Driving the Localized-to-Delocalized Transition in Unsymmetrical Dinuclear Ruthenium Mixed-Valence Complexes

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The degree of delocalization in the symmetrical complexes [{Ru(bpy)2}2(μ-dpb′)]5+ and [{Ru(bpy)2}2(μ-dpb)]5+ (dpb = 2,3-bis(2-pyridyl)-1,4-benzoquinoxaline; dpb′ = dipyrido(2,3-a;3′,2′-c)benzophenazine; bpy = 2,2′-bipyridine) is diminished by the substitution of the terminal bpy ligands at one end of the complex. The results of a classical analysis for the diastereoisomeric forms of the series of complexes [{Ru(bpy)2}2(μ-BL){Ru(pp)2}]5+ (pp = bpy, Me2bpy (4,4′-dimethyl-2,2′-bipyridine), Me4bpy (4,4′,5,5′-tetramethyl-2,2′-bipyridine)) indicate that a greater degree of ground-state delocalization exists in the complexes incorporating the bridging ligand dpb′ compared with the dpb analogue. A two-state analysis in which ΔE0 (the redox asymmetry) is varied at constant Hab (the electronic coupling) and λ (the reorganizational energy) does not adequately describe the properties of the systems due to the importance of a third electronic state corresponding to the bridging ligand.

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Introduction

Electron transfer is fundamental in natural processes such as photosynthesis and in materials science applications such as light-activated devices and non-linear optical materials. Symmetrical dinuclear mixed-valence complexes—which contain atoms of the same element in different formal oxidation states—have received significant attention in this regard. In particular, the characteristics of their light-induced intervalence charge transfer (IVCT) transitions provide a sensitive probe of the factors which affect electronic delocalization in natural and artificial systems. There is also significant interest in the investigation of unsymmetrical mixed-valence systems, as the introduction of a ‘redox asymmetry’ component diminishes the extent of electronic coupling between the metal centres, and induces a degree of valence localization. The present investigation provides a systematic survey of redox asymmetry effects on the IVCT transitions in the stereoisomers of polypyrindiruthenium complexes in order to elucidate how such effects are manifested in the IVCT band-shape.

IVCT transitions are generally observed in the near-infrared (NIR) region of the electronic spectrum, and the characteristics of these transitions—specifically, their energy (νmax), intensity (εmax), and bandwidth (Δν1/2)—may be quantitatively related to the factors which influence electronic delocalization and the activation barriers to electron transfer through the seminal two-state classical formalism pioneered by Hush.1,2 Of particular significance is the relationship between νmax and the Franck–Condon reorganizational energy (λ), the redox asymmetry (ΔE0), and additional energy contributions due to spin–orbit coupling and ligand field asymmetry (ΔE').

\[ ν_{\text{max}} = hν = λ + ΔE_0 + ΔE' \]  \hspace{1cm} (1)

\[ H_{\text{ab}} = \frac{|μ_{12}|}{ε_{\text{ab}}} ν_{\text{max}} \]  \hspace{1cm} (2)

The degree of electronic coupling is quantified by Hab in Eqn (2), where r_{ab} is the distance between the two zero-order (‘adiabatic’) states, ε is the unit electronic charge, and |μ_{12}| is the first-order (‘adiabatic’) transition dipole moment. The latter may be calculated from the integrated intensity of the absorption band.3

According to the Robin and Day classification scheme,4 three classes of mixed-valence systems are distinguished on the basis of the relative magnitudes of λ and 2H_{ab}. Class I systems are characterized by non-interacting centres, ‘localized’ Class II systems by weakly coupled centres (2H_{ab} ≪ λ), and ‘delocalized’ Class III systems by strongly coupled centres (2H_{ab} ≫ λ). Meyer and co-workers5 have recently defined an intermediate regime, ‘Class II–III’, in which the systems literally exhibit both localized and delocalized behaviour. This scenario arises when the time-scale for reorganization of the solvent modes is faster than that for the inner-sphere vibrations, giving rise to solvent averaging and electronic localization. In reality, the transitions between the four regimes are not abrupt, and experimental studies have revealed a gradation in behaviour between the fully localized (Class II) and fully delocalized (Class III) limits, which
is governed by the relative time-scales for intramolecular electron transfer and multiple nuclear and solvent vibrations which are coupled to the electron transfer.[5] The description is further challenged experimentally by the appearance of multiple IVCT and IC (interconfigurational) transitions in transition metal containing chromophores, in addition to contributions from environmental effects such as specific solvation and ion-pairing.[6] While $\Delta E_0$ contributions are typically assessed experimentally within the classical framework (Eqn 1)—which is strictly valid for weakly coupled two-state systems—the development of a conceptual framework that provides a coherent and physically transparent basis for the treatment of mixed-valence systems between the fully localized and delocalized limits is at the forefront of current experimental, theoretical, and computational work in the area. One of the most comprehensive sets of experimental data for the transition between the localized and delocalized regimes has been observed by variation of the peripheral ligands in the series of the Creutz–Taube ion derivatives, trans-$\{[\text{Ru(NH}_3)_5]\}{(\mu-pyz)}\{\text{Ru(NH}_3)_6\}_{\text{L}}\}_{\text{5+}}$ ($L = \text{NH}_3$ (the Creutz–Taube ion itself), py (pyridine), 3,5-Me$_2$py (3,5-dimethylpyridine), 3-Cl–py (3-chloropyridine), 2,6-Me$_2$pyz (2,6-dimethylpyrazine).[13] As shown by Curtis and co-workers,[7] the introduction of a $\Delta E_0$ contribution by the incorporation of increasingly stronger back-bonding ligands results in a broader and blue-shifted IVCT band.

Curtis and co-workers[9–11,23] have proposed a semi-quantitative interpretation for $\Delta E_0$ effects, based on a classical two-state perturbation treatment and electrochemical potential measurements. Central to this two-state classical analysis is the assumption that a $\Delta E_0$ contribution is manifested spectroscopically as an equivalent variation in $\nu_{\text{max}}$ at constant $H_{\text{ab}}$ and $\lambda$.[12] According to Eqn (3), a quantity $m'$ is defined as the ratio of the shift in the electrochemical potential to the indirectly perturbed redox site ‘B’ ($\delta E_{\text{ox}}(\text{RuB})$) to the shift at the directly perturbed redox site ‘A’ ($\delta E_{\text{ox}}(\text{RuA})$), and a quantity $\rho$ is defined as the ratio of the coefficients for the diabatic wave functions ($\Psi_A$ and $\Psi_B$), respectively. The electrochemical shifts are assessed relative to the respective redox potentials in the unperturbed complex.

