Dr. John D. Petersen, now of Kansas State University, for technical advice and assistance. A.W.Z., now of the Joint Sciences Department, the Claremont Colleges, Claremont Calif., thanks that department for partial support during the preparation of this paper.

Registry No. $Co(NH_3)_5(PhCN)^{3+}$, 46343-53-7; $Co(NH_3)_5(CH_3CN)^{3+}$, 44819-13-8; $Co(NH_3)_5Br^{2+}$, 14970-15-1; PhCN, 100-47-0.

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Contribution from the Department of Chemistry,
University of California, Santa Cruz, Santa Cruz, California 95064

Flash Kinetic Spectroscopy of $Mo_2(O_2CCF_3)_4$

VINCENT M. MISKOWSKI, ALLEN J. TWAROWSKI, RONALD H. FLEMING, GEORGE S. HAMMOND,* and DAVID S. KLIGER

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Flash photolysis of $Mo_2(O_2CCF_3)_4$ causes bleaching followed by reappearance of ground-state absorption on a microsecond time scale. In benzene solution recovery follows simple first-order kinetics with $\tau(C_6H_6) = 33\ \mu s$. In nucleophilic solvents reappearance of the original absorption is more complex and appears to be a two-step process. We believe that the principal intermediate present at the end of the 10-ns flash excitation is a triplet having the $\sigma^2\pi^4\delta^1\pi^{*1}$ configuration. We speculate that the triplet reacts with polar solvent molecules (acetonitrile, dimethylformamide, and acetone) forming short-lived adducts in which one trifluoroacetato bridge has been half opened. These intermediates have new absorption near 490 nm, relatively intense maxima in the 385-nm region, and absorption at 360 nm similar to that of the ground state of the parent compound. Half-times for formation of the intermediate adducts are $\tau(CH_3CN) = 5.5$, $\tau(\text{acetone}) = 3.9$, and $\tau(DMF) = 1.5\ \mu s$. Lifetimes for decay of the adducts to $Mo_2(O_2CCF_3)_4$ ground states are respectively 32, 16, and 13 μs. Spectral characteristics of the various transients are discussed.

We recently reported a flash kinetic study[1] of the complex ions $Re_2X_8{}^{2-}$ (X = Cl, Br), which contain quadrupole metal–metal bonds. The lowest excited state had a lifetime of about 100 ns in fluid solution at room temperature and was assigned the $\sigma^2\pi^4\delta^1\pi^{*1}$ configuration. In an earlier communication[2] we reported that photochemical cleavage of the complexes occurred from higher excited states with appreciable quantum yield but that irradiation in the first absorption band gave no permanent chemical change.

We have extended the study to a neutral compound, $Mo_2(O_2CCF_3)_4$, containing a quadruple bond for several reasons. First, spin–orbit coupling will be lower than with the rhenium complexes because the atomic number of the central metallic element is lower; consequently one might expect the lowest lying excited states to have relatively pure triplet character and relatively long lifetimes. Second, dimeric complexes of Re(III)[3,4] and Mo(II)[5-8] containing carboxylate bridges have spectral characteristics considerably different from those of the halide complexes so there may be major differences in the energetic ordering of the excited states of dimers containing bridging ligands and those that do not. Finally, the neutral compound is soluble in a wide range of solvents.

Experimental Section

The flash apparatus employed a Molectron UV-1000 pulsed nitrogen laser, which produced a pulse of 337-nm light which has a half-width of 10 ns. Absorption was monitored using a quartz–iodine lamp with a variable speed shutter to produce analytical light bursts of appropriate duration for the rates of the processes under observation. Transmitted light was passed through a monochromator and the intensity as a function of time was displayed on a Tektronix 474 oscilloscope and photographed. Differences between the intensity of the transmitted beam and the source pulse were read from the photographs and converted to absorbance units for analysis of the kinetics.

A sample of $Mo_2(O_2CCF_3)_4$, purified by two sublimations, was supplied by Dr. William Trogler of the California Institute of Technology. The solid material appeared to be reasonably air stable but was nonetheless stored under argon. Solutions were air sensitive. We therefore designed sample tubes in which the solid compound and the appropriate amount of solvent could be degassed (three freeze–thaw cycles) in separate compartments and mixed only after the entire apparatus had been sealed off under high vacuum. The solution could then be poured into a side arm holding a standard 1-cm optical cell for flash experiments. Solutions were $1–5 \times 10^{-4}$ M in $Mo_2(O_2CCF_3)_4$, and solvents were spectroquality grade, generally subjected to distillation prior to use. One experiment was performed with CH_3CN which had been passed through an alumina column immediately prior to use, and no effect on transient lifetimes was observed.

