Isomerism

Steady-State and Pseudo-Steady-State Photocrystallographic Studies on Linkage Isomers of [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)]: Identification of a New Linkage Isomer**

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Abstract: At temperatures below 150 K, the photoactivated metastable *endo*-nitrito linkage isomer [Ni(Et$_4$dien)(η^2-O,ON)(η^1-ONO)] (Et$_4$dien = N,N,N′,N′-tetraethyldiethylenetriamine) can be generated with 100% conversion from the ground state nitro-(η^1-NO$_2$) isomer on irradiation with 500 nm light, in the single crystal by steady-state photocrystallographic techniques. Kinetic studies show the system is no longer metastable above 150 K, decaying back to the ground state nitro-(η^1-NO$_2$) arrangement over several hours at 150 K. Variable-temperature kinetic measurements in the range of 150–160 K show that the rate of *endo*-nitrito decay is highly dependent on temperature, and an activation energy of $E_{act} = +48.6(4)$ kJ mol^{-1} is calculated for the decay process. Pseudo-steady-state experiments, where the crystal is continually pumped by the light source for the duration of the X-ray experiment, show the production of a previously unobserved, *exo*-nitrito-(η^1-ONO) linkage isomer only at temperatures close to the metastable limit (ca. 140–190 K). This *exo* isomer is considered to be a transient excited-state species, as it is only observed in data collected by pseudo-steady-state methods.

Introduction

The structural determination of short-lived species is a challenge of continued importance in chemistry. In particular, the determination of the structures of reaction intermediates and transition states will enable better understanding of the progress of any particular reaction. For this reason, the technique of photocrystallography has attracted much interest because of its ability to conclusively determine the full, three-dimensional structures of photoactivated excited-state species from diffraction data. Since pioneering studies in the field during the late 1990s,[1] single-crystal photocrystallographic methods have been successfully employed to study a number of photo-induced processes with an increasing range of lifetimes, from metastable species[2] to those existing for a few picoseconds and even less.[3] In particular, the increasing availability of high-flux X-ray sources, including third generation synchrotron and X-ray Free Electron Laser (X-FEL) facilities around the world, has led to a drive to achieve shorter and shorter timescales for the study of faster and faster processes.[4]

Whilst these advancements in resolution and instrumentation are important, it is equally of interest to obtain a thorough understanding of the key physical and chemical processes that affect the progress of the reaction in the solid state. Our previous work has focussed on the study of metastable photoactivated systems, in particular, the process of single-crystal-to-single-crystal linkage isomerism in transition-metal complexes.[5] Since early work by Coppens et al. describing the generation of different nitrosyl isomers in sodium nitroprusside crystals,[1a] a number of such systems have been shown to produce metastable isomers upon photoactivation at low temperature. Other examples of photo-isomerisable ligands include sulfur dioxide, for which metastable η^1-OSO[6] and η^2-(S,O)O[5a] isomers have been characterised by photocrystallographic studies. While others have gone on to investigate the kinetics

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[**] Et$_4$dien = N,N,N′,N′-tetraethyldiethylenetriamine

of sulfur dioxide photoactivated isomerisations in ruthenium complexes,[7] our recent studies have been targeted at maximising conversion levels whilst maintaining single-crystal integrity. By utilising crystal engineering methods, we have aimed to generate a suitable "reaction cavity"[8] in the crystal, within which isomerisable ligands can rearrange without inducing unsustainable levels of strain in the lattice. One method to achieve this is to incorporate bulky, photoinert auxiliary ligands into the target complex; these ligands should dominate the crystal packing and provide freedom for the smaller, photoactive ligand to isomerise. As a result of this approach, in 2009 we reported the first instance of 100% reversible conversion to a metastable nitrito-(η^1-ONO) isomer in the system [Ni(dppe)(η^1-NO$_2$)Cl] (dppe = 1,2-bis(diphenylphosphino)ethane).[5b] We have subsequently developed these methodologies to produce series of nickel(II) and palladium(II) nitrite complexes that readily exhibit high levels of nitro–nitrito conversion in the single crystal.[5d,f,g] High conversion levels have also been achieved in nitrosyl linkage isomer systems; in 2009 Cormary et al. reported 92% excitation to the η^1-ON isomer (MS1) in the complex [RuCl(NO)py$_4$](PF$_6$)·$^1/_2$H$_2$O (py = pyridine).[9] Schaniel and Woike have shown that high levels of conversion are only possible when there is sufficient energy difference between the two forms to avoid an equilibrium becoming established.[10] A high level of excitation, one that is both controllable and reproducible, is highly desirable if such systems are to have any real application, for example, in data storage or opto-electronic devices.[11]

