

# Syntheses, structures and third-order non-linear optical properties of homometal clusters containing molybdenum

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Received 14 June 2004; received in revised form 26 October 2004; accepted 3 November 2004

## Abstract

Both the homometal cluster  $[\text{P}(\text{ph}_4)_2][\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]$  (**1**) and  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Et}_2\text{dtc})_2]$  (**2**) ( $\text{Et}_2\text{dtc}$  = diethyl-dithiocarbamate) were successfully synthesized by low-temperature solid-state reactions. X-ray single-crystal diffraction studies suggest that compound (**1**) is a dinuclear anion cluster, and compound (**2**) is a dinuclear neutral cluster. The two compounds were characterized by elemental analyses, IR spectra and UV-Vis spectra. The third-order non-linear optical (NLO) properties of the clusters were also investigated and all exhibited nice non-linear absorption and self-defocusing performance with moduli of the hyperpolarizabilities  $5.145 \times 10^{-30}$  esu for (**1**) and  $5.428 \times 10^{-30}$  esu for (**2**).

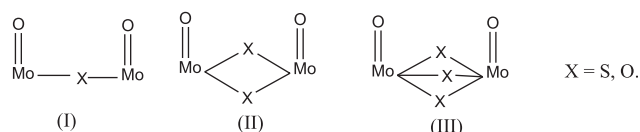
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**Keywords:** Molybdenum(V) clusters; Solid-state reactions; Third-order non-linear optical properties

## 1. Introduction

Early transition-metal complexes, especially those of V, Mo and W, represent a prominent class of compounds involved in many areas of chemistry [1,2]. In particular, such systems are studied extensively for their implications in biological [3,4] and industrial catalytic processes [5,6]. Molybdenum is widely used in biological systems due to the basic forms: nitrogenases [7] and oxotransferases [8,9] or oxomolybdoenzymes [10–13]. Metal–sulfide cluster anions, commonly referred to as thiometalates, exhibit topologies often limited to some archetypal architectures [14], with low nuclearity rarely exceeding four metallic centers. Molybdenum (V) preferentially forms some dinuclear complexes [15], three different types of bridging are

known for oxomolybdenum (V) dinuclear complexes, as drawn below, and these three types of complexes have been prepared with dithiocarbamate ligands [15,16].



An extensive chemistry of the synthesis and structure of molybdenum sulfur compounds has emerged in recent years. Many containing a  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]$  structural complex have been reported [17]. Their spectroscopy characteristics and structures have been studied. However, the third-order non-linear optical (NLO) properties have not been well mentioned. In this study, we report the two examples containing the  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2]$  structural unit with doubly bridged sulfur, in addition to disulfur chelating terminal ligands. Hereinafter, we not

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only describe the syntheses and structures of homometal clusters but also study their NLO properties.

## 2. Experimental

### 2.1. Materials and physical measurements

(NH<sub>4</sub>)<sub>2</sub>MoO<sub>2</sub>S<sub>2</sub> was prepared by a modified published procedure [18]. Other reagents were used as received from commercial suppliers without further purification. Infrared (IR) spectra of the title clusters were recorded as KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer in the 225–4000 cm<sup>-1</sup> region. Element analyses were performed on a Perkin-Elmer 2400LSII element analyzer. Electronic spectra were measured on a Shimadzu UV-3100 spectrophotometer. The NLO measurements were performed with Z-scan technique in the DMF solution, the DMF solution was contained in 5-mm-thick glass cell with concentration of 1.68 × 10<sup>-4</sup> and 1.73 × 10<sup>-4</sup> M for **1** and **2**, respectively. The NLO response of the solution was measured at 532 nm with a 15 ns pulse width produced by a frequency-doubled Q-switched Nd:YAG laser.

### 2.2. Synthesis of compounds

#### 2.2.1. [P(ph<sub>4</sub>)]<sub>2</sub>[Mo<sub>2</sub>O<sub>2</sub>(μ-S)<sub>2</sub>(S<sub>2</sub>)<sub>2</sub>] **1**

A well-ground mixture of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>2</sub>S<sub>2</sub> 259 mg (1.0 mmol), K<sub>2</sub>S 333 mg (3.0 mmol) and [P(ph<sub>4</sub>)]Cl

