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Preparation, Structures, and Redox and Emission Characteristics of the Isothiocyanate Complexes of Hexarhenium(III) Clusters $[Re_6(\mu_3\text{-}E)_8(NCS)_6]^{4-}$ (E = S, Se)

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Hexarhenium(III) complexes with terminal isothiocyanate ligands, $\{(n\text{-}C_4H_9)_4N\}_4[Re_6(\mu_3\text{-}S)_8(NCS)_6]$ (**1**) and $(L)_4[Re_6(\mu_3\text{-}Se)_8(NCS)_6]$ ($L^+ = PPN^+$ (**2a**), $(n\text{-}C_4H_9)_4N^+$ (**2b**)), have been prepared by three different methods. Complex **1** was prepared by the reaction of $\{(n\text{-}C_4H_9)_4N\}_4[Re_6(\mu_3\text{-}S)_8Cl_6]$ with molten KSCN at 200 °C, while **2b** was obtained by refluxing the chlorobenzene–DMF (2:1 v/v) solution of $[Re_6(\mu_3\text{-}Se)_8(CH_3CN)_6](SbF_6)_2$ and $[(n\text{-}C_4H_9)_4N]SCN$. The $[Re_6(\mu_3\text{-}Se)_8(NCS)_6]^{4-}$ anion was also obtained from a mixture of $Cs_2[Re_6(\mu_3\text{-}Se)_8Br_4]$ and KSCN in C_2H_5OH by a mechanochemical activation at room temperature for 20 h and isolated as **2a**. The X-ray structures of **1** and **2a**·4DMF have been determined (**1**, $C_{70}H_{144}N_{10}S_{14}Re_6$, monoclinic, space group $P2_1/n$ (No. 14), $a = 14.464(7)$ Å, $b = 22.059(6)$ Å, $c = 16.642(8)$ Å, $\beta = 113.62(3)°$, $V = 4864(3)$ Å^3, $Z = 2$; **2a**·4DMF, $C_{162}H_{144}N_{14}O_4P_8S_6Se_8Re_6$, triclinic, space group $P\bar{1}$ (No. 2), $a = 15.263(2)$ Å, $b = 16.429(2)$ Å, $c = 17.111(3)$ Å, $\alpha = 84.07(1)°$, $\beta = 84.95(1)°$, $\gamma = 74.21(1)°$, $V = 4098.3(8)$ Å^3, $Z = 1$). All the NCS^- ligands in both complexes are coordinated to the metal center via nitrogen site with the Re–N distances in the range of 2.07–2.13 Å. The redox potentials of the reversible $Re^{III}_6/Re^{III}_5Re^{IV}$ process in acetonitrile are +0.84 and +0.70 V vs. Ag/AgCl for $[Re_6(\mu_3\text{-}S)_8(NCS)_6]^{4-}$ and $[Re_6(\mu_3\text{-}Se)_8(NCS)_6]^{4-}$, respectively, which are the most positive among the known hexarhenium complexes with six terminal anionic ligands. The complexes show strong red luminescence with the emission maxima (λ_{max}/nm), lifetimes ($\tau_{em}/\mu s$), and quantum yields (ϕ_{em}) being 745 and 715, 10.4 and 11.8, and 0.091 and 0.15 for **1** and **2b**, respectively, in acetonitrile. The data reasonably well fit in the energy-gap plots of other hexarhenium(III) complexes. The temperature dependence of the emission spectra and τ_{em} of **1** and $\{(n\text{-}C_4H_9)_4N\}_4[Re_6(\mu_3\text{-}S)_8Cl_6]$ are also reported.

Introduction

The chemistry of hexarhenium(III) chalcogenide cluster complexes has expanded rapidly.[1−15] In addition to their synthetic versatility,[1−8,11−14] photoluminescent[1,2] and redox active properties[1,2,9,10,15] make the hexarhenium complexes particularly attractive for further investigation. Such proper-

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ties can be well controlled by the type and combinations of terminal ligands in addition to the different capping ligands S, Se, Te, and halide ions.[1] The terminal ligands so far introduced onto the hexarhenium centers are halide ions (Cl^-, Br^-, and I^-),[1] CN^-,[1] solvent molecules (DMSO, DMF, and CH_3CN),[1] phosphines,[1,2] and pyridine and its derivative[1,7,12] including a bulky porphyrin ligand 5-(4-pyridyl)-10,15,20-tritolylporphyrin.[6] Complexes with cyano[1,3,4,8,13,14] and bridging dipyridyl ligands[1,7,12] have been used as building blocks of supramolecular assemblies. Some phosphine and pyridyl ligands were introduced in a controlled way with regard to their number and geometrical arrangement. For example, a series of hexarhenium complexes having different numbers of phosphine and pyridyl ligands, $[Re_6(\mu_3\text{-E})_8(X)_{6-n}(L)_n]^{(4-n)-}$ ($L = P(C_2H_5)_3$, E = S, $n = 2-6$; E = Se, $n = 3-6$;[16,17] L = pyridine and some pyridine derivatives, E = S, $n = 2-4$)[18,19] were prepared. In the case of the complexes with $n = 2-4$, geometrical isomers were also isolated. With a diphosphine ligand $(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2$ (dpph), a bridge-chelate coordination mode was found in a series of the complexes, $[Re_6(\mu_3\text{-Se})_8I_{6-2n}(\mu\text{-dpph})_n]^{(2n-4)+}$ ($n = 1-3$).[20]

