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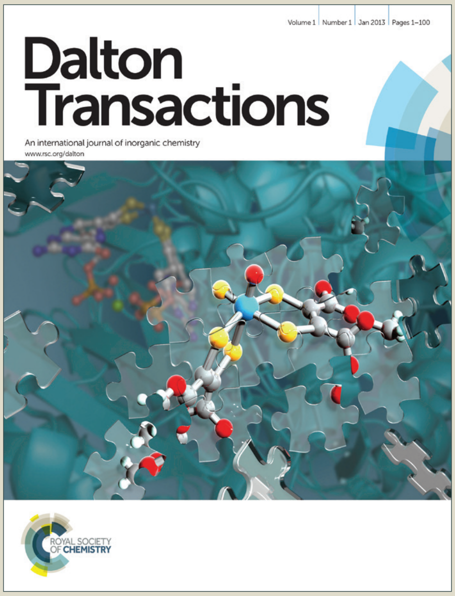

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Cite this: DOI: 10.1039/c0xx00000x

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PAPER

Tin Sulfide and Selenide Clusters soluble in Organic Solvents with the Core Structures of Sn_4S_6 and Sn_4Se_6

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

Reactions of LSnCl (**1**) (L = N(2,6-i$Pr_2C_6H_3$)($SiMe_3$)) with sulfur and selenium, respectively under mild conditions yielded two tin chalcogenide clusters. Surprisingly the tin atoms of the $L_4Sn_4S_6$ (**2**) and $L_4Sn_4Se_6$ (**3**) clusters are oxidized from Sn(II) of the precursor to Sn(IV) of the products under concomitant reduction of elemental sulfur and selenium to sulfide and selenide, respectively. The released chlorine radicals from the precursor RSnCl (**1**) react under oxidative addition with another RSnCl molecule to yield the side product $LSnCl_3$ (**4**). The soluble nature of compounds **2** and **3** in organic solvents is a unique property of this class of compounds and makes them suitable for reactions in organic solvents. Compounds **2** and **3** were characterized by single crystal X-ray diffraction and multinuclear NMR investigations. Furthermore in ROP polymerization, the two products show high catalytic activity. For the first time a tin selenide compound functions in ROP catalysis.

Introduction

In recent years metal chalcogenides have become an important target,[1] due to their solubility in organic solvents, when the inorganic metal chalcogenide core is surrounded by an organic ligand shell. Chalcogenide complexes of the general composition $[(RM)_xE_y]$ (R = organic ligand; M = Ge, Sn; E = S, Se, Te), which are based on an adamantane-(AD) or double-decker-type (DD) inorganic core, have been known for a long time with innocent ligands like Me, Ph, tBu, CF_3, C_6F_5, $C(SiMe_3)_3$.[2] Furthermore, systems with decorated functional organic ligands such as $C_2H_4COO(H)$, $CMe_2CH_2C(O)(Me)$,[3] mono- and bisfunctionalized ferrocenyl units have also been described.[4] The number of organo-wrapped metal chalcogenides on the molecular level are less known due to the limited synthetic approaches and reactivity studies. Further extension of both the inorganic and the organic part of this class of complexes is a challenging target.

In 2006, ligand **L** (N(2,6-i$Pr_2C_6H_3$)($SiMe_3$)) was used for the preparation of high-nuclearity Group 14 metalloid clusters by Power et al.[5] Due to the less sterically hindered ligand, compounds with low-valent tin form easily clusters. To the best of our knowledge the preparation of organic solvent soluble metal chalcogenide clusters through an intermolecular redox process is virtually unexplored. Complexes of low-valent group 14 metals react with sulfur and selenium, respectively, often to the corresponding M=S or M=Se species.[6] Herein, we report on a less hindered ligand to prepare two tin chalcogenide clusters using LSn(II)Cl , sulfur and selenium, respectively, as precursors.

