Synthesis, Crystal Structure and Non-linear Optical Properties of $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ †

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The reaction of $[NH_4]_2[MoO_2S_2]$, CuI and NEt_4Br in the solid state produced $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$. Single-crystal X-ray analysis reveals that the cluster anion consists of two nest-shaped fragments interconnected through a CuI_2Cu bridge with Cu–I and Cu···I bond lengths of 2.502 and 2.972 Å respectively. The cluster forms monoclinic crystals with space group $C2/c$, a = 24.423(9), b = 21.021(2), c = 13.715(5) Å, β = 114.48(3)° and Z = 4; R = 0.067, R' = 0.087. It exhibits interesting optical-limiting and self-defocusing properties.

The chemistry of Cu–Mo(W)–S compounds has been of interest for over a century.[1] Many of these compounds have been extensively studied because of their relevance to biological systems and in catalysis.[2] Recently, it was discovered that some Cu–Mo(W)–S clusters possess very interesting non-linear optical properties.[3]

Traditionally, Cu–Mo(W)–S clusters were synthesized *via* reactions in solution.[4] We explored synthetic routes *via* solid-state reactions at about 100 °C and synthesized over a dozen new clusters.[3,5] In order further to develop this method and study the cluster properties and also as a part of our search for better non-linear optical materials, we studied the compound $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$, a new type of Mo–Cu–S cluster. It is composed of two nest-shaped $Cu_3MoS_3OBrI_2$ moieties interconnected through a CuI_2Cu unit. This paper reports the synthesis, crystal structure, electronic spectra and non-linear optical properties of $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$.

Experimental

Materials.—The salt $[NH_4]_2[MoO_2S_2]$ was prepared according to the literature.[6] Other chemicals were of A.R. grade.

Preparation.—A well ground mixture of $[NH_4]_2[MoO_2S_2]$ (0.23 g, 1 mmol), CuI (0.40 g, 2 mmol) and NEt_4Br (0.42 g, 2 mmol) was placed in a reaction tube and heated at 100 °C for 10 h under a pure nitrogen atmosphere. After extracting the dark red solid product with CH_2Cl_2 (20 cm^3), the deep red extract was filtered and layered with Pr^iOH (10 cm^3). Deep red cubic crystals were obtained several days later. Yield 0.15 g (Found: C, 19.55; H, 4.05; N, 2.75. Calc. for $C_{32}H_{80}Br_2Cu_6I_4Mo_2N_4O_2$: C, 19.35; H, 4.05; N, 2.30%). IR spectrum (KBr pellets): ν_{term}(Mo–O) 913, ν_{br}(Mo–S) 447 cm^{-1}.

Crystal Structure Analysis.—A deep red crystal (0.25 × 0.15 × 0.1 mm) was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed with Mo-Kα radiation (λ = 0.710 73 Å) from a κ-axis Enraf–Nonius CAD diffractometer equipped with a graphite monochromator and controlled by a Micro VAX computer.

Crystal data. $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$, M = 1985.96, monoclinic, space group $C2/c$, a = 24.423(9), b = 21.021(2), c = 13.715(5) Å, β = 114.48(3)°, U = 6408.4(7) Å^3, Z = 4, D_c = 2.058 g cm^{-3}, F(000) = 3808. Diffraction data were collected with the ω–2θ scan mode, μ(Mo-Kα) = 56.9 cm^{-1}.

Lorentz and polarization corrections, an intensity-decay correction and an empirical absorption correction were applied to the diffraction data. The structure was solved by direct methods. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined using a full-matrix least-squares fitting program where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weight $w = 4F_o^2/[\sigma(F_o^2)]^2$ for 2452 observed reflections with $I > 3\sigma(I)$. Final residues were R = 0.067 and R' = 0.087. Final positional parameters with their estimated standard deviations are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Spectroscopic and Other Measurements.—Infrared spectra were recorded on a Fourier Nicolet FT-170SX spectrophotometer with pressed KBr pellets, electronic spectra on a Shimadzu UV-240 instrument. Carbon, hydrogen and nitrogen analyses were performed on a Perkin-Elmer 240C elemental analyser.

