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Article

Self-Exchange Reaction of $[Ni(mnt)_2]^{1-,2-}$ in Nonaqueous Solutions

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The rate constant, *k*, for the homogeneous electron transfer (self-exchange) reaction between the diamagnetic bis(maleonitriledithiolato)nickel dianion, $[Ni(mnt)_2]^{2-}$, and the paramagnetic monoanion, $[Ni(mnt)_2]^{1-}$, has been determined in acetone and nitromethane (CH_3NO_2) using ^{13}C NMR line widths at 22 °C (mnt = 1,2-$S_2C_2(CN)_2$). The values of *k* (2.91×10^6 M^{-1} s^{-1} in acetone, 5.78×10^6 M^{-1} s^{-1} in CH_3NO_2) are faster than those for the electron transfer reactions of other Ni(III,II) couples; the structures of $[Ni(mnt)_2]^{1-}$ and $[Ni(mnt)_2]^{2-}$ allow for a favorable overlap that lowers the free energy of activation. The values of *k* are consistent with the predictions of Marcus theory. In addition to *k*, the spin−lattice relaxation time, T_{1e}, of $[Ni(mnt)_2]^{1-}$ is obtained from the NMR line width analysis; the values are consistent with those predicted by spin relaxation theory.

Introduction

Transition metal bis(dithiolene) complexes have been the focus of a considerable body of research since the 1960s. The initial interest[1] was because of their square planar structures, multiple oxidation states, and the nature of the metal−ligand bonding needed to explain their ESR spectra and large extinction coefficients.[2–4] The oxidation states continue to receive attention for a variety of reasons. Electron transfer plays a key role in determining solid-state conducting and optical properties;[5] the latter make bis(dithiolene) complexes candidates for utilization in optical storage systems, switches, and second-order nonlinear devices.[3,5] Electron transfer also has been shown to be involved in a variety of chemical processes such as ligand exchange,[6] photoinduced ion-pair charge-transfer,[7] and photooxidations;[8] redox-active nickel has been shown to be ligated by S in biological centers[9,10] although Ni-dithiolenes have not been found as they have for Mo and W enzymes.[11]

Given the many areas in which they are important, it is somewhat surprising that the rates of the reactions between $[M(dithiolene)_2]^{Z}$ and $[M(dithiolene)_2]^{Z-1}$ do not appear to have been studied. Any discussion of these rates must start with the simplest type of homogeneous electron transfer (or self-exchange) reaction and in this paper we use ^{13}C NMR line widths to determine the rate constant, *k*, for

$$[Ni(mnt)_2]^{1-} + [Ni(mnt)_2]^{2-} \rightleftharpoons [Ni(mnt)_2]^{2-} + [Ni(mnt)_2]^{1-} \quad (1)$$

between the diamagnetic bis(maleonitriledithiolato)nickel dianion, $[Ni(mnt)_2]^{2-}$, and the paramagnetic monoanion, $[Ni(mnt)_2]^{1-}$, in nitromethane (CH_3NO_2) and acetone (mnt = 1,2-$S_2C_2(CN)_2$). $[Ni(mnt)_2]^{1-}$ and $[Ni(mnt)_2]^{2-}$ are archetypal bis(dithiolene) complexes; the results from an assort-

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ment of techniques can be brought to bear on the interpretation of their *k* values, which are found to be larger than those for other Ni(III,II) complexes and consistent with the predictions of Marcus theory.[12]

The NMR line width analysis is developed in some detail since a considerable number of dithiolene complexes have been synthesized, including those with metals other than nickel and ligands other than mnt.[1–3,5–7] Their electron transfer reactions are potential candidates for this method as well. The criteria that a solvent must meet to be used for these experiments are discussed.

Experimental Section

Preparation and Purification of Chemicals. [Ni(mnt)$_2$]$^{2-}$ and [Ni(mnt)$_2$]$^{1-}$ were prepared as the (n-Bu)$_4$N$^+$ salts following the procedures of Davison and Holm.[13] Acetone (Fisher Optima grade) and CH$_3$NO$_2$ (99+%, Aldrich) were dried over hot 4 Å molecular sieves in a vacuum desiccator prior to NMR sample preparation. Acetone-d$_6$ (Norell) was used as a deuterium lock and was not further purified.

Solvent Criteria. A concentration of 6.0×10^{-2} M was needed for suitably intense ^{13}C spectra. The 1% natural abundance is a factor as is the nonprotonation of the carbon atoms, that is, there is no nuclear Overhauser enhancement.[14] The reduction of the monoanion to the dianion by the solvent is also a potential problem[13] as is the overlap of the solvent spectrum and that of the dianion.

