

Polyhedron 18 (1999) 2157-2162



Synthesis and characterisation of some Ru(II) complexes of 2-carbamoylpyridine derivatives

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Abstract

p-Substituted *N*-phenyl derivatives of 2-carbamoylpyridine (L) have been prepared by the reaction of pyridine-2-carboxylic acid with *p*-substituted aniline. Five complexes of the type $[Ru(L)(DMSO)_2Cl_2]$ have been synthesized by the reaction of $[Ru(DMSO)_4Cl_2]$ with L. The amide ligands have been characterized by elemental analysis, infra red and ¹H NMR spectral studies. The complexes are diamagnetic and show intense absorptions due to metal to ligand charge transfer (MLCT) transitions in the UV–visible spectra. The IR spectra of the complexes show that the amide ligands coordinate to the ruthenium (II) ion as a bidentate ligand coordinating from pyridyl nitrogen and from the carbonyl oxygen of the amide group. The complexes undergo a reversible ruthenium (II)–ruthenium (III) oxidation near 0.55 V in acetonitrile solution. The ruthenium (II)–ruthenium (III) oxidation potentials of the complexes are found to be sensitive to the nature of the substituent on the ligand. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ruthenium complexes; 2-Carbamoylpyridine derivatives; Amide complexes; Electrochemistry; Geometrical isomers

1. Introduction

The chemistry of ruthenium receives ample attention due to the fascinating properties of ruthenium complexes [1,4]. These include the availability of its wide range of oxidation states of ruthenium in its complexes [5,6], occurrence of a ligand mediated intermetallic interaction in binuclear ruthenium complexes [7-9], reactivity of the complexes without changing the coordination sphere as well as reactivity of the complexes causing changes in the coordination sphere [1-3], enhanced catalytic activity towards organic substrates [10-15], and occurrence of some less common reactions [16-21]. The chemistry of the amide complexes of ruthenium also receives considerable attention in the context of metal-peptide chemistry [22–31]. However, these complexes are mostly limited to pentaammineruthenium amido complexes. Here we are reporting the synthesis and characterization of the aromatic amide of pyridine-2-carboxylic acid and their complexes with ruthenium. The general structure of the ligand can be shown as L.



The presence of a pyridyl nitrogen at the adjacent position of the amide linkage helps the ligand (L) to bind to a metal ion in a bidentate fashion forming a five membered chelate ring either through N-bonding **1**. or through O-bonding **2**. from the amide linkage. Both the linkage isomers, Obonded and N-bonded,are known for glycinamide chelated to tetraammineruthenium(III) center [30,31].

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2. Experimental

2.1. Physical measurements

Micro analyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Parkin-Elmer 783 spectrophotometer. Electronic spectra were recorded on a Shimadzu 240-UVvisible spectrophotometer. Magnetic susceptibilities were measured with the help of a PAR 155 vibrating sample magnetometer. The ¹H and ¹³C 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. 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/AgNO3 reference electrode. All electrochemical measurements were performed under dinitrogen atmosphere. Ferrocene was used as an internal standard; all potentials are quoted vs. the ferrocene-ferrocenium couple. Supporting electrolyte used was Tetraethylammonium perchlorate (TEAP)

2.2. Materials

RuCl₃·*x*H₂O (Loba, India) was converted to RuCl₃· 3H₂O by repeated evaporation to dryness with concentrated hydrochloric acid. Pyridine-2-carboxylic acid (Emerk, Germany) was used as received. Aromatic amines (aniline and *p*-substituted aniline, *p*-X-C₆H₄NH₂, X = – CH₃, $-OCH_3$, $-NO_2$ and -Cl) were either distilled over KOH or recrystallized before use. Acetonitrile was distilled over CaH₂ before performing electrochemical experiments. Tetraethylammonium perchlorate (TEAP) was prepared using a reported procedure [32]. Methanol was dried over fused CaO and [Ru(DMSO)₄Cl₂] (DMSO= dimethylsulfoxide) was prepared as reported before [33].

2.3. Syntheses of ligands

All the amide ligands were prepared using the same general method. Specific details are given for representative cases.

