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A Family of Octahedral Rhenium Cluster Complexes $[Re_6Q_8(H_2O)_n(OH)_{6-n}]^{n-4}$ (Q = S, Se; n = 0–6): Structural and pH–Dependent Spectroscopic Studies

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The conversions of hexahydroxo rhenium cluster complexes $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se) in aqueous solutions in a wide pH range were investigated by chemical methods and spectroscopic measurements. Dependences of the spectroscopic and excited-state properties of the solutions on pH have been studied in detail. It has been found that a pH decrease of aqueous solutions of the potassium salts $K_4[Re_6Q_8(OH)_6]\cdot 8H_2O$ (Q = S, Se) results in the formation of aquahydroxo and hexaaqua cluster complexes with the general formula $[Re_6Q_8(H_2O)_n(OH)_{6-n}]^{n-4}$ that could be considered as a result of the protonation of the terminal OH^- ligands in the hexahydroxo complexes. The compounds $K_2[Re_6S_8(H_2O)_2(OH)_4]\cdot 2H_2O$ (**1**), $[Re_6S_8(H_2O)_4(OH)_2]\cdot 12H_2O$ (**2**), $[Re_6S_8(H_2O)_6][Re_6S_6Br_8]\cdot 10H_2O$ (**3**), and $[Re_6Se_8(H_2O)_4(OH)_2]$ (**4**) have been isolated and characterized by X-ray single-crystal diffraction and elemental analyses and infrared (IR) spectroscopy. In crystal structures of the aquahydroxo complexes, the cluster units are connected to each other by an extensive system of very strong hydrogen bonds between terminal ligands.

Introduction

The octahedral chalcogenide rhenium cluster complexes have been in the focus of theorists and experimentalists for a long time. The first studies of Re_6-based compounds were devoted to solid-state chemistry.[1−4] The discovery of the soluble molecular and ionic complexes with the general formula $[Re_6Q_8L_6]$ (Q = S, Se, Te)[5−8] has initiated intensive investigations directed to the solution chemistry of octahedral rhenium cluster compounds.[9−17] The reason for the heightened interest in Re_6 complexes is due to their wide variety of chemical and physical properties, such as their ability to form coordination polymers with various crystal structures,[18−29]

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redox transformations,[13−17,30−33] and luminescent properties both in solutions[15,16,30−39] and in the solid state.[33,36,40]

The intense interest in Re_6-based compounds gives rise to the necessity of developing effective methods of synthesizing new rhenium cluster complexes and the thorough study of their properties.

In this work, we report the study of pH dependences of the spectroscopic and excited-state properties of aqueous solutions of salts $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (**5**) and $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ (**6**) synthesized recently[33] and syntheses, crystal structures, and properties of some new compounds containing cluster complexes with the general formula $[Re_6Q_8(H_2O)_n(OH)_{6-n}]^{n-4}$ ($Q = S$, $n = 2, 4, 6$; $Q = Se$, $n = 4$).

Experimental Section

Materials and Syntheses. The starting cluster salts $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (**5**), $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ (**6**), and $K_2[Re_6S_6Br_8]$ were synthesized as described previously.[33,41] All of the other reagents were used as purchased.

Elemental analyses for H, S, and O were performed by using an EA1108 (Carlo Erba Instrument). Energy dispersive spectroscopy (EDS) was performed on an EDAX equipped (JEOL EX-23000BU) JEOL JSM-6700F field emission scanning electron microscope. X-ray powder diffraction data were collected on a Rigaku diffractometer (Cu Kα radiation, 2θ range was 5−60°, scan rate was 0.02°/s). The X-ray powder patterns of the compounds synthesized are in good agreement with the data calculated on the basis of the results of the single-crystal study. Infrared (IR) spectra were measured on KBr pellets with a Scimitar FTS 2000c spectrometer in the range 4000−400 cm^{-1}.

For the preparation of solutions for spectroscopic measurements, water was distilled and deionized prior to use (Advantec Toyo, GSR-200). The pH of the aqueous solutions was adjusted with an appropriate amount of concentrated solutions of HCl or KOH, and the value was determined by a pH meter (Horiba, D-12). Absorption and emission spectroscopies were conducted using a U-3300 spectrophotometer (Hitachi) and a F-4500 spectrofluorometer (Hitachi), respectively. Corrected emission spectra were recorded on a red-sensitive multichannel photodetector (Hamamatsu Photonics, PMA-11). For emission decay measurements, a sample solution was excited by 355 nm laser pulses (6 ns duration, Continuum Surelite-II), and the emission was analyzed by a streakscope system (Hamamatsu Photonics, C4334 and C5094). For emission measurements, the absorbance of the sample solutions was set <0.05 at 355 nm, and the solutions were deaerated by purging an argon gas stream for 20 min. The emission quantum yields (Φ_{em}) were determined by using tris-(2,2′-bipyridine)ruthenium(II) as a standard: $\Phi_{em} = 0.061$ in deaearated CH_3CN.[42] A refractive index correction was made to calculate the Φ_{em} values.

Synthesis of $K_2[Re_6S_8(H_2O)_2(OH)_4]\cdot 2H_2O$ (1). $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (0.355 g, 0.200 mmol) was dissolved in 5 mL of water, and the solution was left in a closed vessel at room temperature for 1 month. The resulting yellow crystalline precipitate was filtered off, washed with water, and dried in air to give 0.235 g (73.5%) of $K_2[Re_6S_8(H_2O)_2(OH)_4]\cdot 2H_2O$. Anal. Calcd for $H_{12}K_2O_8Re_6S_8$: H, 0.76; O, 8.04; S, 16.11. Found: H, 1.08; O, 7.79; S, 16.56. EDS gave a K/Re/S ratio of 1.6:6:7.5. The IR spectrum, cm^{-1}: 413 s, 750sh vw, 876 m, 1028 m, 1607 s, 3443 s, 3500sh m, 3545sh m.

Synthesis of $[Re_6S_8(H_2O)_4(OH)_2]\cdot 12H_2O$ (2). $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (0.180 g, 0.101 mmol) was dissolved in 20 mL of water, and the solution was left in an open vessel at room temperature for 2 weeks. The resulting yellow crystalline precipitate was filtered off, washed with water, and dried in air to give 0.058 g (34.2%) of $[Re_6S_8(H_2O)_4(OH)_2]\cdot 12H_2O$. The same compound can be also obtained in a quantitative yield as a yellow powder by the acidification of an alkaline aqueous solution of the anionic complex $[Re_6S_8(OH)_6]^{4-}$ with 1M H_2SO_4 until a neutral pH is reached. Anal. Calcd for $H_{34}O_{18}Re_6S_8$: H, 2.02; O, 16.98; S, 15.13. Found: H, 1.93; O, 16.59; S, 15.27. EDS gave a Re/S ratio of 6:7.2. The IR spectrum, cm^{-1}: 407 s, 745 vw, 876 m, 1040 m, 1609 s, 2924 w, 3420 s, 3509 s, 3545sh m.

