

Synthesis and mixed valence aspects of $[(L)ClRu]_2(\mu\text{-tppz})^{n+}$ incorporating 2, 2'-dipyridylamine (L) as ancillary and 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) as bridging ligand †

Nripen Chanda,^a Biprajit Sarkar,^b Jan Fiedler,^c Wolfgang Kaim^{*b} and Goutam Kumar Lahiri^{*a}

^a Department of Chemistry, Indian Institute of Technology -Bombay, Powai, Mumbai-400076, India. E-mail: lahiri@chem.iitb.ac.in

^b Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany. E-mail: kaim@iac.uni-stuttgart.de

^c J. Heyrovsky Institute of Physical Chemistry, Academy of Science of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic

Received 29th May 2003, Accepted 6th August 2003

First published as an Advance Article on the web 19th August 2003

The tppz-bridged diruthenium complex $[(L)ClRu^{II}]_2(\mu\text{-tppz})(ClO_4)_2$, **[1]**(ClO₄)₂ {tppz = 2,3,5,6-tetrakis(2-pyridyl)pyrazine, L = 2,2'-dipyridylamine} and its mononuclear counterpart $[(L)ClRu^{II}(tppz)]ClO_4$, **[2]**(ClO₄) have been synthesized. The 380 mV separation between successive Ru^{II}/Ru^{III} couples in **[1]**²⁺ leads to a comproportionation constant (K_c) of 2.7×10^6 . Consequently, the Ru^{II}Ru^{III} species **[1]**³⁺ exhibits a rather narrow intervalence charge transfer band at 1700 nm, suggesting a class III mixed-valence state, the electronic coupling constant (V_{ab}) is calculated at 2940 cm⁻¹. Complex **[1]**³⁺ displays a rhombic EPR spectrum at 4 K ($g_1 = 3.390$, $g_2 = 2.278$, $g_3 = 1.697$), characteristic of ruthenium(III) in a distorted octahedral environment. Both complexes show two successive tppz-based reduction processes [$(tppz)^{0/-1}$ and $(tppz)^{-1/-2}$]. The one-electron reduced species **[1]**⁺ is a tppz radical anion species with an intense low-energy band at 1105 nm and an axial EPR signal at 4 K ($g_1 = 2.008$, $g_2 = g_3 = 1.994$). **[1]**²⁺ and **[2]**⁺ exhibit moderately strong emissions at 740 nm and 668 nm, respectively, in EtOH–MeOH glass at 77 K.

Introduction

The design of polynuclear metal complexes exhibiting intermetallic electronic coupling in mixed-valence states *via* mediation by suitable bridging functionalities has generated considerable research interest over the past twenty years.¹ This has been primarily due to their relevance for biological processes,² molecular electronics,³ and for theoretical studies of electron transfer kinetics.⁴ The discovery of pyrazine-mediated strong intermetallic coupling in the diruthenium(III,II) Creutz–Taube (CT) ion⁵ has initiated continuous efforts in designing new diruthenium CT analogues which incorporate polyazine-derived heterocyclic bridging moieties such as 2,3-bis(2-pyridyl)quinoxaline,⁶ 2,2'-bipyrimidine,⁷ 2,3-bis(2-pyridyl)pyrazine,⁸ tetrapyrido[2,3-*a*:3',2'-*c*:2'',3''-*h*:3''',2''-*j*]phenazine,⁹ or 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz).¹⁰ In the last fifteen years the efficiency of the non-planar bis-tridentate (tppz) bridge for mediating intermetallic communication in homo- and hetero-polynuclear ruthenium complexes has been scrutinised in combination with a variety of terminal ancillary ligands such as NH₃, 2,2':6',2''-terpyridine, 2,2'-bipyridine or 2-arylazopyridines.¹⁰ In all these cases tppz facilitated the metal–metal interaction through its π^* orbital to a similar extent as the CT ion.¹⁰

Although the amount of metal–metal coupling in mixed-valence states of polynuclear species is largely controlled by the structural and electronic aspects of the bridging ligand, the terminal ancillary ligands in the complex are an additional factor. Thus, a reasonable variation of the comproportionation constants K_c has been observed for the complexes $[(L')Ru^{II}(\mu\text{-tppz})Ru^{III}(L')]^{n+}$, depending on the electronic nature of L': L' = 4'-tolyl-2,2':6',2''-terpyridine (ttrpy), $K_c = 1.2 \times 10^5$;^{10b} L' = 2,2':6',2''-terpyridine (trpy), $K_c = 1.7 \times 10^5$;^{10c} L' = 4'-vinyl-2,2':6',2''-terpyridine (V-trpy), $K_c = 1.3 \times 10^6$;^{10c} L' = NH₃, $K_c = 4.4 \times 10^8$;^{10j} L' = 2,2'-bipyridine (bpy), $K_c = 8.2 \times 10^4$;^{10a} L' =

2-phenylazopyridine, $K_c = 7.9 \times 10^3$.^{10a} The observed effects of L' on the Ru($\mu\text{-tppz}$)Ru core towards the stabilisation of the mixed-valence Ru^{II}Ru^{III} state has initiated the present programme of selective introduction of 2,2'-dipyridylamine (L), which contains a dissociable amine proton and tends to form non-planar six-membered chelate rings on coordination to a metal ion.¹¹

The present work describes the synthesis and characterisation of the diruthenium complex $[(L)ClRu^{II}]_2(\mu\text{-tppz})^{2+}$, **[1]**²⁺, and its mononuclear analogue $[(L)ClRu^{II}(tppz)]^+$, **[2]**⁺, as well as detailed spectroelectrochemical aspects of **[1]**ⁿ⁺ in the accessible states ($n = 1-4$). The effectiveness of L as ancillary ligand in $[(L)ClRu^{II}]_2(\mu\text{-tppz})^{n+}$, particularly with respect to the intermetallic electronic coupling, has been studied in comparison to related complexes¹⁰ having ancillary ligands of a different electronic nature.

