Table III. Electronic Absorption Spectral Data of the Reported Co(III)-(U-EDDA) Complexes

complex	λ_{max}, nm	ϵ, cm^{-1} M^{-1}
trans-[Co(U-EDDA)(tn)]$^+$	537	153
	465 (sh)	
	360	195
cis-[Co(U-EDDA)(tn)]$^+$	503	166
	361	191
trans-[Co(U-EDDA)(mal)]$^-$	569	178
	382	175
cis-[Co(U-EDDA)(mal)]$^-$	531	161
	381	141
cis-[Co(U-EDDA)(CO$_3$)]$^-$	535	169
	379	119
cis-[Co(U-EDDA)(ox)]$^-$	527	160
	375	143

The chemical shifts for H_A and H_B (A more downfield than B) are listed in Table II for each complex.

(2) The Cis U-EDDA Isomers. On the basis of previously established resonance patterns for EDDA uns-cis isomers[3,4] and the Co(III)-ED3A complex[10] (ED3A = ethylenediaminetriacetate), the cis U-EDDA isomers were easily identified. The cis isomers have a characteristic single AB quartet and an AB quartet that has collapsed to a singlet corresponding to the methylene protons of the G_2 and R_2 rings, respectively. In a fresh solution of *cis*-[Co(U-EDDA)(mal)]$^-$ an AB quartet also appears for the malonate protons, but these peaks decrease rapidly with time owing to deuterium exchange. In addition, resonance patterns corresponding to the en backbone protons (E ring) and tn methylene protons are observed at higher fields (δ 3.6-1.9). All cis U-EDDA spectra agree with the corresponding or analogous EDDA complexes except that in [Co(EDDA)(CO$_3$)]$^-$ the resonance for the G_1 ring has not totally collapsed to a singlet.[4] A doublet is observed at δ 3.52 and 3.49. In *cis*-[Co(U-EDDA)(CO$_3$)]$^-$ only a singlet is observed. Tables I and II summarize all the NMR data for the complexes studied.

Assignment of resonances in the cis complexes as being due to R_2 or G_2 rings is based upon C-N magnetic anisotropy effects. Using molecular models of our complexes and the arguments of Blackmer, Hamm, and Legg[10] concerning the [Co(ED3A)NO$_2$]$^-$ complex, we assign the singlet (collapsed AB quartet) to the methylene protons of the R_2 ring and the AB quartet resonances to the protons of the G_2 ring. Where quartets are observed, the low-field proton is designated A in each case.

Electronic Absorption Spectra. Visible absorption data served to provide supporting evidence in the structural assignment of the geometrical isomers. On the basis of the arguments and results presented by Legg and Cooke[12] and Chu, Cooke, and Liu[6] the molar absorptivities for the trans U-EDDA isomers would be expected to be greater than those for the corresponding cis isomers. This behavior was observed with [Co(U-EDDA)(mal)]$^-$. For the trans isomer, $\epsilon_{569} = 178$ and $\epsilon_{382} = 175$, whereas the cis isomer gives $\epsilon_{531} = 161$ and $\epsilon_{381} = 141$. (All λ in nm and ϵ in cm^{-1} M^{-1}.) The [Co(U-EDDA)(tn)]$^+$ isomers are not nearly as clear-cut, however. For *trans*-[Co(U-EDDA)(tn)]$^+$ $\epsilon_{537} = 153$ and $\epsilon_{360} = 195$, whereas for *cis*-[Co(U-EDDA)(tn)]$^+$ $\epsilon_{503} = 166$ and $\epsilon_{361} = 191$. *trans*-[Co(U-EDDA)(tn)]$^+$ exhibits the expected shoulder on the high-energy side of the low-energy peak.[6] Table III lists the pertinent visible spectral data for the complexes studied.

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Registry No. *cis*-K[Co(U-EDDA)(CO$_3$)], 91670-31-4; Na$_3$[Co(CO$_3$)$_3$], 75632-02-9; *cis*-K[Co(U-EDDA)(mal)], 91670-32-5; *trans*-K[Co(U-EDDA)(mal)], 91739-91-2; *cis*-K[Co(U-EDDA)(ox)], 91670-33-6; *cis*-[Co(U-EDDA)(tn)]Cl, 91739-92-3; *trans*-[Co(U-EDDA)(tn)]Cl, 91670-34-7.

