Electronic Absorption and Emission Spectral and Photochemical Studies of Low-Spin d⁶ Metal Hexacarbonyl Anions

MARK S. WRIGHTON,* DAVID I. HANDELI, and DAVID L. MORSE

The electronic absorption spectra of various salts of $M(CO)_6^-$ (M = V, Nb, Ta) have been measured in solution and in KBr pressed disks at 298 and 20 K. For M = Nb, Ta, but not V, we find strongly temperature-dependent optical luminescence upon electronic excitation of the pure solids or the solutions. Quantitative emission measurements (lifetimes and quantum yields) have been made for the pure solids in the range 22–100 K. Maximum emission yields (~0.2) and lifetimes (~10^{-4} sec) are found at the lowest temperature and fall off rapidly, diminishing by nearly 2 orders of magnitude upon warming to 100 K. The overlapping emission and absorption bands and the central metal dependence support a $^3T_{1g}(t_{2g}^5e_g^1) \rightarrow$ $^1A_{1g}(t_{2g}^6)$ assignment for the emission. Except for the absolute energetic position, the lowest absorption bands in $M(CO)_6^-$ correspond closely to those found in the neutral and cationic low-spin d⁶ metal hexacarbonyls. Some photochemical studies have been carried out both in rigid media, KBr or glassy solvents at low temperature, and in solution at room temperature. Photosubstitution in solution is efficient with the formation quantum yields of $V(CO)_5X^-$ (X = CH_3CN, pyridine) equal to 0.5 ± 0.05 for 313-, 366-, or 436-nm irradiation of either $[Ph_4As][V(CO)_6]$ or $[Et_4N][V(CO)_6]$. Spectral changes occurring in rigid media are consistent with dissociative loss of CO to yield coordinatively unsaturated or weakly solvated $M(CO)_5^-$.

Studies of the electronic structure and photochemistry of metal carbonyls have included only a few reports concerning ionic species.[1-3] The photolysis of $M(CO)_6^-$ (M = V, Nb, Ta) in fluid solutions in the presence of nucleophiles leads to substitution products with reasonable chemical efficiency.[4] This report was claimed to be the first photosubstitution reaction of a metal carbonyl anion. The electronic absorption spectrum of $V(CO)_6^-$ has been reported[5] and the lowest energy absorption was associated with the $^1A_{1g}(t_{2g}^6) \rightarrow {}^1T_{1g}(t_{2g}^5e_g^1)$ ligand field (LF) transition expected for O_h, low-spin d⁶ transition metal complexes. The one-electron $t_{2g}^6 \rightarrow t_{2g}^5e_g^1$ excitation should enhance the substitutional lability due to both depopulation of the π-bonding t_{2g} level and population of the σ-antibonding e_g level.[6] For the neutral, low-spin d⁶ $M'(CO)_6$ (M' = Cr, Mo, W) species photoexcitation leads to dissociative loss of CO to give a spectroscopically detectable coordinatively unsaturated $M'(CO)_5$ intermediate.[7] The prospect of dissociative loss of CO from $M(CO)_6^-$ is very exciting as the resulting metal carbonyl fragment is both anionic and coordinatively unsaturated. Such a species should be susceptible to oxidative addition reactions which are important in homogeneous catalysis[8] in general and metal carbonyl photoassisted and photocatalyzed reactions in particular.[1,2,9] Furthermore, cocondensation of metal atoms with CO is not a viable synthetic approach to these anionic systems even though this technique has been elegantly applied to the synthesis, matrix isolation, and spectroscopic characterization of unstable, coordinatively unsaturated, and paramagnetic *neutral* metal carbonyls.[10]

The aim of this paper is to report our results of an investigation of the electronic absorption and emission spectra of the $M(CO)_6^-$ complexes. Additionally, we report some new photochemical studies in solution and rigid media. The data permit comparison of some electronic properties of these anions with the neutral $M'(CO)_6$ analogues.

Results

a. Electronic Spectra. Electronic absorption spectra and emission phenomena of $M(CO)_6^-$ (M = V, Nb, Ta) have been measured. Our basic objective in measuring the electronic absorption spectra of the hexacarbonyl anions was to establish common spectral assignments with the isoelectronic neutral metal hexacarbonyls $M'(CO)_6$ (M' = Cr, Mo, W). In particular we seek to establish similarity in the lowest energy excited states in order consistently to interpret photochemical results.

The electronic absorption bands in $M'(CO)_6$ (M' = Cr, Mo, W) have been assigned previously[5] and are listed in Table I. Except for the energy of the band systems the spectra for the $M(CO)_6^-$ are remarkably similar to those for the neutral hexacarbonyls. This fact was first noted from measurements[5] for $[n\text{-}Bu_4N][V(CO)_6]$. New spectra were recorded for $[Ph_4As][V(CO)_6]$, and band maxima and intensity are very similar to those for the $n\text{-}Bu_4N^+$ salt. The data for several solvents are included in Table I. Electronic spectra for $[K\text{-}(diglyme)_3][Nb(CO)_6]$ are shown in Figure 1 for CH_2Cl_2 at 298 K and in KBr at 25 K. We have encountered considerable difficulty in obtaining high-quality spectra in KBr, but the essential features of the spectrum are revealed and appear to be quite similar to the solution spectra. Also, for neither $Nb(CO)_6^-$ nor salts of $Ta(CO)_6^-$ have we been able to obtain accurate molar extinction coefficients due to the thermal sensitivity of the anions to moisture, oxygen, and other impurities in solutions. The extreme light sensitivity of the complexes also precludes accurate extinction coefficients. To complete the triad of anions, spectra for salts of $Ta(CO)_6^-$ are shown in Figures 2 and 3 for various media and temperatures. The spectra are again remarkably similar to those for $M'(CO)_6$ given in ref 5. Data are summarized in Table I.

For $Nb(CO)_6^-$ and salts of $Ta(CO)_6^-$ structured absorption is observed at low temperatures. Curiously, neither $[Ph_4As][V(CO)_6]$ nor $[Et_4N][V(CO)_6]$ exhibits any structure at temperatures as low as 20 K. While little or no structured absorption was reported in the original work on $M'(CO)_6$, spectra obtained[11] at 20 K in CH_4 matrices for $M'(CO)_6$ (for M' = W, Mo, *but not* Cr) show structured absorption. The structure is logically associated with excitation to various vibrational levels of the electronically excited states. Resolution of the structure is not magnificent, but peak positions can be estimated and these have been tabulated in Table II.

