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Acetic Acid Induced Self-Assembly of Supramolecular Compounds $[Et_4N]_3[(WS_4Cu_2)_2(\mu\text{-}CN)_3]\cdot 2MeCN$ and $[PPh_4][WS_4Cu_3(\mu\text{-}CN)_2]\cdot MeCN$ from Preformed Clusters $[A]_2[WS_4(CuCN)_2]$ ($A = Et_4N, PPh_4$)

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Reactions of two preformed trinuclear W/Cu/S clusters, $[A]_2[WS_4(CuCN)_2]$ (**1**: $A = Et_4N$; **2**: $A = PPh_4$), with different concentrations of acetic acid in MeCN generate two interesting 2D polymeric clusters $[Et_4N]_3[(WS_4Cu_2)_2(\mu\text{-}CN)_3]\cdot 2MeCN$ (**3**), and $[PPh_4][WS_4Cu_3(\mu\text{-}CN)_2]\cdot MeCN$ (**4**), respectively. Compound **4** can also be readily obtained in a high yield from the reaction of **2** with equimolar $[Cu(MeCN)_4]PF_6$ in MeCN. These compounds have been characterized by elemental analysis, IR spectra, thermal analysis, and single-crystal X-ray diffraction. An X-ray analysis reveals that compound **3** retains the WS_4Cu_2 cluster core, which serves as a 3-connecting node to link equivalent nodes via single cyanide bridges, forming an anionic 2D (6,3) net. Compound **4** consists of a T-shaped WS_4Cu_3 core, which also acts as a 3-connecting node, with links to 3 equivalent clusters either through single or double cyanide bridges, affording a different anionic 2D (6,3) network. The acetic acid induced aggregation of **3** and **4** from the two cluster precursors **1** and **2** suggests that this simple synthetic strategy is likely to be applicable to many related systems.

Introduction

Supramolecular compounds using cyanides as linkers have attracted much attention because of the ease with which they can be used to generate 2D and 3D networks.[1−10] Such compounds may have potential applications as host networks for a variety of molecular guests and photo/electronic materials.[7−10] Metal cyanide networks are often prepared by substitution of weak ligands at metal centers with cyanides or cyanide metal complexes. For example, the well-known Hoffmann-type clathrate, $[Ni(NH_3)_2Ni(CN)_4]\cdot 2C_6H_6$, was prepared by replacement of two NH_3 molecules from $[Ni(NH_3)_4]^{2+}$ with cyanides of $[Ni(CN)_4]^{2-}$.[1a] Another example is the substitution of four acetate groups of $[Pd_4(CO)_4(OAc)_4](AcOH)_2$ with four equivalents of $Na[(\eta\text{-}C_5H_4Me)\text{-}$

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$Mn(CN)(CO)_2$]. In the resulting octanuclear cluster, $[(OC)Pd(\mu\text{-}NC)Mn(\eta\text{-}C_5H_4Me)(CO)_2]_4$, cyanide bridges play a key structural role in this beautiful metal−ligand assembly which has approximate S_4 symmetry.[11]

In some cases, partial replacement of monodentate cyanide at metal centers by other ligands may encourage the self-assembly of new cyanide-bridged structures. For example, Py or PPh_3 was found to displace some of the monodentate cyanides within $[PPh_4][Cp^*WS_3(CuCN)_2]$ and enable the formation of the dimeric clusters $[Cp^*WS_3Cu_2(PPh_3)(\mu\text{-}CN)]_2$ and $[PPh_4][\{Cp^*WS_3Cu_2(CN)(Py)\}_2(\mu\text{-}CN)]$, both of which contain bridging cyanide.[12a] Another recent example is a cyanide-bridged supramolecular cube $[(Cp^*WS_3Cu_3)_8(CN)_{12}Cl_8Li_4]$ derived from the reaction of the cluster precursor $[PPh_4][Cp^*WS_3(CuCN)_3]$ with 1,4-pyrazine in the presence of LiCl.[12b] It is worthwhile noting that partial removal of the cyanides from the precursor without coordination of 1,4-pyrazine at copper sites is critical in the formation of this unusual cube. The difficulty arises when determining how one “safely” removes some of the cyanides from cyanide complexes but avoids coordination of the ligand that may facilitate this process. An alternative strategy may be to acidify a parent cyanide complex to remove at least some of the cyanides as hydrocyanic acid and then leave the remaining cyanides to bridge metal centers.

