Reactions of a Tungsten Trisulfido Complex of Hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*)[Et₄N][Tp*WS₃] 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*)[Et₄N][Tp*WS₃] (1) with 3 equiv of CuCl in CHCl₃ afforded a tetranuclear anionic cluster [Et₄N][Tp*W(S³-S)₃ClCl₃] (2), while that of 1 with 3 equiv of CuNCS in MeCN produced a decanuclear neutral cluster (major product) [Tp*W(S³-S)₃Cu₃(μ-NCS)₃(CuMeCN)]₂ (3) along with a binuclear anionic cluster (minor product) [Et₄N][Tp*WO(S²-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(S³-S)(S³-S)₂Cu₂(MeCN)(μ-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*WS₃Cu₃] incomplete cube with one Cl atom coordinated at each Cu center. 3 is composed of an unprecedented centrosymmetric W₂Cu₈ cluster core in which each void of the two single incomplete cubane-like [Tp*W(S³-S)₃Cu₃(μ-NCS)]⁺ cations is partially filled with an extra [Cu(MeCN)(μ-NCS)]⁻ anion via a pair of Cu−μ-NCS−Cu bridges. The cluster anion of 4 contains one WS₂Cu core that is formed by an oxidized [Tp*WO(μ-S)₂] species and one CuNCS fragment. 5 consists of butterfly shaped [Tp*W(S³-S)(μ-S)₂Cu₂(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 n² and the third-order nonlinear optical susceptibility d(3) values being 0.79 × 10⁻¹³ and 3.8 × 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 synths tetrathiotungstate and tetrathiomolybdate, [MS₄]²⁻, have been extensively investigated because of their rich structural chemistry,¹−⁵ potential applications in biological

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systems, and optoelectronic materials. About 12 years ago, another type of organometallic synths, the pentamethylenecyclopentadienyl trisulfilido complexes of tungsten(VI) and molybdenum(VI), \( [\text{PhH}]_3[\text{Cp}^*\text{MS}_3] \) (\( \text{Cp}^* = \eta^5-\text{C}_{25}\text{Me}_{15} \)), were developed.\(^6\) Such synths 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.\(^6\) During this period one more synths \( [\text{Et}_4\text{N}]_2[\text{LWS}_3] \) (\( \text{L} = \text{hydridotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate (Tp)} \) or hydridotris(3,5-dimethyl-1H-pyrazol-1-yl)borate (Tp*) \( (1) \)) was successfully prepared. A series of dinuclear homo- and heterometallic complexes containing \( [\text{Tp}^*\text{WS}_2]\text{M}^+ \text{(M = Pt, Pd, Ir, Rh, and W)} \) and \( [\text{Tp}^*\text{W}^4\text{S}_3]\text{M}^+ \text{(M = Pt, Ir, and Mo)} \) cores has been isolated. \(^7\) In addition, a set of single and double cubanelike Mo(W)/Fe/S clusters derived from \( [\text{Et}_4\text{N}]_2[\text{LWS}_3] \) and \( [\text{Et}_4\text{N}]_2[\text{LMoS}_2\text{S}_2] \) \( (\text{L} = \text{Tp or Tp*}) \) were prepared for the mimicking of the FeMoco and P-cluster structures in the nitrogenases.\(^8\) 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.

We recently were interested in the chemistry and third-order nonlinear optical (NLO) properties of Mo(W)/Cu(Ag)/S clusters originated from \( [\text{MS}_4]^2- \) and \( [\text{Cp}^*\text{MS}_3]^+ \) \( (\text{M = Mo, W}) \), and [Molybdenum Eno\( \ddot{\text{f}} \) Cofactors and Model Systems; Stiefel, E. L., Coucouvanis, D., Newton, W. E., Eds.; ACS Symposium Series 535; American Chemical Society: Washington, DC, 1993.

