(nBu)$_3$)(tBu-DAB), 119878-62-5; Ni(CO)(P(nBu)$_3$)(cHex-DAB), 119878-66-9; Ni(CO)(P(nBu)$_3$)(2,6-iPr$_2$Ph-DAB), 119878-64-7; Ni(CO)(PPh$_3$)(2,6-iPr$_2$Ph-DAB), 119907-57-2; Ni(CO)(P(OPh)$_3$)(2,6-iPr$_2$Ph-DAB), 119878-67-0; Ni(CO)(P(cHex)$_3$)(2,6-iPr$_2$Ph-DAB), 119878-65-8; Ni(CO)(σ-*N*-tBu-DAB)(tBu-DAB), 119878-59-0; Ni(CO)(σ-*N*-2,6-iPr$_2$Ph-DAB)(2,6-iPr$_2$Ph-DAB), 119907-58-3; Ni(tBu-DAB)$_2$, 63576-87-4; Ni(2,6-iPr$_2$Ph-DAB)$_2$, 78802-17-2; Ni(cHex-DAB)(2,6-iPr$_2$Ph-DAB), 119878-63-6; cHex-DAB, 3673-06-1; iPr-DAB, 24764-90-7; 2,6-iPr$_2$Ph-DAB, 74663-75-5; Ni(CO)$_2$(iPr-DAB), 119679-77-5; Ni(CO)$_3$(σ-*N*-tBu-DAB), 119878-57-8; PPh$_3$, 603-35-0; P(OPh)$_3$, 101-02-0; P(cHex)$_3$, 2622-14-2; P(nBu)$_3$, 998-40-3; CO, 630-08-0.

Contribution from the Chemistry Departments, University of Virginia,
Charlottesville, Virginia 22901, and James Madison University, Harrisonburg, Virginia 22807

Intramolecular Excited-State Interactions of Surfactant-Active Osmium(II) Photosensitizers

LouAnn Sacksteder,[†] J. N. Demas,*[,†] and B. A. DeGraff*[,‡]

Received April 29, 1988

A new class of luminescent surfactant-active complexes, *cis*-OsL$_2$(CO)NC(CH$_2$)$_n$CH$_3$$^{2+}$ (n = 0–19; L = 2,2′-bipyridine and 1,10-phenanthroline), were synthesized and characterized. They represent another example of an intramolecular perturbation of excited-state properties by what would normally be considered an electronically passive alkyl ligand. The effect is smaller in the Os(II) case and has a different n dependence than was observed in the *fac*-ReL(CO)$_3$NC(CH$_2$)$_n$CH$_3$$^+$ system. The differences arise from varied geometric constraints on the foldback and the orbital parentage of the emitting state. Foldback must be directly to ligands involved in the emission process in order to perturb the emission. The osmium(II) center highly activates the bound nitrile to thermal nucleophilic attack, and luminescent adducts are formed with alcohols and aliphatic and aromatic amines. Such activation has not been previously observed in complexes with α-diimine ligands. The complexes also photodecompose by labilization of the nitrile.

Introduction

Luminescent transition-metal complexes are used as probes of macromolecular structures[1] and heterogeneous media[2] and as photosensitizers for solar energy conversion[3] and electron-transfer reactions.[4] While Ru(II) complexes, in particular, have found broad application, the excited-state properties of complexes of Re(I),[5,6] Ir(III),[7] Mo(0), W(0),[8] and Os(II)[9] are being increasingly investigated. The metal, ligands, and solvent environment can affect excited-state properties, and variations of one or more of these constituents can "tune" the photophysical and photochemical properties.[10–12] We recently studied the series *fac*-Re(bpy)(CO)$_3$NC(CH$_2$)$_n$CH$_3$$^+$ (n = 0–17). Surprisingly, the emission properties are strongly perturbed by variations in n. We demonstrated that this effect is caused by intramolecular foldback of the alkyl chain onto the face of a bipyridine ligand.[13] The resulting change in solvent environment around the excited portion of the molecule alters the excited-state properties. To further investigate these intramolecular interactions, we synthesized *cis*-OsL$_2$(CO)NC(CH$_2$)$_n$CH$_3$$^{2+}$ (n = 0–19), where L = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen). This allows one to examine foldback in other systems and to determine the effect of differing geometries and energy-level patterns. While foldback does occur, we rationalize the significant differences in the foldback impact.

Experimental Section

Syntheses. Materials and syntheses are described in the supplementary material, *cis*-Os(bpy)$_2$Cl$_2$[14] was converted to *cis*-[Os(bpy)$_2$(CO)Cl]PF$_6$ by using formic acid.[15] The carbonyl was reacted with CF$_3$SO$_3$H to yield *cis*-[Os(bpy)$_2$(CO)(CF$_3$SO$_3$)](CF$_3$SO$_3$), which was converted to the nitriles.[15]

Equipment and Procedures. Absorption spectra and kinetics used a Hewlett-Packard 8452 spectrophotometer. Emission and excitation spectra were recorded as described earlier.[13] Emission spectra were instrument and background corrected, while excitation spectra were only background corrected. Room-temperature emission spectra were typically from aerated solutions (λ_{ex} = 400 nm). Low-temperature, 77 K, spectra were measured by using EPA (5:5:2 diethyl ether–isopentane–ethanol), absolute EtOH, 9:2 DMF–CH$_2$Cl$_2$, 4:1 MeOH–H$_2$O, or 5:4 butyronitrile–propionitrile glasses (λ_{ex} = 300 and 400 nm).

We show a powerful, simple method for assessing emission inhomogeneity. Two uncorrected sample excitation spectra are measured at

---

[†] University of Virginia.

[‡] James Madison University.

(1) (a) Kumar, C. V.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5518. (b) Barton, J.; Lolis, E. *J. Am. Chem. Soc.* **1985**, *107*, 708. (c) Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2172. (d) Barton, J. K.; Basik, L. A.; Danishefsky, A. T.; Alexandrescu, A. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 1961.

(2) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*, Academic Press: New York, 1987.

(3) (a) *Energy Resources through Photochemistry and Catalysis*; Grätzel, M., Ed.; Academic Press: New York, 1983. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (c) Balzani, V. Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr.* Chem. **1978**, *75*, 1.

(4) (a) Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2858. (c) Lin, C.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97.

(5) (a) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104. (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.

(6) (a) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Luong, J. C.; Faltynak, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1597. (c) Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 2257. (d) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415. (e) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *100*, 2888.

(7) (a) Watts, R. J.; Brown, M. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 6029. (b) Watts, R. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 674.

