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SOLVENT INFLUENCES ON THE INFRARED ABSORPTION AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF 4,4-DISUBSTITUTED-2,2′-BIPYRIDINETETRACARBONYLMOLYBDENUM COMPLEXES

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Summary

Proton and carbon NMR spectra of both 4,4′-X_2-bipy and *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)] (X = OMe, CMe_3, Me, H, Cl, CO_2Me) have been recorded in solvents (chloroform, dimethyl sulphoxide) of different polarity. The measurements show that the influence of the solvent on the chemical shifts of the bipyridine ring increases significantly as a result of coordination to the metal. Changes in solvent polarity may discriminate between different carbon atoms and the protons attached to them. Measurements of infrared spectra (2100–1700 cm^{-1}) of the complexes (X = OMe, CMe_3, Me, CO_2Me, NO_2) in solution indicate that there is a preferential interaction between the solvent and the equatorial CO ligands which are *trans* to 4,4′-X_2-bipy.

Introduction

The influence of solvent polarity on the absorption spectra of transition metal complexes of 1,4-diimine ligands is well-documented [1]. Recently we have described [2] the electronic effect of ring substituents in 2,2′-bipyridine (bipy) ligands in complexes of the type *cis*-[M(CO)$_4$(n,n'-X_2-bipy)] (M = Cr, Mo, W; n = 4,5; X = NMe_2, NH_2, OMe, Me, CMe_3, H, Ph, CH : CHPh, CO_2H, Cl, CO_2Me, NO_2) on the solvatochromism of these complexes in a variety of solvents of differing polarity. Both absorption and emission spectra were observed and the redox potentials of the complexes in different solvents were measured. This work showed that it should be possible to control chemistry at the metal centre by a careful choice of both the substituent, X, and the solvent. We have used other spectroscopic measurements which report on specific parts of the complex molecule and now describe the influence of different solvents on the nuclear magnetic resonance (NMR) and infrared spectra of the complexes.

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TABLE 1

^{1}H NMR CHEMICAL SHIFTS (δ (ppm)) OF 4,4′-X_2-bipy (A) and *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)] (B) IN $CDCl_3$ (i) SOLUTION OR IN CD_2Cl_2 (ii) SOLUTION

X	H(3)				H(5)				H(6)				Other			
	A	Δ(A)[a]	B	Δ(B)[b]	A	Δ(A)[a]	B	Δ(B)[b]	A	Δ(A)[a]	B	Δ(B)[b]	A	Δ(A)[a]	B	Δ(B)[b]
OMe (i)	7.98	−0.05	7.53	0.69	6.85	0.18	6.92	0.31	8.48	0.02	8.95	−0.23	3.88	+0.03	3.92	−0.01
CMe_3 (i)	8.41	−0.01	8.04	0.58	7.30	0.17	7.29	0.34	8.59	0.02	8.90	−0.13	1.39	−0.05	1.44	−0.02
Me (i)	8.15	0.08	7.96	0.56	7.10	0.17	7.07	0.40	8.42	0.12	8.93	−0.14	2.34	0.00	2.45	−0.01
H (ii)	8.29	0.06	8.16	0.49	7.04	0.16	7.39	0.25	8.46	0.07	9.12	−0.14	7.56	−0.23	7.95	−0.27
Cl (i)	8.44	0.04	8.06	0.94	7.33	0.45	7.43	0.47	8.57	0.24	9.07	+0.02				
CO_2Me (ii)	8.97	−0.11	8.81	0.22	7.94	0.02	7.96	0.09	8.88	0.08	9.32	0.00	4.04	−0.12	4.67	−0.72

[a] $\Delta(A) = [\delta(DMSO\text{-}d_6) - \delta(CDCl_3 \text{ or } CD_2Cl_2)]$ in 4,4′-X_2-bipy free ligand. [b] $\Delta(B) = [\delta(DMSO\text{-}d_6) - \delta(CDCl_3 \text{ or } CD_2Cl_2)]$ in *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)].

