

Solvatochromism in substituted 2,2'-bipyridinetetracarbonyl-metal complexes of chromium, molybdenum and tungsten

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Received 11 April 1994

Abstract

The influence of various solvents on the electronic absorption spectra in the visible region of complexes of the general type $[M(CO)_4(n,n'-X_2\text{-bipy})]$ ($M = \text{Cr, Mo, W}$; $n = 3, 4, 5, 6$; $X = \text{CH}_3, \text{CN, CO}_2\text{CH}_3$; $\text{bipy} = 2,2'\text{-bipyridine}$) has been measured. Molar absorption coefficients are reported. Attempts to correlate this information with the solvent polarity parameter proposed by Manuta and Lees indicate that the effects of geometric distortion in the substrate complex preclude a simple explanation of the observations in terms of a single parameter.

Keywords: Chromium; Molybdenum; Tungsten; Solvatochromism; Bipyridine; Carbonyl

1. Introduction

The dependence of the energy of absorption in the UV/visible spectrum of $[\text{Mo}(\text{CO})_4(\text{bipy})]$ in solution on changes in the polarity of the solvent was first reported just over 25 years ago [1]. Since then much attention has been given to explaining this and similar observations on other transition-metal α -diimine complexes. The field has been reviewed quite recently [2]. The solvatochromic shift, which is the difference in solvation energy between the initial and final states of the solute in two different solvents, can be considered as a direct experimental indication of the influence of the surrounding medium (solvent, s) on the energy states of the metal complex (solute, m). Various theoretical interpretations have sought to relate the solvatochromic shift to the electron distribution of the solute in its excited state in terms of the total dipole moment, μ , and the average polarizability, α , of the solvent and the solute. The effects of solvent viscosity, temperature and pressure are not taken into consideration. Solvatochromism can occur when there is a change

in either the dipole moment or the polarizability (or both) on going from the ground to the excited state of the solute and the solvent. The dipole-dipole, $\mu_s-\mu_m$, and dipole-polarizability, $\mu_s-\alpha_m$, contributions are considered to be the major components of the observed solvatochromic shift.

Various empirical measures of (relative) solvent polarity have been established, such as Reichardt's E_T -parameter [3], Kosower's Z -parameter [4] and Kamlet and Taft's π^* solvent scale [5], which are derived from studies of organic molecules such as pyridinium betaines, and the E^* scale of Manuta and Lees [6], which is internally referenced to a standard, structurally similar complex, $[\text{W}(\text{CO})_4(\text{bipy})]$, have indicated the need to segregate solvents in terms of certain characteristic solute-solvent interactions [2].

The solvent sensitivity of the visible absorption of a complex of the general type $[M(\text{CO})_4(\text{N-N})]$ depends on the structure of the ligand (N-N). The sensitivity increases as the π -acceptor ability of the ligand decreases [7], and if σ -donation by the ligand is strong in the ground state and increases only slightly in the excited state [8]. Our own contributions in this area started [9] with an examination of the influence of the substituents X in the 2,2'-bipyridine ligand on the solvatochromism of a group of complexes of the type

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[Mo(CO)₄(4,4'-X₂-bipy)]. The influence of the solvent was correlated with π^* , suggesting that the solvent causes redistribution of charge along the axis of the permanent dipole moment of the complex so as to minimize the total energy of the solute in a particular solvent. The substituents on the bipyridine ligand also affect the influence of the solvent on the complex. This was indicated by a decrease in the magnitude of the solvatochromic shift between a donor substituent such as NMe₂ and an acceptor substituent such as NO₂.

We have recently made a much more detailed investigation of the way in which variation in both the position and the nature of the substituent group X on a bipy ligand may be used to control the electronic properties of [M(CO)₄(*n,n'*-X₂-bipy)] (M = Cr, Mo, W) complexes. The groups X include Me, a simple σ -donor; CO₂CH₃, a non-coordinating σ - and π -electron acceptor; and CN, a potentially coordinating σ - and π -electron acceptor substituent. The last two groups were chosen because the work of Kaim's group had indicated [8] that the degree of solvatochromism should increase with decreasing absolute charge-transfer transition energy in a given solvent, i.e. with increasing π -donation from the metal to the ligand π^* molecular orbital.

In order to maintain consistency with a scale which is based on standards similar to the complexes used here, we chose to use the E^* parameter proposed by Manuta and Lees [6] for analysis of the results.

2. Results and discussion

2.1. Synthesis

The standard method [9] of reaction between the particular disubstituted bipyridine ligand and a slight excess of the appropriate bicyclo[2,2,1]hepta-2,4-diene precursor complex [M(CO)₄(η^2, η^2 -C₇H₈)] (M = Cr, Mo, W) in solution was used for the preparation of the complexes. The solvent (generally THF, but sometimes benzene) was carefully dried, deoxygenated and distilled before use in the synthesis. Although we were unable to isolate a complex product containing 3,3'-(CN)₂-bipy, 6,6'-(CN)₂-bipy or 6,6'-(CO₂Me)-bipy, in each of these cases addition of the ligand to the precursor complex results in the formation of an intensely coloured solution, which is taken to indicate that a complex of the substituted bipy ligand is formed but is not stable in solution at room temperature.