Salts of $Ta(CO)_6^-$ and $Nb(CO)_6^-$, but not $V(CO)_6^-$, exhibit luminescence subsequent to electronic excitation at low temperature. Corrected emission spectra are shown in Figures 4 and 5 for pure powders of the salts. The spectral distribution of the emission and the luminescence efficiency are independent of the excitation energy for wavelengths longer than 300 nm. Using a technique recently reported[12] we have measured the absolute quantum efficiency, Φ_e, of the emission of the $Ta(CO)_6^-$ powders as a function of temperature. Emission lifetimes, τ, have been measured over the same temperature range for the same samples. Plots of Φ_e and τ against temperature for three $Ta(CO)_6^-$ salts are shown in Figure 6. Emission data are summarized in Table III. Only one salt exhibited well-resolved vibrationally structured

Table I. Electronic Absorption Spectral Data for Low-Spin d^6 Metal Hexacarbonyls[a]

Compd	Solvent	Energy, kK (ϵ, M^{-1} cm^{-1})		
		$^1A_{1g}(t_{2g}^6) \rightarrow {}^3T_{1g}(t_{2g}^5 e_g^1)$	$^1A_{1g}(t_{2g}^6) \rightarrow {}^1T_{1g}(T_{2g}^5 e_g^1)$	M → π* CO CT
Cr(CO)$_6$[b]	CH$_3$CN	Not obsd	29.50 (700) 31.55 (2670)	35.70 (13100)
Mo(CO)$_6$[b]	CH$_3$CN	28.85 (350)	30.15 (1690) 31.95 (2820)	34.60 (16800)
W(CO)$_6$[b]	CH$_3$CN	28.30 (1000)	29.95 (1680) 31.85 (3250)	34.65 (17600)
[Ph$_4$As][V(CO)$_6$]	CH$_3$CN	Not obsd	25.06 (2090)	28.41 (7150)
	py	Not obsd	25.00 (2340)	28.25 (8160)
	THF	Not obsd	24.87 (2170)	28.41 (7560)
	2-MTHF	Not obsd	25.00 (2200)	28.57 (7500)
	KBr	Not obsd	24.39 (−)	28.41 (−)
[Et$_4$N][V(CO)$_6$]	CH$_3$CN	Not obsd	24.87 (1890)	28.41 (6510)
	py	Not obsd	24.75 (2070)	28.17 (7420)
[K(diglyme)$_3$][Nb(CO)$_6$]	KBr[c]	22.73 (−)	24.39 (−)	26.11 (−)
	CH$_2$Cl$_2$	22.73 (~1500)		26.66 (~6000)
[Ph$_4$As][Ta(CO)$_6$]	CH$_2$Cl$_2$	22.17 (*0.31*)[d]	24.69 (*0.45*)[d]	26.18 (*1.2*)[d]
[(Ph$_3$P)$_3$Au][Ta(CO)$_6$]	KBr	22.22 (*0.65*)[d]	24.39 (*0.8*)[d]	25.97 (*1.5*)[d]
[n-Bu$_4$N][Ta(CO)$_6$]	KBr	22.22	~24.2	26.18
	CH$_2$Cl$_2$	22.22	~24.2	26.18
	EPA	22.22 (920)	24.10 (2400)	26.18 (5800)

[a] For 298 K unless noted otherwise. [b] From ref 5; data are for 300 K. [c] 25 K. [d] Italic values in parentheses are the optical densities taken from a spectrum where the concentration of the species is not known.

Table II. Vibrational Maxima on Low-Temperature Electronic Absorption Bands

Compd	Medium; T, K	Band max, cm^{-1}	$\nu^n - \nu^{n+1}$, cm^{-1}
[n-Bu$_4$N][Ta(CO)$_6$]	EPA; 77	20387	
			403
		20790	
			464
		21254	
			438
		21692	
			419
		22173	
			451
		22624	
			471
		23095	
			379
		23474	
			446
		23920	
			32
		23952	
			320
		24272	
			59
		24331	
			299
		24630	
			184
		24814	
[Ph$_4$As][Ta(CO)$_6$]	KBr; 25	19608	
			392
		20000	
			492
		20492	
			385
		20877	
			400
		21277	
			605
		21822	
			489
		22371	
			512
		22883	
			814
		23697	
			693
		24390	
[(Ph$_3$P)$_3$Au][Ta(CO)$_6$]	KBr; 25	19802	
			902
		20704	
			482
		21186	
			412
		21598	
			428
		22026	
			446
		22472	
			411
		22883	
			1213
		24096	
[K(diglyme)$_3$][Nb(CO)$_6$]	KBr, 25	23584	
			454
		24038	
			352
		24390	
			1584
		25974	
			342
		26313	
			351
		26667	
			360
		27027	

Table III. Emission Characteristics of M(CO)$_6^-$ [a]

Compd	Emission max, kK (width at half-height, kK)	Φ_e(25 K) ± 20%[b]	$10^6 \tau$(25 K) ± 10%, sec
[(n-Bu)$_4$N][Ta(CO)$_6$]	17.20 (3.0)	0.05	23
[Ph$_4$As][Ta(CO)$_6$]	17.36 (2.2)	0.16	63
[(Ph$_3$P)$_3$Au][Ta(CO)$_6$]	17.08 (1.8)	0.25	74
[K(diglyme)$_3$][Nb(CO)$_6$]	17.10 (2.6)		

[a] As pure powders of the indicated salts. [b] These data are for excitation at 370 nm.

Table IV. Vibrational Band Maxima in the Emission Spectrum of [Ph$_4$As][Ta(CO)$_6$] at 25 K

Band max, cm^{-1}	$\nu^n - \nu^{n+1}$, cm^{-1}
19212	
	424
18788	
	424
18364	
	122
18242	
	151
18091	
	152
17939	
	91
17848	
	485
17363 (max)	
	393
16970	
	364
16606	
	439
16167	
	500
15667	

emission, [Ph4As][Ta(CO)6], Figure 5. Careful absorption measurement for the [Ph4As][Ta(CO)6] in a concentrated KBr disk showed that the lowest energy vibrational component of the first absorption system overlaps with the highest energy vibrational component of the emission. The 19608-cm^{-1} lowest absorption maximum and the 19212-cm^{-1} highest emission maximum may thus be used to bracket the position of the O–O transition.

