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# Synthesis, characterization and optical non-linearity of two heterobimetallic copper clusters containing tetraselenometalates

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## Abstract

Cluster [{MoCu<sub>3</sub>Se<sub>3</sub>Br}(PPh<sub>3</sub>)<sub>3</sub>Se]·3THF·H<sub>2</sub>O (1·3THF·H<sub>2</sub>O) was prepared from reaction of [Et<sub>4</sub>N]<sub>2</sub>[MoSe]<sub>4</sub>, Cu(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub> and Et<sub>4</sub>N·Br in CH<sub>2</sub>Cl<sub>2</sub> solution; also, **1** can be also obtained from the reaction of [MoSe<sub>4</sub>Cu<sub>4</sub>Py<sub>6</sub>Br<sub>2</sub>] and excess PPh<sub>3</sub> in a DMF–CH<sub>2</sub>Cl<sub>2</sub> mixture solvent. The <sup>95</sup>Mo NMR technique was used to monitor the above two reaction processes. X-ray crystal-lographic structure determination shows that it contains a strongly distorted cubane-like {MoCu<sub>3</sub>Se<sub>3</sub>Br} core. The coordination of the central Mo atom and each Cu atom are distorted from tetrahedral. Cluster [{WCu<sub>3</sub>Se<sub>3</sub>Cl}(PPh<sub>3</sub>)<sub>3</sub>Se] (**2**) was synthesized by the reaction of [Et<sub>4</sub>N]<sub>2</sub>[WSe]<sub>4</sub> and Cu(PPh<sub>3</sub>)<sub>2</sub>Cl in the solid state for nonlinear optical (NLO) studies. Its structure was reported by Ibers (Inorg. Chem. 31 (1992) 4365). The NLO properties of clusters **1** and **2** were studied. Both NLO absorption and refraction were obtained, and their effective third-order non-linearities were detected with  $\alpha_2 = 3.4 \times 10^{-10}$  and  $5.9 \times 10^{-10}$  m/W and  $n_2 = -1.5 \times 10^{-17}$  and  $-1.3 \times 10^{-17}$  m<sup>2</sup>/W, respectively, for the same concentration CH<sub>2</sub>Cl<sub>2</sub> solution of **1** and **2**. Influence of skeletal atoms to nonlinear absorption is also discussed in the paper. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Synthesis; Crystal structure; 95Mo NMR spectrum; Heteroselenometallic cluster; NLO properties

# 1. Introduction

The chemistry of  $[MS_4]^{2-}$  (M = Mo, W) anions and their related compounds has been extensively investigated owing to their relevance to the biological system, rich structural chemistry and special reaction properties as well as potential applications in nonlinear optical materials [1–7], whereas that of  $[MSe_4]^{2-}$  (M = Mo, W) anions and their related compounds have received attention only in recent years [8,9]. Up to now, a few heteroselenometallic clusters containing  $[MSe_4]^{2-}$  (M = Mo, W) anions have been synthesized and characterized [10–14], however, only few non-linear optical (NLO) results of these clusters have been reported. As part of our interest in NLO properties of Mo(W)–Cu(Ag,Au)–S system, we have characterized a series of clusters and explored their third-order NLO properties [15,16]. Recently we have attempted to synthesize the corresponding heterobimetallic selenide clusters by the solid-state reaction at low heating temperature, and tried to investigate their optical non-linearities based on our previous knowledge. An important reason is that Se-containing compounds are interesting because

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they may be used as precursors for the preparations of low-bandgap semiconductors [17]. Herein, we present synthetic reaction, structural characterization and NLO properties of the two typical cubane-like clusters [ $MoCu_3Se_3Br$ ](PPh<sub>3</sub>)<sub>3</sub>Se](M = Mo (1), W(2)).

