Syntheses and Crystal Structures of the Two New Polychalcogenides $[Mn(C_6H_{14}N_2)_3]Se_6$ and $[Mn(C_6H_{14}N_2)_3]_2[C_6H_{16}N_2](TeSe_2)_2Se$

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Dedicated to Prof. Dr. G.-V. Röschenthaler on the occasion of his 60th birthday

The solvothermal reaction of $MnCl_2 \cdot 4\ H_2O$, K_2Se_3 and Se in *trans*-cyclohexane-1,2-diamine (chxn) at 433 K yields dark blue crystals of $[Mn(chxn)_3]Se_6$ (**1**), and the reaction of $MnCl_2 \cdot 4\ H_2O$, K_2Se_3 and Te under similar conditions gives dark blue crystals of $[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$ (**2**). While compound (**1**) crystallises in the orthorhombic space group *Pbcn* with the lattice parameters $a = 13.7017(9)$, $b = 19.9073(8)$ and $c = 10.8058(5)$ Å, compound (**2**) crystallises in the monoclinic space group $P2_1$ with the lattice parameters $a = 9.4396(6)$, $b = 24.2450(2)$, $c = 12.8170(8)$ Å and $\beta = 91.6(1)^\circ$. In both structures discrete complex cations and polychalcogenide anions are found. In (**1**) the Se_6^{2-} anions form a pseudo-layer arrangement with nearly rectangular pores. The complex cations are encapsulated by the arrangement of the Se_6^{2-} anions. Some short distances between the amino groups of the ligands and the anions indicate weak hydrogen bonding. In compound (**2**) two independent $[Mn(chxn)_3]^{2+}$ and one unique H_2chxn dications, two unique $TeSe_2^{2-}$ as well as one Se^{2-} dianion coexist. The two complex cations exhibit different conformations. One of the two $TeSe_2^{2-}$ anions has the di-protonated chxn molecule in the neighbourhood and short Se···H separations indicate weak hydrogen bonding. The isolated Se^{2-} ion is located above the ring of the di-protonated *trans*-cyclohexane-1,2-diamine molecule and again a short Se···H separation may be due to a weak hydrogen bond. Compound (**1**) decomposes in a single step when heated in an Ar atmosphere. In contrast, the thermal decomposition of compound (**2**) is complex and at least five different steps can be identified.

Key words: Solvothermal Synthesis, Polychalcogenides, Selenides, Telluroselenides, Thermal Decomposition

Introduction

For the synthesis of polychalcogenide anions the solvothermal method is a suitable route. In selenium and tellurium chemistry, *e. g.*, reacting suitable starting compounds at temperatures ranging from 363 – 455 K under an autogenous pressure of $10^5 - 10^6$ Pa for several days in a Teflon-lined autoclave or a glass ampoule can give pure and mixed polyselenides and polytellurides. Examples reported in the literature are $[Mn(en)_3]Se_3$ and $[Mn(en)_3]TeSe_2$ [1] and $[Mn(en)_3]Te_4$ [2, 3]. These compounds were synthesised using ethylene-1,2-diamine (en) as the solvent and chelating amine.

One aspect investigated during our work is the influence of the cation size onto the length of the polychalcogenide anions formed. One would assume that the size and arrangement of the ammonium cations or of complex cations should affect the nature of the polychalcogenide anions. In 1987 Dehnicke *et al.* [4] showed that isolated tetraalkylammonium cations ($N(C_2H_5)_4$, R–$N(CH_3)_3$, R = $C_{16}H_{33}$, $C_{14}H_{29}$, $C_{12}H_{25}$) had no predictable effect on the size and structure of the polyselenide anions in the crystalline products. Judging by the wealth of hexaselenides reported in the literature [4 – 8] the Se_6^{2-} anion seems to represent the most stable of the polyselenide anions. It is noteworthy that no Se_n^{2-} anion longer than the nonaselenide Se_9^{2-} has been synthesised yet. We note that the two compounds presented here are the first $[Mn(chxn)_3]^{2+}$ complexes and the first chalcogenides with a $[M(chxn)_3]^{n+}$ counter cation.

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Table 1. Selected bond lengths [Å] and angles [°] in $[Mn(chxn)_3]Se_6$ (**1**). Estimated standard deviations are given in parentheses.

