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Inorganic Chemistry
Article

Heterometallic Aggregates of Copper(I) with Metalloligand $Sn(edt)_2$ (edt = ethane-1,2-dithiolate): Syntheses and Structures of $[Sn(edt)_2Cl(\mu\text{-}I)(\mu_3\text{-}I)(CuPPh_3)_3]$, $[Sn(edt)_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(CuPPh_3)_4]$, and $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3Cu_5(PPh_3)_8][PF_6]_2$

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The treatment of a slurry of an equimolar mixture of $[Sn(edt)_2]$ (edt = ethane-1,2- dithiolate) and $[Et_4N]Cl\cdot xH_2O$ with CuI in the presence of PPh_3 gave a tetranuclear compound, $[Sn(edt)_2Cl(\mu\text{-}I)(\mu_3\text{-}I)(CuPPh_3)_3]$ (**1**), which consists of a rectangular-pyramidal $[Sn(edt)_2Cl]^-$ moiety ligated by three $[Cu(PPh_3)]^+$ fragments via the sulfur atoms of the edt^{2-} ligands. The treatment of a slurry of $[Sn(edt)_2]$ and excess $[Et_4N]Br$ with $[Cu(MeCN)_4][PF_6]$ in the presence of PPh_3 afforded a pentanuclear compound, $[Sn(edt)_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(CuPPh_3)_4]$ (**2**), which comprises two $[(CuPPh_3)_2\text{-}(\mu\text{-}Br)]^+$ fragments symmetrically ligating an octahedral *trans*-$[Sn(edt)_2Br_2]^{2-}$ moiety via the sulfur and bromide atoms. Reaction of $[Sn(edt)_2]$ with $[Cu(MeCN)_4][PF_6]$ and PPh_3 in a mixed $MeCN/CH_2Cl_2$ solution yielded a novel octanuclear compound, $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3Cu_5(PPh_3)_8][PF_6]_2$ (**3**), which may be described as a triangular $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3]^{3-}$ core chelated by three $[Cu(PPh_3)_2]^+$ species and capped by two $[Cu(PPh_3)]^+$ species. The luminescent properties of compounds **1**, **2**, and **3** were investigated in a CH_2Cl_2 solution at room temperature. Upon excitation at $\lambda > 360$ nm, these compounds are luminescent in CH_2Cl_2 solution with emissions having maxima at 422, 515, and 494 nm, respectively.

Introduction

In contrast to well-documented binary metal−chalcogenides, ternary metal−chalcogenide compounds have been relatively less explored.[1] This may be due to the paucity of suitable binary metal−chalcogenide species that can serve as metalloligand precursors to ternary compounds by way of self-assembly reactions.[1,2] Accordingly, the heterometallic compounds containing both group 11 and 13/14 metals are not many.[1c,3] Of these, only very few compounds containing copper/silver and indium/ gallium/tin have been structurally characterized.[1a,2,4,5] One attractive synthetic approach is the self-assembly of appropriate building blocks such as $[M(SR)_4]^-$ (M = In, Ga) and $[Sn(SR)_4]$ (R = akyl) or those from two different metal components to result in the heterometallic cluster compounds with novel structural modes.[1a,4−7] Remarkably, the homoleptic $[In(SR)_4]^-$ (M = In, Ga) can act

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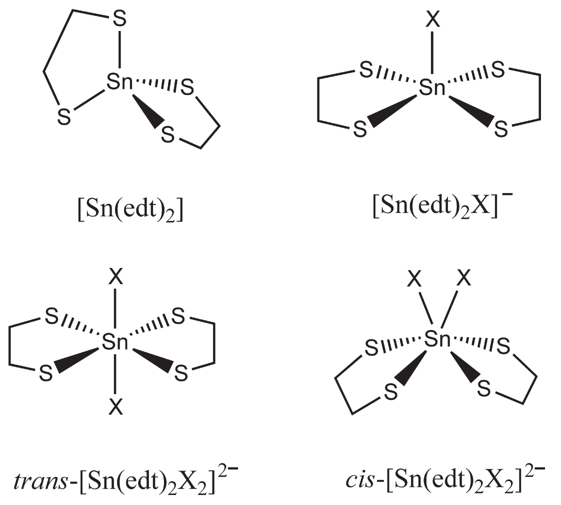
as an excellent metalloligand for coinage metals mainly because of the electron-rich thiolate group and its small steric hindrance.[6] Compared with quite a few reports of heterometallic copper/indium/sulfur(selenium) compounds, analogous heterometallic copper/tin/sulfur(selenium) compounds are even less well exploited. Examples of isolated heterometallic tin/sulfur clusters include $[Sn(Zn_4Sn_4S_{17})]^{6-}$,[8a] $[M_4Sn_4S_{17}]^{10-}$ (M = Mn, Fe, Co, Zn),[8b] $[M_5Sn(\mu_3\text{-}S)_4(SnS_4)_4]^{10-}$ (M = Zn, Co),[8c] and $K_2Ag_6Sn_3S_{10}$,[8d] which were synthesized by solid-state reactions, hydrothermal or solvothermal methods from tin, sulfur, and metal or the corresponding inorganic salt.[9] Wu and co-workers first demonstrated the formation of a novel heptanuclear $Sn^{IV}-Cu^{I}$ compound $[Cu_4Sn_3(edt)_6(\mu_3\text{-}O)(PPh_3)_4](ClO_4)_2$ (edt = ethane-1,2-dithiolate) with a bottle-shaped cluster core by the self-assembly reaction of $Sn(edt)_2$ and $[Cu(PPh_3)]^+$.[7a] In this connection, we are realizing the coordination behavior of neutral spirocyclic $Sn(edt)_2$ in which tin(IV) is four-coordinate with the SnS_4 tetrahedral geometry but may transfer into five-coordinate with the $[SnS_4X]^-$ square-pyramidal geometry and six-coordinate with *trans*-$[SnS_4X_2]^{2-}$ and *cis*-$[SnS_4X_2]^{2-}$ octahedral configurations in the presences of Lewis bases such as halides and hydroxide.[10] Actually, the coordination of spirocyclic $Sn(edt)_2$ with nitrogen- and oxygen-donor ligands has been reported previously.[11] Apart from the coordination ability of the sulfur atoms in $Sn(edt)_2$, the generated species (see Chart 1) may also act as metalloligands to coordinate transition metal atoms via sulfur atoms while the introduced halide groups are partially involved in bridging coordination. Herein, we report three new heterometallic $Sn^{IV}-Cu^{I}$ compounds, $[Sn(edt)_2Cl(\mu\text{-}I)(\mu_3\text{-}I)(CuPPh_3)_3]$ (**1**), $[Sn(edt)_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(CuPPh_3)_4]$ (**2**), and $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3Cu_5(PPh_3)_8][PF_6]_2$ (**3**), formed by the aggregation of copper(I)$-PPh_3$ species with the metalloligand $Sn(edt)_2$ in the presence of halides. Their structural characterizations and spectroscopic properties are also studied in this paper.

