Ultrafast Time-Resolved UV−Visible and Infrared Absorption Spectroscopy of Binuclear Rhenium(I) Polypyridyl Complexes in Solution

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Four binuclear rhenium(I) complexes of the form $[Re(CO)_3Cl]_2BL$, where BL is one of the bridging N_4-donor ligands 2,3-di(2-pyridyl)quinoxaline, 2,3-di(2-pyridyl)-6-methylquinoxaline, 2,3-di(2-pyridyl)pyrido-[2,3-*b*]pyrazine, or 2,3-di(2-pyridyl)pyrido[3,4-*b*]pyrazine, have been studied by femtosecond time-resolved UV−visible and infrared absorption spectroscopies. Photolysis at 606 nm, within the metal-to-ligand charge-transfer (MLCT) absorption band of each complex, produces transient features with lifetimes which vary from 100 to 1800 ps, depending on the structure of the bridging ligand. These transient species are assigned to the ^{3}MLCT excited states of the complexes. A detailed analysis of the time-resolved infrared spectra reveals that the three principal ν(CO) bands of the ground state, which arise from two $Re(CO)_3Cl$ groups in similar environments, split into two sets of three ν(CO) bands in the ^{3}MLCT excited states. This splitting pattern is attributed to asymmetric charge distribution in the excited state, in which one rhenium center is oxidized and the other is a spectator which senses the reduction of the bridging ligand; i.e., the excited state is a class II mixed-valence state, $Re^+(BL^-)Re$. Changes in the transient spectra which occur within ca. 5 ps, and which are observed most clearly as broadening to lower wavenumber of the excited-state infrared bands, are attributed to vibrational relaxation in the excited state. The variation in excited-state lifetime with bridging ligand structure is attributed to changes in the rate constants for nonradiative decay, which correspond qualitatively with changes in the energy of the excited state in accordance with the “energy-gap law” for nonradiative relaxation.

Introduction

The determination of structure and bonding in excited electronic states is a key feature in developing an understanding of the dependence of photochemical reaction mechanisms on molecular structure. Time-resolved resonance Raman (TR^3) and time-resolved infrared (TRIR) spectroscopies have found wide application and success in such studies, including many examples of bimolecular photochemical reactions which require diffusion in solution and which occur on time scales, typically, of >100 ns. Recently, there has been substantial effort in the development of supramolecular photodevices which combine different functional groups and which are designed for specific applications.[1−3] These new supramolecular systems present additional challenges in the study of their excited-state reactions. First, the photochemistry may occur much faster, on the subnanosecond time scale, because the reactions commonly involve intramolecular processes which do not require diffusion. Second, each of several functional groups may need to have distinct marker bands, and may even require complementary spectroscopic techniques, to enable time-dependent changes in their structure and bonding to be observed. The development of experimental strategies for such studies is important if the design of new molecules which contain several functional groups is to be informed by a detailed understanding of the interplay between molecular structure and excited-state properties.

There is current interest in the synthesis and study of polynuclear ligand-bridged complexes of a variety of metals because of the opportunities which they provide to control the photoinduced electron or energy transfer between subunits by supramolecular design.[1−3] The properties of such complexes can be tuned by changing the metal or its oxidation state or by changing the structure of the bridging ligands. Polypyridyl complexes of d^6 transition metals have been widely studied for many years because they display a rich photochemistry arising from their metal-to-ligand charge-transfer (MLCT) excited states, which readily undergo redox reactions.[2] Among these complexes, those containing the $Re(CO)_3L$ group (where the ligand, L, is typically a halide) have received attention because of their high stability, which has enabled them to be used as photocatalysts in bimolecular reactions.[4−7]

The mononuclear $Re(CO)_3L$ polypyridyl complexes exhibit luminescence which often has been used to study the ^{3}MLCT state energies and lifetimes, which range from 10 ns to 100 μs in room-temperature solution.[8−18] In addition, recent nanosecond TRIR[19−24] and TR^3 [25−27] studies of these excited states have yielded important new information on the structure and bonding within the MLCT states. In particular, the ν(CO) bands of the carbonyls attached to the rhenium center are sensitive to the oxidation state of the metal and have proven to be excellent TRIR reporters on the charge redistribution which occurs on excitation.

The attachment of a second $Re(CO)_3L$ group to a polypyridyl ligand has been found, generally, to result in much lower yields of luminescence and much shorter excited-state lifetimes.[11,12,15,28−31] As a result, the excited states of polynuclear complexes are less readily observed by steady-state or nano-

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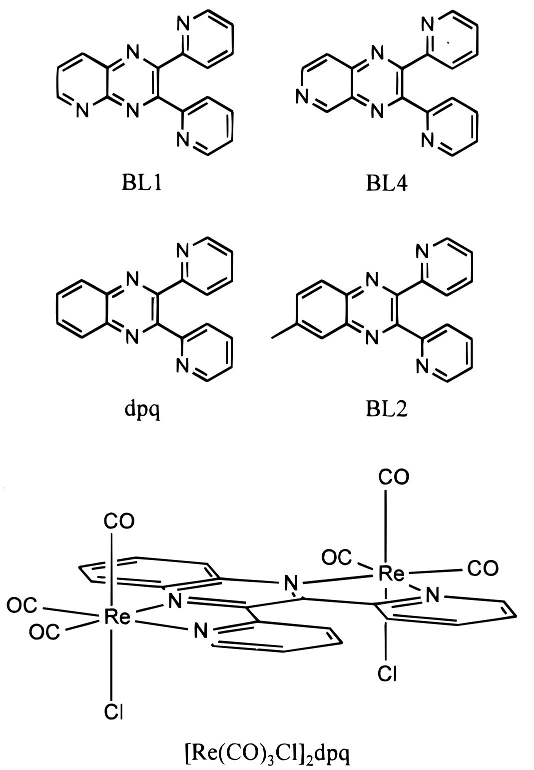

Figure 1. Structures of the bridging ligands (BL) used in this study; schematic structure of *cis*-$[Re(CO)_3Cl]_2dpq$.

second time-resolved techniques than their mononuclear analogues. There is a need for time-resolved studies on a faster time scale in order to determine the effect of attaching a second metal center on both the lifetime and the charge distribution in the excited states of these binuclear complexes.

A recent report described the synthesis of a series of binuclear Re(I) complexes, $[Re(CO)_3Cl]_2BL$ (where BL is a polypyridyl bridging ligand, as shown in Figure 1), and detailed the electrochemical and spectroscopic characteristics of the ground states as a function of bridging ligand structure.[32] This series of complexes offers the opportunity to explore both the structures and the lifetimes of the excited states using a combination of ultrafast time-resolved UV−visible (TRVIS) and TRIR spectroscopies. The aim of this work was to determine the structure and bonding in the ultrashort-lived excited states of this set of binuclear Re(I) complexes and to study the dependence of the excited-state structure and dynamics on bridging ligand structure. In addition to providing information on these particular complexes, this study has wider relevance in the context of studying the excited-state properties of polynuclear metal complexes which have applications as units within supramolecular photodevices.