For optical measurements an acetonitrile solution of $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ was placed in a 1 mm quartz cuvette. The compound is stable toward air and room light. Its non-linear optical response was measured with linearly polarized, 7 ns pulses from a Q-switched frequency-doubled Nd-YAG laser. The spatial profiles of the optical pulses (λ = 532 nm) were nearly Gaussian and the light was focused onto the sample with a mirror of 25 cm focal length. The spot radius of the laser beam was measured as 30 ± 5 μm (half-width at $1/e^2$ maximum). The interval between the laser pulses was chosen to be ≈5 s for operational convenience. The incident and transmitted pulse energies were measured simultaneously by two Laser Precision detectors (RjP-735 energy probes) linked to a computer by an IEEE interface.[7]

An identical set-up was adopted in experiments to measure the Z-scan data except that the sample was moved along the axis of the incident beam instead of being positioned at its focal point.[3] An aperture of 0.5 mm radius was placed in front of the detector to assist measurement of the self-defocusing effect.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Positional parameters and their estimated standard deviations for $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$

Atom	*x*	*y*	*z*
I(1)	0.084 20(6)	0.378 61(7)	0.158 4(1)
I(2)	0.346 22(5)	0.264 80(7)	0.053 0(1)
Mo	0.249 36(6)	0.215 11(8)	0.304 4(1)
Br	0.126 37(9)	0.034 09(9)	0.092 1(2)
Cu(1)	0.181 0(1)	0.126 8(1)	0.176 2(2)
Cu(2)	0.273 2(1)	0.239 3(1)	0.132 4(2)
Cu(3)	0.159 92(9)	0.295 9(1)	0.208 5(2)
S(1)	0.278 4(2)	0.143 2(2)	0.212 6(4)
S(2)	0.257 2(2)	0.311 9(2)	0.241 4(4)
S(3)	0.150 7(2)	0.197 8(2)	0.265 8(4)
O	0.291 7(7)	0.209 8(8)	0.437(1)
N(1)	0.179 9(7)	0.495 6(7)	0.481(1)
N(2)	0.045 5(5)	−0.187 9(7)	0.022(1)
C(1)	0.140 4(9)	0.441(1)	0.475(1)
C(2)	0.106(1)	0.454(1)	0.551(2)
C(3)	0.150(1)	0.559(1)	0.447(2)
C(4)	0.104(2)	0.558(2)	0.344(3)
C(5)	0.210 5(9)	0.477(1)	0.410(2)
C(6)	0.249(1)	0.421(1)	0.446(2)
C(7)	0.226(1)	0.504(1)	0.600(2)
C(8)	0.278(1)	0.551(1)	0.599(2)
C(9)	0.087(1)	−0.218(2)	−0.003(3)
C(10)	0.059(1)	−0.266(1)	−0.098(2)
C(11)	0.011 6(2)	−0.231 9(2)	0.042 2(3)
C(12)	0.033(1)	−0.282(1)	0.131(2)
C(13)	0.0066(2)	−0.1362(2)	−0.0758(2)
C(14)	0.058(1)	−0.102(1)	−0.104(2)
C(15)	0.0728(1)	−0.1456(2)	0.1246(2)
C(16)	0.033(1)	−0.101(1)	0.145(2)

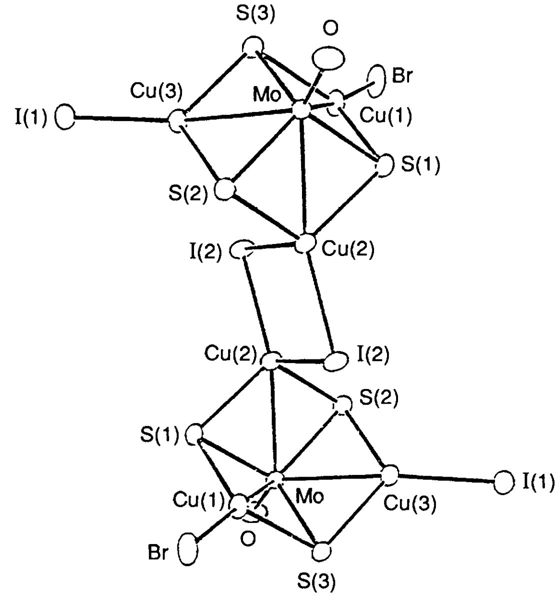

Fig. 1 An ORTEP diagram of the cluster anion of $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$