Experimental Section

Materials and Measurements. 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. $[Sn(edt)_2]$[11] and $[Cu(MeCN)_4][PF_6]$[12] were prepared according to the literature methods. CuI, $[Et_4N]Cl\cdot xH_2O$, $[Et_4N]Br$, and PPh_3 were purchased from Alfa Aesar and used without further purification. All elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. Electronic absorption spectra were obtained on a Shimadzu UV-3000 spectrophotometer. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer with the use of pressed KBr pellets. Positive fast-atom bombardment (FAB) mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ^1H and ^{31}P, respectively, and chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Luminescence properties were measured and recorded using an FLS-920 fluorescence spectrometer.

Chart 1. Structural Types of $Sn(edt)_2$ and Its Halide Adducts (X = Cl, Br)



Preparation of $[Sn(edt)_2Cl(\mu\text{-}I)(\mu_3\text{-}I)(CuPPh_3)_3]$ (1). To a slurry solution of $[Sn(edt)_2]$ (91 mg, 0.30 mmol) and $[Et_4N]Cl\cdot xH_2O$ (62 mg, 0.30 mmol) in EtOH (5 mL) was added a solution of CuI (190 mg, 1.00 mmol) and PPh_3 (262 mg, 1.00 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature for 4 h, during which time the light yellow solution gradually formed. A little precipitate was removed by filtration, and a clear filtrate was obtained. The filtrate was crystallized by layering with Et_2O to obtain yellow block crystals of $\mathbf{1}\cdot CH_2Cl_2\cdot 0.5EtOH\cdot 0.5H_2O$ after 5 days. Yield: 301 mg (59%). Anal. Calcd for $C_{58}H_{53}ClP_3S_4I_2SnCu_3\cdot(CH_2Cl_2)\cdot 0.5(C_2H_6O)\cdot 0.5(H_2O)$: C, 42.7; H, 3.53. Found: C, 42.3; H, 3.47. UV−vis (CH_2Cl_2, λ_{max}/nm, $10^{-3}\ \varepsilon/M^{-1}\cdot cm^{-1}$): 267 (7.4), 374 (1.1). IR (KBr disk, cm^{-1}): $\nu(H_2O)$ 3433 (mbr), ν(O−H) 3047 (m), ν(P−C) 1083 (s), ν(C−S) 623 (m), ν(Sn−S) 421 (w) and 415 (w). ^1H NMR (DMSO-d_6, ppm): δ 1.52 (s, H_2O), 2.83−3.12 (m, CH_2 in edt), 5.34 (s, CH_2Cl_2), 7.37−7.54 (m, PPh_3). ^{31}P NMR (DMSO-d_6, ppm): δ −1.64 (s), −1.12 (s). MS (FAB): *m*/*z* 1570 (M^+), 1535 ($M^+ - Cl$), 1408 ($M^+ - Cl - I$), 1281 ($M^+ - Cl - 2I$).

Preparation of $[Sn(edt)_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(CuPPh_3)_4]$ (2). To a slurry solution of $[Sn(edt)_2]$ (91 mg, 0.30 mmol) and $[Et_4N]Br$ (147 mg, 0.75 mmol) in MeCN (5 mL) was added a solution of $[Cu(MeCN)_4][PF_6]$ (466 mg, 1.25 mmol) and PPh_3 (328 mg, 1.25 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 2 h; the yellow solution was filtered to remove a little precipitate. Yellow block crystals of **2** were obtained by layering with Et_2O on top of the yellow filtrate after 3 days. Yield: 389 mg (67%). Anal. Calcd for $C_{76}H_{68}P_4S_7Br_4\ SnCu_4$: C, 47.4; H, 3.56. Found: C, 47.1; H, 3.52. UV−vis (CH_2Cl_2, λ_{max}/nm, $10^{-3}\ \varepsilon/M^{-1}\cdot cm^{-1}$): 263 (6.1), 378 (0.92). IR (KBr disk, cm^{-1}): ν(P−C) 1088 (s), ν(C−S) 617 (m), ν(Sn−S) 431 (w) and 424 (w). ^1H NMR (DMSO-d_6, ppm): δ 2.89 (br, s, CH_2 in edt), 7.41−7.59 (m, PPh_3). ^{31}P NMR (DMSO-d_6, ppm): δ −2.37 (s). MS (FAB): *m*/*z* 1926 (M^+), 1846 ($M^+ - Br$), 1766 ($M^+ - 2Br$), 1686 ($M^+ - 3Br$), 1606 ($M^+ - 4Br$).

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Table 1. Crystallgraphic Data and Experimental Details for $[Sn(edt)_2Cl(\mu\text{-}I)(\mu_3\text{-}I)(CuPPh_3)_3]\cdot CH_2Cl_2\cdot 0.5EtOH\cdot 0.5H_2O$ (**1**$\cdot CH_2Cl_2\cdot 0.5EtOH\cdot 0.5H_2O$), $[Sn(edt)_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(CuPPh_3)_4]$ (**2**), and $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3Cu_5(PPh_3)_8][PF_6]_2\cdot 6H_2O$ (**3**$\cdot 6H_2O$)

	1$\cdot CH_2Cl_2\cdot 0.5EtOH\cdot 0.5H_2O$	**2**	**3**$\cdot 6H_2O$
formula	$C_{60}H_{59}OCl_3P_3S_4I_2SnCu_3$	$C_{76}H_{68}P_4S_4Br_4SnCu_4$	$C_{156}H_{157}O_9F_{12}P_9S_{12}Sn_3Cu_5$
fw	1686.68	1925.91	3741.04
a, Å	13.9411(3)	19.8088(2)	27.305(4)
b, Å	15.9580(3)	19.3467(2)	24.268(4)
c, Å	16.8180(3)	20.2052(2)	29.046(4)
α, deg	99.561(1)	90	90
β, deg	104.362(1)	90	105.809(7)
γ, deg	101.830(1)	90	90
V, Å^3	3453.50(12)	7743.34(14)	18519(5)
Z	2	4	4
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$Pbca$	$C2/c$
ρ_{calcd}, g cm^{-3}	1.622	1.652	1.342
T, K	296(2)	296(2)	296(2)
μ, mm^{-1}	2.505	3.694	1.233
$F(000)$	1660	3816	7580
no. of reflns	64000	61252	28229
no. of indep. reflns	15819	8860	18209
R_{int}	0.0247	0.0628	0.0908
R_1, wR_2 ($I > 2.0\sigma(I)$)	0.0602, 0.1882	0.0369, 0.0622	0.0685, 0.1289
R_1, wR_2 (all data)	0.0725, 0.2038	0.0583, 0.0768	0.0905, 0.1844
goodness of fit[a]	1.046	0.987	1.003

