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Synthesis of the new binucleating compound pyrazin-2-yl 2-pyridyl sulfide for stepwise or direct approach to asymmetric binuclear ruthenium(II) complexes†

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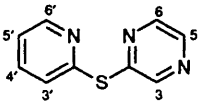
Pyrazin-2-yl 2-pyridyl sulfide (pzpys) has been prepared by reaction of 2-sulfanylpyridine with chloropyrazine. As shown by ^{1}H NMR spectroscopy, its major isomer has two binding sites which are inequivalent, one chelating through the N^1-pyrazine and N-pyridine atoms, the other monodentate through the N^4 atom of the pyrazine ring. By reaction of pzpys with $[RuL_2(NO)(NO_2)][PF_6]_2$ [(L = 2,2′-bipyridine (bipy) or di-2-pyridyl sulfide (dps)] the mononuclear complexes $[RuL_2(pzpys)(NO_2)][PF_6]$ have been obtained in which pzpys is the monodentate. The reactions of pzpys with *cis*-$[RuL_2Cl_2]$ complexes [L = bipy, 1,10-phenanthroline (phen) or dps] have been studied. The dps derivative reacts with a large excess of pzpys affording $[Ru(dps)_2(pzpys)Cl][PF_6]$ in which pzpys is monodentate. On the contrary the bipy and phen (L) derivatives, under the same experimental conditions, undergo substitution of both chloride ligands giving, as major products, $[RuL_2(pzpys)][PF_6]_2$ in which pzpys is chelated. When the reactions were carried out in the presence of a stoichiometric amount of pzpys the binuclear complexes $[L_2Ru(pzpys)RuL_2Cl][PF_6]_3$ (L = bipy or phen) were slowly formed. The mononuclear complexes have been used as ligands in the reactions with $[Ru(bipy)_2Cl_2]$ giving the new binuclear species $[L_2Ru(pzpys)RuL_2(NO_2)][PF_6]_3$ (L = bipy or phen). The compounds have been fully characterized by infrared, UV/VIS, ^{1}H and ^{13}C NMR spectroscopies. In acetonitrile solution $[Ru(bipy)_2(pzpys)Cl][PF_6]$ undergoes a reversible $Ru^{II} \longrightarrow Ru^{III}$ electron transfer. In contrast, the one-electron oxidation of $[Ru(dps)_2(pzpys)Cl][PF_6]$, $[Ru(bipy)_2(pzpys)(NO_2)][PF_6]$ and $[Ru(bipy)_2(pzpys)][PF_6]_2$ is complicated by subsequent chemical reactions. The binuclear complex $[(bipy)_2Ru(pzpys)Ru(bipy)_2Cl][PF_6]_3$ undergoes two consecutive one-electron oxidations ($\Delta E^{o\prime}$ = 0.55 V), which allow the corresponding $Ru^{II}Ru^{III}$ species to be classified as a completely delocalized (Class III) mixed-valence compound.

Binuclear polypyridylruthenium(II) complexes in which the metals are linked by the appropriate N-donor bridging ligands have attracted much attention due to their ability to generate mixed-valence complexes of fundamental interest in the electron-transfer field.[1–5] The construction of homo- and hetero- bi- and poly-nuclear polypyridylruthenium complexes is also of interest in the photochemical and photophysical area because suitable bridging ligands allow electronic communication between the $Ru(bipy)_3$ (bipy = 2,2′-bipyridine) or similar 'antenna' group and the reaction centre.[5,6]

Despite the large body of work devoted to the synthesis and characterization of complexes of the general type $[L_2XRu(L\text{–}L)RuXL_2]^{2+}$ or $[L_2Ru(L\text{–}L)RuL_2]^{4+}$ (L = bipy or bipy-like ligand, X = Cl or NO_2), containing exobidentate bridging ligands[1–3] such as pyrazine, 4,4′-bipyridine or bis(chelating) ligands[4,6] such as 2,3-bis(2-pyridyl)pyrazine, 2,2′-bipyrimidine, 'back to back' bis(bipyridine) and bis(terpyridine), examples of binuclear complexes containing terdentate binucleating ligands are much rarer.[3d] Moreover the preparation of new binuclear complexes requires, as a first step, the design and synthesis of binucleating compounds[6,7] followed by a direct synthesis of the binuclear species or by a stepwise method through the synthesis of mononuclear complexes able to act as ligands.[6,8,9a]

Following our interest in the chemistry of the bipyridine-like ligands[9] we report in this paper the preparation and characterization of the new compound pzpys which may act as mono- or bi-dentate mononucleating and exobidentate or terdentate binucleating ligand. The use of this polyfunctional



pzpys

compound allows the synthesis of mononuclear complexes which can act as monodentate or chelating ligands depending on the attachment mode of pzpys, as well as the one-step synthesis of asymmetric binuclear species containing RuL_2Cl and RuL_2 units. The control of the co-ordination mode of the ligand may be achieved by opportune choice of the starting complex. The complexes $[RuL_2Cl_2]$ [L = bipy[4a,6,7b,8a,b] or 1,10-phenanthroline (phen)[8a,c]] and $[Ru(terpy)Cl_3]$[6,8d] (terpy = 2,2′:6′,2″-terpyridine) are expected to favour the chelation of pzpys by substitution of both chloride ligands, while nitrosyl derivatives $[RuL_2(NO)X][PF_6]_2$[2,3b,c,10] or complexes such as $[RuA_2Cl_2]$ (A = di-2-pyridyl ketone,[11] di-2-pyridyl sulfide[9a] or sterically hindering diimines[12]) are expected to give species in which pzpys is monodentate.

We also report the synthesis and NMR characterization of a series of mono- and bi-nuclear ruthenium(II) complexes containing pzpys as mono- or bi-dentate mononucleating and terdentate binucleating ligand, respectively.

Experimental

Di-2-pyridyl sulfide (dps),[13] $[Ru(bipy)_2Cl_2]$,[14] $[Ru(bipy)_2(NO)(NO_2)][PF_6]_2$,[10] $[Ru(dps)_2Cl_2]$,[9a] $[Ru(dps)_2(NO)(NO_2)][PF_6]_2$[9a] and $[Ru(phen)_2Cl_2]$[15] were prepared by

† *Non-SI unit employed:* mmHg ≈ 133 Pa.

published methods. Elemental analyses were carried out by Redox Microanalytical Laboratory of Cologno Monzese (Milano). Conductivity measurements were done on a Radiometer CDM 3 conductivity meter. Infrared spectra were recorded on an FT-IR 1720X spectrophotometer with samples as Nujol mulls placed between CsI plates, electronic absorption spectra on a Perkin-Elmer Lambda 5 spectrophotometer and the ^1H and ^{13}C NMR spectra on a Bruker AMX 300 spectrometer. Materials and apparatus for electrochemistry were described elsewhere.[16] Potentials are referred to the saturated calomel electrode (SCE). All the syntheses were performed under N_2, and the synthesis and work-up of the binuclear complexes also required protection from light. Crystallization was performed by dissolving the products in acetone and filtering into an excess of stirred diethyl ether. All the complexes obtained were washed with diethyl ether and dried over P_4O_{10} *in vacuo*.

