

solutions varying in the amount of oxidation and were found to be constant.

Electronic Spectroscopic Comparisons. The intense ($\epsilon(\text{Rh}) = (2-3) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) absorption band observed for each oligomer containing at least two Rh(II) centers (in a formal sense) can be assigned to a $\sigma \rightarrow \sigma^*$ transition that is delocalized over the polynuclear rhodium framework. The $\sigma \rightarrow \sigma^*$ transition in the parent complex, Rh_2^{4+} , falls at 311 nm in aqueous sulfuric acid solution.¹¹ Adding two Rh(I) centers to give Rh_4^{6+} shifts the $\sigma \rightarrow \sigma^*$ transition to 558 nm, and further rhodium chain length increases lead to still lower $\sigma \rightarrow \sigma^*$ transition energies [$\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$ (787 nm) > $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ (980 nm) > $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{16+}$ (1350 nm)], as would be expected from simple theoretical considerations.

The electronic structures of the rhodium oligomers are related in a rough sense to those of the platinum blues.^{16,17} The Rh_4^{6+} species may be compared, for example, with Lippard's *cis*-diammineplatinum α -pyridone blue (PPB), where the bulkiness of the α -pyridone ligand restricted the chain length to four platinum atoms with an average formal oxidation state of 2.25.^{16,17} For-

mally, the Pt_4^{9+} unit is $d^8d^7d^8d^8$, whereas Rh_4^{6+} is $d^8d^7d^7d^8$ (the electronic analogue of Pt_4^{9+} is Rh_4^{5+} , which has not been observed as a separate entity, but rather as a higher oligomer, Rh_8^{10+} or $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$). Lippard's ESR studies suggest^{16,17} that the unpaired electron in Pt_4^{9+} is located in a molecular orbital derived from d_{z^2} interactions along the platinum chain. Presumably, this molecular orbital is analogous to the σ^* orbital involved in the allowed $\sigma \rightarrow \sigma^*$ transition in Rh_4^{6+} . However, the characteristic absorption band in the platinum blues in the 550-730-nm region (680 nm in PPB)¹⁷ is much less intense than the 558-nm system in the Rh_4^{6+} spectrum, and it is entirely possible that this particular transition in Pt_4^{9+} is not $\sigma \rightarrow \sigma^*$. Much more extensive spectroscopic studies will be required to elucidate the nature of the lowest electronic excited states in the platinum blues as well as in the rhodium isocyanide oligomers.

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Hydrogen Isotope Effects on the Excited-State Decay Properties of Polynuclear Metal Carbonyl Hydrides. Emission Properties of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{n-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$

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Abstract: The two pairs of complexes $\text{H}_4\text{Re}_4(\text{CO})_{12}$, $\text{D}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{n-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$, $[\text{n-Bu}_4\text{N}]_2[\text{D}_6\text{Re}_4(\text{CO})_{12}]$ have been compared with respect to excited-state decay properties. The $\text{H}_4\text{Re}_4(\text{CO})_{12}$ complex exhibits emission from the lowest excited state at 298 K in hydrocarbon solution or as a solid and also at 77 K in glassy hydrocarbon solution or as a pure solid. The emission maximum is between 13 700 and 14 600 cm^{-1} depending on solvent conditions, and the lifetimes range from <0.02 μs at 298 K in 3-methylpentane solution ($\Phi \approx 0.003$) to 16 μs at 77 K in 3-methylpentane glass ($\Phi = 0.25$). The effect of replacing ^1H by ^2H is to lengthen emission lifetime by 20-30% with an equal percent increase in emission quantum yield. The lowest (emissive) excited state can be rapidly quenched by anthracene (triplet energy ≈ 42 kcal/mol) but not by *trans*-stilbene (triplet energy ≈ 50 kcal/mol), consistent with the high-energy onset (~ 46 kcal/mol) of the structureless emission spectrum of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ attributable to a lowest-lying triplet excited state associated with a Re_4 localized electronic transition. $[\text{n-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$ does not detectably emit in solution or as the solid at 298 K, but emission is detectable at 77 K from the solid or glassy solutions of the salt. The emission is at $\sim 18 000 \text{ cm}^{-1}$ with a lifetime of $\sim 2 \mu\text{s}$ and a quantum yield of ~ 0.01 . The effect of ^1H replacement by ^2H is to increase lifetime and quantum yield by $\sim 50\%$ depending on the medium. Under a given set of conditions for either $\text{H}_4\text{Re}_4(\text{CO})_{12}$ or $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$, the effect of replacing ^1H by ^2H is to lower the rate constant for nonradiative decay; there is no effect on the radiative decay constant.

While studying the photocatalytic activity of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ as a comparison to that for $\text{H}_4\text{Ru}_4(\text{CO})_{12}$,¹ we discovered that $\text{H}_4\text{Re}_4(\text{CO})_{12}$ exhibits visible emission when excited by ultraviolet or high-energy visible light. This discovery afforded us an opportunity to examine the effect of replacing ^1H with ^2H on the excited-state decay properties of the cluster. There are earlier studies of hydrogen isotope effects on excited-state decay of organic molecules and of inorganic complexes where the ligands bear hydrogen atoms.²⁻⁵ The importance of these studies rests in the

fact that the replacement of ^1H by ^2H results in little change in the essential electronic structure or geometry of the molecule while the vibrational energies are altered significantly. Thus, replacing ^1H by ^2H provides a probe of the importance of high-energy vibrations on the rates of nonradiative excited-state decay.

Of particular interest is the fact that the ^1H in $\text{H}_4\text{Re}_4(\text{CO})_{12}$ is directly bonded to the metal.⁶ Often, the highest energy

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Table I. Emission Properties of Polynuclear Rhenium Carbonyl Hydrides

complex	solvent conditions (T, K)	ϵ^a	$\Delta\nu_{1/2}^b$	Φ	τ^c
$\text{H}_4\text{Re}(\text{CO})_{12}$	pure solid (298)	13 700	2000		1.02
	pure solid (77)	14 600	1700		7.09
	3-methylpentane (298)	13 800	2100	0.0034	<0.02
	3-methylpentane (77)	14 600	1700	0.25	12.11
	toluene (298)	13 800	2100	0.032	0.096
$\text{D}_4\text{Re}_4(\text{CO})_{12}$	pure solid (298)	13 700	2100		1.30
	pure solid (77)	14 600	1700		8.65
	3-methylpentane (298)	13 700	2200	0.0039	<0.02
	3-methylpentane (77)	14 600	1700	0.33	15.97
	toluene (298)	13 700	2200	0.037	0.111
$[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-d}$	pure solid (77)	17 900	3600		1.64
	2-MeTHF (77) ^e	17 900	3500	0.012	2.16
$[\text{D}_6\text{Re}_4(\text{CO})_{12}]^{2-d}$	pure solid (77)	17 900	3600		2.35
	2-MeTHF (77) ^e	17 800	3600	0.020	3.42