[a] $GoF = [(\sum w|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Preparation of $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3Cu_5(PPh_3)_8][PF_6]_2$ (3). To a slurry solution of $[Sn(edt)_2]$ (91 mg, 0.30 mmol) in wet MeCN (5 mL) was added a solution of $[Cu(MeCN)_4][PF_6]$ (279 mg, 0.75 mmol) and PPh_3 (393 mg, 1.50 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature overnight, and the yellow solution was filtered to remove the white precipitate. The yellow block crystals of **3** were obtained by the slow diffusion of Et_2O into the yellow filtrate after 2 days. Yield: 253 mg (37%). Anal. Calcd for $C_{156}H_{145}O_3F_{12}P_9S_{12}Sn_3Cu_5\cdot 6(H_2O)$: C, 50.1; H, 4.23. Found: C, 49.6; H, 4.20. UV−vis (CH_2Cl_2, λ_{max}/nm, 10^{-3} ε/M$^{-1}\cdot$cm^{-1}): 260 (7.3), 379 (1.1). IR (KBr disk, cm^{-1}): $\nu(H_2O)$ 3428 (mbr), ν(O−H) 3041 (m), ν(P−C) 1092 (s), ν(C−S) 621 (m), ν(Sn−S) 419 (w) and 407 (w). ^{1}H NMR (DMSO-d_6, ppm): δ 1.54 (br, s, H_2O), 2.84−3.10 (m, CH_2 in edt), 7.37−7.64 (m, PPh_3), 8.14 (br, s, OH). ^{31}P NMR (DMSO-d_6, ppm): δ −142.1 (s), −1.83 (s), 2.37 (s). MS (FAB): m/z 3632 ($M^+ - 1$), 3381 ($M^+ - 3OH - 1$).

X-Ray Crystallography. Crystallographic data and experimental details for $[Sn(edt)_2Cl(\mu\text{-}I)(\mu_3\text{-}I)(CuPPh_3)_3]\cdot CH_2Cl_2\cdot 0.5EtOH\cdot 0.5H_2O$ (**1**$\cdot CH_2Cl_2\cdot 0.5EtOH\cdot 0.5H_2O$), $[Sn(edt)_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(CuPPh_3)_4]$ (**2**), and $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3Cu_5(PPh_3)_8][PF_6]_2\cdot 6H_2O$ (**3**$\cdot 6H_2O$) are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. The collected frames were processed with the software SAINT.[13] The data were corrected for absorption using the program SADABS.[14] Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[15] All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3}−H = 0.96 and C_{sp^2}−H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or nitrogen atoms before the final cycle of least-squares refinement. The solvent molecules in **1**$\cdot CH_2Cl_2\cdot 0.5EtOH\cdot 0.5H_2O$ and **3**$\cdot 6H_2O$ were isotropically refined without hydrogen atoms due to disorder. The six fluorine atoms of the $[PF_6]^-$ anion in **3**$\cdot 6H_2O$ were isotropically refined. Atomic coordinates, complete bond distances and angles, and anistropic thermal parameters of all non-hydrogen atoms for all three clusters are available as Supporting Information.

Results and Discussion

Syntheses and Reactions. Scheme 1 illustrates the structural transformations of $[Sn(edt)_2]$ and synthetic reactions of new $[Sn(edt)_2X_n]^{m-}$ (X = Cl, Br, OH; $n = 1$, $m = 1$; $n = 2$, $m = 2$) species with copper(I) in the presence of PPh_3. It was reported that nucleophilic attack at the tin center in the neutral spirocyclic $[Sn(edt)_2]$ by halides at the tin center affords the 1:1 or 1:2 adducts.[10,11] Thus, it seems reasonable to assume that the anion $[Sn(edt)_2Cl]^-$ is present in an ethanol solution of an equimolar ratio of $[Sn(edt)_2]$ and $[Et_4N]Cl\cdot xH_2O$. Further treatment of as-prepared $[Sn(edt)_2Cl]^-$ with CuI in the presence of PPh_3 led to the formation of the tetranuclear neutral compound $[Sn(edt)_2Cl(\mu\text{-}I)(\mu_3\text{-}I)(CuPPh_3)_3]$ (**1**). As expected, $[Sn(edt)_2Cl]^-$ as a metalloligand binds to Cu(I) via the sulfur atoms of the edt^{2-} moieties, while the introduced terminal chloride is not involved in coordination. Similarly, treatment of $[Sn(edt)_2]$ with excess $[Et_4N]Br$ in an acetonitrile solution resulted in a homogeneous slurry which contained the *trans*-$[Sn(edt)_2Br_2]^{2-}$ anion. The following reaction between the $[Sn(edt)_2Br_2]^{2-}$ anion and the $[Cu(MeCN)_4]^+$ cation in the presence of PPh_3 afforded a pentanuclear neutral compound $[Sn(edt)_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(CuPPh_3)_4]$ (**2**), which features a coplanar openlike $SnCu_4$ core in the solid state. Different from the $[Sn(edt)_2Cl]^-$ species in **1**, the $[Sn(edt)_2Br_2]^{2-}$ as a metalloligand coordinates with copper atoms via both sulfur and bromide atoms in **2**.

