

Neutral Mixed-ligand Complexes of Platinum(II) and Palladium(II) with α -Diimine and Dioxolenes

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Abstract

Ten new mixed-ligand complexes of formula $[M(N-N)(X-X)]$, where M is Pd(II) or Pt(II), N-N is 2,2'-bipyridine, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline or 2,2'-biquinoline, and X-X is the dianion of catechol, 4-tert-butylcatechol or 2,3-dihydroxynaphthalene, have been prepared and characterized by the physical methods. In the visible region of the absorption spectra of these square-planar complexes a ligand–ligand charge-transfer band (13 to 21 kK) with a high extinction coefficient has been observed, which is negatively solvatochromic. Thus these complexes seem to possess a substantial ground state electric dipole which is reduced or reversed by this low-energy transition. Cyclic voltammetry studies show that the above complexes undergo electron transfer reactions with charge +1, 0, –1 and –2. The visible spectral and electrochemical potential data on the above complexes have been interpreted using the qualitative MO theory developed earlier for analogous complexes.

Introduction

Several neutral mixed-ligand complexes of zinc(II), cadmium(II), nickel(II), palladium(II) and platinum(II) containing 2,2'-bipyridine, 1,10-phenanthroline or other α -diimine molecules as one ligand and 3,4-dimercaptotoluene or other dithiolenes as another ligand have been reported [1–8]. These complexes show a visible absorption band due to ligand-to-ligand charge-transfer transitions from the dithiolene ligand to the α -diimine ligand. Several palladium(II) and platinum(II) complexes containing 2,2'-bipyridine as one ligand and dioxolene as another ligand have been reported as good and stable photosensitizers for singlet molecular oxygen (1O_2) production. However, the palladium(II) and platinum(II) complexes containing 2,2'-bipyridine and 3,4-dimercaptotoluene are either poor or unstable photosensitizers for generating 1O_2 [8, 9]. In view

of the importance of these complexes as photosensitizers in inorganic photochemistry, we report here the synthesis, characterization and electrochemical studies of several new complexes of formula $[M(N-N)(X-X)]$, where M = Pd(II) or Pt(II), N-N = 2,2'-bipyridine (bipy), 2,2'-biquinoline (biq), 1,10-phenanthroline (phen) or 4,7-diphenyl-1,10-phenanthroline (dpp), and X-X = the dianion of catechol (CAT), 4-tert-butylcatechol (BCAT) or 2,3-dihydroxynaphthalene (DHN). These complexes have been found to act as photosensitizers for 1O_2 generation [10].

Experimental

Chemicals

Potassium tetrachloroplatinate(II) (Strem, U.S.A.), palladium chloride, 1,10-phenanthroline monohydrate (SRL, India), 2,2'-biquinoline, 4,7-diphenyl-1,10-phenanthroline, 4-tert-butylcatechol (Loba, India), 2,3-dihydroxynaphthalene (Koch-Light, U.K.), 2,2'-bipyridine (Merck, India) and tetra(n-butyl)ammonium perchlorate (Fluka, Switzerland) of reagent grade were bought and used as such. Catechol (SD's, India) was used after recrystallization from benzene. Reagent grade solvents were used after purification by the standard methods [11].

Synthetic Procedure

$[M(N-N)Cl_2]$, where M is Pd(II) or Pt(II), N-N is bipy, phen, biq or dpp, were prepared by the literature methods [10, 12–14]. $[Pt(N-N)(X-X)]$, where N-N is bipy or phen and X-X is the dianion of catechol, 4-tert-butylcatechol or 3,4-dimercaptotoluene (DMT), were prepared and characterized by the reported procedures [7, 12].

$[M(N-N)(X-X)]$, where M is Pd(II) or Pt(II), N-N is bipy, phen, biq or dpp and X-X is the dianion of 2,3-dihydroxynaphthalene, and $[Pt(biq)(BCAT)]$ were prepared by the general method as follows. One mmol of $[M(N-N)Cl_2]$ was dissolved in 20 ml of dimethyl sulphoxide (DMSO) and one mmol of catechol or other dioxolene dissolved in

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2 ml of 1 N NaOH was added to the former solution with constant stirring. The mixture was stirred overnight and then 100 ml of chloroform was added to this mixture with constant stirring. This chloroform solution was later washed repeatedly with distilled water. The chloroform layer was then filtered and dried over anhydrous sodium sulphate. Sodium sulphate was filtered off from the dry chloroform layer. This chloroform solution was slowly concentrated and the complex was recrystallized from solvents such as chloroform, acetone or chloroform-acetone. The crystals after filtration were dried in a vacuum desiccator over anhydrous calcium chloride.

