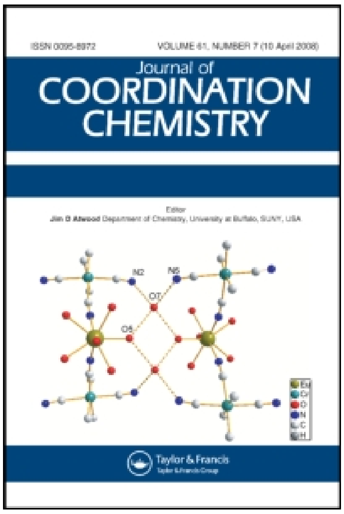

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ANALYSIS OF SOLVENT EFFECTS INDUCED IN PHYSICOCHEMICAL PROPERTIES OF COORDINATION COMPOUNDS

Russell S. Drago[a]; Dimitra Kovala-demertzi[a]; Donald C. Ferris[a]
[a] Department of Chemistry, University of Florida, Gainesville, Florida

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ANALYSIS OF SOLVENT EFFECTS INDUCED IN PHYSICOCHEMICAL PROPERTIES OF COORDINATION COMPOUNDS

RUSSELL S. DRAGO, DIMITRA KOVALA-DEMERTZI and DONALD C. FERRIS

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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The changes in the electronic transitions of three coordination compounds in various solvents are analyzed with the Unified Solvation model. The examples selected illustrate the influence of specific and non-specific solvation on the spectral shift. The Unified Solvation approach provides a quantitative way of determining whether the coordination complex is behaving as a donor, acceptor, or amphoterically in various solvents. The Unified solvation approach provides a quantitative procedure for evaluating the role of solvent, and this understanding allows one to optimize solvent selection for the multitude of physicochemical studies of coordination compounds.

KEYWORDS: solvent effects, *E* and *C* numbers

INTRODUCTION

The analysis[1] of solvent shifts, $\Delta\chi$, on a wide variety of solute molecules in solvents where donor-acceptor interactions are absent has led to a unified scale of solvent polarities, S', for different solvents. The changes induced in probe molecules, $\Delta\chi$, by non-specific solvation are fit to Equation (1),

$$\Delta\chi = S'P + W \qquad (2)$$

where P measures the susceptibility of the solute probe to solvation and W is the value of the measured property of the probe in a solvent where $S' = O$. Solvents which undergo specific interactions with the probes were excluded from data analyzed with Equation (1)[1] and subsequently added[2,3] using Equation (2)

$$\Delta\chi = E_AE_B + C_AC_B + S'P + W \qquad (2)$$

When acceptor probes are studied in donor solvents, the electrostatic and covalent contributions to the specific interaction are accommodated in Equation (2) with an $E_A{}^*E_B$ and $C_A{}^*C_B$ term.[4] The E_B and C_B parameters are the enthalpy based values reported[5] for donor-acceptor interactions in poorly solvating solvents. $E_A{}^*$ and $C_A{}^*$ are physicochemical acceptor parameters that refer to the particular physicochemical property employed when the property is other than a solvation minimized enthalpy.

When donor probes are studied in acceptor solvents, the specific interaction is treated with $E_A{}'E_B{}^*$ and $C_A{}'C_B{}^*$ terms. The $E_A{}'$ and $C_A{}'$ are the counterparts of the poorly solvating, enthalpy based E_A and C_A parameters except they are measured in the pure acceptor solvents.[3] The prime values recognize the possibility that the extent of association of a hydroxylic solvent is different in a poorly solvating solvent than in the pure solvent. The acceptor strength can vary with the degree of association.

The ability of the model to accommodate a wide range of solute probe molecules of different polarity and shape has led to a dynamic cavity model for solvation.[3] In this description, the solvent rearranges to form a cavity to accommodate the probe molecule. In forming the cavity, solvent-solute non-specific dipole and dispersion interactions are maximized at the expense of solute-solute and solvent-solvent interactions. This dynamic cavity model enables the non-specific solvation of the probe to be treated by a simple $S'P$ term. The breakup of solvation into a non-specific component treated by $S'P$ and a specific component treated by $E_AE_B + C_AC_B$ terms is the essence of the Unified Solvation model.

