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# Self-assembly synthesis, crystal structure and nonlinear optical properties of cluster compound containing $PPh_2Py$ ligand

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**Abstract:** Self-assembly cluster compound $[WS_4Cu_3(PPh_2Py)_3Br]_2 \cdot CH_3OH$ (1) was synthesized by the reaction of $(NH_4)_2WS_4$, CuBr and diphenyl-2-pyridyl-phosphine ($PPh_2Py$) in $CH_3OH$ solution under a purified nitrogen atmosphere using standard Schlenk techniques. Its structure was determined by X-ray crystallography. It crystallizes in the triclinic crystal system P-1 space group with $a$=1.178 6 (1) nm, $b$=1.302 6 (1) nm, $c$=1.991 7 (2) nm, $\alpha$=74.671 (7)°, $\beta$=86.188 (8)°, $\gamma$=64.141 (6)°, $V$=2.649 5 (5) nm$^3$, $Z$=1. The W center is slightly distorted from tetrahedral coordination geometry, and the structure is built up from three $[Cu(PPh_2Py)]^+$ units bridged by $WS_4^{2-}$ multifunctional ligand to form a tetranuclear symmetrical cube-like molecule. Measurement of the nonlinear optical (NLO) properties using the $Z$-scan technique with an 8 ns pulsed laser at 532 nm shows that the compound possesses NLO absorption and effective self-focusing effect at $\alpha_2=6.7\times10^{-11}$ m/W and $n_2=5.64\times10^{-18}$ m$^2$/W in a $1.5\times10^{-4}$ mol/L DMF solution.

**Key words:** self-assembly; cluster; Schlenk techniques; $Z$-scan; self-focusing

## 1 Introduction

Transition metal-sulfur cluster chemistry develops rapidly, because clusters have interesting electronic, optical, structural and catalytic properties and are of biological interest and industrial significance in advanced materials[1−3]. Great interest in these clusters has recently been aroused by the search for better materials with third-order non-linear optical(NLO) properties because of their potential applications not only in the protection of optical sensors and the human eye from high-intensity laser beams, but also in the development of optical signal detection techniques such as those utilized in optical computers and broad-band communication[4−5]. For example, $[NBu_4][MoOS_3Cu_3BrCl_2]$, $[NBu_4]_3[MS_4M'_3BrX_3]$ (M=Mo, W; M′=Cu, Ag; X=Cl, Br, I), $[NBu_4]_3[MoOS_3Cu_3BrI_3]$, $[WS_4Cu_4(SCN)_2(Py)_6]$, $[Mo_2Ag_4S_8(PPh_3)_4]$ and $[NEt_4]_4[Mo_2O_2S_6Cu_6Br_2I_4]$ exhibit good NLO properties[6−9].

Although the coordination chemistry of $Ph_2PPy$ is well developed, the corresponding chemistry with heterothiometallic clusters has received less attention [10−11]. In this work, we report the self-assembly synthesis, X-ray crystal structure and NLO properties of cluster compound containing the $PyPPh_2$ ligand.

## 2 Experimental

$(NH_4)_2WS_4$ was prepared according to Ref.[12]. Other chemicals were of A. R. grade and used without further purification. IR spectra were recorded on a Fourier Nicolet FT-170SX spectrophotometer with pressed KBr pellets. Carbon, nitrogen and hydrogen analyses were performed on a PE 240C Elemental Analyser.

### 2.1 Preparation of compound 1

The synthesis of Compound 1 was performed under a purified nitrogen atmosphere using standard Schlenk techniques. A solution of $(NH_4)_2WS_4$ (0.174 g, 0.5 mmol) in 40 mL $CH_3OH$ was added dropwise to a mixture of CuBr (0.216 g, 1.5 mmol) and $PPh_2Py$ (0.234 g, 1.5 mmol). The solution immediately turned deep-red and was stirred for 10 h at room temperature. Single crystal (yield 70%) was obtained after several days by laying the

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filtrate with i-PrOH. The analytical calculation result for $[WS_4Cu_3(PPh_2Py)_3Br]_2\cdot CH_3OH$ (%) is C 44.58, H 3.17, N 3.06. The testing result is C 44.55, H 3.19, N 3.03. IR($cm^{-1}$) of this compound is 448.57(s), 422.72(s), 1 480.22(s), 2 960.64(m).

