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PREPARATION AND ELECTRONIC SPECTRA OF SOME ALKYL- AND ARYL(2,2'-BIPYRIDINE)PLATINUM(II) COMPLEXES

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Summary

A series of alkyl- and aryl-(2,2'-bipyridine)-platinum (II) complexes has been prepared by displacement of the diene ligand in the corresponding cyclooctadiene complexes with 2,2'-bipyridine. Dimethyl(1,10-phenanthroline)platinum(II) was prepared in an analogous way. The electronic spectra of the complexes contain metal to ligand charge transfer bands whose energy is dependent on the nature of the substituents on platinum and on the solvent. It is suggested that π-bonding is important in the phenyl—platinum bond.

Introduction

There has been considerable interest recently in the nature of the transition metal to carbon σ-bond in alkyl and aryl-transition metal complexes. After some controversy, recent reports suggest that in arylplatinum complexes the platinum atom acts as both σ- and π-donor to the aryl groups, but that the π-bonding is weaker than was originally thought and that the extent of such π-bonding is independent of the nature of the other ligands bonded to platinum [1-3]. Similar conclusions have been drawn about the nature of the aryl—nickel and aryl—palladium bonds [3]. Although a number of physical methods have been used to investigate this problem, electronic spectroscopy appears to have been ignored. We recently prepared a number of alkyl- and aryl(2,2'-bipyridine)platinum(II) complexes in order to study their chemical reactivity, and found a correlation between the reactivity of the metal alkyl towards reactions with alkenes and alkynes and the energy of the lowest-energy band in the UV-visible spectrum [4]. This observation led us to study the electronic spectra more carefully and we now report the results of this study as well as the detail-

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ed preparations of the complexes. In an earlier study [1], Stewart and Treichel suggested that π-bonding in arylplatinum compounds might be important when the stabilising ligand was 2,2′-bipyridine and we have found this to be so. We also report solvent effects on the UV-visible spectra of the complexes.

Results and discussion

Preparation of the complexes

Our early attempts to prepare dimethyl(2,2′-bipyridine)platinum(II) by reaction of the corresponding chloride with methyllithium or methylmagnesium iodide were unsuccessful, and we were forced to develop an indirect route to this and related compounds. The compound could be prepared in low yield by replacement of the arsine ligands in *cis*-$PtMe_2(AsMe_3)_2$ or *cis*-$PtMe_2(AsPh_3)_2$, but much better yields (*ca.* 80%) were obtained by replacement of the diene ligand in dimethyl(1,5-cyclooctadiene)platinum(II) by 2,2′-bipyridine. The reaction was usually conducted in ether solution at room temperature, when red needles of the product slowly crystallised, reaction being complete in about three weeks under these conditions. Lower yields could be obtained more rapidly by refluxing the reagents in benzene solution. Similar methods were used to prepare the organo(2,2′-bipyridine)platinum(II) compounds listed in Table 1. The method was unsuccessful for preparation of the compounds $R_2Pt(bipy)$ where R was 2-biphenyl or 4-(dimethylamino)phenyl since the intermediate cyclooctadiene complexes could not be isolated from the usual reaction of diiodo(1,5-cyclooctadiene)platinum(II) with the corresponding Grignard reagent, and also when

