Inorganic Chemistry

Communication

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Catalysis of Proton Reduction by a [BO_4]-Bridged Dicobalt Glyoxime

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Supporting Information

ABSTRACT: We report the preparation of a dicobalt compound with two singly proton-bridged cobaloxime units linked by a central [BO_4] bridge. Reaction of a doubly proton-bridged cobaloxime complex with trimethyl borate afforded the compound in good yield. Single-crystal X-ray diffraction studies confirmed the bridging nature of the [BO_4] moiety. Using electrochemical methods, the dicobalt complex was found to be an electrocatalyst for proton reduction in acetonitrile solution. Notably, the overpotential for proton reduction (954 mV) was found to be higher than in the cases of two analogous single-site cobalt glyoximes under virtually identical conditions.

The reduction of protons to dihydrogen, the reductive half-reaction of water splitting, requires a catalyst to proceed at a suitable rate.[1] Progress in understanding the mechanisms of H_2 production has come from studies of homogeneous catalysts[2] and especially those based on cobalt glyoximes.[3,4]

In acetonitrile with acid sources, the [H]- or [BF_2]-bridged cobaloximes, Co(dmgH)$_2$(L)Cl (**1**) and Co(dmgBF$_2$)$_2$(L)Cl (**2**) (dmg = dimethylglyoximate), (Figure 1) have been shown to reduce protons to dihydrogen. Among the pathways considered for catalysis with **2**, one that is particularly attractive involves a Co^{II}−H intermediate that is readily protonated to form dihydrogen.[2b,5]

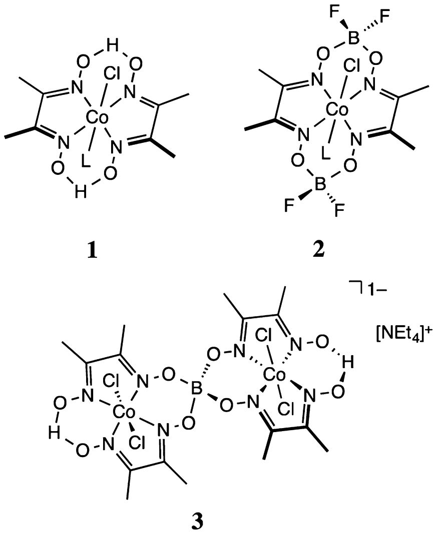

Figure 1. Cobalt(III) dimethylglyoxime complexes.

Pathways involving multiple metal centers also have been proposed because such sites may promote reactivity not accessible with a single site.[6] Along this line, Szymczak and co-workers reported dicobalt pyridazine-bridged complexes that functioned as proton-reduction catalysts.[7] Similarly, our group examined a dicobalt system with octamethylene-linked bis(glyoxime) ligands. In this system, experiments revealed no enhancement of electrocatalytic hydrogen evolution rates over those found for mononuclear analogues.[8]

Synthetic methods remain elusive, however, for derivatizing the glyoxime macrocycle to generate compounds with closely spaced metal atoms or structures amenable to immobilization on electrodes.[9] For this reason, we have recently been investigating new routes to substitution of the macrocyclic structure. Our work has met with success, and we report a novel dicobalt dimethylglyoxime (**3**) bridged by a central [BO_4] moiety (Figure 1) that is active for proton-reduction catalysis.

Synthesis of **3** was accomplished starting with Co^{III}(dmgH)$_2$(MeCN)Cl (**1**). Treatment of **1** with trimethyl borate and tetraethylammonium chloride followed by recrystallization with acetonitrile and diethyl ether yielded brown crystals that were identified as a [BO_4]-bridged dimer of two singly H^+-bridged cobalt(III) glyoxime units.

Nuclear magnetic resonance (NMR) spectroscopy is consistent with the dimeric structure of **3** (Figure S1, Supporting Information). ^1H NMR exhibited two singlets with a 1:1 integration at 2.47 and 2.56 ppm as expected for the methyl groups of the dimethylglyoxime ligands. A singlet was found at 18.4 ppm, attributable to the two bridging protons of the complex, and a triplet and quartet at 1.22 and 3.17 ppm, respectively, that are attributable to the tetraethylammonium countercation. In the ^{13}C NMR spectrum, signals for six unique carbon environments were detected (Figure S2, Supporting Information). Finally, ^{11}B NMR showed a singlet at 7.41 ppm, attributable to the bridging [BO_4] moiety (Figure S3, Supporting Information). Mass spectra also confirmed the expected composition of the isolated material; the negative ion spectrum exhibited a parent peak at 727.1 *m*/*z*, corresponding to the monoanionic dicobalt(III) complex (Figure S4, Supporting Information).