The majority of the probe molecules employed in the solvation analysis[3] to determine S' are flat in shape. Thus, it is desirable to find more probes of different shapes to test the model. Three coordination compounds will be investigated in this report to illustrate the utility of the non-specific (S') and specific (E and C) solvation parameters in understanding the solvent dependence of the physicochemical properties of coordination compounds. This analysis enables one to determine the suitability of these compounds as solvation probes.

cis-Dicyano-bis-1,10 phenanthroline iron(II), $Fe(phen)_2(CN)_2$, has an electronic transition which is sensitive to solvent variation.[6] This sensitivity has led to the use of this complex in establishing the Burgess scale[7] of solvent "polarity." The electronic spectrum consists of two bands. The lower energy band, due to a $t_{2g} - \pi^*$ (phen) transition[8], is sharper and more intense than the higher energy band. Since the band position of the lower energy band is more easily determine, it is used in correlations. In this article, the use of this probe as an indicator of solvent polarity is examined in more detail.

Two transitions, which overlap and distort the position of the band maxima, occur in the electronic spectrum of this complex. The consequences of this overlap are determined by curve resolution. The resolved data are compared to unresolved data.[7] Experimental problems, which may be the cause of deviations in reported literature values, are demonstrated. The application of the S' values are then extended to an analysis of solvent effects on the properties of other coordination compounds to illustrate the insights that can result from such analyses.

RESULTS AND DISCUSSION

cis-$Fe(phen)_2(CN)_2$

The frequencies of the resolved and unresolved bands for the low energy *d-d* electronic transition of $Fe(phen)_2(CN)_2$ in a variety of solvents are listed in Table 1. Results reported by other investigators for the solvents listed are also shown. The analysis of the spectral changes in donor solvents will be considered first. $Fe(phen)_2(CN)_2$ has all of the metal coordination positions occupied by strong donor ligands, which are not expected to be displaced by the solvent. Furthermore, there are no protonic hydrogens for second coordination sphere hydrogen bonding

Table 1 Solvent effects on the electronic transition of dicyano-bis-1,10 phenanthroline iron (II) (kK)

Solvent	$\Delta\nu$(kK) Resolved	$\Delta\nu_{calc}{}^{d}$ Resolved	$\Delta\nu_{calc}$(kK) Unresolved	$\Delta\nu_{calc}$ Unresolved	${}^{e}\Delta\nu_{exp}$(B)	$\Delta\nu_{calc}(E)^{f}$	$\Delta\nu_{exp}(s)$	$\Delta\nu_{calc}(S)^{g}$
C_5H_5N	16.018	(15.67)	16.103	(15.78)			16.12	(15.72)
$(C_2H_5O)_3PO$	15.798	15.85	15.848	15.96				
$(CH_3)_2CO$	16.077	15.89	16.181	16.01	16.000	15.974	16.00	15.94
$CH_3C(O)N(CH_3)_2$	16.013	16.08	16.077	16.11			16.12	16.15
$HC(O)N(CH_3)_2$	16.173	16.24	16.287	16.38	16.290	16.341	16.28	16.31
$CH_2CH_2CH_2C(O)NCH_3$	15.918	15.95	16.000	16.08				
$(CH_3)_2SO$	16.398	16.55	16.502	16.70	16.600	16.674	16.52	16.64
$(CH_3)_2SO^a$	16.920	–	17.065	–				
$(CH_3)_2SO^b$	16.725	–	16.863	–				
CH_3CN	16.653	16.55	16.835	16.70	16.780	16.674	16.68	16.64
CH_3NO_2	16.736	16.66	16.978	16.82			16.85	16.76
$CH_3NO_2{}^h$	16.818	–	17.065	–				
$HCONH_2$	18.053	17.852	18.315	18.072			18.28	18.17
CH_2Cl_2	16.539	16.344	16.666	16.400			16.62	16.41
$CH_2Cl_2{}^c$	16.608		16.694					
$CHCl_3$	16.625	16.626	16.722	16.757			16.80	16.80
CH_3OH	17.962	17.934	18.214	18.205	18.350	18.271	18.35	18.33
C_2H_5OH	17.593	17.655	17.793	17.871	17.950	17.881	17.95	17.97
n-C_3H_7OH	17.455	17.573	17.667	17.776	17.670	17.730	17.76	17.86
t-C_4H_9OH	16.911	16.959	17.064	17.094	17.060	17.009	17.00	17.15
H_2O	19.142	19.227	19.455	19.538	19.380	19.558		

