A cautionary warning on the use of electrochemical measurements to calculate comproportionation constants for mixed-valence compounds†

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The redox potentials for successive oxidations in a series of ligand-bridged dinuclear ruthenium complexes are shown to be dependent on the identity of the anion used as the electrolyte in the electrochemical measurements. Since the differences between these redox potentials (ΔE_{ox}) are often used to calculate the comproportionation equilibrium constants (K_c) in mixed-valence species—and therefore the extent of inter-metal communication between the metal centres—the results demonstrate the need for extreme care in comparison of ΔE_{ox} data and of K_c values derived from them.

Introduction

Mixed-valence complexes have been widely studied because the optical transitions associated with intervalence charge transfer (IVCT) provide a significant insight into the barriers for electron transfer processes.[1,2] Dinuclear ruthenium complexes have received particular attention in this regard. In the comproportionation equilibrium between the mixed-valence form (designated [2,3] to indicate the respective oxidation states of the two metal centres Ru^{II}–Ru^{III}) and the fully-reduced ([2,2]) and fully-oxidised ([3,3]) forms

$$[2, 2] + [3, 3] \rightleftharpoons 2[2, 3]$$
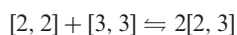
the comproportionation constant K_c is given by the expression

$$K_c = [2, 3]^2/[2, 2][3, 3]$$

When there is no interaction between the metal centres, $K_c = 4$ (the statistical value). However, if the interaction between the metal centres is reasonable, the value of K_c will be higher: a large K_c implies IVCT bands occur at low energy and are of high intensity. The M–M interaction decreases when the bridging ligand is lengthened, twisted or contains a saturated fragment.

K_c can be measured spectrally[3,4] or electrochemically, since

$$\Delta G^\circ = -RT(\ln K_c) = -nF(\Delta E_{ox})$$

where ΔE_{ox} is the separation between the two redox potentials for the successive oxidation processes.[5] The comparison of K_c values for dinuclear complexes has been used extensively as a measure of the stability of the mixed-valence species generated on one-electron oxidation of a dinuclear complex.

A large comproportionation constant, K_c — *i.e.* a substantial value of ΔE_{ox} — is also an essential requirement for the isolation of mixed-valence complexes. In an early investigation of the contributing factors to the magnitude of K_c in ligand-bridged dinuclear complexes of this type, Kaim *et al.*[6] studied a number of complexes with "linear" and "stepped" bridges, and concluded that the metal–metal distance (and the possibility of direct d–d overlap in the case of a small bridge) was unimportant compared with the π* (LUMO) characteristics of the ligand which allowed ligand-mediated interaction.

In subsequent studies, Kalyanasundaram and Nazeeruddin[7] and Giuffrida and Campagna[8] also considered the effect of the identity of the bridging ligand (BL) on electronic interactions in dinuclear complexes. They noted that the extent of electronic coupling depended on a number of factors—including the electronic nature of the bridge, the spectator ligands and the metal centres. Superexchange theory provides a theoretical approach for understanding the M–M interaction, and considers overlaps between metal orbitals with those of BL (through-bond interaction). Bridge-mediated electron transfer (which takes advantage of the LUMO's of bridge) and hole transfer (which takes advantage of HOMO's of bridge) may play a role in assuring electronic interaction (*i.e.* π-backbonding and σ-donation, respectively). Further, the nature of BL plays an important role in electronic coupling *via* through-space interaction by controlling distance and orientation of metal-containing units.

While ΔE_{ox} is a good measure of electronic communication (coupling) between the metal centers in homodinuclear systems, IVCT transitions, if observable, are a better indicator—particularly the intensity and bandwidth of the IVCT bands.[7] Nevertheless, the comparison of K_c values—determined from electrochemical data—has been widely used to assess the extent of inter-metal communication in dinuclear complexes.[5,7–9]

In our studies of the spectral and electrochemical characteristics of the stereoisomers of a range of ligand-bridged dinuclear ruthenium complexes, we have observed a substantial dependence of redox potentials on the identity of the anion used as the electrolyte in electrochemical measurements. Such effects have been reported previously by us[10] and others:[11] however, the implications in terms of comparison of K_c values seem not to be generally appreciated, and the present paper serves to draw attention to the dangers inherent in the use of electrochemical methods for determination of comproportionation contants.

