Fine-tuning of optical properties with salts of discrete or polymeric, heterobimetallic telluride anions $[M_4(\mu_4\text{-Te})(SnTe_4)_4]^{10-}$ (M = Mn, Zn, Cd, Hg) and $^{3}_{\infty}\{[Hg_4(\mu_4\text{-Te})(SnTe_4)_3]^{6-}\}$†‡

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Compounds with first discrete M/Sn/Te anions—exhibiting a series of optical absorption energies in the semiconductor range—are obtained by reactions of K^+ or Rb^+ salts of $[SnTe_4]^{4-}$ with MCl_2 (M = Mn, Zn, Cd, Hg) in H_2O or H_2O–MeOH; larger Cs^+ cations provoke the formation of a polymeric derivative of the ternary anionic structure.

The design and preparation of chalcogenometallate compounds for catalytic purposes is one of the most demanding topics of today's inorganic and material sciences research.[1] The challenge is the development of compounds with both relatively narrow band gaps—that may allow for photocatalytic applications—and suitable chemical properties, *i.e.* stability of respective suspensions or solutions under the desired reaction conditions. Very recently, for instance, Feng *et al.* reported the successful catalytic evolution of hydrogen from water by employing suspended phases with ternary M/13/16 anionic networks.[2]

In order to provide a library of soluble compounds whose electronic excitation energies cover the energy range of the visible spectrum, one of our current aims is the generation of ternary, molecular semiconductor complexes.

We have recently developed a method for the preparation of water-soluble salts of heterobimetallic sulfides or selenides that contain ternary cluster anions of the general type $[M_xE'_yE_z]^{q-}$ (M = Mn, Co, Zn, Cd, Hg; E' = Ge, Sn; E = S, Se).[3] Some of the complexes were also accessible by solvothermal or alkali metal polychalcogenide flux synthesis.[4] Considering the molecular sizes of the anions, $[M_xE'_yE_z]^{q-}$ salts possess relatively small optical absorption energies—compared to ligand-clad, binary relatives—due to their specific M/14/16 elemental combination and the missing organic shell. Similar attempts toward heterobimetallic tellurides have so far produced two compounds containing one-dimensional strands, $Rb_2[HgSnTe_4]$ and $Cs_2[MnSnTe_4]$;[5] reactions under solvothermal conditions yielded related compounds like $K_2[HgSnTe_4]^{6a}$ or $[Mn(en)_3][CdSnTe_4]$.[6b]

By reacting K or Rb salts of the $[SnTe_4]^{4-}$ anion[7] with transition metal chlorides in aqueous solution or H_2O–MeOH mixtures at room temperature, a series of quaternary phases is readily formed in relatively good yields. The preparation of $[A_{10}(H_2O)_{20}][M_4(\mu_4\text{-Te})(SnTe_4)_4]$ with M = Mn (1), Zn (2), Cd (3a, 3b), and Hg (4) is sketched in Scheme 1.

The anionic complexes possess a P1-type supertetrahedral structure in analogy to recently reported $Se^{3a-c,f}$ or $S^{4a,b}$ analogs; this topology has been shown to be favored for both ligand coated clusters and purely inorganic cluster anions. In compounds 1–4, the clusters show perfect T_d symmetry (cubic space group I-43m with Te(3)···Te(3′) edges of 11.6 (2)–11.8 (3a) Å),[8]†§ although they have been generated in solution and crystallize with a counterion aggregate of highly disordered K^+ ions—hinting at ion conductivity—and water molecules. All related phases containing solvent molecules showed both lower crystal and lower molecular point group symmetry. Figs. 1 and 2 show the structure of an anion and the bcc type packing within counterions and solvent molecules.