Chart 1. Designation of Compounds and Abbreviations\(^9\) for 1–5

\[
\begin{align*}
[\text{Et}_4\text{N}][\text{Tp}^*\text{WS}_3] & : 1'^6 \\
[\text{Et}_4\text{N}][\text{Tp}^*\text{W}^4\text{S}_3\text{Pt}^2\text{Cl}_4] & : 2 \\
[\text{Tp}^*\text{W}^4\text{S}_3\text{Cu}^2\text{(µ-NC5)}_2\text{CuMeCN}_2] & : 3 \\
[\text{Et}_4\text{N}][\text{Tp}^*\text{WO}^4\text{S}_3\text{CuNCNS}] & : 4 \\
[\text{Tp}^*\text{W}^4\text{S}_3\text{S}_2\text{CuMeCN}_2\text{(µ-NCNS)}_2] & : 5
\end{align*}
\]

* \( \text{Tp}^* = \text{hydridotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate (Tp*)} \)

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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, 11 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. 1H NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. 1H NMR chemical shifts were referenced to TMS in CDCl3 or to the deuterated dimethyl sulfoxide (DMSO-d6) 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.

**[Et4N][Tp*WS3] with CuX**

A workup similar to that used in the isolation of 1, which were separated under a microscope. Yield for 1: 19 mg (0.025 mmol) in MeCN (5 mL) was added CuCl (0.075 mmol) to the filtrate to form purple red prisms of 2–CHCl3, which were collected by filtration, washed with Et2O, and dried in vacuo. Yield: 16 mg (84%).

**[Et4N][Tp*W(S2C2Cl2)2]2 (3).** To a red solution containing 1 (19 mg, 0.025 mmol) in MeCN (5 mL) was added CuCl (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 3–CHCl3, which were collected by filtration, washed with Et2O, and dried in vacuo. Yield: 12 mg (63%).

**[Tp*W(S2C2Cl2)2]2CHCl3 (4).** To a red solution containing 1 (1 mg, 0.002 mmol) in MeCN (1 mL) was added CuCl (0.0075 mmol). A workup similar to that used in the isolation of 2 afforded dark red blocks crystals of 4–CHCl3, which were separated under a microscope. Yield for 4: 1 mg (75% based on Cu). Anal. Calcd for C18H30BCu2N8S3W: C, 30.75; H, 4.48; N, 15.29. Found: C, 30.91; H, 4.50; N, 15.17. UV–vis spectra were measured on a Varian 500 UV–visible spectrophotometer. Elemental analyses for C, H, and N were performed on a Carlo–Erba CHNO–S microanalyzer.

**[Tp*W(S2C2Cl2)2]2MECN (5).** A red solution containing 1 (1 mg, 0.002 mmol) in MeCN (1 mL) was added CuCl (0.0075 mmol). A workup similar to that used in the isolation of 2 formed a purple-red solution from which a tetranuclear anionic cluster 5–CHCl3 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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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 O2 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. 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 [PPh4][Cp*WS3], comparison of their reactions toward CuX (X = Cl, NCS, CN) merits comment. Reactions of [PPh4][Cp*WS3] with 3 equiv of CuX (X = Cl, or NCS) gave rise to weakly chloride(or thiocyanate)-bridged double incomplete cubane-like clusters [PPh4]2[Cp*WS3(CuX)3]2,10a,c while

\[
\sum \chi [F_o - F_c] / \sum F_o^2, \quad b \quad wR = \left( \sum w(F_o^2 - F_c^2) \right)^{1/2} / \sum F_o^2, \quad c \quad GOF = \left( \sum w(F_o^2 - F_c^2) \right)^{1/2} / (n - p)^{1/2}, \text{ where } n = \text{number of reflections and } p = \text{total number of parameters refined.}
\]