Results and discussion

Geiger and coworkers have promoted the use of weakly-coordinating anions such as tetrakis(pentafluorophenyl)borate $\{B(C_6F_5)_4\}^-$,[12] and the use of solvents with low dielectric constants such as trifluoromethylbenzene (BTF),[13] as a means of probing the influence of possible ion-paring interactions on the potentials of successive redox couples in the oxidation of a number of species. They noted that the separation of successive waves for nickelocene [Cp_2Ni] was greater in BTF than in other media—a feature attributed to an increase in ion-pairing energies of the nickelocene dication with various electrolyte

DOI: 10.1039/b413980a

Table 1 Electrochemical data (in mV) for the dinuclear complexes [{Ru(bpy)$_2$}$_2$(μ-BL)]$^{n+}$ relative to the [FeCp$_2$]$^{0/+}$ couple in 0.02 mol dm^{-3} [(n-C$_4$H$_9$)$_4$N]{B(C$_6$F$_5$)$_4$}/CH$_3$CN, and 0.1 mol dm^{-3} [(n-C$_4$H$_9$)$_4$N]PF$_6$/CH$_3$CN

BL	Diastereoisomer	B(C$_6$F$_5$)$_4^-$				PF$_6^-$			
		$K_c{}^a$	$\Delta E_{ox}{}^b$	E_{ox2}	E_{ox1}	$K_c{}^a$	$\Delta E_{ox}{}^b$	E_{ox2}	E_{ox1}
bpm	*meso*	5230	220	1500	1280	1760	192	1384	1192
	rac	5230	220	1520	1300	1510	188	1380	1192
dpb	*meso*	5230	220	1376	1156	2060	196	1280	1084
	rac	2810	204	1372	1168	944	176	1280	1104
dpo	*meso*			c	1240	1220000	360	1536	1176
	rac			c	1288	478000	336	1536	1200
bpt$^-$	*meso*	409000	332	1068	736	188000	312	992	680
	rac	857000	351	1064	713	161000	308	992	684
dbneil	*meso*	2500	201	1409	1208	1100	180	1268	1088
	rac	2920	205	1403	1198	—	—	—	—
dpi$^-$	*meso*	733000	347	931	584	652000	344	884	540
	rac	793000	349	941	592	188000	312	844	532

^{a} Comproportionation constant, $K_c = \exp\{\Delta E_{ox}F/RT\}$, where F/RT takes the value 38.92 V^{-1} at 298 K.[5] ^{b} $\Delta E_{ox} = E_{ox2} - E_{ox1}$. ^{c} Potential more anodic than the positive potential limit of the electrolyte.

anions (ClO$_4^-$, PF$_6^-$, BF$_4^-$) because of weak association of BTF with the dication. In a subsequent paper, Geiger *et al.* also noted significant medium effects on the separation of sequential redox potentials, and commented on the need for judicious approach to the use of ΔE_{ox} values for the assessment of the degree of electronic interaction between linked metal centres.[11]

Our own laboratory[10] had reported studies of the effect of anions (*viz.* PF$_6^-$, BF$_4^-$, ClO$_4^-$, tosylate$^-$) on the redox potentials of metal-centred oxidations in mono- and di-nuclear ruthenium complexes in acetonitrile solution. The anions gave rise to cathodic shifts in the respective redox potentials for the oxidations in the sequence PF$_6^-$ < BF$_4^-$ ≈ ClO$_4^-$ < tosylate$^-$, which is consistent with known specific interactions of anions with metal complexes of this type.[14,15] Significantly, for the ligand-bridged dinuclear species, the effect was manifested by a difference in the potentials between the [6+/5+] and [5+/4+] couples (ΔE_{ox}). Variation of the electrolyte cation has no effect on the redox potentials.

