Inorg. Chem. **2008**, *47*, 4054−4059

Inorganic Chemistry

Article

Self-Assembly of Luminescent Sn(IV)/Cu/S Clusters Using Metal Thiolates as Metalloligands

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Received September 5, 2007

Through the use of $(Bu_4N)_2[Sn_3S_4(edt)_3]$ (edt = $SCH_2CH_2S^{2-}$) and $Sn(SPh)_4$ as metalloligands, three neutral compounds have been obtained: $[(Ph_3P)_2Cu]_2SnS(edt)_2 \cdot 2CH_2Cl_2 \cdot H_2O$ (**1a**), $[(Ph_3P)_2Cu]_2SnS(edt)_2 \cdot 2DMF \cdot H_2O$ (**1b**), and $[(Ph_3P)Cu]_2Sn(SPh)_6 \cdot 3H_2O$ (**2**). Single-crystal X-ray diffraction studies revealed that compounds **1a** and **1b** contain the same neutral butterfly-like $[(Ph_3P)_2Cu]_2SnS(edt)_2$ cluster, which consists of one central SnS_5 dreich trigonal bipyramid sharing one vertex and two sides with two slightly distorted CuS_2P_2 tetrahedrons. Compound **2** has a linear $[(Ph_3P)Cu]_2Sn(SPh)_6$ cluster that is composed of a central distorted SnS_6 octahedron sharing two opposite planes with two slightly distorted CuS_3P tetrahedrons. Compound **1a** exhibited an emission at 568 nm ($\tau = 12.86\ \mu s$) in the solid state, while in CH_2Cl_2 solution, **1a** exhibited a green emission at 534 nm ($\tau = 4.75\ \mu s$). Compound **2** showed an intense red emission at 696 nm ($\tau = 3.64\ \mu s$) upon excitation at 307 nm in the solid state.

Introduction

Over the past 10-plus years, the synthesis of compounds containing heterometallic M/E′/E (M = transition metal, E′ = group 14 or 15 element, E = S, Se, Te) clusters has become a field of intense research interest.[1] Especially, the chemistry of heterometallic tin chalcogenides has attracted increasing attention because of these compounds' diverse structures and fascinating potential applications in semiconductor, magnetic, optoelectronic, and nonlinear optical materials and solar control devices.[2] Great advances in the field have been achieved by chemists to date. Various structural types of quaternary/ternary tin chalcogenides, from isolated molecular species {e.g., $[Ph_4P]_4[Sn_2(WS_4)_4]$}[3] to solid-state phases {e.g., $Na_2[CdSnS_4]$ and $K_2[AgSbS_4]$},[4] mesostructured phases {e.g., $(CP)_x[Pt_ySn_4E'_{10}]$ ($x = 1.9$–2.8; $y = 0.9$–1.6; E′ = S, Se; CP = cetylpyridinium)},[5] and supertetrahedral isolated inorganic clusters {e.g., $[M_4(\mu_4\text{-Se})$-

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10.1021/ic701741m CCC: $40.75

$(SnSe_4)_4]$[10] (M = Co, Mn, Zn, Cd, Hg)},[6] have been prepared. Various synthetic methods, including high temperature solid-state reactions,[7] molten-salt (flux) methods,[8,9] solvothermal synthesis,[2d,10] and solution methods,[11] have been employed in the search for new quaternary/ternary tin chalcogenides. Among tin chalcogenides, however, the assembly of tin thiolates with transition-metal units has seldom been investigated. To date, only a few examples of heterometal complexes containing thiolate ligands, such as $[Sn(mit)_6Cu_4]$,[12] $[AgSn(\mu\text{-}SC_6H_4PPh_2)_2Me_2(PPh_2Me)]CF_3SO_3 \cdot CH_2Cl_2$,[13] $[Au_2Sn(^tBu)_2(C_6F_5)_2(SC_6H_4PPh_2)_2]$,[14] polymeric $[(Py)_2Eu(2\text{-}S\text{-}NC_5H_4)_2Sn(2\text{-}S\text{-}NC_5H_4)_2]_n$,[15] and $[LFeSnFeL]^{n+}$ [$n = 2, 3$; L = 1,4,7-(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane],[16] have been reported in the literature.

