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Time-resolved Infra-red Spectroscopy Reveals Competitive Water and Dinitrogen Coordination to a Manganese(I) Carbonyl Complex

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Time-resolved infra-red (TRIR) spectroscopy has been used to demonstrate thatphotolysis of [Mn(C^N)(CO)4] (C^N = *bis-*(4‐methoxyphenyl)methanimine) in heptane solution results in ultra-fast CO dissociation and ultimate formation of a rare Mn-containing dinitrogen complex *fac*-[Mn(C^N)(CO)3(N2)] with a diagnostic stretching mode for a terminal-bound N≡N ligand at 2249 cm-1. An isotopic shift to 2174 cm-1 was observed when the reaction was performed under 15N2 and the band was not present when the experiment was undertaken under an atmosphere of argon, reinforcing this assignment. An intermediate solvent complex *fac*-[Mn(C^N)(CO)3(heptane)] was identified which is formed in less than 2 ps, indicating that CO-release occurs on an ultra-fast timescale. The heptane ligand is labile and is readily displaced by both N2 and water to give *fac*-[Mn(C^N)(CO)3(N2)] and *fac*-[Mn(C^N)(CO)3(OH2)] respectively. The *fac*-[Mn(C^N)(CO)3(heptane)] framework showed a significant affinity for N2, as performing the reaction under air produced significant amounts of *fac*-[Mn(C^N)(CO)3(N2)]. Kinetic analysis reveals that the substitution of heptane by N2 (*k =* (1.028 ± 0.004) × 109 mol-1 dm3 s-1), andH2O is competitive on fast (< 1 s) time scales. The binding of water is reversible and, under an atmosphere of N2, some *fac*-[Mn(C^N)(CO)3(OH2)] converts to *fac*-[Mn(C^N)(CO)3(N2)].

Introduction

Coordination of dinitrogen to transition metals plays an important role in N2 fixation. Binding enhances the reactivity of the coordinated ligand, ameliorating the low kinetic reactivity dictated by the strong N≡N bond.1 In addition there has been recent interest in the transition metal-catalysed use of ammonia as an energy carrier and the ruthenium-catalysed conversion of NH3 to N2 has recently been reported.2 Moreover, this process also relies on the ultimate formation of a dinitrogen complex. It is therefore unsurprising that there have been concerted and detailed studies of the synthesis and reactivity of transition metal dinitrogen complexes. Inspired by the active site of the nitrogenase enzyme, there has been a particular focus on dinitrogen complexes of Group 6 metals and molecular species able to catalytically convert N2 to NH3 have been reported.3 There are also many examples of dinitrogen complexes from Groups 4, 5 and 8 which have provided insight into the different binding modes that N2 may exhibit.1

Remarkably, there are only a handful of examples of N2 complexes of the Group 7 metals.3, 4 Indeed the limited examples of manganese dinitrogen complexes are primarily based on two structural frameworks (Figure 1). One such framework is *trans*-[Mn(P-P)2XY] (P-P = chelating phosphorus ligand). For example, Kubas demonstrated that reaction of N2

**Figure 1** Examples of known manganese dinitrogen compounds with NN vibrational mode frequencies, *a* band split due to rotamers, *b* tentative assignment due to band overlap.

with *trans*-[Mn(CO)(dppe)2][BAr’4] (dppe = 1,2-*bis*-(diphenylphosphino)ethane, Ar’ = C6H3-(3,5-CF3)2), in which the formally 16-e Mn-centre is stabilised by two C-H agostic interactions, results in the formation of [Mn(CO)(N2)(dppe)2][BAr’4].5 The related complex *trans*-[MnH(N2)(dmpe)2] (dmpe = 1,2-*bis*-(dimethylphosphino)ethane) may be prepared from the thermal reaction of *trans*-[MnH3(dmpe)2] with N2.6

