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ELECTRONIC SPECTRA AND ELECTROCHEMISTRY OF DISUBSTITUTED 2,2′-BIPYRIDINETETRACARBONYLMOLYBDENUM COMPLEXES. SOLVENT AND SUBSTITUENT EFFECTS

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Summary

Electronic absorption spectra of *cis*-[Mo(CO)$_4$(n,n'-X$_2$-bipy)] ($n = 4$, X = NMe$_2$, NH$_2$, OMe, CMe$_3$, Me, H, Ph, CH:CHPh, CO$_2$H, Cl, CO$_2$Me, NO$_2$; $n = 5$, X = Me, CO$_2$H) have been measured at ambient temperature in a variety of solvents of different polarity. Emission spectra from glasses containing the complexes at 77 K have also been measured. The influence of the substituent X on the spectroscopic properties is correlated with the Hammett parameters, σ_p(X) and σ_p^+(X). The effect of solvent is correlated with the Taft–Kamlet parameter, π^*, indicating charge redistribution along the permanent dipole axis of the complex. The oxidation and reduction potentials in solution are simply related to the electronic effect of the substituent group, X, and are relatively independent of the solvent. The influence of the metal on these properties is not significant.

Introduction

The lowest energy electronic absorption in the spectra of the complexes *cis*-[Mo(CO)$_4$D] (D is 2,2′-bipyridine (bipy), 1,10-phenanthroline and substituted 1,10-phenanthrolines) has been identified as arising from a metal-to-ligand [Mo(4d) → D(π^*)] charge transfer (MLCT) transition. This assignment was based on shifts in the energy of maximum absorption caused by changes in substituents and comparison with similar complexes containing other heterocyclic ligands such as pyridine. Evidence has been presented to show that these [Mo(CO)$_4$D] complexes emit from a state associated with the MLCT state which is populated by absorption [1].

Changes in the solvent medium have been observed to influence the energy of the lowest MLCT absorption in the same *cis*-[Mo(CO)$_4$D] complexes [1,2]. The change

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in the absorption maximum, λ_{max} has been correlated with the polarity of the solvent as represented by the $E_T(30)$ scale [3]. Magnetic circular dichroism and resonance Raman spectroscopy have been used to investigate the component electronic transitions in the lowest energy MLCT absorption of various tetracarbonyl(α,α'-diimine)metal complexes of Group VIB metals [4]. It has been shown that up to four components contribute to the MLCT envelope and that the charge transfer probably extends to the co-planar or *cis*-carbonyl ligands in these complexes.

We have described the preparation and characterisation of a series of complexes containing various 4,4′-disubstituted 2,2′-bipyridines of the general composition $[M(CO)_4(4,4'\text{-}X_2\text{-bipy})]$ (M = Cr, Mo, W) [5], and the influence of solvent and substituent, X, on the physical properties of these complexes has been referred to briefly [6]. A recent paper has reported observations of the effect of changes in solvent and substituent on some *cis*-$[M(CO)_4(\text{diimine})]$ (M = Cr, Mo, W; diimine = substituted 1,10-phenanthroline) complexes [7] using the Kamlet and Taft [8] parameters.

Results

The visible absorption spectra of the complexes *cis*-$[Mo(CO)_4(4,4\text{-}X_2\text{-bipy})]$ were recorded in a range of solvents varying in polarity from methylcyclohexane to dimethylsulphoxide. Values of the energy (in nm) of the lowest energy MLCT transition in these complexes in different solvents are shown in Table 1. Both the substituent, X, and the solvent have a highly significant influence on the position of the absorption maximum. The absorption spectra of two of the more readily soluble complexes (X = CMe_3, CO_2Me) were measured in a wider variety of solvents in order to gain more information concerning the solvent-solute interaction and these results are given in Table 2. The extinction coefficients, ε, of the lowest energy

