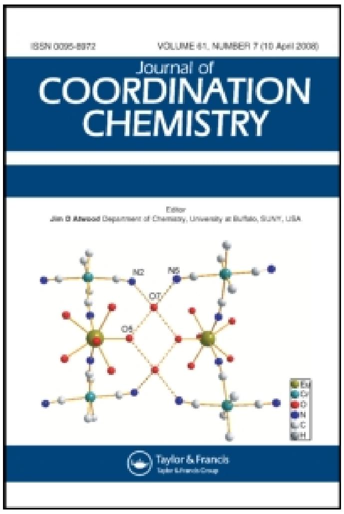

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Synthesis, Crystal Structure and Nonlinear Optical Properties of a new cluster compound: $MoS_4Cu_3(PyPPh_2)_3Cl$

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SYNTHESIS, CRYSTAL STRUCTURE AND NONLINEAR OPTICAL PROPERTIES OF A NEW CLUSTER COMPOUND: $MoS_4Cu_3(PyPPh_2)_3Cl$

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Reaction of $[NH_4]_2[MoS_4]$, CuCl and $PyPPh_2$ in the solid state produces a cube-like cluster. The cluster crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units in a cell of dimensions $a = 12.8980(10)$, $b = 17.6820(10)$, $c = 22.665(2)$ Å. Anisotropic refinement for all nonhydrogen atoms yielded the values $R = 0.0397$ and $R_w = 0.1185$ for 8803 observed reflections. The structure is built up from three $[Cu(Ph_2PPy)]^+$ units bridged by MoS_4^{2-} to form a tetranuclear symmetrical cube-like molecule. Investigation of the third-order optical nonlinear value showed that it exhibits a considerable nonlinear absorptive and self-defocusing effect with $\alpha_2 = 1.3 \times 10^{-11}\,\mathrm{m\,w^{-1}}$ and $n_2 = -3.2 \times 10^{-18}\,\mathrm{m^2\,w^{-1}}$ in a 1.5×10^{-4} M DMF solution.

Keywords: Mo–Cu–S cluster; Crystal structure; Nonlinear optical properties

INTRODUCTION

The chemistry of transition metal–sulfur clusters has attracted much attention owing to their relevance to biological and industrial catalysis, rich structural chemistry, and special reactive properties, as well as potential application in nonlinear optical (NLO) materials [1–3]. The reaction of Cu^+ with MS_4^{2-} in solution has led to syntheses of more than one hundred structurally characterized Cu(Ag)–Mo(W)–S cluster compounds [4]. By exploring the solid state reaction of coordination compounds at mild temperature, we have recently synthesized Cu(Ag)–Mo(W)–S clusters, including linear, cube-like, incomplete cube, butterfly, planar, prism and cage type clusters [5–11]. Although the coordination chemistry of Ph_2PPy is well developed, the corresponding chemistry with heterothiometallic clusters has received less attention [12,13]. Developing superior third-order NLO materials which can utilize the short wavelength

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laser light generated by the newly developed II–IV semiconductor diode laser to perform optical data processing remains a challenge. Both large values of NLO refractive index n_2 and low linear absorptive value α_0 in this wavelength region are key criteria in screening new NLO materials. For example, $[NBu_4][MoOS_3Cu_3BrCl_2]$, $[NBu_4]_2[MoOS_3(CuSCN)_3]$, $[NBu_4]_3[MS_4M'_3BrX_3]$ (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. In this article the synthesis and X-ray crystal structure of a new cluster compound $MoS_4Cu_3(PyPPh_2)_3Cl$ is reported. Bond angles and lengths are discussed and compared to other cubic-like cluster compounds. Investigation of the cluster's NLO properties showed that it exhibits good nonlinear absorptive and refractive properties.