Synthesis of $[Re_6S_8(H_2O)_6][Re_6S_6Br_8]\cdot 10H_2O$ (3). A 1M solution of sulfuric acid was added dropwise to an aqueous solution (10 mL) of $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (0.090 mg, 0.051 mmol) until the complete dissolution of the initially formed precipitate of the sparingly soluble aquahydroxo complex, which resulted in a clear yellow solution. The solution was mixed with an aqueous solution (10 mL) of $K_2[Re_6S_6Br_8]$ (0.103 g, 0.051 mmol) and allowed to stand overnight at room temperature in a covered vessel, resulting in the formation of a yellow crystalline precipitate. The precipitate

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Table 1. Crystal Data and Structure Refinement for $K_2[Re_6S_8(H_2O)_2(OH)_4]{\cdot}2H_2O$ (**1**), $[Re_6S_8(H_2O)_4(OH)_2]{\cdot}12H_2O$ (**2**), $[Re_6S_8(H_2O)_6][Re_6S_6Br_8]{\cdot}10H_2O$ (**3**), and $[Re_6Se_8(H_2O)_4(OH)_2]$ (**4**)

	1	**2**	**3**	**4**
empirical formula	$H_{12}K_2O_8Re_6S_8$	$H_{34}O_{18}Re_6S_8$	$H_{32}Br_8O_{16}Re_{12}S_{14}$	$H_{10}O_6Re_6Se_8$
fw	1591.98	1695.95	3610.78	1854.96
space group	$P\bar{1}$	$R\bar{3}m$	$P\bar{1}$	$Pa\bar{3}$
a (Å)	7.957(2)	14.9959(13)	9.1109(8)	12.084(4)
b (Å)	8.790(2)		9.2467(8)	
c (Å)	9.186(2)	10.9403(19)	15.8877(15)	
α (deg)	78.827(4)		99.966(2)	
β (deg)	64.727(4)		90.343(3)	
γ (deg)	67.085(4)		115.183(2)	
V (Å^3)	534.9(2)	2130.6(5)	1188.2(2)	1764.7(10)
Z	1	3	1	4
ρ_{calcd} (g/cm^3)	4.942	3.965	5.046	6.982
μ (cm^{-1})	350.04	261.14	378.04	575.02
cryst size (mm^3)	0.08 × 0.08 × 0.06	0.09 × 0.08 × 0.06	0.16 × 0.06 × 0.01	0.05 × 0.05 × 0.05
T_{min}; T_{max}	0.0616; 0.1448	0.2021; 0.3033	0.0647; 0.7037	0.1611; 0.1611
θ range (deg)	2.45 to 28.42	2.43 to 28.25	1.31 to 27.48	2.92 to 28.25
reflns collected	3308	4477	8570	9504
unique reflns	2362	650	5085	731
R_{int}	0.0138	0.0291	0.0380	0.1829
params refined	119	32	231	32
$R_1(F)$ $[F_o^2 > 2\sigma(F_o^2)]$	0.0286	0.0204	0.0463	0.0389
$R_w(F^2)$ (all data)	0.0796	0.0554	0.1346	0.0820

was collected by filtration, washed with water, and dried in air to afford 0.120 g (66.5%) of $[Re_6S_8(H_2O)_6][Re_6S_6Br_8]{\cdot}10H_2O$. Anal. Calcd for $H_{32}Br_8O_{16}Re_{12}S_{14}$: H, 0.89; O, 7.09; S, 12.43. Found: H, 0.71; O, 6.64; S, 12.49. EDS gave a Re/S/Br ratio of 6:6.8:3.9. The IR spectrum, cm^{-1}: 413 s, 467 m, 718 s, 1603 s, 2925 s, 3180 s, 3365 m, 3449 m, 3532 m.

Synthesis of $[Re_6Se_8(H_2O)_4(OH)_2]$ (4). An aqueous solution (5 mL) of $K_4[Re_6Se_8(OH)_6]{\cdot}8H_2O$ (0.200 g, 0.093 mmol) was mixed with an aqueous solution (5 mL) of $MgCl_2{\cdot}6H_2O$ (0.200 g, 0.984 mmol) and 1,3,5-trioxane (0.089 g, 0.988 mmol) and left at room temperature in a covered vessel for 1 week. The resulting red octahedral crystals were carefully separated from the reaction mixture and dried in air to give 0.015 g (8.7%) of $[Re_6Se_8(H_2O)_4(OH)_2]$. Anal. Calcd for $H_{10}O_6Re_6Se_8$: H, 0.54; O, 5.18. Found: H, 0.61; O, 5.09. EDS gave a Re/Se ratio of 6:7.8. The IR spectrum, cm^{-1}: 721 m, 879 m, 1038 s, 1605 s, 2924 m, 3400 m, 3512 m, 3543 m.

IR Measurements. In the IR spectra of the presented rhenium cluster complexes, the characteristic bands assigned to the stretching vibrations of Re−OH$_2$ (∼720 cm^{-1}), Re−OH (∼875 cm^{-1}), and O−H in the O−H···O hydrogen bonds (1028−1039 cm^{-1}) were found. Similar assignments for the Re−OH$_2$ and Re−OH frequencies can be made on the basis of the spectra of the complexes $[Re_6S_8(H_2O)_6][Re_6S_6Br_8]{\cdot}10H_2O$ (**3**) and $K_4[Re_6S_8(OH)_6]{\cdot}8H_2O$ (**5**), where only Re−OH$_2$ or Re−OH bonds are presented. For all of the aquahydroxo rhenium complexes, there is a good correlation between the O−H stretching vibrations and O···O hydrogen bond distances established for compounds with strong hydrogen bonding.[43]

Crystallography. The single crystals of **1**−**4** were selected directly from the reaction mixtures and attached to glass fibers using epoxy. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 298 K (**1**), 173 K (**2** and **4**), and 153 K (**3**) on a Bruker SMART APEX CCD diffractometer (structures **1**, **2**, and **4**) and a Bruker Nonius X8Apex equipped with a 4K CCD area detector diffractometer (structure **3**). Absorption corrections were applied using the *SADABS* program.[44] The crystal structures were solved independently by direct methods and were refined by full-matrix least-squares techniques with the use of the *SHELX* package.[45] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the hydroxo groups and water molecules were not located. Crystallographic data and details of the data collection and refinement for complexes **1**−**4** are given in Table 1 and in the Supporting Information. Table 2 tabulates some metrical details for the present and related compounds. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247−808-666; E-mail: crysdata@fiz-karlsruhe.de; http://www.fiz-karlsruhe.de/ecid/Internet/en/DB/icsd/depot_anforderung.html), on quoting the depository numbers CSD-417778 (for **1**), CSD-417779 (for **2**), CSD-417780 (for **3**), and CSD-417781 (for **4**).

