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Electrochemistry and Spectroelectrochemistry (EPR, UV–Vis–Near-IR) of Platinum(II) 2,2′-Bipyridine and Ring-Metalated Bipyridine Complexes: $Pt^{II}(L^-)$ and $Pt^{I}(L^-)$ but Not $Pt^{I}(L)$

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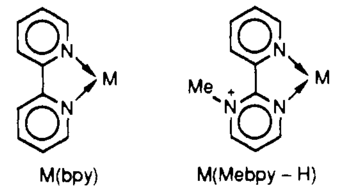
The Pt(II) complexes $[Pt(bpy)(py)_2]^{2+}$ (I), $[Pt(bpy)(Me_2N\text{-}py)_2]^{2+}$ (II), $[Pt(Me_2\text{-}bpy)(py)_2]^{2+}$ (III), $[Pt(bpy)(en)]^{2+}$ (IV), $[Pt(Mebpy-H)(py)_2]^{2+}$ (V), $[Pt(Mebpy-H)(bpy)]^{2+}$ (VI), $[Pt(phen)(py)_2]^{2+}$ (VII), and $[Pt(py)_4]^{2+}$ (VIII) (bpy, 2,2′-bipyridine; py, pyridine; Mebpy − H, *N*-methyl-2,2′-bipyridinyl-*C(3)*,*N′*; Me_2-bpy, 4,4′-dimethyl-2,2′-bipyridine; Me_2N-py, 4-(dimethylamino)pyridine; en, 1,2-diaminoethane; phen, 1,10-phenanthroline) have been investigated by cyclic voltammetry and where possible by EPR spectroelectrochemistry and by UV–vis–near-IR spectroelectrochemistry. All complexes except VIII show at least two reversible reductive one-electron processes; VI shows three, and VIII shows one chemically irreversible process. In all cases, the doubly reduced species showed the characteristic $\pi^* \rightarrow \pi^*$ UV–vis–near-IR absorptions of the ligand anion radicals. For the singly reduced species, EPR spectra show the added electron to be localized on the bipyridine-type ligand. However, the UV–vis–near-IR spectra of these species are not typical of ligand-based reduction products, and the potentials are less negative than expected for such a process. We conclude that the singly reduced species are best formulated as containing Pt(II), with the semioccupied and/or the lowest unoccupied ligand orbitals (corresponding to the LUMO and SLUMO of the unreduced parent species) being perturbed by the presence of metal orbitals. The doubly reduced species, however, are straightforward anion radical complexes of Pt(I).

Introduction

Bidentate aza-aromatic ligands readily form stable complexes with Pt(II) and have long been extensively used in preparative coordination and organometallic chemistry.[1–3] Our earlier investigations[4] of reduced diorganoplatinum Pt(II) complexes with α-diimine ligands, such as $[Pt^{II}(bpy)(Ph)_2]^-$, $[Pt^{II}(bpym)(Ph)_2]^-$ (Ph, phenyl; bpym, 2,2′-bipyrimidine), and $[Pt(bpz)(Ph)_2]^-$(bpz, 2,2′-bipyrazine), show typical ligand-based reductions giving products which are formulated as $[Pt^{II}(diimine)(Ph)_2]^-$. 2,2′-Bipyridine (bpy) can be converted into a potentially monodentate ligand by quaternizing one of nitrogens; the resulting cation is isoelectronic with 2-phenylpyridine[5] and can undergo a similar ortho-metalation at the C(3) position of the ring carrying the quaternized nitrogen to generate the bidentate zwitterionic ligand (Mebpy − H), isoelectronic with bpy[6] (Chart I). In this report we describe the electrochemistry, EPR spectroelectrochemistry, and vis–UV–near-IR spectroelectrochemistry of a range of Pt(II) phen, bpy, and (Mebpy − H) complexes.