Preparations

Pyrazin-2-yl 2-pyridyl sulfide. The compounds 2-sulfanylpyridine (11.3 g, 0.1 mol), chloropyrazine (11.4 g, 0.1 mol) and potassium carbonate (15 g, 0.1 mol) were vigorously stirred in dimethylformamide (30 cm^3) and refluxed for 4 h. The dimethylformamide was then distilled under reduced pressure (100 mmHg) and the residue distilled at 7 mmHg (b.p. 140 °C). The yellow oil obtained was kept at 4 °C to give a waxy solid. Yield 11.4 g (60%) (Found: C, 57.15; H, 3.75; N, 22.20; S, 16.90. $C_9H_7N_3S$ requires C, 57.10; H, 3.75; N, 22.20; S, 16.95%). IR: 3046s, 1605s, 1574vs, 1562s, 1510s, 1451vs, 1419vs, 1387s, 1288s, 1144vs, 1116vs, 1086s, 1047s, 1010s, 988s, 841s, 765vs, 738s, 722vs and 401s cm^{-1}.

[Ru(bipy)$_2$(pzpys)Cl][PF$_6$]·H$_2$O 1. The complex [Ru(bipy)$_2$Cl$_2$]·2H$_2$O (0.520 g, 1 mmol) and $AgPF_6$ (0.253 g, 1 mmol) were dissolved in acetone (30 cm^3) and stirred for 4 h in the dark. The compound pzpys (0.946 g, 5.0 mmol) was then added and the suspension stirred for 2 h. Silver chloride was filtered off and the resulting solution concentrated (10 cm^3) and added to diethyl ether (100 cm^3). The precipitate obtained was washed with diethyl ether, dissolved in acetone (*ca.* 10 cm^3) and added to the top of a chromatography column (diameter 2 cm) packed with aluminium oxide (80 g; Aldrich, neutral, STD grade, 150 mesh) deactivated with water (6 g). Elution with acetone–toluene (3:2) gave a red band which was collected, concentrated (10 cm^3) and treated with diethyl ether. The red solid obtained was crystallized. Yield: 0.32 g (40%) (Found: C, 43.40; H, 3.15; N, 12.15; S 3.90. $C_{29}H_{25}ClF_6N_7OPRuS$ requires C, 43.50; H, 3.15; N, 12.25; S, 4.00%). IR: 1605s, 1569s, 1160s, 844 (br), 765vs, 731s, 759vs and 338ms cm^{-1}. Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 180 Ω^{-1} cm^2 mol^{-1}.

From a second orange band, as described for complex **6**, [Ru(bipy)$_2$(pzpys)][PF$_6$]$_2$ (*ca.* 30%) was obtained.

[Ru(dps)$_2$(pzpys)Cl][PF$_6$]·H$_2$O 2. This complex was obtained as described for **1** starting from [Ru(dps)$_2$Cl$_2$]·2H$_2$O (0.293 g, 0.5 mmol), $AgPF_6$ (0.126 g, 0.5 mmol) and pzpys (0.757, 4 mmol). Yield *ca.* 40% (Found: C, 40.30; H, 3.00; N, 11.30; S, 11.15. $C_{29}H_{25}ClF_6N_7OPRuS_3$ requires C, 40.25; H, 2.90; N, 11.35; S, 11.10%). IR: 1586s, 1569s, 1164s, 845 (br), 768vs, 741ms, 559vs and 335ms cm^{-1}. Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 170 Ω^{-1} cm^2 mol^{-1}.

[Ru(bipy)$_2$(pzpys)(NO$_2$)][PF$_6$]·H$_2$O 3 and [Ru(dps)$_2$(pzpys)(NO$_2$)][PF$_6$]·H$_2$O 4. Potassium azide (0.08 g, 1 mmol) was dissolved in warm methanol (10 cm^3) and added dropwise to a stirred solution of [Ru(bipy)$_2$(NO)(NO$_2$)][PF$_6$]$_2$ (0.78 g, 1 mmol) or [Ru(dps)$_2$(NO)(NO$_2$)][PF$_6$]$_2$·H$_2$O (0.861 g, 1 mmol), in acetone (15 cm^3). The dark red solution obtained was stirred for 20 min. An acetone solution (5 cm^3) of pzpys (0.95 g, 5.0 mmol) was then added. The solution was stirred for 3 h, filtered and added to diethyl ether (150 cm^3). The orange **3** or yellow **4** solid obtained was filtered off, washed copiously with diethyl ether and crystallized. Yield *ca.* 70% for both compounds. Complex **3** (Found: C, 42.80; H, 3.10; N, 13.70; S 4.00. $C_{29}H_{25}F_6N_8O_3PRuS$ requires C, 42.90; H, 3.10; N, 13.80; S, 3.95%); IR 1605s, 1572vs, 1339vs, 1297vs, 1162s, 1116s, 843 (br), 767vs, 732s and 559vs cm^{-1}; Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 180 Ω^{-1} cm^2 mol^{-1}. Complex **4** (Found: C, 39.70; H, 2.95; N, 12.70; S 11.00. $C_{29}H_{25}F_6N_8O_3PRuS_3$ requires C, 39.75; H, 2.90; N, 12.80; S, 11.00%); IR 1629s, 1589vs, 1342vs, 1297vs, 1165s, 1116s, 844 (br), 770vs, 741ms, 726s and 559vs cm^{-1}; Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 160 Ω^{-1} cm^2 mol^{-1}.

Complexes **1** and **2** were obtained in the same way starting from [Ru(bipy)$_2$(NO)Cl][PF$_6$]$_2$ (0.769 g, 1 mmol) or [Ru(dps)$_2$(NO)Cl][PF$_6$]$_2$ (0.833 g, 1 mmol), respectively, potassium azide (0.08 g, 1 mmol) and pzpys (0.946 g, 5.0 mmol). Yields *ca.* 30 (**1**) and *ca.* 40% (**2**).

[Ru(bipy)$_2$(pzpys)(NO)][PF$_6$]$_3$·H$_2$O 5. To a stirred methanol solution (25 cm^3) of the complex [Ru(bipy)$_2$(pzpys)(NO$_2$)][PF$_6$]·H$_2$O (0.203 g, 0.25 mmol) was slowly added a 70% aqueous solution of HPF_6 (1 cm^3). The reaction mixture was stirred for 1 h, then water (10 cm^3) was added and the solid complex **5** obtained filtered off, washed with water (30 cm^3), methanol–water (10 cm^3, 1:1) and diethyl ether (30 cm^3). Yield: *ca.* 60%. (Found: C, 32.10; H, 2.40; N, 10.25; S 3.00. $C_{29}H_{25}F_{18}N_8O_2P_3RuS$ requires C, 32.10; H, 2.30; N, 10.30; S, 2.95%). IR: 1947vs, 1609s, 1573ms, 1506s, 1324s, 1294s, 839 (br), 767vs, 741ms, 726s and 559vs cm^{-1}. Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 425 Ω^{-1} cm^2 mol^{-1}.

