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The First Octahedral Cluster Complexes With Terminal Formate Ligands: Synthesis, Structure, and Properties of $K_4[Re_6S_8(HCOO)_6]$ and $Cs_4[Re_6S_8(HCOO)_6]$

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The hexarhenium anionic cluster complex with terminal formate ligands $[Re_6S_8(HCOO)_6]^{4-}$ was obtained by the room-temperature reaction between $[Re_6S_8(OH)_6]^{4-}$ and formic acid in an aqueous solution. The cluster was crystallized as a potassium or cesium salt and characterized by X-ray single-crystal diffraction and elemental analyses, IR, ^{1}H NMR, UV/vis, and luminescence spectroscopies. In particular, the emission quantum yield of the potassium salt of the Re_6 cluster anion in the solid phase was determined for the first time. The electronic structures of $[Re_6S_8(HCOO)_6]^{4-}$ and $[Re_6S_8(OH)_6]^{4-}$ were also elucidated by DFT calculations.

Introduction

Bi- and trinuclear transition metal cluster complexes with formate ligands have been known for a long time.[1] Generally, the formate ligands in such complexes are coordinated to two metal atoms of the same cluster in a bidentate-bridged mode. A crystal structure of any formate cluster complex with more than three metal atoms in the cluster core has not yet been documented. In the case of a hexanuclear cluster complex, furthermore, only a few compounds with terminal carboxylate ligands have been synthesized: molybdenum and tungsten halogenide complexes $[Mo_6Cl_8(CH_3COO)_6]^{2-}$,[2] $[Mo_6L_8(CF_3COO)_6]^{2-}$ (L = Cl, Br),[3] and $[W_6Cl_8(CH_3COO)_6]^{2-}$.[4] It is clear that bidentate-bridged coordination of carboxylate ligands with adjacent metal atoms in an octahedral cluster complex of the type $\{M_6L_{12}\}$ (M = Nb, Ta, W and L = Cl, Br) or $\{M'_6Q_8\}$ (M′ = Nb and Q = I; M′ = Mo, W and Q = Cl, Br, I, S, Se, Te; M′ = Re and Q = S, Se, Te) is improbable, owing to steric hindrance of the inner ligand environment in the cluster core.

In this paper, we report syntheses, crystal structures, and chemical and physical properties of the potassium and cesium salts of a new octahedral anionic rhenium cluster complex $[Re_6S_8(HCOO)_6]^{4-}$. To the best of our knowledge, this is the first demonstration of the chalcogenide hexanuclear cluster ligated by carboxylic acid anions, and therewith, $[Re_6S_8(HCOO)_6]^{4-}$ is the unique representative of any octahedral cluster complexes with formate ligands.

Experimental Section

Materials and Syntheses. The starting cluster compounds $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and $Cs_4[Re_6S_8(OH)_6]\cdot 6H_2O$ were synthesized as reported previously.[5,6] All other reagents were commercially available products of reagent-grade quality and were used as purchased.

Elemental analyses for H, S, and O were performed by using an EA1108 (Carlo Erba Instrument, Italy) in the Organic Chemistry Research Center of Sogang University, Korea. Energy dispersive spectroscopy (EDS) was performed on an EDAX-equipped (JEOL EX-23000BU) JEOL JSM-6700F field emission scanning electron microscope. Infrared spectra were measured on KBr pellets with a

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Scimitar FTS 2000c spectrometer in the range of 400−4000 cm^{-1}. ^{1}H NMR spectroscopy was conducted by using a JEOL JME-EX270 spectrometer; the ^{1}H chemical shifts are given in parts per million by DSS as an internal standard (0.00 ppm).

For emission spectroscopic measurements, water was distilled and deionized prior to use (Advantec Toyo, GSR-200). Absorption and emission spectroscopies were conducted by using a U-3300 spectrophotometer (Hitachi) and an 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 was excited by 355-nm laser pulses (6 ns duration, LOTIS TII, LS-2137/3), and the emission was analyzed by a streak-scope system (Hamamatsu Photonics, C4334 and C5094). For emission measurements, the absorbance of the sample solution was set <0.05 at 355 nm, and the solution was deaerated by purging an Ar-gas stream over 20 min. The relative emission quantum yield (Φ_{em}) of $K_4[Re_6S_8(HCOO)_6]$ in an aqueous solution was estimated by using $(Bu_4N)_4Re_6S_8Cl_6$ as a standard: $\Phi_{em} = 0.039$ in deaerated acetonitrile.[7] Refractive index correction was made to calculate the Φ_{em} value in solution. The emission quantum yield of $K_4[Re_6S_8(HCOO)_6]$ in the solid state was determined by an Absolute Photo-Luminescence Quantum Yield Measurement System (Hamamatsu Photonics, C9920-03), which comprises an excitation xenon light source (the excitation wavelength was set at 380 nm), an integrating sphere, and a red-sensitive multichannel photodetector (Hamamatsu Photonics, PMA-12).

