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Reactions of a Tungsten Trisulfido Complex of Hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) $[Et_4N][Tp^*WS_3]$ with CuX (X = Cl, NCS, or CN): Isolation, Structures, and Third-Order NLO Properties

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Reactions of a tungsten trisulfido complex of hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) $[Et_4N][Tp^*WS_3]$ (**1**) with 3 equiv of CuCl in $CHCl_3$ afforded a tetranuclear anionic cluster $[Et_4N][Tp^*W(\mu_3\text{-}S)_3(CuCl)_3]$ (**2**), while that of **1** with 3 equiv of CuNCS in MeCN produced a decanuclear neutral cluster (major product) $[Tp^*W(\mu_3\text{-}S)_3Cu_3(\mu\text{-}NCS)_3(CuMeCN)]_2$ (**3**) along with a binuclear anionic cluster (minor product) $[Et_4N][Tp^*WO(\mu\text{-}S)_2(CuNCS)]$ (**4**). Solvothermal reactions of **1** with 3 equiv of CuCN in MeCN at 80 °C for 48 h followed by slowly cooling it to ambient temperature gave rise to a polymeric cluster $[Tp^*W(\mu_3\text{-}S)(\mu\text{-}S)_2Cu_2(MeCN)(\mu\text{-}CN)]_n$ (**5**). Compounds **2**–**5** were characterized by elemental analysis, IR, UV–vis, ^1H NMR, and single-crystal X-ray crystallography. The cluster anion of **2** has a $[Tp^*WS_3Cu_3]$ incomplete cube with one Cl atom coordinated at each Cu center. **3** is composed of an unprecedented centrosymmetric W_2Cu_8 cluster core in which each void of the two single incomplete cubane-like $[Tp^*W(\mu_3\text{-}S)_3Cu_3(\mu\text{-}NCS)]^+$ cations is partially filled with an extra $[Cu(MeCN)(\mu\text{-}NCS)_2]^-$ anion via a pair of Cu–μ-NCS–Cu bridges. The cluster anion of **4** contains one WS_2Cu core that is formed by an oxidized $[Tp^*WO(\mu\text{-}S)_2]$ species and one CuNCS fragment. **5** consists of butterfly shaped $[Tp^*W(\mu_3\text{-}S)(\mu\text{-}S)_2Cu_2(MeCN)]$ fragments that are interconnected via cyanide bridges to form a 1D spiral chain extending along the *c* axis. The successful synthesis of **2**–**5** from **1** suggests that **1** may be an excellent synthon to the W/Cu/S clusters. In addition, the third-order nonlinear optical (NLO) properties of **1**–**3** in solution were also investigated by femtosecond degenerate four-wave mixing (DFWM) technique with a 80 fs pulse width at 800 nm. Although **2** was not detected to have NLO effects, **1** and **3** exhibited relatively good optical nonlinearities with the nonlinear refractive index n_2 and the third-order nonlinear optical susceptibility $\chi^{(3)}$ values being 0.79×10^{-13} and 0.38×10^{-14} esu (**1**) and 2.08×10^{-13} and 1.00×10^{-14} esu (**3**), respectively. The second-order hyperpolarizability γ value for **3** (5.46×10^{-32} esu) is ca. 5 times larger than that of its precursor **1**.

Introduction

In the past four decades, molybdenum(or tungsten)/copper-(or silver)/sulfur clusters derived from the well-known synthons tetrathiotungstate and tetrathiomolybdate, $[MS_4]^{2-}$, have been extensively investigated because of their rich structural chemistry,[1−5] potential applications in biological

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systems,[6] and optoelectronic materials.[7−8] About 12 years ago, another type of organometallic synthons, the pentamethylcyclopentadienyl trisulfido complexes of tungsten(VI) and molybdenum(VI), [PPh$_4$][Cp*MS$_3$] (Cp* = η^5-C$_5$Me$_5$, M = Mo, W), were developed.[9] Such synthons have been employed to react with various copper(I) and silver(I) salts to form a new family of Mo(W)/Cu(Ag)/S clusters in which some structures were found to be unprecedented in the chemistry of the tetrathiometalates and also showed relatively good third-order NLO performances in solution.[10] During this period one more synthons [Et$_4$N][LWS$_3$] (L = hydridotris(pyrazol-1-yl)borate (Tp) or hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) (**1**)) was successfully prepared. A series of dinuclear homo- and heterometallic complexes containing [Tp*WS(μ-S)$_2$M′] (M′ = Pt, Pd, Ir, Rh, and W) and [Tp*W(μ-S)$_3$M′] (M′ = Pt, Ir, and Mo) cores has been isolated.[11] In addition, a set of single and double cubane-like Mo(W)/Fe/S clusters derived from [Et$_4$N][LWS$_3$] and [Et$_4$N][LMoS(S$_4$)] (L = Tp or Tp*) were prepared for the mimicking of the FeMoco and P-cluster structures in the nitrogenases.[12] However, to our knowledge, the chemistry and third-order NLO properties of Mo(W)/Cu/S clusters containing **1** and its derivatives have not been explored yet.

Chart 1. Designation of Compounds and Abbreviations[a] for **1**−**5**

[Et$_4$N][Tp*WS$_3$]	**1**[11a]
[Et$_4$N][Tp*W(μ_3-S)$_3$(CuCl)$_3$]	**2**
[Tp*W(μ_3-S)$_3$Cu$_3$(μ-NCS)$_3$(CuMeCN)]$_2$	**3**
[Et$_4$N][Tp*WO(μ-S)$_2$(CuNCS)]	**4**
[Tp*W(μ_3-S)(μ-S)$_2$Cu$_2$(MeCN)(μ-CN)]$_n$	**5**

[a] Tp* = hydridotris(3,5-dimethylpyrazol-1-yl)borate (1−).

We recently were interested in the chemistry and third-order nonlinear optical (NLO) properties of Mo(W)/Cu(Ag)/S clusters originated from [MS$_4$]$^{2-}$ and [Cp*MS$_3$]$^{-}$ (M = Mo, W).[5,8a,10] We turned our attention to employment of **1** for construction of new W/Cu/S clusters due to the following considerations. First, although Tp* is isoelectronic to Cp*, it binds in a σ rather than π fashion to the W center. The chemistry of **1** toward Cu(I) may be different from that of its Cp* analogue. The second is that because of the bulkiness of Tp*, **1**, when reacted with copper(I) salts, may form more soluble W/Cu/S cluster precursors that may be used for our ongoing assembly of W/Cu/S-based supramolecular compounds.[5d−f,10j−l] Third, the possibly formed W/Cu/S clusters containing **1** are important not only because their NLO properties are reported for the first time, but also because these complexes offer us more chances to explore how structural types and periphery ligands around the cluster framework affect the NLO performances and screen out better cluster-based NLO materials.[5c,8a,10i,l] Therefore, we carried out reactions of **1** with CuX (X = Cl, NCS, CN) and isolated four heterometallic clusters **2**−**5** (Chart 1). Among these compounds, **3** and **5** have no counterparts in either [MS$_4$]$^{2-}$ or [Cp*MS$_3$]$^{-}$. We also examined the third-order NLO properties of **1**−**3** in solution under the femto-

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second degenerate four-wave mixing (DFWM) technique with 80 fs laser pulses at 800 nm. Herein, we report their synthesis, structures, and third-order NLO properties in solution.

