# Electron Spin-Echo Envelope Modulation Spectral Properties of Amidate Nitrogen Coordinated to Oxovanadium(IV) Ion

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Electron spin-echo envelope modulation (ESEEM) measurements have been performed for a $VO^{2+}$-amidate complex, $[V^{IV}O(hybeb)]^{2-}$ ($H_4hybeb$ = 1,2-bis(2-hydroxybenzamido)benzene). ESEEM spectroscopic properties of the amidate $^{14}N$ nucleus have been characterized for the first time ($|A_{iso}|$ = 6.70 MHz; $e^2qQ/h$ = 2.5 MHz, $\eta$ = 0.04) to provide a basis for the studies of vanadium-peptide interactions. The electronic structure of the amidate nitrogen is discussed.

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Increasing evidence shows that vanadium plays a variety of roles in biological systems. For instance, a class of haloperoxidase[1] requires vanadium for their enzymatic activities. Vanadium is also known to have beneficial insulin-mimetic activities, and some vanadium complexes are studied as a candidate for an orally-active anti-diabetic agent.[2,3] These findings have stimulated interests in the interactions of vanadium with biological substances such as amino acids, peptides, and proteins. In the studies on this subject, interests are often focused on carboxylate, imidazole and amine groups for vanadium-coordinating groups. However, recent studies have shown that the amide group can undergo deprotonation/coordination reaction even at physiological conditions when an anchoring group is present.[4,5] Therefore it is possible that vanadium-amidate bonding actually occurs and plays some roles in biological systems.

For characterization of vanadium(IV) coordination environments, electron spin-echo envelope modulation (ESEEM) spectroscopy is suited. It has been demonstrated that ESEEM results not only reveal the presence or absence of nitrogen nuclei coordinated to $VO^{2+}$ ion (and possibly the number of the coordinating nitrogen atoms), but allow identification of equatorial nitrogens based on the empirical correlation between the type of the nitrogen and the $^{14}N$ hyperfine coupling (HFC) parameter.[6] However, neither the HFC parameters nor the nuclear quadrupole coupling (NQC) parameters are known for vanadium-coordinated amidate nitrogens. Here we report the first ESEEM results for a structurally-characterized $VO^{2+}$-amidate complex, $[VO(hybeb)]^{2-}$.

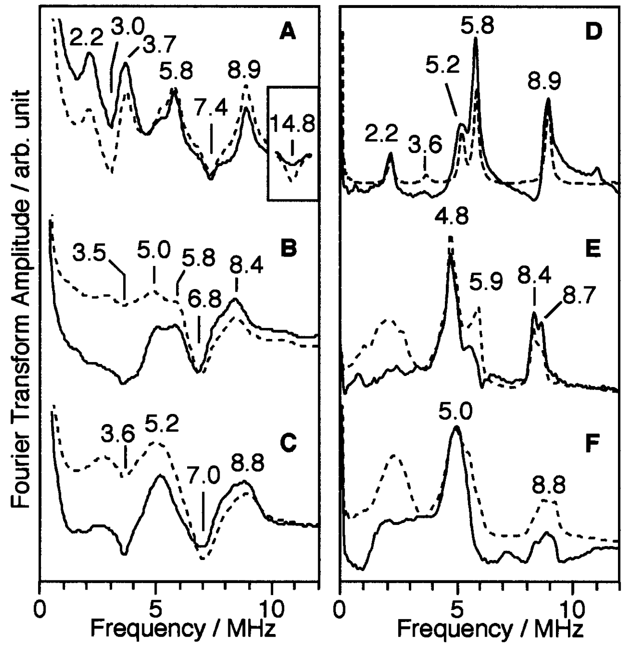

**Figure 1.** Two-pulse (A—C) and three-pulse (D—F) ESEEM spectra of $[VO(hybeb)]^{2-}$ recorded at the $M_I(^{51}V) = -7/2_{\parallel}$ (A and D), $-3/2_{\perp}$ (B and E), and $-1/2_{\parallel\perp}$ (C and F) lines. The dashed lines represent simulated spectra. Conditions: frequency, 8.802 GHz; temperature, 13 K; magnetic field, 260.6 (A and D), 304.9 (B and E), 311.3 mT (C and F); $\tau$ in the three-pulse sequence, 270 (D), 310 (E), 300 ns (F).

Figure 1 shows representative two- and three-pulse ESEEM spectra of $[VO(hybeb)]^{2-}$.[9] Each spectrum exhibits intense peaks attributable to the amidate $^{14}N$ nuclei ($I$ = 1). This type of spectra appears when HFC exceeds NQC and nuclear Zeeman coupling. Major peaks in 4.8—5.8 and 8.4—8.9 MHz are assigned to the lower-frequency and higher-frequency double-quantum (DQ) lines, respectively, where their center frequency provides a rough estimate of the HFC parameter. Other positive peaks in 2.2—5.9 MHz are assigned to single-quantum (SQ) lines. The appearance of SQ lines in spectra A and D indicates a sizable deviation of the NQC axis from the $g_{\parallel}$ axis.[6] In the other spectra, SQ lines are severely broadened, and only the high-frequency edge is resolved at 5.9 MHz in spectrum E (Although simulations predict broad features due to SQ lines in 1—4 MHz, these features are too broad to be observed in the experimental spectra). The negative peaks in spectra A—C are assigned to sum and difference combination lines, which are characteristic of two-pulse spectra. We have carried out spectral simulations based on the Mims formula[7,8] to determine the $^{14}N$ HFC and NQC parameters. The best fits have been achieved with $A_X$, $A_Y$, $A_Z$ = –7.25, –6.80, –6.05 MHz ($|A_{iso}|$ = 6.70 MHz), $Q_X$, $Q_Y$, $Q_Z$ = –0.60, 1.25, –0.65 MHz ($e^2qQ/h$ = 2.5 MHz and $\eta$ = 0.04), and Euler angles[11] of $\alpha$, $\beta$, $\gamma$ = ±45°, 110°, 15° for the two amidate nitrogens.[12] The nitrogen local-axis system $XYZ$ used in the simulation is shown in Figure 2. The Euler angle $\beta$ suggests that the V-N and V=O bond axes (which most likely define the nitrogen $Z$ and molecular $z$ axes, respectively) form an angle of 110° in the solution state, which agrees well with the X-ray result of $\angle(O\text{-}V\text{-}N_{amide})_{av} = 106.3°$.[10]

