

Buffer Assists Electrocatalytic Nitrite Reduction by a Cobalt Macrocycle Complex

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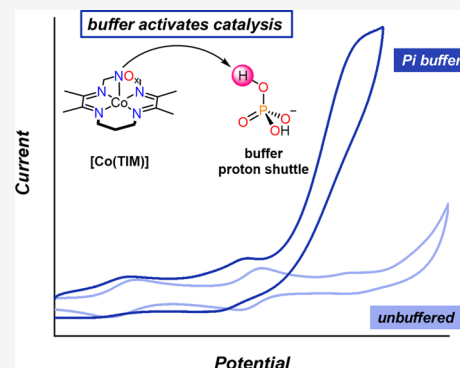


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ABSTRACT: This work reports a combined experimental and computational study of the activation of an otherwise catalytically inactive cobalt complex, $[\text{Co}(\text{TIM})\text{-Br}_2]^+$, for aqueous nitrite reduction. The presence of phosphate buffer leads to efficient electrocatalysis, with rapid reduction to ammonium occurring close to the thermodynamic potential and with high Faradaic efficiency. At neutral pH, increasing buffer concentrations increase catalytic current while simultaneously decreasing overpotential, although high concentrations have an inhibitory effect. Controlled potential electrolysis and rotating ring-disk electrode experiments indicate that ammonium is directly produced from nitrite by $[\text{Co}(\text{TIM})\text{Br}_2]^+$, along with hydroxylamine. Mechanistic investigations implicate a vital role for the phosphate buffer, specifically as a proton shuttle, although high buffer concentrations inhibit catalysis. These results indicate a role for buffer in the design of electrocatalysts for nitrogen oxide conversion.



INTRODUCTION

The Haber-Bosch process makes synthetic ammonia available on an industrial scale, with most of this ammonia used for fertilizers.¹ This ammonia is of critical importance to the survival of humanity, as it is estimated to support almost half of the planet's population.² However, less than 20% of the nitrogen in ammonia fertilizers is converted to food protein, with most of it being lost to the environment.³ The massive influx of anthropogenic nitrogen has severely disturbed the natural nitrogen remediation process, resulting in high concentrations of nitrate in aqueous ecosystems, which in turn leads to a range of deleterious environmental consequences.^{4,5}

A possible strategy for remediating the nitrogen cycle is the development of new methods that recycle nitrate, specifically by reducing it to benign or useful products, including dinitrogen or ammonia. In the biological denitrification process, which reduces nitrate to dinitrogen, the initial step of nitrate processing involves reduction to nitrite by nitrate reductase.⁶ This nitrite is subsequently converted to nitric oxide^{7,8} or ammonia.^{9,10}

As research aimed to better understand the natural denitrification process, efforts have been made toward the synthesis and investigation of molecular electrocatalysts for nitrite reduction.^{11–28} For example, the electrocatalytic reduction of aqueous nitrite by iron porphyrin complexes leads to the formation of multiple products, including ammonia, hydroxylamine, and N_2O ,^{18,22} while a cobalt tripeptide complex forms ammonia, with nitric oxide and hydroxylamine proposed as intermediates.²⁰

We recently reported detailed investigations into the electrocatalytic reduction of nitrogen oxyanions using the Co macrocycle complex, $[\text{Co}(\text{DIM})\text{Br}_2]^+$ (Figure 1), which

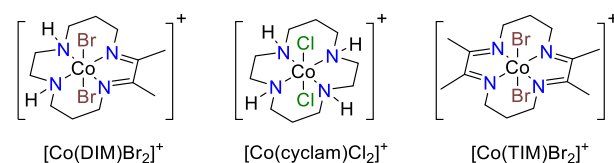


Figure 1. Structures of $[\text{Co}(\text{DIM})\text{Br}_2]^+$, $[\text{Co}(\text{cyclam})\text{Cl}_2]^+$, and $[\text{Co}(\text{TIM})\text{Br}_2]^+$ complexes.

provides ammonia as the sole product of reduction in non-buffered aqueous solution.^{21,29} Mechanistic investigations implicate three critical features of the DIM macrocycle ligand in facilitating the electrocatalytic activity: (1) the flexibility of the macrocycle ligand, which allows for *cis* coordination of the substrate; (2) the redox-noninnocence of the diimine moiety, which allows electrons to be stored on the ligand, thereby promoting two-electron reduction steps; and (3) the presence of the amine proton shuttles, which facilitate intramolecular protonation of the substrate.^{21,30} In support of these

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conclusions, we found that the related complexes, $[\text{Co}(\text{cyclam})\text{Cl}_2]^+$ and $[\text{Co}(\text{TIM})\text{Br}_2]^+$ (Figure 1), which lack the redox-active diimine moiety and amine proton shuttles, respectively, are inferior electrocatalysts for the reduction of aqueous NO_x^- .³¹ Indeed, we found that $[\text{Co}(\text{TIM})\text{Br}_2]^+$ shows no activity toward electrocatalytic NO_x^- reduction.