749 mg (2.0 mmol) was heated in a sealed glass tube filled with N<sub>2</sub> gas at 85 °C for 18 h. The mixture was extracted with the mixed solvent of DMF (40 mL) and CH<sub>3</sub>OH (15 mL), and then filtered. The dark red filtrate was made to stand in the atmosphere of nitrogen at 5 °C for 12 days, and dark red crystals were obtained. Yields: 262 mg (47.9% based on Mo). The compound shows characteristic IR absorption peaks at 942 and 953 cm<sup>-1</sup> for ν (Mo–O<sub>t</sub>), 460 and 420 cm<sup>-1</sup> for ν [Mo–(μ-S)], 520 cm<sup>-1</sup> for ν (S–S). The results of elemental analyses: Anal. calcd. for C<sub>48</sub>H<sub>40</sub>Mo<sub>2</sub>O<sub>2</sub>P<sub>2</sub>S<sub>6</sub>: C, 52.65; H, 3.68; P, 5.66; S, 17.57; Mo, 17.52%. Found: C, 52.63; H, 3.69; P, 5.67; S, 17.55; Mo, 17.53%.

#### 2.2.2. [Mo<sub>2</sub>O<sub>2</sub>(μ-S)<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub>] **2**

A well-ground mixture of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>2</sub>S<sub>2</sub> 259 mg (1.0 mmol), Na(Et<sub>2</sub>dtc) 342 mg (2.0 mmol) and Et<sub>4</sub>NBr 420 mg (2.0 mmol) was heated in a sealed glass tube filled with N<sub>2</sub> gas at 90 °C for 12 h. The mixture was extracted with the mixed solvent of DMF (40 mL) and CH<sub>3</sub>OH (15 mL), and then filtered. The brown red filtrate was made to stand in the atmosphere of nitrogen at 5 °C for 10 days, and yellow brown crystals were obtained. Yields: 171 mg (56.8% based on Mo). The compound shows characteristic IR absorption peak at 951 and 965 cm<sup>-1</sup> for ν (Mo–O<sub>t</sub>), 475 cm<sup>-1</sup> for ν [Mo–(μ-S)], 377 and 340 cm<sup>-1</sup> for ν (Mo–S<sub>dtc</sub>), 1540 and 1457 cm<sup>-1</sup> for ν (C–N)<sub>dtc</sub>. The results of elemental analyses: Anal. calcd for C<sub>10</sub>H<sub>20</sub>Mo<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub>:

Table 1  
Crystal data and structure refinement for the title compounds

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>48</sub> H <sub>40</sub> Mo <sub>2</sub> O <sub>2</sub> P <sub>2</sub> S <sub>6</sub>	C <sub>10</sub> H <sub>20</sub> Mo <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S <sub>6</sub>
Formula weight	1094.98	584.52
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	C2/c
Unit cell dimensions	a = 11.043(2) Å b = 20.620(4) Å c = 21.132(4) Å β = 98.40(3)°	a = 33.961(5) Å b = 6.9879(10) Å c = 18.086(3) Å β = 105.897(3)°
Volume (Å <sup>3</sup> )	4760.3(16)	4127.9(10)
Z	8	8
Calculated density (g cm <sup>-3</sup> )	1.528	1.881
Absorption coefficient (mm <sup>-1</sup> )	0.895	1.826
F <sub>(000)</sub>	2216	2320
Crystal size (mm <sup>3</sup> )	0.473 × 0.264 × 0.230	0.665 × 0.497 × 0.100
θ range for data collection	1.39–27.48°	2.33–23.26°
Limiting indices	0 ≤ h ≤ 14; 0 ≤ k ≤ 26; -27 ≤ l ≤ 27	-19 ≤ h ≤ 37; -7 ≤ k ≤ 7; -20 ≤ l ≤ 18
Reflections collected/unique	10,385/10,385 [R <sub>int</sub> = 0.0573]	6781/2941 [R <sub>int</sub> = 0.0201]
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	10,385/0/541	2941/0/199
Goodness-of-fit on F <sup>2</sup>	0.920	1.091
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0517, wR <sub>2</sub> = 0.1402	R <sub>1</sub> = 0.0262, wR <sub>2</sub> = 0.0627
R indices (all data)	R <sub>1</sub> = 0.0922, wR <sub>2</sub> = 0.1645	R <sub>1</sub> = 0.0300, wR <sub>2</sub> = 0.0646
Largest diff. peak and hole	1.538 and -0.832 e Å <sup>-3</sup>	0.672 and -0.409 e Å <sup>-3</sup>

C, 20.55; H, 3.45; N, 4.79; S, 32.91; Mo, 32.83%. Found: C, 20.57; H, 3.44; N, 4.77; S, 32.89; Mo, 32.85%.

### 2.3. Structure determination

Crystal data were collected with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using a Rigaku R-AXIS RAPID IP diffractometer for **1** and a Siemens SMART CCD diffractometer for **2**. The structures were solved using direct methods with SHEXTL-97 program and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The hydrogen atoms were treated using a riding model. The crystal data and selected parameters are given in Tables 1 and 2.

