Polyhedron 96 (2015) 38-43

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Proton reduction using cobalt glyoximes with isothiocyanate and aniline axial ligands

ABSTRACT

Wai Yip Fan*, Zi Bin Tan, Jingzhi Iris Koh

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

A R T I C L E I N F O

Article history: Received 30 January 2015 Accepted 24 April 2015 Available online 2 May 2015

Keywords: Cobalt glyoxime Aniline Isothiocyanate Proton reduction Cyclic voltammetry

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-dimethylgloxime (dmgBF₂) 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.

© 2015 Elsevier Ltd. All rights reserved.

2. Results and discussion

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.

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].







^{*} Corresponding author. E-mail address: chmfanwy@nus.edu.sg (W.Y. Fan).





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 $v_{asymm NCS}$ 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 $NBu_4^4PF_6^-$ 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).



Fig. 2. ORTEP view of 2. Selected bond lengths (Å): Co(1)–N(1) 1.8862(13), Co(1)–N(5) 2.0030(13), Co(1)–Cl(1) 2.2465(4). Selected bond angles (°): N(5)–Co(1)–Cl(1) 177.34(4), N(1)–Co(1)–Cl(1) 90.30(4), N(1)–Co(1)–N(5) 87.28(6).



Fig. 3. ORTEP view of 3. Selected bond lengths (Å): Co(1)-N(1) 1.887(7), Co(1)-N(5) 1.955(5), Co(1)-N(6) 1.913(7), N(6)-C(18) 1.11(1), S(1)-C(18) 1.629(8). Selected bond angles (°): N(5)-Co(1)-N(6) 178.9(3), N(1)-Co(1)-N(4) 179.3(3), N(1)-Co(1)-N(6) 90.0(3), N(1)-Co(1)-N(5) 89.0(3), Co(1)-N(6)-C(18) 176.4(7), N(6)-C(18)-S(1) 176.9(8).

pathways [1,3,4]. As the four complexes studied here produce similar cyclic voltammograms, we believe that they share a common mechanism for proton reduction. Each of the complex initially undergoes reduction of its Co(III) center to Co(II) and

subsequently Co(II) to Co(I). The anionic axial ligand such as Cl⁻ or NCS⁻ is also detached during the first reduction (Fig. 5). Protonation of the $[Co^{I}(dmgH)_2(NH_2Ph)]^-$ intermediate will then occur, producing a cobalt(III) hydride intermediate, $[HCo^{III}(dmgH)_2(NH_2Ph)]$. In this step, the Co(I) center is considered to have undergone a 2-electron oxidation to form cobalt(III) and the proton undergoes a 2-electron reduction to form a hydride. This cobalt(III) hydride species either reacts with a second proton or undergoes self-recombination to generate dihydrogen. The initial $[Co^{III}(dmgH)_2(NH_2Ph)L]$ catalyst can then be regenerated upon coordination of the anionic axial ligand [12]. This catalytic cycle is an example of an EECC (electrochemical–electrochemical–chemical–chemical) mechanism.

The effect of varying the axial ligands in the cobaloximes is discussed next from the proton reduction overpotential angle. While the overpotentials amongst complexes **1–4** only differ by 0.1 V, the small differences can still be attributed to electronic effects. For example the overpotential exhibited by cobaloximes bearing chloride ligands (**1**, **2** and **4**) decreases with increasing electron-donating power of the neutral axial ligand. The presence of the three methoxy groups of the trimethoxyaniline ligand of **2** increases the electron donation to the Co metal center as compare to **1** and **2**. Consequently, the accumulation of electron density could have increased the Lewis basicity of the $[HCo^{III}(dmgH)_2Y]$ hydride intermediate and facilitated its reaction with a proton to produce dihydrogen.

In contrast, the overpotentials exhibited by **3** and **4** bearing a common pyridine ligand differ only by 0.02 V, indicating that the Cl⁻ and NCS⁻ ligands exert similar effects. This is in agreement with the mechanism in which the first step of proton reduction involves the dissociation of the anionic axial ligand, thus leading to the common cobalt hydride intermediate. As the first step is not considered the rate-determining step, the chemical identity of the ligand may not be crucial as long as it behaves as a good leaving group, thus leading to similar values of the overpotential.

1 [Co(dmgH)₂(NH₂Ph)Cl]

2 [Co(dmgH)₂(NH₂C₆H₂(OMe)₃)Cl]



Fig. 4. Cyclic voltammograms of 1-4 (1 mM) with acetic acid (0-10 equivalence) in 0.1 M Bu₄NPF₆ in acetonitrile with scan rate of 0.1 V/s.



Fig. 5. Proposed mechanism of proton reduction by cobaloximes. X = monoanionic ligand Cl or NCS and Y = neutral N-containing ligand pyridine, aniline or aniline derivatives.

5. Conclusion

In summary, cobalt diglyoxime complexes $Co(dmgH)_2XY$ (dmgH = dimethylglyoxime, X = NCS, Cl and Y = aniline, pyridine) have been prepared and used as proton reduction catalysts. 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, this opens up the possibility of using aniline derivatives as possible pyridine alternatives in

Table 1

The cyclic voltammetry data for complexes 1–4. All potentials are determined with respect to the Fc^{\ast}/Fc couple.

