The IVCT characteristics of the mixed valence forms of the trinuclear complex \([\{\Lambda-Ru(bpy)\},\{\Lambda'-Ru(bpy)(\mu-ppz)\}]^+ (n = 7, 8; t = trans), and the diastereoisomers (meso and rac) of the dinuclear complex \([\{Ru(bpy)\},\{\mu-ppz\}]^{2+}\), display a marked dependence on the nuclearity and extent of oxidation of the assemblies. The dinuclear species are classified as borderline localised–delocalised mixed valence species while the two mixed valence states of the trinuclear complex exhibit localised behaviour. One-electron oxidation of a terminal Ru centre in the trinuclear case gives rise to a broad, low intensity IVCT band for the +7 mixed valence species which is composed of two underlying Gaussian-shaped bands. The transitions are identified as adjacent and remote IVCT transitions, with the former dominating the intensity of the IVCT manifold. The +8 mixed valence species exhibits a single dominant IVCT band arising from the equivalent IVCT transitions from the central Ru to peripheral Ru

### Introduction

The analysis of intervalence charge transfer (IVCT) transitions in mixed valence complexes provides a window to the elucidation of the factors that govern electronic delocalisation and the activation barrier to intramolecular electron transfer. These studies have focused predominantly on dinuclear complexes, and theoretical studies on higher nuclearity polymetallic assemblies are relatively scarce, and the degree to which the IVCT process is influenced by the nuclearity, oxidation state and overall geometry of the systems is not clear.

The elucidation of fundamental electron transfer processes in trinuclear complexes provides the link between the understanding of such processes in dinuclear systems, and in extended arrays and metallosupramolecular systems which form the basis of novel molecular devices.

To date, IVCT studies of trinuclear complexes have focused predominantly on complexes incorporating polypyridyl iron, ruthenium and osmium components, linked by bridging ligands such as cyanide and pyrazine, and polypyridyl bridging ligands including 2,3-dpp, 2,3-bis(2-pyridyl)pyrazine, however, a few reports of extended structures such as cyclic and star-burst cyano-bridged molecular

---

**Interruption charge transfer in a “chain-like” ruthenium trinuclear assembly based on the bridging ligand 4,7-phenanthrolino-5,6:5′,6′-pyrazine (ppz)**

Deanna M. D’Alessandro and F. Richard Keene*

Received 7th September 2005, Accepted 18th October 2005

First published as an Advance Article on the web 17th November 2005

DOI: 10.1039/b512625h

The IVCT characteristics of the mixed valence forms of the trinuclear complex \([\{\Lambda-Ru(bpy)\},\{\Lambda'-Ru(bpy)(\mu-ppz)\}]^+ (n = 7, 8; t = trans), and the diastereoisomers (meso and rac) of the dinuclear complex \([\{Ru(bpy)\},\{\mu-ppz\}]^{2+}\), display a marked dependence on the nuclearity and extent of oxidation of the assemblies. The dinuclear species are classified as borderline localised–delocalised mixed valence species while the two mixed valence states of the trinuclear complex exhibit localised behaviour. One-electron oxidation of a terminal Ru centre in the trinuclear case gives rise to a broad, low intensity IVCT band for the +7 mixed valence species which is composed of two underlying Gaussian-shaped bands. The transitions are identified as adjacent and remote IVCT transitions, with the former dominating the intensity of the IVCT manifold. The +8 mixed valence species exhibits a single dominant IVCT band arising from the equivalent IVCT transitions from the central Ru to peripheral Ru

---

**First published as an Advance Article on the web 17th November 2005**

**Received 7th September 2005, Accepted 18th October 2005**

**DOI: 10.1039/b512625h**

---

**School of Pharmacy and Molecular Sciences, James Cook University, Townsville, Queensland, 4811, Australia. E-mail: Richard.Keene@jcu.edu.au; Fax: +61-(0)7-4781-6078**

† Electronic supplementary information (ESI) available: 1H NMR chemical shifts and spectra for \(\Lambda-[Ru(bpy)(HAT)]^{2+}, \Lambda-[Ru(bpy)(ppz)]^{2+}\) and \(\Delta\Lambda-[\{Ru(bpy)\},\{Ru(bpy)(\mu-ppz)\}]^{2+}\) (Tables S1 and S2, Fig. S1 and S2); ligand-based reduction potentials and \(\Delta\Lambda\) values for the di- and trinuclear complexes (Table S3); CD spectra of \(\Delta\Lambda-\) and \(\Lambda\)-\([Ru(bpy)(HAT)]^{2+}\) and \(\Delta\Lambda-\) and \(\Lambda\)-\([Ru(bpy)(ppz)]^{2+}\) (Fig. S1); a differential pulse voltammogram of \(\Delta\Lambda-[\{Ru(bpy)\},\{Ru(bpy)(\mu-ppz)\}]^{2+}\) (Fig. S4); UV/Vis/NIR spectra of \([Ru(bpy)(ppz)]^{2+}, meso-[Ru(bpy)(ppz)]^{2+}\) and \(\Delta\Lambda-\) \([Ru(bpy)\] \([\{Ru(bpy)(\mu-ppz)\}]^{2+}\) at +25 °C (Fig. S5); and UV/Vis/NIR spectra of meso-\([Ru(bpy)\] \([\{Ru(bpy)(\mu-ppz)\}]^{2+}\) at −35 °C (Fig. S6). See DOI: 10.1039/b512625h

### squares and clusters, polyferrocenes and alkynyl-bridged molecular wires have also appeared. As an illustrative example, Bignozzi and coworkers have extensively investigated the IVCT properties of a series of cyano-bridged systems such as \([\{\text{NH}_3\},\text{Ru}_{\text{trans}}-\text{NC–M}_{\text{trans}}(\text{bpy})–\text{CN–Ru}_{\text{trans}}(\text{NH}_3)\}]^{2+} (M = \text{Ru}, \text{Os}; \text{bpy} = 2,2′-\text{bipyridine}) and their analogues \([\{\text{py}(\text{NH}_3)\},\text{Ru}_{\text{trans}}-\text{NC–Ru}_{\text{trans}}(\text{bpy})–\text{CN–Ru}_{\text{trans}}(\text{NH}_3)\}]^{2+} (X = \text{NH}, \text{py}; \text{cent and term denote the central and terminal metals, respectively}). These studies revealed intriguing differences between the mixed valence forms of the trinuclear complexes and their dinuclear counterparts, including multiple IVCT bands due to the presence of IVCT transitions between adjacent \(\text{Ru}_{\text{trans}}\) and remote \(\text{Ru}_{\text{term}}\) metal centres. However, in these “chain-like” systems, the bridging cyano units are angularly disposed by virtue of the central \(\text{cis-Ru(bpy)}\), chromophore. The influence of the \(\text{cis or trans}\) configuration of trinuclear assemblies was elucidated in IVCT studies of the isomers of the trinuclear complexes \([\{\text{Fe}^{\text{III}}(\text{dppe})\text{Cp}\}–\text{NC–Pt}^{\text{III}}(\text{L})–\text{CN–Ru}^{\text{III}}(\text{PPh}_3)\text{Cp}\}]^{2+} (\text{Cp} = \text{cyclopentadienyl anion}; \text{dppe} = 1,2'-\text{bis(diphenylphosphine)}\ethene; \text{L} = \text{py, CN}^-), which differ only in the \(\text{cis or trans}\) arrangement of the cyano bridging ligands at the central metal. Remote IVCT transitions \(\text{Ru} \rightarrow \text{Fe}^{\text{II}}\) were observed for the \(\text{trans-}\)configured complexes only, so that the metal–metal interaction in the trinuclear species is facilitated by a polynuclear backbone in which the metals and intervening bridging ligands provide a linear (rather than angular) conduit for electron transfer.

While a number of important aspects relating to the influence of the increasing nuclearity and overall oxidation state of the assembly on the IVCT properties have been elucidated, the majority of studies on the physical characteristics of polymetallic assemblies have been conducted without regard for the inherent stereochinematic complexities in such systems. Keene and coworkers provided the first examples of differences in the spectral,
electrochemical and photophysical properties of stereoisomers in mono-, di- and trinuclear systems. Stereochemical effects have also been shown to influence the IVCT properties of a range of dinuclear and trinuclear systems: e.g. the diastereoisomers meso(ΔΔ)- and rac(ΔΔ/ΔΔ)-{[Ru(bpy)3]2+(μ-HAT)}6+ and homochiral (Δ/Δ)- and hetero-chiral (Δ/Δ)-{[Ru(bpy)3]2+(μ-HAT)}n (n = 7, 8), which are based on the bridging ligand HAT (1,4,5,8,9,12-hexaaazatriphenylene; Fig. 1(a)). The characteristics of the IVCT bands in the trinuclear case were markedly different from those of their dinuclear analogues due to extensive electronic communication between the Ru(bpy)2+ chromophores, and varied significantly depending on the extent of oxidation and the overall geometry of the assembly.

