First Examples of Chalcofluoride Rhenium Cluster Complexes with Cubane-Like Anions $[Re_4Q_4F_{12}]^{4-}$ (Q = S, Se)

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Dedicated to Professor James A. Ibers on the occasion of his 75th birthday

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Two rhenium tetrahedral cluster chalcofluoride compounds, $K_4[Re_4S_4F_{12}]\cdot3.4H_2O$ (**1**) and $K_4[Re_4Se_4F_{12}]\cdot6H_2O$ (**2**), have been synthesized for the first time by a reaction of $Re_4Q_4(TeCl_2)_4Cl_8$ (Q = S, Se) with molten KHF_2. Both compounds have been characterized by single-crystal X-ray diffraction methods. Compound **1** crystallizes in the trigonal space group $R\bar{3}$ with 24 formula units per cell [$a = b = 23.6503(3)$ Å, $c = 25.2697(7)$ Å, $V = 12240.6(4)$ Å^3 ($T = 293$ K)]; compound **2** crystallizes in the monoclinic space group $P\bar{1}$ with four formula units per cell [$a = 10.6451(3)$ Å, $b = 14.6853(4)$ Å, $c = 16.9349(5)$ Å, $\alpha = 66.8420(10)°$, $\beta = 84.8460(10)°$, $\gamma = 85.5740(10)°$, $V = 2421.69(12)$ Å^3 ($T = 293$ K)]. Hydrophilic terminal fluoride ligands of cluster anions are included in the hydrogen bond systems of their hydrate shells.

Introduction

Chalcohalide cluster complexes of the early transition metals like triangular $[M_3Q_7L_6]^{2-}$, tetrahedral $[M_4Q_4L_{12}]^{4-}$, and octahedral $[M_6Q_8L_6]^{4-}$ (M = Mo, W, Re; Q = S, Se, Te) complexes are well known in the literature.[1–6] In these complexes the outer ligands L are most often halide ions (Cl^-, Br^-, I^-) and some other simple ligands such as CN^- and SCN^-. Complexes with organic ligands L are known also. Whereas F^- in both inner and outer positions has been known for a long time from the solid state compounds $Nb_6F^i_{12}F^a_{6/2}$,[7] up to now none was known where a fluoride ion played the role of an outer L ligand in complexes, except for the recently described Mo_3 triangular thiofluoride complex $K_5[Mo_3S_4F_7(FHF)_2]\cdot2H_2O$ and Re_6 octahedral thiofluoride complexes $[Re_6S_8F_6]^{4-}$ and $[Re_6S_8F_2(H_2O)_4]$.[8,9]

Here we present the successful syntheses, crystal structures, and some properties of the first representatives of tetrahedral chalcofluoride cluster complexes of rhenium $[Re_4Q_4F_{12}]^{4-}$ (Q = S, Se). Cubane-like chalcofluoride rhenium(IV) complexes with cluster anions $[Re_4S_4F_{12}]^{4-}$ and $[Re_4Se_4F_{12}]^{4-}$ were obtained by the reaction of $Re_4Q_4(TeCl_2)_4Cl_8$ (Q = S, Se) with molten potassium bifluoride KHF_2. These anionic complexes were isolated as potassium salts of compositions $K_4[Re_4S_4F_{12}]\cdot3.4H_2O$ (**1**) and $K_4[Re_4Se_4F_{12}]\cdot6H_2O$ (**2**) from aqueous solutions. Compounds **1** and **2** are the first examples of cubane-like clusters with fluoride ligands in the outer sphere of a cluster core $\{Re_4Q_4\}$.

Results

The prepared anionic complexes **1** and **2** are the first examples of cubane-like clusters with fluoride ligands in the outer sphere of a cluster core $\{Re_4Q_4\}$, namely $[Re_4S_4F_{12}]^{4-}$ and $[Re_4Se_4F_{12}]^{4-}$ (Figure 1).

