

# STEREOCHEMICAL EFFECTS ON INTERVALENCE CHARGE TRANSFER

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Electron transfer is ubiquitous in chemical, physical and biological systems – the phenomenon is fundamental in natural processes such as photosynthesis, and in materials science applications. Mixed-valence dinuclear complexes have received significant attention in electron transfer studies as the characteristics of their intervalence charge transfer (IVCT) bands provide a powerful probe of the factors which govern the barrier to electron transfer (equation 1,  $\nu_{\max}$  = IVCT energy).<sup>1, 2</sup>

$$\nu_{\max} = h\nu = \lambda_i + \lambda_o + \Delta E_0 + \Delta E' \quad (1)$$

The Franck-Condon factors,  $\lambda_i$  and  $\lambda_o$ , correspond to the reorganisational energies within the inner- and outer-sphere (respectively), the redox asymmetry,  $\Delta E_0$ , is the energy difference between the two metal-based chromophores, and  $\Delta E'$  incorporates spin-orbit coupling contributions.

Previously, these factors have been probed by the variation of “global” features of the complexes – such as the identity and coordination environments of the metal centres, or through variation of properties of the solvating medium. The work reported in this thesis is the first to reveal stereochemical effects on the electrochemical, spectral and IVCT characteristics of a range of di- and tri-nuclear complexes incorporating the bridging ligands shown in Figure 1, and challenges prior assertions that the *inherent* stereochemistry of polymetallic assemblies would have no influence on their physical properties.<sup>3</sup>

## The “Stereochemical Problem”

Polymetallic assemblies such as the dinuclear complex  $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-bpm})]^{4+}$  (bpy = 2,2'-bipyridine, bpm = 2,2'-bipyrimidine) may exist in two possible diastereoisomeric forms {Figure 2(a)},<sup>4, 5</sup> which differ only in the nature of the “clefs” between the planes of the bpy ligands {Figure 2(b)}.