EXPERIMENTAL

All syntheses and manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified by conventional methods and degassed prior to use. Electronic absorption spectra were obtained on a Shimazu UV-3000 spectrophotometer. Infrared spectra were recorded on a Fourier Nicolet FT-170SX spectrophotometer with pressed KBr pellets. Carbon, hydrogen and nitrogen analyses were performed on a PE 240C Elemental Analyzer. Molybdenum and copper analyses were performed on a JA-1100 ICP spectrophotometer. $[NH_4]_2[WS_4]$ was prepared according to the literature [14]. Ph_2PPy was purchased from Aldrich. Other chemicals were of A.R. grade and used without further purification.

Preparation of the Compound $[MoS_4Cu_3(PyPPh_2)_3Cl]$

A well ground mixture of CuCl (0.297 g, 3.0 mmol), $(NH_4)_2MoS_4$ (0.348 g, 1 mmol) and 2-(diphenylphosphino)pyridine (0.792 g, 3.0 mmol) was placed in a reaction tube. A dark red solid was generated by heating the mixture at 100°C for 10 h under pure nitrogen. A red solution obtained by extracting the product with ethyl alcohol (50 mL) was allowed to evaporate in air slowly. After several days, 0.45 g (36.3%) of red cubic crystals of the compound suitable for X-ray crystallographic analysis were collected and washed with ethyl ether. Anal. Calcd. for $C_{51}H_{42}ClCu_3MoN_3P_3S_4$(%): C, 49.39; H, 3.41; N, 3.39. Found: C, 49.35; H, 3.45; N, 3.32. IR spectra (KBr), the ν(Mo–μ_2–s) stretching vibration appears at 444.7 cm^{-1}. The elemental analysis and IR spectrum confirmed the formula of the cluster.

Nonlinear Opticals

The optical measurements were performed with linearly polarized 7-ns pulses at 532 nm generated from a frequency-doubled Q-switched Nd: YAG laser; the spatial profiles of the pulses were nearly Gaussian after a spatial filter was employed. A DMF solution of the compound was placed in a 1-mm-thick quartz cell for measurements of NLO properties. The crystal samples of them are stable toward oxygen, moisture and laser light. The laser beam was focused with a 25-cm focal-length focusing mirror. The radius of the beam circumference was measured to be 30 ± 5 μm (half-width at $1/e^2$ maximum in irradiance). The incident and transmitted pulse energy were measured simultaneously by two energy detectors (Laser Precision Rjp-735) which were linked to a computer by an IEEE interface. The interval between the laser pulses was chosen to be ~5 s for operational convenience and controlled by the computer. The NLO properties of the compound were manifested by moving the sample along the axis of the incident laser beam (Z-direction) with respect to the focal point instead of being positioned at its focal point, and an identical setup was adopted in the experiments to measure the Z-scan data. An aperture of 0.5 mm radius was placed in front of the detector to assist the measurement of the NLO refraction effect.

Crystallographic Studies

A single crystal for the compound was carefully chosen, coated with epoxy resin and mounted on a glass fiber. Cell dimension measurements and data collection were performed on a Bruker AXS Smart 1000 X-ray diffractometer equipped with a CCD area detector and graphite-monochromatized Mo radiation ($K_\alpha = 0.71073$ Å) at 293(2) K. Intensity data for the crystal were obtained in the range $3.64 < 2\theta < 50°$ by using an ω scan technique. Data reduction and refinement were performed with Bruker SHELXTL software. Crystallographic data are listed in Table I. Final positional parameters are given in Table II.

RESULTS AND DISCUSSION

Structural Descriptions

The structure of $MoS_4Cu_3(PyPPh_2)_3Cl$ shown in Fig. 1 consists of one molecule in the asymmetric unit. The central unit of the crystal can be described as a slightly distorted cube in which four corners are occupied by one Mo and three Cu atoms (with a $PyPPh_2$ moiety being bonded to each Cu), the other four corners are occupied by one Cl atom and three μ_3-S atoms. Selected bond distances and angles are listed in Table III.

