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Electron Spin Resonance of Tris(2,2′-bipyridyl)vanadium(0)

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Introduction

The isotropic electron spin resonance (ESR) spectrum of tris(2,2′-bipyridyl)vanadium(0), $V(bpy)_3$, was first reported more than 30 years ago by Elschner and Herzog.[1] Although this spectrum was repeated by König,[2] and by Davison et al.,[3] and isotropic spectra have been reported for the Ti(−I),[2] Nb(O),[4] Cr(I),[1,2] and Mo(I)[5] analogs, in no case has a powder, frozen solution, or dilute single-crystal spectrum been obtained. Davison et al.[3] suggested that the odd electron in $V(bpy)_3$ is extensively delocalized into the π^* orbitals of the bipyridyl ligands, but in the absence of a solid-state ESR spectrum, this hypothesis has remained speculative. We report here ESR spectra of $V(bpy)_3$ in fluid and frozen tetrahydrofuran solutions which confirm the delocalization hypothesis.

Experimental Section

$V(bpy)_3$ was prepared by the method of Quirk and Wilkinson[6] by adding 2,2′-bipyridyl to a suspension of sodium amalgam and VCl_3 in THF. The method reported by Herzog[7] failed in our hands; although good yields of $[V(bpy)_3]I_2$ were obtained, we were unable to reduce this compound in aqueous alcohol using either magnesium powder or zinc amalgam. As reported, $V(bpy)_3$ is extremely air-sensitive, although the compound is stable indefinitely in solution in the absence of air.

ESR spectra were obtained using a Bruker ER 220D ESR spectrometer, equipped with a liquid-nitrogen Dewar insert, a Systron-Donner microwave frequency counter, and a Bruker NMR gaussmeter.

Results and Discussion

As reported earlier,[1–3] the isotropic ESR spectrum of $V(bpy)_3$ consists of eight lines, the widths of which exhibit relatively little dependence on m_I. This observation suggests that the g and ^{51}V nuclear hyperfine matrices are rather less anisotropic than is usually found for transition metal complexes. The spectrum is easily analyzed (to third order in perturbation theory) to give $\langle g \rangle = 1.9816 \pm 0.0001$ and $\langle A^V \rangle = (77.5 \pm 0.1) \times 10^{-4}$ cm^{-1} (83.8 G). König[2] observed vestiges of ^{14}N hyperfine structure (the sharpest ^{51}V hyperfine line was somewhat lumpy) with $a^N \approx 2.3$ G; althoughh there was no trace of resolution in our spectra, the lines are non-Lorentzian and the shape is undoubtedly due to unresolved hyperfine structure. Assuming six equivalent ^{14}N nuclei ($I = 1$), our observed line shape is best fit with $a^N \approx 2.8$ G, in satisfactory agreement with König's more direct observation.

The frozen-solution spectrum, shown in Figure 1a, is at first glance very much like an isotropic spectrum with a large m_I^2 line width dependence. However, two small features on either side of the sharpest line provide the key to interpretation. The spectrum is strictly axial with $g_\perp \approx g_\parallel$ and $A_\perp > A_\parallel$, so that the perpendicular features are prominent with all but two of the parallel features superimposed on or obscured by perpendicular features. "Stick spectra" for the parallel and perpendicular orientations are shown in Figure 1b. Analysis of the spectrum is straightforward, and least-squares fitting of the observed features gives $g_\parallel = 1.988 \pm 0.002$, $g_\perp = 1.9805 \pm 0.0005$, $A_\parallel = (42 \pm 1) \times 10^{-4}$ cm^{-1}, and $A_\perp = (86.0 \pm 0.1) \times 10^{-4}$ cm^{-1}. A computer simulation based on these parameters is shown in Figure 1c.

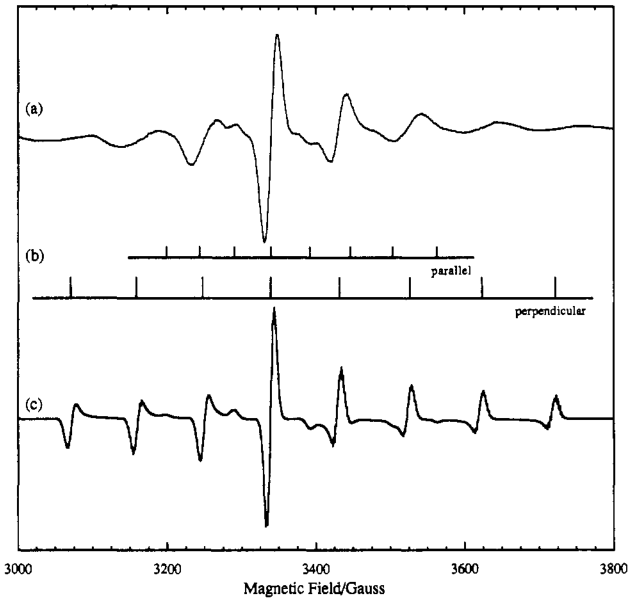

Figure 1. X-band ESR spectrum of $V(bpy)_3$ in THF solution: (a) experimental spectrum at 77 K; (b) stick spectrum showing location of parallel and perpendicular features; (c) computer simulation for $g_\parallel = 1.988$, $g_\perp = 1.9805$, $A_\parallel = 48 \times 10^{-4}$ cm^{-1}, and $A_\perp = 86 \times 10^{-4}$ cm^{-1} with 5-G line widths and Gaussian shapes.

