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WHAT DETERMINES THE SOLVATOCHROMISM OF METAL-TO-LIGAND CHARGE TRANSFER TRANSITIONS? A DEMONSTRATION INVOLVING 17 TUNGSTEN CARBONYL COMPLEXES

WOLFGANG KAIM*, STEPHAN KOHLMANN, SYLVIA ERNST,
BARBARA OLBRICH-DEUSSNER, CHRISTIAN BESSENBACHER, and ANDREAS SCHULZ

Institut für Anorganische Chemie der Universität, Niederurseler Hang,
D-6000 Frankfurt am Main 50 (F.R.G.)

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Summary

A consistent model which permits rationalization and estimation of the solvatochromic behaviour of coordination compounds with metal-to-ligand charge transfer absorption bands is described. The model shows how the changing relationship between metal–ligand bond polarities in the ground and MLCT excited state determines whether negative, positive, or no solvatochromism results. Data for seventeen mononuclear and binuclear tetra- and pentacarbonyltungsten complexes are analyzed in order to illustrate and substantiate the different electronic situations leading to various degrees of solvatochromism. Ligand basicities, calculated Hückel molecular orbital coefficients, ESR coupling constants, and metal fragment oxidation potentials are used to estimate the ability of metal fragments and ligands for charge transfer in the excited state and the resulting solvatochromism of complexes.

Introduction

The continuing interest [1–38] in the phenomenon of solvatochromism [1] results from attempts to understand solvation [2–4] and from the desire to derive generally applicable solvent parameters [1,4–6]. In the field of inorganic and organometallic chemistry, such studies [7–38] were also triggered by efforts to control the photo- and electrochemical behaviour of complexes with metal-to-ligand charge transfer (MLCT) transitions [17,18,29,30,34–42]. The main aim of most of these studies has been to analyze the interaction of selected complexes with the various groups of solvents and to obtain meaningful correlations [29,32,38], while less attention has been given to the relation between the extent of solvatochromism and the electronic structures of ligands and metal fragments [11–13,36,37].

Our own efforts in devising new ligands for coordination compounds with charge transfer and electron transfer activity [36,37,40–43] have led us to reconsider the

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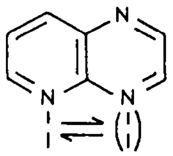
requirements for solvatochromism of such complexes. Previous approaches towards an understanding of the highly variable solvatochromism of tetracarbonylmolybdenum complexes with α-diimine ligands had shown a correlation with the extent of back-bonding within a series of isomeric systems [36], while a study of binuclear complexes had suggested that the relation between the ligand basicities in the ground and MLCT-excited states plays an important role [37]. The rules put forward by us [37] have led to the expectation that pentacarbonyl complexes of the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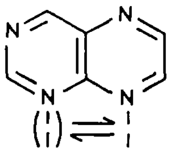
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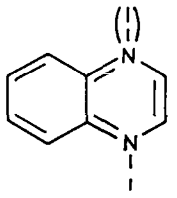
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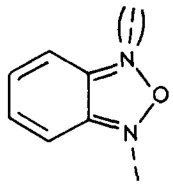
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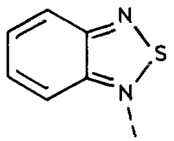
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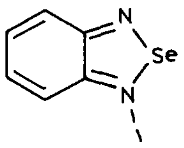
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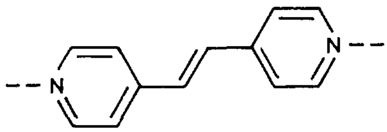
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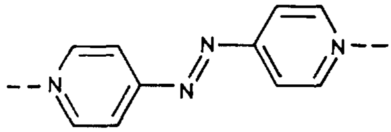
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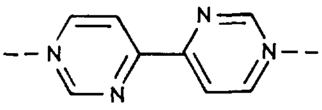
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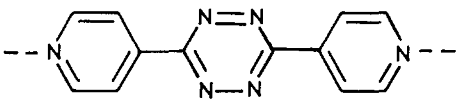
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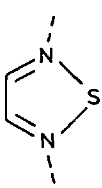
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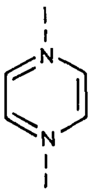
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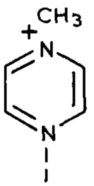
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zerovalent group 6*d* metals should exhibit particularly strong solvatochromism; incidentally, very large medium effects had been observed for the optical absorption of $Cr(CO)_5$ in various inert gas matrices [44]. Furthermore, comparative studies have shown that binuclear complexes without a permanent dipole moment exhibit larger solvatochromatism than their non-centrosymmetric mononuclear analogues [36,37], emphasizing the essential role of induced dipole interactions between aprotic solvents and metal carbonyl complexes.

