

Valence Trapping in Mixed-Valent Quinone and Diimine Complexes

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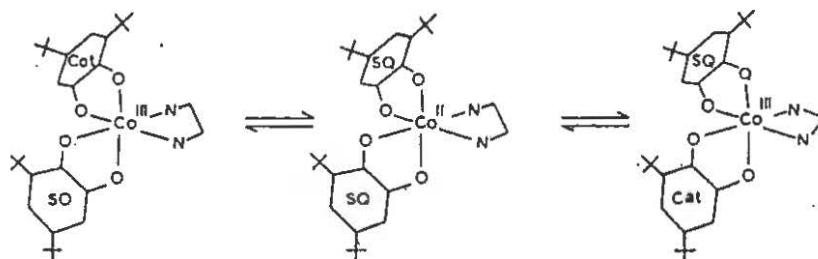
Introduction

A typical mixed-valence complex contains two or more metal centers with different oxidation states such as the Creutz-Taube ion, $([\text{Ru}(\text{NH}_3)_5]_2(\text{pyrazine}))^{5+}$. Coordination compounds exhibiting the mixed-valent ligands are less common. The so called "non-innocent" ligands, such as dithiolenes, quinones and diimines, may form mixed-valent complexes since they may exhibit more than one oxidation state [1]. Transition metal complexes with mixed-valent ligands can be prepared by either ligand-based redox reactions or metal-to-ligand charge transfer (MLCT) transitions.

The question of trapping or detrapping of a particular spin state in mixed-valent ligand complexes, including the MLCT species, with more than one equivalent non-innocent ligand has received considerable attention in recent years. Electron dynamics are affected dramatically by the nature of the ligands. Dithiolene complexes have been shown to be totally valence delocalized, which corresponds to class III in the Robin and Day scheme. For the mixed-valence quinone and diimine complexes, however, there is substantial evidence which allows them to be grouped in the Robin and Day II case, i.e., the electronic interaction between ligands is not strong. In such compounds the valence electron is trapped on one of the ligands.

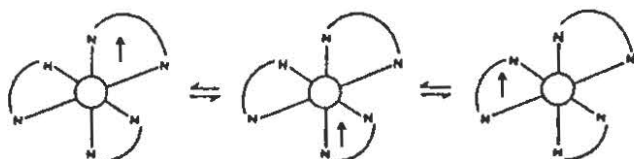
Metal Quinone Complexes

All mixed-valent quinone complexes show the behavior of electron trapped ligand systems [2], in which the electron resides in a single ligand orbital. Intramolecular interligand electron transfer may exist depending on the nature of both the metal center and the ligands. The X-ray structural data on $\{\text{Co}[\text{O}_2\text{-C}_6\text{H}_2(\text{t-Bu})_2]_2(\text{bpy})\}$ indicate that the two quinone ligands are in different oxidation states, one is coordinated as a semiquinone (DBSQ) and the other as a catecholate (DBCat); the cobalt is viewed on a diamagnetic d^6 center and the bipyridyl (bpy) ligand is not involved in the electron dynamics. The solid state magnetic moment is close to the value for $S = 1/2$. Interestingly, the magnetic susceptibility in solution produces a maximum value of $4.3 \mu_B$ at high temperature which suggests an equilibrium between a Co(II) high spin species $\text{Co}(\text{DBSQ})_2(\text{bpy})$ and the Co(III) low spin form found in the solid state. EPR and NMR data also verify the following equilibria in solution.



Metal Diimine Complexes

Transition metal complexes containing aromatic α -diimine ligands show an extended series of electroreductions [3] and multiple state emission [4]. The concept of a "spatially isolated redox orbital" has been used to explain the electron dynamics in the reduced products of d^6 metal tris-diimine complexes. For $[\text{Ru}(\text{bpy})_3]^{2+}$ and its analogues, the first electron resides in redox orbital localized on one of the three near degenerate and non-communicating orbitals. The EPR spectra of the one to three electron reduced species all give free electron g value with $S = 1/2$ [5]. The temperature dependent line-width broadening in the EPR spectrum for the one-electron reduced species suggests the existence of fast interligand electron hopping in which the thermal activation energy is about 1000 cm^{-1} . According to the Hush theory, the low limit of $E_{\text{op}}/E_a = 4$ is predicted for a strongly trapped system so that the optical excitation energy will be around 4000 cm^{-1} . This is confirmed by the IR region electronic spectrum which exhibits an IT band occurring at 4500 cm^{-1} [5a,6]. Cyclic voltammetry [7], resonance Raman, UV-vis [8], and NMR [9] spectral data also support this electron hopping model.



Finally, optically excited $[\text{Ru}(\text{bpy})_3]^{2+}$ has been assigned in terms of the excited electron is trapped on one bipyridyl ligand. Thus the species should be represented as $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{bpy}^-)]^{2+}$ [10]. The time-resolved resonance Raman spectra of this excited species show bands due to Ru-bpy and Ru-bpy⁻ moieties [11]. It is also found that the symmetry of the excited species is lower than the original D_3 $[\text{Ru}(\text{bpy})_3]^{2+}$ species in the ground state [12]. If the detrapped model were correct, the excited state should maintain the D_3 symmetry.

In summary, both mixed-valent quinone and diimine complexes show valence trapped behavior and intramolecular interligand electron hopping may occur via the metal center.

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