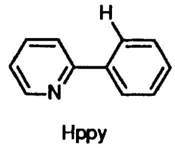
Different Bonding Modes in Octahedral Complexes of 6-(2-Thienyl)-2,2′-bipyridine (HL) with Transition Metal Ions: Crystal Structures of $[Ru(HL)(py)Cl_3]$ (py = pyridine) and $[Ru(HL)_2Cl][BF_4]\cdot CH_2Cl_2$†

Edwin C. Constable,*[a] **Roland P. G. Henney**[a] **and Derek A. Tocher***[b]
[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*
[b] *Department of Chemistry, University College London, 20 Gordon St, London, WC1H 0AJ, UK*

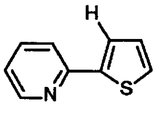
The ligand 6-(2-thienyl)-2,2′-bipyridine (HL) has been shown to adopt terdentate N_2S, bidentate N_2 or terdentate cyclometallated N_2C bonding modes in ruthenium and rhodium complexes. The crystal and molecular structures of the complexes *mer*-$[Ru(HL)(py)Cl_3]$ (py = pyridine) [triclinic, $P\bar{1}$, a = 7.811(1), b = 10.192(1), c = 13.492(2) Å, α = 97.69(1), β = 90.55(1), γ = 110.88(1)°, Z = 2, R = 0.0405, R' = 0.0454] and $[Ru(HL)_2Cl][BF_4]\cdot CH_2Cl_2$ [monoclinic, $P2_1/c$, a = 7.576(1), b = 16.072(3), c = 26.083(4) Å, β = 96.02(1)° Z = 4, R = 0.0504, R' = 0.0585] are reported. The former complex contains a bidentate N_2-bonded HL ligand and a meridional arrangement of the chlorine atoms, whilst the latter contains two independent HL ligands, one of which is a bidentate N_2-donor, and the other a terdentate N_2S-donor, with Ru–S 2.380(2) Å. Cyclometallated complexes with ruthenium(II) and rhodium(III) have been prepared and characterised by ^1H NMR spectroscopy.

Cyclometallated complexes contain polydentate ligands in which at least one of the donor atoms is carbon.[1] Such compounds have been widely investigated in recent years, and examples incorporating a wide combination of donor atoms are known.[2] A particularly common structural feature in such compounds is a ligand in which an anionic carbon donor centre is generated by deprotonation of a C–H bond of an aromatic ring bonded to a heteroaryl ring; the latter acts as the heteroatom donor. The compound 2-phenylpyridine (Hppy) is prototypical of this class, and numerous examples of cyclometallated complexes of Hppy are known. The majority of examples of cyclometallated complexes are with d^8 or d^6 transition metals and incorporate a five-membered chelate ring, although specific examples with other ring sizes are known.

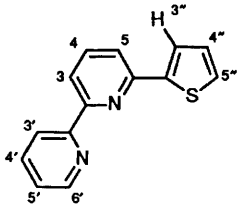
Compounds in which both the carbon and the heterodonor atom are in heteroaryl rings are less common, but are well established. We have been particularly interested in ligands which may act as either cyclometallating CX donors or as 'normal' X or X_2 donors.[3–14] The ligand 2-(2-thienyl)pyridine (Hthpy) may act as a monodentate N donor[15,16] and it has recently been demonstrated that the thiophene ring may be cyclometallated at C-3 to yield complexes with interesting photophysical and electronic properties.[16,17] We have independently been studying a series of 2-(2-thienyl)pyridine derivatives in an attempt to force a thiophene to adopt a chelating S-donor mode. The ligand 6-(2-thienyl)-2,2′-bipyridine (HL) may co-ordinate to a metal ion in a number of different manners, and in this paper we report ruthenium and rhodium complexes in which terdentate N_2S, bidentate N_2 and terdentate cyclometallated N_2C bonding modes are exhibited. We have made a preliminary report concerning the complex $[Ru(HL)_2Cl][BF_4]\cdot CH_2Cl_2$.[10]



Hppy



Hthpy



HL

Experimental

Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform spectrophotometer, with the samples in compressed KBr discs. Proton NMR spectra were recorded on Brüker WM-250 or AM400 spectrometers. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Kratos MS-50 spectrometer, with 3-nitrobenzyl alcohol as matrix for the FAB spectra; ESR spectra were recorded on a Varian E-109 spectrometer as frozen acetonitrile glasses at 90 K. Electrochemical measurements were performed using an AMEL model 4553 potentiostat, model 567 function generator and model 721 integrator connected to an X-Y recorder *via* an AMEL model 560/A interface. A conventional three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and an Ag–AgCl reference. Ferrocene was added at the end of each experiment as an internal standard. Controlled-potential electrolyses were performed using a cylindrical platinum gauze as working electrode and a smaller, coaxial platinum gauze as auxiliary electrode (separated by a frit). The solvent was acetonitrile in all cases, distilled from

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† *mer*-Trichloro(pyridine)[6-(2-thienyl)-2,2′-bipyridine-κ*N*,*N*′]-ruthenium(III) and chloro{bis[6-(2-thienyl)-2,2′-bipyridine]-κ*N*,*N*′; κ*N*,*N*′,*S*}ruthenium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

CaH_2 and then P_4O_{10} and stored over 4 Å molecular sieves. The base electrolyte was 0.1 mol dm^{-3} NBu_4BF_4 recrystallised twice from methanol–water. Potentials are quoted *vs.* ferrocene–ferrocenium couple (= 0.0 V), and all potentials were referenced to internal ferrocene added at the end of each experiment. 2-Acetylpyridine (Aldrich), 2-acetylthiophene (Aldrich), $RuCl_3$·$3H_2O$ and $RhCl_3$·$3H_2O$ (Johnson Matthey) were used as supplied; *6-(2-thienyl)*-2,2′-bipyridine[9] and [Ru(dmso)$_4$Cl$_2$][18] (dmso = dimethyl sulphoxide) were prepared by the literature methods.

Preparations.—[Ru(HL)Cl$_3$]. A solution of $RuCl_3$·$3H_2O$ (0.105 g, 0.4 mmol) in ethanol (5 cm^3) was heated to reflux for 30 min, after which time HL (0.094 g, 0.4 mmol) in ethanol (3 cm^3) was added to the green solution. The mixture was heated under reflux for 7 h, and the brown-black precipitate so formed was then collected by filtration, washed with EtOH and dried *in vacuo* to yield [Ru(HL)Cl$_3$] (0.156 g, 88%). IR: 1595m, 1551m, 1459ms, 1442m, 1293m, 819m, 782s, 720m, 712m, 341m and 319m cm^{-1}, FAB MS: *m/z* 410 {[Ru(HL)Cl$_2$]$^+$}, 375 {[Ru(HL)Cl]$^+$} and 339 {[Ru(HL)]$^+$}. μ_{eff} 2.01 (296 K) (Found: C, 37.75; H, 2.25; N, 6.2. Calc. for $C_{14}H_{10}Cl_3N_2RuS$: C, 37.7; H, 2.25; N, 6.3%).

[Ru(HL)(py)Cl$_3$]. Pyridine (py) (90 µl, 1.1 mmol) was added to a suspension of [Ru(HL)Cl$_3$] (0.050 g, 0.11 mmol) in ethanol (15 cm^3). The mixture was heated under reflux for 6 h and cooled to yield [Ru(HL)(py)Cl$_3$] as a purple powder (0.040 g, 68%). IR: 1603ms, 1561m, 1532m, 1447s, 1233m, 773s, 715m, 695m, 343m and 319m cm^{-1}. FAB MS: *m/z* 491 {[Ru(HL)(py)Cl$_2$]$^+$}, 412 {[Ru(HL)Cl$_2$]$^+$}, 376 {[Ru(HL)Cl]$^+$} and 339 {[Ru(HL)]$^+$} (Found: C, 43.3; H, 2.85; N, 8.0. Calc. for $C_{19}H_{15}Cl_3N_3RuS$: C, 43.5; H, 2.9; N, 8.0%).

[Ru(HL)(dmf)Cl$_3$]. Diethyl ether vapour was allowed to diffuse into a solution of [Ru(HL)Cl$_3$] (0.015 g, 0.031 mmol) in dimethylformamide (dmf) (3 cm^3) over a period of 3 d. The black crystalline precipitate was collected by filtration to give [Ru(HL)(dmf)Cl$_3$] (0.018 g, 97%). IR 1629vs, 1601m, 1559m, 1454s, 1425m, 1377m, 1111m, 769s, 733m, 325ms and 306w cm^{-1}. FAB MS: *m/z* 412 {[Ru(HL)Cl$_2$]$^+$}, 376 {[Ru(HL)Cl]$^+$} and 339 {[Ru(HL)]$^+$} (Found: C, 39.45; H, 3.3; N, 7.85. Calc. for $C_{17}H_{17}Cl_3N_3ORuS$: C, 39.35; H, 3.3; N, 8.1%).

[Ru(HL)$_2$Cl][BF$_4$]·CH_2Cl_2. A solution of $RuCl_3$·$3H_2O$ (0.0275 g, 0.105 mmol) in ethanol (6 cm^3) was heated under reflux for 20 min, after which time HL (0.058 g, 0.24 mmol) was added. The solution was heated under reflux for 44 h, filtered hot through Celite and evaporated to dryness. The residue was extracted with warm water, and the resulting orange aqueous solution treated with an excess of $NaBF_4$. This gave an orange precipitate, which was recrystallised by dissolving it in CH_2Cl_2, adding hexane and then allowing the solvent to evaporate slowly. The complex [Ru(HL)$_2$Cl][BF$_4$]·CH_2Cl_2 was obtained as orange-red crystals (0.052 g, 72%). IR: 1600m, 1560w, 1454ms, 1384ms, 1084s, 775ms and 731m cm^{-1}. FAB MS: *m/z* 613 {[Ru(HL)$_2$Cl]$^+$} and 577 {[Ru(HL)$_2$]$^+$} (Found: C, 44.15; H, 2.75; N, 7.15. Calc. for $C_{28}H_{20}BClF_4N_4RuS_2$·$CH_2Cl_2$: C, 44.4; H, 2.85; N, 7.15%).

[Ru(HL)(L)][BF$_4$]. A solution of [Ru(HL)$_2$Cl][BF$_4$]·CH_2Cl_2 (0.050 g, 0.071 mmol) in glacial acetic acid (8 cm^3) was heated under reflux for 8 h. After this time the dark coloured solution was evaporated to dryness *in vacuo*. The residue was dissolved in the minimum volume of CH_2Cl_2 and purified by TLC (using 1:1 CH_2Cl_2–acetone as eluent); the first (red) band was collected, yielding [Ru(HL)(L)][BF$_4$] (0.016 g, 34%). IR: 1593m, 1455ms, 1384m, 1084s and 771ms cm^{-1}. FAB MS: *m/z* 577 {[Ru(HL)(L)]$^+$} (Found: C, 50.85; H, 2.95. Calc. for $C_{28}H_{19}BF_4N_4RuS_2$: C, 50.7; H, 2.9%).