## 2. Experimental

## 2.1. Synthesis

## 2.1.1. General

All manipulations were conducted using Schlenk techniques under an atmosphere of nitrogen.  $[Et_4N]_2[MoSe_4]$  and  $[Et_4N]_2[WSe_4]$  were prepared by a modification of the literature method [18]. Cu(PPh\_3)\_2NO\_3 and Cu(PPh\_3)\_2Cl were obtained by reaction of Cu(NO\_3)\_2·H\_2O and CuCl, respectively, with PPh\_3 in CH\_2Cl\_2–MeOH. IR spectra were measured on a Digilab FTS-40 spectrophotometer. Electronic spectra were preformed on a Hitachi U-3410 spectrophotometer. <sup>31</sup>P and <sup>95</sup>Mo NMR data were recorded on a Varian Unity-500 spectrometer,

Table 1

Data collections and processing parameters for  $1.3THF \cdot H_2O$  and 2

relative to 85% acid and 2 mol  $dm^{-3}$  Na<sub>2</sub>Mo<sub>4</sub> in D<sub>2</sub>O, respectively.

## 2.1.2. Preparation of

## $[{MoCu_3Se_3Br}(PPh_3)_3Se] \cdot 3THF \cdot H_2O (1 \cdot 3THF \cdot H_2O)$

 $Cu(PPh_3)NO_3$  (0.50 g, 0.75 mmol) in  $CH_2Cl_2$ (10 ml) was added to a CH<sub>2</sub>Cl<sub>2</sub> solution (10 ml) of  $[Et_4N]_2[MoSe_4]$  (0.21 g, 0.25 mmol). The resulting brown solution was stirred for 5 min at room temperature, then Et<sub>4</sub>N·Br (0.09 g, 0.20 mmol) was added and subsequently filtered to afford a reddish-brown filtrate. Block-shaped red crystals of 1.3THF·H<sub>2</sub>O were obtained by layering the filtrate with THF. Yield: 0.18 g (41.6%). Found: C, 47.6; H, 4.29; P, 5.17; Cu, 10.6%; requires for  $C_{66}H_{71}O_4MoCu_{3-}$ Se<sub>4</sub>BrP<sub>3</sub>: C, 46.4; H, 4.19; P, 5.45; Cu, 11.1%. IR  $(KBr, cm^{-1}): 3420.5(vs), 1668.4(vs), 1434.4(vs),$ 1095.1(vs), 744.2(vs), 703.8(vs), 691.3(vs), 521.3(vs), 505.5(vs), 491.8(vs), 384.8(s), 329.3(s). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta = 12.7$  ppm. <sup>95</sup>Mo NMR (CDCl<sub>3</sub>):  $\delta = 1301.4$  ppm.

[MoSe<sub>4</sub>Cu<sub>4</sub>Py<sub>6</sub>Br<sub>2</sub>] was prepared according to the literature method [19]. A mixture of CuBr (0.16 g,

Compound	$1.3THF \cdot H_2O$	2	
Formula	$C_{66}H_{71}O_4P_3BrCu_3Se_4Mo$	$C_{54}H_{45}P_3ClCu_3Se_4W$	
Formula weight	1703.45	1512.57	
Color, habit	Dark-red, prism	Red, prism	
Crystal size, mm <sup>3</sup>	$0.35 \times 0.30 \times 0.28$	$0.48 \times 0.24 \times 0.22$	
Crystal system	Trigonal	Orthorhombic	
Space group	R3 (no. 146)	$P2_12_12_1$ (no. 19)	
<i>a</i> , Å	15.706(2)	13.0809(3)	
<i>b</i> , Å		18.0122(4)	
<i>c</i> , Å	23.887(5)	22.8324(5)	
$V, Å^3$	5103(14)	5379.7(2)	
Ζ	3	4	
F(000)	2523	2912	
$D(\text{calcd}), \text{ g cm}^{-3}$	1.667	1.868	
$\mu, \mathrm{mm}^{-1}$	3.947	6.182	
Collection range; $2\theta_{\text{max}}$ , °	23.28	28.28	
Unique data measured	$3195 \ (R_{\rm int} = 2.61\%)$	13 293 ( $R_{\rm int} = 5.01\%$ )	
Observed data, n	$3007 \ (I > 2.0\sigma(I))$	10 622 $(I > 2.0\sigma(I))$	
No. of variables, p	221	595	
<i>R</i> 1	0.0381	0.0349	
wR2	0.1010	0.0545	
S (goodness of fit on $F^2$ )	1.102	1.030	
Largest diff. peak and	0.849  and  -0.398	0.777 and -0.793	
hole, e Å <sup>-3</sup>			

