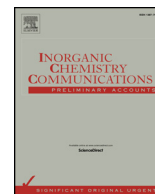




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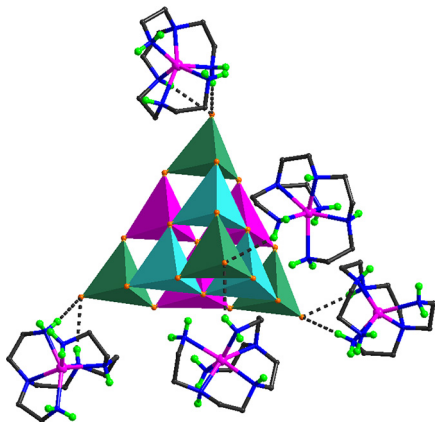
T3 supertetrahedral cluster $[\text{Mn}_4\text{Sn}_6\text{S}_{20}]^{8-}$: Solvothermal syntheses, crystal structures and photocatalytic properties of Mn(II) chalcogenidostannates

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GRAPHICAL ABSTRACT

Chalcogenidostannates $[\text{Mn}(\text{tren})(\text{H}_2\text{O})][\text{Mn}(\text{baen})_3\text{Mn}_4\text{Sn}_6\text{S}_{20}\cdot 9\text{H}_2\text{O}$ (**1**) and $[\text{Mn}(\text{baen})]_2\text{Sn}_2\text{Se}_6$ (**2**) were prepared in tren/tatda mixed solvent by the solvothermal method. The T3 cluster $[\text{Mn}_4\text{Sn}_6\text{S}_{20}]^{8-}$ represents the first ternary anions for the TM-Sn-S phases obtained in the ethylene polyamine solvent and stabilized by TM complex with polyamine ligands. Compound **1** exhibits effective photocatalytic activity in photodegradation of crystal violet.



ARTICLE INFO

InChIKey:

BAMRNKBBALHRKC-UHFFFAOYSA-

GKeywords:

Supertetrahedral cluster

Manganese

Chalcogenidostannate

X-ray structure determination

Photocatalytic properties

ABSTRACT

Solvothermal reaction in tren/tatda mixed polyamines produced a transition metal (TM) thiostannate $[\text{Mn}(\text{tren})(\text{H}_2\text{O})][\text{Mn}(\text{baen})_3\text{Mn}_4\text{Sn}_6\text{S}_{20}\cdot 9\text{H}_2\text{O}$ (**1**) containing a novel T3 supertetrahedral nanocluster $[\text{Mn}_4\text{Sn}_6\text{S}_{20}]^{8-}$. The T3 cluster was constructed by SnS_4 and MnS_4 tetrahedra via corner-sharing with the SnS_4 tetrahedra occupying four corners of the T3 cluster. It has different TM/Sn ratio from the traditional T3 cluster $[\text{TM}_5\text{Sn}_5\text{S}_{20}]^{10-}$ (TM = Zn, Co) prepared by extraction method using alkali cations as the counter ions. Compound **1** is the first T3 cluster of the TM-Sn-Q phase prepared by solvothermal method and stabilized by TM-amino complex counter ions. The same solvothermal reaction with Se instead of S afforded a selenidostannate $[\text{Mn}(\text{baen})]_2\text{Sn}_2\text{Se}_6$ (**2**) containing a dimeric $[\text{Sn}_2\text{Se}_6]^{4-}$ anion. Compound **1** exhibits selective photocatalysis in photodegradation of organic dyes. It has higher photocatalytic effect in the photodegradation of crystal violet (CV) than rhodamine B (RhB) under visible light irradiation at room temperature.

Chalcogenidostannates have been drawn extensively attention not only due to their fascinating topological structures [1,2], but also for their unique physical properties and various potential applications in

photocatalysis [3,4], ion exchange [5–7], nonlinear optics [8], optoelectronic [9] and magnetic [10]. In the past, a large number of binary and multinary chalcogenidostannates were prepared by molten salt

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Received 23 March 2018; Received in revised form 27 April 2018; Accepted 2 May 2018

Available online 12 May 2018

1387-7003/ Published by Elsevier B.V.