Experimental Section

The syntheses of $[Re(CO)_3Cl]_2BL1$, $[Re(CO)_3Cl]_2BL4$, $[Re(CO)_3Cl]_2dpq$, and $[Re(CO)_3Cl]_2BL2$ have been described previously;[32] we have adopted the abbreviations used for the bridging ligands in the earlier work. The cis−trans isomer composition of the samples with respect to the chloride ligands is not known; a schematic structure of *cis*-$[Re(CO)_3Cl]_2dpq$ is shown in Figure 1 for illustration. The complexes were studied at room temperature (ca. 20 °C) in dichloromethane (Aldrich, spectrophotometric grade) solution, at a concentration of ca. $(0.5-1.0) \times 10^{-3}$ M. UV−visible spectra were recorded on a Hitachi U-3000 spectrometer using 1 mm path length cells, and infrared spectra were recorded at 4 cm^{-1} resolution on a Nicolet Impact 410 FTIR spectrometer, using a 500 μm path length cell with KBr windows. Fluorescence spectra were recorded on a Shimadzu RF-1501 spectrofluorimeter using a 1 cm path length quartz cell and front-surface illumination; this instrument was able to detect emission at $<$750 nm. Resonance Raman spectra were recorded using the 514.5 nm line from an argon ion laser (Spectra Physics model 2025), with the sample contained in a spinning quartz cell. Scattered light was collected at 90°, dispersed using a SPEX 1403 double monochromator, and detected with a liquid nitrogen cooled charge-coupled device (CCD) detector (Wright Instruments). A holographic notch filter (Kaiser Optical Systems, Inc.) was used to reject Rayleigh scattering.

The ultrafast laser system used in this study has been described in detail elsewhere.[33] Briefly, an amplified dye laser system was used to provide ultrashort pulses (200 fs, 606 nm, 1050 Hz), and the output was split into two beams. One beam was chopped at 525 Hz and was used to pump the sample with a pulse energy of ca. 8 μJ. The second beam was directed around a variable optical delay line and was used for either probing (TRVIS) or gating (TRIR). For the TRVIS experiments, a white light continuum was generated in a cell of D_2O/H_2O, and the continuum beam was passed through the sample cell coincident with the pump beam using near-collinear geometry. The emerging probe beam was analyzed using 10 nm band-pass interference filters and was detected using a photodiode and two lock-in amplifiers. For the TRIR experiments, the CW output of either a CO laser (used in these studies at 1818−1972 cm^{-1}) or a lead salt diode laser (two diodes used in these studies at 1966−2055 and at 2035−2126 cm^{-1}) was passed through the sample collinear with the pump beam, and the emerging infrared beam was mixed with the gating pulses in a 2 mm $LiIO_3$ crystal to generate an up-converted signal at ca. 540 nm. This signal was analyzed using a spectrometer and was detected with a photomultiplier tube and two lock-in amplifiers. Spectra were collected, point by point, by using a set of interference filters to obtain TRVIS spectra or by tuning the probe laser to obtain TRIR spectra. In all cases the relative polarization of the pump and probe beams was set to the "magic angle" of 54.7°. The solutions (ca. 25 cm^3) were placed under air in a closed gear-pump-driven flow system and were circulated through a 1 mm path length cell with CaF_2 windows. A linear flow rate of $>$100 cm s^{-1} was used to ensure that each pair of laser pulses encountered unphotolyzed sample. Steady-state UV−visible and infrared spectra recorded before and after the experiments were unchanged and confirmed the integrity of the sample.

Kinetic data were fitted to single-exponential or multiexponential decays convoluted with the instrument response function. The output of the diode lasers comprised more than one IR mode at some current/temperature combinations. In these cases, the measured Δabsorbance is represented in the TRIR spectra as a single point at one wavenumber which was obtained by averaging the output mode wavenumbers weighted by their respective intensities: the TRIR bands are sufficiently broad that data obtained with multimode output (which typically encompassed 6 cm^{-1}) did not significantly affect the observed profiles. TRIR spectra obtained with the three different IR lasers were scaled (0.75−1.00) for small changes in experimental parameters before plotting a full-range spectrum; regions of overlap between the different lasers confirmed that the scalings were appropriate. Spectra were analyzed with the Curve Fit

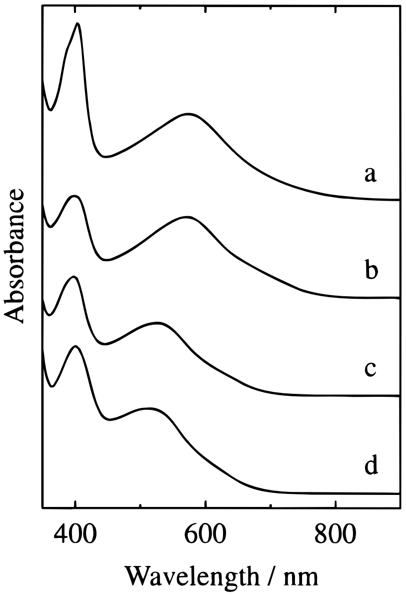

Figure 2. UV−visible absorption spectra of (a) $[Re(CO)_3Cl]_2$BL1, (b) $[Re(CO)_3Cl]_2$BL4, (c) $[Re(CO)_3Cl]_2$dpq, and (d) $[Re(CO)_3Cl]_2$BL2 in dichloromethane solution.

program in the GRAMS/386 package (Galactic Software), using Voigt profiles.

Results

Steady-State Spectroscopy. The steady-state UV−visible absorption spectra of the $[Re(CO)_3Cl]_2$BL complexes in dichloromethane solution are shown in Figure 2, and the infrared spectra in the ν(CO) region are shown in Figure 3 (lower). The UV−visible and infrared band positions are listed in Table 1. Resonance Raman spectra of $[Re(CO)_3Cl]_2$BL1 were recorded in the ν(CO) region and showed a strong band at 2035 cm^{-1} with a shoulder at ca. 2026 cm^{-1}, as shown in Figure 3 (upper). No luminescence was observed at <750 nm on excitation of solutions of the complexes at room temperature.

Time-Resolved UV−Visible Spectroscopy. TRVIS spectra recorded on 606 nm photolysis of solutions of each of the complexes are shown in Figure 4. All of the spectra have a similar shape, comprising bleaching of the ground-state absorption bands at ca. 500−580 nm and transient absorption at ca. 440 nm and at >750 nm. TRVIS kinetics recorded in the region of ground-state bleaching were found to fit well to a single-exponential decay. The kinetics recorded in the region of transient absorption were found to fit well to a dual-exponential decay, with the principal component having the same lifetime (τ_1) as that of the bleaching decay and the small second component having a lifetime (τ_2) of 5 ± 3 ps. This fast component was more evident in the TRIR kinetics (vide infra). Examples of kinetic traces obtained from $[Re(CO)_3Cl]_2$BL1 are shown in Figure 5. The principal component in the TRVIS kinetics of each complex was found to be similar, whether probing in the region of bleaching or of transient absorption. The value of τ_1 was found to be different for each complex, as given in Table 2. The value of τ_2 was found to be similar for each complex.