Results

Solutions of $Mo_2(O_2CCF_3)_4$ in benzene, acetone, acetonitrile, and dimethylformamide (DMF) show an intense absorption system consisting of two overlapping, approximately equally intense ($\epsilon_{max} \simeq 6300\ M^{-1}\ cm^{-1}$) bands at ~330 nm. The lowest energy absorption feature is a much weaker band ($\epsilon_{max} \sim 10^2\ M^{-1}\ cm^{-1}$) peaking between 400 and 450 nm.

Laser pulse irradiation (337 nm) of such solutions results in decreased absorption between 340 and 400 nm. Because our analytical flash lamp has low output below 340 nm, we were unable to monitor transients at shorter wavelengths. The concentrations chosen for study were low enough to effect substantial depopulation of the ground states by the laser pulses but were too low to allow measurement of changes in absorption in the region above 400 nm by the ground-state species with any accuracy. By assuming that there is no absorption by transients in the interval 360–385 nm, we calculated the decrease in the concentration of ground-state molecule after decay of the excitation flash (~10 ns). Concentration changes of $7–8 \times 10^{-5}$ M were obtained with pulses of 10^{16} photons focused on an elliptical area of about 0.24 cm^2 on the surface of 1-cm cells. The solute concentrations were high enough to effect absorption of nearly all of the light so the absorbed photon flux was about 7×10^{-5} einstein L^{-1}, indicating a quantum efficiency for bleaching of about unity. Within the limit of the accuracy of our measurements the result confirms the assumption that there is no competitive absorption by excited species since any such phenomenon would lead to underestimation of the extent of ground-state depopulation and require the unlikely estimate of quantum yields greater than unity.

The kinetics of return of the bleached absorption varied from solvent to solvent. In benzene, absorption returned at the same first-order rates at 360 and 385 nm, with a lifetime of 33 ± 4 μs.

In the other solvents recovery of absorption at 360 nm again gave a reasonable fit to first-order kinetics but was much more rapid than in benzene in each case. However, absorption at 385 nm increased rapidly *to greater than the value in unirradiated solutions* and then fell to the original value. Moreover, in the polar solvents new absorption near 490 nm was observed to grow in and then decay. In acetonitrile the new absorption became sufficiently intense to show a clear maximum at 490 nm and could be used for kinetic analysis. In acetone and DMF only the growing absorption at 385 nm became sufficiently intense to be analyzed with accuracy. In acetonitrile the absorbance changes at 490 nm were fitted to eq 1, where A is absorbance. The tail of the decay curve, which

$$A = e^{-t/\tau_1} - e^{-t/\tau_2} \tag{1}$$

fitted first-order kinetics, was used to estimate τ_2 giving a value of 31.7 ± 0.7 μs. The time of maximum absorption at 490 nm was then used to obtain a first estimate of τ_1 using the relationship

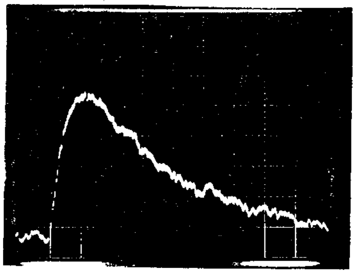
$$t_{max} = \frac{\ln(\tau_2/\tau_1)}{1/\tau_2 - 1/\tau_1} \tag{2}$$

The entire curve was then calculated using the values of τ_1 and τ_2, and τ_1 was varied to improve the fit of the calculated curve to the experimental data. This procedure indicated a value of 5.7 ± 0.5 μs for τ_1. The value of τ_2 was also estimated by fitting the decay of absorption at 385 nm after the maximum to first-order kinetics. This procedure gave a value of 31.8 ± 1.3 μs. The monotonic increase in absorption at 360 nm had a lifetime of 5.5 ± 0.3 μs, i.e., approximately the same as the value of τ_1 estimated by the growth of 490-nm absorption. Figure 1 shows reproductions of typical oscilloscope traces obtained at the three monitoring wavelengths. From these absorption and kinetic characteristics we deduce that in acetonitrile there are two transient species. The first has little absorption at any of the monitoring wavelengths. The second has a low-intensity maximum at 490 nm, a more intense maximum at 385 nm, and absorption similar to that of the ground state at 360 nm.

