3212 *Inorg. Chem.* **1986**, *25*, 3212-3218

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Solvatochromism of the Metal to Ligand Charge-Transfer Transitions of Zerovalent Tungsten Carbonyl Complexes[†]

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Received January 14, 1986

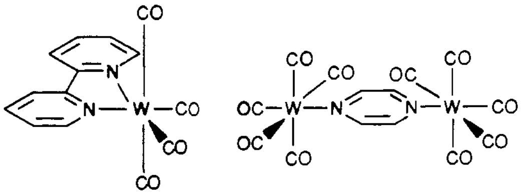
The strong negative solvatochromism of $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ has been studied in a wide range of organic media. The metal to ligand charge-transfer (MLCT) transitions of these complexes are extremely solvent sensitive, exhibiting red shifts of up to 5800 cm^{-1} as the solvent medium becomes less polar. Literature parameters, E_T and π^*, correlate to a high degree with the MLCT energies, but they are based on the transition energy of model compounds and do not provide a further understanding of solvent interaction at the molecular level. Similarly high correlations are also observed with the intrinsic solvent parameters dielectric constant, dipole moment, and polarizability. The strong solvent effects on the energy of the MLCT transition are concluded to be brought about by dipolar and polarizing solvent interactions on the ligand π-electron system.

Introduction

Solvent effects on the absorption spectra of transition-metal complexes have been recognized for a number of octahedral and square-planar systems. Generally, these solvatochromic properties are a result of shifts in the energy of transitions that are predominantly charge-transfer in character. For example, the strong solvent effects on the metal to diimine charge-transfer transition ($M \rightarrow \pi^*$) for *cis*-$M(CN)_2L_2$ (M = Fe, Ru)[1,2] and $M(CO)_4L$ (M = Cr, Mo, W)[3,4] complexes, where L = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 1,4-diazabutadiene (dab), or derivatives, have been noted by several investigators. Correspondingly, the solvatochromic properties of neutral square-planar $M(bpy)X_2$ (M = Pd, Pt; X = Cl, Br, I) complexes have also been shown to be associated with $M \rightarrow \pi^*(bpy)$ transitions.[5] For each of the above complexes the $M \rightarrow \pi^*$ absorption energies have been shown to correlate with Reichardt's E_T solvent polarity scale.[6] Also, solvatochromism attributed to shifts in the energy of interligand charge-transfer transitions have been observed from Ni[S(CN)C=C(Ph)S](phen) complexes.[7]

In recent years we have studied the photochemical and photophysical properties of several classes of group 6 metal carbonyl compounds in detail.[8] Many of these complexes possess low-lying d → d and metal to ligand charge-transfer (MLCT) excited states, and the latter transition is normally observed to be very solvent sensitive. These compounds are particularly suited for studies of solvent phenomena because they are zerovalent and thus soluble in a wide range of organic media. For complexes of the general formula $M(CO)_4$(diimine) (M = Cr, Mo, W) the variation in energy of the MLCT state (E_{MLCT}) is one of the largest known among inorganic or organometallic species.[9] These tetracarbonyl complexes exhibit negative solvatochromism; that is, the MLCT absorption blue shifts in progressively more polar solvent media. Negative solvatochromism for metal carbonyl and other coordination complexes has been interpreted in terms of a reduced excited-state electric dipole.[7,10] This is a consequence of the Franck–Condon principle and implies that there is a substantial electric dipole moment associated with the ground-state solute molecule, which is reduced, reversed, or realigned with the MLCT transition. Subsequently, a polar medium can be considered to stabilize the ground-state species to a greater extent than the excited-state molecule.

Recently, we have prepared a series of binuclear complexes of the general formula $(OC)_5M(pyz)M'(CO)_5$, where M = Cr, Mo, or W and pyz = pyrazine. Infrared data has indicated that the carbonyl ligands in these complexes are arranged in C_{4v} symmetry about the metal centers.[8b] The homonuclear derivatives of these complexes would, in solution, possess no permanent ground-state electric dipole moment, yet these species exhibit negative solvatochromism that is of even greater magnitude than illustrated by the $M(CO)_4$(diimine) system. In this paper we reevaluate the concepts of solvent dependence of the MLCT transitions in the following zerovalent tungsten carbonyl complexes:



Experimental Section

Materials. The parent metal hexacarbonyls (Strem Chemical Co.) and ligands 2,2′-bipyridine (Alfa) and pyrazine (Aldrich) were obtained in high purity and used without further purification. Solvents used were of spectroscopic grade and these are commercially available.

Syntheses. Both the $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ complexes were prepared according to procedures described previously.[3a,8b,8d,11] These complexes are moderately stable as solids, although their long-term stabilities were greatly enhanced by storing under N_2 in the dark at 278 K.

Electronic Absorption Spectra. All spectra were obtained on a microprocessor-controlled diode-array Hewlett-Packard 8450A UV-visible spectrophotometer. The metal carbonyl complexes varied considerably in their solution stability; in general, thermal decomposition was particularly apparent in the more polar coordinating solvents, such as dimethylformamide, dimethyl sulfoxide, and pyridine. In these cases absorption spectra were recorded within 5 s of complex dissolution to

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[†] Presented in part at the Biennial Inorganic Chemical Symposium, Toronto, Canada, June 1985; see Abstract No. 18.