In 2011, we reported the discovery of particularly interesting isomerisation in [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)] (Et$_4$dien = N,N,N′,N′-tetraethyldiethylenetriamine; Figure 1), which undergoes not only photoconversion at low temperature but, additionally, a thermally induced nitro–nitrito isomerisation upon varying the in situ experiment temperature between 100 and 370 K.[5c] In the initial communication, photochemical studies were conducted by using 400 nm LED light and a maximum 86% conversion to a single, endo-nitrito-(η^1-ONO) excited state isomer was achieved. Extensive further studies with this system have been conducted to obtain a stronger understanding of the underlying processes that influence the nitro–nitrito conversion in the single crystal, including kinetic factors and steric effects from the surrounding crystal lattice. The results of these studies are reported herein, including the structural determination of a new, exo-nitrito-(η^1-ONO) excited state isomer, which is believed to be a transient species that is only observed when the system is probed at temperatures close to the metastable limit.

Results and Discussion

[Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)] was synthesised as described previously and single crystals obtained by slow evaporation from a methanolic solution. Figure 1 shows the molecular structures, obtained in earlier studies,[5c] of both the ground state (GS) nitro-(η^1-NO$_2$) isomer and the 86% occupancy metastable state (MS) endo-nitrito-(η^1-ONO) arrangement. Although this level of photoconversion is high in comparison to the ma-
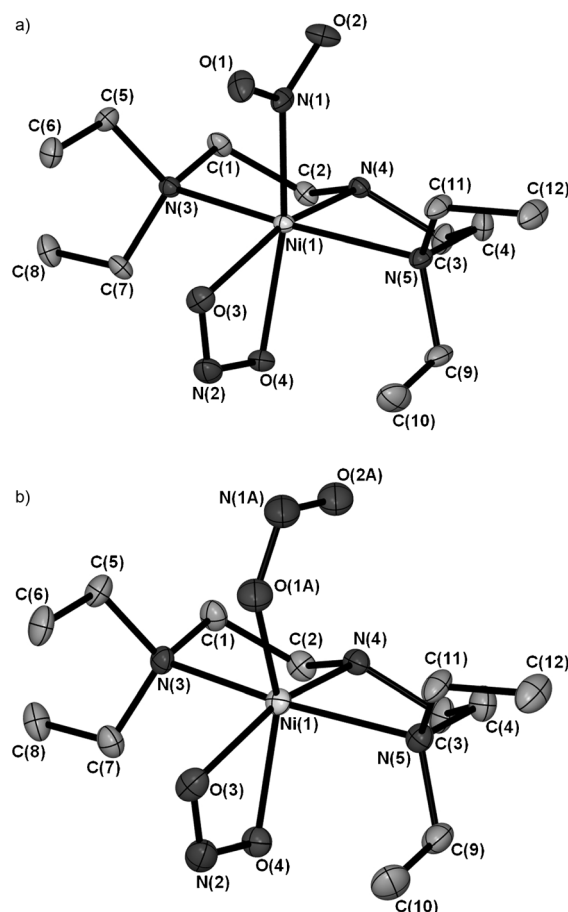

Figure 1. Single crystal X-ray structures showing the atomic arrangement of GS nitro-(η^1-NO$_2$) (a) and MS nitrito-(η^1-ONO) (b) linkage isomers in [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)]. Ellipsoids at 50% probability and hydrogen atoms removed for clarity.

jority of such systems investigated in the literature, it is of interest to better understand why the photoreaction remains incomplete upon irradiation at 400 nm. Reasons for lower single-crystal-to-single-crystal conversion have previously been studied and proposed explanations include the effect of restrictions imposed by steric strain in the lattice,[5b] the relative location of minima on the GS and MS potential energy surfaces,[10] and the absorption properties of the sample.[12] Additionally, it is important to consider that photoactivation will necessarily begin at the crystal surface. If the photoexcited species is strongly absorbing at the activation wavelength, then the excited-state surface layer can effectively block the incident light, limiting the degree to which it can penetrate throughout the crystal and therefore the possible conversion level.