TABLE 1

LOWEST ENERGY MLCT ABSORPTION (λ_{max}(nm)) IN *cis*-$[Mo(CO)_4(n,n'\text{-}X_2\text{-bipy})]$ COMPLEXES IN SOLUTION

$n = n'$	X	Solvent								
		$C_6H_{11}CH_3$	CCl_4	C_6H_6	$CHCl_3$	THF	CH_2Cl_2	Acetone	MeCN	DMSO
4	NMe_2	–	–	463	444	430	405sh	402	385sh	–
4	NH_2	–	–	–	451	427	–	401	397	392
4	OMe	–	494	466	480	453	448	428	420	402
4	CMe_3	538	506	519	510	497	454	444	452	430
5	Me	521	–	476	466	458	455	438	423	418
4	Me	535	520	481	473	464	459	441	431	427
4	H	558	504	493	490	474	469	453	441	440
4	Ph	–	550	516	502	492	488	469	462	460
4	CH=CHPh	546	530	536	523	509	503	486	472	468
4	CO_2H	–	–	–	552	529	548	511	502	494
5	CO_2H	–	–	–	588	558	–	535	528	528
4	Cl	–	580	526	528	502	512	486	477	471
4	CO_2Me	607	598	560	564	536	540	535	508	500
4	Cl/NO_2	–	662	610	625	569	604	552	548	531
4	NO_2	–	656	632	633	594	610	579	576	553

TABLE 2

LOWEST ENERGY MLCT ABSORPTION (λ_{max}(nm)) IN *cis*-[Mo(CO)$_4$(4,4'-X$_2$-bipy)] COMPLEXES IN SOLUTION

Solvent	X = CMe$_3$	X = CO$_2$Me
Triethylamine	490	561
Di-n-propylamine	475	550
n-Pentanol	470	
t-Butanol	470	
N,*N*,*N'*,*N'*-Tetramethyldiaminoethane	469	545
Dioxane	468	542
n-Butanol	466	
n-Propanol	464	
Cyclohexanol	462	
Ethanol	454	540
Methanol	450	530
Pyridine	448	526
N,*N*-Dimethylformamide	415	506
Nitromethane	408	510

MLCT transition of several of the complexes were measured in different solvents. The values of ε (Table 3) are in agreement with the assignment of the transition to a charge transfer process ($\varepsilon > 1000$). The absorption bands are symmetrical and rather broad.

The effect of concentration on the absorption spectrum of *cis*-[Mo(CO)$_4$ (4,4'-(Me$_3$C)$_2$-bipy)] was studied and showed that the absorption maximum of the MLCT transition was not influenced by dilution of ca. 100-fold. This indicates that the transition is not an inter-ligand transition between different complex molecules which might occur [9] as a result of stacking of bipy ligands in more concentrated solutions. The molecular weight of the same complex was measured in chloroform solution: the value obtained (484 dalton) shows that the complex is monomeric (calculated for $C_{22}H_{24}$ MoN$_2$O$_4$, 476 dalton).

In our experience, luminescence from the complexes *cis*-[Mo(CO)$_4$(4,4'-X$_2$-bipy)] is weak and was only observable from solid glass matrices at 77 K (Table 4). All the emission envelopes show shoulders on the low energy side of the main band. In other work, this splitting has been shown to be associated with a vibrational progression

TABLE 3

EXTINCTION COEFFICIENT, ε (dm^3 mol^{-1} cm^{-1}), OF THE LOWEST ENERGY CHARGE TRANSFER TRANSITION IN *cis*-[Mo(CO)$_4$(4,4'-X$_2$-bipy)] COMPLEXES

X	Solvent	ε
OMe	Acetonitrile	3630
CMe$_3$	Benzene	4940
	Acetonitrile	4340
Me	Acetonitrile	4600
Cl	Benzene	5080
	Acetonitrile	4450
CO$_2$Me	Acetonitrile	8450
NO$_2$	Acetonitrile	7850