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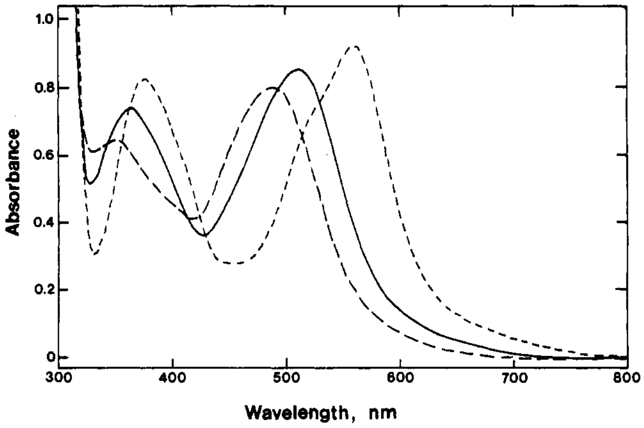

Figure 1. Electronic absorption spectra of $W(CO)_4(bpy)$ in (– –) tetrahydrofuran, (—) benzene, and (- - -) tetrachloroethylene at 298 K.

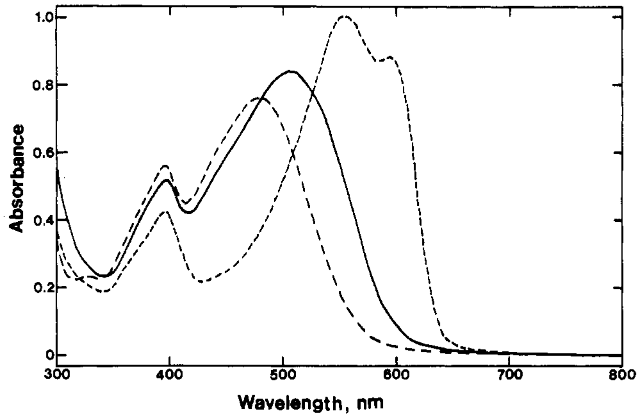

Figure 2. Electronic absorption spectra of $(OC)_5W(pyz)W(CO)_5$ in (– –) tetrahydrofuran, (—) benzene, and (- - -) isooctane at 298 K.

minimize the effects of thermal reaction. All samples were recorded at 298 K with the exception of those in 2-methyl-2-propanol (which is frozen at this temperature), which were recorded at 303 K. The spectral data are considered to be accurate to ±2 nm.

Results and Discussion

The electronic absorption spectra of $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ in various solvents are illustrated in Figures 1 and 2. The lowest energy feature in each of these complexes is extremely solvent sensitive and has been attributed to be of MLCT character. In contrast, the higher energy d → d absorptions are relatively unmoved when solvent is varied.[4] In a very nonpolar medium, such as isooctane, the MLCT transition is substantially red-shifted and depicts the features of two MLCT components. Magnetic circular dichroism and resonance Raman measurements have shown that the MLCT band envelope comprises several electronic transitions.[12] Thus, each absorption maximum of these complexes does not represent a single electronic transition but instead is a composite of several orbitally allowed transitions.

Table I lists the energy positions of the MLCT absorption maxima (E_{MLCT}) of $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ in the full range of solvents studied. The solvents are grouped according to the following classes: aliphatic, aromatic, chlorinated, and alcohol. They also are grouped by increasing E_{MLCT} values for $W(CO)_4(bpy)$.

Table I. Solvent Dependence of MLCT Absorption Maxima (E_{MLCT}) for $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ at 298 K

	E_{MLCT}, kJ mol^{-1}	
solvent	$W(CO)_4(bpy)$	$(OC)_5W(pyz)W(CO)_5$
isooctane	208.4	201.1
	223.2[a]	217.5
triethylamine	219.1	228.7
	235.0[a]	
diethyl ether	231.8	235.5
piperidine	236.4	239.2
tetrahydrofuran	245.1	249.2
cyclohexanone	250.3	255.6
3-pentanone	251.3	254.5
acetone	256.7	260.0
dimethylacetamide	262.3	269.4
dimethylformamide	263.5	268.2
acetonitrile	264.7	260.6
dimethylsulfoxide	265.8	270.6
mesitylene	228.3	226.1
toluene	230.9	235.0
benzene	232.7	234.6
2-picoline	248.2	242.1
pyridine	254.5	248.7
carbon tetrachloride	214.8	203.4[a]
	229.2[a]	218.3
tetrachloroethylene	213.6	203.4[a]
	230.9[a]	217.5
trichloroethylene	227.4	219.5
chloroform	236.9	221.9
chlorobenzene	238.8	227.4
o-dichlorobenzene	239.7	225.7
1,2-dichloroethane	247.7	232.7
methylene chloride	249.2	229.6
1-pentanol	238.3	244.6
2-propanol	238.8	248.2
cyclohexanol	240.2	243.1
2-methyl-2-propanol	241.2[b]	241.2[b]
3-phenyl-1-propanol	242.1	243.1
1-butanol	243.1	242.1
benzyl alcohol	249.2	242.1
ethanol	250.3	247.1
methanol	252.4	251.3

[a] Feature observed as a shoulder. [b] Data recorded at 303 K.

The solvent parameters considered in this work are Kosower's Z parameter,[13] Reichardt and Dimroth's E_T solvent polarity scale,[6] Kamlet and Taft's π^* solvent polarity parameter,[14] the bulk dielectric constant (ϵ_b),[15] the optical dielectric constant (ϵ_{op}),[16] dipole moment values (μ),[17] solvent polarizability values (α), and optical polarizability values (α_{op}).[16] These values are directly obtainable from literature data, or can be derived from such, and are listed in Table II.

The E_{MLCT} data have been correlated with the empirical solvent parameters (S) according to eq 1. The results of least-squares

$$E_{MLCT} = mS + C \qquad (1)$$

fits for individual and combined solvent groups are shown in Tables III–VIII. In these tables, n is defined as the number of solvents used in the correlation, m is the slope of the regression line, and r is the correlation coefficient obtained from the least-squares fits. As noted above, the MLCT absorption maximum of these complexes comprises several electronic transitions. Therefore, in the cases of solutions that exhibit two distinct MLCT components a mean value of E_{MLCT} was used.

