Hydrogen Formation

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Cobalt Clathrochelate Complexes as Hydrogen-Producing Catalysts**

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Dedicated to Doris Lexa

Developing a hydrogen-based economy is one possible scenario to reach a sustainable energy development and also to put ourselves on a path to cut the carbon emissions for obvious climate issues.[1] However, several inherent problems must be overcome, such as production, storage, transport, and efficiency.[2,3]

We are involved in research towards developing metal complexes for the electrocatalysis of hydrogen production. The challenge is to replace the expensive and limited platinum metal with non-noble metal complexes. A bioinorganic approach to tackling this problem wherein metal complexes, based mainly on iron, are designed to mimic the catalytic site of the Fe-hydrogenases, in the hope of simulating their reactivity patterns, has attracted much attention.[4,5] A general trend in the electrocatalytic activity of these complexes is high overpotential. More classical metal coordination complexes for electrocatalysis have also been reported to show interesting activities towards hydrogen evolution.[6–8] Among these examples are the difluoroboryl annulated bis(glyoximato) cobalt derivatives studied by Espenson and Chao.[9] In recent years several groups,[10–12] including ourselves,[13] have demonstrated that this family of complexes can perform electrocatalysis of proton reduction in organic media. Hexacoordinated cobalt complexes have also been reported to act as catalysts for proton reduction.[14] However, no clear-cut mechanism is known for the catalytic activity of these complexes, which was evidenced only on a mercury electrode. In boron-capped tris(glyoximato) cobalt complexes, the metal ion is both coordinatively saturated and encapsulated by a single macrobicyclic ligand. These coordination compounds are classified as clathrochelate complexes, in which the metal ion is locked in a close-knit structure, inhibiting ligand exchange in the more labile oxidation states of the encapsulated metal ion,[15] and, in turn, explaining why the chemical activity of this family of complexes has been particularly elusive. We have been interested in investigating the electrochemical activity of the boron-capped tris(glyoximato) cobalt complexes towards hydrogen evolution. Herein, we report on the synthesis and characterization of three clathrochelate Co^{III} complexes [**1**]$^+$, [**2**]$^+$, and [**3**]$^+$ (Figure 1) together with their involvement in an electrocatalytic hydrogen-forming reaction in solution. X-ray crystallographic data for [**1**]$^+$ and for a derivative Co^{II} complex [**4**] are also discussed.

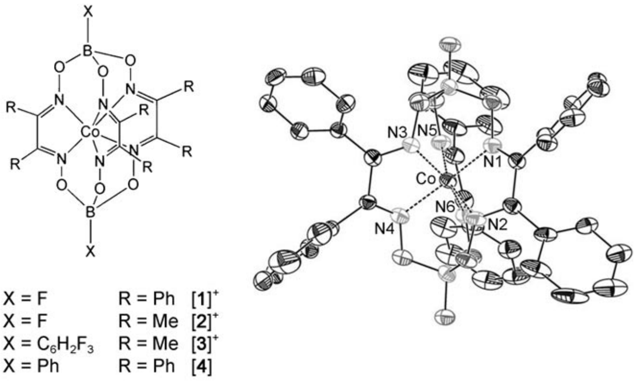

Figure 1. Structure of cobalt clathrochelate complexes (left) and ORTEP representation of complex [**1**]$^+$ (right). Thermal ellipsoids are set at 50% probability. The solvate and hydrogen atoms are omitted for clarity.

The compounds were prepared according to modified literature procedures.[16] After treating three equivalents of the corresponding glyoxime derivatives, diphenylglyoxime (dpgH$_2$) and dimethylglyoxime (dmgH$_2$), with anhydrous cobalt(II) chloride under an argon atmosphere, the mixture was treated with an excess of trifluoroborane in a nonprotic medium for [**1**]$^+$ and [**2**]$^+$, and with a methanolic solution of trifluorophenylboronic acid in the case of [**3**]$^+$. After conventional workup, the corresponding cobalt(III) complexes were isolated. The X-ray crystal structure of [**1**]$^+$ (Figure 1), indicates a mean Co–N distance of 1.88 Å and an average bite angle of 80° that are in agreement with reported bond lengths and angles in similar clathrochelate cobalt(III) complexes.[15] A trigonal twist angle of approximately 31° is evident around the cobalt center, indicating that the coordination environment is intermediate between trigonal prismatic (TP) and trigonal antiprismatic (TAP) geometry. As reported elsewhere[17] and in the case of complex [**4**], the coordination sphere of the cobalt(II) derivatives in this family of complexes is somewhat more dissymmetric than that of

