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Synthesis and substitution reactions of dichlorobis-triphenylphosphine[2-(N-(2-pyridinium-2-yl)- carbamoyl- N^-)-pyridine]ruthenium(II)

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Abstract

Spectroscopic and crystallographic studies show that 2-(N-(2-pyridyl)carbamoyl)pyridine (HL) in both its neutral and deprotonated forms, coordinates ruthenium(II) via the amidato- and pyridine-nitrogen atoms thereby forming five-membered rings. In neutral [Ru(HL)(PPh_3)₂Cl₂], HL exists as a zwitterion and the molecular structure is stabilised, in part, by an intramolecular Cl…N interaction. Reaction of the title complex with bidentate chelating ligands leads to the replacement of two chlorides by the bidentate ligands, resulting in the formation of the mixed-ligand complexes. There is deprotonation of the zwitterionic HL in the mixed-ligand complexes. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Linkage isomers of ruthenium complexes with amide ligands have received due attention in the context of transition metal-peptide chemistry [1]. However, these studies are mainly limited to systems featuring tetraand penta-ammineruthenium(II/III). Both O-bonded and N-bonded linkage isomers are known for glycinamide chelated to the tetraammineruthenium(III) centre [1a,b]. Ruthenium complexes with other amide ligands are also abundant [2,3], but these do not involve the study of linkage isomerisation. In this paper, the syntheses and characterisation of 2-(N-(2-pyridyl)carbamovl)pyridine (HL) and a complex, [Ru(HL)-(PPh₃)₂Cl₂] where HL exists as a zwitterion, are reported. Reactions of the complex with bidentate chelating ligands, leading to the substitution of two chlorides and formation of mixed-ligand complexes of the type

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 $[Ru(L)(PPh_3)_2(L')]ClO_4$ by the deprotonation of HL, are also reported.

The location of an amide linkage between two pyridine rings allows the ligand HL, to function as an ambidentate chelating ligand. Thus, for example, a five-membered chelate ring involving the pyridyl nitrogen, N_a , and either of the oxygen atom (1) or the nitrogen atom (2) of the amide linkage may be envisaged. Participation of the pyridyl nitrogen, N_b , coupled with chelate rings 1 or 2, would lead to a tridentate mode of coordination for HL. HL may also act as a bridging ligand. Additional coordination modes may be envisaged when HL is deprotonated. Analogous chelate rings to 1 and 2 have been reported for ruthenium complexes with other amide ligands [2,3]; and in the present study type 2 is found for complexes containing both neutral HL and its deprotonated form.



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2. Experimental

2.1. Materials

RuCl₃·xH₂O (Loba, India) was converted to RuCl₃·3H₂O by repeated evaporation to dryness with concentrated hydrochloric acid. Pyridine-2-carboxylic acid (E-Merck, Germany), 2-aminopyridine (Sigma) and triphenylphosphine (Loba, India) were used as received. Acetonitrile was distilled over CaH₂ before performing electrochemical experiments and ethanol was dried over fused CaO. All other chemicals were obtained from commercial sources and were used as received. Tetraethylammonium perchlorate [4] (TEAP) and [Ru(PPh₃)₃Cl₂] [5] were prepared as reported before.

2.2. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin-Elmer 240 C elemental analyser. IR spectra were obtained on a Perkin-Elmer 783 spectrophotometer. Electronic spectra were recorded on a Shimadzu 240-UV-Vis spectrophotometer. Magnetic susceptibilities were measured employing a PAR 155 vibrating sample magnetometer. The ¹H NMR spectra were obtained with a 300 MHz Varian Fourier-transform spectrometer, using TMS as an internal standard. The positive ion electrospray mass spectra were recorded on a Micromass Quattro II triple quadruple mass spectrometer (assignments are based on the ¹⁰²Ru isotope). The FAB mass spectrum of LH was recorded on a JOEL SX 102/DD 6000 mass spectrometer. Electrochemical measurements were made using a 174 polarographic analyser, a universal programmer, an X-Yrecorder, a platinum working electrode, a platinum wire auxiliary electrode and Ag | AgNO₃ reference electrode. All electrochemical measurements were performed under a nitrogen atmosphere. Ferrocene was used as an internal standard and all potentials are quoted versus the ferrocene/ferrocenium couple. The supporting electrolyte used was TEAP.