(8) (a) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711. (b) Connor, J. A.; Overton, C.; El Murr, N. *J. Organomet. Chem.* **1984**, *277*, 277. (c) Connor, J. A.; Overton, C. *Inorg. Chim. Acta* **1982**, *65*, L1. (d) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 3385. (e) Wrighton, M. S. *Chem. Rev.* **1972**, *72*, 401.

(9) (a) Kober, E. M.; Marshall, J. L.; Dressick, W. J., Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755. (b) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (c) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

(10) (a) Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 3184. (b) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213. (c) Ford, P. C. *Rev. Chem. Intermed.* **1979**, *2*, 267.

(11) (a) Pankuch, B. L.; Lackey, D. E.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2061. (b) Pankuch, B. J.; Lackey, D. E.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2068.

(12) (a) Sutin, N.; Creutz, C. *Inorganic and Organometallic Chemistry*; Wrighton, M. S., Ed.; Advances in Chemistry 168; American Chemical Society: Washington, DC, 1978; p 1. (b) Creutz, C.; Chou, M.; Netzel, T. L.; Okimura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

(13) (a) Reitz, G. A.; Dressick, W. J.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 5344. (b) Reitz, G. A.; Demas, J. N.; DeGraff, B. A.; Stephens, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 5051.

0020-1669/89/1328-1787$01.50/0

different emission wavelengths (λ_l and λ_s). $R(\lambda)$ is calculated from

$$R(\lambda) = E_l(\lambda)/E_s(\lambda) \qquad (1)$$

where the E's are the emission intensities for excitation at λ and monitoring at the long or short wavelengths (l or s). Since the sample absorbance and excitation intensities are the same at each excitation wavelength, R is related to the relative contribution of different emission components. If the sample and emission are homogeneous, E at each monitored λ arises from only one species, and $R(\lambda)$ is wavelength independent. If there are multiple emissions, $R(\lambda)$ varies with λ.

This procedure has advantages. Low-temperature absorption spectra or calibration of the excitation output is not required. It compensates for solvent absorption, is insensitive to solution absorbance even if the sample is optically dense and dilute in different regions, and works with fractured glasses.

To check for decomposition, several glasses were thawed and kept in the dark at room temperature (2–24 h) following emission measurements. Emission and excitation spectra were then recollected at 77 K.

Oxygen Stern–Volmer quenching constants (K_{SV}) and bimolecular and emission lifetimes (τ) were measured as described elsewhere.[16-19] Decays were single exponential with no fast component. Selected complexes were titrated in water with β-cyclodextrin (β-CD), cetyltrimethylammonium bromide (CTAB), or the nonionic polyether surfactant Brij 58[20] in aerated, deaerated, or O_2-saturated solutions. Data were fit as described earlier.[19,21]

Infrared spectra (KBr pellet) were obtained on a Nicolet 5DXB FTIR spectrometer. ^1H NMR spectra were collected (CD_2Cl_2) on a GE QE-300 FT NMR spectrometer (TMS reference). FAB mass spectra were recorded on a triple-quadrupole mass spectrometer.[22] In a glycerol matrix, samples were bombarded with 10-keV Cs^+ ions.

Reactivity Studies. Once it became clear the nitrile complexes were reactive toward alcohols and amines and were photochemically reactive, thermal and photochemical characterizations were performed. Small-scale reactions (1–2 mg) with selected nitrile complexes demonstrated reactivity toward EtOH, aniline, diethylamine, or isopropylamine. Some CH_2Cl_2 was added to solubilize the complex. Reactions with primary or secondary amines were at room temperature, while the EtOH and aniline reactions were refluxed. To isolate the EtOH reaction product, the reaction between EtOH and the $n = 2$ complex was scaled up (Et_3N catalyst) or all the kinetic runs for the $n = 17$ complex were combined. Orange products were isolated by chromatography.

Room-temperature kinetics were monitored by absorbance versus time (400 and 454 nm). Complexes were predissolved in a minimum volume of acetone. Photochemical decomposition efficiencies were measured by monitoring the emission intensity versus time for the $n = 13$ and 17 bpy complexes at 544 nm in stirred aqueous solutions under CW excitation (337 nm).

For photochemical analyses, an aqueous solution of the $n = 13$ complex was exhaustively photolyzed. The photolyte was extracted with diethyl ether and hexane. The extracts were combined, and the solvent was removed under vacuum. The residues were analyzed by NMR and IR spectroscopies (see supplementary material).

Results

Room-Temperature Spectra of the Nitrile Complexes. Figure 1 shows representative absorption and emission spectra for $Os(bpy)_2(CO)NC(CH_2)_{13}CH_3^{2+}$ and $Os(phen)_2(CO)NC(CH_2)_{17}CH_3^{2+}$. Spectra are virtually independent of n. For the bpy complexes absorptions occur at 260 nm ($\epsilon \sim 32\,000$ M^{-1} cm^{-1}), 300 nm ($\epsilon \sim 24\,000$ M^{-1} cm^{-1}), and 400 nm ($\epsilon = 2500$ M^{-1} cm^{-1}). Spectra in CH_2Cl_2, CH_3OH, diethyl ether–acetone, DMF, and H_2O are similar. The phen derivatives have intense absorptions at 226 nm ($\epsilon = 50\,000$ M^{-1} cm^{-1}) and 272 nm ($\epsilon = 45\,000$ M^{-1} cm^{-1}), and less intense ones at 344 and 392 nm ($\epsilon = 6200$ and 3800 M^{-1} cm^{-1}). Initially it appeared that there was a large absorption shift of the nitrile complexes in EtOH or EPA ($\lambda_{max} \sim 454$ nm for the bpy complex) that was mirrored by large emission changes. These shifts were traced to a rapid room-temperature reaction of the nitriles with EtOH; the spectral

