# Different Effects of a Cotemplate and [(Transition-Metal)-(1,10-Phenanthroline)$_m$]$^{2+}$ ($m$ = 1−3) Complex Cations on the Self-assembly of a Series of Hybrid Selenidostannates Showing Combined Optical Properties of Organic and Inorganic Components

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Ⓢ *Supporting Information*

**ABSTRACT:** 1,10-Phenanthroline (phen) and monoprotonated methylamine molecules were used as a novel cotemplate to direct the formation of a new inorganic−organic hybrid selenidostannate, $(CH_3NH_3)_4(Sn_2Se_6)\cdot6phen$ (**1**); while the utilization of three types of transition-metal (TM) phen complex cations with the TM/phen ration of 1:1, 1:2, and 1:3 as structure directors affords $\{[Mn(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\}\cdot H_2O$ (**2a**), $\{[Fe(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\}$ (**2b**), $\{[Mn(phen)]_2(\mu_4\text{-}Sn_2Se_6)\}_n$ (**3**), $\{[Mn(phen)_2](Sn_2Se_5)\}_n$



(**4**), and $[Fe(phen)_3]_n(Sn_3Se_7)_n\cdot1.25nH_2O$ (**5**). These compounds show diverse structures with the selenidostannate anions varying from discrete, $\mu_2$- and $\mu_4$- $(Sn_2Se_6)^{4-}$ anions, to one-dimensional (1-D) $^1_\infty(Sn_2Se_5^{2-})$ anionic chains, and two-dimensional (2-D) extended $^2_\infty(Sn_3Se_7^{2-})$ anionic layers, demonstrating different structure-directing abilities of the cotemplate and the three types of TM phen complex cations. This work clearly indicates that the approach of modifying the number of the free coordination sites of unsaturated TM phen complex cations is very exciting as a way to synthesize novel hybrid chalcogenidometalates. Of particular interest, the present compounds exhibit interesting optical properties that reflect the combined effects of both photoluminescence-active organic components and semiconducting inorganic chalcogenidometalate anionic networks.
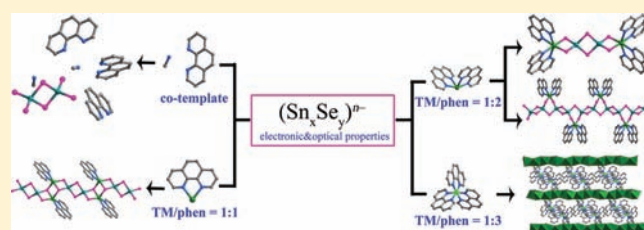
## 1. INTRODUCTION

Recent development on the molecule-based inorganic−organic hybrid materials has revealed that the introduction of organic components, for example, organic species, transition-metal (TM), and rare-earth-metal (Ln) complex cations, into inorganic systems can produce inorganic−organic hybrids with unique topological structures and interesting physical properties.[1] The very important aspect is that the optical, electronic, and magnetic properties of the organic components may integrate with the unique properties of the inorganic components, which can be expected to give rise to complementary properties and synergistic effects.[1p,q,2] On the other hand, previous studies have shown that tin chalcogenides are technically important and show a wide range of interesting electronic and optical properties.[3] Take the tin dichalcogenides, $SnS_2$ and $SnSe_2$, for example; both are semiconductors and have been reported to have numerous applications in thermoelectric generators, detectors, and emitters in the infrared spectral region, as well as switching and memory devices.[3e−o] It is very attractive to incorporate functional organic components into the inorganic Sn-Q (Q = S, Se) system to form inorganic−organic hybrid

chalcogenostannates. In fact, a number of hybrid chalcogenostannates have been prepared up to now,[4] in which the organic components are mainly aliphatic chelating amines or TM/Ln aliphatic chelating amine complexes. As we know, in comparison with the traditional aliphatic chelating amine, $\pi$-conjugated ligands featuring delocalized electrons over their aromatic rings can confer peculiar photochemical and electrochemical properties on their TM complexes, which are of great interest for applications in photoelectronic materials.[5] Thus, the investigation of inorganic−organic hybrid chalcogenidostannates containing $\pi$-conjugated ligand or their TM/Ln complexes is very meaningful, but is still in its infancy. Hitherto, only three hybrid chalcogenostannates containing TM $\pi$-conjugated ligand complexes have been reported,[4aa,6] including a thiostannate prepared by us recently[6] and the other two selenidostannates synthesized by Sheldrick and co-workers.[4aa]

Our recent attention has been devoted to the design and syntheses of inorganic−organic hybrid main-group element

chalcogenides containing TM $\pi$-conjugated ligand complex cations, and we have prepared several such hybrids in the R—As-S and R—Sn-S systems, where R is the organic components.[6,7] Now, we further spread our interest to the R—Sn-Se system, and by using neutral 1,10-phenanthroline (phen) molecule under methylamine aqueous solution we obtained a selenidostannate $(CH_3NH_3)_4(Sn_2Se_6) \cdot 6phen$ (**1**), where the phen ligands coexist with the protonated methylamine molecules acting as a novel cotemplate. While, the utilization of $Mn^{II}$ or $Fe^{II}$ phen complex cations as structure directors yields five hybrid selenidostannates, namely, $\{[Mn(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\} \cdot H_2O$ (**2a**), $\{[Fe(phen)_2]_2\text{-}(\mu_2\text{-}Sn_2Se_6)\}$ (**2b**), $\{[Mn(phen)_2]_2(\mu_4\text{-}Sn_2Se_6)\}_n$ (**3**), $\{[Mn\text{-}(phen)_2](Sn_2Se_5)\}_n$ (**4**), and $[Fe(phen)_3]_n(Sn_3Se_7)_n \cdot 1.25n\text{-}H_2O$ (**5**). In **2a**—**4**, the TM phen complex cations are unsaturated, which further form covalent TM—Se bonds with the selenidostannate anions; while in **5**, each $Fe^{2+}$ ion is chelated by three phen molecules to form a saturated $[Fe(phen)_3]^{2+}$ complex, which acts as a discrete cation in the crystal structure. Herein, we report the solvothermal syntheses, crystal structures, and optical (UV—vis and photoluminescence (PL)) properties of the six new selenidostannates.

## 2. EXPERIMENTAL SECTION

**2.1. Materials and Instruments.** All reagents were purchased commercially and used without further purification. Elemental analyses of C, H, and N were performed on an Elementar Vario EL III microanalyzer. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex II diffractometer using Cu $K\alpha$ radiation. A NETZSCH STA 449C thermogravimetric analyzer was used to obtain thermogravimetry (TG) curves in $N_2$ with a flow rate of 20 mL/min and a ramp rate of 10 °C·min$^{-1}$ in the temperature range 30—700 °C. An empty $Al_2O_3$ crucible was used as the reference. The FT-IR spectra were obtained on a Perkin-Elmer spectrophotometer using a KBr disk in the range 4000—400 cm$^{-1}$. The solid-state fluorescence excitation and emission spectra were measured on an Edinberg FLS920 fluorescence spectrophotometer at room temperature with a wavelength increment of 1.0 nm and an integration time of 0.2 s. Optical diffuse reflectance spectra were measured at room temperature with a PE Lambda 900 UV—vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The samples were ground into fine powder and pressed onto a thin glass slide holder. A $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectra were calculated from reflectance spectrum using the Kubelka—Munk function: $\alpha/S = (1 - R)^2/2R^8$ where $\alpha$ is the absorption coefficient, $S$ is the scattering coefficient (which is practically wavelength independent when the particle size is larger than 5 $\mu$m), and $R$ is the reflectance.

**2.2. Synthesis.** *2.2.1. Preparation of $(CH_3NH_3)_4(Sn_2Se_6) \cdot 6phen$ (1).* A mixture of Sn (0.059 g, 0.50 mmol), Se (0.120 g, 1.52 mmol), phen·$H_2O$ (0.099 g, 0.50 mmol), and ethylenediamine (0.1 mL, 1.50 mmol) in 4 mL of methylamine aqueous solution (28% in $H_2O$) was sealed in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 170 °C for 5 days and finally cooled to room temperature. The product consists of yellow chunk crystals of **1** and a few bits of indefinite powder. The crystals of **1** were selected by hand and washed with ethanol and diethyl ether. The crystals are stable in air and insoluble in common solvents. (Yield: 10% based on Sn). The phase purity of **1** was confirmed by PXRD study (Supporting Information, Figure S1). Elemental analysis calcd. (%) for $C_{76}H_{72}N_{16}Se_6Sn_2$: C 47.53, H 3.78, N 11.67; found: C 46.96, H 3.64, N 11.56.

*2.2.2. Preparation of $\{[Mn(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\} \cdot H_2O$ (2a).* A mixture of $SnCl_4 \cdot 5H_2O$ (0.175 g, 0.50 mmol), $MnCl_2 \cdot 4H_2O$ (0.099 g, 0.50 mmol), Se (0.158 g, 2.00 mmol), and phen·$H_2O$ (0.099 g, 0.50 mmol) in 4 mL of methylamine aqueous solution (28% in $H_2O$) was sealed in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 185 °C for 5 days and finally cooled to room temperature. The product consists of dark-red block crystals of **2a** and a few bits of indefinite powder. The crystals of **2a** were selected by hand and washed with ethanol and diethyl ether. The crystals are stable in air and insoluble in common solvents. (Yield: 15% based on Sn). The phase purity of **2a** was confirmed by PXRD study (Supporting Information, Figure S1). Elemental analysis calcd. (%) for $C_{48}H_{36}Mn_2N_8O_2Se_6Sn_2$: C 36.54, H 2.30, N 7.10; found: C 37.03, H 2.28, N 7.60.

