Synthesis, mixed valence aspects and non-linear optical properties of the triruthenium complexes [{(bpy)₂Ru^II}₃(L)]³⁺ and [{(phen)₂Ru^II}₃(L)]³⁺ (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline and L³⁻ = 1,3,5-triazine-2,4,6-trithiol) †

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The triruthenium complexes [{(bpy)₂Ru^II}₃L]³⁺ [**1**]³⁺ and [{(phen)₂Ru^II}₃L]³⁺ [**2**]³⁺ have been synthesized *via* the reactions of [Ru^II(bpy)₂(EtOH)₂]²⁺ and [Ru^II(phen)₂(EtOH)₂]²⁺ with the trisodium salt of 1,3,5-triazine-2,4,6 trithiol (Na₃L) respectively. In CH₃CN, the complexes [**1**]³⁺ and [**2**]³⁺ exhibit three reversible one-electron redox processes corresponding to successive Ru(II)/Ru(III) couples. The 190–250 mV separation in potential between the successive Ru(II)/Ru(III) couples is indicative of moderate intermetallic electronic coupling in the mixed valence states. The bipyridine and phenanthroline based reductions are observed at −1.58, −1.86 V and −1.77, −2.01, −2.43 V *versus* SCE respectively. The spectroelectrochemical study on the bipyridine derivative [**1**]^n+ (n = 3–6) in acetonitrile medium at 243 K shows a broad and relatively weak intervalence charge-transfer transition (IVCT) near 1900 nm for both the mixed valence states Ru^IIRu^IIRu^III [**1**]⁴⁺ and Ru^IIRu^IIIRu^III [**1**]⁵⁺, characteristic of class II behaviour. The calculated coupling constant (V_{ab}), 560 cm⁻¹ is also supportive of class II mixed-valence states. The electrochemically generated one-electron oxidised species [**1**]⁴⁺ or [**2**]⁴⁺ exhibits an EPR spectrum characteristic of low-spin Ru^III ion in a distorted octahedral environment ($g_1 = 2.246$, $g_2 = 1.993$ for [**1**]⁴⁺ and $g_1 = 2.469$, $g_2 = 2.191$ for [**2**]⁴⁺). The complexes are moderately strongly luminescent at 77 K. Both the complexes have also shown third order non-linear optical properties with $\gamma = -4.5 \times 10^{-29}$ esu for [**1**]³⁺ and -5.09×10^{-29} esu for [**2**]³⁺.

Introduction

The development of newer classes of polynuclear ruthenium polypyridine [2,2′-bipyridine (bpy), 1,10-phenanthroline (phen)] complexes incorporating suitable bridging ligands is of considerable current research interest, which is primarily due to their potential applications in diverse areas such as photo-sensitisers for photochemical conversion of solar energy,[1] molecular electronic devices[2] and as photoactive DNA cleavage agents for therapeutic purposes.[3] Moreover, polynuclear complexes which exhibit stable mixed-valence states due to strong intermetallic electronic coupling across the bridging unit have received special attention because of their relevance to biological electron-transfer processes[4] and for theoretical studies on electron-transfer kinetics.[5] The degree of intermetallic electronic communication in a mixed valence state depends heavily on the electronic nature of the bridging units. π-Acceptor bridging ligands (often neutral in nature) in which the LUMO (i) is close in energy to the metal redox orbitals, and (ii) overlaps effectively with them, facilitate delocalisation of the unpaired electron in the mixed-valence state *via* an electron-transfer mechanism. In contrast, electron-rich bridging ligands (often anionic) have higher-energy orbitals such that the HOMO is close in energy to the metal redox orbitals, thereby facilitating delocalisation of the unpaired electron by a hole-transfer mechanism.[6] Therefore, the extent to which the bridging functions can facilitate inter-metallic coupling in the complex framework is of immense interest.[7]

Although a wide variety of bridging ligands of both the neutral and anionic types have been used as bridging ligands in diruthenium complexes,[8] the study of related trinuclear complexes (triangular, in which all three metal ions share a common bridging ligand) is relatively less.[9] In the present work we explore the ability of the trisodium salt of trithiocyanuric acid (1,3,5-triazine-2,4,6-trithiol) (Na₃L) to bind with three {Ru(bpy)₂}²⁺/{Ru(phen)₂}²⁺ fragments by utilising its three N,S-bidentate sites, which would give four-membered chelate rings. [L]³⁻ is known to be able to function as a versatile ambi-dentate ligand, with a variety of coordination modes available including monodentate N- or S-donor;[10] bidentate chelating [N,S⁻]-donor;[11] bridging two metal ions through the two bidentate [N,S⁻]-donor sets.[12] Only one trinuclear titanium(III) complex [(Ti^III)₃L], is known so far where the L³⁻ unit is reported to bind with the three Ti(III) ions using all three [N,S⁻] donor sets.[12c] Moreover, 1,3,5-triazine-2,4,6-trithiol itself can form supramolecular organic systems with layered and channel structures during co-crystallisation with different organic molecules able to form hydrogen bonding interactions,[13] and both H₃L and its metal complexes have a wide range of industrial applications.[10b]