Thiocyanate ion NCS^- is another interesting ligand which can coordinate via either nitrogen or sulfur sites depending on the nature of metal ions. A bridging coordination mode like CN^- is also possible for NCS^-. It is interesting to see if NCS^- coordinates to a hexarhenium center with a nitrogen or sulfur donor site. Also it is interesting to see how the redox and luminescent properties of the hexarhenium complexes are affected by the coordination of NCS^-, since it could significantly modulate the properties of the host metal cluster centers. We herein report the preparation, X-ray structures, and redox and luminescent properties of two new hexarhenium(III) cluster complex anions, $[Re_6(\mu_3\text{-S})_8(NCS)_6]^{4-}$ and $[Re_6(\mu_3\text{-Se})_8(NCS)_6]^{4-}$.

Experimental Section

Materials. $\{(n\text{-}C_4H_9)_4N\}_4[Re_6(\mu_3\text{-S})_8Cl_6]$, $\{(n\text{-}C_4H_9)_4N\}_3[Re_6(\mu_3\text{-S})_8Cl_6]$,[21] $[Re_6(\mu_3\text{-Se})_8(CH_3CN)_6](SbF_6)_2$,[22] and $Cs_2[Re_6(\mu_3\text{-Se})_8Br_4]$[21] were prepared according to the methods in the literature. Bis(triphenylphosphoranylidene)ammonium bromide ((PPN)Br) was used as received. Tetra-*n*-butylammonium hexafluorophosphate, $n\text{-}(C_4H_9)_4NPF_6$, was recrystallized twice from ethanol. Acetonitrile for the electrochemical measurements was distilled under argon atmosphere. For the photophysical measurements, spectrograde acetonitrile (Dojin) was distilled over CaH_2 under argon atmosphere. Propylene carbonate and butyronitrile were stored at least 1 day with molecular sieves (4A) and then distilled under vacuum.

Preparation of the Complexes. $\{(n\text{-}C_4H_9)_4N\}_4[Re_6(\mu_3\text{-S})_8(NCS)_6]$ (1). A solid mixture of 0.200 g (0.078 mmol) of $\{(n\text{-}C_4H_9)_4N\}_3[Re_6(\mu_3\text{-S})_8Cl_6]$ and 5.0 g (51.58 mmol) of KSCN was heated at 200 °C to obtain a suspension in liquid KSCN which was kept for 1 h. After the sample was cooled to room temperature, 100 mL of water was added to the brown solid and the mixture was stirred for 20 min. The yellow solid was collected by filtration and redissolved in acetonitrile to remove the insoluble solid. On addition of $\{(n\text{-}C_4H_9)_4N\}SCN$ to the filtrate, a yellow precipitate was formed, which was collected by filtration and then washed with water and dried in air. Yield: 84 mg (36%). Anal. Calcd for $C_{70}H_{144}N_{10}Re_6S_{14}$: C, 31.23; H, 5.39; N, 5.20; S, 16.67; Cl, 0. Found: C, 31.08; H, 5.34; N, 5.13; S, 16.60; Cl, 0. FAB-MS: $m/z = 2450$ ($[M - (C_4H_9)_4N]^+$). UV−vis (acetonitrile) [λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: 430 (770, sh), 330 (19 900, sh), 290 (35 700, sh), 260 (91 200, sh), 245 (133 700). Selected IR data (KBr, cm^{-1}): 2092 s (NCS^-). Single crystals were obtained by slow evaporation of acetonitrile−toluene (1:1 v/v) solution at room temperature.

$(PPN)_4[Re_6(\mu_3\text{-Se})_8(NCS)_6]\cdot 4DMF$ (2a·4DMF). A mixture of 2.5 g (1.07 mmol) of $Cs_2[Re_6(\mu_3\text{-Se})_8Br_4]$[21] and 18 g (185.7 mmol) of KSCN in 20 mL of ethanol was loaded in a mechanochemical reactor. Mechanochemical activation of the reaction mixture was carried out for 20 h at room temperature. The product of the reaction was extracted by 50 mL of water. After addition of (PPN)Br to the green solution, the precipitate was isolated by filtration and then washed with water and dried. The solid obtained was dissolved in DMF, and the solution was heated. The green solution became brown, from which single crystals for X-ray diffraction analysis were obtained by slow evaporation of the solvent.

$\{(n\text{-}C_4H_9)_4N\}_4[Re_6(\mu_3\text{-Se})_8(NCS)_6]$ (2b). A chlorobenzene−DMF (2:1 v/v) solution (30 mL) containing $[Re_6(\mu_3\text{-Se})_8(CH_3CN)_6](SbF_6)_2$[22] (100 mg, 0.040 mmol) and $\{(n\text{-}C_4H_9)_4N\}SCN$ (84 mg, 0.280 mmol) was refluxed with stirring under an argon atmosphere for 12 h. After the solution was concentrated in vacuo to ca. 2 mL, 50 mL of water was added to precipitate the product, which was collected by filtration. The solid was then dissolved in 2 mL of dichloromethane and purified through chromatography using a silica gel column to obtain the product. Yield: 106 mg (84%). FAB-MS: $m/z = 3068$ ($[M]^+$). Anal. Calcd for $C_{70}H_{144}N_{10}Re_6S_6Se_8\cdot CH_2Cl_2$: C, 25.80; H, 4.45; N, 4.01; S, 5.51. Found: C, 25.38; H, 4.27; N, 4.34; S, 5.99. UV−vis (acetonitrile) [λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: 455 (1300, sh), 340 (18 800, sh), 310 (32 600, sh), 270 (75 700, sh), 253 (130 400). Selected IR data (KBr, cm^{-1}): 2092 s (NCS^-).

