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LETTER

Spectroelectrochemical studies of bipyridyl and ring-metallated bipyridyl complexes; evidence for mononuclear Pt(I) derivatives

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We have extended our spectroelectrochemical studies of bipyridyls [1] and related [2] complexes to the species $[Pt(bpy)(py)_2]^{2+}$ (**I**), $[Pt(Mebpy\text{-}H)(py)_2]^{2+}$ (**II**), $[Pt(bpy)(Mebpy\text{-}H)]^{2+}$ (**III**) and $[Pt(bpy)_2]^{2+}$ (**IV**) (Fig. 1). The compounds were prepared by standard methods [3]. Reduction potentials are presented in Table 1.

Like previous workers [4], we find that the first reduction of **IV** is chemically irreversible; hence this complex is unsuitable for study by our technique. However, the two reductions reported for each of **I** and **II**, and the three reductions reported for **III**, are all well-behaved electrochemically and chemically reversible one-electron processes over the time-scale of the cyclic voltammetry experiment (several seconds). More importantly for our present purpose, they are fully chemically reversible over the time-scale of our spectroelectrochemical experiments, giving products which are stable in solution for many minutes, and perhaps indefinitely, and from which the starting materials can be regenerated without loss by controlled potential reoxidation. For these complexes, the first reduction is around 0.5 V less cathodic than expected by analogy with $[Ru(bpy)_3]^{2+}$ [5] for bpy or for quaternised (Mebpy-H) (which is isoelectronic with bpy) in a 2+ complex.

TABLE 1. Reduction potentials of Pt(II) complexes in DMF[a]

	$E_{red}^{(2+/+)}$	$E_{red}^{(+/0)}$	$E_{red}^{(0/-1)}$
I	−1.266 (63)[b]	−1.956 (74)	
II	−1.411 (63)	−1.775 (73)	
III	−1.347 (74)	−1.577 (62)	−1.953 (71)
IV	−1.259 (irr)[c]	−1.747 (66)[d]	−1.923 (72)[d]

[a]Data by cyclic voltammetry (20–200 mV s^{-1}, PAR 173/175; *IR* compensation), V vs. ferrocene/ferrocenium$^+$ in stated solvent at 25 °C. Measurements taken vs. Ag/0.01 M $AgNO_3$–0.09 M n-tetrabutylammonium tetrafluoroborate ($TBABF_4$) in stated solvent, but referred to ferrocene/ferrocenium$^+$/0.1 M $TBABF_4$ in solvent/cell combination as used. [b]E_{pa}–E_{pc} (mV) in parentheses. [c]Denotes irreversible redox process with peak potential given (scan rate 200 mV s^{-1}). [d]Reversible and reproducible; but chemical assignment uncertain at this stage.

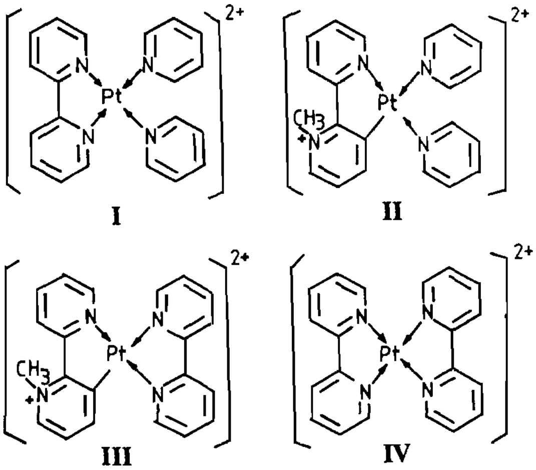

Fig. 1. Structures of **I–IV**.

The parent complexes all show MLCT transitions at approximately 320 nm. These bands disappear on addition of one electron (Table 2). However, the characteristic [2, 6] $\pi(6)\rightarrow\pi(7)$, $\pi(7)\rightarrow\pi(10)$ and $\pi(7)\rightarrow\pi(8,9)$ bands of coordinated bpy^- do not appear at this stage, but only after addition of a second electron (see for example Fig. 2) (the absorption around 10 000 cm^{-1} shown by the singly reduced species is considerably weaker than $\pi(7)\rightarrow\pi(8,9)$ and lacks the characteristic width and vibrational structure).

