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Nonradiative Decay in Rhenium(I) Monometallic Complexes of 2,3-Di-2-pyridylpyrazine

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The nonradiative (k_{nr}) decay rates of the low-lying, emissive metal-to-ligand charge-transfer (MLCT) excited states of a series of complexes of the type $[Re(dpp)(CO)_3L]^+$ (dpp = 2,3-di-2-pyridylpyrazine; L = Cl^-, *N*-methylimidazole, pyridine, 4-phenylpyridine, 4-methylpyridine, trimethylphosphine, acetonitrile) have been investigated. The results show that the "energy gap law" for radiationless decay in the weak coupling limit is obeyed by this series of complexes. The complexes yield a ln k_{nr} vs E_{em} plot with a slope and intercept within experimental error for two separate studies on the series where the acceptor ligand is 2,2′-bipyridine. This is taken as evidence that dpp and bpy differ only in the relative energies of the acceptor orbitals and are vibrationally similar.

Introduction

A growing area of chemistry is that of Re(I) and Ru(II) metal complexes containing ligands of the type 2,3-di-2-pyridylpyrazine (dpp).[1-19] These ligands (shown in Figure 1) were initially developed for the colorimetric analysis of metals[20] and are remarkable in that two of the series, dpp and 2,3-di-2-pyridylquinoxaline (dpq), yield bimetallic complexes of Ru(II) that have relatively long-lived, luminescent excited states.[6-12] These studies have up to this point focused on the location of the excited electron using transient absorbance, electron paramagnetic resonance, and resonance Raman spectroscopy. The results reported to date suggest that while many of the properties critical to the remarkable photochemistry and electrochemistry observed in Ru(II) complexes containing 2,2′-bipyridine (bpy)[21,22] are conserved, there are distinct differences between bpy, dpp, and dpq as well. This interest in the dpp ligands and the continuing activity in the chemistry of Re(I) tricarbonyl complexes containing polypyridyl acceptor ligands[16-19,23-52] has led to reports of Re(I) complexes containing dpp,[17-19] dpq,[19] and dpb[19] (2,3-di-2-pyridylbenzo[*g*]quinoxaline).

The variation of the Re dπ orbital energies with the ligand field strength of L in the $Re(bpy)(CO)_3L$ structure has been utilized to yield a systematic study of the nonradiative decay process of the bpy complexes employing the "energy gap law" (EGL) as the theoretical framework.[24,51,52] These results show that the excited states of these compounds follow the EGL, but they exhibit significantly different slopes and intercepts from Os(II)–bpy or Ru(II)–bpy complexes. This difference was tentatively assigned to the participation of the carbonyl ligand(s) in the decay of the excited state. We report herein the application of this variation in the emission energy with L to gain further insight into the nonradiative decay of the $Re(dpp)(CO)_3L$ (L = Cl^-, N-methylimidazole, pyridine, 4-phenylpyridine, 4-methylpyridine, trimethylphosphine, acetonitrile) series. The details obtained concerning the features of the metal-to-ligand charge-transfer (MLCT) excited states of complexes containing dpp-type ligands should aid in the understanding of the commonalties and differences between bpy and these ligands.

Experimental Section

Materials. All preparative solvents were of reagent grade and were used without further purification. For electrochemical, laser-induced time-resolved luminescence and emission experiments, Burdick-Jackson high-purity acetonitrile and methylene chloride were used. In the electrochemical experiments, the solvent was first dried over activated molecular sieves (4 Å, Davidson). Silver perchlorate (Alfa-Ventron) was used as received. Pyridine (py) was obtained from Fisher Scientific. The ligands dpp, 4-phenylpyridine (Phpy), 1-methylimidazole (MIm) and 4-methylpyridine (Mepy) were purchased from Aldrich. Trimethylphosphine ($P(CH_3)_3$) was obtained as a 1.0 M solution in tetrahydrofuran from Aldrich. These ligands were used as received. Tetrabutylammonium hexafluorophosphate (TBAH) was prepared from tetrabutylammonium bromide (Fluka) and hexafluorophoric acid (Alfa-Ventron). The product was recrystallized from ethanol three times and dried in a vacuum oven at 100 °C for 6 h.