Table 1 presents the redox potentials for the E_{ox1} ([5+/4+]; *i.e.* Ru^{III}–Ru^{II}/Ru^{II}–Ru^{II}) and E_{ox2} ([6+/5+]; *i.e.* Ru^{III}–Ru^{III}/Ru^{III}–Ru^{II}) couples for the series of complexes [{Ru(bpy)$_2$}$_2$(μ-BL)]$^{n+}$ {bpy = 2,2'-bipyridine; BL represents a range of bridging ligands {bpm, dpb, dbneil, dpo, bpt$^-$, dpi$^-$}, the structures of which are shown below) in acetonitrile solutions containing

2,2'-bipyridine (bpm)

2,3-bis(2-pyridyl)benzoquinoxaline (dpb)

3,5-bis(2-pyridyl)-1,2,4-triazolate (bpt$^-$)

3,4-bis(2-pyridyl)-1,2,5-oxadiazole (dpo)

dibenzoeilatin (dbneil)

4,5-di(2-pyridyl)imidalolato (dpi$^-$)
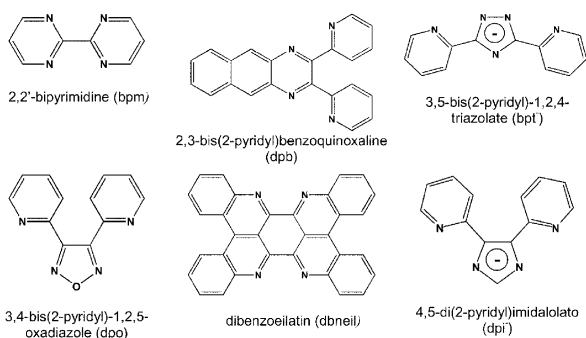
[(n-C$_4$H$_9$)$_4$N]{B(C$_6$F$_5$)$_4$} and [(n-C$_4$H$_9$)$_4$N]PF$_6$ as the supporting electrolyte, together with the respective ΔE_{ox} and K_c values derived from them in the two media.[16] A full listing of the potentials for (metal-based) oxidation and (ligand-based) reduction processes for the complexes in the two media are given in the ESI† (Tables S1 and S2). While the reversibilities of the oxidation and reduction processes were comparable in both electrolyte systems, the relative potentials and separations of the redox processes differed markedly. Slight differences were observed in the potentials for the reduction processes in the

various complexes in the two electrolyte systems, however the effect on the potentials for the oxidation processes was more pronounced.

In all instances, the redox potentials for a particular oxidation in a specified complex occur at more positive potentials in {B(C$_6$F$_5$)$_4$}$^-$ than in PF$_6^-$ media. This arises from the decrease in ion-pairing between the electrolyte anions and the complex cations in the weakly-associating {B(C$_6$F$_5$)$_4$}$^-$ relative to the PF$_6^-$ electrolyte. The pronounced effects of ion-pairing on the redox potentials of mono- and di-nuclear ruthenium complexes in electrolytes containing PF$_6^-$, BF$_4^-$, ClO$_4^-$ and tosylate$^-$ anions have been reported previously (*vide supra*).[10] In all cases for a particular complex, the decrease is greater for E_{ox2} than E_{ox1}: consequently, the value of ΔE_{ox} (and therefore K_c) is invariably greater in {B(C$_6$F$_5$)$_4$}$^-$ than in PF$_6^-$ media. For the individual species, the following specific observations can be made:

BL = 2,2'-Bipyrimidine (bpm). The electrochemical properties of the diastereoisomeric mixture of [{Ru(bpy)$_2$}$_2$(μ-bpm)]$^{4+}$ have been discussed previously.[17–19] From Table 1, no difference is observed in the characteristics of the two diastereoisomers beyond the experimental uncertainty of the potential measurements (± 5 mV). However, the values determined for K_c in the presence of the two anions {5230 *vs.* 1635 (average)} vary significantly.

