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Properties of Osmium(II) Photosensitizers in Aqueous and Sodium Lauryl Sulfate Micellar Media

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The spectroscopy, electrochemistry, and photochemical properties of several cis-$L_2OsXX'^{2+}$ complexes (L = 2,2'-bipyridine and 1,10-phenanthroline; X, X' = nitriles, isocyanides, phosphines, and other strong π-acceptor ligands) and (2,2',2''-terpyridine)$_2Os^{2+}$ in aqueous and sodium lauryl sulfate (NaLS) micellar solutions are described. The quenching of the luminescence by $HgCl_2$ in both media is investigated. Our results are compared to those obtained earlier for the RuL_3^{2+} complexes. The Os(II) photosensitizers are much more reactive electron-transfer photosensitizers than similar Ru(II) complexes. The anionic micelles enhance separation of Hg(I) free-radical photoproducts 3-fold over the surfactant-free system.

Introduction

Numerous schemes have been developed for converting sunlight into electrical or chemical energy.[1-7] Frequently, (polypyridyl)ruthenium(II) complexes are used as sensitizers to achieve this conversion. Comparatively little work has been done on conversion approaches using sensitizers that incorporate other elements, especially the third-row transition metals.

Recently, however, Meyer and co-workers[8,9] have prepared a new series of osmium-based complexes exhibiting room-temperature metal-to-ligand charge-transfer (MLCT) luminescence. These complexes are cis-$L_2OsXX'^{2+}$ where L is 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen). X and X' include various nitriles, isocyanides, phosphines, arsines, and other strong π-acceptor ligands. Properties such as the lifetimes, emission energies, and excited-state redox potentials can be precisely controlled by judicious choice of X and X'.[10-12] In addition, these complexes are more photochemically stable than the analogous RuL_3^{2+} complexes.[13-16] The investigation of the properties of these osmium(II) complexes has been confined largely to nonaqueous solvents.[8-12] Consequently, there exist few data concerning the ground- and excited-state properties of these compounds in the important aqueous media.[17,18] There are no data available for the increasingly important micellar systems.

We describe the spectroscopic, electrochemical, and photochemical properties of several of these complexes in aqueous and sodium lauryl sulfate (NaLS) micellar solutions. In addition, the quenching of the luminescence by $HgCl_2$ in both media is investigated. Our results are compared to those obtained earlier for the RuL_3^{2+} complexes,[19,20] and an attempt is made to interpret the quenching behavior by using Marcus electron-transfer theory. The Os(II) complexes are more reactive electron-transfer sensitizers than similar Ru(II) complexes.

Experimental Section

Laboratory deionized water was distilled from alkaline $KMnO_4$. Electrophoresis grade NaLS from Bio-Red Laboratories was recrystallized from methanol and vacuum-dried. Mercury(II) dichloride was used as received from Mallinckrodt. Vycor double-distilled nitric acid was used in the preparation of the solutions for the quenching experiments. Sodium nitrate, $NaClO_4$, and NaCN were all Fisher ACS reagent grade. Methyl iodide was used as received from Aldrich.

$Ru(bpy)_3Cl_2$ from G. Frederick Smith Chemicals was metathesized to the ClO_4^- salt and recrystallized once from water. The ClO_4^- was judged to be pure on the basis of the results of chromatography and elemental analysis (vide infra). Ligands for the synthesis of the osmium(II) complexes were purchased from Strem and were used without further purification. The ligands and their abbreviations are

Table I. Elemental Analyses for the Complexes[a]

complex	anal. calcd (found)		
	% C	% H	% N
$Ru(bpy)_3(ClO_4)_2$ (Ru(bpy))	56.25 (56.82)	3.12 (3.20)	10.93 (10.94)
$(terpy)_2Os(Cl)_2 \cdot 2H_2O$ (terpy)	47.14 (47.45)	3.23 (3.69)	10.43 (10.20)
$(phen)_3Os(Cl)_2 \cdot 2H_2O$ (phen)	51.61 (50.99)	3.34 (3.80)	10.03 (9.87)
$(phen)_2Os(DPPM)(ClO_4)_2$ (DPPM)	51.92 (52.02)	3.35 (3.29)	4.94 (5.01)
$(phen)_2Os(DPPene)(ClO_4)_2$ (DPPene)	52.42 (52.22)	3.32 (3.34)	4.89 (4.83)
$(bpy)_2Os(CNMe)_2(ClO_4)_2$ (CNMe)	undetermined[12]		
$(phen)_2Os(CO)(Cl)(ClO_4)$ (COCl)	42.08 (41.81)	2.24 (2.30)	7.85 (7.82)

[a] Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA 30366.

as follows: 2,2'-bipyridine (bpy); 1,10-phenanthroline (phen); 2,2',2''-terpyridine (terpy); bis(diphenylphosphino)methane (DPPM); cis-1,2-bis(diphenylphosphino)ethylene (DPPene). Ammonium hexachloroosmate from Alfa was used as received.