Chart I



M(bpy) M(Mebpy − H)

Experimental Section

Materials. The complexes were prepared as described previously.[2a,6a,7] The tetrafluoroborates were used for electro-EPR; all other measurements were carried out on the perchlorates. "Spectrol" grade dimethylforma-

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Table I. Reduction Potentials (V) of Pt(II) Complexes in DMF[a]

complex	$E(1)^{2+/+}$	$E(2)^{+/0}$	$E(3)^{0/1}$
I	–1.381 (0.063)[b]	–2.071 (0.074)	
II	–1.405 (0.064)	–2.121 (irr)[c]	
	–1.415[d] (0.067)	–2.106[d] (0.085)	
III	–1.526 (0.063)	–1.890 (0.073)	
IV	–1.390 (0.064)	–2.082 (0.072)	
V	–1.580 (0.064)	–2.120 (0.075)	
VI	–1.462 (0.064)	–1.692 (0.062)	–2.068 (0.071)
VII	–1.405 (0.063)	–2.105 (0.075)	
X	–1.401 (irr)[c]		

[a] Data from cyclic voltammetry at 200 mV s^{-1}; measurements taken in V vs Ag/0.01 M $AgNO_3$/0.09 M $(TBA)BF_4$ in stated solvent, but referred to ferrocene/ferrocenium/0.1 M $(TBA)BF_4$ in solvent/cell combination used. [b] $E_{pa} - E_{pc}$ (V). [c] Denotes (chemically) irreversible redox processes with peak potentials given (scan rate 200 mV s^{-1}). [d] At –40 °C.

Table II. Main Absorption Bands of Pt(II) Complexes in Acetonitrile at 25 °C [λ/nm ($\nu/10^3$ cm^{-1}) ($\epsilon/10^3$ M^{-1} cm^{-1})]

complex	MLCT	$\pi \rightarrow \pi^*$	MLCT
I	245 (40.8) (10.4)	306 (32.7) (18.5)	343 (29.2) (5.5)^{sh}
II	250 (40.0) (9.2)	314 (31.8) (17.8)	352 (28.4) (5.2)^{sh}
III	248 (40.3) (9.8)	309 (32.4) (18.0)	345 (29.0) (5.4)^{sh}
IV	248 (40.3) (9.0)	321 (31.2) (18.4)	357 (28.0) (5.8)^{sh}
V	260 (38.5) (9.4)	315 (31.7) (18.2)	379 (26.4) (7.2)
VI	246 (40.7) (8.9)[a]	295 (33.9) (17.5)[b]	357 (28.0) (7.1)[a]
	261 (38.3) (8.6)[c]	318 (31.4) (17.2)[d]	360 (27.8) (6.8)[c]
VII		280 (35.7) (17.2)	357 (28.0) (5.2)
VIII	no strong absorption for $\lambda > 250$ nm		

[a] Pt(II) → bpy. sh = shoulder. [b] $\pi(6) \rightarrow \pi(7)$ of bpy. [c] Pt(II) → (Mebpy – H). [d] $\pi(6) \rightarrow \pi(7)$ of (Mebpy – H).

mide (DMF) as purchased from BDH was stored over molecular sieves. Tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$) was prepared from the aqueous acid and hydroxide, recrystallized twice from ethyl acetate/pentane, washed repeatedly with water, and vacuum dried.

Instrumentation. Cyclic voltammetry was performed under argon in a Metrohm cell equipped with the cross section of a 0.1-mm diameter platinum wire as a working electrode and a 5-mm length of similar platinum wire as counter electrode, using a Princeton Applied Research (PAR) Model 173 potentiostat and 175 signal generator with provision for *IR* compensation, results being recorded on a JJ X-Y recorder, Model 151 (the same potentiostat was then used for controlled-potential electrolysis in the spectroelectrochemistry experiments). The reference electrode was Ag/0.01 M $AgNO_3$–0.09 M $TBABF_4$ connected through a porous Vycor frit to a solution of 0.1 M $TBABF_4$, but potentials are referred to the ferrocene/ferrocenium potential obtained under identical conditions. Solutions were 0.005 M for cyclic voltammetry and 0.001 M for spectroelectrochemistry. A 0.1 M $TBABF_4$ solution was used as the supporting electrolyte. For both types of studies, scan rates were varied from 20 to 2000 mV s^{-1}, causing apparent peak positions to vary by at most 10 mV; effects on mean peak positions were negligible. Controlled-potential reduction for spectroelectrochemistry was carried out in a special 1-mm-path quartz cell with a platinum gauze working electrode, as described previously.[8] Spectra were collected on a Perkin-Elmer Lambda 9 spectrophotometer. EPR spectra were recorded in the X-band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter for *g* factor determination. Singly reduced species were generated for EPR measurements in DMF/0.1 M Bu_4NClO_4 by using a Pt electrode in a previously described cell.[9] The potential at the working electrode in this cell was made more negative in steps of 0.1 V until an EPR signal appeared. Electrolysis was then performed at this onset potential until a sufficient concentration of radicals had developed.

