Solvatochromism of Mono- and Dimolybdenum Coordination Compounds of Dipyridyloctatetraene and Linear Solvation Energy Relationship Models Based on the Kamlet−Taft and Drago Scales of Solvent Polarity

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The heteroleptic molybdenum complexes [{Mo(NO)Tp*X}$_n$(L-L)] [Tp* = HB(3,5-$Me_2C_3HN_2$)$_3$; X = Cl, I; L-L = 4-$NC_5H_4(CH{=}CH)_4C_5H_4N$-4′, n = 1, 2; X = Cl; L-L = {4,4′-$NC_5H_4CH{=}CHC(Me){=}CHCH{=}$}$_2$, n = 2] have a low energy absorbance in their electronic spectra which exhibits solvatochromic shifts. These have been analyzed quantitatively by means of linear solvation energy relationships based on Kamlet−Taft solvatochromism parameters, as well as on Drago's "unified scale of solvent polarity". Each of these approaches leads to satisfactory linear models, in qualitative agreement with one another. The solvatochromism is due to a combination of increased solvent dipolarity/polarizability and solvent-to-solute hydrogen bonding, each preferentially stabilizing polar ground states compared with less polar excited states. The latter originate from metal-to-ligand charge transfer. Quantitatively, the Drago and Kamlet−Taft models differ somewhat. The former are statistically slightly better than those based on Kamlet−Taft parameters.

The chemistry of the lower oxidation states of molybdenum (II → −II) is dominated by carbonyl and organometallic species[1] and there are relatively few examples of stable compounds containing Mo(I), but of these many are nitrosyl derivatives containing halide or nitrogen- or phosphorus-based ligands.[2] In these species, the nitrosyl ligand is formally represented as NO^+, acting as a three-electron donor to the metal by provision of the σ lone pair electrons on the N atom *and* the π^* electron of NO. According to this formalism, species containing {Mo(NO)}$^{2+}$ can be regarded as derived from d^5 Mo(I) bonded to an NO^+ group.

One particular series of complexes containing the {Mo(NO)}$^{2+}$ center having the general structure **1** {Tp* is the tridentate ligand **2** (hydrotris-3,5-dimethylpyrazol-1-yl)borate;[3] X is Cl, I} is of particular interest as it includes bimetallic complexes (n = 1) which exhibit measurable interactions between metal centers separated by as much as 20 Å.[4−6] Thus, in **4**, substantial antiferromagnetic interactions (J *ca.* 40 cm^{-1}) have been observed between the remote {Mo(NO)}$^{2+}$ centers {separation 20.764(3) Å}.[6] Furthermore, electrochemical studies of the complexes **1** (n = 1, m = 0−4), in which each metal center has a formal 17-electron configuration, reveal two one-electron reduction processes, separated by 765 mV when m = 0 decreasing to 105 mV when m = 4.[4,5]

Some insight into the way in which these strong interactions may be facilitated can be gleaned from the observation of the increase of 0.3 Å in the Mo−N (amido/amine) bond length between the 16-electron *amido* complexe [Mo(NO)Tp*I({N-$(CH_2)_4$}] {1.937(5) Å} and a 17-electron *amine* analogue [Mo(NO)Tp*I{NH$(CH_2)_5$}] {2.241(6) Å}.[7] The increase is associated with a decrease in formal oxidation state, which may be represented in terms of the formalism described above as {Mo(NO)}$^{3+}$ → {Mo(NO)}$^{2+}$, and is consistent with rehybridization at the N atom, from sp^2 to sp^3, effectively switching off the $p_\pi - d_\pi$ donation from N to Mo in the amido species. An alternative view of this is to regard the "electron deficient" 16-electron Mo center as an acceptor group and the formally reduced 17-electron moiety as at least "electron sufficient" or even as a potential donor. Extending these general considerations to the bimetallic species **1**, it is clear that the bipyridyl ligands should not be regarded as π-donors with respect to the molybdenum nitrosyl group and the N atoms cannot easily rehybridize. However, the ligands could act as π-acceptors with respect to the reduced 17-electron metal centers.

The finding that a low energy band in the electronic spectra of complexes **1** exhibited solvatochromic behavior provided an opportunity to obtain further information about the nature of the interactions of the {Mo(NO)}$^{2+}$ center with the pyridyl ligands. Accordingly a detailed examination of the solvatochromic behavior of the complexes **3** to **7**[7] has been undertaken. In the first instance, the well known Kamlet−Taft (K−T) solvatochromism parameters[8] were employed as quantitative solvent descriptors. However, toward the end of this study,

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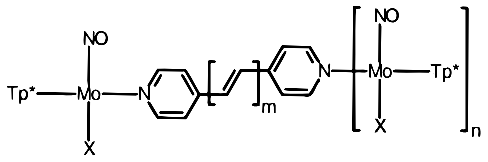
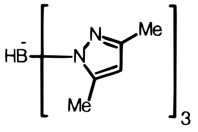
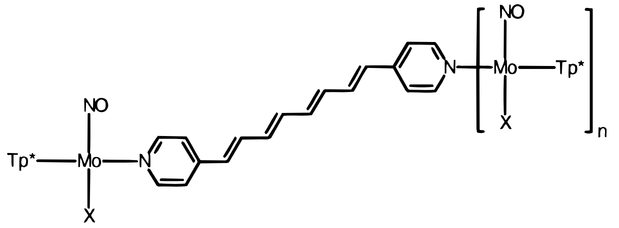


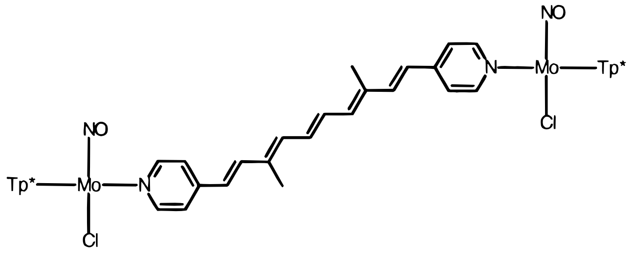
1 m = 0,1,2,3,4; n = 0,1; X = Cl, I



2 = Tp*$^-$



3 X = Cl; n = 0
4 X = Cl; n = 1
6 X = I; n = 0
7 X = I; n = 1



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work was published[9] by Drago and co-workers proposing[9b] a new "unified scale of solvent parameters". Thus a second analysis of the solvatochromism data was undertaken using the parameters described by Drago to allow a comparison of the two formalisms. This constitutes the second goal of the work described here.

