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Reversible Carbon Monoxide Photodissociation from Cu(I) Coordination Compounds

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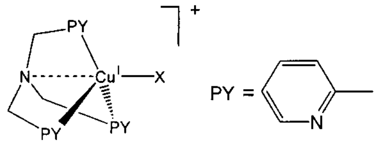
The "phototriggered" release of molecules has been a powerful mechanistic tool for the characterization of excited states, reactive intermediates, and small molecule activation and transport.[1−4] This phenomenon also has practical applications in catalysis and drug delivery.[5] Inorganic coordination compounds are attractive chromophoric molecular donors in that after photodissociation, they often bind a second molecule that can regenerate the initial compound, thereby making the process reversible for potential catalytic applications. The inorganic compounds that undergo such processes are relatively few and are predominately metalloporphyrinic compounds that photorelease CO,[2−4] O_2,[6] or NO.[7] Here we report compelling and unprecedented evidence for CO photodissociation from copper(I) coordination compounds. The results stand as a novel example of dissociative metal-to-ligand charge-transfer (MLCT) excited states[8] and may be exploited for small molecule activation and coordination studies of synthetic[9] and naturally occurring[10] copper systems.

The compounds of interest, $[Cu^I(TMPA)(X)](ClO_4)$, where X is CH_3CN or CO and TMPA is tris((2-pyridyl)methyl)amine, have been previously synthesized and characterized.[11]



$Cu^I(TMPA)(X)^+$

A derivative of TMPA where methoxy substitutents are present in the para position of each pyridine, MeO−TMPA, was also studied. The UV−vis absorbance spectrum for $[Cu^I(TMPA)(CH_3CN)]^+$ in acetonitrile displays an absorption band centered at 350 nm, not present in the free TMPA ligand, that is assigned to a copper-to-pyridine MLCT transition, $(d\pi^{10})(\pi^*)^0 \rightarrow (d\pi^9)(\pi^*)^1$.

The MLCT assignment is based on the molar extinction coefficient, 5600 $M^{-1}\ cm^{-1}$, and comparisons to related compounds.[12] A quasi-reversible wave is observed with cyclic voltammetry at $E°(Cu^{II/I}) = -0.40$ V versus Fc^+/Fc.[13] For $[Cu^I(TMPA)(CO)]^+$, the MLCT absorption band is blue shifted and overlaps with the TMPA ligand electronic transitions. The coordinated CO stretch is observed at $2092 \pm 1\ cm^{-1}$ in CH_3CN. The spectral properties are very similar in THF and Et_2O (Table 1).

Pulsed 355 nm light excitation (fwhm 8−10 ns; 5 mJ/pulse) of $[Cu^I(TMPA)(CO)]^+$ under 1 atm of CO in THF generates the immediate appearance of the absorption difference spectrum shown in Figure 1.[14] Measurements at wavelengths below 325 nm were not made due to the strong $\pi \rightarrow \pi^*$ absorption of the TMPA ligand.

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Table 1. Spectroscopic Data for [Cu^{I}(TMPA)(CO)]$^+$

solvent	k_{obs}, s$^{-1\,a}$	ν (CO), cm^{-1}	anion^b
THF	$1.7 \pm 0.2 \times 10^7$	2092	BArF$^-$
CH_3CN	$1.0 \pm 0.5 \times 10^6$	2091	ClO_4^-
Et_2O	$1.4 \pm 0.4 \times 10^7$	2091	BArF$^-$

[a] Data acquired by time-resolved absorption spectroscopy under 1 atm of CO after pulsed, 355 nm, laser excitation. The error given is the standard deviation from at least three separate measurements. [b] An in-situ metathesis reaction with NaBArF (BArF = tetrakis(3,5-trifluoromethyl)phenyl)borate) was necessary for the ether solvents. Additional details are given in the Supporting Information.

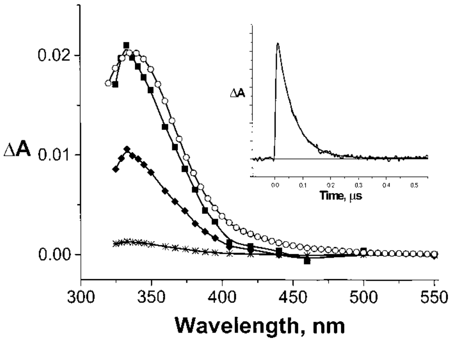

Figure 1. Difference spectra recorded after pulsed 355 nm excitation (8−10 ns fwhm, 5 mJ/pulse) of [Cu^{I}(TMPA)(CO)]$^+$ in THF at 25 °C under 1 atm of CO. The spectra were recorded at the following delay times: 0 ns (squares); 50 ns (diamonds); and 200 ns (stars). For comparative purposes, the spectra calculated as Abs[Cu^{I}(TMPA)(THF)]$^+$ − Abs[Cu^{I}(TMPA)(CO)]$^+$ is shown (open circles). The inset is a single wavelength kinetic trace monitored at 330 nm with a superimposed first-order fit, $k_{obs} = 1.7 \times 10^7$ s^{-1}.