An assessment of the influence of steric strain on the photoisomerisation process has been made by analysis of the crystal packing both before and after irradiation at $\lambda = 400$ nm (Figure 2). The overall packing arrangement is largely unchanged following excitation, with no strong intermolecular interactions, such as hydrogen bonds, altered as a result of the nitro–nitrito rearrangement and only a small increase (2.2%) in the volume of the unit cell is observed following irradiation (Table 1). In addition, the same single crystal may be used for
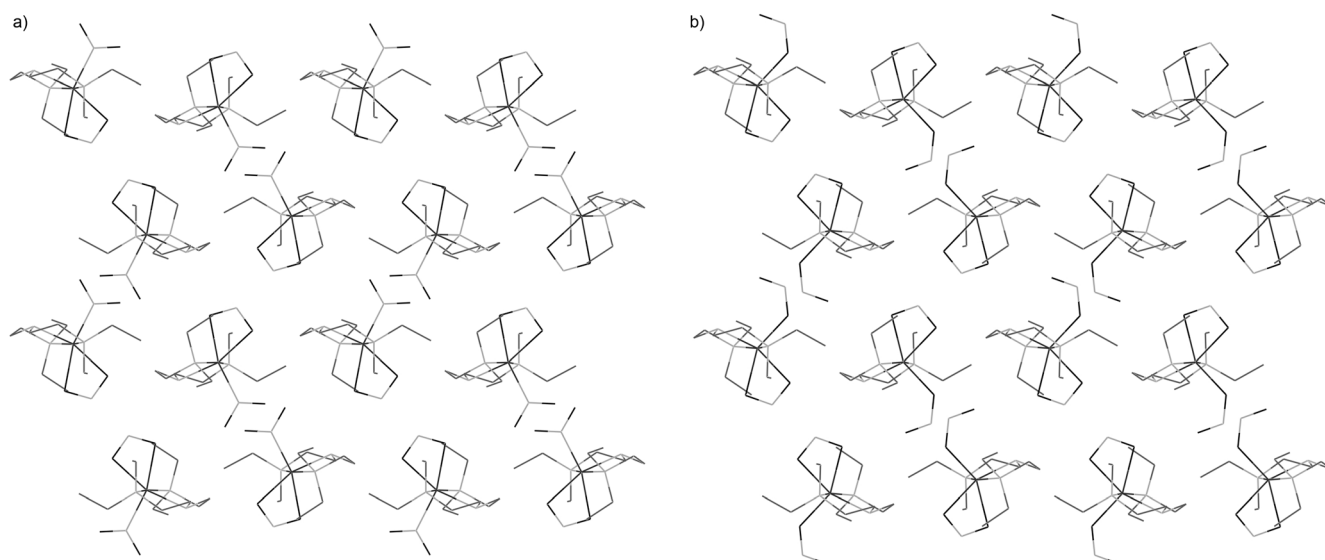
Figure 2. Crystal packing diagrams of GS nitro-(η^1-NO$_2$) (a) and MS *endo*-nitrito-(η^1-ONO) (b) isomers of [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)], obtained from single-crystal X-ray data. Packing arrangements viewed along the *b*-axis, *c*-axis horizontal.

Table 1. Crystal data for the GS and MS structures at 100 K.		
	GS	500 nm MS
Photoconversion [%]	0	100
T [K]	100(2)	100(2)
Radiation source	Mo$_{K\alpha}$	Mo$_{K\alpha}$
λ [Å]	0.71073	0.71073
Empirical formula	C$_{12}$H$_{29}$N$_5$Ni$_1$O$_4$	C$_{12}$H$_{29}$N$_5$Ni$_1$O$_4$
M_r	366.11	366.11
Crystal size [mm^3]	0.40×0.20×0.10	0.30×0.3×0.10
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a [Å]	11.314(5)	11.517(5)
b [Å]	11.597(5)	11.658(5)
c [Å]	12.816(5)	12.799(5)
V [Å^3]	1681.6(12)	1718.5(12)
Z	4	4
ρ_{calcd} [M g m^{-3}]	1.446	1.415
μ [mm^{-1}]	1.178	1.153
Flack parameter	−0.019(14)	0.008(13)
F(000)	784	784
R(int)	0.0729	0.0353
R1 (obs. data)	0.0348	0.0362
wR2 (all data)	0.0671	0.0806
Reflections (indep.)	3434	4706

several repeat photocrystallographic experiments—comprising of multiple irradiation periods, single-crystal X-ray data collections and temperature variation cycles—with no significant sample degradation upon relaxation or reactivation. These observations suggest little evidence of high levels of steric strain in the MS structure that could limit the achievable level of photoconversion.