Synthesis of $K_4[Re_6S_8(HCOO)_6]$ (1). $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ (0.5 g, 0.28 mmol) was dissolved in 50 mL of water, resulting in a clear yellow solution with pH ≈ 8. A total of 10 mL of concentrated formic acid was added to the solution, giving a slightly turbid yellow solution. The solution was left for mixing over 12 h. The resulting clear yellow solution was concentrated to ~5 mL by rotary evaporation and left standing in an open vessel at room temperature. Yellow cubic crystals suitable for X-ray structure determination were obtained after 10 days. The crystals were collected by filtration and dried in the air to give 0.325 g (64%) of $K_4[Re_6S_8(HCOO)_6]$. Anal. calcd for $C_6H_6K_4O_{12}Re_6S_8$: C, 4.00; H, 0.34; S, 14.25. Found: C, 3.89; H, 0.12; S, 13.98. EDS shows a consistent K/Re/S ratio of 4.1:6:7.8. The IR spectrum of the compound comprises the broad and intense bands at 1616 and 1275 cm^{-1} corresponding to the $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ vibrations, respectively. The peak at 404 cm^{-1} was assigned to the Re-(μ_3-S) vibration. UV−vis in H_2O, λ_{max}, nm (ε, mol^{-1} dm^3 cm^{-1}): 407 (sh, 841), 360 (sh, 1691), 258 (sh, 19027), 233 (sh, 35454), 220 nm (72659). ^{1}H NMR (250 MHz, D_2O, 25 °C): δ 8.64, 8.62, 8.60, 8.58, 8.41 (s, CH).

Synthesis of $Cs_4[Re_6S_8(HCOO)_6]$ (2). Compound **2** was prepared by procedures similar to those of **1** except for the use of $Cs_4[Re_6S_8(OH)_6]\cdot 6H_2O$ (0.1 g, 0.047 mmol) as a starting material. Yield: 53 mg (51%). Anal. calcd for $C_6H_6Cs_4O_{12}Re_6S_8$: C, 3.31; H, 0.28; S, 11.79. Found: C, 3.30; H, 0.21; S, 11.92. EDS shows a consistent Cs/Re/S ratio of 3.8:6:7.9. The IR spectrum of the compound comprises the broad and intense bands at 1614 and 1242 cm^{-1} corresponding to the $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ vibrations, respectively. The peak at 403 cm^{-1} was assigned to the Re-(μ_3-S) vibration.

Computational Details. The calculation of the electronic structure for the model complex $[Re_6S_8(HCOO)_6]^{4-}$ with C_i point symmetry was carried out using the ADF 2006 program package.[8] Model Hamiltonians of the density functional are the sum of the LDA (VWN[9]) local density functional and the GGA gradient exchange functional (Becke[10] and Perdew[11]). Slater-type orbitals (ADF/TZP) without core potentials were used as basis wave functions. Geometry optimization was performed with a quasi-Newton method.[12] Relativistic effects were taken into account with the ZORA formalism.[13] The bonding energy of the $[Re_6S_8(HCOO)_6]^{4-}$ complex was determined by the methods described in the literature.[14]

X-Ray Crystallographic Data Collection and Refinement of the Structures. Single-crystal X-ray diffraction data were collected with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 298 K with a Bruker Smart APEX CCD diffractometer with the operating program SMART. Absorption corrections were applied using the SADABS program.[15] The structures were solved by direct methods and refined (full-matrix least squares on F^2) with the SHELX-97 program suite.[16] All nonhydrogen atoms were refined anisotropically. The position of the hydrogen atom of

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(1) See, for example: (a) Yawney, D. B. W.; Doedens, R. J. *Inorg. Chem.* **1970**, *9*, 1626–1632. (b) Koz'min, P. A.; Surazhskaya, M. D.; Larina, T. B. *J. Struct. Chem. (Engl. Trans.)* **1974**, *15*, 56–60. (c) Cotton, F. A.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 688–692. (d) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599–2604. (e) Koz'min, P. A.; Surazhskaya, M. D.; Larina, T. B.; Bagirov, S. A.; Osmanov, N. S.; Kotel'nikova, A. S.; Misailova, T. V. *Koord. Khim.* **1979**, *5*, 1576–1577. (f) Koz'min, P. A.; Larina, T. B.; Surazhskaya, M. D. *Koord. Khim.* **1981**, *7*, 634–638. (g) Beringhelli, T.; Ciani, G.; Dalfonso, G.; Sironi, A.; Freni, M. *J. Organomet. Chem.* **1982**, *233*, C46−C50. (h) Kochetkova, A. P.; Sveshnikova, L. B.; Stepanovich, V. M.; Sokol, V. I. *Koord. Khim.* **1982**, *8*, 529–534. (i) Shapley, J. R.; Stgeorge, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1982**, *21*, 3295–3303. (j) Darensbourg, D. J.; Pala, M.; Waller, J. *Organometallics* **1983**, *2*, 1285–1291. (k) Robbins, G. A.; Martin, D. S. *Inorg. Chem.* **1984**, *23*, 2086–2093. (l) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Vandersluys, W. G.; Kober, E. M.; Lichtenberger, D. L.; Bursten, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 6796–6816. (m) Osmanov, N. S.; Kotelnikova, A. S.; Kozmin, P. A.; Abbasova, T. A.; Surazhskaya, M. D.; Larina, T. B. *Zh. Neorg. Khim.* **1988**, *33*, 810–813. (n) Kelson, E. P.; Henling, L. M.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1993**, *32*, 2863–2873. (o) Boutonnet, F.; Zablocka, M.; Igau, A.; Jaud, J.; Majoral, J. P.; Schamberger, J.; Erker, G.; Werner, S.; Kruger, C. *J. Chem. Soc., Chem. Commun.* **1995**, 823–824. (p) Brorson, M.; Hazell, A.; Jacobsen, C. J. H.; Schmidt, I.; Villadsen, J. *Inorg. Chem.* **2000**, *39*, 1346–1350.

(2) Adams, R. D.; Chen, G.; Huang, J. *J. Cluster Sci.* **1993**, *4*, 151–157.