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Table II. Relevant Solvent Parameters

solvent	Z,[a] kJ mol^{-1}	E_T,[b] kJ mol^{-1}	π^*[c]	ϵ_b[d]	ϵ_{op}[e]	μ,[f] D	$10^2\alpha$[g]	$10^2\alpha_{op}$[e]
isooctane	251.5	129.3	–0.08	1.94	1.94	0	5.70	5.67
triethylamine		139.3	0.14	2.42	1.96	0.80	7.67	5.80
diethyl ether		144.8	0.27	4.34	1.83	1.23	12.5	5.17
piperidine		148.5		5.80	2.12	1.19	14.7	6.44
tetrahydrofuran		156.5	0.58	7.39	1.97	1.69	16.3	5.85
3-pentanone		164.4		17.0	1.94	2.72	20.1	5.69
cyclohexanone		170.7	0.76	18.3	2.10	3.07	20.3	6.08
acetone	274.9	176.6	0.71	20.7	1.85	3.11	20.7	5.25
dimethylacetamide	279.9	182.8	0.88	37.8	2.07	3.81	22.0	6.26
dimethylformamide	286.8	183.3	0.88	36.7	2.05	3.82	22.0	6.14
acetonitrile	298.3	192.5	0.85	37.5	1.81	3.39	22.0	5.06
dimethyl sulfoxide	297.5	188.3	1.00	48.9	2.18	3.90	22.4	6.74
mesitylene		138.5	0.41	2.28	2.25	0.10	7.22	6.98
toluene		141.8	0.54	2.38	2.24	0.37	7.59	6.98
benzene	225.9	144.4	0.59	2.28	2.25	0	7.22	7.04
2-picoline		160.3		9.94	2.24	1.93	17.8	6.98
pyridine	267.8	168.2	0.87	12.3	2.28	2.21	18.8	7.10
carbon tetrachloride		136.0	0.29	2.24	2.13	0	6.80	6.56
tetrachloroethylene		133.5	0.28	2.30	2.27	0	7.22	7.10
trichloroethylene		150.2	0.53	3.42	2.18	0.85	10.6	6.14
chloroform		163.6	0.58	4.81	2.09	1.11	12.1	6.38
chlorobenzene		156.9	0.71	5.62	2.32	1.54	15.9	7.28
o-dichlorobenzene		159.4	0.80	9.93	2.41	2.28	17.8	7.65
1,2-dichloroethane		175.3	0.81	10.4	2.09	2.94	18.1	6.32
methylene chloride	268.6	172.0	0.83	9.08	2.03	1.90	17.4	6.08
1-pentanol		205.4		13.9	1.99	1.66	19.4	5.91
2-propanol	319.2	203.3	0.46	18.3	1.90	1.65	20.3	5.50
cyclohexanol		196.2		15.0	2.14	1.90	19.6	6.56
2-methyl-2-propanol	298.3	183.7	0.41	10.9	1.93	1.67	18.3	5.63
3-phenyl-1-propanol		202.9		11.6	2.33	1.64	18.6	7.34
1-butanol	325.1	210.0	0.46	17.1	1.96	2.96	20.1	5.77
benzyl alcohol		212.6	0.98	13.1	2.37	1.67	19.1	7.46
ethanol	333.0	217.2	0.54	24.3	1.85	1.71	21.1	5.28
methanol	349.8	232.2	0.60	32.7	1.77	2.97	21.8	4.85

[a] Values from ref 13. [b] Values from ref 6. [c] Values from ref 14. [d] Values from ref 15. [e] Derived from refractive index data.[16] [f] Values from ref 17. [g] Derived from bulk dielectric data.[15]

Table III. Least-Squares Regression Parameters for Plots of E_{MLCT} vs. E_T

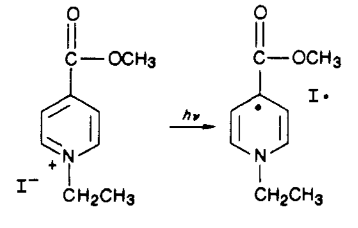
solvent type	n	m	r
(a) $W(CO)_4(bpy)$			
aliphatic (ali)	12	0.781	0.987
aromatic (aro)	5	0.904	0.999
chlorinated (chl)	8	0.671	0.965
alcohol (alc)	9	0.302	0.775
ali + aro	17	0.775	0.986
ali + aro + chl	25	0.773	0.963
ali + aro + chl + alc	34	0.293	0.628
(b) $(OC)_5W(pyz)W(CO)_5$			
aliphatic (ali)	12	0.848	0.949
aromatic (aro)	5	0.630	0.953
chlorinated (chl)	8	0.513	0.951
alcohol (alc)	9	0.177	0.708
ali + aro	17	0.831	0.952
ali + aro + chl	25	0.831	0.811
ali + aro + chl + alc	34	0.357	0.602

Table IV. Least-Squares Regression Parameters for Plots of E_{MLCT} vs. π^*

solvent type	n	m, kJ mol^{-1}	r
(a) $W(CO)_4(bpy)$			
aliphatic (ali)	10	48.22	0.987
aromatic (aro)	4	60.27	0.968
chlorinated (chl)	8	45.06	0.951
ali + aro	14	49.17	0.927
ali + aro + chl	22	48.19	0.885
ali + aro + chl[a]	22	49.67	0.968
(b) $(OC)_5W(pyz)W(CO)_5$			
aliphatic (ali)	10	54.73	0.987
aromatic (aro)	4	47.77	0.990
chlorinated (chl)	8	35.77	0.974
ali + aro	14	54.02	0.916
ali + aro + chl	22	49.88	0.718
ali + aro + chl[a]	22	28.09	0.455

[a] Used π^* values corrected for statistical polarizability (see ref 14).

