Synthesis, Crystal Structure and Third-order Nonlinear Optical Properties of Nest-shaped Cluster $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$

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Nest-shaped cluster $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$ was synthesized by the treatment of $(NH_4)_2MoO_2S_2$, CuBr and Et_4NBr with bpy (2,2'-bipyridyl) in CH_3CN. Its structure has been characterized by X-ray diffraction: monoclinic, space group $P2_1/n$, with $a = 1.0092(4)$, $b = 2.6347(7)$, $c = 1.4087(3)$ nm, $\beta = 91.744(9)°$, $V = 3.7438$ nm^3, $Z = 4$, and final $R = 0.051$, $R_w = 0.053$. It consists of two parts: nest-shaped structural unit $[MoOS_3Cu_3Br_2(bpy)]^-$ and complex ion $[CuBr(bpy)^2]^+$. We determined its third-order nonlinear optical (NLO) properties with a 7-ns pulsed laser at 532 nm. The cluster exhibits strong NLO refractive behavior, its third-order susceptibility $\chi^{(3)}$ was calculated to be 2.7×10^{-11} esu in a 7.8×10^{-4} g/cm^3 DMF solution. The value is comparable to those of inorganic clusters.

Keywords Nest-shaped cluster, crystal structure, nonlinear optical properties

Introduction

The design and synthesis of new molecules with large macroscopic optical nonlinearities represents an active research field in modern chemistry, physics, and material science.[1,2] Mo-Cu-S cluster compounds have been receiving much attention since their biological functions were first recognized in luminants.[3] Recently, studies on these clusters have been expanded to include their nonlinear optical (NLO) properties.[4,5]

It has been found that Mo(W)-S(Se) clusters have very strong third-order NLO effects.[6,7] They have been considered as very promising candidates for nonlinear optical (NLO) applications. Nest-shaped and twin-nest-shaped clusters show strong nonlinear absorption and nonlinear refraction (self-defocusing or self-focusing effect).[8,9] Cubane-like clusters have very large nonlinear absorption and optical limiting effects.[10] The best optical limiting performance is achieved by hexagonal prism-shaped clusters, pentanuclear 'open' structural clusters, supra-cage-shaped cluster $[Bu_4N]_4[Cu_{12}Mo_8O_8S_{24}]$ and two-dimensional network cluster $[MoS_4Cu_6I_4(py)_4]_n$.[11,12] In this paper, we disclose the synthesis of a novel nest-shaped cluster $[CuBr(bpy)]_2[MoOS_3Cu_3Br_2(bpy)]$ and determination of its crystal structure and third-order NLO refractive property. The cluster has very strong NLO refractive effect.

Experimental

The compounds $(NH_4)_2MoO_2S_2$ were prepared according to the literature.[13] Other chemicals were of A. R. grade and used without further purification. IR spectra were recorded on a Perkin-Elmer 983G spectrometer. Electronic spectra were taken on a Perkin-Elmer Lambda 9 spectrophotometer. Elemental analysis was performed

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by a Perkin-Elmer 2400 Elemental Analyser.

It has been proven that nest-shaped, twin-nest-shaped and 'half-open' cubane-like clusters are useful starting materials for Mo-Cu-S clusters containing organic ligands. Typically, treatment of $[n\text{-}Bu_4N]_2[MoOS_3Cu_3BrCl_2]$, $[Et_4N]_3[MoOS_3(CuBr)_3(\mu_2\text{-}Br)]$ or $[Et_4N]_4[Mo_2O_2S_6Cu_6I_6]$ with an excess of py afforded nest-shaped cluster $[MoOS_3Cu_3X(py)_5]$ (X = Br or I).[9] Treatment of $[Et_4N]_3[MoOS_3(CuBr)_3(\mu_2\text{-}Br)]$ or $[Et_4N]_4[Mo_2O_2S_6Cu_6I_6]$ with Phen (1,10-phenanthroline), or bpy, or bMe-bpy (4, 4'-dimethyl-2, 2'-bipyridyl) in CH_3CN solution gave nest-shaped cluster $[MoOS_3Cu_3XR_2]$ (X = Br, I; R = Phen, bpy, bMe-bpy). If we extracted the mixture of $(NH_4)_2MO_2S_2$ (M = Mo, W), CuI and Et_4NI with CH_3CN, and added the solution of R (Phen, bpy or bMe-bpy) in CH_3CN to the extraction, cluster $[MIR_2][MOS_3Cu_3I_2R]$ (The compounds should be $[CuIR_2][MOS_3Cu_3I_2R]$) was obtained in three days later.[8] In the same synthetic method as cluster $[CuIR_2][MOS_3Cu_3I_2R]$ (M = Mo, W; R = Phen, bpy, bMe-bpy), we synthesized the title compound $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$.