During the past thirty years, our group has contributed to research on heterometallic compounds of the Mo(W)/Cu(Ag)/S system by utilizing thiomolybdates and thiotungstates as metalloligands.[17] Recently, our interests have extended to research on M/M′/S compounds (M = main-group metal, M′ = transition metal), especially the study of Sn/Cu/S clusters, for the following two reasons: First, copper/tin reagents are efficient catalysts for allylation, propargylation, alkylation, and benzylation of disulfides and elemental sulfur, but because little structural evidence for intermediates has been given, the study of Sn/Cu/S clusters may be beneficial for the understanding of the catalytic mechanism of copper/tin reagents.[18] Second, polynuclear copper(I) compounds usually demonstrate interesting photoluminescence, so the exploration of novel Sn/Cu/S clusters may provide potential applications for new luminescent materials.[19]

We have previously reported on one novel luminescent bottle-shaped Sn(IV)/Cu/S cluster, $[Sn_3Cu_4(S_2C_2H_4)_6(\mu_3\text{-}O)(PPh_3)_4](ClO_4)_2 \cdot 3CH_2Cl_2$,[20] which was obtained by using $Sn(S_2C_2H_4)_2$ as a metalloligand. Through the use of $(Bu_4N)_2[Sn_3S_4(edt)_3]$ and $Sn(SPh)_4$ as metalloligands, another three novel heterotrinuclear Sn(IV)/Cu(I)/S compounds, $[(Ph_3P)_2Cu]_2SnS(edt)_2 \cdot 2CH_2Cl_2 \cdot H_2O$ (**1a**), $[(Ph_3P)_2Cu]_2SnS(edt)_2 \cdot 2DMF \cdot H_2O$ (**1b**), and $[(Ph_3P)Cu]_2Sn(SPh)_6 \cdot 3H_2O$ (**2**), have been obtained. Herein we report on the syntheses, structures, characterizations, and luminescence properties of these three compounds.

Experimental Section

Materials. The reagents dithioglycol (H_2edt) and thiophenol (HSPh) were purchased from Acros; the other reagents were of analytical quality. All chemicals and solvents were used as received without further purification. $(Bu_4N)_2[Sn_3S_4(edt)_3]$,[21] $Sn(SPh)_4$,[22] and $Cu(PPh_3)_3Br$[23] were synthesized according to the literature.

Syntheses. $[(Ph_3P)_2Cu]_2SnS(edt)_2 \cdot 2CH_2Cl_2 \cdot H_2O$ (1a). To $(Bu_4N)_2[Sn_3S_4(edt)_3]$ (0.125 g, 0.1 mmol) and $Cu(PPh_3)_3Br$ (0.090 g, 0.1 mmol) was added 10 mL of CH_2Cl_2, forming a red solution. The solution was heated for 5 min and then filtered, and the resulting red filtrate was allowed to stand in air. After three days, a large number of yellow block crystals were obtained, washed with ethyl ether, and dried in air. Yield: 0.059 g [69.4% based on $Cu(PPh_3)_3Br$]. Anal. Calcd for $C_{78}H_{74}Cl_4OCu_2P_4S_5Sn$ (1699.12): H, 4.39; C, 55.13. Found: H, 4.72; C, 55.78. IR (KBr pellet) and far-IR (CsI pellet) ν (cm^{-1}): 3448 (w), 3068 (w), 2904 (w), 1585 (w), 1479 (m), 1433 (s), 1093 (m), 742 (s), 694 (vs), 619 (w), 513 (m), 438 (w), 366 (w), 339 (w). Raman (KBr powder) ν (cm^{-1}): 3037 (s), 2856 (s), 1452 (w), 634 (m), 537 (m), 318 (w). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 1.557 (w, 2H, $-H_2O$); 2.945 (br, 8H, $-SCH_2$); 5.285 (m, 4H, CH_2Cl_2); 7.226, 7.301, 7.313 (s, 60H, Ar$-$H). ^{31}P NMR (100 MHz, $CDCl_3$, ppm): –4.48.

$[(Ph_3P)_2Cu]_2SnS(edt)_2 \cdot 2DMF \cdot H_2O$ (1b). $(Bu_4N)_2[Sn_3S_4(edt)_3]$ (0.250 g, 0.2 mmol) and $Cu(PPh_3)_3Br$ (0.180 g, 0.2 mmol) were dissolved in 10 mL of DMF to yield a red solution. The solution was stirred for 10 min and then filtered. The resulting red filtrate was layered with 10 mL of i-PrOH and allowed to stand in air. A few red block crystals were obtained after one month, washed with ether, and dried in air. Yield: 0.016 g [9.6% based on $Cu(PPh_3)_3Br$]. Because of the poor yield and the long crystallization period, only the IR spectrum of **1b** was measured. IR (KBr pellet) ν (cm^{-1}): 3446 (w), 3068 (w), 2904 (w), 1678 (w), 1585 (w), 1477 (m), 1433 (s), 1093 (m), 742 (s), 694 (vs), 619 (w), 513 (s).