TABLE 1

ANALYTICAL DATA AND MELTING POINTS OF COMPLEXES R_2PtL_2

R[a,b,c]	L_2[d]	M.p. (°C)	Analysis Found (Calcd.) (%)		
			C	H	Pt
4-$MeOC_6H_4$	COD	110 — 125d[h]	49.2 (51.1)	4.9 (5.0)	37.5 (37.6)
2-$MeOC_6H_4$	COD	105 — 110d	50.4 (51.1)	5.1 (5.0)	38.6 (37.6)
4-MeC_6H_4	COD	167 — 170d	53.8 (54.4)	5.7 (5.4)	
2-MeC_6H_4	COD	185 — 205d	53.3 (54.4)	5.6 (5.4)	42.3 (40.2)
4-FC_6H_4	COD	169 — 172	48.7 (48.6)	4.2 (4.1)	
3-FC_6H_4	COD	174 — 176d	46.4 (48.6)	4.3 (4.1)	37.2 (39.6)
4-ClC_6H_4	COD	186 — 190d	46.0 (45.6)	3.7 (3.8)	37.0 (37.1)
Me[a]	bipy	190 — 210d	38.0 (37.8)	3.7 (3.7)	50.6 (51.2)[e]
Et[a]	bipy	107 — 110d	40.9 (41.1)	4.8 (4.4)	47.9 (47.7)
Ph[c]	bipy	285 — 305d	52.0 (52.3)	3.4 (3.6)	38.8 (39.6)[f]
4-$MeOC_6H_4$[c]	bipy	218 — 222	52.0 (51.0)	4.0 (3.9)	36.0 (34.5)
2-$MeOC_6H_4$[c]	bipy	228 — 230	50.2 (51.0)	3.7 (3.9)	32.8 (34.5)
4-MeC_6H_4[b]	bipy	250 — 257d	54.0 (54.0)	4.2 (4.2)	35.1 (36.6)
2-MeC_6H_4[b]	bipy	300d	53.1 (54.0)	4.4 (4.2)	37.3 (36.6)
4-FC_6H_4[c]	bipy	267 — 300d	49.4 (48.8)	3.4 (3.0)	32.7 (36.0)
3-FC_6H_4[c]	bipy	285 — 305d	48.2 (48.8)	3.2 (3.0)	36.1 (36.0)
4-ClC_6H_4[c]	bipy	240 — 260d	46.8 (46.0)	3.1 (2.8)	32.5 (34.0)
Me	phen	210d	41.3 (41.5)	3.3 (3.5)	47.9 (48.1)[g]

[a] Colour red. [b] Colour orange. [c] Colour yellow. [d] COD = 1,5-cyclooctadiene, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline. [e] Found: N, 7.6., calcd.: N, 7.3%. [f] Found: N, 5.5., calcd.: N, 5.5%. [g] Found: N, 7.0., calcd.: N, 6.9%. [h] d = decomposition.

TABLE 2

NMR SPECTRA OF DIARYL (CYCLOOCTADIENE)PLATINUM(II) COMPLEXES[a]

Compound	Cyclooctadiene peaks				Aryl peaks		Other
	δ(CH) (ppm)	^{2}J(PtH) (Hz)	δ(CH_2) (ppm)	^{3}J(PtH) (Hz)	δ(H_o)[b] (ppm)	^{3}J(PtH_o)[b] (Hz)	
$(4\text{-}MeOC_6H_4)_2Pt(COD)$	5.59	38	2.95	16	7.70	60	δ(CH_3O) 4.15 ppm
$(4\text{-}CH_3C_6H_4)_2Pt(COD)$	5.56	39	2.93	16	7.50	64	δ(CH_3C) 2.63 ppm ^{6}J(PtH) 4.2 Hz
$(4\text{-}FC_6H_4)_2Pt(COD)$	5.55	39	3.00	16	7.65	67	
$(4\text{-}ClC_6H_4)_2Pt(COD)$	5.47	39	2.88	16	7.55	70	
$(3\text{-}FC_6H_4)_2Pt(COD)$	5.51	39	2.90	16	7.43	77	
$(2\text{-}CH_3C_6H_4)_2Pt(COD)$	5.44	40	2.94	16	7.85	70	δ(CH_3C) 3.03 ppm, ^{4}J(PtH) 7.2 Hz
$(2\text{-}MeOC_6H_4)_2Pt(COD)$	5.52	43	2.89	17	c		δ(CH_3O) 4.21 ppm

[a] Solvent $CDCl_3$ using TMS as external reference. [b] H_o = *ortho*-hydrogen to platinum. [c] Not resolved.

