

AIMS AND BACKGROUND:

Electron transfer (ET) processes are ubiquitous in chemistry, governing the most elementary of bond forming steps, and harnessed in events as complex as the photosynthetic cascade and respiration.¹ In modern

contexts, intra- and inter-molecular ET processes underpin homogeneous, heterogeneous and bio-catalytic processes, are exploited in the design and operation of solar

light harvesting and conversion cells, OLEDs and batteries. Mixed-valence (MV) multinuclear transition-metal complexes (Figure 1) have long been recognised as key models and testing grounds for theories concerning ET in nature (e.g. in metalloenzymes and complex biomachinery such as PSII), in catalysis, and in the design of functional materials.² More recently, possible applications in molecular electronics, e. g. as models for molecular wires, and renewed interest in mixed-valence solids have added further momentum to the field. In addition, organic analogues of the classical metal-based mixed-valence systems are now being increasingly recognised, and studies are shedding considerable new light on the field. It is well-known that methods of analysing the charge transfer characteristics in mixed-valence complexes are also readily extended to more general ET processes. However, regardless of the composition of the system, a central question in all of these fields, and the most fundamental, is that of the localization of charge on a given redox centre, donor or acceptor site or bridge, versus delocalization over the molecular framework.

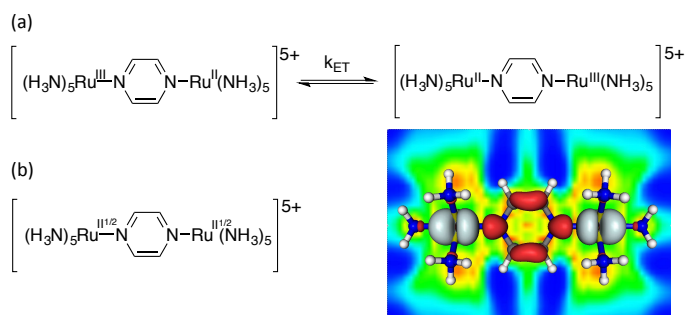


Figure 1. The Creutz-Taube ion as a prototypical mixed-valence (MV) complex in which an element exists in (a) two different formal oxidation states (here, Ru(III) and Ru(II)) or (b) sometimes described as non-integer oxidation state (Ru(II^{1/2})) as a result of extensive delocalisation. The colour plot shows the calculated spin density, which is discussed in more detail below.

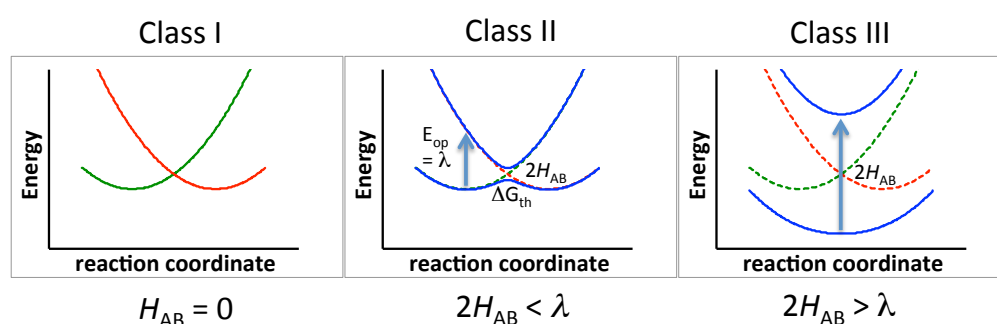


Figure 2. The evolution of the Robin-Day Classes depicted in terms of the coupling of two diabatic states. As the coupling constant H_{AB} increases relative to the reorganisation energy λ , the barrier to thermal electron transfer ΔG_{th} decreases and the system evolves from a localised (Class II) to delocalised (Class III) MV complex.

MV systems have traditionally been characterised in terms of the classification scheme introduced by Melvin Robin and Peter Day, which describe the three most general situations of non-interacting redox centres (Class I), valence-trapped or localised systems (Class II) and valence delocalised systems (Class III) (Figure 2).³

As the optoelectronic properties of a material (here discussed in terms of a MV system) are crucially dependent on the localization/delocalization of charge, the distinctions between compounds in these different broad classes are important, and methods for determining the electronic characteristics of MV compounds through application of an increasingly wide and sophisticated range of spectroscopic and computational techniques and theoretical treatments have been the topic of considerable discussion and exploration for over 50 years, and the various key models continue to attract detailed attention and refinement.⁴ The shape and position of the inter-valence charge-transfer bands (IVCT) in optical or near-infrared (NIR) spectra are typically examined in great detail, but given the importance a degree of delocalization of charge over the bridging unit between the two redox centres plays in many systems, metal-bridge CT (metal-ligand CT, MLCT) transitions are also of interest. Other important spectroscopic techniques for the investigation of the electronic character of MV complexes, which involve somewhat different energy and time scales, include vibrational spectroscopies (IR, Raman), Stark spectroscopy, Mössbauer spectroscopy, and electron spin resonance (ESR) spectroscopy.