Se(1)–Se(2)	2.3129(5)	Se(1)–Se(3)	2.3403(6)
Se(3)–Se(3A)	2.3602(8)		
Mn–N(1)	2.238(3)	Mn–N(1A)	2.238(3)
Mn–N(2A)	2.246(2)	Mn–N(2)	2.246(2)
Mn–N(3)	2.322(2)	Mn–N(3A)	2.322(2)
Se(2)–Se(1)–Se(3)	108.32(2)	Se(1)–Se(3)–Se(3A)	106.08(2)
N(1)–Mn–N(1A)	155.2(2)	N(1)–Mn–N(2A)	100.1(1)
N(1A)–Mn–N(2A)	99.1(1)	N(1)–Mn–N(2)	99.1(1)
N(1A)–Mn–N(2)	100.1(1)	N(2A)–Mn–N(2)	77.6(2)
N(1)–Mn–N(3)	88.9(1)	N(1A)–Mn–N(3)	75.9(1)
N(2A)–Mn–N(3)	165.1(1)	N(2)–Mn–N(3)	89.4(1)
N(1)–Mn–N(3A)	75.9(1)	N(1A)–Mn–N(3)	88.9(1)
N(2A)–Mn–N(3)	89.4(1)	N(2)–Mn–N(3A)	165.1(1)
N(3)–Mn–N(3A)	104.4(2)		

Experimental Section

Syntheses

Dark blue plate like crystals of $[Mn(chxn)_3]Se_6$ (**1**) (estimated yield 60% based on Mn) were obtained from the reaction of 0.198 g $MnCl_2 \cdot 4H_2O$, 0.315 g K_2Se_3 and 0.079 g Se (molar ratio 1:1:3) in 2 ml of *trans*-cyclohexane-1,2-diamine at 433 K heated for 7 d. The product was washed with ethanol and dried in a vacuum. The crystals are not stable on air and decompose within 2 weeks.

The reaction of 0.06 g $MnCl_2 \cdot 4H_2O$, 0.095 g K_2Se_3 and 0.115 g Te (molar ratio 1:1:3) in 2 ml of *trans*-cyclohexane-1,2-diamine at 433 K for 7 d gave dark blue polyhedra of **2** (estimated yield 70% based on Mn). The product was washed with ethanol and dried in a vacuum. Using K_2Se_3 and Te, crystals of $[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$ (**2**) were also formed. The compound is not stable on air and decomposes within 2 weeks. The composition was confirmed by C, H, N analysis and AAS (C calculated 32.31%, found 32.15%; H calculated 6.46%, found 6.23%; N calculated 12.56%, found 12.93%, C:N ratio calculated 2.57, found 2.49; calculated Mn:Se ratio 1:2.5, found 1:2.57).

Structure refinement details

Single crystal X-ray diffractometry: The intensities were collected using a STOE IPDS I diffractometer (λ = 0.7107 Å). The data were corrected for Lorentz and polarisation effects and face indexed absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined with fixed isotropic displacement parameters. In $[Mn(chxn)_3]_2(TeSe_2)_2Se{\cdot}H_2chxn$ (2) the N(13) atom is disordered into two positions and was refined using a split model. The crystal was a racemic twin and refined with a BASF parameter of 0.35(1). The non-centrosymmetry of the structure can clearly be seen in the arrangement of the molecules within the unit cell. Experimental details of data collections and selected refinement results are summarised in Table 3.

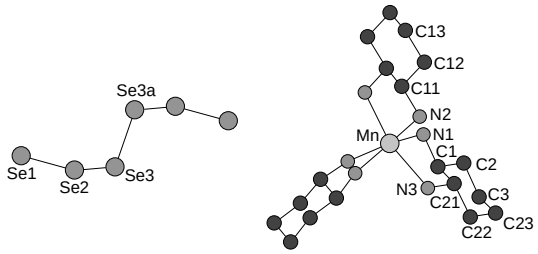

Fig. 1. The Se_6^{2-} anion (left) and the $[Mn(chxn)_3]^{2+}$ cation (right) in compound **1** with atomic labelling. (Hydrogen atoms are omitted for clarity.)

