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NEW MIXED-LIGAND CYANOHYDROXO OCTAHEDRAL CLUSTER COMPLEX *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4–}$, ITS LUMINESCENCE PROPERTIES AND CHEMICAL REACTIVITY

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A new rhenium cyanohydroxo octahedral cluster complex *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4–}$ has been synthesized for the first time starting from $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$. It was crystallized as salts of compositions $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$ (**1**) and $[Cu(NH_3)_4]_2[Re_6S_8(CN)_2(OH)_4]\cdot 2H_2O$ (**2**). By the reaction of *trans*-$[Re_6S_8(CN)_2(H_2O)_4]$, which was prepared by neutralization of **1** by diluted H_2SO_4, with molten 3,5-dimethylpyrazole (3,5-Me_2PzH), the molecular complex *trans*-$[Re_6S_8(3,5\text{-}Me_2PzH)_4(CN)_2]\cdot 2H_2O$ (**3**) was synthesized. Compounds **1**–**3** have been characterized by single-crystal X-ray diffraction and elemental analyses, IR spectroscopy and compounds **1** and **3** – by UV-Vis and luminescence spectroscopy.

Introduction

Hexanuclear rhenium(III) cluster complexes with octahedral core $\{Re_6Q_8\}^{2+}$ (Q = S, Se, Te), which are the objects of interest in the present article, are the most studied among the family of rhenium cluster compounds. Molecular and ionic cluster complexes of this type are represented by numerous compounds containing the general unit $[\{Re_6Q_8\}L_6]$, where apical ligands L are inorganic acido ligands or organic species. Most of these compounds show luminescence in the red and near-infrared regions in both the solid state and solutions that make them interesting for various applications[1]. One of the suitable ways of synthesis of ionic hexarhenium cluster complexes is the excision reactions through interaction of well-known polymeric cluster solids such as $Re_6Q_8X_2$[2] or Re_6Te_{15}[3] with molten salts. This strategy was used, for example, for the preparation of chalcocyanide complexes $[Re_6Q_8(CN)_6]^{4–}$ (Q = S, Se, or Te) and chalcohydroxo complexes $[Re_6Q_8(OH)_6]^{4–}$ (Q = S, Se) by the reactions of the corresponding cluster polymers with molten KCN[4] or MOH (M = K or Cs)[5], respectively. In chalcocyanide complexes CN groups, due to their ambidentate character, can serve as bridging ligands between cluster cores and transition metal cations to give polymeric compounds in different dimensionalities[6], while chalcohydroxo ones can be used both as building blocks for preparation of OH-bridged compounds with alkaline-earth[7] and transition metal cations[8], and as precursors for preparation of new hexarhenium cluster complexes by substitution of relatively labile OH groups by various organic and inorganic ligands[1b, 9]. Recently, a number of compounds containing mixed-ligand cyanohydroxo complexes *trans*-$[Re_6Q_8(CN)_4(OH)_2]^{4–}$ (Q = S, Se) have been prepared and characterized[10]. In particular, it has been shown that reaction of $[Re_6Se_8(OH)_6]^{4–}$ with KCN in an aqueous solution results in the partial ligand substitution giving the anionic cluster complex *trans*-$[Re_6Se_8(CN)_4(OH)_2]^{4–}$ [10c]. The corresponding sulfide complex $[Re_6S_8(CN)_4(OH)_2]^{4–}$ was obtained by a different way through depolymerization reaction of $[Re_6S_8(CN)_4S_{2/2}]^{4–}$ in an aqueous solution of KOH[10a].

In this paper, we report synthesis of a new mixed-ligand anionic cluster complex *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4–}$ isolated as mixed Cs/K salt $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$ (**1**). In addition to the characterization by physical methods, we have carried out two representative reactions to confirm the composition and structure of the anion and ability to demonstrate the properties that are characteristic for cyanocomplexes and hydroxocomplexes. The first reaction was the complexation reaction with Cu(II) ammine ions, which is known to involve the CN/OH apical ligands with the potential to form coordination complexes in different dimensionalities. The second reaction was the substitution of relatively labile hydroxo groups by organic ligands, namely by 3,5-dimethylpyrazole. These reactions yielded two new compounds, $[Cu(NH_3)_4]_2[Re_6S_8(CN)_2(OH)_4]\cdot 2H_2O$ (**2**) and $[Re_6S_8(3,5\text{-}Me_2PzH)_4(CN)_2]\cdot 2H_2O$ (**3**), respectively, that were characterized by single-crystal X-ray diffraction and elemental analyses, IR and UV-Vis spectroscopy. In addition, the luminescence properties of **1** and **3** in solutions and in the solid state have been investigated.

Results and discussion

Syntheses

In the present work, we studied the reaction of $[Re_6S_8(OH)_6]^{4-}$ with an excess of KCN in an aqueous solution intended to obtain $[Re_6S_8(CN)_4(OH)_2]^{4-}$ in consequence of the ligand exchange reaction as it was realized before for selenide cluster complex[10c]. Unexpectedly, the reaction resulted in the formation of a new cyanohydroxo anionic complex having only two CN and four OH apical ligands $[Re_6S_8(CN)_2(OH)_4]^{4-}$. We were not able to separate a pure potassium salt of the anionic cluster complex because of its very high solubility in water. Attempts to precipitate an alkylammonium salt were also unsuccessful. However, it was found that adding CsOH to the aqueous solution followed by its gradual evaporation leads to crystallization of the uncontaminated salt of the composition $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$ (**1**). Compound **1** is insoluble in any common organic solvent. To confirm the composition and structure of newly synthesized cluster anion, we used compound **1** as a starting material for the reaction with $CuCl_2$ in an aqueous ammonia solution. Interestingly, this reaction afforded the complex $[Cu(NH_3)_4]_2[Re_6S_8(CN)_2(OH)_4]\cdot 2H_2O$ (**2**), in which the μ_3-S atoms of the $\{Re_6S_8\}$ cluster core are involved in coordination with Cu(II) ions.