R = benzyl since the reaction of dibenzyl(1,5-cyclooctadiene)platinum(II) with 2,2′-bipyridine gave only decomposition products. Considerable decomposition also took place during the preparation of diethyl(2,2′-bipyridine)platinum(II) from the cyclooctadiene complex, but good yields were obtained in all other cases. Analytical data and melting or decomposition points for the new complexes are given in Table 1, and NMR data for the cyclooctadiene complexes are given in Table 2. Many of the 2,2′-bipyridine complexes were sparingly soluble in organic solvents and satisfactory NMR spectra could not be obtained. The compounds could be stored indefinitely in air without decomposition but dimethyl- and diethyl(2,2′-bipyridine)platinum(II) reacted rapidly with methanol and ethanol, with chlorinated solvents such as dichloromethane and chloroform and with methyl cyanide. In this sense, the compounds are considerably more reactive than similar methyl- or ethyl-platinum complexes stabilised by tertiary phosphines and arsines, which are either stable to or react only slowly with these reagents.

The resonances due to the cyclooctadiene groups in the NMR spectra of the diaryl(cyclooctadiene)platinum(II) complexes (Table 2) were almost identical for all complexes, but the coupling constant from platinum to the *ortho*-hydrogen atoms of the aryl groups varied with different aryl groups. There was a reasonable correlation of this coupling constant with the Hammett σ-values of the substituents on the aryl groups for the *meta*- and *para*-substituted phenylplatinum complexes.

Electronic spectra

The electronic spectra of dihalogeno(2,2′-bipyridine)platinum(II) complexes have been studied previously and four distinct bands were detected [5,6]. Two of these, in the regions 30,500—32,600 cm^{-1} (band 2) [5] and 39,200-39,800 cm^{-1} (band 4) [5], were assigned to π—π^* transitions within the 2,2′-bipyridine ligand shifted slightly from similar bands observed in the free ligand [7-9], and two extra bands in the regions 24,200-29,800 cm^{-1} (band 1) [5] and 33,800-36,800 cm^{-1} (band 3) [5] were assigned as metal to ligand charge transfer transitions (MLCT) from platinum *d*-orbitals to π^*-orbitals of 2,2′-bipyridine. The energies of the MLCT bands were strongly dependent on the solvent while the others were not. Similar assignments can be made for the organoplatinum complexes studied here though the energy of the MLCT bands was very sensitive to the nature of the alkyl or aryl groups bound to platinum. Similar bands have been observed in 2,2′-bipyridine complexes of some main group metal alkyls and have been assigned as σ(MC)—π^* transitions [10-13] but such an assignment is considered unlikely for these compounds.

The MLCT bands for dimethyl(2,2′-bipyridine)platinum(II) in benzene solution were at 19,800 cm^{-1} (shoulder at 21,100 cm^{-1}) and at 29,500 cm^{-1}, while in methyl cyanide the former band had moved to 22,000 cm^{-1} (shoulder at 22,800 cm^{-1}) and the latter was obscured by the first π—π^* transition of 2,2′-bipyridine. In all cases where both MLCT bands could be seen the second band was 9,000-10,000 cm^{-1} higher in energy than the first, while the π—π^* transitions of 2,2′-bipyridine (also 9,000-10,000 cm^{-1} apart) were insensitive to changes in the organic groups bound to platinum and to the solvent. Thus we have studied changes in the lowest energy MLCT band only (band 1) as a func-

TABLE 3

SOLVENT EFFECTS ON THE FIRST MLCT BAND IN THE ELECTRONIC SPECTRA OF SOME ALKYL- AND ARYL(2,2'-BIPYRIDINE)PLATINUM(II) COMPLEXES (UNITS OF $10^3\,\mathrm{cm}^{-1}$)