Complex	Catalytic	Overpotential ^b	E ⁰ (Co ^{III/II})	E ⁰ (Co ^{II/I})
	efficiency ^a	(V)	(V)	(V)
1	0.52	0.14	-0.79	-1.60
2	0.51	0.05	-0.69	-1.51
3	0.49	0.13	-0.89	-1.59
4	0.57	0.11	-0.93	-1.57

^a Catalytic efficiency (C.E.) = $(i_{cat}/i_d)/(c_{HA}/c_{cat})$.

^b Overpotential (V) = $E^{\circ}_{HA/H2} - E_{cat}$, where $E^{\circ}_{HA/H2}$ is the standard reduction potential of the acid. E_{cat} standardized at 5 equivalence of acid.

our continuing search for an even more efficient proton reduction catalyst.

6. Experimental

6.1. General procedures

All syntheses of the cobalt complexes were conducted under a steady stream of inert N_2 gas. The X-ray diffraction of the crystal

obtained was carried out using Bruker-AXS Smart Apex CCD Single-Crystal Diffractometers. Data were obtained at 100(2) K with graphite monochromated Mo K α radiation (λ = 0.7107 Å). Data collection was performed with SMART CCD system. Infrared spectra were obtained on a Shimadzu IR-Prestige 21 spectrometer.

6.2. Electrochemical experiments

Cyclic voltammetry experiments were carried out with the Metrohm Autolab PGSTAT302N potentiostat using a 3-electrode system. The working electrode used was a 1 mm glassy carbon disk (Cypress system), together with a platinum counter electrode (Metrohm) and a silver wire miniature reference electrode (Cypress Systems) immersed in acetonitrile. Before each scan, the sample solution was purged with nitrogen gas and the working electrodes were polished with alumina oxide (0.3 µm grain size) on a Buehler Ultra-pad polishing cloth. The working electrodes were subsequently washed with deionized water, acetone and dried before use. The potentials were calculated with ferrocene as an internal standard added into the sample solution at the start of the measurements [13]. The sample solution consisted of 1 mM of the cobalt complex and 0.1 M of the supporting electrolyte, Bu_4NPF_6 (tetrabutylammonium hexafluorophosphate) in acetonitrile.

For the controlled potential electrolysis experiment, a solution of 1 mM of each of the cobalt complexes with 50 mM CH₃COOH in 0.1 M Bu₄NPF₆ in acetonitrile was electrolyzed at -1.60 V vs Fc⁺/Fc in a gas-tight electrochemical cell. The experiment was carried out three times enabling the average value for the current and electrolysis period to be calculated. The content of the reaction headspace was sampled with a 1 cm³ syringe and injected into a residual analyzer (Pfeiffer PrismaPlus) tuned to monitor signals at m/z = 2, corresponding to H₂ production. The Faraday yield (>80% for all complexes) was determined by calibrating to the signal produced by a known pressure of H₂ from a H₂ cylinder (Soxal, 99.99%).

6.3. Synthesis of [Co(dmgH)₂Cl₂]

 $CoCl_2 \cdot 6H_2O$ (0.50 g, 2.10 mmol) and dimethylglyoxime (0.49 g, 4.202 mmol) were added to 50 mL of acetone. The initial blue solution was aerated and stirred for 6 h before being left to dry overnight under ambient conditions. A green powder was obtained. Yield 0.62 g (82%).

6.4. Synthesis of [Co(dmgH)₂(NH₂Ph)Cl] (complex 1)

Co(dmgH)₂Cl₂ (32.3 mg, 89.7 µmol) and aniline (9.2 mg, 98.7 µmol) were added to 8 mL of methanol and stirred in air at room temperature for 1 h. The initial yellow solution turned red upon aniline addition. The crude product was filtered and the filtrate was column chromatographed on silica gel (100–200 mesh). The product was obtained by eluting out with 100% ethyl acetate. X-ray quality crystals of **1** were grown via solvent diffusion of hexane into a concentrated solution of **1** obtained from column chromatography at room temperature. Yield: 23.6 mg, 63%. ESI-MS (*m*/*z*): 416.0 [CoCl(dmg)(dmgH)(NH₂Ph)]⁻. Elemental analyses (%): C, 44.36 (expected 40.25); H, 5.21 (5.07); N, 14.81 (16.77).

6.5. Synthesis of $[Co(dmgH)_2(NH_2C_6H_2(OMe)_3)Cl]$ (complex 2)

 $Co(dmgH)_2Cl_2$ (36.7 mg, 101.9 µmol) and 3,4,5-trimethoxyaniline (20.5 mg,112.1 µmol) were added to 8 mL of methanol and stirred in air at room temperature for one hour. The initial yellow solution turned red upon the addition of 3,4,5-trimethoxyaniline. The crude product was filtered and the filtrate was column chromatographed on silica gel (100–200 mesh). The product was obtained by eluting out with 1:1 ethyl acetate:acetone. The purified product was dried via rotary evaporation and redissolved in acetone. X-ray quality crystals of **2** were grown by slow evaporation of acetone solvent at room temperature. Yield: 34.7 mg, 67%. ESI-MS (m/z): 505.9 [CoCl(dmg)(dmgH)(NH₂Ph(OCH₃)₃)]⁻. Elemental analyses (%): C, 39.84 (expected 40.21); H, 5.59 (5.36); N 12.00 (13.79).