^a ϵ = emission maximum given in cm^{-1} with an error of $\pm 100 \text{ cm}^{-1}$. ^b $\Delta\nu_{1/2}$ is the full-width at half-height of the emission band given in cm^{-1} with error limits of $\pm 100 \text{ cm}^{-1}$. ^c Error limits are on absolute value of Φ and τ . Relative $^1\text{H}/^2\text{H}$ values have lower error ($\pm 2\%$). τ is given in μs with an error limit of $\pm 10\%$; Φ error limit is $\pm 10\%$. ^d As the $[\text{n-Bu}_4\text{N}]^+$ salt. ^e 2-MeTHF is 2-methyltetrahydrofuran.

vibrations are found to be important in nonradiative decay, but for metal complexes where the excited states can be regarded as "metal-centered", the intraligand vibrations may not be crucial despite being the highest energy vibrations in the complex. An analogy in organic systems might be associated with the $>\text{C}=\text{O}$ $n-\pi^*$ systems that are very localized excited states. The effect on the fluorescence by replacing ^1H with ^2H in H_2CO is much greater than in $(\text{CH}_3)_2\text{CO}$ where the hydrogens are somewhat removed from the transition center.⁷ In metal complexes, metal-ligand vibrations may be most crucial, and of these vibrations, those of highest energy should be most important. The metal-hydrogen stretch is certainly the highest energy metal-ligand stretch, but for metal carbonyls it is possible that the $\text{M}-\text{C}\equiv\text{O}$ vibrational system is important. For $\text{H}_4\text{Re}_4(\text{CO})_{12}$ the effect of heavy hydrogen isotopes is likely to be reduced by the fact that the hydrides are in triply bridging positions⁶ with a low stretching frequency ($\nu(\text{Re}-\text{H}) = 1023 \text{ cm}^{-1}$)^{8a} compared to that found for terminal $\text{Re}-\text{H}$ stretching frequencies ($1900 \pm 300 \text{ cm}^{-1}$).^{8b,c}

Prompted by the discovery of the emissive $\text{H}_4\text{Re}_4(\text{CO})_{12}$, we prepared $[\text{n-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ and found that it too is emissive but only at low temperature. The H atoms in $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ are edge-bridging with a $\text{Re}-\text{H}$ stretching frequency of 1165 cm^{-1} .⁹ For both $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ the emission establishes the energy and lifetime of the lowest excited state. These properties are important in understanding the electronic structure and photochemistry of such systems. The only other metal-metal bonded complexes that have been found to be emissive are $\text{Re}_2(\text{CO})_8(1,10\text{-phenanthroline})$ and related complexes,¹⁰ $\text{Rh}_2(1,3\text{-diisocyanopropane})_4^{2+}$ and related species,¹¹ and $\text{Re}_2\text{Cl}_8^{2-}$, $\text{Mo}_2\text{Cl}_8^{4-}$, and several related complexes having a $\text{M}-\text{M}^4$ quadruple bond.¹² In all cases the emission spectrum has been contributory to an understanding of the electronic structure.

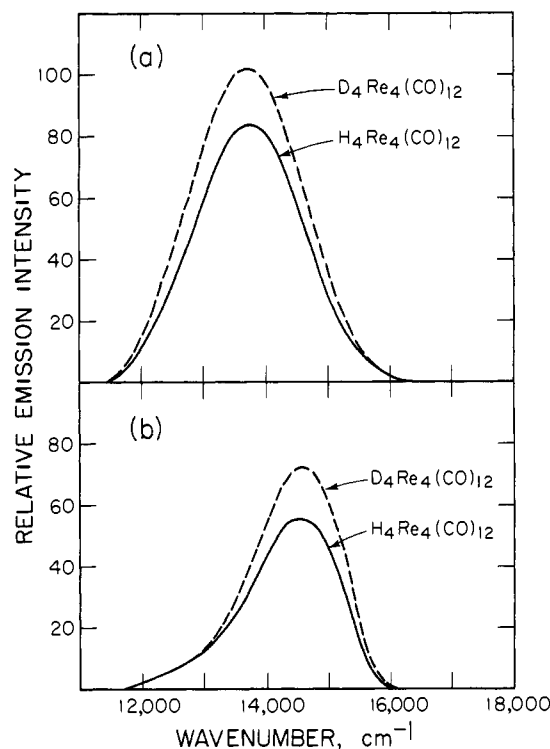


Figure 1. Corrected emission spectral distribution for $\text{H}_4\text{Re}_4(\text{CO})_{12}$ (—) and $\text{D}_4\text{Re}_4(\text{CO})_{12}$ (---) in 3-methylpentane at (a) 298 K and (b) 77 K. The excitation wavelength is 470 nm. The spectra in (a) were recorded at ~ 1000 times the sensitivity as those in (b). See Table I for quantum yields.

$\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ are among¹³ the first metal-metal bonded clusters having a core of more than two metals that are known to be detectably emissive. Generally, the dissociative reaction pathways from the excited states of polynuclear complexes might be expected to be less important than for mononuclear or dinuclear metal complexes since the electronic transitions of the larger clusters involve depopulation and population of orbitals that are more delocalized and less consequential with respect to bonding.¹⁴ Thus, radiative decay should become

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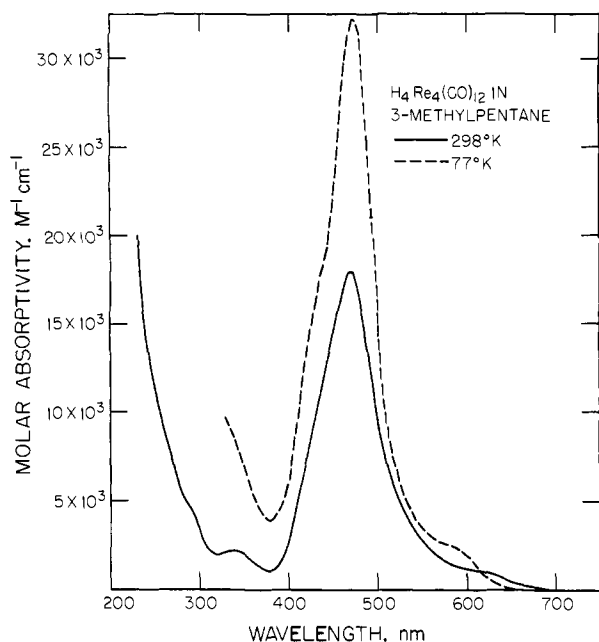


Figure 2. Electronic absorption spectra at 298 K (—) and 77 K (---) in 3-methylpentane for $\text{H}_4\text{Re}_4(\text{CO})_{12}$. The spectral changes upon cooling have not been corrected for solvent contraction.

competitive with chemical-decay paths from the lowest excited states. It is also noteworthy that $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ represent the first examples of emissive transition-metal hydrides. This class of complexes has a rich photochemistry¹⁵ of possible use in catalysis, stoichiometric synthesis, and energy storage.

