DOI: 10.1002/cssc.201300564



Cobalt-Based Particles Formed upon Electrocatalytic Hydrogen Production by a Cobalt Pyridine Oxime Complex

Sanae El Ghachtouli,*^[a] Regis Guillot,^[a] Francois Brisset,^[a] and Ally Aukauloo*^[a, b]

Abstract: An open-coordination-sphere cobalt(III) oximatobased complex was designed as a putative catalyst for the hydrogen evolution reaction (HER). Electrochemical alteration in the presence of acid occurs, leading to the formation of cobalt-based particles that act as an efficient catalyst for HER at pH 7. The exact chemical nature of these particles is yet to be determined. This study thus raises interesting issues regarding the fate of molecular-based complexes designed for the HER, and points to the challenging task of identifying the real catalytic species. Moreover, understanding and rationalizing the alteration pathways can be seen as a new route to reach catalytic particulates.

Research towards molecular catalysts for hydrogen production is a contemporary scientific issue, with the development of cost-effective catalytic materials as its defining target.^[1] This research falls in two main categories: biomimetic models and coordination metal complexes for electrocatalysis. The first approach seeks primarily to understand the intricacies of the relationship between structure and function of the active sites of the hydrogenases, the family of enzymes involved in the metabolism of hydrogen in bacteria and algae.^[2] To their detriment, functional systems in this area are still scarce. However, the development of coordination metal complexes based on first-row transition metals for the hydrogen evolution reaction (HER) has been more successful, and several molecular-based catalysts functioning at modest overpotential have been reported.^[3] Among those, cobalt-based glyoxime complexes figure as one of the most prominent molecular systems for H₂ generation. Artero, Peters, and others have re-examined the chemistry of cobalt glyoximato complexes for their electrocatalytic properties in the HER.^[4] Long and co-workers have reported on robust cobalt polypyridine complexes showing remarkable catalytic properties for H_2 production,^[5] while Gray and collaborators have shown in a recent paper that the cobalt (bisiminopyridine) complex in aqueous solution is a highly active catalyst for the reduction of water.^[6] Based on these results, we

[a]	Dr. S. E. Ghachtouli, Dr. R. Guillot, Dr. F. Brisset, Prof. A. Aukauloo Institut de Chimie Moléculaire et des Matériaux d'Orsav
	UMR-CNRS 8182, Université de Paris-Sud XI
	91405 Orsay (France)
	Fax: (+ 33) 0-169-154-756
	E-mail: ally.aukauloo@u-psud.fr
[b]	Prof. A. Aukauloo CEA, iBiTec-S
	Service de Bioénergétique Biologie Structurale et Mécanismes (SB2SM) 91191 Gif-sur-Yvette (France)
	Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201300564.

reasoned that a ligand set bearing both an oxime and a pyridine functionality may offer attractive properties in the electrocatalytic reduction of protons to H_2 .

We report herein on the synthesis of bis pyridine methyloxime (hereby abbreviated as PyMOH) cobalt complexes. Their electrochemical properties and their activity towards the reduction of protons are discussed. We find that upon electrocatalysis, there is an alteration of the initial cobalt complex to form cobalt-based particles that are at the origin of the electrocatalytic hydrogen production.

The ligand was synthesized by reacting 2-acetylpyridine with NH₂OH.HCl in ethanol, and isolated as a white powder in good yield. Complex **1** was obtained by reacting 2 equiv of the ligand PyMOH with CoBr₂ in ethanol. Upon treatment of complex **1** with an excess of BF₃.Et₂O in dry ether under argon, the BF₂-capped complex **2** was isolated as a green solid. We successfully obtained crystals of both $[Co^{III}(PyMO)(PyMOH)Br_2]$ **1** and $[Co^{III}(PyMO)_2(BF_2)Br_2]$ **2** of sufficient quality to perform X-ray analysis. (see Experimental Section).