The ability to derive not only a general description of the principal electronic character (Robin and Day classes) of a system, but also the crucial ET parameters (H_{AB} , k_{ET} , ΔG_{th} , λ , etc) from spectroscopic observables based on the well-known equations of the Marcus-Hush and Mulliken-Hush theories using two-state models or their extension to a three-state scenario (including bridge states in the latter case) is almost universal in the field. However, while the IVCT transition typically appears as the lowest-energy transition in the NIR region for organic MV systems, the determination of the IVCT band within the NIR band envelope is more complicated in transition metal complexes, not only due the effects of solvent dynamics but also to the potential presence of additional electronic transitions of similar energy (e.g. d-d bands) (Figure 3).⁵

The potential for multiple electronic transitions of similar energy but different electronic origin, together with the asymmetric IVCT band-shapes that characterize strongly coupled MV systems, renders derivation of the ET characteristics and electronic structure from NIR spectra alone very difficult in many MV transition-metal

complexes, despite the popularity of such analyses. A common solution is to deconvolute the band envelope in a sum of a minimum number of Gaussian-shaped bands, with one component of the deconvolution chosen as the ‘true’ IVCT band. However, such analyses are not always achievable, with complications arising from the potential for multiple solutions to the deconvolution arising from overlap of the IVCT band with Ligand-Metal or Metal-Ligand (LMCT or MLCT) charge transfer transitions and localised dd-transitions. The statement below from a recent article by others in *Inorganic Chemistry* illustrates the problems

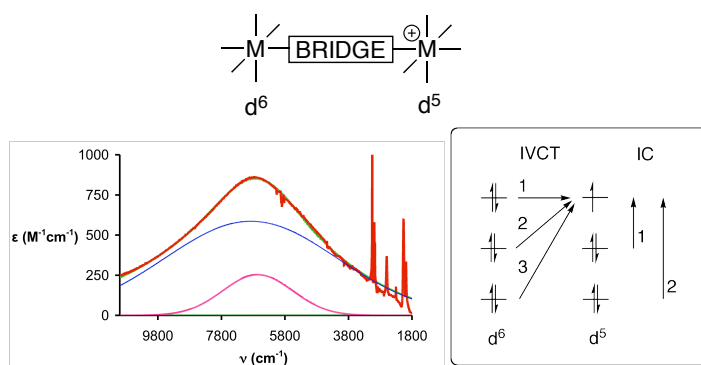


Figure 3. The NIR band envelope of a MV complex can feature multiple transitions of different electronic character.⁵

The overlap of the IVCT with other NIR transitions is quite common for mixed-valence compounds and often complicates data analysis. To locate the IVCT band, we attempted band deconvolution analysis for its NIR envelope. Although the NIR region of the spectrum cannot be described by a single LMCT Gaussian function, the position and width of the possible IVCT band cannot be precisely determined through a fitting algorithm as many possible fitting solutions could be found. Because of the above complication, accurate analysis of the IVCT band is impossible to perform, and therefore, it is difficult to estimate the extent of metal–metal coupling in the mixed-valence complex.⁶

In the case of weakly coupled (Class II) systems, the Hush expressions include the electron transfer distance, d , which is often unknown and approximated by the physical separation of the redox centres. This is known to be a likely over-estimate as a consequence of mixing with the bridge, but few direct methods of measuring d are readily available. The case of compounds which sit close to the borderline between Class II and III is also problematic, and interpretation of the optical spectra from such systems requires considerable care and use of an appropriately modified model.⁷ In addition solvent dynamics, internal vibrational modes and conformational effects within the molecular framework can also play a part in determining the optoelectronic properties of a MV complex (Figure 4).

