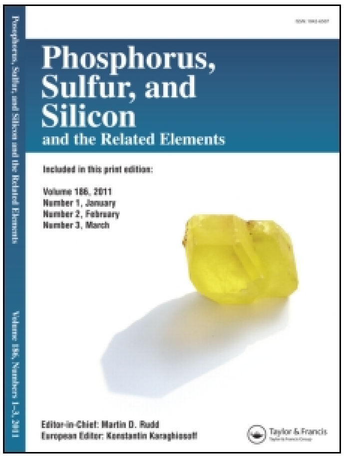

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POLYMERS IN FORM OF LINKED RINGS - A NOVEL TYPE OF STRUCTURES FOR CHALCOGEN POLYCATIONS

THE CRYSTAL STRUCTURES OF $(Se_{4.85}Te_{3.15})[WOCl_4]_2$ AND $(Se_4Te_3)[WOCl_4]_2$

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Among the well developed structural chemistry of the chalcogen polycations polymeric, chainlike entities represent a new feature, known only since 1990. Examples are $(Te_{15}X_4)_n[MOX_4]_{2n}$ (M=Mo, W; X=Cl, Br), $Te_7[MOX_4]X$ (M=W, Nb; X=Cl, Br) or $Te_7[AsF_6]_2$. The reaction of $Te_6[WOCl_4]_2$ with selenium or Se/Te mixtures with $WOCl_4$ yielded $(Se_{4.85}Te_{3.15})[WOCl_4]_2$ (orthorhombic, $P2_12_12_1$, a=782.1(3), b=1549.0(6), c=1824(1) pm, Z=4) and $(Se_4Te_3)[WOCl_4]_2$ (monoclinic, Cc, a=1198.7(5), b=1072.0(6), c=1563.9(7) pm, β=100.80(3)°, Z=4). Both structures contain Se/Te mixed, polymeric cations and square pyramidal $[WOCl_4]^-$ anions linked via W=O····W bridges to linear strands. In $(Se_{4.85}Te_{3.15})^{2+}$ all sites are simultaneously occupied by Se and Te but with different amounts. The cations form five-membered rings linked in 1,3 positions by three-atomic bridges to chains. In $(Se_4Te_3)^{2+}$ the atomic positions are occupied by Se and Te in an ordered way. The cations are built from four-membered rings connected in 1,3 positions by three-atomic bridges to chains. Te atoms are located in the two three-coordinate positions in the rings and the central position in the connecting bridges.

Keywords: chalcogen polycations, main group element clusters, Oxotetrachlorotungstate(V), synthesis, crystal structure

INTRODUCTION

Since the mid-1960s it is known that positively charged clusters of chalcogen atoms are the strongly coloured species that occur in highly electrophilic and acidic media when elemental chalcogens are oxidized. Meanwhile the structural and synthetic chemistry of the chalcogen polycations is well developed and several reviewing articles have appeared [1,2,3]. Most of the known polycations are discrete, molecular entities, e.g. S_4^{2+}, Se_{10}^{2+} or Te_6^{4+}. The polycation Te_8^{2+}, the final member in the series S_8^{2+}, Se_8^{2+}, Te_8^{2+} was first obtained in a vapour transport reaction by oxidation of tellurium with WCl_6 leading to $Te_8[WCl_6]_2$ [4]. The structure turned out to be quite different from its lighter homologues. There are two condensed five-membered rings with a short transannular bond of less than 300 pm. Meanwhile, an isomeric form of Te_8^{2+} could be obtained in $Te_8[ReCl_6]$ [5] which is isostructural to S_8^{2+} and Se_8^{2+}. However, in $Te_8[WCl_6]_2$ for the first time cation-cation interactions with Te-Te distances between cations of 343 pm were observed, still within the range of weak bonding. A similar structural feature occurs in $Te_8[VOCl_4]_2$ [6]. Te_8^{4+} ions form a linear strand reminiscent of a stack of cubes. Te_6^{2+} was first obtained by the oxidation of elemental tellurium with $WOCl_4$ [7], and later by Lewis acid-base reaction between Te_3Cl_2 and $NbOCl_3$ [8]. In the structures of $Te_6[MOCl_4]_2$ the prismatic cations also form strands facing towards each other with the triangular faces.