TABLE 4

LUMINESCENCE SPECTRA OF *cis*-[Mo(CO)$_4$(n,n'-X$_2$-bipy)] COMPLEXES, λ_{max}(nm)

n	X	Emission		Excitation	
		2MTHF [a]	EPA [a]	2MTHF [a]	EPA [a]
4	NMe$_2$	565		406	
4	OMe	590		425	
4	CMe$_3$	595	588		468
4	Me	605	605		477
5	Me	605	603	420	420
4	Cl	677	653	484	465
4	CO$_2$Me	700	722	483	500

[a] 2MTHF = 2-methyltetrahydrofuran, EPA = diethyl ether(5)/isopentane(5)/ethanol(2)

[10]. A very weak emission spectrum was observed from *cis*-[Mo(CO)$_4$(5,5'-Me$_2$-bipy)] in solution at room temperature. The emission maximum of this complex shifts to higher energy and becomes more intense on cooling (λ_{em} 645 nm (293 K); 605 nm (77 K) in 2-methyltetrahydrofuran (MTHF). Similar changes in the populations of component electronic states are probably responsible for shifts in the maxima of absorption (excitation) spectra of the *cis*-[Mo(CO)$_4$(4,4'-X$_2$-bipy)] complexes as a function of temperature, for example λ_{ex} 502 nm (293 K); 484 nm (77 K) in MTHF (X = Cl).

The half-wave redox potentials, $E_{1/2}$ (V), of several of the *cis*-[Mo(CO)$_4$(4,4'-X$_2$-bipy)] (X = Me$_2$N, Me$_3$C, H, Cl, MeO$_2$C) complexes were measured in dichloromethane, tetrahydrofuran and acetonitrile (Table 5). The reduction processes are usually reversible on the electrochemical time scale. The oxidations are chemically irreversible because the lifetime of the resulting molybdenum(I) cation is estimated as approximately 5*s* in solution. Electrolysis of *cis*-[Mo(CO)$_4$(4,4'-X$_2$-bipy)] (X = CMe$_3$, Cl) in acetonitrile solution produces new species as the result of a two-electron process which consumes 2F g^{-1} mol^{-1} of molybdenum. These new species have $E^{ox}_{1/2}$ = 0.30 V (X = Cl), 0.22 V (X = CMe$_3$).

TABLE 5

HALF-WAVE REDOX POTENTIALS ($E_{1/2}$ (V)) of *cis*-[Mo(CO)$_4$(4,4'-X$_2$-bipy)] COMPLEXES IN SOLUTION

X	Solvent		
	CH$_2$Cl$_2$	THF	MeCN
A Oxidation			
NMe$_2$	+0.61	+0.58	+0.50
CMe$_3$	+0.80(r)	+0.76	+0.62
Cl	+0.88(r)	+0.85	+0.70
CO$_2$Me	+0.88	+0.85	+0.69
B Reduction			
NMe$_2$	[a]	−1.90(r)	−1.90
CMe$_3$	−1.68	−1.62(r)	−1.63(r)
Cl	−1.22	−1.22(r)	−1.25
CO$_2$Me	−1.10(r)	−1.07(r)	−1.09(r)

[a] No reduction of complex before reduction of solvent. r = reversible.

Discussion

1. Substituent effect

The results presented in Table 1 show that the maximum of the lowest energy electronic absorption band in the complexes *cis*-$[Mo(CO)_4(4,4'-X_2\text{-bipy})]$ moves to longer wavelength (lower energy) as the ability of the substituent X on the 2,2′-bipyridine ligand to withdraw electron density from the heterocyclic ring increases. The magnitude of this effect is significant: for example, in chloroform solution, the lowest energy absorption maxima of the complexes in which $X = NMe_2$ (λ_{max} 444 nm) and $X = NO_2$ (λ_{max} 633 nm) are separated by 6700 cm^{-1} (0.83 eV) from one another.

