Mixed-valency with cyanides as terminal ligands: Diruthenium(III,II) complexes with the 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine bridge and variable co-ligands (CN⁻ vs. bpy or NH₃)

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ARTICLE INFO

ABSTRACT

New diruthenium complexes (PPN)₄[(NC)₄Ru(μ-bptz)Ru(CN)₄], (PPN)₄ **1**, and [(bpy)₂Ru(μ-bptz)Ru(CN)₄], **2**, (PPN⁺ = bis(triphenylphospine)iminium; bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine; bpy = 2,2′-bipyridine), were synthesised and characterised by spectroscopic and electrochemical techniques. The compro-portionation constant $K_c = 10^{7.0}$ of the mixed-valent species $[(NC)_4Ru(\mu\text{-}bptz)Ru(CN)_4]^{3-}$ as obtained by oxidation of $\mathbf{1}^{4-}$ in CH₃CN is much lower than the $K_c = 10^{15.0}$ previously detected for $[(H_3N)_4Ru(bptz)\text{-}Ru(NH_3)_4]^{5+}$, reflecting the competition between CN⁻ and bptz for the π-electron density of the metals. Comparison with several other bptz-bridged diruthenium(II,III) complexes reveals an approximate corre-lation between K_c and the diminishing effective π acceptor capacity of the ancillary terminal ligands. In addition to the intense MLCT absorption at $\lambda_{max} = 624$ nm, the main IVCT (intervalence charge transfer) band of $\mathbf{1}^{3-}$ was detected by spectroelectrochemistry at $\lambda_{max} = 1695$ nm (in CH₃CN; $\varepsilon = 3200$ M⁻¹ cm⁻¹). The experimental band width at half-height, $\Delta\nu_{1/2} = 2700$ cm⁻¹, is slightly smaller than the theoretical value $\Delta\nu_{1/2} = 3660$ cm⁻¹, calculated from the Hush approximation for Class II mixed-valent species. In agreement with comparatively moderate metal–metal coupling, the mixed-valent intermediate $\mathbf{1}^{3-}$ was found to be EPR silent even at 4 K. The unsymmetrical mixed-valent complex $[(bpy)_2Ru^{II}(\mu\text{-}bptz)Ru^{III}(CN)_4]^+$, obtained in situ by bromine oxidation of **2** in CH₃CN/H₂O, displays a broad NIR absorp-tion originating from an IVCT transition at $\lambda_{max} = 1075$ nm ($\varepsilon \approx 1000$ M⁻¹ cm⁻¹, $\Delta\nu_{1/2} \approx 4000$ cm⁻¹). In addition, the lifetime of the excited-state of the mononuclear precursor complex $[Ru(bptz)(CN)_4]^{2-}$ was measured in H₂O by laser flash photolysis; the obtained value of $\tau = 19.6$ ns reveals that bptz induces a metal-to-ligand electronic delocalisation effect intermediate between that induced by bpy and bpz (bpz = 2,2′-bipyrazine) in analogous tetracyanoruthenium complexes.

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1. Introduction

In addition to their role in retro-Diels-Alder reactions [1], high-energy materials research [2], and crystal engineering [3], the elec-tron transfer [4,5], optical [4,6], and spin accommodation proper-ties [4,7] of 1,2,4,5-tetrazines have been employed to use them as mediating bridging ligands [4] in dinuclear systems, especially containing group 8 metal compounds [4,8–11].

3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) has been extensively used as a bridging ligand, capable of providing strong electronic coupling between chelated metal centres in mixed-valent dinucle-