Received: July 28, 2014
Published: November 19, 2014

dx.doi.org/10.1021/ic501804h | *Inorg. Chem.* 2014, 53, 12668−12670

Brown blade-like crystals of complex **3** analyzed by single-crystal X-ray diffraction revealed a dimeric structure bridged by a tetrahedral [BO_4] moiety (Figure 2). Each cobalt(III) is coordinated by two essentially coplanar dimethylglyoximate ligands and two axial chlorides. The Co−N distances for the two cobalt centers are virtually identical, in the ranges of 1.877−1.888 Å and 1.883−1.890 Å, and the four Co−Cl bond lengths are in the narrow range of 2.226−2.235 Å.

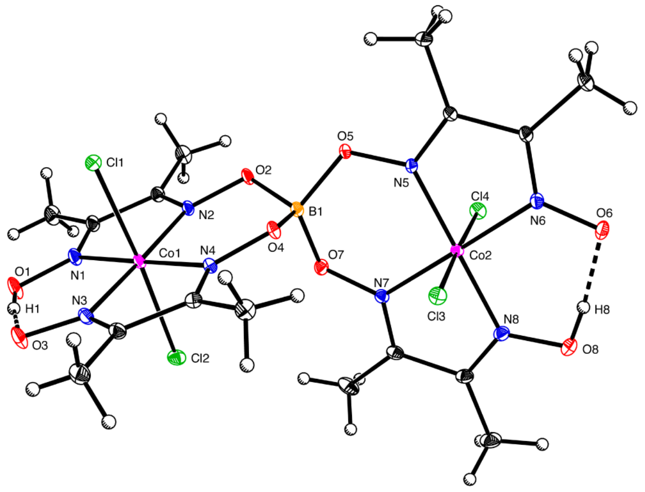

Figure 2. Molecular structure of **3**. Tetraethylammonium counter-cation and one cocrystallized acetonitrile molecule are omitted for clarity. Colors: cobalt, pink; nitrogen, blue; oxygen, red; chloride, green; and boron, yellow. Thermal ellipsoids are shown at 40% probability.

The bridging [BO_4] moiety exhibits a Co−B−Co angle of 145.21° and Co−B distances of 3.211 and 3.210 Å. As a result, the through-space Co−Co distance is rather long, 6.136 Å. Notably, the boron is not in-plane with the macrocycles defined around either Co center, similar to the position adopted by the [BF_2] bridges in **2**. Considering the high degree of symmetry observed by NMR spectroscopy, **3** is likely fluxional in solution at room temperature rather than locked into the conformation observed in the X-ray diffraction study.

Cyclic voltammograms collected for **3** show a broad oxidation event with onset near −0.45 V (all potentials here are reported versus the ferrocenium/ferrocene couple, denoted $Fc^{+/0}$; Figure S6, Supporting Information). We assign this feature to oxidation from Co^{2+} to Co^{3+}. At around −1 V, a reduction appears that we assign to reduction of Co^{3+} to Co^{2+}. At slightly more negative potentials, two closely spaced single-electron couples were observed near −1.2 and −1.3 V (Figure 3). We assign these waves to $Co^{2+}Co^{2+}/Co^{2+}Co^{1+}$ and $Co^{2+}Co^{1+}/Co^{1+}Co^{1+}$ reductions. The $Co^{2+}Co^{2+}$ form is the stable form at the rest potential of −0.5 V; thus, in voltammetr, if sweeping repeatedly from −0.5 V to more negative potentials (Figure 3), the shoulder at −1 V is minimal in comparison to the case of wider sweeps that induce oxidation to Co^{3+} prior to sweeping below −0.5 V (Figure S6, Supporting Information).

Similar to findings for our complex **3**, the bimetallic pyridazine system mentioned above[7] exhibited two one-electron events for the reductions $Co^{2+}Co^{2+}/Co^{2+}Co^{1+}$ and $Co^{2+}Co^{1+}/Co^{1+}Co^{1+}$. Consistent with the shorter Co−Co distance of 3.798 Å in that system, a larger separation (~200 mV) of the one-electron waves was observed, as well as intervalence charge−transfer (IVCT) bands for the mixed valence forms $Co^{3+}Co^{2+}$ and $Co^{2+}Co^{1+}$.[7] Spectroelectrochemical studies with **3** did not reveal the presence of IVCT bands during electrolyses at the relevant negative potentials, suggesting that the significantly larger Co−Co distance of 6.136 Å in **3** disfavors electronic coupling between the metal centers, which in turn results in similar reduction potentials.

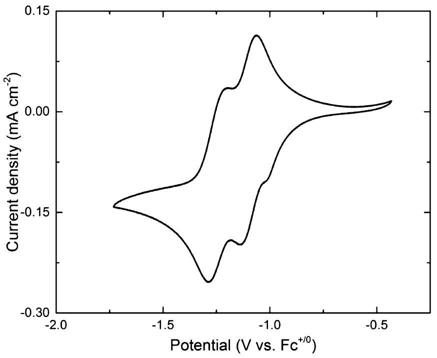

Figure 3. Cyclic voltammetry with **3** showing two closely spaced cobalt(II/I) couples near −1.25 V vs $Fc^{+/0}$. Conditions: [**3**] = 0.5 mM; electrolyte was 0.1 M NBu_4PF_6 in MeCN; scan rate was 100 mV/s.