Results and Discussion

Electrochemistry. Uncoordinated bpy undergoes a reversible one-electron reduction at around –2.57 V vs ferrocene/ferrocenium,[8] but no oxidation processes are observed at potentials up to +1.30 V. Related neutral Pt(II) phenyl complexes exhibit at least one metal-based oxidation step,[4c,10] but for these isoelectronic but charged pyridine complexes no oxidation was observed up to +1.30 V vs ferrocene/ferrocenium in DMF. The reduction potentials of the complexes are given in Table I.

III, IV, V, and VII and at reduced temperature II show two reversible reduction waves, of which the first is somewhat less negative than expected by comparison[11] with other dicationic M(II) complexes. The differences between first and second reduction potentials of about 0.7 V are typical for aromatic α-diimines,[8,12] but the electronic spectra of the doubly reduced species (below) show that one and only one reduction is ligand-based. The reduction potentials of I and VII are very similar, as in other M(II) phen and bpy complexes.[13] VI shows three such waves, and the separation between the first and second of these is typical for the reduction of very similar ligands on the same metal. The first reduction of VIII is completely irreversible under the same conditions.

Absorption Spectra of Parent Pt(II) Complexes. The absorption spectra of the parent Pt(II) complexes in DMF in the region between 200 and 1000 nm contain three main absorptions (Table II). The lowest energy absorption, seen as a shoulder at 343 nm in I, is associated[14,15] with the first metal to ligand charge-transfer transition from a platinum d-orbital to the $\pi^*[\pi(7)\mathrm{LUMO}]$ orbital of the 2,2′-bipyridine ligand. In V, this transition is clearly resolved, lying some 2700 cm^{-1} lower in energy than in I, as expected since C of (Mebpy – H) should be a better σ-donor than N of bpy. In VI, it appears that two MLCT bands are present in this region, as expected.

The highest energy absorption, at approximately 250 nm in each complex except VII and VIII, is assigned to the second intense metal to ligand charge-transfer transition, $d\pi[\mathrm{Pt(II)}] \rightarrow \pi^*[\mathrm{SLUMO};\pi(8)]$. The value of $\nu_{2nd} - \nu_{1st} = 9000$ cm^{-1} found for these complexes is in excellent agreement with the LUMO/SLUMO gap in the bpy system.[16] The most intense bands appearing in the region between 305 and 325 nm of each of the complexes are assigned to the $\pi(6) \rightarrow \pi(7)$ transitions of coordinated bpy, Me_2-bpy and (Mebpy – H).

EPR Spectra of Singly Reduced Species. Complexes I, V, and VI were reduced electrochemically at Pt intra muros, i.e. in an EPR-spectroelectrochemical cell.[9] All three complexes gave intense, fairly narrow (peak-to-peak width ΔH_{pp} ca. 1.5 mT) but incompletely resolved EPR lines in DMF at room temperature (Figures 1a and 2a). While $V^{\bullet-}$ and $VI^{\bullet-}$ exhibit single lines with some structure due to ligand hyperfine splitting (Figure 2a), the reduction of I produces detectable "satellite" lines (Figure 1a) from platinum isotope coupling (^{195}Pt, $I = {}^1/_2$, 33% natural abundance; Table III). In the case of the paramagnetic species containing (Mebpy – H), the platinum hyperfine coupling was too small (<2.5 mT) to produce such separate features. The generally small metal hyperfine splitting as compared to A_{iso} =

