

# Syntheses, crystal structures and non-linear optical responses of two new heteroselenometallic cluster compounds containing dithiocarbamate ligands

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Two novel dialkyldithiocarbamate-containing heteroselenometallic clusters,  $[\text{NET}_4]_2[(\text{WSe}_4)(\text{Et}_2\text{NCS}_2\text{Cu})_3]$  **1** and  $[\text{NET}_4]_2[(\text{WSe}_4)(\text{Me}_2\text{NCS}_2\text{Cu})_4]$  **2**, have been synthesized through reactions of  $[\text{NET}_4]_2[\text{WSe}_4]$  with CuCl and  $\text{R}_2\text{NCS}_2\text{Na}$  ( $\text{R} = \text{Et}$  or  $\text{Me}$ ) in DMF. The  $[(\text{WSe}_4)(\text{Et}_2\text{NCS}_2\text{Cu})_3]^{2-}$  anion in **1** comprises three  $\text{Et}_2\text{NCS}_2\text{Cu}$  fragments ligated by a slightly distorted tetrahedral  $\text{WSe}_4$  moiety. The  $[(\text{WSe}_4)(\text{Me}_2\text{NCS}_2\text{Cu})_4]^{2-}$  anion structure in **2** possesses a nearly planar  $\text{WCu}_4$  core and consists of four  $\text{Me}_2\text{NCS}_2\text{Cu}$  fragments co-ordinated across four edges of the tetrahedral  $[\text{WSe}_4]^{2-}$  moiety. The optical limiting effects of the two clusters were examined at a 0.5 Hz repetition rate. The thresholds of two samples were 6.0 and 1.1  $\text{J cm}^{-1}$  for **1** and **2**, respectively. The non-linear responses for the two clusters in DMF have also been studied in picosecond time-resolved pump-probe experiments.

## Introduction

The coinage-metal chemistry of the  $[\text{MS}_4]^{2-}$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) anions and their related compounds has been well documented owing to their relevance to certain biological systems, rich structural chemistry, and special reactivity as well as potential application in non-linear optical materials.<sup>1–3</sup> However, the chemistry of the corresponding selenide anions  $[\text{MSe}_4]^{2-}$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) and their related compounds has not been well investigated.<sup>4</sup> At present a number of coinage metal/ $\text{MSe}_4^{2-}$  compounds are known, some of which are sketched in Fig. 1.<sup>5–8</sup> As shown, the structural types include linear, butterfly, cubane, incomplete-cubane, T-frame, cross-frame, cage and pin-wheel shape. As part of our interest in thiometalates  $[\text{MO}_n\text{S}_{4-n}]^{2-}$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $n = 0–2$ ), our efforts have been largely devoted to preparing heterobimetallic sulfur-containing clusters by using the low-heating solid-state reaction method and exploring non-linear optical (NLO) properties of different structural mode clusters. Recently, we have noticed that structure alterations of clusters are responsible for the switching of NLO properties and skeleton atom substitution induces larger changes.<sup>9</sup> For examples, nest-shaped clusters  $[\text{NBu}^n_4]_2[\text{MoCu}_3\text{OS}_3\text{BrCl}_2]$  and  $[\text{NBu}^n_4]_2[\text{MoCu}_3\text{OS}_3(\text{NCS})_3]$ , a supercage-shaped cluster  $[\text{NBu}^n_4]_4[\text{Mo}_8\text{Cu}_{12}\text{O}_8\text{S}_{24}]$ , a twin nest-shaped cluster  $[\text{NET}_4]_4[\text{Mo}_2\text{Cu}_6\text{O}_2\text{S}_6\text{Br}_2\text{I}_4]$ , a hexagonal prism-shaped cluster  $[\text{W}_2\text{Ag}_4\text{S}_8(\text{PPh}_3)_4]$ , and linear clusters  $[\text{MAu}_2\text{S}_4(\text{AsPh}_3)_2]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) show strong NLO behaviour.<sup>10</sup> Butterfly-shaped clusters  $[\text{MCu}_2\text{OS}_3(\text{PPh}_3)_n]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $n = 3$  or  $4$ ), half-open cage-shaped clusters  $[\text{NET}_4]_3[\text{W}(\text{CuBr})_3\text{OS}_3\text{Br}]$  and  $[\text{MoCu}_3\text{OS}_3(\text{PPh}_3)_3\{\text{S}_2\text{P}(\text{O}^i\text{Bu})_2\}]$  and one-dimensional linear chain polymeric clusters  $\{[\text{NBu}^n_4][\text{MS}_4\text{Tl}]\}_n$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) exhibit large NLO refraction.<sup>11</sup> Cubane-like clusters  $[\text{NBu}^n_4]_3[\text{MM}'_3\text{S}_4\text{BrX}_3]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $\text{M}' = \text{Cu}$  or  $\text{Ag}$ ;  $\text{X} = \text{Cl}$  or  $\text{I}$ )