[a] Old bottle of $(CH_3)_2SO$.

[b] Old bottle of $(CH_3)_2SO$ dried and distilled once with an empty condenser.

[c] Only slightly soluble. Repeat measurement. Calculated with $W = 13.967$ and $P = 0.820$.

[d] The donor solvents were calculated with Equation (1) using $P = 1.56$, $W = 11.86$.
The acceptor solvents were calculated with Equation (1) using $P = 1.38$ and $W = 12.49$ with $E^{*}_{B} = 1.17$ and $C^{*}_{B} = -0.208$.

[e] The donor solvents were calculated with Equation (1) using $P = 1.64$, $W = 11.78$. The acceptor solvents were calculated with Equation (1) using $P = 1.38$ and $W = 12.49$ with $E^{*}_{B} = 1.22$ and $C^{*}_{B} = -0.087$

[f] The donor solvents were calculated with Equation (1) using $P = 1.67$, $W = 11.67$. The acceptor solvents were calculated with Equation (1) using $P = 1.38$ and $W = 12.49$ with $E^{*}_{n} = 0.91$ and $C^{*}_{B} = 0.26$.

[g] The donor were calculated with Equation (1) using $P = 1.65$, $W = 11.68$. The full set of solvents by this author gave $P = 1.38$ and $W = 12.49$.
The acceptor solvents were calculated with Equation (1) using $P = 1.38$ and $W = 12.49$ with $E^{*}_{B} = 1.23$ and $C^{*}_{B} = -0.014$. The full data set gave $E_B{}^{*} = 1.13$ and $C_B{}^{*} = -0.002$. [h] Nitromethane, which contains 0.2% water.

interactions. Thus, the donor properties of the solvent are omitted in the initial fit, and the data are fit to Equation(1). If a poor fit results, the donor properties can be considered later, *vide infra*. The fist nine solvents, which are not acceptors, are fit to Equation(1) using reported S' values.[3] This fit leads to a sedries of simultaneous equations involving one for each measurement. The solution of these equations produces values for the two unknowns, P and W. The fit of the data is improved by omitting the data for the solvent pyridine. The solution of the resulting simultaneous equations leads to values of $P = 1.56$ and $W = 11.84$ when the frequencies for the curve resolved bands are employed. The quality of the data fit is seen by comparing the experimental shifts with those calculated by substituting the P, W and S' values into Equation (1). These calculated values are listed under ν_{calc}.

When the same set of solvents are fit to Equation (1) using the frequencies for the unresolved bands, values of $P = 1.64$ and $W = 11.77$ result. The $\Delta\chi$ values calculated with these parameters are in excellent agreement with experiment and in good agreement with the parameters from the resolved fit. Little is gained by curve resolution on this system. The data set $\Delta\nu_{\text{exp}}(\text{B})$ was reported in the original work by Burgess. This limited set of solvents leads to $P = 1.67$ and $W = 11.67$.

