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Photocrystallographic Studies on Transition Metal Nitrito Metastable Linkage Isomers: Manipulating the Metastable State

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CONSPECTUS: The design of solid-state materials whose properties and functions can be manipulated in a controlled manner by the application of light is an important objective in modern materials chemistry. When the material changes property or function, it is helpful if a simple measurable response, such as a change in color, can be detected. Potential applications for such materials are wide ranging, from data storage to smart windows. With the growing emphasis on solid-state materials that have two or more accessible energy states and which exhibit bistability, attention has turned to transition metal complexes that contain ambidentate ligands that can switch between linkage isomeric forms when activated by light. Suitable ligands that show promise in this area include nitrosyls, nitro groups, and coordinated sulfur dioxide molecules, each of which can coordinate to a metal center in more than one bonding mode. A nitrosyl normally coordinates through its N atom (η^1-NO) but when photoactivated can undergo isomerism and coordinate through its O atom (η^1-ON). At a molecular level, converting between these two configurations can act as an "on/off" switch. The analysis of such materials has been aided by the development of photocrystallographic techniques, which allow the full three-dimensional structure of a single crystal of a complex, under photoactivation, to be determined, when it is in either a metastable or short-lived excited state. The technique effectively brings the dimension of "time" to the crystallographic experiment and brings us closer to being able to watch solid-state processes occur in real time.

In this Account, we highlight the advances made in photocrystallography for studying solid-state, photoactivated linkage isomerism and describe the factors that favor the switching process and which allow complete switching between isomers. We demonstrate that control of temperature is key to achieving either a metastable state or an excited state with a specific lifetime. We draw our conclusions from published work on the formation of photoactivated metastable states for nitrosyl and sulfur dioxide complexes and from our own work on photoactivated switching between nitro and nitrito groups. We show that efficient switching between isomers is dependent on the wavelength of light used, on the temperature at which the experiment is carried out, on the flexibility of the crystal lattice, and on both the electronic and steric environment of the ambidentate ligand undergoing isomerism. We have designed and prepared a number of nitro/nitrito isomeric metal complexes that undergo reversible 100% conversion between the two forms at temperatures close to room temperature. Through our fine control over the generation of the metastable states, it should be possible to effectively "dial up" a suitable temperature to give a metastable or an excited state with a desired lifetime.

INTRODUCTION

Modern solid-state photochemistry commenced in the 1960s with the pioneering work of Cohen & Schmidt on irreversible [2 + 2] photodimerizations of *trans*-cinnamic acids, which provided the impetus for much of the work that has followed.[1] Their *topochemical postulate* proposed that because of the restrictions imposed by the crystal lattice, the reaction will follow a minimum energy pathway, undergoing the smallest amount of atomic movement possible in order to preserve the crystalline environment. The precept of the stabilizing effect of the crystal lattice has remained at the center of solid-state photochemistry ever since, although the idea is largely qualitative. Later, Cohen introduced the idea of the *reaction cavity* as a more quantitative means of defining the changes that occur within a crystal as a result of photoactivation.[2] Because molecules that will directly undergo a solid-state photochemical reaction occupy a space of a certain size and shape in the starting crystal, the reaction cavity can be defined as the contact surface of molecules within the cavity with surrounding molecules in the crystal lattice. The topochemical postulate can then be interpreted to mean that reactions that occur under lattice control do so with minimal distortion of the surface of the reaction cavity. Ohashi subsequently showed that the reaction cavity displayed flexibility through the process of the reaction, and that changes in temperature could significantly affect the reaction; lowering the

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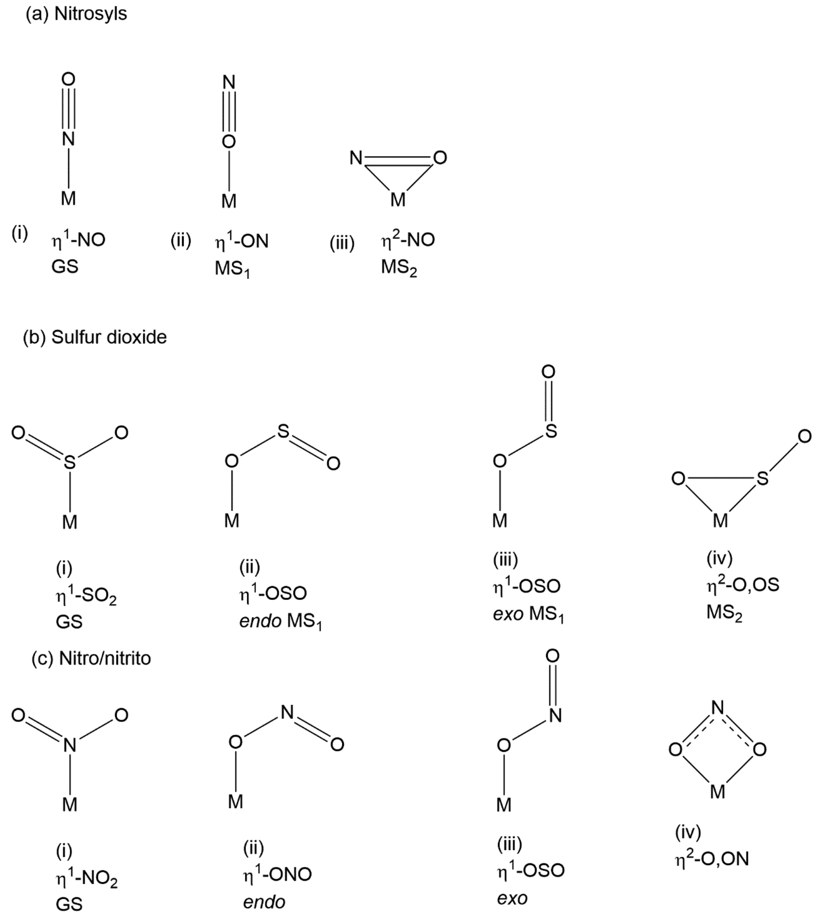