****The second series of compounds are based on a half-sandwich motif. The archetype of this series, [Mn(5-C5H5)(CO)2(N2)], was originally prepared by oxidation of [Mn(5-C5H5)(CO)2(N2H4)] with hydrogen peroxide,7 although displacement of the THF ligand in [Mn(5-C5H5)(CO)2(THF)] by N2 may also be used as a route to this complex.8 The photochemically induced replacement of CO by N2 has been shown to be an effective route to this class of compounds: irradiation of [Mn(5-C5H5)(CO)3] under N2 results in CO loss and formation of [Mn(5-C5H5)(CO)2(N2)].9, 10 This method may be extended to a number of related derivatives. For example George and Poliakoff have shown that photolysis of [Mn(5-C5R4Me)(CO)2L] (R = H, Me; L = CO, PMe3-xPh x = 0-3) in supercritical fluids in the presence of dinitrogen may be used to prepare complexes [Mn(5-C5R4Me)(CO)(N2)L]: evidence for the formation of [Mn(5-C5Me5)(CO)(N2)2] was obtained.11 Similarly photolysis of [Mn(Tp)(CO)3] (Tp = hydrido-*tris*-(1-pyrazolyl)borate) in cyclohexane/HSiEt3 solution under N2 results in CO dissociation and formation of [Mn(Tp)(CO)2(N2)].12 The dinitrogen-bridged dimer [{Mn(5-C5H5)(CO)2}2(N2)] may be prepared from the reaction of [Mn(5-C5H5)(CO)2(THF)] with N2CHCF3.13 An example of P2N2-based complex with a bridging N2 ligand has also been reported.14

Given the current interest in using manganese carbonyl complexes as catalysts for organic transformations,15-20 the observation of new manganese dinitrogen complexes could offer potential for the future development of pathways for nitrogen fixation. We have recently employed time-resolved infra-red spectroscopy to demonstrate that photolysis of [Mn(ppy)(CO)4] (ppy = 2-phenylpyridine) results in ultra-fast loss of a CO ligand and formation of species [Mn(ppy)(CO)3S] within 1 ps, where S is the solvent medium employed.21 If S is a substrate for Mn-catalysed C-H functionalisation, such as an alkyne or an activated alkene, then subsequent C-C bond formation may be observed.16 It was reasoned that if a suitably weakly bound solvent, such as a hydrocarbon, were employed then this could be displaced by a molecule of dinitrogen. TRIR has been used to identify dinitrogen complexes formed by displacement of a coordinated hydrocarbon ligand for a number of different metal complexes and to quantify the rates of substitution.22 In a similar vein, George has demonstrated that using perfluorinated solvents as weakly bound token ligands even allows for the coordination of Xe to photochemically generated [W(CO)5]23 and [Mn(5-C5H5)(CO)2] fragments.24

The implementation of this approach to form a mixed manganese carbonyl/dinitrogen complex is now reported. Instead of the 2-phenylpyridine-substituted complex, the related species [Mn(C^N)(CO)4], [**1**], was employed as it was anticipated that the more sterically demanding cyclometallated imine ligand might favour the coordination of linear N2 to the metal.

Results and Discussion

The photochemical dissociation of CO from [Mn(C^N)(CO)4], [**1**], was studied at the ULTRA facility, Rutherford Appleton Laboratory, using the time-resolved multiple probe (TRMPS)

**Figure 2** (a) ground state spectrum of [**1**] in heptane (b) TRIR spectra of [**1**] in heptane solution recorded with selected pump-probe delays between 1 and 150 ps. Black squares show the bands for [**2**] and arrows indicate the change in intensity of the peaks (c) Expansion of the region between 1880 and 1960 cm-1, showing positive features only.

method. By virtue of using synchronised pump- and probe-lasers, TRMPS permits photo-induced events occurring from 1 ps – 800 s to be observed. A pump wavelength of 355 nm was employed and the changes to the bands in the region 1850 – 2300 cm-1 of the infra-red spectrum used to probe the changes to the metal following irradiation. The resulting data are displayed as difference spectra with negative peaks corresponding to bands lost on irradiation and positive peaks to the photoproducts.

