Figure 1. Transition-state structures (bond lengths in Å, angles in deg) and energetics (kcal/mol) for abstraction reactions.

The saddle-point structures for reactions 1–4 are shown in Figure 1, together with schematics of the potential energy curves. All four structures are found to be linear in X–H–Y. When CH_2 is the attacking group, it is coplanar with the substrate H, while the analogous silicon is pyramidal. This is consistent with the structures of the methyl and silyl radicals.[28] The imaginary frequencies for reactions 1–4 are 2369, 1657, 1729, and 1487 cm⁻¹, respectively. For comparison, the 3-21G C–H and Si–H reactant and product frequencies are about 3200 and 2200 cm⁻¹.[28]

Reaction 1 is predicted to be nearly thermoneutral, with an exothermicity of only 2 kcal/mol, compared with an experimental value of 5 kcal/mol.[30] The predicted abstraction barrier is 17.9 kcal/mol, at the lower end of the range predicted by Bauschlicher et al.[17] but much higher than the MINDO/2 result.[22] When the attacking group is SiH_2 (reaction 2), the transition state moves deeper into the exit channel, and the reaction is endothermic. The larger forward barrier in reaction 2 relative to (1) reflects the weaker Si–H vs. C–H bond.[31]

For reaction 3 the saddle point lies much closer to reactants than products. The smaller barrier relative to reaction 1 reflects the greater ease of abstracting a hydrogen from silane than from methane. Reaction 4 has its transition state more toward the center of the reaction path and is nearly thermoneutral, with a 2.8 kcal/mol endothermicity. The relative ease of abstracting a hydrogen from silane results in a forward barrier half the size of reaction 2. Triplet silylene is less effective than methylene as a hydrogen abstractor, as may be seen by comparing the forward barriers for reaction 4 vs. 3 and reaction 2 vs. 1. Finally, from the parent XH_3YH_3 energies obtained previously,[15] the CC, CSi, and SiSi single-bond energies are calculated to be 95.0, 84.6, and 73.0 kcal/mol, respectively, in good agreement with the experimental values of 88.0, 85.0, and 74.0.[31]

Registry No. H_2, 1333-74-0; CH_4, 74-82-8; SiH_4, 7803-62-5; $:CH_2$, 2465-56-7; $:SiH_2$, 13825-90-6.

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Electron-Transfer Quenching and Outer-Sphere Charge-Transfer Transitions in Mixed-Metal Ion Pairs. The [Eu⊂2.2.1]³⁺-M(CN)₆⁴⁻ Systems[1]

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Electron-transfer quenching (ETQ) of excited states[4] and outer-sphere charge-transfer (OSCT) transitions in ion pairs[5] are playing important roles in the development of electron-transfer theories.[6] A great number of ETQ studies have been performed in the last few years, but with a few exceptions,[7] they have concerned systems where ion pairs are not present. On the other hand, OSCT transitions have only been reported to occur for a few ion pairs,[5] none of which involves complexes having long-lived, luminescent excited states. We report here results concerning systems in which both OSCT transitions and ETQ can be observed.

Encapsulation of Eu^{3+} ion into the 4, 7, 13, 16, 21-pentaoxo-1,10-diazabicyclo[8.8.5]tricosane ligand (Lehn's[8] [2.2.1]cryptand) yields a stable cryptate complex, [Eu⊂2.2.1]³⁺.[9,10] The photophysical properties of this complex have recently been studied.[11] Its lowest excited state, which is the $^5D_0$ metal centered (f → f) excited state, lies 2.1 eV above the $^7F_0$ ground state, exhibits a bright luminescence emission, and has a lifetime of 215 μs in aqueous solution at room temperature. We have found that the luminescence emission of [Eu⊂2.2.1]³⁺ is quenched by M(CN)₆⁴⁻ (M = Fe, Ru, or Os) complexes. At low quencher concentrations the quenching process is *dynamic* in nature and is due to an *electron*-transfer mechanism:[12]

$$[*Eu⊂2.2.1]^{3+} + M(CN)_6^{4-} \rightarrow [Eu⊂2.2.1]^{2+} + M(CN)_6^{3-}$$
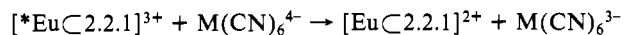
The bimolecular quenching constants (aqueous solutions, 1 M KCl, 295 K) are 7.5×10^8, 2.2×10^8, and 7.8×10^8 M⁻¹ s⁻¹ for the Fe, Ru, and Os cyanides, respectively.

When relatively concentrated aqueous solutions of [Eu⊂2.2.1]³⁺ and M(CN)₆⁴⁻ were used, formation of ion pairs was clearly observed. Addition of 5–500 μL of a 0.5 M Fe(CN)₆⁴⁻

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Table I. Spectral and Thermodynamic Data for the [Eu⊂2.2.1]$^{3+}$-M(CN)$_6$$^{4-}$ Ion Pairs[a]

M(CN)$_6$$^{4-}$, $E_{1/2}$[b], V	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	K_{IP},[c] M^{-1}
Fe(CN)$_6$$^{4-}$, +0.19	530	110	6100	300[d]
Os(CN)$_6$$^{4-}$, +0.40	450	110	7800	800
Ru(CN)$_6$$^{4-}$, +0.70	434	120	6500	400