Physical Measurements. UV−visible absorption spectra were recorded on Hitachi U3410 and U3000 spectrophotometers. Cyclic voltammograms were measured with a BAS-50W potentiostat and a software package at a scan rate of 100 mV/s. The working and counter electrodes were a glassy-carbon disk and a platinum wire, respectively. The sample solutions (ca. 0.001 M) in 0.1 M $(n\text{-}C_4H_9)_4NPF_6$–acetonitrile were deoxygenated with a stream of argon gas. The reference electrode was Ag/AgCl against which the half-wave potential $E_{1/2}$ of Fc^+/Fc was 0.43 V. The absorption spectrum of

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the one-electron oxidized species $[Re_6(\mu_3\text{-}S)_8(NCS)_6]^{3-}$ was obtained in situ by bulk electrolysis of **1** at 1.2 V vs Ag/AgCl by using a BAS CV-50W voltammetric analyzer with a platinum disk as a working electrode. Emission spectra were measured by using a photodiode array detector (Hamamatsu, PMA-11) and an Nd:YAG laser (Continuum minilite or Continuum surelite, 355 nm, 6 ns pulse width) at 355 nm excitation. The absorbance intensity of the complexes was adjusted to ca. 0.05 at 355 nm (the concentration was thus ca. 6×10^{-6} M). The solutions were deoxygenated by purging with an argon gas stream for 15 min and sealed before the measurements. Emission spectra were corrected for instrumental responses. Integrated emission quantum yields ϕ_{em} were estimated relative to that of $\{(n\text{-}C_4H_9)_4N\}_4[Mo_6(\mu_3\text{-}Cl)_8Cl_6]$ ($\phi_{em} = 0.19$) as a reference.[23] Emission lifetimes were measured by using a streak camera (Hamamatsu C3434) as a detector. Temperature of the solutions was controlled within ±1 °C by using a liquid N_2 cryostat (Oxford instruments, DN1704, 3120).

X-ray Structural Determinations. A selected single crystal of **1** was sealed in a glass capillary. X-ray data were collected at room temperature on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by least-squares refinement of 25 reflections ($25 \leq 2\theta \leq 30$). Decay corrections were based on the measured intensities of reflections monitored periodically throughout the course of data collection. The crystal showed no significant decay throughout the course of data collection. The data were corrected for Lorentz and polarization effects. Absorption collection (ψ scans) was applied. The crystal structure was solved by direct methods (SIR92).[24] The positional and thermal parameters of non-hydrogen atoms except for those of the $(n\text{-}C_4H_9)_4N^+$ cation were refined anisotropically by the full-matrix least-squares method. All calculations were performed using TEXSAN.[25]

Unit cell dimensions and X-ray diffraction data for structure determination of $(PPN)_4[Re_6(\mu_3\text{-}Se)_8(NCS)_6]\cdot 4DMF$ (**2a**·4DMF) were obtained by an Enraf-Nonius CAD4 diffractometer (Mo Kα, graphite monochromator, $\omega/2\theta$ scanning, $2\theta \leq 55°$) at room temperature with conventional techniques. An empirical absorption correction was applied by using four ψ scan curves. The structure was solved by direct methods (SHELX-86)[26] with subsequent difference Fourier maps and refined by full-matrix least squares in anisotropic approximation for all non-hydrogen atoms with the SHELXL-97 Release 97-2 software package.[27] The positions of the phenyl hydrogen atoms were calculated with all C−H separations of 0.93 Å and their contributions with $U_{iso}(H) = 1.5U_{eq}(C)$ added to structure factors but not refined. The experimental and refinement details are summarized in Table 1. The selected interatomic distances and angles of **1** and **2a**·4DMF are given in Tables 2 and 3, respectively.

Results and Discussion

Preparation and Characterization of the Complexes. The isothiocyanate complexes of the hexarhenium clusters were prepared by three different methods. The sulfido-capped complex, $[Re_6(\mu_3\text{-}S)_8(NCS)_6]^{4-}$, was prepared by reacting the $[Re_6(\mu_3\text{-}S)_8Cl_6]^{4-}$ salt with molten KSCN for 1 h. The selenido-capped complex was prepared by two different methods. The solid material $Cs_2[Re_6(\mu_3\text{-}Se)_8Br_4]$ was reacted with KSCN in methanol under mechanochemical activation at room temperature for 20 h. Alternatively, the complex anion $[Re_6(\mu_3\text{-}Se)_8(NCS)_6]^{4-}$ was prepared by reacting the hexaacetonitrile complex, $[Re_6(\mu_3\text{-}Se)_8(CH_3CN)_6]^{2+}$, with $\{(n\text{-}C_4H_9)_4N\}SCN$ in chlorobenzene−DMF mixture under refluxing conditions for 12 h. In all these preparations, the complexes were obtained in fairly good yields. The complexes were identified by the X-ray structural analyses of the two samples. For **2a**, PPN^+ was used as the countercation, as it afforded single crystals of good quality for X-ray structure determination. Although the IR stretching of the coordinated NCS^- is by no means instructive in determining which side of the ligand coordinating to the metal ion, X-ray structural analyses clearly show that all the NCS^- ligands are coordinated via the nitrogen side.

