Synthesis, Structure and Optical Limiting (OL) Properties of a Novel Incomplete Cubane-like Cluster $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3(CuBr)(CuI)_2(\mu\text{-dppm})]$

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Reaction of $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3]$ with CuI, CuBr and bis(diphenylphosphino)methane (dppm) (molar ratio = 1∶2∶1∶1) in MeCN gave rise to $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3(CuBr)(CuI)_2(\mu\text{-dppm})]$ (1) in high yield. Compound 1 crystallizes in the monoclinic, space group $P2_1/n$ with lattice parameters: a = 1.2906(4) nm, b = 1.5006(8) nm, c = 3.1484(6) nm, β = 92.12(2)°, V = 6.093(3) nm³, Z = 4. The structure of the anion of 1 contains an incomplete WS_3Cu_3 cubane-like core in which two CuI units are bridged by a dppm ligand. The W—Cu distances vary in the range of 0.2644(1)—0.2793(1) nm. The optical limiting (OL) properties of 1 in MeCN were measured with the laser pulse-width of 12-ns at 532 nm, and the nanosecond OL effect may be due to the reverse saturable absorption (RSA) related to the excited triplet states.

Keywords tungsten cluster, copper cluster, sulfur cluster, crystal structure, optical limiting property

Introduction

Tetrathiometallate anions $[MS_4]^{2-}$ (M = Mo, W) and their clusters with various transition metals are well-known for their rich coordination chemistry,[1-7] and their relation to industrial catalysis process,[8] biological systems,[9] and NLO materials.[10-12] However, the chemistry of the organometallic trisulfide complexes $[PPh_4][(\eta^5\text{-}C_5Me_5)MS_3]$ (M = Mo,[13] W[14]) and their related mixed-metal clusters have been less investigated.[15,16] In order to extend our knowledge about the chemistry of $[PPh_4][(\eta^5\text{-}C_5Me_5)MS_3]$ and continue our study on NLO materials,[10,12] we have carried out the reaction of $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3]$ with CuI, CuBr and bis(diphenylphosphino)methane (dppm) in MeCN and isolated a new tetranuclear anionic cluster, $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3(CuBr)(CuI)_2(\mu\text{-dppm})]$ (**1**). The crystal structure of **1** was determined by X-ray crystallography and its optical limiting (OL) properties in MeCN were further studied with 12-ns laser pulses at 532 nm. Compound **1** is the first example containing organometallic trisulfido tungstate $[(\eta^5\text{-}C_5Me_5)WS_3]^-$, which has been confirmed to possess optical limiting (OL) properties in solution. Herein, we report the synthesis, crystal structure and OL effect of **1**.

Experimental

Materials

All manipulations were carried out under argon using standard Schlenk-line technique. $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3]$ was prepared as reported previously.[14] Other chemicals were of analytical grade. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon. The IR spectra were recorded on a Perkin Elmer 2000 FT-IR spectrometer as KBr disk (4000—400 cm⁻¹). ^1H NMR spectra were recorded on a Varian UNITYplus-500 spectrometer at ambient temperature. ^1H NMR chemical shifts were referenced to the CD_3CN signal. UV-vis spectra were measured on a JASCO V-560 spectrophotometer. The elemental analyses for C, H, N and S were performed on a LECO-CHNS microanalyzer. Bromine and iodine analyses were performed on a PLA-SPECI ICP spectrophotometer.

Preparation of **1**

To a red solution of $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3]$ (0.16

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Received May 12, 2003; revised July 28, 2003; accepted October 8, 2003.
Project supported by the National Natural Science Foundation of China (No. 20271036), the Natural Science Foundation of the Education Committee of Jiangsu Province (No. 02KJB150001), State Key Lab of Coordination Chemistry of Nanjing University, and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry of China.

g, 0.212 mmol) in 40 mL of MeCN was added CuI (0.082 g, 0.414 mmol), CuBr (0.03 g, 0.212 mmol) and dppm (0.081 g, 0.212 mmol). The mixture was stirred at ambient temperature for 1 d to give rise to a dark red clear solution. Layering 25 mL of Et_2O onto the solution afforded $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3(CuBr)(CuI)_2(\mu\text{-}dppm)]$ (**1**) as dark red prisms, which were filtered and washed with Et_2O, and dried *in vacuo*. Yield 0.31 g (87.9 % based on W); UV-vis (MeCN) λ_{max}: 429 nm; ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.23—7.95 (m, 40H), 3.49 (s, 2H), 2.13 (s, 15 H); IR (KBr) ν: 2860, 1460, 1440, 1380, 1260, 1115, 1030, 1005, 780, 760, 740, 725, 695, 528, 430 cm^{-1}. Anal. calcd for $C_{59}H_{57}Cu_3BrI_2P_3S_3W$: C 42.60, H 3.46, S 5.78, Br 4.80, I 15.26; found C 42.51, H 3.40, S 5.59, Br 4.71, I 15.50. Single crystals of **1** were obtained directly from the above preparation.