[Ru(bipy)$_2$(pzpys)][PF$_6$]$_2$ 6. The complex [Ru(bipy)$_2$Cl$_2$]·2H$_2$O (0.520 g, 1 mmol) and pzpys (0.946 g, 5 mmol) were refluxed in ethanol–water (2:1, 30 cm^3) for 2 h, then stirred at room temperature for 2 d. The brown solution obtained was filtered and added to a stirred aqueous solution (100 cm^3) of NH_4PF_6 (1.63 g, 10 mmol). The crude product was collected, washed copiously with cold water, dried overnight and purified by chromatography. The preparation of the column and the elution of **1**, as a red band, was performed as for **1** (yield *ca.* 10%). Elution with acetone–acetonitrile (4:1) gave an orange band which was concentrated (10 cm^3) and precipitated with diethyl ether (100 cm^3). The final yield of **6** was 0.536 g (60%) (Found: C, 39.10; H, 2.60; N, 11.00; S, 3.60. $C_{29}H_{23}F_{12}N_7P_2RuS$ requires C, 39.00; H, 2.60; N, 11.00; S, 3.60). IR: 1605s, 1567s, 1162s, 844 (br), 765vs, 732s and 559vs cm^{-1}. Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 305 Ω^{-1} cm^2 mol^{-1}.

[Ru(phen)$_2$(pzpys)][PF$_6$]$_2$ 7. This complex was obtained in the same way starting from [Ru(phen)$_2$Cl$_2$] (0.266 g, 0.5 mmol) and pzpys (0.474 g, 2.5 mmol). The crude product was purified by chromatography using acetone as eluent. The yield was 0.282 g (60%) (Found: C, 42.30; H, 2.50; N, 10.40; S, 3.40. $C_{33}H_{23}F_{12}N_7P_2RuS$ requires C, 42.15; H 2.45; N, 10.40; S, 3.40%). IR: 1632s, 1568s, 1150s, 850 (br), 772vs, 724s and 559vs cm^{-1}. Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 310 Ω^{-1} cm^2 mol^{-1}.

[(bipy)$_2$Ru(pzpys)Ru(bipy)$_2$Cl][PF$_6$]$_3$·2H$_2$O 8 and [(phen)$_2$Ru(pzpys)Ru(phen)$_2$Cl][PF$_6$]$_3$·2H$_2$O 9. Although these complexes can be obtained as described for **10** starting from **6** and [Ru(bipy)$_2$Cl$_2$] or **7** and [Ru(phen)$_2$Cl$_2$], respectively, they were prepared more easily and in higher yields directly by reaction of [Ru(bipy)$_2$Cl$_2$] or [Ru(phen)$_2$Cl$_2$] (1 mmol) and pzpys (0.104 g, 0.55 mmol) in ethanol–water (2:1, 30 cm^3) for 3 d. The reaction mixture was added to an aqueous solution (100 cm^3) of NH_4PF_6 (1.63 g, 10 mmol). The dark red solid formed was filtered off, washed copiously with cold water and dried overnight. The crude product was dissolved in acetone and

added to the top of a 15 × 2 cm diameter chromatography column (Aldrich, aluminium oxide, neutral, STD grade, 150 mesh deactivated with 11% water). The first orange band of **6** or **7** was eluted with acetone–toluene (3:1) (yield *ca.* 20%). Elution with acetone–acetonitrile (2:1) gave a purple band which was concentrated (10 cm^3) and precipitated with diethyl ether (100 cm^3). Yield *ca.* 55 (**8**) and 35% (**9**). Complex **8** (Found: C, 38.55; H, 2.90; N, 10.00; S, 2.00. $C_{49}H_{43}ClF_{18}N_{11}O_2P_3Ru_2S$ requires C, 38.65; H, 2.85; N, 10.10; S, 2.10%). IR: 1604vs, 1573s, 1163s, 844 (br), 765vs, 731s, 559vs and 344ms cm^{-1}; Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 410 Ω^{-1} cm^2 mol^{-1}. Complex **9** (Found: C, 42.20; H, 2.70; N, 9.50; S, 2.10. $C_{57}H_{43}ClF_{18}N_{11}O_2P_3Ru_2S$ requires C, 42.30; H, 2.70; N, 9.50; S, 2.00%). IR 1634s, 1569ms, 1149s, 830 (br), 775s, 722ms and 559vs cm^{-1}; Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 410 Ω^{-1} cm^2 mol^{-1}.

[(bipy)$_2$Ru(pzpys)Ru(bipy)$_2$(NO$_2$)][PF$_6$]$_3$·2H$_2$O 10. The compound [Ru(bipy)$_2$Cl$_2$]·2H$_2$O (0.520 g, 1 mmol) was refluxed in ethanol–water (2:1, 30 cm^3) for 2 h, then [Ru(bipy)$_2$(pzpys)(NO$_2$)][PF$_6$]$_2$·H$_2$O (0.811 g, 1 mmol) was added. The solution was protected from light and stirred for 2 d. The precipitation of a dark red solid and the preparation of the chromatography column were as described for **8**. A first band of **3** was eluted with acetone–toluene (2:1). Elution with acetone gave a purple band which was concentrated and precipitated with diethyl ether. Yield: *ca.* 30% (Found: C, 38.40; H, 2.80; N, 10.80; S, 2.15. $C_{49}H_{43}F_{18}N_{12}O_4P_3Ru_2S$ require C, 38.40; H, 2.85; N, 10.95; S, 2.10%). IR: 1629ms, 1605s, 1569ms, 1343s, 1314s, 1298s, 1275s, 1162s, 836vs, 766s, 732ms and 559s cm^{-1}. Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 400 Ω^{-1} cm^2 mol^{-1}.

[(phen)$_2$Ru(pzpys)Ru(bipy)$_2$Cl][PF$_6$]$_3$·2H$_2$O 11. This binuclear complex was prepared similarly starting from [Ru(phen)$_2$(pzpys)][PF$_6$]$_2$ (0.47 g, 0.5 mmol) and [Ru(bipy)$_2$Cl$_2$]·2H$_2$O (0.26 g, 0.5 mmol). Yield *ca.* 25% (Found: C, 40.55; H, 2.80; N, 9.65; S, 2.00. $C_{53}H_{43}ClF_{18}N_{11}O_2P_3Ru_2S$ requires C, 40.55; H, 2.75; N, 9.80; S, 2.05%). IR: 1632s, 1604s, 1574s, 1150s, 833 (br), 767s, 724s, 559vs and 344ms cm^{-1}. Λ_M(MeCN, 2 × 10^{-4} mol dm^{-3}, 20 °C) = 410 Ω^{-1} cm^2 mol^{-1}.

Results and Discussion

Synthesis and characterization of pzpys

Pyrazin-2-yl 2-pyridyl sulfide was prepared by reaction of equimolar amounts of 2-sulfanyl pyridine and chloropyrazine in the presence of K_2CO_3. Distillation of the reaction mixture under reduced pressure readily gave the required compound in high yield. It is a yellow oil stable for a long time and well soluble in the most common solvents. Its structure was determined by a combination of elemental analysis, ^{1}H and ^{13}C NMR spectral data.

The ^{1}H NMR spectrum of pzpys in $(CD_3)_2CO$ (Fig. 1) shows the presence of two isomers (ratio 20:1). This means that at room temperature the possibility of free rotation around the C–S bonds is excluded. Moreover the results of theoretical calculations[13,17] for di-2-pyridyl sulfide (dps) as well as experimental data[9,13] indicate that it adopts three equally populated twisted conformations in solution. Molecular models of dps and pzpys show for both compounds similar steric restrictions. However among the three possible rotational conformers[9,13] only two are formed. Furthermore, studies on dps and diphenyl sulfide derivatives indicate a sulfur p_π donation towards aromatic rings bearing electron-withdrawing substituents.[18] To explain the presence of only two isomers we suggest for pzpys the conformations **A** and **B** (Fig. 1) in which the interaction between a sulfur lone pair and the π electrons of the pyrazine ring prevents rotation of this ring which is almost coplanar with the CSC plane, while the pyridine ring is twisted. The relative orientations of the pyrazine and pyridine rings with respect to the CSC plane should be N(1) inside, N(1′) inside and N(1) inside, N(1′) outside in **A** and **B**, respectively. The ^{1}H NMR spectrum of the major isomer shows four sets of resonances in the range δ 8.5–7.25 due to the pyridine ring and three sets in the range δ 8.75–8.45 due to the pyrazine ring. The former pattern is consistent with an almost first-order ABMX system, the latter with an ABX system which is fully resolved by a second-order computer-assisted analysis (Table 1).