ar species [1] which have included the diruthenium ions [(bpy)₂R-u(μ-bptz)Ru(bpy)₂]⁵⁺ and [(H₃N)₄Ru(μ-bptz)Ru(NH₃)₄]⁵⁺ [9,10b]. In previous work, we have also described the formation and partial characterisation of the symmetrical dinuclear complex ion [(NC)₄Ru^{II}(μ-bptz)Ru^{II}(CN)₄]⁴⁻ in aqueous solution [12]. In order to complete the characterisation of this species and of its mono-oxidised mixed-valent derivative [(NC)₄Ru^{II}(μ-bptz)Ru^{III}(CN)₄]³⁻ via essential measurements feasible only in non-aqueous solvents, we attempted the synthesis of the tetraanion using PPN⁺ (bis(tri-phenylphospine)iminium) as a counter-ion and employing a ther-molysis method of formation, similar to that described by Ward et al. for dinuclear [(NC)₄Ru^{II}(μ-bpym)Ru^{II}(CN)₄]⁴⁻ (bpym = 2,2-bipyrimidine) [13]. The mononuclear precursor complex [Ru^{II}(bptz)(CN)₄]²⁻ had been obtained and characterised as a sodium salt [12]. The new dinuclear species (PPN)₄[(NC)₄Ru^{II}

(μ-bptz)Ru^{II}(CN)$_4$], (PPN)$_4$**1**, has been studied by spectroscopic and electrochemical techniques in CH$_3$CN where it is sufficiently soluble. For comparison, the synthesis and characterisation of the unsymmetrical dinuclear complex [(bpy)$_2$Ru^{II}(μ-bptz)Ru^{II}(CN)$_4$], **2**, was also carried out, as well as the generation and *in situ* characterisation of the corresponding mixed-valent species [(NC)$_4$Ru(μ-bptz)Ru(CN)$_4$]$^{3-}$ (**1**$^{3-}$) and [(bpy)$_2$Ru(μ-bptz)Ru(CN)$_4$]$^+$ (**2**$^+$) under conditions where these species are soluble. Additionally, photophysical properties of the mononuclear precursor complex ion [12] [Ru(bptz)(CN)$_4$]$^{2-}$ were determined in order to correlate ground and excited-state results, specifically to assess the electronic effect of bptz as compared to other polypyridyl ligands in cyanoruthenium complexes (Scheme 1).

2. Results and discussion

### 2.1. Synthesis, solubilities and IR spectra

Complex (PPN)$_4$**1** was prepared by following the thermal procedure established by Ward et al. in acidic aqueous solution [13]. Since the K$^+$ salt obtained by this method is soluble in H$_2$O but insoluble in organic solvents, K$^+$ was substituted by PPN$^+$ using the procedure described by Mann et al. [14]. This PPN$^+$ salt is insoluble in H$_2$O and non-polar solvents, but soluble in CH$_3$CN and DMF. Complex **2** was synthesised by following a step-by-step method similar to that described previously for dinuclear unsymmetric ruthenium complexes [15]. It is soluble in a mixture of H$_2$O/CH$_3$CN, 1:1 v/v, but insoluble in pure acetonitrile. The rather selective solubilities of the compounds limited the extent of investigations possible.

Both dinuclear species show the characteristic vibrational bands from coordinated bpy and bptz groups in the IR spectra [16]. Complex (PPN)$_4$**1** shows a single broad band at 2054 cm^{-1} for the cyanide stretching frequencies $\nu_{C \equiv N}$; this value is similar to the one reported for the most intense band of the precursor compound Na$_2$[Ru(bptz)(CN)$_4$]·4H$_2$O [12]. The corresponding band for complex **2** appears at $\nu_{C \equiv N}$ = 2073 cm^{-1}, reflecting diminished charge (4$-$) $\rightarrow$ (0). *Cis*-Tetracyanoruthenium should exhibit four IR-allowed vibrational transitions for $\nu_{C \equiv N}$ [13,18]. However, low interaction force constants [16,17] often cause rather small splitting for $\nu_{C \equiv N}$ in M(CN)$_n$, n = 4,5, and hence band overlap to result in sometimes only one broad feature [13,18–20].
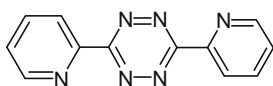
2.2. Electrochemistry

Cyclic voltammetry of complex **1** shows two oxidation processes at $E_{1/2}$ = 0.43 V and $E_{1/2}$ = 0.84 V vs. Fc/Fc$^+$. Although the limited solubility made for rather broad features (Fig. 1), the separation of the waves at ΔE = 0.41 V could be established, both in CH$_3$CN/0.1 M Bu$_4$NPF$_6$ and in DMF/0.1 M Bu$_4$NPF$_6$.