The vibrational maxima in the emission spectrum of [Ph4As][Ta(CO)6] are listed in Table IV. In this connection we have measured the ir absorption spectra of the anions in KBr and some key band maxima are given in Table V. As a final note concerning emission phenomena, we have determined that [n-Bu4N][Ta(CO)6] exhibits luminescence in EPA solution at 77 K with nearly the same spectral distribution as in the solid state. However, the photosensitivity of Ta(CO)6$^-$ under these conditions (vide infra) has precluded our making detailed measurements thus far.

b. Photochemistry of M(CO)6$^-$. Photolysis of M(CO)6$^-$ in solution undoubtedly leads to net photosubstitution.[4] For V(CO)6$^-$ we have carried out quantitative measurements for substitution efficiency for reactions 1 and 2. Reproducible results are only obtained for rigorously degassed solutions.
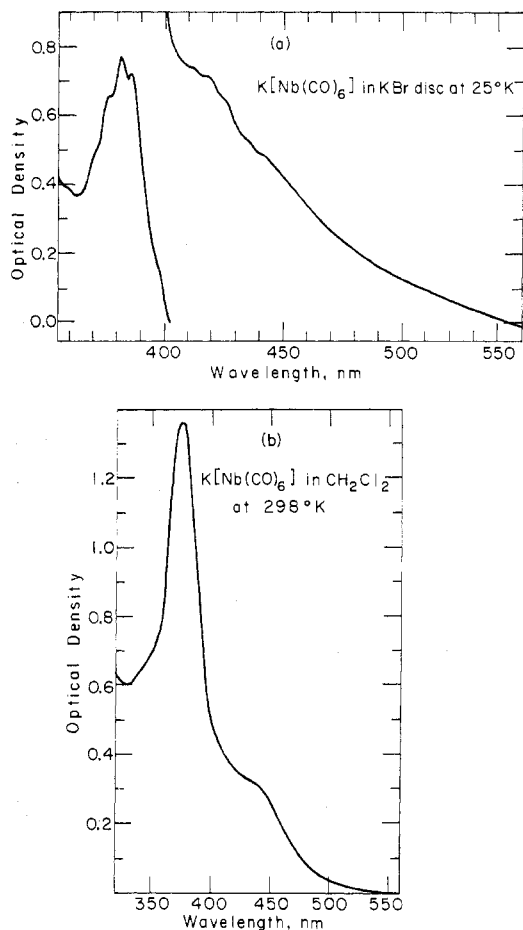
Figure 1. Electronic spectra of $[K(diglyme)_3][Nb(CO)_6]$. The molar absorptivity of the band near 380 nm is ~6000 M^{-1} cm^{-1}. For curve a in KBr the optical density scale above 400 nm begins at 1.0. The peak optical density is 1.77.

Table V. Infrared Absorptions for $M(CO)_6^-$ [a]

Compd	Medium	CO str, cm^{-1}	M–C str, cm^{-1}	M–CO def, cm^{-1}
$[Ph_4As][V(CO)_6]$	KBr	1850 s		
		1870 sh		
		1828 sh		
	CH_2Cl_2	1850 s		
$[K(diglyme)_3][Nb(CO)_6]$	KBr	1838 s	420 w	565 m
$[(Ph_3P)_3Au][Ta(CO)_6]$	KBr	1840 s, br	415 w	550 m
$[(n\text{-Bu})_4N][Ta(CO)_6]$	KBr	1850 s, br	432 w	550 m
	CH_2Cl_2	1850 s		
$[Ph_4As][Ta(CO)_6]$	KBr	1845 s	410 w	555 m
		1865 sh		
		1822 sh		
	CH_2Cl_2	1850 s		

[a] Key: s, strong; m, medium; w, weak; sh, shoulder; br, broad. Assignments are based on those for $M'(CO)_6$ (M' = Cr, Mo, W) in L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963).

Figure 2. Electronic spectra of $[Ph_4As][Ta(CO)_6]$ in CH_2Cl_2 at 298 K and $[(Ph_3P)_3Au][Ta(CO)_6]$ in KBr. The band near 380 nm has a molar absorptivity of ~5800 M^{-1} cm^{-1}.

$$V(CO)_6^- \xrightarrow[\substack{CH_3CN \\ \text{degassed}}]{h\nu} V(CO)_5(NCCH_3)^- + CO \tag{1}$$

$$V(CO)_6^- \xrightarrow[\substack{py \\ \text{degassed}}]{h\nu} V(CO)_5(py)^- + CO \tag{2}$$
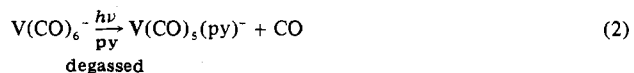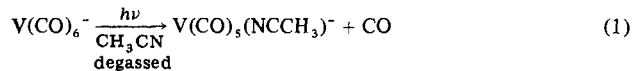
Some solution photochemistry data are given in Table VI, and an example of the clean uv–vis spectral changes accompanying the reaction is given in Figure 7. Infrared spectra for V-

Table VI. Photolysis of $M(CO)_6^-$ in Solution[a]

Compd	Entering group, X	Formation quantum yields for $M(CO)_5X^-$, (±10%)			Isosbestic points, nm	$M(CO)_5X^-$ abs max, nm (ϵ)
		313 nm	366 nm	436 nm		
$[Ph_4As][V(CO)_6]$	CH_3CN		0.51	0.56	333, 423	495 (2470)
	py		0.48	0.57	340, 382	520 (5660)
	4-Et(py)					520
$[Et_4N][V(CO)_6]$	CH_3CN	0.54	0.60	0.63	327, 430	493 (1740)
	py		0.51	0.58		518 (4620)
$[n\text{-Bu}_4N][Ta(CO)_6]$	py				358, 411	536