[Ru(HL)(terpy)Cl]Cl. 2,2′:6′,2″-Terpyridine (terpy) (0.050 g, 0.21 mmol) was added to a solution of [Ru(HL)Cl$_3$] (0.085 g, 0.19 mmol) in ethanol (5 cm^3). The solution was heated to reflux for 3 h, cooled, filtered and evaporated to dryness. The solid residue was extracted with CH_2Cl_2, and the purple solution so obtained allowed to evaporate slowly to yield [Ru(HL)(terpy)Cl]Cl as purple crystals (0.085 g, 69%). IR: 1600m, 1561m, 1448ms, 1384ms and 772s cm^{-1}. FAB MS: *m/z* 608 {[Ru(HL)(terpy)Cl]$^+$}, 574 {[Ru(HL)(terpy)]$^+$} and 370 {[Ru(terpy)Cl]$^+$} (Found: C, 49.15; H, 3.4; N, 9.85. Calc. for $C_{29}H_{21}Cl_2N_5RuS$·CH_2Cl_2: C, 49.45; H, 3.2; N, 9.6%).

[Ru(L)(terpy)]Cl. The complex [Ru(HL)(terpy)Cl]Cl (0.10 g) was dissolved in glacial acetic acid (10 cm^3) and the solution heated to reflux for 14 h. The solvent was then removed *in vacuo* to give crude [Ru(L)(terpy)]Cl.

[Ru(HL)(py)Cl$_2$]. *Method* (*i*). A large excess of NEt_3 (0.52 dm^3) and pyridine (90 µl) were added to a solution of [Ru(HL)Cl$_3$] (0.060 g, 0.135 mmol) in chloroform (15 cm^3). The mixture was heated to reflux for 3 h, evaporated to dryness and the residue extracted first with MeOH and then with CH_2Cl_2. The CH_2Cl_2 extract was separated by TLC (using 3:2:1 acetone–hexane–chloroform as eluent). The purple band was collected and recrystallised from CH_2Cl_2 to yield [Ru(HL)(py)Cl$_2$] (0.013 g, 20%). IR: 1599m, 1481m, 1451m, 733m and 698ms cm^{-1}. FAB MS: *m/z* 491 {[Ru(HL)(py)Cl$_2$]$^+$}, 454 {[Ru(HL)(py)Cl]$^+$}, 412 {[Ru(HL)Cl$_2$]$^+$}, 376 {[Ru(HL)Cl]$^+$} and 339 {[Ru(HL)]$^+$} (Found: C, 44.55; H, 3.15; N, 7.95. Calc. for $C_{19}H_{15}Cl_2N_3RuS$·$0.5CH_2Cl_2$: C, 44.05; N, 3.05; N, 7.9%).

Method (*ii*). An excess of pyridine (100 µl) was added to a solution of [Ru(dmso)(HL)Cl$_2$] (0.064 g, 0.13 mmol) in 2:1 chloroform–ethanol (20 cm^3). The mixture was heated to reflux for 2.5 h and the solvent then removed *in vacuo*. The dark coloured product was extracted first with MeOH and then with CH_2Cl_2. The CH_2Cl_2 fraction was worked up as above to yield [Ru(HL)(py)Cl$_2$] (0.019 g, 30%).

Method (*iii*). To a suspension of [Ru(HL)(py)Cl$_3$] (0.013 g, 0.025 mmol) in EtOH (3 cm^3) was added an excess of *N*-ethylmorpholine (0.15 cm^3). The mixture was heated to reflux for 45 min and then cooled. The purple-black precipitate that formed was collected by filtration and washed with Et_2O to give [Ru(HL)(py)Cl$_2$] (0.010 g, 72%).

[Ru(HL)(py)$_2$Cl][PF$_6$]. *Method* (*i*). An excess of NH_4PF_6 was added to the MeOH extract obtained during the synthesis of [Ru(HL)(py)Cl$_2$] by Method (*i*). An orange-red solid precipitated. This was removed by filtration, washed with MeOH and water and dried *in vacuo*, to give [Ru(HL)(py)$_2$Cl][PF$_6$] (0.011 g, 12%). IR: 1604m, 1486m, 1448ms, 842vs, 772ms, 699ms and 558s cm^{-1}. FAB MS: *m/z* 534 {[Ru(HL)(py)$_2$Cl]$^+$}, 454 {[Ru(HL)(py)Cl]$^+$}, 419 {[Ru(HL)(py)]$^+$}, 376 {[Ru(HL)Cl]$^+$} and 339 {[Ru(HL)]$^+$} (Found: C, 42.3; H, 3.0; N, 8.15. Calc. for $C_{24}H_{20}ClF_6N_4PRuS$: C, 42.5; H, 2.95; N, 8.25%).

Method (*ii*). The method was analogous to that above except that it used the MeOH extract obtained during the synthesis of [Ru(HL)(py)Cl$_2$] by Method (*ii*). The extract yielded [Ru(HL)(py)$_2$Cl][PF$_6$] (0.024 g, 27%).

[Ru(HL)(dmso)Cl$_2$]. Ligand HL (0.065 g, 0.255 mmol) was added to [Ru(dmso)$_4$Cl$_2$] (0.089 g, 0.185 mmol) in warm EtOH (5 cm^3) and the solution was heated to 60 °C for 15 h and then cooled. The purple precipitate was collected by filtration, washed with Et_2O and dried in air, to yield [Ru(HL)(dmso)Cl$_2$] (0.076 g, 85%). IR: 1598m, 1560m, 1465m, 1438m, 1396m, 1082m, 1062m, 1050s, 1024m, 1013m, 774s, 731m and 432m cm^{-1}. FAB MS: *m/z* 490 {[Ru(HL)(dmso)Cl$_2$]$^+$}, 453 {[Ru(HL)(dmso)Cl]$^+$}, 412 {[Ru(HL)Cl$_2$]$^+$}, 376 {[Ru(HL)Cl]$^+$} and 339 {[Ru(HL)]$^+$} (Found: C, 39.3; H, 3.2; N, 5.75. Calc. for $C_{16}H_{16}Cl_2N_2ORuS_2$: C, 39.35; H, 3.3; N, 5.75%). When the above reaction was performed in boiling EtOH for 20 h, an orange solid precipitated. This was collected by filtration, washed with Et_2O and dried, to give the crude product (0.066 g). IR: 1600m, 1553m, 1459ms, 1420m, 1396m, 1094ms, 1086s, 1062m, 1051m, 1013s, 781s, 736ms, 719m and 431m cm^{-1}.

[Rh(L)(MeCN)Cl$_2$]. A solution of HL (0.025 g, 0.105 mmol) in MeCN (3 cm^3) was added to a stirred aqueous solution of $RhCl_3$·$3H_2O$ (0.026 g, 0.10 mmol) in water (3 cm^3). The resulting mixture was maintained at 85 °C under an atmosphere

Table 1 Atomic coordinates (× 10^4) for $[Ru(HL)(py)Cl_3]$

Atom	*x*	*y*	*z*
Ru	2293(1)	1727(1)	3068(1)
Cl(1)	310(2)	−649(1)	2902(1)
Cl(2)	204(2)	2501(1)	3982(1)
Cl(3)	4509(2)	1023(1)	2230(1)
S	4109(3)	5844(2)	1107(1)
N(1)	1032(5)	1755(4)	1672(3)
N(2)	3494(5)	1649(4)	4400(3)
N(3)	4418(5)	3783(4)	3330(3)
C(1)	−822(7)	1354(5)	1579(4)
C(2)	−1763(7)	1217(6)	664(4)
C(3)	−789(8)	1474(6)	−193(4)
C(4)	1121(8)	1914(5)	−86(4)
C(5)	1981(7)	2049(5)	851(3)
C(6)	2790(7)	665(5)	5019(3)
C(7)	3750(7)	641(5)	5880(4)
C(8)	5527(7)	1644(6)	6111(4)
C(9)	6246(7)	2671(5)	5489(4)
C(10)	5182(6)	2662(5)	4655(3)
C(11)	5739(6)	3794(4)	4009(3)
C(12)	7486(7)	4825(5)	4142(4)
C(13)	7907(7)	5936(5)	3585(4)
C(14)	6567(7)	5977(5)	2925(4)
C(15)	4827(6)	4911(4)	2811(3)
C(16)	3422(7)	5073(5)	2165(4)
C(17)	1554(7)	4891(5)	2322(3)
C(18)	801(10)	5327(7)	1534(5)
C(19)	2024(10)	5858(7)	823(6)

Table 2 Selected bond lengths (Å) and angles (°) for $[Ru(HL)(py)Cl_3]$

Ru–Cl(1)	2.343(1)	Ru–Cl(2)	2.345(1)
Ru–Cl(3)	2.344(1)	Ru–N(1)	2.126(4)
Ru–N(2)	2.043(4)	Ru–N(3)	2.141(3)
Cl(1)–Ru–Cl(2)	92.0(1)	Cl(1)–Ru–Cl(3)	89.9(1)
Cl(2)–Ru–Cl(3)	176.7(1)	Cl(2)–Ru–N(1)	92.6(1)
Cl(1)–Ru–N(2)	93.5(1)	Cl(3)–Ru–N(2)	89.1(1)
Cl(1)–Ru–N(3)	170.7(1)	Cl(3)–Ru–N(3)	84.7(1)
N(2)–Ru–N(3)	78.9(1)	Cl(1)–Ru–N(1)	85.3(1)
Cl(3)–Ru–N(1)	90.2(1)	Cl(2)–Ru–N(2)	88.2(1)
N(1)–Ru–N(2)	178.6(1)	Cl(2)–Ru–N(3)	93.0(1)
N(1)–Ru–N(3)	102.2(1)		

of dinitrogen for 16 h, after which period the yellow microcrystalline solid was collected by filtration to give $[Rh(L)Cl_2(MeCN)]$ (0.032 g, 71%). IR: 1597s, 1554m, 1493s, 1460m, 1440m, 876m, 775s and 347m cm^{-1}. FAB MS: *m*/*z* 452 ($\{[Rh(L)Cl_2(MeCN)] + H\}^+$), 410 $\{[Rh(L)Cl_2]^+\}$, 375 $\{[Rh(L)Cl]^+\}$ and 340 $\{[Rh(L)]^+\}$ (Found: C, 42.55; H, 2.65; N, 9.05. Calc. for $C_{16}H_{12}Cl_2N_3RhS$: C, 42.5; H, 2.7; N, 9.3%).

$[Rh(HL)_2Cl_2][PF_6]$. A solution of $RhCl_3{\cdot}3H_2O$ (0.061 g, 0.23 mmol) in water (4 cm^3) was added to a solution of HL (0.179 g, 0.75 mmol) in MeCN (5 cm^3) and the mixture heated to reflux. After 15 h, the solution was filtered hot through Celite and an excess of NH_4PF_6, dissolved in MeOH, was then added to the filtrate. The precipitate that formed on cooling was collected by filtration, washed with water and dried *in vacuo*, to give $[Rh(HL)_2Cl_2][PF_6]$ as an orange crystalline solid (0.142 g, 77%). IR: 1602m, 1561m, 1455s, 841vs, 775m, 736m, 558s and 346w cm^{-1}. FAB MS: *m*/*z* 649 $\{[Rh(HL)_2Cl_2]^+\}$, 614 $\{[Rh(HL)_2Cl]^+\}$, 579 $\{[Rh(HL)_2]^+\}$, 376 $\{[Rh(HL)Cl]^+\}$ and 340 $\{[Rh(L)]^+\}$ (Found: C, 42.55; H, 2.6; N, 7.85. $C_{28}H_{20}Cl_2F_6N_4PRhS_2{\cdot}0.5MeCN$ requires C, 42.7; H, 2.65; N, 7.7%).

Crystal Structure Determinations of $[RuCl_3(HL)(py)]$ *and* $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$.—Suitable single crystals of $[Ru(HL)(py)Cl_3]$ were obtained by the slow crystallisation of a solution in CH_2Cl_2 which had had a layer of hexane carefully added; crystals of $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$ were prepared by the slow diffusion of diethyl ether vapour into a CH_2Cl_2 solution of the compound.

