Synthesis and substitution reactions on dichloro[2-(N-(2-hydroxyphenyl)-carbamoyl)pyridine]bis(dimethylsulphoxide)-ruthenium(II)

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The amide ligand 2-(N-(2-hydroxyphenyl)carbamoyl)pyridine (H2L) has been prepared by condensing pyridine-2-carboxylic acid with 2-aminophenol. This amide ligand has been characterised by elemental analysis, infrared, 1H NMR and mass spectral studies. The complex [Ru(H2L)(dmso)2Cl2] has been synthesised by the reaction of [Ru(dmso)4Cl2] with H2L. Further reaction of I with π-acidic diimines, 2,2'-bipyridine and 1,10-phenanthroline, lead to the substitution of the coordinated dmso molecules in I forming heteroleptic ruthenium complexes [Ru(bpy)(HL)Cl2] and [Ru(phen)(HL)Cl2]. The complex I undergoes a reversible ruthenium(II)/ruthenium(III) oxidation at -0.17 V in acetonitrile solution, while the complexes II and III undergo irreversible ruthenium(II)/ruthenium(IV) oxidation at ca. 0.37 V.

It was shown in our earlier reports that the ability of the amide linkage of the 2-carbamoylpyridyl moiety to coordinate through the oxygen atom or through nitrogen atom leads to the formation of the linkage isomeric chelate rings 1 and 2. For the chelate ring 1, the coordinating atoms are pyridyl nitrogen and amido nitrogen, while for the chelate ring 2, the coordinating atoms are pyridyl nitrogen and the carbonyl oxygen atom of the amide linkage. However, the type of coordination from the amide linkage depends upon the nature of the coligands bound to the metal centre. The substitution of the coordinated dmso molecules of the complexes [Ru(HL)(dmso)2Cl2] by 2,2'-bipyridine leads to the change of the coordination site from amide oxygen to amido nitrogen in the complexes [Ru(L)(bpy)Cl2], together with a change in the oxidation state from (+2) to (+3).

To explore the effect of potential coordinating group at the adjacent position on the phenyl ring in N-phenyl-2-carbamoylpyridyl moiety, a potentially tridentate amide ligand, H2L1 has been synthesised by the condensation of pyridine-2-carboxylic acid and 2-aminophenol. Reaction of H2L1 with [Ru(dmso)4Cl2] yields the complex [Ru(dmso)2(H2L1)Cl2] and further substitution of the coordinated dmso molecules in this complex by π-acidic diimine ligands, bpy and phen, yielded heteroleptic ruthenium complexes [Ru(bpy)(HL)Cl2] and [Ru(phen)(HL)Cl2]. Characterisation and cyclic-voltammetric properties of the complexes are reported in this paper.

Materials and Methods

Micro-analyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyser. IR spectra were obtained on a Perkin-Elmer 783 spectrophotometer. Electronic spectra were recorded on a Shimadzu 240-UV-visible spectrophotometer. Magnetic susceptibilities were measured with the help of a PAR 155 vibrating sample magnetometer. The 1H NMR spectra were obtained with a Varian Fourier-
transform spectrometer, using TMS as an internal standard. The electrospray mass spectra were recorded on a MICROMASS QUATTRO II triple quadruple mass spectrometer (assignments are based on the $^{103}$Ru isotope). Electrochemical measurements were made using the 174A polarographic analyser, a universal programmer, an X-Y recorder, a platinum working electrode, a platinum wire auxiliary electrode and Ag/AgNO$_3$ reference electrode. All electrochemical measurements were performed under nitrogen atmosphere. Ferrocene was used as an internal standard; all the potentials being quoted vs. the ferrocene-ferrocenium couple. Supporting electrolyte used in the experiments was Tetraethylammonium perchlorate (TEAP). The EPR measurements were made using a Varian model 109C E-line X-band spectrometer filled with a quartz dewar for measurements at 77 K (liquid nitrogen). The spectra were calibrated using tetracyanoethylene ($g = 2.0023$). RuCl$_3$·xH$_2$O (Loba, India) was converted to RuCl$_3$·3H$_2$O by repeated evaporation to dryness with concentrated hydrochloric acid. Pyridine-2-carboxylic acid (E-merk, Germany), 2-aminophenol, 2,2'-bipyridine and 1,10-phenanthroline (Loba, India) were used as received. Acetonitrile was distilled over CaH$_2$ before performing electrochemical experiments. Tetraethylammonium perchlorate (TEAP) was prepared using a reported procedure. Methanol was dried over fused CaO and [Ru(dms)$_2$Cl$_2$] (dms = dimethylsulfoxide) was prepared, as reported before.

