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Aqueous Telluridoindate Chemistry: Water-Soluble Salts of Monomeric, Dimeric, and Trimeric In/Te Anions $[InTe_4]^{5-}$, $[In_2Te_6]^{6-}$, and $[In_3Te_{10}]^{11-}$

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Water-soluble salts of monomeric, dimeric, and/or trimeric telluridoindate anions, $[K_5(H_2O)_{2.16}][InTe_4]$ (**1**), $[K_5(H_2O)_5][InTe_4]$ (**2**), $[K_6(H_2O)_6][In_2Te_6]$ (**3**), $[K_{16}(H_2O)_{9.62}][InTe_4]_2[In_2Te_6]$ (**4**), $[K_{133}(H_2O)_{24}][In_3Te_{10}]_{12}Te_{0.5}$ (**5**), and $[Rb_6(H_2O)_6][In_2Te_6]$ (**6**), were prepared by a fusion/extraction method starting from the elements and characterized by single-crystal X-ray diffraction as well as spectroscopic methods. The compounds are the first hydrates of telluridoindate salts and thus point toward an aqueous coordination chemistry with binary In/Te ligands. Both crystallization from the extracts as mixtures of salts as well as preliminary spectroscopic investigation of the solutions indicate the presence of an equilibrium of different anionic species. Here, the indates differ from related stannates, which also show pH-dependent aggregation, but to a much lesser extent and in a better distinguishable manner. We present syntheses and crystal structures and discuss observation of the coexistence of different anions both in the solid state and in solution.

Introduction

Indium chalcogenides possess many interesting properties, such as photocatalytic activity,[1] photoluminescence[2] and ion conductivity,[3] and have found technical application in the field of thin film solar cells, where doped variants of the chalcopyrite $CuInS_2$ hold the record of more than 19% in conversion efficiency.[4] They have been the subject of research since the turn of the last century,[5] and much effort has gone into the preparation of a diverse range of materials, from molecular salts[6] to extended, porous frameworks composed of large supertetrahedral clusters.[7] While indium sulfides have been the focus of attention in the last years, much less is known about the heavier congeners, the least about indium tellurides.

This is exemplified by the fact that, while anionic structures of composition transition metal (TM)/In/S have shown many interesting properties, no example of a similar structure containing TM/In/Te has been known up to now. So, building on the foundation of our experiences with the chemistry of chalcogenidotetrelates[8] and their reactions toward diverse ternary anionic structures, forming ternary clusters and networks of the general type $[TM_xT_yCh_z]^{q-}$ (T = tetrel = group 14 atom; Ch = chalcogen),[9] we attempted to establish a similar route employing telluridoindates. In order to achieve this, water- or alcohol-soluble precursors $[In_xTe_y]^{q-}$ were needed. Although one example of a

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Table 1. Data of the Single-Crystal X-ray Diffraction Analyses of Compounds **1−6**[a]

	1	**2**	**3**	**4**	**5**	**6**
empirical formula	$H_{4.32}InK_5O_{2.16}Te_4$	$H_{10}InK_5O_5Te_4$	$H_{12}In_2K_6O_6Te_6$	$H_{19.25}In_4K_{16}O_{9.62}Te_{14}$	$H_4In_3K_{11.08}O_2Te_{10.4}$	$H_{12}In_2O_6Rb_6Te_6$
fw (g mol^{-1})	859.72	910.80	1337.94	3044.68	2095.17	1616.16
cryst color/shape	yellow block	yellow block	yellow block	brown cube	black cube	yellow block
cryst size (mm^3)	0.06 × 0.05 × 0.04	0.18 × 0.05 × 0.03	0.08 × 0.08 × 0.02	0.05 × 0.05 × 0.05	0.12 × 0.1 2 × 0.06	0.15 × 0.12 × 0.11
cryst syst	monoclinic	orthorhombic	monoclinic	tetragonal	cubic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P4_2/mnm$	I m$\overline{3}$	$P2_1/c$
a (Å)	13.350(3)	8.788(3)	8.993(3)	16.325(4)	22.960(2)	8.881(3)
b (Å)	14.136(4)	11.111(4)	14.372(4)	16.325(4)	22.960(2)	9.693(3)
c (Å)	18.209(4)	20.156(5)	11.602(4)	22.777(5)	22.960(2)	18.728(4)
α (deg)	90	90	90	90	90	90
β (deg)	94.18(3)	90	118.62(3)	90	90	117.71(3)
γ (deg)	90	90	90	90	90	90
V (Å^3)	3427.2(14)	1968.1(11)	1316.3(7)	6070(2)	12104(2)	1427.3(7)
Z	8	4	2	4	12	2
ρ_{calcd} (g cm^{-3})	3.332	3.074	3.345	3.332	3.449	3.747
μ(Mo Kα) (mm^{-1})	9.242	8.066	9.225	9.218	9.963	17.799
abs corrn type	Gaussian	Gaussian	Gaussian	ψ scan	Gaussian	Gaussian
min/max transmn	0.4350/0.6186	0.368/0.794	0.465/0.804	0.411/0.842	0.23174/0.43131	0.052/0.203
max 2θ (deg)	51.82	53.36	51.44	50.00	51.92	53.50
reflns measd	23499	5314	10042	39416	6637	13637
R(int)	0.1090	0.0674	0.0365	0.1961	0.1287	0.1234
indep reflns	6636	3014	2799	2675	2120	3007
indep reflns [$I > 2\sigma(I)$]	4140	2825	2501	2432	867	2757
no, of param	221	126	91	111	74	91
$R1$ [$I > 2\sigma(I)$]	0.0443	0.0418	0.0236	0.0549	0.0709	0.0457
$wR2$ (all data)	0.0700	0.1736	0.0545	0.1381	0.1702	0.1178
S (all data)	0.914	1.046	1.023	0.919	0.818	1.030
res diff peak/hole (e·Å^{-3})	1.35/−1.45	2.80/−3.74	1.02/−1.16	3.44/−2.07	10.05/−4.85	2.36/−3.15