The compounds cis-$(bpy)_2OsCl_2$, cis-$(phen)_2OsCl_2$, and (terpy)$OsCl_3$ were synthesized from $(NH_4)_2OsCl_6$ by using the literature

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(3) Gratzel, M. *Acc. Chem. Res.* **1981**, *14*, 376.
(4) Dressick, W. J.; Meyer, T. J.; Durham, B.; Rillema, D. P. *Inorg. Chem.* **1982**, *21*, 3451.
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(6) Sutin, N. *J. Photochem.* **1979**, *10*, 19.
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(8) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383.
(9) Kober, E. M. Ph.D. Dissertation, The University of North Carolina, Chapel Hill, NC, 1982.
(10) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.
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(18) Balzani, V.; Bolletta, F.; Grandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.
(19) Hauenstein, B. L., Jr.; Mandal, K.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.*, in press.
(20) Dressick, W. J.; Hauenstein, B. L., Jr.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.*, in press.

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methods.[21-23] The osmium(II) complexes listed in Table I were prepared from these starting materials and purified as described previously.[8,9] All complexes were isolated as the perchlorate or chloride salts. The results of the elemental analyses were consistent with the formulations shown in Table I.[24]

The characterization of those complexes listed in Table I was carried out for both aqueous and NaLS solutions. With the exception of the electrochemical measurements (vide infra), all data for the NaLS micellar solutions were obtained at 10 mM NaLS. The micelle concentration, [M], for this solution was estimated to be $> \sim 30 \mu M$.[25] The sensitizer concentrations were $< \sim 20 \mu M$ in order to ensure that the micellar occupancy number did not exceed unity.[27]

Half-wave potentials, $E_{1/2}(III/II)$, for each complex were obtained from differential pulse polarograms. Data were obtained at 23 ± 2 °C in 0.1 M NaNO₃ supporting electrolyte by using a PAR Model 174A waveform programmer. The working and auxiliary electrodes were glassy carbon and platinum gauze, respectively, and the saturated calomel electrode (SCE) was the reference electrode. The $E_{1/2}$-(III/II)'s were calculated from[30]

$$E_{1/2}(III/II) = E_p + \Delta E/2 \tag{1}$$

where E_p is the potential at which the maximum current is noted and ΔE is the modulation voltage. A modulation voltage of 10 mV and a scan rate of 2 mV/s were used in all cases. Adequate signals were obtained for many of the complexes in aqueous solution in spite of the limited solubility ($< \sim 50 \mu M$) of several of the sensitizers. However, the diminished signals noted in the micellar medium required higher sensitizer concentrations (300 μM) in order to acquire usable data. A 50 mM NaLS solution was then used to ensure a subunity micellar occupancy number.[27]

Luminescence lifetimes were acquired with use of a N₂ laser-based system.[31] Samples were excited with the 337-nm laser line of a Molectron UV-14 pulsed nitrogen laser. The emission wavelength was selected with a Jobin-Yvon H-10 monochromator. The detection photomultiplier is an RCA C7164R with an ERMA photocathode. The electrical signals were acquired with a Tektronix 7912 transient digitizer. The digitized data were transferred by a custom interface to a Z-80 based microcomputer. All data reduction was handled in high-level BASIC programs. Lifetimes were determined from the slope of the semilog plot of the intensity vs. time. Such plots were linear over at least 2 half-lives. All solutions were thermostated at 25.0 ± 0.1 °C by using a homemade temperature controller[32] and deoxy-

Table II. Properties of the Sensitizers in Water and 10 mM NaLS Solution

complex	$\lambda_{em}{}^b$	$\lambda_{abs}{}^c$ $(\epsilon)^f$	$\tau_0{}^d$	$E_{1/2}(III/II)^e$
		Aqueous Results		
CNMe[a]	570.0 (588.0) [2.110]	366.0 (7600)[h]	552	>1.6[g]
DPPene	597.0 (612.5) [2.026]	366.0 (9890)	1020	1.41 ± 0.03
DPPM	610.0 (628.5) [1.974]	373.0 (10 100)	554	1.33 ± 0.02
phen	710.0 (727.0) [1.707]	428.5 (15 000)[i]	74	0.84 ± 0.01
terpy	715.0 (726.0) [1.709]	475.0 (14 200)	141	0.99 ± 0.02
Ru(bpy)	607.0 (617.0) [2.010]	452.0 (14 100)	620	1.288 ± 0.003
COCl	646.0 (676.5) [1.839]	365.0 (5745)	223	1.27 ± 0.02
		10 mM NaLS Results		
CNMe	587.5 (598.0) [2.075]	365.5	635	>1.6[g]
DPPene	614.0 (630.0) [1.969]	365.5 (9350)	900	1.45 ± 0.03
DPPM	626.5 (646.0) [1.920]	372.0 (9240)	602	1.35 ± 0.02
phen	733.0 (753.0) [1.648]	430.0 (14 000)	135	0.88 ± 0.02
terpy	722.0 (740.0) [1.677]	476.0 (12 000)	177	1.02 ± 0.03
Ru(bpy)	622.9 (638.2) [1.944]	453.0 (10 500)	772	1.321 ± 0.005
COCl	652.0 (693.0) [1.795]	365.0 (5714)	246	1.24 ± 0.03

