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# One-Size Adjustable-Gap Cluster Anions: Systematic Approach to Multinary, Water-Soluble Chalcogenidometalate Compounds

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Reactions of defined mixtures of ternary salts $[K_4(H_2O)_4][SnSe_4]$ and $[K_4(H_2O)_{0.5}][SnTe_4]$ with transition-metal ions M = $Zn^{2+}$ or $Mn^{2+}$ provide an easy approach to penternary salts of quaternary cluster anions $[M_4Sn_4Se_{17-x}Te_x]^{10-}$, with $x$ corresponding to the Se/Te ratio of the reactant mixture. In this way, it is possible to generate both protic solutions and single crystals with finely adjustable electronic excitation energies $E_g$; the fact that the $E_g$ values cover the whole visible part of the electromagnetic spectrum as a function of the parameter $x$ spotlights these cluster compounds with respect to diverse photocatalytic applications.

The search for metal chalcogenides or chalcogenidometalate compounds with suitable absorption energies besides a suitable structure or surface is one of the most attractive challenges for inorganic chemists at the moment.[1–5] Both the generation of $H_2$ from protic solutions,[6,7] as has been shown impressively by the development of $H_2$ from water using a $Cu^{2+}$-doped In/S lattice,[8] and the trend toward catalytic processes[9] in or at the interface to harmless solvents currently activate the search for water-soluble metal compounds with promising electronic properties.[10] Recently, the fine-tuning of absorption energies in salts of ternary supertetrahedral chalcogenidometalate anions $[M_4Sn_4E_{17}]^{10-}$ of the P1 type was reported.[11–15] These compounds attracted attention because they are water-soluble complexes with relatively narrow optical gaps and increments of 0.1−0.4 eV in $E_g$ upon variation of the incorporated transition-metal $d^5$ $M^{2+}$ or $d^{10}$ $M^{2+}$ ions (M = Mn, Zn, Cd, Hg) or 0.8−1.0 eV when going from S to Se or from Se to Te. However, these increments are still too rough for the requirements of a multipurpose material, and the absorption energies still do not cover the whole visible part of the electromagnetic spectrum owing to a void between the Te and Se domains.

Our latest experiments evidenced that mixtures of $[SnE^1_4]^{4-}$ and $[SnE^2_4]^{4-}$ anions undergo chalcogenide exchange in a protic solution to form a statistical mixture of all possible species $[SnE^1_{4-x}E^2_x]^{4-}$ ($x = 0-3$).[16] The obvious question was, would it be possible to extend the knowledge of preparing these reactive species to generate a library of multinary chalcogenidometalate compounds with consistently tuneable $E_g$?

Here we report our answer to this question by presenting an easy approach to penternary salts of quaternary anions $[Zn_4Sn_4Se_{17-x}Te_x]^{10-}$ ($x = 4, 6, 7$) and $[Mn_4Sn_4Se_{17-x}Te_x]^{10-}$ ($x = 4, 5.4, 6.4$), all showing the preferred P1 cluster type structure, as intended by using $K^+$ ions as a template. All indications are that the ratio of the binary anions $[SnSe_4]^{4-}$ and $[SnTe_4]^{4-}$ in the starting solution directly leads to respective Se/Te ratios in the P1 anionic cluster. This is reflected in both the color of the reaction solution and the color of the single crystals of the penternary compounds. Scheme 1 shows the general pathway for the preparation of solutions (1) and salts of the quaternary anions (2).

Following the pathway sketched in Scheme 1, with stepwise variation of the Se/Te ratio in the starting mixture, it was possible to generate solutions in a wide color range upon reaction with $M^{2+}$: from a light-yellow Zn/Sn/Se combination to dark-red Zn/Sn/Te or from light-orange Mn/Sn/Se to dark-violet Mn/Sn/Te. Preliminary $^{119}$Sn NMR studies give further evidence for the existence of the below-

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**Scheme 1.** Synthesis Pathway for the Preparation of **1**−**3** (M = Zn) and **4**−**6** (M = Mn)[a]

$$[K_4(H_2O)_4][SnSe_4] + [K_4(H_2O)_{0.5}][SnTe_4] \xrightarrow[\text{(2) layering by toluene (1:1)}]{\text{(1) + MCl}_2\text{, MeOH/ H}_2\text{O (19:1)}} [K_{10}(H_2O)_m(MeOH)_n][M_4Sn_4Se_{17-x}Te_x] \text{ (1–6, 73–85\%)} + [K_4(MeOH)_4][Sn_2Se_6] / [K_4(H_2O)_5][Sn_2Te_6] + KCl$$

[a] The respective composition, indicated by *x*, was obtained according to the ratio of the starting compounds.

