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FULL PAPER

Synthesis, structure and redox properties of a new ruthenium(II) complex containing the flexible tridentate ligand *N*,*N*-bis(2-pyridylmethyl)ethylamine, *cis-fac*-Ru(bpea)$_2^{2+}$, and its homologue attached covalently to a polypyrrole film †

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New ruthenium complexes bearing tridentate ligands of general formula *cis-fac*-[Ru^{II}L$_2$][PF$_6$]$_2$ (L = *N*,*N*-bis(2-pyridylmethyl)ethylamine (bpea) **1** or *N*-[3-bis(2-pyridylmethyl)aminopropyl]pyrrole (bpea-pyr) **2**) have been prepared following two different synthetic routes. They have been characterised by elemental analyses, UV-Vis and ^{1}H NMR spectroscopy. Furthermore, the crystal structure of complex **1** has been solved. The Ru is co-ordinated in a distorted octahedral fashion by six N atoms of two bpea ligands which occupy opposite faces of the octahedron. The aliphatic N atoms of the bpea ligands are co-ordinated in a *cis* fashion. 1-D together with 2-D NMR spectra show that in solution **1** has the same structure as in the solid state and that complex **2** has the same structural arrangement. The redox properties of **1** and **2** have been investigated by cyclic voltammetry and coulometry. In the anodic region, the pyrrole group of complex **2** polymerises forming a modified electrode containing **Pt/poly-2**. This new material has been characterised by electrochemical techniques and displays a remarkable chemical and electrochemical stability.

Introduction

Nowadays many research groups are developing the synthetic chemistry related to ruthenium complexes because of their multiple applications in many different scientific fields. Ruthenium complexes containing polypyridyl ligands are widely used for photophysical studies due to the formation of long lived excited states.[1] They are also widely used as catalysts for a variety of purposes including hydrogenation, oxidation, isomerisation, nucleophilic addition to multiple bonds and carbon–carbon bond formation.[2] On the other hand, ruthenium complexes have recently been studied increasingly from a bioinorganic perspective[3] for instance the interaction with DNA sequences.

The heterogenisation of complexes is of interest because it can dramatically improve performance with regard to their homogeneous use and also because it allows one to build tailored solid devices with new applications, for instance molecular photoelectrodes.[4] Thus a variety of different strategies to heterogenise ruthenium complexes, without modifying the intrinsic properties of the original complex, have been developed. Those which involve polymerisation of a spectator group, *e.g.* pyrrole, attached covalently to one or several ligands have been shown to lead to high chemical and electrochemical stability.[5]

In this paper we present the synthesis, spectroscopic and electrochemical characterisation of new ruthenium complexes [Ru(bpea)$_2$][PF$_6$]$_2$ **1** (bpea is the tridentate facial ligand *N*,*N*-bis(2-pyridylmethyl)ethylamine) and [Ru(bpea-pyr)$_2$][PF$_6$]$_2$ **2** (bpea-pyr is the ligand *N*-[3-bis(2-pyridylmethyl)aminopropyl]-pyrrole; bpea-pyr is a new ligand which is similar to bpea but with the ethyl group substituted by a *N*-propylpyrrole group (see Chart 1). Exposing **2** to a sufficiently positive potential produces the electrochemical polymerisation of the pyrrole group, generating new modified electrodes which have also been electrochemically characterised.

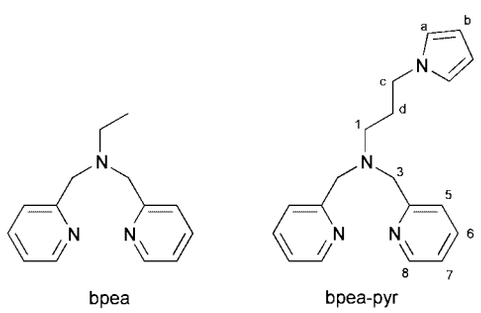


Chart 1 The ligands.

Experimental

Materials and methods

The preparations of bpea[6] and *N*-(3-aminopropyl)pyrrole[7] and the complexes [Ru$_2$Cl(MeCO$_2$)$_4$]$_n$,[8a,b] [RuCl$_3$(bpea)] and [RuCl$_3$(bpea-pyr)][8f] and [Ru(terpy)$_2$][PF$_6$]$_2$ (terpy = 2,2′ : 6′,2″-terpyridine)[8g] have been described.