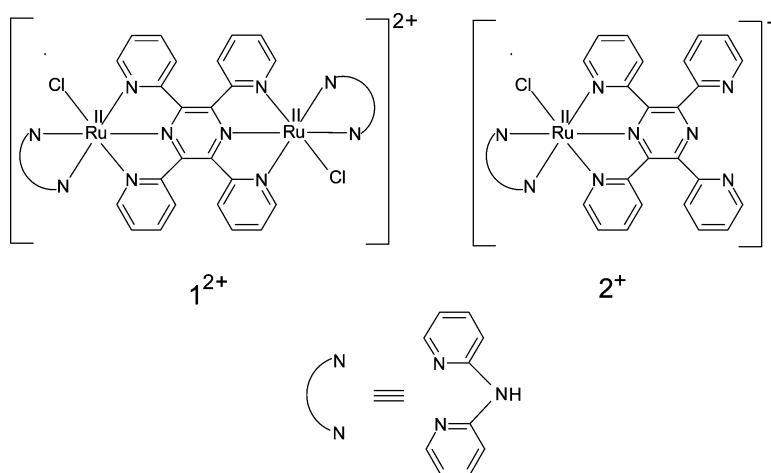
Results and discussion

Synthesis and characterisation of the ruthenium(II) compounds

The dinuclear complex $[(L)ClRu^{II}(\mu\text{-tppz})Ru^{II}Cl(L)]^{2+}$, **[1]**²⁺, was synthesized *via* the reaction of the precursor complex $\{Cl_3Ru^{III}\}_2(\mu\text{-tppz})$ and 2,2'-dipyridylamine (L) in the presence of triethylamine and LiCl in ethanolic medium under a dinitrogen atmosphere. The complex **[1]**²⁺ was isolated as the perchlorate salt **[1]**(ClO₄)₂. During the chromatographic purification of **[1]**(ClO₄)₂ on an alumina column, the pink monomeric complex $[(L)ClRu^{II}(tppz)](ClO_4)$, **[2]**(ClO₄), was eluted initially in about 15% yield, followed by the green dinuclear **[1]**(ClO₄)₂ ($\approx 75\%$; Scheme 1).

The complexes **[1]**(ClO₄)₂ and **[2]**(ClO₄) exhibited satisfactory microanalytical data and displayed 1 : 2 and 1 : 1 conductivities, respectively, in acetonitrile (see Experimental section). The formation of **[1]**(ClO₄)₂ and **[2]**(ClO₄) was confirmed by electrospray mass spectroscopy (Fig. S1 †) which showed maximum molecular ion peaks centred at $m/z = 1103.06$ and 696.09, corresponding to $\{[1](ClO_4)\}^+$ (calculated molecular mass: 1103.3) and $[2]^+$ (calculated molecular mass: 695.59), respectively. The

† Electronic supplementary information (ESI) available: far-IR and electrospray mass spectra of **[1]**(ClO₄)₂ and **[2]**(ClO₄). See <http://www.rsc.org/suppdata/dt/b3/b306065a>



Scheme 1

IR vibrations for $\nu(\text{NH})$ and $\nu(\text{ClO}_4^-)$ were observed near 3300 cm^{-1} and $1100/625\text{ cm}^{-1}$, respectively. The far-IR spectrum of $[\mathbf{1}](\text{ClO}_4)_2$ showed one Ru–Cl stretching band at 312 cm^{-1} which would be consistent with a *trans (anti)* geometry^{10a} (Fig. S2†) (Scheme 1). In the case of other dinuclear complexes $[(\text{L}')\text{ClRu}^{\text{II}}]_2(\mu\text{-tppz})^{2+}$ the *trans (anti)* isomer was found to be the major product for $\text{L}' = \text{bpy}^{10h}$ whereas it was the exclusive product for $\text{L}' = 2\text{-phenylazopyridine}^{10a}$. The Ru–Cl stretching band of complex $[\mathbf{2}](\text{ClO}_4)$ appeared at 322 cm^{-1} (Fig. S2†).

The “aromatic region” of the $^1\text{H-NMR}$ spectrum of $[\mathbf{1}]^{2+}$ in $(\text{CD}_3)_2\text{SO}$ (Fig. 1a) is complicated due to the partial overlapping of several signals in the range between 9.6 and 5.9 ppm. However, direct comparison of the intensities of the aromatic protons with those of the two clearly observable and D_2O -exchangeable NH protons at $\delta = 10.70$ and 10.85 ppm, revealed the presence of 32 “aromatic” protons (sixteen from the bridging tppz and eight from each of the terminal ligands). The pres-

ence of two distinct NH proton signals in 1 : 1 ratio and the appearance of the calculated number of 32 aromatic proton signals suggest either two positional isomers or low symmetry of $[\mathbf{1}]^{2+}$ in solution^{10a,h} due to the non-planarity of tppz and the coordinated L ligands.

The $^1\text{H-NMR}$ spectrum of $[\mathbf{2}]^+$ in $(\text{CD}_3)_2\text{SO}$ (Fig. 1b) shows the expected overlapping signals from 24 protons in the range between 9.5 and 6.0 ppm. The NH signal at 10.75 ppm disappeared on treatment with D_2O .

In both $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^+$, the ancillary ligands L contain dissociable NH protons. Therefore, the pK_a values of the complexes were determined spectrophotometrically. The titration of $[\mathbf{1}]^{2+}$ in aqueous medium resulted in a shift of the lowest energy MLCT band from 590 to 620 nm with increasing pH (Fig. 2a). The plot of absorbance *versus* pH revealed the presence of two pK_a values at 8.5 and 11.6 (Fig. 2a, insert) due to the successive dissociation of the two NH protons.¹² In the case of $[\mathbf{2}]^+$ an increase in pH shifted the lowest energy band from 496 to 532 nm, giving rise to a distinct isobestic point at 517 nm (Fig. 2b)

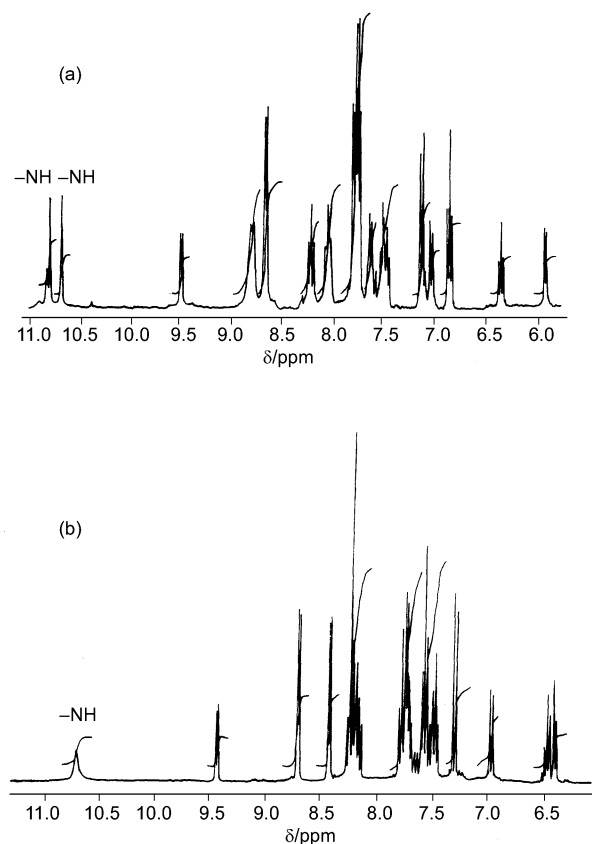


Fig. 1 $^1\text{H NMR}$ spectra of (a) $[\mathbf{1}]^{2+}$ and (b) $[\mathbf{2}]^+$ in $(\text{CD}_3)_2\text{SO}$.