**Synthesis of the ligand**

2-(N-(2-hydroxyphenyl)carbanoyl)pyridine (H$_2$L$^+$)

In a to a solution of pyridine-2-carboxylic acid (3.08 g., 25 mmol) in 10 mL pyridine, 2-aminophenol (2.73 g., 25 mmol) was added and was warmed under stirring condition for 15 min. Into the resulting solution, 6.6 mL (25 mmol) triphenylphosphite was added and the mixture was stirred at 110°C for 4 h. The cold reaction mixture was washed with 100 mL distilled water and the resulting white paste was taken in 40 mL dichloromethane and extracted with 150 mL 1:1 (v/v) aq. hydrochloric acid. The acidic aq. extract was neutralised by saturated aq. sodium bicarbonate solution. The resulting white solid was filtered, washed thoroughly with distilled water and crystallised from aq. methanol as a colourless crystalline solid. Yield 2.84 g. (53%), mp 208°C. [Found C, 66.98; H, 4.35; N, 12.93; Calc. for C$_{12}$H$_{10}$N$_2$O$_2$: C, 67.29; H, 4.67; N, 13.08%].

**Syntheses of the complexes**

**Dichloro [2-(N-(2-hydroxyphenyl)carbanoyl) pyridine]bis(dimethylsulfoxide)ruthenium(II), [Ru(dms)$_2$Cl$_2$]** (H$_2$L$^+$) I: A suspension of [Ru(dms)$_2$Cl$_2$] (0.484 g., 1 mmol) and 2-(N-(2-hydroxyphenyl)-carbanoyl)pyridine (H$_2$L$^+$) (0.214 g., 1 mmol) in 10 mL dry methanol was refluxed for 1 h and 8 mL solvent was distilled out from the reaction mixture. On cooling, an orange coloured microcrystalline product separated. The solid was isolated by filtration, washed with minimum volume of dry methanol and then by (10 x 3) mL diethyl ether, and dried over fused calcium chloride, yield 0.326 g. (60%); [Found C, 35.16; H, 4.02; N, 5.37; Calc. for RuC$_{16}$H$_{22}$N$_2$O$_2$Cl$_2$: C, 36.42; H: 4.06; N, 5.17%].

**Dichloro (2,2'-bipyridine) [2-(N-(2-hydroxyphenyl) carbanoyl)pyridine]ruthenium(III), [Ru(bpy)(H$_2$L$^+$)]Cl$_2$ II:** A solid mixture of I 0.15 g (0.28 mmol) and 2,2'-bipyridine 43.2 mg. (0.28 mmol) was refluxed in dimethylformamide (6 mL) for 4 h. The solvent was evaporated from the deep red coloured reaction mixture. The resulting solid was dissolved in a minimum volume of dichloromethane and was purified by column chromatography using silica gel (60-120 mesh). The desired product was isolated by eluting the column by a 4:1 v/v benzene-acetonitrile mixture. Evaporation of the solvent from the eluate yielded a dark-red coloured crystalline solid. Yield 0.065 g (43%). [Found C, 48.37; H, 3.05; N, 10.13; Calc. for RuC$_{22}$H$_{17}$N$_2$O$_2$Cl$_2$: C, 48.79; H, 3.14; N, 10.35%].

