

Electro- and spectroelectrochemistry of platinum(II) bipyridine complexes and related species

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Abstract

The cyclic voltammetry of 2,4'-bipyridine (I), *N*'-methyl-2,4'-bipyridinium (II), and 4,4'-diphenyl-2,2'-bipyridine (III), together with the platinum(II) complexes Pt(bipy)Cl₂ (IV), [Pt(bipy)(4-NCpy)Cl]⁺ (V), Pt(Ph₂-bipy)Cl₂ (VI), Pt(Me₂-bipy)Cl₂ (VII), Pt(2,4'-bipyOct-i⁺)Cl₂ (VIII), [Pt(2,4'-bipyOct)Cl₃] (IX), [Pt(2,4'-bipyMe-H)(bipy)]²⁺ (X), [Pt(2,4'-bipyMe-H)(py)₂]⁺ (XI), [Pt(terpy)Cl]⁺ (XII), and Pt(DCMB)Cl₂ (XIII) (bipy = 2,2'-bipyridine; 4-NCpy = 4-cyanopyridine; Me₂-bipy = 4,4'-dimethyl-2,2'-bipyridine; Ph₂-bipy = 4,4'-diphenyl-2,2'-bipyridine; 2,4'-bipyOct-H = *N*'-octyl-2,4'-bipyridin-3'-ylium; 2,4'-bipyOct = *N*'-octyl-2,4'-bipyridinium; 2,4'-bipyMe-H = *N*'-methyl-2,4'-bipyridin-3'-ylium; terpy = 2,2':6',2''-terpyridine; DCMB = 3,3'-dicarboxymethyl-2,2'-bipyridine) was carried out in DMF. All the complexes show one (in some cases two) ligand-based reductions, and in many cases a platinum-based reduction at around –2 V vs. FeCp₂–FeCp₂⁺. The difference in reduction potential of a given ligand in different coordination environments can be attributed to metal–ligand and ligand–metal–ligand interactions. Singly and, where possible, doubly reduced states were generated by controlled potential electrolysis, and their electronic absorption spectra taken in situ. Properties were compared with those of 2,2'-bipyridine and [Pt(bipy)py₂]²⁺. In all cases the spectra of the singly reduced complexes show the general features of ligand anion radicals, while the second reduction of VIII is metal-based.

Keywords: Platinum; Electrochemistry; Bipyridyl complexes; Radical anion complexes; Spectroelectrochemistry

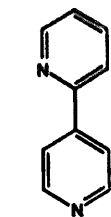
1. Introduction

Platinum(II) and bipyridines and terphenyl readily form stable complexes. These complexes have been extensively investigated in organometallic and inorganic chemistry [1–23]. Our earlier investigations of organoplatinum(II) and platinum(II) pyridine complexes with 2,2'-bipyridine ligands show that they undergo typical ligand-based reductions, giving products which can be formulated as [R₂Pt(II)L[–]][–], or [Pt(II)L[–]L'₂]⁺ (L = e.g. 2,2'-bipy; L'₂ = e.g. 2,2'-bipy, py₂) [24–27]. 2,2'-bipyridine, normally a bidentate ligand, can in general be converted into a monodentate ligand by quater-

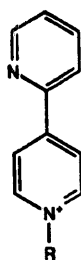
nizing one of its nitrogens, and the resulting cation can undergo ortho-metallation at the C(3) position of the quaternized ring to form the zwitterionic (R–bipy–H) ligand (bipy = 2,2'-bipyridine) [28–30]. 2,4'-bipyridine is different from 2,2'-bipyridine as its two nitrogens are located at unsymmetrical positions, and cannot both be coordinated to the same metal atom. It can act as monodentate ligand in its original form as well as when quaternized. Both neutral and 4'-quaternized 2,4'-bipyridines can undergo ortho-metallation to form bidentate N,C'-coordinated complexes with suitable metal ions [6,31]. In this paper, we report electrochemical and UV–VIS–NIR spectroelectrochemical studies of a group of platinum(II) 2,4'-bipyridine, 2,2'-bipyridine, and terpyridine N- and N–C'-coordinated complexes, together with data for some ligands which have not been examined in this manner before.

