Structure of the light-induced metastable state SII in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$

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The structure of the light-induced metastable state SII of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ was investigated by single-crystal neutron diffraction. The population of SII of 16(3)% was determined by an *in situ* transmission measurement. The final structural refinement yields a *side-on* bonded configuration of NO in the metastable state SII with distances Fe—O, Fe—N, and N—O of 2.01(5) Å, 1.96(5) Å, and 1.11(8) Å, respectively. The angle Fe—N—O is 77(4)°. The population determined from the refinement is 12(2)%, in good agreement with the value of 16(3)% determined from the independent *in situ* transmission measurement.

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I. INTRODUCTION

Light-induced metastable states in nitrosyl compounds are of special interest in the field of photobiology and photonics. It is well known that nitric oxide (NO) plays an important role in biological, biomedical, and medical scientific research and applications. It covers a wide range of important biological functions, such as neurotransmission, penile erection, enzyme, immune, and blood pressure regulation, and even inhibition of tumor growth.^{1–6} Using light irradiation long-lived metastable states can be generated in nitrosyl compounds containing the molecules $[\text{ML}_5\text{NO}]$, where M = Fe, Ru, Os, etc., and L are various ligands, e.g., L = F, Cl, Br, J, CN, NH_3 , OH, etc., including hemoproteins and metalloporphyrins. The bonding energy of the NO ligand is significantly reduced in the metastable states^{7,8} and therefore the NO may be released from the molecule $[\text{ML}_5\text{NO}]$ by an additional small energy supply, in order to fulfill its specific biological function, e.g., for physiological processes or in photodynamic therapy.⁹ Moreover, this photosensitive behavior is highly relevant in the field of photonics, e.g., for the development of optical devices for the telecommunication or future optical data storage systems, such as holographic data storage.^{10,11} In order to efficiently develop and advance these potential applications it is necessary to know the physical nature of the light-induced metastable states. Therefore we investigated the structural properties of the metastable state SII in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ (SNP).

$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ serves as a prototype for all these $[\text{ML}_5\text{NO}]$ -containing compounds. Here the two long-lived metastable states SI and SII can be generated by irradiation with light in the blue-green spectral range below temperatures of about 198 and 147 K, respectively. The long lifetime at sufficiently low temperature allows one to investigate the light-induced structural changes in this compound by neutron or x-ray diffraction. Although the structure of the ground state (GS) is known for a long time,^{12–14} early struc-

tural investigations of the light-induced species, a field in the meantime called photocrystallography,^{15,16} were performed by Rüdinger *et al.*^{17,18} using neutron diffraction. These authors found small increases in the Fe—N and N—O bond lengths in the metastable states SI and SII with respect to the ground state. Later Pressprich and co-workers¹⁹ performed x-ray-diffraction experiments on SI, finding as well an elongation of the Fe—N bond. The following neutron-diffraction study of SII by Schefer *et al.*²⁰ again resulted in rather small changes of bond lengths and angles. The findings of all these studies, however, could not satisfactorily explain the long lifetimes of the metastable states, as already pointed out by Güdel.²¹ A major step toward the understanding of the long lifetime of the metastable states was done in 1997, when Carducci *et al.*²² performed x-ray-diffraction experiments on both metastable states. The astonishing result was that the metastable state SII could be interpreted as a *side-on* (η^2) configuration of the NO ligand, while in the metastable state SI the NO ligand even inverted by 180° to an O-bound configuration Fe—ON (*isonitrosyl*). These large geometrical changes in the Fe—NO bond were supported by calculations based on density functional theory,²³ which found energetic minima for the two configurations, yielding the Fe—N—O angle as the reaction coordinate. A subsequent reinvestigation of the neutron-diffraction results could not confirm this interpretation.²⁴ One major problem during these photocrystallographic experiments was the determination of the population of the metastable states achieved by the *in situ* illumination. Either it was deduced from the illumination time and changes in lattice parameters or it was introduced as a free parameter in the refinement of the data. In order to overcome this uncertainty Schaniel *et al.*²⁵ introduced the *in situ* measurement of the transmitted light intensity, which allows for an independent determination of the population of SI.²⁵ However the associated neutron-diffraction study could not confirm the proposal of the NO inversion for the metastable state SI. In an attempt to finally clarify the issue of the nature of the metastable states we performed neutron-diffraction ex-