BL = 2,3-Bis(2-pyridyl)benzoquinoxaline (dpb).[10,20] In this case, a difference in the value of K_c between the two diastereoisomers is reflected in both media.

BL = 3,4-Bis(2-pyridyl)-1,2,5-oxadiazole (dpo).[21] For this complex, a difference is observed between the two diastereoisomers in terms of ΔE_{ox} and K_c in PF$_6^-$ media, and as reported previously the values of K_c are very large. In {B(C$_6$F$_5$)$_4$}$^-$ media, the anodic shift in the potential of E_{ox2} is so large that the potential is beyond the anodic limit of the [(n-C$_4$H$_9$)$_4$N]{B(C$_6$F$_5$)$_4$}/CH$_3$CN solvent–electrolyte system: the value of ΔE_{ox} and K_c therefore cannot be assessed, but is it clear that since the anodic limit of the medium is ≈ 1900 mV (*vs.* [FeCp$_2$]$^{+/0}$), the value(s) of K_c in this medium will be considerably higher than those reported for PF$_6^-$.

BL = 3,5-Bis(2-pyridyl)-1,2,4-triazolato (bpt$^-$).[22] The electrochemical properties of the diastereoisomeric mixture of [{Ru(bpy)$_2$}$_2$(μ-bpt$^-$)]$^{4+}$ have been discussed previously.[23,24] For this complex, the K_c values for the two separated diastereoisomers are indistinguishable in the presence of PF$_6^-$, but are differentiated in the presence of {B(C$_6$F$_5$)$_4$}$^-$, with the value of the *rac* form being higher.

BL = Dibenzoeilatin (dbneil).[25] For this complex, the K_c values cannot actually be distinguished in {B(C$_6$F$_5$)$_4$}$^-$ media, but (as with the other complexes), the values are higher than in

PF$_6^-$ media (for which only the *meso* diasatereoisomer has been investigated).

BL = 4,5-Di(2-pyridyl)imidazolato (dpi$^-$).[26] The electrochemical measurements in the presence of PF$_6^-$ indicate significant K_c values, which differ for the two diastereoisomers. However, in {B(C$_6$F$_5$)$_4$}$^-$ media, K_c corresponds to the higher of these two values in PF$_6^-$ but is now the same for the two diastereoisomers.

Conclusions

The differences between redox potentials for the successive oxidations (ΔE_{ox}) in ligand-bridged dinuclear ruthenium complexes have been widely used to compute the comproportionation constant (K_c) for the mixed-valence species. These electrochemically-derived values of K_c have been interpreted as a means of assessing the coupling between metal centres in such species. The present work has demonstrated a significant—and sometimes unpredictable—dependence of the redox potentials for these oxidation processes on the identity of electrolyte anions used in such electrochemical experiments, emphasising the need for standard conditions for data from which such comparisons are made, and the danger of over-interpretation of ΔE_{ox} data and K_c values derived from them.

Experimental

Instrumentation

1D and 2D ^{1}H NMR spectra were performed on a Varian Mercury 300 MHz spectrometer. ^{1}H NMR of all complexes are reported relative to 99.9% d$_3$-acetonitrile (CD$_3$CN) at $\delta = 1.93$ ppm. ^{1}H NMR assignments were made with the assistance of COSY experiments to identify each pyridine ring spin system, while individual protons within a ring were assigned on the basis of their chemical shifts and the following typical ^3J coupling patterns for pyridine protons: H3 (d, $J = 8$ Hz), H4 (t, $J = 8$ Hz), H5 (dd, $J = 8, 5$ Hz), H6 (d, $J = 5$ Hz).