2-(*N*-Phenylcarbamoyl)pyridine (L^1) (X=H): Into a solution of pyridine-2-carboxilic acid (3.08 g, 25 mmol) in 10 ml pyridine, aniline (2.28 ml, 25 mmol) was added and was warmed under stirring conditions 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 in 100 ml 1:1 (v/v) aqueous hydrochloric acid. The acidic aqueous extract was neutralized by solid sodium bicarbonate. The resulting

white solid was filtered, washed thoroughly with distilled water and crystallized from aqueous methanol as a colorless crystalline solid. Yield: 3.9 g (80%), mp 79°C. Found C, 72.36; H, 4.9; N, 13.93; calc. for $C_{12}H_{10}N_2O$, C, 72.73; H, 5.05; N, 14.14%.

 L^{2} (X=CH₃), yield 79%; mp 108°C. Found C, 73.85; H, 5.88; N, 12.87; calc. for C₁₃H₁₂N₂O, C, 73.58; H, 5.66; N, 13.2%.

 L^{3} (X=OCH₃), yield 87%; mp 95°C. Found C, 68.73; H, 5.42; N, 11.9; calc. for C₁₃H₁₂N₂O₂, C, 68.42; H, 5.26; N, 12.28%.

 $L^{4}(X=Cl)$, yield 68%; mp. 139°C. Found C, 62.3; H, 3.83; N, 12.37; calc. for $C_{12}H_9N_2OCl$, C, 61.94; H, 4.18; N, 12.04%

 $L^{5}(X=NO_{2})$, From the hot reaction mixture the product was precipitated directly, isolated by filtration, washed thoroughly with methanol, dried over fused calcium chloride, crystallized from large volume of methanol. Yield 78%; mp 233°C. Found C, 59.63; H, 3.89; N, 17.24; calc. for C₁₂H₉N₃O₃, C, 59.26; H, 3.87; N, 17.28%.

2.4. Syntheses of the complexes

Syntheses of the complexes of the type $[Ru(L)(DMSO)_2Cl_2]$ were achieved using same general method. Specific details are given for representative cases:

Dicholoro[2 - (N - phenylcarbamoyl)pyridine]bis(dimethylsulfoxide)ruthenium(II) I: A suspension of [Ru(DMSO)₄Cl₂] (0.242 g, 0.5 mmol) and 2-(N-Phenylcarbamoyl)pyridine (L¹) (0.099 g, 0.5 mmol) in 15 ml dry methanol was refluxed for 1 h. Ten millilitres of solvent was distilled out from the reaction mixture. During this time an orange colored microcrystalline product separated. The solid was isolated by filtration, washed with minimum volume of dry methanol and then by (10×3) ml diethylether, dried over fused calcium chloride, yield 0.22 g (83%); Found C, 36.67; H, 4.02; N, 5.77; calc. for RuC₁₆H₂₂N₂O₃C₁₂S₂; C, 36.5; H, 4.18; N, 5.32%.

For complexes **II–V** the microcrystalline solid was precipitated directly using L^2 , L^3 , L^4 , L^5 instead of L^1 , respectively

II, yield 68%; Found: C, 37.41; H, 4.31; N, 5.56; calc. for $RuC_{17}H_{24}N_2O_3S_2Cl_2$; C, 37.77; H, 4.44; N, 5.18%.

III, yield 73%; Found: C, 36.36; H, 4.32; N, 5.21; calc. for RuC₁₇H₂₄N₂O₄S₂Cl₂; C, 36.69; H, 4.32; N, 5.04%.

IV, yield 76%; Found: C, 34.55; H, 3.71; N, 4.78; calc. for $RuC_{16}H_{21}N_2O_3S_2Cl_3$; C, 34.25; H, 3.75; N, 4.99%.

V, yield 89%; Found: C, 33.82; H, 3.82; N, 7.13; calc. for $RuC_{16}H_{21}N_3O_5S_2Cl_2$; C, 33.62; H, 3.68; N, 7.35%.

Dichlorobipyridine[2 - (N - phenylcarbamoyl)pyridineruthenium(II) VI: A solid mixture of I, 0.1052 g (0.2 mmol) and bipyridine (bpy), 0.0312 g (0.2 mmol) was refluxed in dry toluene for 24 h. The solid thus obtained was isolated by filtration, dissolved in 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 4:1 (v/v) benzene– acetonitrile mixture. Evaporation of the solvent from the eluate yielded dark red colored microcrystalline solid. Yield=55 mg (53%); Found C, 50.08; H, 3.53; N, 10.26 calc. for RuC₂₂H₁₈N₄Cl₂ C, 50.18; H, 3.42; N, 10.64.

