

Solid State Synthesis and Optical Limiting Effect of Two Heteroselenometallic Cubane-Like Clusters (μ_3 -MoSe₄)M₃(PPh₃)₃Cl (M = Cu and Ag)

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Heteroselenometallic cubane-like clusters (μ_3 -MoSe₄)M₃(PPh₃)₃Cl (M = Cu (**I**) and Ag (**II**)) were synthesized by the reactions of [Et₄N]₂[MoSe₄] and M(PPh₃)₃Cl in solid state for nonlinear optical studies. Their optical responses to the incident light exhibit strong optical limiting effect with thresholds of 1.8 J/cm² for cluster **I** and 0.8 J/cm² for cluster **II** in a 0.5 Hz repetition rate condition with nanosecond-duration laser pulses at 532 nm. The optical limiting power of **II** was testified to be an effective broad band optical limiter with the 1064 nm wavelength laser pulses from the nanosecond Na:YAG laser. In this respect, cluster **II** is obviously better than cluster **I** and C₆₀. The nonlinear responses for the two clusters in CH₂Cl₂ have been studied in a picosecond time-resolved pump–probe experiment. The heavy atom effect to the efficiency of nonlinear absorption was also discussed.

Introduction

The coinage metal chemistry of the [MS₄]^{2−} (M = Mo, W) anions and their related compounds has been well-documented, owing to their relevance to certain biological systems, rich structural chemistry, special reactive properties, and strong nonlinear optical characteristics.^{1–3} However, the chemistry of the corresponding selenide anions [MSe₄]^{2−} (M = Mo, W) and their related compounds has not been well-investigated.⁴ Selenium-containing compounds are interesting because they may be used as precursors for the preparation of low band gap semiconductors.⁵ It is speculated that, similar to their sulfur counterparts, selenium-containing clusters may possess large nonlinear optical properties as well.

Up to now, Ibers et al. has reported a number of new coinage metal/MSe₄^{2−} compounds with the structural types including linear, cubane, incomplete-cubane, T-frame, cross-frame, cage, and pinwheel shapes.^{6,7} As part of our interest in thiometalates [MO_nS_{4−n}]^{2−} (M = Mo, W; n = 0–2), our efforts have largely been devoted to preparing heterobimetallic sulfur clusters by using the low-heating solid-state reaction method⁸ and exploring their nonlinear optical properties (NLO) of clusters having different structural modes.⁹ In particular, we have observed strong optical limiting effects in sulfur-containing clusters with cubane-like structure.^{10,11} In this report, the structurally analogous heterobimetallic selenide clusters (μ_3 -MoSe₄)Cu₃(PPh₃)₃Cl (**I**) and (μ_3 -MoSe₄)Ag₃(PPh₃)₃Cl (**II**) have been synthesized by solid-state reaction at low heating temperature and their nonlinear optical properties have been explored. Also, these clusters exhibit manifest optical limiting effects with nanosecond laser pulses. Optical responses of C₆₀ and selenium-containing cubane-like clusters were compared. A picosecond time-resolved

pump probe experiment has also been conducted to give direct evidence on the physical origin of the observed limiting effects.

Experimental Section

General. The compound [Et₄N]₂[MoSe₄] was prepared by modification of the literature method.¹² Cu(PPh₃)₃Cl and Ag(PPh₃)₃Cl were obtained from the reaction of PPh₃ with CuCl and AgCl, respectively, in CH₃OH–CH₂Cl₂ (2:1) mixture solution. Solvents and the solid reagents were purchased as AR grade and used without further purification. Infrared spectra were recorded on a Fourier FT-10SX spectrophotometer with pressed KBr pellets. Electronic spectra were taken on a Hitachi U-3410 spectrophotometer. The ³¹P NMR data were measured in 5 mm round-bottom tubes in CDCl₃ solution on a Varian Unity-500 spectrometer, the chemical shifts are referenced to an external standard of 85% H₃PO₄ acid. Carbon and hydrogen analyses were performed on a PE 240C elemental analyzer. The compositions of copper, silver and molybdenum were analyzed with a JA 1100 + 2000 ICP quantometer. Crystal cell dimensions were measured on a Siemens P4 diffractometer with graphite-monochromitized Mo K α (λ = 0.71073 Å) radiation at 23 ± 1 °C.

