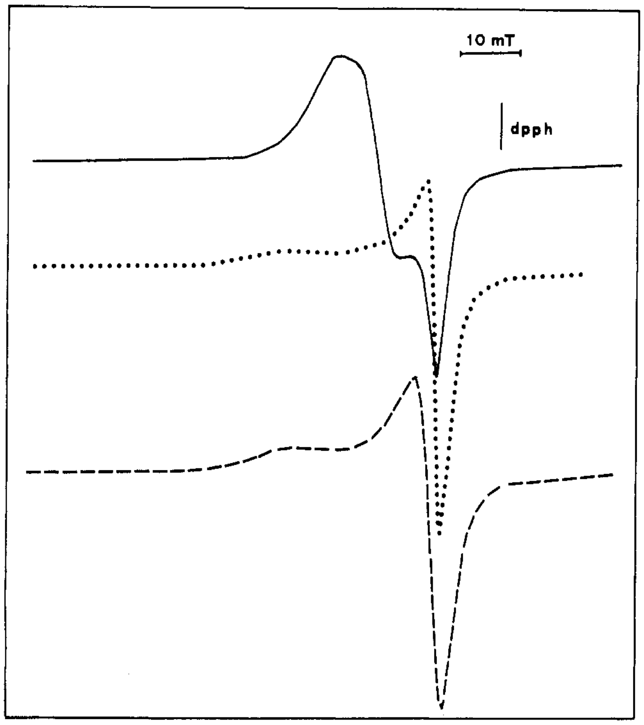

Figure 4. X-Band ESR spectra of $[Cu(Z\text{-}asp)(bpy)]_2 \cdot 2.5H_2O \cdot 0.5NaClO_4$ (—), $[Cu(Ac\text{-}asp)(bpy)] \cdot 2H_2O$ (···), and $[Cu(Bz\text{-}asp)(bpy)] \cdot H_2O$ (- - -).

parallel to the *b* cell axis. These chains are bridged through hydrophobic interactions between bpy molecules and phenyl groups. A comparison with previous structural results[7,20-22] shows very short interatomic distances (3.22 and 3.25 Å) between ring-stacked bpy moieties, whose mean planes make dihedral angles of 1.9 and 16.7°, respectively. The second system of nonbonding ring–ring interactions involves ring-stacking interactions of the $A_1 \cdots B_1 \cdots B_2 \cdots A_2$ type (A = phenyl, B = bpy) and hydrophobic contacts between bpy ligands and other phenyl groups. The shortest interatomic separations between rings and the dihedral angles between stacked ring planes are in the ranges 3.39–3.53 Å and 2.3–11.5°, respectively.

Spectroscopic Properties of Ternary Complexes. The powder ESR spectrum of $[Cu(Z\text{-}asp)(bpy)]_2 \cdot 2.5H_2O \cdot 0.5NaClO_4$ (Figure 4) is rather uninformative as likely affected by either exchange interactions or misalignment of the molecular axes, whereas the electronic absorption spectrum (Table III) is consistent with the square-pyramidal coordination of the metal atom.[24] The other ternary complexes exhibit ESR spectra (Figure 4) which, although again suggestive of weak coupling between the metal centers, as judged by the small line width, support a strongly distorted tetragonal coordination involving nitrogen donors in the metal plane. Instead, the electronic spectra are similar to that of $[Cu(Z\text{-}asp)(bpy)_2]_2 \cdot 2.5H_2O \cdot 0.5NaClO_4$ (Table III). Thus, on the whole, the spectroscopic results suggest that all the adducts have similar coordination geometry and involve the same donor set.

Dissolution of the complexes yields spectral parameters (Table III) that suggest an increase of the axial perturbation, compared to that in the solid state, due to the presence of oxygen donors in the apical positions of a CuN_2O_2-based chromophore. Particularly, the ESR parameters agree very well with those found, in either solution or solid state, for copper(II) ternary complexes of tridentate O donors and 2,2′-bipyridine containing a water molecule in the sixth position.[25]

Registry No. $[Cu(Z\text{-}asp)(H_2O)]_n$, 102922-19-0; $[Cu(Ac\text{-}asp)(H_2O)]_n$, 102922-21-4; $[Cu(Bz\text{-}asp)(H_2O)]_n$, 102922-23-6; Cu(Ac-asp)(bpy), 102922-24-7; Cu(Bz-asp)(bpy), 102922-25-8; $Cu(Z\text{-}asp)(bpy) \cdot {}^5/_2H_2O \cdot 0.25NaClO_4$, 102922-27-0.