Table 1. Crystallographic Data for $\{(n\text{-}C_4H_9)_4N\}_4[Re_6(\mu_3\text{-}S)_8(NCS)_6]$ (**1**) and $(PPN)_4[Re_6(\mu_3\text{-}Se)_8(NCS)_6]\cdot 4DMF$ (**2a**·4DMF)

	1	**2a**·4DMF
formula	$C_{70}H_{144}N_{10}S_{14}Re_6$	$C_{162}H_{144}N_{14}O_4P_8S_6Se_8Re_6$
fw	2692.1	4539.9
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	14.464(7)	15.263(2)
b, Å	22.059(6)	16.429(2)
c, Å	16.642(8)	17.111(3)
α, deg		84.07(1)
β, deg	113.62(3)	84.95(1)
γ, deg		74.21(1)
V, Å^3	4864(3)	4098(1)
Z	2	1
D_{calcd}, g/cm^3	1.838	1.839
μ(Mo Kα), cm^{-1}	77.79	64.00
radiation, Å	0.7107	0.7107
temp, K	296	293
R[a] (wR2[b])	0.096 (0.147)	0.030 (0.065)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $\{(C_4H_9)_4N\}_4[Re_6(\mu_3\text{-}S)_8(NCS)_6]$ (**1**)

	Distances		
Re(1)−Re(2)	2.587(1)	Re(3)−S(1)	2.404(6)
Re(1)−Re(2)*	2.591(1)	Re(3)−S(2)	2.405(6)
Re(1)−Re(3)	2.599(1)	Re(3)−S(3)*	2.417(6)
Re(1)−Re(3)*	2.591(2)	Re(3)−S(4)	2.391(6)
Re(2)−Re(3)	2.595(1)	Re(1)−N(1)	2.12(2)
Re(2)−Re(3)*	2.585(1)	Re(2)−N(2)	2.03(2)
Re(1)−S(1)	2.421(6)	Re(3)−N(3)	2.07(2)
Re(1)−S(2)	2.410(6)	N(1)−C(1)	1.07(2)
Re(1)−S(3)	2.440(6)	N(2)−C(2)	1.13(2)
Re(1)−S(4)*	2.403(6)	N(3)−C(3)	1.12(2)
Re(2)−S(1)*	2.407(6)	C(1)−S(5)	1.63(2)
Re(2)−S(2)	2.393(6)	C(2)−S(6)	1.68(2)
Re(2)−S(3)	2.408(6)	C(3)−S(7)	1.66(2)
Re(2)−S(4)	2.408(6)		
	Angles		
N(1)−Re(1)−S(1)	93.2(6)	N(3)−Re(3)−S(2)	93.7(6)
N(1)−Re(1)−S(2)	95.1(5)	N(3)−Re(3)−S(3)*	92.4(6)
N(1)−Re(1)−S(3)	93.6(6)	N(3)−Re(3)−S(4)	93.6(5)
N(1)−Re(1)−S(4)*	92.0(5)	C(1)−N(1)−Re(1)	176(2)
N(2)−Re(2)−S(1)*	94.5(5)	C(2)−N(2)−Re(2)	166(2)
N(2)−Re(2)−S(2)	91.4(5)	C(3)−N(3)−Re(3)	171(2)
N(2)−Re(2)−S(3)	93.1(5)	N(1)−C(1)−S(5)	175(2)
N(2)−Re(2)−S(4)	92.6(5)	N(2)−C(2)−S(6)	170(2)
N(3)−Re(3)−S(1)	92.5(5)	N(3)−C(3)−S(7)	176(2)

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $(PPN)_4[Re_6(\mu_3\text{-}Se)_8(NCS)_6]\cdot 4DMF$ (**2a**·4DMF)

Distances			
Re(1)−Re(2)	2.6191(7)	Re(3)−Se(1)	2.5227(14)
Re(1)−Re(2)*	2.6231(7)	Re(3)−Se(2)	2.5168(12)
Re(1)−Re(3)	2.6190(7)	Re(3)−Se(3)*	2.5214(14)
Re(1)−Re(3)*	2.6227(7)	Re(3)−Se(4)*	2.5155(12)
Re(2)−Re(3)	2.6178(7)	Re(1)−N(1)	2.095(9)
Re(2)−Re(3)*	2.6236(7)	Re(2)−N(2)	2.069(9)
Re(1)−Se(1)	2.5188(13)	Re(3)−N(3)	2.098(8)
Re(1)−Se(2)	2.5224(13)	N(1)−C(1)	1.122(12)
Re(1)−Se(3)	2.5173(13)	N(2)−C(2)	1.135(12)
Re(1)−Se(4)	2.5174(13)	N(3)−C(3)	1.154(12)
Re(2)−Se(1)*	2.5186(12)	C(1)−S(1)	1.633(12)
Re(2)−Se(2)	2.5183(12)	C(2)−S(2)	1.653(13)
Re(2)−Se(3)*	2.5231(13)	C(3)−S(3)	1.610(11)
Re(2)−Se(4)	2.5249(13)		
Angles			
N(1)−Re(1)−Se(1)	93.2(2)	N(3)−Re(3)−Se(2)	92.3(2)
N(1)−Re(1)−Se(2)	90.4(2)	N(3)−Re(3)−Se(3)*	92.7(3)
N(1)−Re(1)−Se(3)	92.8(2)	N(3)−Re(3)−Se(4)*	90.7(2)
N(1)−Re(1)−Se(4)	90.2(2)	C(1)−N(1)−Re(1)	172.2(10)
N(2)−Re(2)−Se(1)*	92.4(2)	C(2)−N(2)−Re(2)	173.4(10)
N(2)−Re(2)−Se(2)	90.7(2)	C(3)−N(3)−Re(3)	172.4(10)
N(2)−Re(2)−Se(3)*	92.4(3)	N(1)−C(1)−S(1)	178.1(12)
N(2)−Re(2)−Se(4)	91.2(3)	N(2)−C(2)−S(2)	178.6(12)
N(3)−Re(3)−Se(1)	90.7(3)	N(3)−C(3)−S(3)	177.5(11)