Ultra-fast photochemically initiated behaviour of [1]

Photolysis of [**1**] in heptane solution under an atmosphere of dinitrogen results in the formation of intense negative peaks corresponding to the ground state bleach of the complex. These were present at the shortest pump-probe delays employed. At very short pump-probe delays (< 2 ps) the positive peaks were broad, but then sharpened with a lifetime of (7.8 ± 0.4) ps and moved to higher energy to give three new bands with approximately equal intensity at 1918, 1924 and 2024 cm-1 (Figure 2). These data are consistent with the ultra-fast loss of a carbonyl ligand and the formation of a complex *fac*-[Mn(C^N)(heptane)(CO)3], [**2**]. Specifically, the band positions and intensity are typical of a species with three facially coordinated carbonyl ligands – a complex with a meridional arrangement would exhibit a different pattern of bands (both in terms of energy and intensities).21, 25

A close up of a logo

Description automatically generatedThe sharpening and shift in band position at short-pump probe delays is consistent with vibrational cooling.26, 27 As the pump laser energy is greater than that required to dissociate a CO ligand, the resulting photoproducts are formed in a vibrationally excited state which then relaxes to the *v* = 0 level. The anharmonic nature of the vibrational energy well results in the commensurate shift to higher energy on relaxtion. In the spectra recorded between 1 and 150 ps (Figure 2b and 2c) a feature at lower energy than the bands for [**2**] was observed, which decays with a lifetime, , of (26.4 ± 0.8) ps. This was assigned to [**2**] in *v* > 0 vibrational energy levels. The observed shift of *ca*. 14 cm-1 from the longer-lived bands for [**2**] (assigned to the *v* = 0 → 1 transition) support this hypothesis.26 In addition, the ground state bleach bands for [**1**] became less negative at a similar rate,  = (26.7 ± 2.6) ps, consistent with vibrational cooling of excited [**1**].28

At very short pump-probe delays (< 10 ps) broad bands at *ca*. 1949 and 2027 cm-1 (Figure S9) provided evidence for a further short-lived species being generated on photolysis. On the basis of the related behaviour exhibited by [Cr(bpy)(CO)4]25 (bpy = 2,2’-bipyrdyl) and [Mn(ppy)(CO)4]21 theis species was assigned to 3[**1**] which decayed to ground state [**1**].

Identification of a Mn(I) Dinitrogen Complex

Over the course of *ca*. 20 ns, the bands for [**2**] decreased in intensity to be replaced by one major and one minor species, [**3**] and [**4**] respectively (Figure 3). Complex [**3**] exhibited bands at 1929, 1955 and 2013 cm-1 notably blue-shifted from the heptane complex. The intensity of these features was again consistent with the formation of a facially coordinated tricarbonyl complex although the blue-shift in the band positions relative to [**1**] implied that that a -acceptor ligand had coordinated to the metal, resulting in less -backbonding to the three remaining carbonyl ligands.

It was suspected that the formation of [**3**] represented the displacement of the weakly coordinated heptane molecule in [**2**] by dinitrogen to give *fac*-[Mn(C^N)(CO)3(N2)]. This was supported by the observation of a band at 2249 cm-1, which was assigned to the N≡N stretching mode of the complex (Figure 3). This band is at higher energy than in the related mononuclear manganese N2 complexes (Figure 1) and is only shifted by 81 cm-1 from the Raman band in 14N2 (2330 cm-1).29 This may represent the fact that the -accepting dinitrogen and carbonyl ligands are mutually *trans* in [**3**].

In order to fully secure this assignment, two further experiments were undertaken. Firstly, the reaction was performed under an atmosphere of 15N2 (Figure 4c). In this case, the bands in the metal carbonyl region assigned to [**3**] were unchanged compared to the reaction performed at natural isotopic abundance, however the N≡N stretching mode shifted to 2174 cm-1. This is consistent with the isotopic shift to 2173 cm-1 predicted for the 15N≡15N mode on the basis of a harmonic oscillator model. Secondly, when the experiment was

**Figure 3** (a) ground state IR spectrum of [**1**] in heptane solution. (b) TRIR spectrum of [**1**] in heptane under N2 with a pump-probe delay of 500 ns showing the formation of [**3**], red circles, and [**4**] blue diamonds. The bands between 1875 and 2100 cm-1 are assigned to CO stretching modes, whereas the peak at 2249 cm-1 is assigned to the N≡N vibration

performed under an atmosphere of argon, complex [**3**] was not observed although [**4**] was present (Figure 4e). Therefore, the experimental data support the assignment of [**3**] as *fac*-[Mn(C^N)(CO)3(N2)].