Experimental Section

Materials. The syntheses of the molybdenum complexes are reported elsewhere.[6] Solvents were of the highest grade commercially available and were used as received.

Spectroscopy. Spectra were recorded at room temperature on dilute solutions using Shimadzu UV-240 and Cecil CE5501 spectrophotometers. Repeated scans gave absorption maxima within ±2 nm. Multilinear regression analyses were carried out using the commercial SAS and Statistica software packages,[10] taking full advantage of (multi)-colinearity diagnostics present in the routines.

Results and Discussion

The complexes **1** each contain a long wavelength absorbance in the visible region of the electronic spectrum, the λ_{max} of which is very solvent dependent, exhibiting marked negative solvatochromism. That is, more polar solvents induce a more hypsochromic λ_{max} (blue shift). This in turn indicates that the ground state (GS) is more polar than the excited state (ES), the observed solvatochromic shifts resulting from more (di)polar solvents stabilizing the GS more than the ES, leading to an increased transition energy or shorter wavelength absorbance.[11] In order to make a more detailed study of this solvatochromic behavior, the electronic spectra of **3**−**7** were measured at room temperature in a variety of solvents, selected to give as wide a spread of dipolarity/polarizability and H-bond acceptor and donor strengths as possible, consistent with solute solubility. Solvent selection was aided by a hierarchical cluster analysis of the solvent descriptors.[12] This ideally implies use of solvents of such diverse polarity characteristics as fluorocarbons on the one hand, and water, glycol, and formamide on the other. In the event, solubility in these, and a few other chosen solvents, proved to be too low to be useful. Nonetheless the visible spectra were measured for most of the solutes in about 25 solvents and data obtained are presented in Table 1.

Before any detailed analyses of the data were attempted, a preliminary evaluation was carried out. This simply involved plotting the absorbance maxima of one solute against that of each other solute (Figure 1). Direct correlations were observed, but a small number of solvents failed to fall within reasonable proximity of the ideal correlation lines. This was taken to indicate abnormal behavior for one or both the solutes in those particular solvents. In general, deviants were either nonpolar solvents, where poor solubility was accompanied by molecular association of the solute, or polar, strongly H-bonding solvents such as trifluoroethanol. Additionally, preliminary analyses in all cases showed that acetic acid was behaving anomalously. In these cases, data were not included in the statistical analyses reported below, but "omitted" values were then predicted from the derived statistical models, and compared with experiment.

Data Analysis. Besides the experimental λ_{max} values, Table 1 also records the corresponding Kamlet−Taft[8c] and Drago[9c] solvent polarity parameters. As noted in the introduction, one objective of this work was to relate the observed spectral data to these parameters by means of linear solvation energy relationships (LSER).[8a] A basic assumption is that the different intermolecular solvent−solute interactions can be treated separately and are additive. Since the relationship strictly concerns the energy of the electronic transition (E), it is necessary to derive this from the absorption maximum by means of E (10^3 cm^{-1}) = $10^4/\lambda_{max}$ (nm).

K−T based LSER were derived from the form

$$E = c_0 + c_1\pi^* + c_2\delta + c_3\alpha + c_4\beta \qquad (1)$$

where[8] π^* reflects solvent dipolarity and polarizability, α reflects solvent H-bond donor (HBD) ability, β reflects solvent H-bond acceptor (HBA) ability, and δ is a polarizability correction term for aromatic and halogenated solvents.[13] The HBD and HBA terms can also be taken to reflect other specific dipole-based solvent interactions with solute nucleophilic and electrophilic sites, respectively (*i.e.* Lewis acidity and basicity).

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Table 1. Absorbance Maxima and Solvent Parameters

		λ_{max} (nm)					Kamlet−Taft parameters				Drago's parameters		
		3	**4**	**5**	**6**	**7**	α	β	π^*	δ	S'	E_A'	C_A'
1	DMSO	548	555		542	546	0	0.76	1	0	3	0	0
2	CF_3CH_2OH	510	540		512		1.51	0	0.73	0	3.55	1.93	1.31
3	MeOH	535	540		540		0.98	0.66	0.6	0	2.87	1.55	1.59
4	MeCN	537	544	555	536	541	0.19	0.4	0.75	0	3	0	0
5	Me_2CO	550	559	558	547		0.08	0.43	0.71	0	2.58	0	0
6	EtOH	547	548		553		0.86	0.75	0.54	0	2.8	1.33	1.23
7	$CHCl_3$	560	572	573	562	572	0.2	0.1	0.58	0.5	1.74	1.56	0.44
8	py	557	567	570	555	565	0	0.64	0.87	1	2.44	0	0
9	1-PrOH	541	548		551		0.84	0.9	0.52	0	2.68	1.38	1.11
10	2-PrOH		554	560			0.76	0.84	0.48	0	2.66	1.28	0.83
11	EtOAc	563	574	579	560		0	0.45	0.55	0	2.15	0	0
12	Et_2O	581	584				0	0.47	0.27	0	1.73	0	0
13	THF	569	584		565	579	0	0.55	0.58	0	2.08	0	0
14	CH_2Cl_2	554	562	567	552	563	0.13	0.1	0.82	0.5	2.08	0.86	0.11
15	$PhNO_2$	555	575				0	0.3	1.01	1	2.61	0	0
16	ClC_2H_4Cl	553	566	573			0	0.1	0.81	0.5			
17	PhMe	586	598	597			0	0.11	0.54	1	1.66	0	0
18	PhOMe	570	589	564	570		0	0.32	0.73	1	2.04	0	0
19	$BzNMe_2$	591	608		590	602	0	0.64	0.45	1			
20	Et_3N	597	580				0	0.71	0.14	0	1.43	0	0
21	$MeCCl_3$	568	587				0	0	0.49	0.5	1.93	0	0
22	*n*-BuCl	574	594				0	0	0.39	0			
23	CCl_4	598	615	608			0	0.1	0.28	0.5	1.49	0	0
24	c-C_6H_{12}	613		603			0	0	0	0	1.11	0	0
25	HOAc	559	565				1.12		0.64	0	2.39	2.97	0.15

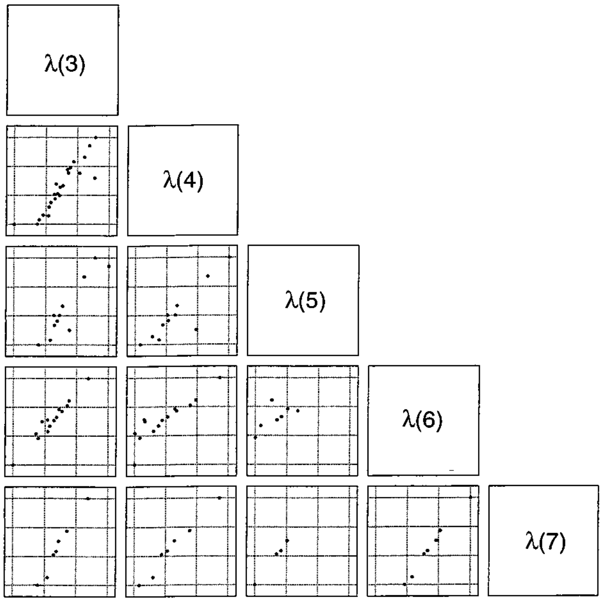

Figure 1. Correlation plots of λ_{max} values for molecules **3**−**7**.

