Syntheses and Characterizations of the New Tetranuclear Rhenium Cluster Compounds Re$_4$(μ_3-Q)$_4$(TeCl$_2$)$_4$Cl$_8$ (Q = S, Se, Te)

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Introduction

Rhenium chalcogeno halides have been studied extensively in recent years,[1−3] in part because of the stability of these Re clusters in a wide array of polyhedra. The majority of the chalcogeno halide clusters contain Re$_6$ octahedra,[4−9] but Re$_4$ tetrahedra, Re$_4$ parallelograms, and Re$_3$ triangles are also known.[10,11] Here we are concerned with Re$_4$ clusters. Re$_4$ clusters occur in systems other than the chalcogeno halides. Thus, Re$_4$ parallelograms are found in ReS$_2$ and ReSe$_2$[12,13] whereas Re$_4$ tetrahedra are observed in a number of systems including mixed rhenium chalcogenides, such as [Re$_4$(μ_3-S)$_4$]Te$_4$,[14] the partly substituted phases [Re$_{4-x}$Mo$_x$(μ_3-S)$_4$]Te$_4$ and [Re$_3$Mo(μ_3-S)$_{4-y}$(μ_3-Se)$_y$]Te$_4$,[15] the chalcogeno cyanide cluster compounds [Re$_4$(μ_3-Q)$_4$(CN)$_{12}$]$^{4-}$ (Q = S,[16,17] Se,[16], Te[18]), and the sulfidorhenate anion [Re$_4$(μ_3-S)$_4$(μ_2-S$_3$)$_6$]$^{4-}$.[19,20]

An interesting feature of some Re clusters, namely Re$_6$(μ_3-Te)$_6$(μ_3-Cl)$_2$(TeCl$_2$)$_2$Cl$_4$, [Re$_6$(μ_3-Te)$_8$(TeBr$_2$)$_6$]Br$_2$,[9] and Re$_4$(μ_3-Te)$_4$(TeBr$_2$)$_4$Br$_8$,[21] is their stabilization of tellurohalide ligands TeX$_2$ (X = Cl, Br) that were previously known only as unstable species in the gas phase.[22,23] The compounds Re$_4$(μ_3-Q)$_4$(TeCl$_2$)$_4$Cl$_8$ (Q = S, Se, Te) reported here extend that list.

Table 1. Crystallographic Data for Compounds **1**−**3**

compd	Re$_4$(μ_3-S)$_4$-(TeCl$_2$)$_4$Cl$_8$ (**1**)	Re$_4$(μ_3-Se)$_4$-(TeCl$_2$)$_4$Cl$_8$ (**2**)	Re$_4$(μ_3-Te)$_4$-(TeCl$_2$)$_4$Cl$_8$ (**3**)
empirical formula	Cl$_{16}$Re$_4$S$_4$Te$_4$	Cl$_{16}$Re$_4$Se$_4$Te$_4$	Cl$_{16}$Re$_4$Te$_8$
fw	1950.64	2138.24	2332.80
a, Å	10.823(3)	10.830(3)	10.742(4)
c, Å	12.920(3)	13.233(4)	13.616(4)
V, Å^3	1513.4(7)	1552.2(8)	1571.2(9)
space group	$I\bar{4}$	$I\bar{4}$	$I\bar{4}$
Z	2	2	2
λ, Å	0.7093	1.540 56	0.7093
ρ_{calc}, g cm^{-3}	4.281	4.575	4.931
μ, cm^{-1}	214	769	240
T, K	113(2)	113(2)	113(2)
R_1^{a}	0.0514	0.0699	0.0390
wR_2^{b}	0.108	0.158	0.079

^{a} $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} w$R(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

Experimental Section

Synthesis. All chemicals were commercial products that were used as supplied unless otherwise noted. Sample purity and homogeneity were assessed by comparison of powder diffraction data (Rigaku DMAX diffractometer, filtered Cu *K*α radiation) with patterns calculated by means of the program XPOW.[24] Samples for ICP analyses for Re, S, Se, and Te were prepared by dissolving the compounds in a 1:1 mixture of concentrated NH$_4$OH and 30% H$_2$O$_2$; the resultant solutions were boiled for 20 min. Analyses were performed on a Thermo Jarrell Ash Atomscan 25 with the use of standards purchased from GFS Chemicals, Inc. Microanalyses for Cl were performed by Oneida Research Services, Whitesboro, NY.