Synthesis of nest-shaped cluster $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$

A well-ground mixture of $(NH_4)_2MoO_2S_2$ (0.23 g, 1 mmol), CuBr (0.29 g, 2 mmol) and Et_4NBr (0.42 g, 2 mmol) was heated at 95 ℃ for 10 h. The mixture was extracted with CH_2Cl_2 (10 mL) and CH_3CN (5 mL) respectively. A solution of bpy (0.04 g, 0.25 mmol) in CH_3CN (5 mL) was added into the above CH_3CN solution. Deep red crystals (0.02 g) can be obtained after three days. It is slightly soluble in CH_3CN, DMF or DMSO. IR spectra: ν (Mo-O_t): 908 cm^{-1}, ν (Mo-S_{br}): 440 and 423 cm^{-1}. Anal. calcd for $C_{30}H_{24}N_6Br_3Cu_4MoOS_3$: C 30.75, H 2.05, N 7.18; found: C 29.77, H 2.06, N 7.23.

Crystal structure analysis

A deep-red prismatic crystal having approximate dimensions of 0.30 × 0.30 × 0.40 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo-K_α radiation. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3375 observed reflections ($I > 2.00\sigma(I)$) and 434 variable parameters. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation (1985 & 1992). Crystallographic data are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Table 1 Crystal data and structure refinement for $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$

Empirical formula	$C_{30}H_{24}N_6Br_3Cu_4MoOS_3$
Formula weight	1170.58
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 1.0092(4) nm
	b = 2.6347(7) nm
	c = 1.4087(3) nm
	β = 91.744(9)°
Volume, Z	3.7438 nm^3, 4
Density	2.077 g/cm^3
$F(000)$	2260
Crystal size	0.30 × 0.30 × 0.40 mm
$2\theta_{max}$	55.0°
No. of reflections measured	4488
No. observations ($I > 2\sigma(I)$)	3375
No. variables	434
Goodness of fit indicator	1.14
Final R indices ($I > 2\sigma(I)$)	R = 0.051, R_w = 0.053
Largest diff. peak and hole	1190 and −1000 e/nm^3

Nonlinear optical measurements

A DMSO solution of $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$ was placed in a 1-mm quartz cuvette for NLO measurements respectively. Their properties were measured with a linearly polarized laser light (λ = 532 nm; pulse width = 7 ns) generated from a Q-switched and frequency-double Nd-YAG laser. The spatial profiles of the optical pulses were nearly Gaussian after passing through a spatial filter. The laser beam was focused with a 25-cm focal-length focusing mirror. The radius of the beam waist 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

Table 2 Selected bond lengths (nm) and bond angles (°) of $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$

Bond distance (nm)					
Mo(1)—O(1)	0.1707(8)	Mo(1)—S(2)	0.2278(3)	Mo(1)—S(1)	0.2285(3)
Mo(1)—S(3)	0.2293(3)	Mo(1)—Cu(2)	0.2670(2)	Mo(1)—Cu(3)	0.2655(2)
Mo(1)—Cu(1)	0.2664(2)	Cu(1)—S(1)	0.2252(3)	Cu(1)—S(3)	0.2265(4)
Cu(2)—N(2)	0.2113(9)	Cu(2)—S(1)	0.2277(3)	S(2)—Cu(2)	0.2265(3)
S(3)—Cu(3)	0.2258(4)	Cu(3)—S(2)	0.2249(4)	Cu(1)—Br(1)	0.2308(2)
Cu(3)—Br(2)	0.2298(2)	Cu(4)—N(6)	0.1984(9)	Cu(4)—N(3)	0.1996(9)
Cu(4)—Br(3)	0.2420(2)				
Bond angle (°)					
O(1)—Mo(1)—S(2)	110.2(3)	O(1)—Mo(1)—S(1)	111.3(3)	O(1)—Mo(1)—S(3)	113.0(3)
S(2)—Mo(1)—S(1)	107.7(1)	S(2)—Mo(1)—S(3)	107.3(1)	S(1)—Mo(1)—S(3)	107.2(1)
O(1)—Mo(1)—Cu(2)	130.1(3)	S(1)—Mo(1)—Cu(2)	54.03(8)	S(2)—Mo(1)—Cu(2)	53.80(9)
Cu(2)—Mo(1)—Cu(3)	82.65(6)	S(1)—Cu(1)—Mo(1)	54.63(8)	Cu(2)—S(1)—Mo(1)	71.63(9)
N(6)—Cu(4)—N(4)	97.2(4)	N(6)—Cu(4)—N(3)	172.5(3)	N(6)—Cu(4)—N(5)	80.1(4)
N(5)—Cu(4)—N(3)	95.5(3)	N(6)—Cu(4)—Br(3)	95.1(3)	N(3)—Cu(4)—Br(3)	92.4(2)

linked to a computer by an IEEE interface. Their NLO properties were manifested by moving the samples along the axis of incident beam (Z-direction) with respect to the focal point.[14] An aperture of 0.5 mm radius was placed in front of the detector measuring transmitted energy when assessment of laser beam distortion was needed.