Synthesis of (μ_3 -MoSe₄)Cu₃(PPh₃)₃Cl (I**).** A well-ground mixture of Cu(PPh₃)₃Cl (1.33 g, 1.5 mmol) and [Et₄N]₂[MoSe₄] (0.34 g, 0.5 mmol) was put into a reaction tube and heated at 80 °C for 4 h under a nitrogen atmosphere. After extracting the resultant black solid with CH₂Cl₂ (30 mL), the extract was filtered to afford a reddish-brown filtrate. Block-shaped dark-red crystals were obtained by diffusing diethyl ether into the filtrate for 2 days. They show characteristic infrared absorptions (KBr pellet) at 373 cm^{−1} for ν (Mo–Se_i) and at 328 cm^{−1} for ν (Mo–Se_b). Calcd. for C₅₄H₄₅P₃ClSe₄Cu₃Mo: C, 45.5; H, 3.16; Cu, 13.4; Mo, 6.74%. Found: C, 45.1; H, 3.12; Cu, 13.6; Mo, 6.68%. ³¹P NMR (CDCl₃): δ = 14.1 ppm.

Synthesis of (μ_3 -MoSe₄)Ag₃(PPh₃)₃Cl (II**).** The preparation method was similar to that of cluster **I** using Ag(PPh₃)₃Cl (1.40

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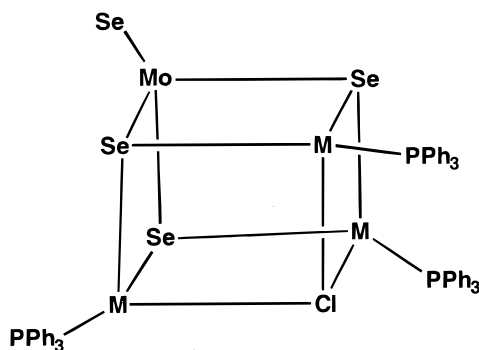


Figure 1. Molecular configurations of clusters **I** ($M = \text{Cu}$) and **II** ($M = \text{Ag}$).

g, 1.5 mmol) instead of $\text{Cu}(\text{PPh}_3)_3\text{Cl}$. The characteristic infrared absorptions (KBr pellet) are at 371 cm^{-1} for $\nu(\text{Mo}-\text{Se}_t)$ and at 331 cm^{-1} for $\nu(\text{Mo}-\text{Se}_b)$. Calcd. for $\text{C}_{54}\text{H}_{45}\text{P}_3\text{ClSe}_4\text{Ag}_3\text{Mo}$: C, 41.6; H, 2.94; Ag, 23.1; Mo, 6.18%. Found: C, 42.1; H, 3.13; Ag, 22.5; Mo, 5.97%. ^{31}P NMR (CDCl_3): $\delta = 3.67\text{ ppm}$.

