

N-(Aryl)picolinamide complexes of rhodium : Synthesis, structure and, spectral and electrochemical properties

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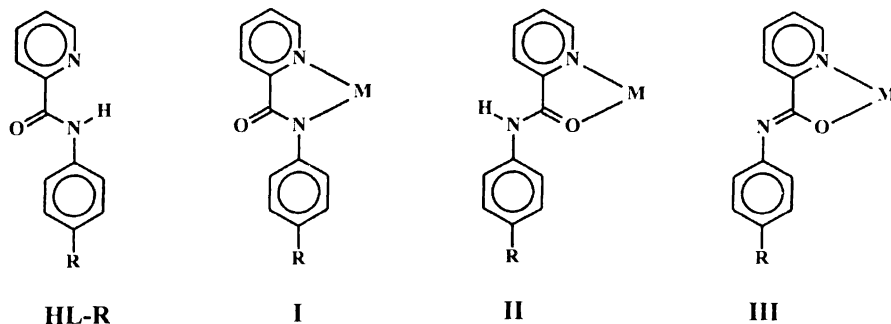
Abstract : Reaction of a series of *N*-(aryl)picolinamide ligands (HL-R, where H denotes the acidic proton and R (R = OCH₃, CH₃, H, Cl and NO₂) is the *para* substituent in the aryl fragment) with RhCl₃·3H₂O in refluxing ethanol in the presence of a base (NEt₃) affords two groups of yellow complexes of type [Rh(HL-R)(L-R)Cl₂] and [Rh(L-R)₂(H₂O)Cl]. In [Rh(HL-R)(L-R)Cl₂], HL-R is coordinated as neutral N,O-donor and L-R as monoanionic N,N-donor, and the two chlorides are mutually *trans*. In [Rh(L-R)₂(H₂O)Cl] both the amide ligands are coordinated as monoanionic N,N-donor, and the chloro and aquo ligands are mutually *cis*. Structures of the [Rh(HL-OCH₃)(L-OCH₃)Cl₂] and [Rh(L-Cl)₂(H₂O)Cl] complexes have been determined by X-ray crystallography. All the complexes show characteristic ¹H NMR signals and intense LLCT transitions in the ultraviolet region. Cyclic voltammetry on the complexes shows an oxidation of the coordinated amide ligand within 0.78–1.80 V vs SCE and a reductive response within –0.20 to –0.75 V vs SCE. DFT calculations have been done to explain the electronic spectral and electrochemical properties.

Keywords : *N*-(Aryl)picolinamides, rhodium complexes, formation, crystal structures, spectral and electrochemical properties.

Introduction

The chemistry of rhodium has been receiving considerable attention primarily because of the fascinating redox¹, photochemical² and catalytic³ properties exhibited by complexes of this metal. As properties of the complexes are dependent mostly on the coordination environment around the metal center, complexation of rhodium by ligands of selected types is of significant importance, and the present work has originated from our continued interest in this area⁴. A group of five *N*-(aryl)picolinamide ligands have been chosen for the present study, which are

abbreviated in general as HL-R, where H stands for the dissociable N–H proton and R (R = OCH₃, CH₃, H, Cl and NO₂) is the *para* substituent in the aryl fragment. Chemistry of the amide ligands is of particular interest with reference to their role in biological processes⁵. Besides, coordination chemistry of the amide ligands is also attractive owing to their variable mode of binding. The selected amide ligands are known to bind to metal ions usually as monoanionic N,N-donors (**I**) via dissociation of the N–H proton. They are also known to display neutral and monoanionic NO-binding modes **II** and **III** res-



pectively. It is relevant to mention here that though coordination chemistry of the selected amide ligands has been extensively studied with many transition metals⁶, that with rhodium appears to have remained unexplored. As the source of rhodium $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ has been chosen, particularly with an aim to prepare tris-chelated complexes via displacement of the chlorides as well the water molecules. Reaction of the selected amides with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ has been found to afford two groups of complexes, where the amides have displayed two different modes of binding. An account of the chemistry of all these complexes is presented in this paper, with special reference to their syntheses, structure and, spectral and electrochemical properties.

Experimental

Materials :

Commercial rhodium trichloride was purchased from Arora Matthey, Kolkata, India. The *para*-substituted anilines were obtained from Aldrich. 2-Picolinic acid was procured from Lancaster, Morecambe, England. All other chemicals and solvents were reagent grade commercial materials and were used as received. The *N*-(aryl)-picolinamides (HL-R) were prepared by following a reported procedure⁷. Tetrabutylammonium perchlorate (TBAP) for electrochemical work was prepared as reported in the literature⁸.

Preparation of the complexes :

$[\text{Rh}(\text{HL-R})(\text{L-R})\text{Cl}_2]$ and $[\text{Rh}(\text{L-R})_2(\text{H}_2\text{O})\text{Cl}]$: The two series of complexes were obtained by following a general procedure. Specific details are given below for a particular pair.

$[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$ and $[\text{Rh}(\text{L-OCH}_3)_2(\text{H}_2\text{O})\text{Cl}]$: To a solution of HL-OCH₃ (260 mg, 1.13 mmol) in absolute ethanol (40 ml), triethylamine (70 mg, 0.70 mmol) followed by $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (100 mg, 0.22 mmol) were added, and the mixture was refluxed for 24 h to yield a golden yellow solution. The solution was evaporated to dryness and the yellow residue, thus obtained, was subjected to purification by thin layer chromatography on a silica plate. With 1 : 1 acetonitrile-benzene as the eluant two yellow bands separated, which were extracted with acetonitrile. Evaporation of the first acetonitrile

trile extract gave $[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$ and that of the second acetonitrile extract gave $[\text{Rh}(\text{L-OCH}_3)_2(\text{H}_2\text{O})\text{Cl}]$ as yellow crystalline solids. Yield : 41% and 37% respectively.

$[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$: Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_4\text{Cl}_2\text{Rh}$: C, 49.52; H, 3.49; N, 8.88. Found : C, 49.63; H, 3.42; N, 8.85%. ¹H NMR⁹ : 9.83 (1H, d, *J* 5.4), 9.15 (1H, d, *J* 5.1), 8.14 (1H, d, *J* 7.5), 7.92–8.02* (2H), 7.64 (4H, d, *J* 7.2), 7.42–7.44* (2H), 7.15–7.18* (2H), 6.46–6.49* (2H), 6.30–6.33* (2H), 6.60* (2H), 3.62 (s, OCH₃), 3.46 (s, OCH₃).

$[\text{Rh}(\text{HL-CH}_3)(\text{L-CH}_3)\text{Cl}_2]$: Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_2\text{Cl}_2\text{Rh}$: C, 52.17; H, 3.67; N, 9.36. Found : C, 52.10; H, 3.72; N, 9.45%. ¹H NMR : 9.66 (1H, d, *J* 5.4), 9.17 (1H, d, *J* 5.1), 8.51 (1H, d, *J* 7.8), 8.17–8.28* (2H), 8.02 (1H, d, *J* 7.9), 7.88 (1H, d, *J* 8.4), 7.80 (1H, d, *J* 6.72), 7.32–7.35* (2H), 7.15–7.18* (2H), 6.69–6.78* (2H), 2.23 (s, CH₃), 2.02 (s, CH₃).

