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Synthesis and crystal structure of $Os_4S_{11}SeCl_8$

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A new quaternary osmium compound, $Os_4S_{11}SeCl_8$, has been synthesized and its crystal structure has been determined by X-ray powder diffraction. The crystal structure of $Os_4S_{11}SeCl_8$ ($Pbcn - d^6$, $oP48$, $Z = 2$, $a = 8.8845(2)$, $b = 11.8108(3)$, $c = 10.9621(3)$ Å; 713 reflections measured, 34 parameters refined, $R_I = 0.0230$, $R_p = 0.0302$, $R_{wp} = 0.0413$, $\chi^2 = 2.87$) represents a new structure type of inorganic compounds. Binuclear clusters with a partly disordered arrangement of S_2 and S-Se ligands are interconnected via double Cl-bridges to form 1D-polymers $[Os_2Cl_4(\mu\text{-}S_2)(\mu\text{-}S(S,Se))_2]_n$.

Inorganic materials / Chemical synthesis / Powder diffraction / Crystal structure

Introduction

Coordination chemistry offers great opportunities for obtaining new sulfur- and selenium-containing semiconductor materials due to the ability of sulfur and selenium to form chain structures. Successful synthesis of solid chalcogen halide compounds of transition metals can be performed in non-aqueous chalcogen halide media. We obtained different types of compound: clusters, molecular and polymeric compounds, and others. Some of them are particularly interesting, *e.g.* the compound $Rh_2Se_9Cl_6$ containing the first nonaselenium ring [1].

The chemistry of osmium chalcogen-halides has not been studied thoroughly. In addition to the complex compounds $(ChalHal_3)_2[OsHal_6]$ (where Chal is S, Se, Te and Hal is Cl, Br), synthesized from chalcogen halogenides with a high content of halogen atoms, also the thiochloride OsS_4Cl_2, which forms during the interaction of OsO_4 with S_2Cl_2 at 150°C, is known [2-4].

For the synthesis of osmium cluster compounds, and in particular heterochalcogen chlorides, solutions of sulfur in Se_2Cl_2 and of selenium in S_2Cl_2 can be used as reaction media with high chalcogen content. The electronic structure of the $Chal_2Cl_2$ (where Chal is S and Se) molecules is characterized by relatively low-lying (~ 12.5 eV) bonding molecular orbitals (MO) with a predominant contribution of the chalcogen atoms, which determine the existence of fragments of chain structure (S-S, Se-Se, S-Se) in these media. The presence of relatively low-lying nonbonding MO defines acceptor properties, *i.e.* the formation of additional bonds (molecular Se_2Cl_2 is a dimer).

The possibility of oxidation-reduction processes, $Chal^{1+} \rightarrow Chal^0 \rightarrow Chal^{2-}$, must be taken into account in the chalcogen chloride medium, and $Chal^{1+} \rightarrow Chal^{4+}$ processes in the presence of oxygen and chlorine. Typically, in a chalcogen chloride medium, at temperatures up to 100°C, formation of the following potential ligands may be considered: chloride ion Cl^-, sulfide ion S^{2-}, selenide ion Se^{2-}. Solvate-complexation involving $Chal_2Cl_2$ molecules is also possible. Their thermal decomposition should be observed at temperatures around 200°C according to the scheme: $Chal_2Cl_2 \rightarrow Chal_n + ChalCl_m$. In the formation of clusters, the most significant role is played by polydentate monoatomic (μ-$Chal^{2-}$, μ_3-S^{2-}), polyatomic (μ-$Chal_2^{2-}$) and polymer ($Chal_n$) ligands.

The aim of this work was to synthesize a mixed chalcogen chloride complex compound with Os, and to determine its crystal structure. Preliminary results have been given in [5,6].