The crystal structure of 1 depicts an octahedral environment around the cobalt(III) ion with two trans-positioned bromide ligands (Figure 1a). The deprotonated form of one oxime function satisfies the electroneutrality of complex 1. We note that the proton bridges the two oxygen atoms O1 and O2. The coordination scheme of the cobalt(III) ion for complex 2 is similar to that of complex 1, with four N atoms in the equatorial belt and two bromide ligands at trans positions. The structure of 2 reveals that the BF₂ bridges the oxime groups, and a contraction of the metric distances in the N4 equatorial plane (Figure 1 b). This shrinking leads at the same time to a pronounced tilt of the pyridine groups, out of the median plane.

The UV/Vis spectra of **1** and **2** (see Supporting Information, Figure S1) show an intense band at 280 nm (16075 m⁻¹ cm⁻¹) and 310 nm (16070 m⁻¹ cm⁻¹) respectively, that we assign to ligand $\pi \rightarrow \pi^*$ transitions. A band of weaker intensity observed at 342 nm (3205 m⁻¹ cm⁻¹) and 400 nm (2355 m⁻¹ cm⁻¹), respectively, probably corresponds to ligand to metal charge-transfer (LMCT) transitions.^[6]

The electrochemical behavior of $[Co^{III}(PyMO)(PyMOH)Br_2]$ **1** and $[Co^{III}(PyMO)_2(BF_2)(Br)_2]$ **2** complexes were studied in acetonitrile (0.1 \bowtie NaClO₄). Cyclic voltrammetry (CV) measurements of **1** display one quasi-reversible wave at 0.45 V vs. SCE, attributed to the Co^{III/II} couple, and an irreversible wave on the cathodic side at around -1 V vs. SCE, for the putative Co^{III/I} couple (Figure 2a). In the case of **2**, we observe a shift of the Co^{III/II} couple towards less-positive potential by ca. 200 mV (Figure 2b). This is in agreement with findings of a stronger interaction between the metal ion and the ligands, leading to a stabilization of the metal *d* orbitals. Intriguingly, the second re-



Figure 1. Crystal structure of a) $[Co^{III}(PyMO)(PyMOH)Br_2]$ 1; Co-N1 (1.9891(19) Å) Co-N2 (1.978(2 Å), Co-N3 (1.9092(19 Å) Co-N4 (1.916(2 Å); and b) $[Co^{III}(PyMO)_2(BF_2)Br_2]$ 2; Co-N1 (1.953(2 Å) Co-N2 (1.957(2 Å), Co-N3 (1.900(2 Å) Co-N4 (1.902(2 Å). Hydrogen atoms and solvent molecules are omitted for clarity.



Figure 2. Cyclic voltammetry in acetonitrile (0.1 mmm of NaClO₄) of 1 mm of a) 1, and b) 2. Glassy carbon: working electrode, $V = 100 \text{ mV s}^{-1}$, T = 293 K.

duction process is also displaced to a less-negative potential (from -1 V to -0.74 V vs. SCE), together with a gain in the electrochemical reversibility. We attribute this shift towards less cathodic values to the electron-withdrawing nature of the difluoroboryl capping group, which confines uptake of the second electron mainly to the ligand skeleton. For comparison, under similar experimental conditions the Co^{II/1} couple of [Co-(DMGBF₂)₂] (DMG: dimethyl glyoxime) was detected at -0.55 V vs. SCE,^[7] supporting the assertion that the pyridine groups are less electron-withdrawing than the boryl-oximato functions. Interestingly, the potential of the Co^{II/1} couple falls within the same potential window (-0.71 V vs. SCE) as in a case where the fluoroboryl-oximato groups were replaced by two iminic functions.^[8]

The CV scans of both 1 and 2 in acetonitrile change strongly upon addition of increasing amounts of trifluroacetic acid (TFA, pK_a 12.7 in acetonitrile).^[9] The absence of a genuine S-shaped electrocatalytic wave, as expected for molecular-based catalysis, and the different reduction processes taking place upon addition of protons prompted us to investigate the effect of proton addition on the cobalt complexes in more detail. For stability reasons (see Figures S2 and S3) we could only study the electrochemical behavior of compound 2. The addition of TFA leads to several marked changes in the shape of the CV curve. Importantly, the electrochemical behavior does not change in the presence of the weaker acids triethylammonium or acetic acid. With TFA, we noticed the increased intensity of the reduction wave in the region of the Co^{II/I} couple, shifted to more positive values by ca. 60 mV (Figure 3, Wa). This wave reaches a maximum upon the addition of two protons and two electrons. A second wave at around -0.9 V vs. SCE (Wb) is also detected, which peaks at the addition of $4e^-$ and $4H^+$ (Figure S4). These electrochemical-chemical processes can be related to, firstly, the hydrogenation of two imine bonds of oximepyridine ligand and, secondly, the hydrogenolysis of two N-O bonds, according to previous studies on the electrochemical behavior of cobalt complexes containing oxime ligands in the presence of acid.^[10] Furthermore, such behavior has recently been reported by Savéant et al. in the electrocatalytic con-



