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3,6-Bis(2′-pyridyl)pyridazine (L) and its deprotonated form $(L - H^+)^-$ as ligands for $\{(acac)_2Ru^{n+}\}$ or $\{(bpy)_2Ru^{m+}\}$: investigation of mixed valency in $[\{(acac)_2Ru\}_2(\mu\text{-}L - H^+)]^0$ and $[\{(bpy)_2Ru\}_2(\mu\text{-}L - H^+)]^{4+}$ by spectroelectrochemistry and EPR†

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Crystallographically characterised 3,6-bis(2′-pyridyl)pyridazine (L) forms complexes with $\{(acac)_2Ru\}$ or $\{(bpy)_2Ru^{2+}\}$ *via* one pyridyl-N/pyridazyl-N chelate site in mononuclear Ru^{II} complexes $(acac)_2Ru(L)$, **1**, and $[(bpy)_2Ru(L)](ClO_4)_2$, **[3]**$(ClO_4)_2$. Coordination of a second metal complex fragment is accompanied by deprotonation at the pyridazyl-C^5 carbon $\{L \rightarrow (L - H^+)^-\}$ to yield cyclometallated, asymmetrically bridged dinuclear complexes $[(acac)_2Ru^{III}(\mu\text{-}L - H^+)Ru^{III}(acac)_2](ClO_4)$, **[2]**$(ClO_4)$, and $[(bpy)_2Ru^{II}(\mu\text{-}L - H^+)Ru^{II}(bpy)_2](ClO_4)_3$, **[4]**$(ClO_4)_3$. The different electronic characteristics of the co-ligands, σ donating $acac^-$ and π accepting bpy, cause a wide variation in metal redox potentials which facilitates the isolation of the diruthenium(III) form in **[2]**(ClO_4) with antiferromagnetically coupled Ru^{III} centres ($J = -11.5\ cm^{-1}$) and of a luminescent diruthenium(II) species in **[4]**$(ClO_4)_3$. The electrogenerated mixed-valent $Ru^{II}Ru^{III}$ states **2** and **[4]**$^{4+}$ with comproportionation constants $K_c > 10^8$ are assumed to be localised with the Ru^{III} ion bonded *via* the negatively charged pyridyl-N/pyridazyl-C^5 chelate site of the bridging $(L - H^+)^-$ ligand. In spectroelectrochemical experiments they show similar intervalence charge transfer bands of moderate intensity around 1300 nm and comparable g anisotropies ($g_1 - g_3 \approx 0.5$) in the EPR spectra. However, the individual g tensor components are distinctly higher for the π acceptor ligated system **[4]**$^{4+}$, signifying stabilised metal d orbitals.

Introduction

The design of polynuclear metal complexes which exhibit strong intermetallic electronic coupling in the mixed-valent states *via* the mediation of suitably bridging functionalities has generated considerable research interest in recent years.[1] This has been primarily due to the relevance for biological processes,[2] for molecular electronics,[3] and for theoretical studies of electron transfer kinetics.[4] In this context we have recently been involved in the design of diruthenium complexes encompassing varying combinations of bridging and ancillary functionalities. The purpose of these efforts has been to scrutinize the effectivity of selective ligand environments for the extent of intermetallic electronic communication in the mixed-valent state(s).[5] The combinations between the bipyridine-like bis-chelating bridging ligand 3,6-bis(2′-pyridyl)pyridazine (bppn, L) and ancillary ligands such as π-acidic 2,2′-bipyridine (bpy) or electron-rich acetylacetonate ($acac^-$) have been chosen for the present work.

The potentially bridging ligand L has been extensively studied in synthesizing a wide range of mononuclear and polynuclear complexes of Cr,[6] Mo,[6,7] W,[6] Rh,[8,10c] Ir,[9] Ru,[10] Ni,[11] Pd,[9a,e,12] Pt,[9b,e,12,13] Cu[9f,14] and Ag,[15] under different aspects. However, diruthenium species of L and the efficiency of L as an electronic mediator between metal termini have not been investigated so far. We therefore, synthesized diruthenium(III) and diruthenium(II) complexes of L, *viz.*, $[(acac)_2Ru^{III}(\mu\text{-}L - H^+)Ru^{III}(acac)_2](ClO_4)$, **[2]**$(ClO_4)$, and $[(bpy)_2Ru^{II}(\mu\text{-}L - H^+)Ru^{II}(bpy)_2](ClO_4)_3$, **[4]**$(ClO_4)_3$, along with their mononuclear counterparts $(acac)_2Ru^{II}(L)$, **1**, and $[(bpy)_2Ru^{II}(L)](ClO_4)_2$, **[3]**$(ClO_4)_2$, respectively. Though the ligand L functions as a neutral N,N′-donor in the mononuclear compounds **1** and **[3]**$(ClO_4)_2$, it bridges the metal complex fragments *via* chemically different N,N′ and N,C^- donor sets in the dinuclear complexes **[2]**(ClO_4) and **[4]**$(ClO_4)_3$. It may be noted that the study of diruthenium complexes based on asymmetric bridging ligands (with inequivalent metal coordination sites) is less common.[5n,16]

The present report describes the synthesis of **1**, **[2]**(ClO_4), **[3]**$(ClO_4)_2$ and **[4]**$(ClO_4)_3$, and the studies of the mixed-valence properties of the diruthenium(II/III) complexes {**[2]** and **[4]**$^{4+}$} by detailed spectroelectrochemical and EPR investigations. In addition we report the magnetic interaction in the paramagnetic diruthenium(III) complex **[2]**(ClO_4) and the luminescence properties of **[4]**$(ClO_4)_3$.

