

Synthesis, chemical reactions and redox properties of ruthenium complexes of a tetradentate *bis* chelating ligand, 2,2'-azobis(pyridine)

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Abstract. The use of silver (I) assisted metal exchange reaction for the synthesis of mononuclear ruthenium (II) complexes of a tetradentate bridging ligand, 2,2'-azobis(pyridine) (L^1) is elaborated. This route has been successfully employed for the direct synthesis of $RuCl_2(L^1)_2$ (2); $[Ru(L^1)_3](ClO_4)_2 \cdot H_2O$ (3) from $RuCl_3 \cdot 3H_2O$ and for the mixed ligand *tris* chelates of general composition $[Ru(L^1)_n(L^2)_{3-n}]^{2+}$ ($n = 0 - 3$; $L =$ neutral N,N donors: 2-(phenylazo)pyridine (L^2), 2,2'-bipyridine (L^3)). The preparation of $[Ru(OH_2)_2(L^1)_2]^{2+}$ (7) from 2 is also described. The diaquo complex, $\underline{7}$, is chemically reactive and undergoes anation, solvolysis and substitution reactions instantaneously with different nucleophiles. All the reactions, described above, occur smoothly and the yields of the products are high. The composition and identities of the complexes are established from their elemental analyses and spectral data. The redox properties of the compounds have been examined. Metal oxidation responses occur at very high positive potentials. Successive reductive responses occur on the negative of the SCE.

Keywords. Ruthenium; silver(I) assisted synthesis; redox.

1. Introduction

The design of effective synthetic procedures for the preparation of polynuclear metal complexes having particular compositions and topologies represents¹⁻⁷ an important area of research. One of the most useful strategies, which has been adopted widely in recent years,^{8,9} for the syntheses of this class of compounds is to connect the reactive basic units ("complexes as ligands" and "complexes as metals" strategy) in a desired fashion. In this regard, design and syntheses of new and reactive mononuclear (basic units) complexes, suitable for step-by-step construction of oligonuclear species, is an essential requirement.

This report describes a general synthetic route to a series of ruthenium(II) mononuclear complexes of 2,2'-azobis(pyridine) (L^1). Our interest in this area arose mainly due to the following reasons. Firstly, the ligand L^1 can act as a bridging ligand and is capable¹⁰⁻¹² of connecting metal centres in stepwise construction of polynuclear arrangements. It is, therefore, expected that suitable monomeric complexes of L^1 , where it coordinates in a bidentate fashion, should be useful synthones for the construction of polynuclear complexes. Secondly, the ruthenium chemistry of monochelating bidentate ligands having

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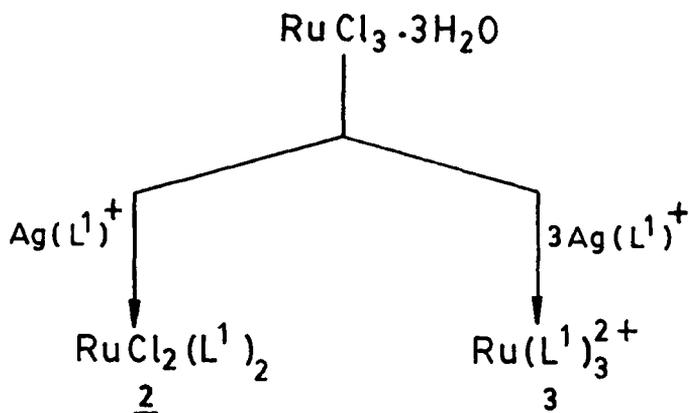
strongly π -acidic diazo chromophore has been recently addressed¹³⁻¹⁹. Multiple electron transfer, low energy charge transfer transitions and interesting chemical reactions are some of the important observations in these compounds.