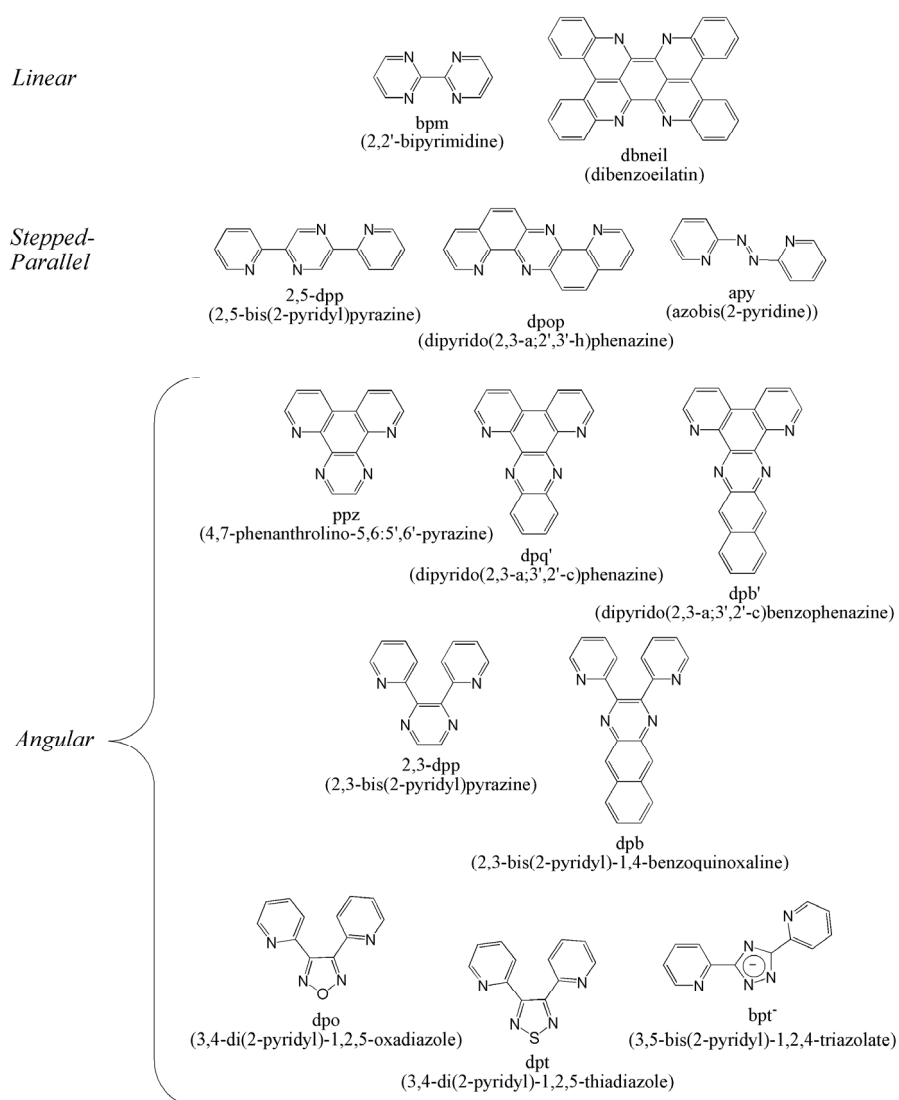


Figure 1

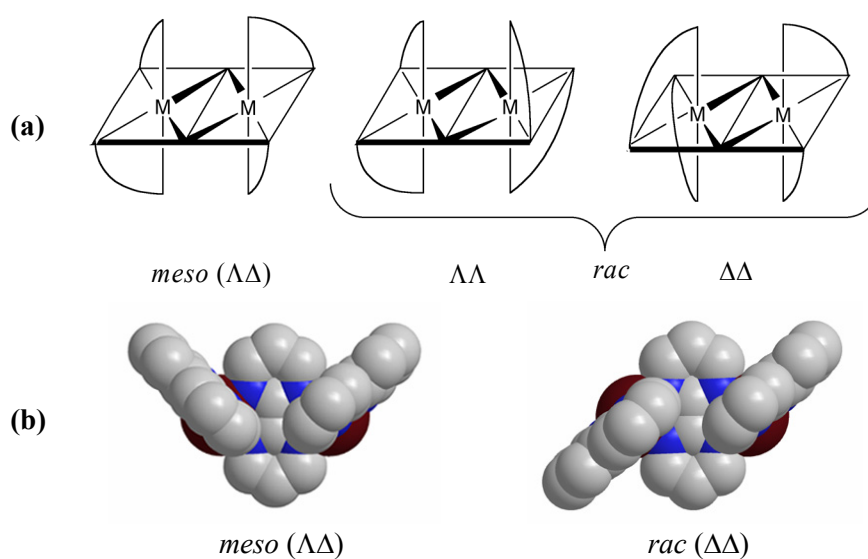
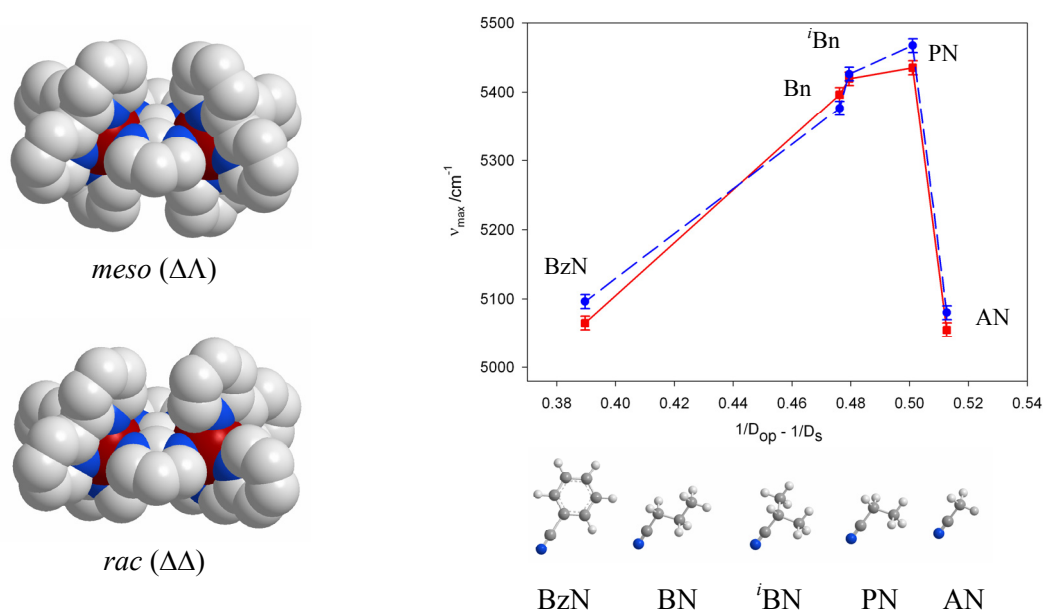


Figure 2

(a) The two diastereoisomers of  $[\{M(pp)_2\}_2(\mu-BL)]^{4+}$   $\{M = Ru, Os; pp = \text{symmetrical bidentate ligand}; BL = \text{linear bridging ligand}\}$ . (b) Views “above” the plane of the bridging ligand in *meso*- and *rac*- $[\{Ru(bpy)_2\}_2(\mu-bpm)]^{4+}$  (bpy ligands “below” the plane are omitted).