Inspired by the previous report on the isolation of a luminescent bottle-shaped heptanuclear Sn^{IV}−Cu^I cluster compound, $[Cu_4Sn_3(edt)_6(\mu_3\text{-}O)(PPh_3)_4](ClO_4)_2$,[7a] together with the knowledge of coordination behaviors of

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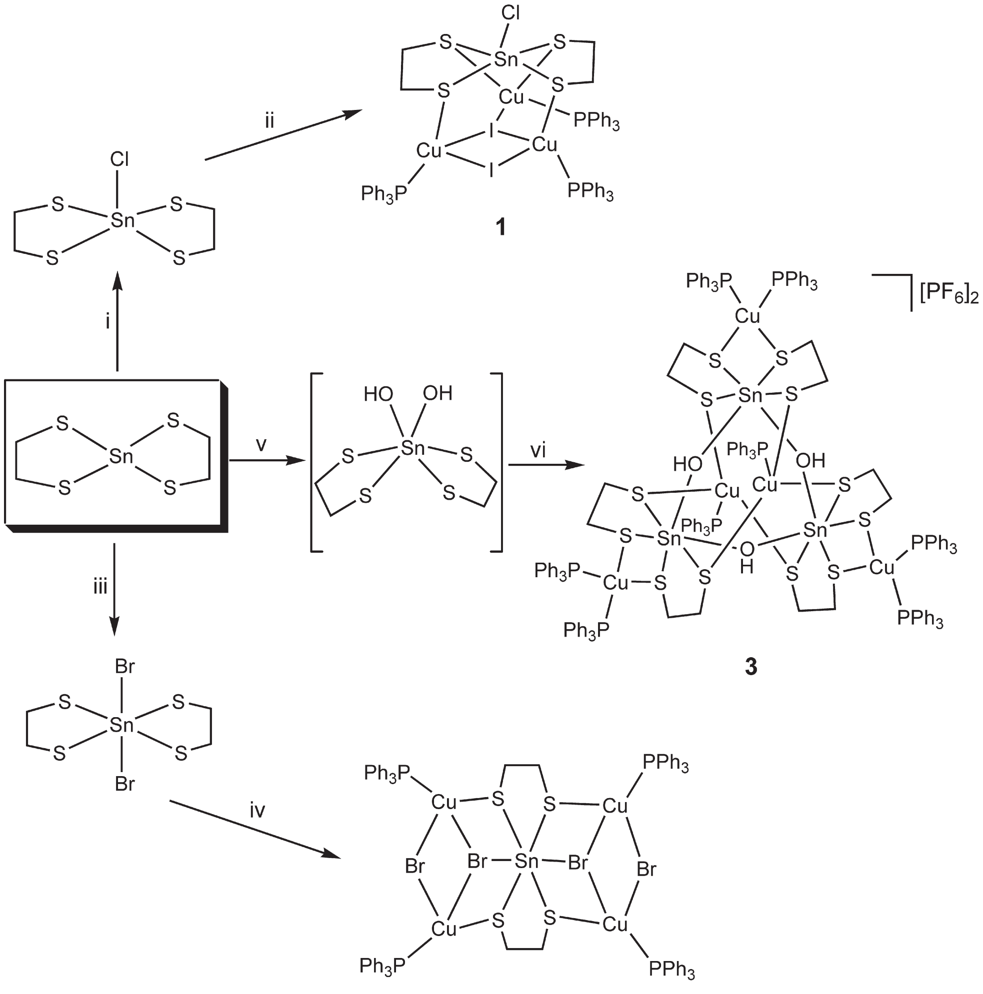
Scheme 1. [a]



[a] Reagents and conditions: (*i*) $[Et_4N]Cl \cdot xH_2O$/EtOH, (*ii*) CuI/PPh_3/CH_2Cl_2, (*iii*) $[Et_4N]Br$/MeCN, (*iv*) $[Cu(MeCN)_4][PF_6]$/PPh_3/CH_2Cl_2, (*v*) H_2O/MeCN, (*vi*) $[Cu(MeCN)_4][PF_6]$/PPh_3/CH_2Cl_2.

$[Sn(edt)_2]$ and its derivatives, we set out to study the reaction of $[Sn(edt)_2]$ and $[Cu(MeCN)_4][PF_6]$ in the presence of PPh_3 in a mixed MeCN/CH_2Cl_2 solution at room temperature, which led to isolation of a novel octanuclear compound $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3Cu_5(PPh_3)_8]$ $[PF_6]_2$ (**3**), which was isolated in 37% yield. It seems that the $[Sn(edt)_2]$ species was transformed to the trimer $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3]^{3-}$ during the formation of **3** over a relatively long reaction time. Further support for this speculation comes from the X-ray crystallographic analysis of **3**. In the present system, it is interesting to note that each of the $[Cu(PPh_3)_2]^+$ species chelates with each of the $[Sn(edt)_2]$ moieties. The two $[Cu(PPh_3)]^+$ species triply cap the three $[Sn(edt)_2]$ moieties in $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3]^{3-}$ by coordination with the sulfur atoms. Compounds **1**−**3** are very air-stable in both the solid state and solutions and soluble in very polar solvents such as dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformide.

Spectroscopic Properties. Infrared and electronic spectra for **1**−**3** are well within the range observed for the reported $[Sn(edt)_2]$ derivatives. The Sn−S stretching modes of the compounds can be identified as weakly sharp peaks in the range of 400−440 cm^{-1}.[16] Thus, the weak peaks at 421 and 415 cm^{-1} for **1**, 431 and 424 cm^{-1} for **2**, and 419 and 407 cm^{-1} for **3** attributed to the corresponding Sn−S stretching vibrations are comparable to those for the related compounds containing $[Sn(edt)_2]$ moieties. The middle peaks at 623 cm^{-1} for **1**, 617 cm^{-1} for **2**, and 621 cm^{-1} for **3** were ascribed to the C−S stretching vibrations.[17] The broad bands at ca. 3430 cm^{-1} for $\nu(H_2O)$ and medium peaks at ca. 3040 cm^{-1} for ν(O−H) in the IR spectra indicated the presences of lattice hydrates in the crystalline products **1** and **3**. The electronic absorption spectra of compounds **1**−**3** in CH_2Cl_2 solution at room temperature display low energy absorption bands at ca. 370−380 nm and higher energy absorptions at ca. 260−270 nm. The latter are assigned as intraligand $\pi \rightarrow \pi^*$ transitions of PPh_3 in the compounds since the free PPh_3 ligand also absorbs at a similar energy.[18] The low energy absorption bands are not of the d−d type but probably arise from S(edt^{2-}) → Cu(I) ligand-to-metal charge transfer (LMCT).[7]

The broad multiplets at 2.80−3.15 ppm in the ^{1}H spectra of **1** and **3** were attributed to the protons of edt^{2-}

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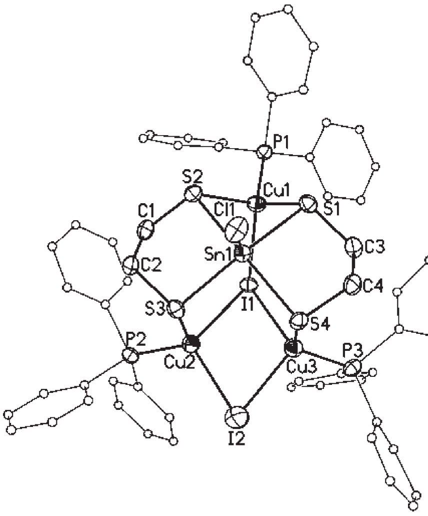