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(a)

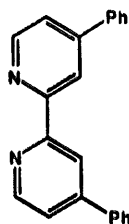


2,4'-bipyridine (I)

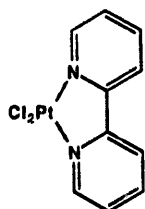
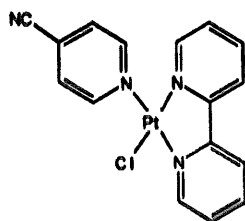
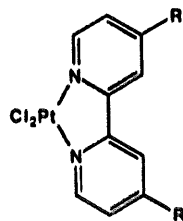


R = Methyl, N'-Methyl-2,4'-bipyridinium (II)

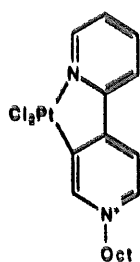
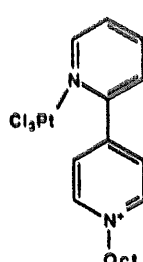
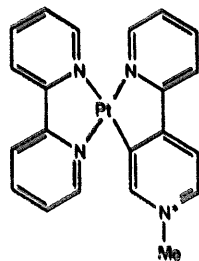
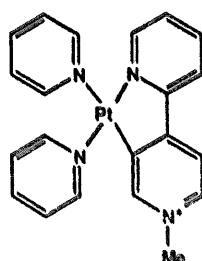
R = Octyl, N'-Octyl-2,4'-bipyridinium



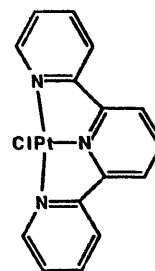
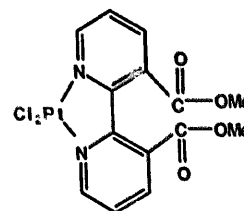
4,4'-diphenyl-2,2'-bipyridine (III)

[Pt(bipy)Cl₂]²⁺ (IV)[Pt(bipy)(NCpy)Cl]⁺ (V)R = Ph, [Pt(phen₂-bipy)Cl₂]²⁺ (VI)R = Me, [Pt(Me₂-bipy)Cl₂]²⁺ (VII)

(b)

[Pt(2,4'-bipyOct-H)Cl₂] (VIII)[Pt(2,4'-bipyOct)Cl₄] (IX)[Pt(bipy)(2,4'-bipyMe-H)]²⁺ (X)[Pt(2,4'-bipyMe-H)(py)₂]²⁺ (XI)

(c)

[Pt(terpy)Cl]⁺ (XII)[Pt(DCMB)Cl₂] (XIII)

2. Experimental

2.1. Materials

Bipyridines, HPLC-grade DMF, and tetrabutylammonium hexafluorophosphate (TBAPF₆) were obtained from Aldrich Chemical Co., and K₂PtCl₄ was from Johnson Matthey. TBAPF₆ was dried under vacuum overnight using a liquid nitrogen trap. 2,4'-bipyridine and DMF were used without further purification, but before each experiment a background cyclic voltammogram was collected to confirm that solvent and electrolyte were satisfactory.

[Pt(2,4'-bipyMe-H)Cl₂] [6], [Pt(2,4'-bipyOct-H)Cl₂] [2], [Pt(2,4'-bipyOct)Cl₃] [2], [Pt(bipy)Cl₂] [1,3], [Pt(DCMB)Cl₂] [4], and [Pt(terpy)Cl]Cl · H₂O [5] (2,4'-bipyMe-H = N'-methyl-2,4'-bipyridin-3'-ylium; 2,4'-bipyOct-H = N'-octyl-2,4'-bipyridin-3'-ylium; 2,4'-bipyOct = N'-octyl-2,4'-bipyridinium; DCMB = 3,3'-dicarboxymethyl-2,2'-bipyridine; terpy = 2,2':6',2''-terpyridine) were prepared as previously reported.

2.1.1. [Pt(2,4'-bipyMe-H)(bipy)](BF₄)₂

[Pt(2,4'-bipyMe-H)Cl₂] (50 mg) and bipy (23 mg) in a mixture of acetone (1 ml) and water (4 ml) were heated gently with stirring until a clear solution was obtained (about 5 min). Aqueous sodium tetrafluoroborate was added to the hot solution until crystals began to form. After crystallization was complete the golden yellow crystals (97%) were collected, washed with ice-

water and ethanol (95%) and dried in vacuo over silica gel. Found: C, 36.2; H, 2.5; N, 8.0%. $C_{21}H_{18}N_4B_2F_8Pt$. Calc.: C, 36.3; H, 2.6; N, 8.1%.

2.1.2. $[Pt(2,4'\text{-bipyMe-H})(py)_2](BF_4)_2$

$[Pt(2,4'\text{-bipyMe-H})Cl_2]$ (65 mg) was suspended in water (7 ml) and pyridine (0.3 g) was added. The mixture was heated gently with stirring until a lemon-yellow solution was obtained (about 5 min). Aqueous sodium tetrafluoroborate was added to the hot solution; on standing, long yellow needles (90%) formed. These were collected by filtration, washed with ice-water and dried in vacuo over silica gel. Found: C, 36.0; H, 2.7; N, 7.9%. $C_{21}H_{20}N_4B_2F_8Pt$. Calc.: C, 36.2; H, 2.9; N, 8.0%.

