Octahedral Hexahydroxo Rhenium Cluster Complexes $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se): Synthesis, Structure, and Properties

Spartak S. Yarovoi,[a] Yuri V. Mironov,[a] Dmitry Y. Naumov,[a] Yuri V. Gatilov,[b] Svetlana G. Kozlova,[a,c] Sung-Jin Kim,[d] and Vladimir E. Fedorov*[a]

Keywords: Rhenium / Hexahydroxo complexes / Cluster compounds / Electronic structure / Luminescence

Two novel rhenium cluster compounds, $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (**1**) and $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ (**2**), containing octahedral cluster chalcogenide anionic complexes $[Re_6Q_8(OH)_6]^{4-}$ with terminal hydroxo ligands have been synthesized by the reaction of $Re_6Q_8Br_2$ (Q = S, Se) with molten KOH. Two chalcohalide compounds, one known ($Cs_4[Re_6S_8Br_6]\cdot 2H_2O$, **3**) and another new ($Cs_3[Re_6Se_8Cl_6]\cdot 2H_2O$, **4**), were prepared by reactions of **1** and **2** with CsX and HX (X = Br, Cl) in an aqueous solution. Compounds **1**, **2**, and **4** have been characterized by the single-crystal X-ray diffraction method. Compounds **1** and **2** are crystallized in triclinic space group $P\bar{1}$ with one formula unit in the cell of dimensions a = 8.4936(8) Å, b = 8.9101(11) Å, c = 10.5940(13) Å, α = 77.935(11)°, β = 75.933(9)°, γ = 71.244(10)°, V = 728.9(1) $Å^3$ (compound **1**) and a = 8.613(1) Å, b = 8.996(1) Å, c = 10.057(1) Å, α = 78.587(2)°, β = 77.811(2)°, γ = 71.728(2)°, V = 715.9(2) $Å^3$ (compound **2**). Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with two formula units in the cell of dimensions a = 9.819(3) Å, b = 12.925(4) Å, c = 11.756(4) Å, β = 113.38(3)°, V = 1369.6(8) $Å^3$. Compounds **1** and **2** display luminescent properties.

Introduction

The chemistry of octahedral rhenium cluster complexes with cluster core $\{Re_6Q_8\}^{2+}$ (Q = S, Se, Te) is in a stage of rapid development.[1] Some solids like $Re_6Q_8X_2$ (Q = S, Se; X = Cl, Br)[2] or Re_6Te_{15}[3] containing similar cluster cores prepared by high temperature solid-state reactions are characterized by extended intercluster bonding. A large number of articles have appeared within the last few years that have reported the preparation of molecular cluster complexes of the $Re_6Q_8L_6$ type (L = Cl, Br, I, or different organic ligands).[4] One way of preparing molecular cluster complexes is the excision reaction through interaction of polymeric solids such as $Re_6Q_8X_2$ or Re_6Te_{15} with molten salts. A similar strategy for the preparation of chalcocyanide complexes $[Re_6Q_8(CN)_6]^{4-}$ by reactions of Re_6Te_{15} or $Re_6Q_8X_2$ with molten KCN have been used earlier.[5] Very recently we suggested molten KOH as a new reaction medium: the reaction of $Re_6Se_8Br_2$ with molten KOH at 280 °C results in formation of the unusual cluster core $\{Re_6Se_4O_4\}^{2+}$, found in $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3\cdot 4H_2O$.[6] Further investigation of reactions of $Re_6Q_8X_2$ with molten KOH results in the preparation of three new cluster compounds: $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (**1**), $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ (**2**), and $Cs_3[Re_6Se_8Cl_6]\cdot 2H_2O$ (**4**), and one known: $Cs_4[Re_6S_8Br_6]\cdot 2H_2O$ (**3**). All new compounds were characterized by X-ray single-crystal analysis.

Results

Syntheses

Compounds **1** and **2** containing hexahydroxo complexes $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se) were obtained from $Re_6S_8Br_2$ (for **1**) and $Re_6Se_8Br_2$ (for **2**) in molten KOH at 280 °C and 200 °C respectively in open vessels following recrystallization of the compounds from water. The only rhenium octahedral cluster complex with OH^- groups as terminal ligands, $[Re_6S_8(OH)_2(H_2O)_4]\cdot 12H_2O$, was described earlier.[7] Compounds **3** and **4** were obtained from aqueous solutions of compounds **1** and **2** by adding CsX and HX and further crystallization. Crystals of diamagnetic compound **3** are orange. Paramagnetic compound **4** crystallizes from the solution as black crystals.