Several solvents did not satisfy these requirements; their purities (and purifications) were of the same quality as those for acetone and CH$_3$NO$_2$. Acetonitrile (MeCN), 2-pentanone, and 3-pentanone failed to give a [Ni(mnt)$_2$]$^{2-}$ concentration of 6.0×10^{-2} M. Dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF) reduced [Ni(mnt)$_2$]$^{1-}$ to [Ni(mnt)$_2$]$^{2-}$. The reduction of the monoanion in DMF was noticed when solutions were allowed to stand overnight. UV−visible spectra confirmed that the monoanion was slowly converted to dianion. The monoanion was not reduced to the dianion in acetone and CH$_3$NO$_2$, solvents in which [Ni(mnt)$_2$]$^{2-}$ was sufficiently soluble; concentrations of 9.0×10^{-2} M were used. The ^{13}C resonances[15] of acetone (30.7, 206.7 ppm) and CH$_3$NO$_2$ (61.2 ppm) do not interfere with those of the dianion (discussed below) nor do those from (n-Bu)$_4$N$^+$ which are all in the approximate range $10 \leq \delta \leq 65$ ppm.

Sample Preparation. [(n-Bu)$_4$N]$_2$[Ni(mnt)$_2$] and 2 mL of acetone-d$_6$ were added to a 10 mL volumetric flask which was then filled to the mark with solvent. Dilute solutions of varying molarities of [Ni(mnt)$_2$]$^{1-}$ were prepared in the same solvent. For the NMR samples, a 1.5 mL aliquot of the [Ni(mnt)$_2$]$^{2-}$ solution was pipetted into a small beaker, followed by 0.50 mL of [Ni(mnt)$_2$]$^{1-}$ solution (or freshly purified solvent in the case of the blank). The CH$_3$NO$_2$ samples, using volume fractions, were 85% CH$_3$NO$_2$ and 15% acetone; this composition has been used to calculate several solution properties in the Discussion section. The samples were run immediately after preparation.

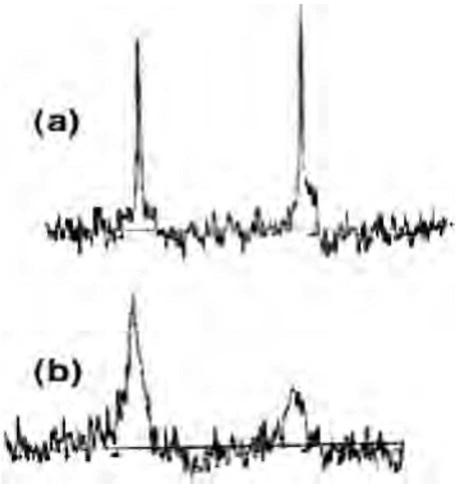

Figure 1. ^{13}C NMR spectra of [Ni(mnt)$_2$]$^{2-}$ in CH$_3$NO$_2$ with (a) no [Ni(mnt)$_2$]$^{1-}$ and (b) 5.0×10^{-5} M [Ni(mnt)$_2$]$^{1-}$.

Table 1. Solvent and Rate Parameters from NMR Line Widths at 22 °C

parameter	acetone	CH$_3$NO$_2$
$10^{-6}m_{125}$, M^{-1} s^{-1}	1.94	3.38
10^4[P]$_{125,\mathrm{max}}$, M[a]	2.50	1.00
$10^{-6}m_{118}$, M^{-1} s^{-1}	2.30	4.22
10^4[P]$_{118,\mathrm{max}}$, M[a]	1.50	0.50
$10^{-6}k$, M^{-1} s^{-1}	2.91	5.78
$10^{-13}\tau_\mathrm{k}$, s	2.16	3.08
$10^{-7}T_{1\mathrm{e}}{}^{-1}$, s^{-1}	4.12	2.94
$2\tau_\mathrm{P}T_{1\mathrm{e}}{}^{-1}$	315	113
$f_\mathrm{D}\tau_\mathrm{P}{}^2(a_{118}{}^2/4)$	1214	307
$f_\mathrm{D}\tau_\mathrm{P}{}^2(a_{125}{}^2/4)$	636	161
η, cP[b]	0.316	0.643
n_i[c]	1.35609	1.37949
ε_s[c]	21.26	36.67

[a] Maximum concentration of [Ni(mnt)$_2$]$^{1-}$ for which line widths could be measured for the indicated chemical shift. [b] From ref 24. [c] From ref 32.