Optical Measurements. Equimolar dichloromethane (CH_2Cl_2) solutions of **I** and **II** (1.0 mmol dm^{-3}) were placed in 1 mm quartz cuvettes for optical measurements. Their optical limiting responses were measured with linearly polarized, 7 ns pulses from a Q-switched frequency-doubled (532 nm) Nd:YAG laser. The spatial profiles of the optical pulses were nearly Gaussian, and the light was focused onto the sample with a 25 cm focal length mirror. The spot radius of the laser beam was measured by a Z-scan technique to be about $35\text{ }\mu\text{m}$ (half width at $1/e^2$ maximum). The samples were tested by the pulses in single shot condition (2 s pulse interval) or with 10 Hz repetition rate. The samples were also tested in the pump-probe experiment in which a Q-switched, mode-locked, frequency-doubled Nd:YAG laser was used to produce 532 nm pulses of 35 ps duration. We employed a standard pump-probe arrangement where the peak irradiance of the probe pulse is approximately 5% of that of the pump pulse.¹³ The pump and probe are orthogonally polarized to avoid interference and are incident at an angle of 10° with respect to each other. The incident and transmitted pulse energies were simultaneously recorded by two laser precision detectors (RJP-735 energy probes), which were linked to a computer by an IEEE interface.¹⁴ The transmission detector was placed at 27 cm from the focus and no aperture was mounted in the both experiments.

Results and Discussion

Synthesis and Characterization. Although the preparations of clusters **I** and **II** have been previously reported by the solution reaction method,¹⁵ they can be readily synthesized by direct heating solid state reactants below 100°C . The color of the starting materials gradually changed from a blue to a dark-red in the course of the reaction. Black selenium powder precipitate from the extractive solution is believed to be generated by partial decomposition of $[\text{Et}_4\text{N}]_2[\text{MoSe}_4]$ in the heating condition. Diffusion of diethyl ether into CH_2Cl_2 extractive filtrates of clusters **I** and **II** led to crystalline products suitable for crystallographic study.¹⁵ The crystals are very air- and moisture-stable. This solid-state reaction at low heating temperature is one of the synthetic methods for these clusters.

Clusters **I** and **II** have the same molecular configuration, as shown in Figure 1. The molecular structure of cluster **I** contains a highly distorted cubane-like cluster core $\{\text{MoCu}_3\text{Se}_3\text{Cl}\}^{2+}$ with one Se^{2-} terminal ligand bound to Mo and PPh_3 ligand bound to each Cu atom. In the core of $\{\text{MoCu}_3\text{Se}_3\text{Cl}\}^{2+}$, both the Cu

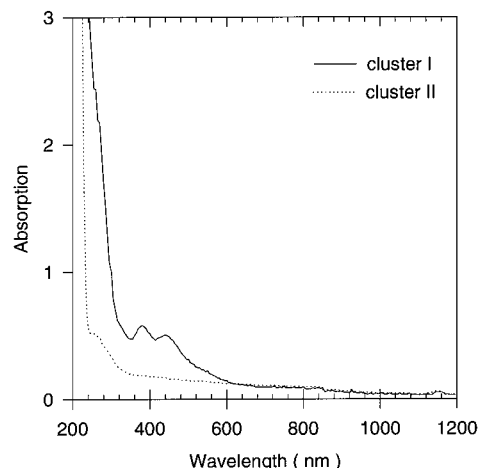


Figure 2. Absorption spectra of metal clusters **I** and **II** in dichloromethane (CH_2Cl_2) with 1 mm optical length.

and Mo atoms are tetrahedrally coordinated. Each Cu center is bonded tetrahedrally to one P, one Cl, and two Se atoms and the Mo center is bonded tetrahedrally to four Se atoms. In cluster **II**, all Cu atoms are replaced by Ag atoms. However, the two structures belong to different space groups, cluster **I** crystallized in the orthorhombic $P2_12_12_1$ space group, while cluster **II** is of triclinic $P-1$ space group. Moreover, there is a large difference in $M-\text{Cl}$ ($M = \text{Cu}, \text{Ag}$) bond distances. Cluster **I** presents two kinds of $\text{Cu}-\text{Cl}$ bond distances: one short and two long bond distances; cluster **II** has three long $\text{Ag}-\text{Cl}$ bonds. This suggests that cluster **II** should have more distorted cubane-like cluster core than cluster **I**. No $^{31}\text{P}-^{107}\text{Ag}$ coupling is observed in **II**, probably because of phosphine exchange. The upfield shift of ^{31}P NMR signal observed in **I** vs in the tungsten-centered cubane cluster $(\mu_3\text{-WSe}_4)\text{Cu}_3(\text{PPh}_3)_3\text{Cl}$ ^{6a} may be due to a smaller orbital overlap in the $[\text{WSe}_4]^{2-}$ than in $[\text{MoSe}_4]^{2-}$. Further withdrawing of electronic density caused by Se atoms in $[\text{MSe}_4]^{2-}$ and Cu interactions may also result in stronger ^{31}P nucleus deshielding effect from Cu atom in $(\mu_3\text{-WSe}_4)\text{Cu}_3(\text{PPh}_3)_3\text{Cl}$ than in **I**. The bands near 370 and 330 cm^{-1} in the low-frequency region are very characteristic for the $\text{Mo}-\text{Se}_t$ and $\text{Mo}-\text{Se}_b$ stretching vibrations, respectively.^{3a, 7}