† Electronic supplementary information (ESI) available: COSY and NOESY NMR spectra of complex **1** and NOE assignments; detailed structural description of **1**. See http://www.rsc.org/suppdata/dt/a9/a909511j/

Infrared spectra were recorded on a Mattson Satellite FTIR spectrometer as KBr pellets, electronic absorption spectra on a Hewlett-Packard 8452A diode array spectrophotometer equipped with a Compaq 286 Computer and a Citizen 120 D printer. Lifetime measurements were carried out in a QUANTA-Master (PTI) instrument at 293 K using either 410 or 608 nm excitation wavelengths. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker 200 or 400 MHz spectrometers using TMS as internal standard. Chemical shifts are reported downfield from the standard in ppm. The FAB mass chromatograms were obtained on a Fisons V6-Quattro instrument. C, H and N elemental analyses were performed using a CHNS-O Elemental Analyser from Fisons.

All electrochemical experiments and the preparation of the modified electrodes were done in an argon atmosphere in a glove-box using a standard three-electrode electrochemical cell. All potentials were referred to a Ag–10 mM Ag^I reference electrode in acetonitrile–tetrabutylammonium perchlorate electrolyte. The working electrode was a platinum disk (5 mm diameter) systematically polished with 1 μm diamond paste.

The purification of NBu_4ClO_4 has been described previously.[9] The electrochemical measurements were carried out using an EG&G PAR MODEL 173 potentiostat equipped with a model 179 digital coulometer and a model 175 programmer with output recorded on a Sefram TGM 164 X-Y recorder.

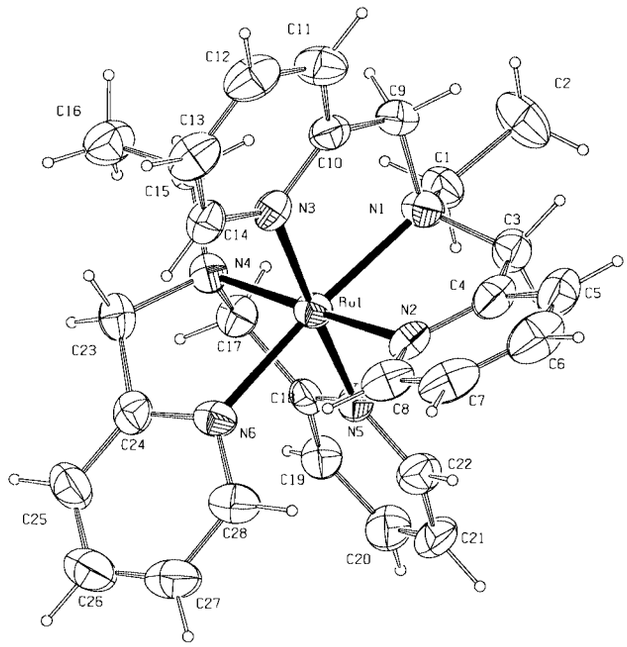


Fig. 1 An ORTEP view (thermal ellipsoids at 50% probability) of the molecular structure of the cation of $[Ru(bpea)_2][PF_6]_2$ **1**.

Preparation of ligands and complexes

bpea-pyr. To an aqueous solution (40 ml) of pyridylmethyl chloride hydrochloride (8.20 g, 0.05 mol) was added *N*-(3-aminopropyl)pyrrole (3.10 g, 0.025 mol). The mixture was stirred and heated to 60 °C. To this solution was added, over 1 h, 10 ml of an aqueous solution of NaOH (4.00 g, 0.010 mol). The brown mixture was stirred for 30 minutes and then cooled to room temperature. The mixture was extracted with chloroform and the brown extract concentrated by rotary evaporation to an oil. The oil was dissolved in 8 ml of chloroform and absorbed on basic alumina (80–200 mesh). Elution with chloroform followed by solvent reduction at low pressure generated a yellow oil. Yield: 5.3 g (69.3%). Calc. for $C_{19}H_{22}N_4{\cdot}0.4H_2O$: C, 72.8; H, 7.3; N, 17.9. Found: C, 72.9; H, 7.3; N, 17.6%. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.55 (d, 2, *J*(H8H7) = 4.8, H8), 7.55 (td, 2, *J*(H6H7) = 7.6, *J*(H6H5) = 1.5, H6), 7.40 (d, 2, *J*(H5H6) = 7.8, H5), 7.15 (ddd, 2, *J*(H7H5) = 1.2, H7), 6.54 (t, 2, *J*(HaHb) = 2.2, Ha), 6.10 (t, 2, Hb), 3.87 (t, 2, *J*(HcHd) = 7.0, Hc), 3.84 (s, 4, H3), 2.61 (t, 2, *J*(H1Hd) = 7.0 Hz, H1) and 1.99 (qnt, 2, Hd). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 158.89 (C4), 148.42 (C8), 135.67 (C7), 122.38 (C5), 121.34 (C6), 119.70 (Ca), 107.28 (Cb), 59.88 (C3), 50.76 (C1), 46.66 (Cc) and 28.59 (Cd). The NMR assignments for this ligand and for the following complexes is keyed in Chart 1 and in the crystal structure displayed in Fig. 1. MS (FAB positive): *m*/*z* 307 (M + 1).

