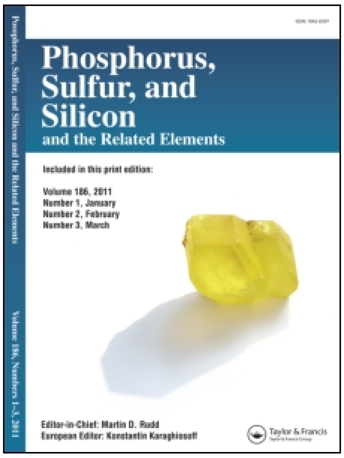

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Synthesis, Crystal Structure, and Luminescence of a Three-Dimensional Supramolecular Compound Based on a Dinuclear Tin Cluster

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Synthesis, Crystal Structure, and Luminescence of a Three-Dimensional Supramolecular Compound Based on a Dinuclear Tin Cluster

Wenxiang Chai,[1] Li Song,[2] Hangyan Shen,[1] and Kangying Shu[1]
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A three-dimensional (3D) supramolecular compound, $[(phen)LSnS]_2{\cdot}(H_2O)_2$ (phen = 1,10-phenanthroline, L = mercaptoacetic acid), has been synthesized and the crystal structure was determined by a single crystal X-ray diffraction study. ***1*** *is triclinic, space group P-1 with* $a = 6.695(1)$ Å, $b = 10.929(2)$ Å, $c = 12.117(2)$ Å, $\alpha = 114.55(3)^\circ$, $\beta = 93.53(2)^\circ$, $\gamma = 104.06(3)^\circ$, *and* $Z = 1$. *The dinuclear cluster of* $[(phen)LSnS]_2$ *and* H_2O *are linked into a 3D supramolecular framework by a combination of O–H. . .O, C–H. . .O hydrogen bonds and π–π stacking interactions. Its luminescence property is discussed.*

Keywords Crystal structure; dinuclear tin cluster; hydrogen bonding; supramolecular; π–π stacking

INTRODUCTION

Self-assembled coordination supramolecular systems and metal–organic frameworks (MOF) through the deliberate selection of metal ions and multifunctional ligands have received considerable recent attention. Such materials not only have potential applications as sensors, in gas storage and catalysis, or as optoelectronic

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and magnetic materials, but also exhibit structural and topological novelty with diverse and intriguing structural motifs.[1–3] Achieving a predictable combination of structural features, however, remains a great challenge.[4] On the efforts to pursue the synthetic strategies for supramolecular framework, some noncovalent interactions have been emphasized repeatedly, such as hydrogen bonding, π–π stacking, and anion–π and C–H…π interactions. These secondary interactions may be very important for different aspects such as molecular recognition and catalysis and, more specifically, for enantioselective processes.[5,6] In this article, a multidentate thiol-carboxylate ligand (mercaptoacetic acid) and an aromatic ligand (1,10-phenanthroline) were selected for assembling supramolecular organization, and a 3D supramolecular compound, $[(\text{phen})\text{LSnS}]_2\cdot(\text{H}_2\text{O})_2$, **1** has been synthesized and characterized. We report herein the crystal structure of a dinuclear tin cluster, the 3D supramolecular framework assembling via hydrogen bonding and π–π stacking, and its ordinary luminescence property.

RESULTS AND DISCUSSION

Structure Description

The single-crystal X-ray diffraction of **1** (Table I) reveals there is a dinuclear tin cluster in the compound and with centrosymmetry in the middle of two tin atoms, and two isolated solvent water molecules located at the two poles of the dinuclear cluster in a centrosymmetric fashion (Figure 1).