Insight into the nature of [**4**] came from a reaction in which a single drop of water was added to an experiment performed under a nitrogen atmosphere. In this case, the proportion of [**4**] formed relative to [**3**] increased significantly (see ESI). It was therefore proposed that [**4**] is *fac*-[Mn(C^N)(CO)3(OH2)] in which trace amounts of water displace the heptane ligand. Similar observations have been made on photolysis of Insight into the nature of [**4**] came from a reaction in which a single drop of water was added to an experiment performed [W(CO)6]30 and [Mn(ppy)(CO)4]21 in hydrocarbon solution. In these experiments, [**4**] underwent further reactions to give a number of new carbonyl-containing products (see ESI). We have tentatively assigned this process to the formation of hydroxy-bridged Mn carbonyl clusters, similar to those observed on catalysis deactivation during C-H functionalisation reactions.18

Nitrogen binding to the putative *fac*-[Mn(C^N)(CO)3] fragment is highly selective. Photolysis of [**1**] under an atmosphere of air again led to the bands for the dinitrogen complex [**3**] dominating the difference spectrum, with [**4**] being observed as the only other significant product (Figure 4d). No evidence of deleterious oxidation and/or the formation of a dioxygen or carbon dioxide adduct was obtained. Qualitatively, this may represent the fact that the formation of [**3**] from [**1**] corresponds to the substitution of isoelectronic CO and N2 ligands.

DFT Calculations

In order to obtain a quantitative view of this process, the energetics of a series of ligand substitutions reactions were calculated using density functional theory at the D3(BJ)-PBE0/def2-TZVPP//BP86/SV(P) level of theory with COSMO solvation in heptane. The isodesmic substitution of the heptane complex, [**2**] was taken as the reference state for the calculations and the resulting energies are shown in Table 1.

The calculations demonstrate that heptane is a far poorer ligand than water, dinitrogen and carbon monoxide. Water and nitrogen have similar binding constants to the manganese and therefore the coordination of these two ligands should be competitive. The calculations indicated that the binding of nitrogen had a small thermodynamic preference when compared to water (G298 = -5 kJ mol-1), although such a small difference must be treated with caution. Carbon monoxide is predicted to coordinate far more strongly to the manganese than either N2 or H2O.

Further insight into the influence of the different ligands coordinated to the *fac*-[Mn(C^N)(CO)3] fragment was obtained by examining the bond metrics within the calculated structures (Table 2). Comparison of carbonyl, [**1**], and dinitrogen, [**3**], complexes confirms that the N2 ligand is a poorer -acceptor than CO as the M-C bond, *a*, (for the CO ligand *trans* to the CO and N2 ligands) is shorter in the case of [**3**]. The calculated N-N bond length (1.125 Å) only shows a small elongation when compared to the dinitrogen (gas phase experimental value 1.0977 Å,31 calculated at BP86/SV(P) 1.112 Å), but is consistent with the corresponding bond length in *trans*-[MnH(N2)(dmpe)2], 1.127(7) Å.6 However, the Mn-N bond length in [**3**] is predicted to be longer (1.907 Å) than in the dmpe-containing complex (1.817(5) Å). This presumably reflects the fact that the N2 is *trans* to an another -accepting ligand despite in *trans*-[MnH(N2)(dmpe)2] the dinitrogen being opposite to a hydride ligand.

The calculated geometry of the heptane complex, [**2**], provides additional information about the binding of this ligand to the manganese. The DFT-predicted structure demonstrates that the hydrogen of the C-H bond is more closely coordinated to the metal than the carbon (Mn-H 1.997 Å, Mn-C 2.871 Å) and the Mn-H-C bond angle is 130.9 °. This behaviour has been observed in the solid-state structure of alkane complexes and indicates that the heptane is best defined as 1 -alkane using the nomenclature of Macgregor and Weller.32 Structures were investigated in which the heptane was bound to the manganese through C-H interactions at each of the four unique carbon atoms. The predicted IR spectra for each complex were identical

**Figure 4** (a) ground state IR spectrum of [**1**] in heptane solution. (b) TRIR spectrum of [**1**] in heptane recorded under an atmosphere of N2 (c) TRIR spectrum of [**1**] in heptane recorded under an atmosphere of 15N2, (d) TRIR spectrum of [**1**] in heptane recorded under an atmosphere of air (b) TRIR spectrum of [**1**] in heptane recorded under an atmosphere of argon. All spectra were recorded with a pump-probe delay of 500 ns. Complex [**2**] is labelled with black squares, [**3**] red circles and [**4**] blue diamonds. The peak for the ground state bleach at 2074 cm-1 omitted for clarity.