Supplementary Material Available: Listings of anisotropic temperature factors, isotropic thermal factors, positional and isotropic thermal parameters for the hydrogen atoms, interatomic distances and angles, nonbonding ring–ring interactions, least-squares planes for $[Cu(Z\text{-}asp)(bpy)]_2 \cdot 2.5H_2O \cdot 0.5NaClO_4$, and variable-temperature magnetic data for the binary complexes (11 pages). Ordering information is given on any current masthead page.

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Exceptionally Variable Solvatochromism of Centrosymmetric Octacarbonyldimolybdenum(0) Complexes. Rules to Estimate the Solvent Sensitivity of Charge-Transfer Absorption Energies

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Solvent sensitivities varying by a factor of more than 6 were observed for the metal-to-ligand charge-transfer (MLCT, $\pi^* \leftarrow d$) absorption bands in four $(\mu\text{-}L)[Mo(CO)_4]_2$ complexes where μ-L are the doubly bidentate bridging ligands 2,2′-bipyrimidine (bpym), 2,5-bis(2-pyridyl)pyrazine (dppz), 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (dptz), and azo-2,2′-bipyridine (abpy). Although the binuclear complexes are centrosymmetric and should, therefore, not possess a permanent dipole moment, they exhibit stronger solvatochromism than their mononuclear, noncentrosymmetric analogues. The highly variable solvatochromic behavior of these complexes may be understood by considering the importance of dispersion interactions in such complexes; changes in molecular polarizability between the respective ground and MLCT excited states depend strongly on the differences in σ donation from the α-diimine ligand in the neutral and anion radical forms and on the possible degeneracy of the ligand π^* molecular orbitals. Some general guidelines are given that allow us to estimate the extent of MLCT absorption band solvent sensitivities from the properties of the ligands and of the metal fragments.

Introduction

After several earlier studies of the solvatochromic behavior of group 6 metal complexes with α-diimine ligands,[1-10] this phenomenon[11-13] has received some renewed attention in connection with approaches toward a more detailed understanding of bonding, electron transfer, and photoreactivity in such compounds.[14-24]

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† Karl Winnacker Fellow, 1982–1987.

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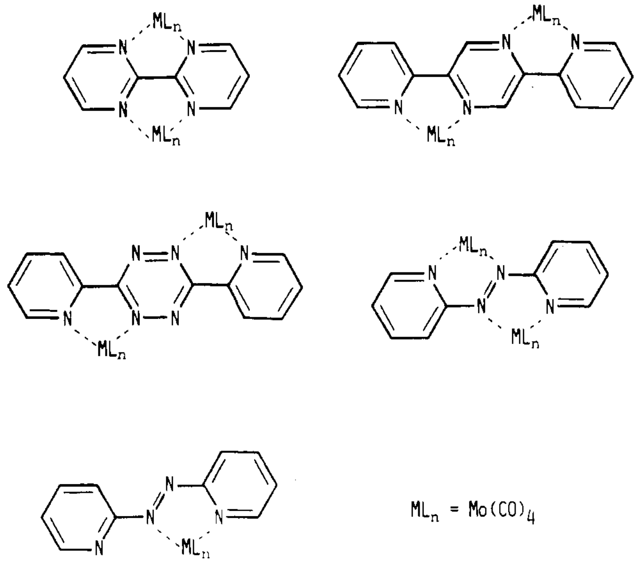
Table I. Metal-to-Ligand Charge-Transfer Absorption Maxima ν_{max}^{MLCT} (cm^{-1}) of Tetracarbonylmolybdenum Complexes in Different Solvents and Linear Correlation Parameters[a] with E^*_{MLCT}[b]

