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Novel pentacoordinated ruthenium(II) complexes with a NNS chelating ligand: synthesis, characterization and electrochemical studies

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Abstract—The NNS chelating donor *N*-2-mercaptophenyl-(2′-pyridyl)methylenimine (PabtH) reacted with $Ru(PPh_3)_3Cl_2$ to give a series of ruthenium(II) complexes Ru(Pabt) $(PPh_3)X$ {X = Cl(**1**), Br(**3**)}, Ru(Pabt) $(PPh_3)_2Cl$ (**2**), [Ru(Pabt) $(PPh_3)L]ClO_4$ {L = 1-Meimz (**2a**), 2-Meimz (**1c**)}, [Ru(Pabt) (PPh_3) $(L')_2]ClO_4$ {L′ = 1-Meimz (**1a**), imz (**1b**), H_2O (**1f**)} and [Ru(Pabt) (PPh_3) (L-L)]ClO_4 {L-L = bpy (**1d**), Phen (**1e**); bpy = 2, 2′-bipyridine, Phen = 1,10-phenanthroline}. They have been characterized using IR, UV–vis, {^{1}H and ^{31}P} NMR, EPR, magnetic susceptibility at room temperature, measurement of molecular weight, molecular conductance in solution and elemental analysis. The stabilisation of the pentacoordinated 16-electron complexes (**1**, **3**, **1c** and **2a**) is attributed to $p\pi$ donation by the sulfur atom of the ligand Pabt. Square pyramidal structure is proposed for these pentacoordinated complexes. Electron transfer behaviour of all the complexes has been explored by cyclic voltammetry in CH_2Cl_2 and CH_3CN using TEAP as the supporting electrolyte. The five-coordinated complexes display cathodically shifted oxidation waves in CH_2Cl_2, when TEACl was used as supporting electrolyte. Linear correlation of electrochemical data in terms of Lever's electrochemical parameter E_L and the energy of metal to ligand charge transfer band has been attempted. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: pentacoordination; ruthenium(II) complexes; mixed ligand complexes; NNS-ligand; chemical reactivity; electrochemical studies.

The chemistry of nitrogen–sulfur chelating ligands has witnessed phenomenal growth during the last decade. This was stimulated particularly by the discovery of the occurrence of similar donor environment in the prosthetic groups of several oxidoreductases [1,2]. However, one of the metal ions that has received little attention in such studies is ruthenium, probably because of its non-availability in biological systems. The relatively small amount of work so far carried out on ruthenium complexes involving such ligands indicate that they exhibit very interesting redox, electronic and structural characteristics [3–9]. It is also well known that chelating nitrogen–sulfur donors can stabilise complexes of unusual oxidation states [10–15] and uncommon coordination numbers of metal ions [13–16]. Such complexes are also known to participate in diverse redox reactions [17–19], sometimes even forming complete electrochemical series [17]. In this chemical milieu, the chemistry of ruthenium ligated to nitrogen–sulfur chelating ligands promises to be quite fascinating. This paper reports the synthesis and reactivity of ruthenium complexes of the NNS chelating ligand N-2-mercaptophenyl (2′-pyridyl) methylenimine (PabtH), which affords a few ruthenium complexes with unusual coordination number. Exploration of the redox behaviour of the ruthenium complexes of PabtH itself and those in which other coligands are present in the first coordination sphere of the ruthenium centre receives appropriate attention in this work.

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EXPERIMENTAL

Physical measurement

Carbon, hydrogen and nitrogen analyses were performed in a Perkin–Elmer 240 C,H,N analyser and halogens were estimated by the reported method.[20] IR spectra were recorded with a Perkin-Elmer 783 Spectrophotometer using the KBr and polythene powder wafer techniques. Thermogravimetric (TG) and differential thermal analysis (DTA) were done in a Shimadzu DT-30 thermal analyser. Electronic spectra of the compounds were taken on a Shimadzu Model UV-2100 UV–vis recording spectrophotometer. Electrical conductance data in solution were collected using a Philips PR-9500 conductivity bridge fitted with a dip-type cell calibrated with 0.02 M KCl solution. Static susceptibility measurements at room temperature were made with the help of a Princeton Applied Research Model 155 vibrating-sample magnetometer using $Hg[Co(SCN)_4]$ as the calibrant. Molecular weight in CH_2Cl_2 was determined by KNAUER model Vapor Pressure Osmometer connected to a Recorder (type 11.15) using benzil as the calibrant. Proton NMR spectra were recorded on a Varian XL100 FT-NMR spectrometer using TMS as internal indicator. $\{^{31}P\}$NMR spectrum was recorded in $CDCl_3$ using 85% H_3PO_4 as external reference. Electron spin resonance spectra were recorded on a Varian E4 X-band EPR spectrometer, using diphenylpicrylhydrazyl (dpph) as an internal field marker. Electrochemical studies were done with the help of a PAR Model 370-4 electrochemistry system, 174A polarographic analyser, 175 universal programmer, RE 0074 X-Y recorder at 298 K. All these experiments were carried out under dry nitrogen. A planar Beckman model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode were used in the three-electrode configuration. The saturated calomel electrode (SCE) was separated from the sample compartment by a salt bridge connected by glass frit filled with the solvent (0.1 M supporting electrolyte) for the measurement. Under these experimental conditions the ferricenium–ferrocene couple was located at 0.42 V. In controlled potential electrolysis, a platinum mesh was used as working electrode and the auxiliary electrode was separated from the solution by a sintered glass disk.