2.1.3. $[Pt(terpy)Cl](BF_4)$

Aqueous sodium tetrafluoroborate was added to $[Pt(terpy)Cl]Cl \cdot H_2O$ (50 mg) in water (6 ml) to give a salmon-pink precipitate. After standing for 1 h, the solid was collected by filtration, washed with water and ethanol and dried in vacuo over silica gel. Found: C, 32.5; H, 1.9; N, 7.4%. $C_{15}H_{11}N_3BClF_4Pt$. Calc.: C, 32.7; H, 2.0; N, 7.8%.

2.1.4. $[Pt(bipy)(4\text{-NCpy})Cl](ClO_4)$ (4-NCpy = 4-cyanopyridine)

4-Cyanopyridine (70 mg) was extracted with hot water (8 ml) and filtered into $[Pt(bipy)Cl_2]$ (100 mg). The mixture was heated with stirring until gently boiling. The solid dissolves over a period of 10 min to give a pale-yellow solution. Aqueous sodium perchlorate was added to the hot solution until crystallization commenced. The pale-yellow needles (55%) were collected by filtration, washed with cold water and dried in vacuo over silica gel. Found: C, 32.4; H, 2.1; N, 9.5%. $C_{18}H_{12}N_4Cl_2O_4Pt$. Calc.: C, 32.6; H, 2.1; N, 9.5%. IR: $347(s) \text{ cm}^{-1}$ (ν_{N-H}).

2.1.5. $[Pt(Ph_2\text{-bipy})Cl_2]$

4,4'-Diphenyl-2,2'-bipyridine (73 mg) was extracted into hot acetone (17 ml) and filtrated into K_2PtCl_4 (90 mg) in water (4 ml). The orange solution was stirred with mild heating for 1 h. The color changed to bright yellow and yellow solid precipitated. The solid (65%) was collected by filtration, washed with water and ethanol and dried in vacuo over silica gel. Found: C, 46.0; H, 2.8; N, 4.5%. $C_{22}H_{16}N_2Cl_2Pt$. Calc.: C, 46.0; H, 2.8; N, 4.9%. 1H NMR (D_6 -DMSO): 9.05 (H-3) d; 8.17 (H-5) d of d; 9.44 (H-6) d; 8.09 (Ph, 2H, m); 7.62 (Ph, 3H, m). $J_{3,5}$ 2.0; $J_{5,6}$ 6.3; $J_{Pt,H}$ 31 Hz.

2.1.6. $[Pt(Me_2\text{-bipy})Cl_2]$

4,4'-Dimethyl-2,2'-bipyridine (65 mg) was dissolved in hydrochloric acid (0.1 M, 3 ml) and added to K_2PtCl_4 in water (5 ml). On heating, a voluminous yellow pre-

cipitate formed. The solid (85%) was collected by filtration, washed with water and ethanol and dried in vacuo over silica gel. Found: C, 32.0; H, 2.7; N, 5.9%. $C_{12}H_{12}N_2Cl_2Pt$. Calc.: C, 32.0; H, 2.7; N, 6.2%. 1H NMR (D_6 -DMSO): 2.46 (Me, s); 3.40 (H-3, d); 7.63 (H-5, d of d); 9.20, (H-6, d). $J_{3,5}$ 1.2; $J_{5,6}$ 6.0; $J_{Pt,H}$ 35.5 Hz. IR: 334 (s), 326 (sh) (ν_{Pt-Cl}).

2.2. Instrumentation

Proton NMR spectra were recorded using a Bruker AC200 spectrometer at ambient temperature. Infrared spectra were recorded as nujol mulls on CsI plates on a Perkin-Elmer 983 spectrophotometer. Cyclic (strictly, staircase cyclic) voltammetry was performed under argon at room temperature in a Metrohm cell with a three-electrode-system using a computer-controlled EG & G Princeton Applied Research Potentiostat Model 273 potentiostat-galvanostat with iR compensation. The working electrode was a platinum disk with diameter of 0.368 mm, and the counter electrode was a piece of platinum wire, of the same diameter, about 5 mm in length. All platinum electrodes were cleaned with concentrated nitric acid and thoroughly dried before use. Potentials are referred to the oxidation of ferrocene potential which was added as an internal standard; the peak to peak separation for this was in all cases within the range 60–80 mV (theoretical value 59 mV). 0.1 M TBAPF₆ was used as supporting electrolyte. The routinely-used potential scan rate was 0.5 V s^{-1} , but the results were verified by changing the scan rate from 20 mV s^{-1} to 4.0 V s^{-1} , which in no case caused significant shifts of the peak potentials. Solutions were typically 10^{-3} M.