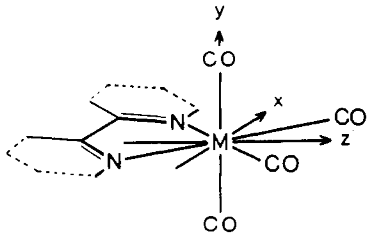
		ν_{max}^{MLCT}: solvent $(E^*_{MLCT})^b$							
complex	band	isooctane (0.00)	toluene (0.30)	THF (0.59)	acetone (log ε)[c] (0.82)	DMF (0.95)	A^a	B^a	r^a
$(\mu\text{-bpym})Mo_2(CO)_8$	I	*d*	15 500	16 500	17 600 (3.71)	18 400	14 070	4410	0.993
	II	*d*	19 300	23 500	24 000 (4.1)[e]	26 000[e]	16 870	9500	0.964
$(\mu\text{-dppz})Mo_2(CO)_8$	I	*d*	14 390	15 200	15 950 (4.22)	16 290	13 360	3110	0.999
	II	*d*	20 410	21 650	22 320 (3.6)	22 930	19 320	3770	0.997
$(\mu\text{-dptz})Mo_2(CO)_8$		*d*	11 100	11 780	12 110 (4.29)	12 200	10 530	1870	0.982
$(\mu\text{-abpy})Mo_2(CO)_8$		10 500	10 890	11 100	11 790 (4.26)		10 450	1460	0.964
$(abpy)Mo(CO)_4$		15 870	15 960	16 130	16 260	16 400	15 830	550	0.983

[a] Parameters for the equation $\nu_{max}^{MLCT} = A + BE_{MLCT}$ and the correlation coefficient r. [b] Solvent parameter E^*_{MLCT} was taken from ref 17. [c] ε in M^{-1} cm^{-1}. [d] Not measurable due to low solubility. [e] Shoulder, overlapping with solvent-insensitive band at 26 000 cm^{-1}.

Chart I



Usually, the negative solvatochromism displayed by these complexes, i.e., the hypsochromic shift of the MLCT absorption bands in polar solvents, is explained by assuming that the transfer of charge in the MLCT excited state occurs antiparallel to the ground-state dipole moment;[4,11,13] the higher transition energy in more polar solvents may thus be attributed to a dominating ground-state stabilization. In fact, nearly all of these studies were carried out with α-diimine complexes that have either idealized C_{2v} or C_s symmetry and should, therefore, possess a nonzero dipole moment; furthermore, the most frequently used ligands 1,10-phenanthroline,[8,16,22] 2,2′-bipyridine,[2,3,7-9,14,15,17,18,21] the 1,4-diazabutadienes,[1,4,7,9,10] and pyridine-2-carbaldehyde imines[5,6,9,10] also provide two identical or rather equivalent coordination sites (**1**).



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We have recently taken advantage of the existence of four isomeric α-diimine ligands with known characteristics, the bidiazine chelate ligands,[24] in order to demonstrate how the sensitivity of the first major MLCT bands toward solvent variation correlates with the back-bonding interaction in those isostructural and isomeric tetracarbonylmetal complexes.[24d] In this work, we present some initially puzzling results on the solvatochromic behavior of four dinuclear, centrosymmetric carbonylmetal complexes (Chart I) with the ligands 2,2′-bipyrimidine (bpym), 2,5-bis(2-pyridyl)pyrazine (dppz), 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (dptz), and azo-2,2′-bipyridine (abpy). These binuclear complexes have D_{2h} (bpym) or C_{2h} symmetry and, therefore, should not possess a permanent dipole moment. Furthermore, the two coordinating nitrogen sites for a $Mo(CO)_4$ fragment are identical in the bpym complex, but are very different in the dptz and abpy systems; compared to pyridine, the tetrazine and azo groups are much poorer σ donors,[25] but may provide for efficient back-donation into their very low lying π* orbitals.[26,27] In order to assess the effect of double coordination, we also studied and report here the solvatochromism of the mononuclear complex $(abpy)Mo(CO)_4$

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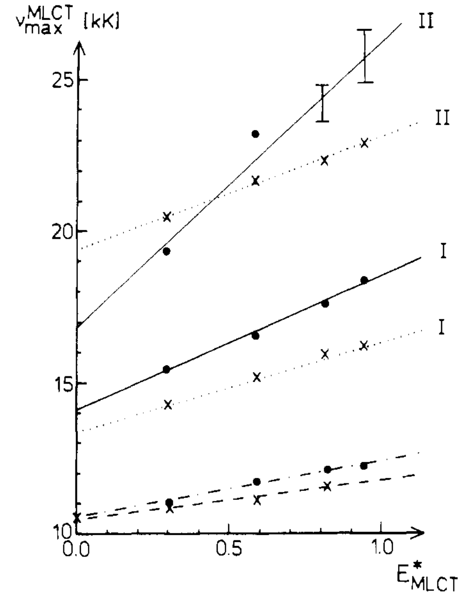


Figure 1. Correlation diagram showing E^*_{MLCT} solvent parameters from ref 17 plotted vs. MLCT absorption energies ν_{max}^{MLCT} (1 kK = 10^3 cm^{-1}) of octacarbonyldimolybdenum(0) complexes with the bridging ligands bpym (—; ●), dppz (···; ×), dptz (–·–; ●), and abpy (– –; ×). Roman numbers refer to the first (I) or second (II) major charge-transfer absorption bands.

