Photocrystallography

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Reversible 100 % Linkage Isomerization in a Single-Crystal to Single-Crystal Transformation: Photocrystallographic Identification of the Metastable [Ni(dppe)(η^1-*O*NO)Cl] Isomer**

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Photocrystallography is a rapidly growing technique that allows the full three-dimensional structures of short-lived and metastable photoactivated species to be determined using X-ray diffraction methods.[1] There has also been considerable research in using ultrafast time-resolved electron diffraction and X-ray absorption spectroscopy.[2] Using photocrystallography it is possible to either determine the structure of a transient species or to follow a dynamic process within a crystal. To date, photocrystallography has required the use of synchrotron radiation coupled with protein-Laue[3] or powder diffraction techniques.[4] Monochromatic radiation, usually from a synchrotron source in conjunction with bright light source, usually a laser, has been used successfully to determine the structures of photoactivated transient species. Coppens has pioneered this area and has determined the structures of a number of metastable linkage isomers that are photoactivated by laser light of the appropriate wavelength. These include metal nitrosyl,[5] metal nitrite,[6] and metal sulfur dioxide complexes.[7] We have also established the structure of a new metastable linkage isomer of the ruthenium sulfur dioxide complex $[Ru(NH_3)_4(H_2O)(\eta^1\text{-}OSO)][MeC_6H_4SO_3]_2$,[8] which forms when single crystals are activated by a broadband tungsten lamp at temperatures below 100 K, and the sulfur dioxide changes from η^1-*S* bound to η^1-*O* bound.

Coppens and co-workers have also developed pump–probe techniques for determining the structure of species that exist in the single crystal, for only a matter of microseconds at low temperature.[9] In this case, a pump laser is used and is synchronized with a mechanical chopper that "chops" the X-ray beam (from a synchrotron source), so that the crystal is excited by the laser and then probed with the X-ray beam only when the crystal is in the photoactivated state. Using this method, a significant change in the Pt–Pt distance in the tetraanion $[Pt_2(pop)_4]^{4-}$ (pop = pyrophosphate $(H_2P_2O_5)^{2-}$) upon activation[10] and a contraction of 0.85 Å in the Rh–Rh distance in $[Rh_2(1,8\text{-diisocyano-}p\text{-methane})_4]^{2+}$ is observed when this complex is irradiated with 355 nm light at 17 K; the excited triplet state has a lifetime of 11.7 μs at 23 K.[11]

One of the drawbacks in all the systems studied is the relatively low conversion rate from the ground-state structure to the excited state and such low conversion is likely to hinder the analysis of the excited-state components. Unlike the light-induced electronic spin state (LIESST) phenomenon,[12] the photoexcitation in the systems studied is not cooperative and the maximum level of excitation observed is 47 % for $[Ni(\eta^5\text{-}C_5Me_5)(NO)]$[13] as is shown in Table 1; although 76 % conversion of the bonding mode of the nitrosyl group has recently been reported in *trans*-$[RuCl(py)_4(NO)][PF_6]_2\cdot0.5\,H_2O$ (py = pyridine) from an IR investigation.[14] The inability to obtain high levels of excitation may be attributed to either the lack of penetration of the laser beam into the crystal or to the generation of unfavorable strain energy within the crystal as the structure changes.[1c] This limitation is unfortunate if such materials are to be exploited as data-storage materials where the control over the linkage

Table 1: Excitation levels in photoactivated metastable metal complexes.

Complex	Irradiation	Conversion [%]	Reference
$[Co(NH_3)_5(NO_2)]Cl_2$	Xe lamp	15	[6a]
$[Ru(bpy)_2(NO)(NO_2)](PF_6)_2$	Ar laser	10	[6b]
$Na_2[Fe(CN)_5(NO)]\cdot H_2O$	laser	37	[5a]
$K_2[Ru(NO_2)_4(NO)(OH)]$	laser	16	[5d]
$[Ni(\eta^5\text{-}C_5Me_5)(NO)]$	laser	47	[13]
$[Ru(NH_3)_4(H_2O)(SO_2)](MeC_6H_4SO_3)_2$	W lamp	44	[8]
$[Ru(NH_3)_4(CF_3CO_2)(SO_2)](MeC_6H_4SO_3)$	Ar laser	38	[7a]

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isomer formed is essential. We have been developing methods to try to improve the percentage of conversion, by either using bulky ligands or metal salts with large counterions that will dominate the crystal packing and, perhaps, reduce the strain within the crystal as the isomerization process occurs.