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cobalt(III). Such complexes exhibit a smaller torsion angle (average value of 16° for [**4**]), and thus a slightly distorted TP local geometry, with two long Co–N bonds, *cis* to each other, resulting from Jahn–Teller distortion (see the Supporting Information).

The electrochemical data of [**1**]$^+$, [**2**]$^+$, and [**3**]$^+$ are given in Table 1. Comparison of the redox behavior of compounds [**1**]$^+$ and [**2**]$^+$ with their corresponding difluoroboryl bis(glyoximato) analogues indicates a quasi-reversible wave for the Co^{III}/Co^{II} process in the case of [**1**]$^+$ and [**2**]$^+$, whereas this process is irreversible and quasi-reversible in the case of [Co(dmgBF$_2$)$_2$] and [Co(dpgBF$_2$)$_2$], respectively.[18] A reasonable interpretation of these results is that the ligands are reorganized in the coordination sphere of the metal ion. In the case of [**1**]$^+$ and [**2**]$^+$, changes in bond lengths on going from Co^{III} to Co^{II} support such behavior, whereas, for [Co(dmgBF$_2$)$_2$], the loss or exchange of axial ligands probably occurs. For [Co(dpgBF$_2$)$_2$], the weaker ligand field would lead to a cobalt(II) complex more strongly bonded to the axial ligands. Both families of complexes undergo a quasi-reversible Co^{II}/Co^{I} redox process.

Table 1: Redox potentials of Co^{III} complexes. Potentials were determined under argon flux in acetonitrile solvent, $T = 20$ °C.

	Co^{III}/Co^{II}		Co^{II}/Co^{I}	
Complex	$E_{1/2}$ [V vs SCE]	ΔE_P [mV]	$E_{1/2}$ [V vs SCE]	ΔE_P [mV]
[1]$^+$	0.46	150	−0.38	70
[2]$^+$	0.38	150	−0.66	80
[3]$^+$	0.28	100	−0.73	90

The effect of the apical substituent on the boron is evidenced by the shift of the redox waves to more negative potentials for [**3**]$^+$ in comparison to [**2**]$^+$, owing to the less electron-withdrawing nature of the trifluorophenyl ring in comparison to the fluorine atom. The nature of the substituents on the periphery of glyoxime ligands is another synthetic handle for the control of the electrochemical behavior, as can be seen upon substitution of the electron-donating methyl groups in [**2**]$^+$ to the electron-withdrawing phenyl groups in [**1**]$^+$. As such, the apical boron sites on the clathrochelate complexes can act as an added synthetic tuning point for redox modulation of the metal complexes, as compared to the difluoroboryl bis(glyoximato) complexes.

Changes in the electronic absorption spectra for the different redox states were monitored by spectroelectrochemistry and show pronounced modifications, especially in the low-energy region. Electrochemical reduction at $E = 0.155$ V and $E = -0.645$ V vs SCE allowed the successive generation of complexes [**1**] and [**1**]$^-$ (Figure 2a, SCE = saturated calomel electrode). The UV/Vis spectrum of [**1**]$^-$ shows two intense overlapping bands at $\lambda = 625$ nm ($\varepsilon = 20 \times 10^3$ mol^{-1} L cm^{-1}) and $\lambda = 680$ nm ($\varepsilon = 20 \times 10^3$ mol^{-1} L cm^{-1}) that are similar to those previously reported for a Co^{I} ion in a clathrochelate system.[17] Notably, similar electronic features are detected for the formal cobalt(I) species in the family of bis(glyoximato) complexes. The presence of different isosbestic points for each one-electron reduction process and for each one-electron re-oxidation process confirms the chemical reversibility of the redox reaction and also the presence of only two species in solution for each redox couple (see the Supporting Information).

