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EPR Study of the Low-Spin [d^3; $S = {}^1/_2$], Jahn−Teller-Active, Dinitrogen Complex of a Molybdenum Trisamidoamine

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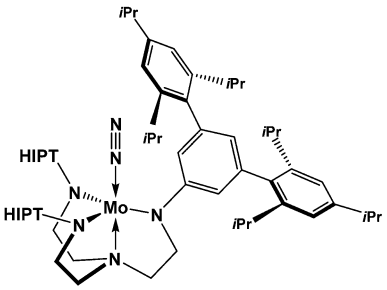
The sterically encumbered trisamidoamine (TAA) complex[1,2] [**Mo**] = Mo[HIPTN$_3$N], Inset 1, is extremely important for its ability to catalyze the reduction of N_2 to NH_3,[3] and for the mechanistic insights into this process that it provides; of the thirteen compounds that are postulated to be 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 [**Mo**]L complexes that underlie their reactivity.

Inset 1

Mo[N_2]

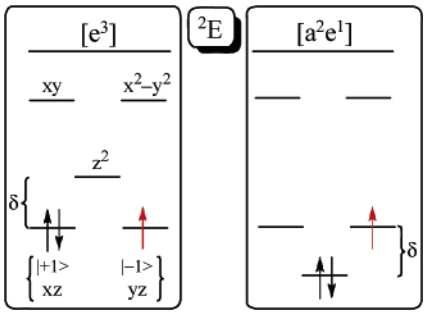


The key first step in the catalytic cycle is N_2-bound [**Mo**]N_2,[6] (Inset 1) which contains a Mo(III) that has been shown by magnetic susceptibility measurements to have a low-spin (ls) [d^3; $S={}^1/_2$] electronic configuration. It has not been emphasized that this is one of the rarest configurations 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 [**Mo**]N_2 exhibits a doubly degenerate ^{2}E 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 [**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]

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

Scheme 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 PJT effect replaces the electronic degeneracy with a vibronic degeneracy in which the complex is distorted (e.g., equilateral → isosceles triangle; axial → nonaxial N_2) and the distortion "pseudorotates". 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" (Figure 1A) with the minimum of the "trough" at ρ_0.[8,9] $V_L \neq 0$ skews the ground APES, (Figure 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, Figure 2,[11,12] 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. The g-values distinguish unambiguously between the [e^3] and [a^2e^1] configurations, and give insights into the vibronic

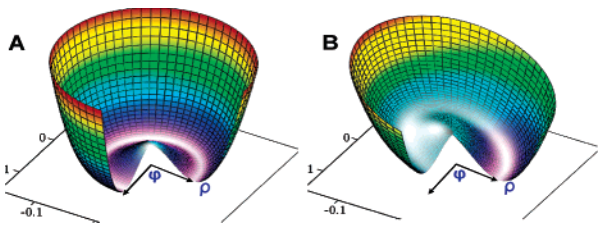


Figure 1. Lower PJT APES (W_-) calculated with (A) $\lambda = 800$ cm^{-1}, $K = 1$ mdyn/A, $F\rho_0 = 0.95\lambda$; (B) as in panel A, but with $V_L = 0.1\lambda$.

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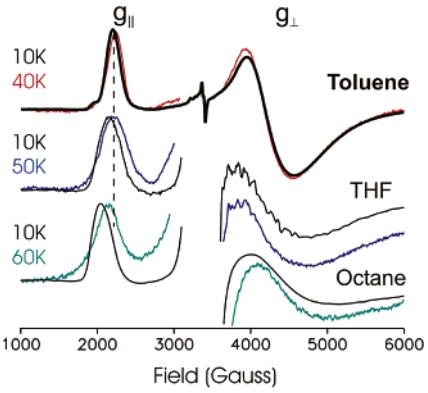

Figure 2. 9.36 GHz EPR of [**Mo**]N_2. The "gaps" at $g \approx 2$ in some spectra eliminate signals from decomposition products and/or precipitated complex in the poorly glassing THF and octane, chosen to vary V_L.

and solvent interactions. We consider 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 $g_{||}$ along the trigonal axis. The [$g_{||}$, $g_\perp$] 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:

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

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

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

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

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 [$0 \le g_\perp \le 2$; $4 \ge g_{||} \ge 2$], while [a^2e^1] gives [$0 \le g_{||} \le g_\perp \le 2$]. 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, $\Delta E(\rho_0) = 2\lambda[(1/2)^2 + ((\tan 2\theta)/2)^2]^{1/2} \approx 2\lambda \approx 1600\ cm^{-1}$.[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 N_2 reduction.

Variations in the g-values with solvent, $g_{||} = 3.03$ (toluene), 3.10 (THF), 3.26 (octane) (Figure 2) reveal an environmental influence.[10] Taking octane as approximating a nonperturbing environment, V_L(octane) ≈ 0, the g-values provide interaction parameters through eq 2: $F\rho_0/\lambda \approx 1$, V_L(THF)/$\lambda \approx 0.3$, and V_L(toluene)/$\lambda \approx 0.4$. The small environmental term, $F\rho_0 > V_L$, contrasts with the PJT-active MCp_2,[10,16] M = Co(II), Fe(I), and Fe(III), where $F\rho_0 \ll V_L$.[10,15−17] The reversal of this inequality for [**Mo**]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 [**Mo**]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 (Figure 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 can cause strong "motional" effects in the Cu(II) g-values. In contrast, $g_{||}$ for [**Mo**]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 (Figure 1B), which is shallower for smaller values of V_L. The EPR signal for [**Mo**]N_2 in toluene does not broaden with increasing temperature; those for [**Mo**]N_2 in THF and octane broaden only slightly (Figure 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 [**Mo**]N_2 has no low-lying excitations (δ, Scheme 1, is large).[18]

In summary, this first EPR study of an [**Mo**]L complex establishes that [**Mo**]N_2 exhibits the ls [e^3] electronic configuration and the JTE in the vibronic strong-coupling (adiabatic) limit. The antibonding 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 [**Mo**]N_2 at low temperatures, even though the complex is highly sterically encumbered. If there is no PJT distortion or a pseudorotating one, hyperfine tensors of the in-plane N atoms as determined by ^{14,15}N ENDOR studies of [**Mo**]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 are in progress to identify the vibrations that contribute to the composite interaction mode. ENDOR studies of [**Mo**]N_2 and other [**Mo**]L also will permit comparison with intermediates trapped during the turnover of nitrogenase.[19,20]

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(13) For large g shifts, as seen here, coupling to the [xy, $x^2 - y^2$] orbitals can be ignored.
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