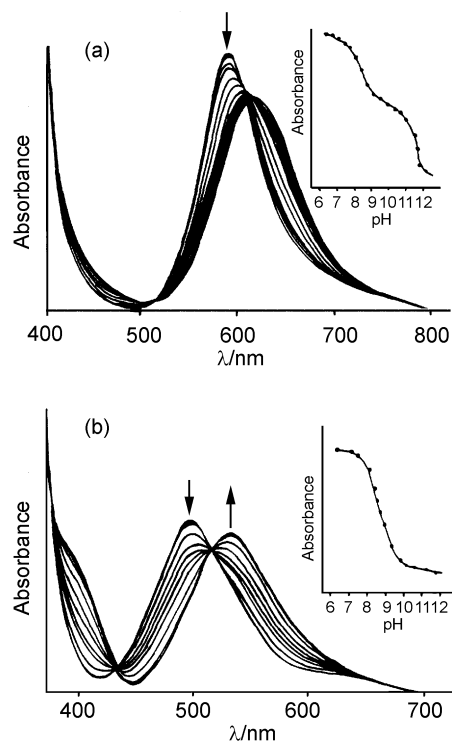


Fig. 2 Changes in the UV-VIS spectra of (a) $[\mathbf{1}]^{2+}$ and (b) $[\mathbf{2}]^+$ as the pH is varied from 6.5 to 12.5 in water. The arrows indicate an increase or decrease in band intensity with increasing pH. The insert shows the variation of absorbance with pH (590 nm for $[\mathbf{1}]^{2+}$ and 496 nm for $[\mathbf{2}]^+$).

and yielding a pK_a value of 8.6 (Fig. 2b, insert). The first pK_a value of $[1]^{2+}$ is almost identical to that of $[2]^+$, however, the second pK_a of $[1]^{2+}$ is much higher.

Electrochemistry and spectroelectrochemistry (UV-VIS-NIR)

The reversible Ru^{III}/Ru^{II} couple for the mononuclear complex $[2]^+$ appeared at $E^\circ = 0.77$ V ($\Delta E_p = 80$ mV, $i_{pa}/i_{pc} \approx 1$) versus SCE (Fig. 3b, couple-I). The dinuclear complex $[1]^{2+}$ exhibited two successive reversible couples at $E_1 = 0.68$ V ($\Delta E_p = 70$ mV, $i_{pa}/i_{pc} \approx 1$, couple-I) and $E_2 = 1.06$ V ($\Delta E_p = 80$ mV, $i_{pa}/i_{pc} \approx 1$, couple-II) versus SCE which are attributed to the stepwise oxidations of the Ru^{II} centres, i.e. $Ru^{II}Ru^{II} \rightleftharpoons Ru^{II}Ru^{III} \rightleftharpoons Ru^{III}Ru^{III}$. The 380 mV separation between the two successive Ru^{III}/Ru^{II} couples ($E_2 - E_1$) leads to a comproportionation constant K_c of the mixed-valent $Ru^{III}Ru^{II}$ state at 2.7×10^6 [using the equation $RT \ln K_c = nF(\Delta E)$]. The relatively high K_c value as well as the 90 mV negative potential shift of the first Ru^{III}/Ru^{II} couple of $[1]^{2+}$ as compared to $[2]^+$ revealed the presence of moderately strong intermetallic coupling in the mixed-valence state $[1]^{3+}$. Related dinuclear complexes involving bipyridine or phenylazopyridine ligands exhibited first Ru^{III}/Ru^{II} couples at 0.96 V^{10h} or 1.28 V, respectively.^{10a} Therefore, a substantial stabilisation of the ruthenium(III) state takes place in the $Ru(\mu\text{-tppz})Ru$ core while moving from π -accepting phenylazopyridine *via* bipyridine to the more donating dipyriddyamine ancillary ligands. The potential difference between the successive Ru^{III}/Ru^{II} couples follows a similar trend, decreasing from the system with dipyriddyamine (380 mV, $K_c = 2.7 \times 10^6$) *via* that with bipyridine (290 mV, $K_c = 8.2 \times 10^4$)^{10a} to the phenylazopyridine-containing complex (230 mV, $K_c = 7.9 \times 10^3$).^{10a} Obviously, increasing competition from π -acidic co-ligands diminishes the electron transfer-type valence exchange^{1a} across the π -acidic tppz bridge with its low-lying π^* orbital. Thus, a significant difference in the degree of intermetallic electrochemical coupling across the tppz bridging unit in $[(L')\text{-}(Cl)Ru]_2(\mu\text{-tppz})^{2+}$ has been observed, depending on the electronic aspects of the co-ligand L' .

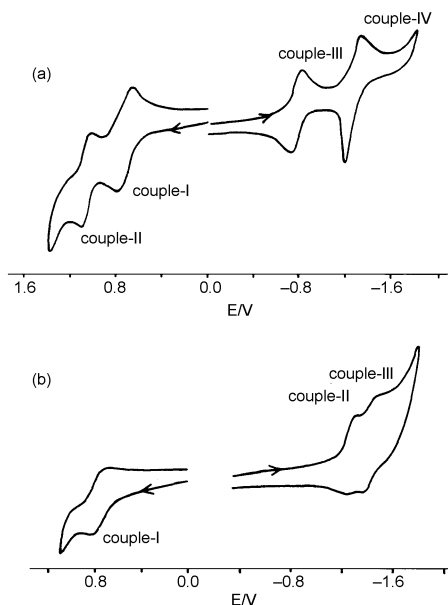


Fig. 3 Cyclic voltammograms of (a) $[1]^{2+}$ and (b) $[2]^+$ in $CH_3CN/0.1$ mol dm^{-3} Et_4NClO_4 .

