

# Synthesis of Two Heterobimetallic Cluster Isomers $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_3\text{S}(\text{CuI})_2]$ and $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuI})_2]$ from *trans*- $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu\text{-S})_2\text{S}_2]$ and Their *trans*-to-*cis* Isomerization, Structures, and Third-Order NLO Properties

Zhi-Gang Ren,<sup>†</sup> Hong-Xi Li,<sup>†</sup> Guang-Fei Liu,<sup>†</sup> Wen-Hua Zhang,<sup>†</sup> Jian-Ping Lang,<sup>\*,†,‡</sup>  
 Yong Zhang,<sup>†</sup> and Ying-Lin Song<sup>\*,§</sup>

School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, Jiangsu, People's Republic of China, State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China, and School of Physical Science and Technology, Suzhou University, Suzhou 215006, Jiangsu, People's Republic of China

Received April 14, 2006

Reaction of *trans*- $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu\text{-S})_2\text{S}_2]$  (**1**) with 2 equiv of CuI in  $\text{CH}_2\text{Cl}_2$  at ambient temperature or in refluxing MeCN afforded two isomeric clusters,  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_3\text{S}(\text{CuI})_2]$  (**2**) and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuI})_2]$  (**3**). Compound **3** could also be prepared either by refluxing an acetonitrile solution of **2** or by heating **2** in the solid state at 120 °C. Compounds **2** and **3** were fully characterized by elemental analysis, IR, UV–vis, <sup>1</sup>H NMR, ESI-MS, and single-crystal X-ray crystallography. The molecular structure of **2** consists of an incomplete cubane-like core in which the *trans* structure of **1** was retained, while that of **3** contains a cubane-like core in which the *trans* structure of **1** was converted into the *cis* structure. The *trans*-to-*cis* isomerization from **2** to **3** either in solution or in the solid state was explored by means of <sup>1</sup>H NMR spectroscopy or X-ray powder diffraction. In addition, the third-order nonlinear optical (NLO) properties of **1–3** in  $\text{CH}_2\text{Cl}_2$  were investigated by using the Z-scan technique. The hyperpolarizability  $\gamma$  values for the two isomers ( $5.65 \times 10^{-30}$  esu (**2**) and  $1.18 \times 10^{-29}$  esu (**3**)) are larger than that of their cluster precursor **1** ( $3.07 \times 10^{-30}$  esu).

## Introduction

The chemistry of clusters consisting of  $[\text{M}_2\text{S}_4]$  (M = Mo, W) cores and transition metals has been of considerable interest because of their rich structural chemistry<sup>1–9</sup> and their potential applications in the industrial hydrodesulfurization (HDS) process,<sup>2</sup> simulating the active site of nitrogenase,<sup>3</sup> and the hydrogenation of unsaturated bonds.<sup>4</sup> In many cases, various

transition metals usually were used to react with species containing  $[\text{M}_2\text{S}_4]$  cores to form various  $[\text{M}_2\text{S}_4\text{M}'_2]$  (M' = Co, Ni, Fe, Cu, Ir, Rh, Pt, Pd) clusters. Among the limited copper complexes,<sup>7–9</sup> one intriguing example is a cubane-like cluster,  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuCl})_2]$ , which was prepared by refluxing a solution containing *trans*- $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu\text{-S})_2\text{S}_2]$  (**1**) and 2 equiv of CuCl in toluene.<sup>7</sup> During this reaction, the original *trans* structure of **1** was converted into its *cis* structure in the cubane-like cluster. However, the mechanism of the *trans*-to-*cis* conversion was not elucidated.

Recently, we have been interested in the preparations of Mo-(W)/Cu/S clusters with the aim of constructing cluster-based supramolecular assemblies<sup>10</sup> and investigating their third-order nonlinear optical (NLO) properties.<sup>11</sup> As clusters derived from tetrathiometalates and pentamethylcyclopentadienyl-coordinated thiometalates have been extensively investigated,<sup>12–15</sup> we have turned our attention to other clusters containing **1** and to related ones. In fact, the chemistry of Mo/Cu/S clusters with **1** has been less explored, and their third-order NLO properties are virtually unknown. As described later in this paper, **1** exhibited relatively

\* Corresponding author. Tel: 86-512-65882865. Fax: 86-512-65880089. E-mail: jplang@suda.edu.cn.

<sup>†</sup> School of Chemistry and Chemical Engineering, Suzhou University.

<sup>‡</sup> Shanghai Institute of Organic Chemistry.

<sup>§</sup> School of Physical Science and Technology, Suzhou University.

(1) Kuwata, S.; Hidai, M. *Coord. Chem. Rev.* **2001**, *213*, 211.

(2) (a) Curtis, M. D.; Druker, S. H. *J. Am. Chem. Soc.* **1997**, *119*, 1027.

(b) Curtis, M. D.; Druker, S. H.; Goossen, L.; Kampf, J. W. *Organometallics* **1997**, *16*, 231. (c) Mansour, M. A.; Curtis, M. D.; Kampf, J. W. *Organometallics* **1995**, *14*, 5460. (d) Curtis, M. D.; Williams, P. D.; Butler, W. M. *Inorg. Chem.* **1988**, *27*, 2853.

(3) (a) Nishibayashi, Y.; Wakiji, I.; Hirata, K.; DuBois, M. R.; Hidai, M. *Inorg. Chem.* **2001**, *40*, 578. (b) Seino, H.; Masumori, T.; Hidai, M.; Mizobe, Y. *Organometallics* **2003**, *22*, 3424.

(4) (a) Birnbaum, J.; DuBois, M. R. *Organometallics* **1994**, *13*, 1014. (b) Allshouse, J.; Kaul, B. B.; DuBois, M. R. *Organometallics* **1994**, *13*, 28. (c) Bernatis, P.; Laurie, J. C. V.; DuBois, M. R. *Organometallics* **1990**, *9*, 1607. (d) Birnbaum, J.; DuBois, M. R. *Organometallics* **1994**, *13*, 1014.

(5) (a) Hidai, M.; Kuwata, S.; Mizobe, Y. *Acc. Chem. Res.* **2000**, *33*, 46. (b) Takei, I.; Suzuki, K.; Enta, Y.; Dohki, K.; Suzuki, T.; Mizobe, Y.; Hidai, M. *Organometallics* **2003**, *22*, 1790. (c) Ikada, T.; Mizobe, Y.; Hidai, M. *Organometallics* **2001**, *20*, 4441.

(6) (a) Coons, D. E.; Laurie, J. C. V.; Haltiwanger, R. C.; DuBois, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 283. (b) Gabay, J.; Dietz, S.; Bernatis, P.; DuBois, M. R. *Organometallics* **1993**, *12*, 3630. (c) Weberg, R. T.; Haltiwanger, R. C.; Laurie, J. C. V.; DuBois, M. R. *J. Am. Chem. Soc.* **1986**, *108*, 6242.

(7) Brunner, H.; Grassl, R.; Wachter, J. Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1990**, *393*, 119.

(8) (a) Lin, P.; Wu, X. T.; Huang, Q.; Wang, Q. M.; Sheng, T. L.; Zhang, W. J.; Guo, J.; Lu, J. X. *Inorg. Chem.* **1998**, *37*, 5672. (b) Lin, P.; Wu, X. T.; Zhang, W. J.; Guo, J.; Sheng, T. L.; Lu, J. X. *Chem. Commun.* **1997**, 1349. (c) Zhu, N. Y.; Zheng, Y. F.; Wu, X. T. *J. Chem. Soc., Chem. Commun.* **1990**, 780.

(9) Wei, Z. H.; Xu, Q. F.; Li, H. X.; Chen, J. X.; Lang, J. P. *J. Organomet. Chem.* **2003**, *687*, 197.

