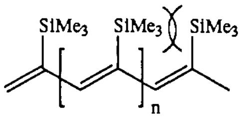
The visible absorption of undoped poly(TMSCOT) solutions shifts to lower energies irreversibly upon exposure to light. This is attributed to a cis–trans isomerization of the polymer.[14] The course of a photolysis experiment[15] was monitored by UV–vis (Figure 1) and ^1H NMR spectroscopy.[16] Differential scanning calorimetry thermograms[12] of the polymer before and after photolysis are shown in Figure 2.[17] An exotherm present at 145 °C in the nascent polymer is not observed after photolysis. Since polyacetylene thermally isomerizes from cis to trans at 150 °C,[18] these data are consistent with the hypothesis that poly(TMSCOT) is undergoing a cis–trans isomerization upon photolysis in solution. The initially formed polymer is expected to have a high cis content since three of the four cis double bonds of the monomer are unlikely to be affected by the metathesis polymerization. Highly reflective soluble polymer films can be cast from a photolyzed purple solution.[19]

Upon doping with iodine, the conductivities of the cis films are less than $10^{-5}\ \Omega^{-1}\ cm^{-1}$, while the conductivities of the trans films are typically $0.2\ \Omega^{-1}\ cm^{-1}$.[18,20,21] By comparing the absorbance maximum of undoped *trans*-poly(TMSCOT) (512 nm) to the maxima of polyenes prepared by Schrock and co-workers,[22] the effective conjugation length of *trans*-poly(TMSCOT) is thought to be greater than that of a polyene containing 15 unsubstituted double bonds. The lowest energy absorption maximum observed for the cis polymer is at 380 nm, implying an average effective conjugation length of less than nine double bonds. *trans*-Poly(TMSCOT) can also be compared to a polymer made from a substituted acetylene, for example, poly(trimethylsilylacetylene),[5] depicted below, which shows a conductivity of $10^{-4}\ \Omega^{-1}\ cm^{-1}$ when saturated with iodine. Presumably, the placement of substituents at every other carbon induces sufficient twisting of the poly(trimethylsilylacetylene) backbone to significantly decrease the effective conjugation length of the polymer π-system.[23] The poly(RCOT) methodology allows placement of the substituents at every eighth carbon atom, on the average, and consequently results in polymers of higher conjugation length. In the present case, where R = Me_3Si, this substitution pattern is sufficient to render the polyene soluble.



poly(trimethylsilylacetylene)

Because of its solubility and conductivity, poly(TMSCOT) is a candidate for study in a variety of investigations. For example, we are examining spin-coated films for third-order nonlinear optical properties.[24] The polymer is amorphous, so losses due to light scattering are less than one observed for crystalline materials. Additionally, we have found that thin transparent films of I_2-doped poly(TMSCOT) can be used in Schottky barrier type solar cells.[25]

In summary, ROMP of trimethylsilylcyclooctatetraene, followed by photolysis in solution, provides a soluble, *trans*-polyacetylene derivative in which the substituents are placed a sufficient distance apart to allow conjugation along the backbone. Work is underway using the RCOT/ROMP methodology to develop other polyacetylene derivatives which are soluble, more conductive, and air-stable.

Acknowledgment. We acknowledge financial support from the Office of Naval Research. S.R.M. thanks the National Research Council and the National Aeronautics and Space Administration for a National Research Council Resident Research Associateship at the Jet Propulsion Laboratory.

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(13) M_n = 137 000 versus polystyrene by gel permeation chromatography.

(14) For a discussion of cis–trans photoisomerization, see: Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 12.

(15) Light from a Pyrex-filtered, 450-W high pressure mercury Hanovia lamp was used for photolyses.

(16) NMR data for the *cis*-poly(TMSCOT) were obtained from a sample containing both isomers of the polymer. *cis*-Poly(TMSCOT): ^1H NMR (THF-d_8, 400 MHz) δ 0.15 (s), 5.8–7.1 (br m). *trans*-Poly(TMSCOT): ^1H NMR (THF-d_8) δ 0.23 (s, 9 H), 6.5 (br s, 5 H), 7.0 (br m, 2 H); $^{13}C\{^1H\}$ NMR (methylene chloride-d^2) δ −0.25 (s), 128–145 (m). Elemental analysis, calculated for $(C_{11}H_{16}Si)_n$: C, 74.93; H, 9.14. Found: C, 74.2; H, 8.9.

