Identification of a Rare Manganese Dinitrogen Complex

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Introduction

Nitrogen fixation, the process of converting readily available gaseous N_2 into useful chemical compounds, is a vitally important industrial and biological process. However, the strong $N{\equiv}N$ bond, coupled with its kinetic inertness means that N_2 is fundamentally an unreactive molecule. Indeed, it is frequently used as a protective atmosphere in sensitive synthetic chemistry. In nature, N_2 fixation is mediated by the nitrogenase enzyme which has a molybdenum-based active site, whereas industrially the Haber-Bosch process is used for the conversion of N_2 to NH_3. Given the vital role of ammonia as a fertilizer precursor, it is perhaps unsurprising that the Haber-Bosch process consumes 1-2% of the world's energy supply.[1]

There is, therefore, a desire to increase the efficiency of industrial nitrogen fixation. Despite its inertness, N_2 binds to a range of different molecular transition metal compounds and, on complexation, is activated to subsequent functionalisation. A number of molybdenum-based complexes have been prepared, inspired by the nitrogenase enzyme, that convert N_2 to NH_3, and there are also a host of examples of complexes based on the elements from Groups 4, 5 and 8 of the periodic table.[2] It is therefore somewhat remarkable that there are only a handful of dinitrogen complexes known of the Group 7 elements, especially when one considers the recent developments in manganese(I)-mediated organic synthesis.[3] Using time-resolved infra-red spectroscopy, we have demonstrated that a new class of manganese-containing dinitrogen compounds are readily available. The spectroscopic insight also demonstrated dynamic competitive binding between N_2 and water and allowed for the rate constants of the processes to be determined.

Methodology

Time-resolved infra-red (TRIR) spectra were recorded on the LIFEtime instrument in the ULTRA facility at the CLF using the time-resolved multiple pump spectroscopy[4] (TR^{M}PS) method with pump-probe delays from 1 ps to 1 ms. A pump wavelength of 355 nm was employed to initiate photodissociation of the CO ligand and the subsequent changes in the IR spectra probed in the region between 1850 and 2310 cm^{-1}. Heptane solutions of manganese compound **1** (Figure 1) were sparged with the appropriate gas (N_2, $^{15}N_2$ or Ar) prior to use. Samples were recorded in continuous flow and raster to ensure that fresh substrate was present for each measurement.

Results and Discussion

Irradiation of a heptane solution of **1** under an atmosphere of N_2 leads to dissociation of a CO ligand in < 1 ps and formation of solvent complex **2**, as demonstrated by the appearance of strong bleach bands for **1** and the appearance of new positive peaks at 1918, 1924 and 2008 cm^{-1} (Figure 2b, blue squares). The intensity and position of these bands is consistent with a *fac*-coordinated $Mn(CO)_3$ complex.[5] Over the course of *ca*. 1 μs, the bands for **2** were replaced by those for two new species, **3** and **4**. Insight into the nature of these species was obtained from a series of control experiments.

The bands in the $MC{\equiv}O$ stretching region for **3** at 1929, 1955 and 2013 cm^{-1} are consistent with the presence of a good π-acceptor ligand (such as N_2) in the coordination sphere of the manganese: this hypothesis is supported by a band at 2249 cm^{-1} which was assigned to an $N{\equiv}N$ stretching mode (Figure 3a). Repeating the reaction under an atmosphere of isotopically enriched $^{15}N_2$ led to a shift in this latter band to 2174 cm^{-1}, in excellent agreement with the predicted value of 2173 cm^{-1} (Figure 3b). The bands in the $MC{\equiv}O$ were unaffected by the use of the isotopically enriched substrate. When the experiment was performed under an argon atmosphere none of the spectroscopic features assigned to **3** were present (Figure 3c). Therefore, the combination of the band at 2249 cm^{-1} which shows the expected isotopic shift and the lack of **3** being formed in the absence of N_2 provided unambiguous evidence for the presence of the dinitrogen complex, **3**, with the structure shown in Figure 1.
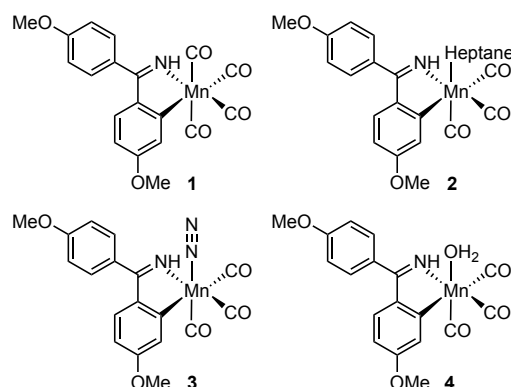

