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Isomerization

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Metastable Linkage Isomerism in [Ni(Et$_4$dien)(NO$_2$)$_2$]: A Combined Thermal and Photocrystallographic Structural Investigation of a Nitro/Nitrito Interconversion**

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Photocrystallography is a rapidly developing technique that enables the full three-dimensional structure of a molecule in a metastable or excited state to be elucidated when a single crystal of the complex is photoactivated by visible or UV light.[1] Pioneering work in the areas of both molecular and macromolecular photocrystallography has allowed the crystallographic characterization of species with microsecond and sub-microsecond lifetimes.[2,3] Of equal importance are the detailed studies on the identification and stabilization of metastable species[4,5] because of potential photorefractive applications, including data storage and optical switching.[6] This area has been pioneered by Coppens et al., and they, and others, have now successfully determined the structures of a number of metastable species including several transition-metal–nitrosyl, –nitro, and –SO$_2$ complexes.[7–9]

A major limitation in the study of these systems has been the relatively low level of conversion from the ground state to the metastable state that can be achieved in the single crystal. Controlled, complete reversible interconversion is desirable if these materials are to find real applications as optical switches or in data-storage devices. Examples of high conversions into metastable species are rare; however, notable studies include the first example of a reversible 100 % conversion of the nickel(II)–nitro complex [Ni(dppe)(η^1-NO$_2$)Cl] (dppe = 1,2-bis(diphenylphosphino)ethane) into the nitrito isomer [Ni(dppe)(η^1-ONO)Cl] when irradiated with UV light-emitting diodes (LEDs)[10] at temperatures below 160 K. A 92 % light-induced conversion from the η^1-NO isomer to the η^1-ON bound isomer of [Ru(py)$_4$Cl(NO)]$^{2+}$ (py = pyridine) also occurs upon irradiation with light of wavelength 473 nm at 80 K.[11] In both these systems, and in systems with lower percentage conversions, once some threshold temperature is reached the structure reverts to the ground-state conformation and no further changes are observed on raising the temperature further.[8,10]

In contrast to photoactivated linkage isomerism, thermally activated linkage isomerism in solution has been known since the time of Alfred Werner. However, single-crystal studies on thermally activated systems remain rare. In a series of solid-state studies on systems with the general formula [NiL$_2$(NO$_2$)$_2$], where L is an N-substituted ethylenediamine ligand, Laskar et al.[12] report the irreversible thermal conversion of [Ni(dipropylethylenediamine)$_2$(NO$_2$)$_2$] from its nitro-(η^1-NO$_2$) isomer into a nitrito-(η^2-O,ON) isomer at room temperature, with displacement of the second nitro ligand. The authors report that conversion is accelerated by higher temperatures, although no crystallographic data of the high-temperature structure was recorded.

We now report the thermal and photoactivation of single crystals of the complex [Ni(Et$_4$dien)(NO$_2$)$_2$] (Et$_4$dien = *N*,*N*,*N*′,*N*′-tetraethyldiethylenetriamine) which, uniquely, undergoes reversible nitro–nitrito linkage isomerism following exposure to either UV light and heat.

The complex [Ni(Et$_4$dien)(NO$_2$)$_2$] was prepared following a modified literature procedure for [NiL$_2$(NO$_2$)$_2$] complexes,[12] and green, platelike crystals were obtained after slow evaporation from methanol (Scheme 1).

A suitable single crystal was mounted at room temperature on an Oxford Diffraction Gemini A Ultra diffractometer and a X-ray data set collected in the absence of light. The structure was solved and refined (structure **1**; Figure 1): at 298 K the complex crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. The metal center adopts a pseudo-octahedral geometry, with the tridentate ligand bound in a meridional arrangement and one nitro ligand bound as nitrito-(η^2-O,ON). The second nitro ligand occupies the remaining coordination site and is disordered, with the major 78 % component adopting the nitro-(η^1-NO$_2$) configuration (isomer **A**) and the minor 22 % component the nitrito-(η^1-ONO) configuration (isomer **B**).