$[\text{Rh}(\text{HL-H})(\text{L-H})\text{Cl}_2]$: Anal. Calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_2\text{Cl}_2\text{Rh}$: C, 50.70; H, 3.16; N, 9.85. Found : C, 50.83; H, 3.12; N, 9.95%. ¹H NMR : 9.67 (1H, d, *J* 5.4), 9.30 (1H, d, *J* 5.2), 9.24 (1H, d, *J* 4.7), 9.124 (1H, t, *J* 6.2), 9.916* (1H), 8.25–8.27* (1H, t), 6.89–8.14* (12H).

$[\text{Rh}(\text{HL-Cl})(\text{L-Cl})\text{Cl}_2]$: Anal. Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_2\text{Cl}_3\text{Rh}$: C, 45.07; H, 2.50; N, 8.76. Found : C, 45.10; H, 2.52; N, 8.71%. ¹H NMR : 9.64 (1H, d, *J* 5.1), 9.07 (1H, d, *J* 7.1), 8.26 (1H, t, *J* 10.8), 7.88–8.02* (2H), 7.78–7.85 (1H), 7.49–7.69* (2H), 7.14–7.31* (3H), 6.94–7.03* (3H), 6.84–6.90* (2H).

$[\text{Rh}(\text{HL-NO}_2)(\text{L-NO}_2)\text{Cl}_2]$: Anal. Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_6\text{O}_6\text{Cl}_2\text{Rh}$: C, 43.63; H, 2.42; N, 12.72. Found : C, 43.83; H, 2.39; N, 12.75%. ¹H NMR : 9.59 (1H, d, *J* 4.5), 9.44 (1H, d, *J* 5.2), 8.28 (1H, t, *J* 7.4), 7.12–8.09* (13H).

$[\text{Rh}(\text{L-OCH}_3)_2(\text{H}_2\text{O})\text{Cl}]$: Anal. Calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_5\text{ClRh}$: C, 50.93; H, 3.91; N, 9.14. Found : C, 50.83; H, 3.92; N, 9.21%. ¹H NMR : 9.87 (1H, d, *J* 5.3), 9.66 (1H, d, *J* 5.2), 9.40 (1H, d, *J* 5.3), 9.18 (1H, t, *J* 6.33), 8.69 (1H, d, *J* 5.3), 6.43–8.46* (11H), 3.68 (s, OCH₃), 3.58 (s, OCH₃).

$[\text{Rh}(\text{L-CH}_3)_2(\text{H}_2\text{O})\text{Cl}]$: Anal. Calcd. for

$C_{26}H_{24}N_4O_3ClRh$: C, 53.74; H, 4.13; N, 9.64. Found : C, 53.65; H, 4.12; N, 9.95%. 1H NMR : 9.37 (1H, d, J 5.5), 9.19 (1H, d, J 5.4), 9.03 (1H, d, J 5.4), 8.36 (1H, t, J 5.9), 8.02–8.05* (2H), 6.13–7.92* (10H), 2.40 (s, CH_3), 2.04 (s, CH_3).

$[Rh(L-H)_2(H_2O)Cl]$: Anal. Calcd. for $C_{24}H_{20}N_4O_3ClRh$: C, 52.31; H, 3.63; N, 10.17. Found : C, 52.33; H, 3.72; N, 10.23%. 1H NMR : 9.26 (1H, d, J 5.2), 9.17 (1H, d, J 5.3), 8.81 (1H, d, J 5.3), 6.68–8.07* (13H).

$[Rh(L-Cl)_2(H_2O)Cl]$: Anal. Calcd. for $C_{24}H_{18}N_4O_3ClRh$: C, 46.33; H, 2.89; N, 9.81. Found : C, 46.83; H, 2.72; N, 9.76%. 1H NMR : 9.24 (1H, d, J 5.4), 9.05 (1H, d, J 5.1), 8.21 (1H, t, J 5.2), 8.12 (1H, d, J 5.7), 6.85–7.99* (12H).

$[Rh(L-NO_2)_2(H_2O)Cl]$: Anal. Calcd. for $C_{24}H_{18}N_6O_7ClRh$: C, 44.82; H, 2.80; N, 13.67. Found : C, 44.83; H, 2.72; N, 13.65%. 1H NMR : 9.70 (1H, d, J 6.2), 9.315 (1H, d, J 4.3), 9.22 (1H, d, J 4.7), 7.78 (2H, d, J 7.7), 8.83 (1H, d, J 5.4), 7.13–8.57* (12H).

Physical measurements :

Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were obtained on a Perkin-Elmer Spectrum RX1 spectrometer with samples prepared as KBr pellets. Electronic

spectra were recorded on a JASCO V-570 spectrophotometer. 1H NMR spectra were recorded in $DMSO-d_6$ solution with a Bruker AV 300 NMR spectrometer. Mass spectra were recorded with a Micromass LCT electrospray (Qtof Micro YA263) mass spectrometer by electrospray ionization method. Electrochemical measurements were made using a CH Instruments model 600A electrochemical analyzer. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. Ground-state structures and energy calculations for the complexes were carried out by density functional theory (DFT) method, based on the crystallographic coordinates, using the Gaussian 03 package using B3LYP/ [SDD/6-31g(d,p)] basis set¹⁰.

Crystallography :

Single crystals of both $[Rh(HL-OCH_3)(L-OCH_3)Cl_2]$ and $[Rh(L-Cl)_2(H_2O)Cl]$ were obtained by slow evaporation of methanolic solution of the complexes. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated

Table 1. Crystallographic data for the complexes

Complex	$[Rh(HL-OCH_3)(L-OCH_3)Cl_2]$	$[Rh(L-Cl)_2(H_2O)Cl]$
Empirical formula	$C_{26}H_{22}N_4O_4Cl_2Rh$	$C_{24}H_{18}N_4O_3Cl_2Rh$
Formula mass	647.31	651.73
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	10.977(3)	30.586(5)
b (Å)	11.476(3)	11.9443(9)
c (Å)	12.364(2)	15.6211(14)
α (deg)	104.380(19)	90
β (deg)	109.98(2)	111.869(13)
γ (deg)	103.95(3)	90
V (Å ³)	1323.9(7)	5296.2(12)
Z	2	8
$D_{calcd.}$ (mg m ⁻³)	1.624	1.635
Crystal size (mm ³)	$0.03 \times 0.17 \times 0.17$	$0.02 \times 0.02 \times 0.15$
T (K)	150	150
μ (mm ⁻¹)	0.892	0.987
Independent reflections	7055	7639

Table-1 (contd.)

R_{int}	0.047	0.034
Collected reflections	8560	18135
R_1^a	0.1013	0.0524
wR_2^b	0.1798	0.1473
GOF ^c	1.16	1.12

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$$

$$^b wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}.$$

$$^c \text{GOF} = [\Sigma [w(F_o^2 - F_c^2)^2] / (M - N)]^{1/2}, \text{ where } M \text{ is the number of reflections and } N \text{ is the number of parameters refined.}$$

Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). X-Ray data reduction and, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs¹¹. The structures were solved by the direct methods. CCDC 844941 and 844942 contain the supplementary crystallographic data.

