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The First Coordination Polymers Based on Octahedral Hexahydroxo Rhenium Cluster Complexes $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se) and Alkaline Earth Metal Cations

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Seven novel octahedral cluster compounds $[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot 6H_2O$ (**1**), $[\{Ca(H_2O)_3\}_2Re_6S_8(OH)_6]$ (**2**), $[\{Ca(H_2O)_3\}_2Re_6Se_8(OH)_6]$ (**3**), $[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6]\cdot 6H_2O$ (**4**), $[\{Sr_2(H_2O)_{10}\}Re_6Se_8(OH)_6]\cdot 6H_2O$ (**5**), $[\{Ba_2(H_2O)_8\}Re_6S_8(OH)_6]$ (**6**), and $[\{Ba_2(H_2O)_8\}Re_6Se_8(OH)_6]$ (**7**) were prepared by the direct reaction of $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ with the cations of the elements of main group II. All compounds have been characterized by single crystal X-ray diffraction. Compound **1** has a discrete molecular structure, compounds **4** and **5** have a one-dimensional chain structure, and compounds **2**, **3**, **6**, and **7** crystallize in two different types of two-dimensional layered structure. This sulfur containing series has been characterized by luminescent spectroscopy.

Introduction

Octahedral rhenium clusters present an attractive class of structural and functional building blocks for the design of solids including coordination polymers and supramolecular constructions.[1] Coordination polymer compounds based on rhenium chalcohalide[2] and chalcogenide[3] clusters have been known for a long time. Others were obtained quite recently. One of the most developed building blocks is the octahedral rhenium chalcogenide cluster complexes of general formula $Re_6Q_8L_6$ where Q = S, Se, Te and L = an acido ligand or an organic donor group. There are two groups of terminal ligand, L, that are suitable for inclusion in such complexes with the appropriate partners. Firstly, there is the ambidentate CN ligand; in this case the $[Re_6Q_8(CN)_6]^{4-/3-}$ building blocks act with the transition or post-transition metals forming cyano-bridged inorganic polymeric structures.[4] Secondly, it is possible to use specific organic molecules that can function as a bidentate-bridge, and in this case mixed organic/inorganic polymers are formed.[5]

Very recently[6] two novel cluster complexes $K_4[Re_6Q_8(OH)_6]\cdot 8H_2O$ (Q = S, Se) were synthesized and characterized. In a preceding contribution, we presented the cluster anions $[Re_6Q_8(OH)_6]^{4-}$ as promising new building blocks for the construction of coordination polymers. In the present work a series of crystalline solids **1**–**7** are prepared by the direct reaction of $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ with the cations of the elements of main group II.

$[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot 6H_2O$ (**1**)
$[\{Ca(H_2O)_3\}_2Re_6S_8(OH)_6]$ (**2**)
$[\{Ca(H_2O)_3\}_2Re_6Se_8(OH)_6]$ (**3**)
$[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6]\cdot 6H_2O$ (**4**)
$[\{Sr_2(H_2O)_{10}\}Re_6Se_8(OH)_6]\cdot 6H_2O$ (**5**)
$[\{Ba_2(H_2O)_8\}Re_6S_8(OH)_6]$ (**6**)
$[\{Ba_2(H_2O)_8\}Re_6Se_8(OH)_6]$ (**7**)

Simple synthetic methods produce these complexes on a large scale. All seven structures were elucidated by single-crystal X-ray diffraction. Compound **1** has a discrete molecular structure, and compounds **4** and **5** are isostructural and form a one-dimensional chain structure. Compounds **2** is isostructural with **3**, and **6** is isostructural with **7**; these compounds form two types of two-dimensional layered structure.

To date, only the ionic alkaline earth aqua complexes $[Ca(H_2O)_7][Re_6Q_6Cl_8]\cdot 3H_2O$ (Q = S, Se), $[Ca(H_2O)_8][Re_6S_6Cl_8]$, and $Mg(H_2O)_6[Re_6S_6Cl_8]\cdot 2H_2O$ have been reported.[7]

Results

Structures

Compounds **1**–**7** contain hexahydroxo cluster anions $[Re_6Q_8(OH)_6]^{4-}$ (Q = S or Se) coordinated to M^{2+} cations, where M = Mg, Ca, Sr, Ba. The structures of the $[Re_6-$