While much attention has been focused on electrocatalysts that incorporate proton shuttles designed to facilitate intramolecular proton transfer, external proton shuttles have also been reported to provide this functionality. For example, a urea-based hydrogen-bond donor has been reported to enhance electrocatalytic CO_2 reduction by $\text{Ni}(\text{cyclam})$ in non-aqueous solution, with the enhancement attributed to intermolecular H-bonding interactions between the urea-based additive and coordinated CO_2 , which help promote substrate protonation.³² More generally, the reaction medium may also provide proton shuttle functionality. For example, buffer has been implicated as a proton shuttle in water splitting electrocatalysis by ruthenium,^{33,34} nickel,^{35–37} and cobalt³⁸ complexes (Figure 2). In this context, it is noteworthy that

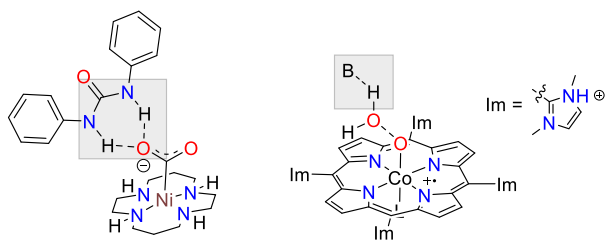


Figure 2. Selected examples of intermolecular proton shuttles in electrocatalysis.

electrocatalytic nitrite reduction by an iron macrocycle complex is observed in buffered solution only, although the origin of this activity was not reported.¹⁹

In this contribution, we report that $[\text{Co}(\text{TIM})\text{Br}_2]^+$, which is inactive in unbuffered solution, becomes an excellent catalyst for the reduction of nitrite to hydroxylamine and ammonium ions when electrocatalysis is conducted in phosphate buffer (Pi). The results of rotating ring-disk electrode (RRDE) experiments suggest that ammonium ion is formed from the electrocatalytic reduction of nitrite and not from the decomposition of hydroxylamine. Mechanistic studies reveal that buffer H_2PO_4^- is a source of protons, although competitive binding to the catalyst can attenuate the catalytic performance.

RESULTS AND DISCUSSION

Electrochemical Properties of $[\text{Co}(\text{TIM})\text{Br}_2]^+$ in Non-aqueous Solution. In contrast to $[\text{Co}(\text{DIM})\text{Br}_2]^+$,^{21,30} three reversible reductive processes are observed in the CV of $[\text{Co}(\text{TIM})\text{Br}_2]^+$ in MeCN solution (Figure S3, Table 1). The first two reductive processes are assigned as $\text{Co}(\text{III})/\text{Co}(\text{II})$ and $\text{Co}(\text{II}) (\text{TIM})/\text{Co}(\text{II}) (\text{TIM}^-)$ in analogy with the

assignments for $[\text{Co}(\text{DIM})\text{Br}_2]^+$ and $[\text{Co}(\text{DIM}) (\text{NO}_2)_2]^+$ complexes.^{21,30} Since $[\text{Co}(\text{TIM})\text{Br}_2]^+$ has two redox-non-innocent diimine moieties, the third reductive wave is tentatively assigned as a second ligand-based reduction, $\text{Co}(\text{II}) (\text{TIM}^-)/\text{Co}(\text{II}) (\text{TIM}^{2-})$. It is notable that the first ligand-based reduction of $[\text{Co}(\text{TIM})\text{Br}_2]^+$ is anodically shifted by over 500 mV from that of the $[\text{Co}(\text{DIM})\text{Br}_2]^+$ analogue, presumably due to the more conjugated electronic structure of the TIM ligand. In comparison with $[\text{Co}(\text{DIM})\text{Br}_2]^+$, $[\text{Co}(\text{TIM})\text{Br}_2]^+$ has superior redox properties as judged by both the number of ligand-based reductions and the accessibility of these processes.

Aqueous Electrochemistry in Phosphate Buffer.

Spectroscopy and mass spectrometry reveal that the cobalt(III) bis(nitro) complex $[\text{Co}(\text{TIM}) (\text{NO}_2)_2]^+$ is formed when $[\text{Co}(\text{TIM})\text{Br}_2]^+$ is dissolved in phosphate buffer containing excess NO_2^- . These characterization data are identical to those observed for the independently synthesized cobalt(III) complex $[\text{Co}(\text{TIM}) (\text{NO}_2)_2]\text{BPh}_4$ (Figures S1,S2,S4 and S5).

The cyclic voltammograms of $[\text{Co}(\text{TIM}) (\text{NO}_2)_2]^+$ in the sodium sulfate electrolyte reveal two reversible processes at $E_{1/2} \approx -0.21$ and -0.60 V vs. SCE (Figure S6). Two cathodic waves are also observed in the CV of $[\text{Co}(\text{TIM}) (\text{NO}_2)_2]^+$ in aqueous phosphate buffer solution at pH 7. The first wave ($E_{1/2} \approx -0.2$ V vs. SCE) is reversible, with a potential that varies significantly with the NO_2^- concentration (Figure 3). The linear dependence of $E_{1/2}$ on $\log[\text{NO}_2^-]$ has a slope of -61 mV/ $\log[\text{NO}_2^-]$, consistent with electron transfer being coupled to the dissociation of at least one nitro ligand (Figure 3).²¹ Analogous redox-coupled binding of NO_2^- has been observed for the related macrocycle complex, $[\text{Co}(\text{DIM}) (\text{NO}_2)_2]^+$.²¹

Density functional theory calculations at the B3LYP + D2/6-311+G** (SDD for Co) level in water modeled *via* the SMD solvation model were performed to support the proposed electrochemical mechanism (see Supporting Information for further details of computational methodology). Baik and co-workers demonstrated that the reduction potential for electron transfer that is coupled with a chemical process can be approximated by adding the energies of each step.^{39–41} The electron transfer coupled with the dissociation of a nitrite ligand for $[\text{Co}(\text{TIM}) (\text{NO}_2)_2]^+$ is expressed as the diagonal pathway (ΔE_D) in Figure S25 and Table S6. The DFT-approximated potentials agree with the experimental cyclic voltammetry results, with less than 0.1 eV difference in the measured concentration range.

