



Research paper

Synthesis and characterization of complexes formed by transition metal ions with thiophene imides as potential precursors to metal ion uptake and release agents



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ABSTRACT

It was found that methyl-2-thienylimide (**L**₁), C₄H₃SC(O)NHC(O)CH₃, could act as a ligand and combine with metal(II) perchlorates (Ni²⁺, Mn²⁺, and Co²⁺) to produce complexes for potential use as metal ion uptake and release agents in polymer form. Methyl-3-thienylimide (**L**₂) formed a similar complex with Co²⁺. The synthesis and structures obtained from single crystal X-ray diffraction data are reported. The carbonyl groups in the ligands are *cis/trans* with respect to the N-H group in the solid state but are necessarily *trans-trans* in the complex. The ligands are bidentate, forming bonds to the metal ions through the imide oxygen atoms; the imide ligands are protonated. The cobalt and nickel complexes have two bidentate ligands in the equatorial positions and two water molecules in the apical positions with the ligands *cis* to each other in the case of methyl-2-thienylimide while they are *trans* in the cobalt complex formed by methyl-3-thienylimide. The manganese complex is seven coordinate with three bidentate ligands and one water molecule. Significant hydrogen bonding is present in all of the complexes leading to the formation of 2D networks in two cases and an infinite chain in one. IR, and UV–Visible spectroscopy along with elemental analyses are also presented.

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1. Introduction

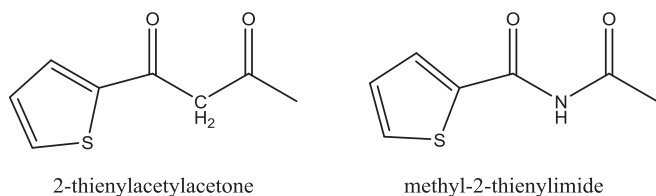
In a previous paper [1], we reported on the preparation, and structural characterization of a series of alkyl-3-thienylimides as well as on their electrochemistry. We had observed that the imide function is an electronic analog of acetylacetone which is often used as a textbook example of a chelating group which coordinates a wide variety of metal ions [2]. Scheme 1 shows the thiophene derivative of acetylacetone and acetylacetone. The acetylacetone moiety in 2-thienyl(trifluoroacetyl)acetone has been used widely as a taggant in biochemical systems [3]. A variety of transition metal complexes, mostly of iron and copper, has been prepared with neutral imide ligands containing both coordinating nitrogen (from associated rings) and oxygen from the imide moiety [4], but only a relatively small number of bidentate acyclic imide metal ion complexes has been reported. These involve complexation of alkali and alkaline earth metal ions [5] and various transition metal ions [6,7] with diacetamide as well as a chain polymer analogue formed by N,N,N',N'-tetra-acetyl-1,4-diaminobutane with selected first row transition metal ions [8]. Three reports [9–11] of complexes

formed by simple acyclic imide anions with transition metal ions have appeared, but to our knowledge no complexes involving transition metal ions with a simple neutral imide ligand of the form RC(O)N(H)C(O)R' where R is thiophene have been reported. It was thus of interest to determine whether the imide group in both methyl-2- and methyl-3-thienyl imides would chelate metal ions. If this could be demonstrated, our long term interest would be to polymerize the 3-substituted thiophene or incorporate the methyl-2-thienylimide and methyl-3-thienylimide monomer in a conducting polymeric material. These polymers could serve as metal-ion uptake and release materials which might be directed by an electrochemical signal (Scheme 2). Such chemistry could have potential applications in environmental remediation [12], charge storage devices [13], and biochemical systems [14].

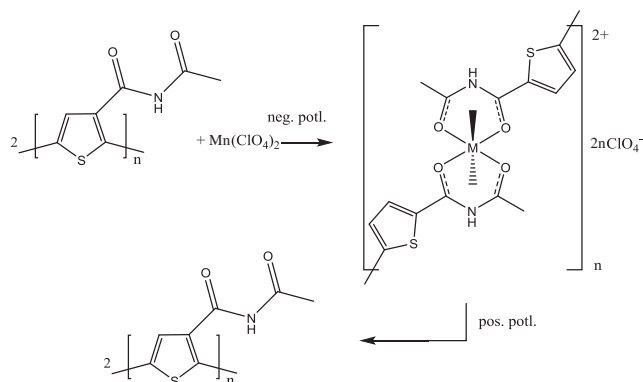
Since the starting material, 2-thiophenecarboxamide, is readily available, methyl-2-thienylimide was used as the preliminary basis for our studies (Scheme 3), and most of our current work has been carried out using this ligand as a test case recognizing that similar chemistry would most probably occur for the methyl-3-thienylimide. In this paper we report on the successful complexation of Mn²⁺, Co²⁺, and Ni²⁺ by methyl-2-thienylimide and the complexation of Co²⁺ by methyl-3-thienylimide demonstrating the feasibility of this approach. The single crystal X-ray structures as

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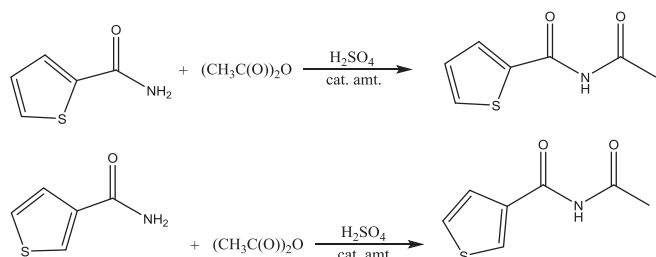
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Scheme 1. 2-Thienylacetylacetone and methyl-2-thienylimide.