Figure 1. Molecular structure of [Sn(edt)$_2$Cl(μ-I)(μ_3-I)(CuPPh$_3$)$_3$] (**1**), showing 50% thermal ellipsoids.

due to the rapid exchange of edt^{2-} in the different coordination environments in DMSO-d_6 solution, while the broad singlet at 2.89 ppm in the ^{1}H spectrum of **2** indicates that all protons exist in the same chemical environment. The ^{31}P{^{1}H} NMR spectra of **1** and **2** show the singlets at δ −1.64 and −2.37 ppm, respectively, which are downfield from that of the free PPh$_3$ ligand. Three ^{31}P signals at δ −142.1, −1.83, and 2.37 ppm are assigned to the phosphorus atoms of the [PF$_6$]$^-$ anion and [Cu(PPh$_3$)]$^+$ and [Cu(PPh$_3$)$_2$]$^+$ species, respectively.[19] Despite the fact that molecular ions of **1**−**3** are detected with a very low intensity, a series of intensive signals assignable to the molecular ions formed by a loss of halides or hydroxide was observed in the FAB$^+$ mass spectra of three compounds.

Crystal Structures. The crystal structure of **1**$\cdot$CH$_2$Cl$_2$$\cdot$0.5EtOH$\cdot$0.5H$_2$O has been established by X-ray crystallography. The molecular structure of **1** is shown in Figure 1, and selected bond lengths and angles are given in Table 2. The unit cell of **1**$\cdot$CH$_2$Cl$_2$$\cdot$0.5EtOH$\cdot$0.5H$_2$O comprises neutral compound **1** and disordered solvent molecules in the crystal lattice. The structure of the neutral **1** consists of a rectangular-pyramidal [Sn(edt)$_2$Cl]$^-$ moiety ligated by three [Cu(PPh$_3$)]$^+$ fragments via the sulfur atoms of the edt^{2-} ligands. Three copper atoms are bridged by a μ_3-I atom with one short (2.6414(8) Å) and two long (2.7991(9) and 2.8046(9) Å) Cu−μ_3-I bonds, of which two are also bridged by a μ-I atom with two unequal Cu−μ-I bonds (short 2.5888(10) and long 2.6333(11) Å). As indicated by the angles around the tin atom (83.84(5)−155.57(5)°), the central tin atom has a distorted rectangular-pyramidal geometry. The Sn−Cl bond length of 2.3822(15) Å in **1** is slightly shorter than that of 2.413(4) Å in [Me$_4$N][(C$_7$H$_6$S$_2$)$_2$SnCl].[10a] There are two types of Sn−S bond lengths: the average value of 2.4996(15) Å chelated by copper atoms is slightly longer than the average value of 2.4762(15) Å terminally bonded by copper atoms. Accordingly, the average Cu−S bond length of 2.4368(16) Å involving chelating sulfur atoms is longer than that of 2.3283(16) Å involving terminal sulfur atoms. By comparison of the Sn−S bond lengths in **1** (av. 2.4879(15) Å) with those in [Sn(edt)$_2$] (av. 2.390(2) Å), elongation of the Sn−S bond length in **1** is due to the coordination of copper atoms with sulfur atoms of edt^{2-} ligands. The average Sn−S bond length of 2.4879(15) Å in **1** is comparable to those in [Sn(edt)$_2$(n-Bu)]$^-$ (av. 2.498(3) Å) and [Sn(edt)$_2$Ph]$^-$ (av. 2.501(4) Å).[10b] There are two kinds of Cu atoms: (i) Cu(1) coordinates to two S atoms, one I atom, and one P atom of PPh$_3$ to form a CuS$_2$PI tetrahedron; (ii) the Cu(2) and Cu(3) atoms bond to one S atom, two I atoms, and one P atom of PPh$_3$ to form the CuSPI$_2$ tetrahedrons. The Cu(2)$\cdots$Cu(3) distance in **1** (3.0390(11) Å) is comparable to those in [Cu$_3$(μ_3-Cl)$_2$(μ-dppa)$_3$]$^+$ (dppa = Ph$_2$PNHPPh$_2$; 2.9909(7) Å)[20] and [Cu$_4$(μ-dppm)$_4$(μ_4-Se)]$^{2+}$ (dppm = Ph$_2$PCH$_2$PPh$_2$; 3.090(4) Å),[21] indicating that weak metal−metal interactions may be observed in **1**. The Cu$_2$I$_2$ four-membered ring is nonplanar with I−Cu−I angles of 106.13(3) and 107.21(3)° and Cu−I−Cu angles of 65.68(2) and 71.17(3)°. All Cu−P bonds are in a similar range and comparable to those found in related Sn^{IV}−Cu^I/PPh$_3$ compounds.[7]

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**$\cdot$CH$_2$Cl$_2$$\cdot$0.5EtOH$\cdot$0.5H$_2$O

Sn(1)−Cl(1)	2.3822(15)	Sn(1)−S(1)	2.4925(15)
Sn(1)−S(2)	2.5067(14)	Sn(1)−S(3)	2.4742(15)
Sn(1)−S(4)	2.4782(14)	Cu(1)−S(1)	2.4301(16)
Cu(1)−S(2)	2.4436(16)	Cu(2)−S(3)	2.3405(17)
Cu(3)−S(4)	2.3161(17)	Cu(1)−P(1)	2.2306(14)
Cu(2)−P(2)	2.2457(17)	Cu(3)−P(3)	2.2416(19)
Cu(1)−I(1)	2.6414(8)	Cu(2)−I(2)	2.5888(10)
Cu(2)−I(1)	2.8046(9)	Cu(3)−I(2)	2.6333(11)
Cu(3)−I(1)	2.7991(9)	Sn(1)$\cdots$Cu(1)	3.1299(7)
Cu(2)$\cdots$Cu(3)	3.0390(11)		
S(1)−Sn(1)−S(2)	83.84(5)	S(3)−Sn(1)−S(4)	90.29(5)
S(3)−Sn(1)−S(1)	155.08(5)	S(4)−Sn(1)−S(1)	87.91(5)
S(3)−Sn(1)−S(2)	87.68(5)	S(4)−Sn(1)−S(2)	155.57(5)
Cl(1)−Sn(1)−S(1)	101.71(6)	Cl(1)−Sn(1)−S(2)	102.61(5)
Cl(1)−Sn(1)−S(3)	102.99(6)	Cl(1)−Sn(1)−S(4)	101.57(5)
S(1)−Cu(1)−S(2)	86.52(5)	S(1)−Cu(1)−I(1)	108.97(4)
S(2)−Cu(1)−I(1)	105.65(4)	S(3)−Cu(2)−I(2)	105.18(5)
S(3)−Cu(2)−I(1)	103.95(4)	S(4)−Cu(3)−I(2)	101.58(5)
S(4)−Cu(3)−I(1)	108.83(5)	P(1)−Cu(1)−S(1)	118.85(6)
P(1)−Cu(1)−S(2)	116.62(6)	P(1)−Cu(1)−I(1)	116.05(5)
P(2)−Cu(2)−S(3)	114.05(6)	P(2)−Cu(2)−I(2)	114.27(5)
P(2)−Cu(2)−I(1)	111.38(5)	I(2)−Cu(2)−I(1)	107.21(3)
P(3)−Cu(3)−S(4)	123.45(7)	P(3)−Cu(3)−I(2)	110.23(6)
P(3)−Cu(3)−I(1)	105.54(5)	I(2)−Cu(3)−I(1)	106.13(3)
Cu(1)−S(1)−Sn(1)	78.95(5)	Cu(1)−S(2)−Sn(1)	78.42(4)
Cu(2)−S(3)−Sn(1)	106.10(6)	Cu(3)−S(4)−Sn(1)	103.11(6)
Cu(1)−I(1)−Cu(3)	109.79(3)	Cu(1)−I(1)−Cu(2)	115.69(3)
Cu(3)−I(1)−Cu(2)	65.68(2)	Cu(2)−I(2)−Cu(3)	71.17(3)