Experimental

The synthesis of osmium thioselenochloride $Os_4S_{11}SeCl_8$ was carried out in an *L*-shaped glass reactor. 15 ml of a 22% solution of Se in S_2Cl_2 were added to 6 g of OsO_4. Upon moderate heating

(40-50°C) OsO_4 completely dissolved in the reaction medium. The exothermic reaction was accompanied by release of gaseous SO_2. The reaction mixture was heated in a moisture-protected open reactor to complete isolation of SO_2 at 60-80°C. After sealing, the reactor was heated at 200°C for 40 h. The resulting solid product was separated from the liquid phase by decantation. Then the part of the reactor containing the liquid was frozen in liquid nitrogen in order to avoid explosion of the reactor during its opening. The solid product was transferred to a Schlenk filter, filtered under a flow of inert gas, washed with S_2Cl_2, CS_2, and CCl_4 and dried in vacuum. A dark-grey microcrystalline diamagnetic powder (11.3 g, 75% yield) of osmium(IV) thioselenochloride $Os_4S_{11}SeCl_8$ was obtained according to the scheme:

$$4OsO_4 + 13Se + 10S_2Cl_2 \rightarrow Os_4S_{11}SeCl_8 + 8SO_2\uparrow + 6Se_2Cl_2 + S$$

Elemental analysis for $Os_4S_{11}SeCl_8$ (%): calc. Os, 51.55; S, 23.89; Se, 5.35; Cl, 19.21%; found Os, 50.74; S, 23.90; Se, 5.30; Cl, 20.06%. Bulk homogeneity of the product was confirmed by X-ray powder diffraction (XRPD). The compound dissolves in pyridine, DMFA and DMSO with the release of the red modification of selenium, which indicates destruction of the original complex.

An infrared (IR) spectrum of $Os_4S_{11}SeCl_8$ (suspension in nujol) was recorded on a Nicolet Magna-IR 750 spectrometer. XRPD data were collected in the transmission mode on a STOE STADI P diffractometer [7]. A calibration procedure was performed utilizing NIST SRM 640b (Si) [8] and NIST SRM 676 (Al_2O_3) [9] standards. Analytical indexing of the powder pattern and determination of the space group were performed using N-TREOR09 [10]. The crystal structure was solved *ab initio*, by direct methods, using EXPO2009 [11] and WinCSD-2010 [12], and was refined by the Rietveld method [13] with the program FullProf.2k (version 4.60) [14] from the WinPLOTR package [15], applying a pseudo-Voigt profile function and isotropic approximation for the atomic displacement parameters. The crystallographic data were standardized with the program STRUCTURE TIDY [16] and the program DIAMOND [17] was used for structural visualization. Further details of the crystal structure investigation can be found in the supporting cif file (including experimental intensities and structure factors).

Results and discussion

Unambiguous interpretation of the IR spectrum (Fig. 1) is difficult owing to the overlap of (Os-Cl) and (Os-S) bond vibrations. The frequencies 583 and 547 cm^{-1} were assigned to (S-S) bond vibrations, while the frequencies 401 cm^{-1} and 380 cm^{-1} were assigned to (Os-S) bond vibrations. Moreover, there are (Os-Cl) and (Os-Se) bond vibrations in the low-frequency region, at 327 and 250 cm^{-1}, respectively. The very strong absorption band at 469 cm^{-1}, with a shoulder at 430 cm^{-1}, was assigned to (>S=S) bond vibrations. The shoulder absorption bands at 360 cm^{-1} were assigned to (>Se=S) bond vibrations.

X-ray experimental and crystallographic data for $Os_4S_{11}SeCl_8$ are summarized in Table 1, while the final atomic positional and displacement parameters are listed in Table 2. Interatomic distances and bond angles are given in Table 3. A comparison of the experimental and calculated powder patterns is presented in Fig. 2.

An $Os_4S_{11}SeCl_8$ "molecule" is shown in Fig. 3. According to the results of the refinement of the population parameter G for site S2, there are on the average two selenium atoms per unit cell and consequently one of the S2 atoms in Fig. 3 can be assumed to be a selenium atom. No indication for further ordering of S and Se atoms was detected.