Crystal structure analysis

A dark red single crystal with approximate dimensions of 0.45 mm × 0.50 mm × 0.25 mm was placed on a glass fiber. Diffraction experiments were performed on a Rigaku AFC7R diffractometer employing graphite-monochromated Mo Kα radiation ($\lambda = 0.071069$ nm) using the ω-2θ scan technique. Cell parameters were obtained from 20 carefully cantered reflections in the range of $6.31° < 2\theta < 30.05°$. The crystal belongs to monoclinic, space group $P2_1/n$ with cell parameters: $a = 1.2906(4)$ nm, $b = 1.5006(8)$ nm, $c = 3.1484(6)$ nm, $\beta = 92.12(2)°$, $V = 6.093(3)$ nm^3, $Z = 4$, $D_{calcd} = 1.813$ g/cm^3, $F(000) = 3224$, $\mu = 48.06$ cm^{-1}. A total of 15215 reflections were collected in the range of $2\theta_{max} = 50.1°$. Empirical absorption corrections were applied based on azimuthal Ψ_{scans}, which resulted in transmission factors ranging from 0.32 to 1.00. The raw intensities were also corrected for the decay, and for LP effects. The structure was solved by direct methods[17] and expanded using Fourier technique.[18] All non-hydrogen atoms were refined anisotropically while hydrogen atoms were put on the calculated positions and not refined. The relatively high thermal parameter for Br atom may be due to disorder. However attempts to model the disorder failed. The final cycle of refinement including 649 variable parameters for 9587 reflections with $I > 3.0\ \sigma(I)$ was converged to $R = 0.045$, $R_w = 0.050$ ($w = [\sigma_c^2(F_o) + 0.000144F_o^2]^{-1}$), $S = 1.97$, and $(\Delta/\sigma) = 0.000$. The maximum and minimum residual peaks on the final difference Fourier map are 1640 and −1960 e/nm^3, respectively. The peak (1640 e/nm^3) is close to that of the W atom (0.084 nm), which may be considered as "ghost peak" of the W atom. All calculations were performed with the teXsan crystallographic software package of Molecular Structure Corporation (1985 & 1992).

Optical limiting measurement

Optical limiting experiments were performed with a Nd:YAG 532-nm laser with a repetition rate of 10 Hz and pulse widths of 12 ns and 35 ps, respectively.[19] The laser beam was focused on the sample, which had been placed in a 2-mm cuvette with a 15-cm lens. An attenuator was used to adjust the incident laser energy. The incident and transmitted laser energy were recorded simultaneously by two identical photodiodes. To avoid other nonlinear optical effects such as self-focusing, self-defocusing, and nonlinear scattering, a lens was set in front of the photodiode to collect all the transmitted energy.

Nonlinear absorption measurement

Nonlinear absorption was measured by the open-aperture Z-scan technique.[20] An Nd:YAG laser (wavelength, 532 nm; pulse width, 12 ns or 35 ps) with near-Gaussian temporal and spatial profiles was focused on a 1 mm optical flat cuvette filled with the MeCN solution of **1** by a lens with focal distance $f = 22$ cm. The variation of the normalized transmission was recorded along with the sample position translated on the optical axis (z-axis).

Results and discussion

Synthesis, IR, UV-vis *and* ^1H NMR *spectra*

The synthesis of **1** is quite straightforward. Reaction of $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3]$ with CuI, CuBr and dppm in the molar ratio of 1:2:1:1 in MeCN gave rise to crystals of **1** in a high yield (87.9%). Compound **1** is soluble in MeCN and stable towards air and moisture. The elemental analysis for **1** is in good agreement with its chemical formula. The IR spectrum shows one band assigned to the W—S stretching vibration at 430 cm^{-1}. The ^1H NMR spectrum of **1** in CD_3CN displays one singlet signal of η^5-C_5Me_5 group at δ 2.13, one singlet signal of methylene of dppm at δ 3.49, and multiple signals for phenyl groups of dppm at δ 7.23—7.95. The UV-vis spectrum of **1** in MeCN has an absorption band at 429 nm, which is red-shifted compared with the S→W(VI) charge-transfer band of $[(\eta^5\text{-}C_5Me_5)WS_3]^-$ (381 nm in MeCN).[14] Therefore, compound **1** is almost transparent at 532 nm, which promises low intensity loss and little temperature change by photon absorption when light propagates in the materials. The identity of **1** was finally confirmed by single-crystal X-ray crystallography.