2.2. Molar absorption coefficients

Although a large amount of information about the energies of the charge-transfer absorptions in the visi-

ble region of the electronic spectra of [M(CO)₄(α -diimine)] complexes has been published, very little of it concerns the molar absorption coefficients, also called extinction coefficients, ϵ (m² mol⁻¹), of the same absorptions. The values of ϵ for compounds described here lie in the range 2000–11000 m² mol⁻¹. The reproducibility of these values has been examined carefully and is estimated to be better than 95% (error less than $\pm 5\%$) across a range of complexes and solvents. The range of values of the molar absorption coefficient of the lower-energy metal–ligand charge-transfer absorption is broader than that of the higher-energy metal–ligand charge-transfer absorption. The latter is sometimes observed as a feature on the low-energy side of the dominant ligand π – π^* transition. Even when more clearly separated from the π – π^* transition, the higher-energy charge-transfer transition will include one (or more) shoulders on the main absorption that indicate that several transitions contribute to the envelope. The lower-energy metal–ligand charge-transfer absorptions usually appear to be more symmetrical in shape, but in solvents of low polarity (benzene, diethylether, for example) the absorption envelope may include a shoulder, thus demonstrating the presence of (at least) two electronic transitions.

The influence of the metal atom on the extinction coefficient of the lower-energy charge-transfer transition, ϵ (LECT), of the [M(CO)₄(*n,n'*-X₂-bipy)] complex is generally that this decreases in the order M = W > Mo > Cr. Again generally, the value of ϵ (LECT), increases as the solvent polarity decreases (benzene > THF > acetone). The influence of the position *n* of the substituent X on the value of ϵ (LECT) is apparent in that $\epsilon(4,4) > \epsilon(5,5) > \epsilon(3,3) \sim \epsilon(6,6)$ for the substituent groups considered here, where measurements were possible. The width of the lower-energy metal–ligand charge-transfer absorption measured at half-peak height (fwhm) is also sensitive to the value of *n*, decreasing in the order fwhm (5,5) > (4,4) > (6,6) $\geq$ (3,3). It should be noted that measurements of the area under the curve/envelope follow the order of the extinction coefficients. Among these complexes the molar absorption coefficients of the two metal–ligand charge-transfer absorptions are not the same, as one would expect. Two groups can be broadly distinguished; one in which ϵ (HECT) > ϵ (LECT) is observed for *n* = 3, 5; the other, in which ϵ (LECT) > ϵ (HECT) is observed for *n* = 4, 6. The metal has a significant influence on the value of ϵ , and consequently the presence of tungsten may result in reversal of these orders.

2.3. Absorption energies

The energies of the two absorptions in the visible/UV region (13 000–28 000 cm⁻¹) are both solvent-sen-

Table 1

Acceptor strength parameter A (cm^{-1}) and solvatochromic coefficient B (cm^{-1}) for $[\text{M}(\text{CO})_4(n,n'\text{-X}_2\text{-bipy})]$ complexes in solution

n,n'	X	M	A	B	r^a
3	Me	Cr	18251	2793	0.999
3	Me	Mo	20137	2672	0.995
3	Me	W	19047	3447	0.997
4	Me	Mo	19379	3989	0.994
5	Me	Mo	19586	4144	0.985
6	Me	Mo	19958	3644	0.993
6	Me	W	18997	3924	0.998
	H	Mo	19190	3520	0.997
3	CO_2Me	Mo	18969	3758	0.999
3	CO_2Me	W	16416	3209	0.999
4	CO_2Me	Mo	16817	3174	0.999
5	CO_2Me	Cr	14091	3614	0.999
5	CO_2Me	Mo	15524	3812	0.998
5	CO_2Me	W	14823	3935	0.999
4	CN	Cr	14762	2877	0.998
4	CN	Mo	15893	3237	0.997
4	CN	W	15567	3053	0.998
5	CN	Cr	12880	3890	0.986
5	CN	Mo	14238	4196	0.986
5	CN	W	13732	4176	0.987
4,5-Diazafluorenone		Mo	18930	3796	0.998

^a r is the multilinear regression correlation coefficient for the data reported in the Experimental Details section.

sitive (solvatochromic). The lower-energy metal–ligand charge-transfer absorption is much more solvent-sensitive than the higher-energy charge-transfer absorption. The latter absorption is observed in a much narrower energy range (26 200–25 500 cm^{-1} in THF solution for the complexes considered here) and is much less sensitive to the nature of the substituent X and the position of that substituent in the bipyridine ring. The most intense absorption in the lower-energy charge-transfer envelope is usually assigned [2,6] to a z -polarized $b_2-b_2(\pi^*)$ transition directed along the dipole vector of the complex. The energy of the lower-energy metal–ligand charge-transfer transition is sensitive to the metal atom, and decreases in the order $\text{M} = \text{Mo} \geq \text{W} > \text{Cr}$, an order that has been explained in terms of relativistic effects [10]. Concentrating on the results for the molybdenum complexes, for which the greatest range of information is available, and using the E^* -scale of Manuta and Lees [6] in the equation

$$\lambda(\text{LECT}) = A + BE^*$$

where A is an index of the π -acceptor strength of the $n,n'\text{-X}_2\text{-bipyridine}$ ligand, and B is a solvatochromism (solvent sensitivity) coefficient, we obtain the results shown in Table 1. In each case, values of λ_{max} recorded in at least five different solvents are included in the correlation. The correlation coefficients, r , are all better than 0.985, and have a mean value of 0.995 for 21 complexes. These results show that the order of π -acceptor strength of the bipy ligand

measured by A is sensitive both to the nature of the substituent X and to its position n on the bipy ring. Thus, A increases in the order CN (strongest acceptor, smallest A value) $< \text{CO}_2\text{Me} < \text{Me}$ (weakest acceptor, largest A value). Although the range of A values for the complexes of the four dimethyl-substituted ligands is rather narrow (758 cm^{-1}) it is also consistent with the broader range (3445 cm^{-1}) of the A values of the complexes of the three di(methoxycarbonyl)-substituted ligands. This shows that the influence of the substituent X on the acceptor strength of the bipyridine increases in the order $3,3' \sim 6,6' < 4,4' < 5,5'$. However, there is no correlation between the acceptor strength parameter A and the solvent sensitivity parameter B .