Crystal data for $[Ru(HL)(py)Cl_3]$. $C_{19}H_{15}Cl_3N_3RuS$, irregular red crystals, crystal size 0.22 × 0.24 × 0.10 mm, M = 524.85, triclinic, space group $P\bar{1}$, a = 7.811(1), b = 10.192(1), c = 13.492(2) Å, α = 97.69(1), β = 90.55(1), γ = 110.88(1)°, U = 992.6(2) $Å^3$, $F(000)$ = 522, Z = 2, D_m not measured, D_c = 1.76 g cm^{-3}, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 12.9 cm^{-1}.

Crystal data for $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$. $C_{29}H_{22}BCl_3F_4N_4RuS_2$, red crystals, crystal size 0.70 × 0.45 × 0.40 mm, M = 782.88, monoclinic, space group $P2_1/c$, a = 7.576(1), b = 16.072(3), c = 26.083(4) Å, β = 96.02(1)°, U = 3158.5(7) $Å^3$, $F(000)$ = 1560, Z = 4, D_m not measured, D_c = 1.65 g cm^{-3}, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 9.2 cm^{-1}.

Data collection and processing. Suitable single crystals of each compound were mounted on glass fibres. All geometric and intensity data were taken from these crystals using an automated four-circle Nicolet R3mV diffractometer equipped with graphite-monochromated Mo-Kα radiation. Lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 $\{[Ru(HL)(py)Cl_3]\}$ or 40 $\{[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2\}$ reflections taken from a rotation photograph and centred by the diffractometer. Axial photography was used to verify unit cell dimensions. The θ–2θ technique was used to measure reflections in the range $5 \leqslant 2\theta \leqslant 50°$. Three standard reflections were remeasured every 97 scans, and showed no significant loss in intensity during the data collection. The data were corrected for intensity and polarisation effects and an empirical absorption correction applied; 4901 $\{$for $[Ru(HL)(py)Cl_3]\}$ and 5496 $\{$for $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2\}$ independent reflections were collected and 3610 $\{$for $[Ru(HL)(py)Cl_3]\}$ and 4313 $\{$for $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2\}$ with $I \geqslant 2\sigma(I)$ were used in the refinement.

Structure analysis and refinement. For $[Ru(HL)(py)Cl_3]$ the position of the ruthenium atom in the asymmetric unit was obtained from a Patterson map; in $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$ the ruthenium atom was located by direct methods. In each case the remaining non-hydrogen atoms were found by iterative application of least-squares refinement and difference Fourier syntheses. No attempt was made to locate the hydrogen atoms in either case. For $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$ the BF_4^- anion is disordered over two sites with an occupancy of 60:40; the geometry was constrained to be approximately tetrahedral and in the final cycle of refinement, positional and thermal parameters of that disordered ion were fixed in order that the important structural features were more precisely defined. All atoms were refined anisotropically. For $[Ru(HL)(py)Cl_3]$ the last cycle of refinement (244 parameters) gave R = 0.0405, R' = 0.0454 [$w^{-1} = \sigma^2(F) + 0.000\,68F^2$] with the largest peak in the final Fourier difference synthesis being 0.70 e $Å^{-3}$; for $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$ (352 parameters), R = 0.0504, R' = 0.0585 [$w^{-1} = \sigma^2(F) + 0.001\,40F^2$] with the largest peak in the final Fourier difference synthesis being 0.57 e $Å^{-3}$. Structure solutions used SHELXTL+ on a Microvax II computer.[19]

Atomic coordinates and selected bond distances and angles for $[Ru(HL)(py)Cl_3]$ are in Tables 1 and 2; atomic coordinates and selected bond distances and angles for $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$ are in Tables 3 and 4. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

The reaction of commercial $RuCl_3{\cdot}3H_2O$ with one equivalent of HL in EtOH results in the formation of the dark brown paramagnetic complex $[Ru(HL)Cl_3]$ **1** (μ_{eff} = 2.01, 296 K). The magnetic moment is typical of a low-spin d^5 octahedral ruthenium(III) complex. The FAB mass spectrum of the complex

Table 3 Atomic coordinates (× 10^4) for $[Ru(HL)_2Cl][BF_4]\cdot CH_2Cl_2$

Atom	*x*	*y*	*z*
Ru	5 480(1)	6 886(1)	1 169(1)
Cl	4 138(2)	5 541(1)	1 179(1)
S(1)	5 369(3)	9 424(1)	2 184(1)
S(2)	2 599(2)	7 380(1)	863(1)
N(1)	6 578(6)	6 656(3)	491(2)
N(2)	6 497(6)	8 072(3)	1 006(2)
N(3)	7 482(6)	6 398(3)	1 651(2)
N(4)	4 533(5)	7 061(2)	1 858(2)
C(1)	6 856(9)	5 893(4)	296(2)
C(2)	7 572(10)	5 775(6)	−172(3)
C(3)	7 977(12)	6 496(7)	−444(3)
C(4)	7 776(11)	7 274(6)	−227(3)
C(5)	7 057(8)	7 340(4)	235(2)
C(6)	6 805(9)	8 128(4)	501(3)
C(7)	6 881(10)	8 902(5)	241(3)
C(8)	6 671(11)	9 614(5)	509(4)
C(9)	6 509(10)	9 580(4)	1 040(3)
C(10)	6 456(8)	8 792(3)	1 274(3)
C(11)	6 528(8)	8 756(3)	1 841(3)
C(12)	7 736(7)	8 297(3)	2 183(2)
C(13)	7 522(12)	8 464(6)	2 709(3)
C(14)	6 296(12)	9 055(5)	2 773(3)
C(101)	9 049(7)	6 123(3)	1 521(2)
C(102)	10 282(8)	5 710(4)	1 874(2)
C(103)	9 856(8)	5 585(4)	2 379(2)
C(104)	8 241(8)	5 882(4)	2 518(2)
C(105)	7 091(7)	6 283(3)	2 148(2)
C(106)	5 413(7)	6 675(3)	2 261(2)
C(107)	4 804(8)	6 664(4)	2 746(2)
C(108)	3 279(9)	7 110(5)	2 816(3)
C(109)	2 390(9)	7 538(4)	2 398(3)
C(110)	3 053(7)	7 492(3)	1 918(2)
C(111)	2 251(7)	7 888(3)	1 436(2)
C(112)	1 516(8)	8 647(4)	1 351(3)
C(113)	1 325(9)	8 868(5)	798(3)
C(114)	1 931(9)	8 252(5)	496(3)
B	137	1 220	1 113
F(1)	−704	714	1 401
F(2)	−435	1 214	625
F(3)	278	1 980	1 322
F(4)	1 924	951	1 152
F(1A)	−1 627	1 528	1 057
F(2A)	58	561	1 418
F(3A)	358	971	634
F(4A)	1 201	1 804	1 290
C(200)	6 849(20)	3 440(10)	985(4)
Cl(2)	7 255(4)	3 590(2)	335(1)
Cl(3)	8 226(4)	3 934(2)	1 413(1)

Table 4 Selected bond lengths (Å) and angles (°) for $[Ru(HL)_2Cl]$-$[BF_4]\cdot CH_2Cl_2$

Ru–Cl	2.390(1)	Ru–S(2)	2.380(2)
Ru–N(1)	2.064(5)	Ru–N(2)	2.116(4)
Ru–N(3)	2.024(4)	Ru–N(4)	2.025(4)
Cl–Ru–S(2)	85.9(1)	Cl–Ru–N(1)	93.3(1)
S(2)–Ru–N(1)	102.2(1)	Cl–Ru–N(2)	168.9(1)
S(2)–Ru–N(2)	88.4(1)	N(1)–Ru–N(2)	78.5(2)
Cl–Ru–N(3)	86.2(1)	S(2)–Ru–N(3)	159.8(1)
N(1)–Ru–N(3)	96.8(2)	N(2)–Ru–N(3)	102.1(2)
Cl–Ru–N(4)	85.7(1)	S(2)–Ru–N(4)	81.6(1)
N(1)–Ru–N(4)	176.1(2)	N(2)–Ru–N(4)	102.9(2)
N(4)–Ru–N(3)	79.3(2)		

shows a highest mass peak at *m*/*z* 410 $\{[Ru(HL)Cl_2]^+\}$ and fragmentation peaks at *m*/*z* 375 $\{[Ru(HL)Cl]^+\}$ and *m*/*z* 339 $\{[Ru(HL)]^+\}$; no parent ion peak was observed. The ^1H NMR spectrum of a solution of the complex in $[^2H_6]$dmso exhibits broadened and shifted peaks in the range δ +12 to −8. Although we have not been able to assign fully the spectrum, three broad peaks centred at δ −3, −6 and −8 form notable and characteristic features. In the absence of any structural data, we assign tentatively an octahedral structure to this complex, in which the HL ligand acts as a *meridional* terdentate N_2S donor to the metal(III) centre. If so, this is the first example of a ruthenium(III) S-bonded thiophene complex. The IR spectrum of the complex exhibits two ν(Ru–Cl) modes at 341 and 319 cm^{-1}, but does not allow us to distinguish unambiguously between *mer* and *fac* isomers {*cf. mer*-$[Ru(py)_3Cl_3]$, 346, 301 cm^{-1}; *fac*-$[Ru(py)_3Cl_3]$, 346, 326 cm^{-1}}.[20] The complex is only soluble in co-ordinating, donor solvents such as dmso or dmf with which it reacts, and we have been unable to obtain X-ray quality crystals of the original compound.

The reaction of $[Ru(HL)Cl_3]$ with dmf or pyridine results in the formation of red-brown solutions, from which the paramagnetic ruthenium(III) complexes $[Ru(HL)(dmf)Cl_3]$ **2** or $[Ru(HL)(py)Cl_3]$ **3** may be obtained as black or purple microcrystals respectively. The FAB mass spectra of these two complexes each show peaks corresponding to $[Ru(HL)Cl_2]^+$, $[Ru(HL)Cl]^+$ and $[Ru(HL)]^+$. The ^1H NMR spectrum of a solution of $[Ru(HL)(dmf)Cl_3]$ in $[^2H_6]$dmso exhibits peaks due to free dmf, but is otherwise identical to that of a solution of $[Ru(HL)Cl_3]$ suggesting $[Ru(HL)(dmso)Cl_3]$ (presumably containing a bidentate N_2-donor HL ligand) as a common solution species. The ^1H NMR spectrum of a $[^2H_6]$dmso solution of $[Ru(HL)(py)Cl_3]$ is also broadened and shifted, but differs from that of a solution containing $[Ru(HL)Cl_3]$. No peaks assignable to free pyridine are observed, and the three high-field resonances are now centred at δ −5.5, −8.5 and −10.5. The IR spectrum of $[Ru(HL)(py)Cl_3]$ exhibits absorptions assigned to ν(Ru–Cl) at 343 and 319 cm^{-1}, whilst those of $[Ru(HL)(dmf)Cl_3]$ are observed at 325 and 306 cm^{-1}. A strong absorption at 1629 cm^{-1} in the vibrational spectrum of $[Ru(HL)(dmf)Cl_3]$ is consistent with the presence of an O-bonded dmf ligand.[21] We believe that $[Ru(HL)(dmf)Cl_3]$ and $[Ru(HL)(py)Cl_3]$ possess similar structures – further evidence comes from the thiophene C–H out-of-plane deformation vibrations at 870, 860 and 815 cm^{-1} in $[Ru(HL)(py)Cl_3]$ and at 864, 854 and 813 cm^{-1} in $[Ru(HL)(dmf)Cl_3]$.