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 230932 for $[Mn(chxn)_3]Se_6$ and CCDC 230931 for $[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

X-ray powder diffractometry

The X-ray powder patterns were recorded with a Siemens D5000 (Cu-K_α radiation, $\lambda = 1.54056$ Å) in Bragg-Brentano geometry.

Thermal analysis

The DTA-TG data were recorded using a Netzsch STA 429 instrument. All measurements were performed under an argon atmosphere in alumina crucibles using Al_2O_3 as the inert reference. Heating rate: 3 K/min.

Results and Discussion

Crystal structures

The compound tris(*trans*-cyclohexane-1,2-diamine)-manganese-hexaselenide (**1**) crystallises in the orthorhombic space group *Pbcn* with four formula units in the unit cell. The crystal structure consists of isolated $[Mn(chxn)_3]^{2+}$ cations and Se_6^{2-} anions each of these being located on centres of inversion. The Mn^{2+} ion is in an octahedral environment of six nitrogen atoms of three amine molecules with Mn−N distances between 2.238(3) and 2.322(2) Å (Fig. 1, Table 1). The Mn-N bond lengths are in the range reported in

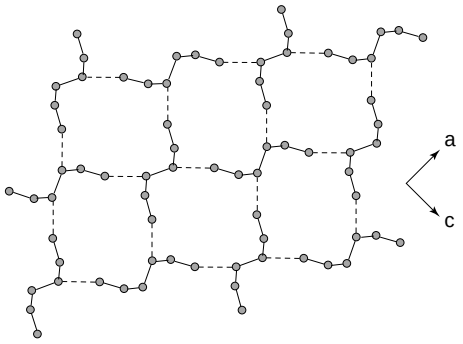

Fig. 2. The pseudo-layers formed by intermolecular Se(1)···Se(1) contacts between neighbouring Se_6^{2-} anions in compound **1**. Dotted lines are the long Se-Se separations.

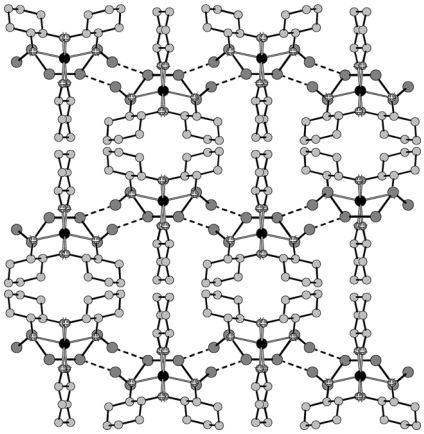

Fig. 3. Crystal structure of compound **1** with view along the c-axis. (Hydrogen atoms are omitted for clarity.) Dotted lines indicate the long Se-Se contacts.

the literature [9 – 11]. The N-Mn-N angles indicate a relatively strong distortion from ideal octahedral geometry (Table 1). The Se–Se bond lengths within the Se_6^{2-} chain (Fig. 1) vary from 2.3129(5) (terminal Se(1)–Se(2)) to 2.3602(8) Å (internal Se(3)–Se(3a)). The angles are 108.32(2)° for Se(2)–Se(1)–Se(3) and 106.08(2)° for Se(1)–Se(3)–Se(3a). These values are comparable with those found in other hexa-selenides [5 – 8]. Between the anions the shortest separation is 3.618 Å (Se(1)-Se(3)) which is slightly smaller than the sum of the van der Waals radii (3.80 Å). When these Se···Se contacts are taken into account two-dimensional layers with large nearly rectangular pores formed by rings of 14 Se atoms present in the (010) plane (Fig. 2). The dimensions of the pores are about 8.9·8.5 Å. The pores are filled with the $[Mn(chxn)_3]^{2+}$ cations with the central Mn^{2+} ion residing within the