[Pd(phen)(DHN)] was prepared by suspending one mmol of [Pd(phen)Cl₂] in 100 ml of methanol; one mmol of 2,3-dihydroxynaphthalene dissolved in 100 ml of methanol and 0.25 ml of triethylamine were added to the above solution. The mixture was refluxed at 60 °C on a water bath for 15 h. The red crystals thus obtained were filtered, washed several times with water and then with methanol. The complex was recrystallized from chloroform. The crystals were dried in a vacuum desiccator over anhydrous calcium chloride.

[Pd(biq)(CAT)] was prepared by the method of [Pd(phen)(DHN)] except that [Pd(biq)Cl₂], catechol

and CH₂Cl₂ were used in place of [Pd(phen)Cl₂], 2,3-dihydroxynaphthalene and CH₃OH respectively.

Chemical analyses of the above complexes were performed at the Microanalytical Laboratory, I.I.T., Bombay or at R.S.I.C., Central Drug Research Institute, Lucknow, India.

Physical Measurements

Physical measurements were carried out as described earlier [15].

Results and Discussion

Ten new mixed-ligand palladium(II) and platinum(II) complexes of the general formula [M(N-N)(X-X)] were prepared. The molar conductance data in dimethylformamide (DMF) and the chemical analyses of the above complexes (Table 1) suggest them to be non-electrolytes [16].

The infrared spectral changes in the ligand moieties of the above complexes as compared to the free ligands suggest the coordination of ligands to metal ions. The presence of two strong bands at about 1265 and 1470 cm⁻¹ in the complexes suggest the binding of ionized hydroxyl groups of catechol and derivatives to metal ions. The band at about

TABLE 1. Colour, yield, molar conductance and chemical analysis data of [M(N-N)(X-X)] complexes

Complex	Colour	Yield	Molar conductance ^a	Calculated (found) (%)		
				C	H	N
[Pd(bipy)(DHN)]	dark brown	51	9.8	57.06 (56.83)	3.33 (3.21)	6.66 (6.52)
[Pd(biq)(DHN)]	dark blue	52	3.0	64.56 (64.51)	3.46 (3.54)	5.38 (5.71)
[Pd(biq)(CAT)]	blue	65	4.8	61.24 (60.16)	3.40 (3.56)	5.95 (5.58)
[Pd(biq)(BCAT)]	green	60	9.8	63.84 (63.41)	4.56 (5.07)	5.32 (5.04)
[Pt(bipy)(DHN)]	brown	50	4.9	47.13 (46.78)	2.75 (2.51)	5.50 (5.42)
[Pt(biq)(DHN)]	blue	70	9.8	55.14 (54.12)	2.95 (2.80)	4.60 (4.31)
[Pd(phen)(DHN)]	red	50	4.9	59.46 (58.97)	3.15 (3.16)	6.31 (5.35)
[Pd(dpp)(DHN)]	dark brown	50	4.5	68.41 (68.34)	3.69 (3.67)	4.70 (3.88)
[Pt(phen)(DHN)]	dark brown	70	4.9	48.53 (48.43)	2.63 (2.55)	5.25 (4.72)
[Pt(dpp)(DHN)]	brown	55	4.9	59.50 (59.05)	3.21 (4.10)	4.08 (4.05)

^acm² ohm⁻¹ mol⁻¹.