(Chart I); data on the mononuclear complex (bpym)Mo(CO)$_4$ had been reported earlier.[24d]

Experimental Section

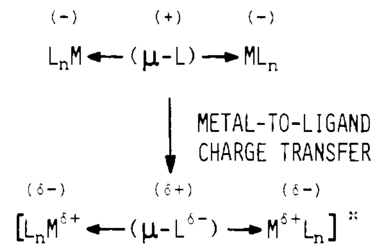
The compounds (μ-bpym)Mo$_2$(CO$_8$),[28] (μ-dptz)Mo$_2$(CO)$_8$,[27] and (μ-abpy)Mo$_2$(CO)$_8$[27] were prepared as reported. Identity and purity of the products were established by IR, NMR, and UV–vis spectroscopy and by elemental analysis.

(μ-dppz)Mo$_2$(CO)$_8$ was obtained by treating the ligand 2,5-bis(2-pyridyl)pyrazine[29] with 6 equiv of an irradiated THF solution of hexacarbonylmolybdenum, which contained Mo(CO)$_5$(THF) and nonconverted Mo(CO)$_6$.[30] After gentle warming to about 35 °C, CO evolution indicated formation first of the purple mononuclear and then of the blue-green binuclear tetracarbonylmolybdenum complex. Crystallization from THF/hexane yielded 70% of the compound. ν_{CO} (cm^{-1}) in THF solution: 2002, 1918, 1895, 1850. ^{1}H NMR (acetone-d_6): δ 10.02 (2 H, s, pyrazine H), 9.21 (2 H, d, H$_6$), 8.89 (2 H, d, H$_3$), 8.32 (2 H, ddd, H$_4$), 7.79 (2 H, ddd, H$_5$); $J_{3,4}$ = 8.1 Hz, $J_{4,5}$ = 7.7 Hz, $J_{5,6}$ = 5.6 Hz, $J_{3,5}$ = 1.2 Hz, $J_{4,6}$ = 1.6 Hz. Anal. C, H, N. UV–vis–near-IR spectra were recorded on Pye-Unicam SP 1800 and Perkin-Elmer Lambda 9 instruments; we thank Dr. D. Ventur and Prof. K. Wieghardt (Ruhr-Universität Bochum) for the near-IR measurements. The complexes were studied in spectrograde solvents; absorption maxima are believed to be correct within ±3 nm on the wavelength scale, which translates to ±36 cm^{-1} at 11 000 cm^{-1} and to ±190 cm^{-1} at 25 000 cm^{-1}.

Results

The absorption spectra of the five complexes (Chart I) were measured in at least four different representative solvents, which cover a broad polarity range (Table I). Excluded from this set were protic and chlorinated solvents, the former because of additional complications expected through hydrogen bonding and the latter because the highly polarizable chlorine centers are known to lead to ill-behaved solvent correlations.[17] As solvent parameters for correlations with the MLCT absorption band maxima, we used the E^*_{MLCT} values that were derived by Manuta and Lees[17] from solvatochromism studies on the related (bpy)M(CO)$_4$ complexes (M = Cr, Mo, W), i.e. standard systems in investigations on solvatochromic behavior.[2,3,7-9,14,15,18,21] E^*_{MLCT} has been defined between 0.00 (isooctane) and 1.00 (dimethyl sulfoxide).[17] While most complexes were not sufficiently soluble in the nonpolar solvent isooctane, the binuclear complex with abpy dissociates rapidly in DMF solution to yield the mononuclear species.

