

of the barrier for axial/equatorial exchange in the exo_3 conformation to the barrier for $\text{exo}_2/\text{exo}_3$ interconversion may be noted, and a correlated process cannot be discounted.

Restricted M-P bond rotation is evident only in a broadening of the cis carbonyl resonance of **1** at -90°C . Thus, unlike PPh_3 ,^{2a,c} phosphorus-carbon bond rotation in $\text{P}(o\text{-tolyl})_3$ complexes appears to represent the process of highest energy. Preliminary results indicate that this is a general phenomenon and that since phosphine helicity is reversed via P-C rotation, variable-temperature NMR spectroscopy may be used to probe the diastereoisomeric relationship between phosphine helicity and other sources of molecular chirality.¹¹

Supplementary Material Available: For **1** and **2**, Table 1S, containing crystallographic data, atomic coordinates, thermal parameters, bond lengths, and bond angles, and ORTEP diagrams, and Figure 1S, containing full calculated and experimental NMR spectra relevant to Table I of the text (36 pages); tables of structure factors (19 pages). Ordering information is given on any current masthead page.

- (9) Crystal structure determinations of the few equatorial $\text{Fe}(\text{CO})_4\text{PR}_3$ complexes which exist show a considerable distortion toward square pyramidal: (a) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7751. (b) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085. (c) Sheldrick, W. S.; Morton, S.; Stelzer, O. Z. *Anorg. Allg. Chem.* **1981**, *475*, 232. (d) Forbes, E. J.; Jones, D. L.; Paxton, K.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1979**, 879. The structures of equatorial exo_2 and exo_3 $\text{Fe}(\text{CO})_4\text{P}(o\text{-tolyl})_3$ were modeled using $\text{CO}_{ax}\text{-Fe-CO}_{ax}$ and $\text{CO}_{eq}\text{-Fe-P}$ angles of 172 and 117° , respectively.
- (10) (a) Sheldrick, G. M. SHELX86, A Computer Program for Crystal Structure Determination. University of Göttingen, 1986. (b) Sheldrick, G. M. A Computer Program for Crystal Structure Determination. University of Cambridge, 1976.
- (11) For example, both (*o*- and (*m*- $\text{MeC}_6\text{H}_4\text{CO}_2\text{Me}$) $\text{Cr}(\text{CO})_2\text{P}(o\text{-tolyl})_3$ exist as 1:1 diastereoisomeric mixtures in solution¹² whereas (cyclohexadiene) $\text{Fe}(\text{CO})_2\text{P}(o\text{-tolyl})_3$ exists as a single diastereoisomer in which helix reversal and iron-diene rotation may be correlated.¹³
- (12) Howell, J. A. S.; Palin, M. G. Unpublished observations.
- (13) Howell, J. A. S.; Palin, M. G.; Tirvengadam, M. C.; Cunningham, D.; McArdle, P.; Goldschmidt, Z.; Gottlieb, H. E. *J. Organomet. Chem.* **1991**, *413*, 269.
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Crown Ether Encapsulation Effects upon Optical Electron-Transfer Energetics in a Symmetrical Mixed-Valence System

A key element in the energetics of many fluid-phase electron-transfer (ET) processes is the reorganization of solvent or other external environment.¹ Experimentally, the solvent energetic effects can be substantial—often comprising the majority of the observed barrier to activated electron transfer.^{2,3} Recently we

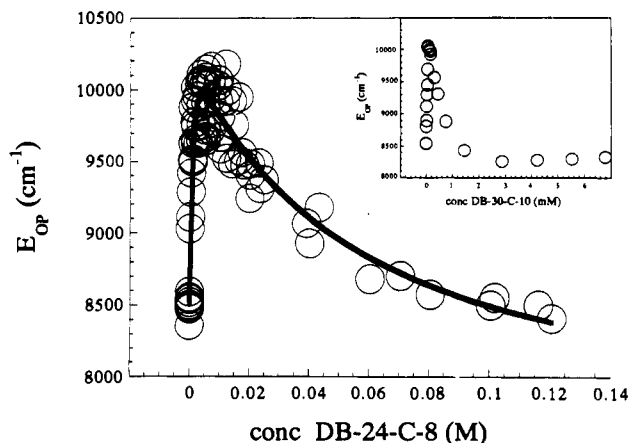
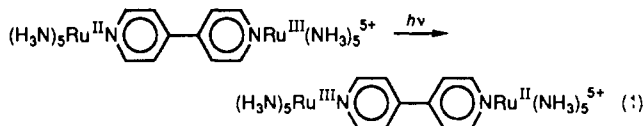