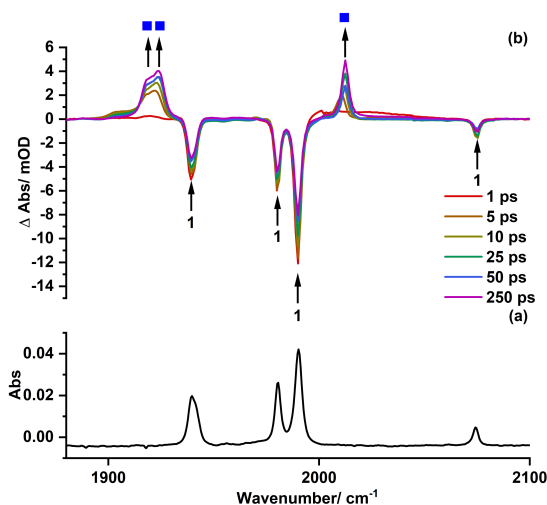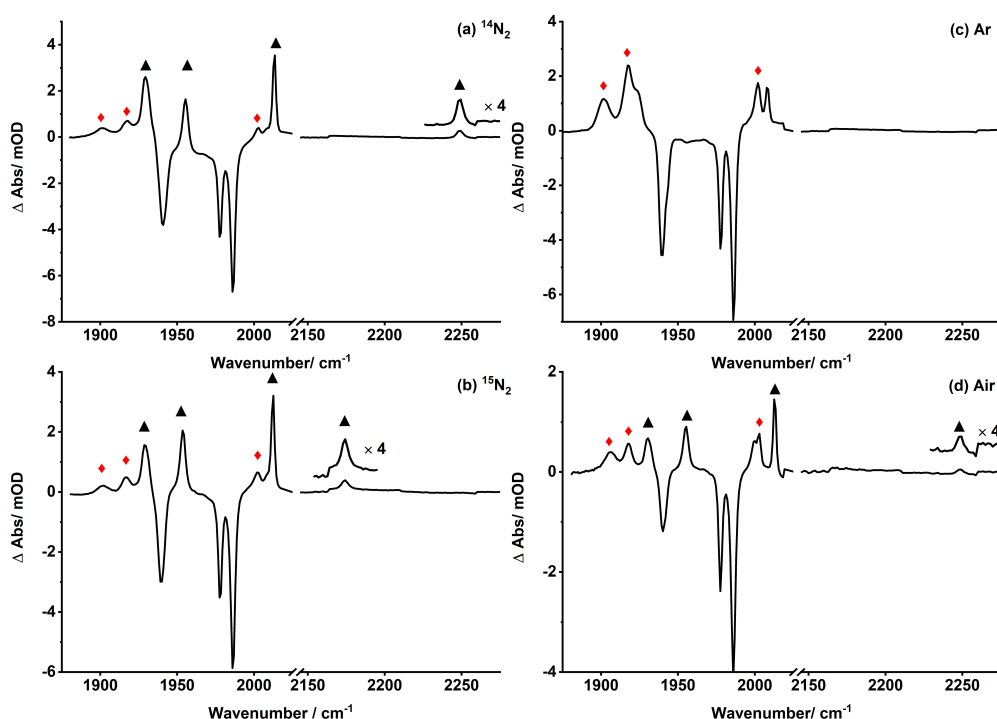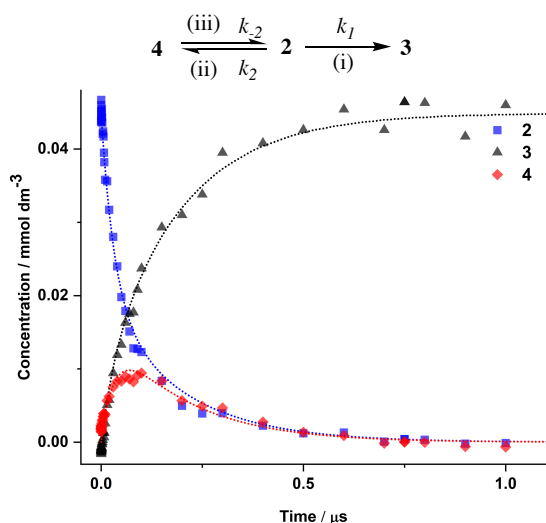**Figure 1** Structure of compounds described in this study.