Subsequent to our carrying out the above measurements, values for the electronic transition of dicyano-bis-1,10 phenanthroline in a variety of solvents were reported.[9] These data are in excellent agreement with the unresolved frequencies reported here. When the non-acceptor solvents that are common to our measurement are fit to Equation (1), values of $P = 1.65$ and $W = 11.68$ result. The data fit[3] of all reported solvents[9] gives $P = 1.38$ and $W = 12.49$. These parameters fit the $\Delta\chi$ values of solvents measured in the more limited sets of solvents nearly as well as the P and W parameters from the limited fits. The more extensive data set should lead to the best parameters, and the parameters $P = 1.38$ and $W = 12.49$ are recommended for future use of equation (1).

Several phenyl substituted derivatives were studied as solvents in all the data sets, and these solvents were omitted from the data fits that result in the above parameters. The S' values for these solvents were previously determined[3] with probes that do not contain π-systems. When these S' values for π-solvents are used with the P and W values of the respective fit to calculate $\Delta\chi$, the calculated values are smaller than the experimental values. The values calculated for the π-solvents with the best parameters reported above are listed in the order experimental/calculated: $C_6H_5NO_2$, 16.48/16.10; $C_6H_5CH_3$, 16.60/16.12; $C_6H_5OCH_3$, 16.20/15.31; C_5H_5N, 16.12/15.86. These deviations suggest that charge transfer interactions occur between this probe and *pi*-solvents. The measured shift has contributions from both coordination and non-specific solvation. Complexation of the solvent as a donor to the π^* orbital of the coordinated phenanthroline would increase the energy of the π^* orbital and of the transition, leading to an experimental value that is higher than the calculated value. As observed, the largest shifts should occur for the aromatic compound with the substituent that makes the π-cloud the best donor. It should be emphasized that if these *pi*-interactions were ignored and the shifts in these solvents were averaged into the fits to determine solvation and probe parameters, the model would not be as effective in detecting these interactions, due to the fact that these deviations would be spread over the entire data fit. In an earlier report from this laboratory[2] it was shown that the Kamlet-Taft solvation parameters average these specific interactions into their non-specific solvation scale.

The three entries for $(CH_3)_2SO$ in Table 1 illustrate the significant influence that solvent purity has on the measurement of the electronic transition. Similar results are obtained with nitromethane when a small amount of water (0.2%) is added. Solvent purity, especially dryness, may be the main cause of the differences in reported values for solvent shifts.

The fit of the calculated and experimental frequencies for aprotic solvents are showns by points 1-6 in Figure 1. The values of protic solvents from Equation (1) are given by open squares. The protic solvents in Table 1 are acceptor solvents that undergo specific donor-acceptor interactions with the nitrogen of the coordinated cyano group. These systems should be fit with Equation (2). The P and W values for the probe in non-hydrogen bonding solvents ($P = 1.38$ and $W = 12.49$) are used