Results and discussion

NMR spectra

The ^1H NMR chemical shifts of the heteroaromatic ligands, 4,4′-X_2-bipy (A) and their complexes *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)] (B) (X = OMe, CMe_3, Me, H, Cl, CO_2Me) in DMSO-d_6 solution have been published [3]. The chemical shifts of the same ligands and complexes have also been measured in $CDCl_3$ (or, occasionally, in CD_2Cl_2); these results are shown in Table 1. This table also includes the chemical shift differences, $\Delta = [\delta(\text{DMSO-}d_6) - \delta(CDCl_3 \text{ or } CD_2Cl_2)]$ ppm. The results show that a change in solvent polarity has only a small and usually insignificant influence on the chemical shifts of the protons in the free ligand. The average values of ΔA are −0.01 (H(3)), +0.13 (H(5)), +0.07 (H(6)) ppm. This is in marked contrast to the significant influence of solvent polarity on the chemical shifts of the same protons in the complex *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)] for which the average values of ΔB are +0.68 (H(3)), +0.31 (H(5)) and −0.11 (H(6)). The electronic effect of the substituent, X, does not appear to influence the value of individual values of ΔB or the pattern of their variation. The absence of a significant influence of the solvent polarity on the chemical shift of protons of the substituent X (with the exception of X = CO_2Me) indicates that a direct interaction between the solvent and the heteroaromatic ring of the 2,2′-bipyridine ligand is involved here. It is unlikely that the solvent dependence of the ring proton chemical shifts in *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)] is explained by changes in the dihedral angle between the heterocyclic ring planes. Such an argument has been used [4] to explain changes in ^1H NMR spectra of free bipyridines when D_2O is used as a co-solvent. It should be recalled that a stereochemical change from the *trans*-configuration of the lone pairs of electrons on the donor nitrogen atoms of the free ligand is required when this ligand forms a complex, and that this may contribute to the particularly large average value of ΔB for H(3).

An alternative, and equally instructive, treatment of the chemical shift data considers the influence of the solvent on the (proton) chemical shift difference between the coordinated and the free ligand, the coordination shift. In chlorocarbon solution, there is only a slight change in the chemical shift of H(5) on coordination (average value, (B-A) 0.08 ppm), but in the same solvents there is a significant coordination shift of H(3) (average value, (B-A) 0.29 ppm) to higher field and an

TABLE 2

INFLUENCE OF SOLVENT ON PROTON NMR COORDINATION SHIFT[a] OF 4,4′-X_2-bipy IN *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)]

Solvent	π^* [b]	X = Me			X = CO_2Me		
		H(3)	H(5)	H(6)	H(3)	H(5)	H(6)
CCl_4	0.294	−0.37	0.15	0.56	−0.23	0.05	0.59
THF-d_8	0.576	−0.33	0.12	0.49	−0.21	0.03	0.51
CD_2Cl_2	0.802	−0.28	−0.03	0.42	−0.16	0.02	0.44
Pyridine-d_5	0.867	[c]	[c]	0.36	[c]	[c]	0.41
DMSO-d_6	1.000	0.29	0.20	0.25	0.17	0.09	0.36

[a] Coordination shift = δ(H(n)) complex − δ(H(n)) free ligand (n = 3,5,6). [b] π^*, solvent polarity parameter of Kamlet and Taft [5]. [c] Signals obscured by solvent.

TABLE 3

^{13}C NMR CHEMICAL SHIFTS (δ (ppm)) OF 4,4'-X_2-bipy (A) AND *cis*-[Mo(CO)$_4$(4,4'-X_2-bipy)] (B) IN DMSO-d_6 SOLUTION

	X = CMe_3				X = Me				X = Cl			
	A	Δ(A)[a]	B	Δ(B)[b]	A	Δ(A)[a]	B	Δ(B)[b]	A	Δ(A)[a]	B	Δ(B)[b]
C(2)	159.07	2.04	163.04	−1.19	155.05	1.63	154.04	1.10	155.72	0.78	155.06	−0.09
C(3)	119.19	1.61	122.94	0.71	124.33	0.74	126.82	−0.07	124.19	0.27	126.60	−0.46
C(4)	154.53	2.27	154.70	−0.02	–	–	150.45	−0.14	143.90	1.48	145.48	−0.43
C(5)	116.04	2.34	120.31	2.83	121.19	1.10	123.97	−0.66	120.82	1.00	124.48	−1.49
C(6)	147.50	1.69	152.28	0.20	148.55	0.88	151.77	1.18	150.13	0.01	153.23	0.42