Complete analysis of the ^{1}H NMR spectrum of the minor isomer is not possible because some signals are masked by those of the major isomer. However the ^{1}H NMR data for the minor isomer are of interest. In fact the $H^{3'}$, $H^{4'}$ and $H^{5'}$ pyridine protons are shielded (δ 7.48, 7.73 and 7.26, respectively) with respect to the same protons of the major isomer (δ 7.53, 7.78 and 7.30, respectively). Conversely the H^3 pyrazine proton (δ 8.76) is deshielded with respect to that of the major isomer (δ 8.69). The molecular model of **B** reveals that a diamagnetic anisotropic interaction should occur because of the short distance between the pyridine protons and the pyrazine ring. This results in a shift of the pyridine proton signals of the minor isomer to higher fields. In contrast a paramagnetic anisotropic interaction should occur between the H^3 pyrazine proton and the pyridine ring.

The ^{13}C NMR spectrum provides further information. In fact the two isomers show overlapped pyrazine carbon signals and different pyridine signals. Furthermore, the pyrazine carbon signals of both isomers (see Table 2) are similar to those of dps[9b] [δ 157.80 (C^2), 150.94 (C^6), 138.10 ($C^{4'}$), 126.57 ($C^{3'}$), 122.77 ($C^{5'}$)]. These data are consistent with a single fixed position of the pyrazine ring because of the interaction between the π electrons of this ring with a lone pair of the sulfur atom.

Looking at the structure of pzpys it is clear that knowledge of its conformational properties is a potential useful tool for the prediction of the stereochemistry of its co-ordination compounds. Conformation **A** is suitable to give mononuclear complexes in which the monoco-ordinating (N^4 pyrazine atom) or chelating binding site (N^1 pyrazine and N pyridine atom) is

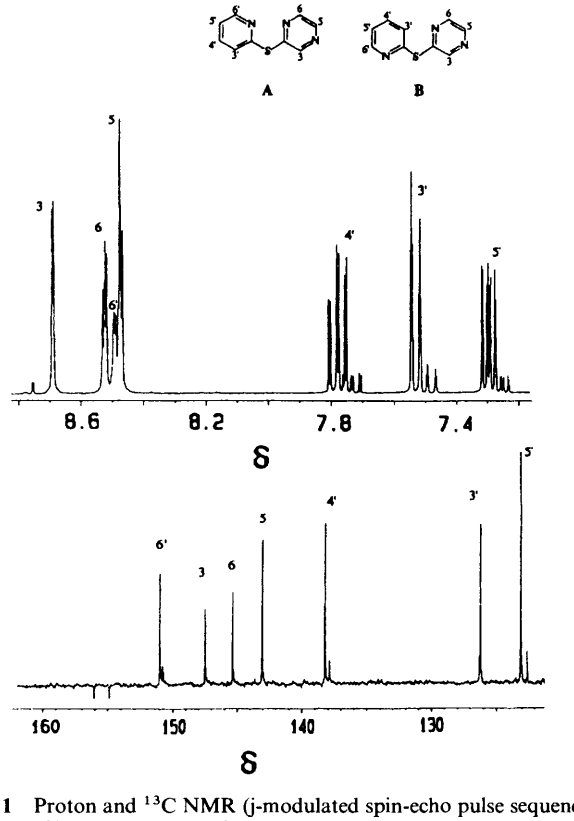


Fig. 1 Proton and ^{13}C NMR (j-modulated spin-echo pulse sequence) spectra of isomers **A** and **B** of pzpys

Table 1 Proton NMR data ($SiMe_4$ as standard) for ruthenium pyrazin-2-yl 2-pyridyl sulfide complexes[a]

	Pyrazine ring			Pyridine ring of pzpys				Other pyridine rings			
Compound	H^3	H^6	H^5	$H^{6'}$	$H^{4'}$	$H^{3'}$	$H^{5'}$	$H^{6''}$	$H^{4''}$	$H^{3''}$	$H^{5''}$
pzpys[b]	8.69[c]	8.53[c]	8.47[c]	8.48	7.78	7.53	7.30				
	$J(H^3H^6) = 1.3$	$J(H^5H^6) = 2.5$	$J(H^3H^5) = 0.3$	$J(H^5'H^6') = 4.9$		$J(H^4'H^6') = 1.9$	$J(H^3'H^6') = 0.9$				
				$J(H^4'H^5') = 7.5$		$J(H^3'H^5') = 1.0$	$J(H^3'H^4') = 8.0$				
1	8.75[d]	8.34	8.78[d]	8.45	7.81	7.48	7.39	9.85	8.22	8.63	7.87
	$J(H^3H^6) = 1.1$	$J(H^5H^6) = 3.4$		$J(H^5'H^6') = 4.9$		$J(H^4'H^6') = 2.0$	$J(H^3'H^6') = 0.8$	8.78	8.17	8.69	7.73
				$J(H^4'H^5') = 7.5$		$J(H^3'H^5') = 1.1$	$J(H^3'H^4') = 8.0$	7.94	7.89	8.51	7.27
								7.68	7.90	8.55	7.27
2	8.29	8.45	8.95	8.38	7.78	7.42	7.36	9.61	7.99	7.90	7.60
	$J(H^3H^6) = 1.1$	$J(H^5H^6) = 3.4$	$J(H^3H^5) = 0.3$	$J(H^5'H^6') = 4.8$		$J(H^4'H^6') = 1.9$	$J(H^3'H^6') = 0.8$	8.91	7.99	7.93	7.42
				$J(H^4'H^5') = 7.5$		$J(H^3'H^5') = 1.0$	$J(H^3'H^4') = 7.9$	8.47	7.87	7.73	7.21
								7.83	7.87	7.75	7.12
3	8.58[d]	8.39	8.61[d]	8.45	7.82	7.50	7.39	9.80	8.29	8.64	7.94
	$J(H^3H^6) = 1.2$	$J(H^5H^6) = 3.3$		$J(H^5'H^6') = 4.8$		$J(H^4'H^6') = 1.9$	$J(H^3'H^6') = 0.8$	8.81	8.29	8.72	7.78
				$J(H^4'H^5') = 7.5$		$J(H^3'H^5') = 1.1$	$J(H^3'H^4') = 7.9$	7.89	8.01	8.54	7.37
								7.76	7.98	8.58	7.31
4	8.10	8.49	8.70	8.33	7.75	7.38	7.33	9.60	8.01	7.86	7.61
	$J(H^3H^6) = 1.2$	$J(H^5H^6) = 3.4$	$J(H^3H^5) = 0.3$	$J(H^5'H^6') = 4.9$		$J(H^4'H^6') = 1.9$	$J(H^3'H^6') = 0.9$	9.07	8.02	7.90	7.49
				$J(H^4'H^5') = 7.5$		$J(H^3'H^5') = 1.1$	$J(H^3'H^4') = 7.9$	8.48	7.90	7.70	7.21
								7.78	7.90	7.70	7.17
6	9.04	7.98	8.25	8.09	7.99	8.01	7.30	9.10	8.31	8.76	7.74
	$J(H^3H^6) = 1.1$	$J(H^5H^6) = 3.4$	$J(H^3H^5) = 0$	$J(H^5'H^6') = 5.9$		$J(H^4'H^6') = 1.6$	$J(H^3'H^6') = 0.7$	8.76	8.35	8.86	7.74
				$J(H^4'H^5') = 7.5$		$J(H^3'H^5') = 1.7$	$J(H^3'H^4') = 7.9$	8.00	8.13	8.75	7.49
								8.00	8.13	8.69	7.53
7	9.05	8.00	8.11	8.19	8.03	7.91	7.19	9.62[e]	8.96[f]	8.15[g]	
	$J(H^3H^6) = 1.1$	$J(H^5H^6) = 3.5$	$J(H^3H^5) = 0$	$J(H^5'H^6') = 5.9$		$J(H^4'H^6') = 1.6$	$J(H^3'H^6') = 0.6$	9.32[e]	9.00[f]	8.18[g]	
				$J(H^4'H^5') = 7.5$		$J(H^3'H^5') = 1.6$	$J(H^3'H^4') = 7.9$	8.64[f]	8.06[e]	7.62[g]	
								8.63[f]	8.04[e]	7.61[g]	
								8.45[h]	8.29[h]		
								8.41[h]	8.33[h]		