***cis-fac*-[Ru(bpea)$_2$][PF$_6$]$_2$·1.5H$_2$O (1·1.5H$_2$O).** This complex was prepared following two different routes.

Method A. A 0.050 g (0.105 mmol) amount of $[Ru_2Cl(MeCO_2)_4]_n$ was added to 0.071 g (0.315 mmol) of the bpea ligand dissolved in 5 ml of MeOH at 25 °C. The solution was then stirred for 3 days at room temperature during which an intense red-violet colour appeared. Addition of an aqueous solution of NH_4PF_6 produced a yellow solid that was filtered off, washed with CH_2Cl_2 and dried in vacuum. Yield: 57.6 mg, 32%. Calc. for $C_{28}H_{37}F_{12}N_6O_{1.5}P_2Ru$: C, 38.5; H, 4.2; N, 9.6. Found: C, 38.6; H, 4.2; N, 9.4%. ^{1}H NMR (d_3-acetonitrile, 400 MHz): δ 8.60 (d, 2, *J*(H8H7) = 5.80, H8), 8.29 (d, 2, *J*(H14H13) = 5.04, H14), 7.76 (t, 2, *J*(H7H6) = 7.40, H6), 7.64 (t, 2, *J*(H13H12) = 7.40, H12), 7.54 (d, 2, *J*(H6H5) = 7.56, H5), 7.20 (t, 2, H7), 7.16 (d, 2, *J*(H12H11) = 7.88, H11), 7.11 (t, 2, H13), 4.58 (d, 2, *J*(H9BH9A) = 18.00, H9B), 4.53 (d, 2, *J*(H3AH3B) = 15.64, H3B), 4.28 (d, 2, H9A), 4.22 (d, 2, H3A), 3.59 (dq, 2, *J*(H1AH1B) = 13.92, *J*(H1BHMe) = 6.96, H1B), 2.90 (dq, 2, *J*(H1AHMe) = 6.96 Hz, H1A) and 1.28 (t, 3, Me). $E_{1/2}(CH_3CN)$ = 0.79 V.

Method B. A 0.375 g (0.880 mmol) sample of $[RuCl_3(bpea)]$ was added to a 100 ml EtOH–water (3 : 1) solution followed by 0.18 ml (1.32 mmol) of NEt_3 under an argon atmosphere. The resulting dark green mixture was then allowed to stir at room temperature for twenty minutes. Afterwards a 0.200 g (0.880 mmol) amount of bpea dissolved in 2 ml of EtOH was added and the mixture heated at reflux for a 3 h. The mixture was allowed to cool to room temperature and the volume reduced to approximately 25 ml under reduced pressure with a rotary evaporator. The mixture was then filtered and upon adding 2 ml of a saturated aqueous solution of NH_4PF_6 a brownish solid immediately precipitated. A yellow solid was obtained upon recrystallisation from MeCN–diethyl ether. Yield: 0.474 g, 61.8%. Analytical and spectroscopic data for complex **1** prepared following this route are in perfect agreement with those obtained by route A.

***cis-fac*-[Ru(bpea-pyr)$_2$][PF$_6$]$_2$·3H$_2$O (2·3H$_2$O).** This complex was also prepared following two different routes.

Method A. A 0.100 g (0.210 mmol) amount of $[Ru_2Cl(MeCO_2)_4]_n$ was added to 0.128 g (0.420 mmol) of bpea-pyr ligand dissolved in 10 ml of MeOH at 25 °C. The solution was stirred for 3 days at room temperature during which an intense brown-violet colour appeared. Addition of an aqueous solution of NH_4PF_6 produced a dark brown solid that was filtered off, washed with MeOH and dried in vacuum. Yield: 107.2 mg, 25%. Calc. for $C_{38}H_{50}F_{12}N_8O_3P_2Ru$: C, 43.2; H, 4.8; N, 10.6. Found: C, 43.3; H, 4.9; N, 10.4%. ^{1}H NMR (d_3-acetonitrile): δ 8.56 (d, 2, *J*(H8H7) = 5.76, H8), 8.20 (d, 2, *J*(H14H13) = 5.36, H14), 7.73 (t, 2, *J*(H7H6) = 7.26, H6), 7.65 (t, 2, *J*(H13-H12) = 7.78, H12), 7.48 (d, 2, *J*(H6H5) = 7.72, H5), 7.17 (t, 2, H7), 7.15 (d, 2, *J*(H12H11) = 7.84, H11), 7.07 (t, 2, H13), 6.57 (t, 2, *J*(HaHb) = 2.08, Ha), 5.99 (t, 2, Hb), 4.45 (d, 2, *J*(H3AH3B) = 15.80, H3B), 4.24 (s, 4, H9A,H9B), 4.04 (d, 2, H3A), 3.91 (t, 4, *J*(HcHd) = 6.44, Hc), 2.85 (dt, 2, *J*(H1A-H1B) = 11.56, *J*(H1BHd) = 5.32, H1B), 2.42 (dt, 2, *J*(H1A-Hd) = 5.32, H1A) and 2.20 (m, 4, Hd).

