Synthesis, Spectroscopy and Electrochemistry of Ruthenium(II) Complexes of Tridentate Pyridylpyrazole Ligands. Predominance of Electronic over Steric Effects

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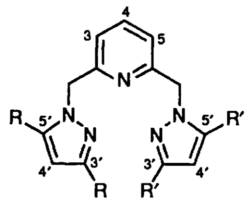
The preparations and properties of bis complexes of ruthenium(II) containing various combinations of the tridentate ligands 2,6-bis(pyrazol-1-ylmethyl)pyridine (L^1) and di- and tetra-methyl substituted derivatives (L^2 and L^3) are described. The absorption spectral properties of the complexes are thoroughly analysed. Full assignments have been made for the ^1H NMR spectra of two representative complexes in CD_3CN and the origins of the co-ordination-induced shifts are discussed. Cyclic voltammetric experiments (MeCN solutions) reveal reversible one-electron Ru^{III}–Ru^{II} redox couples in the potential range 1.00–1.06 V *vs.* saturated calomel electrode (SCE). The occurrence of ligand-based irreversible reductions at low potentials ($E_{p,c}$ values lie in the range: −1.90 to −2.20 V *vs.* SCE) reveals that these pyrazole-rich ligands are very poor π acceptors. The formal potentials of the Ru^{III}–Ru^{II} couples decrease (by *ca.* 8 mV per methyl group) as the number of methyl groups in the ligands are increased. The decreased potential step size for $[RuL(L')]^{2+}$ (L,L′ = L^1–L^3) relative to those observed for non-sterically hindered ruthenium(II) complexes reveals that in the present system steric effects due to 3-Me substituent(s) contribute to the observed effect but that electronic factors predominate over steric effects.

The present work stems from our continued interest[1–3] in the identification of the steric effect of methyl substituent(s) adjacent to donor atoms on the M^{III}–M^{II} redox potentials (M = Mn, Fe or Co) using a new family of tridentate heterocyclic ligands, L^1–L^3. It has been found that the ligand-field strengths of L^2 and L^3 in bis-ligated complexes of iron(II) and nickel(II) are much reduced[1,3–5] compared to that of the corresponding complexes of unsubstituted ligand L^1. Thus while the iron(II) bis complex of L^3 is high spin at all accessible temperatures, the corresponding complex of L^1 displays a temperature-induced singlet $\rightleftharpoons$ quintet transition.[5] In these derivatives the effect of the methyl substituent(s) is to hinder the close approach of the donor atoms to the metal atom and hence to decrease their effective co-ordinating ability. The X-ray structure[5] of the complex $[Fe(L^2)_2][ClO_4]_2$ reveals such reduced bonding interactions.

In the bis-chelate series the ease of oxidation (M^{III}–M^{II} redox couple) follows the order: $[M(L^1)_2]^{2+} < [M(L^2)_2]^{2+} < [M(L^3)_2]^{2+}$ (M = Mn, Fe or Co).[1–3] On electronic grounds this trend is completely unexpected as one would predict redox-potential values less positive for methyl-substituted complexes than for the unsubstituted complex on the basis of the electron-donating property of methyl substituents. The observed opposite effect is a clear demonstration of the predominance of steric factors caused by substitution at the 3 position(s) over the electronic contribution prevailing at the 5 position(s) in L^2 and L^3. Changing the size of the metal ion on going from the first- to the second-transition series might lead to the observation of a predominance of an electronic effect over the steric effect. We thus extended our study to ruthenium. Herein we report a systematic study on the synthesis, spectra and electrochemistry of a novel group of bis-ligated ruthenium(II) complexes using L^1–L^3 ligands.

Experimental

Materials.—Solvents and reagents were obtained from commercial sources and used as received. 2,6-bis(pyrazol-1-ylmethyl)pyridine (L^1), 2-(3,5-dimethylpyrazol-1-ylmethyl)-6-(pyrazol-1-ylmethyl)pyridine (L^2) and 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L^3) were prepared as described in the literature.[1,6] Tetrabutylammonium perchlorate was synthesised as before.[7] Acetonitrile, dimethylformamide (dmf) and ethanol were purified as reported previously.[7,8] Dimethyl sulfoxide (dmso) was purified by distillation over BaO. Water was deionized and then distilled from alkaline $KMnO_4$. Commercial $RuCl_3 \cdot xH_2O$ was treated with concentrated HCl and evaporated to dryness on a hot plate. This was repeated three times to obtain the pure product as $RuCl_3 \cdot 3H_2O$.