In order to gain preliminary insight into the electronic situation, we have investigated the optical absorption behavior of the telluride series in comparison to the closely related compounds
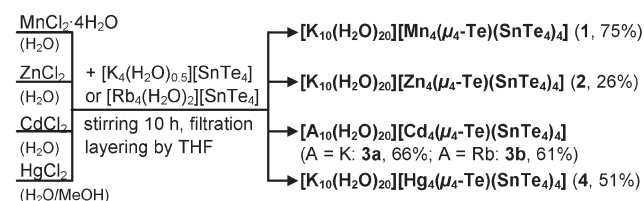
Scheme 1 Synthesis of compounds $[A_{10}(ROH)_n][M_4(\mu_4\text{-Te})(SnTe_4)_4]$ with M = Mn (1), Zn (2), Cd (3a, 3b), Hg (4) from $[K_4(H_2O)_{0.5}][SnTe_4]$ or $[Rb_4(H_2O)_2][SnTe_4]$ and MCl_2 in H_2O or H_2O–MeOH.
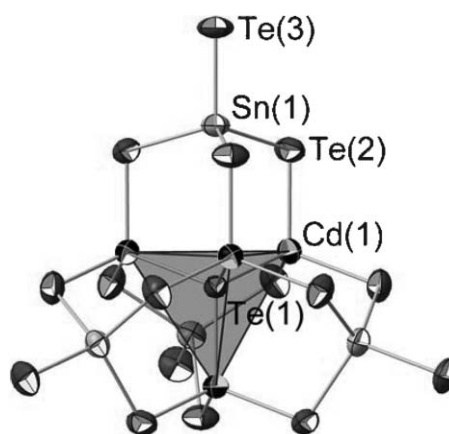
Fig. 1 Thermal ellipsoid drawing (40% probability) of the molecular structure of the ternary anion in 1–4, given for 3a as an example.

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† Electronic supplementary information (ESI) available: Further details of X-ray structural analyses, UV–visible spectroscopy and DFT calculations. See DOI: 10.1039/b610833d
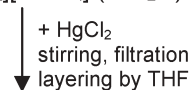‡ The HTML version of this article has been enhanced with color images.
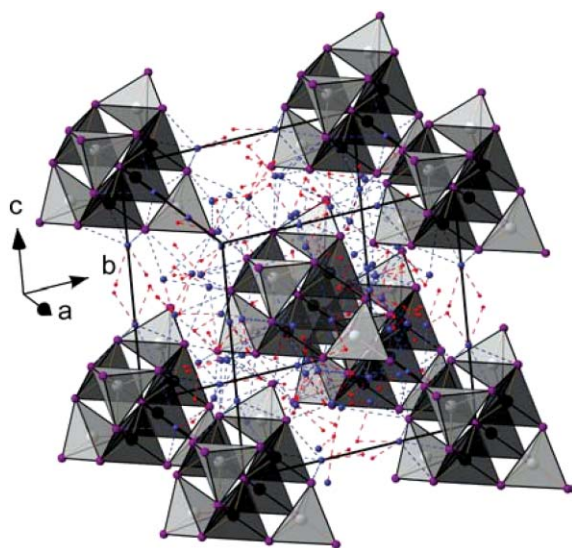
Fig. 2 Illustration of the bcc type crystal packing of anions in **1–4**, and storage of K$^+$ counterions (blue) and solvent molecules (O: red), given for **3a** as representative. For clarity, disorder of K and O atoms is not shown and one anion (top left front corner of the unit cell) is omitted.

[K$_4$(H$_2$O)$_{16}$(MeOH)$_{0.5}$][M$_4$(μ_4-Se)(SnSe$_4$)$_4$].[3b,c] One observes an incremental red-shift of the lowest electronic excitation energy E_g when going from M = Zn through Cd and Mn to Hg for both series, with ΔE_g = 0.05–0.1 eV. Additionally, a significant red-shift is observed for the formal substitution of Te for Se in the anions, with ΔE_g = 0.7–0.9 eV for a given M. The solid state UV–visible spectra of compounds **1–4** are shown in Fig. 3, together with those of the related selenides for comparison.

The energy values of maximum absorption of both series correspond to the visible color of the crystals; according to DFT calculations, the relatively small E_g value of the Mn compounds can be explained by a different charge transfer process (MMCT) when compared to the d^{10} metal compounds (LMCT).[3c]

Employment of the analogous Cs salt [Cs$_4$(H$_2$O)$_2$][SnTe$_4$][7] in a reaction with HgCl$_2$ led to the formation of another anionic substructure in [Cs$_6$(H$_2$O)$_4$][Hg$_4$(μ_4-Te)(SnTe$_4$)$_3$] (**5**) (Scheme 2).

In **5**, fragments of the P1-type cluster anions are linked to form a three-dimensional network. In accordance with the formula of one monomeric unit, the cluster fragments are formally obtained upon removal of one [SnTe$_4$]$^{4-}$ group from each supertetrahedron.