Results and discussion

Synthesis and structure :

Reaction of the selected *N*-(aryl)picolinamides (HL-R, where R = OCH₃, CH₃, H, Cl and NO₂) with RhCl₃·3H₂O in absolute ethanol in the presence of tri-

ethylamine (NEt₃) affords two series of yellow complexes formulated as [Rh(HL-R)(L-R)Cl₂] and [Rh(L-R)₂(H₂O)Cl]. Preliminary characterization data (microanalytical and spectroscopic) on the complexes are found to be in good agreement with their formulations. Compositions of the complexes were further authenticated by mass spectral measurements on two selected complexes, viz. [Rh(HL-OCH₃)(L-OCH₃)Cl₂] and [Rh(L-Cl)₂(H₂O)Cl]. Mass spectra of these two complexes agree well with their respective compositions. In the mass spectrum of [Rh(HL-OCH₃)(L-OCH₃)Cl₂] (Fig. 1), a peak at 615 is

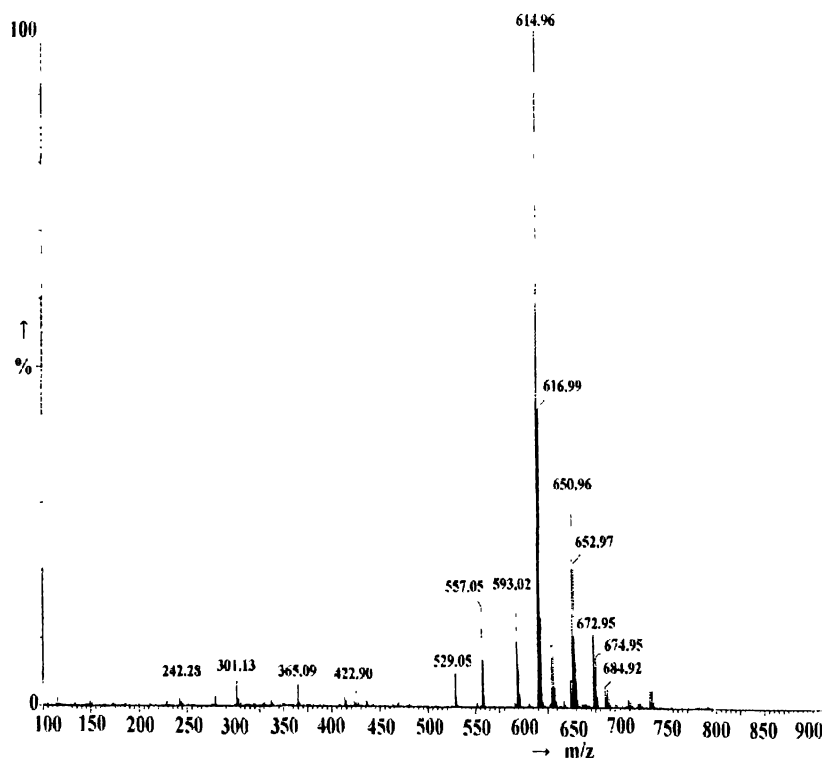


Fig. 1. Mass spectrum of the complex [Rh(HL-OCH₃)(L-OCH₃)Cl₂].

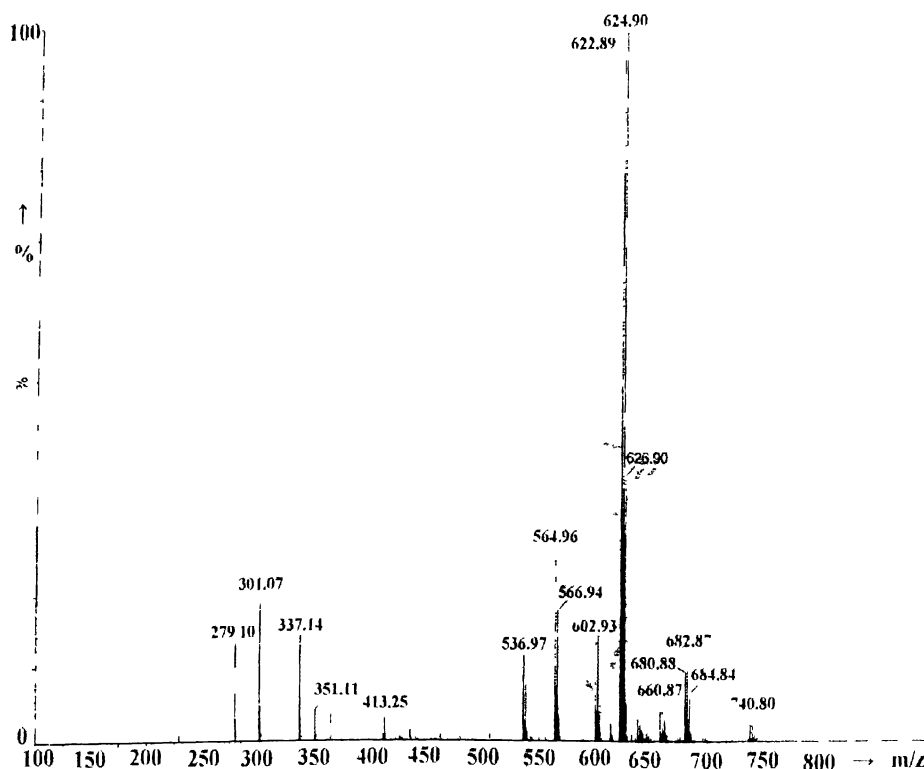


Fig. 2. Mass spectrum of the complex $[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$

observed corresponding to the $[\text{M} - \text{HCl} + \text{Na}]^+$ ion. The peaks corresponding to the $[\text{M} - \text{Cl}]^+$ and $[\text{M} - \text{HCl} - \text{Cl}]^+$ ions are also observed at 593 and 557 respectively. Mass spectrum of $[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$ (Fig. 2) shows a peak at 625, which corresponds to the $[\text{M} - \text{H}_2\text{O} + \text{Na}]^+$ ion. The peaks corresponding to the $[\text{M} - \text{H}_2\text{O} + \text{H}]^+$ ion and $[\text{M} - \text{H}_2\text{O} - \text{Cl}]^+$ ions are also observed at 603 and 565 respectively.

To find out stereochemistry of the $[\text{Rh}(\text{HL-R})(\text{L-R})\text{Cl}_2]$ and $[\text{Rh}(\text{L-R})_2(\text{H}_2\text{O})\text{Cl}]$ complexes, as well as to ascertain coordination mode of the amide ligands in them, structures of the two aforesaid complexes, viz. $[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$ and $[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$, were determined by X-ray crystallography. Structure of $[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$ is shown in Fig. 3 and selected bond parameters are listed in Table 2. The structure reveals that the two amide ligands are coordinated to rhodium in two different coordinating modes, one as monoanionic N,N-donor (as in I) and the other as neutral N,O-donor (as in II). The two coordinated chlorides are mutually

trans, and so are the two pyridine nitrogens. The Rh-N, Rh-O, Rh-Cl distances are found to be quite normal⁴. The C-O and C-N lengths within the two coordinated amide ligands differ significantly, and the observed difference is attributable to the difference in the mode of coordination of these two ligands. Rhodium is thus sitting in an N_3OCl_2 coordination sphere in this complex, and from the bond parameters it is clear that the geometry of the $\text{N}_3\text{OCl}_2\text{Rh}$ core is distorted octahedral in nature.

