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Geometry Changes of a Cu(I) Phenanthroline Complex on Photoexcitation in a Confining Medium by Time-Resolved X-ray Diffraction

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While crystallography is traditionally used for the detailed determination of ground-state structure, recent advances are removing this limitation.[1−4] Among the many processes of interest, photochemically initiated charge separation is of particular importance. It is well known that a change in the conformation of the photoinduced state strongly influences the kinetics of electron transfer and that this change is influenced by the matrix in which the species is embedded, as demonstrated, for example, by the work on dyad molecules in liquid crystals, in which the rate of back transfer of charge varies strongly with environment.[5] For a full understanding of the nature of photoinduced species, detailed knowledge of the molecular distortions that occur is required.

Using a stroboscopic technique,[6−8] in which the molecule is repeatedly excited, and the structural change is probed several thousand times per second immediately after excitation (5.333 kHz in the current study), we have performed a time-resolved single-crystal study of the triplet state of a Cu(I)phenanthroline derivative. [Cu(I)(dmp)(dppe)][PF$_6$] (dppe = 1,2-bis(diphenylphosphino)-ethane) crystallizes in the monoclinic space group $P2_1/c$,[9] with two independent molecules in the asymmetric unit, thus providing an opportunity to study the environment-dependence of the distortion upon excitation. The lowest triplet excited state of the complex has a lifetime τ of 85 μs at 16 K.[10]

The X-ray pulse length must be shorter than the lifetime of the excited species that is to be probed. The experiment was designed such that the 50 ns laser pulses ($\lambda = 355$ nm) each contain a number of photons ($\sim 5 \times 10^{14}$) that exceeds the number of molecules in the $\sim 70 \times 40 \times 40$ μm sample crystals. Monochromatic $\lambda = 0.49594$ Å X-rays are employed throughout. Because of crystal deterioration after several hours of laser exposure, 16 K data sets were collected on three crystals. Correlation plots of the intensity changes of reflections measured in more than one of the data sets showed satisfactory reproducibility within the experimental standard deviations. Although a temperature increase on laser-irradiation is evident from Wilson-type plots[11] of $\ln(I_{\text{on}}/I_{\text{off}})$ versus $(\sin \theta/\lambda)^2$, where I_{on} is the integrated intensity of a particular Bragg reflection after laser excitation and I_{off} is the corresponding ground state intensity, both positive and negative intensity changes were recorded, as required for a structural rearrangement. The effect of the temperature increase on the X-ray intensities is separately allowed for in the refinements of the data. From the cell dimensions and the value of the temperature scale factors (see below), the temperature increase is estimated not to exceed 50 °C in the current experiment, and less for the smaller of the sample crystals.

Simultaneous refinement on data from all three samples was performed on the fractional changes $\eta(hkl) = [I_{\text{on}}(hkl) - I_{\text{off}}(hkl)]/[I_{\text{off}}(hkl)]$ (response ratios[12]) in each of 9154 reflections for which the η values exceeded $2\sigma(\eta)$. In addition to the populations and temperature scale factors, the latter allowing for the temperature increase, excited-state geometric parameters were refined, giving excited-state populations of 0.097(2), 0.073(2), and 0.085(5) in the three experiments. For the excited-state molecules, the counterion, the dmp, and dppe ligands were treated as rigid bodies and were allowed to translate with the corresponding Cu atom and to rotate around three perpendicular axes through the Cu atom. In addition, translations of each of the ligands along their two-fold axes passing through the copper atoms were refined, thus providing additional flexibility of the complex. Exploratory relaxation of the rigid body constraints imposed on the ligands did not lead to significant changes in the observed geometry. To allow for possible variation in ground-state orientation upon partial excitation of the crystal, ground-state molecules were allowed to rotate and translate as rigid bodies, resulting in very small motions of ~0.2° and ~0.01 Å, respectively.

The shift of the atoms for one of the two independent molecules in the crystal is illustrated in Figure 1a. Pronounced shifts on excitation are observed for the Cu atoms, which move in the unit cell by 0.27(1) and 0.25(1) Å in the two independent molecules, respectively.

To describe the conformational changes that occur on excitation, the molecular distortions must be expressed in a molecule-based coordinate system. The intramolecular distortion angles θ_x, θ_y, and θ_z as defined by Dobson et al. in their comparative studies of Cu diimines,[13] which are 90° in the idealized D_{2d} symmetry of the complexes, are illustrated in Figure 1b, together with the changes observed for one of the two independent molecules.