The corresponding Drago formalism for Lewis base solutes is

$$E = W + PS' + E_B{}^*E_A{}' + C_B{}^*C_A{}' \qquad (2)$$

where S' is the solvent dipolarity term, and E_A' and C_A' quantify the electrostatic and covalent contributions, respectively, to Lewis acidity, and thus H-bonding, provided by a HBD solvent.[9c]

The regression coefficients c_1, c_2, and c_3 in the case of the K−T analyses and P, E_B^*, and C_B^* in the Drago formalism reflect the relative contribution of a particular physical interaction to excitation energies, E. Thus they are the parameters which indicate how a solute is interacting with solvent during photoexcitation and hence indicate the nature of the electronic reorganization taking place during photoexcitation. The terms c_0 and W are constants in the two respective treatments. Regression coefficients and constants were determined by multilinear regression analysis (MLRA), using standard software, and the results obtained are recorded in Table 2. The statistics reported are the standard deviation, s, the square of the correlation coefficient, r^2, and Fisher's F statistic.[14] The independent variables used in the MLRA were checked in advance for (multi-)colinearities, and none were found. Regression coefficients are therefore assumed to be reliable, except where noted below. Example plots of experimental excitation energies, E, vs those calculated by the MLRA equations are given in Figure 2 for molecule **3**. The following discussion examines the data for each molecule in turn. The overall picture which emerges from the MLRA based on K−T solvent descriptors is then considered followed by the results obtained using the newer parameters proposed by Drago.

MLRA with Kamlet−Taft Solvatochromism Parameters. Several general observations from the K−T series of MLRA (left-hand side of Table 2) are of immediate note.

(a) In each case, the c_0 term reflects the excitation energy predicted from the model for cyclohexane as solvent, where $\pi^* = \delta = \alpha = \beta = 0$.

(b) The c_1 coefficient of π^* is positive in all cases, reflecting the negative solvatochromism observed.

(c) The coefficient c_2 for the polarizability correction term, δ, is negative in all cases. This behavior is consistent with most previous analyses of negative solvatochromism.[13] Physically, this implies that at least part of the polarizability contribution included inherently in π^* is not operative in these (and other) negatively solvatochromic systems.

(d) The term which quantifies the HBD ability of a solvent (Lewis acidity, α) is relatively important in all molecules **3**−**7**, as reflected by the magnitude of its coefficient c_3. The positive sign of this coefficient indicates that increased H-bonding contributes to increased negative solvatochromism.

(e) Finally, solvent HBA ability ("basicity", β) is unimportant in most molecules. This reflects the situation that there is no

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Table 2. Results of Multilinear Regression Analyses

solvent set	MLRA using Kamlet−Taft parameters										MLRA using Drago parameters								
	entry	c_0	c_1 (π*)	c_2 (δ)	c_3 (α)	c_4 (β)	*n*	r^2	*s*	*F*	entry	*W*	*P* (*S*′)	E_B* (E_A′)	C_B* (C_A′)	*n*	r^2	*s*	*F*
Molecule **3**																			
all	1	16.508 (±0.097)	2.121 (±0.161)	−0.508 (±0.105)	0.984 (±0.105)		23	0.95	0.177	120.2	2	15.242 (±0.137)	1.101 (±0.065)	0.597 (±0.113)	−0.508 (±0.153)	20	0.97	0.145	170.2
	3						*20*	*0.947*	*0.194*	*95.7*									
nonHBD	4	16.516 (±0.097)	2.073 (±0.177)	−0.482 (±0.113)			16	0.916	0.185	70.7	5	15.250 (±0.169)	1.097 (±0.081)			13	0.942	0.153	179.1
	6						*13*	*0.91*	*0.202*	*50.4*									
nonArH	7	16.492 (±0.113)	2.121 (±0.202)	−0.306 (±0.226)	0.992 (±0.113)		18	0.95	0.202	88.2									
	8	16.468 (±0.113)	2.065 (±0.202)		1.048 (±0.113)		18	0.943	0.202	123.6	9	15.226 (±0.169)	1.113 (±0.081)	0.597 (±0.129)	−0.516 (±0.177)	16	0.969	0.169	124.2
	10						*16*	*0.944*	*0.218*	*109.7*									
Molecule **4**																			
all	11	16.274 (±0.161)	2.000 (±0.234)	−0.661 (±0.129)	1.113 (±0.153)		21	0.909	0.210	56.5	12	14.903 (±0.266)	1.089 (±0.121)	0.540 (±0.161)	−0.306 (±0.226)	18	0.915	0.202	50.3
	13						*18*	*0.898*	*0.218*	*40.9*									
nonHBD	14	16.290 (±0.169)	1.911 (±0.274)	−0.621 (±0.145)			14	0.838	0.226	28.4	15	15.032 (±0.331)	1.024 (±0.145)			11	0.841	0.218	47.4
	16						*11*	*0.81*	*0.250*	*17.1*									
Molecule **5**																			
all	17	16.427 (±0.129)	1.831 (±0.202)	−0.629 (±0.145)	0.782 (±0.242)		11	0.94	0.161	36.9	18	15.331 (±0.226)	0.919 (±0.105)	0.548 (±0.185)	−0.750 (±0.419)	10	0.938	0.169	30.3
	19						*10*	*0.949*	*0.153*	*37.5*									
nonHBD	20	16.427 (±0.169)	1.863 (±0.298)	−0.661 (±0.202)			7	0.909	0.202	20.1	21	15.258 (±0.315)	0.968 (±0.161)			6	0.901	0.210	36.2
Molecule **6**																			
all	22	16.782 (±0.274)	2.145 (±0.323)	−0.556 (±0.129)	0.742 (±0.113)	−0.427 (±0.185)	14	0.942	0.169	36.7									
	23	16.444 (±0.282)	2.298 (±0.387)	−0.500 (±0.153)	0.782 (±0.129)		14	0.91	0.210	32.4	24	15.427 (±0.282)	1.065 (±0.113)	0.540 (±0.137)	−0.645 (±0.185)	13	0.929	0.161	39.5
	25						*13*	*0.864*	*0.218*	*19*									

acidic hydrogen or Lewis acid center in **3**−**7** whose charge varies on photoexcitation. (An exception may be the iodo group in **6**; see below).