(3) (a) Johnston, D. H.; Gaswick, D. C.; Lonergan, M. C.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **1992**, *31*, 1869–1873. (b) Malinak, S. M.; Madden, L. K.; Bullen, H. A.; McLeod, J. J.; Gaswick, D. C. *Inorg. Chim. Acta* **1998**, *278*, 241–244.

(4) Weinert, C. S.; Prokopuk, N.; Arendt, S. M.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **2001**, *40*, 5162–5168.

(5) Yarovoi, S. S.; Mironov, Y. V.; Naumov, D. Y.; Gatilov, Y. V.; Kozlova, S. G.; Kim, S. J.; Fedorov, V. E. *Eur. J. Inorg. Chem.* **2005**, 3945–3949.

(6) Brylev, K. A.; Mironov, Y. V.; Fedorov, V. E.; Kim, S.-J. *J. Struct. Chem. (Engl. Trans.)* **2007**, *48*, 1118–1123.

(7) Yoshimura, T.; Ishizaka, S.; Umakoshi, K.; Sasaki, Y.; Kim, H. B.; Kitamura, N. *Chem. Lett.* **1999**, 697–698.

(8) *Amsterdam Density Functional (ADF) program*, release 2005.02; Vrije Universiteit: Amsterdam, The Netherlands, 2005.

(9) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211.

(10) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098–3100.

(11) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822–8824.

(12) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322–328.

(13) van Lenthe, E.; Ehlers, A.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943–8953.

(14) (a) Baerends, E. J.; Branchadell, V.; Sodupe, M. *Chem. Phys. Lett.* **1997**, *265*, 481–489. (b) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1–10.

(15) Sheldrick, G. M. *SADABS*; University of Gottingen: Gottingen, Germany, 1997.

(16) (a) Sheldrick, G. M. *SHELXS-97*; University of Gottingen: Gottingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97*; University of Gottingen: Gottingen, Germany, 1997.

Table 1. Crystal Data and Structure Refinement for $K_4[Re_6S_8(HCOO)_6]$ (**1**) and $Cs_4[Re_6S_8(HCOO)_6]$ (**2**)

	1	**2**
empirical formula	$C_6H_6K_4O_{12}Re_6S_8$	$C_6H_6Cs_4O_{12}Re_6S_8$
fw	1800.19	2175.43
space group	$Pa\bar{3}$	$P2_1/c$
a (Å)	17.6324(3)	9.523(4)
b (Å)		14.625(6)
c (Å)		11.240(5)
β (deg)		107.620(7)
V (Å^3)	5481.94(16)	1492.0(11)
Z	8	2
ρ_{calcd} (g/cm^3)	4.362	4.842
μ (cm^{-1})	276.57	296.57
cryst size (mm^3)	0.10 × 0.10 × 0.10	0.10 × 0.07 × 0.03
θ range (deg)	2.00 to 25.67	2.24 to 25.68
reflns collected	28633	7569
unique reflns	1750	2828
R_{int}	0.0487	0.0365
params refined	111	167
$R_1{}^a/wR_2{}^b$ [$I > 2\sigma(I)$]	0.0208/0.0444	0.0255/0.0580
$R_1{}^a/wR_2{}^b$ (all data)	0.0257/0.0448	0.0336/0.0598

the formate ligand was calculated corresponding to its geometrical conditions and refined using the riding model. The structural parameters are summarized in Table 1. CCDC-702872 (**1**) and CCDC-702873 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis and Structures. Recently, we reported the synthesis of rhenium chalcohydroxo complexes $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se) and predicted their high reactivities in ligand substitution reactions.[5,6,17] In the present experiments, we demonstrated that the room-temperature reaction of $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ or $Cs_4[Re_6S_8(OH)_6]\cdot 6H_2O$ with formic acid in an aqueous solution resulted in substitution of the terminal OH ligands in the parent complex by the acid anions. The salts of $K_4[Re_6S_8(HCOO)_6]$ (**1**) and $Cs_4[Re_6S_8(HCOO)_6]$ (**2**) were crystallized by slow evaporation of the corresponding aqueous solutions and characterized by single-crystal X-ray diffraction. Both salts are well-soluble in water but insoluble in common organic solvents.

Similar reactions have been carried out also between $K_4[Re_6Se_8(OH)_6]\cdot 8H_2O$[5] or $Cs_4[Re_6Se_8(OH)_6]\cdot 8H_2O$[6] and formic acid. However, we were not able to separate a crystalline product: during the evaporation of resultant solutions, their color changed from yellow to green, and a green amorphous precipitate formed. The reason for such a color change and an amorphous precipitate formation is probably oxidation of the selenium cluster complex in an acidic solution. It is known that $\{Re_6Se_8\}^{2+}$-based complexes in comparison with $\{Re_6S_8\}^{2+}$ ones are more inclined to one-electron oxidation, especially in acidic solutions, and a green color is a typical property of $\{Re_6Se_8\}^{3+}$-based compounds.