In an effort to gain further insight into the factors determining the solvent sensitivity of MLCT transitions of organometallic compounds, we have now studied the solvatochromism of 7 mononuclear and 8 binuclear pentacarbonyltungsten complexes with the heterocyclic ligands, 1,4,5-triazanaphthalene (1,4,5-tan), pteridine (pte), 2,1,3-benzoxadiazole (bod), 2,1,3-benzothiadiazole (btd), 2.1.3-benzoselenadiazole (bsd), quinoxaline (quin), *N*-methylpyrazinium cation (mpz^+), 1,2′-bis(4-pyridyl)ethene (4,4′-bpe), azo-4,4′-bipyridine (4,4′-abpy), 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (4,4′-bptz), 4,4′-bipyrimidine (bpm), 1,2,5-thiadiazole (td), and pyrazine (pz).

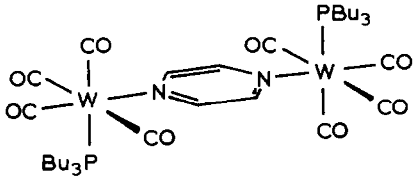
Data for bis(pentacarbonyltungsten)pyrazine were taken from the work of Manuta and Lees [38], for comparison we also studied the *cis*-bis(tetracarbonylphosphane-tungsten) complexes of pyrazine and 4-cyanopyridine (cp) which could be obtained via electron transfer catalyzed carbonyl substitution [45,46].

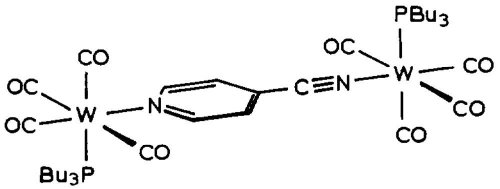
TABLE 1

MLCT ABSORPTION MAXIMA (cm^{-1}) OF TUNGSTEN CARBONYL COMPLEXES IN VARIOUS SOLVENTS

Compound	Solvent ($E^{\star}_{\mathrm{MLCT}}$) [a]				
	i-Octane (0.0)	Toluene (0.30)	THF (0.59)	Acetone (0.82)	DMF (0.95)
$(1,4,5\text{-tan})W(CO)_5$	17760	19800	21140	23090	23420
$(pte)W(CO)_5$	[b]	16230	18520	19420	19690 [c]
$(btd)W(CO)_5$	19230	20490	21740	22520	23260
$(quin)W(CO)_5$	20790	22120	23150	23420	23980
$(bsd)W(CO)_5$	18320	19310	20160	20750	21280
$(bod)W(CO)_5$	18900	19530	20530	21100	21500
$[(mpz^+)W(CO)_5](PF_6)$	[b]	[b]	18730	18870	18660 [c]
$(4,4'\text{-bpe})[W(CO)_5]_2$	20500	21870	22700	23600	~ 24000
$(4,4'\text{-abpy})[W(CO)_5]_2$	16560	17180	18980	19920	20280
$(bpm)[W(CO)_5]_2$	[b]	19310	21190	21830	22490
$(4,4'\text{-bptz})[W(CO)_5]_2$	18120	19460	21500	22470	23200
$(td)[W(CO)_5]_2$	17860	19420	20000 [d]	22830	[f]
$(pz)[W(CO)_5]_2$ [e]	18190	19650	20830	21740	22420
$(bod)[W(CO)_5]_2$	14200	15020	16670	17450	17860
$(quin)[W(CO)_5]_2$	16180	17390	18870	19460	19920 [c]
$(pz)[W(CO)_4(PBu_3)]_2$	14880		16290	16840	[f]
$(cp)[W(CO)_4(PBu_3)]_2$	15500	16980	18120	19120	19840

[a] Solvent parameters $E^{\star}_{\mathrm{MLCT}}$ from ref. 25. [b] Not soluble. [c] In acetonitrile (0.90). [d] In diethyl ether (0.32). [e] From ref. 38. [f] Rapid dissociation.