In contrast to unbuffered conditions, the second wave ($E_{p,c} \approx -0.62$ V vs. SCE at pH 7) in phosphate buffer is irreversible, with a potential that is independent of the NO_2^- concentration (Figure 4). However, the peak potential of this wave changes with pH.⁴² DFT calculations suggest a $2e^-/1H^+$ process ($E_{1/2} = -0.56$ eV vs. SCE at pH 7), leading to a $\{\text{CoNO}\}^9$ complex (see Table S7, and Figure S27 for the detailed scheme). Although five-coordinate $\{\text{CoNO}\}^9$ complexes are extremely

Table 1. Redox Potentials ($E_{1/2}$) for $[\text{Co}(\text{DIM})\text{Br}_2]^+$ and $[\text{Co}(\text{TIM})\text{Br}_2]^+$ (V vs. SCE in MeCN) and the Differences between the Corresponding Redox Couples

	Co(III)/Co(II)	Co(II)L/Co(II)L [−]	Co(II)L [−] /Co(II)L ^{2−}
$[\text{Co}(\text{DIM})\text{Br}_2]^+$	−0.030	−0.90	
$[\text{Co}(\text{TIM})\text{Br}_2]^+$	−0.065	−0.38	−1.23
$\Delta E_{1/2}$	0.035	0.52	

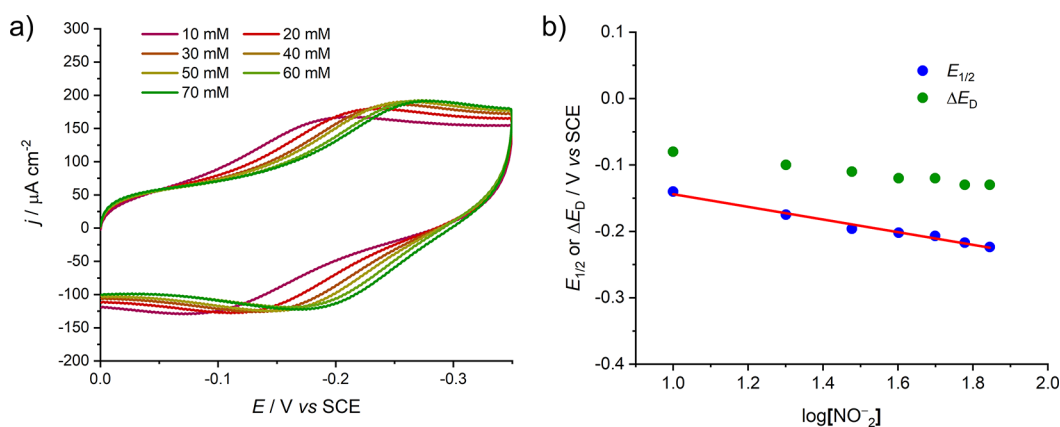


Figure 3. (a) Cyclic voltammetry of 0.5 mM $[\text{Co}(\text{TIM})\text{Br}_2]^+$ and variable concentrations of NaNO_2 in 500 mM Pi buffer, pH = 7. Working electrode: glassy carbon, scan rate = 200 mV/s. (b) Plot of $E_{1/2}$ vs. $\log[\text{NO}_2^-]$ (blue) and ΔE_D vs. $\log[\text{NO}_2^-]$ (green). The plot fits to the equation $y = -0.061(7)x - 0.064(1)$, $R^2 = 0.996$.

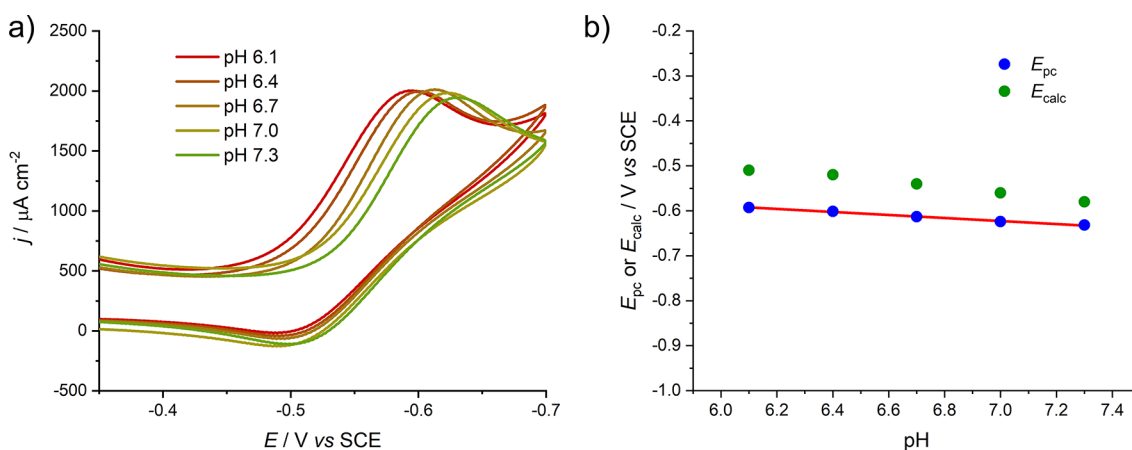


Figure 4. (a) Cyclic voltammograms of 3.0 mM $[\text{Co}(\text{TIM})\text{Br}_2]^+$ and 20 mM NaNO_2 in 100 mM Pi buffer with variable pHs. Working electrode: glassy carbon, scan rate = 200 mV/s; (b) plot of E_{pc} vs. pH (blue) and E_{calc} vs. pH (green). The plot fits to the equation $y = -0.034(1) - 0.387(9)$, $R^2 = 0.99$.