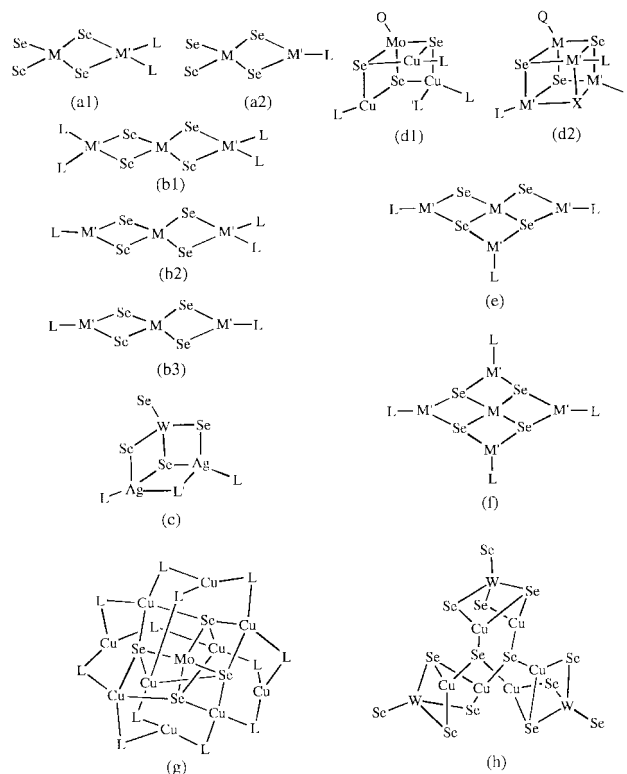


Fig. 1 Connectivities in known heteroselenometalates ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $\text{M}' = \text{Cu}$ ,  $\text{Ag}$  or  $\text{Au}$ ;  $\text{Q} = \text{O}$  or  $\text{Se}$ ;  $\text{L}$ ,  $\text{L}' = \text{ligands}$ ).

possess strong NLO absorption.<sup>12</sup> A very large optical limiting effect has been observed in a hexagonal prism-shaped cluster  $[\text{Mo}_2\text{Ag}_4\text{S}_8(\text{PPh}_3)_4]$  and a cross-frame cluster  $[\text{WCu}_4\text{S}_4(\text{SCN})_2]$

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(py)<sub>6</sub>] (py = pyridine), which is about six times better than that observed in C<sub>60</sub> and is about three times higher than that displayed in phthalocyanine derivatives.<sup>13</sup>

Since few NLO properties of heteroselenometallic clusters have been investigated so far, we found it worthwhile to extend studies on this class of clusters. The strategy is directed towards searching for new optical inorganic cluster materials. Another important reason is that Se-containing compounds may have important applications such as precursors for low-bandgap semiconductors and non-linear optics.<sup>14</sup> In this article we report the syntheses, crystal structures and non-linear optical responses of two new heteroselenometallic cluster compounds [NEt<sub>4</sub>]<sub>2</sub>[(WSe<sub>4</sub>)(Et<sub>2</sub>NCS<sub>2</sub>Cu)<sub>3</sub>] **1** with T-frame structure and [NEt<sub>4</sub>]<sub>2</sub>[(WSe<sub>4</sub>)(Me<sub>2</sub>NCS<sub>2</sub>Cu)<sub>4</sub>] **2** with cross-frame structure.

## Experimental

All syntheses were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by conventional methods and degassed prior to use. The salt [NEt<sub>4</sub>]<sub>2</sub>[WSe<sub>4</sub>] was prepared by an improvement on the literature method,<sup>15</sup> Me<sub>2</sub>NCS<sub>2</sub>Na was synthesized from the reaction of Me<sub>2</sub>NH, NaOH and CS<sub>2</sub> in water and Et<sub>2</sub>NCS<sub>2</sub>Na·3H<sub>2</sub>O and CuCl were purchased from Shanghai Reagents Plant and used without further purification.

## Preparations

[NEt<sub>4</sub>]<sub>2</sub>[(WSe<sub>4</sub>)(Et<sub>2</sub>NCS<sub>2</sub>Cu)<sub>3</sub>] **1**. To a slurry of CuCl (0.152 g, 1.50 mmol) and Et<sub>2</sub>NCS<sub>2</sub>Na·3H<sub>2</sub>O (0.326 g, 1.45 mmol) in DMF (10 cm<sup>3</sup>) was added a solution of [NEt<sub>4</sub>]<sub>2</sub>[WSe<sub>4</sub>] (0.38 g, 0.50 mmol) in DMF (10 cm<sup>3</sup>). The mixture was stirred at room temperature for 20 h, during which time it became brown. The solution was separated from a small amount of black precipitate by filtration. To the resulting filtrate was added Et<sub>2</sub>O (20 cm<sup>3</sup>) and then allowed to stand for one day at 25 °C to cause deposition of inorganic salt. The second filtrate was placed in a refrigerator at -10 °C for two days, and dark red block X-ray quality crystals of complex **1** were obtained. Yield: 0.22 g (31.6%). <sup>1</sup>H NMR [300 MHz, DMSO-*d*<sub>6</sub>, 298 K]: δ 3.86 (*α*-H, Et<sub>2</sub>NCS<sub>2</sub>), 3.23 (CH<sub>2</sub>, Et<sub>4</sub>N), 1.24 (*β*-H, Et<sub>2</sub>NCS<sub>2</sub>) and 1.17 (CH<sub>3</sub>, Et<sub>4</sub>N). IR (KBr pellets, cm<sup>-1</sup>): ν(C=N), 1476s; ν(C-S), 997s, 915m; ν(Cu-S), 349m, 335 (sh); ν(W-Se), 303m and 295w (Found: C, 26.31; H, 4.96; N, 5.12. Calc. for C<sub>31</sub>H<sub>70</sub>Cu<sub>3</sub>N<sub>5</sub>S<sub>6</sub>Se<sub>4</sub>W: C, 26.68; H, 5.02; N, 5.02%).