We infer on both electrochemical and spectroelectrochemical evidence that in complexes **I**, **II** and **III** the first reduction is metal-based, giving what appears to be the first known family of monomeric solution-stable Pt(I) complexes. (We can rule out dimer formation because the process studied by cyclic voltammetry over a wide range of scan rates (down to 20 mV s^{-1}) involves the transfer of only one electron.) The first reduction potentials then show that the (Mebpy-H) ligand is, as expected, a better

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TABLE 2. Main absorption bands: ν (10^3 cm^{-1}); ($10^{-3}\times\epsilon$ (M^{-1} cm^{-1}))

(a) Parent complexes in acetonitrile

	MLCT [d→π(8,9)]	π(6)→π^*(7)	MLCT [d→π(7)]
I	40.8 (18.5)	32.7 (19.0)	29.2 (5.5)
II	38.5 (17.8)	32.4 (11.2)	26.4 (5.7)
III	40.6 (18.2), 38.3 (17.8)	33.9 (15.2), 32.1 (15.0)	28.0 (6.2), 26.2 (5.3)

(b) Complexes [PtLL′]$^+$ in DMF

	π(6)→π^*(7)	MLCT [d→π(8,9)]	MLCT [d→py]	MLCT [d→π(7)]	d→d
I$^-$	35.2 (14.5)	28.7 (7.8)	25.0 (7.2)	20.3 (5.2)	9.1 (2.2)
II$^-$	33.6 (17.3)	28.1 (10.7)	24.0 (8.0)	17.4 (5.1)	10.2 (2.3)
III$^-$	34.5 (16.8)	28.0 (10.3)br		19.8 (5.5)br	10.0 (2.3)br

(c) Doubly and triply reduced complexes in DMF

	π(6)→π^*(7)	MLCT (d→py)	MLCT [d→π^*(7)]	π^*(7)→π^*(10)	π^*(7)→π^*(8,9)
I^{2-}	28.5 (12.2)	24.7 (7.5)		19.8 (5.7)	11.1 (3.2)
II^{2-}	26.9 (18.0)	24.0 (8.3)		18.9 (5.5)	10.1 (3.5)
III^{2-}	26.5 (12.5)		23.3 (6.8)	19.4 (7.0)	9.8 (3.0)
III^{3-}	27.1 (15.5)			19.2 (7.3)	10.0 (3.2)

br = very broad.

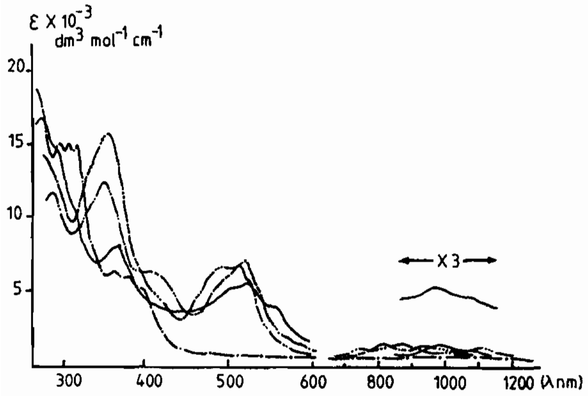

Fig. 2. Absorption spectra of [Pt(bpy)(Mebpy-H)]$^{2+/+/0/-}$ in DMF at 25 °C (V vs. ferrocene/ferrocenium$^+$): – · – · –, parent; ——, single reduced species at -1.365 V; – · · – · · –, doubly reduced species at -1.605 V; – · · · – · · · –, triply reduced species at -1.985 V.

σ-donor than bpy, with the metal-based reduction of **II** being 145 mV more cathodic than that of **I**, while the ligand-based reduction is 180 mV less cathodic. In good agreement with these results, the MLCT band of **II** is at 2800 cm^{-1} lower energy than that in **I**, while **III** shows two separate charge transfers, to bpy and (Mebpy-H), respectively, separated by 1800 cm^{-1}. Thus (Mebpy-H) would appear to be a better π-acceptor than bpy, as well as a better σ-donor, and we would expect it to be a ligand of considerable future interest for its robustness and strong expected ligand-field splitting. The spectra of the singly reduced species can be understood [1] as in Table 2(a), in terms of Pt(I)–(bpy) and Pt(I)–(py) charge transfer bands. The 1000 nm band is provisionally assigned to a d–d transition. The frequency seems rather low, but it should be remembered that the metal is in the +1 oxidation state, and it is possible that there is a distortion away from square planar coordination. It is too weak for assignment to a reduced ligand π^*–π^* transition, and indeed on our interpretation of the electrochemical data, no such ligand is present. The reduced ligand π^*–π^* transitions do, however, occur as expected in the doubly and (for **III**) triply reduced species, for which the reduction potentials are, moreover, as expected for ligand-based reductions in species of the relevant overall charge.

We can now explain the apparently surprising electrochemistry [7] of [Ir(bpy)$_2$(bpy-H)]$^{2+}$ (**V**) (bpy-H, C(3),N′-2,2′-bipyridinyl). Here the bpy ligands show the two expected 1-electron reductions, but the (bpy-H) resists reduction up to potentials at least 0.7 V more negative. This, we can now see, is because (bpy-H), unlike its N-methylated derivative, is not strictly isoelectronic with bpy, but carries an extra formal negative charge. Thus we predict that N-methylation of **V** would give a species showing similar reduction potentials for all three ligands.

Acknowledgements

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