Unusual Capping Chalcogenide Dependence of the Luminescence Quantum Yield of the Hexarhenium(III) Cyano Complexes $[Re_6(\mu_3\text{-}E)_8(CN)_6]^{4-}$, $E^{2-} = Se^{2-} > S^{2-} > Te^{2-}$

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Hexarhenium(III) clusters $[Re_6(\mu_3\text{-}E)_8(CN)_6]^{4-}$ (E^{2-} = S^{2-}, Se^{2-}, Te^{2-}) are luminescent at room temperature with the emission quantum yield and lifetime in the order $E^{2-} = Se^{2-} > S^{2-} >> Te^{2-}$ both in acetonitrile and water.

We have recently shown that the diamagnetic[1] hexarhenium(III) clusters, $[Re_6(\mu_3\text{-}S)_8X_6]^{4-}$ (X^- = Cl^-, Br^-, I^-), are luminescent both in the solid state and in solution.[2] Fairly long emission lifetime in the range of 3.4 - 6.3 μs at room temperature is indicative of the emissive triplet excited state. The emission quantum yield is in the range of 0.015 - 0.039 in the acetonitrile solutions. These emission characteristics are similar to those of halogeno-capped hexatungsten(II) and hexamolybdenum(II) clusters,[3,4] and the excited state that is localized in the hexametal core has been suggested.

A wide variety of hexarhenium(III) complexes are now known with different capping ligands such as $\mu_3\text{-}S^{2-}$, $\mu_3\text{-}Se^{2-}$ and $\mu_3\text{-}Te^{2-}$, and various terminal ligands such as alkylphosphines, acetonitrile, cyanide and pyridine derivatives.[1,5] Mixed-μ_3-chalcogenido complexes have also been reported.[6] Solid state materials with three dimensional networks[7] and supramolecular complexes[8] based on the Re_6 core, are particularly noteworthy. It is thus interesting to see the influence of ligand substitution at the terminal sites as well as the change in the capping chalchogenide on the photoemissive characteristics. In this letter, we wish to report photophysical properties of a series of cyano complexes, $[Re_6(\mu_3\text{-}E)_8(CN)_6]^{4-}$ with different capping chalcogenides (E^{2-} = S^{2-}, Se^{2-}, Te^{2-}), which also show strong emission both in the solid state and in solution. The $\mu_3\text{-}S^{2-}$ cyano complex shows much stronger emission than the previously reported halogeno complexes.[2] The photoemissive behavior is unusual in that the selenide capping complexes show the strongest emission and the longest emission lifetime among the three cyano complexes.

The complexes were isolated as the salts of a tetraphenylphosphonium ion, $(P(C_6H_5)_4)_4[Re_6(\mu_3\text{-}E)_8(CN)_6]$ (E^{2-} = S^{2-}, Se^{2-}, Te^{2-}),[9] and alkali metal ions, $Cs_3K[Re_6(\mu_3\text{-}S)_8(CN)_6]$[10] and $K_4[Re_6(\mu_3\text{-}E)_8(CN)_6]$ (E^{2-} = Se^{2-},[11] Te^{2-}[12]), as described previously. Photophysical measurements were carried out by using a Hamamatsu Photonics Inc. PMA-11 and Nd:YAG laser (Continuum, Surelite, 355 nm, 6 ns pulse width). Emission quantum yields were determined by using $(n\text{-}C_4H_9)_4N)_2[Mo_6(\mu_3\text{-}Cl)_8Cl_6]$ (ϕ_{em} = 0.19)[13] as a standard. Emission spectra were corrected for the instrumental responses.

