

## X-ray Absorption Structural Study of a Reversible, Photoexcited Charge-Transfer State

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Electron-transfer reactions can be accompanied by significant nuclear movements.<sup>4</sup> Nuclear motion appears to be especially vital to the reversible, photoinduced charge-transfer chemistry of cyclopentadienylnickel nitrosyl ( $C_5H_5NiNO$ ). Although extended X-ray absorption fine structure (EXAFS)<sup>5,6</sup> spectroscopy has recorded photoinduced changes in the ligation of myoglobins,<sup>7,8</sup> similar X-ray studies of electron-transfer chemistry have not been reported. Here we examine reversible, photoinduced structural changes in  $C_5H_5NiNO$  by EXAFS and propose a mechanism for the electron-transfer chemistry.

Both microwave spectroscopy in the gas phase<sup>9</sup> and EXAFS spectroscopy in hexane solutions<sup>10</sup> indicate a linear configuration of  $-Ni-N-O$  in ground-state  $C_5H_5NiNO^{GS}$ . FTIR studies on photoirradiated  $C_5H_5NiNO$  in an argon matrix find a  $N-O$  stretching frequency characteristic of  $NO^-$ , suggestive of the charge-separated state  $C_5H_5Ni^{2+}NO^-$ .<sup>11</sup> For the  $C_5H_5Ni^{2+}NO^-$ , a bent  $-Ni-N-O$  is expected because the electrons from Ni are moved to antibonding orbitals in  $NO$ , destabilizing the linear  $-Ni-N-O$  ground-state structure.<sup>12</sup>

An EXAFS spectrum results from the wavelength dependence of the interference between the outgoing photoelectron wave from the central atom and the backscattered photoelectron wave from the surrounding atoms. Because of the "forward focusing" effect in linear  $-Ni-N-O$ , the backscattering amplitude from O will be substantially enhanced compared to that in a bent  $-Ni-N-O$ .<sup>13</sup> As the bending angle increases, this enhancement diminishes rapidly. Thus, the backscattering amplitude of oxygen in the bent photoexcited  $C_5H_5NiNO$  should be much smaller than that of the linear ground state.

EXAFS spectra of  $C_5H_5NiNO$  before and after irradiation with 365-nm light are shown in Figure 1a and b, respectively. The Fourier transform of the EXAFS spectra of Figure 1 (see Figure 2) unambiguously indicates that the amplitude of the oxygen peak is substantially reduced for 365-nm photoirradiated  $C_5H_5NiNO$  compared to its pure ground state as required for a bent configuration of  $-Ni-N-O$  in a charge-transfer state. The EXAFS spectrum almost identical to that of pure ground state reappears (Figure 1c) after a 30-min irradiation by an unfiltered mercury lamp, indicative of the reversibility of the

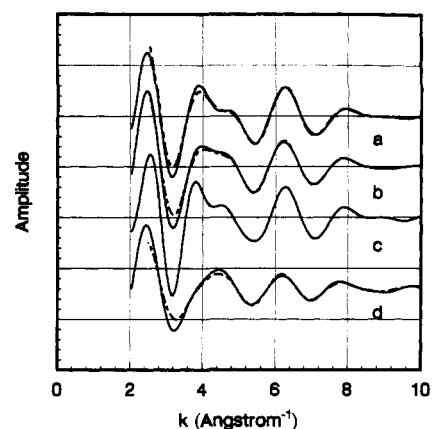


Figure 1. EXAFS spectra of  $C_5H_5NiNO$  in 3-methylpentane solution at 20 K. (—) = experimental; (---) = calculated. (a)  $C_5H_5NiNO^{GS}$ . (b) The photoirradiated mixture (365-nm light irradiation) and the reconstructed spectrum for a mixture of 57%  $C_5H_5NiNO^{GS}$  and 43%  $C_5H_5NiNO^{CT}$ . (c) After 30 min "white light" irradiation by an unfiltered mercury lamp. The resemblance of the spectrum with spectrum a indicates the reversibility of the reaction. (d)  $C_5H_5NiNO^{CT}$ . Solid curve obtained by subtracting 57% of ground-state spectrum a from that of the photoirradiated mixture, b.