(17) The exotherm observed at higher temperatures may be due to a cross-linking reaction, since samples which have been heated above 200 °C are totally insoluble.

(18) Chien, J. C. W. *Polyacetylene: Chemistry, Physics, and Material Science*; Academic: Orlando, FL, 1984.

(19) The polymer is treated as an air-sensitive material. After exposure of a 20–30-μm thick film to air for 2 h, approximately 20% of the material is no longer soluble in tetrahydrofuran.

(20) Conductivities were measured with a four-point probe in a nitrogen drybox or a four-wire probe attached to a Schlenk line. The films were exposed to iodine for several hours and then exposed to vacuum for at least 1 h to remove excess iodine.

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(23) Petit, M. A.; Soum, A. H.; Leclerc, M.; Prud'homme, R. E. *J. Polym. Sci.: Part B: Polym. Phys.* **1987**, *25*, 423.

(24) For discussions of third-order nonlinear optical properties in organic materials, see: *Nonlinear Optical Properties of Organic Molecules and Crystals, Vol. 2*; Chemla, D. S., Zyss, J., Eds.; Academic: Orlando, FL, 1987.

(25) Sailor, M. J.; Lewis, N. S.; Ginsburg, E. J.; Gorman, C. B.; Marder, S. R.; Grubbs, R. H., manuscript in preparation.

[(Benzosemiquinone-18-crown-6)$^{\bullet-}$Li$^+$Na$^+$]$^{\bullet+}$: A Paramagnetic Triple Ion with Two Different Counter Cations[1]

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Received May 1, 1989

The ability of host molecules M to discriminate among various guest cations Me^+ is widely known.[2] Like this shape-selective encapsulation [MMe^+], site-specific complexation at electron-rich centers may also successfully compete with cation solvation, especially, if additional Coulombic attraction by the negative charge, e.g., of a molecular radical anion $M^{\bullet-}$, helps to stabilize the resulting contact ion pair radical $[M^{\bullet-}Me^+]^\bullet$.[3-5] Moreover, if $M^{\bullet-}$ contains several appropriate docking sites and can be generated by single electron transfer in aprotic solution with surplus Me^+X^- content, contact triple ion radical cations, $[Me^+M^{\bullet-}Me^+]^{\bullet+}$, with two identical counter cations readily form.[6-8] They are best

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(1) Electron Transfer and Ion Pairing. 12. Part 11, see: Bock, H.; Herrmann, H. F. *Helv. Chim. Acta* **1989**, *72*, in print.

(2) Cram, D. J. *Science (Washington, D.C.)* **1988**, *240*, 760. Lehn, J. M. *Angew. Chem.* **1988**, *100*, 91; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. Pedersen, C. J. *Pure Appl. Chem.* **1988**, *60*, 450.

(3) Cf. e.g.: Lubitz, W.; Plato, M.; Möbius, K.; Biehl, R. *J. Phys. Chem.* **1979**, *83*, 3402 and the literature survey given.

(4) Bock, H.; Hierholzer, B.; Vögtle, F.; Hollmann, G. *Angew. Chem.* **1984**, *96*, 74; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 57 and literature cited.

(5) Bock, H.; Hierholzer, B.; Schmalz, P. *Angew. Chem.* **1987**, *99*, 811; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 791 and literature cited.

(6) Since their first ESR detection by Gough and Hindle (Gough, T. E.; Hindle, P. R. *Can. J. Chem.* **1968**, *47*, 1698) many triple ion radical cations have been characterized by ESR/ENDOR techniques, cf., e.g.:[7,8] or Hierholzer, B. Ph.D. Thesis University of Frankfurt, 1988.

(7) Bock, H.; Solouki, B.; Rosmus, P.; Dammel, R.; Hänel, P.; Hierholzer, B.; Lechner-Knoblauch, U.; Wolf, H. P. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Horwood Lim.: Chichester, 1985; pp 59–65. See, also: Bock, H. *Polyhedron* **1988**, *7*, 2429 or Hänel, P. Ph.D. Thesis, University of Frankfurt, 1987.

(8) Cf., e.g.: Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution*; VCH Publishers: New York, 1988; and literature cited.