Table 1 shows the emission maxima (λ_{em}), lifetimes (τ_{em}), and quantum yields (ϕ_{em}) of the cyano complexes. The emission maximum tends to shift to a longer wavelength as the capping chalcogenide becomes heavier, but the difference in the value between the $\mu_3\text{-}S^{2-}$ and $\mu_3\text{-}Se^{2-}$ complexes is small. The emission band width in acetonitrile is considerably narrow for the $\mu_3\text{-}Te^{2-}$ complex (f_{whm} = 2500 cm^{-1}) as compared to other complexes (for example, f_{whm} = 4300 cm^{-1} for the $\mu_3\text{-}S^{2-}$ complex) (Figure 1). In considering the effect of the ligand orbitals upon the molecular orbitals associated with the metal-metal bonds in the Re_6 cluster, π-interaction would be important. The sequence of the emission maximum is consistent with that of the π-donating ability of the capping ligand. Thus the heaviest $\mu_3\text{-}Te^{2-}$ ligand gives the highest HOMO to make the emission energy lowest. The conclusion is supported by the oxidation potentials in an $(n\text{-}C_4H_9)_4NPF_6\text{-}CH_3CN$ solution: the reversible oxidation wave is observed at $E_{1/2}$ = 0.60, 0.37, or 0.11 V vs Ag/AgCl for the $\mu_3\text{-}S^{2-}$, $\mu_3\text{-}Se^{2-}$, or $\mu_3\text{-}Te^{2-}$ complex, respectively.[14]

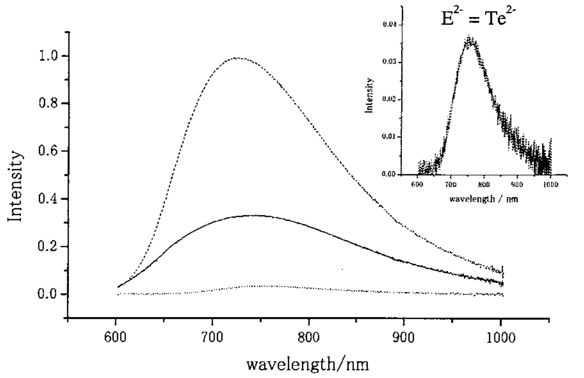

Figure 1. Emission spectra of $[Re_6(\mu_3\text{-}E)_8(CN)_6]^{4-}$ in acetonitrile. $E^{2-} = S^{2-}$ (———), $E^{2-} = Se^{2-}$ (-----), and $E^{2-} = Te^{2-}$ = (•••).

The radiative and non-radiative decay rate constants, k_r and k_{nr}, respectively, as calculated from the τ_{em} and ϕ_{em} values, are listed in Table 1. Corresponding rate constants were also determined from the photophysical data for the terminal halide complexes, $[Re_6(\mu_3\text{-}S)_8X_6]^{4-}$ (X^- = Cl^-, Br^-, I^-).[2] The k_r ($/10^3 s^{-1}$) and k_{nr} ($/10^3 s^{-1}$) values for the Cl^-, Br^-, and I^-

Table 1. Photophysical data of the hexarhenium(III) cyano complexes, $A_4[Re_6(\mu_3\text{-}E)_8(CN)_6]$, at room temperature

A_4	E	λ_{max} /nm	τ / μs	ϕ_{em}	k_r $/10^3 s^{-1}$	k_{nr} $/10^3 s^{-1}$
			in acetonitrile			
$(P(C_6H_5)_4)$	S	720	11.2	0.056	5.5	93
$(P(C_6H_5)_4)$	Se	720	17.1	0.140	8.4	52
$(P(C_6H_5)_4)$	Te	750	0.57	0.004	6.8	1700
			in water			
Cs_3K	S	720	1.2	0.009	7.5	820
K_4	Se	720	1.9	0.015	7.9	520
K_4	Te	750	0.42	0.004	8.3	2400

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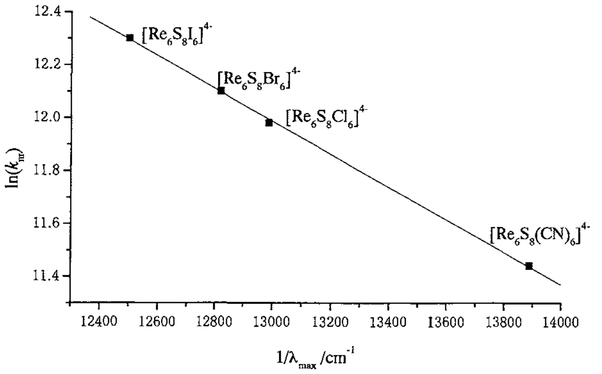