$$\rho = (m')^{1/2} = \frac{b}{a} = \left(\frac{\delta E_{\text{ox}}(\text{RuB})}{\delta E_{\text{ox}}(\text{RuA})}\right)^{1/2}$$

The parameters $a^2$ and $b^2$ represent the fractional valences on the directly and indirectly perturbed metal centres, respectively. Assuming that the overlap between the diabatic wave functions is negligible, $a^2$ and $b^2$ are obtained from the normalization condition $a^2 + b^2 = 1$. Parameter $\rho$ is determined from the slope ($m$) of a plot of the change in the formal potentials of the acceptor versus the donor, which are given by $E_{\text{ox}}(\text{RuB})$ and $E_{\text{ox}}(\text{RuA})$, respectively. From the slope, $b^2 = m/(1 + m)$.[12–14] The parameter $\rho$ provides an alternate measure of the extent of electronic coupling between the metal centres, where $0 \leq \rho \leq 1$, and 0 and 1 are the limits of complete localization and delocalization, respectively. The validity of Eqn (3) is expected to become increasingly invalid as the degree of electronic coupling increases.[7–11] Application of the electrochemical analysis to the series of mixed-valence complexes trans-$\{[\text{Ru(NH}_3)_5]\}{(\mu-pyz)}\{\text{Ru(NH}_3)_6\}_{\text{L}}\}_{\text{5+}}$ yielded a value of $\rho = 0.74$ for the Creutz–Taube ion ($L = \text{NH}_3$), consistent with a delocalized classification and the conclusions of an extensive number of experimental, theoretical, and computational studies.[5,12,15–19]

Recent studies in our laboratory have demonstrated that the diastereoisomers of symmetrical dinuclear mixed-valence complexes such as meso- and rac-$\{[\text{Ru(bpy)}_2]_{2+}\}_{\text{(Bl)}}\text{5+}$ (bpy = 2,2′-bipyridine, BL = dpb (2,3-bis(2-pyridyl)-1,4-benzoquinoloxaline), dpb′ (dipyridido(2,3-a,3,2-c′)-benzophenazine); Fig. 1) provide subtle and systematic probes to examine the microscopic origins of the factors which govern the electron transfer barrier. These include solvent reorganization contributions,[20] ion-pairing and temperature effects,[21] and stereochemically induced structural distortions,[22] which are manifested by different electrochemical and IVCT properties for the diastereoisomeric forms of the same complex.

The introduction of redox asymmetry into the dinuclear complexes $\{[\text{Ru(bpy)}_2]_{2+}\}_{\text{(dpb)}}\text{5+}$ and $\{[\text{Ru(bpy)}_2]_{2+}\}_{\text{(dpb′)}}\text{5+}$ by the substitution of the terminal bpy ligands at one end by Me$_2$bpy (4,4′-dimethyl-2,2′-bipyridine) and Me$_4$bpy (4,4′,5,5′-tetramethyl-2,2′-bipyridine) diminishes the degree of delocalization, and provides a strategy for examining the transition between the delocalized and localized regimes within a closely related series of complexes. In the present study, the electrochemical and spectral analysis of Curtis and co-workers[9–11,23] is applied to investigate the onset of localization in the diastereoisomeric forms of the series of ‘unsymmetrical’ complexes $\{[\text{Ru(bpy)}_2]_{2+}\}_{\text{(Bl)}}\text{5+}$ (BL = dpb, dpb′; pp = Me$_2$bpy, Me$_4$bpy). The work also addresses the limited experimental data which exist to prove the influence of the inherent stereochemical complexities on the physical properties of polynuclear assemblies.[24,25]

There is currently significant interest in elucidating the microscopic origins of redox asymmetry effects for the extension of vibronic coupling models,[16,18] and the potential application of such effects in molecular switching devices.[26] Recently, the elucidation of $\Delta E_0$ contributions to the IVCT properties of mutants of the photosynthetic reaction centre in purple bacteria has enabled a detailed understanding of the relationship between structurally induced perturbations and the mechanism of the photosynthetic function.[18,27]
Experimental

Electrochemistry

Electrochemical measurements were performed under argon using a Bioanalytical Systems (BAS) 100A Electrochemical Analyzer. 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 \( \text{AgCl} \)) solutions. Ag/AgCl. Solutions contained 0.1 M \( \text{KCl} \) as electrolyte. Cyclic voltammetry was performed with a sweep rate of 100 mVs\(^{-1}\); differential pulse voltammetry was conducted with a sweep rate of 4 mVs\(^{-1}\) and a pulse amplitude, width, and period of 50 mV, 60 ms, and 1 s, respectively. All potentials are reported vs \( \text{AgCl} \).

Spectroelectrochemistry

UV/visible/near-infrared (UV/Vis/NIR) spectroelectrochemistry was performed using a Cary 5E spectrophotometer 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.[28] An account of the procedure employed in the spectroelectrochemical measurements has been detailed previously.[29] Solutions for the spectroelectrochemical experiments contained 0.1 M \([n\text{-C}_{4}\text{H}_{9}]\text{PF}_6\) supporting electrolyte in \( \text{CH}_3\text{CN} \) and the complex (about \( 10^{-3} \) M). All solutions were purged with \( \text{N}_2 \) before transferance (via syringe) into the OSTLE cell. The temperature was stabilized to \( \pm 0.3^{\circ}\text{C} \) before commencing electrolysis. The IVCT spectra were scaled as \( f(v/v)dv = \frac{1}{f(v/v)dv} \) and deconvolution of the NIR transitions was performed using the curve-fitting subroutine implemented within the GRAMS32 commercial software package, as described previously.[29] The Gaussian fits were not unique and the underlying components were obtained by fitting a Gaussian peak at the maximum of the absorption band. A minimum number of additional Gaussian-shaped bands were included to obtain convergence in the iterative fitting procedure. Based on the reproducibility of the parameters obtained from the deconvolutions, the uncertainties in the energies \((\nu_{\text{max}})\), intensities \((\nu_{\text{max}})\), and bandwidths \((\Delta \nu_{1/2})\) were estimated as \( \pm 10\text{ cm}^{-1}, \pm 0.001\text{ M}^{-1} \), and \( \pm 20\text{ cm}^{-1} \), respectively. For IVCT bands that exhibit an asymmetric appearance, application of the equations derived from the classical analysis of Hush[23] is not valid as the equations assume a Gaussian-shape: Accordingly, an examination of the first-order moments (\( M_t \)) for the absorption band is required for the IVCT analysis, rather than the experimentally observed quantities \((\nu_{\text{max}}, \Delta \nu_{1/2}, \text{and } (\nu_{\text{max}}))\). \( M_t \) is defined as the average energy of the absorption peak: In the present study, an examination of the moments to first-order (i.e. \( M_0 \)) only was undertaken but it is noted that consideration of the higher-order moments would be necessary in an exact treatment. \( f(v) \) is the line-shape function of the reduced absorption spectrum \((\nu/v) \) versus \( v \) and the limits of the regions are \( v_{1/2} \) and \( v_{2/3} \). The denominator in Eqs (4) is the area under the band of the reduced absorption spectrum, i.e. the zeroth-moment, \( M_0 \).