TABLE 2. ^1H NMR spectral data of $[\text{M}(\text{N-N})(\text{X-X})]$ complexes in DMSO-d_6

Complex	2,2'-Bipyridine/2,2'-Biquinoline protons						Ligand (X-X) protons			
	$\delta\text{H}_{3,3'}$	$\delta\text{H}_{4,4'}$	$\delta\text{H}_{5,5'}$	$\delta\text{H}_{6,6'}$	$\delta\text{H}_{7,7'}$	$\delta\text{H}_{8,8'}$	$\delta\text{H}_{a,a'}/\delta\text{H}_a$	$\delta\text{H}_{b,b'}/\delta\text{H}_b$	$\delta\text{H}_{c,c'}/\delta\text{H}_c$	δH_d
[Pd(bipy)(DHN)]	8.59(d) ^a $J_{3,4} = 7.70^b$ (8.59) ^c	8.37(d) (8.36)	7.84(t) (7.81)	8.68(d) $J_{5,6} = 5.36$ (8.12)			6.62(s) (7.10) ^d	7.35(t) $J_{b,c} = 5.59$ (7.56)	6.86(q) $J_{b,c} = 2.97$ (7.17)	
[Pd(biq)(DHN)]	9.43(d) $J_{3,4} = 8.46$ (8.97)	9.03(d) (8.76)	8.25(d) $J_{5,6} = 7.81$ (8.32)	7.92(d) (8.03)	8.11(t) (8.15)	8.88(d) $J_{7,8} = 8.44$ (8.52)	6.70(s) (6.38(m))	7.39(s) (6.22(m))	6.94(s) (6.22(m))	6.38(m)
[Pd(biq)(CAT)]	9.47(d) $J_{3,4} = 8.58$ (8.97)	9.00(d) (8.76)	8.22(d) $J_{5,6} = 8.00$ (8.32)	7.88(t) (8.03)	8.06(t) (8.15)	8.86(d) $J_{7,8} = 8.00$ (8.52)	6.38(m) (6.75)	6.22(m) (6.75)	6.22(m) (6.75)	6.38(m)
[Pd(biq)(BCAT)]	9.35(t) $J_{3,4} = 8.65$ (8.97)	8.84(d) (8.76)	8.45(d) $J_{5,6} = 8.66$ (8.32)	7.94(d) (8.03)	8.05(d) (8.15)	8.70(d) $J_{7,8} = 8.83$ (8.52)	6.10(m) (6.81)	0.99(s) (1.20)	6.10(m) (6.81)	6.25(s) (6.96)
[Pt(bipy)(DHN)]	8.58 $J_{3,4} = 7.82$ (9.10)	8.40(t) (8.93)	7.82(t) (8.36)	9.15(d) $J_{5,6} = 5.31$ (10.01)			6.83(s) (6.95(s))	7.43(t) (7.48(m))	6.99(t) (7.01(m))	
[Pt(biq)(DHN)]	9.69(d) $J_{3,4} = 8.83$ (9.07)	9.03(d) (8.84)	8.29(d) $J_{5,6} = 7.87$ (8.23)	7.95(t) (7.82)	8.20(t) (8.02)	8.82(d) $J_{7,8} = 8.27$ (8.67)	6.95(s)	7.48(m)	7.01(m)	
1,10-Phenanthroline/4,7-Diphenyl-1,10-phenanthroline protons										
	$\delta\text{H}_{2,9}$	$\delta\text{H}_{3,8}$	$\delta\text{H}_{4,7}$	$\delta\text{H}_{5,6}$	Ligand (X-X) protons		$\delta\text{H}_{a,a'}$	$\delta\text{H}_{b,b'}$	$\delta\text{H}_{c,c'}$	
[Pd(phen)(DHN)]	8.99(d) $J_{2,3} = 4.91$ (9.36)	8.14(q) (8.15)	8.96(d) $J_{3,4} = 8.10$ (8.99)	8.29(s) (8.29)	6.68(s)	7.38(q) $J_{b,c} = 5.90$	6.68(s)	7.38(q)	6.94(q) $J_{b,c} = 2.88$	
[Pd(dpp)(DHN)]	9.34(d) $J_{2,3} = 5.58$ (9.41)	8.10(d) (8.14)	7.67(m) ^e (7.69)	8.09(s) (8.12)	6.62(s)	7.36(t)	6.62(s)	7.36(t)	6.95(t)	
[Pt(phen)(DHN)]	9.37(d) $J_{2,3} = 3.60$ (9.69)	8.12(q) (8.15)	8.99(d) $J_{3,4} = 7.94$ (9.03)	8.27(s) (8.28)	6.86(s)	7.44(s)	6.86(s)	7.44(s)	7.01(s)	
[Pt(dpp)(DHN)]	9.16(s) (9.68)	8.09(d) (8.15)	7.66(m) ^e (7.72)	8.03(s) (8.13)	6.83(s)	7.44(s)	6.83(s)	7.44(s)	7.08(s)	