In this present work we have prepared two cyanide-containing trinuclear clusters, $[A]_2[WS_4(CuCN)_2]$ (**1**: A = Et_4N; **2**: A = PPh_4), with the intention of acidifying these species to produce new cluster-based supramolecular species. Apart from the anticipated partial loss of cyanide through protonation, we also recognize the potential of the acid to interact with the thiotungstate cluster. It is well-established that metal sulfide clusters may be produced from reactions of certain metal sulfide complexes with acids.[13] For example, the trinuclear clusters $[W_3S_9]^{2-}$ and $[W_3S_8]^{2-}$ can be formed by acidification of a CH_2Cl_2 solution of $[PPh_4]_2[WS_4]$ with 3.5 M acetic acid or a diluted aqueous solution of $(NH_4)_2[WS_4]$ with dilute H_2SO_4.[13a,b] These reactions involve the protonation of sulfur atom(s) of $[WS_4]^{2-}$ and subsequent intramolecular redox processes. However, the reactions have limited applicability, as the identity of the product is critically dependent on the acidity of the solution, and in addition, the isolation of the desired products is difficult.

Reactions of **1** or **2** with different concentrations of acetic acid in MeCN resulted in the generation of novel 2D W/Cu/S polymers, $[Et_4N]_3[(WS_4Cu_2)_2(\mu\text{-}CN)_3]\cdot 2MeCN$ (**3**) and $[PPh_4][WS_4Cu_3(\mu\text{-}CN)_2]\cdot MeCN$ (**4**). In this paper we report their preparation and structural characterization.

Experimental Section

Materials and Methods. $(NH_4)_2[WS_4]$ was prepared according to literature procedures.[14] Other chemicals were obtained from commercial sources and used as received. The IR spectra were recorded on a Nicolet MagNa-IR500 FT-IR spectrometer as KBr disks (4000−400 cm^{-1}). The elemental analyses for C, H, and N were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. The thermal analysis was performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer at a heating rate of 10 °C/min and a flow rate of 100 cm^3/min (N_2). All manipulations were carried out in air.

Caution. Due to the production of toxic gases in the preparation of compounds **3** (HCN), and **4** (H_2S and HCN) using acetic acid, it is necessary to perform these syntheses in a well-ventilated fumehood.

Preparation of $[Et_4N]_2[WS_4(CuCN)_2]$ (1). Compound **1** was prepared according to the method reported by Gheller and co-workers.[15] Yield: 80%. Anal. Calcd for $C_{18}H_{40}Cu_2N_4S_4W$: C, 28.76; H, 5.37; N, 7.46. Found: C, 28.53; H, 5.41; N, 7.58. IR (KBr pellet): $\upsilon(C{-}N)$, 2132 (m), $\upsilon(W{-}S_{br})$, 458 (m), 425 (w) cm^{-1}.

Preparation of $[PPh_4]_2[WS_4(CuCN)_2]$ (2). CuCN (0.09 g, 0.10 mmol) was added to a solution of $[PPh_4]_2[WS_4]$ (0.50 g, 0.5 mmol) in 50 mL of MeCN. The mixture was stirred for 2 h, resulting in the formation of a large amount of yellow solid. After filtration, the solid was dissolved in 10 mL of DMF and filtered again. A mixture of MeCN/Et_2O (v/v = 1:2) was layered onto the filtrate to form yellow crystals of **2**. Yield: 0.35 g (60%). Anal. Calcd for $C_{50}H_{40}Cu_2N_2P_2S_4W$: C, 51.32; H, 3.45; N, 2.40. Found: C, 51.12; H, 3.50; N, 2.22. IR (KBr pellet): $\upsilon(C{\equiv}N)$, 2123 (m), $\upsilon(W{-}S_{br})$, 456 (m), 419 (w) cm^{-1}.