Compound **1** crystallizes in the trigonal space group $R\bar{3}$. In the structure there are two different cluster anions $[Re_4S_4F_{12}]^{4-}$ with symmetries C_1 and C_3 respectively, however they are geometrically closely related. Re–Re distances are in the range 2.7277(5)–2.7448(5) Å, and Re–(μ_3-S) distances are in the range 2.310(2)–2.336(2) Å, which are close to those in the starting compound and analogous distances in related cubane rhenium thiohalides. The Re–F distances [1.980(5)–2.020(5) Å] are slightly greater than analogous bond lengths in mononuclear octahedral hexafluororhenates(IV) such as K_2ReF_6 (1.953 Å)[10] and K_3ClReF_6

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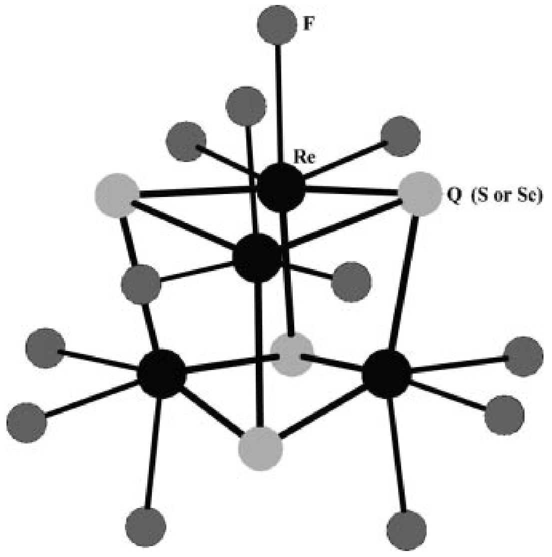

Figure 1. The structure of cluster anions $[Re_4Q_4F_{12}]^{4-}$ (Q = S, Se) in compounds **1** and **2**.

(1.837 Å).[11] In the structure the anions form slightly corrugated hexagonal parallel planes (001) which are linked through potassium cations and hydrogen bonds with additional water molecules.

The K atoms are mainly surrounded by O atoms of water molecules and F atoms of cluster anions. The K8 atom is located on the threefold axis and has a honeycomb-like arrangement of cluster anions (Figure 2).

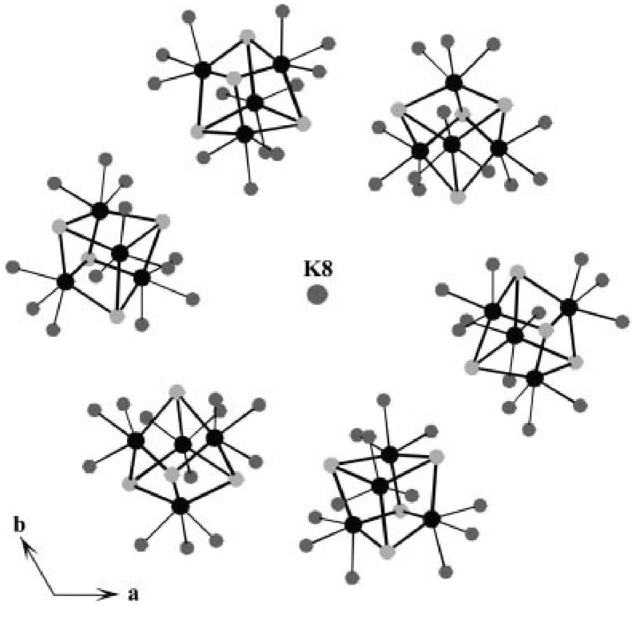

Figure 2. A fragment of the unit cell with honeycomb arrangement of the K8 atom in a projection along the *c* axis in compound **1**.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$. There are two crystallographically independent cluster anions $[Re_4Se_4F_{12}]^{4-}$ in the unit cell. A general view of the mutual arrangement of the clusters in the structure of **2** is given in Figure 3. In the cluster complex the main interatomic distances like Re–Re [2.7527(5)–2.7817(5) Å], Re–(μ_3-Se) [2.4315(10)–2.4454(9) Å], and Re–F [1.987(5)–2.027(5) Å] are in good agreement with those for starting and related compounds. The environment of K atoms consists of fluorine atoms of cluster anions and oxygen atoms of water molecules.