---

[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences,
3 Acad. Lavrentiev pr., 630090 Novosibirsk, Russia
Fax: +7-3832-309489
E-mail: yuri@che.nsk.su
[b] Vorozhtsov Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences,
9 Acad. Lavrentiev pr., 630090 Novosibirsk, Russia
[c] Boreskov Institute of Catalysis, Siberian Branch of Russian Academy of Sciences,
5 Acad. Lavrentiev pr., Novosibirsk 630090, Russia
[d] Department of Chemistry, Ewha Womans University,
Seoul 120-750, Korea
E-mail: sjkim@ewha.ac.kr

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200500284

Structures

The structures of the cluster anions $[Re_6Q_8(OH)_6]^{4-}$, where Q = S (**1**) or Se (**2**) (Figure 1), are similar to the well-known octahedral complexes of $[Re_6Q_8L_6]^{4-}$ type with L = Cl^-, Br^-, I^-, CN^-. There is a nearly regular Re_6 octahedron residing inside a Q_8 (S, Se) cube with the distances Re–Re in the range 2.5906(9)–2.5846(8) Å (**1**) and 2.6085(6)–2.6155(6) Å (**2**) and Re–(μ_3-Q) in the range 2.407(4)–2.420(3) Å (**1**) and 2.527(1)–2.545(1) Å (**2**). Six terminal OH^- ligands are coordinated to Re atoms with bond lengths Re–O 2.07(1)–2.09(1) Å (**1**) and 2.081(6)–2.088(6) Å (**2**). Whereas the Re–Re and Re–(μ_3-Q) bond lengths increase in the order $Re_6S_8 < Re_6Se_8$, the Re–O bond lengths do not appear to vary.

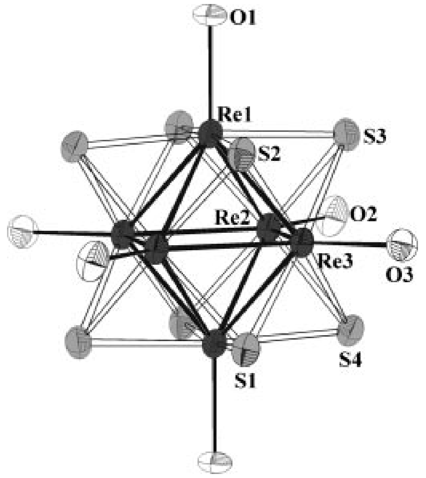

Figure 1. View of the cluster anion $[Re_6(\mu_3\text{-}S)_8(OH)_6]^{4-}$ in **1**. Displacement ellipsoids are drawn at the 50% probability level.

Compound **4** was studied by single-crystal X-ray analysis; the structure of compound **3** was described earlier.[8] The structure of the oxidized cluster anion $[Re_6Se_8Cl_6]^{3-}$ (Figure 2) is also similar to the well-known octahedral complexes $[Re_6Q_8L_6]^{4-}$ where L is a typical acidoligand (Cl^-, Br^-, I^-, CN^-). In the cluster core $\{Re_6Se_8\}$ there is a system of Re–Re and Re–(μ_3-Se) bonds, with lengths in the range 2.606(1)–2.615(1) Å and 2.497(3)–2.525(3) Å, respectively. Six terminal Cl^- ligands are coordinated to Re atoms with bond lengths of 2.414(7)–2.427(6) Å.

To confirm the presence of OH^- groups in the compounds, a solid-state NMR investigation has been carried out at 180 K for $K_4[Re_6Q_8(OH)_6]\cdot 8H_2O$. The wide-line ^1H NMR spectrum was recorded by sweeping the frequency in the neighborhood of 22.8 MHz using a home-made NMR spectrometer with signal accumulation. The experimental NMR spectrum is simulated reasonably by two spectral lines (Figure 3). One line is a classic Pake's line with the parameters: $\alpha = 23.0 \pm 0.5$ kHz and $\beta_1 = 7.4 \pm 0.1$ kHz; these parameters are typical characteristics for H_2O without self-diffusion.[9] The other line is a single one, which can be attributed to H atoms of OH^- groups. This line is simulated by the Gaussian function with $\beta_2 = 7.5 \pm 0.1$ kHz.[10] The ratio of the integral intensities of the two lines (I_2/I_1) is $R = 0.36 \pm 0.02$, which is very close to the composition of $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$. Analogous results were obtained for $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$: $\alpha = 24.5 \pm 0.5$ kHz and $\beta_1 = 9.3 \pm 0.1$ kHz; $\beta_2 = 8.4 \pm 0.1$ kHz and $R = 0.30 \pm 0.02$.

