Single-Crystal X-ray Analysis of an Electronic Excited State: The Structure Determination of a Metastable State of Sodium Nitroprusside

Mark R. Pressprich,* Mark A. White, and Philip Coppens*

Chemistry Department
State University of New York at Buffalo
Buffalo, New York 14214-3094

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While X-ray diffraction has provided a very large body of information on ground-state geometries, it has not been used until now for the determination of the geometry of excited states. In this communication we describe the structural analysis of an extremely long-lived electronic excited state of the nitroprusside ion, $[Fe(CN)_5(NO)]^{2-}$, in single-crystal sodium nitroprusside dihydrate (SNP) by X-ray diffraction at 138 K. The analysis shows a 0.060(9) Å lengthening of the Fe–N bond, a relaxation of the *cis* C–Fe–N angles by an average of –0.9°, and an increase in the *trans* C–Fe–C angles by 1.9(3)°.

A metastable electronic state of SNP, produced by long term laser illumination of single crystals with 350 nm $< \lambda <$ 560 nm, was originally identified by Mössbauer spectroscopy.[1] A metastable population of 37% excited molecules is obtained with $\lambda =$ 488 nm at 100 K. Subsequent Raman and optical spectroscopic studies verified the presence of significantly distorted, metastable nitroprusside ions coexisting with the ground-state species.[2] Large shifts were observed in the ν(NO) and ν(FeN) stretching and the δ (FeNO) bending frequencies indicating charge transfer from the d_{xy} HOMO to the π^* NO LUMO.[3]

In previous work, EXAFS and single-crystal neutron studies were undertaken to determine the distortion. No significant distortion was observed in the EXAFS study,[4] but the neutron results show a significant elongation of the Fe–N bond. The authors recognized that the Fe–N bond increase of 0.019(2) Å was certainly underestimated due to limitations in their structural model, in which only the average of the ground- and excited-state geometries was refined.[5] A complete description of a perturbed crystal must account for the coexistence of ground- and excited-state molecules in the same crystal.

We have followed the protocol for the excitation wavelength and polarization developed in the neutron study. For the purpose of obtaining excited-state structural information a crystal of sodium nitroprusside was cut with a thread saw and ground to 88-μm thickness in the *a* axis direction. The crystal was cooled to 138 K and illuminated by an Ar^+ laser with $\lambda =$ 488 nm, propagation direction $k//a$, and polarization direction $E//c$. The excitation was monitored by periodic X-ray intensity measurements of two reflections, (2 1 2) and (2 3 2), which increase and decrease by 10%, respectively, after laser saturation. These two reflections also served as monitor reflections during subsequent X-ray data collection and showed gradual deexcitation, apparently caused by X-ray exposure. Assuming first-order kinetics, the net fraction of excited molecules decaying to the ground state is $\alpha = 1 - e^{-t/\tau}$. Results shown in Figure 1 correspond to a lifetime, τ, of 73(6) h. This compares with a lifetime of 1.6 – 20 × 10^5 h at 138 K for purely thermal decay with parameters determined from a recent calorimetric study.[6]

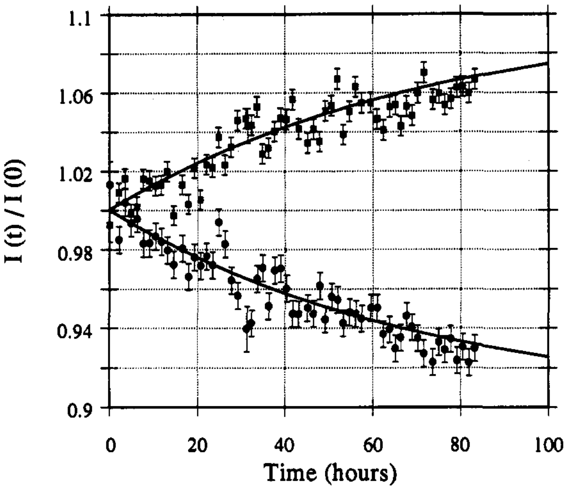

Figure 1. Intensity variation of the (■) (2 3 2) and (●) (2 1 2) reflections, showing the decay of the excited state. The solid lines are a least-squares fit to $I(t)/I_0 = (1 + \delta I) - \delta I \exp(-t/\tau)$. With $\delta I = \pm 10\%$ for (2 3 2) and (2 1 2), respectively, $\tau =$ 73(6) h.