$[(Ph_3P)Cu]_2Sn(SPh)_6 \cdot 3H_2O$ (2). To CuCN (0.027 g, 0.3 mmol) and PPh_3 (0.079 g, 0.3 mmol) was added 20 mL of CH_2Cl_2. Stirring the mixture for 20 min resulted in the formation of a clear solution,

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Table 1. Crystal Data Collection and Structure Refinement Parameters for **1a**, **1b**, and **2**

	1a	**1b**	**2**
empirical formula	$C_{78}H_{74}Cl_4OP_4S_5Cu_2Sn$	$C_{82}H_{84}N_2O_3P_4S_5Cu_2Sn$	$C_{72}H_{66}O_3P_2S_6Cu_2Sn$
formula weight	1699.12	1675.46	1479.32
crystal description	yellow block	yellow block	red rhombic
crystal system	orthorhombic	orthorhombic	rhombohedral
space group	*Pccn*	*Pccn*	$R\bar{3}$
a (Å)	18.147(4)	18.1073(3)	13.5176(10)
b (Å)	19.441(4)	18.6699(2)	13.5176(10)
c (Å)	22.540(5)	23.1699(4)	32.999(4)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	120
V (Å^3)	7952(3)	7832.9(2)	7752(10)
Z	4	4	3
ρ_{calc} (g cm^{-3})	1.419	1.421	1.411
2θ range (deg)	4.18–50.08	3.14−50.30	4.26–50.06
μ (mm^{-1})	1.230	1.118	1.232
F(000)	3464	3448	2268
measured reflns	49354	18664	4204
reflns with $I > 2\sigma(I)$	5649	4218	1575
parameters	429	447	144
independent reflns	7038	6967	2044
R(int)	0.0287	0.0594	0.0485
R^a	0.0672	0.0620	0.0684
$R_w{}^b$	0.1994	0.1421	0.1473
GOF (F^2)	1.011	1.169	1.229
max/min diff. peaks (e Å^{-3})	0.900/–1.155	0.587/–0.544	0.562/–0.490

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$. For **1a**, $a = 0.1330$ and $b = 18.8636$; for **1b**, $a = 0.0214$ and $b = 35.0064$; for **2**, $a = 0.0092$ and $b = 79.8574$.

to which was added a solution of $Sn(SPh)_4$ (0.055 g, 0.1 mmol) in 10 mL of CH_2Cl_2. The resulting mixture was stirred for 5 h and then filtered. The filtrate was allowed to stand in air for one week, during which a large number of red rhombic crystals that were difficult to dissolve in common solvents were obtained. The crystals were washed with ether and dried in air. Yield: 0.0575 g [58% based on $Sn(SPh)_4$]. Anal. Calcd for $C_{72}H_{66}O_3Cu_2P_2S_6Sn$ (mol wt 1479.32): H, 4.50; C, 58.46. Found: H, 4.34; C, 57.26. IR (KBr pellet) and far-IR (CsI pellet) ν (cm^{-1}): 3400 (w), 3053 (w), 1585 (w), 1479 (m), 1435 (s), 1097 (m), 741 (s), 694 (vs), 688 (s), 617 (w), 542 (m), 523 (s), 501 (m), 424 (m), 386 (w), 340 (w), 289 (w), 253 (w), 229 (w). Raman (KBr) ν (cm^{-1}): 2856 (m), 1452 (w), 634 (m), 542 (m), 318 (w).

Physical Measurements. Elemental analyses for carbon and hydrogen were performed using a Vario EL III elemental analyzer. Infrared (IR) and far-infrared (far-IR) spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using pressed KBr and CsI pellets, respectively. Samples for Raman spectroscopy were diluted in KBr powder and placed in NMR tubes, and the Raman spectra were recorded using a Nicolet Magna 950 Raman spectrometer. ^{1}H and ^{31}P NMR spectra were measured using a Unity 500 NMR spectrometer, with 85% H_3PO_4 employed as an external standard for ^{31}P NMR spectra measurements. Luminescence properties were measured and recorded using an FLS-920 fluorescence spectrometer.

X-ray Crystallography. Single crystals suitable for X-ray diffraction, having dimensions of 0.06 × 0.08 × 0.100 mm for **1a**, 0.30 × 0.34 × 0.38 mm for **1b**, and 0.16 × 0.20 × 0.20 mm for **2**, were mounted on the top of a glass fiber. Crystal data for **1a** were measured on a Saturn 70 CCD diffractometer at room temperature [293(2) K], while those for **1b** and **2** were collected on a Siemens SMART CCD diffractometer at room temperature [293(2) K], via the ω scan technique using graphite-monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinements for **1a**, **1b**, and **2** were performed with Smart-CCD software. An absorption correction was applied to the intensity data using SADABS.[24]

The structures were solved by direct or Patterson methods, and the heavy atoms were located from the E-map. The remaining non-hydrogen atoms were determined from successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically except those mentioned otherwise. The hydrogen atoms were generated geometrically. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 program package.[25] Final R and R_w values were computed using the formulas $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$.

A summary of the crystal data and structure refinement parameters for the three compounds is provided in Table 1. Selected bond lengths and bond angles for compounds **1a** and **1b** and compound **2** are listed in Tables 2 and 3, respectively.