Table 2 Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\times 10^3$ ) for 1.3THF·H<sub>2</sub>O

Atom	X	у	z	$\overline{U}(eq)$
Mo	3333	6667	12 431(1)	36(1)
Cu	3940(1)	5894(1)	13 276(1)	55(1)
Se(1)	2613(1)	7583(1)	12 781(1)	46(1)
Br(1)	3333	6667	14 142(1)	56(1)
Se(2)	3333	6667	11 483(1)	73(1)
P(1)	4632(2)	5070(2)	13 630(1)	47(1)
C(11)	4896(6)	4384(6)	13 105(4)	49(2)
C(12)	4786(9)	3485(8)	13 201(5)	80(3)
C(13)	5014(10)	3000(9)	12 803(5)	90(4)
C(14)	5363(8)	3433(9)	12 303(5)	76(3)
C(15)	5504(9)	4343(9)	12 198(5)	80(3)
C(16)	5280(8)	4821(8)	12 588(4)	66(3)
C(21)	5815(6)	5836(7)	13 984(4)	52(2)
C(22)	5995(8)	6722(8)	14 218(4)	70(3)
C(23)	6890(9)	7325(9)	14 512(6)	91(4)
C(24)	7558(9)	7001(11)	14 555(6)	102(4)
C(25)	7398(9)	6165(11)	14 295(6)	100(4)
C(26)	6511(9)	5560(9)	14 036(5)	84(4)
C(31)	3871(7)	4130(6)	14 142(4)	56(2)
C(32)	2962(8)	3405(8)	13 991(6)	86(3)
C(33)	2383(11)	2654(9)	14 346(7)	103(5)
C(34)	2726(14)	2645(11)	14 877(8)	112(6)
C(35)	3580(15)	3338(13)	15 043(6)	113(5)
C(36)	4188(10)	4080(9)	14 668(4)	81(3)
0	6667	3333	14 217(11)	152(9)
O(01)	9222(20)	3496(22)	5905(10)	272(10)
C(02)	9411(20)	4418(19)	6099(14)	220(12)
C(03)	8721(33)	4332(25)	6535(18)	322(22)
C(04)	8029(24)	3272(27)	6646(13)	251(15)
C(05)	8268(24)	2701(18)	6237(15)	244(15)

1.10 mmol) and  $[Et_4N]_2[MoSe_4]$  (0.17 g, 0.25 mmol) in 20 ml pyridine(Py)–DMF (3:1) was stirred for 2 h at room temperature. After filtration, the brown precipitate was removed off to afford a red-brown filtrate. Dark-red microcrystals was obtained by diffusing Et<sub>2</sub>O into the filtrate after 3 days. The crystal were washed with EtOH and dried under vacuum. Yield: 0.15 g (38.7%). Found: C, 21.6; H, 1.82; N, 7.15%; requires for C<sub>20</sub>H<sub>20</sub>N<sub>6</sub>MoCu<sub>4</sub>Se<sub>4</sub>Br<sub>2</sub>: C, 20.5; H, 1.72; N, 7.18%. IR (KBr, cm<sup>-1</sup>): 1595.4(vs), 1442.2(vs), 1217.1(vs), 1152.2(vs), 1070.2(vs), 1037.9(vs), 1006.4(vs), 752.2(vs), 699.1(vs), 650.3(m), 627.1(s), 418.8(s), 334.8(s), 310.7(w), 258.4(w).