Structure of $[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$ (Fig. 4) shows that in this complex both the amide ligands are coordinated to rhodium in the same fashion, viz. as monoanionic N,N-donors (as in I). The coordinated chloride and water molecule are mutually *cis*, while both of them are *trans* to the two amidate-nitrogens. The bond distances around the metal center, as well as those within the two similarly coordinated amide ligands, are found to be quite normal (Table 2)⁴. The N_4OCl coordination sphere Rh core is distorted octahedral in nature.

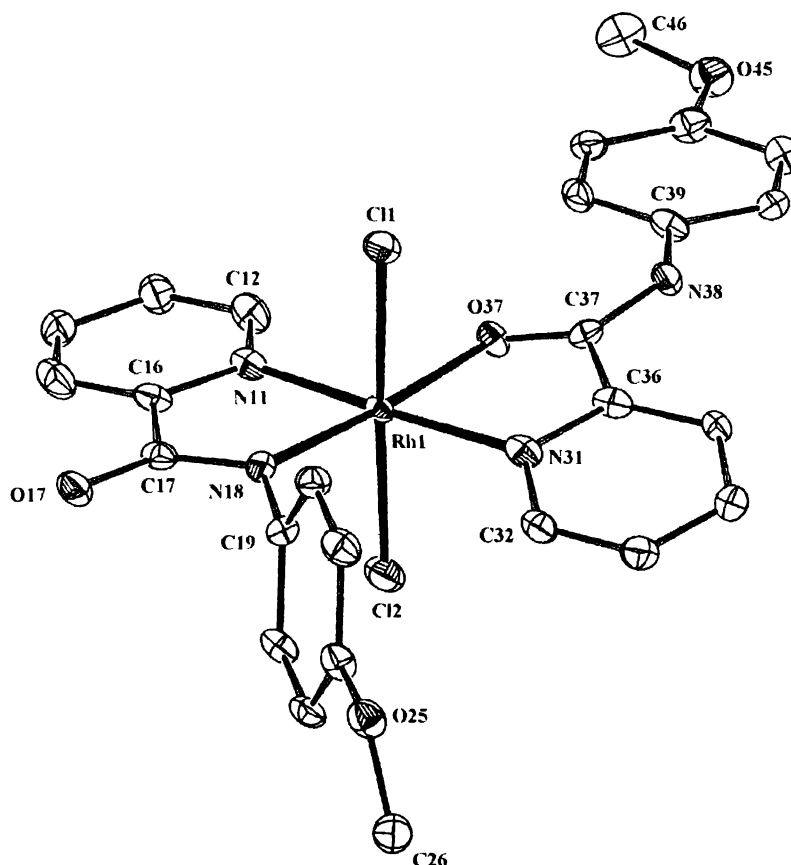
Fig. 3. Structure of the $[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$ complex.

Table 2. Selected bond distances and bond angles of the complexes

$[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$			
Bond distance (Å)			
Rh1-Cl1	2.349(2)	C17-O17	1.264(9)
Rh1-Cl2	2.340(2)	C17-N18	1.333(10)
Rh1-O37	2.112(5)	C37-O37	1.252(10)
Rh1-N11	2.014(7)	C37-N38	1.339(10)
Rh1-N18	2.027(6)		
Rh1-N31	2.070(7)		
Bond angles (°)			
Cl1-Rh1-Cl2	177.29(9)	N11-Rh1-N18	79.5(3)
N18-Rh1-O37	174.8(3)	N11-Rh1-N31	173.9(3)
N31-Rh1-O37	78.5(2)		
$[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$			
Bond distance (Å)			
Rh1-Cl1	2.3419(14)	C37-O37	1.243(7)
Rh1-O1	2.071(3)	C37-N38	1.322(6)
Rh1-N11	2.024(4)	C17-O17	1.249(5)

Table-2 (contd.)

Rh1-N18	2.002(3)	C17-N18	1.315(6)
Rh1-N31	2.019(4)	C39-N38	1.416(6)
Rh1-N38	2.034(4)	C19-N18	1.425(6)
Bond angles (°)			
N38-Rh1-Cl1	174.45(11)	N18-Rh1-N38	174.30(1)
N18-Rh1-O1	173.89(1)	N11-Rh1-N38	98.12(16)
N18-Rh1-N31	80.74(14)		

Formation of the two types of complexes from a single reaction has been quite intriguing, and some speculated steps, that seem probable, are shown in Scheme 1. Upon initial reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with the amide ligand a *trans* dichloro diaquo species (**A**) is believed to form as the active intermediate via elimination of HCl and water. A second molecule of the amide ligand reacts with this intermediate **A** in two different ways, (a) as neutral N,O-donor (as in **II**) it displaces the two aquo ligands and affords $[\text{Rh}(\text{HL-R})(\text{L-R})\text{Cl}_2]$ and, (b) as monoanionic N,N-

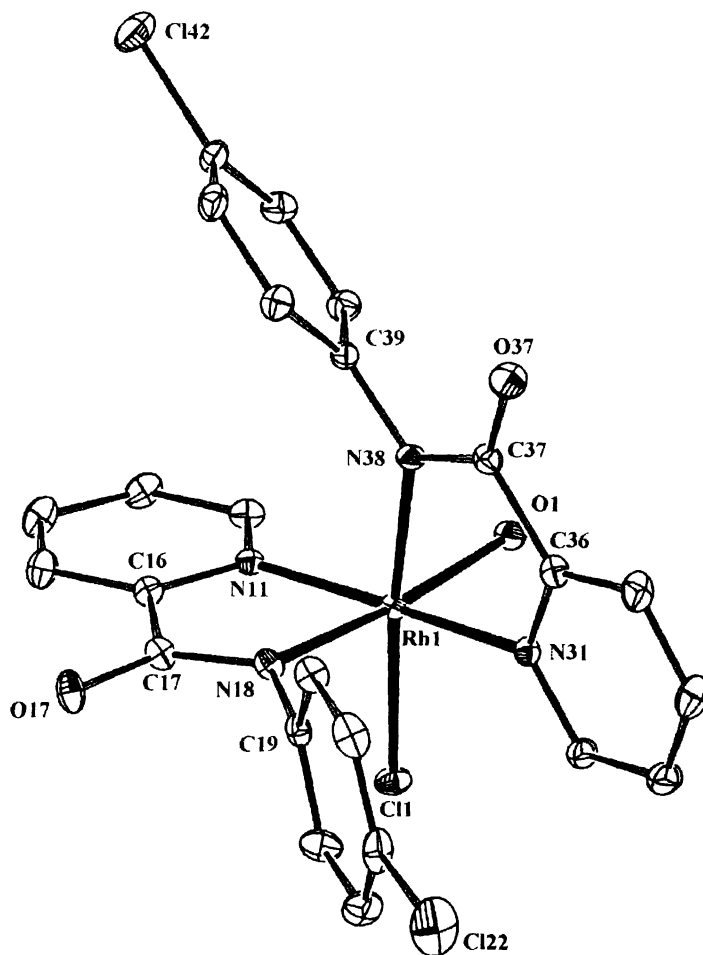
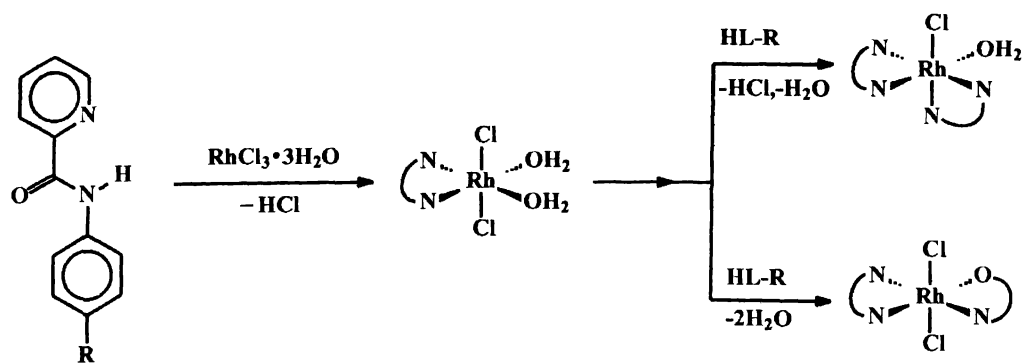


