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Tri- and Pentanuclear Tungsten-(μ-S)-M Clusters (M = W, Cu, Ag)

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The thiotungstate $[Et_4N]_2[OW(WS_4)_2]$, $[Et_4N]_2$·**1**, containing the linear $[\{S_2W^{VI}(\mu\text{-}S)_2\}_2W^{IV}{=}O]$ core, was prepared from $[Et_4N]_2[WS_4]$ in the presence of the sulfide scavenger Cd^{2+}. Addition of 1,2-bis(*o*-diphenylphosphinophenyl)ethane (diphosphine) and Cu^+ or Ag^+ to solutions of **1** in MeCN/DMF led to coordination of the (diphosphine)Cu/Ag fragments to the terminal sulfido ligands of **1**, yielding novel linear pentanuclear, heterometallic clusters $[\mu\text{-}\{OW^{IV}(DMF)(W^{VI}S_4)_2\}\{M(diphosphine)\}_2]$, **2** (M = Cu) and **3** (M = Ag). Along with **2**, the trinuclear cluster $[\{\mu\text{-}(W^{VI}S_4)\{Cu(diphosphine)_2\}]$, **4**, was also obtained. The molecular and crystal structures of $[Et_4N]_2$·**1**, **2**·MeCN, **3**·MeCN, and **4**·2MeCN·CH_2Cl_2 have been determined.

Introduction

The thiometal family containing Mo, W, or V is of interest in relation to the biological significance (molybdo-, tungsto-, or vanadopterin containing oxo-transferases;[1−3] Mo- and V-nitrogenases[4,5]), industrial applications such as hydrodesulfurization in petrochemistry,[6,7] and materials in nonlinear optics.[8] Monomeric oxo-thiometalates of composition $[MO_xS_{4-x}]^{n-}$ (M = V^V, $n = 3$; M = Mo^{VI}, W^{VI}, $n = 2$), dinuclear species containing the $\{E_2M^V(\mu\text{-}S)_2\}$ core (E = O, S; M = Mo, W), and trinuclear clusters such as $[EM^{IV}(M^{VI}S_4)_2]^{2-}$ have been widely used as building blocks in more complex heterometallic transition metal thiocluster compounds,[9−11] as well as in model studies for the redox behavior of biological systems.[12,13]

The synthesis of di- and trinuclear oxothiometalates containing d^1 or d^2 metal centers commonly starts from d^0 tetrathiometalates, which are subjected to internal redox processes by, e.g., thermal decomposition[14] or acidification[15] under aerobic conditions. Cd^{2+} ions can effectively be employed as sulfide scavengers to promote the generation of fragments for the formation and stabilization of new cluster arrangements in the presence of supporting ligands. We have recently reported on the characterization of compounds containing the *syn*-$\{OW(\mu\text{-}S)\}_2$ and $\{OMo(S)(\mu\text{-}S)_2\}$ cores, stabilized by thiocyanate.[16,17] In the present study, we have applied this reaction scheme to synthesize the trinuclear $[\{S_2W^{VI}(\mu\text{-}S)_2\}_2W^{IV}{=}O]^{2-}$, and to explore its ability to act as a bis(bidentate) ligand in the coordination to Cu^+ and Ag^+, supported by 1,2-bis(*o*-diphenylphosphinophenyl)ethane, diphosphine, leading to novel pentanuclear species.

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Table 1. Crystal Structure and Refinement Parameters