Optimisation of the excitation wavelength

To assess the degree to which the absorption properties of the sample affect the level of achievable photoconversion, test experiments were conducted at alternative excitation wavelengths. The solid-state UV/Visible absorption spectrum (Figure S1 in the Supporting Information), obtained at room temperature on a $0.6\times0.6\times0.04$ mm^3 single crystal, was used to guide wavelength selection. Previous work in this area has indicated that exciting a solid-state sample by using a wavelength close to λ_{max} is not beneficial for inducing a high level of photoconversion.[13] At this wavelength, the sample and/or photoproduct are absorbing the incident light. Instead, it has been suggested that a wavelength in the tail of the absorption profile is preferred, as this should penetrate throughout the crystal whilst also minimising sample decay. In line with these theories and our own observations, the excitation wavelength for [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)] was optimised by moving further into the tail of the dominant absorption band, and a value of $\lambda=500$ nm was selected. Test experiments at this new wavelength yielded promising results and so a full, steady-state photocrystallographic experiment was conducted using 500 nm LED light.

Steady-state photocrystallographic studies with $\lambda=500$ nm

At ambient temperature, crystals of [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)] adopt an 88:22 mixture of nitro/nitrito isomers.[5c] Thus, each crystal used for photocrystallographic studies is cooled slowly from 298 to 100 K to produce the clean, 100% nitro-(η^1-NO$_2$) isomer prior to the photocrystallographic experiments. A slow-cooled crystal is first subject to a full, single-crystal X-ray experiment to confirm the presence of the clean GS, and then irradiated in situ at 100 K using a specifically designed LED ring arrangement, as reported previously.[14] After the illumination period, the light is switched off and a second X-ray dataset collected to determine the photoactivated state. After a total of 2 h irradiation with 500 nm light, full conversion to a 100% *endo*-nitrito-(η^1-ONO) linkage isomer was achieved. This isomer is metastable, remaining present when the crystal is held at 100 K, and adopts an identical MS arrangement to

Table 2. Occupancies of nitro and nitrito isomers, determined from steady-state photocrystallographic data, as a function of irradiation time ($\lambda = 500$ nm) and temperature.

Irradiation time [h]	T [K]	Occupancy Nitro-(η^1-NO$_2$)	Nitrito-(η^1-ONO)
0	100	1.00[a]	0.00[a]
2	100	0.00[a]	1.00[a]
2	140	0.00[a]	1.00[a]
2	150	0.14(1)	0.86(1)
2	160	0.85(1)	0.15(1)
2	170	1.00[a]	0.00[a]
2	180	1.00[a]	0.00[a]

[a] No estimated standard deviations (esd) reported for 1.00 or 0.00 occupancy as these ratios are not refined as free variables.

Figure 3. Kinetic curves describing the decay of the *endo*-nitrito-(η^1-ONO) isomer between 150 and 160 K. Least-squares fitting of $y = \exp(-kt^n)$: at 150 K, $k = 0.08(1)$ h^{-1}, $n = 1.05(7)$, $R^2 = 0.994$; at 152.5 K, $k = 0.15(1)$ h^{-1}, $n = 1.02(1)$, $R^2 = 0.999$; at 155 K, $k = 0.27(1)$ h^{-1}, $n = 1.09(9)$, $R^2 = 0.992$; at 157.5 K, $k = 0.48(1)$ h^{-1}, $n = 0.92(3)$, $R^2 = 0.999$.

that depicted in Figure 1. Variable-temperature parametric studies also indicate that the system reverts to the majority GS nitro-(η^1-NO$_2$) isomer at approximately 160 K (Table 2), behaviour that is comparable to that of the MS isomer induced with 400 nm radiation.[5c] This suggests that the same MS state is induced in the system by using both wavelengths.