Scheme 1. Reactions of 1 with CuX (X = Cl, NCS, CN)
those of \([\text{PPh}_4]\)[\(\text{Cp}^*\text{WS}_3\)] with 2 or 3 equiv of \(\text{CuCN}\) afforded discrete trinuclear or tetranuclear anionic clusters \([\text{PPh}_4]\)[\(\text{Cp}^*\text{WS}_3\)(\(\text{CuCN}\)_n)] \((n = 2 \text{ or } 3)\). Although reactions of 1 with \(\text{CuCl}\) gave an incomplete cubane-like cluster 2 whose structure is similar to that of \([\text{PPh}_4]\)[\(\text{Cp}^*\text{WS}_3\)-(\(\text{CuCl}\)_2)], those of 1 with \(\text{CuNCS}\) or \(\text{CuCN}\) produced the decanuclear cluster 3 and the 1D spiral polymeric cluster 5 whose structures are not observed in the \(\text{Cp}^*\) analogue. These results suggest that relative to that of the \(\text{Cp}^*\) analogue, 1 does have somewhat different reactivity toward \(\text{Cu(I)}\), which is probably due to the fact that \(\text{Tp}^*\) binds in a \(\sigma\) fashion to the \(\text{W(VI)}\) center and is more bulky than \(\text{Cp}^*\).

Solids 2-2\(\text{CHCl}_3\), 3-2\(\text{MeCN}\), 4, and 5 are relatively stable toward oxygen and moisture. 2-2\(\text{CHCl}_3\) is readily soluble in \(\text{CHCl}_3\), MeCN, DMF, and DMSO, while 3-2\(\text{MeCN}\) only dissolves in MeCN, DMF, and DMSO. 5 is virtually insoluble in any common organic solvents. Elemental analysis of 2-2\(\text{CHCl}_3\), 3-2\(\text{MeCN}\), and 5 was consistent with their chemical formula. The IR spectra of 2, 3, and 5 exhibited a band assigned to the \(\text{B} - \text{H}\) 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 \(\text{W} - \text{S}\) 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 \(\text{C}=\text{N}\) (\(\mu\)-\(\text{NCS}\)) 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 \(\text{C}=\text{N}\) stretching vibrations, respectively. The \(1^\text{H}\) NMR spectra of 2 in \(\text{CDCl}_3\) and 3 in DMSO-\(d_6\) at ambient temperature showed two sharp singlets with the same intensities at 3.27/2.95 (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 \(\text{Tp}^*\) 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 \(\text{S} \rightarrow \text{W(VI)}\) charge-transfer transitions of the common \(\text{Tp}^*\text{WS}_3\) moiety. \(10a,c\) The identities of 2-2\(\text{CHCl}_3\), 3-2\(\text{MeCN}\), 4, and 5 were further confirmed by X-ray crystallography.

![Figure 1](image1.png)

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

![Figure 2](image2.png)

**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

<table>
<thead>
<tr>
<th>Bond Distance/Angle</th>
<th>Value</th>
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<td>(\text{Cl} - \text{C} )</td>
<td>2.143(4)</td>
</tr>
<tr>
<td>(\text{Cl} - \text{S} )</td>
<td>2.306(3)</td>
</tr>
<tr>
<td>(\text{Cl} - \text{Cl} )</td>
<td>2.131(3)</td>
</tr>
</tbody>
</table>

Crystal Structure of \([\text{Et}_4\text{N}]\)[\(\text{Tp}^*\text{W(S(\text{Me})\text{S})_3}\text{Cu}_3\text{Cl}_3\)]