Figure 2. A linear correlation between $\ln(k_{nr})$ and emission maximum ($1/\lambda_{em}$ /cm^{-1}) for $[Re_6(\mu_3\text{-}S)_8X_6]^{4-}$ (X^- = Cl^-, Br^-, I^-, CN^-) in acetonitrile.

complexes in acetonitrile at room temperature are 6.2 and 160, 3.3 and 180, and 3.4 and 220, respectively. It is noted that, while the k_r values of all the six complexes in acetonitrile are found in a rather narrow range, the k_{nr} values span in two orders of magnitude. The small variation of k_r with the nature of the terminal and capping ligands further supports the view that the electronic transition associated with the photoemission is oriented to the Re_6 core. The change in the k_{nr} values of the four μ_3-S^{2-} complexes is rather modest as compared with the difference in the value among the three cyano complexes. It is thus concluded that the terminal ligands including cyanide do not provide an efficient decay pathway of the excited state.

The plot of $\ln(k_{nr})$ vs $1/\lambda_{em}$ for the four μ_3-S^{2-} complexes determined in acetonitrile gives a good straight line (Figure 2), indicating that the energy-gap law holds for these μ_3-S^{2-} complexes. A similar plot for the three cyano complexes with different capping ligands is not linear. Linear correlation is also found for a series of hexatungsten(II) complexes,[4] $[W_6(\mu_3\text{-}Cl)_8X_6]^{2-}$ (X^- = Cl^-, Br^-, I^-), but not for that of $[W_6(\mu_3\text{-}X)_8Cl_6]^{2-}$. It seems that the energy-gap law holds for the different terminal ligands but not for the capping ligand in these haxanuclear complexes. Thus the electronic states of the hexanuclear complexes are influenced largely by the nature of the capping ligand.

Significant solvent dependencies of the τ_{em} and ϕ_{em} values of the cyano complexes are due to the difference in the k_{nr} values. Since the emission maximum remains the same, the electronic states responsible for the emission are not affected directly by the solvent. Interaction of water molecules possibly with the capping chalcogenide ligands would provide more efficient vibrational decay pathway of the excited state. The heaviest Te^{2-} ligand is expected to cause the strongest interaction with the solvent.

The τ_{em} and ϕ_{em} values depend on the capping chalcogenide ions and decrease in the order of $Se^{2-} > S^{2-} >> Te^{2-}$. Recrystallization of the complexes did not cause appreciable changes in the photophysical properties. Thus we conclude that the unusual capping chalcogenide dependence of the excited state properties must be intrinsic. It is known that isoelectronic hexamolybdenum(II) clusters, $[Mo_6(\mu_3\text{-}X)_8X_6]^{2-}$, show decreases in the $1/\lambda_{em}$ (emission energy), τ_{em}, and ϕ_{em} values as X^- is replaced from Cl^- to Br^-.[13] Opposite trends are observed for the tungsten(II) analogs;[4] the values increase as X^- becomes heavier from Cl^- to I^-. It has been suggested that metal-cluster back bonding to the capping halide is important for the tungsten(II) clusters.[4] It seems that the two factors, π-donating and back-bonding interactions, which would contribute to the photophysical properties in an opposite way, compete in the Re_6-CN complexes to show the unusual chalcogenide dependence. Unusual chalcogenide dependence was also observed for the luminescence of $[Ag_4(\mu_4\text{-}E)(\mu\text{-}dppm)_4]^{2+}$ (E^{2-} = S^{2-}, Se^{2-}, Te^{2-}; dppm = bis(diphenylphosphino)methane) in solution.[15]

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