PHYSICAL REVIEW B **73**, 174108 (2006)

Neutron diffraction shows a photoinduced isonitrosyl linkage isomer in the metastable state *S*I of $Na_2[Fe(CN)_5NO]\cdot 2D_2O$

D. Schaniel,[1,2,*] Th. Woike,[2] J. Schefer,[3] V. Petříček,[4] K. W. Krämer,[5] and H. U. Güdel[5]
[1]*Institut für Experimentalphysik, Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria*
[2]*Institut für Mineralogie und Geochemie, Universität zu Köln, Zülpicherstrasse 49b, D-50674 Köln, Germany*
[3]*Laboratory for Neutron Scattering, ETH Zürich and Paul Scherrer Institute, 5232 Villigen, PSI, Switzerland*
[4]*Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18221 Praha 8, Czech Republic*
[5]*Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3000 Bern 9, Switzerland*
(Received 23 February 2006; published 10 May 2006)

We report neutron diffraction experiments on the light-induced metastable state *S*I in single crystals of $Na_2[Fe(CN)_5NO]\cdot 2D_2O$. It is shown that the metastable state *S*I corresponds to a linkage isomer of the NO group, the so-called isonitrosyl configuration where the NO ligand is oxygen bound to the central iron atom.

DOI: 10.1103/PhysRevB.73.174108 PACS number(s): 61.12.Ld, 42.70.Gi, 64.60.My

I. INTRODUCTION

The nature of the light-induced metastable states in $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (SNP) and related nitrosyl compounds has been a matter of discussion since their discovery in 1977.[1] Due to their almost infinitely long lifetime at sufficiently low temperature it is possible to investigate the light-induced structural changes in this compound by neutron or x-ray diffraction. While the structure of the ground state (GS) has been known for a long time[2–5] the first structural investigations of the light-induced species, a field in the meantime called photocrystallography,[6,7] were performed by Rüdlinger *et al.*[8,9] using neutron diffraction. These authors found small increases in the Fe-N and N-O bond lengths in the metastable states *S*I and *S*II with respect to the ground state. Later Pressprich and co-workers[10] performed x-ray diffraction experiments on *S*I, finding as well an elongation of the Fe-N bond. The following neutron diffraction study of *S*II by Schefer *et al.*[11] 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.[12] A major step toward the understanding of the long lifetime of the metastable states was taken in 1997, when Carducci *et al.*[13] performed x-ray diffraction experiments on both metastable states. The astonishing result was that the metastable state *S*II could be interpreted as a side-on (η^2) configuration of the NO ligand, while in the metastable state *S*I 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 (DFT) by Delley *et al.*,[14] which found energetic minima for the two configurations, yielding the Fe-N-O angle as the reaction coordinate. However, subsequent reinvestigation of the neutron diffraction results could not confirm this interpretation[15] and also a more recent neutron diffraction study could not be interpreted as a linkage isomer for the metastable state *S*I.[16] On the other hand, we recently performed a successful neutron diffraction study on the metastable state *S*II,[17] where we could unambiguously determine the linkage isomer in the side-on configuration in agreement with the earlier x-ray results.[13] In order to finally answer the question about the nature of the metastable states in SNP, we reinvestigated the structure of *S*I, using the photocrystallographic setup which is described in detail in Refs. 7 and 16. With this setup the number of molecules in the metastable state (population) can be determined optically, independent of the structural refinement. The analysis of the neutron diffraction data from a crystal with 40% population of SI clearly shows that SI is indeed formed by the isonitrosyl configuration.

II. EXPERIMENTAL DETAILS

The neutron diffraction experiments were performed on the single-crystal diffractometer[18] TriCS at the Swiss Spallation Source[19] SINQ at PSI/Villigen using a single detector and a high-quality fully deuterated (99% D) single crystal of $Na_2[Fe(CN)_5NO]\cdot 2D_2O$. The crystal was cut perpendicular to the *a* axis to a plate of thickness $d=0.0476$ cm and 0.9 cm diameter. The temperature was kept constant at 50(2) K during data collection. Illumination of the crystal was performed using a xenon lamp filtered to the spectral range 430–470 nm using water, dichroic, and interference filters. After filtering, the blue light was polarized to ensure illumination with light polarization along the *c* axis of the crystal. The total exposure was about $5000\ \mathrm{J/cm^2}$ using an average power of $20\ \mathrm{mW/cm^2}$.