Chemicals

$RuCl_3$ was obtained from Arora-Matthey Limited. 2-(2-Pyridyl)benzothiazoline (PabtH) [15], $Ru(PPh_3)_3Cl_2$ and $Ru(PPh_3)_3Br_2$ were prepared using the published procedure [21,22]. All other chemicals used for preparative work were of reagent grade and were used without further purification. Reagent grade solvents were dried and distilled by the usual methods [23]. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Fluka AG) by following a standard procedure [24]. All reactions were performed under dry nitrogen.

Preparation of $Ru(Pabt)(PPh_3)Cl$ (**1**) *and* $Ru(Pabt)(PPh_3)_2Cl$ (**2**). Solid $Ru(PPh_3)_3Cl_2$ [120 mg, 0.125 mmol] in 20 cm^3 benzene was refluxed with a benzene (5 cm^3) solution of 2-(2-pyridyl) benzothiazoline [54 mg, 0.25 mmol] for 2 h. A brown complex **1** separated from hot solution. The mixture was cooled and filtered under nitrogen. The residue was washed several times with degassed benzene and dried over fused $CaCl_2$. Yield 63 mg (82%).

The volume of the filtrate was reduced to one-third in a rota-evaporator, excess of degassed ether was added to it and the mixture was allowed to settle (5 min). Compound **2** separated out and was filtered, washed thrice with degassed ether and dried *in vacuo*. Yield 10 mg (9%).

When the above reaction was carried out in benzene using (1 : 1) molar ratio of the reactants, compound **1** separated out from the hot solution, being the only product in this reaction. When the reaction was carried out in CH_2Cl_2 using 1 : 1 molar ratio of reactants, the compound **1** had to be precipitated by the addition of excess degassed ether.

Preparation of Ru(Pabt) $(PPh_3)Br$ (**3**). This complex was prepared by a method similar to that of complex **1** using $Ru(PPh_3)_3Br_2$ as the starting material. Yield 70 mg (85%).

Preparation of $[Ru(Pabt)(PPh_3)(1\text{-Meimz})_2]ClO_4 \cdot 1.5CH_2Cl_2$ (**1a**). ***Warning***: Perchlorate salts of metal complexes are potentially explosive [25]. To a stirred solution of Ru(Pabt) $(PPh_3)Cl$ (**1**) [1 mmol] in 40 ml dichloromethane, excess [~100 mmol] 1-methylimidazole (1-Meimz) was added and the mixture was stirred at room temperature for 24 h. The volume was then reduced to 10 cm^3 in a rotaevaporator. To this concentrated solution, excess petroleum ether (60–80°C) was added and the mixture was allowed to settle [10 min] in a refrigerator. When an oily product settled down, the supernatant liquid was decanted off, the oily compound was dissolved in acetone and excess ether was added. The separated oily product was again dissolved in methanol and excess degassed aqueous solution of $LiClO_4$ was added to it. A granular compound precipitated out. It was filtered, washed thoroughly with degassed water and dried over fused $CaCl_2$. The compound was recrystallised from degassed CH_2Cl_2. Yield 600 mg (62%).

Preparation of $[Ru(Pabt)(PPh_3)(imz)_2]ClO_4 \cdot 0.5\,CH_2Cl_2$ (**1b**), $[Ru(Pabt)(PPh_3)(2\text{-Meimz})]\,ClO_4$ (**1C**). ***Warning***: Perchlorate salts of metal complexes are potentially explosive [25]. These two compounds were synthesized and purified by the above procedure using imidazole (imz) and 2-methylimidazole (2-Meimz), respectively, in place of 1-methylimidazole. The complexes **1a, 1b** and **1c** can also be prepared using methanol as the solvent. Yield of **1b** was 495 mg (58%). Yield of **1c** was 360 mg (48%).

Preparation of [Ru(Pabt)(PPh$_3$)(1-Meimz)]ClO$_4$ (**2a**). ***Warning***: Perchlorate salts of metal complexes are potentially explosive [25]. This compound was prepared and purified by reacting Ru(Pabt) (PPh$_3$)$_2$Cl (**2**) with excess 1-methylimidazole following the procedure used for **1a**. Yield 320 mg (42%).

Preparation of [Ru(Pabt)(PPh$_3$)(bpy)]Cl · 1.5CH$_2$Cl$_2$ (**1d**) *and* [Ru(Pabt)(PPh$_3$)(phen)]Cl · CH$_2$Cl$_2$ (**1e**). To a dichloromethane [40 cm^3] solution of Ru(Pabt) (PPh$_3$) Cl (**1**) [1.0 mmol], a solution of 10 ml of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) [1.05 mmol] was added and the mixture was refluxed for 7 h. The volume of the resultant solution was reduced to 5 cm^3 in a rotaevaporator and excess petroleum ether was added. The precipitated compound was allowed to settle and then filtered. The residue was stirred with ether twice to remove excess 2,2′-bipyridine/1,10-phenanthroline. It was then filtered and dried over fused CaCl$_2$. Both **1d** and **1e** were recrystallised from degassed CH$_2$Cl$_2$. Yield of **1d** was 350 mg (39%). Yield of **1e** was 440 mg (49%).