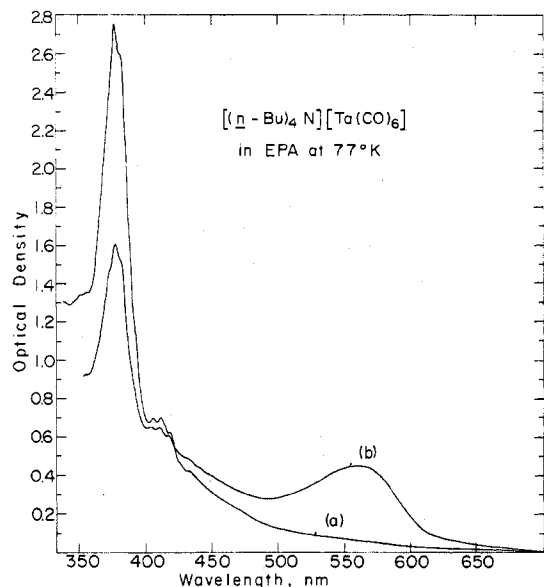[a] Degassed solutions of the $M(CO)_6^-$ salts in the entering group X at 298 K.

Figure 3. Electronic spectrum of EPA solution of [n-Bu$_4$N]-[Ta(CO)$_6$] at 77 K before (a) and after (b) irradiation with near-uv light. The product band near 540 nm is attributed to Ta(CO)$_5$(solvent)$^-$.
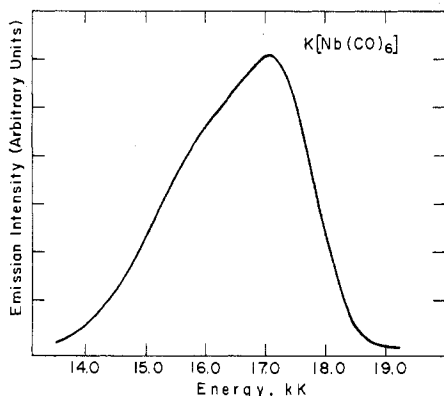

Figure 4. Corrected emission spectrum of [K(diglyme)$_3$]-[Nb(CO)$_6$] powder at 25 K with excitation using the 454-nm line of an argon ion laser.

(CO)$_5$X$^-$ photoproducts are consistent with the C_{4v} products: for X = PPh$_3$, 1951 (m), 1841 (s), 1806 (s) cm^{-1} in CH$_2$Cl$_2$; for X = CH$_3$CN (neat); 1956 (m), 1851 (s), 1811 (m) cm^{-1}. These results are consistent with those in ref 4. No thermal substitution of M(CO)$_6^-$ occurs at room temperature on the time scale of the experiments reported herein.

Electronic spectral changes are also found upon irradiation of the salts of M(CO)$_6^-$ in rigid media, Figures 3, 8, and 9. Generally, the result of irradiation is a decline in the intense near-uv absorption band and the growth of a band maximizing in the 540–600-nm region. Irradiation of V(CO)$_6^-$ in MTHF at ~90°K has previously been reported[13] to yield infrared spectral changes consistent with the formation of V(CO)$_5$-(MTHF)$^-$. Interestingly, there is a degree of reversibility in the spectral changes in KBr for Nb(CO)$_6^-$, Figure 9. Irradiation into the visible band produced by uv photolysis of Nb(CO)$_6^-$ yields substantial regeneration of the original Nb(CO)$_6^-$ spectrum. These results qualitatively parallel those from the low-temperature matrix photochemical studies of neutral M'(CO)$_6$ (M' = Cr, Mo W) species.[7a]

Discussion

Results described above support the general conclusion that the essential nature of the lowest excited states in the M(CO)$_6^-$ species is the same as in the neutral, isoelectronic analogs.

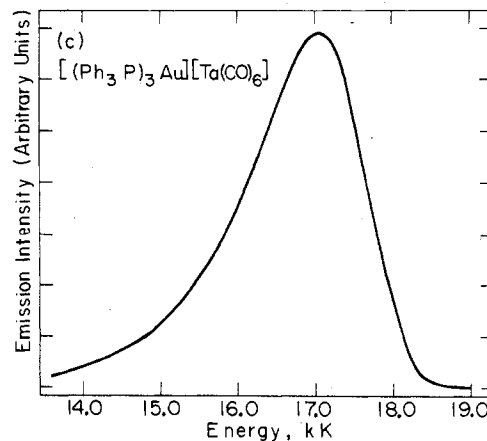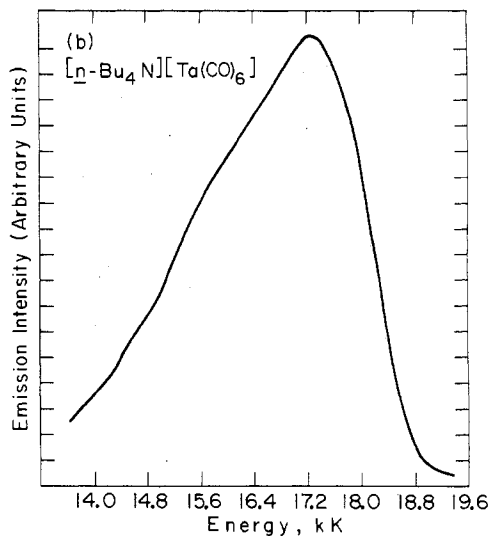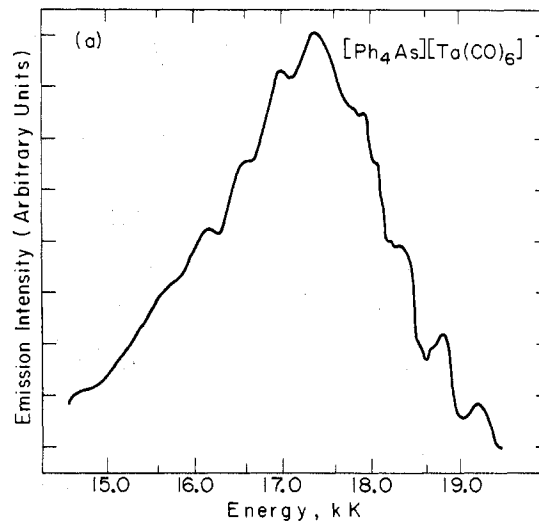**Figure 5.** Corrected emission spectra of powders of Ta(CO)$_6^-$ salts at 25 K using the 454-nm line of an argon ion laser.