Electronic absorption spectra were collected in DMF using a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrometer with computerized control and data acquisition. The reduced species were generated under argon by controlled potential electrolysis with the same potentiostat as used in cyclic voltammetry experiments, inside a 1 mm pathlength spectroelectrochemical cell with a platinum mesh OTTLE electrode, and spectra were taken in situ as described previously [32].

3. Results and discussion

3.1. Electrochemistry of free ligands

Electrochemical data for ligands and complexes are presented in Table 1.

3.1.1. 2,4'-Bipyridine (I)

The cyclic voltammogram of **I** shows two accessible reductions in DMF. The first, at -2.50 V (vs. $FeCp_2-FeCp_2^+$), is a chemically reversible one-electron reduc-

Table 1
Cyclic voltammetry data for platinum(II) complexes ^a

	$E^{0/-1}$ ^b	$E^{0/-1/-2}$ ^b	$E^{0/-2/-3}$ ^b
2,4'-Bipyridine I	–2.50/122	–3.21/irr	
N'-Methyl-2,4'-bipyridinium II	–1.52/92	–2.32/79	
4,4'-Diphen-2,2'-bipyridine III	–2.42/93		
Pt(bipy)Cl ₂ IV	–1.63/90	–2.32/135 ^c	
[Pt(bipy)(4-NCpy)Cl] ⁺ V	–1.47/90	–1.69/100	–2.29/100
Pt(Ph ₂ -bipy)Cl ₂ VI	–1.59/68	–2.18/79	
Pt(Me ₂ -bipy)Cl ₂ VII	–1.64/68	–2.38/irr ^d	
Pt(2,4'-bipyOct-H)Cl ₂ VIII	–1.54/90	–2.23/90	
[Pt(2,4'-bipyOct)Cl ₃] IX	–1.45/90	–2.04/90	
Pt(2,4'-bipyMe-HX(bipy)) ²⁺ X	–1.22/80	–1.57/70	–1.96/80
[Pt(2,4'-bipyMe-HX(py)) ₂] ²⁺ XI	–1.44/60	–2.09/130	
[Pt(terpy)Cl] ⁺ XII	–1.09/76	–1.60/80	–2.36/88
Pt(DCMB)Cl ₂ XIII	–1.16/76	–1.81/100	
2,2':6',2''-Terpyridine	–2.52/92	–2.98/irr	

^a Data taken from cyclic voltammetry at 500 mV s^{–1}, in dry DMF, at room temperature with 0.1 M TBAPF₆ as supporting electrolyte; measurements taken in volts vs. half wave potential of the oxidation of ferrocene. ^b $E^{0}/(E_{pa} - E_{pc})$ (mV); $E^{0} = (1/2)(E_{pa} + E_{pc})$ (V). ^c Return wave only resolved at high scan rate (4 V s^{–1}). ^d Chemically irreversible.

tion. As with 2,2'-bipyridine in DMF [33], the second reduction is chemically irreversible. In the biphenyl system, the $\pi(7)$ orbital has larger electron density at para than at ortho positions, so that nitrogen, being more electronegative than carbon, will stabilize the $\pi(7)$ orbital better at the para position than at the ortho positions. This is consistent with the fact that the potential of the first reduction of **I** is less negative than that of 2,2'-bipyridine, lying between those of 2,2'-bipyridine (–2.56 V) and of 4,4'-bipyridine [33] (–2.40 V) under the same experimental conditions.

3.1.2. N'-Methyl-2,4'-bipyridinium (II)

The cyclic voltammogram of **II**, a singly quaternized derivative of **I**, also shows two reductions, and, in contrast to **I**, both are chemically reversible. The potentials of both first and second reductions shift about 1 V positively on quaternization of 2,4'-bipyridine, as previously reported [33] for the 4,4' analog.

3.1.3. 4,4'-Diphenyl-2,2'-bipyridine (III)

This species shows two accessible reductions in DMF. The first reduction is reversible, as in the other bipyridines. The potential of this reduction is at –2.42 V, slightly less negative than that of 2,2'-bipyridine. This may result either from an inductive effect of the electron-withdrawing phenyl rings, or from delocalization. The second reduction is chemically irreversible, as in the other bipyridines.

3.2. Ligand-based reductions of platinum(II) complexes

In general, the platinum(II) complexes investigated here show two or three single-electron reductions but no accessible oxidation under our experimental conditions. Typical data are shown in Fig. 1. Most of the reductions

are chemically reversible, as shown by their cyclic voltammograms, but the separation of forward and return waves is larger in most cases than the ideal value of 59 mV; in other words, they are not completely electrochemically reversible.