Herein we report the synthesis, spectroelectrochemical and non-linear optical properties of the two trinuclear complexes [{Ru(bpy)₂}₃(L)]³⁺ [**1**]³⁺ and [{Ru(phen)₂}₃(L)]³⁺ [**2**]³⁺, where the bridging unit L³⁻ functions as a tris-bidentate [N,S⁻]-donor ligand. To our knowledge these are the first examples of ruthenium complexes of 1,3,5-triazine-2,4,6-trithiol, and the second set of examples in which L³⁻ functions as a symmetrical tris-bidentate bridging ligand.

† Electronic supplementary information (ESI) available: electrospray mass spectrum of [**1**](ClO₄)₃; emission spectra of [**1**](ClO₄)₃ and [**2**](ClO₄)₃; experimental layout for non-linear absorption and *z*-scan measurement. See http://www.rsc.org/suppdata/dt/b3/b302878j/

Results and discussion

Synthesis and characterisation of complexes

The reaction of an aqueous solution of the trisodium salt of 1,3,5-triazine-2,4,6-trithiol (Na_3L) with the ruthenium precursor complexes $[Ru(bpy)_2(EtOH)_2]^{2+}$ (bpy = 2,2′-bipyridine) and $[Ru(phen)_2(EtOH)_2]^{2+}$ (phen = 1,10-phenanthroline) in ethanol under a dinitrogen atmosphere resulted in formation of the trinuclear complexes, $[\{(bpy)_2Ru^{II}\}_3(L)]^{3+}$, $[1]^{3+}$, and $[\{(phen)_2Ru^{II}\}_3(L)]^{3+}$, $[2]^{3+}$, respectively. Both complexes have the symmetric structure shown in Scheme 1 with each metal fragment coordinated by a bidentate $[N,S^−]$-donor site of $[L]^{3−}$. The complexes were isolated as their perchlorate salts $[1](ClO_4)_3$ and $[2](ClO_4)_3$ (Scheme 1) and are soluble in polar organic solvents such as CH_3CN, dmso and dmf.
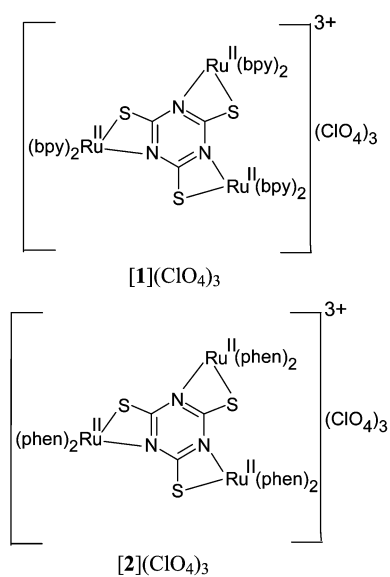
Scheme 1

The complexes gave satisfactory microanalytical data and displayed 1 : 3 conductivities in acetonitrile solution (see Experimental section). The confirmations of the compositions of the complexes were established from the positive ion electrospray mass spectra: $[1](ClO_4)_3$ which showed a strong molecular ion peak centred at $m/z = 1614$ corresponding to $\{[1](ClO_4)_2\}^+$ (calculated molecular weight, 1613.47) (Fig. S1 †) and $[2](ClO_4)_3$ exhibited a molecular ion peak at $m/z = 1760$ corresponding to $\{[2](ClO_4)_2\}^+$ (calculated molecular weight, 1758). The isotopic distribution pattern of the metal ions is shown in the inset of Fig. S1. The ionic perchlorate bands were observed in the IR spectra at 1092 and 630 cm^{-1} for $[1](ClO_4)_3$ and at 1103 and 634 cm^{-1} for $[2](ClO_4)_3$.

The ^1H NMR spectra of $[1]^{3+}$ and $[2]^{3+}$ in $(CD_3)_2SO$ are complicated due to the presence of a large number of aromatic protons with similar chemical shifts (Fig. 1). A few signals are however clearly resolved, and from the integrals of these it appears that this spectrum is consistent with the presence of the low-symmetry $\lambda\lambda\delta/\delta\delta\lambda$ isomer, for which forty-eight signals are expected, rather than the three-fold symmetric $\lambda\lambda\lambda/\delta\delta\delta$ isomer for which only sixteen signals are expected.