Preparation of $[Et_4N]_3[(WS_4Cu_2)_2(\mu\text{-}CN)_3]\cdot 2MeCN$ (3). A 1.5-mL portion of HOAc (99%, d = 1.5 g/cm^3)/MeCN (v/v =

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Table 1. Crystallographic Data for **2**, **3**, and **4**

	2	**3**	**4**
chemical formula	$C_{50}H_{40}Cu_2N_2P_2S_4W$	$C_{31}H_{66}Cu_4N_8S_8W_2$	$C_{28}H_{23}Cu_3N_3PS_4W$
fw	1170.01	1429.28	935.21
space group	$P\bar{1}$	$P2_1/n$	$C2/c$
T, °C	−80	−80	−80
a, Å	12.7724(4)	10.078(4)	30.344(3)
b, Å	14.3104(7)	18.958(7)	10.3195(7)
c, Å	15.4164(6)	13.535(5)	26.170(3)
α, deg	70.926(13)		
β, deg	65.352(11)	101.785(4)	128.202(3)
γ, deg	88.35(2)		
V, Å^3	2401.4(2)	2531.4(17)	6439.6(10)
Z	2	2	8
D_{calcd}, g cm^{-3}	1.618	1.875	1.929
μ, cm^{-1}	35.46	65.42	58.52
R^a ($I > 3\sigma(I)$)	0.055	0.038	0.047
Rw^b ($I > 3\sigma(I)$)	0.070	0.050	0.057

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

1:4) was added to a yellow solution of **1** (0.038 g, 0.05 mmol) in 6 mL of MeCN. This resulted in the rapid formation of an orange-yellow precipitate. The suspension was briefly stirred and filtered to give an orange solution. Diethyl ether (12 mL) was carefully layered onto the solution, which was left to stand at room temperature. After 2 days red-orange crystals (blocks) of **3** were collected by filtration, washed with MeCN and Et_2O, and dried in vacuo. Yield: 20 mg (56%). Anal. Calcd. for $C_{31}H_{66}Cu_4N_8S_8W_2$: C, 26.05; H, 4.66; N, 7.84%. Found: C, 25.58; H, 4.63; N, 7.54%. IR (KBr pellet): υ(C≡N), 2125 (m), $\upsilon(W-S_{br})$, 459 (s) cm^{-1}.

Preparation of $[PPh_4][WS_4Cu_3(\mu\text{-}CN)_2]\cdot MeCN$ (4). Method 1. A 1.5-mL portion of HOAc (99%, d = 1.5 g/cm^3)/MeCN (v/v = 1:1) was added to a yellow solution of **2** (0.064 g, 0.05 mmol) in 6 mL of MeCN. This resulted in the rapid formation of a large amount of orange-yellow precipitate. The resulting mixture was quickly filtered to give an orange-yellow solution. Diethyl ether (12 mL) was carefully layered onto the solution, which was left to stand at room temperature for several days yielding orange prisms of **4** contaminated with some yellow precipitate. Crystals of **4** were mechanically separated from the precipitate under a microscope, and were washed with MeCN and Et_2O and dried in vacuo. Yield: 5.6 mg (12.5%). Anal. Calcd for $C_{28}H_{23}Cu_3N_3PS_4W$: C, 35.96; H, 2.48; N, 4.49%. Found: C, 36.11; H, 2.23; N, 4.36%. IR (KBr pellet): υ(C≡N), 2154 (m), $\upsilon(W-S_{br})$, 467(m), 439 (m) cm^{-1}.

Method 2. A MeCN solution (3 mL) of $[Cu(MeCN)_4]PF_6$ (0.015 g, 0.05 mmol) was added to 6 mL of a yellow solution of **2** (0.064 g, 0.05 mmol). An orange precipitate formed within seconds. The resulting mixture was quickly filtered to give an orange solution. Slow evaporation of MeCN in the filtrate at room temperature for one week gave rise to orange prisms of **4**. Crystals of **4** (6.3 mg) were washed with MeCN and Et_2O and dried in vacuo. The orange precipitate (33.9 mg) was also washed thoroughly with MeCN and Et_2O and dried in vacuo. The orange powder was confirmed to be **4** by elemental analysis, X-ray fluorescence analysis (to obtain W, Cu, S, and P atomic ratios), and IR. The combined yield for **4** was 86%.

