Crystal Structure and Excited Optical Nonlinearity of a 1D Polymeric $[W_2O_2S_6Cu_4(NCMe)_4]_n$ Cluster

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The self-assembly reaction of $(NH_4)_2(WOS_3)$ with CuBr in the presence of PCy_3 (PCy_3 = tricyclohexylphosphane) in MeCN gives rise to a novel 1D polymeric compound $[W_2O_2S_6Cu_4(NCMe)_4]_n$ (**1**) with solvent MeCN coordinated to the copper atom. This situation is unprecedented in the W(Mo)/Cu/S system. The excited state absorption and refraction of **1** in CH_3CN solution were studied by using the Z-scan technique with laser pulses of 40 ps pulse-width at a wavelength of 532 nm. The compound possesses an optical self-focusing performance. The positive nonlinear refraction is attributed to population transitions between singlet states. Compound **1** displays a strong excited-state absorption, which induces an asymmetry between the peak and valley.

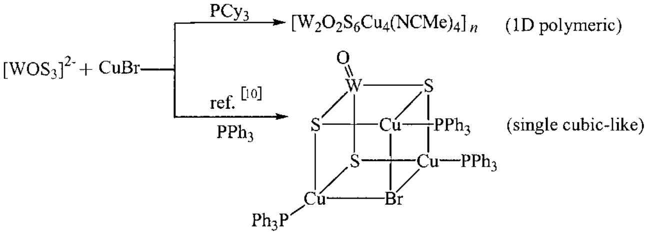
Introduction

Polymeric transition-metal chalcogenides have attracted much attention because of their possible applications as catalysts or nonlinear optical devices directly derived from their peculiar solid-state structures.[1,2] Compared with polyoxometalates, polythiometalates are still in their infancy.[3−5] Mo(W)/Cu/S polymeric clusters are scarce and only a few structures have been reported. For example, the linear one-dimensional chains in $[\{WS_4Ag\}\{[H_3NC(CH_2OH)_3\}_n(dmf)_{2n}]$,[6a] $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_2Ag_3(CN)\}_n]$[6b,6c] or $[WOS_3Cu_3(CN)(py)_4]_n$ (M = Mo, W),[7] the two-dimensional framework in $[\{NEt_4\}\{Mo_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_5\}\cdot MeOH\cdot H_2O]_n$,[8a] $[(PPh_4)_2\{(CuNCS)_4WS_4\}]_n$ [8b] or the three-dimensional cross-framework in $[\{NEt_4\}_2\{(\mu_4\text{-}WSe_4)Cu_4(CN)_4\}]_n$.[9] We report here the synthesis and crystal structure of a novel 1D polymeric cluster $[W_2O_2S_6Cu_4(NCMe)_4]_n$ (**1**) with a novel zigzag chain configuration along the *c* axis and solvent as a ligand. Additionally, the excited state nonlinear refraction and absorption of compound **1** were investigated by using the Z-scan technique with picosecond pulses. We also propose a steady-state model of singlet excited state nonlinear refraction, which agrees well with experimental results of the excited-state refraction and absorption.

Results and Discussion

Synthesis of Compound 1

The reaction of $(NH_4)_2(WOS_3)$ and CuBr in the presence of PCy_3 (molar ratio of 1:2:2) in MeCN solution led to deep-red crystals of $[W_2O_2S_6Cu_4(NCMe)_4]_n$ (**1**) in 65% yield after allowing the orange-red filtrate to stand under an oxygen-free atmosphere for several days. Surprisingly, the PCy_3 ligand is not present in **1**, and solvent MeCN molecules are the only additional co-ligands present. This differs from our previously reported results when an analogous ligand, PPh_3, was used in place of PCy_3. As shown in Scheme 1, reaction of $[WOS_3]^{2-}$ with CuBr and PPh_3 produced a single cubic-like compound $[WOS_3Cu_3(PPh_3)_3Br]$.[10] When the reaction was performed in the absence of PCy_3 we could not isolate compound **1** or obtain good quality crystals, de-



Scheme 1

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spite several attempts. It is possible that PCy_3 plays a role in the crystal growth.