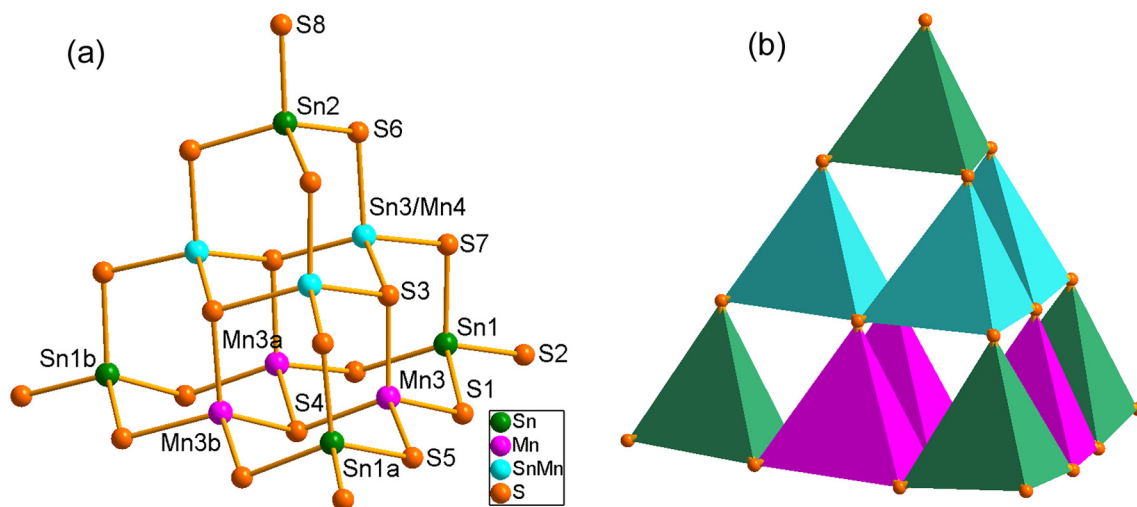


Fig. 1. (a) Crystal structure of the $[\text{Mn}_4\text{Sn}_6\text{S}_{20}]^{8-}$ with labeling scheme in 1. (b) The same view of T3 cluster shown as metal-centered tetrahedra. The SnS_4 , MnS_4 and $(\text{Sn}/\text{Mn})\text{S}_4$ units are shown in green, purple and cyan tetrahedra, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(flux) method, extraction or solvothermal (ionothermal) techniques [1,11]. The rich structural diversities of chalcogenidostannates are believed to be due to the high tendency for self-assembly of SnQ_4 ($\text{Q} = \text{S}, \text{Se}, \text{Te}$) tetrahedra via corner, edge or face-sharing [12]. On the other hand, the SnQ_4 tetrahedra also exhibit high tendency for copolymerization with transition metal (TM) chalcogenide tetrahedra TMQ_4 to form ternary clusters $[\text{TM}_x\text{Sn}_y\text{Q}_z]^{m-}$ with different composition and structures, giving $[\text{Zn}_4\text{Sn}_3\text{S}_{13}]^{5-}$, $[\text{Sn}[\text{Zn}_4\text{Sn}_4\text{S}_{17}]^{6-}]_n$ [13], $[\text{TM}_5\text{Sn}(\mu_3\text{-S})_4(\text{SnS}_4)_4]^{10-}$ ($\text{TM} = \text{Zn}, \text{Co}$) [15] and $[\text{TM}_4(\mu_4\text{-Se})(\text{SnSe}_4)_4]^{10-}$ ($\text{TM} = \text{Mn}, \text{Zn}, \text{Cd}, \text{Hg}$) [16,17], for example. However, the syntheses of this type of TM-containing chalcogenidostannates were usually performed with strict exclusion of air and moisture [15–17]. Solvothermal reactions of Sn/Q with TM in ethylene polyamines had proven to be a successful route to the preparation of TM-containing chalcogenidostannates in the past decade. Although the ethylene polyamines were integrated into the structure with TM centers or as a structure directing agent, they had little effect on the structures of the binary chalcogenidostannates. Binary anions [such as $[\text{Sn}_2\text{Q}_6]^{4-}$ and $[\text{Sn}_3\text{Q}_7]^{2-}$ ($\text{Q} = \text{S}, \text{Se}, \text{Te}$)] other than ternary $[\text{TM}_x\text{Sn}_y\text{Q}_z]^{m-}$ anions are usually obtained by this solvothermal method. The examples include $[\text{TM}(\text{en})_3]_2\text{Sn}_2\text{Q}_6$ ($\text{TM} = \text{Mn}, \text{Co}, \text{Zn}, \text{Ni}$; $\text{Q} = \text{S}, \text{Se}, \text{Te}$; $\text{en} = \text{ethylenediamine}$) [18–20], $[\text{TM}(\text{dien})_2]_2\text{Sn}_2\text{Q}_6$ ($\text{TM} = \text{Ni}, \text{Mn}$; $\text{Q} = \text{S}, \text{Se}$), $[\text{Zn}(\text{dien})_2]_4(\text{Sn}_2\text{Te}_6)_{1.75}(\text{Sn}_2\text{Te}_8)_{0.25}\text{dien}$, $[\text{Mn}(\text{dien})_2]_3\text{Sn}_3\text{Se}_7 \cdot 0.5\text{H}_2\text{O}$ ($\text{dien} = \text{diethylenetriamine}$) [18,21,22], $[\text{TM}(\text{tren})]_2\text{Sn}_2\text{Q}_6$ ($\text{TM} = \text{Ni}, \text{Mn}$), [23,24] and $[\text{Zn}(\text{tren})]_2\text{Sn}_2\text{Te}_6$ ($\text{tren} = \text{tris}(2\text{-aminoethyl})\text{amine}$) [21]. Recently, Yue prepared a quaternary T3 cluster $[\text{Mn}_2\text{Ga}_4\text{Sn}_4\text{S}_{20}]^{8-}$ by introducing 13 group element Ga in the ternary phase Mn/Sn/S using the solvothermal method in ethylene polyamines en and dien [25]. The cluster is composed of SnS_4 , MnS_4 and GaS_4 tetrahedra and stabilized by $[\text{Mn}_2(\text{en})_5]^{4+}$ or $[\text{Mn}(\text{dien})_2]^{2+}$ cations. A Se-analogue $[\text{Zn}_2\text{Ga}_4\text{Sn}_4\text{Se}_{20}]^{8-}$ was synthesized in tepa (tepa = tetraethylenepentamine) solvent under solvothermal condition by Wang's group [26]. The T3 cluster coordinates to the Mn(II) center of $[\text{Mn}(\text{tepa})]^{2+}$ with the terminal Se atoms. Now, we investigated the TM/Sn/S(Se) system in tren/tatda (tatda = 3,6,9,12-tetraazatetradecane-1,14-diamine) mixed polyamines under solvothermal condition, and prepared a novel TM-containing chalcogenidostannates $[\text{Mn}(\text{tren})(\text{H}_2\text{O})][\text{Mn}(\text{baen})]_3\text{Mn}_4\text{Sn}_6\text{S}_{20} \cdot 9\text{H}_2\text{O}$ (1) and $[\text{Mn}(\text{baen})]_2\text{Sn}_2\text{Se}_6$ (2). Compound 1 is the first example of T3 supertetrahedral clusters for the ternary TM-Sn-S phases, which was obtained in ethylene polyamine and stabilized by TM complex with polyamine ligands.

The reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and S in tren/tatda mixed solvent at 190 °C for 5 days yielded compound $[\text{Mn}(\text{tren})(\text{H}_2\text{O})][\text{Mn}$

(baen)]₃ $\text{Mn}_4\text{Sn}_6\text{S}_{20} \cdot 9\text{H}_2\text{O}$ (1). The reaction with Se instead of S under identical conditions afforded compound $[\text{Mn}(\text{baen})]_2\text{Sn}_2\text{Se}_6$ (2) (details in the SI). In FT-IR spectra (Fig. S1, S2), the absorption bands at 2916 cm^{-1} and 3410 cm^{-1} are attributed to the C–H and N–H stretching vibrations, respectively. The characteristic adsorption bands at 1000–1318 cm^{-1} can be assigned to the C–N group. Compound 1 crystallizes in the cubic space group $P2_13$ (no. 198), while 2 crystallizes in the monoclinic space group $P2_1/n$ (Table S1). 1 consists of $[\text{Mn}(\text{tren})(\text{H}_2\text{O})]^{2+}$, $[\text{Mn}(\text{baen})]^{2+}$ and $[\text{Mn}_4\text{Sn}_6\text{S}_{20}]^{8-}$ ions, and nine H_2O molecules. $\text{Mn}(1)^{2+}$ is coordinated to four N atoms of the tren ligand and a H_2O molecule forming a $[\text{Mn}(\text{tren})(\text{H}_2\text{O})]^{2+}$ complex cation. The $\text{Mn}(1)^{2+}$ ion locates in a five-fold coordinate environment with a distorted trigonal bipyramidal geometry (Fig. S3a). $\text{Mn}(2)^{2+}$ is coordinated by a hexadentate chelating ligand baen to form a $[\text{Mn}(\text{baen})]^{2+}$ complex cation (Fig. S3b). It is noteworthy that the linear ethylene polyamine

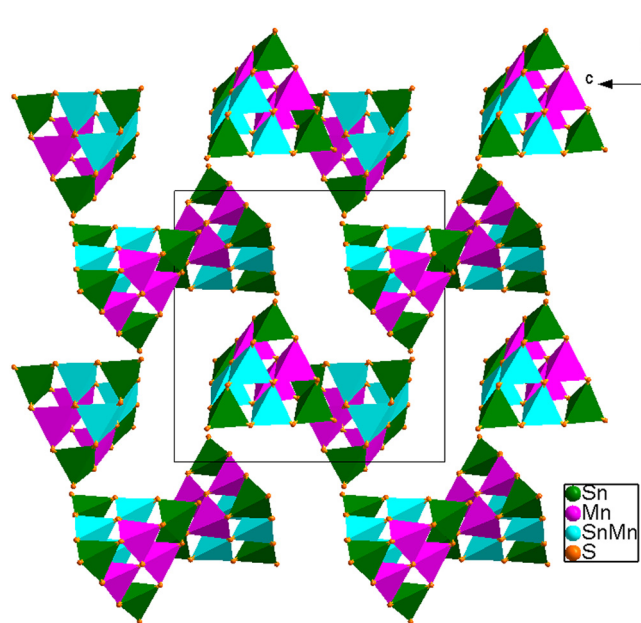


Fig. 2. Packing view of the $[\text{Mn}_4\text{Sn}_6\text{S}_{20}]^{8-}$ T3 clusters in 1. The SnS_4 , MnS_4 and $(\text{Sn}/\text{Mn})\text{S}_4$ units are shown in green, purple and cyan tetrahedra, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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