Decay kinetics

Although the parametric studies indicate that the MS limit exists at approximately 160 K, it is interesting to note that there is a small temperature range over which the system reverts back to the GS arrangement, with the onset of *endo*-nitrito-(η^1-ONO) decay occurring at 150 K (Table 2). As these values are refined from full, time-averaged X-ray datasets, it is not possible to determine whether the *endo*-nitrito occupancies at 150 K and 160 K represent an excited-state population that is static for the duration of the experiment (ca. 4 h). It is possible instead that the system is no longer truly metastable by 150 K and the *endo*-nitrito isomer is actually decaying during the data collection. If this is the case then the refined occupancies are in fact an average of the decaying population over the full experiment time. To study the decay behaviour of the MS state more carefully, decay experiments were conducted at temperatures between 150 and 160 K, using the same crystal. For each experiment, the crystal was first slowly cooled to 100 K and irradiated with 500 nm light for 2 h before a dataset was collected to confirm full excitation to the 100% *endo*-nitrito-(η^1-ONO) isomer. The crystal was then warmed and the data collection started as soon as the required temperature was reached. A separate kinetic experiment was conducted at each of five temperatures; 150, 152.5, 155, 157.5 and 160 K. Each experiment was run for approximately 20 h and within this time the unique data set was recorded four times. This allowed a full single-crystal refinement to be conducted at four time intervals during the decay experiment, and the nitro/nitrito ratio to be determined crystallographically at each of these time points. For each of the five temperatures a decay curve was then constructed, which is a plot of *endo*-nitrito-(η^1-ONO) occupancy versus time (Figure 3). Figure 3 confirms that the photoactivated *endo*-nitrito-(η^1-ONO) isomer is no longer metastable above
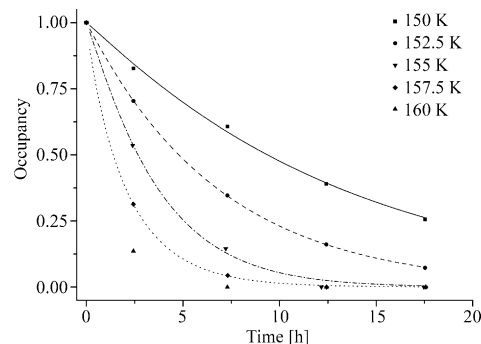
150 K and shows that the decay process is accelerated with increased temperature. The decay is not exponential, but instead the curves are better approximated by a sigmoidal function for all temperatures. A number of studies investigating the progress of photochemical reactions in single crystals with time have employed Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory to model the kinetic behaviour of the excitation.[15] The general Equation (1) of JMAK analysis,

$$\alpha(t) = 1 - \exp(-kt^n) \quad (1)$$

also produces a sigmoidal-shaped curve, making it an attractive choice to model the kinetic behaviour of this type of solid-state photochemical process. $\alpha(t)$ is defined as the "conversion fraction", that is, the amount of the system converted to the excited state at a time, t. If photoactivation in single crystals is well modelled by JMAK theory, it is likely that the decay process of the photoexcited state might occur by a similar mechanism. Therefore, the current decay data have been fitted with a modified JMAK equation,[15c] allowing the initial and final nitrito occupancies to be parameterised [Eq. (2)]:

$$\alpha(t) = \alpha_f - (\alpha_f - \alpha_0)\exp(-kt^n) \quad (2)$$

where k = rate constant, n = order of reaction (or "Avrami constant"), $\alpha(t)$ = nitrito occupancy at time t, α_0 = initial nitrito occupancy and α_f = final nitrito occupancy. The value of n describes the dimensionality (D) of the growth of the decayed phase, where [Eq. (3)]

$$D = n - 1 \quad (3)$$

Thus, a value of $n = 2$ indicates 1-D growth of the phase, $n = 3$ indicates 2-D growth, etc. $n = 1$ suggests a homogeneous transformation where there is equal probability of an event occurring throughout the material.[15d] As [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)] undergoes complete conversion between isomers, $\alpha_f = 0$ and $\alpha_0 = 1$, and the expression simplifies to [Eq. (4)]
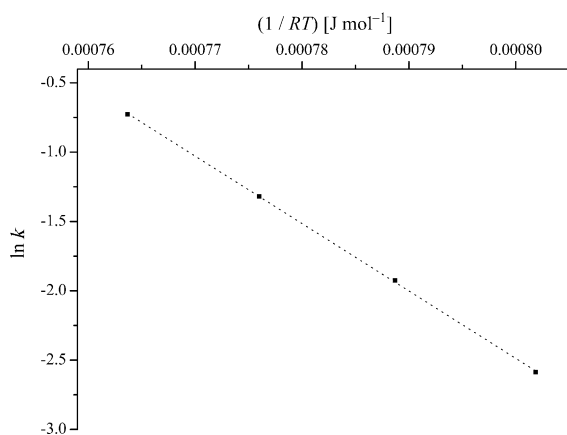
$$\alpha(t) = \exp(-kt^n) \quad (4)$$

Figure 4. Plot of ln(k) versus (1/RT) for kinetic data following nitrito-(η^1-ONO) isomer decay between 150 K and 160 K, E_{act} (−slope) = +48.6(4) kJ mol^{-1}, R^2 = 0.999.