Experimental Section

General Procedures. All manipulations were performed under an argon atmosphere using standard Schlenk-line techniques. **1** was prepared according to the literature method,[11a] while all other chemicals were used as purchased. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon and collected by distillation. ^{1}H NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. ^{1}H NMR chemical shifts were referenced to TMS in CDCl$_3$ or to the deuterated dimethyl sulfoxide (DMSO-d_6) signal. IR spectra were recorded on a Varian 1000 FT-IR spectrometer as KBr disks (4000−400 cm^{-1}). UV−vis spectra were measured on a Varian 50 UV−visible spectrophotometer. Elemental analyses for C, H, and N were performed on a Carlo-Erba CHNO-S microanalyzer.

[Et$_4$N][Tp*W(μ_3-S)$_3$(CuCl)$_3$] (2). To a red solution of **1** (18.7 mg, 0.025 mmol) in CHCl$_3$ (5 mL) was added CuCl (8 mg, 0.075 mmol). The resulting mixture was stirred for 5 min to form a purple-red solution and filtered. Diethyl ether (20 mL) was carefully layered onto the filtrate to form purple red prisms of **2**·2CHCl$_3$, which were collected by filtration, washed with Et$_2$O, and dried in vacuo. Yield: 25 mg (81% based on **1**). Anal. Calcd for C$_{25}$H$_{44}$BCl$_9$Cu$_3$N$_7$S$_3$W: C, 24.15; H, 3.57; N, 7.89. Found: C, 24.32; H, 3.55; N, 7.95. IR (KBr disc): 2564 (w), 1628 (w), 1546 (s), 1453 (s), 1435 (s), 1414 (s), 1348 (s), 1220 (s), 1071 (m), 1035 (m), 860 (w), 821 (w), 790 (w), 691 (w), 651 (w), 481 (w), 410 (w) cm^{-1}. UV−vis (MeCN, λ_{max} (nm (ϵ, M^{-1} cm^{-1}))): 211 (69 000), 254 (18 600), 316 (13 300), 440 (3800). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.36−1.40 (t, 12H, CH$_2$C*H*$_3$), 2.37 (s, 9H, CH$_3$ in Tp*), 2.95 (s, 9H, CH$_3$ in Tp*), 3.33−3.39 (q, 8H, C*H*$_2$CH$_3$), 5.94 (s, 3H, CH in Tp*); the B−H proton was not located.

[Tp*W(μ_3-S)$_3$Cu$_3$(μ-NCS)$_3$(CuMeCN)]$_2$ (3) and [Et$_4$N][Tp*WO(μ-S)$_2$(CuNCS)] (4). To a red solution containing **1** (19 mg, 0.025 mmol) in MeCN (5 mL) was added CuNCS (9 mg, 0.075 mmol). A workup similar to that used in the isolation of **2** afforded dark red block crystals of **3**·2MeCN coupled with several large red plates of **4**, which were separated under a microscope. Yield for **3**·2MeCN: 15 mg (75% based on Cu). Anal. Calcd for C$_{44}$H$_{56}$B$_2$Cu$_8$N$_{22}$S$_{12}$W$_2$: C, 24.29; H, 2.60; N, 14.17. Found: C, 23.97; H, 2.54; N, 13.83. IR (KBr disc): 2564 (w), 2122 (s), 2062 (m), 1631 (w), 1546 (m), 1451 (m), 1439 (m), 1414 (m), 1347 (m), 1221 (m), 1072 (w), 1034 (w), 860 (w), 822 (w), 798 (w), 691 (w), 650 (w), 479 (w), 408 (w) cm^{-1}. UV−vis (MeCN, λ_{max}(nm (ϵ M^{-1} cm^{-1}))): 315 (23 200), 436 (6600). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.04 (s, 9H, CH$_3$CN), 2.32 (s, 18H, CH$_3$ in Tp*), 2.73 (s, 18H, CH$_3$ in Tp*), 6.09 (s, 6H, CH in Tp*), the B−H proton was not located.

[Tp*W(μ_3-S)(μ-S)$_2$Cu$_2$(MeCN)(μ-CN)]$_n$ (5). To a Pyrex glass tube (10 cm in length and 0.5 cm in diameter) was added **1** (18.7 mg, 0.025 mmol), CuCN (7 mg, 0.075 mmol), and 2.0 mL of MeCN. Then the tube was sealed and heated in an oven at 80 °C for 48 h. After being cooled to ambient temperature at a rate of 5 °C/h, the resulting dark red prisms of **5** were eluted with MeCN and Et$_2$O several times and dried in vacuo. Yield: 16 mg (84% based on **1**). Anal. Calcd for C$_{18}$H$_{25}$BCu$_2$N$_8$S$_3$W: C, 28.03; H, 3.27; N, 14.53. Found: C, 28.25; H, 3.30; N, 14.40. IR (KBr disc): 2564 (m), 2160 (m), 2044 (w), 1610 (w), 1545 (s), 1436 (m), 1412 (s), 1384 (m), 1354 (s), 1219 (s), 1073 (m), 1036 (m), 860 (m), 819 (m), 802 (m), 692 (m), 648 (m), 479 (w), 445 (w), 429 (m) cm^{-1}.

X-ray Structure Determinations. X-ray-quality crystals of **2**·2CHCl$_3$, **3**·2MeCN, **4**, and **5** were obtained directly from the above preparations. The measurements of **2**·2CHCl$_3$, **3**·2MeCN, and **4** were made on a Rigaku Mercury CCD X-ray diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å). Single crystals were mounted with grease at the top of a glass fiber and cooled at 193 K in a liquid-N$_2$ stream. Cell parameters were refined using the program CrystalClear (Rigaku and MSC, version 1.3, 2001). The collected data were reduced using the program CrystalStructure (Rigaku and MSC, version 3.60, 2004), while an absorption correction (multiscan) was applied. Measurement of **5** was carried on a CCD-Bruker APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Data reductions and absorption corrections were performed with the SAINT and SADABS software packages. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **2**·2CHCl$_3$, **3**·2MeCN, **4**, and **5** were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with the SHELXTL-97 program.[13] The ethyl groups of the [Et$_4$N]$^+$ cation in **2**·2CHCl$_3$ were found to be disordered over two sites with an occupancy factor of 0.54/0.46 for C18−C20/C18A−C20A, C22/C22A, and C24−C25/C24A−C25A. All non-hydrogen atoms were refined anisotropically. In all four cases, the H atom bound to the B atom was located from the difference Fourier map and refined isotropically. All other hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C). Important crystallographic information for **2**·2CHCl$_3$, **3**·2MeCN, **4**, and **5** are tabulated in Table 1.