Chromatography. Gravity-feed liquid chromatography utilizing Ace

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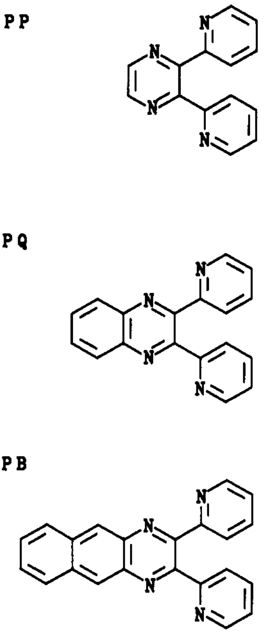

Figure 1. Structures of the ligands 2,3-di-2-pyridylpyrazine (dpp), 2,3-di-2-pyridylquinoxaline (dpq) and 2,3-di-2-pyridylbenzo[*g*]quinoxaline.

Table I. Physical Properties of Re(dpp)(CO)$_3$L^a

L	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	E_p^a, V	$E_{1/2}$, V	ν(CO), cm^{-1}
Cl$^-$	400 (3600)	1.48	−0.97	2021
				1914
				1902
				1889
MIm	410 (2770) sh	1.76	−0.83	2030
	254 (16 500)			1931
	286 (16 900)			1904
py	400 (3130) sh	1.94	−0.79	2033
	332 (10 300) sh			1937
	264 (20 700)			1912
Mepy	408 (2600) sh	1.94	−0.82	2033
	332 (9640) sh			1934
	262 (20 900)			1909
Phpy	398 (3400) sh	2.01	−0.77	2035
	284 (32 300)			1939
				1913
P(CH$_3$)$_3$	394 (3730) sh	2.02	−0.86	2031
	342 (9030) sh			1950
	286 (17 900)			1913
	258 (18 400)			
AN	330 (10 600)	2.05	−0.84	2038
	282 (17 200)			2027
	254 (17 200)			1923
				1915

^{a} All λ_{max}, ϵ, $E_{1/2}$ and E_p^a data were obtained in acetonitrile. The acetonitrile was 0.1 M in TBAH for the electrochemical experiments. E_p^a values were measured via OSWV. $E_{1/2}$ values were measured from cyclic voltammograms. The infrared data were obtained from thin films.

Glass columns and Fisher A-540-500 alumina was used to purify bulk samples of the metal complexes. The chromatography was typically performed using gradient elution (85% CH_2Cl_2/15% CH_3CN to 100% CH_3CN).

Physical Measurements. Elemental analyses were performed by the elemental analysis group at Merck and Co., Rahway, NJ. Infrared spectra were recorded as thin films on a Spectra-Tech Inc. REACT IR-1000 FTIR spectrometer. UV–vis spectra were obtained in acetonitrile on a Hewlett-Packard Model 8452A diode array spectrophotometer controlled by an AT&T 6300 microcomputer.

A Spex Model F222A photon-counting spectrofluorimeter was used to acquire the emission spectra in both acetonitrile and methylene chloride. The photomultiplier tube used to detect the emission was a Hamamatsu R928 side-on tube with an absolute low-energy cut-off of 930 nm. All emission spectra were corrected for detector response with correction files generated on site by the manufacturer. Low-temperature (77 K) spectra were obtained in ethanol freshly distilled from $Mg(OCH_2CH_3)_2$, using a quartz finger Dewar filled with liquid nitrogen. Radiative quantum yields (Φ_r) were determined in deoxygenated (N_2 bubbling for 20 min) methylene chloride at optically dilute sample concentrations (absorbance at the excitation wavelength <0.15). All complexes were excited at 426 nm. The values were calculated relative to $[Ru(bpy)_3](PF_6)_2$ in H_2O (Φ_r = 0.042, at 25 °C)[51] using the areas under the emission spectra obtained from numerical integration. The equation

$$\Phi_r = \Phi_r^{obs}(\eta^2(CH_2Cl_2)/\eta^2(H_2O))$$

was used to correct the observed quantum yield, Φ_r^{obs}, for the differing indices of refraction of the solvents, $\eta(CH_2Cl_2)$ and $\eta(H_2O)$.