Figure 1. Optical intervalence absorption energy versus dibenzo-24-crown-8 concentration in nitromethane as solvent. Solid line represents the four-parameter fit described in the text. Measurement uncertainties ($\pm 100\text{ cm}^{-1}$) are indicated by the diameters of the circles. Reproducibility is indicated by the spread in the points. (Note that the nine points clustered around $8500 \pm 150\text{ cm}^{-1}$ were all measured at zero crown concentration.) The lowest nonzero DB-24-C-8 concentration was $3.6 \times 10^{-4}\text{ M}$ (see refs 8 and 14). Inset: data for dibenzo-30-crown-10.

have begun to examine *molecular* aspects of solvent reorganization and have found that the largest fraction of the reorganization process (in an energetic sense) occurs within the first layer of solvent.⁴ Given these findings, we reasoned that ET barriers, and ultimately kinetics, might be profoundly affected by systematic replacement of local solvent by micellar, polymer, protein, or other "encapsulating" environments. We wish to report here the results of a preliminary exploration of that concept; macrocyclic ethers (dibenzo crown species)^{5,6} have been employed for encapsulation of an ammine-based mixed-valence complex, and ET energetics have been monitored via intervalence absorption measurements.^{2,4,7}



The key findings are first, that only small amounts of crown are required in order to achieve binding or encapsulation; second, that partial encapsulation has significant and unusual energetic consequences; but third, that complete encapsulation leads to only modest changes in total reorganization energy, at least in nitromethane as the reference solvent.

As suggested above, the overall optical barrier to intramolecular charge transfer can be evaluated by simple intervalence absorption energy measurements (eq 1). This energy (E_{op}) is known to be comprised of solvent reorganization (χ_s), vibrational reorganization (χ_i), redox asymmetry (ΔE) and electronic excited state ($\Delta E'$) terms:^{2,4}

$$E_{\text{op}} = \chi_s + \chi_i + \Delta E + \Delta E' \quad (2)$$

Our initial intent with crown encapsulation was chiefly to influence χ_s . As shown below, however, the largest energetic effect is a redox asymmetry effect.

Figure 1 shows a plot of the change in intervalence absorption energy (or optical barrier height) versus concentration of dibenzo-24-crown-8 ($n = 0$; see below) in nitromethane as solvent.⁸

- (4) Blackburn, R. L.; Hupp, J. T. *J. Phys. Chem.* **1988**, *92*, 2817.
 (5) Pederson, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.
 (6) (a) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 487. (b) Colquhoun, H. M.; Lewis, D. F.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1983**, 607.
 (c) Colquhoun, H. M.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 612. (d) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J.; Wolstenholm, J. B.; Zarzycki, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1051.
 (7) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

- (1) Marcus, R. A. *J. Chem. Phys.* **1965**, *45*, 679.
 (2) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 7828.
 (3) See, for example: Brown, G. M.; Sutin, N. S. *J. Am. Chem. Soc.* **1979**, *101*, 883.

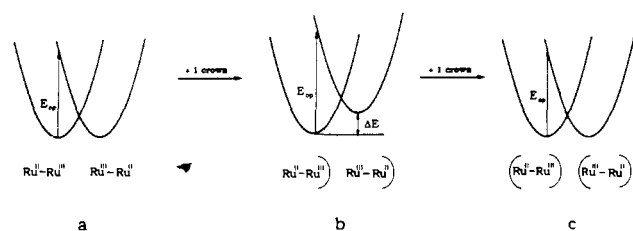
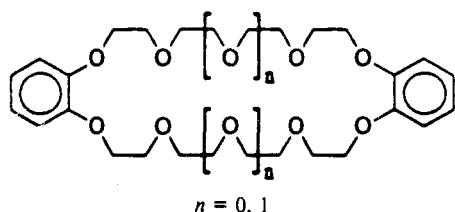


