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Molecular Motion of a Nickel-bis(dithiolato) Complex in Solution

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Abstract

The molecular motion of the planar bis(maleonitriledithiolato)nickel anion, $\text{Ni}(\text{mnt})_2^-$, has been studied as a function of temperature using electron spin resonance (ESR) in several polar solvents; they are ethyl alcohol, eugenol, dimethyl phthalate, tri-*n*-butyl phosphate, tris(2-ethyl-hexyl)phosphate, diglyme, and a dimethylformamide–chloroform mixed solvent. Calculated spectra in agreement with the experimental X-band spectra are obtained using axially symmetric reorientation when the long in-plane axis is the unique (parallel) axis of the rotational diffusion tensor with $D_{\parallel}/D_{\perp} = 3.0\text{--}4.0$; $D_{\parallel}$ and $D_{\perp}$ are the diffusion constants for reorientation about the parallel and perpendicular axes, respectively. The reorientational model required for the simulations is either in or close to the Brownian rotational diffusion limit. In the slow motional (low temperature) region, the spectra can be simulated using the glassy g values. As the temperature increases, however, agreement is obtained only if the intermediate g factor, g_y , for the non-axially symmetric Zeeman interaction increases while g_x , g_z , and the motional model remain unchanged; this scheme and others for which g_x and g_z are possibly temperature-dependent are discussed. The values of $D_{\perp}$ from the simulations are in general agreement with those from earlier analyses of the width of the central spectral feature. The simulations and width analyses indicate (as do electrochemical, conductivity, and vapor-phase osmometry data) that the paramagnetic species reorienting in solution has a shape similar to that of the $\text{Ni}(\text{mnt})_2^-$ ion.

Introduction

The bis(maleonitriledithiolato)nickel anion, $\text{Ni}(\text{mnt})_2^-$, is a prototypical square-planar metallo-bis(dithiolene) complex (Figure 1).¹ This important class of compounds is of current interest because of their possible use in electrically conducting and optoelectronic technologies (such as supramolecular arrays and optical storage devices),^{2,3} the separation of olefin streams,^{4–6} and as models for bioinorganic systems.^{2,3,7} They received considerable initial attention because of their structure, multiple oxidation states,⁸ and intense UV–visible spectra.^{1–3}

Electron spin resonance (ESR),^{9,10} pulsed electron nuclear double resonance, and electron simulated echo envelope modulation⁷ spectroscopies have been used to study $\text{Ni}(\text{mnt})_2^-$ in single crystals and glasses. Maki et al.⁹ measured the three g factors of this $S = 1/2$ radical and assigned them to the molecular symmetry axes ($g_x > g_y > g_z$, Figure 1).

A complete map of the molecule's π electron spin densities was determined from a combination of naturally occurring hyperfine satellites and isotopic enrichment.^{7,9,10}

The temperature-dependent ESR spectra of $\text{Ni}(\text{mnt})_2^-$ in solution, while relatively simple (there is no observable hyper-fine splitting), are a source of information concerning its rotational diffusion.^{11–14} As first observed by Huang and Kivelson in *n*-butyl alcohol (*n*-BuOH),¹⁴ the *principal line* associated with the isotropic g value

$$g_0 = (1/3)(g_x + g_y + g_z) \quad (1)$$

in the motionally narrowed (fast motional) region and the intermediate g value, g_y , in the glassy (rigid limit) region has a well-defined first-derivative shape for all temperatures between these two limits. Figure 2 shows the principal line remaining well-defined as the temperature is lowered in a dimethylformamide–chloroform mixed solvent (DMF– CHCl_3).¹¹ We found similar results in 4-allyl-2-methoxyphenol (eugenol), tri-*n*-butyl phosphate (TBP), ethyl alcohol (EtOH), dimethyl phthalate (DMPT), tris(2-ethyl-hexyl)phosphate (TEHP),^{11,13} and a new solvent, diethylene glycol dimethyl ether (diglyme).