3.2.1. Pt(bipy)Cl₂ (IV)

IV shows two accessible reductions in the potential range studied (from +1.0 to –3.0 V). The first reduction is at –1.63 V, a bipyridine-based reduction, which is 0.93 V less negative than that of free 2,2'-bipyridine [33]. This is due to coordination with the platinum(II) ion, and is typical for bipyridine when coordinating with a metal ion. This first reduction is chemically reversible, but the separation of the forward and return wave is 90 mV, showing incomplete electrochemical reversibility. Klöngler et al. studied the first reduction of **IV** by cyclic voltammetry in acetonitrile in 1982. They described the reduction product as a Pt(I) species, but this assignment seems to have been made in a formal sense only [34].

3.2.2. [Pt(bipy)(4-NCpy)Cl]⁺ (V)

V shows three reduction waves on its cyclic voltammogram. The first one, at –1.47 V, is also a bipyridine-based reduction. The potential of this reduction is about 160 mV less negative than that of **IV**, due to the π acceptor effect of 4-cyanopyridines as against the π donor effect of chlorides. The second reduction at –1.69 V can be assigned as 4-cyanopyridine-based.

3.2.3. [Pt(Ph₂-bipy)Cl₂] (VI) and [Pt(Me₂-bipy)Cl₂] (VII)

The first reduction of **VI** is at –1.59 V, and that of **VII** is at –1.64 V. These are both bipyridine based. This potential is almost the same for **IV** and **VII**, but

shifts positively for **VI** owing to the effect of phenyl groups.

3.2.4. $\text{Pt}(2,4'\text{-bipyOct-H})\text{Cl}_2$ (**VIII**) and $[\text{Pt}(2,4'\text{-bipyOct})\text{Cl}_3]$ (**IX**)

For **VIII**, the first reduction is at -1.54 V , slightly less negative than that of **IV**. The close resemblance here between **IV** and **VIII** parallels that between $[\text{Pt}(\text{bipy})(\text{py})_2]^{2+}$ and $[\text{Pt}(2,2'\text{-bipyMe-H})(\text{py})_2]^{2+}$ [27]. Comparing the azabiphenyl ligands in **IX** and **IV**, that in **IX** carries its most electronegative group at a position where electron density in the LUMO is highest [33], and has one N donating to $\text{Pt}(\text{II})$ and the other, at the same level of formalism, to CH_3^+ ; if we compare metal sites, that in **IX** is coordinated to three chlorides and one nitrogen, rather than to two chlorides and two nitrogens. Thus, the more facile reduction of **IX** is as expected.

3.2.5. $[\text{Pt}(2,4'\text{-bipyMe-H})(\text{bipy})]^{2+}$ (**X**)

X shows three reduction waves, of which the first two are based on the two separate ligands. Since **VIII** is

more readily reduced than **IV**, we assign the first reduction of this complex to the 2,4'-bipyMe-H ligand and the second to the bipyridine. The reduction potential of 2,2'-bipyridine is at -1.57 V here, which is less negative than in **IV** due to the overall charge on the complex and the π -acceptor effect of 1'-methyl-2,4'-bipyridin-3-ylum.

3.2.6. $[\text{Pt}(2,4'\text{-bipyMe-H})\text{py}_2]^{2+}$ (**XI**)

Here the first reduction, on 2,4'-bipyMe-H, is 220 mV more negative than that of **X**. We attribute this difference to the weaker π -accepting ability of pyridine compared with bipyridine.

3.2.7. $[\text{Pt}(\text{terpy})\text{Cl}]^+$ (**XII**)

XII has three accessible reductions. The first two of these are terpyridine-based, and are chemically reversible. Free terpyridine shows a chemically reversible reduction at -2.52 V , and the second reduction with cathodic wave potential at -2.98 V , for which an anodic wave could not be detected even with a scan rate