Results

a. Electronic Emission and Absorption of $\text{H}_4\text{Re}_4(\text{CO})_{12}$. The $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $\text{D}_4\text{Re}_4(\text{CO})_{12}$ complexes are emissive as solids or in hydrocarbon solution at 298 and 77 K. Figure 1 shows corrected emission spectra recorded for the ^1H and ^2H complexes in 3-methylpentane solvent. As shown, the emission spectra are the same for the ^1H and ^2H species, but the emission quantum efficiency for the ^2H species is larger. Quantitative emission data are collected in Table I for various media. The absorption spectra of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ at 298 and 77 K in 3-methylpentane solvent are shown in Figure 2. The onset of the shoulder at ~ 600 nm (16700 cm^{-1}) overlaps the onset of the emission and suggests that the ~ 600 -nm absorption corresponds to the photoexcitation of the ground state to produce the emissive state. The spectral distribution of emitted light is independent of excitation wavelength, and the absorption spectrum in 3-methylpentane and the excitation spectrum of the emission are the same when the optical density of the solution is < 0.1 . These data show that the emission quantum yield is independent of the excitation wavelength, consistent with emission originating from the lowest excited state. The spectral distribution of emitted light is independent of the concentration of the $\text{H}_4\text{Re}_4(\text{CO})_{12}$ complex in a given medium at concentrations in the vicinity of 10^{-6} M. This shows that the emission has a molecular origin. $\text{H}_4\text{Re}_4(\text{CO})_{12}$ does not appear to be photoreactive in solution or in the solid state upon visible or ultraviolet light excitation.

Data in Table I show that the lifetime, quantum yield, emission maximum, and emission width are all sensitive to the medium and temperature. But for a given temperature and medium, the ^2H complex exhibits a higher quantum yield and a longer lifetime than the ^1H complex. While solvent effects do seem large, cf. toluene vs. 3-methylpentane, toluene and toluene- d_8 give decay properties that are the same within experimental error. Thus, the

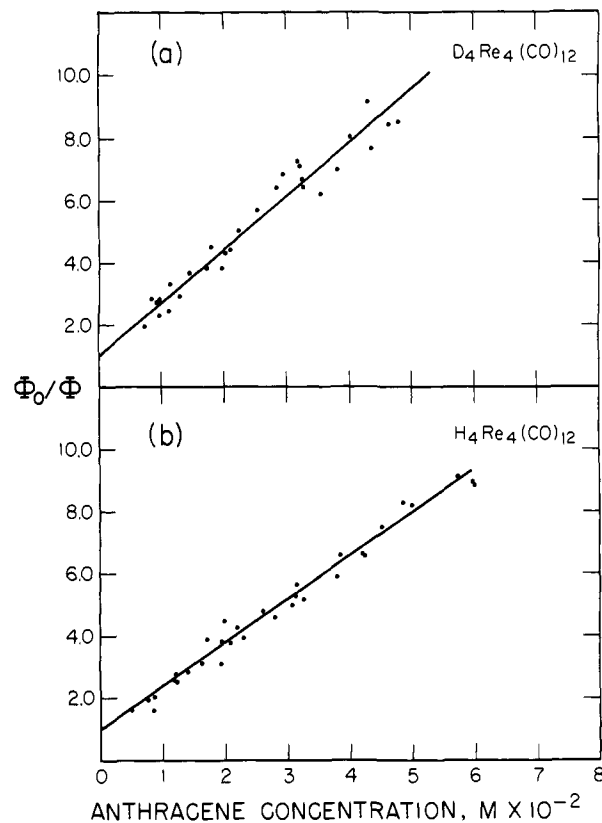


Figure 3. Stern-Volmer plots for (a) $\text{D}_4\text{Re}_4(\text{CO})_{12}$ and (b) $\text{H}_4\text{Re}_4(\text{CO})_{12}$ in toluene at 298 K with use of anthracene as the quencher. The excitation wavelength used was 470 nm.

intramolecular ^2H effect is larger than that associated with the intermolecular effect from perdeuteration of the hydrocarbon solvent. Detailed studies of the medium effects on $\text{H}_4\text{Re}_4(\text{CO})_{12}$ emission have been frustrated by the fact that donor solvents (e.g., MeOH, THF, etc.) rapidly react with $\text{H}_4\text{Re}_4(\text{CO})_{12}$ in the ground state at 25 °C.

The $\text{H}_4\text{Re}_4(\text{CO})_{12}$ emission in toluene solution at 298 K can be quenched by anthracene (Figure 3). As shown, the plots of Φ_0/Φ_Q vs. [anthracene] are linear with an intercept of 1.0, consistent with quenching that obeys the Stern-Volmer relationship (eq 1).¹⁶ The slopes of the plots for the ^1H and ^2H species differ,

$$\Phi_0/\Phi_Q = 1 + k_q\tau[Q] \quad (1)$$

Φ_0 = emission quantum yield in absence of quencher, Q

Φ_Q = emission quantum yield in presence of Q

k_q = bimolecular quenching constant, $\text{M}^{-1}\text{ s}^{-1}$

τ = emission lifetime in absence of Q, s

[Q] = quencher concentration, M

consistent with a different lifetime for the ^1H and ^2H species, 96 and 111 ns, respectively. With the use of these values for the lifetime, anthracene quenches with a k_q of $1.52 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ and $1.45 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ for the ^1H and ^2H species, respectively. The error limits on these numbers are sufficiently large that these values of k_q can be regarded as the same within experimental error. That is, the quenching rate of the excited (emissive) state of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ by anthracene is the same for the ^1H and ^2H complexes. Neither *trans*-stilbene nor *trans*-1,3-pentadiene quench the emission of $\text{H}_4\text{Re}_4(\text{CO})_{12}$. We conclude k_q to be $< 10^6\text{ M}^{-1}\text{ s}^{-1}$ for these species.

b. Infrared Spectrum of $\text{H}_4\text{Re}_4(\text{CO})_{12}$. Figure 4 shows the infrared absorption spectra at 298 K and at low temperature for

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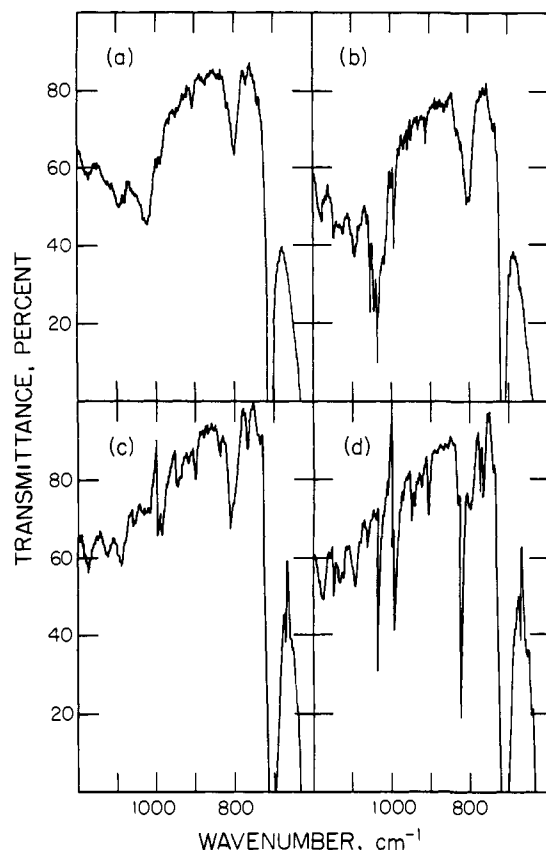


