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Spectral and photophysical properties of mono and dinuclear Pt(II) and Pd(II) complexes: An unusual emission behaviour

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Abstract

Eight mononuclear complexes of the formula [M(N-N)(DHB)] and two binuclear complexes of the formula [M₂(BPY)₂(THB)] {where M = Pd(II) or Pt(II), N-N = 2,2'-bipyridine (BPY), 2,2'-biquinoline (BIQ), 4,7-diphenyl-1,10-phenanthroline (DPP), 1, 10-phenanthroline (PHEN); DHB = dianion of 3,4-dihydroxybenzaldehyde and THB = tetraanion of 3,3',4,4'-tetrahydroxy benzaldazine} were prepared and their electrochemical, spectral and photophysical properties were examined. These complexes were characterized by chemical analysis, IR and proton NMR spectroscopy. A detailed study on the absorption spectroscopy of these complexes was made. These complexes were found to show a low-energy solvatochromic ligand-to-ligand charge-transfer (LLCT) band. The electronic energies of these bands have been analyzed and compared with electrochemical data. Emission behaviour of the complexes of the series, [Pt(N-N)(DHB)], [Pt(N-N)(DHBA)] {where DHBA is the dianion of 3,4-dihydroxybenzoic acid} and [Pt₂(BPY)₂(THB)] was also investigated. These platinum complexes were found to emit from a low-energy state at low temperature and a high-energy state at room temperature. Photophysics of these complexes is also discussed. © 2004 Elsevier Ltd. All rights reserved.

Keywords: LLCT; Luminescence; Phosphorescence; Pt(II) and Pd(II)

1. Introduction

Luminescent transition metal complexes have fascinated photochemists for many decades [1], mainly because of the special features associated with these complexes such as visible light absorption, photoluminescence, long life times and relative inertness toward unimolecular photochemistry [1f]. Growth in this area has been driven by rapid advances in the techniques of studying excited-state transient species and in the theory of photoinduced electron transfer, solar energy conversion, supramolecular assemblies, photocatalysis, nonlinear optics, photonic molecular devices and photoluminescent probes of biological systems [2-7]. By far most work has been carried out on polypyridine complexes of d⁶ metal ions [8] such as Ru(II), Os(II) and Re(I), but not on the d⁸ metal complexes such as Pt(II) or Pd(II). Some of the early studies were on Pt(II) complexes such as $[PtX_4]^{2-}$ {X = halide}, $[Pt(diimine)X_2]$ and [Pt(diimine)]²⁺, for which emission was observed only in frozen solvent glasses or in the solid state [9]. However, a few reports on photophysical properties of d⁸ Pt(II) complexes of diimine in solution are available [10–15]. Three classes of Pt(II) diimine complexes showing fluid solution luminescence are distinguished by the nature of their emissive triplet excited state, namely: (1) diimine localized $\pi - \pi^*$, (2) metal-to-ligand(diimine) charge transfer (MLCT) and (3) mixed metal ligand-to-ligand charge transfer or metal-mediated

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ligand-to-ligand charge transfer (MMLLCT) or ligandto-ligand charge transfer (LLCT). In all these cases the LUMO is predominantly centered on the diimine ligand.

Square-planar complexes containing both easily oxidisable and reducible ligands were found to show a LLCT transition [16]. These transitions were highly solvatochromic, of which some of them exhibit the remarkable property of being luminescent in solution [17]. Metal complexes possessing such a transition have become the focus for numerous photochemical studies due to large molar absorptivity of the transition [16]. The LLCT excited states had previously been noted in some Zn(II) and Pt(II) complexes containing both diimine and aromatic thiolate (dithiolate) ligands [16c,16f]. Dance and Miller [16a] described the observation of a LLCT band for the first time in a Ni(II) complex containing *α*-diimine and dithiolate. In general, both electron-donating substituents on the thiolate and electron-withdrawing substituents on the diimine ligands would lower the LLCT transition energy. On the contrary, electron-withdrawing groups on the thiolate and electron-donating substituents on the diimine increase the transition energy. Thus, selective fine tuning of this excited state could be achieved by altering the ligands (diimine or dithiolate) or changing the substituents on the ligand(s) or the metal ion(s) [16,17].

The LLCT transitions have also been reported for a variety of d^8 metal complexes with catecholate and α -diimine ligands [18], where the charge transfer takes place from the catecholate ligand to the diimine ligand. Here too, the electron-withdrawing substituents on the diimine and the electron-donating substituents on the catechol lower the LLCT transition energy and electron-donating substituents on the diimine and the electron-withdrawing substituents on the catechol increase the LLCT transition energy. However, the solution-state emission from these complexes has not been reported. Many of them were found to be potential candidates for generation of singlet molecular oxygen $({}^{1}O_{2})$ since they produce ¹O₂ upon irradiation at the LLCT band [18b,18c]. Here we report, for the first time, the solution-state luminescence of such complexes. We also report the spectral and electrochemical behaviour of these complexes. An attempt to make a correlation between redox potentials and the energy of the absorption maxima is made. In addition, we synthesized two dinuclear complexes for comparison of the electronic properties since dinuclear complexes have been known to luminesce at higher wavelength compared to related monomers. It has been shown that dinuclear complexes possess a low-lying excited state due to a large decrease in the energy of the lowest π^* orbital of the bridging ligands upon complexation [3]. We also report the solvatochromic LLCT transition and solution state luminescence of these complexes.