L^1 : R = R′ = H
L^2 : R = H; R′ = Me
L^3 : R = R′ = Me

Syntheses of Ruthenium Complexes.—$[Ru(L^1)Cl_3] \cdot 3H_2O$. An ethanolic solution (10 cm^3) of L^1 (183 mg, 0.76 mmol) was added dropwise to a vigorously stirred ethanolic solution (15 cm^3) of $RuCl_3 \cdot 3H_2O$ (200 mg, 0.76 mmol). The mixture was stirred for 1 h at room temperature and the greenish brown powder that separated was filtered off and washed with ethanol followed by acetone and finally dried *in vacuo* (274 mg, yield 72%) (Found: C, 30.3; H, 3.50; N, 14.00. Calc. for $C_{13}H_{19}Cl_3N_5O_3Ru$: C, 30.8; H, 3.80; N, 13.50%). UV/VIS spectrum (in dmso): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 369 (4450), 460 (sh) (3260) and 600 (sh) (657). Molar conductance, Λ_M 36 Ω^{-1} cm^2 mol^{-1}. μ_{eff}(dmf) = 1.98.

The complex $[Ru(L^3)Cl_3] \cdot 3H_2O$ was synthesised similarly (Found: C, 36.3; H, 4.90; N, 12.60. Calc. for $C_{17}H_{27}Cl_3N_5O_3Ru$: C, 36.7; H, 4.90; N, 12.60%).

$[Ru(L^1)_2][ClO_4]_2 \cdot H_2O$.—Two different synthetic pro-

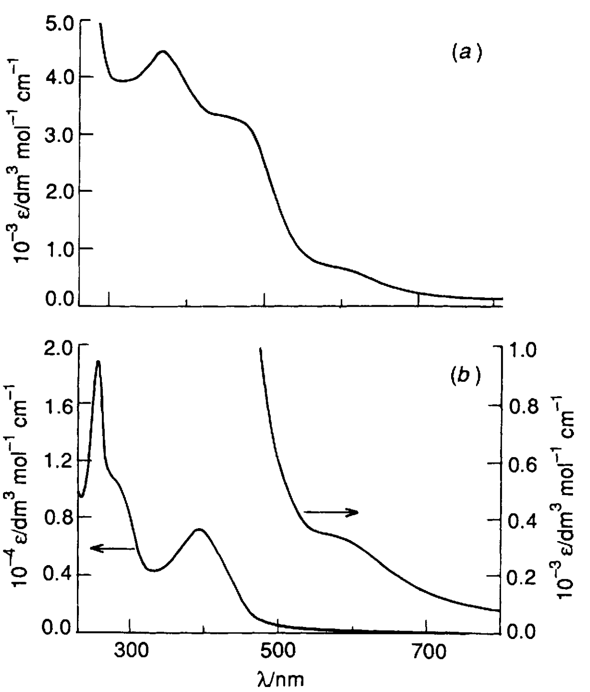


Fig. 1 Electronic spectra of (*a*) $[Ru(L^1)Cl_3]\cdot3H_2O$ in dmso and (*b*) $[Ru(L^1)_2][ClO_4]_2\cdot H_2O$ in CH_3CN

cedures were followed. The method A described below is a modified one to that reported by Watson *et al.*[6]

Method A. An aqueous solution (10 cm^3) of $RuCl_3\cdot3H_2O$ (100 mg, 0.38 mmol) and L^1 (220 mg, 0.92 mmol) was refluxed under a dinitrogen atmosphere for 1 h. The ruthenium was then reduced by the addition of sodium hypophosphite solution [1.8 cm^3; prepared by neutralizing 30% H_3PO_2 (1.2 cm^3) with 2.0 mol dm^{-3} NaOH (3.4 cm^3)]. Concentrated HCl (8 drops) was then added to the green solution which was further refluxed for 2 h and finally filtered. The complex was precipitated as a brownish green microcrystalline solid by dropwise addition of a saturated aqueous solution of sodium perchlorate. The compound was recrystallized from ethanol–water (1:1 v/v) (80 mg, yield 51%).