Preparation of [Ru(Pabt)(PPh$_3$)(H$_2$O)$_2$]ClO$_4$ (**1f**). ***Warning***: Perchlorate salts of metal complexes are potentially explosive [25]. To a methanolic solution 50 cm^3 of Ru(Pabt) (PPh$_3$)Cl (**1**) [0.5 mmol], aqueous silver perchlorate solution [0.6 mmol in 10 cm^3 H$_2$O] was added with stirring. The mixture was refluxed with stirring for about 1 h, cooled and filtered through a sintered bed funnel (G4) to remove AgCl. The volume of the filtrate was reduced to 10 cm^3 and aqueous LiClO$_4$ solution was added in excess. The compound that separated out was filtered, thoroughly washed with water and dried over fused CaCl$_2$. It was recrystallised from CH$_2$Cl$_2$. Yield 370 mg (52%).

RESULTS AND DISCUSSION

The ligand PabtH exists in the benzothiazoline form [26] in the free state and is transformed to the corresponding Schiff base in the presence of either a base or a metal ion (Fig. 1). The complexes **1** and **3** of general formula Ru(Pabt)(PPh$_3$)X [X = Cl, Br respectively] were isolated by the reaction of Ru (PPh$_3$)$_3$X$_2$ with the ligand in 1 : 2 molar ratio in refluxing benzene and Ru(Pabt) (PPh$_3$)$_2$Cl (**2**) was isolated from the filtrate of **1**. When the reaction was carried out in benzene using 1 : 1 molar ratio of the reactants, compound **1** separated out from hot benzene as the only product. When Ru(PPh$_3$)$_3$Cl$_2$ was reacted with one mole of PabtH in refluxing CH$_2$Cl$_2$ **1** was obtained as the sole product, while **3** was isolated as the only product when Ru(PPh$_3$)$_3$Br$_2$ was used. Molecular weight determination in CH$_2$Cl$_2$ [Molecular weight of **1**, Exp. = 601, Calc. = 611.79; **3**, Exp. = 639, Calc = 656.19] clearly indicated the monomeric nature of **1** and **3**. The penta-coordinated complex **1** reacted with excess of different N-donor ligands (imidazole, 1-methylimidazole and 2-methylimidazole) producing hexacoordinated complexes [Ru(Pabt) (PPh$_3$) (B)$_2$]ClO$_4$ [where B = imz, 1-Meimz] and also the pentacoordinated species [Ru(Pabt) (PPh$_3$) (2-Meimz)]ClO$_4$. Moreover, complex **1** reacted with bidentate N—N donor ligands such as 2,2′-bipyridyl or *o*-phenanthroline in 1 : 1 molar ratio to produce hexacoordinated [Ru(Pabt)(PPh$_3$)(L—L)]Cl type complexes [where L—L = bipy, *o*-phen]. Another pentacoordinated complex [Ru(Pabt)(PPh$_3$)(1-Meimz)]ClO$_4$ (**2a**), was obtained by reacting Ru(Pabt) (PPh$_3$)$_2$Cl (**2**) with excess 1-Meimz in CH$_2$Cl$_2$ and subsequent treatment with a concentrated aqueous LiClO$_4$ solution. The aquo complex **1f** was prepared by Cl$^-$ abstraction from Ru(Pabt)(PPh$_3$)Cl using AgClO$_4$ in methanol solution. For convenience the different synthetic routes for the preparation of various ruthenium complexes are summarised in Equation I. The compounds gave satisfactory analytical results (Table 1) which are in good agreement with the assigned formulation. The formula of compounds **1a**, **1c** and **2a** were also checked by {^{1}H}NMR spectrum using the integration ratio of the methyl proton signal to those of the residual proton signals. The conductance data (Table 1) also supports the proposed formulation of the compounds **1a**–**1f** and **2a** as 1 : 1 electrolytes [27] with their anion Cl$^-$ or ClO$_4^-$ not participating in coordination. However compound **1**, **2** and **3** are nonelectrolytes and hence contain coordinated halide. This is supported by the presence of the ν(Ru—Cl) bands in their IR spectra (*vide infra*). The diamagnetic nature of all the complexes suggests the presence of the +2 oxidation state of ruthenium. The complexes (**1a**–**1f**, **2a**) are highly soluble in common organic solvents. The complexes **1**, **2** and **3** are moderately soluble in CH$_3$CN, but fairly soluble in CH$_2$Cl$_2$.

Infrared spectroscopy

The ligand PabtH exhibits a strong band at 3190 cm^{-1} due to ν(N—H) vibration [15], which is absent

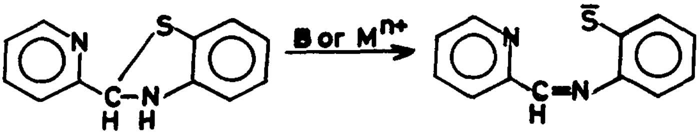

Fig. 1. Metal/base induced conversion of Pabt.