FIG. 1. (Color online) Structure factor F_{107} as a function of the population of SI (P_{SI}) of an SNP crystal ($d=1.0$ mm). The polarization of the light was along the c axis of the crystal. A wavelength of 476.5 nm of an Ar^+ laser with an average power of 50 mW/cm² was used. The total exposure was about 15 000 J/cm². The structure factors F_{107} obtained in the two experiments on TriCS and TOPSI²⁵ are indicated for comparison.

periments on the metastable state SII, as we expect larger changes from the side-on configuration than from the isonitrosyl configuration. During the experiment the population was monitored by the *in situ* transmission measurement, using the photocrystallographic setup, described in detail in Refs. 16 and 25.

II. EXPERIMENTAL DETAILS

The neutron-diffraction experiments were performed on the single-crystal diffractometer TriCS²⁶ at the Swiss Spallation Source SINQ²⁷ at PSI/Villigen using a single detector. The temperature was kept constant at 37(1) K during data collection. The photocrystallographic setup allows for the *in situ* measurement of the transmitted light intensity and, therefore, for the determination of the population of SI during the illumination with the 476.5 nm line of an Ar^+ laser. The total exposure was about 15 000 J/cm² using an average power of 50 mW/cm². Thereby the photovoltage U increased from 0.11(2) mV to 2.19(2) mV, yielding a population of $P_{SI}=29(3)\%$, using

$$P_{SI} = \frac{\alpha_{GS} - \alpha_{GS+SI}}{\alpha_{GS}} = \frac{1}{\alpha_{GS}d} \ln\left(\frac{U_{GS+SI}}{U_{GS}}\right), \quad (1)$$

where α_{GS} and α_{GS+SI} are the absorption coefficients of the ground state and the mixed state GS+SI, respectively (for $\lambda=476.5$ nm $\alpha_{GS}=103$ cm⁻¹),²⁸ d is the thickness of the crystal, and U_{GS} and U_{GS+SI} are the measured photovoltages in the states GS and GS+SI, respectively. As shown in Ref. 25 the structure factor F_{107} of the reflection (h,k,l) = (1,0,7) can be used as a measure of the population as well [see Fig. 1], yielding 30(3)% population of SI in our experiment, using a deuterated single crystal of thickness 1.0 mm. After the generation of SI the sample was illuminated with the unpolarized beam of a Nd-YAG laser (1064 nm) in order to perform the transfer SI $\rightarrow$ SII. This transfer was also moni-

FIG. 2. (a) Photovoltage U measured during illumination with 1064 nm (unpolarized). The transmitted light intensity increases as the population of SI decreases during the transfer SI $\rightarrow$ SII. (b) Transfer SI $\rightarrow$ SII measured by Differential Scanning Calorimetry. The maximal population of SII is obtained after 100 J/cm².

tored by a transmission measurement, as illustrated in Fig. 2(a). The transmission increases as the metastable state SI is transferred into SII. After 300 J/cm² the state SI is completely depleted, and we obtain about 16(3)% SII and 84(3)% GS. This transfer behavior SI $\rightarrow$ SII is known from differential scanning calorimetry (DSC) measurements, as illustrated in Fig. 2(b) for illumination with unpolarized light of a Nd-YAG laser (1064 nm). The metastable state SI decreases exponentially as a function of the exposure Q according to $H_{tot}(\text{SI}) = H_{SI}[\exp(-Q/Q_{SI})] + H_r(\text{SI})$ with $Q_{SI} = 30(2)$ J/cm², $H_r(\text{SI}) = 1.4(6)$ kJ/mol, and $H_{SI} = 45(1)$ kJ/mol, whereas SII increases and subsequently decreases according to $H_{tot} = H_{SII}[1 - \exp(-Q/Q_{SII,inc})]\exp(-Q/Q_{SII,dec})$ with $Q_{SII,inc} = 32(4)$ J/cm², $Q_{SII,dec} = 9(2) \times 10^2$ J/cm², and $H_{SII} = 40(3)$ kJ/mol (1 kJ/mol corresponds to 0.965% population).

