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Synthesis, structure and supramolecular features of cobalt(III) and cobalt(II) complexes, $[CoH_xL](ClO_4)_y$ ($x = y = 3$, 2, 1.50, 1.45, 1 and 0 and $x = 3$, $y = 2$) of a triprotic imidazole containing Schiff base ligand. Effect of protonation state on supramolecular structure

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ABSTRACT

Aerial reaction of cobalt(II) perchlorate with $H_3(1)$ {$H_3(1)$ is the tripodal ligand derived from the condensation of tris(2-aminoethyl)amine with three equivalents of 4-methyl-5-imidazolecarboxaldehyde} in acidic methanol results in isolation of both the orange $[CoH_3(1)](ClO_4)_2$ (trace) and red $[CoH_3(1)](ClO_4)_3$ (2 pseudopolymorphs). An analogous reaction in methanol gives $[CoH_2(1)](ClO_4)_2$. Reaction of $[CoH_2(1)](ClO_4)_2$ (generated in situ) with aqueous sodium hydroxide gives $[CoH(1)](ClO_4)$ (two pseudopolymorphs) and a trace amount of $[CoH_{1.45}(1)](ClO_4)_{1.45}$. Reaction of $[CoH_3(1)](ClO_4)_3$ with 1.5 equivalents of hydroxide gives $[CoH_{1.5}(1)](ClO_4)_{1.5}$. Reaction of $[CoH(1)](ClO_4)$ with methanolic potassium hydroxide in acetonitrile gave [Co(1)] (two pseudopolymorphs). Complexes were characterized by EA and IR if available in sufficient amounts. All ten complexes were structurally characterized and their metrical parameters are consistent with a high spin cobalt(II) for $[CoH_3(1)](ClO_4)_2$ and low spin cobalt(III) for all of the cobalt(III) complexes. $[CoH_3(1)](ClO_4)_2$ and one polymorph of $[CoH_3(1)](ClO_4)_3$ dimerize by hydrogen bonding through three perchlorate anions. $[CoH_2(1)](ClO_4)_2$ and one of the pseudopolymorphs of $[CoH(1)](ClO_4)$ form intermolecular imidazole-H$\cdots$imidazolate hydrogen bonds resulting in hetero and homochiral 1D zig-zag chains, respectively. $[CoH_{1.5}(1)](ClO_4)_{1.5}$ forms a tetrahedral array of octahedral cobalt complexes held together by intermolecular imidazole-H$\cdots$imidazolate hydrogen bonds. $[CoH_{1.45}(1)](ClO_4)_{1.45}$ forms a hexameric structure with a large central channel containing solvent and perchlorate anions. $[CoH(1)](ClO_4)$ and both polymorphs of [Co(1)] form no intermolecular imidazole-H$\cdots$imidazolate hydrogen bonds but do exhibit extensive hydrogen bond formation with water.

1. Introduction

Previous work in this laboratory [1] and others [2] has examined metal complexes of the Schiff bases formed from the reaction of tris-(2-aminoethyl)amine (tren) or analogues with various imidazolecarboxaldehydes (Fig. 1.). These ligands, H_3L, are important due to their ability to bind to metals in different oxidation states, promote spin crossover and form hetero and homochiral supramolecular complexes [3].

The formation of supramolecular complexes of these triprotic ligands is achieved by the selective and partial removal of the imidazole hydrogen atoms to give a $[MHxL]^y$ complex. These partially deprotonated complexes have x hydrogen bonding donors and $3 - x$ hydrogen bonding acceptors and can polymerize to give a wide variety of supramolecular assemblies of differing topologies. The most commonly studied supramolecular assemblies are the hemi-deprotonated complexes, $\{[FeH_{1.5}L]^{x+}\}_n$ ($x = 1.5$ or 0.5, $H_3L = H_3(2)$ or $H_3(3)$), prepared by reacting $[FeH_3L]^{2+/3+}$ with [FeL] or by reacting $[FeH_3L]^{2+/3+}$ with 1.5 equivalents of base [3]. Extensive hydrogen bonding occurs in these systems as each parent complex has either three donor or three acceptor sites. The resulting supramolecular complexes exhibit 2D sheet structures. Similar structures are observed with cobalt(III), $\{[CoH_3(2)][Co(2)]\}(ClO_4)_3$ or $\{[CoH_3(3)][Co(3)]\}(ClO_4)_3$ [4].