The structures of the two complexes $[\text{Mo}(\text{CO})_4(6,6'\text{-Me}_2\text{-bipy})]$ [11] and $[\text{Mo}(\text{CO})_4(3,3'\text{-Me}_2\text{-bipy})]$ [12] as their benzene solvates show that the substituted 2,2'-bipyridine ligand in each complex is significantly distorted. In the case of the 6,6'- $\text{Me}_2\text{-bipy}$ ligand, it is distorted as a consequence of repulsion between the methyl groups and the two carbonyl ligands in the equatorial plane of the complex. The ligand is asymmetrically bound to the metal, and the two pyridine rings are distorted in the *same* direction to pseudo-boat conformations. In the case of the 3,3'- $\text{Me}_2\text{-bipy}$ ligand, it is distorted principally as a consequence of repulsion between the methyl groups. The two pyridine rings in the ligand suffer distortions in *opposite* directions to pseudo-boat conformations.

Comparison with the structure of $[\text{Mo}(\text{CO})_4(1,10\text{-phenanthroline})]$ [13], in which the planar heterocyclic ligand is not distorted and is symmetrically bound to the metal, shows that the Mo–N distance increases from 2.243(2) Å (phen) to 2.258(3), 2.263(4) Å (3,3'- $\text{Me}_2\text{-bipy}$), to 2.290(2), 2.299(2) Å (6,6'- $\text{Me}_2\text{-bipy}$). It is significant also that the structures of the benzene solvates of the two dimethyl-bipy complexes provide no structural evidence for any specific interaction between benzene and the bipy ligand in the solid state: indeed, the benzene molecule lies beyond Van der Waals contact with the bipy ligand in each case. (Separate experiments showed that the benzene is very easily lost by pumping on the crystalline solvate.) The distortions of these ligands suggests that their π -acid strength is thereby reduced, which is consistent with the order of A values. It might have been expected that the solvent sensitivity would also be reduced by the loss of planarity, both within the ligand and between the ligand and the metal, but this is not observed. The B value for $[\text{Mo}(\text{CO})_4(6,6'\text{-Me}_2\text{-bipy})]$ is greater than that for the unsubstituted $[\text{Mo}(\text{CO})_4(\text{bipy})]$. The B value for $[\text{Mo}(\text{CO})_4(\text{bipy})]$ is similar to that for the complex $[\text{Mo}(\text{CO})_4(2\text{-piperidinyl-pyridine})]$, in which the two nitrogen donors are not in conjugation [14].

In general, the bipyridine dinitriles are stronger π

acids, and form complexes which have greater solvent sensitivity, than the analogous 2,2'-bipyridine methyl esters. The close similarity in both the *A* and *B* values of the tetracarbonylmolybdenum complexes of 5,5'-dicyano-2,2'-bipyridine and 4,4'-bipyrimidine [15] on the one hand, and the 4,4'-dicyano-2,2'-bipyridine and 2,2'-bipyrazine [15] complexes on the other, can be used to deduce that 5,5'-dicyano-2,2'-bipyridine is both a superior π -acceptor and is more basic than 4,4'-dicyano-2,2'-bipyridine.

The influence of widening the bite angle NMoN of the coordinated α -diimine on the solvatochromism of its tetracarbonyl Mo complex was assessed by comparing $[\text{Mo}(\text{CO})_4(4,5\text{-diazfluorenone})]$ with $[\text{Mo}(\text{CO})_4(\text{bipy})]$. The *A* values of the two complexes are very similar, but their *B* values (solvent sensitivity) are significantly different. This is probably to be attributed to the presence of a carbonyl group $[\text{Mo}(\text{CO})_4(4,5\text{-diazfluorenone})]$ that lies along the dipole vector of the complex which is the axis of the solvent-sensitive LECT. Transfer of charge from the metal to the ligand is likely to be centred on the cyclopentadienone ring, so that the excited-state dipole moment will be enhanced.

It would appear that when donor substituents are present (on the 2,2'-bipyridine ring) so that the planarity of the rings is disturbed, as in 3,3'-Me₂-bipy, there is a significant decrease in both the π -acceptor ability and the solvent-sensitivity of the complex results. If electron-withdrawing substituents are present that do not significantly disturb the planarity of the rings, as when the substituents are in the 5,5' and 4,4' positions on the rings, then both the π -acceptor ability of the ligand and the solvent sensitivity of the complex are enhanced. Between these limits, adjustment of the position of substitution and the character of the substituent(s) can be used to influence the solvatochromism of the complexes.

The use of a general solvent parameter is inadequate for deriving detailed information about solute-solvent interactions in such complex systems as the α -diimine complexes considered here. Altering the electronic properties of such systems by variation of substituents involves a complex interplay of several variables. The influence of steric effects which may produce structural changes also has to be considered. It is clear, then, that correlation of changes in the parameters *A* and *B* for diimine ligands requires that the ligands should be electronically *and* structurally similar; for example, 4,4'-bipyrimidine, 3,3'-bipyridazine, 2,2'-bipyrazine [15]. The complexity of the solute-solvent interactions appears in the form of deviations from "ideal" behaviour. The apparent anomaly presented by alcohols and dioxane is well-known in this context [2]. The objective of representing solvent polarity by a single number which can apply to a broad

range of different solutes such as $[\text{M}(\text{CO})_4(\alpha\text{-diimine})]$ complexes, even when these may appear to be quite similar, seems not to be realizable because of the inevitable (over-)simplification that is involved.