To a freshly slurry of  $[MoSe_4Cu_4Py_6Br_2]$  (0.19 g, 0.15 mmol) in DMF (8 ml) was slowly added a solution of PPh<sub>3</sub> (0.14 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub>

(15 ml) and the solution was stirred for 4 h, the reaction mixture was filtered to afford a dark-red filtrate. Analytically pure crystals were obtained by  $Et_2O$  vapor diffusion after two days. The product was washed with EtOH and dried under vacuum. Anal. Found: C, 45.7; H, 3.22; P, 6.45%. These elements analytical results are identical to those of **1**.

## 2.1.3. Preparation of $[{WCu_3Se_3Cl}(PPh_3)_3Se]$ (2)

A well-ground mixture of  $Cu(PPh_3)_2Cl$  (1.12 g, 1.5 mmol) and  $[Et_4N]_2[WSe_4]$  (0.38 g, 0.5 mmol) was put into a Schlenk tube and heated at 80°C for 6 h under a nitrogen atmosphere. After extracting the resultant black solid  $CH_2Cl_2$  (30 ml), the extract was filtered to afford a reddish-orange filtrate. Blockshaped red crystals were obtained for 2 days by diffusing the filtrate with diethyl ether. Analytical results of IR spectroscopy and crystal cell dimensions are same as those in Ref. [10].

#### 2.2. X-ray structure determinations

Well-shaped single crystals for 1.3THF·H<sub>2</sub>O and 2 were selected for X-ray data collections which were preformed on a Siemens Smart CCD area-detecting diffractormeter using graphite-monochromated MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation with  $\omega$  scan mode at 293 K. All calculations were carried on a Siemens Computer Station with SHELXTL-97 program [20]. The positions of all metal and selenium atoms were determined by direct methods, and successive difference electron density maps located the remaining nonhydrogen atoms. All non-hydrogen atoms except THF group and O of  $H_2O$  in  $1.3THF \cdot H_2O$  were refined by full-matrix least-squares procedures with anisotropic thermal parameters. The THF group in 1.3THF·H<sub>2</sub>O was rigidly refined. Further details of the structure analyses are listed in Table 1. Because structure of 2 was reported by Ibers, we present only its crystallographic details, which are better than those reported previously. Description of this structure is not too necessary. Positional parameters and selected bond lengths and angles of 1.3THF·H<sub>2</sub>O are given in Tables 2 and 3.

