Published in final edited form as:

J Phys Chem B. 2010 March 4; 114(8): 2760–2765. doi:10.1021/jp906830y.

Electron Spin Resonance Studies of the Reorientational Motion of Ni(mnt)₂[−]

Bruce A. Kowert^{*}, Eva M. Thurman-Keup, Ann Joern Stemmler, Timothy L. Stemmler, Michael J. Fehr, Cassondra V. C. Caldwell, and Stephen J. Gentemann

Department of Chemistry, Saint Louis University, 3501 Laclede Avenue, St. Louis, Missouri 63103

Abstract

Electron spin resonance studies of the planar bis(maleonitriledithiolato)nickel complex ion, Ni(mnt)₂[−], have been carried out from the motional narrowing region to the glassy limit in a series of ethers: 2-methyltetrahydrofuran (MTHF), diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme). Analyses of the spectra show that Ni(mnt)₂[−] is reorienting a factor of 3 faster about its long in-plane axis in all of these solvents; i.e., axially symmetric rotational diffusion produces agreement between the experimental and calculated line widths with $D_{\parallel}/D_{\perp} = 3.0 \pm 0.2$; $D_{\parallel}$ and $D_{\perp}$ are the diffusion constants for reorientation about the long in-plane (parallel) and perpendicular axes, respectively. The temperature dependence of the reorientational correlation time $\tau_2(0) = (6D_{\perp})^{-1}$ determined from the widths is in agreement with the modified Stokes–Einstein–Debye model; the results indicate that Ni(mnt)₂[−] has relatively strong (but not associative) interactions with the ethers. The experimental values of $\tau_2(0)$ and the solvents' viscosities, self-diffusion constants, and dielectric relaxation times are compared and found to have a common temperature dependence. The ESR data also are compared with values of $\langle \tau \rangle_{\text{solv}}$, the correlation time obtained when a fluorescent probe is excited and its emission is monitored as the nonequilibrium solvent distribution relaxes. $\langle \tau \rangle_{\text{solv}}$ and $\tau_2(0)$ are found to have a common temperature dependence in MTHF, tetraglyme, and two other solvents (ethyl alcohol and 1-butanol) in which Ni(mnt)₂[−] has been studied. The factors determining these transport properties are discussed.

Introduction

The bis(maleonitriledithiolato)nickel anion, Ni[S₂C₂(CN)₂]₂[−] or Ni(mnt)₂[−], is a planar, paramagnetic complex with one unpaired electron.^{1–4} The structure and principal axes for its Zeeman interaction ($g_x > g_y > g_z$) are shown in Figure 1.

Electron spin resonance (ESR) has been used to study the solution dynamics of Ni(mnt)₂[−] in a number of polar liquids; they include ethyl alcohol, 4-allyl-2-methoxyphenol (eugenol), tri-*n*-butyl phosphate, dimethyl phthalate, tris(2-ethyl-hexyl)phosphate, 1-butanol, and a 1:1 v/v dimethylformamide–chloroform solution.^{5–10} In all of these solvents,^{5–10} Ni(mnt)₂[−] was found to be reorienting via axially symmetric rotational diffusion with the long in-plane (*y*) axis as the symmetry (or parallel) axis and $D_{\parallel}/D_{\perp} = 3.0$; $D_{\parallel} = D_y$ and $D_{\perp} = D_x = D_z$ are the rotational diffusion constants about the parallel and perpendicular axes, respectively.

The reorientational correlation time^{7,8} $\tau_2(0) = (6D_{\perp})^{-1}$ obtained from the ESR spectra was shown to follow the modified Stokes–Einstein–Debye model^{7–10}

$$\tau_2(0) = C_{\perp}(\eta/T) + \tau_0 \quad (1)$$

where η is the viscosity, T is the absolute temperature, and τ_0 is the zero-viscosity intercept; $C_{\perp} = 4\pi r_0^3 \kappa_{\perp} / 3k_B$ is a constant in a given solvent but varies from solvent to solvent, k_B is Boltzmann's constant, $\kappa_{\perp}$ is a radical-solvent interaction parameter, and $r_0^3 = 78.0 \text{ \AA}^3$ was determined from translational diffusion data.⁹ The values of $C_{\perp}$ and $\kappa_{\perp}$ in the above solvents^{8,9} are given in Table 1 and differ by more than a factor of 3, showing that the viscosity is not the only solvent property determining the reorientation of $\text{Ni}(\text{mnt})_2^-$.

In this paper, we report temperature-dependent X-band ESR studies of $\text{Ni}(\text{mnt})_2^-$ in 2-methyltetrahydrofuran (MTHF) and three polyethers: diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme). Analyses of the spectra show that, as in our previous solvents,^{8,9} $\text{Ni}(\text{mnt})_2^-$ is reorienting with $D_{\parallel} = D_y$ and $D_{\parallel}/D_{\perp} \approx 3.0$. The values of $\tau_2(0)$ can be fitted using eq 1,¹¹ and as discussed below, the values of $C_{\perp}$ and $\kappa_{\perp}$ indicate relatively strong solute–solvent interactions.

Charge and mass transport in the glymes are of interest because they are potential lubricants¹² as well as liquid-state homologues of poly(ethylene oxide), a host matrix for solid-state polymer electrolyte systems with high ionic conductivities.¹³ Consequently, their viscosities,^{14–16} translational self-diffusion constants (D_{self}),¹³ and dielectric relaxation times (τ_{DR})^{17,18} have been determined as a function of temperature as have η , D_{self} , and τ_{DR} for MTHF.^{15,19–21} In a given solvent, a common temperature dependence is found when scaled values of $\tau_2(0)$ for $\text{Ni}(\text{mnt})_2^-$ are compared with those of η , τ_{DR} , $1/D_{\text{self}}$, and $\langle \tau \rangle_{\text{solv}}$, the relaxation time describing the solvent's response to the excitation of a fluorescent probe.^{20,22–27} The mechanisms determining these dynamic properties are compared and found to have factors in common.