Time-Resolved IR Spectroscopy. TRIR spectra recorded on 606 nm photolysis of each of the complexes showed bleaching of the ground-state ν(CO) bands and transient absorption at both higher and lower wavenumbers than these bands. The transient absorption features initially were broad and sharpened over the first few picoseconds, with the peak positions shifting to higher wavenumber. After this broadening, the shapes of the spectra remained similar during the decay. Examples of TRIR spectra recorded from $[Re(CO)_3Cl]_2$BL1 are shown in Figure 6.

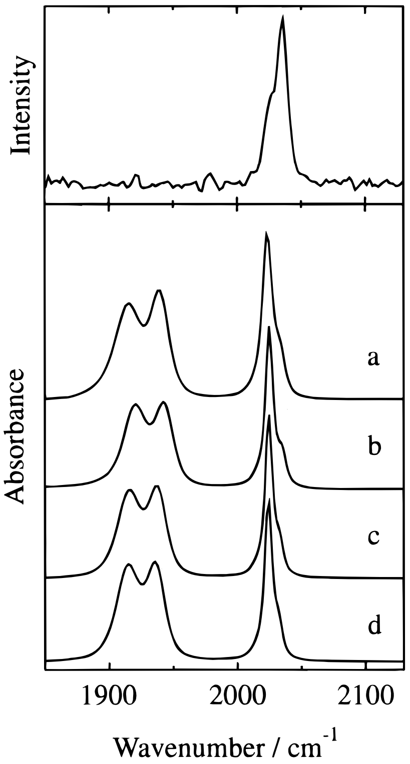

Figure 3. Upper: resonance Raman spectrum of $[Re(CO)_3Cl]_2$BL1 in dichloromethane solution, excited at 514.5 nm. Lower: infrared absorption spectra of (a) $[Re(CO)_3Cl]_2$BL1, (b) $[Re(CO)_3Cl]_2$BL4, (c) $[Re(CO)_3Cl]_2$dpq, and (d) $[Re(CO)_3Cl]_2$BL2 in dichloromethane solution.

TABLE 1: UV−Visible (λ) and Infrared (ν) Band Positions of the Rhenium(I) Complexes in Dichloromethane Solution

complex	λ/nm		ν/cm^{-1}				E^a/eV
$[Re(CO)_3Cl]_2$BL1	574	403	2034	2024	1940	1915	2.16
$[Re(CO)_3Cl]_2$BL4	571	398	2035	2025	1943	1920	2.17
$[Re(CO)_3Cl]_2$dpq	526	398	2033	2025	1938	1916	2.36
$[Re(CO)_3Cl]_2$BL2	510	401	2033	2024	1936	1915	2.43

[a] Energy corresponding to the peak of the long-wavelength UV−visible absorption band.

TRIR kinetics were measured throughout the region 1850−2140 cm^{-1}. All of the TRIR kinetic traces for each complex were found to contain a slow component (τ_1) which is similar to that obtained from the TRVIS kinetics (Table 2). A second component (τ_2) with a lifetime in the range of 2−7 ps, dependent on the probe wavenumber, was observed clearly for all of the complexes as a fast decay on the low-wavenumber side of the transient absorption bands and as a slow rise at the peak of these features. The rise times of the transient absorption bands were <1 ps when measured away from the peaks, in regions where typically two decay components were observed. The rise times of bleaching bands were measured to be 1−2 ps; these bleaching bands overlap with transient absorption bands which may contribute to the observed rise times, whereas the rise times of the transient absorption bands themselves could be measured in regions outside strong overlap with bleaching features. Examples of TRIR kinetic traces from $[Re(CO)_3Cl]_2$BL1, shown in Figure 7, illustrate these features.

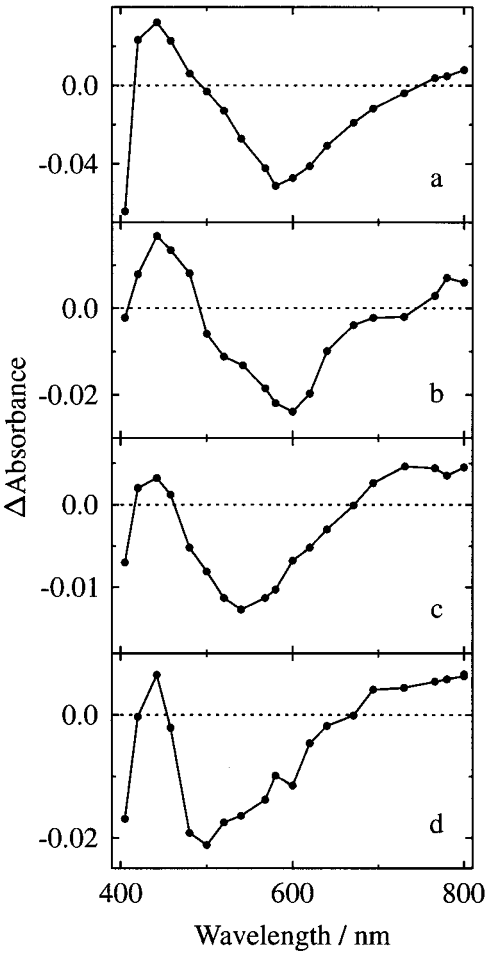

Figure 4. TRVIS spectra of (a) $[Re(CO)_3Cl]_2BL1$, (b) $[Re(CO)_3Cl]_2BL4$, (c) $[Re(CO)_3Cl]_2dpq$, and (d) $[Re(CO)_3Cl]_2BL2$ in dichloromethane solution, recorded at delay times of ca. 5 ps after 606 nm photolysis.

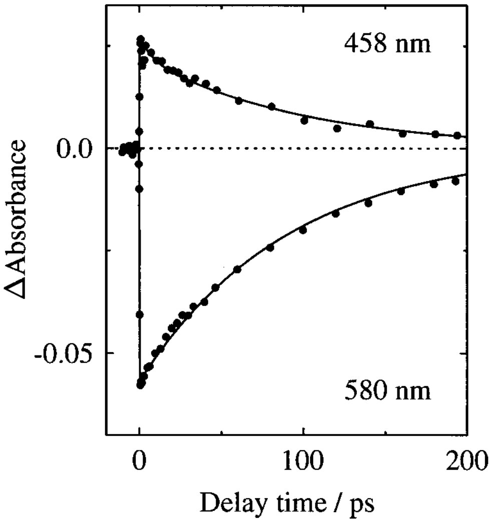

Figure 5. TRVIS kinetics recorded on 606 nm photolysis of $[Re(CO)_3Cl]_2BL1$ in dichloromethane solution. The experimental data are given as points and the solid lines are fits to single-exponential (580 nm, $\tau_1 = 91$ ps) and dual-exponential (458 nm, $\tau_1 = 101$ ps and $\tau_2 = 7$ ps) decays.