Results and Discussion

Crystal Structure of $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$.—This is the first ionic octanuclear cluster (2Mo, 6Cu). Previously reported octanuclear clusters, $[Cu_6Mo_2S_6O_2(PPh_3)_4(SCH_2CH_2OH)_2]$,[8] $[Cu_6W_2S_6O_2(PPh_3)_4(SCMe_3)_2]$[9] and $[Ag_6Mo_2S_6O_2(PPh_3)_4(SCMe_3)_2]$,[10] consist of two nest-shaped groups connected through two S-containing organic ligands acting as triple bridges and all are neutral molecules. An ORTEP[11] diagram of the $[Cu_6Mo_2S_6O_2Br_2I_4]^{4-}$ anion is shown in Fig. 1. A crystallographic centre of symmetry is located at the centre of the anion; each anion can thus be considered to consist of two nest-shaped $[Cu_3MoS_3OBrI_2]^{2-}$ fragments interconnected through a CuI_2Cu unit. Each fragment has one Br atom attached to one of the three copper atoms, two I atoms attached to the remaining two copper atoms respectively and one terminal

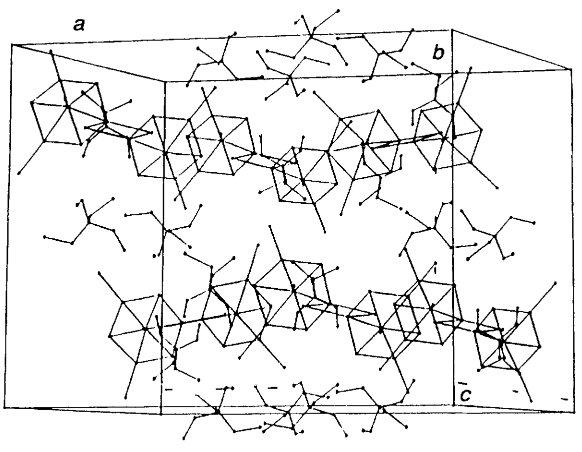

Fig. 2 The crystal packing scheme of $[NEt_4]_4[CU_6Mo_2S_6O_2Br_2I_4]$

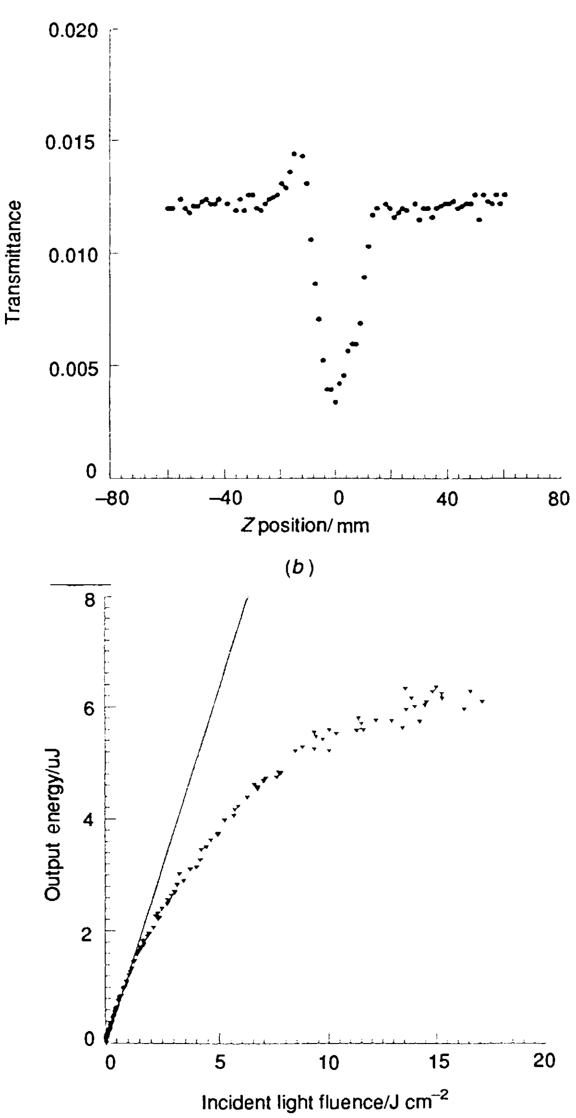

Fig. 3 (*a*) *Z*-Scan data collected for $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ under the closed-aperture configuration. (*b*) Optical limiting data. The straight line is the guide to the situation where Beer's law is obeyed