Experiment

Chemicals and Sample Preparation

$\text{Ni}(\text{mnt})_2^-$ was prepared as the tetrabutylammonium salt following the procedure of Davison and Holm.²⁸ The glymes (Fisher Scientific Co.) and MTHF (Aldrich Chemical Co.) had purities of 99% or better. As described in ref 10, diglyme (bp 162 °C) was purified using multiple distillations and stored on a vacuum line over lithium aluminum hydride before being distilled into an ESR sample tube containing $(n\text{-Bu})_4\text{NNi}(\text{mnt})_2$ and sealed under a vacuum; the same procedure was followed for MTHF (bp 80 °C). Triglyme (bp 216 °C) and tetraglyme (bp 275 °C) were placed over hot 4 Å molecular sieves in a vacuum desiccator before being manually transferred into individual sample tubes containing the solute; the solutions were degassed and sealed on the vacuum line. The $\text{Ni}(\text{mnt})_2^-$ concentration in all samples was $\approx 10^{-3} \text{ M}$.

Viscosities

The temperature dependence of the viscosities of the glymes and MTHF is described by the Vogel–Tamman–Fulcher (VTF) equation^{8,29}

$$\eta = A \exp[D_{\text{VTF}} T_0 / (T - T_0)] \quad (2)$$

The values of A , D_{VTF} , and T_0 obtained from fits to eq 2 are given in Table 2 and were used to calculate the viscosities for the modified Stokes–Einstein–Debye analyses (eq 1). The data for diglyme^{14–16,30,31} are consistent if all temperatures above 273.2 K in Table 2 of ref 14 are lowered by 5 K. Given these changes, the values of η for 313.2 K T 193.2 K from ref 14 (uncertainties of $\pm 1\%$) and $T = 323.3$ and 333.2 K from ref 15 (uncertainties less than $\pm 2\%$) were used with eq 2.

As for diglyme, VTF fits for triglyme and tetraglyme were made after all temperatures above 273.2 K in Table 2 of ref 14 were lowered by 5 K.^{30,31} The values of η (with uncertainties of $\pm 0.5\%$ ¹⁴) for 378.2 K T 248.2 K for both solvents were fitted to eq 2. Two sets of viscosities were used for MTHF: one, from ref 15, was for 183.2–383.2 K (0.236 cP η 2.38 cP) with uncertainties less than $\pm 2\%$. The other, from ref 21 (with the correction noted in ref 20), was for 97.5–107.5 K (2.1×10^5 cP η 1.8×10^9 cP) with somewhat larger uncertainties; the temperatures were given to the nearest 0.5 K and η was said to change by an order of magnitude for $\Delta T = 2$ K. Because there also is a substantial gap between the viscosities for 183.2 K (2.98 cP)¹⁵ and 107.5 K (2.1×10^5 cP),²¹ VTF fits were made for the combined viscosities from refs 15 and 21 and for only the viscosities from ref 15; the rms error for the latter was clearly smaller (Table 2).

ESR Procedures

The X-band ESR spectrometer and temperature control unit are described in ref 8. The analyses in this paper focus on the *principal line*^{5–10} of the temperature-dependent spectra of $\text{Ni}(\text{mnt})_2^-$. It has a well-defined first-derivative line shape for all temperatures in and between the motionally narrowed region and the glassy limit.^{5,10} The position of the principal line is given by the isotropic g factor

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

in the motionally narrowed region and the intermediate g value, g_y , in the glassy limit. Its width is easily measured (with an uncertainty of 1–3%) over the entire range of motional rates. Our early calculations⁷ for $\text{Ni}(\text{mnt})_2^-$ indicated that the principal line remained well-defined only when $D_{\parallel} = D_y$ and $D_{\parallel}/D_{\perp} = 3.0$ –4.0. We then showed that this model gave agreement between the experimental and calculated widths^{8,9} as well as between entire experimental and calculated spectra.¹⁰ The computer program used to calculate the principal line widths and spectra^{7,10} contains the secular (energy level modulation) and nonsecular (lifetime broadening) terms for the anisotropic Zeeman interaction as well as a rotationally invariant width, T_2^{-1} , and the transition moment anisotropy.^{8,10,32–35} In the near-rigid motional limit, T_2^{-1} corresponds to the residual line width in a powder spectrum.³² Reference 10 and the Supporting Information give details of the spectral simulations and show that the values of $D_{\perp}$ from the simulations are in agreement with those from our previous width analyses which used, as we do here, Brownian diffusion, $D_{\parallel} = D_y$, $D_{\parallel}/D_{\perp} \approx 3.0$, and $T_2^{-1} = 0$. For Brownian diffusion, the reorientational correlation times are given by

$$\tau_L(K)^{-1} = [D_{\perp}L(L+1) + (D_{\parallel} - D_{\perp})K^2] \quad (4)$$

where $L = 0, 2, 4, \dots$ and $K = L, L - 2, \dots, -L$.

Results and Discussion

Principal Line Width Analyses

In Figure 2, eq 1 is used to compare the experimental and calculated peak-to-peak principal line widths of $\text{Ni}(\text{mnt})_2^-$ in diglyme. Regression analyses⁸ were used to determine τ_0 and $C_\perp$ after experimental values of $\tau_2(0)$ were obtained from the ESR spectra using the widths calculated for $D_\parallel/D_\perp = 3.0$ and the glassy g_i ($g_x = 2.1355$, $g_y = 2.0413$, and $g_z = 1.9954$ with relative uncertainties of ± 0.0003 ;^{8,10} the uncertainty in $D_\parallel/D_\perp$ is ± 0.2). Good agreement is found for 184.7 K $\leq T \leq$ 261.2 K, a temperature range for which the reorientation rates extend from the slow motional region to the “slow end” of the motional narrowing region where the anisotropic Zeeman interaction still makes the dominant contribution ($\approx 90\%$) to the calculated widths. The spin rotational contribution⁷ is negligible in the slow motional region and is no larger than $\approx 10\%$ for the highest of these temperatures; it is calculated separately and added to the computer-calculated widths.