[a] Recorded at 300 MHz and 298 K in $(CD_3)_2CO$. The pyridine proton signals of bipy and dps appear as a doublet of doublet of doublets. The coupling constants (Hz) of bipy and dps are in the range: $J(H^{5''}H^{6''}) = 5.8–6.2$, $J(H^{4''}H^{6''}) = 1.3–1.7$, $J(H^{3''}H^{6''}) \leqslant 0.7$, $J(H^{4''}H^{5''}) = 7.5–7.8$, $J(H^{3''}H^{5''}) = 1.5–1.8$ and $J(H^{3''}H^{4''}) = 7.8–8.0$. [b] For the minor isomer signals are observed at: δ 8.76 (H^3), 7.73 ($H^{4'}$), 7.48 ($H^{3'}$) and 7.26 ($H^{5'}$). [c] Second-order ABX system. [d] Broad signal. [e] α-Proton of 1,10-phenanthroline. [f] γ-Proton of phen. [g] β-Proton of phen. Four AMX systems with $J(H_\alpha H_\beta) = 5.3$, $J(H_\alpha H_\gamma) = 1.3$ and $J(H_\beta H_\gamma) = 8.3$ Hz. [h] δ-Proton of phen. Two AB systems with $J = 8.9$ Hz.

Table 2 The ^{13}C NMR data[a] ($SiMe_4$ as standard) for ruthenium pyrazin-2-yl 2-pyridyl sulfide complexes

	Pyrazine ring			Pyridine rings							
Compound	C^6	C^3	C^5	$C^{6''}$		$C^{4''}$		$C^{3''}$		$C^{5''}$	
pzpys[b]	143.06	147.48	145.36	150.98	156.07[c]	138.23		126.21		123.07	
			154.90[c,d]								
1	145.46	149.16	146.27	153.42	153.37	138.75[e]	137.78	127.23[e]	124.67	127.82	127.77
			156.68[c,d]	152.70	152.31	137.25	137.17	124.26	124.16	127.35	126.69
				151.45[e]	159.79[c]	136.73	158.66[c]	123.57	158.61[c]	123.94[e]	158.34[c]
2	146.07	150.74	148.72	159.51	159.30[f]	139.43	139.37	130.23	129.03	126.93	125.95
				158.25	151.93[e]	139.13	138.66	128.53	128.23	125.16	124.90
				160.68[c]	160.59[c]	138.60	160.50[c]	127.83	158.36[c]	124.55	158.09[c]
3	145.76	149.21	146.43	154.44	153.22	138.90[e]	138.86	127.33[e]	124.62	128.20	128.01
			157.00[c,d]	152.55[f]	151.56[e]	138.63	138.37	124.46	124.29	127.58	126.97
				158.93[c]	158.77[c]	138.14	157.89[c]	123.78	157.78[c]	124.02[e]	
4	145.95	149.75	148.19	159.38	158.20	139.88	139.51	129.85	129.37	126.44	125.65
				157.97	157.47	139.43	139.10[f]	128.20	127.89	124.94	124.86
				151.56[e]				127.64		124.22	
6	149.52	148.45	145.43	155.99	155.66[e]	139.68[e]	139.52	129.53[e]	125.69	128.61	128.38
				155.24	152.74	139.44	139.18	125.44	125.22	127.99	127.61
				152.57	158.31[c]	139.00	158.22[c]	125.05	156.75[c]	126.38[e]	155.52[c]
				158.28[c]							
7	149.81	148.73	145.08	157.09[g]	156.46[g]	139.29[e]	138.52[h]	129.38[e]	128.89[i]	126.63[e]	126.48[f,j]
			156.68[c,d]	155.83[e]	153.63[g]	138.45[h]	137.84[h]	128.86[i]	128.60[i]	126.20[j]	126.04[j]
				153.49[g]	148.73[c]	137.85[h]	132.00[c]	128.40[i]	131.77[i]	131.72[c]	131.47[c]

[a] Recorded at 75.56 MHz and 298 K in $(CD_3)_2CO$. [b] For the minor isomer signals are observed at: δ 150.75 ($C^{6'}$), 137.98 ($C^{4'}$), 126.31 ($C^{3'}$) and 122.57 ($C^{5'}$). [c] Quaternary carbons. Some signals are not observed. [d] Assigned to pyrazine ring. [e] Assigned to pyridine ring of pzpys. [f] Overlapped signals. [g] α-Carbons of 1,10-phenanthroline. [h] γ-Carbons of phen. [i] δ-Carbons of phen. [j] β-Carbons of phen.

occupied. Furthermore **A**, in binuclear complexes can act as an asymmetric bridging ligand whereas the exobidentate co-ordination mode appears less probable.