In the dinuclear tin cluster of **1**, the tin atoms are located in a distorted octahedral environment of two nitrogen atoms from the phen ligand, one oxygen atom and one sulfur atom from mercaptoacetic acid ligand, and another two inorganic sulfur atoms. The Sn-N1 = 2.321(2) Å, Sn-N2 = 2.300(2) Å, Sn-O1 = 2.129(2) Å, the Sn-S bond lengths range from 2.444(1) Å to 2.461(1) Å, and all of bond lengths are similar to those reported in the literature.[7–10] With a sharing edge fashion, two centrosymmetric SnN_2OS_3 octahedra fused to each other on S2–S2 edge to form a dinuclear cluster, while the Sn(1)-S(2) = 2.461(1) Å, and Sn(1)-S(2)' = 2.4485(9) Å (the details of bond lengths listed in Table II). As far as we know, similar structures of dioctahedron tin–sulfur cluster are rare.[11–15]

In the crystal structure of **1**, hydrogen bonds and offset face-to-face aromatic π–π stacking interactions lead to the formation of a 3D supramolecular framework. First, the dinuclear tin clusters and isolated solvent water molecules connect to each other by hydrogen

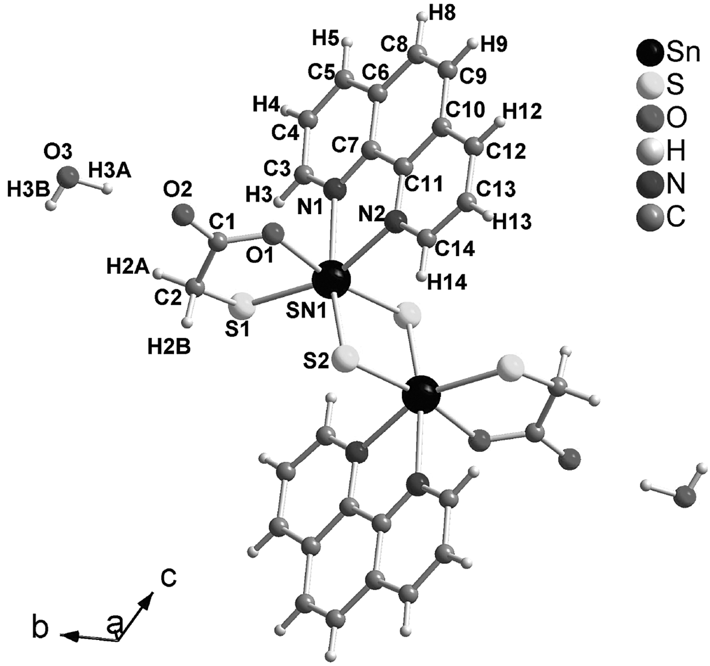

FIGURE 1 A view of the dinuclear tin cluster and two solvent water molecules.

bonding interactions (details listed in Table III),and result in the buildup a supramolecular sheet (Figure 2). The hydrogen bonding data of lengths and angles are in the range of ordinary examples and have been examined by the PLATON program.[16,17] Of them, the hydrogen bond of O(3)-H(3a)...0(2) is obvious with D...A distance 2.798(4) Å, and the other two interactions of C-H...O are both weak hydrogen bonds.[18,19]

And then, adjacent sheets are joined together by virtue of π–π stacking interactions between two phen ligands to form the 3D framework (Figure 3).[20] The phen skeletons are arranged in a perfect parallel fashion; ring A (N1/C3-C7) [symmetry code: (x, y, z)] of one dinuclear cluster stacks with ring B (N1/C3-C7) [symmetry code: (1−x, 1−y, −z)] of neighboring dinuclear molecule with the interplanar distance of 3.4777(40) Å, and ring B stacks with adjacent ring C (N2/C10-C14) [symmetry code: (−x, 1−y, −z)], of a neighboring dinuclear molecule with an interplanar distance of 3.3389(40) Å again (Figure 4). As a result, through these π–π stacking interactions, the supramolecular sheets stack one by one to present a firm 3D supramolecular framework.