2. Results and discussion

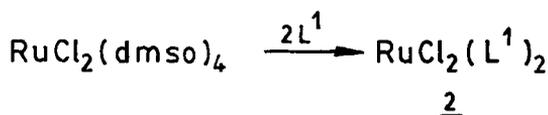
2.1 Reactions studied

We explored our silver assisted metal exchange synthetic route²⁰⁻²² for the syntheses of the mononuclear complexes of 2,2'-azobis(pyridine) (L^1). The ligand L^1 forms a stable complex with silver (I) of type $[Ag(L^1)]ClO_4 \cdot H_2O$. This has been used as the reagent for the following syntheses. The chemical reactions which have been studied are summarised in the schemes 1-5.

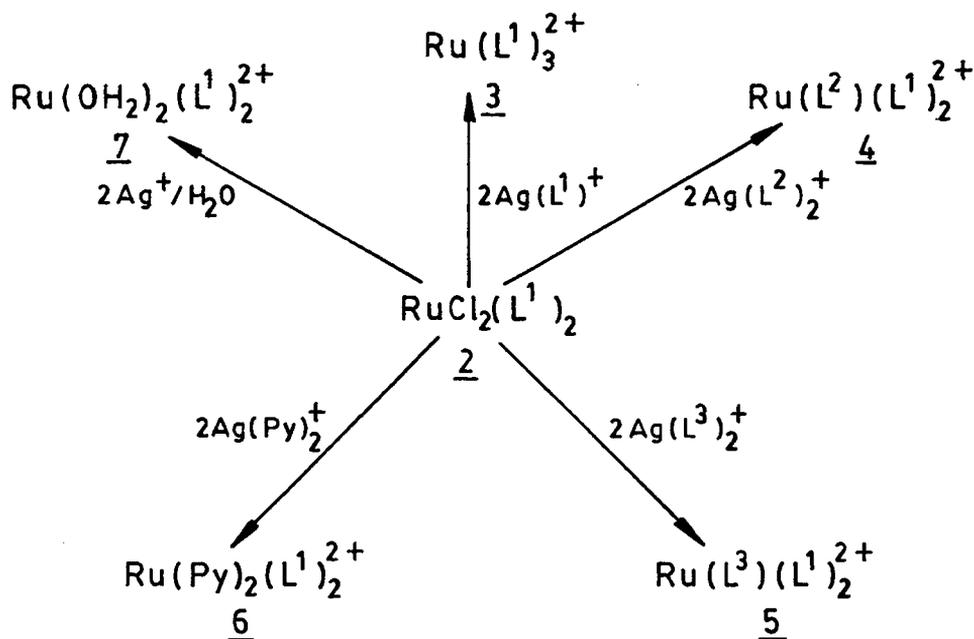
The reaction between hydrated ruthenium trichloride and $Ag(L^1)^+$ in equimolar proportion gave rise to isomeric $RuCl_2(L^1)_2$ (2) in a low yield (30%). This low yield of the product from the above reaction may be due to the lower $[L^1]:[Ru]$ ratio in the reaction mixture (1:1) than the minimum ratio required (2:1) for the formation of $RuCl_2(L^1)_2$. With the increase of reagent, $[Ag(L^1)^+]$, concentration to $[Ag(L^1)_2^+]:[RuCl_3] = 2:1$ many unidentified products were formed. The crude product was purified on a silica gel column. The major bright blue fraction was eluted with a 1:10 $CH_3CN-CHCl_3$ mixture. Its 1H NMR with optical spectral data (vide infra) clearly demonstrate that it is a symmetrical *cis* isomer. Later, we found that the synthesis of isomerically pure sample of 2 can be more conveniently achieved in very high yield (> 85%) by direct reaction of $RuCl_2(dmsO)_4$ (dmsO = dimethylsulfoxide) with neat L^1 at $100^\circ C$ (scheme 2). This neutral dichloro compound 2 has been used as the starting material for the syntheses of mixed ligand complexes having $Ru(L^1)_2$ moiety. The