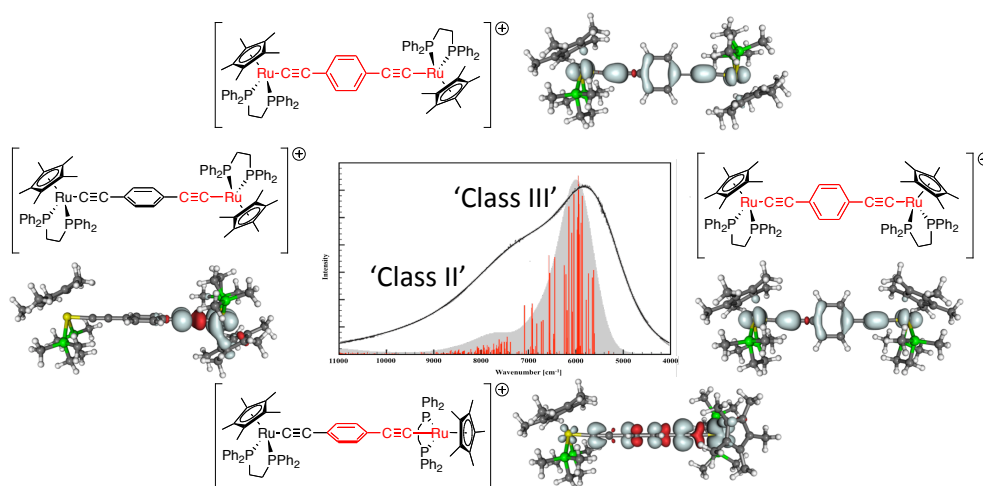


Figure 4. An example of the complications that can arise from the distribution of molecular conformers in a MV compound. Here, rotation of the phenylene bridge and half-sandwich metal end-caps leads to a distribution of electronic characters from strongly coupled / delocalised (Class III) to weakly coupled / localised (Class II) systems within one molecular framework. The figure shows the experimental NIR band envelope (solid black line), stick spectra illustrating the calculated spectral transitions from many individual close-lying local minima and a Boltzman average and broadened simulation of the spectrum (shaded area). The molecular framework is represented by the line figures, whilst calculated spin-density plots are also provided.¹⁰

The identification of these conformational factors in preliminary work from the Kaupp and Low groups prompts reconsideration of other ligand-bridged bimetallic mixed-valence complexes $[M\text{-bridge-M}]^+$ in which $d\text{-}\pi\text{-}d$ overlap along the molecular backbone can be anticipated to be strongly dependent on the relative orientation of the constituent fragments. The thermal population of a conformational phase space encompassing both localized and delocalized charge distributions limits the

usefulness of a description of such complexes in terms of a single, static lowest energy conformation.

The ability to use quantum chemical methods and calculated parameters in concert with directly observable experimental data is highly desirable, and would allow information to be obtained without recourse to simplified models, neglect of molecular dynamics, or broad assumptions inherent in the contemporary interpretations of NIR bands.⁸ However, the use of post-Hartree-Fock (HF) computational methods on systems of chemically interesting size and including relevant aspects of the solvent medium, counter ions and coupled spectator vibrational modes is extremely challenging and represents the state of the art in computational modelling of mixed-valence systems.⁹ The theoretical background knowledge and computational resources necessary to these extraordinarily detailed studies are beyond the realistic capacity of most workers in the field to assess on a reasonable time frame. Accurate interpretations of the spectroscopic properties and electronic characteristics also requires consideration of the internal rotational dynamics and fluxional nature of the molecule, which is not reflected in the static lowest energy structures usually used to interpret spectroscopic information.

RESEARCH PROJECT:

The initial premise of the current proposal is that despite the popularity of the Hush two-state model to analyse and interpret spectroscopic information from MV complexes, or more generally Donor-Bridge-Acceptor molecules, the correct application of the Hush protocols to experimental spectra is often difficult or relies on many significant and not always appropriate approximations. Very often, these approximations are made without due consideration of their appropriateness, or simply for lack of a practical alternative method of interpretation. This project does not seek to redefine new theoretical concepts in the description of mixed-valence complexes, nor does it seek to establish the intricate details of the charge transfer processes in any single compound. Rather, we set out to establish a series of user-friendly protocols that allow the typical experimentalist to better understand their data pertaining to charge transfer processes, which avoid the current pitfalls such as the presence of multiple electronic transitions within the NIR band envelope, ambiguity over the site of the donor and acceptor, and the electron transfer distance, and molecular dynamics and conformational fluxionality. In doing so we will need to step away from the spectroscopically derived coupling parameter H_{AB} as a measure of the interaction between remote sites in the molecular framework, and arrive at an alternative method for the description of electronic structure and charge transfer characteristics.

This project will entail the synthesis of a series of MV complexes, drawn from organometallic, inorganic and organic chemistry. These will be characterised using the spectroelectrochemical facilities at the University of Western Australia, which are among the best in the world. The results will be analysed both at UWA, using Gaussian 09 suite of programs, and in Berlin, but our collaborators in the Kaupp group. Students with experience and interest in any combination of synthetic chemistry, electrochemistry or spectroscopy and computational chemistry are encouraged to apply.

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