\[
M_t = \frac{\int_{v_1}^{v_2} f(v) v dv}{\int_{v_1}^{v_2} f(v) dv}
\]

The transition moment, \( \mu_{12} \) (\( \text{e A} \)), is subsequently defined as

\[
\mu_{12} = 0.02066 \times M_0^{1/2}
\]

For a Gaussian-shaped band, \( M_0 \) is approximated as \((\varepsilon/\nu)_{\text{max}} \Delta \nu_{1/2}/\nu_{\text{max}}\). The consideration of transition moments rather than the ‘raw’ band parameters permits comparisons across a series of complexes and allows for the deviations in the shape of the absorption manifolds from purely Gaussian distributions and permits more meaningful comparisons of experimental data across the series of complexes.

While the IVCT manifolds were adequately fitted using a single Lorentzian band, the results of the deconvolution procedure are reported for fits using purely Gaussian-shaped bands.

Materials

Hydrated ruthenium trichloride (\( \text{RuCl}_3 \cdot 3\text{H}_2\text{O} \), Sterm, 99%), 2,2’-bipyridine (bpy; Aldrich, 99+%), 4,4’-dimethyl-2,2’-bipyridine (Me2bpy; Aldrich), stannous chloride (\( \text{SnCl}_2 \cdot 2\text{H}_2\text{O} \), Ajax), lithium chloride (\( \text{LiCl} \); Aldrich, 99+%), ammonium chloride (\( \text{NH}_4\text{Cl} \); BDH, 98%), ammonium hexafluorophosphate (\( \text{NH}_4\text{PF}_6 \); Aldrich, 99.99%), potassium hexafluorophosphate (\( \text{KF} \); Aldrich, 98%), zinc chloride (\( \text{ZnCl}_2 \cdot 2\text{H}_2\text{O} \); Fluka, 98%), nitrosonium hexafluorophosphate (\( \text{NOPF}_6 \); stored under Ar; Alfa Aesar, 96%), hydrate hydrate (Aldrich), ethylene glycol (Ajax, 95%), sodium octanoate (Aldrich, 98%), sodium benzoate (Aldrich, 98%), sodium toluene-4-sulfonate (sodium tosylate; Aldrich, 98%); DOWEX 1 x 8, 50–100 mesh (Aldrich) and Amberlite IRA-400 (Aldrich) \( \text{CT}^+ \) anion exchange resins, Celite (Aldrich), and laboratory reagent solvents were used as received. Tetra-n-butylammonium hexafluorophosphate (\( \text{[(t-C}_4\text{H}_9]\text{N}]\text{PF}_6 \); Fluka, 99+t% was dried in vacuo at 60°C before use and ferrocene (Fc; BDH) was purified by sublimation before use. \( \text{pp} \) Sephadex C-25 and Sephadex LH-20 (Amersham Pharmacia Biotech), and silica gel (200–400 mesh, 60 A, Aldrich) were employed for the chromatographic separation and purification of ruthenium complexes.[30] Acetonitrile (CH3CN; Aldrich, 99.9+%) was distilled over CaH2 before use. 4’,5.5’-Tetramethyl-2,2’-bipyridine (Me2bpy) was supplied by Dr Bradley Patterson.[31]

Syntheses and Diastereoisomer Separation

The synthesis of dpb[32] and dpb[32] has been described previously. The mononuclear ruthenium complexes \( \text{[Ru(dnnsO)]C}_2 \)[31] cis-\( \text{[Ru(bpy)]C}_2 \) \( 2\text{H}_2\text{O} \) (pp = bpy, \( \text{Me}_2\text{bpy} \))[34] and cis-\( \text{[Ru(Me}_2\text{bpy})\text{C}_2 \text{Cl}_2 \) were prepared according to the literature methods.

\([\text{Ru(bpy)}_2\text{(dpb)}\text{(PF}_6)_2\]

Prepared via a modification of the literature procedure.[36] A suspension of dpb (64.2 mg, 0.192 mmol) in ethylene glycol (4 cm3) was heated in a modified microwave oven on medium high power for 30 s to complete dissolution. cis-\( \text{[Ru(bpy)]C}_2 \) \( 2\text{H}_2\text{O} \) (100 mg, 0.192 mmol) was added and the mixture heated at reflux for a further 2 min on medium-high power during which time the solution attained a deep purple colouration. The mixture was diluted with water (ca. 50 cm3) and separation of the desired mononuclear product from the crude mixture was achieved via a gradient elution procedure on \( \text{SP Sephadex C}-25 \) support using aqueous 0.1–0.3 M NaCl solution as the eluent. The major claret-red band eluted with 0.2 M NaCl, and the complex was precipitated by the addition of saturated aqueous KPF6. The purple solid was isolated by vacuum filtration, washed with chilled water (3 cm3) followed by copious diethyl ether, and dried in vacuo. Yield: 178 mg (89%). The \( ^{1} \text{H NMR} \) and UV/Vis spectral characteristics were identical to those reported previously.[36] (Found C 48.6, H 2.91, N 10.8%. \( \text{C}_{72}\text{H}_{90}\text{F}_{12}\text{N}_{8}\text{P}_{2}\text{Ru} \) requires C 48.4, H 2.90, N 10.8%).

\([\text{Ru(bpy)}_2\text{(dpb)}\text{(PF}_6)_2\]

Prepared according to the method described above for \( \text{[Ru(bpy)}_2\text{-}(\text{dpb})\text{(PF}_6)_2 \) using dpb[34] (128 mg, 0.384 mmol) and cis-\( \text{[Ru(bpy)]C}_2 \text{Cl}_2 \) \( 2\text{H}_2\text{O} \) (200 mg, 0.384 mmol). The mononuclear complex was precipitated as green solid. Yield: 358 mg (90%). (Found C 48.7, H 2.72, N 10.8%. \( \text{C}_{72}\text{H}_{90}\text{F}_{12}\text{N}_{8}\text{P}_{2}\text{Ru} \) requires C 48.5, H 2.72, N 10.8%).