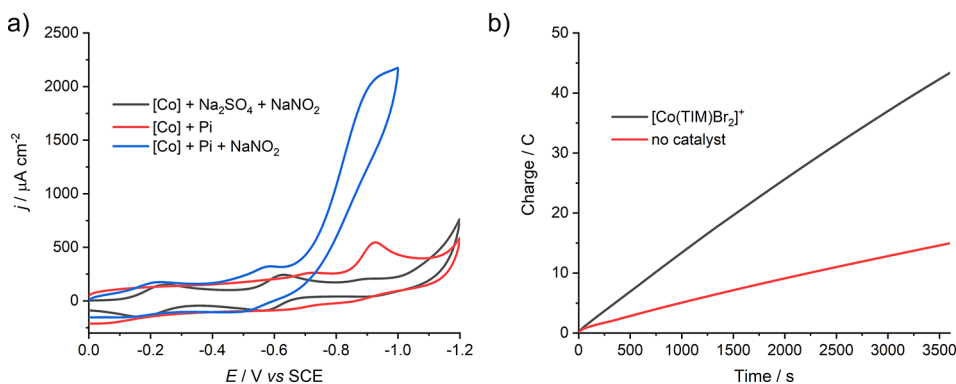


Figure 5. (a) Impact of buffer on the cyclic voltammogram of 0.5 mM $[\text{Co}(\text{TIM})\text{Br}_2]^+$ in pH 7.0 aqueous solution, glassy carbon working electrode, and scan rate = 200 mV/s. Specific conditions: 0.1 M Pi (red), 20 mM NaNO_2 and 0.1 M Na_2SO_4 (black), and 20 mM NaNO_2 and 0.1 M Pi (blue). (b) Charge passed during CPE of 20 mM NaNO_2 without (red) and with 0.05 mM $[\text{Co}(\text{TIM})\text{Br}_2]^+$ (black) in 0.5 M Pi buffer at pH 7.0, carbon rod working electrode.

rare,^{43,44} reduction of the redox-active TIM ligand can allow access to a more stable $\{\text{CoNO}\}^8$ unit.⁴⁵

Electrocatalytic Nitrite Reduction in Phosphate Buffer. As previously reported,²¹ $[\text{Co}(\text{TIM})\text{Br}_2]^+$ shows no activity toward the electrocatalytic reduction of nitrite in unbuffered aqueous solution (Figure 5a, black). An irreversible cathodic process is observed at $E_{p,c} \approx -0.92$ V vs. SCE (Figure

S6), which may correspond to $[\text{Co}(\text{TIM})]^{2+}$ to $[\text{Co}(\text{TIM})]^+$ reduction.³¹ By contrast, electrocatalytic reduction of nitrite is observed in phosphate buffer. For example, at pH 7 (0.1 M Pi), the cyclic voltammogram of 0.5 mM $[\text{Co}(\text{TIM})\text{Br}_2]^+$ in the presence of 20 mM NO_2^- exhibits a catalytic wave having an onset potential of ca. -0.5 V vs. SCE, with the current reaching a maximum at ca. -0.9 V vs. SCE. Remarkably, electrocatalysis

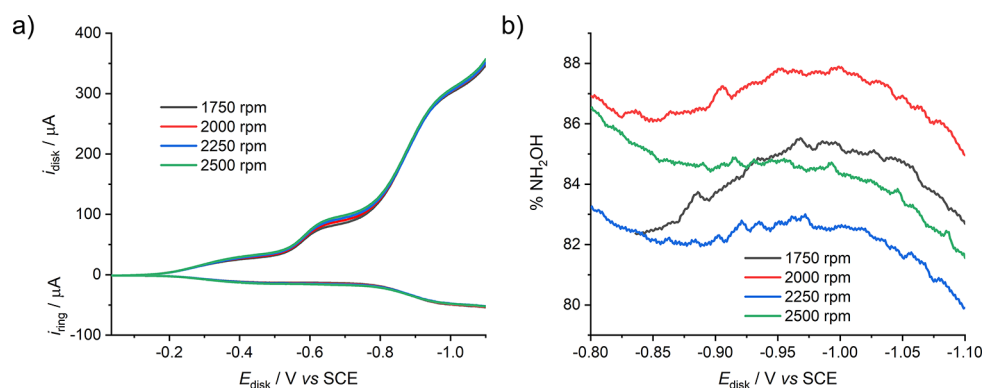


Figure 6. (a) RRDE of 0.5 mM $[\text{Co}(\text{TIM})\text{Br}_2]\text{Br}$ in 0.1 M Pi (pH 7.0) with 20 mM NaNO_2 at a glassy carbon disk/Pt ring electrode, scan rate 100 mV/s, variable rotation rate, $E_{\text{ring}} = 0.5$ V vs. SCE, and collection efficiency = 44.1%, $i_{\text{ring}}/i_{\text{disk}} = 16.4\%$ (b) Faradaic yield for NH_2OH production obtained by the application of eq 1 at different rotation rates.

