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Molecular Nanocluster with a $[Sn_4Ga_4Zn_2Se_{20}]^{8-}$ T3 Supertetrahedral Core

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A multinary molecular nanocluster, in which a T3 supertetrahedral $[Sn_4Ga_4Zn_2Se_{20}]^{8-}$ core was neutralized and covalently terminated by four $[(TEPA)Mn]^{2+}$ (TEPA = tetraethylenepentamine) metal complexes, was synthesized and characterized. The cluster is assembled into, through hydrogen bonding and van de Waals forces, a superlattice that is chemically stable and free of strong covalent coupling. The four different cations were distributed within the cluster in such a manner that both the local charge balance and global charge compensation by the metal complex could be satisfied.

Tetrahedral metal chalcogenide nanoclusters, including supertetrahedral (T*n*), pentasupertetrahedral (P*n*), and capped supertetrahedral (C*n*) series, can behave like artificial atoms and assemble into superlattices via covalent or weak cluster–cluster interactions.[1] The covalently linked nanoclusters tend to form extended open frameworks that are intrinsically endowed with porosity, optical, electrical, and photonic properties. The nanoclusters are isolated in their superlattice structures when there are only weak cluster–cluster interactions, e.g., ionic bonding, hydrogen bonding, or van der Waals forces. In this case, ionic superlattices are more likely to be formed because most of the nanoclusters are negatively charged and only a few neutral isolated tetrahedral nanoclusters with thiolate ligands and their assembled superstructures have been reported.[2] To decouple the quantum effects between covalently linked nanoclusters,[3] superlattices with isolated nanoclusters could be better systems for studying the size-dependent properties.

For supertetrahedral T*n* nanoclusters, most of the recent research interest has been focused on chalcogenides of group 13 and 14 metals including Ga, In, Ge, and Sn. These T*n* clusters could be viewed as fragments of zinc blende ZnS. According to their proposed formula[1d] and in order to maintain negative overall charges, the largest values of *n* are 2 for Ge^{4+} or Sn^{4+} cation-based clusters and 3 for Ga^{3+} or In^{3+} cation-based clusters when the framework metal cations consisted of single metal atoms.[1a,4a] This is to preclude the violation against the bond valence rule when tri- and tetracoordinated chalcogens begin to appear in T3 and T4 nanoclusters. This scenario could be changed when lower-valence (2+ and 1+) metal atoms were incorporated into the clusters. The introduction of low-valence metal atoms could help to augment the cluster sizes from T3 to T4[4] and from T2 to T3.[5] It should be pointed out here that the initial introduction of lower-valence metal atoms was to link T2 clusters of Ge–S and Sn–S into infinite frameworks instead of being incorporated into clusters,[1e] although recent discoveries did verify such feasibility.[6] Despite recent success in incorporating T*n* metal chalcogenide nanoclusters with low-valence (2+ and 1+) metal atoms, few attempts have been made to combine 3+ and 4+ metal cations into one single, large T*n* ($n > 2$) nanocluster partially because these two kinds of high-valent cations tend to form their own T2

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clusters with disordered metal positions.[1a,4a,7] Furthermore, combining different metal atoms into one T*n* nanocluster could also be beneficial for tuning their physical properties such as electrical, optical, magnetic, and so on.

We report here the synthesis of a multinary molecular nanocluster with a T3 core neutralized and terminated by four metal complexes. The 10 metal atomic sites within the T3 core were occupied by tetra-, tri-, and divalent metal cations. These three different cations and the Mn^{2+} cation from a pendant metal complex were distributed within the molecular nanocluster in such a manner that both the local charge balance and global charge compensation by the metal complex could be satisfied. Furthermore, the compound was assembled into, through hydrogen bonding and van de Waals forces, a superlattice that is chemically stable and free of strong covalent coupling.

The title compound was synthesized by mixing tin power (39.6 mg, 0.33 mmol), gallium metal (69.7 mg, 1.00 mmol), selenium (158.0 mg, 2.00 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (99.2 mg, 0.33 mmol), $MnCl_2 \cdot 4H_2O$ (198.0 mg, 1.00 mmol), and 3.0 mL of tetraethylenepentamine (TEPA) in a 17.0 mL Teflon-lined stainless steel autoclave. After stirring for 30 min, the vessel was sealed and heated at 190 °C for 1 week. The resulting yellow square crystals (yield based on Ga added: ~26%) were isolated by washing with ethanol and water and formulated as $[(TEPA)Mn]_4[Sn_4Ga_4Zn_2Se_{20}]$ from single-crystal X-ray diffraction and inductively coupled plasma mass spectrometry (ICP-MS) analysis.[8]