## 3. Results and discussion

### 3.1. Structure description

#### 3.1.1. $[P(\text{ph}_4)]_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]$ **1**

The structure consists of discrete  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$  anions and  $[\text{P}(\text{ph}_4)]^+$  cations. The geometry of the  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$  anion is given in Fig. 1. The dianion is formed by two pentacoordinated molybdenum atoms, the Mo(1)–Mo(2) distance is quite short (2.8177(10) Å). This distance is in the range of that observed for a metal–metal bond in compounds which present the similar  $[\text{Mo}_2(\text{O})_2(\mu\text{-S})_2]$  central core formed of two Mo(V) ions as in the  $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})_2(\text{CS}_4)(\text{CS}_3)]$  [19] complex (Mo–Mo: 2.835(2) Å). Two sulfido groups doubly bridge the two metal centers, the Mo–S distances in the equatorial plane are different for Mo(1), 2.3230(16)–2.340(18) and

Table 2  
Selected bonds lengths (Å) and angles (deg) for the title compounds

<b>1</b>			
Mo(1)–O(1)	1.683(4)	Mo(2)–S(5)	2.3937(18)
Mo(1)–S(4)	2.3230(16)	Mo(2)–S(6)	2.4049(17)
Mo(1)–S(3)	2.3240(18)	S(6)–S(5)	2.069(3)
Mo(1)–S(1)	2.3891(19)	Mo(1)–O(1)	1.683(4)
Mo(1)–S(2)	2.420(2)	Mo(1)–S(4)	2.3230(16)
Mo(1)–Mo(2)	2.8177(9)	Mo(1)–S(3)	2.3240(18)
Mo(2)–O(2)	1.675(4)	Mo(1)–S(1)	2.3891(19)
Mo(2)–S(3)	2.3035(15)	Mo(1)–S(2)	2.420(2)
Mo(2)–S(4)	2.3142(18)	Mo(1)–Mo(2)	2.8177(9)
S(4)–Mo(1)–S(3)	101.92(6)	S(5)–Mo(2)–S(6)	51.08(7)
S(4)–Mo(1)–S(1)	135.60(8)	O(2)–Mo(2)–Mo(1)	105.85(15)
S(3)–Mo(1)–S(1)	88.63(9)	Mo(2)–S(3)–Mo(1)	75.02(5)
S(1)–Mo(1)–S(2)	52.41(10)	S(5)–S(6)–Mo(2)	64.18(7)
O(1)–Mo(1)–Mo(2)	106.41(14)	Mo(2)–S(4)–Mo(1)	74.84(5)
S(3)–Mo(2)–S(4)	102.82(7)	S(6)–S(5)–Mo(2)	68.75(14)
<b>2</b>			
Mo(1)–O(1)	1.670(3)	N(1)–C(1)	1.312(5)
Mo(1)–S(4)	2.3088(12)	N(1)–C(2)	1.468(6)
Mo(1)–S(3)	2.3140(12)	N(1)–C(4)	1.486(6)
Mo(1)–S(1)	2.4613(12)	N(2)–C(6)	1.298(5)
Mo(1)–S(2)	2.4625(11)	N(2)–C(7)	1.474(6)
Mo(1)–Mo(2)	2.8095(5)	N(2)–C(9)	1.768(12)
Mo(2)–O(2)	1.668(3)	S(1)–C(1)	1.725(4)
Mo(2)–S(4)	2.3144(12)	S(2)–C(1)	1.728(4)
Mo(2)–S(3)	2.3146(13)	S(5)–C(6)	1.717(4)
Mo(2)–S(6)	2.4478(13)	S(6)–C(6)	1.730(4)
Mo(2)–S(5)	2.4577(11)		
O(1)–Mo(1)–S(4)	108.91(14)	C(6)–S(5)–Mo(2)	88.06(14)
S(4)–Mo(1)–S(3)	102.08(4)	C(6)–S(6)–Mo(2)	88.10(14)
S(1)–Mo(1)–S(2)	71.01(4)	S(1)–C(1)–S(2)	111.8(2)
O(2)–Mo(2)–S(4)	108.74(13)	S(5)–C(6)–S(6)	111.6(2)
S(4)–Mo(2)–S(3)	101.89(4)	Mo(1)–S(4)–Mo(2)	74.85(4)
S(6)–Mo(2)–S(5)	71.06(4)	C(6)–S(5)–Mo(2)	88.06(14)
C(2)–N(1)–C(4)	116.5(3)	C(6)–S(6)–Mo(2)	88.10(14)
C(7)–N(2)–C(9)	113.6(4)	Mo(1)–S(3)–Mo(2)	74.74(4)
C(1)–S(1)–Mo(1)	88.46(14)	Mo(1)–S(4)–Mo(2)	74.85(4)
C(1)–S(2)–Mo(1)	88.34(14)		

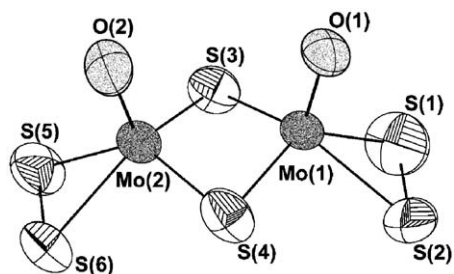


Fig. 1. View of the  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$  anion.