NMR Data Collection Procedures. All spectra were taken at 22 °C using a Gemini 300 MHz multinuclear spectrometer with the proton decoupler off. The dianion's two ^{13}C resonances (at 118 ppm and 125 ppm) were only slightly solvent-dependent; they were assigned by first eliminating the lines due to the solvent and counterion. Further proof was provided by adding a few crystals of [Ni(mnt)$_2$]$^{1-}$ to the [Ni(mnt)$_2$]$^{2-}$ solution in an NMR sample tube; only the lines at 118 and 125 ppm broadened. The nitrile ^{13}C resonances[15] of cyanoethylene (117.2 ppm) and benzonitrile (PhCN, 118.7 ppm) suggested that the 118 ppm line of [Ni(mnt)$_2$]$^{2-}$ was due to ^{13}C≡N and the 125 ppm line to ^{13}C−S. As discussed below, reversing the assignment gives physically unacceptable results when the line widths are analyzed.

A given concentration of [Ni(mnt)$_2$]$^{1-}$ caused the line at 118 ppm to be broader than the line at 125 ppm as seen in Figure 1, which shows the spectra of [Ni(mnt)$_2$]$^{2-}$ in CH$_3$NO$_2$ in the presence and absence of [Ni(mnt)$_2$]$^{1-}$. The maximum concentration of [Ni(mnt)$_2$]$^{1-}$ for which each peak could be measured in acetone and CH$_3$NO$_2$ is given in Table 1.

NMR Line Width Analysis. In the presence of [Ni(mnt)$_2$]$^{1-}$ (S = 1/2), the half-width at half-height of each of the two [Ni(mnt)$_2$]$^{2-}$ lines is given by[16]

$$(1/T_2)_{\mathrm{et},i} = (1/T_2)_{0,i} + f_\mathrm{P}\tau_\mathrm{P}(a_i^{\,2}/4)[1 + f_\mathrm{D}\tau_\mathrm{P}{}^2(a_i^{\,2}/4) + 2\tau_\mathrm{P}T_{1\mathrm{e}}{}^{-1}]^{-1} \quad (2)$$

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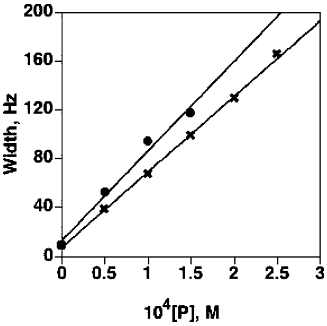

Figure 2. Full width at half-height of the ^{13}C NMR lines with chemical shift 118 (circles) and 125 ppm (x) vs the molar concentration of P = $[\mathrm{Ni(mnt)_2}]^{1-}$ in acetone.

where $(1/T_2)_{0,i}$ is the half-width at half-height in the absence of electron transfer, τ_P is the lifetime of $[\mathrm{Ni(mnt)_2}]^{1-}$, a_i is the isotropic hyperfine splitting constant for ^{13}C nucleus i, T_{1e} is the electron spin−lattice relaxation time for $[\mathrm{Ni(mnt)_2}]^{1-}$, and f_P and f_D are the mole fractions of $[\mathrm{Ni(mnt)_2}]^{1-}$ and $[\mathrm{Ni(mnt)_2}]^{2-}$, respectively; τ_P and τ_D, the lifetime of $[\mathrm{Ni(mnt)_2}]^{2-}$, are given by[16]

$$\tau_P = (k[D])^{-1} \quad \text{and} \quad \tau_D = (k[P])^{-1} \tag{3}$$

where k is the rate constant for eq 1 and [D] and [P] are the molar concentrations of D = $[\mathrm{Ni(mnt)_2}]^{2-}$ and P = $[\mathrm{Ni(mnt)_2}]^{1-}$.

For our ^{13}C NMR solutions, [D] ≫ [P], that is, $f_D \approx 1$, and eq 2 can be rewritten as

$$(1/T_2)_{et,i} = (1/T_2)_{0,i} + k[P][1 + (4/a_i^2)\tau_k]^{-1} \tag{4}$$

where

$$\tau_k = (1 + 2\tau_P T_{1e}^{-1})/\tau_P^2 \tag{5}$$

and $(1/T_2)_{et,i}$ is linear in [P] with a slope

$$m_i = k[1 + (4/a_i^2)\tau_k]^{-1} \tag{6}$$

When $f_D\tau_P^2(a_i^2/4) \gg 1 + 2\tau_P T_{1e}^{-1}$, that is, $(4/a_i^2)\tau_k \ll 1$, eq 4 reduces to the familiar slow exchange (strong pulse) limit,[16] for which

$$(1/T_2)_{et} = (1/T_2)_0 + k[P] \tag{7}$$

The fast exchange (weak pulse) limit[16] corresponds to $f_D\tau_P^2(a_i^2/4) + 2\tau_P T_{1e}^{-1} \ll 1$ in eq 2 and gives, assuming [D] ≫ [P],

$$(1/T_2)_{et} = (1/T_2)_0 + (a_i^2/4k)[P]/[D]^2 \tag{8}$$

Note that the slow and fast exchange limits, as well as the more general result given by eqs 4 and 5, predict that $(1/T_2)_{et}$ is linear in [P]. The slopes, however, have different dependencies on a_i, k, and [D].

