Chalcogen Polycations by Oxidation of Elemental Chalcogens with Transition Metal Halides: Synthesis and Crystal Structure of $[Se_{17}][WCl_6]_2$

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Introduction

Elemental chalcogens can be oxidized by a variety of oxidizing agents to polycationic species. In particular AsF_5 and SbF_5 in liquid SO_2 as solvent have made the isolation of a whole family of polycations stabilized by AsF_6^- or SbF_6^- anions possible.[1] Recently transition metal halides with the metal in high oxidation states turned out to be selective and mild oxidants towards elemental chalcogens, which allowed the synthesis of known but also novel polycations. The reactions are carried out as chemical transports; the compounds of polycations and halogenometalate anions are deposited from the vapour phase.[2] Due to their volatility and oxidation power tungsten(VI) halides and oxidehalides like WCl_6, $WOCl_4$ or $WOBr_4$ are specially suitable for this purpose. The reactions of sulfur and tellurium with WCl_6 have already been investigated and show a marked difference in the reaction behavior. Sulfur with WCl_6 yields S_2Cl_2 and $WSCl_4$ in the molar ratio 3:1 at 100–120 °C,[3] while in the ratio 8:1 at 300 °C one obtains the addition compound $WCl_6{\cdot}S_8$, built of WCl_6 molecules and neutral S_8 rings in a layered structure.[4,5] Tellurium forms with WCl_6 the polycations Te_4^{2+} and Te_8^{2+}. With 2 equiv of tellurium, WCl_6 reacts to give $Te_4(WCl_6)_2$ in two crystalline modifications[6] and with 4 equiv of tellurium to give $Te_8(WCl_6)_2$.[7] We have now studied the reaction of WCl_6 with selenium and obtained $Se_{17}^{2+}(WCl_6^-)_2$ with a novel selenium polycation. Se_{17}^{2+} is a new member in the family of the selenium polycations. The square planar Se_4^{2+} [8] and the two bicyclic ions Se_8^{2+} [9] and Se_{10}^{2+} [10] had so far been structurally characterized. Potentiometric and photometric studies of $Se/SeCl_4$ mixtures in $NaCl{-}AlCl_3$ melts indicate the existence of Se_{12}^{2+} and Se_{16}^{2+}.[11] Selenium-77 NMR studies of Se_{10}^{2+} in SO_2 solution show a disproportionation in Se_8^{2+} and a second polycation of higher nuclearity which was tentatively assigned to Se_{17}^{2+}.[12]

Table 1. Crystallographic Data for $Se_{17}(WCl_6)_2$ (**1**)

chem formula: $Cl_{12}Se_{17}W_2$
fw = 2135.44
$a = 13.21(1)$ Å
$b = 13.06(2)$ Å
$c = 11.44(1)$ Å
$\alpha = 98.85(7)°$
$\beta = 100.26(4)°$
$\gamma = 112.24(6)°$
$V = 1743.4$ Å^3
$Z = 2$
space group: $P\bar{1}$ (No. 2)
$\lambda = 0.7107$ Å
$\rho_{calcd} = 4.07$ g·cm^{-3}
$\mu = 252.6$ cm^{-1}
transm coeff: 0.2454–0.0294
$wR(F^2)^a = 11.5\%$
$R(|F|)^b = 6.8\%$

^{a} $wR(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ with $w = 1/\sigma^2(F_o^2) + (0.057p)^2$ (with $p = (\max(F_o^2) + 2F_c^2)/3$). ^{b} $R(|F|) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

Experimental Section

Reagents. All manipulations were performed in an argon-filled glove box. WCl_6 was obtained from tungsten powder and chlorine at 400–600 °C and was sublimed before use in an evacuated glass ampoule to remove impurities of $WOCl_4$. Selenium powder was used as purchased (MERCK).

$Se_{17}(WCl_6)_2$ (1). A glass ampoule of 15 cm length and 1.5 cm diameter was filled with 0.5 g (1.26 mmol) WCl_6 and 0.84 g (10.7 mmol) Se. The ampoule was evacuated and sealed and placed in a horizontal tube furnace at 350 °C. The content was first converted to a black melt, which was left at 350 °C for 5 days. The ampoule was then drawn 5 cm out of the furnace. The contents were completely transported to the cold end of the ampoule within 1 h as a black crystalline mass. Then the ampoule was placed in a temperature gradient 110 → 100 °C with the charged side at 110 °C. Within 1 day dark red crystals of **1** in a yield of about 30% together with crystals of WCl_6 were transported to the colder part of the ampoule.