[NEt<sub>4</sub>]<sub>2</sub>[(WSe<sub>4</sub>)(Me<sub>2</sub>NCS<sub>2</sub>Cu)<sub>4</sub>] **2**. Copper(I) chloride powder (0.152 g, 1.50 mmol) was added to a solution of [NEt<sub>4</sub>]<sub>2</sub>[WSe<sub>4</sub>] (0.38 g, 0.50 mmol) in DMF (15 cm<sup>3</sup>). After the reaction was stirred overnight, Me<sub>2</sub>NCS<sub>2</sub>Na (0.203 g, 1.42 mmol) was added. Stirring was continued for 8 h at room temperature. The resulting solution was added to Et<sub>2</sub>O (10 cm<sup>3</sup>) and then filtered to afford the dark brown filtrate. Dark red cubic crystals were harvested after the filtrate was cooled to -18 °C for one day. Yield: 0.35 g (46.9%). <sup>1</sup>H NMR [300 MHz, DMSO-*d*<sub>6</sub>, 298 K]: δ 3.41 (CH<sub>3</sub>, Me<sub>2</sub>NCS<sub>2</sub>), 3.21 (CH<sub>2</sub>, Et<sub>4</sub>N) and 1.15 (CH<sub>3</sub>, Et<sub>4</sub>N). IR (KBr pellets, cm<sup>-1</sup>): ν(C=N), 1525s; ν(C-S), 983s, 946s and 911m; ν(Cu-S), 353m; ν(W-Se), 297m (Found: C, 22.15; H, 4.41; N, 5.53. Calc. for C<sub>28</sub>H<sub>64</sub>Cu<sub>4</sub>N<sub>6</sub>S<sub>8</sub>Se<sub>4</sub>W: C, 22.49; H, 4.28; N, 5.62%).

## X-Ray crystallography

Single crystals of complexes **1** and **2** suitable for X-ray diffraction were obtained directly from the reaction solutions. Crystals of **1** with dimensions 0.42 × 0.38 × 0.35 mm and of **2** with dimensions 0.32 × 0.28 × 0.25 mm were mounted in random orientation on glass fibers. Diffraction data were collected on a Siemens Smart CCD area-detecting diffractometer equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) by using the ω scan technique (for **1**, 1.92 < θ < 25.25°; for **2**,

1.57 < θ < 26.31°). The data reductions were performed on a silicon graphics computer station with Smart CCD software.<sup>16</sup> Structures were solved by the direct methods and refined by full-matrix least squares on F<sup>2</sup> using SHELXTL 97 (Vision 5.1).<sup>17</sup> All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C-H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement. For **1**, one carbon atom in an ethyl group of Et<sub>2</sub>NCS<sub>2</sub> was treated as distorted (the site occupancies were each initially set to 0.5, but were then refined with the restriction that they sum to unity; this resulted in site occupancies of 0.511 for C(3) and 0.487 for C(3')) and refined isotropically and others were refined anisotropically. Crystallographic data for **1** and **2** are listed in Table 1.

CCDC reference number 186/1787.

See <http://www.rsc.org/suppdata/dt/a9/a908524f/> for crystallographic files in .cif format.

## Spectroscopic, NLO and other measurements

Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyser in Nanjing University. Electronic absorption spectra were obtained on a Shimadzu UV-3000 spectrophotometer with DMF as solvent, infrared spectra on a Nicolet 170sx FT-IR spectrophotometer with the use of pressed KBr pellets and proton NMR spectra on a Bruker DPX-300 Fourier-transform spectrometer with chemical shifts reported relative to SiMe<sub>4</sub> (external).

The optical limiting characteristics of the compound were investigated with the linearly polarized 7 ns pulses provided by a frequency doubled, mode locked, Q-switched Nd:YAG laser. The spatial distribution of the laser became nearly Gaussian after passing a spatial filter. Each pulse was then divided by a beam splitter into two parts. The reflected part was taken as reference representing the incident light and the transmitted beam was focused onto the sample. Two energy probes (Laser Precision RJP-735) were used to detect the energies of the two laser beams simultaneously.

In the pump probe experiments a Q-switched Nd:YAG laser operating at 532 nm was used to provide 35 ps laser pulses. The set-up was a standard one and the probe peak irradiance was approximately 5% of the pump irradiance.<sup>18</sup> The beam waists of the pump and probe were both 75 μm. The polarization of the pump beam was rotated by 90° with respect to that of the probe beam with a half wave plate to avoid interference. These two beams were then focused onto the sample at an angle of 10° to each other.