Herein, we report that irradiation of the nitro complex [Ni(dppe)(η^1-NO$_2$)Cl] (dppe = 1,2-bis(diphenylphosphino)ethane) with light from a UV light-emitting diode (LED; ca. 400 nm) produces the photoactivated nitrito complex [Ni(dppe)(η^1-ONO)Cl] with a reversible 100 % conversion.

The complex [Ni(dppe)(η^1-NO$_2$)Cl] was synthesized using literature procedures,[15] and red crystals suitable for a synchrotron photocrystallographic experiment were obtained. To facilitate the X-ray experiment, a series of solid-state Raman spectroscopic experiments were undertaken. In each case, a single-crystal sample was cooled to 115 K and the Raman spectrum recorded (Figure 1).

The ground state nitro-(η^1-NO$_2$) isomer has characteristic Raman bands, particularly the δ(NO$_2$) deformation (815 cm^{-1}) and one of the ν(N-O) stretches (1333 cm^{-1}), with the other ν(N-O) band being weak and for these studies less informative.[16] The sample was irradiated at 115 K for 10 min using the visible light from the illuminator on the confocal Raman microscope, resulting in the crystal changing color from red towards yellow. The Raman spectrum was then re-recorded after photolysis. The δ(NO$_2$) band shifts 14 cm^{-1} to 829 cm^{-1} and the ν(N-O) band shifts 71 cm^{-1} to 1404 cm^{-1}. These shifts to higher energy are characteristic of the formation of the nitrito-(η^1-ONO) isomer[16] and show almost complete conversion (Figure 1 a; inset).

The cold photolyzed sample was warmed from 115 K to 300 K and the Raman spectra recorded at regular temperature intervals during warming (Figure 1 b). The 829 cm^{-1} band of the nitrito-(η^1-ONO) isomer decreased with a concomitant increase in the 815 cm^{-1} band of the nitro-(η^1-NO$_2$) isomer. The conversion from the nitrito back to the nitro was complete. The crystal remained intact, and we repeated the cooling to 115 K and subsequent photolysis to again generate the nitrito-(η^1-ONO) isomer. In this experiment, the sample was warmed to 160 K and the Raman spectra obtained at approximately 2 min intervals (Figure 1 c), allowing loss of the nitrito-(η^1-ONO) isomer and recovery of the nitro-(η^1-NO$_2$) isomer to be monitored.[17]

Having established from the single-crystal Raman measurements that photoactivation of the nitrite complex does occur efficiently in a single crystal, and that at sufficiently low temperatures the nitrito-(η^1-ONO) isomer becomes metastable, we examined these changes using X-ray crystallography. A suitable single crystal was placed on an APEX II diffractometer on Station 9.8 at the SRS Daresbury Laboratory and the crystal cooled to 100 K. An X-ray data set was collected in the absence of light at this temperature and the structure solved and refined to obtain an accurate "ground-state" structure (Figure 2 a). The complex crystallizes in the monoclinic space group Cc. The square-planar nickel center is bound to a bidentate dppe ligand, a chlorine atom, and a nitro-(η^1-NO$_2$) group. The crystal was then irradiated at 100 K, using six UV LEDs mounted 1 cm from the crystal in a circle to give uniform irradiation. After a period of approximately 20 min, the irradiation was turned off and a second data set collected. After only 20 min of irradiation, an astonishingly high conversion of 70 % from the nitro-(η^1-NO$_2$) (N1, O1, and O2) into the nitrito-(η^1-ONO) isomer (N1B, O1B, and O2B) was achieved. This metastable component was modeled within the structure as disorder as illustrated in Figure 2 b. Further irradiation for 90 min took

