

Review

Mixed valency in ruthenium complexes—Coordinative aspects

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Received 2 December 2005; accepted 6 June 2006

Available online 15 June 2006

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Abstract

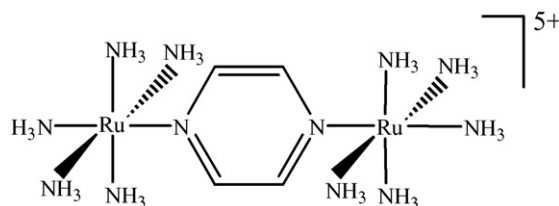
The metal–metal interaction in ligand-bridged diruthenium(II,III) complex intermediates is commonly characterized by using the redox potential difference, usually converted to the comproportionation constant K_c , and by analyzing intervalence charge transfer (IVCT) absorption features and deriving electronic coupling parameters. Although these two kinds of information may yield very different estimates of the extent of metal–metal interaction in any given system, the absolute values have often been used interchangeably to quantify the strength of electronic “coupling”. Using examples from the literature with substantially different coordination arrangements in terms of denticity and donor/acceptor character of the π conjugated bridging ligand we can show that close correlations between electrochemically and spectroscopically determined coupling are only valid within structurally related classes of compounds with qualitatively similar interaction at the metal–ligand interface. Most strikingly, situations with high K_c values but weak, low energy IVCT absorptions have been identified for complexes with bis- and tris-bidentate acceptor bridges whereas intermediates with small comproportionation constants but intense, narrow IVCT bands are typical with bridging bis-tridentate acceptors. © 2006 Elsevier B.V. All rights reserved.

Keywords: Absorption spectroscopy; Bridging ligands; Comproportionation; Mixed valency; Ruthenium

1. Introduction

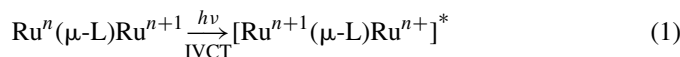
Ever since the first report of the Creutz–Taube ion $[(\text{H}_3\text{N})_5\text{Ru}(\mu\text{-pyrazine})\text{Ru}(\text{NH}_3)_5]^{5+}$, **1** [1] as a small and simple, yet surprisingly stable ligand-bridged $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ coordination compound, there have been numerous experimental and theoretical attempts to understand the stability and physical properties of related symmetrical diruthenium mixed-valent complexes [2,3]. The main focus has been on electronic

spectroscopy, with the intervalence charge transfer (IVCT) transitions (1) and corresponding absorption bands being among the most conspicuous and theoretically challenging features of mixed-valent compounds [4,5].

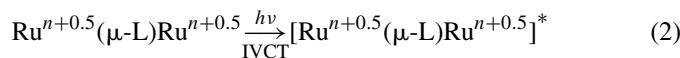


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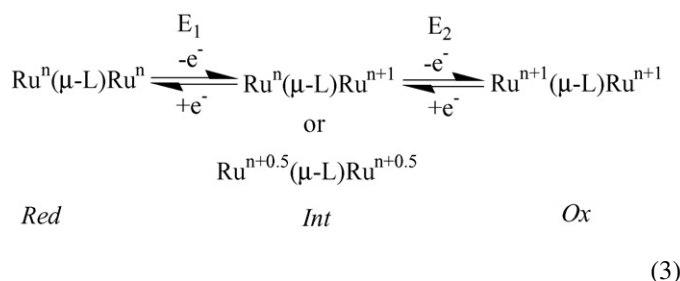
The IVCT designation has also been used for convenience in those symmetrical cases (2) where there is clear valence-averaging, i.e. when both the ground and excited states are electronically delocalized over both metal centers [2,5] on any reasonable spectroscopic time scale [6] (Class III according to Robin and Day [4]):



For a valence-localized situation (“Class II” [4a]) the classical Hush perturbation treatment [5a,c] led to a simple expression for the electronic interaction parameter which involves as essential factors the electron-transfer distance (geometrical or “spectroscopically effective” metal–metal distance) and the oscillator strength of the IVCT band. The latter is rarely reported, however; usually the molar extinction coefficients ϵ and bandwidths $\Delta\nu_{1/2}$ are provided for approximately Gaussian-shaped bands unless very special band shapes are encountered. In an extension of the original Hush approach, Creutz, Newton and Sutin have included formulations from the superexchange concept [18a] to assess the electronic interaction between bridged metals in mixed-valent compounds by using the often easier to determine metal-to-ligand or ligand-to-metal charge transfer spectral data (“CNS model”) [5d].

