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Review

Oxygen and hydrogen photocatalysis by two-electron mixed-valence coordination compounds

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Contents

Abstract

Two-electron mixed valency is a useful design concept for hydrogen and oxygen photocatalysis. As single-electron mixed-valence compounds react in one-electron steps, two-electron mixed-valence compounds may react in two-electron steps at the constituent redox sites, whether they are metal- or ligand-based. With the redox centers working in concert upon photoexcitation, two- and four-electron transformations are promoted along excited-state pathways. Such a strategy is ideally suited to the activation of small molecules. We describe the photochemistry for hydrogen and oxygen activation using two-electron mixed-valence complexes of three different motifs: (a) M^n–M^{n+2} bimetallic complexes, (b) tetrapyrrole macrocycles and (c) externally bridged di-iron(III) μ-oxo porphyrin dimers.

Keywords: Hydrogen; Oxygen; Photocatalysis; Valence; Multielectron; Solar; Proton-coupled electron transfer

1. Introduction

The activation and use of small molecules of energy consequence, including CO_2, N_2 and CH_4 in addition to H_2, H_2O and O_2, share basic chemical commonalities [1]. They are all *multielectron* processes [2–4]. Moreover, for the small

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molecules listed above, proton transfer must accompany electron transfer [5–14], as both *electron and proton inventories* need to be managed for successful small molecule activation [15–19]. Additionally, small molecule transformations confront sizable thermodynamic or kinetic barriers to *bond activation* that must be overcome from electronic excited states if an energy-storing catalytic cycle is to be closed.

Our research efforts have addressed the italicized research themes of the foregoing paragraph by expanding the reactivity of metal complexes in electronic excited states beyond conventional one-electron transfer. Much of the work has been devoted to the concept of two-electron mixed valency. The approach is straightforward: as single-electron mixed-valence compounds react in one-electron steps [20,21] two-electron mixed-valence compounds may react in two-electron steps at the constituent redox sites, whether they are metal- or ligand-based. This approach does not demand that each metal react in a concerted two-electron step, rather, it requires the one-electron mixed-valence species to be kinetically or thermodynamically unstable with respect to the two-electron species. In this manner, even if the primary photoevent involves single electron transfer, an ensuing redox event will be facile, thus driving net multielectron reactivity.

The types of two-electron mixed valency that we are currently investigating are represented schematically in Scheme 1: (a) bimetallic complexes that rely on ligand sets favoring a ground-state M^{n}–M^{n+2} species, which is stabilized relative to its comproportionated and symmetric $M^{n+1}\cdots M^{n+1}$ congener; (b) porphyrinogens that store two-electron equivalency in the framework of a macrocyclic ligand; and (c) M^{III}–O–M^{III} macrocycles tethered to a rigid spacer that upon excitation produce a two-electron mixed-valence metal-oxo intermediate, which is a reactive oxidant. In each case, the two-electron mixed-valence complex is the critical intermediate for promoting discrete two- and four-electron transformations. Recent results in areas (a)–(c) are described in detail below.

2. Two-electron mixed-valence bimetallic complexes

2.1. Hydrogen production using two-electron mixed-valence photocatalysts

The two-electron mixed-valence approach is ideally suited to manage the two-electron chemistry of hydrogen production and activation. Although the occurrence of authentic M^{n}–M^{n+2} compounds is uncommon [22], such complexes can be stabilized by ligand frameworks that juxtapose π-accepting groups directly adjacent to π-donating groups. One such construct is embodied by bis(difluorophosphino)methylamine (dfpma, $CH_3N(PF_2)_2$) and bis(bistrifluoroethoxyphosphino)methylamine (tfepma, $CH_3N[P(OCH_2CF_3)_2]_2$) ligand sets that place an amine bridgehead between two electron-deficient phosphines (PR^F_2) or phosphites ($P(OR^F)_2$). These diphosphazane ligands are distinguished by their ability to drive the internal disproportionation of binuclear $M_2{}^{I,I}$ cores to $M_2{}^{0,II}$ cores [23] for the metals rhodium [24,25] and iridium [26–28]. X-ray crystal structures reveal a pronounced asymmetry in the diphosphazane framework upon ligation to a bimetallic core [24]. The result is consistent with asymmetric donation of the amine bridgehead lone pair to the PR^F_2 bonded to M^{II}. With $M^{II} \rightarrow PR^F_2$ π-backbonding diminished, the PR^F_2 group acts as a σ-donor to stabilize the high-valent M^{II} metal center. Correspondingly, with the nitrogen lone pair electron density channeled away from the second neighboring PR^F_2 group, its strong π-accepting properties are maintained and hence M^0 is stabilized. In this manner, we believe that the dfpma and tfepma ligands accommodate the intramolecular disproportionation of $M_2{}^{I,I}$ to $M_2{}^{0,II}$.

The benefit of designing authentic two-electron mixed-valence complexes is the ability to effect multielectron redox chemistry among discrete molecular species. With the metals working in concert, two- and four-electron transformations are promoted along ground- and excited-state pathways. As shown in Scheme 2, hydrogen halides react with $Rh_2{}^{0,0}(dfpma)_3L_2$ ($L = PPh_3$) in discrete two-electron steps to afford the LRh^0–$Rh^{II}X_2$ and X_2Rh^{II}–$Rh^{II}X_2$ congeners, respectively [24]. An equivalent of H_2 is produced in each step. By incorporating the same $d\sigma^*$ excited state within the electronic structure of the LRh^0–Rh^0L, LRh^0–$Rh^{II}X_2$ and X_2Rh^{II}–$Rh^{II}X_2$ cores [29–32], interconversion among the series members may be accomplished by the elimination of halogen in two-electron steps [24,25]. The LRh^0–Rh^0L starting complex can be regenerated as long as a halogen trap is present, thus permitting the photocycle shown in Fig. 1 to be constructed [33]. In brief, a sacrificial photon removes an axial CO from the $Rh_2{}^{0,0}$ complex, opening a coordination site for HX attack (the axial site may also be opened thermally). Disappearance of the $Rh_2{}^{0,0}$ complex is accompanied by the formation of 1 equiv. of H_2 and the appearance of a blue species that eventually converts to the LRh^0–$Rh^{II}X_2$ complex. Photoactivation of the Rh^{II}–X bond enables the photocycle to be closed.

2.2. Hydrides related to two-electron mixed valence cores

Hydrogen elimination is facile and neither hydrido- nor hydrido-halide intermediates are observed during turnover of the photocycle shown in Fig. 1. With the goal of characterizing hydride species of two-electron mixed-valence cores and understanding their dihydrogen chemistry, we turned our attention to di-iridium complexes owing to the increased stability of third-row metal-hydride bonds relative to their second-row counterparts. Our findings, summarized in Fig. 2 for an $Ir_2{}^{0,II}$ core ligated by tfepma, establish that two-electron mixed-valence bimetallic cores are able to support hydrides and hydrido-halides, and that these species are of consequence to HX photocatalysis [26]. An especially surprising result is the facility with which H_2