Figure 4. Temperature dependence on the infrared spectra for $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $\text{D}_4\text{Re}_4(\text{CO})_{12}$ in KBr pellets: (a) $\text{H}_4\text{Re}_4(\text{CO})_{12}$ at 298 K; (b) $\text{H}_4\text{Re}_4(\text{CO})_{12}$ at 17 K; (c) $\text{D}_4\text{Re}_4(\text{CO})_{12}$ at 298 K; (d) $\text{D}_4\text{Re}_4(\text{CO})_{12}$ at 40 K. A grating change occurs at 1000 cm^{-1} .

$\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $\text{D}_4\text{Re}_4(\text{CO})_{12}$ in KBr disks. The spectra are considerably sharper at low temperature, as has been reported for other transition-metal bridging-hydride systems.^{8c} The ^1H species exhibits absorptions at $\sim 1040\text{ cm}^{-1}$ that can be associated with the triply face-bridging hydride, and the ^2H species exhibits features in the $\sim 800\text{-cm}^{-1}$ range consistent with the isotope effect. The literature assignment for the ^1H species is 1023 cm^{-1} for the Re–H stretch.^{8a} The complexes should exhibit only one Re–H stretch, but as is often found for such species, the spectrum is more complex than would be expected.^{8b,c} Local reduction in symmetry could account for the larger number of bands. We note an unusually large temperature sensitivity for the feature at $\sim 830\text{ cm}^{-1}$ in the $\text{D}_4\text{Re}_4(\text{CO})_{12}$ complex.

c. Electronic Absorption and Emission of $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$. The absorption (Figure 5) and emission (Figure 6) spectra of $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ are very different from those of $\text{H}_4\text{Re}_4(\text{CO})_{12}$. An obvious difference is the higher energy absorption and emission. Further, $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ is only emissive at low temperature. There is no detectable emission at 298 K in solution or in the solid state. As shown by the data in Table I, the ^1H species is shorter lived and has a lower emission quantum yield than the ^2H species. The emission distribution and quantum yield of $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ are independent of the excitation wavelength where the ion absorbs, consistent with emission from the lowest excited state.

The edge-bridging Re– ^1H stretching frequency has been reported⁹ to be at 1165 cm^{-1} and that for Re– ^2H is at 832 cm^{-1} for $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$. These values are somewhat higher than the Re–H stretch for $\text{H}_4\text{Re}_4(\text{CO})_{12}$ where the H atoms are face-bridging.

Discussion

a. Electronic Structure of $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ and $\text{H}_4\text{Re}_4(\text{CO})_{12}$. The main electronic structural features of $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ and $\text{H}_4\text{Re}_4(\text{CO})_{12}$ can be appreciated from simple orbital diagrams adapted from the work of Hoffmann, Schilling, Bau, Kaesz, and

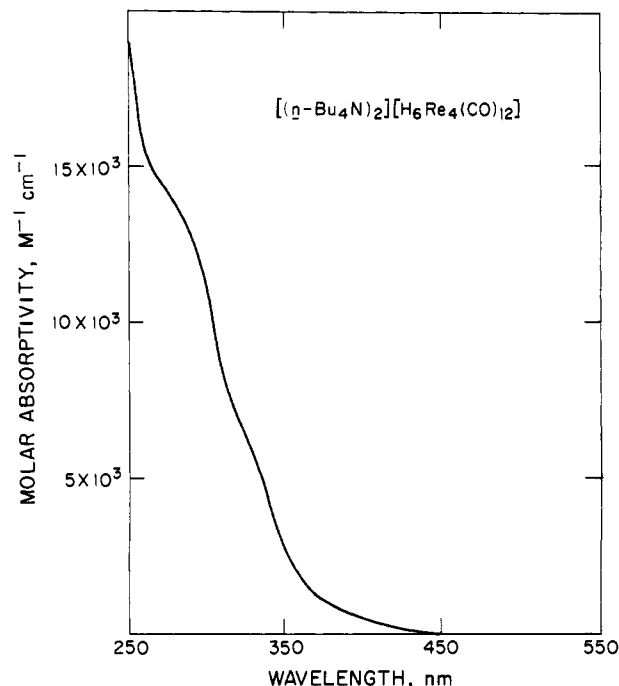


Figure 5. Electronic absorption spectra at 298 K in 2-methyltetrahydrofuran for $[(n\text{-Bu}_4\text{N})_2][\text{H}_6\text{Re}_4(\text{CO})_{12}]$.

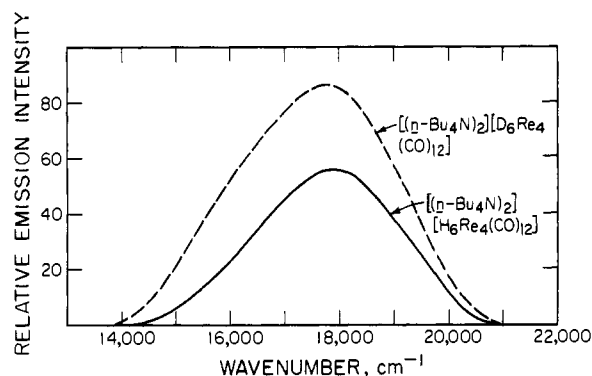


Figure 6. Corrected emission spectral distribution for $[(n\text{-Bu}_4\text{N})_2][\text{H}_6\text{Re}_4(\text{CO})_{12}]$ (—) and $[(n\text{-Bu}_4\text{N})_2][\text{D}_6\text{Re}_4(\text{CO})_{12}]$ (---) in 2-methyltetrahydrofuran at 77 K. The excitation wavelength is 375 nm. See Table I for quantum yields.