TABLE I Crystal data and details of the structure determination for the compound $MoS_4Cu_3(PyPPh_2)_3Cl$

Formula	$C_{51}H_{42}ClCu_3MoN_3P_3S_4$
F_w	1240.14
Space group	$P2_12_12_1$
a(Å)	12.8980(10)
b(Å)	17.6820(10)
c(Å)	22.665(2)
V(Å^3)	5169.0(7)
Z	4
F(000)	2496
D_{calc} (g cm^{-1})	1.593
Crystal system	Orthorhombic
Crystal color	Red
Crystal dimensions (mm)	0.30 × 0.20 × 0.20
Temperature (K)	293(2)
Radiation	Mo-K_α (0.71073 Å)
Flack parameter	0.00
R	0.0397
R_w	0.1185

TABLE II Final coordinates and equivalent isotropic displacement parameters of the nonhydrogen atoms for the compound

Atom	*x*	*y*	*z*	U_{eq}
Mo1	0.83217(3)	1.00486(2)	0.97731(2)	0.0336(1)
Cu1	0.70146(6)	0.90462(4)	0.92709(3)	0.0470(2)
Cu2	0.69731(6)	0.95511(4)	1.06090(3)	0.0441(2)
Cu3	0.65126(6)	1.07857(4)	0.96692(3)	0.0488(2)
Cl	0.54175(10)	0.95203(8)	0.99690(6)	0.0435(4)
S1	0.81110(10)	0.88394(7)	1.00463(5)	0.0367(3)
S2	0.75667(10)	1.07677(7)	1.04743(5)	0.0391(4)
S3	0.74091(10)	1.02223(7)	0.89287(5)	0.0379(4)
S4	0.98535(18)	1.02948(14)	0.96709(12)	0.0882(8)
P1	0.64116(11)	0.81056(7)	0.87245(6)	0.0386(4)
P2	0.65097(11)	0.902277(7)	1.14524(5)	0.0357(3)
P3	0.52472(10)	1.16300(7)	0.96444(6)	0.0375(4)
N1	0.4341(6)	0.8136(5)	0.9063(3)	0.086(3)
N2	0.5983(5)	0.7724(3)	1.0829(2)	0.0623(19)
N3	0.4938(5)	1.1429(4)	1.0828(3)	0.074(2)
C1	0.3304(5)	0.8226(4)	0.8966(3)	0.066(3)
C2	0.2915(6)	0.8351(4)	0.8417(3)	0.067(2)
C3	0.3556(5)	0.8406(5)	0.7956(3)	0.065(3)
C4	0.4612(6)	0.8297(4)	0.8027(3)	0.064(3)
C5	0.5027(5)	0.8196(4)	0.8572(3)	0.0537(19)
C6	0.7298(5)	0.8664(4)	0.7696(3)	0.058(2)
C7	0.7689(6)	0.8611(4)	0.7128(3)	0.064(2)
C8	0.7781(5)	0.7902(4)	0.6852(3)	0.061(2)
C9	0.7515(6)	0.7285(4)	0.7155(3)	0.063(2)
C10	0.7150(6)	0.7311(4)	0.7725(3)	0.067(3)
C11	0.6986(5)	0.8032(4)	0.7998(3)	0.0527(19)