3. Experimental details

3.1. Ligands

The following ligands were prepared by published methods: *n,n'*-dimethyl-2,2'-bipyridines, *n* = 3 [16], *n* = 4, 5, 6 [17]; *n,n'*-dicyano-2,2'-bipyridines, *n* = 3 [18], *n* = 4, 5 [19], *n* = 6 [20]; *n,n'*-di(methoxycarbonyl)-2,2'-bipyridines, *n* = 3 [21], *n* = 4, 5 [16]; 4,5-diazfluorenone [22]. 6,6'-Di(methoxycarbonyl)-2,2'-bipyridine was prepared from the dicarboxylic acid, which in turn was prepared by hydrolysis of 6,6'-dicyano-2,2'-bipyridine [20] with KOH in acetonitrile solution. The finely powdered dicarboxylic acid was suspended in cold dimethoxyethane at -5 to 0°C (ice-salt) and then treated with ethereal diazomethane azeotrope. Removal of the solvent in vacuum after 1.5 h and subsequent sublimation (160°C , 0.05 Torr) followed by recrystallization of the sublimate from propan-1-ol gave colourless rhombic crystals, m.p. $192\text{--}193.5^\circ\text{C}$ (92% yield). Anal. found: C, 61.2; H, 4.3; (I)N, 10.2. C₁₄H₁₂N₂O₄. Calc.: C, 60.9; H, 4.5; N, 10.5%. *m/z* (I) 272 (13, M⁺), 214 (100), 154 (33).

3.2. Complexes

The methods of preparation of the complexes and the instruments used in characterization were standard and as described previously [20]. Generally, the complexes are prepared from the reaction between the disubstituted bipyridine and the norbornadiene complex, $[\text{M}(\text{CO})_4(\eta^2, \eta^2\text{-C}_7\text{H}_8)]$ (M = Cr, Mo, W), which is present in slight excess. The solvents for spectroscopic measurements (benzene, chloroform, tetrahydrofuran, dichloromethane, acetone, acetonitrile) were dried, deaerated, and distilled under dinitrogen before use. Although THF was found to be widely employable as a solvent, we found that the complexes of 3,3'-Me₂-bipy and 6,6'-Me₂-bipy can only be isolated in a pure state using benzene as both the reaction medium and work-up solvent. The use of more polar solvents resulted in decomposition, the rate of which increased with solvent polarity. This behaviour is particularly marked for the complexes of 6,6'-Me₂-bipy, which decompose rapidly in dry, deaerated nitromethane under dinitrogen. Attempts to prepare complexes of 3,3'-(CN)₂-bipy in either THF or benzene readily gave highly coloured solutions, but, despite care and much effort, no complex could be isolated. This is unex-

pected, in view of the ease of isolation and comparative stability of the complexes of 3,3'-(CO₂Me)₂-bipy. However, the structure of 3,3'-(CN)₂-bipy shows [18] that there are attractive intramolecular interactions between the pyridine N atoms and the nitrile C atoms in this molecule which may be responsible for reducing the reactivity of its pyridine nitrogen as a nucleophile. Our attempts to prepare complexes of 6,6'-(CN)₂-bipy and 6,6'-(CO₂Me)-bipy were also unavailing; intensely dark coloured solids were isolated that were only very sparingly soluble in solvents of moderate polarity (THF) and decomposed in more polar solvents (MeCN, DMSO) to liberate the ligand. The following complexes were prepared and characterized for the first time:

(2,2'-Bipyridine-5,5'-dicarbonitrile)tetracarbonylchromium. Purple/black crystals (92% yield). Anal. Found: C, 51.7; H, 1.8; N, 15.0. C₁₆H₆CrN₄O₄ calc.: C, 51.9; H, 1.6; N, 15.1%. δ_{H} (acetone-*d*₆) 8.59 (H(4), ³J₃₄ 7.8), 8.84 (H(3), ³J₃₄ 8.2), 9.59 (H(6)). δ_{C} (acetone-*d*₆) 112.81 (C(5)), 116.05 (CN), 124.89 (C(3)), 141.50 (C(4)), 156.35 (C(6)), 157.72 (C(2)), 213.68 (CO, *trans* to L), 228.81 (CO, *cis* to L). IR (CH₂Cl₂) 2239w, 2013s, 1917vs, 1899sh, 1849s cm⁻¹. λ_{max} (cm⁻¹) (ϵ , m² mol⁻¹) 14085 (3580), 24390 (6290) (C₆H₆); 13736 (3670), 24271 (6450) (CHCl₃); 15361 (3160), 25125 (5570) (THF); 14556 (3490), 24752 (6390) (CH₂Cl₂); 16077 (3120), 25510 (5440) (Me₂CO); 16313 (2930), 25706 (5230) (MeCN).

