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clusively reveals a corresponding strong axial anisotropy of the **g** tensor in agreement with the trigonal site symmetry in the alum lattice. A pronounced anisotropy is also observed for the **A** tensor indicative of the importance of orbital contributions to the hyperfine interaction.

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Photophysics of Metal Carbonyl Complexes. Excited States of a Series of *cis*-$M(CO)_4L_2$ Complexes (M = Cr, Mo, or W; L = Pyridine or a Pyridine Derivative)[1]

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Electronic absorption and emission spectra at 298 K are reported for a series of *cis*-$M(CO)_4L_2$ complexes, where M = Cr, Mo, or W and L = 4-ethylpyridine, 4-methylpyridine, pyridine, 4-phenylpyridine, 3,5-dichloropyridine, 4-benzoylpyridine, or 4-cyanopyridine. Low-lying ligand-field (LF) and metal to ligand charge-transfer (MLCT) transitions are observed in the electronic absorption spectra. The emission centered in the 550–700-nm region is sensitive to the nature of ligand substituent and solvent and for each complex is assigned to originate from the low-energy MLCT state. Emission quantum yields vary greatly with ligand substituent and range from 0.1×10^{-4} to 56×10^{-4}. Photosubstitution quantum yields of *cis*-$W(CO)_4L_2$ complexes are markedly affected by changes in the ligand substituent and excitation wavelength. The low-lying MLCT state is virtually unreactive toward ligand substitution, whereas the higher energy LF state has substantially higher photoreactivity. The spectral and photochemical data lead us to assign that, for L = 4-ethylpyridine, 4-methylpyridine, or pyridine, the LF and MLCT states are approximately at the same energy whereas, for L = 4-phenylpyridine, 3,5-dichloropyridine, 4-benzoylpyridine, and 4-cyanopyridine, the MLCT state is clearly the lowest energy transition. An excited-state scheme based on the experimental observations is presented.

Introduction

There has been considerable interest in the photochemistry of transition-metal complexes that have low-lying metal to ligand charge-transfer (MLCT) excited states. For example, $Ru(NH_3)_5L^{2+}$,[2] $W(CO)_5L$,[3-7] $(\eta^5\text{-}C_5H_5)Re(CO)_2L$,[8] $(\eta^5\text{-}C_5H_5)Mn(CO)_2L$,[8] and $Fe(CN)_5L$[9] complexes, where L is CO or a nitrogen, oxygen, or phosphorus donor, have been extensively studied. The results of these studies have shown that the luminescence and photochemical characteristics of the complexes are dependent on the relative position of the low-lying MLCT excited state. Small changes in the nature of the ligand (L) can have a major effect on the properties of the complex; therefore, the ligand substituent can be used to "tune" the excited states and the photochemical properties of transition metal complexes.[10]

Most investigations of the emissive properties of transition-metal complexes have been carried out at low temperature in a rigid environment, where nonradiative deactivation processes are considerably reduced.[11] As a consequence there are relatively few examples of luminescence from metal complexes in fluid solution, but when such cases are found, valuable information on excited-state processes can be obtained.[12,13] Metal carbonyl complexes in particular have not been considered to be emissive in fluid solution due to the relatively high photoreactivity and efficient nonradiative rates of their excited states. Several $ClRe(CO)_3L$ complexes, where L = 1,10-phenanthroline and related ligands, have been observed to emit in solution.[14] The emission from these complexes was inferred to originate from a low-lying MLCT excited state and to have substantial triplet character. The emission was observed to be remarkably sensitive to the nature of the environment, yielding a red-orange emission in fluid solution at 298 K and a yellow-green emission in rigid glasses at 77 K.[14b] Emission at 298 K has also been reported from a series of $XRe(CO)_3L_2$ complexes, where X = Cl, Br, or I and L =

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4-phenylpyridine, 4,4'-bipyridine, or 3-benzoylpyridine.[15] The emission was significantly affected by medium and temperature. At 77 K the emitting state of several complexes was shown to have considerable intraligand (π–π^*) triplet character, but at 298 K the emission was inferred to be MLCT.[15] Recently a series of $W(CO)_5L$ complexes, where L is a substituted pyridine, have been observed to emit in room-temperature solution. For each complex the emission was assigned to originate from a low-lying MLCT state.[16]

We became interested in *cis*-$W(CO)_4L_2$ complexes (L = pyridine or a pyridine derivative) because their lowest energy absorptions have been reported to be of MLCT character.[17] Replacement of a CO by L in $W(CO)_5L$ can be expected to shift this transition to even lower energy. Furthermore the *cis*-$W(CO)_4L_2$ complexes have been observed to emit in EPA glasses at 77 K.[17] Thus, these complexes were considered to be possible species that would exhibit emission under normally photochemical conditions. Stimulated by the observation of emission of several *cis*-$W(CO)_4L_2$ complexes in solution at 298 K,[18] we have undertaken a complete study of *cis*-$M(CO)_4L_2$ (M = Cr, Mo, W) complexes. In this paper we relate the photophysical properties of these complexes with their photochemistry and report an excited-state model.

Experimental Section

Materials. Chromium hexacarbonyl, molybdenum hexacarbonyl, and tungsten hexacarbonyl were obtained from Strem Chemicals. Pyridine (py) and piperidine (pip) were obtained from Fisher Scientific Co. The ligands 4-ethylpyridine (4-Et-py), 4-methylpyridine (4-Me-py), 4-phenylpyridine (4-Ph-py), 3,5-dichloropyridine (3,5-Cl_2-py), 4-benzoylpyridine (4-Bz-py), 4-cyanopyridine (4-CN-py), and 1,10-phenanthroline (phen) were obtained from Aldrich Chemical Co. Benzene, *n*-hexane, and isooctane were spectroscopic grade; other solvents used were reagent grade. The solvents used in the emission experiments were distilled several times to ensure removal of emitting or quenching impurities. Alumina, 80–200 mesh (Fisher Scientific Co.), was used for column chromatography.