Numerical results are presented in Table 1. In both independent molecules in the crystal, the rocking distortion $(90 - \theta_x)$ decreases to values of 0.4(5)°, not significantly different from zero, in agreement with a decrease from 2.7° to 0.6° calculated with DFT (density functional theory) methods for isolated [Cu(I)(dmp)-(dmpe)]$^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane) ion, which is used as the reference complex. The wagging distortion, defined by $(90 - \theta_y)$, similarly reduces to very small values in molecule 1 (0.4(5)°) and in the isolated reference molecule, but essentially remains constant at the nonzero value of ~5° in molecule 2.

The flattening upon excitation, that is, the deviation of θ_z from 90°, which is more than 30° in the isolated homoleptic [Cu(I)-(dmp)$_2$]$^+$ complex,[14] is observed for molecule 1 at the modest value of 3.2(5)°, as compared to 8° calculated for the isolated [Cu(I)-(dmp)(dmpe)]$^+$ ion. Notably, no further flattening is observed for molecule 2, which in the ground state already shows a flattening distortion of 2.8(1)°, indicating a significant constraint of the molecular conformation even in the ground state. The lack of further

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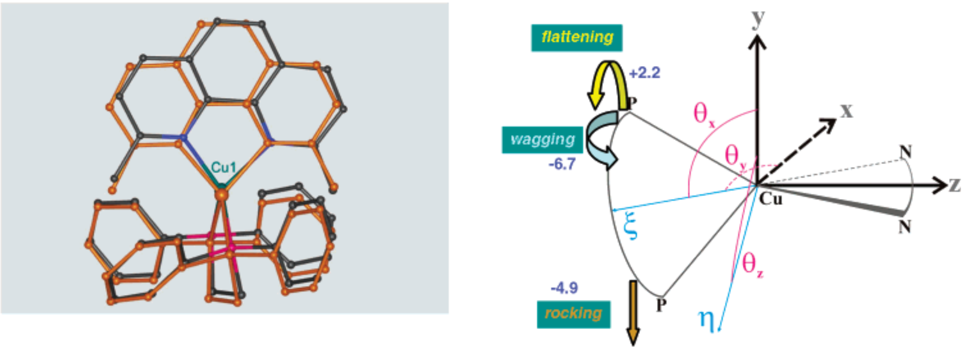

a)

b)

Figure 1. (a) Atomic motion on photoinduced electron transfer: excited-state geometry (orange) of one of the two cations of [Cu(I)(dmp)(dppe)][PF$_6$] superimposed on its ground-state geometry (Cu, green; C, black; P, purple; N, blue). (b) The increase in flattening and decrease in the wagging and rocking distortions of the complex on excitation in the crystal.

Table 1. Distortion Angles of the [Cu(I)(dmp)(dppe)]$^+$ Complex in the Ground and Excited States

	ground state	excited state	change in distortion
	Molecule 1		
θ_x (rocking)	94.5(1)	89.6(5)	−4.9
θ_y (wagging)	95.3(1)	88.6(5)	−6.7
θ_z (flattening)	90.5(1)	93.7(5)	+2.2
	Molecule 2		
θ_x	95.6(1)	90.4(5)	−4.2
θ_y	84.1(1)	85.1(5)	−1.0
θ_z	92.8(1)	92.7(5)	−0.1
	Theory, [Cu(I)(dmp)(dmpe)]$^+$		
θ_x	92.2	89.4	−2.8
θ_y	88.3	90.1	−1.8
θ_z	93.8	101.8	+8.0

flattening of molecule 2, and the modest flattening on excitation of molecule 1 in the crystal as compared to the calculated isolated-molecule value, attest to the constraining influence of the crystalline matrix upon photoexcitation. The observed large displacements of the central Cu atoms make it possible to accommodate a change in the molecular geometry within the constraints imposed by the crystal cavity in which the molecule is located.

The drastic decrease in the geometry change on excitation implies a much diminished reorganization energy (λ) for the complex in the crystalline phase. In this case, the back transfer likely takes place in the inverted region of the Marcus theory ($\lambda < |\Delta G|$) in which the rate constant for back transfer decreases with decreasing λ. We note that a large decrease in reorganization energy on immobilization is also apparent from resonance Raman analysis of the photosensitizer dye *cis*-bis(4,4′-dicarboxy-2,2′-bipyridine)-bis-(thiocyanato)ruthenium(II) absorbed on a TiO$_2$ surface.[15]

The current results are not sufficiently accurate to allow a reliable quantitative estimate of the reorganization energy, mainly because the ligands were by necessity treated as rigid bodies. Nevertheless, they represent the first example of a time-resolved diffraction study of the excited state of a metalloorganic complex in which information on both the metal atom and the ligand geometry has been obtained. We anticipate that with further development of the experimental facilities such quantitative information will become increasingly accessible.

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