The comproportionation constant K_c for the equilibrium:

[Ru^{II}, Ru^{II}] + [Ru^{III}, Ru^{III}] $\leftrightarrow$ 2[Ru^{II}, Ru^{III}]
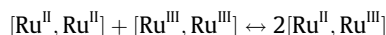
can be calculated as:

$$K_c = \frac{[\text{Ru}^{II}, \text{Ru}^{III}]^2}{[\text{Ru}^{II}, \text{Ru}^{II}][\text{Ru}^{III}, \text{Ru}^{III}]} = 10^{\Delta E/59} \qquad (1)$$
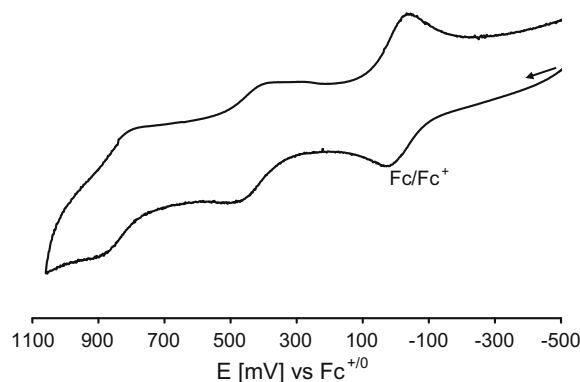
Fig. 1. Cyclic voltammogram of (PPN)**1** in CH$_3$CN/0.1 M Bu$_4$NPF$_6$ at 100 mV s^{-1} scan rate (potential vs. Fc$^{+/o}$).

The value of $K_c = 10^{7.0}$ indicates considerable but no unusual [9,10,20] electrochemical coupling between both metal centres in the symmetrical mixed-valent species [(NC)$_4$Ru(μ-bptz)Ru(CN)$_4$]$^{3-}$ (cf. Table 2 below).

Electrochemical reduction of **1**$^{4-}$ was not observed until -2.3 V vs. Fc/Fc$^+$, probably due to the high negative charge. In contrast, certain mononuclear tetracyanoruthenium(II) complexes such as [Ru(bpz)(CN)$_4$]$^{2-}$, bpz = 2,2′-bipyrazine, were shown to undergo reversible ligand-based reduction [18].

Cyclic voltammetric oxidation of the unsymmetrical complex **2** in aqueous solution (10^{-3} M, 0.1 M KCl) gave a redox potential value $E_{1/2}$ [Ru$_c^{III}$/Ru$_c^{II}$] = 0.80 V vs. Ag/AgCl. The corresponding value for $E_{1/2}$ [Ru$_b^{III}$/Ru$_b^{II}$] was not directly measurable due to insolubility in aprotic solvents (Ru$_c$ = Ru bonded to CN and Ru$_b$ = Ru bonded to bpy). It can be estimated to about 1.40 V, based on several related complexes [9c,21,24a]; the Ru$^{III/II}$ redox potentials of Ru/bpy entities show little solvent sensitivity. These values allow us to calculate $\Delta E_{1/2} \approx E_{1/2}\left(\text{Ru}_b^{III}/\text{Ru}_b^{II}\right) - E_{1/2}\left(\text{Ru}_c^{III}/\text{Ru}_c^{II}\right) \approx 0.60$ V and hence $K_c \approx 10^{10}$.

2.3. UV/Vis/NIR Spectra

Fig. 2 shows the UV/Vis/NIR spectrum of (PPN)$_4$**1** in CH$_3$CN/ 0.1 M Bu$_4$NPF$_6$. The lowest energy MLCT (metal-to-ligand charge transfer) band d$_\pi$ (Ru) $\rightarrow \pi^*$(bptz) appears at λ_{max} = 624 nm (ε_{max} = 1.7 × 10^4 M^{-1} cm^{-1}) with a shoulder at λ_{max} = 700 nm. These values are at lower energies relative to the mononuclear [Ru(bptz)(CN)$_4$]$^{2-}$ with λ_{max} = 521 nm [12] as expected, reflecting a stabilised π^*(bptz) LUMO after double metal coordination [24a]. A second MLCT band [16] occurs at 382 nm, and bands

Scheme 1.

bptz

Table 1
Characteristics of diruthenium(III,II) mixed-valent intermediates.