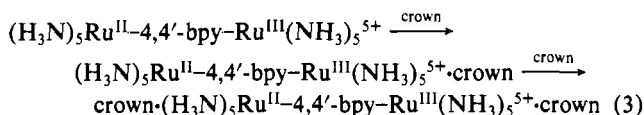
Figure 2. Schematic representation of intervalence absorption energies and potential energy surfaces for (a) $(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}-4,4'\text{-bpy}-\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$, (b) $(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}-4,4'\text{-bpy}-\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}\cdot\text{crown}$, and (c) $\text{crown}\cdot(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}-4,4'\text{-bpy}-\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}\cdot\text{crown}$.

The most striking features of the plot are the initial sharp rise in E_{op} with added crown and the more gradual decrease with further additions, the peak occurring at 3.8 mM in crown concentration. Related studies of metal-to-ligand (bridge) charge transfer (MLCT) within the same system showed a simpler behavior: a monotonic decrease in absorption energy with increasing crown concentration and an asymptotic approach to a constant energy at high crown concentrations (ca. 0.1 M; see supplementary material).



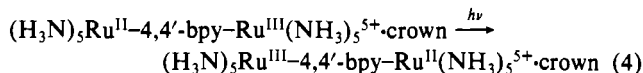
These observations, while clearly unusual, are not unprecedented.^{4,9} They resemble quite closely, in fact, the behavior seen for the same chromophore in mixtures of acetonitrile and dimethyl sulfoxide (DMSO) as solvent.^{4,9} The optical energetic effects there were found to arise from an *unsymmetrical* selective solvation effect—in other words, selective solvation (by DMSO) first at $(\text{NH}_3)_5\text{Ru}^{\text{III}}$ and then at $(\text{NH}_3)_5\text{Ru}^{\text{II}}$. The peak in a plot of intervalence energy versus bulk solvent composition was shown to occur at the point where the two redox sites differed most in terms of primary solvation layer composition.^{4,9,10}

We suggest that a related effect exists here:



Buildup of the partially encapsulated (asymmetric) species (first equilibrium step) would lead to an increase in E_{op} . Further encapsulation (second equilibrium) would lead to a symmetrically bound species and a decrease in E_{op} .¹¹

A more physical interpretation is suggested both by Figure 2 and eq 4. Partial crown encapsulation renders the Ru(II) and Ru(III) sites structurally inequivalent and the thermalized initial



and final states (left- and right-hand sides of eq 4) energetically different. The magnitude of the energy difference should reflect directly the difference in crown binding constant for Ru(II) vs Ru(III) and should be observable as an intervalence effect. In the context of eq 2,¹² this effect would necessarily appear as a positive contribution to E_{op} via the asymmetry term, ΔE .^{9,10} Additional contributions to E_{op} (positive or negative) could arise from crown-induced changes in χ_s or conceivably even χ_i . In principle, these could be evaluated by measuring E_{op} for the doubly encapsulated species. (Note that for this species, as well as the initial chromophore (no crown), asymmetry is absent and ΔE should vanish.)

If stepwise crown encapsulation occurs, as outlined in eq 3, then E_{op} is given by¹²⁻¹⁴

$$E_{\text{op}} = E_i + \frac{\Delta E_{\text{III}}K_{\text{III}}C}{1 + K_{\text{III}}C} + \frac{\Delta E_{\text{II}}K_{\text{II}}C}{1 + K_{\text{II}}C} \quad (5)$$

where E_i is the value of E_{op} without added crown, ΔE_{III} is the difference in intervalence energy for the partially encapsulated complex versus the initial species, ΔE_{II} is the energy difference between fully and partially encapsulated species, C is the crown concentration, and K_{III} and K_{II} are the (stepwise) binding constants for the crown with $(\text{H}_3\text{N})_5\text{Ru}^{\text{III}}$ and $(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}$, respectively. A nonlinear least-squares fit¹⁵ of the experimental data to eq 5 yields the solid line in Figure 1; the fit parameters are $\Delta E_{\text{III}} = 1930 (\pm 150) \text{ cm}^{-1}$, $\Delta E_{\text{II}} = -2790 (\pm 200) \text{ cm}^{-1}$, $K_{\text{III}} = 1620 (\pm 410) \text{ M}^{-1}$, and $K_{\text{II}} = 23 (\pm 7) \text{ M}^{-1}$.