(10) (a) Lang, J. P.; Kawaguchi, H.; Tatsumi, K. *Chem. Commun.* **1999**, 2315. (b) Lang, J. P.; Xu, Q. F.; Chen, Z. N.; Abrahams, B. F. *J. Am. Chem. Soc.* **2003**, *125*, 12682. (c) Lang, J. P.; Xu, Q. F.; Yuan, R. X.; Abrahams, B. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4741. (d) Lang, J. P.; Jiao, C. M.; Qiao, S. B.; Zhang W. H.; Abrahams, B. F. *Inorg. Chem.* **2005**, *44*, 3664.

good third-order NLO properties in  $\text{CH}_2\text{Cl}_2$ . Is it possible to incorporate other metals into the  $[\text{Mo}_2\text{S}_4]$  core of **1** so as to change or improve the NLO performances of **1**? With this question in mind, we carried out the reactions of **1** with 2 equiv of  $\text{CuI}$  in  $\text{CH}_2\text{Cl}_2$  at ambient temperature. To our surprise, we isolated by column chromatography on silica an incomplete cubane-like cluster,  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_3\text{S}(\text{CuI})_2]$  (**2**), in which the original *trans* structure of **1** was retained. Compound **2** could be converted readily into its *cis* isomer  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuI})_2]$  (**3**) by heating it either in solution or in the solid state. Compounds **2** and **3** in  $\text{CH}_2\text{Cl}_2$  showed better NLO effects than those of their cluster precursor **1**. In this paper, we report their synthesis, *trans*-to-*cis* isomerization, crystal structures, and third-order NLO properties.

## Experimental Section

**General Procedures.** All manipulations were performed under an argon atmosphere using standard Schlenk-line techniques. Compound **1** was prepared according to the literature method.<sup>7</sup> Acetonitrile and other solvents were predried over activated molecular sieves and refluxed over  $\text{P}_2\text{O}_5$  under argon. All other chemicals were used as purchased.  $^1\text{H}$  NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer.  $^1\text{H}$  NMR chemical shifts were referenced to TMS in  $\text{CDCl}_3$  or to the solvent signal in  $\text{DMSO-}d_6$ . XRD patterns were carried out on a Rigaku D/MAX-III C X-ray diffractometer. Electrospray ion mass spectra (ESI-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane/methanol as mobile phase. IR spectra were recorded on a Nicolet MagNa-IR spectrometer (4000–400  $\text{cm}^{-1}$ ). Electronic spectra were measured on a Hitachi U-2810 spectrophotometer. Elemental analyses for C, H, and N were performed on a Carlo-Erba CHNO-S microanalyzer.

**Preparation of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_3\text{S}(\text{CuI})_2]$  (**2**).** Compound **1** (30 mg, 0.05 mmol) and  $\text{CuI}$  (19 mg, 0.10 mmol) were mixed and ground in an agate mortar at ambient temperature for 10 min. The resulting mixture was dissolved in 2 mL of  $\text{CH}_2\text{Cl}_2$ , forming

a dark brown solution. The solution was then separated by column chromatography on silica. On elution with  $\text{CH}_2\text{Cl}_2$ , the component in the first band was confirmed to be a small amount of unreacted **1**. The component in the second band was recrystallized from  $\text{CH}_2\text{Cl}_2/n$ -hexane (1:3) to afford dark brown prisms of **2**. Yield: 39 mg (80% based on Mo). Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{Cu}_2\text{I}_2\text{Mo}_2\text{S}_4$ : C, 24.73; H, 3.11. Found: C, 24.69; H, 3.15. MS (ESI):  $m/z$  972.1 (**2** +  $\text{H}^+$ ). IR (KBr disk): 2954 (m), 2904 (m), 1475 (m), 1420 (m), 1375 (s), 1018 (m), 737 (m), 501 (s), 424 (w)  $\text{cm}^{-1}$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm ( $\epsilon$   $\text{M}^{-1}$   $\text{cm}^{-1}$ )): 240 (31 500), 260 (26 500), 348 (16 600), 484 (3800).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  2.029 (s, 15H,  $-\text{CH}_3$ ), 2.237 (s, 15H,  $-\text{CH}_3$ ).

**Preparation of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuI})_2]$  (**3**).** A suspension containing **1** (30 mg, 0.05 mmol) and  $\text{CuI}$  (19 mg, 0.10 mmol) in 4 mL of MeCN was heated at reflux for 20 h, forming a dark green solution. After cooling to room temperature, the resulting mixture was concentrated to dryness in vacuo, and the components were separated by column chromatography on silica. Elution with  $\text{CH}_2\text{Cl}_2$  gave a brown band containing **2** (10 mg, 20% based on Mo). The component in the second green band was eluted with  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  (8:1). The green solution was concentrated to ca. 2 mL in vacuo and then layered by  $\text{Et}_2\text{O}$  (8 mL) for two weeks to form dark green needles of  $3 \cdot 2\text{CH}_2\text{Cl}_2$ . Yield: 39 mg (68% based on Mo). Anal. Calcd for  $\text{C}_{22}\text{H}_{34}\text{Cu}_2\text{Cl}_4\text{I}_2\text{Mo}_2\text{S}_4$ : C, 23.15; H, 3.00. Found: C, 23.24; H, 3.06. MS (ESI):  $m/z$  972.0 (**3** +  $\text{H}^+$ ). IR (KBr disk): 2956 (m), 2910 (m), 1622 (m), 1479 (m), 1423 (m), 1378 (s), 1021 (m), 869 (m), 449 (w)  $\text{cm}^{-1}$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm ( $\epsilon$   $\text{M}^{-1}$   $\text{cm}^{-1}$ )): 232 (53 400), 268 (31 100), 296 (27 300), 388 (9700), 428 (7200), 480 (4500).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  2.071 (s, 30H,  $-\text{CH}_3$ ).

**Conversion of **2** to **3** in MeCN.** **2** (30 mg, 0.03 mmol) was dissolved in 4 mL of MeCN and then heated at reflux for 20 or 40 h. After the solution was cooled to room temperature, a similar workup produced 14.4 mg (48%) of **2** and 15.5 mg (44%) of  $3 \cdot 2\text{CH}_2\text{Cl}_2$  for the 20 h reaction product and 3 mg (10%) of **2** and 26 mg (74%) of  $3 \cdot 2\text{CH}_2\text{Cl}_2$  for the 40 h reaction product.

**Conversion of **2** to **3** in the Solid State.** Powdered **2** (30 mg, 0.03 mmol) was placed in a glass tube and then heated in an oil bath at 120 °C for 20 h. After the reaction product had cooled to room temperature, a similar workup afforded 11.2 mg (37%) of **2** and 18.1 mg (53%) of  $3 \cdot 2\text{CH}_2\text{Cl}_2$ .

**X-ray Crystallography.** All measurements were performed on a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) at  $-80$  °C, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å). A dark brown prism of **2** with dimensions  $0.22 \times 0.20 \times 0.15$  mm and a dark green needle of  $3 \cdot 2\text{CH}_2\text{Cl}_2$  with dimensions  $0.42 \times 0.13 \times 0.05$  mm were mounted on glass fibers with grease. Diffraction data were collected at  $\omega$  mode with a detector distance of 35 mm to the crystal. Indexing was performed from six images, each of which was exposed for 15 s. A total of 720 oscillation images for each were collected in the range  $6.13^\circ < 2\theta < 50.70^\circ$  for **2** and  $6.09^\circ < 2\theta < 50.70^\circ$  for  $3 \cdot 2\text{CH}_2\text{Cl}_2$ . The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver. 1.3, 2001), and an absorption correction (multiscan) was applied, which resulted in transmission factors ranging from 0.358 to 0.490 for **2** and from 0.498 to 0.812 for  $3 \cdot 2\text{CH}_2\text{Cl}_2$ . The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **2** and **3** were solved by direct methods<sup>16a</sup> and expanded using Fourier techniques.<sup>16b</sup> All non-hydrogen atoms were refined anisotropically. Three methyl groups of  $\eta^5\text{-C}_5\text{Me}_5$  groups and a Cl atom of one solvated  $\text{CH}_2\text{Cl}_2$  molecule in  $3 \cdot 2\text{CH}_2\text{Cl}_2$  were found to be disordered over two sites with an occupancy