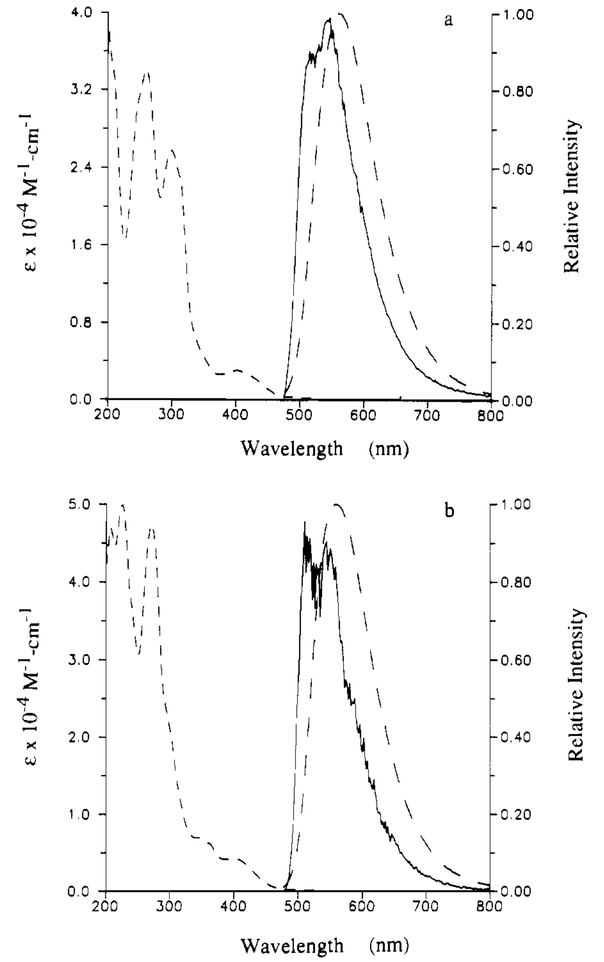

Figure 1. Room-temperature absorption (---) and emission (77 (—) and 298 K (--) of (a) $Os(bpy)_2(CO)NC(CH_2)_{13}CH_3^{2+}$ and (b) $Os(phen)_2(CO)NC(CH_2)_{17}CH_3^{2+}$. Emission spectra intensities have been arbitrarily scaled.

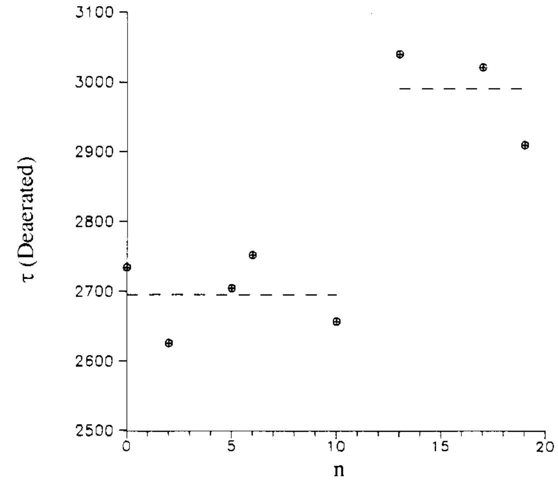

Figure 2. Plot of τ for deaerated CH_2Cl_2 solutions versus n of the $Os(bpy)_2(CO)(NC(CH_2)_nCH_3^{2+}$ series. Precisions were about 50 ns. The dashed lines are the averages for the early and later plateaus.

---

(14) Buckingham, D. A.; Dwyer, F. P.; Goodwin, H. A.; Sargeson, A. M. *Aust. J. Chem.* **1964**, *17*, 325.

(15) Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241.

(16) (a) Turley, T. J. M.S. Thesis, University of Virginia, 1980. (b) Turley, T. J.; Demas, J. N.; Demas, D. J. *Anal. Chim. Acta* **1987**, *197*, 121.

(17) Buell, S. L.; Demas, J. N. *Anal. Chem.* **1982**, *54*, 1214.

(18) Oxygen and Ozone. *IUPAC Solubility Data Series*; Battino, R., Ed.; Pergamon Press: Oxford, Great Britain, 1981; Vol. 7.

(19) Demas, J. N. *Excited State Lifetime Measurements*; Academic Press: New York, 1983.

(20) (a) Cline, J. I., III.; Dressick, W. J.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1985**, *89*, 94. (b) Hauenstein, B. L., Jr.; Dressick, W. J.; Gilbert, T. B.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1984**, *88*, 1902. (c) Buell, S. L.; Demas, J. N. *Rev. Sci. Instrum.* **1982**, *53*, 1298.

(21) Daniels, R. W. *An Introduction to Numerical Methods and Optimization Techniques*; North-Holland Publishing Co.: New York, 1978; Chapter 8.

(22) Hunt, D. F.; Giordani, A. B.; Rhodes, J.; Herold, D. A. *Clin. Chem. (Winston-Salem, N.C.)* **1982**, *28*, 2387.

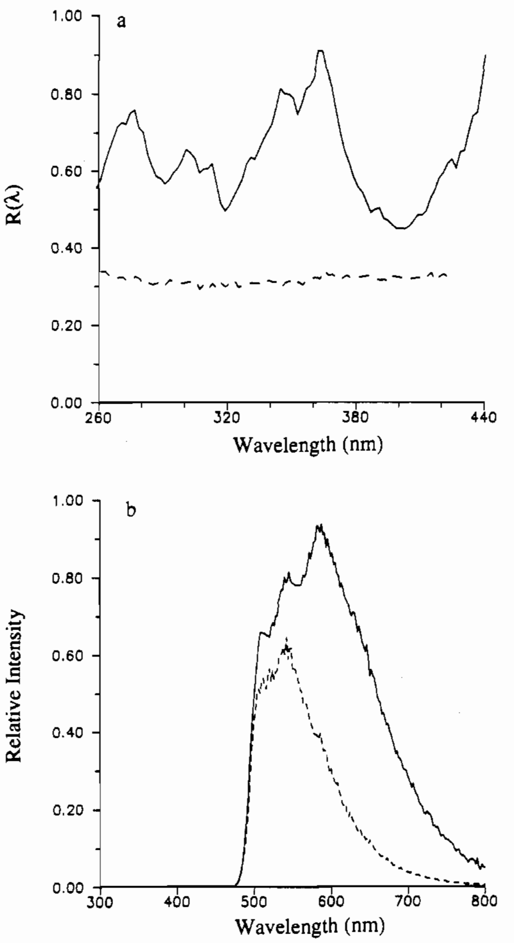

Figure 3. $R(\lambda)$ (a) and emission spectra (b) at 77 K of $Os(bpy)_2(CO)NC(CH_2)_{17}CH_3^{2+}$ in 4:1 $MeOH-H_2O$ glass: (---) quick-frozen solution; (—) solution after thawing and refreezing. Relative intensities cannot be compared.

changes were virtually finished in the dissolution time (<10 min). The reaction was detected by discovering that the EtOD spectra initially matched those for non-alcohol solvents and then changed to that observed for EtOH. The D isotope effect slowed the reaction enough to observe the unreacted complex. In CH_3OH the reaction is much slower.

Emission spectra were independent of oxygenation and of n. Emission maxima (CH_3CN) are 564 nm for the bpy complexes and 560 nm in the phen analogues. Small solvent effects are outside experimental resolution (±2 nm). For example, the $n = 2$ bpy complex emission shifts to 546 nm in CH_2Cl_2.