Compounds **1** and **2** are the simple salts of a $[Re_6S_8(HCOO)_6]^{4-}$ anion (Figure 1). The Re_6 cluster in both structures exhibits a quasi-perfect octahedral geometry, as shown by the similar values of the interatomic Re−Re distances as well as by Re−Re−Re angles close to 60° and 90°: the Re−Re bond lengths range from 2.5768(4) to 2.5864(4) Å in **1** and from 2.5739(9) to 2.5824(10) Å in **2**. Each triangular face of the Re_6 cluster is capped by a sulfur atom, forming the $\{Re_6S_8\}$ cluster core. The Re−S bond lengths vary from 2.401(2) to 2.418(2) Å in **1** and from 2.393(2) to 2.418(2) Å in **2**. Furthermore, each rhenium atom is coordinated with the hydroxyl oxygen atom of a formate anion with the Re−O bonds being varied from 2.095(5) to 2.113(4) Å in **1** and from 2.081(5) to 2.095(6) Å in **2**. The C−O bond lengths, where O is the deprotonated hydroxyl oxygen coordinated to a rhenium atom, range from 1.234(9) to 1.255(8) Å in **1** and from 1.228(11) to 1.272(11) Å in **2**, whereas the C═O bond lengths range from 1.206(8) to 1.207(9) Å in **1** and from 1.205(11) to 1.210(11) Å in **2**.

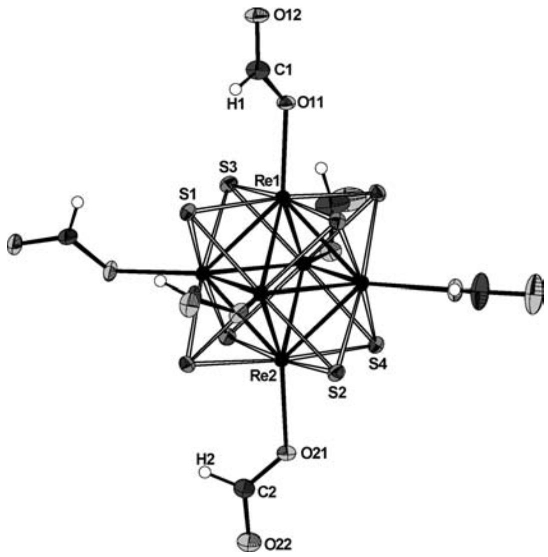

Figure 1. Structure of the cluster anions $[Re_6S_8(HCOO)_6]^{4-}$ in compounds **1** and **2** by the example of **1**. Displacement ellipsoids of the non-hydrogen atoms are drawn at the 30% probability level.

Since structures **1** and **2** both are salts of the same cluster anion, the differences between them are due to big difference in cation (K^+ and Cs^+) sizes. Structure **1** presents a close packing of potassium cations and $[Re_6S_8(HCOO)_6]^{4-}$ anions. The shortest intercluster distances are distances between carbon and oxygen atoms of formate ligands, which are identical in all three directions and equal to ~3.28 Å. The cluster units are tightly connected to each other through potassium cations with the K−O distances ranging from 2.53 to 3.04 Å to form a pseudo three-dimensional polymer framework.

The crystal structure of **2** may be generally described as an alternation of cationic and anionic layers parallel to the *bc* plane (Figure 2). The cationic layers are comprised of Cs^+ ions. While the anionic layers are composed of Cs^+ and $[Re_6S_8(HCOO)_6]^{4-}$ ions in a ratio of 1:1, consequently, the layers have a composition of $\{Cs[Re_6S_8(HCOO)_6]\}^{3-}$. Inside the layers, the cluster anions are connected through cesium cations with Cs−O distances ranging from 3.06 to 3.07 Å (Figure 3). However, the distances between the cesium atoms of cationic layers and oxygen atoms of anionic ones vary from 2.97 to 3.27 Å.

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(17) Brylev, K. A.; Mironov, Y. V.; Yarovoi, S. S.; Naumov, N. G.; Fedorov, V. E.; Kim, S.-J.; Kitamura, N.; Kuwahara, Y.; Yamada, K.; Ishizaka, S.; Sasaki, Y. *Inorg. Chem.* **2007**, *46*, 7414–7422.

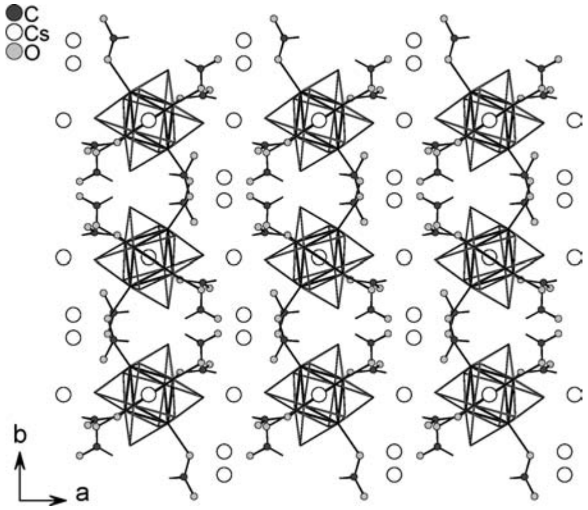

Figure 2. An alternation of cationic and anionic layers in **2**.

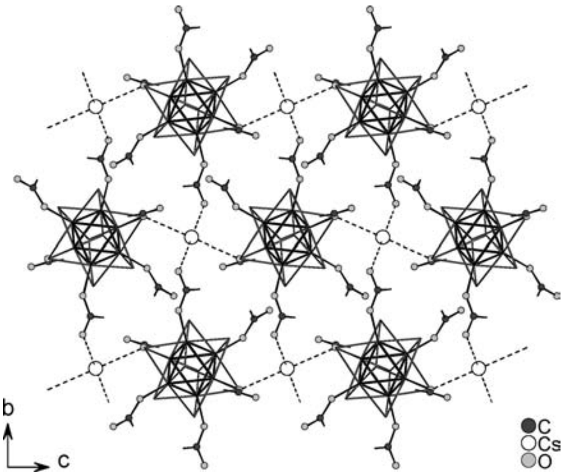

Figure 3. Structure of the anionic layer $\{Cs[Re_6S_8(HCOO)_6]\}^{3-}$ in **2**. Dashed lines indicate bonds between cesium cations and carboxylate ligands of anionic cluster complexes.