[a] The structures were solved and refined using *SHELXTL* software.[12]

sulfidoindate and its homologous selenidoindate hydrate has been reported,[10] the existence of telluridoindates in aqueous phase has been suggested by the works of O'Connor et al.[11] but has only been confirmed by elemental analysis so far. Using an extraction/evaporation route, similar to the one that we established for the generation of analogous selenidoindate[6h] or telluridostannate salts,[8b,c] we succeeded in the synthesis and characterization of the first telluridoindate hydrates, which are presented in this work.

Experimental Section

General Procedures. All synthesis steps were performed under an argon atmosphere. Water was degassed by applying a dynamic vacuum (1×10^{-3} mbar) for several hours. A_5InTe_4 (A = Na, K, Rb, Cs) was prepared according to a modified literature procedure.[11] Na_5InTe_4 was also prepared according to a different literature procedure.[6b]

Synthesis of [K_5InTe_4]. A total of 714 mg (18.3 mmol, 5 equiv) of potassium in small pieces and 3354 mg (29.2 mmol, 5 equiv) of indium powder were mixed and transferred to a quartz ampule. The mixture was fused by heating with a Bunsen burner, yielding the brittle, metallic material K_5In_8. K_5In_8 was ground into a fine black powder in a mortar, and 1864 mg (14.6 mmol, 4 equiv) of tellurium powder was added. Both powders were carefully mixed because the mixture is highly reactive and an exothermic reaction will set in even under strictly inert conditions if there is too much agitation. The mixture was transferred to a quartz ampule and fused to yield the bright-red material K_5InTe_4 and metallic indium fragments.

Synthesis of A_5InTe_4 (A = Na, Rb, Cs). The corresponding sodium, rubidium, and cesium materials were prepared in a fashion similar to that of K_5InTe_4.

Synthesis of [$K_5(H_2O)_{2.16}$][$InTe_4$] (1), [$K_5(H_2O)_5$][$InTe_4$] (2), [$K_6(H_2O)_6$][In_2Te_6] (3), [$K_{16}(H_2O)_{9.62}$][$InTe_4$]$_2$[In_2Te_6] (4), and [$K_{133}(H_2O)_{24}$][In_3Te_{10}]$_{12}Te_{0.5}$ (5). K_5InTe_4 was dissolved in water and filtered to yield a bright-yellow solution. The solvent was removed slowly to yield pale-yellow crystals of **1−3**. Upon standing, brown cubes of **4** and black, metallic cubes of **5** appeared within the mass of yellow crystals.

Synthesis of [$Rb_6(H_2O)_6$][In_2Te_6] (6). Rb_5InTe_4 was dissolved in water and filtered to yield a bright-yellow solution. Slow removal of the solvent yielded small yellow crystals of **6**.

