The Mixed Polychalcogenorhenate(IV) Anions $[Re_4Q_4(S_3)_4(S_4)_2]^{4-}$ (Q = Se, Te): Syntheses and Crystal Structures of $[NMe_4]_5[Me_2NH_2]_3[Re_4Se_4(S_3)_4(S_4)_2]_2 \cdot 2.25H_2O$ and $[NH_4]_4[Re_4Te_4(S_3)_4(S_4)_2] \cdot 8H_2O$

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Introduction

Polynuclear thiocomplexes of transition metals have been intensively studied in recent years.[1−5] Ligands in these clusters are classified as bridging, terminal, or chelating. In studying the possibility of formation of such compounds with ordered mixed chalcogenide and polychalcogenide ligands, we have succeeded in isolating the polychalcogenorhenate(IV) anions $[Re_4Se_4(S_3)_4(S_4)_2]^{4-}$ and $[Re_4Te_4(S_3)_4(S_4)_2]^{4-}$ as hydrated mixed $NMe_4^+/Me_2NH_2^+$ (**1**) and NH_4^+ salts (**2**), respectively. The related sulfidorhenate(IV) anion $[Re_4S_4(S_3)_6]^{4-}$ is known. It contains an analogous $[Re_4S_4]$ core in which six S_3^{2-} ligands span the edges of the Re_4 tetrahedron.[6,7] The existence of $[Re_4S_4(S_3)_n(S_4)_{6-n}]^{4-}$ anions has been claimed, although further details have not been published.[1]

Experimental Section

All reagents were used as purchased. The compounds $Re_4Q_4(TeCl_2)_4Cl_8$ (Q = Se, Te) were synthesized through the reaction of $ReCl_5$ (Strem, 99.9%) with elemental Se (Aldrich, 99.5%) and elemental Te (Aldrich, 99.8%), in the ratio Re:Se:Te = 1:1:1.25, or with elemental Te, in the ratio Re:Te = 1:2.25 at 350 °C.[8] Microanalyses for C, N, S, and H_2O were performed by Oneida Research Services, Whitesboro, NY. Samples for ICP analyses for Re, S, Se, and Te were prepared by dissolving the compounds in a 1:1 mixture of concentrated NH_4OH and 30% H_2O_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.

Synthesis of $[NMe_4]_5[Me_2NH_2]_3[Re_4Se_4(S_3)_4(S_4)_2]_2 \cdot 2.25H_2O$ (1). 0.20 g (6.2 mmol) of elemental S (Johnson Matthey, 99.99%) was dissolved in 10 mL of ammonium polysulfide (10% solution in water). After addition of 0.20 g (0.094 mmol) of $Re_4Se_4(TeCl_2)_4Cl_8$, the reaction mixture was stirred for 5 h at 40 °C. The solution obtained was cooled to room temperature and filtered under Ar. Next, 0.2 g (1.83 mmol) of NMe_4Cl and 0.2 g of Me_2NH_2Cl (2.45 mmol) were added to the solution. The solution was heated to 60 °C and maintained at that temperature for 6 h. Black crystals formed on the walls of the vessel. When the solution was cooled to room temperature, additional black crystals formed. The crystals were separated by filtration under Ar, washed with 10 mL of absolute EtOH, and dried under vacuum at room temperature. Yield: 0.10 g (54%). Anal. Calcd for $C_{26}H_{88.5}N_8O_{2.25}Re_8S_{40}Se_8$: C, 7.90; H, 2.26; N, 2.84; S, 32.44. Found: C, 7.88; H, 2.24; N, 3.06; S, 32.83%.

Synthesis of $[NH_4]_4[Re_4Te_4(S_3)_4(S_4)_2] \cdot 8H_2O$ (2). 0.20 g (6.2 mmol) of elemental S was dissolved in 10 mL of ammonium polysulfide (10% solution in water). After addition of 0.18 g (0.077 mmol) of $Re_4Te_4(TeCl_2)_4Cl_8$, the reaction mixture was stirred for 3 h at 60 °C. The solution obtained was filtered under Ar and stored at 0 °C for 24 h. The black crystals that formed were isolated by filtration under Ar, washed with 10 mL of absolute EtOH, and dried under vacuum at room temperature. Yield: 0.12 g (66%). Anal. Calcd for $H_{32}N_4O_8Re_4S_{20}Te_4$: N, 2.65; Re, 35.25; S, 30.35; Te, 24.16; H_2O, 6.82. Found: N, 2.76; Re, 36.20; S, 30.60; Te, 25.40; H_2O, 6.76%.

Structure Determinations. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer with the program SMART.[9] The crystal−to−detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606 frames at φ settings of 0, 90, 180, and 270°. The exposure time was 15 s/frame. Cell refinement and data reduction were carried out with the use of the program SAINT,[9] and face-indexed absorption corrections were performed numerically with the use of the program XPREP.[10] Then the program SADABS[9] was employed to make incident beam and decay corrections.

