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Assembly of a Heterometallic Polynuclear Sn^{IV}–Cu^{I} Cluster Based on $Sn(edt)_2$ (edt = Ethane-1,2-dithiolate) as a Metalloligand

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Reaction of $[Cu(PPh_3)_2(MeCN)_2]ClO_4$ (**1**) and $Sn(edt)_2$ (edt = ethane-1,2-dithiolate) in dichloromethane afforded a novel compound $[Sn_3Cu_4(S_2C_2H_4)_6(\mu_3\text{-}O)(PPh_3)_4](ClO_4)_2 \cdot 3CH_2Cl_2$ (**2**), which is the first example of the heptanuclear Sn^{IV}–Cu^{I} oxosulfur complex with a bottle-shaped cluster core. Complex **2** gives a blue-green luminescent emission in the solid state. Crystallographic data for **2**: $C_{87}H_{90}Cl_8Cu_4O_9P_4S_{12}Sn_3$, trigonal, space group $R\bar{3}$, $M = 2682.02$, $a = 18.156(2)$ Å, $b = 18.156(2)$ Å, $c = 54.495(10)$ Å, $\gamma = 120°$, $V = 15558(4)$ Å^3, $Z = 6$ ($T = 130.15$ K).

Chalcogenide-based heterometallic clusters have attracted considerable interest because of their rich structural variety and potential applications for fuel cells, nonlinear optical materials, semiconductors, ion exchangers, and electrochemical sensors.[1] Recently, open solid-state structures containing ternary and multinary frameworks, in which binary aggregates of main-group elements $[E'_xE_y]^{q-}$ (e.g., $[E'E_4]^{4-}$, $[E'_2E_6]^{4-}$, or $[E'_4E_{10}]^{4-}$ ions) are stabilized by coordination to M^{n+} (E′ = heavy group 13−15 element; E = S, Se, Te; M = transition metal), have been actively studied because of their zeolite-type and semiconducting properties.[2] During the past 2 decades, our research interest has been focused on the study of the hetero-transition-metallic cluster compounds involving sulfide ligands.[3] By utilizing thiometalates $MS_{4-x}O_x^{2-}$ (M = Mo, W; $x = 0, 1$) as a "metalloligand", we have synthesized and characterized many types of hetero-transition-metal complexes.[3,4] Owing to the importance of tin sulfide based clusters in optoelectronic devices,[5] we recently extended our interest to the study of tin sulfide based heterometallic compounds. Up to now, a few examples of such compounds have been synthesized and structurally characterized, such as $\{Sn[Zn_4Sn_4S_{17}]\}^{6-}$,[1a] $[M_4Sn_4S_{17}]^{10-}$ (M = Mn, Fe, Co, Zn),[6] $[M_5Sn(\mu_3\text{-}S)_4(SnS_4)_4]^{10-}$ (M = Zn, Co),[7] and $K_2Ag_6Sn_3S_{10}$[8] synthesized by solid-state reactions, hydrothermal or solvothermal methods from Sn, S, and metal, or the corresponding inorganic salt.[9] Thus, a new synthetic route is of interest, especially for metal−organic heteropolynuclear tin clusters.

One of the most effective and attractive synthetic approaches is self-assembly from appropriate building blocks or from two different metal components, which could result in a vast number of heterometallic clusters with extraordinary structural varieties.[3b] We are currently interested in developing a Sn/Cu/S cluster formed by self-assembly from metal phosphine and metal thiolate components, where the former component possesses easy substituted solvate sites, whereas the latter shows a potential bridging character. To date, there have been scattered reports on the M/E′/E cluster obtained by employing main-group metal thiolate as a "building

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block".[10] As a part of our work, $Sn(edt)_2$ (edt = ethane-1,2-dithiolate) was chosen as a "metalloligand" to synthesize heterometallic complexes by the solution method. Herein, we report a $Sn(edt)_2$-based heptanuclear $Sn^{IV}-Cu^{I}$ complex, $[Sn_3Cu_4(S_2C_2H_4)_6(\mu_3\text{-}O)(PPh_3)_4](ClO_4)_2\cdot 3CH_2Cl_2$ (**2**), which contains a bottle-shaped cluster core and gives a blue-green luminescent emission in the solid state. To the best of our knowledge, **2** is the first example of the heptanuclear $Sn^{IV}-Cu^{I}$ oxosulfur cluster compound.