^as, d, t, q and m indicate singlet, doublet, triplet, quartet and multiplet (in last only centred position is mentioned respectively). ^b J , coupling constant, is given in Hz. ^cChemical shifts of protons of N-N ligand in $[\text{M}(\text{N-N})\text{Cl}_2]$ are given in parentheses. ^dChemical shifts of protonated X-X ligand's protons are given in parentheses. ^eThe protons of phenyl groups of dpp in the complexes.

1265 cm^{-1} is assigned to the $\nu(\text{C}-\text{O})$ vibration and another at about 1470 cm^{-1} corresponds to skeletal vibration of the aromatic ring [17]. These complexes show the $\nu(\text{M}-\text{O})$ vibration at about 470 cm^{-1} [18].

The ^1H NMR spectral data of the $[\text{M}(\text{N}-\text{N})(\text{X}-\text{X})]$ complexes recorded in deuterated dimethyl sulphoxide ($\text{DMSO}-d_6$) are given in Table 2. The numbering scheme of the ligand protons is given in Fig. 1. The chemical shifts of the protons of diimine ligands in the mixed-ligand complexes have been compared with those in the parent $[\text{M}(\text{N}-\text{N})\text{Cl}_2]$ complexes [15] and they invariably experience an upfield shift in the mixed-ligand complexes with the exception of $[\text{M}(\text{biq})(\text{X}-\text{X})]$. The upfield shifts of α -diimine ligand protons in the mixed-ligand complexes as compared to the corresponding $[\text{M}(\text{N}-\text{N})\text{Cl}_2]$ complexes can be interpreted in terms of the stronger bonding of dianions of catechol and other dioxalenes to metal ions and more backbonding from the metal d_π orbitals to the π^* orbital of the α -diimine ligands to the corresponding chloro complexes [7, 8]. The integrated areas of protons of α -diimine and 2,3-dihydroxynaphthalene dianion are in the ratio of 4:3, 4:3, 2:1 and 8:3 for $[\text{M}(\text{dpp})(\text{DHN})]$, $[\text{M}(\text{phen})(\text{DHN})]$, $[\text{M}(\text{biq})(\text{DHN})]$ and $[\text{M}(\text{dpp})(\text{DHN})]$ respectively. In $[\text{Pd}(\text{biq})(\text{CAT})]$ and $[\text{Pd}(\text{biq})(\text{BCAT})]$ complexes the integrated areas of protons of both the ligands are in the ratio of 3:1 and 1:1 respectively. These data suggest that

both ligands are bonded to metal in the mixed-ligand metal complexes. The sharp ^1H NMR spectral signals observed in these complexes suggest them to be diamagnetic and square planar.

The electronic absorption spectra of $[\text{M}(\text{N}-\text{N})(\text{X}-\text{X})]$ in DMF show several band maxima. The positions of these bands maxima along with their extinction coefficients are given in Table 3. The bands in the region of 250 to 450 nm are assigned on the basis of band assignments of $[\text{M}(\text{N}-\text{N})\text{Cl}_2]$ [19]. The bands 2 and 4 are assigned to charge-transfer transitions from the d orbital of the metal to π -anti-bonding orbitals of the α -diimine. The bands 3 and 5 are assigned to intraligand $\pi-\pi^*$ transitions of α -diimine. These assignments are supported by the blue shift of 10 to 20 nm of bands 2 and 4, and a shift of 0 to 5 nm of bands 3 and 5 from less polar to more polar solvents.