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Solvatochromism of the LMCT Transition of Pentacyanoferrate(III) Complexes

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The pentacyanoferrate(III) and pentaamineruthenium(III) complexes of imidazoles, pyrazoles, and pyridines substituted with functional groups having lone pairs in conjugation with the aromatic ring exhibit ligand-to-metal charge-transfer (LMCT) transitions in the visible region of the absorption spectrum.[1-6] Meyer et al. have shown that the solvatochromism of the pentaammineruthenium(III) complexes arises with specific interaction of hydrogen-bonding acceptor solvents with the coordinated NH_3 ligands.[4] As a consequence, the order of the positions of LMCT for the Ru(III) complexes or the MLCT transitions of the Ru(II) analogues were found to follow a solvent-dependent order related to Gutmann's donor number (DN).[4] The energies of the transitions increase with DN for the pentaammineruthenium(III) series and decrease for pentaammineruthenium(II), as anticipated for an increasingly anionic ligand field due to greater solvent-NH_3 hydrogen bonding. We wish to report here on the solvatochromism of pentacyanoferrate(III) complexes.

Results and Discussion

Unlike the pentaammineruthenium(III) series, we have found that the solvatochromic behavior of pentacyanoferrate(III) complexes is well-correlated with the Reichardt-Dimroth (E_T)[7] and Kosower (Z)[8] scales. The E_T and Z scales of solvents are based on the shift in the charge-transfer transitions of pyridinium *N*-phenolbetaine and ethyl-4-(carbomethoxy)pyridinium iodide dye molecules.[7,8] The solvent scales relate the ability of a dissolved dipole to polarize the solvent.[9] The behavior of the LMCT band of (CN)$_5$FeL^{2-}

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Table I. LMCT Maximum for $(CN)_5FeL^{2-}$ Complexes in Pure Solvents

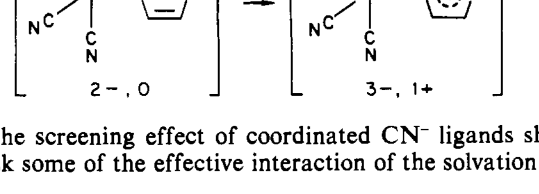
	L				
solvent[a]	imH	bzimH	2-CH_3-bzimH	5,6-CH_3-bzimH	dmapy
H_2O	500	505	515	532.5	662
CH_3OH	457	462	465	484	550
C_2H_5OH	447	454	401	481	526
Me_2SO	433	483.5	412.5	438	491
CH_3CN	430	434	421	433.5	498
DMF	427	430	412.5	432	468
PC	427				

[a] Abbreviations: Me_2SO = dimethyl sulfoxide, DMF = dimethylformamide, PC = propylene carbonate, imH = imidazole, bzimH = benzimidazole, 2-CH_3bzimH = 2-methylbenzimidazole, 5,6-CH_3bzimH = 5,6-dimethylbenzimidazole, dmapy = 4-(dimethylamino)pyridine.

complexes is observed to follow the trend with solvent in which the electronic excited states of the complexes contain a larger dipole moment than their ground-state dipole moments. Therefore, as the systems exhibit an LMCT transition that is solvent dependent, we observe that the influence of the solvent is in reverse of the shifts exhibited for the organic dye molecules used to establish E_T and Z scales.