The absorption maxima of MLCT transitions determined in representative aprotic solvents are summarized in Table 1. Protic and chlorinated solvents are excluded because of their special correlation behaviour [38]; proton transfer processes as well as high solvent molecular polarizabilities in case of chlorinated solvents produce additional complications for the solvent–solute interaction.

Solvatochromism in an MLCT situation

Solvatochromism is observed if the solvent–solute interaction in the ground state differs significantly from that in the excited state of the substrate. The typical "negative" solvatochromism of metal carbonyl complexes with π ligands arises as follows. In the ground state, the metal–ligand bond is polarized as shown in Fig. 1

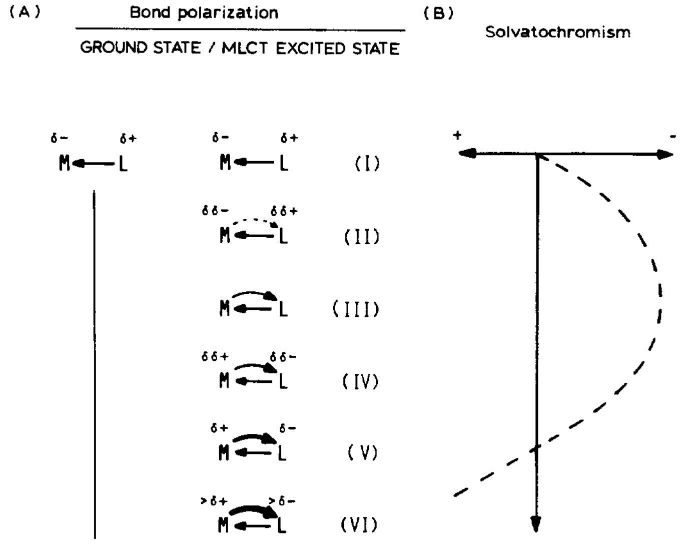
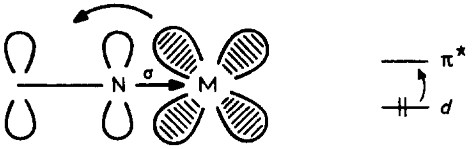


Fig. 1. (A) Effect of increasing metal-to-ligand charge transfer in the excited state on the metal–ligand bond polarization (ground state bond polarization assumed constant). The polarizability differences between ground and excited states determine the sign and the extent of solvatochromism (B); for description of situations (II)–(VI) see the main text.

because of dominating σ donation from the coordinating ligand. On MLCT excitation, this polarization may be reduced, compensated, or even overcompensated by the electron transfer from filled metal *d*-levels into unoccupied π^* orbitals of the ligand, so that a less polar situation results for the complex in the excited state. The stronger stabilization of the ground state by polar solvents is then apparent from increased transition energies in such solvents: "negative solvatochromism" [1].

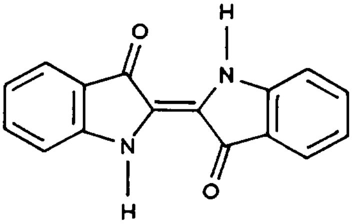
MLCT : Metal-to-Ligand Charge Transfer.



(2)

The crucial factor determining the extent of solvatochromism is the difference between the metal–ligand bond polarities in the ground and MLCT-excited states. If, for the sake of the argument, the ground state situation is kept unchanged, various cases can be distinguished (Fig. 1). Increasing charge transfer in the MLCT excited state first reduces the metal–ligand bond polarity up to complete compensation; this situation, (III), is characterized by maximum negative solvatochromism. Beyond this point, a further increase in MLCT causes a reversal of the bond polarity which, nevertheless, results in a reduction of the polarity difference between ground and MLCT excited state, so that solvatochromism is reduced as well. No solvatochromism at all, despite very strong MLCT, is illustrated by case (V) (Fig. 1), where only the sign of the bond polarization has changed. If charge transfer is still increasing, from this point on "positive solvatochromism", i.e. bathochromic shifts in more polar solvents, will result; this behaviour has been observed for only a few MLCT transitions of metal carbonyl complexes [12,20].