(2,2'-Bipyridine-5,5'-dicarbonitrile)tetracarbonyltungsten. Black crystals (84% yield). Anal. Found: C, 37.8; H, 1.4; N, 11.4. C₁₆H₆N₄O₄W calc.: C, 38.3; H, 1.2; N, 11.2%. δ_{H} (acetone-*d*₆) 8.68 (H(4), ³J₃₄ 8.5, ⁴J₄₆ 1.9), 8.98 (H(3), ³J₃₄ 8.5, ⁵J₃₆ 0.8), 9.63 (H(6), ⁴J₄₆ 1.9, ⁵J₃₆ 0.8). δ_{C} (acetone-*d*₆) 113.95 (C(5)), 115.68 (CN), 126.01 (C(3)), 141.87 (C(4)), 156.26 (C(6)), 158.33 (C(2)), 201.12 (CO, *trans* to L), 215.09 (CO, *cis* to L). IR (CH₂Cl₂) 2240w, 2012s, 1909vs, 1891sh, 1846s cm⁻¹. λ_{max} (cm⁻¹) (ϵ , m² mol⁻¹) 15038 (4780), 23809 (5600) sh, 25974 (6050) (C₆H₆); 14705 (4990), 23640 (5870) sh, 26041 (6140) (CHCl₃); 16393 (4450), 26385 (5890) (THF); 15479 (4740), 24390 (5710) sh, 26315 (6350) (CH₂Cl₂); 17123 (4130), 26737 (5640) (Me₂CO); 17421 (3960), 26881 (5550) (MeCN).

(2,2'-Bipyridine-4,4'-dicarbonitrile)tetracarbonylchromium. Black microcrystalline powder (65% yield). Anal. Found: C, 51.9; H, 1.8; N, 14.2. C₁₆H₆CrN₄O₄ calc.: C, 51.9; H, 1.6; N, 15.1%. δ_{H} (acetone-*d*₆) 8.00 (H(6), ³J₅₆ 5.4), 9.05 (H(3)), 9.52 (H(6), ³J_{5,6} 5.4). δ_{C} (acetone-*d*₆) 116.69 (CN), 121.62 (C(4)), 126.29 (C(3)), 127.83 (C(5)), 154.78 (C(6)), 156.39 (C(2)), 214.12 (CO, *trans* to L), 229.54 (CO, *cis* to L). IR (CH₂Cl₂) 2241w, 2012s, 1921vs, 1908sh, 1851s cm⁻¹. λ_{max} (cm⁻¹) (ϵ , m² mol⁻¹) 15699 (6950), 21739 (7100) (C₆H₆); 15219 (7790), 21008

(8130) (CHCl₃); 16529 (6870), 23364 (7210) (THF); 15748 (7250), 21786 (7510) (CH₂Cl₂); 17065 (6420), 24155 (7250) (Me₂CO); 17241 (6260), 24272 (7200) (MeCN).

(2,2'-Bipyridine-4,4'-dicarbonitrile)tetracarbonyltungsten. Purple-black crystals (90% yield). Anal. Found: C, 38.0; H, 1.3; N, 10.6. C₁₆H₆N₄O₄W calc.: C, 38.3; H, 1.2; N, 11.2%. δ_{H} (acetone-*d*₆) 8.06 (H(5), ⁴J₃₅ 1.6, ³J₅₆ 5.8), 9.21 (H(3), ⁴J₃₅ 1.6, ⁵J₃₆ 0.8), 9.53 (H(6), ⁵J₃₆ 0.8, ³J₅₆ 5.8). δ_{C} 116.65 (CN), 121.78 (C(4)), 127.71 (C(3)), 129.24 (C(5)), 154.21 (C(6)), 156.99 (C(2)), 201.81 (CO, *trans* to L), 215.81 (CO, *cis* to L) p.p.m. (acetone-*d*₆). IR (CH₂Cl₂) 2241w, 2012s, 1913vs, 1895sh, 1849s cm⁻¹. λ_{max} (cm⁻¹) (ϵ , m² mol⁻¹) 16556 (11010), 22989 (8280), 26316 (4730) sh (C₆H₆); 16051 (11070), 22371 (8530), 26316 (4070) sh (CHCl₃); 17422 (10220), 24331 (7760), 26316 (6480) sh (THF); 16639 (10860), 23148 (8520), 26316 (5210) sh (CH₂Cl₂); 18018 (9270), 25641 (7500) (Me₂CO); 18215 (9070), 25907 (7580) (MeCN).

(5,5'-Di(methoxycarbonyl)-2,2'-bipyridine)tetracarbonylchromium. Blue-black microcrystals (84% yield). Anal. Found: C, 49.3; H, 2.8; N, 6.3. C₁₈H₁₂CrN₂O₈ calc.: C, 49.6; H, 2.8; N, 6.4%. δ_{H} (CDCl₃) 4.06 (CH₃), 8.18 (H(3), ³J₃₄ 8.2), 8.48 (H(4), ³J₃₄ 8.4, ⁴J₄₆ 1.9), 9.82 (H(6), ⁴J₄ 1.9). IR (CH₂Cl₂) 2011s, 1907vs, 1890sh, 1838s, 1732 cm⁻¹. λ_{max} (cm⁻¹) (ϵ , m² mol⁻¹) 15314 (2940), 25253 (5460) (C₆H₆); 15314 (3380), 25253 (6600) (CHCl₃); 16260 (2950), 25707 (5220) (THF); 16026 (2810), 25641 (5360) (CH₂Cl₂); 17094 (2750), 26667 (4790) (Me₂CO); 17422 (2760), 27027 (4810) (MeCN).