Synthesis of *cis*-$M(CO)_4L_2$. The complexes were prepared by irradiation of $M(CO)_6$ (1.5 mmol) for approximately 45 min with a 200-W Hg lamp in 125 mL of N_2-purged *n*-hexane containing excess (4 mmol) ligand. The *cis*-$M(CO)_4L_2$ complexes are insoluble in *n*-hexane and precipitate out of solution. The product was washed with *n*-hexane to remove $M(CO)_6$, $M(CO)_5L$, and free L. The *cis*-$W(CO)_4$(4-Bz-py)$_2$ and *cis*-$W(CO)_4$(4-CN-py)$_2$ complexes were prepared by an alternative method: $W(CO)_6$ (0.75 mmol) was irradiated for approximately 10 h with a 200-W Hg lamp in 125 mL of N_2-purged benzene containing excess (2 mmol) ligand. In this case benzene was used as solvent because the $W(CO)_5L$ reaction intermediate was found to precipitate out of *n*-hexane during photolysis; the particularly long irradiation time reflects the extremely low photoreactivities of the $W(CO)_5L$ (L = 4-Bz-py, 4-CN-py) complexes.[3d,16b] After irradiation the volume of the solution was reduced by rotary evaporation, and the complexes were separated by column chromatography on alumina using benzene as eluent.

The *cis*-$M(CO)_4L_2$ compounds were moderately stable in the solid form and were kept in the dark at 273 K; storing under Ar effectively increased their long-term stability. The chromium complexes were particularly susceptible to oxidation, and *cis*-$Cr(CO)_4$(4-Me-py)$_2$ and *cis*-$Cr(CO)_4$(4-Et-py)$_2$ rapidly decomposed on exposure to air. In solution the tungsten complexes were fairly stable, whereas the molybdenum and chromium complexes decomposed significantly over a period of a few minutes.

Elemental analyses for some representative complexes are as follows. Anal. Calcd for *cis*-$Cr(CO)_4$(4-Ph-py)$_2$: C, 65.82; H, 3.82; N, 5.90. Found: C, 65.68; H, 3.87; N, 5.84. Calcd for *cis*-$Cr(CO)_4$(3,5-Cl_2-py)$_2$: C, 36.55; H, 1.31; N, 6.09. Found: C, 36.74; H, 1.29; N, 6.18. Calcd for *cis*-$Cr(CO)_4$(4-CN-py)$_2$: C, 51.62; H, 2.17; N, 15.05. Found: C, 51.50; H, 2.06; N, 15.28. Calcd for *cis*-$Mo(CO)_4$(4-Et-py)$_2$: C, 51.20; H, 4.30; N, 6.63. Found: C, 51.45; H, 4.14; N, 6.43. Calcd for *cis*-$Mo(CO)_4$(4-Ph-py)$_2$: C, 60.24; H, 3.50; N, 5.40. Found: C, 60.02; H, 3.28; N, 5.48. Calcd for *cis*-$Mo(CO)_4$(4-Bz-py)$_2$: C, 58.55; H, 3.16; N, 4.88. Found: C, 58.28; H, 3.04; N, 4.99. Calcd for *cis*-$W(CO)_4$(4-Me-py)$_2$: C, 39.86; H, 2.93; N, 5.81. Found: C, 40.08; H, 2.82; N, 5.68. Calcd for *cis*-$W(CO)_4(py)_2$: C, 37.03; H, 2.22; N, 6.17. Found: C, 36.78; H, 2.40; N, 6.00. Calcd for *cis*-$W(CO)_4$(4-CN-py)$_2$: C, 38.12; H, 1.60; N, 11.11. Found: C, 37.88; H, 1.78; N, 11.35. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Equipment and Procedures. Infrared spectra were recorded from the samples as Nujol mulls with a Perkin-Elmer Model 283B spectrometer and are considered accurate to ±2 cm^{-1}. Electronic absorption spectra were obtained on a Hewlett-Packard 8450A spectrophotometer which incorporates a microprocessor-controlled diode-array detector. We recorded the absorption spectra of thermally sensitive complexes within 5 s of dissolution. Absorption band maxima are considered to be accurate to ±2 nm. Emission spectra were recorded on a Perkin-Elmer MPF-44B spectrofluorometer and were corrected for variation in instrumental response as a function of wavelength. The emission band maxima are considered to be accurate to ±10 nm. Emission quantum yields were determined with the use of a known emitter, $Ru(bpy)_3^{2+}$,[19] and are considered accurate to ±15%.

Photolysis experiments were performed with an Ealing Corp. 200-W mercury–xenon arc lamp. Baird-Atomic and Rolyn Optics Corp. interference filters (10-nm band-pass) were used to isolate irradiation wavelengths at 360, 395, 430, and 465 nm. Typical light intensities were 10^{-9}–10^{-8} einstein s^{-1} determined by ferrioxalate[20] (360, 395, and 430 nm) or Reineckate[21] (465 nm) actinometry. Irradiation at 514 nm was performed with a Lexel Corp. Model 95-4 4-W argon-ion laser. Typical laser power for the 514 nm photolyses was 1 W; incident light intensities were determined by Reineckate actinometry. In all photolysis experiments the concentrations of reactants and products were monitored by UV–vis spectroscopy. Quantum yields (ϕ_{cr}) that were corrected for changing light absorbance were obtained for disappearance of reactant and appearance of product by application of eq 1, where [C] is the concentration of species, I_0 is light intensity,

$$d[C]/dt = -\phi_{cr}I_0(1 - 10^{-D})\epsilon_A l[C]/D \tag{1}$$

ϵ_A and D are extinction coefficient and optical density at photolysis wavelength, l is the cell path length, and t is time of photolysis. Plots of $\ln [(D_t - D_\infty)/(D_0 - D_\infty)]$ vs. $\int_{t_1}^{t_2}[(1 - 10^{-D})/D]\,dt$, where D_0, D_t, and D_∞ are optical densities throughout photolysis at a chosen wavelength, were calculated to yield straight lines of slope α. Here $\alpha = -\epsilon_A\phi_{cr}I_0l$. Reproducibility of quantum yields was within ±10%.