It is known from wavelength-dependent differential scanning calorimetry (DSC) measurements,[20] that illumination in the spectral range of 430 to 470 nm with polarization along the *c* axis of the crystal yields a *S*I population of about 45–50% and a *S*II population of about 3–5%. As the absorption changes concomitant with the generation of the metastable states are known from low-temperature absorption spectroscopy,[21] the change of the transmitted light intensity during illumination can be used to determine the population numbers of the states *S*I and *S*II. The used photocrystallographic setup allows for the in situ measurement of the transmitted light intensity with a Si photodiode.[7,16] In order to have a well-defined signal, the transmitted light was narrowed by an interference filter at 458 nm (full width at half maximum of 2 nm). The detected time-dependent photovoltage $U(t)$ can be described by

$$U(t) = aI_0 e^{-\alpha(t)d} \tag{1}$$

where α denotes the absorption coefficient, d the crystal thickness, and I_0 the constant incident light intensity. a is a proportionality constant, describing the detection efficiency. During illumination the absorption changes as a function of exposure $Q=I_0 t$ due to the change in population of the three involved states GS, *S*I, and *S*II. Hence the total absorption coefficient is given as the sum of the single contributions

$$\alpha(t) = \alpha_{\mathrm{GS}} P_{\mathrm{GS}}(t) + \alpha_{S\mathrm{I}} P_{S\mathrm{I}}(t) + \alpha_{S\mathrm{II}} P_{S\mathrm{II}}(t), \tag{2}$$

where $P_{\mathrm{GS},S\mathrm{I},S\mathrm{II}}$ denote the populations of the different states. It is known from the low-temperature steady-state absorption measurements[21] that $\alpha_{S\mathrm{I}}=0$ at 458 nm (wavelength of experiment), so that Eq. (2) reduces to

$$\alpha(t) = \alpha_{\mathrm{GS}} P_{\mathrm{GS}}(t) + \alpha_{S\mathrm{II}} P_{S\mathrm{II}}(t). \tag{3}$$

Since $P_{\mathrm{GS}}+P_{S\mathrm{I}}+P_{S\mathrm{II}}=1$ we obtain

$$\alpha(t) = \alpha_{\mathrm{GS}} - \alpha_{\mathrm{GS}} P_{S\mathrm{I}}(t) + (\alpha_{S\mathrm{II}} - \alpha_{\mathrm{GS}}) P_{S\mathrm{II}}(t). \tag{4}$$

At the beginning of illumination all molecules are in the ground state and hence $U_0=U(0)=aI_0 e^{-\alpha(0)d}=aI_0 e^{-\alpha_{\mathrm{GS}} d}$. Then we can write the time-dependent voltage as

$$U(t) = U_0 e^{\alpha_{\mathrm{GS}} P_{S\mathrm{I}}(t) d} e^{(\alpha_{\mathrm{GS}} - \alpha_{S\mathrm{II}}) P_{S\mathrm{II}}(t) d}. \tag{5}$$

Equation (5) can be written in the form

$$\ln \frac{U(t)}{U_0} = \alpha_{\mathrm{GS}} P_{S\mathrm{I}}(t) d + (\alpha_{\mathrm{GS}} - \alpha_{S\mathrm{II}}) P_{S\mathrm{II}}(t) d. \tag{6}$$

As a function of exposure Q the population of *S*I and *S*II is given by

$$P_{S\mathrm{I},S\mathrm{II}}(Q) = P_{S\mathrm{I},S\mathrm{II}}^{\mathrm{sat}} \left[1 - \exp\left(\frac{-Q}{Q_{S\mathrm{I},S\mathrm{II}}} \right) \right] \tag{7}$$

with the characteristic exposures $Q_{S\mathrm{I}}$ and $Q_{S\mathrm{II}}$. Fitting the function

$$\ln \frac{U(t)}{U_0} = A_{S\mathrm{I}} (1 - e^{-Q/Q_{S\mathrm{I}}}) + A_{S\mathrm{II}} (1 - e^{-Q/Q_{S\mathrm{II}}}) \tag{8}$$