Figure 2 (a) Ground state IR spectrum of **1** in heptane solution (b) TRIR spectra of **1** in heptane solution recorded at selected pump-probe delays. The blue squares show the bands for **2**.

Figure 3 TRIR spectra of **1** in heptane solutions recorded under (a) an atmosphere of $^{14}N_2$, (b) an atmosphere of $^{15}N_2$, (c) an atmosphere of argon and (d) an atmosphere of air. All spectra were recorded with a pump-probe delay of 500 ns and the bleach band for **1** at 2074 cm^{-1} is omitted. Peaks for **3** are labelled with black triangles, those for **4** with red diamonds.

Photolysis of a heptane solution of **1** which had been spiked with a single drop of water resulted in an increase in the amount of **4** formed in the experiment, relative to **3**. On this basis and on comparison to related species in the literature,[5] complex **4** was assigned as a Mn-aqua complex (Figure 1). The affinity of photochemically generated **2** to bind N_2 was further demonstrated by an experiment performed in air (Figure 3d) which demonstrated that **3** was the major product after 500 ns.

The mechanistic model for these processes involves the initial photodissociation of CO from **1** followed by rapid solvent binding to a resulting putative 16-electron complex. Heptane is a weak ligand for Mn and is therefore substituted by either nitrogen or water to give **3** and **4** respectively. Analysis of the temporal evolution of **3** and **4** (Figure 4) reveals their initial formation over *ca.* 100 ns but then the concentration of **4** decreases and is no longer present after *ca.* 1 μs. This is consistent with initial kinetically controlled substitution of heptane and a slower equilibration to afford **3** as the thermodynamic product.

It was possible to model these exchange processes and determine rate constants for each process. This demonstrates that the substitution of heptane by nitrogen and water had rate constants of $k_1 = (1.028 \pm 0.004) \times 10^9 \ mol^{-1} \ dm^3 \ s^{-1}$ and $k_2 = (1.54 \pm 0.02) \times 10^9 \ mol^{-1} \ dm^3 \ s^{-1}$ respectively. This is close to the diffusion-controlled limit in heptane and reinforces the notion that heptane is only weakly bound to the manganese in **2**. The loss of water from **4**, which leads to the thermodynamically preferred **3** has a smaller rate constant of $k_{-2} = (1.63 \pm 0.03) \times 10^7 \ mol^{-1} \ dm^3 \ s^{-1}$.

Conclusions

These data demonstrate that, despite a dearth of examples, Mn-containing dinitrogen compounds may be readily accessed and TRIR gives insight into the dynamic nature of their formation. Further details of these studies can be found in the related publication.[6]

Figure 4 Kinetic data showing the loss of **2** and formation of **3** and **4**. Dotted lines are a fit to the kinetic model shown. (i) – heptane, + N_2; (ii) – heptane, + H_2O; (iii) – H_2O heptane.

References

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