TABLE 2: Excited-State Lifetimes (τ_1) of the Rhenium(I) Complexes in Dichloromethane Solution[a]

complex	τ_1/ps	complex	τ_1/ps
$[Re(CO)_3Cl]_2BL1$	100 ± 20	$[Re(CO)_3Cl]_2dpq$	1350 ± 150
$[Re(CO)_3Cl]_2BL4$	300 ± 50	$[Re(CO)_3Cl]_2BL2$	1800 ± 200

[a] The fitted values varied between data sets and the given range is that in which satisfactory fits were obtained to both TRVIS and TRIR data; individual fits gave smaller $\pm 2\sigma$ values than the ranges indicated.

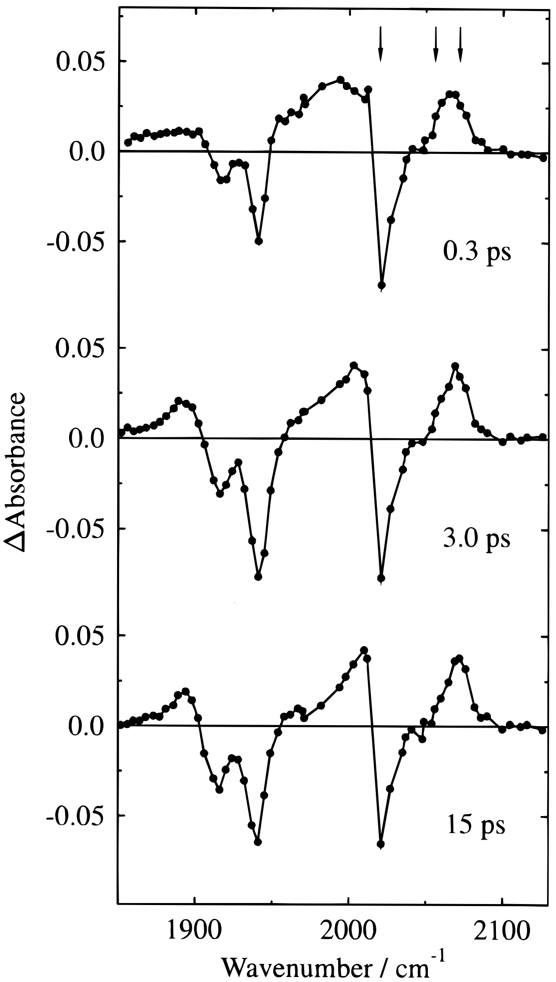

Figure 6. TRIR spectra recorded on 606 nm photolysis of $[Re(CO)_3Cl]_2BL1$ in dichloromethane solution. The solid lines connect the experimental data points. The arrows indicate the positions chosen to illustrate the TRIR kinetics in Figure 7.

Discussion

Steady-State Spectra. The UV−visible absorption spectrum of each of the complexes comprises a broad band at ca. 550 nm and a sharper band at ca. 400 nm (Figure 2), both of which have been assigned to MLCT transitions.[32] The position of the former band shows a strong dependence on the structure of the bridging ligand, shifting to longer wavelength in the order $[Re(CO)_3Cl]_2BL2 < [Re(CO)_3Cl]_2dpq \ll [Re(CO)_3Cl]_2BL4 < [Re(CO)_3Cl]_2BL1$. This shift may be attributed to stabilization of the bridging ligand π^* orbital, which is the acceptor orbital on MLCT excitation. The stabilization is greatest for the complexes $[Re(CO)_3Cl]_2BL1$ and $[Re(CO)_3Cl]_2BL4$, which contain a nitrogen heteroatom within the quinoxaline ring, whereas the electron-donating methyl substituent in $[Re(CO)_3Cl]_2BL2$ destabilizes the π^* orbital relative to that in $[Re(CO)_3Cl]_2dpq$.

All of the complexes give similar infrared spectra, showing three strong bands at ca. 1915, 1940, and 2025 cm^{-1} and a shoulder at ca. 2034 cm^{-1} (Figure 3). Mononuclear rhenium(I) complexes of the form Re(CO)$_3$Cl(diimine) have been found to adopt a facial geometry, which results in a characteristic infrared spectrum comprising three ν(CO) bands.[21] The main features of the infrared spectra of the binuclear complexes

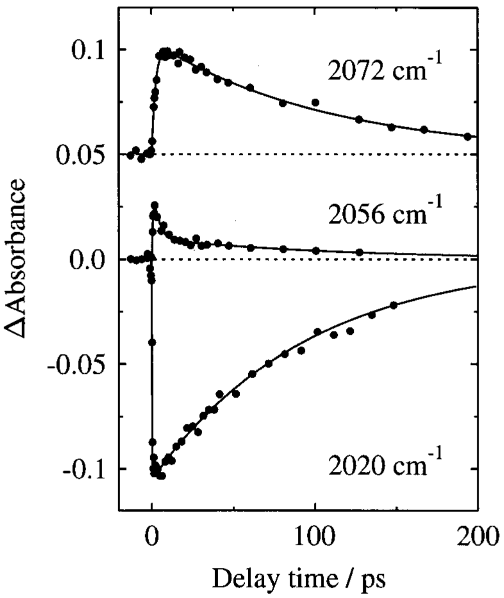

Figure 7. TRIR kinetics recorded on 606 nm photolysis of $[Re(CO)_3Cl]_2BL1$ in dichloromethane solution. The experimental data are shown as points and the solid lines are fits to the data (rise of $\tau_2 = 2.4$ ps and decay of $\tau_1 = 107$ ps at 2072 cm^{-1}; decays of $\tau_2 = 3.3$ ps and $\tau_1 = 115$ ps at 2056 cm^{-1}; rise of 1.0 ps and decay of $\tau_1 = 95$ ps at 2020 cm^{-1}). The kinetics recorded at 2072 cm^{-1} have been offset by Δabsorbance = 0.05 for clarity.

studied here resemble those of such mononuclear complexes, and on this basis, the ν(CO) bands are readily assigned to the in-plane symmetric stretch (2025 cm^{-1}), the in-plane antisymmetric stretch (1940 cm^{-1}), and the out-of-plane stretch (1915 cm^{-1}),[21] where the bridging ligand defines the plane (Figure 1). The presence of the weak infrared band at ca. 2034 cm^{-1} may be considered along with the resonance Raman spectra, which show two bands in this region, at 2026 and 2035 cm^{-1}, with their relative intensities reversed from those observed in the infrared spectra. This observation suggests that these bands arise from coupling between the two metal centers: the in-plane symmetric ν(CO) modes couple in-phase to give a band at 2034 cm^{-1} (strong in the resonance Raman, weak in the infrared) and out-of-phase to give a band at 2025 cm^{-1} (strong in the infrared, weak in the resonance Raman). The presence of two bands in this region for the symmetric $[Re(CO)_3Cl]_2dpq$ complex indicates that the second band does not arise from inequivalent CO ligands resulting from bridging ligand asymmetry.