(11) (a) Shi, S.; Ji, W.; Tang, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 3615. (b) Shi, S.; Ji, W.; Lang, J. P.; Xin, X. Q. *J. Phys. Chem.* **1994**, *98*, 3570. (c) Shi, S.; Ji, W.; Xie, W.; Chong, T. C.; Zheng, H. C.; Lang, J. P.; Xin, X. Q. *Mater. Chem. Phys.* **1995**, *39*, 298. (d) Lang, J. P.; Tatsumi, K.; Kawaguchi, H.; Lu, J. M.; Ge, P.; Ji, W.; Shi, S. *Inorg. Chem.* **1996**, *35*, 7924. (e) Yu, H.; Xu, Q. F.; Sun, Z. R.; Ji, S. J.; Chen, J. X.; Liu, Q.; Lang, J. P.; Tatsumi, K. *Chem. Commun.* **2001**, 2614. (f) Lang, J. P.; Sun, Z. R.; Xu, Q. F.; Yu, H.; Tatsumi, K. *Mater. Chem. Phys.* **2003**, *82*, 493. (g) Lang, J. P.; Xu, Q. F.; Ji, W.; Elim, H. I.; Tatsumi, K. *Eur. J. Inorg. Chem.* **2004**, 86. (h) Yu, H.; Zhang, W. H.; Ren, Z. G.; Chen, J. X.; Wang, C. L.; Lang, J. P.; Elim, H. I.; Ji, W. *J. Organomet. Chem.* **2005**, *690*, 4027. (i) Zhang, W. H.; Chen, J. X.; Li, H. X.; Wu, B.; Tang, X. Y.; Ren, Z. G.; Zhang, Y.; Lang, J. P.; Sun, Z. R. *J. Organomet. Chem.* **2005**, *690*, 394.

(12) (a) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed.* **1981**, *20*, 934. (b) Sarkar, S.; Mishra, S. B. S. *Coord. Chem. Rev.* **1984**, *59*, 239. (c) Müller, A.; Bögge, H.; Schimanski, U.; Penk, M.; Nieradzki, K.; Dartmann, M.; Krickemeyer, E.; Schimanski, J.; Römer, C.; Römer, M.; Dornfeld, H.; Wienböcker, U.; Hellmann, W. *Monatsh. Chem.* **1989**, *120*, 367. (d) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223. (e) Jeannin, Y.; Séheresse, F.; Bernés, S.; Robert, F. *Inorg. Chim. Acta* **1992**, *198–200*, 493.

(13) (a) Stiefel, E. I.; Coucouvanis, D.; Newton, W. E. *Molybdenum Enzymes, Cofactors and Model Systems*; ACS Symp. Ser. 535; American Chemical Society: Washington, DC, 1993. (b) Wu, X. T.; Chen, P. C.; Du, S. W.; Zhu, N. Y.; Lu, J. X. *J. Cluster Sci.* **1994**, *5*, 265. (c) Stiefel, E. I.; Matsumoto, K. *Transition Metal Sulfur Chemistry, Biological and Industrial Significance*; ACS Symp. Ser. 653; American Chemical Society: Washington, DC, 1996.

(14) (a) Wu, D. X.; Hong, M. C.; Cao, R.; Liu, H. Q. *Inorg. Chem.* **1996**, *35*, 1080. (b) Che, C. M.; Xia, B. H.; Huang, J. S.; Chan, C. K.; Zhou, Z. Y.; Cheung, K. K. *Chem. Eur. J.* **2001**, *7*, 3998. (c) Zhang, C.; Song, Y. L.; Kühn, F. E.; Xu, Y.; Xin, X. Q.; Fun, H. K.; Herrmann, W. A. *Eur. J. Inorg. Chem.* **2002**, 55. (d) Zhang, W. J.; Behrens, A.; Gätjens, J.; Ebel, M.; Wu, X. T.; Rehder, D. *Inorg. Chem.* **2004**, *43*, 3020.

(15) Lang, J. P.; Ji, S. J.; Xu, Q. F.; Shen Q.; Tatsumi, K. *Coord. Chem. Rev.* **2003**, *241*, 47.

(16) (a) Sheldrick, G. M. *SHELXS-97, Program for X-ray Crystal Structure Solution*; University of Göttingen: Germany, 1997. (b) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *DIRDIF99, The DIRDIF-99 Program System*, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1999.

**Table 1. Summary of Crystallographic Data of 2 and 3·2CH<sub>2</sub>Cl<sub>2</sub>**

	2	3·2CH <sub>2</sub> Cl <sub>2</sub>
chemical formula	C <sub>20</sub> H <sub>30</sub> Cu <sub>2</sub> I <sub>2</sub> Mo <sub>2</sub> S <sub>4</sub>	C <sub>22</sub> H <sub>34</sub> Cu <sub>2</sub> Cl <sub>4</sub> I <sub>2</sub> Mo <sub>2</sub> S <sub>4</sub>
fw	971.48	1141.34
cryst syst	orthorhombic	triclinic
space group	<i>Pnma</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	21.656(3)	8.9036(18)
<i>b</i> (Å)	15.7285(13)	10.776(2)
<i>c</i> (Å)	8.4351(9)	20.028(4)
$\alpha$ (deg)		83.35(3)
$\beta$ (deg)		87.73(3)
$\gamma$ (deg)		68.51(3)
<i>V</i> (Å <sup>3</sup> )	2873.1(6)	1776.0(6)
<i>Z</i>	4	2
<i>D</i> <sub>calc</sub> (g·cm <sup>-3</sup> )	2.246	2.134
<i>F</i> (000)	1848	1092
$\mu$ (Mo K $\alpha$ , cm <sup>-1</sup> )	47.61	41.59
total no. of reflns	27 181	17 483
no. of unique reflns	2723	6456
no. of obsd reflns	2620	5619
[ <i>I</i> > 2.00 $\sigma$ ( <i>I</i> )]		
no. of variables	155	370
<i>R</i> <sup>a</sup>	0.0244	0.0349
<i>R</i> <sub>w</sub> <sup>b</sup>	0.0501	0.0813
GOF <sup>c</sup>	1.227	1.070
residual peaks (e/Å <sup>3</sup> )	0.613, -0.493	1.944, -0.814

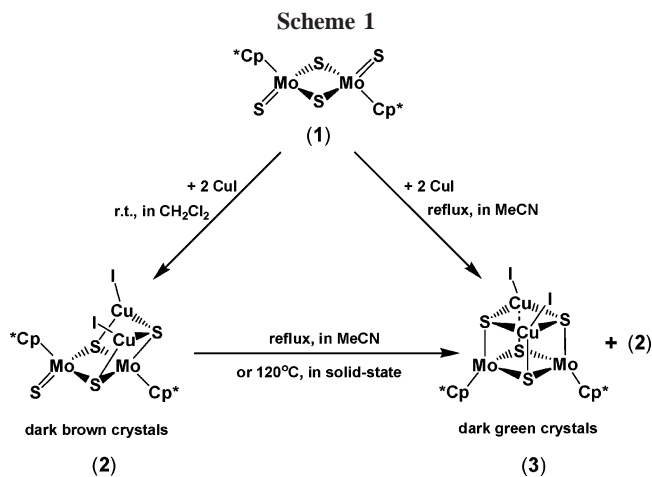
<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^3 \}^{1/2}$ . <sup>c</sup>  $GOF = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$ , where *n* = number of reflections and *p* = total number of parameters refined.

factor of 0.60/0.40 for C17/C17A, C18/C18A, and C19/C19A and 0.44/0.56 for C12/C12A. All other hydrogen atoms were placed in geometrically idealized positions (C–H = 0.98 Å for methyl groups) and constrained to ride on their parent atoms with  $U_{iso}(H) = 1.2U_{eq}(C)$ . All the calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku/MSK, Ver. 3.60, 2004). Important crystal and data collection parameters for **2** and **3**·2CH<sub>2</sub>Cl<sub>2</sub> are summarized in Table 1.