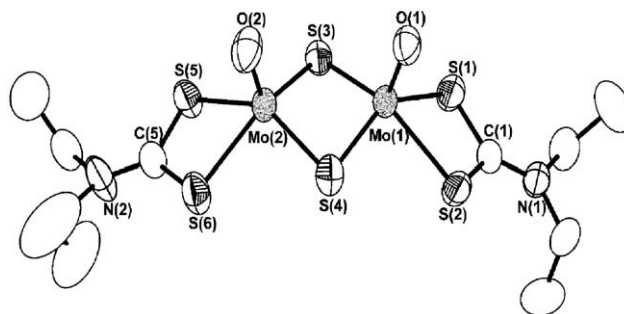


Fig. 2. The molecular structure of compound 2.

2.3891(19)–2.420(2) Å, and for Mo(2), 2.3035(15)–2.3142(18) and 2.3937(18)–2.4049(17) Å. The Mo–S bonds of the sulfido bridging atoms are always shorter than the Mo–S bonds of the terminal ligands, such features were already mentioned by Coucouvanis et al. [19] The coordination sphere is completed by a disulfido group  $\text{S}_2^{2-}$  and a terminal oxygen atom for Mo(1) and Mo(2), the S(1)–S(2) and S(5)–S(6) distance (2.124(4) and 2.069(3) Å) are usual for terminal disulfido groups and is longer than bridging disulfido groups, as in  $[\text{n-Bu}_4\text{N}]_2\{\text{Mo}_2(\eta^2\text{-CS}_3)_4[\mu\text{-}(\text{S}_2)]_2\}$  (2.005(2) Å) [20]. The terminal Mo–O distances are 1.683(4) Å for Mo(1)–O(1) and 1.675(4) Å for Mo(2)–O(2), these values are in the range expected for terminal bonds in such type of compound, in  $[\text{Mo}_2(\text{S})_2(\mu\text{-S})_2(\text{CS}_4)_2]^{2-}$ , the Mo–O distances are 1.672(13)–1.684(9) Å [19]. The complex anion is isostructural to the previously numerous Mo(V) complexes containing the  $[\text{Mo}_2(\text{O})_2(\mu\text{-S})_2]$  core which were reported by Shibahara [21].

### 3.1.2. $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Et}_2\text{dtc})_2] \mathbf{2}$

The structure consists of neutral complex  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Et}_2\text{dtc})_2] \mathbf{2}$  molecules (shown in Fig. 2). The molecule is formed by two pentacoordinated Mo(V) atoms, both the five-coordinate Mo(V) sites possess distorted tetragonal pyramid coordination geometry with S(1)–S(2)–S(3)–S(4) and S(3)–S(4)–S(5)–S(6) based planes for Mo(1) and Mo(2), respectively. The Mo(V) atom lies on a general site, while S(3) and S(4) lie in the equatorial plane. Mo(1) and Mo(2) are related by this equatorial plane, the Mo(1)–Mo(2) distance is quite short (2.8095(5) Å), which is rationalized to have a Mo–Mo single bond [22]. Two sulfido groups doubly bridge the two metal centers, the Mo–S distances in the equatorial plane can be divided into two sets one of which is Mo–S<sub>core</sub> (2.3088(12)–2.3146(13) Å) and the other Mo–S<sub>dtc</sub> (2.4478(13)–2.4625(11) Å). The Mo coordination geometry is identical to that found in the binuclear Mo(V) complexes,  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{C}_4\text{H}_8\text{dtc})_2] \mathbf{[23]}$  and  $[\text{Mo}_2\text{O}_3(\text{OC}_2\text{H}_4\text{S})(i\text{-Bu}_2\text{dtc})_2] \mathbf{[24]}$ , and the corresponding bond lengths are similar to each other in these complexes. The Mo–S bonds of the sulfido bridging atoms are always shorter than the Mo–S bonds