Results and Discussion

For the first time, a structurally characterized octahedral rhenium cluster complex with terminal OH$^-$ ligands, $[Re_6Se_8(H_2O)_4(OH)_2]{\cdot}12H_2O$, was reported by Zheng et al. in 2001.[46] Very lately, we have described a simple and effective method for the preparation of the salts $K_4[Re_6S_8(OH)_6]{\cdot}8H_2O$ (**5**) and $K_4[Re_6Se_8(OH)_6]{\cdot}8H_2O$ (**6**) containing hexahydroxo octahedral rhenium cluster anions $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se).[33] It was shown that the hexahydroxo complexes showed rather high reactivity; terminal OH$^-$ ligands are quite labile and can be substituted by acido ligands, for example by halogenide ions.[33] On the other hand, they can form coordination polymers by means of bonding of the cluster complexes with alkaline-earth atoms via hydroxo ligands.[29] It was found also that the hexahydroxo complexes were luminescent.

This work is the continuation of the study of the chemistry of hexahydroxo complexes $[Re_6Q_8(OH)_6]^{4-}$. During this

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Table 2. Selected Interatomic Distances for $K_2[Re_6S_8(H_2O)_2(OH)_4]\cdot2H_2O$ (**1**), $[Re_6S_8(H_2O)_4(OH)_2]\cdot12H_2O$ (**2**), $[Re_6S_8(H_2O)_6][Re_6S_6Br_8]\cdot10H_2O$ (**3**), and $[Re_6Se_8(H_2O)_4(OH)_2]$ (**4**) and Some Related Compounds

compound	Re−Re, Å	Re−μ_3-Q, Å	Re−O, Å
1	2.5769(7)−2.5953(7)	2.394(2)−2.424(2)	2.095(7)−2.114(6)
	mean: 2.586(6)	mean: 2.410(9)	mean: 2.105(10)
2	2.5813(5), 2.5856(6)	2.403(2)−2.411(2)	2.116(5)
	mean: 2.583(3)	mean: 2.409(4)	
3[a]	2.5728(10)−2.5821(9)	2.398(4)−2.419(4)	2.132(13)−2.145(12)
	mean: 2.576(3)	mean: 2.409(7)	mean: 2.139(7)
4	2.6056(14), 2.6062(14)	2.510(2)−2.526(3)	2.165(10)
	mean: 2.606(1)	mean: 2.517(7)	
$K_4[Re_6S_8(OH)_6]\cdot8H_2O$[33] (**5**)	2.5846(8)−2.5906(9)	2.407(4)−2.420(3)	2.07(1)−2.09(1)
	mean: 2.587(2)	mean: 2.415(4)	mean: 2.08(1)
$K_4[Re_6Se_8(OH)_6]\cdot8H_2O$[33] (**6**)	2.6085(6)−2.6155(6)	2.527(1)−2.545(1)	2.081(6)−2.088(6)
	mean: 2.612(2)	mean: 2.535(5)	mean: 2.084(4)
$[Re_6Se_8(H_2O)_4(OH)_2]\cdot12H_2O$[46]	2.6000(6), 2.6074(6)	2.5187(10)−2.5310(15)	2.146(7)
	mean: 2.604(5)	mean: 2.526(6)	

[a] Distances in the cluster cation $[Re_6S_8(H_2O)_6]^{2+}$.

study, four new compounds containing cluster complexes with the general formula $[Re_6Q_8(H_2O)_n(OH)_{6-n}]^{n-4}$ (Q = S, $n = 2, 4, 6$; Q = Se, $n = 4$) have been isolated and characterized.

In all of the compounds presented, the structure of the units $[Re_6Q_8(H_2O)_n(OH)_{6-n}]$ is typical for octahedral cluster complexes $[Re_6Q_8L_6]$: the octahedron Re_6 is inscribed into a cube of eight inner Q ligands. In addition, every rhenium atom is coordinated with the oxygen atom in the terminal ligand (OH^- or H_2O) (Figure 1). A remarkable feature of the crystal structures of the aquahydroxo complexes is the presence of an extensive system of strong hydrogen bonds, including the terminal ligands of the cluster complexes (OH^- groups and water molecules) and solvate water molecules.

Synthesis and Structures of $K_2[Re_6S_8(H_2O)_2(OH)_4]\cdot 2H_2O$ (1) and $[Re_6S_8(H_2O)_4(OH)_2]\cdot12H_2O$ (2). Depending on reaction conditions, two different aquahydroxo complexes were crystallized starting from an aqueous solution of $K_4[Re_6S_8(OH)_6]\cdot8H_2O$ (**5**). Compound $K_2[Re_6S_8(H_2O)_2(OH)_4]\cdot 2H_2O$ (**1**) is crystallized from a relatively concentrated aqueous solution of the hexahydroxo complex without evaporation (in a tightly closed vessel) and in the absence of an additional amount of KOH. The crystals of **1** are sparingly soluble in water, which apparently could be explained by the presence of very strong hydrogen bonds in the solid. On the other hand, compound **1** is readily dissolved in an alkaline solution, resulting in the highly soluble hexahydroxo complex $[Re_6S_8(OH)_6]^{4-}$; it is also dissolved in a strong acidic solution forming the hexaaqua complex $[Re_6S_8(H_2O)_6]^{2+}$. The neutral aquahydroxo complex $[Re_6S_8(H_2O)_4(OH)_2]\cdot12H_2O$ (**2**) was crystallized from a diluted aqueous solution of **5** left in an open vessel. It seems that the free access of air in the solution is an important factor in the formation of complex **2**; it is probable that CO_2 contained in air promotes the slow pH reduction of the initial solution of **5**, resulting in the crystallization of $[Re_6S_8(H_2O)_4(OH)_2]\cdot12H_2O$ (**2**).

In the cluster anion $[Re_6S_8(H_2O)_2(OH)_4]^{2-}$ (structure **1**), the Re−O bond lengths (2.095(7), 2.105(6), and 2.114(6) Å) are close to that in $[Re_6S_8(OH)_6]^{4-}$. The similarity of the Re−O bond lengths in the aquahydroxo complex is a result of the disorder of the OH^- and H_2O terminal ligands. Because of the disorder, we are not able to distinguish the rhenium atoms coordinated with OH^- from those coordinated with water molecules.

