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Redox Polyether Hybrid Copper Bipyridine Complex Molten Salts

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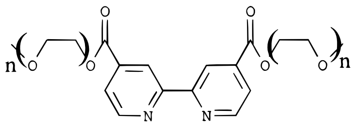
The covalent attachment of poly(ethylene oxide) chains to metal bipyridine complexes produces viscous molecular melts with sufficient ionic conductivity to permit microelectrode voltammetry. This paper describes the use of this chemistry to prepare a new copper complex with “tailed” bipyridine ligands, $[Cu(bpy(CO_2MePEG\text{-}350)_2)_2](ClO_4)_2$, where MePEG-350 is methyl poly(ethylene glycol) with molecular weight 350 g mol^{-1}. The coupling of physical diffusion with electron hopping during voltammetry allows measurement of the electron self-exchange rate constant, k_{EX}, for the Cu(II/I) couple. Activation studies indicate the reaction to be nearly adiabatic, with an activation barrier larger than expected for purely inner-sphere rearrangements. This study also examines the depression of both electron transport and ionic conductivity caused by the addition of 1.4 M $LiClO_4$ to the undiluted room-temperature melt.

Introduction

We have shown[1a] that covalent attachment of oligo(ethylene glycol) chains to the cation or anion of redox salts leads to new room-temperature molten salts. Ionic melts made in this way are structurally versatile media for the investigation of the nature of electron and mass transport in highly viscous, polymer-like phases. The melts can be regarded as bridges between the solid and liquid states. The modified 2,2′-bipyridine ligand in the following structure



n = 3; E_3M
n = 7; MePEG-350
n = 11; MePEG-550
n = 16; MePEG-750

illustrates how a variety of methyl-terminated oligo(ethylene glycol) chains can be attached to a ligand. Coordination of such ligands (L) to different metals yields families of redox-active, room-temperature molten salts whose properties can be manipulated by systematically varying the polyether “tail” content. Thus, series of $[CoL_3](ClO_4)_2$ and $[FeL_3](ClO_4)_2$ complexes with different polyether tail lengths (varied *n*) and of $[Ru(bpy)_{3-x}L_x](ClO_4)_2$ complexes with different numbers of bpy and of tail-bearing ligands have been synthesized and their ion conductivity and viscosity properties examined.[1a,b] It is further possible to use[1a−d,f−i] microelectrodes for the direct voltammetry of the *undiluted* metal complex molten salts. These novel measurements probe the structural sensitivity of the self-diffusivity of the undiluted metal complexes and of the homogeneous electron self-exchange rate constants of the Co(II/I), Fe(III/II), Ru(III/II), and Ru(II/I) redox couples, *i.e.*, how they depend on the number and length of the polyether chains present in the highly viscous metal complex melts and on the addition of lithium electrolyte to them.[1c,d] The objectives are new insights into the effects of a semisolid environment on mass and electron transfer dynamics.

The present paper extends this chemistry to a new copper complex with “tailed” bipyridine ligands for which $n = 7$, *i.e.*, $[Cu(bpy(CO_2MePEG\text{-}350)_2)_2](ClO_4)_2$, designated as $[CuL_2](ClO_4)_2$ in this paper. The copper(II/I) redox couple of this complex offers a rough parallel to the cobalt[1a,c,d] redox couple Co(II/I) in the melt $[CoL_3](ClO_4)_2$. The parallel is, of course, inexact given the stoichiometric coordination shell differences between the two couples and the correspondingly different number of MePEG-350 tails per metal complex. We will describe the similarities and differences in the properties of the Cu and Co complexes, notably the ionic conductivity, mass transport, and electron self-exchange dynamics.

The metal complex melts, by virtue of their polyether tails, will dissolve the electrolyte $LiClO_4$. In dilute solutions, addition of an inert solute does not appreciably change the activity of the original constituents of the solution. The situation is different when adding an electrolyte like $LiClO_4$ to linear polyethers, as in “polymer electrolytes”,[2] and similarly when adding $LiClO_4$ to the undiluted metal complex melts. In both cases, owing to the lithium ion−ether dipole cross- linking, the resulting materials can exhibit substantially altered properties. The present study will explore the change in properties caused by addition of 1.4 M $LiClO_4$ to the undiluted room-temperature $[Cu(bpy(CO_2MePEG\text{-}350)_2)\ ](ClO_4)_2$ melt.

A brief overview of the chemistry of Cu−bpy complexes is in order to complete the introduction. In crystalline $[Cu^{II}(bpy)_2]$-

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$(ClO_4)_2$, the $[Cu(bpy)_2]^{2+}$ unit is square planar with some tetrahedral distortion and with one of the perchlorate ions much closer to the metal ion than the other ($Cu-O = 251.2$ and 274.6 pm),[3] illustrating the tendency of Cu(II) to assume the coordination number 5 and to form complexes of tetragonal pyramidal geometry.[3] The aqueous stability constants of copper bipyridine complexes ($\log K_1 = 8.0$, $\log K_2 = 5.6$, $\log K_3 = 3.5$)[4] indicate that Cu(II) preferentially forms $[Cu(bpy)_2]^{2+}$ if the molar ratio Cu:bpy = 1:2, but there is probably a solvent molecule or an anion occupying the fifth coordination site.[3,5]

The copper(I) bipyridine complex, $[Cu(bpy)_2]^+$, has tetrahedral geometry and is very stable:[5] $\log \beta_2 \simeq 14$. The electron transfer self-exchange rate constant for $[Cu(bpy)_2]^{2+/+}$ is 4.4×10^3 M^{-1} s^{-1} in aqueous medium,[5b] much smaller that of the cobalt complex $[Co(bpy)_3]^{2+/+}$, 10^9 M^{-1} s^{-1}.[6] The kinetic slowness of the Cu(II/I) couple is principally due to the coordination geometry change in the copper complex upon oxidation state change (see above); there is no such change for cobalt.[7] Additionally the spin pairing upon the addition of the electron involves an antibonding orbital in the case of $[Cu(bpy)_2]^{2+}$, but a nonbonding one in the case of $[Co(bpy)_3]^{2+}$.