Excited state lifetimes (τ) were determined by laser flash photolysis with the defocussed 337-nm output of a pulsed Photochemical Research Associates Model LN 100 nitrogen laser as the excitation source (nominal pulse width 300 ps). The luminescence decay following excitation was monitored with a Hamamatsu R928 photomultiplier tube mounted in an EMI-Gencom Inc. Model S photomultiplier housing. An Instruments SA Inc. Model H10 1200 vis monochromator with 2-mm slits (nominal bandpass = 16 nm) was used to select the detection wavelength. The photocurrent was converted to voltage by droppng it across a 50-Ω terminator. The voltage vs time signal was acquired with a Stanford Research Systems SR 255 fast sampler set to a 1-ns gate width interfaced to an IBM personal computer using Stanford Research Systems SR 267 software. The data used for lifetime determinations were the average of 20 decay curves. This data was converted to ASCII format with locally written FORTRAN software. Lifetimes were determined by two-parameter fitting of the exponential intensity vs time curves using the Gauss–Newton algorithm in the ASYSTANT software package (Keithley). The lifetimes of all the compounds examined were determined at optically dilute concentrations in methylene chloride deoxygenated by N_2 bubbling for 20 min.

Electrochemical measurements were carried out in acetonitrile with 0.1 M TBAH as supporting electrolyte. A platinum-disk working electrode (Bioanalytical Systems), a platinum-wire auxiliary electrode (Bioanalytical Systems), and a 3 M NaCl Ag/AgCl reference electrode (+0.20 V vs the normal hydrogen electrode) were used in the voltammetric experiments. All cyclic (CV) and Osteryoung square-wave voltammograms (OSWV) were obtained on a Bioanalytical Systems BAS-100 electrochemical analyzer. The cyclic voltammograms were obtained at a scan rate of 100 mV/s unless otherwise noted. The conditions for OSWV were as follows: square-wave amplitude, 25 mV; sampling points, 256; frequency, 15 Hz; step potential, 4 mV.

Syntheses. ***fac*-[Re(dpp)(CO)$_3$(CH$_3$CN)]ClO$_4$.** In a typical preparation, 0.50 g (9.3 × 10^{-4} mol) of Re(dpp)(CO)$_3$Cl[19] were dissolved in ca. 250 mL of CH_3CN. An 8.9-mL aliquot of 0.1 M $AgClO_4$ in CH_3CN (0.18 g $AgClO_4$, 8.9 × 10^{-4} mol) was then added to the orange solution. This mixture was refluxed with stirring in the dark under a N_2 atmo-

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sphere for 10 h. The resulting solution was yellow, and a white precipitate (AgCl) was evident. After the reaction mixture cooled to room temperature, it was filtered through a 0.45 μm syringe filter (Millipore) and concentrated by rotary evaporation. The concentrate was chromatographed and the resulting residue was precipitated from diethyl ether after dissolving in a minimum volume of CH_2Cl_2. The yellow precipitate was collected by vacuum filtration and washed with ether (yield ca. 70%). *Warning! Perchlorate salts are treacherously explosive. While we encountered no problems, particular caution is strongly recommended.*

***fac*-[Re(dpp)(CO)$_3$(L)]ClO$_4$ (L = Pyridine, 4-Methylpyridine, 4-Phenylpyridine, 1-Methylimidazole, Trimethylphosphine).** These complexes were synthesized according to the procedure developed by Luong.[54] In a representative preparation, 0.25 g (3.9×10^{-4} mol) of [Re(dpp)(CO)$_3$(CH$_3$CN)]ClO$_4$ were dissolved in ca. 250 mL of THF. Approximately 1.0 mL of neat 1-methylimidazole was added to the solution (ca 30× molar excess of ligand) and the mixture was allowed to reflux with stirring under a N_2 atmosphere for 3 h. Since both reactant and product have absorption spectra which only tail into the visible region, essentially no color change is observed and the solution remains yellow. The solution was concentrated, and the product was precipitated by addition of *n*-pentane. After vacuum filtration, the yellow solid was purified by column chromatography and finally precipitated from diethyl ether after the solid was dissolved in a minimum of CH_2Cl_2. The element analyses for all compounds were consistent with the formulations stated above. *Warning! Perchlorate salts are treacherously explosive. While we encountered no problems, particular caution is strongly recommended.*