We also used spectra calculated between the rigid and the fast-motional limits¹² to show that the well-defined principal line was found only for axially symmetric Brownian rotational diffusion (BRD) when the long in-plane (y) axis was the symmetry axis of the rotational diffusion tensor ($D_{\parallel} = D_y$, $D_{\perp} = D_x = D_z$) with $D_{\parallel}/D_{\perp} \approx 3.0$; it was not produced by isotropic or other types of axially symmetric diffusion. When the anisotropic Zeeman interaction makes the dominant contribution to the spin relaxation, this motional model also produced agreement between the experimental and the calculated principal line widths of $\text{Ni}(\text{mnt})_2^-$ in the solvents listed above.^{11–13}

That agreement, while pleasing, was based on quantitative considerations of only a single spectral feature. In this paper, we report the first simulations of the entire X-band ESR spectra of $\text{Ni}(\text{mnt})_2^-$ in eugenol, TBP, EtOH, DMPT, TEHP, diglyme, and DMF– CHCl_3 . The same general model used for the principal line width analyses, $D_{\parallel} = D_y$ and $D_{\parallel}/D_{\perp} \approx 3.0$ – 4.0 , gives calculated spectra in agreement with experiment using either BRD (in EtOH and DMF– CHCl_3) or free diffusion (FD) with small deviations from BRD (in eugenol, DMPT, TBP, TEHP, and diglyme); these models are discussed below. We also find that the glassy g_1 give calculated spectra in agreement with experiment only for the lowest temperatures in the slow motional region. As the temperature is raised, calculated spectra with all line positions in agreement with experiment are found only if g_y increases while g_x , g_z , and the motional model remain temperature-independent; this is consistent with earlier work (by our group^{11,13} and others¹⁴) in which the experimental values of g_0 measured in the motionally narrowed region were found to be larger than those calculated using the glassy g_1 and eq 1. The possibility of g_x and g_z also being functions of temperature is discussed.

The values of $D_{\perp}$ obtained from the simulations are in reasonable agreement with those from the principal line width analyses. This, along with results from other techniques, is consistent with the shape of the paramagnetic species in solution being comparable to that of the free ion.

Experimental Section

Sample Preparation

$\text{Ni}(\text{mnt})_2^-$ was prepared as the tetrabutylammonium salt following the synthesis of Davison and Holm.¹⁵ Details of the sample preparation and purification for solvents other than

diglyme are given in refs 11 and 13; the DMF-CHCl₃ solution¹¹ was 1:1 v/v. Diglyme (Fisher Scientific Co.) was distilled quickly with the fraction within ± 2 °C of the boiling point (162 °C) being collected. This first distillate was refluxed with potassium metal for several hours; the fraction within (± 1 °C of the boiling point) was collected over lithium aluminum hydride (LAH). The second distillate was refluxed over LAH for several hours followed by collection (over LAH) of the fraction within (± 1 °C of the boiling point), then carefully degassed and distilled into a storage vessel containing LAH on the vacuum line. Solvent was distilled from the storage vessel into the ESR sample tube and sealed under vacuum; the radical concentration was $\approx 10^{-3}$ M. The glassy g_i for Ni(mnt)₂⁻ in diglyme are $g_x = 2.1355$, $g_y = 2.0413$, $g_z = 1.9954$; the experimental g_0 2.0605 is larger than the value (2.0574) calculated using the glassy values. The glassy g_i and g_0 in the other solvents are given in refs 11 and 13, where their determination (with relative uncertainties of (0.0003) and other aspects of the ESR methods are discussed.

Calculation of Motionally Averaged Spectra

The procedures used to calculate the spectra are based on Freed's theory¹⁶⁻²² and discussed in refs 11 and 12. For a given calculation, the three g_i , $D_{\parallel}/D_{\perp}$, and $D_{\perp}$ are required as is the designation of the diffusional symmetry axis and reorientational model. BRD, FD, and jump diffusion (JD) were considered, for which the reorientational correlation times are given by^{16,17}

$$\tau_L(K)^{-1} = B_L \left[D_{\perp} L(L+1) + (D_{\parallel} - D_{\perp}) K^2 \right] \quad (2)$$

where L 0, 2, 4, ... and $K = L, L-2, \dots -L$. The model-dependent parameter $B_L = [1 + L(L+1)D_{\perp}\tau^{-m}]$ has $m = 0, 1/2$, and 1 for BRD, FD, and JD, respectively. For FD, a molecule rotates freely for time τ , then reorients instantaneously; for JD, a molecule has a fixed orientation for time τ then jumps instantaneously to a new orientation.^{16,17}