### 2.2 X-ray crystal structure determination

X-ray measurements and data collection were performed on a Siemens Smart CCD diffractometer with graphite monochromated Mo $K_\alpha$ ($\lambda$=0.071 073 nm) radiation at 20 ℃. Intensity data for the crystal were obtained in the range of 4.04°−51.10° using an $\omega$-scan technique. The structure was solved by direct methods and refined by full-matrix least-square methods on $F^2$ using SHELXTL software. All H atoms were geometrically fixed and allowed to ride on their attached atoms. Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No.270021. Copies of these information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax +44-1223-336033 or E-mail:deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.ck

### 2.3 Optical measurement

A well-ground sample was dissolved in $1.5\times10^{-4}$ mol/L DMF solution and placed in a 5 mm-thick quartz cuvette for NLO measurements. Its NLO properties were measured with an 8 ns pulsed laser at 532 nm generated from a Q-switched frequency-doubled Nd-YAG laser. The spatial profiles of the optical pulses were nearly Gaussian after passing through a filter. The pulsed laser was focused onto the sample cell with a 30 cm focal length mirror. Incident and transmitted pulsed energies were measured simultaneously by two energy detectors (RJP-735 energy probes, laser precision). The NLO properties of the sample were determined by performing *Z*-scan measurements[13−14]. The sample was mounted on a translation stage that was controlled by the computer to move along the *Z*-axis with respect to the focal point. An aperture of 0.5 mm in radius was placed in front of the transmission detector. The transmittance was recorded as a function of the sample position on the *Z*-axis (closed aperture *Z*-scan). For measuring the NLO absorption, the transmittance of *Z*-dependent sample was taken without the aperture (open aperture *Z*-scan).

## 3 Results and discussion

### 3.1 Structural descriptions

Table 1 lists the crystallographic data and structure refinements for Compound 1. Selected bond lengths and angles are given in Table 2. The structure of Compound 1 is shown in Fig.1.

The core of $[WS_3Cu_3Br]$ is a slightly distorted cube, in which the four metal atoms and the four non-metal atoms are alternatively distributed. One S is terminal and the other three S and Br are $\mu_3$-bridging atoms. The length