Earlier, it was show that reactions between chalcohalide hexarhenium cluster complexes and various organic substances able to coordinate metal atoms at elevated temperatures (reactions in molten organic media such as 3,5-Me_2PzH, $PnPh_3$ (Pn = P, As or Sb), pyrazine) lead to the substitution of all or some of apical halide ligands by the organic ones[11]. In the current work the reaction of **1** with molten 3,5-dimethylpyrazole, intended to exchange OH ligands by 5-Me_2PzH, has been studied. It was found that direct substitution of OH ligands in molten 3,5-Me_2PzH does not occur. However, the precipitate obtained by an acidification of an aqueous solution of **1**, which according to elemental analyses corresponds to the composition of $[Re_6S_8(CN)_2(H_2O)_4]$, readily reacts with molten 3,5-Me_2PzH to give the molecular compound $[Re_6S_8(3,5\text{-}Me_2PzH)_4(CN)_2]\cdot 2H_2O$ (**3**). Compound **3** was found to be slightly soluble in DMF and insoluble in other common organic solvents and water.

The structures of compounds **1**–**3** were determined by single-crystal X-ray diffraction analysis and their compositions were confirmed by elemental analyses. The structures **1**–**3** unambiguously demonstrated that the similar reactions of $[Re_6S_8(OH)_6]^{4-}$ and $[Re_6Se_8(OH)_6]^{4-}$ with an excess of KCN in boiling aqueous solutions proceed differently, yielding ligand exchange products with different compositions, namely, $[Re_6S_8(CN)_2(OH)_4]^{4-}$ and $[Re_6Se_8(CN)_4(OH)_2]^{4-}$, respectively. In this regard, the $[Re_6S_8(OH)_6]^{4-}$ complex showed a lower reactivity in comparison with selenide analog, which limited the substitution of OH ligands to only two of them.

Crystal structures

The *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4-}$ anion in **1** has the structure typical of other octahedral cluster complexes of the general formula $[M_6Q_8L_6]$. In particular, it consists of a Re_6 octahedron embedded inside a cube of eight capping μ_3-S atoms. The Re atoms are additionally coordinated by terminal ligands: two CN ligands in *trans* positions and four OH ligands (Fig. 1). The **1** adopts a high-symmetry cubic structure (*Pm*–3*m* space group, CsCl type), with the anion's CN groups being disordered over four equivalent *mm*2 positions. Most closely, the structure of the anion resembles those of "4/2" cyanohydroxo complexes, $[Re_6Q_8(CN)_4(OH)_2]^{4-}$ (Q = S, Se)[10]. As expected, the Re–Re, Re–C_{CN} and Re–O_{OH} bond lengths (which are 2.5810(13) and 2.5860(10), 2.07(3), and 2.03(2) and 2.07(3) Å, respectively) are consistent with those observed in the above mentioned compounds.

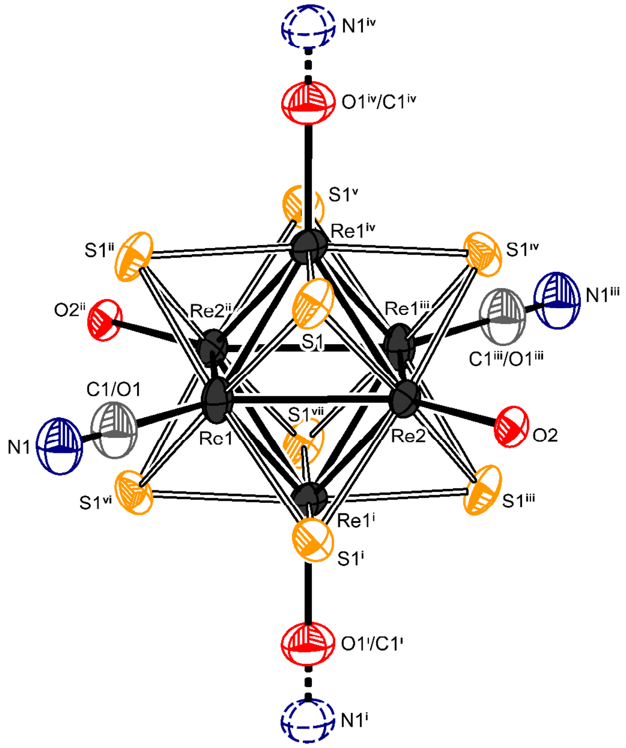

Figure 1. Displacement ellipsoid plot (at the 30% probability level) of the $[Re_6S_8(CN)_2(OH)_4]^{4-}$ cluster anion in **1**. Dashed ellipsoids represent alternative positions of disordered CN groups. Symmetry operations to generate equivalent atoms: (i) $1-y, x, z$; (ii) $x, 1-y, -z$; (iii) $1-x, 1-y, z$; (iv) $y, 1-x, z$; (v) $1-y, 1-x, -z$; (vi) $y, x, -z$; (vii) $1-x, y, -z$.

The cationic part of the structure is represented by two crystallographically independent Cs^+ cations occupying 3*m* positions with the site occupancies of 3/5 and 2/5, and two K^+ cations in *mm*2 and 4*mm* positions with the site occupancies of 1/4 and 1/6, respectively. It is evident that due to the heavy disorder of the cations, the localization of all solvate water molecules belonging to their coordination environments could be a very difficult task. Where possible, partial occupancy water molecules were modelled from electron-density maps, but the full hydrate composition of **1** was assessed on the base of elemental analysis.