## Diastereoisomers as Probes for Reorganisational Effects

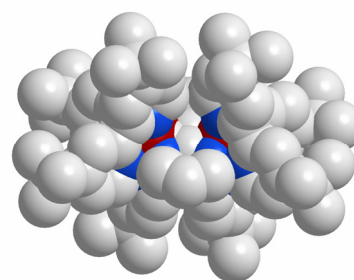
The *subtle* variations in the geometries of the stereoisomers provide a new experimental probe for spatially-directed solvent effects on  $\lambda_0$ . IVCT solvatochromism studies of *meso*- and *rac*- $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-bpm})]^{5+}$  in acetonitrile (AN), propionitrile (PN), *n*-butyronitrile (BN), *iso*-butyronitrile (*i*BN) and benzonitrile (BzN) revealed the predicted linear trend between  $\nu_{\text{max}}$  and the “solvent parameter” ( $1/D_{\text{op}}-1/D_s$ ) in all solvents except AN (Figure 3).<sup>6</sup> The energy disparity was attributed to a *specific* solvent effect which was enhanced for the *rac* relative to the *meso* form: the clefts between the terminal bpy rings allow the AN molecules to approach the metal centres more closely than is permitted by continuum solvation models.



**Figure 3**

IVCT solvatochromism for *meso* (—) and *rac* (---)  $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-bpm})]^{5+}$  in 0.02 M  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\{\text{B}(\text{C}_6\text{F}_5)_4\}$ /solvent at +25°C.

Variations in the dimensions of the clefts through bridging ligand modification<sup>7</sup> and the positioning of alkyl substituents on the terminal ligands<sup>6</sup> revealed that the specific effects depend markedly on the cavity dimensions. *e.g.*, Bulky *tert*-butyl substituents (Figure 4) impede the access of solvent molecules to the clefts leading to negligible IVCT solvatochromism.