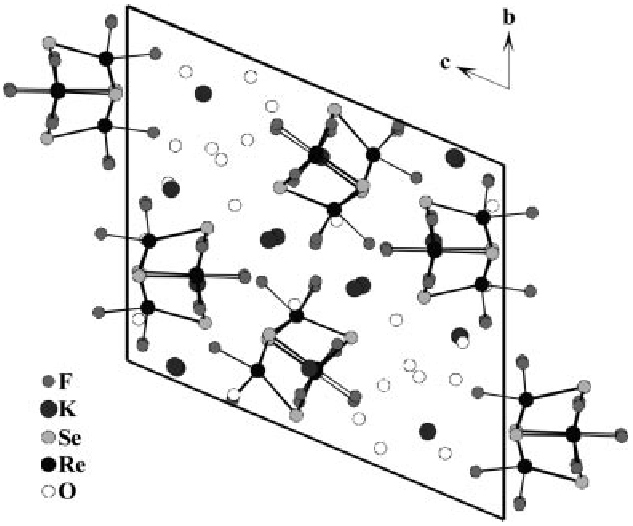

Figure 3. View of the unit cell in a projection along the *a* axis in compound **2**.

In both structures potassium atoms and water molecules connect the cluster anions through potassium ions and hydrogen bonds F···H–O and O···H–O.

NMR

Aqueous solutions of both compounds were studied by NMR on ^{19}F. The spectra of both solutions exhibit only one intensive line with chemical shifts $\delta^{1}_{iso} = -227$ ppm (compound **1**) and $\delta^{2}_{iso} = -252$ ppm (compound **2**) and a number of lines with relative intensities less than 0.5% of the strong lines (Figure 4). This experiment was repeated after one month to test the stability of the compounds in the solution, with no changes found in the spectra. It is worth noting that the experimental difference of the chemicals shifts, $\Delta\delta = \delta^{1}_{iso} - \delta^{2}_{iso} = 25$ ppm, correlates with the

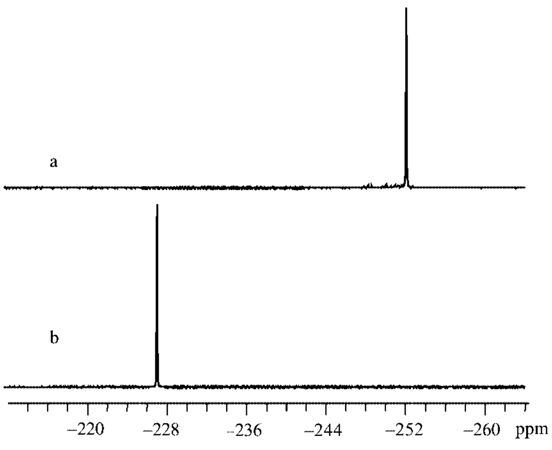

Figure 4. ^{19}F NMR spectra of compounds **1** (a) and **2** (b).

DFT calculated difference of the isotropic NMR nuclear shielding, $\Delta\sigma = \sigma^2_{iso} - \sigma^1_{iso} = 21$ ppm, for the optimized structures of $[Re_4Q_4F_{12}]^{4-}$ models with symmetry T_d ($\sigma^1_{iso} = 337.9$ ppm and $\sigma^2_{iso} = 358.4$ ppm).

Electronic Structure

The calculated bond energies of the complexes $[Re_4Q_4F_{12}]^{4-}$ indicate that the bonding is energetically feasible, and it is stronger for the S complex (–113.40 eV) than for the Se complex (–109.64 eV). The calculated HOMO–LUMO gap is 2.55 eV for $[Re_4S_4F_{12}]^{4-}$ and 2.42 eV for $[Re_4Se_4F_{12}]^{4-}$. The calculated ionization potentials for these complexes are –5.9 eV (S) and –5.8 eV (Se).

The third degenerated HOMOs, $40t_2$ and $46t_2$, are antibonding in character for S and Se complexes and are largely centered on the rhenium atoms (65% of the 5d-valence orbitals), with the F and Q p-valence orbital contributions (Figure 5). The vacant MOs are formed from the valence orbitals of all atoms also. The exception is represented at levels $24a_1$ (for S) and $27a_1$ (for Se), which are formed mainly from atomic s orbitals of rhenium, chalcogen, and fluorine atoms. The calculated charge distribution suggests that these complexes can be formulated as $Re_4^{0.21+}S_4^{0.11-}F_{12}^{0.37-}$ and $Re_4^{0.19+}S_4^{0.09-}F_{12}^{0.37-}$. The value of a charge on Re atoms is slightly positive and on Q is slightly negative. This indicates the essentially covalent nature of bonding for a cluster core $\{Re_4Q_4\}$.