Compound **2** crystallizes in the triclinic space group *P*–1 with one formula unit per cell. The asymmetric unit contains half of the centrosymmetric cluster anion, two halves of the centrosymmetric $[Cu(NH_3)_4]^{2+}$ cations and two half-occupied water molecules of crystallization. The geometric parameters of the anion are similar to those in the compound **1**; nevertheless, they are determined more precisely due to the absence of disorder of the apical ligands. The Re–Re and Re–S bond lengths vary in the intervals 2.5863(7)–2.5991(8) and 2.394(4)–2.429(3) Å, while four Re–C_{CN} bonds have the same length of 2.121(14) Å and two Re–O_{OH} bond lengths are 2.057(9) and 2.095(11) Å.

In each crystallographically independent $[Cu(NH_3)_4]^{2+}$ cation the Cu(II) center is square-planarly coordinated by the nitrogen atoms of four NH_3 molecules with the Cu–N distances ranging from 1.967(14) to 2.029(13) Å. In addition, the coordination sphere of the Cu(II) cation is completed by two weak interactions with the μ_3-S atoms belonging to different cluster anions. The corresponding Cu···S distances are 2.973(4) Å around the Cu1 atom and 2.886(3) Å around the Cu2 atom. These interactions, along with the N_{NH3}–H···O_{OH} hydrogen bonds (3.012(15)–3.08(2) Å), lead to the formation of layers extended parallel to the (-111) plane (Fig. 2).

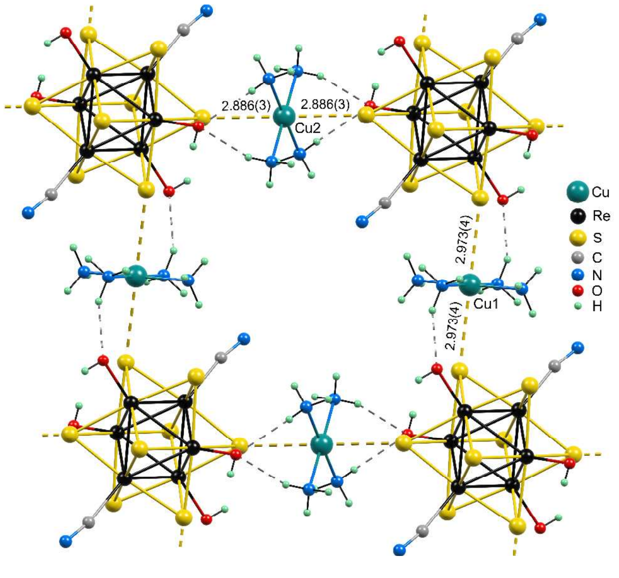

Figure 2. Fragment of the layer formed by $[Cu(NH_3)_4]^{2+}$ cations and $[Re_6S_8(CN)_2(OH)_4]^{4-}$ cluster anions in **2**. Secondary interactions (Cu···S and N–H···O hydrogen bonds) are shown by dashed lines.

The formation of a distorted octahedral environment is often observed in copper(II) complexes, but in the presence of cyanide ions or metal-cyano complexes, it is rather expected that the additional coordination sites of Cu^{2+} may be occupied by nitrogen atoms. However, there are at least several examples where the secondary interactions with μ_3-S atoms (or sulfide ligands) played the similar role in the formation of supramolecular assemblies. The first example is the aquahydroxo complex $[\{Cu(en)_2\}Re_6S_8(H_2O)_2(OH)_4]\cdot 4H_2O$ (en = ethylenediamine) which was obtained by reaction of $[Re_6Se_8(OH)_6]^{4-}$ with $Cu(en)_2Cl_2$ in water[8]. In this case the square-planar geometry of the $\{Cu(en)_2\}^{2+}$ moiety is formed by en nitrogen atoms, and the coordination environment of Cu(II) center is completed to an octahedral by two sulfur atoms of the cluster complexes. The reaction of $[Re_6S_8(OH)_6]^{4-}$ with Cu^{2+} in an aqueous ammonia yielded the second example, $[\{Cu(NH_3)_3\}_2\{Re_6S_8(OH)_6\}]\cdot 8H_2O$, where the octahedral coordination environment of Cu(II) center includes three ammine nitrogen atoms, one hydroxo oxygen and two sulfur atoms originating from two different cluster anions[12].

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with two formula units per cell. It adopts a molecular structure built up from neutral centrosymmetric complexes $[Re_6S_8(3,5\text{-}Me_2PzH)_4(CN)_2]$ and water molecules of crystallization (Fig. 3).

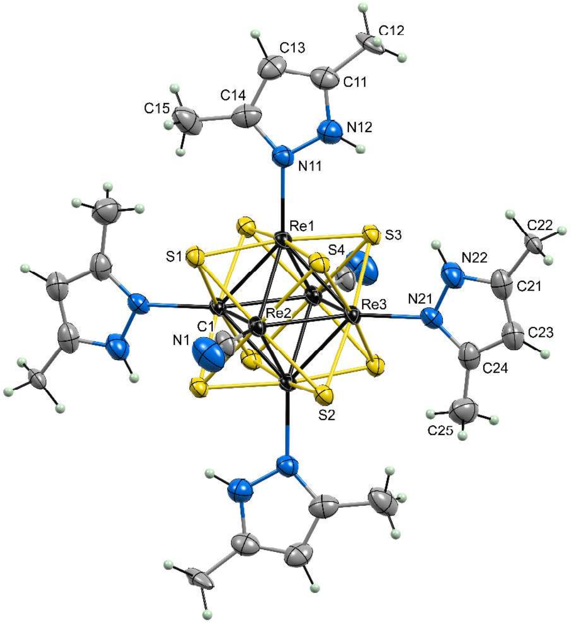

Figure 3. Displacement ellipsoid plot (at the 50% probability level) of the $[Re_6S_8(3,5\text{-}Me_2PzH)_4(CN)_2]$ complex in **3**. Unlabelled atoms are related to labeled atoms by the symmetry code: –*x*, –*y*, 1 – *z*.