Both structures were solved by means of the direct methods program SHELXS, of the SHELXTL-PC suite of programs,[10] and were refined by full-matrix least-squares techniques.[10] The final refinements included anisotropic displacement parameters. The cluster of compound **2** has crystallographically imposed *mm* symmetry, with the result that the ring-bound S atoms of the S_3^{2-} and S_4^{2-} ligands are disordered. The S_3^{2-} ligand exists as either an S(5)−S(6A)−S(7) or S(5)−S(6B)−S(7) linkage. Atoms S(6A) and S(6B) are not related by symmetry. Initially, the site occupancies of atoms S(6A) and S(6B) were refined while constraining their sum to be unity. The values obtained were 0.51(1) for S(6A) and 0.49(2) for S(6B). Subsequently, these were fixed at 1/2. The S_4^{2-} ligands (S(1)−S(2)−S(2)−S(1) and S(3)−S(4)−S(4)−S(3)) are disordered in two parts; the occupancies of atoms S(2) and S(4) have accordingly been fixed at 1/2. In the structure of **1**, the positions of water oxygen atoms O1 and O2 are well defined; both are hydrogen bonded to H atoms of $Me_2NH_2^+$ cations. Atom O3 was placed at a “hole” in the structure. It makes no bonding interactions with other atoms. Occupancy of 0.25 for atom O3 leads to reasonable principal mean-square atomic displacements and 2.25 H_2O molecules per formula unit. In the structure of **2**, the NH_4^+ cation and the H_2O molecules of solvation could not be distinguished. Positions of the non-hydrogen atoms were assigned to the highest residual electron density peaks, with Re:N:O fixed at 4:4:8. Although the resultant positions and displacement parameters refined satisfactorily, there is some disorder among these various positions that precludes the delineation of a hydrogen-bonding scheme. No attempt was made to assign hydrogen-atom positions to the NH_4^+ cation or the H_2O molecules of solvation. Additional experimental details are given in Table 1 and in the Supporting Information.

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Table 1. Crystal Data and Structure Refinement for $[NMe_4]_5[Me_2NH_2]_3[Re_4Se_4(S_3)_4(S_4)_2]_2 \cdot 2.25H_2O$ (**1**) and $[NH_4]_4[Re_4Te_4(S_3)_4(S_4)_2] \cdot 8H_2O$ (**2**)

compound	$[NMe_4]_5[Me_2NH_2]_3[Re_4Se_4(S_3)_4(S_4)_2]_2 \cdot 2.25H_2O$	$[NH_4]_4[Re_4Te_4(S_3)_4(S_4)_2] \cdot 8H_2O$
formula	$C_{26}H_{88.5}N_8O_{2.25}Re_8S_{40}Se_8$	$H_{32}N_4O_8Re_4S_{20}Te_4$
fw	3953.2	2112.7
a, Å	12.555(1)	12.6463(7)
b, Å	38.397(4)	16.2348(9)
c, Å	19.465(2)	19.804(1)
β, deg	93.135(2)	90
V, Å^3	9369.8(16)	4065.9(4)
λ, Å	0.71073	0.71073
$\rho_{calcd.}$,(gcm^{-3})	2.802	3.455
space group	$P2_1/c$	$Cmcm$
Z	4	4
μ (cm^{-1})	143.24	157.44
T, K	153	153
$R(F)$ $(F_o^2 > 2\sigma(F_o^2))^a$	0.056	0.027
$R_w(F^2)^b$	0.123	0.0649

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

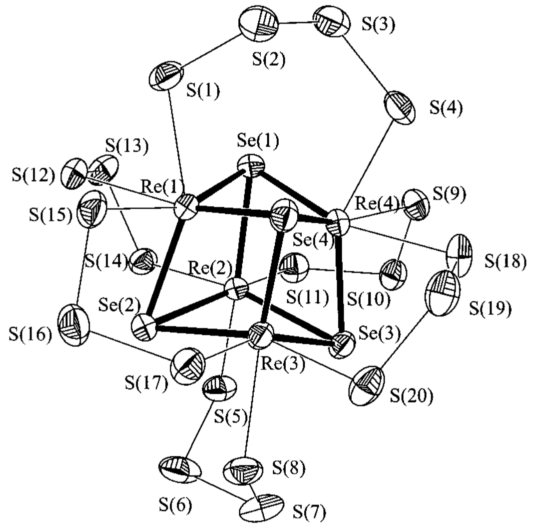

Figure 1. The structure of one of the independent $[Re_4Se_4(S_3)_4(S_4)_2]^{4-}$ anions in $[NMe_4]_5[Me_2NH_2]_3[Re_4Se_4(S_3)_4(S_4)_2]_2 \cdot 2.25H_2O$ (**1**).