Table 2 Selected bond distances (Å) and angles (°)

I(1)–Cu(3)	2.422(2)	Mo–O	1.68(1)	N(1)–C(1)	1.48(3)	C(1)–C(2)	1.61(2)
I(2)–Cu(2)	2.502(2)	Br–Cu(1)	2.374(2)	N(1)–C(3)	1.50(2)	C(3)–C(4)	1.41(3)
I(2)–Cu(2)	2.972(3)	Cu(1)–S(1)	2.244(4)	N(1)–C(5)	1.50(3)	C(5)–C(6)	1.46(2)
Mo–Cu(1)	2.625(2)	Cu(1)–S(3)	2.246(5)	N(1)–C(7)	1.56(2)	C(7)–C(8)	1.60(2)
Mo–Cu(2)	2.703(2)	Cu(2)–S(1)	2.280(4)	N(2)–C(9)	1.35(3)	C(9)–C(10)	1.56(3)
Mo–Cu(3)	2.646(2)	Cu(2)–S(2)	2.282(4)	N(2)–C(11)	1.34(2)	C(11)–C(12)	1.53(2)
Mo–S(1)	2.261(4)	Cu(3)–S(2)	2.252(4)	N(2)–C(13)	1.68(3)	C(13)–C(14)	1.63(2)
Mo–S(2)	2.250(4)	Cu(3)–S(3)	2.250(4)	N(2)–C(15)	1.56(2)	C(15)–C(16)	1.45(2)
Mo–S(3)	2.272(4)						
Cu(2)–I(2)–Cu(2)	75.05(8)	S(2)–Mo–S(3)	107.9(2)	S(1)–Cu(2)–S(2)	105.5(2)	C(1)–N(1)–C(7)	108(1)
Cu(1)–Mo–Cu(2)	81.73(8)	S(2)–Mo–O	111.2(5)	I(1)–Cu(3)–Mo	167.9(1)	C(3)–N(1)–C(5)	110(1)
Cu(1)–Mo–Cu(3)	87.50(7)	S(3)–Mo–O	111.1(4)	I(1)–Cu(3)–S(2)	124.6(1)	C(3)–N(1)–C(7)	106(1)
Cu(1)–Mo–S(1)	54.1(1)	Mo–Cu(1)–Br	118.5(1)	I(1)–Cu(3)–S(3)	125.6(1)	C(5)–N(1)–C(7)	111(1)
Cu(1)–Mo–S(2)	121.0(1)	Mo–Cu(1)–S(1)	54.7(1)	Mo–Cu(3)–S(2)	54.0(2)	C(9)–N(2)–C(11)	108(5)
Cu(1)–Mo–S(3)	54.0(1)	Mo–Cu(1)–S(3)	54.9(1)	Mo–Cu(3)–S(3)	54.6(1)	C(9)–N(2)–C(13)	110(4)
Cu(1)–Mo–O	127.8(5)	Br–Cu(1)–S(1)	124.4(1)	S(2)–Cu(3)–S(3)	108.5(2)	C(9)–N(2)–C(15)	114(5)
Cu(2)–Mo–Cu(3)	82.99(7)	Br–Cu(1)–S(3)	124.4(1)	Mo–S(1)–Cu(1)	71.3(1)	C(11)–N(2)–C(13)	115(6)
Cu(2)–Mo–S(1)	53.8(1)	S(1)–Cu(1)–S(3)	109.6(2)	Mo–S(1)–Cu(2)	73.0(1)	C(11)–N(2)–C(15)	106(7)
Cu(2)–Mo–S(2)	53.9(1)	I(2)–Cu(2)–I(2)	105.0(1)	Cu(1)–S(1)–Cu(2)	100.9(2)	C(13)–N(2)–C(15)	104(6)
Cu(2)–Mo–S(3)	114.8(1)	I(2)–Cu(2)–Mo	150.5(1)	Mo–S(2)–Cu(2)	73.2(1)	N(1)–C(1)–C(2)	110(1)
Cu(2)–Mo–O	134.2(4)	I(2)–Cu(2)–S(1)	119.6(1)	Mo–S(2)–Cu(3)	72.0(1)	N(1)–C(3)–C(4)	112(3)
Cu(3)–Mo–S(1)	122.5(1)	I(2)–Cu(2)–S(2)	119.3(1)	Cu(2)–S(2)–Cu(3)	102.8(2)	N(1)–C(5)–C(6)	115(1)
Cu(3)–Mo–S(2)	54.0(1)	I(2)–Cu(2)–Mo	104.5(1)	Mo–S(3)–Cu(1)	71.0(1)	N(1)–C(7)–C(8)	108(2)
Cu(3)–Mo–S(3)	53.8(1)	I(2)–Cu(2)–S(1)	103.0(1)	Mo–S(3)–Cu(3)	71.6(1)	N(2)–C(9)–C(10)	114(2)
Cu(3)–Mo–O	126.2(5)	I(2)–Cu(2)–S(2)	101.8(1)	Cu(1)–S(3)–Cu(3)	108.3(2)	N(2)–C(11)–C(12)	128(8)
S(1)–Mo–S(2)	107.2(2)	Mo–Cu(2)–S(1)	53.2(1)	C(1)–N(1)–C(3)	117(1)	N(2)–C(13)–C(14)	105(7)
S(1)–Mo–S(3)	108.1(2)	Mo–Cu(2)–S(2)	52.8(2)	C(1)–N(1)–C(5)	106(1)	N(2)–C(15)–C(16)	119(8)
S(1)–Mo–O	111.3(6)						