Solvatochromism of Molecule 3. Monometallic derivative **3** proved insoluble in 2-propanol of the 25 solvents selected for measurement of λ_{max}. Following preliminary MLRA, the measurement in acetic acid was omitted from the statistical analyses. MLRA were run on data measured in the remaining 23 solvents. It was found that the three parameters π*, α, and δ are significant (entry 1, Table 2, and Figure 2a). The H-bond acceptor parameter, β, is insignificant. Regressions based on two or less of the parameters were far inferior (not shown in Table 2).

Since HBD solvents can sometimes give rise to spurious effects due to their self-association,[15] a subset of data measured in 16 non-HBD solvents ($\alpha = 0$) was analyzed to give an MLRA model based on π* and δ only (entry 4, Table 2). The regression coefficients and statistics r^2 and *s* hardly change, indicating that the HBD solvents included in the first MLRA (entry 1) are behaving normally in this system.

A subset of this data set excluding all aromatic solvents also gave essentially the same regression model (entry 7, Table 2), except that the c_2 polarizability correction term is now barely statistically significant. A parallel analysis omitting this parameter resulted in little change to the statistics (entry 8). It would appear that although this term is reportedly applicable to multichlorinated solvents,[13a] which are still included in the series, its importance in this instance is low.

The major deviation from the generally good linear model is the measurement in DMSO, the second most hypsochromic of the solvents studied. The absorbance in DMSO is particularly close to the side of another strong absorbance centered near 400 nm, and thus may be inaccurate. (This latter is probably due to a $\pi \rightarrow \pi$* excitation associated with the dipyridyloctatetraene ligand.) When this point is deleted from the series, the regression coefficients c_n change only slightly, indicating that the DMSO point is not biasing the model.

The solvatochromic behavior of the band at *ca.* 560 nm implies, above all else, that the photoexcitation involves a charge transfer process leading to a change in the polarity of the molecule. The absence of a similar absorption band in the spectrum of $[Mo(NO)Tp^*Cl_2]^-$, along with the variation in the position of the band with changes in the bipyridyl ligand in the complexes **1**,[6] indicates that charge transfer is between the metal and the bipyridyl ligand. There is literature precedent both for photoexcited metal-to-ligand charge transfer (MLCT), as well as the reverse (LMCT),[16−22] and *a priori* there is no reason for knowing which is present in **3**. The solvatochromism results may be used to decide which alternative applies.

Considering first the polarization of the metal−ligand (Mo-bpot) (bpot = bipyridyloctatetraene) system in **3** in the *ground state*, three limiting situations may be defined: (a) polarization (−)Mo-bpot(+); (b) essentially unpolarised, Mo-bpot; and (c) polarization (+)Mo-bpot(−). Any alternative would be intermediate between these or just more extreme cases of a or c. In principle, each of these could undergo either MLCT or LMCT on photoexcitation leading to ES polarization as shown in Figure 3, where py represents one end of the bpot ligand, and other

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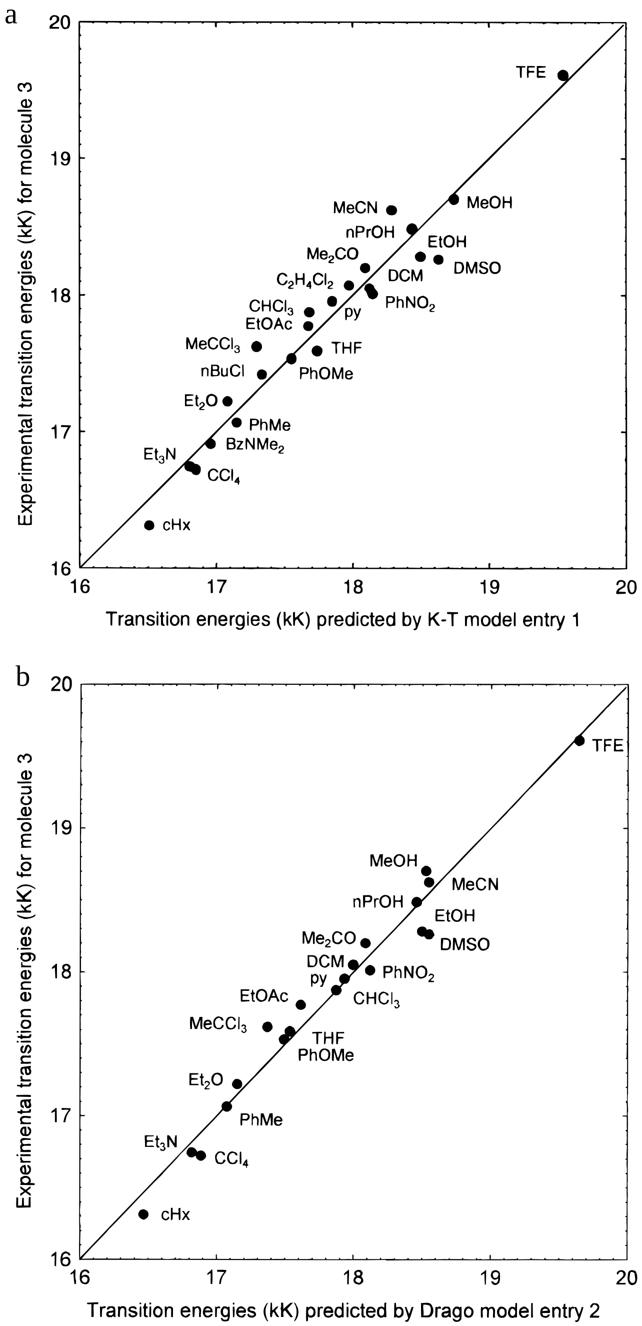

Figure 2. Example plots of experimental excitation energies (10^3 cm^{-1}) against those calculated by multilinear regression models in Table 2 for compound **3**: (a) entry 1 based on Kamlet–Taft solvatochromism parameters; (b) entry 2 based on Drago's parameters. Note: kK = 10^3 cm^{-1}.