τ's of the bpy complexes in deoxygenated CH_2Cl_2 (Figure 2) are approximately 2.7 μs for the bpy n = 0–10 complexes, but exhibit a small, distinct increase between n = 10 and 13 and a new plateau at ~3.0 μs. The $k_q(O_2)$'s show no n dependence ($(1.8-1.9) \times 10^8$ M^{-1} s^{-1}). The n = 2 and 17 phen complexes have unquenched τ's of 11 μs and $k_q(O_2)$'s of 1.7×10^8 M^{-1} s^{-1}.

Titrations of the n = 17, 13, and 6 bpy complexes with Brij 58 or the n = 17 and 13 complexes with β-CD showed no significant changes in τ. However, the n = 13 complex binds weakly to CTAB (K_{DM} = 1300 M^{-1}). CTAB may bind in other cases, but the τ changes were too small to be sure.

Low-Temperature Emission and Excitation Data. The emission spectra of the n = 2, 6, and 17 bpy complexes in $DMF-CH_2Cl_2$ and the nitrile glasses are all very similar (Figure 1). They are slightly structured (λ_{max} = 512 and 542 nm).

Before recognizing the rapid reaction of the nitrile complexes, we measured a full series of emission spectra in EPA (77 K) of the bpy nitriles. For 300-nm excitation, the n = 0 emission was a broad, structureless band at λ = 564 nm. For the n = 2–7 complexes, the emission spectra consisted of two components: a structured emission with maxima at 510 and 540 nm and a lower energy, broad 590-nm band. The intensity ratio of the 590 nm to the 510 nm bands increased with n, and the n = 19 complex showed only the 590-nm band. In pure EtOH glasses, all the complexes had both the structure and the lower energy components with a much smaller n dependence. Exciting at 400 nm favors the 590-nm emission.

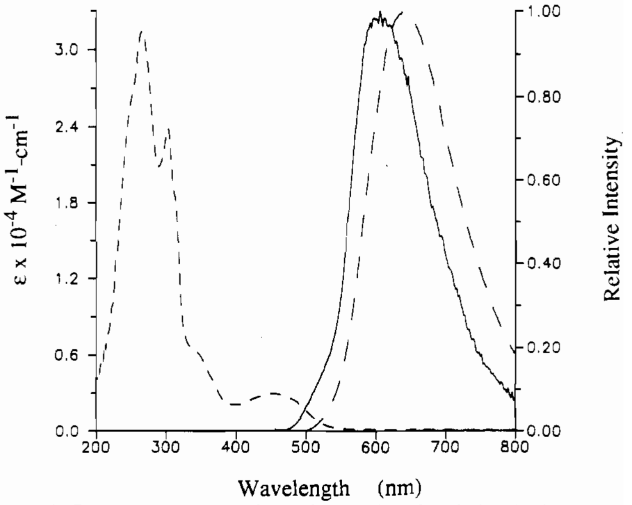

Figure 4. Room-temperature absorption (---) and emission (--) spectra of the n = 2 EtOH adduct in CH_2Cl_2 and 77 K emission spectra (—) in an EtOH glass.

To assess the origins of the different emission components, we measured $R(\lambda)$ (λ_l = 590 nm, λ_s = 514 nm). For the n = 17 bpy complex (Figure 3a), R(λ) shows selective enhancement of the 590-nm emission with lower energy excitation and has several maxima and minima.

Exploiting the much slower reaction of the nitriles in MeOH versus EtOH, we prepared $MeOH-H_2O$ solutions of the nitrile complexes as rapidly as possible and froze them. Figure 3b shows the emission spectra of quick-frozen and aged samples. The emission spectra of the quick-frozen solutions are very similar to those for the $DMF-CH_2Cl_2$ and nitrile glasses. Compare Figures 3b and 1a.

Further, $R(\lambda)$ for the quick-frozen sample is essentially flat (250–425 nm). After the MeOH glasses warmed to room temperature (several hours) and were refrozen, the emission spectra and $R(\lambda)$ closely resembled those of the EPA glasses.

Low-temperature τ's of selected bpy nitrile complexes measured in $DMF-CH_2Cl_2$ or nitrile glasses are ≈6.0 μs and are independent of n and the emission wavelength. EtOH glasses yielded 6.0-μs (514 or 540 nm) and ≈2.4-μs (590 nm) lifetimes.[23]

Thermal and Photochemical Reactions. After the discovery of the EtOH–nitrile complex reaction, a more systematic study was made to delineate the limitations for application of these complexes as sensitizers and molecular probes. In the following, we establish the pathway and relative rates of solvent attack and the mechanism of photodecomposition.

When the Os complexes are dissolved in EtOH or MeOH, the 400-nm band shifts to 454 nm (shoulder at 338 nm). The reactions occur without light and are clean over several half-lives with well-defined isosbestic points (334, 372, and 436 nm for the n = 17 bpy complex, and at 304, 348, 352, 358, and 403 nm for the n = 5 phen complex). In EtOH the lifetime is ~50 s. Rate constants (n = 2 and n = 17 bpy complexes) in different solvents are given in the supplementary material.

In alcoholic solutions, a drop of Et_3N greatly accelerates the reaction and a trace of H_2SO_4 inhibits it. Similar absorbance changes occur when the nitrile complexes are treated with other nucleophilic solvents such as diethylamine, isopropylamine, or aniline. Ethanolic NaOH reacts immediately with the nitrile complexes to form a purple product (λ_{max} = 244, 282, 364, and 526 nm).

---

(23) The n = 0 complex is anomalous. Although the lifetime measured at 590 nm is in line with the other complexes of the series, the 514 and 540 nm τ's are 3.2 μs.

Two products are isolated from the reactions of the $n = 2$ and $n = 17$ bpy complexes with EtOH: a purple complex having an absorption spectrum similar to the product from reaction of the nitrile complexes with OH^- and an orange one (λ_{max} = 268, 302, 340, and 452 nm) (Figure 4). The orange product is the initially formed product of the alcohol–nitrile reaction. The purple complex forms thermally later during workup; this side reaction accounts for the difficulty of isolating the orange material.

The orange nucleophilic adducts have broad room-temperature emissions (λ_{max} = 630–650 nm) in CH_2Cl_2. The $n = 2$ EtOH adduct emits at 638 nm. The $n = 17$ EtOH adduct exhibits similar spectra. The 77 K spectra of the EtOH adducts in EtOH have maxima at 606 nm (Figure 4).

τ of the $n = 2$ EtOH adduct in deoxygenated CH_2Cl_2 is 415 ns with $k_q(O_2) = 4.1 \times 10^8$ M^{-1} s^{-1}. τ at 77 K in an EtOH glass is 2.4 μs; however, the decay is somewhat nonexponential and can be fit with similarly weighted 1.0- and 3.0-μs components.