(5,5'-Di(methoxycarbonyl)-2,2'-bipyridine)tetracarbonylmolybdenum. Blue-black microcrystals (78% yield). Anal. Found: C, 44.8; H, 2.5; N, 5.8. C₁₈H₁₂MoN₂O₈ calc.: C, 45.0; H, 2.5; N, 5.8%. δ_{H} (CD₂Cl₂) 4.03 (CH₃), 8.29 (H(3), ³J₃₄ 8.7, ⁵J₃₆ 0.7), 8.54 (H(4), ³J₃₄ 8.5, ⁴J₄₆ 1.9), 9.65 (H(6), ⁴J₄₆ 1.9, ⁵J₃₆ 0.9). IR (CH₂Cl₂) 2023s, 1911vs, 1887sh, 1840s, 1735s cm⁻¹. λ_{max} (cm⁻¹) (ϵ , m² mol⁻¹) 16807 (3350), 26385 (5440) (C₆H₆); 16892 (3820), 26525 (6500) (CHCl₃); 17857 (3550), 26882 (5340) (THF); 17606 (3670), 26882 (5860) (CH₂Cl₂); 18727 (3200), 27701 (4690) (Me₂CO); 19084 (3280), 28011 (4820) (MeCN).

(5,5'-Di(methoxycarbonyl)-2,2'-bipyridine)tetracarbonyltungsten. Purple-black microcrystals (85% yield). Anal. Found: C, 37.1; H, 2.3; N, 4.9. C₁₈H₁₂N₂O₈W calc.: C, 38.0; H, 2.1; N, 4.9%. IR (CH₂Cl₂) 2010s, 1900vs, 1881sh, 1836s, 1736s cm⁻¹. λ_{max} (cm⁻¹) (ϵ , m² mol⁻¹) 16129 (4190), 26316 (3760) (C₆H₆); 16207 (3740), 26525 (3730) (CHCl₃); 17182 (4140), 26596 (3740) (THF); 16920 (4050), 26738 (3770) (CH₂Cl₂); 18083 (3940), 27100 (3710) (Me₂CO); 18484 (3610), 27473 (3680) (MeCN).

(3,3'-Di(methoxycarbonyl)-2,2'-bipyridine)tetracarbonylmolybdenum. Brown-red needles (77% yield). Anal. Found: C, 44.3; H, 2.4; N, 5.6. $C_{18}H_{12}MoN_2O_8$ calc.: C, 45.0; H, 2.5; N, 5.8%. δ_H ($CDCl_3$) 3.79 (CH_3), 7.49 (H(5), $^3J_{45}$ 7.8, $^3J_{56}$ 5.4), 8.32 (H(4), $^3J_{45}$ 7.8, $^4J_{46}$ 1.5), 9.19 (H(6), $^4J_{46}$ 1.5, $^3J_{56}$ 5.4). δ_C ($CDCl_3$) 53.1 (CH_3), 124.24 (C(5)), 131.33 (C(3)), 138.48 (C(4)), 153.84 (C(6)), 154.49 (C(2)), 165.49 (CO_2R), 204.46 (CO, *trans* to L), 223.14 (CO, *cis* to L). IR (CH_2Cl_2) 2019s, 1911vs, 1881sh, 1836s, 1736s cm^{-1} . λ_{max} (cm^{-1}) (ϵ , $m^2 mol^{-1}$) 18416 (2910), 25575 (6770) (C_6H_6); 18450 (2510), 25773 (5770) ($CHCl_3$); 19231 (2830), 26042 (6350) (THF); 19048 (2870), 26178 (6520) (CH_2Cl_2); 20000 (2770), 26596 (5960) (Me_2CO).

(3,3'-Di(methoxycarbonyl)-2,2'-bipyridine)tetracarbonyltungsten. Purple-black crystals (83% yield). Anal. Found: C, 38.3; H, 2.1; N, 4.7. $C_{18}H_{12}N_2O_8W$ calc.: C, 38.0; H, 2.1; N, 4.9%. δ_H ($CDCl_3$) 3.81 (CH_3), 7.48 (H(5), $^3J_{45}$ 8.0, $^3J_{56}$ 5.5), 8.34 (H(4), $^3J_{45}$ 8.0, $^4J_{46}$ 1.6), 9.31 (H(6), $^4J_{46}$ 1.5, $^3J_{56}$ 5.4). δ_C ($CDCl_3$) 53.13 (CH_3), 124.99 (C(5)), 132.11 (C(3)), 138.14 (C(4)), 153.76 (C(6)), 155.50 (C(2)), 165.27 (CO_2R), 201.07 (CO, *trans* to L), 215.40 (CO, *cis* to L). IR (CH_2Cl_2) 2011s, 1898vs, 1876sh, 1832s, 1734s cm^{-1} . λ_{max} (cm^{-1}) (ϵ , $m^2 mol^{-1}$) 17483 (3330), 24814 (6610) (C_6H_6); 17483 (3660), 24983 (6800) ($CHCl_3$); 18315 (3630), 25445 (6770) (THF); 18248 (3820), 25575 (7070) (CH_2Cl_2); 19084 (3490), 26110 (6480) (Me_2CO); 19342 (3170), 26385 (5930) (MeCN).

(3,3'-Dimethyl-2,2'-bipyridine)tetracarbonylchromium. Brown-red crystals (86% yield). Anal. Found: C, 53.7; H, 3.3; N, 7.9. $C_{16}H_{12}CrN_2O_4$ calc.: C, 55.2; H, 3.5; N, 8.0%. δ_H ($CDCl_3$) 2.35 (CH_3), 7.28 (H(5), $^3J_{45}$ 7.7, $^3J_{56}$ 5.2), 7.70 (H(4), $^3J_{45}$ 7.4), 9.03 (H(6), $^3J_{56}$ 4.4). δ_C ($CDCl_3$) 20.63 (CH_3), 123.42 (C(5)), 133.49 (C(3)), 139.78 (C(4)), 150.65 (C(6)), 155.40 (C(2)), 214.22 (CO, *trans* to L), 229.16 (CO, *cis* to L). IR (CH_2Cl_2) 2010s, 1989vs, 1876sh, 1825s cm^{-1} . λ_{max} (cm^{-1}) (ϵ , $m^2 mol^{-1}$) 19048, 25381 (PhMe); 19231, 25510 (C_6H_6); 19881, 25773 (THF); 20576, 25707 (Me_2CO); 20964, 25907 (MeCN).