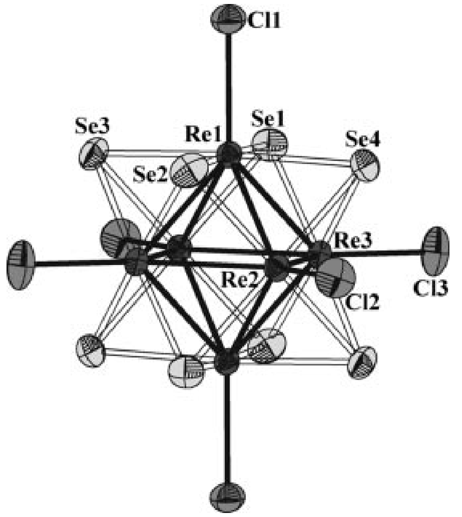

Figure 2. View of the cluster anion $[Re_6(\mu_3\text{-}Se)_8Cl_6]^{3-}$ in **4**. Displacement ellipsoids are drawn at the 50% probability level.

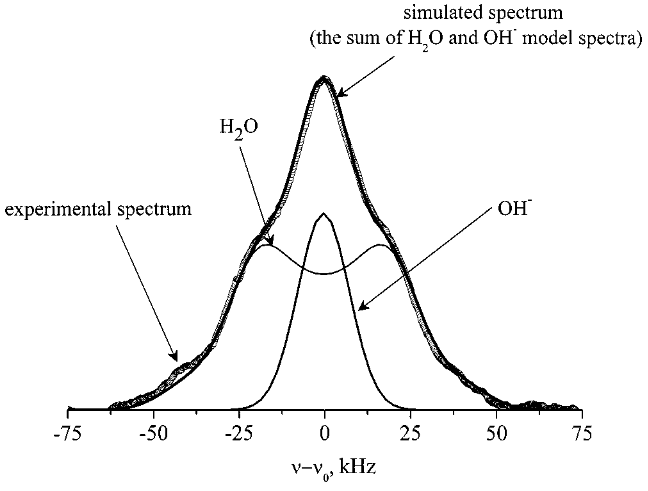

Figure 3. Experimental ^1H NMR absorption at 180 K for $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and the calculated spectra for H_2O and OH^- and their sum. For $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ the figure is analogous.

The most interesting feature of compound **4** is the oxidized state of the cluster core $\{Re_6Se_8\}^{3+}$, where the number of cluster valence electrons is equal to 23. It is known that diamagnetic complexes $[Re_6Q_8L_6]^{4-}$ containing 24 valence electrons in the Re_6 cluster can be transformed into 23-electron paramagnetic $[Re_6Q_8L_6]^{3-}$ forms. The stability of a sulfur-containing complex in comparable experimental conditions can be explained by its higher electrochemical potential in the redox process. For example, it is known that for chalcocyanide complexes $[Re_6Q_8(CN)_6]^{4-}$ the electrochemical potentials of a similar one-electron oxidation reaction are in decreasing order as S > Se > Te; thus for aqueous solutions $E_{1/2}$ are equal to 1.07, 0.82, and 0.53 V respectively for sulfur-, selenium-, and tellurium-containing complexes.[11] Thus, a selenium-containing cluster anion can be oxidized in aqueous solutions rather easily.

The formation of the oxidized anion $[Re_6Se_8Cl_6]^{3-}$ was confirmed by both X-ray analysis (by determination of number of cations in the structure) and magnetic measurements, which showed paramagnetic behavior with one unpaired electron per cluster (see Supporting Information). Simple and high-yield synthesis of this compound opens a path for preparing other compounds containing an oxidized paramagnetic cluster complex. This is rather useful, because oxidized clusters are the most proper starting compounds for the preparation of Re_6 complexes with organic ligands in comparison with rather inert 24-electron complexes.

As seen from our experiments, the hexahydroxo complexes $[Re_6Q_8(OH)_6]^{4-}$ are good precursors for different reactions. They can be transformed into neutral aqua-hydroxo complexes of the type $[Re_6Q_8(OH)_2(H_2O)_4]\cdot nH_2O$. Reactions with halide ions give chalcohalide complexes $[Re_6Q_8L_6]$ where L = Cl, Br, I; in principle, a similar approach for synthesis of chalcohalide complexes may be applied for different variations of μ_3-S or μ_3-Se in the cluster core with terminal Cl, Br, or I ligands. Here we have synthesized only the combinations of S/Br and Se/Cl as the most evident samples in the structure analysis. Beside the substitution of terminal OH^- groups in $[Re_6Q_8(OH)_6]^{4-}$ it is possible to substitute inner μ_3-Q ligands in the cluster core. The first example of a similar reaction is preparation of the compound $Cs_{11}(H_3O)[Re_6Se_4O_4Cl_6]_3\cdot 4H_2O$, containing the cluster core $\{Re_6Se_4O_4\}$.[6] In contrast to easy substitution of terminal OH groups, which is performed in solution, the substitution of inner μ_3-Q ligands in the cluster core requires higher temperatures: for example, substitution of selenium with oxygen was carried out in molten KOH at 280 °C. Finally, selenium-containing complexes can be converted easily in solution in oxidized form.