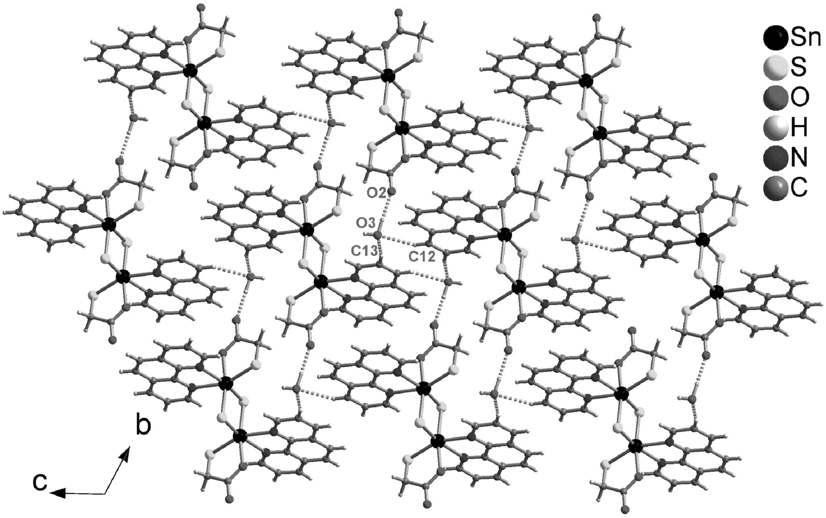

FIGURE 2 A superamolecular sheet and corresponding hydrogen bonds (dashed line), view along *a* axis.

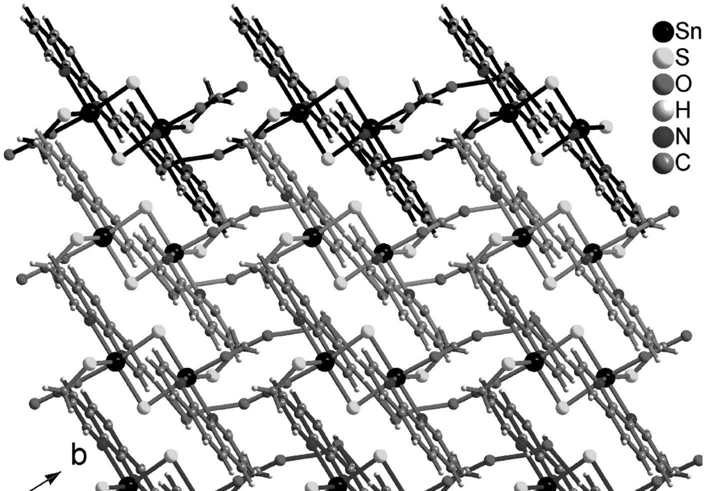

FIGURE 3 A 3D superamolecular framework formed by sheets stacking through π–π stacking interactions, view along [−1 0 1] axis.

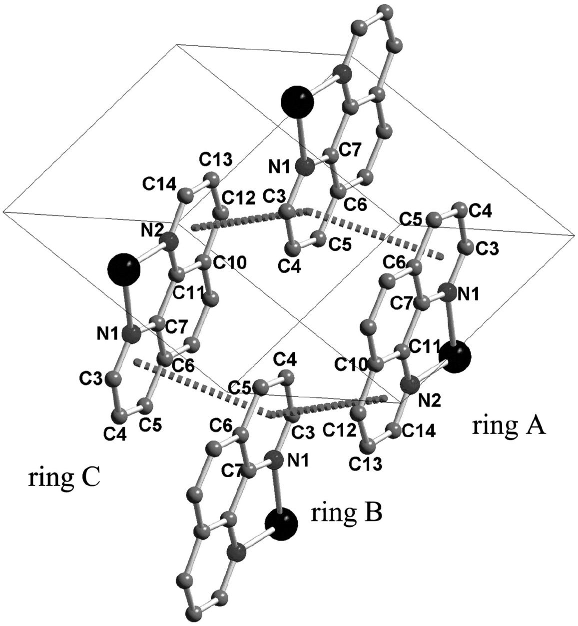

FIGURE 4 Part of the crystal structure of **1**, showing the detail models of π–π stacking interactions. For clarity, all outlying atoms and hydrogen atoms are omitted.

Luminescent Property

The luminescence spectrum of **1** at room temperature shows three broad multipeaks at 486, 496, and 522 nm with excitation maxima at 233 nm (Figure 5). The emissions perhaps derive from the ligand to ligand charge transfer (LLCT) or ligand to metal charge transfer (LMCT).