Experimental Section

Details have been given previously[1a,d–i] of the microelectrode voltammetric and chronoamperometric transport measurements in the mixed-valent diffusion layers at electrode surfaces, ac impedance measurements of ionic conductivity,[1a] and differential scanning calorimetric measurements[1a,d] used for the investigation of the polyether-tailed bipyridine metal complexes. Diffusion in the melts was sufficiently slow as to give generally linear diffusion conditions at the 28 μm diameter Pt microdisk electrode. UV−vis spectra were measured with a Unicam UV-4 spectrophotometer. The synthesis of the polyether-tailed ligand ($n = 7$, see structure) has been published.[1a,d]

The "tailed" metal complex $[Cu(bpy(CO_2MePEG\text{-}350)_2)_2][ClO_4]_2$ was prepared by mixing 500 mg (0.55 mmol) of $bpy(CO_2MePEG\text{-}350)_2$ with 96 mg (0.26 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ (Aldrich), each dissolved in methanol. The deep blue solution was concentrated on a rotary evaporator and the remaining solvent removed in a vacuum oven at 70 °C, leaving a green, highly viscous melt. The density of the undiluted melt, $\rho = 1.34$ g/cm^3 at 25 °C, corresponding to a 0.64 M metal complex concentration, does not change significantly upon $LiClO_4$ electrolyte addition. The $LiClO_4$ concentration added to the $[Cu(bpy(CO_2MePEG\text{-}350)_2)_2](ClO_4)_2$ melt in some experiments was 1.4 M, which corresponds to two MePEG-350 polyether tails per $LiClO_4$ (or an ether O:Li ratio of 14:1). Proton NMR of the complex in acetone solutions shows that the product complex contained less than 2% of uncoordinated tailed ligand.[8] The complex was further identified by its UV−vis spectrum. The UV−vis spectrum of a thin film of $[Cu(bpy(CO_2MePEG\text{-}350)_2)_2][ClO_4]_2$ cast on the optical cell wall exhibits a broad absorption band with $\lambda_{MAX} = ca.$ 670 nm, which agrees with the reflectance spectrum of $[Cu(bpy)_2][ClO_4]_2$.[3] The melt absorbs water readily and must be kept in a dry atmosphere and was additionally dried before use. A shoulder at 480 nm, observed immediately after drying the melt for several days at 70 °C in vacuum, disappears after exposure for 1 day to dry air in a closed vessel. This shoulder may arise from traces of Cu(I),[9] which would be spectrally prominent owing to its intense absorbance. $[Cu(bpy)_2]^+$ has a charge transfer band at *ca.* 440 nm with a molar absorptivity ca. 70-fold larger than that of the 670 nm band of $[Cu(bpy)_2]^{2+}$.[10]

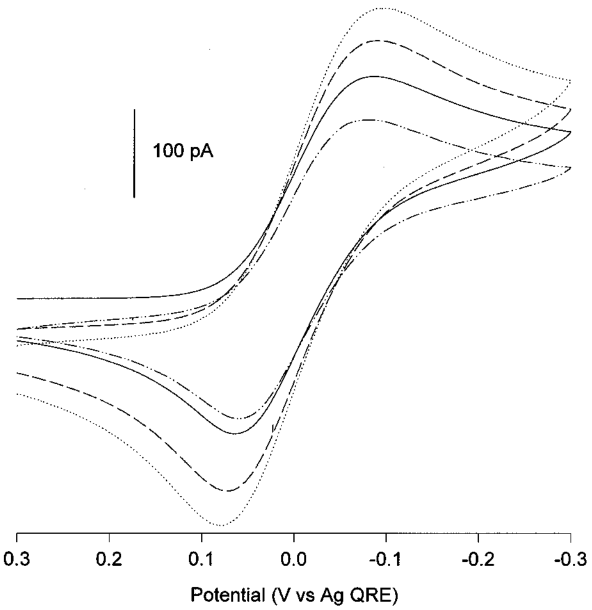

Figure 1. Cyclic voltammetry at a 28 μm diameter Pt microdisk electrode of $[CuL_2](ClO_4)_2$ at 25 °C, at $\nu = 3$ mV s^{-1} (···), $\nu = 2$ mV s^{-1} (- - -), $\nu = 1$ mv s^{-1} (—), and $\nu = 0.7$ mV s^{-1} (- ·· -).

Results

Heterogeneous Electron Transfer Rates Deduced from Cyclic Voltammetry. Polarograms of the Cu(II/I) reaction for $[Cu(bpy)_2]^{2+}$ in dilute aqueous solutions containing excess bpy lie at $E_{1/2} = -0.16$ to -0.21 V vs SCE depending on bpy concentration.[10] A dilute solution of $[Cu(bpy)_2](ClO_4)_2$ in the polyether solvent $(CH_3(OCH_2CH_2)_{7.2}OH)$ (poly(ethylene glycol-350 monomethyl ether)), analogous to the bpy "tail" and containing dissolved $LiClO_4$ electrolyte, gives a voltammetric wave (not shown) lying at $E^o \approx 0$ V vs Ag quasi-reference electrode and with slow Cu (II/I) kinetics as seen in its large cyclic voltammetric peak potential splitting, $\Delta E_p \approx 470$ mV at 100 mV/s.