Single-Crystal X-ray Diffraction. Data were collected on a diffractometer equipped with a STOE imaging-plate detector system IPDS2, using graphite-monochromized Mo Kα radiation (λ = 0.710 73 Å) at 100 K. Structure solution and refinement were performed by direct methods and full-matrix least squares on F^2, respectively, using *SHELXTL* software.[12] Table 1 summarizes the crystallographic data for **1−6**. Details of the refinements: **1**: refinement of K, In, and Te atomic positions employing anisotropic displacement parameters; refinement of O atomic positions employing isotropic displacement parameters; a disordered model was used to describe one O atom and another one was described by a partially occupied position; H atoms were not calculated. **2**: refinement of K, In, and Te atomic positions employing anisotropic displacement parameters; refinement of O atomic positions employing isotropic displacement parameters; a disordered model was used to describe one O atom; H atoms were not calculated. **3**: refinement of K, In, Te and O atomic positions employing anisotropic displacement parameters; H atoms were not calculated. **4**: refinement of K, In, and Te atomic positions employing anisotropic

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displacement parameters; refinement of O atomic positions employing isotropic displacement parameters; H atoms were not calculated. **5**: refinement of K, In, and Te atomic positions employing anisotropic displacement parameters; refinement of O atomic positions employing isotropic displacement parameters; a mixed-site refinement was used to describe occupation of the (0, 0, 0) lattice position by 0.5 equiv of K_2Te per formula unit; H atoms were not calculated. The residual electron densities of $+10.05$ and $-4.84\ e\cdot Å^{-3}$ are located about 1.61 and 0.62 Å from In2, respectively. This indicates that they are mainly artifacts of the cubic symmetry. Upon careful examination of the diffraction data, a larger cell may be found, which possibly represents the superstructure, taking into account the exact occupancy of the (0, 0, 0) site. Unfortunately, we have been unable to gain a structure solution from integration of this cell because of insufficient resolution. **6**: refinement of K, In, Te and O atomic positions employing anisotropic displacement parameters; H atoms were not calculated.

Spectroscopy. UV−vis spectra were recorded on a Perkin-Elmer Cary 5000 UV−vis−near-infrared spectrometer in the range of 800−200 nm employing a double-beam technique. The samples were prepared as suspensions in Nujol oil between two quartz plates.

Results and Discussion

Syntheses. A material of nominal composition K_5InTe_4 was prepared according to a modified literature procedure.[11] In the first step, potassium and indium were fused with a bunsen burner employing a ratio of 5:8. This yields the intermetallic phase K_5In_8, which is the only known one in the K/In system to melt congruously,[13] thus enabling us to get a homogeneous precursor. The resulting brittle, metallic material was finely ground and then mixed with 4 equiv of tellurium powder. This mixture was fused to yield K_5InTe_4 as a reddish powder and the superfluous indium as metallic fragments. K_5InTe_4 was then subjected to aqueous extraction and filtration to yield a bright-yellow solution. Upon slow removal of most of the solvent, pale-yellow crystals of a mixture of compounds **1**−**3** were obtained. Within several days, brown crystals of **4** appeared within the crystalline mass of **1**−**3**. Further standing resulted in the formation of **5** as intergrown, black cubes with a metallic sheen, as shown in Figure 1.

A similar procedure using rubidium instead of potassium resulted in a material of poor crystallinity, from which **6** was isolated in the form of very small, pale-yellow crystals. Employing cesium as the alkali-metal component yielded only material of insufficient crystallinity. In both cases, the formation of significant amounts of $RbInTe_2$ or $CsInTe_2$ could be observed. The only crystalline product that could be isolated from the analogous reaction sequence with sodium was a hydrate of sodium telluride. This could also be observed when employing Na_5InTe_4, which had been prepared by a different literature procedure.[6b]

The general procedure for the reaction employing potassium is shown in Scheme 1. The outlined studies of the influence of the cation on telluridoindate formation indicate that potassium is the ideal counterion for this system. A smaller ion like Na^+ appears to favor formation of the binary alkali-metal telluride, while bigger cations like Rb^+ and Cs^+ seem to induce rapid formation of the ternary phases of composition $AInTe_2$, which has also been observed for the material K_5InTe_4 upon subjection to extended periods of tempering. Yet, in every case, the resulting solid phase could be extracted to yield a yellow solution, an indication that telluridoindate species have formed at least to some extent in solution.

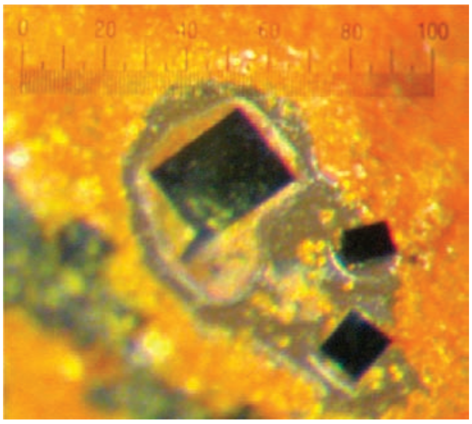

Figure 1. Black cubes of **5** and yellow crystals of compounds **1**−**3**.

