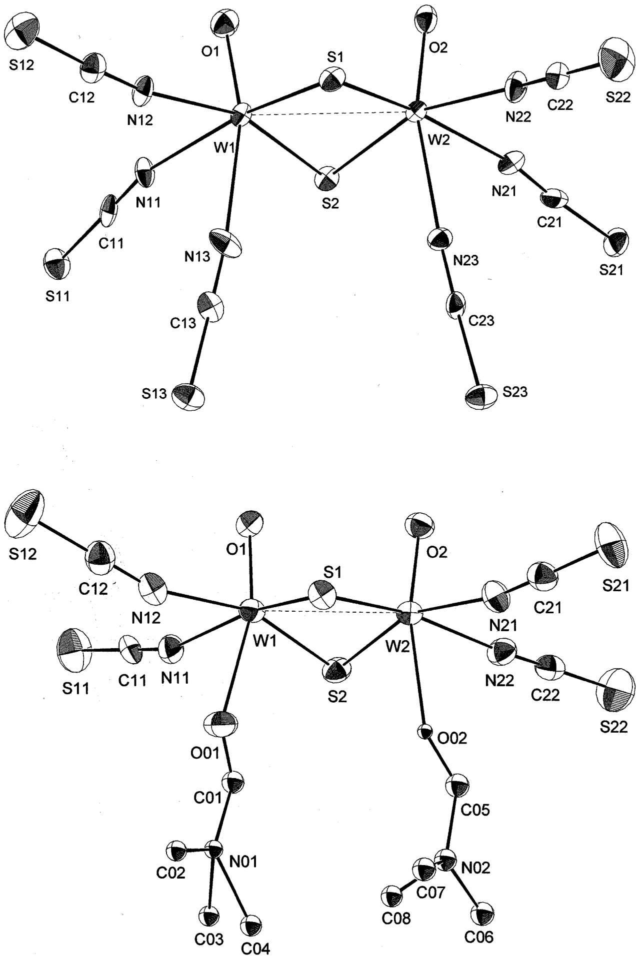

Figure 1. ORTEP plots (30% probability level) of the anions of **1** (top) and **2** (bottom). The structure of **2** is idealized in that the 1:1 DMF/SCN$^-$ disorder is not shown. Selected bond distances (Å) and angles (deg) follow. For **1**: W1−O1 1.690(7), W1−N11 2.142(8), W1−N12 2.146(7), W1−N13 2.290(9), W1−S1 2.331(2), W1−S2 2.323(2), W1···W2 2.8369(5); W1−S1−W2 74.87(7), W1−S2−W2 75.33(7), O1−W1−S1 102.4(3), O1−W1−N13 164.7(3), O1−W1−N12 83.9(3), O1−W1−S2 102.2(3), S1−W1−N11 161.1(2), S1−W1−N12 84.1(2), S1−W1−S2 102.77(8), S1−W1−N13 86.6(2). For **2**: W1−O1 1.703(6), W1−O01 2.284(7), W1−N11 2.132(8), W1−N12 2.137(8), W2−N21 2.133(8), W2−N22 2.148(8), W2−O02/N23 2.262(7), W1−S1 2.333(2), W1−S2 2.331(2), W1···W2 2.8172(5); W1−S1−W2 74.24(6), W1−S2−W2 74.26(6), O1−W1−S1 83.88(18), O1−W1−O01 164.4(3), O1−W1−N12 91.6(3), O1−W1−S2 102.47(19), S1−W1−N11 161.0(2), S1−W1−N12 86.1(2), S1−W1−S2 102.17(8), O2−W2−O02/N23 166.8(3), O01−C01−N01 124.8(15).

as the thiotungstate is deprived of part of its sulfide, and instead of forming cubane-like heterometallic assemblies,[16] one of the thio ligands is substituted by an oxo group. The resulting electrophilic $[(O{=}W)_2(\mu\text{-}S)_2]^{2+}$ core assembles six thiocyanate anions to complement an octahedral coordination sphere and generate the anion of compound **1**, carrying four negative charges, stabilized by the soft tetraethylammonium countercations. The IR spectrum of **1** shows the typical absorptions for the W═O group at 931 and 1001 cm^{-1}, the W−(μ-S)−W mode at 443 cm^{-1}, and a broad ν(CN) band associated with the thiocyanates at 2076 cm^{-1}.

Figure 1, top, is a representation of the molecular structure of the anion of **1**. Selected bonding parameters are given in the figure caption. The W···W distance, 2.8369(5) Å, is consistent with strong coupling of the two d^1 electrons from each of the W^V centers; the compound is thus diamagnetic as are comparable complexes containing the W^V_2 core.[13] The two axial positions in $[(O{=}W(NCS)_3)_2(\mu\text{-}S)_2]^{4-}$ are occupied by the terminal oxo groups (in the *syn* positions) and the nitrogens of NCS$^-$, respectively. Due to the *trans* influence, the values of *d*(W−N) to these axial nitrogens are substantially longer (average 2.285 Å) than the value of *d*(W−N) to the two thiocyanates (average 2.145 Å) which, together with the bridging sulfides, form the basal planes in the distorted octahedron. The dihedral angle between these two planes, spanned by S1,S2,N21,N21 and S1,S2,N12,N11, is 0.9°, the displacement of W from the planes 0.30 Å toward the oxo groups.