Luminescence Properties

Luminescence properties of solid samples of **1** and **2** were recorded at room temperature in wavelength range from 500 to 700 nm. Upon excitation at 440 nm, solid samples of **1** and **2** display photoluminescence with λ_{max} at 618 and 635 nm, respectively (Figure 4). The luminescence spectra of aqueous solutions for both compounds are very similar.[12]

Electronic Structure

The optimized calculated values of the geometric parameters of the $[Re_6Q_8L_6]^{n-}$ complexes are in good qualitative agreement with X-ray experimental data. The highest occupied molecular orbitals (HOMO) of diamagnetic $[Re_6S_8(OH)_6]^{4-}$ and $[Re_6Se_8(OH)_6]^{4-}$ complexes are very much alike (Figure 5). The electronic structure of the HOMO ($21e_g$) in the $[Re_6S_8(OH)_6]^{4-}$ cluster anion in general terms corresponds to the quantum calculations of the electronic structure of related complexes, $[Re_6Q_8L_6]^{4-}$ with Q = S, Se and L = Cl, Br, I, CN.[13] The highest occupied orbitals, $18t_{2u}$ and $24e_g$, in the $[Re_6Se_8(OH)_6]^{4-}$ cluster anion have an energy separation of 0.0015 eV. The use of the SAOP GGA functional[14] revealed that the energy separation is 0.019 eV. In this case it is difficult to predict which one of these orbitals is HOMO in reality. It is interesting to note that this is the first example when the HOMO of $Re_6Q_8L_6$ complexes has a t_{2u} symmetry. The LUMO of both clusters have the symmetry eg [22eg (S) and 25eg (Se)]. The similar result for HOMO may be an artifact, but it challenges further wide theoretical and experimental investigations. In particular, it is well known that luminescent properties of $[Re_6Q_8L_6]^{4-}$ complexes are determined by the frontier orbital symmetry.[13e] For these complexes the HOMO (eg)–LUMO (a_{1g} or t_{1g}) transitions are characterized as forbidden electronic dipole transitions. If the HOMO has t_{2u} symmetry, the HOMO–LUMO transition is allowed and decreasing luminescent excitement may be expected. As can be seen from the luminescent properties of **1** and **2** (Figure 4), this prediction takes place here. Notice that the related complexes $[Re_6Se_8(CN)_6]^{4-}$ showed much stronger emissions than $[Re_6S_8(CN)_6]^{4-}$.[15]

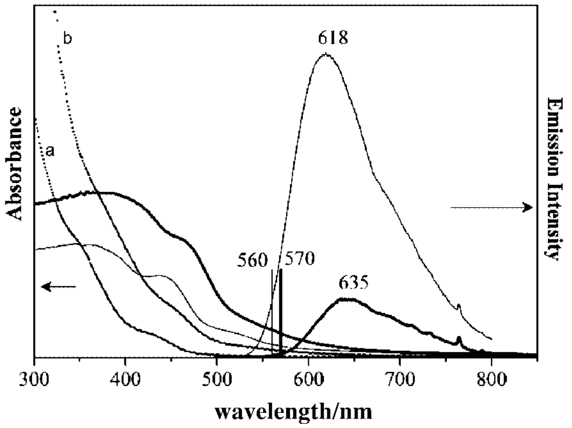

Figure 4. Electronic absorption spectra (at the left) of solids $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (thin line), $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ (bold line), and their aqueous solutions (dots a and b), and emission luminescent spectra (on the right) of solids $K_4[Re_6S_8(OH)_6]$ (thin line) and $K_4[Re_6Se_8(OH)_6]$ (bold line). Spectral intensities are normalized. Vertical lines show the forbidden transitions.