The discovery of this "mixed" nitro/nitrito ground state under ambient conditions suggested the potential for linkage isomerism. Flash-cooling a crystal to 100 K using an Oxford Diffraction cryojet produced the same mixed structure

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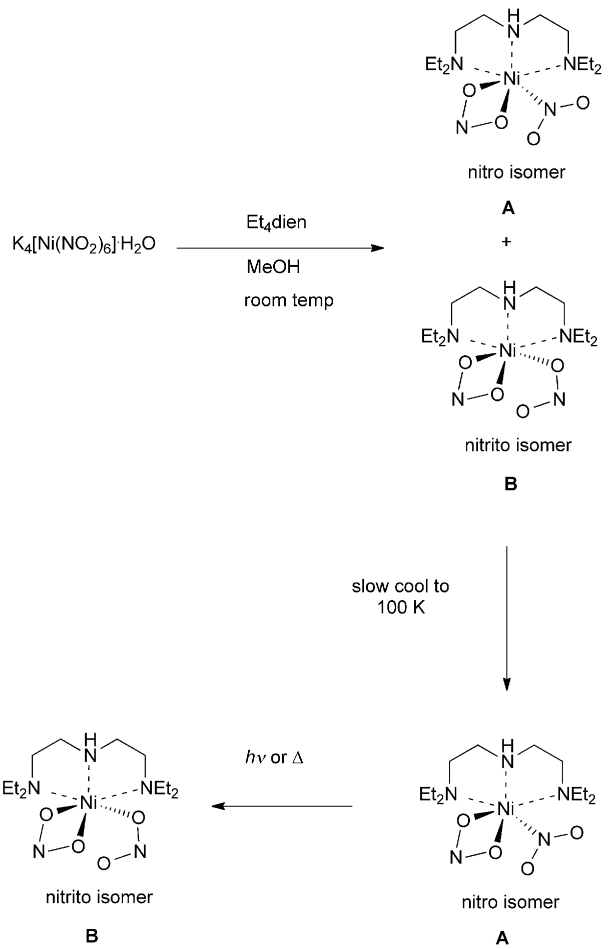


Scheme 1. Synthesis of isomers **A** and **B**.

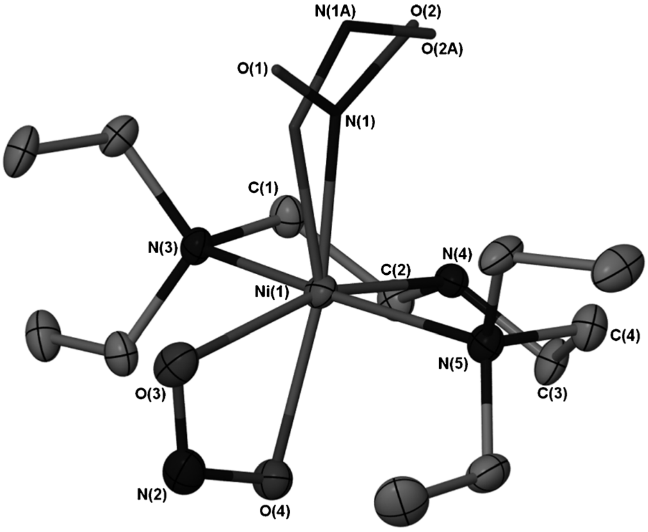
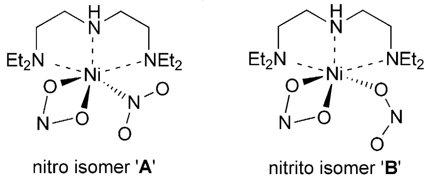


Figure 1. Molecular structure of [Ni(Et$_4$dien)(NO$_2$)$_2$] at 298 K (structure **1**). The two isomers **A** (nitro) and **B** (nitrito) are present in a 78:22% ratio. Hydrogen atoms are removed for clarity and thermal ellipsoids are set at 50% probability, except for the nitro and nitrito group which have been shown as sticks to improve clarity.

Table 1: Crystallographically determined ratios of isomers **A** and **B** in a single crystal as a function of temperature.



T/K	Isomer **A** [%]	Isomer **B** [%]
298	78	22
233	90	10
100	100	0
298[a]	78	22
350	64	36
370	58	42

[a] Reheating.

(structure **2**) with identical occupation of each isomer, thus indicating that the "mixed" state had been "frozen" into the structure. The crystal was next slowly cooled from 298 K to 100 K at a rate of 1 K min^{-1}, in the dark, in situ on the diffractometer. The cooling process was paused at regular intervals and identical data collections were conducted to monitor the relative occupancies of the nitro-(η^1-NO$_2$) and nitrito-(η^1-ONO) isomers (Table 1). At 233 K, the nitrito-(η^1-ONO) component had decreased to 10% (**B**) with the remaining 90% present being the nitro-(η^1-NO$_2$) isomer (**A**; structure **3**), and further cooling below 160 K resulted in the complete removal of the nitrito-(η^1-ONO) component to yield a "clean" nitro-(η^1-NO$_2$) linkage isomer **A**. The slow-cooled structure obtained at 100 K (Figure 2, structure **4**) retains the same space group as the mixed structure at 298 K, and analysis of the intermolecular interactions in both structures using the program CrystalExplorer[13] confirms that the crystal packing is largely unchanged, excluding the isomerization (see the Supporting Information).