The unreacted $n = 17$ bpy nitrile complex exhibits a strong carbonyl stretch at 1972 cm^{-1}, C–H stretches at 2924 and 2859 cm^{-1}, and an intense P–F stretch at 829 cm^{-1}. The nitrile C–N triple-bond stretch should be in the 2100–2300 cm^{-1} range; however, it is generally weak, and we cannot unambiguously assign it.

The orange $n = 17$ EtOH adduct shows many of the same bands as the nitrile complex with a few significant exceptions. A sharp 3334-cm^{-1} peak is observed along with new bands at 1632, 1237, and 1068 cm^{-1}. The carbonyl stretching frequency decreases to 1958 cm^{-1}. A very similar IR spectrum is obtained from the crystalline $n = 2$ EtOH adduct.

The ^1H NMR spectra of the $n = 2$ parent and the $n = 2$ EtOH adduct exhibit similar aromatic resonances (7.39–9.33 ppm). The major difference is the shift of the parent doublet at 9.25 ppm to 8.92 ppm. The triplet at 0.81 ppm and multiplet at 1.60 ppm in the parent shift to 0.76 and 1.48 ppm in the adduct. New adduct peaks are centered at 4.36 and 4.26 ppm (multiplets) and at 2.63 ppm (triplet). In the mass spectrum of the $n = 2$ EtOH adduct, clusters of peaks occur at 502, 531, 644, and 791 mass units. Other prominent peaks are those characteristic of the glycerol matrix.

Under CW 337-nm excitation, all the nitrile complexes decompose. Decomposition quantum yields for the $n = 13$ and 17 bpy nitriles were the same within 2% at 0.022. The triflate complex was 0.072 and the pyridine complex was <0.0025. Photolysis of the $n = 17$ complex at 50 °C quadrupled the rate ($\Delta E = 3000$ cm^{-1}). Qualitatively, the bpy $n = 2$ and phen $n = 5$ complexes were similar. In contrast to shorter chain complexes, the $n = 17$ bpy complex in water was photochemically much more unstable in the 337-nm laser beam (at least 1 order of magnitude), and τ titrations could not be performed.

NMR and IR data for the $n = 13$ photolysis showed complete nitrile loss. No alkyl IR bands were found in the purple product, while NMR spectroscopy and GC of the organic extract revealed only the parent nitrile. The CO stretch in the metal complex product was comparable in intensity to the $n = 13$ nitrile complex, but shifted to 1957 cm^{-1}. We cannot exclude some CO photolabilization, but it would have to be a minor pathway. Only coordinated bpy was found in the aqueous layer, and the NMR data showed a cis configuration.

The triflate and nitrile decomposed photochemically and thermally to the same purple product, which showed reversible acid–base chemistry. We conclude that it is probably *cis*-Os$(bpy)_2CO(H_2O)^{2+}$.

Discussion

Recently we showed that the alkyl chains of nitrile ligands can dramatically perturb the excited states of Re(I) complexes.[13] This effect arises from an alteration of the solvent environment by an intramolecular chain foldback. This change perturbs the relative energies of the metal-to-ligand charge transfer (MLCT) and π–π^* states with a concomitant change in the decay processes.

However, our analogous Os(II) complexes having two cis bipyridines show significant differences. Absorption and emission spectra are independent of n, and the τ changes with n are much smaller with a different n dependence.

Surprisingly, the coordinated nitrile ligands are activated toward nucleophilic addition and react to yield a new class of luminescent imino ether complexes. Alcohol addition to the nitriles occurs at room temperature, which makes these some of the most reactive coordinated nitriles yet observed.

Nucleophilic Reactions of the Coordinated Nitriles. All Os nitrile complexes react with nucleophilic solvents (e.g. alcohols and amines) to yield products with MLCT absorptions at ~460–480 nm. The basic amines react very rapidly at room temperature, while the alcohols, particularly CH_3OH, react more slowly. Heating is required with aniline.

Coordinated nitriles in Ni, Pt, and Re complexes react with nucleophiles (e.g. alcohols, and aliphatic and aromatic amines)[24-26] by addition of RN–H or RO–H across the C–N triple bond to form coordinated R′(RN)C=NH or R′(RO)C=NH species. Et_3N catalyzes these reactions.[25]

For the $n = 17$ bpy EtOH adduct, the sharp 3334-cm^{-1} peak is characteristic of N–H stretches. The 1632-cm^{-1} band is assigned to a C=N stretch. IR bands that occur at frequencies similar to the 1237 and 1060 cm^{-1} bands of the EtOH adduct have been assigned to C–O single-bond stretches in similar Re complexes.[26] The CO stretch decreases by ~14 cm^{-1}, indicating increased electron density at the Os, probably because of the loss of nitrile back-bonding. The $n = 2$ EtOH adduct has the same features.

NMR data confirm the imino ether assignment. The pattern of aromatic resonances for both the nitrile and the adduct are characteristic of the cis configuration.[27] However, there are differences in chemical shifts between the two complexes for some of the multiplets. The largest change is the shift of the doublet at 9.25 ppm to 8.92 ppm. This doublet must correspond to one of the 3 or 3′ protons, and the chemical shift change probably arises from the interaction of the proton with the more sterically bulky imine ligand. The triplet and multiplet at 0.81 and 1.60 ppm in the parent compound correspond to the methyl and the methylene protons of the nitrile ligand, respectively. Both resonances are shifted slightly upfield (~0.12 ppm) in the adduct. The multiplets centered at 4.36 and 4.26 ppm are assigned to the methylene protons of CH_3CH_2O–; these are inequivalent because of the Os center asymmetry. The 2.63 ppm triplet corresponds to the methyl protons of the same group.

In the MS spectrum of the $n = 2$ EtOH adduct, the highest mass component corresponds to the parent minus one PF_6 (791). Additional fragments correspond to the consecutive losses of the second PF_6 counterion (644), the imine ligand (531), and the CO ligand (502).

Thus, IR, NMR, and mass spectra prove the orange $n = 2$ and $n = 17$ EtOH adducts are imino ether complexes. As the spectra are similar for all complexes, the initially formed alcohol adducts are all imino ethers. While no amine products were isolated, the similar chemistry of other coordinated nitriles coupled with our well-characterized alcohol adducts suggests a similar nucleophilic addition.