Time-Resolved UV−Visible and IR Spectra. The TRVIS difference spectrum of each of the complexes shows bleaching of both ground-state bands and transient absorption at ca. 440 nm and at >750 nm (Figure 4). The changes at <700 nm are similar to those observed previously on electrochemical reduction of the bridging ligands of the complexes in the ground state[32] and are consistent with MLCT excitation; for example, reduction of ground-state $[Re(CO)_3Cl]_2BL1$ resulted in an increase in absorbance at 410−480 nm and a decrease in absorbance at >480 nm, similar to the changes observed here on photoexcitation (Figure 4). In contrast, the changes at >700 nm are different from those observed previously on reduction of the ground-state complexes;[32] we observe new absorption features at >750 nm for all four complexes whereas no new bands were observed on electrochemical reduction. The absence of bands in this region for the reduced ligands formed electrochemically suggests that these long-wavelength bands do not arise from intraligand transitions in the reduced ligand formed photochemically. If the excited state is of mixed-valence configuration, then these bands may arise from intervalence transitions between two inequivalent metal centers.

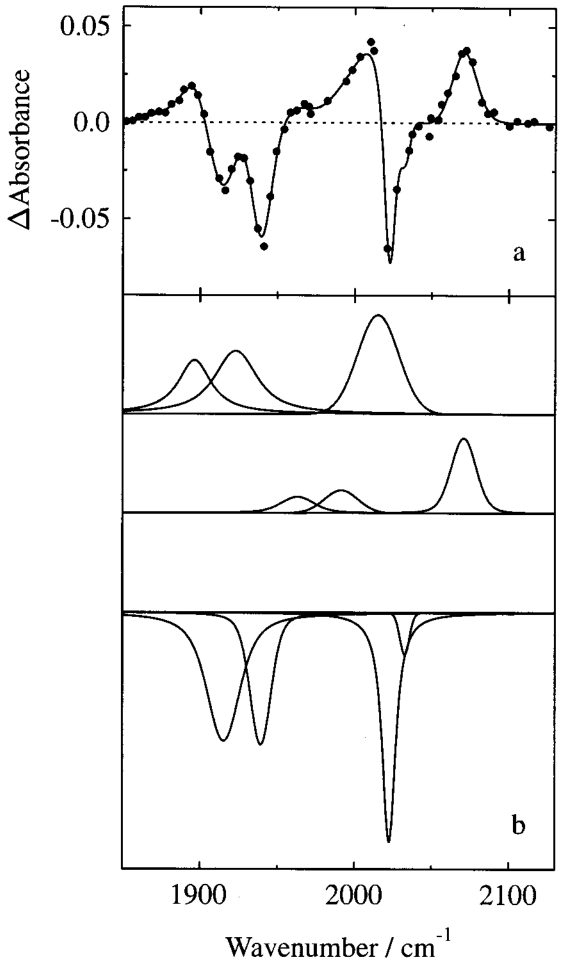

Figure 8. TRIR spectrum recorded 15 ps after 606 nm photolysis of $[Re(CO)_3Cl]_2BL1$ in dichloromethane solution. (a) Points show the experimental data and the solid line is the fitted spectrum. (b) Components of the fitted spectrum, offset for clarity.

For each of the complexes, the shapes of the TRVIS and TRIR spectra did not change significantly at >5 ps, which indicates that only one transient species is present at these longer delay times. The relatively long lifetimes, of up to ca. 2 ns, suggest that these transient species are ^{3}MLCT excited states.

A band-fitting analysis of the TRIR spectra was performed in order to quantify the IR band positions of the excited state present at >5 ps. For $[Re(CO)_3Cl]_2BL1$, the steady-state infrared spectrum was fitted first to determine the positions, bandwidths, relative intensities, and functional forms of the ground-state bands. These ground-state bands were then used, as bleaching features, to fit the TRIR difference spectrum at 15 ps: their positions were allowed to vary by ±1.5 cm^{-1}, their relative heights were fixed, and both the bandwidths and the functional forms were constrained to be similar to those in the fitted ground-state spectrum. Six new absorption bands were required to fit all of the features of the TRIR spectrum. The widths of these transient bands were constrained to be <40 cm^{-1} in the fitting procedure. The fitted spectrum and the fitted component bands for $[Re(CO)_3Cl]_2BL1$ are shown in Figure 8; the band-fitting parameters are listed in Table 3. The transient absorption bands are seen to comprise two sets: three bands are upshifted from the ground-state bands, and three bands are downshifted from the ground-state bands. The transient absorption bands observed at 15 ps were found to be broader than the

TABLE 3: Parameters Used To Fit the TRIR Difference Spectrum of $[Re(CO)_3Cl]_2BL1$ Obtained 15 ps after 606 nm Photolysis

band type	wavenumber/ cm^{-1}	fwhm[a]/ cm^{-1}	rel peak absorbance[b]
ground-state bands	1915	26.8	0.99
	1940	16.3	1.00
	2023	10.4	1.71
	2033	7.4	0.31
downshifted bands	1897	25.3	0.90
	1923	32.4	1.00
	2015	31.3	1.64
upshifted bands	1963	25.0	0.72
	1992	25.2	1.00
	2071	19.0	3.32

[a] Full width at half-maximum. [b] Absorbance relative to the 1940 cm^{-1} ground-state band or the equivalent downshifted (1923 cm^{-1}) or upshifted (1992 cm^{-1}) band.

TABLE 4: Infrared Band Positions Used To Fit the Down- and Upshifted Features in the TRIR Spectra Obtained ≥15 ps after 606 nm Photolysis

	wavenumber/cm^{-1}					
complex	downshift	Δ_{down}[a]	$\Delta_{av\ down}$[b]	upshift	Δ_{up}[a]	$\Delta_{av\ up}$[b]
$[Re(CO)_3Cl]_2BL1$	1897	−18		1963	+48	
	1923	−17	−14	1992	+52	+49
	2015	−8		2071	+48	
$[Re(CO)_3Cl]_2BL4$	1911	−9		1982	+62	
	1933	−10	−12	1993	+50	+52
	2005	−17		2065	+43	
$[Re(CO)_3Cl]_2dpq$	1903	−12		1980	+65	
	1918	−21	−17	1993	+54	+51
	2006	−19		2060	+35	
$[Re(CO)_3Cl]_2BL2$	1896	−19		1966	+51	
	1918	−19	−19	1981	+44	+41
	2006	−19		2054	+29	

[a] Shift from the corresponding ground-state band. [b] Average shift.

ground-state bands; the broadness of these bands, which persists for the lifetime of the excited state, may arise from a wider range of interactions with the solvent in the charge-transfer excited states.

For mononuclear $Re(CO)_3Cl$(diimine) complexes, all three ground-state ν(CO) bands have been found to shift to higher wavenumber on MLCT excitation.[19−24] The loss of electron density at the photoexcited (i.e., oxidized) metal center results in weaker back-bonding to the carbonyl ligands, in strengthening of the CO bonds, and in a shift of the ν(CO) bands to higher wavenumber. The band-fitting analysis of the TRIR spectrum of the binuclear complex $[Re(CO)_3Cl]_2BL1$ shows that one set of bands is shifted to higher wavenumber, and we attribute this shift to MLCT photoexcitation (oxidation) of one of the metal centers. The three transient bands at lower wavenumber than the ground-state bands are characteristic of weaker CO bonds, resulting from increased back-bonding to the carbonyl ligands: they may be assigned to the second metal center, which senses the reduction of the bridging ligand by an increase in electron density. The upshifts are of greater magnitude than the downshifts; this is consistent with the oxidation of one metal center and the second metal center acting as a "spectator". Thus, the approximate form of the excited state may be given as $Re^+(BL^-)Re$.

