DALTON
FULL PAPER

Synthesis, crystal structure and optical limiting property of a novel octanuclear silver cluster complex with an aryl selenolate ligand

Kaluo Tang,[a] Xianglin Jin,[a] He Yan,[a] Xiangjin Xie,[a] Chunling Liu[b] and Qihuang Gong[b]

[a] *Institute of Physical Chemistry, Peking University, Beijing 100871, P. R. China. E-mail: jt1939@pku.edu.cn*
[b] *Department of Physics & National Laboratory for Mesoscopic Physics, Peking University, Beijing 100871, P. R. China. E-mail:qhgong@ibm320h.phy.pku.edu.cn*

Received 15th January 2001, Accepted 6th March 2001
First published as an Advance Article on the web 29th March 2001

The homoleptic silver aryl selenolate complex $[Ag_8(2,4,6\text{–}Pr^i_3C_6H_2Se)_8]$ **1** was synthesized by the reaction of $AgNO_3$ with an equivalent amount of 2,4,6-triisopropylbenzeneselenol ($2,4,6\text{-}Pr^i_3C_6H_2SeH$) in MeCN in the presence of triethylamine at room temperature for 4 h. Recrystallization by slow diffusion of CH_3OH into a CH_2Cl_2 solution gave yellow block crystals. The crystal structure determination indicates that the structure of the Ag_8Se_8 core of complex **1** consists of a compressed distorted Ag_8 hexagonal bipyramid embedded in a distorted rhombohedron formed by eight selenium atoms of the aryl selenolate ligands. The cluster exhibits a strong optical limiting effect with threshold of 0.2 J cm^{-2}, which is about 2.5 times lower than that of C_{60} in toluene under identical experimental conditions.

Introduction

Interest in metal chalcogenolate complexes stems from their potential use as precursors for materials[1] and relevance as models for the active site of metalloproteins.[2] Although a number of silver(I) and copper(I) thiolate complexes have been reported,[3,4] information on the synthesis, structure and properties of copper and silver selenolates remains limited. Arnold and co-workers determined the first structure of a silver alkyl selenolate $Ag_4[SeC(SiMe_3)_3]_4$ and a phosphane complexed copper alkyl selenolate $[(PCy_3)CuSe(SiMe_3)_3]_4$.[5] Then Ohlmann *et al.* reported a hexanuclear copper aryl selenolate $[Cu(2,4,6\text{-}Pr^i_3C_6H_2)Se]_6$, the crystal structure of which consists of a disordered Cu_6 octahedron embedded in an antiprism formed by six selenium centers of the selenolate ligands.[6] They also reported that this hexanuclear complex reacted with 2,2′-bipyridine (bipy) to yield a dinuclear complex $[Cu(2,4,6\text{-}Pr^i_3C_6H_2)Se]_2(bipy)$, the electrochemical behaviour of which was studied.[7] However there are very few reports on the physical properties of this kind of complex.

There is an increasing interest into the synthesis of new non-linear optical (NLO) materials for a variety of potential applications, including optical limiting.[8,9] A series of heterobimetallic sulfur-containing clusters [Mo(W,V)/S/Cu(Ag,Au)] have been prepared by using the low-heating solid-state reaction method and most of them were found to have excellent non-linear optical limiting properties.[10] Recently, interest in this field has been directed towards exploration of the NLO properties of heteroselenometallic cluster complexes.[11–13] However, these are very few reports on NLO properties of homoleptic metal chalcogenolates. We present herein the synthesis, crystal structure and large nanosecond optical limiting property of a new homoleptic silver cluster complex with a sterically hindered aryl selenolate ligand $[Ag_8(2,4,6\text{-}Pr^i_3C_6H_2Se)_8]$ **1**.

Experimental

The reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and freshly distilled under nitrogen. 2,4,6-Triisopropylbenzeneselenol ($2,4,6\text{-}Pr^i_3C_6H_2SeH$) was prepared by the modified literature procedure[14] (bp 98–100 °C/140 Pa. Yield 55.3%. $n_D^{23} = 1.5192$).