The relationship between the electronic character of the substituted 2,2′-bipyridine ligand and the energy of the lowest energy MLCT absorption can be quantified by the Hammett substituent parameter, $\sigma_p(X)$. Previous work has shown that $\sigma_p(X)$ can be used to correlate the ionisation constants and infrared ring stretching absorption frequencies of various $4,4\text{-}X_2$-bipy molecules [11]. If the asymmetrically substituted complex, $[Mo(CO)_4$(4-chloro-4′-nitro-bipy)] (distorted π-system) and $[Mo(CO)_4(4,4\text{-}Ph_2\text{-bipy})]$ (extended π-system in conjugation with the bipy ring) are excluded, then a least-squares regression of the data gives the equation

$$\lambda_{max}(\text{MLCT}) = \left(2.24 - 0.45\,\sigma_p(X)\right)\ \text{eV}$$

with a corrrelation coefficient 0.96.

The position of the substituent on the heterocyclic ring has little influence on the value of λ_{max}(MLCT) as a comparison of results from $[Mo(CO)_4(n,n\text{-}X_2\text{-bipy})]$ ($n = 4$, 5; $X = Me$, CO_2H) (Table 1) shows. Changing the metal atom in *cis*-$[M(CO)_4(4,4\text{-}X_2\text{-bipy})]$ ($M = Cr$, Mo, W; $X = Me$, H, CO_2Me) produces small, systematic changes in λ_{max}(MLCT) of the type $M = Mo < W \lesssim Cr$ (in nm). We do not observe a clearly defined relation between the extinction coefficient, ε (dm^3 mol^{-1} cm^{-1}), of the MLCT absorption and the electronic character of the substituent, X (Table 3). In general, complexes containing mesomeric acceptor substituent groups ($X = CO_2Me$, NO_2), which are able to increase the transition probability of the absorption as a consequence of some charge separation in the ground state have significantly higher extinction coefficients than complexes containing either inductive donor ($X = OMe$, CMe_3, Me) or acceptor ($X = Cl$) substituents.

The emission maxima (λ_{em}) of *cis*-$[Mo(CO)_4(4,4\text{-}X_2\text{-bipy})]$ follow the same pattern as the absorption maxima (Table 4). Electron acceptor substituents ($X = Cl$, CO_2Me) cause λ_{em} to move to longer wavelength (lower energy), whereas donor substituents ($X = NMe_2$, OMe, Me, CMe_3) cause λ_{em} of the complex to appear at higher energy. Correlation of λ_{em} with various substituent parameters for the group X shows that the best correlation is obtained with $\sigma_p^+(X)$, which measures or represents conjugative electronic interaction between X and the heterocyclic ring. The energy difference between the maxima of the emission (λ_{em}) and excitation (λ_{ex}) in the complexes *cis*-$[Mo(CO)_4(4,4'\text{-}X_2\text{-bipy})]$ is almost invariant with changes in the substituent, X.

The electrochemical properties of the complexes *cis*-$[Mo(CO)_4(4,4'\text{-}X_2\text{-bipy})]$ can be interpreted very simply. Complexes containing substituents which release charge into the heterocyclic rings ($X = NMe_2$, CMe_3) are easier to oxidise than those which