Method B. A 0.185 g (0.360 mmol) sample of $[RuCl_3(bpea-pyr)]$ was added to a 100 ml EtOH–water (3 : 1) solution followed by 0.075 ml (0.540 mmol) of NEt_3 under an argon

atmosphere. The resulting dark green mixture was allowed to stir at room temperature for twenty minutes. Afterwards a 0.110 g (0.360 mmol) amount of bpea-pyr dissolved in 3 ml of EtOH was added and the mixture heated at reflux for 3.5 h. It was then allowed to cool to room temperature and the volume reduced to approximately 20 ml under reduced pressure with a rotary evaporator. The mixture was then filtered and upon adding 2 ml of a saturated aqueous solution of NH_4PF_6 a brownish solid immediately precipitated out of the solution which was recrystallised from MeCN–diethyl ether. Yield: 0.235 g, 61.7%. Analytical and spectroscopic data for complex **2** prepared following this route are in perfect agreement with those obtained by route A.

Crystallography

Suitable crystals of complex **1**·1.5MeCN were grown by diffusion of diethyl ether into an acetonitrile solution to give pale yellow blocks. Intensity data were collected on a Stoe Image Plate Diffraction system using Mo-Kα graphite monochromated radiation. A summary of the data collection and structure solution is given in Table 1.

CCDC reference number 186/1927.

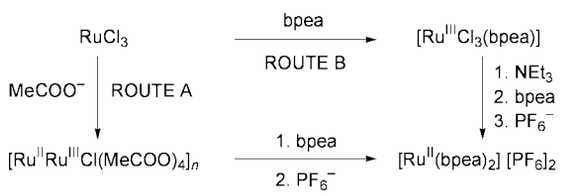
See http://www.rsc.org/suppdata/dt/a9/a909511j/ for crystallographic files in .cif format.

Results and discussion

Synthesis, structure and stereoisomeric analysis

The new bpea-pyr ligand is prepared in an analogous manner to that for bpea. They are prepared by treating 2-pyridylmethyl chloride with *N*-(3-aminopropyl)pyrrole or ethylamine respectively followed by neutralisation with sodium hydroxide and extraction with trichloromethane.

Complexes **1** and **2** have been prepared using $RuCl_3$ as the starting material following two different synthetic routes, as outlined in Scheme 1. In route A the polymeric complex $[Ru^{II}Ru^{III}Cl(MeCO_2)_4]_n$, which has a paddle-wheel structure, is used as intermediate. This complex is obtained when treating $RuCl_3$ with a mixture of acetic acid and sodium acetate in methanol. Its reaction with the bpea or bpea-pyr ligand in MeOH at room temperature produces complexes **1** and **2** respectively. This reaction involves a one electron reduction of the Ru^{II}–Ru^{III} precursor, cleavage of a Ru–Ru bond of order 2.5 and substitution of all bridging carboxylate ligands by bpea.[8a,e] In route B the $[Ru^{III}Cl_3(bpea)]$ complex[8f] is used as intermediate which is obtained by the reaction of $RuCl_3$ and the bpea ligand in a methanolic solution (yield: 58%). The $[Ru^{III}Cl_3(bpea)]$ complex is then treated with NEt_3, which acts as a reducing agent, and further addition of bpea yields the $[Ru^{II}(bpea)_2]^{2+}$ complex.



Scheme 1

Complex **1** has been characterised by single-crystal X-ray diffraction analysis. Table 1, contains crystallographic data, Table 2 selected bond distances and angles. Fig. 1 displays the ORTEP[10] diagram together with the crystallographic numbering scheme for the cation of complex **1** that crystallises in the monoclinic space group *A*2/*n* with eight molecules per unit cell. The Ru atom is co-ordinated by six nitrogen atoms from two facially co-ordinated bpea ligands in an octahedrally distorted fashion. The different electronic nature of the aliphatic and aromatic N-co-ordinating atoms of the bpea ligands induces geometrical distortions from the ideal octahedral geometry which are mainly manifested in the presence of significantly different Ru–N bond lengths. Indeed, all six Ru–N bond distances are different although they are similar to those reported previously for related ruthenium complexes.[8g,11] The two longest correspond to the Ru–N (aliphatic) bonds (Ru–N1 2.148(4), Ru–N4 2.139(3) Å)[11a–c] while the two shortest correspond to the Ru–N (aromatic) bonds *trans* to the other Ru–N (aromatic) bond (Ru–N3 2.053(3), Ru–N5 2.068(3) Å)[8g,11d] consistent with the presence of small Ru–N back bonding. The other two Ru–N bond distances, the Ru–N (aromatic) *trans* to the Ru–N (aliphatic) bond, lie in between (Ru–N6 2.082(4), Ru–N2 2.094(3) Å). The spatially constrained nature of the tridentate facial bpea ligand also produces geometrical distortions from the ideal octahedron which are chiefly manifested in the NRuN bond angles (a more detailed structural description is available as supplementary material).†