The various diimines used are 4,7-diphenyl-1,10phenanthroline, 2,2'-bipyridine, 2,2'-biquinoline and 1,10-phenanthroline. The metal ions used are Pt(II) and Pd(II). 3,4-Dihydroxybenzaldehyde and 3,4-dihydroxybenzoic acid are used as the dianionic ligand. 3,3',4,4'-Tetrahydroxybenzaldazine is used as the tetraanionic ligand to synthesise the dinuclear complexes.

2. Experimental

2.1. Starting materials

Potassium tetrachloroplatinate(II), palladium chloride, 1,10-phenanthroline monohydrate, 4,7-diphenyl-1,10-phenanthroline (Loba-Chemie Indoauatranal Co., India), 2,2'-biquinoline, potassium hydroxide (Merck, India), 3,4-dihydroxybenzoic acid, 3,4-dihydroxybenzaldehyde (Fluka AG, Switzerland), hydrazine hydrochloride, ammonia, acetic acid (s.d.fine-CHEM Ltd., India) and 2,2'-bipyridine (Glaxo Industries, India) were bought, of reagent grade and used as such. The reagent grade solvents were purified before use by standard procedures [19]. Solvents of spectroscopic grade were used for cyclic voltammetry and spectroscopic measurements.

2.2. Physical measurements

The chemical analyses of carbon, hydrogen and nitrogen for the complexes were performed using a Carlo Erba Strumentazion Elemental Analyzer, Model 1106, at R.S.I.C., Central Drug Research Institute, Lucknow. The IR spectra of the complexes in KBr pellets were recorded with a Nicolet 170-Sx FT-IR spectrophotometer in the region $4000-600 \text{ cm}^{-1}$. Electronic absorption spectra of the complexes in various solvents were obtained using a Shimadzu UV-265 UV-VIS spectrophotometer. The proton nuclear magnetic resonance (¹H NMR) spectra of the complexes were acquired using a Varian VXR-300s NMR spectrometer in deuterated dimethyl sulfoxide $[(CD_3)_2SO]$. Tetramethylsilane was used as the internal reference. All the spectra were recorded in the range of 0-11 ppm. The cyclic voltammograms of the complexes in acetonitrile ($\sim 10^{-3}$ M) containing 0.1 M tetra(n-butyl)ammonium hexafluorophosphate as supporting electrolyte were obtained on a Model CV-IB Bioanalytical Cyclic Voltammetry apparatus equipped with an Omnigraphic 2000 Recorder. A single compartment cell was employed with an Ag/AgCl reference-electrode (-0.041 V versus standard calomel)electrode, SCE), a platinum wire counter electrode and a platinum working electrode (6 mm outer diameter). The scan rate used was 200 mV/s. The solutions were degassed for 15 min before recording the cyclic voltammogram. Room-temperature excitation and luminescence spectra of the metal complexes were recorded in a Spex spectrofluorimeter equipped with a Hamamadzu R928 photomultiplier tube (PMT). The PMT was cooled externally by circulating cold water. The emission spectra were corrected for excitation lamp intensity variation and solvent emission. The fluorescence quantum yields were measured by an optically dilute method [24] using tryptophan in water as a standard [25]. The quantum yield values were corrected for solvent refractive index. Fluorescence lifetime measurements were carried out by the single photon counting technique using a nanosecond fluorescence spectrometer from Applied Photophysics (model SP-170) with a bright and stable nanosecond flash-lamp operating at frequencies up to 200 kHz. The lamp was filled with nitrogen gas. The PMT type XP 2020Q was used for photodetection. Output of the multichannel analyzer was analyzed for single, double or multi exponential decay functions. The solutions were excited at 296, 316 or 337 nm. Phosphorescence measurements were made using a SPEX 1934C phosphorimeter with a RCA C13034 photomultiplier attachment having the facility to provide corrected emission spectra. Metal complexes dissolved in EPA mixture (10^{-6} M) were frozen in liquid nitrogen (77 K) in a 10 mm quartz cuvette and the spectra were recorded using different wavelengths of excitation.

2.3. Synthetic procedures

 $[M(N-N)Cl_2]$ {where M = Pd(II) or Pt(II) and N-N is 2,2'-bipyridine (BPY), 2,2'-biquinoline (BIQ), 4,7-diphenyl-1,10-phenanthroline (DPP) and 1,10-phenanthroline (PHEN)} were prepared by the reported procedures [20] and characterized by the methods from the literature [21,22].

2.3.1. [Pd(BPY)(DHB)] (1)

0.2 mmol of $[Pd(BPY)Cl_2]$ was dissolved in 25 cm³ of hot acetonitrile (60 °C). The solution was filtered while hot to remove any undissolved material. To this 0.2 mmol of H₂DHB dissolved in 1.6 cm³ of 0.25 N KOH in methanol was added slowly and stirred for 30 min at the same temperature. Then the solution was cooled to room temperature and kept in a refrigerator overnight to obtain crystals of the complex. The compound was filtered and washed with small amounts of cold acetonitrile, water and methanol successively and dried in a vacuum desiccator over anhydrous calcium chloride. The compound was recrystallized from DMF and 70% yield was obtained. ¹H NMR [(CD₃)₂SO]: 8.58 (d, 2H, 3, 3'), 8.36 (dt, 2H, 4, 4'), 7.81 (t, 2H, 5, 5'), 8.64 (d, 2H, 6, 6'), 6.92 (dd, 1H, B), 6.77 (d, 1H, C), 6.46 (d, 1H, A), 9.5 (s, 1H, D). Anal. Calc. for C₁₇H₁₂N₂O₃Pd: C, 51.21; H, 3.03; N, 7.02. Found: C, 50.87; H, 3.05; N, 6.98%.