	$[Et_4N]_2$·**1**	**2**·MeCN	**3**·MeCN	**4**·2MeCN·CH_2Cl_2
empirical formula	$C_{60}H_{40}N_2OS_8W_3$	$C_{81}H_{74}Cu_2N_2O_2P_4S_8W_3$	$C_{81}H_{74}Ag_2N_2O_2P_4S_8W_3$	$C_{81}H_{72}Cl_2Cu_2N_2P_4S_4W$
M, g mol^{-1}	1613.02	2166.41	2255.07	1707.36
cryst syst	monoclinic	tetragonal	tetragonal	monoclinic
space group	$P2_1/c$	$P\bar{4}2_1c$	$P\bar{4}2_1c$	$C2/c$
a, Å	10.376(10)	17.743(3)	18.3196(17)	14.9271(18)
b, Å	10.689(11)	17.743(3)	18.3196(17)	19.915(2)
c, Å	15.342(15)	28.471(7)	27.835(4)	27.346(3)
β, deg	102.60(3)			100.138(2)
Z	2	4	4	4
V, Å^3	1661(3)	8963(3)	9341.7(17)	8002.4(16)
D_{calcd}, g cm^{-3}	2.169	1.605	1.603	1.417
μ, mm^{-1}	10.88	4.60	4.38	2.25
reflns collected	7983	43770	45515	19333
unique reflns (R_{int})	2924 (0.0427)	7879 (0.0428)	8229 (0.0483)	7025 (0.0423)
R values [$I < 2\sigma(I_0)$]	R1 = 0.0356	R1 = 0.0394	R1 = 0.0429	R1 = 0.0474
	wR2 = 0.0745	wR2 = 0.1063	wR2 = 0.1164	wR2 = 0.1210
R values, all data	R1 = 0.0648	R1 = 0.0441	R1 = 0.0611	R1 = 0.0763
	wR2 = 0.0786	wR2 = 0.1105	wR2 = 0.1232	wR2 = 0.1310
deposition no.	CCDC 185062	CCDC 185063	CCDC 185064	CCDC 185065

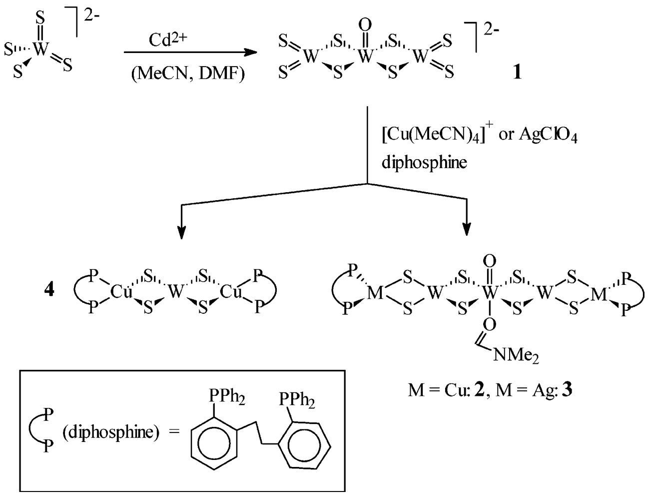
Experimental Section

Materials and Methods. All operations were carried out under aerobic conditions at room temperature. Starting compounds were obtained from commercial sources or prepared according to literature procedures ($[Et_4N]_2[WS_4]$[18]). The elemental analyses of **1** and **2** were carried out by the combustion method. Analyses of **3** (the silver analogue of **2**) and **4** are not reported, since varying conditions of preparation and workup afforded the bulk materials with varying amounts of solvent of crystallization, and thus varying analytical results. IR spectra were obtained as KBr pellets with a Perkin-Elmer spectrometer 1720 FT. NMR spectra were recorded on a Varian Gemini 200 BB spectrometer with the usual spectrometer settings.

Preparation of Complexes. $[Et_4N]_2[O{=}W(WS_4)_2]$, $[Et_4N]_2$·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 was added $CdCl_2·2H_2O$ (0.15 g, 0.65 mmol). The solution was filtered, and the filtrate stirred for about 6 h. Red crystalline bulk material of $[Et_4N]_2$·**1** was obtained by gas diffusion of diethyl ether into the solution, from which single crystals were selected for the structure determination. Overall yield 55 mg (10%). Anal. for $[Et_4N]_2$·**1** Calcd for $C_{60}H_{40}N_2OS_8W_3$ (M = 1613.02 g mol^{-1}): C, 44.68; H, 2.50; N, 1.74; S, 15.95. Found: C, 44.47; H, 2.55; N, 1.78; S, 15.66.