\([\text{Ru(bpy)}_2\text{(dpb)}\text{(Me}_2\text{bpy})\text{(PF}_6)_2\]

Prepared according to the literature procedure.[22,32] Synthesized via an adaption of the literature procedure for \( \text{[Ru(bpy)}_2\text{[(t-HAT)](Ru[phen])]}\text{(PF}_6)_2 \) \( [37] \) \( \text{[Ru(bpy)}_2\text{(dpb)](PF}_6)_2 \) (60 mg, 0.0578 mmol) was added to a \( \text{N}_2 \)-purged solution of aqueous methanol (1:1, 40 cm3) and dissolved
by heating the mixture at reflux for 5 min. [Ru(Me4bpy)2Cl2] (33.4 mg, 0.0578 mmol) was added and the solution heated at reflux for 16 h. During this time the initially purple solution attained a green colouration, suggesting the formation of a dinuclear species. The progress of the reaction was monitored by the TLC analysis of small aliquots of the reaction mixture during the synthesis using thin-layer silica gel plates with 0.1 M NH4Cl in 41% H2O/45% dimethylformamide.

The mixture was cooled to room temperature and the methanol removed by rotary evaporation. A green solid was precipitated on addition of a saturated solution of aqueous KPF6 and the mixture chilled by refrigeration overnight. The solid was isolated by filtration and washed with diethyl ether.

Isolation of the desired dinuclear product from the crude mixture (converted to the Cl– form by stirring an aqueous suspension of the complex with Dowex anion exchange resin) was achieved by cation-exchange chromatography on Sephadex C-25 using a gradient elution procedure with 0.1–0.5 M NaCl solution. A crinkled red band of unretracted mononuclear materials eluted first (0.1–0.2 M NaCl) followed by the desired green product (0.4 M NaCl), which was precipitated as the PF6– salt by addition of a saturated solution of aqueous KPF6. The solid was isolated by vacuum filtration and washed with diethyl ether (3 × 10 cm) yield.

Further characterization was performed following diastereoisomer separation.

Separation of the diastereoisomers was achieved by cation-exchange chromatography on Sephadex C-25 (sodium 0.5 mmol) following this time the initially purple solution attained a green colouration, suggesting the formation of a dinuclear species. The progress of the reaction was monitored by the TLC analysis (as described for the analysis of the desired dinuclear species, the reaction of the progress of the reaction was more effectively established from the TLC analysis (as described for the analogous dinuclear-brided complex).

Prepared according to the literature procedure.[22,23] Synthesized according to the procedure described previously for the analogous dbp-brided complex using [Ru(bpy)2(dpdb)](PF6)2 (90 mg, 0.0868 mmol) and [Ru(Me4bpy)2Cl2] (50 mg, 0.0868 mmol). Given the identical colours of the [Ru(bpy)2(dpdb)](PF6)2 precursor and the desired dinuclear product, the progress of the reaction was more effectively established from the TLC analysis (as described for the analogous dinuclear-brided complex).

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The unsymmetrical complexes \([\{\text{Ru}(\text{bpy})_2(\mu-\text{dpb})\}^2]^{4+}\) (BL = dpb, dpb; \(pp = \text{Me}_2\text{bpy}, \text{Me}_4\text{bpy}\)) were synthesized by the reaction of equimolar amounts of the mononuclear precursors \([\text{Ru}(\text{bpy})_2(\text{BL})]^2\) with \(\text{Ru}(\text{bpy})_2(\text{Cl}_2)\cdot 2\text{H}_2\text{O}\) in ethylene glycol/10\% water for 11 h at 120°C. The reactions were also attempted under microwave conditions with limited success—the preliminary column chromatographic purification of the complexes following synthesis revealed several bands which were indicative of ligand scrambling under the microwave conditions.

Separation of the unsymmetrical complexes from the reaction mixtures was achieved using cation-exchange chromatography with a gradient elution of aqueous sodium chloride solution (0.1–0.5 M). The major band eluted from the column was the desired complex. The diastereoisomers \(\Delta \Lambda/\Delta \Lambda\) - and \(\Delta \Delta/\Delta \Delta\) - were separated by cation exchange chromatography using SP Sphadex C-25 as the support with aqueous 0.25 M sodium octanoate (BL = dpb; \(pp = \text{Me}_2\text{bpy}, \text{Me}_4\text{bpy}\)) and aqueous 0.25 M sodium benzoate (BL = dpb; \(pp = \text{Me}_2\text{bpy}, \text{Me}_4\text{bpy}\)) solutions as eluents.

An additional level of stereoisomeric complexity is present in the \([\{\text{Ru}(\text{bpy})_2(\mu-\text{BL})\}^2]^{4+}\) complexes as the \(\Delta \Lambda\) and \(\Delta \Delta\) forms are no longer equivalent as they are when \(pp = \text{bpy}\) (i.e. a \textit{meso} form). While differences may exist between the physical properties of the stereoisomeric forms, the present study involves the investigation of the mixtures of the both diastereoisomers as the enantiomeric mixtures \(\Delta \Lambda/\Delta \Delta\), and \(\Delta \Delta/\Delta \Delta\).

I. NMR Studies

The assignment of the \(^1\text{H}\) NMR spectra was performed with the assistance of 2D COSY spectra, and by comparison with the spectra for their homoleptic analogues and the structurally related complex \([\{\text{Ru}(\text{bpy})_2(\mu-\text{HAT})\}^2]^{2+}\) (HAT = 1,4,5,8,9,12-hexazatriphenylene)\(^{[40,41]}\). The \(^1\text{H}\) numbering schemes for the terminal and bridging polypryridil ligands are shown in Figure S1 (Accessory Materials) and the designations for the polypryridyl rings are shown in Figure S2 and Table S1 for the diastereoisomers of the symmetrical complex \([\{\text{Ru}(\text{bpy})_2(\mu-\text{dpb})\}^2]^{4+}\).

The \(\Delta \Lambda/\Delta \Delta\) and \(\Delta \Delta/\Delta \Delta\) diastereoisomers both possess \(C_1\) point group symmetry and exhibit \(^1\text{H}\) NMR spectra comprising two non-equivalent bpy ligands (i.e. 16 magnetically non-equivalent proton resonances) and two non-equivalent pp ligands, in addition to 14 non-equivalent dpb proton resonances and 12 non-equivalent dpb proton resonances in their respective complexes. The four different ‘pyridil’ environments for each pp ligand give rise to twelve and eight resonances in the aromatic region for the heteroleptic complexes incorporating \(\text{Me}_2\text{bpy}\) and \(\text{Me}_4\text{bpy}\), in addition to four and eight singlet resonances in the aliphatic region, respectively.

