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Protonation of the N₂-reduction catalyst [HIPTN₃N]Mo(III) investigated by ENDOR spectroscopy

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Abstract

Dinitrogen is reduced to ammonia by the molybdenum complex of $L = [\text{HIPTN}_3\text{N}]^{3-}$ (**Mo**). The mechanism by which this occurs involves stepwise addition of proton/electron pairs, but how the first pair converts **MoN**₂ to **Mo**-N=NH remains uncertain. The first proton of reduction might bind either at N_β of N₂ or at one of the three amido nitrogen (N_{am}) ligands. Treatment of **MoCO** with [2,4,6-Me₃C₅H₃N]BAR'₄ (Ar' = 2,3-(CF₃)₂C₆H₃) in the absence of reductant generates **HMoCO**⁺, whose EPR spectrum has greatly reduced g-anisotropy relative to **MoCO**. ²H Mims pulsed electron-nuclear double resonance (ENDOR) spectroscopy of ²**HMoCO**⁺ shows a signal which simulations show to have a hyperfine tensor with an isotropic coupling, $a_{\text{iso}}(^2\text{H}) = -0.22$ MHz, and a roughly dipolar anisotropic interaction, $\mathbf{T}(^2\text{H}) = [-0.48, -0.93, 1.42]$ MHz. The simulations show that the deuteron is bound to N_{am}, near the Mo equatorial plane, not along the normal, and at a distance of 2.6 Å from Mo, which is nearly identical to the (N_{am})²H⁺-Mo distance predicted by DFT computations.

Molybdenum complexes of the $[L] = [\text{HIPTN}_3\text{N}]^{3-}$ ligand (HIPT=3,5-(2,4,6-*i*Pr₃C₆H₂)₂C₆H₃) catalytically reduce dinitrogen to ammonia under mild conditions.¹ The mechanism proposed for this process, a stepwise addition of proton/electron pairs, rests on the intermediate states that have been isolated and characterized to date. However, the mechanism by which the first proton/electron pair converts **MoN**₂ (**Mo** = $[L]\text{Mo}$) into **Mo**-N=NH (**MoNNH**) is unknown. This transformation occurs rapidly in the presence of a reductant, CoCp₂ or CrCp*₂, and any one of the acids [Et₃NH][OTf], [Et₃NH][BAR'₄], or [2,6-LutH][BAR'₄]. Three mechanistic routes have been considered: (i) reduction followed by protonation, either at N_β on the dinitrogen ligand or an amido N (N_{am}) of $[L]$; (ii) protonation of either type of nitrogen, followed by reduction; (iii) or proton-coupled electron transfer, again with alternate sites for the proton. To achieve a comprehensive understanding of the reduction mechanism, it is of importance to identify the site at which a proton is most likely to interact.

In the absence of reducing agent, addition of one equivalent of LutH⁺ to **MoN**₂ ($\nu(\text{NN}) = 1990$ cm⁻¹) generates a new species, **HMoN**₂⁺, with a $\nu(\text{NN})$ stretch increased to 2057 cm⁻¹. This shift is consistent with decreased backbonding to the dinitrogen ligand; however, no new low-energy band is observed, as would be expected if N_β of the dinitrogen ligand were protonated. Similarly, when **MoCO** ($\nu(\text{CO}) = 1885$ cm⁻¹) is treated with one equivalent of LutH⁺, a new species, **HMoCO**⁺, appears with $\nu(\text{CO})$ increased to 1932 cm⁻¹,² again

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because of diminished backbonding.³ Unfortunately, although the amount of protonated **MoN₂** increases with the amount of **LutH⁺** added, attempts to measure an equilibrium between **MoN₂** and **HMoN₂⁺** failed because the complexes undergo concomitant decomposition,³ most plausibly because loss of protonated [L] is facile.

As an alternative approach to investigating the site at which a proton interacts with **MoAB** (AB = CO, N₂) we have applied EPR and ²H electron-nuclear double resonance (ENDOR) spectroscopy to samples of these **MoAB** treated with **LutD⁺** in the absence of reducing agent.

Treatment of the $S = \frac{1}{2}$ **MoCO** with **LutH/D⁺**⁴ leads to a new signal in the echo-detected EPR spectrum with a small g-spread, $\mathbf{g} = [2.010, 1.974, 1.953]$ (Fig. S1 and Fig. 1, below), in contrast with that of **MoCO**, whose g values are strongly shifted from the free-electron value, $g_{\parallel} = 3.1$, $g_{\perp} = 1.6$, and determined by the Jahn-Teller effect.⁵ Only a small percentage of the **MoCO** is converted, consistent with prior results noted above.