to the observed data shown in Fig. 1 yields the parameters $A_{S\mathrm{I}}=2.017(3)$, $A_{S\mathrm{II}}=-0.133(2)$, $Q_{S\mathrm{I}}=1765(9)\ \mathrm{J/cm^2}$, and $Q_{S\mathrm{II}}=21(1)\ \mathrm{J/cm^2}$. Using $A_{S\mathrm{I}}=\alpha_{\mathrm{GS}} d P_{S\mathrm{I}}^{\mathrm{sat}}$ and $A_{S\mathrm{II}}=(\alpha_{\mathrm{GS}} - \alpha_{S\mathrm{II}}) d P_{S\mathrm{II}}^{\mathrm{sat}}$ we obtain the saturation populations $P_{S\mathrm{I}}^{\mathrm{sat}}$ and $P_{S\mathrm{II}}^{\mathrm{sat}}$ for $Q \rightarrow \infty$, since we know the thickness d and the absorption coefficients α_{GS} and $\alpha_{S\mathrm{II}}$. With $d=0.0476$ cm and $\alpha_{\mathrm{GS}}=103\ \mathrm{cm^{-1}}$ at 458 nm we obtain $P_{S\mathrm{I}}^{\mathrm{sat}}=41\%$ and at $Q=5000\ \mathrm{J/cm^2}$ a population of *S*I of $P_{S\mathrm{I}}=40\%$ is achieved. Using $\alpha_{S\mathrm{II}}=158\ \mathrm{cm^{-1}}$ at 458 nm,[21] a population of $P_{S\mathrm{II}}=5\%$ for *S*II is obtained, which is in reasonable agreement with the values known from the DSC study.[20] We note that by ignoring the small decrease due to *S*II at the beginning and just fitting an exponential law to the population of *S*I the same results for the population of *S*I are obtained, indicating that in a good approximation we could even neglect the influence of *S*II for the population determination of *S*I.

After collection of the first data set with 40% population of *S*I (and about 5% of *S*II) the crystal was heated to 178 K for a few minutes. By this procedure the *S*II population decays completely into the ground state as does also part of the *S*I population. Then we collected a second data set at 50 K for this crystal with now 10(2)% population of *S*I in order to compare the reliability of the refinements with high and low populations. The population for this data set was determined by detecting the change in transmission (488 nm laser light of an argon ion laser) upon heating the sample to room temperature at the end of the measurement. Thereby the photovoltage decreased from 1.0 to 0.6 mV yielding the population of *S*I of 10(2)%. The data collection and refinement parameters for the two data sets are given in Table I.

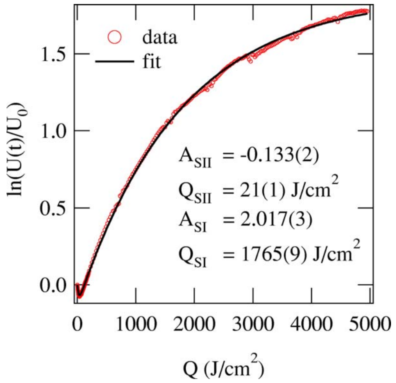

FIG. 1. (Color online) Photovoltage U of the transmitted light at 458 nm as a function of exposure Q. The transmitted light intensity increases as the population of GS decreases and the population of *S*I increases. The initial decrease ($Q < 100\ \mathrm{J/cm^2}$) is due to the population of the state *S*II.

III. RESULTS

As in the previous study of the state *S*II in SNP,[17] in the first refinement step the 14 atoms were refined in their ground-state positions, all with isotropic displacement parameters and ground-state occupation numbers, i.e., especially $o(\mathrm{N4})=o(\mathrm{O1})=1.0$. After convergence of the refinement, a difference Fourier map was calculated. The plane $z=0.5$ is of special interest as it contains the NO ligand and hence exhibits the most significant changes upon a geometrical change of the NO ligand. Figure 2(a) shows the resultant difference map at $z=0.5$ for the data set with $P_{S\mathrm{I}}=40\%$ (the population is known from the transmission measurement). Although some residual features are noted in the vicinity of the NO ligand, the feature is not as clear as in the case of *S*II.[17] In order to estimate the changes, which should be observable due to the inverted NO configuration, we performed simulations using the program package JANA2000.[22] The simulation was performed as follows. A virtual crystal composed of 4% of the NO ligands in the *S*II position, 40% in the *S*I position, and 56% in the GS position was assumed. The fractional coordinates for GS, *S*I, and *S*II were taken from Ref. 13. The populations were chosen to meet the actual experimental conditions (see Sec. II). We calculated the structure factors for the set of reflections that were observed in the experiment. The structure simulation allows also for inclusion of noise by adding random numbers to the individual calculated structure factors. These generated structure