Results

As seen in Figure 2 for acetone, the data for the two chemical shifts show a linear dependence on [P] but have different slopes. This difference indicates that the slow exchange limit, which predicts the same slope for both sets of data (eq 7), is not met. Neither, as we shall show below, is the fast exchange limit, eq 8.

The slopes for the 118 and 125 ppm lines have been analyzed using eq 6; when combined with the values of m_i, they give two equations linear in k and τ_k; T_{1e}^{-1} is calculated from τ_k and eq 5. The values of $a(\mathrm{C{\equiv}N}) = -2.9$ MHz and $a(\mathrm{C{-}S}) = -2.1$ MHz determined by Hoffman et al.[9] using ^{13}C-enriched isotopomers of $[\mathrm{Ni(mnt)_2}]^{1-}$ have been used for the 118 and 125 ppm slopes, respectively. The values of k, τ_k, and T_{1e}^{-1} obtained in this manner (as well as the values of m_i) are shown in Table 1; reversing the association of the chemical shifts with the values of a_i gives unacceptable (negative) values of T_{1e}^{-1} in both solvents.

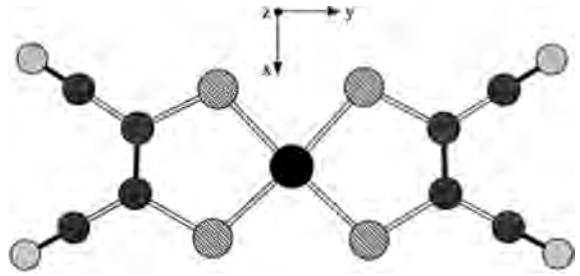

Figure 3. Molecular structure and the right-handed axes of $[\mathrm{Ni(mnt)_2}]^{1-}$.

The values of k in acetone and $\mathrm{CH_3NO_2}$ are discussed in the next section; the values of T_{1e}^{-1} are consistent with values estimated from[17–20]

$$T_{1e}^{-1} = 4j^{(G)}(\omega_0) + \sum_i (g_i - g_e)^2/9\tau_i \tag{9}$$

where $j^{(G)}(\omega_0)$, the spectral density for the nonsecular Zeeman interaction, gives the reorientational contribution (see the Appendix) and the second term is due to the spin rotational interaction; ω_0 is the unpaired electron's Zeeman frequency, g_e is the free electron g value, g_i ($i = x, y, z$) is the g factor for the ith principal axis of $[\mathrm{Ni(mnt)_2}]^{1-}$, and τ_i is the reorientational correlation time about the ith axis. The assignment of the axes is shown in Figure 3. A series of ESR studies[21–23] have shown that the reorientation of $[\mathrm{Ni(mnt)_2}]^{1-}$ is ≈3 times faster about the long in-plane (y) axis. This corresponds to $\tau_x/\tau_y = \tau_z/\tau_y = 3$, which we have used to calculate T_{1e}^{-1} in the magnetic field of our NMR spectrometer ($B_0 = 7.05$ T). Representative values[9,22] of $g_x = 2.140$, $g_y = 2.040$, and $g_z = 1.994$ were employed as were typical correlation times for $[\mathrm{Ni(mnt)_2}]^{1-}$ in room-temperature organic liquids ($5.00 \times 10^{-11} \le \tau_x \le 1.50 \times 10^{-10}$ s).[22] The results, given in Table 2, show that values of the τ_i in this range ($\tau_x = 1.29 \times 10^{-10}$ s and 9.18×10^{-11} s for $\mathrm{CH_3NO_2}$ and acetone, respectively) give values of T_{1e}^{-1} in agreement with experiment. It is encouraging that a shorter value of τ_x was required for the less viscous acetone;[24] the viscosities of $\mathrm{CH_3NO_2}$ and acetone are given in Table 1.

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Table 2. Calculated Values of T_{1e}^{-1} for $[Ni(mnt)_2]^{1-}$

$10^{-11}\tau_x$, s	$10^{-7}T_{1e}^{-1,a}$, s^{-1}
15.0	2.52
12.9	2.94^b
12.0	3.15
10.0	3.78
9.18	4.12^c
9.00	4.21
7.00	5.41
5.00	7.57

[a] Calculated using $g_x = 2.140$, $g_y = 2.040$, $g_z = 1.994$, $B_0 = 7.05$ T, and $\tau_x/\tau_y = 3.0$. [b] The value determined from the ^{13}C line widths in CH_3NO_2. [c] The value determined from the ^{13}C line widths in acetone.