[a] See Table I for the meaning of the abbreviations. [b] Uncorrected emission maxima in nanometers. The values in parentheses represent the emission maxima for spectra that have been corrected for the variation in detector sensitivity with wavelength. Values in brackets are the energies in electronvolts corresponding to the maximum in the corrected emission spectrum. [c] Position of the absorption maximum for the MLCT absorption in nanometers that is located in the visible region of the spectrum. [d] Lifetime of the complex in nanoseconds in N₂-bubble degassed fluid solution at 25.0 ± 0.1 °C. [e] Half-wave potential in volts vs. NHE for the reaction Os(III) + e⁻ → Os(II) calculated from eq 1. [f] Extinction coefficient in units of L mol⁻¹ cm⁻¹. [g] The true value of the potential is masked by the solvent oxidation wave. A lower limit is quoted. [h] Value from ref 9 in MeCN. [i] Note ref 17.

genated with a N₂ purge[33] in the dark for 45 min.

Absorption and emission spectra were acquired for each complex (10 μM) in both aqueous and 10 mM NaLS (aqueous) media. The spectra were unaffected by 0.1 M NaNO₃. Absorption spectra were obtained with use of a Cary 14 spectrophotometer. Corrected emission spectra were recorded on an SLM Model 8000 spectrofluorimeter with 450 ± 10 nm excitation. The emission maxima and band shape were independent of whether the solutions were aerated or deoxygenated.

Luminescence quenching was studied in both aqueous and 10 mM NaLS solutions. NaNO₃ (0.1 M) was employed as an ionic strength

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(22) Buckingham, D. A.; Dwyer, F. P.; Goodwin, H. A.; Sargeson, A. M. *Aust. J. Chem.* **1964**, *17*, 315.
(23) Buckingham, D. A.; Dwyer, F. P.; Sargeson, A. M. *Aust. J. Chem.* **1964**, *17*, 622.
(24) The elemental analysis for (bpy)₂Os(CNMe)₂(ClO₄)₂ is not reported due to an insufficient amount of sample. Although the synthesis of this complex appeared to proceed in moderate yields (25–35%), the presence of a side product (probably (bpy)₂Os(CNMe)(CN)⁺) that eluted with an R_f near that for the desired product precluded clean separation via chromatography in high yields. This problem has been encountered previously for this complex.[9] The complex was judged pure on the basis of (i) the observation of a single exponential decay for the excited-state lifetime and (ii) the observation of only a single peak in the emission spectrum in aqueous solution.
(25) The concentration of micelles in the solution is calculated from [M] = ([NaLS] – cmc)/N, where [M] is the micelle concentration in moles per liter, cmc is the critical micelle concentration, and N is the aggregation number. For NaLS the cmc = 8 mM and N = 70. For a solution containing [NaLS] = 10 mM, we calculate [M] = 3 × 10⁻⁵ M. Since the cmc has been observed to decrease in the presence of electrolytes, our value for [M] represents a lower limit.[26]
(26) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.
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(28) Turro, N. J.; Grätzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675.
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(31) Turley, T. J. M.S. Thesis, University of Virginia, Charlottesville, VA, 1980.
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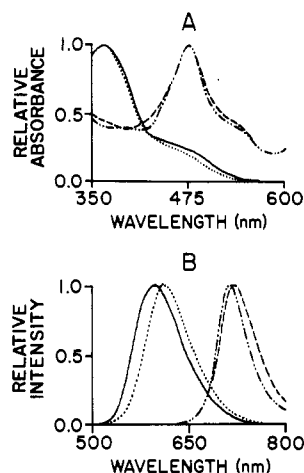(33) Buell, S. L.; Demas, J. N. *Rev. Sci. Instrum.* **1982**, *53*, 1298.

Figure 1. Absorption spectra (A) and emission spectra (B) of (phen)$_2$Os(DPPene)(ClO$_4$)$_2$ in water (—) and 10 mM NaLS (···) and (terpy)$_2$Os(Cl)$_2$ in water (–··–) and 10 mM NaLS (--). Emission spectra are uncorrected.

adjustor in both media. In all cases, solutions contained 0.01 M HNO$_3$ to prevent hydrolysis of the HgCl$_2$. All solutions were deoxygenated.

The Stern–Volmer constants (K_{sv}) for the quenching of the sensitizer luminescence by HgCl$_2$ were determined from the slope of the θ_0/θ vs. [HgCl$_2$] plots according to

$$\theta_0/\theta = 1 + K_{sv}[\text{HgCl}_2] \tag{2}$$

θ_0 and θ are the lifetimes, τ's, or in some cases emission intensities, I's, of the sensitizers in the absence of, and presence of, HgCl$_2$, respectively. The quenching rate constants, k_q (M^{-1} s^{-1}), are calculated from $k_q = K_{sv}/\tau_0$. A linear least-squares routine was used to fit the experimental data, which were linear within experimental error.

The determination of net electron-transfer efficiencies was done by using a flash photolysis system described previously.[34] We report ϕ_{et}^0's, which are the detectable electron-transfer efficiencies corrected to complete quenching of the excited state. A double-jacketed photolysis cell was used with the outer jacket filled with 1.0 M NaNO$_2$ and 0.20 M Cu(NH$_3$)$_4^{2+}$ in 5 M NH$_4$OH. This limited the exciting light pulse to 400 < λ < 500 nm. The aqueous solutions were purged for 45 min with N$_2$ prior to use while the micellar solutions were degassed by the freeze–pump–thaw method.