Figure 3. Cyclic voltammetry in acetonitrile (0.1 mm of NaClO₄) of 0.5 mm of **2** in the presence of increasing trifluoroacetic acid [TFA], 0–11 mm. Glassy carbon: working electrode, $V = 100 \text{ mVs}^{-1}$, T = 293 K.

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version of three glyoximato ligands around a caged cobalt(II) ion in the presence of acid.^[11] Our results evidence that the same electrochemical processes occur for a cobalt complex with an open coordination sphere bearing oximato groups and pyridine groups without any direct activation of the proton at the reduced metallic center.^[12] A more detailed mechanistic study is beyond the scope of this report and will be addressed in the future.

Upon scanning to more-cathodic potentials, we noticed a more intense wave (Wc). The formation of this wave is followed by the appearance of a desorption wave at around 0.07 V vs. SCE. We therefore assign these waves to the catalytic activity of a chemical deposit on the surface of the graphite electrode. Polarizing the electrode at -1.1 V vs. SCE for complex **2** for about 60 s leads to the formation of a new wave at ca. -1 V vs. SCE (Figure 4, blue CV trace). We propose that this



Figure 4. Cyclic voltammograms of **2** (0.5 mM) in acetonitrile (0.1 M of NaClO₄): in the presence of 11 mM of TFA (red line), after electrolysis for 60 s at -0.8 V vs. SCE (green line), after electrolysis for 60 s at -0.98 V vs. SCE (black line) and after electrolysis for 60 s at -1.1 V vs. SCE (blue line); V = 100 mV s⁻¹ at a glassy carbon electrode (0.07 c m²).

process leads to the electrosynthesis of a new species, catalytic towards the HER, at the surface of the electrode. Of note, the initial CV trace is regained after polishing the electrode surface. More importantly, the shape of the CV trace did not change upon polarization of the electrode after Wa and Wb (Figure 4, CV traces in green and black), and the shape of the CV trace changes only upon polarization of the electrode at a potential more negative than Wb. Furthermore, control experiments performed under the same conditions but with only acid or with a solution of the cobalt salt $Co(NO_3)_2$ containing the same acid did not reveal any electrocatalytic activity in the same potential window (see Figure S5), supporting the assertion that the electrochemical route to the formation of the active species emanating from the molecular complex **2** is different from the free cobalt(II) ions source.

Of relevance to this finding, we performed electrolysis of **2** at -1.1 V vs. SCE at a glassy carbon electrode (1 cm^2) in presence of acid. A scanning electron microscopy image of the electrode after electrolysis is shown in Figure 5. The modified electrode with **2**, is decorated with cubic-like particles with an



Figure 5. SEM image of cubes deposited after 18 h of electrolysis at -1.1 V vs. SCE onto glassy carbon (1 cm²) of 2 mm of 2 in an acetonitrile solution (0.1 m NaClO₄) in the presence of 44 mm of TFA.

average size of 1 to 2 μ m. Energy dispersive X-ray spectroscopy (EDS) analysis of a sample of the cubic particles revealed that they are constituted mainly of cobalt and oxygen. (see Figure S7). However, the exact nature of these particles is yet to be determind more precisely.