The data in Figure 3 show very good agreement with [Eq. (4)], producing a value of $R^2 > 99\%$ in all cases. The value of n is refined to be close to unity at all temperatures fitted, indicating homogeneous decay of the *endo*-nitrito-(η^1-ONO) isomer throughout the crystal. Unfortunately, regression analysis could not be completed with the data obtained at 160 K as there are too few data points before full decay to the GS arrangement is achieved.

The rate constants, k, obtained at each temperature fitted were used to obtain an estimate of the activation energy E_{act} for *endo*-nitrito-(η^1-ONO) decay (Figure 4). An Arrhenius plot of the data (ln(k) versus (1/RT), where R = molar gas constant, 8.314 J K^{-1} mol^{-1}) produces a straight line, the gradient of which represents E_{act}. The calculated value of E_{act} was +48.6(4) kJ mol^{-1}, indicating an endothermic process as expected owing to the input of thermal energy (i.e., warming) required for decay to proceed. This result is in agreement with activation energies found in the literature for similar solid-state transformations: in 2010, Cao et al. reported an activation energy of 32.5 kJ mol^{-1} for the photodimerisation of 1,4-dimethyl-2-pyridinone.[15b] Additionally, a recent study by Dumont et al. reports a value of E_{act} = 46 kJ mol^{-1} for cyanide–isocyanide linkage isomerism in iron(II) hexachromate(III) nanoparticles from kinetic data obtained by FTIR measurements.[16] While this comparable energy is calculated for the bulk material, the authors report that the value of E_{act} is highly dependent on the size of the nanoparticles. This highlights how important it is that the current analysis was completed using the same single crystal for every set of data collection.

Pseudo-steady-state photocrystallographic studies

The dramatic increase in the decay rate observed between 150 and 160 K shows that the lifetime of the ES *endo*-nitrito-(η^1-ONO) isomer can be controlled by varying the experiment temperature. This suggests that a spectrum of isomer lifetimes should exist in such systems with longer lifetimes at low temperatures where MS species appear prevalent, to hour/minute lifetimes close to the MS limit, then to more transient linkage

isomers at higher temperatures. This hypothesis is supported by recent work by Woike et al., reporting the observation of nitrosyl linkage isomers with nanosecond lifetimes in single crystals of sodium nitroprusside, at room temperature, by time-resolved absorption spectroscopic measurements using pump-probe techniques.[17] For time-resolved studies with such systems, it should therefore be possible to select the appropriate lifetime of the transient isomer to suit the timeframe of the experimental set-up, simply by controlling the temperature. With this in mind, a series of pseudo-steady-state photocrystallographic experiments were undertaken on [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)], where the sample was continuously pumped by a light source during data collection. Particular focus was given to temperatures close to the MS limit.

Pseudo-steady-state photocrystallographic experiments were first conducted on the Beamline I19 at the Diamond Light Source, UK,[18] in Experimental Hutch 2. Sample irradiation was conducted by using a Vibrant OPO Nd:YAG laser, pumped at 355 nm and tuned to λ = 500 nm, the laser being focussed directly at the crystal position of the diffractometer to allow continuous irradiation of the sample throughout the experiment. Data collections were then conducted for a series of temperatures between 100 and 250 K. As expected from steady-state results, 100% photoconversion was achieved at lower temperatures, with the occupancy of the *endo*-nitrito-(η^1-ONO) isomer decreasing as the temperature was raised. Whilst the corresponding increase in the GS nitro isomer is also observed, the behaviour of these two isomers is not identical to that determined by steady-state methods. The *endo*-nitrito-(η^1-ONO) isomer is present over a wider temperature range in the pseudo-steady-state studies, still detectable at temperatures as high as 190 K (Table S1), whereas no trace of this ES isomer is found in the steady-state data collected at the same temperature. In addition, between 155 and 185 K, that is, very close to the MS limit, new difference electron density peaks could be observed that correspond to the production of a new, *exo*-nitrito-(η^1-ONO) linkage isomer, not observed previously in steady-state experiments using either 500 or 400 nm radiation (Figure 5).