Figure 1. Selected isomeric configurations for (a) nitrosyls, (b) sulfur dioxide, and (c) nitro/nitrito ligands.

temperature caused lattice contraction, reducing the cavity size and thus "switching off" the reaction.[3]

In order to understand the mechanism of reactions in the solid state, it would be enormously useful to watch reactions as they occur and to "see" the reaction intermediates in real time, using single-crystal crystallographic techniques, where the full three-dimensional picture of the structure is obtained. This was not possible in the early developments of the field of solid-state photochemistry, and only the structures of the starting material and reaction products could be determined.[1] However, since then, many technological developments including the availability of high-intensity X-ray synchrotron[4−6] sources, cryogenic technologies,[7,8] high-power lasers,[9] and increased computing power have made the study of solid-state chemical processes in real time, using crystallographic methods, a possibility. The term *photocrystallography* was coined by Coppens to mean the determination of the full three-dimensional structure of a molecule in a metastable or excited state (ES) generated by light irradiation.[10,11] The original definition was applied to single-crystal X-ray diffraction studies under photoactivation. However, the term is now loosely used to refer to photoactivated time-resolved single-crystal and powder diffraction studies where the ES species has a finite lifetime (minutes to picoseconds) or is metastable, in that there is no discernible decay of the ES species over the lifetime of the crystallographic experiment.[12,13] The ES lifetime is temperature dependent, with the lifetime increasing continuously as the measurement temperature is reduced.[14] The term *metastable limit* is used generally to describe a critical temperature above which the ES lifetime is shorter than the measurement time scale. For the photocrystallographic experiments described in this Account, we focus on single-crystal studies, in which the processes are reversible, either with the ES decaying back to the ground state (GS) in a short time or when the temperature is raised above the metastable limit.

A. MOLECULAR PHOTOCRYSTALLOGRAPHY

The pioneering work on molecular photocrystallography was carried out by Coppens. He applied photocrystallographic methods to linkage isomers; these are coordination complexes that contain ambidentate ligands that can coordinate to the metal center in more than one coordination mode. Examples of these ligands include: nitrosyl groups (NO), which can coordinate through either the nitrogen atom or the oxygen atom; nitro groups (NO_2), which can also coordinate either through the nitrogen or one or both of the oxygen atoms; and sulfur dioxide (SO_2), which can coordinate to the metal through either the sulfur or one of the oxygen atoms (Figure 1). Crystallographic studies on these ligands are straightforward to carry out, because their coordination modes change upon isomerization, and the new atom positions are identifiable in electron density difference maps even if only partial isomerization occurs. Additionally, the ligands act as good reporter ligands in IR spectroscopy with changes in the ν(N−O) and ν(S−O) stretches and the δ(O−N−O) and δ(O−S−O) bends providing very useful complementary information to the photocrystallographic studies.[15,16]

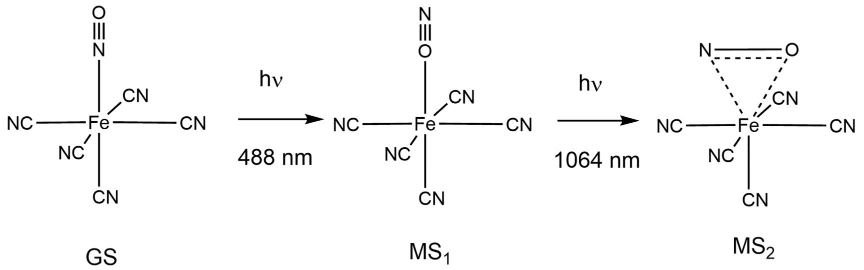

Figure 2. Solid-state linkage isomerism in the SNP anion. The GS η^1-NO nitrosyl transforms to the η_1-ON isonitrosyl and then to the η^2-NO side-bound isomer.

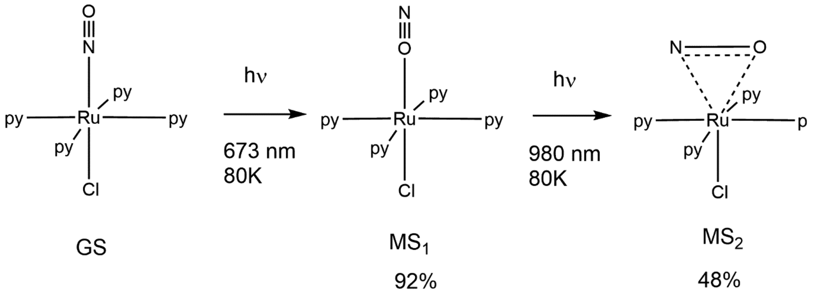

Figure 3. Photoactivated linkage isomerism in $[RuCl(py)_4(NO)][PF_6]_2 \cdot 0.5H_2O$ showing the MS$_1$ and MS$_2$ isomers.

The existence of complexes that display linkage isomerism in solution was established by Jörgensen[17] in the late 19th century. Whereas the first linkage isomeric species were isolated by changing the reaction conditions to favor one isomer over another, conversion between the isomers could be achieved by applying energy from an external source (e.g., heat or light). Later spectroscopic studies indicated that the isomerization process occurred in the solid state, particularly if the structural rearrangements were modest.