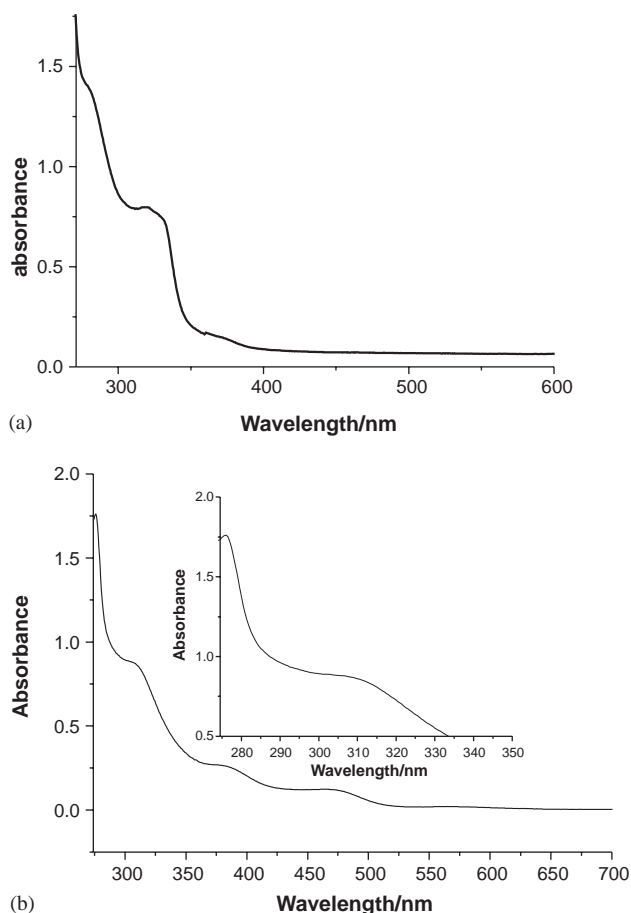


Fig. 3. (a) The UV-visible spectra of complex 1; (b) The UV-visible spectra of complex 2.

of the organic ligands, such features were already mentioned by Coucouvanis et al. [19]. In the structure, the N(1)–C(1) and N(2)–C(5) bond distances (1.312(5) and 1.298(5) Å) are shorter than the other N–C bond distances, which are indicative of considerable double-bond character. Of the four C–S distances, only one is short (1.717(4) Å) compared to the others, the mean C–S distance is 1.725(4) Å, which is shorter than the typical C–S single bond distance; 1.81 Å. Therefore, all the C–S bonds in the present structures are of partial double

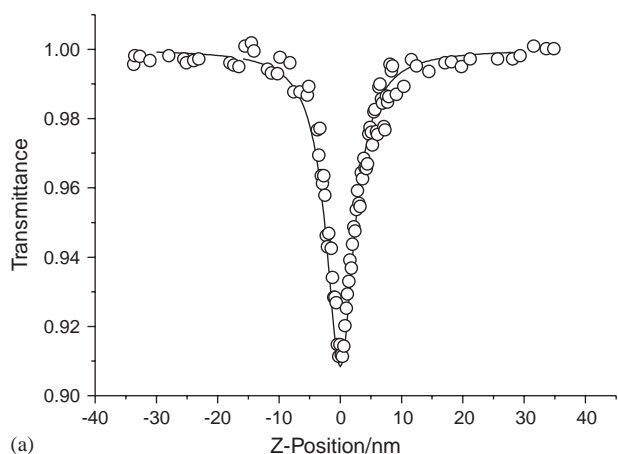
bond character as observed in most of the dithiocarbamates [25].

### 3.2. Non-linear optical properties

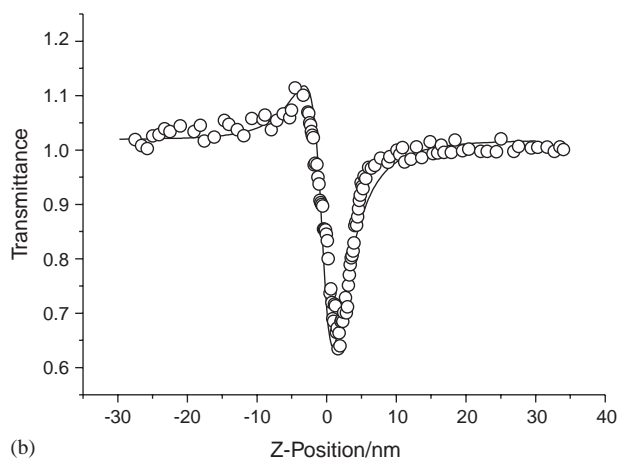
The UV-visible absorption spectra of the title compounds in DMF solution are given in Fig. 3 and the absorption band and attribution are listed in Table 3. (The molar extinction coefficient is in the bracket,  $\text{cm}^{-1} \text{mol}^{-1} \text{dm}^3$ .) It shows that the compounds