Equation 1 also gives satisfactory agreement between the widths calculated for the diglyme fit and the experimental widths in triglyme (246.2 K $\leq T \leq$ 291.2 K) and tetraglyme (240.2 K $\leq T \leq$ 301.2 K). Table 1 gives the values of τ_0 and $C_\perp$ for the ethers,¹¹ including two fits for MTHF. One of the MTHF fits, shown in Figure 2, used the ESR line widths for all of the temperatures at which $\text{Ni}(\text{mnt})_2^-$ was studied (128.2 K $\leq T \leq$ 252.2 K) and the viscosities calculated from the VTF fit to the data in refs 15 and 21; the agreement is comparable to that for the diglyme fit. The other fit used only the ESR temperatures (190.2 K $\leq T \leq$ 252.2 K) within the range (183.2 K $\leq T \leq$ 383.2 K) covered by the ref 15 viscosities (whose VTF fit had a smaller rms error); τ_0 and $C_\perp$ from the two fits are within 5% of each other.

Motional Parameters

A theoretical treatment of reorientation at the molecular level³⁶ showed that $\kappa_\perp$, obtained from $C_\perp$, has a range of $0 \leq \kappa_\perp \leq 1$ and is proportional to $\langle \tau_q^2 \rangle / \langle F^2 \rangle$, where τ_q and F are the intermolecular torques and forces experienced by the solute. The values of $\kappa_\perp$ for $\text{Ni}(\text{mnt})_2^-$ in the glymes and MTHF are large and indicative of relatively strong solute–solvent interactions. They are $\kappa_\perp = 0.82$ (diglyme), 1.07 (triglyme), 0.95 (tetraglyme), and 1.09 (MTHF, an average of the two fits); only $\kappa_\perp = 0.85$ for ethyl alcohol from our previous work is comparable (Table 1). When the uncertainties in $C_\perp$ ($\pm 10\%$) and r_0 (± 0.30 Å) are considered, that for $\kappa_\perp$ is $\pm 15\%$,³⁷ placing the values for MTHF and triglyme near the upper limit.

The value of $\kappa_\perp$ is a function of r_0 , which was determined for the free $\text{Ni}(\text{mnt})_2^-$ ion.^{9,10} Ion pairing is a possibility in the ethers because of their small dielectric constants,³⁸ 6.24 $\leq \epsilon_0 \leq$ 7.70 (Table 1). However, the interactions between $\text{Ni}(\text{mnt})_2^-$ and $(n\text{-Bu})_4\text{N}^+$ are expected to be relatively weak because of the steric hindrance of the positively charged nitrogen atom by the bulky *n*-butyl groups. This is supported by infrared studies of $(n\text{-Bu})_4\text{NCF}_3\text{SO}_3$ in diglyme³⁹ and triglyme,⁴⁰ which showed that only free $(n\text{-Bu})_4\text{N}^+$ and CF_3SO_3^- were present. This was not the case for LiCF_3SO_3 in diglyme³⁹ and triglyme⁴⁰ as well as NaCF_3SO_3 in tetraglyme;⁴¹ mixtures of free ions, ion pairs, triple ions, and aggregates were found.

Specific solvation of $\text{Ni}(\text{mnt})_2^-$ by the ethers also seems unlikely. One of the infrared analyses⁴⁰ (with $(n\text{-Bu})_4\text{N}^+$ as the counterion) showed that there were no associative interactions between CF_3SO_3^- and solvents with relatively weak electron acceptor properties such as triglyme and tetrahydrofuran (THF); the same should hold for $\text{Ni}(\text{mnt})_2^-$ in the glymes and MTHF.

The methyl and methylene groups bonded to the O atoms in the glymes are electropositive and may provide the attractive interactions with $\text{Ni}(\text{mnt})_2^-$ that are responsible for their relatively large $\kappa_{\perp}$ values. The glymes all have comparable numbers of these groups, two of which are bonded to each O atom. The number of O atoms per mL is essentially constant, varying from 1.27×10^{22} for diglyme to 1.37×10^{22} for tetraglyme. The chain-like structures of the glymes also may hinder the motion of $\text{Ni}(\text{mnt})_2^-$ and facilitate the interactions with the CH_2 and CH_3 groups.

Other factors may be at work in MTHF, which has fewer O atoms (6.0×10^{21} per mL) than the glymes. Recent calculations⁴² and neutron diffraction studies⁴³ have revealed the presence of voids in THF with diameters of 2.5–3.0 Å. The dominant components of both the larger and smaller voids' surfaces⁴³ are the H atoms of the CH_2 groups. The O atoms are not found on the surfaces of the larger voids and occupy only a small fraction (0.6%) of the surface of the smaller ones (which also contain C atoms bonded to the O atoms). As a result, the voids' surface has a slightly electropositive character.⁴³ Although the packing in MTHF is somewhat looser because of the methyl group, similar voids could be a source of attractive interactions with an anion. The occurrence of anion–ether interactions has been demonstrated in recent studies of the change in solvation when an electron is ejected from Na^- in THF⁴⁴ and by differences in the peak positions of the optical spectra of Na^- and K^- in THF and diglyme.⁴⁵

In solvents other than the ethers, evidence for the absence of significant interactions between $\text{Ni}(\text{mnt})_2^-$ and either $(n\text{-Bu})_4\text{N}^+$ or the solvent is provided by the low values of $\kappa_{\perp} = 0.50$ – 0.25 in eugenol, dimethyl phthalate, tri-*n*-butyl phosphate, and tris(2-ethyl-hexyl)phosphate (Table 1). Additional discussion of the determination and interpretation of $\kappa_{\perp}$ is found in refs 8, 9, and 46.

Comparison of Transport Properties

The occurrence of similar temperature dependences for different kinetic properties in a given solvent suggests a common rate-determining process.⁴⁷ The values of $\kappa_{\perp}$ for $\text{Ni}(\text{mnt})_2^-$ in the glymes and MTHF indicate relatively strong solute–solvent interactions, and in this section, we will compare $\tau_2(0)$ with properties of the pure solvents such as η , D_{self} , and τ_{DR} .