(3,3'-Dimethyl-2,2'-bipyridine)tetracarbonylmolybdenum. Yellow crystals (65% yield). Anal. Found: C, 49.0; H, 3.2; N, 7.2. $C_{16}H_{12}MoN_2O_4$ calc.: C, 49.0; H, 3.1; N, 7.1%. δ_H ($CDCl_3$) 2.37 (CH_3), 7.32 (H(5), $^3J_{45}$ 7.8, $^3J_{56}$ 5.1), 7.78 (H(4), $^3J_{45}$ 8.0, $^4J_{46}$ 1.1), 8.93 (H(6), $^3J_{56}$ 5.2, $^4J_{46}$ 1.1). δ_C ($CDCl_3$) 20.35 (CH_3), 123.64 (C(5)), 134.14 (C(3)), 140.25 (C(4)), 150.31 (C(6)), 154.91 (C(2)), 205.40 (CO, *trans* to L), 223.58 (CO, *cis* to L). IR (CH_2Cl_2) 2016s, 1903vs, 1873s, 1827s cm^{-1} . λ_{max} (cm^{-1}) (ϵ , $m^2 mol^{-1}$) 21053 (3840), 26042 (6250) (C_6H_6); 21368 (3670), 26385 (5900) ($CHCl_3$); 21739 (3650), 26247

(5560) (THF); 21930 (3410), 26596 (5300) (CH_2Cl_2); 22422 (3440), 26455 (5300) (Me_2CO).

(3,3'-Dimethyl-2,2'-bipyridine)tetracarbonyltungsten.

Red-brown crystals (62% yield). Anal. Found: C, 39.8; H, 2.3; N, 5.8. $C_{16}H_{12}N_2O_4W$ calc.: C, 40.3; H, 2.5; N, 5.8%. δ_H ($CDCl_3$) 2.42 (CH_3), 7.34 (H(5), $^3J_{45}$ 8.0, $^3J_{56}$ 5.2), 7.83 (H(4), $^3J_{45}$ 7.8, $^4J_{46}$ 1.1), 9.04 (H(6), $^3J_{56}$ 5.2, $^4J_{46}$ 1.1). δ_C ($CDCl_3$) 20.73 (CH_3), 124.36 (C(5)), 135.00 (C(3)), 140.41 (C(4)), 150.26 (C(6)), 155.69 (C(2)), 202.59 ($^1J_{WC}$ 525.7) (CO, *trans* to L), 215.92 ($^1J_{WC}$ 669.9) (CO, *cis* to L). IR (CH_2Cl_2) 2008s, 1890vs, 1870sh, 1823s cm^{-1} . λ_{max} (cm^{-1}) (ϵ , $m^2 mol^{-1}$) 20243 (4280), 25773 (6230) (C_6H_6); 20619 (4290), 26110 (6220) ($CHCl_3$); 21052 (3940), 25707 (5390), 28933 (4980) sh (THF); 21368 (3930), 26178 (5530), 27778 (5280) sh (CH_2Cl_2); 21978 (3700), 25907 (5140), 28986 (4530) sh (Me_2CO); 22422 (3800), 26110 (5390) (MeCN).

(6,6'-Dimethyl-2,2'-bipyridine)tetracarbonylchromium.

Red-brown crystals (48% yield). Anal. Found: C, 54.7; H, 3.4; N, 8.1. $C_{16}H_{12}CrN_2O_4$ calc.: C, 55.2; H, 3.5; N, 8.0%. δ_H ($CDCl_3$) 3.09 (CH_3), 7.30 (H(5), $^3J_{45}$ 7.4), 7.72 (H(4), $^3J_{45}$ 7.8), 7.80 (H(3), $^3J_{34}$ 8.0). δ_C ($CDCl_3$) 29.00 (CH_3), 118.54 (C(3)), 125.77 (C(5)), 136.67 (C(4)), 156.66 (C(2)), 163.98 (C(6)), 212.09 (CO, *trans* to L), 228.45 (CO, *cis* to L). IR (CH_2Cl_2) 2010s, 1891vs, 1871sh, 1822s cm^{-1} .

(6,6'-Dimethyl-2,2'-bipyridine)tetracarbonylmolybdenum.

Orange needles (51% yield). Anal. Found: C, 48.5; H, 2.9; N, 7.1. $C_{16}H_{12}MoN_2O_4$ calc.: C, 49.0; H, 3.1; N, 7.1%. δ_H ($CDCl_3$) 3.05 (CH_3), 7.38 (H(5)), 7.79 (H(4), $^3J_{45}$ 7.8), 7.89 (H(3)). δ_C ($CDCl_3$) 29.76 (CH_3), 119.51 (C(3)), 125.88 (C(5)), 137.38 (C(4)), 156.44 (C(2)), 163.07 (C(6)), 203.16 (CO, *trans* to L), 222.88 (CO, *cis* to L). IR (CH_2Cl_2) 2017s, 1904vs, 1875s, 1826s cm^{-1} . λ_{max} (cm^{-1}) (ϵ , $m^2 mol^{-1}$) 21186 (3520), 26110 (3410) (C_6H_6); 22026 (3400), 25840 (3220) (THF); 23905, 25840 (Me_2CO).