A further sense of both the chemical and numerical reliability of the proposed interpretation can be gained from the following additional experiments and analyses. (1) Plots of $1/(E_{\text{op}} - E_i)$ vs $1/C$ were constructed (see eq 5) in the low crown concentration range (primarily binding to Ru(III)). An approximate straight-line fit was obtained, confirming the proposed 1:1 crown:metal binding stoichiometry. (Stoichiometries greater than one would generally be expected to yield either highly curved plots or multiphase plots.)¹⁶ (2) An independent determination of K_{II} from the dependence of E^{MLCT} on crown concentration¹⁵

- (8) Dibenzo-24-crown-8 (2,3,14,15-dibenzo-1,4,7,10,13,16,19,22-octaoxocyclotetradeca-2,14-diene) and dibenzo-30-crown-10 (2,3,17,18-dibenzo-1,4,7,10,13,16,19,22,25,28-decaoxocyclotriaconta-2,17-diene) were purchased from Aldrich and used as received. (One sample of dibenzo-24-crown-8, however, was recrystallized from ethanol; no differences in binding behavior were noted.) HPLC grade nitromethane was purchased from Aldrich and passed through activated alumina just prior to use. (Failure to prepurify the solvent led to shifts of E_{op} (initial) to ca. 9000 cm^{-1} and to hydroxyl overtone (water) interferences in the near-infrared spectrum.) $[(\text{H}_3\text{N})_5\text{Ru}-4,4'\text{-bpy}-\text{Ru}(\text{NH}_3)_5](\text{PF}_6)_4$ was prepared and purified by a literature method.⁴ The mixed-valence form was initially prepared in situ by using bromine vapor as an oxidant. This method led, however, to water contamination (as indicated again by hydroxyl stretching overtones). We subsequently found that dry samples could be reproducibly prepared by (1) dissolving the reduced (4+) dimer in acetone and oxidizing to the 6+ form with excess Br_2 vapor, (2) removing the acetone and unreacted Br_2 by rotary evaporation, (3) redissolving the 6+ ion in acetone and adding an equimolar amount of the 4+ form, and (4) removing the acetone again and redissolving the 5+ ion in prepurified nitromethane. Changes in E_{op} upon crown addition were monitored on an OLIS-modified CARY 14 spectrophotometer. In order to ensure (a) that DB-24-crown-8 concentrations were always at least 5-fold greater than the dimer concentration (and usually much more) and (b) that artifacts due to ion pairing were absent (cf. refs 10 and 15), dilute dimer solutions were employed. This necessitated the use of 4-cm path-length cells to achieve suitable extinction.
- (9) Hupp, J. T.; Weydert, J. *Inorg. Chem.* **1987**, *26*, 2657.
- (10) See also: Ennix, K. S.; McMahon, P. T.; de la Rosa, R.; Curtis, J. C. *Inorg. Chem.* **1987**, *26*, 2660.