We applied pulsed ENDOR spectroscopy⁶ to the new species formed by treatment of **MoCO** with **LutD⁺** to directly determine the presence and location of a bound deuteron. Mims ENDOR spectra⁷ taken at multiple fields across the new EPR signal display a doublet pattern centered at the ²H Larmor frequency, with a hyperfine splitting of approximately $A(^2\text{H}) \sim 1$ MHz (Fig. 1), corresponding to $A(^1\text{H}) = 6.5$ MHz. The assignment of this signal as a ²H ENDOR response is confirmed by its suppression in a spectrum taken with the spacing between the first and second pulses of the Mims sequence of $\tau = 1$ μs . The Mims ENDOR intensity is modulated by the response factor $R \sim [1 - \cos(2\pi A\tau)]$. For an $A = 1$ MHz coupled deuteron, the Mims ENDOR response should be suppressed when $\tau = 1$ μs , as observed in the spectrum collected at $g = 1.974$ (Fig. 1 and Fig. S2).

To confirm that the ²H ENDOR response is associated with ²**HMoCO⁺** and does not arise from the background EPR signal of **MoCO**, we collected the ENDOR-induced-EPR (EIE) spectrum associated with the ²H signal.⁷ A 2D field-frequency pattern of ²H ENDOR spectra was collected at multiple points across the range of fields that yield a ²H ENDOR response. The ²H ENDOR signal does not extend past the narrow range of fields assigned to the ²**HMoCO⁺** EPR signal. A fit of the ν_+ peak intensities from the 2D pattern of ENDOR spectra to a spline curve yielded the EIE spectrum of ²**HMoCO⁺** presented in Fig 1, with g-values corresponding to those given above.

The 2D field-frequency ²H ENDOR pattern of Fig. 1 was simulated⁸ to determine the hyperfine tensor of the bound deuteron, and through this to obtain insight into its location and chemical environment. The pattern is well simulated by a hyperfine tensor having components $\mathbf{A}(^2\text{H}) = [-0.70(10), -1.15(05), 1.2(1)]$ MHz, which is oriented relative to $\mathbf{g}$ by the Euler angles $(\alpha, \beta, \gamma) = (25, 65, 0)$.⁹ This interaction corresponds to an isotropic coupling, $a_{\text{iso}}(^2\text{H}) = -0.22$ MHz, and a roughly dipolar anisotropic interaction, $\mathbf{T}(^2\text{H}) = [-0.48, -0.93, 1.42]$ MHz.¹⁰ To test the assignment of the species being studied as **Mo-N_{am}(²H⁺)**, we performed a DFT optimization on an **Nam-protonated MoCO**, Fig. 2 and Table 1.¹¹ The low g anisotropy of the new spectrum indicates a strong reduction from the threefold symmetry of the parent **MoCO**. The DFT geometry optimization of the **Nam-protonated ²HMoCO⁺** is consistent with such a symmetry reduction; the length of the **Mo-N_{am}(H⁺)** bond is predicted to be approximately 13% longer than the **Mo-N_{am}**. This reduction from three-fold symmetry at Mo readily accounts for the suppression of JT effects implied by the small g anisotropy. If, instead, the oxygen of the axial CO were protonated, DFT computations (Fig. 2 and Table 1) indicate that the resultant species very nearly retains the trigonal symmetry of the parent. Such a complex would exhibit large g anisotropy, like that of **MoCO**, and contrary to observation.

The observed hyperfine tensor also is consistent with N_{am} -protonation. Taking the experimental $T_3 = 1.42$ MHz as an effective through-space dipolar coupling constant, $T_3 = 2T = 2g_{\text{e}}\beta_{\text{e}}g_{\text{n}}\beta_{\text{n}}/r^3$, gives $r = 2.6$ Å, consistent with that predicted for a point-dipole interaction between the Mo spin and $N\text{-}^2\text{H}^+$ at the distance calculated from the DFT geometry optimization (2.7 Å, Table 1), $2T = 1.26$ MHz.¹² In contrast, for protonation at the carbonyl oxygen, the DFT geometry gives $r \sim 3.65$ Å, with $2T \sim 0.50$ MHz, much smaller than observed. More importantly, perhaps, the $\text{Mo-}^2\text{H}^+$ vector for CO protonation would lie roughly along the g_1 direction, $\beta \sim 13^\circ$, whereas the $\text{Mo-}^2\text{H}$ vector for N_{am} -protonation lies at $\beta = 88^\circ$, in acceptable agreement with the simulations, $\beta = 65^\circ$. In short, both the g tensor and ^2H hyperfine tensor are in agreement with N_{am} -protonation, and not with CO protonation. An equivalent argument rules out protonation of the 'distal' axial nitrogen of [L].