Table 1. Analytical and physical data for the ruthenium complexes

Complex	Colour	Molar Conductance^a (ohm^{-1} cm^2 mol^{-1})		Analysis Found (Calc.)%		
			X	C	H	N
1. Ru(Pabt)(PPh$_3$)Cl	Brown	81	5.4 (5.8)	58.5 (58.8)	4.0 (3.9)	4.6 (4.6)
2. Ru(Pabt)(PPh$_3$)$_2$Cl	Violet	79	3.6 (4.1)	65.4 (65.9)	4.4 (4.5)	3.5 (3.2)
3. Ru(Pabt)(PPh$_3$)Br	Brown	74	11.7 (12.2)	54.5 (54.9)	4.2 (4.3)	3.7 (3.7)
1a. [Ru(Pabt)(PPh$_3$)(1-Meimz)$_2$]ClO$_4$ · 1.5 CH$_2$Cl$_2$	Violet	145	—	49.3 (49.0)	3.9 (4.0)	8.4 (8.7)
1b. [Ru(Pabt)(PPh$_3$)(imz)$_2$]ClO$_4$ · 0.5CH$_2$Cl$_2$	Dark Violet	138	—	51.7 (51.3)	3.9 (3.9)	9.5 (9.8)
1c. [Ru(Pabt)(PPh$_3$)(2-Meimz)]ClO$_4$	Dark Violet	124	—	53.7 (53.8)	3.9 (4.0)	7.2 (7.4)
1d. [Ru(Pabt)(PPh$_3$)(bpy)]Cl · 1.5CH$_2$Cl$_2$	Violet	132	3.6 (4.0)	55.5 (55.6)	3.7 (3.9)	6.0 (6.2)
1e. [Ru(Pabt)(PPh$_3$)(Phen)]Cl · CH$_2$Cl$_2$	Dark Violet	118	3.8 (4.1)	58.5 (58.8)	4.0 (3.9)	6.6 (6.4)
1f. [Ru(Pabt)(PPh$_3$)(H$_2$O)$_2$]ClO$_4$	Dark Violet	127	—	51.0 (50.6)	3.8 (3.9)	4.2 (3.9)
2a. [Ru(Pabt)(PPh$_3$)(1-Meimz)]ClO$_4$	Violet	128	—	54.2 (53.8)	4.1 (4.0)	7.6 (7.4)

^{a} = MeCN, X = Cl or Br

in the complexes **1**, **2** and **3**. This strongly suggests that the ligand is present in its Schiff base form, in which it is known [26] to act as a monoanionic tridentate ligand coordinating through pyridine N, imine N and thiolato S. In the spectra of the mixed ligand complexes **1a**–**1e** and **2a**, there seems to be extensive mixing between the bands of the main ligand (Pabt) and those of the coligand bases. This makes precise assignment of the individual vibrations to definite vibrational modes very difficult. However, absence of any band at 2400–2500 cm^{-1} due to ν(S—H) in all these complexes indicates that the ligand is coordinated to the metal through the thiolato sulfur [28]. A medium intensity band at 1585 cm^{-1} assigned to ν(CN) vibration in the ligand is red shifted by ~40 cm^{-1} in the complexes due to coordination [9,29] of the azomethine nitrogen to the Ru^{II} centre. The ν(CS) band present at 750 cm^{-1} in the ligand is lowered by ~5 cm^{-1} on complexation and indicates M—S bond formation [30]. The pyridine ring vibration at 620 cm^{-1} and 420 cm^{-1} are blue shifted by *ca* 10 cm^{-1} because of the coordination through the pyridine ring nitrogen. In addition, the presence of a broad band around 1100 cm^{-1} in the IR spectra of the complexes **1a**–**1c**, **1f** and **2a** indicates that ionic ClO$_4^-$ is present in these complexes [9]. The band at 300 cm^{-1} and 320 cm^{-1} in complexes **1** and **2** respectively can be assigned as ν(Ru—Cl) band [8, 31]. However, we could not detect the ν(Ru—Br) for the compound **3** up to 300 cm^{-1}, which is the detection limit of our instrument.

{^{1}H}*NMR spectroscopy*

The {^{1}H}NMR spectra of the ligand PabtH exhibits a signal at 5.12 ppm which is assigned to the N—H proton and is confirmed by D$_2$O exchange experiment. The complexes **1**, **2** and **3** do not exhibit the characteristic N—H proton signal and indicate that in the metal complexes the ligand is present in its deprotonated form of the Schiff base. All the complexes exhibit proton signals in the aromatic region 6.8–7.6 ppm, which cannot be properly assigned due to overlap of corresponding signals of PPh$_3$ and the ligands. The compound [Ru(Pabt)(PPh$_3$)(1-Meimz)$_2$]ClO$_4$ (**1a**) in CDCl$_3$ exhibits two methyl signals of almost equal intensity at 3.51 ppm and 3.66 ppm indicating *cis* disposition of the two coordinated 1-methylimidazoles. The complex **2a** which contains only one 1-Meimz moiety, exhibits two signals of equal intensity (in CDCl$_3$) at 3.50 ppm and 3.63 ppm, whose combined integration corresponds to one methyl proton. This may indicate that two isomers of square pyramidal geometry (*vide infra*) coexists in solution.

Electronic spectroscopy

The electronic spectrum of 2-(2-pyridyl) benzothiazoline consists of three bands at 232, 255 and 310 nm, characteristic of the cyclic form. These may be attributed to the σ–σ^*, π–π^* and n–π^* benzenoid transitions [32]. All the complexes exhibit rich electronic spectra (Table 2) characteristic of the