Table 3 Comparison of bond lengths (Å) and angles (°) for $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ **A**, $[Cu_6Mo_2S_6O_2(PPh_3)_4(SCH_2CH_2OH)_2]$ **B** and $[NBu_4]_2[MoOS_3(CuSCN)_3]$ **C**

	A	B	C
Mo–O	1.68(1)	1.715(5)	1.704(6)
Mo–Cu	2.703(2), 2.625(5), 2.646(2)	2.658(2), 2.780(2), 2.764(2)	2.650(2), 2.652(2), 2.638(2)
Mo–S	2.250(4), 2.261(4), 2.272(4)	2.251(3), 2.266(4), 2.270(3)	2.248(3), 2.268(4), 2.272(5)
S–Mo–O	111.3(6), 111.2(5), 111.1(4)	112.1(3), 112.0(3), 111.6(3)	112.3(6), 111.9(5), 109.1(5)

oxygen atom attached to the molybdenum. The Mo–O distance of 1.68(1) Å is typical for a Mo=O double bond. The three Mo–S bonds, 2.250(4)–2.272(4) Å, are single bonds. In each fragment the three Cu atoms are linked to the MoS_3O core by S atoms with all Cu–S distances in the range 2.244(4)–2.282(4) Å. Important bond lengths and angles are listed in Table 2. The crystal-packing scheme is shown in Fig. 2.

It is interesting that in a similar nest-shaped cluster, $[NBu_4]_2[MoS_3O(CuSCN)_3]$,[12] trigonal-planar co-ordination is adopted by all of the three Cu atoms. Yet in $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ two distinctly different co-ordination geometries of copper exist: the atoms Cu(1) and Cu(3) adopt trigonal-planar geometry (co-ordinated by two S ligands and one X ligand, X = I or Br), while Cu(2) adopts distorted-tetrahedral geometry (co-ordinated by two S ligands and two I ligands). Owing to the different environments, the Mo–Cu(2) distance of 2.703(2) Å is longer than those of Mo–Cu(1) and Mo–Cu(3) [2.625(2) and 2.646(2) Å respectively]. In the CuI_2Cu unit two Cu–I bond distances are not equivalent [2.502(2) and 2.972(3) Å respectively], and the I–Cu–I bond angle [105.0(1)] is smaller than the value for a perfect tetrahedral geometry.

A similar co-existence of two types of co-ordination geometries was observed before in $[Cu_6Mo_2S_6O_2(PPh_3)_4(SCH_2CH_2OH)_2]$ **B** and $[NBu_4]_2[MoOS_3(CuSCN)_3]$ **C**.[8,12] Four of the six Cu atoms in compound **B** adopt a distorted-tetrahedral geometry, and the other two are in an approximately planar triangular environment. Table 3 gives some bond distances and angles of the three clusters. Compared to the present cluster **A**, the Mo–O and Mo–Cu distances of **B** are all longer, whereas in **C** the former distances are longer and the latter are very similar.