The above complexes show an additional band 1 (see Table 3) above 450 nm in the visible region. The position of the band 1 is highly dependent on the polarity of the solvent and shows a larger blue shift with increase in polarity of solvent (see Table 4). This is consistent with possessing a substantial ground state electric dipole which is reduced by this low energy transition from dioxolene to α -diimine [4]. This band also has a high extinction coefficient (see Table 3). These behaviours suggest it to be a charge-transfer transition involving the HOMO (highest occupied molecular orbital) mainly of dioxolenes and the LUMO (lowest unoccupied molecular orbital) exclusively of α -diimine [4, 6, 20]. Further support in favour of this charge-transfer band came when the two linear plots of Richard's parameter (E_T) [21], for different hydroxylic and non-hydroxylic solvents, versus band 1 maxima in kK of $[\text{Pt}(\text{biq})(\text{DHN})]$ in these solvents was obtained as shown in Fig. 2. Similar plots were obtained earlier for charge-transfer bands of $[\text{Pt}(\text{bipy})\text{Cl}_2]$ and $[\text{Fe}(\text{N}-\text{N})_2(\text{CN})_2]$ where N-N is 2,2'-bipyridine or 1,10-phenanthroline [19, 22].

The qualitative molecular orbital described for analogous mixed-ligand square planar nickel(II), palladium(II) and platinum(II) complexes [4, 6, 20] can be used to explain the above-mentioned trends. According to this model the energy of band 1 has decreased (see Table 2) when the catechol is replaced by 4-tert-butylcatechol in the mixed-ligand complexes. The HOMO of the 4-tert-butylcatechol complexes is expected to have a higher energy than the HOMO of the catechol complexes because of the electron releasing effect of the butyl group. In the 2,3-dihydroxynaphthalene complexes, the HOMO has a lower energy than the corresponding catechol complexes because of the electron withdrawing effect of the additional fused benzene ring in 2,3-dihydroxynaphthalene compared to catechol. In the 2,2'-biquinoline complexes, the

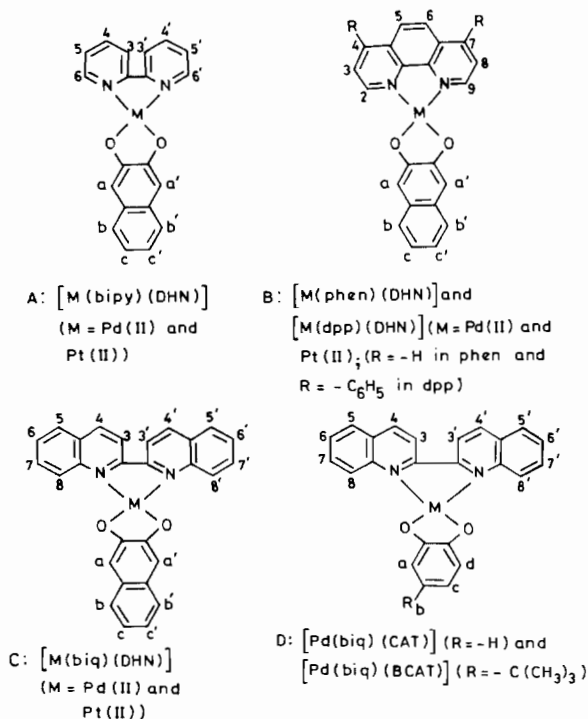


Fig. 1. A to D structures and numbering scheme of $[\text{M}(\text{N}-\text{N})(\text{X}-\text{X})]$ complexes.