*2.2.3. Preparation of $\{[Fe(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\}$ (2b).* A mixture of $SnCl_4 \cdot 5H_2O$ (0.175 g, 0.50 mmol), $FeCl_3$ (0.081 g, 0.50 mmol), Se (0.158 g, 2.00 mmol), and phen·$H_2O$ (0.297 g, 1.50 mmol) in 4 mL of methylamine aqueous solution (7% in $H_2O$) was sealed in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 185 °C for 5 days and finally cooled to room temperature. The product consisted of black chunk crystals of **2b** as the byproduct (Yield: 5% based on Sn) and dark-red block crystals of **5** as the main-product (Yield: about 16% based on Sn). Note that compound **5** with a higher yield (39%) could also be synthesized under the condition as shown below. The crystals of **2b** were selected by hand and washed with ethanol and diethyl ether. The crystals are stable in air and insoluble in common solvents. The phase purity of **2b** was confirmed by PXRD study (Supporting Information, Figure S1). Elemental analysis calcd. (%) for $C_{48}H_{32}Fe_2N_8Se_6Sn_2$: C 37.35, H 2.09, N 7.26; found: C 36.38, H 1.89, N 7.06.

*2.2.4. Preparation of $\{[Mn(phen)_2]_2(\mu_4\text{-}Sn_2Se_6)\}_n$ (3).* A mixture of $SnCl_4 \cdot 5H_2O$ (0.175 g, 0.50 mmol), $MnCl_2 \cdot 4H_2O$ (0.099 g, 0.50 mmol), Se (0.120 g, 1.52 mmol), and phen·$H_2O$ (0.099 g, 0.50 mmol) in 4 mL methylamine aqueous solution (16% in $H_2O$) was sealed in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 170 °C for 6 days and then cooled to room temperature. The product consists of orange chip crystals of **3** and a few bits of indefinite dark-red powder. The crystals of **3** were selected by hand and washed with ethanol and diethyl ether. The crystals are stable in air and insoluble in common solvents. (Yield: 9% based on Sn). The phase purity of **3** was confirmed by PXRD study (Supporting Information, Figure S1). Elemental analysis calcd. (%) for $C_{24}H_{16}Mn_2N_4Se_6Sn_2$: C 24.40, H 1.37, N 4.74; found: C 24.27, H 1.18, N 4.60.

*2.2.5. Preparation of $\{[Mn(phen)_2](Sn_2Se_5)\}_n$ (4).* A mixture of $SnCl_4 \cdot 5H_2O$ (0.175 g, 0.50 mmol), $MnCl_2 \cdot 4H_2O$ (0.099 g, 0.50 mmol), Se (0.158 g, 2.00 mmol), and phen·$H_2O$ (0.099 g, 0.50 mmol) in 4 mL of methylamine aqueous solution (16% in $H_2O$) was sealed in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 185 °C for 5 days and finally cooled to room temperature. The product consists of orange chip crystals of **4** and a few bits of indefinite dark-red powder. The crystals of **4** were selected by hand and washed with ethanol and diethyl ether. The crystals are stable in air and insoluble in common solvents. (Yield: 13% based on Sn). The phase purity of **4** was confirmed by PXRD study (Supporting Information, Figure S1). Elemental analysis calcd. (%) for $C_{24}H_{16}MnN_4Se_5Sn_2$: C 27.52, H 1.54, N 5.35; found: C 27.50, H 1.31, N 5.32.

*2.2.6. Preparation of $[Fe(phen)_3]_n(Sn_3Se_7)_n \cdot 1.25nH_2O$ (5).* A mixture of $SnCl_4 \cdot 5H_2O$ (0.175 g, 0.50 mmol), $FeCl_3$ (0.081 g, 0.50 mmol), Se (0.158 g, 2.00 mmol), and phen·$H_2O$ (0.297 g, 1.50 mmol) in 4 mL of methylamine aqueous solution (28% in $H_2O$) was sealed in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 185 °C for 5 days and finally cooled to room temperature. Dark-red block crystals of **5** were selected by hand

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## Table 1. Crystal and Structure Refinement Data for 1−5

| | 1 | 2a | 2b | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| formula | $C_{76}H_{72}N_{16}Se_6Sn_2$ | $C_{48}H_{36}Mn_2$- $N_8O_2Se_6Sn_2$ | $C_{48}H_{32}Fe_2$- $N_8Se_6Sn_2$ | $C_{24}H_{16}Mn_2$- $N_4Se_6Sn_2$ | $C_{24}H_{16}MnN_4$- $Se_5Sn_2$ | $C_{36}H_{26.5}FeN_6$- $O_{1.25}Se_7Sn_3$ |
| $M_r$ (g mol$^{-1}$) | 1920.64 | 1577.87 | 1543.66 | 1181.43 | 1047.57 | 1527.77 |
| cryst syst | triclinic | monoclinic | monoclinic | triclinic | monoclinic | trigonal |
| space group | $P\bar{1}$ | $P2_1/n$ | $C2/c$ | $P\bar{1}$ | $C2/c$ | $R\bar{3}c$ |
| $D_{calcd}$ (g cm$^{-3}$) | 1.672 | 1.868 | 1.974 | 2.491 | 2.592 | 2.394 |
| $a$ (Å) | 10.594(3) | 11.061(5) | 26.192(3) | 9.721(4) | 16.639(4) | 13.948(3) |
| $b$ (Å) | 12.225(4) | 10.061(4) | 11.248(1) | 10.257(4) | 12.961(3) | 13.948(3) |
| $c$ (Å) | 14.945(4) | 25.207(10) | 17.843(2) | 10.346(5) | 14.088(4) | 75.476(3) |
| $\alpha$ (deg) | 83.589(5) | 90 | 90 | 118.243(14) | 90 | 90 |
| $\beta$ (deg) | 83.133(7) | 90.081(8) | 98.816(7) | 112.53(3) | 117.911(13) | 90 |
| $\gamma$ (deg) | 86.604(6) | 90 | 90 | 95.75(2) | 90 | 120 |
| $V$ (Å$^3$) | 1907.6(10) | 2805(2) | 5194.5(9) | 787.6(6) | 2684.8(12) | 12716.9(6) |
| $Z$ | 1 | 2 | 4 | 1 | 4 | 12 |
| abs coeff (mm$^{-1}$) | 3.571 | 5.256 | 5.744 | 9.305 | 9.111 | 8.132 |
| $F(000)$ | 944 | 1500 | 2928 | 542 | 1932 | 8502 |
| reflns collcd/ unique ($R_{int}$) | 14588/7053 (0.0344) | 17390/5137 (0.0357) | 18940/4842 (0.0418) | 6609/2934 (0.0443) | 9860/2482 (0.1229) | 29156/2623 (0.1027) |
| data/params/restraints | 5814/455/0 | 4648/314/9 | 4268/298/0 | 2544/173/0 | 1926/164/6 | 2041/168/6 |
| $R_1{}^a$ [$I > 2\sigma(I)$] | 0.0377 | 0.0436 | 0.0356 | 0.0336 | 0.0393 | 0.0364 |
| $wR_2{}^b$ [$I > 2\sigma(I)$] | 0.0919 | 0.1320 | 0.0935 | 0.0796 | 0.0932 | 0.0877 |
| goodness of fit | 1.002 | 1.022 | 1.022 | 1.000 | 0.997 | 1.017 |
| $\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.982, −1.510 | 1.450, −1.047 | 1.097, −1.032 | 1.048, −1.012 | 1.287, −2.944 | 1.818, −1.191 |

$^a$ $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b$ $wR_2 = \{\Sigma w[(F_o)^2 - (F_c)^2]^2/\Sigma w[(F_o)^2]^2\}^{1/2}$.

and washed with ethanol and diethyl ether. The crystals are stable in air and insoluble in common solvents. (Yield: 39% based on Sn). The phase purity of **5** was confirmed by PXRD study (Supporting Information, Figure S1). Elemental analysis calcd. (%) for $C_{36}H_{26.5}FeN_6O_{1.25}Se_7Sn_3$: C 28.30, H 1.75, N 5.50; found: C 27.28, H 1.57, N 5.40.

**2.3. Crystal Structure Determinations.** Single crystals of **1−5** suitable for X-ray analyses were mounted at the apex of a glass fiber for data collection. Data collections were performed at 293(2) K on a Rigaku SCXmini CCD diffractometer for **1−3**, a Rigaku Saturn 70 CCD diffractometer for **4**, and a Rigaku Mercury CCD diffractometer for **5**, each diffractometer being equipped with a graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). The intensity data sets were collected with the $\omega$-scan technique and reduced with the CrystalClear program.[9] An empirical absorption correction was applied for **1−5** using the multiscan method. The structures were solved by direct methods using the Siemens SHELXL package of crystallographic software.[10] The difference Fourier maps were created on the basis of these atomic positions to yield the other non-hydrogen atoms. The structures were refined using a full-matrix least-squares refinement on $F^2$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of phen and methylamine molecules were added geometrically and refined as riding on their parent atoms with fixed isotropic displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C, N)$]. The hydrogen atoms of lattice water molecules for **2a** were located by different Fourier maps and refined with O−H distances to a target value of 0.85 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. Hydrogen atoms of water molecules in **5** were not added. Crystallographic data and structural refinements for the title compounds are summarized in Table 1.