Polymeric chalcogen polycations with bonds in the normal single bond range along the chain, occur in the structure family $Te_7[MOX_4]X$ (M=Nb, W; X=Cl, Br) [9] and in $Te_7[AsF_6]_2$ [10]. The two polymeric $(Te_7^{2+})_n$ cations are of substantially different structure (Fig. 1). $Te_7[AsF_6]_2$ contains a chain of six-membered tellurium rings in the chair conformation connected through bridging Te atoms in the 1,4 positions. On the other hand, $(Te_7^{2+})_n$ in $Te_7[MOX_4]X$ is made up from planar Te_7 groups linked by four Te-Te bonds giving a folded band. The central Te atom of the Te_7 groups is in a square-planar environment and interpreted as being in a Ψ^2-octahedral coordination with twelve valence electrons.

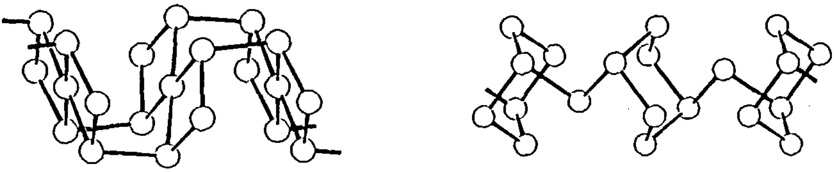

FIGURE 1. The two isomeric $(Te_7^{2+})_n$ ions in $Te_7[MOX_4]X$ (left) and $Te_7[AsF_6]_2$ (right).

The oxidation of elemental chalcogens with transition metal halides is still a productive source for new polycations. Elemental selenium does not react with $WOCl_4$, but with tellurium $Te_6[WOCl_4]_2$ is formed in nearly quantitative yield. So we investigated the reactions of $Te_6[WOCl_4]_2$ with selenium and were able to isolate two new, polymeric Se/Te mixed polycations.

EXPERIMENTAL

The synthesis of $Te_6[WOCl_4]_2$ from tellurium and $WOCl_4$ has already been described [7]. In a typical experiment 0.05 g (0.63 mmol) Se and 0.15 g (0.10 mmol) $Te_6[WOCl_4]_2$ were filled into a glass ampoule, which was evacuated and sealed. The ampoule was placed in a horizontal tube furnace in a temperature gradient 190 → 185°C. Within 8 days black, needle shaped crystals were transported to the cooler part of the ampoule.

Crystal structure analyses [11]

Since the crystals rapidly hydrolyse in moist air they were sealed under argon in glass capillaries. Preliminary X-ray investigations showed that two different compounds had formed. Data were collected with a STOE image plate diffractometer with Mo-K_α radiation at ambient temperature. A numerical absorption correction was applied to both data sets. Both structures were solved by direct methods [12] and refined by full maxtrix least squares with anisotropic displacement parameters for all atoms [13].

$Cl_8O_2Se_{4.85(3)}Te_{3.15(3)}W_2$: orthorhombic, $P2_12_12_1$, a=782.1(3), b=1549.0(6), c=1824(1) pm; V=2210(2) · 10^6pm^3; Z=4; 13767 reflections collected in the range $9<2\theta<52°$; 4288 unique reflections; R_{merge} = 0.064; 4288 reflections in least squares; 191 refined parameters; wR (F^2) = 0.166, $R(|F|)$ for 3854 reflections with $F>4\sigma(F)$ = 0.061, largest difference peak/hole +5.86/-2.14 e/10^6pm^3; inversion twin with 1:1 ratio of the individuals.

$Cl_8O_2Se_4Te_3W_2$: monoclinic, Cc, a=1198.7(5), b=1072.0(6), c=1563.9(7) pm, β=100.80(3)°; V=1974(2) · 10^6 pm^3; Z=4; 7518 reflections collected in the range $10<2\theta<56°$; 4415 unique reflections; R_{merge} = 0.057; 4415 reflections in least squares; 173 refined parameters; wR (F^2) = 0.155, $R(|F|)$ for 4152 reflections with $F>4\sigma(F)$ = 0.057, largest difference peak/hole +2.84/-2.53 e/10^6pm^3; Flack x parameter = 0.07(2).

RESULTS AND DISCUSSION

Elemental selenium does not react with $WOCl_4$ so selenium polycations are not accessible by this way. However, $Te_6[WOCl_4]_2$ takes up selenium and new compounds with mixed selenium/tellurium polycations were formed via vapour transport. X-ray diffraction studies on the black precipitated crystals showed that two different compounds had formed. Both contain square-pyramidal $[WOCl_4]^-$ anions which are linked by linear W=O····W bridges to strands. Chains of this type are also observed in the starting material $Te_6[WOCl_4]_2$ [7] or in $Te_7[WOCl_4]Cl$ [9]. The determination of the magnetic properties of $(Se_4Te_3)[WOCl_4]_2$ showed it to be paramagnetic. It obeys to the Curie-Weiss law in the temperature range 76-295 K with a characteristic temperature of –5(1)K and a magnetic moment of 2.1 B.M., slightly more than expected for one unpaired electron and thus contains W(V).