3. Result and discussion

The synthetic methodology for the ligands has been adapted from Barnes et al. [34] with a modification for the isolation step. The reaction between pyridine-2-carboxylic acid and *p*-substituted anilines in the presence of triphenylphosphite proceeds smoothly in pyridine, resulting in a pale yellow oil (for L⁴ the product precipitated directly). The product was isolated from the reaction mixture by acidification followed by neutralization and finally was crystallized from aqueous methanol. Microanalytical data (experimental section) agree well with the empirical formulae of the compounds. In the IR spectra of the ligands the $\nu_{\rm NH}$ and $\nu_{\rm CO}$ of the amide linkage are observed at ca. 3342 cm⁻¹ and ca. 1677 cm⁻¹, respective-ly.

The reactions of $[Ru(DMSO)_4Cl_2]$ with an equimolar quantity of amide ligands in dry methanol proceed smoothly to precipitate microcrystalline $[Ru(L)(DMSO)_2Cl_2]$ complexes (Eq. (1)) in reasonably good yields. The reaction can be shown as follows.

$$[\operatorname{Ru}(\operatorname{DMSO})_4\operatorname{Cl}_2] + L \rightarrow [\operatorname{Ru}(L)(\operatorname{DMSO})_2\operatorname{Cl}_2] + 2\operatorname{DMSO}$$
(1)

Microanalytical data (C, H, N) correspond to the expected composition of these complexes. Magnetic susceptibility measurements show that these complexes are diamagnetic as expected for complexes of ruthenium (II) (low spin d⁶, S=0). The infrared spectra of these complexes contain many sharp bands of different intensities due to vibrations arising from the coordinated DMSO, L and Cl⁻ ligands and are therefore complex in nature. No attempt has been made to assign the individual bands. However, comparison of the IR spectra of the free ligands, with that of the complexes, shows a negative shift in the ν_{CO} of the amide linkage in the complex, indicating [35] that the oxygen atom of the amide linkage is coordinated to the ruthenium(II) center. In the IR spectra of all the complexes a sharp band is observed at ca. 1095 cm^{-1} . This has been assigned to ν_{SO} . The same band in free DMSO appears at 1055 cm⁻¹ [36]. The positive shift in ν_{SO} indicates that the coordination of the DMSO molecules to the ruthenium(II) center occurs from the sulfur atom [36]. The sharp bands at 306 cm^{-1} (medium intensity) and 274 cm^{-1} are assigned

to $\nu_{\text{Ru-Cl}}$ [37] and $\nu_{\text{Ru-N(pyridine)}}$ [38] stretching mode. The ¹H and ¹³C NMR spectra of one representative complex, **II** and the corresponding ligand, L² (X=CH₃) were recorded in (CD₃)₂SO solvent to confirm the ratio of one bidentate N,O-donor ligand to two co-ordinated DMSO ligands. In the aromatic region of the ¹H NMR spectrum of L² six resonances are found and they are found to integrate to eight protons. The singlet at δ 10.54 is assigned to the NH proton of the amide linkage and the singlet (3H) at δ 2.29 is assigned to the methyl protons. The signals in the aromatic regions are assigned as: δ 7.18 $(2H,d,H^{3'}), \delta$ 7.67 $(1H,td,H^{5}), \delta$ 7.79 $(2H,d,H^{2'}), \delta$ 8.07 $(1H,td,H^4)$, δ 8.16 $(1H,d,H^3)$ and δ 8.74 $(1H,d,H^6)$. In the ¹H NMR spectrum of **II** all the signals due to the ligand protons are retained but are found to be shifted from its position compared to the same in the free ligand. The signal due to the NH proton of the amide linkage is found to appear at δ 11.74 as a singlet and the signal due to the methyl protons appears at δ 2.36 (3H,s). Signals due to the aromatic protons are assigned as: δ 7.33 (2H,d,H^{3'}), δ 7.52 (2H,d, $H^{2'}$), δ 7.94 (1H,t, H^{5}), δ 8.30 (1H,td, H^{4}), δ 8.72 (1H,d,H³) and δ 10.33 (1H,d,H⁶). The methyl protons of the coordinated DMSO molecules appear as two singlets at δ 3.35 and δ 3.26, each of which integrates to six protons. This indicates that two coordinated DMSO molecules are nonequivalent.

In the proton decoupled ¹³C NMR spectrum of L², the signal due to the carbon atom of the amide linkage appears at δ 162.2 while the methyl carbon signal appears at δ 20.5. The spectrum contains nine more signals for 11 aromatic carbon atoms in the region δ 150 to δ 120, assignment of these signals has not been attempted. In the proton decoupled ¹³C NMR spectrum of **II** the signal of the carbon atom of the amide linkage of the bidentate N,O- ligand appears at δ 169.3, while the signal of the aromatic carbon atoms appear at δ 20.6. The signals due to the aromatic carbon atoms appear in the region δ 155 to δ 122, assignment of the individual signals has not been attempted.