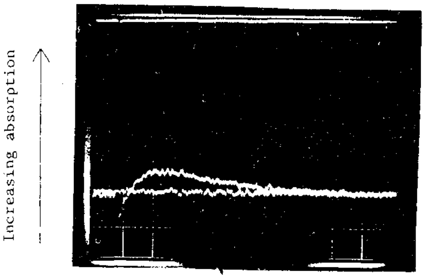
We presume that similar second transients are formed in acetone and DMF. All decay times were more rapid in these solvents but values of τ_1 (1.46 ± 0.07 μs in DMF and 3.9 ± 0.2 μs in acetone) were estimated from the recovery of absorption at 360 nm and those for τ_2 (12.8 ± 0.4 s in DMF and 15.7 ± 1.5 s in acetone) were estimated by decay from the maximum absorption at 385 nm.

Effect of Acid. Since protic acids are potential one-electron oxidants, benzene solutions containing 10% by volume of trifluoroacetic acid were flashed. Only transient bleaching was observed but the first-order recovery of absorption at 385 nm was slowed down considerably (τ = 155 ± 10 μs) in comparison with the rate in pure benzene.[9]

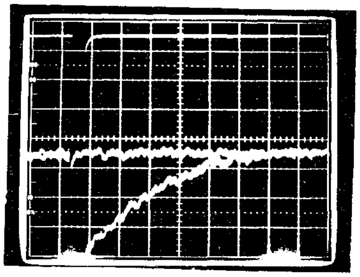
Effect of 1,3-Pentadiene. Since we postulate that the long-lived transient is a triplet of the organometallic compound, we flashed solutions containing concentrations of *cis*-1,3-pentadiene (piperylene) from 10^{-5} to 5×10^{-3} M. No detectable changes in the rates were observed in acetonitrile but in benzene the rate of recovery of absorption was noticeably enhanced. Although quenching was definitely observed in solutions containing 1.0 and 5.2×10^{-3} M diene, the reductions in lifetime were small enough to allow only approximate estimation of a rate constant of about $10^7\ M^{-1}\ s^1$ for interaction



A - 10 μs per horizontal division



B - 10 μs per horizontal division



C - 2 μs per horizontal division

Figure 1. Oscilloscope traces showing changes in absorption at 490 nm (A), 385 nm (B), and 360 nm (C) after flashing a 3.81×10^{-4} M solution of $Mo_2(O_2CCF_3)_4$ in acetonitrile.

of the excited state with the diene. A rate process of this order of magnitude would have been undetectable in competition with the fast first process in acetonitrile even at the highest diene concentrations studied.

Discussion

Our results are compatible with the following mechanism

$$G \xrightarrow{h\nu} I_1 \tag{3}$$

$$I_1 \xrightarrow{k_1} G \tag{4}$$

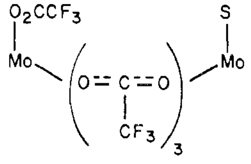
$$I_1 + S \xrightarrow{k_2} I_2 \tag{5}$$

$$I_2 \xrightarrow{k_3} G + S \tag{6}$$

where G is the ground state of the molybdenum complex. I_1 and I_2 are two relatively long-lived phototransients, and S is solvent. The parameter τ_1 in eq 1 would be $(k_1 + k_2[S])^{-1}$ and τ_2 would be k_3^{-1}.