Spectra were calculated as a function of the magnetic field, B , using^{16,17}

$$F_0 = (4\pi\beta_e B/3h) \left[g_y - (1/2)(g_z + g_x) \right] \quad (3a)$$

$$F_2 = \left[2(6)^{1/2} \pi\beta_e B/3h \right] (g_z + g_x) \quad (3b)$$

where β_e is the Bohr magneton, h is Planck's constant, and the y magnetic axis is the symmetry axis of the rotational diffusion tensor.^{11,12} A typical low-temperature calculation involved a 250 G sweep; the line shape equations were solved for each value of B in steps of 1 G. The transition moment anisotropy²² was used as was a rotationally invariant width,¹⁶ T_2^{-1} , in units of F_0 . The resulting magnetic field dependence of T_2^{-1} for our X-band spectra is small, and a field-independent value was not considered; for a typical $T_2^{-1} = 0.050F_0$, T_2^{-1} only changes from 1.2 to 1.4 G across the $\Delta B = 220$ G spanned by the glassy g values of Ni(mnt)₂⁻. A constant T_2^{-1} is an obvious consideration for spectra having larger values of ΔB .

Results

The principal line width analyses all used the glassy g_i , $T_2^{-1} = 0$, BRD, $D_{\parallel} = D_y$, and $D_{\parallel}/D_{\perp} \approx 3.0 - 4.0$ for the calculated widths.¹¹⁻¹³ Figure 3 shows the experimental spectrum of Ni(mnt)₂⁻ in eugenol at -9 °C and one simulated using the width analysis parameters (for which $D_{\parallel}/D_{\perp} = 3.0$) and the glassy g_i (g_x 2.1380, $g_y = 2.0422$, and $g_z = 1.9967$).¹¹ In the calculated spectrum, the principal line's position and the overall line shape clearly differ

from their experimental counterparts. Figure 4 compares the $-9\text{ }^{\circ}\text{C}$ spectrum with one simulated using the glassy g_i , FD with $D_{\perp}\tau = 0.06$, $D_{\parallel} = D_y$, $D_{\parallel}/D_{\perp} = 4.0$, and $T_2^{-1} = 0.050F_0$. In the calculated spectrum, the positions of the low and high field features as well as the overall line shape are in agreement with experiment, but the principal line is still upfield. Increasing g_y to 2.0438 while leaving all other parameters unchanged brings the calculated principal line into coincidence with experiment without producing changes in the positions of the other features or the overall line shape. When the glassy g_i were used, variations in $D_{\parallel}/D_{\perp}$, T_2^{-1} , and the motional model (including JD) failed to produce calculated spectra with the positions of all three features in agreement with experiment.

The six spectra of $\text{Ni}(\text{mnt})_2^-$ in eugenol for $-29.5\text{ }^{\circ}\text{C} \leq T \leq -4\text{ }^{\circ}\text{C}$ could all be simulated by varying only g_y and $D_{\perp}$ among the parameters required for $-9\text{ }^{\circ}\text{C}$; the glassy g_y was appropriate for the three lowest temperatures (-29.5 , -24 , and $-18.5\text{ }^{\circ}\text{C}$) while increasingly larger values were needed for $-13.5\text{ }^{\circ}\text{C}$ (2.0430), $-9\text{ }^{\circ}\text{C}$ (2.0438), and $-4\text{ }^{\circ}\text{C}$ (2.0444). The simulations for -4 and $-13.5\text{ }^{\circ}\text{C}$ are given in Figure 5. This same scheme (g_y is temperature-dependent; g_x and g_z are not), was needed to simulate the spectra in all of our solvents. We refer to it as Scheme 1; others, involving temperature-dependent values of g_x and g_z , are discussed below.

The temperature dependence of the g factors of $\text{Ni}(\text{mnt})_2^-$ complicates the analysis but does not compromise our conclusion that its rotational diffusion is 3–4 times faster about the long axis. The use of $\Delta g_y/\Delta T > 0$ for the simulations is consistent with our finding that the motionally narrowed value of g_0 in all of our solvents is greater than the value calculated using eq 1 and the glassy g_i .^{11,13} a result first obtained by Huang and Kivelson in *n*-BuOH.¹⁴ The values of Scheme 1 $g_y(T)$ are shown with the corresponding values of $D_{\perp}$ in Figure 6. The temperature ranges for the simulations, the number of spectra simulated, and the temperature-independent values of $D_{\parallel}/D_{\perp}$ (± 0.50) used in each solvent are given in Table 1 (as are the values of $D_{\parallel}/D_{\perp}$ used in the width analyses). The uncertainties in $D_{\perp}$ for the simulations are $\pm 10\%$.