[Cs$_4$(H$_2$O)$_2$][SnTe$_4$] (in H$_2$O)

↓ + HgCl$_2$
stirring, filtration
layering by THF

[Cs$_6$(H$_2$O)$_4$][Hg$_4$(μ_4-Te)(SnTe$_4$)$_3$] (**5**) (45%)

**Scheme 2** Synthesis of compound **5** from [Cs$_4$(H$_2$O)$_2$][SnTe$_4$] and HgCl$_2$ in H$_2$O.

Re-saturation of the fourth coordination site at each of the Hg atoms of the open Hg$_3$ face by three terminal Te ligands of three adjacent cluster fragments, and continuation of this formal process results in the observed network (Fig. 4). Disregarding the trigonal distortion into the space group $R3m$,[8]† the barycenters of the cluster fragments represent topologically the simple packing of the α-Po structure.

Whereas for Hg/Sn/Se compounds, both the discrete and the 3D anionic structure were obtained with K$^+$ counterions depending on the reaction conditions,[3c] for the Te analogs, another counterion was necessary to stabilize and thus crystallize the porous substructure. Acting as a template, Cs$^+$ ions fit better to the linked cluster fragments with only six charges per monomeric unit, which is reflected by a smaller number of Te⋯Cs contacts in **5** (18 per 13 outer Te atoms, *i.e.* 1.5 on average) when compared to the number of Te⋯K contacts in **4** (30 per 16 outer Te atoms, *i.e.* 1.9 on average).

5 represents the first Te analog of three related selenide salts, namely [K$_6$(H$_2$O)$_3$][Hg$_4$(μ_4-Se)(SnSe$_4$)$_3$]·MeOH,[3c] and the solvent-free phases K$_6$[Cd$_4$(μ_4-Se)(SnSe$_4$)$_3$],[9a] and K$_6$[Zn$_4$(μ_4-Se)(SnSe$_4$)$_3$],[9b] which possess homologous polar open framework substructures of M/Sn/E anions. As for the salts of discrete anions, the electronic excitation energy E_g decreases upon formal substitution of Te (1.61 eV) for Se (M = Zn: 2.6,[9b] Cd: 2.33,[9a] Hg: 2.20 eV[3c]).

The E_g values for the charge transfer transitions in **1–5** are significantly smaller than those reported until now for d^5 or d^{10} metal telluride cluster complexes of a similar or slightly larger molecular size.[10] This is due to the missing ligand shell on the one hand and the ternary, formally SnTe (E_g: 0.23 eV)[11a] containing composition of **1–5** on the other hand; E_g thus reaches the values of the binary MTe solids (direct gaps for the sphalerite type phases: ZnTe: 2.20 eV, CdTe: 1.48, MnTe: 1.3, HgTe: −0.16 eV).[11a,b]