## Results and discussion

### Synthesis

Cluster **1** was prepared by the direct combination reaction of the [WSe<sub>4</sub>]<sup>2-</sup> anion and the dithiocarbamate-substituted copper(I) species Et<sub>2</sub>NCS<sub>2</sub>Cu in DMF. Cluster **2** was obtained by a two-step reaction, the reaction of [NEt<sub>4</sub>]<sub>2</sub>[WSe<sub>4</sub>] and CuCl in a 1:4 W:Cu ratio and the substitution of Cl<sup>-</sup> by Me<sub>2</sub>NCS<sub>2</sub><sup>-</sup>, which can be regarded as a stepwise addition. However, the two synthetic methods may be used alternatively to prepare clusters **1** and **2**. The final product is independent of the ratio of the starting materials; this is to say, when similar methods were used for the reaction of [NEt<sub>4</sub>]<sub>2</sub>[WSe<sub>4</sub>], CuCl and R<sub>2</sub>NCS<sub>2</sub>Na in DMF solution, Et<sub>2</sub>NCS<sub>2</sub>Na resulted in formation of the tetranuclear cluster [(WSe<sub>4</sub>)(Et<sub>2</sub>NCS<sub>2</sub>Cu)<sub>3</sub>]<sup>2-</sup>, while Me<sub>2</sub>NCS<sub>2</sub>Na gave the pentanuclear cluster [(WSe<sub>4</sub>)(Me<sub>2</sub>NCS<sub>2</sub>Cu)<sub>4</sub>]<sup>2-</sup>. As documented in the corresponding tetrathiometalate system<sup>19</sup> and the tetraselenomolybdate reaction,<sup>6e</sup> it is noteworthy that the Me<sub>2</sub>NCS<sub>2</sub><sup>-</sup> ligand exhibits distinct behavior in all the mentioned reactions systems from the other R<sub>2</sub>NCS<sub>2</sub><sup>-</sup> ligands. An

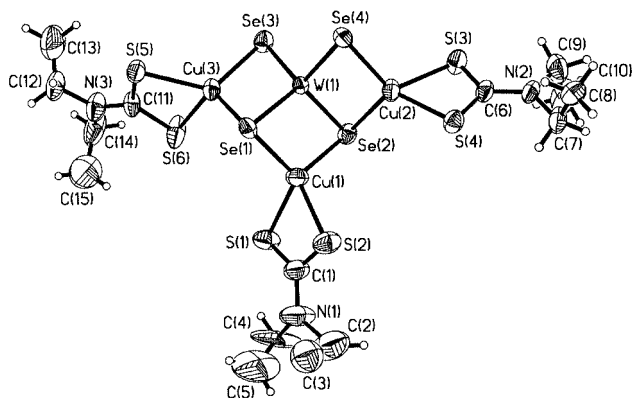


Fig. 2 The  $[(WSe_4)(Et_2NCS_2Cu)_3]^{2-}$  anion of complex 1.

unexpected cluster compound having a special structure was usually obtained when using  $Me_2NCS_2^-$  to replace the other  $R_2NCS_2^-$  ligands. For example, in the  $MS_4^{2-}/CuCl/R_2NCS_2^-$  system ( $M = Mo$  or  $W$ ), the use of  $Me_2NCS_2^-$  led to a heteroheptanuclear cluster  $[M_2Cu_5S_8(Me_2NCS_2)_3]^{2-}$  consisting of two defective cubane units,  $MCu_2S_4$  and  $MCu_3S_4$ ,<sup>20</sup> while other  $R_2NCS_2^-$  ligands lead to a  $MCu_3$  planar cluster  $[MCu_3S_4(R_2NCS_2)_3]^{2-}$ .<sup>21</sup> In the tetraselenometalate reaction system using  $Me_2NCS_2^-$  ligand resulted in  $MCu_4$  ( $M = Mo$  or  $W$ ) core planar clusters which had not yet been observed when using the other  $R_2NCS_2^-$  ligands. These interesting results may be attributed to the smaller steric effect and stronger  $\sigma-\pi$  conjugation effect of the methyl group than those of other alkyl groups in  $R_2NCS_2^-$ , which give rise to the stabilization of the cluster containing  $Me_2NCS_2M$  units and lead to a variety of cluster structures.<sup>22</sup>

### Crystal structures

Compounds **1** and **2** are among the few known  $R_2NCS_2^-$ -containing heterobimetallic clusters.<sup>6e,f,20,21</sup> The two structures consist of well separated cations and anions. The  $[NEt_4]^{2+}$  cations have normal bond distances and angles, which will not be discussed here.