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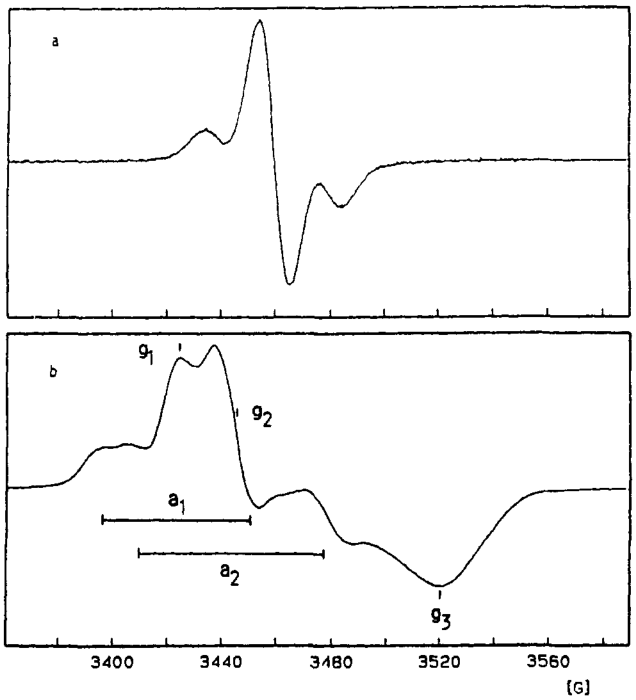

Figure 1. EPR spectra obtained by intra muros electrolysis of I in DMF/0.1 M Bu_4NClO_4 at 290 K (a) and in the frozen state at 150 K (b).

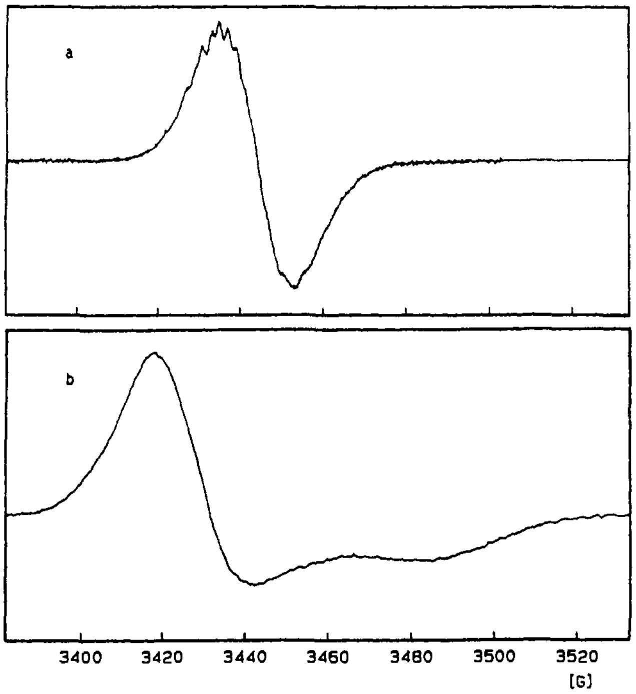

Figure 2. EPR spectra obtained by intra muros electrolysis of V in DMF/0.1 M Bu_4NClO_4 at 290 K (a) and in the frozen state at 150 K (b).