Third-Order Nonlinear Optical (NLO) Measurements of 1−3. Acetonitrile solutions of **1** (2.27 × 10^{-4} M), **2** (2.17 × 10^{-4} M), and **3** (1.17 × 10^{-4} M) were placed in a 1.5 mm quartz cuvette for the third-order NLO measurements. These three compounds were stable toward air and laser light under experimental conditions. As a reference, the optical nonlinearity of the standard sample CS$_2$ was also observed. The third-order NLO properties were measured using the femtosecond DFWM technique with a Ti:Sapphire laser (Spectra-physics Spitfire Amplifier). The pulse width was determined to be 80 fs on a SSA25 autocorrelator. The operating wavelength was centered at 800 nm. The repetition rate of the pulses was 1 kHz. During the measurement the laser was very stable (RMS < 0.1%). The input beam was split into two beams k_1 and k_2 with nearly equal energy by use of a beam splitter (BS) and then focused on a plot of the sample. The beam k_2 passed through a delay line derived by a stepping motor in order that the optical path length difference between the k_2 and k_1 beams could be adjusted during the measurement. The angle between the beams k_1 and k_2 was about 5°. When k_1 and k_2 were overlapped spatially in the sample, the generated signal beam k_3 passed through an aperture, recorded by a photodiode and then analyzed by a lock-in amplifier and computer.

Results and Discussion

Synthetic and Spectral Aspects. Treatment of **1** with 3 equiv of CuCl in CHCl$_3$ produced a purple-red solution from which a tetranuclear anionic cluster **2**·2CHCl$_3$ was isolated in 81% yield (Scheme 1). Similar reactions of **1** with CuCl in 1:2−1:6 molar ratios formed the same product. Analogous

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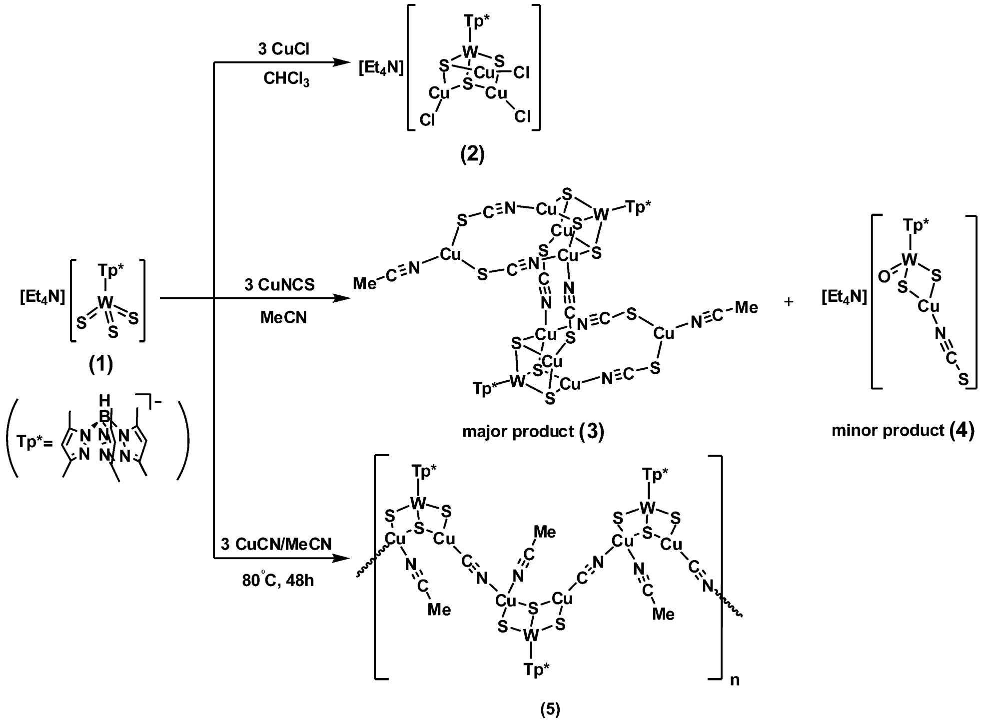
Table 1. Crystallographic Data for **2**·2CHCl$_3$, **3**·2MeCN, **4**, and **5**

	2·2CHCl$_3$	**3**·2MeCN	**4**	**5**
chemical formula	$C_{25}H_{44}BCl_9Cu_3N_7S_3W$	$C_{44}H_{56}B_2Cu_8N_{22}S_{12}W_2$	$C_{24}H_{42}BCuN_8OS_3W$	$C_{18}H_{25}BCu_2N_8S_3W$
fw	1243.23	2175.65	813.07	771.42
cryst syst	triclinic	monoclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	Pbca	$P2_12_12_1$
a (Å)	10.355(2)	10.4069(16)	17.254(4)	9.863(2)
b (Å)	10.390(2)	18.823(3)	18.011(4)	12.442(3)
c (Å)	21.624(4)	17.893(3)	20.956(4)	20.895(5)
α (deg)	83.93(3)			
β (deg)	85.13(3)	93.876(5)		
γ (deg)	75.46(3)			
V (Å^3)	2235.2(8)	3497.0(10)	6512(2)	2564.1(10)
Z	2	2	8	4
D_{calcd} (g·cm^{-3})	1.847	2.066	1.658	1.998
μ(Mo Kα, cm^{-1})	4.679	6.063	4.407	6.387
R^a	0.0789	0.0828	0.0856	0.0326
wR^b	0.2050	0.1868	0.1943	0.0541
GOF^c	1.043	1.202	1.343	0.918

^{a} $R = \sum||F_o| - |F_c|/\sum|F_o|$. ^{b} $wR = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. ^{c} GOF $= \{\sum[w((F_o^2 - F_c^2)^2)/(n - p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

Scheme 1. Reactions of **1** with CuX (X = Cl, NCS, CN)



reactions of **1** with 3 equiv of CuNCS in MeCN afforded a major decanuclear neutral cluster **3**·2MeCN in 75% yield coupled with an unexpected binuclear anionic cluster **4** as a minor product. As discussed later in this paper, **4** contained a terminal O atom, which may have originated from the adventitious moisture or O$_2$ during the reaction and crystallization, though the details about the formation of **4** are not clear. Compound **3** could also be produced from the reactions of **1** with 2 or 4−5 equiv of CuNCS in MeCN. However, when **1** reacted with 3−4 equiv of CuCN in MeCN, a dark red solid was always formed that was almost insoluble in common organic solvents, which precluded its further recrystallization and structural characterization. This crude product was quite messy according to its elemental analysis, IR spectra, and X-ray fluorescence analysis. As it is known, the hydro(solvo)thermal reactions of metal salts with different ligands may generate crystals of products that could not be formed via routine solution methods.[14] Therefore, we attempted reactions of **1** with CuCN in MeCN under solvothermal conditions. Heating a mixture of **1** with 3 equiv of CuCN in a sealed Pyrex tube at 80 °C for 48 h followed by slowly cooling the solution to ambient temperature gave rise to dark red prismatic crystals of **5** in 84% yield (Scheme 1).