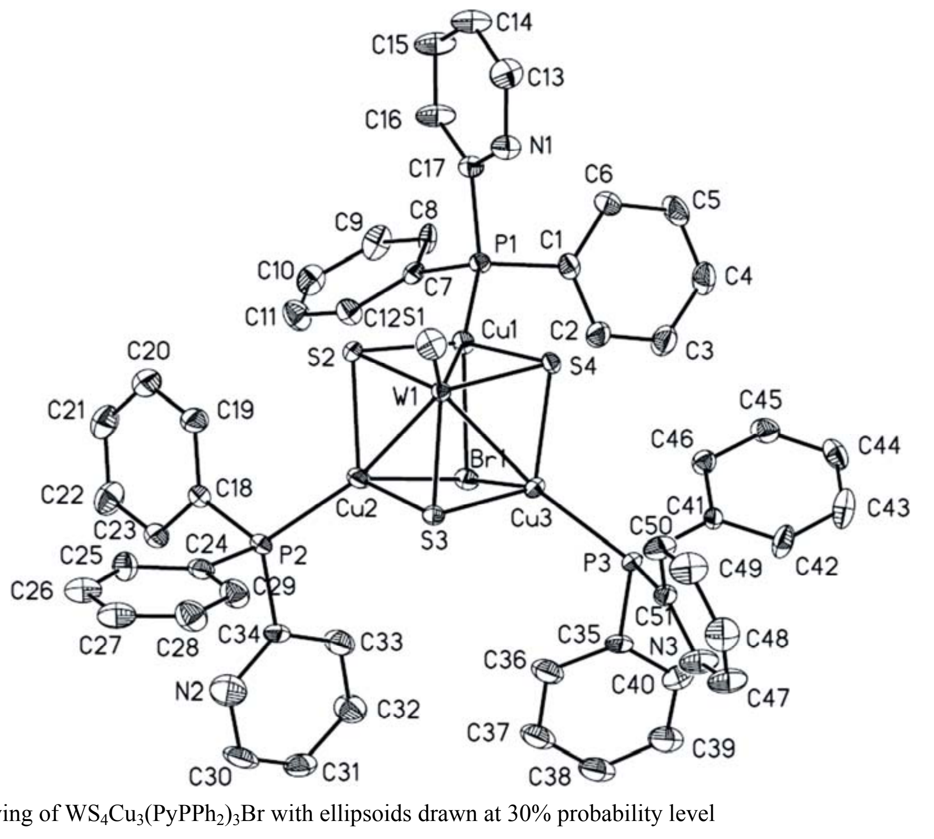

**Fig.1** ORTEP drawing of $WS_4Cu_3(PyPPh_2)_3Br$ with ellipsoids drawn at 30% probability level

**Table 1** Crystal data and structure refinement for $C_{103}H_{88}Br_2Cu_6N_6OP_6S_8W_2$

| Test item | Crystal data |
|---|---|
| Relative formula mass | 2 776.85 |
| Temperature/K | 293(2) |
| Wavelength/nm | 0.071 073 |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimension/nm | $a$=1.178 6 (1)<br>$b$=1.302 6 (1)<br>$c$=1.991 7 (2)<br>$\alpha$=74.671 (7)<br>$\beta$=86.188 (8)<br>$\gamma$=64.141 (6) |
| Volume/nm$^3$ | 2.649 5 (5) |
| $Z$ | 1 |
| $D_{cal}$/(g·cm$^{-3}$) | 1.740 |
| Absorption coefficient/mm$^{-1}$ | 4.393 |
| $F$(000) | 1 366 |
| Crystal size/mm | 0.3×0.2×0.2 |
| $\theta$ range for data collection/(°) | 2.02−25.55 |
| Index range/(°) | $-14\leqslant h\leqslant 14$<br>$-16\leqslant k\leqslant 16$<br>$-24\leqslant l\leqslant 23$ |
| Reflection collected | 27 165 [$R_{int}$=0.028 9] |
| Independent reflection | 10 294 |
| Observed reflection[$I>2\sigma(I)$] | 9 589 |
| Refinement method | Full-matrix least squares on $F^2$ |
| Number of parameters | 615 |
| Goodness-of-fit on $F^2(S)$ | 1.088 |
| Final $R$ indices[$I>2\sigma(I)$] | $R_1$=0.046 3,$wR_2$=0.155 3 |
| $R$ indices(all data) | $R_1$=0.051 0,$wR_2$=0.159 2 |
| Final weighting scheme | (Calculated)<br>$w=1/[S^2(F_0^2)+(0.12P)^2+1.55P]$<br>where $P=(F_0^2+2F_c^1)/3$ |
| Maximum residual diffraction/(e·nm$^{-3}$) | 0.000 909 |
| Minimum residual diffraction/(e·nm$^{-3}$) | −0.000 917 |

of the W=S bond [0.213 49(18) nm] is typical for W══S double bond. The other three W—S bonds are single bonds, and their average bond length of 0.225 07 nm is longer than that of W══S double bond. The central unit of the crystal can be described as a slightly distorted cube, in which four corners are occupied by one W and three Cu atoms, and the other four corners are occupied by one Br atom and three $\mu_3$-S atoms. All the Cu atoms