370.9 mT for ^{195}Pt[17] and the mere presence of relatively narrow EPR signals at 295 K suggest that the reduced forms are complexes of anion radicals[18] with essentially diamagnetic Pt(II).[4a,c] On the other hand, the relatively low isotropic g values, especially for I^-, indicate a nonnegligible contribution from the metal to the singly occupied molecular orbital (SOMO). The approximation (1)[4a,c,18] for $\Delta g = g - g(\text{electron}) = g - 2.0023$ shows that the magnitude of this deviation depends on the spin–orbit coupling factor while the sign is determined by the proximity of intermixing occupied ($g > g(\text{electron})$) or unoccupied ($g < g(\text{electron})$) orbitals. Pt(II) complexes of unsaturated nitrogen ligands are distinguished by the presence of several close-lying unoccupied MOs which may even involve 6p orbitals of the metal.[19] Augmented by the very large spin–orbit coupling constant ζ of about 5000 cm^{-1} for that heavy-metal center,[18] the result is $g < 2$ even for predominantly ligand-based Pt radicals:

$$\Delta g = g - g(\text{electron}) = g - 2.0023 = k\zeta(1/\Delta E_1 - 1/\Delta E_2) \qquad (1)$$

Here ΔE_1 and ΔE_2 are the energy differences between the SOMO and the HOMO and LUMO, respectively.

Table III. EPR Data of Singly Reduced Platinum(II) Complexes[a]

radical	$a(^{195}\text{Pt})$	$\langle g \rangle$ (295 K)	g_1, g_2, g_3 (150 K)	$10^{-4}\Delta g$
$I^{\bullet -}$	3.7	1.9867	2.0084, 1.9964, 1.9540[b]	544
$V^{\bullet -}$	<2.5	1.9957[c]	2.0085,[d] 2.0039, 1.9747	338
$VI^{\bullet -}$	<2.5	1.9979[c]	no anisotropy observable	<300
$[(\text{bpym})\text{PtPh}_2]^{\bullet -}$	<3.0	1.9945[e]	2.0219, 2.0043, 1.9532	687
$[(\text{bpy})\text{PtCl}_2]^{\bullet -}$	6.0	1.98	not reported[9]	
$[(\text{bpy})\text{Pt}(\text{CH}_2)_3]^{\bullet -}$	n.o.	1.98	not reported[9]	

[a] Coupling constants a in mT. [b] ^{195}Pt isotope coupling: $a_1 = 4.7$ mT, $a_2 = 6.9$ mT, $a_3 < 1$ mT. [c] Slightly structured spectrum (ligand hfs). [d] Component calculated via the isotropic g factor. [e] Interpretable hyperfine structure.[4a]

Information on the possibility of even small contributions from a Pt(I) formulation can be obtained from EPR spectra taken in frozen solution (Figures 1b and 2b); a square planar d^9 system such as Pt(I) should have $g_\parallel > g_\perp > 2.0023$.[17] The large spin-orbit coupling constant of platinum is responsible for a substantial divergence of g components; however, in all instances including the radical anions of (α-diimine)diorganoplatinum complexes[4a,c] the general sequence is $g_1 > g_2 \sim 2.00 \gg g_3$ (Table III). The rhombic symmetry and the position of the most separated g component at $g_3 \ll 2.00$ (Figures 1b and 2b) stand in contrast to what would be expected for a d^9 system.[17] A similar difference concerns the metal isotope coupling associated with the individual g components. In contrast to the anisotropic EPR spectra reported previously,[4a] the spectrum of a frozen DMF solution of I^- (Figure 1b) permits the determination of sizable values for $a_1(^{195}\text{Pt})$ and $a_2(^{195}\text{Pt})$ (Table II). The most separate component g_3 at 1.9540 shows no detectable platinum hyperfine splitting; in agreement with that observation, the calculation of $a_3 = 3a_{\text{iso}} - (a_1 + a_2)$ yields a value of -0.5 mT. A square planar d^9 system requires a *large* metal hyperfine splitting $a_\parallel$ for the separate *high-g* component.[17]

Table III contains the data for a clear example, $[(\text{bpym})\text{PtPh}_2]^-$, of a Pt(II) radical complex with appropriate ligand hyperfine structure (bpym = 2,2′-bipyrimidine);[4a] also included are some reduced organoplatinum species of the kind loosely described as "Pt(I)" by Kochi and co-workers.[10] In all these cases, the participation of the metal in the SOMO is at most a few percent, as shown by comparison of the observed small $a(^{195}\text{Pt})$ values with $A_{\text{iso}}(^{195}\text{Pt}) = 370.9$ mT.[17]