Scheme 1. General Synthetic Fusion/Extraction Procedure for the Efficient Generation of Water-Soluble Telluridoindate Salts, Given for Potassium Compounds as an Example

$$5\ K + 8\ In \xrightarrow{\Delta} K_5In_8 \xrightarrow{+4Te,\ \Delta} 'K_5InTe_4' + 7\ In$$

$$'K_5InTe_4' \xrightarrow{H_2O} [In_xTe_y]^{q-}$$

Crystal Structures. All compounds were structurally characterized by means of single-crystal X-ray diffraction (see the Experimental Section). Selected bond lengths, angles, and coordination environments are summarized in Table S5 in the Supporting Information.

The structural aspects of compounds **1**−**3** are in accordance with known solvates such as $K_5InTe_4\cdot KCl$[6c] and $K_6In_2Te_6\cdot 4en$,[6f] yet their formation serves to illuminate several aspects of the aqueous chemistry of these anions, which has before only briefly been touched on and not been accompanied by the evidence of crystallographic data. They represent the first known hydrates of telluridoindates, prove the existence of molecular telluridoindates in aqueous solution, and give the indication that a more complicated equilibrium of telluridoindate species is present in solution than the mere dissolution of K_5InTe_4 into K^+ and $[InTe_4]^{5-}$.

The *ortho*-telluridoindate **1** crystallizes in the monoclinic space group $P2_1/c$ (No. 14). The main structural features are $[InTe_4]^{5-}$ tetrahedra, whose charge is compensated for by partially hydrated potassium ions (Figure 2a). The bond lengths and angles of compound **1** are very similar to those of the related solid phase Na_5InTe_4[6b] [In−Te bond lengths of 2.7660(13)−2.8566(12) Å in **1** and 2.758−2.811 Å in Na_5InTe_4; Te−In−Te angles of 103.27(4)−113.02(4)° in **1** and 104.9−114.5° in Na_5InTe_4]. The barycenters of the $[InTe_4]^{5-}$ tetrahedra form layers of distorted hexagons perpendicular to the crystallographic *b* axis, with an AB stacking order of the layers as enforced by the crystallographic symmetry (Figure 2b).

The closely related *ortho*-telluridoindate **2** (Figure 3a) crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19).

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(13) Thuemmel, R.; Klemm, W. *Z. Anorg. Allg. Chem.* **1970**, *376*, 44–63.

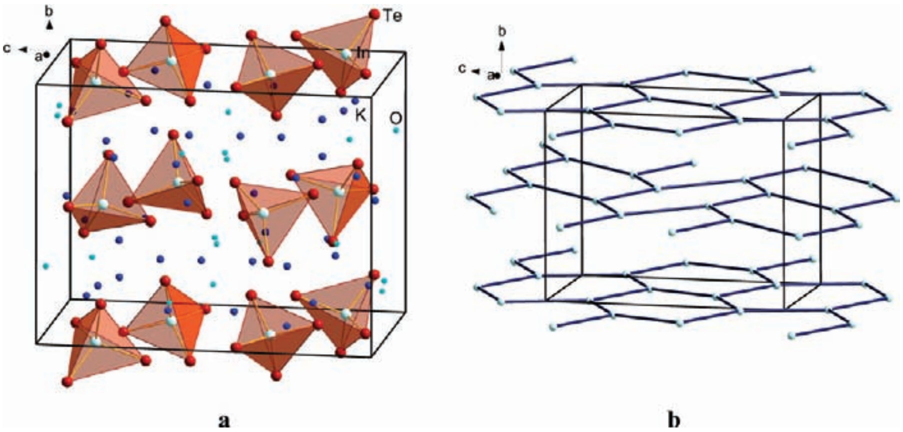

Figure 2. Fragment of the crystal structure in **1** (a) and representation of the arrangement topology of the $[InTe_4]^{5-}$ anions in **1**, illustrated by the position and connection of their barycenters (b).

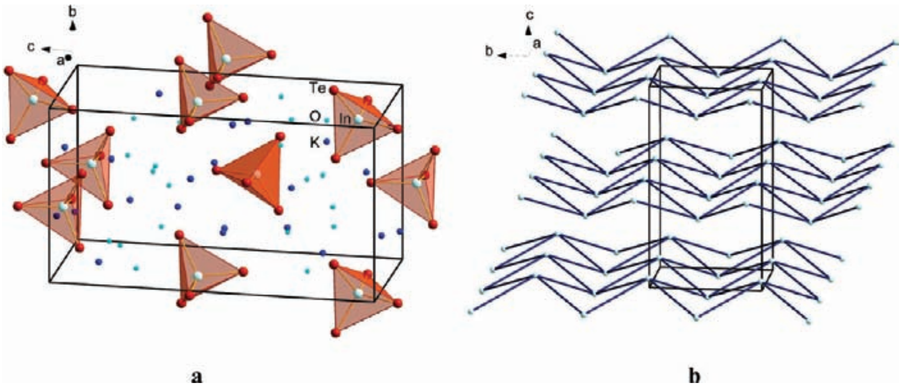

Figure 3. Fragment of the crystal structure in **2** (a) and representation of the arrangement topology of the $[InTe_4]^{5-}$ anions in **2**, illustrated by the position and connection of their barycenters (b).