The molecular structure of **2**, as shown in Figure 2, was determined by single-crystal X-ray diffraction, and the selected bond lengths and bond angles are given in Table 3. Compound **2** crystallized in the orthorhombic space group *Pbca* with centro-symmetry, and the tin atom in **1** is located on a 2-fold rotation axis. The neutral compound **2** comprises two [(CuPPh$_3$)$_2$(μ-Br)]$^+$ fragments symmetrically ligating an octahedral *trans*-[Sn(edt)$_2$Br$_2$]$^{2-}$ moiety via the sulfur and bromide atoms. The five metal atoms are coplanar. The central tin atom has an octahedral coordination geometry with S−Sn−Br angles ranging from 88.41(2) to 91.59(2)°. The average

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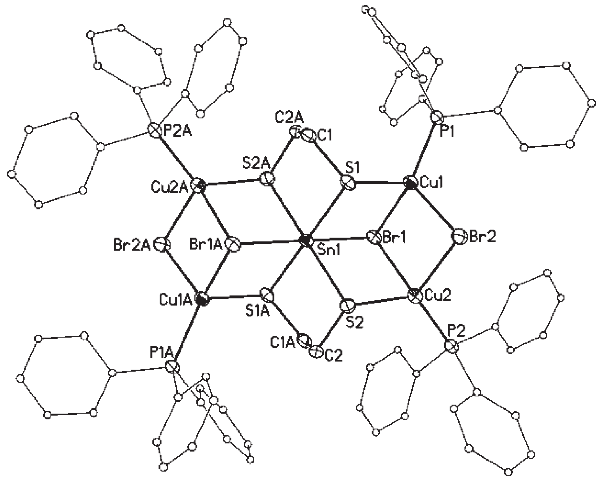

Figure 2. Molecular structure of $[Sn(edt)_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(CuPPh_3)_4]$ (**2**), showing 50% thermal ellipsoids.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**[a]

Sn(1)−S(1)	2.4681(9)	Sn(1)−S(2)	2.5106(9)
Sn(1)−Br(1)	2.8090(4)	Cu(1)−S(1)	2.3444(10)
Cu(2)−S(2)	2.2955(10)	Cu(1)−P(1)	2.2113(10)
Cu(2)−P(2)	2.2164(11)	Cu(1)−Br(1)	2.6505(6)
Cu(1)−Br(2)	2.4737(6)	Cu(2)−Br(1)	2.8613(6)
Cu(2)−Br(2)	2.4445(6)		
S(1)#1−Sn(1)−S(1)	180.00(4)	S(1)#1−Sn(1)−S(2)	88.39(3)
S(1)−Sn(1)−S(2)	91.61(3)	S(1)−Sn(1)−S(2)#1	88.39(3)
S(2)−Sn(1)−S(2)#1	180.00(2)	S(1)−Sn(1)−Br(1)#1	91.41(2)
S(2)−Sn(1)−Br(1)#1	91.59(2)	S(1)−Sn(1)−Br(1)	88.59(2)
S(2)−Sn(1)−Br(1)	88.41(2)	Br(1)#1−Sn(1)−Br(1)	180.000(15)
P(1)−Cu(1)−S(1)	117.70(4)	P(2)−Cu(2)−S(2)	127.40(4)
P(1)−Cu(1)−Br(2)	120.37(3)	P(1)−Cu(1)−Br(1)	122.00(3)
P(2)−Cu(2)−Br(2)	118.71(3)	P(2)−Cu(2)−Br(1)	108.62(3)
S(1)−Cu(1)−Br(2)	95.77(3)	S(1)−Cu(1)−Br(1)	95.17(3)
S(2)−Cu(2)−Br(2)	106.53(3)	S(2)−Cu(2)−Br(1)	91.51(3)
Br(2)−Cu(1)−Br(1)	100.118(19)	Br(2)−Cu(2)−Br(1)	95.273(19)
Cu(1)−Br(1)−Sn(1)	80.994(14)	Sn(1)−Br(1)−Cu(2)	79.486(13)
Cu(1)−S(1)−Sn(1)	94.94(3)	Cu(2)−S(2)−Sn(1)	97.84(3)
Cu(1)−Br(1)−Cu(2)	75.454(16)	Cu(2)−Br(2)−Cu(1)	86.719(19)

[a] #1: $-x, -y, -z + 2$.