Complex $[1]^{2+}$ exhibited two quasi-reversible reduction processes $E^\circ = -0.76$ V ($\Delta E_p = 90$ mV) (couple-III) and -1.27 V ($\Delta E_p = 120$ mV) (couple-IV) (Fig. 3a) which are attributed to successive reductions of the coordinated tppz ligand, $[tppz] \rightleftharpoons [tppz]^-$ and $[tppz]^- \rightleftharpoons [tppz]^{2-}$, respectively.¹⁰ The anodic wave associated with the second reduction couple (couple-IV)

Table 1 Electronic spectral data for $[1]^{n+}$ ($n = 1-4$) in $CH_3CN/0.1$ mol dm^{-3} Bu_4NPF_6 at 298 K

Complex	λ_{max}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$)
$[1]^+$	1105 (5150), 585 (8080), 400 (18000)
$[1]^{2+}$	615 (13570), 365 (25600)
$[1]^{3+}$	1700 (2250), 800(sh), 615 (7020), 370 (20000)
$[1]^{4+}$	895 (1900), 480 (5180), 380 (20500)

showed an adsorption feature at -1.2 V. This is possibly due to the precipitation of the two-electron reduced neutral complex $[(L)ClRu]_2(\mu\text{-tppz}^{2-})$ $[1]$ on the electrode surface.^{10c} A similar electrochemical behaviour was observed earlier for other dinuclear tppz complexes such as $[Ru_2(tppz)_3]^{4+}$ and $[\{Os(trpy)\}_2(tppz)]^{4+}$.

Two tppz based quasi-reversible reductions were also observed for the mononuclear derivative $[2]^+$ at $E^\circ = -1.26$ ($\Delta E_p = 80$ mV, couple-II) and $E^\circ = -1.40$ V ($\Delta E_p = 80$ mV, couple-III) (Fig. 3b). Thus, the first tppz reduction in the dinuclear complex (couple-III) has been shifted to a less negative potential by ≈ 500 mV as compared to the mononuclear analogue $[2]^+$: (couple-II). The consequence of coordination of the available open site of the tppz moiety to the second metal in $[1]^{2+}$ provides an additional stabilisation of the $\pi^*(tppz)$ orbital.¹⁰ The first tppz-based reduction in the corresponding bipyridine and azopyridine containing complexes appeared at -0.60 V^{10h} and -0.44 V,^{10a} respectively. Therefore, the stability of the $\pi^*(tppz)$ orbital in the set, $[(L')(Cl)Ru]_2(\mu\text{-tppz})^{2+}$ follows the order $L' = \text{azopyridine} > \text{bipyridine} > \text{dipyriddyamine}$.

UV-VIS-NIR spectroelectrochemical experiments of complex $[1]^{n+}$ ($n = 1, 2, 3, 4$) were performed in acetonitrile solution at 298 K using an OTTE cell. Spectral data are listed in Table 1 and the spectra are shown in Fig. 4. Complex $[1]^{2+}$ exhibited one moderately strong $Ru^{II} \rightarrow \pi^*(tppz)$ MLCT transition at 615 nm ($\epsilon = 13570$ $dm^3 mol^{-1} cm^{-1}$) and a strong ligand-based transition in the UV region (Fig. 4a).^{10a,h} On one-electron oxidation to the mixed-valence $Ru^{II}Ru^{III}$ state in $[1]^{3+}$ the intensity of the $Ru^{II} \rightarrow \pi^*(tppz)$ MLCT band at 615 nm was reduced to about 50% ($\epsilon = 7020$ $dm^3 mol^{-1} cm^{-1}$) which is compatible with a half-occupied donor orbital in $[1]^{3+}$. Moreover, the mixed-valence $[1]^{3+}$ displayed a new low-energy intervalence charge transfer (IVCT) transition between Ru^{II} and Ru^{III} at 1700 nm ($\epsilon = 2250$ $dm^3 mol^{-1} cm^{-1}$) (Fig. 4a). The width at half height ($\Delta\nu_{1/2}$) was measured at 1390 cm^{-1} . For a localised class II system, the relationship $\Delta\nu_{1/2} = (2310 E_{op})^{1/2}$ as derived from Hush theory¹³ is expected to be valid, which would lead to $\Delta\nu_{1/2} = 3680$ cm^{-1} , considering the absorption maximum of the IVCT band (E_{op}) at 5882 cm^{-1} . However, for a class III system the experimental value of $\Delta\nu_{1/2}$ is known to be much less compared to the value obtained *via* the Hush theory for weakly coupled systems.¹³ The observed $\Delta\nu_{1/2}$ value of 1390 cm^{-1} thus implies class III characteristics of $[1]^{3+}$. This is also in agreement with the observed 380 mV separation between the Ru^{II}/Ru^{III} couples ($K_c = 2.7 \times 10^6$). In view of the class III behaviour of $[1]^{3+}$ the electronic coupling parameter V_{ab} is estimated at 2940 cm^{-1} , considering the relation $V_{ab} = \frac{1}{2} E_{op}$.¹⁴

Spectroelectrochemical results and V_{ab} parameters of three related tppz-bridged diruthenium complexes have been reported in the literature so far.^{10a,b,h} In the case of $[(trpy)Ru]_2(\mu\text{-tppz})^{5+}$, a V_{ab} value of 3200 cm^{-1} was calculated based on a delocalised class III mixed valence situation, although the separation in potentials between the Ru^{II}/Ru^{III} couples was only 300 mV.^{10b} The complexes $[(2\text{-phenylazopyridine})ClRu]_2(\mu\text{-tppz})^{3+}$ ^{10a} and $[(bpy)ClRu]_2(\mu\text{-tppz})^{3+}$,^{10h} the closest analogues of $[1]^{3+}$, displayed narrow and asymmetric IVCT bands at 1890 nm and 1647 nm, respectively; the $\Delta\nu_{1/2}$ values of these IVCT bands are much lower than the calculated values obtained from the Hush formula, in spite of the rather small K_c values of 7.9×10^3 and 8.2×10^4 for the