The concentration of sensitizer was fixed for all experiments. Since there has been no "absolute" determination of ϕ^0 for an Os(II) complex, the results are based on an assumed $\phi_{et}^0 = 1.0$ for the fully quenched (phen)$_2$Os(CO)Cl$^+$/Fe^{3+} system. Since it has been shown that Os(II) complexes usually quench as well as their Ru(II) counterparts[7] and $\phi_{et}^0 = 1.0$ for the Ru(bpy)$_3^{2+}$/Fe^{3+} system,[35] our assumption is probably reasonable. Regardless of this assumption, however, the relative values of ϕ_{et}^0 and the trends they depict are valid. Further experimental details are given elsewhere.[36]

Results

Table I shows the elemental analyses for the complexes described as well as the abbreviations used to identify the sensitizers. All analyses were satisfactory.[24] Table II summarizes the properties in aqueous and 10 mM aqueous NaLS solution.

Several interesting effects are noted in these properties upon proceeding from the aqueous to the micellar solutions. In particular, the lifetimes of the complexes in the micellar environment differ from the corresponding values in aqueous solutions. In addition, red shifts are observed in the emission maxima for all complexes. Emission spectra for (phen)$_2$Os-

Table III. Quenching Results for the Os(II) Sensitizers

complex	*$E_{1/2}$(III/II)[b]	$K_{sv}^{c,d}$	$10^{-6}k_q^{c,d}$
		Aqueous Results	
CNMe[a]	>–0.60[e]	48.0 ± 6.0	87 ± 12
		(55.7 ± 6.5)	(101 ± 20)
DPPene	–0.67 ± 0.10	340 ± 35	333 ± 41
DPPM	–0.70 ± 0.10	380 ± 34	689 ± 76
		(452 ± 50)	(820 ± 100)
phen	–0.91 ± 0.07	f	
terpy	–0.75 ± 0.08	10.7 ± 0.7	66.4 ± 6.7
Ru(bpy)	–0.76 ± 0.08	107 ± 9[g]	22.9 ± 3.6
COCl	–0.57 ± 0.08	153 ± 8	689 ± 70
		10 mM NaLS Results	
CNMe	>–0.50[e]	1.69 ± 0.15	2.66 ± 0.32
DPPene	–0.57 ± 0.10	2.93 ± 0.36	3.28 ± 0.52
		(3.34 ± 0.30)	(3.74 ± 0.42)
DPPM	–0.63 ± 0.10	3.40 ± 0.40	5.34 ± 0.81
		(4.07 ± 0.40)	(6.40 ± 0.70)
phen	–0.81 ± 0.10	<1.50	<11.1
		(1.57 ± 0.07)	(1.14 ± 0.12)
terpy	–0.70 ± 0.10	0.28 ± 0.04	10.4 ± 3.1
Ru(bpy)	–0.67 ± 0.10	1.42 ± 0.14[h]	1.84 ± 0.26
COCl	–0.56 ± 0.10	11.1 ± 0.4	45.1 ± 5.0

^{a} See Table I for the meaning of the abbreviations. ^{b} Excited-state reduction potential in volts vs. NHE calculated by using eq 3. ^{c} K_{sv}'s in M^{-1} and k_q's in M^{-1} s^{-1}. ^{d} Values measured by either the lifetime or intensity methods. Intensity values are in parentheses. ^{e} The uncertainty in the $E_{1/2}$(III/II) value for this complex (note Table II) prohibits the determination of this value. An upper limit is given. ^{f} Values undetermined due to precipitation. ^{g} From ref 19. ^{h} From ref 20.

(DPPene)(ClO$_4$)$_2$ and (terpy)$_2$Os(Cl)$_2$ are shown in Figure 1.

Absorption spectra of the Os(II) complexes in both aqueous and micellar environment are remarkably similar. The complexes, (phen)$_3$Os(Cl)$_2$ and (terpy)$_2$Os(Cl)$_2$, exhibit small but definite red shifts in their absorption maxima. Such shifts have been noted for the analogous RuL$_3^{2+}$ complexes under similar conditions.[37] The extinction coefficients of the complexes in micellar solution are only slightly altered (<15% change) over the corresponding aqueous values. Absorption spectra for (phen)$_2$Os(DPPene)(ClO$_4$)$_2$ and (terpy)$_2$Os(Cl)$_2$ are shown in Figure 1.