Results and Discussion

In view of the greater stability and better solubility of tin thiolates as opposed to thiostannates in organic solvents, tin thiolates instead of thiostannates were selected as the tin source in the synthesis of heterometallic tin chalcogenides. In our recent work,[20] the luminescent bottle-shaped Sn(IV)/Cu/S cluster $[Sn_3Cu_4(S_2C_2H_4)_6(\mu_3\text{-}O)(PPh_3)_4](ClO_4)_2 \cdot 3CH_2Cl_2$ was obtained by reaction of $Sn(S_2C_2H_4)_2$ as a metalloligand with $(Ph_3P)_2Cu(CH_3CN)_2(ClO_4)$. In this work, $Sn(SPh)_4$ and $(Bu_4N)_2[Sn_3S_4(edt)_3]$ were selected as tin sources, and $Cu(PPh_3)_3Br$ and $Cu(PPh_3)CN$ (synthesized in situ from CuCN and PPh_3 in CH_2Cl_2) were used as copper sources.

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Table 2. Selected Bond Lengths and Bond Angles for Compounds **1a** and **1b** [a]

1a		**1b**	
bond	length (Å)	bond	length (Å)
Sn(1)−S(1)	2.364(2)	Sn(1)−S(1)	2.350(2)
Sn(1)−S(2)	2.6058(16)	Sn(1)−S(2)	2.5844(15)
Sn(1)−S(3)	2.4222(18)	Sn(1)−S(3)	2.418(2)
Cu(1)−P(1)	2.2952(16)	Cu(2)−P(1)	2.290(2)
Cu(1)−P(2)	2.2752(15)	Cu(2)−P(2)	2.270(2)
Cu(1)−S(1)	2.4486(8)	Cu(2)−S(1)	2.4523(7)
Cu(1)−S(2)	2.3944(17)	Cu(2)−S(2A)	2.3763(17)
angle	measure (deg)	angle	measure (deg)
S(1)−Sn(1)−S(3)	121.96(6)	S(1)−Sn(1)−S(3)	121.46(6)
S(1)−Sn(1)−S(2)	90.76(3)	S(1)−Sn(1)−S(2)	91.26(4)
S(3)−Sn(1)−S(3)	116.07(11)	S(3)−Sn(1)−S(3A)	117.08(11)
S(3)−Sn(1)−S(2)	87.18(5)	S(3A)−Sn(1)−S(2)	87.05(7)
S(3)−Sn(1)−S(2A)	92.02(5)	S(3)−Sn(1)−S(2)	91.63(7)
S(2)−Sn(1)−S(2A)	178.48(7)	S(2)−Sn(1)−S(2A)	177.48(8)
S(2)−Cu(1)−S(1)	93.97(6)	S(2A)−Cu(2)−S(1)	93.97(7)
P(1)−Cu(1)−S(2)	107.36(6)	P(1)−Cu(2)−S(2A)	107.84(8)
P(1)−Cu(1)−S(1)	107.74(5)	P(1)−Cu(2)−S(1)	107.52(6)
P(2)−Cu(1)−S(1)	114.30(5)	P(2)−Cu(2)−S(1)	114.28(6)
P(2)−Cu(1)−S(2)	115.31(6)	P(2)−Cu(2)−S(2A)	117.40(8)
P(2)−Cu(1)−P(1)	115.82(6)	P(2)−Cu(2)−P(1)	113.82(6)
Sn(1)−S(1)−Cu(1)	89.76(5)	Sn(1)−S(1)−Cu(2)	89.12(5)
Cu(1)−S(1)−Cu(1A)	179.52(9)	Cu(2)−S(1)−Cu(2A)	178.24(10)
Cu(1)−S(2)−Sn(1)	85.45(5)	Cu(2A)−S(2)−Sn(1)	85.48(5)

[a] Symmetry code: A = $-x + 3/2$, $-y + 3/2$, z.

Table 3. Selected Bond Lengths and Bond Angles for Complex **2**[a]

bond	length (Å)
Sn(1)−S(1)	2.5657(17)
Sn(1)−Cu(1)	3.1452(16)
Cu(1)−P(1)	2.198(4)
Cu(1)−S(1)	2.421(2)
angle	measure (deg)
S(1)−Sn(1)−S(1A)	81.43(6)
S(1)−Sn(1)−S(1D)	98.57(6)
S(1B)−Sn(1)−S(1E)	180.0
S(1A)−Sn(1)−S(1D)	180.0
S(1E)−Sn(1)−S(1D)	81.43(6)
S(1)−Sn(1)−S(1C)	180.0
Cu(1)−Sn(1)−Cu(1C)	180.0
P(1)−Cu(1)−S(1)	127.02(5)
S(1)−Cu(1)−S(1A)	87.49(7)
S(1)−Cu(1)−Sn(1)	52.98(5)
Cu(1)−S(1)−Sn(1)	78.15(6)

[a] Symmetry code: A = $-y + 1$, $x - y$, z; B = $-x + y + 1$, $-x + 1$, z; C = $-x + 4/3$, $-y + 2/3$, $-z + 2/3$; D = $y + 1/3$, $-x + y + 2/3$, $-z + 2/3$; E = $x - y + 1/3$, $x - 1/3$, $-z + 2/3$.