The labilization of the axial thiocyanates by the *trans* influence implies reactivity of **1** in that these ligands might be exchanged by other nucleophiles or exhibit, via the thiocyanate sulfur, nucleophilicity toward suitable thiophilic metal ions, thus acting as bidentate bridging ligands. With the formation of compounds **2** and **3**, we have observed both reactivity patterns.

Compound **1** can be converted to a dinuclear anion carrying only 2.5 negative charges via exchange of the greater part of the axial thiocyanates by neutral dimethylformamide. This conversion is achieved, as Mn^{2+} is added to a solution of **1**. In this process, the intermediate formation of an insoluble compound is observed, which might be a polymeric mixed metal (W/Mn) compound analogous to **3** (vide infra); this compound produces solutions of **2** on addition of excess DMF, from which it can be isolated with diethyl ether by the gas diffusion method. In **2**, according to charge calculations, there are 1.5 DMF and 0.5 SCN$^-$ distributed over the axial positions (*trans* to the oxo group) of the two tungsten ions. The structure determination indicates that one of the positions is completely occupied by DMF while, in the second position, there is a 1:1 disorder of DMF and SCN$^-$. Apart from this, the anions of **1** and **2** are isostructural. The presence of DMF in **2** is further evidenced by IR [ν(C═O) = 1662 cm^{-1}] and ^{1}H NMR of solutions of **2** in CD_3CN [δ = 7.8 (formyl) and 2.88/2.72 (methyl protons)]. The remaining IR pattern of **2** [ν(W═O) = 955 and 1000 cm^{-1}; ν(W−S−W) = 440, ν(CN) = 2081 cm^{-1}] compares to that of **1**.

The presence of 0.5 Ag per dinuclear tungsten unit in **3** has been verified by ICP-MS. The presence of DMF is indicated by its ν(C═O) at 1654 cm^{-1}. Additional selected IR data [ν(W═O) = 944 and 1001 cm^{-1}; ν(W−S−W) = 441 cm^{-1}, ν(CN) = 2090 cm^{-1}] correspond to the patterns observed for **1** and **2**. In **3** (with tungsten still in the oxidation state +V), axial thiocyanate in part is replaced by DMF, and in part acts as a bridging ligand coordinated to silver ions via the sulfur. In the average structure, the ratio of DMF and SCN$^-$ in the axial position of W1 strictly is 1:1. The overall appearance of the structure (Figure 2) is that of two

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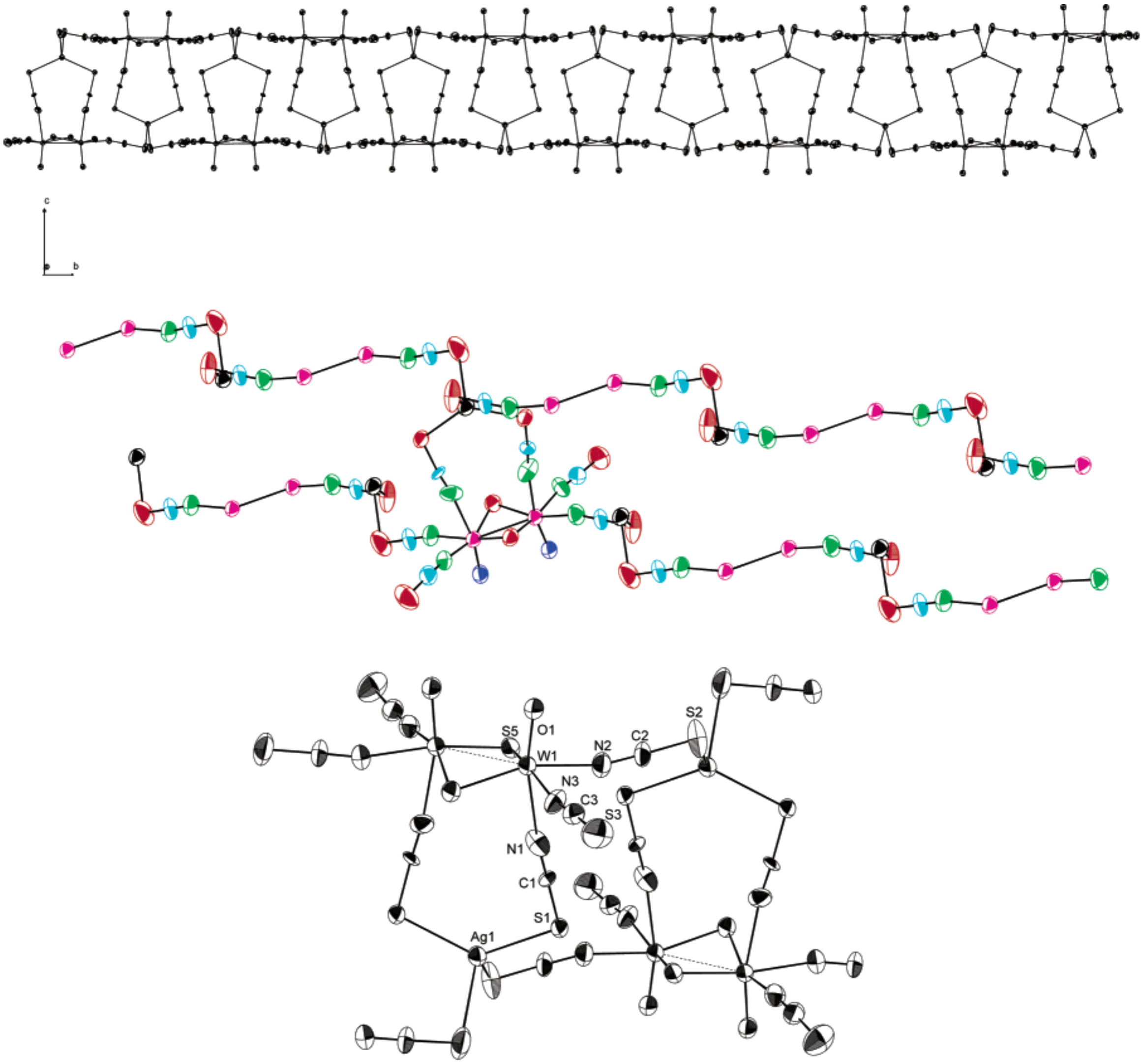