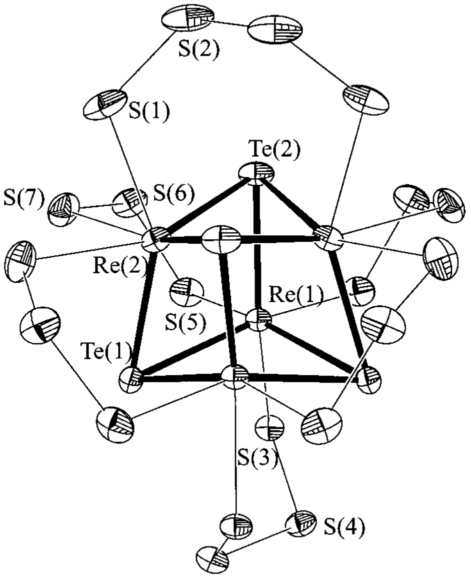

Figure 2. The structure of the $[Re_4Te_4(S_3)_4(S_4)_2]^{4-}$ anion in $[NH_4]_4[Re_4Te_4(S_3)_4(S_4)_2] \cdot 8H_2O$ (**2**). The anion has crystallographically imposed *mm* symmetry. The disorder in the S_3^{2-} and S_4^{2-} ligands is not shown.

Table 2. Ranges of Selected Bond Distances (Å) and Angles (deg) for $[NMe_4]_5[Me_2NH_2]_3[Re_4Se_4(S_3)_4(S_4)_2]_2 \cdot 2.25H_2O$ (**1**) and $[NH_4]_4[Re_4Te_4(S_3)_4(S_4)_2] \cdot 8H_2O$ (**2**)

bond or angle	compound **1**	compound **2**
Re−Re	2.7805(8)−2.8773(8)[a] 2.7794(7)−2.8786(8)[a]	2.8440(4)−2.9319(5)
Re−Se	2.4303(15)−2.4617(15)	
Re−Te		2.6014(4)−2.6324(6)
Re−S	2.465(3)−2.503(4)	2.479(2)−2.5171(14)
S−S	2.042(6)−2.105(8)	2.000(5)−2.069(6)
Re−Re−Re	58.745(8)−62.21(2) 58.723(19)−62.274(19)	58.973(6)−62.055(12)

[a] There are two independent Re_4 clusters in the asymmetric unit.

Results and Discussion

The title compounds $[NMe_4]_5[Me_2NH_2]_3[Re_4Se_4(S_3)_4(S_4)_2]_2 \cdot 2.25H_2O$ (**1**) and $[NH_4]_4[Re_4Te_4(S_3)_4(S_4)_2] \cdot 8H_2O$ (**2**) have been synthesized by the reaction of the Re clusters $Re_4Q_4(TeCl_2)_4Cl_8$ (Q = Se, Te) with ammonium polysulfide. Compound **1** crystallizes as black needles from a hot solution that contains an excess of NMe_4Cl and Me_2NH_2Cl. Our attempts to obtain analogous crystals of $[NMe_4]_5[Me_2NH_2]_3[Re_4Te_4(S_3)_4(S_4)_2]_2 \cdot 2.25H_2O$ in this way led to powders. In the presence of Me_2NH_2Cl or Me_3NHCl, the formation of the ammonium salt $[NH_4]_4[Re_4Te_4(S_3)_4(S_4)_2] \cdot 8H_2O$ (**2**) occurs. The most interesting feature of the present syntheses is the formation of mixed Se/S and Te/S complexes from concentrated solutions of ammonium polysulfide. This demonstrates the very high stability of the cluster units $[Re_4Q_4]^{8+}$ (Q = Se, Te) in the presence of a high concentration of S_n^{2-}. Previously, the high stability of these cluster units was observed in the reactions of $Re_4Q_4(TeCl_2)Cl_8$ with KSCN melts.[11]

Compound **1** contains two independent $[Re_4Se_4(S_3)_4(S_4)_2]^{4-}$ anions in the asymmetric unit. One such anion is shown in Figure 1. The related $[Re_4Te_4(S_3)_4(S_4)_2]^{4-}$ anion of compound **2** is shown without disorder in Figure 2. Each anion comprises a Re(IV) metal−metal bonded tetrahedron. Each tetrahedral face is capped by an Se^{2-} (**1**) or a Te^{2-} (**2**) ligand. Each Re_4Q_4 core is additionally bis-chelated by two trans S_4^{2-} ligands and four S_3^{2-} ligands. The four Re_2S_3 rings have an envelope conformation, as previously observed in the $[Re_4S_4(S_3)_6]^{4-}$ anion.[6] The ReS_4 rings also contain planar Re_2S_2 moieties, with the two remaining S atoms trans to the Re_2S_2 plane. Ranges of selected bond distances and angles are presented in Table 2. These are consistent with literature values.[1,6−8]

The polysulfide ligands, S_3^{2-} and S_4^{2-}, were previously found in the binuclear rhenium cluster compound $[NH_4]_2[Re_2S_2(S_3)_2(S_4)_2] \cdot 4H_2O$.[12] Of course, a variety of polysulfide ligands, especially S_2^{2-} and S_4^{2-}, are found in molybdenum clusters.[5]

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $[NMe_4]_5[Me_2NH_2]_3[Re_4Se_4(S_3)_4(S_4)_2]\cdot2.25H_2O$ and $[NH_4]_4[Re_4Te_4(S_3)_4(S_4)_2]\cdot8H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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