The dipole-allowed excitation energies for systems with a T_d symmetry are depicted in Figure 5. The energies calculated for proposed transitions are in qualitative agreement with experimental UV/Vis spectra. The uninterrupted weak absorption in the visible range (700–400 nm, $\varepsilon \leqslant 2\times10^2$) can be explained by electron-dipole transitions between HOMO and a nearby vacant MO (LUMO_LUMO2). The most intensive transitions occur in the UV region of absorption ($\varepsilon > 1\times10^3$) and can involve electron-dipole transitions between the HOMO and vacant MOs.

Experimental Section

$Re_4Q_4(TeCl_2)_4Cl_8$ (Q = S, Se) compounds were prepared as described previously.[12] All other reagents used were commercially available products of reagent grade quality. All experiments were performed in air. UV/Vis spectra were recorded in H_2O with an Ultraspec 3300 Pro spectrometer at room temperature in the range 200–1100 nm. Infrared spectra were recorded with a Bruker IFS-85. ^{19}F NMR spectra of aqueous solutions were obtained with a Bruker MSL-400 spectrometer in a magnetic field of 9.4 T at room temperature. The resonance frequency for ^{19}F was 376.308 MHz, pulse width (90°) 8 μs with a 2-s repetition rate for 3000 transients. Chemical shifts are reported with respect to an external standard C_6F_6. EMA = Electron microprobe analysis.

Preparation of $K_4[Re_4S_4F_{12}]\cdot3.4H_2O$ (1): $Re_4S_4(TeCl_2)_4Cl_8$ (0.35 g, 0.18 mmol) was heated with an excess of KHF_2 (5 g, 64 mmol) in a carbon glass vessel in air for 2 h at 300–310 °C. The fusion cake was washed with water (20 mL), and the remaining solid was dissolved in water (40 mL) to yield a green solution which was filtered and left for a day. A green precipitate formed; it was filtered and dried in air. Yield: 0.19 g (76%). Single crystals of **1** were obtained by dissolving the pure product in water with the addition of a small amount of KHF_2. The solution was left for 3 days in an open polyethylene tube. Dark brown crystals that formed were filtered and dried in air. EMA: $K_{4.1}Re_4S_{3.9}F_{12.1}$. Microanalysis for $H_{6.8}F_{12}K_4O_{3.4}Re_4S_4$: calcd. F 17.29, S 9.73; found F 16.95, S 9.90. IR (KBr): $\tilde{\nu}$ = (Re–F) = 512 (s), 466 (s) cm^{-1}. ^{19}F NMR (ppm): –227. UV/Vis (H_2O): λ, nm (ε, $L\,mol^{-1}cm^{-1}$): 230 (5458), 267 (5368), 317 (1965), 363 (1143) (700–400 uninterrupted weak absorption).

Preparation of $K_4[Re_4Se_4F_{12}]\cdot6H_2O$ (2): $Re_4Se_4(TeCl_2)_4Cl_8$ (0.6 g, 0.31 mmol) was treated as described for compound **1** (Yield: 0.29 g (58%)) and single dark green plate crystals of **2** were obtained in the same way as for compound **1**. EMA: $K_{4.1}Re_4Se_{3.8}F_{12.5}$. Microanalysis for $H_{12}F_{12}K_5O_6Re_4Se_4$: calcd. F 14.32; found F 14.68. IR