Infrared spectra were recorded from KBr pellets with a Nicolet-550 spectrometer, ^1H and ^{13}C NMR spectra on a Bruker DMX-300 (WB) spectrometer. Melting points were measured on a Buchi 535 melting point instrument.

Preparation of complex 1

A solution of $AgNO_3$ (0.17 g, 1.0 mmol) in CH_3CN (5 mL) was added to a solution of $2,4,6\text{-}Pr^i_3C_6H_2SeH$ (0.2 mL, 1.0 mmol) and Et_3N (0.18 mL, 1.0 mmol) in CH_3CN (3 mL). A greenish yellow precipitate formed immediately. After stirring for 4 h at room temperature, the precipitate was filtered off, washed with acetone, then dried. Yield 70%. The greenish yellow powder is soluble in CH_2Cl_2, DMF, CH_2I_2, cyclohexane, pyridine, *etc.* and insoluble in benzene, acetone, diethyl ether, methanol, ethanol, *etc.* Yellow block crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of CH_3OH into a CH_2Cl_2 solution. The crystals can be handled briefly in air, but should be stored under an inert atmosphere under exclusion of light. mp 155.7–157.9 °C. IR (KBr): 2957s, 2930m, 2868m, 1460m, 1419w, 1383m, 1360m, 1305w, 1100m, 1054w, 1012m, 875w cm^{-1}. ^1H NMR (solvent $CDCl_3$, standard TMS): δ 1.11 (d, J(HH) = 6.6, 12H, Me of *o*-Pr^i), 1.20 (d, J(HH) = 6.6, 6H, Me of *p*-Pr^i), 2.79 (m, J(HH) = 6.6, 1H, CH of *p*-Pr^i), 4.10 (m, J(HH) = 6.6 Hz, 2H, CH of *o*-Pr^i), 6.85 (s, 2H, aromatic CH). ^{13}C NMR (solvent $CDCl_3$): δ 23.8 (s, Me of *o*-Pr^i), 24.0 (s, Me of *p*-Pr^i), 34.0 (s, CH of *o*-Pr^i), 35.4 (s CH of *p*-Pr^i), 121.7 (s, *m*-C), 125.5 (s, CSe), 146.7 (s, *o*-C), 150.6 (s, *p*-C).

Crystal structure determination

The crystallographic measurement of complex **1** was made on a Rigaku R-AXIS RAPID image plate diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). An absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.[15] The structure was solved by direct methods and successive difference maps (SHELXS 97)[16] and refined by full-matrix

DOI: 10.1039/b100565k

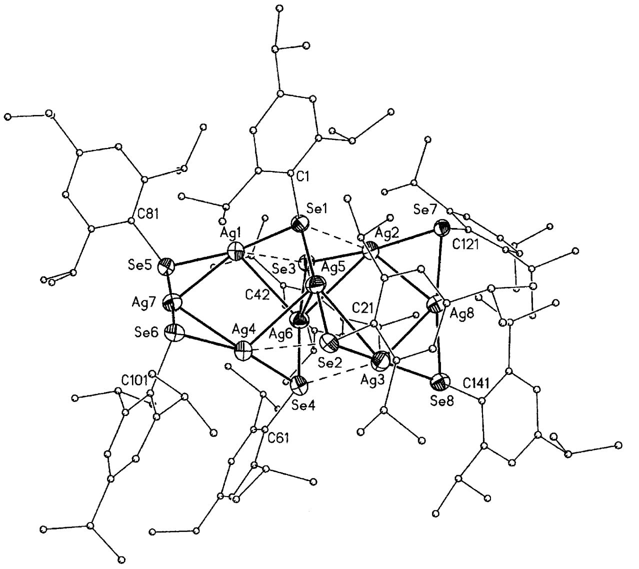

Fig. 1 Perspective view of the molecular structure of $[Ag_8(2,4,6\text{-}Pr^i_3C_6H_2Se)_8]$ **1**.

