Published in final edited form as:

J Am Chem Soc. 2007 March 28; 129(12): 3480–3481. doi:10.1021/ja068546u.

EPR Study of the Low-Spin [d^3 ; $S = 1/2$], Jahn-Teller-Active, Dinitrogen Complex of a Molybdenum Trisamidoamine

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Abstract

The first EPR study of the trisamidoamine complex, $[\mathbf{Mo}]N_2$, where $[\mathbf{Mo}] = [\text{Mo(III)}(\text{HIPTN}_3\text{N})]^{3-} = [3,5-(2,4,6\text{-i-Pr}_3\text{-C}_6\text{H}_2)_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2]_3\text{N}^{3-}$, reveals that this low-spin ($S = 1/2$) [d^3] complex exhibits a 2E state that undergoes a pseudo Jahn-Teller distortion in the adiabatic limit, modified by interactions with the solvent, and gives approximate values of interaction energies. The experiments establish that $[\mathbf{Mo}]N_2$ exhibits the low-spin $[e^3]$ electronic configuration, not $[a^2e^1]$, with the $a(z^2)$ antibonding orbital substantially higher in energy than the $e[xz, yz]$ orbitals.

The sterically encumbered trisamidoamine (TAA) complex^{1,2} $[\mathbf{Mo}] = \text{Mo}(\text{HIPTN}_3\text{N})$, Inset 1, is extremely important for its ability to catalyze the reduction of N_2 to NH_3 ,³ and for the mechanistic insights into this process that it provides; of the thirteen compounds that are postulated to be involved in the formation of $2NH_3$, the structures of eight already have been determined by x-ray diffraction.^{4,5} Nonetheless, at present there is little understanding of the particular features of the electronic structure of the $[\mathbf{Mo}]L$ complexes that underlie their reactivity.

The key first step in the catalytic cycle is N_2 -bound $[\mathbf{Mo}]N_2$,⁶ (Inset 1) which contains a Mo (III) that has been shown by magnetic susceptibility measurements to have a low-spin (ls) [d^3 ; $S = 1/2$] electronic configuration. It has not been emphasized that this is one of the rarest configurations in coordination chemistry. To our knowledge, there is only one report of a ls- $[d^3]$ complex of any transition ion prior to the synthesis of the TAA complexes.⁷ Nor has it been noted that a ls- $[d^3]$ ion in the trigonal-bipyramidal coordination environment of $[\mathbf{Mo}]N_2$ exhibits a doubly-degenerate 2E ground state, Scheme 1, that is subject to a Jahn-Teller (JT) distortion by vibronic coupling to doubly-degenerate e_2 vibrations.^{8,9} Indeed, as shown in the scheme, this ls- $[d^3]$ complex has two possible electronic configurations: $[e^3]$ and $[a^2e^1]$, each doubly degenerate. Although the former is suggested to apply,⁴ this has not been tested. This report first describes the possible vibronic behaviors of $[\mathbf{Mo}]N_2$. It then presents an EPR study that characterizes the electronic configuration and vibronic properties of this complex.

Both $[d^3; S=1/2]$ configurations of Scheme 1 exhibit unquenched orbital angular momentum, and splitting of the orbital degeneracy by spin-orbit coupling (SOC) competes with the JT effect (JTE). Linear vibronic coupling is describable in terms of a single composite ('interaction') e_2 mode,⁸ in which the molecule undergoes a 'pseudo-Jahn-Teller' (PJT) distortion, ρ_0 .⁸

$$\rho_0 = [(F/K)^2 - (\lambda/2F)^2]^{1/2} \quad (1)$$

provided the JT vibronic coupling is strong enough, namely ρ_0 is real. Here K is the effective force constant of the interaction mode, F is the linear coefficient of vibronic coupling to this mode, and λ is the SOC constant. This JTE replaces the electronic degeneracy with a vibronic degeneracy in which the complex is distorted (e.g.: equilateral $\rightarrow$ isosceles triangle; axial $\rightarrow$ non-axial N_2) and the distortion 'pseudo-rotates'. If the JT vibronic coupling is weak (ρ_0 is imaginary) the JT distortion is quenched and $[Mo]N_2$ retains the trigonal symmetry.