Half-wave potentials measured in the micellar solution exhibit anodic shifts when compared to the corresponding values in aqueous solution. The change in $E_{1/2}$(III/II) is usually 20–30 mV. The anomalous 50-mV shift seen for (phen)$_3$Os(Cl)$_2$ has been noted previously.[38] In many instances, the polarographic waves are partially masked by the solvent oxidation wave. This leads to rather large uncertainties in the E_p's and the fwhm's (full widths at half maximum) and prohibits a quantitative treatment of the effects of the micellar environment on the $E_{1/2}$(III/II)'s.[39–41]

The differential pulse polarograms of the complexes listed in Table I display the fwhm of 93 ± 2 mV in aqueous solution expected for reversible systems.[30] In the micellar solution, however, a definite broadening (fwhm = 106 ± 7 mV) is observed. Such behavior may be attributed to either of two effects: (i) irreversible charge transfer during the oxidation

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(35) Taylor, D. G.; Demas, J. N. *J. Chem. Phys.* **1979**, *71*, 1032.

(36) DeGraff, B. A.; Demas, J. N.; Taylor, D. G. "Solar Energy—Chemical Conversion and Storage"; Hautala, R. R., King, R. B., Kutal, C., Eds.; Humana: Clifton, NJ, 1979; p 189.

(37) Buell, S. L.; Mandal, K.; Demas, J. N., unpublished observations.

(38) Ohsawa, Y.; Shimazaki, Y.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *114*, 235.

(39) A number of qualitative and semiquantitave explanations have been proposed in order to explain the changes in the observed positions and shapes of the polarographic waves upon micellization. Most of these are based on electrostatic arguments.[40,41]

(40) Jacobsen, E.; Lindseth, H. *Anal. Chim. Acta* **1976**, *86*, 123.

(41) Shinozuka, N.; Hayano, S. In "Solution Chemistry of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York 1979; Vol 2, p 599 and references therein.
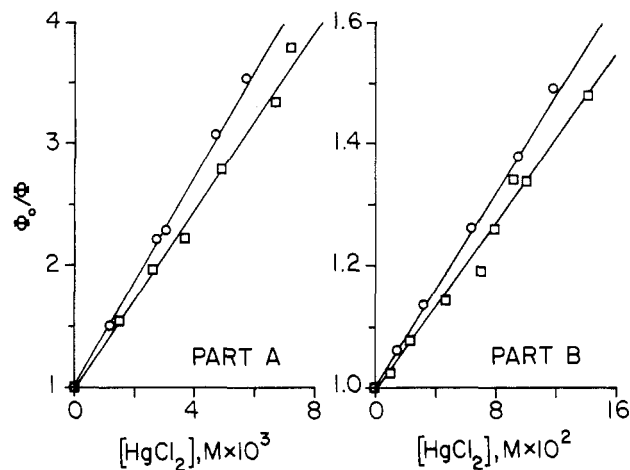
Figure 2. Stern–Volmer plots for (phen)$_2$Os(DPPM)(ClO$_4$)$_2$ quenched by HgCl$_2$ in aqueous (A) and 10 mM NaLS solution (B). All solutions contained 0.1 M NaNO$_3$ and 0.01 M HNO$_3$. O = intensity quenching data; □ = lifetime quenching data.

at the electrode or (ii) reversible charge transfer from a distribution of sensitizer–micelle states. The inherent uncertainty in our data unfortunately precludes the determination of the mode of charge transfer.

Table III illustrates the results of the quenching experiments performed using HgCl$_2$. Differences in the k_q's obtained from lifetime and intensity measurements were usually about 10%. In those cases where sufficient HgCl$_2$ could be dissolved to yield I_0/I values >3.5, no deviations from Stern–Volmer behavior were found. Typical results are shown in Figure 2 for (phen)$_2$Os(DPPM)(ClO$_4$)$_2$. This behavior indicates that quenching of the MLCT states occurs predominantly via a dynamic, rather than a static, mechanism.[18]

Also shown in Table III are the values for the excited-state reduction potentials, $*E_{1/2}$(III/II)'s. The $*E_{1/2}$(III/II)'s are calculated from the relation[18]

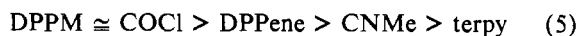$$*E_{1/2}(\text{III}/\text{II}) = E_{1/2}(\text{III}/\text{II}) - E_o \qquad (3)$$

where E_o is the observed emission energy in electronvolts and $*E_{1/2}$(III/II) and $E_{1/2}$(III/II) are in volts. Equation 3 has been verified previously.[12,18]

We have previously shown that the electron-transfer quenching of RuL$_3{}^{2+}$ complexes by HgCl$_2$ in both the aqueous and micellar environments is adequately described by Marcus theory.[19,20] k_q increases monotonically as $*E_{1/2}$(III/II) becomes less positive. A limiting value (i.e., the diffusion plateau) for k_q is reached, and further decreases in $*E_{1/2}$(III/II) do not affect k_q. Thus, it is interesting to compare the relative quenching rates observed in both media with those expected (note Table III).

The k_q should be ordered as

phen > terpy > DPPM > DPPene > CNMe $\cong$ COCl   (4)

In water the observed sequence is

DPPM $\cong$ COCl > DPPene > CNMe > terpy   (5)

Data are unavailable for (phen)$_3$Os(Cl)$_2$ since precipitation of HgCl$_2$ occurs in the aqueous solution. In the micellar solution, the sequence

COCl > phen $\cong$ terpy > DPPM > DPPene > CNMe   (6)

is noted. The behavior predicted in eq 4 is clearly not observed in either the micellar or the aqueous media. Possible reasons for these differences are discussed below.

