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Communications to the Editor

The First Crystallographic Evidence for Side-On Coordination of N_2 to a Single Metal Center in a Photoinduced Metastable State

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While common crystallographic methods give information on the geometry of stable molecules and solids, the *photocrystallographic* technique allows the study of metastable or transient species formed by in situ laser irradiation of diffractometer-mounted samples at low temperature.[1,2] Using this technique we have now obtained the first structural evidence for the existence of a metastable η^2 side-on binding mode of the N_2 molecule. Supporting evidence on its stability has been obtained from low-temperature IR and Differential Scanning Calorimetry (DSC) measurements and from quantum mechanical calculations.

Molecular nitrogen is a simple and relatively inert molecule, the binding modes of which have been extensively studied since the discovery of a metal-bound dinitrogen complex $[Ru(NH_3)_5(N_2)]^{2+}$ in 1965.[3] The η^2 (side-on) binding mode of N_2 to a single metal atom has never been observed crystallographically, an earlier claim[4] having been refuted by more detailed analysis,[5] though its existence has been invoked in a number of studies.[6]

A simple osmium complex, $[Os(NH_3)_5(N_2)]^{2+}$, was chosen for this study, as maximal overlap between d orbitals of the metal and 2p orbitals of the (η^2) bound N_2, and thus maximal stability, can be expected for third row transition metals. The pentammine complex was selected, as Armor and Taube interpreted IR spectra of isotopically labeled $[Ru(NH_3)_5(^{15}NN)]^{2+}$ in terms of end-to-end rotation of N_2 taking place through the side-on bound state of N_2.[7]

The UV/vis spectrum of $[Os(NH_3)_5(N_2)]^{2+}$ in water consists of one intense band at 218 nm ($\epsilon \approx 11000$ $cm^{-1}\cdot L\cdot mol^{-1}$). This band has a broad long wavelength shoulder extending to 380 nm. A new IR band is generated at 1838 cm^{-1} upon irradiation into this shoulder ($330 < \lambda < 460$ nm; Xe lamp) of a polycrystalline sample[8] of $[Os(NH_3)_5(N_2)][PF_6]_2$ at 100 K. The band is downshifted by 187 cm^{-1} from the one at 2025 cm^{-1} assigned to the stretching vibration of (η^1) N_2. The downshift is comparable to that observed on photoinduced formation of linkage isomers of the transition metal nitrosyl complexes.[1] With time, the intensity of the new band increases at the expense of the parent band. The process is thermally reversible as the light-induced band disappears and the intensity of the original stretch of (η^1) N_2 is restored when the light is switched off and the sample warmed to room temperature.

The formation of a new species is also detected by DSC of a sample consisting of several small crystals, irradiated at 100 K. It shows a peak centered at about 218 K, corresponding to the thermal decay of the light-induced species. Assuming an energy difference between the metastable and ground states of 1 eV, as for (η^2) NO in sodium nitroprusside,[9] the area of the peak corresponds to a metastable state population of 19%.[10]

To identify the photochemical product, diffraction intensities were collected at 100 K on the same crystal of $[Os(NH_3)_5(N_2)][PF_6]_2$ before and after irradiation with a He/Cd laser ($\lambda = 325$ nm).[11] Each set was collected within 1 day, using an area detector. On this time scale the metastable species does not decay at 100 K. As in our previous studies on nitrosyl complexes, no new reflections occur upon generation of the metastable state, but a small though significant change in cell dimensions is observed ($\Delta a = 0.005(1)$ Å, $\Delta b = -0.138(3)$ Å, $\Delta c = 0.020(2)$ Å). Since the N_2 ligand is oriented along the *b*-axis of the unit cell, this is a first indication of a change in its orientation upon irradiation. A *photodifference map*, reflecting the effect of the irradiation on the electron density distribution, shows a reduction of density in the N_2 region of the ground-state complex, and an enhancement of density along a line perpendicular to the ground-state N−N axis (Figure 1). A similar map in the vicinity of Os shows a 32 e/Å^3 peak displaced from the position of the Os atom toward the N_2 group and a hole in the opposite direction, indicating shift in the position of Os toward the dinitrogen ligand. In the least-squares analysis of the photoexcited crystal, the geometry of the ground-state component is taken from the analysis of the crystal