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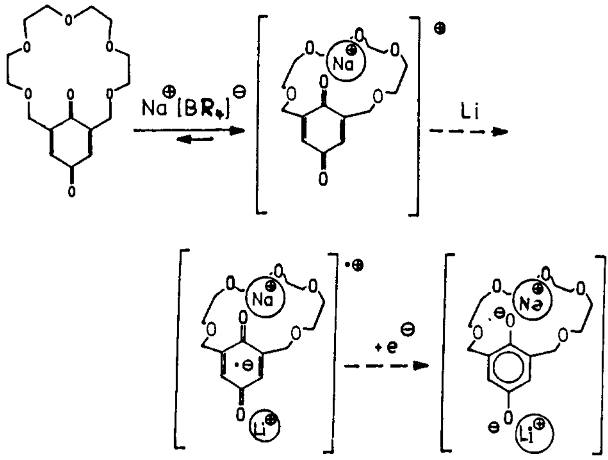
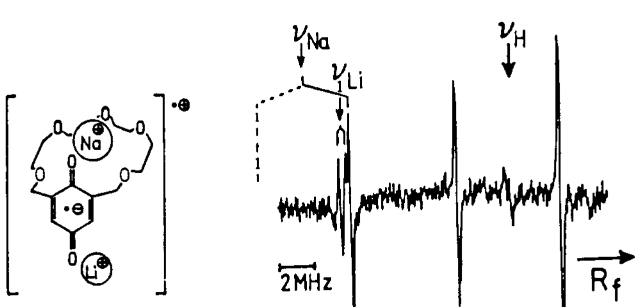
identified and characterized by ENDOR spectroscopic determination of their metal hyperfine couplings, although identical counter cations can only be distinguished if they dock at nonequivalent centers of low-symmetry radical anions.[7] Here we report on shape-selective Na^+ complexation and additional Li^+ contact ion pair formation with the radical anion of benzosemiquinone-18-crown-6,[9-11] for which a combined cyclovoltammetric and ENDOR spectroscopic study[9] provides conclusive evidence.



(1)

The reversible first half-wave reduction potentials, $E_{1/2}^{\text{Red}\,1}$, are negative[9] and shifted in the positive direction with increasing counter cation concentration c_{Me^+}. The resulting linear regressions, exp $(\Delta E_{1/2}^{\text{Red}\,1}F/RT)$ vs c_{Me^+},[9] yield "averaged" association contants[12] for radical ion pair formation, $M_{\text{solv}} + Me_{\text{solv}}^+ \rightarrow [M^{\bullet-}Me^+]_{\text{solv}}^{\bullet}$, which are about 50 times higher[9] than the stability constants[10] of the neutral crown ether, $M_{\text{solv}} + Me_{\text{solv}}^+ \rightarrow [MMe^+]_{\text{solv}}$, and increase in the sequence $Li^+ < Na^+ < K^+$ (cf.[11]) of the cation radii r_{Me^+}. This demonstrates both the enhancement of complex formation by additional Coulombic attraction, $[MMe^+] < [M^{\bullet-}Me^+]^{\bullet}$, as well as the dominating shape-selective encapsulation of the respective counter cations by the 18-crown-6,[10] part of which is the *p*-benzosemiquinone radical anion with high electron density at the $>C{=}O^{\delta-}$ oxygen centers.

The question of whether *p*-benzoquinone-18-crown-6 on single electron transfer in aprotic solutions with surplus Me^+X^- salt content forms radical ion pairs $[M^{\bullet-}Me^+]^{\bullet}$ or triple ion radical cations $[Me^+M^{\bullet-}Me^+]^{\bullet+}$ can be answered by its reduction in $Na[B(C_6H_5)_4]$/THF solution using a lithium metal mirror.[9] As is convincingly demonstrated by the ENDOR spectrum recorded for the title triple ion, two metal couplings are observed: a relatively large $a_{\text{Na}} = 0.158$ mT and a rather small $a_{\text{Li}} = 0.012$ mT, each centered around the respective metal Larmor frequency.



