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Tetranuclear Rhenium Chalcochloride Cluster Complexes $Cs_3H[Re_4Q_4Cl_{12}] \cdot 3.33H_2O$ (Q = Se and Te): Synthesis and Structures

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Abstract—The tetranuclear cluster rhenium complexes $Cs_3H[Re_4Q_4Cl_{12}] \cdot 3.33H_2O$ (Q = Te (**I**) and Se (**II**)) with the Cl atoms as terminal ligands were obtained and structurally characterized. The structures of complexes **I** and **II** were determined by X-ray diffraction analysis. Their isostructural crystals are monoclinic; space group *C*2, $Z = 6$; $a = 26.403(8)$ Å, $b = 16.495(5)$ Å, $c = 11.744(3)$ Å, $\beta = 91.25(2)°$, $V = 5113(2)$ Å^3 (**I**); $a = 26.573(3)$ Å, $b = 16.461(3)$ Å, $c = 11.726(2)$ Å, $\beta = 91.381(4)°$, $V = 5127.6(14)$ Å^3 (**II**).

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The chemistry of tetrahedral rhenium(IV) chalcogenide cluster complexes of the type $[Re_4Q_4L_{12}]$ (Q = S, Se, or Te) has been under intensive development in the last few years [1–3]. In these complexes, the trigonal faces of the tetrahedron Re_4 are coordinated by chalcogen atoms (S, Se, or Te) to form the cluster core $\{Re_4Q_4\}$. Each Re atom is additionally coordinated by three terminal ligands L. At present, many relevant complexes with both inorganic [4–10] and organic ligands [11, 12] are known. However, complexes with halide ions as terminal ligands L were not obtained. Only recently, we have synthesized chalcofluoride complexes $[Re_4Q_4F_{12}]^{4-}$ [4].

Proceeding further in our investigations, here we obtained two new complexes $Cs_3H[Re_4Q_4Cl_{12}] \cdot 3.33H_2O$ (Q = Te (**I**) and Se (**II**)) with chloride ions as all terminal ligands. Since the formation of such complexes occurs only in strongly acidic media, complexes **I** and **II** are acid salts.

EXPERIMENTAL

The starting cluster chalcogenides $Re_4Te_8Cl_{16}$ and $Re_4Se_4Te_4Cl_{16}$ were prepared from $ReCl_5$ and Te or from $ReCl_5$, Se, and Te [5].

Synthesis of complex I. The chalcogenide $Re_4Te_8Cl_{16}$ (0.15 g) and CsCl (0.2 g) were refluxed in 6 M HCl (20 ml) for 1 h. The resulting dark brown solution was filtered, concentrated to 5 ml, and cooled. Black crystals of complex **I** were filtered off, washed with methanol, and dried. The yield was 0.08 g (57.6%).

Synthesis of complex I. The chalcogenide $Re_4Se_4Te_4Cl_{16}$ (0.05 g) was heated in concentrated HCl ($HCl : H_2O = 1 : 1$) for 1 h. The solution turned brown. The resulting solution was filtered and left with CsCl (0.05 g) in an open beaker. After 24 h, dark needle-shaped crystals of complex **II** were filtered off and dried in air. The yield was 23 mg (52%).

X-Ray diffraction analysis. X-ray diffraction data were obtained on single-crystal automated diffractometers (Siemens P4 for **I** and Bruker-Nonius X8APEX CCD for **II**) at room temperature according to a standard procedure (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). Absorption correction was applied in a semiempirical way from five azimuthal scan curves for **I** or from the intensities of equivalent reflections for **II** (SADABS [13]).

Structures **I** and **II** were solved by the direct method and refined from difference electron-density maps. The atomic coordinates and anisotropic thermal parameters were refined by the full-matrix least-squares method (SHELX-97) [14, 15]. The coordinates of the hydrogen atoms were not refined. Crystallographic parameters and a summary of data collection are given in table.

The atomic coordinates have been deposited with the FIZ Karlsruhe Crystallographic Data Collection for inorganic compounds (Nos. 419 787 and 419 786 for **I** and **II**, respectively) and can be made available from the authors upon request.

RESULTS AND DISCUSSION

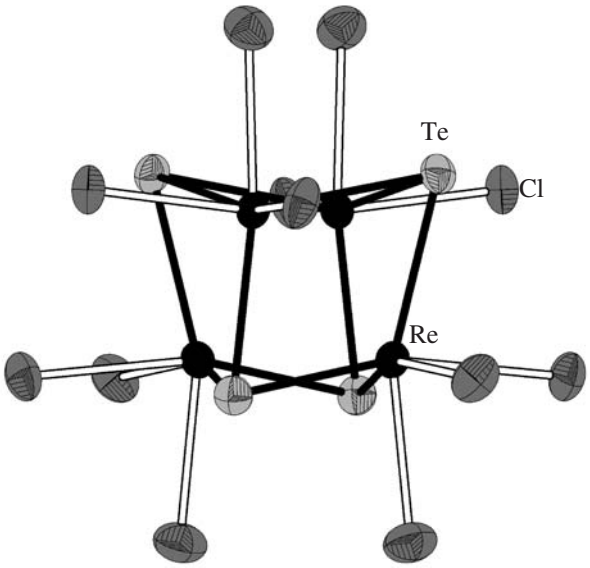
First tetrahedral rhenium complexes were obtained nearly contemporaneously with octahedral ones. However, in contrast to octahedral metal clusters extensively studied by various groups of researchers in the last few decades, the chemistry of tetrahedral Re(IV) cluster