The above discussion suggests that the dmf ligand in $[Ru(HL)(dmf)Cl_3]$ is only weakly co-ordinated to the metal and may be readily displaced by donor solvents. Further evidence for this comes from the electrochemical behaviour; the cyclic voltammograms of acetonitrile solutions of $[Ru(HL)Cl_3]$ and $[Ru(HL)(dmf)Cl_3]$ are identical and exhibit a quasi-reversible process at +1.11 V (*vs.* ferrocene–ferrocenium). The reductive cyclic voltammogram exhibits a single reduction wave centred at −0.56 V on the outgoing wave, and two processes on the return wave centred at −0.46 and −0.23 V. In contrast to the above, the electrochemical properties of $[Ru(HL)(py)Cl_3]$ are different. In acetonitrile solution, the complex exhibits a quasi-reversible oxidation process at +1.05 V and a reversible reductive process at −0.60 V. These latter results closely resemble those reported for *mer*-$[Ru(py)_3Cl_3]$ (+1.13 and −0.66 V) in which the metal is in a six-co-ordinate N_3Cl_3 co-ordination environment.[22]

Recrystallisation of the complex $[Ru(HL)(py)Cl_3]$ from dichloromethane yielded X-ray quality crystals, and in order to clarify the nature of these compounds, we have determined the crystal and molecular structure. The crystal and molecular structure of $[Ru(HL)(py)Cl_3]$ is shown in Fig. 1; atomic coordinates are reported in Table 1 and bond lengths and angles in Table 2. The ruthenium(III) centre is in an approximately octahedral N_3Cl_3 environment, with the HL ligand acting as an N_2 donor. There is a *meridional* arrangement of the three chloride ligands about the metal. The thienyl group is not co-ordinated to the metal [Ru(1) $\cdots$ S(1) 5.042 Å]. The pyridine ligand is co-ordinated *trans* to the terminal pyridine ring of the HL ligand. The co-ordination site which would have been occupied by a sulphur atom in $[Ru(HL)Cl_3]$ (assuming an octahedral structure) is now occupied by the pyridine nitrogen

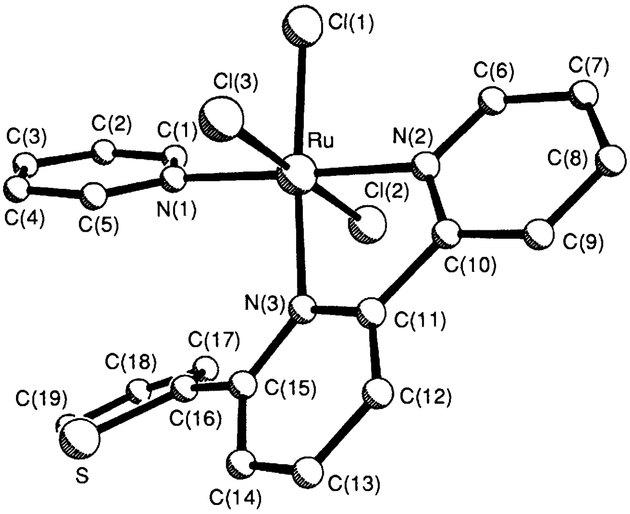


Fig. 1 The crystal and molecular structure of $[Ru(HL)(py)Cl_3]$ showing the numbering scheme adopted

donor. This would involve the smallest molecular rearrangements in the conversion of $[Ru(HL)Cl_3]$ to $[Ru(HL)(py)Cl_3]$.

The Ru–Cl bond lengths of 2.343(1), 2.344(1) and 2.345(1) Å are significantly shorter than those of 2.38 Å observed in *fac*-$[Ru(NH_3)_3Cl_3]$[23] but slightly longer than those of 2.321 and 2.328 Å in $[Ru(bipy)_2Cl_2]Cl{\cdot}2H_2O$ (bipy = 2,2′-bipyridine).[24] The Ru(1)–N(3) bond, *trans* to chlorine, of 2.141(3) Å is slightly but significantly longer than those in $[Ru(bipy)_2Cl_2]Cl{\cdot}2H_2O$ (2.045–2.063 Å),[24] but the others [Ru–N(2) 2.043(4), Ru–N(1) 2.126(4) Å] are typical. In $[Ru(bipy)_2Cl_2]Cl{\cdot}2H_2O$ the Ru–N bond *trans* to chlorine is shorter than that *trans* to nitrogen; we ascribe this difference to steric interactions between the thienyl ring and the directly bonded pyridyl ring in $[Ru(HL)(py)Cl_3]$ which result in the non-planarity of the HL ligand. The torsion angle between the two pyridyl rings of the HL ligand is 14.0° which is greater than in $[Ru(bipy)_2Cl_2]Cl{\cdot}2H_2O$, and that between the central pyridyl ring and the directly bonded thienyl ring of HL is 39.3°. This results in the thienyl ring and the pyridine ligand exhibiting van der Waals interactions; the two rings are at 23.8° to each other and the inter-ring distance (centroid to centroid) is 3.624 Å. This distance is similar to those which we have observed in a range of other oligopyridine complexes which exhibit intramolecular 'stacking' interactions. The 'bite' angle N(2)–Ru–N(3) of 78.9(1)° closely resembles those of 78.5 and 78.8° in $[Ru(bipy)_2Cl_2]Cl{\cdot}2H_2O$.[24] There are no short contacts between the ruthenium and any atoms of the thienyl ring (including H atoms when placed in idealised positions).

The prolonged reaction of $RuCl_3{\cdot}3H_2O$ with an excess of HL in ethanol results in the formation of a deep orange solution, from which an orange ruthenium(II) salt of stoichiometry $[Ru(HL)_2Cl][BF_4]$ **4** may be obtained by the addition of $NaBF_4$. If the $NaBF_4$ is not added, the chloride salt is obtained as an orange powder upon cooling the solution. The FAB mass spectrum exhibits peaks at *m/z* 613 $\{[Ru(HL)_2Cl]^+\}$, 578 $\{[Ru(HL)_2]^+\}$ and 339 $\{[Ru(HL)]^+\}$. The ^1H NMR spectrum of this complex (Fig. 2) initially led us to believe that it contained a metallated ligand. Specifically, the ^1H NMR spectrum clearly illustrates the presence of two non-equivalent HL ligands in the complex, but an examination of the double-quantum filtered COSY spectrum (Fig. 2) indicates the presence of only 19 protons, which could be assigned to two terminal pyridine rings, two central pyridine rings, a thiophene ring bearing three protons and a thiophene ring bearing two protons. This is superficial evidence for the formation of a cyclometallated complex, and in order to clarify the nature of this compound we determined the crystal and molecular structure of $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$, and demonstrated that the compound is *not* cyclometallated.

The molecular structure of the cation in $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$ is shown in Fig. 3; atomic coordinates are presented in Table 3 and selected bond lengths and bond angles in Table 4. The metal is in a six-co-ordinate N_4SCl environment. One of the two HL ligands acts as a bidentate N_2 donor, whilst the other is bonded in a *meridional* terdentate N_2S maner. The co-ordinated chlorine is *trans* to the central pyridine ring of the bidentate HL ligand. The Ru–Cl distance of 2.390(1) Å is slightly shorter than that of 2.426 Å observed in $[Ru(bipy)_2Cl_2]{\cdot}H_2O$[24] but closely resembles those observed in $[Ru(papy)Cl_2]$ (papy = 2-phenylazopyridine)[25] and $[Ru(bipy)_2(CO)Cl][ClO_4]$.[26] The Ru–N distances [2.064(5) and 2.116(4) Å] and N–Ru–N 'bite' [78.5(2)°] of the bidentate HL ligand closely resemble those observed in $[Ru(bipy)_2Cl_2]{\cdot}H_2O$ (2.053 Å, 79.11°).

Neither of the two HL ligands is planar. The two pyridyl rings of the bidentate ligand are approximately coplanar (interplanar angle 16.1°), but the non-co-ordinated thienyl ring is twisted at an interplanar angle of 45.3° with respect to the adjacent pyridine. There are no short contacts between the ruthenium atom and any of the atoms of the non-co-ordinated thienyl ring, the closest calculated approaches of 3.586 and 5.396 Å being between Ru and H(12) and H(13) respectively. In the terdentate ligand the 'bipyridyl' fragment resembles that of the bidentate ligand [Ru–N(3) 2.024, Ru–N(4) 2.025 Å, N(3)–Ru–N(4) 79.3°]. The co-ordinated thienyl ring is twisted with respect to the adjacent pyridine, and forms an interplanar angle of 35.2° with it, whilst the two pyridyl rings exhibit an interplanar angle of 8.3°. The consequence is that the non-co-ordinated thienyl ring interacts with the central pyridine ring of the other HL ligand, in a manner reminiscent of that observed in $[Ru(HL)(py)Cl_3]$ (interplanar angle, 22.4°; interplanar distance, 3.821 Å). The Ru(1)–S(2) vector is not coplanar with the co-ordinated thienyl ring, but makes an angle of 123.6° with it. This appears to indicate a distorted pyramidal geometry about the sulphur which could be interpreted in terms of loss of aromaticity of the thienyl ring and adoption of a sp^3 hybridisation scheme, or promotion of the 'lone pair' into an orbital with considerable d character. A consideration of the bond lengths and angles in the free and co-ordinated thienyl groups supports the former explanation. Both thienyl rings are approximately planar, but the reduction of the C–S–C bond angle from 93.8(4) to 91.9(3)° upon co-ordination is consistent with greater s character. The co-ordinated thienyl ring shows a marked alternation of bond lengths within the ring [S(2)–C(111) 1.746(6), C(111)=C(112) 1.350(9), C(112)–C(113) 1.478(12), C(113)=C(114) 1.374(11), C(114)–S(2) 1.742(7) Å] consistent with a localised bonding scheme. Significantly, there is a lengthening of the S–C bonds and the C–C formal single bond upon co-ordination to the metal. Only two other ruthenium complexes containing a co-ordinated thiophene have been structurally characterised, and a similar pyramidal geometry about sulphur is observed in each case, with angles between the Ru–S vector and the mean plane of the thienyl group of 132.0,[27] 130.1[27] and 126°.[28] The changes in bond lengths of the co-ordinated thienyl ring are more noticeable in $[Ru(HL)_2Cl][BF_4]{\cdot}CH_2Cl_2$ than in the other reported cases. The Ru–S(2) bond distance is 2.380(2) Å, which is comparable to those reported in the two other examples of thienyl groups S-bonded to ruthenium (2.343, 2.402[27] and 2.408 Å[28]) and also to those reported for an S-bonded phenothiazine (2.343–2.396 Å).[29]

With a knowledge of the structure of the complex, the ^1H NMR spectrum may be fully interpreted. Comparison with the ^1H NMR spectrum of $[Ru(bipy)_2Cl_2]$[30] allows the most downfield double doublet (δ 10.120) to be assigned to $H^{6'}$ of the bidentate ligand. The COSY spectrum then allows assignment of $H^{5'}$, $H^{4'}$ and $H^{3'}$ of this ring. The doublet at δ 8.28 is also seen from the COSY spectrum to be part of a four proton spin system, and the coupling constant ($^3J_{HH'}$ 7.7 Hz) allows unambiguous assignment of this to $H^{3'}$ of the terdentate ligand.