Crystal structure

X-ray diffraction analysis revealed that **1** is composed of one independent $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3BrI_2(dppm)]^-$ anion and one $[PPh_4]^+$ cation in an asymmetric unit. A perspective view of the anion is shown in Fig. 1, and the selected bond lengths and angles are listed in Table 1. The anion of **1** contains an incomplete WS_3Cu_3 cubane-like core in which two CuI units are linked by a dppm ligand. The

(η^5-C_5Me_5)WS_3 moiety adopts a slightly distorted three-legged piano-stool structure. The mean W—μ_3-S bond length of (η^5-C_5Me_5)WS_3(0.2273 nm) is 0.008 nm longer than that of [PPh_4][(η^5-C_5Me_5)WS_3],[14] but very close to that of [PPh_4]$_2$[(η^5-C_5Me_5)$WS_3Cu_3Br_3$]$_2$(0.2282 nm).[15] The three Cu atoms show different coordination geometry. The Cu(1) and Cu(2) atoms have a distorted tetrahedral geometry, coordinated by one terminal I, one P (dppm), and two μ_3-S atoms, while the Cu(3) atom has a trigonal planar geometry, coordinated by one terminal Br and two μ_3-S atoms. Because of the different coordination geometries of the Cu atoms, the W—Cu(3) distance (0.2644 nm) is 0.0138 nm shorter than the mean value of W—Cu(1) and W—Cu(2), but close to those found in [PPh_4]$_2$ [(η^5-C_5Me_5) $WS_3Cu_3Br_3$](0.2661 nm)[14] and (NEt_4)$_3$[WOS_3($CuBr$)$_3$(μ-Br)]·$2H_2O$ (0.2676 nm).[21] The Cu—μ_3-S distances reflect the mode of coordination of the copper atoms, av. 0.2210 nm for trigonal geometry, av. 0.2288 nm for a tetrahedral environment. However, the mean Cu—μ_3-S length (0.2228 nm) is similar to those reported in [PPh_4]$_2$ [(η^5-C_5Me_5) $WS_3Cu_3Br_3$]$_2$ (0.2234 nm) and (NEt_4)$_3$[WOS_3($CuBr$)$_3$(μ-Br)]·$2H_2O$ (0.2293 nm). The terminal Cu(3)—Br(1) length (0.2354 nm) is close to the corresponding ones in [PPh_4]$_2$[(η^5-C_5Me_5)-$WS_3Cu_3Br_3$]$_2$ (0.2308 nm) and [(n-Bu)$_4$N]$_3$-[$MoS_4Cu_5Br_6$] (0.2272 nm).[22] The Cu—I lengths of 0.2621(2)—0.2635(2) nm are comparable with those observed in compounds containing tetrahedrally-coordinated copper (*e.g.* 0.2629(1)—0.2639(1) nm in [$MoS_4Cu_4I_2$(Py)$_6$]).[23] The mean Cu—P length (0.2274 nm) is normal compared with those found in [WS_4Cu_4-(dppm)$_4$](PF_6)$_2$ (av. 0.2269 nm).[24]

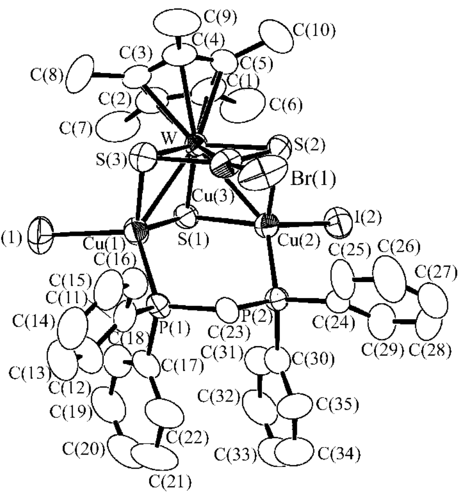

Fig. 1 Perspective view of the anion of [PPh_4][(η^5-C_5Me_5)-WS_3($CuBr$)(CuI)$_2$(μ-dppm)] (**1**). Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths (nm) and angles (°) for **1**