2.3. Ligand synthesis

2-(N-(2-Pyridyl)carbamoyl)pyridine (HL). Into a solution of pyridine-2-carboxylic acid (1.54 g, 12.5 mmol) in 5 ml pyridine, 2-aminopyridine (1.18 g, 12.5 mmol) was added and warmed with stirring for 15 min. Into the resulting solution triphenylphosphite (3.3 ml, 12.5 mmol) was added and the mixture was stirred at 110°C for 4 h. The cold reaction mixture was washed with 100 ml distilled water. The resulting light brown oil was taken in 50 ml dichloromethane and was extracted in 150 ml 1:1 (v/v) aqueous hydrochloric acid. The acidic aqueous extract was neutralised by solid sodium bicar-

bonate. The resulting white solid was filtered, washed thoroughly with distilled water and crystallised from aqueous methanol as colourless needles. Yield: 1.65 g (67%), m.p. 110°C. *Anal.* Found C; 66.16; H, 4.28; N, 20.81. Calc. for $C_{11}H_9N_3O$: C, 66.33; H, 4.52; N, 21.10%.

2.4. Syntheses of the complexes

Caution: Although no problems were encountered in the present study, perchlorate salts are potentially explosive and should be handled in small quantities.

Dichlorobis-triphenylphosphine[2-(N-(2-pyridinium-2yl)-carbamoyl-N⁻)-pyridine]ruthenium(II) [Ru(HL)-(PPh₃)₂Cl₂] (I). To a solution of HL (21 mg, 0.1 mmol) in 15 ml dry ethanol, [Ru(PPh₃)₃Cl₂] (0.1 g, 0.1 mmol) was added. The resulting suspension was refluxed for 2 h with stirring. From the cold reaction mixture the deep brown coloured microcrystalline product was isolated by filtration, washed thoroughly with dry ethanol, and dried over fused CaCl₂. Yield: 66 mg (71%). Anal. Found C; 62.87; H, 4.27; N, 4.65. Calc. for C₄₇H₃₉Cl₂N₃OP₂Ru: C, 63.01; H, 4.36; N, 4.69%.

[2 - (N - (2 - pyridyl)carbamoyl)pyridine]bis - triphenylphosphine(2,2' - bipyridine)ruthenium(II) - perchlorate, $[Ru(L^{-})(bpy)(PPh_{3})_{2}]ClO_{4}$ (II). To a solution of 2,2'bipyridine (bpy) (18 mg, 0.11 mmol) in 10 ml dry ethanol, I (0.1 g, 0.11 mmol) and triethylamine (12 mg, 0.11 mmol) were added. The resulting suspension was refluxed for 2 h. The resulting deep red coloured solution was filtered to reject any impurity and the solution was subjected to distillation to obtain a concentrated solution. Into this cold solution 5 ml saturated aqueous sodium perchlorate solution was added. The red coloured solid product was isolated by filtration, washed thoroughly with distilled water, dried over fused CaCl₂. Yield: 95 mg (85%). Anal. Found C; 63.64; H, 4.48; N, 6.21. Calc. for C₅₇H₄₆ClN₅O₅P₂Ru: C, 63.42; H, 4.26; N, 6.49%.