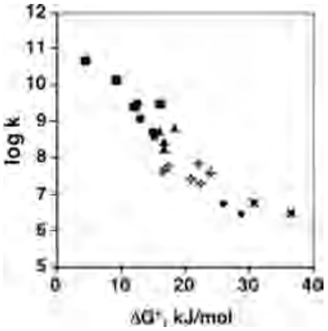

Figure 4. Logarithm of k vs the Marcus theory free energy of activation for systems (a) (squares), (b) (circles), (c) (triangles), (d) (+), and $[Ni(mnt)_2]^{1-,2-}$ assuming a charge of $-e$ (diamonds) and $-2e$ (x) for $[Ni(mnt)_2]^{2-}$.

The values of k and T_{1e}^{-1} in acetone as well as $f_D = 1$ and $[D] = 9.0 \times 10^{-2}$ M give values of $2\tau_P T_{1e}^{-1} = 315$ and $f_D\tau_P^2(a_i^2/4) = 1214$ and 636 for 118 and 125 ppm, respectively, showing that the data for both lines are in neither the slow exchange ($f_D\tau_P^2(a_i^2/4) \gg 1 + 2\tau_P T_{1e}^{-1}$) nor the fast exchange ($f_D\tau_P^2(a_i^2/4) + 2\tau_P T_{1e}^{-1} \ll 1$) limit; the same is true in CH_3NO_2 (see Table 1). Because of the non-negligible $2\tau_P T_{1e}^{-1}$ term, the values of k are noticeably different from those of the slopes. In acetone, $10^{-6}m_{125} = 1.94$ M^{-1} s^{-1}, $10^{-6}m_{118} = 2.30$ M^{-1} s^{-1}, and $10^{-6}k = 2.91$ M^{-1} s^{-1}; similar differences are found in CH_3NO_2. The slow exchange limit has been found to be appropriate in several studies of the electron transfer reactions of organic radicals, for which T_{1e}^{-1} is typically an order of magnitude (or more) smaller (for similar τ_i values) because of their smaller g factor anisotropies.[16,20,25] Additionally, the values of the $|a_i|$ for protons in organic radicals[26] are often larger than those for the ^{13}C nuclei of $[Ni(mnt)_2]^{1-}$.

Discussion

In this section the rate constants for eq 1 are compared with the predictions of Marcus theory and with those for the electron transfer reactions of other Ni(III,II) complexes. The data for the Marcus comparison, shown in Figure 4, were chosen to span a wide range of k values; they are for eq 1 in CH_3NO_2 and acetone and for the reactions between (a) the pyrene anion radical and 9,10−dimethylanthracene in diethylamine, ethylenediamine, isopropyl alcohol and ethyl alcohol (EtOH),[27] (b) the naphthalene anion radical and naphthalene in hexamethylphosphoramide, tetrahydrofuran (THF), and a mixture of dimethoxyethane (44 mol %) and THF (56 mol %),[28] (c) the PhCN anion radical and PhCN in DMF, MeCN, DMSO, propylene carbonate, and dioxane,[29] and (d) the cobaltocenium cation radical and cobaltocene in MeCN, acetone, pyridine, DMF, PhCN, and *N*-methylformamide.[30] The values of log k are plotted against ΔG^*, the Marcus theory free energy of activation[12,31]

$$\Delta G^* = (w^r + w^p)/2 + \lambda/4 + \Delta G^0/2 + (\Delta G^0 + w^p - w^r)^2/4\lambda \tag{10}$$

where w^r and w^p are the work needed to bring the reactants and products together in the activated complex, ΔG^0 is the standard free energy of reaction, and[31]

$$\lambda = \lambda_{os} + \lambda_{is} \tag{11}$$

where λ_{os} and λ_{is} are the outer- and inner-sphere contributions, respectively. The outer-sphere (solvent reorganization) contribution is given by[31]

$$\lambda_{os} = [(2r_1)^{-1} + (2r_2)^{-1} - r^{-1}][(\varepsilon_{op})^{-1} - (\varepsilon_s)^{-1}](ne)^2 \tag{12}$$

where r_1 and r_2 are the effective radii of the reactants, $r = r_1 + r_2$, and n is the number of electrons transferred. ε_{op} and ε_s are the solvent's optical dielectric constant (the square of its refractive index, n_i) and static dielectric constant, respectively; the values of n_i and ε_s for CH_3NO_2 and acetone[32] are given in Table 1. The values of ε_s and n_i for the CH_3NO_2 NMR samples were calculated as described in the Experimental section, that is, $\varepsilon_s(CH_3NO_2)_{NMR} = 0.85\varepsilon_s(CH_3NO_2) + 0.15\varepsilon_s(\text{acetone})$.