6.6. Synthesis of [Co(NCS)₂]

KSCN (0.5756 g, 5.92 mmol) was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.5788 g, 2.43 mmol) in 30 mL of acetone. The mixture was stirred at room temperature for 2 h, and filtered to remove the precipitate. The solvent was removed via rotary evaporation to obtain the product. Yield: 0.25 g, 38%. IR (DMF): $v_{SCN} = 2075 \text{ cm}^{-1}$.

6.7. Synthesis of [Co(dmgH)₂(NCS)₂]

 $Co(NCS)_2$ (0.2202 g, 1.26 mmol) was dissolved in 15 mL of acetone, and dimethylglyoxime (0.3275 g, 2.82 mmol) was added to the resulting blue solution. The mixture was stirred for 3.5 h in the presence of air. The precipitated product was filtered by suction filtration, washed with cold acetone and air dried to give a brown product. Yield: 0.312 g, 61%. IR (DMF): v_{SCN} = 2109 cm⁻¹.

6.8. Synthesis of [Co(dmgH)₂(py)(NCS)] (complex 3)

Co(dmgH)₂(NCS)₂ (0.4893 g, 1.20 mmol) was suspended in 25 mL of methanol and pyridine (0.2023 g, 2.56 mmol) was added. The mixture was stirred at room temperature for 1 h. 40 mL of water was added with stirring, and the suspension was cooled in an ice bath for 10 min. The precipitated product was collected via suction filtration, washed with 2:1 water/methanol, followed by diethyl ether, and air dried to give an orange product. X-ray quality crystals of **6** were grown via solvent diffusion of Et₂O into a concentrated solution of **6** in CHCl₃ at room temperature. Yield: 0.2564 g, 50%. IR (DMF): $v_{SCN} = 2113 \text{ cm}^{-1}$. ESI-MS (*m*/*z*): 424.7 [Co(NCS)(dmg)(dmgH)(py)]⁻. Elemental analyses (%): C, 39.84 (expected 39.44); H, 4.88 (4.49); N, 16.91 (19.71); S, 6.23 (7.52).

6.9. Synthesis of [Co(dmgH)₂(py)Cl] (complex 4)

 $Co(dmgH)_2Cl_2$ (0.1773 g, 0.491 mmol) was suspended in 10 mL of methanol before adding pyridine (0.0396 g, 0.501 mmol). The mixture was stirred at room temperature for 1.5 h and filtered to remove the precipitate. The solvent of the resultant filtrate was removed via rotary evaporation to obtain a brown product. Yield: 0.1036 g, 52%. ESI-MS (*m*/*z*): 404.9 [CoCl(dmg)(dmgH)(py)]⁻.

Acknowledgment

W.Y. Fan thanks NUS for a research grant 143-000-553-112.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015.04.030.

References

- [1] J.R. McKone, S.C. Marinescu, B.S. Brunschwig, J.R. Winkler, H.B. Gray, Chem. Sci. 5 (2014) 865.
- [2] G. Li, D.P. Estes, J.R. Norton, S. Ruccolo, A. Sattler, W. Sattler, Inorg. Chem. 53 (2014) 10743.

- [3] J.L. Dempsey, B.S. Brunschwig, J.R. Winkler, H.B. Gray, Acc. Chem. Res. 42 (2009) 12.
- M. Razavet, V. Artero, M. Fontecave, Inorg. Chem. 44 (2005) 4786.
 A. Mahammed, B. Mondal, A. Rana, A. Dey, Z. Gross, Chem. Commun. 50 (2014)

- [5] A. Mahammed, B. Mondal, A. Kana, A. Dey, Z. Gross, Chem. Commun. 50 (2014) 2725.
 [6] J. Connolly, J.H. Espenson, Inorg, Chem. 25 (1986) 2684.
 [7] B.D. Gupta, R. Yamuna, D. Mandal, Organometallics 25 (2006) 706.
 [8] P. Wu, J. Schneider, G. Luo, W.W. Brennessel, R. Eisenberg, Inorg. Chem. 48 (2009) 4952.
- [9] S. Meghdadi, K. Mereiter, M. Amirnasr, F. Karimi, A. Amiri, Polyhedron 68 (2014) 60.
- [10] H. Xile, B.S. Brunschwig, J.C. Peters, J. Am. Chem. Soc. 129 (2007) 8990.
 [11] G.A.N. Felton, R.S. Glass, D.L. Lichtenberger, D.H. Evans, Inorg. Chem. 45 (2006) 9181.
- C. Baffert, V. Artero, M. Fontecave, Inorg. Chem. 46 (2007) 1817.
 E.S. Rountree, B.D. McCarthy, T.T. Eisenhart, J.L. Dempsey, Inorg. Chem. 53 (2014) 9983.