The distance between two neighboring Os atoms in $Os_4S_{11}SeCl_8$ is 2.708 Å, which corresponds to a single Os-Os bond, and the structure consequently contains binuclear clusters. The coordination polyhedron around the Os atoms is a distorted octahedron, $Os[S(S,Se)_2Cl_3]$, formed by three sulfur (selenium) atoms on one side, all of them part of a S-S or (S,Se)-S dumbbell, and three chlorine atoms on the other side. If the neighboring osmium atom is included in the coordination polyhedron, the coordination sphere around the osmium atom will be extended to form an $Os[(S,Se)_3Cl_3Os]$ pentagonal bipyramid. A non-collinear two-atom environment $S1[SOs]$ is observed for the S1 atom, while non-coplanar triangles $(S,Se)[SOs_2]$ correspond to the $S2 = 0.75S + 0.25Se$ atoms. The atom environment type for the atoms S3 and Cl2 (see Table 3) is a single atom (coordination number 1), whereas a non-collinear two-atom environment, $Cl1[Os_2]$, can be assigned to Cl1.

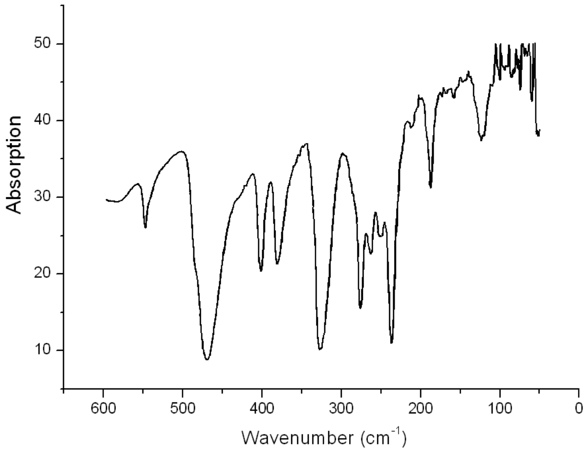

Fig. 1 IR spectrum of $Os_4S_{11}SeCl_8$.

Table 1 Experimental details and crystallographic data for $Os_4S_{11}SeCl_8$.

Formula / name	$Os_4S_{11}SeCl_8$ / tetraosmium monoselenium undecasulfur octachloride
Space group – Wyckoff sequence / Pearson symbol	*Pbcn* (No. 60) – d^6 / *oP*48
Structure type	$Os_4S_{11}SeCl_8$ (own)
M_r / Z	1476.25 / 2
Lattice parameters a, b, c (Å)	8.8845(2), 11.8108(3), 10.9621(3)
Cell volume V (Å^3)	1150.29(5)
F_{000} (electrons)	1300
Calculated density D_x (g/cm^3)	4.262
Absorption coefficient μ(Cu $K\alpha$) (mm^{-1})	60.35
Specimen shape / particle morphology / color	Flat sheet (8×8×0.1 mm) / loose powder, grain size < 0.04 mm / dark-grey
Data collection temperature T (K)	297(1)
Diffractometer	STOE STADI P (transmission mode)
Radiation, wavelength λ (Å)	Cu $K\alpha_1$, 1.540598
Angular range for data collection / Increment (°2θ)	$5.500 \leq 2\theta \leq 100.945$ / 0.015
Linear PSD step (°2θ) / Time (sec/step)	0.180 / 280
Number of measured reflections	713
Number of refined parameters	34
Half width parameters η_0, U, V, W	0.783(5), 0.89(3), -0.218(13), 0.0635(13)
Asymmetry parameters As1, As2	0.0233(7), -0.0002(2)
Reliability factors:	
$R_I = \Sigma\lvert I_{obs}-I_{calc}\rvert / \Sigma\lvert I_{obs}\rvert$	0.0230
$R_F = \Sigma\lvert F_{obs}-F_{calc}\rvert / \Sigma\lvert F_{obs}\rvert$	0.0175
$R_p = \Sigma\lvert y_i - y_{c,i}\rvert / \Sigma y_i$	0.0302
$R_{wp} = [\Sigma w_i \lvert y_i - y_{c,i}\rvert^2 / \Sigma w_i y_i^2]^{1/2}$	0.0413
$R_{exp} = [n-p / \Sigma w_i y_i^2]^{1/2}$	0.0244
$\chi^2 = \{R_{wp}/R_{exp}\}^2$	2.87