**Nonlinear Optical Measurements.** The CH<sub>2</sub>Cl<sub>2</sub> solutions of **1**, **2**, and **3** were placed in a 2 mm quartz cuvette for NLO measurements. The clusters were stable toward air and laser light under the experimental conditions. The nonlinear absorption and refraction were investigated with a linearly polarized laser light ( $\lambda = 532$  nm; pulse widths = 8 ns; repetition rate = 1 Hz) provided by a frequency-doubled, mode-locked, Q-switched 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 30 cm focal length focusing mirror. The radius of the beam waist was measured to be  $35 \pm 5$   $\mu$ m (half-width at  $1/e^2$  maximum). The incident and transmitted pulse energies were measured simultaneously by two energy detectors (Laser Precision Rjp-735), which were linked to a computer by an IEEE interface.<sup>17</sup> The NLO properties of the samples were manifested by moving the samples along the axis of the incident laser irradiance beam (*z*-direction) with respect to the focal point and with incident laser irradiance kept constant (*Z*-scan methods). The closed-aperture curves are normalized to the open-aperture curves. An aperture of 0.2 mm radius was placed in front of the detector to measure the transmitted energy when assessment of laser beam distortion was needed. To eliminate scattering effects, a lens was mounted after the samples to collect the scattered light.

## Results and Discussion

**Synthesis and Characterization.** Compound **1** was mixed with 2 equiv of CuI and ground at ambient temperature for 10



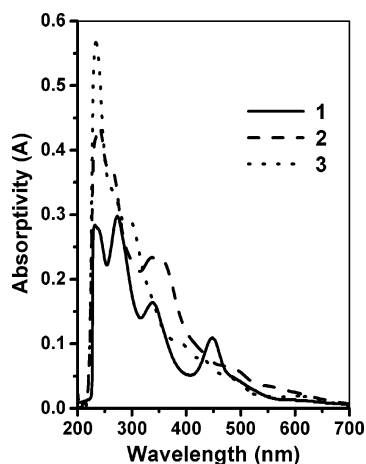
min. It seems that no reaction took place according to XRD patterns of the mixtures before and after grinding (see Figure S1). When the solid mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the two compounds reacted rapidly to form a dark brown solution (Scheme 1). Column chromatography on silica was used to separate a small amount of the unreacted **1** and the major product **2** (80% yield). On the other hand, when the suspension of **1** and 2 equiv of CuI were heated at reflux in MeCN for 20 h, the color of the solution changed slowly from dark brown to dark green. Column chromatography on silica was used to separate the major product **3** (68% yield) and the minor product **2** (20% yield). Furthermore, compound **3** could be readily produced in higher yields by refluxing the acetonitrile solution of **2** for up to 40 h or directly heating solid **2** at 120 °C for 20 h.

Compounds **2** and **3**·2CH<sub>2</sub>Cl<sub>2</sub> were relatively stable toward air and moisture and readily soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, or DMSO, slightly soluble in MeCN, benzene, or acetone, and insoluble in Et<sub>2</sub>O and hexane. In the case of **3**·2CH<sub>2</sub>Cl<sub>2</sub>, the two solvated CH<sub>2</sub>Cl<sub>2</sub> molecules can be removed in vacuo at 60 °C. The elemental analysis was consistent with the chemical formula of **2** and **3**·2CH<sub>2</sub>Cl<sub>2</sub>. In the IR spectrum of **2**, bands at 501 and 424 cm<sup>-1</sup> may be assigned as the terminal Mo=S and the bridging Mo–S stretching vibrations, respectively.<sup>18a</sup> The IR spectrum of **3** showed only one weak bridging Mo–S stretching vibration at 449 cm<sup>-1</sup>. The UV–vis spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub> was characterized by four bands, while those of **2** and **3** had four absorptions for **2** and six absorptions for **3** (Figure 1). Relative to the bands at 338 and 448 nm (**1**), those at 348 and 484 nm (**2**) and 388, 428 and 480 nm (**3**) are red-shifted, and they are probably dominated by the S→Mo(V) charge-transfer transitions of the [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>S<sub>4</sub>] moiety.<sup>18b</sup> The <sup>1</sup>H NMR spectrum of **2** in CDCl<sub>3</sub> at room temperature showed two sharp singlets due to the protons of two  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> groups at 2.029 and 2.237 ppm, while that of **3** had one singlet due to the protons of  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> at 2.071 ppm (see Figures S3 and S4). The positive ion ESI mass spectra of **2** or **3** (see Figures S8 and S9) exhibited the protonated parent molecular ion signal at *m/z* = 972.1 for **2** + H<sup>+</sup> or at *m/z* = 972.0 for **3** + H<sup>+</sup>. The identities of **2** and **3**·2CH<sub>2</sub>Cl<sub>2</sub> were further confirmed by single-crystal X-ray analysis.

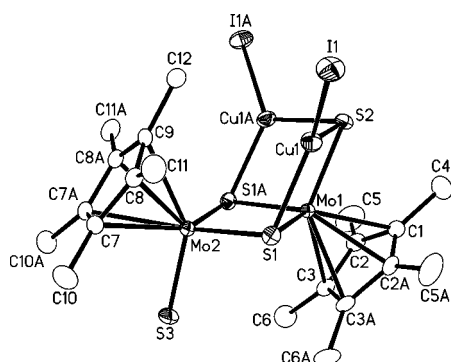
**Crystal Structures of 2 and 3·2CH<sub>2</sub>Cl<sub>2</sub>.** Compound **2** crystallizes in the orthorhombic space group *Pnma*, and the asymmetric unit contains half of the [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>( $\mu_3$ -S)<sub>3</sub>S-

(17) (a) Sherk-Bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760. (b) Sherk-Bahae, M.; Said A. A.; Van Stryland, E. W. *Opt. Lett.* **1989**, *14*, 955.

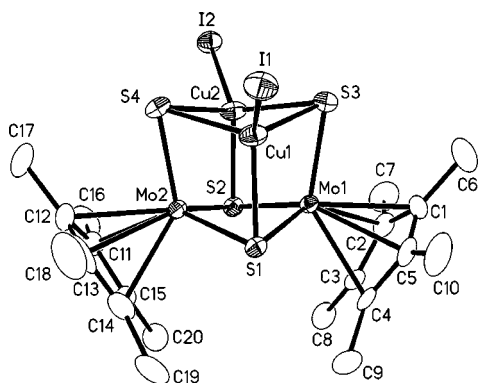
(18) (a) Bruce, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 3433. (b) Kawaguchi, H.; Yamada, K.; Lang, J. P.; Tatsumi, K. *J. Am. Chem. Soc.* **1997**, *119*, 10346.



**Figure 1.** Electronic spectra of **1** ( $1.08 \times 10^{-5}$  M), **2** ( $1.40 \times 10^{-5}$  M), and **3** ( $1.07 \times 10^{-5}$  M) in  $\text{CH}_2\text{Cl}_2$  in a 1 cm thick glass cell.