Table 1 Crystal data and refinement of complex **1**

Formula	$C_{120}H_{184}Ag_8Se_8$
M	3121.31
T/K	173
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	20.051(4)
b/Å	21.300(4)
c/Å	15.898(3)
α/°	110.70(3)
β/°	90.96(3)
γ/°	96.63(3)
V/Å^3	6297(2)
Z	2
μ/mm^{-1}	3.572
No. of reflections collected/unique	81378/21676
R_{int}	0.0560
Data/restraints/parameters	21676/0/1274
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0608$, $wR2 = 0.1470$
R indices (all data)	$R1 = 0.0998$, $wR2 = 0.1647$

least squares on F^2 using all unique data (SHELXL 97).[17] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in their calculated positions with geometrical constraints and refined in the riding model. Crystal data and the structure refinement are presented in Table 1.

CCDC reference number 153093.

See http://www.rsc.org/suppdata/dt/b1/b100565k/ for crystallographic data in CIF or other electronic format.

Results and discussion

Molecular structure of complex 1

The crystal structure determination indicates that complex **1** is a neutral cluster, which consists of eight silver atoms linked through eight aryl selenolate ligands. Figs. 1 and 2 give the molecular configuration and the structure of the Ag_8Se_8 core and its arrangement, respectively. Selected interatomic distances and angles are in Table 2. In order to describe the novel structure of **1,** we chose the selenium atoms as edges of a distorted rhombohedron with the atoms Se1–Se5–Se3–Se7 and Se2–Se6–Se4–Se8 facing top and bottom respectively [Se · · · Se distances (edges) mean 4.83 Å (4.484–5.006 Å), but the diagonals are rather short (Se1 · · · Se3 3.395, Se2 · · · Se4 3.716 Å)]. Both rhombuses are linked by somewhat longer Se · · · Se distances [mean 4.97 Å (4.915–5.008 Å)]. A compressed (along its axis) distorted Ag_8 hexagonal bipyramid is embedded into this distorted Se_8 rhombohedron (Fig. 2b). In the Ag_8 polyhedron six silver atoms (Ag1, Ag2, Ag3, Ag4, Ag7, Ag8) are in the equatorial plane, coplanar within 0.081 Å,[18] and the other two silver atoms (Ag5, Ag6) are on its axis. (The distances from Ag5 and Ag6 to the plane are 1.590 and 1.475 Å, respectively.) The eight Ag atoms are almost at the midpoints of eight edges of the Se_8 rhombohedron respectively (Se–Ag–Se angles mean 164.88°, Ag–Se distances are close and average 2.499 Å). The silver atoms are displaced toward the centre of the Se_8 core. While Ag1, Ag2 are under the plane of Se1, Se5, Se3, Se7, the distances being 0.1370 and 0.2564 Å, respectively, Ag3, Ag4 are above the plane of Se2, Se6, Se4, Se8, the distances being 0.1333 and 0.2342 Å, respectively. The Ag–Ag contacts vary between 2.885 and 4.733 Å. Only two silver atoms Ag5, Ag6 bond to three silver atoms respectively, the Ag–Ag distances averaging 3.144 Å (3.047–3.258 Å). Each of the other six silver atoms bond two silver atoms, the Ag–Ag distances averaging 2.980 Å (2.885–3.161 Å). The distance between Ag5 and Ag6, unbridged by Se, is 3.258 Å. These Ag–Ag distances are shorter than the sum of the van der Waals radii of two Ag atoms (3.44 Å), and may suggest they are related by so-called agentophilicity.[19] The distances between other non-bonding Ag atoms average 4.208 Å, which indicates that they are involved in weak interactions.