The present study broadens this previous investigation of the IVCT properties of “cluster-like” homo-dinuclear and homo-trinuclear ruthenium systems and hetero-dinuclear and hetero-trinuclear ruthenium and osmium systems based on the bridging ligand HAT (Fig. 1(a)), to the “chain-like” trinuclear complex ΔΔΔ-[{Ru(bpy)3}2(μ-ppz)2][{Ru(bpy)3}2(μ-ppz)2]6+, shown in Fig. 1(b). The mononuclear “core” [Ru(bpy)3(ppz)3]2+ possesses two geometric isomers, trans and cis, in addition to the Δ and Λ enantiomeric forms of each, and the “t” denotes the trans arrangement of the ppz ligands at the central metal.

The bridging ligand ppz (4,7-phenanthroline-5,6:5′,6′-pyrazine) is closely related electronically and structurally to HAT and the bridging ligand 2,3-dpp which have been utilised extensively in the construction of tri-, tetra- and higher nuclearity assemblies. The planarity of the ligand overcomes the problem of conformational lability in complexes incorporating 2,3-dpp, and permits the assessment of the influence of the overall “chain-like” geometry of the assembly by comparison with the IVCT properties for the closely related trinuclear “cluster-like” systems based on HAT.

Experimental

General

1D and 2D 1H NMR spectra were performed on a Varian Mercury 300 MHz spectrometer. Chemical shifts for all complexes are reported relative to 99.9% d3-acetonitrile (CD3CN; Cambridge Isotope Laboratories (CIL)) at δ = 1.93 ppm. 1H NMR assignments were performed with the assistance of COSY experiments to identify each pyridine ring system. Elemental microanalyses were performed at the Microanalytical Unit in the Research School of Chemistry, Australian National University.

Circular dichroism (CD) spectra were recorded in acetonitrile solution at concentrations of ca. 2–3 × 10−5 M in a 1.0 cm path length cell, using a JASCO J-715 spectropolarimeter. CD spectra are presented as ∆ε (M−1 cm−1) vs. wavelength λ (nm).

Electrochemical measurements were performed under argon using a Bioanalytical Systems (BAS) 100A electrochemical analyser. Cyclic (CV) and differential pulse (DPV) voltammograms were recorded in a standard three-electrode cell using a glassy carbon or platinum button working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode (0.1 M [n-C4H9]4NPF6 in CH3CN). Ferrocene was added as an internal standard on completion of each experiment (the ferrocene/ferrocenium couple (Fc+/Fc−) occurs at +550 mV vs. Ag/AgCl). Solutions contained 0.1 M [n-C4H9]4NPF6 as the electrolyte. Cyclic voltammetry was performed with a sweep rate of 100 mV s−1; differential pulse voltammetry was conducted with a sweep rate of 4 mV s−1 and a pulse amplitude, width and period of 50 mV, 60 ms and 1 s, respectively. All potentials are reported ±0.3 mV.

UV/visible/near-infrared (UV/Vis/NIR) spectrophotometry was performed using a CARY 5E spectrophotometer.

Fig. 1 The bridging ligands HAT and ppz, and Chem 3D representations of (a) “cluster-like” ΔΔΔ-{[Ru(bpy)3]2(μ-HAT)}6+ and (b) “chain-like” ΔΔΔ-{[Ru(bpy)3]2(μ-ppz)2][{Ru(bpy)3}2(μ-ppz)2]}6+. Hydrogen atoms are omitted for clarity.
interfaced to Varian WinUV software. The absorption spectra of the electrogenerated mixed valence species were obtained in situ by the use of a cryostatted optically semi-transparent thin layer electrosynthetic (OSTLE) cell mounted in the path of the spectrophotometer. An account of the procedure employed in the spectrophotometric measurements has been detailed previously. Solutions for the spectrophotometric experiments contained 0.1 M \([n-(C_8H_17)_2N]PF_6\) supporting electrolyte in CH_3CN and the complex \((ca. 1 \times 10^{-3} \text{ M})\). All solutions were purged with N_2, prior to transference \((via a syringe)\) into the OSTLE cell. The temperature was stabilised to \(\pm 0.3 \degree C\) prior to commencing electrolysis. The dinuclear systems required approximately 6 h for data collection at \(-35 \degree C\), while the trinuclear systems required approximately 10 h and were conducted at \(-15 \degree C\) due to limitations on the continuous supply of coolant gas. The integrity of the spectral data was checked by the observation of stable isosbestic points, and the complete regeneration of the starting spectrum following each stage of oxidation.

The IVCT spectra were scaled as \(\int \alpha(t)/\nu \; \text{d}v\) and deconvolution of the NIR transitions was performed using the curve-fitting subroutine implemented within the GRAMS32 commercial software package, as described previously. Based on the reproducibility of the parameters obtained from the deconvolutions, the uncertainties in the energies (\(\nu_{\text{max}}\)), intensities \(\{\alpha/\nu_{\text{max}}\}\) and bandwidths \(\{\Delta\nu_{\text{b}}\}\) were estimated as \(\pm 10 \text{ cm}^{-1}\), \(\pm 0.001 \text{ M}^{-1}\) and \(\pm 10 \text{ cm}^{-1}\), respectively.

Materials
Hydrated ruthenium trichloride (RuCl_3 \cdot 3H_2O; Strem, 99%), 2,2'-bipyridine (bpv; Aldrich, 99+%), 2,3-diaminonaphthalene (Fluka), 4,7-phenanthroline (Aldrich), 3-nitrobenzenesulfonic acid (Na^+ salt, Aldrich, 98%), 2-methoxy-1,4-phenylenediamine hydrate (Aldrich, 95%), glycerol (APS Fineschluf), sulfuric acid (H_2SO_4; Ajax, 98%), ammonium hydrogen carbonate (NH_4HCO_3; May and Baker), stannous chloride (SnCl_2 \cdot 2H_2O; Aldrich), lithium perchlorate (LiClO_4; Aldrich, 99+%), ammonium hexafluorophosphate (NH_4PF_6; Aldrich, 99.99%), potassium hexafluorophosphate (KF; Aldrich, 98%), zinc chloride (ZnCl_2 \cdot xH_2O; Fluka, 98%), hydrazine hydrate (Aldrich), ethylene glycol (Ajax 95%), sodium toluene-4-sulfonate (Aldrich, 98%), DowEx® 1 × 8, 50–100 mesh (Aldrich) and Amberlite® IRA-400 (Aldrich) anion exchange resins. Celite (Aldrich) and laboratory reagent solvents were used as received. Tetra-n-butylammonium hexafluorophosphate \([n-(C_8H_17)_2N]PF_6; \text{Fluka}, 99+\%\) was dried in vacuo at 60 \degree C prior to use and ferrocene (Fc; BDH) was purified by distillation

ligand synthesis

The synthesis of ppz involved a three-stage procedure:

(a) 5-Methoxy-4,7-phenanthroline hydrogen sulfate. This compound was prepared via a modification of the literature procedure. A two-necked 3 dm³ round bottom flask was fitted with a mechanical stirrer and condenser, and 3-nitrobenzenesulfonic acid (Na^+ salt; 100 g, 0.444 mol), 2-methoxy-1,4-phenylenediamine-sulfate (50 g, 0.212 mol) and glycercol (934.7 g, 9.53 mol) were added to the flask. A solution of 98% H_2SO_4 (510 cm³) in H_2O (270 cm³) was prepared, allowed to cool to room temperature, and added in a single portion. The mixture was heated at reflux (~140 \degree C) for 6 h, during which time the mixture attained a dark red colouration. The solution was cooled to room temperature, poured over ice (540 g) and basified to pH 10 with 50% NaOH (ca. 1200 cm³).