We believe that I_1 is an excited state of $Mo_2(O_2CCF_3)_4$; if so, its lifetime indicates that it is a triplet. This is consistent with the fact that it is quenched by piperylene, a well-known triplet quencher having[11] a triplet excitation energy estimated from the onset of oxygen-perturbed absorption[12] of 59.9 kcal mol^{-1} (21 000 cm^{-1}). The fact that the quenching rate is substantially less than the diffusion-controlled limit would indicate that the excitation energy of the organometallic species is $\sim 10^3$ cm^{-1} lower than that of the diene[13,14] if the excitation process in the diene is assumed to be "vertical"; otherwise a still lower excitation energy might be assigned to the energy donor.[14]

There is no indication that a second transient, I_2, is produced in benzene so we infer that formation of such species in the other media involves direct participation of solvent molecules. Since all of the other solvents have higher nucleophilic reactivity than benzene, we postulate that molecules of solvent become bound to metal centers as ligands, producing the electronic ground states of short-lived adducts. We suggest that the adducts have structures (**1**) in which one carboxylate bridge has been opened. The second decay process, reaction 5, would then become expulsion of the weakly bound ligands from intermediates I_2 to regenerate the ground state of $Mo_2(O_2CCF_3)_4$.



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Electronic Structures. Gray et al.[7] have recently assigned the lowest energy absorption of $Mo(O_2CCF_3)_4$ as a $\delta \rightarrow \pi^*$ transition with a 0–0 component at 21 862 cm^{-1}. Emission from the crystalline compound at 1.3 K had a lifetime of 2 ns as was assigned to a triplet lying about 1600 cm^{-1} below the lowest excited singlet. Decrease of the lifetime of such a species by about 2 orders of magnitude in fluid solutions at room temperature is not unreasonable. Assignment of the excitation energy at about 20 300 cm^{-1} is consistent with the marginally detectable quenching by piperylene.

Assignment of the $\sigma^2\pi^4\delta^1\pi^{*1}$ configuration to the triplet is consistent with lack of significant absorption by the first transient in the visible region. The ground-state absorption at 330 nm (30 300 cm^{-1}) has been assigned as $\delta \rightarrow \delta^*$ transition.[7,8] In the complex $Mo_2(SO_4)_4{}^{3-}$, the δ orbital is singly occupied and the $\delta \rightarrow \delta^*$ transition is observed[15] in the near-infrared region, red shifted by 13 000 cm^{-1} from the $\delta \rightarrow \delta^*$ transition of the $\sigma^2\pi^4\delta^2$ complex $Mo_2(SO_4)_4{}^{4-}$. Evidently, loss of a δ-bonding electron, and resultant metal–metal bond lengthening,[16] causes a very large decrease in the $\delta \rightarrow \delta^*$ transition energy. The same result can be expected in the thermally equilibrated $\sigma^2\pi^4\delta^1\pi^{*1}$ excited state of $Mo_2(O_2CCF_3)_4$ and may account for the $\delta \rightarrow \delta^*$ "bleaching".[17] Furthermore, a longer metal–metal bond may strain the bridging carboxylate rings and account for the high reactivity of the transient towards nucleophilic solvents.

Assignment of structure **1** to the intermediates formed in nucleophilic solvents is based largely upon kinetic evidence. It does not seem possible that any process involving merely axial ligation of solvent molecules could be as slow as indicated by the observed τ_1 values because solvents are believed to be weakly bound to the metals even in the ground state.[18] However, the spectra of the transients are also consistent with the assignment. The weak absorption near 490 nm (20 410 cm^{-1}) and the more intense band near 385 nm (26 000 cm^{-1}) would be assigned, respectively, to $\delta \rightarrow \pi^*$ and $\delta \rightarrow \delta^*$ transitions. Both should be red shifted from the corresponding bands in $Mo_2(O_2CCF_3)_4$ because breaking one of the carboxylate bridges should cause lengthening of the Mo–Mo bond.

Effect of Trifluoroacetic Acid. The apparent strong inhibition of nonradiative decay of I_1 by CF_3CO_2H in benzene is a remarkable phenomenon for which we have no easy explanation. We are led to suspect that the transient observed in these experiments is *not* the same as that observed in pure benzene but coincidentally also lacks strong absorption in the visible. Possibly it is an unstable "metal–hydride" complex formed by protonation of the metal-localized excited state. Such a complex is a likely intermediate produced by irradiation of several other dinuclear Mo(II) complexes in acidic solution,[15,19] processes that ultimately yield gaseous hydrogen as a product.

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Registry No. $Mo_2(O_2CCF_3)_4$, 36608-07-8.