Solvent	RR' in RR'Pt(bipy)						
	Et, Et	Me, Me	Me, Cl	Cl, Cl	Ph, Ph	Me, I	Me, Me[h]
Acetonitrile	21.3[a] 21.9	22.0 22.8	23.9 25.0	26.2	23.4 23.9	23.8	22.0 23.3 24.3
Acetone	20.4[b] 22.1	21.2 22.2	23.3 24.4	25.3	22.8 23.4	23.1 23.9 (sh)	21.2 23.0 24.1
Dichloromethane	20.8 22.0	21.4 22.3			22.7 23.5		21.7 23.1 24.3
Pyridine	20.3 21.3		23.4	25.2 26.5 28.4	22.3 23.1		21.0 22.7 23.8
Tetrahydrofuran	19.8[c] 20.9		22.3 23.5		21.9 22.8		
Diethyl ether	19.2[d] 20.7						
Benzene	19.3[e] 20.7	19.8[f] 21.1	21.8 23.1		21.2 22.4	19.8 (sh) 21.5 22.8 (sh)	20.0 21.7 22.9
Toluene		19.6[g] 20.9	21.5 22.8		21.0 22.2		19.7 21.4 22.6

[a] Band 3 at 30,900 cm^{-1} (sh), band 2 at 32,400, cm^{-1}, 33,300 cm^{-1}, band 4 at 41,800 cm^{-1}. [b] Band 3 at 30,500 cm^{-1} (sh). [c] Band 3 at 29,800 cm^{-1}. [d] ϵ = 1130 l mol^{-1} cm^{-1}; band 3 at 29,100 cm^{-1} ϵ = 2090 l mol^{-1} cm^{-1}. [e] ϵ = 1430 l mol^{-1} cm^{-1}, band 3 at 29,100 cm^{-1}, ϵ = 2600 l mol^{-1} cm^{-1}. [f] ϵ = 3430 l mol^{-1} cm^{-1}; band 3 at 29,800 cm^{-1}, ϵ = 6100 l mol^{-1} cm^{-1}; [g] ϵ = 3720 l mol^{-1} cm^{-1}; band 3 at 29,500 cm^{-1}, ϵ = 6770 l mol^{-1} cm^{-1}. [h] 1,10-phenanthroline complex.

tion of the organic groups bound to platinum and of the solvent. The data are given in Tables 3 and 4, which also contain selected values of the energies of the other bands observed.

An attempt to correlate the energies of band 1 for the complexes RR'Pt(bipy) (where R,R' = methyl, phenyl, chloride or iodide) with the Taft σ_I values [14] and the Hammett σ_p values [15] of the groups R and R' is shown in Fig. 1. As might be expected for this system which is very different from those for which the σ-parameters were devised, the correlation is not perfect in either case. However, the correlation with σ_p values, which take account of both inductive and resonance effects, is considerably better than that with σ_I values, which take account of inductive effects only. In particular the energy of band 1 for diphenyl(2,2'-bipyridine)platinum(II) is considerably higher than that predicted from the σ_I value of the phenyl group, suggesting that the phenyl groups are acting as π-acceptors thus stabilising the *d*-orbitals on platinum and increasing the energy of the d—π^* transition. The effect is probably exaggerated since in the halide complexes the *d*-orbitals on platinum will be destabilised by the π-

TABLE 4

SOLVENT EFFECTS ON THE FIRST MLCT BAND IN THE ELECTRONIC SPECTRA OF THE COMPLEXES $(XC_6H_4)_2Pt(2,2'\text{-bipyridine})$ (units of 10^3 cm^{-1})

Solvent	Substituent X						
	4-MeO	2-MeO	4-Me	2-Me	4-Cl	4-F	3-F
Acetonitrile	22.7	23.5	23.1	22.9	24.0	23.6	24.4
	23.3		23.6	23.5	24.4	24.2	24.8
Acetone	22.2	22.7	22.4	22.4	23.5	23.2	23.9
	23.0		23.0	23.0	23.9	23.9	24.4
Dichloromethane	22.2	22.9	22.4	22.0	23.3	23.0	23.5
	22.8		23.0	22.9	23.7	23.5	24.1
Pyridine	21.8	22.5	22.0	21.9	23.1	22.7	23.4
	22.4		22.8	22.7	23.6	23.3	24.1
Tetrahydrofuran	21.8	22.0	21.6	21.7	22.7	22.0	23.0
	22.2		22.6	22.5	23.4	23.1	23.9
Diethyl ether	20.5	21.6	20.7		21.8	21.6	22.2
	21.7		21.9		22.8	22.7	23.3
Benzene	20.4	21.5	20.8	20.8	21.7	21.5	22.0
	21.7		21.8	22.0	22.7	22.6	23.0
Toluene	20.4	21.4	20.6	20.7	21.6	21.4	22.0
	21.7		21.7	21.8	22.7	22.6	23.1