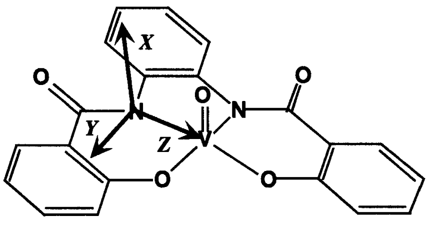

**Figure 2.** Schematic drawing of the orientation of the nitrogen local axes *XYZ* defining the HFC and NQC tensors.

The HFC and NQC parameters can provide invaluable information concerning the electronic structure of the amidate nitrogen. From the HFC parameters, the spin populations of the nitrogen lone-pair and π orbitals can be estimated as $\rho_n$ = –1.1% and $\rho_\pi$ = –0.3%, respectively, and the V-N bond length can be estimated as $r$ = 2.05 Å using eqs. 4 in Ref. 13.[14] This bond length agrees very well with the X-ray result of $r(\text{V-N}_{\text{amide}})_{\text{av}}$ = 2.022 Å.[10] From the NQC parameters, the electron populations of the nitrogen lone-pair and π orbitals can be estimated as $P_n$ = 1.70 and $P_\pi$ = 1.55, respectively, using eqs. 7 in Ref. 13,[14] where the electron population of the nitrogen C-N bond σ-orbital is set as $P_\sigma$ = 1.28 as reported previously.[13] In the formal valence scheme, $P_n$ and $P_\pi$ would equal 2 for the amidate nitrogen. The decrease of $P_n$ from the formal value is consistent with the donation of the lone-pair electrons to vanadium orbitals, which simultaneously induces the negative spin populations on the nitrogen orbitals. The decrease of $P_\pi$ is consistent with the charge delocalization onto the π-linked oxygen in the amidate group.[15] In $[\text{VO(hybeb)}]^{2-}$, where the four equatorial donor atoms are all anionic, remarkable charge redistribution is likely to occur. Hence it is reasonable that $P_\pi$ is notably less than 2.

Compared with other $sp^2$-hybrid nitrogens, the amidate nitrogen has an $|A_{\text{iso}}|$ value substantially smaller than those of the phthalocyanate indole[13] and porphynate[16] nitrogens, but larger than those of the Schiff-base nitrogens.[6] The value is, however, very similar to those of imidazoles,[17,18] which makes it difficult to distinguish between amidate and imidazole coordinations only from the $|A_{\text{iso}}|$ values. Nevertheless, the present results show that the amidate nitrogen has NQC distinctly different from those of imidazoles. The difference in the orientation of the unique axis (the axis containing the largest magnitude NQC component) should be noted. The unique axis in the amidate nitrogen is perpendicular to the V-N axis within the amide plane (the *Y* axis in Figure 2) whereas the unique axis is parallel to the V-N axis in imidazoles.[18] Interestingly, this unique-axis orientation in the amidate nitrogen is equivalent to that in the porphynate nitrogen. These variations in NQC can be attributed to the variations of $P_\pi$. The $P_\pi$ dependence of NQC based on eqs. 7 in Ref. 13 is shown in Figure 3, where sets of experimental data are also plotted versus their estimated $P_\pi$ values. This clear correlation may also help to characterize the ligand type.

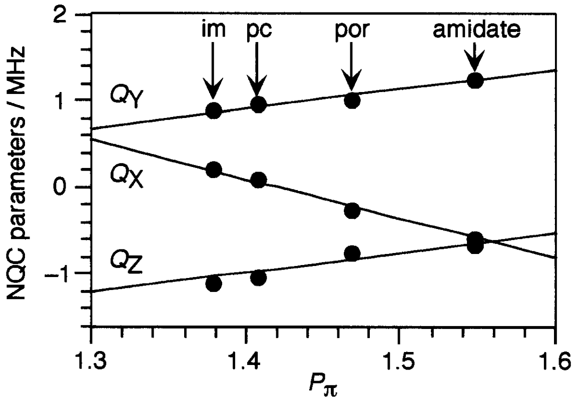

**Figure 3.** $P_\pi$ dependence of the NQC parameters for $sp^2$-hybrid nitrogen. The solid lines represent theoretical results (with $P_n$ = 1.70 and $P_\sigma$ = 1.28 fixed). The solid circles represent experimental data: "im", $\text{VO(imidazoleacetate)}_2$ from Ref. 18; "pc", VO(tetrabutylphthalocyanate) from Ref. 13; "por", VO(octaethylporphynate) from Ref. 16; "amidate", $[\text{VO(hybeb)}]^{2-}$ from the present data.

## References and Notes

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14 Note that *x*, *y* and *z* in Ref. 13 correspond to *Z*, *Y* and *X*, respectively, in this paper.

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