Result and Discussion

Treatment of LSnCl with equiv amounts of S and Se, respectively, under ambient temperature results in compounds $L_4[Sn_4S_6]$ (**2**) and $L_4[Sn_4Se_6]$ (**3**) (Scheme 1). The metal chalcogenide clusters **2** and **3** were prepared uniquely by the reaction of low-valent tin complex (**1**) with sulfur and selenium, respectively. Previously reports on the preparation of such compounds are using salt elimination reaction or treatment of the precursor under stronger conditions.[7] The byproduct $LSnCl_3$ (**4**) was characterized using ESI-MS(+) analysis of the mother liquor from the reaction of **3** ($LSnCl_3$: m/z 473.35, $[LSnCl_3]^+$) (Figure S1). After removal of all volatiles and extraction of the residue with n-hexane, crystalline colorless solid of **2** and crystalline yellow solid of **3** were obtained in yields of 42% and 37%, respectively. They are thermally quite stable (268 °C and 247 °C(dec.)). Previously we tried the traditional method (reaction of LSnCl with Li_2S, Li_2Se, Na_2S, and Na_2Se, respectively) for preparing the desired compounds. However, this method was not successful for achieving the target complexes but rather a mixture of compounds was formed. Furthermore compounds **2** and **3** were characterized by elemental analysis, single crystal X-ray diffraction, and ^{119}Sn NMR spectroscopy. For compound **3** was also employed ^{77}Se NMR spectroscopy. Compounds **2** and **3** show each only one resonance in the ^{119}Sn NMR spectrum (Figure, S4, S5). This indicates that all tin atoms are equivalent on the nmr time scale, reflecting their high symmetrical structure of both **2** and **3**. The ^{77}Se NMR spectrum of **3** reveals one resonance at δ 55.49 ppm, indicating the equivalent of all the selenium atoms (Figure, S5). Compounds **2** and **3** are both soluble in toluene and THF, but only slightly soluble in n-hexane.

The structures of **2** and **3** were further confirmed by X-ray single crystal diffraction and contain co-crystallizing solvent molecules in the crystal structures comprising compounds **2** and **3** as **2**·*n*-hexane and **3**·2THF. **2** crystallizes in the orthorhombic space group *Pnma*, which contains a quasi-tetrahedral, AD-type $[Sn_4S_6]$ core with amido ligands (Figure 1). All Sn atoms have the same coordination sphere, where each is surrounded by three S atoms and one amido ligand. The Sn−S bond lengths (2.3890(11)-2.4137(9)Å) are in a narrow range and in agreement with those reported for $(C_6F_5Sn)_4S_6$ (2.40(1)-2.41(1)Å).[8] The Sn−N bond lengths (2.018(5)-2.032(3)Å) are slightly shorter, when compared with that of the starting material (2.068(2)Å).[5] Compound **3** crystallizes in the monoclinic space group *C*2/*c*, the Sn−Se bond lengths are in a narrow range (2.5233(5)-2.5409(5)Å) and comparable to those in $[(PhSe)_3Sn{-}Fc{-}Sn(SePh)_3]$ (2.5058(11)-2.5413(11)Å) (Fc = ferrocenyl) (Figure 2).[9]

Dehnen et al. studied the influence of various specific organometallic ligands on the structural and electrochemical properties of complexes containing the inorganic Sn/S as well as the Sn/Se core.[4,10] They found that $(RFcSn)_4Sn_6S_{10}]$ [RFc = $CMe_2CH_2C(Me){=}N{-}N{=}C(Me)Fc$] resembles that in the gas phase. Consequently, we investigated the spectrometric properties of complexes **2** and **3** (See the SI, Figure S6, S7). However, compounds **2** and **3** were found to dissociate under APCI-MS conditions (see the SI, Figure S2, S3).

Main-group molecular clusters are interesting because the coordination of their constrained atoms may resemble atoms at elemental surfaces.[11-14] The stoichiometric reaction of cluster $Sn_8(ArMe_6)_4$ ($ArMe_6$ = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$) with small molecules under ambient conditions has been reported.[15] The known catalytic properties of metal clusters in organic processes are mostly reported with metallasiloxanes,[16] while other main-group metal clusters are less studied. It is well known that metal-alkyl and metal-alkoxide are used as initiators in ROP.[17] However, metal selenide compounds have never been studied for this process. We investigated the ROP with **2** and **3**, respectively as novel initiators (See Table 2). The two catalysts show high activity in toluene of the polymerization at 100 °C. All polymerizations are complete within 6 h, giving polymers with M_n (obsd) values and low polydispersities (M_w/M_n = 1.08−1.42). It is noteworthy that alcohol is normally added, which leads to a dramatically acceleration of the polymerization process yielding polymers of narrower PDI_S.[19] However in our case, polymers of relatively narrow dispersities are obtained without adding alcohol, which implies that a better control is possible by the catalysts **2** and **3**, respectively. Considering the importance of Group 14 polymerization catalysts, in most of the cases low valent germanium(II),[20] tin(II)[17c, 21] and lead(II)[22] ROP catalysts are used. All of the initiators exhibit a similar bias toward ROP catalysts, which is attributed to a chain-end control mechanism influenced predominantly by the presence of the lone pair of electrons. Compared with other tin(II) compounds, **2** and **3** have open coordination sites for substrate binding and activation. We assume that the bulky ligand with harder donors could affect the Lewis acidity of the metal center, with the consequence of showing remarkable effects on the catalytic performance.