Though compound **1** is ionic by nature, it is possible to denote the layers parallel to the *ab* plane composed of the cluster anions connected via the strong hydrogen bonds, with O···O distances of 2.60 and 2.69 Å (Figure 2). These layers are also connected to each other with the very strong hydrogen bonds (the O···O distances between the terminal ligands of the cluster anions of the adjacent layers are equal to 2.49 Å), giving an extended 3D hydrogen-bonding

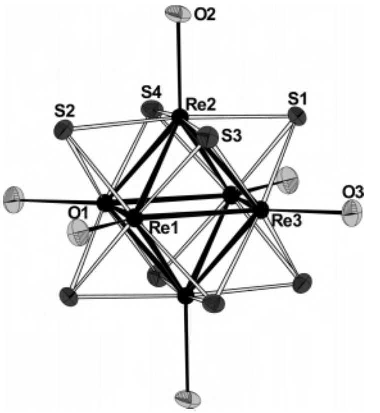

Figure 1. Structure of the cluster units $[Re_6Q_8(H_2O)_n(OH)_{6-n}]$ in compounds **1**−**4** by the example of $[Re_6S_8(H_2O)_2(OH)_4]^{2-}$ in **1**. Displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms of the terminal ligands have been omitted.

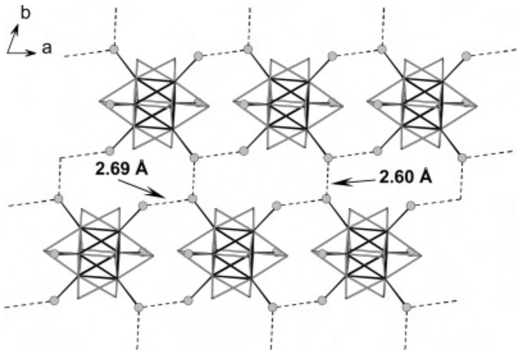

Figure 2. Linking of the cluster anions $[Re_6S_8(H_2O)_2(OH)_4]^{2-}$ (structure **1**) in polymer layers with a system of hydrogen bonding. Dashed lines indicate hydrogen bonds. Hydrogen atoms are not shown.

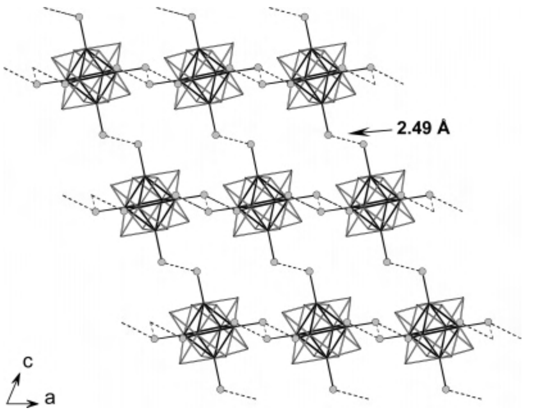

Figure 3. Scheme of the formation of a hydrogen-bonded 3D network based on the anionic cluster units $[Re_6S_8(H_2O)_2(OH)_4]^{2-}$ in **1**. Dashed lines indicate hydrogen bonds. Hydrogen atoms have been omitted.

network (Figure 3). The space between the layers is filled with potassium cations and solvate water molecules. The solvate water molecules also take part in the formation of the hydrogen-bonding system. However, the distances between them and the terminal H_2O/OH ligands are longer (the shortest O···O distance is 2.82 Å) than those between the ligands of the adjacent cluster complexes.

Compound $[Re_6S_8(H_2O)_4(OH)_2]\cdot 12H_2O$ (**2**) is isostructural to the selenium analogue $[Re_6Se_8(H_2O)_4(OH)_2]\cdot 12H_2O$ previously described.[46] The structure presents the packing of neutral cluster aquahydroxo complexes $[Re_6S_8(H_2O)_4(OH)_2]$ and solvate water molecules connected with an extensive system of strong hydrogen bonds. The shortest O···O contacts of a given type include hydrogen bonds between the terminal ligands of the cluster complexes (2.51 Å), hydrogen bonds between the oxygen atoms of the terminal ligands and solvate water molecules (2.73 Å), and hydrogen bonds between adjacent solvate water molecules (2.69 Å). In the selenium analogue $[Re_6Se_8(H_2O)_4(OH)_2]\cdot 12H_2O$ for comparison, the corresponding distances are 2.56, 2.76, and 2.72 Å, respectively. A fragment of crystal structure **2** with the indication of the hydrogen-bonding scheme is shown in Figure 4.

Earlier, similar exceptionally short intermolecular hydrogen bonds were found in the related octahedral aquahydroxo cluster complexes $NEt_4[Nb_6C1_{12}(OH)_3(H_2O)_3]\cdot 3H_2O$[47] and *trans*-$[Ta_6Cl_{12}(OH)_4(H_2O)_2]\cdot 10H_2O$,[48] where strong hydrogen bonds are formed between the coordinated water molecule of one cluster complex and the coordinated OH^- group from a neighboring one, with O···O distances equal to 2.54 Å. Their values are very close to the intercluster hydrogen bond lengths found in the rhenium aquahydroxo complexes **1** and **2** presented here and fall in the range of exceptionally short intermolecular hydrogen bonds usually formed between the OH^- ligand coordinated to one metal atom and the H_2O ligand coordinated to another metal atom, thus forming the bridging ligand $H_3O_2^-$, as discussed by Bino et al.[49−51]

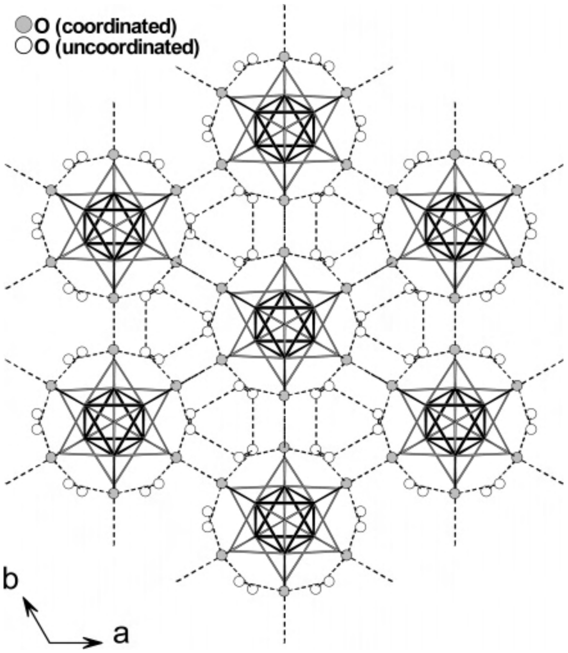

Figure 4. Hydrogen-bonding interactions (indicated by dashed lines) between solvate water molecules and terminal OH ligands of the cluster complexes in **2** (view down [001]). Hydrogen atoms have been omitted.