2-\(\text{CHCl}_3\), 2-\(\text{CHCl}_3\). Compound 2-\(\text{CHCl}_3\) crystallizes in the triclinic space group \(\text{P}\)\(\text{I}\) and the asymmetric unit contains one discrete \([\text{Tp}^*\text{W(S(\text{Me})\text{S})_3}\text{Cu}_3\text{Cl}_3]\) anion, one \([\text{Et}_4\text{N}]^+\) cation, and two \(\text{CHCl}_3\) 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 \([\text{Tp}^*\text{W(S(\text{Me})\text{S})_3}\text{Cu}_3\text{Cl}_3]\) core structure, which was found in \([\text{PPh}_4]\)[\(\text{Cp}^*\text{MS}_3\text{Cu}_3\text{Cl}_3\)] \((M = \text{Mo}, X = \text{Br}; M = \text{W}, X = \text{Cl}, \text{Br}, \text{NCS})\). \(10a,c,i,l\) The oxidation states of \(\text{W}\) and \(\text{Cu}\) atoms in 2 are assumed to be +6 and +1,\(4b,10c\) respectively. The \(\text{W}\) center in the \(\text{Tp}^*\text{WS}_3\) unit has a distorted octahedral configuration coordinated by three pyrazolyl N atoms and three sulfur atoms. The mean \(\text{W} - \mu - \text{S}\) bond length (2.314-3 Å) is elongated by 0.12 Å relative to that of \([\text{Et}_4\text{N}]\)[\(\text{Tp}^*\text{W(S(\text{Me})\text{S})_3}\text{Cu}_3\text{Cl}_3\)] \((3.134 - 3.143\) Å) due to coordination of the sulfur atoms at the \(\text{Cu}\) centers. Each \(\text{Cu}\) atom adopts a trigonal-planar geometry coordinated by two \(\mu - \text{S}\) atoms and one terminal \(\text{Cl}\) atom.

The mean \(\text{W} - \text{Cu}\) distance (2.6404(18) Å) is slightly shorter than those found in three-coordinate \(\text{Cu}\) clusters such as \([\text{PPh}_4]\)[\(\text{Cp}^*\text{WS}_3\text{Cu}_3\text{Cl}_3]\] \((2.654(3)\) Å) and \([\text{PPh}_4]\)[\(\text{Cp}^*\text{WS}_3\text{Cu}^\text{II}\text{Cl}_3\)] \((2.653(14)\) Å). \(10d\) The average \(\text{Cu} - \text{S}\) bond length (2.118(5) Å) is comparable to those of \([\text{PPh}_4]\)[\(\text{Cp}^*\text{WS}_3\text{Cu}_3\text{Cl}_3]\] and \([\text{PPh}_4]\)[\(\text{Cp}^*\text{WS}_3\text{Cu}^\text{II}\text{Cl}_3\)] and \([\text{PPh}_4]\)[\(\text{Cp}^*\text{WS}_3\text{Cu}^\text{II}\text{Cl}_3\)] \((2.188(7)\) Å) and \([(\text{n-Bu}_2\text{N})_4]\)[\(\text{WS}_4(\text{CuCl}_4)\)] \((2.159(6)\) Å). \(15\)
...CuMeCN) fragments, which are linked via a pair of Cu located at the center of the cluster. Each [Tp*W(t̂_3-S)Cu_3(μ-NCS)]_2(CuMeCN)_2 molecule contains a similar [Tp*W(t̂_3-S)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-S atoms), while Cu2 has a distorted tetrahedral geometry (coordinated by two N atoms of thiocyanates and two μ-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^2-C_5Me_3)WS_3Cu]_6 and [WS_4-Cu_4(dppm)]_2([PF_6])_2. The Cu–μ-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-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 (1.966(6) Å for L = 2-methylpyridine; 2.00(1) Å for L = quinoline). Correspondingly, the average Cu–μ-S(NCS) bond length (2.221–(5) Å) is somewhat shorter than those of [Cu(μ-NCS)(L)]_2 (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.