Based on the ^{1}H NMR (Figure S8) described above, a mechanism has been proposed to elaborate on the cooperation between the Sn atoms of the inorganic core supported by the organic ligand shell. A brief coordination-insertion mechanism is proposed in which an acyl−oxygen bond cleavage occurs and one monomer inserts into one Sn−E (S, Sn) bond. A second monomer coordinates to an adjacent Sn atom, which is activated for insertion into the newly formed Sn−O bond. The polymer chain thus shuttles between different Sn atoms, leading to a highly efficient polymerization process (Scheme S1).

Experimental Section

General Procedures. All manipulations were carried out under a dry argon or nitrogen atmosphere using Schlenk line and glovebox techniques. Solvents including THF, toluene and n-hexane were dried by refluxing with sodium/potassium benzophenone under N_2 prior to use. ε-Caprolactone was stirred over CaH_2 for 18 h and distilled under vacuum. Commercially available chemicals were purchased from J&K and used as received. Elemental analyses were performed by the Analytical Instrumentation Center of the Beijing Institute of Technology. Melting points of the compounds were measured in a sealed glass tube using the Büchi-540 instrument. Raman spectra were recorded on Horiba Jobin Yvon XploRa instrument. Infrared spectra of **2** and **3** were recorded on a Perkin Elmer spectrophotometer. UV-visible absorption spectra were recorded on a 4802 UV/VIS Double Beam Spectrophotometer. Mass spectra were acquired with an Agilent Accurate-Mass-Q-TOF MS 6520 system equipped with an atmospheric pressure chemical ionization (APCI) source. Molecular weight and the polydispersities of polymers were determined by Shimadzu CTO-20A Gel Penetration Chromatography (GPC) equipped with polystyrene gel columns using THF as an eluent (1 mL/min), calibrated by polystyrene standards at 25 ℃. Compound LSnCl (L=N(2,6-iPr$_2$C$_6$H$_3$)(SiMe$_3$)) was prepared according to the literature.[23]

Preparation of [L$_4$[Sn$_4$S$_6$] (**2**). A solution of LSnCl (0.401 g, 1.0 mmol) in THF (10 mL) was added drop by drop to a suspension of sulfur (0.032g, 1.0 mmol) in THF (10 mL) at room temperature. After the addition was complete, stirring of the reaction mixture was continued overnight. Then the solvent was removed in vacuo. The solid was extracted with n-hexane (20 mL), and the extract was stored at room temperature for 2 d to afford **2** as colorless crystals. An additional crop of **2** was obtained from the mother liquor. Total yield: 0.116g (42%), mp 268 °C (decomp). ^{1}H NMR (400 MHz, CDCl$_3$ 298 K, ppm): δ = 0.27 (s, 36H, SiMe$_3$), 1.33 (d, 48H, CH$_3$), 3.58 (sept, 8H, $^3J_{H\text{-}H}$ = 6.5 Hz, 4 H, CHMe$_2$), 7.12-7.25 (m, 12H, C$_6$H$_3$). ^{13}C NMR (400 MHz, CDCl$_3$ 298 K, ppm): δ =148.04, 140.41, 125.40, 123.57 (*p*-, *m*-, *o*-, *i*-*C* of Ar), 27.65 (*C*HMe$_2$), 22.51 (CH*Me*$_2$), 2.79(Si*Me*$_3$). ^{119}Sn NMR (186 MHz, C$_4$D$_8$O), δ = 43.1 ppm. Anal. calcd (%) for $C_{60}H_{104}N_4Si_4Sn_4S_6$ (Mr =1661.07): C, 43.34; H, 6.26; N, 3.37. Found: C, 43.23; H, 5.95; N, 3.49.

