

Editorial

Electron spin aspects of Ru and V=O complexes for drugs

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Abstract

In the field of biology, drugs, and bioinorganic materials, magnetism or spin states may be an important physical viewpoint such as blood under magnetic field and magnetic controlled DDS. Magnetic role and detection of hybrid systems of metal complexes and proteins will be mentioned in this short review. From the viewpoint of pure physical chemistry, excited state changing spin state is important for photo-induced electron transfer especially for Ru complexes. In addition, redox active V=O complexes were also investigated as molecule based magnets, in which the numbers of unpaired electrons are essential. Finally, future perspective will be stated potential application of typical types of Ru or V=O complexes.

Keywords: Ru complex; V=O complex; electron spin; photo-induced electron transfer; magnetism.

Introduction

In the field of biology, drugs, and bioinorganic materials, magnetism or spin states may be an important physical viewpoint such as blood under magnetic field and magnetic controlled DDS. Magnetic role and detection of hybrid systems of metal complexes and proteins will be mentioned in this short review. From the viewpoint of pure physical chemistry, excited state changing spin state is important for photo-induced electron transfer especially for Ru complexes. Indeed, Ru complexes have been studied from the viewpoint of docking to DNA [1,2] and anticancer agents [3,4] for far. However, detailed factors such as redox (electron transfer) against biomolecules by central metal ions and molecular recognition for biomolecules by organic ligands were not clear, and detection or analysis should be carried out to reply such questions. Herein, we focused on how to arrive back physicochemical factors to develop biological functions reasonably.

Excited state of Ru complexes in electron transfer

As for electron transfer of Ru complexes having pi-conjugate ligand systems, Ohno and co-workers have elucidated systematically. Photo-induced electron transfer reactions [5] of Ru(II) complexes basically depends on life-time (phosphorescent quenching [6, 7]) of (triplet) photo-excited states by metal-to-ligand charge transfer transitions [8], because (not only mononuclear but also dinuclear [9]) Ru(II) (or mixed valence states Ru(II/III) [10]) exhibit suitable redox potentials and light absorption potentially. Not only solutions (mass spectroscopy [11, 12] was also used for detection of ligand substitution) but also crystalline states [13] were target of such studies. Electron transfer between Ru and other metal ions are possible for intramolecular Ru-Rh systems [14] as well as intermolecular Ru-Co [15-18] and Ru-Os [19] systems.

Comparison with V=O complexes as potentially redox catalysts

As a future perspective, we would like to compare with V=O (oxovanadium) (VI/V) complexes, which may exhibit redox, magnetic and catalytic behaviors similar to Ru(II/III) complexes. As a mediator for electron transfer between the biofuel cell electrode and laccase, two oxovanadium complexes were used in our previous study (Figure 1) [20]. Besides the literature preparation procedures of diamagnetic V(V) d0 and paramagnetic V(IV) d1 complexes [21, 22], respectively, their valences in solutions electrochemically characterized with cyclic voltammetry were prepared by heating solutions to 363 K after isolating precipitates. However, these complexes exhibited ESR signals in the solid state at 300 K, and the effective magnetic moments at 300 K were 1.03 and 1.64 B.M., respectively, indicating middle of S=0 (V(IV) d0) and S=1 (V(V) d1) valence states. The results suggested both oxovanadium complexes are easy to occur redox reactions and the resulting precipitates were mixture of V(V) and V(IV) complexes. Furthermore, magnetic properties of laccase from *Trametes versicolor*

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having trinuclear active type 2 and type 3 Cu sites and a type 1 Cu site accepting electron from a mediator has been reported so far [23].

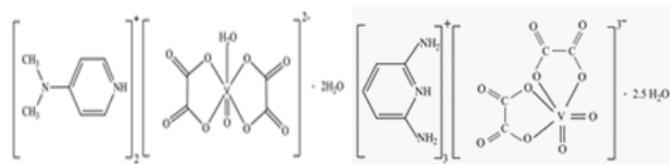


Figure 1: Two V=O complexes investigated from the viewpoint of both magnetism and redox properties with metalloproteins.

For a long time, Tsuchimoto *et al.* have reported V=O complexes for their redox behavior (oxovanadium (VI) (in many cases) or (V) [24]), reaction with oxygen [25], magnetic properties in the solid state [26, 27], thermal behavior, stereochemistry [28], and solid-state isomerization [29] based on their crystal structures. They mentioned that “The solution chemistry of oxovanadium complex attract the interest of many researchers these days because of their catalytic properties and biological relevance” and “Oxo-bridged metal complexes which include a unit structure of magnetic metal oxides play an important role in transition metal chemistry. However, little is known about other metallocomplexes with doublet spin states such as the d1 configuration”. In this way, catalytic and biological functions have reasons to be achieved. It is based on a static electronic structure. The same is true for other metal ions. This is the common-sense view of coordination chemistry.

Conclusions

Coordinating compounds aimed at biological function will be driven by redox reactions, unless they use a mechanism of shape-based inhibition of the target protein. They are usually synthesized using a vacuum line. Preliminary characterization of metal complexes is measured using NMR and infrared spectroscopy. Redox properties are measured by voltammetry, which, if confirmed by UV-Vis spectro-electrochemistry, are investigated in conjunction with electronic properties. Molar conductivity measurements help determine neutral or cationic species in solution. The solid structure of the metal complex is elucidated by single crystal X-ray diffraction. However, the kinetics of unstable coligand substitution of metal complexes with biological reagents will be investigated using the UV-Vis spectrophotometry, albeit the more essential physicochemical properties and their physicochemical properties should be also investigated and discussed to establish a molecular design strategy. That is “spin” really? In this short review, we considered the possibilities of “spin” as supporting methods.

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