Redox properties of the complexes

The redox properties of the complexes were studied in acetonitrile solvent by cyclic voltammetric and differential pulse voltammetric techniques (Fig. 2). The oxidation processes at the positive side of SCE were recorded by using a platinum working electrode; a glassy-carbon working electrode was used for recording the reduction processes.
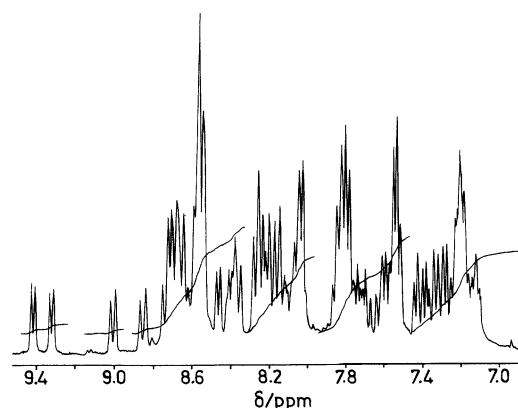
Fig. 1 ^1H NMR spectrum of $[\{(bpy)_2Ru^{II}\}_3(L)](ClO_4)_3$, $[1](ClO_4)_3$ in $(CD_3)_2SO$.
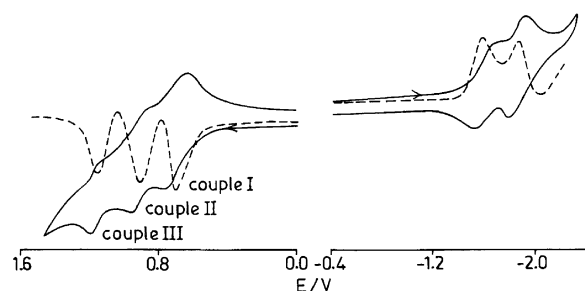
Fig. 2 Cyclic voltammograms and differential pulse voltammograms of $[\{(bpy)_2Ru^{II}\}_3(L)](ClO_4)_3$, $[1](ClO_4)_3$, in CH_3CN (Pt-working electrode for the positive side of SCE and glassy-carbon working electrode for the negative side of SCE).

Complex $[1]^{3+}$ exhibited three successive quasi-reversible oxidative couples: E^0_{298}/V ($\Delta E_p/mV$): 0.72 (80) (couple I); 0.94 (80) (couple II); 1.18 (65) (couple III) *versus* SCE. The same three couples for complex $[2]^{3+}$ appeared at 0.77 (130) (couple I); 0.96 (70) (couple II); 1.20 (80) (couple III). The observed three responses are assigned as stepwise electron-transfer processes involving the metal centres, $Ru^{II}Ru^{II}Ru^{III}/Ru^{II}Ru^{II}Ru^{II}$ (couple I); $Ru^{II}Ru^{III}Ru^{III}/Ru^{II}Ru^{II}Ru^{III}$ (couple II); $Ru^{III}Ru^{III}Ru^{III}/Ru^{II}Ru^{III}Ru^{III}$ (couple III),[14] and the slightly less positive redox potentials for $[1]^{3+}$ compared to $[2]^{3+}$ indicates slight stabilisation of the lower oxidation state in the latter case, although the effect is marginal. The potential separations between the successive couples in $[1]^{3+}$ and $[2]^{3+}$ are 215 mV and 190 mV for couple I/couple II, and 250 mV and 240 mV for couple II/couple III. These separations of *ca.* 200 mV between the successive redox couples are indicative of moderately strong electronic coupling between the ruthenium centres across the bridging unit in the respective mixed-valence states.[15] For the homologous mononuclear complex $[Ru^{II}(bpy)_2(2-NC_5H_4S)]^+$ incorporating a 2-thiopyridonate co-ligand with a 4-membered chelate ring, the Ru(III)/Ru(II) couple appears at 0.59 V *versus* SCE.[16] Therefore, the Ru(II) states are stabilised with respect to the Ru(III) states on moving from a mononuclear to a trinuclear environment, which is ascribable to the increase in overall charge of the complex molecule from +1 to +3.

The complex $[1]^{3+}$ displayed two quasi-reversible reductions, at E^0_{298}/V ($\Delta E_p/mV$): −1.58 (140) and −1.86 (100) *versus* SCE, which we assign as ligand-based, associated with either the terminal bipyridine ligands or the central triazine ring. The phenanthroline derivative $[2]^{3+}$ showed three irreversible reductions at peak potentials of E_{pc}/V: −1.77, −2.01 and −2.43 *versus* SCE.