Mingos¹⁷ and the difference in the total valence electron count in the two species:

$\text{H}_4\text{Re}_4(\text{CO})_{12}$		$[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$	
4H	4e ⁻	6H	6e ⁻
12CO	24e ⁻	12CO	24e ⁻
4Re	28e ⁻	4Re	28e ⁻
		2 ⁻ charge	2e ⁻
total	56e ⁻	total	60e ⁻

The appropriate orbital diagrams are represented by Scheme I. The key is that the 56-valence-electron cluster has four fewer electrons than what would be regarded as a "saturated" 60-valence-electron system.¹⁸ Further, $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ likely has edge-bridging H atoms with a staggered orientation of the CO's relative to the Re–Re bonds, while $\text{H}_4\text{Re}_4(\text{CO})_{12}$ has triply face-bridging H atoms with an eclipsed orientation of the CO groups.^{6,9} The a_1, e, t_2 orbital set can be viewed as the bonding orbitals associated with the six metal–metal bonds of the Re_4 -

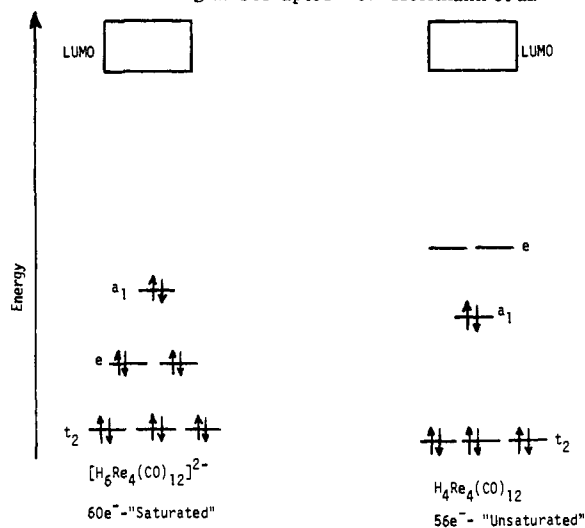
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Table II. Summary of Hydrogen Isotope Effects on Excited-State Decay of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$

complex	medium (T, K)	$10^{-4}k_{\text{nr}}, \text{s}^{-1}$ ^a		$10^{-4}k_{\text{r}}, \text{s}^{-1}$ ^b		$\tau^2_{\text{H}}/\tau^1_{\text{H}}$	$\Phi^2_{\text{H}}/\Phi^1_{\text{H}}$ ^d
		¹ H	² H	¹ H	² H		
$\text{H}_4\text{Re}_4(\text{CO})_{12}$	pure solid (298)					1.27	
	pure solid (77)					1.22	
	3-methylpentane (298)						1.15
	3-methylpentane (77)	6.18	4.20	2.07	2.06	1.32	1.31
$[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-e}$	toluene (298)	1.01×10^3	8.68×10^2	33.3	33.3	1.16	1.16
	pure solid (77)					1.43	
	2-MeTHF (77) ^f	4.6×10^1	2.87×10^1	0.56	0.58	1.58	1.63

^a Rate constant for nonradiative decay for ¹H and ²H complexes. ^b Rate constant for radiative decay for ¹H and ²H complexes. ^c Ratio of emission lifetimes of ¹H and ²H complexes (see Table I). ^d Ratio of emission quantum yields of ¹H and ²H complexes. ^e As the $[\text{n-Bu}_4\text{N}]^+$ salt. ^f 2-MeTHF is 2-methyltetrahydrofuran.

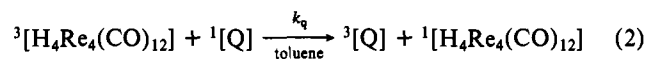
Scheme I. Orbital Diagrams Adapted from Hoffmann et al.¹⁷

($\text{CO})_{12}^{4-}$ or $\text{Re}_4(\text{CO})_{12}^{8-}$ core that are then perturbed by binding four or six H^+ to these clusters. Calculations¹⁷ show that the next set of unoccupied orbitals, LUMO's in Scheme I, are far removed from the fully occupied ($[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$) or partially occupied ($\text{H}_4\text{Re}_4(\text{CO})_{12}$) a_1 , e , t_2 set. The orbital schemes are qualitatively consistent with the optical spectrum: $\text{H}_4\text{Re}_4(\text{CO})_{12}$ exhibits very low-energy absorption compared to the $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$. The low-energy absorption is logically associated with excitations to the low-lying vacant e orbital. The $a_1 \rightarrow e$ transition is not fully allowed and may be the $\sim 600\text{-nm}$ shoulder while the intense feature at $\sim 470\text{ nm}$ may be associated with the allowed $t_2 \rightarrow e$ transition. An alternative assignment is to attribute the $\sim 600\text{-nm}$ shoulder to the singlet to triplet $t_2 \rightarrow e$ transition while the $\sim 470\text{ nm}$ is the corresponding singlet feature. In any case the $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ absorption is clearly very different in absorption, and we attribute this difference to the fact that low-lying empty orbitals are not available.

The lack of any measurable photochemistry for $\text{H}_4\text{Re}_4(\text{CO})_{12}$ in solution at 298 K and the observation of emission are consistent with a relatively nonlabile lowest excited state. The $a_1 \rightarrow e$ and $t_2 \rightarrow e$ transitions merely involve redistribution of electrons among orbitals that are relatively close in energy; the e level is not antibonding. Also, the orbital scheme for $\text{H}_4\text{Re}_4(\text{CO})_{12}$ accords well with the sensitivity of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ to donor solvents that disrupt the cluster. The low-lying e orbital makes the cluster especially susceptible to nucleophilic attack as expected from the 56-valence-electron count as well. Finally, the low-lying e orbital may make the cluster especially sensitive to the solvent used, rationalizing the rather strong medium effects on excited-state decay rates (Table I).

The lower energy absorption for the 56-valence-electron system compared to the saturated cluster is interesting and possibly general. We note that $\text{Os}_3(\text{CO})_{11}\text{H}_2$ (48 valence-electrons) is yellow whereas the unsaturated $\text{Os}_3(\text{CO})_{10}\text{H}_2$ (46 valence-electrons) is purple. These systems will be the object of study in this laboratory in the future.

The emission of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ can be associated with the radiative decay of the lowest excited state to the ground state. The lifetime of the emission at low temperature accords well with the lifetimes found for other third-row metal-carbonyl systems where the lowest excited state has considerable triplet character.^{15a} We assign the emission as principally triplet in character. Quenching of the emission by anthracene (triplet energy = 42 kcal/mol)¹⁹ is consistent with a triplet assignment. The singlet state of anthracene (76 kcal/mol) is well above the onset of the emission of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ (46 kcal/mol), and quenching by singlet-singlet transfer would not be expected to be fast since it would be so endothermic. However, the triplet-triplet transfer would be expected to be fast with the exothermic energy transfer. Thus, we associate the quenching of the excited (emissive) state of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ with triplet-triplet transfer (eq 2). The lack of



Q = anthracene ($E_T = 42\text{ kcal/mol}$); $k_q = 1.5 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$

Q = *trans*-stilbene ($E_T = 50\text{ kcal/mol}$); $k_q < 10^6\text{ M}^{-1}\text{ s}^{-1}$

Q = *trans*-1,3-pentadiene ($E_T = 59\text{ kcal/mol}$); $k_q \ll 10^6\text{ M}^{-1}\text{ s}^{-1}$

quenching by the *trans*-stilbene and *trans*-1,3-pentadiene is consistent with the triplet-triplet mechanism since these two olefins have triplet energies that are higher than that for $\text{H}_4\text{Re}_4(\text{CO})_{12}$.¹⁹ The triplet character of the lowest excited state is thus confirmed by the quenching studies. The orbital character is ambiguous; the excited state has either the $t_2^6a_1^1e^1$ or $t_2^5a_1^2e^1$ configuration as indicated above.