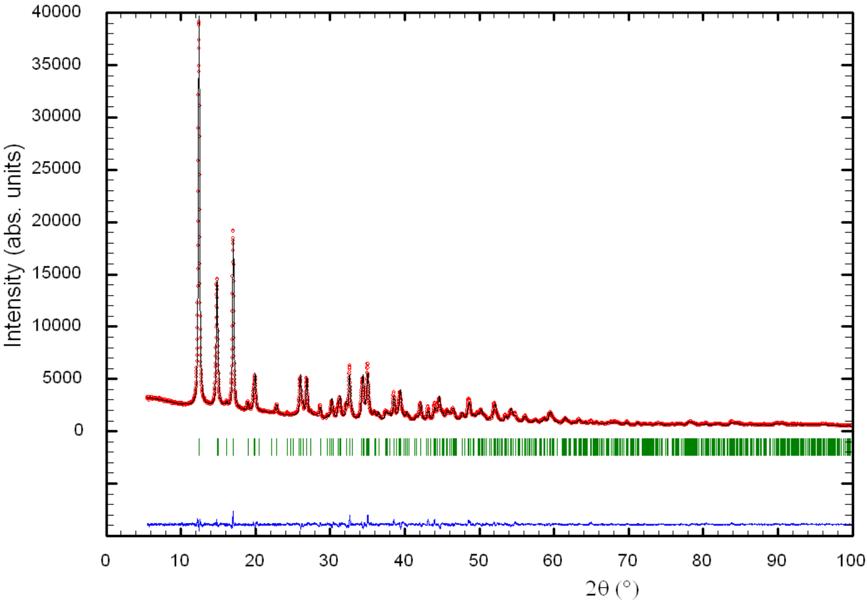

Fig. 2 Observed and calculated X-ray powder profiles for $Os_4S_{11}SeCl_8$. Experimental data (circles) and calculated profile (solid line through the circles) are presented together with the calculated Bragg positions (vertical ticks) and difference curve (bottom solid line). (Diffractometer STOE STADI P, Cu $K\alpha_1$ radiation, WinPLOTR graphic).

Table 2 Fractional atomic coordinates and equivalent isotropic displacement parameters for $Os_4S_{11}SeCl_8$.

Site	Wyckoff position	*x*	*y*	*z*	U_{iso} (Å^2)
Os1	8*d*	0.04938(14)	0.09352(10)	0.13314(14)	0.0162(2)
S1	8*d*	0.0469(9)	0.2740(5)	0.1625(6)	0.030(3)
S2[a]	8*d*	0.1949(6)	0.0426(4)	0.3046(6)	0.040(2)
S3	8*d*	0.3468(7)	0.1664(5)	0.3392(7)	0.028(3)
Cl1	8*d*	0.0601(7)	0.1095(6)	0.5803(6)	0.038(3)
Cl2	8*d*	0.2883(8)	0.1044(7)	0.0346(5)	0.034(3)

[a] S2 = 0.75S + 0.25Se. Refinement of the site occupancy gave 0.742(13)S + 0.258(13)Se; in the last cycle the values were fixed to 0.75 and 0.25.

Table 3 Interatomic distances (δ), coordination numbers (CN) and selected bond angles (ω) for $Os_4S_{11}SeCl_8$.

Bond	δ(Å)	CN	Angle	ω(°)
Os1 – 1S1	2.156(6)	6(7)	S2–Os1–Os1	54.8(2)
Os1 – 1S2*	2.353(6)		S2–Os1–Os1	55.0(2)
Os1 – 1S2	2.359(6)		S2–Os1–Cl1	83.5(2)
Os1 – 1Cl2	2.385(7)		Cl1–Os1–Cl2	84.9(2)
Os1 – 1Cl1	2.469(7)		S2–Os1–Cl1	85.3(2)
Os1 – 1Cl1	2.541(7)		S1–Os1–Cl2	91.3(3)
Os1 – 1Os1	2.708(2)		S1–Os1–S2	98.0(2)
S1 – 1S1	2.092(10)	2	S1–Os1–S2	101.5(2)
S1 – 1Os1	2.156(6)		S2–Os1–S2	102.1(2)
S2 – 1S3	2.026(8)	3	S1–Os1–Cl1	174.7(2)
S2 – 1Os1	2.353(6)		Os1–S1–S1	98.1(3)
S2 – 1Os1	2.359(6)		Os1–S2–Os1	70.15(18)
S3 – 1S2	2.026(8)	1	Os1–S2–S3	109.3(3)
Cl1 – 1Os1	2.469(7)	1(2)	Os1–S2–S3	112.1(3)
Cl1 – 1Os1	2.541(7)			
Cl2 – 1Os1	2.385(7)	1		