	[L$_4$Ru(μ-bptz)RuL$_4$]^n		[L$_5$Ru(μ-pz)RuL$_5$]^n	
	L = CN$^-$	L = NH$_3$	L = CN$^-$	L = NH$_3$
n	3$-$	5+	5$-$	5+
K_c[a]	10$^{7.0}$	10$^{15.0}$	10$^{4.7}$	10$^{7.3}$
λ_{max} (nm)	1695	1453	1760	1600
ν_{max} (cm^{-1})	5900	6880	5680	6250
ε_{max} (M^{-1} cm^{-1})	≈3200	500	2600	5000
$\Delta\nu_{1/2}$ (cm^{-1}) (exp)	2700	1600	4200	1250
$\Delta\nu_{1/2}$ (cm^{-1}) (calc)[b]	3660	3990	3620	3800
EPR	silent	active	silent	active
References	this work	[9c]	[21]	[24]^c

pz = pyrazine.
[a] Comproportionation constant according to Eq. (1).
[b] According to $\Delta\nu_{1/2} = (2310 \cdot \nu_{max})^{1/2}$ (see Ref. [22]).
[c] C. Creutz, M.H. Chou, Inorg. Chem. 26 (1987) 2995.

Table 2
Mixed-valence properties[a] of complexes [$L_nRu(\mu$-bptz)RuL_n]^m.

L_n	m	K_c	λ_{IVCT} (nm)	ε_{IVCT} (M^{-1} cm^{-1})	References
(CN)$_4$	3–	$10^{7.0}$	1695	3200	this work
Cl{[9]$_{ane}$S$_3$}[b]	3+	$10^{8.2}$	1852	519	[10a]
(bpy)$_2$	5+	$10^{8.5}$	1483	2800	[9a,10b]
(acac)$_2$[c]	+	10^{13}	1238	20	[11a]
(NH$_3$)$_4$	5+	$10^{15.0}$	1453	500	[9b,c]

[a] Comproportionation constants K_c and intervalence charge transfer absorption data.
[b] [9]$_{ane}$S$_3$ = 1,4,7-trithiacyclononane.
[c] acac = acetylacetonate = 2,4-pentanedionate.
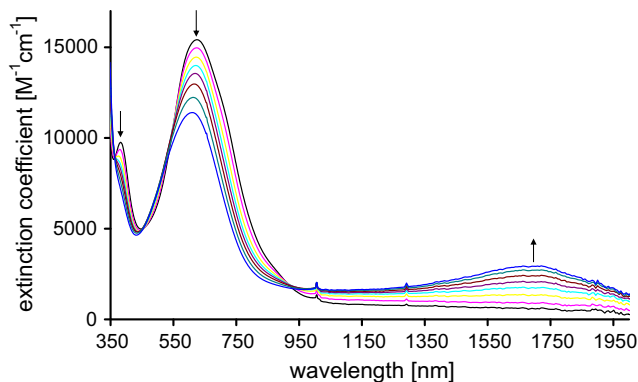
Fig. 2. Spectroelectrochemical oxidation of (PPN)**1** in CH$_3$CN/0.1 M Bu$_4$NPF$_6$.

between 250 and 350 nm can be assigned to LC (ligand centered) transitions of bptz.

The UV/Vis spectrum of [(bpy)$_2$Ru(μ-bptz)Ru(CN)$_4$] (**2**) in CH$_3$CN/H$_2$O 1:1 v/v exhibits a band at λ_{max} = 503 nm (ε_{max} = 3.4 × 10^3 M^{-1} cm^{-1}), comprising MLCT transitions d_π(Ru$_c$) → π^*(bptz), d_π(Ru$_b$) → π^*(bptz) and d_π(Ru$_b$) → π^*(bpy) [9,24a]. The charge transfer transition pattern resulting from coordination of two different metal donor entities to one π acceptor bridge has been discussed previously [25,26], however, in the present case the absorptions are not sufficiently resolved to warrant further interpretation.