The value of $D_{\perp}\tau = 0.06 \pm 0.03$ for FD represents a small deviation from BRD but is necessary to bring the calculated line shape into agreement with experiment in eugenol as well as in DMPT, TBP, TEHP, and diglyme. BRD was appropriate in EtOH and DMF- CHCl_3 ; the experimental and calculated spectra in DMF- CHCl_3 at -80 and $-86\text{ }^{\circ}\text{C}$ are shown in Figure 2. X-band and 250 GHz studies of nitroxides^{16–21} as well as X-band studies of vanadyl (VO^{2+}) complexes²² also have shown that the overall spectral line shape is a function of the reorientational model; our value of $D_{\perp}\tau = 0.06$ is small compared with $D_{\perp}\tau \approx 1$ (for either FD or JD) needed to simulate the ESR spectra of 2,2,6,6-tetramethyl-4-piperidone- d_{16} (PDT),^{16,19,20} peroxyamine disulfonate (PADS),¹⁷ and the VO^{2+} complexes.²²

The 250 GHz ESR spectra of PDT²⁰ were shown to be more sensitive to differences in the motional models than those at X band. The enhanced g -factor resolution at the higher frequency gave a clearer indication of the type and rate of motion about the molecular axes.²¹ At 250 GHz, the separations between the features in the glassy spectrum of PDT in toluene ($g_z = 2.00233$, $g_y = 2.00633$, $g_x = 2.00936$)²⁰ are $\Delta B_{zy} = B(g_z) - B(g_y) = 178\text{ G}$ and $\Delta B_{yx} = B(g_y) - B(g_x) = 134\text{ G}$ but are only $\Delta B_{zy} = 6.7\text{ G}$ and $\Delta B_{yx} = 5.1\text{ G}$ at X band. The sensitivity of our X-band spectra to the choice of motional model may be because the large differences between the g values of $\text{Ni}(\text{mnt})_2^-$ (compared with those of the nitroxides) give relatively large separations between the features in its glassy spectra; for example, $\Delta B_{zy} = 76\text{ G}$ and $\Delta B_{yx} = 145\text{ G}$ in diglyme.

T_2^{-1} was found to be $0.050F_0$ in all solvents except EtOH where $0.050F_0$ was used for the three lowest temperatures (-111 , -118 , and -125 °C) while $0.025F_0$ was appropriate for -104 °C T -88 °C. A width of $0.050F_0$ corresponds to 1.34 G for the magnetic field for the glassy value of g_y in all solvents. These values are between the X-band values of 2.0 G for the VO^{2+} complexes²² and 0.2–0.9 G for PADS¹⁷ and PDT.^{16,19}

Discussion

Simulation Results

Axially symmetric reorientation with $D_{\parallel} = D_y$, $D_{\parallel}/D_{\perp} = 3.0$ – 4.0 produces simulations in agreement with experiment in all of our solvents, indicating a common, near-prolate-ellipsoidal shape for $\text{Ni}(\text{mnt})_2^{-}$,¹³ which does not appear to have strong associative (or bonding) interactions with solution components, as do its one-electron oxidation and reduction products, $\text{Ni}(\text{mnt})_2$ and $\text{Ni}(\text{mnt})_2^{2-}$, respectively.

The interaction found for $\text{Ni}(\text{mnt})_2$ but not for $\text{Ni}(\text{mnt})_2^{-}$ (in the solvents we have studied) is crucial to Wang and Stiefel's olefin separation process.^{4–6} The neutral complex undergoes an addition reaction with 1-hexene (in CH_2Cl_2) to form a single, well-defined product which, upon electrochemical reduction, quickly releases the olefin and free $\text{Ni}(\text{mnt})_2^{-}$.