Figure 2. Anion of compound **3**. Top: full view (*bc* plane). Center: view of the backbones of the two helices with one of the interstrand linkages indicated [color code: W (magenta), Ag (black) S (red), N (green), O (blue), C (cyan)]. Bottom: section showing the intra- and interstrand linkages. Partial occupancy of axial SCN^- positions by DMF not shown; N1 and S1 of SCN^- correspond to O01 and N01 of DMF. Selected bond distances (Å) and angles (deg): W1−O1 1.706(9), W1−N1 2.31(3), W−O01 2.21(2), W−N2 2.128(12), W1−N3 2.132(13), W1−S5 2.344(4), W1···W1# 2.8204(10), Ag1−S1 2.535(7), Ag1#−S2 2.746(6); O1−W1−N1 168.2(9), O1−W1−O01 162.4(6), O1−W1−N2 90.0(4), O1−W1−S5 102.7(3), S5−W1−S5# 102.18(11), S1−Ag−S1# 130.0(4), S1−Ag−S2# 106.8(2).

helices, constituted by $(O_2W_2S_2)(\mu\text{-NCS})Ag(\mu\text{-SCN})(W_2O_2S_2)$ chains, linked together alternately via the $\{O{=}W(\mu\text{-S})\}_2$ unit of one of the chains and a silver ion of the other chain through bridging SCN^-. The silver is in a tetrahedral environment of (on an average basis) three thiocyanates and one DMF, while the tungsten centers retain their geometry pertinent in **1** and **2**, leaving two of the thiocyanates per dinuclear unit in the terminal, nonbridging coordination mode. The *d*(W−N) to the axial, chain-bridging thiocyanate is somewhat elongated [2.31(3) Å] with respect to the corresponding distances in **1** and **2**, while all of the other distances of the ditungsten unit in **3** are about the same as in **1** and **2**. The distance *d*(W−O) to DMF, 2.219 Å, is in the expected range for DMF *trans* to W=O. The distance *d*(Ag−S) to the thiocyanates bridging the two strands is 2.535(7) Å, while the *d*(Ag−S) to the bridging SCN^- within the strand, 2.746(6) Å, is substantially elongated and should hence be considered a comparatively weak bonding interaction. We may thus view the chain structure of the anion of **3** to consist of heterometallic $\{(SCN)_2WO(\mu\text{-S})\}_2(\mu\text{-NCS/DMF})\{Ag_{0.5}(SCN)_2\}$units (Figure 2), linked in moderate bonding interaction to a one-dimensional polymeric double-chain. The periods of this helical double-chain have a length of 13.9 Å.

Conclusion

Transition metal ions such as Cd^{2+} can be used to abstract sulfido ligands from tetrathiomolybdate(VI) to form, in the presence of air and alternative nucleophilic ligands such as thiocyanate, and with concomitant reduction of W^{VI} to W^{V}, dinuclear, strongly antiferromagnetically coupled assemblies of composition $[\{O{=}W(\mu\text{-S})(NCS)_3\}_2]^{4-}$. These are starting products for ligand exchange of the axial (*trans* to the doubly bonded oxo group) thiocyanate by dimethylformamide, stimulated by Mn^{2+} or Ag^{+}. Thiophilic Ag^{+} further generates aggregation to polymeric double chains through strongly linking interstrand and moderately linking intrastrand μ-SCN^{-} bridges.

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Supporting Information Available: Crystallographic data of **1**, **2**, and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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