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$Q_8(OH)_6]^{4-}$ (Q = S, Se) cluster anions are similar to those observed in the starting materials, and to the well known octahedral complexes of type $[Re_6Q_8L_6]^{4-}$ with L = Cl^-, Br^-, I^-, CN^-. The Re_6 octahedron that resides inside a cube of Q_8 (S, Se) forms a system of Re–Re and Re–(μ_3-Q) bonds. Six terminal OH^- ligands are coordinated to the Re atoms with Re–O bond lengths in the following ranges: 2.090(6)–2.093(6) Å (**1**), 2.100(4) Å (**2**), 2.124(3) Å (**3**), 2.077(7)–2.096(6) Å (**4**), 2.080(6)–2.110(5) Å (**5**), 2.059(9)–2.093(11) Å (**6**) and 2.083(7)–2.100(8) Å (**7**). The structures of complexes with M^{2+} demonstrate a strong dependence on the atomic size of the metal used.

Compound **1** has a discrete molecular structure (Figure 1) where the cluster anion $[Re_6S_8(OH)_6]^{4-}$ is coordinated to by two aqua cationic $[Mg(H_2O)_5]^{2+}$ complexes in a *trans* arrangement about the OH bridges. In this way each Mg atom is coordinated to by 5 water molecules, with Mg–O distances in the range of 2.052(7)–2.216(7) Å, and by the O atom of the OH ligand of the cluster anion. The Mg–O(OH) distance is equal to 2.046(7) Å, and the ∠Re–O–Mg is equal to 138.0(3)°.

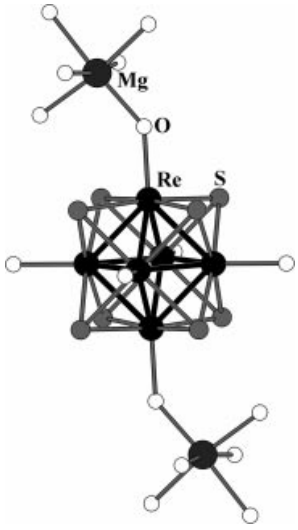

Figure 1. Structure of molecular complex $[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]$ in (**1**).

Compounds **2** and **3** have a two-dimensional layered structure (Figure 2). Each Ca atom of compounds **2** and **3** is coordinated to by three water molecule O atoms with Ca–O distances of 2.377(5) Å, and by three O atoms from the OH ligands of three different cluster anions with Ca–O distances of 2.338(4) Å. This results in the formation of the *fac*-isomer. Whereas each Ca atom is coordinated to by three cluster anions, and each cluster anion is coordinated to by six Ca atoms giving a Ca/cluster anion ratio of 2:1. Interlayer distances are in the range excepted for hydrogen bonds between the O atoms of the water molecules coordinated to the Ca atoms and the O atoms of the OH groups of the cluster anions in an adjacent layer (2.745 Å in **2** and 2.804 Å in **3**).

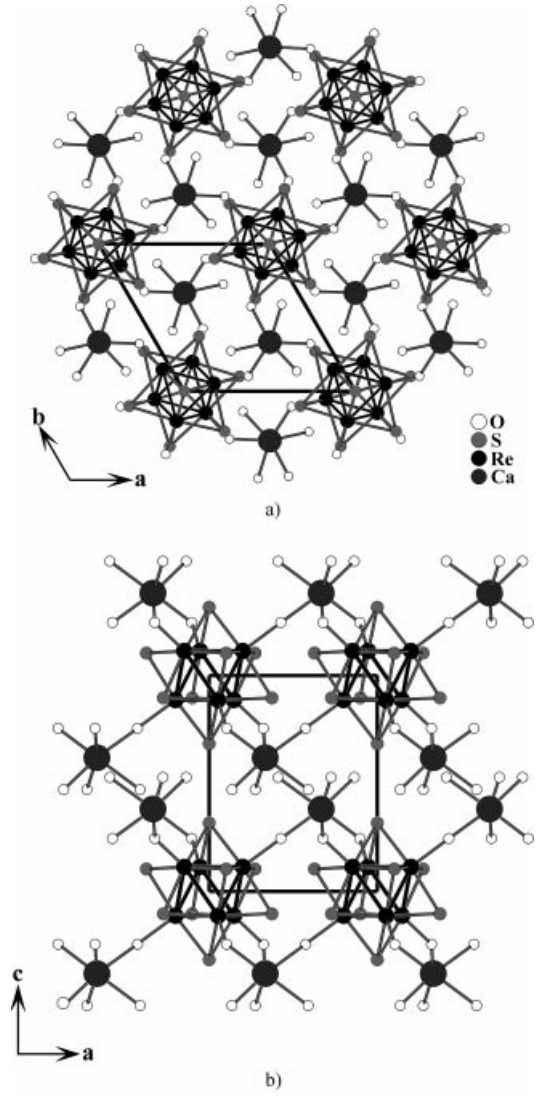

Figure 2. Structure of $[\{Ca(H_2O)_3\}_2Re_6S_8(OH)_6]$ (**2**): a) view along the *c*-axes; b) view along the *b*-axes.