The calorimetric study also shows the presence of two metastable levels. Therefore, following the laser illumination and prior to X-ray data collection the crystal was warmed to 165 K for 5 min to eliminate the fastest decaying excited state, which lies 1 eV above the ground state.[6] The saturated population of the remaining level at 138 K, p_0^{excited}, was derived from Mössbauer[1] and calorimetric data.[6,7] The elimination of the fastest decaying excited state decreases the net excited population fraction by less than 0.01, based on the ratio of saturated enthalpies (λ = 488 nm) corresponding to the two states. The saturated enthalpy of the remaining state is temperature dependent above 120 K.[6,7] With λ = 457.9 nm $H_\infty(138\ \text{K})/H_\infty(100\ \text{K}) = 0.76$ and with λ = 530.9 nm the ratio is 0.89. Linear interpolation between these values gives $p_0^{\text{excited}} = 0.30(2)$ for λ = 488 nm.

The ground-state structure of the nitroprusside ion at the same temperature was determined from a separate data collection.[8]

The spherical atom refinement of the perturbed crystal was based on a model designed to account for the coexistence of ground and excited molecules. The ground-state nitroprusside structure determined from the unperturbed crystal was incorporated into the perturbed crystal refinement as a rigid body with refinable rotational and translational displacement parameters and fixed anisotropic thermal parameters. The atomic coordinates of the excited-state nitroprusside ion, the sodium ions, and the water oxygen were also refined but with thermal parameters fixed to those values determined from the ground-state study.[9] The population of the excited nitroprusside ions was described by $p = p_0^{\text{excited}} e^{-t/\tau}$, where t is the net X-ray exposure time. Least-squares refinement of the parameters in this model were carried out with a computer program, LASER,[10] which accounts for the time dependent populations using time-labeled X-ray diffraction

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(8) Details on the data collections are given in the supplementary material.

(9) The nitroprusside ion lies on an *xy* mirror plane, so a test refinement was made in which the U_{33} parameters of the atoms in the mirror plane were varied to see if the excited nitroprusside ion breaks the imposed C_s symmetry. The changes in the parameters were small and/or not statistically significant. Introduction of an additional group anisotropic thermal parameter for the ground nitroprrusside/excited nitroprusside ion to account for the slightly different environments between the ground- and excited-state crystals had no significant effect on the positional parameters.

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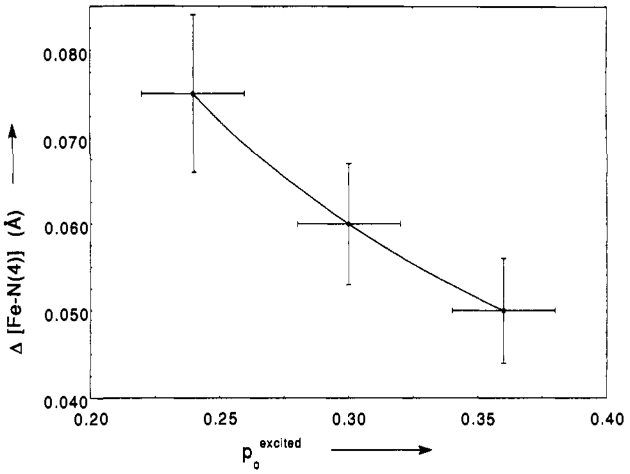

Figure 2. Dependence of the refined Fe–N(4) bond length distortion on the starting fractional excited-state population.