2.4. Mixed-valent intermediates and spectroelectrochemistry

By oxidation of **2** with Br$_2$ vapour in CH$_3$CN/H$_2$O 1:1 v/v, a new broad band at $\lambda_{max} \approx 1075$ nm ($\varepsilon \approx 1000$ M^{-1} cm^{-1}, $\Delta\nu_{1/2} \approx 4000$ cm^{-1}) is observed. This near IR band is assigned to the metal-to-metal charge transfer (MMCT) or intervalence charge transfer (IVCT) transition d_π(Ru$_b^{II}$) → d_π(Ru$_c^{III}$), involving the two different ruthenium atoms of the unsymmetrical mixed-valent species **2$^+$**. The observations are in agreement with that obtained by controlled potential electrolysis of **2**, and the results, especially the relatively high-energy and the large bandwidth for the IVCT transition are typical for a situation of coupled centres which are appreciably different (Class I/II) [22,27]. The more facile oxidation of the [Ru^{II}(CN)$_4$]$^{2-}$ side of the unsymmetrical complex **2** is attributed to the charge effect from four cyanide anion ligands, which were calculated to be weak π acceptors [28].

By following the Marcus–Hush formalism applied to mixed-valent species [22] values of the reorganisation energy (λ = 0.28 eV) and the electronic coupling (H_{AB} = 570 cm^{-1}) can be obtained according to Eqs. (2) and (3) for the intramolecular electron transfer through the bptz bridge in **2$^+$**. The value of λ is lower than that of $-\Delta G^0$, suggesting that the charge recombination process falls into the Marcus inverted region [23]. The value of H_{AB}

indicates a considerable interaction between both metallic centres, even though the distance is estimated at $r \sim 7$ Å [11a]. Indeed, for an unsymmetrical mixed-valent species [(trpy)(bpy)Ru^{II}-(μ-pz)-Ru^{III}(NH$_3$)$_5$]$^{5+}$ (trpy = 2,2':6',2"-terpyridine), bridged by pyrazine (pz) and with a similar metal–metal distance as complex **2$^+$**, the calculated value of H_{AB} is similar at 614 cm^{-1} [24b].

$$\lambda = E_{op} - \Delta G^0 - \Delta E_{ex} \tag{2}$$

$$H_{AB} = \frac{2.06 \times 10^{-2}}{r}(\varepsilon_{max} \cdot \Delta\tilde{\nu}_{1/2} \cdot \tilde{\nu}_{max})^{1/2} \tag{3}$$

E_{op} is the energy of the absorption maximum (in eV), ΔG^0 is the free energy difference between both redox sites (approximated as the difference in the redox potentials $\Delta E_{1/2}$), ΔE_{ex} is an excited-state energy difference, estimated as 0.25 eV, ε_{max} is the absorption coefficient of the MMCT band, $\tilde{\nu}_{max}$ is the energy maximum of the same band (in cm^{-1}), $\tilde{\nu}_{1/2}$ is the bandwidth at half-height, and r is the metal–metal distance in Å.

Spectroelectrochemical measurement of (PPN)$_4$**1** in CH$_3$CN/ 0.1 M Bu$_4$NPF$_6$ was affected by adsorption of the doubly oxidised form on the Pt-grid electrode. Results can be therefore guaranteed only for the one-electron oxidised species **1^{3-}**. Unfortunately, but not unexpectedly [18–20], the CN stretching bands in the IR are not well resolved, and hence they cannot be used to establish valence localisation or delocalisation [28]. In the UV/Vis spectra, a shift from 624 to 610 nm reflects the decrease of negative charge. Spectral analysis of the electronic transition in the near-IR region (Fig. 2) yields ν_{max} = 5900 cm^{-1} (1695 nm), ε_{max} = 3200 M^{-1} cm^{-1}, $\Delta\nu_{1/2}$ = 2700 cm^{-1} for the asymmetric IVCT band. The IVCT band disappears and the MLCT band shifts from 610 nm to about 550 nm on further oxidation of **1^{3-}**, however, this process is not 100% reversible in the spectroelectrochemical experiment.