Compounds **4** and **5** form one-dimensional chain-like structures (Figure 3). In these compounds cluster anions are bonded by cationic dimers $[Sr_2(H_2O)_{10}]^{4+}$. Two Sr atoms are bridged by two water molecules to form a dimer with an Sr–Sr separation of 4.3140(19) Å in **4** and 4.3016(16) in **5** and Sr–O distances of 2.675(8) Å and 2.680(8) Å in **4** and 2.666(6) Å and 2.686(7) Å in **5**. Additionally each Sr atom is coordinated to by 4 terminal water molecules (Sr–O distances are in the ranges of 2.555(8)– 2.603(9) Å in **4** and 2.551(7)–2.622(7) Å in **5**) and two O atoms of the OH ligands of the cluster anion [Re–O(OH) distances equal 2.532(7) Å in **4** and 2.547(6) Å in **5**]. Each Sr atom is connected to the Q atom of the cluster anion with Sr–Q distances equal to 3.260(3) Å (**4**) and 3.3649(12) Å (**5**).

In compounds **6** and **7** (Figure 4) the Ba atoms also form dimers but of a different type to the Sr dimers: two O atoms of the OH ligands of the cluster anions bridge the Ba atoms. The Ba–Ba distances in these compounds are equal to

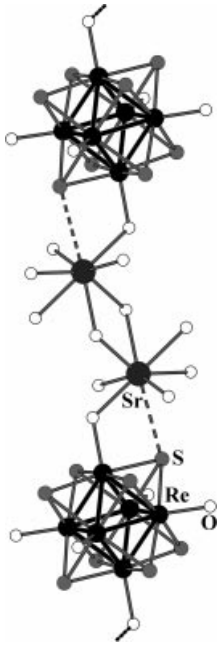

Figure 3. Structure of fragment of the $[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6]_n$ chain in (**4**).

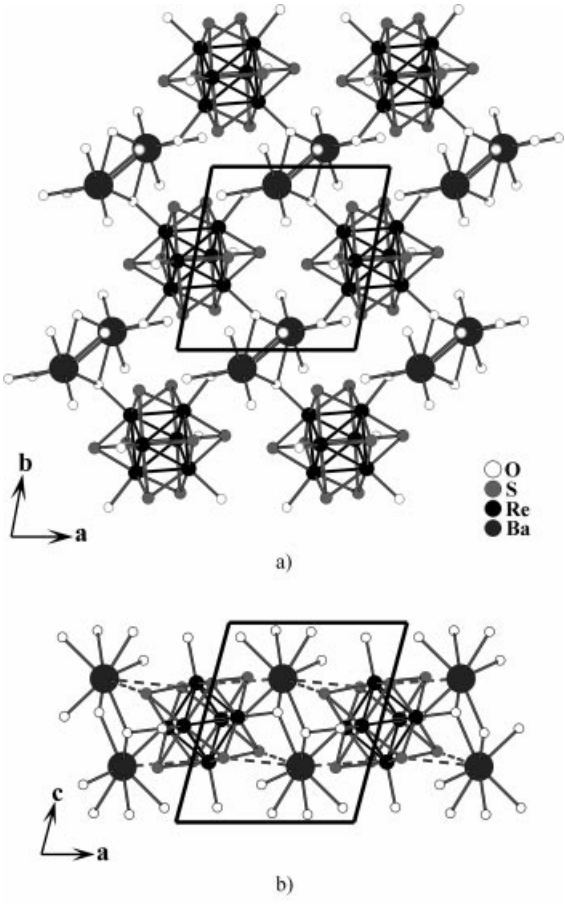

Figure 4. Structure of $[\{Ba_2(H_2O)_8\}Re_6S_8(OH)_6]$ (**6**): a) view along the *c*-axes; b) view along the *b*-axes.

