COMMUNICATION

β-Oxochlorin cobalt(II) complexes catalyze the electrochemical reduction of CO_2

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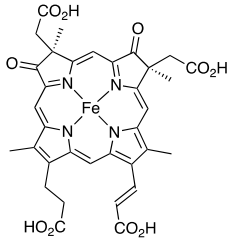
Inspired by the architecture of the macrocycle of heme d_1, a series of synthetic mono-, di- and tri-β-oxo-substituted porphyrinoid cobalt(II) complexes were evaluated as electrocatalytic CO_2 reducers, identifying complexes of unusually high efficiencies in generating multi-electron reduction products, including CH_4.

The efficient reduction of the greenhouse gas CO_2 into useful carbon-based molecules will help alleviate its environmental impact.[1-3] Generating fuels from CO_2, such as CH_4, particularly when using electrical energy from renewable resources, may also contribute to solving other timely problems: the dwindling of our non-renewable energy sources and the storage of energy from highly fluctuating renewable energy sources.[4]

Among the challenges associated with using CO_2 as a feedstock is that the linear, non-polar CO_2 molecule is thermodynamically stable and kinetically inert.[5] Fortunately, promising approaches for overcoming the kinetic challenges have been reported.[6-10] Thermal, electrochemical and photochemical reduction of CO_2 have become possible using both heterogenous and homogeneous systems.[11-18]

Irrespective of the progress in the field, systems that are able to reduce CO_2 by more than two electrons are rare, particularly, when considering systems that are based on earth-abundant metals.[15, 19-22] Porphyrin iron and cobalt complexes possess some electrocatalytic CO_2 reduction properties.[23-28] In addition, the superior activity of select hydrometalloporphyrins in electrocatalytic reductions of H^+ (hydrogen evolution reaction)[29-31] or CO_2[32, 33] over their saturated porphyrin analogues has begun to be explored.

Bacteria accomplish multi-electron reductions of nitrite or sulfate using heme d_1, the iron porphyrinoid prosthetic group of dissimilatory nitrite and sulfite reductases, respectively.[34-36] The porphyrinic framework of heme d_1 contains a unique 2,7-dioxoisobacteriochlorin framework.[§]



heme d_1

Aside from the generally recognized non-innocence of the porphyrinic framework in the catalytic action of their metal complexes,[37] the complex roles of the β-oxo-functionalities during nitrite reduction catalysis have only recently begun to become clear; they affect the iron reduction potential, metal axial ligand binding, and proton transfer reactions.[38] The question arises whether the presence and regiochemistry of one, or more, β-oxo-functionalities impart beneficial properties with respect to the ability to reduce CO_2, also. We therefore prepared the Co(II) complexes of known β-mono-oxo-, all di-oxo-isomers, and some trioxo-isomers derived from β-octaethylporphyrin,[39] and studied their characteristics in the electrocatalytic CO_2 reduction reaction, some of which proved to be competent in affecting the 8-electron reduction of CO_2 to CH_4. Thusly, we introduce herein a new family of earth-abundant metal-based CO_2 catalysts. This study also delineates the degree number, and position of the oxo-substituents on the macrocycle affect the reduction of CO_2, guiding the further development of more efficient catalysts.

All free base oxochlorins were prepared using an established method (treatment of octaethylporphyrin **1** with H_2O_2 in conc. H_2SO_4) (Scheme 1).[39, 40] The chromatographic separation of the products formed in this non-selective oxidation allowed the isolation of the monoketone, all isomers of the diketones (of the bacteriochlorin and isobacteriochlorin series)[‡], and two triketone isomers.[39] Insertion of cobalt(II) under thermal conditions provided the complexes, most of which are novel (see ESI for their characterization).[41]