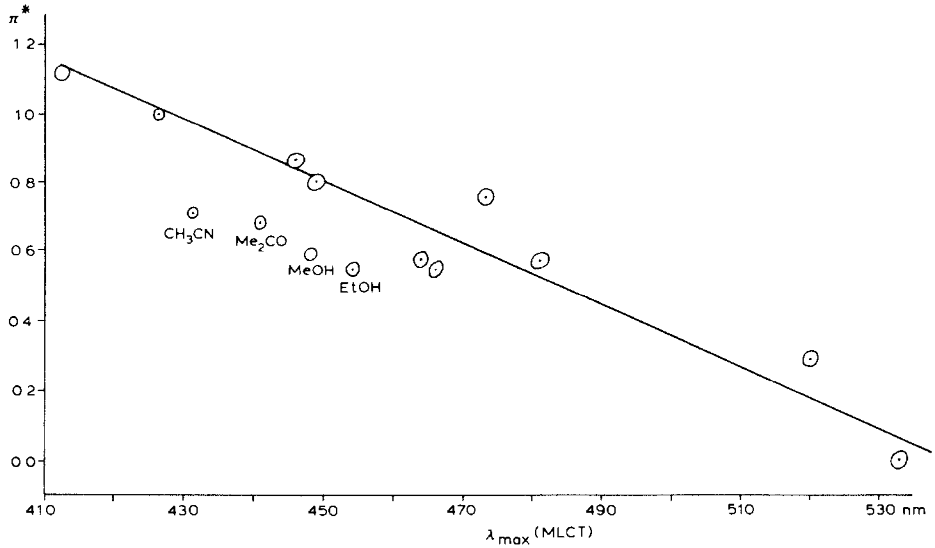

Fig. 1. Plot of λ_{max}(MLCT) vs. π^*, the Taft–Kamlet solvent polarity parameter, for *cis*-[Mo(CO)$_4$(4,4′-Me$_2$-bipy)] in different solvents.

contain electron accepting groups (X = Cl, CO$_2$Me). The opposite holds true for reduction (Table 5). Similar results, showing the predictable influence of remote substituents on values of $E_{1/2}$ have been noted in other systems [12]. However, it is remarkable that in the diazenido complexes [Mo(N$_2$C$_6$H$_4$X) (S$_2$CNMe$_2$)$_3$] (X is *o*-, *m*- or *p*-Cl, NO$_2$, Me, OMe etc). although $E_{1/2}^{ox}$ varies predictably with the nature of X, the lowest energy MLCT absorption is almost insensitive to these changes [12].

2. *Solvent effects*

As the solvent in which the *cis*-[Mo(CO)$_4$(4,4-X$_2$-bipy)] complex is dissolved becomes more polar, the MLCT absorption band, λ_{max} shifts to higher energy. For example, the complex (X = CMe$_3$) shows a shift of 4700 cm^{-1} (0.58 eV) between methylcyclohexane (λ_{max} 538 nm) and dimethylsulphoxide (λ_{max} 430 nm). Solutions of the complex (X = CO$_2$Me) appear green, purple or red-orange when it is dissolved in carbon tetrachloride, dichloromethane or dimethylsulphoxide respectively. This behaviour is in marked contrast with that of *cis*-[Mo(CO)$_4$(NC$_5$H$_4$-X-4)$_2$] (X = NH$_2$, Me, H, Cl, CO$_2$Me), where the lowest energy transition is metal-localised and shows almost no variation with solvent.

It appears that the general polarisability (i.e. dielectric constant) of the solvent determines the value of λ_{max}(MLCT). Acetonitrile and dimethylsuphoxide produce similar values of λ_{max}, as do tetrahydrofuran and dichloromethane, because their dielectric constants are similar. A plot of λ_{max}(MLCT) against the Gutmann donor or acceptor [13] number of the solvent shows no correlation at all. Solvatochromism of *cis*-[Ru(CN)$_2$(bipy)$_2$] can be correlated strongly ($c = 0.98$) with the acceptor number of the solvent [14]. Further evidence for the absence of specific solute-solvent interaction in *cis*-[Mo(CO)$_4$(4,4′-X$_2$-bipy)] is provided by our observation that neither triethylamine nor boron trifluoride give anomalous values of λ_{max}(MLCT) for the complex (X = CMe$_3$). However, there is evidence for preferential solvation; a small decrease in the mole fraction of the less polar component in a mixed solvent system causes a large change in λ_{max}(MLCT). For example (X = CO_2Me), λ_{max}(pure CCl_4) 644 nm, (0.93 mol% CCl_4 in DMSO) 601 nm, (pure DMSO) 544 nm.