Fig. 4. Structure of the $[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$ complex.



Scheme 1

donor (as in **I**) it affords $[\text{Rh}(\text{L-R})_2(\text{H}_2\text{O})\text{Cl}]$ via elimination of HCl and water. It needs to be mentioned here that

though our initial target was to obtain tris-chelated complexes from these reactions, no such tris complex could

be obtained even on using excess (five-fold) amide ligand during the synthesis.

Presence of the coordinated water in the $[\text{Rh}(\text{L-R})_2(\text{H}_2\text{O})\text{Cl}]$ complexes makes them attractive candidates for exploring displacability of the rhodium-bound aquo ligand by neutral monodentate ligands, and thereby utilizing them as synthon for the preparation of new complexes. Several such reactions were attempted using many monodentate ligands (such as acetonitrile, 4-picoline, triphenylphosphine, etc.), but the rhodium-bound aquo ligand could not be displaced at all. The non-displacability of the coordinated water is attributable to the intra-molecular $\text{O-H}\cdots\text{Cl}$ and $\text{O-H}\cdots\text{N}$ hydrogen-bonding existing between the water-hydrogen atoms and the rhodium-bound chloride and amidate-nitrogen respectively (Fig. 5). It also needs to be mentioned in this context that our attempts to displace both the chloro and aquo-ligands from $[\text{Rh}(\text{L-R})_2(\text{H}_2\text{O})\text{Cl}]$ by several mono-anionic bidentate ligands (such as 2-picolinic acid, 8-hydroxyquinoline, or, even another molecule of *N*-(aryl)picolinamide) has failed to afford the targeted mixed-tris or tris complexes.

Spectral properties :

^1H NMR spectra of the complexes show many signals, most of which are overlapping, and hence assignment of each signal to a specific proton has not been possible. In all the rhodium complexes signals for the aromatic protons, arising from the two coordinated amide-ligands, appeared within 6.0–9.9 ppm. Among these, some were clearly detected in the 8.5–9.8 ppm region, while the rest appeared as broad signals within 6.0–8.5 ppm due to overlap problem. Signals for the methoxy and methyl substituents in the amide ligands are observed within 3.46–3.68 ppm and 2.02–2.39 ppm respectively.

Infrared spectra of two selected complexes, viz. $[\text{Rh}(\text{HL-Cl})(\text{L-Cl})\text{Cl}_2]$ and $[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$, have been recorded. Both the spectra show many bands of different intensities within 400–4000 cm^{-1} . Assignment of each individual band to a specific vibration has not been attempted. However, comparison of the spectrum of $[\text{Rh}(\text{HL-Cl})(\text{L-Cl})\text{Cl}_2]$ with that of the uncoordinated HL-Cl ligand shows that the N–H stretch, observed at 3142 cm^{-1} in the

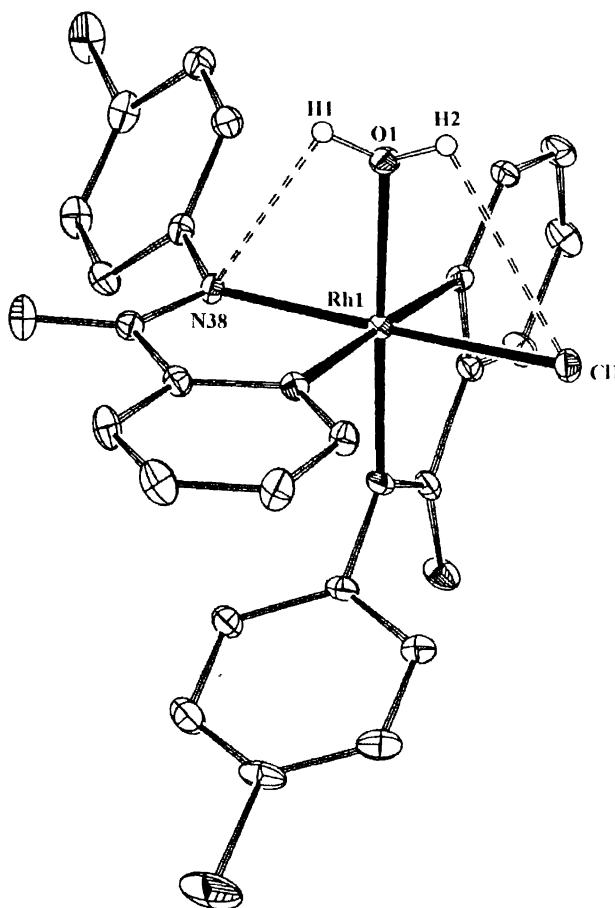


Fig. 5. Intramolecular $\text{O-H}\cdots\text{Cl}$ and $\text{O-H}\cdots\text{N}$ hydrogen bonding in the $[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$ complex. The $\text{H2}\cdots\text{Cl1}$ distance = 2.915 Å, O1-H2-Cl1 angle = 98.63° and the $\text{H1}\cdots\text{N38}$ distance = 2.788 Å and O1-H1-N38 angle = 84.70° .

uncoordinated ligand, is still present in the complex as a rather weak band at 3121 cm^{-1} , indicating the presence of N–H fragment in the N,O-coordinated amide. In the other $[\text{Rh}(\text{L-R})_2(\text{H}_2\text{O})\text{Cl}]$ complex, however, this N–H stretch was totally absent, as expected. Similarly the amide C=O stretch, observed at 1681 cm^{-1} in the uncoordinated HL-Cl ligand, is also found to be shifted to 1624 and 1565 cm^{-1} in the $[\text{Rh}(\text{HL-Cl})(\text{L-Cl})\text{Cl}_2]$ complex, and to 1624 and 1594 cm^{-1} in $[\text{Rh}(\text{L-R})_2(\text{H}_2\text{O})\text{Cl}]$. For the dichloro complex several bands, which appear at 1565 to 467 cm^{-1} (1565, 1484, 1401, 1341, 1294, 1265, 1133, 1090, 1012, 911, 824, 762, 724, 684, 510, 467 cm^{-1}) are attributed to the coordinated amide ligands. For the chloro-aquo species the bands from 1623 to 444

cm^{-1} (1623, 1593, 1483, 1393, 1295, 1150, 1087, 1012, 968, 820, 763, 726, 684, 509, 444 cm^{-1}) are attributed to the coordinated amide ligands.