The chemical shifts of the bpy ligands in the two diastereoisomers for a given unsymmetrical complex are approximately identical to those of the corresponding bpy ligands in the symmetrical complex with the same relative stereochemistries. Minor differences were observed in the chemical shift resonances for the \(\text{H}5\) and \(\text{H}6\) protons of bpy rings \(b\) and \(d\) oriented over the bridging ligand, as they experience slightly different anisotropic interactions with the adjacent pp ligand. The chemical shifts of the protons in the methyl-substituted ligands experience a 0.2–0.3 ppm upfield shift relative to the corresponding resonance of the stereochemically related bpy ligand.

Electrochemical and UV/Vis/NIR Characterization

The electrochemical characteristics of the diastereoisomers of the unsymmetrical complexes \([\{\text{Ru}(\text{bpy})_2(\mu-\text{BL})-\{\text{Ru}(\text{pp})_2\}]^{4+}\) (BL = dpb, dpb; \(pp = \text{Me}_2\text{bpy}, \text{Me}_4\text{bpy}\)) were investigated by cyclic and differential pulse voltammetry in acetonitrile solution containing 0.1 M \([\text{LiClO}_4]_{\text{PF}_6}\) as the electrolyte. The redox potentials for the metal-based oxidation processes are reported in Table 1, in addition to the lowest energy MLCT transitions in the +4 states. The...
The electrochemical and NIR spectroscopic data for the series of unsymmetrical complexes are provided in Tables S2 and S3 and in Tables S4 and S5 (Accessory Materials), respectively. The electrochemical and UV/Vis/NIR (Table S6, Accessory Materials) data for the symmetrical systems is displayed for comparison. The NIR spectra for the series of complexes are shown in Fig. 2.

On the basis of the electrochemical method reported by Curtis and co-workers,[8–11] the extent of coupling between the metal centres is related to the ratio of the redox perturbation directly induced by ligand substitution at one end of the dimer to that indirectly induced at the other end. For both series of complexes, [([Ru(bpy)3]2(μ-BL)[Ru(pp)2])4+ (BL = dbp, dbp')] linearity was observed in the plots of \(E_{\mathrm{ox}1}\) versus \(E_{\mathrm{ox}2}\) for pp = bpy, Me2bpy, and Me4bpy, and the slopes were identical (within experimental error) for the meso and rac diastereoisomers of each series. The slope enables an assignment of \(b^2\) according to \(b^2 = m/(1 + m)\).

From the slopes \(m\), the \(p^2\) and resulting \(b^2\) values are reported in Table 6. Physically, \(b^2\) quantifies the fraction of a valence electronic charge that has been transferred from the donor to the acceptor metal centre in the electronic ground state, and represents the difference between the minima of the diatomic and diatomic surfaces in the two-state model depicted in Fig. 3. The results of the electrochemical analysis suggest that the degree of valence delocalization in the ground state is greater for the dbp'-bridged diastereoisomers relative to their dbp-bridged analogues. In addition, the degree of delocalization is greater for meso-([Ru(bpy)3]2(μ-Bl)[Ru(pp)2])4+ and rac-([Ru(bpy)3]2(μ-dbpc)5+) relative to their corresponding diastereomeric forms. \(p\) represents the ratio of the coefficients for the diatomic wave functions which is unity when mixing is complete, 0.5 at the transition between the localized and delocalized regimes, and zero in the absence of mixing. The relative values for \(p\) in Table 6 indicate that the diastereoisomers lie at the transition between the localized and delocalized regimes.

According to the classical two-site model, \(H_{ab}\) should remain constant for each series of complexes involving the dbp and dbp' bridging ligands. If this holds, the actual amount of charge transferred in the IVCT process, \(\Delta q\), is given by \(1 - 2b^2\) (Table 6), and the diabatic reorganization energy \(\lambda'\) is a fraction only of the diabatic reorganization energy \(\lambda\), Eqn (6),[142]

\[
\lambda' = \lambda(1 - 2b^2)^2 = \lambda(\Delta q)^2
\]

From Table 6, it is evident that the actual amount of charge transferred is significantly less than a unit electronic

**Table 1.** Electrochemical data and energies of the first MLCT transition in the +4 state \((E_{\mathrm{MLCT}}(1))\) for \([([Ru(bpy)3]2(μ-dbpc)[Ru(pp)2])4+\) and \([([Ru(bpy)3]2(μ-dbpc)[Ru(pp)2])4+\)

<table>
<thead>
<tr>
<th>pp</th>
<th>Diastereoisomer</th>
<th>BL = dbp</th>
<th>BL = dbp'</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta E_{\text{ox}})</td>
<td>(E_{\text{ox}1})</td>
<td>(E_{\text{ox}2})</td>
</tr>
<tr>
<td>Me4bpy</td>
<td>meso</td>
<td>292</td>
<td>1260</td>
</tr>
<tr>
<td></td>
<td>rac</td>
<td>284</td>
<td>1248</td>
</tr>
<tr>
<td>Me2bpy</td>
<td>meso</td>
<td>244</td>
<td>1260</td>
</tr>
<tr>
<td></td>
<td>rac</td>
<td>224</td>
<td>1256</td>
</tr>
<tr>
<td>bpy</td>
<td>meso</td>
<td>196</td>
<td>1280</td>
</tr>
<tr>
<td></td>
<td>rac</td>
<td>176</td>
<td>1280</td>
</tr>
</tbody>
</table>

\(\Delta E_{\text{ox}} = E_{\text{ox}2} - E_{\text{ox}1}\).
Driving the Localized-to-Delocalized Transition

<table>
<thead>
<tr>
<th>Diastereoisomer</th>
<th>Electrochemical parameters</th>
<th>Spectral parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta E_{ox1}$ [mV]</td>
<td>$\delta E_{ox2}$ [mV]</td>
</tr>
<tr>
<td>bpy</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>rac</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Me$_2$bpy, meso</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Me$_4$bpy, meso</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Me$_4$bpy, rac</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

$^\lambda m'$ is determined as the ratio of the potential shift ratio $m' = \delta E_{ox2}/\delta E_{ox1}$.