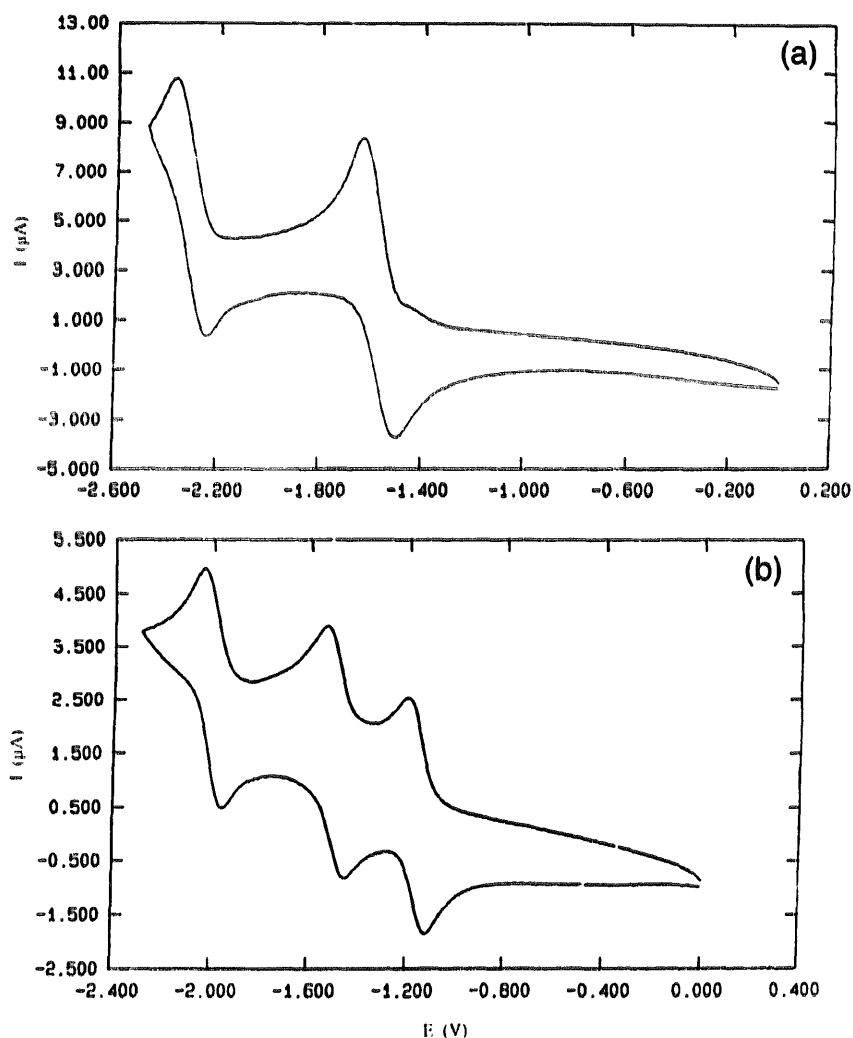


Fig. 1. (a) Cyclic voltammogram of **IV** in DMF-0.1 M TBAPF₆ (scan rate 2 V s^{-1}); (b) Cyclic voltammogram of **X** in DMF-0.1 M TBAPF₆ (scan rate 500 mV s^{-1}). Both voltammograms plotted vs. $\text{Ag}-0.01\text{ M AgNO}_3 + 0.09\text{ M TBAPF}_6$, but tabulated vs. internal Fc^+/Fc (not shown).

of 4 V s^{-1} . As in other cases, the reversibility of the second reduction of terpyridine is improved on coordination to the metal ion. The first reduction of **XII** is at -1.09 V . The first reduction potential of free terpyridine, -2.52 V , is close to the value of 2,2'-bipyridine, -2.56 V . However, perhaps because there are three nitrogens coordinating with platinum(II) ion, constraining the ligand to be planar, the positive shift of reduction potentials of terpyridine due to coordination is larger than in the other cases discussed here.

3.2.8. $\text{Pt}(\text{DCMB})\text{Cl}_2$ (**XIII**)

XIII has its first reduction at -1.16 V , which is DCMB ligand-based. It is not surprising that the elec-

tron-withdrawing carboxymethyl group greatly lowers the LUMO of the bipyridine.

3.3. Metal-based reductions of platinum(II) complexes

Platinum(II) complexes of bipyridine radical anion ligands can undergo metal-based electrochemical reduction, forming platinum(I) [27]. In the complexes investigated here, most of them have their metal-based reduction located at around -2.0 V , as expected [27]. The metal-centered reduction of **IV** was at -2.32 V . The product of this reduction is not very stable, the return wave being resolved only at high scan rate (4 V s^{-1}). This potential is quite negative, owing to the charge and

Table 2

Spectroscopic data and proposed assignments for platinum complexes and related species in DMF ^a