Differences between $\text{Ni}(\text{mnt})_2^{-}$ and $\text{Ni}(\text{mnt})_2^{2-}$ were found when we measured their translational diffusion constants, D , at 25 °C.²³ The Stokes–Einstein relation ($D = k_B T / 6\pi\eta r_t$) was used to obtain r_t , a length determined by the solute's shape and size;¹³ k_B is Boltzmann's constant, T is the absolute temperature, and η is the viscosity. The values of r_t for $\text{Ni}(\text{mnt})_2^{-}$ were essentially the same in EtOH (3.55 ± 0.22 Å),¹³ acetonitrile (ACN, 3.55 ± 0.10 Å),²³ acetone (3.77 ± 0.20 Å),¹³ and *n*-BuOH (3.44 ± 0.10 Å),²³ the values¹³ for $\text{Ni}(\text{mnt})_2^{2-}$ were larger in EtOH (4.76 ± 0.31 Å) and acetone (4.54 ± 0.15 Å), in agreement with electrochemical,²⁴ conductivity,^{25,26} and vapor-phase osmometry²⁴ data in ACN, which showed that $\text{Ni}(\text{mnt})_2^{2-}$ but not $\text{Ni}(\text{mnt})_2^{-}$ was ion paired with Et_4N^+ (we used (*n*-Bu)₄N⁺). The dielectric constants, ϵ_0 , of ACN, EtOH, acetone, and *n*-BuOH (Table 2), range from 37.45 (ACN) to 17.1 (*n*-BuOH). While eugenol, DMPT, TBP, TEHP, and diglyme all have $\epsilon_0 < 10$, the similar motional models used for the simulations and width analyses^{11,13} do not seem to suggest an association with counterion. In fact, the interaction of $\text{Ni}(\text{mnt})_2^{-}$ with (*n*-Bu)₄N⁺ would be expected to be relatively weak because the positively charged nitrogen is sterically hindered by the bulky *n*-butyl groups. Infrared studies of the trifluoromethanesulfonate salt (*n*-Bu)₄NCF₃SO₃ in diglyme ($\epsilon_0 = 7.65$)²⁷ and triethylene glycol dimethyl ether (triglyme, $\epsilon_0 = 7.75$)²⁸ showed that only free (*n*-Bu)₄N⁺ and CF₃SO₃[−] ions were present.

The absence of strong $\text{Ni}(\text{mnt})_2^{-}$ –(*n*-Bu)₄N⁺ attractions is consistent with the temperature dependence of the reorientational data determined from the principal line widths, for which the Vogel–Tammann–Fulcher (VTF) equation (discussed later in this section) and the Stokes–Einstein–Debye (SED) model were used.^{11–13} For the SED model, the reorientation is determined by the probe's hydrodynamic interaction with the bulk solvent (represented by the viscosity) as well as its intermolecular interactions with the nearest neighbor solvent molecules; it gives

$$\tau_2(0) = C_{\perp} (\eta/T) + \tau_0 \quad (4)$$

where $\tau_2(0) = (6D_{\perp})^{-1}$ and τ_0 is the zero-viscosity intercept. The parameter $C_{\perp} = 4\pi r_0^3 \kappa_{\perp} / 3k_B$ is a constant in a given solvent but varies from solvent to solvent; $r_0^3 = 78.0$ Å³ was determined from r_t and the radical's geometry,¹³ and $\kappa_{\perp}$ is a radical–solvent interaction parameter ($0 \leq \kappa_{\perp} \leq 1$).²⁹ The values of $C_{\perp}$, τ_0 , and $\kappa_{\perp}$ for $\text{Ni}(\text{mnt})_2^{-}$ are given in Table 2.

Some of the smallest values of $\kappa_{\perp}$ are found for solvents with $\epsilon_0 < 10$, for example, 0.38 for TBP and 0.25 for TEHP.^{11,13} The quantity $4\pi r_0^3 \kappa_{\perp}/3$ is often taken to be the effective probe volume; ion pairing would be expected to give larger probe volumes and larger, not smaller, values of $\kappa_{\perp}$.

The different values of $\kappa_{\perp}$ are the result of varying degrees of solute–solvent interaction but also suggest, as do the motional model and the near-constant values of r_t , that the association of $\text{Ni}(\text{mnt})_2^-$ with solvent is unlikely. For example, the value of r_t is the same (within experimental error) in EtOH and *n*-BuOH, but the values of $\kappa_{\perp}$ are appreciably different (0.85 in EtOH, 0.48 in the larger *n*-BuOH); also, as mentioned above, two of the smallest values of $\kappa_{\perp}$ are found for TBP and TEHP, two of the larger solvent molecules.^{11,13} $\text{Ni}(\text{mnt})_2^-$ would not tend to be solvated by the electronegative oxygens of diglyme, which is well-known for complexing alkali metal cations.³⁰