Electronic Spectra.—Earlier studies showed that a certain extent of delocalization exists in many Mo(W)–Cu–S clusters.[13] This is consistent with the notion that the central atoms (Mo or W) possess open d shells. The assignment of the electronic transition bands for such systems can only be approximated. The characteristic absorption bands of $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ at 500, 410, 310, 288 and 240 nm are roughly comparable to those of $[MoOS_3]^{2-}$ at 465 (ν_1, $1a_2 \longrightarrow 6e$), 392 (ν_2, $5e \longrightarrow 6e$), 313 (ν_3, $1a_2 \longrightarrow 7e$), 260 (ν_4, $4e \longrightarrow 6e$) and 243 nm (ν_5, $5a_1 \longrightarrow 6e$).[14] Since the strong S→Mo charge-transfer bands are significantly affected by the co-ordination of $[MoOS_3]^{2-}$ to $Cu(CuS_2Mo)$, a shifting of three of the prominent electronic transition bands is observed. Thus, ν_1, ν_2 and the ν_4 bands of $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ are at longer wavelengths compared to those of $[MoOS_3]^{2-}$ (500, 410 and 288 *vs.* 465, 392 and 260 nm), whereas the positions of the ν_3 and ν_5 bands are almost unchanged.

Optical-limiting Properties.—As a part of our search for optical-limiting materials we have recently studied the non-linear optical properties of a number of inorganic clusters and discovered that cage-shaped clusters $[NBu^n{}_4]_3[MM'_3S_4BrX_3]$ exhibit very large non-linear absorption and a small optical self-focusing effect.[3,15] Over a wide range of compositional variation where M = Mo or W, M′ = Ag or Cu, and X = Cl, Br or I, such non-linear optical effects persist. We also discovered that the nest-shaped molecule $[NBu^n{}_4]_2[MoS_3O(CuNCS)_3]$ possesses the ability to cause self-defocusing of a light beam propagating through it. Geometrically, a nest-shaped (*nido*) cluster can be derived from a cubic cage-shaped (*closo*) one by removing only one vertex. Yet the contrast between the non-linear optical behaviour of $[NBu^n{}_4]_3[Cu_3MoS_4BrX_3]$ and that of $[NBu^n{}_4]_2[MoS_3O(CuNCS)_3]$ is sharp. It seemed that the structure alternation of cubic cage and nest (or *closo* and *nido*) could induce a switch in non-linear optical property from self-focusing to self-defocusing. The problem in basing the above structure–non-linear optical property relation on the comparison between these two clusters is that the copper atoms in the two types are co-ordinated by different ligands: S and X in the former, S and NCS in the latter. The successful synthesis of $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ has placed the correlation on a firmer basis because NCS does not exist in this cluster. The co-ordination environments of Mo and Cu can be described by S_4 and BrX_3 respectively in both $[NBu^n{}_4]_3[Mo_3S_4BrX_3]$ and $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$. Preliminary *Z*-scan data of $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ reveal that the compound possesses self-defocusing ability too, as illustrated in Fig. 3(*a*), adding support to the above proposed correlation. No reliable theory is available at this stage to explain why such a correlation should exist. Extended data fitting based on a multiple energy-level diagram and rate equations and molecular-orbital calculations are underway.

In addition to the self-defocusing effect, $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ also exhibits strong non-linear absorption at 532 nm. The combination of the self-defocusing and non-linear absorption makes the cluster an interesting case for optical-limiting study. An ideal optical-limiting material should be able to respond quickly to the incident light and become increasingly opaque as the incident fluence increases.[16] The compound $[NEt_4]_4[Cu_6Mo_2S_6O_2Br_2I_4]$ possesses such desired optical-limiting ability, as demonstrated in Fig. 3(*b*). The light energy transmitted starts to deviate from Beer's law as the input light fluence reaches about 1.5 J cm^{-2}, and the material becomes increasingly less transparent as the fluence rises. The limiting threshold[3] was measured as 2 J cm^{-2} with a saturation fluence transmitted of 8.5 J cm^{-2}.

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