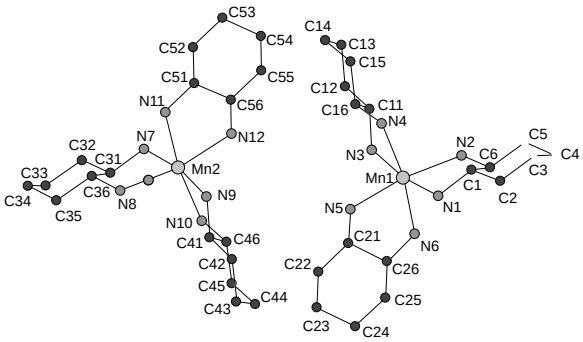

Fig. 4. The two cations in $[Mn(C_6H_{14}N_2)_3]_2[C_6H_{16}N_2](TeSe_2)_2Se$ (**2**) with atomic labelling.

plane of the pores and the ligands pointing outwards (Fig. 3). The layers are stacked perpendicular to [010] with a shortest interlayer separation of 9 Å. The terminal Se(1) atom has two relatively short contacts to H atoms of the amino groups of 2.61 and 2.66 Å with corresponding angles of 158.6° and 170.5°. The arrangement of the cations and anions may be viewed as an encapsulation of the $[Mn(chxn)_3]^{2+}$ cations by the Se_6^{2-} anions.

Compound **2** crystallises in the monoclinic space group $P2_1$ with two formula units in the cell. Two crystallographically independent $[Mn(chxn)_3]^{2+}$ cations, two crystallographically independent Se_6^{2-} anions, one selenide anion and one di-protonated ligand are found, and all are located in general positions. The two crystallographically independent Mn^{2+} cations are each sixfold coordinated by the nitrogen atoms of three 1,2-cyclohexanediamine molecules (Fig. 4), and the complex cations show the lel^3-$\lambda(\lambda\delta\delta)$ and lel^3-$(\lambda\lambda\delta)$ conformation. The Mn–N distances are between 2.227(5) and 2.284(5) Å for Mn(1) and range from 2.254(5) to 2.291(5) Å for Mn(2), being comparable with the values found in **1** and in [9 – 11]. Again, the N-Mn-N angles indicate a rather strong distortion of the octahedral environment (Table 2). The Se–Te distances between 2.4781(8) and 2.4888(8) Å and Se–Te–Se angles of 106.44(3) and 109.41(3)° (Table 2) found in the two distinct V-shaped $TeSe_2^{2-}$ anions are in the range observed for other isolated $TeSe_2^{2-}$ anions [1, 12].

The shortest separations between the $TeSe_2^{2-}$ anions amount to 5.529 (Se(2)···Se(3)) and 5.480 Å (Se(1)···Se(4)) which are shorter than the distance of 6.029 Å found in $[Mn(en)_3]TeSe_2$ [1]. The two different $TeSe_2^{2-}$ anions are stacked in rods along [100],

Table 2. Selected bond lengths (Å) and angles [°] in $[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$ (**2**). Estimated standard deviations are given in parentheses.

Te(1)–Se(1)	2.478(1)	Te(1)–Se(2)	2.480(1)
Te(2)–Se(4)	2.483(1)	Te(2)–Se(3)	2.489(1)
Mn(1)–N(5)	2.227(5)	Mn(1)–N(6)	2.256(5)
Mn(1)–N(2)	2.262(5)	Mn(1)–N(4)	2.265(6)
Mn(1)–N(1)	2.275(5)	Mn(1)–N(3)	2.284(5)
Mn(2)–N(12)	2.254(5)	Mn(2)–N(8)	2.258(5)
Mn(2)–N(11)	2.261(5)	Mn(2)–N(10)	2.272(5)
Mn(2)–N(7)	2.286(5)	Mn(2)–N(9)	2.291(5)
Se(1)–Te(1)–Se(2)	106.44(3)	Se(4)–Te(2)–Se(3)	109.41(3)
N(5)–Mn(1)–N(6)	79.3(2)	N(5)–Mn(1)–N(4)	92.6(2)
N(5)–Mn(1)–N(6)	79.3(2)	N(5)–Mn(1)–N(2)	170.4(2)
N(6)–Mn(1)–N(2)	93.0(2)	N(5)–Mn(1)–N(4)	92.4(2)
N(6)–Mn(1)–N(4)	170.3(2)	N(2)–Mn(1)–N(4)	95.8(2)
N(5)–Mn(1)–N(1)	97.3(2)	N(6)–Mn(1)–N(1)	90.3(2)
N(2)–Mn(1)–N(1)	76.9(2)	N(4)–Mn(1)–N(1)	95.8(2)
N(5)–Mn(1)–N(3)	89.2(2)	N(6)–Mn(1)–N(3)	98.1(2)
N(2)–Mn(1)–N(3)	97.6(2)	N(4)–Mn(1)–N(3)	76.7(2)
N(1)–Mn(1)–N(3)	170.3(2)		
N(12)–Mn(2)–N(8)	169.4(2)	N(12)–Mn(2)–N(11)	79.0(2)
N(8)–Mn(2)–N(11)	91.7(2)	N(12)–Mn(2)–N(10)	93.2(2)
N(8)–Mn(2)–N(10)	96.5(2)	N(11)–Mn(2)–N(10)	170.5(2)
N(12)–Mn(2)–N(7)	96.9(2)	N(8)–Mn(2)–N(7)	78.2(2)
N(11)–Mn(2)–N(7)	91.3(2)	N(10)–Mn(2)–N(7)	95.0(2)
N(12)–Mn(2)–N(9)	92.4(2)	N(8)–Mn(2)–N(9)	93.7(2)
N(11)–Mn(2)–N(9)	96.5(2)	N(10)–Mn(2)–N(9)	78.3(2)
N(7)–Mn(2)–N(9)	168.9(2)		