Method B. A suspension of $[Ru(L^1)Cl_3]\cdot3H_2O$ (100 mg, 0.20 mmol) and L^1 (48 mg, 0.20 mmol) in water (10 cm^3) was refluxed for 30 min under a dinitrogen atmosphere. After the addition of sodium hypophosphite solution (1.2 cm^3; prepared as described above) it was further refluxed for 2 h and filtered. The desired complex was precipitated and recrystallized as described above (78 mg, yield 48%). The product obtained by both methods gave similar microanalyses (Found: C, 39.2; H, 3.60; N, 17.60. Calc. for $C_{26}H_{28}Cl_2N_{10}O_9Ru$: C, 39.2; H, 3.50; N, 17.60%).

$[Ru(L^1)(L^3)][ClO_4]_2\cdot H_2O$.—This complex was prepared by a procedure similar to that described above (Method B) for $[Ru(L^1)_2][ClO_4]_2\cdot H_2O$, using L^3 as ligand in place of L^1 (yield 48%) (Found: C, 42.1; H, 4.30; N, 16.50. Calc. for $C_{30}H_{36}Cl_2N_{10}O_9Ru$: C, 42.2; H, 4.20; N, 16.40%).

CAUTION: Although no problems were experienced in handling these complexes, perchlorate salts of complexes with organic groups should be regarded as potentially explosive.

Physical Measurements.—Infrared and electronic spectra were recorded on Perkin Elmer 1320 and Lambda-2 spectrophotometers respectively. Conductivity measurements were made with an Elico (Hyderabad, India), type CM-82T conductivity bridge. Solution-state magnetic susceptibility measurements were done by the NMR technique[9] of Evans in acetonitrile or dmf with a PMX-60 JEOL (60 MHz) NMR spectrometer. Solvent susceptibility and diamagnetic corrections were obtained as before.[10] The 400 MHz ^1H NMR spectra were measured in CD_3CN on a Brüker WM-400 (400 MHz) NMR spectrometer at the Regional Sophisticated Instrumentation Centre, Lucknow, India. Cyclic voltammetric measurements for dinitrogen flushed solutions containing ruthenium complexes (1.0×10^{-3} mol dm^{-3}) and NBu_4ClO_4 (0.2 mol dm^{-3}) as supporting electrolyte were done by using a PAR model 370–4 electrochemistry system incorporating the following: model 174A, polarographic analszer; model RE0074 *x–y* recorder. The working electrode was either a Beckman planar platinum model 39273 or a PAR model G0021 glassy carbon electrode. Potentials are referenced to a saturated calomel electrode (SCE) and are uncorrected for any junction contributions. The formal potentials (E_f) are calculated as the average of cathodic (E_{pc}) and anodic (E_{pa}) peak potentials. Under our experimental conditions, the reversible couple $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ (E_f = 0.40 V *vs.* SCE in acetonitrile) has ΔE_p of 80 mV, which was used as the criterion for electrochemical reversibility.[8] The details of the electrochemical cell are the same as described earlier.[7]

Results and Discussion

Syntheses and Selected Properties.—The general synthetic approach that was employed for the preparation of the ruthenium(II) complexes with various combinations of the ligands reported in this work has involved the reactions of $[RuLCl_3]$ ($L = L^1$–L^3) with the tridentate ligands (L^1–L^3) in the presence of sodium hypophosphite as reducing agent. The successful syntheses of these complexes demonstrate the generality of substitution reactions that the complexes $[RuLCl_3]$ can undergo. The synthesis and a very limited characterization of the complex $[Ru(L^1)_2]^{2+}$ has been reported in the literature[6] following a direct reaction between the ligand and $RuCl_3\cdot3H_2O$ in the presence of NaH_2PO_2 as reducing agent.

