Solvent Effects on the Electronic Spectra of Some 2,2′-Bipyridyl Palladium(II) and Platinum(II) Complexes

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Solvent effects on the electronic spectra of the complexes $[Pt(bipy)X_2]$ (bipy = 2,2′-bipyridyl; X = Cl, Br, or I), $[Pd(bipy)Cl_2]$, and $[Pt(bipy)(py)_2]^{2+}$ (py = pyridine) are reported and correlated with the E_{T} parameters of the solvents. The assignments of the electronic spectra are discussed.

ALTHOUGH the electronic spectra of metal complexes are generally assumed to be relatively independent of the solvent,[1] it has recently been shown that the positions of the metal ⟶ ligand charge-transfer (MLCT) bands in the complexes $[M(bipy)(CO)_4]$ (M = Mo or W),[2] $[Ru(bipy)_2Y_2]$ (Y = CN or ½ox),[3] $[FeL_2(CN)_2]$, $[FeL(CN)_4]^{2-}$ (L = 2,2′-bipyridyl or 1,10-phenanthroline),[1,4,5] $[FeL'_2(CN)_2]$ (L′ = Schiff base), and $[FeL_2(CN)_2]^+$,[6] are strongly solvent dependent and can be correlated with E_{T} values[7] for the solvents. We now report a similar variation in the electronic spectra of some palladium(II) and platinum(II) 2,2′-bipyridyl complexes. Although the spectra of a number of square-planar complexes are appreciably affected by the solvent,[8,9] the effects described in the present work are of much larger magnitude.

EXPERIMENTAL

Dihalogeno-complexes of platinum(II) were prepared by methods of Morgan and Burstall,[10] $[Pd(bipy)Cl_2]$ by the method of Livingstone,[11] and the preparation of $[Pt(bipy)(py)_2](ClO_4)_2$ will be described elsewhere.[12] Spectra were recorded on a Unicam SP 800B spectrophotometer, the wavelength scale of which was calibrated against a standard holmium glass filter.

RESULTS

The electronic spectra of the complexes $[Pt(bipy)X_2]$ (X = Cl, Br, or I) were strongly effected by the solvent (Tables 1 and 2 and Figure 1). In the case of the dichloro-complex, the band which appears as a shoulder at *ca.* 29 kK in aqueous solution (band 1) showed a large shift to lower energy in less polar solvents (Table 1), appearing at 24·3 kK in 1,4-dioxan, the least polar solvent used. The two peaks at *ca.* 32 kK (band 2) underwent shifts (*ca.* 0·7 kK) to lower energy on changing the solvent from water to 1,4-dioxan. Band 3, which we assume to overlap with band 4 in water, appeared at 36·8 kK in methanol and shifted to 35·1 kK in 1,4-dioxan. All spectra showed a peak at *ca.* 40 kK (band 4). Similar effects were observed for the dibromo- and di-iodo-complexes and $[Pd(bipy)Cl_2]$, but in the latter case the shifts were smaller. The electronic spectrum of $[Pt(bipy)(py)_2]^{2+}$ was almost independent of solvent. A graph of E_{T} against $\nu_{\mathrm{max.}}$ for $[Pt(bipy)Cl_2]$ (Figure 2) shows two straight lines, one for hydroxylic and one for non-hydroxylic solvents, similar to those found by Burgess[2,5,6] for the molybdenum, tungsten, and iron complexes men-

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Table 1

Solvent effects on the electronic spectrum of the complex [Pt(bipy)Cl_2]