IR Spectroscopy. FT-IR spectra were recorded with a BRUKER IFS 120 in the range 50–375 cm^{-1}. Samples were prepared as Nujol suspensions between polyethylene windows.

X-ray Structure Determination of 1. Due to the high sensitivity towards moist air, opening of the reaction ampoules and selection of crystals were performed in the glove box. Crystals of **1** were filled into glass capillaries. Precession photographs showed no symmetry higher than $\bar{1}$. The space group $P\bar{1}$ was confirmed by the structure analysis. Most of the tested crystals were only poorly diffracting. The best one of the size 0.39 × 0.23 × 0.08 mm was choosen for intensity measurements. Details of data collection and the crystallographic data are presented in Table 1. A numerical absorption correction with description of the crystal shape by 16 faces was applied to all data.[13] The structure was solved by direct methods[14] and refined by full-matrix least-squares with anisotropic displacement factors for all atoms.[15] The atomic coordinates and temperature factors are given in Table 2, and some selected distances and angles listed in Table 3.

Results and Discussion

In the reaction of WCl_6 with selenium no liberation of Se_2Cl_2 is observed, and in contrast to the reaction with sulfur no formation of $WSeCl_4$ occurs. $WSeCl_4$ can be obtained from WCl_6 and Sb_2Se_3 under evolution of $SbCl_3$.[16] The reaction behavior of selenium towards WCl_6 is more related to that of tellurium, which yields polycation-containing compounds. From WCl_6 and selenium we obtained $Se_{17}(WCl_6)_2$ (**1**) as dark red

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(1) Corbett, J. D. *Prog. Inorg. Chem.* **1976**, *21*, 129; Gillespie, R. J. *J. Chem. Soc. Rev.* **1979**, *8*, 315; Burford, N., Passmore, J., Sanders, C. P. S. *Mol. Struct. Energ.* **1989**, *11*, 53.

(2) Beck, J. *Angew. Chem.* **1994**, *106*, 172; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 163.

(3) Cotton, F. A.; Kibala, F. A.; Sandor, R. B. W. *Inorg. Chem.* **1989**, *28*, 2487.

(4) Cotton, F. A.; Kibala, F. A.; Sandor, R. B. W. *Acta Crystallogr.* **1989**, *C45*, 1287.

(5) We observed an equilibrium between $WCl_6{\cdot}S_8$ and $WSCl_4 + S_2Cl_2$. Prolonged contact of S_2Cl_2 with $WSCl_4$ over several weeks leads even at room temperature to the formation of $WCl_6{\cdot}S_8$. Heating to 100 °C yields again the mixture of $WSCl_4 + S_2Cl_2$. With higher amounts of sulfur the formation of $WCl_6{\cdot}S_8$ is favored at all temperatures.

(6) Beck, J. *Z. Naturforsch.* **1990**, *B45*, 413. Beck, J. *Z. Naturforsch.* **1994**, *B49*, 1159.

(7) Beck, J. *Angew. Chem.* **1990**, *102*, 301. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 293.

(8) Brown, I. D.; Crump, D. B.; Gillespie, R. J. *Inorg. Chem.* **1971**, *10*, 2319.

(9) McMullan, R. K.; Prince, D. J.; Corbett, J. D. *Inorg. Chem.* **1971**, *10*, 1749.

(10) Burns, R. C.; Chan, W. C.; Gillespie, R. J.; Luk, W. C.; Sawyer, J. F.; Slim, D.R. *Inorg. Chem.* **1980**, *19*, 1432.

(11) Fehrmann, R.; Bierrum, N. J. *Inorg. Chem.* **1977**, *16*, 2089.

(12) Burns, R. C.; Collins, M. J.; Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1986**, *25*, 4465.

(13) Baernighausen, H.; Herrendorf, W. HABITUS, Program for optimization of the crystal shape using ψ scanned reflections. University of Karlsruhe, Germany, 1993. Sheldrick, G. M. SHELX-76, Program for crystal structure determination, University of Cambridge, U.K., 1976.

(14) Sheldrick, G. M. SHELXS-86, Program for crystal structure solution. University of Göttingen, Germany, 1986.

(15) Sheldrick, G. M. SHELXL-93, Program for crystal structure determination. University of Göttingen, Germany, 1993.