(b) 4,7-Phenanthroline-5,6-dione. This compound was prepared according to a modification of the literature method. 5-Methoxy-4,7-phenanthroline hydrogen sulfate (40.63 g; 0.132 mol) was dissolved in 98% H_2SO_4 (150 cm³). With ice bath cooling, fuming HNO_3 (60 cm³) was added dropwise with stirring. The mixture was refluxed at 96 \degree C for 10 h, then cooled to room temperature, poured onto ice (ca. 900 g), and neutralised to pH 6.8–7.0 (pH meter) by the stepwise addition of ammonium
bicarbonate, maintaining the temperature below 10 °C throughout by vacuum filtration. Washed with chilled H2O (1500 cm³), chilled acetone (250 cm³) and chilled diethyl ether (250 cm³), and dried in vacuo overnight. Yield: 24.0 g (86%). The 1H NMR and melting point were identical to those reported previously.53

(c) 4,7-Phenanthrolino-5,6:5′,6′-pyrazine (ppz). This compound was prepared according to a modification of the literature procedures.52,53 4,7-Phenanthrolino-5,6-dione (21.95 g, 0.104 mol) was dissolved in freshly distilled methanol (380 cm³) at 30 °C. Freshly distilled ethylenediamine (7.3 cm³, 0.110 mol) was added in a single portion, at which point the mixture attained a red colouration. The reaction was stirred at 30 °C for 2 h, and the solvent removed by rotary evaporation to yield an orange solid. The residue was dissolved in H2O (500 cm³) and extracted with chloroform (3 × 100 cm³). The solution volume was reduced in vacuo and chromatographed on silica gel via gradient elution using 10% methanol–1% NH4OH in dichloromethane. The ppz was isolated as the light yellow band which eluted prior to a deep purple band (which presumably contained the non-aromatic tetrahydroquinoline analogue).54 The solvent was removed in vacuo and the beige solid was washed with acetone. Yield: 15.7 g (65%). The 1H NMR and melting point were identical to those reported previously.52,53

Complex syntheses and diastereoisomer separations

The mononuclear ruthenium complexes [Ru(DMSO)Cl2]−, cis-[Ru(bpy)Cl2]2+ and the carbonyl complexes [Ru(CO)Cl2]−, [Ru(bpy)(CO)Cl2]− and [Ru(bpy)(CO)2Cl2]− were prepared according to the literature procedures. [Ru(bpy)Cl2]− was supplied by Dr Bradley Patterson.

[Ru(bpy)(HAT)]2+,[PF6]−. This complex was synthesised via a procedure analogous to that reported previously for [Ru(bpy)(2,3-dppz)][PF6]−.49 A suspension of HAT (200 mg, 0.854 mmol) was heated in ethylene glycol (10 cm³) for 5 min via microwave heating to complete dissolution. [Ru(bpy)Cl2] (45 mg, 0.113 mmol) was added in four portions over 10 min with heating, during which time the solution attained an orange colouration. The mixture was heated for a further 5 min, then quenched with distilled water (ca. 50 cm³) and filtered to recover the excess HAT ligand. One major band was collected from the Sephadex C-25 cation exchange column (20 × 2 cm) using 0.1 M NaCl solution as eluent. Following the addition of a saturated solution of aqueous KPF6 to the eluate the mixture was chilled by refrigeration overnight. The orange precipitate was isolated by filtration, washed with chilled water (3 cm³), diethyl ether (3 × 1 cm³) and dried in vacuo. Yield: 7.02 mg (61%). Anal.: Calcd for C₃₂H₂₅F₃N₃P₂Ru: C, 39.6; H, 1.98; N, 19.3%. Found: C, 40.0; H, 2.05; N, 19.2%. Further structural characterisation was performed following the separation and chiral resolution of the geometrical isomers and their enantiomeric forms.

Resolution of [Ru(bpy)(HAT)]2+,[PF6]−. The mononuclear complex was resolved via an analogous procedure to that described previously for [Ru(bpy)2(HAT)]57. The PF6− salt was converted to the corresponding aqueous Cl− form by stirring with DOWEX® 1 × 8 anion exchange resin (50–100 mesh, Cl− form). The aqueous solution was sorbed onto SP Sephadex C-25 cation exchanger (96 × 1.6 cm) and chromatographed using 0.10 M (+)-di-O-4-toluoyl-D-tartrate solution as eluent. Resolution of the enantiomeric forms was achieved with ~50 cm of travel down the column. The products from the two bands were precipitated on addition of aqueous KPF6; the mixtures were refrigerated overnight and the solids isolated by filtration, washed with chilled water (3 cm³), diethyl ether (3 × 10 cm³) and dried in vacuo. By comparison with similar complexes of known configuration,58 band 1 was assigned as Δ−([Ru(bpy)(HAT)]2+) and band 2 as Δ−([Ru(bpy)(HAT)]2+). UV/Vis in CH3CN, λ/nm {νmax[M−1 cm−1 (band 1 = band 2)}: 210 (52089), 275 (54956), 408 (11326), 466 (11089). CD spectra in CH3CN, λ/nm {Δε[M−1 cm−1 (band 1, band 2)}: 206 (−18.0, + 19.6), 224 (+8.85, −8.51), 259 (+7.58, −8.02), 297 (−49.4, +47.2), 318 (−53.0, +52.0), 392 (−15.8, +15.6), 482 (−9.73, +10.1).

{[Ru(bpy)2]+,[μ-ppz]}[PF6]−. The synthesis and purification were performed under similar conditions to those described previously for {[Ru(bpy)2]+,[μ-HAT]}[PF6]− using cis-[Ru(bpy)(Cl2)2]H2O (111 mg, 0.213 mmol) and ppz (24 mg, 0.103 mmol). The dinuclear species was isolated as a purple solid. Yield: 140 mg (83%). Anal.: Calcd for C63H72F24N12P4Ru2: C, 39.6; H, 2.46; N, 10.3%. Found: C, 39.4; H, 2.44; N, 10.1%. Further characterisation was performed following the diastereoisomer separation.

Separation of the diastereoisomers was achieved as described above using aqueous 0.25 M sodium toulene-4-sulfonate solution as the eluent. Bands 1 and 2 were determined to be the meso and rac diastereoisomers, respectively, as established by NMR characterisation. 1H NMR (6 ppm; CD3CN): (band 1; meso) 7.25 (H5d, 2H, = 8, 5 Hz, dd), 7.39 (H5b, 2H, = 8, 5 Hz, dd), 7.42 (H5c, 2H, = 8, 5 Hz, dd), 7.50 (H5a, 2H, = 8, 5 Hz, dd), 7.54 (H6d, 2H, = 5, 1.5 Hz, dd), 7.73 (H6a, 2H, = 5, 1.5 Hz, dd), 7.75 (H6c, 2H, = 5, 1.5 Hz, dd), 7.85 (H6b, 2H, = 5, 1.5 Hz, dd), 7.93 (H2/3 ppz, 2H, s), 7.99 (H4d, 2H, = 8, 8 Hz, dd), 8.01 (H7/10 ppz, J = 10, 8 Hz, dd), 8.06 (H4c, 2H, = 8, 8 Hz, dd), 8.09 (H4b, 2H, = 8, 8 Hz, dd), 8.15 (H3a, 2H, = 8, 8 Hz, dd), 8.23 (H6/11 ppz, J = 5, 1.5 Hz, dd), 8.39 (H3d, 2H, = 8, 5 Hz, dd), 8.43 (H3c, 2H, = 8, 1.5 Hz, dd), 8.52 (H3b, 2H, = 8, 1.5 Hz, dd), 8.58 (H3a, 2H, = 8, 1.5 Hz, dd), 9.32 (H9/8 ppz, J = 8, 1.5 Hz, dd), (band 2; rac) 7.02 (H5b, 2H, = 8, 5 Hz, dd), 7.36 (H5d, 2H, = 8, 5 Hz, dd), 7.38 (H5c, 2H, = 8, 5 Hz, dd), 7.42 (H6d, 2H, = 5, 1.5 Hz, dd), 7.51 (H5a, 2H, = 8, 5 Hz, dd), 7.61 (H6b, 2H, = 5, 1.5 Hz, dd), 7.66 (H6c, 2H, = 5, 1.5 Hz, dd), 7.76 (H6a, 2H, = 5, 1.5 Hz, dd), 7.96 (H2/3 ppz, 2H, s), 8.00 (H4d, 2H, = 8, 8 Hz, dd), 8.01 (H7/10 ppz, J = 10, 8 Hz, dd), 8.07 (H4b, 2H, = 8, 8 Hz, dd), 8.13 (H4a, 2H, = 8, 8 Hz, dd), 8.15 (H4c, 2H, = 8, 8 Hz, dd), 8.23 (H6/11 ppz, J = 5, 1.5 Hz, dd), 8.48 (H3d, 2H, = 8, 1.5 Hz, dd), 8.51 (H3b, 2H, = 8, 1.5 Hz, dd), 8.53 (H3a, 2H, = 8, 1.5 Hz, dd), 8.55 (H3c, 2H, = 8, 1.5 Hz, dd), 9.31 (H9/8 ppz, J = 8, 1.5 Hz, dd).