Results

Electrochemistry. Table I contains the half-wave potentials for the first (most positive) reductions as well as the peak potentials from OSWV for the first (least positive) oxidations of all complexes examined. The most positive reductions are assigned to an electrochemically reversible dpp-localized reduction,[19] consistent with the observed $|E_p^a - E_p^c|$ values of ca. 60–75 mV. The $E_{1/2}$ values for the dpp$^{0/-}$ process were calculated from cyclic voltammetry using the equation

$$E_{1/2} = (E_p^a + E_p^c)/2$$

The least positive oxidations are assigned to a Re-centered oxidation, based on analogous complexes.[19] The Re$^{II/I}$ process is irreversible in cyclic voltammetry, so the E_p^a values were estimated from OSWV peaks.

Absorption Spectroscopy. The characteristic ultraviolet–visible absorption maxima, extinction coefficients, and infrared carbonyl stretching frequencies for the Re(dpp)(CO)$_3$L molecules can be found in Table I. The absorption spectra show complex structure with intraligand (IL) bands (principally $\pi^* \leftarrow \pi$) in the UV region. Lower energy shoulders overlap these UV absorbances. On the basis of the previously published[19] correlation between the electrochemical and spectroscopic properties of Re(I) complexes containing the same and related chromophores, the MLCT transitions arising from the

$$[\mathrm{Re^{II}(dpp^{\bullet -})(CO)_3L}]^+ \leftarrow [\mathrm{Re^{I}(dpp)(CO)_3L}]^+$$

process were estimated to occur between ca. 350 and 380 nm. The extinction coefficients appearing in Table I in the region of 400 nm should therefore correspond to values measured on the low-energy shoulder of the unresolved MLCT maxima.

Table II. Photophysical Data for Re(dpp)(CO)$_3$L and Re(bpy)(CO)$_3$L[a]

L	E_{em}, eV	τ, ns	$10^4\Phi_r$	10^3k_r, s^{-1}	10^6k_{nr}, s^{-1}
		Re(dpp)(CO)$_3$L			
Cl$^-$	1.72	15 (5)	18 (2)	120	67
MIm	1.86	46 (5)	60 (8)	130	22
Mepy	1.97	170 (10)	270 (30)	160	5.9
Phpy	1.96	190 (20)	270 (30)	150	5.3
py	1.98	200 (10)	300 (40)	150	4.9
P(CH$_3$)$_3$	2.05	280 (30)	290 (40)	100	3.5
AN	1.98	200 (10)	95 (10)	48	5.0
		Re(bpy)(CO)$_3$L			
Cl$^-$	2.00	51	50	98	20
4-DMApy	2.04	95	170	178	10
4-Apy	2.08	129	520	406	7.34
MIm	2.11	161	580	359	5.85
4-Etpy	2.19	604	1800	296	1.39
py	2.23	669	1600	236	1.26
P(CH$_3$)$_3$	2.28	1169	2700	232	0.623
AN	2.32	1201	4100	343	0.490

[a] All data were obtained in deoxygenated methylene chloride. Emission spectral data were calculated from spectra corrected for detector sensitivity. Data for [Re(bpy)(CO)$_3$L]$^+$ were obtained from ref 51. Numbers in parentheses represent errors (±) obtained from an error analysis using the method of propagation of error. 4-DMApy = 4-(dimethylamino)pyridine; 4-Apy = 4-aminopyridine; 4-Etpy = 4-ethylpyridine.

