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CORRELATION BETWEEN SOLVATOCHROMISM AND BACK-BONDING IN FOUR ISOMERIC (α-DIIMINE)M(CO)$_4$ COMPLEXES, M = Cr, Mo, W

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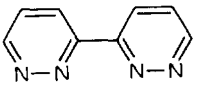
Summary

Long-wavelength charge transfer absorption energies of isomeric complexes (bidiazine)M(CO)$_4$, (bidiazine = 3,3′-bipyridazine, 2,2′- and 4,4′-bipyrimidine, 2,2′-bipyrazine; M = Cr, Mo, W) were measured in various solvents and compared with those for corresponding 2,2′-bipyridine complexes. Linear correlations of energies of absorption maxima with solvent parameters E^{*}_{MLCT} revealed that the solvent dependence $\Delta\nu/\Delta E^{*}_{\mathrm{MLCT}}$ within the bidiazine series increases with decreasing absolute charge transfer transition energy in a given solvent, i.e. with increasing back-donation into the ligand π^{*} orbital. Complexes of the most strongly back-bonding ligand, 4,4′-bipyrimidine, thus display by far the most pronounced solvent dependence, with $\Delta\nu/\delta E^{*}_{\mathrm{MLCT}}$ 4100 cm^{-1} for the molybdenum system.

Introduction

We have recently revealed the strong back-bonding exerted by 4,4′-bipyrimidine (bpm) [1] and 3,3′-bipyridazine (bpdz) [2] towards d^6 metal fragments. Complexes of these two less studied isomers of the bidiazine family have metal-to-ligand charge transfer (MLCT, $\pi^{*} \leftarrow d$) absorptions at longer wavelengths than corresponding complexes of the two better known and commercially available ligands in that series, viz., 2,2′-bipyrimidine (bpym) [3,4] and 2,2′-bipyrazine (bpz) [5,6].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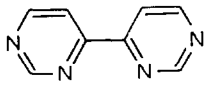
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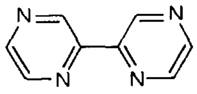
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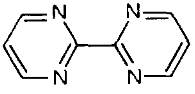
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It was noted that tetracarbonyl-chromium, -molybdenum and -tungsten complexes of bpym [3,4] and bpz [6], as well as of bpm [1] and bpdz [2], exhibit the negative solvatochromism which is typical for such α-diimine tetracarbonylmetal species [6–18]; the current renewed interest [6,9,17,18] in more quantitative approaches towards this phenomenon has now prompted us to look for a correlation between the extent of solvatochromism and the established [1,2] order of back-bonding in the series of isomeric coordination compounds (bidiazine)M(CO)$_4$.

Results and discussion

For the related complexes (bpy)M(CO)$_4$ (bpy = 2,2′-bipyridine), Manuta and Lees recently published a large number of absorption data in various solvents from which they derived a modified solvent parameter (E^{*}_{MLCT}) scale, especially suited to correlate MLCT absorption energies [18]. E^{*}_{MLCT} values ranged between those of isooctane ($E^{*}_{\mathrm{MLCT}} = 0.00$) and dimethylsulfoxide ($E^{*}_{\mathrm{MLCT}} = 1.00$). We have used these results as well as published data for (bpym)M(CO)$_4$ [4] and for (bpz)Mo(CO)$_4$ [6] in addition to our own measurements (Table 1) in the three representative aprotic solvents toluene ($E^{*}_{\mathrm{MLCT}} = 0.30$), tetrahydrofuran, THF ($E^{*}_{\mathrm{MLCT}} = 0.59$), and dimethylformamide, DMF ($E^{*}_{\mathrm{MLCT}} = 0.95$); unfortunately, many complexes were insufficiently soluble in the non-polar iso-octane ($E^{*}_{\mathrm{MLCT}} = 0.00$). MLCT energies recorded in chlorinated solvents (methylene chloride, chloroform, tetrachloromethane) are not included [9] because the E^{*}_{MLCT} values given for these solvents [18] seem to be somewhat too large.

TABLE 1

LONG-WAVELENGTH ABSORPTION MAXIMA (cm^{-1}) OF (α-DIIMINE)M(CO)$_4$ COMPLEXES IN VARIOUS SOLVENTS

Compound	Solvent (E^{*}_{MLCT}) [a]			
	i-Octane (0.0)	Toluene (0.30)	THF (0.59)	DMF (0.95)
(bpy)Cr(CO)$_4$ [b]	18350	18720	19760	21370
(bpdz)Cr(CO)$_4$	*c*	15970	17010	18080
(bpm)Cr(CO)$_4$	*c*	14490	15870	16980
(bpz)Cr(CO)$_4$	15240	16670	17300	18220
(bpym)Cr(CO)$_4$ [d]		18080 [d]		20040 [d]
(bpy)Mo(CO)$_4$ [b]	19300	20120	21180	22620
(bpdz)Mo(CO)$_4$	*c*	17240	18120	19550
(bpm)Mo(CO)$_4$	*c*	15870	17240	18550
(bpz)Mo(CO)$_4$	16260	17670	18650 [e]	19650 [e]
(bpym)Mo(CO)$_4$	*c*	19080	20410	21280
(bpy)W(CO)$_4$ [b]	18660	19300	20490	22030
(bpdz)W(CO)$_4$	*c*	16950	17860	18620
(bpm)W(CO)$_4$	*c*	15150	16450	17860
(bpz)W(CO)$_4$ [f]	*c*	17300	18120	19010
(bpym)W(CO)$_4$ [d]		18690 [d]		20920 [d]

[a] Solvent parameters E^{*}_{MLCT} from ref. 18. [b] Ref. 18. [c] Not soluble. [d] Values in benzene (0.34) and acetonitrile (0.98) from ref. 4. [e] From ref. 6.