In emission and photochemical experiments, sample solutions were filtered immediately before use through a 0.22-μm Millipore filter and transferred to a 1 × 1 cm four-clear-sided quartz cell. The solutions were deaerated by argon purging for 20 min. The temperature of the solution in the cell was controlled to ±0.1 K by circulating thermostated water.

Results and Discussion

Synthesis of *cis*-$M(CO)_4L_2$. The *cis*-$M(CO)_4L_2$ complexes were prepared photochemically (reactions 2 and 3).[22] Although the *cis*-$W(CO)_4L_2$ complexes have been previously obtained by this method, this is the first report of the synthesis of the corresponding chromium and molybdenum complexes. Infrared spectra of the carbonyl stretching region are consistent with the C_{2v} symmetry of the four CO ligands; see Table I. Furthermore the data appear to rule out the possibility of 4-Bz-py and 4-CN-py being bound through the substituent

$$M(CO)_6 \xrightarrow[L]{h\nu = 313\ nm} M(CO)_5L + CO \tag{2}$$

$$M(CO)_5L \xrightarrow[L]{h\nu = 313\ nm} cis\text{-}M(CO)_4L_2 + CO \tag{3}$$

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Table I. Infrared Spectral Data for the *cis*-$M(CO)_4L_2$ Complexes[a]

complex	bands, cm^{-1}					
		A_1^{1a}	B_1	A_1^{1b}	B_2	
cis-$Cr(CO)_4(py)_2$		2001	1885	1869	1828	
cis-$Cr(CO)_4(4\text{-Ph-py})_2$		2003	1888	1868	1812	
cis-$Cr(CO)_4(3,5\text{-}Cl_2\text{-py})_2$		2004	1898	1883	1857	
cis-$Cr(CO)_4(4\text{-Bz-py})_2$		2003	1890	1875	1840	1668[b]
cis-$Cr(CO)_4(4\text{-CN-py})_2$	2235[c]	2001	1900	1880	1855	
cis-$Mo(CO)_4(4\text{-Et-py})_2$		2005	1889	1868	1817	
cis-$Mo(CO)_4(4\text{-Me-py})_2$		2003	1889	1869	1821	
cis-$Mo(CO)_4(py)_2$		2002	1899	1871	1828	
cis-$Mo(CO)_4(4\text{-Ph-py})_2$		2003	1884	1867	1823	
cis-$Mo(CO)_4(3,5\text{-}Cl_2\text{-py})_2$		2008	1890	1878	1858	
cis-$Mo(CO)_4(4\text{-Bz-py})_2$		2008	1900	1875	1864	1674[b]
cis-$Mo(CO)_4(4\text{-CN-py})_2$	2240[c]	2007	1890	1872	1841	
cis-$W(CO)_4(4\text{-Et-py})_2$		2003	1874	1863	1812	
cis-$W(CO)_4(4\text{-Me-py})_2$		2003	1868	1850	1813	
cis-$W(CO)_4(py)_2$		2002	1885	1868	1820	
cis-$W(CO)_4(4\text{-Ph-py})_2$		2001	1880	1865	1820	
cis-$W(CO)_4(3,5\text{-}Cl_2\text{-py})_2$		2005	1892	1882	1842	
cis-$W(CO)_4(4\text{-Bz-py})_2$		2004	1887	1864	1851	1670[b]
cis-$W(CO)_4(4\text{-CN-py})_2$	2238[c]	2002	1895	1870	1850	

[a] In Nujol mulls at 298 K. [b] Ketone stretch of pyridine ligand. [c] Cyano stretch of pyridine ligand.

Table II. Electronic Absorption Spectra of *cis*-$M(CO)_4L_2$ Complexes in Benzene at 298 K[a]

complex	band max λ, nm (ε, M^{-1} cm^{-1})		
cis-$Cr(CO)_4(4\text{-Ph-py})_2$	393 (sh)	454	
cis-$Cr(CO)_4(4\text{-Bz-py})_2$	406 (sh)	510	
cis-$Cr(CO)_4(4\text{-CN-py})_2$	406 (sh)	506	
cis-$Mo(CO)_4(4\text{-Et-py})_2$	350	395	
cis-$Mo(CO)_4(4\text{-Me-py})_2$	345	395	
cis-$Mo(CO)_4(py)_2$	355	398	
cis-$Mo(CO)_4(4\text{-Ph-py})_2$	375 (sh)	424	
cis-$Mo(CO)_4(3,5\text{-}Cl_2\text{-py})_2$	375 (sh)	426	
cis-$Mo(CO)_4(4\text{-Bz-py})_2$	385 (sh)	468	
cis-$Mo(CO)_4(4\text{-CN-py})_2$	385 (sh)	468	
cis-$W(CO)_4(4\text{-Et-py})_2$	359 (6650)	406 (7320)	~455 (sh)
cis-$W(CO)_4(4\text{-Me-py})_2$	358 (6760)	406 (7390)	~455 (sh)
cis-$W(CO)_4(py)_2$	367 (6340)	412 (7580)	~460 (sh)
cis-$W(CO)_4(4\text{-Ph-py})_2$	~382 (sh)	434 (8580)	~475 (sh)
cis-$W(CO)_4(3,5\text{-}Cl_2\text{-py})_2$	~382 (sh)	438 (7920)	~492 (sh)
cis-$W(CO)_4(4\text{-Bz-py})_2$	~387 (sh)	490 (8810)	~554 (sh)
cis-$W(CO)_4(4\text{-CN-py})_2$	~392 (sh)	490 (7670)	~556 (sh)

[a] Spectra of chromium and molybdenum complexes recorded within 5 s of dissolution.