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(11) Crystal data for $[Os(NH_3)_5(N_2)][PF_6]_2$ in the ground state: formula, $H_{15}N_7P_2F_{12}Os$; molecular weight $M = 593.33$; space group *Cmcm* (No. 63); 100 K, $a = 8.4920(7)$ Å, $b = 20.0480(18)$ Å, $c = 8.1450(8)$ Å; $V = 1386.6$ Å^3; $D_{calc} = 2.842$ $g\cdot cm^{-1}$; $Z = 4$; $\mu = 9.57$ mm^{-1}; numerical absorption correction (T_{min}/T_{max} 0.38924/0.75248); Mo Kα with graphite monochromator, Bruker CCD diffractometer; 20916 measured reflections; 1543 reflections used with $I > 2\sigma(I)$; maximum diffraction angle $2\theta = 71.60°$; 77 variables; non-H atoms refined anisotropically; H atoms fixed in calculated positions, except for the axial NH_3 group; $R_1 = 1.29\%$; $wR_2 = 2.87\%$. Crystal data for $[Os(NH_3)_5(\eta^2\text{-}N_2)][PF_6]_2$: formula, $H_{15}N_7P_2F_{12}Os$; molecular weight $M = 593.33$; space group *Cmcm* (No. 63); $Z = 4$; 100 K, $a = 8.4968(9)$ Å, $b = 19.9100(28)$ Å, $c = 8.1646(12)$ Å; $V = 1381.1$ Å^3; $D_{calc} = 2.853$ $g\cdot cm^{-1}$; $\mu = 9.61$ mm^{-1}; numerical absorption correction (T_{min}/T_{max} 0.38703/0.75311); Mo Kα with graphite monochromator, Bruker CCD diffractometer; 21783 measured reflections; 1583 reflections used with $I > 2\sigma(I)$; maximum diffraction angle $2\theta = 71.94°$; 72 variables; 6 bond length restraints introduced to fix the geometry of the ground-state component; temperature factors of all atoms comprising ground-state component fixed; population of the metastable state refined; temperature factors of the Os atom in the metastable state structure refined anisotropicaly, $N(N_2)$ isotropically, $N(NH_3)$ fixed at ground-state values; as the N_2 ligand in the ground state occupies a position of *mm* symmetry, two equivalent side-on configurations included in the refinement. $R_1 = 1.40\%$; $wR_2 = 3.06\%$.

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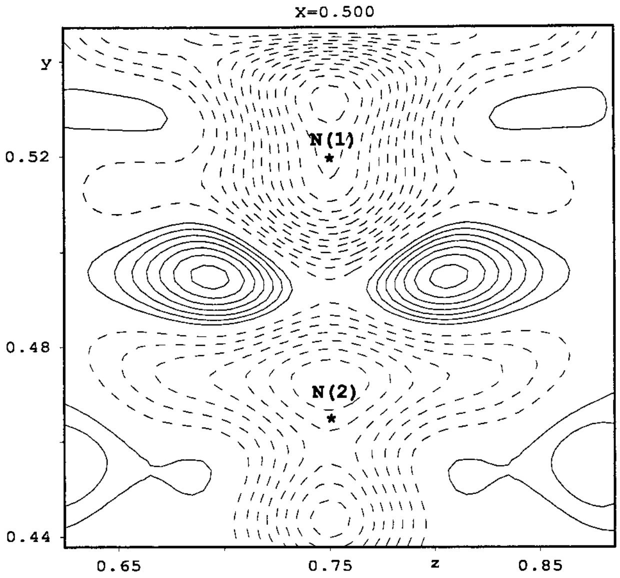

Figure 1. Difference between the electron density in the excited crystal and the ground-state density in a plane containing the N_2 ligand. The change in orientation of the ligand is manifested by electron deficient regions (broken lines) around the original positions of the nitrogen atoms and two new peaks (solid lines) at the atomic positions of the light-induced side-on bound ligand. Contour interval 0.2 e/Å^3.