[a] $\Delta(A) = [\delta(CDCl_3) - \delta(DMSO\text{-}d_6)]$ in 4,4'-X_2-bipy free ligand. [b] $\Delta(B) = [\delta(CDCl_3) - \delta(DMSO\text{-}d_6)]$ in *cis*-[Mo(CO)$_4$(4,4'-X_2-bipy)].

even larger coordination shift of H(6) (average value, (B-A) 0.46 ppm) to lower field. These differences are in contrast to those observed in the more polar solvent, DMSO. In this solvent, coordination of the ligand to the metal produces a general shift of the ring protons to lower field. The average values of the coordination shift in DMSO-d_6 are 0.30 (H(3), H(6)) and 0.20 (H(5)) ppm.

The effect of solvent polarity on the coordination shift was studied in more detail. The ^{1}H NMR spectra of *cis*-[Mo(CO)$_4$(4,4′-X$_2$-bipy)] (X = Me, CO$_2$Me) were measured in solution in CCl$_4$, THF-d_8, CD$_2$Cl$_2$, pyridine-d_5 and DMSO-d_6. Imperfect deuteration of the pyridine resulted in partial obscuration of the bipy ring proton signals. The results of these measurements are summarised in Table 2. The coordination shifts of H(3) and H(6) in both of the complexes change in opposite senses with changing solvent polarity. Increasing the polarity of the solvent, as indicated by the π^*-scale of Kamlet and Taft [5], for example, causes the coordination shift of H(3) to become increasingly positive ($B > A$), whereas the coordination shift of H(6) decreases. The correlation between the coordination shifts of H(3) and H(6) and the solvent polarity parameter π^* are not strictly linear, the deviation being most marked for H(3) in DMSO. The correlation between these shifts and other solvent parameters such as the Gutmann Donor number is very poor. These observations suggest that the solute/solvent interaction is principally dielectric rather than donor/acceptor in nature.

The influence of solvent (CDCl$_3$, DMSO-d_6) on ^{13}C NMR spectra was investigated in three cases (Table 3). This number was limited largely by the solubility of the complexes and the inevitable long accumulation times for the FT spectra of the less soluble complexes. The changes in the chemical shifts of the bipy ring carbon atoms, either on coordination to molybdenum or in different solvents are rather small (less than 5 ppm) but they are reproducible. In most cases, coordination causes a shift to lower field and this coordination shift is greater (in most cases) in the more polar solvent. Whereas the ^{13}C resonances of all the bipy ring carbon atoms move to higher field in the more polar solvent (DMSO), coordination to molybdenum may cause the bipy ring carbon resonances to appear at lower field in the more polar solvent. These changes are small and some are not significant. In general, the ^{13}C NMR spectra of the free ligands are slightly more sensitive to solvent polarity than the coordinated ligands. The coordination shift of the bipy ring carbon atoms bearing a hydrogen atom (C(3), C(5), C(6)) are more sensitive to the influence of solvent polarity than those (C(2), C(4)) which do not. The coordination shift of C(3) is significantly greater in the more polar solvent (DMSO); this is similar to the solvent influence on H(3) in the ^{1}H NMR spectra already discussed.

We succeeded in recording the ^{13}CO signals in two different solvents only in the case of *cis*-[Mo(CO)$_4$(4,4′-(Me$_3$C)$_2$-bipy)]. Increasing the polarity of the solvent causes the resonance of the two *cis*-CO ligands to appear at slightly higher field ($\Delta\delta$ -0.42 ppm) and the signal of the two *trans*-CO ligands move to lower field ($\Delta\delta$ $+0.38$ ppm).