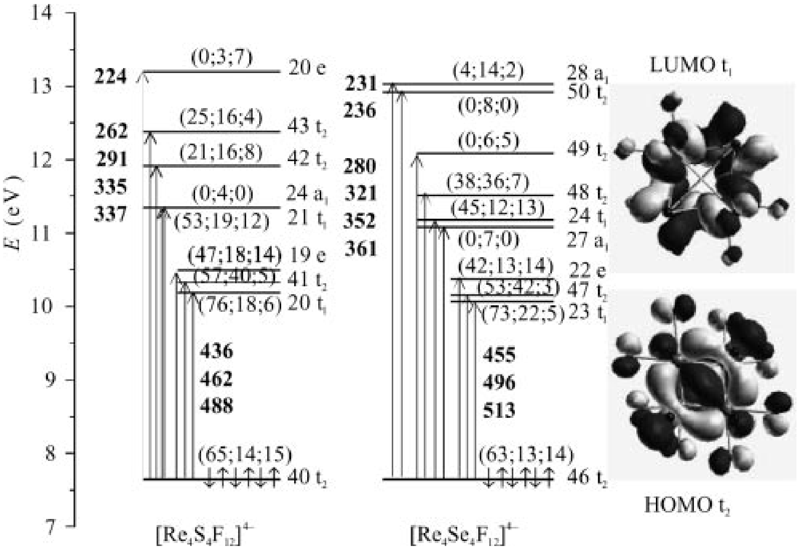

Figure 5. Electronic level schemes for $[Re_4Q_4F_{12}]^{4-}$ models and schematic figures of one from third degenerated HOMO and LUMO. The numbers and symmetry types of the calculated MOs are indicated. Numbers in brackets indicate the percentage of the contributing valence orbitals – 5d Re; 3p S; 4p Se; 2p F, respectively. The vertical arrows and integers (nm) show the calculated transitions.

(KBr): $\tilde{\nu}$ = (Re–F) = 500 (s), 455 (s) cm^{-1}. ^{19}F NMR (ppm): –252. UV/Vis (H_2O): λ, nm (ε, L mol^{-1} cm^{-1}): 265 (2667), 294 (3686), 334 (2429), 381 (sh) (750–430 uninterrupted weak absorption).

X-ray Structure Determination: Diffraction data for **1** and **2** were collected with a Bruker–Nonius X8Apex equipped with a 4-K CCD area detector with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at room temperature using standard techniques (Table 1). An empirical absorption correction using the SADABS program was applied. The structures were solved by direct methods employing difference Fourier syntheses and refined anisotropically by full-matrix least-squares techniques on F^2 using the SHELXL-97 Release 97-2 software package.[13] The hydrogen atoms of water molecules were not located. Crystal data, experimental details, and refinement results are summarized in Table 1 and have been deposited with the Fachinformationszentrum Karlsruhe.[14]

Table 1. Crystal data and structure refinement for $K_4[Re_4S_4F_{12}]\cdot 3.4\,H_2O$ (**1**) and $K_4[Re_4Se_4F_{12}]\cdot 6\,H_2O$ (**2**).

Compound	**1**	**2**
Chemical formula	$H_{6.76}F_{12}K_4O_{3.38}Re_4S_4$	$H_{12}F_{12}K_4O_6Re_4Se_4$
Formula mass	1318.24	1553.14
a [Å]	23.6503(3)	10.6451(3)
b [Å]		14.6853(4)
c [Å]	25.2697(7)	19.763(3)
α [°]	66.8420(10)	66.842(1)
β [°]		84.846(1)
γ [°]		85.574(1)
V [Å^3]	12240.6(4)	2421.7(1)
$d_{calcd.}$ (g cm^3)	4.292	4.260
Space group	$R\bar{3}$	$P\bar{1}$
Z	24	4
μ (mm^{-1})	24.991	26.735
T (K)	293(2)	293(2)
$R_1(F)$ ($F_o{}^2 > 2\sigma(F_o{}^2)$)	0.0374	0.0415
$R_w(F^2)$ (all data)	0.0886	0.1010

DFT Calculations: Density functional spin-restricted calculations (DFT) were carried out on $[Re_4Q_4F_{12}]^{4-}$ models by using the ADF2002 code.[15] The local-exchange VWN correlation potential was used for the local density (LDA) approximation;[16] Becke's nonlocal corrections to the exchange energy[17] and Perdew's nonlocal corrections to the correlation energy were added.[18] The ZORA (zeroth-order relativistic approximation) method was used to account for the scalar relativistic effects.[19] The STO basic set without core potentials was used for all atoms (ZORA/TZ2P). The tetrahedral symmetry, T_d, was imposed on the full geometry optimization of the ground electronic states for the $[Re_4Q_4F_{12}]^{4-}$ and $[Re_4Q_4F_{12}]^{3-}$ models. Calculations of the electronic binding energy were performed as $\Delta E_n = [Re_4Q_4F_{12}]^{n-} - (4Re + 4Q + 12F)$. The ionization potentials were computed as the energy differences between the $[Re_4Q_4F_{12}]^{3-}$ and $[Re_4Q_4F_{12}]^{4-}$, IP = $\Delta E_3 - \Delta E_4$. The atomic net charges for $[Re_4Q_4F_{12}]^{4-}$ complexes were obtained using the Hirshfeld analysis.[20] The isotropic NMR nuclear shieldings (^{19}F σ_{iso}) were calculated by the method of gauge including atomic orbitals (GIAO) with scalar relativistic effects.[21]

Acknowledgments

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