The polarity of solvents has been described in terms of a variety of scales: the Z-scale of Kosower [15], the $E_T(30)$ scale of Dimroth and Reichardt [3] and, most recently, the π^*-scale of Taft and Kamlet [8]. Figure 1 shows the variation of λ_{max}(MLCT) for the complex (X = Me) with the parameter π^* for the range of solvents given in Table 1. This variation is represented by the solvent polarity–polarisability equation:

$$\lambda_{max}(\text{MLCT}) = (2.314 + 0.596\,\pi^*)\ \text{eV}$$

with a correlation coefficient, $c = 0.886$. However, if the alcohol solvents (MeOH, EtOH), acetone and acetonitrile are removed from the data set, the value of c increases to 0.96, and the regression equation becomes:

$$\lambda_{max}(\text{MLCT}) = (2.266 + 0.605\,\pi^*)\ \text{eV}.$$

The effect of different solvents on λ_{max}(MLCT) for *cis*-[Mo(CO)$_4$(4,4-X$_2$-bipy)] is similar to the betaine indicator of Dimroth [3]. In both cases, more polar solvents cause an increase in the electronic absorption energy so that the absorption maxima are hypsochromically shifted. This behaviour can be explained by reference to the fact that in the molybdenum(0) complexes (and in Dimroth's betaine) the direction of electron density transfer (metal to ligand) is opposed to the dipole moment in the ground state of the complexes. Polar solvents induce the electron density to move in the direction of the dipole moment, so that the ground state of the complex is stabilised on going from a less polar to a more polar solvent. This stabilisation is less in the MLCT excited state because the dipole moment is reduced (and may be reversed) by the transition [16].

The influence of solvent on emission spectra of *cis*-[Mo(CO)$_4$(4,4′-bipy)] is more difficult to determine because of the requirement to form a glass at 77 K, at which temperature weak emission is detectable. The emission spectrum of the complex (X = CMe_3) was also measured in diethylether (E), isopentane (P), methanol (M) solvent mixtures at 77 K, in which the maximum emission was observed at 608 (1/1/4 EPM) and 606 nm (1/1/2 EPM). These results with those in Table 4 indicate that the solvent dependence of the emission is insignificant.

The reversible reduction half-wave potentials show very little solvent dependence. The apparent solvent dependence of the half-wave potentials for oxidation, which are not reversible, may be explained rather by reaction of the cation with the solvent (ECE mechanism).

Conclusion

The remote substituent, X, in *cis*-[Mo(CO)$_4$(4,4-X$_2$-bipy)] complexes has a profound effect on the electronic absorption and emission spectra of the complexes and also on their redox potentials. The influence of the group X on these properties is well-correlated by the Hammett substituent parameters σ_p(X) and σ^+(X). The effect of solvent on these spectroscopic properties causes redistribution of charge along the axis of the permanent dipole moment of the complex, so as to minimise the energy of the complex in the particular solvent. This redistribution of charge is also evident from other spectroscopic measurements (infrared and NMR) which we shall report separately. Conjugation between the bonded pyridine ligands is also a significant factor.

Experimental

The complexes *cis*-[M(CO)$_4$(n,n'-X$_2$-bipy)] (M = Cr, Mo, W; $n = 4$, X = NMe$_2$, NH$_2$, OMe, CMe$_3$, Me, H, Ph, CH=CHPh, Co$_2$H, Cl, CO$_2$Me, NO$_2$; $n = 5$, X = Me, CO$_2$H) were prepared and characterised as we have described previously [5]. The electronic absorption spectra were measured with a Pye Unicam SP800 or Perkin–Elmer PE402 spectrometer in carefully purified, deoxygenated, dry solvents. Emission and excitation spectra were recorded on a purpose-built spectrometer [17], on a Perkin–Elmer MPF4 or on a Schoffel spectrometer at 77 K or at room temperature. The source was always tuned to the excitation maximum when recording emission spectra; however, high amplifier gain was required in some cases in order to observe the rather weak emission. Care was taken to ensure that the solvents used in the emission spectroscopic measurements were of the highest purity and showed no emission above 350 nm. The electrochemical apparatus has been described elsewhere [18].

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