$\tau_2(0)$ will also be compared with $\langle \tau \rangle_{\text{solv}}$, which is determined using time-dependent fluorescence techniques. In those experiments, a nonequilibrium solvent distribution is created by exciting a probe and monitoring its emission spectrum as the solvent relaxes;^{23,48–50} analysis of the Stokes shifts gives $\langle \tau \rangle_{\text{solv}}$, which often involves multiple time constants (τ_j) and weighting factors (a_j), i.e., $\langle \tau \rangle_{\text{solv}} = \sum_j a_j \tau_j$. Representative values of $\langle \tau \rangle_{\text{solv}}$ obtained using coumarin 153 (C153, Figure 3) are given in Table 3.⁵⁰ The range of solvation times for a given probe in different solvents (<3 orders of magnitude for C153) is much larger than the range of $\langle \tau \rangle_{\text{solv}}$ values for different probes in a common solvent (a factor of <3).^{23,51,52} The latter range, however, is roughly the same as our spread of $\kappa_{\perp}$ values for $\text{Ni}(\text{mnt})_2^-$. The solvent relaxation involves reorientation,⁴⁹ and it seemed reasonable to ask how closely the reorientation of $\text{Ni}(\text{mnt})_2^-$ follows the solvent's response to the excited probe.

With regard to the glymes, Argaman and Huppert²² found that the solvation dynamics of di-, tri-, and tetraglyme were determined by multiple relaxations. At room temperature, relatively long (≈ 100 ps) and short relaxation times (≈ 10 ps) were attributed to cooperative motion of the solvent matrix and intramolecular segmental motions, respectively. This interpretation of the shorter time and the values²² of 11.8, 15.4, and 18.2 ps obtained using diethylthiatricarbocyanine for di-, tri-, and tetraglyme, respectively, and 10 ps for tetraglyme

using C153 at 283 K are consistent with dielectric results also attributed to segmental motions; Scheutz and Stockhausen¹⁸ found $\tau_{\text{DR}} = 9.7$ and 15.4 ps at 293 K for diglyme and tetraglyme, respectively, while Kaatz and co-workers¹⁷ obtained $\tau_{\text{DR}} = 15.0$ ps at 298 K for tetraglyme. Eyring, Petrucci, and co-workers³⁸ determined $\tau_{\text{DR}} = 6.9$ and 12.2 ps at 298 K for diglyme and tetraglyme, respectively. The uncertainties for the τ_{DR} values are ± 5 –10%.⁵³

The fast and slow solvation times of tetraglyme had the same activation energy (~ 7 kJ/mol), and the possible control of the slow process by the segmental motions was suggested.²² The combination of the faster segmental and slower cooperative motions may well be the determining factor for the structural relaxation in tetraglyme as well as the reorientation of $\text{Ni}(\text{mnt})_2^-$; as seen in Figure 4, the values of η , $1/D_{\text{self}}$, τ_{DR} , $\langle \tau \rangle_{\text{solv}}$ (determined using C153²²), and $\tau_2(0)$ have the same temperature dependence. The inverse of D_{self} is used, since $1/D_{\text{self}} = 6\pi\eta R/kT$ (the Stokes–Einstein relation) has the same dependence on η and T as eq 1 for $\tau_2(0)$. The factor η/T might be expected to produce a difference when $1/D_{\text{self}}$ and $\tau_2(0)$ are compared with η , but the change in $1/T$ is small compared with the exponential variation in η . Each data set in Figures 4–6 is scaled using a temperature-independent multiplier given in Table 4 or 5.

The dynamics in diglyme also appear to be determined by the segmental and cooperative motions. Figure 4 shows that the data for $\tau_2(0)$, η , $1/D_{\text{self}}$, and τ_{DR} have a common temperature dependence; $\langle \tau \rangle_{\text{solv}}$ was not determined as a function of temperature.

The values of $\tau_2(0)$ for $\text{Ni}(\text{mnt})_2^-$, η , $1/D_{\text{self}}$, τ_{DR} , and $\langle \tau \rangle_{\text{solv}}$ in MTHF also have a common temperature dependence; $\tau_2(0)$, η , $1/D_{\text{self}}$, and τ_{DR} are shown in Figure 5, while $\tau_2(0)$ is compared with $\langle \tau \rangle_{\text{solv}}$ in Figure 6. The self-diffusion data are given as $\tau_T = 2\eta_H^2/(9D_{\text{self}})$, with $\eta_H = 2.0$ Å;¹⁹ 4-aminophthalimide (4-AP) was used to determine $\langle \tau \rangle_{\text{solv}}$.²⁰ The dielectric relaxation in MTHF was considered to be determined by the overall molecular reorientation, as is usually the case for rigid, polar molecules.^{20,54} The common temperature dependence of $\tau_2(0)$, η , $1/D_{\text{self}}$, τ_{DR} , and $\langle \tau \rangle_{\text{solv}}$ indicates that, as was concluded in an earlier study,²⁰ both the reorientational and translational motions in MTHF are determined by the solvent's structural relaxation, i.e., the α process responsible for viscous flow.^{20,47,55} In related work, Richert et al.^{56,57} found that the rotational motion of probes excited to long-lived triplet states and the solvation dynamics induced by the excitation had the same temperature dependence near the glass transition temperature in several solvents (including MTHF).

We also have found agreement between the temperature dependences of $\langle \tau \rangle_{\text{solv}}$ and $\tau_2(0)$ for $\text{Ni}(\text{mnt})_2^-$ in ethyl alcohol and 1-butanol. Figure 6 shows the comparisons for those solvents as well as for tetraglyme and MTHF. The solvation probes used for ethyl alcohol are 3-methyl-2,3,6,7,8-pentahydro-quinolizino-4h-(1,9-g,h)-1-benzoxazine-1,4-2-one (MPQB),²⁴ rhodamine 6G (R6G),^{23,25} and 2-aminoanthracene (2-AA);²³ the values of $\langle \tau \rangle_{\text{solv}}$ in 1-butanol were obtained using *p*-dimethyl-laminobenzonitrile (DMABN)²⁶ and the benzophenone anion radical (BAR).²⁷

There are differences between $\tau_2(0)$ and $\langle \tau \rangle_{\text{solv}}$ even though they have common temperature dependences and appear to be determined by the same dynamic factors. $\langle \tau \rangle_{\text{solv}}$ describes the time-dependent change in the electrical component of the solute–solvent interaction energy subsequent to a probe's electronic excitation;⁵⁸ $\tau_2(0)$ describes the interaction of $\text{Ni}(\text{mnt})_2^-$ with the bulk of the solvent via the viscosity and with nearby solvent molecules via $\kappa_{\perp}$. The determination of one does not obviate the determination of the other; rather, the value of one sets limits on the other. $\langle \tau \rangle_{\text{solv}}$ is the relaxation time for a collective response, and while the nature of the probes employed and the cross-correlations involved in them can introduce

ambiguities,^{56,57} collective correlation times usually are shorter than those for a single-particle reorientation, i.e., $\tau_2(0)$.