The calculated HOMO–LUMO energy gaps are 2.20 and 2.17 eV, the binding energies are –158.0 and –152.3 eV, and ionization potentials (IP) are –6.1 and –5.9 eV for $[Re_6S_8(OH)_6]^{4-}$ and $[Re_6Se_8(OH)_6]^{4-}$ complexes respectively. (IP = –4.5 eV for the $[Re_6Se_8Cl_6]^{4-}$ complex.) The charge distribution of calculated octahedral clusters is presented in Table 1.

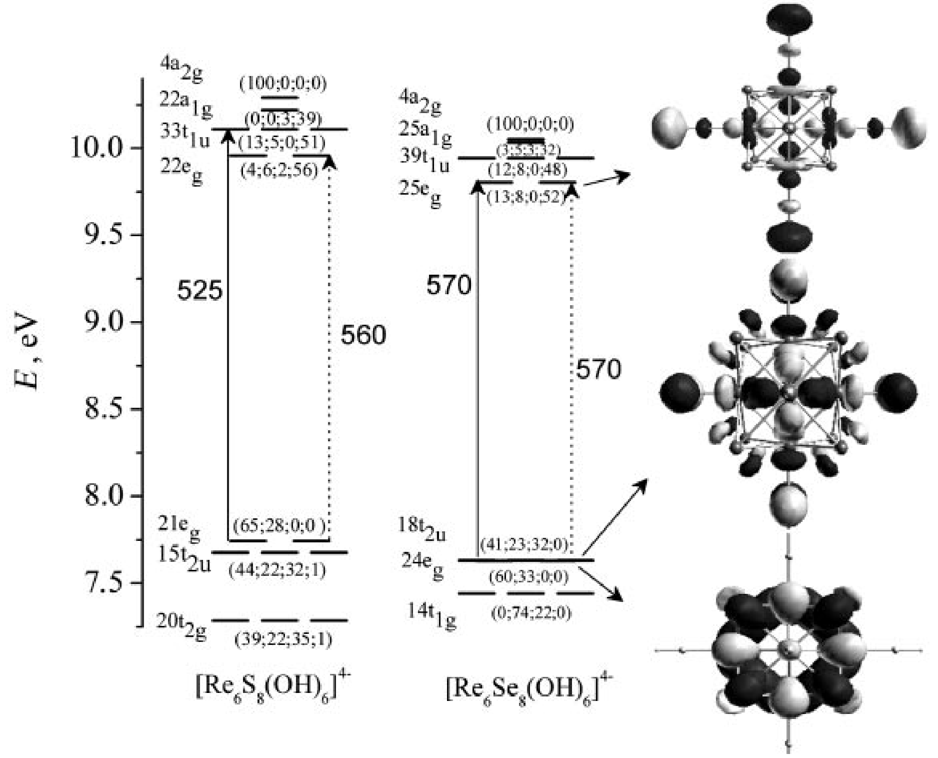

Figure 5. The energy level diagram and schematic figures of MO calculated at the DFT level of theory for $[Re_6S_8(OH)_6]^{4-}$ and $[Re_6Se_8(OH)_6]^{4-}$ complexes. The numbers and symmetry types of the calculated MOs are indicated. Numbers in brackets indicate the percentage of the valent orbitals: 5d Re; 3p S; 4p Se; 2p O; and 1s H, respectively. Arrows show the electronic forbidden (dotted lines) and allowed (solid lines) transitions.

Table 1. The charge distribution in the $[Re_6Q_8L_6]^{4-}$ (Q = S, Se; L = OH, Cl) complexes.

Complex	Re	Q	O; (Cl)	H
$[Re_6S_8(OH)_6]^{4-}$	0.118	–0.283	–0.447	0.039
$[Re_6Se_8(OH)_6]^{4-}$	0.099	–0.276	–0.439	0.041
$[Re_6Se_8Cl_6]^{3-}$	0.069	–0.115	–0.416	–
$[Re_6Se_8Cl_6]^{4-}$	0.054	–0.179	–0.481	–

Experimental Section

$Re_6S_8Br_2$ and $Re_6Se_8Br_2$ were prepared as described.[2] All other reagents were commercially available products of reagent grade quality and were used as purchased. All experiments were performed in an open vessel in air.

$K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (1) and $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ (2): Compounds **1** and **2** were obtained by heating $Re_6Q_8Br_2$ (Q = S, Se) (1 g) and KOH (1.5 g) at 280 °C (**1**) and 200 °C (**2**) in carbon glass vessels for 30 min in air. After cooling, the resulting melt was washed with *i*PrOH (3 × 20 mL portions), dissolved in water (30 mL), filtered, evaporated to 7 mL by heating, and cooled to room temperature. After 12 h red crystals were filtered off and air-dried. Yields: $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (0.78 g, 66%), $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$ (0.9 g, 79%). Electron microprobe analysis (EMA): $K_{4.0}Re_6S_{8.0}$ (**1**), $K_{4.1}Re_6Se_{7.98}$ (**2**).