Electrochemical measurements were performed under argon using a Bioanalytical Systems BAS 100A Electrochemical Analyser. Cyclic and differential pulse voltammograms were recorded under Ar in 0.02 M [(*n*-C$_4$H$_9$)$_4$N]{B(C$_6$F$_5$)$_4$}/CH$_3$CN at +25 °C using a glassy carbon working electrode, a platinum wire auxiliary electrode and an Ag/AgCl (0.02 M [(*n*-C$_4$H$_9$)$_4$N]{B(C$_6$F$_5$)$_4$} in CH$_3$CN) reference electrode; or in 0.1 M [(*n*-C$_4$H$_9$)$_4$N]PF$_6$/CH$_3$CN using an Ag/AgCl (0.1 M [(*n*-C$_4$H$_9$)$_4$N]PF$_6$ in CH$_3$CN) reference electrode. Ferrocene was added as an internal standard on completion of each experiment {the ferrocene/ferrocenium couple (FeCp$_2^+$/FeCp$_2^0$) occurred at +550 mV *vs.* Ag/AgCl}: all potentials quoted in mV *versus* FeCp$_2^+$/FeCp$_2^0$.[27] Cyclic voltammetry was performed with a sweep rate of 100 mV s^{-1}; differential pulse voltammetry was conducted with a sweep rate of 4 mV s^{-1} and a pulse amplitude, width and period of 50 mV, 60 ms and 1 s, respectively.

In order to obtain reasonable electrochemical response, measurements in the 0.02 mol dm^{-3} [(*n*-C$_4$H$_9$)$_4$N]{B(C$_6$F$_5$)$_4$}/CH$_3$CN electrolyte required a concentration of complex which was approximately double that in 0.1 mol dm^{-3} [(*n*-C$_4$H$_9$)$_4$N]PF$_6$/CH$_3$CN.

Materials

2,2-Bipyrimidine (bpm; Lancaster), ammonium hexafluorophosphate (NH$_4$PF$_6$; Aldrich, 99.99%), potassium hexafluorophosphate (KPF$_6$; Aldrich, 98%), ethylene glycol (Ajax), sodium toluene-4-sulfonate (Aldrich, 98%), DOWEX 1×8 (50–100 mesh) Cl$^-$ anion exchange resin, and laboratory reagent solvents were used as received. SP Sephadex C-25 (Amersham Pharmacia Biotech), Sephadex LH-20 (Pharmacia) and silica gel 200–400 mesh (Aldrich) were employed for the chromatographic separation and purification of ruthenium complexes.[15]

Syntheses and diastereoisomer separation

cis-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O[28] and 3,5-bis(2-pyridyl)-1,2,4-triazole (Hbpt)[23,29] were prepared according to the literature procedures. The syntheses of the complexes [{Ru(bpy)$_2$}$_2$(μ-BL)]$^{n+}$ {bpy = 2,2′-bipyridine; BL represents a range of bridging ligands (dpb,[10,20] dbneil,[25] dpo,[21] bpt$^-$,[22] dpi$^-$ [26]), and the separation of the stereoisomers, were undertaken as described elsewhere.

[{Ru(bpy)$_2$}$_2$(μ-bpm)](PF$_6$)$_4$. [{Ru(bpy)$_2$}$_2$(μ-bpm)](PF$_6$)$_4$ was synthesised by an adaption of the procedure reported for the analaogous [{Ru(phen)$_2$}$_2$(μ-bpm)](PF$_6$)$_4$ complex (phen = 1,10-phenanthroline) by Hua.[30] [Ru(bpy)$_2$Cl$_2$]·2H$_2$O (300 mg, 0.5765 mmol) and bpm (41.4 mg, 0.262 mmol) were heated at reflux ($\approx$120 °C) in 10% water/ethylene glycol (20 cm^3) for 5 h. Upon cooling, the dark green solution was diluted with distilled water (50 cm^3) and loaded onto a column (dimensions: 15 cm × 3.5 cm) containing SP Sephadex C-25 support. Separation of the dinuclear product from the crude mixture was achieved *via* a gradient elution procedure using aqueous 0.1–0.5 mol dm^{-3} NaCl as the eluent. An orange band of mononuclear material eluted first (0.2–0.3 mol dm^{-3} NaCl), followed by the desired dark green product (0.5 mol dm^{-3} NaCl), which was precipitated as the PF$_6^-$ salt by addition of a saturated solution of aqueous KPF$_6$. The dark green solid was isolated by vacuum filtration, washed with chilled water and diethyl ether, and dried *in vacuo* at 40 °C for 4 h. Yield: 385 mg (94%). The NMR spectrum of the product was identical to that reported previously by Hua.[31]