The fact that linkage isomerism occurs in the solid state inspired the idea that, with their two stable equilibrium states, these compounds might act as solid-state molecular switches with one isomer representing the "on" position and the other in the "off" position. This possibility suggests applications as photochromic and photorefractive materials for use in nonlinear optics and holographic data storage[18−20] as well as in developing a better understanding of processes such as light-induced NO release[21] for photodynamic therapy.[22]

In this Account, we highlight the advances in photocrystallographic studies of metastable linkage isomers and discuss the factors that allow us to manipulate the metastable state of transition metal nitrito complexes.

B. PHOTOCRYSTALLOGRAPHIC STUDIES ON NITROSYL AND SULFUR DIOXIDE LINKAGE ISOMERS

Initial solid-state studies on linkage isomerization involved sodium nitroprusside (SNP). Mössbauer spectroscopy was used to identify the presence of two unexpectedly long-lived isomers when a sample of SNP was irradiated with light.[23] The photoactivated isomers were metastable (MS) at cryogenic temperatures, which is when a given isomer is stable indefinitely at low temperatures but returns to the original GS structure upon warming. A satisfactory explanation for the existence of two metastable isomers for SNP could not be resolved fully until Coppens carried out the first photocrystallographic study in 1997.[11] He established that photoactivation of SNP resulted in a change in the coordination mode of the NO ligand. Irradiation of a single crystal using 488 nm light, at 50 K, resulted in a 37% conversion from the GS (η_1-NO) form to a metastable form, in which the nitrosyl had inverted its coordination mode to link through the oxygen (η_1-ON) (Figure 2). This isomer was designated MS$_1$. The ligand rearrangement was identified from an analysis of the anisotropic displacement parameters of the nitrosyl N and O atoms in the metastable state; they became more physically reasonable when the atomic scattering factors were reversed to give the isonitrosyl form. Subsequently, the same crystal, in the MS$_1$ state, was exposed to 1064 nm light, still at 50 K, and conversion to a new side-on-bound isomer (η_2-NO), designated MS$_2$, occurred. This isomer could be observed at a 10% conversion level.

Coppens expanded the range of ruthenium nitrosyl complexes that showed the formation of metastable linkage isomers under photoactivation, at low temperatures, in the solid-state.[24−26] All the systems showed evidence of the presence of the MS$_1$ and MS$_2$ species. He also showed that other metal nitrosyls exhibited photoactivated linkage isomerism[27] and that dinitrogen ligands displayed "end-on" (η^1-N_2) and metastable "side-on" (η^2-N_2) isomers when irradiated at low temperature with 325 nm light.[28]

In a parallel series of studies, Schaniel and Woike extended the range of photoactive ruthenium nitrosyl and iron nitrosyl linkage isomers studied using powder and single-crystal X-ray diffraction studies coupled with detailed IR and DSC measurements and underpinned by computational studies. Their objective was to establish the factors that governed the level of interconversion between the ground and metastable states. All the systems studied essentially showed the presence of the (η_1-ON) (MS$_1$) and (η_2-NO) (MS$_2$) states under different illumination conditions, at different temperatures. However, conversion levels were generally low in the solid state, below 50%. One exception is a photocrystallographic analysis of $[RuCl(py)_4(NO)][PF_6]_2 \cdot 0.5H_2O$ using laser light of 673 nm, at 80 K, which gave a 92% conversion to MS$_1$ that could then be converted to 48% of MS$_2$ using 980 nm light (Figure 3).[29] Because of the high conversion obtained in this system, a series of related complexes, with the general formula $[RuX(py)_4(NO)][Y]_2 \cdot nH_2O$ with different halides, pyridine ligands, and counterions were studied, and the results from photocrystallography and IR studies were compared. The results showed that the shorter the distance between the counterion and the NO ligand in the GS structure, the higher the population of the photoinduced metastable state obtained. This suggests that the contacts between the counterion and the NO ligand are reduced in the metastable state, reducing unfavorable packing effects within the crystal. It was also established that the lower the donating character of the ligand *trans* to the NO ligand, the higher the photoconversion yield.[30]

Another ambidentate ligand that has been studied photocrystallographically is sulfur dioxide. SO_2 can coordinate to a metal center as illustrated in Figure 1. The most common coordination mode is η^1-SO_2 (Figure 1b, (i)) with the central sulfur atom bonded to the metal. The first evidence for linkage isomerism in transition metal SO_2 complexes came from spectroscopic studies carried out by Johnson and Drew,[31] in solution-based photochemical IR studies on *trans*-$[Ru(NH_3)_4Cl(SO_2)]Cl$, and they observed changes in the $\nu(SO_2)$ upon irradiation with 365 nm light, at 195 K. They attributed these changes to the formation of a photoexcited, metastable, side-bound η^2-(O,SO) isomer (Figure 1b, (iv)), which was later designated as MS_2, to be consistent with the side-bound nitrosyl species described above.

The first crystallographic evidence for the side-bound η^2-(O,SO) linkage isomer was obtained in 2002 when Coppens obtained the structure of the MS_2 isomer from a steady-state photocrystallographic study on *trans*-$[Ru(NH_3)_4Cl(SO_2)]Cl$ using 300−500 nm light at 150 K.[32,33] The first photocrystallographic observation of a second type of SO_2 linkage isomerism occurred in 2006 when Bowes confirmed the presence of a bent η^1-OSO isomer (Figure 1b, (ii)) in $[Ru(NH_3)_4(H_2O)(SO_2)][MeC_6H_4SO_3]_2$ at 13 K, with a maximum conversion level of 36%.[34] This isomer was designated MS_1 by analogy to the η^1-ON arrangement of the nitrosyl ligand.