A chemically modified glassy carbon (GC) electrode with the cobalt-based particles using complex **2** as starting material was prepared, rinsed under inert conditions and used as a working electrode for catalytic hydrogen production in an aqueous solution containing 0.1 μ phosphate buffered at pH 7. We found that the overpotential for proton reduction is 400 mV for a geometric current density of 2 mA cm⁻² at pH 7, and the shift in the overpotential when compared to the blank electrode is around 750 mV towards more positive value at the same pH for a similar current density (Figure 6). As a comparison, the overpotential value we found is lower than those re-



Figure 6. Linear sweep voltammetry in 0.1 m phosphate buffer at pH 7. in the absence of catalyst (black line); of working electrode washed with water and placed into a pure phosphate electrolyte after 60 s of electrolysis at -1.1 V vs. SCE in acetonitrile in the presence of **2** (0.5 mm) and 11 mm of TFA (red line). Glassy carbon: working electrode, V = 100 mVs⁻¹, T = 293 K.

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ported for the majority of cobalt molecular complexes and slightly higher than that of the film of H₂-CoCat deposited on FTO electrode reported recently.^[13] However, any further comparison would be risky given the fact that we do not know the actual amount of catalytically active cobalt sites at the surface of the electrode, and because the morphologies of the deposited materials are different.

Bulk electrolysis of particles deposited in acetonitrile at the surface of the glassy carbon electrode (1 cm^2) was performed in an aqueous solution containing 0.1 M phosphate buffered at pH 7 at a controlled potential (-1.1 V vs. SCE). A quasilinear dependence of the charge with time was observed during ca. 4 h with 80% Faradaic yield of H₂ production (see Figure S6).

As mentioned earlier, the challenge behind developing molecular-based catalyst is to provide a more cost-efficient catalytic material for hydrogen production than platinum. In proton exchange membrane technology, hydrogen is produced in acidic medium with platinized electrodes. With this in mind we prepared a modified glassy carbon electrode (0.07 cm^2) by depositing a drop of a solution of **2** dissolved in acetonitrile (2 mM) and leaving the sample to dry in air. The disc was then smeared with a perfluorosulfonate ion-exchange polymer (Nafion117) to prevent leaching of deposit at the surface of the electrode. Cyclic voltammograms obtained after continual cycling between 0 and -1 V vs. SCE in a 0.5 m aqueous solution of H₂SO₄ under argon at a scan rate 5 mV s⁻¹ are given in Figure 7. The current density steadily increases to



Figure 7. Linear sweep voltammetry obtained in aqueous solution of H_2SO_4 (0.5 m) of a glassy carbon modified electrode with Nafion (blue line); and of a glassy carbon modified electrodes with **2** (2 mm) and Nafion. GC (0.07 cm²), V = 5 mVs⁻¹.

reach a value of ca. 21 mA cm⁻² at around -1 V vs. SCE. This gradual increase in the current density of the catalytic wave for the reduction of protons can be directly inferred to the chemical changes observed for complex **2** in solution at the surface of the electrode.

We have shown in this study that an acid-stable cobalt(III) complex bearing pyridine and oximato groups in its coordination sphere is electrochemically converted to cobalt-based particles at the surface of the electrode in the presence of acid. The modified electrode exhibits good catalytic activity towards the hydrogen evolution reaction (HER) at pH 7. This study thus raises interesting issues regarding the fate of molecular-based complexes designed for the HER, and points to the challenging task of identifying the real catalytic species given the primary importance of the outcome of this research area in the development of new catalytic materials. Moreover, understanding and rationalizing the alteration pathways can be seen as a new route to reach catalytic particulates.

Experimental Section

Pyridine methyloxime (PyMOH): To a solution of 2-acetyl pyridine (2 g, 14.7 mmol) in ethanol (15 mL) was added one equivalent of hydroxylamine hydrochloride in ethanol (15 mL). The solution was stirred under reflux for 24 h, the mixture was concentrated, and cold water (120 mL) was added to the reaction mixture at room temperature. The white precipitate was filtered, washed with cold water, and dried by suction (1.36 mg, 60% yield). ¹H NMR (300 MHz, CDCl₃): δ = 8.668 (d, 1H), 7.868 (d, 1H), 7.706 (t, 1H), 7.296 (t, 1H), 2.429 ppm (s, 3H). Elemental analysis for: C₇H₈N₂O calcd (%): C 61.75, H 5.92, N 20.58; found (%): C 61.69, H 6.03, N 20.58.