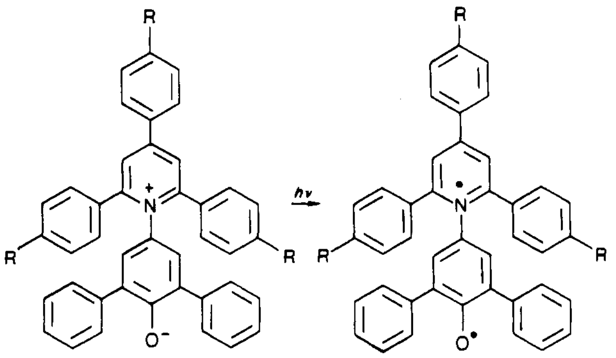
Kosower's *Z* Parameter. The *Z* scale arises from the energy of a highly solvent-dependent intermolecular charge-transfer transition from 1-ethyl-4-carbomethoxypyridinium iodide (eq 2).[13]



(2)

Following excitation of this molecule, an electron is transferred from the iodide to the pyridinium ring. A "dipole-flip" mechanism is thought to occur in this system; the ground-state dipole was found to be perpendicular to the plane of the pyridinium ring, while the excited-state dipole is considered to be parallel to this plane. Moreover, the magnitude of the dipole is reduced in proceeding from the ground state to the excited state. The solvent dependence of the charge-transfer transition of the pyridinium iodide molecule was found to hold only for media of the same family type; e.g., aromatic solvents would behave differently from aliphatic solvents.[13] However, the most significant drawback of the *Z* parameter is that the model compound is barely soluble in nonpolar media and only a few such values were obtained. As a consequence, there is insufficient data for *Z* in each of the solvent classes (see Table II) to obtain a meaningful correlation.

Reichardt's E_T Parameter. The E_T solvent polarity parameter is based on the transition energy of an intramolecular charge-transfer transition (eq 3) for a pyridinium *N*-phenol betaine molecule [4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenoxide].[6]



(3)

Analogous to the *Z* scale pyridinium compound, the dipole moment of the ground state is greater than that of the excited state and the betaine compound thus exhibits negative solvatochromism. The charge-transfer transition in this betaine molecule is highly solvent sensitive, and the E_T parameters are more useful than the *Z* scale because the betaine (especially the trimethyl derivative) is soluble in a wide range of solvents.

The E_T parameters correlate strongly with the E_{MLCT} values for $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$; the results of least-squares fits for individual and combined solvent families are illustrated in Table III. The correlation data show that the best least-squares lines are obtained when the solvent classes are plotted separately. This result implies that the change in dipole moment and polarizability of the betaine during the charge-transfer process must be somewhat different in the four solvent families, and this gives rise to useful subgroups of E_T parameters. In alcohol solvents, hydrogen bonding is known to take place with interaction between the betaine oxygen and acidic protons of the solvent.[6] An aromatic solvent may also be expected to interact strongly with the betaine oxygen atom. Liptay et al. have reported a reduction in dipole moment from 15 to 6 D on going from the ground state to the excited state for these betaines.[18] In addition, these workers have shown that the change in resonance structure of the solute betaine is equal to the change in polarization for the solute. Thus, if the solute and solvent molecules are treated as point dipoles in a homogeneous dielectric continuum, the solvent dependence is related to dispersion effects.

Kamlet and Taft's π^* Solvent Scale. Briefly, the π^* solvent parameter is based on the solvatochromism of the $\pi \rightarrow \pi^*$ transition in seven nitrobenzene and benzophenone derivatives.[14a] The averaging of the absorption energies has minimized some of the solvation problems encountered in the single model compound parameters. The π^* scale is dimensionless as the values have been normalized from 0 (cyclohexane) to 1 (dimethyl sulfoxide) according to eq 4, where XYZ = average electronic absorption

$$\pi^* = (XYZ - XYZ_0)/s\ ;\ s = XYZ_1 - XYZ_0 \qquad (4)$$

energy in a given solvent, XYZ_0 = average electronic absorption energy in cyclohexane, XYZ_1 = average electronic absorption energy in dimethyl sulfoxide, *s* = solvatochromic coefficient, and π^* = solvent polarity or solvatochromic parameter. Equation 4 has been shown to be only useful for solvents that possess closely related physical properties. Kamlet and Taft have recognized the varying degrees of charge delocalization in the dye molecules associated with the different families of solvents, and they have modified their equation to incorporate a number of correction factors[14b]

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (5)$$

Table V. Least-Squares Regression Parameters for Plots of E_{MLCT} vs. ϵ_b

solvent type	*n*	*m*, kJ mol^{-1}	*r*
	(a) $W(CO)_4(bpy)$		
aliphatic (ali)	12	0.908	0.951
aromatic (aro)	5	2.371	0.991
chlorinated (chl)	8	2.806	0.912
alcohol (alc)	9	0.514	0.684
ali + aro	17	0.891	0.887
ali + aro + chl	25	0.938	0.869
ali + aro + chl + alc	34	0.888	0.852
	$(OC)_5W(pyz)W(CO)_5$		
aliphatic (ali)	12	0.974	0.861
aromatic (aro)	5	1.580	0.903
chlorinated (chl)	8	2.173	0.911
alcohol (alc)	9	0.428	0.884
ali + aro	17	0.977	0.877
ali + aro + chl	25	1.176	0.853
ali + aro + chl + alc	34	1.119	0.844