The complexes [2-(N-(2-pyridyl)carbamoyl)pyridine]bis-triphenylphosphine(1,10-phenanthroline)ruthenium- $[Ru(L^{-})(phen)(PPh_{3})_{2}]ClO_{4}$ (II)-perchlorate, (III). [2-(N-(2-pyridyl)carbamoyl)pyridine]bis-triphenylphosphine(1,2 - diaminoethane)ruthenium(II) - perchlorate, $[\operatorname{Ru}(L^{-})(\operatorname{en})(\operatorname{PPh}_{3})_{2}]ClO_{4}$ (IV) and $[2-(N-(2-\operatorname{pyridy}))$ carbamoyl)pyridine]bis-triphenylphosphine(2-(2-aminoethylpyridine)ruthenium(II)-perchlorate, $[Ru(L^{-}) (amepy)(PPh_3)_2|ClO_4$ (V) were prepared by a method similar to that used for the preparation of II, using an equivalent amount of 1,10-phenanthroline (phen), 1,2-(en) and 2-(2-aminoethyl)pyridine diaminoethane (amepy), respectively, instead of 2,2'-bipyridine. Yields: 104 mg, (91%) for III, 90 mg, (88%) for IV, and 102 mg, (94%) for V. Anal. Found for III: C; 64.20; H, 4.24; N, 6.13. Calc. for C₅₉H₄₆ClN₅O₅P₂Ru: C, 64.16; H, 4.17; N, 6.34%; for IV: C; 59.73; H, 4.41; N, 6.87. Calc. for $C_{49}H_{46}ClN_5O_5P_2Ru$: C, 59.84; H, 4.68; N, 7.12%; for V: C; 61.87; H, 4.68; N, 6.32. Calc. for $C_{54}H_{48}ClN_5O_5P_2Ru$: C, 62.04; H, 4.60; N, 6.70%.

2.5. X-ray crystallography

Intensity data for a colourless prism $(0.20 \times 0.20 \times 0.40 \text{ mm}^3)$ were collected at 293 K on a Rigaku AFC7R diffractometer employing Mo K α radiation ($\lambda = 0.71073$ Å) and the $\omega - 2\theta$ scan technique such that θ_{max} was 30.5°. Corrections were made for Lorentz and polarisation effects [6a] but not for absorption. Of the 13 345 reflections measured, 12 848 were unique ($R_{\text{int}} = 0.039$) and of these, 6875 with $I \ge 3.0\sigma(I)$ were used in the subsequent analysis.

 $C_{47}H_{39}Cl_2N_3OP_2Ru$, M = 895.8, monoclinic, $P2_1/c$, a = 15.786(2), b = 19.848(2), c = 13.085(2) Å, $\beta = 90.52(2)^\circ$, V = 4099.6(8) Å³, Z = 4, μ (Mo K α) = 6.31 cm⁻¹, F(000) = 1832, 463 refined parameters, $\rho_{max} = 0.75$ e Å⁻³.

The structure was solved by heavy-atom methods [6b] and refined by a full-matrix least-squares procedure based on F [6a]. Non-hydrogen atoms were refined employing anisotropic displacement parameters and C-bound H atoms were included in the model at their calculated positions; the N-H atom was located from a difference map but included in a calculated position. A weighting scheme of the form $w = 1/[\sigma^2(F)]$ was employed and at convergence, final R = 0.040 and $R_W = 0.033$. Fig. 3, showing the crystallographic numbering scheme, was drawn with ORTEP at the 35% probability level [6c].

3. Results and discussion

3.1. Synthesis and characterisation of the ligand

The ligand, HL, has been prepared by an analogous procedure to that reported [7a] for the preparation of picolinic acid amides with a slight modification in the isolation of the product [7b]. The reaction between pyridine-2-carboxylic acid and 2-aminopyridine proceeds smoothly in pyridine medium in presence of triphenylphosphite. In the FAB mass spectrum the maximum peak is observed at m/z 200, which corresponds to the molecular ion (calculated molecular weight 199). In the IR spectrum the NH and CO stretching of the amide linkage are observed at 3347 and 1695 cm⁻¹, respectively. The ¹H NMR spectrum (CHCl₃-d) shows a singlet at δ 10.56, which disappears upon the addition of H₂O-d₂ and is thus, assigned to the NH proton of the amide. In the aromatic region eight resonances are found to integrate to eight protons. The signals in the aromatic region are assigned as: δ 8.65 (d, 1H, J = 4.56, H⁶), 8.43 (d, 1H, J = 7.30, H⁶),

8.38 (d, 1H, J = 4.56, H³), 8.30 (d, 1H, J = 7.33, H³), 7.95 (t, 1H, J = 4.60, H⁴), 7.89 (t, 1H, J = 4.58, H⁵), 7.51 (t, 1H, J = 7.38, H⁵) and 7.09 (1H, t, J = 7.27, H⁴).