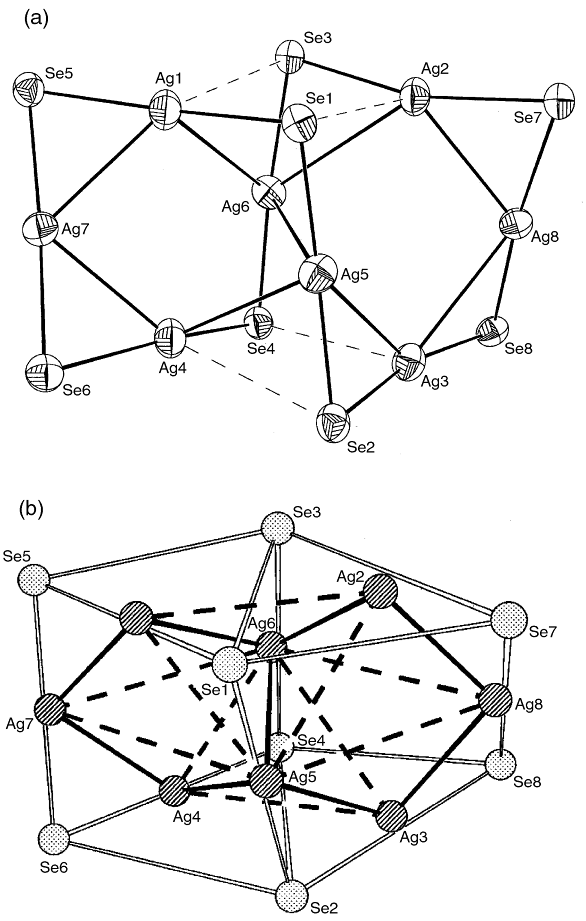

Fig. 2 (a) The structure of the Ag_8Se_8 core of $[Ag_8(2,4,6\text{-}Pr^i_3C_6H_2Se)_8]$ **1**. (b) Arrangement of the distorted Ag_8 hexagonal bipyramid within the distorted Se_8 rhombohedron. Ag–Ag distances are shown as solid (<3.44 Å) and dashed lines (>3.44 Å), respectively.

The atoms Ag1, Ag2, Ag3, Ag4 are trigonal planar coordinated by three selenium atoms, each with two short [mean 2.491 Å (2.459–2.518 Å)] and one long Ag–Se distances [mean 3.116 Å (3.043–3.272 Å)], which means weak interactions between these Ag and Se atoms. The other four silver atoms Ag5, Ag6, Ag7, Ag8 are coordinated in a nearly linear fashion by two selenium atoms (Se–Ag–Se angles average 172.44°) with typical Ag–Se bond lengths between 2.458 and 2.510 Å (mean 2.489