For example, fluorescence up-conversion methods were used to determine values of $\langle \tau \rangle_{\text{rot}}$, C153's single-particle rotational correlation time, in the probe's S_1 electronic state.^{50,51,58} When the values of $\langle \tau \rangle_{\text{rot}}$ in Table 3 are compared with the values of $\langle \tau \rangle_{\text{solv}}$ in common solvents, they do indeed give $\langle \tau \rangle_{\text{rot}}/\langle \tau \rangle_{\text{solv}} > 1$. A similar comparison (Table 5) shows $\tau_2(0)$ for $\text{Ni}(\text{mnt})_2^-$ to be slightly to clearly longer than $\langle \tau \rangle_{\text{solv}}$ for each of the solvation probes in each of the four solvents. The inequalities $\langle \tau \rangle_{\text{rot}}/\langle \tau \rangle_{\text{solv}} > 1$ and $\tau_2(0)/\langle \tau \rangle_{\text{solv}} > 1$ are not a consequence of comparing $\langle \tau \rangle_{\text{solv}}$, the correlation time for the dipolar solvation dynamics ($L = 1$, eq 4)⁵⁶ and relaxation times with $L = 2$ ($\tau_2(0)$ and $\langle \tau \rangle_{\text{rot}}$). If correlation times of the same order were compared, $\tau_1(0)/\langle \tau \rangle_{\text{solv}}$ and $\langle \tau_1 \rangle_{\text{rot}}/\langle \tau \rangle_{\text{solv}}$ would be even larger; eq 4 gives $\tau_1(0) = 3\tau_2(0)$ for Brownian diffusion. Dielectric relaxation is another collective process with $L = 1$.⁵⁶ The values of $\tau_2(0)$ and τ_{DR} in Table 4 also give $\tau_2(0)/\tau_{\text{DR}} > 1$; $\tau_2(0)/\tau_{\text{DR}} \approx 30$ in MTHF, 10 in diglyme, and 14 in tetraglyme.

Tables 3 and 5 show that even though $\tau_2(0)$ and $\langle \tau \rangle_{\text{solv}}$ were determined using different probes there are parallels between the values of $\tau_2(0)/\langle \tau \rangle_{\text{solv}}$ and $\langle \tau \rangle_{\text{rot}}/\langle \tau \rangle_{\text{solv}}$ for C153. In 1-butanol, $\langle \tau \rangle_{\text{rot}}/\langle \tau \rangle_{\text{solv}} = 2.2 \pm 0.5$ for C153, while $\tau_2(0)/\langle \tau \rangle_{\text{solv}} = 1.8 \pm 0.4$ for BAR and 1.6 ± 0.3 for DMABN. In ethyl alcohol, $\langle \tau \rangle_{\text{rot}}/\langle \tau \rangle_{\text{solv}} = 3.9 \pm 0.9$ for C153, while $\tau_2(0)/\langle \tau \rangle_{\text{solv}} = 4.2 \pm 0.8$ for MPQB and 2.4 ± 0.5 for 2-AA; R6G does give a larger value of $\tau_2(0)/\langle \tau \rangle_{\text{solv}} = 22.5 \pm 4.5$.

Richert et al.^{56,57} found the reorientation of their triplet-state probes to be slower than the solvent relaxation by a temperature-independent factor. In MTHF, they determined $\langle \tau \rangle_{\text{rot}}/\langle \tau \rangle_{\text{solv}} = 14$ for four different probes; our results for $\text{Ni}(\text{mnt})_2^-$ and $\langle \tau \rangle_{\text{solv}}$ determined using 4-AP give $\tau_2(0)/\langle \tau \rangle_{\text{solv}} = 22.5 \pm 4.5$.

Summary and Conclusions

The planar complex ion $\text{Ni}(\text{mnt})_2^-$ has been studied using X-band ESR in MTHF, diglyme, triglyme, and tetraglyme. Spectra taken from the motionally narrowed to the slow motional region show that the rate of reorientation about the long in-plane (parallel) axis of $\text{Ni}(\text{mnt})_2^-$ is 3 times faster than that about the two perpendicular axes. This motional model produces agreement between the experimental and calculated ESR line widths of $\text{Ni}(\text{mnt})_2^-$ when the anisotropic Zeeman interaction makes the dominant contribution to the widths.

The temperature dependence of $\tau_2(0)$, the reorientational correlation time obtained from the line widths, is consistent with the modified Stokes–Einstein–Debye model. The analyses give large values of the anisotropic interaction parameter $\kappa_{\perp}$ that indicate appreciable (but not associative) interactions between $\text{Ni}(\text{mnt})_2^-$ and the ethers.

Transport properties of the solvents have been compared with the reorientational data for $\text{Ni}(\text{mnt})_2^-$. Scaled values of the temperature-dependent viscosities are shown to be in agreement with those of $\tau_2(0)$ as are the solvents' self-diffusion constants and dielectric relaxation times. The values of $\tau_2(0)$ in MTHF, tetraglyme, ethyl alcohol, and 1-butanol also are compared to $\langle \tau \rangle_{\text{solv}}$, a collective relaxation time obtained from time-resolved studies of a solvent's response to the excitation of a fluorescent probe. The solvent's adjustment to the electronic structure of the probe's excited state involves reorientation and, in a given solvent, the scaled temperature-dependent values of $\langle \tau \rangle_{\text{solv}}$ also are in agreement with those of $\tau_2(0)$.

Consideration of the factors contributing to the various transport processes in the ethers suggest that τ_{DR} , $\langle \tau \rangle_{\text{solv}}$, and $\tau_2(0)$ are determined by the solvent's overall structural

relaxation in MTHF, while the segmental motions of the carbon–oxygen chains are important for the glymes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The ESR temperature-control unit used in this work was purchased with funds provided by the Beaumont Faculty Development Fund and the Department of Chemistry, St. Louis University.