3.2. Syntheses and characterisation of the complexes

The reaction of $[Ru(PPh_3)_3Cl_2]$ with an equimolar quantity of HL in dry ethanol proceeds smoothly to precipitate microcrystalline $[Ru(HL)(PPh_3)_2Cl_2]$ (I) in reasonably good yield. Further reaction of I with neutral chelating ligands, L', in presence of an equivalent amount of triethylamine and sodium perchlorate leads to the formation of complexes of the form $[Ru(L^-)(PPh_3)_2(L')]ClO_4$, II–V (L' = bidentate chelating ligands bpy, phen, en and amepy). When conducted in the absence of triethylamine, the same products were obtained but in lower yields. The complexes II–V were isolated as perchlorate salts and the molar conductivity data (Table 1) indicate that these are 1:1 electrolytes.

Microanalytical data (see Section 2) correspond to the expected composition. Magnetic susceptibility measurements show the complexes to be diamagnetic as expected for ruthenium(II) (low spin d^6 , S = 0). In the IR spectrum of I the CO stretching is found at 1639 cm^{-1} . The lowering of the CO stretching compared to the free LH is typical for coordination of the amide-nitrogen in its deprotonated form [8]. A NH stretching band for I appears as a broad band centred at 3442 cm^{-1} , an indication of hydrogen bonding [9]. This indicates that in the neutral complex I, HL exists as a zwitterion with the deprotonation of the amide NH and protonation of the pyridyl nitrogen. There is hydrogen bond formation between the protonated pyridyl nitrogen and one of the coordinated chloride ligands. The existence of the hydrogen bonding has been further confirmed by the X-ray studies, discussed later. The NH stretching band does not appear for II and III, while for IV and V the band around 3311 cm⁻¹ may be attributed to NH of the coordinated primary amines. The bands around 520, 690 and 740 cm⁻¹ arise due to coordinated triphenylphosphine [10,11]. Two intense vibrations are observed at ca. 1091 and 622 cm⁻¹, in the IR spectra of II-V, which are ascribed to non-coordinated perchlorate anions.

The ¹H NMR spectra of I-V were recorded in CHCl₃-d solution. In the spectrum of I, a signal due to a NH proton is found at d 14.46, as a broad singlet. This signal disappears on H₂O-d₂ exchange. The low field proton signal supports the hydrogen bonding of the pyridinium NH with one of the coordinated chloride ligands as indicated in the IR studies. The signal due to the NH proton does not appear in the ¹H NMR spectra of the other complexes, II-V, thereby confirming deprotonation of the ligand. From the above, it can

Table 1				
Characterisation	data	for	I–	1

Complex	Electronic spectral data ^a λ_{max} (nm) (ϵ^{b} (dm ³ mol ⁻¹ cm ⁻¹)	Molar conductivity data ^c $L_{\rm M}$ (W ⁻¹ dm ³ mol ⁻¹ cm ²)	Cyclic voltammetric data ^d E ⁰ ₂₉₈ , V (DE _p , mV)	
			Ru ^{II/III}	$Ru^{\mathrm{III}/\mathrm{IV}}$
I	479(2299.8),308(10696.5)°, 274(28590.7),230(31760.6)	_	0.44(60)	0.98(60)
П	436(6865.8),293(30773.7), 230(36622.6)	86	0.40(07)	0.88(70)
ш	437(8493.4),266(41011.6), 231(52173.3)	95	0.42(70)	0.93(70)
IV	464(2421.3),401(331706), 258(21968.4),231(37480.9)	115	0.59(70)	0.88(70)
v	386(5861.6),312(9661.4)°, 254(2453408)°,230(40167.9)	114	0.76(60)	-

^a In dichloromethane solution

^b Extinction coefficient

^c In acetonitrile solution

^d Conditions: solvent, acetonitrile; supporting electrolyte, tetraethylammonium perchlorate; working electrode, platinum; reference electrode, Ag | Ag +; $E_{298}^{\circ} = 0.5(E_{pa} + E_{pc})$; DE_p = $E_{pa} - E_{pc}$.