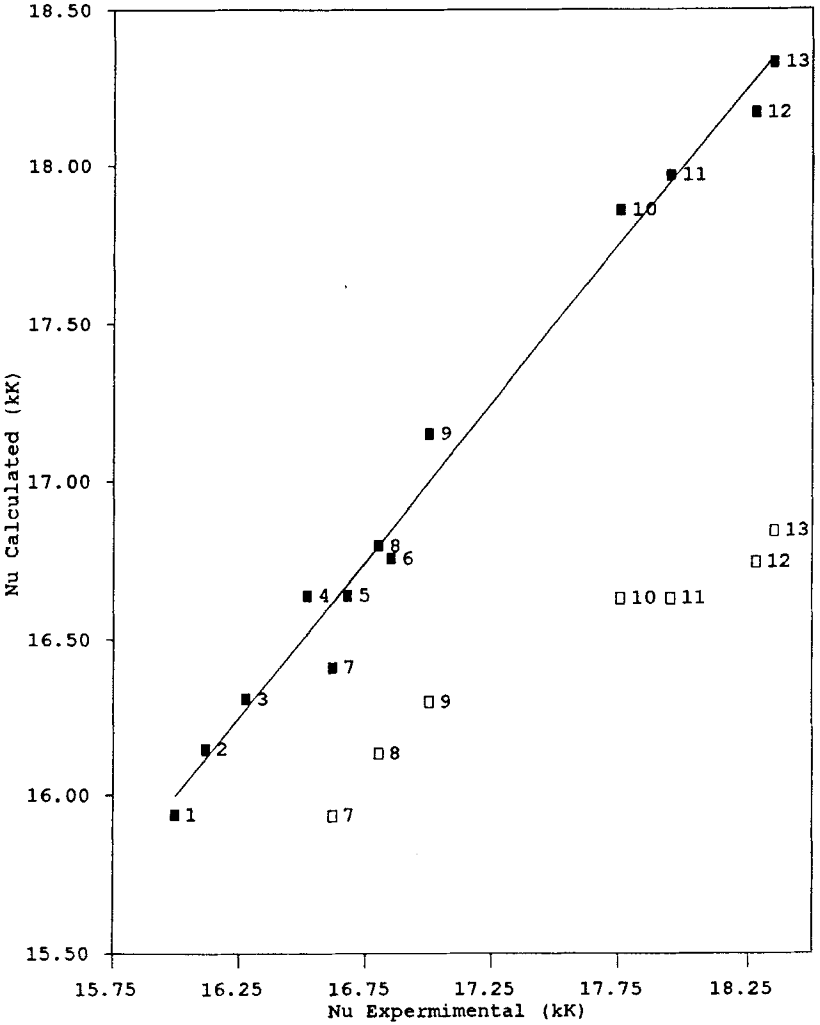

Figure 1 Plot of calculated values *vs.* experimental values of Burgess Dye using data from ref 9. The solid squares are the best fit data from Table 1. The open squares are the calculated values for the hydrogen bonding solvents using Nu(Calc) = $S'P + W$. The solid line represents the ideal case where Nu(Calc) = Nu (Exp). Key to solvents: 1, $(CH_3)_2CO$; 2, $CH_3C(O)N(CH_3)_2$; 3, $HC(O)N(CH_3)_2$; 4, $(CH_3)_2SO$; 5, CH_3CN; 6, CH_3NO_2; 7, CH_2Cl_2; 8, $CHCl_3$; 9, t-C_4H_9OH; 10, n-C_3H_7OH; 11, C_2H_5OH; 12, $HC(O)NH_2$; 13, CH_3OH.

to calculate the non-specific contribution to the shift in hydrogen bonding solvents. Reported S', E_A' and C_A' values for each solvent are substituted into Equation (2) along with the measured $\Delta\chi$. The resulting series of equations is solved for E_B^* and C_B^* of the donor probe. E_B^* and C_B^* are spectral donor parameters which include conversion units to convert the enthalpy based E_A' and C_A' parameters to (kK). Each data set yields E_B^* and C_B^* parameters that produce excellent agreement between the calculated and observed values. The solid squares in Figure 1 can be compared to the open squares for the same solvent to appreciate the correction made by adding the specific interaction term. The values of E_B* and C_B* indicate that shift of the electronic transition to higher energy by the specific interaction is dominated by the electrostatic bond forming tendencies of the hydrogen bonding solvent. The variation observed in the E_B* and C_B* values from the different data fits is expected because of the narrow range in the C_A'/E_A' ratio of the acceptors employed. The narrow range leads to a shallow minimum[4a] in the set of simultaneous equations used to solve for E_B* and C_B*. Accordingly, the use of these E_B* and C_B* parameters to predict specific interactions should be limited to hydrogen bonding solvents.

The specific hydrogen bonding contribution to the shift increases the energy of the metal to ligand d → π* transition. Hydrogen bonding to the coordinated cyanide weakens the metal-cyanide bond, increases the partial positive charge on the metal, lowers the energy of the metal *d*-orbitals and increases the energy of the transition.

The analysis of the solvent influence on the electronic spectra of $Fe(phen)_2(CN)_2$ with the Unified Solvation model has provided details about the behavior of this solute in polar-, *pi-* and acceptor-solvents. This information is essential to the understanding of the spectroscopy and reactivity of this and similar phenanthroline and bipyridine complexes.