New monochelate ruthenium(III) starting complexes used in this work were prepared following direct reactions between the appropriate ligand and $RuCl_3\cdot3H_2O$ in ethanol. The molar conductance value (see Experimental section) of $[Ru(L^1)Cl_3]\cdot3H_2O$ in dmf solution reveals a partial dissociation of the supposedly neutral complex. Measurement of the magnetic susceptibility of this complex in dmf solution gives a μ_{eff} value of 1.98 (see Experimental section), consistent with the presence of monomeric octahedral d^5 low-spin ($S = \frac{1}{2}$) ruthenium(III). The bis-chelate complexes were isolated as crystalline perchlorate salts. All the ruthenium(II) complexes are diamagnetic.

Absorption Spectra.—The absorption spectral data for all the ruthenium(II) complexes are presented in Table 1. The absorption spectrum of $[Ru(L^1)Cl_3]\cdot3H_2O$ in dmso and a representative ruthenium(II) bis complex in CH_3CN are shown in Fig. 1. For $[Ru(L^1)Cl_3]$ the shoulders at 460 and 600 nm are assigned as ligand(π)-to-metal(t_2) charge-transfer transitions. The band at 369 nm is due to a $Cl^- \rightarrow Ru(t_2)$ charge-transfer transition. The spectral feature observed for this mononuclear ruthenium(III) complex is well documented in the literature.[11]

All the ruthenium(II) bis complexes show three types of bands. A comparatively low-intensity shoulder at ≈580 nm is seen in addition to absorptions of medium intensity in the region 350–430 nm and very strong bands due to intraligand transitions at higher energies.

The occurrence of only a moderately intense shoulder at ≈580 nm is of interest since $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) shows an absorption tail at 546 nm with a molar absorption coefficient of ≈700 dm^3 mol^{-1} cm^{-1}. This absorption is responsible for the luminescence shown by $[Ru(bipy)_3]^{2+}$ and is assigned to a spin-forbidden metal-to-ligand charge transfer, ^{3}m.l.c.t. transition.[12,13] We believe that the weak-field nature of ligands $L^{1,3-5}$ makes the low-lying

Table 1 Characterization data of ruthenium(II) complexes in acetonitrile at 298 K

Complex	Molar conductivity[a] Λ_M/Ω^{-1} cm^2 mol^{-1}	UV/VIS data λ/nm(ε/dm^3 mol^{-1} cm^{-1})	Ru^{III}–Ru^{II} couple[b] E_f/V (ΔE_p/mV)
$[Ru(L^1)_2][ClO_4]_2 \cdot H_2O$	274	256 (19 000), 285 (sh) (10 250), 395 (7 250), 586 (sh) (330)	1.06 (80)
$[Ru(L^2)_2][ClO_4]_2 \cdot H_2O$	280	257 (18 000), 285 (sh) (9 700), 404 (5 900), 580 (sh) (787)	1.03 (80)
$[Ru(L^3)_2][ClO_4]_2 \cdot H_2O$	281	257 (19 050), 285 (sh) (9 950), 350 (sh) (3 070), 419 (8 420), 605 (sh) (919)	1.00 (80)
$[Ru(L^1)(L^2)][ClO_4]_2 \cdot H_2O$	270	257 (17 750), 286 (sh) (9 900), 392 (6 050), 591 (sh) (635)	1.05 (90)
$[Ru(L^1)(L^3)][ClO_4]_2 \cdot H_2O$	281	257 (18 800), 286 (sh) (8 000), 350 (sh) (3 100), 409 (6 200), 580 (sh) (280)	1.04 (90)
$[Ru(L^2)(L^3)][ClO_4]_2 \cdot H_2O$	283	257 (18 100), 285 (sh) (9 600), 403 (5 800), 600 (sh) (730)	1.01 (90)

[a] Expected 1:2 electrolyte range: 220–300 Ω^{-1} cm^2 mol^{-1}. [b] Supporting electrolyte 0.2 mol dm^{-3} NBu_4ClO_4; scan rate, 50 mV s^{-1}; potentials are *vs.* saturated calomel electrode (SCE).