Photocrystallographic studies on ruthenium−sulfur dioxide complexes were extended to systems with a series of different ligands *trans* to the coordinated SO_2 group and a range of counterions. These showed that the side-bound η^2-(O,SO) isomer was readily formed with the bent η^1-OSO isomer (MS_1) appearing at temperatures below 130 K. The isomerizations were strongly influenced by the environment around the SO_2 group and by the electronic properties of the metal and the *trans* ligand.[32,33,35,36] Again, conversion levels were generally below 50%.

One of the main reasons for undertaking photocrystallographic studies on transition metal linkage isomers is to produce new functional materials for "real world" applications. The crystallographic studies act as benchmarks for the design of polycrystalline or amorphous materials. An obvious application for materials that can undergo photoactivated linkage isomerism is in the optoelectronics industry. Optoelectronic materials can provide light of desired wavelengths and provide binary data storage through their ability to exist in switchable "on/off" states, with, in principle, access to these applications at the molecular level.[37] In this context, photoswitchable hybrid materials have been prepared successfully by embedding guanidinium nitroprusside (GuNP, $(CN_3H_6)_2[Fe(CN)_5(NO)]$) into the mesopores of xerogel monoliths. Irradiation of the structures with blue-green light results in 15% conversion of the (η^1-NO) isomer into the (η^1-ON) isomer.[38] The "fingerprint" of the embedded complex was confirmed by the analysis of neutron powder diffraction data.[39] The effect of the particle size of SNP embedded in silica xerogels has also been investigated using powder diffraction, absorption, and IR spectroscopy. The electronic structure and the activation energies of the metastable isomers appear to be independent of particle size down to a single isolated molecule.[40]

Sulfur dioxide metastable linkage isomers have also shown promise as functional materials. In $[Ru(NH_3)_4(\eta^1\text{-}SO_2)(3\text{-Cl-pyridine})][tosylate]_2$, a phototriggered molecular rotation of one of the counterion tosylate phenyl rings occurs, which can be described as a nanomechanical transduction. The decay of this anionic molecular rotor follows a nontraditional decay path.[41] The complex $[Ru(NH_3)_4(H_2O)(SO_2)][MeC_6H_4SO_3]_2$, which exhibits the side-on (η^2-OSO) coordination mode at temperatures between 100−250 K,[34] has been incorporated into a poly(vinyl alcohol) (PVA) polymer host. This was achieved by the in situ reaction of *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ and *p*-toluenesulfonic acid in the PVA matrix and an in situ precipitating crystallization. Transmission electron microscopy, diffraction, and UV−vis spectroscopy indicated that the photoactivated linkage isomerization was uncompromised by inclusion in polymer thin films.[42] The size of the crystallites was optimized within the polymer, having dimensions between 1 and 10 μm.

C. FACTORS FAVORING THE FORMATION OF SOLID-STATE METASTABLE LINKAGE ISOMERS

An analysis of the data obtained on the NO and SO_2 linkage isomers indicates that there are many complementary and opposing factors that determine whether or not linkage isomerism will occur in the solid-state under photoactivation.

(1) The isomerization is strongly dependent on the wavelength of light used as has been seen for several of the systems;[11,34] changing the wavelength causes one metastable state (e.g., (η_1-ON)) to convert to another (e.g., (η_2-NO)) or to revert to the GS.

(2) The isomerization is also highly temperature dependent, with the metastable isomer reverting to the GS above a certain temperature, and there is a temperature range in which the ES has a finite lifetime.

(3) For the isomerization to occur, the environment around the ligand undergoing the transformation is of key importance. There must be enough flexibility in the crystal lattice for the ligand to move, and intermolecular interactions between the ligand and surrounding groups should not be strong. There is compelling evidence for this in the $[RuX(py)_4(NO)][Y]_2 \cdot nH_2O$[30] and $[Ru(SO_2)(NH_3)_4X]Y$[35] series investigated.

(4) When considering single-crystal photocrystallographic studies, the GS and metastable structures need to be determined, so the isomerization must involve a single-crystal to single-crystal transformation. Therefore, the change in the unit cell dimension must be small so that little strain is placed on the crystal lattice. In all the examples discussed above, the maximum change in cell volume is ca. 2%.

(5) Electronic factors are also important in determining whether or not isomerization occurs. To trigger the photoconversion in the linkage isomers, a metal-to-ligand charge transfer (MLCT) or a d → d transition must occur to change the bond between the ligand and the metal.