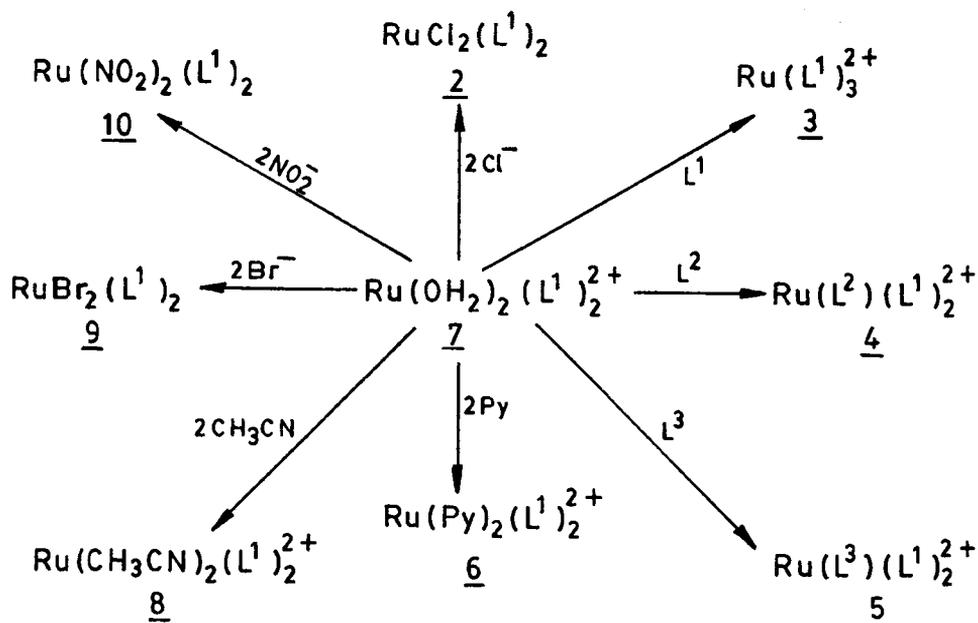
Scheme 1.



Scheme 2.

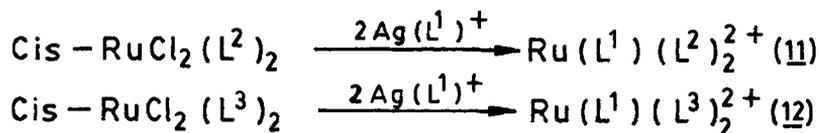


Scheme 3.



Scheme 4.

preparation of the *tris* chelated compound, $\text{Ru}(\text{L}^1)_3^{2+}$, was readily accomplished from a single step reaction (scheme 1) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $[\text{Ag}(\text{L}^1)]^+$ in 1:3 molar proportion in ethanol at reflux. Recrystallisation of the crude product from water produces analytically pure $[\text{Ru}(\text{L}^1)_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (3). The compound 3 also may be



Scheme 5.

obtained in a better yield from the reaction of (2) and two moles of $[\text{Ag}(\text{L}^1)]^+$ in ethanol (scheme 3). The major success of the present synthetic strategy lies in the controlled syntheses of mixed ligand complexes of varied compositions. The syntheses of these were readily achieved by following the routes described in schemes 3–5. We selected two terminal bidentate N,N donors viz. 2-(phenylazo)pyridine (L^2) and 2,2'-bipyridine (L^3) as the coligand for this purpose. In fact, the compounds of all possible combinations in the pairs of ligands viz. (L^1 and L^2), (L^1 and L^3) and can easily be synthesised in almost quantitative yields ($\approx 90\%$).

In order to obtain a diaquo complex, $[\text{Ru}(\text{OH}_2)_2(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (7), the dichloro compound 2 was treated with two moles of AgNO_3 in refluxing 1:2 water-ethanol mixture. Addition of excess of aqueous NaClO_4 (in 1 M HClO_4) to the filtrate gave rise to the desired product. The compound 7 is reactive and undergoes (i) solvolysis in acetonitrile, (ii) anation reactions with monodentate nucleophiles like Cl^- , Br^- , NO_2^- etc. to yield dichloro (2), dibromo (9), dinitro (10) compounds respectively, and (iii) substitution reactions with neutral ligands viz. L^1 – L^3 to yield *tris* chelated compounds (scheme 4).