Reaction of $Sn(edt)_2$[11] with 1 equiv of $[Cu(PPh_3)_2(MeCN)_2]ClO_4$ (**1**)[12] in dichloromethane produced a yellow solution. The yellow prismatic crystals of complex **2** were obtained upon slow diffusion of diethyl ether into the dichloromethane solution.[13] The complex is air stable and soluble in dimethyl sulfoxide (DMSO) and dimethylformamide. X-ray single-crystal analysis reveals that complex **2** crystallizes in the space group $R\bar{3}$.[14] It contains one heptanuclear $Sn^{IV}-Cu^{I}$ oxosulfur cluster cation with a strict threefold axis, two perchlorate anions, and three dichloromethane solvent molecules. The P2, Cu2, and O1 atoms and the Cl atom of ClO_4^- lie on the threefold axis that passes through the center of the Sn_3 plane (Sn1, Sn1A, and Sn1B) and the Cu_3 plane (Cu1, Cu1A, and Cu1B) (Figure 1a). The Sn^{IV} and Cu^{I} atoms are connected by edt ligands to afford a unique "bottle-shaped" cage. As shown in Figure 1b, the $\{Sn_3Cu_4(S_2C_2H_4)_6\}$ cage looks like a bottle, of which the Cu_3 plane is the bottom and Cu2 is the neck connected to P2. The μ_3-O atom acts as a guest filled in the bottle. The three Sn^{IV} atoms are bridged by the edt ligands and one central μ_3-O atom and construct an equilateral triangle (Sn_3 plane) with the Sn···Sn separation of 3.543 Å. The O1 protrudes only 0.2666 Å from the Sn_3 plane, indicating that the central O1 atom bridges three Sn atoms [Sn−O: 2.0626(6) Å] in an almost trigonal-planar mode. By contrast with the four-coordinate Sn in the precursor mononuclear tin complex,[11] each of the tin atoms in **2** affords an approximately octahedral coordination environment. The bottom three Cu^{I} atoms linked by the three edt S atoms are staggered with respect to the three Sn atoms (Figure 1c) and form another equilateral triangle (Cu_3 plane) with the Cu···Cu separation of 3.924 Å. The Cu2 apex and Cu_3 plane are located above and below the Sn_3 plane at 3.3083 and 3.2841 Å, respectively. It is noteworthy that two types of Cu^{I} coordination environments are present: the apex Cu2 atom has a distorted tetrahedral environment with a S_3P chromophore, while each of the bottom three Cu^{I} atoms has an almost trigonal-planar environment with a S_2P chromophore. All of the Cu−P bonds are in a similar range and are comparable to those found in other phosphanides.[15] The Cu−O distance of 2.482 Å suggests the presence of a weak interaction between the Cu (Cu1, Cu1A, and Cu1B) atoms and the ClO_4^- anion, which may play an important role in the stabilization of the whole structure.

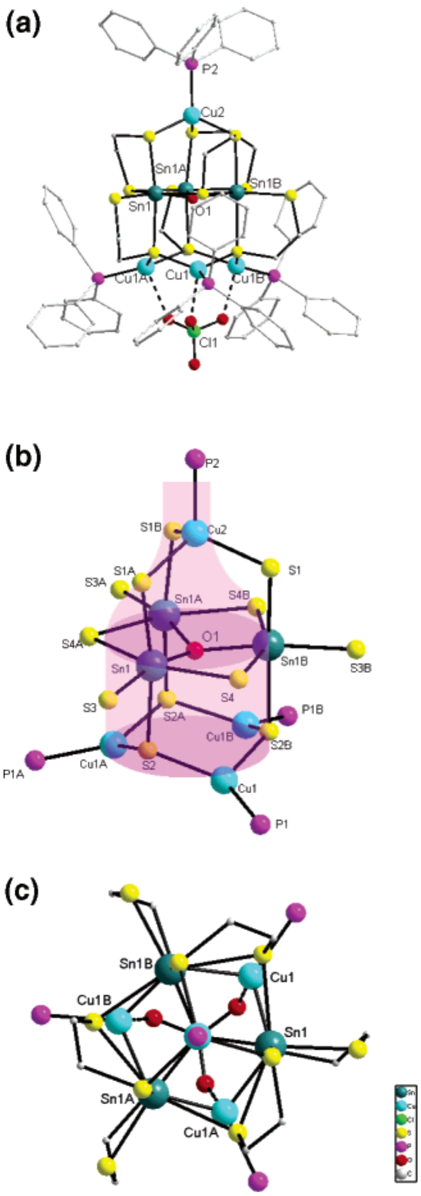

Figure 1. (a) Structure of complex **2**. (b) Cluster core of **2** with a bottle shape. (c) Structure of complex **2** viewed along the C_3 axis.

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(14) Crystal data for **2**: $C_{87}H_{90}Cl_8Cu_4O_9P_4S_{12}Sn_3$, trigonal, space group $R\bar{3}$, $M = 2682.02$, $a = 18.156(2)$ Å, $b = 18.156(2)$ Å, $c = 54.495(10)$ Å, $\gamma = 120°$, $V = 15558(4)$ Å^3, $Z = 6$, $T = 130.15$ K, $D_c = 1.718$ g cm^{-3}, $F(000) = 8028$, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 2.077$ mm^{-1}, R1 = 0.0496 and wR2 = 0.1042 for 7653 observed reflections from 7923 independent reflections, GOF = 1.114. The crystal data collection was performed on a Mercury CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using *SHELXTL-97*.[20] All non-H atoms were treated anisotropically. The positions of H atoms attached to C atoms were generated geometrically.