In the undiluted $[CuL_2](ClO_4)_2$ melt, without added electrolyte, the Cu(II/I) voltammetric wave also evidences slow kinetics. Figure 1 shows microdisk (28 μm diameter Pt) voltammetry of the undiluted, room-temperature molten salt $[CuL_2](ClO_4)_2$ at several scan rates. The voltammogram is stable and well formed and has, qualitatively, the appearance of a quasi-reversible (but chemically reversible) electron transfer reaction. That is, the Cu(II/I) peak potential splittings (ΔE_{PEAK}) are >59 mV. The Nicholson−Shain treatment[11] was applied to the ΔE_{PEAK} results for cyclic voltammograms like those in Figure 1 and, when taken as a function of temperature, produced heterogenous electron transfer rate constants k^o and barrier energies as shown in Figure 2 and Table 1. The data were taken at very slow potential scan rates and hence small currents (see scale in Figure 1), and the rate constants k^o were invariant with potential scan rate (Table 1 footnotes) as expected for minimal

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(8) In the ^{1}H NMR spectrum, the bipyridine protons in the free, uncomplexed ligand appear as three peaks 9−10 ppm, whereas the bpy protons of the bound ligand are shifted downfield and do not appear in the spectrum. Purity of the complex (within ±2% excess ligand) is confirmed when the bpy protons no longer appear.

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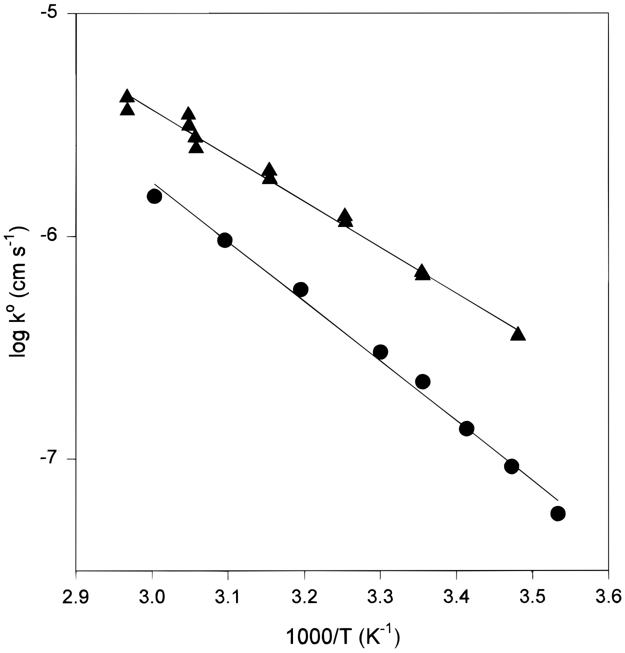

Figure 2. Activation plots of the heterogeneous rate constant, *k*°, for $[CuL_2](ClO_4)_2$ neat (▲) and containing 1.4 M $LiClO_4$ (●).

Table 1. Heterogeneous Electron Transfer Results in $[CuL_2](ClO_4)_2$

redox system	*k*° at 298 K[a] (cm/s)	$E_{A,HET}$ (kJ mol^{-1})
Cu(II/I) neat	6.5×10^{-7}	37
Cu(II/I) + 1.4 M $LiClO_4$	2.2×10^{-7}	46[b]

[a] Average *k*° value over several potential scan rates. The rate constant was found to be independent of scan rate; for example in neat $[CuL_2](ClO_4)_2$, at 14 °C, at $\nu = 0.7$, 1.0, 2.0, and 3.0 mV s^{-1}, $k^o = 6.1 \times 10^{-7}$, 8.0×10^{-7}, 7.2×10^{-7}, 6.2×10^{-7}, and 3.4×10^{-7} cm s^{-1}. Similarly, in $[CuL_2](ClO_4)_2$ containing $LiClO_4$, at 25 °C, at $\nu = 0.6$, 1.0, 2,0, and 5.0 mV s^{-1}, $k^o = 2.2 \times 10^{-7}$, 2.2×10^{-7}, 2.3×10^{-7}, and 2.2×10^{-7} cm s^{-1}. [b] Results of measurements at temperatures below 25 °C were not included because of possible distortion by the low ionic conductivity of the melt there.

distortions by uncompensated resistance effects. The rate constant of the heterogeneous Cu(II/I) reaction is quite small (Table 1), in the range of 10^{-7} cm/s, and is depressed somewhat by the addition of $LiClO_4$ electrolyte. The activation barrier to electron transfer is large and is enhanced further by the addition of electrolyte. The electrolyte sensitivity of the heterogeneous kinetics is qualitatively like that seen in measurements of homogeneous electron transfer rates, which are discussed next.

Sometimes voltammetry in the melts was not as well formed as in Figure 1; the post-reduction current decayed more slowly, and the oxidation peak was broader than ideal for a quasi-reversible process. This behavior was not seen consistently, and its origin is obscure.