The synthetic strategy used in the present work is based on chloride substitution reaction. The silver complexes in the above reactions are a source of $\text{Ag}(\text{I})$ for abstraction of chloride and also a source of ligand, required for the formation of the compound. Following this strategy, the degree of substitution of chloride and thus, the compositions of the products can be monitored by just varying the stoichiometric ratio of the reactants. For example, the reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with equimolar $\text{Ag}(\text{L}^1)^+$ yielded partial chloride substituted product, $\text{RuCl}_2(\text{L}^1)_2$ (2), whereas, the formation of *tris* chelated compound from ruthenium trichloride needs complete substitution of chlorides and reasonably, therefore, three moles of $\text{Ag}(\text{L}^1)^+$ are required per mole of RuCl_3 . The starting material for the mixed ligand compound is RuCl_2L_2 ($\text{L} = \text{L}^1$ – L^3) and the optimum ratio of the reagents required for the above reaction $[\text{RuCl}_2\text{L}_2]:[\text{AgL}^+]$ is 1:2, as expected.

2.2 Characterisation and properties

The compounds were obtained in high yields and purity (experimental). Formulation of these are made based on their analytical and spectral (table 1) analyses. Selected data are collected in table 1. Far IR spectrum of $\text{RuCl}_2(\text{L}^1)_2$ shows two absorptions at 325 and 300 cm^{-1} due to $\nu_{\text{Ru-Cl}}$, indicating a *cis* geometry with respect to the two coordinated Cl. The ^1H spectrum of the above dichloro compound displays a total of eight resonances in the range 7.0–9.5 δ . The free ligand, L^1 is a symmetrical ligand and shows four pyridyl proton resonances in the range, 6.25–8.25 δ . Upon coordination, in a bidentate fashion, the two pyridyl groups become nonequivalent and eight proton resonances are expected²³ from each L^1 . With the *cis*- RuCl_2 moiety, there could be three isomeric possibilities²⁴ of $\text{RuCl}_2(\text{L}^1)_2$, two of which are symmetrical (C_2) and the

Table 1. Molar conductivity and spectral data

Compound	Λ_M^a $\Omega^{-1} \text{ cm}^2 \text{ M}^{-1}$	IR, cm^{-1c}		$\lambda_{\text{MLCT}}, \text{nm}^a$ ($10^{-3} \epsilon, \text{M}^{-1} \text{ cm}^{-1}$)
		$\nu_{\text{C=N}}$	$\nu_{\text{N=N}}$	
$\text{RuCl}_2(\text{L}^1)_2$ (2)		1595	1300	585(0.92), 472 sh
$[\text{Ru}(\text{L}^1)_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (3)	285	1600	1350	515(0.96), 475 sh
$[\text{Ru}(\text{L}^2)(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (4)	292	1595	1355	510(0.94), 472 sh
$[\text{Ru}(\text{L}^3)(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (5)	287	1595	1345	532(0.97), 466(0.61)
$[\text{Ru}(\text{py})_2(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (6)	278	1600	1342	530(0.96), 462 sh
$[\text{Ru}(\text{OH}_2)_2(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (7)	260 ^b	1600	1320	560(0.97) ^b , 372(1.01) ^b
$[\text{Ru}(\text{CH}_3\text{CN})_2(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (8)	292	1600	1352	510(0.98), 374 sh
$\text{RuBr}_2(\text{L}^1)_2$ (9)		1600	1300	587(0.89), 470 sh
$[\text{Ru}(\text{L}^1)(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (10)	279	1605	1355	512(0.95), 474 sh
$[\text{Ru}(\text{L}^1)(\text{L}^3)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (11)	282	1600	1340	510(0.60), 375 sh
$\text{Ru}(\text{NO}_2)_2(\text{L}^1)_2$ (12)		1605	1365	545(0.87), 465 sh

^aIn CH_3CN . ^bIn 0.1 molar aqueous H_2SO_4 . ^cAs KBr disk.