Band-fitting analyses of the TRIR spectra of the other three complexes produced similar results (Table 4). In each case, two sets of transient bands were obtained which showed analogous shifts from the ground-state bands, i.e., ca. +50 cm^{-1} for the upshifted bands and ca. −15 cm^{-1} for the downshifted bands. The similarity of these shifts and of the TRIR spectra suggests that the structure and bonding of the ^{3}MLCT state is similar for each of the complexes.

The ν(CO) bands of the mononuclear complex $Re(CO)_3Cl$-(2,2′-bpy) (bpy = bipyridine) have been reported to shift by an average of +55 cm^{-1} on MLCT excitation.[20] This value is similar to the average upshift of the ν(CO) bands on excitation of the binuclear complexes studied here and indicates that the change in electron density at the photoexcited (oxidized) metal center is similar in mono- and binuclear complexes.

The lowest unoccupied molecular orbital of the ground-state complexes is a bridging ligand π* orbital, and one-electron reduction of the ground state has commonly been used to obtain indirect information on the MLCT excited state. For $Re(CO)_3Cl$(2,2′-bpy), one-electron reduction causes the ν(CO) bands to shift an average of −30 cm^{-1};[20] preliminary studies of $[Re(CO)_3Cl]_2BL1$ have shown that the ν(CO) bands shift an average of −28 cm^{-1}.[34] The metal center may be considered to act as a spectator in the reduction of the ground-state complex, in a similar way to the nonphotoexcited (nonoxidized) metal center present in the MLCT excited states of the binuclear complexes studied here. The average downshift on MLCT excitation is ca. 50% of that observed on one-electron reduction of the ground state, which indicates that the presence of the oxidized metal center decreases the electron density on the bridging ligand, and thereby at the spectator metal center, in comparison with the reduced complex in the ground state.

The dual splitting pattern of the ν(CO) bands of the excited states of the binuclear $[Re(CO)_3Cl]_2BL$ complexes studied here is similar to that reported for the MLCT excited states of binuclear $[W(CO)_5]_2BL$ complexes[35] which have recently been studied on the nanosecond time scale by both TRIR[36,37] and TR^3[38] spectroscopies. Our interpretation, that the dual splitting pattern of the ν(CO) bands of the excited-state rhenium complexes arises from a localized charge-transfer state, is consistent with the earlier interpretation for the excited-state tungsten complexes; our studies provide new examples of asymmetric charge distribution for different transition-metal complexes in much shorter-lived excited states. The asymmetric charge distribution in the excited states of the $[Re(CO)_3Cl]_2BL$ complexes indicate that they are mixed-valence states of the type $Re^+(BL^-)Re$, comprising both Re^{II} and Re^I metal centers. Although there have been many studies of charge distribution and localization/delocalization in mixed-valence ground electronic states,[39,40] there have been relatively few examples where charge distribution has been studied in mixed-valence excited electronic states.

The magnitudes of the band shifts on photoexcitation of the $[Re(CO)_3Cl]_2BL$ complexes can reveal further information. In particular, they provide an interesting contrast with the shifts reported for the $[W(CO)_5]_2$(4,4′-bipy) complex.[36,37] The shifts of the ν(CO) bands at the photoexcited (oxidized) metal center of $[W(CO)_5]_2$(4,4′-bipy) are reported to be similar to those of the photoexcited mononuclear complex, as we also observe for $[Re(CO)_3Cl]_2BL$. However, the shifts of the ν(CO) bands of the "spectator" metal center of $[W(CO)_5]_2$(4,4′-bipy) are greater (ca. 140%) than those of the reduced ground-state complex, which is different from our observations with the $[Re(CO)_3Cl]_2BL$ complexes. It has been proposed that the excited states of the binuclear tungsten complexes display spectra which are more characteristic of class I than class II species (Robin and Day classification[39]), i.e., that any coupling between the metal centers is very weak.[37] This proposal was made on the basis of the larger shift in the ν(CO) bands at the "spectator" metal center on photoexcitation than on electrochemical reduction and because there is no evidence for an intervalence transition. Our observation of a smaller shift in the ν(CO) bands at the "spectator" metal center on photoexcitation than on electrochemical reduction and our observation of a long-wavelength band in the TRVIS spectrum which may arise from an intervalence transition both indicate that the excited states of the binuclear rhenium complexes may best be described as class II. In other words, our TRIR and TRVIS data suggest that the coupling between the metal centers is stronger for these rhenium complexes than for the tungsten complexes.

The specificity of the ν(CO) marker bands and their use to provide information on structure and bonding in ultrashort-lived excited states clearly offers a useful tool with which to study the photochemistry of these polynuclear metal complexes. This technique would seem to be particularly appropriate for complexes containing the $Re(CO)_3L$ unit, for which the IR bands are relatively few and the band shifts easily observed; examples of supramolecular systems including this unit have already been reported.[41−47]

Time-Resolved UV−Visible and IR Kinetics. TRVIS and TRIR kinetics recorded in regions of ground-state bleaching were found to fit well to single-exponential decays, giving the lifetimes (τ_1) of the ^{3}MLCT states. However, TRVIS and TRIR kinetics recorded in regions of transient absorption showed an additional fast component with a lifetime of 2−7 ps (τ_2). This fast component was most clearly evident in the TRIR data as a fast decay when recorded at the low-wavenumber side, or as a slow rise when recorded near the peak, of a transient absorption band (Figure 7). Thus, the TRIR spectra recorded at the earliest times showed broad transient absorption bands which sharpened over the first few picoseconds, with the peak positions shifting to higher wavenumber (Figure 6). These changes in IR band shape and position are indicative of vibrational relaxation in the excited state. Photoexcitation results initially in the formation of excited electronic states with excess vibrational energy. The ν(CO) bands of the vibrationally excited species occur at lower wavenumber than those of the vibrationally relaxed species because of anharmonicity, resulting initially in very broad transient bands in the TRIR spectra. The ν(CO) bands shift to higher wavenumber as vibrational relaxation occurs, giving the sharpening to higher wavenumber which we observe. The time scale observed here for vibrational relaxation, of ca. 5 ps, is reasonable for such processes in solution,[48,49] although relaxation of vibrationally excited ν(CO) modes can occur on longer time scales of up to a few hundred picoseconds.[50−52]

Another possibility for the ca. 5 ps process is the decay of a first-formed ^{1}MLCT state to the longer-lived ^{3}MLCT state. This seems less likely for two reasons. First, the infrared bands of a ^{1}MLCT state may be expected to have a bandwidth similar to those of the ^{3}MLCT state, whereas the TRIR spectra indicate that the transient bands are broadened considerably at early times. Second, a change in spin state may be expected to result in distinct changes in the UV−visible spectrum, whereas the TRVIS spectra showed only small changes and a similar profile at all delay times. Intersystem crossing has been reported to occur in $\ll$1 ps on photoexcitation of related polypyridyl complexes of Fe(II).[53] Thus, our proposal that ultrafast intersystem crossing occurs for polypyridyl complexes of Re(I) is reasonable because spin−orbit coupling will be strong for this third-row transition metal; indeed, we recognize that "singlet" and "triplet" may be poor descriptors of the electronic states, but we follow common practice in using them as labels.