- (11) Binding in both instances is presumably driven chiefly by ammine hydrogen/ether oxygen interactions (although we have not been able to rule out a stability contribution from favorable bipyridine/benzene π interactions: Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *25*, 487). Note that the profound oxidation-state sensitivity of the binding equilibrium is fully consistent with the anticipated effect of central metal ion charge upon the electron-accepting (Lewis acidity) or H-bond donating ability of the coordinated ammonias.
- (12) In the context of eq 6 the asymmetric crown effect could conceivably appear instead as a new component of the reorganization energy (see ref 10). The results in ref 23, however, suggest otherwise.
- (13) Strictly speaking, eq 5 should also contain a term for the formation of $\text{crown}\cdot(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}-4,4'\text{-bpy}-\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$. If we assume that the extent of formation of this species can be adequately determined from a knowledge of K_{II} and the total amount of unbound dimer at any particular crown concentration, we find (at all concentrations) the fraction of $\text{crown}\cdot(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}-4,4'\text{-bpy}-\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$ to be negligible.
- (14) The assumptions made in deriving eq 5 were (1) that only three species absorb, (2) that they are interrelated by eq 4, (3) that the absorption lineshapes and extinction coefficients are similar for the three chromophores, (4) that ΔE_{III} and ΔE_{II} are relatively small compared with the width of any individual absorption, and (5) that binding does not appreciably diminish the concentration of free crown.
- (15) Parameters and associated standard errors for eq 5 were determined by a non-linear least-squares (χ^2 minimization) program (Kaleida Graph, Synergy Software).
- (16) See, for example: Blackburn, R. L.; Hupp, J. T. *Chem. Phys. Lett.* **1988**, *150*, 399.

(supplemental Figure S1) yielded $K_{II} = 20 (\pm 1) M^{-1}$, in very good agreement with the four-parameter fit above. (3) An electrochemical experiment with the model complex, $Ru(NH_3)_5(py)^{3+/2+}$ (essentially half of the mixed-valence system), yielded a negative shift in formal potential (E_f) with crown addition and a maximum shift of -44 to -67 mV (replicate experiments) in a saturated crown solution (ca. 0.15 M). Insertion of these data into the Lingane equation

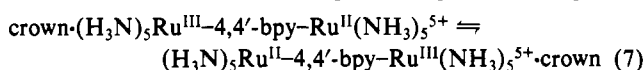
$$E_f = E^0 - (RT/F) \ln(1 + K_{II}C) \quad (6)$$

yields a K_{II} estimate of $30\text{--}80 M^{-1}$, in fair agreement with the spectroscopic measurements. Taken together, these three observations strongly support the proposed model of crown encapsulation and energetic interaction.

With the preceding analysis in hand, we turn our attention to the original inquiry: the effect of crown encapsulation upon χ_s . From the four-parameter fit we derive an E_{op} value of $7640 \pm 250 \text{ cm}^{-1}$ for the doubly encapsulated complex. This differs significantly from the initial value of E_{op} ($8500 \pm 150 \text{ cm}^{-1}$), suggesting that χ_s is at least moderately decreased by crown binding. Some caution is called for, however. Note that the smallest measured value of E_{op} is 8400 cm^{-1} (see Figure 1). Clearly, extraction of the limiting "final" value from the four-parameter fit entails a lengthy extrapolation. We suggest, therefore, that $E_{op}(\text{final})$ may possibly be less reliable than implied by the fitting statistics.

A more definitive measure of $E_{op}(\text{final})$ (albeit for a slightly different system) can be obtained from the inset in Figure 1. Shown there are data for dibenzo-30-crown-10 ($n = 1$; see above), a species which binds much more strongly than dibenzo-24-crown-8. For DB-30-crown-10, $E_{op}(\text{final})$ (double encapsulation) is directly measured as 8250 cm^{-1} , i.e. only slightly less than the initial (crown free) value. In retrospect, this latter result is perhaps not too surprising. The crown species might, for example, provide only partial shielding from solvent.¹⁷ Perhaps more importantly, the crown itself may serve as a polar medium (or pseudosolvent) requiring reorganization. For moderate to high polarity solvents, χ_s is known to vary approximately with n^{-2} , where n is the refractive index.^{2,18} For nitromethane, n^{-2} is 0.524.¹⁹ For molten²⁰ dibenzo-24-crown-8 at 119°C (melting point = 103°C ; data were not obtained for DB-30-crown-10), we find $n^{-2} = 0.432$. Admittedly, one must exercise some caution on account of both temperature²¹ and possible "molecularity"²² effects; however, the refractive index measurements do suggest that significant reorganizational demands may exist for the crown as "solvent".