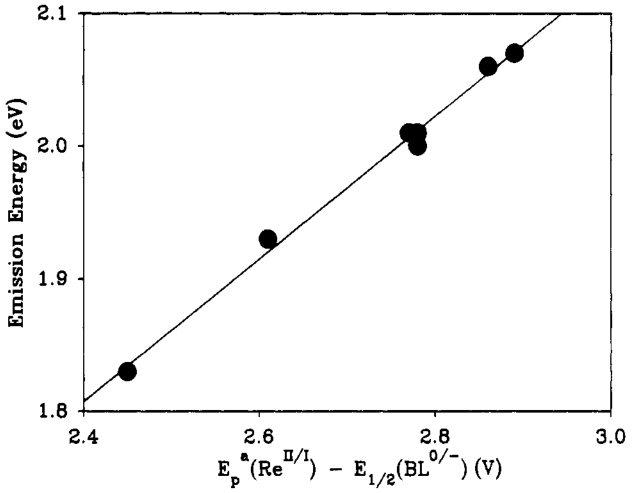

Figure 2. Plot of E_{em} vs $\Delta E_{1/2}$ ($=E_p^a(\mathrm{Re^{II/I}}) - E_{1/2}(\mathrm{dpp^{0/-}})$). The dpp line has a slope of 0.54, an intercept of 0.51, and a correlation coefficient of 0.996. All data in this graph were acquired in acetonitrile. The emission energies were not corrected for detector response.

Emission Spectroscopy. The complexes all exhibit unstructured luminescence in both fluid solution at room temperature and in glassy ethanol at 77 K. Table II contains the emission energies and radiative quantum efficiencies in methylene chloride at room temperature for all complexes examined. The emission energies in these complexes are consistent with expectations based on the relative ligand strengths. As discussed in previous works,[26,59,68] the linear correlation of the emission energy (E_{em}, eV) with the difference ($\Delta E_{1/2}$) between the first reduction (most positive reduction; $E_{1/2}$(dpp/dpp$^{\bullet -}$)) and first oxidation (least positive oxidation; E_p^a; Re(II/I)) potentials can be used as supporting

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evidence for the MLCT nature of the emissive state. This observation is also consistent with the electrochemical reductions being ligand-centered and the oxidations being metal-centered processes as stated above. The linearity of this plot is demonstrated in Figure 2. Bivariate regression statistics were employed in the analysis of the data in order to establish the degree of correlation between the variables since both coordinates are dependent variables (presumably effects of a common cause) and are subject to experimental uncertainty.[19,55] The best-fit line had a slope of 0.54, an intercept of 0.51, and a correlation coefficient of 0.996. Slopes of less than 1 for such plots are expected due to the differing Coulombic attraction of the $(d\pi)^5$ core and the $(p\pi^*)^1$ ligand observed in the excited state and the $(d\pi)^6$ core and the $(p\pi^*)^1$ ligand observed in the electrochemical measurement.[2] This correlation indicates that the same orbitals are involved in both the electrochemical and emission processes throughout the two series where the chromophoric ligand remains constant.

Infrared Spectroscopy in the Carbonyl Region. The infrared spectra of the complexes show strong absorptions in the carbonyl region (2100 – 1800 cm^{-1}). The values for these stretches are listed in Table I. The cationic complexes show a band centered around 2030 cm^{-1}, with two poorly resolved bands centered around 1930 cm^{-1}. In three cases, a weaker band is observed around 1913 cm^{-1}, which may be due to partial crystallization in the thin films. The occurrence of this pattern of carbonyl stretches in tricarbonylrhenium(I) complexes of this type is typical of a degraded C_{3v} local environment, which is consistent with a facial isomer.[19]

Excited-State Lifetimes. The excited-state lifetimes can be found in Table II and were obtained from two-parameter fitting of the exponential decay curves using the Gauss–Newton (GN)[56,57] algorithm. Most of the experimental data had a correlation coefficient of greater than 0.99 for two to three lifetimes. To establish the shortest detectable lifetime, the excited-state lifetime of the IAPS recommended standard[58] anthracene was measured in cyclohexane at room temperature. The literature value is τ = 5.24 ns under these conditions. A value of τ = 6.4 ns (the average of 5.8 and 7.0 ns) was obtained with our instrument.