Results and discussion

The ligand bppn (L) was prepared according to the reported procedure,[17] its crystal structure is shown in Fig. 1. The bond distances and angles (Table S1, ESI†) are in the expected

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† Electronic supplementary information (ESI) available: Fig. S1: ^1H NMR spectrum of $NC_5H_4C_4H_2N_2NC_5H_4$ (L) in $CDCl_3$. Fig. S2: Electrospray mass spectra of **1** in CH_2Cl_2 and **[2]**(ClO_4), **[3]**$(ClO_4)_2$, **[4]**$(ClO_4)_3$ in CH_3CN. Fig. S3: ^1H NMR spectrum of **1** in $(CD_3)_2SO$. Table S1: Bond distances (Å) and angles (°) for L. See http://www.rsc.org/suppdata/dt/b4/b417530a/

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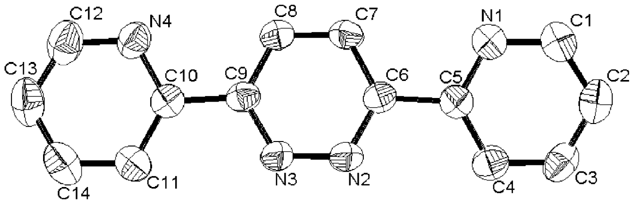


Fig. 1 Crystal structure of bppn (L).

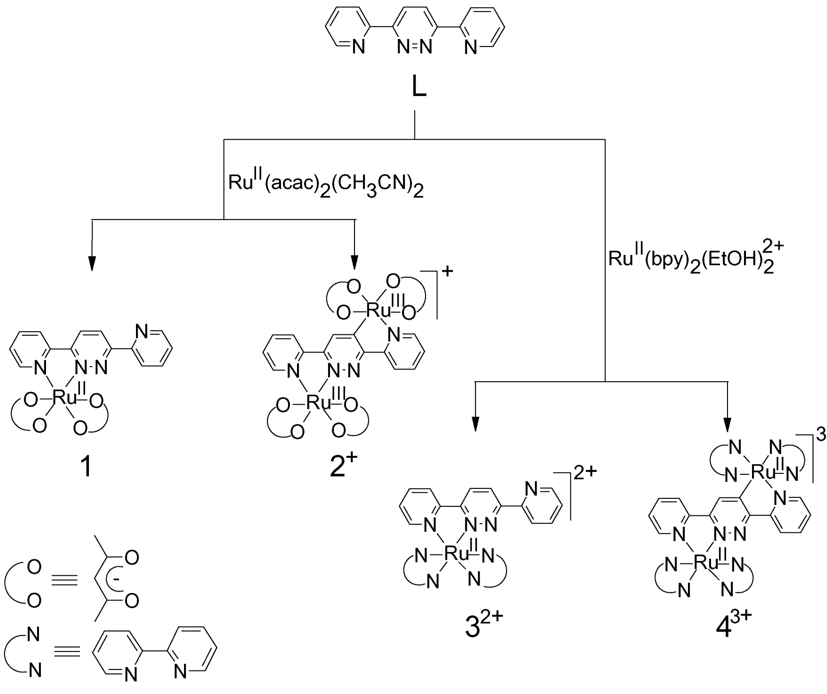
range[18] with an approximate *s-trans*/*s-trans*-conformation of the rings (Fig. 1). The NMR spectrum of L is shown in Fig. S1 (ESI†). The complexation reactions of L were carried out with the ruthenium precursors $Ru^{II}(acac)_2(CH_3CN)_2$ and $[Ru^{II}(bpy)_2(EtOH)_2]^{2+}$. The reactions of L with $Ru(acac)_2(CH_3CN)_2$ or $[Ru(bpy)_2(EtOH)_2]^{2+}$ in a 1 : 2 molar ratio in EtOH under a dinitrogen atmosphere, followed by chromatography using alumina, yielded mononuclear $(acac)_2Ru^{II}(L)$, **1**, with dinuclear $[(acac)_2Ru^{III}(\mu\text{-}L - H^+)Ru^{III}(acac)_2](ClO_4)$, [**2**]($ClO_4$), or $[(bpy)_2Ru^{II}(L)](ClO_4)_2$, [**3**]$(ClO_4)_2$, with $[(bpy)_2Ru^{II}(\mu\text{-}L - H^+)Ru^{II}(bpy)_2](ClO_4)_3$, [**4**]$(ClO_4)_3$, respectively $\{(L - H^+)^-$ originates *via* the deprotonation of pyridazyl-C^5 in L$\}$ (Scheme 1). It should be noted that the monomeric bipyridine complex [**3**]$(PF_6)_2$ was reported earlier.[10c] The electronic spectrum and cyclic voltammograms of [**3**]$(ClO_4)_2$ are well in agreement with the reported results (see later). In the mononuclear complexes **1** and [**3**]$(ClO_4)_2$, L is bonded to the metal ion by neutral N,N′ donors whereas the dinuclear species [**2**](ClO_4) and [**4**]$(ClO_4)_3$ have the two ruthenium ions linked to the deprotonated bridging ligand $(L - H^+)^-$ in its *s-cis*/*s-trans* orientation *via* neutral N,N′ and anionic N,C^- donor sets (cyclometallation). The alternative, the binding of two metal ions *via* the available two N,N′ donor sets of L in the *s-cis*/*s-cis* orientation seems to be unlikely from the steric point of view, particularly for essentially octahedrally coordinated metal ions as in [**2**](ClO_4) and [**4**]$(ClO_4)_3$. Thus, in other dinuclear complexes of L involving Ru, Rh[10c,8a] or Ir,[9c] similar deprotonation reactions with *s-trans* orientation and coordinating N,N′ and N,C^- donor sets were reported. However, for tetra- or penta-coordinated metal complexes in dinuclear systems the *s-cis*/*s-cis* geometry of bridging L with two N,N′ donor atoms has also been observed.[9a–c,e,f,12,14a–c,e,15]

The complexes showed satisfactory microanalyses. Compound **1** is neutral while [**2**](ClO_4), [**3**]$(ClO_4)_2$ and [**4**]$(ClO_4)_3$ exhibited 1 : 1, 1 : 2 and 1 : 3 conductivities, respectively (see Experimental section). The formation of the four complexes was confirmed by their electrospray mass spectral data. Complexes **1**, [**2**](ClO_4), [**3**]$(ClO_4)_2$ and [**4**]$(ClO_4)_3$ exhibited molecular masses m/z at 534.03, 831.88, 747.16 and 1256.28 (Fig. S2, ESI†), respectively, corresponding to $\mathbf{1}^+$ (calculated molecular weight, 533.55), $[\mathbf{2}]^+$ (831.83), $\{[\mathbf{3}](ClO_4)\}^+$ (747.04) and $\{[\mathbf{4}](ClO_4)_2\}^+$ (1259.04), respectively.