### Table 3. Comparison of the calculated parameters from the electrochemical and spectral analyses for the diastereoisomers of [({Ru(bpy)$_2$}(μ-dpb)-(bpy)$_2$])$^{5+}$ (pp = bpy, Me$_2$bpy, Me$_4$bpy)

<table>
<thead>
<tr>
<th>Diastereoisomer</th>
<th>$M_0$ [cm$^{-1}$]</th>
<th>$M_1$ [cm$^{-1}$]</th>
<th>$M_1 - \Delta E_0$ [cm$^{-1}$]</th>
<th>$\mu_{12}$ [e Å]</th>
<th>$\Gamma$</th>
<th>$\Delta v_{\gamma1,2}\pm 0.20$ [cm$^{-1}$]</th>
<th>$H_{ab}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>640</td>
<td>5655</td>
<td>5655</td>
<td>0.521</td>
<td>0.382</td>
<td>3090</td>
<td>395</td>
</tr>
<tr>
<td>rac</td>
<td>870</td>
<td>5450</td>
<td>5450</td>
<td>0.608</td>
<td>0.426</td>
<td>3030</td>
<td>440</td>
</tr>
<tr>
<td>meso</td>
<td>385</td>
<td>6020</td>
<td>5470</td>
<td>0.405</td>
<td>0.230</td>
<td>3135</td>
<td>315</td>
</tr>
<tr>
<td>rac</td>
<td>560</td>
<td>5780</td>
<td>5390</td>
<td>0.487</td>
<td>0.263</td>
<td>3180</td>
<td>390</td>
</tr>
<tr>
<td>bpy</td>
<td>330</td>
<td>6150</td>
<td>5210</td>
<td>0.375</td>
<td>0.245</td>
<td>3085</td>
<td>280</td>
</tr>
<tr>
<td>rac</td>
<td>350</td>
<td>6125</td>
<td>5250</td>
<td>0.385</td>
<td>0.270</td>
<td>3110</td>
<td>295</td>
</tr>
</tbody>
</table>

$^\lambda H_{ab}$ estimated from Eqn (2) assuming $r_{ab} = 6.870 \text{ Å}$ for both diastereoisomers of [({Ru(bpy)$_2$}(μ-dpb)-(bpy)$_2$])$^{5+}$ (the average of the Ru-Ru distances from the crystal structure determinations of meso-([Ru(bpy)$_2$](μ-dpb))(PF$_6$)$_2$ and meso-([Ru(bpy)$_2$](μ-dpb))(ZnCl$_4$)$_2$).$^{[21]}$

### Table 4. Summary of the experimental electrochemical and spectral parameters for the diastereoisomers of [({Ru(bpy)$_2$}(μ-dpb)-(bpy)$_2$])$^{5+}$ (pp = bpy, Me$_2$bpy, Me$_4$bpy)

<table>
<thead>
<tr>
<th>Diastereoisomer</th>
<th>Electrochemical parameters</th>
<th>Spectral parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta E_{ox1}$ [mV]</td>
<td>$\delta E_{ox2}$ [mV]</td>
</tr>
<tr>
<td>bpy</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>rac</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>meso</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>rac</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>bpy</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>rac</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

$^\lambda m'$ is determined as the ratio of the potential shift ratio $m' = \delta E_{ox2}/\delta E_{ox1}$.

### Table 5. Comparison of the calculated parameters from the electrochemical and spectral analyses for the diastereoisomers of [({Ru(bpy)$_2$}(μ-dpb)-(bpy)$_2$])$^{5+}$ (pp = bpy, Me$_2$bpy, Me$_4$bpy)

<table>
<thead>
<tr>
<th>Diastereoisomer</th>
<th>$M_0$ [M$^{-1}$]</th>
<th>$M_1$ [cm$^{-1}$]</th>
<th>$M_1 - \Delta E_0$ [cm$^{-1}$]</th>
<th>$\mu_{12}$ [e Å]</th>
<th>$\Gamma$</th>
<th>$\Delta v_{\gamma1,2}\pm 0.20$ [cm$^{-1}$]</th>
<th>$H_{ab}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy</td>
<td>1010</td>
<td>5510</td>
<td>5510</td>
<td>0.655</td>
<td>0.657</td>
<td>3115</td>
<td>500</td>
</tr>
<tr>
<td>rac</td>
<td>900</td>
<td>5510</td>
<td>5510</td>
<td>0.619</td>
<td>0.653</td>
<td>3115</td>
<td>475</td>
</tr>
<tr>
<td>meso</td>
<td>510</td>
<td>5725</td>
<td>5435</td>
<td>0.466</td>
<td>0.542</td>
<td>3090</td>
<td>350</td>
</tr>
<tr>
<td>rac</td>
<td>735</td>
<td>7570</td>
<td>7275</td>
<td>0.559</td>
<td>0.588</td>
<td>3070</td>
<td>415</td>
</tr>
<tr>
<td>bpy</td>
<td>484</td>
<td>8640</td>
<td>8125</td>
<td>0.452</td>
<td>0.462</td>
<td>3115</td>
<td>350</td>
</tr>
<tr>
<td>rac</td>
<td>360</td>
<td>5930</td>
<td>5280</td>
<td>0.389</td>
<td>0.392</td>
<td>3075</td>
<td>290</td>
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</tbody>
</table>

$^\lambda H_{ab}$ estimated from Eqn (3.2) assuming $r_{ab} = 6.887 \text{ Å}$ for both diastereoisomers of [({Ru(bpy)$_2$}(μ-dpb)-(bpy)$_2$])$^{5+}$ (the Ru-Ru distance from the crystal structure determinations of meso-([Ru(bpy)$_2$](μ-dpb)-(bpy)$_2$])$^{5+}$.[21]
Fig. 2. (a) Overlay of the IVCT bands for meso- (solid lines) and rac-\([\text{Ru}(\text{bpy})_2(\mu-\text{BL})\{\text{Ru}(\text{pp})_2\}]^{5+}\) (dashed lines) (pp = bpy, Me₂bpy, Me₄bpy; BL = dpb, dpb′) in 0.1 M\([\text{n-C}_4\text{H}_{10}]_4\text{N}\)PF₆/CH₃CN at −35°C. (b) Overlays of the IVCT bands for meso- and rac-\([\text{Ru}(\text{bpy})_2(\mu-\text{BL})\{\text{Ru}(\text{pp})_2\}]^{5+}\) in addition to the bands obtained from Gaussian deconvolution for the meso diastereoisomers.

Table 6. Comparison of the calculated parameters from the electrochemical and spectral analyses on the diastereomeric forms of \([\text{Ru}(\text{bpy})_2(\mu-\text{BL})]\)³⁺ (BL = dpb, dpb′)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\rho^2)</th>
<th>(\rho)</th>
<th>(b^2)</th>
<th>(\Delta q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>meso-([\text{Ru}(\text{bpy})_2(\mu-\text{dpb})])³⁺</td>
<td>0.18 ± 0.08</td>
<td>0.43 ± 0.19</td>
<td>0.15 ± 0.09</td>
<td>0.66</td>
</tr>
<tr>
<td>rac-([\text{Ru}(\text{bpy})_2(\mu-\text{dpb})])³⁺</td>
<td>0.23 ± 0.06</td>
<td>0.48 ± 0.13</td>
<td>0.19 ± 0.07</td>
<td>0.63</td>
</tr>
<tr>
<td>meso-([\text{Ru}(\text{bpy})_2(\mu-\text{dpb′})])³⁺</td>
<td>0.43 ± 0.03</td>
<td>0.68 ± 0.04</td>
<td>0.30 ± 0.03</td>
<td>0.40</td>
</tr>
<tr>
<td>rac-([\text{Ru}(\text{bpy})_2(\mu-\text{dpb′})])³⁺</td>
<td>0.33 ± 0.01</td>
<td>0.57 ± 0.02</td>
<td>0.25 ± 0.01</td>
<td>0.50</td>
</tr>
</tbody>
</table>

charge (e). The adiabatic (\(r_{12}\)) and diabatic (\(r_{ab}\)) charge transfer distances are related by Eqn (7). The former is the effective transfer distance for unit electronic charge. The difference between the diabatic and adiabatic distances illustrates that partial charge delocalization decreases the effective charge transfer distance relative to the geometrical through-space distance between the metal centres.