The $[Re_6S_8(3,5\text{-}Me_2PzH)_4(CN)_2]$ complex is characterized by the following geometric parameters: the Re–Re and Re–S bond lengths are in the ranges of 2.5943(4)–2.6044(4) and 2.395(2)–2.414(2) Å, respectively, while the Re–C_{CN} bond lengths are equal to 2.116(8) Å and the Re–N bond lengths are 2.156(6) and 2.168(7) Å. The structure of **3** can be represented as a pseudo-cubic CsCl-type packing in which the cluster complexes are interconnected through the N–H···O (2.794(10) and 2.814(10) Å) and O–H···N_{CN} (2.792(12) Å) hydrogen bonds between pyrazole NH groups and H_2O molecules, and H_2O molecules and CN groups, respectively.

Infrared data

Assignments of the vibrational spectra of compounds **1**–**3** were made according to literature data[13]. The strong absorption bands at 2107 in **1**, 2112 cm^{-1} in **2** and 2105 cm^{-1} in **3** are assigned to the CN stretching frequencies. In the spectra of **1**–**3**, the band near 413 cm^{-1} may be assigned to the Re–S vibrations. The H_2O solvent molecules in **1** are characterized by the bands at 1625 and 3411 cm^{-1} assigned to $\delta(H_2O)$ and $\nu(OH_{aq})$, respectively. In the spectrum of **3**, these bands are at 1570 and 3382 cm^{-1}. Due to the overlap of the bands of H_2O solvent molecules with the bands of NH_3 molecules in **2**, definitive assignments could not be made. The presence of strong bands in the range assignable to the N–H vibrations in the spectrum of **3** confirms the coordination of 3,5-Me_2PzH ligands in the neutral monodentate form. The characteristic bands of the C–C and C≡N stretching modes, observed at 1640 and 1558 cm^{-1} in uncoordinated 3,5-Me_2PzH, are shifted to considerable lower frequencies 1598 and 1518 cm^{-1}, respectively. It is consistent with the somewhat longer C–C and C≡N bond lengths in the complex **3** in comparison to those in uncoordinated 3,5-Me_2PzH[14].

Luminescence study

Similar to the previously studied hexanuclear chalcogenide rhenium cluster complexes[1a, 9a, 10c, 15], compounds **1** and **3** show broad and featureless emissions in the wavelength region from about 550 to longer than 950 nm in solutions as well as in the solid state. The emission spectra of **1** and **3** are shown in Figs. 4 and 5, respectively, and the emission maximum wavelengths (λ_{em}), quantum yields (Φ_{em}) and lifetimes (τ_{em}) of the compounds are summarized in Table 1.

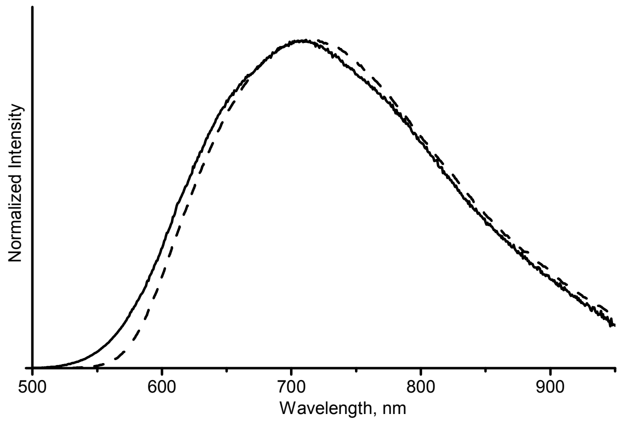

Figure 4. Emission spectra of **1** in the solid state (dash line) and in a basic aqueous solution (solid line).

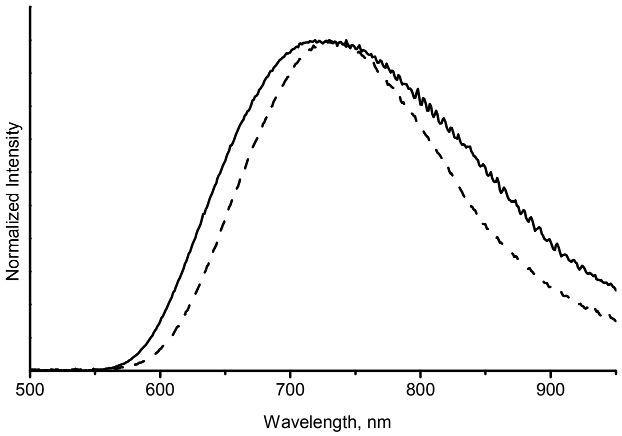

Figure 5. Emission spectra of **3** in the solid state (dash line) and in DMF solution (solid line).

Table 1. Spectroscopic and photophysical data of compounds **1**, **3** and related $\{Re_6S_8\}^{2+}$-based complexes

Sample	λ_{em} (nm)	τ (μs)	$\Phi_{em}{}^{a}$
1 (pH ~ 13)	~710	1.2	0.012
1 (pH ~ 7)	~715	1.1	0.011
1 (pH ~ 1)	~720	1.6	0.014
trans-$[Re_6S_8(CN)_4(OH)_2]^{4-}$ (pH ~ 13, 7 or 1)[50]	~730	1.1	0.005
$[Re_6S_8(CN)_6]^{4-}$ (pH ~ 13, 7 or 1)[46, 50]	~720	1.2	0.009
$[Re_6S_8(OH)_6]^{4-}$ (pH ~ 13)[48]	~655	2.2	0.010
$[Re_6S_8(OH)_6]^{4-}$ (pH ~ 7)[48]	~665	1.1	0.003
$[Re_6S_8(OH)_6]^{4-}$ (pH ~ 1)[48]	~685	2.35	0.005
1 in solid phase	~715	2.2	0.038
3 in DMF	~725	5.9	0.016
3 in solid phase	~730	3.9, 1.3	0.013

The emission quantum yields in solution and solid samples phases were determined by $(Bu_4N)_4[Re_6S_8Cl_6]$ as a standard (Φ_{em} = 0.039) in deaerated acetonitrile and an emission photon counter, respectively. See also the experimental section.