4.352(2) Å in **6** and 4.4016(16) Å in **7**, the Ba–O distances for the bridged OH ligands are equal to 2.724(10) Å and 2.795(11) Å for **6**, 2.708(7) Å and 2.799(7) Å for **7**. Additionally each Ba atom is coordinated to by four water molecule O atoms [Ba–O distances are in range of 2.761(12)–2.86(3) Å (**6**) and 2.809(12)–2.92(2) Å (**7**)], and one atom of a OH ligand of a cluster anion [Ba–O distances are equal to 2.648(11) Å in **6** and 2.632(8) Å in **7**]. The coordination spheres of the Ba atoms are expanded by three Q atoms of the cluster core [Ba–S distances in **6** are 3.537(4), 3.660(3) and 3.878(4) Å, and the Ba–Se distances in **7** are 3.5715(14), 3.7457(13) and 3.7883(14) Å]. In this way each Ba dimer is coordinated to four cluster anions resulting in the formation of two-dimensional layered structures. Finally, in compounds **6** and **7** four OH ligands coordinated to the Ba atoms are associated with the anion clusters, whereas the other two are terminal and are in a *trans* arrangement about the dimer unit. The terminal OH groups are hydrogen bonded to the O atoms of water molecules coordinated to Ba atoms in an adjacent layer causing close packing of the layers. The closest interlayer distances are $O(H_2O)$–O(OH) = 2.748 Å in **6** and 2.813 Å in **7**.

Thus, the coordination numbers of the metal atoms in these compounds vary from 6 for Mg and Ca to 8 for Sr, and 10 for Ba.

Luminescence

The luminescent properties of the starting cluster compound $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and the thio complexes **1**, **2**, **4**, **6** were studied. All compounds show similar behavior; for example, upon excitation at 440 nm, the solid sulfur containing samples $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and **1**, **2**, **4** and **6** displayed photoluminescence maxima at 618, 621, 618, 619 and 625 nm, respectively (Figure 5). These results are consistent with those previously reported for sulfide rhenium clusters.[5f,6] Figure 6 shows a comparison of the emission spectra for the rhenium sulfide (**2**) and selenide (**3**) cluster compounds. The emission maximum of the selenide

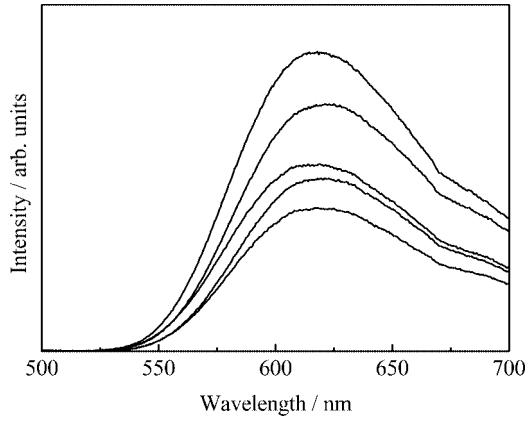

Figure 5. Solid-state emission (λ_{exc} = 440 nm) spectra of the compounds $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and **1**, **2**, **4**, **6** (from top to bottom). The maxima are observed at 618, 621, 618, 619 and 625 nm.

cluster is shifted by about 40 nm to a longer wavelength relative to the sulfide cluster, which is consistent with previous reports.[5f,8]

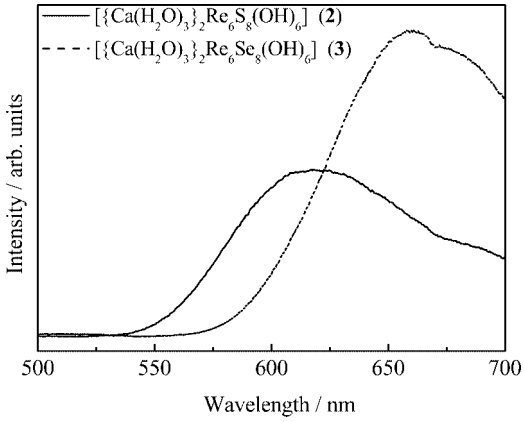

Figure 6. Solid-state emission (λ_{exc} = 440 nm) spectra of compounds $[\{Ca(H_2O)_3\}_2Re_6S_8(OH)_6]$ (**2**) and $[\{Ca(H_2O)_3\}_2Re_6Se_8(OH)_6]$ (**3**). The maxima are observed at 619 and 659 nm.