In Table I the maxima for the LMCT transitions of the pentacyanoferrate(III) complexes of imidazole, benzimidazole, 2-methylbenzimidazole, 5,6-dimethylbenzimidazole, and 4-(dimethylamino)pyridine are given for the $Na_2[Fe(CN)_5L]$ salts dissolved in the following solvents: H_2O, CH_3OH, C_2H_5OH, $(CH_3)_2SO$, CH_3CN, $(CH_3)_2NC(O)H$ (DMF), and $C_3H_6CO_3$ (propylene carbonate). Consider the ligand-to-metal charge-transfer excitation for $(CN)_5Fe^{III}L^{2-}$ complexes. The ground-state complex has a solvent cage optimal for solute–solvent interactions (H bonding, dipole–dipole, etc.). The excited-state complex retains the solvent cage of the ground state due to the Franck–Condon rule. The solvated excited state will be nonoptimal. Therefore, an energy difference exists between the ground and excited state due to the solvation differences. The potential wells of the ground- and excited-state $(CN)_5FeL^{2-}$ species are anticipated to be of similar curvature; even when the obvious differences in back-bonding of Fe(II) vs. Fe(III) are recognized, the CN vibrations in $(CN)_5FeL^{2-}$ and $(CN)_5FeL^{3-}$ salts are similar,[15] as well as other ligand vibrations.[16] The LMCT excitation creates an Fe(II)-like complex from an Fe(III)-like center of the ground state. Due to the approximate similarity of the $(CN^-)_5$(N-heterocycle) ligand donor set in bonding to either Fe(II) or Fe(III) the potential wells or their configurational coordinate analogues will not be greatly displaced.[17] If one compares complexes of comparable oscillator strength, *f*, for the LMCT transition, the transition energy, E_{LMCT}, will be proportional to the separation of states produced by the various solvation shells as the solvent is changed. In this study the values of *f* are found to be fairly insensitive to L. For example, with $(CN)_5FeL^{2-}$ in water, *f* is found as follows for L: 0.30 (dmapy), 0.052 (bzimH), 0.013 (2-CH_3bzimH), 0.015 (imH). With use of the $(CN)_5Fe(dmapy)^{2-}$ complex as a probe of the influence of changing the solvent, *f* is found to be 0.30 (H_2O), 0.19 (CH_3OH), 0.081 (DMF), 0.068 (C_2H_5OH), 0.067 (Me_2SO), and 0.065 (CH_3CN). *f* values have not been obtained for complexes in all solvents. The solubilities of some of them are low, requiring long path lengths to observe accurate values of λ_{max} for the LMCT band. Also, equilibrium shifts of ion pairs and ion triples in the nonaqueous medium from solvent to solvent makes the task of determining accurate ϵ_{max} values, and hence *f*, an extremely formidable task. The similarity of *f* values with changing L or with changing solvent assure that the E_{LMCT} energies provide a justifiable measure of the energy differences due to solvation as a perturbation to the Fe(III)-like and Fe(II)-like ground- and excited-state species immersed in a solvent bath. It might be noted here that mixed-solvent systems of a pure nonaqueous solvent doped with a certain fraction of water exhibit band broadening and reductions of ϵ_{max} for a complex in the mixed solvent. Even in mixed solvents the *f* values remain comparable to those with either pure solvent or 100% water. Thus modifications to the solvent cage appear as an average effect in the mixed media. In Table II the LMCT transition energies in kcal/mol are compared with the dye transition energies (also in kcal/mol) for the Z and E_T scales. If the value of the LMCT transition energy of a particular $(CN)_5FeL^{2-}$ complex is plotted vs. either E_T or Z in a respective solvent, we observe an excellent linear correlation. The slope is negative in the range of −0.366 to −0.831 depending on L. The error bars of the slopes do not exceed 9.5% for six solvents. The values of the slope and intercept found for plotting E_{LMCT} vs. E_T or Z are given in Table III. The intercept relates to the ideal case of the $(CN)_5FeL^{2-}$ complex dissolved in a noninteractive, nonpolarizable solvent with $E_T = Z = 0$. As the nature of the LMCT transition produces a greater dipole moment, the same solvent would create the largest energy barrier to the LMCT excitation. Solvents of low E_T or Z value are predominantly those of very low dielectric constant and generally would not dissolve $(M^+)_2A^{2-}$ salts. Therefore, the value of the intercept represents a condition that is not likely to be achieved in the laboratory.