As illustrated previously by the example of $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se), decreases in the pH values of initially basic aqueous solutions of the complexes lead to gradual protonation of the OH ligands and transformation of the hexahydroxo units to the aquahydroxo units $[Re_6Q_8(H_2O)_n(OH)_{6-n}]^{n-4}$ and finally to the hexaaqua $[Re_6Q_8(H_2O)_6]^{2+}$ clusters[15c]. In addition, protonation of the OH ligands as the result of acidification of the aqueous solution was observed for the cyanohydroxo complex $[Re_6S_8(CN)_4(OH)_2]^{4-}$, resulting in formation of the aquacyano cluster $[Re_6S_8(CN)_4(H_2O)_2]^{2-}$ [16]. It was found that protonation of $[Re_6S_8(OH)_6]^{4-}$ accompanied an appreciable red-shift of the emission spectrum and changes in the τ_{em} and Φ_{em} values, while the emission properties of an aqueous solution of $[Re_6S_8(CN)_4(OH)_2]^{4-}$ were not affected by pH: *trans*-$[Re_6S_8(CN)_4(H_2O)_2]^{2-}$, *trans*-$[Re_6S_8(CN)_4(OH)(H_2O)]^{3-}$, and *trans*-$[Re_6S_8(CN)_4(OH)_2]^{4-}$ anionic clusters exhibit the almost similar spectroscopic and excited-state characteristics (λ_{em}, τ_{em}

and Φ_{em}) to those of an aqueous $[Re_6S_8(CN)_6]^{4-}$ solution. The emission properties of $[Re_6S_8(CN)_6]^{4-}$ were found to be independent of the pH of the solution[16](Table 1) that allowed us to conclude that the photophysical properties of *trans*-$[Re_6S_8(CN)_4(OH)_{2-n}(H_2O)_n]^{n-4}$ were mainly defined by the CN ligands and not appreciably affected by the OH or H_2O ligand(s).

In the present investigation, we studied the emission properties of **1** in aqueous solutions at pH ~1, ~7 and ~13. Based on the previous studies[15c, 16], it is expected that an *trans*-$[Re_6S_8(CN)_2(H_2O)_4]^0$, *trans*-$[Re_6S_8(CN)_2(H_2O)_n(OH)_{4-n}]^{n-4}$ or *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4-}$complex predominates in an aqueous solution at pH ~1, ~7 or ~13, respectively. The relevant emission spectra are shown in Fig. 6. The spectroscopic/photophysical parameters summarized in Table 1 clearly demonstrate that the emission maximum wavelength of *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4-}$ in an aqueous solution is red-shifted gradually along with a decrease in pH similar to the above mentioned $[Re_6S_8(OH)_6]^{4-}$, while the τ_{em} and Φ_{em} values are slightly varied in an irregular way with a change in the solution pH. Furthermore, the λ_{em} values of aqueous *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4-}$ solutions at different pH values are very close to those (~720 nm) of $[Re_6S_8(CN)_6]^{4-}$ and *trans*-$[Re_6S_8(CN)_4(OH)_2]^{4-}$ in aqueous solutions at the relevant pH values and is far from λ_{em} of $[Re_6S_8(OH)_6]^{4-}$ (665 nm). This one more time corroborates our statement[16] that the emission properties of cyanohydroxo complexes with the general formula $[Re_6S_8(CN)_n(OH)_{6-n}]^{4-}$ (n = 1–4) are mainly defined by the presence of the apical CN ligands.

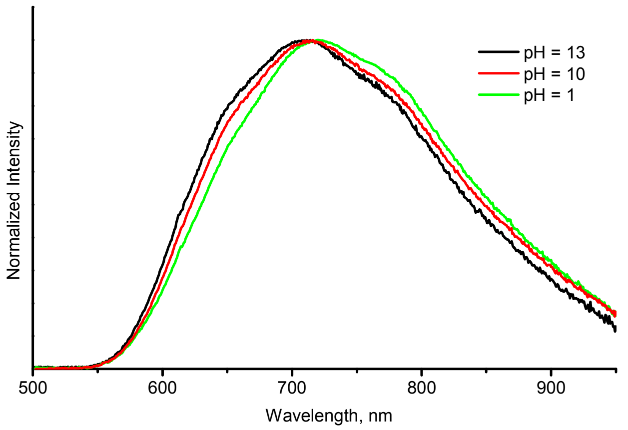

Figure 6. Emission spectra of *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4-}$ in aqueous solutions at pH 1, 7 and 13.

On the other hand, the emission properties of the complex **1** in the solid state were best characterized by higher Φ_{em} and τ_{em} values than the relevant values in an aqueous solution (Table 1), similar to those of other water-soluble hexarhenium cluster complexes[9a, 10c, 15d].

The emission properties of **3** were also studied in both DMF solution and in the solid state. It gave evidence that substitution of the OH apical ligands (complex **1**) by 3,5-Me_2PzH molecules resulted in an appreciable red-shift of λ_{em} (Table 1). The emission decay profile of a DMF solution of **3** was fitted by a single exponential function with the τ_{em} value of 5.9 µs, whereas the powdered sample exhibited double exponential emission decay with the decay constants of 3.9 and 1.3 µs with the amplitude values ~0.7 and ~0.3, respectively. Non-single exponential decay of **3** in the solid phase could be explained by efficient excitation migration in the crystal and subsequent energy trapping/emission in the crystal defects.