Table 2. Electronic spectral data for the ruthenium complexes

	Bands λ_{max} (nm) [ε (dm^3 mol^{-1} cm^{-1})]		
Complex	Solvent CH_3CN	Solvent CH_2Cl_2	Nujol mull spectra
1. Ru(Pabt)(PPh_3)Cl	523(b)(2012), 466(b)(2468) 343(sh)(10,934), 322(14,150) 276(sh)(12,298), 222(48,224)	522(2878), 355(sh)(8080), 328(sh)(13,343), 276(12,626) 246(sh)(27,090), 233(34,565)	
2. Ru(Pabt)$(PPh_3)_2$Cl	537(sh)(>1844), 453(>3926) 351(sh)(>11,685), 306(>17,111) 276(sh)(>22,035), 226(>69,092)	522(1958), 326(9958) 274(20,021), 230(37,687)	541, 331(sh), 280
3. Ru(Pabt)(PPh_3)Br	520(b)(1395), 456(2120) 347(sh)(8594), 321(11,763) 240(25,000)	520(2076), 352(sh)(6939) 332(10,279), 252(sh)(23,336) 230(30,105)	
1a. [Ru(Pabt)(PPh_3)(1-Meimz)$_2$] $ClO_4 \cdot 1.5CH_2Cl_2$	521(b)(2837), 434(4293) 314(19,353), 275(14,100) 223(56,109)	524(sh)(2621), 442(3654), 318(16,934), 275(sh)(12,595), 232(39,745)	534, 439, 318
1b. [Ru(Pabt)(PPh_3)(imz)$_2$] $ClO_4 \cdot 0.5CH_2Cl_2$	504(b)(3503), 355(sh)(9312), 323(18,777), 275(12,968) 221(57,775)	526(b)(3474), 356(sh)(9069) 328(16,552), 275(sh)(11,715) 231(41,095)	548, 352, 243
1c. [Ru(Pabt)(PPh_3)(2-Meimz)]ClO_4	480(b)(2229), 352(sh)(8077) 318(11,437), 271(sh)(9375), 226(34,854)	493(2946), 356(sh)(8492), 325(12,969), 274(sh)(11,201) 231(30,575)	497, 336, 276(sh)
1d. [Ru(Pabt)(PPh_3)(bpy)]Cl $\cdot$ 1.5CH_2Cl_2	502(3909), 362(sh)(12,040) 332(19,702), 307(sh)(17,351) 235(49,646)	503(3601), 353(sh)(10,979) 327(17,313), 298(sh)(14,645) 247(sh)(28,451)230(39,683)	
1e. [Ru(Pabt)(PPh_3)(phen)]Cl $\cdot$ CH_2Cl_2	486(b,sh)(3921), 426(b) (4690), 351(sh)(8996), 322(sh)(14,071), 291(sh) (18,065), 265(sh)(39,721), 224(82,173)	497(4210), 427(5152), 355(sh)(9529), 333(sh)(14,088) 319(15,380), 292(sh)(19,759) 268(42,188), 232(67,219)	
1f. [Ru(Pabt)(PPh_3)$(H_2O)_2$]ClO_4	477(b)(2026), 351(sh)(7978) 315(10,873), 273(sh)(11,070) 222(sh)(35,175), 211(43,275)	493(b)(1948), 357(sh)(7431) 322(9968), 274(sh)(10,485), 230(24,537)	490(b) 399, 262(sh)
2a. [Ru(Pabt)(PPh_3)(1-Meimz)]ClO_4	515(b)(2569), 351(sh)(8284) 319(14,103), 273(sh)(11,485) 223(50,319)	532(2632), 357(sh)(6638), 321(12,790), 274(sh)(10,515) 231(36,137)	530, 307(sh), 266

b = broad, sh = shoulder

complexes of Pabt with other metals [15]. However, correct assignment of the bands is difficult without detailed analysis. In the UV-visible region there are generally two bands near 460–550 nm and 350–450 nm regions. The high extinction coefficient of the bands indicate that they are mainly of charge transfer origin. Among them, the lower energy band is probably due to a MLCT transition from the Ru^{II} centre to the Pabt ligand. This is supported by the fact that the plot (Fig. 4(a) and Fig. 4(b)) of $E_{Ru^{III}/Ru^{II}}$ (*vide infra*) *vs* the above MLCT transition expressed in eV gives a straight line, as has been observed for similar systems [5,33]. However, for bipyridine and orthophenanthroline complexes the above assignments are not unambiguous as transitions from Ru^{II} $d\pi$ to π^* of bpy or phen occur in the same region [33]. The band at 220–325 nm region is due to intraligand transitions.

Proposed structure of the complexes

The complexes $Ru(Pabt)(PPh_3)X$ [X = Cl (**1**) and X = Br (**3**)] are five-coordinated and probably square pyramidal. The five-coordinated nature of these complexes is supported by the molecular weight determination of $Ru(Pabt)(PPh_3)Cl$. TG-DTA traces clearly exhibit the absence of any water or solvent molecule in the complexes. The formation of such five-coordinated square pyramidal complexes is supported by Sellmann's work on a series of complexes of sulfur and nitrogen-sulfur donors. Sellmann reported the reaction of $[Ru(PPh_3)_2(dttd)]$ and $[Ru(PPh_3)_2(bmae)]$ [where $dttd^{2(-)}$ = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(−2), $bmae^{2(-)}$ = 1,2-bis(2-mercaptoanilino)ethane(−2)] with CO proceeds through the unsaturated 5-coordinated intermediate [3,34]. Moreover, he succeeded in isolating the distorted square pyramidal $[Ru(^{bu}bmae)]_2$ [where $^{bu}bmae^{2(-)}$ = 1,2-bis(2-mercapto-3,5-di-^{t}butyl-anilino)ethane (2−)] having a vacant coordination site [35]. The formation of stable five-coordinated complexes **1** and **3** and lability of the six-coordinated complex **2** [to form five-coordinated **2a**] is probably due to the stabilisation of five-coordinated 16 electron species through $p\pi$ donation by sulfur as suggested by Sellmann [3,34,35].