The complexes **1**, [**3**]$(ClO_4)_2$ and [**4**]$(ClO_4)_3$ are diamagnetic whereas [**2**](ClO_4) showed $\mu = 2.45\ \mu_B$ at 300 K (see later). In the former, the ruthenium ions are stabilised in the +II state whereas [**2**](ClO_4) has the unpaired electrons associated with the low-spin Ru^{III} ions, antiferromagnetically coupled at 300 K. The stabilisation of the +III states in chemically nonequivalent $[Ru^{III}O_4N_2]^+$ and $[Ru^{III}O_4NC]^-$ sites of [**2**](ClO_4) suggests that the formation of the strongly π-donating C^- donor centre in $(L - H^+)^-$ stabilises not only the ruthenium(III) ion directly linked to it but also facilitates the oxidation of the other ruthenium centre coordinated by the *s-trans* oriented bridging ligand. On the other hand, the neutral form L in the mononuclear derivative **1** stabilises the Ru^{II} state of the same $[RuO_4N_2]$ site.

The ^1H NMR spectrum of **1** in $(CD_3)_2SO$ exhibits ten distinct aromatic signals which includes six doublets [δ/ppm (J/Hz): 8.14 (8.7); 8.44 (7.8); 8.51 (7.8); 8.63 (9.0); 8.67 (6.6); 8.80 (6.0)] and four triplets [δ/ppm (J/Hz): 7.43 (6.0, 6.0); 7.57 (6.0, 6.0); 7.74 (6, 8.1); 8.07 (4.5, 3.3)]. The expected four CH_3 and two CH protons of $acac^-$ appear as six distinct singlets at 1.50/1.54/2.15/2.19 and 5.26/5.37 ppm, respectively (Fig. S3, ESI†). The corresponding dinuclear species [**2**](ClO_4) failed to show a conventional ^1H NMR spectrum due to its paramagnetic nature. The bipyridine-containing complexes [**3**]$(ClO_4)_2$ and [**4**]$(ClO_4)_3$ display complicated ^1H NMR spectra due to the overlapping of >25 signals with similar chemical shifts in the aromatic region.

The magnetic susceptibility of [**2**](ClO_4) as a function of temperature was recorded between 6 to 300 K. It exhibits a magnetic moment (per dinuclear unit) of 2.45 μ_B at 300 K which drops to 0.5 μ_B at 6 K. On lowering the temperature, the magnetic susceptibility first increases up to a maximum at 20 K, then decreases (Fig. 2). The maximum in the susceptibility is a



Scheme 1

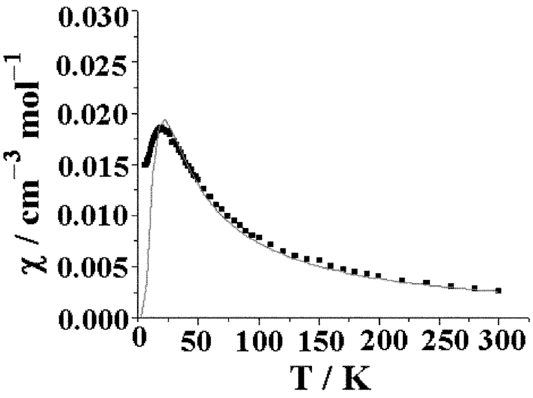


Fig. 2 Plot of magnetic susceptibility *vs.* temperature for [**2**](ClO_4). The solid line results from least-squares fit using equation (1) and the parameters from the text.

signature of moderate antiferromagnetic exchange interaction. The model used to fit the magnetic data considers a general isotropic spin exchange Hamiltonian $H = -2J\boldsymbol{S}_1\cdot\boldsymbol{S}_2$ where $S_1 = S_2 = \frac{1}{2}$, using the van Vleck equation (eqn. (1)):[19]

$$\chi_{\mathrm{M}} = \frac{Ng^2\beta^2}{3kT}\frac{1}{1+(1/3)\exp(-2J/kT)} \qquad (1)$$

The obtained parameters are: $g = 2.06 \pm 0.05$, $J = -11.5 \pm 2$ cm^{-1}, TIP $\approx 1 \times 10^{-3}$ cm^3 mol^{-1}. The J value indicates intramolecular antiferromagnetic coupling between the unpaired electrons of the Ru^{III} centres in each dinuclear molecule.[5c]