Experimental Section

Characterization techniques

Elemental analysis was performed using a MICRO CORDER JM10. Energy dispersive X-ray spectroscopy (EDS) was performed on an EDAX equipped (JEOL EX-23000BU) JEOL JSM-6700F field emission scanning electron microscope. IR spectra in KBr pellets were recorded on Scimitar FTS 2000c spectrometer in 4000–375 cm^{-1} range. Electronic absorption spectrum in a range 200–600 nm was recorded on a U-3300 Hitachi spectrophotometer.

Synthesis Procedures

$K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ was prepared as described previously[5a]. All other reagents used were commercially available products of reagent grade quality. All synthetic procedures were performed in air.

Preparation of $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$ (1)

$K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (1 g, 0.563 mmol) and KCN (1 g, 15.357 mmol) were dissolved in 20 mL of water resulting in a clear orange solution. The solution was boiled for 2 hours and then CsOH (1 g, 6.670 mmol) was added. The solution was evaporated by heating to the volume of ~5 mL. After cooling down the solution was left for 5 hours at room temperature resulting in the formation of a red crystalline precipitate. The crystals were filtered off and dried in air to give 0.70 g (yield 63 %) of $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$. Found: C, 1.0; H, 0.7; N, 1.1, S, 12.5. Calc. for $C_2H_{12}N_2Cs_{2.67}K_{1.33}O_8Re_6S_8$: C 1.2, H 0.6, N 1.4, S, 13.0. EDS showed the consistent Cs : K : Re : S ratio of 3.3 : 1.6 : 6 : 7.2. IR (KBr, cm^{-1}): 3490(w), 3411(w), 3239 (m), 2107 (s), 1730 (w), 1625(m), 1590(m), 1396 (m), 1301(m), 1011(w), 833(w), 743(w), 684(w), 415 (m). UV-Vis in 0.1 M aqueous solution of H_2SO_4: λ_{max}, nm (ε, $mol^{-1}dm^3cm^{-1}$) = 360 (sh, 1664), 266 (sh, 10177), 238 (sh, 20570). UV-Vis in 0.1 M aqueous solution of KOH: λ_{max}, nm (ε, $mol^{-1}dm^3cm^{-1}$) = 428 (sh, 455), 352 (sh, 2801), 238 (sh, 34502). The X-ray powder diffraction pattern for **1** showed a good agreement with that simulated from the crystal structure (Fig. 7).

Preparation of $[Cu(NH_3)_4]_2[Re_6S_8(CN)_2(OH)_4]\cdot 2H_2O$ (2)

0.02 g (0.011 mmol) of compound **1** was dissolved in 5 mL of water and mixed with a solution of $CuCl_2\cdot 2H_2O$ (0.02 g, 0.117 mmol) in 5 mL of concentrated aqueous ammonia (25 %). The resulting mixture was left for 1 week at room temperature in a capped vessel. Black crystals formed were filtered and dried in air. Yield 0.013 g (72 %). Found: C, 1.2; H, 2.0; N, 7.6; S, 13.8. Calc. for $C_2H_{32}Cu_2N_{10}O_6Re_6S_8$: C, 1.3; H, 1.8; N, 7.8; S, 14.3. IR (KBr, cm^{-1}): 3536 (m), 3437 (w), 3307 (w), 3152 (w), 2924 (m), 2856 (w), 2112 (s), 1730 (s), 1600 (s), 1467 (m), 1402 (m), 1234 (s), 1076 (w), 845 (m) 703 (m), 466 (m), 407 (m). EDS showed the consistent Cu:Re:S ratio of 2.2:6:7.8.

Preparation of $[Re_6S_8(3,5\text{-}Me_2PzH)_4(CN)_2]\cdot 2H_2O$ (3)

Compound **1** (0.24 g, 0.12 mmol) was dissolved in 5 mL of water giving an orange solution. 0.5 mL of 0.1 M H_2SO_4 was added to the solution resulting in the formation of a yellow precipitate. The precipitate was separated by centrifugation, washed by water and then dried in air. Found: C, 1.5; H, 0.7; N, 1.8; S, 16.8. Calc. for $C_2H_8N_2O_4Re_6S_8$: C, 1.6; H, 0.5; N, 1.9; S, 17.1. EDS shows the absence of potassium and caesium in the sample. For the preparation of **3**, all the obtained precipitate was mixed with 0.32 g (3.33 mmol) of 3,5-dimethylpyrazole and heated in a sealed glass ampoule at 180 °C for 48 hours. The ampoule was cooled down with a rate of 20 °C/h resulting in formation of red crystals on the walls of the ampoule. The crystals were washed with diethyl ether to remove the excess of 3,5-dimethylpyrazole. Yield: 0.14 g (62 % based on **1**). Found: C, 14.4; H, 2.0; N, 7.6; S, 13.8. Calc. for $C_{22}H_{36}N_{10}O_2Re_6S_8$: C, 14.3; H, 2.0; N, 7.6; S, 13.9. IR (KBr, cm^{-1}): 3382 (m), 3289 (w), 3132 (w), 2921 (w), 2852 (w), 2105 (s), 1598 (s), 1570 (s), 1518 (w), 1268 (m), 1150(m), 1023(w), 807(m), 723(w), 618 (w), 413 (m). UV-Vis in DMF: λ_{max}, nm (ε, $mol^{-1}dm^3cm^{-1}$) = 430 (sh, 623), 325 (sh, 11096).