As **1** has a very similar structure to its Cp* analogue [PPh$_4$][Cp*WS$_3$], comparison of their reactions toward CuX (X = Cl, NCS, CN) merits comment. Reactions of [PPh$_4$][Cp*WS$_3$] with 3 equiv of CuX (X = Cl, or NCS) gave rise to weakly chloride(or thiocyanate)-bridged double incomplete cubane-like clusters [PPh$_4$]$_2$[Cp*WS$_3$(CuX)$_3$]$_2$,[10a,c] while

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[14] (a) Rabenau, A. *Angew. Chem., Int. Ed.* **1985**, *24*, 1026. (b) Feng, S. H.; Xu, R. R. *Acc. Chem. Res.* **2001**, *34*, 239. (c) Chen, X. M.; Tong, M. L. *Acc. Chem. Res.* **2007**, *40*, 162.

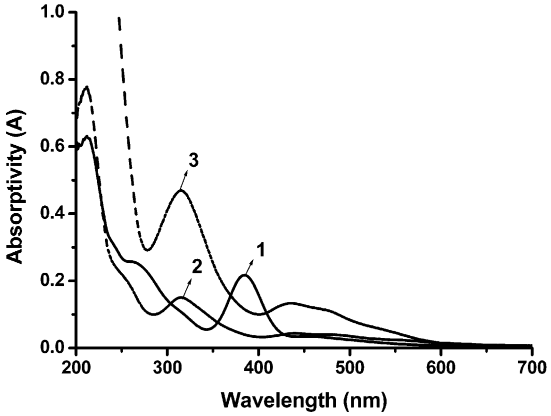

Figure 1. Electronic spectra of **1** (2.31×10^{-5} M), **2** (1.13×10^{-5} M), and **3** (2.02×10^{-5} M) in MeCN in a 1 cm thick glass cell.

those of [PPh_4][Cp*WS_3] with 2 or 3 equiv of CuCN afforded discrete trinuclear or tetranuclear anionic clusters [PPh_4][Cp*WS_3(CuCN)$_n$] (n = 2 or 3).[10i,j] Although reactions of **1** with CuCl gave an incomplete cubane-like cluster **2** whose structure is similar to that of [PPh_4]$_2$[Cp*WS_3($CuCl$)$_3$]$_2$, those of **1** with CuNCS or CuCN produced the decanuclear cluster **3** and the 1D spiral polymeric cluster **5** whose structures are not observed in the Cp* analogue. These results suggest that relative to that of the Cp* analogue, **1** does have somewhat different reactivity toward Cu(I), which is probably due to the fact that Tp* binds in a σ fashion to the W(VI) center and is more bulky than Cp*.

Solids **2**·$2CHCl_3$, **3**·2MeCN, **4**, and **5** are relatively stable toward oxygen and moisture. **2**·$2CHCl_3$ is readily soluble in $CHCl_3$, MeCN, DMF, and DMSO, while **3**·2MeCN only dissolves in MeCN, DMF, and DMSO. **5** is virtually insoluble in any common organic solvents. Elemental analysis of **2**·$2CHCl_3$, **3**·2MeCN, and **5** was consistent with their chemical formula. The IR spectra of **2**, **3**, and **5** exhibited a band assigned to the B−H stretching vibration at ca. 2564 cm^{-1}. In the IR spectra of **2**, **3**, and **5** bands at 481/410 (**2**), 479/408 (**3**), and 479/445/429 cm^{-1} (**5**) may be assigned as the bridging W−S stretching vibrations. In addition, a band at 2062 and 2122 cm^{-1} in the IR spectrum of **3** was assigned to be the terminal (MeCN) and bridging C≡N (μ-NCS) stretching vibrations, while those at 2044 and 2160 cm^{-1} in the IR spectrum of **5** were assumed to be the terminal (MeCN) and bridging C≡N stretching vibrations, respectively. The ^{1}H NMR spectra of **2** in $CDCl_3$ and **3** in DMSO-d_6 at ambient temperature showed two sharp singlets with the same intensities at 2.37/2.95 (**2**) and 2.32/2.73 ppm (**3**) and one singlet at 5.94 (**2**) and 6.09 ppm (**3**), which may be assigned to be the methyl protons and the pyrazolyl methine protons of the Tp* species, respectively. As shown in Figure 1, the UV−visible absorption spectra of **1**−**3** in MeCN are characterized by four absorption bands. Relative to the band at 386 nm (**1**), those at 316 (**2**) and 315 nm (**3**) are blue shifted and are probably originated from the S → W(VI) charge-transfer transitions of the common Tp*WS_3 moiety.[10a,c,j] The identities of **2**·$2CHCl_3$, **3**·2MeCN, **4**, and **5** were further confirmed by X-ray crystallography.

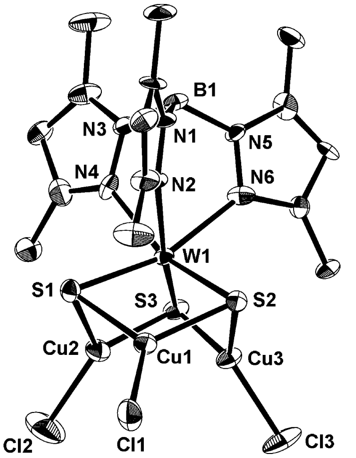

Figure 2. Perspective view of the cluster anion of **2** with labeling scheme and 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**

W(1)···Cu(1)	2.6391(19)	W(1)···Cu(2)	2.6435(18)
W(1)···Cu(3)	2.6385(18)	W(1)−S(1)	2.314(3)
W(1)−S(2)	2.306(3)	W(1)−S(3)	2.321(3)
Cu(1)−S(1)	2.213(4)	Cu(1)−S(2)	2.213(4)
Cu(2)−S(1)	2.211(3)	Cu(2)−S(3)	2.214(3)
Cu(3)−S(2)	2.215(3)	Cu(3)−S(3)	2.208(3)
Cu(1)−Cl(1)	2.141(5)	Cu(2)−Cl(2)	2.150(4)
Cu(3)−Cl(3)	2.143(4)		
S(1)−W(1)−S(2)	104.15(12)	S(1)−W(1)−S(3)	103.96(11)
S(2)−W(1)−S(3)	104.08(11)	S(1)−Cu(1)−S(2)	110.85(13)
S(1)−Cu(1)−Cl(1)	124.1(2)	S(2)−Cu(1)−Cl(1)	124.0(2)
S(1)−Cu(2)−S(3)	111.23(13)	S(1)−Cu(2)−Cl(2)	123.66(14)
S(3)−Cu(2)−Cl(2)	123.93(14)	S(2)−Cu(3)−S(3)	111.13(13)
S(2)−Cu(3)−Cl(3)	124.04(15)	S(3)−Cu(3)−Cl(3)	123.74(15)

Crystal Structure of [Et_4N][Tp*W(μ_3-S)$_3$($CuCl$)$_3$]·$2CHCl_3$ (2·$2CHCl_3$). Compound **2**·$2CHCl_3$ crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit contains one discrete [Tp*W(μ_3-S)$_3$($CuCl$)$_3$]$^-$ anion, one [Et_4N]$^+$ cation, and two $CHCl_3$ solvent molecules. The structure of the cluster anion of **2** is shown in Figure 2, and its selected bond lengths and angles are given in Table 2.