This is usually assigned to an M(d) → π*(L) or a M(d) → d_{z2} transition, which changes the σ-bonding to the metal.[43]

(6) In terms of the energy surface of the transformation, the ES potential must exhibit a minimum close to the saddle point of the GS surface between the ground and metastable states or a cross surface, such that the relaxation from an ES into the metastable state can occur (Figure 4).[43]

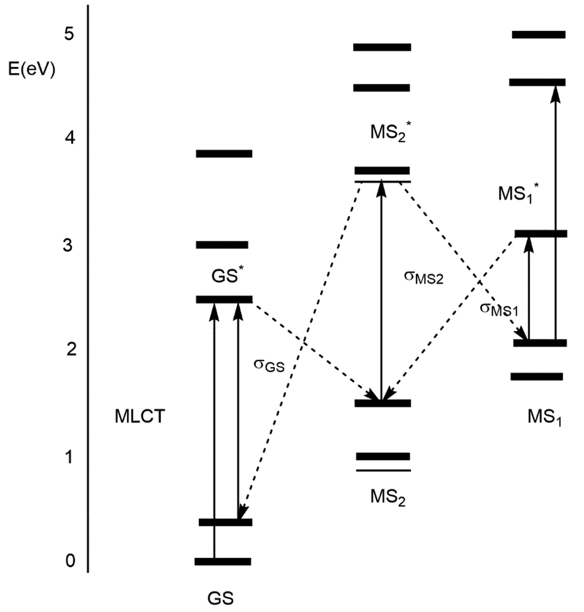

Figure 4. Diagram of the pathway for the formation of a metastable linkage isomer (example for a $ML_5(NO)$ complex).[43] Adapted with permission from ref 43. Copyright (2009) Royal Society of Chemistry.

(7) Because the ground and metastable states will be formally in an equilibrium, depending on factors such as temperature and illumination, the depletion rate of the metastable state must be smaller than its population rate for the metastable state to be maintained.

(8) One of the issues identified is the difficulty in achieving 100% conversion to one or more of the metastable states within the single crystal. The majority of excitation levels are below 50%. In addition to points (1), (2), (3), (5), (6), and (7), above incomplete excitation may be caused by the penetration depth of the light used to photoactivate the crystals, which is of course linked to their size. Light absorbed by the surface layers cannot be transmitted onward and so is not available to excite molecules deeper in the crystal. Typically, single crystals for these experiments have volumes between 0.001−0.06 mm^3. Although X-rays will pass through crystals of this size, the light may be stopped within a few nm of the crystal surface if the wavelength of light used is close to the absorption λ_{max}, which for materials with strong charge transfer bands may have extinction coefficients that exceed 50 000 L mol^{-1} cm^{-1}. This problem can be reduced if the irradiation wavelength is chosen to be in the tail of the absorption peak, and then, the absorption coefficients are reduced below 20 L mol^{-1} cm^{-1}. In the successful experiments where high conversions occur, light of a wavelength in the absorption tail has been used. Lack of penetration also depends on the relative positions of the absorption bands of the GS and ES molecules, because the ES species may absorb the same wavelengths as the GS complex, preventing light from penetrating the crystal fully or causing a reverse reaction.

Only if all or most of the factors are favorable can 100% conversion from the ground to the metastable (excited) state occur. However, complete conversion is important if solid-state linkage isomeric materials are to find real applications as molecular switches.

D. LINKAGE ISOMERS INVOLVING THE NO_2 GROUP

Another ligand that can undergo linkage isomerization in a complex is the nitro group. The NO_2 group can coordinate to a metal center through either the nitrogen atom (η^1-NO_2-nitro) or one or both of the oxygen atoms (η^1-ONO or μ^2-O,ON-nitrito). In the monodentate nitrito form, the ligand can adopt either the *endo* form with the second oxygen pointing toward the metal center or the *exo* form where it points away (Figure 1c). The ambidentate nature of the NO_2 group has been known since the time of Jörgensen[17] with his pioneering studies on $[Co(NH_3)_5(NO_2)]Cl_2$. The solution-state photochemistry of nitro complexes was first established in 1944 when it was found that while individual nitro-((η^1-NO_2) and nitrito-(η^1-ONO)

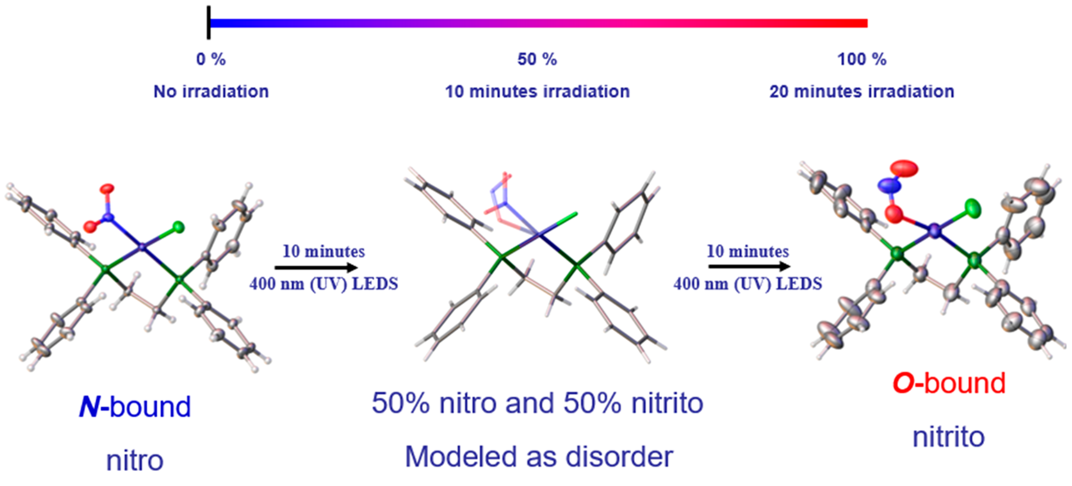

Figure 5. Reversible 100% conversion of $[Ni(dppe)(\eta^1\text{-}NO_2)Cl]$ to $[Ni(dppe)(\eta^1\text{-}ONO_2)Cl]$