is observed for phosphate buffer concentrations as low as 2 mM (see below). Importantly, no catalytic current is observed in the absence of nitrite, and therefore, the observed catalysis does not correspond to proton reduction (Figure 5a). This is consistent with previous studies that showed that $[\text{Co}(\text{TIM})\text{Br}_2]^+$ is not an electrocatalyst for proton reduction, albeit under more acidic conditions.⁴⁶

To assess the reduction products, controlled potential electrolysis (CPE) was performed on a 0.5 M phosphate buffer solution of 0.05 mM $[\text{Co}(\text{TIM})\text{Br}_2]^+$ and 20 mM NaNO_2 at pH 7 (Figure 5b). Following electrolysis at -0.9 V vs. SCE for 1 h, NH_2OH is characterized as the primary reduction product (2.1 mM, 42 turnovers, Faradaic efficiency 85%),⁴⁷ while NH_4^+ is characterized as a secondary product (0.28 mM, 5.8 turnovers, Faradaic efficiency 17%).⁴⁸ Consistent with the CV experiments, no dihydrogen is formed as determined by gas chromatography-thermal conductivity detector (GC-TCD) analysis of the headspace gas. Chemiluminescence analysis⁴⁹ of the headspace following electrocatalysis shows minimal ($<0.001\%$ Faradaic efficiency) $\text{NO}(\text{g})$ production (Table S1). There is no evidence for loss of catalytic activity over the course of the CPE experiment. Control experiments do not show the formation of nanoparticles or electrode-deposited materials, strongly supporting homogeneous catalysis (see Supporting Information for details).

While other electrocatalysts for nitrite reduction have similarly been reported to produce both ammonium and hydroxylamine,^{13–16,18,50,51} it is worth noting that hydroxylamine has low thermodynamic stability.⁵² Moreover, transition metal complexes that are electrocatalysts for nitrite reduction have been reported to affect the catalytic disproportionation of aqueous hydroxylamine under non-electrocatalytic conditions, providing ammonium ion as one of the disproportionation products.⁵³

In light of these concerns, we undertook RRDE experiments to determine the Faradaic efficiency for hydroxylamine formation. Here, the potential of the glassy carbon disk was swept negatively while the platinum ring potential was kept constant at 0.50 V vs. SCE. This potential is sufficient to oxidize hydroxylamine by two electrons, while ammonium cannot be oxidized under these conditions.⁵²

The Faradaic efficiency for hydroxylamine production as a function of potential is determined according to:

$$\% \text{NH}_2\text{OH}(E) = \frac{\frac{2i_r(E)}{N}}{i_d(E) + \frac{i_r(E)}{N}} \times 100\% \quad (1)$$

where $i_r(E)$ and $i_d(E)$ are the ring and the disk current, respectively, at potential E , while N is the collection efficiency of the RRDE.⁵⁴

As observed in the CV experiments, sweeping the disk potential negatively reveals the two cobalt-based reduction processes, followed by a steep increase in the current (commencing at *ca.* -0.8 V vs. SCE) as a result of electrocatalytic nitrite reduction (Figure 6a). The corresponding Faradaic yield for hydroxylamine production across the potential range of nitrite reduction catalysis shows a small variance that is independent of the rotation rate (Figure 6b) and matches that obtained from CPE experiments. This variance ($\pm 5\%$) is likely due to the collection efficiency of the RRDE. Since the Faradaic efficiency is the same at different rotation rates, hydroxylamine is unlikely to be an intermediate in the reduction of nitrite to ammonium ion *via* disproportionation on the timescale of this experiment. While the RRDE experiment does not allow us to quantify ammonium formation under these conditions, the collection efficiency at the ring (16%) is lower than would be expected (22%) if hydroxylamine is the only product of reduction, suggesting that both ammonium ion and hydroxylamine are directly formed from the catalytic reduction of nitrite.

Experimental Mechanistic Investigations. The catalytic current for nitrite reduction shows an S-shaped response at relatively slow scan rates (200 mV/s), which indicates homogeneous electrocatalysis under pure kinetic conditions. Under these conditions, the catalytic plateau current i_c is described by:^{55,56}

$$i_c = nFAC_P\sqrt{DkC_A} \quad (2)$$

where k is the rate constant of NO_2^- reduction, C_P is the bulk concentration of $[\text{Co}(\text{TIM})\text{Br}_2]^+$, and C_A is the bulk concentration of NO_2^- . For the reduction of nitrite to hydroxylamine, $n = 4$ is the number of electrons involved in the reduction. Note that a similar analysis will apply for the formation of ammonium ($n = 6$), but the resulting rate constants will be 2.25 times slower (see eq 2).