Pronounced transient photochemistry was associated with the HgCl$_2$ quenched systems. The spectroscopic changes were consistent with production of Os(III) and HgCl$_2^-$. Os(terp)$_2{}^{2+}$

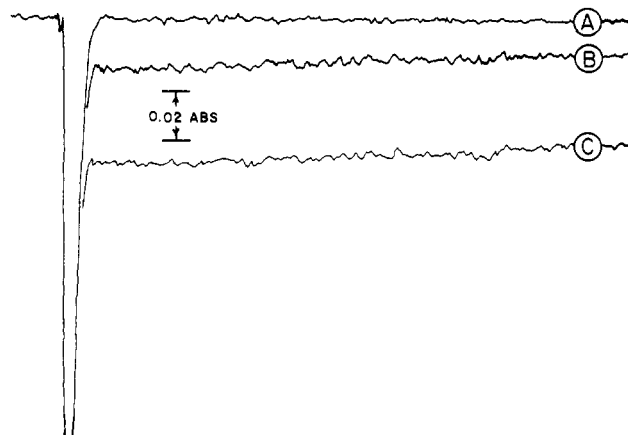**Figure 3.** Flash photolysis transients for *cis*-(phen)$_2$Os(CO)Cl$^+$ (12 μM) with HgCl$_2$ in aqueous and NaLS media (absorbance monitored at 436 nm in a 10-cm cell; full-scale time 1 ms): A, baseline in the absence of HgCl$_2$; B, HgCl$_2$ without NaLS; C, HgCl$_2$ with 10 mM NaLS. All solutions contained 20 mM HNO$_3$. The absorbance data for curve B have been corrected to the same degree of quenching as for curve C.

and Os(phen)$_2$(CO)Cl$^+$ exhibited reversible photochemistry in water. Os(phen)$_2$(CO)Cl$^+$ also exhibited even more efficient photochemistry in the micellar media. The Os(phen)$_2$(CO)Cl$^+$ systems were studied quantitatively in both media. The results are shown in Figure 3. The aqueous data are corrected to the same degree of quenching as the micellar system so that a direct comparison of the transients can be made. The $\phi_{et}{}^0$'s were 0.07 and 0.20 for the aqueous and micellar media, respectively. The reference was the Fe^{3+} system with an assumed value of 1.00. In the event that the $\phi_{et}{}^0$ of the reference reaction is less than one, the $\phi_{et}{}^0$'s reported here represent lower limits.

Discussion

The data of Tables II and III reveal a number of interesting features for the L$_2$OsXX'$^{2+}$ systems. The ground- and excited-state properties vary smoothly with changes in the π-acceptor ability of X and X' for both the micellar and aqueous media. Such behavior is consistent with that reported earlier for these species in acetonitrile.[8,9,12] These effects have been attributed to changes in the energy of the d(Os) levels and, consequently, the energy of the π^*(L) $\leftarrow$ dσ(Os) MLCT transition.[9]

The emission energies, lifetimes, and redox potentials change on going from the micellar to the aqueous media. Analogous behavior has been noted for the tris(polypyridyl)ruthenium(II) systems.[19,20] Such changes indicate strong binding of the complexes to the NaLS micelles.

In a recent study, we have shown that a series of tris(polypyridyl)ruthenium(II) complexes are bound to the nonionic surfactant Triton X-100.[42] The binding is relatively strong and is related to the hydrophobicity of the complexes. Strong binding of metal cations to the anionic NaLS micelles is also known to occur due to the electrostatic attractions between the species.[28,29] It is not surprising to observe strong binding of the Os(II) complexes to the NaLS micelles since both hydrophobic and electrostatic interactions are present.

That both hydrophobic and electrostatic interactions are important in the binding of our complexes to the NaLS micelles is supported by experiment. Studies using (phen)$_3$Os^{2+} have shown that solvent interactions play a critical role in determining excited-state properties such as τ_0 and E_o.[11] We have shown that, on the average, approximately one-third of

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the micelle-bound Os(II) sensitizer is exposed to the aqueous environment near the micelle's surface.[43] The hydrophilicity of the solvent environment around the complex is radically decreased upon binding to the micelle. The changes noted in Table II must arise at least in part from this solvent effect.
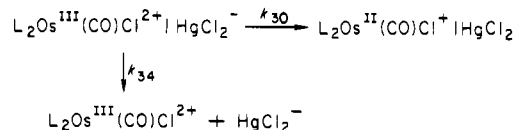
Electrostatic interactions are also important in the binding process. In solvents of low dielectric constant where ion pairing is prevalent, Meyer and Vining[44] have demonstrated that τ_0 and E_o for $(phen)_3Os^{2+}$ depend on the counterion. Larger anions exhibiting good donor properties such as LS^- led to decreased τ_0's and increased E_o's when compared to less polarizable and smaller counterions such as Cl^-. Masuda et al.[45] have reached similar conclusions in their investigation of the hydrophobic interaction between the hexanesulfonate anion and a number of metal phen complexes in aqueous solution. Recent evidence and calculations indicate that the dielectric constant of the NaLS micellar surface at the polar sulfonate groups is $< \sim 32$.[46,47] For sensitizers binding in this region,[43] ion pairs can thus be expected to form between the sensitizer and the LS^- anion. Consequently, changes in the properties of the sensitizers relative to the aqueous solution are expected although we cannot resolve the relative importance of solvent and ion-pairing effects at this point.