Table 3  
The UV-spectra absorption (nm) and attribution

1		2	
Absorption	Attribution	Absorption	Attribution
275.5 nm ( $1.7 \times 10^4$ )	(d)Mo ← ( $\pi$ )O	276.5 nm ( $2.0 \times 10^4$ )	(d)Mo ← ( $\pi$ )O
321.5 nm ( $9.4 \times 10^3$ )	(d)Mo ← ( $\pi$ )S	310 nm ( $1.0 \times 10^4$ )	(d)Mo ← ( $\pi$ )S
365.5 nm ( $2.1 \times 10^3$ )	d ← d	380 nm ( $3.1 \times 10^3$ )	d ← d
		476 nm ( $1.4 \times 10^3$ )	$\pi^* \leftarrow \pi$



(a)



(b)

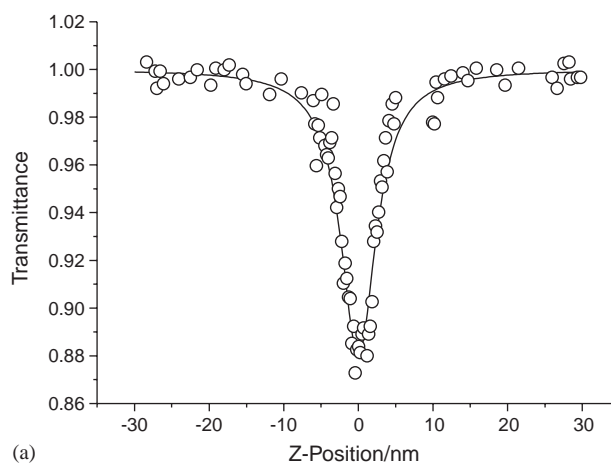
Fig. 4. Z-scan data of **1** dissolved in DMF with a concentration of  $1.68 \times 10^{-4} \text{M}$ . The circles represent experimental data and solid curve is theoretical fit. (a) The data were collected under an open aperture configuration showing NLO absorption; (b) the data were obtained under a closed aperture configuration.

display broad transparent range that cover visible and near-IR regions, promising low intensity loss and little temperature change caused by photon absorption when pulse light propagates in the materials. It shows that the clusters have potential as optical limiters [26].

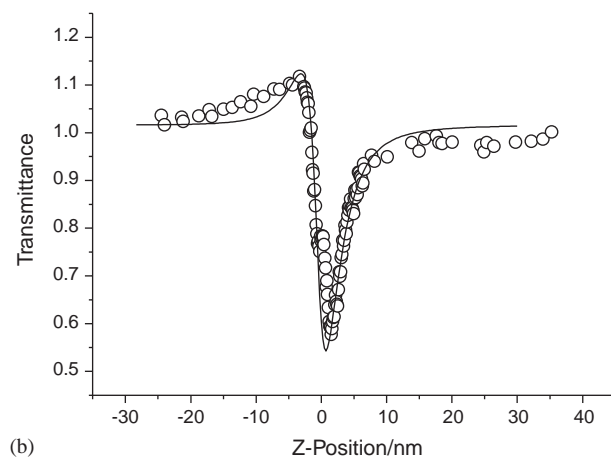
The third-order NLO properties of the title compounds were investigated by using a Z-scan technique. The cell selected to place the sample is a 5 mm-thick glass. The obtained experimental data and theoretical fit [27] are depicted in Figs. 4 and 5, respectively. In accordance with the observed effective third-order NLO absorptive coefficient  $\alpha_2$  and refractive coefficient  $n_2$ , the modulus of the effective third-order non-linear susceptibility  $\chi^{(3)}$  can be calculated by

$$|\chi^{(3)}| = [(9 \times 10^8 n_0^2 \epsilon_0 c \lambda \alpha_2 / 8\pi^2)^2 + (n_0 c n_2 / 80\pi^2)^2]^{1/2}, \quad (1)$$

where  $\lambda$  is the laser wavelength,  $n_0$  is the linear refractive index of the sample ( $n_0$  can be replaced by one of the solvents during calculation if the concentration of the



(a)



(b)

Fig. 5. Z-scan data of **2** dissolved in DMF with a concentration of  $1.73 \times 10^{-4} \text{M}$ . The circles represent experimental data and solid curve is theoretical fit. (a) The data were collected under an open aperture configuration showing NLO absorption; (b) the data were obtained under a closed aperture configuration.