Transport Measurements and Homogeneous Electron Exchange. Charge transport measurements are accomplished by chronoamperometry, in which the applied potential is stepped well past the peak of the voltammetric wave so as to produce a purely transport-limited Cu(II/I) electrode reaction. The resulting current–time curves when analyzed according to the Cottrell equation[12]

$$i = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} \tag{1}$$

produce linear current vs [time]$^{-1/2}$ plots as exemplified in

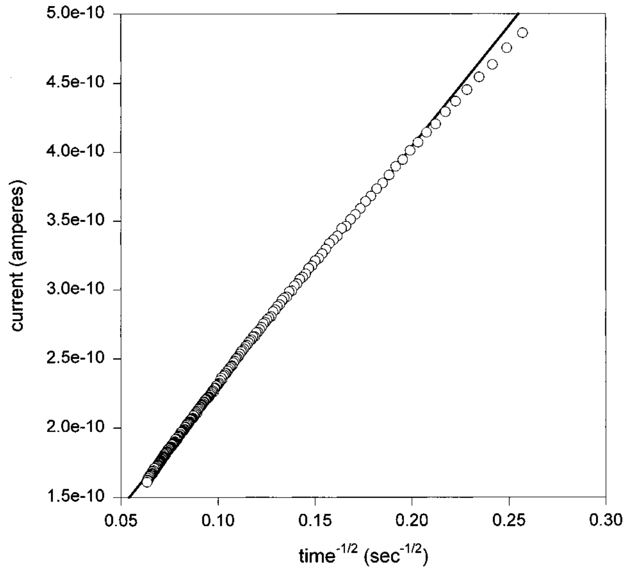

Figure 3. Cottrell plot for neat $[CuL_2](ClO_4)_2$ at 25 °C using a 28 mm diameter Pt microelectrode (○) with linear regression (—), giving slope = 1.7×10^{-9} A s^{-1} and intercept 5.6×10^{-11}A.

Figure 3. The current–time traces were typically analyzed out to several hundred seconds.

Evaluation of chronoamperograms taken at 298 K of the undiluted (no added electrolyte) molten salt $[CuL_2](ClO_4)_2$ gave an apparent diffusion coefficient for the Cu(II/I) reaction of $D_{APP} = 7.1 \times 10^{-11}$ cm^2/s. Analogous experiments with melt samples to which 1 equiv of $LiClO_4$ per ligand L had been added (1.4 M) gave a 30-fold smaller transport rate, $D_{APP} = 2.1 \times 10^{-12}$ cm^2/s (Table 2, column 3). Depression of charge transport rates by addition of electrolyte is also seen for other metal complex melts[1c,d] of polyether-tailed bipyridine ligands and appears to be a general effect, probably associated with the Li$^+$-induced coordinative polyether chain cross-linking well-known in polymer electrolytes.[2] The change in D_{APP} caused by addition of electrolyte is not an artifact caused by an ionic migration effect, since it is far too large to be accounted for that way. Also, other assessments[1a–d] of transference numbers in polyether-tailed metal bipyridine complexes show that ionic charge transport in the electrolyte-free melts is dominated by the smaller, mobile perchlorate counterion (*i.e.*, ionic migration enhancement of the Cu(II/I) reduction currents and of D_{APP} should be minor or absent).

Let us next consider the nature of diffusive charge transport in the copper complex melt. The potential step and electrolysis in Figure 3 produce a mixed-valent Cu(II/I) layer of metal complexes around the microelectrode. It is well-known that when physical diffusion of an electrode reactant is very slow yet electron self-exchange between the members of the redox couple is facile, electron self-exchange reactions in the mixed-valent layer can enhance the observed, apparent (D_{APP}) diffusion coefficient. This is commonly described by a hopping model in a fictitious octahedral framework called the Dahms–Ruff relation:[13]

$$D_{APP} = D_{PHYS} + (k_{EX}\delta^2 C)/6 \tag{2}$$

Here D_{PHYS} is the true physical diffusion coefficient of the electrode reactant, k_{EX} (M^{-1} s^{-1}) is the second-order (*i.e.*, Cu(II/I)) self-exchange rate constant, and δ (cm) and C (M) are the average center-to-center distances between the metal com-

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Table 2. Diffusion and Electron Self-Exchange in Undiluted Molten Salts $[CoL_3](ClO_4)_2$ and $[CuL_2](ClO_4)_2$

redox system	D_{PHYS} at 298 K (cm^2/s)	D_{APP} at 298 K (cm^2/s)	k_{EX} at 298 K ($M^{-1}\ s^{-1}$)	A ($M^{-1}\ s^{-1}$)	E_A (kJ mol^{-1})
Cu(II/I)[a] neat melt	4.7×10^{-13} [b] (10^{-12})[c]	7.1×10^{-11}	2.3×10^4 (2.2×10^4)	1.3×10^{13}	50
Cu(II/I)[d] + $LiClO_4$	$<10^{-13}$ [e]	2.1×10^{-12}	6.8×10^2	3.1×10^{12}	55
Co(III/II)[f] neat melt	1.3×10^{-11}	N.A.	N.A.	N.A.	73
Co(III/II)[g] + $LiClO_4$	7.0×10^{-14}	N.A.	N.A.	N.A.	125
Co(II/I) neat melt	1.3×10^{-11}	1.46×10^{-9}	6.7×10^5	3.0×10^{12}	36

[a] Density at 298 K, 1.343 g/cm^3, gives a 0.644 M Cu complex concentration. [b] D_{PHYS} of Cu(II) complex, estimated from ionic conductivity using eq 7. [c] Estimated by analogy to Co(III/II) neat melt. See text. [d] $[Cu(bpy(CO_2MePEG\text{-}350)_2)_2](ClO_4)_2$ containing 1.4 M $LiClO_4$ (O:Li = 14:1). [e] D_{PHYS} for Cu(II) complex estimated by comparison to Co(III/II) melt with added $LiClO_4$ (see below in table). [f] The neat $[Co(bpy(CO_2MePEG\text{-}350)_2)_3](ClO_4)_2$ complex; data from ref 1a. [g] $[Co(bpy(CO_2MePEG\text{-}350)_2)_3](ClO_4)_2$ containing 1.3 M $LiClO_4$; data from ref 1c.

plexes and their concentration in the melt, both of which are evaluated from melt density (see Table 1, footnote). Equation 2 shows that if D_{PHYS} is known and is smaller than D_{APP}, it is possible to evaluate the electron self- exchange rate constant k_{EX} for the metal complex redox couple. We[1] and others[14] have exploited the Dahms–Ruff relation for this purpose in a variety of media including other examples of polyether-tailed metal complex melts.