donor ligand, but the above conclusion is confirmed by a study of the effect of substituents on the phenyl groups of diphenyl(2,2'-bipyridine)platinum(II) on the energy of band 1. A good correlation is observed between the energy of band 1 and the Hammett σ-values for the substituents (Fig. 2), again suggesting that the energies of the *d*-orbitals on platinum are sensitive to both σ- and π-bonding effects in the aryl—platinum bonds. The points for the *meta*- and *para*-substituted phenyl groups all correlate well, and that for the *ortho*-tolyl group

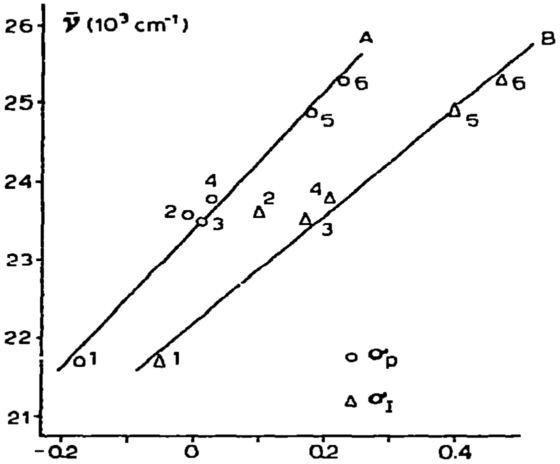

Fig. 1. Correlation of the energy of band 1 for the compounds RR'Pt(bipy) with (A) the mean Hammett σ_p values and (B) the mean Taft σ_I values of the substituents R and R'. 1, R = R' = Me; 2, R = R' = Ph; 3, R = Me, R' = I; 4, R = Me, R' = Cl; 5, R = R' = I; 6, R = R' = Cl.

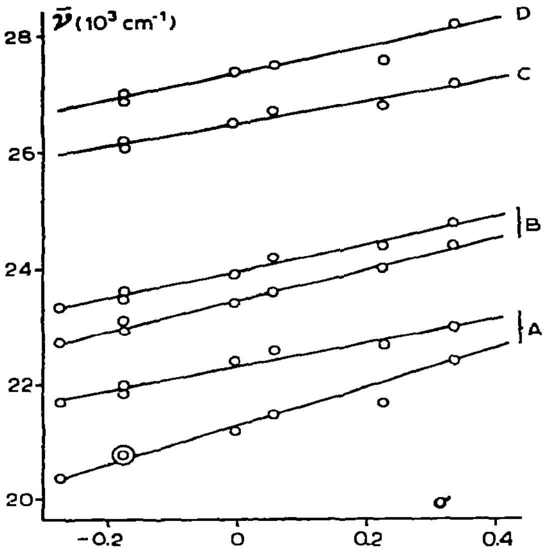

Fig. 2. Correlation of the energies of the MLCT bands in the electronic spectra of the compounds $(XC_6H_4)_2Pt(bipy)$ with the Hammett σ values of the substituents X. (A) band 1 in benzene solution (B) band 1 in acetonitrile solution (C) band 5 in tetrahydrofuran solution (D) band 5 in acetonitrile solution.

also falls on this line suggesting that there is no specific electronic interaction between the *ortho*-methyl group and the platinum atom. However, the energy of band 1 for the *o*-methoxyphenylplatinum complex is higher than expected, so that there probably is a direct interaction between the methoxy group and the platinum atom in this compound.