The molecular adiabatic potential energy surface (APES) of an isolated molecule is a function of the PJT distortion, ρ , but is independent of the phase angle (ϕ) that defines the direction of the distortion. One must further allow for a solvent-dependent environmental contribution to the e -orbital splitting, the 'solvent potential', V_L ,¹⁰ resulting in APES energies, $W_{\pm} = K\rho^2/2 \pm 2[(\lambda/2)^2 + (F\rho \sin\phi)^2 + (F\rho \cos\phi + V_L)^2]^{1/2}$. When $V_L = 0$, the ground APES (W_-) is the well-known 'modified Mexican hat', Fig 1A, with the minimum of the 'trough' at ρ_0 .^{8,9} $V_L \neq 0$ skews the ground APES, Fig 1B, favoring a particular distortion. At low temperatures, the dynamic PJT distortion will localize at the skewed APES minimum; localization also is favored by quadratic JT coupling.⁸

The X-band CW EPR spectrum of $S = 1/2$ $[Mo]N_2$ in toluene, Fig 2, exhibits axial symmetry, with $g_{\perp} = 1.61 < 2 < g_{\parallel} = 3.03$; identical values were obtained from Q-band CW and spin echo-EPR spectra.^{11,12} The g -values distinguish unambiguously between the $[e^3]$ and $[a^2e^1]$ configurations, and give insights into the vibronic and solvent interactions. We begin by considering a two-orbital model Hamiltonian in which vibronic coupling with the interaction mode combines with SOC to mix and split the $e(xz, yz; m_S = \pm 1)$ orbitals.¹³ This PJT model gives an axial g -tensor for the ground APES with $g_{\parallel}$ along the trigonal axis. The $[g_{\parallel}, g_{\perp}]$ components at the APES minimum depend on the ratio of the sum of equilibrium distortion and environmental energies to the SOC, $[(F\rho_0) + V_L/2]/\lambda$, through the fictitious angle 2θ ;

$$\tan 2\theta = 2[F\rho_0 + V_L/2]/\lambda. \quad (2)$$

$$[e^3] \quad g_{\parallel} = 2(1 + k \cos 2\theta) \quad (3a)$$

$$[a^2e^1] \quad g_{\parallel} = 2(1 - k \cos 2\theta) \quad (3b)$$

$$g_{\perp} = (2 \sin 2\theta) \quad (3c)$$

the quantity $(1 - k)$ corresponds to d -electron delocalization. As 2θ increases from 0 (JTE quenched; no distortion) to $\pi/2$ (SOC quenched), the $[e^3]$ configuration gives $[0 \leq g_{\perp} \leq 2; 4 \geq g_{\parallel} \geq 2]$, while $[a^2e^1]$ gives $[0 \leq g_{\parallel} \leq g_{\perp} \leq 2]$. The observed g -values thus require the $[e^3]$ configuration for $[Mo]N_2$. Analysis further gives d -electron delocalization of $(1 - k) = 15\%$ and a distortion energy with $\tan 2\theta = 1.4$. The PJT splitting between the lower APES minimum and the upper APES is large, $\Delta E(\rho_0) = 2\lambda[(1/2)^2 + ((\tan 2\theta)/2)^2]^{1/2} \sim 2\lambda \sim 1600 \text{ cm}^{-1}$.¹⁴ As a result, the ground and excited APES should be vibronically decoupled ('strong-coupling' or adiabatic limit), and the system well-described by the ground APES and its g -values.^{8,9} The JT energies may even be large enough to have an influence on the energetics of reaction.