The quasi-reversible Ru^{III} $\rightleftharpoons$ Ru^{II} couple (I) and an irreversible Ru^{III} $\rightarrow$ Ru^{IV} oxidation (II) of **1** appear at 0.022 and at E_{pa} = 1.53 V *vs.* SCE in CH_3CN, respectively (Fig. 3(a), Table 1). The one-electron nature of couple I was confirmed by constant-potential coulometry whereas the same for the irreversible process II was established by comparing its differential pulse voltammetric current height with that of couple I. The Ru^{III} $\rightleftharpoons$ Ru^{II} couple for the corresponding mononuclear bipyridine complex, [**3**]$(ClO_4)_2$, appears at 1.33 V (reported value: 1.35 V[10c]). Thus, a potential shift of ~1.3 V has taken place on moving from acac$^-$ to bpy ancillary ligands, as expected from their difference in electronic nature. The appearance of the Ru^{III} $\rightleftharpoons$ Ru^{II} couples of $[Ru(acac)_2(bpy)]^+$ and $[Ru(bpy)_3]^{2+}$ at −0.05 V[20] and 1.29 V,[21] respectively, implies a slightly greater ligand field strength of L relative to bpy. Complex [**3**]$(ClO_4)_2$ exhibits three reversible reductions at −1.15, −1.56 and −1.81 V which match well with reported values.[10c] The dinuclear complex [**2**](ClO_4) exhibits two irreversible oxidation processes at E_{pa} = 1.10 (I) and 1.49 V (II) and two reversible reduction couples at −0.16 (III) and −0.66 V (IV) which are assigned as successive metal based oxidations (Ru^{III}Ru^{III} → Ru^{III}Ru^{IV} and Ru^{III}Ru^{IV} → Ru^{IV}Ru^{IV}) and reductions (Ru^{III}Ru^{III} $\rightleftharpoons$ Ru^{III}Ru^{II} and Ru^{III}Ru^{II} $\rightleftharpoons$ Ru^{II}Ru^{II}), respectively (Fig. 3(b), Table 1). The successive metal based couples for the analogous bipyridine complex [**4**]$(ClO_4)_3$, Ru^{II}Ru^{II} $\rightleftharpoons$ Ru^{II}Ru^{III} (I) and Ru^{II}Ru^{III} $\rightleftharpoons$ Ru^{III}Ru^{III} (II) appear at 0.77 and 1.25 V, respectively (Fig. 3(c), Table 1). Besides, the compound also shows four bpy based reductions at −1.33 (III), −1.55 (IV), −1.68 (V) and −1.88 V (VI). Thus, moving from an electron-rich acetylacetonate environment in [**2**](ClO_4) to the π-acidic bipyridine ancillary ligands in [**4**]$(ClO_4)_3$, a substantial stabilisation of the Ru^{II} state has taken place. The potentials of the first Ru^{III}/Ru^{II} and Ru^{IV}/Ru^{III} redox processes for the dinuclear complex [**2**](ClO_4) and of the first Ru^{III}/Ru^{II} potential for [**4**]$(ClO_4)_3$ are appreciably lower than those of the corresponding mononuclear complexes **1** and [**3**]$(ClO_4)_2$. This justifies the identification of the first oxidation waves in the dinuclear systems with the RuO_4NC^- site, the additional destabilisation of the Ru^{II} states in the dinuclear complexes arises

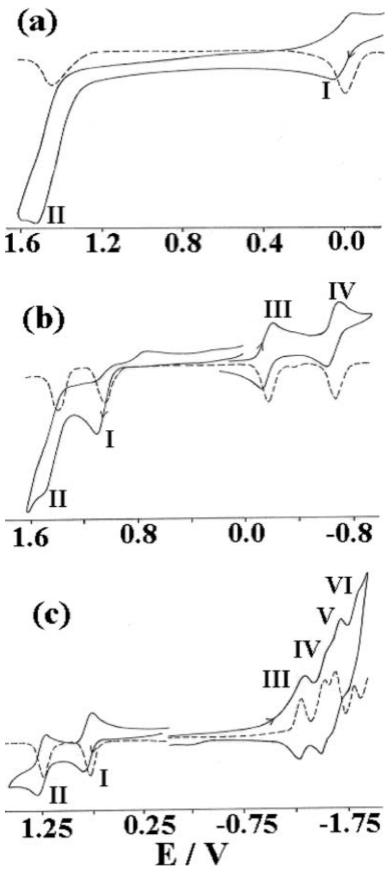


Fig. 3 Cyclic voltammograms (—) and differential pulse voltammograms (---) of (a) **1**, (b) [**2**](ClO_4) and (c) [**4**]$(ClO_4)_3$ in CH_3CN.

Table 1 Redox potentials for complexes[a]

Compound	Couple	$E°_{298}$/V (ΔE_p/mV)
1	Ru^{III} $\rightleftharpoons$ Ru^{II} (I)	0.022 (70)
	Ru^{III} → Ru^{IV} (II)	1.53[b]
[**2**](ClO_4)	Ru^{III}Ru^{III} → Ru^{III}Ru^{IV} (I)[c]	1.1[b]
	Ru^{III}Ru^{IV} → Ru^{IV}Ru^{IV} (II)	1.49[b]
	Ru^{III}Ru^{III} $\rightleftharpoons$ Ru^{III}Ru^{II} (III)[d]	−0.16 (90)
	Ru^{III}Ru^{II} $\rightleftharpoons$ Ru^{II}Ru^{II} (IV)	−0.66 (90)
[**3**]$(ClO_4)_2$	Ru^{III} $\rightleftharpoons$ Ru^{II}	1.33 (90)
	bpy reductions	−1.15 (70), −1.56 (90), −1.81 (100)
[**4**]$(ClO_4)_3$	Ru^{II}Ru^{II} $\rightleftharpoons$ Ru^{II}Ru^{III} (I)[c]	0.77 (60)
	Ru^{II}Ru^{III} $\rightleftharpoons$ Ru^{III}Ru^{III} (II)	1.25 (90)
	bpy reductions (III–VI)	−1.33 (60), −1.55 (60), −1.68 (60), −1.88 (60)

[a] Measured in $CH_3CN/(Et_4N)ClO_4$, potentials E/V *vs.* SCE. [b] E_{pa} (irreversible process). [c] First oxidation at the cyclometallated site. [d] First reduction at the non-cyclometallated site.

Table 2 UV-Vis-NIR Data of $\mathbf{2}^n$ [n = 1, 0, −1] and $\mathbf{4}^n$+ [n = 1, 2, 3, 4, 5] from spectroelectrochemistry[a]

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
$[\mathbf{2}]^+$	298 (28800), 398 (9200), 521 (6690)
2	294 (26000), 415 (sh), 532 (9600), 685 (sh), 1295 (1800)
$[\mathbf{2}]^-$	285 (24400), 310 (sh), 445 (14450), 525 (sh), 610 (sh), 750 (2900)
$[\mathbf{4}]^{5+}$	245 (37400), 310 (45500), 665 (sh)
$[\mathbf{4}]^{4+}$	248 (29500), 288 (49000), 435 (8670), 1335 (2830)
$[\mathbf{4}]^{3+}$	245 (25500), 291 (64000), 342 (sh), 469 (15180)
$[\mathbf{4}]^{2+}$	246 (29600), 295 (53500), 367 (19350), 395 (sh), 513 (12400), 830 (2400)
$[\mathbf{4}]^{+}$	245 (27200), 295 (42600), 365 (27000), 500 (sh), 535 (14050), 865 (3090)

[a] Measurements in CH_3CN/0.1 mol dm^{-3} Bu_4NPF_6 (OTTLE spectroelectrochemistry).

obviously from the strong σ-donor effect of the carbanion centre in the cyclometallated arrangement.