The properties of the ^2H hyperfine tensor for $N_{\text{am}}(^2\text{H}^+)$ of the LutH^+ -treated **MoCO** complex provide support for our recent assignment of the species trapped in frozen solutions when **MoN₂** is treated with H_2 gas. This species was assigned as the hydrido-Mo(III) anion formed by heterolytic cleavage of H_2 and loss of H^+ . If instead, this species were the neutral complex formed by heterolytic $^2\text{H}_2$ cleavage, with the proton bound as $N_{\text{am}}(\text{H}^+)$ and the hydride bound to Mo(III), it would necessarily show an ENDOR signal equivalent to that seen here from $N_{\text{am}}(^2\text{H}^+)$, but it does not.

We were unsuccessful in trapping the analogous protonated **MoN₂** at low temperature in an EPR tube, the complex instead presumably decomposing to unidentified species through loss of the protonated organic ligand. Following our earlier discussion of modes of decomposition of the product(s) of reaction of H_2 with **Mo**,¹³ it seems likely that protonation of **MoN₂**, like protonation of **MoCO**, occurs at the amido nitrogen, and that the bond between Mo and $N_{\text{am}}(\text{H}^+)$ of amido-protonated **MoN₂** cleaves to form an 'arm-off' species that is unstable to total ligand loss, possibly through bimolecular processes. An alternative is that dinitrogen is lost from the cationic species more readily than CO is lost, again with overall decomposition. The same type of frequency change to the N-N and C-O stretches upon treatment of the respective parent species with LutH^+ suggest that protonation occurs at the same site in both systems.

In summary, a combination of EPR/ENDOR spectroscopy and DFT computations shows that treatment of **MoCO** with the acid LutH^+ results in protonation of the amido nitrogen of the $\text{HIPTN}_3\text{N}^{3-}$ ligand. Infrared spectroscopic measurements show that **MoCO** and **MoN₂** behave similarly when treated with LutH^+ in the absence of reductant, which strongly suggests that N_{am} is protonated in the same way, although protonated **MoN₂** is too unstable to be trapped for EPR/ENDOR analysis. That N_{am} is the site of protonation for **MoAB**, $\text{AB} = \text{CO}$ and N_2 , further indicates that when acid *and* reductant are both present, then reduction of **MoN₂** proceeds either by protonation of N_{am} followed by electron transfer or by proton-coupled electron transfer. This finding also provides evidence for N_{am} -protonation as the first step in the acid-induced decomposition of $[\text{HIPTN}_3\text{N}]\text{Mo(III)N}_2$.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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9. The quadrupole splitting for the deuteron is not resolved in the ENDOR spectra, but its incorporation into the simulations is necessary to obtain quality fits. From the simulations we predict principal values of $P = [-0.075, 0.034, 0.039]$ MHz, with an orientation relative to g of $(\alpha, \beta, \gamma) = (0, 55, 0)$.
10. The isotropic and dipolar hyperfine couplings are calculated from the expression $A = a_{iso}1 + T$. Absolute signs for the principal hyperfine values were not directly determined. Rather, the sign of a_{iso} is expected to be negative because spin polarization to this proton should be indirect through the Nam nucleus.
11. Density Functional Theory (DFT) calculations were performed with the Amsterdam Density Functional (ADF) software package (ADF version 2007.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>) with a BLYP functional in the spin-unrestricted formalism. Geometry optimizations used a TZ2P basis set with a small core potential for all atoms. A reduced structure for Mo in which the HIPT groups were replaced with phenyls was used for the geometry optimizations.
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Figure 1.

35 GHz Mims ^2H ENDOR field-frequency pattern for $^2\text{HMoCO}^+$: $\mathbf{A} = [-0.70, -1.15, 1.2]$ MHz; orientation relative to $\mathbf{g}$, $(\alpha, \beta, \gamma) = (25, 65, 0)$. Hyperfine suppression holes are indicated with red arrows for the $\tau = 1000$ ns spectrum taken at $g = 1.974$. The ENDOR-induced-EPR spectrum was generated by plotting the intensity of the ν_+ ^2H ENDOR response versus field, then applying a spline fit to the data.

Figure 2.

DFT optimized structures for CO-protonated (left) N_{ami}-protonated (right) **MoCO**. The predicted values of r , β are 3.65 Å, 13° for the CO-proton, and 2.7 Å, 88° for the N_{ami}-proton (g_1 is expected to be nearly coincident with the MoC bond axis).

Scheme 1.

Table 1

Selected DFT-optimized bond lengths^a and angles for MoCO protonated either at an amido nitrogen or the carbonyl oxygen.

	MoH ⁺	MoN _{am}	MoN _{ax}	MoC	C-MoH ⁺	N _{am} -MoN _{am}	N _{ax} -MoC
N _{am} -H ⁺	2.690	2.302	2.006	1.977	2.315	2.017	88.2
CO-H ⁺	3.647	2.057	2.055	2.053	2.348	1.189	13.1
							117.7
							115.3
							120.8
							177.3
							179.3

^a See reference 4 for computational details.