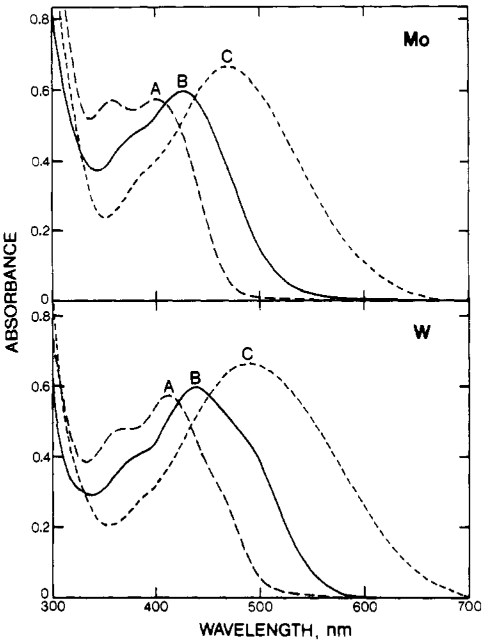

Figure 1. Electronic absorption spectra at 298 K of (A) *cis*-$M(CO)_4(py)_2$, (B) *cis*-$M(CO)_4(3,5\text{-}Cl_2\text{-py})_2$, and (C) *cis*-$M(CO)_4(4\text{-Bz-py})_2$ in benzene. M = Mo (maxima scaled arbitrarily) and M = W (complexes at equal concentration).

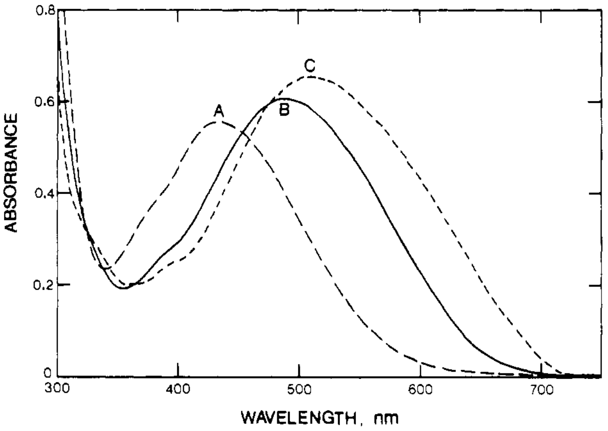

Figure 2. Solvent effects on the electronic absorption spectra at 298 K of *cis*-$W(CO)_4(4\text{-Bz-py})_2$. Complexes are at equal concentration in (A) dimethyl sulfoxide, (B) benzene, and (C) benzene/*n*-hexane (1:10 v/v).

heteroatom. The carbonyl stretching vibrations of *cis*-$M(CO)_4L_2$ where L = 4-Bz-py or 4-CN-py are similar to those of the other complexes in this series, and the C≡N and C═O stretching frequencies (see Table I) are close to those of the free ligands (2241 and 1653 cm^{-1}, respectively). The chromium complexes where L = 4-Me-py and 4-Et-py decomposed too rapidly in Nujol mulls to obtain infrared data.

Electronic Absorption Spectra. The electronic absorption spectra of *cis*-$M(CO)_4L_2$ (M = Mo, W; L = py, 3,5-Cl_2-py, 4-Bz-py) in benzene are shown in Figure 1. The absorption data obtained from all the complexes studied are summarized in Table II, although spectra were not obtained from several of the chromium complexes due to rapid thermal reaction.

The low-lying absorption bands of *cis*-$W(CO)_4L_2$ have been previously assigned to be due to overlapping ligand-field (LF) and metal to ligand charge-transfer (MLCT) transitions.[17] The position of the lowest energy absorption for *cis*-$M(CO)_4L_2$ depends on the nature of L; as the substituent on L becomes more electron withdrawing, the lowest energy features shift to longer wavelength (see Figure 1 and Table II). On this basis the lowest energy absorption of each complex is assigned to contain a significant proportion of a MLCT transition. In contrast, the higher energy features are relatively unshifted and are assigned to LF transitions, although they overlap substantially with the MLCT transition. For any particular ligand, the energies of the MLCT absorption are ordered Mo > W > Cr, congruent with other classes of group 6B metal carbonyl complexes.[4,7b,23]

The LF and MLCT transitions can be expected to exhibit quite different solvent sensitivities.[24] This we observed in our absorption experiments; the absorption spectra of *cis*-$W(CO)_4(4\text{-Bz-py})_2$ in dimethyl sulfoxide, benzene, and benzene/*n*-hexane (1:10 v/v) are shown in Figure 2. The spectra show a blue shift of the lowest energy transition as the solvent becomes more polar. This observation appears to be a general one for the *cis*-$M(CO)_4L_2$ complexes and is attributed to the solvatochromic character of the MLCT transition. Similarly large solvent and substituent effects on the energy of the MLCT transition have been observed in the electronic ab-