Scheme I



In agreement with MO perturbation calculations,[31] the abpy and dptz complexes exhibit only one major[31,32] MLCT transition in the visible-to-near-infrared region; the bpym and dptz systems, on the other hand, have two solvent-sensitive MLCT bands in that range as expected from the calculations.[31] The spectra of the bpym complex in various solvents are further dominated by an intense ($\epsilon \simeq 4.15$) solvent-insensitive band at 26 000 cm^{-1}; a similar observation was made by Moore and Petersen for the corresponding binuclear tungsten complex.[33]

Linear correlations between measured energies of absorption band maxima and the solvent parameters E^*_{MLCT} are illustrated in Figure 1, the correlation parameters derived from least-squares fit analyses are summarized in Table I. The correlation coefficients indicate good linear behavior except for the second MLCT band in (bpym)Mo$_2$(CO)$_8$, which is obscured by the overlapping transition at 26 000 cm^{-1}, particularly in polar solvents; the abpy complexes display the smallest solvatochromism so that the experimental uncertainties strongly affect the correlation coefficients.

Discussion

Double coordination of Mo(CO)$_4$ fragments to the very π-electron-deficient α-diimine ligands bpym, dppz, dptz, and abpy yields complexes with exceptionally low energy MLCT absorptions.[27,28,34] Although these complexes should have a center of symmetry and hence a zero ground-state dipole moment, they all exhibit the typical negative solvatochromism of MLCT bands,[13] albeit to a widely varying degree. The highest solvent sensitivity is displayed by the second MLCT band of the bpym complex, while the ratio $\Delta\nu/\Delta E^*_{MLCT} = B$ for the binuclear abpy system is smaller by a factor of more than 6. In contrast to the results obtained for the series of four isomeric bidiazine complexes,[24d] the solvent sensitivity of the first MLCT band decreases along with decreasing absolute MLCT absorption energies, i.e. following the order bpym > dppz > dptz, abpy complexes.

Another remarkable result is the significant increase in solvent sensitivity of centrosymmetric binuclear systems with respect to their noncentrosymmetric mononuclear analogues; in the bpym series, the parameter B increases from 3340[24d] to 4410, and in the two abpy compounds, the parameters are 570 for the mononuclear species and 1460 for the binuclear species.

These results as well as the fact that large solvatochromic effects are observed at all for the centrosymmetric binuclear systems in contrast to expectations[13] suggest the necessity to modify the conventional explanation of solvatochromism, which invokes the dipole moment change between the ground state and the excited state.[4,11,13] Since there is no evidence that the dipole moment should be nonzero in the excited state either (which would imply, e.g., a localized transition from only one metal center to the ligand π system),[34] the effect responsible for the pronounced solvato-

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(32) The broad bands of (α-diimine)M(CO)$_4$ complexes were shown by resonance Raman and MCD studies to comprise several differently polarized transitions,[10a] the major allowed component being $\pi^*(b_2) \leftarrow d_{yz}$.

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chromism in such complexes must involve their polarizability.[20b,c] On the molecular level, the polarizability α (the proportionality constant between the induced dipole moment μ_{ind} and an inducing electric field E) describes to what extent external electric fields as exerted, e.g. by a solvent medium, will affect the shift of charge within the molecular framework through dispersion forces (induced dipole moment interactions).[2,11b] Charge-transfer complexes with their delicate balance between σ donation and π back-bonding should obviously be strongly polarizable also in the absence of a permanent dipole moment; other examples of solvatochromic, centrosymmetric charge-transfer complexes include, e.g., the pyrazine complexes $\mathrm{L}_n\mathrm{M{-}pz{-}ML}_m$,[35] for which B is estimated from the available data to be about 4500 for ML_n = W(CO)$_5$[20] and 1600 for ML_n = MnCp(CO)$_2$.[36]

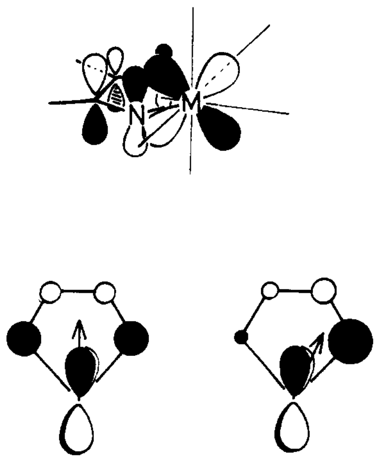
The polarizability argument explains straightforwardly why binuclear complexes have higher solvent sensitivities than those of mononuclear species: The polarizing interaction between ligand and metal fragment occurs twice (Scheme I)! The exact ratio of B values between binuclear and mononuclear species depends on several factors such as changes in ligand properties upon the first coordination or steric effects; thus, the ligand abpy adopts different conformations in mononuclear and binuclear complexes.[27b]