The flexibility of the N-co-ordinating arms of the tridentate bpea or bpea-pyr ligands allows them to act as meridional[12] and also as facial ligands when co-ordinating to transition metal complexes. In the present case both ligands co-ordinate in a facial fashion as shown by X-ray crystallography for **1** (Fig. 1) and by ^1H NMR analysis for **1** and **2** (see below).

Facial co-ordination of two bpea ligands to a ruthenium(II) centre with an octahedral type of symmetry can take place so that the amino nitrogens are situated *cis* or *trans* with regard to one another. If the two amino nitrogens co-ordinated in a *trans* fashion then the molecule would have a plane of symmetry that would contain the Ru atom and the two amino N atoms thus transforming the aromatic pyridyl rings of each ligand. The molecule would also have an inversion centre that would transform pyridyl rings of different bpea ligands. As a result all the aromatic rings would end up being equivalent and therefore only one set of aromatic resonances would be observed in the NMR. The fact that both complexes **1** and **2** display two sets of aromatic signals (Fig. S1 of supplementary material and Fig. 2) clearly indicates that for **1** the solid state structure is basically

Table 1 Crystal data for the complex $[Ru^{II}(bpea)_2][PF_6]_2$·1.5MeCN (**1**·1.5MeCN)

Empirical formula	$C_{31}H_{38.5}F_{12}N_{7.5}P_2Ru$
Formula weight	907.20
Crystal symmetry	Monoclinic
Space group	*A*2/*n*
a/Å	15.4749(13)
b/Å	11.6232(6)
c/Å	41.920(4)
β/°	97.861(10)
V/Å^3	7469.3(10)
Formula units per cell	8
T/K	223(2)
λ(Mo-Kα)/Å	0.71073
μ/mm^{-1}	0.600
R^a	0.0426
$R_w{}^b$	0.0753

Table 2 Selected bond lengths (Å) and angles (°) for the complex $[Ru(bpea)_2][PF_6]_2$·1.5MeCN (**1**·1.5MeCN)

Ru(1)–N(3)	2.053(3)	Ru(1)–N(2)	2.094(3)
Ru(1)–N(5)	2.068(3)	Ru(1)–N(4)	2.139(3)
Ru(1)–N(6)	2.082(4)	Ru(1)–N(1)	2.148(4)
N(2)–Ru(1)–N(1)	79.38(14)	N(5)–Ru(1)–N(6)	81.04(13)
N(6)–Ru(1)–N(4)	80.22(14)	N(5)–Ru(1)–N(4)	82.35(13)
N(3)–Ru(1)–N(2)	80.26(12)	N(3)–Ru(1)–N(1)	82.82(14)
N(5)–Ru(1)–N(1)	93.93(13)	N(3)–Ru(1)–N(4)	95.36(12)
N(6)–Ru(1)–N(2)	99.42(15)	N(5)–Ru(1)–N(2)	102.11(13)
N(4)–Ru(1)–N(1)	101.41(13)	N(3)–Ru(1)–N(6)	102.31(14)
N(6)–Ru(1)–N(1)	174.50(13)	N(3)–Ru(1)–N(5)	175.61(13)
N(2)–Ru(1)–N(4)	175.44(13)		

Table 3 UV-Vis spectral data for the bpea and bpea-pyr ligands and for complexes **1** and **2**

Compound	Solvent	λ/nm	ε/M^{-1} cm^{-1}	Assignment
bpea	0.1 M HCl (water)	258	10274	π–π*
bpea-pyr	0.1 M HCl (water)	260	7406	π–π*
$[Ru(bpea)_2][PF_6]_2$	MeCN	250	18057	π–π*
		380	14472	dπ–π*
		566	167	d–d
$[Ru(bpea\text{-}pyr)_2][PF_6]_2$	MeCN	250	18107	π–π*
		380	12640	dπ–π*
		566	975	d–d