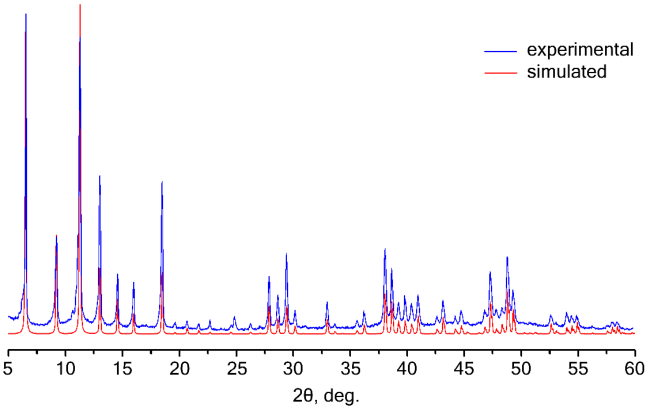

Figure 7. Comparison of experimental and simulated XRD patterns of **1**.

X-ray crystallography

Crystal structures of the title compounds were solved by single-crystal X-ray diffraction analysis. Suitable crystals were selected from the mother liquors, fixed to the tips of glass fibers with epoxy resin, and mounted on a Bruker-Nonius X8 Apex 4K CCD diffractometer (graphite monochromatized Mo-Kα radiation, λ = 0.71073 Å). The data were collected by the standard technique. Data reduction and multi-scan absorption were carried out using the SADABS[17]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package[17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of OH, NH_3 and 3,5-dimethylpyrazole ligands in **2** and **3** were located geometrically and refined as riding; hydroxo hydrogen atoms in **1** could not be located due to disorder of OH groups. Hydrogen atoms of lattice water molecules were not located. Crystallographic data, data collection and selected refinement details are given in Table 2. Selected bond lengths are listed in Table 3.

The complete crystallographic data for **1** and **2** have been deposited with the Inorganic Crystal Structure Database under the reference CSD-numbers 428064 and 428065, respectively. These data can be obtained free of charge *via* http://www.fiz-karlsruhe.de/request_for_deposited_data.html. The crystallographic data for **3** have been deposited with the Cambridge Crystallographic data Centre under the reference number CCDC 1013350. These data can be obtained free of charge from CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.

X-ray powder diffraction analysis of **1** was performed on a Shimadzu XRD-7000 diffractometer (Cu-Kα radiation, λ = 1.54178 Å, Ni filter, 5 – 60° 2θ range, 0.03° step, 10 s per step, room temperature). A polycrystalline sample was ground with hexane in an agate mortar, and the resulting suspension was deposited on a standard quartz sample holder. A thin polycrystalline layer was formed after drying.

Luminescence

For emission spectroscopic measurements, water and DMF were distilled prior to use. The absorbance of aqueous and DMF sample solutions was set ~0.1 at an excitation wavelength (355 nm). The solutions were deaerated by purging an Ar gas stream over 30 min and then sealed. To investigate emission properties in the solid state, fine-crystalline compounds **1** and **3** were powdered by using an agate mortar and the obtained powders were placed between two nonfluorescent glass plates. The solutions and solid samples were excited by 355-nm laser pulses (6 ns duration, LOTIS TII, LS-2137/3). Corrected emission spectra were recorded on a red-sensitive multichannel photodetector (Hamamatsu Photonics, PMA-11). For emission decay measurements, the emission was analyzed by a streakscope system (Hamamatsu Photonics, C4334 and C5094). The emission quantum yields (Φ_{em}) of **1** in an aqueous solution and **3** in a DMF solution were estimated by using $(Bu_4N)_4[Re_6S_8Cl_6]$ as a standard: Φ_{em} = 0.039 in deaerated acetonitrile[15a]. Refractive index correction was made to calculate the Φ_{em} value in solutions. The emission quantum yields of **1** and **3** in the solid state were determined by an Absolute Photo-Luminescence Quantum Yield Measurement System (Hamamatsu Photonics, C9920-03), which comprised of an excitation Xenon light source (the excitation wavelength was set at 400 nm), an integrating sphere, and a red-sensitive multichannel photodetector (Hamamatsu Photonics, PMA-12).

Conclusions

In conclusion, in the present work we have reported the simple synthesis of new *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4-}$ anionic rhenium cluster complex by the reaction of a hexahydroxo complex $[Re_6S_8(OH)_6]^{4-}$ with KCN in a boiling aqueous solution. The cluster anion *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4-}$ has two types of terminal ligands: two kinetically inert cyano ligands and four labile hydroxo groups. According to our recent studies on $\{Re_6Q_8\}$-based complexes (Q = S, Se), the terminal OH ligands can be substituted by other ligands, opening a way to preparation of new *trans*-$[Re_6S_8(CN)_2L_4]^{n-}$ complexes, that was already realized in this work (compound **3**). On the other hand, apical CN^- ligands are able to coordinate with transition metal cations forming cyano-bridged compounds. Surprisingly, by the reaction with Cu^{2+} we obtained S-bridged compound **2**. The luminescence properties of **1** and **3** were studied in detail and the results were compared with those of related compounds.