W—Cu(1)	0.2770(1)	W—Cu(2)	0.2793(1)
W—Cu(3)	0.2663(6)	W—S(1)	0.2258(2)
W—S(2)	0.2272(2)	W—S(3)	0.2289(2)
I(1)—Cu(1)	0.2621(1)	I(2)—Cu(2)	0.2635(2)
Br(1)—Cu(3)	0.2354(2)	Cu(1)—S(1)	0.2269(2)
Cu(1)—S(3)	0.2281(3)	Cu(2)—S(1)	0.2283(2)
Cu(2)—S(2)	0.2290(2)	Cu(3)—S(2)	0.2211(3)
Cu(3)—S(3)	0.2208(2)	Cu(1)—P(1)	0.2268(2)
Cu(2)—P(2)	0.2279(2)		
S(1)-W-S(2)	104.78(7)	S(1)-W-S(3)	105.65(8)
S(2)-W-S(3)	105.35(8)	Cu(1)-W-Cu(2)	77.29(3)
Cu(1)-W-Cu(3)	78.72(3)	Cu(2)-W-Cu(3)	77.62(3)
I(1)-Cu(1)-S(1)	104.16(6)	I(1)-Cu(1)-S(3)	106.94(7)
I(1)-Cu(1)-P(1)	111.29(7)	S(1)-Cu(1)-S(3)	104.69(8)
S(1)-Cu(1)-P(1)	112.58(8)	S(3)-Cu(1)-P(1)	116.25(9)
I(2)-Cu(2)-S(1)	109.48(6)	I(2)-Cu(2)-S(2)	103.87(7)
I(2)-Cu(2)-P(2)	108.98(6)	S(2)-Cu(2)-S(1)	103.36(8)
S(1)-Cu(2)-P(2)	114.14(8)	S(2)-Cu(2)-P(2)	116.37(8)
Br(1)-Cu(3)-S(2)	117.86(8)	Br(1)-Cu(3)-S(3)	131.40(8)
S(2)-Cu(3)-S(3)	110.30(8)	W-S(1)-Cu(1)	74.93(7)
W-S(1)-Cu(2)	75.91(6)	Cu(1)-S(1)-Cu(2)	98.70(8)
W-S(2)-Cu(2)	75.50(7)	W-S(2)-Cu(3)	72.28(7)
Cu(2)-S(2)-Cu(3)	98.45(10)	W-S(3)-Cu(1)	74.62(7)
W-S(3)-Cu(3)	72.00(7)	Cu(1)-S(3)-Cu(3)	99.85(9)

Optical limiting effect

The optical limiting (OL) properties were obtained by varying the input energy and measuring the transmitted energy. No other apparent nonlinear optical effects such as self-focusing, self-defocusing, and nonlinear scattering, contribute to the OL effect for the lens set in front of the detectors. Fig. 2 displays the measurement of OL effects of the MeCN solution of **1** at different concentrations with laser pulses of 12 ns duration. There is a linear response of transmitted energy to the very low incident laser intensity, and the obvious deviation from the linear response can be observed as the incident intensity increases. A reduction in transmission is also observed as the concentration of the sample increases. However, no obvious OL effect was observed on picosecond (ps) laser pulses. It indicates that the nanosecond OL effect may be due to the reverse saturable absorption (RSA) related to the excited triplet states, which can occur when the absorption cross-section of the excited states is larger than that of the ground states.[25]

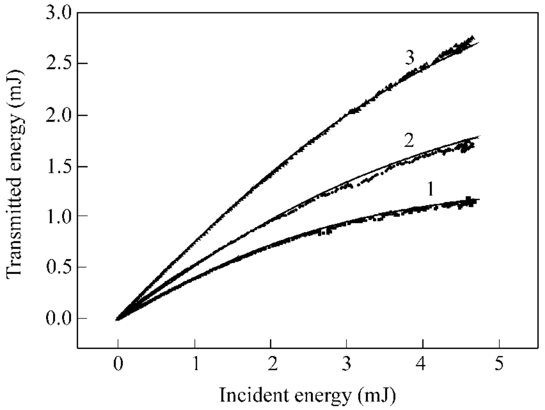

Fig. 2 Optical limiting responses for **1** at 1.05×10^{-3} mol/L (line 1), 2.63×10^{-4} mol/L (line 2), and 5.25×10^{-4} mol/L (line 3) in MeCN with 12 ns laser and 2 mm cell.

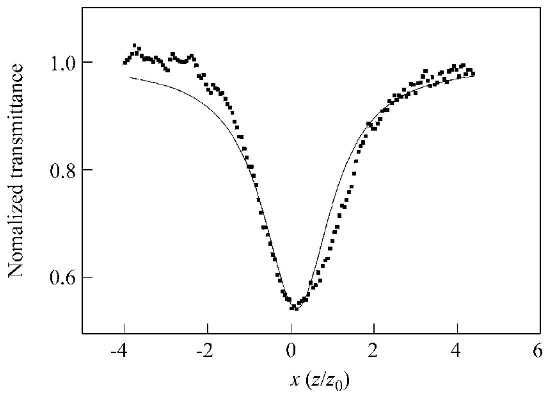

Fig. 3 Open aperture Z-scan data for MeCN solution of **1** with concentration of 5.00×10^{-4} mol/L (filled sqaure). Each solid curve is theoretical fit.