Optical Response. The UV-visible absorption spectra of clusters **I** and **II** in CH_2Cl_2 solution are shown in Figure 2. Sample **I** has two absorption peaks positioned at 422 and 388 nm. Compared to cluster **I**, cluster **II** has a relatively flat absorption spectrum in the visible region with a fundamental absorption edge at 240 nm. This difference results in a relatively lower transmittance at 532 nm laser light for cluster **I** (62%) than for cluster **II** (78%) with the same concentration.

The optical limiting effects in clusters **I** and **II** are depicted in Figure 3. The transmittance is normalized to its linear transmittance for each sample measured when the fluence is low. The transmittances of the samples start to drop down as the input light fluence reaches about 0.1 J/cm^2 , and the samples become increasingly less transparent as the light fluence rises. The thresholds for these two samples in the 0.5 Hz repetition rate condition are 1.8 and 0.8 J/cm^2 for cluster **I** and **II**, respectively. As the pulse repetition rate increases to 10 Hz, the samples become less effective in optical limiting and larger threshold values have been observed. In optical limiting experiments, the fluence is so high that some of the molecules are actually damaged. The damaged molecules have to be replaced by fresh molecules through heat diffusion. This is a very slow process depending on the viscosity, temperature, etc. of the solvent. Usually, a time from one to several seconds is

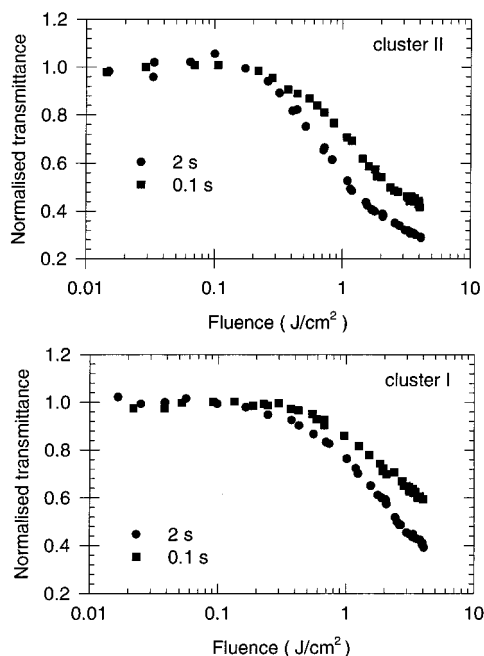


Figure 3. Optical limiting response to 7 ns, 532 nm laser pulses, with clusters **I** (lower graph) and **II** (upper graph) in dichloromethane (CH_2Cl_2) with 1 mm optical length: (filled circle) single shot; (filled box) 10 Hz. Linear transmittance is 62% for cluster **I** and 78% for cluster **II**. Both samples have identical concentration.