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be concluded that, L^- coordinates to ruthenium(II) centre forming a chelate ring of type 2 in complexes **II**-**V**. The aromatic region of the ¹H NMR spectra of all complexes are quite complicated owing to significant overlap of the signals due to both HL, L^- , L' and triphenylphosphine ligands.

The electrospray mass spectra of two representative complexes, III and V were recorded. The peaks observed at m/z 1104.2 for III and at m/z 1046.2 for V correspond to the molecular ions of the corresponding complexes; calculated molecular weight: 1103.6 for III and 1045.6 for V.

3.3. Electronic spectra

Electronic spectra have been recorded in dichloromethane solution. Spectral data are collected in Table 1 and a representative spectrum is shown in Fig. 1. All complexes display intense absorption in the visible region. On the basis of the magnitudes of the extinction coefficients, these bands are assigned to the $t_2^6 \rightarrow \pi^*$ metal to ligand charge-transfer (MLCT) transitions [11]. For I two absorptions are found at 308 and 479 nm. The band at 308 nm disappears after conversion of I into the other complexes, while the band at 479 nm remains for II-IV. For IV, a new band appears at 401 nm and for V two new bands appear at 312 and 386 nm. Two intense absorptions at ca. 266 and 230 nm, which also appear in the spectrum of HL due to intraligand transitions, appear in the UV region of the spectra of all the complexes; for V the band at 254 nm appears as a shoulder. In the complexes the intraligand bands are found to appear with a minor shift in the position compared to those for HL.

3.4. Electrochemical properties

The electrochemical properties of I were studied in dichloromethane solution (0.1 M TEAP) and those for II-V were studied in acetonitrile solution (0.1 M TEAP) by cyclicvoltammetry. The voltammetric data are collected in Table 1 and a selected voltammogram is shown in Fig. 2. Complexes I-IV show two reversible responses in the potential range 0.35-1.0 V. The first response is assigned to the ruthenium(II)/ruthenium(III) oxidation and the second is due to the ruthenium(III)/ruthenium(IV) oxidation. For all the voltammetric responses, the $\Delta E_{\rm p}$ values lie within the range 60 - 70 mV, which do not change with changes in the scan rate. The i_{pa}/i_{pc} (i_{pa} = anodic peak current



Fig. 1. Representative UV-Vis spectrum for III in dichloromethane.





Fig. 2. Representative voltammogram for III in acetonitrile (0.1 M TEAP); scan rete 100 mV s⁻¹.



Fig. 3. An ORTEP representation of \mathbf{I} showing the atomic numbering scheme.

and i_{pc} = cathodic peak current) ratio is close to 1.0, as expected for reversible response.

For **I** the responses due to Ru(II)/Ru(III) and Ru(III)/Ru(IV) couples appear at 0.44 and 0.98 V, respectively. In the complexes **II** and **III** the same oxidation couples appear at a lower potential value compared to **I**, whereas in case of complex **IV** they appear at a more positive potential. For complex V, the response due to Ru(II)/Ru(III) couple appears at a higher positive potential compared to **I**, while the Ru(III)/Ru(IV) oxidation couple does not appear within the solvent window. The difference in the oxida-

tion potentials for the substituted complexes II-V can be attributed to the following reasons: (i) in all the complexes the coordination from the negatively charged nitrogen atom of the amide linkage, which is a strong s-donor, increases the electron density over the ruthenium(II) centres; (ii) in II and III there is substitution of the chloride ligands of I by the π -accepting diimine ligands; (iii) all the complexes II–V have one unit positive charge; and (iv) the higher molar conductance values for IV and V indicate that they are more ionic i.e. the formal positive charge over these complexes are greater compared to the same over II and III.

