Proton reduction using cobalt glyoximes with isothiocyanate and aniline axial ligands

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ABSTRACT

Cobaloxime model complexes containing aniline derivatives and isothiocyanate as the axial ligands $Co(dmgH)_2XY$ (dmgH = dimethylglyoxime, X = NCS, Cl and Y = aniline, pyridine) have been synthesized and used as proton reduction catalysts. Using acetic acid as the proton source in acetonitrile, cyclic voltammetry studies have shown that these complexes are comparable to the well-known $Co(dmgH)_2(pyridine)Cl$ complex as a potent catalyst in terms of the overpotential and catalytic efficiency of proton reduction. In particular, we have shown that aniline derivatives can be used as possible pyridine alternatives in cobaloximes in our continuing search for an even more efficient proton reduction catalyst.

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1. Introduction

There has been much research carried out on the use of renewable energy resources to replace fossil fuels. One of the most studied systems is the generation of hydrogen gas from photochemical or electrochemical proton reduction catalyzed by earth-abundant transition metal complexes [1]. A class of such hydrogen evolution electrocatalyst is cobaloxime complexes $Co(dmgh)_2XY$ with the bidentate dimethylglyoxime (dmgH) or its derivatives as the equatorial ligands. The commonly used axial ligands X and Y are acetonitrile, pyridine, water and chloride [1–5].

Conolly and Espenson first showed that difluoroboryl-dimethyl-gloxime ($dmgBF_2$) analogues of cobaloxime are able to catalyze the reduction of strong acids [6]. More recently, much work has been focused on varying the electronic properties of the ligands and how they influence the overpotential of proton reduction [4]. In particular, pyridine-containing cobaloximes have been shown to catalyze proton reduction efficiently [7].

In this work, we have explored the use of aniline derivatives (NH_2Ar) and isothiocyanate (NCS) as replacements for pyridine and chloride as the axial ligand in cobaloximes while retaining dimethylglyoxime as the equatorial ligand (Scheme 1). The preparation and structural characterization of these complexes will be described. The overpotential of proton reduction catalyzed by these complexes will be evaluated via cyclic voltammetry with acetic acid as the proton source in acetonitrile. Using the previously-studied $Co(dmgh)_2(pyridine)Cl$ as the comparison [8], our study shows that these complexes have comparable proton reduction efficiency, hence increasing the repertoire of cobaloxime complexes that can be used for proton reduction.

2. Results and discussion

All cobalt complexes studied here have been prepared in good yields via a two-step reaction. The first step involves the reaction of $CoCl_2$ or $Co(NCS)_2$ salt with two equivalents of dmgh to generate $CoCl_2(dmgh)_2$ or $Co(NCS)_2(dmgh)_2$ complexes. The complex is then isolated and reacted with a mole equivalent of an axial ligand Y for example pyridine or aniline, to generate $Co(dmgh)_2YCl$ or $Co(dmgh)_2Y(NCS)$. The reaction progress is easily followed by the color change of the complexes. In the case of complexes containing the NCS ligand, infrared absorption spectroscopy via the intense NCS stretch around 2100 cm^{-1} region can be used to monitor the reaction as well.

The structures of complexes **1**, **2** and **3** have been obtained via X-ray crystallography (More details can be found in the Supporting Information). As seen in previously reported cobaloximes, an octahedral complex **1** is obtained with two dmgh groups coordinated to the Co(III) center in the equatorial plane (Fig. 1). The amine group of the axial aniline ligand is coordinated to the metal center with a Co(1)–N(5) distance of 2.0095 Å [9]. The chloride and aniline group are the trans ligands with a bond angle N(5)–Co(1)–Cl(1) of 178.61°. Fig. 2 shows the structure of complex **2** in which the axial 3,4,5-trimethoxyaniline ligand is trans to the chloro ligand. The Co(1)–N(5) bond length of 2.0030 Å is similar to that of complex **1** [9].

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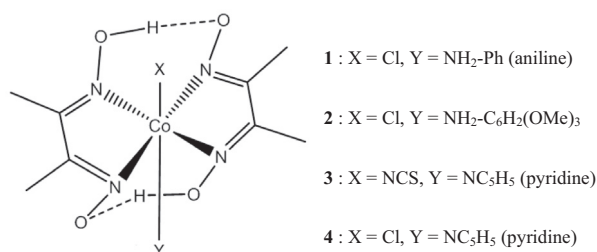
Scheme 1. The cobalt dimethylglyoxime complexes Co(dmgh)₂XY labelled as **1–4**.

1 : X = Cl, Y = NH₂-Ph (aniline)

2 : X = Cl, Y = NH₂-C₆H₂(OMe)₃

3 : X = NCS, Y = NC₅H₅ (pyridine)

4 : X = Cl, Y = NC₅H₅ (pyridine)

Fig. 3 shows the structure of complex **3** which contains an isothiocyanato-NCS ligand coordinated to the metal center via the nitrogen atom with a Co(1)–N(6) bond length of 1.913 Å [10]. The observed cobalt–pyridine (Co(1)–N(5)) bond length at 1.955 Å is very close to its counterpart in the known complex **4** [9]. The pyridine and NCS ligands are trans to each other while the dmgh ligands are also coordinated to cobalt in an equatorial plane. The almost linear coordination of the isothiocyanato ligand as indicated by the Co(1)–N(6)–C(18) and N(6)–C(18)–S(1) bond angles of 176.4° and 176.9° respectively provides further evidence that the coordination mode of the ambidentate isothiocyanato ligand is indeed via the N atom rather than the S atom. In addition, complex **3** has an intense $\nu_{asymm\ NCS}$ infrared absorption band observed at 2113 cm⁻¹ (in DMF).