The transient absorption signals were observed to rise in $<$1 ps, when measured away from the peaks, but at a rate which was slower than the instrument response time. The TRIR technique used for this study, with a CW infrared probe and up-conversion detection, gives IR bleaching signals which rise instantaneously and transient IR absorption signals which rise with the vibrational dephasing time of the excited state.[54] The excited-state bandwidths observed here correspond to dephasing times on the order of 500 fs, consistent with the observed $<$1 ps rise time. The ca. 10 times difference in rate and the clearly observed asymmetry in the broadening enables us to discount vibrational dephasing as the origin of the ca. 5 ps process. We attribute the 1−2 ps rise time measured in the IR bleaching signals to a contribution from the overlying transient absorption bands.

The shifts of the ν(CO) bands are of similar magnitudes on excitation of each of the four binuclear complexes studied here, indicating that the charge distribution in their ^{3}MLCT states is similar. This suggests that the acceptor orbitals for the MLCT transitions are similar, despite the differences in the structures of the bridging ligands, although the data presented here do not enable us to determine the excited-state charge distribution within the ligands or the extent of communication between the pyridyl and quinoxaline rings. Crystal structures of several mononuclear metal complexes containing dpq ligands have shown that the pyridyl rings are twisted by ca. 30° out of the plane of the quinoxaline ring,[55−57] resulting in poor overlap between the π systems of the pyridyl and quinoxaline ring systems, and it has been suggested that the extent of communication between these two moieties is small in the ground states of the complexes studied here.[32]

The similarities in the TRIR spectra of the ^{3}MLCT states of the binuclear complexes suggest that differences in the excited-state lifetimes do not arise from differences in structure. The "energy gap law"[58] has been applied widely to interpret the dependence of excited-state lifetime on excited-state energy for many metal polypyridyl complexes,[9,10,13−15, 17,18,30,59] including several sets of mononuclear $Re(CO)_3L(BL)$ complexes (L = *N*-methylimidazole, trimethylphosphine, acetonitrile, or substituted pyridines) containing the same BL.[17] In its simplest form, the energy gap law relates $\ln(k_{nr})$, where k_{nr} is the rate constant for nonradiative decay of the excited state, to the energy gap between the excited and ground states. Such studies have usually considered the effect within a series of complexes in which the polypyridyl ligand (BL) remains unchanged while L is varied. However, if the normal modes which couple the excited and ground states are similar for each of several bridging ligands while L is unchanged, then the energy gap law may apply approximately. Indeed, as BL is varied, we observe a decrease in excited-state lifetime as the steady-state MLCT absorption band maximum shifts to longer wavelength (Tables 1 and 2). Luminescence from binuclear Re(I) polypyridyl complexes of this type is usually reported to be unobservable or very weak in solution at room temperature,[11,15,28−30] and we observed no luminescence at $<$750 nm from these complexes in solution at room temperature. Consequently, we have been unable to determine the energy gap between the ground and excited ^{3}MLCT states of these binuclear complexes. However, if the minima of the ground- and excited-state potential energy surfaces are displaced by similar amounts for each complex, then the variation of the energy corresponding to the steady-state MLCT absorption maximum (E, Table 1) will reflect the variation of ^{3}MLCT state energy. The quantum yield of luminescence is given by $\phi_L = k_r/(k_r + k_{nr})$, where k_r is the rate constant for radiative decay. We observe that $\phi_L \approx 0$, which indicates that $k_{nr} \gg k_r$ and that the observed lifetime of the

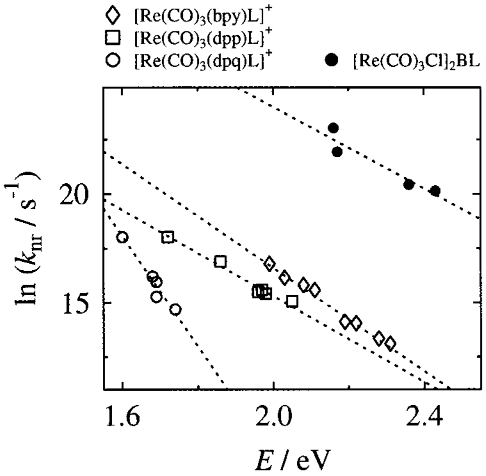

Figure 9. Plot of $\ln(k_{nr})$ vs E, where E is either the energy corresponding to the MLCT absorption band maximum (for the binuclear complexes) or the energy of the ^{3}MLCT excited state (reported for the mononuclear complexes). Data for the mononuclear complexes taken from refs 9 and 17.

excited state $\tau_1 \approx 1/k_{nr}$. The usual test of whether the energy gap law is obeyed is the linearity of a plot of $\ln(k_{nr})$ versus the energy of the excited state (E). Figure 9 shows such a plot for the binuclear complexes studied here, using the energy values corresponding to the steady-state absorption maxima. Values reported for three sets of $[Re(CO)_3(BL)L]^+$ complexes, where the excited-state energies have been determined from luminescence data and where BL is bpy,[9] dpp,[17] or dpq,[17] are included in Figure 9 for comparison. It is notable that the values for the binuclear complexes vary qualitatively according to the energy gap law and that the data for these binuclear complexes would lie within the range predicted from an extrapolation of the trends for the mononuclear complexes if the energy of the excited ^{3}MLCT state were to lie at 0.7−0.9 eV below the energy of the steady-state absorption maximum. A difference of ca. 1 eV between the absorption maximum and the energy of the excited state is commonly observed for $Re(CO)_3(BL)L$ complexes; for the binuclear complexes studied here, such a difference would place any luminescence at 700−1000 nm.

Conclusions

Ultrafast TRVIS and TRIR spectroscopies have been used to study the structure and dynamics of the excited states formed on visible photolysis of four binuclear rhenium(I) polypyridyl complexes. A detailed analysis of the TRIR spectra has shown that the excited states may be attributed to localized ^{3}MLCT states which have an asymmetric charge distribution, i.e., that they are of the form $Re^+(BL^-)Re$. The changes in charge distribution are similar on excitation of each of the four complexes studied, whereas the lifetime of the excited state was found to depend strongly on the structure of the bridging ligand, ranging from 100 to 1800 ps in the order $[Re(CO)_3Cl]_2BL1 < [Re(CO)_3Cl]_2BL4 < [Re(CO)_3Cl]_2dpq < [Re(CO)_3Cl]_2BL2$. This variation in lifetime has been attributed to variation in the rate constant for nonradiative decay of the excited state; the variation in this rate constant was found to obey the energy gap law qualitatively. In addition, vibrational relaxation within the ^{3}MLCT excited states was observed as a ca. 5 ps component in the TRVIS and TRIR kinetics and as a sharpening of the excited-state TRIR bands. The specificity of the ν(CO) bands in the TRIR spectra and the use of their positions to report on changes in structure and bonding in ultrashort-lived excited states indicate that the experimental strategy used in this study may be applied to probe the photochemistry of more complex, supramolecular systems incorporating several metal centers.