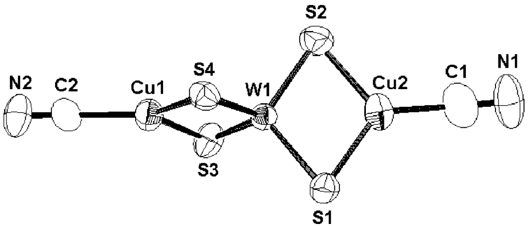

Figure 1. Dianion of $[PPh_4]_2[WS_4(CuCN)_2]$ (**2**) (50% thermal ellipsoids). Selected atomic separations (Å) and angles (deg): W1···Cu1 2.655(2), W1···Cu2 2.645(2), W1−S1 2.222(2), W1−S2 2.198(3), W1−S3 2.215(4), W1−S4 2.226(2), Cu1−S1 2.247(4), Cu1−S2 2.229(4), Cu2−S3 2.223(3), Cu2−S4 2.232(4), Cu1−C1 1.89(2), Cu2−C2 1.90(1), Cu1···W1···Cu2 175.00(5), S1−W1−S2 107.7(1), S1−W1−S3 111.9(1), S1−W1−S4 111.0(1), S2−W1−S3 108.2(1), S2−W1−S4 110.9(1), S3−W1−S4 107.2(1).

X-ray Crystallography. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) using graphite monochromated Mo Kα radiation (λ = 0.71070 Å). The structures were solved by direct methods[16] and refined against F for all independent reflections.[17] In **3** and **4**, the bridging cyanides were modeled as disordered units with each of the atomic sites assigned as 50% C and 50% N. Crystallographic data are presented in Table 1.

Results and Discussion

As shown in Figure 1, the cluster dianion of **1** and **2** consists of a central WS_4 unit coordinated symmetrically to two CuCN groups. The resulting WS_4Cu_2 cluster has a linear arrangement of metal atoms (Cu···W···Cu), which is similar to that found for the molybdenum analogue.[15]

The reaction of **1** with HOAc in a solution of MeCN, which contains 4% (by volume) HOAc, produces an orange precipitate over a period of 30 min. When the precipitate is filtered off, the slow diffusion of diethyl ether into the filtrate yields the compound $[Et_4N]_3[(WS_4Cu_2)_2(\mu\text{-}CN)_3]\cdot 2MeCN$ (**3**) as orange-red prisms (56% yield). The same reaction of **1** with different HOAc concentrations (2−7%) produces **3** but in lower yields. If the concentration of HOAc is lower than 2%, almost no reaction is observed, and if the concentration is higher than 7% the reaction begins to yield a product of composition $[Et_4N][WS_4Cu_3(\mu\text{-}CN)_2]\cdot MeCN$ which has a composition similar to that of compound **4** (described below). Direct treatment of **1** with concentrated acids such as HOAc,

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H_3PO_4, HPF_6, $HClO_4$, and H_2SO_4 completely destroys **1** and is accompanied by the strong smell of H_2S in addition to the formation of large amounts of unidentified insoluble materials. Interestingly, the reaction with excess citric acid produces crystals of **3** in about 10% yield. The addition of other weak organic acids such as benzoic acid and benzene-1,4-dicarboxylic acid to a MeCN solution of **1** results in no apparent reaction.

The inability to obtain good quality crystals of $[Et_4N][WS_4Cu_3(\mu\text{-}CN)_2]\cdot MeCN$ for structural investigations prompted the use of **2** as a starting material. The reaction of **2** with HOAc in a solution of MeCN which contains 10% (by volume) HOAc produces an orange-yellow precipitate, accompanied by the smell of H_2S gas. When the solid is filtered off and diethyl ether is allowed to diffuse slowly into the resulting orange filtrate, prismatic crystals of $[PPh_4][WS_4Cu_3(\mu\text{-}CN)_2]\cdot MeCN$ (**4**) (12.5% yield) along with a large amount of unidentified yellow powder are formed after 10 days. Elemental analyses indicate that **4** and $[Et_4N][WS_4Cu_3(\mu\text{-}CN)_2]\cdot MeCN$ have similar compositions.

