Synthesis, characterisation and absorption spectroscopy of mono and dinuclear complexes of platinum(II) and palladium(II)

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Two mononuclear complexes of the formula [M(bpy)(dhb)] and two dinuclear complexes of the formula [(M(bpy)Mthb)] (where M=Pd(II) or Pt(II), bpy is 2,2’-bipyridine, dhb is the dianion of 3,4-dihydroxybenzaldehyde and thb is the tetraanion of 3,3’,4,4’-tetrahydroxybenzaldazine) have been prepared and characterized by chemical analysis, IR and proton NMR spectroscopy. These complexes are found to show a low lying, solvent-dependent, ligand-to-ligand charge-transfer (LLCT) band. A comparison on the spectroscopic behaviour of mononuclear and dinuclear complexes is made.

Mixed-ligand complexes with a more readily oxidisable donor ligand and an acceptor ligand with energetically low-lying empty orbitals exhibiting an inter ligand-to-ligand charge-transfer transition (LLCT) have been investigated during the past decade. Metal complexes containing such electronic transition have become focus for numerous photochemical studies due to the large molar absorptivity of such transition. Selective fine tuning of an excited state is an added advantage of such transitions which can be achieved by changing either the ligand(s) or the metal ion(s). A number of mononuclear $d^4$ metal complexes with catecholate and α-dimine ligands were found to show the LLCT transition and exhibited a remarkable photochemical activity on irradiation at this LLCT band. However, very few dinuclear complexes of $d^5$ metal ion which show this typical LLCT transition have been reported in literature.

The above said considerations combined with the interest in spectroscopy have led to the synthesis and characterisation of new dinuclear and mononuclear complexes which exhibit LLCT transition. Here, 2,2’-bipyridine is used as the α-dimine ligand, 3,4-dihydroxybenzaldehyde is used as the dianionic ligand and 3,3’,4,4’-tetrahydroxybenzaldazine is used as the tetraionic ligand. The metal ions used are Pt(II) and Pd(II).

**Experimental**

Potassium tetrachloroplatinate(II), palladium chloride (Loba-Chemie Indoasian Co., India), 3,4-dihydroxybenzaldehyde, potassium hydroxide (Merck, India), 2,2’-bipyridine (Glaxo Industries, India) and hydrazine hydrochloride, ammonia and acetic acid (S.D. fine-chem Ltd., India) were of reagent grade and used as such. The reagent grade solvents were purified before use by standard procedures. Spectroscopic grade solvents were used for all measurements.

The starting material [M(bpy)Cl$_2$] (where M=Pd(II) and Pt(II)) was prepared and characterised by the literature method.

**Synthesis of complexes**

$[\text{Pd(bpy)}(\text{dhb})] \quad (1)$

$[\text{Pd(bpy)}\text{Cl}_2] \quad (0.2 \text{ mmol}, 66.6 \text{ mg})$ was dissolved in hot (60°C) acetonitrile (50 cm$^3$) and the yellow coloured solution was filtered while hot to remove any undissolved material. To this, 0.2 mmol (27.6 mg) of H$_2$dhb dissolved in 1.6 cm$^3$ of 0.25 $N$ KOH in methanol was added slowly with stirring. The solution...
was stirred for further 30 min at the same temperature during which the yellow coloured solution changed to deep red. The solution was then brought to room temperature and cooled to about 7°C. The dark red coloured crystals formed were filtered and washed with small amounts of cold water followed by cold methanol. The compound was dried in a vacuum desiccator over anhydrous calcium chloride. The yield obtained was 70%. The compound was insoluble in water but soluble in most of the organic solvents. 

[H NMR \[\{(CD_3)_2SO\}\]: 8.55 (d, 2H, 3,3'), 8.36 (dd, 2H, 4,4'), 7.81 (m, 2H, 5,5'), 9.12 (d, 2H, 6,6'), 6.90 (d, 1H, B), 7.76 (d, 1H, C), 6.77 (d, 1H, A), 9.50 (s, 1H, D). Anal: [Found: C, 50.87; H, 3.14; N, 6.35. Calc.: C, 51.21; H, 3.03; N, 7.03%] \[\Lambda_m\], 7 ohm⁻¹ cm⁻¹ mol⁻¹.] 

\[(Pt(bpy)(dhb)}\] (2)

\[Pt(bpy)(Cl)_2\] (0.2 mmol, 84.4 mg) was dissolved in 25 cm³ of DMF and filtered. To this, 0.2 mmol (27.6 mg) of H₂dhb dissolved in 1.6 cm³ of 0.25 N KOH in methanol was added slowly. The solution was stirred for 24 h at 60°C, during which the yellow coloured solution changed to brownish red. The solvent was then evaporated at 40°C. The brown coloured crude product obtained is recrystallised from chloroform and dried in a vacuum desiccator over anhydrous calcium chloride. The yield obtained is 55%. The compound was insoluble in water but soluble in most of the organic solvents. 