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References and Notes

(1) Balzani, V.; Scandola, F. *Supramolecular Chemistry*; Ellis Horwood Ltd.: London, 1991.
(2) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, 1992.
(3) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995.
(4) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536.
(5) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401.
(6) Meyer, T. J. *Acc. Chem. Res* **1989**, *22*, 163.
(7) Ishitani, O.; George, M. W.; Ibusuki, T.; Johnson, F. P. A.; Koike, K.; Nozaki, K.; Pac, C.; Turner, J. J.; Westwell, J. R. *Inorg. Chem.* **1994**, *33*, 4712.
(8) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.
(9) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.
(10) Lees, A. J. *Chem. Rev. (Washington, D.C.)* **1987**, *87*, 711.
(11) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J.-M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007.
(12) Lin, R.; Guarr, T. F.; Duesing, R. *Inorg. Chem.* **1990**, *29*, 4169.
(13) Worl, L. A.; Duesing, R.; Chen, P.; Ciana, L. D.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849.
(14) Baiano, J. A.; Murphy, W. R., Jr. *Inorg. Chem.* **1991**, *30*, 4594.
(15) Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1992**, *31*, 5.
(16) Wallace, L.; Rillema, D. P. *Inorg. Chem.* **1993**, *32*, 3836.
(17) Baiano, J. A.; Kessler, R. J.; Lumpkin, R. S.; Munley, M. J.; Murphy, W. R., Jr. *J. Phys. Chem.* **1995**, *99*, 17680.
(18) Rossenaar, B. D.; Stufkens, D. J.; Vlcek, A. J. *Inorg. Chem.* **1996**, *35*, 2902.
(19) Glyn, P.; George, M. W.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1655.
(20) George, M. W.; Johnson, F. P. A.; Westwell, J. R.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2977.
(21) Gamelin, D. R.; George, M. W.; Glyn, P.; Grevels, F.-W.; Johnson, F. P. A.; Klotzbücher, W.; Morrison, S. L.; Russell, G.; Schaffner, K.; Turner, J. J. *Inorg. Chem.* **1994**, *33*, 3246.
(22) Schoonover, J. R.; Strouse, G. F.; Dyer, R. B.; Bates, W. D.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 273.
(23) Schoonover, J. R.; Strouse, G. F.; Omberg, K. M.; Dyer, R. B. *Comments Inorg. Chem.* **1996**, *18*, 165.
(24) Chen, P.; Palmer, R. A. *Appl. Spectrosc.* **1997**, *51*, 580.
(25) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067.
(26) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyde, S.; Jones, W. E.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473.
(27) Schoonover, J. R.; Bates, W. D.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 6421.
(28) Ruminski, R.; Cambron, R. T. *Inorg. Chem.* **1990**, *29*, 1575.
(29) Van Wallendael, S.; Shaver, R. J.; Rillema, D. P.; Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 1761.
(30) Baiano, J. A.; Carlson, D. L.; Wolosh, G. M.; DeJesus, D. E.; Knowles, C. F.; Szabo, E. G.; Murphy, W. R. J. *Inorg. Chem.* **1990**, *29*, 2327.
(31) Lee, Y. F.; Kirchhoff, J. R.; Berger, R. M.; Gosztola, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3677.
(32) Simpson, T. J.; Gordon, K. C. *Inorg. Chem.* **1995**, *34*, 6323.
(33) Ye, T.-Q.; Arnold, C. J.; Pattison, D. I.; Anderton, C. L.; Dukic, D.; Perutz, R. N.; Hester, R. E.; Moore, J. N. *Appl. Spectrosc.* **1996**, *50*, 597.
(34) Gordon, K. C., unpublished results.
(35) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1139.
(36) George, M. W.; Turner, J. J.; Westwell, J. R. *J. Chem. Soc., Dalton Trans.* **1994**, 2217.
(37) George, M. W.; Johnson, F. P. A.; Turner, J. J.; Westwell, J. R. *J. Chem. Soc., Dalton Trans.* **1995**, 2711.
(38) McNicholl, R.; McGarvey, J. J.; Al-Obaidi, A. H. R.; Bell, S. E. J.; Jayaweera, P. M.; Coates, C. G. *J. Phys. Chem.* **1995**, *99*, 12268.
(39) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.
(40) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(41) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 3885.

(42) Tapolsky, G.; Duesing, R.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 2285.

(43) Schoonover, J. R.; Gordon, K. C.; Argazzi, R.; Woodruff, W. H.; Peterson, K. A.; Bignozzi, C. A.; Dyer, R. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 10996.

(44) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 2725.

(45) Bardwell, D. A.; Barigelletti, F.; Cleary, R. L.; Flamigni, L.; Guardigli, M.; Jeffery, J. C.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 2438.

(46) Slone, R. V.; Hupp, J. T.; Stern, C. L.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **1996**, *35*, 4096.

(47) Berg-Brennan, C. A.; Yoon, D. I.; Slone, R. V.; Kazala, A. P.; Hupp, J. T. *Inorg. Chem.* **1996**, *35*, 2032.

(48) Doorn, S. K.; Dyer, R. B.; Stoutland, P. O.; Woodruff, W. H. *J. Am. Chem. Soc.* **1993**, *115*, 6398.

(49) Owrutsky, J. C.; Raftery, D.; Hochstrasser, R. M. *Annu. Rev. Phys. Chem.* **1994**, *45*, 519.

(50) Heilweil, E. J.; Cavanagh, R. R.; Stephenson, J. C. *Chem. Phys. Lett.* **1987**, *134*, 181.

(51) Grubbs, W. T.; Dougherty, T. P.; Heilweil, E. J. *Chem. Phys. Lett.* **1994**, *227*, 480.

(52) Arrivo, S. M.; Dougherty, T. P.; Grubbs, W. T.; Heilweil, E. J. *Chem. Phys. Lett.* **1995**, *235*, 247.

(53) McCusker, J. K.; Walda, K. N.; Dunn, R. C.; Simon, J. D.; Magde, D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 298.

(54) Wynne, K.; Hochstrasser, R. M. *Chem. Phys.* **1995**, *193*, 211.

(55) Rillema, D. P.; Taghdiri, D. G.; Jones, D. S.; Keller, C. D.; Worl, L. A.; Meyer, T. J.; Levy, H. A. *Inorg. Chem.* **1987**, *26*, 578.

(56) Rasmussen, S. C.; Richter, M. M.; Yi, E.; Place, H.; Brewer, K. J. *Inorg. Chem.* **1990**, *29*, 3926.

(57) Gordon, K. C.; Al-Obaidi, A. H. R.; Jayaweera, P. M.; McGarvey, J. J.; Malone, J. F.; Bell, S. E. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1591.

(58) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145.

(59) Treadway, J. A.; Loeb, B.; Lopez, R.; Anderson, P. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2242.