	Solvent	E_T [a]/ kcal mol^{-1}	$\nu_{max.}$/kK (ε/l mol^{-1} cm^{-1}) Band 1	Band 2		Band 3		Band 4
1	Water	63·1	29·0—29·8sh (2,500)	31·4 (13,000)	32·6 (11,000)			39·8 (18,000)
2	Methanol	55·5	27·0	31·0	32·2	36·8		39·7
3	Methyl cyanide	46·0	26·2	31·1	32·2	36·4		39·8sh
4	Dimethyl sulphoxide	45·0	26·1	30·6	31·8	35·7sh	*b*	
5	Ethanol	51·9	25·9	30·8	32·1	35·8		39·5
6	2-Methoxyethanol	52·3	25·8	30·8	32·0	36·4		39·5sh
7	n-Propanol	50·7	25·6	30·8	32·2	35·7	36·4sh	39·7
8	Dichloromethane	41·1	25·4	31·0	32·1	35·5		39·4
9	Acetone	42·2	25·3	*b*				
10	1,2-Dichloroethane	41·9	25·3	30·8	32·0	35·2		39·2
11	Pyridine [c]	40·2	25·2, 26·5sh, 28·4	*b*				
12	Chloroform	39·1	25·1, 26·3sh (3100)	30·8 (5200)	32·0 (5200)	35·1 (18,000)		39·2 (11,000)
13	Ethyl acetate	36·0	24·6	30·8	31·8sh	35·1	36·4sh	*b*
14	1,4-Dioxan	36·0	24·3	30·7	31·8sh	35·1	36·4sh	
15	Chlorobenzene	37·5	24·2	30·5sh	31·7sh	33·8sh	*b*	

sh = Shoulder

[a] From Ref. 7. [b] Solvent absorbs. [c] Freshly prepared solution.

Table 2

Absorption maxima for band 1 in the complexes [Pt(bipy)Br_2], [Pt(bipy)I_2], [Pd(bipy)Cl_{27}, and $[Pt(bipy)(py)_2]^{2+}$

Solvent	E_T [a]/ kcal mol^{-1}	$\nu_{max.}$/kK [Pt(bipy)Br_2]	[Pt(bipy)I_2]	[Pd(bipy)Cl_2]	$[Pt(bipy)(py)_2]^{2+}$ [b]
Water	63·1	28·6—29·8sh	27·8—30·3sh	31·5sh [c]	30·0sh
Dimethyl sulphoxide	45·0	25·4sh, 26·6sh	26·4		
Methanol	55·5	25·3sh, 27·1	25·6		
Ethanol	51·9	25·3, 27·1sh	25·7		
n-Propanol	50·7	25·2, 27·8sh	25·6		
Chloroform	39·1	24·4, 25·8sh, 27·3sh	23·7—24·8br	29·4sh	29·8sh
1,4-Dioxan	36·0	24·1, 25·4sh, 27·0sh	22·7sh, 25·0	28·8sh	

[a] From ref. 7. [b] Perchlorate salt. [c] NaCl added (*ca.* 2M) to suppress hydrolysis.

tioned previously. Similar graphs were obtained for the dibromo- and di-iodo-complexes of platinum.

DISCUSSION

The electronic spectrum of the complex [Pt(bipy)Cl_2] in chloroform has been reported previously.[13] Band 1 was assigned to MLCT, 2 to spin-allowed $d \longrightarrow d$ transitions, and 3 and 4 to the first and second internal $\pi \longrightarrow \pi^*$ type transitions of the ligand 2,2′-bipyridyl. With the aid of the spectra in a range of solvents, we are able to suggest new assignments for bands 2 and 3.

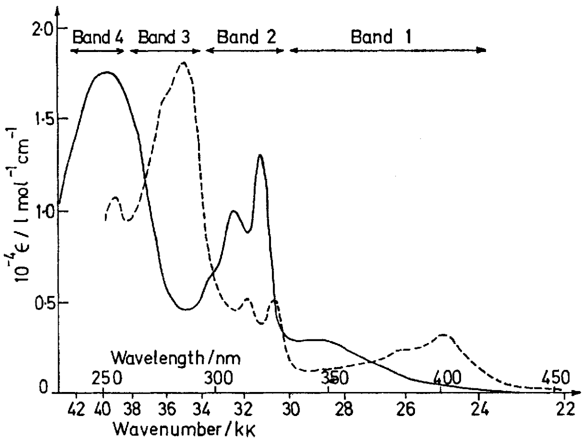

Figure 1 Electronic spectra of the complex [Pt(bipy)Cl_2] in water (——) and chloroform (– – – –)