\[
er_{12} = (\Delta q)r_{ab}
\]

where

\[
r_{12} = r_{ab}(1 - 2b^2)
\]

As a consequence, the value of \(H_{ab}\) determined from Eqn (2) represents a lower limit only.[5] A more accurate estimate of \(H_{ab}\) may be obtained by incorporating the effective charge transfer distance, which results in an upwards revision of the values, reported in Tables 3 and 5, of 820 and 1000 cm⁻¹ for meso- and rac-\([\text{Ru}(\text{bpy})_2(\mu-\text{dpb})]\)³⁺ and of 3180 and 1870 cm⁻¹ for meso- and rac-\([\text{Ru}(\text{bpy})_2(\mu-\text{dpb′})]\)³⁺, respectively. These values are closer to those expected in the delocalized limit, where \(H_{ab}\) is estimated as 2600
and 2500 cm\(^{-1}\) for *meso-* and *rac-\([\{Ru(bpy)\_2\}_2(m\_dpb')\]^{5+}\), and 2640 and 2645 cm\(^{-1}\) for *meso-* and *rac-\([\{Ru(bpy)\_2\}_2(m\_dpb')\]^{5+}\), respectively, since \(v\max = 2H\lambda\).\(^{[12]}\)

The results from the electrochemical analysis indicate that the dpb\(^{-}\)-bridged diastereoisomers exhibit a greater degree of delocalization relative to the dpb-bridged analogues, and the degree of delocalization differs between the diastereoismeric forms of the same species. While the electrochemical method has been shown to provide reasonable measures of the trends in the degree of delocalization (on the basis of the parameter \(b^2\)), the method is based upon the two-site model and is valid only in the limit of small overlap. As a result, the electrochemical method is unlikely to yield reliable quantitative measures of the degree of delocalization. In addition, differential ion-pairing and solvent interactions with the different complexes, and the diastereoismeric forms of the same complex, may confound the results.

**Comparisons with IVCT Spectroscopic Parameters**

A linear correlation is observed between \(v\max\) and \(\Delta E\_\text{ox}\) for the diastereoisomers of \([\{Ru(bpy)\_2\}_2(m\_BL)(Ru(ppp)\_2)\]^{5+}\) (BL = dpb, dpb\(^{-}\), pp = bpy, Me\(_2\)bpy, Me\(_4\)bpy), which suggests that the peripheral ligand variation predominates to change the redox asymmetry contribution \((\Delta E_0)\) to the IVCT process.\(^{[7\text{-}11]}\) As shown in Fig. 2, the introduction of Me\(_2\)bpy and Me\(_4\)bpy terminal ligands leads to increasingly localized IVCT behaviour, and the appearance of more Gaussian-shaped IVCT bands. The transition is accompanied by an increase in \(v\max\) and \(\Delta v\_1/2\), and a decrease in \((\epsilon/\nu)\_\text{max}\) and \(M_0\) of the IVCT band as pp is varied through the series bpy, Me\(_2\)bpy, and Me\(_4\)bpy. In addition, the observed bandwidth \((\Delta v\_1/2)\) approaches the value expected in the localized limit \((v\_1/2)^0\) in Eqn 8, where \(R\) is the gas constant, \(T\) is the temperature [K], and the term \(16RT\ln 2\) is 1836 cm\(^{-1}\) at 238 K [\(-35^\circ\text{C}\)].

\[
\Delta v\_1/2 = \left[16RT \ln 2(\lambda)^1/2\right] = \left[16RT \ln 2(\nu\max - \Delta E_0 - \Delta E')\right]^{1/2} \quad (8)
\]

For the diastereoisomers incorporating the dpb\(^{-}\) bridging ligand, the \(v\max\) and \(\Delta v\_1/2\) are comparable for the two diastereoismeric forms over the series, and \((\epsilon/\nu)\_\text{max}\) and \(M_0\) are consistently greater for the *meso* versus the *rac* diastereoisomer (Table 5). The variation in the qualitative appearance of the IVCT bands also signals the transition from the delocalized to localized regimes (Fig. 2). The skewed appearance of the IVCT bands for the symmetrical complex towards higher energies was previously rationalized by the contributions of multiple underlying Gaussian-shaped components in the Gaussian deconvolution procedure. For the unsymmetrical complex \([\{Ru(bpy)\_2\}_2(m\_dpb')\]^{5+}\), the IVCT band is also skewed towards higher energies. By comparison, the IVCT line-shape for \([\{Ru(bpy)\_2\}_2(m\_dpb')\]^{5+}\) is approximated by a single Gaussian band, with additional minor components to reproduce the line-shape at the ‘tails’ of the IVCT manifolds. The results for the band parameters obtained from the Gaussian deconvolution procedure are reported in Table S5 (Accessory Materials). The IVCT properties for the series of complexes bridged by dpb follow similar trends to their dpb\(^{-}\)-bridged analogues. Qualitatively, the increase in the degree of localization as pp is varied through the series bpy, Me\(_2\)bpy and Me\(_4\)bpy is reflected by the increasingly Gaussian-shaped appearance of the IVCT bands. While the \(v\max\) and \(M_0\) values for the diastereoisomers of \([\{Ru(bpy)\_2\}_2(m\_dpb')\]^{5+}\) (pp = bpy, Me\(_2\)bpy) are greater than for the corresponding *rac* forms, the IVCT band parameters for both diastereoisomers of \([\{Ru(bpy)\_2\}_2(m\_dpb')\]^{5+}\) are almost identical. The results suggest that differential spectroscopically induced structural distortions \((\Delta E\_\text{struct})\) exist between the diastereoismeric forms, in addition to the induced redox asymmetry contribution \((\Delta E_0)\). \(\Delta E\_\text{struct}\) varies over the series complexes and between the diastereoisomers of the same complex, due to differential bridging ligand distortion. Such effects have been observed in the crystal structures of the dinuclear cations \([\{Ru(bpy)\_2\}_2(m\_BL)\]^{5+}\) (BL = dpb, dpb\(^{-}\)).\(^{[21]}\)