Interestingly the electronic spectra of the arylplatinum complexes contain an extra band (band 5) which is not shown by the alkylplatinum or halogenoplatinum complexes some 3,500 cm^{-1} higher in energy than band 1. The energy

TABLE 5

SOLVENT EFFECTS ON BAND 5 IN THE ELECTRONIC SPECTRA OF THE COMPLEXES $(XC_6H_4)_2$-Pt(2,2'-bipyridine) (units of 10^3 cm^{-1})

Solvent	Substituent X						
	2-MeO	4-Me	2-Me	H	4-Cl	4-F	3-F
Acetonitrile	26.9	26.9	27.0	27.4	27.4	27.5	28.2
Acetone	26.4	26.7	26.9	26.9	27.2	27.2	27.8
Dichloromethane	26.3	26.4	26.4	26.8	26.9	26.9	27.5
Pyridine	26.3	26.2	26.3	26.6	26.9	26.8	27.5
Tetrahydrofuran	26.0	26.1	26.2	26.5	26.8	26.7	27.2
Diethyl ether	[a]	25.6			26.2	26.3	26.7
Benzene	[a]	[a]	25.8	25.9	26.1	26.1	26.5
Toluene	[a]	[a]	25.8	25.8	26.0	26.0	26.5

[a] band too weak to be observed. Band 5 was not observed in any solvent when X = 4-MeO.

of this band also shows a reasonable correlation with the Hammett σ-values of the substituents on the phenyl groups (Fig. 2). It is also solvent dependent (see later, Fig. 4) and so is almost certainly another MLCT band. The band may well arise from a transition from a d-orbital on platinum to a π^*-orbital of the aryl group, thus explaining its absence in the alkyl- and halogeno-platinum compounds. However, the correlation with the Hammett σ-values would not be expected to hold for such a band [14], and the alternative assignment that the band may be due to a transition from a lower energy d-orbital on platinum to the π^*-orbital of 2,2'-bipyridine cannot be disregarded. In the ion $PtCl_4^{2-}$ the d_z^2 orbital is known to be 3,500 cm^{-1} lower in energy than the d_{xz}, d_{yz} orbitals [16] though there is no reason to expect this order to be the same in complexes containing π-acceptor ligands.

The energy of band 1 is also dependent on the metal, following the series Pd > Pt > Ni for analogous compounds RR'M(bipy) where M = Ni, Pd or Pt. Thus in benzene solution band 1 for Me_2M(bipy) is at 15,000 cm^{-1} when M = Ni and at 19,300 cm^{-1} (with a shoulder at 20,700 cm^{-1}) when M = Pt. We have been unable to prepare Me_2Pd(bipy) for a similar comparison, but in benzene solution band 1 for MeClM(bipy) is at 21,800 cm^{-1} (with a shoulder at 23,100 cm^{-1}) for M = Pt and at 29,400 cm^{-1} for M = Pd, while for MeIM(bipy) the corresponding bands are at 21,500 cm^{-1} (with shoulders at 19,800 and 22,800 cm^{-1}) for M = Pt and at 28,800 cm^{-1} for M = Pd. The order Pd > Pt > Ni for the energy of band 1 is the same as the order of the second ionisation energies for these elements (but not of the first ionisation energies for which the order is Pt > Pd > Ni) and is the reverse of the order of reactivity of the corresponding methyl(2,2'bipyridine)metal compounds towards alkenes and alkynes [4].

Finally, we note that the compounds $Pt(C_2F_4)$(bipy) [17] and $Pt(CF_3)_2$(bipy) [18] are reported to be pale-yellow compounds, so that band 1 for these compounds must be at higher energy than for $PtMe_2$(bipy) which is red. The d-orbitals on platinum in $Pt(C_2F_4)$(bipy) are therefore lower in energy than in $PtMe_2$(bipy) adding further evidence to the theory that the former complex should be regarded as a platinum(II) complex of $C_2F_4^{2-}$ rather than as a platinum(0) complex of tetrafluoroethylene.

The complex dimethyl(1,10-phenanthroline)platinum(II) gave MLCT bands similar to but more complex than those of the 2,2'-bipyridine complexes in its electronic spectrum. The data are included in Table 3.