These observations allude to a thermally controlled equilibrium between the two isomers **A** and **B**. At low temperatures (specifically 100 K and below), and significantly in the absence of light, the position of the equilibrium is such that the nitro isomer **A** is the only isomer present in the crystals. Isomer **A** can, therefore, be considered to be the thermodynamic ground-state configuration.

Increasing the temperature of the crystal to 233 K, 298 K, 350 K (structure **5**), and 370 K (structure **6**) induced a shift in the equilibrium position such that the percentage of isomer **B** present in the single crystal increased to 10%, 22%, 36%, and 42%, respectively (Table 1). At temperatures above 370 K, the crystal decomposed to such an extent that crystallinity was irretrievably lost.

Photocrystallographic studies were next undertaken on the slow-cooled clean nitro-(η^1-NO$_2$) isomer at 100 K. Using a specifically designed LED ring[14] that positioned six 400 nm LEDs 1 cm from the sample, the crystal was irradiated in situ for a period of 1 h at 100 K. The subsequent X-ray data set showed that a photochemical linkage isomerization reaction had occurred with, remarkably, 86% of the crystal now converted into the nitrito-(η^1-ONO) isomer **B**. The Fourier electron density difference map between the starting clean

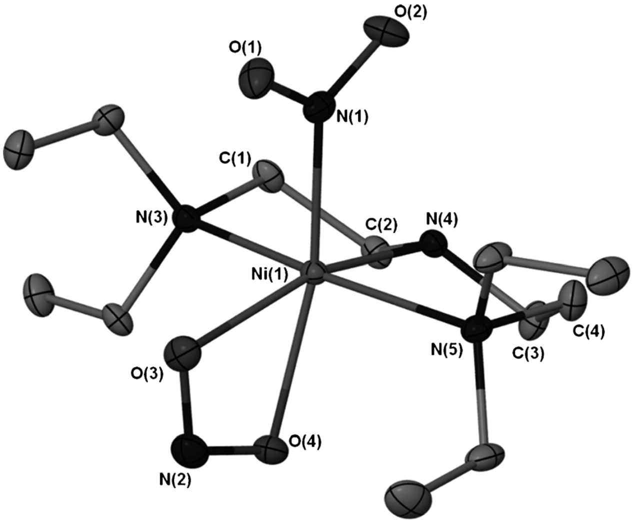
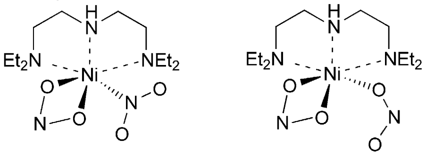


Figure 2. Structure **4**: structure of the "clean" nitro-(η^1-NO_2) isomer (**A**) of [Ni(Et_4dien)(NO_2)$_2$] with thermal ellipsoids set at 50% probability and hydrogen atoms removed for clarity.

nitro-(η^1-NO_2) structure (isomer **A**) and the photoexcited data clearly shows the increased occupation of the nitrito-(η^1-ONO) (isomer **B**) component in the metastable state, and confirms that both components lie in the same plane (see the Supporting Information). An analysis of the displacement ellipsoids for the nitrite components shows no trend in shape or directionality that would suggest a pathway for the isomerization reaction. This is perhaps not surprising since in this study it is the structures of photostationary states that are being determined. Further irradiation at 100 K caused no appreciable change in the conversion level, thereby confirming that the photostationary point had been achieved. The conversion levels for all the photoexcitation experiments conducted for the complex are summarised in Table 2.

Again, the space group and crystal packing remain largely unchanged excluding the isomerization. In addition to analysis with CrystalExplorer,[13] a summary of the intermolecular contacts around the nitrite ligand for the ground and photoexcited states (included in the Supporting Information) support this observation. Analysis of the void spacing in all seven structures was also conducted with the program Mercury.[15] Employing the default limits that a volume with a void radius greater than 1.20 Å constitutes a void indicates that no significant void space is present in any of the structures.

Table 2: Crystallographically determined ratios of isomers **A** and **B** in a single crystal as a function of exposure time to 400 nm wavelength radiation and temperature.



t/h	*T*/K	Isomer **A** [%]	Isomer **B** [%]
0	100	100	0
1	100	14	86
2	100	14	86
2	140	23	77
2	160	33	67
2	180	100	0

To determine if the species is truly metastable, variable-temperature photocrystallographic parametric studies were undertaken. Although a slight decrease in the conversion level was observed, the nitrito-(η^1-ONO) component exists on warming up to 160 K, above which the system returns to the clean nitro-(η^1-NO_2) isomer **A**. This result confirms that the photochemical isomerization is also a reversible process.