The trends in the IVCT band parameters \((v\max, \Delta v\_1/2, \text{and } M_1)\) as a function of \(\Delta E_0\) for the series of complexes are shown in Figure S3 (Accessory Materials). Estimates for the redox asymmetry contribution (reported in Tables 2 and 4) were obtained from the electrochemical measurements, as the difference between the potentials of the first metal-based oxidation process in a given diastereoisomer of the unsymmetrical complexes compared with the same diastereoisomer of the symmetrical complex. The \(\Delta E_0\) estimates which were determined according to the method of Curtis and co-workers\(^{[7]}\) represent the combination of the induced redox asymmetry due to peripheral ligand variation, the structurally induced redox asymmetry, and additional sources of peak splitting such as resonance stabilization and differential solvation energies.\(^{[9,43,44]}\)

According to the semi-classical theory of Brunsvig, Creutz, and Sutin\(^{[12]}\) the trends in the \(\Gamma\) parameters\(^{[12]}\) (\(\Gamma = 1 - (\Delta v\_1/2/\Delta v\_1/2^0)\)) reported in Tables 3 and 5 provide an additional measure of redox asymmetry contributions to the line-width. The magnitude of the \(\Gamma\) parameter distinguishes the class of a mixed valence system: \(0 < \Gamma < 0.1\) for weakly coupled Class II systems, \(0.1 < \Gamma < 0.5\) for moderately coupled Class II systems, \(\Gamma \approx 0.5\) at the transition between Classes II and III, and \(\Gamma > 0.5\) for Class III systems. In the present case, the decrease in \(\Gamma\) as pp is varied through the series bpy, Me\(_2\)bpy, and Me\(_4\)bpy demonstrates that the introduction of a relatively small redox perturbation results in a relatively dramatic increase in the bandwidth. However, the \(\Gamma\) values remain appreciable for the complexes incorporating Me\(_4\)bpy ligands, which indicates that the corresponding \(\Delta E_0\) contributions are not sufficient to induce complete localization.

**Theoretical Implications and Considerations**

The trends in the spectral parameters obtained from the classical analysis reveal that the introduction of redox asymmetry has profound effects: The IVCT bands shift to higher energies, broaden, and decrease in intensity. The onset of
localization is accompanied by a significant decrease in $H_{db}$, and an increase in $\lambda$.[12] Based on classical theory, both quantities should remain constant for a given series of complexes, since the expectation is that a variation in the redox asymmetry contribution should be manifested spectroscopically as an equivalent variation in the energy of the IVCT band (Eqn 1) at constant $H_{db}$ and $\lambda$. [12] In the present case, the variations in these quantities across the series suggest that different diabatic descriptions exist for each of the complexes. In addition, the results indicate that a classical two-state description is inappropriate, and electronic delocalization is governed by superexchange effects rather than direct donor–acceptor orbital overlap. For the dpb-bridged diastereoisomers, the increase in $\Delta E_0$ is also accompanied by a fundamental change in electronic structure, due to the non-zero contribution of $\Delta E_{\text{struct}}$. Clearly, the development of an adequate theory to describe the transition between the localized and delocalized regimes for the full series of complexes requires a theoretical model incorporating both symmetric and antisymmetric modes, in which $\Delta E_0$ is varied at constant $H_{db}$ and $\lambda$. Application of the model to the series of unsymmetrical analogues of the Creutz–Taube ion, trans-[[Ru(NH$_3$)$_5$]($\mu$-pyz)]([Ru(NH$_3$)$_3$]($\mu$-pyz))$^3+$(L = NH$_3$ (the Creutz–Taube ion itself), py, 3,5-Me$_2$py, 3,5-CI$^-$, py, 2,6-Me$_2$pyz), revealed qualitative agreement between the trends in the calculated parameters and the experimental data. However, it was evident that a more sophisticated model was required in which $H_{db}$ and $\lambda$ were permitted to vary with $\Delta E_0$. The results for the present series of complexes support this contention, and provide an experimental basis for testing the validity of future theoretical models which incorporate redox asymmetry effects.

Conclusions

The degree of delocalization in the symmetrical complexes $[[\text{Ru(bpy)}_2]_2(\mu-dpb')]^{3+}$ and $[[\text{Ru(bpy)}_2]_2(\mu-dpb)]^{3+}$ is diminished by the substitution of the terminal bpy ligands at one end of the complex. The results of a classical analysis for the series of complexes $[[\text{Ru(bpy)}_2](\mu-BL)[\text{Ru(pp)}_2]]^{5+}$ (BL = dpb', dpb; pp = bpy, Me$_2$bpy, Me$_4$bpy) according to the electrochemical method proposed by Curtis and co-workers[7–11] support the conclusion that a greater degree of ground state delocalization exists in the complexes incorporating the fused bridging ligand dpb' compared with the unfused dpb analogue. A two-state analysis in which $\Delta E_0$ is varied at constant $H_{db}$ and $\lambda$, is not sufficient to describe the properties of the systems due to the importance of a third electronic state corresponding to the bridging ligand.

Acknowledgements

We gratefully acknowledge Professor Joe Hupp (Northwestern University, Chicago) for inspiring these experiments, and Dr Jeff Reimers and Professor Noel Hush (University of Sydney) for helpful discussions on their analysis. This work was supported by the Australian Research Council.

References

[14] $\beta^2$ is equivalent to the delocalization parameter $\omega^2$, as defined by N. S. Hush, Coord. Chem. Rev. 1985, 54, 135. doi:10.1016/0010-8545(85)80047-3

Accessory Materials

Accessory Figures (NMR numbering for ligands, representations of meso-(\Delta\Delta)- and rac-(\Delta\Delta)-[[Ru(bpy)2]2-(\mu-dpb')]4+ and representations of $\nu_{\text{max}}$, $\Delta\nu_{1/2}$, and $M_1$ as a function of $E_0$ and Tables (NMR shifts for [[Ru(bpy)]2]$_2$-(\mu-dpb')]4+, reduction potentials for [[Ru(bpy)]2(\mu-dpb')-([Ru(pp)]2)]4+ and [[Ru(bpy)]2(\mu-dpb')([Ru(dp)]2)]4+, spectroelectrochemical data for [[Ru(bpy)]2(\mu-BL)[Ru(dp)]2]4+ and [[Ru(bpy)]2(\mu-BL)]4+, and NIR data of the reduced absorption spectra for [[Ru(bpy)]2(\mu-BL)[Ru(dp)]2]4+] available from the author or, until November 2010, the Australian Journal of Chemistry.