required. Before the molecules are replaced, the optical limiting performance is very poor, and hence different results between 10 Hz and single shot are observed. Additionally, the fluence of the 10 Hz laser pulses is a heat accumulation in the irradiated area, which keeps molecules in this area at high temperature. Molecules with such high temperatures tend to decompose easily, resulting in a lower effective concentration.¹⁶ Compared with sulfur-containing clusters having similar structures we had studied before,^{3c,10,11} where the optical limiting effect can only be achieved in 15–20 s intervals, photodegradation becomes a less prominent problem for the two selenium-containing clusters. Further support for the stability of the two samples arises from the fact that the samples remained effective even if the samples were prepared several months before. Several NMR experiments over a period of four months showed nearly no change of ^{31}P NMR signal for the samples in solution being determined. To testify their effectiveness as broad band optical limiters, the 1064 nm wavelength laser pulses from the nanosecond Nd:YAG laser have been used. At 1064 nm, the limiting threshold for cluster **II** was about 3 times larger than that at 532 nm, while cluster **I** did not show an obvious limiting effect. The limiting power for $\text{Mo}_2\text{Ag}_4\text{S}_8(\text{PPh}_3)_4$ measured at 1064 nm is a factor of ~ 30 less effective than at 532 nm.^{13a}

This decrease in effectiveness may be attributed to the obvious reduction in the linear absorption coefficients (the linear transmittance for both samples is about 98% at 1064 nm). Recent experiments on a hexagonal prism-shaped inorganic metal cluster $\text{Mo}_2\text{Ag}_4\text{S}_8(\text{PPh}_3)_4$ have indicated that strong limiting responses originate from nonlinear scattering processes that are associated with photothermal processes,¹⁶ which is similar to those observed in carbon black suspension (CBS)¹⁷ and silver-containing nanocrystalline particles.¹⁸ In the nonlinear scattering process, the linear absorption initiates heating, which can vaporize and ionize the cluster molecules. As a result, the cluster molecules scatter light, further leading to the limiting effect. At 1064 nm, where the linear-absorption coefficient becomes much smaller, the heating is less effective and so the nonlinear

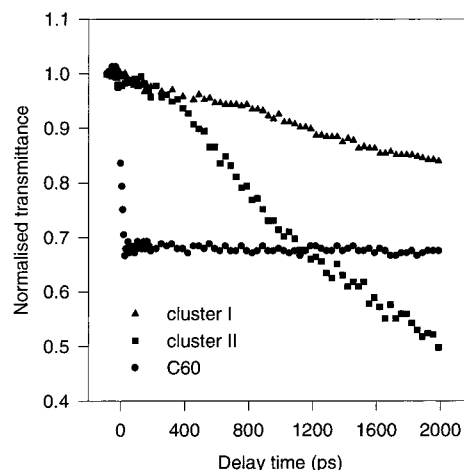


Figure 4. Normalized transmittance of the probe as a function of time delay for pump fluence of 1.14 J/cm^2 : (filled circle) C_{60} in toluene; (filled triangle) cluster **I**; (filled box) cluster **II**.

loss at 1064 nm is higher than that at 532 nm. This leads to degrading of the limiting effect.