The inner-sphere (vibrational) contributions are given by[31]

$$\lambda_{is} = \sum_i f_i(r_d - r_a)_i^2 \tag{13}$$

where $f_i = f_a f_d/(f_a + f_d)$ is the reduced force constant for the ith inner-sphere vibration, f_a and f_d are the force constants for the ith vibration in the anion and dianion, respectively, and $(r_a - r_d)_i$ is the difference in the ith equilibrium bond length.

The work terms for $[Ni(mnt)_2]^{1-}$ and $[Ni(mnt)_2]^{2-}$ in eq 1 are assumed to arise from the electrostatic interaction between the ions moderated by ε_s; they are appreciably larger than those for the reactions between an ion and neutral species, that is, (a)−(d) above, for which we have set $w^r = w^p = 0$. Also, reactions (b)−(d) and eq 1 have $\Delta G^0 = 0$ while those in (a) have $\Delta G^0 = -8.41$ kJ mol^{-1}. The values of λ_{os} for (a), (b), and (c) are from ref 29, those for (d) are from ref 30, and those for eq 1 were calculated using

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$r([\mathrm{Ni(mnt)_2}]^{1-}) = 3.77$ Å and $r([\mathrm{Ni(mnt)_2}]^{2-}) = 4.54$ Å from capillary-flow determinations of the ions' translational diffusion constants, D, in acetone.[23] The Stokes−Einstein relation ($D = k_BT/6\pi\eta r$) was used to obtain r, a length determined by the solute's shape and size; k_B is Boltzmann's constant, T is the absolute temperature, and η is the viscosity. Similar determinations for $[\mathrm{Ni(mnt)_2}]^{1-}$ and $[\mathrm{Ni(mnt)_2}]^{2-}$ in MeCN and EtOH gave sizes that were essentially the same as those in acetone.[23,33] The larger size of $[\mathrm{Ni(mnt)_2}]^{2-}$ was attributed to ion pairing; electrochemical,[34] conductivity,[35,36] and vapor phase osmometry[34] data have shown this to be the case in MeCN where $\mathrm{Et_4N^+}$ was the counterion (we used $(n\text{-Bu})_4\mathrm{N}^+$). Because of the ion pairing, the work terms were calculated using a charge of $-e$ as well as $-2e$ for the dianion. Both results are shown in Figure 3; the less negative charge gives a better correlation with the data for (a)−(d), particularly in acetone, which has a smaller value of ε_s (21.26) than $\mathrm{CH_3NO_2}$ (36.67).[32] The value of ΔG^* for eq 1 in acetone with a dianion charge of $-2e$ is the largest in Figure 4.

The force constants[37] and bond lengths[38] for $[\mathrm{Ni(mnt)_2}]^{2-}$ and $[\mathrm{Ni(mnt)_2}]^{1-}$ have been determined and show that the inner-sphere contributions are small. For example, the largest difference in bond lengths is for the Ni−S bonds ($\Delta r = r_d - r_a = 2.175 - 2.149$ Å $= 0.026$ Å).[38] This value of Δr and the stretching force constants $K(\mathrm{Ni{-}S}) = 153$ and 127 N m^{-1} in the anion and dianion, respectively,[37] contribute 0.28 kJ mol^{-1} to λ_{is}, much less than $\lambda_{os} \approx 85$ kJ mol^{-1} for both $\mathrm{CH_3NO_2}$ acetone. Other bond length differences, such as those for the S−C and C═C bonds, are 0.01 Å or less and give contributions of 0.1 kJ mol^{-1} or less to λ_{is}. Only the outer-sphere contributions are included in Figure 4.

Given the variety of reactants and solvents involved in Figure 4, the general trend in log k is predicted by ΔG^*_{os}. Our results also can be compared with the prediction of the Marcus relation $[k/Z_{soln}]^{1/2} \geq k_{el}/Z_{el}$,[39] where k and k_{el} are the rate constants in homogeneous solution and at an electrode, respectively. The use of $Z_{soln} = 10^{11}$ M^{-1} s^{-1} and $Z_{el} = 10^4$ cm s^{-1} gives $[k/10^3]^{1/2} \geq k_{el}$. Lingane[34] found $k_{el} \geq 1$ cm s^{-1} for $[\mathrm{Ni(mnt)_2}]^{1-,2-}$ in MeCN, which gives $k \geq 10^3$ M^{-1} s^{-1}; this is consistent with our rate constants of $\approx 10^6$ M^{-1} s^{-1}.