Table 2 Selected interatomic distances (Å) and angles (°) for complex **1**

Ag(1)–Ag(6)	3.047(1)	Ag(1)–Ag(7)	2.885(2)
Ag(2)–Ag(6)	3.248(2)	Ag(2)–Ag(8)	2.972(1)
Ag(3)–Ag(5)	3.107(1)	Ag(3)–Ag(8)	3.161(2)
Ag(4)–Ag(5)	3.060(2)	Ag(4)–Ag(7)	2.901(1)
Ag(5)–Ag(6)	3.258(1)	Ag(1)–Se(5)	2.526(1)
Ag(1)–Se(1)	2.505(1)	Ag(1)–Se(3)	3.104(2)
Ag(2)–Se(3)	2.509(1)	Ag(2)–Se(1)	3.043(2)
Ag(3)–Se(2)	2.518(2)	Ag(2)–Se(7)	2.501(1)
Ag(3)–Se(8)	2.503(1)	Ag(3)–Se(4)	3.047(1)
Ag(4)–Se(4)	2.498(4)	Ag(4)–Se(6)	2.502(1)
Ag(5)–Se(2)	2.465(1)	Ag(5)–Se(1)	2.458(1)
Ag(6)–Se(4)	2.483(1)	Ag(6)–Se(3)	2.491(1)
Ag(7)–Se(6)	2.501(2)	Ag(7)–Se(5)	2.497(1)
Ag(8)–Se(8)	2.509(1)	Ag(8)–Se(7)	2.511(1)
Ag(1) · · · Ag(2)	4.433(2)	Ag(1) · · · Ag(4)	3.916(2)
Ag(1) · · · Ag(5)	3.776(1)	Ag(2) · · · Ag(3)	4.691(2)
Ag(3) · · · Ag(4)	4.275(2)	Ag(2) · · · Ag(5)	3.912(1)
Ag(4) · · · Ag(6)	3.413(1)	Ag(3) · · · Ag(6)	4.007(1)
Ag(5) · · · Ag(8)	4.398(1)	Ag(5) · · · Ag(7)	4.733(1)
Ag(6) · · · Ag(8)	4.521(1)	Ag(6) · · · Ag(7)	4.426(1)
Se(1) · · · Se(3)	3.395(2)	Se(1) · · · Se(7)	4.705(2)
Se(1) · · · Se(5)	5.006(2)	Se(2) · · · Se(4)	3.716(2)
Se(2) · · · Se(6)	4.744(2)	Se(2) · · · Se(8)	4.990(2)
Se(3) · · · Se(5)	4.765(2)	Se(3) · · · Se(7)	4.957(2)
Se(4) · · · Se(6)	4.958(2)	Se(4) · · · Se(8)	4.484(2)
Se(1) · · · Se(2)	4.915(2)	Se(3) · · · Se(4)	4.961(2)
Se(5) · · · Se(6)	4.988(2)	Se(7) · · · Se(8)	5.008(2)
Se(2)–C(21)	1.958(8)	Se(1)–C(1)	1.958(8)
Se(4)–C(61)	1.959(9)	Se(3)–C(41)	1.954(8)
Se(6)–C(101)	1.961(9)	Se(5)–C(81)	1.955(8)
Se(8)–C(141)	1.976(8)	Se(7)–C(121)	1.955(8)
Se(1)–Ag(1)–Se(5)	168.77(4)	Se(1)–Ag(1)–Ag(7)	124.03(5)
Se(5)–Ag(1)–Ag(7)	54.48(3)	Se(1)–Ag(1)–Ag(6)	75.71(4)
Se(5)–Ag(1)–Ag(6)	115.19(4)	Ag(7)–Ag(1)–Ag(6)	96.49(4)
Se(1)–Ag(1)–Se(3)	73.63(3)	Se(5)–Ag(1)–Se(3)	115.27(4)
Ag(7)–Ag(1)–Se(3)	138.33(4)	Ag(6)–Ag(1)–Se(3)	47.78(3)
Se(7)–Ag(2)–Se(3)	163.32(4)	Se(7)–Ag(2)–Ag(8)	53.79(3)
Se(3)–Ag(2)–Ag(8)	135.85(4)	Se(7)–Ag(2)–Se(1)	115.80(4)
Se(3)–Ag(2)–Se(1)	74.72(3)	Ag(8)–Ag(2)–Se(1)	114.64(4)
Se(7)–Ag(2)–Ag(6)	145.67(4)	Se(3)–Ag(2)–Ag(6)	49.25(3)
Ag(8)–Ag(2)–Ag(6)	93.15(3)	Se(1)–Ag(2)–Ag(6)	66.07(3)
Se(8)–Ag(3)–Se(2)	167.47(4)	Se(8)–Ag(3)–Se(4)	107.41(4)