The cluster anion consists of an incomplete cubane-like [Tp*W(μ_3-S)$_3$$Cu_3$] core structure, which was found in [PPh_4]$_2$[Cp*MS_3(CuX)$_3$]$_2$ (M = Mo, X = Br; M = W, X = Cl, Br, NCS).[10a,c,i,l] The oxidation states of W and Cu atoms in **2** are assumed to be +6 and +1,[4b,10c] respectively. The W center in the Tp*WS_3 unit has a distorted octahedral configuration coordinated by three pyrazolyl N atoms and three sulfur atoms. The mean W−μ_3-S bond length (2.314(3) Å) is elongated by 0.12 Å relative to that of [Et_4N][Tp*WS_3][11a] due to coordination of the sulfur atoms at the Cu centers. Each Cu atom adopts a trigonal-planar geometry coordinated by two μ_3-S atoms and one terminal Cl atom. The mean W···Cu distance (2.6404(18) Å) is slightly shorter than those found in three-coordinate Cu clusters such as [PPh_4]$_2$[Cp*$WS_3Cu_3Cl_3$]$_2$ (2.654(3) Å)[10c] and [PPh_4][Cp*WS_3($CuCN$)$_2$] (2.6661(14) Å).[10j] The average Cu−S length (2.212(3) Å) is comparable to those of [PPh_4]$_2$[Cp*$WS_3Cu_3Cl_3$]$_2$ and [PPh_4][Cp*WS_3($CuCN$)$_2$]. The average terminal Cu−Cl length (2.145(5) Å) is slightly shorter than those observed in [PPh_4]$_2$[Cp*WS_3($CuCl$)$_3$]$_2$ (2.188(7) Å) and [(n-Bu)$_4$N]$_2$[WS_4($CuCl$)$_4$] (2.159(6) Å).[15]

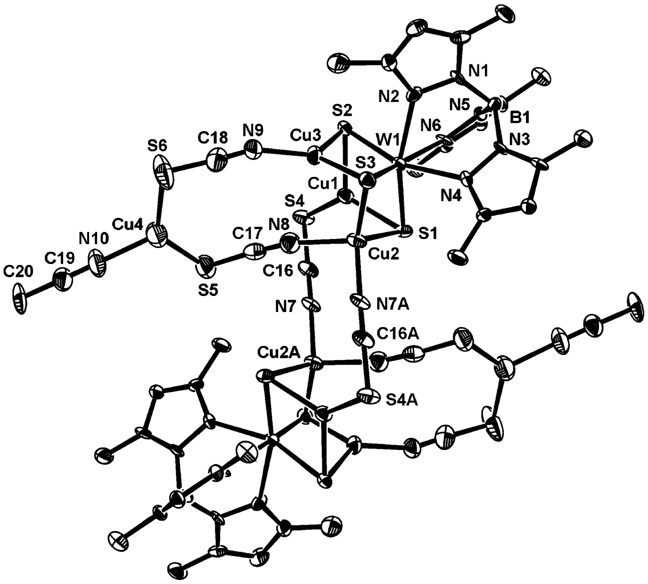

Figure 3. Molecular structure of **3** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Symmetry code: A $-x + 1$, $-y$, $-z + 1$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3**

W(1)···Cu(1)	2.6412(16)	W(1)···Cu(2)	2.7193(16)
W(1)···Cu(3)	2.6287(16)	W(1)−S(1)	2.298(3)
W(1)−S(2)	2.304(3)	W(1)−S(3)	2.305(3)
Cu(1)−S(1)	2.224(4)	Cu(1)−S(2)	2.191(3)
Cu(1)−S(4)	2.208(4)	Cu(2)−S(1)	2.259(4)
Cu(2)−S(3)	2.264(4)	Cu(2)−N(8)	2.107(13)
Cu(2)−N(7A)	1.939(11)	Cu(3)−S(2)	2.210(4)
Cu(3)−S(3)	2.221(4)	Cu(3)−N(9)	1.894(13)
Cu(4)−N(10)	1.956(13)	Cu(4)−S(5)	2.224(5)
Cu(4)−S(6)	2.230(6)		
S(1)−W(1)−S(2)	104.25(11)	S(1)−W(1)−S(3)	103.46(12)
S(2)−W(1)−S(3)	104.92(12)	S(1)−Cu(1)−S(2)	110.75(13)
S(1)−Cu(1)−S(4)	126.97(14)	S(2)−Cu(1)−S(4)	120.79(14)
S(1)−Cu(2)−S(3)	106.10(13)	S(1)−Cu(2)−N(8)	112.5(4)
S(1)−Cu(2)−N(7A)	112.0(4)	S(3)−Cu(2)−N(8)	109.7(4)
S(3)−Cu(2)−N(7A)	119.2(4)	N(8)−Cu(2)−N(7A)	97.4(5)
S(2)−Cu(3)−S(3)	111.12(13)	S(2)−Cu(3)−N(9)	126.2(4)
S(3)−Cu(3)−N(9)	121.6(4)	N(10)−Cu(4)−S(5)	113.8(5)
N(10)−Cu(4)−S(6)	115.9(5)	S(5)−Cu(4)−S(6)	130.15(19)

Crystal Structure of [Tp*W(μ_3-S)$_3$Cu$_3$(μ-NCS)$_3$(CuMeCN)]$_2$·2MeCN (3·2MeCN). Compound **3**·2MeCN crystallizes in the monoclinic space group $P2_1/c$, and the asymmetric unit contains one-half of the [Tp*W(μ_3-S)$_3$Cu$_3$(μ-NCS)$_3$(CuMeCN)]$_2$ molecule and one MeCN solvent molecule. The molecular structure of **3** is shown in Figure 3, and its selected bond lengths and angles are listed in Table 3.