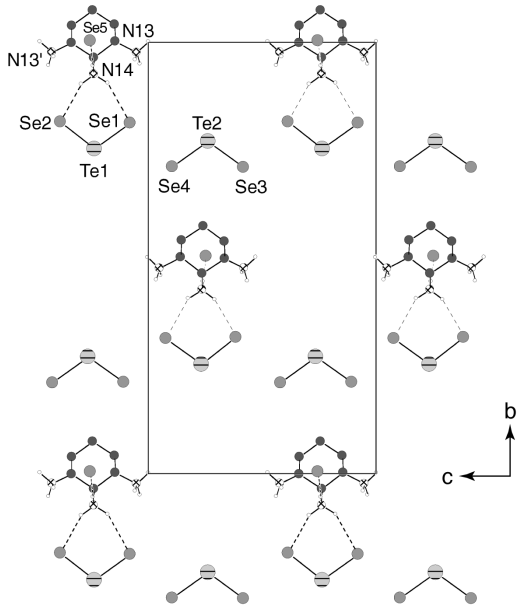

Fig. 5. Packing of the di-protonated *trans*-cyclohexane-1,2-diamine molecules, the $TeSe_2^{2-}$ and Se^{2-} anions showing Se···H contacts in compound (**2**). The nitrogen atom N13 is disordered in two positions and the C-H hydrogen atoms are omitted for clarity.

with an identical orientation within the rods and an alternating orientation in neighbouring rods. The shortest distance between the isolated Se^{2-} anion and a Se atom of the $TeSe_2^{2-}$ anion amounts to 5.978 Å.

Charge neutrality of the compound requires that the isolated *trans*-cyclohexane-1,2-diamine molecule is di-protonated. The Se atoms of only one of the $TeSe_2^{2-}$ anions (Te(1), Se(1), Se(2)) and the isolated Se^{2-} ion (Se(5)) have relatively short contacts to the H atoms of the amino groups of the *trans*-cyclohexane-1,2-diammonium cation. The arrangement of the anions around the ammonium cation is displayed in Fig. 5. All cations point into the same direction which can be regarded as an evidence for the non-centrosymmetry of the structure. Two of the three H atoms of N(14) have a contact to one Se atom of one $TeSe_2^{2-}$ anion (Se(1)-H28N: 2.597 Å; Se(2)-H29N: 2.533 Å). As expected the H atoms point towards the lone-pairs of Se(1) resp. Se(2). The third H atom makes a short contact to the isolated Se^{2-} anion (Se(5)-H30N: 2.498 Å). Obviously, there is no ammonium cation in the neighbourhood of the second $TeSe_2^{2-}$ anion which can act as a donor for hydrogen bonds. Because the H atoms of N13 have no contacts to acceptors they are disordered and both orientations are energetically more or less identical.