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Notes and references

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Table 2. Crystal data and structure refinement details for **1** – **3**

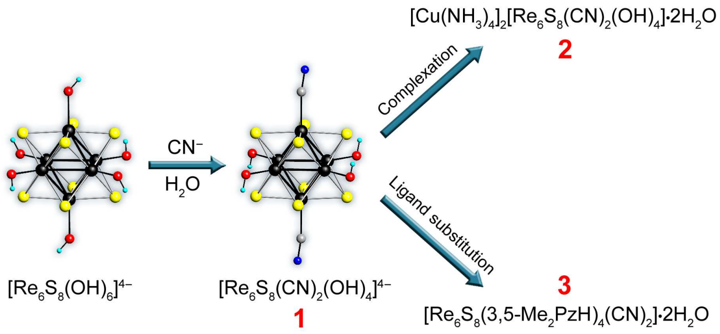
Compound	**1**	**2**	**3**
Empirical formula	$C_2H_{12}Cs_{2.67}K_{1.33}N_2O_8Re_6S_8$	$C_2H_{32}Cu_2N_{10}O_6Re_6S_8$	$C_{22}H_{36}N_{10}O_2Re_6S_8$
Formula weight	1972.38	1793.14	1846.29
Temperature (K)	120(2)	173(2)	150(2)
Crystal size (mm^3)	0.10 × 0.10 × 0.06	0.30 × 0.12 × 0.08	0.10 × 0.08 × 0.08
Crystal system	Cubic	Triclinic	Monoclinic
Space group	*Pm*–3*m*	*P*–1	$P2_1/n$
Z	3	1	2
a (Å)	13.5676(13)	8.5493(6)	11.0552(10)
b (Å)		9.3230(6)	12.0620(12)
c (Å)		11.1684(7)	14.0743(15)
α (º)		92.188(5)	
β (º)		111.206(6)	97.116(3)
γ (º)		101.782(6)	
V (Å^3)	2497.5(4)	806.27(9)	1862.3(3)
$D_{\mathrm{calcd.}}$ (g cm^{-3})	3.934	3.693	3.292
μ(Mo Kα) (mm^{-1})	25.289	24.266	19.910
θ range (º)	2.12 – 27.46	2.80 – 27.48	2.21 – 26.38
h, k, l indices range	$-13 \le h \le 14$; $-7 \le k \le 17$; $-17 \le l \le 1$	$-11 \le h \le 11$; $-12 \le k \le 12$; $-13 \le l \le 14$	$-9 \le h \le 13$; $-15 \le k \le 14$; $-17 \le l \le 17$
F(000)	2556	798	1664
Reflections collected	4166	7837	12970
Unique reflections	634 (R_{int} = 0.0360)	3531 (R_{int} = 0.0526)	3801 (R_{int} = 0.0253)
Observed reflections [$I > 2$	525	2585	3228
Parameters refined	40	172	221
$R[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0433$ $wR_2 = 0.1214$	$R_1 = 0.0455$ $wR_2 = 0.1158$	$R_1 = 0.0255$ $wR_2 = 0.0667$
$R(F^2)$ (all data)	$R_1 = 0.0544$ $wR_2 = 0.1295$	$R_1 = 0.0658$ $wR_2 = 0.1207$	$R_1 = 0.0342$ $wR_2 = 0.0691$
GOOF on F^2	1.097	1.000	1.084
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.832, –1.989	4.217, –3.626	2.611, –0.822

Table 3. Selected bond lengths (*d*, Å) for the $[Re_6S_8(CN)_2(OH)_4]^{4-}$ anion in **1** and **2**, and for the $[Re_6S_8(3,5\text{-}Me_2PzH)_4(CN)_2]$ complex in **3**

1	*d*	**2**	*d*	**3**	*d*
Re1—Re1^{i}	2.5810(13)	Re1—Re2	2.5881(8)	Re1—Re2	2.6026(5)
Re1—Re2	2.5860(10)	Re1—Re2^{i}	2.5873(7)	Re1—Re2^{i}	2.5971(4)
Re1—S1	2.407(3)	Re1—Re3	2.5881(8)	Re1—Re3	2.6044(4)
Re2—S1	2.406(4)	Re1—Re3^{i}	2.5912(7)	Re1—Re3^{i}	2.6039(4)
Re1—C1	2.07(3)	Re2—Re3	2.5991(8)	Re2—Re3	2.5943(4)
Re1—O1	2.07(3)	Re2—Re3^{i}	2.5863(7)	Re2—Re3^{i}	2.6017(5)
Re2—O2	2.03(2)	Re1—S1	2.418(4)	Re1—S1	2.402(2)
N1—C1	1.09(2)	Re1—S2^{i}	2.402(4)	Re1—S2^{i}	2.413(2)
		Re1—S3	2.404(4)	Re1—S3	2.414(2)
		Re1—S4	2.413(3)	Re1—S4	2.404(2)
		Re2—S1	2.417(4)	Re2—S1	2.395(2)
		Re2—S2	2.394(4)	Re2—S2	2.413(2)
		Re2—S3^{i}	2.414(3)	Re2—S3^{i}	2.408(2)
		Re2—S4	2.429(3)	Re2—S4	2.412(2)
		Re3—S1^{i}	2.417(3)	Re3—S1^{i}	2.401(2)
		Re3—S2	2.418(4)	Re3—S2	2.412(2)
		Re3—S3	2.411(3)	Re3—S3	2.408(2)
		Re3—S4	2.418(3)	Re3—S4	2.411(2)
		Re1—C1	2.121(14)	Re1—N11	2.155(6)
		Re2—O1	2.095(11)	Re2—C1	2.116(8)
		Re3—O2	2.057(9)	Re3—N21	2.167(7)
		N1—C1	1.18(2)	N1—C1	1.136(11)

Equivalent positions for **1**: (i) $y, 1 - x, z$; for **2**: (i) $1 - x, 1 - y, -z$; for **3**: (i) $-x, -y, 1 - z$.

Graphical abstract



Synopsis

A new mixed-ligand anionic cluster complex *trans*-$[Re_6S_8(CN)_2(OH)_4]^{4-}$ isolated as mixed Cs/K salt $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$ has been synthesized and characterized by different physical methods. In addition, two representative reactions confirming the composition and structure of the anion and its ability to show reactivity similar to that of cyano- and hydroxocomplexes have been carried out.