It is worth emphasizing that the formate anion in the cluster coordinates with a rhenium atom as a monodentate ligand, as demonstrated by the X-ray crystal structure. This can also be confirmed by the IR spectra of compounds **1** and **2**. It is known that the peak separation between the asymmetric ($\nu_{asym}(COO^-)$) and symmetric ($\nu_{sym}(COO^-)$) COO^- stretching modes, observed for the metal complex coordinated with monodentate carboxylate ligands, is much larger than that with chelating or bridging carboxylate ligands.[18] In the cases of **1** and **2**, indeed, the IR peak separations between $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ were found to be 341 and 372 cm^{-1}, respectively (see the Experimental Section), while that value is usually less than 200 cm^{-1} in the complexes with bidentate carboxylate ligands.[18]

Several rhenium mononuclear and binuclear cluster complexes with formate or acetate anions coordinated as bidentate (μ) or bidentate-bridged (μ_2) ligands have been hitherto reported, as confirmed by the Cambridge Structural Database.[19] However, carboxylate rhenium cluster complexes with a nuclearity higher than two or any rhenium compounds with monodentate coordination of formate or acetate ligands have not been deposited in the Database. Consequently, as far as we know, the compounds described here are the first structurally characterized examples of hexanuclear rhenium cluster complexes with terminal carboxylate ligands. Moreover, it is the first example of any rhenium complexes or any transition metal octahedral cluster complexes with monodentate coordinated formate ions.

^{1}H NMR Study. In order to reveal the chemical stability of the cluster in an aqueous solution, we conducted repeated ^{1}H NMR measurements on $K_4[Re_6S_8(HCOO)_6]$ (**1**) in D_2O. The ^{1}H NMR spectrum of a freshly prepared solution displayed peaks attributed to several $HCOO^-$ species, as shown in Figure 4a. A strong singlet peak at 8.64 ppm and three signals at 8.62, 8.60, and 8.58 ppm were attributed to the coordinated formate ligands, while the weak signal at 8.41 ppm was responsible for that of a free $HCOO^-$ ion in D_2O. This spectrum demonstrates quick substitution of the terminal formate ligands in $[Re_6S_8(HCOO)_6]^{4-}$ by D_2O molecules, leading to the release of $HCOO^-$ ions (signal at 8.41 ppm) and the subsequent formation of mixed-ligand complexes with the general formula $[Re_6S_8(D_2O)_n(HCOO)_{6-n}]^{n-4}$ (signals at 8.62, 8.60, and 8.58 ppm). Furthermore, successive ^{1}H NMR measurements of the sample revealed a gradual increase in the signal intensity at 8.41 ppm along with decreases in the signal intensities attributed to the coordinated formate ligands. About 8 weeks after sample preparation, yellow amorphous flakes precipitated in the NMR tube. The ^{1}H NMR spectrum of the solution, separated from the precipitate, showed the proton signal of free $HCOO^-$ (at 8.41 ppm), whose intensity was much stronger than those of the multiplet attributed to the protons of the coordinated formate ligands (at around 8.60 ppm, see Figure 4b). The integrated intensity of the proton of the free formate ion was ~7.5 times stronger than the total integrated intensity of the coordinated formate protons, confirming substitution of the formate ligands in **1** by D_2O. Thus, the precipitated solids in D_2O are predicted to be a poorly soluble low-charged or neutral cluster complex, owing to substitution of the anionic formate ligands by neutral water molecules. The precipitate was obtained again from an aqueous solution of **1** (instead of D_2O solution) and analyzed. The following data were found: C, 0.61; H, 1.08; S, 16.35%. Such an element ratio is close to the $[Re_6S_8(H_2O)_4(OH)(HCOO)]\cdot 4H_2O$ composition. The calculated elemental analysis for $[Re_6S_8(H_2O)_4(OH)(HCOO)]\cdot 4H_2O$ ($CH_{18}O_{11}Re_6S_8$) is as follows: C, 0.76; H, 1.15; S, 16.24%.

Luminescence Study. Luminescence properties of **1** were studied in both aqueous solution and the solid state, and the results are shown in Figure 5. In both aqueous solution and the solid phase, **1** shows broad and structureless emission in the wavelength region of 550−950 nm, with maximum wavelengths (λ_{em}) of 672 and 655 nm, respectively, similar to those of other hexarhenium clusters.[7,17,20−24] Furthermore, the emission quantum yields (Φ_{em}) in an aqueous solution

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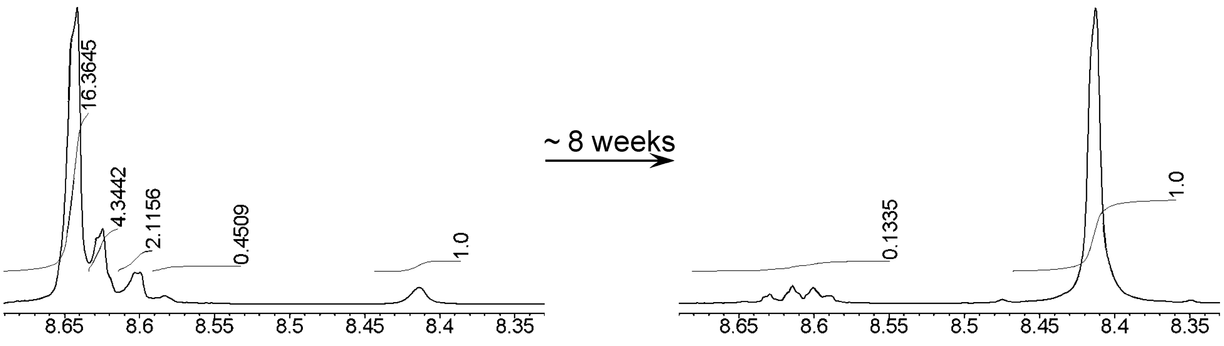
(18) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227–250.