It has also been proposed that complexes of five-coordinated d^6 ions are best classified as square-pyramidal [36] which is in agreement with the second-order Jahn–Teller effect [37,38]. This view, taken along with the fact that most of the reported five-coordinated complexes of ruthenium are square pyramidal with varying degree of distortions, has induced us to propose that the five-coordinated complexes reported in this study also possess square pyramidal coordination geometry. As the ligand (Pabt) is planar [25] due to conjugation of all the atoms present, two isomeric arrangements are possible for the square pyramidal geometry (Fig. 2). Among these two possibilities, isomer "**a**" containing PPh_3 in axial position is expected to be more stable, both from steric as well

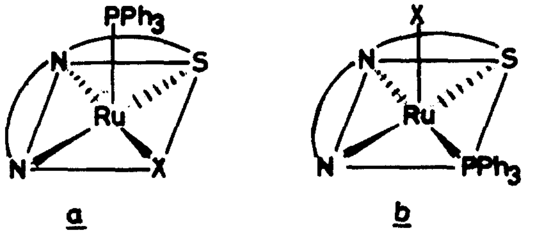

Fig. 2. Two possible isomeric arrangements of $Ru(Pabt)(PPh_3)Cl$ (**1**)

as electronic point of view. The isomer "**b**" may be stabilised from the agostic interaction of H atom from the PPh_3 ligand [39] which is known to stabilise $Ru(PPh_3)_3Cl_2$. Formation of **1a**, **1b**, **1d** and **1e** can then be easily explained by replacement of equatorial X and occupation of the vacant axial position by two N donor atoms of two imidazoles or a bipyridyl/phenanthroline.

The structure of six-coordinated complexes $[Ru(pabt)(PPh_3)_2Cl]$ (**2**) is established by $\{^{31}P\}$NMR spectrum in $CDCl_3$, which exhibits a single sharp peak at 20.2 ppm indicating that the two PPh_3 groups are trans to each other [40]. Thus the square plane is occupied by the ligand Pabt and a chloride (Fig. 3(a)).

The probable structure of the complex $[Ru(pabt)(PPh_3)(2\text{-Meimz})]ClO_4$ (**1c**) is shown in (Fig. 3(b)). Molecular model shows that the CH_3^- group on the ligated 2-Meimz sterically restricts the access of a second 2-Meimz at the vacant sixth position of Ru.

Cyclic voltammetry. The electron transfer behaviour of all the complexes has been examined in dichloromethane and acetonitrile solvents, containing 0.1 M TEAP using cyclic voltammetric technique (scan rate 200 mV s^{-1}). The results are summarised in Table 3.

The complexes exhibit reversible oxidative responses in the potential range 0.3–1.0 V. The compound **1** exhibits a one electron anodic wave at a $E_{1/2}$ of 0.40 V *vs* SCE in both the solvents which corresponds to the process (**I**).

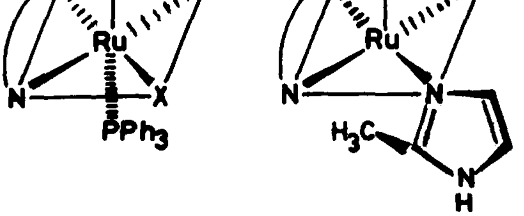

Fig. 3. (a) Possible structure of $Ru(Pabt)(PPh_3)_2Cl$ (**2**); (b) Possible structure of $[Ru(Pabt)(PPh_3)(2\text{-Meimz})]ClO_4$ (**1c**).

Table 3. Cyclic voltammetric results for [a,b] Ru^{II} complexes in 0.1 M TEAP at 298 K

Complex	In CH_2Cl_2 $E_{1/2}$, V[ΔE_p(mV)]	In CH_3CN $E_{1/2}$, V[ΔE_p(mV)]
1. Ru(Pabt) $(PPh_3)Cl$	0.40(70), 0.19(60)[c]	0.40(60), 0.14(75)[c]
2. Ru(Pabt) $(PPh_3)_2Cl$	−0.08(60), 0.65(69)	−0.07(60), 0.62(68)
3. Ru(Pabt) $(PPh_3)Br$	0.44(60), 0.21(50)[c]	$E_{pa} = 0.66$[d]
1a. [Ru(Pabt) (PPh_3) $(1\text{-Meimz})_2]ClO_4 \cdot 1.5\ CH_2Cl_2$	0.75(62)	0.74(81)
1b. [Ru(Pabt) (PPh_3) $(imz)_2]ClO_4 \cdot 0.5CH_2Cl_2$	0.76(100)	0.74(63)
1c. Ru(Pabt) (PPh_3) $(2\text{-Meimz})]ClO_4$	0.85(60), 0.52[c]	1.02(125)
1d. [Ru(Pabt) (PPh_3) (bpy)]$Cl \cdot 1.5CH_2Cl_2$	0.90(70)	0.96(76)
1e. [Ru(Pabt) (PPh_3) (phen)]$Cl \cdot CH_2Cl_2$	1.03(125)	0.98(118)
1f. [Ru(Pabt) (PPh_3) $(H_2O)_2]ClO_4$	$E_{pa} = 0.94$	1.00(80)
2a. [Ru(Pabt) (PPh_3) $(1\text{-Meimz})]ClO_4$	0.72(62), 0.31[c]	0.70(75)

[a] Working electrode platinum; reference electrode SCE; $E_{1/2} = 0.5\ (E_{pa} + E_{pc})$; $\Delta E_{pc} = E_{pc} - E_{pa}$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively.

[b] Supporting electrolyte 0.1 M TEAP, solute concentration $\sim 10^{-3}$ M, scan rate 200 $mV^{-1}s^{-1}$.

[c] Supporting electrolyte TEACl (0.1 M).