TABLE I. Experimental data collection and refinement parameters for SNP for the two data sets with 40% and 10% population of *S*I. The populations were determined optically.

	GS+SI(40%)	GS+SI(10%)
Space group	*Pnnm*	*Pnnm*
Z	4	4
Wavelength λ(Å)	1.1757(13)	1.1757(13)
T(K)	50	50
a(Å)	6.1581(7)	6.1642(4)
b(Å)	11.9013(14)	11.8869(1)
c(Å)	15.6328(18)	15.5749(1)
V(Å^3)	1145.7(2)	1141.2(4)
d(g/cm^3)	1.727(4)	1.734(6)
$[\sin(\theta)/\lambda]_{\max}$ (Å^{-1})	0.544	0.627
Absorption coefficient (mm^{-1})	0.0034	0.0034
$T_{\min}$ (minimum transmission)	0.9714	0.9737
$T_{\max}$(maximum transmission)	0.9964	0.9967
Crystal size (mm^3)	$\pi \times 4.5^2 \times 0.476$[a]	$\pi \times 4.5^2 \times 0.476$[a]
$h_{\max}$	5	5
$k_{\max}$	12	16
$l_{\max}$	16	20
Measured reflections	937	774
Unique reflections	774	587
Refined reflections	774	587
Observed reflections ($I > 3\sigma$)	704	525
$g_{\text{iso}}(10^{-4})$[b]	0.004	0.009
Refined population of *S*I, P_{SI}(%)	40(5)	5(6)
No of variables	53	53
$R_w(\lvert F \rvert)$	0.074	0.066
$R(\lvert F \rvert)$	0.080	0.0882
Goodness of fit S	8.00	7.07

[a] Circular sample of diameter 9 mm.

[b] Isotropic extinction correction of type I (Lorentzian distribution) is used (Ref. 23).

factors were then used as input for the refinement. The refinement was performed in the same manner as for the experimental data and the correspondingly obtained difference Fourier map is shown in Fig. 2(b). One notes the similarities with the experimental data in the region of the N and O atoms, providing a first hint to the proposed inverted geometry of the nitrosyl ligand.

In the second refinement step the occupation numbers for the N4 and O1 atom were released, i.e., they became fit parameters. The obtained occupation numbers for these positions can then be regarded as composed of two parts: the GS NO and the *S*1 ON configurations, i.e., at both positions we have a sum of the two scattering lengths for oxygen (5.803 fm) and nitrogen (9.36 fm), according to their real occupation or population. We then would expect a decrease of the occupation at the N4 position and an increase at the O1 position. Indeed the refinement of the experimental data set yielded $o(\text{N4})=0.824(18)$ and $o(\text{O1})=1.20(4)$. The weighted R value R_w and the goodness of fit (GOF) improved from $R_w=0.077$ to 0.074 and from GOF of 8.30 to 8.00 during this refinement step. The same refinement was performed using the simulated data set, yielding $o(\text{N4})=0.840(14)$ and $o(\text{O1})=1.20(2)$, in perfect agreement with the experimental results. Hence the isonitrosyl model seems to be correct. Additionally we noted that the isotropic displacement parameters U_{iso} at the N4 and O1 positions changed considerably during this second refinement step. $U_{\text{iso}}[\text{N4}]$ decreases from $21(1)\times 10^{-3}$ Å^2 to $8(3)\times 10^{-3}$ Å^2 while $U_{\text{iso}}[\text{O1}]$ increases from $3(2)\times 10^{-3}$ Å^2 to $16(3)\times 10^{-3}$ Å^2 (see Table II for final refinement parameters). Since the scattering length of the nitrogen ($b_{\text{N}}=9.36$ fm) is larger than that of the oxygen ($b_{\text{O}}=5.803$ fm), the scattering power at the N4 position is overestimated if we assume a 100 % nitrogen occupation of this position (step 1 of refinement). The increase in the displacement parameter corrects for this overestimation, as it effectively reduces the scattering power at this position. The situation is reversed for the O1 position where the scattering power is underestimated.