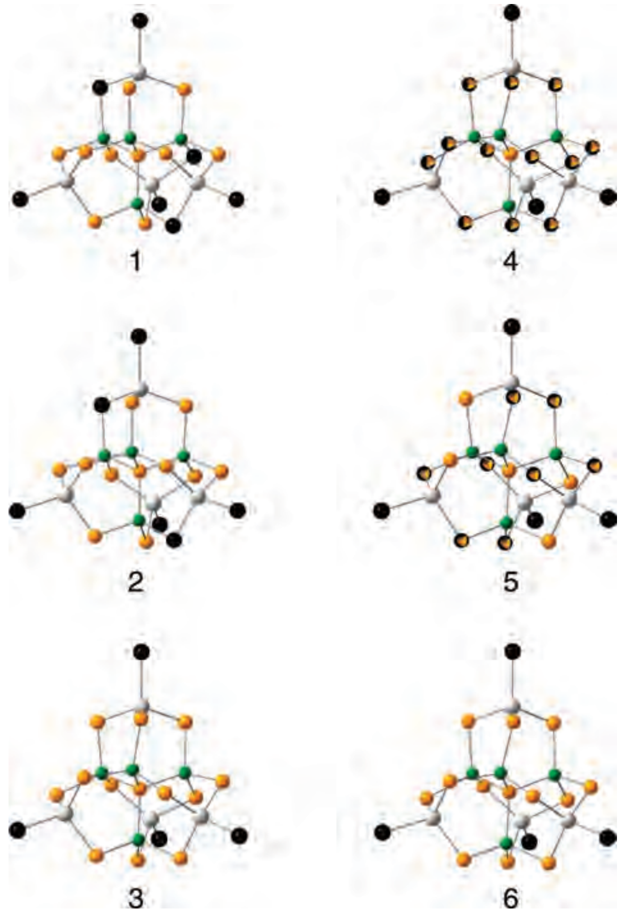

**Figure 1.** Structures of the quaternary anions $[Zn_4Sn_4Se_{17-x}Te_x]^{10-}$ **1**−**3** (left-hand side) and $[Mn_4Sn_4Se_{17-x}Te_x]^{10-}$ **4**−**6** (right-hand side). Color code: Sn, gray; Zn or Mn, green; Se, orange; Te, black spheres. Yellow spheres denote positions with statistical occupation by Se or Te atoms (see the Supporting Information).

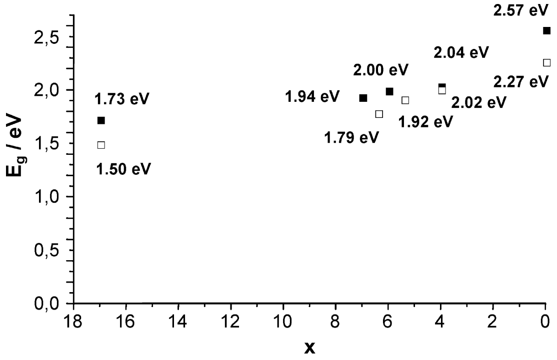

**Figure 2.** Variation of the absorption energy $E_g$ with the number of Te atoms *x* in the cluster anions[12] $[M_4Sn_4Se_{17-x}Te_x]^{10-}$ received by solid-state UV−vis spectra of **1**−**3** (black squares) and **4**−**6** (open squares), recorded as suspensions of single crystals in Nujol oil, together with those of $[K_4(H_2O)_{20}][Zn_4Sn_4Te_{17}]$ (**C**),[13] $[K_4(H_2O)_{16.5}(MeOH)_{0.5}][Zn_4Sn_4Se_{17}]$ (**A**),[12] $[K_4(H_2O)_{20}][Mn_4Sn_4Te_{17}]$ (**D**),[13] and $[K_4(H_2O)_{16.5}(MeOH)_{0.5}]$ $[Mn_4Sn_4Se_{17}]$ (**B**).[12]

discussed quaternary anions in these solutions. Table 1 summarizes the $[SnTe_4]^{4-}$/$[SnSe_4]^{4-}$ ratios in the reaction mixtures and the composition of the solid products. Semiquantitative energy-dispersive X-ray spectroscopy analyses (EDX analyses) served to confirm the outcomes of the nontrivial X-ray investigations, which were complicated by a tendency of statistical disorder of E$^1$ or E$^2$ over certain positions in the cluster.