3.1. Geometry of the ruthenium(II) center

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



A single ν_{Ru-Cl} band is expected for a linear grouping of the *trans*-RuCl₂ moiety (as in *a*), whereas, two ν_{Ru-Cl} bands of equal intensity are expected for a *cis*-RuCl₂ moiety (as in *b*, *c* and *d*) [39]. Appearance of a single ν_{Ru-Cl} band excludes isomers *b*, *c* and *d*, hence the arrangement of the donor atoms around the ruthenium(II) center is as depicted in a(Y=DMSO). Further, in the ¹H NMR spectrum of **II**, the appearance of two different signals for the coordinated DMSO molecules indicates that they are non-equivalent. This is expected when the coordinated DMSO molecules are in *cis*-geometry, as is suggested in *a*.

Electronic spectra of these complexes have been recorded in mixed solvent, dichloromethane-acetonitrile 4:1 v/v mixture. Spectral data are collected in Table 1 and representative spectra are shown in Fig. 1. All the complexes display two intense absorptions, one of which is in the visible region and the second one extends to the UV region. These two intense bands are assigned to the metal to ligand charge transfer transitions. The corresponding parent ligands display an intense absorption in the UV region, assigned to the intraligand transition. The absorption due to the intraligand transition appears as a shoulder in the electronic spectra of the complexes I, II and IV with a minor shift in the position along with the second absorption in the UV region, whereas for III the intraligand transition appears as a separate band at 273 nm (Fig. 1) and for V the same probably merges with the metal to ligand charge transfer band.

The electro-spray mass spectra of two representative complexes, **II** and **IV** were recorded. The peaks observed at m/z 542.9 for **II** and at m/z 559.9 for **IV** corresponds to the molecular ion of the corresponding complexes **II** and **IV**, (calculated molecular weight 540.5 for **II** and 560.6 for **IV**).

Thus the mass spectral data along with ¹H and ¹³C NMR spectroscopic result, microanalytical, magnetic moment and IR data collectively establish the suggested composition and stereochemistry of the complexes.

3.2. Electrochemical properties

The electrochemical properties of the complexes were studied in acetonitrile (0.1 M in TEAP) by cyclic voltammetry. The voltammetric data are presented in Table 1. Each complex shows a reversible response, due to ruthenium(II)/ruthenium(III) couple (Eq. (2)) in the potential range 0.54–0.60 V.

Table 1				
Cyclic-voltammetric	and	optical	spectral	data



Fig. 1. Electronic spectra of II (\longrightarrow) and III (- - -) in dichloromethane-methanol 4:1 (v/v) mixture.

$[\operatorname{Ru}(L)(\mathrm{DMSO})_2\mathrm{Cl}_2] \rightleftharpoons [\operatorname{Ru}(L)(\mathrm{DMSO})_2\mathrm{Cl}_2]^+ + \mathrm{e}^- \qquad (2)$

The $\Delta E_{\rm p}$ values of these couples lie in the range 60–70 mV, which do not change with change in the scan rate and the $i_{\rm pa}/i_{\rm pc}$ ($i_{\rm pa}$ =anodic peak current and $i_{\rm pc}$ =cathodic peak current) ratio is close to 1.0, as expected for reversible couples. To establish the one electron stoichiometry of this couple, constant potential coulometric oxidation of one representative complex, I was carried out.

Cycle voluminetie and optical spectral data				
Complexes	Electronic spectra ^a λ_{max} (nm) (ε , M ⁻¹ cm ⁻¹)	Cyclic-voltammetric data ^b E_{298}° , V (ΔE_{p} , mV) Ru ^{II/III}		
I	425(2360); 293(11437); 277(10302) ^c	0.55 (70)		
П	419(2431); 305(10713); 275(8134) ^c	0.55 (70)		
III	404(2559); 317(9293); 273(6497)	0.54 (70)		
IV	414(2183); 297(11312); 275(9764) ^c	0.57 (60)		
V	446(2239); 309(15830)	0.60 (70)		
VI	516(1928); 376(5351); 296(16930)	0.83 (63)		

^a For I-V solvent used is dichloromethane-methanol 4:1 (v/v) mixture and for VI dichloromethane.