[d] Corresponding cathodic wave $E_{pc} = 0.45$ V.

$$Ru(NNS^-)(PPh_3)Cl \underset{+e}{\overset{-e}{\rightleftharpoons}} [Ru^{III}(NNS^-)(PPh_3)Cl]^+. \qquad \textbf{(I)}$$

This assignment is justified by the fact that, when compound **1** is oxidised chemically with iodine in dichloromethane solution, the EPR spectrum of the oxidised species at 77 K is found to be highly anisotropic. It is known that Ru^{III} compounds give rise to highly anisotropic EPR spectra [23]. The g values ($g_1 = 2.12$, $g_2 = 2.29$ and $g_3 = 2.59$), as well as a large separation of 530 G between the lowest and highest field peak indicates that the unpaired electron is predominantly metal centred [41]. So the above oxidation involves a metal based redox orbital. Complex **3**, the bromo analogue of **1**, exhibits a peak at $E_{1/2} = 0.44$ V in dichloromethane, which is consistent with a reaction similar to the one described by process **(I)**. But when compound **3** is scanned in MeCN it reveals an irreversible anodic wave at $E_{pa} = 0.66$ V. The anodic shift of this peak is probably due to the solvent participation [42].

When the scanning is extended to higher positive potentials, it reveals ill-defined peaks which may be due to ligand oxidation or can be attributed to oxidation of triphenyl phosphine [43].

When the voltammogram of **1** is run in dichloromethane with TEACL as the supporting electrolyte a cathodic shift of the anodic peak is observed (Table 3). The negative shift of the first anodic peak ($E_{1/2} = 0.19$ V) can be explained considering direct coordination of Cl ion to the metal centre of the coordinatively unsaturated complex, prior to its participation in electrolysis [19]. The involvement of the Cl facilitates the oxidation of the complex by decreasing the overall positive charge of the complex ion [process **(II)**].

$$Ru^{II}(NNS^-)(PPh_3)Cl \underset{-Cl^-}{\overset{+Cl^-}{\rightleftharpoons}} [Ru^{II}(NNS^-)(PPh_3)Cl_2] \underset{+e}{\overset{-e,0.19}{\rightleftharpoons}} Ru^{III}(NNS^-)(PPh_3)Cl. \qquad \textbf{(II)}$$

The corresponding bromo complex **3** exhibits similar behaviour. The five coordinated complexes **1c** and **2a** similarly display cathodically shifted oxidation waves in dichloromethane when TEACL used as supporting electrolyte.

The six-coordinated complex **2** displays an anodic wave at 0.63 V. Here, due to the presence of additional PPh_3 in the sixth position, Ru^{III}/Ru^{II} potentials are anodically shifted [44]. This happens because the presence of an extra PPh_3 results in a HOMO with different energy. The reductive couple at −0.08 V of same current height may be due to Ru^{II}/Ru^{I} reduction as reported earlier [45].

As expected, the $E_{1/2}$ values of the cationic complexes (**1a**–**1f**) and **2a** are more positive compared to the neutral [46] parent complexes **1** and **3**. The one-electron change of the complexes **1d** and **1e** was checked coulometrically [for **1d** $n = 0.98$ (1.15 V); for **1e** $n = 1.03$ (1.15 V)]. It is obvious that in all the complexes the oxidation potential values in CH_2Cl_2 are greater than those in MeCN, due to the difference in solvent polarity.

During the cyclic voltammetric study of the complex **1e** in acetonitrile solution using TEAP as the supporting electrolyte, attention was drawn to an interesting observation. Gradual addition of PPh_3 to the solution of the complexes caused an increase in the i_{pa}/i_{pc} value at 0.98 V accompanied by a small anodic shift. This may happen due to the interaction between **1e** or its oxidised species with PPh_3, the latter