(6,6'-Dimethyl-2,2'-bipyridine)tetracarbonyltungsten.

Brown crystals (91% yield). Anal. Found: C, 39.6; H, 2.4; N, 5.6. $C_{16}H_{12}N_2O_4W$ calc.: C, 40.3; H, 2.5; N, 5.8%. δ_H ($CDCl_3$) 3.10 (CH_3), 7.42 (H(5)), 7.80 (H(4)), 7.91 (H(3)). δ_C ($CDCl_3$) 30.83 (CH_3), 119.77 (C(3)), 126.09 (C(5)), 137.28 (C(4)), 157.62 (C(2)), 163.47 (C(6)), 199.46 (CO, *trans* to L), 214.82 (CO, *cis* to L). IR (CH_2Cl_2) 2010s, 1891vs, 1869sh, 1823s cm^{-1} . λ_{max} (cm^{-1}) (ϵ , $m^2 mol^{-1}$) 20325, 25641 (C_6H_6); 21322, 25840 (THF); 22321, 25641 (Me_2CO).

(4,5-Diazafluoren-9-one)tetracarbonylmolybdenum.

Dark brown crystals (83% yield). Anal. Found: C, 46.5; H, 1.4; N, 7.1. $C_{15}H_6MoN_2O_5$ calc.: C, 46.2; H, 1.6; N,

7.2%. δ_{H} (CDCl_3) 7.53 (H(2), $^3J_{12}$ 7.7, $^3J_{23}$ 5.5), 8.06 (H(1), $^3J_{12}$ 7.4, $^4J_{13}$ 1.1), 8.93 (H(3), $^3J_{23}$ 5.5, $^4J_{13}$ 1.1). δ_{C} 129.01 (C(2), C(6)), 130.05 (C(8)), 133.52 (C(1), C(7)), 156.70 (C(3), C(5)), 164.54 (C(4)), 205.53 (CO, *trans* to L), 222.57 (CO, *cis* to L). λ_{max} (cm^{-1}) (ϵ , $\text{m}^2 \text{mol}^{-1}$) 20243 (5780), 25641 (2610), 28571 (4020) sh (C_6H_6); 20000 (6020), 25641 (2780) (CHCl_3); 20747 (5670), 25641 (2730) (CH_2Cl_2); 22026 (4880), 25641 (3330) (Me_2CO); 22321 (4550), 25641 (3330) (MeCN).

The molar absorption coefficients were also measured for compounds which have been described in previous papers [9,19], as follows.

$[\text{Mo}(\text{CO})_4(4,4'-(\text{CN})_2\text{-bipy})]$ [19]. λ_{max} (cm^{-1}) (ϵ , $\text{m}^2 \text{mol}^{-1}$) 16920 (7830), 23364 (6210), 26316 (4660) sh (C_6H_6); 16393 (9260), 22676 (7670), 26316 (5140) sh (CHCl_3); 17857 (7590), 25510 (6600) (THF); 17065 (7940), 23529 (6480) (CH_2Cl_2); 18519 (6810), 26110 (6390) (Me_2CO); 18727 (6670), 26247 (6460) (MeCN).

$[\text{Mo}(\text{CO})_4(5,5'-(\text{CN})_2\text{-bipy})]$ [19]. λ_{max} (cm^{-1}) (ϵ , $\text{m}^2 \text{mol}^{-1}$) 15456 (2110), 25974 (3210) (C_6H_6); 15082 (2580), 26109 (3960) (CHCl_3); 16892 (3990), 26455 (5850) (THF); 16025 (4170), 26315 (6470) (CH_2Cl_2); 17699 (3870), 26809 (5600) (Me_2CO); 18115 (2480), 27027 (3810) (MeCN).

$[\text{Mo}(\text{CO})_4(4,4'\text{-Me}_2\text{-bipy})]$ [9]. λ_{max} (cm^{-1}) (ϵ , $\text{m}^2 \text{mol}^{-1}$) 20790 (8950), 25974 (8175) (C_6H_6); 21141 (8700), 25602 (9540) sh (CHCl_3); 21551 (8600), 25510 (7510) sh (THF); 21786 (7950), 26110 (5800) sh (CH_2Cl_2); 22675 (8360), 26250 (6390) sh (Me_2CO); 23201 (7300), 26840 (8200) sh (MeCN).

$[\text{Mo}(\text{CO})_4(5,5'\text{-Me}_2\text{-bipy})]$ [9]. λ_{max} (cm^{-1}) (ϵ , $\text{m}^2 \text{mol}^{-1}$) 21008 (4410) (C_6H_6), 21459 (4400) (CHCl_3); 21834 (4300) (THF); 21978 (4300) (CH_2Cl_2); 22831 (4200) (Me_2CO); 23640 (4200) (MeCN).

$[\text{Mo}(\text{CO})_4(4,4'-(\text{CO}_2\text{Me})\text{-bipy})]$ [9]. λ_{max} (cm^{-1}) (ϵ , $\text{m}^2 \text{mol}^{-1}$) 17857 (5690), 24814 (6870) (C_6H_6); 17730 (5640), 24716 (6700) (CHCl_3); 18656 (5620), 25320 (7000) (THF); 18518 (5560), 25475 (6890) (CH_2Cl_2); 18690 (5420), 25930 (6650) (Me_2CO); 19680 (5400), 26125 (6420) (MeCN).

Acknowledgements

We thank the Science and Engineering Research Council for the award of a studentship to PNWB and for allowing us to use the Mass Spectrometry Service at the University College of Swansea (Dr. J.A. Ballantine). We thank Dr. D.O'N. Smith for measuring the NMR spectra.

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