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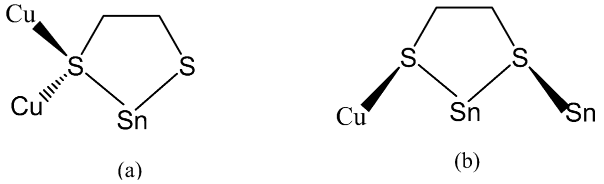
Chart 1. Two Coordination Modes of edt Ligands in **2**



(a)

(b)

Also noteworthy is the two kinds of distinct bridging coordination modes of the edt ligands in **2**, as shown in Chart 1. In each of the three Sn(edt)$_2$, one Sn-chelating edt ligand bridges two Cu^I atoms by one S$_{edt}$ atom (Chart 1a), while the other bridges one Cu^I and one Sn^{IV} of another Sn(edt)$_2$ by two S$_{edt}$ atoms (Chart 1b), respectively.[16] The Sn−S bond lengths range from 2.4367(12) (Sn1−S3) to 2.6152(13) (Sn1−S4) Å and are longer than those in Sn(edt)$_2$ [average: 2.390(1) Å].[11] We can conclude that the Sn−S bond becomes weaker when Sn(edt)$_2$ coordinates to other metals (Cu) as a metalloligand. Furthermore, the Sn−S bond distance increases as the coordination number of the edt S atom increases, being in the order Sn−μ_3-S2 > Sn−μ_2-S1 > Sn−μ_1-S3. In addition, the Sn−μ_2-S4 distance is the longest, which may be because S4 bridges two Sn atoms with a larger atomic radius than the Cu atom.

Owing to rapid PPh$_3$ exchange in a DMSO solution,[17a] the ^{31}P NMR spectrum of complex **2**,[17b] recorded at room temperature, shows only one signal at −1.878 ppm, which is shifted upfield by 3.573 ppm relative to the free PPh$_3$ ligand.[17c]

For polynuclear Cu^I complexes, one of the interesting properties is their luminescence.[18] Besides the novelty of the structure, as expected, the complex **2** possesses fluorescent properties. The emission spectrum of the precursor complex **1** was measured for the purpose of better comparison; the emission has been suggested to originate from a metal-to-ligand charge transfer (MLCT) Cu → phosphine in nature.[19] The solid-state spectra of complexes **1** and **2** are shown in Figure 2. Compound **2** emits a blue-green luminescence with a peak maximum band at 495 nm with an approximate 10-nm bathochromic shift compared to that of **1** (λ_{max} = 485 nm, excited at 337 nm). A similar assignment is possible. However, the coordination of the S donors to the Cu^I atom would lower the energy level of the dπ orbitals of the Cu^I center, thus increasing the energy gap between the highest occupied molecular orbital (dπ of Cu) and the lowest unoccupied molecular orbital (π* of phosphine) and inducing a blue shift. The relatively long Cu···Cu (3.924 Å) distances exclude the possibility of substantial metal−metal interactions. From the asymmetrical profile of the emission spectrum, it can be concluded that at least two charge-transfer processes occur in the emission; hence, admixtures of a MLCT Cu → phosphine transition and a ligand-to-metal CT S → Cu transition are likely.[18] A theoretical calculation for the detailed assignment is necessary.

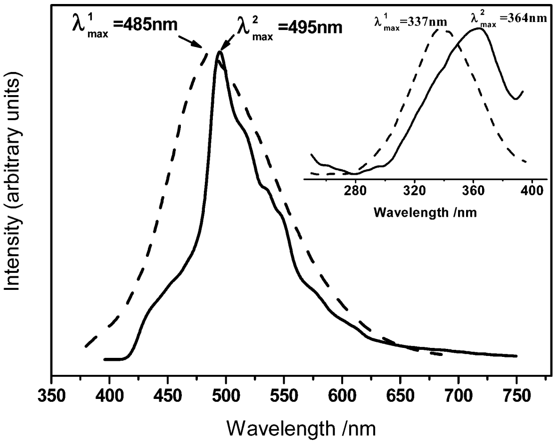


Figure 2. Emission and excitation (inset) spectra for **1** (dashed line) and **2** (solid line) in the solid state at room temperature.

In conclusion, we have successfully designed and synthesized a novel heteroheptanuclear Sn^{IV}−Cu^I oxosulfur cluster using metal phosphine and metal thiolate as metalloligands, which give a blue-green luminescent emission in the solid state. Compound **2** exhibits a novel structure with a bottle-shaped core. The search for other heteronuclear clusters with different ratios of the reactants, different dithiolate ligands, and different metals is underway in our laboratory.

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Supporting Information Available: X-ray crystallographic file for **2** in CIF format, bond lengths and angles, detailed synthesis process and some supplementary figures, including powder XRD patterns (Figure S2), a ^{1}H NMR spectrum (Figure S3), a ^{31}P NMR spectrum (Figure S4), an IR spectrum (Figure S5), a Raman spectrum (Figure S6), and a low-frequency IR spectrum (Figure S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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