Single-Crystal X-ray Diffraction Studies

Compound **1** crystallizes in the monoclinic system with space group *P*2_1/*c*. An ORTEP drawing is shown in Figure 1. The configuration of the polymeric compound can be viewed as a helical chain which is propagated along the crystallographic *c* axis. For clarity, a simplified diagram is shown in Figure 2, with S atoms omitted; the packing diagram of the unit cell is shown in Figure 3. It should be noted that the chain turns at each W atom. The main core in compound **1** may be described as containing a nest-shaped $W_2S_6Cu_4$ fragment, which has been previously been observed in $[(C_7H_7)_3P]_4Cu_4W_2S_6O_2$ [11] and $[Et_4N]_4[Mo_2S_6Cu_6O_2I_6]$.[12] Each approximately tetrahedral W atom is coordinated by one terminal O and three μ_3-S atoms with angles subtended at W of 108.61(10)−110.8(3)°. However, the coordination tetrahedron around the Cu(1) atom, formed by two μ_3-S and two N atoms from MeCN, is much more distorted, the angles of Cu ranging from 105.14(11)° to 116.0(3)°. The average W−Cu−W and Cu−W−Cu angles are 177.05(6)° and 85.80(2)°, respectively. The W=O bond length of 1.718(8) Å is typical of a double bond and is similar to those observed in $[(C_7H_7)_3P]_4Cu_4W_2S_6O_2$,[11] and $[(PPh_3)_4(SCMe_3)_2Cu_6W_2S_6O_2]$.[13] The W−$\mu_3$-S bond lengths are 2.244(2), 2.245(3), and 2.238(3) Å.

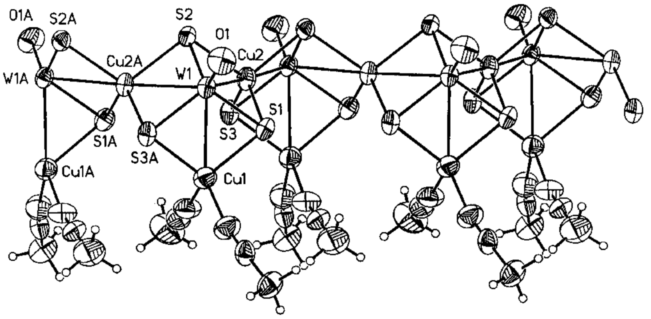

Figure 1. ORTEP drawing of a portion of the anion of $[W_2O_2S_6Cu_4(NCMe)_4]_n$ (**1**) with atomic labeling (30% displacement ellipsoids)

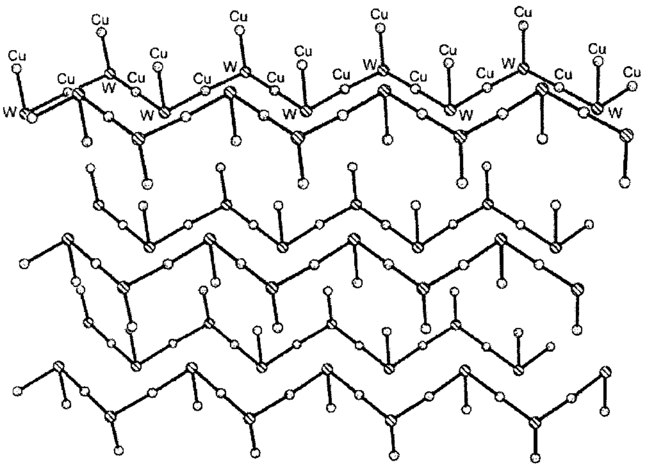

Figure 2. Simplified diagram of the anionic helical chain of **1**; sulfur atoms omitted for clarity