The electronic spectra of $\text{Ni}(\text{mnt})_2^-$ also argue against its association with solvent³¹ although some metallo-bis(dithiolene) complexes do exhibit specific solvent effects. The electronic spectra of $\text{Ni}(\text{S}_2\text{C}_6\text{X}_2\text{Y}_2)_2^-$ (X and Y are H or CH₃) show no variation in solvents ranging from CH₂Cl₂ to pyridine (py)³² but when X = Y = Cl major spectral bands have clearly different peak positions.^{31,32} $\text{Co}(\text{mnt})_2^-$ has a triplet ground state in dimethyl sulfoxide but is diamagnetic in cyclohexanone. It also is diamagnetic in py³³ with an electronic spectrum different from that in cyclohexanone; the salt of the five-coordinate complex $[\text{Co}(\text{mnt})(\text{py})]^-$ was isolated. Our $\text{Ni}(\text{mnt})_2^-$ ESR spectra showed none of the changes seen when py is combined with the $\text{Ni}(\text{emi})^-$ complex ion; emi^{4-} is a four-coordinate amide-thiol ligand.³⁴ The *g* factors of free $\text{Ni}(\text{emi})^-$ (*S* = 1/2) have the rhombic symmetry of $\text{Ni}(\text{mnt})_2^-$; those for $[\text{Ni}(\text{emi})(\text{py})]^-$ have axial symmetry with hyperfine structure from the ¹⁴N of py on the *g*_{||} feature.³⁴

All of the non-ESR data discussed here were obtained at (or near) room temperature. The simulated spectra were taken at temperatures 20 °C or more lower (Table 1), where the interactions of $\text{Ni}(\text{mnt})_2^-$ with the solution components may change the *g* factors but do not appear to cause major alterations of its shape or size. In addition to the common increase in *g_y* as the temperature increases, the rate of change appears to be about the same from solvent to solvent. Plots of *g_y*(*T*) – *g_y*(glass) versus *T* (Figure 7) have approximately the same slope once *g_y*(*T*) becomes greater than *g_y*(glass).

Possible Schemes for the Temperature-Dependent *g* Factors

If a single *g* factor is temperature-dependent, only Scheme 1 ($\Delta g_y/\Delta T > 0$) is consistent with experiment.³⁵ It is possible (if not likely) that all three *g_i* are temperature-dependent and some qualitative observations can be made. The features are shifted in the appropriate directions provided $\Delta g_y/\Delta T > 0$ while (a) $\Delta g_x/\Delta T > 0$ and $\Delta g_z/\Delta T < 0$ (Scheme 2) or while (b) $\Delta g_x/\Delta T < 0$ and $\Delta g_z/\Delta T > 0$ (Scheme 3). Spectra obtained at spectrometer frequencies higher than X band may yield more information concerning the *g_i*(*T*).^{20,21} For example, if X-band and higher frequency spectra were taken at a given temperature, the separations between the high and the low field features could be compared. If the spectrum at the higher frequency was wider (or narrower) than that predicted by the Scheme 1 X-band simulation, Scheme 2 (or 3) would be suggested.

Comparison of the Simulations and Principal Line Width Results

Figure 8 compares the values of $\tau_2(0)$ from the Scheme 1 simulations with those calculated for the corresponding temperatures from the fits for the principal line widths to the VTF equation,^{11,13} $\tau_2(0) = A \exp[B/(T - T_0)]$. The VTF equation was used because the temperature dependence of $\tau_2(0)$, like that of η , shows deviations from the Arrhenius

equation ($T_0 = 0$). The values of A , B , and T_0 for the solvents except for diglyme are given in refs 11 and 13 (along with more discussion of the VTF equation); those for diglyme (261.2 K T 179.2 K) are $10^{12}A = 6.30$ s, $B = 436.4$ K, and $T_0 = 131.8$ K. The SED and VTF fits gave similarly good agreement between the experimental and the calculated widths.^{11,13}

Given that results from a single feature (the principal line) are being compared with those from the entire spectrum, the overall agreement is good. The differences in the motional models used for the line width analyses and simulations tend to offset each other.³⁶ The temperature-dependent values of g_y from the Scheme 1 simulations have no effect on $\delta g_2 = g_z - g_x$ in F_2 , eq 3b; F_2 is larger than $\delta g_0 = g_y - (1/2)(g_z + g_x)$ in F_0 , eq 3a, which does not change appreciably. As g_y for eugenol increases from the glassy value (2.0422) to the value needed to simulate the spectrum at -4.0 °C (2.0444), $\delta g_2 = -0.1413$ while δg_0 changes from -0.0251_5 to -0.0229_5 .