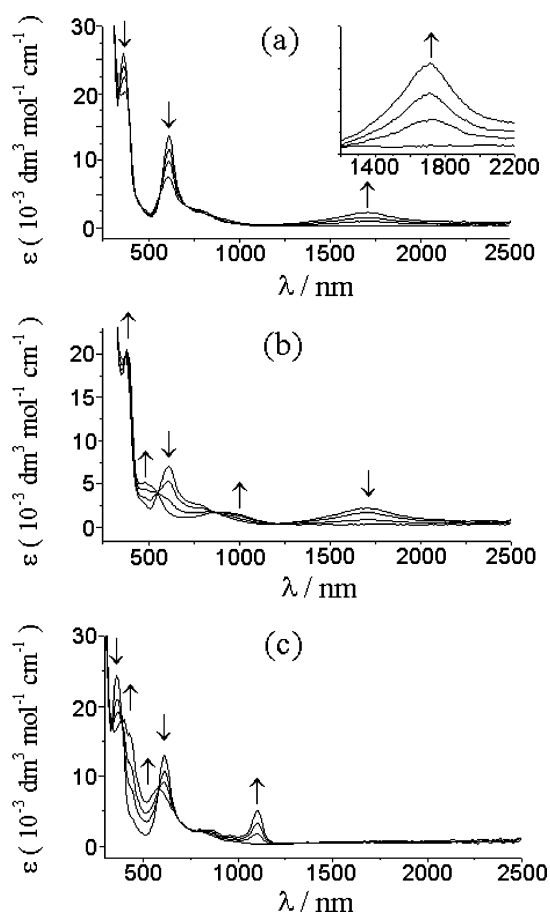


Fig. 4 UV-VIS-NIR spectroelectrochemistry of the conversions (a) $[I]^{2+} \rightarrow [I]^{3+}$, (b) $[I]^{3+} \rightarrow [I]^{4+}$, and (c) $[I]^{2+} \rightarrow [I]^+$ in $CH_3CN/0.1 \text{ mol dm}^{-3} Bu_4NPF_6$.

2-phenylazopyridine and bipyridine complexes, respectively. The dichotomy between the comproportionation constant value and the profile of the IVCT band was addressed in terms of a class-II/-III hybrid nature of the mixed-valence state,^{10a,h} however, it must be realised that the charge-related electrochemical coupling (K_c) and the orbital-controlled electronic coupling (V_{ab}) pertain to different physical phenomena.^{1d} In any case, the 380 mV separation of the Ru^{II}/Ru^{III} couples in combination with the observed narrow IVCT band in $[I]^{3+}$ is a clear indication of a class III system, a 390 mV separation had been observed for the Creutz-Taube ion.^{1i,5a,b}

On further one-electron oxidation to the isovalent Ru^{III}/Ru^{III} state $[I]^{4+}$, the IVCT band and the Ru^{II} -based residual MLCT transition disappeared completely with the concomitant growth of a weak Ru^{III} -based LMCT band at 895 nm ($\epsilon = 1900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (Fig. 4b) which was just visible as a shoulder in $[I]^{3+}$ (Fig. 4a).^{1a,15}

On one-electron reduction to $[I]^+$, the $Ru^{II} \rightarrow tppz$ based MLCT transition was blue shifted from 615 nm ($\epsilon = 13570 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) to 585 nm ($\epsilon = 8080 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) with a drop in intensity which is the expected consequence of putting one electron into the previously empty acceptor orbital (π^* LUMO) of $tppz$.^{1j,k} Moreover, the reduction of $tppz$ in $[I]^+$ yielded an intense transition at 1105 nm ($\epsilon = 5150 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (Fig. 4c). In the absence of any other π -acidic ancillary ligands in complex $[I]^+$ it may be assumed that this low-energy band reflects an internal transition associated with the $tppz$ radical anion.^{1j,16} It is to be noted that in the $tppz$ -based radical complex $\{[(2\text{-phenylazopyridine})ClRu]_2(\mu\text{-}tppz)\}^{3+}$, an exclusive case where spectroelectrochemical studies on the reduced state(s) were performed, the observed low-energy band at 990 nm was assigned to a $\pi\{(\text{SOMO } tppz^{\cdot-}) \rightarrow \pi^*\{(\text{LUMO} + 1)\text{arylazopyridine}\}$ transition, based on the spectroelectrochemistry of the reduced states in combination with ZINDO calculations.^{10a}

It should be noted that the spectra are comparable in different solvents which indicates little or no change in the molecular or electronic structure.

EPR spectra of $[I]^{3+}$ and $[I]^+$

The *in-situ* generated one-electron oxidised $Ru^{II}Ru^{III}$ derivative $[I]^{3+}$ exhibited a rhombic EPR spectrum at 4 K in acetonitrile ($g_1 = 3.390$, $g_2 = 2.278$, $g_3 = 1.697$) (Fig. 5). The complex $[I]^{3+}$, however, failed to show any EPR signal at room-temperature due to rapid relaxation. The large g anisotropy exceeding that of the Creutz-Taube ion ($g_1 = 2.799$, $g_2 = 2.489$, $g_3 = 1.346$)^{17a}) points to a considerably distorted octahedral environment around the ruthenium centres in $[I]^{3+}$ ¹⁷ as would be expected considering the non-planarity of both the $tppz$ and L ligands. An average g factor of $\langle g \rangle = 2.53$ is derived from $\langle g \rangle = [1/3(g_1^2 + g_2^2 + g_3^2)]^{1/2}$. On the other hand, the one-electron reduced species $[I]^+$ in acetonitrile showed an axial EPR spectrum at 4 K with a rather small g tensor splitting ($g_1 = 2.008$, $g_2 = g_3 = 1.994$) (Fig. 5). The isotropic g value of 1.999 is very close to the free electron value of 2.0023 which implies that the unpaired electron is preferentially confined to the $tppz$ ligand.^{1j,10a,17a,18} Remarkably, however, there is no EPR signal observed at room temperature which has been similarly noted for the radical complex $\{(\mu\text{-}bptz)[Ru(NH_3)_4]_2\}^{3+}$, $bptz = 3,6\text{-bis}(2\text{-pyridyl})\text{-}1,2,4,5\text{-tetrazine}$, and which signifies rapid relaxation due to paramagnetic states lying close to the radical ground state.^{17a}

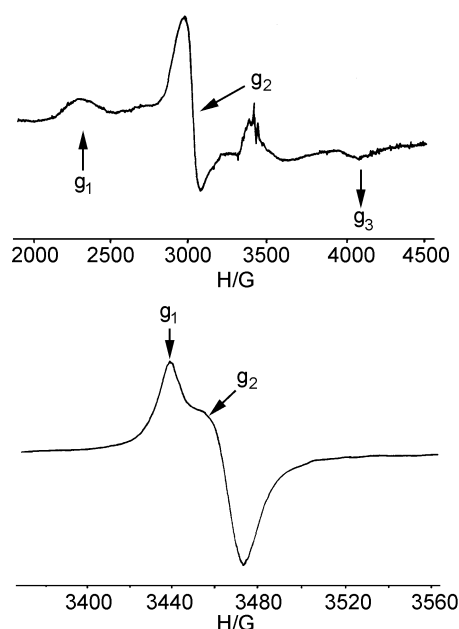


Fig. 5 EPR spectra of $[I]^{3+}$ (top) and $[I]^+$ (bottom) in $CH_3CN/0.1 \text{ mol dm}^{-3} Bu_4NPF_6$ at 4 K (impurity signals at $g \approx 2$ for the oxidation process).