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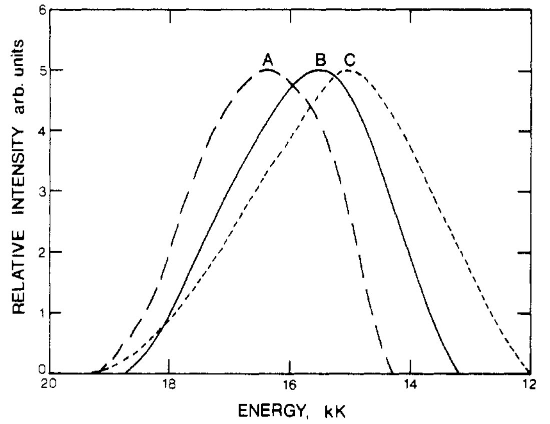

Figure 3. Corrected emission spectra at 283 K of (A) *cis*-$Mo(CO)_4(py)_2$, (B) *cis*-$Mo(CO)_4(3,5\text{-}Cl_2\text{-}py)_2$, and (C) *cis*-$Mo(CO)_4(4\text{-}Bz\text{-}py)_2$ in benzene. Excitation wavelength is 400 nm. Intensities are scaled to make maxima equal.

Table III. Emission Spectral Data of *cis*-$M(CO)_4L_2$ Complexes in Benzene at 298 K[a,b]

	emission[c]		
complex	max, nm	half-width[d] $cm^{-1} \times 10^3$	$10^4 \times$ quantum yield[e]
cis-$Mo(CO)_4(4\text{-}Et\text{-}py)_2$	*f*		
cis-$Mo(CO)_4(4\text{-}Me\text{-}py)_2$	*f*		
cis-$Mo(CO)_4(py)_2$	610	2.8	0.1
cis-$Mo(CO)_4(4\text{-}Ph\text{-}py)_2$	636	3.2	3.0
cis-$Mo(CO)_4(3,5\text{-}Cl_2\text{-}py)_2$	645	3.1	0.2
cis-$Mo(CO)_4(4\text{-}Bz\text{-}py)_2$	665	4.1	0.4
cis-$Mo(CO)_4(4\text{-}CN\text{-}py)_2$	650	3.4	1.4
cis-$W(CO)_4(4\text{-}Et\text{-}py)_2$	565	5.7	0.5
cis-$W(CO)_4(4\text{-}Me\text{-}py)_2$	575	6.0	0.3
cis-$W(CO)_4(py)_2$	629	5.1	1.4
cis-$W(CO)_4(4\text{-}Ph\text{-}py)_2$	641	6.5	56.4
cis-$W(CO)_4(3,5\text{-}Cl_2\text{-}py)_2$	678	3.5	0.9
cis-$W(CO)_4(4\text{-}Bz\text{-}py)_2$	>700		
cis-$W(CO)_4(4\text{-}CN\text{-}py)_2$	>700		

[a] Recorded at 283 K for molybdenum complexes. [b] 8×10^{-5}–4×10^{-4} M deaerated solutions. [c] Spectra were corrected for variation in instrumental response as a function of wavelength. The excitation wavelength is 400 nm. [d] Width of emission band at half-height. [e] Measured relative to the emission of $Ru(bpy)_3^{2+}$. Accurate to within ±15%. [f] Emission not observed.

sorption spectra of isoelectronic $Mo(CO)_5L$,[25] $W(CO)_5L$,[3-7] $M(CO)_4L$ (M = Cr, Mo, W),[24,26] $Ru(NH_3)_5L^{2+}$,[2] and $Fe(CN)_5L^{3-}$[9] complexes.

Emission Spectra. Emission spectra were recorded from *cis*-$M(CO)_4L_2$ complexes in benzene, at 298 K (M = W) or at 283 K (M = Mo) to minimize thermal reaction. The chromium complexes decomposed too rapidly in solution to yield emission data. Emission spectra recorded from *cis*-$Mo(CO)_4L_2$ (L = py, $3,5\text{-}Cl_2\text{-}py$, 4-Bz-py) complexes in benzene are shown in Figure 3. The emission spectra obtained from all of the complexes studied were similarly broad and unstructured, and their data are summarized in Table III. We observed a weak onset of emission increasing from 550–700 nm for *cis*-$W(CO)_4(4\text{-}Bz\text{-}py)_2$ and *cis*-$W(CO)_4(4\text{-}CN\text{-}py)_2$; their emission maxima may be too red shifted to be detected on our apparatus.

The spectral distribution of the emission of each complex was observed to be independent of excitation wavelengths longer than 300 nm; this is consistent with emission from a single low-lying excited state. The emission data illustrate that as L becomes more electron withdrawing, the emission maxima shift to lower energies. This effect is parallel to that seen in the absorption spectra (see Table II); therefore, we assign the emission to be from the MLCT excited state of each complex. Furthermore, the onset of emission for each complex is consistent with the position of the lowest energy absorption; for example, compare Figures 1 and 3. For any given ligand the emission maxima energies are ordered Mo > W, corresponding to that observed in absorption.

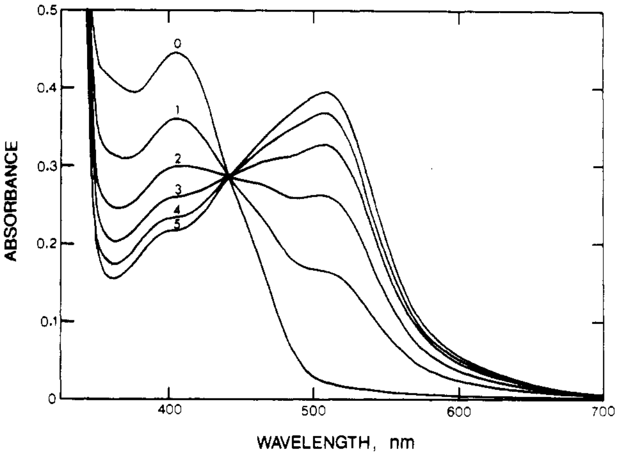

Figure 4. Electronic absorption spectral changes accompanying the 465-nm irradiation (equal time intervals) at 298 K of *cis*-$W(CO)_4(4\text{-}Me\text{-}py)_2$ in benzene containing 0.01 M phen.