Complex **1a** was obtained by reaction of an equimolar ratio of $(Bu_4N)_2[Sn_3S_4(edt)_3]$ and $Cu(P(Ph)_3)_3Br$ in dichloromethane at room temperature. It is obvious that the tin thiolate component $[SnS(edt)_2]^{2-}$ that exists in **1a** is not found in the $[Sn_3S_4(edt)_3]^{2-}$ reactant. It is possible that a rearrangement from $[Sn_3S_4(edt)_3]^{2-}$ to $[SnS(edt)_2]^{2-}$ occurred during the formation of **1a** in the presence of $Cu(PPh_3)_3Br$.

X-ray structure determination revealed that the asymmetric unit of compound **1a** contains one neutral $[(Ph_3P)_2Cu]_2[SnS(edt)_2]$ cluster, two CH_2Cl_2 solvent molecules, and one crystal water molecule. The molecular structure of compound **1a** is shown in Figure 1. Selected bond lengths and bond angles for compound **1a** are listed in Table 2. As shown in Figure 1, the three metal atoms (Sn1, Cu1, Cu1A) in the neutral cluster form an isosceles trigonal metal skeleton with an Sn···Cu separation of 3.349 Å. Sn1 is five-coordinate, surrounded by four sulfur atoms from two 1,2-ethanedithiolate ligands and one μ_3-S atom to form a dreich trigonal bipyramid. As one consequence of coordination of the axial sulfur atoms (S2, S2A) of 1,2-ethanedithiolato to two-sided copper atoms (Cu1, Cu1A), the Sn1–S2 bond length (2.606 Å) is longer than that of Sn1−S3 (2.422 Å). The μ_3-S−Sn1 bond length (2.364 Å) is not only slightly shorter than that in $(Bu_4N)_2[Sn_3S_4(edt)_3]$[21] but also slightly shorter than that in $[PhSn(\mu_3\text{-}S)]_3[Cu_6(PPhMe_2)]_6$ (2.399 Å on average).[11b] The Cu1 atom is four-coordinate, surrounded by two P atoms from PPh_3 ligands, one μ_3-S atom, and one S atom from a 1,2-ethanedithiolato ligand to form a slightly distorted tetrahedron. The Cu−S and Cu−P bond lengths are in the ranges 2.3944(17)−2.4486(8) and 2.2752(15)−2.2952(16) Å, respectively. Therefore, the cluster skeleton can be viewed as a "butterfly" consisting of one central $[SnS(edt)_2]^{2-}$ unit as the body and two $Cu(PPh_3)_2$ units as the wings.

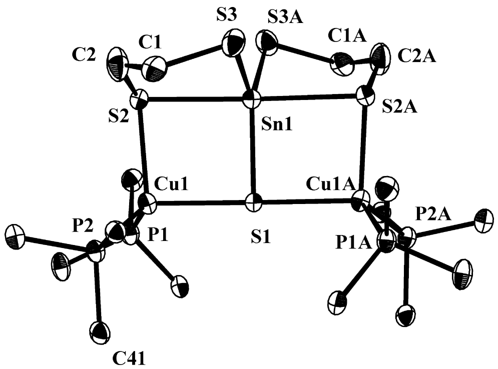

Figure 1. ORTEP drawing (50% thermal ellipsoids) of the neutral cluster **1a**, including an atom labeling scheme. The phenyl rings attached to the phosphorus atoms as well as the hydrogen atoms have been omitted for clarity. Symmetry code: A = $-x - 1/2$, $-y - 1/2$, z.

Complex **1b** possesses the same neutral $[(Ph_3P)_2Cu]_2SnS(edt)_2$ cluster as in complex **1a** along with two DMF solvent molecules and one water solvent molecule. For the purpose of comparison, selected bond lengths and bond angles for compound **1b** are also listed in Table 2. The Sn···Cu distance (3.370 Å) is slightly longer than that in compound **1a**.