It is possible in principle to form complexes of H_2L^- and HL^{2-} with either a M(II) or M(III) but production of all possible species is hampered by the fact that the products at an intermediate state

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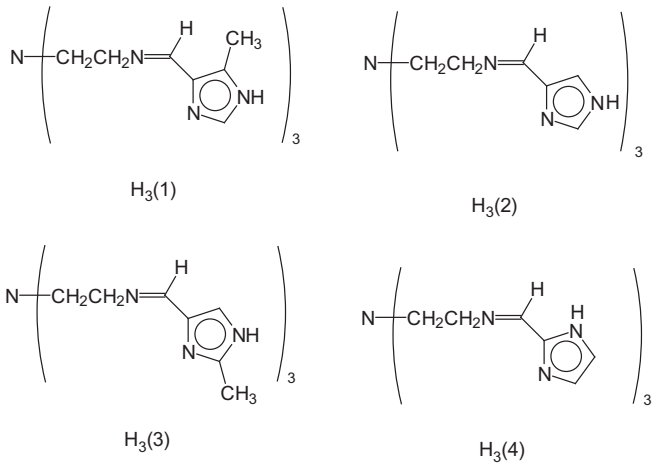

Fig. 1. Schiff base ligands formed between tren and imidazolecarboxaldehydes.

of protonation may be difficult to produce in a rational manner and the products of one oxidation state may be unstable under the reaction conditions. Recently rational synthesis of $[CoH_2(4)](ClO_4)_2{\cdot}H_2O$ and $[FeH(4)]ClO_4{\cdot}CH_3CN$ [5] were achieved through a combination of acid base and redox chemistry. The coupling of proton transfer at a coordinated ligand with a metal-centered electron transfer (proton coupled electron transfer, PCET) [6] was successful for these systems but cannot be guaranteed to produce any intermediate protonation state for a specified metal/ligand combination. Another literature example documenting the production of a single partially deprotonated complex is the iron(II) complex, [FeH(4)] [7] (hexagonal supramolecular assembly), prepared in mg quantities for XRD analysis but not otherwise characterized.

The most important feature of the supramolecular complexes is the topology, which is determined by the protonation state of the ligand and the space group. An examination of the structures of all protonation states of the cobalt complexes of $H_3(1)$ was carried out to survey the topologies. The structures of the perchlorate salts of $[CoH_3(1)]^{2+}$, $[CoH_3(1)]^{3+}$ (2 pseudopolymorphs), $[CoH_2(1)]^{2+}$, $[CoH_{1.5}(1)]^{1.5}$, $[CoH_{1.45}(1)]^{+1.45}$, $[CoH(1)]^{2+}$ (2 pseudopolymorphs), and [Co(1)] (2 pseudopolymorphs) are reported. Pseudopolymorphs are polymorphs that differ in the amount or type of solvent in the lattice [8]. These complexes exhibit homochiral dimeric, linear 1D zig zag homo and heterochiral chains, homochiral tetrahedral and heterochiral hexagonal topologies.

2. Experimental

2.1. General

Elemental analyses were determined by MHW Laboratory, Phoenix, AZ. ESI-MS were obtained by HT Laboratory, San Diego, CA. Tris(2-aminoethyl)amine, 4-methyl-5-imidazole-4-carboxaldehyde, cobalt(II) perchlorate hexahydrate, methanol, dichloromethane, acetonitrile, 0.10 M aqueous hydrochloric acid, 0.10 M aqueous sodium hydroxide and .10 M methanolic potassium hydroxide were obtained from Aldrich. Neutral alumina and sodium perchlorate were obtained from Fisher scientific. IR spectra were obtained as KBr pellets on a Perkin–Elmer 1600 FT IR spectrometer.