**Dichloro (1, 10-phenanthroline) [2-(N-(2-hydroxy- phenyl)carbanoyl)pyridine]ruthenium(III), [Ru(phen)(H$_2$L$^+$)]Cl$_2$ III:** The complex was synthesised by a method similar to that described for II. Yield 0.072 g (46%). [Found C, 50.73; H, 3.17; N, 9.67; Calc. for RuC$_{23}$H$_{19}$N$_2$O$_2$Cl$_2$: C, 50.97; H, 3.01; N, 9.91 %].

**Result and Discussion**

The synthetic methodology for the ligands has been adapted from Barnes et al. with a modification in the isolation step. The reaction between pyridine-2-carboxylic acid and 2-aminophenol in presence of triphenylphosphite proceeds smoothly in pyridine medium, resulting in a brown oil. The product was isolated by acidifying the reaction mixture by 1:1 (v/v) aqueous hydrochloric acid, followed by neutralisation by saturated aq. sodium bicarbonate solution and finally was crystallised from aqueous methanol.
Microanalytical data (Experimental Section) agree well with the empirical formula of H₂L₁. In the FAB mass spectrum the maximum peak is observed at m/z 214, which corresponds to the molecular ion (calculated molecular weight 214). The ¹H NMR spectrum was recorded in dmso-d₆ solvent. Six resonances in the aromatic region of ¹H NMR spectrum of H₂L₁ are found to integrate to eight protons; three doublets due to three protons, two triplets due to two protons and a multiplet due to three protons. Two singlets, which disappear on D₂O exchange, at δ 10.55 and 9.73, have been assigned to NH proton of the amide linkage and the phenolic proton of the phenol ring, respectively. In the IR spectrum of H₂L₁, the bands due to the NH stretching and CO stretching appear at 2997 and 1651 cm⁻¹, respectively. The band due to the OH stretching of the phenolic hydroxyl group appears at 3308 cm⁻¹.

The complex [Ru(H₂L₁)(dmso)₂Cl₂] I has been synthesised by substituting two coordinated dmso molecules from the starting complex [Ru(dmso)₂Cl₂] by the amide ligand, H₂L₁. The reaction of [Ru(dmso)₂Cl₂] with an equimolar quantity of H₂L₁ proceeds smoothly, in dry methanol, to precipitate the microcrystalline complex, I in good yield. Further reactions of I with π-acidic chelating diimine ligands, bpy and phen in refluxing dimethylformamide lead to the substitution of the coordinated dmso molecules forming the substituted complexes II and III. The complexes were isolated from the reaction mixture by column chromatography.

The elemental analytical data correspond to the expected composition of these complexes. Magnetic susceptibility measurements show that complex I is diamagnetic, as expected for the complexes of ruthenium(II) (low spin d⁶, S = 0), while the complexes II and III are paramagnetic, due to one unpaired electron, as expected for the complexes of ruthenium(III) (low spin d⁵, S = ½).

The infrared spectrum of I contains many sharp bands of different intensities due to the vibrations arising from the coordinated dmso, H₂L₁ and Cl⁻ ligands, and are, therefore, complex in nature. No attempt has been made to assign the individual bands. However, comparison of the IR spectrum of I with that of the free ligand shows a negative shift in ν₁ (1651 cm⁻¹ in H₂L₁ and 1627 cm⁻¹ in I) of the amide linkage in the complex, indicating that oxygen atom of the amide linkage is coordinated to the ruthenium(II) centre. The sharp band at 1082 cm⁻¹ has been assigned to ν₅0. The same band in free dmso appears at 1055 cm⁻¹. The positive shift in ν₂ shows that sulphur atom of the dmso molecule coordinates to the ruthenium(II) centre. The bands at 3449 and 3397 cm⁻¹ have been assigned to the stretching vibration of NH bond of the amide linkage and OH bond of the phenolic hydroxyl group of H₂L₁, respectively. The appearance of NH stretching band, in the IR spectrum of the complex I, indicate that ruthenium(II) centre is not coordinated by the amidato nitrogen of H₂L₁ and indirectly supports that the coordination is from the oxygen atom of the amide linkage of H₂L₁. The sharp bands at 307 cm⁻¹ (medium intensity) and 270 cm⁻¹ are assigned to ν₁(Ru=Cl) and ν₂(Ru=O(pyridine)) stretching modes. Thus in complex I, the amide ligand H₂L₁ coordinates from the pyridyl nitrogen and oxygen atom of the amide linkage, forming the chelate ring 2.