Whereas the deviation of the Se/Te ratio in the quaternary cluster anions from that of the reactant mixtures is negligible for **2** and **5** (4.5 and 3.5%) or **3** and **6** (2.2%), it is more signifcant for **1** and **4** (30 or 37%); this is due to the cocrystallization of the byproduct $[K_4(H_2O)_5][Sn_2Te_6]$ in a 15% yield in these two cases, whereas the other byproduct, $[K_4(MeOH)_4][Sn_2Se_6]$, is only observed in trace amounts under the given conditions. Thus, increasing the Se percentage decreases the total amount of crystalline byproduct.

Compounds **1** and **2** crystallize in the monoclinic space group *C*2/*c*, and **3**−**6** crystallize in the tetragonal space group $P4_32_12$, isotypically to **A** or **B**.

According to shorter Sn−Se and M−Se bonds in comparison to Sn−Te and M−Te, the edges of the P1 supertetrahedra diminish when going from **1** to **3** or from **4** to **6**, following the decreasing number of Te atoms: from 11.0−11.4 Å in **1** to 10.7−10.9 Å in **3** and from 11.1−11.3 Å in **4** to 11.0−11.2 Å in **6**. The smaller edge lengths of the Zn clusters in **1**−**3**, when compared to the Mn clusters in **4**−**6**, are due to the smaller volume of the central $Zn_4Se$ tetrahedron in comparison to the $Mn_4Se$ unit. Figure 1 depicts the molecular structures of the quaternary anions in **1**−**6**.

The preferences for a distribution of Se and Te atoms over the three different chalcogenide positions of the P1 clusters ($\mu_4$, $\mu$, and terminal) that are observed in the molecular structures of the anions are in good agreement with quantum chemical investigations using density functional theory (DFT) methods[17] within the program system Turbomole:[18,19] (1) terminal positions are always occupied by Te atoms, enabling a better delocalization of the relatively high charge of the corner atoms in larger Te orbitals, (2) the $\mu_4$ ligand forming four highly ionic bonds to transition-metal ions is best represented by the more electronegative Se atom, and (3) both atoms can take up $\mu$-bridging positions so that a statistical disorder of these chalcogenide ligands over this position is also possible, as observed for **4** and **5**. Calculated energy differences for the different species according to a 13:4 ratio of Se/Te, for instance, amount to up to 63.7 kJ mol$^{-1}$ if the chalcogenide ligands are distributed differently with respect to the experimental findings. The maximum

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**Table 1.** Se/Te Ratios in the Reaction Mixture and in the P1 Cluster Anions in **1**−**6**, As Observed by X-ray and EDX Analyses, together with That of Previously Reported $[K_{10}(H_2O)_{16}(MeOH)_{0.5}][M_4Sn_4Se_{17}]$ [M = Zn (**A**), M = Mn (**B**)][11,12] as References

| | | | Se/Te (X-ray) | | Se/Te (EDX) | |
|---|---|---|---|---|---|---|
| Zn | Mn | Se/Te (provided) | Zn | Mn | Zn | Mn |
| **A** | **B** | | 17:0 | 17:0 | 17:0 | 17:0 |
| **1** | **4** | 1:1 | 10:7 | 10.6:6.4 | 9.8:7.2 | 10.1:6.9 |
| **2** | **5** | 2:1 | 11:6 | 11.5:5.5 | 11.3:5.7 | 11.8:5.2 |
| **3** | **6** | 3:1 | 13:4 | 13:4 | 13.3:3.7 | 13.6:3.4 |

destabilization is observed if a Te atom is placed on the $\mu_4$-bridging position and Se atoms are terminal ligands in the same molecule.

The optoelectronic properties of **1**−**6** were examined by means of UV−vis spectroscopy (Figure 2).

It is obvious that the increments between the absorption engergies $E_g$ of the novel penternary compounds (0.15−0.04 eV for a given **M**) are considerably smaller than those of the quaternary compounds.[11−13] Additionally, the absorption energies are situated right between those of the pure tellurido- or selenidometalates.

As shown exemplary by these preliminary studies, the aim of succeeding in a user-defined composition of chalcogenide ligands in the solutions or salts of P1 cluster anions was successful in enabling a well-selective adjustment of $E_g$ for a given cluster type. The investigations are complementary to recent reports on the preparation and fine-tuning of optical properties in mixed Zn/Cd/E clusters.[20] Current studies focus on the use of these compounds and their protic solutions in diverse photocatalytic reactions.

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**Supporting Information Available:** Crystallographic and refinement details, experimental details, methods of spectroscopy, and EDX analyses (PDF and CIF), and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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