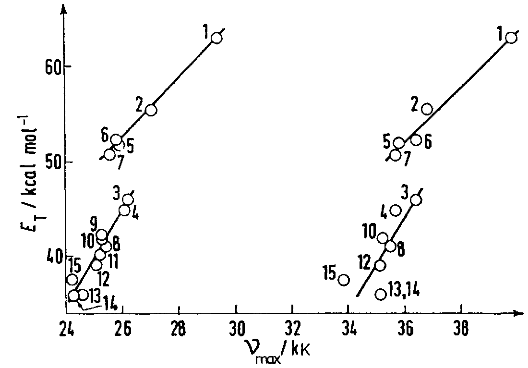

Figure 2 Correlation of $\nu_{max.}$ with E_T for bands 1 and 3 of the spectra of the complex [Pt(bipy)Cl_2] in various solvents: 1, water; 2, methanol; 3, methyl cyanide; 4, dimethyl sulphoxide; 5, ethanol; 6, 2-methoxyethanol; 7, n-propanol; 8, dichloromethane; 9, acetone; 10, 1,2-dichloroethane; 11, pyridine; 12, chloroform; 13, ethyl acetate; 14, 1,4-dioxan; 15, chlorobenzene

The solvent-dependent bands in the molybdenum, tungsten, ruthenium, and iron complexes described previously have been assigned to metal $\longrightarrow$ (aromatic) ligand charge transfer.[2,5,14] This suggests that band 1

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of the [Pt(bipy)Cl$_2$] complex is also due to an MLCT transition (from platinum to a π-antibonding orbital of 2,2′-bipyridyl) in agreement with the previous assignment.[13] The extinction coefficient of this band (*ca.* 3000 l mol^{-1} cm^{-1}) is also consistent with such an assignment and in the spectra of the dibromo- and di-iodo-complexes the band appears at progressively lower energies, in accordance with the order of electronegativities of the halide ions; Cl > Br > I. The spectrum of the complex [Pd(bipy)Cl$_2$] in chloroform (Table 2) shows a shoulder at *ca.* 29·4 kK which shifts to higher energy in aqueous solution (*ca.* 31·3 kK). This solvent-dependent band is again assigned to MLCT. The position of the band is consistent with the relative ease of oxidation of platinum(II) as compared with that of palladium(II). The shift in $\nu_{max.}$ (*ca.* 2·5 kK from water to 1,4-dioxan) for this complex is somewhat smaller than that in the platinum complexes (5·1, 5·1, and 4·1 kK for the dichloro-, dibromo-, and di-iodo-complexes respectively).

The spectrum of the [Pt(bipy)Cl$_2$] complex in water shows the two peaks of band 2 at 31·4 and 32·6 kK (ε 1·3 × 10^4 and 1·1 × 10^4 l mol^{-1} cm^{-1} respectively) and these are identified with the peaks at 30·8 and 32·0 kK (ε 5200 l mol^{-1} cm^{-1}) in chloroform. The position and extinction coefficient of band 2 in water indicate an assignment to the first internal $\pi \longrightarrow \pi^*$ type transition of the ligand 2,2′-bipyridyl ($\nu_{max.}$ 35·5 kK, ε 1·3 × 10^4 l mol^{-1} cm^{-1} for the free ligand in ethanol; the band usually moves to lower energy on complex formation[15]). Although the first $d \longrightarrow d$ spin-allowed band of a *cis*-[PtN$_2$Cl$_2$] chromophore is expected at *ca.* 33 kK,[16] the extinction coefficient should be *ca.* 100 l mol^{-1} cm^{-1} and therefore such a band will be masked by the much more intense ligand band.

Band 3 in the spectrum of the complex [Pt(bipy)Cl$_2$] shows a strong solvent effect in the same sense and, in energy terms, of about the same magnitude as the shift of band 1 (*ca.* 5 kK from water to 1,4-dioxan; in the spectrum in water, band 3 is assumed to have shifted so far to higher energy that it overlaps with band 4). It therefore seems likely that band 3 is also a MLCT band, perhaps from a common orbital on platinum to a higher π-antibonding orbital on the 2,2′-bipyridyl ligand.

Burgess[5] has discussed evidence that the solvent effect operates through non-aromatic ligands (CN, CO, or in the present case the halide ions). It is probable that this is also true in the cases of the palladium(II) and platinum(II) complexes, since the complex [Pt(bipy)(py)$_2$]$^{2+}$ shows only a very slight solvent effect (Table 2). The latter observation also suggests that, for the square-planar dihalogeno-complexes, direct interaction of solvent molecules with the metal atom at the ‘ vacant ’ co-ordination sites is of secondary importance compared with that *via* the halide ligands.

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