To further confirm the nonlinear origin of these two clusters, we have conducted the pump probe experiment. The pump probe experimental results with a pump fluence of 1.14 J/cm^2 are given in Figure 4. The transmittance of the weak probe light is normalized to its linear transmittance. These two samples in CH_2Cl_2 solution have an identical concentration while different transmittance is due to the shoulders in the linear absorption of cluster **I**. The response of the C_{60} -toluene solution has also been used to test the same apparatus. The fast drop of the probe signal is typical for C_{60} being due to excited singlet state absorption, while the very slow recovery results from excited triplet state absorption, which can be explained by a five-energy-level model.^{17b} Clusters **I** and **II**, however, have different responses. The turn-on time of the nonlinear response is much effectively slower with all of the nonlinear response occurring well after at least 1.5 ns is gone. These results are consistent with their poor performance in the 35 ps laser pulse optical limiting experiments and similar to the responses of CBS and metal cluster $\text{Mo}_2\text{Ag}_4\text{S}_8(\text{PPh}_3)_4$.^{16,17} The relatively slow responses for CBS and metal cluster $\text{Mo}_2\text{Ag}_4\text{S}_8(\text{PPh}_3)_4$ in the pump-probe experiments were explained by a model of direct heating of the microscopic sized particles by linear absorption. As the pump energy increases, the limiting performance improves both in increasing maximum loss and in reducing turn-on time. After heating till the generation of plasma, rapid expansion of the microscopic plasma can effectively scatter the input light.¹⁶ From Figure 4, the maximum nonlinear transmission loss for cluster **II** is much higher than that of cluster **I** and C_{60} . Although the nonlinear response is much slower than C_{60} , the maximum nonlinear transmission for cluster **II** is much higher. Therefore, this nanosecond-responded nonlinearity is very effective for nanosecond laser pulses, as we observed in the optical limiting experiments.

It is interesting to compare these two new clusters with other well-known optical limiting materials. Table 1 gives the limiting thresholds of clusters **I** and **II**, other cubane-like clusters, hexagonal prism-shaped cluster, and C_{60} .¹⁹ All the silver-containing clusters have lower thresholds than those of the copper-containing clusters. The significant improvement of limiting capability by replacing skeleton Cu atoms with Ag atoms implies a heavy atom effect. The importance of the heavy atom effect to the efficiency of nonlinear absorption has already been noticed in the cases of metallophthalocyanine systems.²⁰

TABLE 1: Limiting Thresholds of Clusters with Cage-Shaped Structure Measured at 532 nm with 7 ns Laser Pulses

compound	solvent	linear transmission (%)	limiting threshold (J/cm ²)	ref
C ₆₀	toluene	62	1.6	19
[NBu ⁿ ₄] ₃ [WCu ₃ Br ₄ S ₄]	MeCN	70	1.1	10
[NBu ⁿ ₄] ₃ [WAg ₃ Br ₄ S ₄]	MeCN	70	0.6	10
[NBu ⁿ ₄] ₃ [WAg ₃ BrI ₃ S ₄]	MeCN	70	0.5	11
[NBu ⁿ ₄] ₃ [WAg ₃ BrCl ₃ S ₄]	MeCN	70	0.6	11
Mo ₂ Ag ₄ S ₈ (PPh ₃) ₄	MeCN	92	0.1	16
(μ ₃ -MoSe ₄)Cu ₃ (PPh ₃) ₃ Cl	CH ₂ Cl ₂	62	1.8	this work
(μ ₃ -MoSe ₄)Ag ₃ (PPh ₃) ₃ Cl	CH ₂ Cl ₂	78	0.8	this work

The results from clusters **I** and **II**, where nonlinear scattering plays an important role in agreement with metal cluster Mo₂-Ag₄S₈(PPh₃)₄,¹⁶ imply that the heavy atom effect also exists in scattering-induced nonlinearity. This obvious nonlinearity improvement may arise from the fact that the silver-containing cluster molecule has much lower pump energy than the copper-containing cluster molecule and hence plasma of the silver-containing cluster molecule may be more easily generated.

In summary, solid-state syntheses and optical limiting effects of two cubane-like clusters, (μ₃-MoSe₄)Cu₃(PPh₃)₃Cl (**I**) and (μ₃-MoSe₄)Ag₃(PPh₃)₃Cl (**II**), have been investigated. With nanosecond-duration laser pulses, the limiting thresholds for the two clusters are comparable to that of C₆₀. The nonlinear responses for the two clusters in CH₂Cl₂ have also been studied in picosecond time-resolved pump-probe experiment. The relatively slow turn-on time (1.5 ns) of the nonlinearity and very poor limiting with 35 ps laser pulses implies that nonlinear scattering may play an important role in the nonlinear process.

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