The molecular structure of complex **2** is shown in Figure 2, and selected bond lengths and bond angles for **2** are summarized in Table 3. As shown in Figure 2, X-ray structure determination indicated that compound **2** possesses a linear Cu−Sn−Cu metal skeleton. A similar linear metal skeleton has been observed in some heterometallic trinuclear clusters with transition metal as the central metal, such as $(PPh_3Cu)_2M(SAr)_6$ (M = W, Mo, U; Ar = Ph, p-C_6H_4Me, p-C_6H_4F, p-C_6H_4Cl, p-C_6H_4Br).[26] To date, only one example of a main-group metal-centered linear trinuclear cluster has been reported, namely, $[LFeMFeL]^{n+}$ [M = Ge, Sn; n = 2,

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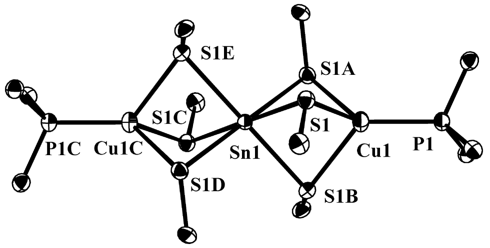

Figure 2. ORTEP drawing (50% thermal ellipsoids) of the cluster metal skeleton of **2**, including an atom labeling scheme. The phenyl rings and the hydrogen atoms have been omitted for clarity. Symmetry code: A = $-x + y + 1, -x + 1, z$; B = $-y + 1, x - y, z$; C = $-x + {}^{4}/_{3}, -y + {}^{2}/_{3}, -z + {}^{2}/_{3}$; D = $x - y + {}^{1}/_{3}, x - {}^{1}/_{3}, -z + {}^{2}/_{3}$; E = $y + {}^{1}/_{3}, -x + y + {}^{2}/_{3}, -z + {}^{2}/_{3}$.

3; L = 1,4,7-(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane], in which the trinuclear cluster is bridged and stabilized by the trident-chelated ligand L.[16]

The Cu1−Sn1−Cu1C bond angle is 180°. The separation between Sn1 and Cu1 is 3.14 Å. The central Sn1 atom is six-coordinate, surrounded by six phenylthiolate ligands that form an octahedron. The two Cu atoms are each bonded to one PPh_3 ligand and three bridging phenylthiolate ligands, forming two slightly distorted tetrahedrons that share the opposing S1−S1A−S1B and S1C−S1D−S1E faces with the SnS_6 octahedron. In the SnS_6 octahedron, the S1−Sn1−S1C, S1A−Sn1−S1D, and S1B−Sn1−S1E bond angles are all equal to 180.0° while the S1−Sn1−S1B and S1B−Sn1−S1D bond angles are 81.43(6) and 98.57(6)°, respectively, implying that the octahedron is slightly distorted. The P−Cu−S and S−Cu−S bond angles in the CuS_3P tetrahedron are 127.02(5) and 87.49(7)°, respectively, which deviate severely from the ideal angles of a regular tetrahedral configuration (109.47°).

The Sn−S bond length in **2** (2.5657 Å) is slightly longer than those in $Sn(SPh)_4(2,2'\text{-bipy})$ (2.497–2.502 Å)[27] and $Sn(SPh)_4$ (2.379–2.401 Å).[22] The Cu−P and Cu−S bond lengths are 2.196 and 2.420 Å, respectively. Therefore, the whole cluster can be viewed as a highly distorted SnS_6 octahedron sharing two parallel faces with two slightly distorted $CuPS_3$ tetrahedrons. The Sn···Cu distances in compounds **1a**, **1b**, and **2** are 3.349, 3.37, and 3.144 Å, respectively. The Sn···Cu separation in compound **2** (3.1452 Å) is shorter than those found in the literature.[11,28]

In the IR and far-IR spectra of the three compounds (see Figures S-1, S-2, and S-4−S-6 in the Supporting Information), the broad band at 3400 cm^{-1} indicates the presence of crystallization water in their unit cells. The medium peak at 1673 cm^{-1} in the IR spectrum of **1b** suggests the presence of C=O. The strong peaks at 1093 cm^{-1} for **1a**, 1093 cm^{-1} for **1b**, and 1096 cm^{-1} for **2** were ascribed to the C−P stretching vibration.[29] The weak peaks at 619 cm^{-1} for **1a**, 619 cm^{-1} for **1b**, and 617 cm^{-1} for **2** were attributed to the corresponding C−S stretching vibration and are comparable to those for previously reported compounds containing C−S bonds.[29] The peaks at 438 cm^{-1} for **1a** and 424 cm^{-1} for **2** were ascribed to the Sn−S stretching vibration.[30] The absorption bands at 336–340 cm^{-1} for **1a**, **1b**, and **2** could be attributed to the stretching vibration of the Cu−S bond.[31]

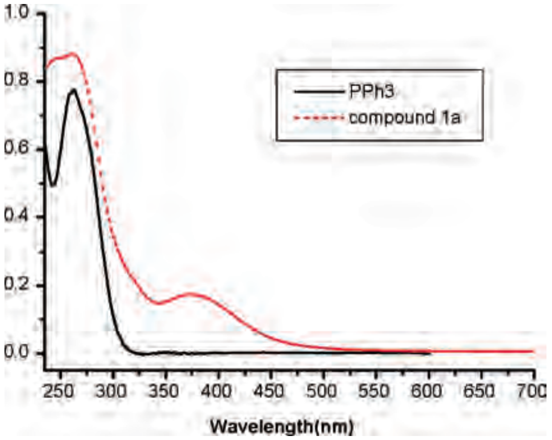

Figure 3. UV–vis absorption spectra of compound **1a** and free PPh_3 in CH_2Cl_2 solution at room temperature.