Compound **3** contains two [Tp*W(μ_3-S)$_3$Cu$_3$(μ-NCS)$_3$(CuMeCN)] fragments, which are linked via a pair of Cu−μ-NCS−Cu bridges. A crystallographic inversion center is located at the center of the cluster. Each [Tp*W(μ_3-S)$_3$Cu$_3$(μ-NCS)$_3$(CuMeCN)] fragment consists of one [Tp*W(μ_3-S)$_3$Cu$_3$(μ-NCS)]$^+$ cation and one [Cu(MeCN)(μ-NCS)$_2$]$^-$ anion that are held together via another pair of Cu−μ-NCS−Cu bridges. Such a decanuclear W$_2$Cu$_8$ core structure is unprecedented in the chemistry of tetrathiometalates [MS$_4$]$^{2-}$ and Cp*-substituted trithiometalates [Cp*MS$_3$]$^-$ (M = Mo, W). Although the [Tp*W(μ_3-S)$_3$Cu$_3$(μ-NCS)]$^+$ cation in **3** contains a similar [Tp*W(μ_3-S)$_3$Cu$_3$] core to that of **2**, the three Cu atoms show different coordination geometries. Cu1 and Cu3 adopt an approximately trigonal-planar geometry (coordinated by one S (or N) of thiocyanate and two μ_3-S atoms), while Cu2 has a distorted tetrahedral geometry (coordinated by two N atoms of thiocyanates and two μ_3-S atoms). Owing to the different coordination environments of copper atoms, the three W···Cu contacts are different. The shorter W1···Cu1 and W1···Cu3 contacts are comparable to those observed in **2**, while the longer W1···Cu2 contact is close to those in clusters containing tetrahedrally coordinated Cu such as [(η^5-C$_5$Me$_5$)WS$_3$Cu]$_4$[16] and [WS$_4$Cu$_4$(dppm)$_4$](PF$_6$)$_2$.[5b] The Cu−μ_3-S bond lengths also reflect the mode of coordination of copper atoms: av. 2.212(4) Å for a trigonal geometry and av. 2.262(4) Å for a tetrahedral environment. The mean W−μ_3-S bond length (2.302(3) Å) is slightly shorter than that of **2**. In addition, Cu4 is coordinated by one N of the terminal MeCN molecule and two sulfur atoms of each NCS, forming a trigonal-planar geometry. The mean Cu−N(NCS) bond length (1.980(13) Å) is between those of the copper(I) complexes containing bridging thiocyanates [Cu(μ-NCS)(L)$_2$]$_n$ (1.966(6) Å for L = 2-methylpyridine; 2.00(1) Å for L = quinoline).[17] Correspondingly, the average Cu−μ-S(NCS) bond length (2.221(5) Å) is somewhat shorter than those of [Cu(μ-NCS)(L)$_2$]$_n$ (2.349(2) Å for L = 2-methylpyridine; 2.290(4) Å for L = quinoline), suggesting the two pairs of Cu(NCS)Cu linkages in **2** are relatively strong.

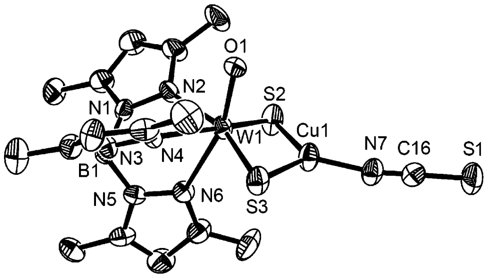

Figure 4. Perspective view of the cluster anion of **4** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Crystal Structure of [Et$_4$N][Tp*WO(μ-S)$_2$(CuNCS)] (4). Compound **4** crystallizes in the orthorhombic space group *Pbca*, and the asymmetric unit contains one discrete [Tp*WO(μ-S)$_2$(CuNCS)]$^-$ anion and one [Et$_4$N]$^+$ cation. The cluster anion of **4** consists of one [Tp*WOS$_2$] species and one CuNCS fragment linked by a pair of μ-S atoms, forming a WS$_2$Cu ring structure (Figure 4).

The W and Cu centers in **4** again kept their +6 and +1 oxidation states. The Cu1 adopts a trigonal-planar geometry coordinated by one N of thiocyanate and two μ-S atoms. As shown in Table 4, the WS$_2$Cu ring is asymmetrical and puckered slightly with a dihedral angle of 166° around the W1···Cu1 vector, which may lead to the existence of the

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Table 4. Selected Bond Distances (Å) and Angles (deg) for **4**

W(1)⋯Cu(1)	2.5630(15)	W(1)−O(1)	1.948(7)
W(1)−S(2)	2.258(3)	W(1)−S(3)	2.184(3)
Cu(1)−S(2)	2.107(3)	Cu(1)−S(3)	2.190(4)
Cu(1)−N(7)	1.849(10)		
O(1)−W(1)−S(2)	100.9(2)	O(1)−W(1)−S(3)	100.3(2)
S(2)−W(1)−S(3)	104.44(12)	S(2)−Cu(1)−S(3)	109.57(13)
S(2)−Cu(1)−N(7)	122.7(3)	S(3)−Cu(1)−N(7)	127.5(3)

shortest W⋯Cu contact (2.5630(15) Å) among the known W/Cu/S clusters containing trigonally coordinated Cu. The WS$_2$Cu ring in **4** resembles those found in [Me$_4$N]$_2$[WOS$_3$(CuCl)][18a] and [PPh$_4$][WO$_2$S$_2$(CuPPh$_3$)]·acetone.[18b] However, those in the latter two clusters are almost symmetrical and planar. The mean W−μ-S (2.221(3) Å) bond length in **4** is close to that in [Me$_4$N]$_2$[WOS$_3$(CuCl)] (2.227(3) Å), while that for the Cu−μ-S bonds (2.149(3) Å) is shorter than that of [Me$_4$N]$_2$[WOS$_3$(CuCl)] (2.219(3) Å). The terminal W1−O1 bond length is much longer than that found in [Cp*WO(μ-S)$_2$RuCl(PPh$_3$)$_2$] (1.746(4) Å)[11b] and [Me$_4$N]$_2$[WOS$_3$(CuCl)] (1.775(3) Å). The Cu1−N7 bond length is shorter than that of [Cu(imt)$_2$(NCS)] (1.956(4) Å, imt = imidiazolidine-2-thionate).[18c]