The value of D_{PHYS} of the $[CuL_2]^{2+}$ ion in the $[CuL_2](ClO_4)_2$ copper complex melt is needed in order to measure the electron transfer behavior of the Cu(II/I) couple using eq 2. D_{PHYS} for the $[CuL_2]^{2+}$ ion was estimated in two ways, one being from ionic conductivities using the Stokes–Einstein equation (*vide infra*). The result (Table 2, column 2) in the neat $[CuL_2](ClO_4)_2$ melt is 4.7×10^{-13} cm^2/s; note in the context of eq 2 that this value is smaller than the $D_{APP} = 7.1 \times 10^{-11}$ cm^2 s^{-1} measured for the Cu(II/I) reaction in the neat $[CuL_2](ClO_4)_2$ melt. The second estimate is based on analogy to the physical diffusivity (i.e., D_{PHYS}) of the $[CoL_3]^{2+}$ ion in the structurally similar cobalt complex melt $[CoL_3](ClO_4)_2$. The k_{EX} for the Co(III/II) redox system is very small,[1a,d] and therefore the D_{APP} value resulting from Co(III/II) chronoamperometry in the $[CoL_3](ClO_4)_2$ melt can be taken as equal to D_{PHYS} of the $[CoL_3]^{2+}$ ion. D_{PHYS} of the $[CoL_3]^{2+}$ ion depends strongly on the "tail" content of the complex and is[1a] 1.3×10^{-11} and 2×10^{-13} cm^2/s for $n = 7$ and 3, respectively (corresponding to *ca.* 42 and 18 ethylene oxide (EO) units/complex, see structure above). The tail content of the $[CuL_2]^{2+}$ ion is *ca.* 28 EO units/complex, so its D_{PHYS} should have an intermediate value, e.g., *ca.* 10^{-12} cm^2/s, which is not very different from the Stokes–Einstein estimate. Again, the D_{PHYS} estimate is much smaller than the D_{APP} measured from Cu(II/I) chronoamperometry in the neat $[CuL_2](ClO_4)_2$ copper complex melt. Similarly estimated (by comparison to $[CoL_3](ClO_4)_2$) D_{PHYS} values in $[CuL_2](ClO_4)_2$ melts that contain added $LiClO_4$ electrolyte are also smaller than D_{APP} values measured in those melts (Table 2, column 2).

From the preceding assessment it is reasonable to conclude that D_{APP} values measured from Cu(II/I) chronoamperometry in $[CuL_2](ClO_4)_2$ melts are dominated by values of the electron self-exchange rate constant of the Cu(II/I) redox couple, so that eq 2 can be used to calculate that rate constant. Resulting (Table 2, column 4) values of the room-temperature rate constant k_{EX} for electron self-exchange between $[CuL_2]^{2+}$ and $[CuL_2]^+$ in the $[CuL_2](ClO_4)_2$ melt, neat and with added $LiClO_4$ electrolyte, are 2×10^4 and 7×10^2 M^{-1} s^{-1}, respectively.

It is always useful to compare results obtained in unusual environments (i.e., electron transfer dynamics in a semisolid melt) to those known for analogous redox systems in more familiar ones (such as dilute solutions in fluid solvents). Unfortunately, k_{EX} has not been reported for the copper bipyridine complex in an ether solvent, and the only pertinent result[5b] is $k_{EX} = 4.4 \times 10^3$ M^{-1} s^{-1} for the aqueous solution reaction

$$[Cu(bpy)_2OH_2]^{2+} + e^- = [Cu(bpy)_2]^+ + H_2O \qquad (3)$$

This k_{EX} value is smaller than the measured k_{EX} in the room-temperature $[CuL_2](ClO_4)_2$ melt, 2×10^4 M^{-1} s^{-1}, which in the melt ostensibly corresponds to the reaction

$$[Cu(bpy)_2OR_2]^{2+} + e^- = [Cu(bpy)_2]^+ + R_2O \qquad (4)$$

Previous comparisons[15] have uniformly produced solid-state electron transfer rate constants smaller than those of couples within identical coordination but in a fluid solvent. The difference in the metal ion coordination between reactions 3 and 4 makes comparison in this case more tenuous.

A more complete picture of Cu(II/I) electron transfer kinetics was sought by repeating the above measurements in $[CuL_2](ClO_4)_2$ melts as a function of temperature over a range of *ca.* 10–60 °C. In analysis of the activation parameters, D_{PHYS} was again taken as negligible[16] with respect to D_{APP}, and k_{EX} was calculated directly from the latter using eq 2. The temperature dependence of k_{EX} is represented by the standard activation expression[17]

$$k_{EX} = A \exp\left[-\frac{E_A}{RT}\right] \qquad (5)$$

where the pre-exponential term $A = K_A\kappa\nu$, in which K_A is the donor–acceptor precursor complex formation constant, κ the electronic factor or transmission coefficient, and ν the frequency factor, and where E_A is the activation enthalpy (ΔH^*). Activation plots of k_{EX} for neat and electrolyte-containing $[CuL_2](ClO_4)_2$ melts are shown in Figure 4, with slopes and intercepts presented in Table 2 (columns 5, 6) along with data[1a,c] for the $[CoL_3](ClO_4)_2$ melt.