Se(2)–Ag(3)–Se(4)	83.21(4)	Se(8)–Ag(3)–Ag(5)	138.20(4)
Se(2)–Ag(3)–Ag(5)	50.67(3)	Se(4)–Ag(3)–Ag(5)	72.09(3)
Se(8)–Ag(3)–Ag(8)	50.98(4)	Se(2)–Ag(3)–Ag(8)	132.20(4)
Se(4)–Ag(3)–Ag(8)	110.80(4)	Ag(5)–Ag(3)–Ag(8)	89.12(3)
Se(4)–Ag(4)–Se(6)	165.06(5)	Se(4)–Ag(4)–Ag(7)	125.39(4)
Se(6)–Ag(4)–Ag(7)	54.55(4)	Se(4)–Ag(4)–Ag(5)	80.64(4)
Se(6)–Ag(4)–Ag(5)	114.19(4)	Ag(7)–Ag(4)–Ag(5)	105.11(3)
Se(1)–Ag(5)–Se(2)	173.10(4)	Se(1)–Ag(5)–Ag(4)	109.78(4)
Se(2)–Ag(5)–Ag(4)	71.71(4)	Se(1)–Ag(5)–Ag(3)	133.99(4)
Se(2)–Ag(5)–Ag(3)	52.18(4)	Ag(4)–Ag(5)–Ag(3)	87.76(3)
Se(1)–Ag(5)–Ag(6)	72.31(4)	Se(2)–Ag(5)–Ag(6)	113.95(5)
Ag(4)–Ag(5)–Ag(6)	65.31(4)	Ag(3)–Ag(5)–Ag(6)	78.00(3)
Se(4)–Ag(6)–Se(3)	171.48(4)	Se(4)–Ag(6)–Ag(1)	120.96(4)
Se(3)–Ag(6)–Ag(1)	67.32(4)	Se(4)–Ag(6)–Ag(2)	128.76(4)
Ag(1)–Ag(6)–Ag(2)	89.47(3)	Se(3)–Ag(6)–Ag(2)	49.73(3)
Se(3)–Ag(6)–Ag(5)	108.80(5)	Se(4)–Ag(6)–Ag(5)	76.91(5)
Ag(2)–Ag(6)–Ag(5)	73.93(4)	Ag(1)–Ag(6)–Ag(5)	73.50(3)
Se(5)–Ag(7)–Ag(1)	55.41(4)	Se(5)–Ag(7)–Se(6)	172.68(4)
Se(5)–Ag(7)–Ag(4)	130.84(4)	Se(6)–Ag(7)–Ag(1)	124.60(5)
Ag(1)–Ag(7)–Ag(4)	85.19(3)	Se(6)–Ag(7)–Ag(4)	54.58(4)
Se(8)–Ag(8)–Ag(2)	132.43(4)	Se(8)–Ag(8)–Se(7)	172.44(4)
Se(8)–Ag(8)–Ag(3)	50.82(4)	Se(7)–Ag(8)–Ag(2)	53.49(3)
Ag(2)–Ag(8)–Ag(3)	99.76(3)	Se(7)–Ag(8)–Ag(3)	136.08(4)
C(1)–Se(1)–Ag(1)	114.6(2)	C(1)–Se(1)–Ag(5)	105.3(2)
C(1)–Se(1)–Ag(2)	133.4(2)	Ag(5)–Se(1)–Ag(1)	99.07(5)
Ag(1)–Se(1)–Ag(2)	105.67(4)	Ag(5)–Se(1)–Ag(2)	90.02(5)
C(21)–Se(2)–Ag(3)	98.4(2)	C(21)–Se(2)–Ag(5)	110.5(3)
C(41)–Se(3)–Ag(6)	100.7(2)	Ag(5)–Se(2)–Ag(3)	77.15(5)
Ag(6)–Se(3)–Ag(2)	81.02(4)	C(41)–Se(3)–Ag(2)	116.5(3)
Ag(6)–Se(3)–Ag(1)	64.91(4)	C(41)–Se(3)–Ag(1)	134.8(3)
C(61)–Se(4)–Ag(6)	113.9(2)	Ag(2)–Se(3)–Ag(1)	103.82(4)
Ag(6)–Se(4)–Ag(4)	86.49(5)	C(61)–Se(4)–Ag(4)	99.1(2)
Ag(6)–Se(4)–Ag(3)	92.31(5)	C(61)–Se(4)–Ag(3)	148.1(2)
C(81)–Se(5)–Ag(7)	95.4(2)	Ag(4)–Se(4)–Ag(3)	100.42(4)
Ag(7)–Se(5)–Ag(1)	70.11(4)	C(81)–Se(5)–Ag(1)	102.9(3)
C(101)–Se(6)–Ag(4)	98.2(3)	C(101)–Se(6)–Ag(7)	114.0(3)
C(121)–Se(7)–Ag(2)	102.0(3)	Ag(7)–Se(6)–Ag(4)	70.88(5)
Ag(2)–Se(7)–Ag(8)	72.72(4)	C(121)–Se(7)–Ag(8)	103.5(2)
C(141)–Se(8)–Ag(8)	114.2(3)	C(141)–Se(8)–Ag(3)	96.0(2)
Ag(3)–Se(8)–Ag(8)	78.20(5)		