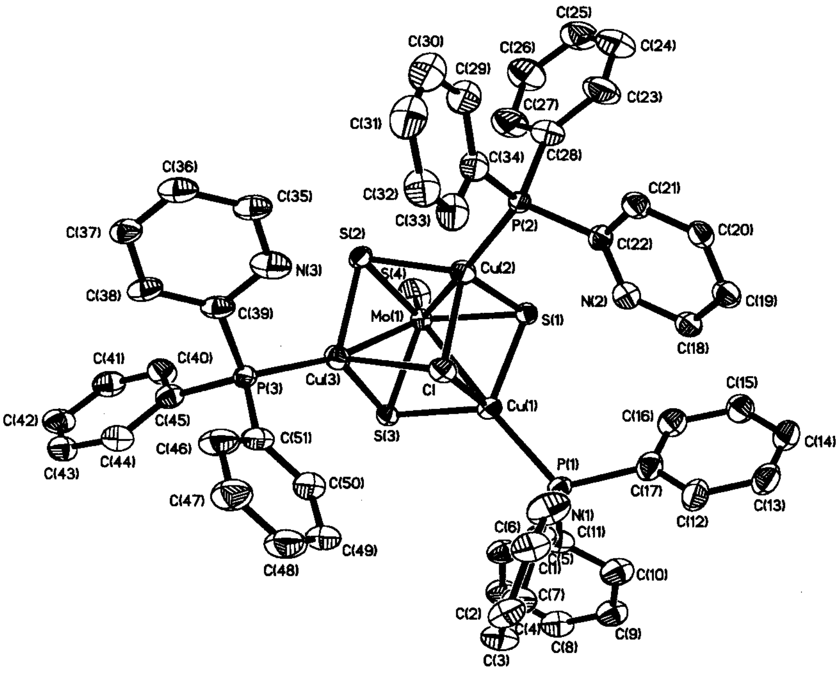

FIGURE 1 Diagram of the crystal structure of $MoS_4Cu_3(PyPPh_2)_3Cl$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 40% probability level.

TABLE III Selected bond lengths (Å) and angles (°) for the titled compound

Mo(1)–S(4)	2.036(2)	Cu(3)–S(3)	2.2685(14)
Mo(1)–S(1)	2.2425(12)	Cu(3)–Mo(1)	2.6830(8)
Mo(1)–S(2)	2.2563(13)	Cl–Cu(1)	2.7294(15)
Mo(1)–S(3)	2.2677(13)	Cl–Cu(2)	2.4764(14)
Cu(1)–P(1)	2.2146(14)	Cl–Cu(3)	2.7319(15)
Cu(2)–P(2)	2.2101(13)	P(1)–C(5)	1.826(6)
Cu(3)–P(3)	2.2126(14)	P(1)–C(11)	1.809(6)
Cu(1)–S(1)	2.2853(14)	P(1)–C(17)	1.835(6)
Cu(1)–S(3)	2.2772(14)	P(2)–C(22)	1.839(5)
Cu(1)–Mo(1)	2.6981(8)	P(2)–C(28)	1.848(7)
Cu(2)–S(1)	2.3160(14)	P(2)–C(34)	1.819(6)
Cu(2)–S(2)	2.3037(14)	P(3)–C(39)	1.790(5)
Cu(2)–Mo(1)	2.7183(7)	P(3)–C(45)	1.789(6)
Cu(3)–S(2)	2.2758(15)	P(3)–C(51)	1.804(6)
Cu(2)–Cl–Cu(1)	74.63(4)	P(3)–Cu(3)–S(3)	130.81(5)
Cu(2)–Cl–Cu(3)	73.07(4)	P(3)–Cu(3)–S(2)	118.06(5)
Cu(1)–Cl–Cu(3)	73.57(4)	S(3)–Cu(3)–S(2)	106.41(5)
P(1)–Cu(1)–S(3)	125.02(6)	P(3)–Cu(3)–Mo(1)	166.28(5)
P(1)–Cu(1)–S(1)	121.82(6)	S(3)–Cu(3)–Mo(1)	53.72(4)
S(3)–Cu(1)–S(1)	105.65(5)	S(2)–Cu(3)–Mo(1)	53.37(4)
P(1)–Cu(1)–Mo(1)	161.57(5)	P(3)–Cu(3)–Cl	100.23(5)
S(3)–Cu(1)–Mo(1)	53.42(4)	Cu(3)–Mo(1)–Cu(2)	70.24(2)
S(1)–Cu(1)–Mo(1)	52.70(3)	Cu(1)–Mo(1)–Cu(2)	71.43(2)
P(1)–Cu(1)–Cl	106.85(5)	Mo(1)–Cu(3)–Cl	91.72(4)
S(3)–Cu(1)–Cl	94.91(5)	S(4)–Mo(1)–S(1)	110.66(8)
S(1)–Cu(1)–Cl	94.03(5)	S(4)–Mo(1)–S(2)	112.24(9)
Mo(1)–Cu(1)–Cl	91.44(3)	S(1)–Mo(1)–S(2)	106.88(5)
P(2)–Cu(2)–S(2)	126.81(5)	S(4)–Mo(1)–S(3)	112.25(8)
P(2)–Cu(2)–S(1)	114.71(5)	S(1)–Mo(1)–S(3)	107.42(5)
S(2)–Cu(2)–S(1)	102.93(5)	S(2)–Mo(1)–S(3)	107.10(5)
P(2)–Cu(2)–Cl	106.16(5)	S(4)–Mo(1)–Cu(3)	136.88(7)
S(2)–Cu(2)–Cl	102.25(5)	S(1)–Mo(1)–Cu(3)	112.46(4)
S(1)–Cu(2)–Cl	100.31(5)	S(2)–Mo(1)–Cu(3)	54.04(4)
P(2)–Cu(2)–Mo(1)	155.89(5)	S(3)–Mo(1)–Cu(3)	53.75(4)
S(2)–Cu(2)–Mo(1)	52.61(3)	S(4)–Mo(1)–Cu(1)	134.33(8)
S(1)–Cu(2)–Mo(1)	52.16(3)	S(1)–Mo(1)–Cu(1)	54.16(4)
Cl–Cu(2)–Mo(1)	96.74(4)	S(2)–Mo(1)–Cu(1)	113.43(4)
S(1)–Mo(1)–Cu(2)	54.65(4)	S(3)–Mo(1)–Cu(1)	53.75(4)
S(2)–Mo(1)–Cu(2)	54.21(4)	Cu(3)–Mo(1)–Cu(1)	74.85(3)
S(3)–Mo(1)–Cu(2)	107.45(4)	S(4)–Mo(1)–Cu(2)	140.29(8)