Electrocatalysis conducted with variable catalyst ($[\text{Co}(\text{TIM})\text{Br}_2]^+$) concentrations at pH 7 revealed a first-order dependency in the catalytic peak current (Figure S8); however,

there is no dependence on substrate (NaNO_2) concentration (Figure S9), indicating that nitrite is not involved in the rate-determining step. For the same phosphate buffer concentration, the peak current of the electrocatalytic wave increases as the solution is acidified (Figure S10), suggesting that catalysis is facilitated by proton transfer. More interestingly, at constant pH, the peak current has a strong dependence on the phosphate buffer concentration (Figure 7a). Specifically, the

peak current increases with increasing buffer concentration up to ca. 500 mM, with further increases in concentration leading to a decrease in the peak current (Figure 7b).⁵⁷

The overall rate of reduction (k_{cat}) for a buffer-assisted mechanism can be expressed as the sum of the rates in unbuffered solution (k_w) and the rate dependent on the buffer ($k_b[\text{B}]$, where B is HPO_4^{2-})

$$k_{\text{cat}} = k_w + k_b[\text{B}] \quad (3)$$

As noted above, low buffer concentrations enhance the rate of nitrite reduction catalysis, while high buffer concentrations are inhibitory. This observed biphasic behavior is well described by a model that rationalizes the inhibitory effects of buffer in terms of multiple equilibria involving binding of the buffer anion to cobalt (Scheme 1)

$$\left(\frac{i_{\text{cat}}}{i_w}\right)^2 = \left(\frac{c_{\text{cat}}}{c_{\text{cat}}^0}\right)^2 \frac{k_{\text{cat}}}{k_w} = \frac{1 + \frac{k_b[\text{B}]}{k_w}}{\left(1 + \frac{K_1[\text{B}]}{[\text{NO}_2^-]} + \frac{K_1K_2[\text{B}]^2}{[\text{NO}_2^-]^2}\right)^2} \quad (4)$$

where i_{cat} and i_w are the catalytic currents observed in the presence and absence of buffer, respectively (Figure 7c). A similar model has been used to describe the inhibiting effects of buffer on water oxidation by a cobalt porphyrin electrocatalyst.³⁸

Modeling the experimental data by eq 4 provides $K_1 = 0.057 \pm 0.006$ and $K_2 = 0.014 \pm 0.006$, which compares well with the values determined by DFT ($K_1 = 0.015$ and $K_2 = 0.002$, Figure S28). The error between the experimentally measured parameters and computed parameters corresponds to a free energy difference of only 1 kcal/mol.

A catalytic Tafel plot^{55,56} for the reduction of nitrite to hydroxylamine with different phosphate buffer concentrations reveals that the onset potential for catalysis as well as the maximum rate of catalysis (TOF_{max})⁵⁵ are dependent on the buffer concentration (Figure 8a). A linear correlation between TOF_{max} and $[\text{H}_2\text{PO}_4^-]$ is observed for buffer concentrations up to 200 mM, suggesting that electron transfer is facilitated by the proton source H_2PO_4^- (Figure 8b). The catalyst performance at pH 7 is optimal for a phosphate buffer concentration of ca. 500 mM. Under these conditions, $\text{TOF}_{\text{max}} = 72 \text{ s}^{-1}$ for the reduction of nitrite to hydroxylamine at an overpotential of 0.56 V. In contrast to the electrocatalytic wave, the first and second reductive processes for $\text{Co}(\text{TIM})$ are invariant for different buffer concentrations, indicating that the buffer is not directly involved in the first two reductive processes (Figure S17).

It is important to note that the nitrite reduction electrocatalytic activity of $\text{Co}(\text{TIM})$ is induced by other buffers. Specifically, the catalytic rates and onset potentials for both [(2-*N*-morpholino)ethane sulfonic acid] (MES) and imidazole buffers at pH 7 are dependent on the buffer concentration (Figures S16–S21). Fitting these data to the same model used for the phosphate buffer reveals the sensitivity of the catalyst to inhibitory binding of the buffer, with imidazole showing the greatest extent of inhibition.

Mechanism of Electrocatalytic Nitrite Reduction. The experimental and computational results lead to a plausible mechanism for electrocatalytic nitrite reduction (Scheme 2). One-electron reduction of the *in situ*-formed cobalt(III) complex $[\text{Co}(\text{TIM})(\text{NO}_2)_2]^+$ is coupled with the loss of a nitro ligand, providing entry to the catalytic cycle in the form of the five-coordinate cobalt(II) complex $[\text{Co}(\text{TIM})(\text{NO}_2)]^+$.