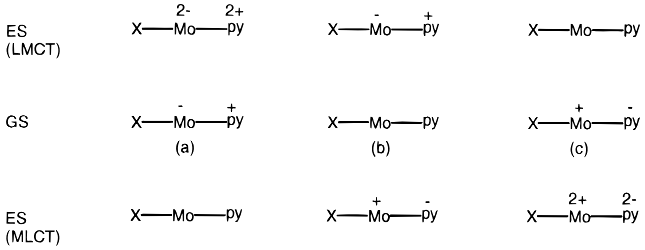

Figure 3. Three limiting ground state polarizations for molybdenum centers in compounds **3**–**7**, and corresponding idealized excited state polarizations after LMCT or MLCT.

ligands to Mo are abbreviated X. In general, if the GS is more polar than the ES, increasingly dipolar solvents will lead to hypsochromic shifts, reflected by a positive value for the c_1 coefficient of π^*. The reverse applies for a more polar excited state.

Table 3. Anticipated Signs of Regression Coefficients c_1 and c_3 Depending on Different Ground State Polarizations (Figure 3), Direction of Charge Transfer on Excitation, and Solvent H-Bonding Site in Solute

entry	excitation and polarization type	c_1 (π^*)	c_3 (α) Cl/NO···HBD	py···HBD
i	MLCT (a)	+	+	−
ii	MLCT (b)	−	+	−
iii	MLCT (c)	−	+	−
iv	LMCT (a)	−	−	+
v	LMCT (b)	−	−	+
vi	LMCT (c)	+	−	+

There are three feasible HBA sites in **3**: the *uncomplexed* bpot nitrogen atom, the nitrosyl oxygen, and the chloride ligand. For a HBD solvent H-bonding to the free pyridine ring in **3** in the GS, an energetically less favorable situation will result if charge is transferred from the bpot ligand to Mo on photoexcitation (LMCT). This will result in a hypsochromic solvatochromic shift, reflected by a positive c_3 coefficient for the HBD term. MLCT will lead to a negative c_3 value under the same conditions. The exact opposite will apply for HBD solvents H-bonding to the other HBA ligands (NO, Cl) attached to Mo, since their H-bonding propensity is expected to be reflected in turn by inductive polarization by the Mo atom. All these options are summarized in Table 3, where the + and − signs refer to the signs of the c_1 and c_3 coefficients. (Of course it is possible that the uncomplexed pyridine and the NO/Cl ligands are all H-bonded to HBD solvents in the GS. The observed effect on solvatochromism in such a case will therefore be dependent on the relative contributions deriving from the different H-bonding sites. We will return to this point later and, for the present, continue the discussion assuming a single H-bonding site).

There are only two options present in Table 3 consistent with the statistical analysis (entry 1, Table 2) of the experimental data which indicates both c_1 and c_3 are positive. These correspond to (i), which represents MLCT with H-bonding to the NO or Cl ligands in the GS, and (vi), which represents LMCT and H-bonding to the uncoordinated pyridine nitrogen. Results from **4**, the bimetallic analogue of **3**, may be used to show that the former is in fact the situation which pertains. Additionally, the exact nature of the H-bonding site in **3** only becomes clearer on consideration of the results for **6**, the iodo analogue of **3**, as described below. Furthermore, this analysis says nothing about the strength of the H-bond between solvent and molecule **3** in the GS, merely that there is one. However, its strength is less than that required to break apart the acetic acid dimer, as the following result indicates. If the π^* and α values for acetic acid are substituted into the MLRA equation (entry 1, Table 2), the estimated transition energy corresponds to λ_{max} = 528 nm, clearly at variance with the measured λ_{max} (559 nm). However, if *no* H-bonding is assumed for this solvent (α set equal to 0 for HOAc), the calculated λ_{max} is now 560 nm, equal to experiment. This implies that the strength of the Mo–X···HOAc interaction is too weak to cause rupture of the very strong solvent···solvent H-bonds in the 8-membered acetic acid cyclic dimer. This phenomenon has been noted previously.[15] The energy of self-association of the other hydroxylic HBD solvents is not sufficient to prevent solvent···X–Mo H-bonding in the GS.

Solvatochromism of Molecule 4. This species is the bimetallic analogue of **3**. Both trifluoroethanol and acetic acid were omitted from the data analysis. Furthermore it was clear from the preliminary plots that λ_{max} measured in triethylamine was anomalous, and this was also omitted. Since the solubility of **4** in cyclohexane was minimal the λ_{max} value for this solvent was considered unreliable and was not used. The MLRA analysis of the remaining 21 data points gave the result of entry 11 in Table 2. It is significant that the form of the regression equation is very similar to that for the monometallic analogue **3**. The same overall interpretation of the regression coefficients applies.

The fact that the c_3 coefficient of α, the HBD term, is essentially the same for **3** and **4** excludes the possibility that the solute HBA site responsible for solvatochromism is uncoordinated pyridine in **3** since this is no longer present in **4**. This leads to the conclusion that H-bonding to NO and/or Cl contributes to the observed solvatochromism. Furthermore, it now follows from Table 3 that the first excitation of **3** and **4** is a MLCT process. The MLRA equation (entry 11) predicts a transition energy corresponding to λ_{max} values of 531 nm for **4** in H-bonding glacial acetic acid, and 570 nm with $\alpha = 0$ (to mimic no H-bonding), compared with 565 nm (experimental). The situation is the same as for **3**; HOAc does not H-bond to **4**. The prediction of λ_{max} for trifluoroethanol is 564 nm ($\alpha = 0$), and 514 nm (H-bonding), compared to 540 nm (experimental). Although this prediction is not good, the indication is that trifluoroethanol does, at least partially, H-bond to **4**. The extrapolated value for triethylamine is 604 nm (experimental 580 nm), and for cyclohexane is 614 nm (experimental very roughly 580 nm). It is believed that **4** is aggregating in these solvents and that the experimental λ_{max} in triethylamine and cyclohexane may no longer be compared with those for the other solvents.

Repeating the MLRA for the absorption maxima of **4** in solely non-HBD solvents gives the results of entry 14 (Table 2). The regression coefficients are again hardly altered, although the s and r^2 statistics are somewhat inferior.

Solvatochromism of Molecule 5. This bimetallic compound is very similar to **4**, differing by one extra C=C unit and the presence of two methyl groups on the pentaene linking chain. (The presence of these substituents was necessary for synthetic convenience.) For the 10 solvents which are common to **4** and **5**, the absorption maxima of the latter are on average 3 nm more bathochromic than those for **4**. Clearly increasing the polyene chain length by 1 unit has little effect on the spectra.