As can be seen, the optical transfer SI $\rightarrow$ SII with 1064 nm is much faster than the population of SI with 476.5 nm. After about 100 J/cm² the maximal population of SII is achieved, which afterward decreases slowly with increasing exposure Q . At 300 J/cm² about 55% of the original SI population (50% in this case) is transferred into SII, the rest has relaxed to the ground state except for a small fraction $H_r(\text{SI}) = 1.4(6)$ kJ/mol, which remains in SI. Therefore for our neutron diffraction experiment we obtain a popu-

TABLE I. Experimental data collection and refinement parameters for SNP.

	GS	GS+SII
Space group	<i>Pnnm</i>	<i>Pnnm</i>
Z	4	4
Wavelength λ (Å)	1.1757(13)	1.1757(13)
<i>T</i> (K)	37	37
<i>a</i> (Å)	6.0802(7)	6.0878(4)
<i>b</i> (Å)	11.7985(14)	11.781(1)
<i>c</i> (Å)	15.4750(18)	15.436(1)
<i>V</i> (Å ³)	1110.1(2)	1107(4)
<i>d</i> (g/cm ³)	1.7821(4)	1.787(6)
$[\sin(\theta)/\lambda]_{\max}$ (Å ⁻¹)	0.488	0.627
Abs. coeff. (mm ⁻¹)	0.004	0.004
<i>T</i> _{min} (min. transm.)	0.9705	0.9694
<i>T</i> _{max} (max. trans.)	0.9934	0.9949
Crystal size (mm ³)	10 × 1 ^a	10 × 1 ^a
<i>h</i> _{max}	5	7
<i>k</i> _{max}	10	14
<i>l</i> _{max}	14	19
Meas. rflcns	743	1944
Unique rflcns	474	1146
Refined rflcns	655	1730
Obs. rflcns (<i>I</i> > 3 σ)	596	1623
<i>g</i> _{iso} (10 ⁻⁴) ^b	0.002735	0.001891
Pop. of SII <i>P</i> _{SI} (%)	0	12(2)
No. of variables	51	60
<i>R</i> _w (<i> F </i>)	0.0863	0.1070
<i>R</i> (<i> F </i>)	0.0876	0.0853
GOF <i>S</i>	5.66	7.52

^aCircular sample of 10 mm diam.^bIsotropic extinction correction of type I (Lorentzian distribution) is used (Ref. 30).

lation of SII of about 16(3)%, assuming that 55% of the measured SI population [30(3)%] has been transferred into SII. The small rest population $H_r(\text{SI}) = 1.4(6)$ kJ/mol in the state SI will be neglected for the analysis of the data.

III. RESULTS

A. Ground state

The structural analysis was performed using the program JANA2000.²⁹ The refinement of the ground state GS is straightforward and yields agreement factors of $R = 0.086$ and $S = 5.66$, using isotropic displacement parameters U_{iso} and an extinction correction of type I (Lorentzian distribution).³⁰ The results are in agreement with earlier refinements of the GS structure based on neutron¹⁸ and x-ray²² measurements. The details of the data collection are presented in Table I.

B. Mixed state GS+SII

First, we performed a refinement, using the parameters of the GS as starting values. The refinement converged at R

FIG. 3. (Color online) Fourier difference map after refinement of S2 data with ground-state configuration. Top: Shows the plane defined by the atoms O1 and N4 and the direction (0 0 1). Bottom: Shows the plane perpendicular to the plane in the upper picture, at the position indicated by the line. Contours are 0.2 barn Å⁻³.