and, in line with our our previous work on [Mn(ppy)(CO)3(heptane)],21 the energetics of binding to these different sites has a significant dependence on the DFT method employed (see ESI for details). Consequently it was not possible to determine which site(s) of the heptane ligand bind to the metal. Examination of the Mn-C and C-O bond lengths within the carbonyl ligands of [**2**] (*a*-*f* Table 2) indicates that the carbonyl ligands are more tightly held in this complex than in

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| **Entry** | **L** | **Product Complex** | **Experimental (CO)a / cm-1** | **E / kJ mol-1** | **G298 / kJ mol-1** |
| 1 | CO | [**1**] | 1940 (1934)  1980 (1967)  1990 (1969)  1974 (2066) | -113 | -116 |
| 2 | Heptane | [**2**] | 1918 (1895)  1924 (1915)  2024 (1999) | 0 | 0 |
| 3 | N2 | [**3**] | 1929 (1929)  1955 (1956)  2013 (2017) | -29 | -33 |
| 4 | H2O | [**4**] | 1900 (1902)  1913 (1911)  2012 (1998) | -23 | -28 |

**Table 1** Calculated energy differences for the substitution of heptane by CO, N2 and H2O at the D3(BJ)-PBE0/def2-TZVPP//BP86/SV(P) level of theory with COSMO solvation in heptane. E corresponds to the zero-point energy-corrected SCF energy change, G298 includes corrections for the chemical potential (calculated at the BP86/SV(P) level). a calculated values at the BP86/SV(P) level in brackets, these have been scaled using an empirical correction factor.16

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | | | | | | | |
| **Complex** | **Mn-C*a*** | **Mn-C*b*** | **Mn-C*c*** | **C-O*d*** | **C-O*e*** | **C-O*f*** | ***Mn-Cg*** | ***Mn-Nh*** | ***Mn-LI*** |
| [**1**] | 1.841 | 1.801 | 1.822 | 1.160 | 1.166 | 1.165 | 2.078 | 2.036 | 1.840 |
| [**2**] | 1.759 | 1.792 | 1.824 | 1.168 | 1.170 | 1.169 | 2.049 | 2.015 | 1.997 |
| [**3**] | 1.808 | 1.803 | 1.829 | 1.162 | 1.166 | 1.166 | 2.073 | 2.035 | 1.907[a] |
| [**4**] | 1.772 | 1.794 | 1.824 | 1.169 | 1.169 | 1.169 | 2.058 | 2.021 | 2.173 |

**Table 2** Structures and calculated bond lengths in Å at the BP86/SV(P) level for complexes [**1**], [**2**], [**3**] and [**4**]. [a] N-N bond length = 1.125 Å.

any of the species investigated: the Mn-C bond trans to the heptane ligand, Mn-C*a*, is the shortest of the all species investigated. In addition, the bond lengths between the two metal-atoms of the cyclometallated ligand in [**2**] are shorter than in the other complexes investigated (Mn-Cg 2.049 Å, Mn-N*h* 2.015 Å). These latter structural effects may be viewed as the donor groups having a stronger interaction with the metal when a poor ligand (in this case heptane) is bound to the metal.

Kinetic profile of the formation of [3] and [4] from [2]

The kinetic profile for the conversion of [**2**] to [**3**] and [**4**] is shown in Figure 5. Inspection of the data indicated that [**2**] appeared to convert into both [**3**] and [**4**] over the course of *ca*. 500 ns. Then, over approximately 1 s, the amount of [**3**] increased further with commensurate loss of [**4**]. In order to quantify the processes which underpin this behaviour, the data were fitted to a series of kinetic models using the COPASI software.33 Care must be taken in the construction of kinetic models based on TRIR data, especially when bimolecular pathways may be involved. Specifically, it is not possible to determine the absorption coefficients of the bands for short-