In addition, ESR, ENDOR, and GENERAL TRIPLE spectra have been recorded for the *p*-benzosemiquinone-18-crown-6 radical anion $M^{\bullet-}$ with $[K^+(2.2.2\ \text{cryptand})]$ as shielded and largely interaction-free counter cation,[9] for the radical ion pair $[M^{\bullet-}Na^+]^{\bullet}$, generated by stoichiometric reduction at a sodium metal mirror,[9] and for the disodium triple ion radical cation $[Na^+M^{\bullet-}Na^+]^{\bullet+}$, generated analogously in a $Na[B(C_6H_5)_4]$/THF solution.[9]

The ESR/ENDOR data[9] provide the following clues for the structure of the paramagnetic species in aprotic THF solution and their spin distribution: For the "naked" radical anion $M^{\bullet-}$ $[K^+(2.2.2)]$, the degenerate methylene proton couplings suggest an "averaged" leveling of the fluxional 18-crown-6 skeleton with the *p*-benzoquinone subunit approximately "in plane". However, their large split[9] in all radical contact ions indicates (eq 1) canting of the quinone moiety. Fitting of the two different coupling constants of the sodium radical ion pair $[M^{\bullet-}Na^+]^{\bullet}$, $a_H^{CH_2} = +0.087$ and 0.010 mT,[9] into the Heller/McConnell equation, $a_H = (B_0 + B_2 \cos^2 \theta)\rho_\pi$, for the angular dependence of hyperconjugative spin ρ_π transfer yields a dihedral angle $\theta \sim 50°$ between the quinone molecular plane and the $C{-}O_{\text{crown}}$ bond (eq 1). Concomitantly, a positive sign for the sodium coupling is determined by GENERAL TRIPLE measurements,[9] which suggests direct spin transfer[8] to the Na^+ counter cation, i.e., its location in the π cloud of the quinone C=O bond as proven by a structure determination.[13] The coupling of the two equivalent semiquinone protons[9] rises from $M^{\bullet-}$ to $[M^{\bullet-}Na^+]^{\bullet}$ due to the considerable structural change which diminishes hyperconjugation and is lowered again with increasing effective charge $1/r_{\text{Me}^+}$ of the additional ion pairing counter cation (eq 1:Li^+). In the triple ions, the coupling of the crown-complexed Na^+ remains of comparable magnitude, whereas that of the more loosely ion-paired Li^+ is rather small. Altogether, the ESR/ENDOR data[9] support the structure sketched out for the title triple ion radical cation (eq 1).

The second one-electron reduction step from the triple radical cation $[Me^+M^{\bullet-}Me^+]^{\bullet+}$ to the hydroquinone dianion salt $[Me^+M^{2-}Me^+]$, expectedly,[4,5,7,11,12] strongly depends on the effective ionic charge $1/r_{\text{Me}^+}$ of the respective counter cations: relative to the second half-wave reduction potential of −1.27 V

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[9] Part of the Herrmann, H. F. Ph.D. Thesis University of Frankfurt, 1989. The neutral *p*-benzoquinone-18-crown-6 (3,6,9,12,15-pentaoxabicyclo[15.3.1]heneicosa-17,20-dien-19,21-dione) has been synthesized starting from 2,6-bis(hydroxymethyl)-1,4-dimethoxyphenol, adding the crown by condensation with tetraethyleneglycolditosylate using NaH as base and accomplishing the final oxidative demethylation using $(NH_4)_2Ce(NO_3)_6$ in H_3CCN/H_2O (see[10,11]). CV measurements were performed in aprotic ($c_{H^+} < 1$ ppm) DMF (GCE vs SCE, v = 100 mV/s) and yield for *p*-benzoquinone-18-crown-6 with 0.1 N $R_4N^+PF_6^-$ as conducting salt $E_{1/2}^{\text{Red}\,1} = -0.440$ V (ΔE = 70 mV). The concentration-dependent half-wave potentials have been determined by adding to 5 mL of DMF/0.1 N R_4NPF_6 solutions containing 2×10^{-4} M *p*-benzoquinone-18-crown-6 dropwise (0.01 mL) and 10^{-2} M solutions of $Li[B(C_6H_5)_4]$, $Na[B(C_6H_5)_4$, or $KClO_4$ and yield the complex formation constants $K(K^+) = 2.0 \times 10^4$, $K(Na^+) = 2.8 \times 10^3$, $K(Li^+) = 1.4 \times 10^2$ [L/mol]. ESR, ENDOR, and GENERAL TRIPLE spectra are recorded in aprotic ($c_{H^+} < 1$ ppm) THF solutions (with all manipulations carried out either under 10^{-4} mbar vacuum or dry Ar) with a Bruker 220 D spectrometer. For the various paramagnetic species, the following hydrogen coupling constants $(a_H^{\text{quinone}}/a_H^{CH_2})$ are measured: $[M^{\bullet-}]^{\bullet-}[K^+(2.2.2)]^+$: −0.256/+0.097, +0.097; $[M^{\bullet-}Na^+]^{\bullet}$: −0.311/+0.087, 0.010; $[Na^+M^{\bullet-}Na^+]^{\bullet+}[BR_4]^-$: 0.248/0.156, < 0.01 and $[Na^+M^{\bullet-}Li^+]^{\bullet+}[BR_4]^-$: 0.197/0.197, 0.008.