Emission properties

Both complexes $[I]^{2+}$ and $[2]^+$ were found to be luminescent at 77 K in EtOH–MeOH (4 : 1) glass (Fig. 6). Excitation of $[I]^{2+}$ at the lowest energy MLCT band maximum (λ_{ex} , 610 nm) resulted in a moderately strong emission at 740 nm (quantum yield, $\Phi = 4.1 \times 10^{-2}$; the quantum yield was determined using a previously described method¹⁹) (Fig. 6a). The emission energy is substantially red-shifted with respect to $Ru^{II}(tppz)_2^{2+}$ (λ_{abs} , 480 nm and λ_{em} at 77 K, 628 nm), indicating the additional stabilisation of the $\pi^*(tppz)$ orbital in $[I]^{2+}$, which is also consistent with the absorption data.

Excitation of the mononuclear complex $[2]^+$ at the MLCT band (λ_{ex} , 520 nm) led to a moderately strong emission at 668 nm (quantum yield, $\Phi = 3.6 \times 10^{-2}$) (Fig. 6b). As is observed for

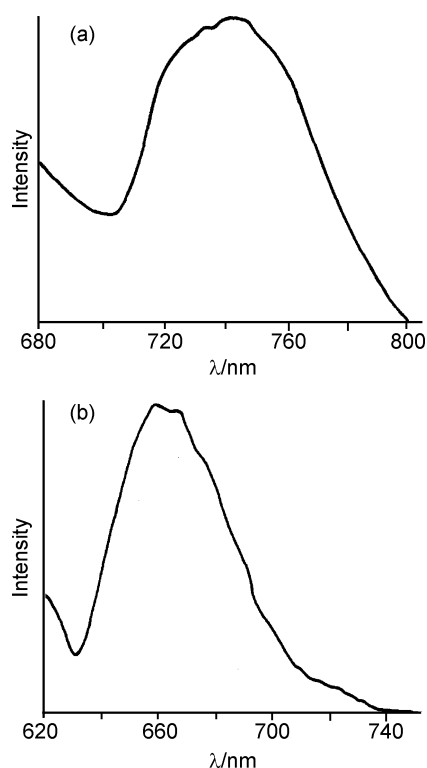


Fig. 6 Emission spectra of (a) $[1]^{2+}$ and (b) $[2]^+$ in 4 : 1 EtOH–MeOH glass at 77 K.

the absorption process, the emission energy of the dinuclear complex $[1]^{2+}$ is reasonably red-shifted relative to that of the monomeric analogue $[2]^+$, indicating the stabilisation of the tppz π^* -acceptor orbital through the second metal coordination at the vacant site of tppz in $[2]^+$. The observed luminescence is consistent with emission from a ${}^3\text{MLCT}$ excited state involving the tppz ligand.^{10c} Negligibly small absorption band shifts were observed in the different solvent systems used for emission spectroscopy and spectroelectrochemistry, suggesting comparable molecular and electronic structure.

Conclusions

A new 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz)-bridged diruthenium complex $\{[(\text{L})\text{ClRu}^{\text{II}}]_2(\mu\text{-tppz})\}(\text{ClO}_4)_2$, $[1](\text{ClO}_4)_2$, incorporating 2,2'-dipyridylamine (L) ancillary ligands and its mononuclear analogue $\{[(\text{L})\text{ClRu}^{\text{II}}(\text{tppz})]\text{ClO}_4$, $[2](\text{ClO}_4)$, have been synthesized. The present work illustrates the following features: (i) the use of possibly non-planar 2,2'-dipyridylamine in $[1]^{2+}$ reduces the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ potentials appreciably as compared to analogous complexes having more π -acidic, planar 2,2'-bipyridine or arylazopyridine ancillary ligands. The use of L increases the K_c value of the mixed-valence $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ state in $[1]^{3+}$ to $K_c = 2.7 \times 10^6$. (ii) Although spectroelectrochemical studies of the analogous bipyridine and arylazopyridine complexes suggest a class-II/-III hybrid behaviour of the mixed-valence $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ state, the $[1]^{3+}$ ion represents a genuine class III system based on the narrow IVCT band at 1700 nm. (iii) The π^* -orbital of the tppz ligand is more stabilised in the dinuclear complex $[1]^{2+}$ relative to the corresponding mononuclear derivative $[2]^+$. (iv) The EPR spectrum of the reduced species $[1]^+$ suggests that the unpaired electron is preferentially localised on tppz whereas the highly anisotropic EPR spectrum of the mixed-valent species $[1]^{3+}$ indicates metal-based electron spin and a distorted coordination geometry. (v) Both the mononuclear and dinuclear complexes are moderately luminescent at 77 K, the emission energy being substantially red-shifted while moving from mononuclear $[2]^+$ to dinuclear $[1]^{2+}$. Future efforts will be made to investigate the electrochemical and spectro-

scopic responses of oxidised, reduced and excited states to deprotonation in suitable media.

Experimental

Materials

The precursor complex $[\text{Cl}_3\text{Ru}^{\text{III}}(\mu\text{-tppz})\text{Ru}^{\text{III}}\text{Cl}_3]$ was prepared as reported.^{1h} 2,2'-Dipyridylamine (L) was purchased from Aldrich, USA. Other chemicals and solvents were reagent grade and used as received. For spectroscopic and electrochemical studies HPLC grade solvents were used. Water of high purity was obtained by distillation of deionised water from KMnO_4 under dinitrogen atmosphere.