$= 0.1106$. The subsequent inspection of Fourier difference maps revealed two significant features near the NO (N4 and O1) position of the GS, as illustrated in Fig. 3 for the plane containing the NO (upper picture) and a plane perpendicular to it (lower picture) containing the residual maxima. The maxima in the difference map with densities of 2.3 barn Å⁻³ and 2.2 barn Å⁻³ are found at the positions (0.80, 0.34, 0.46) and (0.72, 0.42, 0.5), respectively. These positions may be compared to those found by Carducci *et al.*,²² where a residual peak of 0.6 e Å⁻³ after rigid-body refinement lead to the finding of the N4 atom at the position (0.794, 0.342,

FIG. 4. (Color online) Fourier difference map for GS. Planes and contours as in Fig. 3.

0.5313) and O1 at (0.755, 0.406, 0.479) for the metastable state SII. We note that maxima of slightly smaller size occur also near the Fe and CN positions. However, features of this size are also present in the final difference maps of the refined ground state (see Fig. 4) and can therefore be excluded as originating from the light irradiation. Note that the Fourier difference map of the final refinement for the GS (Fig. 4) is flat, i.e., it does not exhibit distinguished minima or maxima as found in the residual map obtained from the GS+SII measurement [Fig. 3].

In a second step we introduced two additional atoms N4' and O1' at positions (0.80, 0.34, 0.46) and (0.72, 0.40, 0.50), respectively. Refinement of all parameters, including the occupation o of N4' and O1', converged at $R=0.1073$. The refined occupation of N4' and O1' is 0.14(2), whereby the constraints $o[\text{N4}] + o[\text{N4}'] = 1$ and $o[\text{O1}'] = o[\text{N4}']$ were used. The positions of N4' and O1' are [0.7707(6),

0.3550(3), 0.4657(1)] and [0.7234(8), 0.4059(4), 0.5], respectively. The refined isotropic displacement for these two atoms are rather large: $U_{\text{iso}}(\text{N4}') = 0.042(14) \text{ \AA}^2$ and $U_{\text{iso}}(\text{O1}') = 0.063(21) \text{ \AA}^2$. Since also the N4'—O1' distance of 0.85(9) Å is too short, in the third and last step, we moved the oxygen atom O1' out of the mirror plane, obtaining a stable refinement with $R=0.1070$. The positions of N4' and O1' are then [0.782(2), 0.348(4), 0.466(4)] and [0.730(8), 0.401(5), 0.478(3)], respectively. The occupation for these two atoms is 0.12(2), and their isotropic displacement parameters read $U_{\text{iso}}(\text{N4}') = 0.030(14) \text{ \AA}^2$ and $U_{\text{iso}}(\text{O1}') = 0.003(15) \text{ \AA}^2$. All parameters of the final refinement are given in Table II. The N4'—O1' distance is 1.11(8) Å for this configuration. Angles and distances are given in Table III.