Although the scheme in Fig. 1 refers to a single metal–ligand linkage and the model can be discussed in terms of varying dipole moments, there is strong evidence that the essential contribution to the solvatochromism of metal carbonyl complexes comes from induced-dipole interactions [9,37,38]; accordingly, large and highly anisotropic polarizabilities were found for complexes with MLCT characteristics [47]. The most convincing evidence for the contribution of induced-dipole interactions between solvent and solute has come from the large effects observed for centrosymmetric systems without a permanent dipole moment [37,38]; incidentally, a most prominent example from the field of organic dye molecules is centrosymmetric indigo, which exhibits distinct positive solvatochromism [48].



μ(ground state) = μ(exc. state) = 0

Mononuclear pentacarbonyltungsten complexes

Applying the scheme illustrated in Fig. 1 to complexes $(OC)_5WL$, we first evaluated their solvatochromism graphically (see Fig. 2A) and numerically (see Table 2); as solvent parameters we used the $E^{\star}_{\mathrm{MLCT}}$ values derived by Manuta and Lees from a study of (2,2′-bipyridine)$M(CO)_4$ complexes (M = Cr, Mo, W; 0.00 (i-octane) $\leqslant E^{\star}_{\mathrm{MLCT}} \leqslant$ 1.00 (DMSO)) [25].

The decreasing solvent sensitivity $B = \Delta\tilde{\nu}_{\mathrm{MLCT}}/\Delta E^{\star}_{\mathrm{MLCT}}$ of the mononuclear complexes as arranged in Table 2 correlates with decreasing ligand basicity in the ground state and with increasing Hückel molecular orbital coefficients c^2_{N} at the coordinating nitrogen center in the ligand $\pi^{\star}$ orbital (LUMO) (Table 2). The calculated values c^2_{N} serve as an approximate measure of the amount of charge transferred in the MLCT-excited state since this state may be formulated as containing the excited electron in the ligand $\pi^{\star}$ orbital [40] (eq. 2). A good experimental approach to MLCT is to consider the ESR coupling constants $a_{14_{\mathrm{N}}}$ of the corresponding anion radicals; a_{N} and c^2_{N} are related by the approximation (3) [49]:

$$a_{\mathrm{N}} \simeq Q \cdot \rho^{\pi}_{\mathrm{N}} \simeq Q \cdot c^2_{\mathrm{N}} \tag{3}$$

$\rho^{\pi}_{\mathrm{N}} = \pi$ spin density at nitrogen atom
Q = proportionality constant

Within the series of chalcogenadiazole complexes, the lowest a_{N} value for the sulfur system correlates with the strongest solvatochromism of the neutral complex.

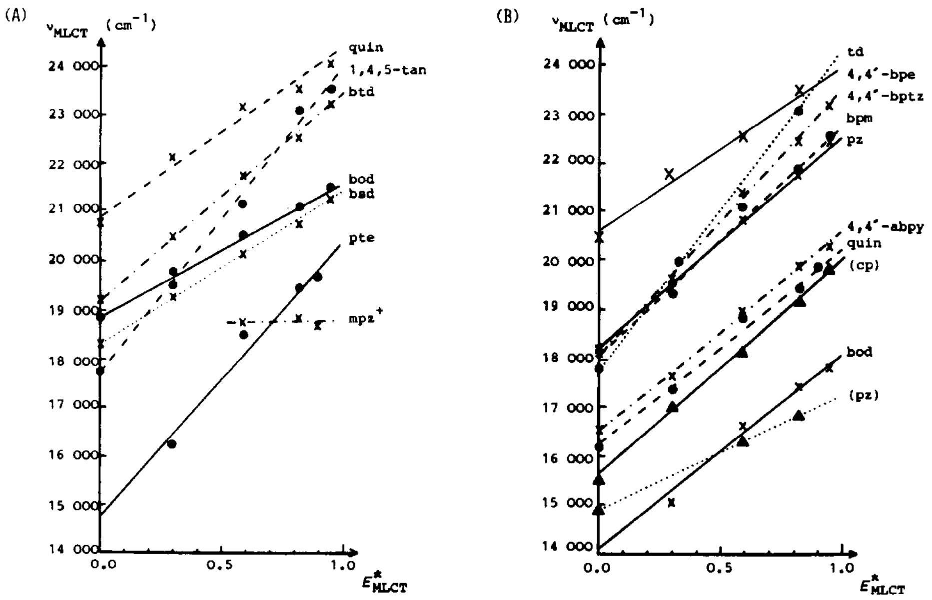


Fig. 2. Metal-to-ligand charge transfer absorption maxima $\tilde{\nu}_{\mathrm{MLCT}}$ of mononuclear (A) and binuclear (B) tungsten carbonyl complexes of heterocyclic ligands, plotted against the solvent parameter $E^{\star}_{\mathrm{MLCT}}$ [25]. Triangles refer to tetracarbonyl(phosphane)tungsten complexes.