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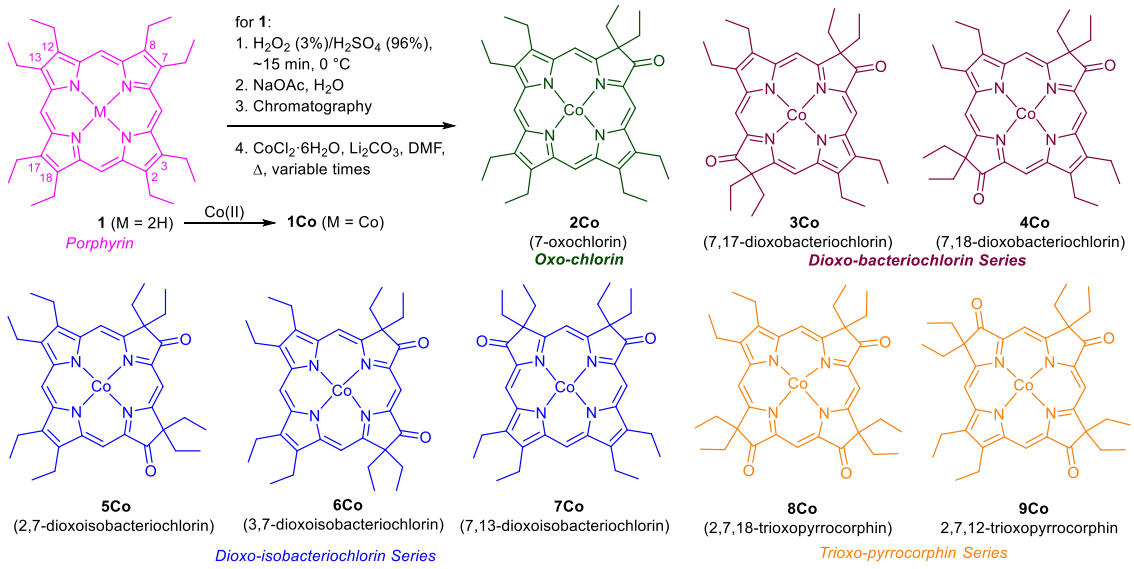

Scheme 1. Synthesis of the oxoporphyrinoid cobalt(II) complexes investigated, also indicating by color the general porphyrinoid class the macrocycles belong to.

The cyclic voltammograms (CVs) of solutions of the complexes in acetonitrile sparged with N_2 show two quasi-reversible reductions separated by ~1.1 V from each other (Figure 1, Table 1). The first reductions for the trioxopyrrocorphin complexes **8Co** and **9Co** appear at less negative potentials than those of oxochlorin **2Co** or all dioxo(iso)bacteriochlorin isomers (**3Co** through **7Co**). Based on recent literature reports, we assign these reductions to a ligand-based and a metal-based process that produce $[\mathbf{XCo^{II}}]^-$ and $[\mathbf{XCo^{I}}]^{2-}$ intermediates, respectively.[27, 42-44] A third, non-reversible, reduction is observed for the dioxochlorin cobalt complexes **3Co**, **4Co**, and **5Co**, and the two trioxochlorin complexes **8Co** and **9Co**.

Table 1. Electrochemical reduction potentials (vs $Fc^{+/0}$) of cobalt complexes indicated under N_2 and catalytic current enhancement in presence of CO_2.[a]

Complex	1st red	2nd red	3rd red	4th red	i_{CO2}/i_{N2}
1Co[b]	N.D.	N.D.	N.D.	N.D.	N.D.
2Co	-1.32	-2.52	-2.72		9
3Co	-1.16	-2.31	-2.46	-2.75	7
4Co	-1.24	-2.37	-2.82		9
5Co	-1.25	-2.36	-2.75		3
6Co	-1.18	-2.26			9
7Co	-1.27	-2.35			9
8Co	-1.15	-2.22	-2.71		6
9Co	-1.13	-2.17	-2.72		5

[a] Conditions: N_2 or CO_2 atmospheres, electrolyte 0.1 M $[^nBu_4N]PF_6$ in acetonitrile, glassy carbon working electrode, Pt wire counter electrode, 25 °C. [b] The solubility of **1Co** in CH_3CN was too low to allow a determination of its electrochemical and electrocatalytic properties under comparable conditions to those of the oxo-porphyrinoids.

