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Photoredox Decomposition of $(PPh_3)_3Cu^I(\mu\text{-}Cl)Fe^{III}Cl_3$ Induced by Metal-to-Metal Charge Transfer Excitation

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Introduction

The electronic spectra and photochemistry of copper(I) complexes have attracted much interest in recent years.[1-3] Metal-centered ds, MLCT, LMCT, IL, and CTTS transitions[4] of Cu(I) compounds have been identified and characterized. In addition, various Cu(I)/Cu(II) mixed-valence complexes are known to display low-energy MMCT bands in their absorption spectra.[5-10] However, these MMCT transitions have not yet been shown to induce any photoreaction. Moreover, while many redox active metals partipicate in optical MMCT not only in mixed-valence[5,6] but also in heteronuclear complexes,[11,12] MMCT transitions involving Cu(I) as a donor and a different metal as an acceptor have been identified in solid state materials such as Cu_2WO_4[13] but not in simple binuclear complexes. In the case of binuclear complexes of the type $[(NH_3)_5Co^{III}\text{-}NH_2(CH_2)_nCH{=}CH_2Cu^I]^{4+}$ a photoredox reaction resulting in the formation of Co^{2+} and Cu^{2+} was observed.[14] However, this reaction is not initiated by a MMCT transition. Light absorption is associated with the population of a (Cu to olefin) MLCT state which subsequently undergoes electron transfer to Co(III).

According to these considerations the identification of a photoreactive MMCT state which involves Cu(I) as the donor should be a valuable extension of the photochemistry and spectroscopy of Cu(I) compounds. We explored this possibility and selected the complex $(PPh_3)_3Cu^I(\mu\text{-}Cl)Fe^{III}Cl_3$[15] for the present study which is also of interest for other reasons. Cytochrome c oxidase catalyzes the reduction of oxygen to water in biological systems.[16-18] This enzyme contains iron and copper which may be bridged by chloride.[19-21] In addition to the fully reduced, active state (Cu^I/Fe^{II}) and the fully oxidized, resting state (Cu^{II}/Fe^{III}) several semireduced forms involving the combination Cu^I/Fe^{III} are known. Although the ligands and the structure of cytochrome c oxidase and $(PPh_3)_3Cu^I(\mu\text{-}Cl)Fe^{III}Cl_3$ are quite different, the latter complex might serve as a simple model for the Cu^I/Fe^{III} CT interaction in the enzyme which has not yet been reported to display a copper-to-iron MMCT absorption band.

Experimental Section

Materials. The compound $(PPh_3)_3Cu^I(\mu\text{-}Cl)Fe^{III}Cl_3$ was prepared according to a published procedure.[15] CH_2Cl_2 was spectrograde.

Photolyses. The photolyses were carried out at room temperature in 1-cm spectrophotometer cells. The light source was a Hanovia Xe/Hg 977 B-1 (1kW) lamp. Monochromatic light was obtained by means of a Schoeffel GM 250-1 high-intensity monochromator. For quantum yield determinations the complex concentrations were such as to have essentially complete lightabsorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with a RkP-345 detector.

Progress of photolysis was monitored by UV–visible spectrophotometry, using a 8452 Hewlett Packard diode array spectrophotometer.

Analyses. On the basis of the spectral changes only the photoproducts could not be identified. However, a qualitative and quantitative analysis showed that the photolysis led to a photoredox decomposition with the formation of Cu(II) and Fe(II). For this analysis 5 mL of a 5×10^{-3} M solution of $(PPh_3)_3Cu^I(\mu\text{-}Cl)Fe^{III}Cl_3$ was photolyzed for 10 min under argon with $\lambda_{irr} = 546$ nm. According to the decrease of the extinction at this wavelength 9.9% ($4.9 \cdot 10^{-4}$ M) of the binuclear complex was photodecomposed. To 2.5 mL of the photolyzed solution was added 50 mL of cold pentane. A precipitate was formed, separated by filtration, dried, and dissolved in 2 mL of acetone. Upon addition of 4 mL of 0.1 M aqueous HCl, a white precipitate consisting of $(PPh_3)_3CuCl$ and PPh_3 formed. The remaining solution was yellow owing to the presence of a large excess of iron(III) chloro complexes. This solution was analyzed for Cu^{2+} and Fe^{2+} spectrophotometrically as $Cu(NH_3)_4^{2+}$ ($\lambda_{max} = 616$ nm; $\epsilon = 63$ M^{-1} cm^{-1}) and $Fe(o\text{-}phen)_3^{2+}$ ($\lambda_{max} = 510$ nm, $\epsilon = 11500$),[22] respectively. With regard to the original solution the analysis yielded concentrations of 3.06×10^{-4} M Cu^{2+} and 4.08×10^{-4} M Fe^{2+}.