Table 4  
Third-order non-linear optical properties of some clusters

Compound	$\alpha_2$ (m W <sup>-1</sup> )	$n_2$ (m W <sup>-1</sup> )	$ \chi^{(3)} $ (esu)	$\gamma$ (esu)	Ref.
[P(ph <sub>4</sub> ) <sub>2</sub> ][Mo <sub>2</sub> O <sub>2</sub> ( $\mu$ -S) <sub>2</sub> (S <sub>2</sub> ) <sub>2</sub> ] (a)	$5.7 \times 10^{-11}$	$-7.8 \times 10^{-18}$	$6.356 \times 10^{-12}$	$5.145 \times 10^{-30}$	This work
[Mo <sub>2</sub> O <sub>2</sub> ( $\mu$ -S) <sub>2</sub> (Et <sub>2</sub> dtc) <sub>2</sub> ] (b)	$4.5 \times 10^{-11}$	$-8.6 \times 10^{-18}$	$6.705 \times 10^{-12}$	$5.428 \times 10^{-30}$	This work
[MoOS <sub>3</sub> Cu <sub>3</sub> I(2,2'-bipy) <sub>2</sub> ] (c)	$6.2 \times 10^{-10}$	$-3.8 \times 10^{-17}$	$2.1 \times 10^{-11}$	$1.7 \times 10^{-29}$	[28]
[WAg <sub>3</sub> OS <sub>3</sub> (Pph <sub>3</sub> ) <sub>3</sub> S <sub>2</sub> P(OP <sup>i</sup> ) <sub>2</sub> ] (d)	$2.9 \times 10^{-10}$	$-1.74 \times 10^{-17}$	—	$7.8 \times 10^{-30}$	[29]
[WCu <sub>3</sub> S <sub>4</sub> (Pph <sub>3</sub> ) <sub>3</sub> {S <sub>2</sub> P(OCH <sub>2</sub> ph) <sub>2</sub> }] (e)	$2.53 \times 10^{-10}$	$-6.03 \times 10^{-17}$	—	$3.0 \times 10^{-29}$	[29]

Concentrations of samples (M). (a)  $1.68 \times 10^{-4}$ ; (b)  $1.73 \times 10^{-4}$ ; (c)  $3.7 \times 10^{-4}$ ; (d)  $1.16 \times 10^{-3}$ ; (e)  $8.74 \times 10^{-4}$ .

sample is very dilute),  $\epsilon_0$  and  $c$  are the permittivity and the speed of light in a vacuum, respectively. The corresponding moduli of the third-order non-linear molecular susceptibilities (or hyperpolarizabilities) were obtained from

$$|\gamma| = |\chi^{(3)}|/NF^4, \quad (2)$$

where  $F^4 = [(n^2 + 2)/3]^4$ ,  $N$  is the molecular number density of the compound in the sample (i.e. molecular number of the solute in each mL of the solution) and  $F^4$  is the local Lorents field correction term. All the calculated results and some literature data on the NLO properties are listed in Table 4, from which we can see that NLO performances of the clusters containing sulfur atoms are better than those of the cluster containing no sulfur atom, and the more sulfur atoms, the stronger NLO performances. It also has been proved that both the cluster skeletons and the heavy atoms are responsible for the NLO effects [30], but which one plays more important role is still not clear and needs to be further explored. The  $\gamma$  value in the table indicates that the title compounds have nicer third-order NLO performance, and displays reverse saturation absorption ( $\alpha_2 > 0$ ) and self-defocusing property ( $n_2 < 0$ ). The material possessing the self-defocusing performance may be an excellent one for the application in protection of optical sensors. As for the interrelation between structure and optical performance, we can attribute the nicer NLO properties of the title compounds to the crystal structures and the presence of large delocalized electron cloud in the cluster skeleton and ligands of the compounds. This very fact strongly implies that the heterothiometallic clusters may be designed and synthesized to obtain predictable and controllable NLO properties.

#### 4. Supplementary data

Supplementary data have been deposited with the Cambridge Crystallographic Centre, CCDC No. 240648 for **1** and No. 240649 for **2**. 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; E-mail address: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

#### Acknowledgments

This research was supported by grants from the National Natural Science Foundation of China (Nos. 20271021 and 20333070) and the State Key Basic Research Project of China (No. 2001CB 108906).