All the complexes are found to be insoluble in dichloromethane, chloroform, etc., but readily soluble in acetone, acetonitrile, methanol, ethanol, etc., producing golden-yellow solutions. Electronic spectra of the complexes have been recorded in methanolic solution. All the complexes show two intense absorptions in the ultraviolet

found to be delocalized predominantly over the coordinated amide ligands. Hence the lower energy absorptions are attributable to transitions within the orbitals of these two amide ligands.

Electrochemical properties :

Electrochemical properties of the complexes have been studied by cyclic voltammetry in acetonitrile solution (0.1 M TBAP). All the complexes show two oxidative responses at positive potentials of SCE (reference electrode) and a

Table 3. Electronic spectral and cyclic voltammetric data of the complexes

Complex	Electronic spectral data ^a	Cyclic voltammetric data ^b
	λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)	E , V vs SCE
[Rh(HL-OCH ₃)(L-OCH ₃)Cl ₂]	232(19500), 330(8000)	-0.35 ^c , 0.84 ^d , 1.23 ^d
[Rh(HL-CH ₃)(L-CH ₃)Cl ₂]	234(31900), 334(13200)	-0.45 ^c , 1.03 ^d , 1.50 ^d
[Rh(HL-H)(L-H)Cl ₂]	245(11100), 338(3800)	-0.60 ^c , 1.11 ^d , 1.40 ^d
[Rh(HL-Cl)(L-Cl)Cl ₂]	238(2700), 354(9300)	-0.61 ^c , 0.80 ^d , 1.30 ^d
[Rh(HL-NO ₂)(L-NO ₂)Cl ₂]	265(10400), 368(7100)	-0.65 ^c , 0.83 ^d
[Rh(L-OCH ₃) ₂ (H ₂ O)Cl]	265(10000), 348(3700)	-0.54 ^c , 0.75 ^d , 1.07 ^d , 1.26 ^d
[Rh(L-CH ₃) ₂ (H ₂ O)Cl]	264(12700), 351(3200)	-0.54 ^c , 1.18 ^d , 1.43 ^d
[Rh(L-H) ₂ (H ₂ O)Cl]	241(13100), 342(4700)	-0.66 ^c , 0.85 ^d , 1.16 ^d
[Rh(L-Cl) ₂ (H ₂ O)Cl]	264(14000), 363(4100)	-0.75 ^c , 0.80 ^d , 1.28 ^d
[Rh(L-NO ₂) ₂ (H ₂ O)Cl]	267(5500), 368(4100)	-0.58 ^c , 0.82 ^d , 1.23 ^d

^aIn methanolic solution.

^bSolvent, acetonitrile; supporting electrolyte, TBAP; scan rate 50 mV s^{-1} .

^cAnodic peak potential (E_{pa}) value.

^dCathodic peak potential (E_{pc}) value.

let region (Table 3). Though the complexes do not have any absorption band with a λ_{max} in the visible region (Table 3), yet they display a yellow color, which is attributable to the portion of absorption profile that resides within the visible window. A representative spectrum is shown in Fig. 6. To have an understanding of the origin of the lower-energy absorption DFT calculations have been performed on two representative complexes, viz. [Rh(HL-OCH₃)(L-OCH₃)Cl₂] and [Rh(L-Cl)₂(H₂O)Cl]. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of these two complexes are shown in Fig. 7 and Fig. 8 respectively, and their compositions are given in Table 4.

For both the complexes, the HOMO and LUMO are

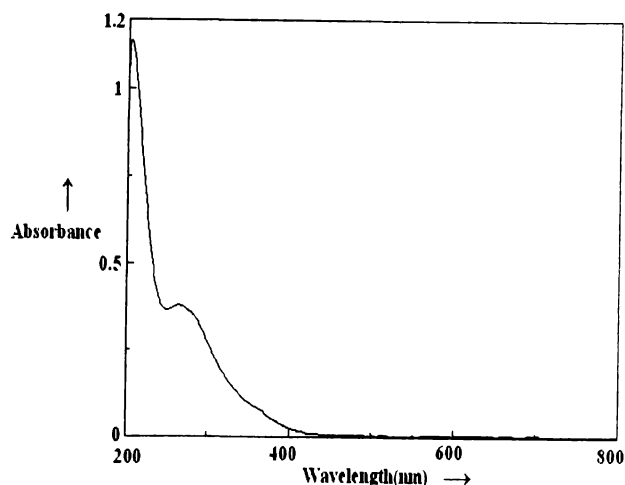


Fig. 6. Absorption spectrum of the complex [Rh(HL-OCH₃)(L-OCH₃)Cl₂].

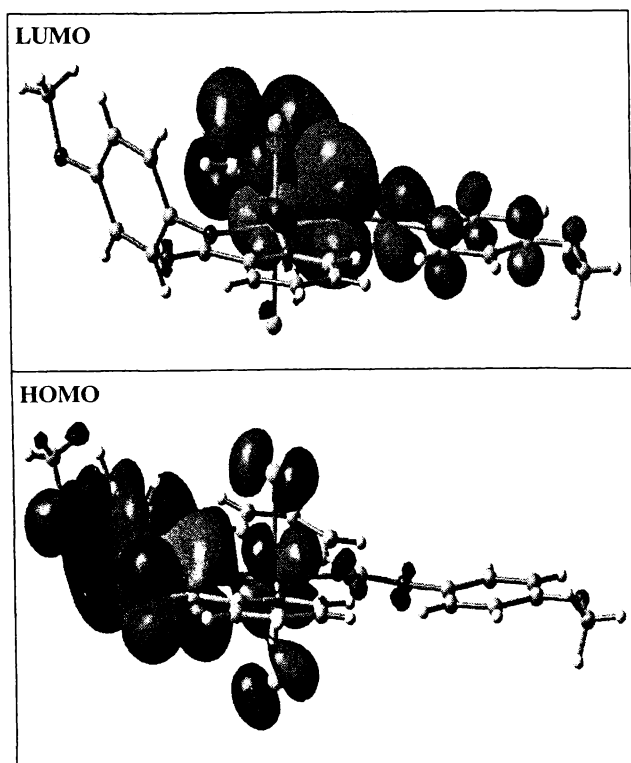


Fig. 7. Contour plot of HOMO and LUMO of the $[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$ complex.