X-ray Structures of the Complexes. Both of the complex anions $[Re_6(\mu_3\text{-}S)_8(NCS)_6]^{4-}$ in **1** and $[Re_6(\mu_3\text{-}Se)_8(NCS)_6]^{4-}$ in **2a**·4DMF take a centrosymmetrical structure, as shown in Figures 1 and 2, respectively. The structural characteristics of the two complex anions are very similar to each other and are consistent with the coordination of NCS^- at its nitrogen site. There is no need to consider any disorder of nitrogen and sulfur atoms in the crystals. The Re−N bond lengths span in the range 2.03(2)−2.12(2) Å for **1** and 2.069(9)−2.098(8) Å for **2a**. The N−C (1.07(2)−1.13(2) and 1.122(12)−1.154(12) Å for **1** and **2a**, respectively) and C−S distances (1.63(2)−1.68(2) and 1.610(11)−1.653(13) Å for **1** and **2a**, respectively) are consistent with the coordination of the nitrogen site. Thiocyanate ligands are approximately perpendicular to the faces of the S_8 and Se_8 cubes and practically linear while Re−N−C angles only slightly decline from 180°.

The six rhenium atoms form nearly regular octahedrons with Re−Re distances of 2.6178(7)−2.6238(7) and 2.618(1)−2.625(1) Å for **1** and **2a**, respectively. The average values of the Re−Re−Re bond angles are nearly 90 and 60° for the meridional and facial partners, respectively. The Re−S and Re−Se bond distances are in the range 2.391(6)−2.440(6) and 2.5155(12)−2.5249(13) Å, respectively. No appreciable difference in the bond distances is found from those of $[Re_6(\mu_3\text{-}S)_8X_6]^{4-}$ ($X^- = Cl^-, Br^-, I^-$),[21,28−30] so that the terminal isothiocyanides are not influential on the hexarhenium core structurally.

The mutual arrangement of the constituent components in **2a**·4DMF is shown in Figure S1 (Supporting Information). The DMF molecules are in the voids of cation−anion packing. Two independent PPN^+ cations and two sorts of DMF molecules have the usual geometrical parameters though slightly differing in their details.

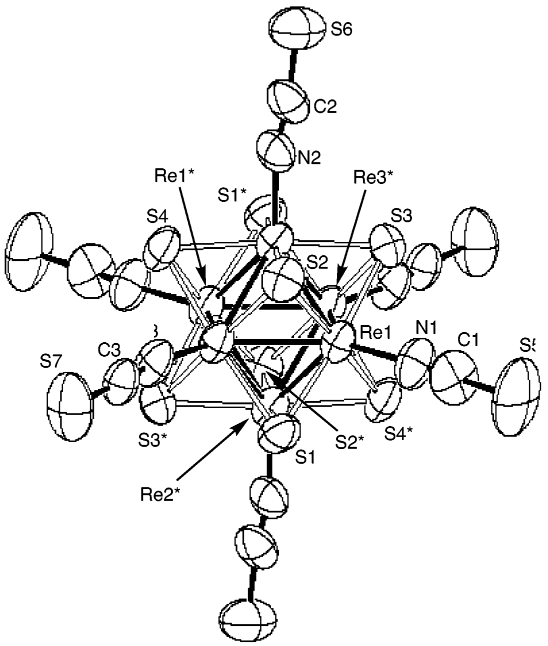

Figure 1. ORTEP drawing of the anionic part of **1** at the 50% probability level.

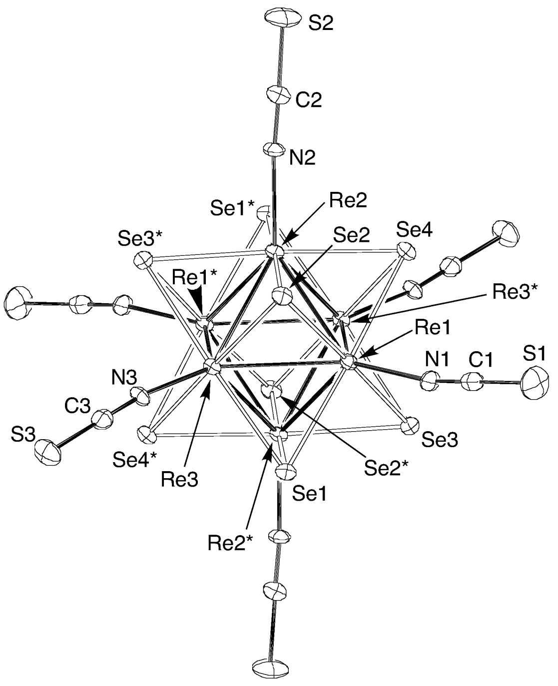

Figure 2. ORTEP drawing of the anionic part of **2a**·4DMF at the 50% probability level.