Table 2. Electrochemical data

Compound	$E^\circ_{298}{}^{a,b}$	
	Metal oxidation, V ($\Delta E_p/\text{mv}$)	Ligand based reductions, V ($\Delta E_p/\text{mv}$)
(2)	1.07(110)	-0.49(140), -0.77(140)
(3)	1.97(130)	-0.025(150), -0.36(200), -0.83(140), -1.37(200), -1.59(170), -1.78(120)
(4)	2.12(200)	+0.03(100), -0.35(100), -0.82(140) -1.36(230), -1.54(150), -1.73(130)
(5)	1.86(130)	-0.05(120), -0.55(120), -1.33(140), -1.77(130)
(6)	1.87(140)	-0.11(100), -0.60(120), -0.865(130), -1.105(130)
(8)	2.015(150)	-0.125(110), -0.58(120)
(9)	1.09(110)	-0.485(90), -0.645(210)
(10)	2.10(280)	+0.015(110), -0.36(120), -0.85(130), -1.35(140), -1.655(150)
(11)	1.62(110)	-0.35(110), -1.05(90), -1.66(80)
(12)	1.42, ^c 1.65(120)	-0.39(110), -0.91(180)

^aIn CH_3CN . ^b Supporting electrolyte: TBAP (conc. 0.1 mol dm^{-3}), working electrode: platinum, $u = 50 \text{ mV s}^{-1}$. ^cIrreversible anodic response.

rest is unsymmetrical (C_1). The above ^1H NMR data, therefore, clearly reveals that the geometry of $\text{RuCl}_2(\text{L}^1)_2$ is one of the two symmetrical isomers.

The solutions of the complexes are intensely coloured and the visible range absorption spectra are dominated by highly intense metal-to-ligand charge transfer (MLCT) transitions¹⁷. Interestingly, the lowest energy of the above transitions linearly correlate²⁵ with the difference between the metal oxidation and the first ligand reduction potentials ΔE (redox).

All the complexes are electroactive and characterized by multiple step electron transfers (table 2). There are two types of processes observed in the present systems.