Table VI. Least-Squares Regression Parameters for Plots of E_{MLCT} vs. $(1 - \epsilon_b)/(2\epsilon_b + 1)$

solvent type	*n*	*m*, kJ mol^{-1}	*r*
	(a) $W(CO)_4(bpy)$		
aliphatic (ali)	12	−157.2	0.953
aromatic (aro)	5	−104.4	0.980
chlorinated (chl)	8	−115.9	0.944
alcohol (alc)	9	−211.8	0.568
ali + aro	17	−134.2	0.940
ali + aro + chl	25	−133.9	0.929
ali + aro + chl + alc	34	−116.6	0.864
	(b) $(OC)_5W(pyz)W(CO)_5$		
aliphatic (ali)	12	−179.4	0.963
aromatic (aro)	5	−69.0	0.885
chlorinated (chl)	8	−92.6	0.972
alcohol (alc)	9	−203.5	0.848
ali + aro	17	−145.2	0.917
ali + aro + chl	25	−147.5	0.801
ali + aro + chl + alc	34	−135.7	0.791

Table VII. Least-Squares Regression Parameters for Plots of E_{MLCT} vs. μ

solvent type	*n*	*m*, kJ mol^{-1} D^{-1}	*r*
	(a) $W(CO)_4(bpy)$		
aliphatic (ali)	12	12.03	0.979
aromatic (aro)	5	10.72	0.975
chlorinated (chl)	8	9.29	0.915
alcohols (alc)	9	3.72	0.397
ali + aro	17	10.38	0.952
ali + aro + chl	25	10.42	0.945
ali + aro + chl + alc	34	10.03	0.918
	(b) $(OC)_5W(pyz)W(CO)_5$		
aliphatic (ali)	12	13.50	0.974
aromatic (aro)	5	7.21	0.897
chlorinated (chl)	8	7.50	0.951
alcohols (alc)	9	1.88	0.312
ali + aro	17	11.47	0.948
ali + aro + chl	25	12.12	0.861
ali + aro + chl + alc	34	11.65	0.838

where α = scale of hydrogen bond donor acidities, β = scale of hydrogen bond donor basicities, δ = statistical polarizability correction term ($\delta = 0$ for aliphatic solvents, $\delta = 0.5$ for polychlorinated aliphatic solvents, $\delta = 1.0$ for aromatic solvents), *a* = susceptibility of absorption maximum to hydrogen bond donor acidities, *b* = susceptibility of absorption maximum to hydrogen bond acceptance basicities, and *d* = coefficient that accounts for the difference between the polarity-statistical polarizability effect and the π^* effect for a given absorption energy XYZ. The *d* coefficient is defined as

$$d = 2[XYZ_{aliphatics} - XYZ_{aromatics}]/[(slope)_{aliphatics} + (slope)_{aromatics}] \qquad (6)$$

The average π^* value for the aliphatic and aromatic solvents is 0.7.

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Table VIII. Least-Squares Regression Parameters for Plots of E_{MLCT} vs. α

solvent type	n	m, kJ mol^{-1}	r
(a) $W(CO)_4(bpy)$			
aliphatic (ali)	12	1.637	0.974
aromatic (aro)	5	1.144	0.982
chlorinated (chl)	8	1.198	0.945
alcohols (alc)	9	1.612	0.580
ali + aro	17	1.412	0.958
ali + aro + chl	25	1.400	0.952
ali + aro + chl + alc	34	1.208	0.884
(b) $(OC)_5W(pyz)W(CO)_5$			
aliphatic (ali)	12	1.845	0.972
aromatic (aro)	5	0.755	0.887
chlorinated (chl)	8	1.021	0.965
alcohols (alc)	9	1.536	0.857
ali + aro	17	1.524	0.932
ali + aro + chl	25	1.575	0.839
ali + aro + chl + alc	34	1.433	0.824

The π^* values were correlated with the E_{MLCT} data for $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ according to eq 1, where $S = \pi^*$. The least-squares regression parameters are shown in Table IV, and these illustrate that π^* correlates with E_{MLCT} to a high degree. There is an insufficient range of π^* values available for the alcohol solvents to obtain a meaningful correlation.[14b] The data indicates that the best least-squares fits are obtained when the solvent families are segregated, although considerable improvement was noted in the single-line fit for $W(CO)_4(bpy)$ when corrections were made for statistical polarizability.[14b]

In summary, while the Z, E_T, and π^* parameters are helpful in predicting solvent effects on a wide range of organic transformations[14a] and yield good fits with our metal carbonyl MLCT energies, they are statistically based (on the mean transition energies of a number of model compounds) and offer little to an understanding of solvent phenomena on the molecular level.

Dielectric Constant, ϵ. To briefly summarize relevant theory, Onsager has considered a nonpolarizable point dipole solute molecule in the center of a spherical cavity of radius a. This solute molecule is completely surrounded by solvent molecules, which impart an electric field (E_R) on the solute molecule. This electric field is otherwise known as the reaction field (RF).[14a,19] If the solute molecule has a dipole moment, μ_A, the potential ψ generated by the solute and first-coordination-sphere solvent molecules is governed by LaPlace's equation ($\Delta\psi = 0$), where ψ is finite and continuous.[14a] The solutions of ψ are further restricted because a boundary condition exists such that the functions relating the dielectric constant just inside and outside the boundary are equal. These relationships are shown in eq 7 and 8, where a = radius

$$\epsilon_{a-0}(\sigma\psi/\sigma r)_{r=a-0} = \epsilon_{a+0}(\sigma\psi/\sigma r)_{r=a+0} \qquad (7)$$

$$\epsilon_r = (\sigma\psi/\sigma r)_{r=a-0} = \epsilon_r(\sigma\psi/\sigma r)_{r=a+0} \qquad (8)$$

of cavity, r = distance from center of cavity, ϵ_{a-0} = dielectric constant just inside the cavity, and ϵ_{a+0} = dielectric constant just outside the cavity. In this model ϵ_r is a step-function; outside the cavity the dielectric constant takes on its bulk value, whereas within the cavity the dielectric constant equals unity.[19]

