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Transition Metal Complexes as Linkages for Assembly of Supertetrahedral T4 Clusters

Yu-Hong Wang,[†,‡] Ming-Hui Zhang,[†] Yun-Meng Yan,[†] Guo-Qing Bian,[†] Qin-Yu Zhu,*[,†] and Jie Dai*[,†]

[†]*Department of Chemistry and Key Laboratory of Organic Synthesis of Ji-angsu Province, Soochow University, Suzhou 215123, P. R. China, and* [‡]*School of Chemistry and Bioengingeering, Suzhou University of Science and Technology, Suzhou 215009, P. R. China*

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T*n* clusters are usually connected into frameworks by sulfur bridges. A new type of T4 compounds in which the clusters are linked by both sulfur bridges and transition metal complexes are described.

Main-group metal chalcogenido supertetrahedral clusters (T*n*) have become increasingly interesting since the initial report of the assembly of germanium sulfide clusters, $[Ge_4S_{10}]^{4-}$, into polymeric frameworks.[1] A significant progress has been made subsequently in these novel chalcogenides.[2,3] Large supertetrahedral clusters, such as T3 clusters $[In_{10}S_{20}]^{10-}$,[4] T4 clusters $[M_4In_{16}S_{33}]^{10-}$ (M = Mn, Co, Zn, Cd),[5] together with the largest T5 clusters $[Cu_5In_{30}S_{54}]^{13-}$ and $[In_{34}S_{54}]^{6-}$,[6] have been reported in the early part of this decade. The noticeable limitation existing in known superlattices built from T*n* clusters is the intercluster linkage mode. So far, T*n* clusters are mainly joined together by biconnected sulfur atoms. Some T2 clusters, such as $[Ge_4S_{10}]^{4-}$, form three-dimensional frameworks through divalent metal ions.[1,7] Compounds UCR-18 and UCR-8 are rare examples, in which clusters are linked by polysulfur chain and three-connected sulfur atoms, respectively.[8,5d] Very recently, T*n* clusters assembled by organic ligand 1,2-di(4-pyridyl)ethylene have been reported.[9] To obtain new structural types, it is necessary to devise alternative ways of linking the clusters.

In general, the organic directing molecules used in the solvothermal synthesis of metal chalcogenides enter the structure as space filling or template. In extended chalcogenido structures, covalent bonding of organic molecules to the inorganic framework has been found in a number of hybrid chalcogenides containing metals coordinated both by sulfur and amines.[10,11] These transition metal (TM) complexes are not only mainly responsible for many interesting properties but also contribute to the generation of new structural types. Therefore it is an attractive way for integrating TM complexes and linkages into structures of main group metal chalcogenides. However, only a small number of TM complexes act as structural linkages in this field.[11g,12] T2 and

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*To whom correspondence should be addressed. E-mail: zhuqinyu@suda.edu.cn. (Q.-Y.Z.), daijie@suda.edu.cn (J.D.).

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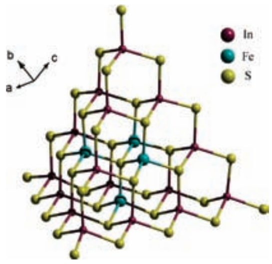

Figure 1. Structure of the $[Fe_4In_{16}S_{34}]^{8-}$ anion in **1** showing the position of Fe atoms.

T3 clusters decorated with TM amine complexes have been reported.[11b,13] However, large T*n* supertetrahedral clusters, with $n > 3$ and decorated with TM complexes, remain unknown. To the best of our knowledge, prior to the work reported here a TM complex has never been found as a linkage between supertetrahedral clusters.

In our continual efforts to explore the rich synthetic and structural chemistry of chalcogenidometalates using transition metal coordination compounds as structural decorating moieties,[11] we have been increasingly interested in developing chalcogenido-clusters with new linkages and bonding patterns other than commonly observed structures of supertetrahedra. In this Communication, we report the preparation of a new type of T4 cluster compounds with $[M(dach)_2]$ linkages (dach = 1,2-diaminocyclohexane), compounds **1** (M = Fe) and **2** (M = Co). The structural characterization and electronic spectra of the synthesized compounds are discussed.