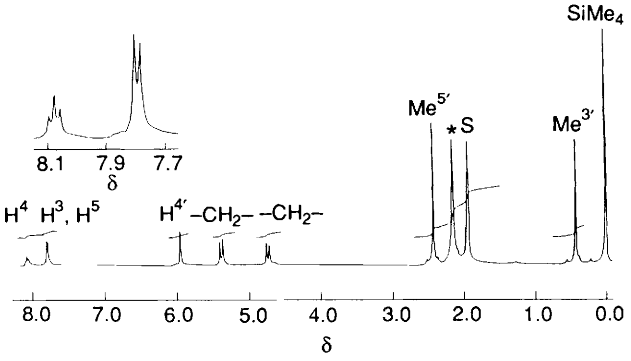


Fig. 2 400 MHz ^{1}H NMR spectrum of $[Ru(L^3)_2][ClO_4]_2 \cdot H_2O$ in CD_3CN (peaks for a solvent and water present therein are marked by S and * respectively)

metal–ligand antibonding orbital d_{σ^*} thermally accessible and that the shoulder at ≈580 nm is due to a $(d_\pi)^6 \longrightarrow (d_\pi)^5 (d_{\sigma^*})^1$ transition. We rule out the possibility of this being a spin-forbidden charge-transfer (^{3}m.l.c.t.) transition since these ligands are very poor π acceptors (see below).

The absorptions in the region 350–430 nm are attributed to spin-allowed charge-transfer transitions from the metal d_π orbitals to ligand π* orbitals (m.l.c.t.). Inspection of Table 1 shows that in going from $[Ru(L^1)_2]^{2+}$ to $[Ru(L^3)_2]^{2+}$ a significant red shift in the band maxima is observed as the number of methyl substituents near the donor site increases. A similar trend has been observed in other complexes containing ligands with substituents in sterically hindering positions.[14,15]

The m.l.c.t. band positions of the present complexes are comparable to those for a related group of complexes containing 2,6-bis(*N*-pyrazolyl)pyridine ligands.[16] It is worth noting here that the m.l.c.t. band energy for $[Ru(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) is 476 nm.[16] This indicates an increase in separation of the energy levels of the metal d and ligand π* orbitals in these complexes of pyrazole-rich ligands compared to the pyridine-rich planar terpy ligand. Since the same orbitals are well known[13] to be involved in redox processes this is also reflected by an increase in the potential gap between the Ru^{III}–Ru^{II} redox couple and the first ligand-reduction process (see below). Furthermore, it appears that this increase in orbital separation results from both an increase in the energy of the metal *d* orbitals, as shown by the decrease in Ru^{III}–Ru^{II} reduction potentials (cathodically shifted), and a large rise in of the energy level of the ligand π* orbitals (see below). The band at ≈250 nm and the shoulder at ≈285 nm are assigned to ligand-localized transitions.

Proton NMR Spectra.—To throw light on the bonding interactions between the metal and the ligands L^1–L^3 in these diamagnetic complexes we have examined the ^{1}H NMR spectral properties of two representative bis complexes, *viz*., $[Ru(L^1)_2][ClO_4]_2 \cdot H_2O$ and $[Ru(L^3)_2][ClO_4]_2 \cdot H_2O$ in CD_3CN. Table 2 lists the ^{1}H NMR chemical shifts for the complexes with co-ordination-induced shifts Δδ ($\Delta\delta = \delta_{complex} - \delta_{ligand}$).[17–19] A typical spectrum is shown in Fig. 2. Assignments were made by comparison with the spectra of the free ligands and of related complexes from the literature.[18] In both the complexes studied here it is expected that the six-membered chelate rings exist in boat conformations.[5,6] In the spectra of $[Ru(L^1)_2]^{2+}$ and $[Ru(L^3)_2]^{2+}$ the CH_2 protons give rise to an AB quartet, which confirms the presence of two diastereotopic protons, axial and equatorial. Thus it is obvious that these two protons are not interconverting on the NMR time-scale, otherwise a singlet would have resulted.