2.3.2. [Pd(PHEN)(DHB)] (2)

[Pd(PHEN)Cl₂] (0.2 mmol) was dissolved in 50 cm³ of DMF. To this, 0.2 mmol of H₂DHB dissolved in 1.6 cm³ of 0.25 N KOH in methanol was added slowly. The solution was stirred for 30 min. Then the solution was evaporated to 5 cm³ and cooled overnight. The precipitate formed was filtered and recrystallized from DMF and dried in a vacuum desiccator over anhydrous CaCl₂. The yield obtained was 45%. ¹H NMR [(CD₃)₂SO]: δ 8.85 (d, 2H, 2, 9), 8.91 (d, 2H, 4, 7), 8.23 (s, 2H, 5, 6), 8.08 (m, 2H, 3, 8), 6.64 (d, 1H, B), 6.68 (s, 1H, C), 6.39 (d, 1H, A), 9.5 (s, 1H, D). *Anal.* Calc. for C₁₉H₁₂N₂O₃Pd: C, 53.98; H, 2.86; N, 6.63. Found: C, 53.54; H, 2.85; N, 6.59%.

2.3.3. [Pd(BIQ)(DHB)](3)

This complex was prepared according to the protocol given for **1**, replacing [Pd(BIQ)Cl₂] with [Pd(BPY)Cl₂]. The yield obtained was 60%. ¹H NMR [(CD₃)₂SO]: δ 9.35 (d, 1H, 3), 9.25 (d, 1H, 3'), 9.01 (d, 2H, 4, 4'), 8.85 (d, 2H, 5, 5'), 8.23 (d, 2H, 6, 6'), 7.89 (t, 2H, 7, 7'), 8.07 (m, 2H, 8, 8'), 6.92 (dd, 1H, B), 6.82 (d, 1H, C), 6.51 (d, 1H, A), 9.55 (s, 1H, D). *Anal.* Calc. for C₂₅H₁₆N₂O₃Pd: C, 60.19; H, 3.23; N, 5.62. Found: C, 59.80; H, 3.25; N, 5.66%.

2.3.4. [Pd(DPP)(DHB)] (4)

The complex was prepared by the procedure described for **2** using $[Pd(DPP)Cl_2]$ in place of $[Pd(PHEN)Cl_2]$. The yield obtained was 52%. ¹H NMR $[(CD_3)_2SO]$: δ 8.89 (m, 2H, 2, 9), 7.74 (s, 2H, 4, 7), 7.88 (s, 2H, 5, 6), 7.66 (m, 2H, 3, 8), 6.66 (d, 1H, B), 6.49 (s, 1H, C), 6.17 (d, 1H, A), 9.40 (s, 1H, D). *Anal.* Calc. for $C_{31}H_{20}N_2O_3Pd$: C, 64.76; H, 3.51; N, 4.87. Found: C, 64.96; H, 3.49; N, 4.86%.

2.3.5. [*Pt*(*BPY*)(*DHB*)] (5)

[Pt(BPY)Cl₂] (0.2 mmol) was dissolved in 25 cm³ of DMF and filtered. To this 0.2 mmol of H₂DHB dissolved in 1.6 cm³ of 0.25 N KOH in methanol was added. The solution was stirred for 24 h at 60 °C, then the solvent was evaporated at 40 °C. The crude product obtained was recrystallized from chloroform and dried in a vacuum desiccator over anhydrous calcium chloride. The yield obtained was 62%. ¹H NMR [(CD₃)₂SO]: 8.55 (d, 2H, 3, 3'), 8.38 (dt, 2H, 4, 4'), 7.78 (t, 2H, 5, 5'), 9.08 (d, 2H, 6, 6'), 6.96 (d, 1H, B), 6.94 (s, 1H, C), 6.64 (d, 1H, A), 9.6 (s, 1H, D). *Anal.* Calc. for C₁₇H₁₂N₂O₃Pt: C, 41.89; H, 2.48; N, 5.75. Found: C, 41.60; H, 2.45; N, 5.79%.

2.3.6. [Pt(PHEN)(DHB)] (6)

This complex was prepared by the method described for **5** using [Pt(PHEN)Cl₂] instead of [Pt(BPY)Cl₂]. The yield obtained was 42%. ¹H NMR [(CD₃)₂SO]: δ 9.59 (d, 2H, 2, 9), 8.99 (d, 2H, 4, 7), 8.23 (s, 2H, 5, 6), 8.12 (q, 2H, 3, 8), 6.94 (d, 1H, B), 6.90 (s, 1H, C), 6.60 (d, 1H, A), 9.62 (s, 1H, D). *Anal.* Calc. for $C_{19}H_{12}N_2O_3Pt$: C, 44.62; H, 2.37; N, 5.48. Found: C, 45.21; H, 2.35; N, 5.48%.

2.3.7. [*Pt*(*BIQ*)(*DHB*)] (7)

Preparation of this complex was made possible by following the procedure given for **5** using [Pt(BIQ)Cl₂] instead of [Pt(BPY)Cl₂]. The yield obtained was 62%. ¹H NMR [(CD₃)₂SO]: δ 9.49 (d, 2H, 3), 9.40 (d, 1H, 3'), 8.94 (d, 2H, 4, 4'), 8.19 (d, 2H, 5, 5'), 8.03 (d, 2H, 6, 6'), 7.85 (dt, 2H, 7, 7'), 8.64 (m, 2H, 8, 8'), 6.96 (d, 1H, B), 6.94 (s, 1H, C), 6.64 (d, 1H, A), 9.63 (s, 1H, D). *Anal.* Calc. for C₂₅H₁₆N₂O₃Pt: C, 51.11; H, 2.75; N, 4.77. Found: C, 51.27; H, 2.75; N, 4.80%.