Cu (tmen) aca$^+$

The complex N,N,N′,N′-tetramethylethylenediamine acetylacetanato copper(II) is suggested[10] as a probe of solvent donor strength. The color of the square planar complex is assigned to a d-d transition d_{xy}, $d_{yz} \rightarrow d_{x^2-y^2}$. Coordination of ligand on the *z*-axis raises the energy of the d_{xz} and d_{yz} *orbitals to a greater extent than the energy of the* $d_{x^2-y^2}$ orbital, increasing the transition energy. Values for this electronic transition in the complex dissolved in several donor solvents are given in Table 2. When the data are substituted into Equation (1) along with the S' values of the solvents and solved for P, a very poor fit results. Non-specific solvation is not the dominant contribution to the observed shift. Specific donor-acceptor interactions involving coordination of the donor on the *z*-axis probably are involved when the complex is dissolved in donor solvents. To test this proposal, the data are fit to the E, C, W model, *i.e.*, Equation (2) with $S'P$ set to zero, because non-specific solvation contributions are presumed absent. An excellent data fit results with an averge deviation, $\bar{x}$, of 0.13 and a percent fit[11] (100 × $\bar{x}$/Range) of 4.2%. This result suggests that non-specific solvation plays a minor role in influencing the electronic

Table 2 Electronic transition of Cu tmen $acac_2^+$ in various solvents (in kK)

	ν_{calc}				ν_{calc}
Solvent(S')	ν_{exp}	ECW[a]	Solvent (S')	ν_{exp}	ECW[a]
CH_3NO_2 (3.07)	18.80	–	$(CH_2)_4O$(2.08)	17.27	17.07
$C_6H_5NO_2$ (2.61)	18.76	19.03	$(CH_3O)_3PO$ (2.55)	16.69	16.60
$PrCO_3$[b] (2.87)	18.05	17.89	$HCON(CH_3)_2$(2.80)	16.58	16.71
$(CH_3)_2CO$ (2.58)	17.51	17.59	$(CH_3)_2SO$ (3.00)	16.31	16.20
$CH_3C(O)C_2H_5$ (2.15)	17.33	(18.03)	C_5H_5N (2.44)	15.67	15.77

[a] Calculated with E_A* = -1.87, C_A* = -0.77 and W = 21.81.
[b] Propylene carbonate.

transition. The data fit was not improved by using Equation (2) and adding an $S'P$ term. A P-value of 0.07 ± 0.16 resulted for this complex, which is zero within experimental error. It would be desirable to double the number of solvents studied in order to fit the data to Equation (2) and to determine the small but expected non-specific solvation contribution for this system.

Ni (tfd) phen

The complex 1,10-phenanthroline trifluorodithiolene nickel(II) undergoes spectral changes when added to various solvents.[12] In the earlier evaluation of S' parameters[3], this system produced a fair fit for non-specific solvation, the data in Table 3 provide an alternate interpretation of the spectral shifts. Both specific and non-specific interactions are proposed to influence the shift in donor solvents. Furthermore, steric problems with diethyl ether and incomplete complexation by toluene decreases the magnitude of the shift contribution from specific interactions with these donors. Aggregation of probe molecules in these solvents may lead to the low experimental values. The data are fit to Equation (2) with $E_A^* = 0.133$, $C_A^* = 0.137$, $P = 4.32$ and $W = 45.02$. The parameters indicate that non-specific solvation makes the dominant contribution to the shift with smaller contributions from weak donor-acceptor interactions. The donor-acceptor component has appreciable contributions from both the covalent and electrostatic bond formation tendencies of the donor ($C_A/E_A = 1$). DMSO and nitromethane have comparable shifts because of the stronger donor properties of the former and the stronger solvating properties of the latter.