Generally, the effect of countercation is fairly small. The low-energy regions of the electronic absorption spectra are very similar in the number of bands and their relative intensity. Adopting the earlier assignments[5] for the d^6 metal hexacarbonyls, the lowest absorption band system in M(CO)$_6^-$ is ascribed to the $^1A_{1g}(t_{2g}^6) \rightarrow {}^{1,3}T_{1g}(t_{2g}^5e_g^1)$ transitions. As expected for the lower oxidation state central metal, the anionic species have a smaller LF strength, and thus the lowest energy absorption system falls at lower energy than in the neutral species. Likewise, the fairly sharp, intense absorption near
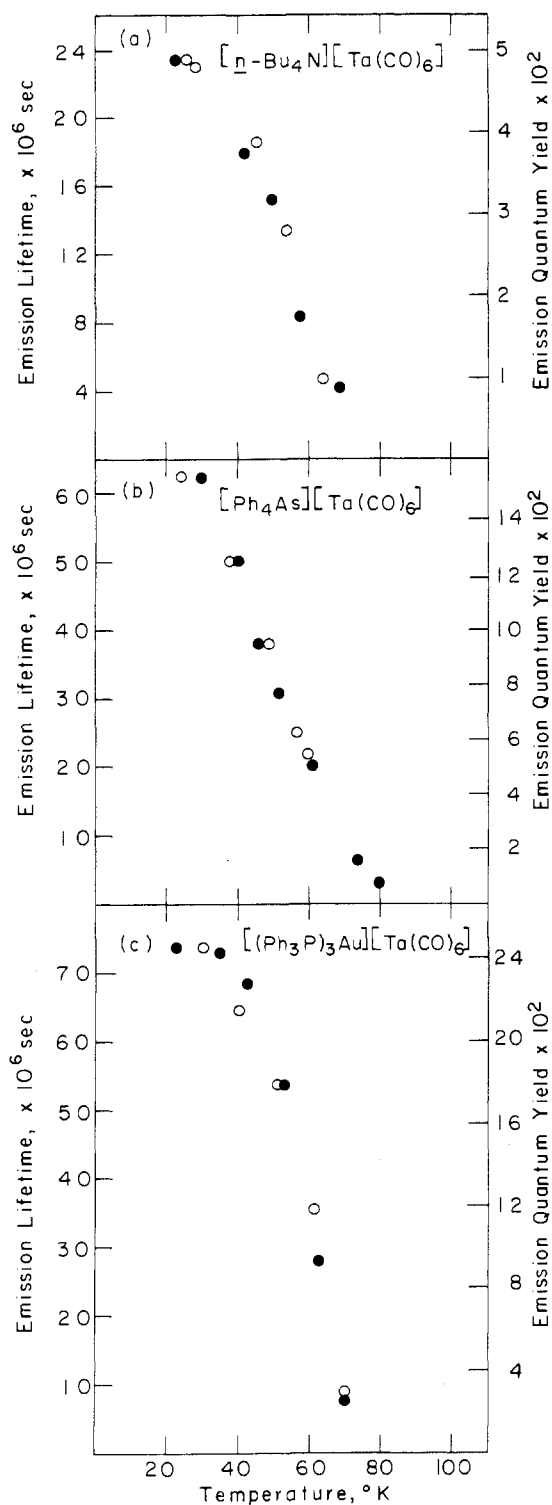
Figure 6. Temperature dependence of emission quantum yields (● and right scale) and emission lifetimes (○ and left scale) for pure powdered salts of Ta(CO)$_6$⁻.

Figure 7. Electronic spectral changes accompanying 366-nm photolysis of [Ph$_4$As][V(CO)$_6$] in CH$_3$CN to yield V(CO)$_5$-(NCCH$_3$)⁻. Irradiation times are (a) 0 sec; (b) 63 sec, (c) 144 sec, (d) 226 sec, (e) 300 sec, (f) 427 sec, (g) 621 sec, (h) 887 sec, and (i) 1221 sec. Quantum yield for formation of V(CO)$_5$(NCCH$_3$)⁻ is 0.51 (Table IV).

Figure 8. Electronic absorption spectra of [Ph$_4$As][V(CO)$_6$] at 75 K in 2-methyltetrahydrofuran after (1) 0 min, (2) 5 min, (3) 10 min of irradiation with a near-uv black light source.

Figure 9. Absorption spectra of [K(diglyme)$_3$][Nb(CO)$_6$] in KBr at 25 K after (1) 2-min irradiation with a near-uv source and then (2) 30 sec of visible light irradiation from an argon ion laser. The spectrum prior to any irradiation is shown in Figure 1a.

360 nm in M(CO)$_6$⁻ ascribed to a M → π* CO CT transition is lower in energy than for the neutral M'(CO)$_6$ M' → π* CO CT which is found near 290 nm.