$Cs_4[Re_6S_8Br_6]\cdot 2H_2O$ (3) and $Cs_3[Re_6Se_8Cl_6]\cdot 2H_2O$ (4): Compounds **3** and **4** were obtained by heating $Re_6Q_8Br_2$ (Q = S, Se) (1 g) and KOH (1.5 g) at 280 °C (**3**) and 200 °C (**4**) in carbon glass vessels for 30 min in air. After cooling, the resulting melt was washed with *i*PrOH (3 × 20 mL portions), dissolved water (50 mL), and filtered. CsBr (1 g, for **3**) or CsCl (1 g, for **4**), and 10 mL of concentrated HBr (for **3**) or HCl (for **4**) were added to the solutions and boiled for 10 min. After this the solutions were filtered and evaporated to 20 mL and cooled to room temperature. After 12 h the orange crystals of **3** or black crystals of **4** were filtered off and air-dried. Yields: $Cs_4[Re_6S_8Br_6]\cdot 2H_2O$ (1.1 g, 70%); $Cs_3[Re_6Se_8Cl_6]\cdot 2H_2O$ (0.91 g, 58%). EMA: $Cs_{4.0}Re_6S_{7.98}Br_{6.1}$ (**3**), $Cs_{3.1}Re_6Se_{7.9}Cl_{6.1}$ (**4**).

X-ray Crystallography: Single-crystal X-ray diffraction data were collected on compounds **1**, **2**, and **4** with the use of graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 273 K (**1** and **4**) and 170 K (**2**) with Enraf Nonius CAD4 (**1**), Bruker Smart CCD with the operating program SMART (**2**) and Siemens P4 (**4**) diffractometers. All structures were solved by direct methods by means of the SHELX-97 program set and were refined by full-matrix least-squares techniques.[16] An empirical absorption correction was applied by measuring three azimuthal scan curves for compound **1**. Face indexed absorption correction was performed numerically with the use of XPREP for compounds **2** and **4**. The program SADABS (**4**) was then employed to make incident beam and decay corrections.

$K_4Re_6S_8(OH)_6\cdot 8H_2O$ (1): M = 1776.26, crystal size 0.25 × 0.20 × 0.15 mm, triclinic space group $P\bar{1}$, a = 8.4936(8) Å, b = 8.9101(11) Å, c = 10.5940(13) Å, α = 77.935(11)°, β = 75.933(9)°, γ = 71.244(10)°, V = 728.9(1) Å^3, Z = 1, $\rho_{calcd.}$ = 4.120 g cm^{-3}, μ = 26.011 mm^{-1}, $2 < \theta < 24.98°$, T = 293(2) K. Reflections: 2746 collected, 2557 unique (R_{int} = 0.0186), 2105 observed [$I > 2\sigma(I)$]; 158 parameters refined with R = 0.0439 [$I > 2\sigma(I)$], wR_2 = 0.1218 (all data), Gof = 1.032, residual electron density: +3.983, –2.509 e Å^{-3}.

$K_4Re_6Se_8(OH)_6\cdot 8H_2O$ (2): (M = 2151.46), crystal size 0.12 × 0.06 × 0.02 mm, triclinic space group $P\bar{1}$, a = 8.613(1) Å, b =

8.996(1) Å, c = 10.057(1) Å, α = 78.587(2)°, β = 77.811(2)°, γ = 71.728(2)°, V = 715.9(2) Å^3, Z = 1, $\rho_{\text{calcd.}}$ = 4.990 g cm^{-3}, μ = 36.058 mm^{-1}, 2.09 < θ < 28.20°, T = 170(2) K. Reflections: 4461 collected, 3174 unique (R_{int} = 0.0186), 2461 observed [$I > 2\sigma(I)$]; 146 parameters refined with R = 0.0329 [$I > 2\sigma(I)$], wR_2 = 0.0941 (all data), Gof = 0.992, residual electron density: + 2.783, –2.382 e Å^{-3}.