[Ru(bpy)2(py)2][PF6]−. This complex was prepared according to a minor variation on the literature procedure.63 [Ru(bpy)2(py)2]Cl2.H2O (0.164 g, 0.315 mmol) and pyridine (0.655 cm³, 8.10 mmol) were combined in aqueous methanol (13 cm³, 1 : 1 v/v) and the mixture heated at reflux for 4 h during which time the solution attained an orange-red colouration. The mixture was cooled to room temperature and the solvent was removed by rotary evaporation. The resultant red residue was
dissolved in a minimum volume of methanol (ca. 1 cm³) and the complex was precipitated by the addition of diethyl ether. The precipitate was collected by vacuum filtration and washed with diethyl ether (3 × 10 cm³).

The complex was purified by cation-exchange chromatography (SP Sephadex C-25). The solid was converted to the chloride salt by stirring an aqueous suspension with DOWEX® 1 × 8 anion exchange resin (50–100 mesh, Cl⁻ form), and the solution was loaded onto the Sephadex column (20 × 2 cm) and eluted with 0.2 M NaCl solution. The orange band was precipitated as the PF₆⁻ salt by the addition of aqueous KPF₆. The complex was isolated by filtration, washed with copious amounts of diethyl ether and dried in vacuo. Yield: 0.290 g (80%). The ¹H NMR was identical to that reported previously.⁸⁰

Resolution of [Ru(bpy)₂(py)₂](PF₆)₆. [Ru(bpy)₂(py)₂](PF₆)₆ was converted to the Cl⁻ salt by stirring the complex with DOWEX® 1 × 8 anion exchange resin (50–100 mesh, Cl⁻ form), and the solution applied to a cation-exchange column (SP Sephadex C-25; 96 × 1.6 cm). The two enantiomers were resolved on elution with an aqueous solution of sodium (→)-O,O-dibenzoyl-L-tartarate (0.10 M). The complex in each band was precipitated using a saturated solution of KPF₆ and collected by filtration.

Purification was achieved on silica gel as described below. The complex was washed with water (3 × 5 cm³) then copious amounts of diethyl ether and dried in vacuo. Bands 1 and 2 were assigned as Δ(-) and Δ(+), respectively, based on excitation analysis of their CD spectra and comparisons with related compounds with known absolute configurations.⁶³,⁶⁴

[Ru(bpy)(ppz)(CO)₂](PF₆)₆. This complex was prepared according to an adaptation of the literature method.⁷⁷ [Ru(bpy)(CO)₂(CF₃SO₃)₂](0.180 g, 0.294 mmol) and ppz (136.7 mg, 0.589 mmol) were dissolved in 95% ethanol (30 cm³) under N₂. The solution was refluxed for 30 min during which time the mixture attained a yellow colouration. The mixture was refluxed for a further 60 min and evaporated to dryness by rotary evaporation. The precipitate was dissolved in boiling water and filtered to remove unreacted ligand (ppz). A saturated aqueous solution of NH₄PF₆ was dissolved in boiling water and filtered to remove the beige residue. The mixture was refluxed for a further 60 min and evaporated to dryness by rotary evaporation. The precipitate was collected by vacuum filtration and washed with copious amounts of diethyl ether and dried in vacuo. Yield: 0.290 g (80%). The ¹H NMR was identical to that reported previously.⁸⁰

Separation and resolution of trans-[Ru(bpy)(ppz)₂](PF₆)₆. The separation of the geometric isomers and chiral resolution of their enantiomeric forms was achieved during a single column chromatographic procedure. The complex (ca. 90 mg) as the Cl⁻ form (obtained by stirring an aqueous suspension with DOWEX® 1 × 8 anion exchange resin; 50–100 mesh, Cl⁻ form) was absorbed onto a column of SP Sephadex C-25 cation exchanger and eluted using aqueous 0.10 M sodium tolulene-4-sulfonate solution. The column was sealed at the top and bottom to permit recycling of the broadening band and small portions of the front and back of the band were collected on each pass down the column. The complex was extracted from each fraction using dichloromethane following the addition of a saturated solution of aqueous KPF₆. The organic layers were dried over Na₂SO₄, filtered and the solvent removed by rotary evaporation. Purification of the solids was achieved on a short column of silica gel (3 × 2 cm). A solution of the complex in acetone was loaded onto the column and washed alternately with acetone, water and acetone and eluted with acetone containing 5% NH₄PF₆. Addition of water and removal of the acetone under reduced pressure afforded an orange solid which was collected by filtration through Celite and washed with diethyl ether (3 × 5 cm³). The precipitate was washed off the Celite into a test tube with acetone (ca. 2 cm³), evaporated under a stream of dry nitrogen and dried in vacuo for 3 h at 50 °C. By using ¹H NMR and CD spectroscopies, as well as by comparison with similar complexes of known configurations, the identities of the front and back fractions of the eluting band (bands 1 and 4, respectively) were established as the Δ-[Ru(bpy)(ppz)₂]²⁺ and Δ'-[Ru(bpy)(ppz)₂]²⁺ isomers, respectively (t = trans). The other fractions contained various admixtures of the Δ-[Ru(bpy)(ppz)₂]²⁺ and Δ'-[Ru(bpy)(ppz)₂]²⁺ isomers (c = cis).

By comparison with similar complexes of known configurations, band 1 was assigned as Δ-[Ru(bpy)(ppz)₂]²⁺ and band 4 as Δ'-[Ru(bpy)(ppz)₂]²⁺. UV/Vis in CH₃CN, ν/cm⁻¹ {λmax/M⁻¹ cm⁻¹ (band 1 = band 4)}: 464 (12 850), 426 (13 110), 279 (53 333), 264 (60 520), 257 (50 344), 243 (54 710). CD spectra in CH₃CN, λ/νm {Δε/M⁻¹ cm⁻¹ (band 1, band 4)}: 250 (10.0, −8.00), 270 (29.4, −26.8), 294 (−81.5, 80.5), 380 (11.8, −10.20), 420 (17.7, −16.6), 470 (−13.9, 14.5).

Stereoselective synthesis of [Δ-[Ru(bpy)₃]Cl₂][Δ'-Ru(bpy)(μ-ppz)] (PF₆)₆. The complexes Δ-[Ru(bpy)(ppz)₂][PF₆]₆ (7.0 mg, 6.92 μmol) and Δ'[Ru(bpy)(ppz)₂][PF₆]₆ (17.4 mg, 15.2 μmol) were combined in ethylene glycol (1 cm³ containing 10% water) and the mixture was heated at 120 °C for 5 h in the absence of light. During this time the initially orange solution attained a deep purple colouration. The reaction mixture was cooled to room temperature, followed by the addition of water (ca. 5 cm³). The isolation of the desired trinuclear product from the crude mixture was achieved via a gradient elution procedure with SP Sephadex C-25 cation exchanger (20 × 2 cm) using aqueous NaCl solution (0.2–0.8 M) in the absence of light. Two bands were
Results and discussion

Synthesis and structural characterisation

Mononuclear precursors for a stereochemically pure trinuclear assembly. The synthesis of [Ru(bpy)(ppz)]{2+ was based on the previously reported synthetic methodology for tris(heteroleptic) complexes of ruthenium(II), [Ru(pp)(pp)(ppz)]{2+. This involved the reaction of [Ru(bpy)(HAT)]{2+ with excess HAT under microwave conditions according to the previously reported procedure for the synthesis of [Ru(bpy)(2,3-dpp)]{2+ via the dicarbonylation of [Ru(pp)(ppz)]{2+ and [Ru(bpy)(HAT)]{2+ isomers and chiral resolution of the corresponding ∆- and Λ- enantiomeric forms, was achieved in a single step by cation-exchange chromatography (SP Sephadex C-25) using 0.10 M sodium toluene-4-sulfonate solution as eluent. Since the anion is achiral, the concurrent resolution of the ∆- and Λ enantiomeric forms with geometric isomer separation arises from the inherent chirality of the polydextran Sephadex support.