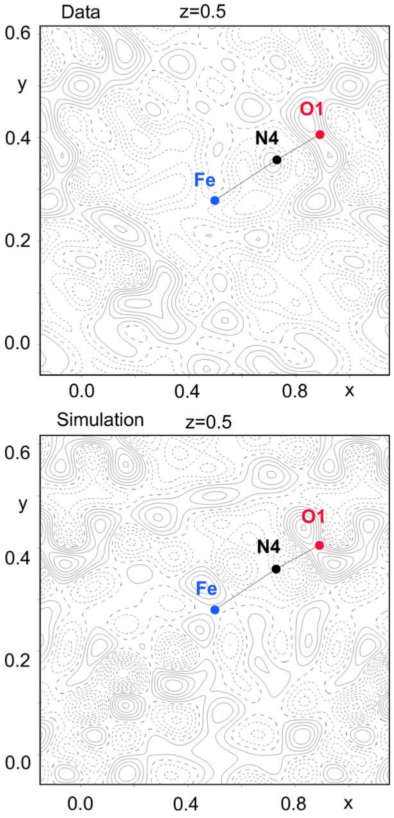

FIG. 2. (Color online) Difference Fourier maps after refinement step 1, i.e., 14 atoms in the ground-state nitrosyl configuration with occupation of N4 and O1 positions fixed to 1. Top, experimental data set; bottom, simulated data set with expected noise added. Contours are 0.2 b Å^{-3}.

TABLE II. Structural parameters of the mixed state GS+*S*I in SNP for the data set with 40% population of *S*I after final refinement. The isotropic displacement parameters U_{iso} are given in 10^{-3} Å^2.

Atom	Occupation	x	y	z	U_{iso}
Na1	1	0.5	0	0.2455(9)	12(3)
Na2	1	0	0	0.3781(9)	10(3)
Fe	1	0.4972(10)	0.2787(4)	0.5	5(1)
C1	1	0.2483(14)	0.1826(6)	0.5	10(2)
N1	1	0.0979(10)	0.1233(5)	0.5	11(1)
C2	1	0.6067(9)	0.1789(4)	0.5880(3)	6(1)
N2	1	0.6672(6)	0.1194(3)	0.6420(3)	11(1)
C3	1	0.3448(9)	0.3613(4)	0.5893(3)	7(1)
N3	1	0.2498(7)	0.4054(3)	0.6443(2)	12(1)
N4	0.824(18)	0.7271(12)	0.3568(5)	0.5	8(3)
O1	1.20(4)	0.8863(15)	0.4065(7)	0.5	16(3)
D1	0.80(3)	0.1872(15)	0.1971(8)	0.7151(6)	29(3)
D2	0.81(3)	0.0642(15)	0.1241(7)	0.7767(5)	27(3)
O2	1	0.1723(11)	0.1206(5)	0.7311(4)	10(2)

Using the isonitrosyl geometry (40%), the scattering powers are correctly estimated and hence yield the expected larger displacement parameter for the outer position O1. This observation is in perfect agreement with the earlier x-ray results[13] and supports the interpretation of *S*I as an isonitrosyl geometry.

A further stringent test for the validity of the inverted nitrosyl geometry can be made by comparing the refined populations (occupations) with the population determined from the transmission measurement ($P_{SI}=40\%$). This can be done by considering a simple formula to calculate the population of *S*I from the refined occupation value at the N4 position (or alternatively at the O1 position). The scattering length at the N4 position is given by the nitrogen atom $b_{\mathrm{N}}=9.36$ fm, as we assume a sole occupation $o(\mathrm{N4})$ by this atom. In reality we have a mixed occupation with the number n_{N} of nitrogen atoms having the scattering length $b_{\mathrm{N}}=9.36$ fm and with the number n_{O} of oxygen atoms having the scattering length $b_{\mathrm{O}}=5.803$ fm. Neglecting the state *S*II we can therefore write the following equation for the scattering power at the N4 position:

$$o(\mathrm{N4})b_{\mathrm{N}} = n_{\mathrm{N}}b_{\mathrm{N}} + n_{\mathrm{O}}b_{\mathrm{O}}. \tag{9}$$