**Figure 2.** View of **2** with labeling scheme and 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.



**Figure 3.** View of **3**, where only the disordered C17–C19 atoms with a site occupancy factor of 0.60 are shown. The thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

(CuI)<sub>2</sub> molecule, while compound **3**·2CH<sub>2</sub>Cl<sub>2</sub> crystallizes in the triclinic space group  $P\bar{1}$  and the asymmetric unit contains one independent  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu\text{-S})_4(\text{CuI})_2]$  molecule and two CH<sub>2</sub>Cl<sub>2</sub> solvate molecules. Figures 2 and 3 show perspective views of the molecular structures of **2** and **3**, and Tables 2 and 3 list their selected bond lengths and angles, respectively. The formal oxidation states for the Cu and Mo atoms in **2** and **3** are assumed to be +1 and +5, respectively. **2** consists of one *trans*- $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu\text{-S})_2\text{S}_2]$  moiety and two CuI units that are held together by four Cu– $\mu_3$ -S bonds, forming an incomplete cubane-like [Mo<sub>2</sub>S<sub>4</sub>Cu<sub>2</sub>] core structure with one terminal Mo–S bond intact. There is a crystallographic mirror plane running through atoms Mo1, Mo2, S2, S3, C1, C4, C9, and C12. Such

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **2**

Mo(1)···Mo(2)	2.9359(6)	Mo(1)···Cu(1)	2.6525(5)
Mo(1)···Cu(1A)	2.6525(5)	Mo(1)–S(1A)	2.3332(9)
Mo(1)–S(1A)	2.3332(9)	Mo(1)–S(2)	2.2721(12)
Mo(2)–S(1)	2.3534(9)	Mo(2)–S(1A)	2.3534(9)
Mo(2)–S(3)	2.1202(13)	Cu(1)–S(1)	2.2385(9)
Cu(1)–S(2)	2.2145(9)	Cu(1)–I(1)	2.4496(5)
S(1)–Mo(1)–S(1A)	102.99(4)	S(1)–Mo(1)–S(2)	105.65(3)
S(1A)–Mo(1)–S(2)	105.65(3)	S(1)–Mo(2)–S(1A)	101.76(4)
S(1)–Mo(2)–S(3)	102.03(3)	S(1A)–Mo(2)–S(3)	102.03(3)
S(1)–Cu(1)–S(2)	110.99(4)	S(1)–Cu(1)–I(1)	126.83(3)
S(2)–Cu(1)–I(1)	121.72(3)		

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **3**

Mo(1)···Mo(2)	2.8456(12)	Mo(1)···Cu(1)	2.7827(11)
Mo(1)···Cu(2)	2.7870(13)	Mo(2)···Cu(1)	2.7828(9)
Mo(2)···Cu(2)	2.7802(11)	Mo(1)–S(1)	2.3267(13)
Mo(1)–S(2)	2.3269(13)	Mo(1)–S(3)	2.2346(14)
Mo(2)–S(1)	2.3271(14)	Mo(2)–S(2)	2.3233(13)
Mo(2)–S(4)	2.2275(14)	Cu(1)–S(1)	2.2522(14)
Cu(1)–S(3)	2.3959(16)	Cu(1)–S(4)	2.3831(16)
Cu(1)–I(1)	2.4821(9)	Cu(2)–S(2)	2.2522(14)
Cu(2)–S(3)	2.3874(16)	Cu(2)–S(4)	2.3922(16)
Cu(2)–I(2)	2.4861(12)		
S(1)–Mo(1)–S(2)	100.77(5)	S(1)–Mo(1)–S(3)	106.12(5)
S(2)–Mo(1)–S(3)	105.68(6)	S(1)–Mo(2)–S(2)	100.86(6)
S(1)–Mo(2)–S(4)	105.74(5)	S(2)–Mo(2)–S(4)	106.18(6)
S(1)–Cu(1)–S(3)	103.29(6)	S(1)–Cu(1)–S(4)	103.13(6)
S(1)–Cu(1)–I(1)	115.26(5)	S(3)–Cu(1)–S(4)	96.29(6)
S(3)–Cu(1)–I(1)	120.93(4)	S(4)–Cu(1)–I(1)	114.97(5)
S(2)–Cu(2)–S(3)	103.15(6)	S(2)–Cu(2)–S(4)	103.14(6)
S(2)–Cu(2)–I(2)	115.19(4)	S(3)–Cu(2)–S(4)	96.28(6)
S(3)–Cu(2)–I(2)	123.04(5)	S(4)–Cu(2)–I(2)	112.89(5)

a cluster core framework is unprecedented in the chemistry of **1** and other related species containing a [Mo<sub>2</sub>S<sub>4</sub>] core. Within the structure of **2**, the *trans* configuration of **1** is basically retained, but the Mo–S bonds are changed due to the coordination of two Cu atoms at the three S atoms. Each Cu atom adopts approximately trigonal planar geometry, coordinated by a terminal iodine atom and two  $\mu_3$ -S atoms. The mean Mo···Cu (2.6525(5) Å, Cu– $\mu_3$ -S (2.2265(9) Å), and Cu–I (2.4496(5) Å) bond lengths are comparable to those of the corresponding ones of [PPh<sub>4</sub>]<sub>2</sub>[( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)MoS<sub>3</sub>Cu<sub>3</sub>Br<sub>3</sub>]<sub>2</sub>,<sup>19a</sup> [MoOS<sub>3</sub>Cu<sub>3</sub>I(2,2'-bipy)<sub>2</sub>]<sub>2</sub>,<sup>19b</sup> and [MoOS<sub>3</sub>Cu<sub>3</sub>I(phen)<sub>2</sub>]<sub>2</sub> (phen = 1,10-phenanthroline).<sup>19c</sup> Relative to the corresponding ones in **1**,<sup>20</sup> the Mo1···Mo2 separation (2.9359(6) Å) in **2** is 0.03 Å longer than that of **1**, while the terminal Mo2–S3 bond is shortened and the change from terminal sulfido to bridging  $\mu_3$ -sulfido increases the Mo1–S2 bond length from 2.144(2) to 2.2721(12) Å. For the two S atoms bridging two Mo atoms, an increase in their Mo–S bond lengths is also observed from an average of 2.299(2) to 2.3433(9) Å. The mean Mo–S length (2.3196(9) Å) is slightly longer than that in [PPh<sub>4</sub>]<sub>2</sub>[( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)MoS<sub>3</sub>-Cu<sub>3</sub>Br<sub>3</sub>]<sub>2</sub> (2.230(2) Å).

The molecular structure of **3** closely resembles that of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuCl})_2]$ <sup>7</sup> and  $[(\text{dte})_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuBr})_2]$  (dte = diethyldithiocarbamate).<sup>9</sup> The mean Mo···Cu contact (2.7832(11) Å) and Cu– $\mu_3$ -S (2.3438(14) Å) and Mo– $\mu_3$ -S (2.2943(13) Å) bond lengths are close to those of the corresponding ones of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mo}_2(\mu_3\text{-S})_4(\text{CuCl})_2]$ . The Mo1···Mo2 contact (2.8456(12) Å) is longer than that of  $[(\text{dte})_2\text{Mo}_2(\mu_3\text{-S})_4$

(19) (a) Lang, J. P.; Kawaguchi, H.; Ohniski, S.; Tatsumi, K. *Inorg. Chim. Acta* **1998**, *283*, 136. (b) Li, Y.; Lu, J.; Xu, J. Q.; Cui, X. B.; Sun, Y. H.; Yang, Q. Q.; Pan, L. Y. *J. Mol. Struct.* **2004**, *690*, 131. (c) Hou, H. W.; Ang, H. G.; Ang, S. G.; Fan, Y. T.; Low, M. K. M.; Ji, W.; Lee, Y. W. *Inorg. Chim. Acta* **2000**, *299*, 147.