## 3. RESULTS AND DISCUSSION

**3.1. Synthetic Considerations.** Hydro(solvo)thermal techniques have been successfully used in synthesizing a large number of inorganic−organic hybrid materials, because the difficulties of differential solubility for organic and inorganic precursors can be overcome under hydro(solvo)thermal condition.[1g,11] In the present work, the mild solvothermal reaction has been conducted to prepare these six compounds. As we know, in a special hydro(solvo)thermal process, many factors can affect the formation and crystal growth of the product phases, such as reactant stoichiometry, initial reactants, pressure, pH value, temperature, reaction time, and so forth. We have studied the influence of several synthetic parameters on the obtained compounds. (1) Note that methylamine aqueous solution, acting as an organic base, offers the indispensable alkaline condition in the syntheses of **1−5**. In case of **1**, besides 28% methylamine aqueous solution, additional ethylenediamine (0.1−0.2 mL) was also used to justify the alkalinity of the reaction solution; otherwise the yield of **1** was lowered. Compounds **2a** and **4** were obtained from the same starting materials with $SnCl_4 \cdot 5H_2O/MnCl_2 \cdot 4H_2O/Se/phen \cdot H_2O$ in the molar ratio of 1:1:4:1, but with methylamine aqueous solution of different concentrations (28% for **2a** and 16% for **4**). Compound **2b** can be obtained in a very low yield with a 7% methylamine aqueous solution. Attempts to improve the yield of **2b** by changing the concentration of the methylamine aqueous solution were unsuccessful. Compound **3** can be obtained with the optimized concentration of the methylamine aqueous solution in the range 11−28%; otherwise, the expected crystal was not formed. Compound **5** can be isolated in a good yield with the concentration of the methylamine aqueous solution spanning widely from 11% to 28%; otherwise the yield of **5** was lowered. (2) The temperature does not play a decisive role in the formation of these six compounds, although it is directly related to the yields of the products. Compound **1** can also be well
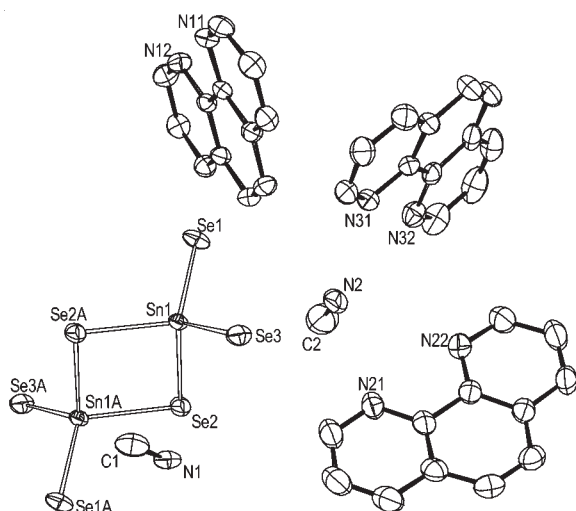
**Figure 1.** ORTEP drawing of **1** with 30% thermal ellipsoids and hydrogen atoms being omitted for clarity. Symmetry code: A ($-x$, $-y$, $1-z$).
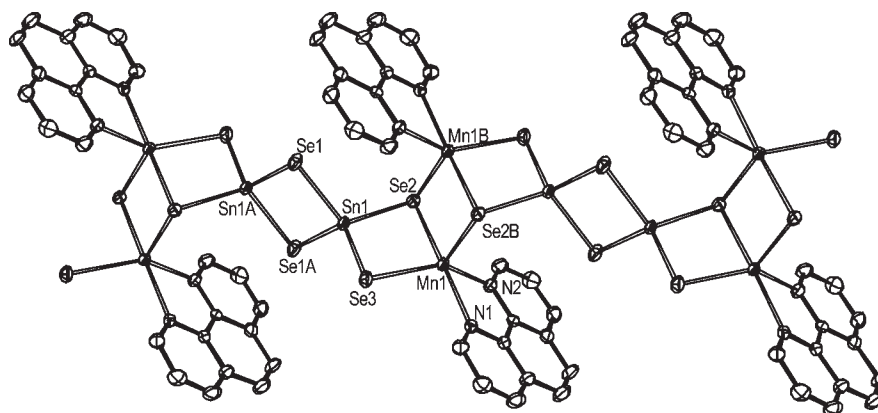


**Figure 2.** ORTEP drawing of the $\{[Mn(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\}$ molecular in **2a** with 30% thermal ellipsoids and hydrogen and oxygen atoms being omitted for clarity. Symmetry code: A ($-x$, $-y$, $1-z$).

isolated in the optimized temperature of 150–170 °C. Compounds **2a**, **2b**, **4**, and **5** still can be obtained in a lower yield in the temperature range of 170–185 °C. While, compound **3** can also be isolated between 160 and 180 °C. (3) The Sn powder used in the synthesis of **1** or $SnCl_4 \cdot 5H_2O$ used in the syntheses of **2a–5** is perfect as the Sn source in our experiments; when the Sn source is replaced, that is, Sn powder is replaced by $SnCl_4 \cdot 5H_2O$ in the synthesis of **1** and $SnCl_4 \cdot 5H_2O$ is replaced by Sn powder in the syntheses of **2a–5**, the yields of their corresponding products are lowered. Detailed experiments also show that compounds **2a** and **5** still can be formed in a lower yield with $FeCl_3$ been replaced by $FeCl_2 \cdot 4H_2O$.

**3.2. Crystal Structures.** *3.2.1. Crystal Structure of 1.* Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in triclinic space group $P\bar{1}$ and consists of one-half $(Sn_2Se_6)^{4-}$ anion, two monoprotonated methylamines, and three phen molecules in the asymmetric unit (Figure 1). The dimeric $(Sn_2Se_6)^{4-}$ anion is formed by two edge-sharing distorted $(SnSe_4)$ tetrahedra with four terminal Se atoms. The average $Sn–Se_t$ ($Se_t$ = terminal Se atom) bond distance of 2.453 Å is noticeable shorter than the average $Sn–Se_b$ ($Se_b$ = bridging Se atom) bond distance of 2.591 Å. Both the $Sn–Se_t$ and $Se–Se_b$ bond distances agree well with those in the selenidostannate containing discrete $(Sn_2Se_6)^{4-}$ anions.[4y,12] The bond angles of the $(Sn_2Se_6)^{4-}$ anion match well with those of analogous dimeric $(M_2Q_6)^{4-}$ (M = Ge, Sn) anions,[4c,g,l,12a,13] with bond angles always in the order of $Q_t$ $-M-Q_t$ > $Q_b$ $-M-Q_b$ > M1$-$Q$-$M2. The methylamine molecules are monoprotonated for charge balance, which is confirmed by the IR spectrum as discussed in the Supporting Information. It should be noted that there are three types of face-to-face $\pi \cdots \pi$ stacking interactions between two neighboring phen molecules in **1** with the centroid–centroid distances varying from 3.561(1) to 3.647(1) Å and dihedral angles in the range of 0.00(14)–1.40(9)°, which lead to three types of (phen)$_2$ pairs, as depicted in Supporting Information, Figure S2a. The values of the centroid–centroid distances are in the ranges of those reported in the literature.[14] The C–H$\cdots$Se, N–H$\cdots$Se, and N–H$\cdots$N hydrogen bonds further link the (phen)$_2$ pairs, $(Sn_2Se_6)^{4-}$ anions,
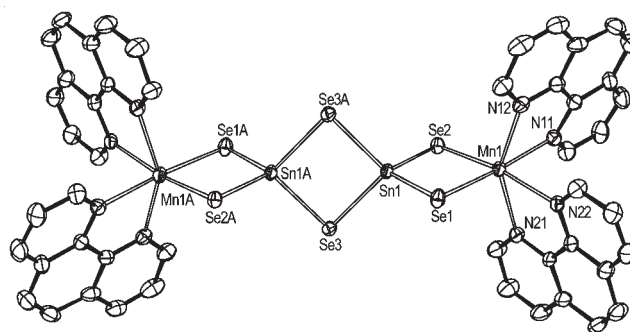
and the monoprotonated molecules into a three-dimensional (3-D) supramolecular framework of **1** ( Supporting Information, Figure S2b). The donor$\cdots$acceptor distances and the donor–H$\cdots$acceptor angles of these hydrogen bonds are comparable with the corresponding values in the literature.[15]

It is worth mentioning that although a large number of inorganic–organic hybrids (including hybrid metal halides, metal chalcogenides, and metal oxide-based materials) templated with organic species have been synthesized, the examples containing discrete phen molecules as a structure director have been rarely reported.[16] In **1**, the neutral phen molecule coexists with the monoprotonated methylamine molecule as an unprecedented cotemplate directing the formation of $(Sn_2Se_6)^{4-}$ anions. The dimeric $(Sn_2Q_6)^{4-}$ anions have been widely reported in hybrid group 14 chalcogenidometalates,[4c,r–t,v–x,17] where the structure directors are always organic amine cations[4c,v,w,z,17a] and metal complex cations.[4r–t,x,17b]

*3.2.2. Crystal Structures of 2a and 2b.* Compounds **2a** and **2b** crystallize in the monoclinic crystal system with the space group $P2_1/n$ for **2a** and the space group $C2/c$ for **2b**. In both compounds, the dimeric $(Sn_2Se_6)^{4-}$ anions locate at a center of inversion and bridge two unsaturated $[TM(phen)_2]^{2+}$ complex cations via the four terminal Se atoms to form neutral $\{[TM(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\}$ (TM = Mn (**2a**), Fe (**2b**)) moieties (Figure 2 and Supporting Information, Figure S3). In **2a**, there are one-half of a dimeric $(Sn_2Se_6)^{4-}$ anion, one [Mn-(phen)$_2$]$^{2+}$ complex cation, and one water molecule in the asymmetric unit; while in **2b**, there are one-half of a $(Sn_2Se_6)^{4-}$ anion and one $[Fe(phen)_2]^{2+}$ cation in the asymmetric unit. The TM complex cations in both compounds are in a distorted octahedral environment, which is formed by four N atoms from two chelating phen ligands and two Se atoms from the chelating $(Sn_2Se_6)^{4-}$ anion. As shown in Supporting Information, Figures S4 and S5, the $\{[TM(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\}$ molecules pack differently in their corresponding crystal structures. In **2a**, every $\{[Mn(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\}$ molecule interacts with four neighboring molecules by C–H$\cdots$Se hydrogen bonds and face-to-face $\pi \cdots \pi$ stacking interactions (Supporting Information, Figure S7a) to produce 2-D extended layers parallel to the *ab* plane, which are further stacked along the *c* direction through the van der Waals force (Supporting Information, Figure S5c). Structural analysis indicates that there are no significant hydrogen bonds between the lattice water molecules and the 2-D supramolecular layers. As for **2b**, each $\{[Fe(phen)_2]_2(\mu_2\text{-}Sn_2Se_6)\}$ molecule interacts with 10 neighboring molecules (Supporting

**Figure 3.** ORTEP drawing of **3** with 30% thermal ellipsoids and hydrogen atoms being omitted for clarity. Symmetry codes: A ($-x$, $-y$, $1-z$); B ($1-x$, $1-y$, $1-z$).