Reactivity of pzpys

$$[RuL_2Cl_2] \xrightarrow{(i)} [RuL_2(pzpys)Cl][PF_6] \xleftarrow{(ii)} [RuL_2(NO)Cl][PF_6]_2$$

1 (L = bipy), **2** (L = dps)

$$[RuL_2(NO)(NO_2)][PF_6]_2 \xrightarrow{(ii)} [RuL_2(pzpys)(NO_2)][PF_6] \xrightarrow{(iii)}$$

3 (L = bipy), **4** (L = dps)

$$[RuL_2(pzpys)(NO)][PF_6]_3$$

5 (L = bipy)

$$[RuL_2Cl_2] \xrightarrow{(iv)} [RuL_2(pzpys)][PF_6]_2$$

6 (L = bipy), **7** (L = phen)

$$[RuL_2Cl_2] \xrightarrow{(v)} [L_2Ru(pzpys)RuL_2Cl][PF_6]_3$$

8 (L = bipy), **9** (L = phen)

$$[Ru(bipy)_2Cl_2] \xrightarrow{(vi)} [L_2Ru(pzpys)Ru(bipy)_2X][PF_6]_3$$

8 (X = Cl, L = bipy), **10** (X = NO_2, L = bipy), **11** (X = Cl, L = phen)

Scheme 1 Synthetic pathways for the preparation of the complexes: (*i*) Me_2CO, $AgPF_6$, pzpys (excess); (*ii*) N_3^-, pzpys (excess); (*iii*) HPF_6; (*iv*) ethanol–water (2:1), pzpys (excess); (*v*) ethanol–water (2:1), $\frac{1}{2}$ pzpys; (*vi*) ethanol–water (2:1), $[Ru(bipy)_2(pzpys)][PF_6]_2$, $[Ru(bipy)_2(pzpys)(NO_2)][PF_6]$ or $[Ru(phen)_2(pzpys)][PF_6]_2$

As shown in Scheme 1 the $[Ru(bipy)_2(pzpys)Cl][PF_6]$ **1** and $[Ru(dps)_2(pzpys)Cl][PF_6]$ **2** complexes have been obtained by treating $[Ru(bipy)_2Cl_2]$ or $[Ru(dps)_2Cl_2]$ dissolved in acetone with $AgPF_6$ (ratio 1:1) in the presence of a large excess of pzpys, while $[Ru(bpy)_2(pzpys)(NO_2)][PF_6]$ **3** and $[Ru(dps)_2(pzpys)(NO_2)][PF_6]$ **4** have been prepared through solvento species generated *in situ* from the nitrosyl derivatives. Compounds **1** and **2** can be prepared in the same way from $[Ru(bipy)_2(NO)Cl][PF_6]_2$ and $[Ru(dps)_2(NO)Cl][PF_6]_2$, respectively. Further reaction of **3** with HPF_6 leads to the formation of $[Ru(bipy)_2(pzpys)(NO)][PF_6]_3$ **5** whereas the same reaction of **4** gives an unstable product. All the above complexes contain pzpys co-ordinated in a monodentate fashion. The compounds $[Ru(bipy)_2(pzpys)][PF_6]_2$ **6** and $[Ru(phen)_2(pzpys)][PF_6]_2$ **7** containing pzpys chelated to ruthenium can be obtained by several methods. In fact the reaction of **5** with the azide ion (or **1** with $AgPF_6$) in 1:1 ratio gives **6** (see also the syntheses of **1**, **8** and **9** in the Experimental section). However the synthetic pathway (*iv*) gives **6** and **7** in higher yields. The binuclear complexes $[(bipy)_2Ru(pzpys)Ru(bipy)_2Cl][PF_6]_3$ **8** and $[(phen)_2Ru(pzpys)Ru(phen)_2Cl][PF_6]_3$ **9** were obtained straightforwardly from $[Ru(bipy)_2Cl_2]$ or $[Ru(phen)_2Cl_2]$ and pzpys. By treating $[Ru(bipy)_2Cl_2]$ with the mononuclear complex **3**, containing the monodentate pzpys, the complex $[(bipy)_2Ru(pzpys)Ru(bipy)_2(NO_2)][PF_6]_3$ was obtained, while from $[Ru(bipy)_2Cl_2]$ and the mononuclear complex **6** or **7** containing chelated pzpys the complexes $[L_2Ru(pzpys)Ru(bipy)_2Cl][PF_6]_3$ (L = bipy or phen) were prepared. In contrast, no tractable products were obtained under comparable conditions from the reactions between $[Ru(bipy)_2Cl_2]$ and $[Ru(dps)_2(pzpys)X][PF_6]$ (X = Cl or NO_2).

All the compounds are soluble in methanol, acetone and acetonitrile. Most are stable for some months in the solid state and for some days in solution; **5** and **9** are much less stable in solution (*ca.* 20 and 60 min, respectively).

NMR spectroscopy

Compounds **1**–**4**, containing monodentate pzpys, consistent with their *cis* configuration, have five inequivalent pyridine rings which give five ABMX systems in the ^1H NMR spectrum and 25 carbon signals in the ^{13}C NMR spectrum. Moreover the pyrazine ring produces an ABX system and four carbon signals. Complete assignment of the signals present in the ^1H NMR spectra is mainly based on the analysis of the correlation (COSY) spectra (which clarify the connectivity patterns of the rings) and ring-current effects.[19]

We assign the more deshielded $H^{6''}$ protons, observed for compounds **1**–**4** in the range δ 9.85–9.60, to ring a next to a Cl or

NO_2 group (Fig. 2 and Table 1). Consequences of the ring-current effects are: (*i*) a moderate upfield shift of the *o*-protons (range δ 9.07–8.78) assigned to ring b above the pyrazine ring; (*ii*) a higher upfield shift of the *o*-protons lying above the plane of the adjacent bipy rings ($H^{6''}$ of rings c and d, Fig. 2 and Table 1); (*iii*) a downfield shift of the pyridine protons at the 3 position of bipy (rings a–d) of **1** and **3** relative to those of the pyridine ring of dps in **2** and **4**. The last shift may be also due to a steric interaction between the $H^{3''}$ protons of the coplanar rings. The assignment of the proton pyrazine signals of pzpys follows from COSY spectra as well as the splitting patterns.[20] In fact when pzpys is co-ordinated to the ruthenium centre the H^3 and H^5 protons are not coupled to each other whereas they are coupled with H^6.

On comparing the ^1H NMR spectra of compounds in which pzpys is monodentate with those of compounds containing chelated pzpys, we observe (Table 1) that the H^6 pyrazine protons of **1**–**4** fall in the range δ 8.3–8.5 whereas in **6** and **7** these resonances are shifted to lower frequencies in agreement with the N^1 co-ordination of the pyrazine ring and as a consequence of the diamagnetic anisotropic effect of the adjacent ring of bipy (or phen). A similar effect, when pzpys is chelated, shields the $H^{6'}$ proton of the pyridine ring of pzpys. Conversely the H^3 proton resonances, which for the chelated compounds **6** and **7** are observed at high frequencies (δ 9.04 and 9.05, respectively), are shifted to lower frequencies for complexes **1**–**4**. All the above results suggest that in **6** and **7** pzpys is chelated to the ruthenium centre through the N^1-pyrazine and the N-pyridine atoms, while in **1**–**4** co-ordination occurs *via* the N^4 atom of the pyrazine ring. Furthermore, broad signals for the H^3 and H^5 protons in the ^1H NMR spectra of **1** and **3** suggest that a rotation of the pyrazine ring around the Ru–N^4 bond is operative. Unfortunately this process is not frozen even at low temperature.

In the ^{13}C NMR spectra of complexes **1** and **3** the $C^{6''}$, $C^{4''}$, $C^{5''}$ and $C^{3''}$ signals of bipy are in the ranges δ 154.5–152.0, 139.0–136.5, 128.0–126.5 and 125.0–123.5, respectively. In the spectrum of the dicationic compound **6** the above carbon atoms are significantly deshielded in accordance with the increasing transfer of electron density from bipy to the metal. Also in the dps derivatives (**2**–**4**) the pyridine carbons are deshielded as observed in similar compounds.[9a]

The ^{13}C NMR spectra confirm the co-ordination mode of pzpys in compounds **1**–**4**, **6** and **7**. The pyridine and pyrazine carbon signals of pzpys were assigned with the help of C–H correlation experiments (Fig. 3). The N(1) co-ordination of pyrazine and the N co-ordination of pyridine in chelated compounds **6** and **7** deshield the C^6 pyrazine and $C^{6'}$ pyridine carbons. In particular, the pyrazine C^6 signals are up to 6 ppm higher than that of free pzpys. Furthermore the C^6 carbons are deshielded with respect to the C^3 and C^5 pyrazine carbons, whereas in the monodentate compounds the opposite trend occurs (Fig. 3).