The structure of $(Se_{4.85}Te_{3.15})[WOCl_4]_2$ contains polymeric chainlike $(Ch_8)^{2+}$ ions (Ch=chalcogen). The cationic and anionic strands are running along the *a*-axis of the unit cell and form a tetragonal rod packing (Fig. 2). Se and Te are statistically distributed over all atomic sites of the cation in various amounts. As expected the highest amount of tellurium is observed in the three-coordinate positions Ch(4) and Ch(6) with 86(2) and 64(2) % respectively. The occupancy ratio Se:Te of all sites was introduced in the refinement calculations, resulting in the composition $(Se_{4.85(3)}Te_{3.15(3)})^{2+}$. The cation consists of five-membered rings connected in the 1,3 ring positions by three-atomic bridges. The mean Ch-Ch bond length of 262 pm is between Se-Se and Te-Te bond lengths of 235 and 275 pm and shows the mixed composition (Fig. 3).

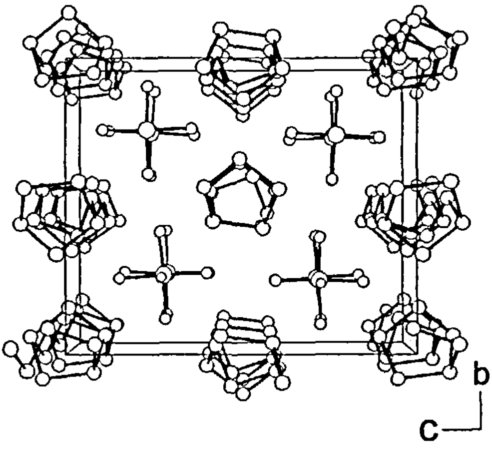

FIGURE 2.
The unit cell of $(Se_{4.85}Te_{3.15})[WOCl_4]_2$ in a perspective view along [100].

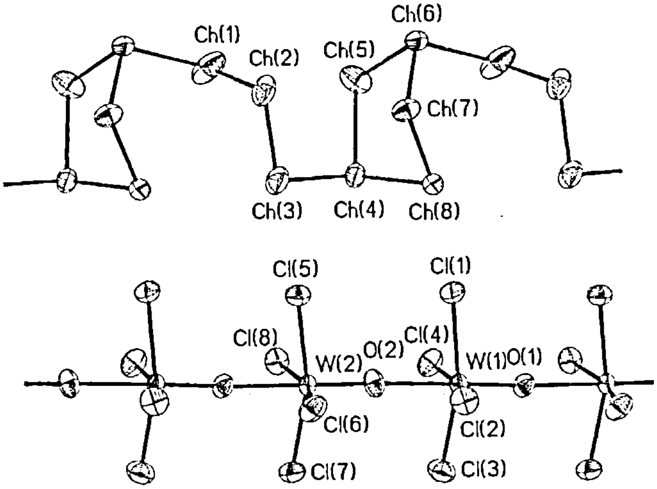

FIGURE 3. Section of the chains of the polymeric $(Ch_8)^{2+}$ cation (top) and the $[WOCl_4]^-$ anion (bottom) in the structure of $(Se_{4.85}Te_{3.15})[WOCl_4]_2$. Thermal ellipsoids represent 50 % probability. The amount of Se on the sites of the cation is (1)=0.89, (2)=0.66, (3)=0.93, (4)=0.14, (5)=0.57, (6)=0.36, (7)=0.92, (8)=0.38 with e.s.d. of 0.03. Bond lengths [pm]: Ch(1)-Ch(2) 261.3(4), Ch(2)-Ch(3) 248.6(4), Ch(3)-Ch(4) 266.4(3), Ch(4)-Ch(5) 266.2(3), Ch(5)-Ch(6) 271.3(3), Ch(6)-Ch(7) 257.2(3), Ch(7)-Ch(8) 248.9(3), Ch(8)-Ch(4) 272.9(2), Ch(6)-Ch(1) 263.5(4), W-Cl from 232.5(5) to 237.6(5), W-O 172(2) and 219(2); Ch-Ch-Ch angles from 93.5(1) to 105.6(1)°.