reductive response at the negative potential of SCE (Table 3)¹². All the redox responses are found to be irreversible in nature. A representative cyclic voltammogram is shown in Fig. 9. In view of the composition of the HOMO and LUMO, the first oxidative response and the reductive response are assignable respectively to oxidation and re-

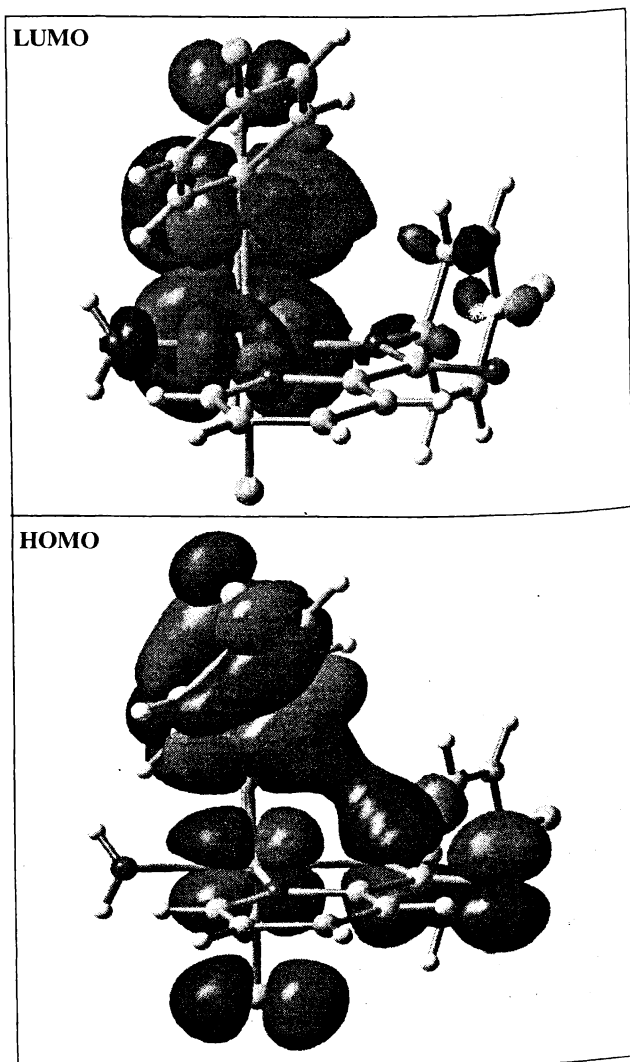


Fig. 8. Contour plot of HOMO and LUMO of the $[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$ complex.

Table 4. Composition of selected molecular orbitals of $[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$ and $[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$

Complex	Contributing fragments	% Contribution to	
		HOMO	LUMO
$[\text{Rh}(\text{HL-OCH}_3)(\text{L-OCH}_3)\text{Cl}_2]$	Rh	4.99	2.06
	L-OCH ₃	74.54	13.63
	HL-OCH ₃	6.29	81.65
	2 Cl	12.17	2.64
$[\text{Rh}(\text{L-Cl})_2(\text{H}_2\text{O})\text{Cl}]$	Rh	7.23	14.00
	L-Cl ^a	52.01	70.68
	L-Cl ^b	34.73	13.31
	Cl	5.93	0.00
	H ₂ O	0.00	2.00

L-Cl^a : The amide ligand with its imine-nitrogen *trans* to the coordinated chloride.

L-Cl^b : The amide ligand with its imine-nitrogen *trans* to the coordinated water.

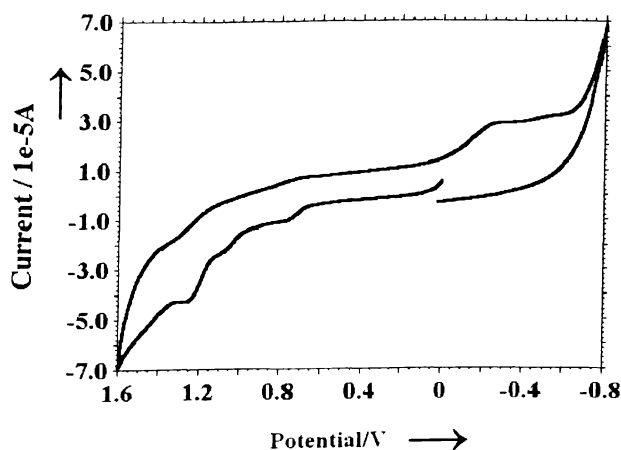


Fig. 9. Cyclic voltammogram of the $[\text{Rh}(\text{L}-\text{OCH}_3)_2(\text{H}_2\text{O})\text{Cl}]$ complex.

duction of the amide ligands. The other redox responses are also believed to be amide ligand based.

Conclusion :

The present study shows that the *N*-(aryl)picolinamide ligands (HL-R) readily react with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and afford complexes of two types (viz. $[\text{Rh}(\text{HL}-\text{R})(\text{L}-\text{R})\text{Cl}_2]$ and $[\text{Rh}(\text{L}-\text{R})_2(\text{H}_2\text{O})\text{Cl}]$) via two different kinetic routes. The neutral amide ligands show N,O-mode of binding, while the monoanionic amidate ligands display N,N-binding mode. The coordinated aquo ligand is found to be too strongly bound to be displaced by other ligands.

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Appendix A

Supplementary data :

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC numbers 844941 and 844942.

References

- (a) D. W. Shaffer, S. A. Ryken, R. A. Zarkesh and A. F. Heyduk, *Inorg. Chem.*, 2011, **50**, 13; (b) B. C. de Pater, E. J. Zijp, H. W. Frühauf, J. M. Ernsting, C. J. Elsevier, K.