0020-1669/95/1334-6202$09.00/0

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **1** with Standard Deviations Given in Parentheses

atom	*x/a*	*y/b*	*z/c*	B_{eq},[a] pm^2
W1	0.5211(2)	0.7295(2)	0.3138(2)	1.98(5)
W2	0.0006(2)	0.2834(2)	−0.8356(2)	2.11(5)
Se1	0.0187(4)	0.1697(5)	−0.4801(4)	3.4(1)
Se2	0.0444(4)	0.0930(5)	−0.3167(4)	3.3(1)
Se3	−0.1419(4)	−0.0267(5)	−0.3230(5)	3.9(1)
Se4	−0.2157(4)	0.1001(5)	−0.2610(4)	2.9(1)
Se5	−0.2577(4)	0.1482(5)	−0.4499(4)	3.0(1)
Se6	−0.1565(4)	0.3395(5)	−0.3938(4)	2.8(1)
Se7	0.0384(3)	0.3574(5)	−0.3904(4)	2.5(1)
Se8	0.0708(4)	0.3718(5)	−0.1789(4)	2.6(1)
Se9	0.2604(4)	0.4042(5)	−0.1439(4)	3.0(1)
Se10	0.3460(4)	0.6007(5)	−0.1110(4)	3.1(1)
Se11	0.3461(4)	0.6190(5)	−0.3118(4)	2.7(1)
Se12	0.3334(4)	0.8045(5)	−0.2593(4)	3.5(1)
Se13	0.5115(4)	0.9347(5)	−0.2361(4)	3.5(1)
Se14	0.5975(4)	0.9527(6)	−0.0302(4)	5.1(2)
Se15	0.7347(4)	0.8896(5)	−0.0593(4)	3.5(1)
Se16	0.6324(4)	0.6927(5)	−0.1210(4)	3.7(1)
Se17	0.5392(4)	0.6612(5)	−0.3203(4)	3.3(1)
Cl1	0.4923(9)	0.580(1)	0.1504(9)	3.3(3)
Cl2	0.3829(8)	0.604(1)	0.388(1)	3.8(3)
Cl3	0.5472(9)	0.881(1)	0.470(1)	3.9(3)
Cl4	0.6597(9)	0.851(1)	0.241(1)	4.6(3)
Cl5	0.6533(8)	0.685(1)	0.4307(9)	3.0(3)
Cl6	0.3820(9)	0.760(1)	0.1905(9)	3.4(3)
Cl7	−0.1131(9)	0.120(1)	−0.787(1)	3.6(3)
Cl8	−0.1507(9)	0.278(1)	−0.9712(9)	3.8(3)
Cl9	0.1154(9)	0.449(1)	−0.883(1)	3.6(3)
Cl10	0.1539(8)	0.304(1)	−0.6864(9)	3.4(3)
Cl11	−0.0457(9)	0.389(1)	−0.6776(9)	3.6(3)
Cl12	0.039(1)	0.171(1)	−0.982(1)	4.8(4)

[a] Equivalent isotropic *B* [10^4 pm^2] = $8\pi^2 U_{eq}$ with U_{eq} defined as one third of trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (pm) and Angles (deg) in **1**, with Standard Deviations Given in Parentheses[a]

Se1−Se2	228.4(6)		
Se2−Se3	234.3(7)		
Se3−Se4	230.2(7)		
Se4−Se5	237.1(6)		
Se5−Se6	226.1(8)	W1−Cl1	235(1)
Se6−Se7	248.7(5)	W1−Cl2	233(1)
Se7−Se1	240.4(8)	W1−Cl3	232(1)
Se7−Se8	234.5(6)	W1−Cl4	231(1)
Se8−Se9	232.4(5)	W1−Cl5	231.4(8)
Se9−Se10	231.5(8)	W1−Cl6	230.9(8)
Se10−Se11	234.6(6)		
Se11−Se12	248.1(8)		
Se12−Se13	226.0(7)	W2−Cl7	232(1)
Se13−Se14	235.9(6)	W2−Cl8	227.3(8)
Se14−Se15	230.9(6)	W2−Cl9	233(1)
Se15−Se16	232.7(9)	W2−Cl10	230.1(8)
Se16−Se17	228.3(6)	W2−Cl11	241(1)
Se17−Se11	242.1(6)	W2−Cl12	231(1)
Se14−Se14^{I}	337.8(8)		
Se6−Se7−Se1	106.1(3)	Cl−W−Cl angles of the two independent WCl_6^- anions between 87.0(3) and 93.0(4) and between 174.4(5) and 179.3(5)	
Se6−Se7−Se8	88.2(2)		
Se8−Se7−Se1	105.5(3)		
Se10−Se11−Se12	89.8(3)		
Se10−Se11−Se17	104.0(2)		
Se12−Se11−Se17	106.9(3)		

all other Se−Se−Se angles between 96.3(2) and 103.8(3)

[a] Symmetry operation: I = $-x + 1, -y + 2, -z$.