* S2=0.75S+0.25Se

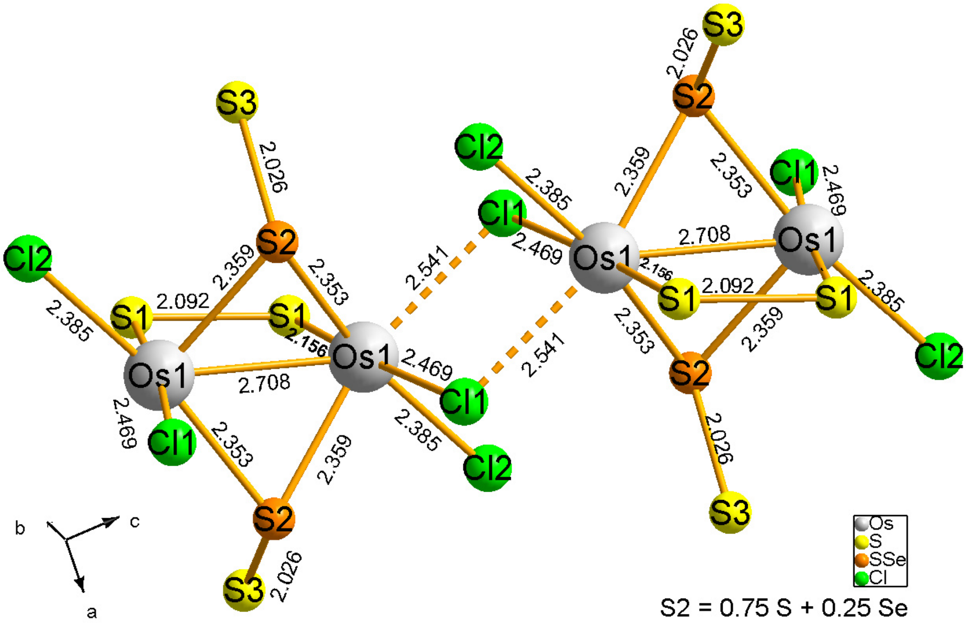

Fig. 3 Two binuclear clusters $Cl_2Os(\mu\text{-}S_2)(\mu\text{-}S(S,Se))_2OsCl_2$.