Variations in the g -values with solvent, $g_{\parallel} = 3.03$ (toluene), 3.10 (THF), 3.26 (octane) (Fig 2) reveal the presence of an environmental influence.¹⁰ Taking octane as approximating a non-perturbing environment, $V_L(\text{octane}) \rightarrow 0$, the g -values provide interaction parameters through eq 2: $F\rho_0/\lambda \sim 1$; $V_L(\text{THF})/\lambda \sim 0.3$, and $V_L(\text{toluene})/\lambda \sim 0.4$. The small environmental term, $F\rho_0 > V_L$, contrasts with the PJT-active MCp_2 ,^{10,16} $M = \text{Co(II)}$, Fe(I) , and Fe(III) , where $F\rho_0 \ll V_L$.^{10,15-17} The reversal of this inequality for $[\text{Mo}]\text{N}_2$ is noteworthy, as the bulky HIPT substituents were in fact incorporated to shield the metal center from its environment.

The g -values of $[\text{Mo}]\text{N}_2$ in toluene do not shift significantly as temperature increases, whereas in THF and octane, solvents with smaller V_L , the g -values shift slightly (Fig 2). Unlike the well-studied JTE for Cu(II) ,^{8,9,17} this behavior cannot be used as evidence regarding possible reorientation of a trapped JT distortion. Warping of the ground APES of Cu(II) ions leads to three alternate JT distortion orientations with different g -tensor orientations, and thermally activated reorientation of the distortion causes strong ‘motional’ effects in the Cu(II) g -values. In contrast, $g_{\parallel}$ for $[\text{Mo}]\text{N}_2$ is oriented along the trigonal axis for all orientations of the PJT distortion (angles, ϕ), so reorientation has no effect. We instead attribute g -shifts to thermal excitations within the energy ‘well’ of the skewed APES (Fig 1B), which is shallower for smaller values of V_L . The EPR signal for $[\text{Mo}]\text{N}_2$ in toluene does not broaden with increasing temperature; those for $[\text{Mo}]\text{N}_2$ in THF and octane broaden only slightly (Fig 2). This contrasts with the substantial broadening from Orbach relaxation by low-lying states of the PJT-active MCp_2 ,^{10,15} and indicates that $[\text{Mo}]\text{N}_2$ has no low-lying excitations (δ , Scheme 1, is large).

In summary, this first EPR study of an $[\text{Mo}]\text{L}$ complex establishes that $[\text{Mo}]\text{N}_2$ exhibits the $1s[e^3]$ electronic configuration and the JTE in the vibronic strong-coupling (adiabatic) limit. The anti-bonding $a(z^2)$ orbital is considerably higher in energy than $e(xz, yz)$, presumably because of interactions with the axial nitrogen atoms. It appears that interactions with the solvent localize the PJT distortion of $[\text{Mo}]\text{N}_2$ at low temperatures, even though the complex is highly sterically encumbered. If there is no PJT distortion or a pseudo-rotating one, hyperfine tensors of the in-plane N atoms as determined by ^{14,15}N ENDOR studies of $[\text{Mo}]\text{N}_2$ (in progress) will be identical; if skewing of the APES selects a particular distortion, as proposed, they will not be equal. DFT computations also are in progress to identify the vibrations that contribute to the composite interaction mode. ENDOR studies of $[\text{Mo}]\text{N}_2$ and other $[\text{Mo}]\text{L}$ also will permit comparison with intermediates trapped during the turnover of nitrogenase.^{19,20}

Acknowledgements

This work was supported by the NIH (HL13531, BMH; GM31978, RRS; GM067349, RLM) and NSF (MCB0316038, BMH). We thank Prof. J. Telser for insightful remarks and Mr. Clark Davoust for technical assistance.

References

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Figure 1. Lower PJT APES (W_-) calculated with (A) $\lambda = 800 \text{ cm}^{-1}$, $K = 1 \text{ mdyn/\AA}$, $F\rho_0 = 0.95\lambda$; (B) as in A, but with $V_L = 0.1\lambda$.

Figure 2. 9.36 GHz EPR of $[\text{Mo}]\text{N}_2$. The ‘gaps’ at $g \sim 2$ in some spectra eliminate signals from decomposition products and/or precipitated complex in the poorly-glassing THF and octane, chosen to vary V_L .

Scheme 1.

Mo[N₂]

Inset 1.