Intra muros oxidation of **1^{4-}** inside an X band EPR spectrometer did not produce a detectable signal, even if the measurement was done at 4 K for a glassy frozen solution of **1^{3-}** in CH$_3$CN/0.1 M Bu$_4$NPF$_6$. EPR "silence" of mixed-valent species involving heavier transition elements is not uncommon, it has been observed similarly for [(NC)$_5$Ru(μ-pz)Ru(CN)$_5$]$^{5-}$ [19]. The effect is attributed to the presence of several additional states lying close to the doublet ground-state which allow for very rapid relaxation of electron spin, enhanced also by spin–orbit coupling. The resulting massive line broadening can then lead to the absence of an observable EPR response.

EPR silence is typical for weakly coupled mixed-valent systems [19,20,27b,28] where the energy difference between close lying states near the SOMO is small. The fact that **1^{3-}** exhibits no EPR spectrum at 4 K whilst the analogous [(H$_3$N)$_4$Ru(μ-bptz)Ru(NH$_3$)$_4$]$^{5+}$ shows such a signal [9c] suggests that **1^{3-}** involves a weaker metal–metal coupling, interpreted as the result of competition from both bptz and the eight cyano acceptor ligands for the metal π donor capability.

Table 1 shows the properties of this new mixed-valent complex **1^{3-}** in comparison to those of related diruthenium species (CN$^-$ vs. NH$_3$ as terminal ligand).

Both the electrochemical and IVCT absorption data in Table 1 suggest that the mixed-valent [(NC)$_4$Ru(μ-bptz)Ru(CN)$_4$]$^{3-}$ ion lies in between the clearly delocalised ammineruthenium species [9c] [(H$_3$N)$_4$Ru(μ-bptz)Ru(NH$_3$)$_4$]$^{5+}$ and the localised decacyanodiruthenium(III,II) dimer [(NC)$_5$Ru(μ-pz)Ru(CN)$_5$]$^{5-}$ bridged by pyrazine [19]. In effect, the value of K_c = 10$^{7.0}$ for **1^{3-}** indicates a diminished electrochemical coupling relative to the octaammine diruthenium species [(H$_3$N)$_4$Ru(bptz)Ru(NH$_3$)$_4$]$^{5+}$ (Table 1), in conformity with the competition between CN$^-$ and bptz for the π-electron density of the metals (electron transfer mechanism of valence

delocalisation [27b]). Interestingly, the K_c value is almost identical to that of the Creutz–Taube ion, and a borderline case (Class II/III) may be discussed [27].

Comparison with several other symmetrical bptz-bridged diruthenium(II,III) complexes in Table 2 reveals an approximate correlation between Kc and the diminishing π acceptor competition of the ancillary terminal ligands. Table 2 reflects this correlation in a straightforward way for K_c (which depends on the relative stabilities of the oxidation states), showing a terminal ligand sequence from the cyanide, thioether and 2,2'-bipyridine acceptors to the donating acac- and NH₃ ligands. However, the long-wavelength IVCT absorptions do not quite exhibit the same correlation; energies and intensities of these transitions depend strongly on orbital overlap and thus on the spatial circumstances dictated by the co-ligands.