^b Supporting electrolyte, TEAP (0.1 M); reference electrode Ag/Ag⁺; $E_{298}^{\circ} = 0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potential; $\Delta E_p = E_{pa} - E_{pc}$; scan rate 100 mV s⁻¹; solvent: acetonitrile.

^c Shoulder.

The observed Coulomb count corresponds to one electron transfer (n=0.98; n=Q/Q', where Q' is the calculated Coulomb count for one electron transfer and Q is that for exhaustive electrolysis).

Though stable in the cyclic voltammetric time scale attempts for the isolation of $[Ru(L)(DMSO)_2Cl_2]^+$ by chemical oxidation were not successful. The chemical oxidation was tried in 1:1 (v/v) aqueous acetonitrile by ammonium ceric sulphate. The color of the reaction mixture changed from orange to green after stirring the reaction mixture for 24 h, but no product could be isolated from the reaction mixture by the addition of the negative counter ion ClO_4^- . This may be attributed to the degradation of the complex.

For the five complexes the potential of the ruthenium(II)–ruthenium(III) couple were found to be sensitive to the nature of the substituents, X, on the ligand. In case of **V** with X=electron withdrawing NO₂, higher oxidation potential value (0.60 V) of the ruthenium(II)–ruthenium(III) couple is observed, whereas lower ruthenium(II)–ruthenium(III) oxidation potential (0.54 V) is observed for **III** (X=OCH₃), reflects the electron donating nature of the substituent (Fig. 2).

3.3. Substitution reaction

To explore the reactivity of two *cis*-DMSO ligands, reaction of complex **I**, with the bidentate chelating ligand 2,2'-bipyridine (bpy) was carried out. Reaction between **I** and bpy in dry toluene lead to the formation of **VI** according to Eq. (3)

$$[\operatorname{Ru}(\operatorname{DMSO})_4(\operatorname{L}^1)\operatorname{Cl}_2] + \operatorname{bpy} \to [\operatorname{Ru}(\operatorname{L}^1)(\operatorname{bpy})\operatorname{Cl}_2] + 2\operatorname{DMSO}.$$
(3)

Composition of **VI** was confirmed by microanalytical data (experimental section). In the UV spectrum of **VI** three intense absorption bands are found. Two intense bands at 516 nm and 376 nm are assigned to metal to ligand charge transfer transitions while the band at 296 nm is assigned to intraligand transition. The cyclic voltammogram of **VI** was recorded on acetonitrile (0.1 M in TEAP). The reversible



Fig. 2. The plot of E_{298}^0 versus σ [σ =Hammett constant of X [40]; OCH₃=-0.27; CH₃=-0.17; H=0.0; Cl=0.23 and NO₂=0.78] is linear Fig. 2 with ρ =0.05 (ρ =reaction constant for this couple).

response in the anodic side of the voltammogram (initial scan anodic), presumably due to ruthenium(II)/ruthenium(III) couple, Eq. (4), occurs at 0.83 V.

$$[\operatorname{Ru}(\operatorname{L}^{1})(\operatorname{bpy})\operatorname{Cl}_{2}] \to [\operatorname{Ru}(\operatorname{L}^{1})(\operatorname{bpy})\operatorname{Cl}_{2}]^{+} + e^{-}$$
(4)

The $\Delta E_{\rm p}$ value of this couple is 63 mV and it does not change with the change in scan rate and the ratio $I_{\rm pa}/I_{\rm pc}$ is close to one as expected for a reversible couple. Thus the ruthenium (II)/ruthenium (III) couple for **VI** is shifted to a more positive potential (by 0.28 V) compared to **I**, indicating substitution of the DMSO groups by bpy stabilizes the oxidation state, (II) of the ruthenium center in the complex.

Acknowledgements

The authors gratefully acknowledge the financial assistance provided by DST, New Delhi, Govt. of India. Acknowledgments are made to the Regional Sophisticated Instrumentation Centre (RSIC), Indian Institute of Technology, Bombay, for providing NMR and IR facility, RSIC, Central Drug Research Institute, Lucknow, for providing the electrospray mass spectra and RSIC, Roorkee University for room temparature magnetic moment determination. We are thankful to Dr. Samaresh Bhattacharya of Jadavpur University for helpful discussion, Dr. Amitava Das CSMCRI, Bhavnagar for providing the facility of constant potential coulometric experiment and to the Head, Department of Chemistry, for providing the laboratory facilities. Refrees' suggestion at the revision stage were very helpful.

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