Although there are some differences related to the small but to some extent varying contributions form the metal to the SOMO, *all* these paramagnetic species contain essentially Pt(II) coordinated to anion radicals of α-diimines. Indicators are the magnitude of the Pt hyperfine coupling, the resolution of the line due to ligand hyperfine splitting, and the g anisotropy $\Delta g = g_1 - g_3$. Not surprisingly, the largest such contribution seems to exist for the complex with the electron-poor dichloroplatinum fragment. Increasing donation from coordinated bases such as py or bpy or from covalently bonded organic groups causes the Pt isotope coupling and g anisotropy to diminish. An almost vanishing metal contribution is found for VI^-, which does not even exhibit g anisotropy in frozen solution and which has a $\langle g \rangle$

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Table IV. Main Absorption Bands of Singly Reduced Pt(II) Complexes in DMF–$(TBA)BF_4$ at 25 °C [λ/nm ($\nu/10^3$ cm^{-1}) ($\epsilon/10^3$ M^{-1} cm^{-1})]

complex	$\pi(6) \rightarrow \pi(7)$ (L^-)	LMCT	$\pi(7) \rightarrow \pi(10)$ (L^-)	$\pi(7) \rightarrow \pi(8,9)$ (L^-)
I^-	348 (28.7) (8.4)	400 (25.0) (7.2)	492 (20.3) (6.8)	1090 (9.2) (3.3)
II^-	344 (29.1) (9.9)	404 (24.8) (5.6)	492 (20.3) (7.1)	1030 (9.7) (3.3)
III^-	345 (29.0) (9.1)	395 (25.3) (7.0)	485 (20.6) (7.2)	1070 (9.3) (3.3)
IV^-	347 (28.8) (10.8)	407 (24.6) (7.0)	485 (20.6) (6.5)	980 (10.2) (3.3)
V^-	356 (28.1) (10.5)	416 (24.0) (7.3)	575 (17.4) (7.0)	980 (10.2) (3.1)
VI^-	357 (28.0) (9.7)	420 (23.8) (5.4)^{br}	535 (19.8) (7.0)	1000 (10.0) (3.0)
VII^-	380 (26.3) (9.0)^a	417 (24.0) (6.4)	560 (17.9) (7.3)^b	990 (10.1) (3.7)^b

[a] $\pi(7) \rightarrow \pi^*(8,9)$ of phen$^-$. br = broad. [b] $\pi(8,9)$ to higher π^* orbitals [$\pi(10)$ through $\pi(14)$] of phen$^-$.

Table V. Main Absorption Bands of Doubly and Triply Reduced Pt(II) Complexes in DMF–$(TBA)BF_4$ at 25 °C [λ/nm ($\nu/10^3$ cm^{-1}) ($\epsilon/10^3$ M^{-1} cm^{-1})]

complex	$\pi(6) \rightarrow \pi(7)$ of L^-	Pt(I) → py CT	$\pi(7) \rightarrow \pi(10)$ of L^-	$\pi(7) \rightarrow \pi(8,9)$ of L^-
I^{2-}	351 (28.5) (12.4)	405 (24.7) (7.3)	481 (20.8) (7.2)	900 (11.1) (3.4)
III^{2-}	349 (28.7) (12.2)	401 (24.9) (7.2)	475 (21.1) (7.4)	890 (11.2) (3.3)
IV^{2-}	350 (28.6) (12.1)		480 (20.8) (7.0)	890 (11.2) (3.2)
V^{2-}	372 (26.9) (14.3)	407 (24.5) (7.5)	514 (19.4) (7.8)	990 (10.1) (3.5)
VI^{2-}	377 (26.5) (13.5)		516 (19.4) (9.0)	1020 (9.8) (3.3)
VI^{3-}	369 (27.1) (24.0)		520 (19.2) (9.3)	1000 (10.0) (3.5)

very close to 2. The reason could be a certain delocalization of spin over the (Mebpy – H) *and* the bpy ligands in an essentially coplanar situation; such a competition would reduce the possible contribution from the metal center. In general, the smaller ^{195}Pt coupling constants in V^- and VI^- relative to I^- suggest that it is the more easily reduced, zwitterionic ligand which accommodates the unpaired electron in both radical complexes containing (Mebpy – H).

