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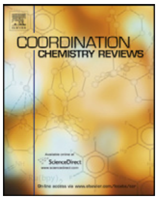

Review

Inter- or intramolecular electron transfer between triruthenium clusters: we'll cross that bridge when we come to it

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ABSTRACT

The purpose of this review is to examine the fundamental differences between intermolecular self-exchange vs. intramolecular ET in mixed-valence complexes based on similar triruthenium structural units. The role of orbital overlap between ancillary ligands of the electron donor and acceptor are considered in self-exchange reactions which are found to be strongly adiabatic and again in bridged mixed-valence systems. The method of infrared (IR) reflectance spectroelectrochemistry for the determination of extremely fast (10^{11}–10^{13} s^{-1}) ET rate constants is reviewed as a tool to provide quantitative information about the time scales of localization and delocalization. The role of internal vibrations of the bridging ligand in strongly delocalized mixed-valence ions is investigated by resonance Raman and IR spectroscopies. The role of solvent dipolar relaxation times in determining the rates of ultrafast intramolecular ET reactions is reviewed in the context of inorganic mixed-valence chemistry. Finally, the concept of Robin–Day Class II/III "borderline" complexes is considered, and a concise definition of the localized to delocalized transition is provided in terms of the relative contributions of external solvent and internal complex ion vibrational modes to ET.

1. Introduction

Electron transfer (ET) is not only the simplest reaction in the field of coordination chemistry, but also the most important as all life processes and many technologies depend on it. In this review, we consider 12 years of work on intramolecular electron transfer (ET) reactions within mixed-valence ions of the general type $[Ru_3O(OAc)_6(L)(CO)(\mu\text{-BL})Ru_3O(OAc)_6(L)(CO)]^-$ (L = pyridyl or isocyanide ligand; BL = 4,4′-bipyridine or pyrazine) [1–21]. There are two key concepts that we wish to discuss and illustrate with examples from our work. The first is the fundamental difference between intermolecular self-exchange and intramolecular electron transfer through a donor-bridge-acceptor assembly. The second concept is the localized to delocalized transition, the transition that occurs at the borderline between Robin–Day [22] Class II and Class III systems [23]. We will take the liberty of not presenting the work in a historical sequence, but will begin by considering some of our more recent work on electron self-exchange reactions of the ruthenium clusters of the type $[Ru_3O(OAc)_6(L)_2(CO)]$ (Fig. 1) which constitute "half" of the dimer of trimer mixed-valence ions (Fig. 12) [21]. Our intent here is to determine the rates of self-exchange, individual cluster reorganization energies, and general features that will shed light on the unusual intramolecular ET properties of the pyrazine-bridged mixed-valence ions that are based on the same structural and redox unit. We will then move on to consider these latter systems in which the electron donor and acceptor are covalently joined by a pyrazine or similar bridging ligand. We will review the importance

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of energetic alignment of donor-bridge-acceptor triad, the importance of bridging ligand modes of vibration as probed by resonance Raman and IR spectroscopies, and the role of solvent dynamics in controlling the rates and degrees of localization/delocalization in very rapidly exchanging Class II/III borderline systems.

2. Self-exchange—take the bridge or the tunnel?

Within the context of the Marcus–Hush theory of electron transfer (ET) [24,25], rates of electron self-exchange can be related directly to the total reorganization energy for ET, λ, and by the Marcus cross relation, to rates of intermolecular ET with other redox agents [26,27]. Here, we examine the self-exchange ET reactions of ruthenium clusters of the type $[Ru_3O(OAc)_6(CO)(L)_2]$ (Fig. 1) which constitute "half" of the dimer of trimer mixed-valence ions discussed in more detail later in this review. We will show examples of *inter*molecular electron exchange reactions that are best described as coupled systems that are strongly adiabatic.

The three different ancillary pyridine ligands used dictate the redox potentials of the clusters, as shown in Fig. 2. The redox events are typically discussed as metal cluster-based, with the reduction of the neutral complex to the monoanion at around −1500 mV vs. the ferrocene/ferrocenium couple, corresponding formally to the reduction of $Ru^{III}Ru^{III}Ru^{II}$ to $Ru^{III}Ru^{II}Ru^{II}$. As can be seen, the redox potential is sensitive to the identity of the ancillary pyridyl ligand (specifically the pK_a of the conjugate acid). An initial question then is how the intermolecular ET rate for electron exchange between the neutral and anionic species in solution depends on changes in the ancillary ligands.