#### References

- [1] C. Simonnet-Jégat, F. Sécheresse, Chem. Rev. 9 (2001) 2601.
- [2] (a) D. Coucouvanis, Adv. Inorg. Chem. 45 (1998) 1;  
(b) E.I. Stiefel, in: E.I. Stiefel, K. Matsumoto (Eds.), Transition Metal Sulfur Chemistry, Biological and Industrial Significance, ACS Symposium Series 653, American Chemical Society, Washington, DC, 1996, pp. 2–38.
- [3] T.G. Spiro (Ed.), Molybdenum Enzymes, Wiley, New York, 1985.
- [4] E.I. Stiefel, D. Coucouvanis, W.E. Newton (Eds.), Molybdenum Enzymes, Cofactors and Model Systems, ACS Symposium Series 535, American Chemical Society, Washington, DC, 1993.
- [5] (a) H. Topsoe, B.S. Clausen, Catal. Rev.—Sci. Eng 26 (1984) 395;  
(b) R.R. Chianelli, M. Daage, M.J. Ledoux, Adv. Catal. 40 (1994) 177.
- [6] (a) D.A. Vivic, W.D. Jones, J. Am. Chem. Soc. 121 (1999) 7606;  
(b) M. Cindrić, V. Vrdoljak, N. Strukan, P. Tepeš, P. Novak, A. Brbot-Šaranović, G. Giester, B. Kamenar, Eur. J. Inorg. Chem. 8 (2002) 2182;  
(c) A.J. Arce, Y. De Sanctis, A. Karam, A.J. Deeming, Angew. Chem. Int. Ed. Engl. 116 (1994) 1459.
- [7] (a) R.H. Holm, Chem. Soc. Rev. 10 (1981) 455;  
(b) D. Coucouvanis, Acc. Chem. Res. 14 (1981) 201.
- [8] (a) B. Fischer, H. Schmalle, E. Dubker, Inorg. Chem. 34 (1995) 5726;  
(b) R. Hille, Chem. Rev. 96 (1996) 2757.
- [9] M.J. Johnson, D.C. Rees, M.W.W. Adams, Chem. Rev. 96 (1996) 2817.
- [10] A.G. Wedd, Coord. Chem. Rev. 5 (1996) 154.
- [11] R.H. Holm, J. Am. Chem. Soc. 120 (1998) 3259.
- [12] K. Sung, R.H. Holm, Inorg. Chem. 39 (2000) 1275.
- [13] M.L. Mader, M.D. Carducci, J.H. Enemark, Inorg. Chem. 39 (2000) 525.
- [14] T. Shibahara, Coord. Chem. Rev. 123 (1993) 73.
- [15] E.I. Stiefel, in: S.J. Lippard (Ed.), Progress in Inorganic Chemistry, vol. 22, Wiley-Interscience, New York, 1977, p. 1.
- [16] J.M. Manoli, C. Potvin, Inorg. Chem. Acta 133 (1987) 27.
- [17] E.I. Stiefel, Prog. Chem. 22 (1975) 1.

- [18] J.W. McDonald, G.D. Friesen, L.D. Rosenhein, W.E. Newton, *Inorg. Chim. Acta* 72 (1983) 205.
- [19] D. Coucouvanis, M.E. Draganjac, S.M. Koo, A. Toupadakis, A.I. Hadjikyriacou, *Inorg. Chem.* 31 (1992) 1186.
- [20] C. Simonnet-Je'gat, E. Cadusseau, R. Dessapt, F. Se'cheresse, *Inorg. Chem.* 38 (1999) 2335.
- [21] T. Shibahara, *Coord. Chem. Rev.* 123 (1993) 73.
- [22] F.A. Cotton, R.A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York, 1982.
- [23] S.F. Lu, J.Q. Huang, H.B. Chen, Q.J. Wu, *Acta Chim. Sin.* 51 (1993) 885 (in Chinese).
- [24] K. Unoura, T. Suzuki, A. Nagasawa, A. Yamazaki, Y. Fukuda, *Inorg. Chem. Acta* 292 (1999) 7.
- [25] J.T. Huneke, K. Yamanouchi, J.H. Enemark, *Inorg. Chem.* 17 (1978) 3695.
- [26] C. Zhang, Y.L. Song, F.E. Kuhn, Y. Xu, X.Q. Xin, H.K. Fun, W.A. Herrmann, *Eur. J. Inorg. Chem.* (2002) 55.
- [27] A. Muller, H. Bogge, U. Schimanski, *Inorg. Chim. Acta* 69 (1983) 5.
- [28] Y. Li, J. Lu, J.Q. Xu, X.B. Cui, Y.H. Sun, Q.X. Yang, L.Y. Pan, *J. Mol. Struct.* 690 (2004) 131.
- [29] H.G. Zheng, W.L. Tan, M.K.L. Low, W. Ji, D.L. Long, W.T. Wong, K.B. Yu, X.Q. Xin, *Polyhedron* 18 (1999) 3115.
- [30] C. Zhang, Y.L. Song, B.M. Fung, Z.L. Xue, X.Q. Xin, *Chem. Commun.* (2001) 843.