The value of the slope in the plot of E_{LMCT} vs. E_T or Z is negative due to the reverse nature of the dipole moments for the $(CN)_5FeL^{2-}$ complexes compared to those of the dye molecules used to develop the solvent scales. If both species types were equally sensitive or able to polarize a solvent, a slope of −1.0 would be predicted. However, the fractional slopes between −0.37 and −0.83 show that the $(CN)_5FeL^{2-}$ dipole moments are not equivalently polarizing of solvents as the dye molecules used to construct the E_T and Z scales. In each case the betaine dye is more polarizing than the pyridinium iodide salt ($E_T > Z$) as compared to any particular $(CN)_5FeL^{2-}$ complex, yielding a more negative slope of E_{LMCT} vs. E_T. It is quite logical that the $(CN)_5FeL^{2-}$ entity should be less sensitive to solvent than the dye molecules. As the excitation of the LMCT band takes place, positive charge is formally transferred to the ligand as shown in eq 1 for the imidazole complex.



(1)

The screening effect of coordinated CN^- ligands should mask some of the effective interaction of the solvation cage

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Table II. Energies of Charge-Transfer Transitions for Scales of E_T, Z and $(CN)_5FeL^{2-}$ Complexes (E_{LMCT})[a]

					E_{LMCT}				
solvent	DN	AN	E_T	Z	imH	bzim	2-CH_3-bzimH	5,6-CH_3-bzimH	dmapy
H_2O	18.0	54.8	63.1	94.6	57.2	56.6	55.5	53.7	43.2
CH_3OH	19.0	41.3	55.5	83.6	62.6	61.9	61.5	59.1	52.0
C_2H_5OH	20.0	37.1	51.9	79.6	64.0	63.0	(71.3)[b]	59.5	54.4
Me_2SO	29.8	19.3	45.0	71.1	66.1	(59.2)[b]	69.3	65.3	58.3
CH_3CN	14.1	18.9	46.0	71.3	66.5	65.9	67.9	66.0	57.4
DMF	26.6	16.0	43.8	68.5	67.0	66.5	69.3	66.2	61.1

[a] Abbreviations from Table I. [b] Omitted from plotting procedures.

Table III. Correlation of E_T or Z vs. E_{LMCT}

	L				
E_T/Z	imH	bzimH	2-CH_3bzimH	5,6-CH_3bzimH	dmapy
E_T slope	−0.366 ± 0.029	−0.377 ± 0.026	−0.547 ± 0.023	−0.502 ± 0.040	−0.630 ± 0.055
intercept on E_T scale	92.5 ± 2.3	92.7 ± 2.1	107.3 ± 2.3	100.8 ± 3.1	103.6 ± 3.9
Z slope	−0.482 ± 0.046	−0.506 ± 0.042	−0.726 ± 0.025	−0.663 ± 0.058	−0.831 ± 0.077
intercept on Z scale	88.4 ± 2.4	89.1 ± 2.2	101.5 ± 1.3	95.4 ± 3.0	96.7 ± 4.0

with the increased dipole of the excited state. The dye molecules, being planar aromatic molecules, are less shielded in terms of the interaction of the reduced dipole of its excited state (greater dipole of the ground-state dye) with its solvent cage. Therefore, the inorganic unit should be less sensitive to changing solvent. Additionally, the extent of charge transfer in the LMCT state may be less than complete compared to the nonpolar resonance form of the excited dye unit.[9c] Either influence will reduce the slope of E_{LMCT} vs. E_T or Z to values less negative than −1.0.

If the slopes are compared as a function of the coordinated ligand L, the order imH $\lesssim$ bzimH < 5,6-CH_3bzimH $\lesssim$ 2-CH_3bzimH < dmapy is found. The $(CN)_5Fe(dmapy)^{2-}$ complex is about twice as sensitive toward the nature of the solvent as is the $(CN)_5Fe(imH)^{2-}$ complex. Since the lone pair in the dmapy complex is about 1.5 Å more remote, and the positions of the LMCT band in any solvent is at lower energy than for the imidazole complex, it would appear that a larger change in dipole moment occurs for the $(CN)_5Fe(dmapy)^{2-}$ complex on excitation than for $(CN)_5Fe(imH)^{2-}$. If this assumption is correct, $(CN)_5Fe(dmapy)^{2-}$ should behave more like the organic dye systems and the plot of L_{LMCT} vs. E_T or Z should more closely approach −1.0 than for the $(CN)_5Fe(imH)^{2-}$ case. This anticipated result is confirmed by the data in Table III.