Infrared spectra of II and III are very similar; each spectrum shows many vibrations of different intensity below 1650 cm⁻¹ due to the presence of coordinated amide ligand and the chelating diimines. No attempt has been made for the individual band assignment. The ν₁(C=O) of the coordinated amide ligand is found to appear at ca. 1631 cm⁻¹. A broad band, centred at 3344 cm⁻¹ in case of II and at 3340 cm⁻¹ in case of III, in the IR spectra of the corresponding complexes, has been assigned to the ν₁(H₂L₁). The appearance of ν₁(NH) indicates the presence of noncoordinated phenolic moiety of H₂L₁, while the disappearance of ν₁(ν₃) band indicates the amidato nitrogen atom coordinating to the ruthenium(III) centre in these substituted complexes. Thus in II and III, H₂L₁ coordinates to ruthenium(III) centre from the amidato nitrogen and pyridyl nitrogen atoms, forming the chelate ring 1. This may be because the π-acidic bpy ligand reduces the electron density at the ruthenium centres, forcing the amidic ligand to coordinate from the σ-donor amidato nitrogen atom.

The ¹H NMR spectrum of I was recorded in dmso-d₆ solvent to confirm the ratio of one bidentate N,O-donor ligand to two coordinated dmso ligands. In the ¹H NMR spectrum of I all the signals due to the ligand protons are retained but are found to be shifted from their positions compared to the same in the free ligand. Two singlets, which disappear on D₂O exchange, at δ 11.57 and 10.31 have been assigned to NH proton of the amide linkage and the phenolic hydroxyl group of H₂L₁ in the complex I. Two singlets at δ 3.38 and 3.17, each of which integrates to six protons, have been assigned to the two coordinated dmso molecules. The appearance of two different sig-
nals for the two coordinated dmos molecules indicate that they are magnetically nonequivalent. Seven resonances in the aromatic region of the $^1$H NMR spectrum of I are found to integrate to eight protons; three doublets due to three protons, three triplets due to three protons and a multiplet due to two protons.

**Geometry around ruthenium centre:**

The ruthenium(II) center in I may, in principle, exist in the following four geometrical isomeric forms:

- **A**: \( \text{N} \quad \text{Ru} \quad \text{Cl} \quad \text{Y} \quad \text{Cl} \quad \text{Y} \)
- **B**: \( \text{Cl} \quad \text{Y} \quad \text{Ru} \quad \text{Cl} \quad \text{Y} \quad \text{N} \)
- **C**: \( \text{Cl} \quad \text{Y} \quad \text{Ru} \quad \text{Y} \quad \text{Cl} \quad \text{N} \)
- **D**: \( \text{Cl} \quad \text{Y} \quad \text{Ru} \quad \text{N} \quad \text{Cl} \quad \text{Y} \)

In the IR spectra, a single \( v_{\text{Ru-Cl}} \) band is expected for a linear grouping of the trans-RuCl$_2$ moiety (as in \( a \)), whereas, two \( v_{\text{Ru-Cl}} \) bands are expected for a cis-RuCl$_2$ moiety (as in \( b, c \) and \( d \)). Appearance of a single \( v_{\text{Ru-Cl}} \) band excludes the isomers \( b, c \) and \( d \), hence the arrangement of the donor atoms around the ruthenium(II) centre is as depicted in \( a \) (Y= dmos). This is further supported by the appearance of two different signals for the methyl groups of the coordinated dmos molecules in the $^1$H NMR spectrum of I, indicating that they are magnetically non-equivalent.