## 2.3. Optical measurements

A  $CH_2Cl_2$  solution of  $1.5\times10^{-3}\ mol\ dm^{-3}$  of

Mo-Se(2)	2.265(2)	Mo-Se(1)	2.3831(9)
Mo-Se(1) <sup>a</sup>	2.3832(9)	Mo-Cu <sup>a</sup>	2.7577(12)
Mo-Cu	2.7578(12)	Cu-P(1)	2.231(2)
Cu-Se(1) <sup>a</sup>	2.3896(13)	Cu–Se(1) <sup>b</sup>	2.3917(12)
Cu-Br(1)	2.795(2)	P(1)–C(11)	1.832(9)
P(1)-C(21)	1.839(9)	P(1)-C(31)	1.828(9)
Se(2)-Mo-Se(1)	110.54(3)	$Se(1)-Mo-Se(1)^{b}$	108.38(3)
Se(1) <sup>a</sup> -Mo-Cu <sup>b</sup>	54.87(3)	Se(1) <sup>b</sup> -Mo-Cu <sup>b</sup>	112.38(5)
Se(2)-Mo-Cu	137.03(3)	Se(1) <sup>a</sup> -Cu-Mo	54.60(3)
Se(1)-Mo-Cu	112.43(5)	Se(1) <sup>a</sup> –Mo–Cu	54.81(3)
Cu <sup>a</sup> -Mo-Cu	72.36(5)	$P(1)-Cu-Se(1)^{a}$	119.82(8)
$P(1)-Cu-Se(1)^{b}$	117.97(7)	$Se(1)^{a}-Cu-Se(1)^{b}$	107.89(5)
Se(1) <sup>b</sup> -Cu-Mo	54.58(3)	P(1)-Cu-Br(1)	109.96(7)
$Se(1)^{a}-Cu-Br(1)$	98.70(4)	$Se(1)^{b}-Cu-Br(1)$	98.65(4)
Mo-Cu-Br(1)	94.76(4)	Mo-Se(1)-Cu <sup>b</sup>	70.59(3)
Mo-Se(1)-Cu <sup>a</sup>	70.56(3)	Cu <sup>b</sup> -Se(1)-Cu <sup>a</sup>	85.83(6)
Cu <sup>a</sup> -Br(1)-Cu	71.25(5)	C(31)-P(1)-Cu	114.3(3)
C(11)-P(1)-Cu	113.6(3)	C(21)-P(1)-Cu	115.0(3)

Table 3 Selected bond lengths (Å) angles (°) for 1.3THF·H<sub>2</sub>O

<sup>a</sup> Symmetry code: -y + 1, x - y + 1, z.

<sup>b</sup> Symmetry code: -x + y, -x + 1, z.

cluster 1 or 2 was placed in a 1-mm quartz cuvette for optical measurements. Their nonlinear absorption and nonlinear refraction were measured with a linearly polarized laser light ( $\lambda = 532$  nm, pulse width = 7 ns) generated from a Q-switched and frequencydoubled Nd:YAG laser. The spatial profiles of the optical pulses were nearly Gaussian. The laser beam was focused with a 25-cm focal-length focussing mirror. The radius of the laser beam waist was measured to be 30  $\mu$ m (half-width at  $1/e^2$  maximum). The incident and transmitted pulse energy were measured simultaneously by two Laser Precision detectors (RjP-735 energy probes) communicating to a computer via an IEEE interface [21]. The details of the set-up can be found elsewhere [22].

#### 3. Results and discussion

#### 3.1. Synthesis and reaction

In the present reaction system, the reaction of  $[Et_4N]_2[MoSe_4]$  and  $Cu(PPh_3)_2NO_3$  in a ratio of 1:3 in  $CH_2Cl_2$ ,  $[MoSe_4]^{2-}$  anion was coordinated by  $[Cu(PPh_3)]^+$  fragment to afford an intermediate product  $[MoSe_4(CuPPh_3)_3]^+$  which has a non-coordination terminal Mo–Se bond; when halide anion is additionally supplied, the neutral cubane-like cluster was formed (Scheme 1).

When cluster [MoSe<sub>4</sub>Cu<sub>4</sub>Py<sub>6</sub>Br<sub>2</sub>] is reacted with excess PPh<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>, the same cubane-like cluster is also obtained (see Scheme 2). The reaction processes involve: (i) a change of the cluster



Scheme 1.



Scheme 2.

skeleton from the cross  $MoSe_4Cu_4$  to the cubane-like (Se) $MoSe_3Cu_3$ ; (ii) the substitute reaction of Py by PPh<sub>3</sub>; (iii) the formation of the Cu–P bond enhancing the ability for the Br atom to assume a  $\mu_3$ -position.