Reactions involving other HOAc concentrations up to 16% also produce **4** but in much lower yields. Direct addition of concentrated acids such as HOAc, H_3PO_4, HPF_6, $HClO_4$, and H_2SO_4 fails to give isolable products.

The composition of the anion appears to be dependent upon the concentrations of acetic acid used in the reactions. In the reaction that produces **3**, the acetic acid serves only to protonate cyanide, thereby reducing the availability of coordinated cyanide ions, while in the reaction that produces **4**, the higher concentration of acid results in protonation of cyanide and sulfide. The liberation of H_2S is associated with the decomposition of some of the WS_4Cu_2 clusters—a process that generates Cu(I) ions which are then available for binding to other WS_4Cu_2 clusters. We propose that the tetranuclear cluster, $[WS_4Cu_3]^+$, which is present in **4**, is generated through such a process.

This work prompted an investigation of a more direct synthetic route for the preparation of **4**. The reaction of **2** with an equimolar amount of $[Cu(MeCN)_4](PF_6)$ in MeCN results in an immediate orange precipitate. After filtration, slow evaporation of the filtrate gives rise to orange-red prismatic crystals of **4**. The yield in this procedure is 86%.

Crystals of **3** and **4** are air-stable and insoluble in common organic solvents. The IR spectra show cyanide bands at 2125 and 2154 cm^{-1} for **3** and **4**, respectively. For **1** and **2** the corresponding bands are at 2132 and 2124 cm^{-1}, respectively. Both compounds show bridging W−S stretching vibrations at 448 (**3**) and 467/439 (**4**) cm^{-1}. Thermogravimetric analyses of **3** and **5** (see Supporting Information) reveal weight losses of 4.8% (**3**) and 3.6% (**4**) in the region 30−115 °C, consistent with the loss of MeCN. The compound is stable until ~200 °C, after which a series of decomposition steps commence.

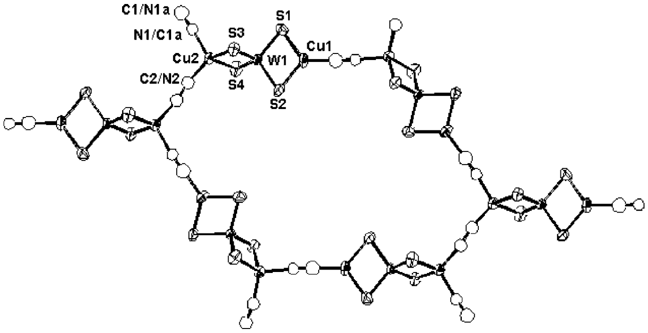

Figure 2. Part of the 2D anionic network within **3**. Selected atomic separations (Å) and angles (deg): W1···Cu1 2.643(1), W1···Cu2 2.7331(9), W1−S1 2.226(2), W1−S2 2.224(2), W1−S3 2.194(2), W1−S4 2.201(2), Cu1−S1 2.234(4), Cu1−S2 2.232(4), Cu2−S3 2.311(3), Cu2−S4 2.306(4), Cu1···W1···Cu2 177.13(2), S1−W1−S2 107.49(8), S1−W1−S3 108.91(7), S1−W1−S4 111.67(8), S2−W1−S3 109.96(6), S2−W1−S4 109.71(7), S3−W1−S4 109.08(7).

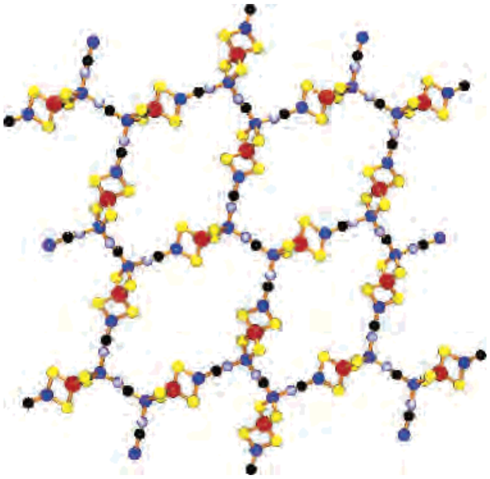

Figure 3. View along the *a* axis of **3** showing the extended 2D network.