EPR spectra of $[1]^{4+}$ and $[2]^{4+}$

In order to record the EPR spectra of the first-stage oxidised one-electron paramagnetic $Ru^{II}Ru^{II}Ru^{III}$ species $[1]^{4+}$ and $[2]^{4+}$,

Table 1 Summary of electronic spectral data for $[1]^{n+}$ (n = 3–6) from an OTTLE experiment in MeCN at 243 K

Charge	λ_{max}/nm ($10^{-3}\varepsilon$/dm³ mol⁻¹cm⁻¹)
+3	243 (47), 292 (100), 350 (26), 456 (21), 491 (19)
+4	241 (46), 289 (86), 339 (16), 457 (17), 576 (2.8), 1900 (2.3)
+5	240 (46), 289 (70), 426 (12), 593 (3.6), 1900 (2.4)
+6	240 (53), 303 (54), 314 (54), 350 (sh), 624 (5.5)

the bulk electrolysis of the starting diamagnetic $Ru^{II}Ru^{II}Ru^{II}$ complexes $[1]^{3+}$ and $[2]^{3+}$ in acetonitrile solvent were performed inside the EPR tube at 243 K. The oxidised one-electron paramagnetic species exhibited poorly resolved EPR spectra when cooled to 110 K. The signals due to the g_1 and g_2 components were clearly observed but the expected g_3 signal was not properly resolved possibly due to a high noise to signal ratio {Fig. 3; g_1 = 2.246, g_2 = 1.993 for $[1]^{4+}$ and g_1 = 2.469, g_2 = 2.191 for $[2]^{4+}$}. The splitting of the EPR signal confirms that the unpaired electron in the mixed valence $Ru^{II}Ru^{II}Ru^{III}$ state ($[1]^{4+}$ or $[2]^{4+}$) is primarily localised on the metal centre.[17]
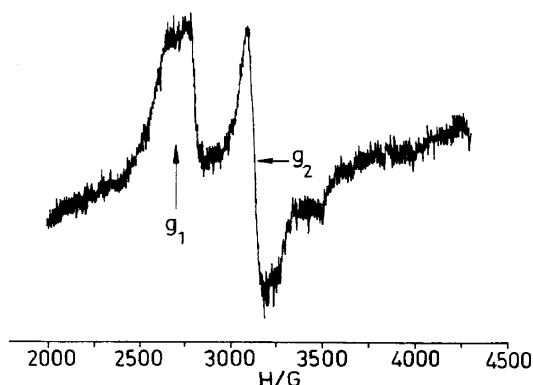
**Fig. 3** X-Band EPR spectrum of electrochemically generated $[1]^{4+}$ in CH_3CN solution at 110 K.

Emission properties

The $Ru^{II}Ru^{II}Ru^{II}$ complexes $[1]^{3+}$ and $[2]^{3+}$ exhibited moderately strong emissions at 77 K. Excitations of the complexes near the lowest energy MLCT transitions in an ethanol/methanol (4 : 1) glass showed moderately strong emission bands with maxima at 661 nm (quantum yield, Φ = 2.02 × 10^{-2}) and 652 nm (Φ = 5.5 × 10^{-2}) for $[1]^{3+}$ and $[2]^{3+}$ respectively (Fig. S2 †). The observed luminescence is consistent with emission from a ^{3}MLCT excited state involving the bpy or phen ligands.[18] The quantum yield data suggest that the phenanthroline derivative $[2]^{3+}$ is approximately three times more strongly luminescent than the bipyridine analogue $[1]^{3+}$.

UV-Vis-NIR spectroelectrochemistry

A spectroelectrochemical study was conducted only in the case of complex $[1]^{n+}$. Electronic spectra of $[1]^{n+}$ (n = 3–6) were recorded in MeCN at 243 K in an OTTLE cell (see Table 1) in which the higher oxidation states were generated electrochemically. All redox conversions were chemically reversible under these conditions as shown by (i) the presence of clean isosbestic points during each conversion, and (ii) the fact that re-reduction generated the starting spectrum with no significant changes. The results are shown in Fig. 4.

The spectrum of $[1]^{3+}$ contains intense transitions in the UV region at 243 and 292 nm, and three weaker transitions of similar intensity to one another at 350, 456 and 491 nm of which at least the latter two can be assigned as MLCT transitions. Given the presence of different π* acceptor levels involving the bpy and triazine ligands, and the low symmetry which will split the t_{2g} orbital set, a range of MLCT transition energies is to be
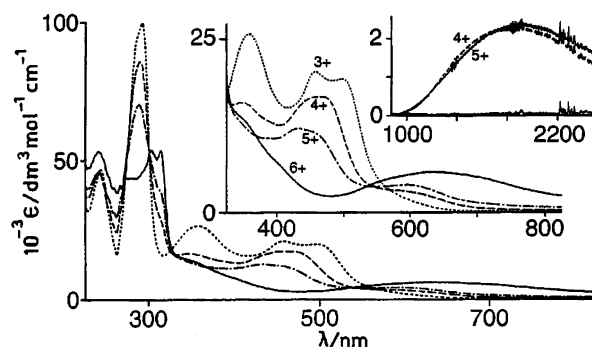
Fig. 4 Electronic spectra (from an OTTLE experiment in MeCN at 243 K) of $[1]^{n+}$: n = 3 (· · ·), 4 (- - -), 5 (- · -), 6 (—).

expected. This spectrum is generally similar to that of the mononuclear analogue $[Ru^{II}(bpy)_2(2\text{-}NC_5H_4S)]^+$,[16] apart from the greater intensity of the transitions due to the presence of three metal chromophores.