[a] Aqueous solutions, KCl 1 M, 295 K. [b] Reference 5e. [c] From spectrophotometric titrations; uncertainty, ±10%. [d] 250 ± 50 M^{-1} from electrochemical measurements.
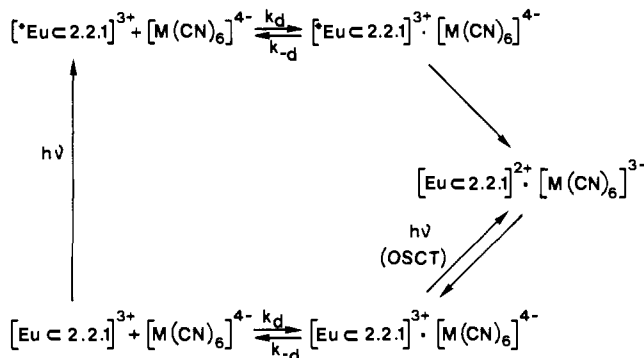

Figure 1. Scheme of the light-induced and thermal reactions occurring in the [Eu⊂2.2.1]$^{3+}$-M(CN)$_6$$^{4-}$ systems (M = Fe, Ru, or Os).

solution to 3 mL of a 5.0 × 10^{-3} M [Eu⊂2.2.1]$^{3+}$ solution caused the appearance of a violet color owing to the formation of a broad band with maximum at 530 nm. Ru(CN)$_6$$^{4-}$ and Os(CN)$_6$$^{4-}$ exhibited a similar behavior, giving rise to bands with maxima at 434 and 450 nm. The displacement of the absorption maximum toward the UV region as the cyanide complex becomes more difficult to oxidize (Table I) suggests that the new band is due to CT transitions within [Eu⊂2.2.1]$^{3+}$-M(CN)$_6$$^{4-}$ ion pairs. Spectrophotometric and potentiometric titrations in 1 M KCl showed that the ion pairs have a 1:1 stoichiometry[13] and allowed us to obtain the values of the formation constants which are reported in Table I together with the parameters of the observed OSCT bands. It should be noted that such bands are very broad and asymmetric, as expected because of their composite nature due to the splitting of the d^5 core of the oxidized hexacyano ion caused by spin–orbit coupling.[5e,14] The Gaussian analysis of the observed bands and a discussion of the kinetic parameters that can be obtained from the spectroscopic data[4b,5e,6a,c] will be reported in a later publication. As far as the formation of ion pairs and the appearance of OSCT transitions are concerned, our systems are quite similar to the Ru^{III}(amine)–M(CN)$_6$$^{4-}$ systems recently described by Curtis and Meyer.[5e] A noticeable difference is that the ion pairs described in this paper are quite stable both in the dark and under light excitation, while Curtis and Meyer's ion pairs are not stable, giving rise to cyano-bridged species in a few minutes.

Figure 1 summarizes the dark and light-induced reactions taking place between [Eu⊂2.2.1]$^{3+}$ and M(CN)$_6$$^{4-}$ and shows some important features of these systems where both ETQ and OSCT transitions can be observed. In sufficiently concentrated solutions the two complexes give rise to ground-state ion pairs. OSCT transitions can then occur, which lead to ion-pair species where the europium ion is reduced and the metal of the cyanide complex is oxidized. Since no net chemical effect is observed upon excitation in the OSCT band, the photoinduced OSCT reaction must be followed by a fast back-electron-transfer process which leads the system in its original situation. In diluted solutions ion pairs are not present, and light excitation of [Eu⊂2.2.1]$^{3+}$ (e.g., at 394 nm) leads to the long-lived $^5D_0$ excited state of the europium complex, which is dynamically quenched by M(CN)$_6$$^{4-}$ via formation of an encounter (precursor) complex.[15] Such a reductive

quenching leads to a successor complex which is exactly the same species as that obtained upon OSCT excitation of the ground-state ion pair. It is interesting to note that the thermal and the two light-induced electron-transfer reactions (Figure 1) are expected to exhibit the same intrinsic barrier and orbital overlap because the $^5D_0$ excited state of the europium complex has the same equilibrium geometry and the same orbital configuration as the $^7F_0$ ground state. These reactions, however, are not expected to behave in the same way as far as spin is concerned. The possible spin values are in fact 3 for the ground-state ion pair, 3 and 4 for the successor complex, and 2 for the precursor complex. Thus, the reductive quenching process is spin forbidden while the other two reactions are spin allowed. A very large influence of the spin factor, however, cannot be expected in these systems because of the presence of heavy atoms.

Further investigations on systems showing OSCT transitions and ETQ are needed in order to elucidate the role of the nuclear, orbital, and spin factors in these electron-transfer processes.

(15) In principle, the same precursor complex could be obtained via excitation of [Eu⊂2.2.1]$^{3+}$ moiety of the ground-state ion pair. In practice, however, this is difficult because the weak absorption bands of [Eu⊂2.2.1]$^{3+}$ are hidden by the broad and intense OSCT band.

Imidazole–Trimethyl Phosphate System: Characterization of the Hydrogen Bonding by Fast-Atom-Bombardment Mass Spectrometry and X-ray Crystallography

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The hydrogen-bonding properties of imidazole and its derivatives are of considerable importance in biochemistry. Of special interest is the ability of imidazole to form strong, easily polarizable hydrogen bonds as this may play an important role in a number of biochemical functions including proton conductivity in membranes[1] and protein oxygen binding.[2] An apparently simple example of a strong, easily polarizable hydrogen bond to imidazole has recently been reported to occur in the imidazole–trimethyl phosphate system.[3,4] Infrared and multinuclear NMR spectroscopy revealed the presence of the hydrogen bond and several other features of interest in the system but gave little information on the structure

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