As would be anticipated, the MLRA results for **5** (entry 17, Table 2) are similar to those for **4**. The physical interpretation is the same. However, the regression coefficients for **5** are less reliable since they have been derived from a much smaller data set. One small difference is the fact that the datum for cyclohexane now fits the MLRA model satisfactorily. Presumably, the methyl substituents on the dipyridyl ligand in **5** inhibit aggregation in this solvent at the concentration studied.

Solvatochromism of Molecules 6 and 7. These are the iodo analogues of the chloro derivatives **3** and **4**, respectively. These compounds were studied in the hope that it might prove possible to distinguish between the NO and Cl ligands as the H-bond acceptor site. H-bonding to I−Mo would be expected to be much weaker than to Cl−Mo and, if present, should show up in the corresponding MLRA. In the event, MLRA of the excitation energies of **6** gave an expression similar to that for **3** (entry 35, Table 2). The goodness of fit as reflected by s and r^2 is inferior to that for **3**, but the regression coefficients are very similar. We take this to indicate a common HBA site in **3** and **6**, and this can only be nitrosyl oxygen.

Further study of the data for **6** revealed that the solvent HBA term, β, may also be significant in this series (entry 34, Table 2). Given the limited amount of data in the data set (14 solvents only), it is not clear if this is experimentally significant, or merely a statistical artifact. We can offer no meaningful chemical rationalization.

The bimetallic diiodo analogue **7** proved too insoluble to measure in more than a small number of solvents, and no MLRA was attempted. However, a plot of the limited data available against that for **4** revealed no surprising outliers. As far as can be determined, **7** parallels **4** in its solvatochromic behavior.

MLRA with the Unified Scale of Solvent Parameters. In order to obtain an alternative interpretation of the solvatochromism data for **3**−**7** which might lend further support to the proposed model involving MLCT with NO as a Lewis base site, the data were also analyzed using the "unified scale of solvent parameters" proposed by Drago.[9] This also provides a timely opportunity to compare the K−T and Drago models. A possible source of confusion in the application of these two models derives from the conflicting meanings of "donor" and "acceptor" as used by K−T and by Drago. The former apply these terms to H-bonding characteristics, while Drago refers to electron pair properties, with the opposite connotations. We try to avoid this confusion by explicitly refering to H-bond donor (HBD) and H-bond acceptor (HBA) systems, or Lewis acids and bases. Solvents included in the MLRA are those used in the K−T analyses, above, assuming Drago parameters were available (Table 1).

The results are tabulated on the right-hand side of Table 2 opposite the corresponding K−T MLRA results. Since warnings have been published regarding the use of some solvent classes,[9c] subsets of the whole series were again analyzed. For example aromatic solvents can display extra interaction with π-acceptor solutes, and other solvents can interact anomalously with some strong electron donor solutes. In view of the relative consistency of the results obtained, the analyses are not discussed in the same detail as the K−T MLRA, above. (However, this should not be taken to indicate a preference for the former; we compare the two series of results below.) In general, MLRA analyses of the full data sets revealed dependence on both the dipolarity/polarizability parameter S' and both components of the Lewis acid quantification, E_A' and C_A'. The statistics indicated that these parameters gave good models of the form of eq 2 (see also Figure 2b). Furthermore, the regression coefficients were unchanged between the full data sets and the respective subsets, indicating that neither Lewis acid nor aromatic solvents are behaving anomalously toward the solutes. The sign of the dipolarity/polarizability coefficient, P, is positive, consistent with the MLCT interpretation already given. The positive sign of the $E_B{}^*$ coefficient implies that the electrostatic component of the specific solute−solvent interaction is contributing to a negative solvatochromic effect. However, the negative sign of the $C_B{}^*$ coefficient corresponding to the covalent part implies the opposite. This reversal of sign has been observed in earlier published work involving these parameters,[9c] and is discussed in a recent paper.[23] Despite the negative sign of $C_B{}^*$, the combined $E_B{}^*E_A' + C_B{}^*C_A'$ solvent−solute Lewis acid−base interaction term for the MLRA of **3**, **4**, and **5** is overall positive, implying that specific solvent−solute interaction (H-bonding to the solutes) adds to the nonspecific dipolarity/polarizability-induced negative solvatochromism. We believe this specific solute−solvent interaction has its origins in H-bonding. Thus the Drago and K−T solvent parameters give at least qualitatively similar models. However,

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Table 4. Components of Solvatochromism MLRA (10^3 cm^{-1}) for Compounds **3**, **4**, and **6**

	MLRA components for **3**				MLRA components for **4**				MLRA components for **6**			
	entry 1		entry 2		entry 11		entry 12		entry 23		entry 24	
	$c_1\pi^* + c_2\delta$	$c_3\alpha$	$PS' - 1.226$	$E_B{}^*E_A' + C_B{}^*C_A'$	$c_1\pi^* + c_2\delta$	$c_3\alpha$	$PS' - 1.210$	$E_B{}^*E_A' + C_B{}^*C_A'$	$c_1\pi^* + c_2\delta$	$c_3\alpha$	$PS' - 1.185$	$E_B{}^*E_A' + C_B{}^*C_A'$
DMSO	2.121	0.000	2.081	0.000	2.000	0.000	2.058	0.000	2.298	0.000	2.012	0.000
CF_3CH_2OH	1.548	1.486	2.686	0.486	1.460	1.680	2.656	0.641	1.678	1.181	2.597	0.198
MeOH	1.273	0.964	1.937	0.117	1.200	1.091	1.916	0.350	1.379	0.767	1.874	−0.188
MeCN	1.591	0.187	2.081	0.000	1.500	0.211	2.058	0.000	1.724	0.149	2.012	0.000
Me_2CO	1.506	0.079	1.618	0.000	1.420	0.089	1.600	0.000	1.632	0.063	1.565	0.000
EtOH	1.145	0.846	1.860	0.169	1.080	0.957	1.840	0.342	1.241	0.673	1.799	−0.075
$CHCl_3$	0.976	0.197	0.694	0.707	0.829	0.223	0.686	0.708	1.083	0.156	0.671	0.559
py	1.337	0.000	1.464	0.000	1.079	0.000	1.448	0.000	1.500	0.000	1.416	0.000
1-PrOH	1.103	0.826	1.728	0.260	1.040	0.935	1.709	0.405	1.195	0.657	1.671	0.030
2-PrOH	1.018	0.748	1.706	0.342	0.960	0.846	1.687	0.437	1.103	0.595	1.650	0.156
EtOAc	1.167	0.000	1.145	0.000	1.100	0.000	1.132	0.000	1.264	0.000	1.107	0.000
Et_2O	0.573	0.000	0.682	0.000	0.540	0.000	0.675	0.000	0.621	0.000	0.660	0.000
THF	1.230	0.000	1.068	0.000	1.160	0.000	1.056	0.000	1.333	0.000	1.033	0.000
CH_2Cl_2	1.485	0.128	1.068	0.457	1.309	0.145	1.056	0.431	1.635	0.102	1.033	0.394
$PhNO_2$	1.634	0.000	1.651	0.000	1.359	0.000	1.633	0.000	1.821	0.000	1.597	0.000
ClC_2H_4Cl	1.464	0.000			1.289	0.000			1.612	0.000		
PhMe	0.637	0.000	0.605	0.000	0.419	0.000	0.599	0.000	0.741	0.000	0.585	0.000
PhOMe	1.040	0.000	1.024	0.000	0.799	0.000	1.012	0.000	1.178	0.000	0.990	0.000
$BzNMe_2$	0.446	0.000			0.239	0.000			0.534	0.000		
Et_3N	0.297	0.000	0.352	0.000	0.280	0.000	0.348	0.000	0.322	0.000	0.341	0.000
$MeCCl_3$	0.785	0.000	0.903	0.000	0.649	0.000	0.893	0.000	0.876	0.000	0.873	0.000
n-BuCl	0.827	0.000			0.780	0.000			0.896	0.000		
CCl_4	0.340	0.000	0.418	0.000	0.229	0.000	0.414	0.000	0.394	0.000	0.405	0.000
c-C_6H_{12}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HOAc	1.357		1.409		1.280		1.394		1.471		1.363	