TABLE 3. Electronic absorption spectral data of [M(N-N)(X-X)] complexes in DMF

Complex	Band maxima (kK)				
	Band 1	Band 2	Band 3	Band 4	Band 5
[Pd(bipy)(DHN)]	20.76 (1.60) ^a	28.90 (10.56)	30.48 (7.60)	33.33 (15.28)	37.26 (22.00)
[Pd(biq)(DHN)]	16.61 (2.12)	26.80 (22.20) 28.84 (28.50)	30.30 (sh) ^b	33.90 (sh)	36.36 (42.16)
[Pd(biq)(CAT)]	14.86 (1.53)	26.77 (26.43) 27.78 (sh)	29.41 (sh)	33.48 (sh)	36.85 (50.65)
[Pd(biq)(BCAT)]	13.93 (1.28)	26.75 (19.11) 27.78 (19.11)	29.41 (11.26)	32.72 (18.81)	36.85 (42.64)
[Pt(bipy)(DHN)]	19.71 (6.74)	29.04 (14.12)	30.47 (11.01)	33.16 (23.94)	37.40 (41.66)
[Pt(biq)(DHN)]	15.91 (0.76)	26.62 (3.80)	29.59 (33.50) 30.68 (40.49)	31.75 (35.80)	37.12 (44.32)
[Pt(bipy)(CAT)]	18.18 (5.00)	26.88 (1.70)	30.58 (4.10)	33.78 (26.10)	37.59 (11.70)
[Pt(bipy)(BCAT)]	17.54 (2.70)	22.33 (1.90)	30.40 (6.30)	33.45 (16.20)	37.18 (13.10)
[Pt(bipy)(DMT)]	17.64 (7.40)	27.17 (1.50)	32.36 (26.00)	34.88 (19.90)	37.31 (26.00)
[Pd(phen)(DHN)]	20.85 (3.56)	28.94 (19.50)	30.23 (12.29)	33.90 (sh)	35.46 (50.22)
[Pd(dpp)(DHN)]	20.86 (1.71)	27.03 (4.00)	28.99 (19.50) 30.77 (sh)	34.82 (44.54)	37.04 (sh)
[Pt(phen)(DHN)]	19.94 (7.88)	26.71 (4.85)	28.91 (19.34) 30.21 (12.62)	33.90 (sh)	36.13 (68.00)
[Pt(dpp)(DHN)]	19.22 (4.20)	28.82 (5.20)	31.25 (sh)	33.90 (sh)	35.11 (7.30) 36.10 (37.15)
[Pt(phen)(CAT)]	18.52 (4.50)	25.32 (sh)	27.78 (2.80)	33.67 (15.80)	37.31 (24.40)
[Pt(phen)(BCAT)]	17.73 (3.30)	25.00 (sh)	28.01 (2.30)	33.33 (sh)	37.31 (22.40)
[Pt(phen)(DMT)]	17.54 (4.60)	24.39 (2.30)	27.78 (sh)	30.77 (sh)	36.36 (20.00)

^aMolar extinction coefficient in $1 \text{ mol}^{-1} \text{ cm}^{-1} \times 10^{-3}$ are given in parentheses. ^bsh is shoulder.

TABLE 4. Solvent effect on frequency of maximum absorption (ν_{\max}) of band 1 in [M(N-N)(X-X) complexes

Complex	ν_{\max} (kK) ($1 \times 10^{-3} \text{ cm}^{-1}$)				
	Methanol	n-Butanol	Acetonitrile	Dimethylformamide	Chloroform
[Pd(bipy)(DHN)]	22.88	21.74	19.61	20.76	18.81
[Pd(biq)(DHN)]	21.74	a	17.02	16.61	15.38
[Pd(biq)(CAT)]	16.74	a	15.18	14.86	13.82
[Pd(biq)(BCAT)]	16.13	15.04	14.73	13.93	12.82
[Pt(bipy)(DHN)]	21.37	20.27	20.43	19.71	18.51
[Pt(biq)(DHN)]	17.25	16.00	16.45	15.91	14.71
[Pd(phen)(DHN)]	23.87	21.96	22.01	20.85	19.61
[Pd(dpp)(DHN)]	20.83	22.06	20.83	20.86	19.40
[Pt(phen)(DHN)]	21.50	20.92	20.87	19.94	18.52
[Pt(dpp)(DHN)]	20.66	21.28	20.62	19.22	19.51

^aComplex is insoluble in n-butanol.