2.3.8. Pt(DPP)(DHB) (8)

The complex was prepared according to the procedure described for **5** using [Pt(DPP)Cl₂] in place of [Pt(BPY)Cl₂]. The yield obtained was 48%. ¹H NMR [(CD₃)₂SO]: δ 9.09 (t, 2H, 2, 9), 7.79 (s, 12H, 4, 7, 3, 8), 7.79 (s, 2H, 5, 6), 6.83 (m, 2H, B, C), 6.47 (d, 1H, A), 9.56 (s, 1H, D). *Anal.* Calc. for C₃₁H₂₀N₂O₃Pt: C, 56.11; H, 3.04; N, 4.22. Found: C, 55.96; H, 3.01; N, 4.18%.

2.3.9. Synthesis of 3,3',4,4'-tetrahydroxybenzaldazine (H_4THB)

A solution of H₂DHB (276 mg, 2 mmol in 10 cm³ of methanol) was added dropwise to a solution containing a mixture of 0.05 cm³ of hydrazinehydrochloride, 9 cm³ of distilled water and 1.5 cm³ of concentrated ammonia solution. The contents were stirred for 3h at room temperature, then the solution was neutralized with 1N acetic acid to remove excess ammonia and cooled to get yellow crystals of the compound. The product was recrystallized from 50% methanol and the yield was 62%. The purity of the compound was checked using TLC. ¹H NMR [(CD₃)₂SO]: δ 9.54 (s, 2H, E, E'), 9.25 (s, 2H, F, F'), 8.46 (s, 2H, D), 7.29 (d, 2H, C), 7.08 (dd, 2H, B), 6.81 (d, 2H, A). *Anal.* Calc. for C₁₄H₁₂N₂O₄: C, 61.76; H, 4.44; N, 10.29. Found: C, 62.02; H, 2.49; N, 10.21%.

2.3.10. $[Pd_2(BPY)_2(THB)]$ (9)

This complex was prepared according to the method reported for **1** by adding 0.1 mmol of H₄THB instead of 0.2 mmol of H₂DHB. The compound was recrystallized twice from acetonitrile and dried in a vacuum desiccator over anhydrous calcium chloride. The yield was 25%. ¹H NMR [(CD₃)₂SO]: δ 8.52 (d, 2H, 3, 3'), 8.31 (dt, 4H, 4, 4'), 7.78 (m, 4H, 5, 5'), 8.59 (d, 4H, 6, 6'), 6.87 (dd, 2H, B), 6.72 (d, 2H, C), 6.41 (d, 2H, A), 9.52 (s, 2H, D). *Anal.* Calc. for C₃₄H₂₄N₆O₄Pd₂: C, 51.47; H, 3.05; N, 10.59. Found: C, 51.27; H, 3.05; N, 10.57%.

2.3.11. $[Pt_2(BPY)_2(THB)]$ (10)

[Pt(BPY)Cl₂] (0.2 mmol) was dissolved in 25 cm³ DMF and filtered. To this 0.1 mmol of H₄THB dissolved in 1.6 cm³ of 0.25 N KOH in methanol was added. The solution was stirred for 24 h at 60 °C, then the solvent was evaporated at 40 °C. The crude product obtained was recrystallized from chloroform and dried in a vacuum desiccator over anhydrous calcium chloride. The yield obtained was 62%. ¹H NMR [(CD₃)₂SO]: δ 8.58 (d, 2H, 3, 3'), 8.40 (d, 4H, 4, 4'), 7.83 (m, 4H, 5, 5'), 9.48 (d, 4H, 6, 6'), 6.94 (dd, 2H, B), 6.65 (d, 2H, C), 6.65 (d, 2H, A), 9.6 (s, 2H, D). *Anal.* Calc. for C₃₄H₂₄N₆O₄Pt₂: C, 42.07; H, 2.49; N, 8.66. Found: C, 41.89; H, 2.53; N, 8.72%.

The complexes [Pt(BPY)(DHBA)] (11), $[Pt(PHEN)-(DHBA)] \cdot H_2O$ (12) [Pt(BIQ)(DHBA)] (13) and $[Pt(DPP)(DHBA)] \cdot H_2O$ (14) were prepared and characterized as reported in the literature [23].

3. Results and discussion

3.1. Syntheses and characterization

Eight complexes of the formula, [M(N-N)(DHB)]{where M = Pd(II) or Pt(II), N-N = 2,2'-bipyridine (BPY), 2,2'-biquinoline (BIQ), 4,7-diphenyl-1,10-phenanthroline (DPP), 1,10-phenanthroline (PHEN) and DHB = dianion of 3,4-dihydroxybenzaldehyde (H₂DHB)} were prepared and characterized. In general these complexes were prepared by reacting stoichiometric quantities of the starting material, $[M(N-N)Cl_2]$ with H₂DHB in the presence of an appropriate amount of KOH under a nitrogen atmosphere. An illustrative example of the synthesis of [M(BPY)(DHB)] is shown in Scheme 1.

The various complexes prepared are [Pd(BPY)(DHB)] (1), [Pd(PHEN)(DHB)] (2), [Pd(BIQ)-(DHB)] (3), [Pd(DPP)(DHB)] (4), [Pt(BPY)(DHB)] (5), [Pt(PHEN)(DHB)] (6), [Pt(BIQ)(DHB)] (7) and [Pt(DPP)(DHB)] (8).