The  $[(WSe_4)(Et_2NCS_2Cu)_3]^{2-}$  anion of complex **1**, shown in Fig. 2, comprises three neutral  $Et_2NCS_2Cu$  fragments ligating a tetrahedral  $[WSe_4]^{2-}$  moiety across three of its edges leaving the other Se–W–Se angle open. The W(1) and Cu(3) atoms lie on a crystallographic twofold axis. The W has a nearly tetrahedral geometry (Se–W–Se angles varying from 108.16(7) to 110.05(7) $^\circ$ ); it shows smaller distortion than the known cubane-like cluster  $[(WSe_4)(CuPPh_3)_3Cl]$ .<sup>5a</sup> The geometry about the Cu atom is a highly distorted tetrahedron consisting of two Se atoms from the  $[WSe_4]^{2-}$  anion and two S atoms from one  $Et_2NCS_2^-$  ligand with an average bite angle of 74.5(2) $^\circ$  in the four-membered chelating ring. The four metal atoms W(1), Cu(1), Cu(2) and Cu(3) lie approximately in a plane with deviations of 0.05 Å from the idealized  $WCu_3$  plane. This structural characterization is identical to those of the similar clusters  $[(MS_4)(CuL)_3]^{2-}$  ( $M = Mo$  or  $W$ ;  $L = Cl, SCN$  and  $Et_2NCS_2$ ).<sup>21,23</sup>

The W–Se bond lengths show two types: the average value of 2.732(2) Å involving  $\mu_3$ -Se is obviously longer than that of 2.320(2) Å involving  $\mu_2$ -Se. The average W–Cu distance, 2.738(2) Å, is significantly shorter than that in  $[(WSe_4)\{(PMe_2Ph)_2Cu\}_2]$  (average 2.872(2) Å).<sup>5a</sup> Although the formally  $W^{VI}$  and  $Cu^I$  in cluster **1** and  $[(WSe_4)\{(PMe_2Ph)_2Cu\}_2]$  are tetrahedrally co-ordinated, interaction between W and Cu atoms with the  $\pi$ -conjugated ligand  $Et_2NCS_2$  in the former is slightly stronger than that between W and Cu atoms with the  $\sigma$ -donor ligand  $PMe_2Ph$  in the latter. The Cu–Se distances are not clearly influenced by the different selenium co-ordination modes and are similar to those reported for analogous cluster compounds.

Table 1 Crystallographic data for complexes **1** and **2**

	1	2
Empirical formula	$C_{31}H_{70}Cu_3N_5S_6Se_4W$	$C_{28}H_{64}Cu_4N_6S_8Se_4W$
Formula weight	1395.59	1495.18
$T/K$	293	293
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$Pbca$ (no. 61)
$a/\text{Å}$	12.974(2)	14.592(3)
$b/\text{Å}$	13.358(2)	18.645(4)
$c/\text{Å}$	29.736(3)	37.561(8)
$V/\text{Å}^3$	5153.4(12)	10219.1(37)
$Z$	4	8
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	6.540	7.084
$D/\text{g cm}^{-3}$	1.799	1.943
Unique reflections/ $R(\text{int})$	7246/0.0394	9020/0.0619
Data/restraints/ parameters	7245/0/450	9018/0/460
$R1, wR2 [I > 2\sigma(I)]$	0.0617, 0.1308	0.0815, 0.1446
[all data]	0.0795, 0.1448	0.1059, 0.1542
Residual $\rho/e \text{ Å}^{-3}$	+1.080, –0.577	+1.137, –1.387

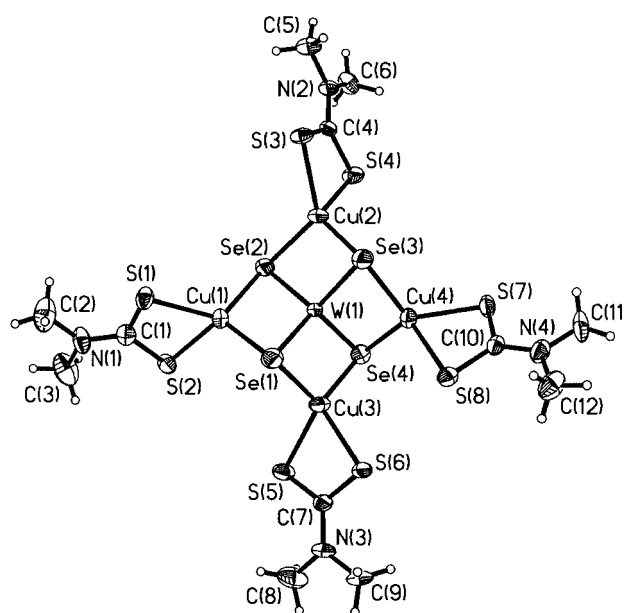


Fig. 3 The  $[(WSe_4)(Me_2NCS_2Cu)_4]^{2-}$  anion of complex 2.