The ^1H NMR spectrum of compound **1a** in $CDCl_3$ solution was also studied (see Figure S-8 in the Supporting Information). The signal at 1.557 ppm could be attributed to the proton of solvent water.[32] The broad signal at 2.945 ppm was attributed to the protons of SCH_2. The signal at 5.285 ppm was ascribed to the proton of CH_2Cl_2,[32] and the three signals at 7.226, 7.301, and 7.313 ppm could be attributed to PPh_3 Ar−H. The integration matched well with the measured structure. The ^{31}P NMR spectrum of compound **1a** in dichloromethane solution at room temperature showed one signal at −4.49 ppm (see Figure S-9 in the Supporting Information).

The electronic absorption spectrum of compound **1a** in dichloromethane solution at room temperature demonstrated a strong absorption band at 264 nm and a weak absorption band at 380 nm (as shown in Figure 3). The free PPh_3 ligand in CH_2Cl_2 solution showed a strong absorption band with a maximum at 263 nm that could originate from intraligand $\pi \rightarrow \pi^*$ transitions in the phenyl groups of the PPh_3 ligand and usually remains unshifted upon coordination to Cu(I). In view of the fact that $Cu^I(PPh_3)_3Cl$ does not absorb at wavelengths above 350 nm,[33] the weak band at 380 nm did not originate from the Cu^IPPh_3 moiety, and therefore, it might be attributed to $S^{2-} \rightarrow Cu(I)$ or $SC_2H_4S^- \rightarrow Cu(I)$ ligand-to-metal charge transfer (LMCT).

The luminescence properties of complexes **1a**, **1b**, and **2** were also studied. As shown in Figure 4, upon excitation at 360 nm, compound **1a** in the solid state exhibited a green-yellow emission (λ_{max} = 568 nm, τ_{em} = 12.86 μs), while a CH_2Cl_2 solution of **1a** exhibited a green emission (λ_{max} = 534 nm, τ_{em} = 4.75 ns) upon the excitation at 378 nm. For the purpose of

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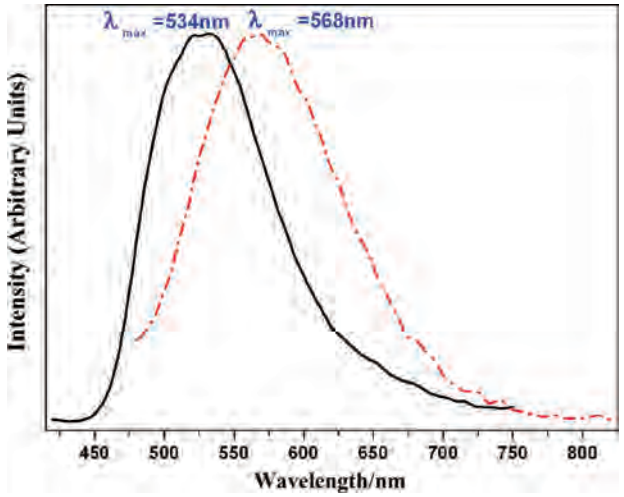

Figure 4. Emission spectra of compound **1a** at room temperature: (black solid line) in CH_2Cl_2 solution upon excitation at 378 nm; (red dashed line) in the solid state upon excitation at 360 nm.

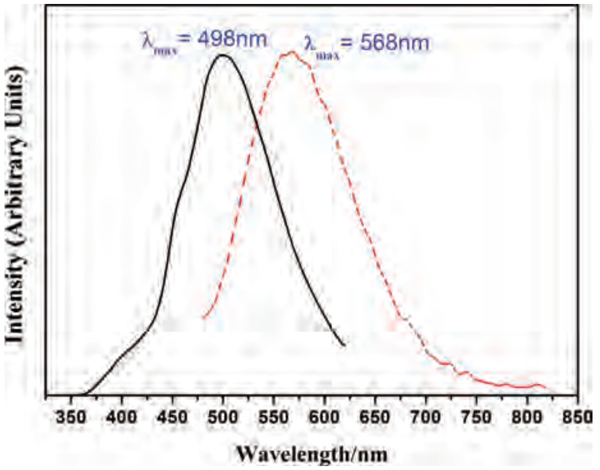

Figure 5. Emission spectra of compound **1a** excited at 360 nm (red dashed line) and $Cu(PPh_3)_3Br$ excited at 337 nm (black solid line) in the solid state at room temperature.