Crystal Structure of [Tp*W(μ_3-S)(μ-S)$_2$Cu$_2$(MeCN)(μ-CN)]$_\infty$ (5). Compound **5** crystallizes in the orthorhombic space group $P2_12_12_1$, and the asymmetric unit contains one [Tp*W(μ_3-S)(μ-S)$_2$Cu$_2$(MeCN)(μ-CN)] molecule. X-ray analysis revealed that **5** has a 1D spiral chain extending along the crystallographic *c* axis in which the repeating [Tp*W(μ_3-S)(μ-S)$_2$Cu$_2$(MeCN)] units are linked via Cu−μ-CN−Cu bridges (Figure 5). There is a 2$_1$ axis (parallel to the *c* axis) running through the center of the chain. The [Tp*W(μ_3-S)(μ-S)$_2$Cu$_2$(MeCN)] unit may be viewed as being a butterfly shaped [WS$_3$Cu$_2$] core structure, which is similar to those found in [WOS$_3$Cu$_2$(PPh$_3$)$_3$]·0.8CH$_2$Cl$_2$,[1b] [PPh$_4$][Cp*WS$_3$(CuCN)$_2$], [Cp*WS$_3$Cu$_2$(PPh$_3$)(μ-CN)]$_2$, and [PPh$_4$][{Cp*WS$_3$Cu$_2$(CN)(Py)}$_2$(μ-CN)].[10j] The two Cu atoms in **5** are not equivalent, and their coordination variability ranges from a nearly trigonal- planar (Cu1) to a distorted tetrahedron coordination (Cu2). Because of the different coordination geometries of the Cu atoms, the W1⋯Cu separations are different (Table 5). The trigonally coordinated W1⋯Cu1 contact is similar to those of the corresponding ones in [Cp*WS$_3$Cu$_2$(PPh$_3$)(μ-CN)]$_2$ and [PPh$_4$][{Cp*WS$_3$Cu$_2$(CN)(Py)}$_2$(μ-CN)]. The tetrahedrally coordinated W1⋯Cu2 contact is shorter than those of the corresponding ones in [Cp*WS$_3$Cu$_2$(PPh$_3$)(μ-CN)]$_2$ (2.768(2) Å) and [PPh$_4$][{Cp*WS$_3$Cu$_2$(CN)(Py)}$_2$(μ-CN)] (2.714(2) Å). It is noted that the Cu1−μ_3-S1−Cu2 angle (79.68(6)°) in **5** is 17.6° smaller than that of the cationic cluster [PPh$_4$][Cp*WS$_3$(CuCN)$_2$], which may make the cyanide groups of **5** able to access the Cu centers in the adjacent [WS$_3$Cu$_2$] cores to form a 1D spiral chain. In the structure of [PPh$_4$][Cp*WS$_3$(CuCN)$_2$], the Cu−μ_3-S−Cu bond angle is too large to have further coordination at the Cu sites of the neighboring cluster cores, which makes it only a discrete cluster. The Cu−μ-CN−Cu portions in **5** are slightly bent, with Cu1−C16−N7 and C16−N7−Cu2B angles of 176.2(7)° and 171.6(6)°. We assigned the atom coordinated at Cu1 to carbon and that bound to Cu2 to nitrogen on the basis of peak heights on the Fourier map and bond lengths. The Cu1−C16 and Cu2−N7A distances of the bridging cyanide groups are comparable to those of the corresponding ones in {[PPh$_4$][Cp*WS$_3$Cu$_3$(μ_3-Cl)(CN)(μ-CN)]·py}$_n$ and slightly shorter than those found in [Cp*WS$_3$Cu$_3$(μ-CN)$_2$(py)]$_n$[10k] and KCu(CN)$_2$.[19] The mean W1−μ-S, W1−μ_3-S, Cu−μ-S, and Cu−μ_3-S bond lengths in **5** are comparable to those of the corresponding ones in [Cp*WS$_3$Cu$_2$(PPh$_3$)(μ-CN)]$_2$ and [PPh$_4$][{Cp*WS$_3$Cu$_2$(CN)(Py)}$_2$(μ-CN)].

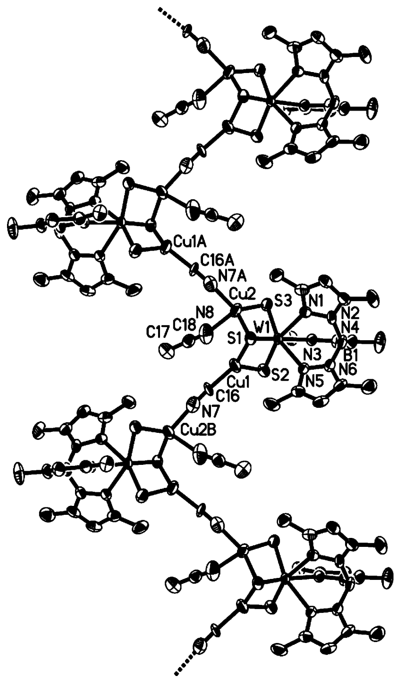

Figure 5. View of a section of the 1D spiral chain of **5** (extending along the *c* axis) with labeling scheme and 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Symmetry codes: A $-x+1$, $1/2+y$, $1/2-z$; B $-x+1$, $-1/2+y$, $1/2-z$.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **5**

W(1)⋯Cu(1)	2.6560(9)	W(1)⋯Cu(2)	2.6694(10)
W(1)−S(1)	2.3358(14)	W(1)−S(2)	2.2255(18)
W(1)−S(3)	2.2132(17)	Cu(1)−S(1)	2.2276(19)
Cu(1)−S(2)	2.199(2)	Cu(1)−C(16)	1.866(6)
Cu(2)−S(1)	2.2469(18)	Cu(2)−S(3)	2.208(2)
Cu(2)−N(8)	2.425(7)	Cu(2)−N(7A)	1.930(7)
S(1)−W(1)−S(2)	104.46(6)	S(1)−W(1)−S(3)	104.00(6)
S(2)−W(1)−S(3)	103.51(7)	S(1)−Cu(1)−S(2)	109.10(7)
S(1)−Cu(1)−C(16)	128.9(2)	S(2)−Cu(1)−C(16)	119.1(2)
S(1)−Cu(2)−S(3)	107.18(6)	S(1)−Cu(2)−N(8)	105.90(17)
S(1)−Cu(2)−N(7A)	127.1(2)	S(3)−Cu(2)−N(8)	101.27(17)
S(3)−Cu(2)−N(7A)	119.8(2)	N(8)−Cu(2)−N(7A)	88.3(2)
Cu(1)−S(1)−Cu(2)	79.68(6)		

Third-Order Nonlinear Optical (NLO) Properties of 1−3. As indicated in Figure 1, **1**−**3** showed relatively low linear absorption in the range of 600−800 nm. The laser

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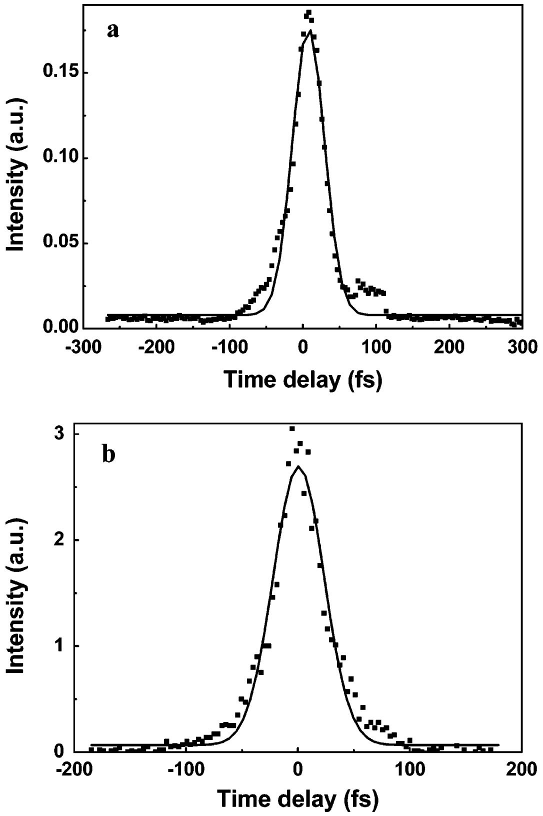