To validate these observations, experiments were repeated with 500 nm LED light on a larger crystal, by using the specially designed LED ring arrangement.[14] This facilitates continuous illumination of the sample during data collection. These laboratory-based experiments were conducted on the same single crystal as used for the steady-state experiments with 500 nm LED light reported above. Excepting a small, systematic discrepancy in temperatures between the two pseudo-steady-state datasets, the results are reproducible between the two methods indicating that the new, *exo*-nitrito ES isomer cannot be the product of non-linear processes, such as two-photon excitation, which might have been induced by the higher incident flux available with laser irradiation. The temperature discrepancy between the two pseudo-steady-state experiments could be attributed to the differing sizes of the crystals, as this has been reported to have an effect on the progress of isomerisation processes in other single-crystal studies.[16] Figure 6 shows that, with this slightly larger crystal, the new *exo* isomer
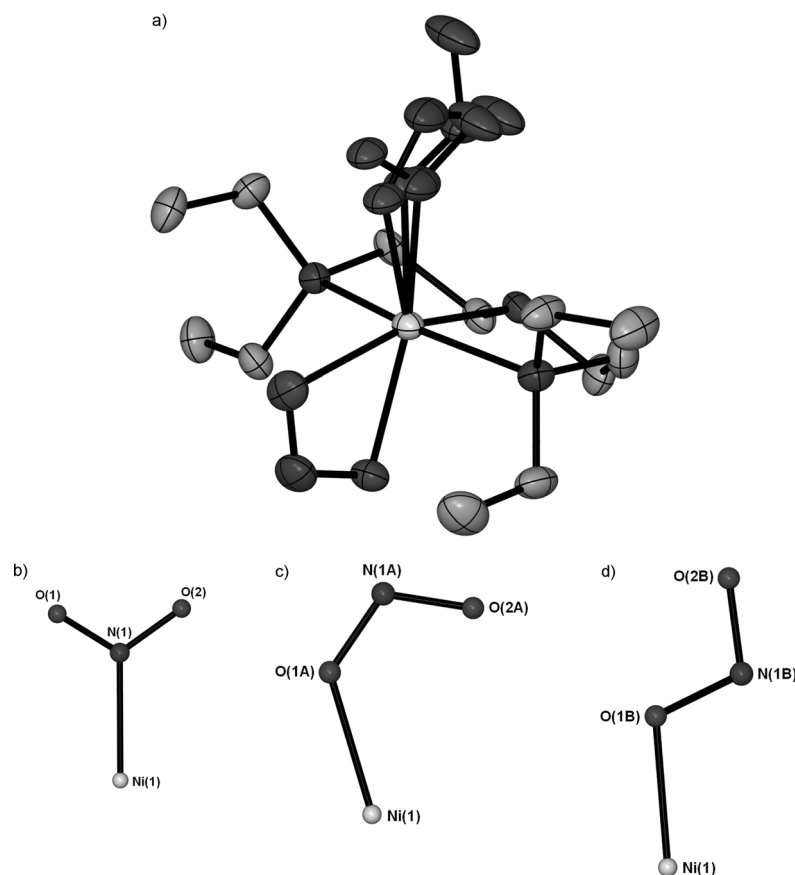
Figure 5. (a) Single-crystal X-ray structure showing the atomic arrangement determined in pseudo-steady-state experiments at 155–185 K, ellipsoids at 50% probability and hydrogen atoms removed for clarity; Individual atomic arrangements for (b) GS nitro, (c) ES *endo*-nitrito and (d) ES *exo*-nitrito linkage isomers.
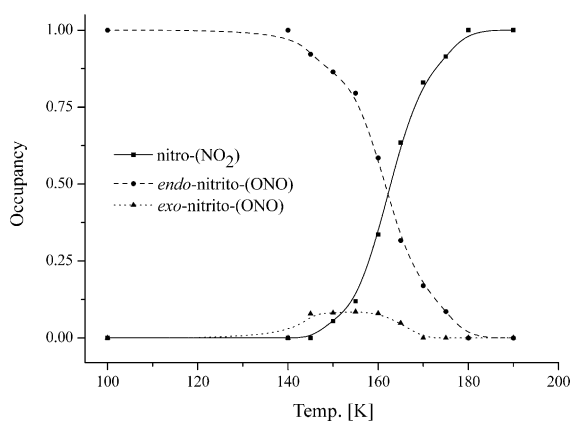

Figure 6. Nitrite isomer occupancies, determined in pseudo-steady-state experiments with [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)], as a function of temperature.

is detectable between 145 and 165 K, with a maximum occupancy of 8.5(1)% achieved at 155 K. The fact that the *exo*-nitrito arrangement is only detected under pseudo-steady-state conditions indicates that it is a transient isomer, with a lifetime too short to be observed by standard, time-averaged X-ray techniques. Under pseudo-steady-state conditions, however, continuous optical pumping retains the *exo* isomer at a high

enough occupancy level that it can be refined from the diffraction data.