Synthesis and Structure of $[Re_6S_8(H_2O)_6][Re_6S_6Br_8]\cdot 10H_2O$ (3). Earlier, it was shown that the hexaaqua complex $[Re_6S_8(H_2O)_6]^{2+}$ could be obtained in a strong acidic solution.[52] To date, however, this cluster cation was not structurally characterized. Here, we describe for the first time the crystal structure of the compound containing the unit $[Re_6S_8(H_2O)_6]^{2+}$. Only the use of the anionic cluster complex $[Re_6S_6Br_8]^{2-}$ allowed us to isolate the hexaaqua cation $[Re_6S_8(H_2O)_6]^{2+}$ in solid phase. It has been demonstrated that in reactions with large ionic cluster complexes choosing of counterions with the same charge and similar size facilitates the crystallization of ionic compounds with 1:1 cation−anion ratios, which agrees with the present result.[53−55]

The structure of the compound $[Re_6S_8(H_2O)_6][Re_6S_6Br_8]\cdot 10H_2O$ (**3**) consists of crystallographically independent cluster ions $[Re_6S_8(H_2O)_6]^{2+}$ and $[Re_6S_6Br_8]^{2-}$ and solvate water molecules. In the cluster anion $[\{Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2\}Br_6]^{2-}$ (Figure 5), an octahedron Re_6 is surrounded by a pseudo-cube $[S_6Br_2]$; each rhenium atom in addition is ligated with a bromine atom. The two μ_3-Br ligands are disordered over the eight face-capping ligand sites. So, the four independent inner ligands occupying the general positions of space group $P\bar{1}$ are composite sulfur/bromine atoms. The site occupation factors are 0.813(12), 0.688(12), 0.627(12), and 0.875(11) for the S(5), S(6), S(7), and S(8) atoms,

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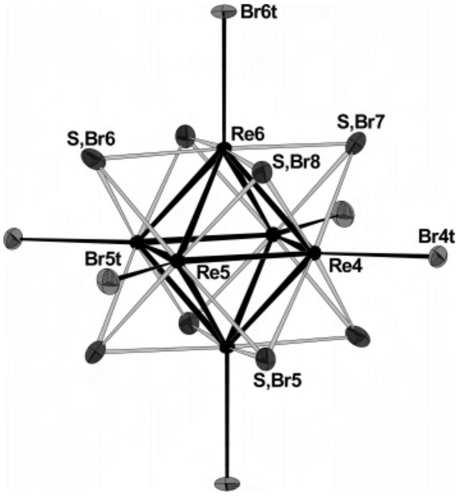

Figure 5. Structure of the cluster anion $[\{Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2\}Br_6]^{2-}$ in **3**. Displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

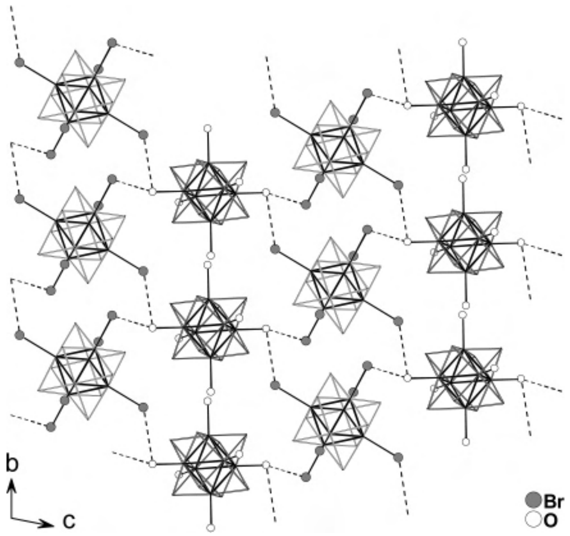

Figure 6. Hydrogen-bonding interactions (indicated by dashed lines) between terminal ligands of cluster ions in **3** (view down [100]). Hydrogen atoms have been omitted.

respectively, and the total S/Br ratio (for the eight position of the cube) being 6.01:1.99 is close to the expected ratio (6:2). The interatomic distances in the $[\{Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2\}\text{-}Br_6]^{2-}$ anion do not differ significantly from the starting material and related cluster compounds: the Re−Re distances range from 2.5934(9) to 2.6030(9) Å, the Re−(μ_3-L) distances (where μ_3-L are mixed disordered inner ligands) range from 2.409(4) to 2.533(3) Å, and the Re−$Br_{terminal}$ distances range from 2.526(2) to 2.537(2) Å.

The cluster counterions in **3** are connected to each other by hydrogen bonds between H_2O and bromine terminal ligands (the O···Br distances are 3.24 and 3.53 Å) to form the layers parallel to the crystallographic *bc* plane (Figure 6). Solvate water molecules also participate in the formation of an extended hydrogen-bonding system; the shortest O···O distances include hydrogen bonds between solvate water and the terminal H_2O ligands of the cluster cations (2.58 Å) and those between adjacent solvate water molecules (2.71 Å). Besides these, there are O···Br hydrogen bonds between solvate water and the bromine terminal ligands of the cluster anions (3.23 Å).

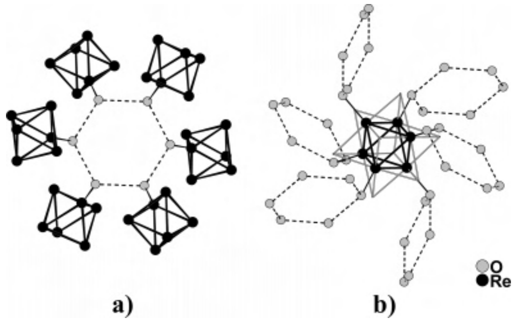

Figure 7. Scheme of the formation of a hydrogen-bonding system in **4**. Bonding of the cluster complexes $[Re_6Se_8(H_2O)_4(OH)_2]$ through the terminal ligands (a) and the environment of the single cluster unit (b). Dashed lines indicate hydrogen bonds. Hydrogen atoms are not shown.

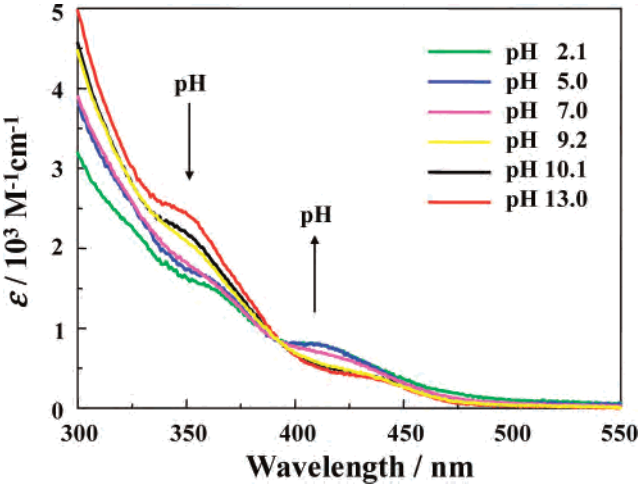

Figure 8. pH dependence of the absorption spectrum of **5** in aqueous solution.