Re$_4$(μ_3-S)$_4$(TeCl$_2$)$_4$Cl$_8$ (1). ReCl$_5$ (0.073 g, 0.20 mmol; Strem, 99.9%), elemental S (0.0064 g, 0.20 mmol; Johnson Matthey Electronics 99.99%), and elemental Te (0.032 g, 0.25 mmol; Aldrich, 99.8%) were combined in a fused-silica tube that was evacuated to 10^{-4} Torr and sealed. The tube was heated to 400 °C for 12 h, held at this temperature for 48 h, and then cooled to room temperature at 4 °C/h. The reaction mixture, after being washed with 20 mL of acetonitrile and then 10 mL of diethyl ether, was dried under vacuum. Yield: 0.090 g (93%). Anal. Calcd for Cl$_{16}$Re$_4$S$_4$Te$_4$: Re, 38.2; Te, 26.2; Cl, 29.1; S, 6.6. Found: Re, 40.3; Te, 26.3; Cl, 26.9; S, 6.7.

Re$_4$(μ_3-Se)$_4$(TeCl$_2$)$_4$Cl$_8$ (2). The procedure for the synthesis of **1** was followed, except for the substitution of elemental Se (0.016 g, 0.20 mmol; Aldrich, 99.5%) for S. Yield: 0.10 g (91%). Anal. Calcd for Cl$_{16}$Re$_4$Se$_4$Te$_4$: Re, 34.8; Te, 23.9; Cl, 26.5; Se, 14.8. Found: Re, 36.0; Te, 23.5; Cl, 23.9; Se, 14.9.

Re$_4$(μ_3-Te)$_4$(TeCl$_2$)$_4$Cl$_8$ (3). ReCl$_5$ (0.72 g, 1.98 mmol) and elemental Te (0.56 g, 4.39 mmol) were combined in a fused-silica tube that was evacuated to 10^{-4} Torr and sealed. The tube was heated to 350 °C for 12 h, held at this temperature for 48 h, and then cooled to room temperature at 4 °C/h. The reaction mixture was washed with 20 mL acetonitrile and 10 mL of diethyl ether and was dried under vacuum. Yield: 1.05 g (91%). Anal. Calcd for Cl$_{16}$Re$_4$Te$_8$: Re, 31.9; Te, 43.8; Cl, 24.3. Found: Re, 32.5; Te, 43.9; Cl, 22.9.

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Table 2. Metrical Comparisons of Re−Re and Re−Q Distances (Å) in the Re_4Q_4 Cores (Q = S, Se, Te) of Known Structures[a,b]

dist	Re_4S_4, compd	Re_4Se_4, compd	Re_4Te_4, compd
Re−Re	2.706(1)−2.742(1), **1**	2.737(2)−2.785(2), **2**	2.783(1)−2.843(1), **3**
	2.784(1), **6**	2.805(5), **11**	2.876(1)−2.883(1), **4**
	2.736(3)−2.753(3), **7**		2.774(3)−2.831(3), **5**
	2.755(5), **8**		
	2.764(3), **9**		
	2.768(2), **10**		
Re−Q	2.332(4)−2.349(5), **1**	2.433(3)−2.449(3), **2**	2.602(1)−2.613(1), **3**
	2.349(2), **6**	2.46(1), **11**	2.641(1)−2.650(1), **4**
	2.329(7)−2.361(7), **7**		2.585(3)−2.605(4), **5**
	2.34(1), **8**		
	2.319(7)−2.463(12), **9**		
	2.324(5)−2.481(9), **10**		