The crystal structural analysis revealed that the compound crystallized in $P\bar{4}b2$. As shown in Figure 1, it is a neutral isolated molecular cluster built up from one T3 supertetrahedral core and four $[(TEPA)Mn]^{2+}$ metal complexes in which the core is covalently terminated by four $[(TEPA)Mn]^{2+}$ via four Se atoms. The Mn−Se distance is 2.701(4) Å and is comparable with reported values in antimony selenide containing manganese amino complexes.[9] In the discrete T3 anionic core, the Sn−Se distances of the four corners range from 2.494(2) to 2.526(2) Å, which are close to previously reported values[10] and are larger than the remaining M−Se bond lengths [2.385(2)−2.456(2) Å]. The shorter bond lengths are similar to those of Zn−Se or Ga−Se found in the literature.[11] The $[Sn_4Ga_4Zn_2Se_{20}]^{8-}$ formula of such an anionic cluster was deduced from the number of total negative charges and defined number of Sn atoms in this T3 core. The overall 1:1:1:0.5 atomic ratio of Mn:Sn:Ga:Zn derived from the charge balance agrees well with that of the elemental analysis (1:1.03:0.96:0.47) from ICP-MS analysis. However, it is impossible to distinguish Ga^{3+} and Zn^{2+} ions by X-ray diffraction because they are isoelectronic. The valence sum[12] surrounding the μ_3-Se^{2-} ions on the surface of T3 is 1.969. The values for the four terminal and remaining 12 μ_2-Se^{2-} ions are 1.452 and in the range of 1.712−1.761, respectively. Prior to this work, only one or two metal ions were involved for the synthesis of tetrahedral chalcogenide clusters. To our knowledge, the present case represents the first multinary molecular nanocluster in the T*n*, P*n*, and C*n* series with four metal ions.

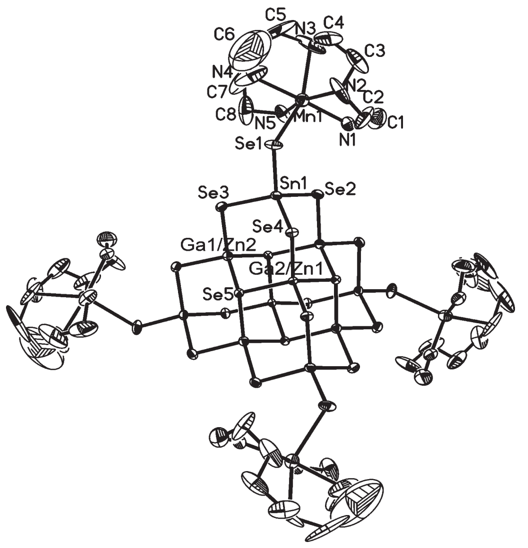

Figure 1. Molecular nanocluster. Displacement ellipsoids are drawn at the 30% probability level, and all H atoms have been omitted for clarity.

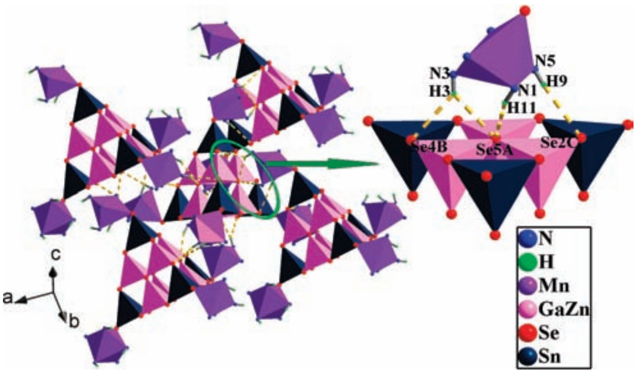

Figure 2. View of a two-dimensional layered structure with magnified hydrogen-bonding interactions (dashed yellow lines): N1−H11···Se5A; N3−H3···Se5A; N3−H3···Se4B; N5−H9···Se2C. Symmetry codes: A, $x + {}^1/_2, -y + {}^1/_2, z$; B, $-x + {}^1/_2, y + {}^1/_2, z$; C, $-x + {}^1/_2, -y + {}^1/_2, -z$. H atoms not involved in hydrogen bonding and C atoms have been omitted for clarity.

In the metal complex of $[(TEPA)Mn]^{2+}$, the Mn atom is coordinated by five N atoms from TEPA and one Se atom from the T3 core and shows a distorted octahedral environment. The distribution of Mn and Zn atoms in the molecular cluster partially results from their different coordination tendencies. Taking the whole neutral cluster into consideration, the dimensional sizes of six edges of the whole cluster are 15.96 Å (×2) and 13.52 Å (×4) as measured between metal sites of the complexes. These values are comparable to the lateral dimensions of $Zn_4Ga_{16}Se_{33}^{10-}$, the only known selenide T4 cluster.[11]

Each neutral isolated cluster interacts with neighboring clusters via weak intercluster N−H···Se hydrogen bonds, resulting in a layered arrangement parallel to the (001) plane (Figure 2). The N···Se distances [3.65(2)−3.89(2) Å], the

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(8) Crystallographic data: $[(C_8H_{23}N_5)Mn]_4[Sn_4Ga_4Zn_2Se_{20}]$, tetragonal, space group $P\bar{4}b2$, a = 17.4951(5) Å, c = 13.5849(8) Å, V = 4158.0(3) Å^3, Z = 8, Mo Kα, T = 123 K, 23 338 reflections measured, 4113 unique (R_{int} = 0.0875), 2739 observed [$I > 2\sigma(I)$], R1 = 0.0517, wR2 = 0.1531, GOF = 1.067. Elem anal. Calcd: C, 11.17; H, 2.70; N, 8.14. Found: C, 11.35; H, 2.72; N, 7.97.