more detailed quantitative breakdown of the various components reveals the differences between the two treatments. Relevant data are recorded in Table 4. Figure 4a shows the $c_1\ \pi^* + c_2\ \delta$ dipolarity−polarizability term from the K−T treatment, plotted against the corresponding PS_A' term from the Drago analysis, for **3**. (The latter term is adjusted by −1.226, the cyclohexane value, to ensure the same zero reference.) The plot of $E_B{}^*E_A' + C_B{}^*C_A'$ vs $c_3\alpha$ representing the respective specific solvent−solute interactions, for **3**, is given in Figure 4b. Figure 4a shows the inevitable equality of the contributions for non-HBD solvents. Superimposed on this are the H-bonding solvents, and it is clear that their dipolarity/polarizability effects are represented quite differently by the K−T and Drago parameterizations. Figure 4b reveals that these deviations are compensated by the solvatochromic contributions of these solvents to differing degrees. Thus K−T assigns a much higher influence due to H-bonding for alcohols than Drago's *E*/*C* parameters for this solute. Furthermore both acetone and acetonitrile are assumed to be HBD solvents by K−T but have no specific Lewis acid effect according to Drago. (This is one of several central points of contention in Drago's critique of the K−T formalism.[9]) In contrast, Drago's parameters lead to a much greater solvatochromic effect for both chloroform and dichloromethane than the K−T α. The most counterintuitive observation is the interpretation from the Drago analysis that nominally strong HBD solvents such as methanol cause a relatively minor specific solvation solvatochromic effect in **3** (*cf.* Figure 4b) and also **4** and **5**, due to the negative $C_B{}^*$ coefficient. Indeed this effect becomes even more extreme for the iodo derivative **6** where the $E_B{}^*E_A' + C_B{}^*C_A'$ contributions for methanol and ethanol are now overall negative. This is a result of the negative covalent interaction now assuming the dominant part in the electrostatic-plus-covalent combination, presumably as a result of the weaker inductive effect of iodide in **6**, compared with chloride in **3**. The physical interpretation of the Drago analysis, that nominally similar HBD solvents can cause both positive (*e.g.* methanol) and negative (*e.g.* 2-propanol) contributions to overall solvatochromic shifts for the same solute, is a fundamental difference between the K−T and Drago formalisms. (While we refrain from commenting on which approach is "best", we note that Drago's use of two parameters to describe Lewis acid−base interactions is more in line with theoretical views of the H-bond, which recognize stabilizing contributions from two or more interactions.[24])

To allow fair comparison of the statistics of the models based on the two sets of solvent parameters, the K−T based MLRA were repeated on data sets containing exactly those solvents included in the Drago-based MLRA. The results are recorded on the left-hand side of Table 2, in italics. Regression coefficients are not reported; they differ little from those derived for the full data sets. For six of the comparable pairs of MLRA, the Drago parameters give statistically superior models. In the one other case, the K−T parameters give the better model. Parts a and b of Figure 2 clarify the deviations for **3** from the respective MLRA models for the two approaches

H-Bonding to Uncomplexed Pyridine in 3. More detailed analysis of the difference in absorption maxima between monometallic **3** and bimetallic **4**, $\Delta\lambda_{34}$, allows further consideration of the question of H-bonding at the uncomplexed pyridine of the dpot ligand present in **3**. In the case of 14 non-HBD solvents, the effect of the second, electropositive Mo center in **4** gives mean $\Delta\lambda_{34}$ shifts of 14 nm (SD 5.3 nm) compared with **3**. If HBD solvents are indeed H-bonding to the free pyridine of **3** the induced shift $\Delta\lambda_{34}$ is expected to be less, since conceptually one electropositive unit (the HBD solvent) would have to be removed before the second Mo center could be added to give **4**. In fact, the mean $\Delta\lambda_{34}$ value for 7 HBD solvents is 7 nm (SD 3.8 nm). Thus the indications are that HBD solvents might be interacting with uncomplexed pyridine in **3** to the extent of causing a *ca.* 7 nm. shift. However, this value is well within the combined SDs of the $\Delta\lambda_{34}$ estimates. (This analysis can be stretched a little further by considering the value of the C_3 regression coefficients of α for **3** and **4**. Any interaction of HBD solvent with free pyridine in **3** should attenuate the solvatochromic effect as reflected by the magnitude of the C_3 coefficient for **3** compared with **4**. This is in fact observed to