a better comparison, the emission spectra of $Cu(PPh_3)_3Br$ in the solid state (excitation at 337 nm) and CH_2Cl_2 solution (excitation at 380 nm) were measured. The solid-state emission spectra of complex **1a** and $Cu(PPh_3)_3Br$ are shown in Figure 5. Compound **1a** emitted a lower-energy luminescence band with a maximum at 568 nm, a bathochromic shift of 70 nm compared to that of $Cu(PPh_3)_3Br$ ($\lambda_{max} = 498$ nm). As shown in Figure 6, however, the energy luminescence shift was 94 nm from $Cu(PPh_3)_3Br$ to compound **1a** in CH_2Cl_2 solution. Given the reducing nature of thiolate ligands,[19,34] the lower-energy emission of compound **1a** in both the solid state and CH_2Cl_2 solution are tentatively assigned to an admixture of $RS^- \rightarrow Cu$ and/or $S^{2-} \rightarrow Cu$ LMCT and $Cu \rightarrow PPh_3$ metal-to-ligand charge transfer (MLCT).[20] The luminescence properties of complex **1b** were similar to those of complex **1a**.

Compound **2** exhibited an intense red emission ($\lambda_{max} = 696$ nm, $\tau_{em} = 3.64\ \mu s$) upon excitation at 307 nm in the solid state and a higher-energy luminescence band with a maximum at 419 nm upon excitation at 370 nm in CH_2Cl_2 solution, as shown in Figure 7. These emissions were also tentatively assigned to an admixture of $RS^- \rightarrow Cu$ and/or $S^{2-} \rightarrow Cu$ LMCT and $Cu \rightarrow PPh_3$ MLCT.[20] The large Stokes shift (3.19 eV) between the excitation wavelength and the emission maximum of the lower-energy emission for compound **2** indicates that the cluster skeleton undergoes a significant distortion upon excitation. The longer luminescence lifetime ($\tau_{em} = 3.64\ \mu s$) and the large Stokes shift of the complex show that the emission may suggest a phosphorescence nature.

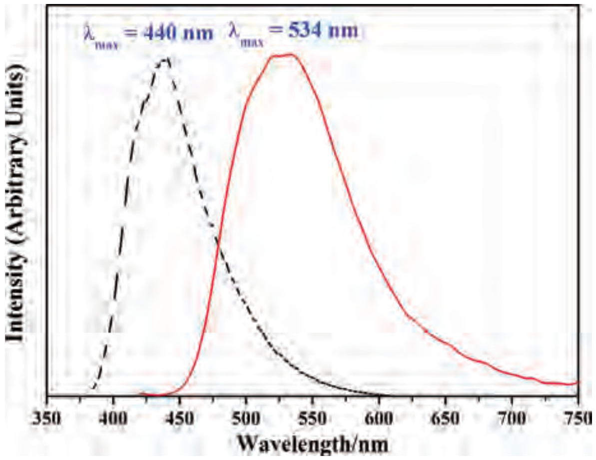

Figure 6. Emission spectra of compound **1a** excited at 378 nm (red solid line) and $Cu(PPh_3)_3Br$ excited at 380 nm (black dashed line) in CH_2Cl_2 solution at room temperature.

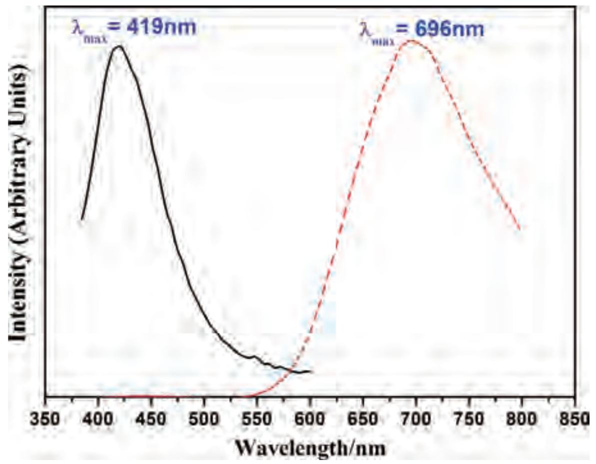

Figure 7. Emission spectra of compound **2** at room temperature: (black solid line) in CH_2Cl_2 solution upon excitation at 370 nm; (red dashed line) in the solid state upon excitation at 307 nm.

Acknowledgment. This work was supported by grants from the 973 Program (2007CB815301 and 2006CB932904), the National Science Foundation of China (20733003 and 20673118), and the Science Foundation of CAS (KJCX2-YW-M05) and of Fujian Province (2006F3132 and 2006L2005).

Supporting Information Available: X-ray crystallographic data in CIF format for compounds **1a**, **1b**, and **2** and various IR, Raman, NMR, and emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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