Infrared absorption spectra in the 2100–1700 cm^{-1} region in solution

The CO ligand stretching absorption wavenumbers of the full range of *cis*-[Mo(CO)$_4$(4,4′-X$_2$-bipy)] complexes in acetonitrile solution were published earlier [3]. These showed the electronic influence of the substituent, X. As the substituent becomes a better acceptor, the values of ν(CO) increase. We have measured the

TABLE 4

INFRARED ABSORPTIONS IN THE 2100–1700 cm^{-1} REGION OF *cis*-[Mo(CO)$_4$(4,4'-X$_2$-bipy)] IN SOLUTION AND DERIVED FORCE CONSTANTS. INFLUENCE OF SOLVENT (Experimental error in measurement ±2 cm^{-1})

X	Solvent	Absorption wavenumbers ν(CO) (cm^{-1})				Force constant (mdyn Å^{-1})		
		A_1	B_1	A_1	B_2	k_1	k_2	k_i
OMe	CS_2	2008s	1887vs	1880sh	1840s	14.088	15.364	0.416
	CH_2Cl_2	2016s	1900vs	1872sh	1827s	13.918	15.486	0.454
	CH_3CN	2017s	1895vs	1870sh	1819s	13.930	15.448	0.450
CMe_3	CCl_4	2012s	1907vs	1889sh	1847s	14.196	15.525	0.419
	CH_2Cl_2	2013s	1902vs	1874sh	1828s	13.945	15.509	0.450
	CH_3CN	2014s	1901vs	1875sh	1830s	13.966	15.508	0.457
Me	CCl_4	2014s	1910vs	1890sh	1848s	14.213	15.544	0.422
	CH_2Cl_2	2015s	1905vs	1875sh	1824s	13.936	15.597	0.472
	CH_3CN	2019s	1900vs	1868sh	1824s	13.946	15.540	0.481
CO_2Me	CCl_4	2020s	1921vs	1905sh	1862s	14.415	15.730	0.414
	CH_2Cl_2	2016s	1912vs	1890sh	1939s	14.115	15.685	0.461
	CH_3CN	2017s	1907vs	1887sh	1931s	14.022	15.714	0.483
NO_2	CCl_4	2016s	1934s	1920vs	1875vs	14.381	15.738	0.395
	CH_2Cl_2	2022s	1929s	1909vs	1855vs	13.978	15.624	0.469
	CH_3CN	2023s	1924s	1900vs	1846vs	13.930	15.600	0.496