2.5. Photophysical properties of the precursor

The [Ru(bpy)(CN)₄]²⁻ ion and its derivatives exhibit remarkable photophysical behaviour [29]. We have previously reported that the mononuclear species [Ru(bptz)(CN)₄]²⁻ emits at room temperature in a solution of CH₃OH/C₂H₅OH, 5:1 v/v, whilst the emission in water was not detected [12]. In an attempt to correlate the ground-state properties mentioned with excited-state properties, we have now determined the lifetime in a N₂-saturated aqueous solution for the lowest lying excited-state of [Ru(bptz)(CN)₄]²⁻ by using a laser flash photolysis technique. Fig. 3 shows the excited-state difference spectra following excitation into the MLCT absorption [12] of the complex at 355 nm. The transient spectrum shows a maximum at 410 nm, typical of Ru^{III}-(diimine·⁻) triplet excited species. The measured lifetime, τ = 19.5 ± 0.5 ns, is almost five times lower than that of [Ru(bpy)(CN)₄]²⁻ (τ = 101 ns) [29a], but nearly four times higher than that of [Ru(bpz)(CN)₄]²⁻ (τ = 5 ns) [30]. These changes can be accounted for by the energy gap law [31]: the *ln* of the rate for the non-radiative decay from the excited-state is inversely proportional to the energy of that state. In effect, as the energy of the singlet first excited-state of [Ru(L)(CN)₄]²⁻ decreases (λ_{max} = 400, 454 and 465 nm, in H₂O, for L = bpy, bptz and bpz, respectively) [12,29a,30], the lifetime of the corresponding triplet excited-states shortens. The following order of (Ru → L) π-backbonding effect in [Ru(L)(CN)₄]²⁻ is thus disclosed: bpy < bptz < bpz, in consistency with previous IR results [12].
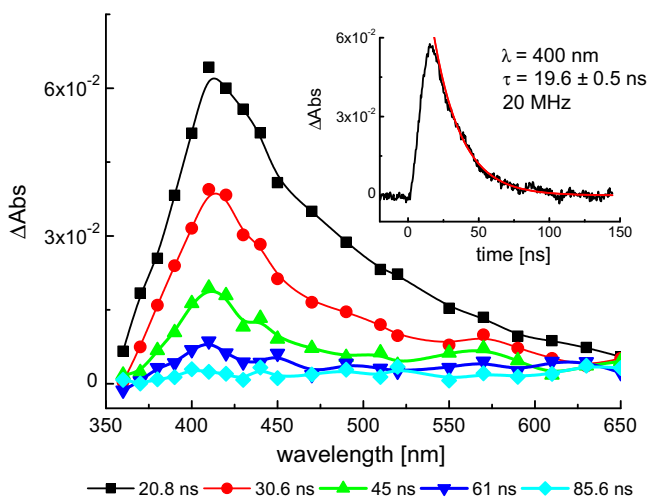
Fig. 3. Transient spectra and exponential decay for the lowest-lying excited-state of [Ru(bptz)(CN)₄]²⁻ in N₂-deareated aqueous solution at room temperature (λ_{exc} = 355 nm).

2.6. Conclusions and outlook

In both symmetrical and unsymmetrical mixed-valent complexes [(NC)₄Ru(bptz)Ru(CN)₄]³⁻, **1**³⁻, and [(bpy)₂Ru^{II}(bptz)-Ru^{III}(CN)₄]⁺, **2**⁺, the first tetracyanoruthenium species with characterised ground-state mixed-valency (cf. the excited-state descriptions by Ward et al. [13b,c]), the bridging ligand bptz induces strong electronic communication between both metal centres, although the competition between the bptz acceptor bridge and the eight terminal cyanide ligands for the metal π donor capacity reduces the comproportionation constant K_c to a relatively low value of 10^{7.0}. Applying the Hush equation to **1**³⁻ shows only a rather small discrepancy between experimental and theoretical $\Delta\nu_{1/2}$ values, suggesting a Class II or perhaps borderline [27] species. The unsymmetrical **2**⁺ is most probably oxidised first at the Ru(CN)₄ fragment; it shows a very broad IVCT absorption at a comparatively high-energy.

In contrast to the numerous mixed-valent systems of the Prussian Blue type in which the cyano functions act as bridges (case A in Scheme 2) [32], the examples presented here contain the CN⁻ groups as terminal ligands (case B). In this configuration, the π acceptor potential of cyanide manifests itself by attenuation of the metal–metal interaction across an acceptor bridge such as bptz. It remains to be studied how mixed-valent systems with other bridges respond, and how, solubility permitting, the well-known sensitivity of polycyano complexes towards the environment [10c,13] (solvent molecules, hydrogen bridge donors, counter-ions) will affect the mixed-valence properties.