As each metal centre in turn is oxidised from Ru(II) to Ru(III), the MLCT transitions at 456 and 491 nm steadily diminish in intensity as the number of Ru(II) centres is reduced. They are replaced by a much weaker region of absorbance at *ca.* 600 nm which steadily grows in intensity until, for the fully-oxidised species $[1]^{6+}$ [three Ru(III) centres)], it is a well-defined peak at 624 nm. This may be ascribed to an $S^- \longrightarrow Ru(III)$ LMCT transition which becomes allowed due to the presence of a low-energy hole in the d_π orbital set of each metal ion.[19] At higher energy, the intense transition at 292 nm also diminishes in intensity during the successive metal-centred oxidations, indicating that it has Ru(II) $\longrightarrow$ bpy MLCT character, and is replaced by a shoulder which becomes apparent on the low-energy side of it (*ca.* 300 nm), which becomes a clearly-developed maximum in the fully-oxidised form $[1]^{6+}$.

The electronic interaction between the Ru(II) and Ru(III) sites in the mixed-valence species $[1]^{4+}$ and $[1]^{5+}$ is apparent from the broad, relatively weak IVCT (intervalence charge transfer) transitions in the near-IR region which are present for these two oxidation states, but absent for the two isovalent states (Fig. 4). In both $[1]^{4+}$ and $[1]^{5+}$ the IVCT is very broad and of relatively low intensity, centred at *ca.* 1900 nm in each case and with similar intensities: for $[1]^{4+}$, ε = 2300 dm³ mol⁻¹ cm⁻¹; for $[1]^{5+}$, ε = 2400 dm³ mol⁻¹ cm⁻¹. The width of these transitions is consistent with class II mixed-valence states, for which the relationship in eqn. (1)

$$\Delta\bar{v}_{1/2} = [2310(\bar{v}_{max})]^{1/2} \qquad (1)$$

is expected to hold: this predicts full width at half maximum height (FWHM) values of *ca.* 3500 cm⁻¹ for both $[1]^{4+}$ and $[1]^{5+}$, in reasonable agreement with the observed values of *ca.* 4400 cm⁻¹ for both $[1]^{4+}$ and $[1]^{5+}$ respectively.[6f] It is common (indeed, normal) for IVCT transitions in class II complexes to be slightly broader than predicted by eqn. (1), because the splitting of the d_π orbital set in ligand fields which are not exactly octahedral, as here, results in three closely-spaced (but individually unresolved) IVCT transitions.[20] In contrast, class III (fully delocalised) behaviour is characterised by much narrower transitions because the transition associated with the delocalised electron is not accompanied by solvent repolarisation.[6f] It follows from this that both $[1]^{4+}$ and $[1]^{5+}$ are displaying class II behaviour, and it is therefore appropriate to use eqn. (2)

$$V_{ab} = [2.05 \times 10^{-2}(\varepsilon_{max}\bar{v}_{max}\Delta\bar{v}_{1/2})^{1/2}]/R\sqrt{2} \qquad (2)$$

to estimate the electronic coupling constants V_{ab} for the two mixed-valence states.[6f] In eqn. (2) the factor of $\sqrt{2}$ in the denominator, which is not present when dinuclear complexes are being considered, is a statistical correction for the fact that

in both mixed-valence forms there are two equivalent routes for the Ru(II) → Ru(III) intervalence electron transfer.[20] The values so obtained are 560 cm^{-1} in each case, assuming a Ru · · · Ru separation of 5.9 Å (taken from the crystal structure of a structurally related dinuclear complex with thiouracil as bridging ligand).[2g] These coupling constants are typical of those observed for class II mixed-valence states,[6d,f] in agreement with the redox separations seen in the electrochemical measurements. The fact that the values obtained for [1]$^{4+}$ and [1]$^{5+}$ are essentially the same is presumably related to the fact that the bridging pathway (between two N atoms of the triazine unit *via* a metal-substituted linkage) is the same in each case.