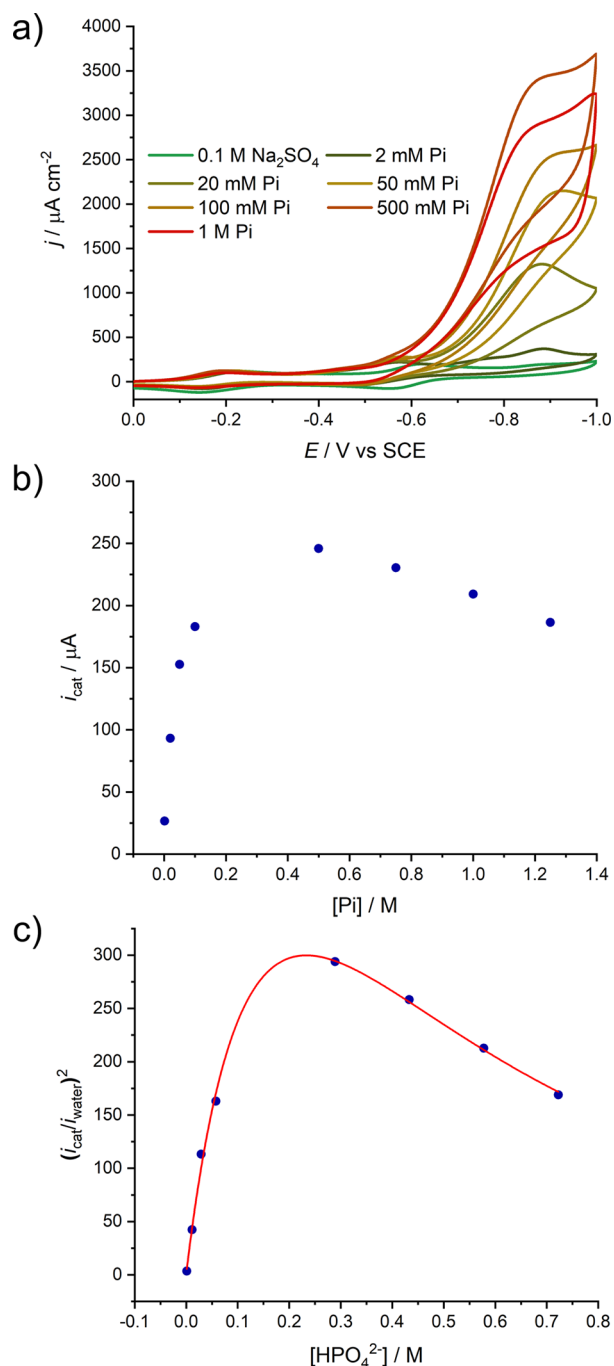
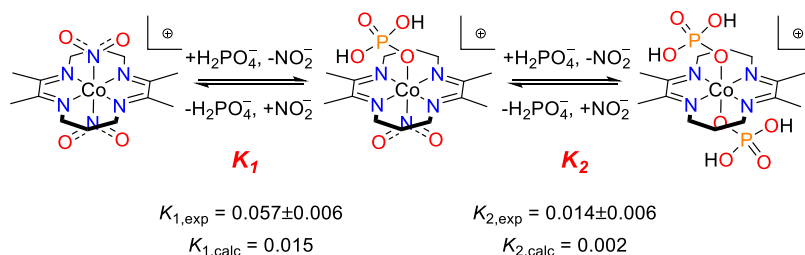


Figure 7. Effect of phosphate buffer concentration on electrocatalysis of 0.5 mM $[\text{Co}(\text{TIM})\text{Br}_2]^+$ with 20 mM NaNO_2 : (a) variable Pi buffer concentration, pH 7; (b) plot of peak current density vs. $[\text{Pi}]$; (c) plot of $(i_{\text{cat}}/i_w)^2$ vs. $[\text{HPO}_4^{2-}]$. The red line is the least squares fit according to the model described in the text, providing parameters $k_b/k_w = (4.0 \pm 0.2) \times 10^3$; $K_1 = 0.057 \pm 0.006$; $K_2 = 0.014 \pm 0.006$; $R^2 = 0.996$. Glassy carbon electrode, scan rate = 200 mV/s.

Scheme 1. Potential Equilibria for Buffer Binding of Catalyst^a

^aExperimentally and computationally determined equilibrium constants shown.

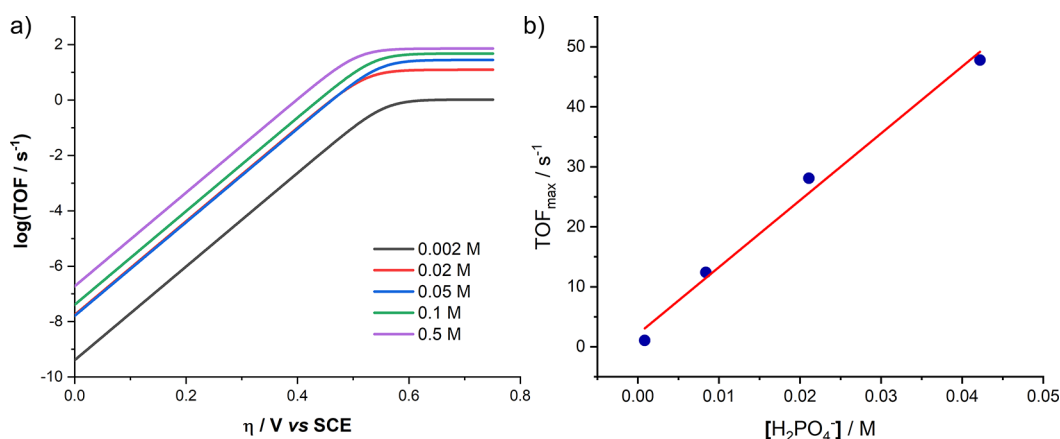
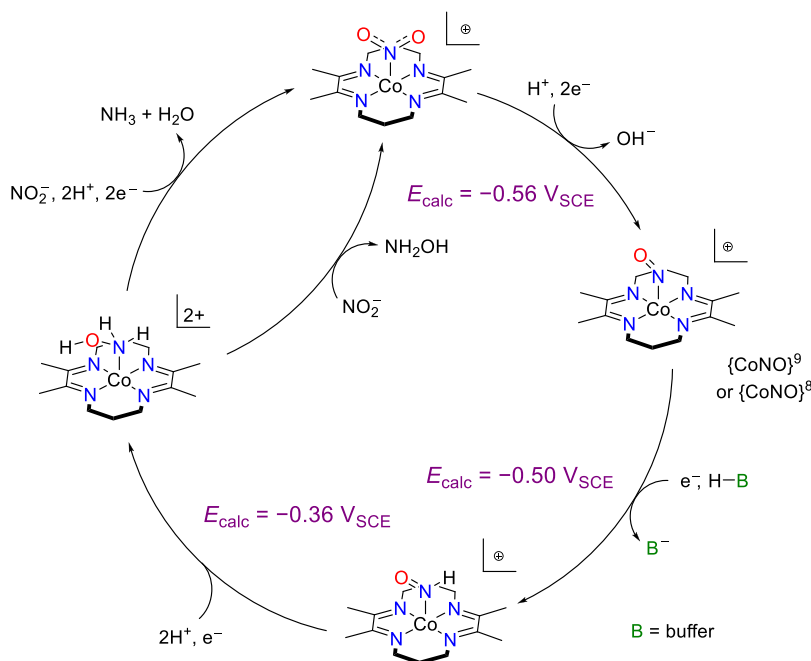