The absorption and emission of $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ is associated with an electronic transition between the filled bonding $t_2^6e^4a_1^2$ set and the empty antibonding levels. The lifetime suggests a triplet assignment but this could not be confirmed by quenching studies, since the complex does not emit in fluid solution. Interestingly, $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ and $\text{H}_4\text{Re}_4(\text{CO})_{12}$ belong to the same point group but have different orbital orderings due to the differing orbital interactions associated with the different ligand orientation. The main conclusion is that the saturated, 60-valence-electron $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ understandably absorbs at higher energy compared to $\text{H}_4\text{Re}_4(\text{CO})_{12}$ owing to the absence of the low-lying vacant orbital. The excited state of $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ should be more labile than that of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ since strongly antibonding orbitals are populated. However, it is now clear that one-electron excitations of tetranuclear (tetrahedrane structure) complexes generally do not labilize ligands or metal-metal bonds sufficiently to give efficient net reaction within the lifetime of the excited state.¹⁴

b. Effect of ²H on Excited-State Decay of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$. The effects on excited-state decay by replacing ¹H by ²H in $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ are summarized in Table II. The values of the nonradiative, k_{nr} , and radiative k_{r} , rate constants are calculated from the quantum yields and lifetimes by using eq 3 and 4. The complexes do not undergo

$$\Phi = k_r / (k_{nr} + k_r) \quad (3)$$

$$\tau = 1 / (k_{nr} + k_r) \quad (4)$$

net chemical change upon irradiation, and thus the nonradiative decay rates represent nonchemical, nonradiative decay paths. Under all conditions, the effect of replacing ^1H by ^2H is to lower k_{nr} while there is no measurable effect on k_r . The smaller value of k_{nr} with a constant value of k_r results in a longer excited state lifetime and a larger quantum yield. It is interesting to note that the effect of replacing ^1H by ^2H is larger for $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ than for $\text{H}_4\text{Re}_4(\text{CO})_{12}$. The six H atoms in $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ are believed to be edge-bridging while the four H atoms in $\text{H}_4\text{Re}_4(\text{CO})_{12}$ are face-bridging.^{6,9} Thus, both complexes have 12 Re–H bonds. As indicated above, the edge-bridging system has a Re–H stretch at $\sim 1165 \text{ cm}^{-1}$ ⁹ whereas for the triple-face bridging system the Re–H stretch is at lower energy at $\sim 1023 \text{ cm}^{-1}$.^{8a} Thus, the 12 Re–H bonds in $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ could be argued to be of more importance than in $\text{H}_4\text{Re}_4(\text{CO})_{12}$ with respect to nonradiative decay rates, consistent with the fact that the ^2H effect on nonradiative decay rates is greater for $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ than for $\text{H}_4\text{Re}_4(\text{CO})_{12}$. However, there are two other important differences in the $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ complexes that may cause the isotope effects to differ. First, the excited-state energy is higher for the $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ (see Table I). This would have the effect of lowering nonradiative decay rates, all other factors constant. Second, the geometrical structure of the “ $\text{Re}_4(\text{CO})_{12}$ ” core differs and the orbital nature of the lowest excited states differ. These differences have consequences with respect to the importance of ^2H effects on the excited-state decay, but we are not in a position to predict the magnitude or direction of the effect.

$\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ are the first metal–hydride complexes to be studied with respect to ^2H effects on excited-state decay. However, a number of complexes have been examined that have H atoms on the ligand.^{3–5} In most of the systems examined thus far where ^2H effects are observed, H_2O solvent is a potential complication. The vibrational modes of solvent have been established to be important in the $[\text{RhBr}_2(\text{py})]^+$ system where exchange of protons on pyridine with the $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ solvent is not observed, though the effect from perdeuteration of the four pyridine ligands is greater.³ By way of contrast, the $\text{Ru}(2,2'\text{-bpy})^{2+}$ lowest excited state is more affected by changing solvent from H_2O to D_2O than by perdeuteration of the three 2,2'-bipyridine ligands.^{4d} Perhaps surprisingly, there appears to be little effect on decay properties of $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$ upon changing solvent from H_2O to D_2O .^{4c} But perdeuteration of $\text{Rh}(\text{NH}_3)_5\text{X}^{2+}$ does give a significant change in lifetime.^{3,4c} Our results for $\text{H}_4\text{Re}_4(\text{CO})_{12}$ in toluene vs. toluene- d_8 show that there is no measurable effect on the $\text{H}_4\text{Re}_4(\text{CO})_{12}$ decay properties upon perdeuteration of solvent. This result is similar to that for aromatic hydrocarbons that are only affected to a small extent by solvent deuteration.^{2,7a} We are presently searching for more examples of luminescent metal hydrides to develop greater understanding of the nonradiative decay. We hope to find systems where there are a large number of terminal hydrides where the M–H stretching frequency can be about a factor of 2 higher than for the bridging systems reported here. The $\sim 50\%$ diminution of k_{nr} in $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ and $\text{H}_4\text{Re}_4(\text{CO})_{12}$ is already fairly large given the small number of hydrogens and the low energy ($\sim 1000 \text{ cm}^{-1}$) of the associated vibrations.

The irradiation of mononuclear polyhydrides generally results in the loss of H_2 .¹⁵ Irradiation of such complexes could provide a mechanism for hydrogen isotope separation, but isotope effects on the quantum efficiency of H_2 elimination have not been reported. Isotope effects of the magnitude that we have observed here on k_{nr} might prove useful for isotope enrichment in reversible systems such as $\text{H}_2\text{IrCl}(\text{PPh}_3)_3 \rightleftharpoons \text{IrCl}(\text{PPh}_3)_3 + \text{H}_2$.

Experimental Section

General Procedures. Reagent grade solvents were dried over CaH_2 prior to use. Toluene, toluene- d_8 , NaBH_4 , NaBD_4 , $\text{Re}_2(\text{CO})_{10}$, $n\text{-Bu}_4\text{NBr}$, H_2 (99.95%), D_2 (99.5 atom % minimum), and 3-methylpentane (99+%) were commercially available and used as received. 2-Methyltetrahydrofuran (Aldrich) was passed through Al_2O_3 prior to use. An-

thracene (J. T. Baker Chemical Co.) was recrystallized from toluene. ^1H NMR spectra (60 MHz) were recorded on a Varian T-60 NMR spectrometer and (90 MHz) on a Joel FX-90Q NMR spectrometer. Chemical shifts are reported in τ with use of Me_4Si as an internal standard. ^2H NMR spectra (13.7 MHz) were recorded on a Joel FX-90Q NMR spectrometer, and chemical shifts are reported in τ with use of either an acetone- d_6 or CDCl_3 internal standard. Mass spectra were obtained on a Varian MAT 122 mass spectrometer.