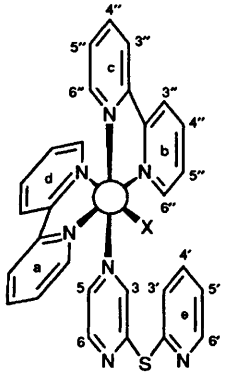


Fig. 2 View of the $[Ru(bipy)_2(pzpys)X]^+$ cation in complexes **1** and **3** with atomic numbering

Electronic spectroscopy

The UV/VIS absorption maxima of the complexes are reported in Table 3. The spectra of all compounds contain intense absorptions in the range 295–220 nm assigned as π ⟶ π* ligand transitions. They also contain lower-energy bands assigned as metal-to-ligand charge-transfer (m.l.c.t.) transitions. For the mononuclear compounds containing monodentate pzpys the absorption spectra are similar to those of the corresponding pyrazine compounds.[3a,b] In particular the m.l.c.t. bands for $[Ru(bipy)_2(pzpys)Cl][PF_6]$ are observed at 478, 458, 393 and 335 nm and the same number of bands of similar energy are observed for $[Ru(bipy)_2(pyz)Cl][PF_6]$ (pyz = pyrazine).[3a] Moreover the band at 393 nm can be assigned to the d ⟶ π*(pzpys) transition just as that at 385 nm for the pyrazine derivative is assigned to the d ⟶ π* (pyrazine) transition. For the $[Ru(dps)_2(pzpys)Cl][PF_6]$ and $[Ru(dps)_2(pzpys)(NO_2)][PF_6]$ complexes blue shifts of the m.l.c.t. bands (415 and 373 nm, respectively) are observed

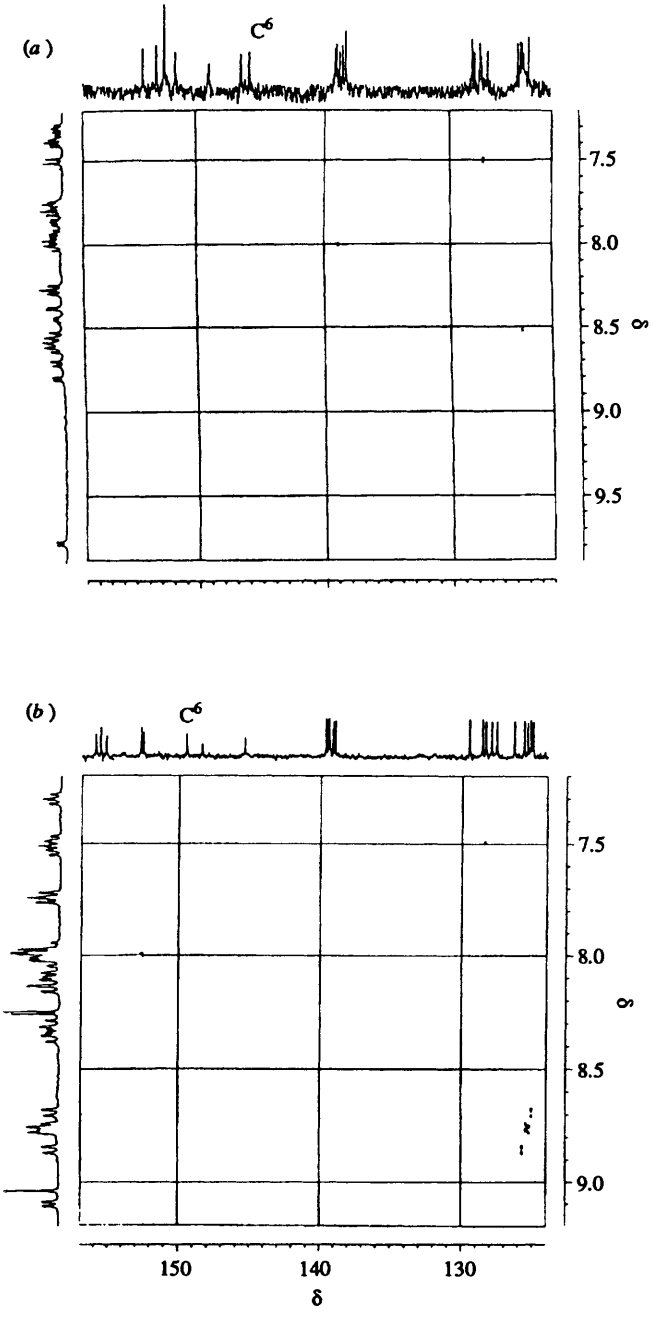


Fig. 3 The C–H correlation NMR spectra of $[Ru(bipy)_2(NO_2)(pzpys)][PF_6]$ (*a*) and $[Ru(bipy)_2(pzpys)][PF_6]_2$ (*b*)

Table 3 The UV/VIS data for ruthenium pyrazin-2-yl 2-pyridyl sulfide complexes in MeCN

Complex	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})
1	478 (11.4), 458 (sh), 393 (8.0), 335 (10.6), 292 (65.6), 241 (32.9)
2	415 (15.8), 287 (36.4), 241 (20.8)
3	438 (11.0), 380 (sh), 330 (sh), 286 (55.2), 243 (28.5)
4	373 (12.7), 274 (26.9)
5	320 (sh), 292 (26.3)
6	441 (13.9), 285 (58.9), 243 (25.7)
7	435 (16.0), 410 (sh), 263 (87.0), 223 (70.0)
8	540 (25.5), 450 (17.7), 288 (91.6), 244 (41.9)
9	523 (17.5), 439 (18.8), 286 (98.5), 243 (47.4)
10	536 (21.0), 438 (21.4), 263 (135.4), 222 (113.8)
11	538 (26.9), 441 (22.2), 390 (sh), 290 (78.7), 263 (108.5)

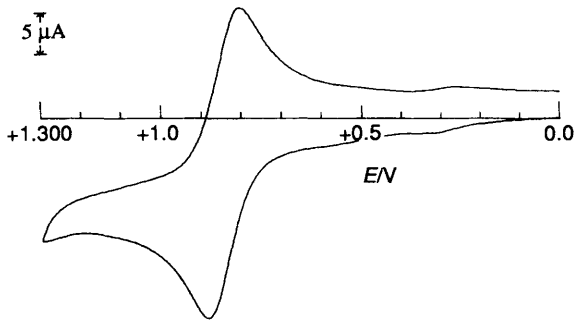


Fig. 4 Cyclic voltammogram recorded at a platinum electrode for a MeCN solution containing complex **1** (1.4×10^{-3} mol dm^{-3}) and $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}). Scan rate 0.2 V s^{-1}