The electronic transition is mainly dithiolene $b_2(2b_{1u})$ diimine in character. The ground state is polar, and the electronic transition reverses the direction of polarity causing an increase in the energy of the transition from non-specific solvation. Coordination to nickel functions in the opposite manner from electron releasing substituents on the dithiolene[12]. Coordination increases the dithiolene contribution to the ground state orbital and increases the transition energy.[12]

The complexities involved when this probe is studied in acceptor solvents are greater than those in donor solvents. The shifts calculated for the non-specific component of solvation in CH_2Cl_2 and $CHCl_3$ (*i.e.*, $PS' + W$) are 55.7 and 54.6, respectively, compared to experimental values of 54 and 48.6. Since $CHCl_3$ is not

Table 3 Solvent shifts of ni(tfd)(phen)

Solvent	$\Delta\chi_{exp}$	$\Delta\chi_{calc}$	Solvent	$\Delta\chi_{exp}$	$\Delta\chi_{calc}$
$(C_2H_5)_2O$	51.5	(52.0)[b]	CH_3NO_2	58.6	58.7[b]
EtOAc	54.7	54.7[a]	C_5H_5N	56.4	56.3[a]
$(CH_3)_2CO$	57.0	56.6[a]	CH_3OH	56.8	56.0[c]
$(CH_2)_4O$	54.2	54.5[a]	C_2H_5OH	55.7	56.1[c]
$HCON(CH_3)_2$	57.8	57.6[a]	n-C_3H_7OH	55.5	55.8[c]
$(CH_3)_2SO$	58.3	58.5[a]	i-C_4H_7OH	55.2	56.0[c]
CH_3CN	58.1	58.3[a]	$CHCl_3$	53.7	52.7[c]
$O(C_2H_4)_2O$	53.8	53.8[a]	CH_2Cl_2	55.3	54.3[c]
$C_6H_5CH_3$	50.8	(52.1)[b]	CH_3CO_2H	55.8	56.6[c]

[a] Calculated with $W = 45.0$, $E_A^* = 0.133$, $C_A^* = 0.137$, $P = 4.33$.
[b] Omitted from the fit and calculated with the parameter in footnote a.
[c] Calculated with $W = 45$, $E_B^* = 0.49$, $C_B^* = -1.36$ and $P = 4.33$.

expected to be a donor toward acids of weak or moderate strength, the larger calculated value than the observed value suggests that hydrogen bonding interactions occur and increase the transition energy above that calculated for non-specific solvation. Deviations in the same direction are not obtained when the non-specific solvation component of the solvation is calculated for alcohol solvents and the calculated shift is compared to the experimental result. Thus, the data in hydrogen bonding solvents are fit to Equation (2) using E_A', C_A' and S' for the solvents and $W = 45.0$ and $P = 4.33$ for the probe.

A poor fit of the solvent shift for Ni(tfp)(phen) toward hydrogen bonding solvents results as shown in Table 3. In view of the quality of the fit, few conclusions can be drawn regarding the influence of alcohol solvents on the electronic spectrum of Ni(tfd)(phen). Alcohol solvents can behave as donors or acceptors. However, both hydrogen bonding and coordination to nickel (II) by the alcohol solvents should increase the transition energy which in all instances is even lower than that predicted by S' above. The observed deviations for these solvents are in the direction that is consistent with aggregation of the nickel(II) complex in these solvents. In the case of the donor solvents, aggregation in $(C_2H_5)_2O$ and toluene led to low values for the transition energy.

In this manner, a consistent explanation of the spectral shifts of Ni(tfd)(phen) in donor and acceptor solvents is provided. More systems should be studied to test the tentative explanations that have been offered. The Unified Solvation model provides a means of quantitatively examining the many possible reactions that this complex can undergo in solution. This extensive reaction chemistry makes Ni(tfd)(phen) a poor probe for evaluating solvent properties.

SUMMARY

The three examples provided in this study illustrate the variety of molecular interactions that coordination compounds can undergo in solution and the application of the Unified Solvation model in differentiating between these interactions. The Unified Solvation model can be employed to correlate observed physicochemical changes under circumstances where the coordination compound is a donor or an acceptor. The procedure to be employed for fitting data for these different scenarios is illustrated with the examples selected. Deviations in the calculated and experimental values signal the presence of unusual interactions. Proposals for these interactions can be offered if patterns in the deviations can be detected. Experiments can then be designed to support or reject the proposed cause of the deviation.