The band 1 and 2 eluates obtained from the resolution of [Ru(bpy)(2,3-dpp)]{2+ were assigned as the ∆(-) and Λ(+)- enantiomers, respectively, while bands 1 and 4 for trans-[Ru(bpy)(ppz)]{2+ were assigned as the ∆(-) and Λ(+)- enantiomers, respectively.

1H NMR studies. The proton labelling schemes employed in the assignment of the 1H NMR spectra of [Ru(bpy)(HAT)]{2+ and trans-[Ru(bpy)(ppz)]{2+ are shown in Fig. 2. The coordinated bpy ligands exhibit the expected coupling constant values and coupling patterns based on the symmetry requirements of the complexes.

The 1H NMR chemical shifts of the mononuclear [Ru(bpy)(BL)]{2+ (BL = HAT, ppz) complexes (Fig. S2 and Table S1 of the ESIF) were determined by 1H COSY spectra and assigned by comparisons with the structurally-related complex [Ru(bpy)]{2+ and consideration of the relative degree of diamagnetic anisotropic interactions between the stereochemically-related ligands.

Fig. 2  Proton numbering scheme for (a) ∆-[Ru(bpy)(HAT)]{2+ and (b) Λ-[Ru(bpy)(ppz)]{2+.
constant values and comparisons with the previously assigned related complex [Ru(bpy)_2(HAT)]^{2+}. The C_2 point group symmetry of trans-[Ru(bpy)(ppz)]^{2+} is expected to give rise to 12 non-equivalent proton resonances, while the C_1 point group symmetry for the corresponding cis geometric isomers would give rise to 24 non-equivalent proton resonances. As shown in Fig. S2,† the 1H NMR spectrum of $\Delta$-[Ru(bpy)(ppz)]^{2+} is similar to that for $\Delta$-[Ru(bpy)(HAT)]^{2+}, with two additional resonances due to the H8 and H9 protons of ppz. The chemical shifts for the bpy resonances are similar to those in [Ru(bpy)(HAT)]^{2+}, with the H5 and H4 resonances experiencing upfield shifts of 0.05 ppm due to the increased shielding influence of ppz relative to HAT. The H3 protons of ppz are oriented over the adjacent bpy ligand, and occur slightly upfield (8.11 ppm) of the resonance at 8.22 ppm for the H6 ppz which is oriented over the plane of the adjacent ppz ligand. The ppz H8 and H9 protons, which are oriented away from the shielding influence of the adjacent bpy and ppz ligands, are assigned as the most downfield resonances (cf. H6 and H7 HAT resonances in [Ru(bpy)(HAT)]^{2+}. The remaining assignments were based on coupling constant values and comparisons with the assignments for [Ru(bpy)(HAT)]^{2+}.†

**Stereoselective synthesis of a trinuclear assembly.** The synthesis of $\Delta\Delta\Delta$-[{Ru(bpy)}_2{[Ru(bpy)(HAT)]}_{2}]{Ru(bpy)(HAT)}^{2+} was performed via a modification of the stereoretentive synthetic method reported by Patterson‡ involving the reaction of 2.2 equivalents of $\Delta$-[Ru(bpy)(py)]^{2+} with $\Delta$-[Ru(bpy)(py)]^{2+}.

†1H NMR studies. The proton labelling for the ligands employed in the assignment of the 1H NMR spectrum is shown in Fig. 3. The 1H NMR chemical shifts of $\Delta\Delta\Delta$-[{Ru(bpy)}_2{[Ru(bpy)(HAT)]}_{2}]{Ru(bpy)(HAT)}^{2+} (Table S2 and Fig. S3(c) of the ESI†) were assigned by comparison with the structurally-related complexes [Ru(bpy)_2(ppz)]^{2+} and meso- and rac-[{Ru(bpy)}_2{[Ru(bpy)(μ-ppz)]}_{2}]^{2+}. The 1H NMR assignments of the latter are shown in Fig. S3(a) and (b).†

**Fig. 3 Proton numbering scheme for $\Delta\Delta\Delta$-[{Ru(bpy)}_2{[Ru(bpy)(μ/ppz)]}_{2}]^{2+}.**

The C_2 point group symmetry of $\Delta\Delta\Delta$-[{Ru(bpy)}_2{[Ru(bpy)(HAT)]}_{2}]{Ru(bpy)(μ/ppz)}^{2+} gives rise to five non-equivalent bpy pyridyl rings in addition to eight non-equivalent ppz proton resonances, resulting in 36 non-equivalent proton environments. As expected, the spectrum bears a striking resemblance to that for rac-(Δ/Δ/Δ)-[{Ru(bpy)}_2{[Ru(bpy)(μ/ppz)]}_{2}]^{2+} (Fig. S3(b)†). The complexes trans-[Ru(bpy)(ppz)]^{2+} and rac-(Δ/Δ/Δ)-[{Ru(bpy)}_2{[Ru(bpy)(μ/ppz)]}_{2}]^{2+} also possess a C_2 symmetry, and the spectrum of the trinuclear complex may be interpreted as the summation of the spectra for the mono- and dinuclear analogues. Ring b is oriented over the plane of the ppz and adjacent bpy ring e (rather than bpy (ring d) for the dinuclear case) so that the H5 proton is assigned as the most upfield resonance at 7.17 ppm (cf. 7.08 ppm in the dinuclear complex). The 1H chemical shifts for pyridyl rings a and c are comparable to those in the dinuclear analogue as they are oriented away from the bridging ligand, while ring d exhibits slight shifts relative to the dinuclear analogue due to the influence of the ppz (rather than bpy) ligand across the bridge. The H5 and H6 resonances of ring e are oriented over the plane of the ppz ligand in a similar environment to the corresponding protons of ring d. Accordingly, the protons of the two rings possess similar 1H chemical shifts; however, the ring e protons experience a slightly greater shielding influence due to the adjacent bpy (rather than ppz) ligand across the bridge, and thus lie slightly upfield of the ring d resonances.

The ppz resonances for H2, H9, H10 and H11 experience the most pronounced shifts relative to the mononuclear analogue, as these protons are now oriented towards the terminal Ru centre, and therefore experience the shielding influence of the terminal bpy rings. For example, the H11 resonance occurs at 9.26 ppm in the mononuclear complex compared with 9.36 ppm in the trinuclear complex, since the proton is now situated over the shielding ring of ring a. In the dinuclear complex, the H2/3, H6/11, H7/10 and H8/9 protons are related by a C_1 axis. In the trinuclear complex, distinct resonances are observed for each proton of the ppz ligand. For instance, the H8 and H9 protons of the two rings possess similar 1H chemical shifts; however, the ring e protons experience a slightly greater shielding influence due to the adjacent bpy (rather than ppz) ligand across the bridge, and thus lie slightly upfield of the ring d resonances.

**Electrochemistry and electronic spectroscopy**

Electrochemical data for trans-[Ru(bpy)(ppz)]^{2+}, meso- and rac-[{Ru(bpy)}_2{[Ru(bpy)(μ/ppz)]}_{2}]. The relative peak currents and areas are clearly discernible from the differential pulse voltammogram (Fig. S4, Supporting Information†) are consistent with this assignment. The approximately simultaneous oxidation of the metal centres to Ru^{II} is followed by one-electron oxidation of the central Ru^{III}. The relative peak currents and areas are clearly discernible from the differential pulse voltammogram (Fig. S4, Supporting Information†) are consistent with this assignment. The approximately simultaneous oxidation of the metal centres to Ru^{II} is followed by one-electron oxidation of the central Ru^{III}. The relative peak currents and areas are clearly discernible from the differential pulse voltammogram (Fig. S4, Supporting Information†) are consistent with this assignment. The approximately simultaneous oxidation of the metal centres to Ru^{II} is followed by one-electron oxidation of the central Ru^{III}. The relative peak currents and areas are clearly discernible from the differential pulse voltammogram (Fig. S4, Supporting Information†) are consistent with this assignment. The approximately simultaneous oxidation of the metal centres to Ru^{II} is followed by one-electron oxidation of the central Ru^{III}. The relative peak currents and areas are clearly discernible from the differential pulse voltammogram (Fig. S4, Supporting Information†) are consistent with this assignment. The approximately simultaneous oxidation of the metal centres to Ru^{II} is followed by one-electron oxidation of the central Ru^{III}.
redox process is more anodic in the trinuclear complex vs. the mononuclear analogue.