Information, Figure S7b) through C—H···Se hydrogen bonds and face-to-face $\pi$···$\pi$ stacking interactions to form a 3-D supramolecular structure (Supporting Information, Figure S6a). The values of the centroid—centroid distances between the parallel aromatic rings (3.521(1) Å for **2a** and 3.562(1)—3.673-(1) Å for **2b**) are comparable with those in the literature.[14] The C···Se separations and the C—H···Se angles are in the ranges of corresponding values reported in the literature.[15c,d]

Dimeric $(Sn_2Q_6)^{4-}$ anion containing two edge-sharing $(SnQ_4)$ tetrahedra represents the predominant Sn-containing species in inorganic—organic hybrid group 14 chalcogenides, where the $(Sn_2Q_6)^{4-}$ anion is usually structurally characterized as a discrete anion[4c,g,j−m,o,p,r,s,v−z,12,13,17b,18] or a bridging anionic ligand connecting two unsaturated TM[4f−h,n,p,q,19] or Ln complex cations[4t] through its two trans terminal Q atoms; however, the examples of the $(Sn_2Q_6)^{4-}$ anion using all its four terminal Q atoms to coordinate to TM complexes are very limited.[4aa] For **2a** and **2b**, the prominent structural feature is that the bridging $(Sn_2Se_6)^{4-}$ anion chelating to two TM complex cations via its four terminal Se atoms. Similar compounds can only be found in two known selenidostannates,[4aa] in which the $(Sn_2Se_6)^{4-}$ anion bridges two $[Mn(cyclam or terpy)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; terpy = 2,2′;6′,2″-terpyridine) complexes. The $(Sn_2Se_6)^{4-}$ anions in **2a**, **2b** and the known selenidostannates all show a $\mu-1\kappa Se:1\kappa Se':2\kappa Se'':2\kappa Se'''$ linkage mode.

*3.2.3. Crystal Structure of* **3**. Compound **3** crystallizes in the triclinic space group $P\overline{1}$ and is composed of 1-D $\{[Mn(phen)]_2$-$(\mu_4\text{-}Sn_2Se_6)\}_n$ neutral wavelike chains. The Mn atoms in the chain adopt trigonal bipyramid configuration, MnSe$_3$N$_2$, in which the N atoms come from one phen molecule and the Se atoms come from two $(Sn_2Se_6)^{4-}$ anions (Figure 3). Two Mn1 trigonal bipyramids edge-share to form a $(Mn)_2$ dimer with a crystallographic inversion center and the Mn1···Mn1A distance of 3.521(1) Å. The dimeric $(Sn_2Se_6)^{4-}$ anion acts as a bridging ligand linking the $(Mn)_2$ dimers to form a novel 1-D four-membered ring chain extending along the $a$ axis. The Sn—Se bond distances varying from 2.338(1) to 2.431(1) Å are comparable with those in **1**— **2b** and can be grouped into three types: the longest Sn—$\mu_2$-Se1 bond distance of av. 2.554 Å, the medium Sn—$\mu_3$-Se2 bond distance of av. 2.510 Å, and the shortest Sn—$\mu_2$-Se3 bond distance of av. 2.468 Å. Interestingly, there exist interchain face-to-face $\pi$···$\pi$ stacking interactions between the aromatic rings of phen ligands with the centroid—centroid distance of 3.712(2) Å and dihedral angle of 1.21(11)°, which

are comparable with corresponding values in the literature[14a,20] and link the chains in **3** into a 2-D layer structure parallel to the $ab$ plane (Supporting Information, Figure S9a). The layers are interconnected in parallel fashion via weak C—H···Se hydrogen bonds along the $c$ direction to yield a 3-D supramolecular framework (Supporting Information, Figure S9b). The C···Se distances and the C—H···Se angles are consistent with the values observed in the literature.[15c,d]

The most striking structural feature of **3** is the presence of a tetradentate $(Sn_2Se_6)^{4-}$ anion, which connects four TM complex cations, showing an unprecedented $\mu_4$–1,2$\kappa S':2\kappa S'':3\kappa S''':$-3,4$\kappa S''''$ linkage mode. Before this work, $(Sn_2Q_6)^{4-}$ anion connecting four TM complex cations could only be observed in $\{[Mn(terpy)]_2(\mu_4\text{-}Sn_2Se_6)\}_n$ with the $(Sn_2Se_6)^{4-}$ anion exhibiting a different $\mu_4$–1$\kappa S':2\kappa S'':3\kappa S''':4\kappa S''''$ linkage mode.[4aa]

*3.2.4. Crystal Structure of* **4**. Compound **4** crystallizes in the triclinic centrosymmetric crystal system with space group $P\overline{1}$ and comprises a neutral $\{[Mn(phen)_2](Sn_2Se_5)\}_n$ chain, which can be regarded as the unsaturated $[Mn(phen)_2]^{2+}$ complex cations bonding to the opposite side Se atoms of the $^1_\infty(Sn_2Se_5{}^{2-})$ anionic backbone chain. As shown in Figure 4, each Sn atom is coordinated by four Se atoms to form a $(SnSe_4)^{4-}$ tetrahedron, which is further self-condensed in an alternating (corner-sharing)-(edge-sharing) sequence to form the $^1_\infty(Sn_2Se_5{}^{2-})$ chain along the $c$ direction. Alternatively, the anionic $^1_\infty(Sn_2Se_5{}^{2-})$ chain can also be described as the further condensation of the ditetrahedral $(Sn_2Se_6)^{4-}$ species via sharing two trans terminal Se atoms. The $^1_\infty(Sn_2Se_5{}^{2-})$ chain adopts a *zweier* configuration, which contains two corner-sharing $(Sn_2Se_6)^{4-}$ species in a repeating unit. The period of the repeating unit is 14.088(1) Å, which is equal to the unit cell length of the $c$ axis. In the crystal structure of **4**, each Mn$^{2+}$ ion has a distorted octahedral environment and is coordinated by four N atoms of two chelating phen ligands and two Se atoms of the $^1_\infty(Sn_2Se_5{}^{2-})$ chain. The average Sn—Se$_b$ (Se$_b$ = bridging Se bonding with two Sn atoms) bond distance of 2.570 Å is about 0.116 Å longer than the Sn—Se$_b'$ (Se$_b'$ = bridging Se bonding with a Mn atom) bond distance of 2.454 Å. Notably, the Se atoms in **4** all acting as a $\mu_2$-ligand bridging two Sn atoms, or one Sn and one Mn atoms to form the 1-D inorganic $(MnSn_2Se_5)_n$ chain with fused four-membered $(Sn_2Se_2)$ rings and six-membered $(MnSn_2Se_3)$ rings in an alternating fashion. The Mn—N and Mn—Se bond distances, as summarized in Supporting Information, Table S1, are in their normal ranges.[6,21] In the crystal structure of **4**, the interchain
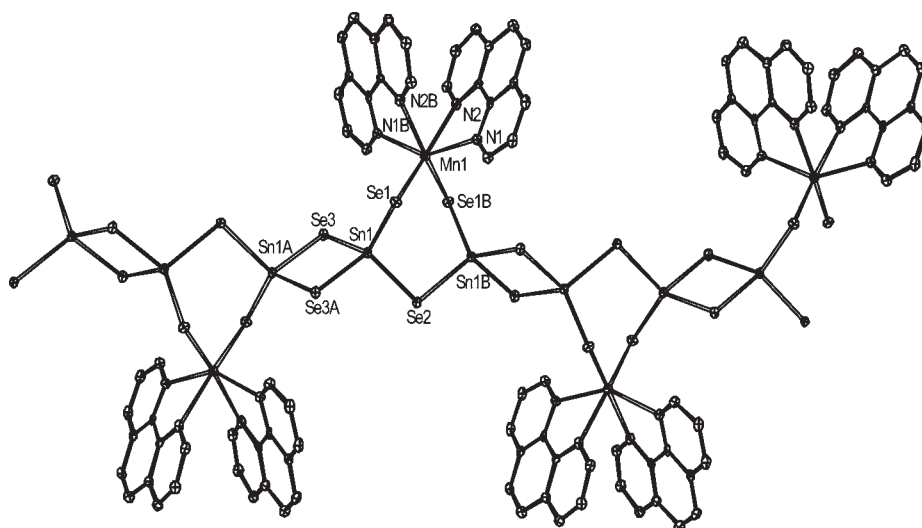
**Figure 4.** ORTEP drawing of **4** with 30% thermal ellipsoids and hydrogen atoms being omitted for clarity. Symmetry codes: A $(1-x, -y, 1-z)$; B $(1-x, y, 3/2-z)$.



(a)

(b)                    (c)
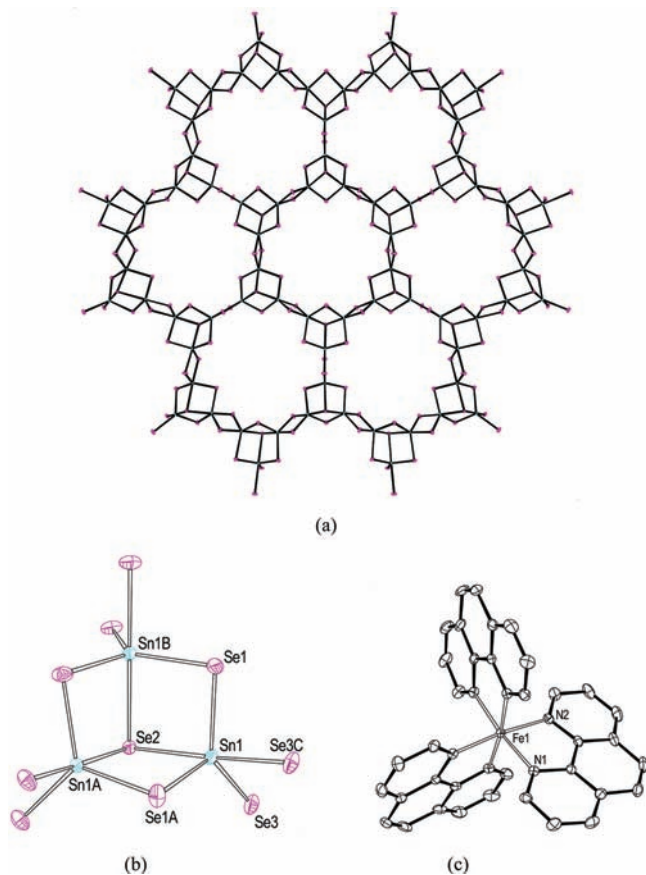
**Figure 5.** (a) Structure of the $^2_\infty(Sn_3Se_7{}^{2-})$ anionic layer of **5**. (b) ORTEP drawing of the $(Sn_3Se_{10})$ unit containing incomplete cubane-like $(Sn_3Se_4)$ unit. Symmetry codes: A $(-1-x+y, 1-x, z)$; B $(1-y, 2+x-y, z)$; C $(-2/3+y, 2/3+x, 1/6-z)$. (c) ORTEP drawing of the $[Fe(phen)_3]^{2+}$ complex cation in **5**.