TABLE 2

PARAMETERS OF EQUATION $\tilde{\nu}_{MLCT} = A + B \cdot E^{\star}_{MLCT}$ FOR TUNGSTEN CARBONYL COMPLEXES, LIGAND BASICITIES pK_{BH^+}, CALCULATED LIGAND LUMO COEFFICIENTS c_N^2 [a] AND ESR COUPLING CONSTANTS a_N (mT) FOR METAL COMPLEX ANION RADICALS

Compound	A (cm^{-1})	B (cm^{-1})	r [b]	pK_{BH^+}	c_N^2	a_{14_N}
(1,4,5-tan)W(CO)$_5$	17820	6060	0.995	1.2 (N^5) [c] ~ 0 (N^4)	0.106 0.188	[d]
(pte)W(CO)$_5$	14730	5720	0.983	~ −2 (N^1) [e] ~ −4 (N^8)	0.097 0.165	[d]
(btd)W(CO)$_5$	19240	4150	0.999	[d]	0.206	0.640 [f]
(quin)W(CO)$_5$	20980	3410	0.987	0.56 [g]	0.200	0.708 [h]
(bsd)W(CO)$_5$	18350	3040	0.999	−1.41 [i]	[d]	0.700 [f]
(bod)W(CO)$_5$	18830	2790	0.997	[d]	[d]	0.703 [f]
[(mpz$^+$)W(CO)$_5$](PF$_6$)	18780	−40	0.94	−5.78 [k]	0.270	0.80
(4,4′-bpe)[W(CO)$_5$]$_2$	20590	3680	0.996	5.92 [l]	0.093	0.321 [h]
(4,4′-abpy)[W(CO)$_5$]$_2$	16340	4220	0.988	3.5 [m]	0.075	0.23
(bpm)[W(CO)$_5$]$_2$	18040	4752	0.986	1.5 [n]	0.117	0.378 [o]
(4,4′-bptz)[W(CO)$_5$]$_2$	18040	5460	0.997	[d]	0.082	[d]
(td)[W(CO)$_5$]$_2$	17830	6090	0.996	[d]	0.272	[d]
(pz)[W(CO)$_5$]$_2$ [e]	18240	4360	0.999	0.65 [g]	0.268	0.823 [h]
(bod)[W(CO)$_5$]$_2$	14090	4040	0.993	[d]	0.225	0.703 [f]
(quin)[W(CO)$_5$]$_2$	16240	3980	0.995	0.56 [g]	0.219	0.708 [h]
(pz)[W(CO)$_4$(PBu$_3$)]$_2$	14880	2390	0.999	0.65 [g]	0.268	0.815 [p]
(cp)[W(CO)$_4$(PBu$_3$)]$_2$	15540	4460	0.999	1.90 [g]	0.219 (N^1) 0.140 (CN)	0.668 [q] 0.220

[a] Hückel MO parameters $h_{N(coordinating)} = 0.8$, $h_{N'} = 0.5$, $h_{RN^+} = 1.2$, $h_S = 1.1$, $k_{CN} = 1.0$, $k_{NS} = 0.7$. [b] Correlation coefficient. [c] Ref. 50. [d] Not reported or determined. [e] Estimated, ref. 51. [f] Values for binuclear complexes, ref. 52. [g] From ref. 53. [h] Values for binuclear complexes, ref. 54. [i] Ref. 55. [k] pK_{BH^+} of protonated pyrazine, ref. 53. [l] Value for 4-styrylpyridine, from ref. 53. [m] Value for 4-phenylazopyridine, from ref. 53. [n] Ref. 40. [o] Ref. 56. [p] Ref. 45. [q] Values for W(CO)$_5$ complex, ref. 57.

