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Solvent Influences on the Spectra of Tetracarbonyl (4,4′-disubstituted-2,2′-bipyridine)molybdenum Complexes

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The solvent dependence of the frequency of maximum absorption of the metal-to-ligand charge transfer (MLCT) band in the visible region of the spectra of the complexes $[M(CO)_4(bpy)]$ (M = Cr, Mo, W; bpy is 2,2′-bipyridine) was described many years ago [1]. Similar observations have been made of the solvatochromism of other α-diimine complexes [2]. So far as we are aware, the nature of the solute–solvent interaction has not been specified in greater detail.

In order to gain a clearer understanding of the solute–solvent interaction we have investigated the solvent dependence of nuclear magnetic resonance (^1H and ^{13}C), infrared, and visible absorption and emission spectra of a range of 4,4′-disubstituted-2,2′-bipyridine complexes, in which the electronic donor/acceptor character of the substituents was varied widely.

We wish to draw particular attention to the influence of solvent polarity on the NMR spectra of these complexes. The effect of solvent polarity ($CDCL_3$, d_6-DMSO) on the chemical shifts of the protons of the free ligands (which exist in the *trans*/*anti* configuration) is small (less than 0.1 p.p.m.). Coordination to a metal involves a rearrangement to the *cis*/*syn* configuration. One would expect that the ring protons H3, H3′ and H6, H6′ should be most sensitive to the change in their environment as a result of coordination; this can be measured by the coordination shift, Δ defined as [δ(complex – δ(free)] p.p.m. The results (Table I) show that in all cases there are large incremental changes in the chemical shift of these protons as the polarity of the solvent increases. In chloroform, a solvent of low polarity, H3/3′ is more shielded than in the free ligand but H6/6′ resonates to lower field than in the free ligand. In constrast to this, in the more polar solvent dimethylsulphoxide, H3/3′ in the complex resonates at lower field than in the free ligand but H6/6′, while deshielded compared to the free ligand, is less deshielded than in chloroform. The values of Δ for H3/3′ and H6/6′ are very similar (*ca.* 0.3 p.p.m.) in the more polar solvent.

TABLE I Coordination Shift, Δ/p.p.m. = [δ(complex) – δ(free)] in $CDCL^3$ and d_6-DMSO, for $[Mo(CO)_4(4,4'\text{-}X_2\text{-}bpy)]$

X	H3/H3′		H6/H6′	
	$CDCl_3$	d_6-DMSO	$CDCl_3$	d_6-DMSO
MeO	–0.45	0.29	0.47	0.22
Me_3C	–0.37	0.22	0.40	0.25
H	–0.13	0.33	0.66	0.45
Cl	–0.38	0.52	0.50	0.28
MeD_2C	–0.16	0.17	0.44	0.36

The electronic influence of the substitutent is immediately apparent from the colour of the solid complexes. Thus, with a donor substituent the MLCT absorption moves to higher energy (*e.g.*, $[Mo(CO)_4\{4,4'\text{-}(Me_2N)\text{-}bpy\}]$ is golden yellow) and with an acceptor substituent the MLCT absorption moves to lower energy (*e.g.* $[Mo(CO)_4\{4,4'\text{-}(O_2N)\text{-}bpy\}]$ is deep blue). The energy of MLCT absorption shows a strong correlation with the Hammett parameter, σ_p, of the substituent (correlation coefficient 0.96) according to the relation $\lambda(MLCT) = (2.24 - 0.45\ \sigma_p)$ eV. For a given substituent, the variation of the MLCT absorption maximum shows a strong correlation with the solvent polarity [3] parameter, π^*; for example, in the case of $[Mo(CO)_4\{4,4\text{-}Me_2\text{-}bpy\}]$, the equation $\lambda(MLCT) = (2.31 + 0.596\ \pi^*)$ eV produces a correlation coefficient, 0.96. The emission spectra (77K) of the complexes are sensitive to the substituent. The energy difference between the maxima of the emission and excitation spectra is independent of both substituent and solvent/matrix polarity with a value of (0.80 ± 0.07) eV. These results suggest that the chemistry of bpy complexes in solution will be subject to more precise control than has been recognised hitherto. Details of these measurements together with results of other relevant experiments will be reported.

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