The crystals **1** were synthesized from element Fe, In, and S in a water solution of 80% dach by solvothermal reaction at 140 °C for 9 days (Supporting Information). The single-crystal X-ray diffraction study shows that the basic structure of **1** is composed of T4 clusters, a first reported Fe-T4 example. The bond lengths of the inner sulfur to Fe sites in the T4 cluster ranging from 2.344(3) to 2.355(4) Å are shorter than the average tetrahedral S−Fe distances (2.417(4) Å). For the remaining sites, the inner In−S bond lengths are typical for a tetrahedral In−S bond length (about 2.47 Å). Both experimental data of the bond distances and the calculation results of the bond valence sum (BVS) indicate that four metal sites surrounding the tetrahedral sulfur atom are occupied by divalent cations, Fe(II) (Figure 1, Supporting Information). Several related compounds constructed from T4 supertetrahedral clusters, $[M_4In_{16}S_{35}]^{14-}$ (Cd^{2+}, Zn^{2+}, Mn^{2+}, or Co^{2+}), have been reported and discussed elsewhere in detail.[5]

The T4 clusters are usually linked in a four-connected topology constructing 3-D porous frameworks, in which the corner sulfur atoms adopt a two-connected bridging mode. In the case of **1**, T4 clusters share two corner sulfur atoms with two neighboring T4 clusters forming a 1-D zigzag chain (Figure 2a). There are two free corner sulfur atoms in each T4 cluster. The free terminal In−S distances, 2.482(5) Å for In(1)−S(1) and 2.466(4) Å for In(17)−S(31), are longer than the distances of the bridging corner, In(11)−S(21) (2.452(3) Å) and In(20)−S(21) (2.447(3) Å), respectively. Although hydrogen atoms cannot be located in the Fourier maps, the longer terminal In−S distances imply that the terminal sulfur atoms might be protonated.[14] In the IR spectrum of **1**, a weak peak at 2640 cm^{-1} can be attributed to the presence of −SH groups (SI-Fig. 1 in the Supporting Information).

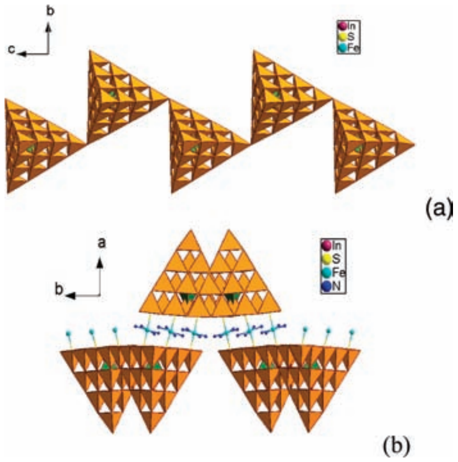

Figure 2. (a) The 1-D zigzag structure of **1** formed by T4 clusters sharing two corner sulfur atoms with neighboring clusters. (b) The T4 cluster chains connect to a 2-D structure by $[Fe(dach)_2]$ linkages viewed along the *c* axis (the direction of the 1-D chain).

The structure of this compound is intriguing since it represents a new level of complexity in the linkage of the supertetrahedral clusters. In addition to the 1-D sulfur bridged structure, the in situ formed $[Fe(dach)_2]^{2+}$ complex cations join the T4 clusters into a 2-D framework through Fe−S bonds. The thioantimonate(III) $[Fe(C_6H_{14}N_2)_2][Sb_6S_{10}]$ is an example with $[Fe(dach)_2]$ linkage, but it is not a T*n* compound.[12a] The solvothermal system provides a reducing environment in which only Fe(II) can be formed. It has also been confirmed by BVS calculation (Supporting Information). Each T4 cluster connects with three neighboring clusters by three $[Fe(dach)_2]$ linkages. Figure 2b shows the connection viewed along the *c* axis (the direction of the 1-D chain). In the $[Fe(dach)_2]$ complex, the Fe(II) ion is coordinated by two chelating dach molecules which are arranged in the equatorial plane. The octahedral coordination sphere is completed by two sulfur atoms of the T4 clusters in axial positions. The octahedral Fe−N and Fe−S bond lengths are comparable with those found in $[Fe(C_6H_{14}N_2)_2][Sb_6S_{10}]$.[12a] It should be noted that all the sulfur atoms involved in the coordination connection are those on the edge of T*n* clusters and near the corner.

There are isolated $[Fe(dach)_3]^{2+}$ complex cations and protonated dach molecules in the crystal structure, which act as charge balancing and space filling cations. The final composition of **1**, $\{[In_{16}Fe_4S_{34}H_2]_2[Fe(dach)_2]_3\}\cdot 4[Fe(dach)_3]\cdot 6Hdach\cdot 6H_2O$, has been determined using a combination of single-crystal data analysis and elemental microanalysis. The positions of Fe, In, and S of the cluster are determined accurately, the cations and guest molecules filling the space and residing between the clusters are not all located because of the disorder problems usually encountered in this kind of structure.[4−6] Carefully obtained data on elemental microanalysis (Supporting Information) and the charge balance rule are very helpful to confirm the final composition.