[H NMR \[\{(CD_3)_2SO\}\]: 8.55 (d, 2H, 3,3'), 8.38 (dt, 2H, 4,4'), 7.78 (m, 2H, 5,5'), 9.12 (d, 2H, 6,6'), 6.90 (d, 1H, B), 6.94 (d, 1H, C), 6.64 (d, 1H, A), 9.60 (s, 1H, D). Anal: [Found: C, 51.60; H, 2.43; N, 5.24. Calc.: C, 41.89; H, 2.48; N, 5.75%] \[\Lambda_m\], 5 ohm⁻¹ cm⁻¹ mol⁻¹.

3,3',4,4'-tetrahydroxymbenzaldehyde (H₂dhb)

3,4-Dihydroxybenzaldehyde (2 mmol, 276 mg) was dissolved in 10 cm³ of methanol. This was added dropwise to a solution of 0.05 cm³ of hydrazine hydrochloride in 9 cm³ of distilled water and 1.5 cm³ of conc. ammonium solution. The contents were stirred for 3 h at room temperature during which the light brown coloured solution changed to yellow. The solution was then neutralised with 1 N acetic acid to remove excess ammonia and kept at 7°C for 24 h to obtain yellow crystals of the compound. The product was recrystallised from 50% methanol and dried in vacuum desiccator. Yield: 62%. 

[H NMR \[\{(CD_3)_2SO\}\]: 9.58 (s, 2H, E,E'), 9.30 (s, 2H, F,F'), 7.31 (d, 2H, C,C'), 7.10 (dd, 2H, B,B'). 8.28 (d, 2H, A,A'), 8.45 (s, 2H, D,D'). Anal: [Found: C, 62.05; H, 4.56; N, 10.34. Calc.: C, 61.75; H, 4.44; N, 10.29%] m.pt, 174°C.]

\[(Pd(bpy)(thb)}\] (3)

\[Pd(bpy)(Cl)_2\] (0.2 mmol, 66.6 mg) was dissolved in hot (60°C) acetonitrile (50 cm³). The solution was filtered while hot to remove any undissolved material. To this 0.1 mmol (27.2 mg) of H₂thb dissolved in 1.6 cm³ of 0.25 N KOH in methanol was added slowly with stirring. The solution was stirred for further 30 min at the same temperature during which the yellow coloured solution changed to deep red. The solution was then brought to room temperature and the dark red coloured solution then filtered and recrystallised twice from acetonitrile and washed with small amounts of cold water followed by cold methanol. The compound was dried in a vacuum desiccator over anhydrous calcium chloride and the yield was 25%. The compound was soluble in DMSO, DMF, acetonitrile, ethanol, chloroform, methanol and CCl₄ but insoluble in most of the other solvents. 

[H NMR \[\{(CD_3)_2SO\}\]: 8.52 (d, 4H, 3,3'), 8.31 (dt, 4H, 4,4'), 7.78 (m, 4H, 5,5'), 8.59 (d, 4H, 6,6'), 6.72 (d, 2H, C,C'), 6.87 (dd, 2H, B,B'). 6.41 (d, 2H, A,A'), 9.52 (s, 2H, D,D'). Anal: [Found: C, 51.76; H, 2.76; N, 10.45. Calc.: C, 51.47; H, 3.05; N, 10.59%] \[\Lambda_m\], 4 ohm⁻¹ cm⁻¹ mol⁻¹.

\[(Pt(bpy)(thb)}\] (4)

\[Pt(bpy)(Cl)_2\] (0.2 mmol, 84.4 mg) was dissolved in 20 cm³ of DMF. To this, 0.1 mmol (27.2 mg) of H₂thb dissolved in 1.6 cm³ of 0.25 N KOH in methanol was added slowly. The solution was stirred for 24 h during which the yellow coloured solution changed to brownish red. Then the solution was evaporated to 5 cm³ at room temperature and cooled to about 7°C for 12 h. The dark brown solid formed was filtered and recrystallised twice from DMF and dried in a vacuum desiccator over anhydrous calcium chloride. The yield obtained was 23%. The compound was insoluble in most of the solvents but soluble in DMSO, DMF, CCl₄, acetonitrile, ethanol, chloroform and methanol. 