For the furtherance of understanding the reactivity and reaction mechanism in the above two reactions, the <sup>95</sup>Mo NMR technique was used to monitor the reaction processes. Fig. 1(a) shows <sup>95</sup>Mo NMR spectrum of the sample drawn from the synthetic reaction mixture for [Et<sub>4</sub>N]<sub>2</sub>[MoSe<sub>4</sub>] and Cu(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub> in a molar ratio of 1:3 in CH<sub>2</sub>Cl<sub>2</sub>, only one resonance peak at 1316 ppm ( $\Delta \nu_{1/2} = 125$  Hz), which may be assigned to  $[MoSe_4(CuPPh_3)_3]^+$  intermediate [23]. After the addition of Et<sub>4</sub>N·Br salt to the above reaction mixture, nearly no change of the  $^{95}\mbox{Mo}$  NMR signal was observed. This fact may infer that the final product [{MoCu<sub>3</sub>Se<sub>3</sub>Br}(PPh<sub>3</sub>)<sub>3</sub>Se] was formed through the Br<sup>-</sup> anion attaching to the [MoSe<sub>4</sub>-(CuPPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> species. The <sup>95</sup>Mo NMR spectrum of the sample [MoSe<sub>4</sub>Cu<sub>4</sub>Py<sub>6</sub>Br<sub>2</sub>] in DMF is depicted in Fig. 2(a), only one resonance peak at -1.92 ppm  $(\Delta v_{1/2} = 48 \text{ Hz})$  was found, which is similar to the <sup>95</sup>Mo NMR results of the cluster compounds containing MoCu<sub>4</sub> core plane [14]. When an excess PPh<sub>3</sub> ligand was reacted with [MoSe<sub>4</sub>Cu<sub>4</sub>Py<sub>6</sub>Br<sub>2</sub>] in

(a)	-many many many many many many many many
(b)	Contraction of the second seco

800

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1400 1200 1000

Fig. 1. (a) <sup>95</sup>Mo NMR spectrum of the sample drawn from the reaction mixture of  $[Et_4N]_2MoSe_4$  with 3 equiv of Cu(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> ( $\delta = 1316$  ppm,  $\Delta \nu_{1/2} = 125$  Hz). (b) Addition of equal equiv of Et<sub>4</sub>N·Br salt to (a) ( $\delta = 1301$  ppm,  $\Delta \nu_{1/2} = 113$  Hz).

600

400

200

ppm

DMF–CH<sub>2</sub>Cl<sub>2</sub> for 2 h, the single at -1.92 ppm disappeared and a new one at 1307 ppm appeared, and the signal was independent of the reaction time. Based on the above results, it may be suggested that the great change from the high field to the low field for the Mo nucleus deshielding effect came from the cluster skeleton transformation. Thus, the reaction processes are undergoing structural change from MoCu<sub>4</sub> core cross-plane to MoCu<sub>3</sub> core distorted-cubane.

Although cluster 2 was previously prepared by the solution reaction method [10], it can be readily synthesized by the solid state reaction at low heating temperature. The fact that the reaction was carried out in the solid state, may be inferred from the starting material  $[Et_4N]_2[WSe_4]$  color varying from a violet-red to a red-brown, accompanied by disappearance of white complex Cu(PPh<sub>3</sub>)<sub>2</sub>Cl and gas evolution generated from partial decomposition of  $[Et_4N]_2[WSe_4]$ . Different from the molybdenum-containing cluster 1, the crystal product of tungsten-containing cluster 2 is very air- and moisture-stable.

### 3.2. Structure of $1.3THF \cdot H_2O$

The molecular cluster of 1.3THF·H<sub>2</sub>O crystallized



Fig. 2. (a) The <sup>95</sup>Mo NMR spectrum of the sample [MoSe<sub>4</sub>Cu<sub>4</sub>. Py<sub>6</sub>Br<sub>2</sub>] in DMF ( $\delta = -1.92$  ppm,  $\Delta \nu_{1/2} = 48$  Hz). (b) <sup>95</sup>Mo NMR spectrum of the sample drawn from the reaction mixture of [MoSe<sub>4</sub>Cu<sub>4</sub>Py<sub>6</sub>Br<sub>2</sub>] and excess PPh<sub>3</sub> in DMF-CH<sub>2</sub>Cl<sub>2</sub> ( $\delta = 1307$  ppm,  $\Delta \nu_{1/2} = 119$  Hz).