Absorption Spectra of Reduced Species. The band energies and assignments of the reduced Pt(II) complexes are summarized in Tables IV and V, and representative results are shown in Figure 3.

The electronic absorption spectra of the doubly and triply reduced species are easiest to understand and will be discussed first. The electronic absorption spectra of the doubly reduced species derived from I–V and of the doubly and triply reduced species derived from VI clearly show the $\pi(7) \rightarrow \pi(8,9)$ band around 10 000 cm^{-1} characteristic of bpy$^-$ and related species[8,13,16] and their complexes.[20] No such band is present in species related to bpy^{2-}, for which the lowest energy characteristic band [$\pi(7) \rightarrow \pi(10)$] occurs around 25 000 cm^{-1}.[8,16,21a] Thus, the second added electron is located on the metal. In IV, no other assignment is possible, while in I, III, V, and VII location on py can be ruled out on grounds of energy. But according to our electrochemical results, the second reduction of these species is a reversible one-electron process in all cases. We conclude that the doubly reduced species are, at least over the time scale of our spectroelectrochemical experiments, ranging up to 30 min, solution-stable monomeric complexes of Pt(I) with anion radical diimine ligands. The other bands [$\pi(7) \rightarrow \pi(10)$, $\pi(6) \rightarrow \pi(7)$] expected for the reduced ligand are found in more or less their expected positions, although $\pi(6) \rightarrow \pi(7)$ is lowered remarkably little on reduction relative to the neutral ligand. The remaining band at around 25 000 cm^{-1} is also present in the singly reduced species and is discussed further below.

Singly reduced I, II, and IV also show the expected intraligand $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$ transitions of coordinated bpy$^-$, but there are shifts in the appearance of the spectrum relative to more characteristic anion radical spectra, the band around 10 000 cm^{-1} is weaker and narrower than usual, and the high values of the $\pi(6) \rightarrow \pi(7)$ frequency and the unexpected band at ca. 25 000