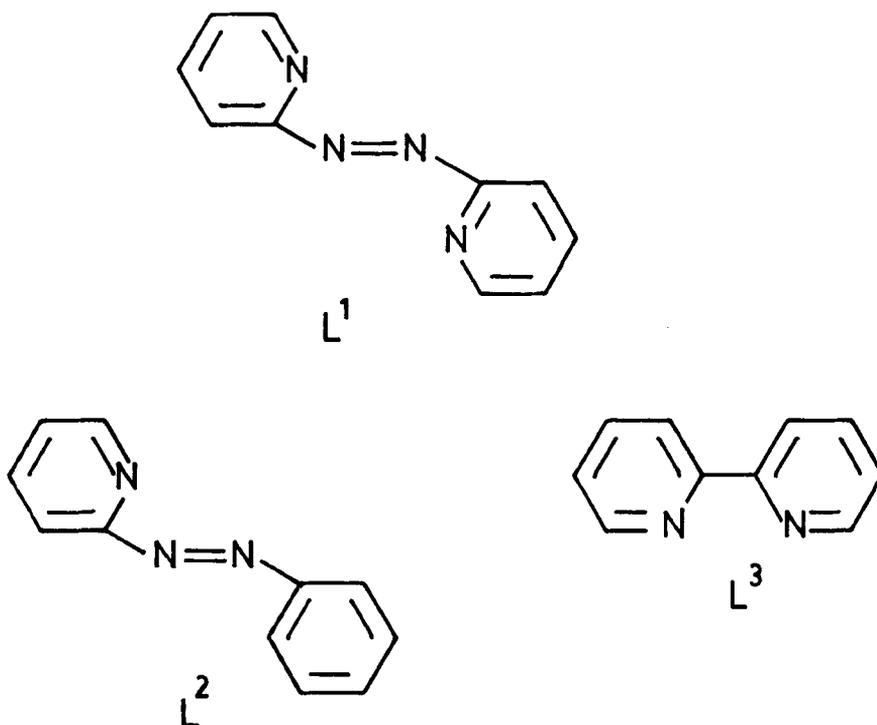


Figure 1. Structures L¹, L², L³

One reversible oxidative response, occurring at high to very high positive potential, is assigned to Ru^{III}/Ru^{II} couple. Series of reductive waves, which are believed to be ligand centered, are also observed. In the case of Ru(NO₂)₂(L¹)₂, the first Ru^{II} → Ru^{III} oxidative response is irreversible which is followed by a reversible response at a higher potential. This type of redox behaviour of a ruthenium dinitro complex has been documented¹³. Interestingly, the first ligand reduction process, in some cases, even occurs at a positive potential of the SCE. It is known that the ligands used for the present work can accept two electrons each and the ligands containing the *azo* chromophore, viz. L¹ and L², are very susceptible to reduction due to the presence of low lying acceptor orbitals^{12,26}. Here we wish to note an interesting trend. The compound, which is oxidised at a relatively high positive potential, is reduced at a relatively low negative potential. Thus, the oxidation potential for the complex, [Ru(L¹)₂(L²)]²⁺ is as high as 2.12 V and its first reduction occurs at a positive potential, 0.03 V. A parallel trend is also observed in the MLCT energies. These above trends may be rationalised by the consideration of different degrees of *dπ-pπ* interactions in the above complexes.

3. Conclusion

In conclusion, it may be stated that the primary aim of the present synthetic work to develop a simple and a general approach to synthesise mononuclear complexes of a tetradentate *bis* chelating ligand (L¹) has been achieved. Although there have been

few reports of Ru–L¹ complexes in the literature ^{11,23}, no systematic approach in regard to the syntheses of the mononuclear basic units have been made. The available routes which involve multiple steps, require chromatographic purification and are obtained in relatively poorer yields. In the present compounds L¹ binds to ruthenium(II) as a monochelate bidentate ligand. Therefore, it is quite likely that these compounds, in general, and the reactive solvento species (7 and 8), in particular, would be useful basic units for the stepwise tailoring of polynuclear compounds. Efforts to synthesise mixed-ligand and mixed-metal polynuclear complexes of L¹ are on.

4. Experimental

4.1 Materials and measurements

The salt, RuCl₃·nH₂O was obtained from Arora Matthey, Calcutta and was digested thrice with concentrated HCl before use. The ligand L¹ and the silver complexes of the ligands L¹–L³ were synthesised as before ^{27–29}. The ruthenium complexes, RuCl₂(dmsO)₄ ³⁰, *cis*-RuCl₂(L²)₂ ³¹ and *cis*-RuCl₂(L³)₂ ³² were prepared by published procedures. All other chemicals and solvents used for the preparative work were of reagent grade and were used as received. Physical measurements were performed as described earlier ²¹.

4.2 Preparations

Caution! Perchlorate salts of metal complexes are generally explosive. Care should be taken in handling of such samples.

(i) (a) *Synthesis of RuCl₂(L¹)₂ from RuCl₃·3H₂O.* A sample of RuCl₃·3H₂O (1 mmol) dissolved in 20 ml of ethanol was added to a solution of [AgL¹]ClO₄·H₂O (1 mmol) in 15 ml of ethanol. The mixture was heated on a water bath for 15 min. It was cooled and filtered through a G-4 sintered-glass funnel to remove insoluble AgCl. The filtrate was concentrated to 10 ml and a dark mass was precipitated on addition of diethyl ether. The crude product was then subjected to column chromatography on a silica gel (60–120 mesh) column using different mixtures of CH₃CN–CHCl₃ as eluant. A major blue band was eluted with 1:10 solvent mixture. The solution was then evaporated and shining crystals of *cis*-RuCl₂(L¹)₂ were obtained on crystallisation of CHCl₃–C₆H₁₄ mixture. Yield 23%. Three other minor bands of different colours were also observed on the column. Due to serious overlap we are unable to get pure compounds from the eluates. Anal. calcd. for RuC₂₀H₁₆N₈Cl₂: C, 44.40; H, 2.96; N, 20.74. Found: C, 44.38; H, 3.15; N, 20.92.