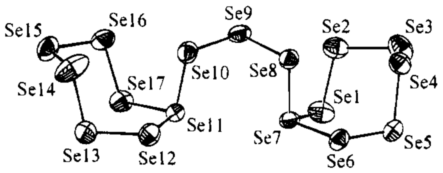

Figure 1. View of the polycation Se_{17}^{2+} in the structure of $Se_{17}(WCl_6)_2$. Thermal ellipsoids are scaled to enclose a 70% probability density.[29]

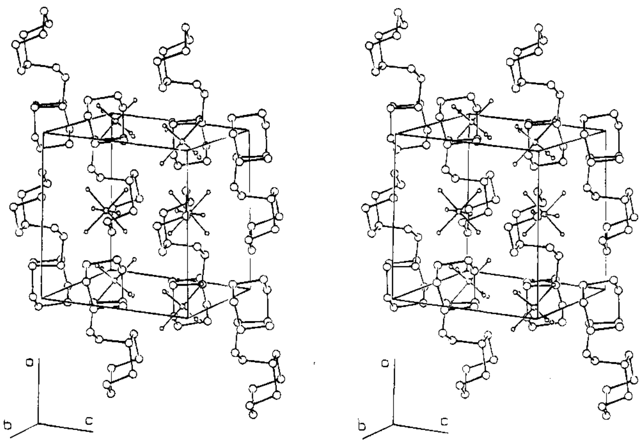

Figure 2. Stereoscopic view of the packing of ions in $Se_{17}(WCl_6)_2$.

air-sensitive crystals. The reaction is carried out in a sealed evacuated ampoule. First the content of the ampoule is converted at 350 °C to a black melt that is quenched to 110 °C. In a temperature gradient 110 → 100 °C the crystals of **1** are transported to the colder side. The yield reaches only about 30%, and large amounts of WCl_6 were obtained in all performed reactions, which shows that **1** exists at all temperatures in an equilibrium with Se and WCl_6. Other compounds of chalcogen polycations and halogenometallate anions of transition metals show a similar but not as extreme behavior in their thermal stability. $Te_8(WCl_6)_2$,[7] $Te_6(WOCl_4)_2$, and $Te_6I_2(WCl_6)_2$,[17] for example, have small ranges of thermal stability and decompose at elevated temperatures into elemental tellurium and tungsten halide. The crystals of **1** are in colour and shape very similar to those of WCl_6. The formation of **1** was only discovered by the occurence of additional lines in the powder diffraction diagrams and subsequent x-ray studies on a series of single crystals, of which the majority turned out to be α- and β-WCl_6.[18] The IR spectra, however, of the mixtures of **1** and WCl_6 show significant differences to pure WCl_6. The T_{1u} modes of WCl_6 are observed at 372 and 172 cm^{-1}.[19] Additional absorptions are attributed to **1**. Bands at 327 cm^{-1} with a sholder at 315 cm^{-1} and 356 cm^{-1} show clearly the presence of hexachlorotungstate(V) with a strong distortion of the octahedral symmetry.[20] Weak bands at 140, 161, and 165 cm^{-1} are assigned to the vibrations of the cation. Of the selenium polycations only Se_4^{2+} shows a characteristic IR spectrum[21] while Se_8^{2+} gives weak bands in the region 330−250 cm^{-1}.[22] Absorption bands of Se_{17}^{2+} in this region could be hidden by the strong bands of the WCl_6^- anions.

The crystal structure of **1** is composed of Se_{17}^{2+} and WCl_6^- ions. Figure 1 gives a view of the ion and Figure 2 a

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(16) Britnell, D.; Fowles, G. W. A.; Rice, D. A. *J. Chem. Soc., Dalton Trans.* **1974**, 2191. We have performed a crystal structure determination of $WSeCl_4$ and found it to be isotypic to β-$WSCl_4$.[3] Beck, J.; Wetterau, J. To be submitted for publication.

(17) Beck, J. *Chem. Ber.* **1995**, *128*, 23.

(18) Ketelaar, J. A. A.; van Oosterhout, G. W. *Recl. Trav. Chim. Pays-Bas* **1943**, *62*, 197. Taylor, J. C.; Wilson, P. W. *Acta Crystallogr.* **1974**, *B30*, 1216.