CONCLUSION

A 3D supramolecular framework, assembling from tin dinuclear molecules of $[(phen)LSnS]_2$ and isolated solvent water molecules, has been synthesized and their crystal structure was determined. The details of O–H...O, C–H...O hydrogen bonds and π–π stacking interactions were carefully investigated and described. The luminescence property of the 3D supramolecular framework has also been reported.

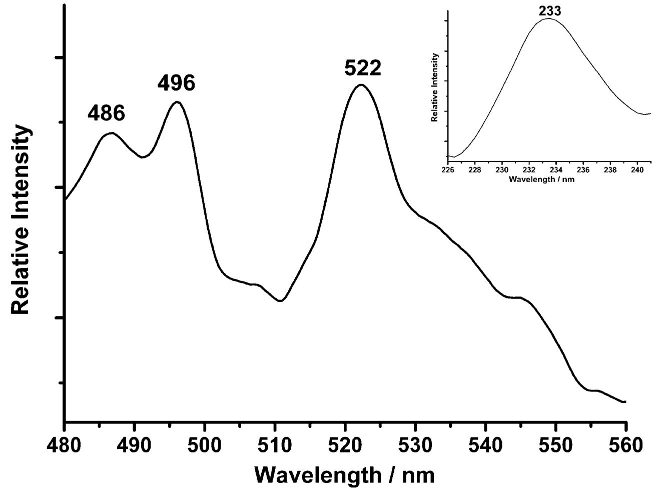

FIGURE 5 The solid-state photon emission spectrum of polycrystalline **1** (λ_{ex} = 233 nm) at 298 K, and the inset is the corresponding excitation spectrum.

EXPERIMENTAL

Materials and General Methods

All the reagents for synthesis were commercially available and employed without further purification. Elemental analysis was carried out on a Flash EA 1112 element analyzer, and the IR spectrum was recorded on a Nicolet Avatar 370 FT-IR spectrophotometer in the range of 4000–400 cm^{-1}. The luminescence spectrum measurement was performed on a pure polycrystalline sample with a LS45 Instrument by Perkin-Elmer at room temperature.

Synthesis

1 was synthesized by hydrothermal reaction of mercaptoacetic acid (0.12 mL, 1.8 mmol), NaOH (150 mg, 3.6 mmol), $SnCl_4{\cdot}5H_2O$ (212 mg, 0.6 mmol), $Nd(NO_3)_3{\cdot}6H_2O$ (176 mg, 0.4 mmol), and 1,10-phenanthroline (240 mg, 1.2 mmol) in a water (6 mL) and alcohol (4 mL) mixed solution. The mixture was heated to 110°C at the rate of 20°C/h, and kept at this temperature for 2 days and then cooled to room temperature at the rate of 2°C/h. The pale yellow crystals of **1**, suitable for X-ray crystallography, were obtained in a yield of 18% (95 mg). Anal. Calc. for $C_{28}H_{24}N_4O_6S_4Sn_2$ (%): C, 38.51; H, 2.84; N, 6.26; O, 10.77. Found: C, 38.30; H, 2.75; N, 6.38; O, 10.93. IR (KBr, cm^{-1}):

TABLE I Crystal Data and Structure Refinement for 1

Compound	**1**
CCDC deposit No.	704530
Empirical formula	$C_{28}H_{24}N_4O_6S_4Sn_2$
Formula weight	878.21
Temperature	293 (2)
Wavelength	0.71075
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions (Å°)	$a = 6.6953$ (13) $b = 10.929$ (2) $c = 12.117$ (2) $\alpha = 114.55$ (3) $\beta = 93.53$ (2) $\gamma = 104.06$ (3)
Volume (Å^3)	768.9 (4)
Z	1
Density (calculated) (g cm^{-3})	1.896
Absorption coefficient (cm^{-1})	1.945
F(000)	432
Crystal size (mm^3)	0.26 × 0.22 × 0.17
Crystal color/shape	Pale yellow/block
θ range for data collection (°)	3.19–27.44
Limiting indices	$-8 \leq h \leq 8$ $-14 \leq k \leq 14$ $-15 \leq l \leq 15$
Independent reflections	7586/3518[*R*(int) = 0.0177]
Absorption correction	multiscan
Data/restraints/parameters	3518/0/247
Goodness-of-fit on F^2	1.243
Final *R* indices [*I*>2sigma(*I*)]	$R_1 = 0.0201$ $\omega R_2 = 0.0631$
R indices (all data)	$R_1 = 0.0234$ $\omega R_2 = 0.0662$
Largest diff. peak and hole (eÅ^{-3})	0.416 and −0.608