The 500 and 480 mV separations between the two successive Ru^{III}/Ru^{II} couples for [**2**](ClO_4) and [**4**]$(ClO_4)_3$, respectively, are a result of combined effects of the built-in donor centre asymmetry around the metal ions and of the bridging ligand mediated intermetallic coupling. The resulting comproportionation constant (K_c) values of the mixed-valent $Ru^{III}Ru^{II}$ states are 3 × 10^8 and 1.4 × 10^8, respectively [using the relation $RT\ln K_c = nF(\Delta E)$[22]]. The related diruthenium complexes involving 3,6-substituted tetrazine based bridging ligands, 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) and 3,6-bis(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine (bpytz) exhibited much more pronounced effects on the K_c values as a function of the ancillary ligands: K_c = 3 × 10^8 (bpy)[23] and 1 × 10^{13} (acac)[24] or $10^{7.6}$ (bpy)[5a] and $10^{13.9}$ (acac),[5a] respectively, in the mixed-valent $Ru^{III}Ru^{II}$ states. The fact that no such bpy/acac-based shift has been observed with the present bridging ligand, $(L - H^+)^-$, suggests that the asymmetry effect is primarily responsible for the fairly large K_c values.

UV-Vis-NIR spectroelectrochemical experiments for $[\mathbf{2}]^n$+ (n = −1, 0, 1) and $[\mathbf{4}]^n$+ (n = 1, 2, 3, 4, 5) were performed in acetonitrile solution at 298 K using an OTTLE cell. Spectral data are listed in Table 2 and the spectra are shown in Figs. 4 and 5. In agreement with the assignment of redox processes the native $Ru^{III}Ru^{III}$ species $[\mathbf{2}]^+$ exhibits a moderately intense $(L - H^+)^- \rightarrow Ru^{III}$ based LMCT transition at 521 nm (ε = 6690 dm^3 mol^{-1} cm^{-1}), in addition to intense ligand based transitions in the UV region. In the one-electron reduced species **2** ($Ru^{III}Ru^{II}$), the charge-transfer transition is slightly red-shifted to 532 nm (ε = 9600 dm^3 mol^{-1} cm^{-1}) with a substantial increase in intensity. Moreover, the mixed-valent $Ru^{III}Ru^{II}$ species **2** displays a low-energy intervalence charge-transfer (IVCT) band at 1295 nm (ε = 1800 dm^3 mol^{-1} cm^{-1}) (Fig. 4(a)). The width at half height ($\Delta\nu_{1/2}$) was measured at 2790 cm^{-1}. Following the above arguments we attribute this IVCT band to a largely localised transition from $[Ru^{II}O_4N_2]$ to $[Ru^{III}O_4NC^-]$. On further one-electron reduction to the $Ru^{II}Ru^{II}$ state in $[\mathbf{2}]^-$, the IVCT band disappears and a strong MLCT absorption appears at 445 nm (ε = 14500 dm^3 mol^{-1} cm^{-1}) with shoulders at the lower energy side at 525 and 610 nm and an additional weak band at 750 nm (Fig. 4(b)). The pronounced asymmetry is responsible for the various MLCT absorptions of **2**.

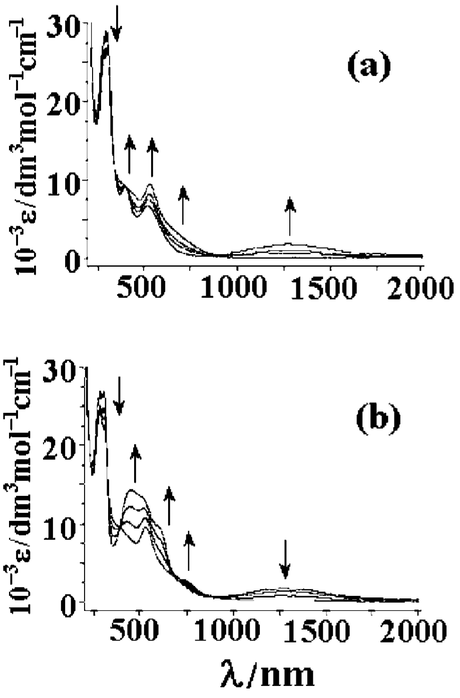


Fig. 4 UV-VIS-NIR spectroelectrochemistry for the conversions (a) $[\mathbf{2}]^+ \rightarrow \mathbf{2}$ and (b) $\mathbf{2} \rightarrow [\mathbf{2}]^-$ in CH_3CN/Bu_4NPF_6.

The Ru^{II} based intense MLCT band for $[\mathbf{4}]^{3+}$appears at 469 nm (ε = 15180 dm^3 mol^{-1} cm^{-1}). On oxidation to the mixed-valent $Ru^{II}Ru^{III}$ state in $[\mathbf{4}]^{4+}$, the MLCT band is blue shifted to 435 nm (ε = 8670 dm^3 mol^{-1} cm^{-1}) with appreciably lowered intensity due to a diminished number of Ru^{II} centres. In addition, an IVCT band appears at 1335 nm (ε = 2830 dm^3 mol^{-1} cm^{-1}), with a width at half height ($\Delta\nu_{1/2}$) of 2660 cm^{-1} (Fig. 5(a)). This absorption is attributed to a localised transition from the $[Ru^{II}N_6]$ centre to the $[Ru^{III}N_5C^-]$ site, in agreement with the similar IVCT features for **2**. On further oxidation to the isovalent $Ru^{III}Ru^{III}$ state $[\mathbf{4}]^{5+}$, the Ru^{II} based MLCT and IVCT bands disappear, only a weak band remains at 665 nm (Fig. 5(b)).