As the following discussion will show, the values of $10^{-6}k = 2.91$ and 5.78 M^{-1} s^{-1} for eq 1 in acetone and $\mathrm{CH_3NO_2}$, respectively, are faster than those for the electron transfer reactions of other Ni(III,II) couples. The molecular and electronic structures of $[\mathrm{Ni(mnt)_2}]^{1-}$ and $[\mathrm{Ni(mnt)_2}]^{2-}$ allow for a favorable overlap that facilitates the electron transfer. The singly occupied molecular orbital (SOMO) of the anion and the highest occupied molecular orbital (HOMO) of the dianion have appreciable contributions from the noninnocent mnt ligand.[4] ESR[40,41] and ENDOR/ESEEM[9] have been used to determine the spin density for every atom of $[\mathrm{Ni(mnt)_2}]^{1-}$ and show that ≈0.75 of the electron resides on the ligands (with 0.60 on the sulfurs) although the nickel atom has the largest single value (≈ 0.25). X(α) MO calculations indicate that the HOMO of $[\mathrm{Ni(mnt)_2}]^{2-}$ has ≈70% ligand and ≈30% nickel character.[42]

Margerum and co-workers obtained rate constants that were smaller than ours for a number of Ni(III,II) peptide complexes. Using stopped-flow techniques, cross-reactions, and the Marcus cross-relation,[12] they found values of k as large as 1.2×10^5 M^{-1} s^{-1} for tripeptideamides and 1.3×10^4 M^{-1} s^{-1} for tripeptides at 25 °C in aqueous solutions.[43] An ESR line broadening technique using ^{61}Ni gave $k = 450$ M^{-1} s^{-1} at 24 °C in aqueous solution for the $[\mathrm{Ni^{III}(H_{-2}\text{-}Aib_3)(H_2O)_2}]^0$ and $[\mathrm{Ni^{II}(H_{-2}Aib_3)}]^{1-}$ couple where $\mathrm{Aib_3}$ is the tripeptide of α−aminoisobutyric acid and $\mathrm{H_{-2}}$ denotes two deprotonated-N(peptide) groups.[44] For these systems, the Ni(III) complexes have a tetragonally distorted octahedral structure with two $\mathrm{H_2O}$ molecules in the axial sites; the Ni(II) complexes are square planar with no axial solvation; a water bridge was proposed to facilitate the electron transfer between the tripeptideamide and tripeptide complexes while this type of interaction was hindered in the $\mathrm{Aib_3}$ complex.[44]

McAuley and co-workers also determined k values for a number of Ni(III,II) electron transfer reactions in aqueous solutions using cross-reactions and the Marcus cross-relation;[12] they too are smaller than ours. For example $[\mathrm{Ni(cyclam)(NO_3)_2}]^{+,0}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) has $10^{-5}k = 1.4$ M^{-1} s^{-1} at 20 °C[45] while $[\mathrm{Ni(cyclam)Cl_2}]^{+,0}$ has $10^{-4}k = 3.4$ M^{-1} s^{-1} at 25 °C[45–47] and $[\mathrm{Ni(cyclam)\text{-}(H_2O)_2)}]^{3+,2+}$ has $10^{-3}k = 2.0$ M^{-1} s^{-1} at −16 °C.[45,48] The related $[\mathrm{Ni([9]aneN_3)_2}]^{3+,2+}$ couple ($\mathrm{[9]aneN_3}$ = 1,4,7-triazacyclononane) has $10^{-3}k = 6.0$ M^{-1} s^{-1} at 25 °C.[45,47] Unlike $[\mathrm{Ni(mnt)_2}]^{2-}$ and $[\mathrm{Ni(mnt)_2}]^{1-}$, which are square planar, these complexes have octahedral coordination and unconjugated ligands.

McAuley did find a nickel-centered electron transfer reaction with a k value comparable to those for eq 1 although it was not between Ni(III,II) complexes. It involved the bicyclic $[\mathrm{Ni_2(L4)}]^{4+,3+}$ complexes (L4 = 1,1′-enebicyclo-3,6,10,13-tetraazadeca-2,13-dienylidene), which have electron delocalization across the large conjugated portion of the ligand linking the two Ni(II) ions in $[\mathrm{Ni_2(L4)}]^{4+}$; $[\mathrm{Ni_2(L4)}]^{3+}$

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has some Ni(I) character. The rate constant of $10^{-6}k = 5.1$ M^{-1} s^{-1} in aqueous solution at 9 °C[49] was taken to be consistent with a reduced reorganizational barrier due to the delocalization.