[10] Sugihara, K.; Kamiya, H.; Yamaguchi, M.; Misumi, S. *Tetrahedron Lett*. **1981**, *22*, 1619. The stability constants measured for both 18-crown-6 (log *K*: K^+ 6.19 and Na^+ 4.33) and *p*-benzoquinone-18-crown-6 (log *K*: K^+ 2.67 and Na^+ 1.80) clearly show the preferred K^+ complexation by the macrocyclic ring.

[11] Wolf, and Cooper (Wolf, R. E. Jr.; Cooper, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 4646) have studied cyclovoltammetrically the complexation of counter cations by the radical anion of the dimethyl derivative and assigned the ESR spectrum of the paramagnetic species, generated electrochemically in $NaClO_4$/DMF solution, to a "canted" crown ether ion pair radical $[M^{\bullet-}Na^+]^{\bullet}$. Insufficient ESR solution (cf. Table (I)) did not permit detection of the smaller of the two Na^+ couplings of the triple ion $[Na^+M^{\bullet-}Na^+]^{\bullet+}$ formed. Furthermore, extrapolation of the regressions exp $(\Delta E_{1/2}^{\text{Red}\,1}F/RT)/c_{\text{Me}^+}$ to 0.1 m Me^+ solutions of the unmethylated parent compound yield more reasonably spaced shifts of 190 mV (K^+) > 140 mV (Na^+) > 70 mV (Li^+),[9] avoiding the limiting dissociation of higher concentrated $KClO_4$ solutions in DMF (cf.: Ames, D. P.; Sears, P. G. *J. Phys. Chem.* **1955**, *59*, 16).

[12] Extensive electrochemical investigations by Gokel, G. W. and collaborators (cf.: e.g., *J. Am. Chem. Soc.* **1985**, *107*, 1958 or **1968**, *108*, 7553) succeeded—among other interesting results—in recording time-resolved cyclovoltammetric redox potentials for both reduction steps of lariat ethers and their metal complexes with relatively large formation constants (*Anal. Chem.* **1988**, *60*, 2021). Therefore, the exchange rate of counter cations with the surrounding solution can be beyond the cyclovoltammetric time scale and "averaged" reduction potentials result for both M and $[MMe^+]$ complexes.

[13] Bock, H.; Hermann, H.-F.; Fenske, D.; Goesmann, H. *Angew. Chem.* **1988**, *100*, 1125; *Angew. Chem., Int. Engl.* **1988**, *27*, 1067 and literature cited.

in the presence of innocent tetra(*n*-butyl)ammonium, Na^+ lowers the half-wave reduction potential by 400 mV to −0.86 V and Li^+ by 600 mV to −0.67 V.

Summarizing, cyclovoltammetric and ESR/ENDOR information[9] has been gathered on triple ion intermediates along the two-step single electron transfer pathway of *p*-benzoquinone-18-crown-6 to its dihydroquinone dianion salt (eq 1) in aprotic solutions with surplus Me^+X^- salt content (cf. also ref 7). Shape-selective Me^+ encapsulation, depending on the optimum cation radius r_{Me^+} and accompanied by drastic structural changes, has been found, together with weaker ion pairing, inversely proportional to the counter cation radius, $1/r_{Me^+}$. It has been pointed out before[7,11] that redox-active chelating agents capable of considerable structural changes—like the one investigated here—and their ion pairs might have biological as well as industrial implications. Presumably, this applies even more to triple ions with different binding sites for different cations, which should allow for additional fine-tuning of molecular carriers and "turn on–turn off" switches.[1]

Acknowledgment. The research project "electron transfer and ion pairing" is supported by the Deutsche Forschungsgemeinschaft, Land Hessen, Fonds der Chemischen Industrie and the A. Messer Foundation.