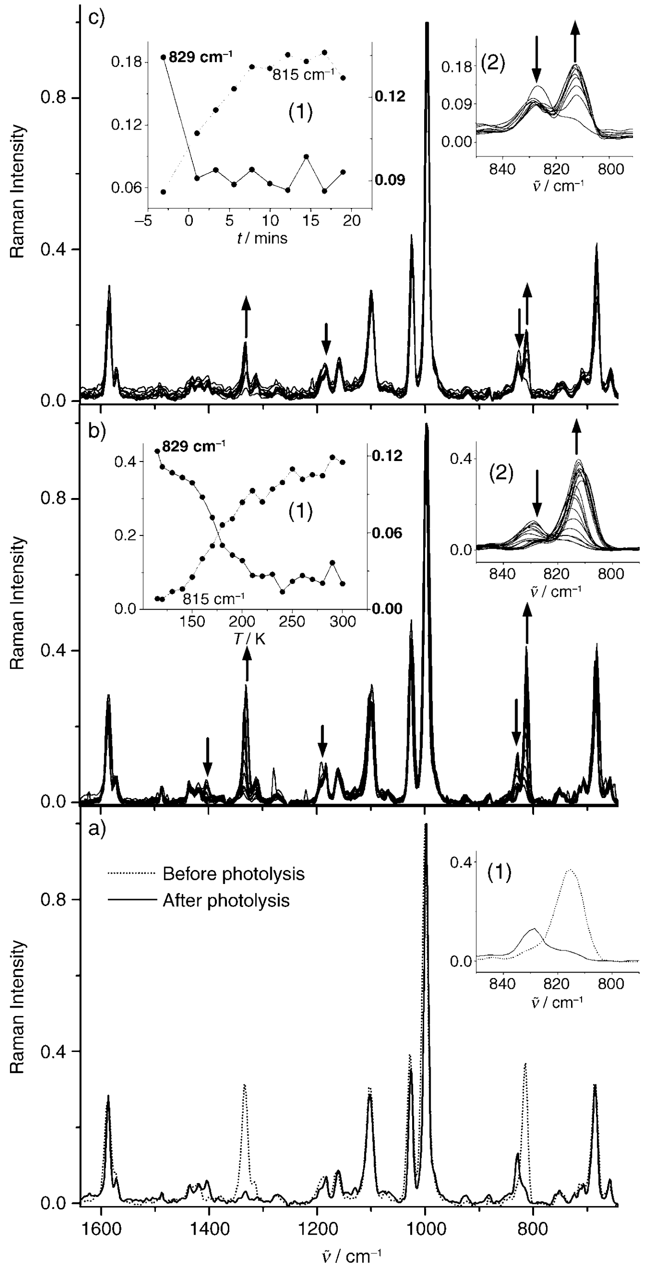

Figure 1. Solid-state Raman spectra of [Ni(dppe)(NO$_2$)Cl] a) at 115 K before and after photolysis, inset: expansion of the δ(NO$_2$) spectral region; b) after photolysis at 115 K, recorded at 10 K intervals from 120 K to 300 K. Inset 1): temperature dependence of the δ(NO$_2$) bands of the nitro-(η^1-NO$_2$) isomer (815 cm^{-1}, left y axis) and the nitrito-(η^1-ONO) isomer (829 cm^{-1}, right y axis). Inset 2): an expansion of that region; c) at 160 K after photolysis. Inset 1): time dependence of the δ(NO$_2$) bands of the nitro-(η^1-NO$_2$) isomer (815 cm^{-1}, left y axis) and the nitrito-(η^1-ONO) isomer (829 cm^{-1}, right y axis). Inset 2): an expansion of that region.