Inspection of the chemical shifts and Δδ values in Table 2 allows a number of observations to be made. The Δδ values are, in general, positive except for protons on carbon atoms adjacent to the co-ordinating nitrogens and the methylene protons. The former protons show significant negative (upfield) Δδ values. A large range of Δδ values (+1.06 to −1.64 ppm) reflects some dramatic changes in the ^{1}H NMR chemical shifts upon co-ordination of ligands L^1–L^3 to ruthenium. The sign and magnitude of Δδ values depend on several factors[17–19] such as ligand-to-metal σ donation, metal-to-ligand π back donation, chelation-imposed conformational changes, co-ordinative disruption of inter-ring conjugation and through-space ring-current anisotropy.

The large negative Δδ values observed for protons adjacent to co-ordinating pyrazole nitrogens (R$^{3'}$ position) result from interligand through-space ring-current anisotropy effects since on complexation the protons involved all lie over the shielding plane of the central pyridine ring of the other co-ordinated ligand. This is clearly seen when the 3′ position is methyl substituted.

The large positive Δδ values for pyridine protons (H^{3,4,5}) (downfield shifts) suggest that the ligand-to-metal σ donation is more important (as this will decrease the electron density at those sites and lead to positive Δδ values) than metal-to-ligand π-back donation in the ground state of these complexes (see below). Since ring-current-induced fields depend on the aromaticity and π polarisability of the heterocycle these effects will differ significantly for different types of heterocycle.[20] Thus, in contrast to pyrdine-ring protons, pyrazole-ring protons are shifted upfield. This is in accord with the well established fact that pyrazole-containing ligands are expected to be weaker[16] donors than the analogous pyridine-containing ligands, given

Table 2 Proton NMR chemical shifts[a] and co-ordination-induced shifts[b]

	^{1}H NMR					
Compounds	H^4	H^3,H^5	$H^{4'}$	CH_2	$R^{3'c}$	$R^{5'c}$
L^1	7.43	6.80	6.23	5.33	7.33	7.60
	(q, J 8)	(d, J 8)	(t, J 2.5)	(s)	(d, J 2.5)	(d, J 2.5)
$[Ru(L^1)_2][ClO_4]_2 \cdot H_2O$	8.15	7.78	6.25	5.15	6.25	7.80
	(t, J 8)	(d, J 8)	(m)	(AB, q, J 16)	(m)	(s,br)
$\Delta\delta$	+0.72	+0.98	+0.02	−0.18	−1.08	+0.20
L^3	7.50	6.73	5.80	5.16	2.06	2.13
	(q, J 8)	(d, J 9)	(s)	(s)	(s)	(s)
$[Ru(L^3)_2][ClO_4]_2 \cdot H_2O$	8.08	7.79	5.95	5.06	0.42	2.42
	(t, J 8)	(d, J 8)	(s)	(AB, q, J 16)	(s)	(s)
$\Delta\delta$	+0.58	+1.06	+0.15	−0.10	−1.64	+0.29

[a] For deuteriated acetonitrile solutions, J/Hz. [b] $\Delta\delta = \delta_{complex} - \delta_{ligand}$. [c] H or Me.