Physical measurements

Solution electrical conductivity was checked using a Systronic conductivity bridge 305. Infrared spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets, far-IR spectra were recorded with samples prepared as polyethylene discs. ${}^1\text{H-NMR}$ spectra were recorded for $(\text{CD}_3)_2\text{SO}$ solutions using a 300 MHz Varian FT spectrometer. UV-VIS-NIR spectroelectrochemical studies were performed in MeCN/0.1 mol dm^{-3} Bu_4NPF_6 at 298 K using an optically transparent thin layer electrode (OTTLE) cell mounted in the sample compartment of a Bruins Omega 10 spectrophotometer. Cyclic voltammetric and coulometric measurements were carried out using a PAR model 273A electrochemistry system. A platinum wire working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. Tetraethylammonium perchlorate (TEAP) was the supporting electrolyte and the solution concentration was ca. 10^{-3} mol dm^{-3} ; the scan rate used was 50 mV s^{-1} . A platinum gauze working electrode was used in the coulometric experiments. All electrochemical experiments were carried out under a dinitrogen atmosphere and all redox potentials are uncorrected for junction potentials. The EPR measurements were made at a single temperature (4 K) with an X-band Bruker system ESP300, equipped with a Bruker ER035M gaussmeter and an HP 5350B microwave counter. The elemental analyses were carried out with a Perkin-Elmer 240C elemental analyser. Electrospray mass spectra were recorded on a Micromass Q-ToF mass spectrometer. Emission measurements were made using a Perkin Elmer L S 55 luminescence spectrofluorimeter.

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

Preparation of complexes $\{[(\text{L})\text{ClRu}^{\text{II}}]_2(\mu\text{-tppz})\}(\text{ClO}_4)_2$, $[1](\text{ClO}_4)_2$, and $[(\text{L})\text{ClRu}^{\text{II}}(\text{tppz})]\text{ClO}_4$, $[2](\text{ClO}_4)$

The precursor complex $[\text{Cl}_3\text{Ru}^{\text{III}}(\mu\text{-tppz})\text{Ru}^{\text{III}}\text{Cl}_3]$ (100 mg, 0.12 mmol) and the free ligand L (54 mg, 0.32 mmol) were taken in ethanol (15 cm^3) and refluxed for 4 h under a dinitrogen atmosphere in the presence of excess LiCl (54 mg, 1.3 mmol) and NEt_3 (0.4 cm^3). The initial light green solution gradually changed to deep green. A saturated aqueous solution of NaClO_4 was then added to the concentrated acetonitrile solution of the product. The solid precipitate thus obtained was filtered off and washed thoroughly with cold ethanol followed by ice-cold water. The dried product was purified by using an alumina column. The mononuclear complex $[2](\text{ClO}_4)$ and dinuclear complex $[1](\text{ClO}_4)_2$ were eluted with 5 : 2 CH_2Cl_2 – CH_3CN and 5 : 3 CH_2Cl_2 – CH_3CN mixtures, respectively. After removal of the solvents under reduced pressure the complexes were further purified by recrystallisation from benzene–acetonitrile mixture.

Anal. calcd. for $\text{C}_{44}\text{H}_{34}\text{Cl}_4\text{N}_{12}\text{O}_8\text{Ru}_2$ $[1](\text{ClO}_4)_2$: C, 43.9; H, 2.8; N, 13.9; found: C, 43.6; H, 2.6; N, 14.2%. Conductivity: A_M

($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in acetonitrile at 298 K: 260.^{1d,10a} IR data: $\nu(\text{ClO}_4^-)$, cm^{-1} : 1091, 619; $\nu(\text{NH})$, cm^{-1} : 3280. Yield: 75% (110 mg).

Anal. calcd. for $\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{N}_9\text{O}_4\text{Ru} [2](\text{ClO}_4)$: C, 51.3; H, 3.2; N, 15.8; found: C, 51.1; H, 2.8; N, 16.0%. Conductivity: Λ_{M} ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in acetonitrile at 298 K: 110.^{1d,10a} IR data: $\nu(\text{ClO}_4^-)$, cm^{-1} : 1092, 621; $\nu(\text{NH})$, cm^{-1} : 3295. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 518 (4700), 340 (29000), 287 (34000), 252 (29000), 198 (60000). Yield, 15% (14.8 mg).

Acknowledgements

Financial support received from the council of Scientific and Industrial Research, New Delhi (India), the DAAD, the DFG and the FCI (Germany) is gratefully acknowledged. Special acknowledgement is made to the Regional Sophisticated Instrumentation Centre, RSIC, Indian Institute of Technology, Bombay, for providing the NMR and far-IR facilities.