3.5. Crystal structure of I

The molecular structure of I is illustrated in Fig. 3 and selected interatomic parameters are collected in Table 2. The structure confirms the spectroscopic results obtained for I, i.e. type 2 coorindation, is also found in the solid state. The transfer of the amide-proton to a pyridine-nitrogen retains the electrical neutrality of the complex so that coordinated LH functions as a zwitterion. The ruthenium atom exists in a distorted octahedral geometry with a Cl₂N₂P₂ donor set. The maximum deviation from the ideal geometry is manifested in the N(1)-Ru-N(8) chelate angle of 77.89(9)°. The five-membered chelate ligand is planar to 0.067 Å but there is some buckling in this ring, notably about the amide-nitrogen atom as seen in the Ru-N8-C7-C6 torsion angle of 13.1(3)°. The dihedral angle between the pyridine rings is calculated to be 29.5° suggesting that there is no extensive delocalisation of p-electron density over LH. This is further borne out by the geometric parameters characterising the backbone of

Table 2 Selected bond lengths (Å) and angles (°) for ${\bf I}$

Bond lengths			
Ru–Cl(1)	2.4503(9)	Ru–Cl(2)	2.4197(9)
Ru-P(1)	2.3804(8)	Ru-P(2)	2.3708(8)
Ru-N(1)	2.067(2)	Ru–N(8)	2.152(2)
C(7)–O(7)	1.232(4)	N(1)-C(2)	1.344(4)
N(1)-C(6)	1.337(4)	N(8)–C(7)	1.375(4)
N(8)-C(9)	1.362(4)	N(10)-C(9)	1.358(4)
N(10)-C(11)	1.353(4)		
Bond angles			
Cl(1)-Ru-Cl(2)	90.34(3)	Cl(1)-Ru-P(1)	90.21(3)
Cl(1)-Ru-P(2)	86.39(3)	Cl(1)-Ru-N(1)	178.24(6)
Cl(1)-Ru-N(8)	100.40(6)	Cl(2)-Ru-P(1)	90.48(3)
Cl(2)-Ru-P(2)	88.00(3)	Cl(2)-Ru-N(1)	91.36(7)
Cl(2)-Ru-N(8)	169.19(6)	P(1)-Ru-P(2)	176.27(3)
P(1)- Ru - $N(1)$	90.23(7)	P(1)-Ru-N(8)	90.69(7)
P(2)-Ru-N(1)	93.21(7)	P(2)-Ru-N(8)	91.44(7)
N(1)-Ru-N(8)	77.89(9)	Ru–N(1)–C(2)	126.6(2)
Ru–N(1)–C(6)	116.3(2)	C(2)-N(1)-C(6)	117.1(2)
Ru–N(8)–C(7)	113.5(2)	Ru-N(8)-C(9)	130.3(2)
C(7)-C(8)-C(9)	116.0(2)		

the ligand (Table 2). The Ru–N(amidato) distance of 2.152(2) Å is [4a,5b] longer, as expected, than the Ru–N(pyridine) distance of 2.067(2) Å and both fall in the ranges expected for such interactions[2]. A key feature of the molecular structure is the presence of a short intramolecular N–H…Cl interaction that provides additional stability to the ligand donor set.

The N–H atom was located in the X-ray study and is separated from Cl(1) by 2.17 Å so that Cl(1)…N(10) is 3.016(3) Å. The participation of the Cl(1) atom in this contact has the result that its distance to the ruthenium centre has elongated significantly, i.e. by approximately 0.03 Å, compared to the Ru–Cl(2) distance (Table 2). The closest intermolecular contact involving non-H atoms of 3.290(4) Å between the O(7) and C(116)^{*i*} atoms corresponds to an O…H separation of 2.74 Å; symmetry operation *i*: *x*, 0.5 – *y*, -0.5 + z.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 149895. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam. ac.uk or www:http://www.ccdc.cam.ac.uk).

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