Again, the bond lengths and angles are similar to those found in **1** and in Na_5InTe_4. As can be deduced from the sum formula, the degree of solvation of the potassium ions is greater than that in **1**. Curiously, as we have also found in our studies of the selenidoindates,[6h] more solvent molecules do not necessarily induce a reduction of the crystallographic symmetry but may instead afford a higher symmetry in the salt containing more solvent. In this compound, the barycenters of the anions form waved layers along the crystallographic *c* axis (Figure 3b). It seems remarkable that the anions in both **1** and **2** form layerlike structures within a similar range of distances between barycenters [6.9307(3)−7.9027(4) Å in **1** and 7.4045(9)−7.7899(10) Å in **2**]. This should result in a pronounced optical anisotropy and, because of the noncentrosymmetric symmetry adopted by **2**, possibly even nonlinear optical properties.

The dimeric telluridoindate **3** (Figure 4a) crystallizes in the monoclinic space group $P2_1/c$ (No. 14). The dimeric $[In_2Te_6]^{6-}$ anions have been reported in solid-phase structures as well as in the solvate $K_6In_2Te_6 \cdot 4en$. Unsurprisingly, the bond lengths and angles of the anion are similar in all three compounds. The potassium cations are only partly hydrated, affording a helical chain of potassium and water molecules along the *a* axis. The barycenters of the dimeric anions form a network of distorted, completely edge-sharing octahedra (Figure 4b).

4 represents the first known mixed chalcogenidoindate anion salt in the chemistry of chalcogenidoindates. It crystallizes in the tetragonal space group $P4_2/mnm$ (No. 136). **4** features *ortho*-telluridoindate anions as well as dimeric units, being in essence a less hydrated double salt of compounds **1** and **3** (Figure 5a). The barycenters of the dimeric units are located on the $(^1/_2, 0, 0)$ lattice position, forming a primitive tetragonal lattice that is interwoven by waved layers of the barycenters of the *o*-telluridoindate anions, occupying the lattice position (0.77322, 0.22678, 0.21819), similar to those in **2**, perpendicular to the crystallographic *c* axis (Figure 5b).

Compound **5** contains the previously unknown decatelluridotriindate anion $[In_3Te_{10}]^{11-}$, consisting of three corner-sharing $[InTe_4]$ tetrahedra (Figure 6). The formation of this species underlines yet again the diversity of the chemistry of the telluridoindates and their complex solution behavior. Yet, it is also remarkable for its low degree of condensation. In all multinuclear molecular chalcogenidoindate anions, the single $[InTe_4]$ tetrahedra are connected through edge or even face sharing. To find a related structure, one has to look as far up the periodic table as the oxoindates. Here, a tetrameric chain fragment of composition $K_{14}[In_4O_{13}]$ has been reported, which is made up of four corner-sharing InO_4 units.[14] Trimeric chains of conformation similar to that of $[In_3Te_{10}]^{11-}$ can

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[14] Lulei, M.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1818–1826.

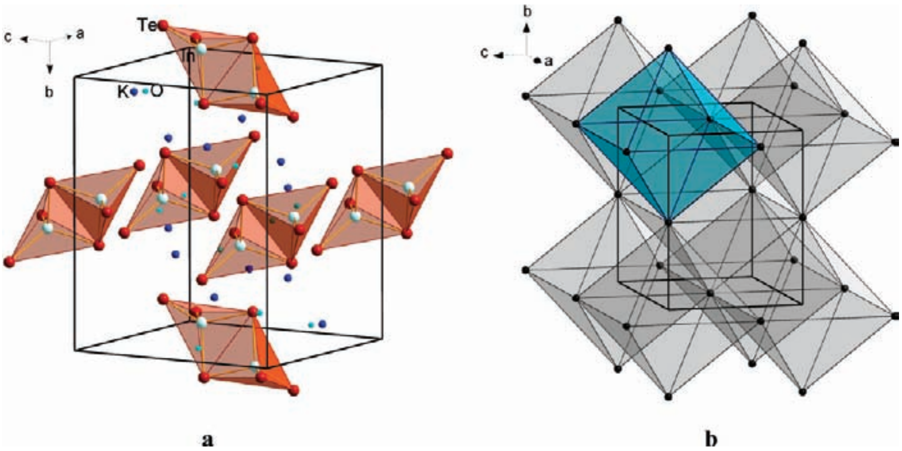

Figure 4. Fragment of the crystal structure in **3** (a) and representation of the arrangement topology of the $[In_2Te_6]^{6-}$ anions in **3**, illustrated by the position and connection of their barycenters (b).