The rate constants for radiative and nonradiative decay of the excited-state, k_r and k_{nr}, respectively, can also be found in Table II. The quantities k_r and k_{nr} were calculated using the following equations, assuming that the quantum efficiency for intersystem crossing is equal to unity, $\Phi_{isc} \approx 1$,[51] and τ is temperature independent or has the same temperature dependence in all complexes

$$k_r = \Phi_r/\tau$$

$$k_{nr} = 1/\tau - k_r = (1 - \Phi_r)/\tau$$

Discussion

Electrochemistry. Within a series of complexes where L is varied, the first reduction potentials show only minor (70–90 mV within the same charge type), apparently unsystematic variations. This observation is consistent with the first reduction process being principally localized on the dpp ($dpp/dpp^{\bullet-}$).[51,59,61] The first oxidation potentials, however, are considerably more sensitive to the identity of L. As Table I illustrates, the first oxidations span a range of 290 mV. This trend indicates substitution at the metal center and is consistent with the first oxidation being predominantly metal-centered (Re(II/I)) in character.[24,51,61] The data in Table I also show that complexes containing the stronger field ligands (L) possess the more positive metal oxidations, due primarily to stabilization of the Re $d\pi$ orbitals as a result of back-bonding to these π-accepting ligands.

Excited-State Decay. The energy gap law (EGL) for the radiationless decay of excited states in large molecules was developed by Siebrand and others[62-65] and modified by Jortner, Englman, and Freed.[66,67] It has been applied previously to a number of inorganic complexes of Ru(II), Os(II), and Re(I).[22,24,51,52,60,68-70]

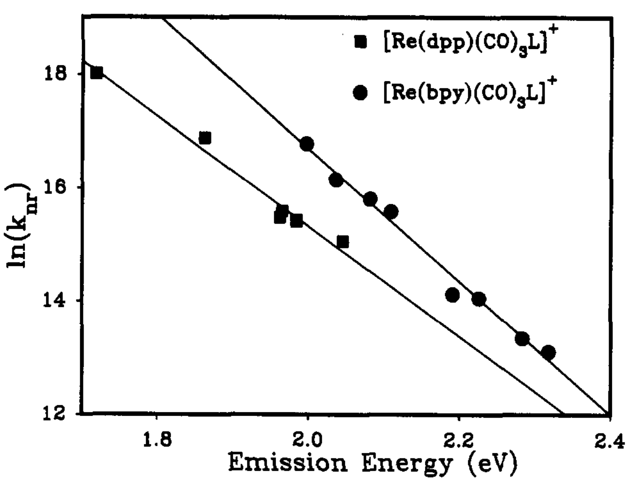

Figure 3. Plot of ln k_{nr} vs E_{em} for $[Re(dpp)(CO)_3L]^+$ and $[Re(bpy)(CO)_3L]^+$. The lines have slopes of –9.9 and –11.9 eV^{-1}, for the dpp and bpy complexes, respectively. Please note that two of the points for the dpp series overlap and are not clearly distinguishable.

This correlation essentially states that the nonradiative decay rate constant (k_{nr}) should decay exponentially with the increasing difference in energy between the emitting and ground-state levels ($\approx E_{em}$, see below) for a series in which the luminescent chromophore remains unchanged. Clearly the dpp complexes whose preparation is described above form such a series of MLCT emitters. The form of the energy gap law adopted for this work is[59,68]

$$\ln k_{nr} = \ln \beta_0 - [\ln (\hbar\omega_m E_{em})]/2 - S_m + (\gamma + 1)^2(\Delta\nu_{1/2}/\hbar\omega_m)^2/(16\cdot\ln 2) - \gamma E_{em}/\hbar\omega_m \quad (1a)$$