face-to-face $\pi\cdots\pi$ stacking interactions between the aromatic rings of phen ligands with centroid–centroid distance varying from 3.566(1) to 3.593(1) Å and dihedral angles in the range of

0.00(10)–3.50(9)° lead to 2-D extended layer structure parallel to the $bc$ plane (Supporting Information, Figure S10a), which are further linked via C–H$\cdots$Se hydrogen bonds along the $a$ direction to form a 3-D supramolecular structure of **4** (Supporting Information, Figure S10b). The values of the centroid–centroid distances and the C$\cdots$Se separations are comparable with corresponding values observed in the literature.[14,15c,15d]

The prominent structural feature of **4** is the presence of a rarely reported $^1_\infty(Sn_2Se_5{}^{2-})$ anionic chain.[4ab,22] Chalcogenidostannates synthesized in the past years display intriguing crystal structures and have attracted substantial attention. The majority of the known chalcogenidostannates contain tetrahedral $(SnQ_4)^{4-}$ unit that is usually stabilized by coordinating to TM/Ln ions or TM/Ln complex cations, or the polyanions formed by the self-condensation of the $(SnQ_4)^{4-}$ unit, such as ditetrahedral $(Sn_2Q_6)^{4-}$, tetranuclear $(Sn_4Q_{10})^{4-}$, and the polymeric 2-D $^2_\infty(Sn_3Q_7{}^{2-})$ and $^2_\infty(Sn_4Q_9{}^{2-})$. A reaction mechanism proposed by Sheldrick and coworkers[4ab,23] for the formation of $^2_\infty(Sn_3Q_7{}^{2-})$ and $^2_\infty(Sn_4Q_9{}^{2-})$ sheets from individual $(Sn_2Q_6)^{4-}$ anion suggests that the $^1_\infty(Sn_2Q_5{}^{2-})$ anion is an intermediate of these chalcogenidostannates anionic sheets. Selecting a proper structure-director or templates and adjusting the proper reaction conditions (e.g., temperature, pH value of the solution) are very important to isolate the $^1_\infty(Sn_2Q_5{}^{2-})$ anions, but difficult to perform. Hitherto, the $^1_\infty(Sn_2Q_5{}^{2-})$ anionic chains are only characterized in very limited number of compounds,[4ab,22] in which the templates are alkali metal cation or the protonated organic amine cation.

*3.2.5. Crystal Structure of **5***. Compound **5** crystallizes in the trigonal centrosymmetric crystal system with space group $R\bar{3}c$ and consists of $^2_\infty(Sn_3Se_7{}^{2-})$ sheet, $[Fe(phen)_3]^{2+}$ complex cation, and lattice water molecules. In the $^2_\infty(Sn_3Se_7{}^{2-})$ sheet, all the Sn atoms are five-coordinated by Se atoms giving a distorted trigonal bipyramidal symmetry, while the Se atoms are two- and three-coordinated by Sn atoms (Figure 5a). Three $(SnSe_5)$ polyhedra share edges to form a $(Sn_3Se_{10})$ unit, in which the triangular trinuclear Sn atoms are capped by one $\mu_3$-Se atom, bridged by three $\mu_2$-Se atoms to form an incomplete cubane-like $(Sn_3Se_4)$ core with each Sn atom further bonding a pair of

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"terminal" Se atoms (Figure 5b). Six $(Sn_3Se_{10})$ units circularly link each other by sharing its two pair of "terminal" Se atoms to form a 24-membered ring with the cross sectional dimensions being 11.305 Å, which share the third pair of "terminal" Se atoms to form a (6, 3) honeycomb-like $^2_\infty(Sn_3Se_7^{2-})$ slab with hydrogen-bonding connected water clusters $(H_2O)_4$ being accommodated inside the rings (Figure 5a and Supporting Information, Figure S10a). The slabs are stacked along the $c$ direction in an -ABCABC- fashion with the $[Fe(phen)_3]^{2+}$ complex cations being located between the slabs to form the framework of 5 (Supporting Information, Figure S11c).

As expected, the $Sn-\mu_3$-Se bond distances of 2.798(1) Å is significantly longer than the average $Sn-\mu_2$-Se bond distance of 2.581 Å, which is consistent with those found in the $^2_\infty$-$(Sn_3Se_7^{2-})$ sheet-containing selenidostannates. The shortest $O\cdots Se$ separation between the water clusters and the $^2_\infty$-$(Sn_3Se_7^{2-})$ anionic framework is 3.580 Å, which is slightly longer than the sum of the van der Waals radii of O and Se atom, 3.42 Å, indicating that there are no significant hydrogen bonds. In 5, the Fe atom is coordinated by six N atoms from three chelating phen molecules to form a slightly distorted octahedron (Figure 5c) with the Fe-N bond distances in the narrow range of 1.970-(3)-1.977(3) Å and the axial trans N-Fe-N bond angles having the same value of 173.22 (10)°. It should be noteworthy that each $[Fe(phen)_3]^{2+}$ complex cation interacts with three neighboring ones through face-to-face $\pi\cdots\pi$ stacking interactions between the aromatic rings of phen ligands to form 2-D extended $[Fe(phen)_3]_n^{2n+}$ supramolecular layers (Supporting Information, Figure S11b) that also have a (6, 3) topological network, where each $[Fe(phen)_3]^{2+}$ complex cation acts as a 3-connected node (Supporting Information, Figure S12).

Recently, considerable interest has been focused on the utilization of chiral metal complex cations as templates or structure directors in making chiral inorganic−organic hybrid compounds such as hybrid metal halides, metal chalcogenides, and metal oxide-based materials, where the metal complex can transfer the chiral information to the inorganic host through hydrogen-bonding interactions or/and induce the hybrid compound to crystallize in a chiral space group.[1i,24] In 5, three phen ligands chelate to a $Fe^{2+}$ ions to form a pinwheel-shaped $[Fe(phen)_3]^{2+}$ complex conferring chirality on the metal center; however, a mixture of enantiomeric $[Fe(phen)_3]^{2+}$ complexes with opposite configurations, Λ and Δ, were found in a single crystal, where each Λ-Fe complex cation is surrounded by three Δ-Fe complexes and vice versa, leading to achiral supramolecular $[Fe(phen)_3]_n^{2n+}$ layers (Supporting Information, Figure S12). These supramolecular layers and the $^2_\infty$-$(Sn_3Se_7^{2-})$ anionic layers are stacked along the $c$ direction in an alternating fashion to form an achiral 3-D supramolecular structure; meanwhile, there is no any chiral character in the inorganic $^2_\infty(Sn_3Se_7^{2-})$ anionic framework. All these indicate that the $[Fe(phen)_3]^{2+}$ complex does not preserve its chirality to a higher dimensionality in the crystal structure of 5, which may be due to the lack of effective supramolecular interactions for chiral transfer.

Lamellar $^2_\infty(Sn_3Q_7^{2-})$ anions have been reported in a number of chalcogenidostannates,[4a,b,z,12b,25] where the structure directors are usually alkylammonium cations,[4b,25a] alkali metal cations[26] and protonated organic amine cations.[4a,12b,25b−25d] The example of $^2_\infty(Sn_3Q_7^{2-})$ sheet-containing compound directed by TM complex cations is only found in $[Mn(C_{10}H_{28}N_6)]$-$(Sn_3Se_7)$,[25e] where a Mn aliphatic chelating amine complex

cation acts as a structure director. To the best of our knowledge, compound 5 represents the first example of TM $\pi$-conjugated ligand complex cations as a structure director to direct the formation of lamellar $^2_\infty(Sn_3Q_7^{2-})$ anions.

**3.3. Different Structure-Directing Abilities of the Cotemplate (Phen + Methylamine) and the $[TM(phen)_m]^{2+}$ ($m$ = 1−3) Complex Cations on the Self-Assembly of 1−5.** In this work, a novel cotemplate and three types of TM phen complexes, which feature four, two, and no free coordination sites on the $TM^{2+}$ centers, were used to direct the formation of the title compounds, and their different structure-directing abilities can be clearly observed. Furthermore, the three types of TM phen complexes exhibit different structure-directing abilities from the conventional TM aliphatic chelating amine complexes, which are also discussed below.

Similar to discrete single-template cations, the cotemplate of phen and monoprotonated-methylamine in 1 acts as a charge-compensating agent and a space filler to exert a structure directing effect via the formation of supramolecular interactions, for example, hydrogen bonding with the inorganic chalcogen-idometalate anions.[1e] Generally, in comparison with the conventional single templates, cotemplates featuring the integration of two or more single templates may have different charge, size and shape to direct the formation of hybrids with unusual inorganic anionic network.[11c,27] However, the novel cotemplate in 1 modulates the formation of a well-known dimeric $(Sn_2Se_6)^{4-}$ discrete anion, which indicates that novel templates are not always related with novel inorganic anions and other factors may also play an important role in determining the structure of the inorganic anionic network.[1e]

On the other hand, unsaturated TM complex cations as structure directors are of particular interest, because they can modify the inorganic chalcogenidometalate anionic network directly via forming covalent TM−Q bonds. Generally, the more free coordination sites the unsaturated TM complex leaves, the more flexibility and unpredictability the coordination between unsaturated TM complexes and inorganic chalcogenidometalate anions displays. In 3, the $[TM(phen)]^{2+}$ complex formed by the phen chelating to $TM^{2+}$ in a 1:1 ratio attracted more attention in that it has as many as four free coordination sites, and it is worthwhile to note that such an unsaturated complex is very difficultly to form when a bidentate aliphatic chelating amine was used instead, because of its strong inclination to form saturated TM complexes. Therefore, the flexible and unpredictable coordination between the $[TM(phen)]^{2+}$ complex and the inorganic chalcogenidometalate anion can be manifested by 3, where the $[TM(phen)]^{2+}$ complex is coordinated by two $(Sn_2Se_6)^{4-}$ anions in two different fashions (monodentate and bidentate-chelating) leading to a five-coordinated $(TMNQ_3)$ coordination sphere, and each $(Sn_2Se_6)^{4-}$ anion shows an unprecedented $\mu_4-1\kappa S':2\kappa S'':3\kappa S''':4\kappa S''''$ link mode.