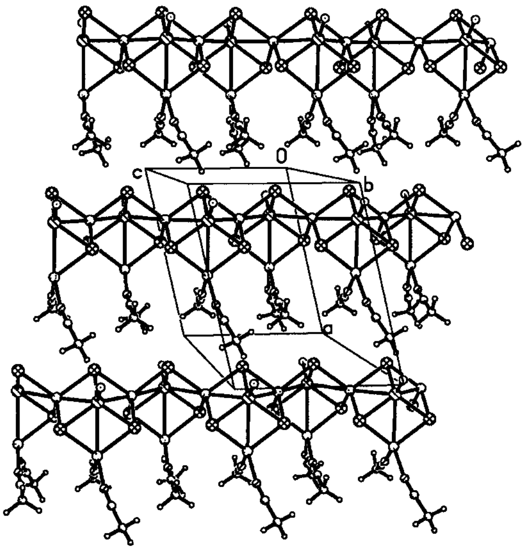

Figure 3. Packing drawing of the unit cell of **1** viewed along the *b* axis

There are two types of copper atoms in the $W_2S_6Cu_4$ core. The Cu(1) atom is tetrahedrally coordinated by two μ_3-S atoms and two nitrogen atoms of the MeCN ligands, resulting in a $(\mu_3\text{-S})_2Cu(NCMe)_2$ arrangement, while the Cu(2) atom is tetrahedrally coordinated by the four μ_3-S atoms resulting in a $(\mu_3\text{-S})_4Cu$ arrangement. Owing to the different coordination modes of the copper atoms, the W−Cu lengths are slightly different; for example, the W1−Cu1 bond length [2.6999(16) Å] is shorter than those for the W1−Cu2 bonds [av. 2.7489(15) Å]. The Cu−S distances also reflect the different coordination modes of the copper atoms, the Cu(2)−S bonds [av. 2.3264(3) Å] are longer than those for Cu(1) [av. 2.292(3) Å]. Selected bond lengths and angles are listed in Table 1.

Nonlinear Optical Properties

The UV/Vis spectrum of the polymeric compound **1** is depicted in Figure 4. It shows two absorption peaks with the first maximum located at 367 nm. The polymer has a relatively low linear absorption in the visible and near-IR regions. Indeed, the solution is nearly transparent in the visible and near infrared range, which qualifies the cluster as a potential optical limiting material.

The open-aperture Z-scan results are shown in Figure 5. The nonlinear transmittances of the sample are dependent only on the incident intensity for nanosecond and picosecond laser pulses, which indicates that the metal cluster possesses excited state absorption and not two-photon absorption. The details will be reported elsewhere. The nonlinear absorption of about 90% at the focus shows that the metal cluster possesses strong excited state absorption and a large optical limiting response. The normalized closed-aperture Z-scan curve (Figure 6) has a pair of sharp peaks and valley and the occurrence of the peak at positive Z indicates that

Table 1. Selected bond lengths (Å) and angles (°) of $[W_2O_2S_6Cu_4(NCMe)_4]_n$ (**1**)

Cu1−N2	2.006(11)	Cu1−N1	2.027(12)	Cu1−S3A	2.291(3)
Cu1−S1	2.293(3)	Cu1−W1	2.6999(16)	Cu2−S3	2.322(3)
Cu2−S2	2.322(3)	Cu2−S2A	2.329(3)	Cu2−S1	2.330(3)
Cu2−W1	2.7479(15)	Cu2A−W1	2.7494(15)	O1−W1	1.718(8)
S1−W1	2.244(2)	S2−W1	2.245(3)	S2−Cu2	2.329(3)
S3−W1	2.238(3)	S3−Cu1	2.291(3)	W1−S3	2.238(3)
W1−Cu2	2.7494(15)				
N2−Cu1−N1	105.8(4)	N2−Cu1−S3A	116.0(3)	N1−Cu1−S3A	111.7(3)
N2−Cu1−S1	106.3(3)	N1−Cu1−S1	111.9(3)	S3A−Cu1−S1	105.14(11)
S3−Cu2−S2	114.46(11)	S3−Cu2−S2A	103.14(11)	S2−Cu2−S2A	107.88(12)
S3−Cu2−S1	115.21(11)	S2−Cu2−S1	103.36(11)	S2−Cu2−S1A	112.87(11)
O1−W1−S3A	110.3(3)	O1−W1−S1	109.5(3)	S3A−W1−S1	108.61(10)
O1−W1−S2	110.8(3)	S3A−W1−S2	108.72(10)	S1−W1−S2	108.79(10)
Cu1−W1−Cu2	86.45(4)	Cu1−W1−Cu2A	85.84(4)	Cu2−W1−Cu2	85.76(2)