3422w, 3057w, 2976w, 2884w, 1633s, 1518m, 1430s, 1290sh, 1222m, 1148m, 1102m, 919m, 855s, 779m, 721s.

X-Ray Crystal Structure Determination

A suitable single crystal of **1** was selected and mounted on a thin glass fiber with the aid of an epoxy resin. The XRD data were collected with ω scan mode at 293(2) K on a Rigaku RAXIS-RAPID CCD diffractometer (Mo Kα, $\lambda = 0.71075$ Å). The structure was solved using direct

TABLE II Selected Bond Lengths (Å) and Angles (°) for Compound 1

Sn(1)-O(1)	2.129 (2)	Sn(1)-N(2)	2.300 (2)
Sn(1)-N(1)	2.321 (2)	Sn(1)-S(1)	2.444 (1)
Sn(1)-S(2)#1	2.4485 (9)	Sn(1)-S(2)	2.461 (1)
S(2)-Sn(1)#1	2.4485 (9)	S(1)-C(2)	1.811 (4)
O(1)-C(1)	1.282 (3)	O(2)-C(1)	1.220 (4)
N(1)-C(3)	1.332 (3)	N(1)-C(7)	1.351 (3)
N(2)-C(14)	1.326 (3)	N(2)-C(11)	1.356 (3)
O(1)-Sn(1)-N(2)	79.59 (8)	O(1)-Sn(1)-N(1)	81.36 (8)
O(1)-Sn(1)-S(1)	83.28 (6)	O(1)-Sn(1)-S(2)	93.08 (6)
O(1)-Sn(1)-S(2)#1	169.85 (5)	N(1)-Sn(1)-S(1)	92.16 (6)
N(1)-Sn(1)-S(2)	162.42 (6)	N(1)-Sn(1)-S(2)#1	90.09 (6)
N(2)-Sn(1)-N(1)	71.63 (7)	N(2)-Sn(1)-S(1)	157.91 (6)
N(2)-Sn(1)-S(2)	91.01 (6)	N(2)-Sn(1)-S(2)#1	92.57 (6)
S(1)-Sn(1)-S(2)	103.79 (3)	S(1)-Sn(1)-S(2)#1	102.62 (3)
S(2)#1-Sn(1)-S(2)	93.49 (4)		

Symmetry code is #1: −x, −y, −z−1.

methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were added at calculated positions and refined using a riding model, except that two hydrogen atoms of water were picked out by difference Fourier syntheses. The structure was refined on F^2 using the SHELXTL-97 software package[21,22] without any unusual events. Some crystal data and refinement details are gathered in Table I. Selected bond lengths and bond angles are given in Table II for **1**. CCDC-704530 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/ retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223–336033; email: deposit@ccdc.cam.ac.uk].

TABLE III Typical Hydrogen Bond Lengths (Å) and Bond Angles (°) for Compound 1

D-H. . .A	D-H(Å)	H. . .A(Å)	D. . .A(Å)	D-H. . .A(deg.)
O(3)-H(3a). . .0(2)	0.94 (5)	1.90 (5)	2.798 (4)	160 (4)
C(12) #1-H(12) #1. . .0(3)	0.90 (3)	2.39 (3)	3.230 (4)	156 (3)
C(13) #2-H(13) #2. . .0(3)	0.93 (4)	2.45 (4)	3.360 (5)	165 (3)

Symmetry codes are #1: −x, 1−y, −z; #2: 1+x, 1+y, z.

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