Solvent effects on the electronic spectra

Strong solvent effects on the energy of the MLCT bands in a number of bipyridine complexes of the transition elements have been observed but there is some disagreement on the cause of the effect [5,19-22]. Thus Burgess showed that the MLCT bands of $Fe(bipy)_2(CN)_2$ were solvent dependent but those of $Fe(bipy)_3^{2+}$ were not and suggested that the solvent effect operated through the cyanide groups [20]. Similar effects were proposed [21] for some octahedral complexes $M(CO)_4$(bipy) where M = Mo or W, and Gillard and co-workers [5] suggested a similar effect to account for the solvent dependence of the electronic spectra of compounds PtX_2(bipy) where X = Cl, Br, I. On the other hand, Yamamoto and co-workers [22] showed that the energies of the

MLCT bands of square planar complexes NiR_2(bipy) where R = Me, Et were solvent dependent while those for octahedral $Et_2Fe(bipy)_2$ were not, and suggested that direct solvation of nickel in the square planar complexes was responsible for the effect. We observe similar solvent effects on band 1 for a variety of alkyl-, aryl- and halogeno(2,2'-bipyridine)platinum(II) complexes (Tables 2 and 3). It seems unlikely that solvent effects could be transmitted to similar extents through such different groups, so that we favour direct solvation of platinum to account for the results. If this theory is correct then one might expect the *ortho*-substituted phenylplatinum complexes to show lower solvent effects due to steric hindrance to the approach of solvent molecules to the platinum centre, but no significant lowering of the solvent effect was observed for the *o*-tolyl and *o*-methoxyphenyl derivatives. Our attempts to prepare complexes containing bulkier substituents in the *ortho*-position have been unsuccessful, so that an unequivocal test for the above theory is not yet possible.

As found for other 2,2'-bipyridine complexes the frequency of the MLCT bands for a given 2,2'-bipyridineplatinum complex in different solvents can be correlated with the E_T values of the solvents, which can be considered as measures of the polarity of the solvents [23]. Typical correlations are shown in Fig. 3 and 4. Fig. 3 illustrates the similar solvent dependence on band 1 and band 3

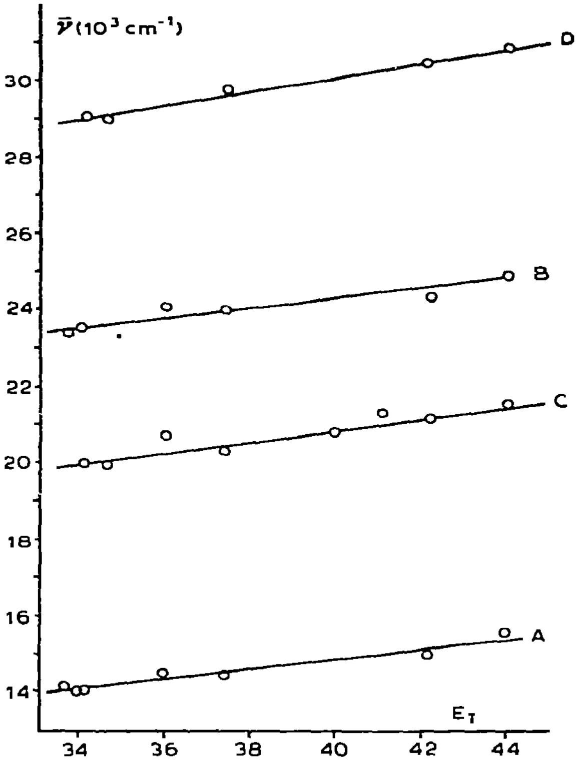

Fig. 3. Correlation of the energies of the MLCT bands in the electronic spectra of $Et_2Ni(bipy)$ (A) band 1 (B) band 3 and $Et_2Pt(bipy)$ (C) band 1 (D) band 2 with the solvent E_T values.