References

- (a) W. Kaim, A. Klein and M. Glöckle, *Acc. Chem. Res.*, 2000, **33**, 755; (b) J. A. McCleverty and M. D. Ward, *Acc. Chem. Res.*, 1998, **31**, 842; (c) D. Astruc, *Acc. Chem. Res.*, 1997, **30**, 383; (d) M. D. Ward, *Chem. Soc. Rev.*, 1995, **24**, 121; (e) R. J. Crutchley, *Adv. Inorg. Chem.*, 1994, **41**, 273; (f) G. Giuffrida and S. Campagna, *Coord. Chem. Rev.*, 1994, **135–136**, 517; (g) C. Creutz, *Prog. Inorg. Chem.*, 1983, **30**, 1; (h) W. Kaim, *Coord. Chem. Rev.*, 2002, **230**, 126; (i) K. D. Demandis, C. M. Hartshorn and T. J. Meyer, *Chem. Rev.*, 2001, **101**, 2655; (j) S. Chakraborty, R. H. Laye, R. L. Paul, R. G. Gonnade, V. G. Puranik, M. D. Ward and G. K. Lahiri, *J. Chem. Soc., Dalton Trans.*, 2002, 1172; (k) B. Sarkar, R. H. Laye, B. Mondal, S. Chakraborty, R. L. Paul, J. C. Jeffery, V. G. Puranik, M. D. Ward and G. K. Lahiri, *J. Chem. Soc., Dalton Trans.*, 2002, 2097; (l) S. Chakraborty, R. H. Laye, P. Munshi, R. L. Paul, M. D. Ward and G. K. Lahiri, *J. Chem. Soc., Dalton Trans.*, 2002, 2348; (m) P. Passaniti, W. R. Browne, F. C. Lynch, D. Hughes, M. Nieuwenhuyzen, P. James, M. Maestri and J. G. Vos, *J. Chem. Soc., Dalton Trans.*, 2002, 1740; (n) P. J. Mosher, G. P. A. Yap and R. J. Crutchley, *Inorg. Chem.*, 2001, **40**, 1189; (o) R. H. Laye, S. M. Couchman and M. D. Ward, *Inorg. Chem.*, 2001, **40**, 4089; (p) W. E. Meyer, A. J. Amoroso, C. R. Horn, M. Jaeger and J. A. Gladysz, *Organometallics*, 2001, **20**, 1115; (q) J. E. Ritchie and R. W. Murray, *J. Am. Chem. Soc.*, 2000, **122**, 2964; (r) T. Weyland, K. Coustas, L. Toupet, J. F. Halet and C. Lapinte, *Organometallics*, 2000, **19**, 4228; (s) J.-P. Launay, S. Frayssé and C. Coudret, *Mol. Cryst. Liq. Cryst.*, 2000, **344**, 125; (t) S. Baitalik, U. Florke and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1999, 719; (u) B. S. Brunschwig, C. Creutz and N. Sutin, *Chem. Soc. Rev.*, 2002, **31**, 168.
- E. I. Solomon, T. C. Brunold, M. I. Davis, J. N. Kemsley, S. K. Lee, N. Lehnert, F. Neese, A. J. Skulan, Y. S. Yang and J. Zhou, *Chem. Rev.*, 2000, **100**, 235.
- (a) F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1998, **178–180**, 431; (b) M. D. Ward, *Chem. Ind.*, 1996, 568; (c) M. D. Ward, *Chem. Ind.*, 1997, 640.
- (a) B. S. Brunschwig and N. Sutin, *Coord. Chem. Rev.*, 1999, **187**, 233; (b) A. Bencini, I. Ciofini, C. A. Daul and A. Ferretti, *J. Am. Chem. Soc.*, 1999, **121**, 11418.
- (a) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1969, **91**, 3988; (b) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1973, **95**, 1086; (c) U. Fuerholz, S. Joss, H. B. Büergi and A. Ludi, *Inorg. Chem.*, 1985, **24**, 943.
- D. P. Rillema, D. G. Taghdiri, D. S. Jones, C. D. Keller, L. A. Wori, T. J. Meyer and H. A. Levy, *Inorg. Chem.*, 1987, **26**, 578.
- (a) J. D. Petersen, W. R. Murphy, Jr., R. Sahai, K. Brewer and R. R. Ruminiski, *Coord. Chem. Rev.*, 1985, **64**, 261; (b) E. V. Dose and L. J. Wilson, *Inorg. Chem.*, 1978, **17**, 2660; (c) M. Hunziker and A. Ludi, *J. Am. Chem. Soc.*, 1977, **99**, 7370; (d) R. R. Ruminiski and J. D. Petersen, *Inorg. Chem.*, 1982, **21**, 3706.
- (a) C. H. Braunstein, A. D. Baker, T. C. Streckas and H. D. Gafney, *Inorg. Chem.*, 1984, **23**, 857; (b) R. R. Ruminiski, T. Cockroft and M. Shoup, *Inorg. Chem.*, 1988, **27**, 4026; (c) V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759; (d) S. Serroni, S. Campagna, G. Denti, T. E. Keyes and J. G. Vos, *Inorg. Chem.*, 1996, **35**, 4513.
- (a) A. Gourdon and J.-P. Launay, *Inorg. Chem.*, 1998, **37**, 5336; (b) P. Bonhote, A. Lecas and E. Amouyal, *Chem. Commun.*, 1998, 885.
- (a) N. Chanda, R. H. Laye, S. Chakraborty, R. L. Paul, J. C. Jeffery, M. D. Ward and G. K. Lahiri, *J. Chem. Soc., Dalton Trans.*, 2002, 3496; (b) J. P. Collin, P. Laine, J. P. Launay, J. P. Sauvage and A. Sour, *J. Chem. Soc., Chem. Commun.*, 1993, 434; (c) C. R. Arana and H. D. Abruna, *Inorg. Chem.*, 1993, **32**, 194; (d) R. P. Thummel and S. Chirayil, *Inorg. Chim. Acta*, 1988, **154**, 77; (e) L. M. Vogler, B. Scott and K. J. Brewer, *Inorg. Chem.*, 1993, **32**, 898; (f) J.-D. Lee, L. M. Vrana, E. R. Bullock and K. J. Brewer, *Inorg. Chem.*, 1998, **37**, 3575; (g) T. S. Akasheh, D. Marji and Z. M. Al Ahmed, *Inorg. Chim. Acta*, 1988, **141**, 125; (h) C. M. Hartshorn, N. Daire, V. Tondreau, B. Loeb, T. J. Meyer and P. S. White, *Inorg. Chem.*, 1999, **38**, 3200; (i) L. M. Vogler and K. J. Brewer, *Inorg. Chem.*, 1996, **35**, 818; (j) R. Ruminiski, J. Kiplinger, T. Cockroft and C. Chase, *Inorg. Chem.*, 1989, **28**, 370; (k) D. M. Dattelbaum, C. M. Hartshorn and T. J. Meyer, *J. Am. Chem. Soc.*, 2002, **124**, 4938.
- D. E. Morris, Y. Ohsawa, D. P. Segers, M. K. DeArmond and K. W. Hanck, *Inorg. Chem.*, 1984, **23**, 3010.
- A. M. Bond and M. Haga, *Inorg. Chem.*, 1986, **25**, 4507.
- N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 391; M. B. Rabin and P. Day, *Adv. Inorg. Radiochem.*, 1967, **10**, 247.
- N. S. Hush, *Coord. Chem. Rev.*, 1985, **64**, 135.
- (a) Z. Shirin and K. Mukherjee, *Polyhedron*, 1992, **11**, 2625; (b) K. S. Murray, A. M. van der Bergen and B. O. West, *Aust. J. Chem.*, 1978, **31**, 203; (c) G. S. Rodman and J. K. Nagle, *Inorg. Chim. Acta*, 1985, **105**, 205.
- (a) N. C. Fletcher, T. C. Robinson, A. Behrendt, J. C. Jeffery, Z. R. Reeves and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1999, 2999; (b) A. K. Ghosh, S.-M. Peng, R. L. Paul, M. D. Ward and S. Goswami, *J. Chem. Soc., Dalton Trans.*, 2001, 336; (c) P. R. Auburn and A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 2551; (d) G. A. Heath, L. J. Yellowlees and P. S. Braterman, *Chem. Phys. Lett.*, 1982, **92**, 646.
- (a) J. Poppe, M. Moscherosch and W. Kaim, *Inorg. Chem.*, 1993, **32**, 2640; (b) N. Bag, G. K. Lahiri, P. Basu and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1992, 113.
- (a) N. Bag, A. Pramanik, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.*, 1992, **31**, 40; (b) M. D. Ward, *Inorg. Chem.*, 1996, **35**, 1712.
- (a) R. Alsasser and R. van Eldik, *Inorg. Chem.*, 1996, **35**, 628; (b) P. Chen, R. Duesing, D. K. Graff and T. J. Meyer, *J. Phys. Chem.*, 1991, **95**, 5850.