It has been pointed out that in trinuclear mixed-valence complexes of this sort, two distinct IVCT transitions are expected in the diradical form (here, Ru^{II}Ru^{III}Ru^{III}) because of the presence of magnetic exchange between the two radical centres.[20] The Ru^{II}Ru^{III}Ru^{III} species [1]$^{5+}$ will have two energetically distinct electronic states depending on whether the two Ru(III) centres have their spins mutually aligned or opposed. Whether the dominant coupling is ferromagnetic or antiferromagnetic is immaterial; unless the coupling is extraordinarily strong, both states will be occupied at 243 K (the temperature of the spectroelectrochemical measurements), leading to two slightly different energies for the Ru(II) → Ru(III) IVCT process. The effect of this will be to broaden the envelope for the IVCT transition in [1]$^{5+}$ compared to that of (monoradical) [1]$^{4+}$. However, we could not clearly detect the effect here, presumably because the effect is much smaller than the broadening of the IVCT manifold caused by the non-degeneracy of the d$_\pi$ orbitals on the metal atoms, although we note that at the long-wavelength limit of our measurements (2500 nm) the IVCT peak for [1]$^{5+}$ is tailing off more slowly than that of [1]$^{4+}$.

Non-linear optical properties

The non-linear optical properties of the complexes [1]$^{3+}$ and [2]$^{3+}$ were studied using the *z*-scan technique.[21] In this technique, the sample is scanned across the beam waist of a focused Gaussian beam along its propagation direction, *z*. The intensity dependent non-linear phase front distortions of the beam are measured as a function of *z* in terms of the transmittance variations through an aperture placed in the exit beam. The resulting scan (closed aperture scan) contains the information of both the absorptive and refractive non-linearity. The absorptive part of the non-linearity can be obtained from the intensity dependent transmission of the sample measured without an aperture (open aperture scan). The ratio of the normalised closed and open aperture scan generates a *z*-scan due to purely refractive non-linearity. The prefocal maximum followed by postfocal minimum in the generated *z*-scan is the signature of the negative (self defocusing) non-linearity and *vice versa* for the positive (self focusing) non-linearity. Thus this method provides a direct measurement of the real and imaginary parts of the non-linearity along with its sign.

The open aperture *z*-scan (●) of [2]$^{3+}$ at 532 nm is shown in Fig. 5a. The sample was scanned 15 mm on either side of the focus. The intensity of the input beam at focus was 85.49 MW cm^{-2}. The normalised power transmittance increases at the focus nearly 1.3 times compared to that of the low power transmittance indicating saturable absorber behaviour. Similar behaviour is also observed for the bipyridine analogue [1]$^{3+}$. This saturable absorber behaviour may arise due to the presence of an excited state having a lifetime greater than the pulse width. The origin of this saturable absorption can be understood using a three-level model of this kind of system as shown in Fig. 6. Laser radiation at 532 nm excites the molecules from the singlet ground state ^{1}A$_{1g}$ to a first electronic singlet MLCT band, ^{1}CT . The excited molecules undergo internal conversion and intersystem crossing to ^{3}CT. As the intersystem crossing
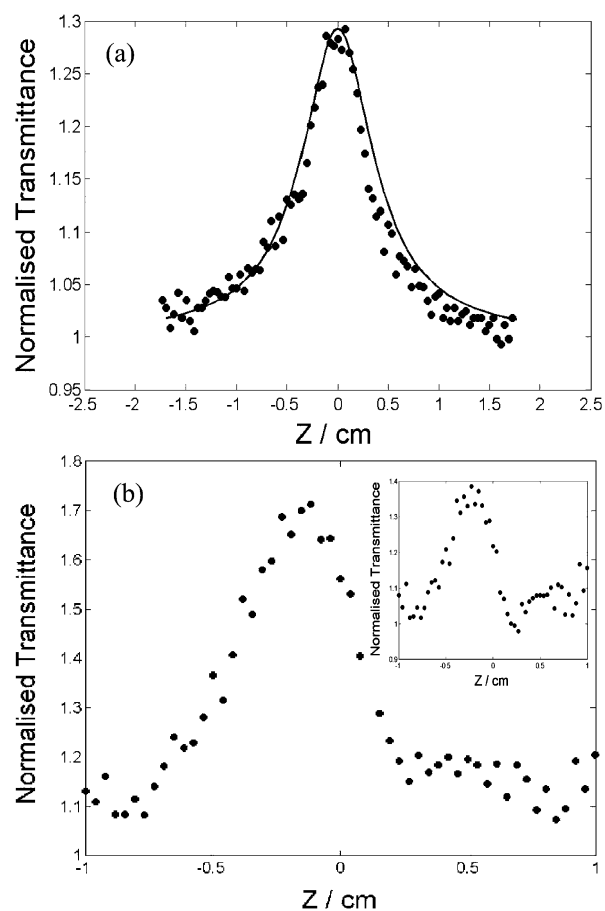