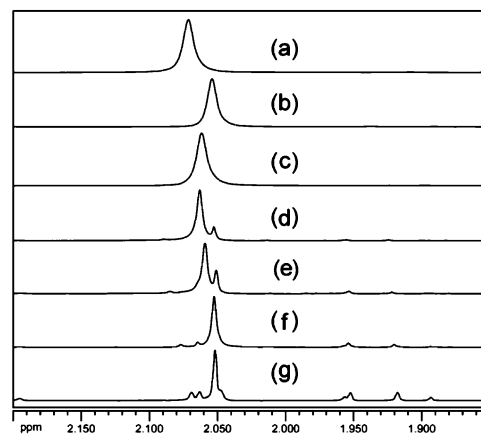
(20) Dubois, M. R.; Dubois, D. L.; Vanderveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

(CuBr)<sub>2</sub>] (2.766(2) Å), but comparable to those in other Mo<sub>2</sub>S<sub>2</sub>M'<sub>2</sub> cubane-like clusters (M' = Cu, 2.865(1) Å,<sup>8c</sup> M' = Fe, 2.822(2) Å,<sup>21a</sup> M' = Co, 2.838(1) Å,<sup>2b</sup> M' = Ni, 2.829(2) Å<sup>21b</sup>). The mean terminal Cu–I length (2.4842(9) Å) is similar to those of clusters containing tetrahedrally coordinated Cu.<sup>22</sup>

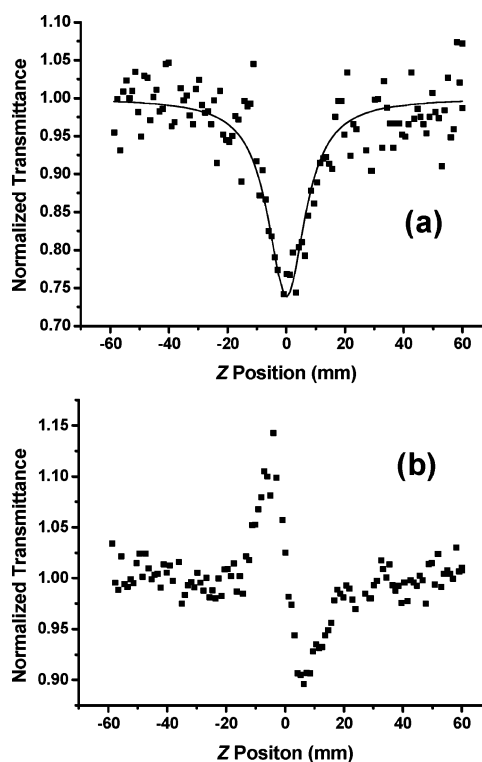
**Trans-to-Cis Isomerization.** The *cis*–*trans* isomerizations of coordination compounds either in solution<sup>23–25</sup> or in the solid state<sup>18a,26,27</sup> have been extensively investigated. There have been numerous examples that are involved in the *cis*–*tran* isomerization reactions of the homometallic mono-, di-, or polynuclear complexes. There is no example related to those of heterometallic clusters in the solid state, but only a few have been reported to take place in solution.<sup>25</sup>

As discussed earlier in this paper, while **2** was readily obtained at ambient temperature, **3** could be obtained by refluxing the acetonitrile solution of **2** or directly by heating solid **2** at 120 °C. Therefore **2** may be assumed to be a kinetically controlled product, while **3** may be a thermodynamically controlled product. **2** and **3** have the same composition, but have different core structures. Compound **2** retained the *trans*–[(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>(μ-S)<sub>2</sub>S<sub>2</sub>] structure of **1**, while **3** had a *cis*–[(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>(μ-S)<sub>2</sub>S<sub>2</sub>] moiety in its structure. Evidently there existed a *trans*–to–*cis* isomerization of **2** to **3** either in solution or in the solid state. To confirm this, we used <sup>1</sup>H NMR spectroscopy to monitor the conversion of **2** to **3**.

In view of the low boiling point of CDCl<sub>3</sub>, we employed DMSO-*d*<sub>6</sub> as the solvent to monitor the **2**–to–**3** conversion at higher temperatures. The <sup>1</sup>H NMR spectrum of **2** in DMSO-*d*<sub>6</sub> showed a sharp singlet at 2.079 ppm for the η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> groups at room temperature. The same solution of **2** was heated at 80 °C for different times, then cooled to ambient temperature, and the corresponding <sup>1</sup>H NMR spectra were measured. As shown in Figure 4, when the solution was heated to 80 °C for 1 h, the signal due to the η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> group shifted to 2.065 ppm and became somewhat broad, which may be due to partial replacement of iodine atoms in **2** by a DMSO-*d*<sub>6</sub> molecule. After being heated for 4 h, there appeared a weak single resonance at 2.050 ppm, which could be assigned to be the η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> group of **3**.



**Figure 4.** <sup>1</sup>H NMR spectra of the conversion of **2** to **3** in DMSO-*d*<sub>6</sub>, in which pure **2** (a), pure **3** (b), and a solution of **2** (5 × 10<sup>−3</sup> M) in DMSO-*d*<sub>6</sub> was heated at 80 °C for 1 h (c), 4 h (d), 8 h (e), 16 h (f), and 48 h (g).



**Figure 5.** Z-scan data of a 1.05 × 10<sup>−3</sup> M CH<sub>2</sub>Cl<sub>2</sub> solution of **2** at 532 nm. (a) The data were evaluated under the open-aperture configuration. (b) The data were assessed by dividing the normalized Z-scan data obtained under the closed aperture by the normalized Z-scan data in (a). The black dots are the experimental data, and the solid curve is the theoretical fit.

It was found that continued heating of this solution gradually increased the ratio of **3** to **2** in this system, and the **2**–to–**3** isomerization was almost complete after 16 h. Compound **3** decomposed after a heating period of 48 h, and the formation of some unknown species became evident in the <sup>1</sup>H NMR spectrum. The free energy Δ*G* of this conversion at 80 °C was roughly calculated to be −7.44 ± 0.01 kJ·mol<sup>−1</sup>. This *trans*–to–*cis* isomerization was found to be irreversible, as cooling the solution of **3** in DMSO or MeCN to 25 °C for 1 day did not produce any **2**, suggesting that **3** is thermodynamically more stable than **2**.

To monitor the *trans*–to–*cis* isomerization in the solid state, solid **2** was heated for 48 h at different temperatures and then

(21) (a) Kawaguchi, H.; Yamada, K.; Ohnishi, S.; Tatsumi, K. *J. Am. Chem. Soc.* **1997**, *119*, 10871. (b) Mansour, M. A.; Curtis, M. D.; Kampf, J. W. *Organometallics* **1997**, *16*, 275.

(22) (a) Diller, H.; Keck, H.; Wunderlich, H.; Kuchen, W. *J. Organomet. Chem.* **1995**, *489*, 123. (b) Lu, S. F.; Chen, H. B.; Huang, J. Q.; Wu, Q. J.; Sun, Q. L.; Li, J.; Lu, J. X. *Inorg. Chim. Acta* **1995**, *232*, 43.

(23) (a) Agaskar, P. A.; Cotton, F. A.; Derringer, D. R.; Powell, G. L.; Root, D. R.; Smith, T. J. *Inorg. Chem.* **1985**, *24*, 2786. (b) McVitie, A.; Peacock, R. D. *Polyhedron* **1992**, *11*, 2531. (c) Raptis, R. G.; Murray, H. H.; Staples, R. J.; Porter, L. C.; Fackler, J. P., Jr. *Inorg. Chem.* **1993**, *32*, 5576. (d) Chen, H.; Cotton, F. A.; Yao, Z. *Inorg. Chem.* **1994**, *33*, 4255. (e) Heinrich, D. D.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **1995**, *229*, 61. (f) Wu, W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **1996**, *242*, 81. (g) McArdle, P.; O'Neill, L.; Cunningham, D. *Organometallics* **1997**, *16*, 1335. (h) Jean, Y.; Lledos, A. *Chem. Commun.* **1998**, 1443. (i) Trylus, K. H.; Kernbach, U.; Brüdgam, I.; Fehlhammer, W. P. *Inorg. Chim. Acta* **1999**, *291*, 266.