(b) *Reaction of RuCl₂(dmsO)₄ in neat L¹.* The complex RuCl₂(dmsO)₄ (1 mmol) and L¹ (2 mmol) were thoroughly mixed in a 25 ml round bottom flask heated on a water-bath for 3–5 min till the mass became bright blue. It was extracted with minimum volume (50 ml) of CHCl₃, the volume of the solution was reduced to 15 ml and hexane (50 ml) was added. Dark shiny crystals of *cis*-RuCl₂(L¹)₂ separated, collected by filtration. Yield 85%.

(ii) (a) *Synthesis of [Ru(L¹)₃](ClO₄)₂·H₂O from RuCl₃·3H₂O.* To a sample of RuCl₃·3H₂O (1 mmol) dissolved in 15 ml of ethanol was added a solution of

$[\text{Ag}(\text{L}^1)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (3 mmol) in 15 ml ethanol. The mixture was heated to reflux for 1 h. It was cooled and filtered through a G-4 sintered-glass funnel to remove insoluble products. The filtrate was concentrated to 10 ml and to it was added 1 ml of an aqueous saturated solution of NaClO_4 . The brown precipitate thus formed was filtered out and washed thoroughly with diethyl ether. Recrystallisation of the precipitate from water yielded crystalline compound. Yield 76%. Anal. calcd. for $\text{RuC}_{30}\text{H}_{26}\text{N}_{12}\text{O}_9\text{Cl}_2$: C, 41.38; H, 2.99; N, 19.31. Found: C, 41.45; H, 3.01; N, 19.45.

(b) *Synthesis of $[\text{Ru}(\text{L}^1)_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ from $\text{RuCl}_2(\text{L}^1)_2$.* To a suspension of $\text{RuCl}_2(\text{L}^1)_2$ (1 mmol) in 20 ml ethanol was added a solution of $[\text{Ag}(\text{L}^1)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (2 mmol) in 15 ml ethanol. The mixture was heated to reflux for 15 min. The rest of the procedure was the same as that described in section ii(a). Yield 92%.

(iii) *Synthesis of mixed-ligand tris complexes from RuCl_2L_2 ($\text{L} = \text{L}^1 - \text{L}^3$).* The syntheses of this class of complexes were performed by using a general procedure using a combination of appropriate reagents. A representative example is described below.

$[\text{Ru}(\text{L}^2)(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. To a suspension of $\text{RuCl}_2(\text{L}^1)_2$ (1 mmol) in 20 ml ethanol was added a solution of $[\text{Ag}(\text{L}^2)]\text{ClO}_4$ (2 mmol) in 15 ml ethanol, and the mixture was heated to reflux for 15 min. The rest of the procedure was the same as that described in section ii(a). Yields and analytical data for the mixed ligand compounds are collected below.

$[\text{Ru}(\text{L}^2)(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: Yield 91%. Anal. calcd for $\text{RuC}_{31}\text{H}_{27}\text{N}_{11}\text{O}_9\text{Cl}_2$: C, 42.80; H, 3.11; N, 17.72. Found: C, 42.92; H, 3.24; N, 17.75.

$[\text{Ru}(\text{L}^3)(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: Yield 89%. Anal. calcd for $\text{RuC}_{30}\text{H}_{26}\text{N}_{10}\text{O}_9\text{Cl}_2$: C, 42.76; H, 3.09; N, 16.63. Found: C, 42.82; H, 3.15; N, 16.72.

$[\text{Ru}(\text{L}^1)(\text{L}^2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: Yield 86%. Anal. calcd for $\text{RuC}_{32}\text{H}_{28}\text{N}_{10}\text{O}_9\text{Cl}_2$: C, 44.24; H, 3.23; N, 16.13. Found: C, 44.32; H, 3.33; N, 16.25.

$[\text{Ru}(\text{L}^1)(\text{L}^3)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: Yield 90%. Anal. calcd for $\text{RuC}_{30}\text{H}_{26}\text{N}_8\text{O}_9\text{Cl}_2$: C, 44.23; H, 3.19; N, 13.76. Found: C, 44.32; H, 3.24; N, 13.86.