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(17) We have obtained a difference spectrum for solutions in benzene after excitation. There are a λ_{max} at 680 nm for which ϵ_{max} is $\simeq 500$, no significant absorption in the interval 400–600 nm, and sharply decreasing absorbance at the region 400–360 nm. The last is due to ground-state depletion. The 680-nm maximum is assigned to a $\delta \rightarrow \delta^*$ transition of the $\sigma^2\pi^4\delta^1\pi^*$ triplet. The shift of the $\delta \rightarrow \delta^*$ transition by about 15 000 cm^{-1} from that of the ground-state molecule (330 nm) is consistent with this analysis.

(18) This conclusion is based upon the variation in absorption spectra of $Mo_2(O_2CCF_3)_4$ in different solvents and on the known structure of a bis(pyridine) adduct (F. A. Cotton and J. G. Norman, Jr., *J. Am. Chem. Soc.*, **94**, 5697 (1972)).

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Contribution from the Department of Chemistry,
Kansas State University, Manhattan, Kansas 66506

Photochemistry of Pentacyanoferrate(II) Complexes Containing Aromatic Nitrogen Heterocyclic Ligands

JOSEPH E. FIGARD and JOHN D. PETERSEN*

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Charge-transfer-to-ligand (CTTL) excitation of pentacyanoferrate(II) complexes, $(CN)_5Fe^{II}L^{n-}$ (where L is an aromatic, nitrogen, heterocyclic base), leads to the photosubstitution of L at room temperature in aqueous solution. The nature of the excited state responsible for the photosubstitution reaction is assigned as ligand field (LF) in character. Efficient interconversion between LF and CTTL excited states is observed with the magnitude of the quantum yield dependent on whether the LF ($0.1 < \Phi_L < 1.0$) or CTTL ($\Phi < 0.05$) excited state is lowest in energy. Interconversion between internal ligand excited states and LF or CTTL excited states is apparently not a very efficient process.

Introduction

The photochemical reactivity of transition-metal complexes is dependent, in many cases, on the nature of the excited state generated by photon absorption.[1] The ligand field (LF) excited states of low-spin, d^6 complexes generally undergo ligand labilization, owing to the increase in σ^* orbital population.[2-9] The charge-transfer-to-ligand (CTTL) excited states of d^6 complexes, which may be conceptualized as an oxidized metal/reduced ligand species, are usually unreactive toward photosubstitution reactions and either interconvert to lower energy excited states or deactivate directly back to the ground state.[10,11]

The extreme sensitivity[12] of the wavelength maxima of the CTTL transitions in $(NH_3)_5Ru^{II}L^{2+}$ to substituents on L (where L is a substituted pyridine) enabled Malouf and Ford[10] to vary the magnitude of the photosubstitution reactions markedly by varying the energy of the CTTL excited state with respect to the energy of the LF state. A similar type of tuning of excited states is apparent in metal carbonyl photochemistry. Wrighton and co-workers[11] have studied the photochemistry and emission spectroscopy of $(CO)_5WL$ (where L = substituted pyridine) with the result that changes in the nature of the lowest excited state affect the quantum yield of photochemical substitution and the emission lifetime.

We report herein a study of the photosubstitution reactions of a series of pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles. The major emphasis of this work will center on answering the following two questions. (1) Can the photosubstitutional quantum yield be substantially changed for $(CN)_5Fe^{II}L^{n-}$ complexes by modifying the nature of the lowest excited state? (2) How efficient is the interconversion from an internal ligand (IL) excited state to a LF excited state or from a LF excited state to a CTTL excited state?

Experimental Section

Materials. The recrystallized sodium salts of $(CN)_5Fe^{II}L^{n-}$ (L = pyridine, 4,4′-bipyridine, isonicotinamide, pyrazine, 4-cyanopyridine, 4-acetylpyridine, 4-pyridylpyridinium, *N*-methyl-4,4′-bipyridinium, and *N*-methylpyrazinium) were prepared from $Na_3[(CN)_5Fe(NH_3)]$ by previously described procedures.[13,14] Nonmethylated ligands were commercially available as analytical reagent grade and were used without further purification. Monomethylated ligands were prepared from the reaction of methyl iodide (Fisher AR) with the corresponding heterocycle in chloroform and recrystallized from chloroform prior to complexation. Purity of the ligands was determined by ^1H and ^{13}C NMR spectroscopy. The electronic absorption spectra of the recrystallized $(CN)_5Fe^{II}L^{n-}$ complexes had absorption maxima and molar absorptivities which agreed with previously reported values.[13,14]