The quenching data are also consistent with the sensitizer being tightly bound to the micelle. Once again, the behavior is identical with that noted for the tris(polypyridyl)ruthenium(II) species.[19,20] A 10 to 100-fold decrease in quenching rate is observed when the micellar solution is compared to the aqueous case. Quenching occurs via collision of the unbound $HgCl_2$[20] with the micelle-bound sensitizer. This decrease is consistent with our geometric shielding model proposed earlier for Ru(II) photosensitizers.[20]

The relative quenching order observed for the Os(II) complexes by $HgCl_2$ is similar in both the micellar and aqueous solutions. The same behavior is noted for the Ru(II) complexes.[19,20] However, unlike the case of the Ru(II) complexes, the quenching order for the Os(II) complexes does not follow Marcus theory.[19] Marcus theory requires that the systems being examined be similar structurally and electronically. Although our Os(II) complexes exhibit electronic similarities,[9] basic structural differences exist. These differences are sufficiently large to preclude quantitative fitting of the data using a common set of kinetic parameters. In contrast, Marcus theory does fit the quenching data for a single Os(II) complex by a series of structurally and electronically similar pyridinium quenchers.[12]

In sharp contrast to our results with both aqueous and micellar $RuL_3^{2+}/HgCl_2$ systems,[19,20] we observe net redox chemistry with at least two of the Os(II) complexes. Further, as hoped, the use of micellar media significantly enhanced the net yield of photoproducts over that observed for the simple aqueous case. While ϕ_{et}^0 is modest and the absolute values are subject to some uncertainty, there is no doubt that net redox occurs and that micelles are effective in increasing the yield.

The differences between the Ru(II) and Os(II) sensitizers cannot be accounted for by differences in oxidizing power of the Ru(III) or Os(III) photoproducts. $E^\circ(III/II)$ for $(phen)_2Os(CO)Cl^+$ is the same as for $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$. These latter complexes show no net redox with $HgCl_2$ despite the fact that they bracket the Os(II) complex in terms of k_q and τ_0. The back-electron-transfer in the encounter pair from $HgCl_2^-$

$$L_2Os^{III}(CO)Cl^{2+} | HgCl_2^- \xrightarrow{k_{30}} L_2Os^{II}(CO)Cl^+ | HgCl_2$$
$$\downarrow k_{34}$$
$$L_2Os^{III}(CO)Cl^{2+} + HgCl_2^-$$

should be as highly driven for the Os(III) as for the Ru(III) complexes, and yet $k_{30} \gg k_{34}$ for the Ru(II) case. While it is not known when the Cl^- is expelled from the incipient $HgCl_2^-$,[48] the timing would be expected to be the same for both the Os(III) and Ru(III) cases. It is not clear at this point whether a decrease in k_{30} or an increase in k_{34} on going from RuL_3^{2+} to OsL_3^{2+} is resposible for the observed redox. It is clear that electrochemical and photophysical data alone do not, at present, allow complete prediction of which systems will produce observable products.

The significant increase in ϕ_{et}^0 that occurs in micellar medium suggests that some of the initially formed $HgCl_2^-$ exists long enough to be expelled by the anionic micelle surface. If all the Cl^- was lost while the geminate pairs were still in the solvent cage, it is doubtful that the micelle surface would have such a dramatic effect.

Conclusions

The examination of the properties of the $L_2OsXX'^{2+}$ species in micellar and aqueous solutions leads to several important conclusions:

(i) The ability to systematically alter the properties of these MLCT states in water through changes in the π-acceptor ability of X and X' has important ramifications for solar energy conversion. Although solubility problems encountered for some of the complexes may ultimately limit their usefulness in water-based commercial energy storage schemes, they should nonetheless prove useful in theoretical and mechanistic studies. However, water solubility is not a consideration in nonaqueous photocatalytic energy conversion systems.[49] Further, micelles can frequently solubilize otherwise insoluble complexes.

(ii) The changes in the ground state and photophysical properties of the complexes on proceeding from an aqueous to a micellar environment are consistent with those observed[19,20] earlier for the Ru(II) polypyridine complexes. In conjunction with other studies,[43] this indicates that the Os(II) complexes are strongly bound to the micelles.[28,29]

(iii) The quenching of the Os(II) MLCT states by $HgCl_2$ parallels that observed previously for the Ru(II) polypyridine complexes in aqueous[19] and micellar[20] solutions. Quenching occurs via electron transfer and is dynamic. The decreases in the quenching rate on proceeding from the aqueous to the micellar environment are entirely consistent with the behavior expected for a strongly bound sensitizer and very weakly bound $HgCl_2$ quencher.[20]

(iv) Attempts to relate the quenching rate to the driving force for the $^*Os^{II}-HgCl_2$ reactions were unsuccessful. Since these complexes exhibit electronic similarities,[9] we conclude that structural differences lead to the deviations observed in the quenching rate from that predicted using Marcus theory. It is likely that this aberrant behavior is due to structural changes that lead to variations in both solvation[11] and ion pairing.[44] Indeed, subtle structural changes can result in unsatisfactory fits using Marcus theory. For example, with RuL_3^{2+} complexes the bipyridine complexes were not fit by the same parameters as the phenanthroline complexes.[19,20] These results underscore the importance of selecting a homologous family of structurally and electronically related sensitizers/quenchers when attempting to apply Marcus theory to electron-transfer reactions.