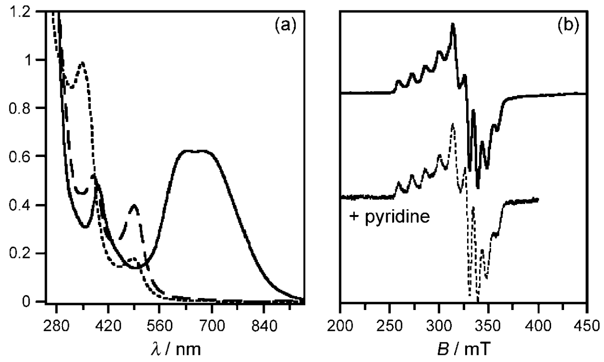

Figure 2. a) UV/Vis spectra of 1 mM acetonitrile solution of [1]$^+$ (•••••), showing evolution upon successive reduction at $E = 0.155$ V (– – –, [1]), and $E = -0.645$ V vs SCE (——, [1]$^-$); $T = -30$ °C. b) X-band EPR spectra of a 1 mM acetonitrile solution of [1] (——) and in presence of 2.5 equivalents of pyridine (-----); $T = 100$ K, microwave power = 2 mW, attenuation = 20 dB, $\nu = 9.4$ GHz.

The X-Band EPR spectrum at 100 K of an electrochemically generated solution of [**1**] is typical for a low-spin hexacoordinated cobalt(II) complex (Figure 2b). Furthermore, no spectral change occurs upon addition of an exogenous ligand, such as pyridine, indicating that further coordination is not possible at the metal center (see the Supporting Information), in sharp contrast with the X-band EPR spectrum of the complex [Co(dmgBF$_2$)$_2$], wherein the binding of a nitrogen-containing ligand to the metal center is evidenced by the presence of superhyperfine coupling on the signals.[19] The X-Band EPR spectrum of the doubly reduced species [**1**]$^{-1}$ shows no signal under the same experimental conditions as for [**1**]. The formation of either a high-spin ($S = 1$) or a low-spin ($S = 0$) cobalt(I) species can account for this result. Notably, a high-spin cobalt(I) complex has been magnetically characterized within the same coordination sphere but with more electron-withdrawing substituents on the glyoxime skeleton.[17]

Figure 3 shows the evolution of the cyclic voltammograms of [**1**]$^+$ and [**2**]$^+$ upon addition of protons. Addition of acid ($HClO_4$ in acetonitrile) triggered the formation of a catalytic wave on the more cathodic process attributed to the Co^{II}/Co^{I} redox couple. The same catalytic wave appears for compound [**3**]$^+$ at the Co^{II}/Co^{I} couple, which supports the fact that the cobalt(I) species is the catalytically active form in our systems, as is the case for the difluoroboryl bis(glyoximato) Co complexes. A general trend in the catalytic activity for this family of complexes with strong acids is the appearance of a catalytic wave near the Co^{II}/Co^{I} couple at low acid concentrations. Upon increasing the acid concentration, a weak shift of the catalytic wave to more negative potentials occurred, together with an increasing intensity, without reaching a plateau. This reactivity pattern has been termed as a “total” catalysis situation, whereby the catalytic reaction proceeds so quickly that the current is controlled by the diffusion of acid to the electrode surface.[20–22] A preliminary run to test the catalytic activity of [**2**]$^+$ in the presence of HCl showed no marked shift to higher potentials, as indicated by Peters and

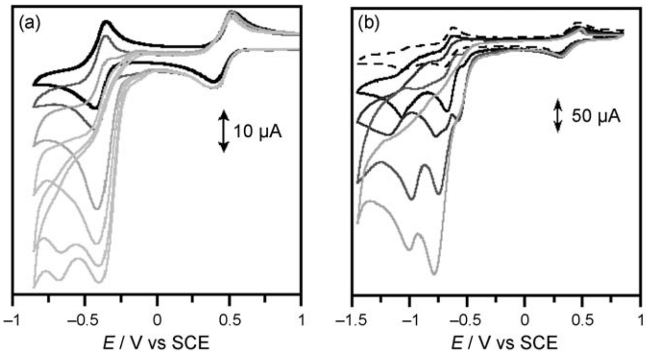

Figure 3. a) Cyclic voltammogram of a 0.87 mM acetonitrile solution of [**1**]$^+$ at a glassy carbon electrode (——), and evolution upon addition of successive aliquots of 2 equivalents of $HClO_4$. b) Cyclic voltammogram of a 2 mM acetonitrile solution of [**2**]$^+$, and evolution upon addition of 1, 2, 4, and 6 equivalents of $HClO_4$. Scan rate = 100 mV s^{-1}, T = 20 °C.