All complexes exhibited multiple reversible ligand-based reductions in the cathodic region (Table S3, Supporting Information†). In the dinuclear complexes, the first two reductions are assigned to sequential one-electron reduction of the ppz bridging ligand, due to the greater stabilisation of its π* level relative to the peripheral bpy ligands, followed by sequential one-electron reduction processes associated with the terminal bpy ligands. The assignments for the subsequent reduction processes are ambiguous, however comparison with the related mono- and dinuclear complexes suggests that the third two-electron process consists of overlapping contributions from a second ppz reduction and a bpy-based reduction process for the bpy coordinated to the central [Ru(bpy)(μ-ppz)]. Chromophore. These assignments are consistent with those reported for meso- and rac-[Ru(bpy)(μ-HAT)](μ-ppz)2. In the trinuclear complex, the first two one-electron reduction processes correspond to the reduction of the two equivalent (and slightly interacting) ppz bridging ligands. The assignments for the subsequent reduction processes are ambiguous, however comparison with the related mono- and dinuclear complexes suggests that the third two-electron process consists of overlapping contributions from a second ppz reduction and a bpy-based reduction process for the bpy coordinated to the central [Ru(bpy)(μ-ppz)].

The first two one-electron reduction processes in [Ru(bpy)(μ-ppz)]2+ are assigned to the sequential reduction of the ppz ligands, while the third one-electron process is bpy-based (by comparison with the bpy-based reduction potentials for [Ru(bpy)]2+). The splitting of 246 mV between the ppz reductions indicates electronic communication between the bpy ligands. In the trinuclear complex, the lesser splitting between the two ppz-based reduction processes (168 mV) implies decreased coupling between the ppz ligands relative to the mononuclear species, as there is diminished electronic communication between the ppz ligands. The two ppz-based reduction processes are shifted anodically in the trinuclear complex relative to [Ru(bpy)(μ-ppz)]2+ due to the decrease in the electron density of the ppz ligands through backbonding interactions with the terminal Ru centres.

The complete UV/Vis/NIR spectral data for the mono-, di- and trinuclear systems (for the range 3050–30 000 cm−1) are provided in Table 2, and an overlay of the spectra for the unoxidised forms of the complexes is shown in Fig. S5 of the ESI.† The spectral characteristics for the mixed valence states of the di- and trinuclear complexes are presented in Fig. 4 and S5, respectively.† Low temperature spectroelectrochemical generation of the complexes was required in each case as the electrogenerated species were unstable at room temperature.

The spectra of meso- and rac-[Ru(bpy)(μ-ppz)]2+ exhibit comparable features to the diastereoisomers of [Ru(bpy)]2+(μ-HAT)4+ described previously. The spectra over the region 15 000–30 000 cm−1 are characterised by a combination of overlapping dπ(Ru3+) → π*(ppz) and dπ(Ru4+) → π*(bpy) singlet metal-to-ligand (MLCT) transitions, with the former occurring at lower energy. The spectrum of the diastereomeric mixture has been

<table>
<thead>
<tr>
<th>Complex</th>
<th>ΔE_{n1−n2} (K_v × 10^−3)</th>
<th>ΔE_{n2−n3} (K_v × 10^−3)</th>
<th>E_{n3}</th>
<th>E_{n2}</th>
<th>E_{n1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[Ru(bpy)(ppz)]2+</td>
<td>53450 (0.5590)</td>
<td>17740 (0.3253)</td>
<td>13320 (0.1400)</td>
<td>11670 (0.1566)</td>
<td></td>
</tr>
<tr>
<td>meso-[Ru(bpy)2]2+</td>
<td>5370 (0.8721)</td>
<td>16950 (0.2601)</td>
<td>23420 (0.8987)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rac-[Ru(bpy)2]2+</td>
<td>5590 (0.8494)</td>
<td>16930 (0.2600)</td>
<td>18210 (0.6440)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 UV/Vis/NIR spectral data for the di- and trinuclear complexes in 0.1 M [n-C4H9]4PF6–CH3CN at −35 and −15 °C, respectively. The NIR spectral data are indicated in bold type.
completely assigned previously on the basis of resonance Raman studies.\textsuperscript{28} In the present work, minor differences were observed in the band energies and intensities between the diastereoisomeric forms. The 1MLCT energies in meso- and rac-\{[Ru(bpy)]\}_2{([μ-ppz])}_2+ are red-shifted by ca. 300 cm\(^{-1}\) relative to their related \{[Ru(bpy)]\}_2{([μ-HAT])}_2+ species, which is consistent with the more delocalised nature of ppz (and the stabilisation of the lowest unoccupied π* molecular orbital) compared with HAT. The mixed valence (+5) species is characterised by an IVCT band in the region 3500–5000 cm\(^{-1}\), as shown in Fig. S5.\textsuperscript{†} The intense absorption bands in the region 10 000–16 000 cm\(^{-1}\) for meso- and rac-\{[Ru(bpy)]\}_2{([μ-HAT])}_4+ exhibit a broad absorption band between 15 000–20 000 cm\(^{-1}\), as shown in Fig. 4. The band receives contributions from three underlying transitions of approximately equal intensities at 17 560, 16 150 and 19 930 cm\(^{-1}\) (obtained by Gaussian deconvolution) which are assigned as dσ(Ru\(^{III}\)) → π*(ppz) 1MLCT transitions. The 1MLCT energy is red-shifted relative to the analogous mono- and dinuclear complexes due to the increased stabilisation of the π*(ppz) orbitals in the trinuclear complex. The higher energy transitions in the region 20 000–30 000 cm\(^{-1}\) involve overlapping dσ(Ru\(^{III}\)) → π*(ppz) and dσ(Ru\(^{IV}\)) → π*(bpy) 1MLCT transitions.

Spectroelectrochemical oxidation of the trinuclear complex allowed the generation of the mixed valence +7 and +8 forms, and fully-oxidised +9 forms at −15 °C (Fig. 4). Stable isosbestic points were observed in the spectral progressions accompanying each stage of oxidation. On one-electron oxidation, the lowest energy component of the 1MLCT manifold at 17 560 cm\(^{-1}\) (which is assigned as a dσ(Ru\(^{III}\)) → π*(ppz) transition) decreases in intensity while the two higher energy components are undiminished. The band at 23 710 cm\(^{-1}\) decreases in intensity and experiences a slight blue-shift on one-electron oxidation, consistent with its dσ(Ru\(^{IV}\)) → π*(bpy) assignment. Further oxidation of the second terminal Ru\(^{III}\) centre to Ru\(^{IV}\) generates the +8 mixed valence state and results in a decrease in the intensity of the lowest energy band at 17 560 cm\(^{-1}\) in the 1MLCT manifold. A relatively narrow absorption band appears at 21 860 cm\(^{-1}\) which is due predominantly to a dσ(Ru\(^{IV}\)) → π*(ppz) 1MLCT transition associated with the central (unoxidised) Ru\(^{III}\) centre. This band collapses on further oxidation to the +9 state. Oxidation of the formally Ru\(^{IV}\) centres to Ru\(^{V}\) was accompanied by an increase in the intensity of the LMCT transitions in the region 10 000–16 000 cm\(^{-1}\).

**Intervalance charge transfer**

The NIR spectra of the di- and trinuclear systems are shown in Fig. 4 and S6,\textsuperscript{†} respectively. The results for the IVCT band parameters derived from the deconvolution procedure are summarised in Table 3.