Catalytic proton reduction was observed in cyclic voltammograms of **3** in the presence of a buffered organic acid. Specifically, we used a 1:1 mixture of protonated dimethylformamide ([DMFH]$^+$) and dimethylformamide (DMF). This buffered organic acid allows control of the reversible thermodynamic potential for the H^+/H_2 couple under conditions set here at −389 mV vs $Fc^{+/0}$.[10] The change in the cyclic voltammogram upon buffered acid addition is shown in Figure 4.

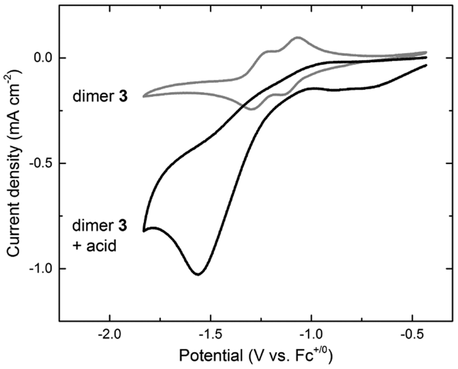

Figure 4. Cyclic voltammetry of **3** in the absence and in the presence of 5 mM of the 1:1 mixture of [DMFH]$^+$:DMF.

Cyclic voltammetry of **3** in the presence of acid showed onset of an irreversible catalytic response. A small irreversible current onsets near −0.5 V, and a larger current more characteristic of catalysis onsets near −1.25 V. Control experiments with **1** and **2** under virtually identical conditions also showed onset of catalytic currents (Figures S8 and S9, Supporting Information). Notably, conditions were not found to achieve a plateauing catalytic current by variation of reagent concentrations or scan rate. However, we estimated the overpotential for catalyst **3** to be ~954 mV at half-max current of the larger catalytic wave.[10] For comparison, the overpotentials of **1** and **2** under our conditions (5 mM 1:1 [DMFH]$^+$:DMF, 0.5 mM [catalyst]) were found to be 851 and 497 mV, respectively. Direct acid reduction in the absence of catalyst was observed at potentials slightly more negative than the catalytic response of **3** (Figure S10, Supporting Information).

Dihydrogen was confirmed as the product associated with the observed catalytic current with **3** by gas chromatography. Analysis of headspace gas following a 1.25 h electrolysis at −1.5 V gave 1.26 mL of H_2. On the basis of the charge transferred during electrolysis (minus the charge to reduce the dimer to the [$Co^{2+}Co^{2+}$] state), 1.43 mL of H_2 could have been produced; the Faradaic yield of H_2 production was 88% (±10% error). The total charge transferred corresponds to a TON of 3.3 (based on dimer). Analogous electrolysis data in the absence of catalyst showed significantly less charge passed, consistent with the voltammetry (Figure S11, Supporting Information).

Strikingly, **3** has a higher overpotential than either of the monomeric analogues. This finding was surprising to us because **3** is composed of two cobalt units closely resembling **1**. We anticipated that the bridging [BO_4] moiety would perform a similar role to the [BF_2] moieties in **2**, resulting in less negative reduction potentials and consequently catalysis at lower overpotentials. We also note, however, that the small irreversible currents for **3** in the presence of acid near −0.75 V may suggest multiple catalytic pathways, and thus, direct comparisons are challenging.

The cobalt centers in **3** are sufficiently closely spaced to result in electronic coupling that separates their respective cobalt(II/I) reductions by ~100 mV. Thus, the increased overpotential may be due to a higher potential requirement for reaching the key hydride-forming intermediate necessary for catalysis ([$Co^{1+}Co^{1+}$] rather than [$Co^{2+}Co^{1+}$]). This observation highlights that both the spatial arrangement of metal centers and their electronic coupling should be considered in future efforts aimed at generating catalysts with multiple metal centers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data for complex **3** in CIF format, synthetic details, and electrochemistry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Ivonne Ferrer for helpful discussions and Aaron Sattler for assistance in preparation of Figure 2. This research was carried out in part at the Molecular Materials Research Center of the Beckman Institute at Caltech. The research was supported by the Resnick Sustainability Institute at Caltech (Postdoctoral Fellowship to J.D.B.) and the NSF CCI Solar Fuels Program (CHE-1305124 and a CCI Postdoctoral Fellowship to J.D.B.). The Bruker KAPPA APEXII X-ray diffractometer was purchased via an NSF CRIF:MU award to the California Institute of Technology (CHE-0639094). Gas chromatographs were collected at the Joint Center for Artificial Photosynthesis at Caltech.

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