in the trigonal R3 space group possible due to the presence of solvent molecules THF and H<sub>2</sub>O. There are no any contacts among the solvent and cluster molecules. The molecular structure possesses a crystallographic  $C_3$  axis passing through the terminal Se(2), Mo, Br(1) and O atoms. The neutral cluster molecular [ $\{MoCu_3Se_3Br\}(PPh_3)_3Se\}$  contains a highly distorted cubane-like [MoCu<sub>3</sub>Se<sub>3</sub>Br]<sup>+</sup> cluster core with Se<sup>2-</sup> terminal ligand to the Mo, and PPh<sub>3</sub> ligand bound to each Cu atom. The Mo-Se<sub>b</sub> (bridging) distance of 2.384(1) Å is greater than the Mo–Se<sub>t</sub> (terminal) distance of 2.264(2) Å. The average Mo-Cu distance of 2.757(1) Å in 1.3THF $\cdot$ H<sub>2</sub>O is slightly longer than that of 2.712(2) Å in  $[(\mu_3-Cl)(\mu_3-MoS_4)(CuPPh_3)_3]$  [24], and shorter than the sum of the van der Waals radii of Mo and Cu atoms, which may be considered that an interaction exists between two metal atoms. The average Cu-Se bond length of 2.391(1) Å in 1.3THF·H<sub>2</sub>O agrees well with that of 2.394(3) Å in  $[(\mu_3-Cl)(\mu_3-WSe_4)(CuPPh_3)_3]$  [10]. The Cu-Br distance of 2.797(1) Å is normal. The Se<sub>t</sub>-Mo-Se<sub>b</sub> angles are ca. 2.1° more obtuse than the Se<sub>b</sub>-Mo-Se<sub>b</sub> angles, each of which along with the average Se-Cu-Se angle of 107.9(1)° is near 109.4° of tetrahedral angle. The Br atom is at one vertex of [MoCu<sub>3</sub>. Se<sub>3</sub>Br]<sup>+</sup> cubane, however, the average Cu-Br-Cu bond angle of 71.2(2)° is much deviated from 90° of the standard cubane angle. A view of the structure is presented in Fig. 3.

### 3.3. NLO properties

The electronic spectra of clusters **1** and **2** exhibit a moderately intense absorption band positioned at 381 and 338 nm, respectively. The bands have been assigned as charge-transfer bands of the type  $(\pi(Se) \rightarrow d(M))$  arising from the MSe<sub>4</sub> moiety (M = Mo, W). It is interesting to note that the Se  $\rightarrow$  M charge-transfer transition peaks are



Fig. 3. A view of the inner core of  $[{MoCu_3Se_3Br}(PPh_3)_3Se]$  in 1·3THF·H<sub>2</sub>O. Only inequivalent atoms are labeled. Displacement ellipsoids are plotted at the 50% probability level.



Fig. 4. Z-scan data of  $1.5 \times 10^{-3}$  M of **1** in CH<sub>2</sub>Cl<sub>2</sub> at 532 nm with  $I_0$  being  $2.6 \times 10^{12}$  W/m<sup>2</sup> : (a) collected under the open aperture configuration showing NLO absorption; (b) obtained by dividing the normalized Z-scan data obtained under the closed aperture configuration by the normalized Z-scan data in (a) (it shows the self-defocusing effect).

obviously blue shifted when Mo is replaced by W in the clusters. Peak at  $\sim$ 380 nm was shifted by  $\sim$ 40 nm to shorter wavelength. This is a demonstration of metal dependence on the NLO performances of clusters.