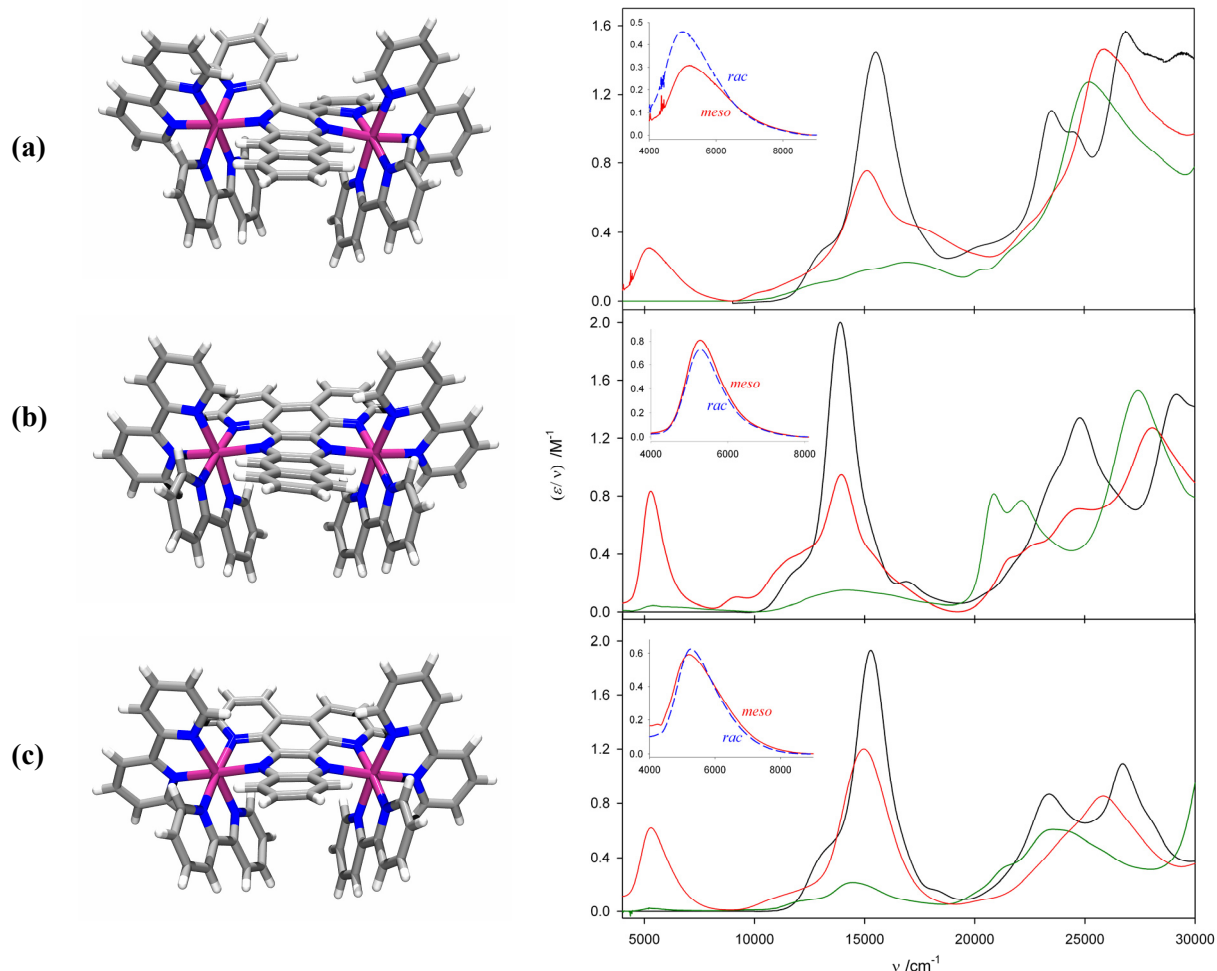


**Figure 4**

*meso*( $\Delta\Delta$ )- $[\{\text{Ru}(\text{Bu}_2\text{bpy})_2\}_2(\mu\text{-bpm})]^{4+}$   
( $\text{Bu}_2\text{bpy}$  = 4,4'-*di-tert*-butyl-2,2'-bipyridine)

## Stereochemical Effects on the Factors that Govern the Electron Transfer Barrier

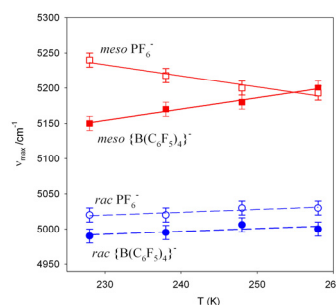
(1) **Structural distortions** in the bridging ligands contribute a redox asymmetry ( $\Delta E_0$ ) to the electron transfer barrier which enhances the differences between the IVCT characteristics of the diastereoisomers of the same complex.<sup>8-10</sup> *e.g.*, Electronic delocalisation was reduced for both diastereoisomers of  $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-dpb})]^{4+}$  relative to their dpb'- and dpq'-bridged analogues due to bridging ligand distortion (Figure 5).



**Figure 5**

X-ray crystal structures of  $\text{meso}-(\Delta\Delta)-[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-BL})]^{4+}$  and UV/Vis/NIR spectra of  $\text{meso}-[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-BL})]^{n+}$ , BL = dpb (a), dpb' (b) and dpq' (c)  $\{n = 4$  (—),  $5$  (—),  $6$  (—)} in 0.1 M  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$  at  $-35^\circ\text{C}$ . Insets: overlays of IVCT bands for the diastereoisomers.

(2) **IVCT Solvatochromism,<sup>11,12</sup> Thermochromism and Ion-Pairing.<sup>13-15</sup>** Differential ion-pairing interactions with the diastereoisomers – which are a crucial factor in their chromatographic separation<sup>4,5</sup> – were manifested by differences in their IVCT thermochromism in the presence of relatively strongly,  $\text{PF}_6^-$ , and weakly,  $\{\text{B}(\text{C}_6\text{F}_5)_4\}^-$ , ion-pairing anions.



**Figure 6**

IVCT thermochromism for  $\text{meso}$  (—) and  $\text{rac}$  (---)  $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-dpb})]^{5+}$  in 0.1 M  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6$  or 0.02 M  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\{\text{B}(\text{C}_6\text{F}_5)_4\}/n\text{-butyronitrile}$ .