[μ-{OW(DMF)(WS_4)$_2$}{M(diphosphine)}$_2$] (M = Cu, 2; M = Ag, 3) and [{μ-($W^{VI}S_4$)}{Cu(diphosphine)$_2$}], 4. To a solution of **1** prepared as described above, 40 mL of CH_2Cl_2 solution containing diphosphine (0.20 g, 0.4 mmol) and $[Cu(NCMe)_4]ClO_4$ (0.13 g, 0.4 mmol; for **2** and **4**) or $AgClO_4$ (0.11 g, 0.5 mmol; for **3**) were added. The mixtures were stirred for 5 min. Red crystals of **2** or **3**, and yellow crystals of **4**·2MeCN·CH_2Cl_2, were obtained by gas diffusion of diethyl ether. Compounds **2** and **4** were separated manually by sorting out red crystals of **2** and yellow crystals of **4**. Yields: **2**, 265 mg (25%); **3**, 221 mg (20%); **4**, 84 mg (10%). Anal. for **2** Calcd for $C_{81}H_{74}Cu_2N_2O_2P_4S_8W_3$ (M = 2166.41 g mol^{-1}): C, 44.90; H, 3.44; N, 1.29; S, 11.84. Found: C, 44.17; H, 3.55; N, 1.08; S, 11.66. For ^{31}P NMR results see later in the text. ^1H NMR patterns for the coordinated diphosphine (3.11 CH_2, 7.77−6.85 phenyl-H) do not significantly deviate from those of the free phosphine. For DMF of **2** an **3**, the ^1H NMR resonances ($CDCl_3$) at 7.82 (formyl) and 2.80 (methyl) indicate coordination. **CAUTION:** Perchlorates bear the risk of uncontrolled explosions when heated in contact with inflammable materials.

Scheme 1



X-ray Crystallography. Data collection was carried out on a Bruker SMART Apex CCD diffractometer at 293(2) K 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. The program ASP (Chen, Jiutong, Fujian Institute, P.R. China) was used to plot the molecular structures. Disorder of the central W═O was treated with the following occupancies: **1**, 1/1; **2**, 0.9/0.1, **3**, 0.93/0.07. The oxygen of DMF in **2** and **3** was refined in a defined position without disorder. The C and N atoms of DMF in **2** and **3** were treated with a 1:1 disorder model. Atoms of solvent molecules were refined anisotropically; the phenyl carbons C21−C26, C51−C56, C61−C66 in **2**, and all of the phenyl carbons in **3** were fitted into rectangular hexagons with C−C distances of 1.39 Å and refined anisotropically. H atoms were placed into calculated positions and included in the last cycles of refinement. Crystal structure and refinement data, and the CCDC deposition numbers, are collated in Table 1.

Results and Discussion

Scheme 1 summarizes the reactions. Treatment of $[Et_4N]_2[WS_4]$ in a mixture of acetonitrile and dimethylformamide, DMF, with Cd^{2+} leads to partial removal of sulfido ligands

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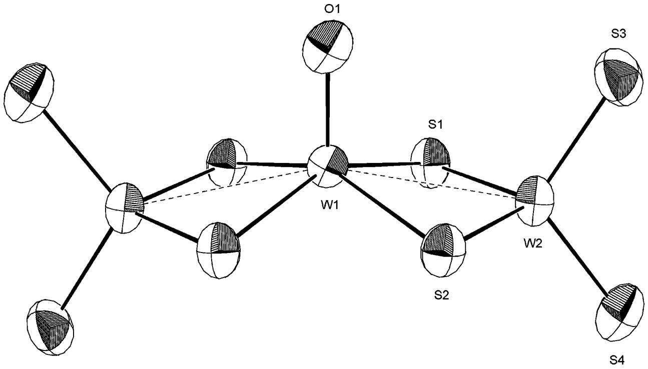

Figure 1. Molecular structure of **1**. The W═O unit is evenly disordered over two positions, pointing upward (shown) and downward (not shown).