Fig. 5 (a) Open aperture *z*-scan for [{(phen)$_2$Ru^{II}}$_3$(L)](ClO$_4$)$_3$, [2](ClO$_4$)$_3$. Dots represent experimental points and the solid curve is the theoretical fit. (b) Closed aperture *z*-scan for [{(phen)$_2$Ru^{II}}$_3$(L)](ClO$_4$)$_3$, [2](ClO$_4$)$_3$. Figure in inset represents the refractive part of the *z*-scan.
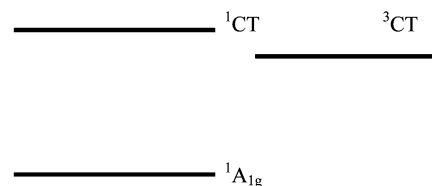

Fig. 6 A general three level model for ruthenium polypyridine complexes.

time is comparable to the pulse width and the lifetime of the ^{3}CT (at 652 nm) state is much longer than the pulse width, this gives rise to saturable absorber behaviour. The intensity dependent absorption coefficient can be defined as $a(I) = a_0 + \beta_{eff}I$. Here β_{eff} is the effective intensity dependent absorption coefficient, a_0 (cm^{-1}) is the linear absorption coefficient and I (W cm^{-2}) is the incident radiation intensity. The experimental data were fitted to the normalised transmittance given by eqn. (3).[22]

$$T_{norm}(z) = \frac{1}{\sqrt{\pi}q_0} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-t^2})dt \qquad (3)$$

In this, q_0 is given by the equation

$$q_0 = \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{(1 + z^2/z_0^2)\alpha_0} \qquad (4)$$

where I_0 is the on-axis intensity at the focus, l is the path length of the sample, and z_0 is the Rayleigh range of the beam. Values

of $\beta_{eff} = -5.96 \times 10^{-8}$ cm W^{-1} for [1]$^{3+}$ and -6.42×10^{-8} cm W^{-1} for [2]$^{3+}$ were determined and the representative fitted curve for [2]$^{3+}$ is shown in Fig. 5a.

The normalised closed aperture z-scan data for [2]$^{3+}$ is shown in Fig. 5b. Here, the greatly enhanced prefocal peak and fully suppressed postfocal valley are the consequence of large saturable absorption. Thus absorptive and refractive contributions to the far field beam profile are coupled. The ratio of normalised closed to open aperture z-scan is depicted in the inset of Fig. 5b. The signature of prefocal maximum and postfocal minimum represent the negative non-linearity in this system. The same is true for [1]$^{3+}$. This refractive part of non-linearity (n_2) was determined from the peak–valley transmittance difference [22] ΔT_{p-v} using $n_2 = \dfrac{\lambda \alpha_0}{0.405(1-S)^{0.25}2\pi I(1-\mathrm{e}^{-\alpha_0 l})}\Delta T_{p-v}$. The modulus of the effective third order susceptibility ($\chi^{(3)}$) was calculated [22] using $|\chi^{(3)}| = \sqrt{\left(\left|\dfrac{c\lambda n_0^2 \beta_{eff}}{64\pi^3}\right|^2 + \left|\dfrac{c n_0^2 n_2}{16\pi^2}\right|^2\right)}$. Here n_0 and λ are the linear refractive index of the solvent and the excitation wavelength respectively. The corresponding modulus of hyperpolarisability can be obtained from $|\chi^{(3)}| = N\left(\dfrac{n_0^2+2}{3}\right)^4 |\gamma|$.

This analysis yields values of $\gamma = -4.5 \times 10^{-29}$ esu for [1]$^{3+}$ and -5.09×10^{-29} esu for [2]$^{3+}$. The magnitude of γ for samples [1]$^{3+}$ and [2]$^{3+}$ are comparable to those observed for many other ruthenium complexes.[23]

Conclusions

The complexes [1]$^{3+}$ and [2]$^{3+}$ represent the first examples of a triruthenium series incorporating 1,3,5-triazine-2,4,6-trithiol as a trinucleating bridging function which have so far been reported only with the titanium metal ion. The electrochemical results in combination with spectroelectrochemical and EPR observations unequivocally establish that the mixed valence states Ru^{II}Ru^{II}Ru^{III} [1]$^{4+}$ and Ru^{II}Ru^{III}Ru^{III} [1]$^{5+}$ are in moderately coupled class II systems. The complexes are moderately strongly luminescent and exhibit reasonably good second molecular hyperpolarisabilities, suitable for photonic device applications.