 $[Co^{III}(PyMO)(PyMOH)Br_2] \ 1: \ CoBr_2 \cdot 2\,H_2O \ (200 mg, \ 0.78 mmol) \ dissolved in ethanol/methanol (1:1, 4 mL) was added to 2 equiv of the ligand PyMOH dissolved in ethanol (4 mL). The brown mixture was stirred at room temperature overnight and concentrated by evaporation. A brown precipitate was filtered, washed with ethanol and diethyl ether, and the powder was dried by suction (306 mg, 80% yield). The powder was further dissolved in acetonitrile, and after slow diffusion of diethyl ether, brown monocrystals of 1 suitable for X-ray analysis were obtained. Elemental analysis for: CoC₁₄H₁₅Br_2N_4O_2 calcd (%): C 34.31, H 3.09, N 11.43; found (%): C 34.62, H 3.39, N 11.39.$

 $[Co^{III}(PyMO)_2(BF_2)Br_2]$ **2**: To a solution of complex **1** (200 mg, 0.41 mmol) in diethyl ether (10 mL) was added 1.2 equiv of CH₃COONa, and the mixture was stirred under argon atmosphere at room temperature for 30 min. BF₃·Et₂O (1 mL) was added to the mixture, and the brown–green suspension was stirred for 24 h at room temperature under argon. The green precipitate was collected by filtration, washed with water and diethyl ether, and the powder was dried by suction (154 mg, 70% yield). Green monocrystals of **2** suitable for X-ray analysis were obtained via diethyl ether vapor into a acetonitrile solution of **2**. Elemental analysis for **2**: $CoC_{14}H_{14}Br_2BF_2N_4O_2$ calcd (%): C 31.26, H 2.62, N 10.42; found (%): C 31.72, H 2.53, N 10.54.

Acknowledgements

This work was supported by CNRS project Commerce $H_{2^{n}}$ ANR TechbBioPhyp and the LABEX CHARMMMAT.

Keywords: cobalt · electrocatalysis · homogeneous catalysis · hydrogen · oximes

- [1] V. Balzani, A. Credi, M. Venturi, ChemSusChem 2008, 1, 26-58.
- [2] a) C. Tard, X. Liu, S. K. Ibrahim, M. Bruschi, L. D. Gioia, S. C. Davies, X. Yang, L.-S. Wang, G. Sawers, C. J. Pickett, *Nature* 2005, 433, 610–613; b) F. A. Armstrong, N. A. Belsey, J. A. Cracknell, G. Goldet, A. Parkin, E. Reisner, K. A. Vincent, A. F. Wait, *Chem. Soc. Rev.* 2009, 38, 36–51; c) F.

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Gloaguen, T. B. Rauchfuss, *Chem. Soc. Rev.* **2009**, *38*, 100–108; d) S. Kaur-Ghumaan, L. Schwartz, R. Lomoth, M. Stein, S. Ott, *Angew. Chem.* **2010**, *122*, 8207–8211; *Angew. Chem. Int. Ed.* **2010**, *49*, 8033–8036; e) Ö. Erdem, L. Schwartz, M. Stein, A. Silakov, S. Kaur-Ghumaan, P. Huang, S. Ott, E. Reijerse, W. Lubitz, *Angew. Chem.* **2011**, *123*, 1475–1479; *Angew. Chem. Int. Ed.* **2011**, *50*, 1439–1443; f) J.-F. Capon, F. Gloaguen, F. Y. Pétillon, P. Schollhammer, J. Talarmin, *Coord. Chem. Rev.* **2009**, *253*, 1476–1494.