Crystallographic parameters and a summary of data collection for $Cs_3(H)[Re_4Te_4Cl_{12}] \cdot 3.33H_2O$ (**I**) and $Cs_3(H)[Re_4Se_4Cl_{12}] \cdot \cdot 3.33H_2O$ (**II**)

Parameter	Value	
	I	**II**
Empirical formula	$H_{7.67}Cl_{12}Cs_3O_{3.33}Re_4Te_4$	$H_{7.67}Cl_{12}Cs_3O_{3.33}Re_4Se_4$
M	2140.38	1945.82
Crystal size, mm	$0.6 \times 0.4 \times 0.2$	$0.02 \times 0.03 \times 0.12$
Crystal system	Monoclinic	Monoclinic
Space group	*C*2	*C*2
a, Å	26.403(8)	26.573(3)
b, Å	16.495(5)	16.461(3)
c, Å	11.744(3)	11.726(2)
β, deg	91.25(2)	91.381(4)
V, Å^3	5113(2)	5127.6(14)
Z	6	6
ρ_{calcd}, g/cm^3	4.169	3.781
μ, mm^{-1}	21.617	22.470
Ranges of *h*, *k*, and *l* indices	$0 \le h \le 36$	$-36 \le h \le 18$
	$-22 \le k \le 0$	$-23 \le k \le 23$
	$-16 \le l \le 16$	$-16 \le k \le 16$
Transmittance factors	0.0965; 0.0267	0.6621; 0.0833
Number of measured/independent reflections, R_{int}	7176/7033, 0.0500	23499/15126, 0.0279
Number of parameters refined	371	370
R (reflections with $I > 2\sigma(I)$)	$R_1 = 0.0517$	$R_1 = 0.0623$
	$wR_2 = 0.1169$	$wR_2 = 0.1972$
R (for all reflections)	$R_1 = 0.0716$	$R_1 = 0.0734$
	$wR_2 = 0.1269$	$wR_2 = 0.2066$

complexes remained stagnant for a long period of time. Its development was spurred by the synthesis of chalcogenides with the general formula $Re_4Q_4(TeCl_2)_4Cl_8$ (Q = S, Se, and Te) [5]. These chalcogenides proved to be excellent precursors for new similar complexes. Complexes **I** and **II** ($Cs_3H[Re_4Q_4Cl_{12}] \cdot 3.33H_2O$; Q = Te (**I**) and Se (**II**)) also relate to this series of complexes. They were obtained by reactions of $Re_4Q_4(TeCl_2)_4Cl_8$ with CsCl in boiling HCl through replacement of the neutral ligands $TeCl_2$. On heating, rhenium chalcochlorides dissolved; concentration of the resulting solution gives black crystals of salts **I** and **II**.

Structures **I** and **II** were determined from X-ray diffraction data. Crystals of complexes **I** and **II** are isostructural (monoclinic, space group *C*2). According to the crystallographic data, complexes **I** and **II** contain only three Cs^+ ions, whereas the charge of the cluster anion is –4 (from the magnetic properties of these complexes). In addition, an electrochemical study in an available potential range revealed no redox transformations of these clusters. Such a behavior correlates with the known resistance of similar cluster complexes to redox reactions. Therefore, one can state that complexes **I** and **II** contain a proton compensating for the anionic charge.



Structure of the cluster anion $[Re_4Te_4Cl_{12}]^{4-}$ with atomic thermal displacement ellipsoids (50% probability).

The structure of the cluster anion in complex **I** is shown in figure. Its structure contains two independent clusters, one of which is symmetrical. The cluster core $[Re_4Q_4]$ is structurally similar to this fragment in other tetrahedral rhenium complexes. The Re–Re distances in the cluster range from 2.848(2) to 2.879(2) Å in **I** and from 2.854(1) to 2.880(1) Å in **II**. The Re–(μ_3-Q) distances range from 2.587(2) to 2.612(2) Å in **I** and from 2.580(2) to 2.620(2) Å in **II**. The Re–Cl distances range from 2.437(12) to 2.493(10) Å in **I** and from 2.435(8) to 2.501(7) Å in **II**.

Complexes **I** and **II** are soluble in water; however, they are unstable in solution and decompose rapidly. In aqueous solutions acidified with HCl, both complexes are stable for a long period of time and can be recrystallized.

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