3. Cyclic voltammetry and comparison

We have used cyclic voltammetry to determine the overpotential and catalytic efficiency (C.E.) for proton reduction catalyzed by the cobalt complexes. The complexes were dissolved in acetonitrile with acetic acid, CH₃COOH as the proton source and tetrabutylammonium hexafluorophosphate NBu₄⁺PF₆⁻ as the electrolyte. The

thermodynamic potential for free acetic acid reduction in acetonitrile has been determined to be −1.46 V with respect to the Fc⁺/Fc couple (Fc = ferrocene) [11]. All potentials quoted henceforth are referenced to the ferrocene couple.

The cyclic voltammetry data obtained for **1–4** are shown in Fig. 4 and tabulated in Table 1. In the absence of an acid, an irreversible molecular reduction peak attributed to the Co^{III/II} couple is observed around −0.7 to −0.9 V for each of the complexes. As the scan proceeds to more negative potentials, a reversible reduction peak which corresponds to the Co^{II/I} couple is seen in the range of −1.5 to −1.6 V.

Upon the addition of acetic acid, a large peak in the vicinity of the Co^{II/I} couple is observed for complexes **1–4**. This peak continues to increase in magnitude upon subsequent addition of acid and is thus regarded as the catalytic proton reduction peak. Controlled potential electrolysis at these potentials also confirms the generation of dihydrogen gas. The catalytic peak tends to show a small negative shift of about −0.1 V at the highest acid concentration.

In our case, the overpotential for proton reduction is determined as the difference between the catalytic peak potential and −1.46 V which is the thermodynamic reduction potential of free acetic acid in acetonitrile. The calculated overpotentials for all four complexes are similar to within 0.1 V, and fall in the range of 0.05–0.15 V with complex **2** exhibiting the lowest value. Very good agreement was also found between the proton reduction overpotential for complex **4** and a previously determined value [8]. The proton reduction catalytic efficiencies have been determined at a fixed acetic acid concentration for the complexes. Similar to the overpotentials, complexes **1–4** show comparable catalytic efficiency with values ranging from 0.49 to 0.57.

4. Mechanism

Previous extensive studies on the mechanism of proton reduction by cobaloximes have revealed some possible
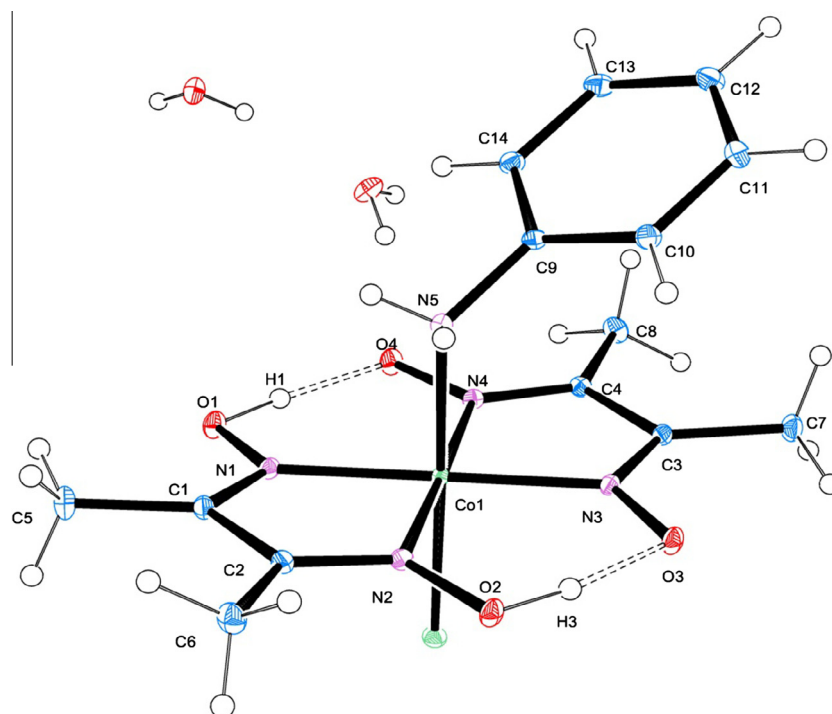
Fig. 1. ORTEP view of **1**. Selected bond lengths (Å): Co(1)–Cl(1) 2.2561(3), Co(1)–N(5) 2.0095(9), Co(1)–N(1) 1.9066(9). Selected bond angles (°): N(5)–Co(1)–Cl(1) 178.61(3), N(1)–Co(1)–Cl(1) 89.90(3), N(1)–Co(1)–N(5) 88.76(4).