Table I. Bond Lengths and Angles of the Nitroprusside Ion[a]

distance	ground	excited
Fe–N4	1.662(2)	1.722(9)
Fe–C1	1.924(2)	1.914(9)
Fe–C2	1.931(1)	1.937(6)
Fe–C3	1.939(1)	1.933(6)
N4–O1	1.125(2)	1.145(11)
C1–N1	1.152(3)	1.154(12)
C2–N2	1.151(2)	1.141(8)
C3–N3	1.154(2)	1.161(9)

angle	ground	excited
N4–Fe–C1	176.79(8)	177.2(4)
C2–Fe–C3	168.97(5)	170.8(3)
C2–Fe–C2a[b]	90.23(5)	89.8(3)
C2–Fe–N4	93.44(5)	92.6(3)
C2–Fe–C3a[b]	88.21(5)	89.0(2)
C3–Fe–C3a[b]	91.24(5)	90.7(3)
C3–Fe–N4	97.55(5)	96.6(3)
C1–Fe–C2	84.30(5)	85.5(3)
C1–Fe–C3	84.68(5)	85.4(3)
Fe–C1–N1	179.76(17)	179.6(7)
Fe–C2–N2	178.55(11)	177.2(6)
Fe–C3–N3	176.58(11)	176.6(6)
Fe–N4–O1	176.06(5)	174.3(7)

[a] Distances are in Å; angles are in deg. [b] C2a and C3a are related to C2 and C3 by an *xy* mirror plane.

data. A small change in $p_0^{excited}$ in the refinement leads to proportionate changes in the nitroprusside distortion, i.e., for any bond length or angle distortion $\Delta_i' \approx \Delta_i(p_0{}^{exc}/p_0^{exc'})$. This is shown explicitly in Figure 2 for the distortion of the Fe–N(4) bond length.

Bond lengths and angles for both states are listed in Table I. The esds for the excited-state parameters include the uncertainty in $p_0^{excited}$; i.e., for a parameter x_i with least-squares determined $\sigma^2(x_i)$, the corrected $\sigma^2{}_{corr}(x_i) = \sigma^2(x_i) + 2\sigma^2(p_0^{excited})(\Delta_i/p_0^{excited})^2$. The distortion of the excited nitroprusside ion from its ground-state geometry is best described with reference to Figure 3, in which the ground-state and the excited-state ion with displacements exaggerated by a factor of ten are shown superimposed. The primary effect of the excitation is the elongation of the Fe–N4 bond by 0.060(9) Å. This elongation agrees qualitatively with the decrease in ν(FeN) from 663 to 566 cm^{-1} as determined by Raman spectroscopy[2] and can be compared with that predicted by Badger's rule[11] from which an elongation of 0.082 Å is expected.[5] The reported decrease in ν(NO) from 1950 to 1832 cm^{-1} yields an expected increase in the N–O length of 0.025 Å, which can be compared with the directly determined (but not statistically significant) increase of 0.020(11) Å. Besides these bond length changes, bond angle distortions occur leading to a smaller deviation from D_{4h} symmetry in the excited state. The *cis* N4–Fe–C2 and N4–Fe–C3 bond angles decrease by –0.9(3)° and –1.0(3)°, respectively, and the *trans* C2–Fe–C3 angle increases by 1.9(3)°.

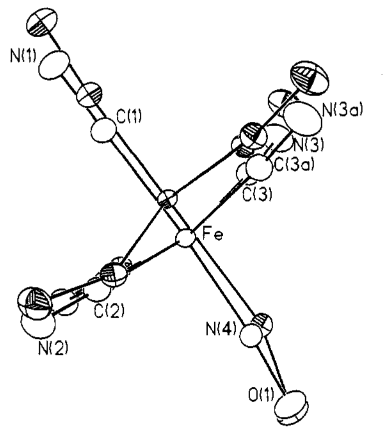

Figure 3. Thermal ellipsoid plot at 50% probability of the nitroprusside ion: exaggerated excited-state ion (shaded ellipsoids) superimposed on the ground-state ion (open ellipsoids). The *c*-axis is along the line of view. The *x* direction is down; *y* is to the right.

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Supplementary Material Available: Details on data collection and refinement and a listing of positional and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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