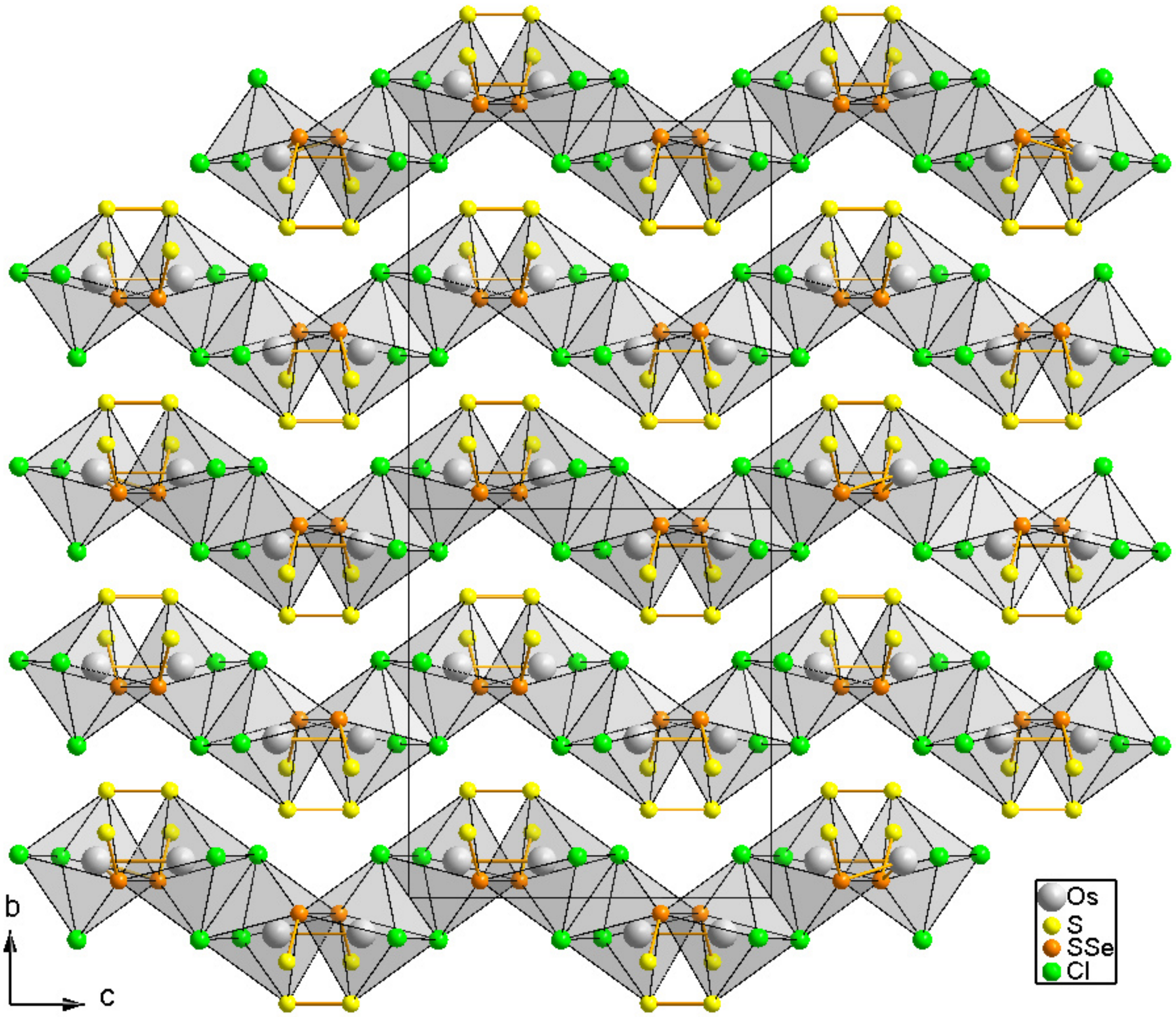

Fig. 4 Projection of the crystal structure of the $Os_4S_{11}SeCl_8$ linear polymer on the (100) plane showing the packing of $Os[(S,Se)_3Cl_3]$ octahedra.

The binuclear clusters, $Cl_2Os\{S_2\}\{S(S,Se)\}_2OsCl_2$, are interconnected via double Os-Cl1-Os bridges to form infinite polymer chains. The Os-Cl1 bonds are longer (2.469 and 2.541 Å) than the Os-Cl2 bonds (2.385 Å). The $Os[S(S,Se)_2Cl_3]$ octahedra are interconnected via a common edge Cl1-Cl1 on one side and via a common edge S2-S2 and a homonuclear bond S1-S1 on the other side (Fig. 4). Connection of octahedra via two Cl-bridges is also observed, for example, in the “classical” inorganic compound $OsCl_4$ [18] and in $RhSCl_5$ [19]. The general structural formula for the new cluster compound can be written as $[Os_2Cl_4(\mu\text{-}S_2)(\mu\text{-}S(S,Se))_2]_n$.

Conclusions

The osmium(VIII) oxide was reduced in a non-aqueous chalcogen halide medium ($Se+S_2Cl_2$) to obtain the osmium thioselenochloride $Os_4S_{11}SeCl_8$. The crystal structure of $Os_4S_{11}SeCl_8$ represents a new structure type of inorganic compounds. The interatomic distance Os-Os is 2.708 Ǻ, which corresponds to a single Os-Os bond. Binuclear clusters with a partly disordered arrangement of S_2 and S-Se ligands are interconnected via double Cl-bridges to form 1D-polymers $[Os_2Cl_4(\mu\text{-}S_2)(\mu\text{-}S(S,Se))_2]_n$.

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