Experimental Section

$K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ were prepared as previously described.[6] All other reagents were commercially available products of reagent grade quality, and were used as obtained. All experiments were not performed under controlled atmospheric conditions.

All compounds were obtained in 70–90% yield by mixing an aqueous solution of $K_4[Re_6Q_8(OH)_6]\cdot 8H_2O$ with the chloride or nitrate salt of the corresponding metal. Crystals of compound **1** were obtained in the presence of 1,3,5-trioxane. The formation of compounds **2**–**5** may be forced by adding a few drops of DMF to the reaction mixture.

Luminescence Measurements: The emission spectra of solid samples of **1**, **2**, **3**, **4**, **6** were recorded in the wavelength range of 500 nm to 700 nm using a UV-Spectrofluorimeter equipped with a ORIEL 77200 monochromator and a Hamamatsu R928 PMT detector. The Xe lamp (ORIEL photomax, 75 W) was used as a light source, which emitted intense and relatively stable radiation in a continuous range of 200 nm to 800 nm. The excitation slit width was 1.56 mm, and the emission slit width was 60 μm.

X-ray Crystallography: Single crystal X-ray diffraction data were collected on $[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]$ (**1**), $[\{Ca(H_2O)_3\}_2Re_6Q_8(OH)_6]$ where Q = S (**2**), Se (**3**), $[\{Sr_2(H_2O)_{10}\}Re_6Q_8(OH)_6]$ where Q = S (**4**), Se (**5**), and $[\{Ba_2(H_2O)_8\}Re_6Q_8(OH)_6]$ where Q = S (**6**), Se (**7**). Data were collected with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 170 K (**1**, **3**) and 293 K (**2**, **4**, **5**, **6**, **7**) with a Bruker Smart APEX CCD diffractometer with the operating program SMART. A face-indexed absorption correction was performed numerically with the use of XPREP. The program SADABS was then employed to perform incident beam and decay corrections. All structures were solved by direct methods and refined (full-matrix least-squares on F^2) with the SHELX-97 program suite.[9]

$[\{Mg(H_2O)_5\}_2Re_6S_8(OH)_6]\cdot 6H_2O$ (1): (M = 1812.60), crystal size 0.28 × 0.06 × 0.05 mm, triclinic space group $P\bar{1}$, a = 8.4986(18) Å, b = 8.6593(19) Å, c = 10.920(2) Å, α = 78.179(4)°, β = 85.273(3)°, γ = 76.809(3)°, V = 765.3(3) Å^3, Z = 1, $\rho_{calcd.}$ = 3.933 g cm^{-3}, μ = 24.294 mm^{-1}, 1.91 < θ < 28.22°, T = 173(2) K. Reflections: 4799 collected, 3406 unique (R_{int} = 0.0229), 2893 observed [$I > 2\sigma(I)$]; 173 parameters refined with R = 0.0333 [$I > 2\sigma(I)$], wR_2 = 0.0882 (all data), GOF = 0.996, residual electron density: +2.814 e Å^3, –2.745 e Å^3.

$[\{Ca(H_2O)_3\}_2Re_6S_8(OH)_6]$ (2): (M = 1663.98), crystal size 0.16 × 0.14 × 0.026 mm, trigonal space group $P\bar{3}$, a = 8.3359(8) Å, c = 9.3100(18) Å, V = 560.25(13) Å^3, Z = 1, $\rho_{calcd.}$ = 4.932 g cm^{-3}, μ = 33.527 mm^{-1}, 2.19 < θ < 28.03°, T = 293(2) K. Reflections: 3450 collected, 904 unique (R_{int} = 0.0394), 832 observed [$I > 2\sigma(I)$]; 56 parameters refined with R = 0.0246 [$I > 2\sigma(I)$], wR_2 = 0.0608 (all data), GOF = 1.046, residual electron density: +3.390 e Å^3, –1.795 e Å^3.

$[\{Ca(H_2O)_3\}_2Re_6Se_8(OH)_6]$ (3): (M = 2039.18), crystal size 0.28 × 0.20 × 0.01 mm, trigonal space group $P\bar{3}$, a = 8.4729(6) Å, c = 9.4353(14) Å, V = 586.61(11) Å^3, Z = 1, $\rho_{calcd.}$ = 5.772 g cm^{-3}, μ = 43.719 mm^{-1}, 2.78 < θ < 28.13°, T = 293(2) K. Reflections: 3667 collected, 927 unique (R_{int} = 0.0288), 859 observed [$I > 2\sigma(I)$]; 44 parameters refined with R = 0.0222 [$I > 2\sigma(I)$], wR_2 = 0.0572 (all data), GOF = 1.13, residual electron density: +1.551 e Å^3, –1.616 e Å^3.