Previous Structural Information on Rhenium NCS^- Complexes. A number of Re complexes with NCS^- ligand(s) have been structurally characterized by X-ray diffraction studies. The two coordination modes, Re−NCS and Re−SCN, are definitely distinguished by X-ray crystallography. The nitrogen-bonded Re−NCS is dominant with virtually linear Re−N−C and Re−N bonds of ca. 2.0 Å. On the other

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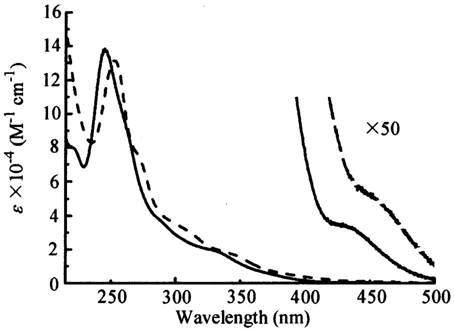

Figure 3. Electronic absorption spectra of **1** (solid lines) and **2b** (broken lines) in acetonitrile.

hand, the bent Re−S−C (ca. 110°) and Re−S bonds of ca. 2.4 Å have been found in sulfur-bonded Re−SCN complexes. Two NCS^- complexes with mixed Re−N and Re−S coordination modes, *trans*- and *cis*-$[Re^{IV}Br_4(NCS)(SCN)]^{2-}$,[31] display typical examples. There are some Re cluster complexes with nitrogen-bonded NCS^- ligands, $[Re^{III}Re^{IV}(NCS)_{10}]^{3-}$ [32,33] and $[Re^{III}_2(NCS)_8L_2]^{2-}$ (L = acetone, pyridine),[34] and a series of tetranuclcear complexes with a cubanelike core, $[Re_4Q_4(NCS)_{12}]^{4-}$ (Q = S, Se, Te).[35]

It is also noted that molybdenum(II) analogues of the hexarhenium isothiocyanate complexes, $[Mo_6(\mu_3\text{-}X)_8(NCS)_6]^{2-}$ (X = Cl,[36] Br,[37] I[38]), have been characterized by X-ray crystallography, in which nitrogen sites are coordinated to the molybdenum centers.

Redox Potentials. Cyclic voltammograms of **1** and **2b** were measured in 0.1 M $(n\text{-}C_4H_9)_4NPF_6$−acetonitrile solution. Complexes **1** and **2b** show reversible one-electron waves at +0.84 V (ΔE_p = 70 mV) and +0.70 V (90 mV) vs Ag/AgCl, respectively, which are assignable to the $Re^{III}_6/Re^{III}_5Re^{IV}$ process. The potentials are the most positive for the hexarhenium complexes with six terminal anionic ligands, $[Re_6(\mu_3\text{-}E)_8(X)_6]^{4-}$, X = Cl (E = S, +0.27 V vs. SCE),[18] Br^- (E = S, +0.31 V vs. SCE),[21] I^- (E = S, +0.36; E = Se, +0.12 V),[39] and CN^- (E = S, +0.60; E = Se, 0.37 V)[40] in acetonitrile (V vs Ag/AgCl unless otherwise mentioned).

Absorption Spectra and Luminescence Characteristics. Electronic absorption spectra of **1** and **2b** are shown in Figure 3. The spectrum of μ_3-S complex **1** in acetonitrile is featured by a strong peak at 245 nm with four prominent shoulders at 260, 290, 330, and 430 nm. That of the μ_3-Se complex **2b** is similar to **1** with all the absorptions shifting to a longer wavelength (253, 270, 310, 340, and 455 nm). Intense shoulders at 330 (**1**) and 340 nm (**2b**) may be assigned to the charge transfer between NCS^- and the metal cluster core, since the corresponding strong peak is not seen in other hexarhenium(III) complexes. Excited-state molecular orbitals associated with other transitions may be of a complicated mixture of the contribution from Re and ligands (primarily capping chalcogenide) as indicated by theoretical studies.[5,10] While the absorptions at least in the region >300 nm have been suggested to have characters of the mixture of capping ligand-to-metal and metal-to-metal transitions on one hand,[5] the orbitals near the HOMO−LUMO energy region are indicated to have mainly metal-centered character in another theoretical treatment.[10,41,42]

The spectrum of one-electron oxidized species $[Re_6(\mu_3\text{-}S)_8(NCS)_6]^{3-}$ is characterized by a near-infrared band at 1304 nm in addition to the bands at 583, 521, 326 (sh), and 247 nm. Similar near-infrared bands were reported for other $Re^{III}_5Re^{IV}$ species and ascribed primarily to the intervalence transition of the mixed valence state.[18] It is interesting to note that the $23e^-$ clusters are suggested to cause structural Jahn−Teller distortion as revealed by both experimental and theoretical studies.[9,10]