[a] Only the structure of **6** is extended. [b] **1**, $Re_4(\mu_3\text{-}S)_4(TeCl_2)_4Cl_8$, this work; **2**, $Re_4(\mu_3\text{-}Se)_4(TeCl_2)_4Cl_8$, this work; **3**, $Re_4(\mu_3\text{-}Te)_4(TeCl_2)_4Cl_8$, this work; **4**, $Cs_4[Re_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 4H_2O$, ref 18; **5**, $Re_4(\mu_3\text{-}Te)_4(TeBr_2)_4Br_8$, ref 21; **6**, $Re_4(\mu_3\text{-}S)_4Te_4$, ref 14; **7**, $Cs_2K_2[Re_4(\mu_3\text{-}S)_4(CN)_{12}]\cdot 2H_2O$, ref 17; **8**, $[PPh_4]_4[Re_4(\mu_3\text{-}S)_4(CN)_{12}]\cdot 3H_2O$, ref 16; **9**, $[NH_4]_4[Re_4(\mu_3\text{-}S)_4(\mu_2\text{-}S_3)_6]\cdot 0.3NH_4Cl\cdot 0.7H_2O$, ref 19; **10**, $[NH_4]_4[Re_4(\mu_3\text{-}S)_4(CN)_{12}]\cdot 2H_2O$, ref 20; **11**, $[PPh_4]_4[Re_4(\mu_3\text{-}Se)_4(CN)_{12}]\cdot 3H_2O$, ref 16.

Table 3. Metrical Data for TeX_2 (X = Cl, Br) Molecules and Ligands

compd	M−Te (TeX_2), Å	Te−X, Å	X−Te−X, deg	ref
$TeCl_2$[a]		2.329(3)	97.0(6)	22
$Re_4(\mu_3\text{-}S)_4(TeCl_2)_4Cl_8$	2.725(1)	2.328(5)	96.5(2)	this work
$Re_4(\mu_3\text{-}Se)_4(TeCl_2)_4Cl_8$	2.724(2)	2.33(1)−2.34(1)	96.5(4)	this work
$Re_4(\mu_3\text{-}Te)_4(TeCl_2)_4Cl_8$	2.709(1)	2.329(3)−2.367(3)	94.5(1)	this work
$Re_6(\mu_3\text{-}Te)_6(\mu_3\text{-}Cl)_2(TeCl_2)_2Cl_4$	2.634(3)−2.667(3)	2.330(9)−2.363(10)	88.8(4)−91.9(4)	9
$TeBr_2$[a]		2.51(2)	98(3)	23
$Re_4(\mu_3\text{-}Te)_4(TeBr_2)_4Br_8$	2.738(3)	2.509(7)−2.543(7)	95.5	21
$[Re_6(\mu_3\text{-}Te)_8(TeBr_2)_6]Br_2$	2.634(3)	2.484(6)−2.503(6)	92.0(2)	9

[a] Electron diffraction determination.

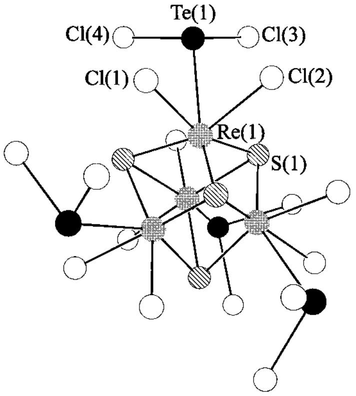

Figure 1. Structure of $Re_4(\mu_3\text{-}S)_4(TeCl_2)_4Cl_8$. The molecule has crystallographically imposed $\bar{4}$ symmetry.

Single crystals of all three compounds formed in higher quality than normal in the cool ends of the reaction tubes in the presence of a small excess of $ReCl_5$, which suggests that $ReCl_5$ acts as a vapor-transport agent in these reactions.

Crystallographic Studies. Preliminary crystallographic information for all three compounds was obtained from Weissenberg photographs taken at room temperature. Final unit cells were obtained at 113 K from the setting angles of 25 reflections that had been centered on a Picker diffractometer[25] (compounds **1** and **3**, Mo Kα radiation) or on an Enraf-Nonius CAD4 X-ray diffractometer (compound **2**, Cu Kα radiation). For each data collection, the intensities of six standard reflections remained constant. Intensity data for all compounds were processed and corrected for absorption by the analytical method.[26] The structures were solved by direct methods and refined with the use of the SHELXTL PC[24] crystallographic program package. The chosen crystals of **1** and **2** have opposite directions of their polar axes whereas **3** is an enantiomeric twin. Some crystallographic details are listed in Table 1. Additional details are available as Supporting Information.