$[\{Sr_2(H_2O)_{10}\}Re_6S_8(OH)_6]\cdot 6H_2O$ (4): (M = 1939.22), crystal size 0.26 × 0.20 × 0.16 mm, triclinic space group $P\bar{1}$, a = 8.7027(12) Å, b = 9.2442(13) Å, c = 10.8666(15) Å, α = 87.545(2)°, β = 74.635(2)°, γ = 73.721(2)°, V = 808.70(19) Å^3, Z = 1, $\rho_{calcd.}$ = 3.982 g cm^{-3}, μ = 26.214 mm^{-1}, 1.94 < θ < 28.25°, T = 293(2) K. Reflections: 5077 collected, 3587 unique (R_{int} = 0.0271), 3192 observed [$I > 2\sigma(I)$]; 173 parameters refined with R = 0.0386 [$I > 2\sigma(I)$], wR_2 = 0.1085 (all data), GOF = 1.057, residual electron density: +4.172 e Å^3, –3.669 e Å^3.

$[\{Sr_2(H_2O)_{10}\}Re_6Se_8(OH)_6]\cdot 6H_2O$ (5): (M = 2314.42), crystal size 0.26 × 0.14 × 0.02 mm, triclinic space group $P\bar{1}$, a = 8.8380(13) Å, b = 9.3615(13) Å, c = 11.0489(16) Å, α = 86.906(2)°, β = 73.821(2)°, γ = 72.735(2)°, V = 838.0(2) Å^3, Z = 1, $\rho_{calcd.}$ = 4.586 g cm^{-3}, μ = 33.488 mm^{-1}, 2.28 < θ < 28.26°, T = 293(2) K. Reflections: 5255 collected, 3732 unique (R_{int} = 0.0199), 2981 observed [$I > 2\sigma(I)$]; 173 parameters refined with R = 0.0317 [$I > 2\sigma(I)$], wR_2 = 0.0935 (all data), GOF = 1.069, residual electron density: +2.536 e Å^3, –1.956 e Å^3.

$[\{Ba_2(H_2O)_8\}Re_6S_8(OH)_6]$ (6): (M = 1894.54), crystal size 0.18 × 0.03 × 0.02 mm, triclinic space group $P\bar{1}$, a = 8.2413(14) Å, b = 8.4332(15) Å, c = 9.4651(17) Å, α = 81.879(3) , β = 74.242(3) , γ = 77.937(3) , V = 616.63(19) Å^3, Z = 1, $\rho_{calcd.}$ = 5.102 g cm^{-3}, μ = 33.185 mm^{-1}, 2.24 < θ < 28.24°, T = 293(2) K. Reflections: 3898 collected, 2757 unique (R_{int} = 0.0253), 2166 observed [$I > 2\sigma(I)$]; 137 parameters refined with R = 0.0426 [$I > 2\sigma(I)$], wR_2 = 0.1139 (all data), GOF = 1.008, residual electron density: +4.294 e Å^3, –3.040 e Å^3.

$[\{Ba_2(H_2O)_8\}Re_6Se_8(OH)_6]$ (7): (M = 2269.74), crystal size 0.30 × 0.03 × 0.02 mm, triclinic space group $P\bar{1}$, a = 8.4020(12) Å, b = 8.5735(12) Å, c = 9.6420(14) Å, α = 81.049(3)°, β = 73.639(2)°, γ = 77.308(2)°, V = 646.88(16) Å^3, Z = 1, $\rho_{calcd.}$ = 5.826 g cm^{-3}, μ = 42.241 mm^{-1}, 2.21 < θ < 28.26°, T = 293(2) K. Reflections: 4076 collected, 2882 unique (R_{int} = 0.0279), 2225 observed [$I > 2\sigma(I)$]; 137 parameters refined with R = 0.0340 [$I > 2\sigma(I)$], wR_2 = 0.0879 (all data), GOF = 0.957, residual electron density: +2.288 e Å^3, –1.875 e Å^3.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository CSD number filenames 415688–415694 (for **1**–**7**).

Acknowledgments

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