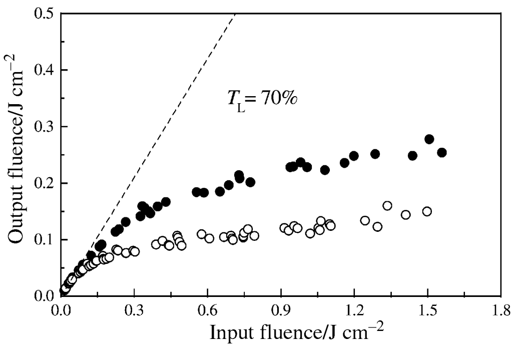

Fig. 3 Comparison of optical limiting properties of [Ag$_8$(2,4,6-Pr$_3^i$C$_6$H$_2$Se)$_8$] in dichloromethane (open circles) and C$_{60}$ in toluene (solid circles) with the same linear transmission of 70% at 532 nm.

Å), which is similar to the average Ag–Se distance of 2.480 Å in Ag$_4$[SeC(SiMe$_3$)$_3$]$_4$.[5] Ignoring the weak interactions of Ag and Se atoms, the Ag$_8$Se$_8$ core can also be considered as a twisted 16-membered ring of alternating silver and selenium atoms. The twisted centre of the 16-membered ring is located between Ag5 and Ag6. The structure of the Ag$_8$Se$_8$ ring is somewhat similar to that of the Cu$_8$S$_8$ ring in the corresponding copper thiolate Cu$_8$(2,4,6-Pr$_3^i$C$_6$H$_2$S)$_8$,[20] However, the structure of the complex **1** is different from that of the copper selenolate with the same ligand [Cu(2,4,6-Pr$_3^i$C$_6$H$_2$Se)]$_6$,[6] which is a hexanuclear copper cluster. Compared with the corresponding silver thiolate {[Ag(2,4,6-Pr$_3^i$C$_6$H$_2$S)]$_4$·CHCl$_3$}$_n$, which consists of a one-dimensional double (Ag–SR)$_n$ strand belt polymer,[21] silver selenolate **1** is a discrete octanuclear cluster. From these examples, it seems that selenolate has a lower degree of aggregation than thiolate when coordinated to the same metal. Furthermore, the copper selenolate complex with the same ligand has a lower degree of aggregation than the silver selenolate complex. The same trend has been observed in copper and silver thiolates.[3] However, more examples are needed to verify it.

Optical limiting property study

For optical property measurements the complex **1** was dissolved in dichloromethane and placed in a 2 mm thick glass cell with linear transmission of 70% at 532 nm. The optical limiting behaviour was observed by measuring the fluence-dependent transmission in a collimated optical setup,[22] using 10 ns laser pulses at 532 nm. For comparison, a solution of C$_{60}$ in toluene with the same linear transmission was measured under identical experimental conditions. Fig. 3 presents a comparison of optical limiting properties between complex **1** and C$_{60}$. It is clear that the optical limiting capability of **1** is significantly stronger than that of C$_{60}$ under the same linear transmissivity. The optical limiting threshold, defined as the input fluence at which the transmission is 50% of the linear transmission, is about 0.2 J cm^{-2} for the complex **1** and about 0.5 J cm^{-2} for C$_{60}$. The measured fluence-dependent transmission was well fitted by an approximate expression[23] obtained from a reverse saturable absorption five-level rate-equation model in which ionization and germinate recombination are included. Thus it was believed that the observed optical limiting behavior of complex **1** was mainly attributed to strong reverse saturable absorption induced by triplet–triplet transition. In addition, a broad transparent window is found in the ground-state absorption spectrum, which is also an important factor for optical limiting materials. In conclusion, all the linear and non-linear optical properties make **1** a promising candidate for optical limiting applications. The experimental details and theoretical analysis of the optical limiting property will be reported elsewhere.[24]