As we have pointed out before,[1a,b] the nature of the electron transfers in the mixed-valent metal complex melts affords a straightforwardly simplified interpretation of the activation relation eq 5. First, since the melt is undiluted and the reacting molecules are essentially in contact, work terms should be

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(16) Activation energy barriers for physical diffusion are (near room temperature) larger than those for electron transfer[1a,c,d;] (Table 2), but calculations readily show that in Figure 4 temperatures have not been elevated enough for D_{PHYS} to increase to values approaching D_{APP}.

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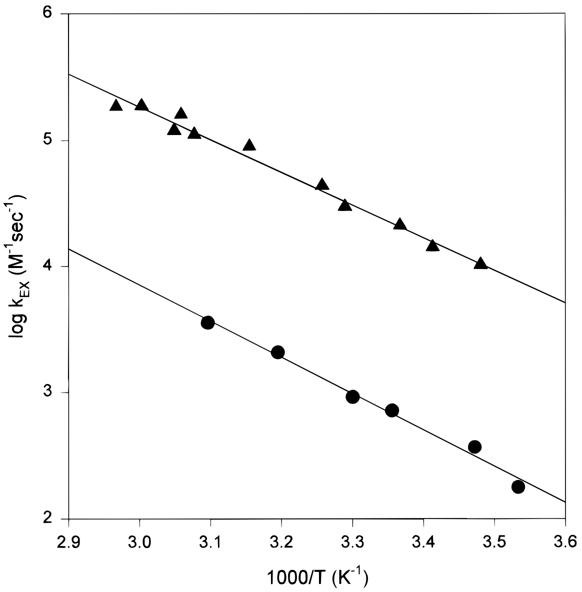

Figure 4. Activation plots of the self-exchange rate constant, k_{EX}, for $[CuL_2](ClO_4)_2$ neat (▲) and containing 1.4 M $LiClO_4$ (●).

unimportant and are thus ignored in calculation[18] of the precursor complex formation constant, which gives a value near unity: $K_A = 1.4\ M^{-1}$. Second, since the reaction is an isotopic self-exchange,[17b,19] the reaction entropy and the entropy of activation (ΔS^*) are zero,[15b] so that activation energy barriers E_A in Table 2 (column 6) for the Cu(II/I) and Co(II/I) electron self-exchanges are the same as activation free energies ΔG^*. Third, since $K_A \approx 1$, the numerical values of the intercepts (A) are within experimental uncertainty, the same as $\kappa\nu$, so that the values of A (Table 2, column 5) divided by K_A give values of $\kappa\nu$ (s^{-1}) = $10^{12}-10^{13}\ s^{-1}$ for the Cu(II/I) reaction. Since reactions with $\kappa\upsilon = 10^{12}-10^{13}\ s^{-1}$ are generally considered to be adiabatic,[17] the E_A results in Table 2 indicate that the Cu(II/I) electron self-exchange reactions are adiabatic, especially in the neat melt. The significance of this result is its implication of the absence of a significant electron tunneling barrier, *i.e.*, that the polyether chains attached to the bipyridine ligands do not appreciably impede close approach of the metal complex reaction centers to one another. The Co(II/I) and Fe(III/II) complex melt reactions are similarly behaved,[1a,c,d] and additionally their k_{EX} results showed no systematic dependency on the length of the attached polyether tails.[1a]

We draw from the observed reaction adiabaticity a picture of these melts in which the metal complex cores move within their soft, deformable polyether shells on time scales faster than the frequencies of electron transfer steps. The picture further drawn from $D_{APP} \gg D_{PHYS}$ is that net diffusion motions of the entire complex-plus-polyether shell (*i.e.*, motion over many metal complex diameters) occur on time scales slower than the frequencies of electron transfers. It follows that motion of the metal complexes within their deformable, polyether shells is much faster than net physical diffusion of the complex-plus-polyether shell in the $[CuL_2](ClO_4)_2$ melt.

If we turn to the free energy of activation (E_A) of the $[CuL_2]^{2+/+}$ electron transfer reaction, Table 2 (column 5) shows that the observed value is quite large. The electron transfer barrier energies observed previously[1a] for the $[CoL_3]^{2+/+}$ (Table 2, column 5) and $[FeL_3]^{3+/2+}$ reactions are also large but not as large as that for $[CuL_2]^{2+/+}$. In considering the $[CoL_3]^{2+/+}$ and $[FeL_3]^{3+/2+}$ reactions, it was noted[1a] that the large barriers should not represent classical inner-sphere reorganizational barrier terms arising from metal−bipyridine bonding geometry differences between the oxidized and reduced forms, since metal−bipyridine geometries of analogous untailed complexes are essentially identical. The tailed complexes present an unusual circumstance, however, in that the bipyridine and the poly-ether "solvent" are in fact a single ligand entity. Thus, the enlarged free energy of activation may be composed of an "outer-sphere reorganization" term of magnitude characteristic of an ether "solvent" plus either[1a] a peculiar "inner-sphere reorganization"-like barrier term associated with the solvent−ligand coupling or, functionally equivalent, a barrier associated with the dipolar longitudinal relaxation of the attached polyether "solvent" chains.

The above hypothesis concerning the activation barrier energies of tailed metal complexes should also apply to electron transfers of the Cu complex. Unlike the Co and Fe complexes, the Cu complex should in addition exhibit a more conventional, inner-sphere energy barrier contribution associated with the transition between tetragonal pyramidal and tetrahedral coordination geometry that accompanies the Cu(II/I) electron transfer reaction. This expectation qualitatively rationalizes the large difference (Table 2) between E_A values for the Cu(II/I) and Co(II/I) complexes.