Scheme 2. Anticipated electrochemical uptake and release of metal ions.



Scheme 3. Synthesis of methyl-2-thienylimide (**L1**, top) and methyl-3-thienylimide, (**L2**, bottom).

well as the infrared and visible spectra of the complexes are discussed.

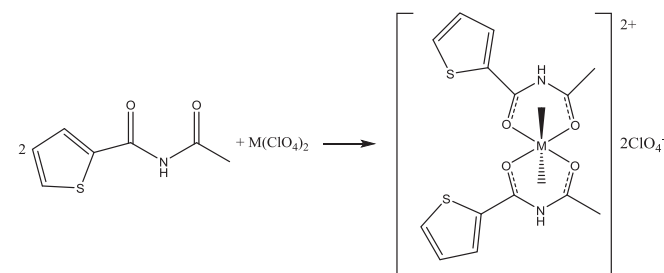
2. Results and discussion

2.1. Synthesis

Methyl-2-thienylimide (**L1**) was synthesized initially in a yield of almost 50% by microwave irradiation of the reactants for three minutes. The previously reported method for the synthesis of methyl-3-thienylimide (**L2**) gave a better yield of methyl-2-thienylimide (68%) [1] but required two hours of reflux. Methyl-2-thienylimide had been previously synthesized [15,16], but the structure had not been determined. Formation of the complexes resulted upon mixing solutions of the metal perchlorate with those of the ligands (Scheme 4). In some cases slow evaporation of the solvent was necessary to grow crystals suitable for X-ray analysis; in others, the crystals grew from the undisturbed solution. Some trials resulted in precipitation of powders.

2.2. Crystallography

Both ligands **L1** and **L2** form monoclinic crystals in space group $P2_1/c$ (#14). Both molecules crystallize in the *cis-trans* configuration (with respect to the NH function) with the formation of



Scheme 4. Formation of methyl-2-thienylimide (**L1**) complexes of (a) Ni^{2+} and Co^{2+} (b) Mn^{2+} .

intermolecular hydrogen-bonds through the N–H hydrogen atom on one molecule and the carbonyl oxygen atom adjacent to the methyl group on another molecule to form dimers. Such dimers have been observed in other acyclic imides [17]. Since the structure of **L2** has been described previously, **L2** will not be discussed here but Fig. 1 shows the thermal ellipsoid plots for both molecules. Selected data for **L1** and complexes **1–4** are presented in Tables 1–3. Molecular plots and packing diagrams are presented in Figs. 1–5. The C=O bond distances in **L1** are 1.218(1) and 1.222(1) Å, the C–N distances are 1.384(2) and 1.393(1) Å, and the C–C distances are 1.494(2) Å (methyl) and 1.470(2) Å (2-thienyl). **L2** has similar bond distances [1]. Single crystal X-ray structures of diacetamide [18,19], acetylbenzamide [20], isobutrylbenzamide [21], dibenzamide [22], and dipivalamide [23] have been reported and the interatomic distances listed above are similar with allowance for differences in the substituents.

Complex **1** crystallizes in the triclinic system, space group $P-1$ (#2) with one $[\text{Ni}(\text{C}_7\text{H}_7\text{NO}_2\text{S})_2(\text{H}_2\text{O})_2]^{2+}$ cation and two perchlorate ions per asymmetric unit. The bidentate ligands of the cation occupy equatorial positions, with the thiophene rings *cis* to each other, and each water is bonded to the metal ion through oxygen. The nitrogen atom is protonated, and the neutral ligand undergoes hydrogen bonding through the N–H hydrogen atom with two perchlorate anions. Two water molecules are *trans* to each other in the apical positions and each water is also hydrogen-bonded to two perchlorate ions. One of the perchlorate ions is disordered with a single (fully occupied) oxygen atom serving as a pivot point for two alternate (83/17%) orientations of a ClO_3 group. The average O=C bond distance for **1** is 1.234 (2,4,7,4) Å (the four numbers in parentheses are the RMS value of the ESD for an individual datum, the mean and maximum deviations and the number of individual values used to determine the average value). This bond lengthening is expected for coordination of the metal ion by oxygen. The average C–N bond length is 1.380(2,6,13,4) Å while that for the ligand is 1.389(2,4,5,2) Å; the bond shortening would also be expected owing to greater delocalization over the —O—C—N—C—O— system. The carbonyl-carbon to methyl-carbon bond distances are essentially unchanged within the measurement error limits, but the carbonyl-carbon to thiophene-carbon distance decreases from that in the free ligand (1.470(2) to 1.455(3,1,1,2) Å) probably as a result of extended resonance over the C—C bond in the complex. Bond lengths in acetylbenzamide [20] as a ligand compare well with methyl-2-thienylimide, but the only crystal structure of a metal ion complex (CCDC and Scifinder) was that of a tetrahedral metal silver(I) complex containing one acetylbenzamide ligand and two phosphine ligands which is not relevant for a direct structural comparison [24]. A low precision crystal structure of diacetamide is available, but only the crystal structure of its complex with Ba^{2+} has been reported [5d,5e]. The complex involved five bidentate diacetamide molecules and the precision was such that bond distance changes between the ligand and the complex were almost negligible. A useful comparison is with

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