Compound	$\pi(6) \rightarrow \pi(7)$	$\pi(7) \rightarrow \pi(10)$	$\pi(7) \rightarrow \pi(8,9)$	MLCT	Other (see text)
I	273(36.6)(20.1)				
I ⁻	388(25.8)(36.7)	545(18.3)sh 580(17.2)(11.6)	970(10.3)(0.54) 1128(8.9)(0.54)		
II	290(34.5)(21.2)				
II ⁻	368(27.1)(33.4)	480(20.8)sh 524(19.1)(7.35)			
III	300(33.3)				
III ⁻	347(28.8)(17.9) 375(26.6)(17.5)	665(15.0)(8.7)			
IV	313(31.9)(7.9) 325(30.8)(9.1)			278(36.0)(18.9) 388(25.8)(3.6)	
IV ⁻	359(27.9)(10.7)	463(21.6)(5.1) 500(20.0)(6.0)	913(10.1)(1.5)	424(23.6)(5.3)	
V	311(32.2)(13.9) 323(31.0)(16.6)			333(30.0)sh	
V ⁻				273(36.6)	
VI	338(29.6)(12.9)			400(25.0)(7.8) 297(33.7)(47.5)	
VI ⁻	367(27.2)(34.9)	430(23.3)(8.5)	1117(8.9)(4.8) 1279(7.8)(4.4)	524(19.1)(5.0) 562(17.7)(5.7)	
VII	311(32.1)(6.7) 322(31.1)(7.7)			280(35.7)(17.7) 363(27.5)sh	
VII ⁻	358(27.9)(5.3)	474(21.1)(2.4)	632(15.9)(0.35) 700(14.3)(0.34)	384(26.0)(3.39) 418(23.9)(2.4) 510(19.6)(2.8)	
VIII	295(33.9)(9.3)			268(37.3)(11.4) 372(26.9)sh	343(29.2)sh
VIII ⁻	319(31.3)(5.4)	473(21.1)(2.7)	887(11.3)(0.35)	432(23.1)(1.2) 451(22.2)(1.2) 375(26.7)(2.2)	260(38.5) 538(18.6)(2.2) 580(17.2)sh 635(15.7)(0.89) 696(14.4)(0.71)
VIII ²⁻					
IX	319(31.3)(5.4)			393(25.4)(4.3) 380(26.3)sh 420(23.8)sh	
IX ⁻	371(26.9)(25.2)	525(19.0)(8.2)			
X	312(32.1)(20.2)			373(26.8)(7.6)	
XI	305(32.8)(9.1) 316(31.6)(9.2)			359(27.8)(3.6)	
XIII				373(26.8) 436(22.9)	
XIII ⁻		450(22.2)	900(11.1)		

^a $\lambda/\text{nm}(\bar{\nu}/10^3 \text{ cm}^{-1})(\epsilon/10^3)$

π donor effect of the chloride ligands. In contrast, the platinum(II)-centered reduction of **XIII** is reversible at -1.81 V, which is about 550 mV less negative than in **IV**. This is because of the electron-withdrawing effect of the carboxymethyl group. The metal-centered reduction of **VIII** is 160 mV less negative than in **IV** for a similar reason; the lower LUMO of 2,4'-bipyOct-H makes it a better π -acceptor than bipyridine. The first (ligand-based) reduction of **XI** is 60 mV more negative than that of $[\text{Pt}(\text{bipy})\text{py}_2]^{2+}$ [27], but the second reductions, which we assign as metal-based, are at almost the same potential. It would appear that metal to ligand π -donation has a greater effect on the metal potential in the neutral chloro complexes **IV** and **VIII** than in the cationic bis(pyridine) complexes **V** and **XI**. The metal-centered reduction of **V** appears as the third wave in its cyclic voltammogram, at -2.29 V, which is much more negative than in other similar complexes. As mentioned above, the first reduction is bipyridine-based and the second reduction is 4-cyanopyridine-based, so that the platinum(II) ion being reduced is coordinated to three negatively charged ligands.

3.4. Spectroscopy and spectroelectrochemistry of bipyridines

As shown in the tabulated data (Table 2), in DMF, the electronic absorption spectra of the neutral bipyridines generally show a single strong band near 300 nm, assigned as $\pi(6) \rightarrow \pi(7)$. This absorption commonly shifts to a lower energy, in the region of 370 – 400 nm, if the bipyridines are singly reduced [33]. This is because the added electron in $\pi(7)$ increases the bond order between the two pyridyl rings, thus lowering $\pi(7)$ (antibonding for the molecule as a whole but bonding between the two pyridyl rings), and raising $\pi(6)$ (for which the reverse is true) [33]. The other bands in the spectra of reduced bipyridines are assigned as $\pi(7) \rightarrow \pi(10)$, and $\pi(7) \rightarrow \pi(8,9)$. The first of these is around 600 nm, and usually is broad and about half as intense as $\pi(6) \rightarrow \pi(7)$. $\pi(7) \rightarrow \pi(8,9)$ is broad and comparatively weak due to the near cancellation of local transition dipole moments. These assignments can be extended to the spectra of **I**, **II** and **III**, and their reduction products, which are reported here for the first time. The $\pi(7) \rightarrow \pi(8,9)$ bands of **I**[−] show vibrational structure similar to that of 2,2'-bipy[−] and 4,4'-bipy[−] [33].