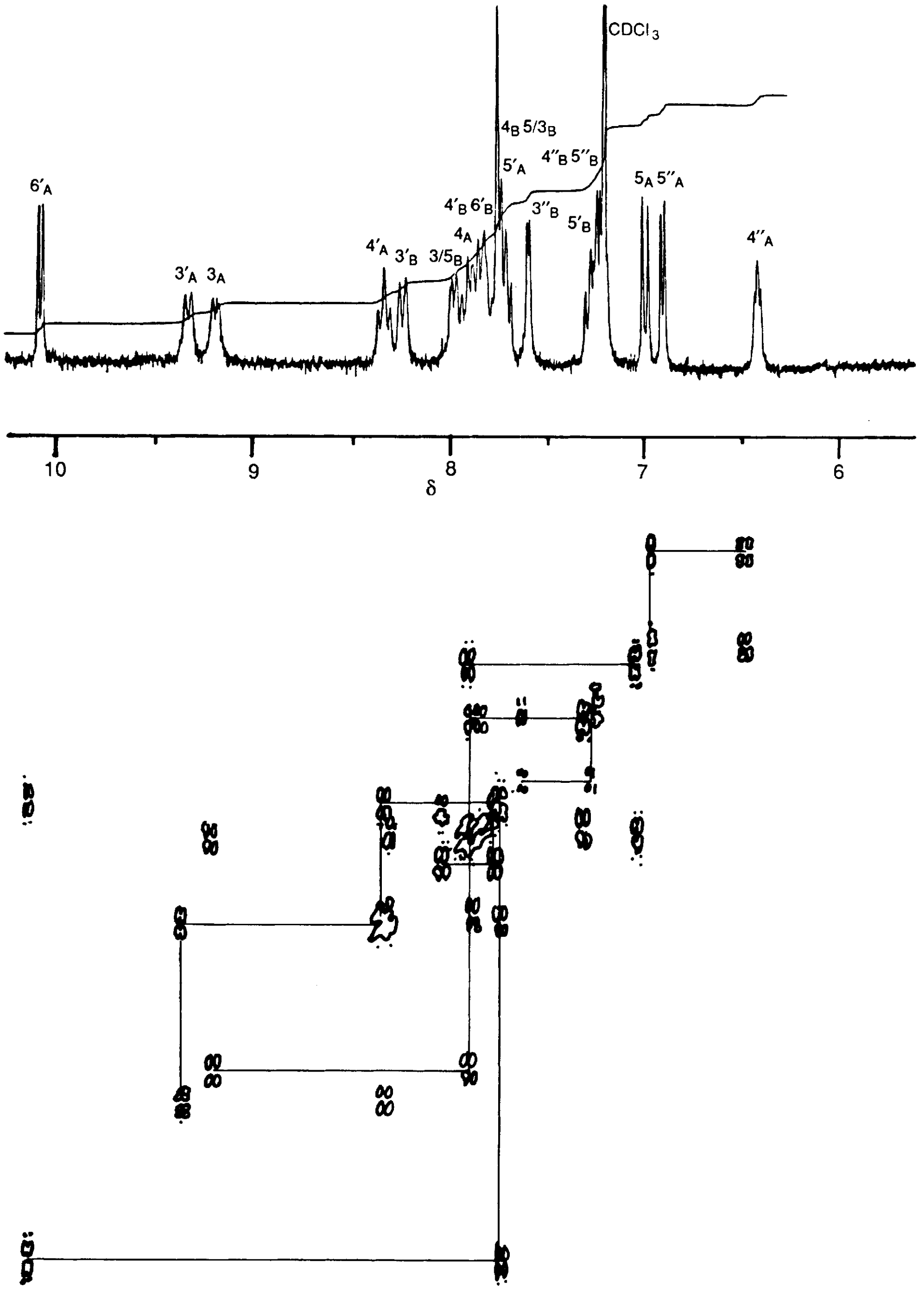


Fig. 2 The one- and two-dimensional phase-sensitive double quantum filtered COSY ^1H NMR spectra of $CDCl_3$ solutions of $[Ru(HL)_2Cl][BF_4]$

The assignment of $H^{4'}$, $H^{5'}$ and $H^{6'}$ of this ligand follows from the COSY spectrum. Only five thiophene protons are evident in the spectrum (δ 6.47–7.64). The most upfield resonance (δ 6.47) is a broadened doublet of doublets typical for $H^{4''}$ of a thiophene. However, the COSY spectrum indicates a single coupling to a doublet (*J* 4.7 Hz) at δ 6.96, which is thus $H^{5''}$ of this ring. Use of the coupling constant is a reliable method for the assignment of protons within a thiophene ring; with very few exceptions, $^3J_{H^3H^4}$ is in the range 3.0–3.5 Hz, whereas $^3J_{H^2H^3}$ ($^3J_{H^4H^5}$) is in the range 4.5–5.0 Hz.[31] The observation of additional coupling to $H^{4''}$ confirms that we have not got a metallated ring, but the lack of observation of the resonance for $H^{3''}$ is initially puzzling. We have observed similar phenomena in other ruthenium(II) complexes which incorporate ligands with non-co-ordinated aryl rings. The broadening (or in this case, non-observation) of signals is due to a restricted rotation or rocking of the non-co-ordinated aryl ring about an interannular C–C bond. We thus assign the signals at δ 6.47 and δ 6.96 to $H^{4''}$ and $H^{5''}$ of the non-co-ordinated thienyl ring. Upon warming the solution to 318 K (Fig. 4), a broad signal appears at δ 5.9, which we assign to $H^{3''}$ of this ring; at the same time, the peak assigned to $H^{4''}$ is sharpened. In contrast to this behaviour, the resonances assigned to the protons of the co-ordinated thiophene ring are sharp and well resolved. This phenomenon is somewhat unusual, but is a recurring feature in complexes containing a stacked non-co-ordinated aryl ring. The rotation (or restricted rotation) about the interannular C–C bond results in some (but not all) of the aryl protons experiencing significantly different chemical environments. In the case of $[Ru(HL)_2Cl]^+$, the rotation results in a range of environments for $H^{3''}$ of the thienyl ring, whilst $H^{4''}$ and $H^{5''}$ remain in relatively similar environments. The consequence is that the resonance assigned to $H^{3''}$ exhibits classical site-exchange broadening, whereas those for $H^{4''}$ and $H^{5''}$ do not. It so happens that at ambient temperature $H^{3''}$ is in coalescence. Although the site-exchange results in the broadening of the

Table 5 Proton NMR spectroscopic properties [chemical shifts (δ), coupling constants (*J*/Hz)] of the complexes

	$H^{6'}$	$H^{5'}$	$H^{4'}$	$H^{3'}$	H^{3}	H^{4}	H^{5}	$H^{3''}$	$H^{4''}$	$H^{5''}$	$J_{H^{3''}H^{4''}}$	$J_{H^{4''}H^{5''}}$
HL[a]	8.67	7.32	7.87	8.56	8.30	7.84	7.70	7.68	7.16	7.45	3.6	5.1
HL[b]	8.70	7.48	8.01	8.45	8.26	7.97	7.97	7.89	7.20	7.69		
$[Ru(HL)(py)Cl_2]$[a]												
HL	8.64	7.38	7.79	8.17	8.08	7.83	8.03	7.78	7.43	7.69	3.7	5.2
py	9.73	7.54	7.95									
$[Ru(HL)(dmso\text{-}S)Cl_2]$[a]												
HL	10.09	7.48	7.85	8.16	8.17	8.09	8.09	7.71	7.55	7.66	3.7	5.3
$[Ru(HL)(dmso\text{-}O)Cl_2]$[a]												
HL	9.66	7.63	8.01	8.14	8.00	8.00	8.00	7.77	7.48	7.86	3.7	5.2
$[Ru(HL)(py)_2Cl]^+$[c]												
HL	8.75	7.66	8.11	8.66	8.59	8.15	8.30	7.83	7.51	7.99	3.8	5.2
py (1)	9.06	7.67	8.14									
py (2)	7.33	6.96	7.59									
$[Ru(HL)(py)_2Cl]^+$[d]												
HL	8.66	7.46	8.02	8.45	8.38	7.97	7.62	6.70	7.03	7.51	3.7	4.8
py (1)	8.66	7.41	7.91									
py (2)	7.81	7.16	7.76									
$[Ru(HL)(terpy)Cl]^+$[a]												
HL	10.25	7.80	8.31	9.02	8.79	7.88	6.98	5.69	6.55	7.07	3.4	5.1
terpy	7.66[e]	7.27	7.88	8.17	8.02	7.73						
$[Ru(HL)_2Cl]Cl$[f]												
N,N-bonded	10.12	7.76	8.38	9.37	9.24	7.95	7.05	*g*	6.47	6.96		4.7
N,N,S-bonded	7.90	7.32	7.90	8.28	8.01	7.80	7.80	7.64	7.26	7.26	3.2	
$[Ru(HL)_2Cl][BF_4]$[a]												
N,N-bonded	10.19	7.90	8.31	8.55	8.32	7.91	7.11	*g*	6.48	7.00		5.1
N,N,S-bonded	7.90	7.33	7.86	7.90	8.18	7.79	7.90	7.66	7.30	7.18	3.7	5.2
$[Ru(HL)L][BF_4]$[a]												
N,N,C-bonded[h]	7.52	7.16	7.87	8.25	8.29	8.10	8.29	—	6.02	7.21		4.7
N,N,S-bonded[h]	7.48	7.08	7.68	8.19	7.94	7.94	7.68	7.83	7.12	7.07	3.7	5.1
$[Rh(L)(MeCN)Cl_2]$[a]	9.20	7.71	8.10	8.18	7.65	7.84	7.44	—	7.55	7.73		4.9
$[Rh(L)(MeCN)Cl_2]$[b]	9.25	7.85	8.28	8.63	8.12	8.00	7.64	—	7.51	7.85		4.8
$[Rh(HL)_2Cl_2][PF_6]$[i]	9.49	7.78	8.26	8.67	8.44	8.41	7.75	7.00[e]	6.66	7.37		5.0

[a] In CD_2Cl_2. [b] In $(CD_3)_2SO$. [c] In CD_3OD. [d] In CD_3CN. [e] Broad. [f] In $CDCl_3$. [g] Not observed. [h] Ambiguity between the pyridine resonances of the two ligands. [i] In $(CD_3)_2CO$.