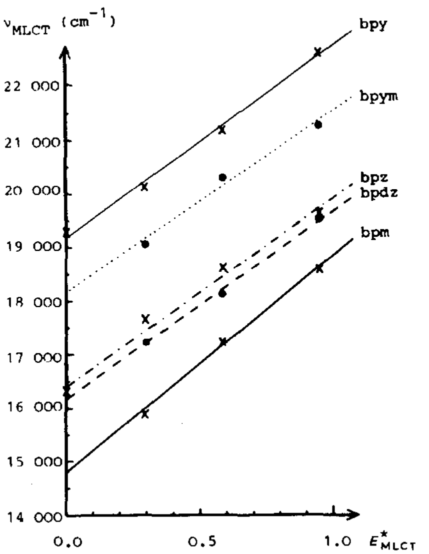


Fig. 1. Metal-to-ligand charge transfer absorption maxima ν_{MLCT} of (α-diimine)Mo(CO)$_4$ complexes plotted against the solvent parameter E^*_{MLCT} [18].

Although the first MLCT bands in such α-diimine complexes comprise several electronic transitions [16,18], we observed only one absorption maximum in each case at room temperature (Table 1). A comparison among related systems differing only in the metal shows that the solvatochromic shifts, $\Delta\nu$, for a given solvent pair are fairly constant [13], although the absolute absorption energies vary in the order $\nu(\mathrm{Mo}) > \nu(\mathrm{W}) > \nu(\mathrm{Cr})$, in accordance with geometrical and effective nuclear charge effects [19]. In the Mo(CO)$_4$ series, for which the most data are available [6,17], we have correlated the long-wavelength charge transfer absorption energies of the four bidiazine complexes and of the bpy system with the respective E^*_{MLCT} values and observed approximately linear behaviour (Fig. 1); the parameters of the straight lines obtained via least-squares fit are given in Table 2.

For the four bidiazine complexes, the slope B, i.e. the sensitivity towards solvent change, decreases as the intercept A, the absorption maximum wavenumber at $E^*_{MLCT} = 0.00$ increases. Hence, the sequence of $\Delta\nu/\Delta E^*_{MLCT} = B$ in Table 2 is also in agreement with the established sequence of back-bonding interaction among the

TABLE 2

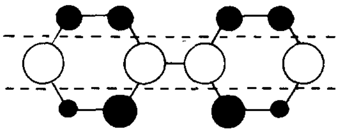
PARAMETERS OF EQUATIONS $\nu_{MLCT} = A + B \cdot E^*_{MLCT}$ FOR (α-DIIMINE)Mo(CO)$_4$ COMPLEXES BASED ON DATA FROM TABLE 1

α-diimine	A (cm^{-1})	B (cm^{-1})	r[a]
bpy	19190	3520	0.997
bpdz	16110	3570	0.997
bpm	14700	4100	0.997
bpz	16430	3530	0.992
bpym	18210	3340	0.984

[a] Correlation coefficient.

(bidiazine)M$(CO)_4$ and (bpy)M$(CO)_4$ complexes [1,2], mononucleating bpym displaying a rather weak effect and bpm exerting by far the strongest such interaction with d^6 metal fragments [1]. As a result of these tendencies, the MLCT transition energies of the bidiazine systems are drawn closer together in more polar solvents such as DMF; further extrapolation shows that the MLCT absorption energies should even converge at $E^{\star}_{\text{MLCT}} > 1.2$, i.e., in a region of little chemical significance.

The correlation between absolute MLCT energies and the extent of solvatochromism may be understood by considering the origin of this solvent effect. All other parameters such as geometry, composition, and nodal properties of the π^* level being comparable, the stronger back-donation in a given system means that more charge will be transferred between the metal and the ligand in the excited state of the complex. Accordingly, the differences between the dipole moments on going from the ground states to the MLCT excited states should increase, eventually leading to higher sensitivity towards change of solvent [8,9]. Figure 1 and Table 1 demonstrate the success of this simple approach within the (bidiazine)Mo$(CO)_4$ complex series. The 2,2′-bipyridine complexes also seem to obey the rule (Fig. 1), even though the absolute MLCT energies are higher than in the bidiazine series because of absence of two electronegative nitrogen centers. In all these five cases the symmetrical α-diimine chelate arrangement and the nodal properties of the ligand π^* LUMOs (lowest unoccupied molecular orbitals) [20] are alike, so that the amount of back-donation becomes the sole determining factor for the degree of solvatochromism.



Generalizing, the extent of solvent dependence of MLCT absorptions correlates directly with the degree of back-bonding interaction; for the metal carbonyl complexes studied, the largest spread of MLCT absorption energies is found in the least polar solvents, where solvent-solute interactions are small and intramolecular effects dominate. Solvatochromism of α-diimine molybdenum carbonyl complexes has now been studied as a function of (i) the steric situation at the ligand [14]; (ii) further substitution at the metal centre [14,16]; and (iii), ligand MO variations (this work); further investigations will be needed to reveal the way in which other factors, such as the symmetry of the α-diimine ligand, affect the solvatochromic behaviour of (α-diimine)carbonylmetal complexes.

Experimental

The synthesis of the complexes has been described previously [1–3,5]. 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 ±60 cm^{-1}.

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