The complexes II and III may, in principle, exist in the following two geometrical isomeric forms 'A' and 'B'.

- **A**: \( \text{N} \quad \text{Ru} \quad \text{N} \quad \text{Cl} \quad \text{Cl} \quad \text{N} \)
- **B**: \( \text{N} \quad \text{Ru} \quad \text{Cl} \quad \text{Cl} \quad \text{N} \quad \text{N} \)

The EPR spectra of complexes II and III were recorded in 1:1 (v/v) dichloromethane-toluene solution at 77 K. A representative spectrum is shown in Fig. 1. Each complex shows rhombic EPR spectrum with three distinct g values (Table I). However, both the spectra may be regarded as pseudo-axial, consisting of two very closely spaced signals (\( g_1 \) and \( g_2 \), rhombic component of \( g \)-perpendicular) and a rather isolated signal (\( g_3 \), \( g \)-parallel in the axial case). Thus the axial distortion, that splits the 't$_2$' level into 'a' and 'e' components, is expected to be much larger than the rhombic distortion, which splits 'e$^{10}$'.

The complex I is insoluble in chloroform, dichloromethane and methanol but is partially soluble in acetonitrile and is totally soluble in DMSO. The complex is soluble in 4:1 (v/v) dichloromethane-methanol, dichloromethane-acetonitrile, chloroform-methanol and chloroform-acetonitrile mixtures. The electronic spectrum of this complex has been recorded in mixed solvent, dichloromethane-methanol 4:1 (v/v) mixture and the spectral data are collected in Table I. The complex shows two intense bands at 318 and 436 nm. On the basis of the values of the extinction coefficients, these bands are assigned to the metal to ligand charge transfer (MLCT) transitions.

The complexes II and III are readily soluble in polar organic solvents such as methanol, ethanol, acetonitrile, dichloromethane and chloroform, but are insoluble in non-polar solvents, such as benzene, toluene and n-hexane. The electronic spectra of these
### Table 1—Characterisation data of the complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Electronic spectra*</th>
<th>Magnetic moment</th>
<th>Cyclic voltammetric data*</th>
<th>‘γ’ values*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$, nm (ε, M$^{-1}$ cm$^{-1}$)</td>
<td>$\mu$(BM)</td>
<td>$E'_a$, V ($\Delta E_p$, mV)</td>
<td>$g_1$</td>
</tr>
<tr>
<td>I</td>
<td>318(7480.2), 436(2187.5)</td>
<td>—</td>
<td>0.17(60)</td>
<td>—</td>
</tr>
<tr>
<td>II</td>
<td>295(12016.6), 375(3482.1), 447(1502.1), 595(409.7)</td>
<td>1.77</td>
<td>+0.38</td>
<td>-1.26(60)</td>
</tr>
<tr>
<td>III</td>
<td>291(20240.7), 377(9755.2), 457(3464.2), 593(912.2)</td>
<td>1.78</td>
<td>+0.39</td>
<td>-1.26(60)</td>
</tr>
</tbody>
</table>

*in 4:1 (v/v) dichloromethane-methanol solution for I and in dichloromethane solution for II and III.

*Solvent, acetonitrile; supporting electrolyte, TEAP; scan rate 100 mV s$^{-1}$; $E'_{250}$ = 0.5 ($E_{pa}$ + $E_{pc}$), where $E_{pa}$ and $E_{pc}$ are anodic and cathodic peak potentials respectively. $\Delta E = E_{pa} - E_{pc}$.

*The anodic peak potential.

*in 1:1 (v/v) dichloromethane-toluene solution, at 77 K.

The electronic spectra of these complexes have been assigned to the MLCT transitions, on the basis of high extinction coefficient values of these bands. Another intense band (at 295 nm for II and at 291 nm for III) appears in the UV region of the electronic spectra of these complexes. In the electronic spectra of free bpy and phen, an intense band appears at 290 and 289 nm, respectively. Thus the band at ca. 290 nm, in the electronic spectra of the complexes II and III, has been assigned to the intraligand transition in the coordinated π-acidic diimine ligands. An intense band is found to appear in the electronic spectrum of the free amide ligand $H_2LI$ at 279 nm. This band due to the intraligand transition does not appear in the electronic spectrum of any of these three complexes.