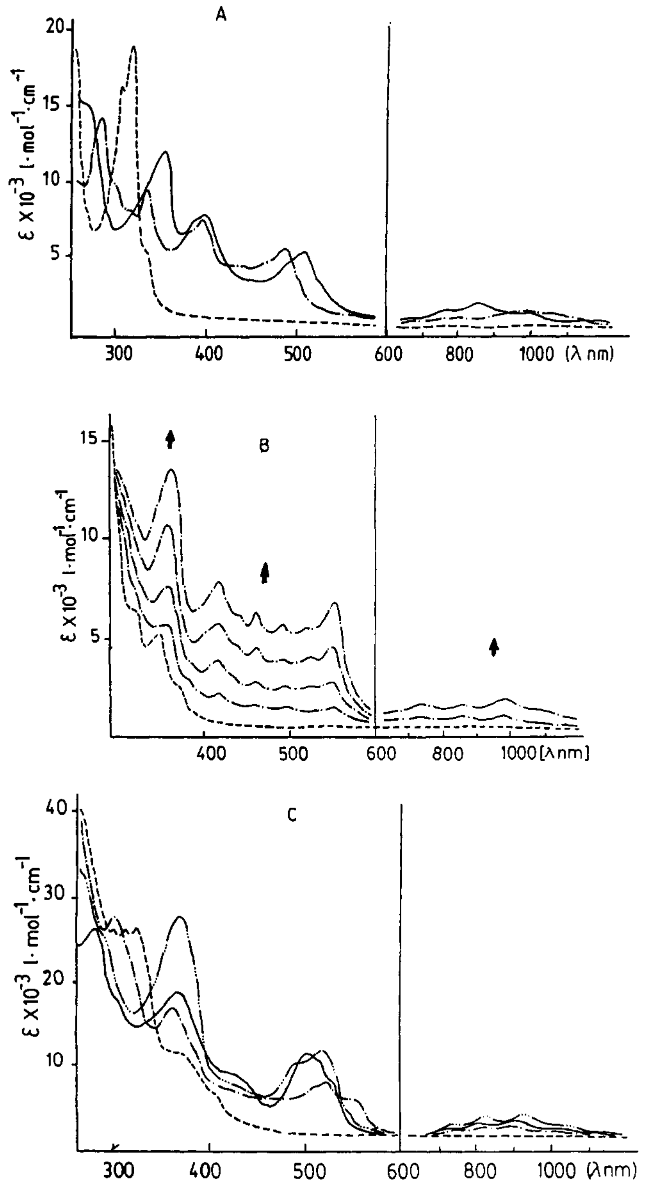

Figure 3. Absorption spectra of (A) $[Pt(bpy)(py)_2]^{2+/+/0}$ at -1.481 and -2.171 V, (b) $[Pt(phen)(py)]^{2+/+}$ at -1.505 V, and (c) $[Pt(bpy)(Mebpy - H)]^{2+/+/0/-}$ at -1.462, -1.792, and -2.168 V in DMF–$TBABF_4$ solution (V vs ferrocene/ferrocenium). Key: - - -, parent; – · –, singly reduced species; —, doubly reduced species; – ··· –, triply reduced species.

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cm^{-1}, already noted for the doubly reduced species, are present here also. For these reasons, some of us[21b] originally located the first reduction on the metal, a conclusion that we now withdraw in the face of the compelling EPR evidence. It would appear that some of the near-LUMO orbitals [in particular, perhaps, one of $\pi(8,9)$] are perturbed by closeness to orbitals on the metal. It would also appear by analogy with this and our earlier work[4] that the formal Pt(I) species described by Kochi's group[10a] were also in fact bpy^- complexes of Pt(II). The nature of the bands around 400 nm in both singly and doubly reduced species remains unclear.

Similar arguments apply to the spectra of III^- and V^-. In singly reduced VI^-, the EPR results (above) show that the first reduction is based on (Mebpy – H) rather than bpy, in accord with the lower MLCT energy in V compared with I, although the electrochemical data for these species would have suggested otherwise.

The assignments of the spectrum of VII^- are more complicated than those of I^-, because the phen system is characterized by two low-lying unoccupied molecular orbitals [$\pi(8)$ and $\pi(9)$] of comparable energies.[22] The band at 380 nm is associated with the intraligand HOMO [$\pi(7)$] → LUMOs [$\pi(8,9)$] $\pi \rightarrow \pi^*$ transitions of the coordinated $phen^-$. Transitions between the LUMOs and higher orbitals [presumably $\pi(10)$ through $\pi(14)$] are observed in the near-IR and vis regions. The bands that we assigned to coordinated $phen^-$ in this complex, as in $phen^-$ complexes of Fe(II) and Ru(II),[13] agree well those reported by Shida[23] in his important compilation of radical ion spectra, for free $phen^-$ in MTHF. Further studies are required for precise assignment of these bands, but the energies and ordering of LUMO orbitals in phen are not much affected by complexation.

Conclusions

The first reduction of I, V, and VI is ligand-based, as shown by the EPR spectra, and we assume that this is so for the other complexes discussed here. The electronic spectra of the singly reduced species are considerably distorted from those of other $diimine^{\bullet-}$ derivatives. We attribute this to interaction between LUMO or near-LUMO levels on the ligand and orbital(s) (probably $6p_z$ in particular) on the metal and retract our previous assignment of these species as Pt(I) derivatives of neutral ligands. The second reduction, however, does indeed appear to give rise to monomeric Pt(I) complexes of $diimine^{\bullet-}$.

We note that with UV–vis–near-IR spectroelectrochemistry, as with other spectroscopic methods, positive evidence is persuasive but negative evidence can be misleading. In particular, we can only expect to recognize characteristic features if *both* orbitals involved in the relevant transition are essentially unperturbed. Coordinatively unsaturated systems, such as square planar Pt(II) are thus particularly likely to present problems of interpretation.

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