References and Notes

1. Maki AH, Edelstein N, Davison A, Holm RH. *J Am Chem Soc.* 1964; 86:4580–4587.
2. Beswick, CL.; Schulman, JM.; Stiefel, EI. *Progress in Inorganic Chemistry: Dithiolene Chemistry.* Stiefel, EI., editor. Vol. 52. Wiley; New York: 2004. p. 55-110.
3. Kirk, ML.; McNaughton, RL.; Helton, ME. *Progress in Inorganic Chemistry: Dithiolene Chemistry.* Stiefel, EI., editor. Vol. 52. Wiley; New York: 2004. p. 111-212.
4. Huyett JE, Choudury SB, Eichorn DM, Bryngelson PA, Maroney MJ, Hoffman BM. *Inorg Chem.* 1998; 37:1361–1367. [PubMed: 11670347]
5. Huang R, Kivelson D. *J Magn Reson.* 1974; 14:202–222.
6. Huang R, Kivelson D. *Pure Appl Chem.* 1972; 32:207–219.
7. Kowert BA, Broecker GK, Gentemann SJ, Fehr MJ. *J Magn Reson.* 1992; 98:362–380.
8. Kowert BA, Higgins EJ, Mariencheck WI, Stemmler TL, Kantorovich V. *J Phys Chem.* 1996; 100:11211–11217.
9. Kowert BA, Stemmler TL, Fehr MJ, Sheaff PJ, Gillum TJ, Dang NC, Hughes AM, Staggemeier BA, Zavich DV. *J Phys Chem B.* 1997; 101:8662–8666.
10. Kowert BA, Broecker GK, Gentemann SJ, Stemmler TL, Fehr MJ, Joern Stemmler A, Thurman-Keup EM, Whittington McCoo P, Everett TB, Lupo DJ, Fitzsimmons PK, Barros Cordero A. *J Phys Chem B.* 2007; 111:13404–13409. [PubMed: 17979269]
11. The results of the line width fit for diglyme using eq 1 were mentioned in ref 10, but details of the analysis were not given and the results were not correlated with other motional properties as is done in this paper.
12. Lopez ER, Daridon JL, Baylaucq A, Fernandez J. *J Chem Eng Data.* 2003; 48:1208–1213.
13. Hayamizu K, Akiba E, Bando T, Aihara Y. *J Chem Phys.* 2002; 117:5929–5939.
14. Canters GW. *J Am Chem Soc.* 1972; 94:5230–5235.
15. Canters, GW. PhD Thesis. University of Nijmegen; Nijmegen, NL: 1969.
16. Powles JG, Mosley MH. *Proc Phys Soc.* 1961; 78:370–376.
17. Kaatz U, Loennecke-Gabel V, Pottel R. *Z Phys Chem.* 1992; 175:165–186. The value of τ_{DR} was obtained using a Cole–Cole distribution.
18. Scheutz G, Stockhausen M. *Z Phys Chem.* 1992; 175:187–200. The values of τ_{DR} were obtained using a Cole–Cole distribution.
19. Qi F, El Goresy T, Boehmer R, Doesz A, Diezermann G, Hinze G, Sillescu H, Blochowicz T, Gainaru C, Roessler E, Zimmerman H. *J Chem Phys.* 2003; 118:7431–7438. The values of τ_{DR} were obtained from the loss peak maxima using $\tau_{DR} = (2\pi\nu_{peak})^{-1}$.
20. Richert R, Stickel F, Fee RS, Maroncelli M. *Chem Phys Lett.* 1994; 229:302–308. The mean dielectric relaxation time ($\tau_m = \tau_{DR}$) was obtained using the Havriliak–Negami function.
21. Ling AC, Willard JE. *J Phys Chem.* 1968; 72:1918–1923.
22. Argaman R, Huppert D. *J Phys Chem A.* 1998; 102:6215–6219.
23. Maroncelli M. *J Mol Liq.* 1993; 57:1–37.
24. Declémy A, Rullière C, Kottis P. *Laser Chem.* 1990; 10:413–429.
25. Kinoshita S, Nishi N. *J Chem Phys.* 1988; 89:6612–6622.