In accordance with a MLCT assignment, the emission of *cis*-$M(CO)_4L_2$ was observed to be solvent sensitive. For solutions of *cis*-$W(CO)_4(4\text{-}Ph\text{-}py)_2$ at 298 K, the emission maxima were recorded at 641 nm in benzene and at 671 nm in tetrachloroethylene. Emission was not observable from *cis*-$M(CO)_4L_2$ in more polar solvents, e.g. dimethyl sulfoxide; we attribute this to be due to an increased rate of nonradiative decay from the MLCT excited state in more polar solutions.

Emission quantum yields (ϕ_e) were measured for the *cis*-$M(CO)_4L_2$ complexes; see Table III. We note that, for both series of complexes, ϕ_e varies by approximately 2 orders of magnitude, and we attribute this to be a result of competition between the radiative and reactive rate processes of these complexes (vide infra). The emission quantum yields were observed to be independent of temperature in the 283–303 K range, indicating that the emission process is not thermally activated.

Photosubstitution Reactivity. The following photosubstitution reaction was monitored for the series of *cis*-$W(CO)_4L_2$ complexes:

$$cis\text{-}W(CO)_4L_2 \xrightarrow[0.01\ M\ phen,\ C_6H_6]{h\nu\ \lambda} W(CO)_4phen + 2L \tag{4}$$

$$\lambda = 360, 395, 430, 465, 514\ nm$$

$$phen = 1,10\text{-phenanthroline}$$

Figure 4 illustrates the spectral sequence accompanying the 465-nm photolysis of *cis*-$W(CO)_4(4\text{-}Me\text{-}py)_2$ in benzene, showing a clear progression to the spectrum of $W(CO)_4phen$. This reaction was observed to proceed cleanly at all of the irradiation wavelengths, and we found no evidence for photodissociation of CO. Furthermore, quantum yields (ϕ_{cr}) were found to be independent of phen concentration in the 0.01–0.1 M range. It has been previously established that the primary photoprocess of reaction 4 is loss of L, forming $W(CO)_4L$,[17] which in turn thermally reacts with phen to give $W(CO)_4phen$. Quantum yields of reaction 4 therefore measure the efficiency of removal of the first ligand.

We undertook a study of the wavelength dependence of reaction 4 to evaluate the photoefficiencies of the LF and

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Table IV. Photosubstitution Quantum Yields of *cis*-$W(CO)_4L_2$ Complexes in Benzene at 298 K[a]

	irradiation wavelength, nm				
L	360	395	430	465	514
4-Et-py	0.32	0.38	0.40	0.14	*b*
4-Me-py	0.32	0.38	0.35	0.13	*b*
py	0.30	0.36	0.33	0.12	*b*
4-Ph-py	0.005	0.006	0.004	0.002	0.0002
3,5-Cl_2-py	0.07[c]	0.06[c]	0.02[c]	0.011[c]	0.008[c]
4-Bz-py	0.004	0.004	0.003	0.002	0.0001
4-CN-py	0.01	0.01	0.007	0.003	0.0003

[a] Photolyses carried out in $\sim 10^{-4}$ M solutions of *cis*-$W(CO)_4L_2$ containing 0.01 M phen. [b] These complexes absorb insufficiently at 514 nm to determine accurate quantum yields. [c] Recorded at 283 K.

Table V. Temperature Dependence of Photosubstitution Quantum Yields for *cis*-$W(CO)_4(py)_2$ in Benzene[a]

	irradiation wavelength, nm			
T, K	360	395	430	465
283	0.28	0.33	0.32	0.10
288	0.29	0.34	0.32	0.11
293	0.30	0.35	0.34	0.11
298	0.30	0.36	0.33	0.12
303	0.30	0.36	0.36	0.13

[a] Photolyses carried out in $\sim 10^{-4}$ M solutions of *cis*-$W(CO)_4(py)_2$ containing 0.01 M phen.

MLCT states; the results are shown in Table IV. The *cis*-$W(CO)_4L_2$ complexes are significantly less photoreactive during long-wavelength (465, 514 nm) irradiation. We attribute this to be due to direct population of the MLCT state exclusively, which is virtually unreactive. In contrast, the quantum yields at short wavelengths (360, 395, 430 nm) indicate that the higher energy LF states are substantially more photoreactive than the MLCT state. The relative efficiencies of the LF and MLCT excited states for the *cis*-$W(CO)_4L_2$ series are in agreement with recently published values for closely related $W(CO)_5L$ complexes.[16b]

The quantum yields are markedly dependent on ligand substituent. For L = 4-Ph-py, 3,5-Cl_2-py, 4-Bz-py, and 4-CN-py, the extremely low values are characteristic of carbonyl complexes in which the MLCT state lies below the LF state.[3d,16,24] For L = 4-Et-py, 4-Me-py, and py, the values are considerably greater and reflect significant population of the LF state. The results imply that in the former complexes the lowest lying absorption is clearly MLCT, but in the latter complexes this absorption comprises LF and MLCT transitions.