Experimental

Materials

The starting complexes cis-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O and cis-[Ru(phen)$_2$Cl$_2$]·2H$_2$O were prepared according to the reported procedure.[24] The trinucleating bridging ligand, trisodium salt of 1,3,5-triazine-2,4,6-trithiol (Na$_3$L) was purchased from Fluka, Switzerland. Other chemicals and solvents were of reagent grade and used as received. For electrochemical studies HPLC grade acetonitrile was used. Commercial tetraethylammonium bromide was converted to pure tetraethylammonium perchlorate (TEAP) by following an available procedure.[25]

Physical measurements

The 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. Magnetic susceptibility was checked with a PAR vibrating sample magnetometer. ^{1}H-NMR spectra were obtained on a 300 MHz Varian FT-NMR spectrometer. UV-Vis-NIR spectroelectrochemistry studies were performed at 243 K in an optically transparent thin layer electrode (OTTLE) cell mounted in the sample compartment of a Perkin-Elmer Lambda 19 spectrophotometer, the cell and the method used have been described previously.[26] Cyclic voltammetry 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 three-electrode configuration. A glassy-carbon working electrode was used while recording the voltammograms at potentials negative of SCE. Tetraethylammonium perchlorate (TEAP) was the supporting electrolyte and the concentration of the solution was 10^{-3} M. The half wave potential E^0_{298} was set equal to 0.5 ($E_{pa} + E_{pc}$), where E_{pa} and E_{pc} are the anodic and cathodic cyclic voltammetric peak potentials, respectively. The scan rate used was 50 mV s^{-1}. A platinum gauze working electrode was used in coulometric experiments. All electrochemical experiments were carried out under a dinitrogen atmosphere and are uncorrected for junction potentials. The elemental analyses were carried out using a Perkin-Elmer 240C elemental analyser. The EPR measurements were made with a X-band Bruker system ESP300, equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. The electrospray mass spectrum was recorded on a Finnigan LCQ ADVANTAGE mass spectrometer, USA. Solution emission properties were checked using a SPEX-fluorolog spectrofluorometer with fluorescence quantum yields being determined using a previously described method.[27]

Preparation of complexes [1](ClO$_4$)$_3$ and [2](ClO$_4$)$_3$

Both of the complexes were prepared by the same general procedure: the details are given for [1](ClO$_4$)$_3$.

[{(bpy)$_2$Ru^{II}}$_3$(L)](ClO$_4$)$_3$, [1](ClO$_4$)$_3$. The starting complex Ru(bpy)$_2$Cl$_2$ (100 mg, 0.19 mmol) and AgClO$_4$ (90 mg, 0.39 mmol) were taken in absolute ethanol (15 cm^3) and the mixture was heated to reflux with stirring for 1.5 h. The initial violet solution changed to orange-red; it was then cooled and filtered through a sintered glass funnel. The ligand Na$_3$L (175 mg, 0.06 mmol) was then added to the above [Ru(bpy)$_2$(EtOH)$_2$]$^{2+}$ solution. The resulting mixture was heated to reflux under a dinitrogen atmosphere for 6 h. The precipitate which formed on cooling was filtered off and washed thoroughly with ice-cold water followed by cold ethanol and diethyl ether. The product was recrystallised from acetonitrile–benzene (1 : 4). Yield: 59% (196 mg); Anal. Calcd for C$_{63}$H$_{48}$N$_{15}$Cl$_3$O$_{12}$S$_3$Ru$_3$: C, 44.18; H, 2.82; N, 12.27%. Found: C, 44.09; H, 2.49; N, 11.96% Λ_M (Ω^{-1} cm^2 mol^{-1}) in acetonitrile at 298 K: 328.

[2](ClO$_4$)$_3$. Yield: 62% (205 mg); Anal. Calcd for C$_{75}$H$_{48}$N$_{15}$Cl$_3$O$_{12}$S$_3$Ru$_3$: C, 48.51; H, 2.61; N, 11.31%; Found: C,48.39; H, 2.00; N, 10.62% Λ_M, (Ω^{-1} cm^2 mol^{-1}) in acetonitrile at 298 K: 342; λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1}cm^{-1}) in CH$_3$CN at 298 K: 498 (27), 449 (36), 265 (190), 223 (177).

Non-linear optical parameter measurement

A schematic of the z-scan set up employed for our studies is shown in Fig. S3.† Second harmonic pulses (6 ns duration) of an indigenously developed Q-switched Nd:YAG laser were focused using a 25 cm focal length lens onto a spot ($2\omega_0 \approx 56$ μm). Samples in acetonitrile solution (5.0×10^{-4} mol dm^{-3}) were placed in 3 mm quartz cuvettes and were scanned over its focal region by a motorised translational stage. Incident and transmitted pulse energies were measured on a digital storage oscilloscope using two calibrated photodiodes operating in a linear regime. For the closed aperture measurement, an aperture having linear transmittance factor $s = 0.1$ was kept before the photodiode PD2. Input pulse energy was restricted to keep the maximum phase change to less than 1 radian.

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