The tetradentate ligand H_4 THB was synthesized by coupling two molecules of H_2 DHB with hydrazinehydrochloride in the presence of liquid ammonia as depicted in Scheme 2.

Two complexes of the formula $[M_2(BPY)_2(THB)]$ {where M is Pd(II) or Pt(II) and BPY is 2,2'-bipyridine and THB is the tetraanion of tetrahydroxy benzaldazine} were prepared using the starting material H₄THB. The complexes prepared were $[Pd_2(BPY)_2-(THB)]$ (9) and $[Pt_2(BPY)_2(THB)]$ (10). Four more platinum complexes, namely [Pt(BPY)(DHBA)] (11), $[Pt(PHEN)(DHBA)] \cdot H_2O$ (12), [Pt(BIQ)(DHBA)] (13) and $[Pt(DPP)(DHBA)] \cdot H_2O$ (14) were prepared for luminescence studies, according to the reported procedure [23].



Scheme 1. Synthesis of [M(N-N)(DHB)] complexes.



Scheme 2. Synthesis of H₄THB.

Changes in the IR spectra in the ligand segment of the [M(N-N)(DHB)] complexes are compared with that of the parent chloro compounds of the formula [M(N-N)Cl₂], as well as with the free ligands. The ring frequency of the α -diimine moiety is shifted to higher frequency on complexation as compared to the free ligand. The presence of two additional sharp bands around 1250 and 1460 cm^{-1} confirms the bonding of DHB to the metal ion through ionized hydroxyl groups [26,27]. The band at 1460 cm^{-1} is due to the skeletal stretching vibration of the aromatic ring of DHB and the band at 1250 cm⁻¹ corresponds to the C–O stretching vibration of DHB. In the case of binuclear complexes, the IR spectra show a peak around 1560 cm^{-1} due to the – CH=N- group. There are strong peaks at 1275 cm^{-1} (which is due to the -C-O- stretching) and around 1475 cm^{-1} (which is due to the aromatic ring stretching of THB). Observation of these two peaks indicates the binding of THB to the metal ion through the -O⁻ group.

The ¹H NMR spectra of the complexes are compared with the parent dichloro compounds in order to determine the bonding mode and stoichiometry of the complexes. The signals are assigned on the basis of chemical shifts and spin-spin interaction. The structure and numbering scheme of the ligand protons of the complexes are given in Figs. 1 and 2. The α -diimine protons of the complexes generally experience upfield shifts when compared to the parent chloro compound. This could be due to stronger binding of DHB to the metal ion than the chloride ions, or more back bonding from the metal d-orbital to π^* orbitals of the α -diimine ligands as compared to chloride ions [20c,28]. The upfield shift is remarkable (0.48 and 0.93 ppm for 1 and 5, respectively) for the $H_{6,6'}$ protons of [M(BPY)(DHB)] complexes. The H_{2,9} protons of [M(PHEN)(DHB)] complexes experience maximum upfield shift (0.51 and 0.1 ppm for 2 and 6, respectively). A similar trend is also observed in [M(DPP)(DHB)] complexes. The H_{2.9} protons of 4 and 8 show upfield shifts of 0.52 and 0.66 ppm, respectively. The phenyl protons in the fourth and seventh positions experienced little upfield shifts when compared to their parent chloro compounds. In the ¹H NMR spectra of [M(BIQ)(DHB)] complexes, all the protons of BIQ experience up- or downfield shifts except the $H_{6,6'}$ protons. The protons $H_{4,4'}$ and $H_{8,8'}$ of 3 experience downfield shifts of 0.25 and 0.33 ppm, respectively, whereas the $H_{5.5'}$ and $H_{7.7'}$ protons experience upfield shifts of 0.09 and 0.26 ppm correspondingly as compared to the parent chloro compound. The protons H_3 and $H_{3'}$ of complexes 3 and 6 appear as two separate doublets rather than a single doublet as in the parent chloro compound. This could be due to the fact that the compound lacks planarity in solution which



Fig. 1. Structure and numbering scheme of the protons of [M(N-N)(DHB)] and [Pt(N-N)(DHBA)] complexes.



Fig. 2. Structure and numbering scheme of the protons of H_4THB and $[M_2(BPY)_2(THB)]$ complexes.

makes the protons have different electronic environments. Thus, the protons H_3 and $H_{3'}$ could resonate at different frequencies. Similar behaviour was observed earlier in the case of [M(BIQ)(DHBA)] [23]. The free ligand, 3,4-dihydroxybenzaldehyde shows two peaks at 10.11 and 9.55 ppm due to the phenolic -OH protons, but they are absent in the metal complexes. All other protons (H_A, H_B, H_C and H_D) experience upfield shifts in the complexes as compared to the free ligand, indicating the bonding of DHB to the metal ions. Similarly, H₄THB shows two peaks for the four phenolic -OH protons at 9.54 and 9.29 ppm. These two peaks are absent in the metal complexes. The protons H_D, H_C and H_B experienc considerable upfield shifts in the complex as compared to the free ligand. The structure and numbering scheme of the protons in the ligand and complexes are given in Figs. 1 and 2. The ${}^{3}J$ (${}^{195}Pt-{}^{1}H$) couplings in these complexes have not been observed due to a decrease of chemical shielding anisotropy with an increase in the magnetic field strength [28].