(19) McDowell, R. S.; Kennedy, R. C.; Asprey, L. B.; Shermann, R. J. *J. Mol. Struct.* **1977**, *36*, 1. Brown, T. L.; Mc Dugle, W. G.; Kent, L. G. *J. Am. Chem. Soc.* **1970**, *92*, 3645.

(20) Uhl, G.; Hey, E.; Becker, G.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1983**, *497*, 213.

(21) Gillespie, R. J.; Pez, G. P. *Inorg. Chem.* **1969**, *8*, 1229.

(22) Prince, D. J.; Corbett, J. D.; Garbisch, B. *Inorg. Chem.* **1970**, *9*, 2731.

stereoscopic view of the unit cell. The so far unknown Se_{17}^{2+} polycation consists of two seven-membered selenium rings in the chair conformation connected by a Se_3 chain.

The Se−Se distances within the Se_7 rings show a marked alternation. The bonds to the triply bound Se atoms Se1−Se7, Se6−Se7, Se11−Se12, and Se11−Se17 are the longest with a mean length of 245 pm, followed by very short bonds Se1−Se2, Se5−Se6, Se12−Se13, and Se16−Se17 of average length 227 pm. The bond length alternation decreases with the distance from the triply bound atoms. The bonds Se2−Se3, Se4−Se5, Se13−Se14, and Se15−Se16 are with an average length of 235 pm slightly elongated; Se3−Se4 and Se14−Se15 with a mean of 231 pm are in the range of normal Se−Se single bonds as in the element modification γ-Se_8 with 233.4 pm.[23] The bond length alternation is typical for the seven membered sulfur ring S_7[24] and for polycationic species with a triply bound chalcogen atom in the ring as e.g. S_7I^+ [25] and $Se_7SeSeCl^+$.[26] The structure of Se_{17}^{2+} in **1** shows a very close relationship to the structure of S_{19}^{2+} [27] which consists of seven-membered sulfur rings connected by a S_5 bridge. The WCl_6^- anions are distorted from octahedral symmetry. Both crystallographically independent ions have an average W−Cl bond length of 232 pm which is typical for W(V).[7] Together with the two triply bound Se atoms in the cations that carry formally the positive charges, this reveals unequivocally the ionic formulation $Se_{17}^{2+}(WCl_6^-)_2$. The individual bond lengths in the anions however vary in a wide range from 227 to 241 pm with the bond length around W(1) being much less distorted than around W(2). In the structure of **1** significant cation-anion interactions with Se−Cl distances significantly less than the sum of the van der Waals radii (380 pm[28]) are observed.

The distortion of the WCl_6^- octahedra is caused by these interactions. The shortest Se−Cl contact, of 321 pm, is observed between Se(9) and Cl(1). Typically the W−Cl(1) bond is the longest in the $W(1)Cl_6^-$ ion. Cl(11) has the longest W−Cl bond (241 pm) and on the other side four short contacts to Se atoms, two of them to the triply bound Se(7) which carries formally the positive charge. Se(14) exhibits no such short contacts to Cl atoms and has accordingly the largest thermal motion, displayed by an elongated thermal ellipsoid. A fairly close contact of Se(14) to the corresponding atom of the neighboring cation of 338 pm is observed, similar to the shortest contact between Se atoms in $Se_7SeSeCl^+$ [26] (336 pm).

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Supporting Information Available: Tables listing complete details of the structure determination, atomic coordinates, thermal parameters, and bond distances and angles and figures showing the independent anions and a stereoscopic view of the cation for **1** (8 pages). Ordering information is given on any current masthead page.

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(23) Foss, O.; Janickis, V. *J. Chem. Soc., Dalton Trans.* **1980**, 624.

(24) Steudel, R.; Reinhardt, R.; Schuster, F. *Angew. Chem.* **1977**, *89*, 756; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 716.

(25) Passmore, J.; Taylor, P.; Whidden, T. K.; White, P. *J. Chem. Soc., Chem. Commun.* **1976**, 689.

(26) Faggiani, R.; Gillespie, R. J.; Kolis, J. W.; Malhotra, K. C. *J. Chem. Soc., Chem. Commun.* **1987**, 591.

(27) Burns, R. C.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1980**, *19*, 1423. Faggiani, R.; Gillespie, R. J.; Sawyer, J. F.; Vekris, J. E. *Acta Crystallogr. Sect. C* **1989**, *45C*, 1847.

(28) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(29) Johnson, C. K. *ORTEP, Program for Crystal Structure Illustrations*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.