To confirm the origins of the RSA, we measured the nonlinear absorption of **1** in MeCN by the open-aperture Z-scan technique. The results of nonlinear absorption are shown in Fig. 3. The tremendous change of transmission in the open aperture case indicates that the laser pulses experienced strong excited state absorption and RSA at 532 nm wavelength.[26,27] The optical absorption behavior of a metal sulfide cluster like **1** can be well described by a system with five energy levels (including three singlet states and two triplet states).[28] The attenuation of the incident light is described by:

$$\frac{\partial I}{\partial z} = -\sigma_0 S_0 N I - \sigma_1 S_1 N I - \sigma_2 T_1 N I \tag{1}$$

where I is the light intensity, N is the total number density of molecules, and σ_0, σ_1, σ_2 are the absorption cross sections for the ground state, the first excited singlet state, and the first excited triplet state, respectively. The dimensionless quantities $S_0 = N_{S_0}/N$, $S_1 = N_{S_1}/N$, $S_2 = N_{S_2}/N$, $T_1 = N_{T_1}/N$, $T_2 = N_{T_2}/N$; and N_{S_0}, N_{S_1}, N_{S_2}, N_{T_1}, N_{T_2} are the population densities of the S_0, S_1, S_2, T_1, and T_2 states. In nanosecond case, there should be a significant amount of population transfer from S_1 to T_1, and thus the relaxation time from the higher excited singlet states S_n to the first excited singlet state S_1 is extremely short (< ps). Consequently, the three-level model seems to be inadequate to describe the result. The energy transfer processes can be described as:

$$\frac{\partial S_0}{\partial t} = -\frac{\sigma_0 I}{\eta\omega} S_0 + \frac{S_1}{\tau_{10}} + \frac{T_1}{\tau_3} \tag{2}$$

$$\frac{\partial S_1}{\partial t} = \frac{\sigma_0 I}{\eta\omega} S_0 - \frac{\sigma_1 I}{\eta\omega} S_1 + \frac{S_2}{\tau_{21}} - \frac{S_2}{\tau_{21}} - \frac{S_1}{\tau_{10}} - k_{\mathrm{isc}} S_1 \tag{3}$$

$$\frac{\partial S_2}{\partial t} = \frac{\sigma_1 I}{\eta\omega} S_1 - \frac{S_2}{\tau_{21}} \tag{4}$$

$$\frac{\partial T_1}{\partial t} = k_{\mathrm{isc}} S_1 - \frac{\sigma_2 I}{\eta\omega} T_1 + \frac{T_2}{\tau_4} - \frac{T_1}{\tau_3} \tag{5}$$

$$\frac{\partial T_2}{\partial t} = \frac{\sigma_2 I}{\eta\omega} T_1 - \frac{T_2}{\tau_4} \tag{6}$$

Here τ_{21}, τ_{10}, τ_3, and τ_4 are the life-time of S_1, S_2, T_1 and T_2 states, and k_{isc}[29] is the transfer rate of the intersystem transition $S_1 \rightarrow T_1$. According to Eqs. (1)—(6), we can find an agreement between the experiment data and the theoretical fitting results as shown in Fig. 3. When $\sigma_0 = 5.6 \times 10^{-19}$ cm^2 and $I_0 = 4.9 \times 10^{12}$ W/m^2, $k_{\rm isc}$ and σ_2 are thus determined to be 3.0×10^9 s^{-1} and 4.9×10^{-17} cm^2, respectively. As the σ_2 is larger than σ_0, the OL effect for nanosecond laser pulses appears obvious, and can be easily observed in the experiment.

Conclusions

We have demonstrated that a 1∶2∶1∶1 reaction mixture of [PPh$_4$][(η^5-C$_5$Me$_5$)WS$_3$], CuI, CuBr and dppm in MeCN produced compound **1** in a relatively high yield. The structure of the anion of **1** contains an incomplete WS$_3$Cu$_3$ cubane-like framework in which two CuI units are linked by a dppm ligand. Compound **1** exhibits good OL effects and nonlinear absorption properties in solution. Its OL performance may be attributed to the RSA related to the excited triplet states. Therefore compound **1** may be optimized for the photonic devices and may have potential application in optical switches and OL materials.

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(E0305129 PAN, B. F.; LING, J.)