These data suggest that both ligands are bonded to the metal ion in the mixed-ligand complexes. The integrated areas obtained for the protons of α -diimine and DHB indicate the stoichiometry of these complexes corresponds to [M(N-N)(DHB)]. Similarly, the proton ratio of BPY and THB indicate a stoichiometry of [M₂(BPY)₂(THB)]. The sharp ¹H NMR spectral signals observed in these complexes suggest them to be diamagnetic. The proton NMR spectral, the IR and the elemental analysis data confirm the synthesis and the structures assigned to them as shown in Figs. 1 and 2.

3.2. Electronic absorption spectra

The electronic absorption spectral data of these complexes are given in Table 1. A representative spectrum is shown in Fig. 3. The chloro complexes of the formula, [M(N-N)Cl₂] show four bands (bands are numbered in increasing order of energy), whereas the complexes of the formula [M(N-N)(DHB)] show five band maxima. The bands in the UV region have been assigned on the basis of band assignments of chloro complexes [20c,29,30]. Thus, the bands 2 and 4 have been assigned to charge-transfer transitions from a metal d-orbital to π -antibonding orbitals of the α -diimine (MLCT). Bands 3 and 5 are assigned as the intra-ligand π - π * transition of the α -diimine (IL). In addition, these complexes exhibit a band in the visible region, which is strongly dependent on the polarity of the solvent (band 1). The absorption maximum of this band is found to shift with a change of solvent. The energy of this band increases with an increase in the polarity of the solvent (hydroxylic as well as non-hydroxylic). The observed shift in band maxima to higher energy in solvents of increasing polarity is indicative of a polar ground state and nonpolar excited state as reported by Cummings and Eisen-

Table 1	
Electronic absorption spectral data of [M(N-N)(DHB)], [Pt(N-N)(DHBA)] and [M ₂ (BPY) ₂ (THB)] complexes in DMF at 298 1	K

Complex	Band maxima (λ_{max}/nm)							
	Band 1	Band 2	Band 3	Band 4	Band 5			
1	478 (3.73) ^a	364 (17.49)	316 (21.50)	304 (26.20)	266 (46.12)			
2	476 (3.07)	363 ^b (14.48)		300 (17.80)	270 (40.66)			
3	598 (2.42)	372 (38.57)	360 (38.57)	300 (19.62)	267 (72.60)			
4	492 (4.17)	350 (19.76)	325 (sh) ^c	293 (51.18)	267 (37.30)			
5	496 (8.22)	361 (17.39)	322 (16.87)	310 (sh)	272 (35.95)			
6	475 (1.65)	360 (25.24)	300 (sh)	271 (8.93)	264 (9.31)			
7	622 (2.86)	374 (18.30)	339 (28.62)	314 (28.96)	267 (51.75)			
8	518 (8.97)	360 (sh)	344 (21.75)	296 (45.82)	269 (47.12)			
9	465 (7.041)	362 (33.52)	316 (44.53)	304 (51.17)	266 (83.51)			
10	510 (5.66)	388 (17.99)	326 (34.85)	313 (32.97)	280 (65.59)			
11	510 (7.15)	330 (22.42)	305 (sh)	289 (35.63)	259 (29.03)			
12	512 (3.14)	325 (27.49)		280 (34.39)	265 (47.12)			
13	640 (1.74)	377 (36.50)	360 (sh)	327 (28.00)	266 (59.59)			
14	531 (1.45)	410 (sh)	333 (sh)	309 (sh)	274 (sh)			

^a Molar absorptivity in $\varepsilon \times 10^{-3}$ L mol⁻¹ cm⁻¹ is given in parentheses.

^b Broad band.

^c Shoulder.



Fig. 3. Electronic absorption spectrum of 6 in DMF.

berg [12b]. This is in contrast to the small degree of solvatochromism observed for the MLCT band of transition metal diimine complexes such as $[Ru(bpy)_3]^{2+}$ and related systems [8]. The effect of various solvents on the λ_{max} of this band is given in Table 2. An excellent correlation of absorption band energy with solvent polarity was found using Reichardt's scale [31]. The plots of Reichardt's parameter (E_T) of the solvents against absorption maxima gave two separate lines, one for hydroxylic solvents and the other for non-hydroxylic solvents [18,29,30]. A typical plot for **2** is given in Fig. 4. This band was not observed in a solution containing a 1:1 mixture of [M(N-N)Cl₂] and H₂DHB.

The energy of this band decreases when the α -diimine is changed from BPY to BIQ. However, small changes

were observed when N-N was replaced from BPY to PHEN or DPP. An increase in energy of this band was observed when compared to [M(N-N)(DHBA)] [23] and [M(N-N)(CAT)] [32]. Based on these observations this band has been assigned as a LLCT transition from the HOMO of DHB to the LUMO of α-diimine via the metal [23,32]. The observed trends in the energy of this band can also be explained based on the above assignment. Thus, the decrease in energy of [M(BIQ)(DHB)] complexes when compared to [M(BPY)(DHB)] complexes can be explained to be due to the additional fused rings on the bipyridine, which pulls down the LUMO to lower energy. The two phenyl groups are perpendicular to the plane of 1,10-phenanthroline in the DPP complexes and are therefore not expected to contribute much to conjugation in the complex [33]. Hence, there is a small change in the energy of transition between PHEN and DPP complexes. Because of the electron-withdrawing group (-CHO) on the phenyl ring of DHB, the HOMO of the complexes, [M(N-N)(DHB)] further drops to lower energy. Thus, the energy of transition for [M(N-N)(DHB)] complexes increases when compared to the unsubstituted catechol complexes, [M(N-N)(CAT)] or those substituted with a carboxylic group, [M(N-N)(DHBA)] complexes [23]. This band assignment is supported by the solvent studies. With the increase in polarity of the solvent, the HOMO is stabilized more and leads to an increase in the energy of transition [29,30]. The LLCT band of palladium complexes is at higher energy as compared to the platinum counterparts. This is due to increase in the ligand field of Pt(II) by 30–50% when compared to Pd(II).