Vibrational structure observed for Nb(CO)$_6$⁻ and Ta(CO)$_6$⁻ is not resolved well enough to make a detailed analysis, but the results (Table II) do seem to show that the vibrational spacings are fairly close to the M–C stretching frequency found in the ground-state infrared spectra (Table V). If the structure can be ascribed to the population of higher vibrational levels associated with M–C stretching, one can conclude that there
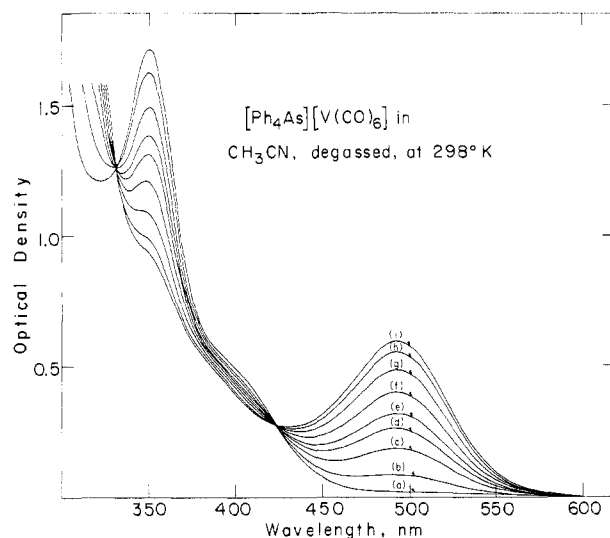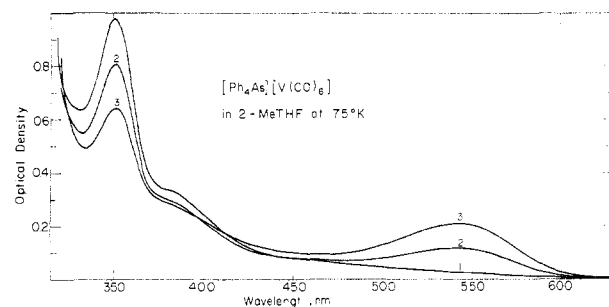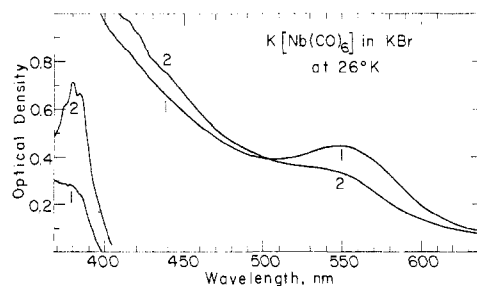
is not a great deal of distortion of the excited state compared to the ground state. Lack of substantial geometrical distortion in the excited state also follows from the overlap of the lowest energy absorption and the highest energy vibrational component of the emission in [Ph4As][Ta(CO)6]. Energetic spacing of the structure in the emission is very close to the ground-state Ta–C stretching frequency. Structured emission from the O_h, low-spin d⁶ Co(CN)$_6$³⁻ has also been observed and the spacings corresponded to the Co–C stretching frequency.[14] For the Co(CN)$_6$³⁻ the emission was first[15] assigned to the ³T$_{1g}$(t$_{2g}$⁵e$_g$¹) → ¹A$_{1g}$(t$_{2g}$⁶) transition, but this assignment was later refined[14] to include the fact that spin–orbit coupling is a substantial perturbation. The ³T$_1$ state splits into A$_1$, T$_1$, T$_2$, and E upon application of spin–orbit coupling, and it has

been suggested[14] that emission occurs from a Boltzman distribution of these spin–orbit states accounting for the temperature dependence of the emission properties. We adopt the $^3T_{1g}(t_{2g}{}^6) \rightarrow {}^1A_{1g}(t_{2g}{}^5e_g{}^1)$ assignment for the emission of Nb(CO)₆⁻ and Ta(CO)₆⁻, but with the understanding and realization that the spin–orbit coupling is so large as to preclude real meaning for the spin state. Additionally, as discussed below, the emitting state likely has some considerable CT character. Temperature dependencies that we find for τ and Φ_e, Figure 6, show that the ratio of τ at a temperature T_1 to τ at T_2 is equal to the ratio of the Φ_e's at these same temperatures; i.e., eq 3 obtains within experimental error.

$$\frac{\tau(T_1)}{\tau(T_2)} = \frac{\Phi_e(T_1)}{\Phi_e(T_2)} \tag{3}$$

From the definition of τ, eq 4, and Φ_e, eq 5, eq 3 holds when

$$\tau = \frac{1}{k_r + k_{nr}} \tag{4}$$

$$\Phi_e = \frac{k_r}{k_r + k_{nr}} \tag{5}$$

the radiative decay constant, k_r, is invariant. Therefore, all variations in τ and Φ_e over the temperature range investigated can only be ascribed to variation in the nonradiative decay constant, k_{nr}. Similar results have been found for ruthenocene[16] and Re(CO)₅X (X = Cl, Br, I).[17] These results may mean that the spin–orbit coupling is so large that the second spin–orbit state lies far enough above the lowest spin–orbit state that "activated" nonradiative decay processes set in well before the second spin–orbit state gains any substantial population by thermal activation. It would be interesting to extend the temperature-dependent studies down to 4.2 K or lower to determine whether eq 3 obtains over the complete region where luminescence is observed. Such measurements are beyond our own capabilities.

Luminescence has never been reported for any other O_h, low-spin d⁶ hexacarbonyl. In particular, we have attempted to observe emission from pure Mo(CO)₆ and W(CO)₆ down to 20 K. While we are hesitant to conclude that emission is *completely* absent in any compound, these neutral metal hexacarbonyls certainly are not obviously luminescent. Emission results for the Nb(CO)₆⁻ and Ta(CO)₆⁻ show that there is little distortion in the excited state despite the facts that the complexes undergo efficient photosubstitution and the lowest excited state is strongly σ antibonding. The Co(CN)₆³⁻ apparently undergoes considerable expansion in its lowest excited state.[14] Likewise, other low-spin d⁶ complexes (Rh(III) and Ir(III) complexes) which exhibit LF luminescence[18] often have significantly red-shifted emission and typically low-emission quantum yields. These results suggest that LF excited states do distort away from the ground-state geometry. However, in the d⁶ W(CO)₅(NH₃) and related complexes LF emission obtains[19] which overlaps the lowest absorption band, but in M(CO)₆⁻ the LF and CT bands are closer energetically than in W(CO)₅(NH₃). Thus, we attribute M → π* CO CT character to the emitting state in M(CO)₆⁻ to account for the small distortion and the apparent difference in radiative decay efficiency compared to that of M'(CO)₆. While it has been shown[18] in the low-spin d⁶ Ru(NH₃)₅X²⁺ (X = pyridine or substituted pyridine) complexes that pure Ru → X CT states *do not* lead to efficient photosubstitution, it is apparent[18,19] that, when the Ru → X CT and LF states are close energetically, fairly efficient photosubstitution can obtain despite the fact that the absorption spectrum is completely dominated by the CT absorption. In the case at hand, M(CO)₆⁻, the emitting state and the reactive state may be different. The data are not conclusive in this regard.