The degree of solvatochromism should, therefore, depend on the *change in molecular polarizability*, α, when going from the ground state to the excited state.[37] In keeping with the argument using dipole moment changes,[4,13] it may be assumed that, in complexes displaying MLCT transitions, the polarizability in the ground state, α_{gr}, should be large because the shift of charge occurs from the usually negatively polarized low-valent metal center to the positively polarized ligand; this will then lower the polarizability in the MLCT excited state, α_{ex} (Scheme I). The relation between α_{gr} and α_{ex} may vary, however, and even be reversed; i.e., $\alpha_{\mathrm{ex}} > \alpha_{\mathrm{gr}}$ will cause positive solvatochromism. The latter or a virtually solvent-independent situation ($\alpha_{\mathrm{gr}} = \alpha_{\mathrm{ex}}$) has been observed with dicarbonylbis(phosphane)molybdenum complexes of α-diimines[4c,10a,34b] for which ESR studies on anion radicals still indicate the MLCT character of the first MLCT transition;[7,34b] very negatively charged metal fragments such as M(CO)$_2$(PR$_3$)$_2$ or very weakly σ-donating α-diimine ligands render the polarization in the ground state rather small.

As concerns the other component, the polarizability in the excited state, it will depend to a large extent on the σ-donor strength acquired by the α-diimine ligand during the MLCT transition. The excited electron will be added into a π^* orbital of the ligand, thereby causing a tremendous increase of its basicity,[38] and the higher this ligand σ donation in the excited state, the higher should be the polarizability α_{ex}. We have recently proposed[24c,31] that this additional basicity acquired by a heterocyclic π system in the reduced or MLCT excited state may be conveniently estimated by using Hückel MO coefficients $c_{\mathrm{N}}{}^2$ (LUMO) at the corresponding π centers;[39] useful experimental indicators for these estimations are the ESR coupling constants of the ^{14}N nuclei, which reflect the distribution of the unpaired electron in the π^* orbital.[40]

Two extreme cases may now be considered: Complexes containing α-diimine ligands that are strongly basic in the ground state but which acquire a relatively small amount of basicity in the excited (or reduced) state as indicated by calculations or by small ESR coupling constants $a_{^{14}\mathrm{N}}$ in the anion radicals should exhibit strong solvatochromism. Such a behavior is displayed by the 2,2′- and 4,4′-bipyrimidine (bpym and bpm[24]) complexes and, to a lesser extent, by the classical 2,2′-bipyridine and 1,10-phenanthroline systems; the experimental ESR coupling constants $a_{^{14}\mathrm{N}}$ at the α-diimine nitrogen centers in the ligand anion radicals are 0.143 (bpym$^{\bullet-}$),[41] 0.158 (bpm$^{\bullet-}$),[40] 0.261 (bpy$^{\bullet-}$), and 0.280 mT (phen$^{\bullet-}$).[42]

Chart II



On the other hand, complexes containing ligands that are very poor σ donors in the ground state but which acquire a large amount of basicity in the MLCT excited (or reduced) states should exhibit only weak solvatochromism; i.e., α_{gr} should then be not that much larger than α_{ex}. Prototypes for this kind of compounds are the abpy and dptz complexes; their dominant chromophors, the azo and s-tetrazine moieties, are very poor bases in the ground state.[25,43] However, the ESR[34,44] and calculation results[31] indicate a particularly strong increase of electron density at the coordinating centers in the reduced or MLCT excited states of the d^6 metal complexes. Since ESR studies show that the spin in the anion radicals of these complexes is strongly localized at the azo nitrogen centers,[34] the MLCT transition moments in these chelate-bonded complexes with two very inequivalent coordination sites will presumably be directed to the area of this localization as illustrated in Chart II. Between the extremes of abpy and dptz complexes on one side ($B \simeq 1600$) and of bpm and binucleating bpym systems ($B \simeq 4200$) on the other side (Table I), there are, of course, intermediate cases such as the bppz binuclear complexes or the bpz and bpdz mononuclear species;[24d] the tetracarbonylmetal complexes of 1,4-diazabutadienes constitute a special case due to their conformational flexibility, and consequently, tom Dieck and co-workers have detected strong steric effects on their solvatochromic behavior.[4b]