The structure of $(Se_4Te_3)[WOCl_4]_2$ is closely related to the structure of $(Se_{4.85}Te_{3.15})[WOCl_4]_2$ and contains polymeric $(Ch_7)^{2+}$ cations. Cationic and anionic strands are running along the c-axis of the unit cell and also form a tetragonal rod packing (Fig. 4).

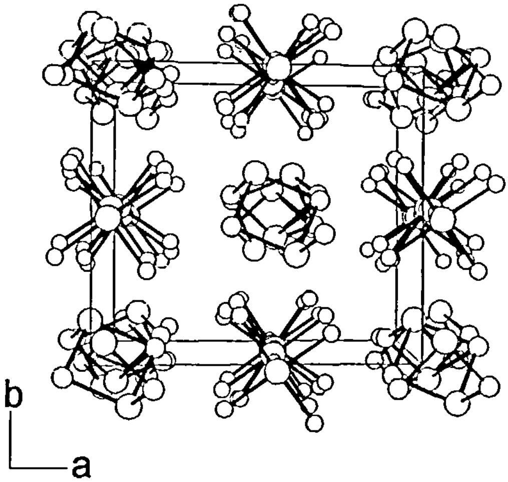

FIGURE 4.
The unit cell of $(Se_4Te_3)(WOCl_4]_2$ in a perspective view along [001].

In the cationic strands all chalcogen atom positions are occupied by Se and Te in an ordered alternating way. Te atoms are found in the three-coordinate positions and in the central position of the Ch_3 bridge. The cations are built of four-membered planar Te_2Se_2 rings (sum of angles 360.1(1)°) connected via three-atomic -Se-Te-Se-bridges (Fig. 5) in the 1,3 positions of the rings. Bond lengths within the cationic strand are in the range of 247 to 260 pm and indicate Se and Te simultaneously present in all bonds.

The polycations $(Se_{4.85}Te_{3.15})^{2+}$ and $(Se_4Te_3)^{2+}$ have a „Zintl-precise" [3] structure. Both have a precise number of three-coordinate chalcogen atoms with respect to the two-coordinate ones, in each ion two for eight and seven atoms in total, respectively. Since the three-coordinate atoms formally carry the positive charges, the total charge of the cations can easily be derived from the structure.

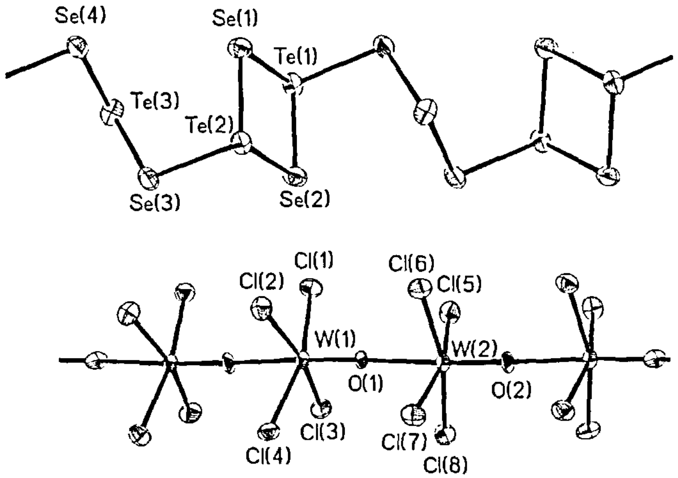

FIGURE 5. Sections of the chains of the polymeric $(\mathrm{Ch}_7)^{2+}$ cation (top) and the $[\mathrm{WOCl}_4]^-$ anion (bottom) in the structure of $(\mathrm{Se}_4\mathrm{Te}_3)[\mathrm{WOCl}_4]_2$. Thermal ellipsoids represent 50 % probability. Bond lengths [pm]: Te(1) - Se(1) 260.1(4), Te(1) - Se(2) 254.5(4), Te(2) - Se(1) 253.8(4), Te(2) - Se(2) 259.7(4), Te(2) -Se(3) 258.9(3), Te(3) -Se(3) 246.8(4), Te(3) - Se(4) 247.1(4), Se(4) - Te(1^I) 259.1(3); W-Cl from 233.0(6) to 239.8(7), W-O 172(2) and 220(2); Ch-Ch-Ch angles from 89.0(1) to 106.3(1)°.

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