
STEREOCHEMICAL EFFECTS ON INTERVALENCE CHARGE TRANSFER

Thesis submitted by
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DECLARATION



I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is provided.

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STATEMENT OF CONTRIBUTION OF OTHERS



The work reported in this thesis was conducted under the supervision of Prof. Richard Keene, using the facilities in the Department of Chemistry at James Cook University.

Collaborations with Prof. Joe Hupp (Centre for Nanofabrication and Materials Science, Northwestern University, U.S.A.), Prof. Peter Steel (University of Canterbury, N.Z.), and Dr Jeff Reimers (University of Sydney) have been instrumental in providing intellectual and experimental support for this work. Electroabsorption (Stark effect) measurements were conducted by the candidate under the skilful guidance of Dr Peter Dinolfo and Dr Keith Walters during a three-month research visit to Prof. Hupp's laboratory. Prof. Steel supplied a number of novel bridging ligands which have been employed in this work. The preliminary Density Functional Theory calculations reported in Chapter 2 were conducted by the candidate under Dr Reimers' expert guidance.

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“While the difficult takes time, the impossible just takes a little longer.”
Art E. Berg

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ABSTRACT

This thesis reports the first observation of stereochemical effects on intervalence charge transfer (IVCT) in di- and trinuclear mixed-valence complexes. The differential IVCT characteristics of the diastereoisomers of polypyridyl complexes of ruthenium and osmium offer a new and intimate probe of the fundamental factors that govern the extent of electronic delocalisation and the barrier to electron transfer. These findings challenge prior assertions that the inherent stereochemical identity of such complexes would have no influence on the intramolecular electron transfer properties of polymetallic assemblies. *Chapter 1* addresses these issues within the context of the existing theoretical and experimental framework for IVCT.

Solvatochromism studies on the *meso* and *rac* diastereoisomers of $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-bpm})]^{5+}$ {bpy = 2,2'-bipyridine; bpm = 2,2'-bipyrimidine} reported in *Chapter 2*, reveal striking differences between their IVCT characteristics due to stereochemically-directed specific solvent interactions. Such effects are inconsistent with dielectric continuum theories of solvation which are typically used to assess the contribution of the Franck-Condon outer-sphere reorganisational energy to the electron transfer barrier. Solvent proportion experiments demonstrate that the magnitude of the specific interaction is enhanced for the *rac* relative to the *meso* form, as the dimensionality of the “clefts” between the planes of the terminal polypyridyl ligands are ideally disposed to accommodate discrete solvent molecules. Subtle and systematic variations in the size and shape of the clefts through bridging ligand modification and the judicious positioning of alkyl substituents on the terminal ligands reveal that the magnitudes of the effects are dependent on the different cavity dimensions, and the number, size, orientation and location of solvent dipoles within the clefts.

Chapter 3 discusses stereochemically-directed solvent and anion interactions in systems of the type $[\{\text{M}(\text{bpy})_2\}_2(\mu\text{-BL})]^{5+}$ {M = Ru, Os} where BL denotes an extensive series of N-heterocyclic di- and tri-bidentate polypyridyl bridging ligands. NIR region electroabsorption (Stark effect) measurements of the mixed-valence complexes reveal small dipole moment changes for the IVCT transitions. In all cases, the *effective* charge transfer distances are negligible compared with the geometrical metal-metal separations, in support of a moderately- to strongly-delocalised assignment for the systems. This contrasts previous assertions in the literature which favoured a localised (“Class II”) classification for complexes of the genre.

IVCT solvatochromism and thermochromism studies on the mixed-valence species reveal that a subtle increase in the extent of inter-metal coupling with bridging ligand modification reduces the reorganisational barrier to electron transfer and leads to a transition between the localised (“Class II”) and localised-to-delocalised (“Class II-III”) regimes. The importance of the bridging ligand in mediating the IVCT process necessitates a three-state theoretical analysis for the IVCT line-shape which explicitly includes the symmetric vibration mode.

The comproportionation constants (K_c) which are typically used to assess the degree of metal-metal coupling are markedly dependent on the electrolyte anion and the stereochemical identity of the complex. This emphasises the need for standard conditions for data from which analyses based on the magnitude of K_c are made, and the danger of over-interpretation of the values. The differential anion interactions between the diastereoisomers are also manifested in their IVCT characteristics and represent a redox asymmetry contribution to the electron transfer barrier.

The magnitude of the differences between the IVCT characteristics of the diastereoisomeric forms of the same complex are more pronounced in the presence of inherent structural distortions in the bridging ligands, which are evident in their solid-state X-ray crystal structures. Such distortions decrease the extent of delocalisation through their redox asymmetry contribution to the electron transfer barrier. The interconfigurational (IC) transitions in the fully-oxidised forms of the dinuclear osmium complexes indicate that stereochemical effects modulate the energy levels of the metal-based $d\pi$ orbitals themselves, which are split by spin-orbit coupling and ligand field asymmetry.

Chapter 4 extends the IVCT probe to stereochemically-pure trinuclear assemblies through a systematic investigation of the influence of the oxidation state, nuclearity and overall geometry of the systems on their intramolecular electron transfer processes. The IVCT properties of the dinuclear complexes [$\{\text{Ru}(\text{bpy})_2\}(\mu\text{-HAT})\{\text{M}(\text{bpy})_2\}]^{5+}$ $\{\text{M} = \text{Ru, Os}\}$ and [$\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-ppz})]^{5+}$ are contrasted with their trinuclear analogues, which are “cluster-type” [$\{\text{Ru}(\text{bpy})_2\}_2\{\text{M}(\text{bpy})_2\}(\mu\text{-HAT})]^{n+}$ or “chain-like” [$\{\text{Ru}(\text{bpy})_2\}_2\{\text{Ru}(\text{bpy})(\mu\text{-ppz})_2\}]^{n+}$ $\{n = 7, 8; \text{M} = \text{Ru, Os}; \text{BL} = \text{HAT (1,4,5,8,9,12-hexaazatriphenylene) and ppz (4,7-phenanthroline-5,6:5',6'-pyrazine)}\}$. While the diastereoisomers of the dinuclear complexes possess similar electrochemical and IVCT characteristics, the trinuclear “cluster-type” system bridged by HAT exhibits significantly greater electronic coupling than the “chain-like” assembly based on ppz. The IVCT transitions in the singly-oxidised (+7) and doubly-oxidised (+8) trinuclear mixed-valence species are markedly different to those in their dinuclear analogues due to appreciable second-order interactions which depend on the overall geometry and oxidation state of the assemblies.

The observation of stereochemical effects on IVCT illustrates the subtle interplay of factors that govern the localised-to-delocalised transition, and addresses the limited experimental data which exist to probe the microscopic factors that facilitate this transition. The recognition of such effects on intramolecular electron transfer processes has significant implications for the elucidation of spatial influences on electron migration in biological systems such as metalloenzymes in nature. Ultimately, stereochemical modifications may be exploited in materials science applications to “fine-tune” the physical properties of novel molecular devices such as artificial photosynthetic systems for solar energy harvesting.

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