The temperature dependency of the photoreaction of *cis*-$W(CO)_4(py)_2$ was investigated at each photolysis wavelength; the data are shown in Table V. The quantum yields are not very temperature dependent; the least-squares line of an Arrhenius type plot ($\ln \phi_{cr}$ vs. $1/T$) at each of the excitation wavelengths corresponds to activation energies in the range 0.6–2.1 (± 1) kcal mol^{-1}. These low values indicate that the photoreaction of *cis*-$W(CO)_4(py)_2$ proceeds directly from the LF state and is not thermally activated through higher energy states. For *cis*-$W(CO)_4(4\text{-Bz-py})_2$ the MLCT state is clearly of lower energy than the LF state (we estimate an energy difference of 8 ± 2 kcal mol^{-1} on the basis of the absorption and emission data). Quantum yields were obtained for the 514-nm photolysis of *cis*-$W(CO)_4(4\text{-Bz-py})_2$ as a function of temperature. At this excitation wavelength it is assumed that the MLCT state is populated exclusively. The results at 283, 288, 293, 298, and 303 K are 5.1×10^{-5}, 6.7×10^{-5}, 8.1×10^{-5}, 8.8×10^{-5}, and 12.3×10^{-5}, respectively. This corresponds to an apparent activation energy of 6.8 ± 1 kcal mol^{-1}, a value within experimental error of the estimated 8 ± 2 kcal mol^{-1} needed to thermally populate the higher energy LF excited state. It is concluded that the MLCT state is virtually unreactive and that photosubstitution proceeds via the LF state. Although the LF state reacts efficiently, the quantum yields following excitation at long wavelength are small because of competition with nonradiative decay at the MLCT state.

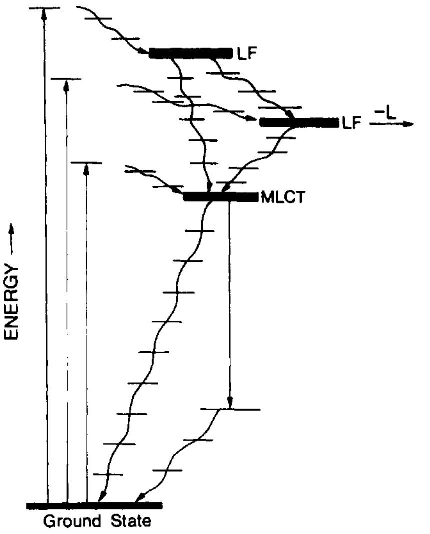

Figure 5. Excited-state scheme for *cis*-$M(CO)_4L_2$ complexes. Vertical and wavy lines denote radiative and nonradiative processes respectively. Heavy horizontal lines represent thermally equilibrated excited states. Light horizontal lines represent successive complex–solvent cage energies as vibrationally excited states relax (only a few of these lines are shown).

Excited-State Scheme. The experimental observations have led us to propose a scheme of the low-energy excited states of *cis*-$M(CO)_4L_2$; see Figure 5. In Figure 5 the MLCT state is shown below that of the lowest lying LF state. This is the case for L = 4-Ph-py, 3,5-Cl_2-py, 4-Bz-py, and 4-CN-py, where the MLCT state is clearly the lowest energy absorption. However, for L = 4-Et-py, 4-Me-py, and py, the absorption, emission, and photochemical data imply that whereas the MLCT is still the lowest lying state, it is very close in energy to the LF state. It is also noted that the relative positions of the LF and MLCT states are dependent on the solvent medium.

Emission was observed from *cis*-$M(CO)_4L_2$ following LF excitation. The emission was assigned to originate from the MLCT state; the vertical line from this state denotes this process. The LF state therefore populates the emitting MLCT state by nonradiative processes; the wavy line between these states denotes this process.

The photoreactivity data are interpreted in terms of this excited-state scheme. Excitation at 514 nm of *cis*-$W(CO)_4(4\text{-Bz-py})_2$ or *cis*-$W(CO)_4(4\text{-CN-py})_2$ can be assumed to exclusively populate the low-lying MLCT state. This state is therefore virtually unreactive ($\phi_{cr} < 0.0003$). In contrast, excitation at 395 nm results in appreciable population of the LF state and their reactivities are significantly higher (ϕ_{cr} = 0.004–0.01). For the complexes where the LF and MLCT states are at approximately the same energy, the ligand substitution reaction is considerably more efficient (ϕ_{cr} = 0.12–0.40). The LF state is thus assigned as a reactive excited state and this is denoted by the loss of ligand.

Finally, the emission of *cis*-$W(CO)_4(4\text{-Ph-py})_2$ requires further comment. The emission efficiency for this molecule is substantially higher than that of the other complexes and is accompanied by a reduction in the photosubstitution efficiency. Apparently the nonradiative processes that intercommunicate the LF and MLCT excited states become more competitive in this molecule. This trend appears to be a general one for the *cis*-$W(CO)_4L_2$ series; as ϕ_{cr} is reduced, ϕ_e is increased.

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Registry No. phen, 66-71-7; *cis*-$Cr(CO)_4(py)_2$, 43118-74-7; *cis*-$Cr(CO)_4(4\text{-Ph-py})_2$, 90245-53-7; *cis*-$Cr(CO)_4(3,5\text{-}Cl_2\text{-py})_2$, 90245-54-8; *cis*-$Cr(CO)_4(4\text{-Bz-py})_2$, 90245-55-9; *cis*-$Cr(CO)_4(4\text{-CN-py})_2$, 90245-56-0; *cis*-$Mo(CO)_4(4\text{-Et-py})_2$, 90245-57-1; *cis*-$Mo(CO)_4(4\text{-Me-py})_2$, 16244-56-7; *cis*-$Mo(CO)_4(py)_2$, 16742-99-7; *cis*-$Mo(CO)_4(4\text{-Ph-py})_2$, 90245-58-2; *cis*-$Mo(CO)_4(3,5\text{-}Cl_2\text{-py})_2$, 90245-59-3; *cis*-$Mo(CO)_4(4\text{-Bz-py})_2$, 90245-60-6; *cis*-$Mo(CO)_4(4\text{-CN-py})_2$, 90245-61-7; *cis*-$W(CO)_4(4\text{-Et-py})_2$, 67951-65-9; *cis*-$W(CO)_4(4\text{-Me-py})_2$, 84076-49-3; *cis*-$W(CO)_4(py)_2$, 16743-01-4; *cis*-$W(CO)_4(4\text{-Ph-py})_2$, 67921-71-5; *cis*-$W(CO)_4(3,5\text{-}Cl_2\text{-py})_2$, 67921-72-6; *cis*-$W(CO)_4(4\text{-Bz-py})_2$, 67921-74-8; *cis*-$W(CO)_4(4\text{-CN-py})_2$, 67921-75-9; $W(CO)_4$phen, 14729-20-5; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