Thermal properties

Single crystals of $[Mn(chxn)_3]Se_6$ were heated up to 873 K in an argon atmosphere. The sample decomposed in one step, accompanied by a mass loss of 34.9% (calculated mass loss for the three amine molecules is 39.3%). In the grey product obtained after the treatment MnSe could be identified with X-ray powder diffraction. According to the C, N, H analysis only traces of organic material are present. Hence, it must be assumed that amorphous elemental Se is present in the residue explaining the difference between the expected and measured mass change.

A SEM-EDX-analysis of the decomposition product showed three different phases: octahedral-like crystals with composition MnSe, ellipsoidal and shapeless crystals which both are selenium-rich.

A more complex behaviour was found for $[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$. Upon heating single crystals in an argon atmosphere decomposition occured in at least five not well separated steps (Fig. 6),

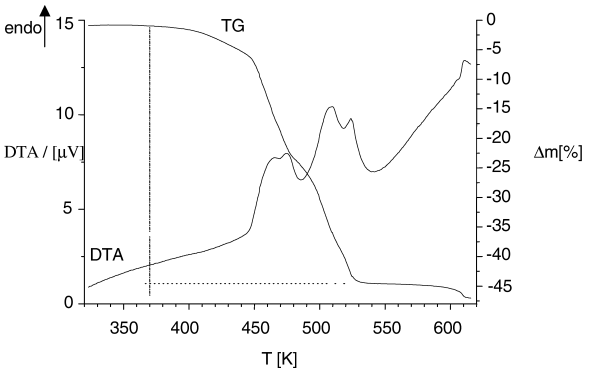

Fig. 6. DTA-TG curves for $[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$ (**2**) in argon atmosphere.

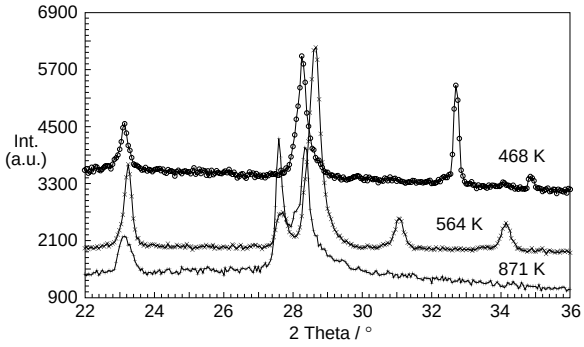

Fig. 7. X-ray powder patterns of the decomposition products of $[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$ (**2**) after heating the sample to 468 K (first trace), to 564 K (second trace) and to 871 K. Note that the patterns are shifted on the intensity scale for clarity.

each step being accompanied by an endothermic signal in the DTA curve. The total mass loss of 45.9% is about 10% lower than expected assuming a decomposition according to equation (1) (expected: 56.3%).

$$[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se \rightarrow 2\,MnSe_2 + 2\,Te + H_2Se\uparrow + 7\,C_6H_{14}N_2\uparrow \quad (1)$$

To acquire more information about this complex thermal decomposition, several experiments were conducted where the heat treatment was stopped after each reaction step. The resolution of individual steps is not good and the assignment of distinct temperatures to each step is somewhat arbitrary. The products were analysed by X-ray powder diffractometry.

A selected region of the X-ray powder patterns (XPD) recorded after quenching samples from 468 K, 564 K and 871 K are displayed in Fig. 7. The background of the patterns recorded below 564 K is strongly modulated in the range from about 10 to 40° 2θ. In this 2θ range the most intense reflections of the different modifications of elemental Se and Te are located. The main difficulty for a definite assignment of the reflections is that different manganese selenides and tellurides as well as elemental Se and Te show the strongest reflections in the region between 20 and 40° 2θ. In addition, the formation of crystalline Te/Se solid solutions makes the assignment more difficult. Therefore, we can only qualitatively discuss the changes of the X-ray powder patterns. After the first thermal event (468 K) the XPD shows the reflections of elemental Te and one intense peak at about 28.3° 2θ which cannot be explained considering simple compounds like MnTe, MnSe, Se or $MnSe_2$. In the XPD of the reactions stopped after 475 and 500 K only small alterations are seen compared to that obtained after the first stop. Interestingly, in the pattern of the residue obtained at 564 K the background is more flat and two new reflections occur between 30 and 40° 2θ which match well with the most intense peaks of $MnSe_2$. We note that the formation of $MnSe_2$ and elemental Te is known from the thermal decomposition of $[Mn(en)_3]TeSe_2$ [1]. In addition, the intensity ratio of the "doublet" around 28 – 30° 2θ has drastically changed and the reflection at about 38.3° 2θ has disappeared. In the pattern of the grey material obtained at 871 K several reflections can be explained with crystalline MnSe, but the remaining peaks do not match with Te, Se or other Mn chalcogenides. It cannot be excluded that at this temperature reactions within the genuine material lead to the formation of unknown Mn compounds. From the literature it is known that the decomposition of $MnSe_2$ into MnSe starts at 863 K in vacuum which takes between 2 and 5 days until completion. At 948 K complete decomposition was observed [13].