Returning to the crown asymmetry effects, there are some significant implications for charge-transfer kinetics. The observation that the optical barrier height is increased upon addition of small amounts of crown implies a corresponding increase in the thermal electron-transfer barrier height (see Figure 2). This, in turn, implies the existence of rate attenuation effects for the overall thermal electron-transfer process (eq 7). The magnitude



of the expected rate effect is difficult to predict, as it surely must

depend on the detailed reaction pathway chosen. (For example, does crown migration occur synchronously with electron transfer or does it precede or follow? What role is played by binding dynamics? Etc.)²³ Nevertheless, given the size of the optical effects, a factor of 5 or 10 in rate attenuation would not be an unreasonable prediction. Presumably the issue could be investigated experimentally by resorting to bimolecular, pseudo-self-exchange rate measurements³ (e.g. $(H_3N)_5Ru(py)^{2+}/(H_3N)_5Ru(\text{methylpyridine})^{3+}$, etc.).

The focus of continuing work, however, is not self-exchange measurements. Instead we are attempting to understand in greater detail the nature of the binding effect—especially the roles played by crown size and by various solvent properties. Preliminary studies indicate stronger binding for larger crowns (see Figure 1) but weaker binding in solvents of higher basicity. Other work emphasizes encapsulation in more rigid supramolecular environments.

To summarize, encapsulation of donor and acceptor charge-transfer sites in a mixed-valence complex can be achieved with dibenzo-24-crown-8 at modest crown concentrations. Incomplete encapsulation (acceptor site only) leads to significant optical intervalence energy effects which may be significant also for thermal ET kinetics. Complete encapsulation leads to only modest changes in E_{op} or reorganization energy.

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Registry No. $[(H_3N)_5Ru\text{-}4,4'\text{-bpy-Ru}(NH_3)_5]^{5+}$, 54065-65-5; dibenzo-24-crown-8, 14174-09-5.

Supplementary Material Available: A figure (Figure S1) showing the dependence of MLCT energy on crown concentration (1 page). Ordering information is given on any current masthead page.

(23) Some sense of the relative time scales involved is available, in principle, from dynamic electrochemical experiments. For example, in cyclic voltammetric studies with DB-36-crown-12 we observe *distinct* waves for oxidation of $Ru(NH_3)_5(\text{pyridine})^{2+}$ (504 mV vs SSCE) and $Ru(NH_3)_5(\text{py})\text{-crown}^{2+}$ (178 mV vs SSCE), indicating that crown exchange between metal complexes is occurring on a time scale longer than 1 s. (The dimer itself has not yet been examined.)

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Tetrabutylammonium

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as a Noncoordinating Electrolyte: Reversible $1e^-$ Oxidations of Ruthenocene, Osmocene, and $Rh_2(TM4)_4^{2+}$ (TM4 = 2,5-Diisocyano-2,5-dimethylhexane)

The interpretation of electrochemical data is often complicated by interactions between electrochemically generated species and the surrounding ionic medium.¹ For example, our group recently

(17) For a related report, see: Tabib, J.; Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1986**, *25*, 1918.

(18) Hupp, J. T.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 2332.

(19) *CRC Handbook of Chemistry and Physics*, 64th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1983; p C-373.

(20) Because relative refractive index values for any given substance as a function of temperature, pressure, phase or state of matter, etc. largely reflect relative densities, we reasoned that a molten (liquid) crown sample would provide a better model for the crown in liquid solution (nitromethane) than would a (presumably) higher volume, crystalline (room-temperature) sample.

(21) Refractive index measurements at three liquid temperatures (135, 129, and 119°C), followed by a lengthy extrapolation, led to $n^{-2} = 0.416$ at 25°C .

(22) Our previous work⁴ with mixed solvents suggests that "molecularity" effects may not be significant. In the earlier work we found, somewhat surprisingly, that a single molecular layer of DMSO solvent in contact with the mixed-valence ion behaved very similarly to bulk DMSO.

(1) (a) Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker, Inc.: New York, 1984; p 483. (b) Fry, A. J.; Britton, W. E. In ref 1a, p 367. (c) Lever, A. P. B. *Inorg. Chem.* **1990**, *29*, 1271. (d) O'Toole, T. R.; Younathan, J. N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 3923. (e) Pickett, C. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 1. (f) Boyd, D. C.; Rodman, G. S.; Mann, K. R. *J. Am. Chem. Soc.* **1986**, *108*, 1779.