The activation of our nitriles probably arises because of the 2+ charge on Os enhanced by the strong π-accepting CO. Increased positive charge on the nitrile carbon enhances nucleophilic reactivity. Nucleophilic attack and protonation of the nitrile nitrogen leads to the imine. Our results represent the first direct demonstrations of such a reaction for an α-diimine complex, although a similar reaction was suggested for the hydrolysis of $[Os(terpy)(bpy)(NCCH_3)]^{3+}$ to $[Os(terpy)(bpy)(OH)]^{2+}$.[28]

---

(24) (a) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1. (b) Habib, M.; Trujillo, H.; Alexander, A. A.; Storhoff, B. N. *Inorg. Chem.* **1985**, *24*, 2344. (c) Suzuki, K.; Nakamura, S. *Inorg. Chim. Acta* **1977**, *25*, L21. (d) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1971**, *10*, 2699.

(25) Wada, M.; Shimohigashi, T.; *Inorg. Chem.* **1976**, *15*, 954.

(26) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 489.

(27) Birchall, T. D.; O'Donoghue, T. D.; Wood, J. R. *Inorg. Chim. Acta* **1979**, *37*, 1461.

(28) Buckingham, D. A.; Dwyer, F. P.; Sargeson, A. M. *Aust. J. Chem.* **1964**, *17*, 622.

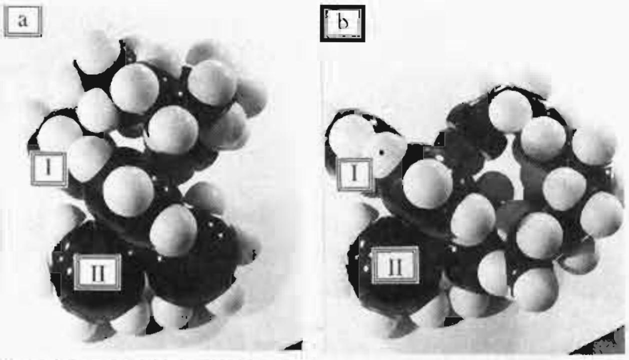

Figure 5. Space-filling models showing the limiting overlap of the n = 9 complex with bpy I (a) and bpy II (b). The coverage of I is much greater than II.

Room-Temperature Absorption and Emission Results. The intense, high-energy absorptions (260–300 nm) for the bpy complexes are assigned to ligand π–π^* transitions in analogy to those observed from protonated bpy[29] and similar Os(II) and Ru(II) bpy complexes.[30] The 400-nm absorption has been assigned to a $d\pi(Os) \rightarrow \pi^*(bpy)$ transition in the parent CH_3CN complex.[15] For the phen complexes, the ligand π–π^* transitions are at 226 and 272 nm, and the 392-nm transition is assigned as $d\pi(Os) \rightarrow \pi^*(phen)$. The 344 absorption maximum is probably a result of overlap of transitions of both types.

Some degree of solvent dependence is expected for CT transitions,[31] but $Os^{II}(bpy)_2X_2$ species show a very small solvent effect. λ_{abs} shifts <200–300 cm^{-1} over the range of solvents used. For example, the lowest energy CT maxima shift to the red by 40–150 cm^{-1} when the solvent is changed from CH_2Cl_2 to DMF.[32] We observed similar shifts (magnitude and direction) for the $[Os(bpy)_2(CO)(NC(CH_2)_nCH_3)]^{2+}$ series; the full range was <5 nm for CH_2Cl_2 to DMF. A slightly more pronounced solvent effect is observed in the room-temperature emission spectra (λ_{max} blue shifts by ~500 cm^{-1} from CH_3CN to CH_2Cl_2).

The n-dependence of the CT absorption or emission for our series of Os complexes is not detectable. Either intramolecular foldback does not occur or, more likely, the solvent effect of the bpy–alkyl-chain interaction is imperceptible. However, as with the Re(I) complexes, we do see a break in τ as a function of alkyl-chain length (Figure 2); the magnitude is smaller and the break for the *fac*-Re complexes occurs between n = 5 and 10 while for the Os complexes it is between n = 10 and 13.

We attribute the different breakpoints to the very different geometric constraints of foldback in the *cis*-$Os(bpy)_2(CO)NC(CH_2)_nCH_3^{2+}$ complexes versus the *fac*-$Re(bpy)(CO)_3NC(CH_2)_nCH_3^+$ complexes. The cis complexes have two inequivalent bpy's. Figure 5 shows $[Os(bpy)_2(CO)NC(CH_2)_9CH_3]^{2+}$. One bpy (I) is geometrically equivalent to the bpy of the Re(I) complexes (i.e. both bpy nitrogens are cis to the nitrile). The other bpy (II) is more distant from the nitrile and has one nitrogen that is cis and one that is trans to the NCR. There are two limiting foldback cases: the alkyl chain can fold onto bpy I or onto bpy II. See Figure 5, parts a and b, respectively, where we assume the maximum overlap of the chain with each bpy. Also, compare Figure 5a and Figure 2 in ref 13a.

On the basis of the Re results, we expected a large excited-state perturbation for the long-chained Os complexes (n = 5–10). This was not observed probably because the two bpy's are electronically inequivalent. There are energetically two distinct MLCT transitions, one to bpy I and the other to bpy II. Because CO is a better π-acid than NCR, the lowest lying π^* orbital and, thus, the CT state, arises from bpy II. This assignment is supported by the effect of trans CO on MLCT states of $Ru(bpy)_2(CO)_2$[33] and the origin of the lowest MLCT state of $Os(bpy)_2(CO)X$ with X.[15] Thus, we conclude that the lowest CT state in our nitrile complexes, the one responsible for the emission, is an MLCT state originating on bpy II. As supported by our models, n must exceed 9 for appreciable chain interaction with bpy II. Environmental changes around a bpy not involved in the emission can have little effect on the emission, and as expected, we do not observe an n effect for $n < 11$. For the longer chains ($n > 10$), however, the alkyl chain can overlap strongly with the bpy involved in the emission, and we would expect the observed change in the emission properties.

Thus, for intramolecular foldback to affect emission properties not only must a favorable geometric interaction exist with the ligands involved in the absorption process, but the interaction must be with the ligand actively involved in the emission. In the Os complexes, foldback to bpy I affects higher energy absorptions but has no effect on the emission. An emission effect can only arise when the chain is long enough to reach the more distant bpy II, which has the lowest CT state and is the one responsible for emission. In the Re complexes, there is only a near bpy and any interaction must affect the emission.

The τ changes on foldback are much smaller than those for Re(I) species. This is not surprising, however, since the MLCT absorption spectra of analogous Os(II) species[32] and our complexes are largely insensitive to environment.