(19) *Cambridge Structural Data Base*, version 5.29; Cambridge Crystallographic Data Center: Cambridge, United Kingdom, 2008.

(20) Gray, T. G.; Rudzinski, C. M.; Nocera, D. G.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 5932–5933.



a) **b)**

Figure 4. ^{1}H NMR spectra of **1** in D_2O for the freshly prepared solution (a) and the solution kept standing for 8 weeks (b).

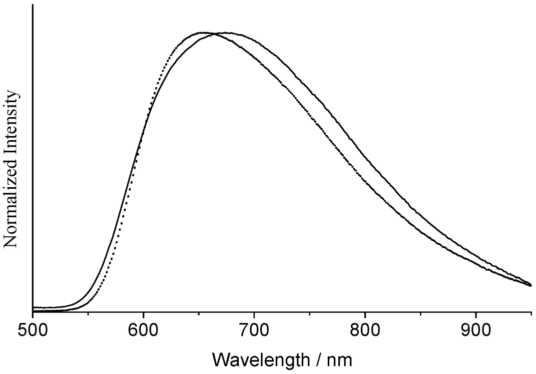


Figure 5. Emission spectra of **1** in the solid state (dot line) and in aqueous solution (solid line).

Table 2. Optimized Geometries and Experimental Parameters of the $[Re_6S_8(HCOO)_6]^{4-}$ Complex (Average Interatomic Distances (Å) and Valent Angles (deg))

	calculated	complex in **1**	complex in **2**
Re—Re	<2.628>	<2.580>	<2.579>
Re—S	<2.452>	<2.411>	<2.408>
Re—O	<2.136>	<2.104>	<2.087>
O—C	<1.303>	<1.245>	<1.253>
O^a—C	<1.246>	<1.207>	<1.208>
∠Re—O—C	<126.3>	<129.3>	<129.2>
∠O—C—O	<125.3>	<125.4>	<126.4>

[a] Terminal oxygen atom in $HCOO^-$ ligand.

and in the solid phase were estimated to be 0.028 (deaerated) and 0.091 (aerated), respectively. It is worth pointing out that, although relative quantum yields of various hexarhenium(III) cluster complexes in solutions have been reported in a number of papers,[7,17,20,22,23] to the best of our knowledge, there is only one paper reporting the Φ_{em} values of several Re_6 clusters in the solid phase.[23] However, the Φ_{em} values reported by Gray et al.[23] are those relative to the Φ_{em} of $(Bu_4N)_2[Mo_6Cl_{14}]$ as a standard sample and consequently are not the absolute values. In the present experiments, we determined the absolute Φ_{em} value of **1** in the solid phase on the basis of an integrating sphere equipped with a Xe lamp as an excitation light source and a red-sensitive photodetector (see the Experimental Section for details). As a result, the Φ_{em} value of **1** in the solid phase was determined to be as large as 0.091, even under aerated conditions, which was 3.25 times higher than that in a deaerated aqueous solution: 0.028. Since intramolecular vibrations inducing nonradiative decay from the emitting excited triplet state are restricted considerably in a solid phase as compared with those in solution,[25] the higher Φ_{em} value of **1** in the solid phase as compared with that in an aqueous solution is a reasonable consequence.

The emission of **1** in both aqueous and solid phases exhibited double exponential decays. The short (τ_{em}(s)) and long lifetime components (τ_{em}(l)) in the aqueous solution (deaerated) were ~0.30 μs (amplitude value (A) = ~0.10) and ~3.1 μs (A = ~0.90), respectively, while those in the solid state (aerated) were 1.3~1.5 μs (A = 0.16~0.27) and 6.1~6.5 μs (A = 0.73~0.84), respectively. The longer emission lifetime(s) in the solid phase as compared with that in an aqueous solution is understood by reasons analogous with those of Φ_{em} as mentioned above. Furthermore, the nonsingle exponential decay in the solid phase could be explained by efficient excitation migration in the crystal and subsequent energy trap/emission in the crystalline defects. On the other hand, the emission from a hexarhenium(III) cluster in solution exhibits in general a single exponential decay with a typical example being that from $[Re_6Q_8L_6]^{4-}$ (Q = S or Se; L = Cl, Br, or I) in acetonitrile.[7,20,23] An exceptional case is the emission decay of $[Re_6Q_8(OH)_6]^{4-}$ (Q = S or Se) in water. As reported recently, $[Re_6Q_8(OH)_6]^{4-}$ undergoes chemical equilibria between $[Re_6Q_8(OH)_6]^{4-}$ and

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(21) (a) Guilbaud, C.; Deluzet, A.; Domercq, B.; Molinie, P.; Coulon, C.; Boubekeur, K.; Batail, P. *Chem. Commun.* **1999**, 1867–1868. (b) Kitamura, N.; Ueda, Y.; Ishizaka, S.; Yamada, K.; Aniya, M.; Sasaki, Y. *Inorg. Chem.* **2005**, *44*, 6308–6313. (c) Mironov, Y. V.; Shestopalov, M. A.; Brylev, K. A.; Yarovoi, S. S.; Romanenko, G. V.; Fedorov, V. E.; Spies, H.; Pietzsch, H. J.; Stephan, H.; Geipel, G.; Bernhard, G.; Kraus, W. *Eur. J. Inorg. Chem.* **2005**, 657–661. (d) Mironov, Y. V.; Brylev, K. A.; Shestopalov, M. A.; Yarovoi, S. S.; Fedorov, V. E.; Spies, H.; Pietzsch, H. J.; Stephan, H.; Geipel, G.; Bernhard, G.; Kraus, W. *Inorg. Chim. Acta* **2006**, *359*, 1129–1134.