On one-electron reduction to $[\mathbf{4}]^{2+}$, the $Ru^{II} \rightarrow$ bpy MLCT transition was found to be slightly red-shifted to 513 nm (ε = 12400 dm^3 mol^{-1} cm^{-1}) with a slight drop in intensity. This is a consequence of placing an electron in the LUMO (which thus becomes a singly occupied MO, SOMO).[25] In addition to that the reduction results in a moderately intense low-energy absorption at 830 nm (ε = 2400 dm^3 mol^{-1} cm^{-1}) (Fig. 5(c)) which corresponds to an internal transition associated with the bpy radical anion, π(SOMO) → π^*(LUMO + 1). On further reduction to $[\mathbf{4}]^+$, the MLCT transition and the low energy radical anion transition are further red-shifted to 535 and 865 nm (Fig. 5(d)), respectively. These are consistent with the second reduction associated with a second bpy co-ligand.

On excitation at the lowest energy MLCT band at 469 nm, the dinuclear complex [**4**]$(ClO_4)_3$ containing bipyridine co-ligands displays a strong emission at 664 nm (quantum yield of ϕ = 0.14) at 77 K in 4 : 1 EtOH–MeOH glass with vibrational fine structure characteristic of emission from a ^{3}MLCT excited state (Fig. 6). The origin of the emission band at 469 nm was confirmed *via* its excitation spectrum (Fig. 6, inset). The quantum yield of [**4**]$(ClO_4)_3$ is less than that for $[Ru(bpy)_3]^{2+}$ (ϕ = 0.34)[26] but much greater than that of the monomeric species [**3**]$(PF_6)_2$ (λ_{em} = 630 nm in 1 : 1 1,2-dichloroethane–dichloromethane, ϕ = 0.03).[10c]

The *in situ* oxidised mononuclear complexes $[\mathbf{1}]^+$ and $[\mathbf{3}]^{3+}$ display EPR signals in frozen CH_3CN at 4 K with a rhombic {$[\mathbf{1}]^+$: g_1 = 2.311, g_2 = 2.214, g_3 = 1.852} and an axial *g*

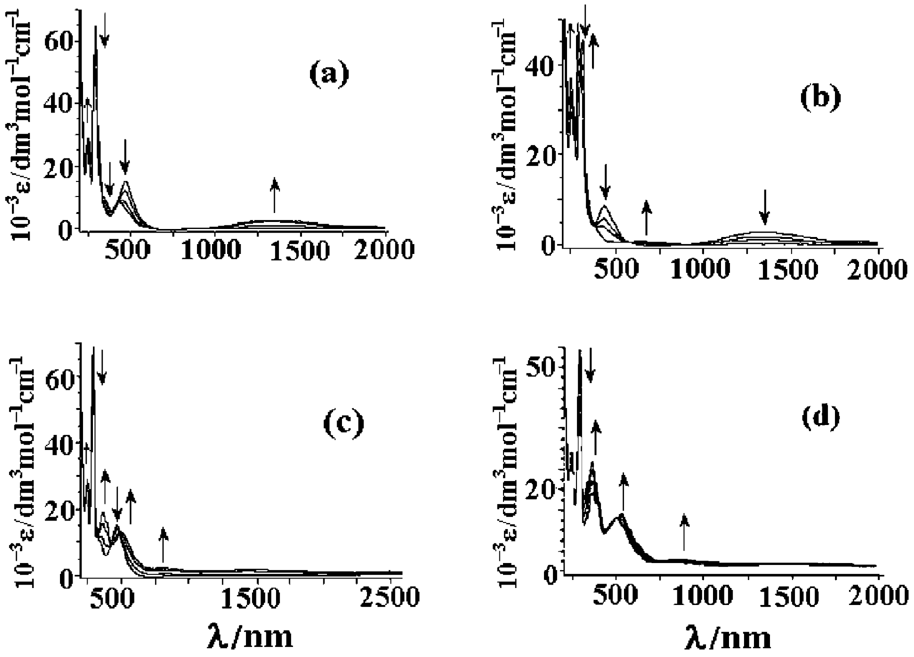


Fig. 5 UV-VIS-NIR spectroelectrochemistry for the conversions of (a) $[\mathbf{4}]^{3+} \rightarrow [\mathbf{4}]^{4+}$, (b) $[\mathbf{4}]^{4+} \rightarrow [\mathbf{4}]^{5+}$, (c) $[\mathbf{4}]^{3+} \rightarrow [\mathbf{4}]^{2+}$ and (d) $[\mathbf{4}]^{2+} \rightarrow [\mathbf{4}]^{+}$ in CH_3CN/Bu_4NPF_6.

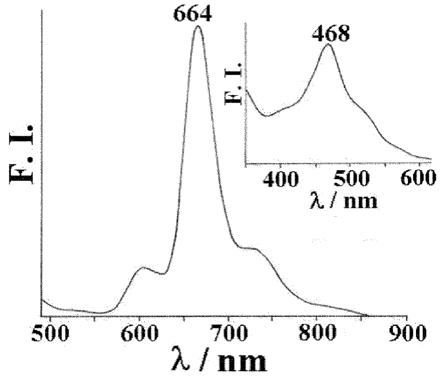


Fig. 6 Emission spectrum of $[\mathbf{4}](ClO_4)_3$ in EtOH–MeOH (4 : 1) at 77 K ($\lambda_{\text{excitation}} = 469$ nm). Inset shows the corresponding excitation spectrum ($\lambda_{\text{excitation}} = 664$ nm).

tensor component splitting $\{[\mathbf{3}]^{3+}: g_{1,2} = 2.631, g_3 = 2.173\}$, respectively (Fig. 7(a)). Both systems have a distorted octahedral arrangement around the ruthenium(III) ion (low-spin $4d^5$ configuration),[27] however, the higher g values for the π acceptor ligated system $[\mathbf{3}]^{3+}$ signify stabilised metal d-orbitals. The one-electron reduced species $[\mathbf{3}]^{+}$ shows a free radical-type EPR signal at $g = 1.997$, characteristic of $bpy^{\bullet-}$ bound to Ru^{II}.[23]