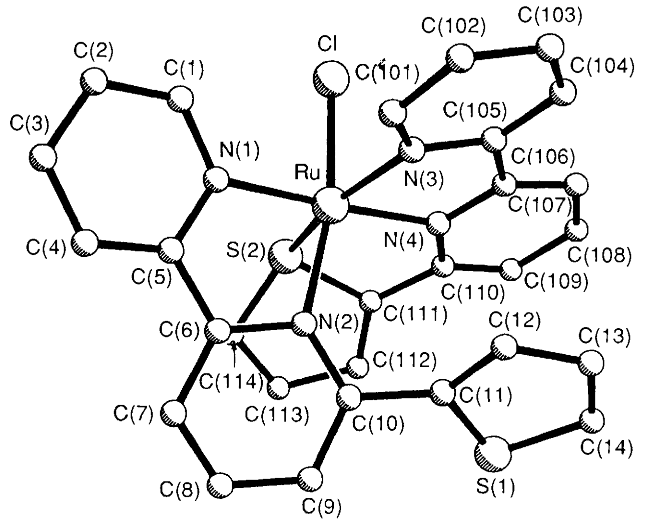


Fig. 3 The crystal and molecular structure of the $[Ru(HL)_2Cl]^+$ cation in the complex $[Ru(HL)_2Cl][BF_4]\cdot CH_2Cl_2$ showing the numbering scheme adopted

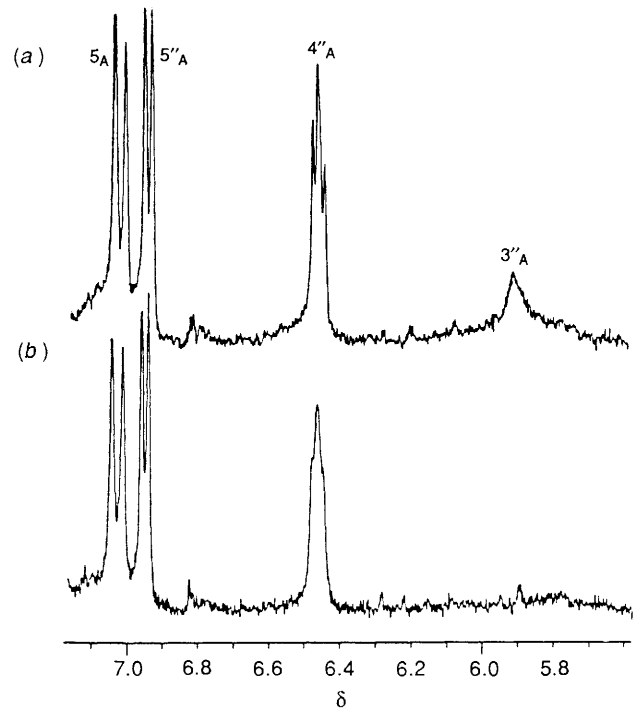


Fig. 4 The ^1H NMR spectra of a CD_2Cl_2 solution of $[Ru(HL)_2Cl][BF_4]$ at (*a*) 318 and (*b*) 295 K

signal, the coupling constants are unaffected – and coupling to the non-observed (coalesced) signal is unaffected. Assignments are presented in Fig. 2 and Table 5. It is significant to note that the spectrum of this cation is markedly and sometimes dramatically dependent upon both the solvent and the counter ion (Table 5). The cyclic voltammogram of the tetrafluoroborate salt exhibits an irreversible reduction centred at −1.85 V and a reversible oxidation at +0.49 V. This is compatible with the oxidations reported for the analogous complex cations $[Ru(terpy)(bipy)Cl]^+$ (+0.50 V) and $[Ru(bipy)_2(py)Cl]^+$ (+0.46 V).[32]

Preparations of $[Ru(HL)_2Cl][BF_4]$ consistently (but in

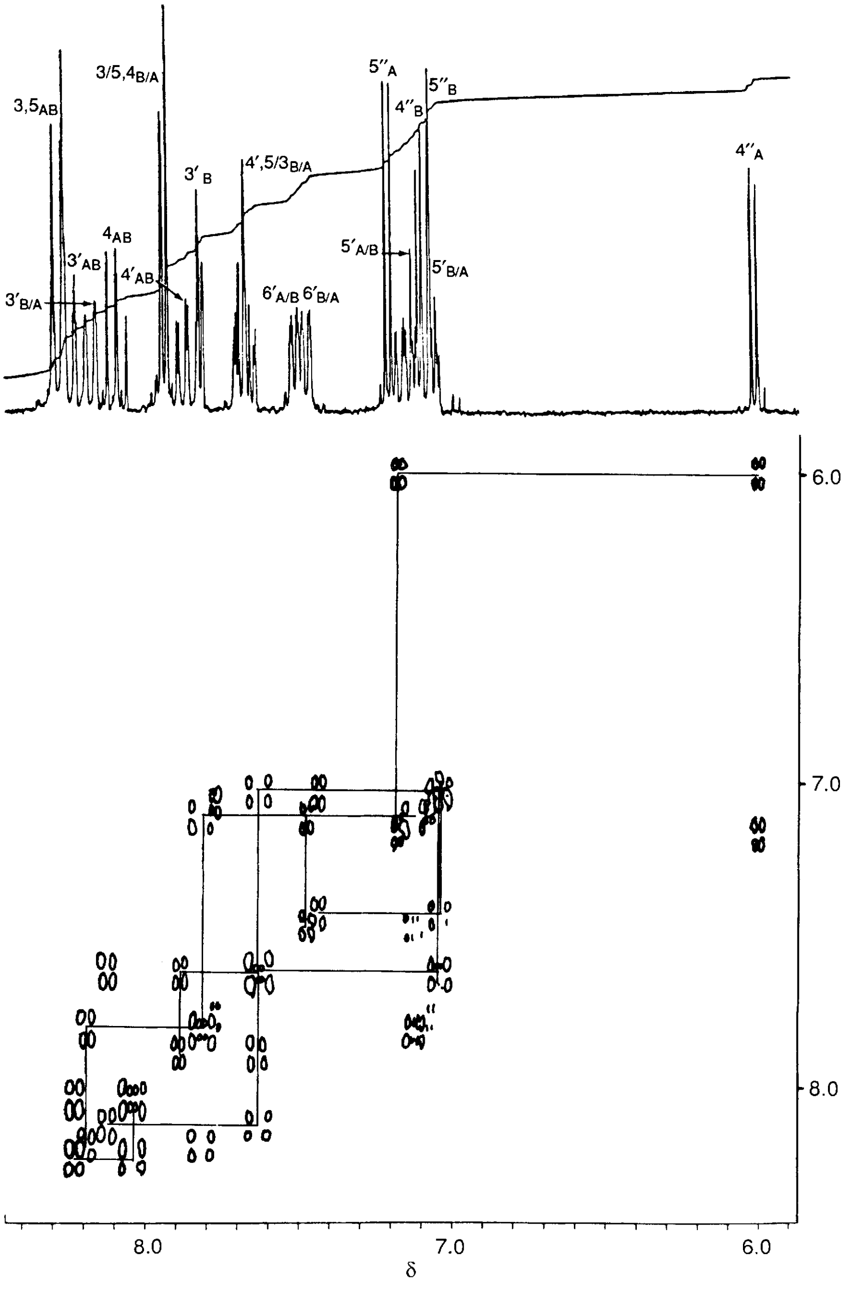


Fig. 5 The one- and two-dimensional phase-sensitive double quantum filtered COSY ^1H NMR spectra of CD_2Cl_2 solutions of $[Ru(HL)L][BF_4]$. The resonances indicated A are those due to the metallated ligand, and those indicated B are due to the N,N,S-bonded ligand

variable and low yield) also gave small amounts of a red complex, which we thought contained the metallated $[Ru(HL)L]^+$ ion **5**. Attempts to prepare this complex in a controlled manner by the reaction of $[Ru(HL)_2Cl][BF_4]$ with halide ion abstractors ($AgClO_4$, $AgPF_6$ or $TlPF_6$) were unsuccessful, as was the reaction of $[Ru(HL)_2Cl][BF_4]$ with bases or photolysis in various media. However, the complex could be obtained in satisfactory yield by heating $[Ru(HL)_2Cl][BF_4]$ in glacial acetic acid (a route that we have previously utilised for the preparation of cyclometallated palladium complexes).[3] The FAB mass spectrum of $[Ru(HL)_2Cl][BF_4]$ showed a peak at *m/z* 577 $\{[Ru(HL)(L)]^+\}$. The ^1H NMR one-dimensional and double quantum filtered COSY) spectra are shown in Fig. 5, and clearly illustrate the presence of 19 sharp resonances. An AX multiplet (δ 6.02 and 7.21), this time genuinely consisting of two doublets, is observed for the metallated thiophene ring. The coupling constant of 4.7 Hz unambiguously establishes these resonances to be due to $H^{4''}$ and $H^{5''}$ of a thiophene, and the chemical shifts allow assignment of the δ 6.02 resonance to H^4 and the δ 7.21 resonance to H^5. The other thiophene ring exhibits three sharp and well resolved resonances. Assignments are presented in Fig. 5 and Table 5. The formation of the cation $[Ru(HL)L]^+$ combined with the tendency for the d^6 ruthenium(II) ion to form octahedral complexes suggest that in this cation the HL ligand is co-ordinated in an N_2S terdentate manner. This complex is also electrochemically active, exhibiting an irreversible reduction centred at −1.89 V and a reversible oxidation at + 0.07 V. This oxidation process is at a potential very similar to that reported for the related monocyclometallated complex $[Ru(bipy)_2(ppy)]^+$ (+0.07 V).[4] There is also an oxidation process observed at +0.30 V on the oxidative sweep only.

Some other ruthenium(II) complexes were obtained directly from $[Ru(HL)Cl_3]$ in the presence of reducing agents such as triethylamine, ethanol or *N*-ethylmorpholine. The reaction of $[Ru(HL)Cl_3]$ with pyridine in chloroform in the presence of triethylamine leads to the complex $[Ru(HL)(py)Cl_2]$ **6**. This