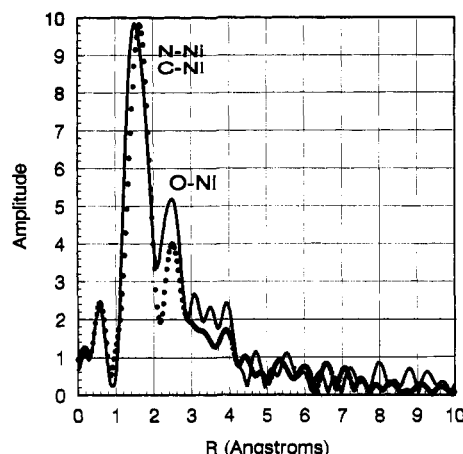


Figure 2. Fourier transform of EXAFS spectra for Figure 1a (—) and b (•).

reaction. By irradiating with light of the proper wavelength, the sample can be repeatedly cycled between ground and charge-transfer states without any noticeable changes in the spectra of Figure 1a or b. The combined evidence suggests that during irradiation with 365-nm light  $NO$  movement converts some of the photoexcited state,  $C_5H_5NiNO^*$ , into the charge-transfer state,  $C_5H_5NiNO^{CT}$ , resulting in a mixture of  $C_5H_5NiNO^{GS}$  and  $C_5H_5NiNO^{CT}$ . On the other hand, with irradiation by unfiltered light the  $NO$  motion essentially transforms almost all of the photoirradiated  $C_5H_5NiNO^{CT}$  back to ground-state  $C_5H_5NiNO^{GS}$ . With warming to 90 K the mixture of  $C_5H_5NiNO^{GS}$  and  $C_5H_5NiNO^{CT}$  returns to pure  $C_5H_5NiNO^{GS}$ . The  $-Ni-N-$ ,  $-C-Ni-$ , and  $-Ni-O$  distances in  $C_5H_5NiNO^{GS}$  at 20 K are  $1.65 \pm 0.03$ ,  $2.15 \pm 0.02$ , and  $2.78 \pm 0.04$  Å, respectively.

The EXAFS spectrum of the photoirradiated mixture of  $C_5H_5NiNO^{GS}$  and  $C_5H_5NiNO^{CT}$  is shown in Figure 1b. The EXAFS spectrum of pure  $C_5H_5NiNO^{CT}$  is obtained by subtracting various fractions of the ground-state EXAFS spectrum (Figure 1a) from the mixed spectrum (Figure 1b). The resulting difference spectra are analyzed using conventional EXAFS functions.<sup>14</sup> A reconstructed EXAFS spectrum (Figure 1b, dashed line), based on

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57% ground state (Figure 1a) and 43% charge-transfer state (Figure 1d), agrees best with the observed spectrum of the mixture (Figure 1b). Thus, Figure 1d provides a reasonable approximation of the EXAFS spectrum for the pure  $C_5H_5NiNO^{CT}$ .

The  $Ni-N$  and  $C-Ni$  distances in the  $C_5H_5NiNO^{CT}$  are determined to be  $1.77 \pm 0.03$  and  $2.15 \pm 0.02$  Å, respectively. The 0.12-Å increase of the  $Ni-N$  distance in the  $C_5H_5NiNO^{CT}$  compared to that in the ground state is consistent with the  $Ni-N$  bond order decrease resulting from electron transfer from Ni to NO. The unchanged  $C-Ni$  distance upon photoexcitation implies that the molecular orbitals contributing mostly to the bonding between Ni and  $C_5H_5$  are not significantly involved in the photoinduced electron transfer.

Lacking a nickel reference compound, the  $Ni-O$  distances determined for  $C_5H_5NiNO^{CT}$  and  $C_5H_5NiNO^{GS}$  rely on the reference phases from  $Co-O$  in  $Co_4(CO)_{12}$ . Also, the enhanced noise level created by the subtraction process that provides the difference spectrum of Figure 1d may contribute additional error to the  $Ni-O$  distance determination. Thus, the approximated  $Ni-O$  distance for the charge-transfer state,  $2.82 \pm 0.04$  Å, likely has uncertainty additional to that indicated by the standard deviation. Assuming limits of 1.13 (from  $C_5H_5NiNO^{CT}$ ) and

1.208 Å (from isoelectronic  $O_2$ ) for the bond length of  $N-O$ , the bond angle of  $Ni-N-O^{CT}$  lies between 142 and 152°.

This work demonstrates that EXAFS can measure distance changes accompanying photoinduced electron transfer to provide new details of the geometry of photoexcited states and suggests that electron transfer occurs in the transient, optically excited states of  $C_5H_5NiNO$  and  $C_5H_5NiNO^{CT}$  as dictated by the NO movement that produces either  $C_5H_5NiNO^{CT}$  or  $C_5H_5NiNO^{GS}$ . Time domain EXAFS experiments at higher temperatures where the lifetime of  $C_5H_5NiNO^{CT}$  is decreased should provide new information on the potential of EXAFS in probing the structure of transient molecules.

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