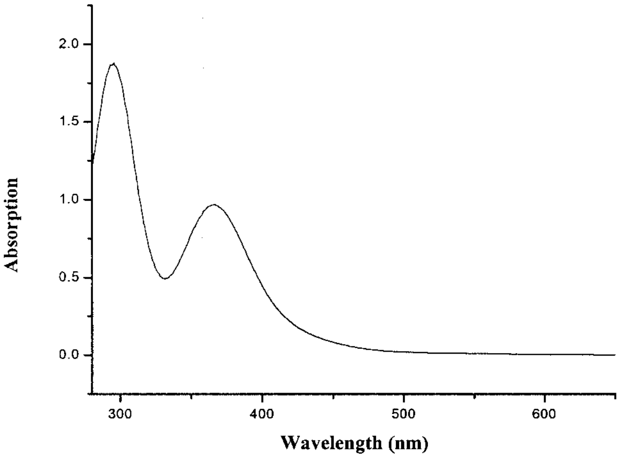

Figure 4. Electronic spectrum of **1** in acetonitrile; concentration 1.2 × 10^{-4} M

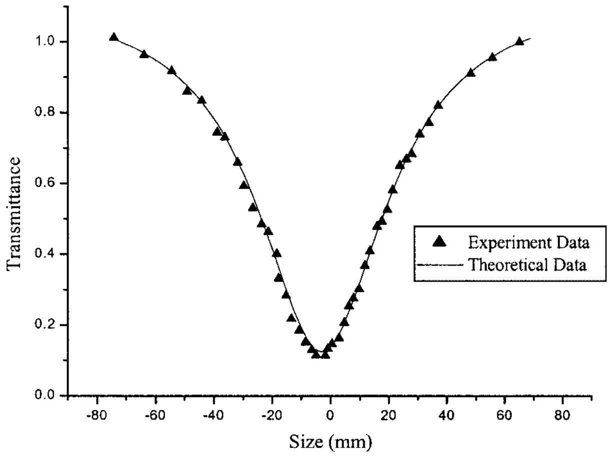

Figure 5. The open-aperture Z-scan results of compound **1**

the cluster possesses positive nonlinear refraction or is self-focusing. Both the peak and the valley are asymmetric, and the width of the valley is widened. The asymmetry of the peak and valley of the normalized Z-scan curve is caused by the strong excited-state absorption. The excited-state optical nonlinearity can be studied by excited-state theory.

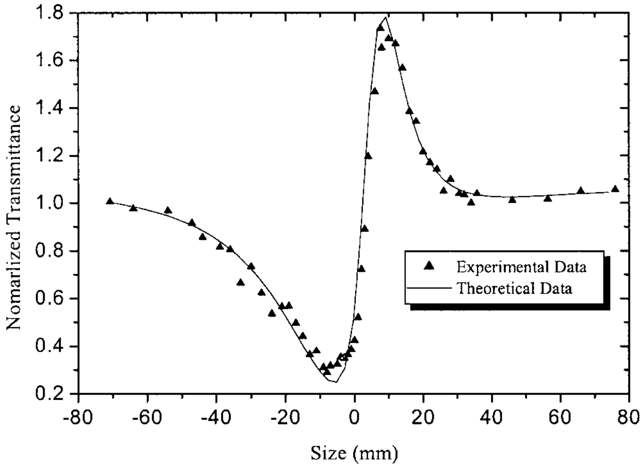

Figure 6. The Z-scan results of compound **1** observed under a closed-aperture configuration divided by those obtained under the open-aperture configuration

Under the excitation of picosecond laser pulses, the contribution of population of the singlet states to optical nonlinearities predominate and that of the triplet is negligible.[14] The nonlinear absorption index and refraction index can be written as shown in Equation (1)[15]

$$\begin{cases}\alpha = \alpha_0 + N_0\sigma_0 + N_1\sigma_S \\ \beta = \beta_0 + N_0\eta_0 + N_1\eta_S\end{cases} \tag{1}$$

where α_0 and α are the absorption coefficients of solvent and solute, respectively, σ_0 and σ_S are the absorption cross-sections of the ground and first singlet excited states, respectively, β_0 and β are the refractive indices of solvent and solution, respectively, and η_0 and η_S are the refrangibilities of the ground and first singlet excited states, respectively.

