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