Sn−S bond length in **2** (av. 2.4894(9) Å) is longer than that in $[Sn(edt)_2]$ (av. 2.390(2) Å)[11] but comparable to that in *trans*-$[Sn(edt)_2(py)_2]$ (py = pyridine) (av. 2.465(3) Å).[11] The Sn−Br bond length of 2.8090(4) Å in **2** is obviously longer than that of 2.537(2) Å in *cis*-$[Sn(S_2COEt)_2Br_2]$ containing the terminal bromides,[22] due to the bridging bromide atoms linking two $[Cu(PPh_3)]^+$ species. The geometry about the copper atoms has a highly distorted tetrahedral structure with angles varying from 91.51(3) to 127.40(4)°. The Cu_2Br_2 four-membered ring is approximately coplanar with deviations of 0.132 Å from the least-squares plane. Each ring contains a pair of long and short Cu−μ_3-Br bonds [Cu(2)−Br(1) = 2.8613(6) Å ("long") and Cu(1)−Br(1) = 2.6505(6) Å ("short")] and two nearly equivalent Cu−μ-Br bonds [Cu(1)−Br(2) = 2.4737(6) Å and Cu(2)−Br(2) = 2.4445(6) Å]. The Cu−μ-Br−Cu bond angle of 86.72(2)° is larger than the Cu−μ_3-Br−Cu bond angle of 75.45(2)°. The average Cu−Br−Sn and Cu−S−Sn bond angles are 80.24(1) and 96.39(3)°, respectively. Similar to **1** and other related Sn^{IV}−Cu^{I} compounds,[7] the distance of Sn···Cu separation in **2** (3.587(3) Å) is too long for the metal−metal bond.

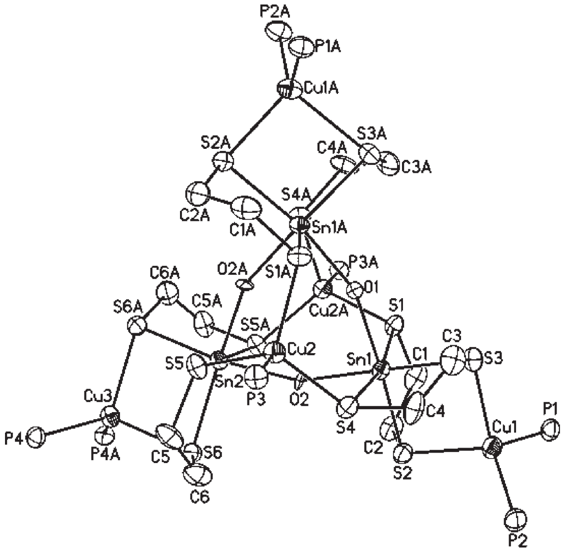

Figure 3. Molecular structure of the $[\{Sn(edt)_2\}_3(\mu\text{-}Cl)_3Cu_5(PPh_3)_8]^{2+}$ cation in **3**, showing 50% thermal ellipsoids. All phenyl rings were omitted for clarity. Symmetry code: (A) $-x + 1, y, -z + {}^1/_2$.

The structure of cationic $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3Cu_5(PPh_3)_8]^{2+}$ is illustrated in Figure 3, and selected bond lengths and angles are given in Table 4. It contains one octanuclear Sn^{IV}−Cu^{I} cluster cation with a strict 2-fold axis, two $[PF_6]^-$ anions, and six disorder water molecules in the crystal lattice. The O(1), Sn(2), and Cu(3) atoms lie on the 2-fold axis. Three tin atoms are connected by three μ-OH ligands, forming a $Sn_3(\mu\text{-}OH)_3$ core with average O−Sn−O and Sn−O−Sn bond angles of 82.6(3)° and 157.5(3)°, respectively. Similar to the formation of $[Sn_3(\mu\text{-}OH)S_3(edt)_3]^-$,[23] the bridging OH^- in the present compound might come from trace water in the solvents. All the tin atoms are six-coordinated by four sulfur atoms of edt^{2-} moieties and the two μ-OH in an octahedral geometry. The bond lengths of Sn−O are from 2.145(4) to 2.152(2) Å, while those of Sn−S are from 2.479(2) to 2.511(3) Å. Both Sn−O and Sn−S bond lengths are in the normal ranges for the related compounds such as $[n\text{-}Bu_4N]_4[Sn_8(\mu_4\text{-}O)_2(\mu\text{-}OH)_2S_{12}Cl_6]$,[24] $[(n\text{-}BuSn(OH)O_2P(Cy)_2O)][(n\text{-}BuSnCl_2O_2P(Cy)(OH)]$ (Cy = cyclohexyl),[25] and $[n\text{-}Bu_4N]_4[Sn_3(\mu_3\text{-}OH)S_3(edt)_3]$.[25] Three $[Cu(PPh_3)_2]^+$ species bind three $Sn(edt)_2$ fragments from the periphery of the $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3]^{3-}$ via the two sulfur atoms of the edt^{2-} moieties, forming CuS_2P_2 tetrahedra. Two $[Cu(PPh_3)]^+$ species cap the $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3]^{3-}$ via the three sulfur atoms from each of three $Sn(edt)_2$ fragments, forming CuS_3P tetrahedra. Thus, the structure of the cluster cation in **3** can be described as one triangle $[\{Sn(edt)_2\}_3(\mu\text{-}OH)_3]^{3-}$ chelated by three $[Cu(PPh_3)_2]^+$ species and capped by two $[Cu(PPh_3)]^+$ species. The average Cu−S bond length of 2.506(3) Å in the CuS_2P_2 tetrahedra is longer than the 2.348(3) Å in the CuS_3P

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Table 4. Selected Bond Distances (Å) and Angles (deg) for $\mathbf{3}\cdot 6H_2O^a$