The electronic spectra of the dinuclear complexes are similar to the mononuclear complexes. There is a little change in the position of the LLCT band but the molar

Table 2	
Effect of hydroxylic and non-hydroxylic solvents on the LLCT band of [M(N-N)(DHB)] complexes	

Solvent	Band maxima (λ_{max}/nm)							
	1	2	3	4	5	6	7	8
Ethylene glycol	416 (24.06) ^a	426 (23.49)	544 (18.38)	427 (23.43)	430 (23.26)	431 (23.19)	541 (18.48)	429 (23.33)
Methanol	421 (23.74)	431 (23.18)	555 (18.03)	440 (22.71)	437 (22.87)	433 (23.08)	559 (17.90)	483 (20.71)
Ethanol	444 (22.53)	439 (22.78)	568 (17.60)	448 (22.34)	454 (22.03)	443 (22.57)	581 (17.20)	492 (20.34)
<i>n</i> -Propanol	451 (22.16)	454 (22.01)	603 (16.58)	459 (21.81)	473 (21.16)	454 (22.01)	608 (16.45)	505 (19.81)
Acetonitrile	459 (21.80)	450 (22.23)	578 (17.31)	481 (20.79)	491 (20.35)	450 (22.23)	587 (17.03)	485 (20.62)
N,N-Dimethyl sulfoxide	468 (21.36)	464 (21.54)	588 (17.01)	484 (20.66)	478 (20.91)	464 (21.54)	602 (16.61)	510 (19.62)
N,N-Dimethyl formamide	478 (20.90)	476 (20.99)	598 (16.71)	492 (20.33)	496 (20.15)	476 (21.03)	622 (16.09)	518 (19.31)
Acetone	485 (20.61)	482 (20.76)	600 (16.68)	497 (20.14)	500 (20.01)	482 (20.76)	638 (15.68)	526 (19.00)
Dichloromethane	502 (19.94)	495 (20.20)	622 (16.09)	504 (19.83)	502 (19.94)	495 (20.20)	663 (15.09)	513 (19.51)
Chloroform	510 (19.61)	498 (20.07)	638 (15.68)	506 (19.78)	510 (19.61)	498 (20.07)	681 (14.68)	522 (19.16)

^a Band maxima in kK mol⁻¹ is given in parentheses.



Fig. 4. Plot of $E_{\rm T}$ vs. $v_{\rm max}$ for the LLCT band of 2.

extinction coefficient of this band is higher for the dimer as compared to the monomer, and the position of the MLCT band is considerably red-shifted in the dimer. Since the binuclear complexes were found be soluble in very few solvents, a complete solvent-studies could not be made.

3.3. Electrochemical studies

The cyclic voltammetric data of complexes 1-8 are given in Table 3. In general these complexes show diffuse, irreversible and successive two one-electron reductions and one quasi-reversible one-electron oxidation. Irreversibility of the reduction peaks was confirmed by the

Table 3							
Electrochemical	data	of	[M(N-N)(DHB)]	complexes	in	CH_3CN	at
298 K							

Complex	Reduction		Oxidation	
	I	II	Ι	II
1	-0.825^{a}	-1.213	0.750	0.950
2	-0.838	-1.250	0.725	0.950
3	-0.850	-1.250	0.700	
4	-0.950	-1.275	0.750	
5	-0.985	-1.270	0.725	
6	-0.900	-1.450	0.700	
7	-0.915	-1.250	0.780	
8	-0.875	-1.350	0.650	

^a Potentials in volts vs. Ag/AgCl.

absence of the peak in the reversible scan or by the large difference in potentials between two counter peaks. The general electron transfer series for the complexes can be represented by the following equations:

$$[\mathbf{M}(\mathbf{N}-\mathbf{N})(\mathbf{D}\mathbf{H}\mathbf{B})]^+ \stackrel{+e^-}{\underset{-e^-}{\longleftarrow}} [\mathbf{M}(\mathbf{N}-\mathbf{N})(\mathbf{D}\mathbf{H}\mathbf{B})]^0 \tag{1}$$

$$[\mathbf{M}(\mathbf{N}-\mathbf{N})(\mathbf{D}\mathbf{H}\mathbf{B})]^{0} \stackrel{+\mathbf{e}^{-}}{\underset{-\mathbf{e}^{-}}{\overset{-}}} [\mathbf{M}(\mathbf{N}-\mathbf{N})(\mathbf{D}\mathbf{H}\mathbf{B})]^{-1}$$
(2)

$$[\mathbf{M}(\mathbf{N}-\mathbf{N})(\mathbf{D}\mathbf{H}\mathbf{B})]^{-1} \stackrel{+\mathbf{e}^{-}}{\stackrel{-}{\rightleftharpoons}} [\mathbf{M}(\mathbf{N}-\mathbf{N})(\mathbf{D}\mathbf{H}\mathbf{B})]^{-2}$$
(3)