Synthesis and Structure of $[Re_6Se_8(H_2O)_4(OH)_2]$ (4). The formation of compound **4** is a rather unexpected result. The purpose of the experiment was the synthesis of a magnesium salt of the cluster anion $[Re_6Se_8(OH)_6]^{4-}$ by analogy with the recently described salts[29] in the presence of 1,3,5-trioxane. The yield of this complex is low. Its formation is probably due to a water−organic medium used in this experiment. In addition to known $[Re_6Se_8(H_2O)_4\text{-}(OH)_2]\cdot 12H_2O$, new compound **4** is one more example of a compound built from neutral cluster aquahydroxo complex $[Re_6Se_8(H_2O)_4(OH)_2]$. However, it is important to underline that, in contrast to $[Re_6Se_8(H_2O)_4(OH)_2]\cdot 12H_2O$, compound **4** does not contain solvate water molecules. The crystal packing of **4** is shown in Figure 7. The complex units are connected to each other by hydrogen bonds between the oxygen atoms of the terminal ligands, forming the hexa-member ring O_6 with O···O distances of 2.73 Å.

pH-Dependences of the Spectroscopic and Excited-State Properties. Figure 8 shows the pH dependence of the absorption spectrum of **5** in aqueous solutions, where ϵ denotes the molar absorption coefficient of the cluster. The absorption characteristics of **5** at pH ~13 are very similar to those of $[Re_6S_8Cl_6]^{4-}$, indicating that the absorption band observed for **5** at around 400−450 nm is assigned to the

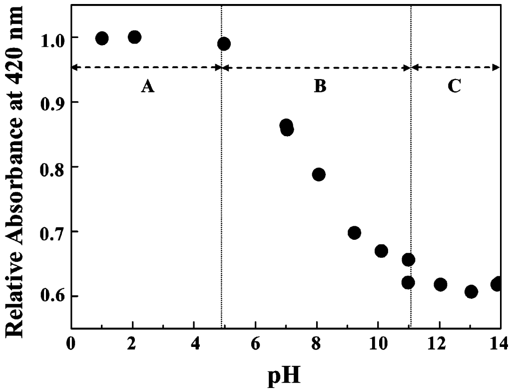

Figure 9. pH dependence of the absorbance at 420 nm observed for **5** in aqueous solution. The data are taken from Figure 8.

ligand-to-metal charge transfer transition.[36,56−58] When the the solution pH is decreased from ∼13 to ∼2, the absorbance at around 420 nm increases, whereas that at around 350 nm decreases, showing an isosbestic point at 392 nm. The presence of the isosbestic point in Figure 8 clearly indicates that **5** reached an acid−base equilibrium in the ground state. Thus, the relative absorbance at 420 nm is plotted against the solution pH as the data are presented in Figure 9. The results demonstrate that the absorbance is almost constant in the pH region of ∼1 to ∼5 (region A) or ∼11 to ∼14 (region C), whereas it decreases gradually when the pH is increased from ∼6 to ∼11 (region B). The pH titration curve in Figure 9 suggests that, at least three chemical species participate in the ground-state acid−base equilibrium of the cluster. We have also explored experiments analogous to those in Figure 8 for aqueous solutions of **6**. However, the solubility of **6** greatly depends on the solution pH, and, in particular, the cluster is almost insoluble at pH ∼6−9. Therefore, we could not obtain an absorption titration curve for **6**.

Figure 10 shows the pH effects on the emission spectra of **5** and **6**. At pH ∼14, **5** and **6** show broad and structureless emissions at the maximum wavelengths (λ_{em}) of 653 and 657 nm, and the Φ_{em} of **5** and **6** are estimated to be 0.010 and 0.017, respectively.

The data in Figure 10 demonstrate that the emission intensities of **5** or **6** depend on the solution pH. As the data are summarized in Figure 11a, the emission intensity of **5** is marginally dependent on the pH in the range of ∼1 to ∼5 (region A) and ∼11 to ∼14 (region C), whereas an increase in the solution pH gives rise to a sharp decrease (pH ∼6 to ∼8) and subsequent sharp increase in the emission intensity of the cluster (pH ∼8 to ∼10, region B). Although it is discernible from Figure 10a, furthermore, the emission maximum wavelength (λ_{em}) also shows a pH dependence as the data are shown in Figure 12a. Analogous to the pH effects on the emission intensity in Figure 11a, the pH dependence of λ_{em} is categorized into three pH regions. In the pH region of A or C, λ_{em} is almost constant at ∼685 or ∼655 nm, respectively, whereas it shifts from ∼660 to ∼680 nm with a decrease in the pH from ∼10 to ∼6 (region B). On the other hand, although the data of **6** in the pH region of ∼6 to ∼10 are lacking, the pH dependences of the emission characteristics of **6** are somewhat different from those of **5**.