The geometry of the Mo atom is a slightly distorted tetrahedron. The angle between the terminal S and the bridging S atoms (110.66(8) and 112.25(8)°) is larger than the angles between the bridging atoms themselves (107.10(5) and 107.42(5)°). The three Cu atoms are not equivalent. The coordination variability ranges from a strongly distorted tetrahedron (Cu3) to a nearly trigonal planar coordination (Cu1 and Cu2) with a weak fourth Cu–Cl interaction. The Cu–S distances are similar, but Cu–P distances are longer than those in [$MoS_4Cu_3(PPh_3)Cl$] [15]. This can be attributed to the difference between PPh_3 and $PyPPh_2$.

Nonlinear Optical Properties

The electronic absorption spectrum for the compound shows two big absorption peaks at 282 and 454 nm and no absorption from 650 to 1000 nm. The cluster has relatively low linear absorption in the visible and near IR region.

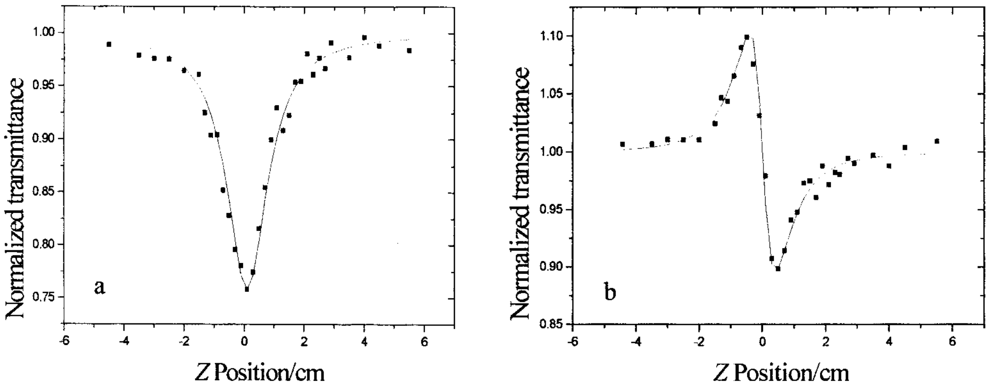

FIGURE 2 Z-scan measurement of the title compound in a 1.5×10^{-4} M DMF solution: (a) the data were collected with an open aperture configuration; (b) the data were obtained by dividing the normalized Z-scan measured with a closed aperture configuration.