Table 2. Selected IR Bands of Complexes **1**−**4**

	1	**2**	**3**	**4**
ν(C═O)		1643	1644	
ν(W═O)	972	961	962	
ν(W−S_{term})	494			
δ(W−S−W)	466	466	464	
δ(Cu/Ag−S−W)		494	498	503

Table 3. Selected Bond Lengths (Å) and Angles (deg)

	1	**2**	**3**	**4**
W1−O1	1.772(12)	1.673(9)	1.667(13)	
W1−O01		2.314(10)	2.338(12)	
W1−S1	2.475(3)	2.432(2)	2.437(2)	2.2091(17)
W1−S2	2.406(3)	2.446(2)	2.424(2)	2.1988(15)
W2−S1	2.272(3)	2.233(2)	2.240(3)	
W2−S2	2.269(3)	2.238(2)	2.239(3)	
W2−S3	2.148(3)	2.190(2)	2.181(3)	
W2−S4	2.152(3)	2.190(2)	2.183(3)	
W1···W2	3.000(2)	2.9692(6)	2.9686(6)	
Cu/Ag−S3		2.347(2)	2.608(3)	2.3239(17)[a]
Cu/Ag−S4		2.361(3)	2.625(3)	2.3521(18)[a]
Cu/Ag−P1		2.332(3)	2.494(3)	2.3502(17)
Cu/Ag−P2		2.318(2)	2.471(3)	2.3440(18)
W2···Cu/Ag		2.8289(11)	3.0789(9)	2.8358(7)
S1−W1−S2	94.15(8)	94.92(7)	95.29(9)	107.03(6)
S1−W1−S1#	151.45(5)	162.77(13)	163.53(17)	112.07(9)
W1−S1−W2	78.25(7)	78.97(6)	78.69(8)	
S1−W2−S2	103.86(8)	107.00(8)	106.66(9)	
av of other angles at W2	110.54	109.97	110.00	
Cu/Ag−S3−W2		77.06(8)	79.48(9)	77.41(5)[b]
S3−Cu/Ag−S4		97.88(9)	88.25(9)	98.55(6)
S3−Cu/Ag−P1		110.36(9)	112.24(10)	111.07(7)[a]
P1−Cu/Ag−P2		123.06(10)	123.73(11)	116.11(6)[a]

[a] In **4**, the bridging S atoms connecting to Cu are labeled S1 and S2. [b] Angle Cu−S1−W1.

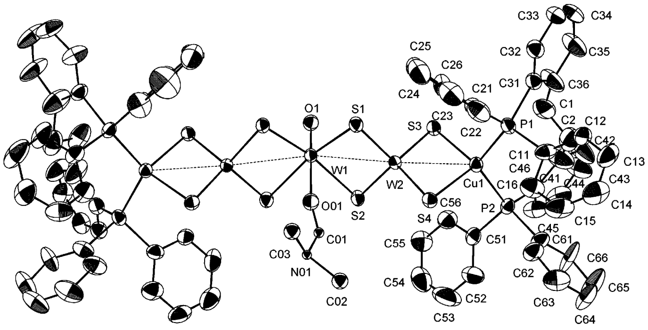

Figure 2. Molecular structure for the pentanuclear compound **2**. The corresponding silver complex **3** is isostructural. The dashed line indicates the slight deviations from linearity in the alignment of the five metal centers.

from the tetrathiotungstate and partial reduction (presumably by S^{2-} or HS^{-}) of W^{VI} to W^{IV} to yield the well-known[11,19] d^2 intermediate $\{O{=}W^{IV}\}^{2+}$. This electrophile coordinates to two yet unaffected tetrathiotungstates, forming the trinuclear, mixed-valent anion $[OW^{IV}(W^{VI}S_4)_2]^{2-}$, **1**, which was isolated as the tetraethylammonium salt $[Et_4N]_2\cdot$**1**. The origin of the oxo group is not clear. Most probably, however, it is supplied by water in the reaction mixture. In the IR spectrum of $[Et_4N]_2\cdot$**1**, there are characteristic bands at 972 (W═O), 494 (W−S_{term}), and 466 (W−S−W) cm^{-1}; Table 2.