Sn(1)−O(1)	2.1517(15)	Sn(1)−O(2)	2.134(4)
Sn(2)−O(2)	2.145(4)	Sn(1)−S(1)	2.479(2)
Sn(1)−S(2)	2.511(3)	Sn(1)−S(3)	2.486(2)
Sn(1)−S(4)	2.485(2)	Sn(2)−S(5)	2.486(2)
Sn(2)−S(6)	2.498(2)	Cu(1)−S(2)	2.418(2)
Cu(1)−S(3)	2.605(3)	Cu(2)−S(1)#1	2.345(3)
Cu(2)−S(4)	2.350(3)	Cu(2)−S(5)	2.349(2)
Cu(3)−S(6)	2.494(3)	Cu(1)−P(1)	2.315(3)
Cu(1)−P(2)	2.321(3)	Cu(2)−P(3)	2.262(3)
Cu(3)−P(4)	2.316(3)		
O(2)−Sn(1)−O(1)	82.4(2)	S(1)−Sn(1)−S(4)	167.71(9)
O(2)#1−Sn(2)−O(2)	82.8(3)	S(1)−Sn(1)−S(3)	99.65(8)
O(2)−Sn(1)−S(1)	92.50(14)	S(4)−Sn(1)−S(3)	88.91(8)
O(1)−Sn(1)−S(1)	78.30(7)	S(1)−Sn(1)−S(2)	88.65(9)
O(2)−Sn(1)−S(4)	78.33(14)	S(4)−Sn(1)−S(2)	99.58(9)
O(1)−Sn(1)−S(4)	92.26(8)	S(3)−Sn(1)−S(2)	94.16(9)
O(2)−Sn(1)−S(3)	166.83(14)	S(5)−Sn(2)−S(5)#1	166.56(10)
O(1)−Sn(1)−S(3)	95.06(18)	S(5)−Sn(2)−S(6)#1	100.52(8)
O(2)−Sn(1)−S(2)	91.16(16)	S(5)−Sn(2)−S(6)	88.69(8)
O(1)−Sn(1)−S(2)	165.11(10)	S(6)#1−Sn(2)−S(6)	94.00(11)
O(2)#1−Sn(2)−S(5)	78.15(14)	S(1)#1−Cu(2)−S(5)	108.30(9)
O(2)−Sn(2)−S(5)	91.71(14)	S(1)#1−Cu(2)−S(4)	109.74(10)
O(2)#1−Sn(2)−S(6)#1	93.02(15)	S(5)−Cu(2)−S(4)	107.51(10)
O(2)−Sn(2)−S(6)#1	166.03(13)	S(2)−Cu(1)−S(3)	93.44(9)
O(2)#1−Sn(2)−S(6)	166.03(13)	P(4)−Cu(3)−P(4)#1	115.12(13)
O(2)−Sn(2)−S(6)	93.02(15)	P(4)−Cu(3)−S(6)	112.11(8)
P(1)−Cu(1)−P(2)	116.25(12)	P(4)#1−Cu(3)−S(6)	110.74(9)
P(1)−Cu(1)−S(2)	113.94(10)	P(4)−Cu(3)−S(6)#1	110.74(9)
P(2)−Cu(1)−S(2)	111.25(9)	P(4)#1−Cu(3)−S(6)#1	112.11(8)
P(1)−Cu(1)−S(3)	109.82(10)	S(6)−Cu(3)−S(6)#1	94.16(11)
P(2)−Cu(1)−S(3)	109.75(11)	Cu(2)#1−S(1)−Sn(1)	113.93(10)
P(3)−Cu(2)−S(1)#1	108.80(10)	Cu(1)−S(2)−Sn(1)	87.93(9)
P(3)−Cu(2)−S(5)	111.95(9)	Sn(1)−S(3)−Cu(1)	84.44(8)
P(3)−Cu(2)−S(4)	110.50(10)	Cu(2)−S(4)−Sn(1)	113.60(10)
Cu(2)−S(5)−Sn(2)	114.42(9)	Sn(1)#1−O(1)−Sn(1)	157.4(3)
Cu(3)−S(6)−Sn(2)	85.92(8)	Sn(1)−O(2)−Sn(2)	157.5(3)

[a] #1: $-x + 1, y, -z + {}^1/_2$.

tetrahedral. Accordingly, the average S−Cu−S angle of 93.80(10)° in the CuS_2P_2 tetrahedra is obviously smaller than that of 108.52(10)° in the CuS_3P tetrahedra. The Cu−P bond lengths, in the range of 2.262(3)−2.321(3) Å, are not clearly influenced by the different copper coordination environments and are similar to those reported for analogous cluster compounds.

Luminescent Properties. The luminescent properties of compounds **1**−**3** in CH_2Cl_2 solutions have been studied. Similar to reported heterometallic $Sn^{IV}-Cu^I$ compounds with PPh_3 ligands,[7] compounds **1**−**3** are luminescent, with emission maxima at ca. 420−520 nm upon excitation at $\lambda > 360$ nm. The emission spectra for **1**−**3** at room temperature in degassed CH_2Cl_2 solutions are shown in Figure 4. The emission maximum for octanuclear compound **3** at 494 nm is comparable to that for heptanuclear $[Cu_4Sn_3(edt)_6(\mu_3\text{-}O)(PPh_3)_4]^{2+}$ (ca. 495 nm).[7a] Previously, the luminescence of $[Cu_4Sn_3(edt)_6(\mu_3\text{-}O)(PPh_3)_4]^{2+}$ has been tentatively attributed to admixtures of a MLCT Cu → phosphine transition and a LMCT S → Cu transition. By comparison of **3** with **1** and **2**, a similar emission blue-shift has been found for the tetranuclear $[Sn(edt)_2Cl(\mu\text{-}I)(\mu_3\text{-}I)(CuPPh_3)_3]$ ($\lambda_{max} = 422$ nm), while a similar emission red-shift has been found for the pentanuclear $[Sn(edt)_2(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(CuPPh_3)_4]$ ($\lambda_{max} = 515$ nm). Previously, it was reported that $[(Ph_3P)Cu]_2Sn(SPh)_6$ exhibited a higher-energy luminescent band at 419 nm upon excitation at 370 nm in CH_2Cl_2 solution.[7b] We therefore tentatively assign the emission of **1** and **2** to an admixture of S^{2-} → Cu LMCT and Cu → PPh_3 MLCT. Similar observations have been reported for a related heterometallic complex, $[(Ph_3P)Cu]_2Sn(edt)_2$.[7b] The design and syntheses of new heterometallic $Sn^{IV}-Cu^I$ compounds based on $[Sn(edt)_2]$ as a metalloligand would well elucidate the nature of excited states involved in the photoluminescence of this class of compounds. Research along these derivatives is in active progress in the laboratory.

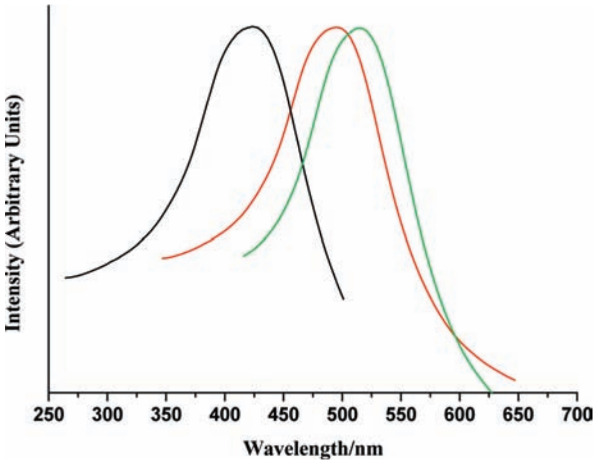

Figure 4. Emission spectra of compounds **1** (black), **2** (green), and **3** (red) in CH_2Cl_2 at room temperature.

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Supporting Information Available: Tables of crystal data; final atomic coordinates; anisotropic thermal parameters; and complete bond lengths and angles for compounds $\mathbf{1}\cdot CH_2Cl_2\cdot 0.5EtOH\cdot 0.5H_2O$, **2**, and $\mathbf{3}\cdot 6H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.