The structure of the anion  $[(WSe_4)(Me_2NCS_2Cu)_4]^{2-}$  of complex **2** is shown in Fig. 3. This anion is most closely related structurally to the anions in the  $Cu/MS_4$  ( $M = Mo$  or  $W$ )<sup>24</sup> and  $Cu/MoSe_4$  systems.<sup>6e</sup> The present anion possesses a pseudo- $D_{2d}$  symmetry because angles of the *trans*-Cu atoms through the W center Cu(1)–W(1)–Cu(4) (168.24(6) $^\circ$ ) and Cu(2)–W(1)–Cu(3) (174.04(6) $^\circ$ ), are greatly deviated from the standard angle 180 $^\circ$ . The anion structure consists of four  $Me_2NCS_2Cu$  fragments ligating through four of six edges of the tetrahedral  $[WSe_4]^{2-}$  moiety. In the  $WCu_4$  core, W and Cu atoms are tetrahedrally coordinated, and five metal atoms are nearly coplanar with deviations of not more than 0.1 Å from the least squares plane. Distances from the W to the four Se atoms range from 2.337(2) to 2.349(2) Å, while the Se–W–Se angles range from 106.34(7) to 110.88(6) $^\circ$ . The Cu–Se bond lengths in **2** agree with those in **1**, which suggests that Cu–Se distances are not affected by the co-ordination geometries of Cu atoms and different  $R_2NCS_2^-$  ligands. The average W–Cu distance of 2.707(2) Å in **2** with tetrahedral copper geometry is shorter than those in related clusters with the same co-ordination environment and slightly longer than that of 2.696(2) Å in  $[NEt_4]_2[(WSe_4)\{(SC_4H_3)SeCu\}_2]$  with trigonal copper geometry,<sup>5c</sup> which may be a manifestation of a weak  $W^{VI}$ – $Cu^I$  interaction. Selected structural

**Table 2** Comparison of selected bond parameters for related W–Cu–S compounds<sup>a</sup>

Compound	W–Se	Cu–Se	W–Cu	Se–W–Se	Se–Cu–Se	Ref.
[WSe <sub>4</sub> ] <sup>2-</sup>	2.307(1)–2.310(1) av. 2.308(1)					7
[(WSe <sub>4</sub> ) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> Cu] <sub>2</sub>	2.317(1)–2.327(1) av. 2.322(1)	2.427(1)–2.430(1) av. 2.428(1)	2.868(1)–2.877(2) av. 2.872(1)	108.85(5)–110.01(3) av. 109.36(4)	101.93(7)–102.60(7) av. 102.26(7)	5(a)
[(WSe <sub>4</sub> ) <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> Cu] <sub>2</sub> Cl	2.201(4)–2.390(3) av. 2.332(3)	2.385(4)–2.431(4) av. 2.408(4)	2.733(3)–2.771(3) av. 2.753(3)	108.13(8)–111.4(1) av. 109.46(5)	104.2(1)–108.6(1) av. 106.8(1)	5(a)
[(WSe <sub>4</sub> ) <sub>2</sub> (SC <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SeCu] <sub>2</sub> <sup>2-</sup>	2.338(1)–2.344(1) av. 2.341(1)	2.331(1) <sup>b</sup>	2.699(2)	109.14(6)–109.97(4) av. 109.43(4)	109.83(6)	5(c)
[(WSe <sub>4</sub> ) <sub>2</sub> (Cu(dppm)) <sub>4</sub> ] <sup>2+</sup>	2.3206(7)	2.4202(11)–2.4513(11) av. 2.4357(11)	2.8172(8)	108.12(4)–111.40(2) av. 109.76(3)	108.11(2)–109.07(2) av. 108.43(2)	28
<b>1</b>	2.316(2)–2.373(2) av. 2.346(2)	2.369(3)–2.388(3) av. 2.381(3)	2.731(2)–2.747(2) av. 2.737(2)	108.16(7)–110.05(7) av. 109.47(7)	107.60(10)–109.06(11) av. 108.32(11)	This work
<b>2</b>	2.337(2)–2.349(2) av. 2.342(2)	2.348(2)–2.406(2) av. 2.374(2)	2.693(2)–2.720(2) av. 2.707(2)	106.34(7)–110.88(6) av. 109.48(6)	108.01(8)–108.90(8) av. 108.37(8)	This work

<sup>a</sup> Bond distances in Å and bond angles in ° with e.s.d.s in parentheses. <sup>b</sup> Cu–Se<sub>ligand</sub> (2.284(2) Å) is not included.

parameters of related W–Cu–Se compounds are compiled in Table 2 for comparison.

### Spectral features

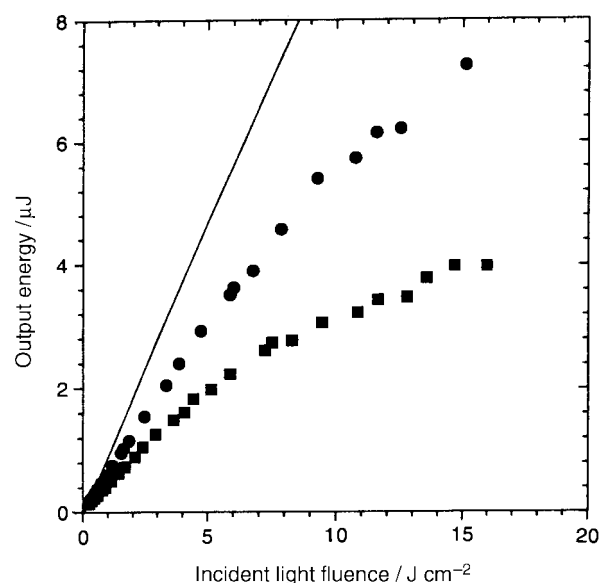
The bands near 1500 and 1000 cm<sup>-1</sup> are very characteristic for the C=N and C–S stretching vibrations of the R<sub>2</sub>NCS<sub>2</sub> ligand.<sup>25</sup> For cluster **1**, the strong absorption at 1476 cm<sup>-1</sup> is assigned to the stretching vibration of the C=N bond with a considerable double-bond character. This is consistent with the C–N bond distances of 1.32–1.38 Å. For cluster **2**, it is interesting that the stretching vibration of the C=N bond at 1525 cm<sup>-1</sup> has shifted evidently to a higher wavenumber region than that of **1**. This indicates an important effect of the mass of the alkyl substituents. The absorptions at 330–350 cm<sup>-1</sup> are assigned to Cu–S vibrations. In the region 290–310 cm<sup>-1</sup> where the W–Se vibrations are expected the W–Se stretching vibrations for **1** and **2** are only slightly red-shifted compared to that of [WSe<sub>4</sub>]<sup>2-</sup> (305 cm<sup>-1</sup>).<sup>1a</sup> For **1**, two types of W–Se absorptions at 303 and 295 cm<sup>-1</sup> are observed, which is consistent with the W–μ<sub>2</sub>-Se and W–μ<sub>3</sub>-Se bond modes in the solid-state structure.