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Early Stages of the Hydrolysis of Chromium(III) in Aqueous Solution. 2. Kinetics and Mechanism of the Interconversion between Two Tetrameric Species

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The hydrolytic chromium(III) tetramer in acidic solution is predominantly $Cr_4(OH)_6^{6+}$ (HTO). On deprotonation (pK_a = 3.53 ± 0.08), the resulting complex, $Cr_4(OH)_7^{5+}$ (TO), slowly isomerizes to $Cr_4O(OH)_5^{5+}$ (TC), which contains a tetracoordinate oxo bridge. Protonation of TC gives HTC (pK_a = 0.89 ± 0.01) as an unstable intermediate. HTO is then formed by cleavage of the oxo bridge. The isomerization constants are K_i = [TC]/[TO] = 8.8 ± 2.3 and $K_{i,H}$ = [HTC]/[HTO] = 0.020 ± 0.003, respectively. The following rate constants were determined: $k_o = 0.027 \pm 0.004\ s^{-1}$ for TC + H_2O → TO; $k_{o,H} = 4.35 \pm 0.05\ s^{-1}$ for HTC + H_2O → HTO; $k_c = 0.24 \pm 0.07\ s^{-1}$ for TO → TC + H_2O; $k_{c,H} = 0.087 \pm 0.014\ s^{-1}$ for HTO → HTC + H_2O. These data were determined from spectrophotometric kinetics at 25.0 ± 0.1 °C and I = 1.0 ($NaClO_4$) in the pH range 0.3–4.0. The pK_{a1} of the tetramer deduced from these parameters is consistent with that previously determined by potentiometric determination (2.55 ± 0.06). The proposed reaction sequence is consistent with the slow equilibration observed in these titrations and confirms the structural assignments made earlier. Both formation and cleavage of the oxo bridge in the tetramer are much faster than known cases of hydroxo bridge formation and cleavage in other Cr(III) species. Contrary to substitution in monomeric Cr(III), deprotonation of coordinated water does not appreciably accelerate substitution in the reaction TO → TC + H_2O.

Introduction

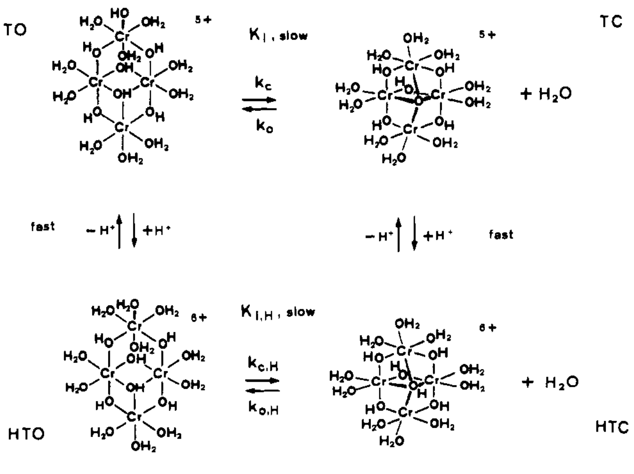
In previous work,[2] a complete series of hydrolytic oligomers of Cr(III) up to, and including, the hexamer has been obtained in solution by ion-exchange chromatography. The configuration of the tetramer, $Cr_4O(OH)_5^{5+}$, has been deduced from a series of buildup and cleavage reactions involving other, known oligomers and from the general trends in pK_a values.

In the course of potentiometric pK_a determinations of the tetramer, the electrode potentials reached equilibrium unusually sluggishly compared with the lower oligomers. This was explained by a reversible, intramolecular condensation reaction accompanying deprotonation of the tetramer. As this presumed process provided an important argument in deducing the configuration of the tetramer, we have now studied its kinetics in more detail. This has enabled us to explore, for the first time, the reactivity pattern of an oxo bridge in a hydrolytic species of Cr(III).

Results

Description of the Reaction System and Data Collection. The hydrolytic tetramer, $Cr_4(OH)_6^{6+}$, was synthesized by dimerization of $Cr_2(OH)_2^{4+}$ with base and isolated in solution by ion-exchange chromatography as described.[2] The purity of these fractions was checked by UV/vis spectroscopy, using the distinctive, high intensity ratio of the maxima, $\epsilon_{426}/\epsilon_{580}$ = 1.95 ± 0.04 at [H^+] = 0.04 M of the tetramer. The band positions for this species and for the essentially monodeprotonated tetramer are nearly the same, but there are small changes in intensity.[2]

Scheme I. Interconversion of Forms of the Tetramer, $Cr_4O(OH)_5^{5+}$



The potentiometric pK_a determinations (pK_{a1} = 2.55, pK_{a2} = 5.08, 25 °C, I = 1.0 ($NaClO_4$))[2] also established the stoichiometry of the deprotonation reaction. Thus, one proton per tetramer is lost in the buffer region up to pH 3.8. These titrations showed that this reversible protonation–deprotonation

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[2] Part 1: Stünzi, H.; Marty, W. *Inorg. Chem.* **1983**, *22*, 2145.

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