(24) (a) Bitterwolf, T. E.; Scallorn, W. B.; Li, B. *Organometallics* **2000**, *19*, 3280. (b) Sun, S. S.; Lees, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 8956. (c) Yamaguchi, T.; Ueno, K.; Ogino, H. *Organometallics* **2001**, *20*, 501. (d) VandeVondele, J.; Magistrato, A.; Rothlisberger, U. *Inorg. Chem.* **2001**, *40*, 5780. (e) Shiu, K. B.; Yu, S. J.; Wang, Y.; Lee, G. H. *J. Organomet. Chem.* **2002**, *650*, 37. (f) Soler, M.; Wernsdorfer, W.; Sun, Z.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Chem. Commun.* **2003**, 2672. (g) Teo, S. H.; Weng, Z. Q.; Hor, T. S. A. *Organometallics* **2006**, *25*, 1199. (h) Iwatsuki, S.; Ito, T.; Ito, H.; Mori, H.; Uemura, K.; Yokomori, Y.; Ishihara, K.; Matsumoto, K. *Dalton Trans.* **2006**, 1497.

(25) (a) Hattersley, A. D.; Housecroft, C. E.; Liable-Sands, L. M.; Rheingold, A. L.; Waller, A. *Polyhedron* **1998**, *17*, 2957. (b) Chivers, T.; Parvez, M.; Schatte, G. *Inorg. Chem.* **1999**, *38*, 5171. (c) Gimeno, J.; Lastra, E.; Madrigal, C.; Graiff, C.; Tiripicchio, A. *J. Organomet. Chem.* **2002**, *663*, 204. (d) Jin, G. X.; Wang, J. Q.; Zhang, C.; Weng, L. H.; Herberhold, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 259.

cooled to ambient temperature. Subsequently, it was dissolved in DMSO- $d_6$  for measuring the  $^1\text{H}$  NMR spectra. As indicated in Figure S5, **2** remained almost unchanged at 40 °C. When the temperature was increased to ca. 80 °C, a small amount of **3** appeared with its  $\eta^5\text{-C}_5\text{Me}_5$  signal at 2.053 ppm. Increasing the temperature up to 120 °C evidently increased the ratio of **3** to **2** in this system. However, it also resulted in the formation of some unidentified species with  $\eta^5\text{-C}_5\text{Me}_5$  NMR resonances at 2.059, 2.068, and 2.074 ppm. From their XPD patterns (see Figure S2), it is noted that some main peaks of **2** became weakened while those of **3** were strengthened when solid **2** was heated from ambient temperature to 80 °C. This tendency became more evident when **2** was heated to 120 °C. At this stage, a large part of **2** was converted into its *cis* isomer **3**.

Although it is difficult to determine the actual mechanism for the *trans*-to-*cis* isomerization in solution or in the solid state, we suggest that, from a topological view, the terminal Mo1–S3 bond of **2** may have to rotate around the Mo1⋯Mo2 vector by 180° so as to fill into the void of the incomplete cubane-like structure of **2**. This may be followed by the formation of the two extra Cu–S bonds, thereby affording the cubane-like structure of **3**. Evidently, higher temperatures may activate and expedite this process either in solution or in the solid state.

**Nonlinear Optical Properties of 1–3.** As shown in Figure 1, the electronic spectra of **1–3** showed relatively low linear absorption at 532 nm, which promises low intensity loss and little temperature change by photon absorption during the NLO measurements. The nonlinear absorption performance of **1–3** in  $\text{CH}_2\text{Cl}_2$  was evaluated by the Z-scan technique under an open-aperture configuration (Figures S8a, 5a, S9a). Although the detailed mechanism is still unknown, it is interesting to note that the NLO absorption data obtained under the conditions used in this study can be well described by eqs 1 and 2, which are derived to describe a third-order NLO process.<sup>17</sup>

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

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

where light transmittance  $T(Z)$  is a function of the sample's Z position (with respect to the focal point at  $Z = 0$ ).  $I(Z)$  is the incident light irradiance.  $\alpha_0$  and  $\alpha_2$  denote linear and effective third-order NLO absorptive coefficients, respectively.  $L$  is the optical path and  $\tau$  is the time. The solid lines in Figures S4a, 5a, and S5a are theoretical curves from eqs 1 and 2. The data collected under the open-aperture configuration indicate that they all exhibit good nonlinear absorption properties with effective  $\alpha_2$  values of  $2.81 \times 10^{-10} \text{ m}\cdot\text{W}^{-1}$  (**1**),  $6.18 \times 10^{-10} \text{ m}\cdot\text{W}^{-1}$  (**2**), and  $3.47 \times 10^{-10} \text{ m}\cdot\text{W}^{-1}$  (**3**).

The nonlinear refractive properties of **1–3** were assessed by dividing the normalized Z-scan data obtained under closed aperture by the normalized Z-scan data collected under the open-aperture configuration (Figures S8b, 5b, and S9b). The effective third-order NLO refractive indexes  $n_2$  can be derived from the difference between normalized transmittance values at valley and peak positions ( $\Delta T_{V-P}$ ) by using eq 3:<sup>28,29</sup>

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

where  $\lambda$  is the wavelength of the laser,  $\alpha_0$  is the linear coefficient,  $L$  is the sample thickness, and  $I$  is the peak irradiation intensity at focus. The effective third-order NLO refractive indexes  $n_2$  values are  $-8.61 \times 10^{-11} \text{ esu}$  (**1**),  $-8.27 \times 10^{-11} \text{ esu}$  (**2**), and  $-11.17 \times 10^{-11} \text{ esu}$  (**3**), respectively, indicating that **1–3** all exhibit strong self-defocusing effect.

In accordance with the observed  $\alpha_2$  and  $n_2$  values, the effective third-order susceptibility  $\chi^{(3)}$  and the hyperpolarizability  $\gamma$  value can be calculated by eqs 4 and 5:<sup>28,29</sup>

$$|\chi^{(3)}| = \sqrt{\left( \left| \frac{9 \times 10^8 \epsilon_0 n_0^2 c^2}{2\nu} \alpha_2 \right|^2 + \left| \frac{cn_0^2 n_2}{80\pi} \right|^2 \right)} \quad (4)$$

$$\gamma = \chi^{(3)}/NF^4 \quad (5)$$

where  $c$  is the speed of light in a vacuum,  $n_0$  is linear refractive indexes of the sample,  $N$  is the number density (concentration) of the clusters in the samples, and  $F^4$  ( $=3.25$ ) is the local field correction factor. The effective third-order susceptibilities  $\chi^{(3)}$  for **1–3** are calculated by eq 4 to be  $0.94 \times 10^{-11} \text{ esu}$  (**1**),  $2.03 \times 10^{-11} \text{ esu}$  (**2**), and  $1.15 \times 10^{-11} \text{ esu}$  (**3**), while the corresponding hyperpolarizabilities  $\gamma$  values are  $3.07 \times 10^{-30} \text{ esu}$  (**1**),  $5.65 \times 10^{-30} \text{ esu}$  (**2**), and  $1.18 \times 10^{-29} \text{ esu}$  (**3**), respectively. These results showed that **1–3** possess strong third-order optical nonlinearities.