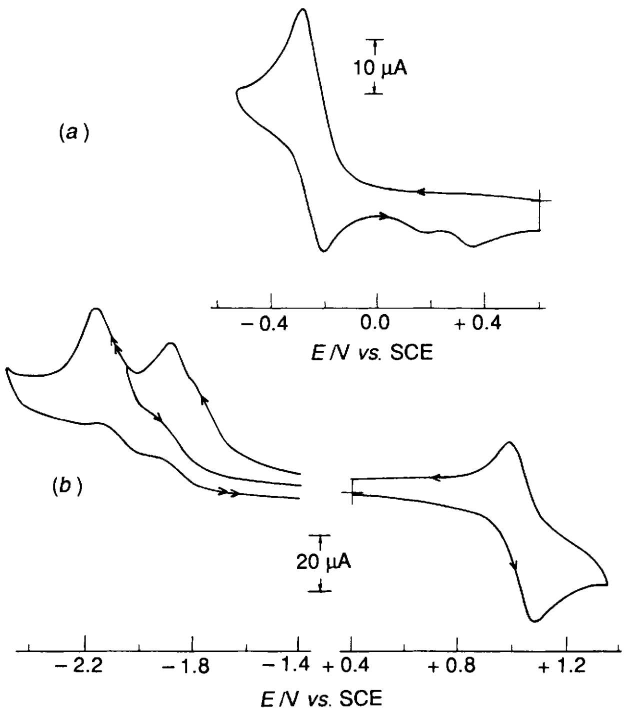


Fig. 3 Cyclic voltammograms of (*a*) $[Ru(L^1)Cl_3] \cdot 3H_2O$ in dmf at a platinum electrode and (*b*) $[Ru(L^1)(L^3)][ClO_4]_2 \cdot H_2O$ in CH_3CN at a glassy carbon electrode; scan rate = 50 mV s^{-1}

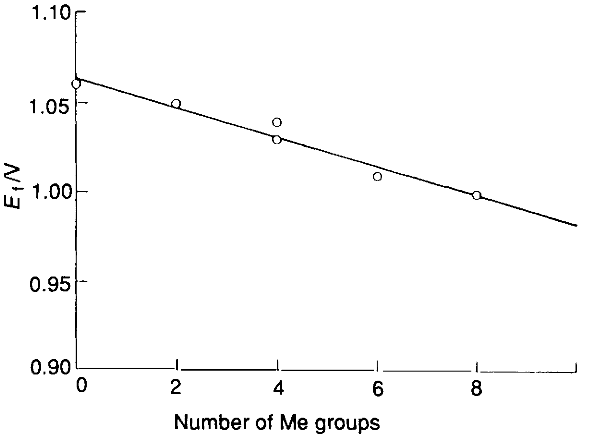


Fig. 4 Plot of the Ru^{II}–Ru^{III} couple *vs.* total number of methyl groups in the complex. The complexes are $[Ru(L^1)_2]^{2+}$, $[Ru(L^1)(L^2)]^{2+}$, $[Ru(L^2)_2]^{2+}$, $[Ru(L^1)(L^3)]^{2+}$, $[Ru(L^2)(L^3)]^{2+}$ and $[Ru(L^3)_2]^{2+}$ (in the order of decreasing potential)

the difference in ligand basicities for pyridine- and pyrazole-ring systems. The reduced donor ability of pyrazole relative to pyridine-ring systems may also be a result of the geometric constraints on the chelate bite. For $[Ru(L^1)_2]^{2+}$ the $\Delta\delta$ values for the pyrazole ring protons ($H^{4'}$ and $R^{5'}$) are less positive than those for $[Ru(L^3)_2]^{2+}$ suggesting that compared to L^1 the ligand L^3 is a better donor to ruthenium (see below).

In ligands L^1 and L^3 the π-excessive (pyrazole) heterocycle is not directly bound to a π-deficient (pyridine) heterocycle. Due to this disrupted conjugation the co-ordinated ruthenium can act as an alternative acceptor of π-electron density from the pyrazole and as a donor to the pyridine.[20]

Electrochemistry.—The electrochemical behaviour of $[Ru(L^1)Cl_3]$ in dmf solution was investigated by cyclic voltammetry to examine the extent of stabilization of the ruthenium(III) oxidation state by L^1 with respect to reduction. The cyclic voltammogram exhibits a quasi-reversible (ΔE_p = 100 mV at a scan rate of 50 mV s^{-1}; with a ten-fold increase in scan rate ΔE_p increases by 70 mV) one-electron reduction wave at −0.24 V *vs.* SCE with two additional oxidative responses during the anodic (reoxidative) scan (Fig. 3). This behaviour is a prototype of electron transfer followed by chemical reaction.[21] When studied in dmso, the Ru^{III}–Ru^{II} formal potential (E_f) increases by 100 mV. The formal potential for this couple justifies the successful use of sodium hypophosphite ($H_3PO_3 + 2H^+ + 2e^- \rightleftharpoons H_3PO_2 + H_2O$, −0.75 V *vs.* SCE)[22] as reducing agent in the syntheses of the ruthenium(II) complexes. Even though the syntheses were carried out in acidic aqueous medium and the electrochemical experiments were done in dmf or dmso, a qualitative measure of the ease of reducibility of $[Ru(L^1)Cl_3]$ can be obtained.