It seems that the proposed crude model, which involves only σ contributions and neglects, in this first approximation, the different charge shifts via π back-bonding, gives a sufficiently reliable first indication of the degree of solvatochromism in α-diimine tetracarbonylmetal complexes. Spectroscopic studies have shown that the π^* levels in such α-diimine carbonylmetal complexes may interact with various other orbitals of appropriate symmetry, with occupied d$_{yz}$ metal orbitals (Chart II) but also with the π^* orbitals of the equatorial carbonyls[13] and with the $\sigma^*_{\mathrm{M-C}}$ orbitals involving the axial (cis) carbonyl ligands.[45] In fact, more subtle studies in the fortunate case of four isomeric

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(43) Electron density at coordinated d^6 metal centers may be estimated from oxidation potentials (Ru$^{\mathrm{II}}$ or Cr^0 complexes) or from heteronuclear NMR (e.g. ^{95}Mo NMR): Alyea, E. C.; Ernst, S.; Kohlmann, S.; Kaim, W., unpublished results.

(44) ESR coupling constants of azo nitrogen centers amount to 0.495 mT in dptz$^{\bullet-}$ (ref. 34) and to about 0.46 mT in the abpy anion radical.

(45) Kaim, W. (a) *Inorg. Chim. Acta* **1981**, *53*, L151. (b) Kaim, W. *Chem. Ber.* **1982**, *115*, 910. (c) Kaim, W. *J. Organomet. Chem.* **1984**, *262*, 171.

and isostructural α-diimine complexes have revealed the significance of the contributions from π back-bonding;[24d] however, it seems that the extent of sovatochromism in the series of α-diimine tetracarbonylmetal complexes with their relatively similar π back-bonding depends largely on the differences in σ-donation behavior of the ligands in their respective ground and MLCT excited states.

This result thus illustrates still another use of calculated or ESR-estimated charge distributions in π^* molecular orbitals; previous studies[24c] have demonstrated the value of these data in estimating reduction potential changes, absorption band energies and intensities, and MLCT excited-state lifetimes.

A further result that requires explanation concerns the very strong solvent sensitivity of the second MLCT absorption band in (μ-bpym)$Mo_2(CO)_8$; this band at 26 000 cm^{-1} yields a value of $B \simeq 9500$, which is about twice as large as the B parameter for the first MLCT band. To understand this result, one has to consider the D_{2h} symmetry of the system and the resulting degeneracy of the second lowest unoccupied molecular orbitals,[40] a_u and b_{3g}, if the z axis is chosen as the coordination axis (**1**) (connecting the two metal centers in the binuclear complex).[4,10] Besides the first long-wavelength transition $\pi^*(b_{2u}, \text{LUMO}) \leftarrow 2d_{yz}$ (Chart II), two symmetry-allowed MLCT transitions of virtually equal energy are possible, viz. $\pi^*(b_{3g}) \leftarrow 2d_{yz}$ and $\pi^*(a_u) \leftarrow 2d_{xy}$. The two degenerate second lowest molecular orbitals each have similar small $c_N{}^2$ values as the LUMO,[24c] and accordingly, the solvent sensitivity of these degenerate transitions becomes about twice as large as that of the first band. Apparently, there is an almost additive dependence of the degree of solvatochromism on the number of allowed metal orbital/ligand orbital interactions; thus, interaction of *two* metal fragments in (bpym)$[M(CO)_4]_2$ with a *doubly degenerate* ligand MO increases the polarizability difference $\alpha_{gr} \gg \alpha_{ex}$ to an unusually large extent.

Finally, attention should be drawn to the solvent-insensitive absorption band at 26 000 cm^{-1} in (bpym)$[M(CO)_4]_2$ complexes (M = Mo, W). Moore and Petersen[33] attributed this absorption band to a ligand field transition with considerable MLCT admixture,[46] which seems reasonable because *two* metal centers are now present in the complex; nevertheless, the fact that this strong spectral feature occurs *only* in the bpym complex and not in the other binuclear species that have metal–metal distances larger (dppz, dptz) or smaller (abpy)[27] than those in the bpym system should be related to the special coordination arrangement and the high symmetry. In speculating, we may assume a connection of this spectral feature with the low-lying excited state inferred from the unusually low g values found for the anion radical complexes.[41] Clearly, further photochemical or resonance Raman studies are needed to elucidate the nature of this conspicuous absorption band.