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(v) Surprisingly, the Os(II) photosensitizers show much richer and more efficient photochemical behavior with $HgCl_2$ than similar Ru(II) photosensitizers. Thus, the Os(II) complexes may well prove to be better photosensitizers than the widely used Ru(II) systems.

(vi) Anionic NaLS micelles have proved useful in enhancing product separation by accelerating the expulsion of $HgCl_2^-$ before back-reaction with Os(III) can occur.

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Optical Spectra of Exchange-Coupled Manganese(II) Pairs in Cesium Magnesium Trichloride and Cesium Magnesium Tribromide

PAUL J. McCARTHY*[1] and HANS U. GÜDEL

Mixed crystals $CsMg_{1-x}Mn_xX_3$ (X = Cl, Br; x = 0.04–0.20) were prepared and investigated by optical spectroscopy. Manganese(II) pair excitations were observed in the regions of $^4A_1(G)$, $^4T_2(D)$, and $^4E(D)$ in the absorption spectra. They were studied as a function of temperature and applied magnetic field. Ground-state exchange parameters of 14.2 and 19.6 cm^{-1} were determined for $Mn_2Br_9^{5-}$ and $Mn_2Cl_9^{5-}$, respectively. The corresponding values for the singly excited $^4A_1$ pair state were found to be 18.6 and 26.8 cm^{-1}. Estimates of the orbital contributions to the net exchange were made.

Introduction

The study of pairs of paramagnetic transition-metal ions remains an active area of solid-state research. Ground-state properties are usually investigated by magnetochemical techniques. Valuable information about exchange splittings in the ground and excited states can, however, also be obtained from optical spectroscopy. This is particularly true for systems exhibiting sharp and structured spin-forbidden absorption or emission bands.

Reports have appeared on several systems related to those treated in this research. The optical spectra of the $^4A_1$ pair states of manganese(II) in $KMgF_3$ and $KZnF_3$ have been studied in detail.[2-6] Trutia et al.[7] have measured the optical spectra at 77 K of single crystals of $CdCl_2$ containing 15 and 0.1 mol % manganese(II). In the 15% crystals they observed bands not found in the 0.1% crystals, bands that had also been observed by Pappalardo[8] in pure $MnCl_2$. They noted that these bands do not belong to isolated $MnCl_6^{4-}$ groups. The spectra of $CsMnCl_3$ have been studied,[9] as well as those of some similar antiferromagnetic insulators: $RbMnCl_3$,[9] $TlMnCl_3$,[10] $((CH_3)_4N)MnCl_3$ (TMMC),[11] and Rb_2MnCl_4.[9,12] No report

has appeared on the spectra of $CsMg_{1-x}Mn_xCl_3$.

The electronic spectra and magnetic properties of the one-dimensional antiferromagnet $CsMnBr_3$ and of the diluted analogue $CsMg_{1-x}Mn_xBr_3$ (x = 0.08, 0.26), between 77 and 300 K, have been reported by McPherson et al.[13] Since the spectra are only of low resolution, they show no traces of the pair effects reported here. A more detailed study of the optical spectrum of pure $CsMnBr_3$ has appeared,[14] as well as that of the analogous $((CH_3)_4N)MnBr_3$ (TMMB).[15]

In this research we have made a systematic study of the optical absorption spectra of the mixed crystals $CsMg_{1-x}Mn_xX$ (X = Br, Cl; $x \leq 0.2$) in the region of the spin-forbidden d–d transitions. Emphasis has been placed on features arising from $Mn_2X_9^{5-}$ pairs. The matrix used has some notable advantages: the crystal symmetry is high, and the symmetry of the $Mn_2X_9^{5-}$ pairs in the crystal is also high (D_{3h}). The threefold axis of the pairs coincides with the crystal c axis, and all dimers are parallel. This latter fact permits the measurement of the polarization of the pair bands, a unique advantage. It was not possible, for example, to do this for the manganese(II) pairs in $KMg_{1-x}Mn_xF_3$, which has the perovskite structure.[6]

Our aims in this research have been (1) to determine the energy splittings in the ground state and in as many excited pair states as possible, (2) to study the intensity mechanisms of the pair excitations, and (3) to attempt a rationalization of exchange splittings in terms of orbital parameters. From this, information can be obtained concerning the dominant exchange mechanism and exchange pathways, information not available from a magnetochemical study alone.

Experimental Section

Crystal Preparation. Crystals were prepared by the Bridgman technique. The bromide crystals contained 20, 14, 8, and 4 mol % manganese, while only a 5 mol % chloride sample was prepared. The

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