Table II also lists the value of Gutmann's donor number (DN) and Gutmann's acceptor number (AN) for the solvents in our study. It is readily seen that no linear correlation exists between DN and E_{LMCT} for the $(CN)_5FeL^{2-}$ complexes. If one compares E_{LMCT} values with DN, the only obvious trend is that potential H-donating solvents (H_2O, alcohols) have E_{LMCT} values lower than non-H-donating solvents, but no ordering of E_{LMCT} is achieved on the basis of DN for even the latter group (Me_2SO, DMF, CH_3CN, PC). Therefore, the $(CN)_5FeL^{2-}$ series does not respond to changes in solvent as do the $(NH_3)_5RuL^{3+}$ complexes of Meyer's study.[4] The pentaammineruthenium(III) complexes follow DN for E_{LMCT} and correlate with the acceptor character of the solvent (solvent lone pairs attracted to the H atom of coordinated NH_3). The CN^- ligands do not have a proton susceptible to interaction with lone pairs of a solvent molecule, but the reverse case is possible for CN^-. The terminal lone pair would be available to enter into H-bonding with an H-donating solvent (H_2O or alcohols). Therefore, it is reasonable that, as a class, H_2O and alcohols will be in a separate group if one attempts any correlation based on DN. Values of E_{LMCT} are linearly correlated with Gutmann's acceptor parameter for the solvent (AN). However, since AN is linearly related to both E_T and Z,[10] the same apparent property must be influenced in forming the LMCT state. The success of the correlation of E_{LMCT} for the $(CN)_5FeL^{2-}$ series with both E_T and Z for all solvents in Table II shows that the major feature that dominates the energetics of LMCT excitation is the polarizability of the solvent by the changing magnitude of the dipole moment.

A major concern in reporting spectral LMCT maxima for a series of pure solvents rests with the ubiquitous impurity of water in solvents. It is difficult to achieve bulk solvents that are lower than millimolar in H_2O content, particularly for solvents such as C_2H_5OH, Me_2SO, CH_3CN, and DMF. Since the $(CN)_5FeL^{2-}$ complex is dissolved at ca. 1×10^{-3} M, the extent of selective solvation of the anion by H_2O in greater proportion than its statistical mole fraction is a serious concern in studies of solvatochromic behavior of a charge-transfer band. We obtained spectra for $(CN)_5FeL^{2-}$ (L = bzimH, 5,6-CH_3bzimH, 2-CH_3bzimH, and dmapy) in DMF, C_2H_5OH, CH_3OH, Me_2SO, and CH_3CN as a function of the volume percent of water from 80.0% solvent/20.0% H_2O up to 100.0% solvent (dried over molecular sieves). The data obtained for this region may be extrapolated backwards to 100.0% H_2O for comparison with the value of λ_{max} in H_2O. If a statistical solvation shell is formed, a straight tie line should be achieved between the value of λ_{max} in H_2O to that of λ_{max} in a pure solvent. This situation appears to be nearly realized for the four $(CN)_5FeL^{2-}$ complexes (benzimidazoles and dmapy) in CH_3OH. A very slight bathochromic shift, higher than the statistical value predicted by the pure solvent tie line, is found in CH_3OH for all of the benzimidazole derivatives. This indicates a slight preferential incorporation of H_2O in the solvation cage. Approximately 23% of the total shift as one goes from pure CH_3OH to pure H_2O occurs in the first 20% H_2O enrichment. Thus the discrimination of H_2O over CH_3OH is small. For C_2H_5OH, Me_2SO, and CH_3CN data points in the range of 80.0–100.0% solvent exhibit greater bathochromic shifts as the percent of H_2O increases than predicted on a statistical substitution in the solvent cage for the bzimH, 5,6-CH_3bzimH, and dmapy complexes (about 27% of the total shift in the first 20% of H_2O enrichment). The 2-CH_3bzimH complex exhibited behavior different from any of the other complexes studied. A distinct decrease in λ_{max} (hypsochromic shift) occurs as the percentage of H_2O increases in the 80.0–100.0% solvent range for DMF, C_2H_5OH, Me_2SO, and CH_3CN. This effect is particularly large in CH_3CN. The only other complex to exhibit a slight hypsochromic shift in the 80.0–100.0% solvent range was the benzimidazole complex in DMF. DMF produced a distinctly hypsochromic shift for the 2-CH_3bzimH complex but behaves bathochromically in the 80.0–100.0% DMF range for the dmapy and 5,6-CH_3bzimH complexes. The hypsochromic effect on the 2-CH_3bzimH complex in the 80.0–100.0% range follows the order CH_3CN (21, 5.3) >> Me_2SO (8, 2.0) > DMF (5, 1.3) $\gtrsim$ C_2H_5OH (4, 1.0) > CH_3OH (0, 0.0). Values in parentheses refer to the shifts at 80% solvent in nm and normalized shifts based on C_2H_5OH as a standard, respectively. Thus CH_3CN shifts 5.3 times more hypsochromically for a given enrichment in H_2O within the 80.0–100.0% solvent range, and a net shift of −21 nm is observed at 80.0% CH_3CN.