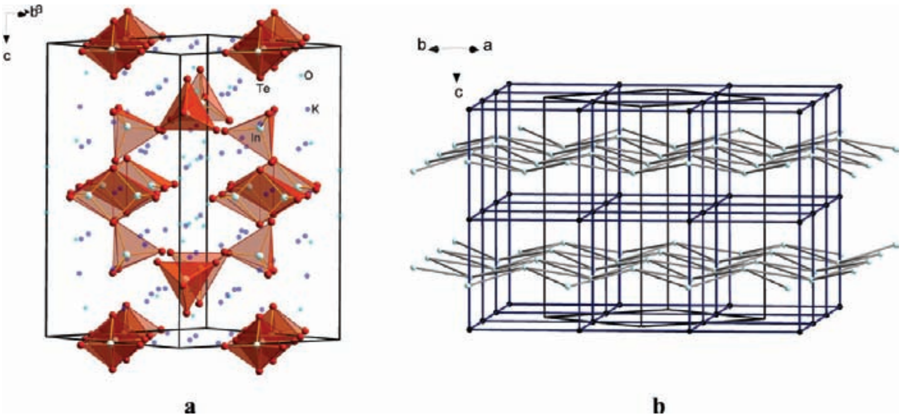

Figure 5. Fragment of the crystal structure in **4** (a) and representation of the arrangement topology of the $[InTe_4]^{5-}$ and $[In_2Te_6]^{6-}$ anions in **4**, illustrated by the position and connection (gray, $[InTe_4]^{5-}$; blue, $[In_2Te_6]^{6-}$) of their barycenters (b).

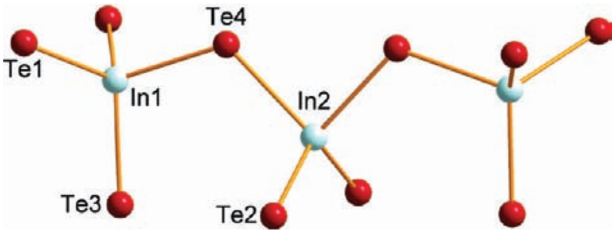

Figure 6. Molecular structure of the $[In_3Te_{10}]^{11-}$ anion in **5**.

be found in the chemistry of the silicates, namely, the mineral ardennite[15a] and the rare-earth silicate $Ho_4[Si_3O_{10}]$-$[SiO_4]$;[15b] further silicates containing the $[Si_3O_{10}]^{11-}$ unit, such as those of the fluorothalenite-type $M_3F[Si_3O_{10}]$,[16] prefer a horseshoe-type conformation of the trimer instead of a linear chain.

Yet, if the search for related structural motifs is broadened to extended anionic structures, an example from the chemistry of solid-state telluridoindates can be found. Here, the one-dimensional structure of $Na_5[InTe_3]_2$ gives an example of a polymeric chain of corner-sharing $[InTe_4]$ tetrahedra, although an additional condensation into double chains via Te−Te bonds is present here.[6b]

Compound **5** crystallizes in the cubic space group *Im*$\bar{3}$ (No. 204). Within the crystal lattice, the barycenters of the trimeric $[In_3Te_{10}]^{11-}$ units are arranged in an octahedral way around mixed sites containing one K and 0.5 Te atoms (Figure 7b). The mixed sites are a sign of a superstructure that we have not been able to account for in the structure solution because of the large cell size and the fact that potassium and a half-occupied tellurium position are indistinguishable as a result of equal electron numbers. Yet, we are sure that, while some uncertainty remains regarding the mixed sites, we were able to obtain an accurate picture of the main structural features of this compound.

Compound **6** (Figure 8a), which represents the first Rb^+ salt of the dimeric telluridoindate anion, crystallizes in the monoclinic space group $P2_1/c$ (No. 14). While compounds **6** and **3** show homologous compositions, and both contain dimeric telluridoindate units, the two are not isostructural. This is clearly illustrated by the arrangement of the barycenters of the dimeric units: As in **3**, a network of distorted, edge-sharing octahedra is formed, yet the distortion is much more pronounced in this case (Figure 8b), being better described as an arrangement of edge-sharing tetrahedra. Thus, the supramolecular