**Table 2** Selected bond lengths and angles for $C_{103}H_{88}Br_2Cu_6N_6OP_6S_8W_2$

| Bond | Bond length/nm | Bond | Bond length/nm |
|---|---|---|---|
| W1—S1 | 0.213 49 (18) | S4—Cu3 | 0.229 89 (16) |
| W1—S2 | 0.224 84 (14) | W1—Cu3 | 0.271 87 (9) |
| W1—S3 | 0.224 91 (15) | Br1—Cu1 | 0.273 92 (10) |
| W1—S4 | 0.225 46 (14) | Br1—Cu2 | 0.280 34 (11) |
| Cu1—P1 | 0.221 47 (16) | Br1—Cu3 | 0.275 24 (11) |
| Cu2—P2 | 0.222 77 (17) | P1—C1 | 0.181 8 (7) |
| Cu3—P3 | 0.221 51 (16) | P1—C7 | 0.181 8 (6) |
| Cu1—S2 | 0.230 12 (16) | P1—C17 | 0.182 4 (7) |
| Cu1—S4 | 0.228 89 (15) | P2—C18 | 0.182 3 (7) |
| W1—Cu1 | 0.271 76 (7) | P2—C24 | 0.182 7 (7) |
| S2—Cu2 | 0.231 56 (16) | P2—C34 | 0.182 5 (6) |
| S3—Cu2 | 0.230 63 (17) | P3—C35 | 0.182 4 (7) |
| W1—Cu2 | 0.273 31 (8) | P3—C41 | 0.181 6 (6) |
| S3—Cu3 | 0.229 57 (16) | P3—C51 | 0.182 7 (6) |
| **Bond** | **Bond angle/(°)** | **Bond** | **Bond angle/(°)** |
| S1—W1—S2 | 112.49 (7) | S3—W1—Cu3 | 54.05 (4) |
| S1—W1—S3 | 111.56(7) | S4—W1—Cu3 | 54.09 (4) |
| S1—W1—S4 | 110.75 (7) | S1—W1—Cu2 | 138.16 (6) |
| S2—W1—S4 | 107.12 (5) | S2—W1—Cu2 | 54.35 (4) |
| S3—W1—S4 | 107.19 (5) | S3—W1—Cu2 | 54.10 (4) |
| S2—W1—S3 | 107.46 (5) | S4—W1—Cu2 | 111.09 (4) |
| S1—W1—Cu1 | 136.90 (6) | Cu1—W1—Cu2 | 72.47 (3) |
| S2—W1—Cu1 | 54.22 (4) | Cu1—W1—Cu3 | 72.36 (3) |
| S3—W1—Cu1 | 111.51 (4) | Cu3—W1—Cu2 | 72.13 (3) |
| S4—W1—Cu1 | 53.85 (4) | Cu1—Br1—Cu2 | 71.07 (3) |
| S1—W1—Cu3 | 136.08 (6) | Cu1—Br1—Cu3 | 71.52 (3) |
| S2—W1—Cu3 | 111.42 (4) | Cu3—Br1—Cu2 | 70.56 (3) |

are coordinated by one P, two $\mu_3$-S, and one $\mu_3$-Br atoms. The Cu-S distances are similar, but Cu-P distances are longer than those in compound [$MoS_4Cu_3(PPh_3)_3Cl$][15]. This can be contributed to the difference of $PPh_3$ and $PPh_2Py$.

### 3.2 Nonlinear optical properties

The NLO properties of Compound 1 were determined by using $Z$-scan techniques. A $Z$-scan measurement is shown in Fig.2 and Fig.3. The optical propagation equation for the pulsed light intensity is given by Eqn.(1)[16]:

$$\frac{\mathrm{d}I}{\mathrm{d}z}=-\alpha I \tag{1}$$

where $\alpha$ is the non-linear absorption coefficient of the sample, which can be expressed as the function of the incident pulsed light intensity $I$ from Eqn.(2)[16]:

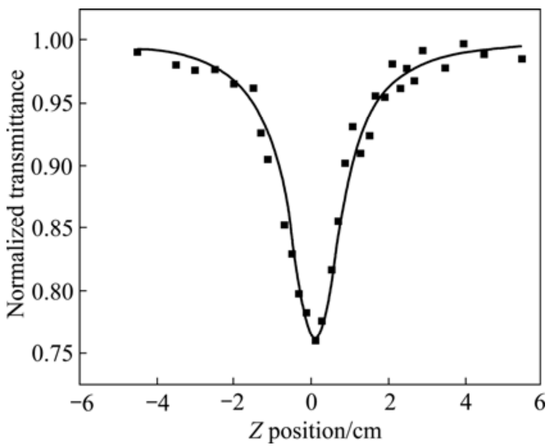


**Fig.2** Open-aperture $Z$-scan results of Compound 1 in $1.5\times10^{-4}$ mol/L DMF solution

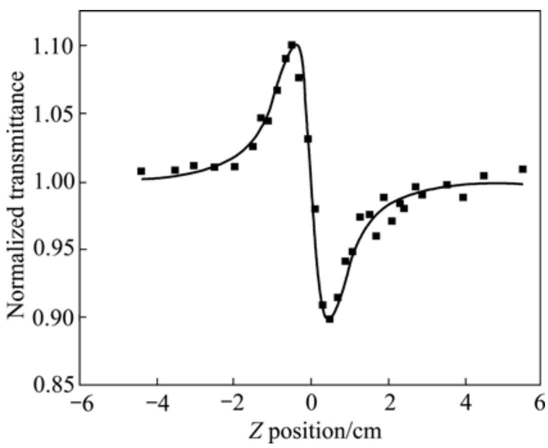


**Fig.3** $Z$-scan results of Compound 1 in $1.5\times10^{-4}$ mol/L DMF solution observed under closed-aperture configuration