co-workers for the $[Co(dmgBF_2)_2]$ complex.[10] This result is in agreement with the fact that no direct coordination of the chloride ion to the metal center is feasible in the case of the [**2**]$^+$ (see the Supporting Information). As a reference, no catalysis occurred at a glassy carbon electrode in the presence of acid, scanning at a more negative potential than −1 V versus SCE. Bulk electrolysis of a 0.4 mM acetonitrile solutions of [**2**]$^+$ and [**1**]$^+$ in the presence of 33 mM $HClO_4$ were run at −0.85 V and −0.55 V, respectively. Hydrogen production was confirmed by gas chromatography analysis with a faradaic yield comparable with that of (5,10,15,20-tetraphenylporphyrinato)iron(III) chloride, measured in the same conditions (see the Supporting Information).[22] A challenging task ahead of us is to decipher the mechanistic routes explaining the patterns of reactivity for these complexes. For steric reasons, a bimetallic mechanism seems improbable, although we cannot exclude consequent structural changes around the metal ion leading to such cooperative action. The situation is also unclear for a monometallic mechanism. It is possible that two mechanisms may be operating; in one a purely metal-centered activation of the substrate, and in the other an intimate cooperation between the ligand scaffold and the metal for the formation of hydrogen.[23]

In summary, coordinatively saturated boron-capped tris(glyoximato) cobalt complexes have shown catalytic activity for hydrogen-forming reactions at potentials as positive as −0.55 V. The synthetic versatility of this family of complexes provides new perspectives for the fine tuning of their electrochemical reactivity, together with the elaboration of modified electrodes or photoelectrodes. Investigations into such applications are currently underway.

Experimental Section

$[Co(dmg(BF)_2)_3](BF_4)$ ([**2**](BF_4)): Dimethylglyoxime (1.47 g, 12.6 mmol) and $CoCl_2$ (540 mg, 4.2 mmol) were suspended in ether (100 mL) under argon. After a few minutes, trifluoroborane etherate (5.3 mL, 42 mmol) was added. The mixture was stirred overnight at room temperature. The resultant brown precipitate was isolated by filtration and re-crystallized from acetonitrile/methanol (1:1), affording [**2**](BF_4) as a brown powder (770 mg, 2.81 mmol, 67 %). MS (ESI) m/z (%): 461.1 (100) $[M]^+$. Elemental analysis calcd (%) for $C_{12}H_{18}B_3CoF_6N_6O_6$: C 26.32, H 3.31, B 5.92, Co 10.76, F 20.81, N 15.35; found: C 26.95, H 3.40, B 6.01, Co 10.49, F 20.63, N 15.17.

Crystal data of **1**: $C_{44}H_{37}B_3Co_1F_6N_7O_8$; $M_r = 997.17$; crystal size $0.21 \times 0.13 \times 0.09$ mm^3; monoclinic; space group Cc (9); $a = 16.967(3)$, $b = 20.124(3)$, $c = 15.681(2)$ Å; $\alpha = 90$, $\beta = 116.530(4)$, $\gamma = 90°$; $V = 4790.2(13)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.383$ g cm^{-3}; $\mu(Mo_{K\alpha}) = 0.440$ mm^{-1}; $T = 100(1)$ K; $2\theta_{max} = 61.46°$; 36736 reflections measured; 13464 unique reflections ($R_{int} = 0.0749$); 6358 ($I > 2\sigma(I)$) of which were used in all calculations. $R(F_2) = 0.0790$ and $wR(F_2) = 0.1963$; $\rho_{max} = 0.755$ e$^-$ Å^{-3}, $\rho_{min} = -0.414$ e$^-$ Å^{-3}.

CCDC 674980 and 674981 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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