The [{Ru(bpy)$_2$}$_2$(μ-bpm)](PF$_6$)$_4$, which was a diastereoisomeric mixture, was converted to the chloride salt by stirring an aqueous suspension with DOWEX® 1×8 anion exchange resin (50–100 mesh; Cl$^-$ form). The complex was sorbed onto the top of the SP Sephadex C-25 support and separation of the diastereoisomers was achieved by cation exchange chromatography using aqueous 0.25 mol dm^{-1} sodium toluene-4-sulfonate solution as the eluent.[32] The diastereoisomers separated after passing through an effective column length[14] of approximately 180 cm. The two dark green bands were collected and precipitated as the PF$_6^-$ salts by addition of a saturated solution of KPF$_6$.

Rigorous purification methods were employed prior to characterisation due to the potentially strong associations between the complex cations and the anions present in the eluents used for the chromatographic separations.[14,32] The solid product from each band was dissolved in a minimum volume of acetone and loaded onto a short column of silica gel, washed alternately with copious amounts of water and acetone, and then eluted with acetone containing 5% NH$_4$PF$_6$. Following the addition of an equal volume of water, and removal of the acetone under reduced pressure, the precipitates were isolated by vacuum filtration and washed with chilled water and diethyl ether. Bands 1 and 2 exhibited different NMR spectra, and were assigned as the *meso* and *rac* diastereoisomers, respectively (see Table 2).

The numbering scheme adopted for the proton assignments is provided below.
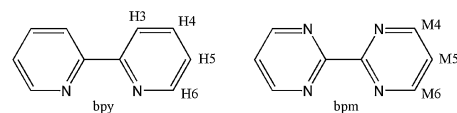
[{Ru(bpy)$_2$}$_2$(μ-bpt$^-$)](PF$_6$)$_3$. [{Ru(bpy)$_2$}$_2$(μ-bpt$^-$)](PF$_6$)$_3$ was synthesised by an adaptation of the literature procedure[23] (*Method A*), or by an alternative method detailed below (*Method B*).

Method A. Hbpt (11 mg, 0.050 mmol) was dissolved in ethanol/water (2 : 1, 2.5 cm^3) with heating, and the solution purged with N$_2$ for 20 min. [Ru(bpy)$_2$Cl$_2$]·2H$_2$O (50 mg, 0.10 mmol) was added and the mixture refluxed for 10 h under N$_2$, during which time the solution attained a red-brown coloration. The hot solution was filtered and evaporated to

Table 2 ^{1}H NMR chemical shifts (ppm) for the diastereoisomeric forms of [{Ru(bpy)$_2$}$_2$(μ-bpt$^-$)]$^{4+}$ in CD$_3$CN