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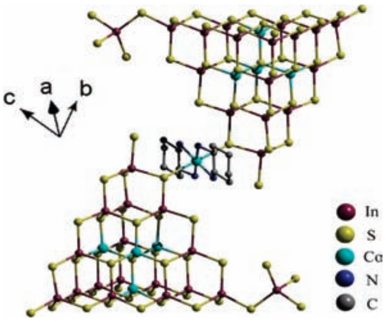

Figure 3. Structure of the $\{[In_{17}Co_4S_{38}H_3]_2[Co(dach)_2]\}^{26-}$ anion in **2** showing the coordination linkage.

Figure 4. The molecular packing of **2** showing the relationship of the cations and anions.

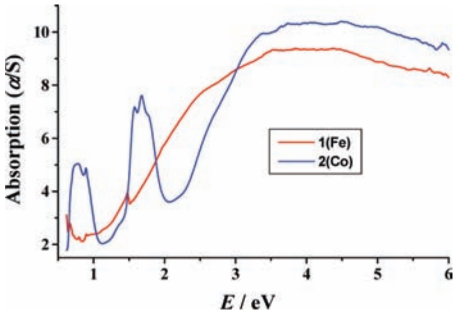

Figure 5. Solid-state optical absorption spectra of **1** and **2** at room temperature.

The structure of **2** is also composed of T4 clusters but with four inner Co ions. The terminal sulfur atom (S35) in one corner of the T4 cluster bridges to a T1 tetrahedral InS_4. (Supporting Information). The structure is depicted in Figure 3. Bond lengths of the T4 cluster are comparable with the distances in the reported T4-Co compound.[5b] The free terminal In−S distances in the cluster are 2.494(3), 2.486(3), and 2.493(3) Å for In(1)−S(1), In(11)−S(21), and In(17)−S(31), respectively, longer than the bibridging bond of the corner, 2.470(3) Å for In(20)−S(35). The distances imply that three terminal sulfur atoms of the T4 cluster might be protonated. In the crystal structure, every two clusters form a pair connected by a $[Co(dach)_2]^{2+}$ complex cation. Other components filling the space are also not all located. On the basis of information from the X-ray data analysis, careful elemental analysis, charge balance, and BVS calculation (Supporting Information), the composition of **2** is determined as $\{[In_{17}Co_4S_{38}H_3]_2[Co(dach)_2]\}\cdot 8[Co(dach)_3]\cdot 10Hdach\cdot 2H_2O$ (**2**). Figure 4 is the molecular packing of compound **2**, viewed along the *a* direction.

Optical diffuse-reflection spectra of **1** and **2** were measured at room temperature using $BaSO_4$ as a standard reference (Figure 5). The absorption data were calculated from the reflectance. Compound **1** shows a broad band with an edge at about 1.2 eV, while **2** exhibits two sharp peaks and a broad band with an edge at about 1.8 eV. There are two main contributions that may be considered in the spectra. One is the absorption of InS_4 framework that appears above 2.8 eV because the inorganic In_xS_y clusters are usually colorless or pale-yellow. The edge of this band extends into the visible region by charge-transfer absorptions of the central tetrahedral TMS_4.[15a] The coordination field absorption (single peak) for tetrahedral Fe(II) (d^6) should be at about 0.7 eV (only half of the peak appeared in Figure 5).[15b] Three peaks (ν_1 outside the measuring range) for tetrahedral Co(II) (d^7) are expected and the ν_2 and ν_3 are at 0.8 and 1.68 eV, respectively.[15] These intense TM bands might be useful in improving the optical absorption of the main group metal chalcogenides. The contribution of the octahedral coordination field of the dach complexes (symmetrically forbidden) can be ignored in comparison with that of the tetrahedral TM centers and charge-transfer absorption.[16]

In summary, significant progress in supertetrahedral clusters have been reached in the early part of this decade. However, new achievements in this field are limited in these years for the noticeable limitation in intercluster linkage modes. Herein a new type of T4 supertetrahedral compounds has been synthesized. In addition to the 1-D sulfur bridged structure of T4 clusters in **1**, the in situ formed $[Fe(dach)_2]^{2+}$ complex cations act as linkages joining the T4 clusters into a 2-D framework. Compound **2** is also composed of T4 clusters with paired structure connected by the $[Co(dach)_2]^{2+}$ cation. The structures of these compounds are intriguing since they represent a new level of complexity in the linkage of supertetrahedral clusters. Furthermore, integrating TM into the structure of main group metal chalcogenides clearly improves the optical functionality of these compounds.

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Supporting Information Available: Experimental preparation, figures of IR spectra, powder X-ray diffraction, VBS calculation, and CIF table. This material is available free of charge via the Internet at http://pubs.acs.org.

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