The results of correlations of E_{MLCT} for $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ with bulk solvent dielectric data[15] are shown in Table V. Overall, the regression lines for either complex correlate to a considerable extent, with the exception of the alcohol group. Modifications to Onsager's point dipole theory have been suggested by Kirkwood[20] and by Block and Walker.[21] Kirkwood's theory of solvation is based on an ellipsoidal cavity and yields effective dielectric constants in the cybotactic region.[13b,22] The theory developed by Block and Walker utilizes a decay function rather than a step function to describe the dielectric constant at the cavity boundary. These solvation theories, however, are concerned with an ionic or highly polar solute.

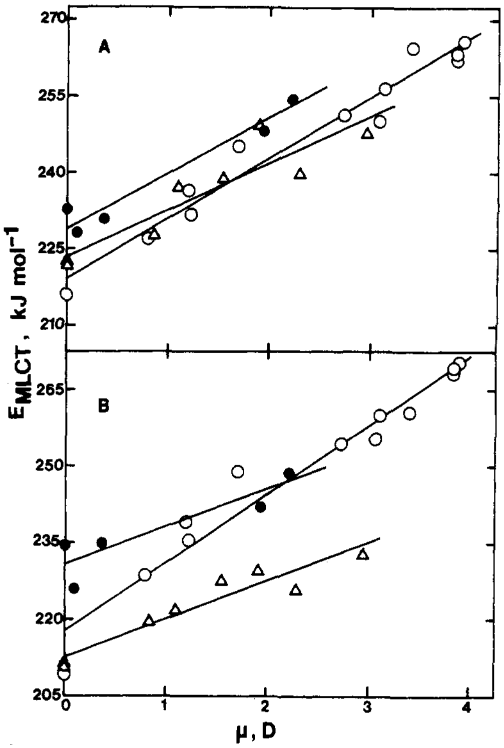

Figure 3. Least-squares plots of E_{MLCT} vs. solvent dipole moment, μ, for (A) $W(CO)_4(bpy)$ and (B) $(CO)_5W(pyz)W(CO)_5$. Lines indicate separate plots for aliphatic (○), aromatic (●), and chlorinated (△) solvent groups.

Meyer et al. have correlated the transition energies of $Ru(bpy)_3^{2+}$ with the dielectric function $(1 - \epsilon_b)/(2\epsilon_b + 1)$.[21,23] Least-squares plots of E_{MLCT} for $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ vs. $(1 - \epsilon_b)/(2\epsilon_b + 1)$ (according to eq 1) yield regression parameters shown in Table VI. These results indicate that the correlation fits are not improved when the bulk dielectric data are included as this function. Replacement of the bulk dielectric constant (ϵ_b) by the optical dielectric constant ($\epsilon_{op} = n^2$, where n = refractive index) yields the function $(1 - \epsilon_{op})/(2\epsilon_{op} + 1)$, which is derived from a theory that assumes localization in the excited state initially formed after excitation.[21,23,24] This function, however, does not correlate with E_{MLCT} for a significant number of solvents in any of the solvent groups studied here.

Solvent Dipole Moment, μ. Least-squares plots of E_{MLCT} for each complex vs. solvent dipole moment μ are illustrated in Figure 3. The alcohol solvents correlate poorly and are not included. The corresponding regression parameters for the solvent groups are shown in Table VII. As expected, the results closely parallel the data obtained for the correlations with dielectric constant and good least-squares fits are observed.

Solvent Polarizability, α. A number of authors have reported theoretical studies describing the solvation of nonpolar molecules.[25] The Longuet-Higgins and Pople theory predicts the red shift of a low-lying absorption band of a nonpolar solute in a nonpolar solvent.[25d] Equation 9 has been derived from perturbation theory,

$$\Delta\nu_{red} = \tfrac{1}{6}(\alpha_B Z\bar{R}^{-6})(\tfrac{1}{4}(E\alpha_A + M^2)) \qquad (9)$$

where $\Delta\nu_{red}$ = frequency shift (to lower energy) relative to the gas-phase frequency, α_A = molecular polarizability of the solvent,

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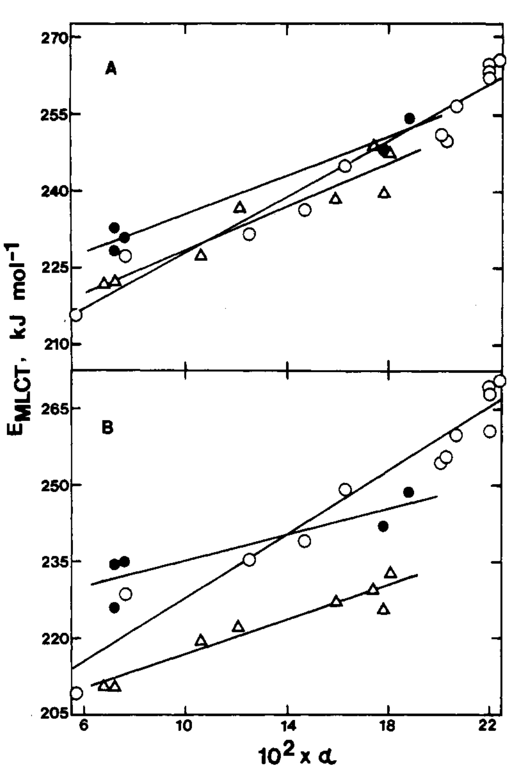

Figure 4. Least-squares plots of E_{MLCT} vs. solvent polarizability, α, for (A) $W(CO)_4(bpy)$ and (B) $(OC)_5W(pyz)W(CO)_5$. Lines indicate separate plots for aliphatic (○), aromatic (●), and chlorinated (△) solvent groups.