Not unexpectedly, the absorption peaks of the <sup>1</sup>H NMR spectra for clusters **1** and **2** are very close to those of the free R<sub>2</sub>NCS<sub>2</sub><sup>-</sup>, which indicates the geometric structures of the cluster core have little influence on the proton chemical shielding of the ligands.

The electronic spectra of complexes **1** and **2** are characterized by two absorptions in the 280–560 nm range, while there appear three absorptions in the spectrum of [NEt<sub>4</sub>]<sub>2</sub>[WSe<sub>4</sub>]. The high energy absorption may be attributed to charge transfer from R<sub>2</sub>NCS<sub>2</sub><sup>-</sup> ligand to Cu<sup>I</sup>, which is typical of R<sub>2</sub>NCS<sub>2</sub><sup>-</sup>-containing complexes and cluster compounds. The strong broad peak can be assigned as the internal Se-to-W charge-transfer transitions of the [WSe<sub>4</sub>]<sup>2-</sup> moiety, which are red-shifted compared to that of the free [WSe<sub>4</sub>]<sup>2-</sup> anion.<sup>26</sup>

### Optical properties

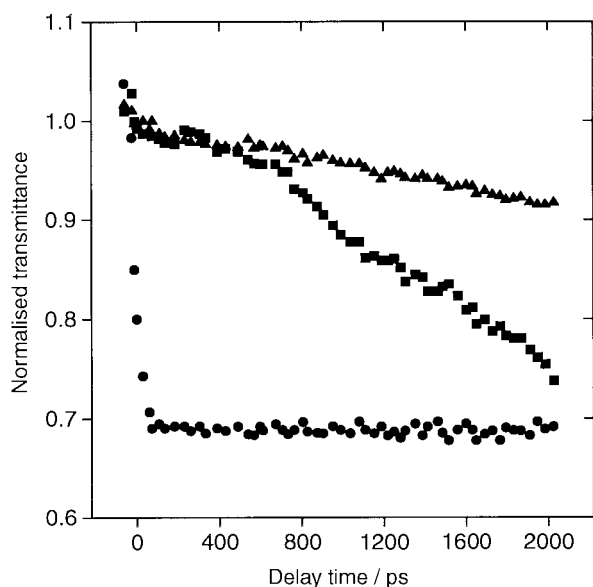
As a part of our research for optical-limiting materials we have studied the NLO properties of a number of inorganic clusters with different structural modes. Up to now, we have discovered that Ag-containing cubane-like clusters [NBu<sub>4</sub>]<sub>3</sub>[MS<sub>4</sub>Ag<sub>3</sub>-XX'<sub>3</sub>]<sup>12</sup> and [MSe<sub>4</sub>Ag<sub>3</sub>X(PPh<sub>3</sub>)<sub>3</sub>]<sup>27</sup> (M = Mo or W; X = Cl or Br; X' = Cl, Br or I), a hexagonal prism-shaped cluster [Mo<sub>2</sub>Ag<sub>4</sub>S<sub>8</sub>(PPh<sub>3</sub>)<sub>4</sub>]<sup>13a</sup> and open cross-frame clusters [WCu<sub>4</sub>S<sub>4</sub>(SCN)<sub>2</sub>(py)<sub>6</sub>]<sup>13b</sup> and [(WSe<sub>4</sub>)<sub>2</sub>(Cu(dppm))<sub>4</sub>][ClO<sub>4</sub>]<sub>2</sub> (dppm = bis(diphenylphosphino)methane)<sup>28</sup> have large optical limiting effects. With reference to these results, we have tried to synthesize some heterobimetallic sulfido- and selenido-clusters of similar structural types and to explore their optical limiting effects.



**Fig. 4** Optical limiting effect of clusters **1** (filled circles) and **2** (filled squares). The straight line is an eye guide with 89% transmittance.