Results and Discussion

Syntheses. $ReCl_5$ reacts with elemental Te at 350 °C to form $Re_4(\mu_3\text{-}Te)_4(TeCl_2)_4Cl_8$ (**3**) (eq 1). The reaction of the necessary amount of elemental S (eq 2) or Se (eq 3) and Te with $ReCl_5$ at 400 °C results in the formation of mixed chalcogeno halides $Re_4(\mu_3\text{-}Q)_4(TeCl_2)_4Cl_8$ (Q = S (**1**), Se (**2**)). These Re(IV) compounds can be prepared directly from the elements as was $Re_4(\mu_3\text{-}Te)_4(TeBr_2)_4Br_8$.[21]

$$4ReCl_5 + 9Te \rightarrow Re_4(\mu_3\text{-}Te)_4(TeCl_2)_4Cl_8 + TeCl_4 \quad (1)$$

$$4ReCl_5 + 4Se + 5Te \rightarrow Re_4(\mu_3\text{-}Se)_4(TeCl_2)_4Cl_8 + TeCl_4 \quad (2)$$

$$4ReCl_5 + 4S + 5Te \rightarrow Re_4(\mu_3\text{-}S)_4(TeCl_2)_4Cl_8 + TeCl_4 \quad (3)$$

In contrast, reactions of $ReCl_5$ or Re_3Br_9 with Te at 450−550 °C produce the Re_6 clusters $Re_6(\mu_3\text{-}Te)_4(\mu_3\text{-}Cl)_4Cl_6$,[8] $Re_6(\mu_3\text{-}Te)_6(\mu_3\text{-}Cl)_2(TeCl_2)_2Cl_4$,[9] and $[Re_6(\mu_3\text{-}Te)_8(TeBr_2)_6]Br_2$,[9] compounds of Re(III).

Compounds **1**−**3** are insoluble in organic solvents and water. They react slowly with DMF to form $Re_4(\mu_3\text{-}Q)_4(DMF)_4Cl_8$,[27] and they react with KCN in water at room temperature to form $K_4[Re_4(\mu_3\text{-}Q)_4(CN)_{12}]$.[18]

Structures. $Re_4(\mu_3\text{-}Q)_4(TeCl_2)_4Cl_8$ (Q = S, Se, Te) are isostructural with $Re_4(\mu_3\text{-}Te)_4(TeBr_2)_4Br_8$.[21] All of the molecules possess crystallographically imposed $\bar{4}$ symmetry. Each contains a Re_4Q_4 cubane-like core formed from a nearly regular Re_4 tetrahedron with each triangular face capped symmetrically by a μ_3-Q ligand. Table 2 summarizes the bond distances in the Re_4Q_4 core in these three compounds and in previously reported structures. In the present compounds each Re atom is further ligated by two terminal chloro ligands and one terminal

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(27) Compounds **1**−**3** react slowly with coordinating solvents such as DMF and pyridine: Mironov, Y. V.; Albrecht-Schmitt, T. E.; Ibers, J. A. Results to be published.

$TeCl_2$ ligand. The average Re−Re bond lengths increase in the order $Re_4S_4 < Re_4Se_4 < Re_4Te_4$, with ranges of 2.706(1)−2.742(1), 2.737(2)−2.785(2), and 2.783(1)−2.843(1) Å, respectively. As expected, Re−(μ_3-Q) distances increase in the same order with ranges of 2.332(4)−2.349(5), 2.433(3)−2.449(3), and 2.602(1)−2.613(1) Å, respectively. Re−Cl distances also increase in the same way, with ranges of 2.426(4)−2.443(4), 2.444(7)−2.451(6), and 2.474(3)−2.479(3) Å, respectively. The Re−Te($TeCl_2$) distances at 2.725(1) (**1**), 2.725(2) (**2**), and 2.709(1) Å (**3**) do not appear to vary.

The most prominent feature of these clusters is the presence of TeX_2 (X = Cl, Br) ligands. Whereas these TeX_2 molecules are unstable in the gas phase,[22,23] they are stabilized upon being bonded to the Re atoms in these clusters.[28] The metrical changes that occur in these molecules on ligation are minor, as the data of Table 3 indicate. It is remarkable that the resultant clusters are robust; they have shown no observable decomposition after 1 year of exposure to air.

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Supporting Information Available: Tables of crystal data and refinement details, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for **1**−**3** (15 pages). Ordering information is given on any current masthead page.

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