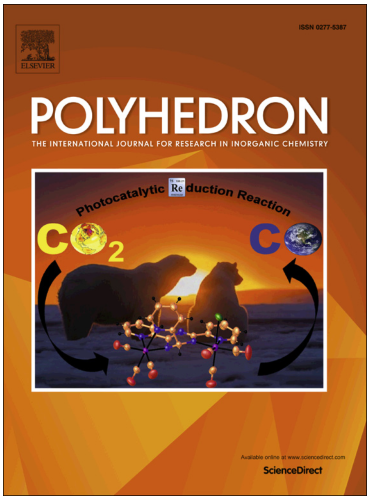

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Synthesis and Crystal Structures of Transition Metal Ion Complexes of Di(2-thienyl)imide

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Keywords: di(2-thienyl)imide; metal complexes; crystal structures; polymer; metal ion uptake and release

Abstract

Di(2-thienyl)imide, **1**, has been shown to chemically polymerize, and, if metal complexes of 1 could be synthesized, the polymer could have potential applications as an ion sensor and environmental remediation agent. As a first step towards this goal, di(2-thienyl)imide is shown to form complexes with Mn (II), Co (II), and Zn (II) perchlorates. The complexes of Mn^{2+} and $Co^{2+}$are isostructural with two di(2-thienyl)imide ligands in equatorial positions and two perchlorate ions axial. The Zn^{2+} complex has two water molecules in the axial positions and the thiophene rings in the two equatorial ligands are tilted in the same direction from the median plane due to intra- and intermolecular contacts. The crystal structures and infrared spectra, as well as an improved synthesis and polymerization of di(2-thienyl)imide, are reported and discussed.

1. Introduction

Di(2-thienyl)imide, **1**, was recently prepared [1] in low yield and attempts were made to polymerize this monomer electrochemically. No polymerization occurred unless a large amount of catalytic bithiophene was added to the electrolyte; the copolymer that formed contained about 12% of **1**. If metal ions bind to the polymer *via* the imide function, the material could have applications as a metal ion sensor and an environmental remediation agent by virtue of electrochemically controlled uptake and release (Scheme 1). Although many coordinating groups have been attached to conducting polymers as agents to bind metal ions in metal ion sensor applications as detailed in a recent review [2, 3], fewer systems involving a coordinating group as part of the thiophene conducting polymer backbone itself have been reported [3-7]. A pertinent example involves the imide analog, 1,3-propanedione, in the thiophene chain which optical evidence indicates does bind metal ions by anionic-cationic interaction [8]. Other related materials are an *alt*-pyridine-imide oligomer [9] and imide-urea structures [10] which were synthesized for their hydrogen bonding capabilities; however, coordination with metal ions was not investigated. A number of polymers containing N-substituted cyclic imides has been prepared but these do not have metal-ion binding capability through the imide function [11]. A system involving the use of overoxidized polypyrrole, containing pendant carboxylate and sulfonate substituents, has been used as a solid-phase extraction media [12]. Electrochemical switching was employed to extract and desorb selected alkaline earth metal ions as well as Ni^{2+} and Cd^{2+} [12]. Polypyrrole has been used to remove heavy metal ions from wastewater by a counterion effect which releases the ions on