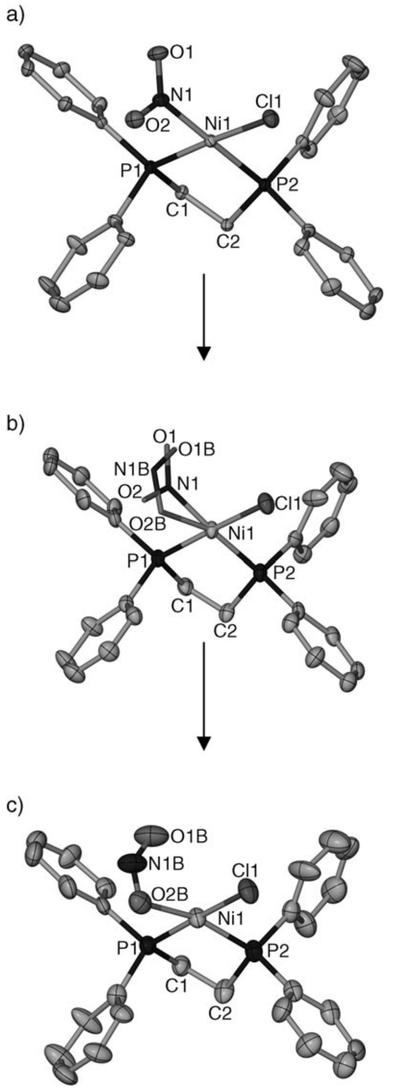

Figure 2. a) Ground-state structure of [Ni(dppe)(η^1-NO$_2$)Cl] with thermal ellipsoids set at 50% probability; b) Metastable structure of [Ni(dppe)(NO$_2$)Cl] with thermal ellipsoids set at 50% probability, except for the nitro and nitrito group which have fixed radii for clarity; c) Metastable state structure of [Ni(dppe)(η^1-ONO)Cl] with thermal ellipsoids set at 50% probability showing the complete conversion into the metastable state.

the process to completion, with a structure containing 100% nitrito-(η^1-ONO) conformation as shown in Figure 2c. The structure remains in the same *Cc* space group and little change to the unit cell or packing arrangement is observed. A comparison of the molecular parameters between the nitro and nitrito complexes showed no significant differences except for the clear change in bonding mode of the NO$_2$ group (an overlay of the nitro and nitrito structures is provided in the Supporting Information).

In neither the ground-state nitro nor the metastable state nitrito structure are there any particularly short intermolecular contacts. In the nitro complex there is a C–H···O hydrogen bond of 2.45 Å between O(2) and an arene proton on an adjacent molecule, while in the nitrito complex the shortest C–H···O hydrogen bond, which is between O(1B) and an arene proton on an adjacent molecule, is 2.56 Å. The lack of any strong intermolecular interactions involving the NO$_2$ group in either the ground or metastable state may facilitate the isomerization upon photoactivation as disruption to the crystal lattice will be relatively small.

To definitively establish the existence of the metastable state, the crystal was kept in the dark for 1 h at 100 K, after which time the structure was recollected and the metastable state remained completely unchanged. When the structure is briefly warmed to room temperature by blocking the cryostream for 10 s, the metastable state completely converted back into the ground state and a re-determination of the "ground-state" structure, at 100 K, was essentially identical to that obtained prior to irradiation with no evidence of the oxygen-bound isomer.

Structural determination as a function of temperature showed that the metastable structure is stable between temperatures of 100 K to 160 K. Above 160 K, the metastable state converted back into the ground state, consistent with the early Raman measurements, and presumably because the thermal energy is sufficient to overcome the energy barrier between the two states and fully convert into the more thermodynamically favorable nitro-(η^1-NO$_2$) conformation.

In this series of experiments we have identified a new metastable oxygen-bound nitrito isomer of [Ni(dppe)(η^1-ONO)Cl] in the solid state using Raman and photocrystallographic techniques and, for the first time, identified a system which undergoes reversible 100% conversion from the "ground-state" nitrite complex to the metastable nitrito complex under photocrystallographic conditions. The demonstration that the use of bulky auxiliary ligands on the metal complex that dominate the packing and provide free regions of space within the crystal for the photoactivated ligand to rearrange yielding a system which undergoes 100% reversible conversion opens up this approach for more widespread utilization and is likely to be important in future time-resolved X-ray measurements.