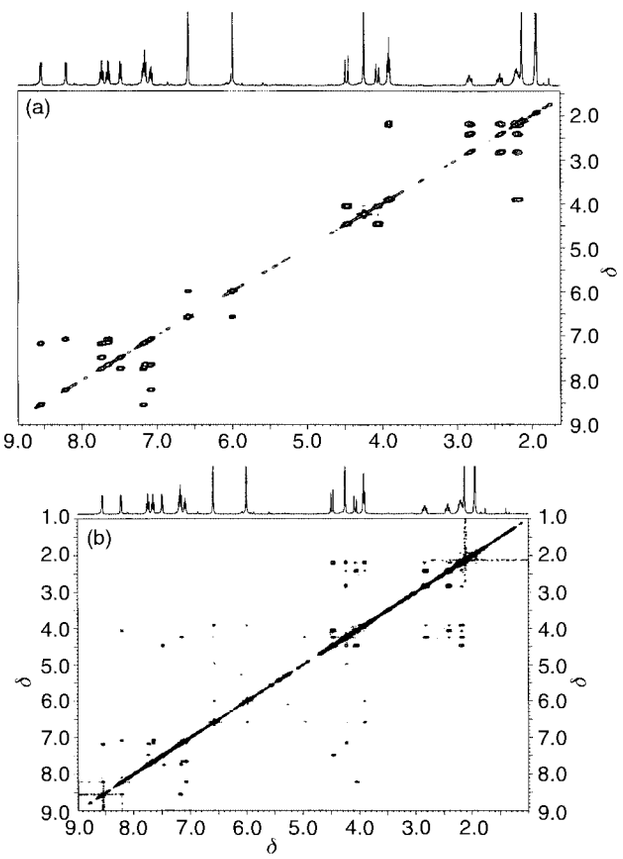


Fig. 2 ^{1}H NMR spectra of complex **2** in d_3-acetonitrile solution recorded on a Bruker 400 MHz instrument at 298 K. (a) COSY, (b) NOESY.

maintained in solution and that **2** has essentially the same structural arrangement as that of **1**.

The *cis* co-ordination of complex **1** (N1RuN4 bond angle of 101.41(13)°) transforms the aliphatic N atoms (N1 and N4) into two chiral centres. In the structure displayed in Fig. 1 they adopt the *S* configuration. Furthermore, since the molecule does not have any rotation axis the Ru also becomes a chiral centre. In the "free" bpea ligand the two pyridylmethyl arms are identical, thus the chirality of N1 and N4 arises from the relative location of the three co-ordination positions of the opposite facially co-ordinated bpea ligand. As a consequence of these restrictions, the *cis-fac* arrangement of $Ru(bpea)_2^{2+}$ gives rise to only two possible stereoisomers: the Λ-*S*-*S* and the Δ-*R*-*R* which are enantiomers. In the unit cell both isomers can be found in equal proportions and therefore a racemic mixture of **1** is obtained.

Spectroscopic properties

Fig. 2 displays both 1-D and 2-D ^{1}H NMR spectra of complex **2** registered in d_3-acetonitrile, which allow one unambiguously to assign its solution structure. The 2-D COSY map is presented in Fig. 2(a) whereas the 2-D NOESY is shown in Fig. 2(b) with the 1-D ^{1}H NMR spectrum on top. NMR spectra of complex **1** are available as supplementary material.†

The ^{1}H NMR spectrum of complex **2** in the δ 7.0–8.7 zone clearly shows eight separate resonances revealing the presence of only two distinct pyridyl rings. This indicates that the two bpea ligands are magnetically equivalent through a C_2 axis (contained in the equatorial plane where the N1, N2, N4 and N6 atoms are lying). This C_2 axis does not rigorously exist in the solid state, hence the different labelling for the two bpea ligands used in Fig. 1. The 2-D COSY spectrum, Fig. 2(a), allows one to assign the resonances of each pyridyl group as well as the hydrogen atoms belonging to the two distinct diastereotopic methylenic groups. It also allows one to identify fully the aliphatic chain linking the pyrrole group with the amine.

From the 2-D NOESY spectrum, Fig. 2(b), it is interesting that of the two resonances at δ 8.56 and at 8.20, which are due to the hydrogen atoms bonded to the carbon atoms in the alpha position with regard to the co-ordinating nitrogen atom, only one exhibits a NOE effect with protons of the aliphatic region. Examination of the crystal structure allows one to conclude that those two protons can only be H14 and H23A (d = 2.822 Å), thus there is an inter-ligand NOE effect. The information obtained from the 2-D COSY map together with that given by this NOE effect allows us unambiguously to assign all the resonances observed in the spectrum (a listing of all NOEs observed is available as supplementary material).†

Finally, the NOE pattern observed for complexes **1** and **2** is not compatible with the bpea ligands co-ordinating in a meridional fashion since in this geometry the aliphatic–aromatic inter-ligand NOE effect is not possible. This further corroborates that the solid state structure is also maintained in solution.