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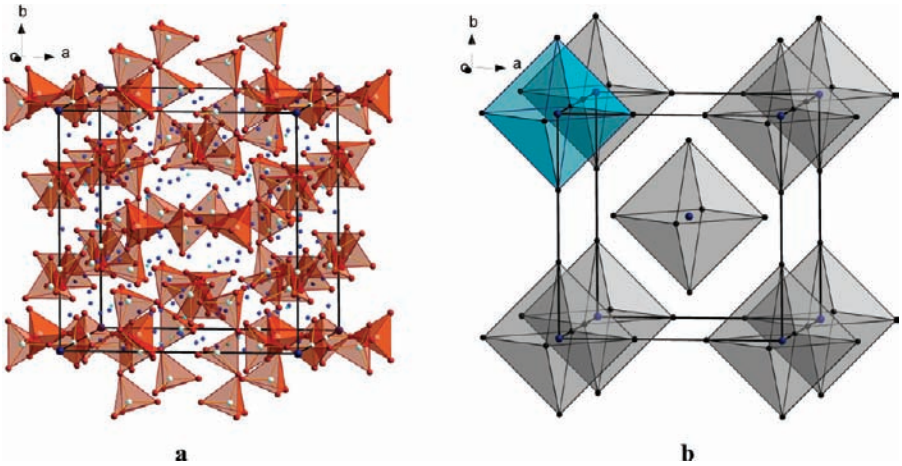

Figure 7. Fragment of the crystal structure in **5** (a) and representation of the arrangement topology of the $[In_3Te_{10}]^{11-}$ anions in **5**, illustrated by the position and connection of their barycenters (black), which form octahedra around the K atoms (blue) on (0, 0, 0) and symmetry-equivalent positions (b).

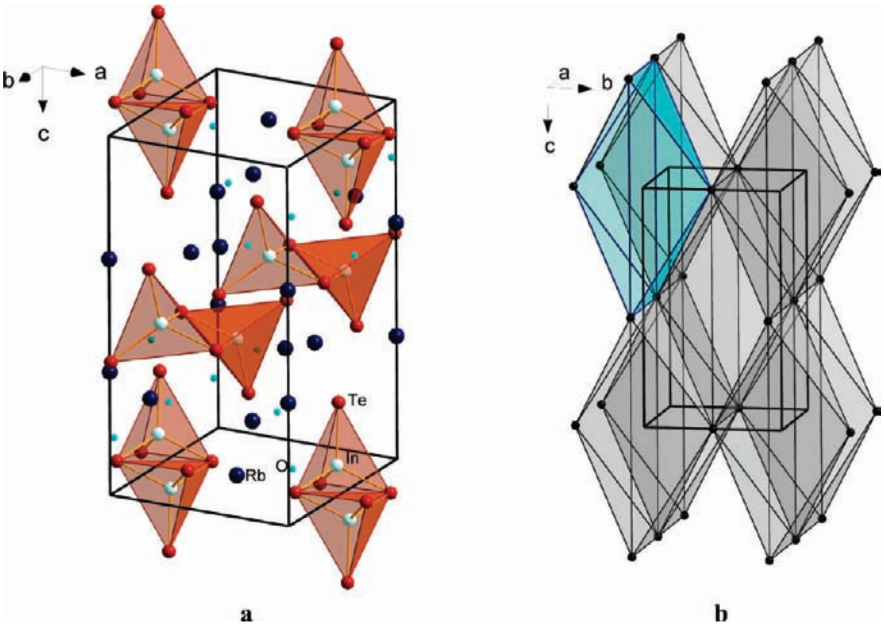

Figure 8. Fragment of the crystal structure in **5** (a) and representation of the arrangement topology of the $[In_3Te_{10}]^{11-}$ anions in **5**, illustrated by the position and connection of their barycenters (b).

arrangement of the anions self-resembles their molecular structure, a feature that was previously observed, for instance, at the crystal structure of the selenidogermanate salt $[K_4(H_2O)_3][Ge_2Se_6]$.[17]

The surprising number of different anions and corresponding telluridoindate salts that may be isolated from a single reaction mixture is in good accordance with similar observations in different areas of chalcogenidoindate chemistry[18] and gives further evidence to a trend that has already been noted in the chemistry of the borates in comparison with silicates:[19] the chalcogenidotrielates have a much broader phase width than their tetrelate analogues. Yet, while this has enabled us to isolate all of the above compounds using a single method, it also gives evidence to a complex equilibrium of anions in solution,

Scheme 2. Possible Condensation Pathways for Telluridoindate Anions in Solution

$$[InTe_4]^{5-} + [In_2Te_6]^{6-} \rightleftarrows [In_3Te_{10}]^{11-}$$

$$2[InTe_4]^{5-} \rightleftarrows [In_2Te_6]^{6-} + 2\,Te^{2-}$$

as depicted in Scheme 2. This has thus far hindered the isolation of the products of further reactions of the telluridoindate anions with TM cations toward multinary clusters by leading to complex reaction mixtures with little tendency to crystallize. We intended to explore the behavior in solution by ^{125}Te NMR spectroscopy; however, probably because of the high quadrupole moment of indium,[20] only very tentative results were obtained, which are summarized in the Supporting Information.