In summary, the decomposition process of **2** is complex with the experimental mass loss significantly smaller than expected. The changes in the XPD provide also evidence for the complex nature of the thermal reactions. Further experiments using mass spectrometry are required to acquire a better understanding of the thermal degradation of the material.

In the introduction we mentioned that one aim of our study is the investigation of the influence of the size of the cation onto the polychalcogenide chain length. Using the *in situ* formed $[Mn(en)_3]^{2+}$ cation

Table 3. Crystallographic data, details of the data collection and selected results of the structure refinement for $[Mn(chxn)_3]Se_6$ (**1**) and $[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$ (**2**). Estimated standard deviations are given in parentheses.

	$[Mn(chxn)_3]Se_6$ (**1**)	$[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$ (**2**)
Lattice parameters	$a = 13.7017(9)$ Å	$a = 9.4396(6)$ Å
	$b = 19.9073(8)$ Å	$b = 24.2450(2)$ Å
	$c = 10.8058(5)$ Å	$c = 12.8170(8)$ Å
		$\beta = 91.6(1)$
Unit cell volume/Å^3	2947.4(3)	2932.3(3)
Crystal system, space group	orthorhombic, *Pbcn*	monoclinic, $P2_1$
Formula units per unit cell	4	2
Density (calculated)/ g·cm^3	1.963	1.768
μ/mm^{-1}	7.88	4.55
Scan range	$4^\circ \leq 2\theta \leq 56^\circ$	$3^\circ \leq 2\theta \leq 52^\circ$
Temperature of data collection	150 K	150 K
No. refined parameters	142	590
Reflections measured	15536	21249
Independent reflections	3421	10653
Independent with $F_o > 4\sigma(F_o)$	2908	9623
R_{int}	0.0774	0.0286
Min./max. transmission	0.1183/0.4270	0.4207/0.6178
$R1$ ($F_o > 4\sigma(F_o)$)	0.0362	0.0429
$R1$ (all)	0.0447	0.0480
$wR2$ ($F_o > 4(F_o)$)	0.0893	0.1175
$wR2$ (all)	0.0938	0.1217
ΔF/e$^-$/Å^3	$1.57/-1.28$	$1.96/-1.13$

and applying K_2Se_3/Se or K_2Te_3/Se mixtures, well separated Se_3^{2-} resp. $TeSe_2^{2-}$ anions are observed in the products. Under similar conditions and using K_2Te_3/Te as the chalcogenide source, the compound $[Mn(en)_3]Te_4$ is formed with Te_4^{2-} anions which form infinite chains through interchain interactions [1]. With the larger $[Mn(chxn)]^{2+}$ cation the reaction with K_2Se_3/Se leads to the formation of $[Mn(chxn)_3]Se_6$ with the Se_6^{2-} anion which shows weak inter-anionic interactions in a two-dimensional arrangement. With the same cation, and using K_2Te_3/Se, the compound $[Mn(chxn)_3]_2[H_2chxn](TeSe_2)_2Se$ is obtained with isolated anions. Attempted syntheses with $MnCl_2 \cdot 4H_2O$, K_2Te_3/Te in a solution of chxn were unsuccessful and only amorphous powders were formed. Hence, the results of the present study as well as of previously published work demonstrate that there is no simple relation between cation size and the final polychalcogenide chain lengths. It seems that besides the geometrical factors hydrogen bonding cannot be neglected even for the very weak Se···H and Te···H bonds.

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