According to eq 5,  $N$  represents the number density (concentration) of a compound. Therefore the hyperpolarizability  $\gamma$  value can be used to represent NLO properties of neat materials. The  $\gamma$  values of **1**, **2**, and **3** are comparable to those of the metal sulfide clusters derived from  $[\text{MoS}_4]^{2-}$  or  $[\text{MoOS}_3]^{2-}$ ,<sup>11c,i,14c,29</sup> such as  $[(n\text{-Bu})_4\text{N}]_2[\text{MoOS}_3(\text{Cu}(\text{NCS})_3)]$  ( $4.8 \times 10^{-29} \text{ esu}$ ) and  $[\text{MoOS}_3\text{Cu}_3(4\text{-pic})_6] \cdot 0.5[\text{Mo}_2\text{O}_7]$  ( $1.32 \times 10^{-30} \text{ esu}$ ), and are better than those observed in  $\text{C}_{60}$  ( $7.5 \times 10^{-34} \text{ esu}$ ) and  $\text{C}_{70}$  ( $1.3 \times 10^{-33} \text{ esu}$ ),<sup>30a</sup> organometallic compounds such as *trans*- $[\text{Mo}(\text{CO})_4(\text{PPh}_3)_2]$  ( $8.49 \times 10^{-32} \text{ esu}$ ) and *cis*- $[\text{Mo}(\text{CO})_4(\text{PPh}_3)_2]$  ( $4.38 \times 10^{-31} \text{ esu}$ ),<sup>30b</sup> and their films such as TiOPc ( $1.04 \times 10^{-33} \text{ esu}$ ).<sup>31</sup> It seems true that the NLO performances of **1–3** may depend on their core frameworks. When two CuI units were incorporated into the  $[\text{Mo}_2\text{S}_4]$  core of **1** to form the incomplete cubane-like cluster **2**, an obvious increase of the  $\gamma$  value was found; that is, the  $\gamma$  value of **2** is 1.84 times larger than that of **1**. The *trans*-to-*cis* isomerization from **2** to the

(27) (a) Bogadi, R. S.; Levendis, D. C.; Coville, N. J. *J. Am. Chem. Soc.* **2002**, *124*, 1105. (b) Suh, M. P.; Ko, J. W.; Choi, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 10976. (c) Eda, K.; Fukiharu, S.; Suzuki, T.; Sotani, N. *J. Solid State Chem.* **2002**, *164*, 157. (d) Lee, E. Y.; Suh, M. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2798. (e) Toh, N. L.; Nagarathinam, M.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2237. (f) Ma, J. P.; Dong, Y. B.; Huang, R. Q.; Smith, M. D.; Su, C. Y. *Inorg. Chem.* **2005**, *44*, 6143.

(28) Yang, L.; Dorsinville, R.; Wang, Q. Z.; Ye, P. X.; Alfano, R. R.; Zamboni, R.; Taliani, C. *Opt. Lett.* **1992**, *17*, 323.

(29) (a) Chen, Z. R.; Hou, H. W.; Xin, X. Q.; Yu, K. B.; Shi, S. *J. Phys. Chem.* **1995**, *99*, 8717. (b) Zhang, C.; Song, Y. L.; Jin, G. C.; Feng, G. Y.; Wang, Y. X.; Rag, S. S. S.; Fun, H. K.; Xin, X. Q. *J. Chem. Soc., Dalton Trans.* **2000**, 1317.

(30) (a) Wang, Y.; Cheng, L. T. *J. Phys. Chem.* **1992**, *96*, 1530. (b) Zhai, T.; Lawson, C. M.; Gale, D. C.; Gray, G. M. *Opt. Mater.* **1995**, *4*, 455. (c) Guha, S.; Frazier, C. C.; Porter, P. L.; Kang, K.; Finberg, S. E. *Opt. Lett.* **1989**, *14*, 952. (d) Blau, W. J.; Byrne, H. J.; Gardin, D. J.; Davey, A. P. *J. Mater. Chem.* **1991**, *1*, 245.

(31) (a) Rao, D. V. G. L. N.; Aranda, F. J.; Roach, J. F.; Remy, D. E. *Appl. Phys. Lett.* **1991**, *58*, 1241. (b) Hosoda, M.; Wada, T.; Yamada, A.; Garito, A. F.; Sasabe, H. *Mater. Res. Soc. Symp. Proc.* **1990**, *175*, 89. (c) Hosoda, M.; Wada, T.; Yamada, A.; Garito, A. F. *Jpn. J. Appl. Phys.* **1991**, *30*, L1486.

(26) (a) Ageskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1986**, *25*, 15. (b) Filippou, A. C.; Winter, J. G.; Kociok-Köhn, G.; Hinz, I. *J. Organomet. Chem.* **1997**, *542*, 35. (c) Filippou, A. C.; Winter, J. G.; Feist, M.; Kociok-Köhn, G.; Hinz, I. *Polyhedron* **1998**, *17*, 1103. (d) Maresca, L.; Natile, G. *Inorg. Chim. Acta* **1999**, *285*, 301.

cubane-like cluster **3** also led to an increase of the  $\gamma$  value; that is, the  $\gamma$  value of **3** is 2.08 times larger than that of **2**. These enhancements in  $\gamma$  value may be attributed to skeletal extension of the metal cluster.<sup>11a,32</sup> It is noted that the  $\gamma$  values for **1–3** were obtained from a dilute solution, and much larger  $\gamma$  values can be expected if these clusters could be engineered into a thin film.

### Conclusions

In summary, the reactions of **1** with 2 equiv of CuI in solution have been investigated, and two isomeric compounds **2** and **3** were isolated in relatively high yields. Compounds **2** and **3** were characterized by elemental analysis, IR, UV–vis, <sup>1</sup>H NMR, ESI-MS, and X-ray analysis. **2** has an incomplete cubane-like core structure in which the *trans* structure of **1** is retained, while **3** contains a cubane-like core structure in which the *trans* structure of **1** was turned into the *cis* structure. The *trans*-to-*cis* isomerization from **2** to **3** either in solution or in the solid state was also explored. Compounds **1–3** showed excellent third-order NLO absorption and NLO self-defocusing effects. More importantly, the third-order NLO performance of **1** was enhanced to some extent when **1** combined with two CuI units to form **2** or **3**, which supports our original idea that incorporation of other metals into the structure of **1** may result in improvement of the

(32) (a) Shi, S.; Lin, Z.; Mo, Y.; Xin, X. Q. *J. Phys. Chem.* **1996**, *100*, 10695. (b) Zhang, Q. F.; Niu, Y. Y.; Lueng, W. H.; Song, Y. L.; Williams, I. D.; Xin, X. Q. *Chem. Commun.* **2001**, 1126.

NLO properties of **1**. Furthermore, as **2** and **3** have terminal iodides, which may be replaced by strong donor ditopic ligands such as 4,4'-bipyridine, they may serve as potential structural and optical building blocks for [Mo<sub>2</sub>S<sub>4</sub>Cu<sub>2</sub>]-based supramolecular assemblies. Studies on these respects are in progress in this laboratory.

**Acknowledgment.** This work was supported by the NNSF of China (Nos. 20271036 and 20525101), the NSF of Jiangsu Province (No. BK2004205), the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20050285004), the State Key Laboratory of Organometallic Chemistry (No. 06-26), and the Qing-Lan Project of Jiangsu Province in China. We thank Prof. Zhong-Ning Chen of FJIRSM for measuring the ESI-MS spectra of **2** and **3**. We are grateful to the reviewers for their helpful suggestions.

**Supporting Information Available:** Crystallographic data of **2** and **3**·2CH<sub>2</sub>Cl<sub>2</sub> (CIF); XRD patterns of **1**, CuI, and the 1:2 mixture of **1** and CuI before and after grinding; XRD patterns of **2** and **3**·2CH<sub>2</sub>Cl<sub>2</sub>, as well as XRD patterns of **2** that was heated in the solid state at 40, 80, and 120 °C for 48 h; <sup>1</sup>H NMR spectra of **2** and **3** in CDCl<sub>3</sub>, <sup>1</sup>H NMR spectra of **2** in DMSO-*d*<sub>6</sub> after **2** was heated at 40, 80, and 120 °C for 48 h in the solid state, ESI-MS spectra of **2** and **3**, and Z-scan data of the CH<sub>2</sub>Cl<sub>2</sub> solutions of **1** and **3** at 532 nm (in pdf format) are available free of charge via the Internet at <http://pubs.acs.org>.

OM060335A