The electrospray mass spectra of all the complexes were recorded. The peaks observed at m/z 543.1 for I, m/z 542 for II and at m/z 566 for III, correspond to the molecular ions of the corresponding complexes. (Calc. mol. Wt. : 542.57 for I, 541.47 for II and 565.49 for III.)

Thus the mass spectral data, along with microanalytical, magnetic moment, $^1H$ NMR, ESR and IR spectral results, collectively establish the suggested composition and the stereochemistry of the complexes.

The electrochemical properties of the complexes were studied in acetonitrile (0.1 M in TEAP) by cyclic voltammetric technique. All the potentials are quoted vs. the ferrocene-ferrocenium couple. The voltammetric data are presented in Table 1 and a representative voltamogramme is shown in Fig. 2. The complex I shows a reversible response, due to ruthenium(II)/ruthenium(III) couple (Eq. 1) at −0.17 V.

![Fig. 2 — Cyclic voltammogram of I in acetonitrile solution (0.1 M TEAP) at a scan rate of 200 mV s$^{-1}$](image-url)
[Ru(H2L')\(\text{dms}\text{o})\text{Cl}_2]^{+}\text{e}^{-} \rightarrow [\text{Ru}(\text{H2L'})\text{dms}\text{o})\text{Cl}_2]^+\text{e}^{-} \ldots (1)

The \(\Delta E_p\) values of this couple is 60 mV, which does not change with change in the scan rate and the \(i_{p+1/2} = \text{anodic peak current and } i_{p-1} = \text{cathodic peak current}\) ratio is close to 1.0, as expected for reversible systems. This potential of the ruthenium(II)/ruthenium(III) couple can be compared with that for the complexes [Ru(HL)(\text{dms}\text{o})\text{Cl}_2], which bear \(p\)-substituted \(N\)-phenyl-2-carbamoylpyridine as the ligand (HL). For these complexes the potential of the ruthenium(II)/ruthenium(III) couple lies in the potential range 0.54 to 0.60 V vs the ferrocene-ferrocnium couple\(^a\). The presence of a phenolic hydroxyl group at the \(\alpha\)-position of the phenyl ring of the ligand \(\text{H}_2\text{L}'\), in the complex I, increases the electron density at the ruthenium(II) centre making it more prone to undergo oxidation. As a consequence, the ruthenium(II)/ruthenium(III) oxidation potential in the complex I is much lower compared to the same for the complexes [Ru(HL)(\text{dms}\text{o})\text{Cl}_2].

In the cyclic voltammogram of the complexes II and III, an irreversible response appears at a potential \(ca. +0.38\) V, due to the irreversible oxidation of the ruthenium(III) centres (Eq. 2)

\[
[\text{Ru}(\text{HL'})\text{L}^2\text{Cl}_2]\rightarrow [\text{Ru}(\text{HL'})\text{L}^2\text{Cl}_2]^+\text{e}^{-} \ldots (2)
\]

\(\text{L}^2 = \text{bpy, phen}.\)

The irreversibility of the ruthenium(III)/ruthenium(IV) couple for these complexes may be due to the instability of the oxidised species within the cyclic voltammetric time scale. In the cathodic side of the cyclic voltammograms of these complexes a reversible response appears at \(ca. -1.25\) V. This reversible response has been attributed to the reduction of the coordinated dimine ligands (bpy, phen). It is well known\(^{12,13}\), that bpy or phen can successively accept two electrons in the lowest unoccupied molecular orbital. In the complexes II and III only the first reduction has been observed experimentally. The second reduction, which usually takes place at a more negative potential\(^b\), is not observed due to solvent cut off\(^c\).

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**References**