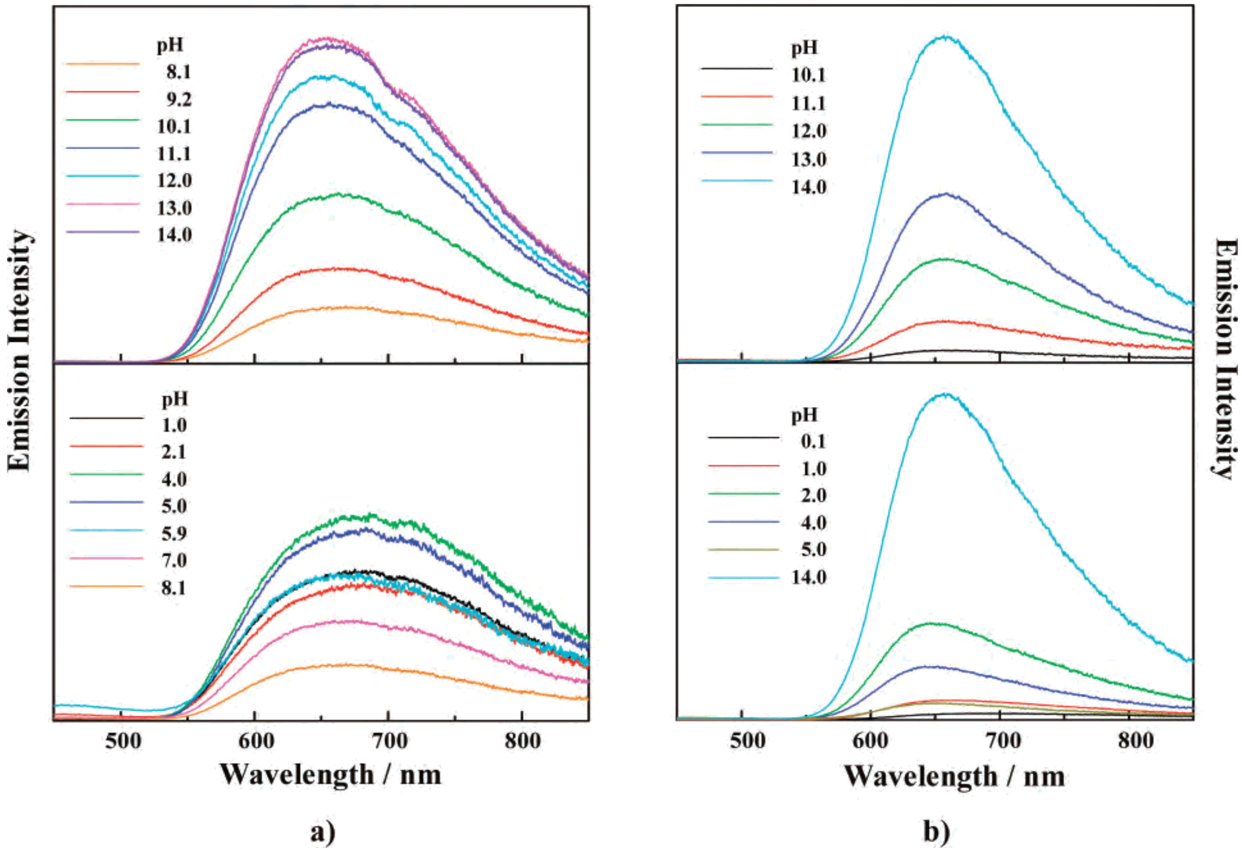

Figure 10. pH dependence of the emission spectrum of **5** (a) or **6** (b) in aqueous solutions.

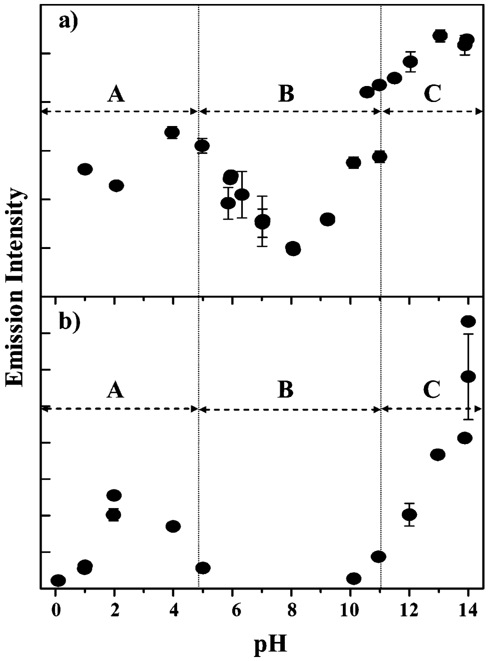

Figure 11. pH dependence of the emission intensity of **5** (a) or **6** (b) in aqueous solutions.

When the solution pH decreases from $\sim$14 to $\sim$10 (region C), the emission intensity decreases very sharply and is also highly dependent on the pH in region A (Figure 12b). Furthermore, the λ_{em} of **6** shifts to the longer wavelength by $\sim$20 nm at pH $<$ 2, which is markedly in contrast to the pH effects on λ_{em} of **5**.

Reflecting the pH effects on the emission spectrum, the emission decays of both clusters are dependent on the solution pH. As a typical example, the pH dependence of the emission decay profile of **5** is displayed in Figure 13, and the decay parameters evaluated are summarized in the Table in the Supporting Information. At a high ($\sim$11 to $\sim$14), neutral ($\sim$7), or low pH condition ($\sim$1), the emission decay profile of **5** can be fitted by a single exponential function with the decay time constant (i.e., emission lifetime = τ_{em}) of $\sim$1.8 to $\sim$2.1, $\sim$1, or $\sim$2.3 μs, respectively. In other pH regions, the emission from **5** exhibits a double-exponential decay with the short ($\tau_{em}(s)$) and long-lifetime components ($\tau_{em}(l)$) being $\sim$0.1 to $\sim$0.4 μs (amplitude value (A) = $\sim$0.15 to $\sim$0.30) and $\sim$1.8 to $\sim$1.6 μs (A = $\sim$0.70 to $\sim$0.90), respectively (Table in the Supporting Information). In the case of **6**, although the data are limited owing to the low solubility of the cluster in several pH solutions, the emission decay is also dependent on the pH (Table in the Supporting Information). For further discussion, we plotted the long-lifetime component ($\tau_{em}(l)$) of **5** or **6** against the solution pH (emission lifetime titration curves in Figure 14).Although the lifetime data of **6** in the pH range of $\sim$5 to $\sim$9 are not available, overall pH dependence of $\tau_{em}(l)$ of **5** (Figure 14a) or **6** (Figure 14b) can be categorized into approximately three pH regions (A, B, and C) analogous to the data in Figures 9, 11, and 12.

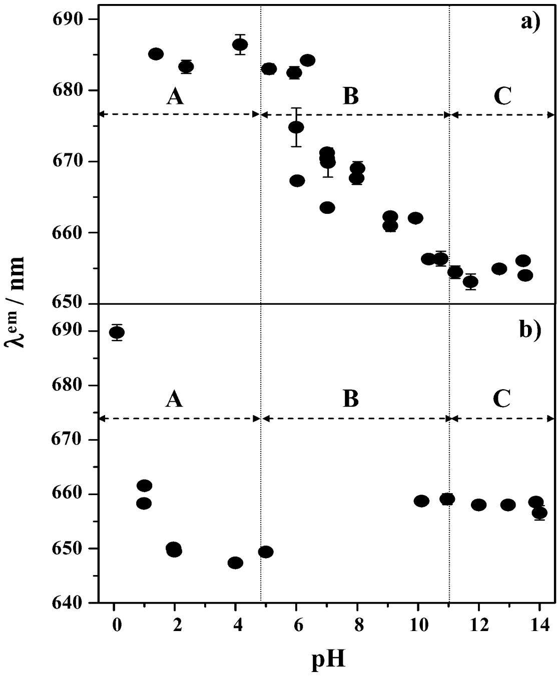

Figure 12. pH dependence of the emission maximum wavelength of **5** (a) or **6** (b) in aqueous solutions.