Conclusion

Crystals of [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)] show complicated photoinduced linkage isomerism on excitation across a range of temperatures. At low temperatures ($<$150 K) photoactivation produces 100% conversion to a metastable *endo*-nitrito-(η^1-ONO) isomer; whereas, on warming the system above 150 K, this isomer decays to the nitro-(η^1-NO$_2$) GS. Decay experiments show that the lifetime of this ES *endo*-nitrito isomer is temperature dependent, with the rate of decay increasing on warming. An activation energy of $+48.6(4)$ kJ mol^{-1} was determined for the decay process between 150 and 160 K, where the isomer lifetime is now reduced to be on a timescale of a few hours. Of particular interest is the observation of a new, transient *exo*-nitrito linkage isomer during pseudo-steady-state photocrystallographic experiments, using both laser and LED irradiation at $\lambda = 500$ nm. To the best of the authors' knowledge this is the first observation of an ES *exo*-nitrito-(η^1-ONO) isomer under such conditions and the results open up the opportunity to investigate linkage isomers over a range of different timescales, merely by careful control of the experiment temperature.

Experimental Section

Synthesis of [Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)]

[Ni(Et$_4$dien)(η^2-O,ON)(η^1-NO$_2$)] was synthesised by a modified literature procedure.[17] Potassium hexanitronickelate(II) monohydrate[20] (0.51 g, 1 mmol) was suspended in methanol (25 mL) and treated with stoichiometric amounts of *N,N,N',N'*-tetraethyldiethylenetriamine (0.26 mL, 1 mmol). The reaction mixture was stirred for 2 h, during which time the initially orange suspension dissolved to a dark green solution. The mixture was concentrated in vacuo to approximately. 5 mL and the green crystalline precipitate was isolated by filtration. Crystals were obtained by slow evaporation of a methanolic solution. Yield: 90% (0.55 g, 1.50 mmol). FTIR: (NO$_2$) $\tilde{v} = 1363$, 1208, 974 cm^{-1}, (NH) $\tilde{v} = 3238$ cm^{-1}; UV/Vis (single crystal): $\lambda_{max} = 646$, 366 nm; elemental analysis calcd (%) for C$_{12}$H$_{29}$N$_5$Ni$_1$O$_4$ (366.08): C 39.37, H 7.98, N 19.13; found: C 39.20, H 8.10, N 19.32.

X-ray crystallography

At the University of Bath, single-crystal X-ray diffraction data were recorded on an Agilent Technologies Gemini A Ultra CCD diffractometer, using monochromatic radiation, $\lambda = 0.71073$ Å. The sample temperature was controlled by using an Oxford Diffraction Cryojet apparatus. On the Beamline I19 at Diamond Light Source,[18] data were recorded by using a Newport diffractometer equipped with an Agilent Technologies Atlas CCD detector, and the sample temperature was controlled by using an Oxford Cryosystems Cobra Cryostream. The program CrysAlis Pro was used for collecting frames of data, indexing reflections and determining lattice parameters. Structures were solved by Direct Methods using SHELXS-86[21] and refined by full-matrix least-squares on F^2 using SHELXL-97.[22] In photocrystallographic studies, excited-state species were treated as a disorder model, allowing the occupancies for each linkage isomer to be refined freely from the diffraction data by using free variables. Figures showing the atomic arrangement determined from single-crystal X-ray data were created by using POV-Ray v3.6[23] and crystal packing diagrams by using Mercury.[24] At the University of Bath, sample illumination was achieved by using six 500 nm LEDs (1200 mcd, 3.5 V, 20 mA), positioned 1 cm from the crystal. On I19, illumination was achieved with a Vibrant OPO Nd:YAG laser, pumped at 355 nm and tuned to 500 nm. The pulsed system operates at 10 Hz, with a pulse width of 6–7 ns. The laser was attenuated by an aperture, producing an output of 0.5 mJ per pulse after the aperture. The beam was guided through a fibre optic cable and focussed onto the sample position. CCDC 968636–968655 contain the supplementary crystallographic data for all structures in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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