UV-Vis spectral features for the bpea and bpea-pyr ligands and for complexes **1** and **2** are summarised in Table 3. For the ligands only π–π* bands are observed above 250 nm. Both complexes present these bands at relatively similar energies and an intense and broad dπ–π* band at 380 nm due to a series of MLCT transitions and their vibronic components. Finally both complexes also have a low intensity band at 566 nm due to a forbidden d–d transition.[13] Lifetime measurements show that the MLCT based excited state of complex **1** ($t_{1/2}$ = 17.0 ns at 293 K, using an excitation wavelength of 410 nm) is comparable to that of other polypyridyl complexes of Ru like $[Ru(terpy)_2]^{2+}$ ($t_{1/2}$ = 4.6 ns at 293 K, using an excitation wavelength of 608 nm). These results indicate that a π delocalisation between the pyridyl units of polypyridyl ligands is not indispensable in order to achieve relatively long lived excited states.[13]

Redox chemistry and modified electrodes

The electrochemical behaviour of complexes **1** and **2** (1 mM) was investigated by means of cyclic voltammetry on platinum electrodes using 0.1 M NBu_4ClO_4 as the supporting electrolyte in acetonitrile. Fig. 3 summarises the most significant features of the electrochemical properties of complex **2** and its polymeric derivatives.

Complex **1** displays a single chemical and electrochemical reversible redox process at $E_{1/2}$ = 0.79 V ($E_{p,a}$ = 0.82 V, $E_{p,c}$ = 0.76 V, ΔE = 60 mV) which is assigned to the Ru^{III}–Ru^{II} redox

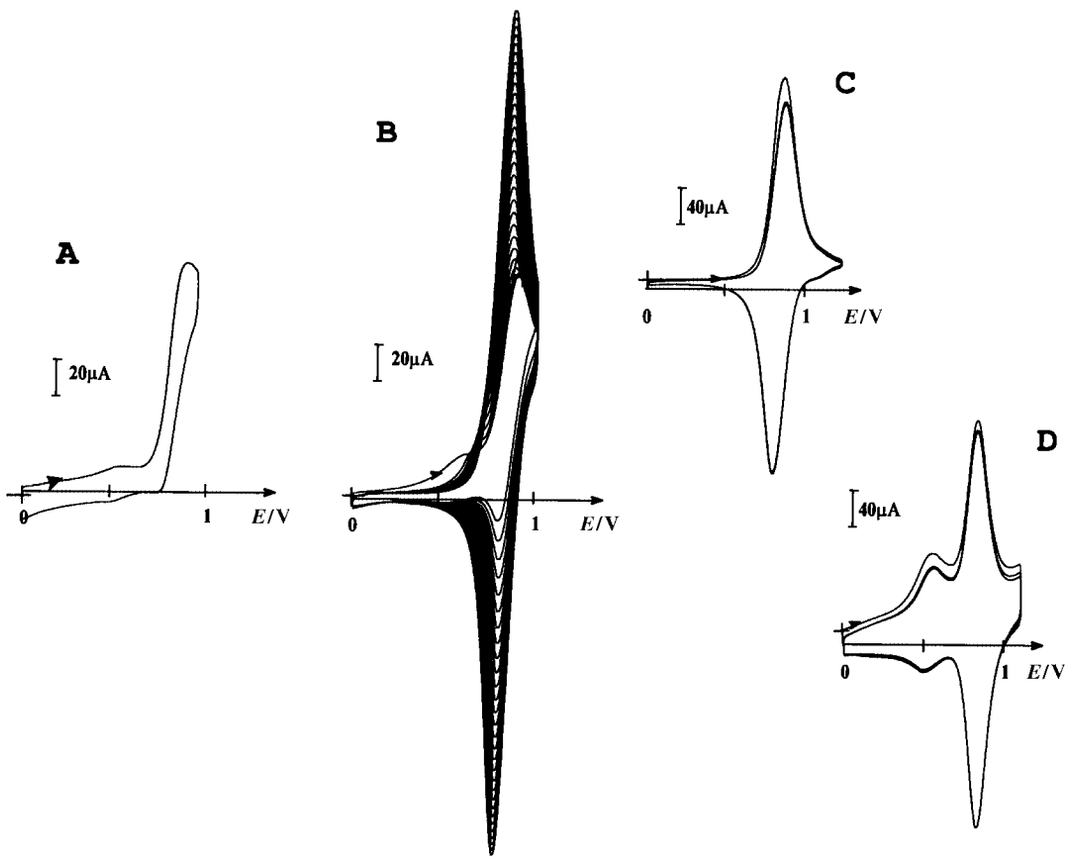


Fig. 3 Cyclic voltammograms at a platinum electrode (5 mm diameter) of complex **2** (1 mM) and **Pt/poly-2** in MeCN + 0.1 M NBu_4ClO_4 at $v = 0.1$ V s^{-1}. (A) Cyclic voltammetry of **2**, showing the first cycle. (B) Growth of a **Pt/poly-2** film by oxidative electropolymerisation of **2,** showing the following 29 repeated cyclic voltammetric scans between 0 and 1.0 V. (C) **Pt/poly-2** ($\Gamma = 9.78 \times 10^{-9}$ mol cm^{-2}) modified electrode after transfer to a clean electrolyte solution: first scan and several consecutive scans. (D) Cyclic voltammetry of **Pt/poly-2** film on a clean electrolyte solution, grown upon applying a constant potential of 0.8 V and passing a total charge of 3 mC: first scan and several consecutive scans.