$Cs_3[Re_6Se_8Cl_6]\cdot 2H_2O$ (4): (M = 2396.34), crystal size 0.24 × 0.19 × 0.18 mm, monoclinic space group $P2_1/n$, a = 9.819(3) Å, b = 12.925(4) Å, c = 11.756(4) Å, β = 113.38(3)°, V = 1369.6(8) Å^3, Z = 2, $\rho_{\text{calcd.}}$ = 5.811 g cm^{-3}, μ = 41.554 mm^{-1}, 2.3 < θ < 29.99°, T = 293(2) K. Reflections: 4202 collected, 3993 unique (R_{int} = 0.0445), 2861 observed [$I > 2\sigma(I)$]; 116 parameters refined with R = 0.0782 [$I > 2\sigma(I)$], wR_2 = 0.2203 (all data), Gof = 1.027, residual electron density: + 5.211, –9.385 e Å^{-3}.

Computational Details: Density functional calculations (DFT) were carried out on $[Re_6Q_8(OH)_6]^{4-}$ models using the ADF2002 code.[14] The local-exchange VWN correlation potential was used for the local density approximation (LDA),[17] and Becke's nonlocal corrections to the exchange energy[18] and Perdew's nonlocal corrections to the correlation energy were added.[19] The zeroth-order relativistic approximation (ZORA) method was used to account for the scalar relativistic effects.[20] The STO basic set without core potentials was used for all atoms (ZORA/TZ2P). The octahedral O_h symmetry was imposed on the full geometry optimization of the ground electronic states for $[Re_6Q_8(OH)_6]^{4-}$ models, a prototype of the analyzed clusters. Calculations of the electronic-binding energy have been performed for the reactions $6\,Re + 8\,Q + 6\,O + 6\,H + 4\,e^- \rightarrow [Re_6Q_8(OH)_6]^{4-}$. The ionization potentials were computed as the energy differences between the $[Re_6Q_8L_6]^{3-}$ and $[Re_6Q_8L_6]^{4-}$, IP = $\Delta E_3 - \Delta E_4$. The atomic net charges for several $[Re_6Q_8(OH)_6]^{n-}$ complexes have been obtained using the Hirshfeld analysis.[21]

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 415278 (for **1**), 415279 (for **2**), and 415280 (for **4**).

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (grants 05-03-08090 and 05-03-32123), Division of Chemistry and Materials Science of RAS (project No. 15 of Program 4.1), and the International Cooperation Research Program of the Ministry of Science & Technology of Korea. The authors are grateful to V. N. Ikorsky for magnetic measurements.

---

[1] a) A. Perrin, M. Sergent, *New J. Chem.* **1988**, *12*, 337–356; b) T. Saito, *J. Chem. Soc., Dalton Trans.* **1999**, 97–105; c) Y. V. Mironov, V. E. Fedorov, *J. Struct. Chem. (Engl. Trans.)* **1999**, *40*, 959–974; d) N. G. Naumov, A. V. Virovets, V. E. Fedorov, *J. Struct. Chem. (Engl. Trans.)* **2000**, *41*, 499–520; e) J.-C. P. Gabriel, K. Boubekeur, S. Uriel, P. Batail, *Chem. Rev.* **2001**, *101*, 2037–2066; f) H. D. Selby, B. K. Roland, Z. Zheng, *Acc. Chem. Res.* **2003**, *36*, 933–944.

[2] a) C. Fischer, N. Alonso-Vante, S. Fiechter, H. Tributsch, G. Reck, W. Schulz, *J. Alloys Comp.* **1992**, *178*, 305–314; b) N. L. Speziali, H. Berger, G. Leicht, R. Sanjines, G. Chapuis, F. Levy, *Mater. Res. Bull.* **1988**, *23*, 1597–1604; c) S. S. Yarovoi, Y. I. Mironov, Y. V. Mironov, A. V. Virovets, V. E. Fedorov, U.-H. Paek, S. C. Shin, M.-L. Seo, *Mater. Res. Bull.* **1997**, *32*, 1271–1277.

[3] F. Klaiber, W. Petter, F. Hulliger, *J. Solid State Chem.* **1983**, *46*, 112–120.

[4] Selection of research papers: a) J. R. Long, L. S. McCarty, R. H. Holm, *J. Am. Chem. Soc.* **1996**, *118*, 4603–4616; b) Z. Zheng, J. R. Long, R. H. Holm, *J. Am. Chem. Soc.* **1997**, *119*, 2163–2171; c) Z. Zheng, T. G. Gray, R. H. Holm, *Inorg. Chem.* **1999**, *38*, 4888–4895; d) Y. V. Mironov, J. A. Cody, E. Albrecht-Schmitt, J. A. Ibers, *J. Am. Chem. Soc.* **1997**, *119*, 493–498; e) Y. V. Mironow, M. A. Pell, J. A. Ibers, *Inorg. Chem.* **1996**, *35*, 2709–2710; f) Y. V. Mironov, M. A. Pell, J. A. Ibers, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2854–2856; g) Z.-N. Chen, T. Yoshimura, M. Abe, K. Tsuge, Y. Sasaki, S. Ishizaka, H.-B. Kim, N. Kitamura, *Chem. Eur. J.* **2001**, *7*, 4447–4455; h) A. Itasaka, M. Abe, T. Yoshimura, K. Tsuge, M. Suzuki, T. Imamura, Y. Sasaki, *Angew. Chem. Int. Ed.* **2002**, *41*, 463–466; i) B. K. Roland, C. Carter, Z. Zheng, *J. Am. Chem. Soc.* **2002**, *124*, 6234–6235.