In the series of the aza-quinoxaline complexes, the increase in c_N^2 at the predominant coordinating centers N^5 (1,4,5-tan), N^8 (pte) and N^1 (quin) [58] also corresponds to decreasing solvatochromism, but the situation is complicated for 1,4,5-tan and pte complexes because of NMR-detectable site exchange [58] between the peri coordination centers [59]. The ligand with the largest c_N^2 and a$_N$ values and the

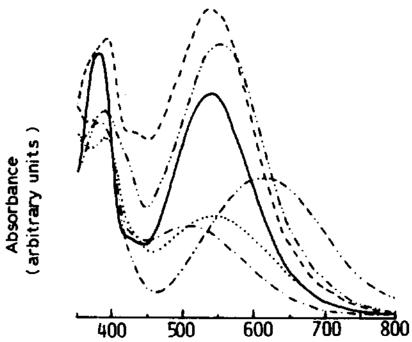


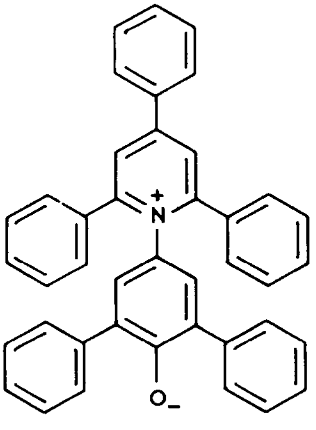
Fig. 3. Absorption spectra of two complexes with very different solvent sensitivity of the MLCT band: Spectra of (pte)W(CO)$_5$ in acetonitrile (–·–·), THF (····) and toluene (––··), and of [(mpz$^+$)W(CO)$_5$](PF$_6^-$) in water (–··), acetonitrile (———) and THF (– – – –).

lowest basicity in the ground state is mpz$^+$ [60,61], which forms a pentacarbonyltungsten complex without virtually any solvatochromic behaviour ($\tilde{\nu}_{\mathrm{MLCT}}$ 18 180 cm^{-1} in water); this result corresponds to situation (V) in Fig. 1. The series of mononuclear pentacarbonyltungsten complexes reported here thus covers the region between cases (III) and (V) of the scheme in Fig. 1; Figure 3 illustrates the range of solvent sensitivity as exhibited by the two extreme examples.

Binuclear pentacarbonyltungsten complexes

Complexes with relatively little charge transfer in the excited state have their absorption bands often overlapping with other transitions: e.g., ligand field (LF, $d \leftarrow d$) transitions which occur at 25 000 cm^{-1} for W(CO)$_5$ complexes [31,39,43]. However, the use of binucleating ligands has allowed solvatochromism to be studied (see Fig. 4) also for examples falling into category (II) of Fig. 1; the sequence in Tables 1 and 2 was derived by considering decreasing ground state basicity of the ligand, increasing charge transfer as indicated by c_{N}^2 and a_{N} values, and monotonously increasing and then decreasing the solvent sensitivities $B = \Delta\tilde{\nu}_{\mathrm{MLCT}}/\Delta E^{\star}_{\mathrm{MLCT}^\circ}$.

It is assumed that the situation in the td complex can be adequately described by case (III) in Fig. 1; solvatochromism greater than that corresponding to B 6000 cm^{-1} has so far been observed in only one instance, involving degenerate ligand orbitals [37]. Even the widely employed dipolar betain solvent indicator, which



μ (ground state) = 14.7 Debye
μ (exc. state) = 6.0 Debye [1]

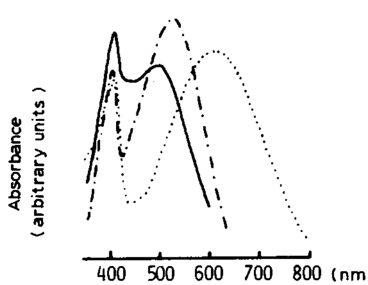


Fig. 4. Absorption spectra of (4,4′-abpy)[W(CO)$_5$]$_2$ in DMF (———), THF (–·–·) and i-octane (····), displaying the broad, solvent-sensitive MLCT band and the narrow, solvent-insensitive LF band at 25 000 cm^{-1}.

serves as basis for the E_T scale [1,63] and which has been assumed to hold the world record for solvatochromism [1], has a value of B of only 4870 cm^{-1} (A 10570 cm^{-1}, r 0.991). Compared to the td system, the complexes with 4,4'-bpe, 4,4'-abpy, bpm and 4,4'-bptz ligands are distinguished by relatively small c_N^2 and a_N values while retaining a significant amount of basicity at the pyridine or pyrimidine nitrogen centers (Table 2). Pz, bod and quin ligands, on the other hand, are relatively poor bases in the ground state but may accept large amounts of charge in the MLCT excited state, as is evident from their c_N^2 and a_N values. Accordingly, the complexes with the latter group of ligands resemble situation (IV) in Fig. 1, while complexes of the first mentioned ligands are better characterized by case (II), despite comparable solvatochromism in both sets of complexes.