The optical limiting effects in clusters **1** and **2** are depicted in Fig. 4. The transmittance is normalized to its linear transmittance for each sample measured when the fluence is low. Using 532 nm laser light, the relatively lower transmittances are 82% for **1** and 65% for **2** with the same concentration. The straight line is an eye guide with 89% transmittance. Under the experimental conditions used, cluster **2** performs much better than **1**. For **2**, the light energy transmitted starts to deviate from Beer's law as the input light fluence reaches about 1.2 J cm<sup>-2</sup>, and the sample solution becomes increasingly less transparent as the fluence rises. The threshold for **2** was measured as 1.1 J cm<sup>-2</sup> with a saturation fluence transmission of 8 J cm<sup>-2</sup>. The threshold of **1** was measured to be about 6 J cm<sup>-2</sup> under similar experimental conditions.

Further to confirm the non-linear origin we have conducted pump probe experiments. The results with a pump fluence of 1.14 J cm<sup>-2</sup> are given in Fig. 5. The transmittance of the weak probe light is normalized to its linear transmittance. These two samples have an identical concentration, the different transmittance being due to the shoulders in the linear absorption of cluster **1**. The response of a C<sub>60</sub>-toluene solution has also been used to test the same apparatus. The fast drop of the probe signal is typical for C<sub>60</sub> due to the excited singlet state absorption, while the very slow recovery results from the excited triplet state absorption, which can be explained by a five-energy-level model.<sup>29</sup> Clusters **1** and **2**, however, have different responses. From Fig. 5 we can see that the maximum



**Fig. 5** Pump-probe result for  $C_{60}$  in toluene solution (filled circles) and clusters **1** (filled triangles) and **2** (filled squares) in DMF solution. Pump fluence is  $1.14 \text{ J cm}^{-2}$ .

non-linear transmission loss for cluster **2** is much higher than that of **1**. Although the non-linear response of **2** is slower than that of  $C_{60}$ , the maximum non-linear transmission for **2** is slightly higher than that for  $C_{60}$ .<sup>30</sup> Therefore, this non-linearity is very effective for nanosecond laser pulses as we observed in optical limiting experiments.<sup>18</sup>

It is interesting to compare the optical limiting abilities of clusters **1** and **2** with those of other clusters of similar structural types. The T-frame shaped cluster **1**, as well as the nest-shaped clusters  $[\text{MoCu}_3\text{OS}_3\text{BrCl}_2]^{2-}$  and  $[\text{MoCu}_3\text{OS}_3(\text{NCS})_3]^{2-}$ ,<sup>10a</sup> has a relatively high threshold. From previous study, the nest-shaped cluster is positioned over a six-membered  $\text{Cu-S-Cu-S-Cu-S}$  ring which appears like a doughnut, and the  $\text{M=O}$  group is not responsible for the non-linear refractive property change. Thus, this kind of metal cluster has a relatively small optical limiting capability. The T-frame shaped cluster has two different types of co-ordinated Se atoms: two- and three-co-ordinated. The electronic interactions between  $\mu$ -Se and  $\mu_3$ -Se bridged metal atoms may result in different electron delocalizations in the cluster molecule, which needs a higher pump energy to generate the plasma, further leading to degradation of the limiting effect. In comparison with the limiting effects of the cross frame clusters with planar  $\text{WCu}_4$ , cluster **2** containing ligand  $\text{Et}_2\text{NCS}_2^-$  has a higher threshold than those of clusters with similar structure, such as  $[\text{WCu}_4\text{S}_4(\text{SCN})_2(\text{py})_6]$  and  $[\text{WSe}_4\{\text{Cu}(\text{dppm})\}_4][\text{ClO}_4]_2$ . A previous conclusion was that only minor modifications of the NLO effects were observed when all of the three replaceable peripheral ligands of the cubane cage shaped cluster were replaced.<sup>11b</sup> It is now preferable to reconsider the limiting effects influenced by the properties of the peripheral ligands on the basis of the present study on optical response. The strong  $\sigma$ -donor ligands, such as py,  $\text{PPh}_3$  and dppm, result in transfer of electron density from the copper-complex fragments toward the  $[\text{WE}_4]^{2-}$  ( $\text{E} = \text{S}$  or  $\text{Se}$ ) moiety. However, the  $\pi$ -conjugated ligand  $\text{R}_2\text{NCS}_2^-$  leads to delocalization of electron density to both Cu and W atoms. In other words, the change of the extent of electron delocalization between the HOMOs and the LUMOs in the cluster is more significant. Consequently, a greater change in the strength of interaction between the cluster molecules and propagation optical field is induced by photoexcitation.<sup>31</sup> Further theoretical analyses are underway in our laboratories.

In summary, we have synthesized and characterized two heteroselenometallic cluster compounds containing dithiocarb-

amate ligands. With nanosecond-duration laser pulses, the limiting thresholds for the two clusters were obtained and compared with those of  $C_{60}$ . The non-linear responses for the clusters in DMF have also been studied in picosecond time-resolved pump-probe experiments. Influences of structural types and peripheral ligands on the non-linear optical properties were discussed and renewed. We are currently investigating more versatile co-ordination geometries and structure types of heteroselenometallic clusters and further studying their NLO properties so that some desired NLO functions will be achieved.

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