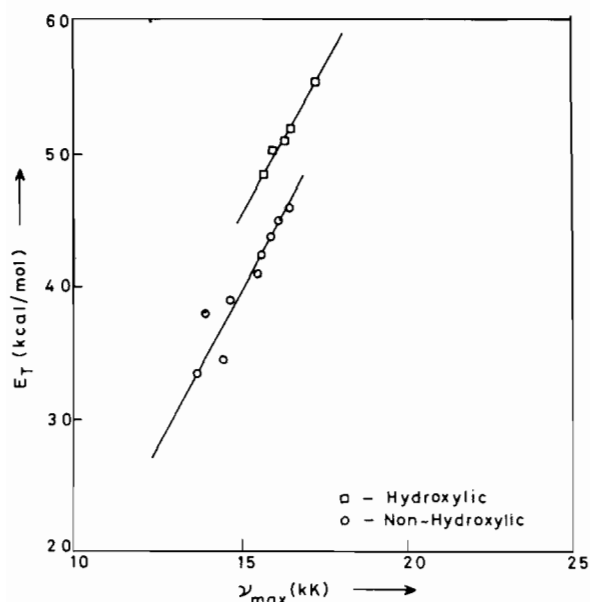


Fig. 2. Plot of E_T against ν_{\max} for the lowest energy charge transfer band of [Pt(biq)(DHN)].

energy of band 1 has decreased as compared to corresponding 2,2'-bipyridine complexes. This results in a lowering of the energy of the LUMO in 2,2'-biquinoline complexes compared to the corresponding 2,2'-bipyridine complexes because of an increased conjugation in 2,2'-biquinoline compared to 2,2'-bipyridine.

There is a small increase in the energy of the LUMO in 1,10-phenanthroline complexes as compared to the corresponding 2,2'-bipyridine complexes even though there is some increase in conjugation in 1,10-phenanthroline compared to 2,2'-bipyridine. The above statement seems to be true only in complexes containing dioxolenes because there is a small decrease in energy of the LUMO in the 1,10-phenanthrolineplatinum(II) complex containing 3,4-dimer-

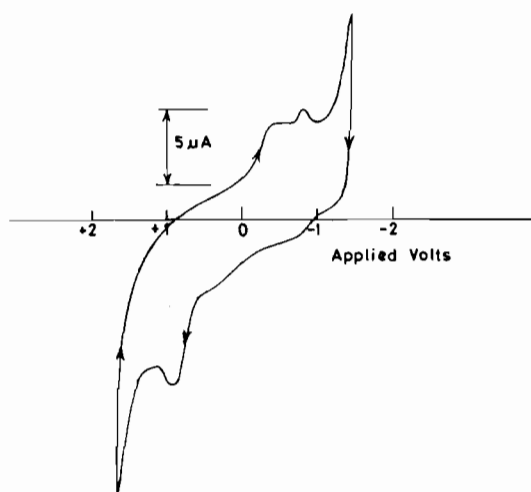
captotoluene compared to the corresponding 2,2'-bipyridineplatinum(II) complex. The above-mentioned behaviour of 1,10-phenanthroline complexes containing dioxolenes can be explained in terms of the different extent of backbonding from the d-orbital of the metal to the π^* orbitals of the α -diimine. In the 4,7-diphenyl-1,10-phenanthroline complexes, the two phenyl groups of 4,7-diphenyl-1,10-phenanthroline are perpendicular to the 1,10-phenanthroline plane [23], and, therefore, they are not expected to contribute to conjugation in the complexes. They can only contribute as electron withdrawing groups. Therefore, the energy of the LUMO is expected to be lower in 4,7-diphenyl-1,10-phenanthroline complexes than in the corresponding 1,10-phenanthroline complexes. The stronger ligand field in the platinum(II) complexes compared to the corresponding palladium(II) complexes [24] pushes the HOMO to a higher energy in the former complexes than in the latter complexes because some of the metal d character prevails in the HOMO. This explains the lower energy of band 1 in the platinum(II) complexes than in the corresponding palladium(II) complexes.

The cyclic voltammetry data of the mixed-ligand complexes in acetonitrile using tetra(n-butyl)ammonium perchlorate as supporting electrolyte are presented in Table 5. One of the representative voltammograms is given in Fig. 3. In general the mixed-ligand complexes show diffuse and irreversible two or some times three successive one-electron reduction and one sometimes two or three one-electron oxidation. The irreversibility of potentials was determined on the basis of the absence of a counter peak on the reverse scan or on the basis of a large difference in potentials between two counter peaks. However, the complex [Pt(phen)(DMT)] shows a reversible cathodic peak.