Preparation of L$_4$[Sn$_4$Se$_6$]. A solution of LSnCl (0.401g, 1.0 mmol) in THF (10 mL) was added drop by drop to a suspension of selinium (0.079g, 1.0 mmol) in THF (10 mL) at room temperature. After the addition was complete, stirring of the reaction mixture was continued overnight. Then the solvent was removed in vacuo. The solid was extracted with n-hexane (20 mL), and the extract was stored at room temperature for 3 d to afford **3** as yellow crystals. An additional crop of **3** was obtained from the mother liquor. Total yield: 0.119g (37%), mp 247 °C (decomp). ^{1}H NMR 400 MHz, CDCl$_3$ 298 K, ppm): δ = 0.18 (s, 36H, SiMe$_3$), 1.11 (d, 48H, CH$_3$), 3.40 (sept, 8H, $^3J_{H\text{-}H}$ = 6.5 Hz, 4 H, CHMe$_2$), 6.88-7.01 (m, 12H, C$_6$H$_3$). ^{13}C NMR (400 MHz, CDCl$_3$ 298K, ppm): δ = 148.27, 141.51, 125.27, 123.60 (*p*-, *m*-, *o*-, *i*-*C* of Ar), 27.76 (*C*HMe$_2$), 25.32 (CH*Me*$_2$), 3.43 (Si*Me*$_3$). ^{119}Sn NMR (186 MHz, C$_4$D$_8$O), δ = -168.4 ppm; ^{77}Se NMR (95 MHz, C$_4$D$_8$O), δ = 55.5ppm. Anal. calcd (%) for $C_{60}H_{104}N_4Si_4Sn_4Se_6$ (Mr = 1942.44): C, 37.07; H, 5.35; N, 2.88. Found: C, 36.77; H, 5.17; N, 2.97.

Ring-Opening Polymerization of ε-Caprolactone Catalyzed by 2 and 3, respectively. A 50 mL Schlenk flask was charged with the desired amount of initiator in toluene. The solution was stirred for 2 min in a glovebox, and toluene along with ε-CL was added to the solution. The solution was stirred for the time given in the table of the manuscript. During the stirring an increased viscosity was observed. The reaction mixture was quenched by addition of 1M HCl-ethanol solution, and poured into methanol to precipitate the polymer, which was dried under vacuum and checked by weight.

Single Crystal X–ray Structure Determination and Refinement.

Single crystals of **2** and **3** were mounted with glue on glass fibers and crystal data were collected on the Rigaku AFC10 Saturn724 + (2 × 2 bin mode) diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical absorption correction was applied using the SADABS program.[24] Structures were solved by direct methods[25] and refined by full-matrix least squares on F^2 using the SHELXL-97 program.[26] A summary of the crystal data is given in Table **1**

Table 1 Crystallographic Data for Compounds **2 and 3**

	2·*n*-hexane	**3**·2THF
Empirical formula	$C_{66}H_{118}N_4S_6Si_4Sn_4$	$C_{68}H_{120}N_4O_2Se_6Si_4Sn_4$
Formula weight	1747.12	2086.56
Temperature (K)	153(2)	173(2)
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*	*C*2/*c*
a (Å)	14.2045(18)	23.528(5)
b (Å)	27.355(4)	14.278(3)
c (Å)	23.153(3)	27.858(5)
α (°)	90	90.00
β (°)	90	112.960(2)
γ (°)	90	90.00
V ($Å^3$)	8997(2)	8617(3)
Z	4	4
Dcalcd. (Mg/m^3)	1.290	1.608
Absorption coefficient (mm^{-1})	1.324	3.776
F(000)	3576	4128
θ range for data collection(°)	2.25 to 31.51	2.032 to 31.504
Index ranges	$-20 \leq h \leq 20$	$-34 \leq h \leq 34$
	$-39 \leq k \leq 37$	$-14 \leq k \leq 20$
	$-34 \leq l \leq 31$	$-37 \leq l \leq 40$
Reflections collected	86324	50082
R (int)	0.0441	0.0386
Data / restraints / parameters	15131 / 15 /440	14139 / 17 /440
Goodness-of-fit on F^2	1.001	1.003
Final Rint [$I > 2\sigma(I)$]	$R1^a = 0.0620$	$R1^a = 0.0485$
	$wR2^b = 0.1637$	$wR2^b = 0.1276$
Rint (all data)	$R1^a = 0.0651$	$R1^a = 0.0563$
	$wR2^b = 0.1670$	$wR2^b = 0.1335$
CCDC number	1406396	1406397

Conclusions

Herein, we report on amido ligand supported tin sulfide and selenide clusters. Compared with the traditional route, where LiCl or NaCl are eliminated, **2** and **3** are prepared from a Sn(II) complex with sulfur and selenium, respectively. This is a novel method for preparing soluble Group 14 clusters. Both **2** and **3** show high activity for initiating the polymerization of ε-caprolactone. This is the first example of a tin selenide compound being used in the ROP process.