The formation of a charge transfer to the α -diimine excited state formally involves the oxidation of the HOMO and reduction of the α -diimine-based LUMO [12b]. Thus, the potentials of the first reduction and oxidation of the complexes can be related to the nature of the orbitals in these redox processes. These orbitals are the LUMO, consisting exclusively of α -diimine [34,35], and the HOMO of DHB, and they are involved in the charge-transfer transition (band 1) as described above. The first reduction potential of [M(BIQ)(DHB)] complexes lies at lower values as compared to [M(BPY)(DHB)] complexes. This can be explained in terms of the electron-withdrawing effect with increased delocalizing effect of additional fused rings in the former

compared to the latter. Similarly, the oxidation potentials of [M(BIQ)(DHB)] are higher than that of the [M(BPY)(DHB)] counter parts. The [M(DPP)(DHB)] complexes have a much smaller negative value for the first reduction potential than [M(PHEN)(DHB)] complexes. This could be due to the electron-withdrawing nature of the substituted phenyl groups in DPP [33]. However, only a small change was noticed in the position of the absorption bands (band 1) of [M(PHEN)(DHB)] and [M(DPP)(DHB)]. The observed difference in redox potentials of an electron transfer process is normally controlled by both kinetic and thermodynamic parameters [36,37], whereas the absorption band position is purely thermodynamically controlled. Similar observations were found for another series of complexes [23]. Cyclic voltammograms on the dinuclear complexes could not be recorded due to insufficient solubility of these complexes in acetonitrile.

3.4. Luminescence studies

The luminescence studies of the complexes were carried out in acetonitrile at room temperature. These complexes do not show emission on excitation at the LLCT band at room temperature. However, these complexes were found to be luminescent at room temperature on excitation at the MLCT/ILCT band. Only the platinum derivatives were found to show emission at room temperature. This may be due to the lack of structural rigidity of the Pd(II) complexes as compared to the Pt(II) complexes. The parent dichloro complexes of Pt(II) did not show emission at room temperature. The luminescence band maxima of these complexes are given in Table 4. Representative luminescence and excitation spectra are given in Fig. 5(a) and (b). The energies of the MLCT (band 2) and IL (band 3) lie very close to each other in the electronic spectra of these complexes. On excitation at these bands, these complexes show luminescence at room temperature. The energy of the emission maxima of these complexes lies in the following order: $4 \sim 8 > 6 \sim 10 > 5 \sim 7 \sim 9$. This order can be explained in terms of π -conjugation. The difference in energy between 5, 7 and 9 is very small. This may be due to the only one additional double bond present in 5 and 9 as compared to 7. The difference in energy between 6, 10 and 5, 9 can be attributed to the presence of two additional phenyl groups in DPP. Similar behaviour has earlier been observed by Watts and Crosby [38] for ruthenium complexes. In the case of 4 and 8 the larger red shift in emission maximum is due to the additional fused rings in the BIQ system. The large Stokes shift observed in the excitation spectra of these complexes indicates that the ground state geometry of these complexes differs largely with the excited state. The quantum yields of luminescence (ϕ_L) of these complexes are included in Table 4. The $\phi_{\rm L}$ values were determined with reference

Photophysical data of [Pt(N-N)(DHB)], $[Pt_2(BPY)_2(THB)]$ complexes in CH_3CN

Complex	Luminescence maxima (λ_{max}/nm)	Luminescence excitation maxima (λ_{max}/nm)	τ^{a} (ns)	$\Phi_{\rm L}{}^{\rm a}$ (×10 ²)
5	364	294	2.40 8.68	0.188
6	368	291	2.80 7.30	0.278
7	419	333	4.28 4.29	0.295
8	416 398	355 319 284	3.49 10.70	0.409
10	470 422	370 336 295	9.20	0.204
11	364	291	1.40 8.77	0.881
12	363	290	1.53 8.74	0.232
13	422	332	3.80 5.60	0.292
14	414 394	350 319 299	4.80 12.20	2.788

^a Experimental error is less than 5%.

to tryptophan in water [25]. The DPP derivative is found to show a larger quantum yield than any other complex. Similar behaviour was earlier reported for DPP complexes of ruthenium [39].

Two of the complexes were tested for phosphorescence at low temperature. Both complexes 1 and 5 were found to show phosphorescence at 77 K. They were excited at various wavelengths to obtain the same spectrum. The phosphorescence spectrum of 5 is shown in Fig. 6. The phosphorescence spectrum of 5 shows a band around 600 nm which is due to the emission from the lowest excited state, namely the LLCT state as reported earlier for a similar complex [40].

The fluorescence lifetime measurements were done in acetonitrile. The fluorescence lifetime shows a bi-exponential decay. The multiple lifetimes found for these complexes suggest the possibility of more than one emitting state for these complexes. Multiple state luminescence has been reported for a number of metal complexes [41]. Hence, it is concluded that there is a mixing of MLCT and IL excited states as proposed by Balzani and co-workers [42] for a different set of Pt(II) complexes.



Fig. 5. (a) Luminescence spectrum of 7 in acetonitrile at 298 K. (b) Excitation spectrum of 7 in acetonitrile at 298 K.



Fig. 6. Phosphorescence spectrum of 5 in EPA glass at 77 K.

4. Conclusion

This study shows that various mixed-ligand complexes of Pt(II) and Pd(II) can exhibit a LLCT band. The platinum complexes of this series were found to emit from a low-energy state at low temperature and a high-energy state at room temperature.

Appendix A. Supplementary data

A representative lifetime trace is available from the publishers. Supplementary data associated with this arti-

cle can be found, in the online version at doi:10.1016/ j.poly.2004.09.029.

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