- Vrieze, P. H. M. Budzelaar and A. W. Gal, *Organometallics*, 2004, **23**, 269; (c) A. N. Belyaev, S. A. Simanova, M. Y. Garlov and V. I. Viyatkin, *Russ. J. Gen. Chem.*, 2001, **71**, 1186; (d) M. F. C. Guedes da Silva, A. M. Trzeciak, J. J. Ziolkowski and A. J. L. Pombeiro, *J. Orgmet. Chem.*, 2001, **620**, 174; (e) T. V. Magdesieva and K. P. Butin, *Russ. Chem. Rev.*, 1993, **62**, 359.
- (a) S. K. Leung, K. Y. Kwok, K. Y. Zhang and K. K. Wing Lo, *Inorg. Chem.*, 2010, **49**, 4984; (b) H. A. Ho, J. F. Dunne, A. Ellernand and A. D. Sadow, *Organometallics*, 2010, **29**, 4105; (c) S. Tanaka, S. Masaoka, K. Yamauchi, M. Annaka and K. Sakai, *Dalton Trans.*, 2010, **39**, 11218; (d) D. Loganathan and H. Morrison, *Photochem. Photobiol.*, 2006, **8**, 237; (e) G. Ferraudi, S. Oishi and S. Muralidharan, *J. Phys. Chem.*, 1984, **88**, 5261; (f) M. A. Bergkamp, J. Brannon, D. Magde, R. J. Watts and P. C. Ford, *J. Am. Chem. Soc.*, 1979, **101**, 4549; (g) J. D. Petersen, R. J. Watts and P. C. Ford, *J. Am. Chem. Soc.*, 1976, **98**, 3188.
- (a) M. Vasylyev and H. Alper, *J. Org. Chem.*, 2010, **75**, 2710; (b) N. Ahlsten and B. M. Matute, *Adv. Synth. Catal.*, 2009, **351**, 2657; (c) Y. Sumida, Y. Takada, S. Hayashi, K. Hirano, H. Yorimitsu and K. Oshima, *Chem. Asian J.*, 2008, **3**, 119; (d) M. Rubio, A. Suarez, E. Alvarez, C. Bianchini, W. Oberhauser, M. Peruzzini and A. Pizzano, *Organometallics*, 2007, **26**, 6428; (e) J. U. Rhee and M. J. Krische, *J. Am. Chem. Soc.*, 2006, **128**, 10674.
- (a) P. Majumder, S. Baksi, S. Halder, H. Tadesse, A. J. Blake, M. G. B. Drew and S. Bhattacharya, *Dalton Trans.*, 2011, **40**, 5423; (b) C. GuhaRoy, M. G. B. Drew and S. Bhattacharya, *J. Chem. Sci.*, 2009, **121**, 257; (c) C. GuhaRoy, R. J. Butcher and S. Bhattacharya, *J. Organomet. Chem.*, 2008, **693**, 3923; (d) S. Baksi, R. Acharyya, F. Basuli, S. M. Peng, G. H. Lee, M. Nethaji and S. Bhattacharya, *Organometallics*, 2007, **26**, 6596; (e) S. Baksi, R. Acharyya, S. Dutta, A. J. Blake, M. G. B. Drew and S. Bhattacharya, *J. Organomet. Chem.*, 2007, **692**, 1025; (f) S. Basu, S. Dutta, M. G. B. Drew and S. Bhattacharya, *J. Organomet. Chem.*, 2006, **691**, 3581; (g) R. Acharyya, S. Dutta, F. Basuli, S. M. Peng, G. H. Lee, L. R. Falvello and S. Bhattacharya, *Inorg. Chem.*, 2006, **45**, 1252; (h) S. Basu, I. Pal, R. J. Butcher, G. Rosair and S. Bhattacharya, *J. Chem. Sci.*, 2005, **117**, 167; (i) S. Basu, S. M. Peng, G. H. Lee and S. Bhattacharya, *Polyhedron*, 2005, **24**, 157; (j) R. Acharyya, F. Basuli, G. Rosair and S. Bhattacharya, *New J. Chem.*, 2004, **28**, 115; (k) I. Pal, S. Dutta, F. Basuli, S. Goverdhan, S. M. Peng, G. H. Lee and S. Bhattacharya, *Inorg. Chem.*, 2003, **42**, 4338; (l) S. Dutta, F. Basuli, S. M. Peng, G. H. Lee and S. Bhattacharya, *New J. Chem.*, 2002, **26**, 1607; (m) A. Das, F. Basuli, S. M. Peng and S. Bhattacharya, *Inorg. Chem.*, 2002, **41**, 440; (n) S. Dutta, S. M. Peng and S. Bhattacharya, *J. Chem. Soc., Dalton Trans.*, 2000, 4623; (o) S. Dutta, S. M. Peng and S. Bhattacharya, *Inorg. Chem.*, 2000, **39**, 2231.
- (a) S. M. Redmore, C. D. F. Rickard, S. J. Webb and L. J. Wright, *Inorg. Chem.*, 1997, **36**, 4743; (b) M. H. Chou, D.

- J. Szalda, C. Creutz and N. Sutin, *Inorg. Chem.*, 1994, **33**, 1674; (c) M. H. Chou, B. S. Brunshwig, C. Creutz, N. Sutin, A. Yeh, R. C. Chang and C.-T. Lin, *Inorg. Chem.*, 1992, **31**, 5347; (d) M. H. Chou, C. Creutz and N. Sutin, *Inorg. Chem.*, 1992, **31**, 2318; (e) H. Y. Huang, W. J. Chen, C. C. Yang and A. Yeh, *Inorg. Chem.*, 1991, **30**, 1862; (f) Y. Ilan and M. Kapon, *Inorg. Chem.*, 1986, **25**, 2350; (g) Y. Ilan and H. Taube, *Inorg. Chem.*, 1983, **22**, 1655; (h) T. Matsubara and P. C. Ford, *Inorg. Chem.*, 1976, **15**, 1107; (i) A. W. Zanella and P. C. Ford, *Inorg. Chem.*, 1975, **14**, 42; (j) P. Ford, D. E. P. Rudd, R. G. Gaunders and H. Taube, *J. Am. Chem. Soc.*, 1968, **90**, 1187.
6. (a) R. A. Eikey and M. M. Abu-Omar, *Coord. Chem. Rev.*, 2003, **243**, 83; (b) J. R. Fulton, A. W. Holland, D. J. Fox and R. G. Bergman, *Acc. Chem. Res.*, 2002, **35**, 44; (c) K. Severin, R. Berge and W. Beck, *Angew. Chem. Int. Ed.*, 1998, **37**, 1634; (d) O. Clement, B. M. Rapko and B. P. Hay, *Coord. Chem. Rev.*, 1998, **170**, 203; (e) M. D. Fryzuk and C. D. Montgomery, *Coord. Chem. Rev.*, 1989, **95**, 1; (g) H. E. Bryndza and W. Tam, *Chem. Rev.*, 1988, **88**, 1163; (h) H. E. Bryndza and W. Tam, *Chem. Rev.*, 1988, **88**, 1163; (i) H. Sigel and R. B. Martin, *Chem. Rev.*, 1982, **82**, 385.
7. S. Dutta, S. Pal and P. K. Bhattacharya, *Polyhedron*, 1999, **182**, 157.
8. (a) M. Walter and L. Ramaley, *Anal. Chem.*, 1973, **45**, 165; (b) D. T. Sawyer and J. L. Roberts, "Jr. Experimental Electrochemistry for Chemists", Wiley, New York, 1974, 167.
9. Chemical shifts are given in ppm and multiplicity of the signals along with the associated coupling constants (*J* in Hz) are given in parentheses. Overlapping signals are marked with an asterisk.
10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery (Jr.), T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, O. G. Navarro, R. A. Kelly, III and S. P. Nolan, *J. Am. Chem. Soc.*, 2003, **125**, 16194; A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, I. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskroz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, revision D01; Gaussian Inc. : Pittsburgh, PA, 2003.
11. G. M. Sheldrick, SHELXS-97 and SHELXL-97, Fortran programs for crystal structure solution and refinement, University of Gottingen, Gottingen, Germany, 1997.
12. For the $[\text{Rh}(\text{L}-\text{OCH}_3)_2(\text{H}_2\text{O})\text{Cl}]$ complex three oxidative responses were observed, and for the $[\text{Rh}(\text{HL}-\text{NO}_2)(\text{L}-\text{NO}_2)\text{Cl}_2]$ complex the second oxidative response could not be observed, probably because it occurs outside the voltage window.