(22) (a) Yoshimura, T.; Ishizaka, S.; Sasaki, Y.; Kim, H. B.; Kitamura, N.; Naumov, N. G.; Sokolov, M. N.; Fedorov, V. E. *Chem. Lett.* **1999**, 1121–1122. (b) Yoshimura, T.; Umakoshi, K.; Sasaki, Y.; Ishizaka, S.; Kim, H.-B.; Kitamura, N. *Inorg. Chem.* **2000**, *39*, 1765–1772. (c) Chen, Z.-N.; Yoshimura, T.; Abe, M.; Tsuge, K.; Sasaki, Y.; Ishizaka, S.; Kim, H.-B.; Kitamura, N. *Chem.—Eur. J.* **2001**, *7*, 4447–4455. (d) Yoshimura, T.; Chen, Z. N.; Itasaka, A.; Abe, M.; Sasaki, Y.; Ishizaka, S.; Kitamura, N.; Yarovoi, S. S.; Solodovnikov, S. F.; Fedorov, V. E. *Inorg. Chem.* **2003**, *42*, 4857–4863.

(23) Gray, T. G.; Rudzinski, C. M.; Meyer, E. E.; Holm, R. H.; Nocera, D. G. *J. Am. Chem. Soc.* **2003**, *125*, 4755–4770.

(24) Shestopalov, M. A.; Mironov, Y. V.; Brylev, K. A.; Kozlova, S. G.; Fedorov, V. E.; Spies, H.; Pietzsch, H. J.; Stephan, H.; Geipel, G.; Bernhard, G. *J. Am. Chem. Soc.* **2007**, *129*, 3714–3721.

(25) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Herndon, VA, 1991.

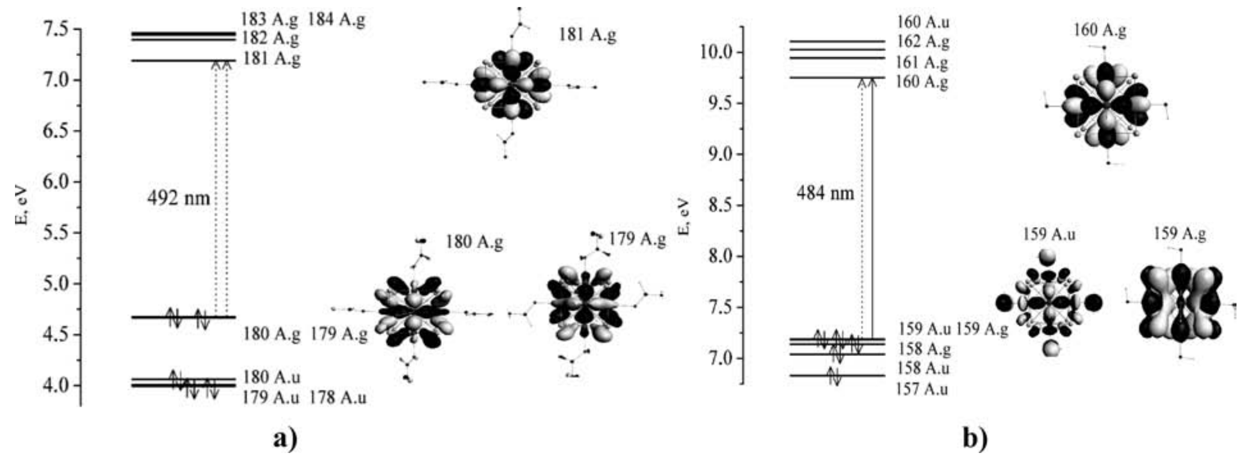

Figure 6. The energy level diagrams and schematic illustrations of MOs calculated for $[Re_6S_8(HCOO)_6]^{4-}$ (a) and $[Re_6S_8(OH)_6]^{4-}$ (b) complexes. Both complexes possess C_i point symmetry. The dashed arrows show the electronically forbidden transitions. The numbers and symmetry types of the calculated MOs are indicated.

$[Re_6Q_8(H_2O)_n(OH)_{6-n}]^{n-4}$ ($n = 0-6$), and reflecting such chemical equilibria in water, the emission from the cluster exhibits a double exponential decay at certain pH regions.[17] $[Re_6S_8(HCOO)_6]^{4-}$ in water also undergoes chemical equilibria, as demonstrated by the present ^{1}H NMR study. Therefore, the double exponential decay of the cluster could be explained by the terminal ligand substitution reactions, with the major and longer lifetime component being primarily the emission lifetime of the parent cluster complex $[Re_6S_8(HCOO)_6]^{4-}$. Participation of the ligand substitution reaction of the cluster was also confirmed in the course of spectroscopic measurements of H_2O samples, by which yellow cubic crystals were precipitated in a very diluted aqueous solution of $K_4[Re_6S_8(HCOO)_6]$. A single-crystal X-ray study revealed that the crystals were $[Re_6S_8(H_2O)_4(OH)_2]\cdot 12H_2O$, reported recently,[17] demonstrating substitution of all of the terminal formate ligands in **1** by water molecules and subsequent precipitation as the poorly soluble neutral aquahydroxo complex.