IV. DISCUSSION

The structural changes induced by the generation of the metastable state SII in SNP can be explained by a side-on configuration of the NO ligand with distances $d(\text{Fe—N4}') = 1.96(5) \text{ \AA}$, $d(\text{Fe—O1}') = 2.01(5) \text{ \AA}$, and $d(\text{N4'—O1}') = 1.11(8) \text{ \AA}$ and an angle $\angle(\text{Fe—N4'—O1}')$ of $77(4)^\circ$. These findings are in agreement within experimental errors with those from the x-ray study,²² where distances $d(\text{Fe—N4}') = 1.893(19) \text{ \AA}$, $d(\text{Fe—O1}') = 2.067(15) \text{ \AA}$, and an angle $\angle(\text{Fe—N4'—O1}')$ of $82.0(13)^\circ$ were found. The occupation of the metastable state can be refined, converging at 12(2)%. This is in reasonable agreement with the population of 16(3)% obtained from the *in situ* transmission measurement, which allows for an independent determination of the population. Although the determined fractional coordinates are in good agreement with those from the x-ray study,²² we note that some problems occur with the determination of the displacement parameters in our study. The values for N4, O1, and Fe (GS) are rather small, while that of N4' (SII) is rather large. The large value $U_{\text{iso}}(\text{O1}') = 0.063(21) \text{ \AA}^2$ of the displacement parameter for O1' obtained in the refinement, where O1' was located in the mirror plane ($z=0.5$) could be reduced to the value $U_{\text{iso}}(\text{O1}') = 0.003(15) \text{ \AA}^2$ by releasing O1' from the mirror plane, indicating that the latter position is reasonable, even if the improvement of R values obtained from this out-of-plane movement is negligible. Simulated Fourier maps with the atom O1' located out of the mirror plane yield also the broad peak at (0.72, 0.4, 0.5), as observed in Fig. 3. Therefore the Fourier map itself could not give a unique conclusion concerning the O1' split. However, the obtained N4'—O1' distance of 1.11(8) Å is a much more reasonable value for the NO distance than the 0.85(9) Å obtained from the refinement with O1' in the mirror plane. The large-displacement parameter of N4' may also origin in some disorder at this position. One could think even of the possibility that the N4' and O1' interchange to some extent their position. This should lead to a decrease of the displacement parameters for N4', while those of O1' would increase. Such a refinement, however, is not possible with the current data set and the comparatively low occupation at these positions. The overall improvement

TABLE II. Fractional coordinates and isotropic displacement parameters U_{iso} ($10^{-3} \text{ \AA}^2$) of the mixed state GS+SII in SNP.

Atom	site	Occ.	x	y	z	U_{iso}
N4	4g	0.88(2)	0.7281(6)	0.3582(4)	0.5	1(1)
O1	4g	0.88	0.8869(8)	0.4051(4)	0.5	3(2)
N4'	8h	0.12	0.782(8)	0.348(4)	0.466(4)	30(14)
O1'	8h	0.12	0.730(8)	0.401(5)	0.478(3)	3(15)
Fe	4g	1	0.5014(4)	0.2807(2)	0.5	0.8(5)
C1	4g	1	0.2506(6)	0.1831(3)	0.5	3.9(7)
N1	4g	1	0.1010(4)	0.1234(2)	0.5	6.7(6)
C2	8h	1	0.6078(4)	0.1801(2)	0.5880(2)	3.4(6)
N2	8h	1	0.6679(3)	0.1200(1)	0.6419(1)	6.8(5)
C3	8h	1	0.3452(4)	0.3618(2)	0.5889(2)	3.8(6)
N3	8h	1	0.2504(3)	0.4053(1)	0.6444(1)	8.0(5)
Na1	4f	1	0.5	0	0.2460(4)	5.7(5)
Na2	4e	1	0	0	0.3784(4)	7(1)
D1	8h	0.48(2)	0.187(1)	0.1981(6)	0.7142(5)	26(3)
D2	8h	0.48(1)	0.062(1)	0.1247(5)	0.7748(4)	20(2)
O2	8h	1	0.1719(5)	0.1225(3)	0.7309(2)	5.5(7)

TABLE III. Distances and angles in GS and GS+SII of SNP.