This question was answered using a standard NMR kinetic study [28], in which the shifts and line broadening in ^1H NMR signals were examined as a function of the concentrations and mole fractions of the neutral and reduced clusters to determine rate constants for self-exchange. The mole fractions of diamagnetic neutral clusters and paramagnetic singly reduced clusters in solution were initially determined by IR spectroscopy, by integration of the $\nu(CO)$ bands for the neutral cluster (~1940 cm^{-1}) and the singly reduced cluster (~1900 cm^{-1}). Spectra for **1** in CD_2Cl_2 are shown in Fig. 3(a). The $\nu(CO)$ region for the mixed solutions was not coalesced and could be fit to two well resolved bands, giving an upper bound to k_{ET} of ~10^{10}–10^{11} s^{-1} M^{-1} [11]. However, the exchange was in the fast regime on the NMR timescale (where $k(C_{tot}) \gg 2\pi(\Delta\nu)$),

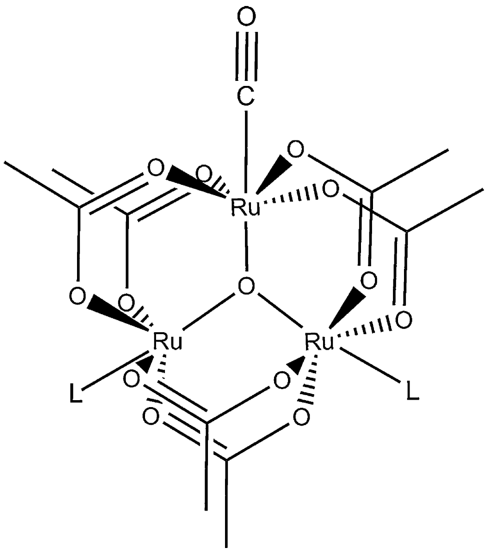

Fig. 1. The three clusters used in Section 1: **1**, L = 4-cyanopyridine (cpy); **2**, L = pyridine (py); **3**, L = 4-(dimethyl)aminopyridine (dmap) [21].

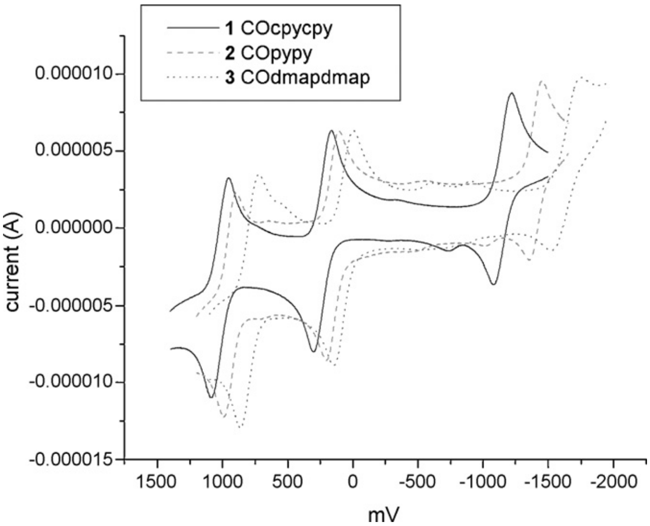

Fig. 2. Electrochemistry of ruthenium trimers with different pyridyl ligands in CH_2Cl_2 with 0.1 M TBAH, glassy carbon working, platinum wire counter, and Fc/Fc^+ reference electrodes [21].

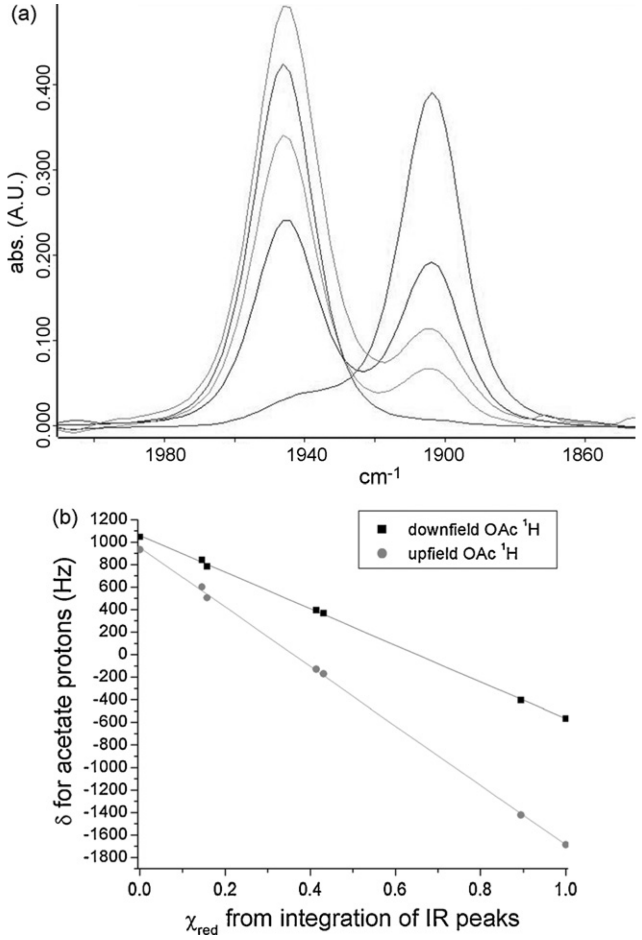

Fig. 3. (a) IR spectra of the $\nu(CO)$ region for **1** in CD_2Cl_2, with varying mole fractions, χ_{red}, of [red]/[ox]. (b) Plot of χ_{red} determined from integration of IR peaks vs. chemical shift of acetate protons [21]. The linear relationship confirms fast exchange on the NMR timescale.