[H NMR \[\{(CD_3)_2SO\}\]: 8.58 (d, 4H, 3,3'), 8.40 (d, 4H, 4,4'), 7.83 (m, 4H, 5,5'), 9.48 (d, 4H, 6,6'), 6.65 (d, 2H, C,C'), 6.60 (dd, 2H, B,B'). 9.60 (s, 2H, A,A'), 9.60 (s, 2H, D,D'). Anal: [Found: C, 41.84; H, 2.55; N, 7.25. Calc.: C, 42.06; H, 2.49; N, 7.33%.] \[\Lambda_m\], 5 ohm⁻¹ cm⁻¹ mol⁻¹.

The chemical analyses of carbon, hydrogen and nitrogen for the complexes were performed using a Carlo Erba Strumentazione Elemental Analyser, Model...
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1106, at RSIC, CDRI, Lucknow. The conductivity measurements of $10^{-3}$ molar solution of the complexes in DMF were carried out using Toshniwal digital conductivity meter. A conductivity cell consisting of two platinum electrodes having cell constant 0.885 was used. The IR spectra of the complexes in KBr pellets were recorded with Nicolet 170-Sx FT-IR spectrophotometer in the region 4000-600 cm$^{-1}$. Electronic spectra of the complexes were recorded using a Shimadzu UV-265 UV-Vis recording spectrophotometer. The proton nuclear magnetic resonance (1H NMR) of the complexes were recorded with Varian VXR-300s NMR spectrometer in DMSO-d$_6$. TMS was used as the internal reference. All the spectra were recorded in the range of 0-10 ppm. Mass spectrum of the ligand was recorded on Shimadzu QP 1000 spectrometer, at an ionisation potential of 70 eV.

Results and discussion

Mononuclear complexes

Two complexes of the formula [M(bpy)(dhb)] (1,2) and two complexes of the formula [(M(bpy)h(thb)] (3,4) {Where bpy is 2,2'-bipyridine, dhb is the dianion of 3,4-dihydroxybenzaldehyde, thb is the tetraanion of 3,3',4,4'-tetrahydroxybenzaldazine and M is Pd(II) and Pt(II)} were prepared and characterised.

The molar conductivity of these complexes lie in the range of 4-7 ohm$^{-1}$ cm$^2$ mol$^{-1}$ and suggests them to be non-electrolytes. The changes in the IR spectra in the ligand moiety of the above complexes were compared with the parent chloro compounds, as well as with the free ligands. On complexation, the ring frequency of bpy is shifted to higher frequency. When the spectra of the complexes were compared with corresponding chloro complexes, two additional sharp bands at 1250 and 1460 cm$^{-1}$ were observed. The presence of these two bands confirms the bonding of dhb to the metal ion through ionized hydroxyl groups.$^{10}$ The band at 1460 cm$^{-1}$ is due to skeletal stretching vibration of the aromatic ring of dhb and the band at 1250 cm$^{-1}$ corresponds to C-O stretching vibration of dhb.

The structure and numbering scheme of the ligand Protons of the complexes are given in Structure I. The bpy protons of the complexes generally experience upfield shifts when compared to the parent chloro compound. This may be due to stronger binding of dhb to the metal than the chloride ions, or more back bonding from the metal d-orbital to π-antibonding orbitals of the bpy as compared to chloride ions.$^{12}$ The $^{2}$J($^{10}$Pd-$^{1}$H) couplings in these complexes have not been observed due to decrease of chemical shielding anisotropy with increase in magnetic field strength.$^{12}$

The free ligand, H$_2$dhb shows two broad peaks at 10.11 and 9.55 ppm due to -OH protons. This assignment was verified with D$_2$O exchange studies. These two peaks were absent in the metal complexes. A sharp peak, which was observed at 9.7 ppm due to CHO proton in the free ligand is observed at 9.5 ppm for 1 and at 9.6 for 2. All other protons (H$_A$, H$_B$ and H$_C$) experience an upfield shift in the range of 0.20 to 0.50 ppm as compared to the free ligand indicating the binding of the ligand with metal ion.

These data suggest that both ligands be bonded to metal ion in the mixed-ligand complexes. The integrated areas obtained for the protons of bpy and dhb indicate the stoichiometry, [M(bpy)(dhb)].

Dinuclear complexes

The binucleating ligand, 3,3',4,4'-tetrahydroxybenzaldazine (H$_2$thb) has been synthesised and the purity of the compound was checked by thin layer chromatography (TLC). The mass spectrum shows the molecular ion peak at 272 and the molecular weight of the compound is 272.3. The $^1$H NMR spectrum of H$_2$thb shows a sharp peak at 8.45 ppm, which is due to the -CH=N- group. The absence of a sharp peak at 9.7 ppm (due to -CHO group) which is present in the parent compound (3,4-dihydroxybenzaldehyde),

Fig. 1—Plot of $E_T$ versus $\nu_{max}$ for the LLCT band of 2.
indicates the formation of the product, H4thb. The D2O exchange studies reveal the presence of four -OH groups. The integrated area obtained for these protons corresponds to the total number of protons in the compound.