The light propagation equations are shown in Equation (2)

$$\begin{cases}\dfrac{\partial I}{\partial z} = -\alpha I \\ \dfrac{\partial \phi}{\partial z} = k\beta\end{cases} \tag{2}$$

where k is the wave vector and I is the incident laser density. We performed a Z-scan measurement using TEM_{00}-mode laser pulses with a beam-waist radius of ω_0, a Gaussian temporal profile of duration τ, and a propagation direction along positive z. The irradiance I thus varies with z, r, and t according to Equation (3)

$$I(z,r,t)=\frac{\omega_0^2}{\omega^2(z)}I_{00}\exp\left[-\left(\frac{t}{\tau}\right)^2\right]\exp\left[-\left(\frac{2r^2}{\omega^2(z)}\right)\right] \tag{3}$$

where $\omega(z) = \omega_0[1 + (z/z_0)^2]^{1/2}$ is the beam waist radius at z, $z_0 = \pi\omega_0^2/\lambda$ is the diffraction length of the beam, and I_{00} is the on-axis peak irradiance at the focus.

The lifetime of the second excited singlet-state is of the order of sub-picosecond, and is much shorter than the duration of the picosecond pulses. Hence this problem can be dealt with by a stable-state approximation. For the sake of simplicity, only the case of steady state is considered. In this event, the outcome may be expressed by Equation (4)

$$\begin{cases} \alpha=\alpha_0+\dfrac{1+K_a\dfrac{I}{I_s}}{1+\dfrac{I}{I_s}}\sigma_0 N \\ \beta=\beta_0+\dfrac{1+K_r\dfrac{I}{I_s}}{1+\dfrac{I}{I_s}}\eta_0 N \end{cases} \tag{4}$$

where $I_S = (\eta\nu)/(\sigma_0\tau_{S0})$ is a saturable intensity, and K_a and K_r are defined by $K_a = \sigma_S/\sigma_0$ and $K_r = \eta_S/\eta_0$, which are the ratios of the singlet excited-state absorption cross section and refrangibility to those of the ground state, respectively.

From Equations (1)−(4) we studied the nonlinear optical properties of the excited state of metal clusters, and successfully fitted the experimental results shown in Figure 5 and 6 (solid lines). The ratios K_r and K_a are calculated to be 1.1 and 18 by the fitting curve for picosecond pulses. It can be seen that the ratio of refraction volumes of the singlet excited-state to the ground-state is greater than one for picosecond pulses, so it is self-focusing. The ratio of the singlet excited-state absorption cross-section to the ground-state is very large, so the compound possesses a strong excited-state absorption, which induces the asymmetry of the peak and valley.

Conclusions

In summary, a novel 1D polymeric compound $[W_2O_2S_6Cu_4(NCMe)_4]_n$ (**1**) with solvent MeCN coordinated to the copper atom was obtained through the self-assembly reaction of $(NH_4)_2(WOS_3)$ with CuBr in the presence of PCy_3. Compound **1** exhibits a strong excited-state absorption performance, the ratio of absorption cross-section of the singlet excited-state to that of the ground-state was about 18. Compound **1** is therefore considered to be a promising candidate for picosecond optical-limiting. The ratio of refrangibility of the singlet excited-state to that of the ground state is about 1.1; thus, it possesses a self-focusing property with picosecond pulses. The asymmetry of the peak and valley of the Z-scan curve is caused by the excited-state absorption. The nonlinear refraction and absorption model of the excited-states is presented to simulate the experiment results.