EXPERIMENTAL

Fresh solvents were purchased from either Fisher-Scientific or Aldrich. A solution of Burgess Dye ($\sim 1.1 \times 10^{-4}$ M) was made in each solvent. The UV/vis spectrum of each solution was taken using a Perkin-Elmer Lambda 6 spectrophotometer. The spectra were resolved using Peak Fit^{TM} by Jandel Scientific.

The calculations were done using a least square minimum routine as reported in our earlier paper.[3] The data fit for Table 1 was done as follows. The known S'

parameters for the donor solvents were used to calculate the best P and W. For the data fit of the H-bonding solvents, the W (12.49) was subtracted from the χ_{exp}. Using the reported[3] E_A, C_A and S' and holding P (1.38) fixed, the series of simultaneous equations was solved for the best $E_B{}^*$ and $C_B{}^*$ values. This procedure is referred to as a data fit.

A data fit of the results in Table 2 was carried out using the above program to find the best $E_A{}^*$, $C_A{}^*$ and W. The W obtained was subtracted from ν_{exp}, and the data were fit again to obtain the best $E_A{}^*$, $C_A{}^*$ and P. No improvement in the data fit resulted. Since the numbers for $E_A{}^*$ and $C_A{}^*$ were statistically equivalent to the original data fit, the original parameters are reported.

The fit in Table 3 is carried out using a least squares program that best fits the data to the four unknowns in Equation (2). For hydrogen bonding solvents, the W and P from the donor solvent fit are used along with the known E_A', C_A' and S' to determine the best $E_B{}^*$ and $C_B{}^*$.

References

1. R.S. Drago, *J. Chem. Soc. Perkins Trans 2* **114**, 9527 (1992).
2. R.S. Drago, *J. Org. Chem.* **57**, 6547 (1992).
3. R.S. Drago, M.S. Hirsch, D.C. Ferris, C.W. Chronister, *J. Chem Soc. Perkin Trans*, **2**, 219 (1994).
4. a) R.S. Drago, *Coord. Chem. Rev.* **33**, 251 (1980).
   b) R.S. Drago, N. Wong, C. Bilgrien, G.C. Vogel, *Inorg. Chem.* **26**, 9 (1987).
   c) R.S. Drago, G.C. Vogel, *J. Am. Chem. Soc.* **114**, 9527 (1992).
   d) R.S. Drago, M.K. Kroeger, J.R. Stahlbush, *Inorg. Chem.* **20**, 306 (1981).
5. R.S. Drago, A.P. Dadmun, G.C. Vogel, *Inorg. Chem.* **32**, 2473 (1993).
6. A.A. Shilt, *J. Am. Chem. Soc.* **82**, 3000 (1960).
7. a) Burgess, *J. Spectrochim. Acta 26A* **1369**, 957 (1969).
   b) Burgess, *J. Organometal. Chem.* **19**, 218 (1969).
8. D.F. Shriver, J.J. Posner, *J. Am. Chem. Soc.* **88**, 1672 (1966).
9. S. Spange, D. Kentel, *Lebigs Ann. Chem.*, **1192**, 423.
10. a) V. Gutmann, R. Resch, *Monatsch fur Chemie*, **119**, 1251 (1988).
    b) A.A.G. Tomlinson, R.J. Hathaway, *J. Chem. Soc. A 1905 (1968).*
    c) K. Sono, Y. Fukuda, Stud in Phy and Theort. Chem, **27**, 254 (1982) and references therein.
    d) R.W. Soukup, R. Schmid, *J. Chem. Educ.* **62**, 454 (1985).
11. See reference 5 for a more complete discussion of these quantities.
12. T.R. Miller, I.G. Dance, *J. Am. Chem. Soc.* **95**, 6970(1973).