Summary and General Rules

This study provides strong evidence for the conception that the solvatochromism in the kind of complexes at hand, viz. uncharged carbonylmetal complexes with α-diimine ligands,[1-24] depends mainly on polarizability differences[20b,c] between the ground and MLCT excited states. The results presented here draw new attention to the conclusions obtained in the early study of Saito, Fujita, and Saito,[2] who reported that the MLCT absorption bands owe their distinct solvatochromism to the large contribution of dispersion force, i.e., to induced-dipole interactions involving the polarizability α according to the relation $\mu_{ind} = \alpha E$.

The wide range of solvent sensitivities of MLCT absorption bands as reported in this investigation allows us to propose a few rules for estimating the degree of solvatochromism. Strong solvent sensitivity can be expected if (a) the number of allowed metal-to-ligand transitions in one molecule at one energy is large (i.e., polynuclear (ligand-bridged) complexes and species containing ligands with π^* orbital degeneracy should exhibit particularly strong solvatochromism), (b) the σ donation exerted by the ligand (basicity!) is high in the ground state (large α_{gr}), and the σ donation capability increases relatively little in the excited state (small α_{ex}), as may be inferred from π MO calculations or from ESR data of reduced systems, (c) the π back-donation is sufficiently large, and (d) the metal fragment is electron poor, as may be estimated, e.g., from electrochemical oxidation potentials. The validity of the last point may be illustrated by several additional results. According to this rule, pentacarbonylmetal complexes should display higher solvent sensitivities than corresponding tetracarbonylmetal species because $M(CO)_5$ fragments are less electron rich than $M(CO)_4$ fragments. Pertinent examples for this rule include the pair (pyrazine)$[W(CO)_5]_2$ with $B \simeq 4500$[20] and (dppz)$[W(CO)_4]_2$ with $B \simeq 3200$[47] where one CO ligand is replaced by a 2-pyridyl group; another related example concerns the two complexes (bpm)$W(CO)_4$ with $B \simeq 4000$[24d] and (bpm)$[W(CO)_5]_2$[24a,c] with $B \simeq 5000$.[47] Increasing the electron density at the metal center in going from $Mo(CO)_4$ via $Mo(CO)_3(PR_3)$ to $Mo(CO)_2(PR_3)_2$ causes a reduction and, in some instances, even a reversal of negative solvatochromism in the corresponding α-diimine complexes.[4c,10a,34b] Other examples of this kind are the binuclear d^6 metal complexes of μ-pyrazine; for instance, the use of $W(CO)_5$ fragments gives a value of $b \simeq 4500$[20] whereas lower values of $B \simeq 1600$ are obtained with the much more electron rich fragments $(\eta^5\text{-}C_5R_5)Mn(CO)_2$.[36] Even less solvatochromic are, therefore, ruthenium(II) complexes that cannot undergo hydrogen bonding.[48]

The guidelines to estimate solvent sensitivities of charge-transfer absorption bands as given here may, with due precautions, also be applicable to other such complexes without α-diimine ligands; the very small solvatochromism of the $\pi^*(CO) \leftarrow d$ bands in group 6 metal hexacarbonyls[49] may thus be understood by considering the extremely poor nucleophilicity of CO in the ground state and the large amount of charge transferred to this ligand in the MLCT excited states, which results in a situation where $\alpha_{gr} \sim \alpha_{ex}$. The frequently observed thermochromism of MLCT complexes[50] may also be explained by assuming dominating dispersion interactions; increasing solvent association at lower temperatures leads to a higher dielectric constant of the medium and hence to the usually observed hypsochromic shifts on cooling.[50] Eventually, after inclusion of additional important aspects such as hydrogen bonding in protic solvents,[48a] the rules presented in this work should provide a practical basis for better approaches toward the extremely complex phenomenon of absorption band sensitivity toward solvvents.[11-13]

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Registry No. (μ-bpym)$Mo_2(CO)_8$, 81986-03-0; (μ-dppz)$Mo_2(CO)_8$, 102869-01-2; (μ-dptz)$Mo_2(CO)_8$, 97374-20-4; (μ-abpy)$Mo_2(CO)_8$, 97374-25-9; (abpy)$Mo(CO)_4$, 102869-02-3; THF, 109-99-9; DMF, 68-12-2; isooctane, 540-84-1; toluene, 108-88-3; acetone, 67-64-1.

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