The τ's of the nitrile complexes show little, if any, changes in solutions of Brij 58 or β-CD. Earlier binding studies with Ru(II)[20a,b,34] and Re(I) complexes[13] leave little doubt that the Os complexes with longer chains ($n > 6$) must be binding to the micelles and CD, but the τ changes are too small to detect. Because the solvent effect of the nitrile chain is very small, binding of the hydrocarbon to CD or micelles, which will remove the alkyl chain from the bpy, cannot greatly affect τ.

Initially, it was surprising that the CD or Brij 58 micelles did not protect the complexes from O_2 quenching. There are very plausible reasons. We showed that only RuL_3^{2+} complexes with hydrophobic L's efficiently bind to nonionic surfactants. For example, $Ru(bpy)_3^{2+}$ is too hydrophilic to bind to nonionic surfactants. For the n = 17 and n = 13 Os(II) complexes, the very hydrophobic nitrile ligands certainly bind, but the emitting divalent hydrophilic $Os(bpy)_2^{2+}$ center is in too aqueous an environment and is too far removed from the CD or micelle to be affected. Also, excitation resides predominantly on bpy II, which is more remote from the point of binding and, thus, exhibits little shielding.

The n = 13 complex binds weakly to cationic CTAB micelles. This is expected. The hydrophobic tail of the alkyl chain can bind to the micelle, even if the positive metal center is repelled.

The high photochemical reactivity of $[Os(bpy)_2(CO)NC(CH_2)_nCH_3]^{2+}$ complexes compared to $[Os(bpy)_2(CO)(py)]^{2+}$ is in keeping with the well-known photoactivity of thermally accessible d–d states. We suggest that our Os nitrile complexes labilize nitrile from a d–d state. Although d–d states are normally not thermally accessible in Os(II) complexes because of the large ligand-field splitting,[12b,35] experimental evidence suggests that a strong back-bonding CO ligand in combination with other ligands can decrease the d–d energies relative to the emitting CT state.[31a] For example, $Os(bpy)_2CO(DMSO)^{2+}$ is quite photosensitive, presumably via a nearby d–d state.[31b] The large increase in photoreactivity with increasing temperature is similar to that for d–d-assisted decomposition of Ru(II) complexes.[36] The anomalously high photochemical sensitivity of the n = 17 complex under

---

(29) Gondo, Y.; Kanda, Y. *Bull. Chem. Soc. Jpn.* **1965**, *4*, 39.

(30) (a) Fergusson, J. E.; Harris, G. M. *J. Chem. Soc. A* **1966**, 1293. (b) Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.* **1971**, *24*, 275. (c) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(31) (a) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (b) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755.

(32) Kober, E. M.; Sullivan, B. P. *Inorg. Chem.* **1984**, *23*, 2098.

(33) Pinnick, D. V.; Durham, B. *Inorg. Chem.* **1984**, *23*, 1440.

(34) (a) Mandal, K.; Hauenstein, B. L., Jr.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1983**, *87*, 328. (b) Dressick, W. J.; Demas, J. N.; DeGraff, B. A. *J. Photochem.* **1984**, *24*, 45. (c) Dressick, W. J.; Cline, J., III.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 7567.

(35) Allen, G. H.; Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc. Chem. Commun.* **1981**, 793.

(36) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17*, 3381.

pulsed conditions may arise from multiphoton excitation of aggregates that permit energy pooling and open decomposition paths not available with single molecules.

Low-Temperature Emission Data. The emission energies, the τ's, and the structure of the 77 K emission spectra leave no doubt that all the emissions are MLCT in nature. The broad emission is slightly structured ($\Delta E \sim 1000$ cm^{-1}), and the highest energy maximum is $\sim$1800 cm^{-1} higher in energy than the 298 K emission maximum. The energy of the vibrational structure is consistent with framework stretching modes characteristic of bpy or phen rings;[37] this is a common characteristic of MLCT emissions.

The emissions of the nitrile complexes in EPA, EtOH, or aged $MeOH/H_2O$ glasses also have a 590-nm component, which arises from the imino ether complex formed by nucleophilic attack of the alcohol on the nitrile ligand. This is shown by the fact that the emission spectra of the alcoholic glasses can be reconstructed as a sum of the parent nitrile complex and the pure EtOH adduct spectra (Figure 4). If the $MeOH/H_2O$ glasses are frozen quickly after complex dissolution, the emission spectra are similar to those in non-hydroxylic solvents. However, when solutions were held at room temperature for short periods before freezing, or thawed and refrozen, the 590-nm emission dominates. The "chain-length effect" on the 77 K emission spectra simply reflected different reaction times in solution.

Further, the alcoholic reaction products have two τ's. The τ of the high-energy component is 6 μs, which matches the values of the nitrile complex in DMF and nitrile glasses or the unreacted MeOH glass. The 590-nm emission τ is 2.9 μs, which matches the 2.4 μs of the pure adduct in an EtOH glass.

The $R(\lambda)$'s are flat in non-hydroxylic solvents and for controls such as $Ru(bpy)_3^{2+}$, while glasses having a predominant $\sim$590-nm emission show significant structure. Minima correspond roughly to absorption maxima of the nitrile complex, and maxima correspond roughly to the maxima of the pure adduct. Thus, the excitation results are fully explainable by a mixture of the adduct and the parent nitrile.

Lifetimes measured at 590 or 514 nm for the pure nitrile complexes are independent of n except for the $n = 0$ complex, which is somewhat shorter at 77 K. The $n = 0$ Re(I) complex from an analogous series has been shown to give anomalous emission data relative to data for the longer chain homologues; this has been attributed to a difference in the inductive effect of a-CH_2 versus a-CH_3 group.[13b]

In the Re(I) series, alkyl-chain foldback radically affected the emitting state at 77 K; the relative amounts of CT and $^3\pi$–π^* emissions depend strongly on n.[13] There is no analogous effect in the Os(II) systems. State energetics explain this effect. The emitting CT states are too far below the $^3\pi$–π^* state to be thermally populated at room temperature. The 0–0 emission maxima are 458 nm for the $^3\pi$–π^* phosphorescence of bound bpy and 510 nm for the CT emissions of the Os nitrile complexes. Also, the CT states of the nitriles are insensitive to even gross solvent changes, and foldback cannot push the emitting MLCT states close enough to the $^3\pi$–π^* state to allow $^3\pi$–π^* phosphorescence.

A useful predictor of systems that will exhibit larger perturbation of luminescence properties due to alkyl-chain foldback is significant solvatochromism. We suggest that a possible explanation of the large n dependence in the Re(I) species is an energy gap law effect. Changes in the emitting-state energy change the radiationless rates and, thus, the quantum yield and τ. The Re(I) complexes exhibit large absorption and emission solvatochromism and, therefore, are susceptible to large changes in luminescence properties on foldback. The Os(II) nitriles are virtually insensitive to even gross solvent changes, and foldback can only minimally perturb the luminescence. Thus, in any search for new systems exhibiting intramolecular foldback interactions, one must seek core molecular frameworks with large solvatochromic effects.