The potentials of the first reduction and oxidation of the mixed-ligand metal complexes may be related

TABLE 5. Electrochemical data of [M(N-N)(X-X)] complexes in CH₃CN^a

Complex	Reduction			Oxidation			
	I	I	III	I'	II'	III'	IV'
[Pd(bipy)(DHN)]	-0.75	-1.25		+0.90			
[Pd(biq)(DHN)]	-0.80	-1.45		+0.95			
[Pd(biq)(CAT)]	-0.40	-0.80		+0.75	+1.05		
[Pd(biq)(BCAT)]	-0.40	-1.15		+0.75			
[Pd(bipy)(DMT)]	-0.45	-0.72	-1.32	+0.68			
[Pt(bipy)(DHN)]	-0.85	-1.10		+0.80			
[Pt(biq)(DHN)]	-0.70	-1.00		+0.85			
[Pt(bpy)(CAT)]	-0.50	-0.98	-1.32	+0.45	+0.70	+1.20	
[Pt(bipy)(BCAT)]	-0.50	-1.00		+0.45	+0.70	+1.00	
[Pt(bipy)(DMT)]	-0.40	-1.30		+0.42	+0.55	+0.68	+0.97
[Pd(phen)(DHN)]	-0.70	-1.25		+0.98	+1.20		
[Pd(dpp)(DHN)]	-0.35	-0.80		+0.92			
[Pd(phen)(TSA)]	-0.45	-0.78	-1.25	+0.87	+1.04	+1.50	
[Pt(phen)(DHN)]	-0.70	-1.38		+0.82	+1.45		
[Pt(dpp)(DHN)]	-0.45	-1.25		+0.75			
[Pt(phen)(CAT)]	-0.50	-1.35		+0.45	+0.72		
[Pt(phen)(BCAT)]	-0.45	-1.30		+0.40	+0.78	+1.10	
[Pt(phen)(DMT)]	-0.43	-1.30		+0.70	+0.95		

^aPotentials in V vs. Ag/AgCl.Fig. 3. Cyclic voltammogram of 3 mM of [Pd(dpp)(DHN)] in 0.1 M (C₄H₉)₄NClO₄ in acetonitrile, scan rate 0.2 V s⁻¹ at 6 mm outer diameter platinum electrode; potential in V vs. Ag/AgCl.

to the nature of the orbitals involved in these redox processes. These orbitals are the HOMO consisting exclusively of α -diimine [4, 6, 20], and they are also involved in the charge-transfer transition (band 1) as described above. In [Pd(biq)(CAT)] and [Pd(biq)(BCAT)] the first oxidation potential has a much smaller positive value and the first reduction potential has a smaller negative value than [Pd(biq)(DHN)]. This can be interpreted in terms of the large increase

in the HOMO energy and the small decrease in the LUMO energy in the former complexes compared to the latter complex. These variations of HOMO and LUMO energies are in accord with the band 1 red shift in the former complexes compared to the latter complex. A similar effect is seen in the [Pt(phen)(X-X)] and [Pt(bipy)(X-X)] complexes. The effect of substitution on catechol in mixed-ligand metal complexes is small for the energy of band 1 and negligible for the electrochemical data.

The [M(dpp)(DHN)] complexes have much smaller negative values for the first reduction potential than [M(phen)(DHN)]. This is due to the electron withdrawing nature of the substituted phenyl groups in 4,7-diphenyl-1,10-phenanthroline. A similar behaviour was observed earlier in Fe(phen)₃²⁺ and Fe(dpp)₃²⁺ [23]. However, the absorption band 1 positions in [M(phen)(DHN)] and [M(dpp)(DHN)] are similar. The observed differences in redox potentials of an irreversible electron transfer process are controlled both by kinetic and thermodynamic parameters [25, 26], whereas the absorption band 1 position is totally a thermodynamic parameter. However, the oxidation potentials of these complexes are similar showing the HOMO is mainly from X-X ligands. [M(bipy)(DHN)] and [M(biq)(DHN)] show a considerable change in the band 1 position but they have no change in redox potentials. These observations are not explained by the above model.

The electronic structure of the above mixed-ligand metal complexes is very similar to the analogous mixed-ligand metal complexes reported earlier [6–8]

because they have a similar spectroscopic behaviour as well as analogous solvatochromatic properties of absorption bands. The low-energy charge-transfer absorption bands and one-electron redox potentials of these complexes are interpreted in terms of a qualitative MO model.

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