

Redox reactions of an Mo(V) tetrasulfophthalocyanine

G. Ferraudi*, T. Nyokong[†] and M. Feliz^{††}

Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556 (USA)

M. Perkovic and D.P. Rillema

Department of Chemistry, University of North Carolina, Charlotte, NC 28223 (USA)

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Abstract

The preparation of an Mo(V) tetrasulfophthalocyanine and some of its thermal and photochemical reactions have been investigated in this work. Electrochemical processes have been followed by means of the UV-Vis spectral changes and compared with those observed in flash photolysis. Mo(IV) and Mo(V)-ligand-radical species are common intermediates of the electrochemical and photochemical reactions. In 254 nm irradiations of the Mo(V) tetrasulfophthalocyanine in aqueous solutions of 2-propanol, the macrocycle can be photohydrogenated and the product of the photolysis can be reoxidized with O₂ back to the parent complex.

Key words Electrochemistry, Molybdenum complexes; Macrocyclic ligand complexes; Phthalocyanine complexes

Introduction

A number of examples of metal ion catalyzed hydrogenation and dehydrogenation reactions of macrocyclic ligands have been reported in the literature [1]. Common to these processes, is the participation of coordination complexes with metal ions in unstable oxidation states. For example, Me₄[4]4,11-dieneN₄ coordinated to Fe(II), eqn. (1), undergoes a dehydrogenation reaction which is mediated by an Fe(III) complex.

The same macrocycle coordinated to Ni(II) undergoes dehydrogenation, eqn. (2), or hydrogenation, eqn. (3), reactions under appropriate chemical conditions.

If such ligand hydrogenation/dehydrogenation processes are made labile and reversible by coordination of the macrocycle to a given metal ion, the complex may have a number of practical applications, e.g. as a catalyst of redox reactions and/or in cycles for the storage of solar energy [2]. The reversibility exhibited by some redox reactions involving phthalocyanine complexes is appealing from such a standpoint. Several literature reports about the preparation of molybdenum phthalocyanines have shown that compounds of Mo(IV) and Mo(V) exhibit sufficient thermal stability for their isolation as pure products [3–5]. There is little information, however, about the thermal and photochemical reactivity of the Mo macrocycles in general and phthalocyanines in particular [6]. In this work, we report experimental observations about the reversible thermal and photochemical hydrogenation of the Mo(V) macrocycle.

*Author to whom correspondence should be addressed
[†]Visiting fellow from the National University of Lesotho.
^{††}On leave from CICBA