couple. For related complexes[8g,14] like for instance $[Ru(terpy)_2][PF_6]_2$ this wave appears shifted to higher potentials by roughly 300 mV. This phenomenon is due to both a decrease of π-back bonding and an increase of the σ-bonding capacity of the bpea ligand *vs*. the terpy ligand. The one electron nature of the wave at 0.79 V was further corroborated by bulk electrolysis experiments ($E_{app} = 1.0$ V; 1.04 mol of electrons per mol of complex) that quantitatively formed the corresponding chemically stable ruthenium(III) species.

In sharp contrast, complex **2** presents a chemically irreversible redox process at $E_{p,a} = 0.92$ V (Fig. 3A) which is due to both the reversible oxidation of the Ru^{III}–Ru^{II} couple and the chemically irreversible oxidation of the pyrrole monomer with concomitant polymerisation to form the resulting modified electrode **Pt/poly[Ru(bpea-pyr)$_2$]$^{2+}$ (Pt/poly-2)**. Fig. 3B exhibits the growth of a film of the latter from **2**, by repeatedly scanning (30 times) over the 0.0–1.0 V potential range. As expected, the resulting modified electrode displays the regular electroactivity of the immobilised redox system but with no polypyrrole response except for a prepeak at the foot of the Ru^{III}–Ru^{II} couple. This prepeak is observed for the first 9 to 10 scans but then progressively fades away as the number of scans increases, and finally disappears. The prepeak phenomenon is a consequence of the weak conductivity of the polymer skeleton when the polypyrrole is obtained in an overoxidised form.[15] Fig. 3C shows the response of the **Pt/poly[Ru(bpea-pyr)$_2$]$^{2+}$** modified electrode upon transferring to a clean electrolyte solution. Again no electrochemical response is obtained for the polypyrrole backbone and only a wide wave due to the Ru^{III}–Ru^{II} redox couple is observed at $E_{1/2} = 0.83$ V ($E_{p,a} = 0.86$ V, $E_{p,c} = 0.80$ V, $\Delta E = 60$ mV). The film thus obtained is stable after repeatedly scanning over the potential range of 0 to 1.2 V. In the second scan the intensity of the anodic peak slightly decreases but in the following scans the intensity of both anodic and cathodic peaks remains practically constant for at least 15 cycles.

The **Pt/poly[Ru(bpea-pyr)$_2$]$^{2+}$** modified electrode can also be generated in a controlled-potential oxidation as shown by the cyclic voltammetric experiment of Fig. 3D. The best results were obtained by applying a constant potential of 0.8 V and a total charge of 3×10^{-3} Coulombs giving a film with an electropolymerisation efficiency of 18% and an apparent surface coverage of $\Gamma = 2.01 \times 10^{-9}$ mol cm^{-2}. Interestingly, under these low potential polymerisation conditions, the electroactivity of the polypyrrole polymer is clearly manifested in the form of a quasi-reversible peak system at $E_{1/2} = 0.53$ V ($E_{p,a} = 0.56$ V, $E_{p,c} = 0.50$ V, $\Delta E = 60$ mV) which is within the expected value for related polypyrrole modified electrodes.[5a,16] The other electroactive wave is due to the Ru^{III}–Ru^{II} couple that was also observed in the films obtained by repeated cyclic voltammetric scanning (see above). This new modified electrode is also stable under repeated scanning (for at least 30 cycles) in the potential range 0.0–1.1 V in a clean electrolyte solution as shown in Fig. 3D.

It is worth noting the high stability to repetitive voltammetry of the **Pt/poly[Ru(bpea-pyr)$_2$]$^{2+}$** modified electrode described in the present paper taking into account that there are only two pyrrole groups per metal center. The stability of this type of material generally improves on increasing the number of pyrrole groups per metal centre.[17]

In conclusion, two new ruthenium complexes (**1**, **2**) bearing flexible tridentate ligands have been prepared following two different synthetic routes. 1-D and 2-D NMR analysis allow us unambiguously to determine their structures in solution which coincide with that found for **1** in the solid state by X-ray diffraction analysis. The Ru atom has a distorted octahedral

geometry with the two bpea ligands co-ordinated in a facial fashion and with their aliphatic N atoms situated *cis* with respect to one another. The pyrrole group of complex **2** undergoes anodic polymerisation at platinum electrodes generating **Pt/poly-2,** which is a new, chemically and electrochemically stable, modified electrode.

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