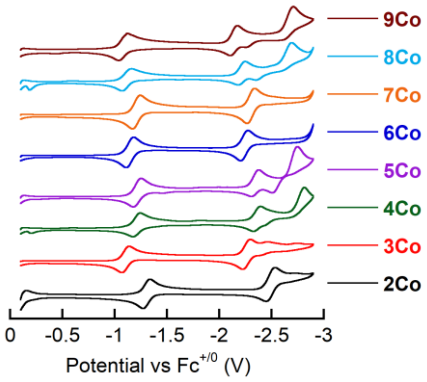

Figure 1. Cyclic voltammograms of 1 mM oxoporphyrinoid cobalt complexes. Conditions: see Table 1.

When the solutions were saturated with CO_2, the peaks corresponding to the first reduction event ($[\mathbf{XCo^{II}}]/[\mathbf{XCo^{II}}]^-$) remained unaffected. However, strong catalytic currents, i_{CO2}, were observed for the second reduction events ($[\mathbf{XCo^{II}}]^-/[\mathbf{XCo^{I}}]^{2-}$) in all cases, indicating the electrocatalytic reduction of CO_2 is promoted by the cobalt complexes. This behavior is reminiscent of cobalt porphyrinic systems,[45] For example, cobalt(II) tetraphenylporphyrin also showed an 8-fold current increase (i_{CO2}/i_{N2}) on the wave corresponding to the second reduction (butyronitrile solution saturated with Ar at a scan rate of 0.1 V s^{-1}).[45] The oxochlorin cobalt complex **2Co** and the dioxoisobacteriochlorin complexes **6Co**, **7Co** and dioxobacteriochlorin **4Co** exhibit the highest current enhancements, 9-fold (Table 1). All other dioxo complexes show only about 3- to 7-fold current enhancements. This clearly shows the strong influence of the number and position of the β-dioxo substituents. The regiochemical influences of the β-oxo substituents on the electronic properties of these,[39, 40] and related,[46] chromophores was shown before. Both of the triketone isomers provided catalytic current enhancements that were larger than that of weakest diketone (**5Co**), but

smaller than that of the other diketone regioisomers, showing that more β-oxo substituents is not necessarily better.

We also tested these complexes with respect to the effect on their catalytic potential ($E_{cat/2}$) for CO_2 activation and product selectivity in the presence of different concentrations of Brønsted acid. In general, the catalytic current tends to increase linearly with increasing [TFE] (pK_a (CH_3CN) = 35.4)[47] across the series tested, with positive shifts in the $E_{cat/2}$ values at the highest TFE concentration tested (0.42 M). One example of these studies for oxochlorin complex **2Co** is shown in Figure 2 (all data are tabulated in Table S2 and shown in Figs. S33-64). For example, titrimetric analysis of the electrochemical solution of 6Co with TFE (in the range up to 0.42 M) reveals the largest positive shift across the series in Ecat/2 from -2.45V vs Fc+/0 to -2.35V vs Fc+/0. The catalytic enhancement ratio (iCO2/iN2) increased from 9 (0.0 M TFE) to 37 (0.42 M TFE), representing a 4-fold enhancement in catalytic activity. Since the catalytic waves represent three reactions, they do not allow foot-of-the-wave analyses to extract catalytic rates.[48] We thus used preparative-scale electrolysis experiments to compare the electrocatalytic CO_2 reduction activity and product selectivity of the complexes.

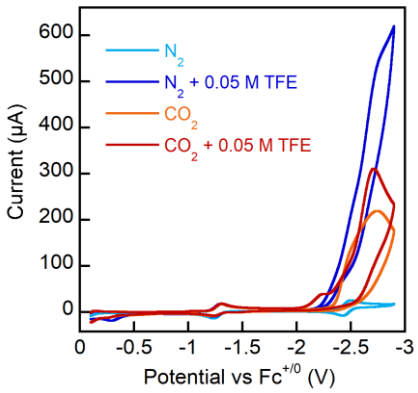

Figure 2. Cyclic voltammograms of 1 mM **2Co** in the absence and presence of CO_2, in the absence and presence of 0.05 M trifluoroethanol (TFE). Conditions: N_2 or CO_2 atmospheres, electrolyte 0.1 M $[^nBu_4N]PF_6$, glassy carbon working electrode, platinum wire counter electrode, reference $Fc^{+/0}$, 25 °C.