We have determined the rate constant for the reaction between a nickel bis(dithiolene) anion and dianion. Neutral dithiolene complexes have been prepared and there are four ligands for which all three members of the redox chain $[NiL_2]^{0,1-,2-}$ have been isolated; it would be interesting to compare the *k* value for the $[NiL_2]^{0,1-}$ reaction with that for $[NiL_2]^{1-,2-}$. The series are[50] $[Ni(S_2C_2(CF_3)_2)_2]^{0,1-,2-}$, $[Ni(S_2C_2Ph_2)_2]^{0,1-,2-}$, $[Ni(3,5\text{-}Bu^t{}_2bdt_2)_2]^{0,1-,2-}$ (bdt = benzene−1,2-dithiolate(2−)), and $[Ni(S_2C_2Me_2)_2]^{0,1-,2-}$. The composition of the relevant molecular orbitals, one of the factors that could cause differences in the *k* values, varies among the members of these series. For example, DFT calculations carried out by Holm et al.[50] showed that the $5b_{2g}$ orbital, which is the lowest unoccupied molecular orbital (LUMO) of $[Ni(S_2C_2Me_2)_2]^0$, the SOMO of $[Ni(S_2C_2Me_2)_2]^{1-}$, and the HOMO of $[Ni(S_2C_2Me_2)_2]^{2-}$, has 13.3, 19.5, and 38.9% $Ni(3d_{yz})$ character for the neutral species, anion, and dianion, respectively. The assignment of the *x* and *y* axes in ref 48 is the reverse of ours; the $3d_{yz}$ we use here is $3d_{xz}$ there. The $6b_{1u}$ HOMO of $[Ni(S_2C_2Me_2)_2]^0$ has only a small (5.6%) contribution from $Ni(4p_z)$.[50] X-ray absorption spectroscopy also has been used to show[4] that the neutral complex has significant differences in electronic structure compared to the mono- and dianion.

Conclusions

The rate constant, *k*, for the homogeneous electron transfer (self-exchange) reaction between the planar $[Ni(mnt)_2]^{1-}$ and $[Ni(mnt)_2]^{2-}$ complexes has been determined using ^{13}C NMR line width measurements. The *k* values in CH_3NO_2 and acetone are faster than those for the reactions of other Ni(III,II) complexes. The outer-sphere contributions to the Marcus theory free energy of activation are consistent with those for other inorganic and organic redox couples. The spin−lattice relaxation time, T_{1e}, of the paramagnetic $[Ni(mnt)_2]^{1-}$ must be included in the line width analysis to obtain a consistent interpretation of the data; the values obtained are in general agreement with those estimated using the known motional properties of $[Ni(mnt)_2]^{1-}$ in other polar solvents. The analysis can be applied to the electron transfer reactions of the large number of dithiolene complexes involving ligands other than mnt, transition metals other than Ni, and nuclei with $I = 1/2$ other than ^{13}C, that is, ^1H, ^{19}F, and ^{195}Pt.

Appendix

The Zeeman interaction between the magnetic field, B_0, and the unpaired electron of $[Ni(mnt)_2]^-$ is anisotropic ($g_x \neq g_y \neq g_z$). The spectral density, $j^{(G)}(\omega_0)$, is responsible for the contributions to T_{1e}^{-1} from the reorientationally induced electron spin flips and is given by[19]

$$j^{(G)}(\omega_0) = (1/20)[(d^2\tau_x)/(1+\omega_0^2\tau_x^2) + (2e^2\tau_{xy})/(1+\omega_0^2\tau_{xy}^2)] \quad \text{(A1)}$$

with

$$d = (6)^{-1/2}[2g_y - (g_z + g_x)](\omega_0/g_0) \quad \text{(A2)}$$

$$e = (1/2)(g_z - g_x)(\omega_0/g_0) \quad \text{(A3)}$$

$$\omega_0/g_0 = (\beta_e B_0)/(h/2\pi) \quad \text{(A4)}$$

$$g_0 = (1/3)(g_x + g_y + g_z) \quad \text{(A5)}$$

$$\tau_{xy} = 3\tau_x(1 + 2\tau_x/\tau_y)^{-1} \quad \text{(A6)}$$

where β_e is the Bohr magneton and *h* is Planck's constant. We have assumed axially symmetric rotational diffusion of $[Ni(mnt)_2]^{1-}$ with the *y* magnetic axis as the diffusional symmetry axis, that is, $\tau_x = \tau_z \neq \tau_y$ and $\tau_x/\tau_y = 3.0$. The relative contributions to T_{1e}^{-1} from the anisotropic Zeeman (32%) and spin rotation (68%) interactions are the same in both solvents. Equations 9 and A1 are valid in the motionally narrowed (fast motional) limit[17–19] and are appropriate for nonviscous liquids such as acetone and CH_3NO_2 at (or near) room temperature.[20,22]

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