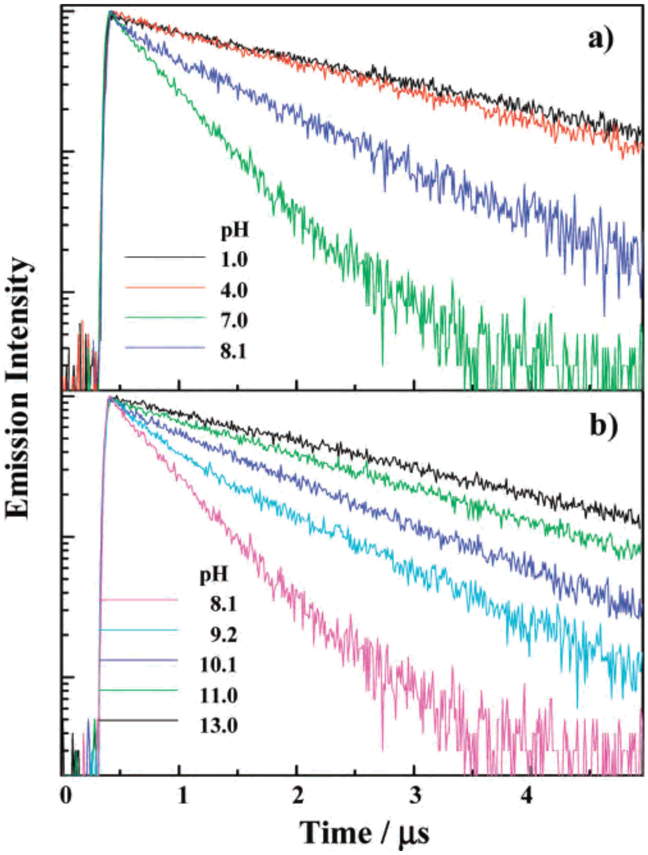

Figure 13. pH dependence of the emission decay profile of **5** in aqueous solution.

Chemical Equilibria Between $[Re_6Q_8(OH)_6]^{4-}$ and $[Re_6Q_8(H_2O)_6]^{2+}$ in Aqueous Solutions. All of the pH-dependent data on the absorption (Figures 9 and 10b) and

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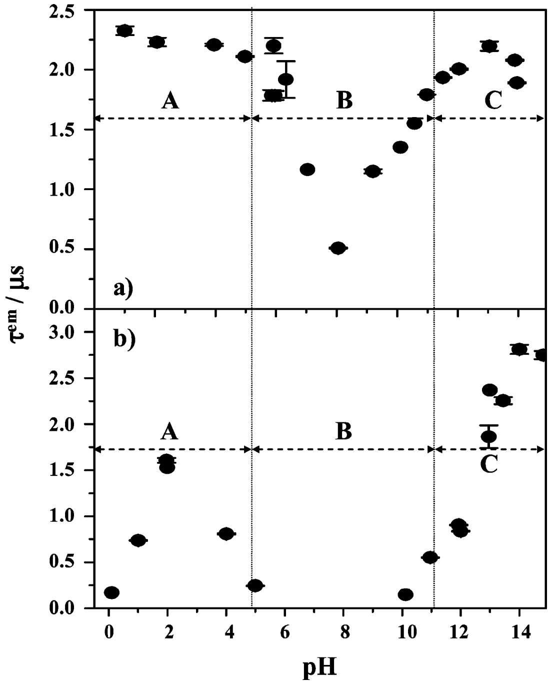

Figure 14. pH dependence of the long-emission-lifetime component (τ_{em}-(l)) of **5** (a) or **6** (b) in aqueous solutions.

Scheme 1

$$\text{pH region: }\underset{\mathbf{A}}{\underset{(\text{in }\mathbf{3})}{[Re_6S_8(H_2O)_6]^{2+}}} \rightleftarrows \underbrace{\underset{(\text{in }\mathbf{2})}{[Re_6S_8(H_2O)_4(OH)_2]^{0}} \rightleftarrows \underset{(\text{in }\mathbf{1})}{[Re_6S_8(H_2O)_2(OH)_4]^{2-}}}_{\mathbf{B}} \rightleftarrows \underset{\mathbf{C}}{\underset{(\text{in }\mathbf{5})}{[Re_6S_8(OH)_6]^{4-}}}$$

emission characteristics (Figures 11, 12, and 14) are categorized into three pH regions (A, B, and C) as described above. This indicates that, at least three chemical species derived from **5** or **6** are involved in the acid−base equilibrium in the pH region studied. In the case of **5**, the only chemical specimen involved at pH ∼14 is $[Re_6S_8(OH)_6]^{4-}$, whereas the relevant absorption spectrum at pH ∼1 resembles very well that of $[Re_6S_8(H_2O)_6]^{2+}$.[52] At pH ∼1 or ∼14, because the emission from **5** exhibits a single exponential decay, a single chemical specimen should be involved at each pH value. Therefore, the spectroscopic and excited-state characteristics of **5** at pH ∼ 1 or ∼14 could be responsible for $[Re_6S_8(H_2O)_6]^{2+}$ or $[Re_6S_8(OH)_6]^{4-}$, respectively. On the other hand, non-single exponential decays of the emission from **5** at pH ∼2 to ∼11 will be explained by the participation of **1** and **2** as shown in Scheme 1. Because the pH-dependent data observed for **6** are similar to those of **5**, the pH dependences of the spectroscopic and excited-state characteristics of **6** can also be explained by assuming the equilibria between the hexahydroxo, aquahydroxo, and hexaaqua complexes similar to Scheme 1.

In conclusion, the anionic hexahydroxo complex $[Re_6S_8(OH)_6]^{4-}$ is stable in alkaline solutions, whereas it can turn into the aquahydroxo complexes $[Re_6S_8(H_2O)_2(OH)_4]^{2-}$, $[Re_6S_8(H_2O)_4(OH)_2]$, and finally into the hexaaqua complex $[Re_6S_8(H_2O)_6]^{2+}$ when the pH is decreased. Despite the fact that selenium-containing analogs are less documented, it seems that the behavior of $[Re_6Se_8(OH)_6]^{4-}$ in water is similar. The conversions between the chemical species are very fast and therefore can be regarded as the result of the protonation of the terminal hydroxo ligands in the starting hexahydroxo complex. These processes have been studied in a wide pH range by chemical methods. pH-dependent data on the absorption and emission characteristics were obtained, and the equilibrium between different chemical forms has been confirmed. The new solid aquahydroxo complexes $K_2[Re_6S_8(H_2O)_2(OH)_4]\cdot 2H_2O$, $[Re_6S_8(H_2O)_4(OH)_2]\cdot 12H_2O$, and $[Re_6Se_8(H_2O)_4(OH)_2]$ have been synthesized; the compound $[Re_6S_8(H_2O)_6][Re_6S_6Br_8]\cdot 10H_2O$ containing cationic hexaaqua complex $[Re_6S_8(H_2O)_6]^{2+}$ was isolated from a strong acidic solution. Structural and IR spectroscopy studies of the aquahydroxo complexes revealed that they are characterized by strong hydrogen bonding with very short O···O contacts between the terminal ligands of neighboring cluster complexes. The strong interaction of the cluster complexes leads to low solubilities of the aquahydroxo complexes.

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Supporting Information Available: X-ray crystallographic data (CIF) and a table with the pH dependences of the emission lifetimes of $[Re_6Q_8(OH)_6]^{4-}$ (Q = S or Se) in aqueous solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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