To the best of our knowledge this is the first generation of fully reversible nitro–nitrito linkage isomers in a single crystal, with both light and heat used as the stimulus for excitation. As both phenomena have been shown to occur in the same crystal, the question of whether some common underlying processes are responsible for both thermal and photoexcitation seems pertinent.

These studies both complement and contrast the extensive work on spin-crossover metal complexes which show both thermal and light-induced (LIESST) reversible interconversions between high- and low-spin states.[16] In the case of the spin-crossover systems, it is the size and local coordination geometry of the metal ion that changes, whereas in the present study it is the ligand conformation that interconverts reversibly upon the application of light or heat.

Experimental Section

Single-crystal X-ray diffraction experiments were conducted either on an Oxford Diffraction Gemini A Ultra CCD diffractometer using monochromatic $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), or on a Rigaku Saturn CCD diffractometer ($\lambda = 0.68890$ Å) on Station I19 at the Diamond Light Source.[17] The sample temperature was controlled using an Oxford Diffraction Cryojet apparatus, or using an Oxford Cryosystems Cobra Cryostream at the Diamond Light Source. The programs CrystalClear and CrysAlis Pro were used for collecting frames of data, indexing reflections, and determining lattice parameters, and structures were solved by direct methods using SHELXS-86[18] and refined by full-matrix least-squares on F^2 using SHELXL-97.[19]

The crystals were irradiated using six 400 nm LEDs (350 mcd, 3.7 V, 20 mA) positioned 1 cm from the crystal.

Crystal data (data in common): $C_{12}H_{29}N_5NiO_4$, $M_r = 366.11$, orthorhombic, $P2_12_12_1$, $Z = 4$, green plate. Structure **1**, 298 K: 11.422(5), 11.735(5), 12.972(5) Å, 1738.7(13) Å^3, 298(2) K, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.399$, $\mu = 1.14$, $2\theta_{max} = 58.48°$, 11069 reflections collected, 4137 unique, $R_{int} = 0.0216$, $R_1 = 0.0312$, $wR_2 = 0.0574$. Structure **2**, flash-cooled to 100 K: 11.409(2), 11.677(2), 12.891(3) Å, 1717.5(6) Å^3, 100(2) K, synchrotron, $\lambda = 0.6889$ Å, $\rho_{calcd} = 1.416$, $\mu = 1.154$, $2\theta_{max} = 63.06°$, 21175 reflections collected, 5873 unique, $R_{int} = 0.0665$, $R_1 = 0.0293$, $wR_2 = 0.0674$. Structure **3**, slow-cooled to 233 K: 11.377(5), 11.693(5), 12.918(5) Å, 1718.5(12) Å^3, 233(2) K, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.415$, $\mu = 1.153$, $2\theta_{max} = 58.29°$, 10282 reflections collected, 4058 unique, $R_{int} = 0.0191$, $R_1 = 0.0244$, $wR_2 = 0.0486$. Structure **4**, slow-cooled to 100 K: 11.321(5), 11.613(5), 12.829(5) Å, 1686.6(12) Å^3, 100(2) K, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.442$, $\mu = 1.175$, $2\theta_{max} = 58.36°$, 9827 reflections collected, 4012 unique, $R_{int} = 0.0168$, $R_1 = 0.0197$, $wR_2 = 0.0443$. Structure **5**, 350 K: 11.466(6), 11.792(7), 13.051(7) Å, 1764.6(17) Å^3, 350(2) K, synchrotron, $\lambda = 0.6889$ Å, $\rho_{calcd} = 1.378$, $\mu = 1.123$, $2\theta_{max} = 63.54°$, 23529 reflections collected, 6178 unique, $R_{int} = 0.0414$, $R_1 = 0.054$, $wR_2 = 0.1225$. Structure **6**, 370 K: 11.455(5), 11.799(5), 13.058(5) Å, 1764.8(12) Å^3, 370(2) K, synchrotron, $\lambda = 0.6889$ Å, $\rho_{calcd} = 1.378$, $\mu = 1.123$, $2\theta_{max} = 63.8°$, 23594 reflections collected, 6213 unique, $R_{int} = 0.0478$, $R_1 = 0.0732$, $wR_2 = 0.1369$. Structure **7**, photoexcited: 11.493(5), 11.656(5), 12.808(5) Å, 1715.8(12) Å^3, 100(2) K, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.417$, $\mu = 1.155$, $2\theta_{max} = 58.38°$, 7977 reflections collected, 3976 unique, $R_{int} = 0.0372$, $R_1 = 0.0399$, $wR_2 = 0.0828$. CCDC 817676–817682 contain the supplementary crystallographic data for structures **1**–**7** 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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