5. Summary and Conclusions

The X-band ESR spectra of $\text{Ni}(\text{mnt})_2^-$ have been simulated as a function of temperature in seven different solvents. The general motional model ($D_{\parallel} = D_y$, $D_{\parallel}/D_{\perp} = 3.0\text{--}4.0$) produces entire calculated spectra in agreement with experiment. Our ESR results (as well as those from other techniques) suggest that the shape of the species reorienting in solution is similar to that of the free ion. The particular reorientational model required for the simulations is solvent-dependent; BRD was used in EtOH and DMF- CHCl_3 while FD (with small deviations from BRD) was necessary for eugenol, TBP, DMPT, TEHP, and diglyme. It also is necessary to include rotationally invariant width contributions and temperature-dependent g factors in all solvents. The spectra can be simulated only if g_y is allowed to increase as the temperature increases while g_x and g_z are temperature-independent; this scheme (Scheme 1) produced values of $D_{\perp}$ in agreement with those from the width analyses. Two possible temperature variations for g_x and g_z are (a) g_x increases while g_z decreases (Scheme 2) and (b) g_x decreases while g_z increases (Scheme 3). The combination of the X-band results with spectra taken at higher spectrometer frequencies is suggested as a means of obtaining further information concerning these schemes.

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- (35). Consider the case when only g_x (associated with the low field feature) is temperature-dependent. In the spectrum calculated using the glassy g_i in Figure 4, the central feature, as noted previously, is up field from the experimental value. The separations between it and the low and high field features are greater than and less than the observed values, respectively. The only way to bring these separations into agreement with experiment is to decrease both g_x and $D_{\perp}$. The decrease in g_x is unacceptable and also causes the absolute positions of the three features to be slightly upfield from their experimental values. If g_z (associated with the high field feature) is temperature-dependent, one matches the experimental separations by decreasing it and increasing $D_{\perp}$, which again is unacceptable. As for $g_x(T)$, the calculated positions of the three features are larger than the experimental values.
- (36). The differences in the motional models used for the line width analyses and simulations tend to counterbalance each other, giving essentially the same value of $D_{\perp}$ in a given solvent at a given temperature. The use of FD and nonzero T_2^{-1} for the simulations (as opposed to BRD and $T_2^{-1} = 0$ for the width analyses) causes compensating changes in the values of $D_{\perp}$ needed to give calculated positions of the high and low features in agreement with experiment. If only T_2^{-1} is changed and increased, these two features move toward each other as they do for an increase in $D_{\perp}$ (or for an increase in $D_{\parallel}/D_{\perp}$ at constant $D_{\perp}$); if only τ for FD is changed and increased, the motional rate decreases (eq 2), and they move away from each other (as they do for a decrease in $D_{\perp}$ or for a decrease in $D_{\parallel}/D_{\perp}$ at constant $D_{\perp}$).

Figure 1. Molecular structure of $\text{Ni}(\text{mnt})_2^-$ ($\text{Ni}[\text{S}_2\text{C}_2(\text{CN})_2]_2^-$) and the right-handed principal axes of the anisotropic Zeeman interaction. Values of $g_x > g_y > g_z$ for $\text{Ni}(\text{mnt})_2^-$ in eugenol and diglyme are given in the text.

Figure 2.

Experimental and calculated ESR spectra for $\text{Ni}(\text{mnt})_2^-$ in DMF-CHCl_3 . The calculated spectra were obtained using BRD, $D_{\parallel} = D_y$, $D_{\parallel}/D_{\perp} = 4.0$, $T_2^- = 0.050F_0$, the indicated values of $\tau_2(0) = (6D_{\perp})^{-1}$, and $g_y = 2.0449$ (-80°C) and 2.0437 (-86°C); the glassy values is $g_y = 2.0429$. The magnetic field increases left to right.

Figure 3.

Experimental and calculated ESR spectra for $\text{Ni}(\text{mnt})_2^-$ in eugenol at -9°C . The calculated spectrum was obtained using the glassy g_i (see the Results section) BRD, $D_{\parallel} = D_y$, $D_{\parallel}/D_{\perp} = 3.0$, $T_2^- = 0$, and $D_{\perp} = 3.90 \times 10^7 \text{ s}^{-1}$.