Photolysis of the M(CO)₆⁻ species seems to parallel closely the results for the neutral species. Electronic spectral changes accompanying the photolysis of M(CO)₆⁻ in rigid media at low temperature, Figures 3, 8, and 9, show that a visible absorption band grows (near 550 nm) at the expense of bands that are associated with M(CO)₆⁻. We ascribe the visible absorption band to the $^1A_1(e^4b_2{}^2) \rightarrow {}^{1,3}E(e^3b_2{}^2a_1{}^1)$ LF transitions for a C_{4v} M(CO)₅⁻ or M(CO)₅(solvent)⁻ species. The difference in energy of the $^1A_{1g} \rightarrow {}^{1,3}T_{1g}$ and $^1A_1 \rightarrow {}^{1,3}E$ transitions is about that expected for the reduction of symmetry and LF strength as compared to the analogous neutral O_h and C_{4v} complexes.[7a] Quantum efficiency for the substitution of V(CO)₆⁻ by pyridine or CH₃CN is very high as typically found for the mononuclear metal carbonyls.

Experimental Section

Materials. All solvents used are commercially available. [Ph₄As][Ta(CO)₆], [n-Bu₄N][Ta(CO)₆], [(Ph₃P)₃Au][Ta(CO)₆], [K(diglyme)₃][Nb(CO)₆], and [Ph₄As][V(CO)₆] were generously supplied by Professor Alan Davison of M.I.T. The samples of these complexes used are just those prepared, characterized, and described previously.[21] The [Et₄N][V(CO)₆] was prepared by metathesis of commercially available [Na(diglyme)₂][V(CO)₆].

Spectroscopic Measurements. All electronic absorption spectra were recorded on a Cary 17 uv–vis–near-ir spectrophotometer. Low-temperature spectra were recorded using the Cary 17 with (1) an all-quartz liquid N₂ sample Dewar fitted with optical-quality flats for windows or (2) a Cryogenic Technology, Inc., Spectrim II sample conditioner. Infrared absorption spectra were recorded on either a Perkin-Elmer 521 or 337 grating spectrometer. Electronic emission spectra were recorded using (1) an Aminco-Bowman emission spectrophotometer equipped with a 150-W xenon excitation source or (2) the Cary 17 placing the sample where the source is usually placed. For Cary 17 detected emission the excitation source was typically a beam expanded (6×) Spectra Physics Model 164 argon ion laser tuned to the 454-nm line. Temperature variation was achieved using the Spectrim II. Quantum yields for emission were determined as previously reported,[12,16,17] and all emission spectra have been corrected for variation in detector sensitivity as a function of wavelength. The detector systems were calibrated using the equipment described previously.[16,17] Emission lifetimes were measured using equipment previously described.[16,17]

Photochemical Measurements. Irradiations in rigid media were carried out by irradiation of the sample while in the liquid N₂ Dewar or in the Spectrim II sample conditioner. The irradiation source was either the argon ion laser or a G.E. Black Lite equipped with two 15-W black lite bulbs (spectral output principally between 300 and 400 nm). Quantitative irradiations carried out at room temperature were done using appropriately filtered Hanovia 450-W medium-pressure Hg arc lamps equipped with merry-go-rounds[22] for irradiation at 313, 366, or 436 nm. For merry-go-round irradiations the [Et₄N][V(CO)₆] or [Ph₄As][V(CO)₆] was dissolved in neat pyridine or CH₃CN and 3.0-ml aliquots were placed in 13 × 100 mm test tubes with constrictions. The ampules were then freeze–pump–thaw degassed in five cycles and hermetically sealed. Irradiation was then carried out and light intensity was measured using ferrioxalate actinometry.[23] Analysis of the samples was by monitoring uv–vis absorption spectral changes (as in Figure 7). The quantum efficiency for formation of the V(CO)₅X⁻ species was determined to be equal to the V(CO)₆⁻ disappearance.

References and Notes

(1) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).
(2) E. A. Koerner von Gustorf and F.-W. Grevels, *Top. Current Chem.*, **13**, 366 (1969).
(3) V. Balzani and V. Carassiti, "Photochemistry of Coordination

Compounds", Academic Press, New York, N.Y., 1970.
(4) A. Davison and J. E. Ellis, *J. Organomet. Chem.*, **31**, 239 (1971).
(5) N. A. Beach and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5713 (1968).
(6) M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).
(7) (a) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971); (b) A. G. Massey and L. E. Orgel, *Nature (London)*, **191**, 1387 (1961); (c) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Am. Chem. Soc.*, **84**, 3589 (1962); **85**, 1013 (1963); (d) J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organomet. Chem.*, **29**, 269 (1971); (e) J. M. Kelly, H. Hermann, and E. A. Koerner von Gustorf, *J. Chem. Soc., Chem. Commun.*, 105 (1973); (f) J. A. McIntyre, *J. Phys. Chem.*, **74**, 2403 (1970).
(8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, pp 770–800.
(9) (a) M. S. Wrighton, D. S. Ginley, M. A. Schroeder, and D. L. Morse, *Pure Appl. Chem.*, **41**, 671 (1975); (b) M. S. Wrighton and M. A. Schroeder, *J. Am. Chem. Soc.*, **96**, 6235 (1974); **95**, 5764 (1973); (c) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Organomet. Chem.*, **70**, 283 (1974); *J. Am. Chem. Soc.*, **92**, 6068 (1970); **93**, 3285 (1971); (d) W. Jennings and B. Hill, *ibid.*, **92**, 3199 (1970); (e) B. Hill, K. Math, D. Pillsbury, B. Voecks, and W. Jennings, *Mol. Photochem.*, **5**, 195 (1973); (f) J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organomet. Chem.*, **27**, C13 (1971); (g) G. Platobrood and L. Wilputte-Steinert, *ibid.*, **70**, 393, 407 (1974); (h) P. Krausz, F. Garnier, and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 437 (1975); (i) A. Agapiou and E. McNelis, *J. Chem. Soc., Chem. Commun.*, 187 (1975).