Crystal Structure of [Tp*W(t̂_3-S)Cu_3(μ-NCS)]_2(CuMeCN)_2·2MeCN (3). Compound 3·2MeCN crystallizes in the monoclinic space group P2_1/c, and the asymmetric unit contains one-half of the [Tp*W(t̂_3-S)Cu_3(μ-NCS)]_2(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(t̂_3-S)Cu_3(μ-NCS)]_2(CuMeCN)_2 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(t̂_3-S)Cu_3(μ-NCS)]_2(CuMeCN)_2 fragment consists of one [Tp*W(t̂_3-S)Cu_3(μ-NCS)]^+ cation and one [Cu(MeCN)(μ-NCS)]^- anion that are held together via another pair of Cu–μ-NCS–Cu bridges. Such a decanuclear W_3Cu_8 core structure is unprecedented in the chemistry of tetrathiolactimic species [M(S)_2]^2-


shortest W−μ−Cu contact (2.5630(15) Å) among the known W/Cu/S clusters containing trigonally coordinated Cu. The WS2Cu ring in 4 resembles those found in [Me4N][WOS3−(CuCl)]18a and [PPh4][WOS3(CuPPh3)]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 [Me4N][WOS3(CuCl)] (2.227(3) Å), while that for the Cu−μ−S bonds (2.149(3) Å) is shorter than that of [Me4N][WOS3(CuCl)] (2.219(3) Å). The terminal W1−O1 bond length is much longer than that found in [Cp*WO(μ-S)2RuCl(PPh3)2] (1.746(4) Å)18b and [Me4N][WOS3−(CuCl)] (1.775(3) Å). The Cu1−N7 bond length is shorter than that of [Cu(imt)2(NCS)] (1.956(4) Å, imt = imidazolidine-2-thione).18c

**Crystal Structure of [Tp*W(t3-S)(μ-S)2Cu2(MeCN)(μ-CN)]n (5).** Compound 5 crystallizes in the orthorhombic space group P212121, and the asymmetric unit contains one [Tp*W(t3-S)(μ-S)2Cu2(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(t3-S)(μ-S)2Cu2(MeCN)] units are linked via Cu−μ−CN−Cu bridges (Figure 5). There is a 21 axis (parallel to the c axis) running through the center of the chain. The [Tp*W(t3-S)(μ-S)2Cu2(MeCN)] unit may be viewed as being a butterfly shaped [WS2Cu2] core structure, which is similar to those found in [WOS3Cu2(PPh3)0.89CH2Cl2]18 [PPh4][Cp*WS3−(CuCN)2], [Cp*WS2Cu2(PPh3)(μ-CN)], and [PPh4][Cp*WS3−(CuCN)(Py)]2(μ-CN).18e 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 neighboring 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*WS3Cu2(PPh3)(μ-CN)]2 and [PPh4][Cp*WS3−(CuCN)]2. The tetrahedrally coordinated W1−Cu2 contact is shorter than those of the corresponding ones in [Cp*WS3Cu2(PPh3)(μ-CN)]2 and [PPh4][Cp*WS3−(CuCN)]2(μ-CN). It is noted that the Cu1−μ−S−1−Cu2 angle (79.68(6)°) in 5 is 17.6° smaller than that of the cationic cluster [PPh4][Cp*WS3(CuCN)2], which may make the cyanide groups of 5 able to access the Cu centers in the adjacent [WS2Cu2] cores to form a 1D spiral chain. In the structure of [PPh4][Cp*WS3(CuCN)2], the Cu−μ−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 {PPh4}[Cp*WS3Cu2(μ-CN)(CN−(μ-CN)]py}, and slightly shorter than those found in [Cp*WS3Cu2(μ-CN)2(py)]10e and KCu(CN)2.19 The mean W1−μ−S, W1−μ−S, Cu−μ−S, and Cu−μ−S bond lengths in 5 are comparable to those of the corresponding ones in [Cp*WS3Cu2(PPh3)(μ-CN)]2 and [PPh4][Cp*WS3Cu2(CN−(Py))2(μ-CN)].