- [3] a) M. L. Helm, M. P. Stewart, R. M. Bullock, M. Rakowski DuBois, Daniel L. DuBois, *Science* 2011, 333, 863–866; b) G. M. Jacobsen, J. Y. Yang, B. Twamley, A. D. Wilson, R. M. Bullock, R. M. DuBois, D. L. DuBois, *Energy Environ. Sci.* 2008, 1, 167–174; c) G. A. N. Felton, A. K. Vannucci, J. Chen, L. T. Lockett, N. Okumura, B. J. Petro, U. I. Zakai, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *J. Am. Chem. Soc.* 2007, *129*, 12521–12530; d) P. Du, R. Eisenberg, *Energy Environ. Sci.* 2012, *5*, 6012–6021; e) O. Pantani, E. Anxolabéhe're-Mallart, A. Aukauloo, P. Millet, *Electrochem. Commun.* 2007, *9*, 54–58.
- [4] a) X. Hu, B. S. Brunschwig, J. C. Peters, J. Am. Chem. Soc. 2007, 129, 8988–8998; b) C. C. L. McCrory, C. Uyeda, J. C. Peters, J. Am. Chem. Soc. 2012, 134, 3164–3170; c) M. Razavet, V. Artero, M. Fontecave, Inorg. Chem. 2005, 44, 4786–4795; d) C. Baffert, V. Artero, M. Fontecave, Inorg. Chem. 2007, 46, 1817–1824; e) M.-T. Dinh Nguyen, A. Ranjbari, L. Catala, F. Brisset, P. Millet, A. Aukauloo, Coord. Chem. Rev. 2012, 256, 2435–2444; f) V. Artero, M. C. -Kerlidou, M. Fontecave, Angew. Chem. 2011, 123, 7376–7405; Angew. Chem. Int. Ed. 2011, 50, 7238–7266, and references therein.

- [5] a) Y. Sun, J. P. Bigi, N. A. Piro, M. Lee. Tang, J. R. Long, C. J. Chang, J. Am. Chem. Soc. 2011, 133, 9212–9215; b) A. E. King, Y. Surendranath, N. A. Piro, J. P. Bigi, J. R. Long, C. J. Chang, Chem. Sci. 2013, 4, 1578–1587.
- [6] B. D. Stubbert, J. C. Peters, H. B. Gray, J. Am. Chem. Soc. 2011, 133, 18070–18073.
- [7] X. Hu, B. M. Cossairt, B. S. Brunschwig, N. S. Lewis, J. C. Peters, Chem. Commun. 2005, 4723–4725.
- [8] a) P.-A. Jacques, V. Artero, J. Pécaut, M. Fontecave, Proc. Natl. Acad. Sci. USA 2009, 106, 20627–20632.
- [9] I. Kosuke, in Acid-Base Dissociation Constants in Dipolar Aprotic Solvents, Blackwell Scientific Publications, Oxford, 1990.
- [10] a) F. Ma, D. Jagner, L. Renman, *Anal. Chem.* 1997, *69*, 1782–1784;
 b) L. A. M. Baxter, A. Bobrowski, A. M. Bond, G. A. Heath, R. L. Paul, R. Mrzljak, J. Zarebski, *Anal. Chem.* 1998, *70*, 1312–1323.
- [11] E. Anxolabéhère-Mallart, C. Costentin, M. Fournier, S. Nowak, M. Robert, J.-M. Savéant, J. Am. Chem. Soc. 2012, 134, 6104–6107.
- [12] J. L. Dempsey, B. S. Brunschwig, J. R. Winkler, H. B. Gray, Acc. Chem. Res. 2009, 42, 1995–2004.
- [13] S. Cobo, J. Heidkamp, P-A. Jacques, J. Fize, V. Fourmond, L. Guetaz, B. Jousselme, V. Ivanova, H. Dau, S. Palacin, M. Fontecave, V. Artero, *Nat. Mater.* 2012, *11*, 802–807.

Received: June 11, 2013 Revised: July 29, 2013 Published online on ■■ ■, 0000

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S. E. Ghachtouli,* R. Guillot, F. Brisset, A. Aukauloo*

Cobalt-Based Particles Formed upon Electrocatalytic Hydrogen Production by a Cobalt Pyridine Oxime Complex



Cobalt based particles

Unexpected Co-operation: An open-coordination-sphere cobalt(III) pyridine oxime complex is designed as catalyst for the hydrogen evolution reaction (HER). However, electrochemical alteration in presence of acid leads to the formation of cobalt-based particles that act as efficient HER electrocatalyst at pH 7, pointing to the challenging task of identifying the real catalytic species in the development of new materials.