The outcome of these studies is that "pure solvents", which contain only the most minimal H_2O that cannot be removed by drying procedures, appear to provide data that are meaningful measurements of E_{LMCT} in these solvents. The presence of H_2O in larger abundance, in synthetic mixtures in the 80.0–100.0% solvent range, produces shifts of a few nanometers per percent solvent change. These data show the existence of preferential solvation of H_2O for all except the $(CN)_5Fe(2\text{-}CH_3bzimH)^{2-}$ complex. Since this complex is the only one to be sterically hindered in the vicinity of the pyrrole N–H and pyrrole lone-pair region, it is tempting to assign the effect of the hypsochromic shift to changes in solvation of the hindered NH and lone pair. However, further studies are necessary to confirm this conjecture. That the tabulated values of λ_{max} of the LMCT transition follow E_T and Z linearly with E_{LMCT} to within a maximum deviation of any slope of ±9.5% supports the conclusion that the "pure solvent" data are not plagued by artifacts introduced by preferential solvation of trace water. These studies lend further support to the assignment of the transitions observed for $(CN)_5FeL^{2-}$ complexes (L = imidazoles, pyrazoles, and electron-releasing substituted pyridines) as LMCT transitions.[1] Although neutral complexes of the type $Fe^{II}(bpy)_2(CN)_2$[11] $M^0(bpy)(CO)_4$ (M = Mo, W),[12,18] and $M^{II}(bpy)X_2$ (M = Pt; X = halide ion)[13] have been shown previously to follow the Reichardt–Dimroth and Kosower scales for their solvatochromic behavior, the present study is the first to be carried out on anionic transition-metal complexes having LMCT excitations.

Experimental Section

Solvents. DMF, CH_3OH, and C_2H_5OH were J. T. Baker Spectral/Analytical grade. These solvents were distilled under N_2 and dried over molecular sieves for 1 week prior to preparation of solutions used to obtain spectral data. Purified Me_2SO, CH_3CN, and propylene carbonate were gifts from Professor J. Coetzee.[10] These solvents had been rigorously purified in Coetzee's laboratory by spinning-band distillations. Karl Fischer analysis estimated the H_2O content at less than 3 mM. Transfers to containers were carried out in a dry glovebox to avoid contamination with atmospheric moisture. H_2O was the department distilled and laboratory ion exchanged water.

$Na_2[Fe(CN)_5L]$ Complexes. Preparations of the complexes were reported previously.[2,5,9c,14] Spectra were obtained by dissolving freshly weighed samples in an appropriate solvent. Spectra were obtained on a Varian-Cary 118C spectrophotometer at room temperature (ca. 22 °C) in quartz cells.