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[20] ^{115}In, 95.7%, $I = {}^{9}/_{2}$, $\Xi = 21.914$ MHz, $Q = 1.16 \times 10^{-28}$ m^2, $D_c = 1890$: Mason, J. *Multinuclear NMR*; Plenum: New York, 1987.

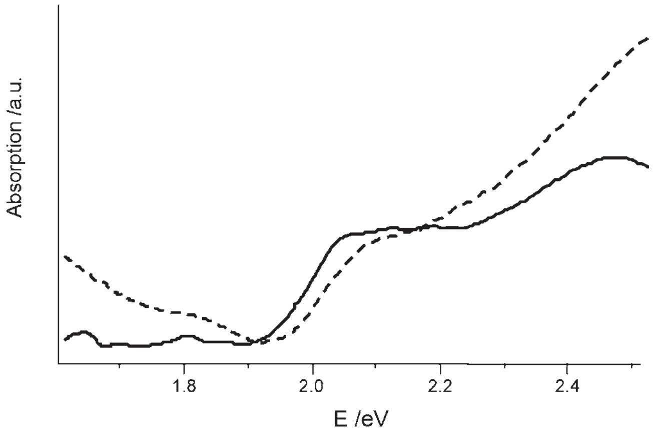

Figure 9. Solid-state UV−vis spectra of as-prepared K_5InTe_5 (solid line) and of a mixture of as-prepared compounds **1**−**4** (dashed line), recorded from suspensions of the solid material in Nujol oil.

Optical Absorption Behavior. We have investigated the optical absorption behavior of the title compounds by measuring solid-state absorption spectra of the starting material K_5InTe_4 and of compound **1** (Figure 9). As outlined above, the salts have a high tendency for cocrystallization. Thus, the sample of **1** also contains nonnegligible amounts of **2**−**4**, which is reflected in the UV−vis spectrum. Both lines show an onset of absorption between 1.92 eV (K_5InTe_4) or 1.96 eV (**1**−**4**) and 2.01 eV (K_5InTe_4) or 2.09 eV (**1**−**4**) before reaching a small plateau. This corresponds well with the visible dark-red and brownish color of K_5InTe_5 and compound **4**, respectively. The mixture of the latter with yellow compounds **1**−**3** is, however, reflected in the stronger increase of absorption in the UV region when compared to the starting material. The excitations are presumably based on Te(5p) → In(5p) charge transfer. The color of compounds **1**−**3** corresponds well with the prior findings of O'Connor et al.,[11] indicating that K_5InTe_4 dissolves to give "an orange solution". The reddish color of K_5InTe_4 is in accordance with the color of Na_5InTe_4 described by Eisenmann et al.[6b] In agreement with the decreasing band gap going from In_2Se_3 (1.3−1.8 eV, depending on its modification)[21] to In_2Te_3 (1.2 eV),[22] there is a deepening of color going from the selenidoindate hydrates, which are colorless even as tetrameric aggregates,[6h] to the telluridoindate hydrates, whose color ranges from yellow for the monomeric and dimeric anions to black for the trimeric one.

Conclusions and Outlook

In summary, we have succeeded in preparing the first telluridoindate hydrates from the solid-state material K_5InTe_4 via a simple extraction and evaporation route. The obtained structural motifs range from single $[InTe_4]^{5-}$ tetrahedra through the classic dimeric $[In_2Te_6]^{6-}$ unit to the previously unknown trimeric $[In_3Te_{10}]^{11-}$ anion. Our findings point toward a complex equilibrium in aqueous solution, which is also reflected by a strong tendency for the cocrystallization of different $K_x[In_yTe_z]$ salts in one single-crystalline compound. Although "neighbors" in the periodic system, this is in contrast to all observations concerning stannate chemistry but is in agreement with the phase width of borates. The coexistence of different anions in solution has thus far hindered the selective utilization of the $[InTe_4]^{5-}$ anion as a starting material for the preparation of multinary cluster compounds, such as was previously reported for chalcogenidostannte anions. Therefore, we are now aiming to use these building blocks by employing different reaction conditions, like other solvents or solvothermal reaction techniques, to obtain multinary materials.

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Supporting Information Available: CIFs for **1**−**6**, structural details of **1**−**6** (Table S5), and ^{125}Te NMR and Raman spectroscopy along with corresponding quantum chemical investigations. This material is available free of charge via the Internet at http://pubs.acs.org.

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