Moreover, the values observed for **1–5** are only about 0.7–1.0 eV higher in energy than the optical gaps of recently
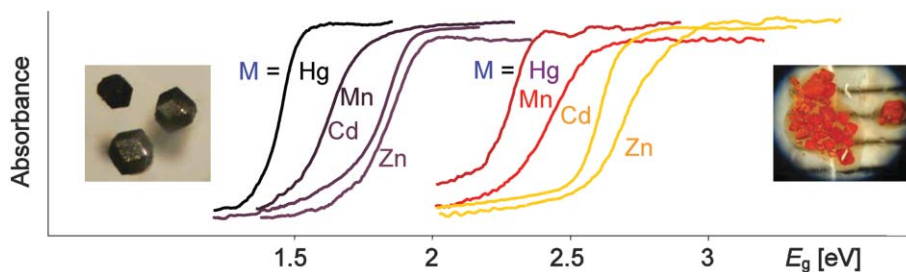
Fig. 3 Normalized solid state UV–Vis spectra of compounds with ternary anions [M$_4$(μ_4-E)(SnE$_4$)$_4$]$^{10-}$, recorded as suspensions of single crystals in nujol oil; **1–4** (left hand side), related selenides [K$_4$(H$_2$O)$_{16}$(MeOH)$_{0.5}$][M$_4$(μ_4-Se)(SnSe$_4$)$_4$] (M = Zn, Cd, Mn, Hg)[3b,c] (right hand side). Electronic excitation energies E_g for a given M are [eV]: E = Se:[3c] 2.57 (Zn), 2.53 (Cd), 2.27 (Mn), 2.12 (Hg); E = Te: 1.73 (Zn), 1.68 (Cd), 1.50 (Mn), 1.39 (Hg). The photos show corresponding crystals of the Mn compounds with E = Te (top left) or E = Se (top right), respectively.
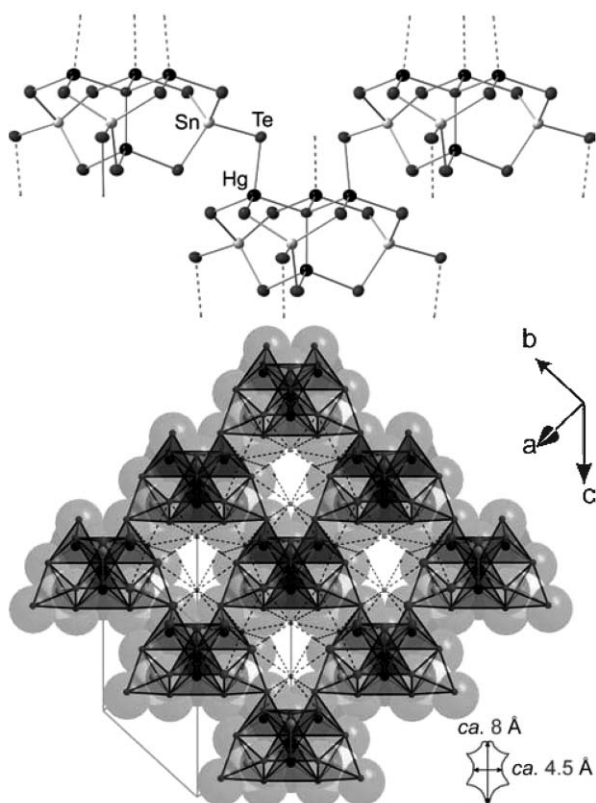
Fig. 4 Thermal ellipsoid drawing (70% probability) of one monomeric unit in **5** and space-filling/polyhedral model of the ternary anionic network sketching the channel sizes and the position of counterions and water molecules within the channels.
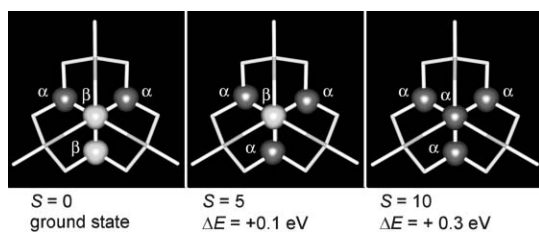
Fig. 5 Illustration of the spin density for the different spin states of $[Mn_4Sn_4Te_{17}]^{10-}$ anions as calculated using DFT methods. α or β labelled clouds represent residual alpha or beta spins, respectively, up to 0.2 e^- Å^{-3}.

reported inorganic–surfactant composites with extended $Pt_xSn_yTe_z$ networks (*e.g.* CTEA[$Pt_{0.5}SnTe_{3.5}$], $E_g = 0.75$),[12] suggesting a comparable semiconductor situation.

To the best of our knowledge, the magnetism of μ₄-Te-bridged Mn complexes has not been investigated so far. Preliminary information can be gathered from DFT calculations of the open-shell anion in **1**.† According to analyses of the spin density (*i.e.* the difference of all α and β spins per volume element), localization of the unpaired electrons at the Mn atoms was evident, which is tantamount to the presence of intact d⁵ shells. The possible spin orientations at the four Mn centers lead to three species fulfilling the *aufbau* principle with a resulting total spin of $S = 0$, $S = 5$, and the ferromagnetically coupled high spin species with $S = 10$ (Fig. 5). The $S = 0$ state with two Mn atoms possessing $S = +\frac{5}{2}$ and two

Mn atoms possessing the inverse spin $S = -\frac{5}{2}$ is the lowest in energy; the excited states are destabilized by 0.1 eV ($S = 5$) or 0.3 eV ($S = 10$), indicating a weak antiferromagnetic coupling *via* the μ₄-Te atom. This is in qualitative agreement with MnTe (NiAs structure) being an antiferromagnet,[13] and accords with experimental as well as theoretical investigations of the Se analogs;[3c] the coupling constant J of the telluride anions will have to be explored experimentally.

In this paper, we have presented a series of K⁺ or Rb⁺ salts of discrete M/Sn/Te anions and the Cs⁺ salt of a porous anionic Hg/Sn/Te network. Whereas the latter represents a so-called "zeotype" compound, the K/M/Sn/Te series comprises water-soluble compounds with a high contact surface in the solid state which might be of special interest for catalytic application[14] and will thus be the subject matter of our future research activities.

Notes and references

§ CCDC 616329–616334. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610833d

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