Just like the electrochemical parameters (cf. below), the absorption data are often significantly dependent on the environment (general and specific solvent–solute interactions, ion-pairing for the often highly charged species). Considering dipole moment changes it is evident that centrosymmetric valence-delocalized systems should exhibit smaller solvatochromism of the IVCT band than localized analogues with their built-in polarity, an argument which has even been taken as valid criterion for the Class II/Class III distinction [2a]. However, specific substrate–solvent interactions like hydrogen bonding may still lead to substantial solvent dependence of IVCT bands of clearly valence-averaged species [7], and the situation with faster thermal electron-transfer than the solvent reorganization has given rise to a new “Class II/III borderline” category [2d].

Another physical property immediately connected to the *stability* of mixed-valent intermediates [2b] is the comproportionation constant K_c according to (3)–(5) [2c,8].



$$K_c = \frac{[\text{Int}]^2}{[\text{Red}][\text{Ox}]} = 10^{\Delta E/59 \text{ mV}} \text{ at } 298 \text{ K}; \quad \Delta E = E_2 - E_1 \quad (4)$$

$$RT \ln K_c = nF(\Delta E) \quad (5)$$

Although the free energy of comproportionation is not only determined by the resonance exchange as delocalization parameter but also by contributions from electrostatic forces, ion-pairing, antiferromagnetic exchange, inductive effects and entropy (“statistical factor”) [2b,c,8,18a], the ΔE or K_c values have been “widely used”, often in an unreflected way, to describe “the extent of inter-metal communication between the metal centres” [9]. The variable (“sometimes unpredictable” [9]) dependence of redox potentials and their differences (and hence of K_c) on the solvent and on the counter-ions has been pointed out by D’Alessandro and Keene [9], following the ground-breaking work by LeSuer and Geiger [10]. Not surprisingly, higher charges lead to more pronounced effects from the medium. The case for standard conditions [9] in reporting E and K_c values is thus strongly advised in order to allow for reasonable comparison and to avoid the “danger of over-interpretation” [9]. For synthetic chemists, the positioning of a new compound relative to known systems is often more important than absolute numbers from rigorous theoretical treatment.

The prototypical Creutz–Taube ion **1**, for example, has $K_c \approx 10^7$ in various solvents and a major [2c,d], somewhat asymmetrical IVCT absorption band at about $\lambda_{\text{max}} \approx 1560 \text{ nm}$ with $\epsilon \approx 5000 \text{ M}^{-1} \text{ cm}^{-1}$ [1,2,11] (see Table 1). There are other, very weak IVCT transitions at still lower energies [2c,d]. Studies using additional spectroscopic methods pertaining to different time scales [6] such as EPR, Mössbauer, XPS, Stark or vibrational spectroscopy have also been used successfully to assess intramolecular electron exchange rates, the valence (de)localization, and the degree of electronic coupling for the Creutz–Taube ion [2,12] and for mixed-valent compounds in general [2,4b,6,13].

The inertness and general chemical stability of ruthenium in both the +II (4d⁶) and the +III (4d⁵) configurations [14] have largely contributed to the focus on these two states in mixed-valency research [2]. Following several reviews on diruthenium(II,III) chemistry with many listed examples, mostly containing bis-monodentate bridges [2], and an account [3] of efforts to expand the chemistry of the Creutz–Taube ion we intend to focus on the *role of the coordination mode of the bridging ligand* and the apparent contradictions between electrochemical and spectroscopic results for the metal–metal “interaction”. Several previous reviews [2c,i] and articles have suggested that certain ranges for K_c values or IVCT band intensities or widths are associated with Class II or Class III category. It is one purpose of this article to show that such generalizations are unwarranted and that correlations can only be drawn within specific kinds of coordinatively related molecular systems.

2. Results and discussion

2.1. Atom-bridged complexes

Although the focus of this survey lies on *molecule-bridged* mixed-valent diruthenium compounds there are many such com-

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