$$\beta_0 = C_k^2\omega_k(\pi/2)^{1/2} \quad (1b)$$

$$\gamma = \ln (E_{em}/S_m\hbar\omega_m) - 1 \quad (1c)$$

$$C_k = \hbar\langle\Psi_g|\partial/\partial Q_k|\Psi_e\rangle \quad (1d)$$

$$\hbar = h/2\pi$$

In eq 1a–d above, k_{nr} is the rate constant for nonradiative decay, $\hbar\omega_m$ is the quantum spacing for the single or averaged "acceptor" mode, m (i.e. the mode in the ground state which is the acceptor of the majority of the excited-state energy), and E_{em} is the observed emission energy. S_m ($=(\Delta_m)^2/2$) is the Huang–Rhys factor for mode m where (Δ_m) is the dimensionless distortion of mode m in the excited state relative to the ground state. $\Delta\nu_{1/2}$ is the width at half-maximum of the highest energy vibronic band resolved in the emission spectrum. C_k, as given in eq 1d, is the vibronic coupling matrix element. The $\partial/\partial Q_k$ operator represents the change in the mass weighted normal coordinate associated with the excited-state "promoting" mode, k, which removes the orthogonality of the zero-order Born–Oppenheimer electronic states and "allows" the radiationless transition to take place. Ψ_g and Ψ_e correspond to the ground and excited electronic wave functions, respectively. The term ω_k is the angular frequency of the promoting mode, k.

It has been shown previously by the work of Meyer et al.[68] on Os(II) complexes involving polypyridyl ligands that S_m increases linearly with increasing E_0 ($\approx E_{em}$) throughout a series of related complexes. Assuming that $\hbar\omega_m$ is essentially invariant throughout a series of emitters and that the C_k term is relatively constnat, eq 1a predicts that ln k_{nr} should be linearly dependent on E_{em}, particularly due to the covariance of S_m and E_{em}. A plot of ln k_{nr} vs E_{em} for the $[Re(dpp)(CO)_3(L)]ClO_4$ series is displayed in Figure 3. The bpy series is included for comparison.[51] The best-fit line obtained by bivariate regression analysis has a slope of –9.9 eV^{-1}, an intercept of 35.1, and a correlation coefficient of –0.99.

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These data show good linearity, demonstrating that these complexes obey the energy gap law both qualitatively and quantitatively. Good EGL correlations can also be found in the literature for the other inorganic systems alluded to above.[22,24,51,52,59,60,68-70,73] The slope of analogous plots for the Re(bpy)(CO)$_3$L series exhibit slopes of -11.9[51] and -8.7 eV^{-1}[24] as compared to a value of -9.9 eV^{-1} for the dpp series. These slopes are within experimental error of our value.[71]

The slopes of $\ln k_{\rm nr}$ vs $E_{\rm em}$ plots for osmium(II) and ruthenium(II) polypyridyl complexes tend to be more negative when carbonyl ligands are present in the coordination sphere. Complexes of Os(II) and Ru(II) with polypyridyl acceptor ligands and phosphine ligands[59,68,72] typically have slopes in the range of -7.8 to -6.6 eV^{-1}, while incorporation of a carbonyl ligand lowers the slope to -12.9 eV^{-1} for [Os(AA)$_2$(CO)Cl]$^+$ (AA = substituted bpy or phen)[70] and -8.7 eV^{-1} for [Os(bpy)$_2$(CO)L]$^+$ (L = H$^-$, D$^-$, Cl$^-$, py).[74] As noted above, [Re(bpy)(CO)$_3$L]$^+$ complexes have slopes of -8.7[24] and -11.9 eV^{-1}.[51] This suggests that the presence of carbonyl ligands in the inner coordination sphere of Os(II) and Re(I) complexes has a significant effect on the nonradiative decay of these molecules.

From the data presented in Figure 3 and in refs 24 and 51, it is clear that the slopes for the dpp and bpy series are essentially indistinguishable given the number and the general quality of the data points. It is therefore likely that the smaller lifetimes and radiative quantum yields for the dpp derivatives relative to the bpy derivatives are simply due to the generally smaller energy gap of the former complexes.[68]