Two new dinuclear complexes of the formula [(M(bpy)(thb))] were synthesised by starting with the corresponding dichloro precursors. The IR spectra of these complexes show a peak ~1580 and 1600 cm⁻¹ due to –CH=N– group. There are strong peaks at 1275 (due to the –C=O stretching) and at 1475 cm⁻¹ (due to the aromatic ring stretching of thb). The peaks at 1275 and at 1475 cm⁻¹ indicate that the binding of thb to the metal ion through –O group¹⁴.

In the ¹H NMR spectra of [(M(bpy)(thb)], all the bpy protons experience upfield shift, when compared to the parent chloro compounds¹⁵. However, the effect is more pronounced in the H₄⁺ protons. The complexes, [(Pd(bpy)(thb)) and [(Pt(bpy)(thb)] experience an upfield shift of 0.53 and 0.96 ppm respectively. The H₄thb shows two peaks at 9.58 and 9.30 ppm due to –OH protons, which is confirmed by D₂O exchange studies. These two peaks were absent in the metal complexes. A sharp peak at 8.45 ppm observed due to –CH=N– proton in the free ligand is observed at 9.52 for 3 and at 9.60 for 4. However, all other protons (H₉, H₁₀ and H₁₁) experienced an upfield shift in the range 0.20 to 0.70 ppm as compared to the free ligand.

These data suggest that both ligands are bonded to metal ion in the mixed-ligand metal complexes. The integrated areas obtained for the protons of bpy and thb indicate the stoichiometry [(M(bpy)(thb)]. The ³J (¹⁹Pt¹H) couplings in these complexes have not been observed due to earlier mentioned reason¹⁵. The proton NMR spectral data, the IR data and the elemental analysis data confirm the synthesis and the structure assigned to these complexes as shown in Fig. 1.

**Absorption spectroscopy of mono and dinuclear complexes**

The electronic absorption spectra of the mono and dinuclear complexes are recorded. These mono and dinuclear complexes show five band maxima. These bands are numbered in the increasing order of energy. The bands in the UV region have been assigned on the basis of band assignments of chloro complexes⁸. Thus, bands 2 and 4 have been assigned to charge-transfer (CT) transitions from metal d-orbital to π-antibonding orbitals of the bpy. Bands 3 and 5 are assigned as the intra-ligand π-π* transition of the bpy. In addition, these complexes exhibit a band (band 1) in the visible region, which is strongly dependent on the polarity of the solvent. Further, this band is absent in 1:1 mixture of [(M(N–N)Cl₂] and H₂thb or 2:1 mixture of [(M(bpy)Cl₂] and H₂thb. There is an increase in the energy of this band when compared to [(M(bpy)(dhba)]²³ and [M(bpy)(cat)]¹¹ [where dhba is 3,4-dihydroxybenzoic acid and cat is catechol]. From these observations, this band has been assigned as ligand-to-ligand charge-transfer (LLCT) transition from HOMO of dhba to LUMO of bpy via metal⁻¹³,¹⁴. The trends observed in energy of this band can also be explained based on the above assignment. Because of the electron-withdrawing group (–CHO) on the phenyl ring of dhb, the HOMO of the complex further goes to lower energy, so the energy of transition increases when compared to the catechol complexes¹¹ or dhba complexes²⁵.

These band assignments are supported by the solvent studies. The absorption maximum of this band shifts with the change of solvent. The v_max of band 1 can be correlated with Reichardt’s parameter of solvent polarity (Er). A plot of Er values of solvents against absorption maxima gave two separate lines⁶, one for hydroxylic solvents and other for non-hydroxylic solvents, which confirms the assignments made. A typical plot for [Pt(bpy)(dhb)] is given in Fig. 2. Some of the solvents and their Er (in k.cal/mol) values are given below: Methanol, 55.5; ethanol, 51.9; acetonitrile, 46.0; DMSO, 45.0; acetone, 42.2; DMF, 43.8; chloroform, 39.1.

There is a little change in the position of the band 1 of the dinuclear complexes when compared with the mononuclear complexes. However, the molar extinction coefficient of this band in 4 is considerably higher than that of the 2. The position of MLCT band is considerably red-shifted in 4.

This study shows that various mono and dinuclear complexes of Pt(II) and Pd(II) can exhibit LLCT band. The MLCT bands are substantially red shifted in dinuclear complexes of platinum indicating larger delocalisation of the π-system in the dinuclear complex as compared to mononuclear complex. These complexes also show luminescence on excitation at the MLCT band and the detailed studies on luminescence are underway.

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References