Since the population of the GS corresponds to the occupation of the N4 position with nitrogen, i.e., n_{N}, we obtain the population of GS or *S*I by (using $n_{\mathrm{O}}=1-n_{\mathrm{N}}$)

$$P_{\mathrm{GS}} = n_{\mathrm{N}} = \frac{o(\mathrm{N4})b_{\mathrm{N}} - b_{\mathrm{O}}}{b_{\mathrm{N}} - b_{\mathrm{O}}} = 1 - P_{SI}. \tag{10}$$

Inserting the refinement results we obtain $P_{SI}=46(4)\%$ using $o(\mathrm{N4})=0.824(18)$. The same arguments can be applied to the occupation $o(\mathrm{O1})$ of the O1 position with nitrogen and oxygen. Here $P_{SI}=33(6)\%$ is obtained from $o(\mathrm{O1})=1.20(4)$. The average value is 40(5)% in agreement with the result from the transmission measurement.

The second data set with 10% population of *S*I (see Table I) was evaluated in the same manner. The difference Fourier map after the first refinement step showed no unique features, but rather an overall noisy behavior. The subsequent refinement of the occupation numbers yielded $o(\mathrm{N4})=1.00(2)$ and $o(\mathrm{O1})=1.06(4)$ and therefore populations of 0(5)% and 10(7)%, respectively. The average of 5(6)% is well below the result from the transmission measurement (10 %) and shows that the error for this low population is too large using this simple approach. Also here the R values did not improve during the second refinement step.

IV. DISCUSSION

The refinement of the first data set with 40% population of *S*I clearly shows, that NO is in the isonitrosyl configuration in *S*I. The high population allows us to use a rather simple method for the refinement and thereby to extract the main feature of the structure, without refinement of the atomic positions of the inverted NO in *S*I by introduction of a second molecule as in the x-ray study of Carducci and co-workers.[13] However, it is exactly this simple approach which makes the evidence for the isonitrosyl so stringent and also important. Up to now all the studies concerned with this question suffered from the fact that the quality of the refinement did not really improve upon introduction of an inverted

NO compared to one in the GS configuration with slightly elongated bonds (compare discussions in Refs. 13 and 16). The arguments for or against the isonitrosyl configuration were found in the displacement parameters. While being very plausible due to the fact that *S*II is a side-on bound NO and being supported by the DFT results, this situation was not satisfying, as direct methods should yield more direct evidence. It is therefore a relief that finally x-ray and neutron diffraction results agree on this fundamental question, especially as neutron diffraction is supposed to be superior in determining structural changes involving N and O, because of their significantly different scattering lengths. On the other hand, neutron data sets are generally much smaller than corresponding x-ray collections due to the much longer counting times and lack of beamtime. From our comparably small data set we can therefore not compete with the published structural parameters obtained from the x-ray study. Nevertheless, the presented neutron diffraction evidence for the isonitrosyl configuration of *S*I is convincing because it does not rely on the interpretation of displacement parameters or other indirect arguments. Furthermore, the in situ determination of the population via a transmission measurement ensures that we had a population of 40%. Concerning earlier failures of neutron diffraction in determining the isonitrosyl structure,[16] the second experiment reported here hints to some pitfalls, as obviously low populations of a structurally nearly degenerate NO (ON) moiety are hard to detect. A population of 40% was never achieved in the earlier experiments.

V. CONCLUSIONS

Neutron diffraction experiments on the light-induced metastable state *S*I in SNP show that it corresponds to the linkage isomer of the NO ligand in the isonitrosyl configuration as proposed from x-ray measurements[13] and DFT calculations.[14] This result resolves a long controversy concerning the nature of the metastable states, as now the direct methods of structure determination agree with the DFT results. As DFT is able to predict the existence and the main properties of such metastable linkage isomers it offers the possibility to screen potential candidate systems before really synthesizing them, a valuable help in the search for optimized properties for applications.