**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

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

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distances (Å)</th>
<th>Bond</th>
<th>Distances (Å)</th>
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<tr>
<td>W1(1)−Cu1(1)</td>
<td>2.5630(15)</td>
<td>W1(1)−O1(1)</td>
<td>1.948(7)</td>
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<td>W1(1)−S(3)</td>
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<td>Cu1(1)−S(3)</td>
<td>2.190(4)</td>
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<tr>
<td>Cu1(1)−N(7)</td>
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<td>O1(1)−W1(1)−S(2)</td>
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<td>S(2)−W1(1)−S(3)</td>
<td>104.44(12)</td>
<td>S(2)−Cu1(1)−S(3)</td>
<td>109.57(13)</td>
</tr>
<tr>
<td>S(2)−Cu1(1)−N(7)</td>
<td>122.7(3)</td>
<td>S(3)−Cu1(1)−N(7)</td>
<td>127.5(3)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distances (Å)</th>
<th>Bond</th>
<th>Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1(1)−Cu1(1)</td>
<td>2.6560(9)</td>
<td>W1(1)−Cu2(1)</td>
<td>2.6694(10)</td>
</tr>
<tr>
<td>W1(1)−S(1)</td>
<td>2.3358(14)</td>
<td>W1(1)−S(2)</td>
<td>2.2225(18)</td>
</tr>
<tr>
<td>W1(1)−S(3)</td>
<td>2.2112(17)</td>
<td>Cu1(1)−S(1)</td>
<td>2.2276(19)</td>
</tr>
<tr>
<td>Cu1(1)−S(2)</td>
<td>2.1992(18)</td>
<td>Cu1(2)−S(1)</td>
<td>1.8666(6)</td>
</tr>
<tr>
<td>Cu2(1)−S(1)</td>
<td>2.2460(18)</td>
<td>Cu2(2)−S(3)</td>
<td>2.2082(2)</td>
</tr>
<tr>
<td>Cu2(2)−N(8)</td>
<td>2.4245(7)</td>
<td>Cu2(2)−N(7A)</td>
<td>1.930(7)</td>
</tr>
<tr>
<td>S(1)−W1(1)−S(2)</td>
<td>104.46(6)</td>
<td>S(1)−W1(1)−S(3)</td>
<td>104.00(6)</td>
</tr>
<tr>
<td>S(2)−W1(1)−S(3)</td>
<td>103.51(7)</td>
<td>S(1)−Cu1(1)−S(2)</td>
<td>109.10(7)</td>
</tr>
<tr>
<td>S(1)−Cu1(1)−S(16)</td>
<td>128.9(2)</td>
<td>S(2)−Cu1(2)−S(16)</td>
<td>119.1(2)</td>
</tr>
<tr>
<td>S(1)−Cu1(2)−S(3)</td>
<td>107.18(6)</td>
<td>S(1)−Cu2−N(8)</td>
<td>105.90(17)</td>
</tr>
<tr>
<td>S(1)−Cu2−N(7A)</td>
<td>127.1(2)</td>
<td>S(3)−Cu2−N(8)</td>
<td>101.27(17)</td>
</tr>
<tr>
<td>S(3)−Cu2−N(7A)</td>
<td>119.8(2)</td>
<td>N(8)−Cu2−N(7A)</td>
<td>88.3(2)</td>
</tr>
<tr>
<td>S(1)−Cu1−S(2)</td>
<td>79.68(6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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.\(^{3b,5c,8,10j,l}\) 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 \(\exp(-t/T_s)\). 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 \(^{20a}\)

\[
\chi^{(3)} = \left(\frac{I}{I_0}\right)^{1/2} \cdot \frac{L}{n} \cdot \frac{\alpha \cdot \exp(\alpha L/2)}{1 - \exp(-\alpha L)} \cdot \alpha^{(3)}
\]

(1)

where the subscripts \(s\) and \(r\) represent the parameters for the sample and CS\(_2\) and \(\alpha\) 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 \(\chi^{(3)}\) and \(n_s\) for CS\(_2\) are \(6.7 \times 10^{-11}\) 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 \(3.8 \times 10^{-14}\) (1) and \(1.0 \times 10^{-14}\) 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 \(^{20c}\)

\[
n_2(\text{esu}) = \frac{12\pi\chi^{(3)}}{n^2}
\]