An X-ray analysis revealed that the asymmetric unit of **3** is represented by one-half of the formula unit $[Et_4N]_3[(WS_4Cu_2)_2(\mu\text{-}CN)_3]\cdot 2MeCN$. As indicated in Figure 2, Cu2 is coordinated by two bridging cyanides and two sulfur atoms (from the cluster) resulting in a tetrahedral Cu(I) center. The other Cu center of the cluster is in an approximately trigonal environment formed from a single bridging cyanide and two sulfur atoms. The oxidation states of the W and Cu atoms in **1**, +6 and +1, respectively, are retained in **3**. As a consequence of C/N disorder within cyanide, the clusters within the network cannot all be coordinated by the same donor atom set, despite the fact that they are related by crystal symmetry. The W(1)···Cu(1) separation (2.643(1) Å) in **3** is similar to that found in **1**, while the other W···Cu2 separation (2.7331(9) Å) is significantly longer. This is consistent with the higher coordination number of the Cu2 center leading to longer bond distances.

From a topological perspective, the WS_4Cu_2 cluster may be considered as a 3-connecting node, which is linked to equivalent nodes to form a 2D (6,3) net that extends in the *bc* plane (Figure 3). The networks are ca. 10 Å apart with Et_4N^+ cations and MeCN solvent molecules lying between the sheets.

Compound **4** also consists of an anionic 2D polymer formed by linking WS_4Cu_3 clusters with cyanide bridges (Figures 4 and 5). The asymmetric unit of **4** consists of the formula unit $[PPh_4][WS_4Cu_3(\mu\text{-}CN)_2]\cdot MeCN$. A T-shaped $[WS_4Cu_3]$ core within **4** may be considered as being derived from the addition of a Cu atom to the WS_4Cu_2 cluster of **2**.

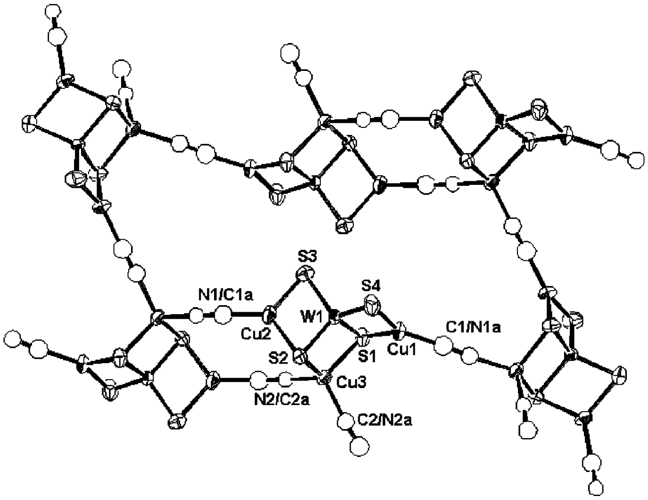

Figure 4. Part of the 2D anionic network within **4**. The C/N assignment of the cyanide units is arbitrary. Selected atomic separations (Å) and angles (deg): W1···Cu1 2.6395(9), W1···Cu2 2.6362(9), W1···Cu3 2.732(1), W1−S1 2.241(3), W1−S2 2.246(2), W1−S3 2.200(2), W1−S4 2.212(3), Cu1−S1 2.254(3), Cu1−S4 2.235(4), Cu2−S2 2.250(2), Cu2−S3 2.243(2), Cu3−S1 2.307(2), Cu3−S2 2.327(3), Cu(1)···W(1)···Cu(2) 168.61(4), Cu(1)···W(1)···Cu(2) 87.02(3), Cu(2)···W(1)···Cu(3) 81.60(3), S1−W1−S2 108.71(9), S1−W1−S3 108.9(1), S1−W1−S4 107.9(1), S2−W1−S3 108.15(7), S2−W1−S4 109.2(1), S3−W1−S4 114.0(1).