Experimental Section

General: The reagent $(NH_4)_2(WOS_3)$ was prepared according to a literature procedure.[16] Other chemicals were of AR grade and used without further purification. Infrared spectra were recorded with a Fourier transform Nicolet FT-170SX spectrophotometer (KBr pellets). The electronic spectrum was taken on a Shimadzu UV-240 spectrophotometer and elemental analyses (C and H) were performed on a PE-240C elemental analyzer. The ^1H NMR spectra were recorded on a Bruker AC400 spectrometer.

Nonlinear Optical Measurements: The nonlinear optical properties of the metal cluster solution were measured by the Z-scan technique at 532 nm. A continuum ns/ps Nd:YAG laser system with a pulse width of 40 ps was used. The metal complex **1** in CH_3CN solution was filled into a 2-mm cuvette with a linear transmittance of 92%. The input and the output energies of beams were measured with energy meters (Laser Precision Corporation Rjp-735). The focal length of the lens was 90 mm. The laser beam waist was about 36 μm at focus point, and the corresponding Rayleigh length was thus much larger than the thickness of sample. The aperture diameter was 2 mm and this corresponds to a far-field transmittance of 9.8%. The experimental data were collected utilizing a single shot at a rate of 1 pulse per minute to avoid thermal effects. The input pulse energies were 700 μJ for picosecond pulses.

Preparation of Compound 1: A solution of PCy_3 (560 mg, 2 mmol) in MeCN (10 mL) was added to a mixture of $(NH_4)_2(WOS_3)$ (332 mg, 1 mmol) and CuBr (287 mg, 2 mmol) in MeCN (40 mL). The resulting mixture was stirred for 24 h and then filtered. The red filtrate was layered with hexane (20 mL) and allowed to stand at room temperature for several weeks. Deep-red crystals were obtained; yield: 65%. Characteristic infrared absorptions were found at 420 cm^{-1} and 440 cm^{-1} for ν(W−S), 910 cm^{-1} for ν(W−O), and 2100 cm^{-1} for ν(C≡N). ^1H NMR ($[D_6]$DMSO, 25 °C): δ = 1.93 (s, CH_3). $C_4H_6Cu_2N_2OS_3W$ (505.22): calcd. C 9.51, H 1.20, N 5.54; found C 9.21, H 1.23, N 5.32.

Crystal Structure Determination and Refinement: A well-developed single crystal of the polymeric compound with suitable dimensions was mounted on a glass fiber. Cell dimension measurements and data collection were performed on a Siemens Smart CCD diffractomer with graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å) at 20 °C. Intensity data for the crystal were obtained in the range $4.56° < 2\theta < 50°$ using the ω-scan technique. The structure was solved by direct methods using SHELXTL software and refined by full-matrix least-square methods on F^2.[17] All H atoms were geometrically fixed and allowed to ride on their attached atoms. Selected bond lengths and angles are listed in Table 1 and details of the data collection and structure refinement are summarized in Table 2.

CCDC-223470 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road,

Table 2. Crystal data and standard refinement details for $[W_2O_2S_6Cu_4(NCMe)_4]_n$ (**1**)

Empirical formula	$C_4H_6Cu_2N_2OS_3W$
Molecular mass	505.22
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å)	$a = 9.075(2)$
	$b = 17.827(2)$
	$c = 7.481(2)$
β (°)	102.780(10)
Volume (Å^3)	1180.3(4)
Z	4
$D_{\mathrm{calcd.}}$ (Mg·m^{-3})	2.843
Absorption coefficient (mm^{-1})	13.786
$F(000)$	928
Crystal size (mm)	0.30 × 0.20 × 0.20
Crystal colour	red
θ range for data collection (°)	2.28 to 24.99
Reflections collected	5980
Independent reflections	2074
Observed reflections	1643 $[I > 2\sigma(I)]$
Absorption correction	empirical
Transmission factors	$T_{\mathrm{min}} = 0.052$; $T_{\mathrm{max}} = 0.064$
Data/restraints/parameters	2074/0/120
Goodness-of-fit on F^2	1.057
Final difference map extremes	0.915; −0.633
R_1, wR_2 (all data)	0.0718, 0.0832
R_1, wR_2 $[I > 2\sigma(I)]$	0.0437, 0.0792

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