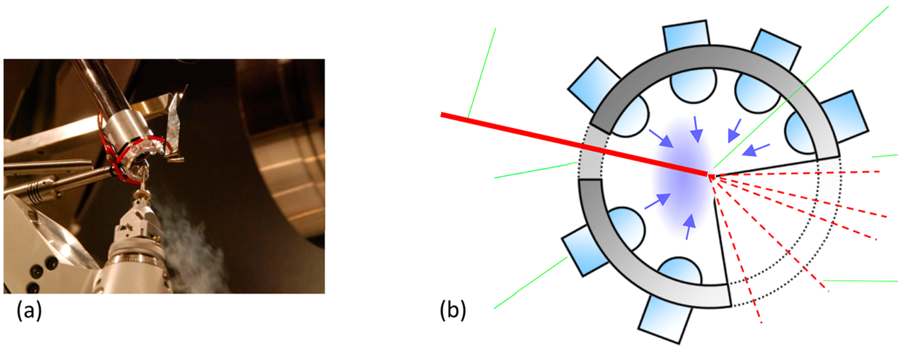

Figure 6. (a) LED holder mounted on diffractometer and (b) schematic showing the six LEDs in a ring 1 cm from the crystal.

isomers could be prepared selectively under specific reaction conditions; conversion between the two forms could be photoinduced by irradiation of the nitro form under UV light.[44] Then in 1979, detailed powder X-ray diffraction studies on microcrystalline samples of $[Co(NH_3)_5(NO_2)]Cl_2$ showed that both thermal and photoactivated nitro−nitrito isomerization occurred.[45,46] By following the gradual shift in peak positions in sequential powder patterns, which reflect the changes in crystallographic cell dimensions associated with the nitro−nitrito conversion, the level of interconversion could be assessed.

Prompted by the photocrystallographic studies on nitrosyl and sulfur dioxide linkage isomers, we began a program to study photoactivated linkage isomerism in metal nitro compounds in 2007. Our dual aim was to design systems that underwent 100% conversion to the nitrito species and that had an isomeric switch that occurred near room temperature so that they might be useful for "real world" applications. The ideas on the design features required for good switchable materials ((1)−(8) above) were being developed during the latter half of the 2000s. Our initial strategy was to use bulky auxiliary ligands that would control the solid-state crystal packing and provide space within the lattice for the nitro → nitrito conversion to occur. We chose $[Ni(dppe)(\eta^1\text{-}NO_2)Cl]$ (dppe = 1,2-bis(diphenylphosphino)ethane) and studied its solid-state photoactivation using a combination of photocrystallographic and Raman methods.[47] The solid-state Raman spectrum recorded at 115 K, under 400 nm light, showed changes in the spectrum consistent with the formation of the nitrito isomer. In a photocrystallographic experiment, irradiation of a single crystal for 20 min with 400 nm LEDs, below 160 K, followed by a data collection without irradiation, resulted in a structure showing 100% conversion from the nitro form to the *endo*-nitrito form (Figure 5). Raising the temperature of the sample above 160 K resulted in the regeneration of the GS structure. This process could be cycled more than 10 times without any observable crystal degradation. In these experiments, we used 400 nm LEDs (Figure 6) as the radiation source rather than lasers.[48] We found the use of LEDs to be advantageous, because any sample heating issues resulting from the use of lasers were substantially reduced.

As a general point, the measure of whether 100% conversion to the metastable species in these studies had been achieved is that in the final, crystallographically obtained, electron density difference map, there should be no residual peaks corresponding to the GS ligand structure, and no significant residual electron density above approximately 1 eÅ^{-3}. At this level, the error on the percentage conversion is less than 5%.

The 100% photocrystallographic nitro → *endo*-nitrito conversion was also achieved by extending the range of the bulky bidentate phosphine ligands used. With 400 nm LEDs, at 100 K, both *cis*-$[Ni(dppe)(NO_2)_2]$ and *cis*-$[Ni(dcpe)(NO_2)_2]$ (dcpe = $Cy_2PCH_2CH_2PCy_2$; Cy = cyclohexyl) showed complete conversion to the metastable nitrito form.[49] Above 180 K, the nitrito isomer reverted to the GS nitro isomer. The presence of other bulky chelating groups also facilitated the complete nitro → *endo*-nitrito conversion.[50]

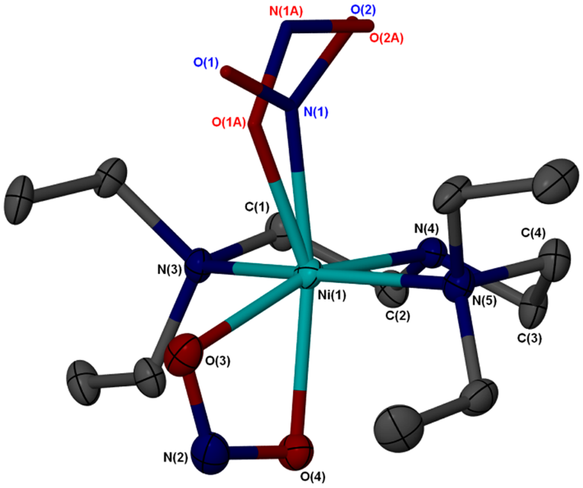

Figure 7. Disordered room temperature structure of $[Ni(Et_4\ dien)(NO_2)_2]$.