Oxidant-Dependent Nonadiabatic Intervalence Transitions

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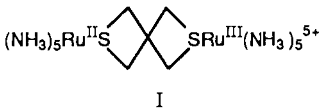
Received July 18, 1988
Revised Manuscript Received July 19, 1989

We have found evidence that the reduced oxidant used to generate the mixed valence species I apparently serves as a necessary "cofactor" in the observation of an intervalence transfer (IT) band. Such metal cofactors are commonly present in redox processes in nature although their precise role often is not well understood. Our system may usefully serve as a model for such processes.



I

Compounds such as I containing two transition-metal atoms in different oxidation states often have bands in the near-infrared region of the spectrum. These light-induced transitions between the metal centers have been designated IT bands, and they are present only for the mixed-valence state.[1-6] Considerable work has been performed on these types of complexes, and much is now known about the effect of distance[7-12] between the metal centers on the electron-transfer process as well as the influence of the bridging ligand or "intervening matter" on the extent of electronic coupling that is possible.[8,9,13]

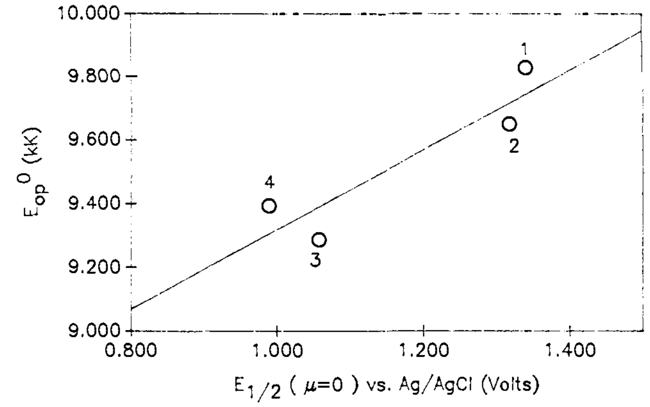


Figure 1. Oxidant potential dependence of intervalence transfer bands extrapolated to zero ionic strength. Oxidants shown are (1) $[Ru(bpy)_3]^{3+}$, (2) $[Ru(bpy)_2(py)_2]^{3+}$, (3) $[Ru(bpy)_2(CN)_2]^+$, and (4) $[Ru(bpy)_2(PPh_3)Cl]^{2+}$. Potentials were measured in DMSO by Osteryoung square wave voltammetry at a series of ionic strengths for each oxidant, and the potential at zero ionic strength was determined graphically. The range of ionic strengths employed was the same as that used in the spectroscopy experiments.

The simple dielectric continuum model has been used widely[14-23] to evaluate the relative importance of inner-sphere reorganizational energies (changes in internuclear bond distances) and outer-sphere reorganizational energies (influence of solvent and ionic species in solution). Recently, it has been recognized that there are severe problems associated with the application of this model. Drickamer and Hendrickson et al.[24,25] have shown that the simple dielectric continuum model does not explain the solvent dependence of the energy band maximum of the intervalence transfer electronic absorption band (E_{op}) since only small changes in the energy of the IT band were seen for solutions of mixed-valence complexes when pressure-induced freezing was employed to dramatically vary D_s. The same group later showed[26] that there is a strong concentration dependence of E_{op} for mixed-valence biferrocenium triiodide dissolved in either nitrobenzene or dichloromethane. This was assigned to the effects of ion aggregation, and it was concluded that the increase in E_{op} with increasing concentration reflects an increasing percentage of ion-paired mixed-valence cations that have a higher energy IT band than the non-ion-paired cation because the ion pairing probably introduces a zero-point energy separation between the two vibronic states of the cation. We also recently have demonstrated[27] that there is an ionic strength dependence on the value of E_{op} obtained in dimethyl sulfoxide and *N*-methylformamide for μ-2,6-dithiaspiro[3.3]heptanedecaamminediruthenium(II,III) (complex I). At zero ionic strength, the values of E_{op} were identical, within experimental error, in the

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