$$\alpha=\alpha_0+\frac{1+K_\alpha\dfrac{I}{I_s}}{1+\dfrac{I}{I_s}}\sigma_0 N \tag{2}$$

where $\alpha_0$ is the linear absorption coefficient of the sample; $\sigma_0$ is the absorption cross-section of the ground-state molecular solution; $N$ is the concentration of the sample solution; $I_s=(h\gamma/\sigma_0\tau_{e0})$ is the saturation intensity, with $\tau_{e0}$ being the lifetime of the excited-state, $K_\alpha=\sigma_e/\sigma_0$ is the ratio of the excited-state absorption cross-section to the ground-state cross-section.

The nonlinear absorption components were evaluated by the $Z$-scan method under an open aperture configuration and the NLO absorptive experimental data obtained under the conditions used in this study can be well described by Eqns.(3) and (4)[17], which are used to describe a third-order NLO absorptive process:

$$T(z)=\frac{1}{\sqrt{\pi q(z)}}\int_{-\infty}^{+\infty}\ln[1+q(z)]\exp(-\tau^2)\mathrm{d}\tau(z) \tag{3}$$

$$q(Z)=\int_0^{+\infty}\int_0^{+\infty}\alpha_2\frac{I_0}{1+(Z/Z_0)^2}\exp[-2(\gamma/\omega_0)-(t/t_0)^2]\cdot\frac{1-\exp(-\alpha_0 L)}{\alpha_0}r\mathrm{d}r\mathrm{d}t \tag{4}$$

where light transmittance $T$ is a function of the $Z$-position (against the focal point $Z$=0) of the sample; $Z$ is the distance of the sample from the focal point; $L$ is the sample thickness; $I_0$ is the peak irradiation intensity at focus. $Z_0=\pi\omega_0^2/\lambda$, where $\omega_0$ is the spot radius of the laser pulse at focus and $\lambda$ is the laser wavelength; $\gamma$ is the radial coordinate; $t$ is the time; and $t_0$ is the pulse width.

The nonlinear refractive properties were assessed by dividing the normalized $Z$-scan data obtained under the closed aperture configuration by the normalized $Z$-scan data obtained under the open aperture configuration. The valley/peak patterns of the corrected transmittance curves show characteristic self-focusing behaviors of the propagating light in the sample. An effective third-order nonlinear refractive index $n_2$ of this compound can be derived from the difference between normalized transmittance values at valley and peak position ($\Delta T_{\text{v-p}}$) by use of Eqn.(5)[18]:

$$n_2=\frac{\lambda\alpha_0}{0.812\pi I[1-\exp(-\alpha_0 L)]}\Delta T_{\text{v-p}} \tag{5}$$

where $I$ is the peak irradiation intensity at focus and $\lambda$ is the wavelength of the laser. The filled boxes in Fig.2 and Fig.3 are the optical limiting experimental data measured with linear transmittance. The effective nonlinear absorptive indexes $\alpha_2$ and $n_2$ of this compound are $6.7\times10^{-11}$ m/W and $5.64\times10^{-18}$ m$^2$/W. The $n_2$ value of the title compound is comparable with that of the heterobimetallic polymeric compound $\{[n\text{-}Bu_4N][W_2Ag_3S_8]\}_n$ ($3.67\times10^{-18}$ m$^2$/w)[19]. Therefore, this cluster compound exhibit considerable NLO absorption properties. The valley/peak pattern of the normalized transmittance curve, obtained under a closed aperture configuration, shows characteristic self-focusing behavior of propagating light in the sample. This property shows that this cluster compound can be promising material for applications such as protection of optical sensors.

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