Figure 6. DFWM signal for acetonitrile solutions of 2.27×10^{-4} M for **1** (a) and 2.17×10^{-4} M for **3** (b) with 80 fs laser pulses and a 1.5 mm cell. The black solid squares are experimental data, and the solid curves are the theoretical fit.

wavelength (800 nm) used in the experiment of DFWM was out of the absorption region. Thus, the off-resonant third-order optical nonlinearities of the compounds could be measured. Previously, the third-order NLO properties of Mo(W)/Cu(Ag)/S clusters were measured by nanosecond or picosecond DFWM or Z-scan techniques.[3b,5c,8,10j,1] In this paper, we carried out our first attempt on the measurement of the third-order NLO properties of W/Cu/S clusters **1**−**3**. The dependence of time-resolved DFWM signal intensity on the delay time of the input beam is shown in Figure 6. The curves were obtained via fitting the time convolution between autocorrelation function of pulse and single-exponent decline function $\exp(t/-T_2)$. Intriguingly, **2** was not detected to have third-order NLO effects, implying that its NLO effects are weak in our experimental conditions.

The third-order nonlinear optical susceptibility $\chi^{(3)}$ is measured via a comparison with that of a reference sample CS_2, calculated from the DFWM signal (I), the linear refractive index (n), the sample thickness (L), and absorption correction factor using eq 1[20a]

$$\chi_s^{(3)} = \left(\frac{I_s}{I_r}\right)^{1/2} \cdot \frac{L_r}{L_s} \cdot \left(\frac{n_s}{n_r}\right)^2 \cdot \frac{\alpha \cdot L \cdot \exp(\alpha L/2)}{1 - \exp(-\alpha L)} \cdot \chi_r^{(3)} \qquad (1)$$

where the subscripts s and r represent the parameters for the sample and CS_2 and α is the linear absorption coefficient. The last fraction comes from the sample absorption and equals 1, while the sample has no absorption around the employed laser wavelength. The values of $\chi_r^{(3)}$ and n_r for CS_2 are 6.7×10^{-14} esu and 1.632, respectively.[20b] The third-order nonlinear optical susceptibility $\chi^{(3)}$ for **1** and **3** are calculated by eq 1 to be 0.38×10^{-14} (**1**) and 1.00×10^{-14} esu (**3**), respectively. The response times of **1** and **3** obtained from Figure 6 are 44 fs (**1**) and 45 fs (**3**). These results showed that **1** and **3** possess relatively good third-order optical nonlinearities.

The third-order nonlinear refractive index n_2 in isotropic media is estimated through eq 2[20c]

$$n_2(esu) = \frac{12\pi\chi^{(3)}}{n^2} \qquad (2)$$

where n is the linear refractive index of the solution. The nonlinear refractive index n_2 values are 0.79×10^{-13} esu (**1**) and 2.08×10^{-13} esu (**3**), respectively.

The second-order hyperpolarizability γ of a molecule in isotropic media is related to the solution $\chi^{(3)}$ by eq 3[20d]

$$\gamma = \frac{\chi^{(3)}}{Nf^4} \qquad (3)$$

where N is the number density of the solute per milliliter, and f^4 is the local field correction factor which is $[(n^2 + 2)/3]^4$ (n is the linear refractive index of solution). The second-order hyperpolarizability γ values are 1.07×10^{-32} esu (**1**) and 5.46×10^{-32} esu (**3**). According to eq 3, N represents the number density (concentration) of a compound and the γ value can be used to represent NLO properties of neat materials. Therefore, the third-order NLO performance for **3** was enhanced relative to that of **1**, which may be due to formation of the characteristic cluster skeleton of **3** from **1** and Cu^+ ions.[8a,d,f,20e] When compared with the nanosecond and picosecond measurement values, femtosecond values are roughly 2−3 orders of magnitude lower.[21] Therefore, the γ values of **1** and **3** are comparable to those of the Mo(W)/Cu/S clusters derived from $[MS_4]^{2-}$ or $[Cp^*MS_3]^-$ (M = Mo, W), such as $[(Et_4N)_2\{WS_4Cu_4(CN)_4\}]_n$ (1.26×10^{-29} esu),[8e] $[PPh_4][(\eta^5\text{-}C_5Me_5)MoS_3(CuNCS)_3]\cdot DMF$ (3.09×10^{-29} esu),[10l] and $[MoS_4Cu_4(\alpha\text{-}MePy)_5Br_2]\cdot 2(\alpha\text{-}MePy)_{0.5}$ (1.06×10^{-31} esu),[22b] and larger than those of C_{60} (7.5 ×

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10^{-34} esu) and C_{70} (1.3×10^{-33} esu),[23a] organometallic compounds such as *trans*-$[Mo(CO)_4(PPh_3)_2]$ (8.49×10^{-32} esu) and *cis*-$[Mo(CO)_4(PPh_3)_2]$ (4.375×10^{-31} esu),[23b] and TiOPc (Pc = phthalocyanie) films before and after thermal annealing (1.04×10^{-33} and 5.35×10^{-34} esu).[23c] As the γ values for **1** and **3** were obtained from a diluted solution, better NLO effects would be anticipated for higher concentrations of these compounds.

Conclusions

In the work reported here we investigated the reactions of **1** with CuX (X = Cl, NCS, CN) and isolated four new W/Cu/S clusters **2**−**5** containing the $[Tp^*WS_3]^-$ anion of **1**. For **5**, we successfully applied the solvothermal synthesis into the system of **1** and CuCN, which produced it in a relatively high yield that could not be isolated via the common solution method. Compounds **2**−**5** were characterized by elemental analysis, IR, UV−vis, ^1H NMR, and X-ray crystallography. The anion of **2** contains a $[WS_3Cu_3]$ incomplete cube, while **3** consists of an unusual W_2Cu_8 cluster core. The cluster anion of **4** has a WS_2Cu core with a rather short W···Cu contact, and **5** has a 1D spiral chain formed from the $[Tp^*W(\mu_3\text{-}S)(\mu\text{-}S)_2Cu_2(MeCN)]$ fragments that are linked via cyanide bridges. Formation of **2**−**5** suggested that **1** could be an excellent synthon, and its chemistry related to Cu(I)/Ag(I) is anticipated to be at least as rich as that of its Cp* analogue. Compounds **1** and **3** showed good third-order optical nonlinearities, and the third-order NLO performance of **3** was enhanced when the $[Tp^*WS_3]^-$ anion of **1** binds more Cu^+ ions to form **3**. Furthermore, as **2** and **3** have terminal chlorides and acetonitrile molecules, they may be replaced by strong donor multitopic ligands such as 4,4′-bipyridine. They may serve as potential structural and NLO building blocks for W/Cu/S-based supramolecular assemblies. Studies on these aspects are in progress in this laboratory.

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Supporting Information Available: Crystallographic data of compounds **2**−**5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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