It has been reported that the hexarhenium(III) complexes with various capping and terminal ligands are luminescent.[1,2,19,20,40−46] The present NCS^- complexes are also strongly luminescent both in the solid state and in solution at room temperature. The emission decays exponentially in solution, solvents used for the measurements being acetonitrile, dichloromethane, and acetone for **1** and acetonitrile for **2b**. The emission maximum of **1** is almost independent of the solvent. Table 4 summarizes the photophysical data (emission maximum (λ_{max}), quantum yield (ϕ_{em}), and lifetime (τ_{em})) for the two complexes together with those of other octachalcogenidohexarhenium complexes with anionic terminal ligands. The two complexes **1** and **2b** are among the most strongly luminescent hexarhenium(III) complexes with fairly long emission lifetimes. For the sulfido-capped $Re_6(\mu_3\text{-}S)_8$ complexes, photophysical data are available for those with terminal anionic ligands and those with mixed terminal ligands of chloride and pyridine derivatives.[19,40,45,46] The present complex **1** (ϕ_{em} = 0.091, τ_{em} = 10.4 μs) and $\{(C_6H_5)_4P\}_4[Re_6(\mu_3\text{-}S)_8(CN)_6]$ (0.056, 11.2 μs)[40] show the strongest luminescence among the μ_3-S complexes. For the selenido-capped $Re_6(\mu_3\text{-}Se)_8$ complexes, data are available for those with wider variety of terminal ligands.[2,20,40,46] Those with neutral terminal ligands such as pyridine, DMF, DMSO, and CH_3CN tend to show luminescence centered at much shorter wavelengths (<700 nm) with fairly high quantum

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Table 4. Photophysical Data of the Hexaanionohexarhenium(III) Clusters, [Re$_6$(μ_3-S, -Se or -Te)$_8$X$_6$]$^{4-}$ (X$^-$ = NCS$^-$, CN$^-$, Cl$^-$, Br$^-$, I$^-$) in Acetonitrile at 298 K

complex	λ_{max}/nm	ϕ_{em}	τ_{em}/μs	$10^{-3}k_r$/s^{-1}	$10^{-4}k_{nr}$/s^{-1}	refs
[Re$_6$(μ_3-S)$_8$(NCS)$_6$]$^{4-}$	745	0.091	10.4	8.8	8.6	this work
[Re$_6$(μ_3-S)$_8$(CN)$_6$]$^{4-}$	720	0.056	11.2	5.0	8.4	40
[Re$_6$(μ_3-S)$_8$Cl$_6$]$^{4-}$	770	0.039	6.3	6.2	15.3	43
[Re$_6$(μ_3-S)$_8$Br$_6$]$^{4-}$	780	0.018	5.4	3.3	18.2	43
[Re$_6$(μ_3-S)$_8$I$_6$]$^{4-}$	800	0.015	4.4	3.4	22.4	43
[Re$_6$(μ_3-Se)$_8$(NCS)$_6$]$^{4-}$	ca. 730	0.15	11.8	13.1	7.2	this work
[Re$_6$(μ_3-Se)$_8$(CN)$_6$]$^{4-}$	720	0.14	17.1	8.2	5.0	40
[Re$_6$(μ_3-Te)$_8$(CN)$_6$]$^{4-}$	750	0.0039	0.57	6.8	175.0	40

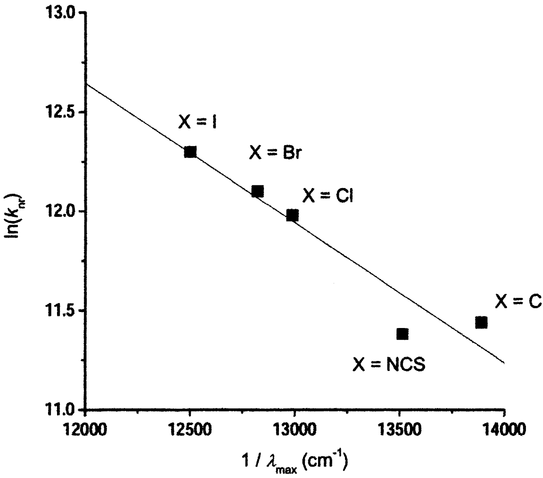

Figure 4. Correlation between ln(k_{nr}) and emission maximum (1/λ_{max} (cm^{-1})) for [Re$_6$(μ_3-S)$_8$X$_6$]$^{4-}$ (X$^-$ = Cl$^-$, Br$^-$, I$^-$, CN$^-$, NCS$^-$).

yields (0.100−0.238) and long lifetimes (14.0−22.4 μs).[46] The isothiocyanato complex **2b** (0.15, 11.8 μs) shows somewhat weaker luminescence than that with terminal neutral ligands but still the strongest luminescence among those with terminal anionic ligands.

Table 4 also lists radiative (k_r) and nonradiative (k_{nr}) decay rate constants of the photoexcited state as calculated from the relations $k_r = \phi_{em}/\tau_{em}$ and $k_{nr} = (1 - \phi_{em})/\tau_{em}$. Previously, we have pointed out a good linear correlation between 1/λ_{max} and ln(k_{nr}) for the series of four complexes [Re$_6$(μ_3-S)$_8$(X)$_6$]$^{4-}$ (X$^-$ = Cl$^-$, Br$^-$, I$^-$, CN$^-$).[40] As shown in Figure 4, the data point for **1** reasonably well fit in the straight line. Gray and co-workers also reported the linear correlation for wider range of 16 hexarhenium complexes including both μ_3-S and μ_3-Se complexes.[46] From the linear correlation they concluded the Re$_6$(μ_3-E)$_8$ (E = S, Se) excited states predominated for these hexarhenium(III) complexes. Similar arguments may be applied to the NCS$^-$ complexes **1** and **2b**.