**Dinuclear systems.** The first oxidation process for the diastereoisomers of the dinuclear complex \{[Ru(bpy)]\}_2{([μ-ppz])}_2+ was characterised by the appearance of an intense new band in the region 3500–8000 cm\(^{-1}\) (\(ν_{max} = 5370\) (meso) and 5390 cm\(^{-1}\) (rac)), which collapsed completely on removal of the second electron: on this basis, the band was assigned as an IVCT transition (Table 3, Fig. 4). The bands appear asymmetrical and narrower on the lower energy side with bandwidths at half-height of 1560 cm\(^{-1}\) for both diastereoisomers. The IVCT transitions are qualitatively similar to those observed for \{[Ru(bpy)]\}_2{([μ-HAT])}_4+ \textsuperscript{41} Quantitative analysis of the bands according to the classical two-state theory\textsuperscript{29} suggests that the \{[Ru(bpy)]\}_2{([μ-ppz])}_2+ diastereoisomers may be similarly described as borderline localised–delocalised systems, since the experimental bandwidths are significantly narrower than
the predicted bandwidths ($\Delta v_{1/2}$) of 3140 and 3150 cm\(^{-1}\) for the meso and rac forms, respectively ($\Delta v_{1/2} = [16 R T \ln(2)]^{1/2}$ for a weakly-coupled two-state system). From eqn (1), the lower limits for $H_{\text{ab}}$ are 610 cm\(^{-1}\) for both diastereoisomers, where $r_{\text{ab}}$ is approximated as the geometrical-metal–metal separation of 6.65 Å.

$$H_{\text{ab}} = \frac{2.06 \times 10^{-2} (v_{\max}-v_{\text{min}})^{1/2}}{r_{\text{ab}}}$$ (1)

Since electronic coupling decreases the effective electron transfer distance, $H_{\text{ab}}$ is likely to lie closer to the value in the fully-delocalised limit (i.e. $H_{\text{ab}} = \frac{1}{2} v_{\max}$) of 2625 and 2620 cm\(^{-1}\) for the meso and rac diastereoisomers, respectively. On the basis of the electronic coupling values, the diastereoisomers exhibit a slightly greater degree of delocalisation compared with the corresponding diastereoisomer of $[\text{Ru}(\text{bpy})_2]_2(\mu-\text{HAT})$.$^{41}$ Spectral deconvolution of the NIR bands reveals three underlying Gaussian-shaped components (Fig. 4(b) and Table 3) which may be assigned as the three underlying spin–orbit coupling components observed previously for the IVCT bands in $[\text{Ru}(\text{bpy})_2]_2(\mu-\text{HAT})$.$^{41}$ Alternatively, according to a delocalised description in which the bridging ligand is included as a third electronic state, the IVCT transition arises from electron transfer between the bonding and non-bonding molecular orbitals within the molecular orbital manifold of the system.$^{76,82}$

### Trinuclear system

The two mixed valence states of the trinuclear diastereoisomers were generated upon one- and two-electron oxidation of the +6 species at $-15$ °C. The NIR spectra of the +7 and +8 mixed valence forms (Fig. 4) exhibit striking differences from one another (which lie well outside the limits of experimental error), and from their diinuclear analogues.

The generation of the +7 mixed valence species was accompanied by the appearance of a broad absorption band in the range 3500–12 000 cm\(^{-1}\) (Fig. 4, Tables 2 and 3). Spectral deconvolution revealed the presence of three underlying transitions at 5310, 8255, and 2500 cm\(^{-1}\), separated by 2945 and 2500 cm\(^{-1}\), respectively. The lowest energy component dominates the manifold and is assigned as an adjacent IVCT transition between the central Ru$^+$ and terminal Ru$^{III}$ centres. This transition occurs in the same region as the IVCT band for $[\text{Ru}(\text{bpy})_2]_2(\mu-\text{ppz})]^+$.$^{76}$ The second component is assigned as a remote IVCT transition between the two terminal Ru centres, since the 2945 cm\(^{-1}\) separation between IVCT(1) and (2) is inconsistent with their assignment as spin–orbit components (as was the case for $[\text{Ru}(\text{bpy})_2]_2(\mu-\text{HAT})$)$^{41}$. The 2500 cm\(^{-1}\) separation between the second and third components suggests that the latter is an LMCT rather than an IVCT band; it occurs at approximately the same position as the LMCT bands at 10 940 cm\(^{-1}\) in the +9 state, and at 11 670 and 13 320 cm\(^{-1}\) in $\text{meso-}[\text{Ru}(\text{bpy})_2]_2(\mu-\text{ppz})]^+$. A classical analysis of the IVCT bands yields the following parameters: IVCT(1) $- \Delta v_{1/2} = 3250$ cm\(^{-1}\) and $H_{\text{ab}} = 480$ cm\(^{-1}\) assuming $r_{\text{ab}} = 6.65$ Å; IVCT(2) $- \Delta v_{1/2} = 4050$ cm\(^{-1}\) and $H_{\text{ab}} = 60$ cm\(^{-1}\) assuming $r_{\text{ab}} = 13.3$ Å (i.e. twice the through-bond

### Table 3

Spectral data for the di- and trinuclear complexes at $-35$ and $-15$ °C, respectively. For the dinuclear species, the parameters for the overall NIR band envelopes are shown in bold type. Details of the deconvoluted bands are in normal type.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Component</th>
<th>$v_{\text{max}}$ ± 10 cm(^{-1})</th>
<th>($\varepsilon/v_{\text{max}}$)* ± 0.001 M(^{-1})</th>
<th>$\Delta v_{1/2}$ ± 10 cm(^{-1})</th>
<th>$\Delta v_{1/2}^2$ * cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{meso-}[\text{Ru}(\text{bpy})_2]_2(\mu-\text{ppz})]^+$</td>
<td>5370</td>
<td>0.8721</td>
<td>1560</td>
<td>3140</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3960*</td>
<td>0.1037</td>
<td>920</td>
<td>2695</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5220</td>
<td>0.3981</td>
<td>775</td>
<td>3095</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5715</td>
<td>0.4893</td>
<td>1410</td>
<td>3240</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6825</td>
<td>0.1885</td>
<td>3055</td>
<td>3540</td>
<td></td>
</tr>
<tr>
<td>$\text{rac-}[\text{Ru}(\text{bpy})_2]_2(\mu-\text{ppz})]^+$</td>
<td>5390</td>
<td>0.8494</td>
<td>1560</td>
<td>3150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3940*</td>
<td>0.1487</td>
<td>1110</td>
<td>2690</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5250</td>
<td>0.3683</td>
<td>960</td>
<td>3100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5730</td>
<td>0.5539</td>
<td>1490</td>
<td>3240</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7330</td>
<td>0.1677</td>
<td>2560</td>
<td>3670</td>
<td></td>
</tr>
<tr>
<td>$\Delta \Lambda \Delta-[\text{Ru}(\text{bpy})_2]_2(\text{Ru}(\text{bpy})(\mu-\text{ppz})_2)]^+$</td>
<td>17560</td>
<td>1.293</td>
<td>1510</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16150</td>
<td>1.617</td>
<td>2070</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19930</td>
<td>1.497</td>
<td>1460</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21230</td>
<td>0.5235</td>
<td>1470</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>23370</td>
<td>0.6790</td>
<td>2090</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta \Lambda \Delta-[\text{Ru}(\text{bpy})_2]_2(\text{Ru}(\text{bpy})(\mu-\text{ppz})_2)]^+d$</td>
<td>5310*</td>
<td>0.2099</td>
<td>3980</td>
<td>3250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8255*</td>
<td>0.0892</td>
<td>2530</td>
<td>4050</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10755</td>
<td>0.0599</td>
<td>2730</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12970</td>
<td>0.0435</td>
<td>2215</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15755</td>
<td>0.6550</td>
<td>2415</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta \Lambda \Delta-[\text{Ru}(\text{bpy})_2]_2(\text{Ru}(\text{bpy})(\mu-\text{ppz})_2)]^+d$</td>
<td>3410</td>
<td>0.0649</td>
<td>2680</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5590</td>
<td>0.0747</td>
<td>1880</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8230*</td>
<td>0.3694</td>
<td>2765</td>
<td>4050</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12080</td>
<td>0.0798</td>
<td>3390</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16660</td>
<td>0.3318</td>
<td>3650</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta \Lambda \Delta-[\text{Ru}(\text{bpy})_2]_2(\text{Ru}(\text{bpy})(\mu-\text{ppz})_2)]^+$</td>
<td>5090</td>
<td>0.0775</td>
<td>3865</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8195</td>
<td>0.1218</td>
<td>2710</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10940</td>
<td>0.6995</td>
<td>2010</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12935</td>
<td>0.2147</td>
<td>2410</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15690</td>
<td>0.2314</td>
<td>3075</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The corresponding molar absorption coefficients ($\varepsilon_{\text{m}}$/M cm\(^{-1}\)) are given by the product of ($\varepsilon/v_{\text{max}}$) and $v_{\text{max}}$. \* Artifact peak at detector limit. $\Delta v_{1/2} = [16 R T \ln(2)]^{1/2}$ for a weakly-coupled two-state system where $16 R T \ln(2) = 1836$ cm\(^{-1}\) at $-35$ °C (dinuclear systems) and 1990 cm\(^{-1}\) at $-15$ °C (trinuclear systems). Transitions of IVCT origin are indicated by asterisks.
distance for the adjacent transition). The experimental bandwidths ($\Delta \nu_{1/2}$) are comparable to those predicted from theory, and the magnitudes of $\tilde{H}_{ab}$ indicate that both transitions are localised. For IVCT(1), $\Delta \nu_{1/2} > \Delta \nu_{1/2}^{0}$, which suggests the presence of underlying spin–orbit components beneath the Gaussian-shaped IVCT manifold. As shown in Fig. 5(b), the results are in marked contrast to the borderline localised–delocalised IVCT in the dinuclear analogues, and the $\{[\text{Ru(bpy)}_2]_2 (\mu\text{-HAT})\}^{n\pm}$ mixed valence species (Fig. 5(a)). From the electrochemical studies, the presence of the third Ru chromophore in the ppz-bridged trinuclear complex reduces the electron density at the central Ru, giving rise to decreased coupling of the bridging ligands through the central metal in the trinuclear compared with the mononuclear complex. This decreased coupling is also manifested in the IVCT properties by a significantly reduced coupling between the adjacent metal centres in the trinuclear relative to the dinuclear species.