Acknowledgements

This work was supported by the Beijing Natural Science Foundation (2132044), the Deutsche Forschungsgemeinschaft (RO224/64-1), and the International Science & Technology Cooperation Program of China (2012DFR40240, 2014DFR61080).

Notes and references

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† Electronic Supplementary Information (ESI) available: CCDC 1406396–1406397. For ESI and CIF see DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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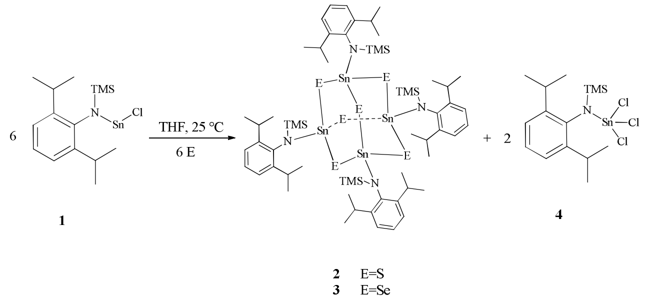
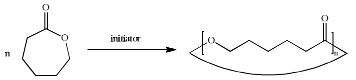


Scheme 1. **Preparation of Compound 2 and 3**

Table 2. Ring-opening polymerization of ε-caprolactone (CL) catalyzed by 2 and 3[a]



Entry	Initiator	[CL]/[Sn]	Time (h)	Conv (%)[b]	M_w (g/mol)[c]	M_n (g/mol)[c]	PDI[c]
1	**2**	500:1	4.0	43	9879	7734	1.28
2	**2**	1000:1	4.0	51	10287	8662	1.19
3	**2**	1500:1	6.0	57	11324	8804	1.27
4	**2**	2000:1	6.0	62	14822	10448	1.42
5	**3**	500:1	4.0	63	4527	4203	1.08
6	**3**	1000:1	4.0	78	15659	12776	1.22
7	**3**	1500:1	6.0	82	19896	17006	1.17
8	**3**	2000:1	6.0	88	21252	17832	1.19

[a]Conditions: 30 mL toluene as solvent, 100 ºC. [b]Obtained from ^{1}H NMR analysis. [c]Experimental M_n, M_w and PDI values determined by GPC in THF *vs* Polystyrene standards, using a correcting factor of 0.56 [18].

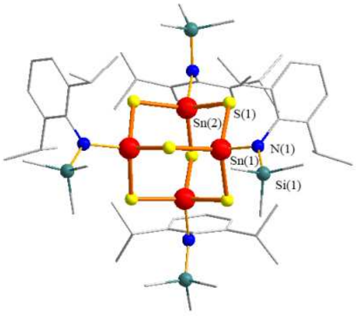


Figure 1. Molecular structure of 2 without H atoms

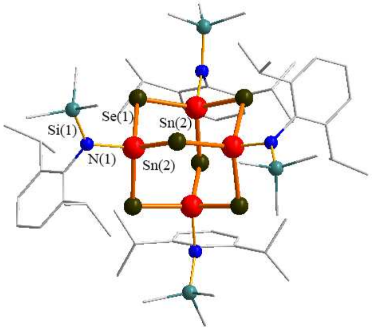


Figure 2. Molecular structure of 3 without H atoms

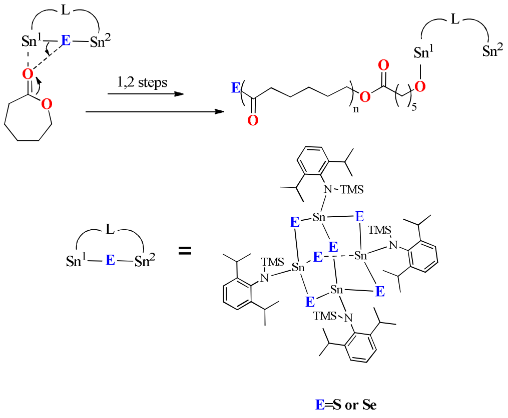


Table of Content

Reactions of LSnCl (**1**) (L = N(2,6-iPr$_2$C$_6$H$_3$)(SiMe$_3$)) with sulfur and selenium, respectively under mild conditions yielded 5 two tin chalcogenide clusters. The two products show high catalytic activity in ROP catalysis.