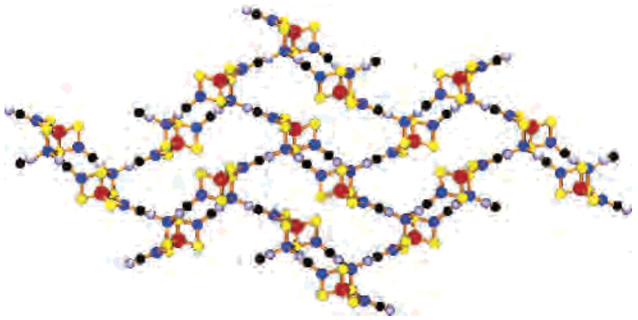

Figure 5. View along the *c* axis of **4** showing the extended 2D network.

This type of unit is similar to that found in $[MS_4(CuX)_3]^{2-}$ (M = Mo, W; X = Cl, Br, I),[18a,b] $[VS_4Cu_3(PPh_3)_4]$,[18c] $[WS_4(CuNCS)_3]^{2-}$,[18d] $[MS_4Cu_3(C_5H_{10}dtc)_3]^{2-}$ (M = Mo, W),[18e] and $[WS_4Cu_3Br_2(dppm)_2]$.[18f] As illustrated in Figure 4, Cu1 and Cu2 are each in approximately trigonal coordination environments formed by two sulfur atoms and a single bridging cyanide. In contrast, Cu3 is 4-coordinate with two bridging cyanides and a pair of sulfur atoms from the WS_4 unit completing the coordination environment. As seen in **3**, the W···Cu separations appear to be dependent on the coordination number of the Cu. The W···Cu separations of 2.6395(9) and 2.6362(9) Å found for Cu1 and Cu2 respectively are significantly shorter than the W···Cu3 separation of 2.732(1) Å.

Each cluster is linked to 3 crystallographically equivalent clusters either through single or double cyanide bridges. From a topological perspective each cluster may be considered as a 3-connecting node within a 2D (6,3) network (Figure 5). The six-membered rings within this network (as depicted in Figure 4) resemble the chair conformation of cyclohexane. The average layer-to-layer separation is ca. 16 Å with the $[\{WS_4Cu_3(\mu\text{-CN})\}_2(\mu'\text{-CN})_2]_n^{2n-}$ anionic layers separated by $[PPh_4]^+$ cations and MeCN molecules. The oxidation states for W and Cu atoms remain at +6 and +1, respectively.

Although **4** and $[Et_4N][WS_4Cu_3(\mu\text{-CN})_2]\cdot MeCN$ share a similar composition, the structural influence of the cation is very difficult to gauge. Accordingly, the connectivity of the anion may be different in **4** and $[Et_4N][WS_4Cu_3(\mu\text{-CN})_2]\cdot MeCN$.

Conclusion

In the work reported here, we have demonstrated the acid-induced assembly of two interesting W/Cu/S supramolecular compounds, **3** and **4**, from preformed clusters **1** and **2**, respectively, via control of acetic acid concentrations. The general strategy of using a weak acid to remove cyanide without causing decomposition of the cluster appears to be suitable only at lower concentrations (∼4 vol %) of acetic acid. At concentrations higher than 7% the acid plays a far less innocent role and begins to attack WS_4Cu_2 clusters. Nevertheless, under these conditions it is still possible to generate crystals of a quality suitable for X-ray crystallography.

We anticipate that the synthetic methodology may be applied to other Mo(W)/Cu/S clusters and other metal complexes containing cyanide, sulfide, thiocyanide, phenolate, and benzenethiolate with a view to accessing new types of supramolecular assemblies. Furthermore, the formation of **4** and $[Et_4N][WS_4Cu_3(\mu\text{-CN})_2]\cdot MeCN$ through the addition of Cu^+ to the WS_4Cu_2 unit suggests that **1** and **2** may be good precursors for the generation of supramolecular compounds containing the $[WS_4Cu_2(M')_n]$ (M'^+ = Cu, Ag, Tl, n = 1, 2) core. Research is continuing in these areas.

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Supporting Information Available: Crystallographic data of **2**, **3**, and **4** (CIF), details of the synthesis and characterization of $[Et_4N][WS_4Cu_3(\mu\text{-CN})_2]\cdot MeCN$ and thermogravimetric analysis results for **3** and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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