The paramagnetic $Ru^{III}Ru^{III}$ state in $[\mathbf{2}](ClO_4)$ did not exhibit any EPR signal even at 4 K in frozen CH_3CN solution. This EPR silence is in agreement with the relatively large antiferromagnetic spin–spin coupling as described above. The *in situ* generated $Ru^{III}Ru^{II}$ reduced species **2** shows a rhombic EPR spectrum in acetonitrile at 4 K with $g_1 = 2.399$, $g_2 = 2.259$ and $g_3 = 1.798$ (Fig. 7(b)). The g anisotropy ($g_1 - g_3$) and the average g factor ($<g>$) are calculated at 0.601 and 2.167, respectively, the corresponding values for the mononuclear analogue $[\mathbf{1}]^{+}$ are 0.459 and 2.135. In comparison, the bipyridine analogue $[\mathbf{4}]^{4+}$ ($Ru^{II}Ru^{III}$) exhibits a rhombic signal with $g_1 = 2.748$, $g_2 = 2.468$ and $g_3 = 2.176$ leading to $g_1 - g_3 = 0.572$ and $<g> = 2.475$ (Fig. 7(c)), the corresponding values are 0.458 and 2.488 for the mononuclear $[\mathbf{3}]^{3+}$. The higher g anisotropy for both dinuclear systems in relation to corresponding mononuclear species reflects increased participation of the metals at the singly occupied MO, suggesting strong ruthenium(III)/carbanion interaction and, perhaps, a partial valence delocalisation. Again, however, the individual g

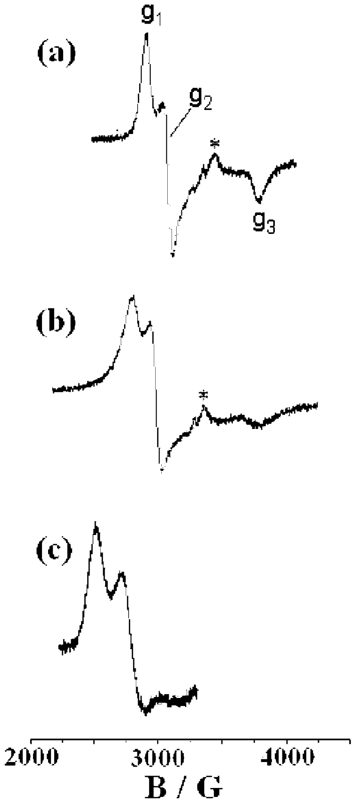


Fig. 7 X-Band EPR spectra of (a) $\mathbf{1}^{+}$, (b) **2** and (c) $[\mathbf{4}]^{4+}$ in $CH_3CN/0.1\ mol\ dm^{-3}\ Bu_4NPF_6$ at 4 K (* = cavity signal).

tensor components are distinctly higher for $[\mathbf{4}]^{4+}$, in accordance with stabilised metal d orbitals in that π acceptor ligated system. Reduction to $[\mathbf{4}]^{2+}$ produced an unresolved EPR signal at $g = 2.0017$, typical for a $bpy^{\bullet-}/Ru^{II}$ situation.[23]

In conclusion, both the intervalence charge transfer (IVCT) bands in the near infrared and the g anisotropies $g_1 - g_3$, obtained from EPR are comparable for mixed-valent **2** and $[\mathbf{4}]^{4+}$ because these values reflect energy differences and suggest a similar qualitative description of the frontier orbitals situation in these mixed-valent species. As compared to the electronically rich acac$^-$ species **2**, the individual g tensor components are distinctly higher for the π acceptor (bpy) ligated system [**4**]$^{4+}$ as are the redox potentials. Though different homovalent forms were isolated as [**2**]$^+$ (Ru^{III}Ru^{III}) and [**4**]$^{3+}$ (Ru^{II}Ru^{II}), the Ru^{II}Ru^{III} mixed-valent intermediates are easily generated through reduction and oxidation, respectively. The asymmetric coordination of the metal centres by (μ-L − H$^+$)$^-$ is assumed to be the main cause of the fairly high comproportionation constants $K_c > 10^8$.

Experimental

Materials

The precursor compounds Ru(acac)$_2$(CH$_3$CN)$_2$,[28] *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O[21] and 3,6-bis(2′-pyridyl)pyridazine (L)[17] were prepared according to the reported procedures. Other chemicals and solvents were reagent grade and used as received. For spectroscopic and electrochemical studies HPLC grade solvents were used.

Physical measurements

UV-Vis-NIR spectroelectrochemical studies were performed in CH$_3$CN/0.1 mol dm^{-3} Bu$_4$NPF$_6$ at 298 K using an optically transparent thin layer electrode (OTTLE) cell[29] mounted in the sample compartment of a Bruins Instruments Omega 10 spectrophotometer. FTIR spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. Solution electrical conductivity was checked using a Systronic 305 conductivity bridge. ^{1}H NMR spectra were obtained with a 300 MHz Varian FT spectrometer. The EPR measurements were made in a two-electrode capillary tube[30] with an X-band (9.5 GHz) Bruker system ESP300, equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. Cyclic voltammetric, differential pulse voltammetric and coulometric measurements were carried out using a PAR model 273A electrochemistry system. Platinum wire working and auxiliary electrodes and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. The supporting electrolyte was [NEt$_4$]ClO$_4$/0.1 mol dm^{-3} and the solute concentration was *ca.* 10^{-3} mol dm^{-3}. The half-wave potential E°_{298} was set equal to 0.5(E_{pa} + E_{pc}), where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials, respectively. A platinum wire-gauze working electrode was used in coulometric experiments. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyser. Electrospray mass spectra were recorded on a Micromass Q–ToF mass spectrometer. Emission experiments were made using a Perkin-Elmer LS 55 spectrometer fitted with a cryostat and the quantum yield (ϕ) was determined by following a previously described method.[31] The magnetic susceptibility of [**2**](ClO$_4$) as a function of temperature was recorded from 6 to 300 K using a 0.1 T applied field on a Quantum Design MPMS XL7 SQUID magnetometer. The data were corrected for the diamagnetic contributions to the magnetic susceptibility using Pascal's constants, for the diamagnetic contribution of the sample holder, and for temperature independent paramagnetism (TIP).