Absorbance measurements before and after pulsed laser excitation gave no evidence for photochemical products. Excitation of the solvento complexes in the absence of CO did not yield nanosecond difference spectra. The transient spectra shown have a positive absorption band, $\lambda_{max} = 333$ nm, and are within experimental error of that calculated from (Abs[Cu^{I}(TMPA)(THF)]$^+$ − Abs[Cu^{I}(TMPA)(CO)]$^+$), indicating that the transiently generated intermediate in Figure 1 is [Cu^{I}(TMPA)(THF)]$^+$. Absorption difference spectra generated for [Cu^{I}(TMPA)(CO)]$^+$ in CH_3CN and Et_2O also show positive absorption changes in the UV region, consistent with CO loss and transient solvent binding to the Cu(I) ion.

The formation of the transient intermediate occurs within the instrument response function, indicating that CO loss occurs in less than 10 ns. The observed rate constants for CO rebinding, k_{obs}, under pseudo first-order conditions, inset of Figure 1, were independent of the monitoring wavelength, the [Cu^{I}(TMPA)(CO)]$^+$ concentration (0.2−6.0 mM), and the laser excitation energy (5−10 mJ cm^{-2}) in all conditions studied. At low [CO] concentrations (1−5 mM), the process was also shown to be first order in [CO]. The observed rate constants under 1 atm of CO were found to be solvent dependent (Table 1). Carbon monoxide coordination is the slowest in the highly coordinating CH_3CN solvent and is over an order of magnitude faster in THF and Et_2O.

Carbon monoxide coordination was also quantified for [Cu^{I}(MeO−TMPA)(CH_3CN)]$^+$. The electron donating methoxy groups increase the electron density at the copper center, as reflected in an ∼90 mV negative shift in the Cu(II/I) reduction potentials. Analogous to the parent compound, pulsed light excitation of [Cu^{I}(MeO−TMPA)(CO)]$^+$ in CH_3CN transiently generates the solvento compound. The kinetics for CO rebinding are about a factor of 4 slower, $k_{obs} = 2.6 \pm 0.5 \times 10^5$ s^{-1}, which we attribute to the stronger Cu−NCCH$_3$ bond that results from a more π-basic cuprous center.

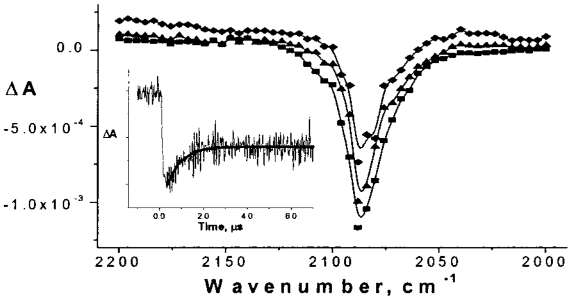

Figure 2. TRIR difference spectra observed from 0 to 1 μs (squares); 1−2 μs (triangles); and 2−4 μs (diamonds) following laser photolysis (355 nm, fwhm 90 ns, 0.4 mJ/pulse) of [Cu^{I}(TMPA)(CO)]$^+$ in CH_3CN. The inset shows a kinetic trace observed at 2088 cm^{-1} with a superimposed first-order fit to a nonzero baseline, $k_{obs} = 1.5 \times 10^6$ s^{-1}.

Additional evidence for CO photodissocation was obtained with time-resolved infrared (TRIR) spectroscopy.[15] A bleach of the coordinated CO stretch was observed at 2088 cm^{-1}, after pulsed 355 nm light excitation of Cu^{I}(TMPA)(CO)$^+$ in CH_3CN under 1 atm of CO, Figure 2. The recovery of the bleach is well described by a first-order kinetic model with a nonzero baseline, $k_{obs} = 1.5 \pm 0.9 \times 10^6$ s^{-1}, in reasonable agreement with the time-resolved UV measurements. Some sample decomposition was observed under these conditions, presumably due to the intense IR source and/or the significant number of laser flashes required for signal averaging.

Taken together, the spectroscopic data provides compelling evidence for CO photodissociation in a copper coordination compound for the first time. The time-resolved IR and UV spectra are completely consistent with CO photodissociation. Excited state dissociation might be expected since Cu(II) complexes, like those formally generated in MLCT excited states, are not known to form stable carbonyl adducts. Previous workers have found that light excitation of copper(I) diimine compounds results in luminescent excited states or an increase in the copper coordination number.[12,16] An advantage of the photodissociative behavior reported here is that it is amenable to the “flash and trap” techniques that have been so powerful for characterizing hemes.[2,3] Here we in fact show that the kinetics for carbon monoxide coordination to the “trapped” solvento compound can be quantified. In the future, this approach will be extended to study copper reactivity with O_2, NO, and organohalides. Studies of this type are currently underway in our laboratories.

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Supporting Information Available: The synthesis of the MeO−TMPA ligand and coordination compounds and the metathesis procedure to yield the BArF salts (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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