(10) (a) E. P. Kündig, D. McIntosh, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **95**, 7234 (1973); (b) E. P. Kündig and G. A. Ozin, *ibid.*, **96**, 3820 (1974); (c) H. Huber, E. P. Kündig, and G. A. Ozin, *ibid.*, **96**, 5585 (1974); (d) H. Huber, E. P. Kündig, G. A. Ozin, and A. J. Poe, *ibid.*, **97**, 308 (1975); (e) G. A. Ozin, H. Huber, E. P. Kündig, and M. Moskovits, *ibid.*, **97**, 2097 (1975).
(11) R. Perutz, Ph.D. Thesis, University of Newcastle-upon-Tyne, 1974.
(12) M. S. Wrighton, D. S. Ginley, and D. L. Morse, *J. Phys. Chem.*, **78**, 2229 (1974).
(13) P. S. Braterman and A. Fullarton, *J. Organomet. Chem.*, **31**, C27 (1971).
(14) K. W. Hipps and G. A. Crosby, *Inorg. Chem.*, **13**, 1543 (1974).
(15) M. Mingardi and G. B. Porter, *J. Chem. Phys.*, **44**, 4354 (1966).
(16) M. S. Wrighton, L. Pdungsap, and D. L. Morse, *J. Phys. Chem.*, **79**, 66 (1975).
(17) M. S. Wrighton, D. L. Morse, H. B. Gray, and D. K. Ottesen, *J. Am. Chem. Soc.*, in press.
(18) M. K. De Armond, *Acc. Chem. Res.*, **7**, 309 (1974), and references therein.
(19) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 4336 (1971).
(20) (a) G. Malouf and P. C. Ford, *J. Am. Chem. Soc.*, **96**, 601 (1974); (b) D. S. Chaisson, R. E. Hintze, D. H. Stuermer, J. D. Petersen, D. P. McDonald, and P. C. Ford, *ibid.*, **94**, 6665 (1972).
(21) J. E. Ellis, Ph.D. Thesis, M.I.T., 1966.
(22) F. G. Moses, R. S. H. Liu, and M. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).
(23) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

Reactions of the *trans*- and *cis*-Diaquobis(oxalato)chromate(III) Ions in Solutions Which Contain Oxalic Acid

THOMAS W. KALLEN

When *trans*-Cr(C₂O₄)₂(H₂O)₂⁻ is added to acidic solutions that contain H₂C₂O₂ and HC₂O₄⁻, rapid isomerization of the trans complex occurs. This step is followed by the slower anation of the resulting cis complex by oxalate species. Anation proceeds to an equilibrium mixture of species described by the equilibrium quotient $K_3 = [Cr(C_2O_4)_3{}^{3-}][H^+]^2/[cis\text{-}Cr(C_2O_4)_2(H_2O)_2{}^-][H_2C_2O_4]$. At 50°C and $\mu = 1.00$ M, maintained with potassium nitrate, $K_3 = 0.890 \pm 0.012$ M. The kinetics of the two-step reaction at $\mu = 1.00$ M, between 35 and 55°C, are reported. Both steps of the reaction obey simple first-order kinetics. Observed pseudo-first-order rate constants for the trans–cis isomerization in sodium perchlorate and potassium nitrate were fit to the form $k_{obsd} = k_{H_2O} + k_M[M^+] + k_H[H^+]$, where M is sodium or potassium. Activation enthalpies for the various constants are 15.1 ± 0.5 (k_{Na}), 14.7 ± 0.8 (k_K), and 18.5 ± 0.3 (k_H) kcal/mol. Activation entropies are −23.9 ± 1.6 (k_{Na}), −26.0 ± 2.6 (k_K), and −8.5 ± 0.8 (k_H) cal/(mol deg). Data interpretations are based on $\Delta H^\ddagger = 17.9$ kcal/mol and $\Delta S^\ddagger = -14.7$ cal/(mole deg) for k_{H_2O}. Hydrogen ion and ligand dependencies of the observed pseudo-first-order anation rate constants are medium-dependent and slower rates are observed in perchlorate media. In perchlorate media, $k_{obsd} = k_b[HC_2O_4^-] + k_4[H^+]$, while in nitrate media, $k_{obsd} = \{k_1[H_2C_2O_4] + (k_2k_4/k_3)[H^+]^2\}/\{1 + (k_2/k_3)[H^+]\}$. At 50°C in potassium nitrate, $k_1 = 2.84 \times 10^{-2}$ M⁻¹ sec⁻¹, $k_2/k_3 = 73.8 \pm 11.3$ M⁻¹, and $k_4 = 4.38 \times 10^{-4}$ M⁻¹ sec⁻¹. Activation enthalpies are 20.7 ± 0.4 and 21.9 ± 0.4 kcal/mol, and activation entropies are −1.9 ± 1.0 and −6.5 ± 1.4 cal/(mol deg), for k_1 and k_4, respectively. A steady-state mechanism, which describes k_1 and k_3 as anation steps and k_2 and k_4 as aquation steps, is proposed for the anation reaction in both media. This mechanism identifies k_b as a composite constant equal to k_1k_3/k_2K_1, where K_1 is the first dissociation constant of oxalic acid. The anation rate constant, k_1, is limited by k_H for the trans–cis isomerization. Other mechanistic similarities between the isomerization process and aquation and anation processes are described, and a new conformation for the bidentate oxalate ligand is proposed as a precursor to each process.

Introduction

The trans–cis isomerization of Cr(C₂O₄)₂(H₂O)₂⁻ has been investigated by a variety of research groups. Uncatalyzed pathways,[1,2] hydrogen ion catalyzed pathways,[3–5] multivalent cation catalyzed pathways,[5] and univalent cation catalyzed pathways[6] have been identified for this superficially simple process. Isomerization is generally thought to involve generation of a half-bonded oxalate intermediate which may be stabilized by association with a hydrogen ion or other cations. Operation of the deuterium isotope effect upon the hydrogen ion catalyzed pathway, for example, may be explained by a preequilibrium involving the hydrogen ion, followed by a rate-determining step which is not subject to an isotope effect.

The anation reaction of *cis*-Cr(C₂O₄)₂(H₂O)₂⁻ with oxalate species is not as well characterized. Anation reactions involving the oxalate ion[7,8] and hydrogen oxalate ion[8] have been examined and an ion-pairing mechanism was proposed to rationalize the dependence of the rate upon the ligand concentration.[8]

Aquation of Cr(C₂O₄)₃³⁻ to the *cis*-Cr(C₂O₄)₂(H₂O)₂⁻ complex ion has been studied under a wide variety of conditions, with the majority of investigators agreeing upon a two-term rate law which involves first- and second-order hydrogen ion catalysis.[9–12] The deuterium isotope effect,