Acknowledgment. We gratefully acknowledge the National Science Foundation, Grant No. CHE 802183, for support of this work. The assistance of Tim Yashika in obtaining several early spectra and preparing the benzimidazole complex is appreciated.

Registry No. DMF, 68-12-2; PC, 108-32-7; H_2O, 7732-18-5; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; Me_2SO, 67-68-5; CH_3CN, 75-05-8; $(CN)_5Fe(imH)^{2-}$, 61332-60-3; $(CN)_5Fe(bzimH)^{2-}$, 91209-20-0; $(CN)_5Fe(2\text{-}CH_3bzimH)^{2-}$, 91209-21-1; $(CN)_5Fe(5,6\text{-}CH_3bzimH)^{2-}$, 91209-25-5; $(CN)_5Fe(dmapy)^{2-}$, 91209-30-2.

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Solvent Effects on the ^{11}B and ^1H NMR Spectra of Decaborane(14), $B_{10}H_{14}$

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In the past it has been commonly presumed that the ^{11}B NMR chemical shifts of boron hydrides (boranes) and their derivatives are for the most part independent of the nature of the solvent. While this may be true of many boranes, we have recently found that several of the ^{11}B resonances of decaborane(14), $B_{10}H_{14}$, exhibit substantial chemical shift differences as a function of the nature of the solvent. In addition we have recorded the resolved ^{11}B–^{11}B coupling in $B_{10}H_{14}$, obtained via line narrowing, and have observed that the nature of the solvent and the temperature influences the resolution of such fine structure. Solvent effects on the ^1H NMR chemical shifts of $B_{10}H_{14}$ are also illustrated.

Experimental Section

$B_{10}H_{14}$ was sublimed prior to use. Most solvents were used as received. C_6D_6 and C_6F_6 were dried over $LiAlH_4$ and distilled prior to use. THF was dried over potassium and distilled prior to use. All solutions were saturated in $B_{10}H_{14}$ unless specified otherwise and were contained in 5-mm o.d. thin-walled Pyrex NMR tubes.

The instruments used were a Bruker 270-MHz (86.6 MHz ^{11}B) NMR spectrometer, an IBM 270-MHz (86.6 MHz ^{11}B) NMR spectrometer, and a Bruker 360-MHz (115.5 MHz ^{11}B) NMR spectrometer. Line narrowing and data refinements were performed with each instrument's accompanying software.

Results and Discussion

Solvent–Chemical Shift Effects. Figure 1 shows the structure and atom numbering for $B_{10}H_{14}$. In the ^{11}B NMR spectra of $B_{10}H_{14}$, the most dramatic solvent effects are associated with the B(1,3) and B(6,9) resonances at the lowest field positions (Table I). The spectral appearances can be conveniently grouped into three categories on the basis of the solvent polarizabilities. The largest chemical shift differences, between the B(1,3) and B(6,9) resonances, occur in the least polarizable solvents such as butane and *n*-pentane. In addition, the fine structure associated with the B(6,9) resonance is most readily resolved in these solvents (vide infra). Somewhat more polarizable solvents such as benzene and dichloromethane give rise to intermediate shift differences, which in solvents having a permanent dipole such as acetone and acetonitrile the B(1,3) and B(6,9) resonances are coincident. These shift differences in the three classes of solvents are illustrated in Figure 2 for the solvents pentane, benzene-d_6, tetrahydrofuran, and acetonitrile-d_3. While the B(5,7,8,10) and B(2,4) resonances also shift as a function of solvent polarizability, as shown in Table I, these shifts are not as visually dramatic. The largest and most discontinuous shift is that of the B(6,9) resonance in the Lewis base solvents acetone, tetrahydrofuran, and acetonitrile. All three solvents give rise to B(6,9) resonance shifts of over 1.00 ppm to lower field, while the B(1,3) resonance shifts to higher field and is coincident with the B(6,9) resonance in acetone and acetonitrile. In THF the resonances are very nearly coincident, but a slight shoulder can be discerned on the high-field member of the doublet. The B(5,7,8,10) reso-

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