(2)

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

The second-order hyperpolarizability \(\gamma\) of a molecule in isotropic media is related to the solution \(\chi^{(3)}\) by eq \(^{30d}\)

\[
\gamma = \frac{\chi^{(3)}}{N_f}
\]

(3)

where \(N\) is the number density of the solute per milliliter, and \(f^0\) is the local field correction factor which is \([n^2 + 2]^{1/2}\) (\(n\) is the linear refractive index of solution). The second-order hyperpolarizability \(\gamma\) values are \(1.07 \times 10^{-32}\) esu (1) and \(5.46 \times 10^{-32}\) esu (3). According to eq 3, \(N\) represents the number density (concentration) of a compound and the \(\gamma\) 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.\(^{8a,d,l,20k}\) When compared with the nanosecond and picosecond measurement values, femtosecond values are roughly 2–3 orders of magnitude lower.\(^{21}\) Therefore, the \(\gamma\) values of \(1\) and \(3\) are comparable to those of the Mo(W)/Cu/S clusters derived from [MNS\(_4\)]\(^{2-}\) or [Cp*MS\(_3\)]\(^-\) (M = Mo, W), such as [Et(N\(_2\))\(_2\)(WS\(_3\)Cu(CN)\(_3\))]\(_n\) \((1.26 \times 10^{-29}\) esu),\(^{5e}\) [PPh\(_4\)]\((\eta^5-C_5\text{Me}_5)\text{MoS}_2\text{(CuNCS)}_3\)\(_n\) \((3.09 \times 10^{-29}\) esu),\(^{10}\) and [MoS\(_2\text{Cu}(\text{MePy})_2\text{Br}_2](2\text{-}(\alpha\text{-MePy})_2\text{CS}_2)\) \((1.06 \times 10^{-31}\) esu),\(^{22b}\) and larger than those of C\(_{60}\) \((7.5 \times\)

---


10^{-34} \text{ esu}) and \text{C}_70 (1.3 \times 10^{-33} \text{ esu}),\text{23a} organometallic compounds such as trans-[Mo(CO)_{4}(PPh_3)_2] (8.49 \times 10^{-32} \text{ esu}) and cis-[Mo(CO)_{4}(PPh_3)_2] (4.375 \times 10^{-31} \text{ esu}),\text{23b} and TiOPc (Pc = phthalocyanine) films before and after thermal annealing (1.04 \times 10^{-33} and 5.35 \times 10^{-34} \text{ esu}).\text{23c} As the \gamma values for \text{1} and \text{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 \text{1} with CuX (X = Cl, NCS, CN) and isolated four new W/Cu/S clusters \text{2}–\text{5} containing the [Tp^*WS_3^-] anion of \text{1}. For \text{5}, we successfully applied the solvothermal synthesis into the system of \text{1} and CuCN, which produced it in a relatively high yield that could not be isolated via the common solution method. Compounds \text{2}–\text{5} were characterized by elemental analysis, IR, UV–vis, \text{1H} NMR, and X-ray crystallography. The anion of \text{2} contains a [WS_3Cu_3] incomplete cube, while \text{3} consists of an unusual W_2Cu_8 cluster core. The cluster anion of \text{4} has a WS_2Cu core with a rather short W–Cu contact, and \text{5} has a 1D spiral chain formed from the [Tp^*W(\mu_3-S)(\mu-S)_2Cu_2(MeCN)] fragments that are linked via cyanide bridges. Formation of \text{2}–\text{5} suggested that \text{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 \text{1} and \text{3} showed good third-order optical nonlinearities, and the third-order NLO performance of \text{3} was enhanced when the [Tp^*WS_3^-] anion of \text{1} binds more Cu^+ ions to form \text{3}. Furthermore, as \text{2} and \text{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 \text{2}–\text{5} (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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