The NLO properties of [$MoS_4Cu_3(PyPPh_2)_3Cl$] was investigated using the Z-scan technique [16]. Figure 2 shows typical Z-scan measurements of the cluster in a 1.5×10^{-4} M DMF solution. The filled boxes are the experimental data measured under an open aperture, clearly illustrating that the absorption increases as the incident light irradiance rises. Since light transmittance (T) is a function of the sample's Z position (with respect to the focal point at $Z = 0$). Nonlinear absorption ($\alpha = \alpha_2(I_i)$) and linear absorption (α_0) can be well described by Eqs. (1) and (2), where α and α_0 are linear and effective third-order NLO absorptive coefficients, τ is the time, and L is the optical path. The solid line is the theoretical curve from Eqs. (1) and (2). The effective nonlinear absorptive index α_2 is estimated to be 1.3×10^{-11} m w^{-1}.

$$T(Z) = \frac{1}{\sqrt{\pi} q(Z)} \int_{-\infty}^{\infty} \ln[1 + q(Z)] e^{-r^2} d\tau \tag{1}$$

$$q(Z) = \alpha_2^{\mathrm{eff}} I(Z) \frac{1 - e^{-\alpha_0 L}}{\alpha_0} \tag{2}$$

The nonlinear refractive components of the compound were assessed by dividing the normalized Z-scan data obtained under open aperture configuration (Fig. 2). An effective third-order nonlinear refractive index n_2 can be derived from the difference between normalized transmittance values at valley and peak positions (ΔT_{V-P}) by using Eq. (3) [17], where ΔT_{V-P} is the difference between normalized transmittance values at valley and peak position, α_0 is the linear coefficient, L is the sample thickness, I is the peak irradiation intensity at focus and λ is the wavelength of the laser. The data show that these two clusters have a negative sign for refractive nonlinear value, which indicates self-defocusing behavior.

$$n_2 = \frac{\lambda \alpha_0}{0.812 \pi I (1 - e^{-\alpha_0 L})} \Delta T_{V-P} \tag{3}$$

The cluster exhibits good NLO refractive properties. The valley–peak pattern of the normalized transmittance curve shows characteristic self-defocusing behavior of the propagating light in the sample. The n_2 value was estimated from these data to be $-3.2 \times 10^{-18}\,\mathrm{m^2\,w^{-1}}$.

Inorganic clusters uniquely combine the merits of inorganic semiconductors and organic molecules. They resemble organic molecules in that they are discrete molecules. Both the skeleton atoms and peripheral ligands can be changed to achieve desired structures and to tailor linear optical properties. On the other hand, they resemble inorganic semiconductors in having large numbers of heavy atoms. These heavy atoms introduce large numbers of excited states positioned close to the ground state and therefore enhance the NLO performance of the materials [18]. Although these measured values of α_2 and n_2 were obtained with a 1.5×10^{-4} M DMF solution of the titled cluster, they are comparable with many of the best known third-order materials in neat solid form, such as SiO_2 ($2 \times 10^{-20}\,\mathrm{m^2\,w^{-1}}$) and CdS ($2.5 \times 10^{-18}\,\mathrm{m^2\,w^{-1}}$) [19] or $SrLaGa_3O_7$ ($11.1 \times 10^{-20}\,\mathrm{m^2\,w^{-1}}$) and $Ca_2Ga_2SiO_7$ ($6.5 \times 10^{-20}\,\mathrm{m^2\,w^{-1}}$) [20]. The origins of these good NLO properties can be attributed to the third-order bound-electronic effect, excited-state effect, two-photon absorption and nonlinear scattering [21,22]. A much larger n_2 value may be expected with more concentrated solutions. Further work on the NLO mechanism is in progress.

Acknowledgments

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[17] $\Delta\Phi_0 = (2\pi/\lambda)\Delta n_0(t)(1 - e^{-\alpha_0 L})/\alpha_0$, $\Delta T_{p-v} = 0.406|\Delta\Phi_0|$, $\Delta n_0 = n_2 I$. From above equations, we can obtain the formula: $|n_2| = (\lambda\alpha_0/0.812\pi I(1 - e^{-\alpha_0 L}))\Delta T_{p-v}$.

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