3.5. Spectroscopy and spectroelectrochemistry of platinum(II) complexes

In DMF, the electronic absorption spectra of unreduced platinum(II) complexes can contain at least three kinds of bands in the UV–VIS–NIR region, namely ligand-based $\pi \rightarrow \pi^*$ bands, metal to ligand charge

transfer (MLCT) bands, and d–d bands; see Table 2. For all species listed, except **X**, **XI** and **XII**, we were able to collect spectra for the singly reduced species, with satisfactory (greater than 90%) regeneration of parent on re-oxidation. In all these cases, our data imply a bipyridine-based reduction, with the expected $\pi(7) \rightarrow \pi(10)$ and $\pi(7) \rightarrow \pi(8,9)$ transitions. The ligand-based $\pi(6) \rightarrow \pi(7)$ transition, like that of the free ligand, shifts to a lower energy on reduction, which is consistent with the assumption that the added electron is localized at the bipyridine. For the singly reduced $\text{Pt}(2,4'\text{-bipyOct-H})\text{Cl}_2$, the origin of the 260 nm band is not very clear; it may be a ligand (reduced bipyridine) to metal charge transfer [35]. **VIII** was the only complex for which we are confident of having collected the spectrum of both the singly and the doubly reduced species (Fig. 2), as shown by satisfactory regeneration of the parent spectrum on re-oxidation. **VIII**[−] (but not **VIII**^{2−}) was unique in showing absorption from $18\,600\text{ cm}^{-1}$ to $14\,400\text{ cm}^{-1}$, with a clear vibrational progression in steps of 1400 cm^{-1} , which we attribute to a ring–ring stretching frequency. We assign this absorption as charge transfer from the reduced ligand to the metal. Presumably it is found only in **VIII**[−] because of the weak ligand field of chloride. The progression is consistent with transfer of an electron from $\pi(7)$, which is bonding between the two pyridyl rings, and is thus related with that generally observed (but for these complexes not well pronounced) in the $\pi(7) \rightarrow \pi(8,9)$ transition. Compared with **VIII**[−], **VIII**^{2−} shows

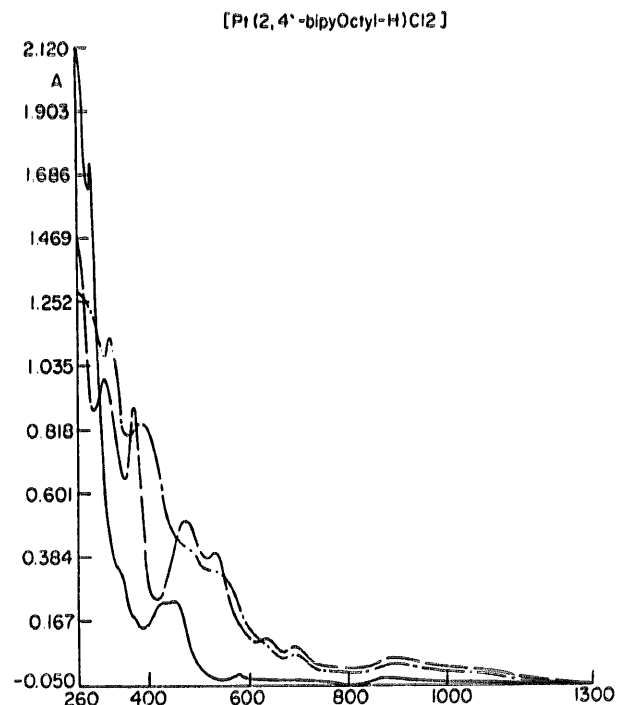


Fig. 2. Absorption spectra of **VIII** (—), **VIII**[−] (---), and **VIII**^{2−} (- · -) in DMF-0.1 M TBAPF₆.

the reduced bipyridine-based $\pi(6) \rightarrow \pi(7)$ band unchanged at 319 nm, the platinum to bipyridine anion radical charge transfer band shifted to lower energy at 393 nm, and loss of the LMCT band in VIII⁻. All these data are consistent with the second reduction being metal-based.

4. Conclusions

From the cyclic voltammetry and the electronic absorption spectra, we can conclude that in all cases the first reductions of these platinum(II) complexes are bipyridine ligand-based. Subsequent reductions are in most cases metal-based. The reduction potentials are influenced by the ligand–metal interactions, and also by other ligands coordinated at the same metal center.

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