The TM complexes with two free coordination sites of the $TM^{2+}$ center represent the most common unsaturated TM complex cationic structure-directors used in the syntheses of hybrid chalcogenidometalates, which are usually formed by a tetradentate aliphatic chelating amine (e.g., teta = triethylenete-tramine, tren = tris(2-aminoethyl)amine) chelating to a $TM^{2+}$ center;[1e,2d] however, the unsaturated TM $\pi$-conjugated ligand complex with two free coordination sites in 2a, 2b, and 4 is formed by two phen ligands chelating to a $TM^{2+}$ center. Despite having the same number of the free coordination sites, the tetradentate aliphatic amine-containing unsaturated TM complexes
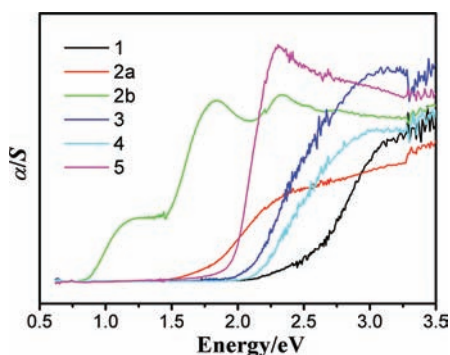
**Figure 6.** Optical diffuse reflectance spectra for **1**−**5**.

show different structure-directing ability from the phen-containing one when coordinating with dimeric $(Sn_2Q_6)^{4-}$ anions, which can be evidenced by the fact that the $[TM(tren/teta)]^{2+}$ complex cations usually form one TM−Q bond with the $(Sn_2Q_6)^{4-}$ anion leading to a trigonal bipyramidal $(TMN_4Q)$ coordination sphere in related hybrid chalcogenostannates.[4g,19] While, as for the $[TM(phen)_2]^{2+}$ complexes in **2a** and **2b**, each is chelated by a $(Sn_2Q_6)^{4-}$ anion in a chelating mode showing an octahedral $(TMN_4Q_2)$ coordination sphere. Such different coordination behaviors are ascribed to their different steric hindrances. Similar to **2a** and **2b**, the $[TM(phen)_2]^{2+}$ complex in **4** is further coordinated by two terminal Se atoms of the $^1_\infty$-$(Sn_2Se_5^{2-})$ anionic backbone chain and also adopts an octahedral coordination sphere around the $TM^{2+}$ center. Note that similar $[TM(phen)_2]^{2+}$ cations direct the formation of different inorganic chalcogenostannate anions in **2a**−**2b** and **4**, again suggesting that some other factors (e.g., hydro(solvo)thermal parameters) also greatly influence the structure of the inorganic anionic network.

For saturated TM complex cationic templates, although the ones of aliphatic chelating amines have been widely used in the syntheses of main-group element hybrid chalcogenidometalates, the ones of π-conjugated ligands as structure directors are still rarely reported.[1u,21c,28] To our knowledge, compound **5** represents the first example of the utilization of saturated TM π-conjugated ligand complex cation as a structure director in the syntheses of group 14 hybrid chalcogenidometalates, where the $[TM(phen)_3]^{2+}$ complex directing the formation of a $^2_\infty$-$(Sn_3Se_7^{2-})$ sheet behaves differently from saturated TM aliphatic chelating amine complexes usually directing the formation of dimeric $(Sn_2Q_6)^{4-}$ anions in the literature.[4g,l,m,29]

**3.4. Optical Spectroscopy and Photoluminescence.** Solid state UV−vis absorption spectra of the present compounds calculated from the diffuse reflectance data by using the Kubelka−Munk function are plotted in Figure 6. The band gaps ($E_g$) can be estimated as 2.52 eV (492 nm) for **1**, 1.75 eV (709 nm) for **2a**, 1.34 eV (925 nm) for **2b**, 2.30 eV (539 nm) for **3**, 2.22 eV (559 nm) for **4**, and 1.97 eV (629 nm) for **5**, which are consistent with their yellow, dark-red, black, orange, orange, and dark-red colors of the crystals, respectively and also suggests that the present compounds are semiconductors. There is a noticeable blue shift of the absorption edges of the title compounds compared with the energy gap of 0.9 eV for binary 2-D SnSe₂.[3c,l,n] Interestingly, for **2b**, a significant absorption feature is observed at about 1.13 eV (1097 nm), which can be attributed to midgap states associated with $Fe^{2+}$ d-d electronic transitions.
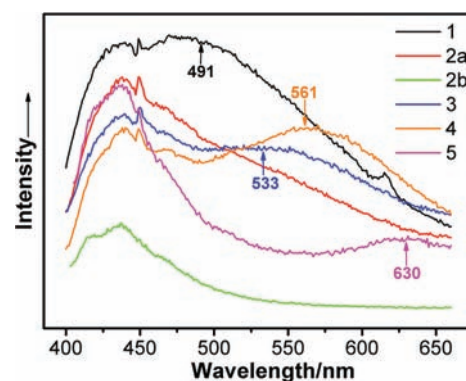


**Figure 7.** Solid-state photoluminescence spectra of **1**−**5** measured at room temperature; the peak positions of **1** and **3**−**5** were determined by the multipeak Gaussian fitting method.

The emission spectra of **1**−**5** in the solid state were investigated at room temperature with photoexcitation at 350 nm. The title compounds all exhibit blue emission bands around 440 nm, which are consistent with our previous investigation on the sold-state luminescence of other similar compounds (Figure 7).[6,30] We consider that the 440 nm-emission probably originates from an intraligand transition because similar emission is also observed for the pure phen ligand (Supporting Information, Figure S14). It is worthy of notice that, besides the emission at 440 nm, compounds **1** and **3**−**5** also exhibit the other emissions with the maxima at 491, 533, 561, and 630 nm, respectively, that differ from those of our previously reported main-group element hybrid chalcogenides in the R−Sn-S and R−As-S systems, which usually show a single emission peak. These emissions are comparable with their corresponding band gaps and are ascribed to the band-to-band luminescence, that is, the electrons excite across the band gap followed by radiative relaxation directly to the ground state.[31] The other two members of the R−Sn-Se system in this study, **2a** and **2b**, may also have the similar emission from band-to-band transitions, but were not observed in our test, which is ascribed to their smaller band gaps: 709 nm for **2a** being close to the $2\lambda_{ex}$ that is undetectable for our machine, and 925 nm for **2b** that is outside the detection range of 200−900 nm for our machine.

## 4. CONCLUSION

In summary, phen and protonated methylamine molecules as a cotemplate and three types of TM phen complexes with the TM/phen ratio of 1:1, 1:2, and 1:3 were used to direct the formation of a series of new hybrid selenidostannates, where the inorganic selenidostannate anions vary from discrete, $\mu_2$- and $\mu_4$-$(Sn_2Se_6)^{4-}$ anions, to 1-D $^1_\infty(Sn_2Se_5^{2-})$ anionic chain, and 2-D extended $^2_\infty(Sn_3Se_7^{2-})$ anionic layer, displaying their different structure-directing abilities. The title compounds are semiconductors with the band gaps in the range of 1.34−2.52 eV showing a blue shift compared with the band gap of binary SnSe₂, and exhibit PL originating from the phen ligand and the band-to-band transition. All these results indicate that the incorporation of π-conjugated ligands or their TM complexes into the inorganic selenidostannate system can produce novel hybrid selenidostannates with diverse structures and interesting optical properties that reflect the combined effects of both PL-active organic components and semiconducting inorganic chalcogenidometalate

anionic network. More fascinating inorganic—organic hybrid chalcogenidometalates with interesting optical properties are expected by incorporating other functional organic components such as SHG-pores (SHG = second harmonic generation) photochromophores into inorganic chalcogenidometalates systems. Work in these directions is underway in our laboratory.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Crystallographic data (CIFs; CCDC reference numbers 829516 (**1**), 829517 (**2a**), 829518 (**2b**), 829519 (**3**), 829520 (**4**), and 829521 (**5**)), additional structural figures, TGA curves, IR spectra, and PXRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ ACKNOWLEDGMENT

## ■ REFERENCES

(1) (a) Dehnen, S.; Melullis, M. *Coord. Chem. Rev.* **2007**, *251*, 1259. (b) Drake, G. W.; Kolis, J. W. *Coord. Chem. Rev.* **1994**, *137*, 131. (c) Sheldrick, W. S.; Wachhold, M. *Coord. Chem. Rev.* **1998**, *176*, 211. (d) Li, J.; Chen, Z.; Wang, R.-J.; Proserpio, D. M. *Coord. Chem. Rev.* **1999**, *190—192*, 707. (e) Seidlhofer, B.; Pienack, N.; Bensch, W. *Z. Naturforsch.* **2010**, *65b*, 937. (f) Stephan, H. O.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1996**, *118*, 12226. (g) Zhou, J.; Fang, W.-H.; Rong, C.; Yang, G.-Y. *Chem.—Eur. J.* **2010**, *16*, 4852. (h) Morgan, K. R.; Gainsford, G. J.; Milestone, N. B. *Chem. Commun.* **1997**, 61. (i) Wang, Y.; Yu, J.; Li, Y.; Shi, Z.; Xu, R. *Chem.—Eur. J.* **2003**, *9*, 5048. (j) Sekine, T.; Okuno, T.; Awaga, K. *Inorg. Chem.* **1998**, *37*, 2129. (k) Calabrese, J.; Jones, N. L.; Harlow, R. L.; Herron, N.; Thorn, D. L.; Wang, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2328. (l) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (m) Kagan, C. R.; Mitzi, D. B.; Dimitrakopoulos, C. D. *Science* **1999**, *286*, 945. (n) Mitzi, D. B. *Chem. Mater.* **1996**, *8*, 791. (o) Feng, M.-L.; Kong, D.-N.; Xie, Z.-L.; Huang, X.-Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 8623. (p) Zhang, Z.-J.; Xiang, S.-C.; Zhang, Y.-F.; Wu, A.-Q.; Cai, L.-Z.; Guo, G.-C.; Huang, J.-S. *Inorg. Chem.* **2006**, *45*, 1972. (q) Wang, M.-S.; Xu, G.; Zhang, Z.-J.; Guo, G.-C. *Chem. Commun* **2010**, *46*, 361. (r) Bu, X.; Zheng, N.; Feng, P. *Chem.—Eur. J.* **2004**, *10*, 3356. (s) Bu, X.; Feng, P.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 1811. (t) Zheng, N.; Bu, X.; Vu, H.; Feng, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 5299. (u) Zheng, N.; Lu, H.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2006**, *128*, 4528.