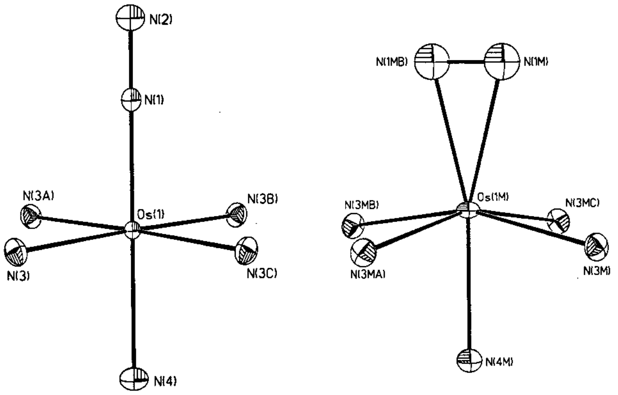

Figure 2. ORTEP diagrams of the $[Os(NH_3)_5(N_2)]^{2+}$ ion in $[Os(NH_3)_5(N_2)][PF_6]_2$. Left: Ground state. Right: Light-induced metastable state. Only one of two symmetry-related orientations of the N_2 ligand is shown. Hydrogen atoms omitted for clarity. The bending of the equatorial ligands away from the side-bound dinitrogen is evident. Selected bond lengths (Å) and angles (deg). (A) Ground-state structure: Os−N(1), 1.848(2); Os−N(3,4,5,6), 2.135(1); Os−N(4), 2.151(3); N(1)−N(2), 1.128(3); Os(1)−N(1)−N(2) 180. (B) Metastable state structure: Os−N(1M,1MB), 2.111(16); Os−N(3MA,B,C,D), 2.169(7); Os−N(4M), 2.097(14); N(1M)−N(1MB), 1.058(30); Os−N(1M)−N(1MB) 75.3(4).

before irradiation.[1] In agreement with the photodifference map, the least-squares results show the light-induced state to correspond to a species with an (η^2) bound N_2 group (Figure 2), located in an almost eclipsed, rather than a staggered conformation with respect to the equatorial ligands. Unlike in the ground state, the N_2 ligand is no longer located on the intersection of the two mirror planes. As the metastable molecule retains the 2-fold axis, two chemically equivalent N_2 orientations occur in the photoinduced state. Upon irradiation the Os atom moves by 0.189(3) Å toward N_2, while the equatorial nitrogen atoms are displaced by 0.23(1) Å away from N_2 and the nitrogen atom of the axial ligand by 0.22(2) Å, in the same direction as Os. The population of the metastable state refined to 17.4(5)%, in qualitative agreement with the DSC results. Changes in the bond lengths upon transition from the (η^1) N_2 to (η^2) N_2 configuration are quite large: the axial $Os-N(NH_3)$ bond shortens by 0.054(14) Å, while the equatorial $Os-N(NH_3)$ bonds are elongated by 0.034(7) Å. The most pronounced change occurs for the $Os-N(N_2)$ bond which lengthens by 0.263(17) Å. The observed shortening of the N−N bond by 0.070(31) Å is not significant, given the large esd in this light-atom to light-atom bond length in the presence of the heavy Os atom and the fractional conversion percentage.

Parallel Density Functional Theory (DFT) quantumchemical calculations[12] were undertaken with the ADF package.[13] Results of the calculations confirm that the side-on geometry, $[Os(NH_3)_5(\eta^2\text{-}N_2)]^{2+}$, corresponds to a local minimum on the potential energy surface located ~0.82 eV above the ground-state energy. Geometry differences between the metastable and ground states are in general agreement with those found experimentally. In particular the lengthening of the $Os-N(N_2)$ bond of 0.263 Å is almost exactly reproduced by the calculation. The N−N bond is slightly lengthened (by 0.02 Å) according to the theoretical result, in agreement with the observed downshift of the stretching frequency.

The study of the binding modes of small molecules to transition metals is of importance given the crucial function of molecules such as N_2 and NO in biological[14,15] and industrial[16] processes. We are currently extending photocrystallographic methods to include the study of short-lived transient species using pulsed X-ray and laser sources.[2,17]

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Supporting Information Available: Description of the refinement procedure, tables (for both states) with crystallographic information, atomic coordinates and thermal parameters, bond lengths and angles, hydrogen atom coordinates; UV and IR spectra, DSC curve; a packing diagram of the ground-state structure, and a photodifference map in the region of the Os atom (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) All calculations were performed with the Amsterdam Density Functional package (ADF, version 2.3). Complete geometry optimizations of the structures of $[Os(NH_3)_5(\eta^1\text{-}N_2)]^{2+}$ and $[Os(NH_3)_5(\eta^2\text{-}N_2)]^{2+}$ were performed using the VWN (Vosko, Wilk, and Nusair) functional. Standard ADF libraries were used to create Os, N, and H atoms. The effective core potential approximation has been used in the description of Os and N atoms. Triple-ξ basis sets were employed in the description of the 4f, 5s, 5p, 5d, 6s, and 6p shells of Os and the 2s, 2p, and 3d shells of N. A double-ξ basis set with 2p polarization functions was used in the case of the H atom. The Pauli formalism was utilized to take into account relativistic effects on Os.

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