DFT Calculations. In order to optimize the geometrical structure of $[Re_6S_8(HCOO)_6]^{4-}$ and to evaluate the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO/LUMO) energies of the cluster, we conducted DFT calculations. According to the geometry optimization data, the bonding energy of $[Re_6S_8(HCOO)_6]^{4-}$ is equal to -260.0 eV. Table 2 shows characteristic interatomic geometry parameters of the optimized structure of **1**, together with those determined by X-ray crystal measurements. The table demonstrates clearly that the calculated parameters agree well with the experimental data. It is worth noting, furthermore, that the $HCOO^-$ ligand coordinated to the $\{Re_6S_8\}$ cluster core does not possess C_{2v} symmetry.

Figure 6 shows the molecular orbital (MO) energy diagrams of $[Re_6S_8(HCOO)_6]^{4-}$ and $[Re_6S_8(OH)_6]^{4-}$, where the numbers and symmetry types of the calculated MOs are indicated. A.g and A.u designation correspond to even (gerade in German) and odd (ungerade in German) orbitals, respectively.

For $[Re_6S_8(HCOO)_6]^{4-}$ (Figure 6a), the 5d orbitals of Re and the 2p orbitals of S contribute largely to the 180 A.g HOMO (~ 58% and ~ 25%, respectively). However, the 180 A.g MO is not necessarily a sole HOMO, since the 179 A.g HOMO_1 lies below the 180 A.g HOMO only by 0.007 eV in energy. The 181 A.g LUMO is composed primarily of the 5d orbitals of Re (~100%) to form the antibonding orbital. The energy gap between HOMO−LUMO and HOMO_1−LUMO in $[Re_6S_8(HCOO)_6]^{4-}$ is about 2.52 eV (or 492 nm), and the optical transitions between these MOs are predicted to be forbidden (Laporte rule[26]). On the other hand, although the HOMO/LUMO energies of $[Re_6S_8(OH)_6]^{4-}$ were recently reported,[5] we recalculated thoroughly the electronic structures of the hydroxo cluster to compare them with those of **1** in the present study. As seen in Figure 6, the electronic structure of **1** (Figure 6a) is very similar to that of $[Re_6S_8(OH)_6]^{4-}$ (Figure 6b). The energy gap between the 159 A.u HOMO and 159 A.g HOMO_1 was only 0.005 eV, and the HOMO_1 might also contribute to the optical transition to the 160 A.g LUMO. These calculations for the hydroxo cluster indicate that the HOMO—LUMO electronic transition is allowed, owing to the symmetry of the LUMO being 160 A.g, while the HOMO_1−LUMO transition is predicted to be forbidden.[26] The energy gap between HOMO−LUMO and HOMO_1−LUMO in $[Re_6S_8(OH)_6]^{4-}$ is about 2.56 eV (or 484 nm).

The forbidden/allowed characteristics of the HOMO−LUMO transitions in hexarhenium clusters have been considered to be responsible for phosphorescent/non- (or weak-)phosphorescent properties of the complexes.[5,23,27] The present DFT calculations predict that the HOMO−LUMO transition of $[Re_6S_8(HCOO)_6]^{4-}$ is forbidden, and the cluster displays phosphorescence as described above. Furthermore, the emission quantum yield of **1** ($\Phi_{em} = 0.028$) was found to be higher than that of $[Re_6S_8(OH)_6]^{4-}$ ($\Phi_{em} = 0.010$ in H_2O at pH = ~14),[17] whose HOMO−LUMO electronic transition is predicted to be allowed as mentioned above. In the case of $[Re_6S_8(OH)_6]^{4-}$, both 159 A.g−160 A.g (HOMO_1−LUMO) forbidden and 159 A.u−160 A.g (HOMO−LUMO) allowed transitions contribute to lower energy absorption, and this will give rise to a lower Φ_{em} of

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(26) Cory, M. G.; Zerner, M. C. *Chem. Rev.* **1991**, *91*, 813–822.
(27) Gray, T. G.; Rudzinski, C. M.; Meyer, E. E.; Nocera, D. G. *J. Phys. Chem. A* **2004**, *108*, 3238–3243.

the hydroxo cluster. A similar correlation between the phosphorescence characteristics and the arrangement of the MO was observed recently in triphenylphosphine Re_6 cluster complexes.[24]

In conclusion, the potassium and cesium salts of a hexanuclear rhenium thiocluster complex anion with terminal formate ligands can be easily prepared by room-temperature reactions of $K_4[Re_6S_8(OH)_6]\cdot 8H_2O$ and $Cs_4[Re_6S_8(OH)_6]\cdot 6H_2O$, respectively, with formic acid in aqueous solutions. The compounds obtained were studied by X-ray single-crystal diffraction analysis and IR, ^{1}H NMR, UV/vis, and luminescence spectroscopies, and the electronic structure of $[Re_6S_8(HCOO)_6]^{4-}$ was also elucidated by DFT calculations. It was found that terminal formate ligands were very labile and gradually substituted by water molecules in an aqueous solution. Consequently, the complex $[Re_6S_8(HCOO)_6]^{4-}$ has high potential as a starting material for the synthesis of new rhenium cluster complexes by terminal ligand substitution reactions.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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