**Figure 5** Top Kinetic model for the formation of [**4**] and subsequent reaction to form Mn clusters. Bottom Kinetic profile for the loss of [**2**] and formation of [**4**]. The dotted lines show the fit to the kinetic model with parameters [**Mn**]0 = 4.49 × 10-5 mol dm-3 , [H2O]0 = (6.24 ± 0.14) mmol dm-3, *k1* =(1.028 ± 0.004) × 109 mol-1 dm3 s-1, *k2 =* (1.54 ± 0.02) × 109 mol-1 dm3 s-1,*k-2 =* (1.63 ± 0.03) × 107 mol-1 dm3 s-1, [N2] = 9.54 mmol dm-3. Inset shows the behaviour and fit up to 270 ns.

lived intermediates and therefore the absorption values in the difference spectra cannot be converted to absolute concentration values. In order to address this, the absorption coefficients for the four vibrational modes of [**1**] were measured. The intensity of the bleach band at 1980 cm-1 in the difference spectrum (recorded with a pump-probe delay of 50 ps) was then used to determine the concentration of [**1**] lost on irradiation. This was defined as [**Mn**]0 as at this time point it was argued that all of the [**1**] which had been consumed on photolysis had been converted to [**2**], and that the concentration of the heptane complex at this point was also equivalent to [**Mn**]0. As the complexes [**2**], [**3**] and [**4**] are all based on the same *fac*-[Mn(C^N)(CO)3(S)] framework, it was assumed that the absorption coefficients of the high-energy symmetric stretching modes would be similar, and that [**2**]t+[**3**]t+[**4**]t = [**Mn**]0, where [**X**]t is the concentration of a given complex at time *t*. Therefore, the change in absorbance of each species with time could be converted into changes in concentration.

A number of models were simulated and the best fit to the experimental data is shown in Figure 5. In this model, the substitution of heptane by nitrogen is irreversible with a second order rate constant, *k1 =* (1.028 ± 0.004) × 109 mol-1 dm3 s-1 (based on the concentration of N2 in heptane at 1 atmosphere and 25 °C being 9.54 mmol dm-3).34 This is a very fast reaction, approaching the diffusion controlled rate limit in heptane solution calculated to be 2.35 × 1010 mol-1 dm3 s-1 at 20 °C35 and may simply represent how weakly the hydrocarbon is bound to the manganese. Extrapolation of the second order rate constant for the substitution of heptane by water is more problematic as the rate of this process will depend on the rate constant *k2* and the (unknown) concentration of water in the sample. However, it was assumed that value of *k2* would be similar to *k1*. Both *k2* and [H2O] were iterated in independent fits to the kinetic model which then converged on values of *k2 =* (1.54 ± 0.02) × 109 mol-1 dm3 s-1,*k-2 =* (1.63 ± 0.03) × 107 mol-1 dm3 s-1 and [H2O]0 = (6.24 ± 0.14) mmol dm-3.36

These data represent a picture where the substitution of heptane by either water or nitrogen is extremely rapid and the subsequent establishment of an equilibrium position between [**3**] and [**4**] occurs on a longer timescale. There are two further mechanistic points to highlight. Firstly, no evidence for the existence for the formally 16-electron complexes *fac*-[Mn(C^N)(CO)3] or *fac*-[Mn(ppy)(CO)3] has been obtained in any TRIR experiments which implies they have a lifetime of less than 1 ps.21 It is argued that such species would be highly Lewis acidic and in the condensed phase: solvation is extremely rapid following photochemical CO-loss. It is therefore difficult to argue that the substitution of heptane is formally a dissociative pathway. Secondly, models in which [**4**] converted directly to [**3**] did not give satisfactory fits to the experimental data, ruling this out as a potential mechanistic pathway. In any event, the data illustrate that [**3**] is thermodynamically more stable than [**4**].

Conclusions

The selective formation of a rare manganese dinitrogen complex has been observed on photo-induced CO-dissociation from [Mn(C^N)(CO)4] in heptane solution. The kinetic data present a mechanistic picture in which substitution at the initially formed heptane complex, *fac*-[Mn(C^N)(CO)3(heptane)], occurs close to the diffusion controlled limit and therefore the proportion of dinitrogen and water complexes obtained is controlled by the relative concentration of the two substrates. An equilibrium position is obtained on a microsecond timescale and indicates that the dinitrogen complex is more stable than the aqua complex. This situation is also predicted by the DFT calculations, although the energetic difference is very small. These results demonstrate that it is possible to access dinitrogen complexes containing reactive cyclometallated ligands and may offer a new potential pathway for N2 fixation.