Preparation of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $\text{D}_4\text{Re}_4(\text{CO})_{12}$. $\text{H}_4\text{Re}_4(\text{CO})_{12}$ was prepared according to a modification of literature methods.^{6,18} $\text{Re}_2(\text{CO})_{10}$ was heated to 170°C for 4 h in dry decalin while slowly bubbling H_2 through the solution and then refluxed for 40 min, yielding a dark red solution. Any $\text{Re}_2(\text{CO})_{10}$ and $\text{H}_3\text{Re}_3(\text{CO})_{12}$ present was removed by filtration after cooling to -20°C . Dry benzene was added dropwise to the dark red solution precipitating $\text{H}_4\text{Re}_4(\text{CO})_{12}$, which was recrystallized from CH_2Cl_2 . $\text{D}_4\text{Re}_4(\text{CO})_{12}$ was prepared in the same manner, with use of D_2 in place of H_2 .

$\text{H}_4\text{Re}_4(\text{CO})_{12}$: ^1H NMR (60 MHz, CCl_4) τ 14.95 (s); infrared (isooctane solution) $\nu(\text{CO})$ 2044 (s), 1990 (s) cm^{-1} (KBr pellet) (cf. Figure 4); UV-vis (3-methylpentane solution, 298 K) 292 (sh), 336 (2200 $\text{M}^{-1} \text{cm}^{-1}$), 470 (18000 $\text{M}^{-1} \text{cm}^{-1}$), ~ 615 (sh) nm (cf. Figure 2). The mass spectrum exhibits the following isotope distribution for P^+ [m/e (relative abundance)]: 1082 (1.47), 1083 (0.74), 1084 (3.15), 1085 (1.05), 1086 (3.57), 1087 (0.84), 1088 (1.68). This is followed by sequential loss of 12 CO's.

$\text{D}_4\text{Re}_4(\text{CO})_{12}$: ^2H NMR (13.7 MHz, CCl_4) τ 15.08 (s) measured relative to CDCl_3 assuming τ 2.75; infrared (isooctane solution) $\nu(\text{CO})$ 2044 (s), 1990 (s) cm^{-1} (KBr pellet) (cf. Figure 4); UV-vis (3-methylpentane solution, 298 K) 290 (sh), 335 (2100 $\text{M}^{-1} \text{cm}^{-1}$), 470 (17800 $\text{M}^{-1} \text{cm}^{-1}$), ~ 615 (sh) nm. The mass spectrum exhibits the following isotope distribution for P^+ [m/e (relative abundance)]: 1086 (1.35), 1087 (0.93), 1088 (3.00), 1089 (1.35), 1090 (3.31), 1091 (0.93), 1092 (1.45). This is followed by the sequential loss of 12 CO's. The mass spectrum shows $\text{D}_4\text{Re}_4(\text{CO})_{12}$ to be $>95\%$ ^2H .

Preparation of $[n\text{-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$ and $[n\text{-Bu}_4\text{N}]_2[\text{D}_6\text{Re}_4(\text{CO})_{12}]$. $[n\text{-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$ was prepared according to the literature.^{9,20a} A heterogeneous mixture of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and excess NaBH_4 in dried, degassed cyclohexane was stirred under an Ar atmosphere for days. After all the $\text{H}_4\text{Re}_4(\text{CO})_{12}$ had reacted as indicated by IR, the solid was filtered from solution. The excess NaBH_4 present was hydrolyzed by dissolution in H_2O , yielding a yellow solution. $[n\text{-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$ was precipitated from the yellow solution by the addition of an aqueous $n\text{-Bu}_4\text{NBr}$ solution. The product was recrystallized from acetone/water. $[n\text{-Bu}_4\text{N}]_2[\text{D}_6\text{Re}_4(\text{CO})_{12}]$ was prepared from $\text{D}_4\text{Re}_4(\text{CO})_{12}$ and NaBD_4 by the above method.

$[n\text{-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$: ^1H NMR (90 MHz, acetone- d_6) τ 27.25 (s) plus resonances between τ 6.5 and τ 9 for $n\text{-Bu}_4\text{N}^+$ cation. Infrared (acetone solution) $\nu(\text{CO})$ 1995 (s), 1905 (s) cm^{-1} (KBr pellet) $\nu(\text{Re-H})$ 1165 cm^{-1} ; UV-vis (2-methyltetrahydrofuran solution, 298 K): ~ 290 (sh), ~ 330 (sh) (cf. Figure 5).

$[n\text{-Bu}_4\text{N}]_2[\text{D}_6\text{Re}_4(\text{CO})_{12}]$: ^2H NMR (13.7 MHz, acetone) τ 27.31 (s) measured relative to acetone- d_6 assuming τ 7.93; infrared (acetone solution) $\nu(\text{CO})$ 1995 (s), 1905 (s) cm^{-1} (KBr pellet) $\nu(\text{Re-D})$ 828 cm^{-1} ; UV-vis (2-methyltetrahydrofuran solution, 298 K) ~ 290 (sh), ~ 330 (sh). Integration of NMR signals shows the $[\text{D}_6\text{Re}_4(\text{CO})_{12}]^{2-}$ samples to be $>80\%$ ^2H .

Emission Spectra and Quantum Yields. All emission spectra were recorded with use of a Perkin-Elmer MPF-44 fluorescence spectrophotometer equipped with a Perkin-Elmer Model 150 xenon power supply and a Hamamatsu HR777 PMT detector. The relative sensitivity of the entire detection system and the PMT has been calibrated from 300–900 nm with use of a standard lamp obtained from and calibrated by E.G. & G., Inc., Salem, MA. The standard lamp is a 200-W tungsten halogen lamp operated at 6.50 A having serial no. B115A and was calibrated from NBS standards Qm 197, Qm 198, and Qm 199. All emission samples were placed in Pyrex tubes and the 298-K solution samples were freeze-pump-thaw-degassed (5 cycles) and hermetically sealed. The emission quantum yields of the complexes at 298 and 77 K were determined relative to rhodamine B ($\Phi_0 = 0.69$)²¹ in EtOH with the use of the following procedure. The absorbance of the complex whose quantum yield is to be measured is set equal to that of rhodamine B in EtOH (o.d. < 0.10 in 1.00-cm path length) at the desired wavelength (470 nm for $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $\text{D}_4\text{Re}_4(\text{CO})_{12}$; 375 nm for $[n\text{-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$ and $[n\text{-Bu}_4\text{N}]_2[\text{D}_6\text{Re}_4(\text{CO})_{12}]$). The emission spectra of the complex and the standard were recorded by exciting with the desired wavelength. The