After 2 h of controlled potential electrolysis (CPE) experiments at -2.9 V (vs $Fc^{+/0}$), the liquid and gas phases were analysed by ^1H NMR and GC-MS, respectively (Table 2).

Table 2. Faradaic efficiencies, TON and TOF for oxoporphyrinoid cobalt complexes indicated based on controlled potential electrolysis (CPE) experiments. Conditions: $[^nBu_4N]PF_6$ (0.1 M) in CH_3CN with a glassy carbon working electrode, a Pt counter electrode, a Ag/Ag^+ reference electrode ($Fc^{+/0}$ used as an internal calibrant), held at -2.9 V vs $Fc^{+/0}$ for 2 h.

Catalyst	FE (%)				TON				TOF (h^{-1})			
	H_2	CO	CH_4	$HCOO^-$	H_2	CO	CH_4	$HCOO^-$	H_2	CO	CH_4	$HCOO^-$
2Co	<3	59 ± 3	4 ± 2	< 3	-	35	1.3	-	-	17.5	0.7	-
3Co	<3	53 ± 1	12 ± 2	< 2	-	28	3.1	-	-	14	1.5	-
4Co	<4	66 ± 2	15 ± 1	< 1	-	37	3.5	-	-	18.5	1.8	-
5Co	<3	49 ± 3	14 ± 2	< 3	-	24	3.1	-	-	12	1.5	-
6Co	<3	57 ± 4	10 ± 3	< 4	-	29	2.9	-	-	14.5	1.5	-
7Co	<3	63 ± 2	16 ± 2	<2	-	36	3.7	-	-	18	1.8	-
8Co	< 5	51 ± 1	8 ± 3	< 3	-	26	2.2	-	-	13	1.1	-
9Co	<3	52 ± 3	9 ± 2	< 1	-	27	2.7	-	-	13.5	1.8	-

The primary reduction product using any of the catalysts is CO, with turnover numbers (TON) for the formation of CO ranging from 24 to 35. The highest TON_{co} was determined for oxochlorin complex **2Co**. Smaller fractions of H_2, CH_4, and HCO_2^- (formate) were detected in the reaction products of all catalysts. Isotope labelling studies using $^{13}CO_2$ produced $^{13}CH_4$ (*m/z* = 17), confirming that the CH_4 originated from CO_2 reduction (Figure S65). The TON for CH_4 formation ranged from 1.3 to 3.7. The highest CH_4 producing catalysts are any of the dioxo(iso)bacteriochlorin. Dioxo-bacterio- and isobacterio-chlorin complexes **4Co** and **7Co** were found to be the best catalysts for CH_4 production. Overall, the increase in the over-potential required to reduce CO_2 to CO leads to larger relative TOF, as expected based on data of other porphyrinoids.[15, 19-21]

In conclusion, the series of cobalt β-oxo-porphyrinoid complexes investigated here provide a new macrocycle modification motif for the search of efficient CO_2 activation catalyst that can reduce CO_2 beyond CO or formate. As in many other Co(II) porphyrinoids, the reduction event occurs when $[\mathbf{XCo}^{I}]^{2-}$ is formed. The highest catalytic current increases were registered for the mono-oxochlorin complex **2Co** and the dioxoisobacteriochlorin complexes **6Co**, **7Co** and dioxo-bacteriochlorin **4Co**. Our studies demonstrate that – firstly for any Co(II) complex – CH_4 can be produced using the β-oxoporphyrinoid complexes, whereby the all dioxo species proved to be the most active CH_4-generating catalysts (in terms of TON and TOF) for this 8-electron reduction process, perhaps pointing at the special nature of their dioxoporphyrinoid frameworks. However, any evidence that the 2,7-dioxoisobacteriochlorin framework for heme d_1 is superior compared to that of the other dioxoporphyrnoids could not be provided. Our data demonstrate the complex structure-activity relationships that are operative within this family of structurally related but electronically much differentiated compounds. Detailed mechanistic studies are the focus of continuing studies.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

§ In the context of the β-oxo-porphyrinoids discussed here, the terms chlorin, bacteriochlorin, and isobacteriochlorin are purely to describe their substitution pattern.

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