A comparison between mononuclear and binuclear complexes of the quin and bod ligands demonstrates again the stronger response of the latter species arising from double metal–ligand bond polarization [37].

Binuclear tetracarbonyl(phosphane)tungsten complexes

Substitution of one *cis*-carbonyl ligand by a phosphane affects the metal fragment by increasing its ability to transfer charge, as is evident from the lowering of the potentials for metal-centered oxidation. A study of the binuclear pyrazine complex with the electron-rich $W(CO)_4(PBu_3)$ fragments (E_{ox} 0.70 V vs. SCE) reveals considerably reduced solvatochromism when compared to the corresponding $W(CO)_5$ complex (E_{ox} 1.05 V); such reduction as the result of increased MLCT demonstrates that the situation (IV) in Fig. 1 is indeed a valid description for the pyrazine complexes. Incidentally, the coordination of the even more electron rich $(\eta^5\text{-}C_5R_5)(CO)_2Mn$ fragments [64] to the pyrazine ligand ($E_{ox} \simeq 0.4$ V [65]) reduces the solvatochromism of the binuclear system even further ($B \simeq 1600$ cm^{-1} [65]).

When the bridging ligand is changed from pyrazine to 4-cyanopyridine, which was also recently found to form binuclear complexes with carbonylmetal fragments [66], the solvatochromism of the $W(CO)_4(PBu_3)$ complex increases again (Table 2). This reflects the higher basicity and lower π acceptor ability of 4-cyanopyridine relative to pyrazine; both effects combine to move the system back, in the direction of situation (III) in Fig. 1, i.e. to cause larger solvatochromism.

Conclusion

Data for a series of seventeen tungsten carbonyl complexes with *N*-heterocycles has been used to derive and substantiate a consistent model for the solvatochromism of MLCT transitions. The relation between the metal–ligand bond polarities in the ground and MLCT excited state of a complex determines whether negative, positive, or no solvatochromism at all is observed. In view of the various possible situations (I)–(VI) (Fig. 1), the rationalization or even prediction of the extent of solvatochromism is not simple, and should preferably be restricted to a series of related systems. Useful criteria for such a perturbation approach are the ligand basicities, calculated Hückel MO coefficients c^2 or ESR coupling constants from the ligand coordination center(s), and redox potentials of the coordinated metal fragments.

The rational approach presented here for MLCT transitions may also be applied to LMCT transitions, for which there are fewer reports on solvatochromic behaviour [30,39]. In view of the requirements necessary for particularly large solvatochromism, one would like to have sufficient metal–ligand polarization in the ground state and a virtual compensation of this polarization through charge transfer in the excited state. The ground state polarizability is effectively increased by multiple coordination, so that multinuclear coordination compounds may exhibit pronounced solvatochromism even if they do not possess a permanent dipole moment [37,38]. Solvatochromism may thus provide at least indirect information on the polarizabilities in the ground and charge transfer-excited states [67], information which can be of great interest in such diverse areas as photochemistry and photocatalysis [39] and the development of materials for non-linear optics [68].

Experimental

The pentacarbonyltungsten complexes were prepared by treating the heterocyclic ligands [60,70–72] with the appropriate amount of photogenerated (THF)W(CO)$_5$ [40,43,52,58,73,74]. Binuclear tetracarbonyl(phosphane)tungsten complexes were obtained via electron-transfer-catalyzed carbonyl substitution [45,46]; detailed NMR, ESR and electrochemical studies will be the subjects of forthcoming reports.

Electronic absorption spectra were recorded in Spectrograde solvents on a Pye-Unicam SP 1800 instrument; wavenumbers for absorption maxima are believed to be correct within ± 180 cm^{-1} at 24000 cm^{-1} and ± 50 cm^{-1} at 14000 cm^{-1}.

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