Conclusions

A new class of surfactant-active Os(II) complexes were synthesized. These species show intramolecular perturbation of excited-state properties by what are normally considered electronically passive ligands and demonstrate that the effect is not restricted to Re(I) complexes. However, for the appearance of an intramolecular foldback effect, the chain must interact with a ligand directly involved in the emission. For optimal effect, the emission should be highly solvatochromic. Further, we have demonstrated a previously unobserved, highly activated, bound RCN in an α-diimine complex. Also, the complexes are photochemically labile. These are highly photoactive Os(II) complexes in what is normally a photochemically robust series. Presumably decomposition is through the intervention of proximal d–d states. Unfortunately, these reactions make these species less useful as sensitizers and as probes of macromolecular structure. Work on less reactive, environmentally sensitive photosensitizers is in progress.

Acknowledgment. We gratefully acknowledge support by the National Science Foundation (Grant CHE 8600012). We thank Jeff Shabanowitz for running the mass spectrum and assisting in its interpretation, Hewlett-Packard for the gift of the 8452 spectrometer, H. Wilson for assistance, and W. L. S. Andrews for use of his BH-6 lamp.

Registry No. Brij 58, 9004-95-9; β-CD, 7585-39-9; CTAB, 5306-78-5; *cis*-$[Os(bpy)_2(CO)(CF_3SO_3)](CF_3SO_3)$, 89689-72-5; EtOH, 64-17-5; MeOH, 67-56-1; *cis*-$Os(bpy)_2(CO)NCCH_3^{2+}$, 119816-15-8; *cis*-$Os(bpy)_2(CO)NCCH_2CH_3^{2+}$, 119742-73-3; *cis*-$Os(bpy)_2(CO)NC(CH_2)_2CH_3^{2+}$, 119742-74-4; *cis*-$Os(bpy)_2(CO)NC(CH_2)_3CH_3^{2+}$, 119742-75-5; *cis*-$Os(bpy)_2(CO)NC(CH_2)_4CH_3^{2+}$, 119742-76-6; *cis*-$Os(bpy)_2(CO)NC(CH_2)_5CH_3^{2+}$, 119742-77-7; *cis*-$Os(bpy)_2(CO)NC(CH_2)_6CH_3^{2+}$, 119742-78-8; *cis*-$Os(bpy)_2(CO)NC(CH_2)_7CH_3^{2+}$, 119742-79-9; *cis*-$Os(bpy)_2(CO)NC(CH_2)_8CH_3^{2+}$, 119787-16-5; *cis*-$Os(bpy)_2(CO)NC(CH_2)_9CH_3^{2+}$, 119742-80-2; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{10}CH_3^{2+}$, 119742-81-3; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{11}CH_3^{2+}$, 119742-82-4; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{12}CH_3^{2+}$, 119742-83-5; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{13}CH_3^{2+}$, 119742-84-6; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{14}CH_3^{2+}$, 119742-85-7; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{15}CH_3^{2+}$, 119742-86-8; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{16}CH_3^{2+}$, 119742-87-9; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{17}CH_3^{2+}$, 119742-88-0; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{18}CH_3^{2+}$, 119742-89-1; *cis*-$Os(bpy)_2(CO)NC(CH_2)_{19}CH_3^{2+}$, 119742-90-4; *cis*-$Os(phen)_2(CO)NCCH_3^{2+}$, 119742-91-5; *cis*-$Os(phen)_2(CO)NCCH_2CH_3^{2+}$, 119742-92-6; *cis*-$Os(phen)_2(CO)NC(CH_2)_2CH_3^{2+}$, 119742-93-7; *cis*-$Os(phen)_2(CO)NC(CH_2)_3CH_3^{2+}$, 119742-94-8; *cis*-$Os(phen)_2(CO)NC(CH_2)_4CH_3^{2+}$, 119742-95-9; *cis*-$Os(phen)_2(CO)NC(CH_2)_5CH_3^{2+}$, 119742-96-0; *cis*-$Os(phen)_2(CO)NC(CH_2)_6CH_3^{2+}$, 119742-97-1; *cis*-$Os(phen)_2(CO)NC(CH_2)_7CH_3^{2+}$, 119742-98-2; *cis*-$Os(phen)_2(CO)NC(CH_2)_8CH_3^{2+}$, 119742-99-3; *cis*-$Os(phen)_2(CO)NC(CH_2)_9CH_3^{2+}$, 119743-00-9; *cis*-$Os(phen)_2(CO)NC(CH_2)_{10}CH_3^{2+}$, 119743-01-0; *cis*-$Os(phen)_2(CO)NC(CH_2)_{11}CH_3^{2+}$, 119743-02-1; *cis*-$Os(phen)_2(CO)NC(CH_2)_{12}CH_3^{2+}$, 119743-03-2; *cis*-$Os(phen)_2(CO)NC(CH_2)_{13}CH_3^{2+}$, 119743-04-3; *cis*-$Os(phen)_2(CO)NC(CH_2)_{14}CH_3^{2+}$, 119743-05-4; *cis*-$Os(phen)_2(CO)NC(CH_2)_{15}CH_3^{2+}$, 119743-06-5; *cis*-$Os(phen)_2(CO)NC(CH_2)_{16}CH_3^{2+}$, 119743-07-6; *cis*-$Os(phen)_2(CO)NC(CH_2)_{17}CH_3^{2+}$, 119743-08-7; *cis*-$Os(phen)_2(CO)NC(CH_2)_{18}CH_3^{2+}$, 119743-09-8; *cis*-$Os(phen)_2(CO)NC(CH_2)_{19}CH_3^{2+}$, 119743-10-1; $CH_3(CH_2)_{17}CN$, 28623-46-3; $CH_3(CH_2)_2CN$, 109-74-0; *cis*-$Os(bpy)_2(CO)[NH{=}C(OEt)(CH_2)_2CH_3]$, 119743-13-4; *cis*-$Os(bpy)_2(CO)[NH{=}C(OEt)(CH_2)_{17}CH_3]$, 119743-14-5; *cis*-$[Os(phen)_2(CO)(CF_3SO_3)](CF_3SO_3)$, 119743-12-3; D_2, 7782-39-0; aniline, 62-53-3; diethylamine, 109-89-7; isopropylamine, 75-31-0.

Supplementary Material Available: Experimental details and a listing of nucleophilic addition rate constants (Table I) (2 pages). Ordering information is given on any current masthead page.

---

(37) (a) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 106. (b) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.