(2) (a) Xu, G.; Guo, G.-C.; Wang, M.-S.; Zhang, Z.-J.; Chen, W.-T.; Huang, J.-S. *Angew. Chem., Int. Ed.* **2007**, *46*, 3249. (b) Zhang, Z.-J.; Xiang, S.-C.; Guo, G.-C.; Xu, G.; Wang, M.-S.; Zou, J.-P.; Guo, S.-P.; Huang, J.-S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4149. (c) Zhang, Q.; Bu, X.; Lin, Z.; Biasini, M.; Beyermann, W. P.; Feng, P. *Inorg. Chem.* **2007**, *46*, 7262. (d) Zhou, J.; Dai, J.; Bian, G.-Q.; Li, C.-Y. *Coord. Chem. Rev.* **2009**, *253*, 1221.

(3) (a) Mitzi, D. B.; Kosbar, L. L.; Murray, C. E.; Copel, M.; Afzali, A. *Nature* **2004**, *428*, 299. (b) Chun, D.; Walser, R. M.; Bene, R. W.; Courtney, T. H. *Appl. Phys. Lett.* **1974**, *24*, 479. (c) Bhatt, V. P.; Gireesan, K.; Pandya, G. R. *J. Cryst. Growth* **1989**, *96*, 649. (d) Xue, M.-Z.; Yao, J.; Cheng, S.-C.; Fu, Z.-W. *J. Electrochem. Soc.* **2006**, *153*, A270. (e) Mooser,

E.; Pearson, W. B. *Phys. Rev.* **1956**, *101*, 492. (f) Domingo, G.; Itoga, R. S.; Kannewur, Cr *Phys. Rev.* **1966**, *143*, 536. (g) Irene, E. A.; Wiedemeier, H. *Z. Anorg. Allg. Chem.* **1975**, *411*, 182. (h) Alalamy, F. A. S.; Balchin, A. A. *J. Cryst. Growth* **1977**, *38*, 221. (i) Leveque, G.; Bertrand, Y.; Robinkandare, S. *Solid State Commun.* **1981**, *38*, 759. (j) Harbec, J. Y.; Powell, B. M.; Jandl, S. *Phys. Rev. B* **1983**, *28*, 7009. (k) Shibata, T.; Muranushi, Y.; Miura, T.; Kishi, T. *J. Phys. Chem. Solids* **1991**, *52*, 551. (l) Trifonova, E.; Yanchev, I. Y.; Manou, P.; Kambas, K.; Anagnostopoulos, A. N. *J. Mater. Sci.* **1996**, *31*, 3647. (m) Manou, P.; Kalomiros, J. A.; Anagnostopoulos, A. N.; Kamba, K. *Mater. Res. Bull.* **1996**, *31*, 1407. (n) Aguiar, M. R.; Caram, R.; Oliveira, M. F.; Kiminami, C. S. *J. Mater. Sci.* **1999**, *34*, 4607. (o) Bindu, K.; Nair, P. K. *Semicond. Sci. Technol.* **2004**, *19*, 1348.

(4) (a) Jiang, T.; Lough, A.; Ozin, G. A. *Adv. Mater.* **1998**, *10*, 42. (b) Jiang, T.; Lough, A.; Ozin, G. A.; Bedard, R. L.; Broach, R. *J. Mater. Chem.* **1998**, *8*, 721. (c) Jiang, T.; Lough, A.; Ozin, G. A.; Bedard, R. L. *J. Mater. Chem.* **1998**, *8*, 733. (d) Parise, J. B.; Ko, Y. H.; Rijssenbeek, J.; Nellis, D. M.; Tan, K. M.; Koch, S. *Chem. Commun.* **1994**, 527. (e) Pienack, N.; Näther, C.; Bensch, W. *Eur. J. Inorg. Chem.* **2009**, 937. (f) Pienack, N.; Lehmann, S.; Lühmann, H.; El-Madani, M.; Näther, C.; Bensch, W. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2323. (g) Behrens, M.; Scherb, S.; Näther, C.; Bensch, W. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1367. (h) Pienack, N.; Näther, C.; Bensch, W. *Z. Naturforsch.* **2008**, *63*, 1243. (i) Pienack, N.; Näther, C.; Bensch, W. *Eur. J. Inorg. Chem.* **2009**, 1575. (j) Näther, C.; Scherb, S.; Bensch, W. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *59*, M280. (k) Puls, A.; Näther, C.; Bensch, W. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *61*, M868. (l) Jia, D.-X.; Zhang, Y.; Dai, J.; Zhu, Q.-Y.; Gu, X.-M. *Z. Anorg. Allg. Chem.* **2004**, *630*, 313. (m) Jia, D.-X.; Dai, J.; Zhu, Q.-Y.; Zhang, Y.; Gu, X.-M. *Polyhedron* **2004**, *23*, 937. (n) Gu, X.-M.; Dai, J.; Jia, D.-X.; Zhang, Y.; Zhu, Q.-Y. *Cryst. Growth Des.* **2005**, *5*, 1845. (o) Zhao, Q.-X.; Jia, D.-X.; Zhang, Y.; Song, L.-F.; Dai, J. *Inorg. Chim. Acta* **2007**, *360*, 1895. (p) Zhou, J.; Bian, G.-Q.; Dai, J.; Zhang, Y.; Tang, A.-B.; Zhu, Q.-Y. *Inorg. Chem.* **2007**, *46*, 1541. (q) Zhou, J.; Zhang, Y.; Tang, A.-B.; Bian, G.-Q.; Jia, D.-X.; Dai, J. *Inorg. Chem. Commun.* **2007**, *10*, 348. (r) Jia, D.-X.; Zhu, A.-M.; Deng, J.; Zhang, Y. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1246. (s) Zhu, A.-M.; Jin, Q.-Y.; Jia, D.-X.; Gu, J.-S.; Zhang, Y. *Eur. J. Inorg. Chem.* **2008**, 4756. (t) Chen, J.-F.; Jin, Q.-Y.; Pan, Y.-L.; Zhang, Y.; Jia, D.-X. *Chem. Commun.* **2009**, 7212. (u) Dehnen, S.; Zimmermann, C.; Anson, C. E. *Z. Anorg. Allg. Chem.* **2002**, *628*, 279. (v) Dehnen, S.; Zimmermann, C. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2463. (w) Nayek, H. P.; Lin, Z.; Dehnen, S. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1737. (x) Melullis, M.; Brandmayer, M. K.; Dehnen, S. *Z. Anorg. Allg. Chem.* **2006**, *632*, 64. (y) Ruzin, E.; Zent, E.; Matern, E.; Massa, W.; Dehnen, S. *Chem.—Eur. J.* **2009**, *15*, 5230. (z) Sheldrick, W. S.; Braunbeck, H. G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1300. (aa) Kromm, A.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1005. (ab) Loose, A.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1999**, *625*, 233. (ac) Lehman, S. E.; Schimek, G. L.; Cusick, J. M.; Kolis, J. W. *Inorg. Chim. Acta* **1997**, *260*, 173. (ad) Park, C. W.; Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 4555.

(5) (a) Scaltrito, D. V.; Thompson, D. W.; O'Callaghan, J. A.; Meyer, G. J. *Coord. Chem. Rev.* **2000**, *208*, 243. (b) Polo, A. S.; Itokazu, M. K.; Iha, N. Y. M. *Coord. Chem. Rev.* **2004**, *248*, 1343. (c) Nazeeruddin, M. K.; Zakeeruddin, S. M.; Lagref, J. J.; Liska, P.; Comte, P.; Barolo, C.; Viscardi, G.; Schenk, K.; Graetzel, M. *Coord. Chem. Rev.* **2004**, *248*, 1317. (d) Laine, P. P.; Campagna, S.; Loiseau, F. *Coord. Chem. Rev.* **2008**, *252*, 2552. (e) Youngblood, W. J.; Lee, S. H. A.; Maeda, K.; Mallouk, T. E. *Acc. Chem. Res.* **2009**, *42*, 1966. (f) Gratzel, M. *Nature* **2001**, *414*, 338. (g) Kim, J. J.; Choi, H.; Kim, C.; Kang, M. S.; Kang, H. S.; Ko, J. *Chem. Mater.* **2009**, *21*, 5719. (h) Konig, E. *Coord. Chem. Rev.* **1968**, *3*, 471. (i) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Vonzelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (j) Armaroli, N. *Chem. Soc. Rev.* **2001**, *30*, 113. (k) Lavie-Cambot, A.; Cantuel, M.; Leydet, Y.; Jonusauskas, G.; Bassani, D. M.; McClenaghan, N. D. *Coord. Chem. Rev.* **2008**, *252*, 2572. (l) Pomeranc, D.; Heitz, V.; Chambron, J. C.; Sauvage, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 12215.