Results and discussion

Crystal structure of $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$

The cluster consists of nest-shaped structural unit $[MoOS_3Cu_3Br_2(bpy)]^-$ and complex ion $[CuBr(bpy)_2]^+$ (Fig. 1). The nest-shaped skeleton is composed of one Mo, three μ_3-S and three Cu atoms. The seven atoms occupy all of important positions of the nest-shaped structure. Compared to free $MoOS_3^{2-}$ ion, the $MoOS_3$ fragment deviates slightly from C_3 symmetry, with three O—Mo—S bond angles of 109.9(4), 110.9(4) and 113.4(4)°. The Mo—O bond length of 0.170(1) nm is typical for a double bond. The three Mo—S bond distances, 0.2286(4), 0.2276(4) and 0.2290(5) nm, are in the range of a single bond. In $[MoOS_3Cu_3Br_2(bpy)]^-$, two distinctly different coordination geometries of copper coexist. Two CuBr groups and one Cu(bpy) group are bonded to the $[MoOS_3]^{2-}$ group across three S—S edges. Cu(1) and Cu(3) atoms are three-coordinate bonding to two S and one Br atoms. Atom Cu(2) is four-coordinate bonding to two N and two S atoms.

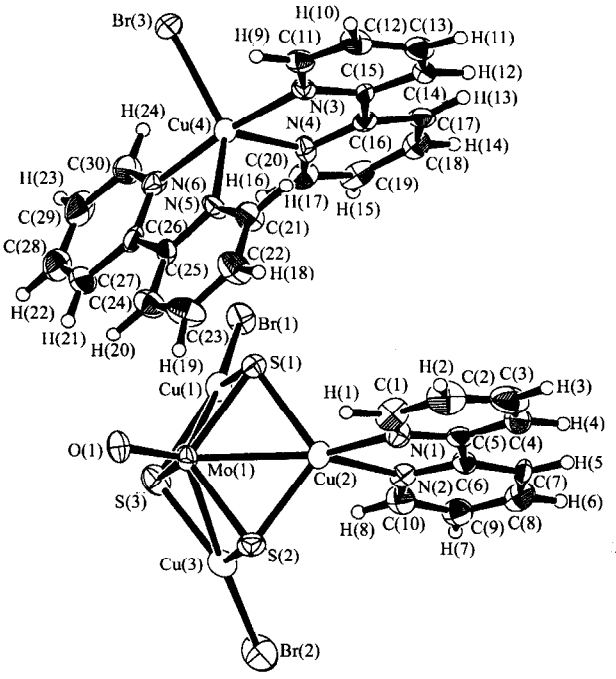

Fig. 1 Crystal structure of $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$.

Compared with the known nest-shaped cluster $[CuI(bpy)_2][MoOS_3Cu_3I_2(bpy)]$,[8] $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$ shows difference. $[CuBr(bpy)_2][MoO-$

$S_3Cu_3Br_2(bpy)]$ has longer Mo—S and Mo—Cu bond lengths, but S(O)—Mo—S bond angles are similar to those of $[CuI(bpy)_2][MoOS_3Cu_3I_2(bpy)]$.

The complex ion $[CuBr(bpy)_2]^+$ shows a distorted trigonal bipyramid structure, axial N(3) and N(6) atoms, and equatorial N(4), N(5) and Br atoms. The Cu atom is coordinated by the five atoms, and the Cu atom slightly deviates the plane consisting of N(4), N(5) and Br atoms.

Nonlinear optical (NLO) *properties*

Cluster $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$ displays two absorption peaks (355 nm and 410 nm) in its UV-vis spectrum. It has relatively low linear absorption in the range of 500 nm to 1000 nm. Fig. 2 depicts its

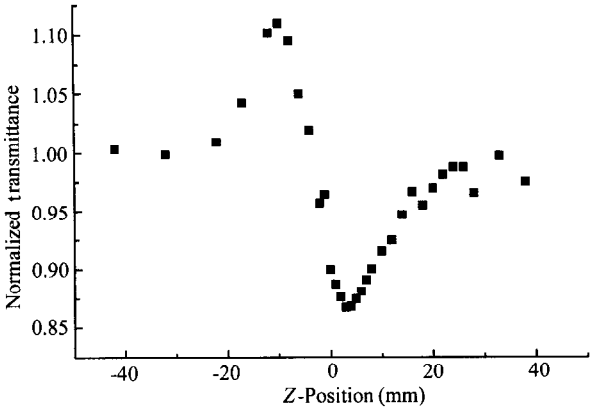

Fig. 2 Nonlinear optical refractive behavior of $[CuBr(bpy)_2][MoOS_3Cu_3Br_2(bpy)]$ in DMF solution of 7.8×10^{-4} g/cm^3 DMF solution at 532 nm with incident energy of 150 μJ.

NLO data 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 data show that the cluster has a negative sign for the refractive nonlinearity, which gives rise to self-defocusing behavior. The third-order susceptibility $\chi^{(3)}$ can be calculated to be 2.7×10^{-11} esu in a 7.8×10^{-4} g/cm^3 DMF solution. These data are comparable to those of inorganic clusters and other nest-shaped clusters.[15,16] The cluster can be considered as a very promising candidate for nonlinear optical applications, but it is obvious too that more NLO data need to be accumulated about the cluster.

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