(3) **Spin-orbit coupling ( $\Delta E'$ ) contributions** were quantified from interconfigurational transitions in the osmium complexes  $[\{\text{Os}(\text{bpy})_2\}_2(\mu\text{-BL})]^{5+/6+}$  {BL = dpb', dpq', ppz, dpb, 2,3-dpp} and showed that stereochemical effects modulate the energy levels of the component metal centres.<sup>16</sup>

(4) **The effective charge transfer distances** from electroabsorption (Stark effect) measurements on  $[\{\text{M}(\text{bpy})_2\}_2(\mu\text{-BL})]^{5+}$  {M = Ru, Os} were negligible compared with the metal-metal separations, supporting a borderline localised-delocalised classification.<sup>16, 17</sup>

### Trinuclear Polymetallic Assemblies

The extension of the IVCT probe to stereochemically-pure trinuclear assemblies reveals the contribution of “second-order” interactions due to multiple coupled centres, and provides the link between electron transfer in dinuclear species and in extended arrays and metallosupramolecular systems.<sup>18</sup>

The dinuclear complexes  $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-BL})]^{5+}$  {BL = HAT (1,4,5,8,9,12-hexaazatriphenylene) and ppz} possess similar electrochemical and IVCT characteristics, while the properties of the mixed-valence forms of the trinuclear systems  $[\{\text{Ru}(\text{bpy})_2\}_3(\mu\text{-HAT})]^{n+}$  and  $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Ru}(\text{bpy})(\mu\text{-ppz})_2\}]^{n+}$  { $n = 7, 8$ }<sup>19-21</sup> differ markedly from their dinuclear analogues and depend on the overall geometry and oxidation state of the assemblies. The three Ru centres in  $[\{\text{Ru}(\text{bpy})_2\}_3(\mu\text{-HAT})]^{n+}$  are equivalently disposed, and share in the available electron density.<sup>19-21</sup> By comparison, the “chain-like” assembly in  $\Delta\Delta^t\Delta\text{-}[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Ru}(\text{bpy})(\mu\text{-ppz})_2\}]^{n+}$  gives rise to a decreased coupling through the central metal.<sup>20</sup>

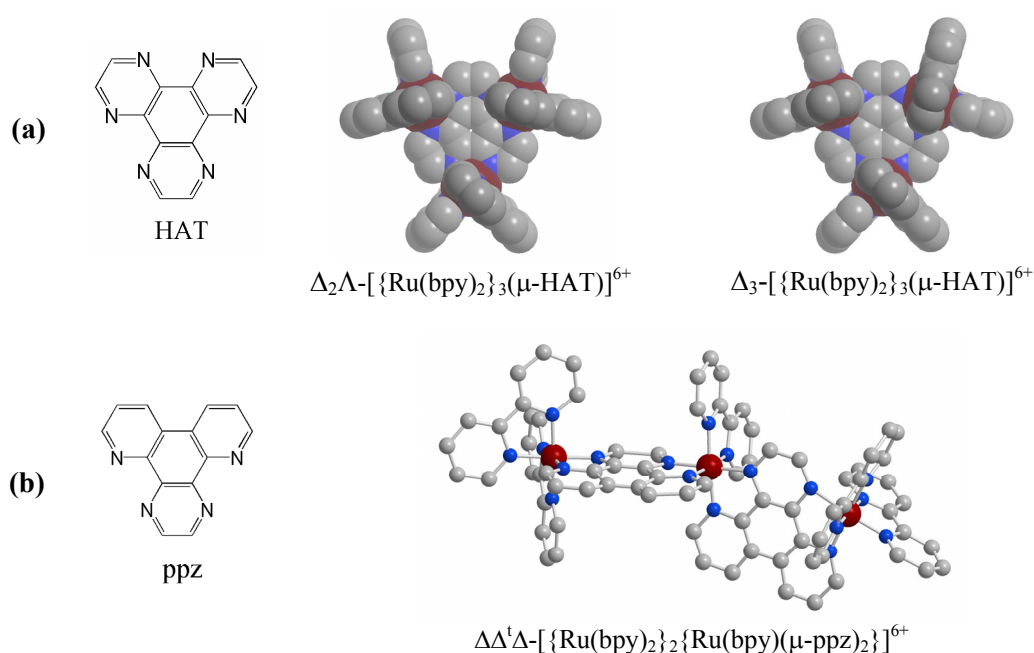


Figure 7

The elucidation of stereochemical effects on IVCT illustrates the subtle interplay of factors that govern intramolecular electron transfer and electronic delocalisation. The findings have significant implications for understanding spatial influences on electron migration in natural systems. At an applied level, stereochemical effects could be exploited in the design of novel molecular materials such as artificial photosynthetic systems for solar energy harvesting.

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