(6) Liu, G.-N.; Guo, G.-C.; Chen, F.; Guo, S.-P.; Jiang, X.-M.; Yang, C.; Wang, M.-S.; Wu, M. F.; Huang, J.-S. *CrystEngComm* **2010**, *12*, 4035.

9668

dx.doi.org/10.1021/ic201413h |*Inorg. Chem.* 2011, 50, 9660–9669

(7) Liu, G.-N.; Jiang, X.-M.; Wu, M.-F.; Wang, G.-E.; Guo, G.-C.; Huang, J.-S. *Inorg. Chem.* **2011**, *50*, 5740.

(8) Wendlandt, W. M.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience: New York, 1966.

(9) *CrystalClear*, Version 1.35; Rigaku Corp.: Tokyo, Japan, 2002.

(10) *SHELXTL Reference manual*, Version 5; Siemens Energy & Automaion Inc.: Madision, WI, 1994.

(11) (a) Chen, Z.; Wang, R. J.; Li, J. *Chem. Mater.* **2000**, *12*, 762. (b) Huang, X.; Li, J.; Zhang, Y.; Mascarenhas, A. *J. Am. Chem. Soc.* **2003**, *125*, 7049. (c) Feng, M.-L.; Xiong, W.-W.; Ye, D.; Li, J.-R.; Huang, X.-Y. *Chem.—Asian J.* **2010**, *5*, 1817. (d) Pichon, C.; Dolbecq, A.; Mialane, P.; Marrot, J.; Riviere, E.; Goral, M.; Zynek, M.; McCormac, T.; Borshch, S. A.; Zueva, E.; Secheresse, F. *Chem.—Eur. J.* **2008**, *14*, 3189.

(12) Zimmermann, C.; Melullis, M.; Dehnen, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 4269. (b) Fehlker, A.; Blachnik, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 411. (c) Ahari, H.; Lough, A.; Petrov, S.; Ozin, G. A.; Bedard, R. L. *J. Mater. Chem.* **1999**, *9*, 1263. (d) Campbell, J.; Devereux, L. A.; Gerken, M.; Mercier, H. P. A.; Pirani, A. M.; Schrobilgen, G. J. *Inorg. Chem.* **1996**, *35*, 2945.

(13) (a) Li, J. Q.; Marler, B.; Kessler, H.; Soulard, M.; Kallus, S. *Inorg. Chem.* **1997**, *36*, 4697. (b) Jia, D.; Zhu, A.; Zhang, Y.; Deng, J. *Monatsh. Chem.* **2007**, *138*, 191. (c) Liu, G.-N.; Guo, G.-C.; Wang, M.-S.; Cai, L.-Z.; Huang, J.-S. *J. Mol. Struct.* **2010**, *983*, 104.

(14) (a) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885. (b) Balboa, S.; Carballo, R.; Castiñeiras, A.; González-Pérez, J. M.; Niclós-Gutiérrez, J. *Polyhedron* **2008**, *27*, 2921. (c) Spodine, E.; Paredes-García, V.; Gaune, S.; Saldías, M.; Garland, M. T.; Baggio, R.; Vega, A.; El Fallah, M. S.; Escuer, A.; Le Fur, E.; Venegas-Yazigi, D. *Inorg. Chim. Acta* **2008**, *361*, 3681.

(15) (a) Zhou, J.; Zhang, Y.; Bian, G.-Q.; Li, C.-Y.; Chen, X.-X.; Dai, J. *Cryst. Growth Des.* **2008**, *8*, 2235. (b) Jia, D.; Jin, Q.; Chen, J.; Pan, Y.; Zhang, Y. *Inorg. Chem.* **2009**, *48*, 8286. (c) Liu, C. W.; Sarkar, B.; Wen, S. Y.; Wang, J. H.; Chiou, L. S.; Liao, P. K.; Santra, B. K.; Wang, J. C. *Inorg. Chem.* **2009**, *48*, 5129. (d) Lippolis, V.; Arca, M.; Aroz, T.; Gimeno, M. C.; Kulcsar, M.; Laguna, A.; Lasanta, T.; Lopez-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E. *Eur. J. Inorg. Chem.* **2011**, 2288.

(16) (a) Pan, Y. L.; Jin, Q. Y.; Chen, J. F.; Zhang, Y.; Jia, D. X. *Inorg. Chem.* **2009**, *48*, 5412. (b) Xu, X.; Cao, Q.; Luo, F.; Wang, G. Z. *Naturforsch.* **2008**, *63*, 1352. (c) Zurkova, L.; Kucsera, R.; Gyepes, R.; Sivak, M. *Monatsh. Chem.* **2003**, *134*, 1071. (d) Qi, Y.; Li, Y.; Wang, E.; Zhang, Z.; Chang, S. *Dalton Trans.* **2008**, 2335. (e) Wang, Q.-W.; Shi, L. F.; Gao, G.-G.; Li, C.-B.; Han, L. *Chin. J. Struct. Chem.* **2006**, *25*, 979. (f) Mafra, L.; Paz, F. A. A.; Shi, F. N.; Ferreira, R. A. S.; Carlos, L. D.; Trindade, T.; Fernandez, C.; Klinowski, J.; Rocha, J. *Eur. J. Inorg. Chem.* **2006**, 4741. (g) Joniakova, D.; Gyepes, R.; Rakovsky, E.; Schwendt, P. B.; Zurkova, L.; Marek, J.; Micka, Z. *Polyhedron* **2006**, *25*, 2491.

(17) (a) Jia, D.-X.; Dai, J.; Zhu, Q.-Y.; Cao, L.-H.; Lin, H.-H. *J. Solid State Chem.* **2005**, *178*, 874. (b) Duan, H.-B.; Hu, Z.; Jia, B.; An, Y.-L. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *62*, M2709.

(18) (a) Sportouch, S.; Tillardcharbonnel, M.; Belin, C. *J. Chem. Soc., Dalton Trans.* **1995**, 3113. (b) Haddadpour, S.; Melullis, M.; Staesche, H.; Mariappan, C. R.; Roling, B.; Clerac, R.; Dehnen, S. *Inorg. Chem.* **2009**, *48*, 1689.

(19) Kromm, A.; Sheldrick, W. S. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *62*, M2767.

(20) (a) García-Báez, E. V.; Martinez-Martínez, F. J.; Höpfl, H.; Padilla-Martínez, I. I. *Cryst. Growth Des.* **2003**, *3*, 35. (b) Ghosh, A. K.; Ghoshal, D.; Zangrando, E.; Ribas, J.; Chaudhuri, N. R. *Dalton Trans.* **2006**, 1554.

(21) (a) Wang, X.; Sheng, T.-L.; Hu, S.-M.; Fu, R.-B.; Chen, J.-S.; Wu, X.-T. *J. Solid State Chem.* **2009**, *182*, 913. (b) Wang, X.; Sheng, T.-L.; Hu, S.-M.; Fu, R.-B.; Wu, X.-T. *Inorg. Chem. Commun.* **2009**, *12*, 399. (c) Pan, Y.; Jin, Q.; Chen, J.; Zhang, Y.; Jia, D. *Inorg. Chem.* **2009**, *48*, 5412.

(22) Sheldrick, W. S.; Wachhold, M. *Angew. Chem., Int. Ed.* **1997**, *36*, 207.

(23) Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **2000**, 3041.

(24) (a) Morgan, K.; Gainsford, G.; Milestone, N. *Chem. Commun.* **1995**, 425. (b) Wang, Y.; Yu, J. H.; Guo, M.; Xu, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 4089. (c) Lin, Z. E.; Zhang, J.; Zhao, J. T.; Zheng, S. T.; Pan, C. Y.; Wang, G. M.; Yang, G. Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 6881.

(25) (a) Fehlker, A.; Blachnik, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1128. (b) Parise, J. B.; Ko, Y. H.; Tan, K. M.; Nellis, D. M.; Koch, S. *J. Solid State Chem.* **1995**, *117*, 219. (c) Lu, S.-M.; Ke, Y.-X.; Li, J. M.; Zhou, S.-X.; Wu, X.-T.; Du, W.-X. *Struct. Chem.* **2003**, *14*, 637. (d) Wang, X.; Sheng, T.-L.; Xiang, S.-C.; Hu, S.-M.; Fu, R.-B.; Wu, X.-T. *Chin. J. Struc. Chem.* **2010**, *29*, 260. (e) Xu, G.-H.; Wang, C.; Guo, P. *Acta Crystallogr., Sect. C* **2009**, *65*, M171.

(26) (a) Sheldrick, W. S.; Braunbeck, H. G. *Z. Naturforsch.* **1990**, *45*, 1643. (b) Marking, G. A.; Kanatzidis, M. G. *Chem. Mater.* **1995**, *7*, 1915.

(27) (a) Kong, D.-N.; Xie, Z.-L.; Feng, M.-L.; Ye, D.; Du, K.-Z.; Li, J.-R.; Huang, X.-Y. *Cryst. Growth Des.* **2010**, *10*, 1364. (b) Zhang, Z.-J.; Guo, G.-C.; Xu, G.; Fu, M.-L.; Zou, J.-P.; Huang, J.-S. *Inorg. Chem.* **2006**, *45*, 10028.

(28) (a) Zhao, J.; Liang, J.; Chen, J.; Pan, Y.; Zhang, Y.; Jia, D. *Inorg. Chem.* **2011**, *50*, 2288. (b) Lei, Z.-X.; Zhu, Q.-Y.; Zhang, X.; Luo, W.; Mu, W.-Q.; Dai, J. *Inorg. Chem.* **2010**, *49*, 4385.

(29) Li, J.; Chen, Z.; Emge, T. J.; Yuen, T.; Proserpio, D. M. *Inorg. Chim. Acta* **1998**, *273*, 310.

(30) Fu, M.-L.; Guo, G.-C.; Liu, X.; Chen, W.-T.; Liu, B.; Huang, J.-S. *Inorg. Chem.* **2006**, *45*, 5793.

(31) Axtell, E. A.; Hanko, J.; Cowen, J. A.; Kanatzidis, M. G. *Chem. Mater.* **2001**, *13*, 2850.