Table 2 (column 5) shows that the Cu(II/I) electron transfer barrier E_A increases by *ca.* 10% when $LiClO_4$ electrolyte is added to the $[CuL_2](ClO_4)_2$ melt, and the reaction adiabaticity (A) is somewhat smaller. These two effects conspire to decrease the room temperature k_{EX} in the presence of electrolyte. $LiClO_4$ electrolyte could produce these changes in a variety of ways. Addition of $LiClO_4$ to oligo(ethylene oxide) melts is known to elevate viscosity, and to depress glass transition temperatures and physical diffusion coefficients.[2,20] These effects presumably are consequences of coordinative interactions between the Li^+ ions and the polyether oxygen dipoles,[2,20] which lead to reduced polyether chain segmental mobility. The orders of magnitude decrease in D_{PHYS} in the $[CoL_3](ClO_4)_2$ melt with added $LiClO_4$ electrolyte is also attributed[1c] to Li^+−ether coordination, and the generally enhanced electron transfer barrier energies seen in tailed metal complex melts may also originate in part from changes in the energetics of polyether tail motions.[1a] There are additional possible effects including changes in the nature of cation−anion associations (which may have an as yet unappreciated role in the electron transfer dynamics in these melts) and changes in the dynamics of motion of the metal bipyridine complex core within its less "soft" polyether shell (*vide supra*). The changes in the $[CuL_2](ClO_4)_2$ melt electron transfer dynamics upon addition of $LiClO_4$ may thus reflect the concerted action of multiple effects, and their interpretation is more difficult. This topic will receive a fuller discussion in a larger body of results for $[CoL_3](ClO_4)_2$ melts containing electrolyte.[1c]

As an incidental note, the density and concentration changes accompanying electrolyte addition are far too small to account for the observed 30-fold change in the room-temperature D_{APP} for Cu(II/I) in Table 2.

Ionic Conductivities. Table 3 presents results for ionic conductivity of $[CuL_2](ClO_4)_2$ melts together with those[1a] of

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(18) K_A may be calculated using the following equation:[17d]

$$K_A = \frac{4\pi N_A \overline{r^2}\delta\bar{r}}{10^3}$$

Here *r* is the average metal center-to-center distance, 15.5 Å, and δr is 0.8 Å.[17d]

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(20) (a) Frech, R. *Solid State Ionics* **1988**, *28/30*, 958. (b) McLin, M. G.; Angell, C. A. *J. Phys. Chem.* **1991**, *95*, 9464.

Table 3. Ionic Conductivity and DSC Results for Metal Complex Melts

redox system	σ_{ION}[a] at 25 °C (S cm^{-1})	[ClO$_4^-$] (M)	$E_{\mathrm{A,ION}}$ (kJ mol^{-1}) Arrhenius[b]	VTF[c]	T_o[d] (°C)	T_g[e] (°C)
Cu(II/I) neat	3.1×10^{-6}	1.288	63	12.0	−99	−40
Cu(II/I) + LiClO$_4$	3.9×10^{-7}	~2.7	113	14.2	−77	−20
Co(II/I)[f] neat	6.4×10^{-7}	0.89	48	9	−86	−56
Fe(III/II)[g] neat	6.9×10^{-7}	0.89	54	11	−92	−48

[a] Ionic conductivity, from AC impedance spectroscopy measurements. [b] Activation barrier for σ_{ION} from linear regression of the Arrhenius plot. [c] Activation barrier for σ_{ION} from VTF analysis. [d] Reduced temperature from VTF analysis of σ_{ION} Arrhenius plot. [e] Glass transition temperature, from differential scanning calorimetry. [f] [Co(bpy(CO$_2$MePEG-350)$_2$)$_3$](ClO$_4$)$_2$; data from ref 1a. [g] [Fe(bpy-(CO$_2$MePEG-350)$_2$)$_3$](ClO$_4$)$_2$; data from ref 1a.

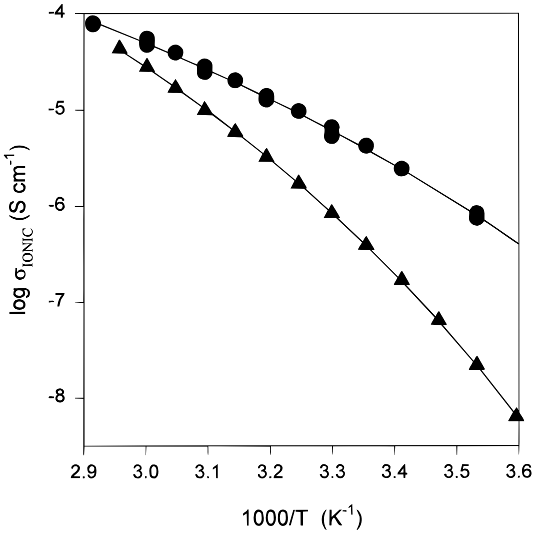

Figure 5. Activation plot of ionic conductivity, σ_{ION}, for neat [CuL$_2$](ClO$_4$)$_2$ (●) and for [CuL$_2$](ClO$_4$)$_2$ containing 1.4 M LiClO$_4$ (▲), with VTF fit (—).