Furthermore, we realize that for photocrystallographic experiments it is advantageous to have independent means to determine the amount of generated metastable isomers, as otherwise the interpretation of the results might not be unambiguous, especially in the case of low populations or as in the present case where the N and O atoms simply interchange positions. However, our results also clearly show that the determination of the isonitrosyl configuration from x-ray diffraction,[13] which was mainly based on a detailed analysis of the involved displacement parameters, is correct. Thus the careful analysis of the displacement parameters of the involved photoexcited atoms allows for the identification of such linkage isomers.[6]

ACKNOWLEDGMENTS

The neutron diffraction was performed at SINQ, Paul Scherrer Institute, Villigen, Switzerland. Financial support from the DFG (Grant No. Wo618/5-3) and the Grant Agency of the Czech Republic (Grant No. 202/06/0575) is gratefully acknowledged. D.S. is indebted to the University of Vienna for support that considerably facilitated this work.

---

*Electronic address: dominik.schaniel@uni-koeln.de

[1] U. Hauser, V. Oestreich, and H. D. Rohrweck, Z. Phys. A **280**, 17 (1977).

[2] P. T. Manoharan and W. C. Hamilton, Inorg. Chem. **2**, 1043 (1963).

[3] F. Bottomley and P. S. White, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **35**, 2193 (1979).

[4] M. Yu. Antipin, V. G. Tsirelson, M. P. Flyugge, Yu. T. Stuchkov, and R. P. Ozerov, Sov. J. Coord. Chem. **13**, 67 (1987).

[5] A. Navaza, G. Chevrier, P. M. Alzari, and P. J. Aymonino, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **45**, 839 (1989).

[6] P. Coppens, I. Novozhilova, and A. Kovalevski, Chem. Rev. (Washington, D.C.) **102**, 86 (2002).

[7] J. Schefer, D. Schaniel, Th. Woike, and M. Imlau, Physica B **350**, 87 (2004).

[8] M. Rüdlinger, J. Schefer, T. Vogt, T. Woike, S. Haussühl, and H. Zöllner, Physica B **180-181**, 293 (1990).

[9] M. Rüdlinger, J. Schefer, G. Chevrier, N. Furer, H. U. Güdel, S. Haussühl, G. Heger, P. Schweiss, T. Vogt, T. Woike, and H. Zöllner, Z. Phys. B: Condens. Matter **83**, 125 (1991).

[10] M. R. Pressprich, M. A. White, Y. Vekhter, and P. Coppens, J. Am. Chem. Soc. **116**, 5233 (1994).

[11] J. Schefer, Th. Woike, S. Haussühl, and M. D. Fernandez Diaz, Z. Kristallogr. **212**, 29 (1997).

[12] H. U. Güdel, Chem. Phys. Lett. **175**, 262 (1990).

[13] M. D. Carducci, M. R. Pressprich, and P. Coppens, J. Am. Chem. Soc. **119**, 2669 (1997).

[14] B. Delley, J. Schefer, and Th. Woike, J. Chem. Phys. **107**, 10067 (1997).

[15] J. Schefer, Th. Woike, M. Imlau, and B. Delley, Eur. Phys. J. B **3**, 349 (1998).

[16] D. Schaniel, J. Schefer, M. Imlau, and Th. Woike, Phys. Rev. B **68**, 104108 (2003).

[17] D. Schaniel, Th. Woike, J. Schefer, and V. Petříček, Phys. Rev. B **71**, 174112 (2005).

[18] J. Schefer, M. Könnecke, A. Murasik, A. Czopnik, T. Strässle, P. Keller, and N. Schlumpf, Physica B **276-278**, 168 (2000).

[19] W. E. Fischer, Physica B **234-236**, 1202 (1997).

[20] Th. Woike, W. Krasser, H. Zöllner, W. Kirchner, and S. Haussühl, Z. Phys. D: At., Mol. Clusters **25**, 351 (1993).

[21] D. Schaniel, J. Schefer, B. Delley, M. Imlau, and Th. Woike, Phys. Rev. B **66**, 085103 (2002).

[22] V. Petříček, M. Dušek, and L. Palatinus, *The Crystallographic Computing System JANA2000* (Institute of Physics, Praha, 2000).

[23] P. J. Becker and P. Coppens, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **30**, 129 (1974).