		meso	rac
bpy			
ring a (over bpy)	H6′	7.728 (ddd, J = 6.3, 1.5, 0.6 Hz, 4H)	7.765 (ddd, J = 6.3, 1.5, 0.6 Hz, 4H)
	H5′	7.488 (ddd, J = 8.0, 7.2, 1.2 Hz, 4H)	7.442 (ddd, J = 8.0, 7.2, 1.2 Hz, 4H)
	H4′	8.131 (dd, J = 8.0, 1.5 Hz, 4H)	8.136 (dd, J = 8.0, 1.5 Hz, 4H)
	H3′	8.507 (d, J = 8.0 Hz, 4H)	8.564 (d, J = 8.0 Hz, 4H)
ring b (over bpm)	H3	8.526 (d, J = 8.0 Hz, 4H)	8.591 (d, J = 8.0 Hz, 4H)
	H4	8.156 (dd, J = 8.0, 1.5 Hz, 4H)	8.232 (dd, J = 8.0, 1.5 Hz, 4H)
	H5	7.645 (ddd, J = 8.0, 7.2, 1.2 Hz, 4H)	7.463 (ddd, J = 8.0, 7.2, 1.2 Hz, 4H)
	H6	8.062 (ddd, J = 6.3, 1.5, 0.6 Hz, 4H)	7.799 (ddd, J = 6.3, 1.5, 0.6 Hz, 4H)
bpm	M4	8.045 (d, J = 5.7 Hz, 2H)	8.100 (d, J = 5.7 Hz, 2H)
	M5	7.466 (t, J = 5.7 Hz, 2H)	7.455 (t, J = 5.7 Hz, 2H)
	M6	8.045 (d, J = 5.7 Hz, 2H)	8.100 (d, J = 5.7 Hz, 2H)

Table 3 ^{1}H NMR chemical shifts (ppm) for the diastereoisomeric forms of [{Ru(bpy)$_2$}$_2$(μ-bpt$^-$)]$^{3+}$ in CD$_3$CN

	meso				rac			
	H3	H4	H5	H6	H3	H4	H5	H6
bpy	8.33	8.04	7.56	7.88	8.54	7.89	7.31	8.13
	8.52	7.89	7.23	7.63	8.60	7.92	7.38	7.98
	8.52	7.89	7.23	7.98	8.3–8.6	7.7–8.0	6.9–7.2	7.7–8.0
	8.48	7.94	7.33	7.66				
	8.48	7.94	7.23	7.76				
	8.43	7.85	7.27	7.81				
	8.45	7.85	7.33	7.74				
	8.36	7.89	7.12	7.98				
bpt$^-$	6.40	7.04	6.92	7.53	6.54	7.06	6.86	7.44
	6.82	7.00	7.79	8.44	6.98	7.42	7.89	8.38

dryness. Distilled water (20 cm^3) was added to the red-brown residue and the compound was precipitated from the resultant solution by the addition of an excess of aqueous KPF$_6$. The solid was isolated by filtration and washed with distilled water and diethyl ether. Purification of the crude mixture was achieved by gel permeation chromatography on Sephadex LH-20 support with ethanol as eluent. The first fraction was collected and evaporated to dryness. Yield: 27 mg (37%) Separation of the diastereoisomers was achieved *via* the method described below.

Method B. A suspension of Hbpt (21 mg, 0.094 mmol) in ethylene glycol (10 cm^3) was heated in a modified microwave oven (Model R-2V55; 600 W, 2450 MHz) on medium-high power[33] for 20 s to complete dissolution. *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O (100 mg, 0.207 mmol) was added and the mixture heated at reflux for a further 8 min during which time the solution attained a red-orange coloration. Upon cooling, the mixture was diluted with distilled water (50 cm^3) and the product precipitated by the addition of a saturated aqueous solution of KPF$_6$, and collected by filtration. Purification of the crude mixture was achieved by exclusion chromatography on Sephadex LH-20 support with ethanol as eluent. The first fraction was collected and evaporated to dryness. Yield: 93 mg (66%).

Separation of the diastereoisomers was achieved by cation exchange chromatography as described above, using 0.15 mol dm^{-3} sodium toluene-4-sulfonate solution as the eluent.[32] Purification was achieved as described above. Bands 1 and 2 exhibited different NMR spectra, and were assigned as the *meso* and *rac* diastereoisomers, respectively (see Table 3).

The numbering scheme adopted for the proton assignments is provided below.
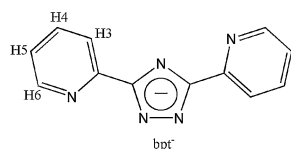
bpt$^-$

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