The central $O{=}WS_4$ unit of **1** is square pyramidal, with tungsten displaced from the plane spanned by the four thio ligands (S1, S2, S1#, and S2#; # indicates symmetry-related atoms) by 0.596 Å toward the apical, doubly bonded O, Figure 1. There is a crystallographically imposed inversion center, giving rise to an even distribution of the W═O unit above and below the tetragonal plane. The plane W2, S1, S2, S1#, S2#, W2# is perpendicular to the planes formed by W2, S3, and S4. The distance *d*(W1···W2) is 3.000(2) Å. With 156.83(3)°, the angle W2−W1−W2# significantly deviates from linearity; the compound thus attains a flattened butterfly conformation. For selected bond lengths and angles, see also Table 3. The *d*(W−S) decrease in the order W1-μS > W2-μS > W2−S_{term}, reflecting, as far as the bridging thio ligands are concerned, a stronger bonding to W^{VI} (=W2) than to W^{IV} (=W1), an observation which also applies to compounds **2** and **3** (cf. Table 3), and supports, along with the diamagnetism of the compounds, the assignment of the oxidation states.

The reactivity of **1** focuses onto two aspects: (i) There is a free coordination site at the central tungsten, which can be occupied by a suitable nucleophile, such as DMF; (ii) the terminal sulfido ligands are potential coordination sites for electrophiles, such as Cu^+ and Ag^+. Both of these functions are realized as **1** is reacted with $[Cu(NCMe)_4]ClO_4$ or $AgClO_4$ in DMF/MeCN/CH_2Cl_2, and in the presence of the auxiliary diphosphine ligand. The neutral, pentanuclear, isostructural complexes [μ-{OW(DMF)$(WS_4)_2$}{M(diphosphine)}$_2$] (M = Cu, **2**; M = Ag, **3**) are generated, which have been isolated and structurally characterized (Figure 2) as the acetonitrile adducts **2**·MeCN and **3**·MeCN. The ^{31}P NMR signal of diphosphine (−14.6 in $CDCl_3$) shifts to +32.6 ppm on coordination. The coordination of DMF is revealed by the ν(C═O) = 1643 (free DMF, 1677 cm^{-1}), by ^1H NMR (δ = 7.82 and 2.80 in $CDCl_3$; free DMF = 8.02 and 2.90), and by the X-ray diffraction analysis.

Coordination of DMF in *trans* position to the oxo group O1 of the central tungsten (W1) reduces the displacement of W1 from the plane S1, S2, S1#, S2# from 0.596 Å in **1** to 0.3543 Å (**2**) and 0.3491 Å (**3**). The *d*(W1···W2) remains practically unaffected. The deviations from linearity in the alignment of the three tungsten ions in the precursor compound **1** are essentially alleviated: the angles at the

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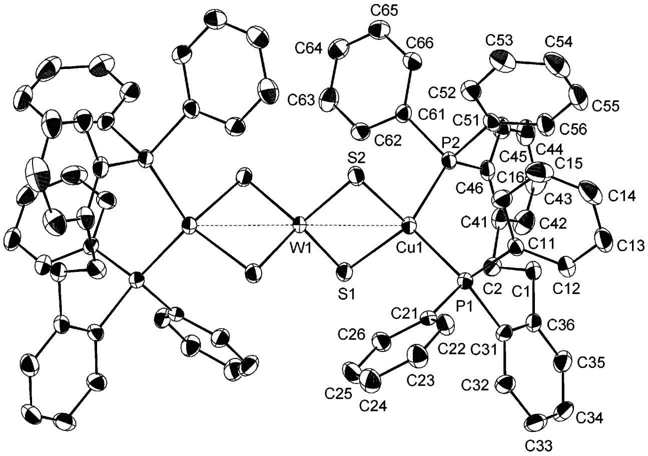

Figure 3. Molecular structure of **4**.

central W1 in **2** and **3** amount to 162.77(13)° and 163.53(17)°. The angles at the flanking tungstens, Cu/Ag−W2−W1, are 175.31(3)° for the copper, and 176.10(4)° for the silver complex. The *d*(Cu···W2) and the *d*(Ag···W2) are 2.8289 and 3.0789 Å, respectively; the average *d*(Cu−S) (2.354 Å), *d*(Ag−S) (2.613 Å), *d*(Cu−P) (2.325 Å), and *d*(Ag−P) (2.482 Å) are in the expected range.