An interesting feature of complexes that undergo nitro to nitrito linkage isomerism is that the interconversion can be controlled by temperature as well as by illumination. $[Ni(Et_4\ dien)(NO_2)_2]$ (Et_4 dien = *N,N,N′,N′*-tetraethyldiethylenetriamine) adopts *pseudo*-octahedral structure with the tridentate Et_4 dien ligand in a meridional arrangement with one bidentate nitrito-(η^2-O,ON). The second nitro ligand is monodentate but is disordered at room temperature with the major 78% component adopting the nitro conformation and the minor 22% component in the nitrito conformation (Figure 7).[51] We discovered that slow cooling of a crystal of $[Ni(Et_4\ dien)(NO_2)_2]$ to 160 K resulted in the complete removal of the nitrito component. Warming of the crystal to around 370 K affords an isomer ratio of 58:42 nitro/nitrito. Therefore, there is a thermally controlled equilibrium between the two isomers, and the nitro form can be considered as the thermodynamic GS.[52] In a photocrystallographic experiment with 500 nm LEDs, at 100 K, 100% conversion to the nitrito isomer was achieved

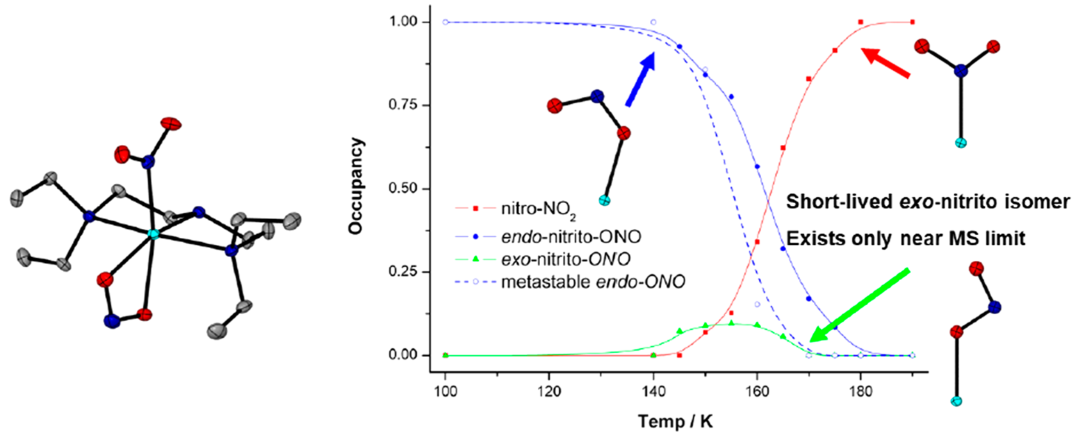

Figure 8. Results of the pseudo-steady-state experiment showing the formation of the transient *exo*-nitrito species (in green).

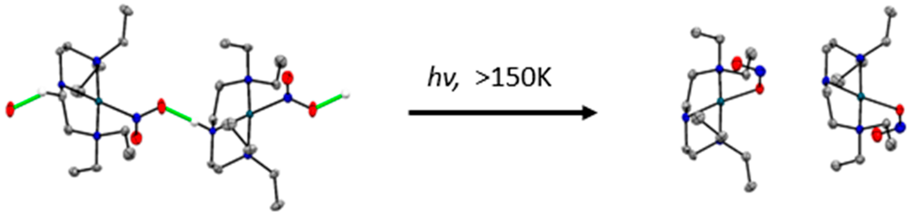

Figure 9. Loss of hydrogen bonding in [Pd(Et$_4$ dien)(NO$_2$)][OTf] as the temperature is increased to above 150 K.

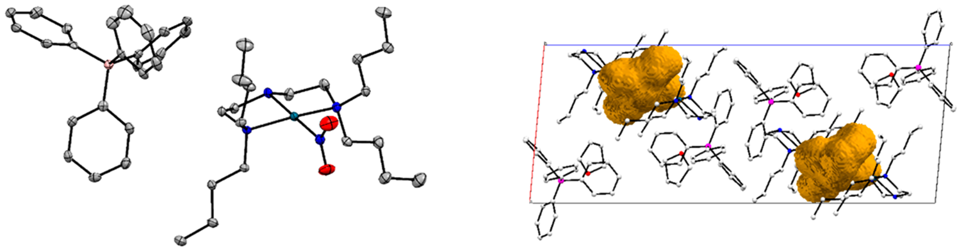

Figure 10. Structure of [Pd(Bu$_4$ dien)(η^1-NO$_2$)][BPh$_4$] and a packing diagram showing the volume available to the nitro/nitrito group.

after 2 h, and when the temperature was raised to around 160 K, the GS nitro isomer was regenerated.[14]

Because of the thermal and photocontrol that we had established for [Ni(Et$_4$ dien)(NO$_2$)$_2$] it was possible to undertake variable-temperature kinetic measurements in the 150−160 K range. This showed that the endonitrito decay is dependent on temperature and an activation energy of E_{act} = 48.6(4) kJ mol^{-1} (0.5 eV) was obtained. It was also possible, to carry out pseudo-steady-state photocrystallography experiments in which the illumination is continued during the crystallographic data collection. This experiment showed the presence of a previously unobserved *exo*-nitrito linkage isomer at temperature close to the metastable limit (Figure 8).[14] This isomer may be a transient-state species.