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Registry No. Re(dpp)(CO)$_3$Cl, 136301-20-7; [Re(dpp)(CO)$_3$(MIm)]ClO$_4$, 136301-22-9; [Re(dpp)(CO)$_3$(Mepy)]ClO$_4$, 136301-24-1; [Re(dpp)(CO)$_3$(Phpy)]ClO$_4$, 136301-26-3; [Re(dpp)(CO)$_3$(py)]ClO$_4$, 136301-28-5; [Re(dpp)(CO)$_3$(P(CH$_3$)$_3$)]ClO$_4$, 136327-65-6; [Re(dpp)(CO)$_3$(AN)]ClO$_4$, 136301-30-9; Re(bpy)(CO)$_3$Cl, 55658-96-3; [Re(bpy)(CO)$_3$(4-DMApy)]$^+$, 84028-75-1; [Re(bpy)(CO)$_3$(4-Apy)]$^+$, 84028-72-8; [Re(bpy)(CO)$_3$(MIm)]$^+$, 84028-70-6; [Re(bpy)(CO)$_3$(4-Etpy)]$^+$, 84028-68-2; [Re(bpy)(CO)$_3$(py)]$^+$, 84028-66-0; [Re(bpy)(CO)$_3$(P(CH$_3$)$_3$)]$^+$, 84028-64-8; [Re(bpy)(CO)$_3$(AN)]$^+$, 62972-14-9.

Supplementary Material Available: A listing of the elemental analyses for each new compound described (1 page). Ordering information is given on any current masthead page.

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Synthesis and Reduction of Osmium(VI) Nitrido Complexes and X-ray Crystal Structure of Tetra-*n*-butylammonium Octachlorodinitrido(μ-pyrazine)diosmate(VI)

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Anionic and neutral osmium(VI) nitrido complexes are prepared by the substitution of mono- or polypyridyl ligands on [n-Bu$_4$N][OsNCl$_4$] (**1**) in nonaqueous solvents. The cationic complex [OsNCl$_2$(terpy)]$^+$ (**11**) is formed by chelate ring closure of OsNCl$_3$(η^2-terpy) (**9**) in H$_2$O. The complexes were characterized by UV-vis, ^{1}H NMR, and IR spectroscopy. ^{15}N-labeled complexes were prepared to assign ν(Os≡N) unambiguously. Reduction of the nitrido complexes in protic media produced the monoammine complexes with intact coordination spheres. The structure of the pyrazine-bridged nitrido binuclear species (**3**) was determined by a single-crystal X-ray structure analysis. It crystallizes in the space group $P\bar{1}$ with $a = 11.557$ (4) Å, $b = 11.582$ (3) Å, $c = 11.028$ (2) Å, $\alpha = 113.02$ (2)°, $\beta = 108.67$ (2)°, $\gamma = 91.81$ (2)°, $V = 1266$ Å^3, and $Z = 1$. The structure was refined to $R = 0.049$ and $R_w = 0.066$ for 3906 reflections with $F_o^2 > 3\sigma(F_o^2)$. The pyrazine nitrogen atoms coordinate to two OsNCl$_4$ fragments in the position trans to the nitride, resulting in a tetragonally distorted octahedral geometry about each osmium center. The Os≡N bond length is 1.630 (7) Å with the osmium atoms displaced 0.365 Å from the plane containing the four chloride ligands.

Introduction

The capability of some transition metals to stabilize the nitrogen atom by the formation of discrete molecular complexes has been known for some time and is well documented in the literature.[1] An example of such a metal is osmium, which in the +VI oxidation state forms stable terminal nitrido complexes. Of particular current interest is the reactivity of the terminal nitrido ligand. Oxidation of free phosphines to give phosphinimates[2-4] and S$_2$Cl$_2$ to give thionitrosyls[5] by osmium(VI) nitrido complexes are two examples and can be viewed as intermediates in N-atom-transfer reactions analogous to the reactions of metal-oxo complexes. In addition, the implication of molybdenum nitrido complexes as intermediates in the reduction of dinitrogen to ammonia in nitrogenase model systems[6] and the proposal that the internal disproportionation of a μ-dinitrogen bimetallic complex to give two metal nitrido species may be a possible mechanism for dinitrogen fixation[6,7] has made the study of metal nitrido complexes important.

In this paper the systematic substitution of one, two, or three pyridyl groups into the coordination sphere of [OsNCl$_4$]$^-$ is described. The synthesis and characterization of anionic, neutral, and cationic complexes corresponding to the mono-, di-, and trisubstituted [Os≡N] moiety, respectively, is given. The structure of a binuclear (μ-pyrazine)nitridoosmate species has been determined by X-ray methods and compared with other osmium(VI)

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