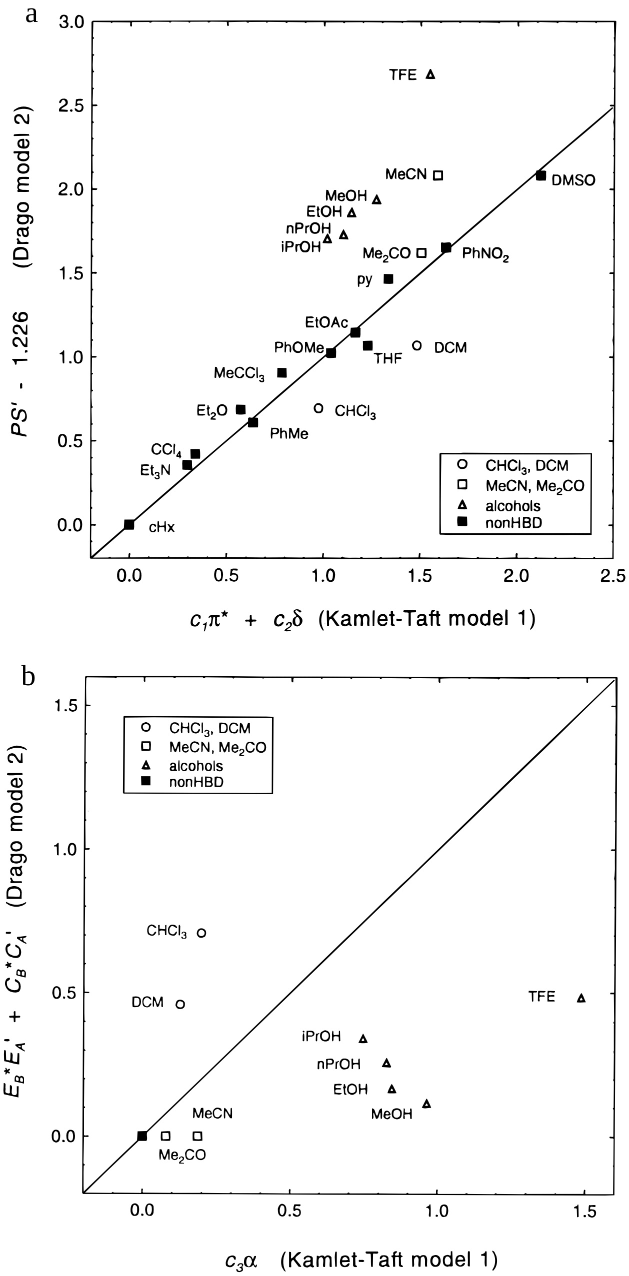

Figure 4. Plots of contributions to solvatochromic shifts (10^3 cm^{-1}) for molecule **3** as modelled by Kamlet–Taft and Drago parameters: (a) solvent dipolarity/polarizability; (b) solvent H-bond donor ability. The straight lines shown correspond to $y = x$. Note kK = 10^3 cm^{-1}.

be the case (*cf.* entries 1 and 11, Table 2), but again the difference is within the deviations calculated for the C_3 values. In contrast, the relative E_B* and C_B* magnitudes from the parallel series of analyses go in the opposite direction, although again the differences are slight (entries 2 and 12, Table 2). Thus this attempted analysis is also inconclusive.) Thus the data do not establish the presence or absence of an H-bonding interaction between HBD solvent and pyridine but show that, if present, it is having minimal effect on the spectra of **3**. The major solvatochromic effect of HBD solvents is associated with solvent H-bonding to the NO ligand attached to Mo.

Comparisons with Data for Other Complexes. The results obtained in this study of $\{Mo(NO)\}^{2+}$ compounds may be compared with those from earlier studies of solvatochromism in transition metal coordination compounds. The molybdenum(0) complexes, $[M(CO)_4(L\text{-}L)]$ (L = bpy, substituted *o*-phenanthrene), also exhibit negative solvatochromism which has been correlated with the K–T π* parameter.[17] In this earlier study the solvents were divided into different classes to produce acceptable correlations. We have now carried out multiparameter correlation analyses on this data and find that the transition energies of the bpy complexes correlate with π*, δ, and β, the solvent HBD parameter, α being insignificant. The influence of the first two terms is to be expected but the importance of β is unexpected. The only potential HBD sites in the molecules are the aryl hydrogens, although these would not normally be expected to be strong hydrogen bond donors. On the basis of data from another study, the solvatochromism of $[W(CO)_4(phen)]$ has been found to correlate with π* and δ alone, which is more in accord with expectation.[13b] A further example of negative solvatochromism has been found in the spectra of $[Fe(L\text{-}L)_2(CN)_2]$ (L-L = a bidentate Schiff base ligand)[18] and the data have been analyzed by a multiparameter relationship based on both π* and the HBD term α,[15] as well as the Drago S' plus $E_B{}^*E_A{}' + C_B{}^*C_A{}'$ model.[25] The K–T statistical model derived is the nearest to that found in the study described here, although in this case the δ term is unnecessary since the analysis included no polarizable aromatic or chlorinated solvents. Contrasting behavior is found in the spectra of the ruthenium complexes $[(NH_3)_5RuL]^{2+}$ (L = substituted pyridine). These contain a solvatochromic CT band which is strongly influenced by hydrogen bond acceptor solvents which weaken the H–N bonds of the NH_3 ligands.[16] The data have been correlated with single solvent parameters and the solvatochromism associated with a LMCT process.[19] The solvatochromism of mixed-ligand dithiolene/α-diimine complexes of nickel[22] and that of a mixed tetramethylethylenediamine/acetylacetonato copper(II) complex[25] have both been analyzed using the Drago parameters. Other studies of solvatochromism which relate less closely to the work described here involve the complexes $[M(\eta^5\text{-}C_5H_5)(CO)_2X]$ (M = Mn, Re; X = CO, alkylamine, substituted pyridine),[20] $[M(bipy)X_2]$ (M = Pt, Pd; X = Cl, Br, I, py) and $[Pt(bipy)(py)_2]$, [21] and a series of mixed-valence ruthenium ammine complexes.[26]

Conclusions

Two independent approaches to linear solvation energy relationships have both shown that the lowest energy electronic absorbances of molybdenum complexes **3**–**7** are due to MLCT. The negative solvatochromic shifts are caused by a combination of general solvent dipolarity/polarizability and solvent H-bonding to the nitrosyl ligands of **3**–**7**. The parameters of the Drago formalism lead to slightly better statistical models than those of Kamlet and Taft. Furthermore, the Drago analysis leads to a counterintuitive conclusion that Lewis acid (*e.g.* H-bonding) interactions of solvents with a basic solute can give both negative and positive contributions to the overall solvatochromic shifts. This results from the balance between opposite electrostatic and covalent interactions which are sometimes present in a given system, as exemplified by the nitrosyl molybdenum complexes described in this paper.

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