$[\text{Ru}(\text{PY})_2(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: Yield 87%. Anal. calcd for $\text{RuC}_{30}\text{H}_{28}\text{N}_{10}\text{O}_9\text{Cl}_2$: C, 42.65; H, 3.32; N, 16.59. Found: C, 42.76; H, 3.40; N, 16.65.

(iv) *Synthesis of $[\text{Ru}(\text{OH}_2)_2(\text{L}^1)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ from $\text{RuCl}_2(\text{L}^1)_2$.* To a suspension of $\text{RuCl}_2(\text{L}^1)_2$ (1 mmol) in 20 ml ethanol was added an aqueous solution of AgNO_3 (3 mmol in 15 ml 0.5 M aqueous HClO_4). The mixture was heated to reflux for 30 min. The cold red solution was then filtered through G-4 sintered-glass funnel to remove insoluble AgCl . The solution was concentrated to 15 ml and a saturated aqueous solution of NaClO_4 (2 ml) was added. The mixture was kept overnight in the refrigerator. Dark needle-shaped crystals were obtained which were dried *in vacuo* over P_4O_{10} . Yield 76%. Anal. calcd for $\text{RuC}_{20}\text{H}_{22}\text{N}_8\text{O}_{11}\text{Cl}_2$: C, 33.24; H, 3.05; N, 15.51. Found: C, 33.50; H, 3.15; N, 15.42.

(v) Reactions of $[Ru(OH_2)_2(L^1)_2](ClO_4)_2 \cdot H_2O$ (7)

(a) Solvolysis. Formation of $[Ru(CH_3CN)_2(L^1)_2](ClO_4)_2 \cdot H_2O$. The salt **7** (1 mmol) was dissolved in 10 ml CH_3CN and heated to reflux for 15 min. To the resultant orange brown solution an aqueous solution of $NaClO_4$ (1g in 15 ml water) was added and left at room temperature overnight. An orange crystalline compound was obtained which was dried *in vacuo* over P_4O_{10} . Yield: 92%. Anal. calcd. for $RuC_{24}H_{24}N_{10}O_9Cl_2$: C, 37.50; H, 3.13; N, 18.23. Found: C, 37.58; H, 3.28; N, 18.19.

(b) Anation reactions. Formation of $RuX_2(L^1)_2$ $X = Cl, Br, NO_2$. These were performed by using a general procedure. A representative example is described below.

$RuBr_2(L^1)_2$. To an ethanolic solution of **7** (1 mmol in 15 ml) 2.5 mmol of LiBr was added and the mixture was heated to reflux for 1 h. On cooling, the resultant blue solution, highly crystalline compounds with bronze-sheen separated out from the solution. This was collected by filtration and dried *in vacuo*. Yield: 86%. Anal. calcd for $RuC_{20}H_{16}N_8Br_2$: C, 38.16; H, 2.54; N, 17.80. Found: C, 38.25; H, 2.75; N, 17.95.

$RuCl_2(L^1)_2$: Yield 91%.

$Ru(NO_2)_2(L^1)_2$: Yield: 72%. Anal. calcd for $RuC_{20}H_{16}N_{10}O_4$: C, 42.78; H, 2.85; N, 24.96. Found: C, 42.71; H, 2.92; N, 25.04.

(c) Reactions with neutral ligands. These were performed following a general procedure. Experimental details for a representative example are described below.

Formation of $[Ru(L^3)(L^1)_2](ClO_4)_2$. The salt **7** (1 mmol) was dissolved in 25 ml of ethanol and to it was added a solution of BPY (1 mmol) in 5 ml of ethanol. The mixture was heated to reflux for 30 min. The red brown solution was then cooled and to it was added 1 ml of an aqueous saturated solution of $NaClO_4$. The mixture was then left overnight for crystallisation. Dark crystals thus formed, were filtered out and washed thoroughly with diethyl ether. Yield 90%.

Acknowledgements

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