Experimental Section

Raman spectra were recorded on a Nicolet Almega XR Dispersive Raman Microscope using a 780 nm laser, each spectrum consisting of 3 × 30 second scans. Temperature control was achieved using a Linkam FTIR600 variable-temperature stage with CaF$_2$ windows and modified tubing to fit the Raman spectrometer.

Preliminary X-ray diffraction investigations were carried out on Station 11.3.1 of The Advanced Light Source (ALS), Lawrence Berkeley National Laboratory.[18]

Single-crystal X-ray diffraction collections were carried out on a Bruker APEXII CCD diffractometer equipped with a silicon (111) monochromated beam ($\lambda = 0.6940$) on Station 9.8 of Daresbury Synchrotron Radiation Source.[19] The program SMART[20] was used for collecting frames of data, indexing reflection, and determination of lattice parameters, SAINT[20] for integration of the intensity of reflections and scaling, and SADABS[21] for absorption correction. The structures were solved by direct methods using SHELXS-86[22] and refined by full-matrix least-squares on F^2 using SHELXL97.[23]

Irradiation of the single crystals was carried out using six 400 nm UV LEDs (350 millicandela at 3.7 V and 20 mA) placed at a distance of 1 cm from the crystal.

Crystal data: Ground-state structure for [Ni(dppe)(η^1-NO$_2$)Cl], $T = 100$ K, $C_{26}H_{24}ClNNiO_2P_2$, $M_r = 538.56$, monoclinic, space group Cc (No. 9), $Z = 4$, $a = 13.4279(18)$, $b = 11.4341(16)$, $c = 17.039(2)$ Å, $\beta = 110.546(2)°$, $V = 2449.7(6)$ Å^3, Station 9.8, Daresbury Laboratory, $\lambda = 0.6940$ Å, $\mu = 1.056$ mm^{-1}, $T_{min}/T_{max} = 0.765$, $2\theta_{max} = 61.36°$, 13 952 reflections collected, 7372 unique [$R_{int} = 0.064$], $wR_2 = 0.129$, $R_1 = 0.0525$ ($I > 2\sigma(I)$), Flack parameter $= 0.035(11)$. 70% converted structure of [Ni(dppe)(NO$_2$)Cl], $T = 100$ K, $C_{26}H_{24}ClNNiO_2P_2$, $M_r = 538.56$, monoclinic, space group Cc (No. 9), $Z = 4$, $a = 13.653(8)$, $b = 11.460(7)$, $c = 16.869(13)$ Å, $\beta = 110.178(6)°$, $V = 2477(3)$ Å^3, Station 9.8, Daresbury Laboratory, $\lambda = 0.6940$ Å, $\mu = 1.044$ mm^{-1}, $T_{min}/T_{max} = 0.764$, $2\theta_{max} = 51.46°$, 10 080 reflections collected, 4885 unique [$R_{int} = 0.093$], $wR_2 = 0.176$, $R_1 = 0.0734$ ($I > 2\sigma(I)$), Flack parameter $=$ 0.05(3). 100% converted structure of [Ni(dppe)(NO$_2$)Cl], $T = 100$ K, $C_{26}H_{24}ClNNiO_2P_2$, $M_r = 538.56$, monoclinic, space group Cc (No. 9), $Z = 4$, $a = 13.803(5)$, $b = 11.283(4)$, $c = 17.008(6)$ Å, $\beta = 111.264(4)°$, $V = 2468.5(14)$ Å^3, Station 9.8, Daresbury Laboratory, $\lambda = 0.6940$ Å, $\mu = 1.048$ mm^{-1}, $T_{min}/T_{max} = 0.733$, $2\theta_{max} = 47.72°$, 8346 reflections collected, 4012 unique [$R_{int} = 0.073$], $wR_2 = 0.184$, $R_1 = 0.0722$ ($I > 2\sigma(I)$), Flack parameter $= 0.03(4)$. CCDC 724867 (ground state), 724868 (30%:70% conversion to nitrito), 724869 (100% nitrito) contain the supplementary crystallographic data for 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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