	GS	GS+SII
N4—O1	1.126(9)	1.11(8)
N4'—O1'		1.1(6)
Fe—N4	1.658(7)	1.655(4)
Fe—N4'		1.96(5)
Fe—O1	2.782(9)	2.768(5)
Fe—O1'		2.01(5)
Fe—C1	1.898(8)	1.912(3)
Fe—C2	1.915(5)	1.915(3)
Fe—C3	1.921(5)	1.923(3)
C1—N1	1.161(8)	1.151(4)
C2—N2	1.154(5)	1.151(3)
C3—N3	1.162(5)	1.153(3)
Fe—N4—O1	176.0(3)	176.3(4)
Fe—N4'—O1'		77(4)
C1—Fe—N4	176.6(4)	176.5(2)
C1—Fe—N4'		160.30(16)
C2—Fe—N4	93.4(2)	93.39(15)
C3—Fe—N4	97.3(2)	97.94(15)
C3—Fe—C1	85.0(2)	84.48(13)
C3—Fe—C2	169.2(3)	168.64(17)
C3—Fe—C2'	88.1(2)	88.28(10)
C3—Fe—C3'	91.5(3)	90.90(14)
Fe—C1—N1	179.4(6)	179.3(3)
Fe—C2—N2	178.7(4)	178.6(2)
Fe—C3—N3	176.3(4)	176.5(2)

of R values from 0.1106 in the configuration with atoms as in GS to 0.1070 in the configuration with the additional side-on NO ligand is small but significant. Especially the Fourier difference maps after the first refinement step indicates clearly the presence of scattering density at the subsequently refined positions of N4' and O1'. Furthermore, the fact that the refinement converges at a population corresponding to that determined by the independent transmission measurements convincingly underlines the final refinement.

The ground state was measured after the state SII was thermally depopulated in order to demonstrate that the crystal had not been damaged by the illumination and cooling procedure. The refinement of this basic data set is in agreement with published data^{18,22} and clearly shows that the crystal was still in very good shape at the end of the measurement (see Tables I and III).

The crystal in the mixed state SII+GS has the same space group $Pnnm$ as the GS. The space group can only be kept when we assume a statistical distribution of the SII molecules over the crystal. The local symmetry of the SII molecule is C_s compared to C_{4v} of the GS molecule. Since the NO group is displaced from the mirror plane, the SII nitrosyl group must exist in at least two orientations, as indicated in Fig. 5. There is the possibility that the kinked NO molecule in SII occurs in two configurations, namely, eclipsed and staggered. In the eclipsed configuration, which is obtained from the refinement, N4' is located over the equatorial ligand C2 and O1' over C3. In the staggered configuration the NO molecule would be rotated by about 45° compared to the eclipsed configuration, i.e., it would be lying between the equatorial ligands. The eclipsed geometry is slightly lower in energy than the staggered one, as calculated by DFT.²³ One could imagine that tunneling processes between these different SII configurations occur, which might also be responsible for the observed problems in the displacement parameters.

FIG. 5. (Color online) Molecule $\text{Fe}(\text{CN})_5\text{NO}$ in the metastable state SII.

The existence of such tunneling processes is supported by Mössbauer spectroscopy, where a significant line broadening is observed in SII at a temperature of 80 K.^{31,32} The reduced symmetry of the SII molecule should be observable in polarized infrared spectroscopic (IR) measurements, as the selection rules for the $\delta(\text{FeNO})$ vibration are different for the linear NO configuration of GS and the kinked NO configuration of SII. IR measurements on normal and isotopic sub-

stituted powdered samples of SNP were interpreted on the basis of the side-on configuration of SII.³³

V. SUMMARY

The structure of the metastable state SII in SNP was investigated by single-crystal neutron diffraction. 16(3)% of the metastable state SII were generated *in situ* by successive illumination with blue and infrared laser light. The population of the generated metastable states was monitored by transmission measurements. The refinement is in excellent agreement with published data^{18,22} for the ground-state structure and shows that the structure of the metastable state SII has a side-on bonded configuration of the NO ligand as proposed by Carducci *et al.*²² and as supported by calculations based on density functional theory.²³ Direct evidence for this side-on bonding of the NO ligand is given by Fourier difference maps and the subsequent successful refinement of a side-on bonded NO configuration with 12(2)% population, which is in reasonable agreement with the population of 16(3)% determined from the *in situ* transmission measurement.

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