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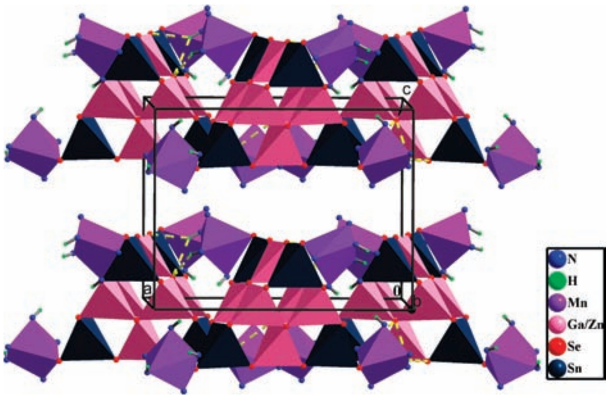

Figure 3. Crystal packing view of the layers. H atoms not involved in hydrogen bonding and C atoms have been omitted for clarity.

H···Se distances [2.85(2)−3.03(4) Å], and the N−H···Se angles [137.3(1)−161.0(1)°] are in accordance with the values reported in the literature.[13] The layered structure was further packed into a three-dimensional superlattice with a A···A···A sequence along the *c* axis through van der Waals forces instead of hydrogen bonds (Figure 3).

Both charge balance and covalent termination by the metal complex appeared to be the most fascinating features in this compound. To reduce the high negative charge of tetrahedral metal chalcogenide clusters, thiolates were previously utilized to substitute the chalcogens on the surface of the clusters.[1b,2f,14] An alternative to this is the use of amine ligands to partially or fully replace the four terminal S^{2-} ions.[2d,15] In our case, the 8− valence of the T3 cluster was completely counteracted by four complexes with 2+ valence, and the special arrangement of cations in the T3 core revealed the self-adjustability for T*n* to satisfy the charge balance. Besides this, they also act as structure-directing agents for assembly of the molecular nanocluster.

The molecular nanocluster is a wide-gap semiconductor with an energy gap of 1.99 eV (Figure 4), as calculated from reflectance data by using the Kubelka−Munk function.[16] The band gap lies between the band gaps (1.4−1.7 eV) of gallium selenide derived T*n* frameworks[11] and those (2.5−2.9 eV) of ternary P*n* $[M_4(\mu_4\text{-Se})(SnSe_4)_4]^{10-}$ (M = Zn, Mn) anions[10] and demonstrates the feasibility of tuning the band gap of clusters via the combination of different metal cations. The compound is insoluble in common polar and nonpolar solvents, e.g., water, ethanol, tetrahydrofuran, toluene, and cyclohexane. Thermogravimetric analysis (TGA) indicates that, under a N_2 atmosphere, it is stable up to 260 °C.

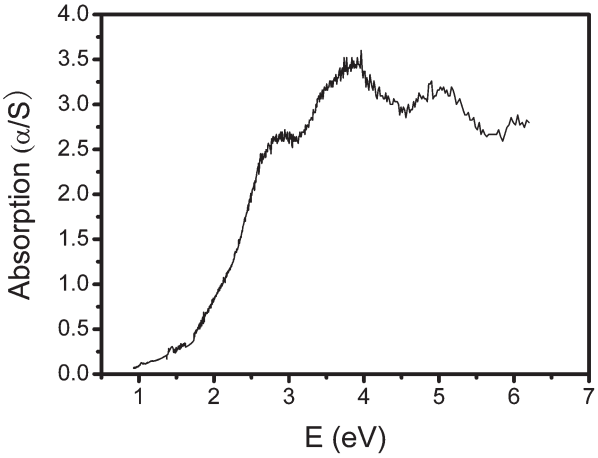

Figure 4. Optical absorption spectrum of the molecular nanocluster.

In a $[Sn_4Ga_4Zn_2Se_{20}]^{8-}$ T3 core, the four tetracoordinated Sn^{4+} cations only occupied the four corner metal sites of the T3 cluster. Such an arrangement of 4+ metal ions in the T*n* series is acceptable no matter whether the other 3+ metal sites are replaced by 2+ and 1+ metal ions or not because no violation against Pauling's electrostatic valence rule would occur. This finding suggests that it is possible to combine both 3+ and 4+ metal cations into one single T*n* ($n > 2$) cluster. By using 4+ metal atoms to substitute 3+ metal atoms at the four corners of T*n* clusters, the high negative charge of the T*n* cluster could be lowered by 4. Consequently, larger clusters might be stabilized and open frameworks consisting of such clusters could be achieved using organic amines as templates with less stringent requirements on their volume and C/N ratio.

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Supporting Information Available: Hydrogen-bonding parameters, crystallographic data in CIF format, observed and simulated powder X-ray diffraction data, and TGA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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