All the ruthenium(II) bis complexes $[RuL_2]^{2+}$ exhibit well defined nearly reversible Ru^{III}–Ru^{II} oxidative responses (Fig. 3 and Table 1) when examined by cyclic voltammetry. The Ru^{III}–Ru^{II} formal potentials for the present complexes are about 200 mV more cathodic than those of related complexes studied by Jameson *et al.*[16] ($E_{\frac{1}{2}}$ 1.06–1.25 V *vs.* SCE). This trend points toward a destabilization of the filled t_2 orbitals by the present ligands. Thus compared to the 2,6-bis(*N*-pyrazolyl)pyridine ligands studied by Jameson *et al.*[16] the present ligands are better donors towards ruthenium(II). It is worth mentioning here that ligands L are weak-field ligands towards iron(II) as a result of the increased metal–pyridine bond distance caused by steric requirements.[5]

Two ill defined irreversible ligand-based reductions were observed for all the complexes when scanned cathodically (Fig. 3). The potentials are very negative ($E_{p,c}$ values lie in the range −1.90 to −2.20 V *vs.* SCE) revealing that the lowestunoccupied molecular orbitals (LUMOs) are relatively high in energy compared to those of terpy.[16] It is worth noting that for the 2,6-bis(*N*-pyrazolyl)pyridine ruthenium(II) complexes studied by Jameson *et al.*[16] irreversible ligand reductions were observed at −1.66 V *vs.* SCE. Thus ligands L are even weaker as π acceptors. The poorer π-accepting property of pyrazole-containing ligands relative to polypyridine ligands has also been noted previously.[16,17,20,23,24]

Correlations.—A steady decrease in the Ru^{III}–Ru^{II} formal potentials from 1.06 to 1.00 V *vs.* SCE was observed (Table 1) upon increasing the total number of methyl groups from 0–8. A plot of E_f (Ru^{III}–Ru^{II}) *vs.* the total number of methyl groups is shown in Fig. 4. The trend is understandable given the electron-releasing nature of the methyl groups. An average potential step size of *ca.* 8 mV per methyl group is obtained from the slope of this plot. Interestingly, when the pyrazole rings are attached directly to the pyridine ring this potential step size is much larger (24 mV per methyl group).[16,18] We believe that the reduced inductive effect of the methyl groups observed here is due to a partial contribution of a steric effect.[1–3] In the case of the first-row transition-metal bis-chelate complexes of L^1–L^3 we observe[1–3] that the M^{III}–M^{II} redox potential (M = Mn, Fe or Co) increases as the number of methyl groups near the donor site increases so demonstrating the predominance of a steric effect over the electronic effect. Thus we believe that for a second-row transition-metal ion such as Ru^{II} the larger size of the metal ion has caused a better metal–ligand orbital overlap and hence overrides the steric effect. The decreased potential step size for $[RuL(L')]^{2+}$ relative to those observed for the non-sterically hindered ruthenium(II) complexes[16] indicates that the steric factor as observed for the first-row complexes is still operative in the ruthenium(II) bis-chelate complexes, although it is now outweighed by the electronic effect.

Conclusion

The successful syntheses of a group of similar complexes $[RuL(L')]^{2+}$ (L, L′ = L'–L^3) has been accomplished by the use of substitutionally labile ruthenium(III) precursors and the ^1H NMR spectra of two representative complexes have been assigned. The derived co-ordination-induced shift values, Δδ, have been shown to provide useful structural and bonding information which complements that obtained from absorption spectroscopy and electrochemical measurements. By observation of the Ru^{III}–Ru^{II} redox couples it has been nicely demonstrated that in the present system steric effects due to 3-Me substituents also contribute in addition to the inductive effect of the methyl groups. Due to the larger size of the ruthenium(II) ion, a better metal–ligand orbital overlap takes place allowing the electronic effect of the methyl groups to predominate over steric factors. We are not aware of any previous low-spin $Ru^{II}N_6$ system in which this kind of effect has been observed.

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