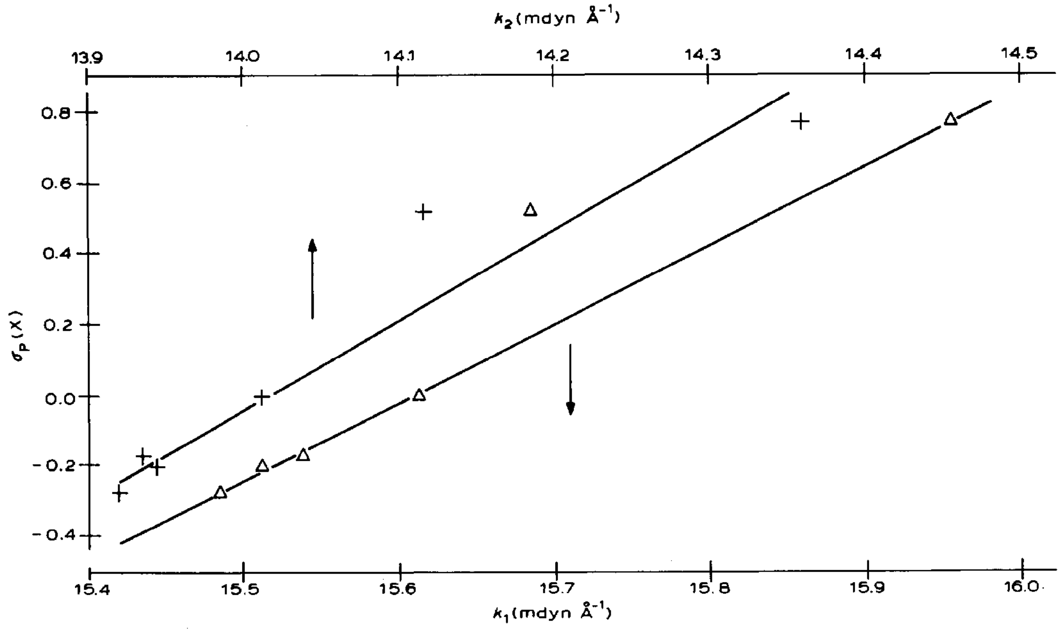

Fig. 1. Variation of Cotton–Kraihanzel CO stretching force constants, k_1 and k_2, with Hammett substituent parameter σ_P(X), in *cis*-[Mo(CO)$_4$(4,4'-X$_2$-bipy)] complexes.

ν(CO) wavenumbers of a selection of these complexes in two other solvents, tetrachloromethane and dichloromethane, of lower polarity than acetonitrile. In order to assist in the interpretation of the data, the approximate force constants of the two pairs of CO ligands (*cis* and *trans*) have been calculated using the simple force field model of Cotton and Kraihanzel [6]. The force constants, k_1, (Table 4), of the equatorial carbonyl ligands which are *trans* to the 4,4′-X_2-dipy ligand (and mutually *cis*) usually decrease as the polarity of the solvent increases. The force constants, k_2, of the axial carbonyl ligands vary very little with solvent polarity and then randomly. This behaviour suggests that the solvent molecules interact with (solvate) preferentially the equatorial CO ligands which are in the same plane as the bipyridine ligand and *trans* to it. This is in direct contrast to the electronic effect of the substituent, X, in the complexes *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)] where both k_1 and k_2 are·effected. Figure 1 shows the linear relation between the Taft substituent constant, σ_p(X), and the force constants k_1 and k_2 of complexes in dichloromethane solution. The value of the interaction force constant, k_i, in these complexes generally increases with solvent polarity. This is consistent with more efficient transmission of the relative motions of the axial and equatorial CO ligands through a more rigid polar solvent cage in which the complex is more highly solvated and solute–solvent interaction is thereby increased.

Conclusions

The ensemble of the measurements reported in this and the previous paper [2] show that there are specific solute–solvent interactions which can be probed in detail by spectroscopic studies of *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)] complexes in solution. The importance of the interannular connection in the bipyridine ligand is emphasised by the observations we have made on some of the analogous *cis*-[Mo(CO)$_4$(4-X-pyridine)$_2$] complexes. The spectroscopic properties of these substituted pyridine complexes generally show insignificant dependence on solvent polarity [7]. The interaction between a *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)] complex and the solvent is remarkably specific and basically dielectric rather than donor/acceptor in nature. The solvent polarity influences those properties (MLCT transition energies, ^{1}H and ^{13}C NMR chemical shifts, and IR ν(CO) absorption wavenumbers) which originate within the perimeter of the $\{(C_{10}H_6N_2)Mo(CO)_2\}$ plane; that is, those properties which are associated with metal–ligand π-bonding interactions. Properties of non-hydrogen substituents on the bipyridine ring which do not interact with the π-system are not significantly changed by the solvent polarity. CO ligands which are perpendicular to the $\{MoN_2C_2\}$ plane are not significantly affected by the solvent polarity either.

Experimental

The complexes *cis*-[Mo(CO)$_4$(4,4′-X_2-bipy)] (X = OMe, CMe$_3$, Me, H, Cl, CO$_2$Me, NO$_2$) were prepared and characterised as we have described previously [3]. Infrared spectra were recorded using either Perkin–Elmer PE257 or 577 spectrometers. The spectra were calibrated using a thin polystyrene film or the internal wave-marker. The solutions were contained in 0.1 mm sodium chloride cells. The NMR spectra were recorded on a Bruker WP80 instrument (^{1}H 80 MHz, ^{13}C 20.1 MHz). When tetramethylsilane was not used, as an internal reference, the proton impurity of the deuterated solvent served as a reference. Solvents used for spectroscopic measurements were deaerated with dry, deoxygenated dinitrogen gas and dried before use, and the solutions were prepared in conventional Schlenk tubes under an inert atmosphere.

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