In an alternative strategy to probe the importance of the crystal environment in complexes that can undergo solid-state photoactivated linkage isomerism, the two salts [Pd(Et$_4$ dien)(NO$_2$)][OTf] and [Pt(Et$_4$ dien)(NO$_2$)][OTf] have been investigated. Both the GS structures contain significant N−H···O hydrogen bonds involving a nitro O atom. Irradiation with 400 nm LEDs, at 100 K, results in a mixture of both *endo*- and *exo*-(η^1-ONO) isomers, and only overall conversion levels of 56% (Pd) and 29% (Pt) are observed. However, on warming to 150 K, when the Pd salt crystals are irradiated for 1 h, 100% conversion to the *endo*-(η^1-ONO) form occurs. When the Pt salt is irradiated for 3 h, at 200 K, 93% of the *endo*-(η^1-ONO) form is obtained along with 7% of the ground state. Variable temperature studies show that the metastable limit for the Pt complex is around 240 K, whereas for the lighter Pd complex, it is 190 K.[53] For both complexes, the amine···NO$_2$ hydrogen bonds become longer at higher temperatures (Figure 9). If the hydrogen bonds do inhibit photoisomerization at lower temperatures, raising the temperature would facilitate isomerization, as is observed. Similarly, the volume of the reaction cavity should increase at higher temperatures. This suggests that temperature-regulated photoactivation may provide a new method to control single-crystal to single-crystal linkage isomeric transformations.

These series of studies on the nitro/nitrito linkage isomers suggest that using bulky auxiliary ligands or bulky counterions, which will strongly influence the crystal packing, will favor high levels of conversion to the metastable isomers. The electronic factors also seem to be acceptable for the isomerization to occur, although the kinetics for isomerization for complexes of the second and third row of the d-block are slower than those for the first row, with some of the conversions for the heavier metal complexes only occurring at higher temperatures. The objective remains, can complexes be engineered where 100% conversion occurs and switching is achieved close to room temperature?

The packing efficiency in the crystal structure of metal complexes can be further reduced by moving to ionic systems, cations and anions, one or both of which may contain bulky groups. In [Pd(Bu$_4$ dien)(η^1-NO$_2$)][BPh$_4$] (Bu$_4$ dien = *N*,*N*,*N*′,*N*′-tetrabutyldiethylenetriamine), 100% conversion to the metastable *endo*-nitro-(η^1-ONO) isomer (Figure 10) is achieved in only 15 min upon irradiation with 400 nm LEDs at 100 K,[54] and significantly, the system is metastable until 240 K. Under pseudo-steady-state photocrystallographic conditions, the nitrito isomer is observed at temperatures up to 260 K. This result suggests that complexes containing heavier transition metals may raise the temperature of the metastable limit close to room temperature.

Because of the fine control over the generation of the metastable states in [Pd(Bu$_4$ dien)(η^1-NO$_2$)][BPh$_4$], we have been able to extract quantitative kinetic information for both the excitation and decay processes from the data,[55] building on the previous kinetic studies on linkage isomers.[14,36,54,56] We found that the photoactivation process is weakly temperature dependent, which may be due to the effect of the crystal environment on the isomerization process. However, the reverse decay process has an activation energy of 55 ± 5 kJ mol^{-1} and is strongly dependent on temperature, which leads to lifetimes that are tunable through several orders of magnitude by careful temperature control.[55] Over the temperature range of 175–325 K the decay time, $t_{1/2}$, ranges from 10^7 s to 100 ms.[55] It should now be possible to effectively "dial up" a suitable temperature to give a desired ES lifetime. Because of the fine control over temperature vs lifetime, these linkage isomeric materials may prove to be useful benchmark materials for the development of time-resolved diffraction methodologies.

E. CONCLUDING REMARKS

Over the last two decades, we and others have shown how it is possible to use photocrystallographic techniques to study photoactivated linkage isomerism in solid-state transition metal coordination complexes containing ambidentate ligands such as NO, NO$_2$, and SO$_2$. All these ligands have been shown to undergo isomerism to produce metastable isomers. The percentage of conversion achieved and the isomer obtained are strongly dependent on the wavelength of light used and the temperature at which the experiment is carried out. In all cases, there is a temperature at which the metastable limit is reached, above which the excited state has a finite lifetime before returning to the ground state. The interconversion is also dependent on the flexibility of the crystal lattice and on the steric and electronic environment of the ambidentate ligand and the metal center. There needs to be sufficient space in the lattice for the ligand to switch between one form and the other, and intermolecular interactions should either not be particularly strong or be flexible perhaps through a change in temperature.[30,54]

For transition metal nitro/nitrito complexes, the use of bulky bidentate phosphines and amines as auxiliary ligands, which are largely responsible for the crystal packing motif, favor high levels of conversion to the metastable state as does the inclusion of bulky counterions when dealing with salts. Additionally, the inclusion of a second or third row transition metal in the complex favors a higher temperature for the isomerization to occur. In these cases, the decay process from the excited or metastable state back to the ground state has an activation energy of ca. 55 kJ mol^{-1} and is dependent on temperature, which leads to lifetimes that are tunable through several orders of magnitude by careful control of temperature. This should make accessing a particular GS lifetime a much more straightforward process.

With the design features that have been established, it should be possible to convert the knowledge gained from the photocrystallographic studies to the design of switchable materials. Because of the relationship that we have established between temperature and lifetime in these linkage isomers, they should be useful benchmark materials as time-resolved diffraction methodology continues to develop. The successful incorporation of some of the nitrosyl and sulfur dioxide linkage isomers into polymers and xerogels without the loss of their switching function[40,42] suggests that these systems may have optical device applications. Schaniel et al. have shown that it is possible to write short-lived phase gratings with identically and orthogonally polarized waves using nanosecond laser pulses in crystals of iron nitrosyl complexes. The isomerization leads to a change of modulation of the polarizability and with it a measurable change in refractive index of the crystal.[57]

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