CAUTION! Perchlorate salts of metal complexes are generally explosive. Care should be taken while handling such complexes.

Synthesis of (acac)$_2$Ru^{II}(L) 1 and [(acac)$_2$Ru(μ-L − H$^+$)Ru(acac)$_2$](ClO$_4$) [2](ClO$_4$). The starting complex Ru(acac)$_2$(CH$_3$CN)$_2$ (100 mg, 0.26 mmol), and the ligand L (30 mg, 0.13 mmol) were dissolved in 20 cm^3 of ethanol and the mixture was heated to reflux for 6h under a dinitrogen atmosphere. The initial orange solution gradually changed to purple. The solvent of the reaction mixture was evaporated to dryness under reduced pressure. The solid mass thus obtained was dissolved in minimum volume of acetonitrile, then excess aqueous NaClO$_4$ solution was added to it and the mixture kept at 0 °C overnight. Filtration yielded a precipitate which was washed with ice-cold water followed by cold ethanol, and dried under vacuum. It was then purified using a neutral alumina column. Initially, a red compound corresponding to Ru(acac)$_3$ was eluted by CH$_2$Cl$_2$–CH$_3$CN (25:1), followed by a brown compound with CH$_2$Cl$_2$–CH$_3$CN (5 : 1) corresponding to **1**. With CH$_2$Cl$_2$–CH$_3$CN (1 : 1), a purple compound corresponding to [**2**](ClO$_4$) was eluted. Evaporation of solvent under reduced pressure yielded pure complexes **1** and [**2**](ClO$_4$), respectively.

Anal. Calc. for **1**: C, 53.92; H, 4.53; N, 10.49. Found: C, 53.67; H, 4.47; N, 10.03%. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) in CH$_3$CN at 298 K: 526 (11760), 428 (11800), 388 (12530), 304 (32220), 278 (35960). Yield: 30% (42 mg).

Anal. Calc. for [**2**](ClO$_4$): C, 43.78; H, 4.00; N, 6.01. Found: C, 43.52; H, 3.97; N, 5.98%. Conductivity: Λ_M/Ω^{-1} cm^2 mol^{-1} in acetonitrile at 298 K: 115. Yield: 55% (67 mg).

Synthesis of [(bpy)$_2$Ru(L)](ClO$_4$)$_2$ [3](ClO$_4$)$_2$ and [(bpy)$_2$Ru(μ-L − H$^+$)Ru(bpy)$_2$](ClO$_4$)$_3$ [4](ClO$_4$)$_3$. The starting complex *cis*-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O (100 mg, 0.21 mmol) and AgClO$_4$ (108.6 mg, 0.52 mmol) were taken in 15 cm^3 absolute ethanol and the mixture was refluxed for 2 h with stirring. The initial violet solution changed to orange–red; it was then cooled and filtered through a sintered glass funnel. The ligand L (24 mg, 0.10 mmol) was then added to the above solution containing [Ru(bpy)$_2$(EtOH)$_2$]$^{2+}$. The resulting mixture was heated to reflux for 20 h under dinitrogen atmosphere. The initial orange-red solution gradually changed to brown. The reaction mixture was reduced to 5 cm^3 and kept at 0 °C overnight. The precipitate was filtered and washed with ethanol. The solid mass thus obtained was purified by using a neutral alumina column. Initially, an orange compound corresponding to [**3**](ClO$_4$)$_2$ was eluted with CH$_2$Cl$_2$–CH$_3$CN (1.5 : 1). With CH$_2$Cl$_2$–CH$_3$CN (1 : 3), a brown compound corresponding to [**4**](ClO$_4$)$_3$ was then separated. Evaporation of solvent under reduced pressure yielded the pure complexes [**3**](ClO$_4$)$_2$ and [**4**](ClO$_4$)$_3$, respectively.

Anal. Calc. for [**3**](ClO$_4$)$_2$: C, 48.23; H, 3.10; N, 13.24. Found: C, 48.53; H, 3.99; N, 12.82%. Λ_M/Ω^{-1} cm^2 mol^{-1} in acetonitrile at 298 K: 264. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) in CH$_3$CN at 298 K: 480 (2430), 434 (4400), 286 (37100), 206 (30340). Yield: 25% (44 mg).

Anal. Calc. for [**4**](ClO$_4$)$_3$: C, 47.68; H, 3.11; N, 12.36. Found: C, 47.28; H, 3.01; N, 12.23%. Λ_M/Ω^{-1} cm^2 mol^{-1} in acetonitrile at 298 K: 342. Yield: 50% (70 mg).

Crystallography

Single crystals of bppn (L) were grown by slow diffusion of a dichloromethane solution into hexane, followed by slow evaporation. X-ray data of L were collected on a PC-controlled Enraf-Nonius CAD-4 (MACH-3) single-crystal X-ray diffractometer using Mo-Kα radiation. The structure was solved and refined by full-matrix least-squares on F^2 using SHELX-97 (SHELXTL).[32] Hydrogen atoms were included in the refinement process as per the riding model.

Crystal data for bppn: C$_{14}$H$_{10}$N$_4$, M = 234.26, monoclinic, space group Pn, a = 5.7084(5), b = 6.5938(4), c = 15.3455(10) Å, β = 91.693(6)°, V = 577.35(7) Å^3, T = 293(2) K, Z = 2, μ = 0.085 mm^{-1}, e data (R_{int}) = 1122 (0.000), $R1$ ($I > 2\sigma(I)$) = 0.0322, $wR2$ (all data) = 0.0888.

CCDC reference number 256270.

See http://www.rsc.org/suppdata/dt/b4/b417530a/ for crystallographic data in CIF or other electronic format.

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