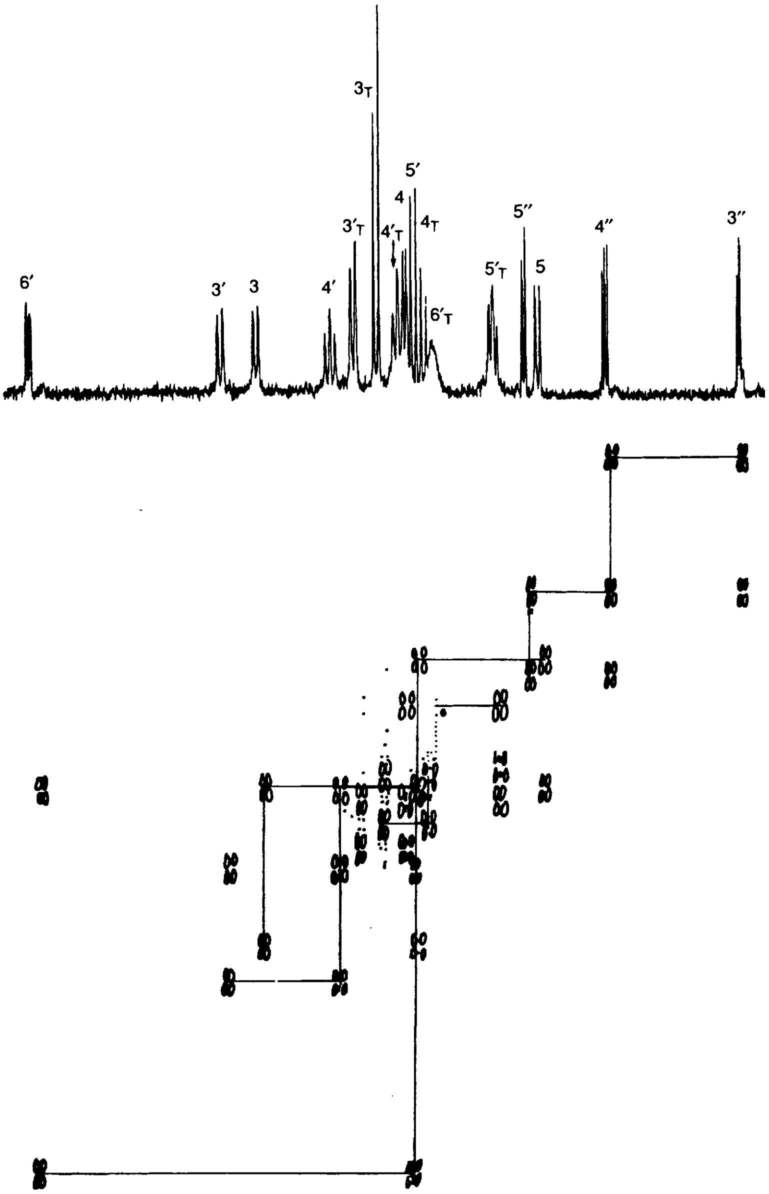
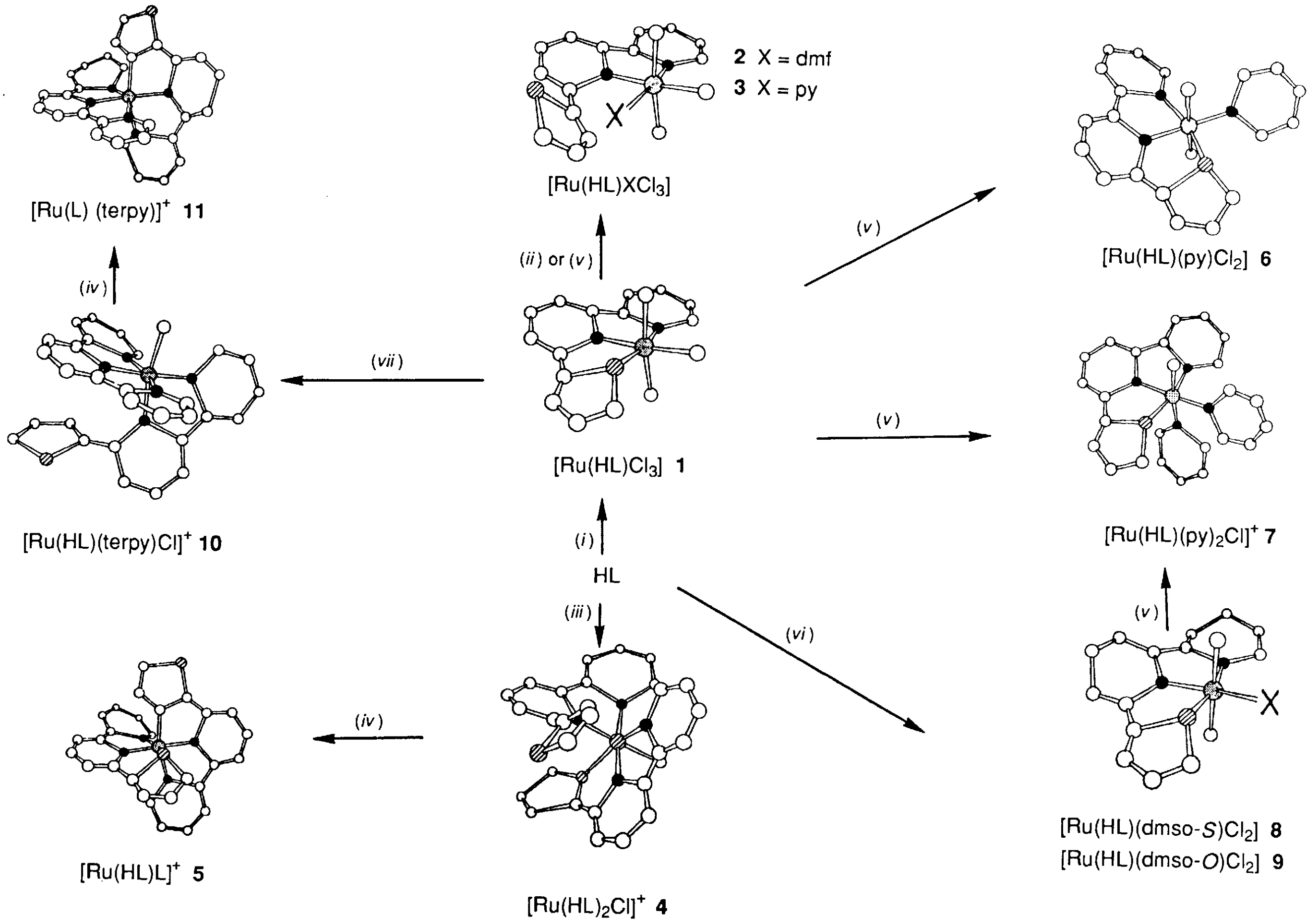


Fig. 6 The one- and two-dimensional phase-sensitive double quantum filtered COSY ^1H NMR spectra of CD_2Cl_2 solutions of [Ru(HL)(terpy)Cl]Cl. The resonances indicated T are those due to the 2,2′:6′,2″-terpyridine ligand

same complex may also be obtained by the reduction of $[Ru(HL)(py)Cl_3]$ with *N*-ethylmorpholine or by the reaction of $[Ru(HL)(dmso)Cl_2]$ (see later) with pyridine. Small amounts of $[Ru(HL)(py)_2Cl]^+$ **7** are also formed during these reactions, and the salt $[Ru(HL)(py)_2Cl][PF_6]$ may be isolated by the addition of ammonium hexafluorophosphate to solutions after removal of $[Ru(HL)(py)Cl_2]$. The ^1H NMR spectra of solutions of the complex $[Ru(HL)(py)Cl_2]$ (Table 5) together with the observed stoichiometry are consistent with a terdentate N_2S-bonded HL ligand at an octahedral ruthenium(II) centre, with the three remaining co-ordination sites occupied by the two chloride ligands and the pyridine. The pyridine is rotating about the Ru–N vector freely on the NMR time-scale, as only three resonances are observed for the α, β and γ protons, at δ 9.73, 7.54 and 7.95 respectively. Analysis of the ^1H NMR spectra and IR spectra did not allow us to distinguish unambiguously between the *cis* and *trans* arrangement of chloride, although the latter seems more likely from the shifts associated with the pyridine and HL protons. The ^1H NMR spectrum of a $(CD_3)_2SO$ solution of the related complex $[Ru(HL)(py)_2Cl][PF_6]$ is sharp (Table 5) and indicates that the two pyridine ligands are inequivalent but freely rotating about the Ru–N bond on the NMR time-scale. Assuming a *meridional* arrangement of an N_2S bonded HL ligand, this is consistent with a *cis* arrangement of the two pyridine ligands. Solutions of the salt in CD_3CN exhibit broadened ^1H NMR spectra consistent with displacement of the thiophene by solvent. Specifically, the resonance at δ 6.7, assigned to $H^{3''}$ of the thiophene, is broadened, as expected for a non-co-ordinated thienyl ring. Both of the pyridine complexes are electrochemically active. The cyclic voltammogram of $[Ru(HL)(py)Cl_2]$ shows an irreversible reduction centred at −1.85 V and a reversible process at −0.06 V, whereas that of $[Ru(HL)(py)_2Cl][PF_6]$ shows a similar irreversible reduction but a reversible oxidation at +0.45 V. This is consistent with the larger number of anionic ligands, and compares favourably with the analogous complexes $[Ru(bipy)_2Cl_2]$ (0.00 V) and $[Ru(terpy)(bipy)Cl]^+$ (+0.50 V).

The closely related complex $[Ru(HL)(dmso)Cl_2]$ **8** may be prepared as a purple powder by the reaction of HL with $[Ru(dmso)_4Cl_2]$ in ethanol at 60°. The ^1H NMR spectrum is sharp and well resolved (Table 5) and indicates that a single isomer of this complex is formed, and exhibits a singlet at δ 3.60 assigned to an S-bonded co-ordinated dmso ligand. The purple form slowly converts to an orange compound **9** in CH_2Cl_2 solution, and if the original preparation in ethanol is repeated at higher temperatures mixtures of purple and orange products



Scheme 1 Interconversion of ruthenium complexes of HL showing proposed structures for compounds. (*i*) Excess $RuCl_3{\cdot}3H_2O$; (*ii*) dmf; (*iii*) $RuCl_3{\cdot}H_2O$; (*iv*) heat in $MeCO_2H$; (*v*) pyridine; (*vi*) $[Ru(dmso)_4Cl_2]$; (*vii*) terpy

may be obtained. The ^1H NMR spectra of this mixture shows two separate sub-spectra, one of which is due to the previously described purple $[Ru(HL)(dmso)Cl_2]$. The other sub-spectrum contains all of the resonances of the purple compound, with aromatic resonances all within 0.2 ppm of the purple compound. The only exception is for $H^{6'}$ of the terminal pyridine ring of HL which is shifted upfield by 0.43 ppm (Table 5). The methyl groups of the dmso are now observed as two singlets at δ 2.62 and 2.71, typical of an O-bonded dmso ligand with inequivalent methyl environments. We propose that the orange compound is simply an O-bonded isomer. The stoichiometry of the complexes strongly suggests that the HL ligand is acting as an N_2S donor in each case.

The reaction of 2,2′:6′,2″-terpyridine with $[Ru(HL)Cl_3]$ yields orange solutions, from which the salt [Ru(HL)(terpy)Cl]Cl **10** may be isolated. Attempts to prepare this same complex by the reaction of $[Ru(terpy)Cl_3]$ with HL in a range of solvents were unsuccessful. The ^1H NMR spectrum of $[Ru(HL)(terpy)Cl]^+$ (Fig. 6) exhibits a low-field resonance at δ 10.25 which is characteristic of the α position of a 2,2′-bipyridine *cis* to a chloride; this, and the similarity of chemical shifts of the terminal pyridine ring of HL to those observed for the structurally characterised cation $[Ru(HL)_2Cl]^+$ allow an unambiguous assignment of structure to the complex, in which the non-co-ordinated thienyl lies close to the terpyridine rather than the chloride ligand. The significant upfield shift of the thienyl protons with respect to the free ligand arise from the anisotropy of the ruthenium and the terpyridine which it lies close to. It is worthy of note that the thienyl protons in this complex are all observed and are sharp and well resolved, in contrast to those for $[Ru(HL)_2Cl]^+$; one feature of the ^1H NMR spectrum of [Ru(HL)(terpy)Cl]Cl is the broadening of H^6 of the terpyridine, for which we have no satisfactory explanation, although it is possible that it is again associated with rotation of the thienyl group. In this complex, the HL ligand is acting as a bidentate N_2 donor.

When a solution of [Ru(HL)(terpy)Cl]Cl in glacial acetic acid is heated to reflux, a cyclometallation reaction analogous to that observed with $[Ru(HL)_2Cl]^+$ occurs, to yield $[Ru(L)(terpy)]^+$ **11**, which may be isolated as the tetrafluoroborate salt. This salt shows a characteristic AM pattern for the two protons of the cyclometallated thienyl ring, with a coupling constant of 4.8 Hz confirming the site of metallation.

The formation and interconversion reactions of ruthenium complexes of HL are summarised in Scheme 1.