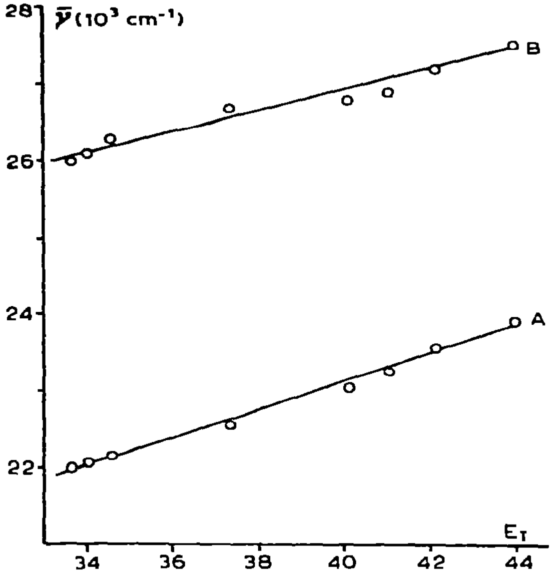

Fig. 4. Correlation of the energies of the MLCT bands in the electronic spectra of $(4\text{-}FC_6H_4)_2Pt(bipy)$ with the solvent E_T values (A) band 1 (B) band 5.

for $Et_2M(bipy)$ where M = Ni or Pt, and Fig. 4 illustrates the similar solvent dependence of band 1 and band 5 for a typical diaryl(2,2'-bipyridine)platinum(II) complex.

The electronic spectrum of MeClPt(bipy) in pyridine contained bands at 27,500 and 29,000 cm^{-1} which may be assigned to band 1 in the ion $[MePt(bipy)(py)]^+$, as well as weaker bands due to the parent MeClPt(bipy). $PtCl_2(bipy)$ undergoes a similar ionisation reaction in pyridine solution [5]. In each case band 1 moves to higher energy in the cationic platinum complex as would be expected.

Experimental section

Infrared spectra were obtained using a Perkin—Elmer 577 spectrophotometer, NMR spectra using a Perkin—Elmer R12B spectrometer, and electronic spectra using a Unicam SP8000 spectrophotometer.

$Me_2Pt(COD)$, $Et_2Pt(COD)$, $Ph_2Pt(COD)$ and MeClPt(bipy) where COD = 1,5-cyclooctadiene were prepared by known methods [18,24].

Dimethyl(2,2'-bipyridine)platinum(II) was prepared by treating $Me_2Pt(COD)$ (2.5 g) in ether (40 ml) with 2,2'-bipyridine (1.0 g). Red needles of the product slowly separated and reaction was complete in three weeks at room temperature (yield 90%). In some cases the product was contaminated with a yellow solid, and separation from this was effected by recrystallisation from acetone.

Diethyl(2,2'-bipyridine)platinum(II) was prepared in best yield by treating $Et_2Pt(COD)$ (0.7 g) with 2,2'-bipyridine (0.7 g) in ether (15 ml) in a sealed Carius tube. After 3 weeks at room temperature the impure precipitate was extracted with acetone, and the acetone slowly evaporated to yield red needles of the product (yield 40%).

Bis(4-fluorophenyl)(1,5-cyclooctadiene)platinum(II) was prepared by reaction of $PtI_2(COD)$ (1.0 g) with 4-fluorophenylmagnesium bromide [from Mg (0.5 g) and 4-fluorobromobenzene (1.5 g) in ether (50 ml)]. After stirring for 12 h under nitrogen at room temperature, the mixture was hydrolysed with ammonium chloride solution, the ether layer was separated, dried over $MgSO_4$, decolourised by adding charcoal and finally the ether was evaporated to yield the required product as a colourless oil, which solidified to a white solid on scratching with pentane (yield 75%). Other complexes were prepared similarly; occasionally the product was insoluble in ether and the hydrolysed reaction mixture was extracted with dichloromethane to obtain the desired product.

Diaryl(2,2'-bipyridine)platinum(II) was prepared as for $Me_2Pt(bipy)$. If the cyclooctadiene complex was insoluble in ether, benzene was used as solvent. Yields were in the range 50-80%.

Dimethyl(1,10-phenanthroline)platinum(II) was prepared from dimethyl(cyclooctadiene)platinum(II) (0.2 g) and 1,10-phenanthroline (0.4 g) in ether (50 ml) at room temperature. Bright red crystals of the product slowly formed.

After 2 weeks these were filtered off, washed thoroughly with ether and dried under vacuum. Yield 70%.

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