Figure 4.

Experimental and calculated ESR spectra for $\text{Ni}(\text{mnt})_2^-$ in eugenol at -9°C . The calculated spectrum was obtained using the glassy g , FD with $D_\perp\tau = 0.06$, $D_\parallel = D_y$, $D_\parallel/D_\perp = 4.0$, $T_2^{-1} = 0.050F_0$, and $D_\perp = 3.98 \times 10^7 \text{ s}^{-1}$.

Figure 5. Experimental and calculated ESR spectra for Ni(mnt)_2^- in eugenol at -4°C (A) and -13.5°C (B). The calculated spectra were obtained using the same parameters as in Figure 4 with the exception of (A) $g_y = 2.0444$, $D_\perp = 5.64 \times 10^7 \text{ s}^{-1}$, and (B) $g_y = 2.0430$, $D_\perp = 2.42 \times 10^7 \text{ s}^{-1}$.

Figure 6.
Plots of $\Delta g_y = g_y(T) - g_y(\text{glass})$ vs $\tau_2(0) = (6D_{\perp})^{-1}$ in eugenol (circle), TBP (triangle), EtOH (diamond), DMF-CHCl₃ (x), DMPT (inverted triangle), TEHP (square), and diglyme (+).

Figure 7. Plots of $\Delta g_y = g_y(T) - g_y(\text{glass})$ vs T in eugenol (circle), TBP (triangle), EtOH (diamond), DMF-CHCl₃ (x), DMPT (inverted triangle), TEHP (square), and diglyme (+).

Figure 8.

Comparison of $\tau_2(0)$ for the simulations and the principal line width analyses using the VTF equation in eugenol (circle), TBP (triangle), EtOH (diamond), DMF-CHCl₃ (x), DMPT (inverted triangle), TEHP (square), and diglyme (+).

TABLE 1

Temperature Ranges and Values of $D_{\parallel}/D_{\perp}$ for $\text{Ni}(\text{mnt})_2^-$ Simulations

solvent	$T(\text{low}), (\text{high}), ^\circ\text{C}$	N^a	$D_{\parallel}/D_{\perp}(\text{sim})$	$D_{\parallel}/D_{\perp}(\text{widths})^b$
eugenol	−29.5, −4.0	6	4.0	3.0
DMPT	−14.5, +0.5	5	3.0	2.85
TBP	−69.0, −44.0	6	3.5	3.0
TEHP	−43.0, −37.0	2	3.0	3.0
diglyme	−88.5, −65.5	7	3.0	3.0
DMF- CHCl_3	−92.0, −80.0	4	4.0	4.0
EtOH	−125.0, −88.0	7	4.0	3.5
<i>n</i> -BuOH				2.5–3.5 ^c

^aNumber of spectra simulated in the indicated temperature range.^bFrom refs 11 – 13 except for diglyme (this work).^cBased on calculations in ref 12 and line width data from Huang, R.; Kivelson, D. *Pure Appl. Chem.* **1972**, 32, 207–219.

TABLE 2

Solvent-Dependent Reorientational Parameters for $\text{Ni}(\text{mnt})_2^-$ from the Stokes–Einstein–Debye Model

solvent	$10^6 C^a$ (s K P ⁻¹)	$\kappa_{\perp}^a$	$10^{11} \tau_0^a$, S	ϵ_0^b
diglyme	1.95	0.82	1.70	7.65 ₂₅
EtOH	2.01	0.85	−3.01	24.3 ₂₅
eugenol	1.38	0.58	9.13	9.7 ₂₀
DMPT	1.18	0.50	5.74	8.5 ₂₄
<i>n</i> -BuOH	1.13	0.48	0.226	17.1 ₂₅
TBP	0.899	0.38	8.01	8.1 ₂₅
TEHP	0.583	0.25	13.5	≈8.0 ₂₅
ACN				37.45 ₂₀
acetone				21.3 ₂₅
triglyme				7.75 ₂₅

^aFrom refs 11 and 13 except for diglyme (this work).^bFrom ref 23 except for diglyme and triglyme from Firman, M.; Xu, M.; Eyring, E. M; Petrucci, S. *J. Phys. Chem.* **1993**, 97, 3606–3613.