Results and Discussion

The absorption spectrum of $(PPh_3)_3Cu^I(\mu\text{-}Cl)Fe^{III}Cl_3$[23] (Figure 1) in CH_2Cl_2 displays band maxima at $\lambda = 540$ ($\epsilon = 90$ M^{-1} cm^{-1}), 364 (6000), 312 (sh, 6700), and 256 nm (sh, 37000). In solvents of low polarity the binuclear complex was thermally stable[24] but light sensitive. The spectral changes which accompanied the photolysis (Figure 1) were independent of the irradiating wavelength. The long-wavelength band at $\lambda = 540$ nm which is indicative for the presence of the Cu^IClFe^{III} moiety (see below) disappeared completely upon product formation. The quantum yield for disappearance of the binuclear complex was $\phi = 0.02$ at $\lambda_{irr} = 546$ nm. According to a quantitative analysis the photodecomposition of $(PPh_3)_3Cu^I(\mu\text{-}Cl)Fe^{III}Cl_3$ led to the formation of nearly stoichiometric amounts of Cu^{2+} and

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(4) Abbreviations: MLCT (metal-to ligand charge-transfer), LMCT (ligand-to-metal charge-transfer), MMCT (metal-to-metal charge-transfer), CTTS (charge transfer-to-solvent), IL (intraligand).

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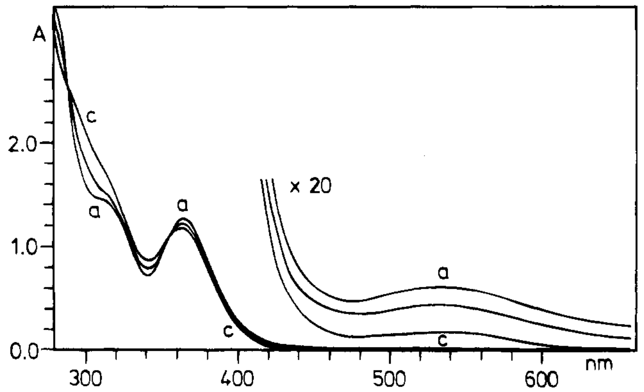

Figure 1. Spectral changes during the photolysis of 2.11×10^{-4} M $(PPh_3)_3Cu^I(\mu$-Cl)Fe^{III}Cl$_3$ in CH_2Cl_2 after 0 (a) and 4 min (c) irradiation time with $\lambda_{irr} > 340$ nm (Osram HBO 100 W/2 lamp), 1-cm cell.

Fe^{2+}. A blind test showed that the dark solution did not contain Cu^{2+} and Fe^{2+}.

The absorption spectrum of $(PPh_3)_3Cu^I(\mu$-Cl)Fe^{III}Cl$_3$ (Figure 1) contains the same strong absorption bands characteristic of its mononuclear components. $Cu(PPh_3)_3Cl$ shows intraligand absorptions[1,25,26] at $\lambda_{max} = 261$ ($\epsilon = 25\,300$) and 274 nm (sh, 22 600) while the spectrum of $FeCl_4^-$ is characterized by long-wavelength LMCT bands at $\lambda_{max} = 364$ (7350) and 317 nm (7600).[27,28] It follows that the metal–metal interaction in the binuclear complex is rather weak and the metal centers exist in well-defined oxidation states.[6,7,11,12] However, $(PPh_3)_3Cu^I(\mu$-Cl)Fe^{III}Cl$_3$ displays an additional band at $\lambda_{max} = 540$ nm (Figure 1) which is logically assigned to a MMCT transition from the reducing Cu^I to the oxidizing Fe^{3+} ion. The ability of Cu(I) to serve as a donor in CT transitions is well-known. Copper(I) polypyridyl complexes display low-energy MLCT bands in their absorption spectra.[29]

The MMCT assignment of the long-wavelength absorption of $(PPh_3)_3Cu^I(\mu$-Cl)Fe^{III}Cl$_3$ is also supported by the photochemical behavior of this complex. The MMCT excitation leads to a photoredox decomposition with the formation of Cu(II) and Fe(II). This reaction should be facilitated by the structural changes with accompany the MMCT transition. A relatively large reorganizational energy is indicated by a remarkable expansion of the Fe–Cl bonds ($\Delta = 0.11$ Å)[30] which occurs upon reduction of the $FeCl_4^-$ moiety to $FeCl_4^{2-}$. Moreover, the oxidation of Cu(I) to Cu(II) is certainly also associated with a considerable distortion in the CT state.[29] However, the relatively small quantum yield of the photoredox decomposition suggests that back electron transfer which regenerates the starting binuclear complex is still rather efficient.

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