The NLO properties of clusters 1 and 2 were investigated by using the Z-scan technique. Two clusters show both non-linear absorption and refraction. The nonlinear absorption component was evaluated under an open aperture configuration. Theoretical curves of transmittance against the Z-position, Eqs. (1) and (2), were

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

$$q(Z) = \alpha_2 I_i(Z) \frac{(1 - e^{-\alpha_0 L})}{\alpha_0}$$
(2)

fitted to the observed Z-scan data by varying the effective third-order NLO absorptivity  $\alpha_2$  value, where the experimentally measured  $\alpha_0$  (linear absorptivity), L (the optical path of sample) and  $I_i(Z)$  (the on-axis irradiance at Z-position) were adopted. The solid lines in Figs. 4(a) and 5(a) are the theoretical curve calculated with  $\alpha_2 = 3.4 \times 10^{-10}$  and  $5.9 \times 10^{-10}$  m/W, respectively, for the same concentration CH<sub>2</sub>Cl<sub>2</sub> solution of **1** and **2**. The non-linear refractive components of clusters **1** and **2** were assessed by dividing the normalized Z-scan data obtained in the close-aperture configuration by those obtained in the open-aperture configuration. They are plotted in Figs. 4(b) and 5(b) for **1** and **2**, respectively; the solid curves are an eye guide for comparison where the effective NLO refractivity  $n_2$  values estimated therefore are  $-1.5 \times 10^{-17}$  m<sup>2</sup>/W for **1** and  $-1.3 \times 10^{-17}$  m<sup>2</sup>/W for **2**, respectively.

Comparing the NLO data of 1 and 2, the non-linear absorption capability of 2 is obviously stronger than that of 1, while their non-linear refractive effects are almost identical. Such a significant improvement of non-linear absorption capability by replacing skeletal Mo atom with W atom implies a heavy atom effect, which is similar to those observed in the same structure clusters  $[MS_4(AuAsPh_3)_2]$  and  $[n-Bu_4N]_3[WS_4M'_3Br_3]$  (M = Mo, W; M' = Cu, Ag) [25,26]. Together with electronic spectral data of 1 and 2, it may be inferred that substitution of Mo



Fig. 5. Z-scan data of  $1.5 \times 10^{-3}$  M of 2 in CH<sub>2</sub>Cl<sub>2</sub> at 532 nm with  $I_0$  being  $2.9 \times 10^{12}$  W/m<sup>2</sup> : (a) collected under the open aperture configuration showing NLO absorption; (b) obtained by dividing the normalized Z-scan data obtained under the closed aperture configuration by the normalized Z-scan data in (a) (it shows the self-defocusing effect).

atom by heavier W atom allows more efficient spinorbital coupling and ionization/geminate recombination between the W and Se atoms than between the Mo and Se atoms. However, non-linear refraction effects of 1 and 2 are not influenced by substitution of the center atom. Based on our previous results from the theoretical analyses, the reason may be that an intense charge transfer may not necessarily give rise to a large refractive index [27].

The negative values of non-linear refraction in 1 and 2 indicate that there are self-defocusing effects in NLO behaviors of the present cubane clusters. A combination of their NLO refractive properties (selfdefocusing) and NLO absorptive properties is in contrast to the behavior of the corresponding sulfur cluster compound,  $[MCu_{3}S_{4}X_{4}]^{3^{-1}}$ cubane-like (M = Mo, W) [28], which typically shows a combination of strong NLO absorptive and very weak selffocusing characteristics. Thus, a slightly significant improvement of NLO absorptive capability is seen when S atoms are replaced by Se atoms in the cluster skeleton. Heavy atom effect arises from the fact that Se atoms can facilitate intersystem crossing more effectively via spin-orbit coupling than S atoms [29]. Meanwhile, NLO refractive effects change from self-focusing of S-containing clusters to selfdefocusing of Se-containing clusters although they are of a similar structural type. A considerable interruption may be that the bigger the atomic radius is, the looser the structure shows. This makes the cage structure to have bigger electronic displacements coming from larger bond parameters.

## 4. Supplementary materials

Crystal data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133092/3(0119) and also available from the authors.

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