α_B = molecular polarizability of the solute, Z = number of solvent molecules at $\bar{R}$, $\bar{R}$ = mean distances of solvent molecules from the solute molecule, E = energy of the transition, and M = dipole moment of the transition. This theory predicts that the solvatochromism of a nonpolar solute in a nonpolar solvent is proportional to the molecular polarizability of the solvent. Furthermore, the red shift of the lowest lying absorption is inversely dependent on R^6. Thus, the distance R between solute and solvent molecules decreases as the transition is red-shifted.[25d] The Longuet-Higgins and Pople theory is closely related to that for London dispersion forces, eq 10,[26] where U_D = force of attraction between molecules

$$U_D = -3h\nu_0\alpha^2/4r^6 \qquad (10)$$

without a permanent dipole, h = Planck's constant, ν_0 = frequency of transition, α = molecular polarizability, and r = distance between molecules.

Solvent polarizability is a function of the bulk solvent dielectric constant. The polarization of a solvent molecule can be expressed as

$$\alpha = (3/4\pi)(\epsilon_b - 1)/(\epsilon_b + 2) \qquad (11)$$

where ϵ_b = dielectric constant of bulk solvent. Solvent polarizability values (α), based on a single solvent molecule, were obtained from bulk dielectric data[15] by using eq 11. Least-squares plots of E_{MLCT} vs. α for $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ are depicted in Figure 4. The corresponding regression parameters shown in Table VIII illustrate that good correlations are obtained for the individual solvent families. Poor fits were obtained for the alcohol solvents indicating the importance of hydrogen bonding, and they are not plotted in Figure 4. The E_{MLCT} least-squares fits based on solvent polarizability are of the order of that generated with π^*.

Bayliss and McRae have discussed solvation theory of the four combinations of polar and nonpolar solutes and solvents.[27] Their case I theory corresponds to a nonpolar solute in a nonpolar solvent. In this approach the Franck–Condon excited state will be composed of orientation strain and packing strain. The orientation strain will change only if the excited-state dipole moment is significantly different from the ground-state dipole moment. The packing strain is related to the ability of the solvent molecules to surround the solute molecule and is important if the excited-state molecule is considerably larger than the ground-state molecule. Neither of these strain effects are expected to be sizeable for the tungsten carbonyl complexes. As a consequence, the solvent polarizability interaction with the ground and excited states is an important factor in determining the solvatochromism. Although this phenomenon has been reported for organic molecules,[28] it has not been well recognized for the solvation of transition-metal complexes.

Optical polarizabilities can be obtained by substitution of optical dielectric data ($\epsilon_{op} = n^2$, where n = refractive index) into eq 11, yielding

$$\alpha_{op} = (3/4\pi)(n^2 - 1)(n^2 + 2) \qquad (12)$$

However, as was found for optical dielectric constant, inclusion of α_{op} does not correlate to a significant degree with E_{MLCT}.

Conclusions

In this contribution we have endeavored to further understand the nature of solvent interaction with transition-metal carbonyl complexes. Previously the solvent dependence of these complexes has been explained in terms of a reduced excited-state electric dipole moment.[7,10] Our correlation data for the $W(CO)_4(bpy)$ complex do not invalidate this interpretation. However, in the case of $(OC)_5W(pyz)W(CO)_5$, which does not possess a permanent dipole moment, the exceptionally strong solvatochromism has lead us to conclude that induced dipolar and polarizability interactions in the ground and excited states are important. Indeed, the solvent-dependent MLCT transition of both complexes has been correlated to a high degree with simple bulk dielectric, solvent dipole moment, and solvent polarizability properties. In general, the protic solvents correlate poorly with these solvent parameters due to the additional hydrogen-bonding interactions.

There exists substantial variation in solvatochromic properties, even between closely related metal carbonyl complexes. For instance, the MLCT solvent dependencies of $W(CO)_4(bpy)$ and $(OC)_5W(pyz)W(CO)_5$ reported here are substantially greater than corresponding $W(CO)_4(dab)$ complexes (dab = 1,4-diazabutadiene, or their derivatives).[3c,4a,c] These differences in solvatochromic behavior may be associated with the character of the MLCT transition. In the simplest sense a MLCT transition can be considered to result in a formal oxidation of the metal and reduction of the ligand. For the bpy or pyz complexes the MLCT state consists of excitation from a d_π orbital to an orbital of mainly $\pi^*(L)$ character. On the other hand, the π^* orbital of the dab ligand is at lower energy, and there is more overlap between the d_π and π^* orbitals. Excitation of the dab complex thus leads to population of a LUMO orbital which is primarily of d_π–$\pi^*(L)$ character from a HOMO orbital of d_π–$\pi^*(L)$ character. The large MLCT solvent dependence for the bpy complex is attributed to a substantial change in the dipolar or polarization interaction of the solvent with the π-electron diimine ring system between the ground and excited states. When the charge is primarily localized along the metal–nitrogen bond, as in the dab complex, the solvent dipolar and polarization effects are changed much less on going from the ground to the excited state.