26. Heisel F, Miehe JA. Chem Phys Lett. 1986; 128:323–329.
27. Xujia Z, Jonah CD. J Phys Chem. 1996; 100:7042–7049.
28. Davison, A.; Holm, RH. Inorganic Syntheses. Muetterties, EL., editor. Vol. 10. McGraw-Hill; New York: 1967. p. 8-26.
29. Angell CA. Science. 1995; 267:1924–1935. [PubMed: 17770101]
30. Pal A, Singh YP. J Chem Eng Data. 1996; 41:1008–1011.
31. Conesa A, Shen S, Coronas A. Int J Thermophys. 1998; 19:1343–1358.
32. Freed, JH. Spin Labeling: Theory and Applications. Berliner, LJ., editor. Vol. I. Academic Press; New York: 1976. p. 53-132.
33. Goldman SA, Bruno GV, Polnaszek CFJH, Freed JH. J Chem Phys. 1972; 56:716–735.
34. Freed JH, Bruno GV, Polnaszek CF. J Phys Chem. 1971; 75:3385–3399.
35. Campbell RF, Freed JH. J Phys Chem. 1980; 84:2668–2680.
36. Kivelson D, Kivelson MG, Oppenheim I. J Chem Phys. 1970; 52:1810–1821.
37. In ref 9, we showed that η_0 , the effective size of $\text{Ni}(\text{mnt})_2^-$, was related to the size r_l obtained from its translational diffusion constant via $(\eta_0/r_l)^3 = 1.59$. The uncertainty in r_l given in that paper ($\pm 0.30 \text{ \AA}$) was too large by a factor of 2. When the smaller uncertainty is used with an uncertainty of $\pm 10\%$ for $C_\perp$, the uncertainty in $\kappa_\perp$ is $\pm 15\%$.
38. Firman P, Xu M, Eyring EM, Petrucci S. J Phys Chem. 1993; 97:3606–3613. The values of τ_{DR} were obtained using a Cole–Cole distribution.
39. Petrowsky M, Frech R, Suarez SN, Jayakody JRP, Greenbaum S. J Phys Chem B. 2006; 110:23012–23021. [PubMed: 17107139]
40. Frech R, Huang W. J Solution Chem. 1994; 23:469–481.
41. Dong H, Hyun JK, Rhodes CP, Frech R, Wheeler RA. J Phys Chem B. 2002; 106:4878–4885.
42. Bedhard-Hearn MJ, Larsen RE, Schwartz BJ. J Chem Phys. 2005; 122:134506. [PubMed: 15847480]
43. Bowron DT, Finney JL, Soper AK. J Am Chem Soc. 2006; 128:5119–5126. [PubMed: 16608347]
44. Bragg AE, Cavanagh MC, Schwartz BJ. Science. 2008; 321:1817–1822. [PubMed: 18818354]
45. Lok MT, Tehan FJ, Dye JL. J Phys Chem. 1972; 76:2975–2981.
46. Kowert BA, Hughes AM, Dang NC, Martin MB, Cheung GH, Tran HD, Reed JP. Chem Phys. 1999; 247:435–443.
47. Ediger MD, Angell CA, Nagel SR. J Phys Chem. 1996; 100:13200–13212.
48. Maroncelli M, Fleming GR. J Chem Phys. 1987; 86:6221–6239.
49. Maroncelli M, Kmar VP, Papazyan A. J Phys Chem. 1993; 97:13–17.
50. Horng ML, Gardecki JA, Papazyan A, Maroncelli M. J Phys Chem. 1995; 99:17311–17337.
51. Chapman CF, Fee RS, Maroncelli M. J Phys Chem. 1995; 99:4811–4819.
52. Stratt RM, Maroncelli M. J Phys Chem. 1996; 100:12981–12996.
53. We have used $\pm 5\text{--}10\%$ for the uncertainties in τ_{DR} because values were reported only for tetraglyme in ref 17 ($\pm 7\%$); the complex permittivity of the pure solvents in ref 18 was “measured within a few percent”. Larger uncertainties have been given for other organic liquids in which $\text{Ni}(\text{mnt})_2^-$ has been studied, i.e., $\pm 10\%$ in a study of dimethyl phthalate: Nayak SK, Murthy SSN. J Chem Phys. 1993; 99:1607–1613.
54. Shears MF, Williams G, Barlow AJ, Lamb J. J Chem Soc, Faraday Trans 2. 1974; 70:1783–1793.
55. Williams G, Crossley J. Annu Rep Prog Chem. 1977; 74:77–105.
56. Yang M, Richert R. Chem Phys. 2002; 284:103–114.
57. Wang LM, Richert R. J Chem Phys. 2004; 120:11082–11089. [PubMed: 15268138]
58. Horng ML, Gardecki JA, Maroncelli M. J Phys Chem A. 1997; 101:1030–1047.

Figure 1. Molecular structure of $\text{Ni}(\text{mnt})_2^-$ and the right-handed principal axes of the anisotropic Zeeman interaction.

Figure 2. Principal line widths for $\text{Ni}(\text{mnt})_2^-$ in MTHF and diglyme. The experimental widths for diglyme (black circles) and MTHF (gray triangles) were fitted to the calculated widths (open squares) using eq 1.

Figure 3.
The commonly used solvation probe coumarin 153 (C153).

Figure 4.

Transport properties in (a) tetraglyme and (b) diglyme. The same labels are used for both solvents. The properties and their symbols are as follows: viscosity (black squares), $\tau_2(0)$ for $\text{Ni}(\text{mnt})_2^-$ (gray circles), τ_{DR} (white diamonds), and $1/D_{\text{self}}$ (gray triangles); the scale factors are given in Table 4. For tetraglyme, open squares are used for $\langle \tau \rangle_{\text{solv}}$; the scale factor is given in Table 5.

Figure 5.

Transport properties in MTHF. The properties and their symbols are as follows: viscosity (gray diamonds), $\tau_2(0)$ for $\text{Ni}(\text{mnt})_2^-$ (black squares), τ_{DR} from ref 19 (open squares), τ_{DR} from ref 20 (gray circles), and τ_T (white triangles). The scale factors are given in Table 4.

Figure 6.

Comparison of $\tau_2(0)$ for $\text{Ni}(\text{mnt})_2^-$ with values of $\langle \tau \rangle_{\text{solv}}$ obtained using solvatochromic probes. Black squares are used for $\tau_2(0)$ of $\text{Ni}(\text{mnt})_2^-$ in all solvents except for ethyl alcohol (black triangles). In (a) tetraglyme, the probe is C153 (gray circles). In (b) 1-butanol, the probes are BAR (white circles) and DMABN (gray circles). In (c) ethyl alcohol, the probes are MPQB (gray circles), 2-AA (open circles), and R6G (open rectangles). In (d) MTHF, the probe is 4-AP (gray circles). The values of $\tau_2(0)$ and $\langle \tau \rangle_{\text{solv}}$ were multiplied by the scale factors in Table 5 before the logarithms were taken.

TABLE 1

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

solvent ^a	$10^6 C_L$, s K P ⁻¹	κ_L	$10^{11} \tau_0$, s	rms error ^b	ϵ_0^c
MTHF ^d	2.65	1.12	5.55	0.098	6.24 ₂₅
MTHF ^e	2.53	1.07	5.11	0.054	6.24 ₂₅
triglyme	2.54	1.07	-2.10	0.076	7.75 ₂₅
tetraglyme	2.25	0.95	-5.20	0.072	7.70 ₂₅
diglyme	1.95	0.82	1.70	0.097	7.65 ₂₅
ethyl alcohol	2.01	0.85	-3.01	0.161	24.3 ₂₅
eugenol ^f	1.38	0.58	9.13	0.102	9.7 ₂₀
DMPT ^f	1.18	0.50	5.74	0.086	8.5 ₂₄
1-butanol	1.13	0.48	0.226	0.114	17.1 ₂₅
TBP ^f	0.899	0.38	8.01	0.088	8.1 ₂₅
TEHP ^f	0.583	0.25	13.5	0.104	≈8.0 ₂₅

^aFrom refs 8 and 9 except for MTHF, diglyme, triglyme, and tetraglyme; see also ref 11.