Fig. 5 Comparison of the IVCT transitions for the di- and trinuclear mixed valence systems: (a) heterochiral-$\{[\text{Ru(bpy)}_2]_2 (\mu\text{-HAT})\}^{n\pm}$ ($n = 7, 8$) and meso-$\{[\text{Ru(bpy)}_2]_2 (\mu\text{-HAT})\}^{n\pm}$; (b) $\Delta \lambda \Delta \lambda \{[\text{Ru(bpy)}_2]_2 (\mu\text{-ppz})\}^{n\pm}$ ($n = 7, 8$) and meso-$\{[\text{Ru(bpy)}_2]_2 (\mu\text{-ppz})\}^{n\pm}$.

The intensity of the IVCT bands decreased on subsequent oxidation of the second terminal Ru centre in the +8 mixed valence species, with the appearance of a new band at 8230 cm$^{-1}$ (Fig. 4 and 5(b), Tables 2 and 3) which is assigned to two degenerate adjacent IVCT transitions from the central Ru$^n$ to terminal Ru$^{n\pm}$ centres. A classical analysis yields $H_{ab} = 860$ cm$^{-1}$ (eqn (1)) assuming $r_{ab}$ is 6.65 Å. The transitions are localised and occur at higher energy than the corresponding adjacent IVCT in the +7 mixed valence form due to the decreased electron delocalisation in the system, and hence destabilisation of the acceptor Ru$^{n\pm}$ orbitals. This is consistent with previous observations for the +7 and +8 states for the trinuclear $\mu$-HAT complex, and with previous literature reports for IVCT transitions in related di- and trinuclear systems.

The assignment of the bands in the region at energies lower than 7000 cm$^{-1}$ is ambiguous due to the presence of comproportionation equilibria, however these may be reasonably ascribed to the residual absorptions of the mono-oxidised $+7$ species.

The transition at 12 080 cm$^{-1}$ may correspond to an IVCT transition to the singlet or triplet “exciton” state of the 8230 cm$^{-1}$ transition, as discussed previously for $\{[\text{Ru(bpy)}_2]_2 (\mu\text{-HAT})\}^{n\pm}$. However, an assignment as an LMCT absorption is more probable as LMCT bands of similar energy are present in the +9 species, and in the dinuclear analogues. Since the two holes are situated on remote localised Ru$^{n\pm}$ centres, the coupling of the spins (parallel or antiparallel) should be significantly weaker given the ~13.3 Å separation of the metals, compared with the “cluster” arrangement in $\{[\text{Ru(bpy)}_2]_2 (\mu\text{-HAT})\}^{n\pm}$. Nevertheless the possibility of an IVCT transition to the second “exciton” state cannot be discounted, and the relatively weak transition may be obscured by the low-lying LMCT and MLCT transitions.

Conclusions

The IVCT properties of the mixed valence forms of the trinuclear complex $\Delta \lambda \Delta \lambda \{[\text{Ru(bpy)}_2]_2 (\mu\text{-ppz})\}^{n\pm}$ ($n = 7, 8$) and the diastereoisomers (meso and rac) of the dinuclear complex $\{[\text{Ru(bpy)}_2]_2 (\mu\text{-ppz})\}^{n\pm}$ display a marked dependence on the nucularity and extent of oxidation of the mixed valence assemblies. The IVCT properties of the diastereoisomeric forms of $\{[\text{Ru(bpy)}_2]_2 (\mu\text{-ppz})\}^{n\pm}$ are similar, and are comparable to those in $\{[\text{Ru(bpy)}_2]_2 (\mu\text{-HAT})\}^{n\pm}$. Both dinuclear complexes are classified as borderline localised–delocalised mixed valence species.

By comparison, the two mixed valence states of the trinuclear complex $\Delta \lambda \Delta \lambda \{[\text{Ru(bpy)}_2]_2 (\mu\text{-ppz})\}^{n\pm}$ exhibit localised behaviour. One-electron oxidation of a terminal Ru centre gives rise to a broad, low intensity IVCT band for the +7 mixed valence species which is composed of two underlying Gaussian-shaped bands. The transitions are identified as adjacent and remote IVCT transitions, with the former dominating the intensity of the IVCT manifold. The +8 mixed valence species exhibits a single dominant IVCT band arising from the equivalent IVCT transitions from the central Ru$^n$ to peripheral Ru$^{n\pm}$ centres, shown in Fig. 6.
Despite the similarity in the IVCT properties of the dinuclear complexes \([\{Ru(bpy)\}_2\{\mu-ppz\}]^{2+}\) and \([\{Ru(bpy)\}_2\{\mu-HAT\}]^{2+}\), the ICT characteristics of the mixed valence forms of \(\Delta\Delta\Lambda\cdot\{[Ru(bpy)]_2\{[Ru(bpy)\{\mu-ppz\}_2}\}\}^{2+}\) are markedly different from those of the corresponding mixed valence forms of \(\{[Ru(bpy)]_2\{\mu-HAT\}]^{2+}\) reported previously.\(^{41}\) As shown in Fig. 1(a), the three Ru centres in the latter are equivalently disposed, and share the available electron density. By comparison, a “chain-like” arrangement of the three metal centres in \(\Delta\Delta\Lambda\cdot\{[Ru(bpy)]_2\{[Ru(bpy)\{\mu-ppz\}_2}\}\}^{2+}\) suggests a decreased coupling through the central metal. As a result, the \([\{Ru(bpy)\}_2\{\mu-HAT\}]^{2+}\) complex exhibits a comparable degree of electronic coupling to its dinuclear analogue, while the degree of electronic coupling in \(\Delta\Delta\Lambda\cdot\{[Ru(bpy)]_2\{[Ru(bpy)\{\mu-ppz\}_2}\]\}^{2+} is reduced relative to its dinuclear counterpart.

Qualitatively, a localised description based on the geometrical properties of the \(d\pi(Ru^{2+})\) orbitals provides a reasonable rationale for the IVCT behaviour in the localised trinuclear system. However, treatment of the full vibronic coupling problem is necessary in order to provide a quantitative analysis of these borderline localised-to-delocalised dinuclear complexes.

The existence of high quality experimental data that will test and guide developments in the conceptual theories for IVCT in higher nuclearity systems, and the extension of the IVCT probe to stereochemically unambiguous trimetallic species, are extremely significant to our understanding of fundamental intramolecular electron transfer phenomena. This represents a key step in the rational design of higher nuclearity polymeric assemblies in which the electron transfer processes may be controlled and ultimately exploited for novel practical applications.

Acknowledgements

We are grateful to Dr Rob Gauci for his assistance with the synthesis of ppz. This work was supported by the Australian Research Council.

References

67 B. T. Patterson, PhD thesis, James Cook University, Townsville, Queensland, Australia, 2002.
68 B. T. Patterson, *Honours dissertation*, James Cook University, Townsville, Queensland, Australia, 1997.