Recently, Stufkens et al. have studied the resonance Raman spectra of $W(CO)_4(4,7\text{-}Ph_2\text{-}phen)$ and $W(CO)_4(mes\text{-}dab)$, and their data strongly supports this interpretation.[30] Following MLCT excitation, the resonance Raman spectrum of $W(CO)_4(4,7\text{-}Ph_2\text{-}phen)$ illustrates a substantial enhancement of the ligand

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C=N stretching modes but only weak W–N stretching modes. This result is consistent with an electronic transition of strong MLCT character, as discussed above for the bpy and pyz complexes. In contrast, the resonance Raman spectrum of $W(CO)_4$(mes-dab) exhibits strong W—N stretching and ligand deformation modes, and the ligand C=N stretching modes were too weak to be detected. These observations imply that the excitation results in little transfer of charge to the mes-dab ligand π^* orbital.

In this vein, Kaim et al. have studied the ligand π^* level in a series of chelated $Mo(CO)_4L$ complexes, where L = 4,4′-bipyrimidine (bpm), 3,3′-bipyradazine (bpdz), 2,2′-bipyrazine (bpz), and 2,2′-bipyrimidine (bpym). Hückel MO calculations for these ligands have illustrated that they are π-electron deficient in the order bpm > bpz > bpym > bpdz.[31] The solvent sensitivity of these $M(CO)_4L$ complexes has been reported to closely follow this order (i.e., complexes of bpm display the most pronounced solvatochromism[32]) concordant with varying degrees of MLCT character.

Also relevant is the study by Van Eldik et al. on the piezochromic and thermochromic behavior of $Mo(CO)_4L$ complexes (L = bpy, phen, dab).[33] Observed spectral changes at elevated pressure and temperature have been shown to be associated with solvent polarity changes. An increase in solvent polarity at increasing pressure is accompanied by a blue shift in the MLCT transition, whereas a decrease in solvent polarity at increasing temperature red shifts this band.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for supporting this research.

Registry No. $W(CO)_4$(bpy), 15668-66-3; $(OC)_5W(pyz)W(CO)_5$, 70738-71-5.

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Reversible CO Binding by $Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}$. A Spectroscopic and Electrochemical Investigation

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Received December 12, 1985

The binding constants for carbon monoxide addition to a series of dirhodium complexes of the form $Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}$, where n = 0, 2, 3, and 4, were determined in 1,2-dichloroethane and in acetonitrile. At room temperature, either 1:1 or 1:2 CO adducts are observed depending upon the particular combination of bridging ligands and the nature of the solvent. In addition, the stability constants of the CO adducts were found to increase with increasing number of acetamidate bridging ions in the dirhodium complex. Cyclic voltammetry was carried out for the oxidation of $Rh_2(ac)_n(acam)_{4-n}$ in acetonitrile and dichloroethane under various CO partial pressures. The value of $E_{1/2}$ for the formation of $Rh^{II}Rh^{III}$ shifted positively with increasing CO pressure. This positive shift can be associated with log K for the 1:1 CO adduct formation. A linear relationship between log K and $E_{1/2}$ for the first oxidation of $Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}$ under nitrogen was observed for complexes having n = 0, 1, and 2. Finally, solution infrared spectroscopy of $Rh_2(O_2CCH_3)_n(HNOCCH_3)_{4-n}CO$ species showed that the CO stretching frequencies are lowered as the number of $HNOCCH_3$ bridging ligands is increased. The lowest CO stretching frequency in this series occurs for $Rh_2(HNOCCH_3)_4CO$, which has ν_{CO} = 2028 cm^{-1}.

Introduction

The extent of π interaction between axially coordinated π-acid ligands and the rhodium(II) centers in dirhodium(II) carboxylates has been a subject of debate in recent years.[1-5] Reversible CO binding by some dirhodium complexes and infrared spectroscopic data of the CO adducts have been reported to suggest a weak π interaction.[1,2,6] However, the primary argument against any axial π interaction comes from a low-temperature crystal structure which shows that $Rh_2(O_2CCH_3)_4(CO)_2$ has unusually long Rh–C and short C–O bond lengths.[4,7]

There is no doubt that the interaction between CO and dirhodium(II) carboxylates is quite weak. At room temperature, CO adduct formation only occurs in nonbonding solvents under an atmosphere of CO. At lower CO partial pressures the CO adduct is converted to the axially uncomplexed dimer. Thus, dirhodium complexes having electron-donating bridging ligands which are stronger donors than carboxylates should more clearly demonstrate the existence of any significant π-back-donation from the dirhodium(II) center to a π acceptor axial ligand.

Recently, we reported the syntheses of dirhodium complexes that contain stronger electron-donor bridging ligands than those in dirhodium carboxylates.[8,9] These dirhodium complexes are represented as $Rh_2(ac)_n(acam)_{4-n}$ where n = 0–4, ac = $[O_2CCH_3]^-$, and acam = $[HNOCCH_3]^-$. Increasing the number of acetamidate (acam) bridging ligands on $Rh_2(ac)_n(acam)_{4-n}$ leads to an increased ease of electrooxidation, as shown in reactions 1 and 2, as well to a lowering of the $3d_{5/2}$ binding energy of the neutral complex.

$$Rh^{II}_2 \rightleftarrows Rh^{II}Rh^{III} + e^- \qquad (1)$$

$$Rh^{II}Rh^{III} \rightleftarrows Rh^{III}_2 + e^- \qquad (2)$$

In addition, electrochemical and XPS studies of $Rh_2(ac)_n(acam)_{4-n}$ show that the energies of the HOMO and the core electrons are raised considerably as a result of amidate binding.[8,9] Therefore, the acetamidate and acetate/acetamidate complexes should be better π donors than $Rh_2(O_2CCH_3)_4$. This was investigated in the present study, which demonstrates that $Rh_2(ac)_n(acam)_{4-n}$ complexes reversibly bind CO. At room tem-

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