2.2. Syntheses

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

2.2.1. Synthesis of $[CoH_3(1)](ClO_4)_3$ and $[CoH_3(1)](ClO_4)_2$

Tren (0.250 g, 1.71 mmol) and 4-methyl-5-imidazolecarboxaldehyde (0.565 g, 5.14 mmol) were mixed in methanol (50 mL) and the mixture was refluxed for ten minutes to give a clear yellow solution. A solution of $Co(ClO_4)_2{\cdot}6H_2O$ (0.626 g, 1.71 mmol) in methanol (30 mL) was added. The mixture immediately turned orange. The reaction mixture was split into two halves (please see Section 2.2.2 for treatment of the second half). Aqueous hydrochloric acid (0.10 M, 8.55 mL, 0.855 mmol) was added to one half. The solution was left to stand and after seven days orange-red crystals (0.277 g, 42%) were removed by filtration. IR absorptions were observed at 3300 cm^{-1} for the imidazole N–H stretch, at 1637 cm^{-1} for the imine bond and at 1107, 1088 and 624 cm^{-1} for absorptions of perchlorate anion. Microscopic examination of the initial reaction product showed small amounts of pinkish orange hexagonal crystals, which were removed manually. These were not produced in sufficient quantity for more detailed analysis but were satisfactory for single crystal analysis. These orange hexagonal crystals were shown to be $[CoH_3(1)](ClO_4)_2$ and exhibited IR peaks at ~3300 (N–H), 1640 cm^{-1} (imine) and ~1100 and 624 (perchlorate). Elemental analysis of the reaction product found: 30.57, C; 3.78, H; 16.48, N. $[C_{21}H_{30}CoN_{10}](ClO_4)_3{\cdot}3H_2O$ requires 30.25, C; 4.35, H; 16.80, N%. Some diffraction quality crystals (orthorhombic form) were obtained directly from the reaction mixture. Recrystallization of a portion of the sample from a methanol/propanol mixture afforded a few dark red (rhombohedral) crystals which gave imidazole absorptions identical to those of the orthorhombic form given above.

2.2.2. Synthesis of $[CoH(1)](ClO_4)$ (orthorhombic $Pna2_1$ and Pbca forms)

Aqueous sodium hydroxide (0.10 M, 17.0 mL, 1.70 mmol) was added to the other half of the reaction mixture described in Section 2.2.1. The reaction mixture darkened to a deeper red immediately and the solution was left to stand. After seven days very thin orange brown hair like crystals were removed by filtration (0.395 g, 80% yield). An absorption corresponding to the imine bond appears in the IR spectrum at 1635 and 1596 cm^{-1} and absorptions of perchlorate at 1089 and 623 cm^{-1}. Elemental analysis for $[C_{21}H_{28}CoN_{10}](ClO_4){\cdot}0.5CH_3OH$ requires: 43.41, C; 5.08, H; 23.54, N. Found: 43.85, C; 5.39, H; 23.75, N%. Recrystallization of this complex from methanol afforded orange needles of $[CoH(1)](ClO_4){\cdot}2H_2O$ (orthorhombic $Pna2_1$) as the dominant form which gave two imine absorptions in the IR as provided above. Microscopic examination of the bulk methanol recrystallized form revealed the presence of trace amounts of other products that differed in the level of protonation, $[CoH_{1.5}(1)](ClO_4)_{1.5}$ (rhombohedral, $R3c$), $[CoH_{1.45}(1)](ClO_4)_{1.45}{\cdot}3H_2O$ (trigonal $P\bar{3}$), and $[Co(1)]{\cdot}3.14H_2O$ (monoclinic, $C2/c$). None of these products were produced in sufficient amounts from this procedure by characterization by means other than diffractometry. However both $[CoH_{1.5}(1)](ClO_4)_{1.5}$ (see Section 2.2.3) and [Co(1)] (see Section 2.2.5) were produced by other procedures that isolated these complexes as the sole product and IR data is provided in Sections 2.2.3 and 2.2.5. Recrystallization of the initial hair like needles ($[CoH(1)](ClO_4){\cdot}2H_2O$ orthorhombic $Pna2_1$ form) from ethanol afforded another pseudopolymorph, $[CoH(1)](ClO_4){\cdot}EtOH$ (orthorhombic $Pbca$) which also exhibited two imine absorptions as discussed above.

2.2.3. Synthesis of $[CoH_{1.5}(1)](ClO_4)_{1.5}$

An aqueous solution of sodium hydroxide (0.10 M, 2.70 mL, 0.270 mmol) was added to a solution of $[CoH_3(1)](ClO_4)_3$ (0.140 g, 0.180 mmol) (from Section 2.2.1) in boiling methanol (50 mL) in a Erlenmeyer flask. The solution darkened slightly and began to produce large orange cubic crystals within a day. These