We have also investigated the co-ordination behaviour of HL with rhodium compounds. The addition of an acetonitrile solution containing one equivalent of HL to an aqueous solution containing one equivalent of $RhCl_3{\cdot}3H_2O$ at 85 °C resulted in the precipitation of a yellow microcrystalline solid, formulated $[Rh(L)(MeCN)Cl_2]$ **12** on the basis of elemental analysis. The FAB mass spectrum also supports this formulation, showing peaks at *m/z* 410, 375 and 340, corresponding to $[RhLCl_2]^+$, $[RhLCl]^+$ and $[RhL]^+$ respectively. The ^1H NMR spectrum of the complex in CD_2Cl_2 shows resonances assigned to nine non-equivalent protons. In the COSY spectrum (Fig. 7) an AM pattern ($^3J_{HH'}$ 4.8 Hz) for the thiophene ring is clearly observed, and confirms unambiguously the presence of a thienyl ring metallated at the 3 position. The resonances assigned to $H^{6'}$ and $H^{5'}$ are shifted downfield ($\delta\Delta$ +0.52 and +0.40 ppm respectively) with respect to free HL. This suggests that the terminal pyridine is co-ordinated to the metal. In contrast, $H^{3'}$ and H^3 both move upfield with respect to the free ligand; similar upfield shifts are observed upon cyclopalladation and cycloplatination of HL. The ^1H NMR spectrum also shows a single environment for the methyl group

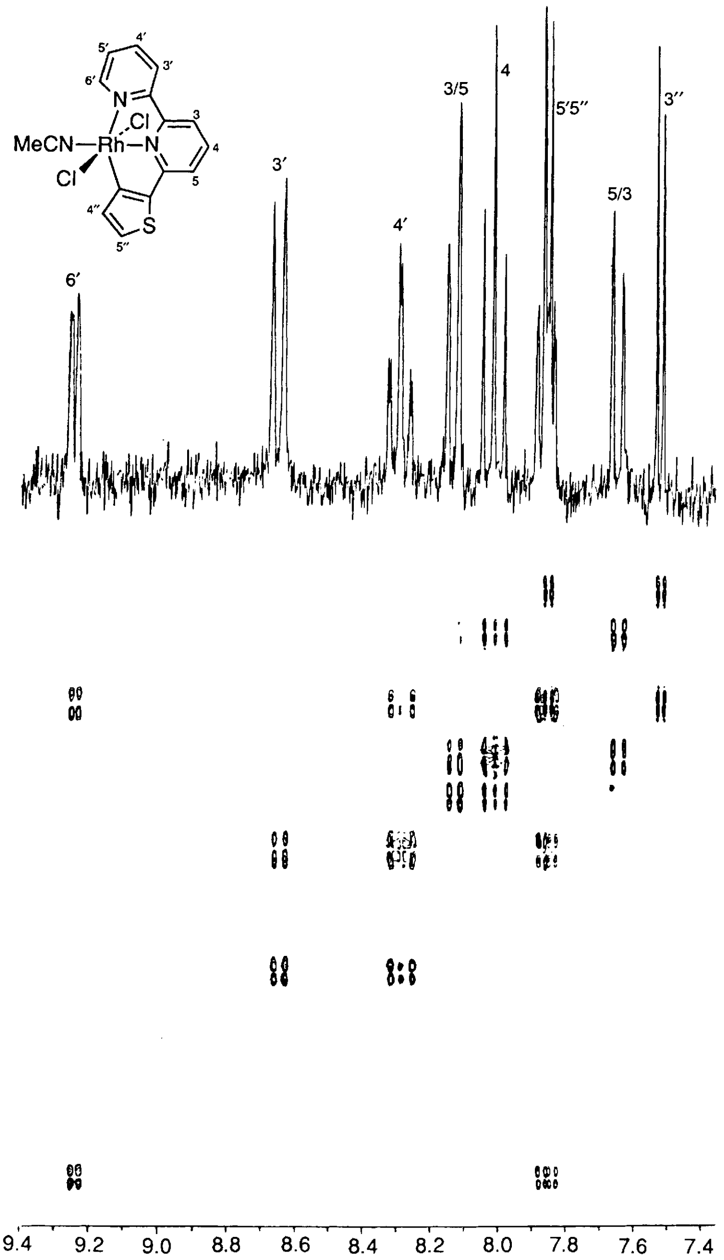


Fig. 7 The one- and two-dimensional phase-sensitive double quantum filtered COSY ^1H NMR spectra of $(CD_3)_2SO$ solutions of $[Rh(L)(MeCN)Cl_2]$

of the co-ordinated acetonitrile (δ 2.65). We propose an approximately octahedral structure for this complex, with L acting as a terdentate N_2C donor. The complex exhibits a single ν(Rh–Cl) stretch in the IR spectrum at 347 cm^{-1}, which is consistent with the two chlorines being *trans* to each other. If this is correct, the structure is somewhat similar to the cyclometallated complex produced with the N_2C-donor ligand 1,3-$(Me_2NCH_2)_2C_6H_4$.[33] Acetonitrile solutions of the complex show two irreversible oxidation processes centred at + 0.60 and + 1.00 V, and an irreversible reduction centred at − 1.53 V.

Reaction of $RhCl_3{\cdot}3H_2O$ with an excess of HL followed by treatment with NH_4PF_6 yielded an orange crystalline product. Elemental analysis indicated a formulation $[Rh(HL)_2Cl_2][PF_6]$ **13**, and the FAB mass spectrum exhibited an intense peak at *m/z* 649 $\{[Rh(HL)_2Cl_2]^+\}$. The IR spectrum exhibits a broad, weak ν(Rh–Cl) stretch at 346 cm^{-1}, in contrast to the single, sharp absorption observed for the *trans*-$[RhL(MeCN)Cl_2]$. This observation, combined with modelling studies lead us to propose a *cis* arrangement of the two chloride ligands in this complex. The ^1H NMR spectrum of the complex [Fig. 8(*b*)] indicates the presence of a single isomer of the complex, in which two bidentate N_2-bonded HL ligands are chemically and magnetically equivalent. Two possible configurations with equivalent ligands are possible [Fig. 9(*a*) and 9(*b*)]. The lowest-field resonance (δ 9.49) is assigned to $H^{6'}$ of the terminal pyridine ring on the basis of the coupling constant. In $[Ru(bipy)_2Cl_2]$ one of the H^6 environments is such that the proton lies above a pyridine ring and is shielded (δ 7.45) and the other such that it lies close to a chlorine ligand and is deshielded (δ 9.89). The downfield shift observed for $H^{6'}$ in $[Rh(HL)_2Cl_2][PF_6]$ suggests that it is in an environment close to the chlorine ligand hence isomer **a** has been formed. This is consistent with the presence of stacking type interactions between the free thienyl rings and the central pyridine rings of the other ligand, and also with the configuration of the structurally characterised complex $[Ru(Hpbpy)_2Cl_2]$ (Hpbpy = 6-phenyl-2,2′-bipyridine). It is noticeable that in Fig. 8(*b*) the resonance assigned to $H^{3''}$ is considerably broadened,

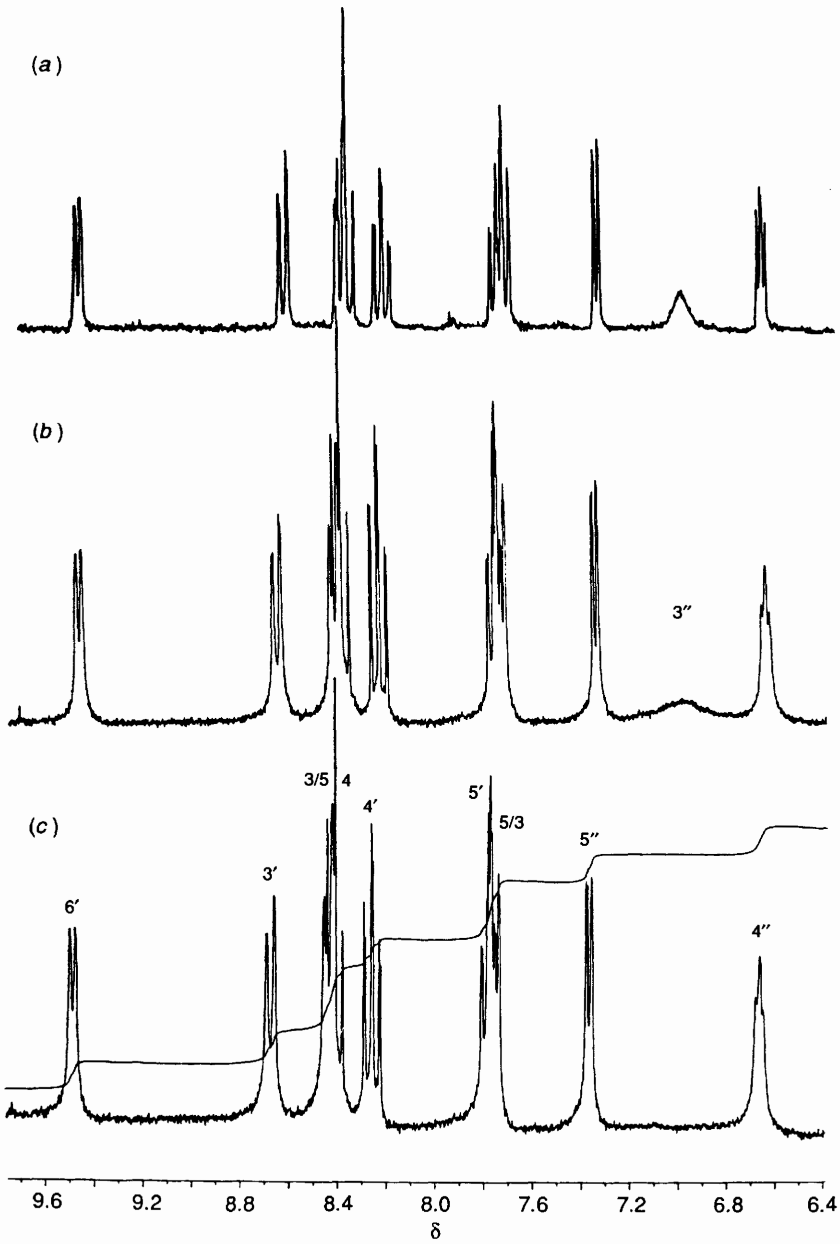


Fig. 8 ^{1}H NMR spectra of a $(CD_3)_2CO$ solution of $[Rh(HL)_2Cl_2][PF_6]$ at (*a*) 318, (*b*) 295 and (*c*) 280 K

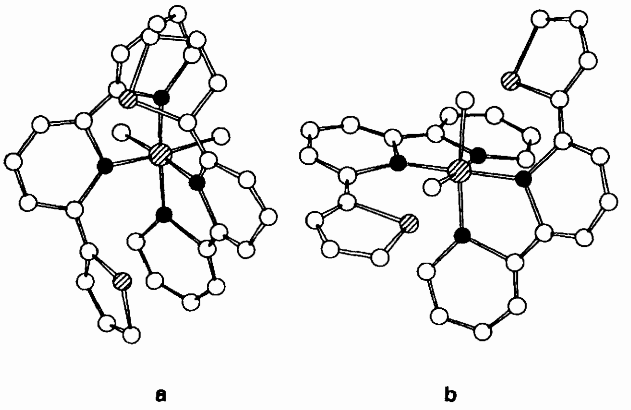


Fig. 9 Possible isomers of the complex cation $[Rh(HL)_2Cl_2]^+$ with two chemically and magnetically equivalent ligands and a *cis* arrangement of the halides

reminiscent of the behaviour of $[Ru(HL)_2Cl][BF_4]$, and consistent with a restricted 'rocking' motion of the free thienyl group. Upon cooling the sample [Fig. 8(*c*)] complete coalescence of $H^{3''}$ occurs, whilst upon warming the signal is sharpened [Fig. 8(*a*)]. The cyclic voltammogram of the complex exhibits no oxidation features between 0 and +1.4 V, and an irreversible process at −1.14 V on the outgoing reduction wave only.

In conclusion, we have shown that ruthenium and rhodium complexes of HL may exhibit a wide range of different co-ordination modes, and that interconversions between these are facile.

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