Acknowledgements

The work was supported by the NNSF of China (Grant Nos. 29873080, 29873001, 19525412, and 19884001). Professor K. Tang would like to thank Professor G.-D. Zhou for helpful discussion.

References

1 M. G. Kanatzidis and S. Huang, *Coord. Chem. Rev.*, 1994, **130**, 509.
2 N. Baidya, B. C. Noll, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.*, 1992, **31**, 2999.
3 K. Tang and Y. Tang, in *Heteroatom Chemistry*, VCH Publishers, New York, 1990, pp. 345–369.
4 K. Tang, X. Jin and Y. Tang, in *Reviews on Heteroatom Chemistry*, ed. S. Oae, MYU, Tokyo, 1996, vol. 15, pp. 83–114.
5 P. J. Bonasia, G. P. Mitchell, F. J. Hollander and J. Arnold, *Inorg. Chem.*, 1994, **33**, 1797.
6 D. Ohlmann, H. Pritzkow, H. Grutzmacher, M. Anthamatten and R. Glaser, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1011.
7 D. Ohlmann, C. M. Marchand, H. Schonberg and H. Grutzmacher, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1349.
8 L. W. Tutt and T. F. Boggess, *Prog. Quant. Electron.*, 1993, **17**, 299.
9 Y. P. Sun and J. E. Riggs, *Int. Rev. Phys. Chem.*, 1999, **18**, 43.
10 C. Zhang, G. C. Jin and X. Q. Xin, *Chin. J. Inorg. Chem.*, 2000, **16**, 229.
11 Q. F. Zhang, M. T. Bao, M. C. Hong, R. Cao, Y. L. Song and X. Q. Xin, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 605.
12 Q. F. Zhang, W. H. Leung, X. Q. Xin and H. K. Fun, *Inorg. Chem.*, 2000, **39**, 417.
13 Q. F. Zhang, S. S. S. Raj, H. K. Fun and X. Q. Xin, *Chem. Lett.*, 1999, 619.
14 M. Bochmann, K. J. Webb, M. B. Hursthouse and M. Mazid, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 2317.
15 T. Higashi, ABSCOR, Empirical Absorption Correction based on Fourier Series Approximation, Rigaku Corporation, Tokyo, 1995.
16 G. M. Sheldrick, SHELXS 97, Program for the Solution of Crystal Structures, University of Göttingen, 1997.
17 G. M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures, University of Göttingen, 1997.
18 Least-squares plane equation: $19.758X - 0.885Y - 2.962Z = 13.0258$. Deviations from the plane: Ag1 0.1362, Ag2 −0.0636, Ag3 0.1063, Ag4 −0.0681, Ag7 −0.0630, Ag8 −0.0478 Å. Mean deviation = 0.0809 Å.
19 N. Kaltsoyannis, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1.
20 Q. Yang, K. Tang, H. Liao, Y. Han, Z. Chen and Y. Tang, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 1076.
21 K. Tang, J. Yang and Q. Yang and Y. Tang, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 2297.
22 C. L. Liu, G. Z. Zhao, Q. H. Gong, K. Tang, X. Jin, P. Cui and L. Li, *Opt. Commun.*, 2000, **184**, 309.
23 W. Ji, H. J. Du, S. H. Tang and S. Shi, *J. Opt. Soc. Am. B*, 1995, **12**, 876.
24 C. L. Liu, X. Wang, Q. H. Gong, K. Tang, X. Jin, Y. He and P. Cui, submitted.