3. Experimental

3.1. Materials and techniques

All chemicals were p.a grade. CH₃CN was distilled over P₄O₁₀. IR spectra were recorded (as KBr pellets) on a Perkin–Elmer FTIR Spectrum RX-1 spectrophotometer. UV–visible spectra were obtained with Shimadzu UV-160 A and Varian Cary 50 spectrophotometers, provided with 1-cm cells. Cyclic voltammetry was carried out on a BAS-Epsilon equipment, provided with vitreous carbon as a working electrode, Pt wire as auxiliary electrode and Ag/AgCl (3 M KCl) as reference electrode. In acetonitrile, ferrocene (FeCp₂/FeCp₂⁺ couple) was used as internal reference. An OTTLE (optically transparent thin layer electrode) cell from BAS and a previously described constructed cell [33] were used for spectroelectrochemical measurements. Luminescence lifetime measurements were determined by using a Luzchem m-LFP (Laser Flash Photolysis) equipment from the University of Santiago del Estero, Argentina, which was provided with a Q-switched Nd:YAG laser generating 355-nm pulses (fwhm: 10 ns; 5 mJ per pulse). The lifetimes were obtained without deconvolution of the laser pulse response and were quite reproducible and higher than the dead time values. EPR measurements were done using a two-electrode capillary cell [34]. Chemical analyses (C, H, and N) were done at INQUIMAE, University of Buenos Aires, Argentina, with an estimated error of ±0.5%.

3.2. Syntheses

(PPN)₄[(NC)₄Ru(μ-bptz)Ru(CN)₄], (PPN)₄**1**. 500 mg (1.07 mmol) of K₄[Ru(CN)₆]·3H₂O and 126 mg (0.53 mmol) of bptz were heated

$$M^x\text{-}(\mu\text{-CN})\text{-}M^{x+1} \qquad \qquad (\textbf{A})$$

$$(NC)_n M^x\text{-}(\mu\text{-L})\text{-}M^{x+1}(CN)_n \qquad \qquad (\textbf{B})$$

Scheme 2.

at reflux under Ar in 42 mL of MeOH/H$_2$O, 1:3 v/v, at pH 1.3 (HCl) during 24 h. The dark violet solution was neutralised with KOH, filtered to eliminate unreacted bptz and reduced to a minimum volume. EtOH was then added to eliminate excess K$_4$[Ru(CN)$_6$], which was removed by filtration. The solvent was removed until complete dryness, the residue redissolved in the minimum amount of water and chromatographed on a Sephadex G-25 column (24 × 4 cm), which was eluted with water. The first fraction was collected, reduced in volume and precipitated with acetone. The obtained K$^+$ salt was filtered, washed with acetone and ether, and dried under vacuum over P$_4$O$_{10}$. The dry solid was dissolved in the minimum amount of water and excess (PPN)Cl in warm water was added to give the water-insoluble PPN$^+$ salt. The precipitate was filtered, washed with water, dissolved in acetonitrile and reprecipitated with ether. The solid was filtered and dried in vacuum over P$_4$O$_{10}$. Further redissolution in acetonitrile and slow evaporation at room temperature gave a dark violet crystalline product. Yield: 99 mg (7%). *Anal.* Calc. for C$_{164}$H$_{128}$N$_{18}$P$_8$Ru$_2$: C, 70.3; H, 4.6; N, 9.0. Found: C, 70.1; H, 4.4; N, 9.2%.

[(bpy)$_2$Ru(μ-bptz)Ru(CN)$_4$], **2**. 13 mg (0.025 mmol) of [Ru(bpy)$_2$Cl$_2$]·2H$_2$O were heated at reflux under Ar in 10 mL of EtOH/H$_2$O, 1:1 v/v during 1 h. 14 mg (0.025 mmol) of Na$_2$[Ru(bptz)(CN)$_4$]·4H$_2$O, prepared as in Ref. [12], were added under Ar and heated at reflux for 1 h. Ethanol was evaporated and the neutral complex precipitated overnight at 0 °C. The light violet solid was filtered and dried under vacuum over P$_4$O$_{10}$. Yield: 17 mg (80%). *Anal.* Calc. for C$_{36}$H$_{24}$N$_{14}$Ru$_2$: C, 50.6; H, 2.8; N, 22.9. Found: C, 50.8; H, 3.0; N, 22.5%.

Acknowledgements

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