^bThe rms error is $\{N^{-1}[\sum(\ln \tau_2(0)_{\text{exptl}} - \ln \tau_2(0)_{\text{calcd}})^2]\}^{1/2}$.

^cFrom ref 9 except for MTHF [Nicholls, D.; Surphen, C.; Szwarc, M. *J. Phys. Chem.* **1968**, 72, 1021–1027] and diglyme, triglyme, and tetraglyme (ref 38).

^dObtained using the ESR data for 128.2 K T 252.2 K and the viscosities from refs 15 and 21.

^eObtained using the ESR data for 190.2 K T 252.2 K and the viscosities from ref 15.

^fThe abbreviations used are eugenol (4-allyl-2-methoxyphenol), DMPT (dimethyl phthalate), TBP (tri-*n*-butyl phosphate), and TEHP (tris(2-ethyl-hexyl)phosphate).

TABLE 2

Fits to the Vogel–Tamman–Fulcher Equation for the Solvent Viscosities

solvent	$10^4 A, P$	D_{VTF}	T_0, K	rms error ^a
diglyme	5.44	4.09	123.5	0.0250
triglyme	5.50	5.16	122.0	0.011
tetraglyme	7.30	4.32	139.5	0.0075
MTHF ^b	7.50	4.72	81.6	0.251
MTHF ^c	2.31	−19 040	−0.0468	0.0013

^aThe rms error is $\{N^{-1}[\sum(\ln \eta_{\text{exptl}} - \ln \eta_{\text{calcd}})^2]\}^{1/2}$.

^bDetermined using the data from refs 15 and 21.

^cDetermined using only the data from ref 15; the fit parameters show Arrhenius behavior, i.e., $T_0 = -0.0468 \text{ K}$ is near zero; the fit equation is $\ln \eta = -8.373 + 890.35/(T + 0.04676)$.

TABLE 3

Representative Values of $\langle \tau_{\text{rot}} \rangle$ and $\langle \tau \rangle_{\text{solv}}$ for C153

solvent	$\langle \tau \rangle_{\text{rot}}^a$ ps	$\langle \tau \rangle_{\text{solv}}^b$ ps	$\langle \tau_{\text{rot}} \rangle / \langle \tau \rangle_{\text{solv}}^c$
benzonitrile	93	5.1	18 ± 4
chloroform	42	2.8	15 ± 3
DMC ^d	35	6.9	5.1 ± 1.1
formamide	185	15.3	12 ± 3
methanol	35	5.0	7.0 ± 1.5
ethyl alcohol	63	16	3.9 ± 0.9
1-butanol	140	63	2.2 ± 0.5
1-decanol	818	245	3.3 ± 0.7

^aFrom ref 58 at 22 ± 2 °C; the uncertainties are ± 4 –8%.^bFrom ref 50 at 22 ± 2 °C; the uncertainties are ± 15 –25%. The uncertainties for other determinations of $\langle \tau \rangle_{\text{solv}}$, e.g., refs 24, 27, and 48, are comparable.^cThe uncertainties are calculated using $\pm 8\%$ for $\langle \tau_{\text{rot}} \rangle$ and $\pm 20\%$ for $\langle \tau \rangle_{\text{solv}}$.^dDMC is dimethyl carbonate.

TABLE 4

Scale Factors for Dynamic Properties in the Glymes and MTHF

MTHF		
$1.00 \times 10^{10} \tau_2(0),^a \text{ s}$	$3.00 \times 10^{11} \tau_{\text{DR}},^b \text{ s}$	$3.00 \times 10^{11} \tau_{\text{T}},^c \text{ s}$
$1.50 \times 10^2 \eta^d \text{ P}$		
Diglyme		
$1.10 \times 10^{10} \tau_2(0),^a \text{ s}$	$1.10 \times 10^{11} \tau_{\text{DR}},^e \text{ s}$	$1.05 \times 10^{-5} (D_{\text{self}})^{-1},^f \text{ s/cm}^2$
$1.00 \times 10^2 \eta^d \text{ P}$		
Tetraglyme		
$1.50 \times 10^{10} \tau_2(0),^a \text{ s}$	$2.10 \times 10^{11} \tau_{\text{DR}},^e \text{ s}$	$9.00 \times 10^{-6} (D_{\text{self}})^{-1},^f \text{ s/cm}^2$
$1.00 \times 10^2 \eta^d \text{ P}$		

^aThe values of $\tau_2(0)$ are from this work.^bFrom ref 20.^cFrom ref 19.^dThe values of η are from the references given in the text.^eFrom ref 18.^fFrom ref 13.

TABLE 5

Scale Factors for Comparisons of $\tau_2(0)$ for $\text{Ni}(\text{mnt})_2^-$ and $\langle \tau \rangle_{\text{solv}}$

solvent	$\tau_2(0),^a \text{ s}$	$\langle \tau \rangle_{\text{solv}},^b \text{ s (probe)}$	$\tau_2(0)/\langle \tau \rangle_{\text{solv}}^c$
tetraglyme	1.50×10^{10}	1.00×10^{11} (C153)	6.7 ± 1.4
MTHF	1.00×10^{10}	2.25×10^{11} (4-AP)	22.5 ± 4.5
ethyl alcohol	1.00×10^{10}	4.17×10^{10} (MPQB)	4.2 ± 0.8
		2.25×10^{11} (R6G)	22.5 ± 4.5
		2.40×10^{10} (2-AA)	2.4 ± 0.5
1-butanol	1.00×10^{10}	1.80×10^{10} (BAR)	1.8 ± 0.4
		1.60×10^{10} (DMABN)	1.6 ± 0.3

^aThe values of $\tau_2(0)$ are from this work (tetraglyme, MTHF) and refs 7 (1-butanol) and 8 (ethyl alcohol).

^bThe values of $\langle \tau \rangle_{\text{solv}}$ are from the references given in the text.

^cThe uncertainties, calculated using representative values of $\pm 3\%$ for $\tau_2(0)$ and $\pm 20\%$ for $\langle \tau \rangle_{\text{solv}}$ (see the text and Table 3).