with respect to those of the bipy derivatives in agreement with the suggestion that the dps ligand[9a] is a weaker π acceptor than bipy. Similar bands assigned as $d_\pi(Ru) \longrightarrow \pi^*$ (dps) transitions have been previously observed for $[Ru(dps)_2(pyz)X][PF_6]$ complexes (X = Cl or NO_2).[9a] These spectral similarities indicate that the electronic environment at the ruthenium(II) site is little changed by substitution of pyrazine by the monodentate pzpys ligand. Although the exact position of the $d \longrightarrow \pi^*$(pzpys) transitions for the complexes $[Ru(bipy)_2(pzpys)][PF_6]_2$ and $[Ru(phen)_2(pzpys)][PF_6]_2$ is masked by intense $d \longrightarrow \pi^*$(bipy) or $d \longrightarrow \pi^*$(phen) transitions, the slight blue shifts of the last bands with respect to those of $[Ru(bipy)_3][PF_6]_2$ and $[Ru(phen)_3][PF_6]_2$[8a] suggest that chelated pzpys is a comparable π-acceptor ligand to bipy (or phen). The spectra of the binuclear compounds are consistent with this. In particular, in the spectrum of $[(bipy)_2Ru(pzpys)Ru(bipy)_2Cl][PF_6]_3$ the band observed at 540 nm can be assigned to the $d \longrightarrow \pi^*$(pzpys) transition. The red shift of this band with respect to those of the mononuclear compounds **1** and **6** is attributed to stabilization of the m.l.c.t. excited state by the positive charge of the remote ion. In addition complex **8** exhibits another m.l.c.t. band at 450 nm {452 nm for $[Ru(bipy)_3][PF_6]_2$} in accord with the suggestion that pzpys and bipy are comparable π-acceptor ligands and evidencing that the $d \longrightarrow \pi^*$(bipy) transition is not influenced by the remote ion. Similar considerations apply on comparing the bi- and mono-nuclear chelated compounds containing 1,10-phenanthroline. The energy of the m.l.c.t. bands of both the bipy and dps derivatives is dependent on the nature of the ligand *cis* with respect to pzpys. In fact blue shifts are observed on replacing Cl^- by a stronger π-acceptor ligand such as NO_2 or NO. Also in the spectrum of the binuclear compound $[(bipy)_2Ru(pzpys)Ru(bipy)_2(NO_2)][PF_6]_3$ the m.l.c.t. bands, assigned as $d \longrightarrow \pi^*$ transitions (pzpys, 536 nm, bipy 438 nm) are blue shifted with respect to those of the corresponding compound containing Cl.

Electrochemistry

A preliminary electrochemical investigation of the redox properties of the present complexes has been performed on the mononuclear derivatives **1**–**3**, **6** and the binuclear species **8**.

Fig. 4 shows the cyclic voltammetric anodic profile exhibited by complex **1** in acetonitrile solution. As confirmed by controlled-potential coulometry (E_w = +1.1 V), this process involves a chemically reversible one-electron removal, which we confidently assign to the Ru^{II}–Ru^{III} couple. Closely grouped reduction waves typical of processes centred on the π-conjugated ligand are present in the cathodic region from −1.3 to −2.0 V.[21]

Analysis[22] of the cyclic voltammetric responses corresponding to the anodic process at various scan rates from 0.02 to 2.00 V s^{-1} shows that the i_{pc}/i_{pa} ratio is constantly equal to 1 : 1, $i_{pa}v^{-\frac{1}{2}}$ is substantially constant and the peak-to-peak separation progressively increases from 82 to 216 mV. Taking into account that under the same experimental conditions the electrochemically reversible oxidation of ferrocene ($E^{o\prime}$ = +0.38 V) exhibits a progressive ΔE_p increase from 67 to 128 mV, these features are diagnostic of an electrochemically quasi-reversible Ru^{II}–Ru^{III} electron transfer. Significant geometrical reorganization probably occurs upon removing one electron from complex **1**.[23]

Although qualitatively similar behaviour is displayed by complexes **2**, **3** and **6** in cyclic voltammetry, there are some significant differences as far as controlled-potential macroelectrolysis experiments are concerned. In the case of complexes **2** and **3** their electrogenerated dications are not completely stable and decompose to oxidizable species with an overall consumption of two electrons per molecule. On the other hand, the oxidized product of **6** apparently undergoes self-reduction, in that the electrolysis current progressively decreases with time, but after one electron per molecule the residual current remains higher than the background current and even after the consumption of three electrons it does not disappear, although cyclic voltammetric tests coupled to direct-current voltammograms at a platinum electrode with periodical renewal of the diffusion layer do not reveal the presence of unknown species.

Table 4 summarizes the formal electrode potentials for Ru^{II}–Ru^{III} oxidation of all the complexes studied. Comparison between **6** and $[Ru(bipy)_3]^{2+}$ indicates that the new ligand pzpys is somewhat more electron withdrawing than is bipy.

Fig. 5 illustrates the anodic profile of the binuclear complex **8**. Step-by-step controlled-potential coulometric tests show that each oxidation process involves one eletron per molecule. Both processes are chemically reversible and their redox potentials are included in Table 4. Since these anodic steps are assigned to the sequence $Ru^{II}Ru^{II}$–$Ru^{II}Ru^{III}$–$Ru^{III}Ru^{III}$, which is rather common for polypyridylruthenium complexes,[24] a K_{com} of 2×10^9 is computed, which allows the mixed-valence $Ru^{II}Ru^{III}$ complex to be classified as a completely delocalized Robin-Day Class III compound.[25]

Table 4 Electrochemical characteristics for the oxidation processes exhibited in MeCN

Complex	$E^{o\prime}{}_1$/V	$\Delta E_p{}^a$/mV	$i_{pc}/i_{pa}{}^a$
1	+0.85	102	1
2	+0.97	82	0.9
3	+1.09	112	0.4
6	+1.38	84	1
8[b]	+0.90	72	1
$[Ru(bipy)_3]^{2+}$	+1.29[c]	60[c]	1

[a] Measured at 0.2 V s^{-1}. [b] Also $E^{o\prime}{}_2$ = +1.45 V, ΔE_p = 90 mV and i_{pc}/i_{pa} = 1 : 1. [c] From ref. 21.

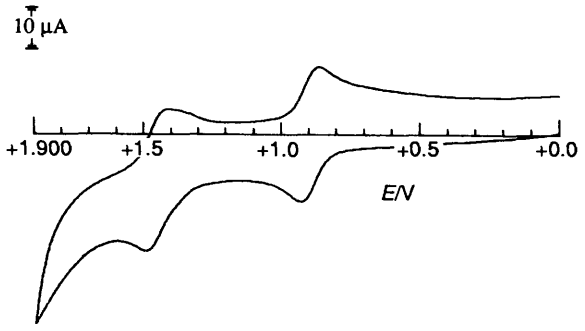


Fig. 5 Cyclic voltammogram recorded at a platinum electrode for a MeCN solution containing complex **8** (0.5×10^{-3} mol dm^{-3}) and $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}). Scan rate 0.5 V s^{-1}

Conclusion

The data reported indicate that pzpys acts as a very interesting bridging ligand which has a conformation (**A**) favouring one-step or stepwise assembly of RuL_2 and RuL_2X subunits. This is an interesting way to obtain asymmetric binuclear species containing significantly different ruhenium centres. It remains to be established if such differences between the ruthenium polypyridine subunits may play a role in determining selectivity in reactions like the oxidation of polynuclear complexes. Preliminary results show that the complex $[(bipy)_2Ru(pzpys)Ru(bipy)_2Cl][PF_6]_3$ undergoes single-electron oxidation to give a stable mixed-valence compound.

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