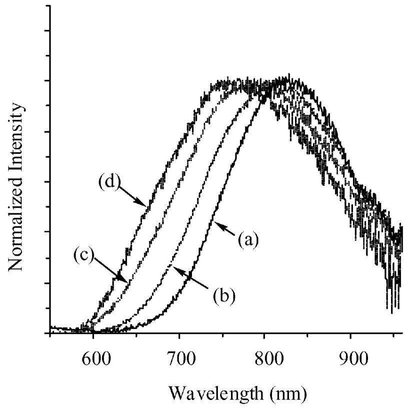

Figure 5. Temperature dependence of the emission spectra of **1** in butyronitrile: (a) 80 K; (b) 150 K; (c) 210 K; (d) 250 K.

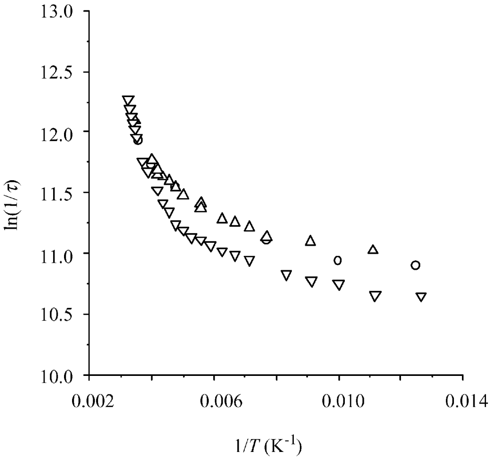

Figure 6. Temperature dependence of the emission spectra of {(n-C$_4$H$_9$)$_4$N}$_4$[Re$_6$(μ_3-S)$_8$Cl$_6$] in the solid (○) and in propylene carbonate solution (△) and **1** in butyronitrile solution (▽).

The temperature dependence of the emission spectra and emission lifetimes have been measured for **1** and {(n-C$_4$H$_9$)$_4$N}$_4$[Re$_6$(μ_3-S)$_8$Cl$_6$]. Figure 5 shows the temperature dependence of the emission spectra of **1** in butyronitrile. The emission maximum shifts to longer wavelength and the emission intensity increases as temperature decreases. The reciprocal emission lifetimes are plotted against the reciprocal of temperature in Figure 6. Similar temperature dependence has been observed for {(n-C$_4$H$_9$)$_4$N}$_4$[Re$_6$(μ_3-Se)$_8$Cl$_6$] in the solid state and in propylene carbonate. The temperature dependence of the emission properties of hexamolybdenum(II) and hexatungsten(II) complexes [M$_6$(μ_3-X)$_8$Y$_6$]$^{2-}$ (M = Mo, W; X$^-$, Y$^-$ = Cl$^-$, Br$^-$, I$^-$) that are isoelectronic to the hexarhenium(III) complexes were studied previously.[47−50] In these studies, temperature dependence of the emission lifetimes as well as emission spectral shape were successfully analyzed quantitatively in terms of the contribution of three excited triplet state sublevels.[47−49] The simple simulation of the data for the hexarhenium(III) complexes by considering up to three excited triplet state sublevels with different lifetimes has not been successful, however. Nevertheless, we

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thought it may be worth describing here our observation, since the temperature dependences of photophysical properties of hexarhenium(III) complexes have never been reported previously. As theoretical studies indicate, more densely populated excited-state energy levels would be involved in the case of hexarhenium(III) clusters.[5,10,41,42] Although more sophisticated treatments by considering a higher number of sublevels would superficially solve the problem, such treatments would not be very realistic without further evidences for the excited-state orbitals. We leave the results for future interpretation with the aid of more systematic studies of the excited state of the hexarhenium(III) and related complexes.

Conclusions

Two hexarhenium(III) complexes have been prepared by using NCS^- as terminal ligands. From the X-ray structural studies of $\{(n\text{-}C_4H_9)_4N\}_4[Re_6(\mu_3\text{-}S)_8(NCS)_6]$ (**1**) and $(PPN)_4[Re_6(\mu_3\text{-}Se)_8(NCS)_6]\cdot 4DMF$ (**2a**·4DMF), the ligands exclusively coordinate to the rhenium atoms via the nitrogen donor site. By considering the nitrogen-bonded structures of previously reported di- and tetranuclear rhenium complexes of NCS^-, it appears that rhenium clusters of the oxidation states of III and IV including the present hexanuclear ones all behave as a hard metal center toward the NCS^- ligand. The new complex anions exhibit the most positive redox potentials toward one-electron oxidation among the terminal aniono complexes with the same capping ligands, μ_3-S or μ_3-Se. They are also among the most strongly luminescent hexarhenium complexes. The temperature dependence of the emission spectra and lifetimes indicates a rather complicated nature of the excited states involved.

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Supporting Information Available: Figure S1, showing the mutual arrangement of independent species in the crystal structure of **2a**·4DMF, and X-ray crystallographic data in CIF format for **1** and **2a**·4DMF. This material is available free of charge via the Internet at http://pubs.acs.org.

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