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relative emission quantum yield of the complex is the integrated area under the corrected emission spectrum divided by that for the rhodamine B standard, after correction for differences in the index of refraction of the solvents.²²

Emission Lifetimes. The emission lifetimes, τ , were measured with use of a TRW Model 75A decay time fluorometer having a Hamamatsu R446UR PMT detector powered by a Kepco Model 2500 ABC regulated high-voltage supply. A Xenon Corp. Nanopulser excitation source was used for samples with $\tau > 0.5 \mu\text{s}$. Output from the PMT was monitored by a Tektronix 453 oscilloscope and recorded with a Polaroid camera. Samples with $\tau < 0.5 \mu\text{s}$ were excited by the third harmonic of a Quanta Ray DCR Nd:YAG laser equipped with a PHS-1 prism harmonic separator. Output from the PMT following a 7-ns excitation pulse was monitored by a Tektronix 545A oscilloscope or a Tektronix digital oscilloscope (7912AD programmable digitizer, 624 monitor, 634 monitor, 7B50 amplifier, and 7A15A time-base plug ins) and recorded with a Polaroid camera. Plots of \log (emission intensity) vs. time were linear in every case over at least two lifetimes. The value of τ is taken as the time required for the emission intensity to decay to $1/e$ of its original intensity.

Quenching of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $\text{D}_4\text{Re}_4(\text{CO})_{12}$ Emission. Quenching of the emission of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $\text{D}_4\text{Re}_4(\text{CO})_{12}$ obeys the Stern-Volmer expression (eq 1).¹⁴ Degassed toluene solutions of the complex of interest at a constant concentration and the quencher (anthracene, $E_T = 42 \text{ kcal/mol}$) were placed in $13 \times 100 \text{ mm}$ Pyrex tubes and stoppered with septa in a Vacuum Atmospheres drybox. With the use of a 470-nm excitation wavelength, the emission spectra of each sample were recorded, and the relative emission intensities were determined as a function of

quencher concentration (Figure 3). Plots of Φ_0/Φ_Q against quencher concentration are linear, and the line passes through $\Phi_0/\Phi_Q = 1.0$ at zero quencher concentration. From the slope $k_q\tau$ of the plots of the quenching constant, k_q , can be calculated, after determination of the donor lifetime in the absence of quencher ($\tau = 96 \text{ ns}$ for $\text{H}_4\text{Re}_4(\text{CO})_{12}$, $\tau = 111 \text{ ns}$ for $\text{D}_4\text{Re}_4(\text{CO})_{12}$).

Absorption and Excitation Spectra. All UV-vis absorption spectra were recorded with use of a Cary 17, and low-temperature spectra were obtained with use of an all-quartz liquid- N_2 Dewar equipped with optical quality flats for windows. Excitation spectra were recorded with the use of a Perkin-Elmer MPF-44 fluorescence spectrophotometer equipped with a Hamamatsu HR 777 PMT detector and a Perkin-Elmer Model 150 xenon power supply. The lamp output was calibrated with use of a rhodamine B quantum counter or internally by placing total-white-reflectance coating in the sample chamber, scanning the excitation and emission wavelengths simultaneously, and correcting for the PMT sensitivity throughout the wavelength region scanned.

Infrared Spectra. All infrared spectra were recorded with the use of a Perkin-Elmer Model 180 grating infrared spectrophotometer. Solution spectra were recorded in 1.0-mm matched path length NaCl cells, and solid-state spectra were recorded as KBr pellets. A Cryogenic Technology, Inc., Spectrim II sample conditioner was used in recording low-temperature infrared spectra of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $\text{D}_4\text{Re}_4(\text{CO})_{12}$ in KBr pellets.

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Siderophilin Metal Coordination. 1. Complexation of Thorium by Transferrin: Structure-Function Implications

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Abstract: As part of a program to develop actinide-specific sequestering agents, the coordination of actinide ions by human transferrin is being investigated. Therapeutically useful synthetic ligands must be able to compete with this iron-transport protein for the bound actinide ion. As in the Fe(III) complex of the native protein, two Th(IV) ions bind at pH 7. This coordination has been monitored at several pH values by using difference ultraviolet spectroscopy. The corresponding coordination of a phenolic ligand, ethylenebis(*o*-hydroxyphenylglycine) (EHPG), has been used to determine $\Delta\epsilon$ for a tyrosyl group coordinated to Th(IV), in contrast to the common practice of assuming the $\Delta\epsilon$ for protons and all metal ions is the same. This in turn is used to determine, from the observed $\Delta\epsilon$ upon protein coordination, the number of transferrin tyrosine residues that coordinate. Maxima in the Th(IV) + EHPG difference UV spectra occur at 292 and 238 nm, with corresponding $\Delta\epsilon$ values per phenolic group of 2330 and 8680 $\text{cm}^{-1} \text{M}^{-1}$, respectively. At pH 7.2, the Th(IV) transferrin spectrum is closely similar to the Th^{IV}EHPG spectrum, with maxima at 292 and 240 nm. The $\Delta\epsilon$ at 240 nm reaches a maximum of 24700 $\text{cm}^{-1} \text{M}^{-1}$, which corresponds to coordination of three tyrosine residues in the dithorium-transferrin complex; the stronger binding site ("A" or C-terminal) coordinates via two tyrosines and the weaker ("B" or N-terminal) via one. There is evidence suggesting that the N-terminal site is slightly smaller than the C-terminal site; while Th(IV) easily fits into the C-terminal site, the large ionic radius of Th(IV) makes this ion of borderline size to fit into the N-terminal site. This may be an important biological difference between Th(IV) and the slightly smaller Pu(IV), which should easily fit into both sites. At pH values below 7, the complexation of Th(IV) by transferrin decreases rapidly. At pH 6 and a Th(IV)/transferrin ratio of 2, only ~ 0.3 Th(IV) are bound per protein ($[\text{Th}] = 10^{-5} \text{ M}$). The N-terminal site is more rapidly affected by lowering the pH, so that coordination is entirely at the C-terminal site at low pH. Above pH 9, the conformation at the C-terminal site (two tyrosines) changes such that only one tyrosine is bound, the same that pertains at the N-terminal site at neutral pH. In addition to the three protons released by the coordinating tyrosine residues, the complexation of two Th(IV) ions releases two more protons at pH 8.6, which are ascribed to hydrolysis, so that the metal is bound as a monohydroxo species. It is suggested that diferric transferrin undergoes a similar reaction, and the other implications of these results for the structure and function of the native ferric transferrin are discussed.

A major concern associated with nuclear power has been the radiation hazards associated with the nuclear fuel cycle. The principal long-term hazards are the transuranium elements, es-

pecially plutonium. Previous biological studies have shown that Pu^{4+} tends to follow the ferric ion metabolic pathways in mammalian systems. When plutonium first enters the blood, it binds to the iron transport protein transferrin.⁴⁻⁶ It then circulates as

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