[CoL$_3$](ClO$_4$)$_2$ and [FeL$_3$](ClO$_4$)$_2$ melts, within which the predominant ionic charge flow is thought[1a] to be carried by the ClO$_4^-$ ion.[1a] It is thus unsurprising that the ionic conductivity of the neat copper complex melt, having a larger ClO$_4^-$ concentration, is larger. However, when perchlorate is added in the form of LiClO$_4$, the ionic conductivity of the [CuL$_2$](ClO$_4$)$_2$ melt actually *decreases*. This contrary phenomenon is also seen with the other tailed metal complexes[1c,d] and is associated with the depression of the mobility of all constituents, including of perchlorate, due to Li$^+$−polyether coordination.

The temperature dependencies of ionic conductivities of the neat and LiClO$_4$ containing [CuL$_2$](ClO$_4$)$_2$ melts are shown in Figure 5. The curvature of the plots is typical for transport processes involving strong coupling with polyether chain segmental motions. The experimental points were fitted to the Vogel−Tammann−Fulcher (VTF) equation,[21]

$$\sigma_{\mathrm{ION}} = \frac{A'}{T^{1/2}}\exp\left[\frac{-E_{\mathrm{A,ION}}}{R(T - T_{\mathrm{o}})}\right] \qquad (6)$$

where T_{o} is the reduced temperature, related to the glassing temperature, and A' is a parameter related to the number of ionic charge carriers.

In order to (roughly) compare ionic thermal activation to that of the Cu(II/I) electron transfer reaction, linear fits of log(σ_{ION}) = $f(1/T)$ were made over the same temperature ranges as for measurement of D_{APP} values by chronoamperometry. The Arrhenius activation energies for ionic conductivity, 63 kJ mol^{-1} for the neat melt and 113 kJ mol^{-1} for the LiClO$_4$-containing melt, are much larger than those for electron transfer (50 and 55 kJ mol^{-1}, respectively) (Table 2, column 6). Similar differences have been seen for ionic conductivity versus homogeneous electron exchange barrier energy results for tailed Fe$^{\mathrm{III/II}}$L$_3$ and Co$^{\mathrm{II/I}}$L$_3$ metal complex melts.[1c,d] The difference in ionic conductivity and electron energy transfer barriers argues against the importance of the rate of ionic motions (as dipolar sources in the reorganization barrier energy, for example) in the electron transfer reactions.

The rough similarity of activation energy barriers $E_{\mathrm{A,ION}}$ for the ionic conductivities of the Cu, Co, and Fe complexes in Table 3 is in line with the perchlorate ion being the dominant charge carrier in all three melts. It is therefore not unreasonable to assume that its diffusion coefficient is similar in the three melts. If we use the previously estimated[1a] $D_{\mathrm{ClO_4^-}} = 1.7 \times 10^{-10}$cm^2 s^{-1}, D_{PHYS} of [CuL$_2$]$^{2+}$ in the neat [CuL$_2$](ClO$_4$)$_2$ melt can be calculated using the Nernst−Einstein equation:[22]

$$\sigma_{\mathrm{ION}} = \frac{F^2}{RT}\left(z^2_{\mathrm{CLO_4^-}} D_{\mathrm{ClO_4^-}} C_{\mathrm{CLO_4^-}} + z^2_{\mathrm{ML_2^{2+}}} D_{\mathrm{ML_2^{2+}}} C_{\mathrm{ML_2^{2+}}}\right) \qquad (7)$$

Here z, D, and C are ionic charge, diffusion coefficient, and concentration, respectively. The calculation yields $D_{\mathrm{PHYS}} = 4.7 \times 10^{-13}$ cm^2/s, which, being much smaller than the D_{APP} measured for the Cu(II/I) reaction, supports the assumption that D_{PHYS} can be taken as negligible in the above evaluation of the homogeneous electron exchange rate constants from eq 2.

Finally, ion pairing probably occurs in the melts, but its presence, qualitatively, would lead to an underestimation of $D_{\mathrm{ClO_4^-}}$ from ionic conductivity data[1a,b,d] and an overestimation of D_{PHYS} above. Ion-pairing effects could not therefore invalidate the $D_{\mathrm{APP}} \gg D_{\mathrm{PHYS}}$ assertion.

That the ionic conductivity of the LiClO$_4$-containing [CuL$_2$](ClO$_4$)$_2$ melt is less than that of the neat metal complex melt was noted above. Estimation of the contributions of Li$^+$ and ClO$_4^-$ to the conductivity of this melt is not possible because the diffusion coefficients ($D_{\mathrm{ClO_4^-}}$ and D_{Li}) cannot be determined independently. If, as a very conservative approximation, they are taken as equal, the Nernst−Einstein equation gives $D_{\mathrm{Li}} = D_{\mathrm{ClO_4^-}} = 2.4 \times 10^{-11}$ cm^2/s, which is 50-fold larger than the D_{PHYS} estimated in the neat [CuL$_2$](ClO$_4$)$_2$ melt. This rough comparison is consistent with the view that the mobility of the [CuL$_2$]$^{2+}$ ion contributes little if any to the ionic conductivity of the LiClO$_4$-containing melt. The very similar conductivities of [CuL$_2$](ClO$_4$)$_2$, [FeL$_3$](ClO$_4$)$_2$, and [CoL$_3$](ClO$_4$)$_2$ melts that contain LiClO$_4$ at a ratio of Li:ether oxygen = 1:16 (3.9×10^{-7} S cm^{-1} for the Cu, 2.4×10^{-7} S cm^{-1} for the Fe, and 3.9×10^{-7} S cm^{-1} for Co complex[1a,c,d]) are yet other observations that are consistent with the assumption that the metal complex cation contributes little to the ionic conductivity of all these melts, *i.e.*, that the metal complexes have very small transference numbers. This final point means that the measured D_{APP} values are not distorted by ionic migration effects.

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(22) In ref 11, p 66.