Experimental

Complex [**1**] was prepared as described previously.37 Heptane (anhydrous, stored and handled under N2) and 15N2 were supplied by Sigma Aldrich. Time-resolved infra-red spectra were recorded on the LIFEtime instrument in the ULTRA facility at the Rutherford Appleton Laboratories.38 The pump source was the output of a Yb:KGW amplifier providing 15W, 260 fs pulses at 1030 nm with a 100 kHz repetition rate (Pharos). This was used to drive a BBO-based 515 nm pumped optical parametric amplifier (OPA) to deliver pulses at 355 nm. The pump beam was collimated, travelled over a computer programmable 0 - 16 ns optical delay (1200 mm long, double pass), and focused onto the sample. The pump energy at the sample was attenuated down to 500 nJ and focused down to a 120 × 120 μm2 spot. The probe source was the output of a Yb:KGW amplifier providing 6 W, 180 fs pulses at 1030 nm with a 100 kHz repetition rate (Pharos). This drove two 3 W BBO/KTA based OPAs. The two Pharos sources share a common 80 MHz oscillator to allow for pump-probe delay steps of 12.5 ns. The probe beam was split to provide probe and reference pulses. To go beyond pump-probe delays of 12.5 ns, subsequent seed pulses were selected from the 80 MHz oscillator. Data were collected using pump-probe delays ranging from 1 ps to 988.5 μs. The probe beams were collimated, synchronised by a fixed optical delay, and focused by a gold parabolic mirror onto the sample. The three beams were overlapped on the sample using a 50 μm pinhole. The probe beams were measured by two separate 128-element detectors. To cover the full spectroscopic window required, data from different detector positions were combined to generate the required spectra.

Solutions of [**1**] were prepared in heptane (typically 16.5 mg of [**1**] in 20 ml heptane) in a thick-walled Duran flask. Samples under N2, 15N2 and Ar were prepared by sparging these solutions for *ca*. 20 mins whilst flowing (peristaltic pump) through a Harrick cell fitted with a 100 m Teflon spacer. The samples where then sealed, light excluded (either by covering in aluminium foil or employing an amberised flask) and transferred to the LIFEtime instrument. To ensure that the photoproducts were not themselves irradiated, data were acquired while continuously flowing and rastering the sample.

Data were initially visualised in the ULTRA View version 2 software,39 where baseline-correction was undertaken. The resulting spectra were then exported as comma-separated variable files into Origin2019.40 The spectra were calibrated against samples of polystyrene (200 m thick) and 1,4-dioxane.

Kinetic analysis was performed in COPASI. Absorbance data were converted to concentration by using the bleach band at 1980 cm-1 to determine total concentration of manganese, **[Mn]0**, following photolysis at a pump-probe delay of 50 ps. Absorbance data were then scaled so that [**2**]t+[**3**]t+[**4**]t = [**Mn**]0. These data were then imported into COPASI and used to iterate against the parameter *k1*, *k2*, *k-2* and, independently, against [H2O]0. The resulting data are quoted with 95 % confidence limits.

DFT calculations were performed using the TURBOMOLE V6.4 package using the resolution of identity (RI) approximation.41-47 Initial optimisations were performed at the (RI-)BP86/SV(P) level, followed by frequency calculations at the same level. All minima were confirmed as such by the absence of imaginary frequencies. Single-point calculations on the (RI-)BP86/SV(P) optimised geometries were performed using the hybrid PBE0 functional and the def2-TZVPP basis set. The (RI-)PBE0/def2-TZVPP SCF energies were corrected for their zero-point energies, thermal energies and entropies (obtained from the (RI-)BP86/SV(P)-level frequency calculations). No symmetry constraints were applied during optimisations. Solvent corrections were applied with the COSMO48 dielectric continuum model and dispersion effects modelled with Grimme’s D3 method.49, 50 Energies, xyz coordinates and the first 50 lines of the vibrational spectra are presented in the electronic supporting information.

Conflicts of interest

There are no conflicts to declare.

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