Along with red crystals of **2**·NCMe, yellow crystals of the trinuclear complex $[\{\mu\text{-}(WS_4)\}\{Cu(diphosphine)\}_2]\cdot 2MeCN\cdot CH_2Cl_2$, **4**·$2MeCN\cdot CH_2Cl_2$, were isolated. Compound **4**, which contains a tetrahedrally coordinated W^{VI} center, apparently forms in a competing reaction from tetrathiotungstate(VI) and the copper precursor along with **2** (containing the mixed-valence $W^{IV}(W^{VI})_2$ core). W and the two Cu atoms are linearly arranged (the angle Cu1−W1−Cu1# is 179.18(3)°). To the best of our knowledge, there are only three cases where this apparently rare basic trinuclear WS_4Cu_2 unit has been characterized, the supporting ligands on each copper being $2PPh_3$,[20] *o*-phenanthroline,[21] and PPh_3 + tetrahydropyrimidine-2-thione.[22] In **4**, the steric conditions imposed by the bulky diphosphine favor this arrangement (Figure 3). The steric demand of diphosphine is reflected by the fact that the angle P1−Cu−P2 = 116.11(6)° is substantially larger than the S3−Cu−S4 angle (98.55(6)°). These differences are even more pronounced in **2** with P1−Cu−P2 = 123.06(10)° and S3−Cu−S4 = 97.88(9)°. The *d*(Cu···W1) in **4**, 2.8358 Å, compares to the corresponding distance in **2**, as do the average *d*(Cu−S) and *d*(Cu−P), Table 3.

Conclusion

Employing the sulfide scavenger Cd^{2+}, tetrathiotungstate is activated to the extent where oligonuclear, essentially linear thiotungstate clusters form, accompanied by redox ($W^{VI} \rightarrow W^{IV}$) and oxygenation processes (of W^{IV}) and, in the presence of Cu^+/Ag^+ plus the stabilizing diphosphine ligand, incorporation of these metal ions. Rearrangements in the coordination environment and oxidation state of the tungsten ions go along with chracteristic variations of several of the structure parameters: The trinuclear cluster **1**, with a square pyramidal central oxo-tetrathiotungstate, exhibits the largest deviation from a strictly linear arrangement of the three tungsten centers. The angle at the central W1, 151.5°, is diminished to 162.8° in the copper compound **2** and to 163.5° in the silver compound **3** as a consequence of supplementing the coordination sphere of W1 by dimethylformamide. The angles at the flanking tetrahedrally coordinated tungstens of **2** and **3**, linking to Cu or Ag, are 175.3° and 176.1°. Tungsten−sulfur distances reflect the oxidation states (and, to a certain extent, also the geometries) of the tungsten ions: The longest distances (averaging 2.437 Å in compounds **1**−**3**) are found for the central, tetragonally coordinated W^{IV}, the shortest (av 2.150 Å in **1**, 2.186 Å in **2** and **3**) for the flanking, tetrahedral W^{VI} ligated to the terminal, doubly bonded sulfides (**1**), or linking, via μ-S, to Cu/Ag (**2** and **3**). The $d(W^{VI}-\mu\text{-}S)$ values reflecting linking to the central W^{IV} (av 2.211 Å for **1** to **3**) are between these. The corresponding distances in **4**, where the central tungsten is in the oxidation state VI and tetrahedrally coordinated, amount to 2.204 Å.

The linear arrangement within the tungsten−copper/silver clusters is favored by the large steric requirement of the auxiliary diphosphine ligand, and the restriction to the finite size (pentanuclearity) by the fact that the bidentate phosphine coordinatively saturates the Cu/Ag sites. We have shown previously that unlimited chains can form when bifunctional bridging ligands such as thiocyanate are employed,[17] while nonlinear ("closed") assemblies are obtained in the absence of auxiliary ligands.[16] Compounds **2** and **3** appear to be the first linear pentanuclear thiometalates reported.

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