[5] a) A. Slougui, Yu. V. Mironov, A. Perrin, V. E. Fedorov, *Croat. Chem. Acta* **1995**, *68*, 885–890; b) Yu. V. Mironov, A. V. Virovets, V. E. Fedorov, N. V. Podberezskaya, O. V. Shishkin, Yu. T. Struchkov, *Polyhedron* **1995**, *14*, 3171–3173; c) N. G. Naumov, A. V. Virovets, Y. I. Mironov, S. B. Artemkina, V. E. Fedorov, *Ukr. Khim. Zh.* **1999**, *65*, 21–27; d) N. G. Naumov, A. V. Virovets, N. V. Podberezskaya, V. E. Fedorov, *J. Struct. Chem. (Engl. Trans.)* **1997**, *38*, 857–863.

[6] S. S. Yarovoi, Y. V. Mironov, S. F. Solodovnikov, D. Y. Naumov, N. K. Moroz, S. G. Kozlova, A. Simon, V. E. Fedorov, *Chem. Commun.* **2005**, 719–721.

[7] Z. Zheng, H. D. Selby, B. K. Roland, *Acta Crystallogr., Sect. E* **2001**, *57*, i77–i79.

[8] S. S. Yarovoi, S. F. Solodovnikov, Y. V. Mironov, V. E. Fedorov, *J. Struct. Chem. (Engl. Trans.)* **2003**, *44*, 355–358.

[9] G. E. Pake, *J. Chem. Phys.* **1948**, *16*, 327.

[10] A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford, **1961**.

[11] N. G. Naumov, PhD thesis, Novosibirsk, **2004**.

[12] The emission spectra of the samples were recorded with a UV-Spectrofluorimeter equipped with an ORIEL 77200 monochromator and a Hamamatsu R928 PMT detector. A Xe lamp (ORIEL photomax, 75 W) was used as a light source. The excitation slit width was 1.56 mm and the emission slit width was 60 µm. Both compounds were also measured in aqueous solutions with concentrations in the region of 10^{-5}–10^{-3} mol L^{-1}.

[13] Selection of research papers: a) A. Deluzet, H. Duclusaud, P. Sautet, S. A. Borshch, *Inorg. Chem.* **2002**, *41*, 2537–2542; b) S. G. Kozlova, S. P. Gabuda, K. A. Brylev, Yu. V. Mironov, V. E. Fedorov, *J. Phys. Chem. A* **2004**, *108*, 10565–10567; c) S. A. Baudron, A. Deluzet, K. Boubekeur, P. Batail, *Chem. Commun.* **2002**, 2124–2125; d) R. Arratia-Perez, L. Hernandez-Acevedo, *J. Chem. Phys.* **1999**, *111*, 168–172; e) T. G. Gray, C. M. Rudzinski, E. E. Meyer, R. H. Holm, D. G. Nocera, *J. Am. Chem. Soc.* **2003**, *125*, 4755–4770.

[14] *Amsterdam Density Functional (ADF) program*, Release 2002.02, Vrije Universteit, Amsterdam, The Netherlands, **2002**.

[15] T. Yoshimura, S. Ishizaka, Y. Sasaki, H.-B. Kim, N. Kitamura, N. G. Naumov, M. N. Sokolov, V. E. Fedorov, *Chem. Lett.***1999**, *28*, 1121–1122.

[16] a) G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, Universität Göttingen; b) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany.

[17] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.

[18] A. D. Becke, *Phys. Rev. A.* **1988**, *38*, 3098–3100.J. P. Perdew, *Phys. Rev. B.* **1986**, *33*, 8822–8824.E. van Lenthe, A. E. Ehlers, E. J. Baerends, *J. Chem. Phys.* **1999**, *110*, 8943–8951.

[21] F. L. Hirshfeld, *Theor. Chim. Acta* **1977**, *44*, 129–138.

Received: April 2, 2005