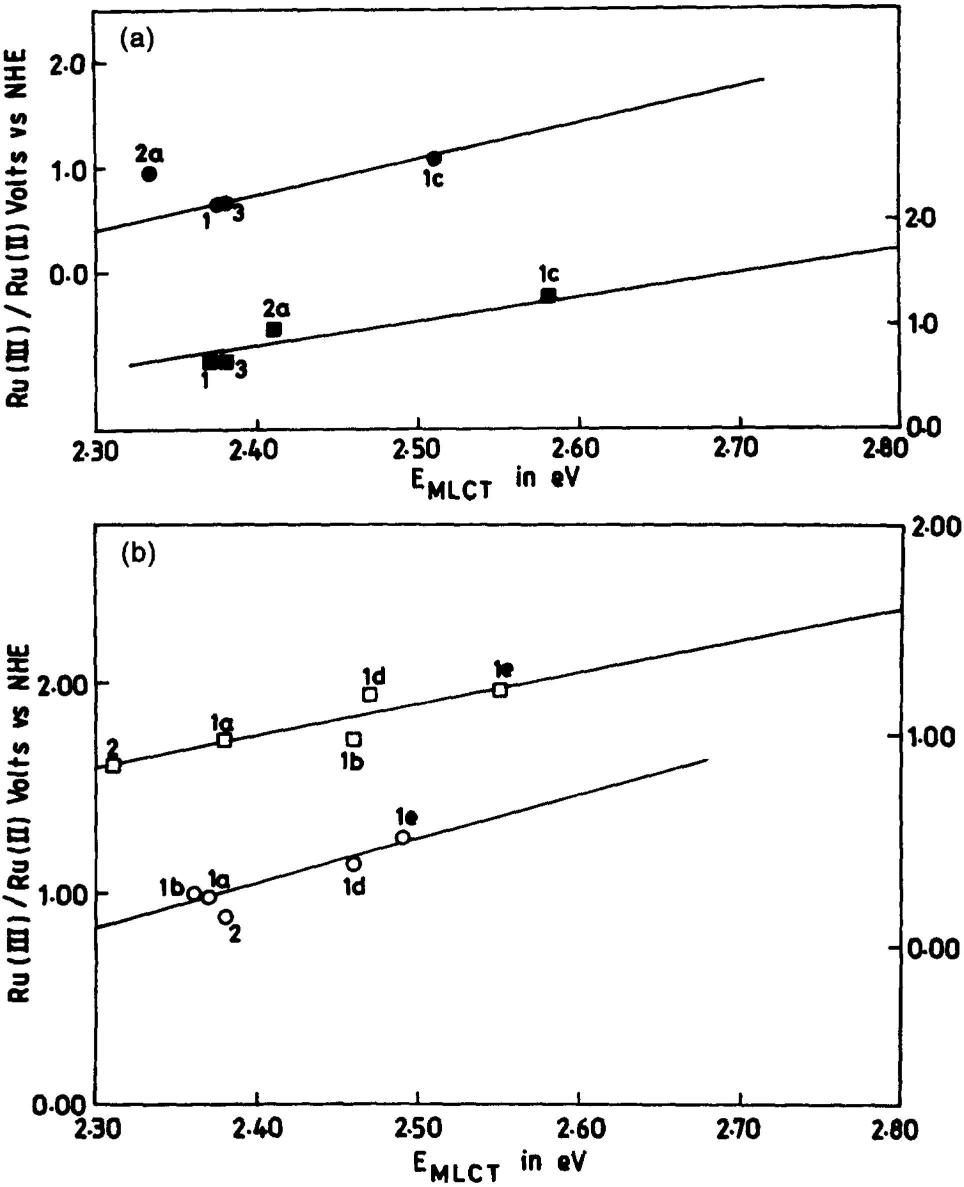

Fig. 4. Plots of observed Ru^{III}/Ru^{II} potentials ($E_{1/2}$) against the energy of the metal-to-ligand charge transfer transition (E_{MLCT}) of (a) six-coordinated complexes: (bottom, open circles) measured in CH_2Cl_2 and referred to left-hand y-axis; (top, open square) measured in CH_3CN and referred to right-hand y-axis. All data are *vs* NHE (1 V *vs* SCE = 1.242 V *vs* NHE); (b) five-coordinated complexes: (top, closed circles) measured in CH_2Cl_2 and referred to left-hand y-axis; (bottom, closed square) measured in CH_3CN and referred to right hand y-axis. All data are *vs* NHE (1 V *vs* SCE = 1.242 V *vs* NHE).

undergoing catalytic oxidation. The complex **1d** also behaves similarly. Similar observations were made in dichloromethane solution. Such observations were recorded previously for electrochemical reduction of molybdenum complexes [47–49].

It is possible to compare the observed $E_{1/2}$ values of Ru^{III}/Ru^{II} couples of the six-coordinated complexes with that calculated according to the linear relation given by Lever in organic solvents, based on his electrochemical ligand parameter E_L [50]. Two least-square lines (Fig. 5) obtained are as follows: dichloromethane: $E_{Ru^{III/II}} = 0.73\,[\Sigma E_L] + 0.30$; acetonitrile: $E_{Ru^{III/II}} = 0.80[\Sigma E_L] + 0.22$.

This linear correlation of $E_{1/2}$ values with ΣE_L parameter suggests that the assignment of $E_{1/2}$ values for Ru^{III}/Ru^{II} couples in these complexes are self-consistent and there are no synergic interactions between the metal and the ligand.

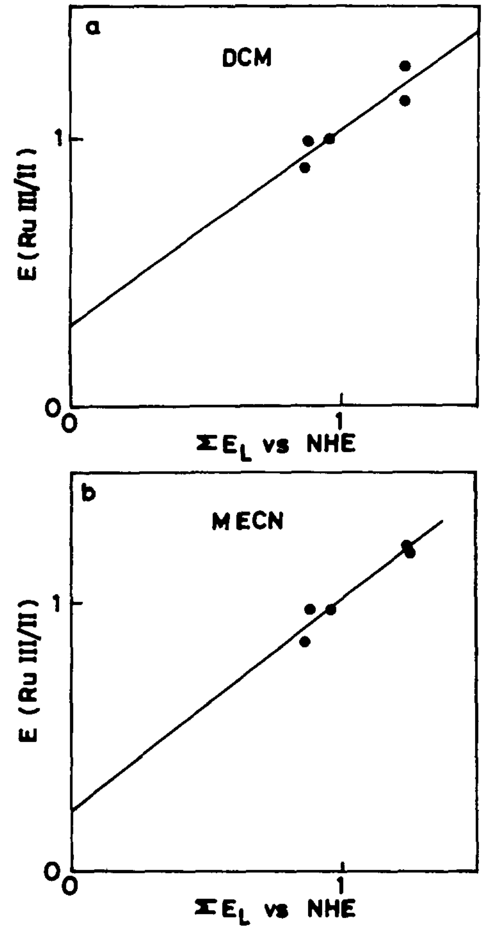

Fig. 5. Plot of observed Ru^{III}/Ru^{II} potentials against ΣE_L of six-coordinated complexes (a) measured in CH_2Cl_2, (b) measured in CH_3CN. All data are *vs* NHE (1 V *vs* SCE = 1.242 V *vs* NHE). Taking $E_{Pabt} = 0.33$, calculated from Lever's equation [50].

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