In D_3 symmetry, the metal d-orbitals belong to the a_1 and e representations, with the a_1 orbital identified as d_{z^2} (z along the C_3 axis). Since the spectrum is easily observed at room temperature, $V(bpy)_3$ clearly does not have a degenerate ground state, and since the symmetry is D_3,[8] we conclude that the metal contribution to the singly-occupied molecular orbital (SOMO) must be d_{z^2}. If spin–orbit coupling contributions are ignored (since the g-matrix is so nearly isotropic, spin–orbit coupling contributions are probably quite small), the hyperfine matrix components are given by

$$A_\parallel = \langle A \rangle + {}^4/_7\, P\rho^d \tag{1a}$$

$$A_\perp = \langle A \rangle - {}^2/_7\, P\rho^d \tag{1b}$$

where $P = 146.0 \times 10^{-4}$ cm^{-1} is the dipolar coupling parameter[9] for ^{51}V and ρ^d is the 3d spin density. Subtracting these equations, we obtain

$$\rho^d = \frac{7}{6P}(A_\parallel - A_\perp) \tag{2}$$

Substituting the experimental values of $A_\parallel$ and $A_\perp$ (assuming both are negative), we obtain $\rho^d = 0.30$.

Vanadium 4s character is symmetry-allowed if the SOMO is a_1. If all the spin density were in 4s, the expected coupling would be 1389×10^{-4} cm^{-1},[9] so that at least 5.6% 4s character would be required to account for the observed coupling. This is not impossible for vanadium(0), but it would imply that $\langle A^V \rangle > 0$ and that $A_\parallel > A_\perp$, inconsistent with the assumption that the 3d contribution is d_{z^2}.. Accordingly, we conclude that the coupling is negative and arises through spin polarization of inner-shell vanadium s-orbitals by the 3d spin and by the spin density on the adjacent nitrogen atoms. Although 84 G seems a large coupling through this route, we must recall that for $[VO(H_2O)_5]^{2+}$, with

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the odd electron in d_{xy} so that 4s character is symmetry-forbidden, the isotropic coupling, ca. 116 G,[10] must arise entirely from spin polarization.

If the SOMO were a_1 and purely d_{z^2} with filled orbitals of *e* symmetry somewhat lower in energy and empty e orbitals at much higher energy (the simple ligand-field model), we would expect $g_{\parallel} = g_e$, $g_{\perp} > g_e$. Since the SOMO apparently is a_1, but largely ligand-based, $g_{\parallel}$, $g_{\perp} < g_e$ implies that there are empty orbitals of a_2 and e symmetry with which the SOMO is coupled by L_z and L_x, L_y, respectively. The a_2 orbital must be rather low-lying since the departure of $g_{\parallel}$ from g_e must be proportional to the relatively small nitrogen or carbon spin–orbit coupling constants, metal d-character being symmetry-forbidden. Since several orbitals of e symmetry are expected, some filled and some empty and most with some metal 3d character, the balance of couplings which results in $g_{\perp} < g_e$ is clearly more complex. Given our understanding of the *g*-matrix components, we should not be surprised that $\langle g \rangle$ varies somewhat over the series of isoelectronic tris(bipyridyl) complexes: Ti(−I), 2.007;[2] Nb(0), 1.974;[4] Cr(I), 1.997;[2] Mo(I), 2.037.[5] These variations most likely reflect changes in $g_{\perp}$ as the balance shifts between coupling to filled and empty e orbitals.

Davison et al.[3] suggested low metal 3d participation in the SOMO of $V(bpy)_3$ by analogy with the formal vanadium(IV) thietene complex $[V\{S_2C_2(CN)_2\}_3]^{2-}$, which has qualitatively similar isotropic m_I-dependent line widths and parameters, $\langle g \rangle = 1.980 \pm 0.001$ and $\langle A^V \rangle = (58.5 \pm 0.5) \times 10^{-4}$ cm^{-1}. Earlier work by the same authors[11] had shown that this complex has a nearly isotropic *g*-matrix, with $A_{\parallel} = 92 \times 10^{-4}$ cm^{-1} and $A_{\perp} = 41 \times 10^{-4}$ cm^{-1}. Since $|A_{\parallel}| > |A_{\perp}|$, and for several other reasons discussed by Davison et al.,[11] it is unlikely that the metal contribution to the SOMO is d_{z^2}. There was speculation that the SOMO is a ligand-based orbital of a_2 symmetry, which in D_3 could only have $4p_z$ metal character, but this is inconsistent with the anisotropic ^{51}V coupling. This issue apparently has not been resolved.

The results $V(bpy)_3$ do not share these difficulties, and the SOMO can be understood quite simply as an extensively delocalized orbital of a_1 symmetry with about 30% metal 3d character.

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