Figure 8. Effect of the phosphate buffer concentration on electrocatalysis: (a) catalytic Tafel plot at varied $[P_i]$; (b) plot of TOF_{max} vs. $[\text{H}_2\text{PO}_4^-]$ for buffer concentrations up to 200 mM. Red line is the least squares linear fit to the equation $y = (1.12 \pm 0.08 \times 10^3)x + (2 \pm 2)$; $R^2 = 0.990$. Experimental conditions: 0.5 mM $[\text{Co}(\text{TIM})\text{Br}_2]^+$ with 20 mM NaNO_2 , pH 7, glassy carbon electrode, scan rate = 200 mV/s.

Scheme 2. Proposed Catalytic Cycle for Electrocatalytic Nitrite Reduction by $\text{Co}(\text{TIM})$ at pH 7.0^a

^aInhibition of the catalyst by the buffer is not shown.

Formal hydride transfer generates the $\{\text{CoNO}\}^9$ complex $[\text{Co}(\text{TIM})(\text{NO})]^+$, where the proton is provided by the solvent. The redox-active macrocycle may also stabilize this complex as $\{\text{CoNO}\}^8 [\text{Co}(\text{TIM}^-)(\text{NO})]^+$. A subsequent

proton transfer step provides $[\text{Co}(\text{TIM})(\text{HNO})]^+$, with H_2PO_4^- from the buffer serving as the proton source, as suggested by the mechanistic experiments described above. Investigations of model complexes have shown that proto-

nation of a five-coordinate $\{\text{CoNO}\}^9$ complex leads to the corresponding nitrosyl hydride ligand.^{43,58} Buffer ions have similarly been shown to act as proton reservoirs in proton and CO_2 reduction electrocatalysis.^{59–61}

We propose that subsequent transfer of two electrons and two protons provides the cobalt(II) hydroxylamine complex $[\text{Co}(\text{TIM})(\text{NH}_2\text{OH})]^{2+}$. The proton binding and the reduction steps from $[\text{Co}(\text{TIM})(\text{NO})]^+$ to $[\text{Co}(\text{TIM})(\text{NH}_2\text{OH})]^{2+}$ are mapped in Figure S30. At pH 7, binding of a proton to $[\text{Co}(\text{TIM})(\text{NO})]^+$ is accessible at room temperature (5.5 kcal/mol). The reduction potential of the resulting $[\text{Co}(\text{TIM})(\text{HNO})]^{2+}$ complex is -0.26 V vs. SCE. Once reduced, the introduction of a second proton becomes a spontaneous process (-5.2 kcal/mol); this complex can then be reduced at -0.36 V vs. SCE. After that, spontaneous binding of another proton to the complex produces the hydroxylamine complex $[\text{Co}(\text{TIM})(\text{NH}_2\text{OH})]^{2+}$. From this complex, there is a bifurcation of the reaction mechanism (Scheme 2). In one pathway, an additional two protons and two electrons are transferred, which fully reduces nitrite to ammonium ion and turns over the catalyst. Alternatively, the catalytic cycle is short-circuited via the substitution of hydroxylamine by an additional nitrite substrate. This mechanistic proposal is consistent with the RRDE experiments, which suggest that both hydroxylamine and ammonia are directly formed from catalytic nitrite reduction.

In addition to serving as a source of protons, our calculations also suggest a potential role of phosphate in accelerating the proton binding process. Phosphate can bind directly to Co and increase the overall electron density of the complex, which helps facilitate proton transfer to the nitrosyl ligand. Further details are discussed in the Supporting Information.

CONCLUSIONS

In appropriately buffered aqueous solution, the cobalt macrocycle complex $[\text{Co}(\text{TIM})\text{Br}_2]^+$ is an efficient catalyst for the electrochemical reduction of nitrite. Both hydroxylamine and ammonia are the final reduction products, with RRDE experiments suggesting that they are formed through a bifurcated reaction pathway. Experimental and computational investigations suggest that catalysis commences from the six-coordinate Co(III) complex $[\text{Co}(\text{TIM})(\text{NO}_2)_2]^+$, which is reduced by three electrons in two steps to afford $\{\text{CoNO}\}^9$ $[\text{Co}(\text{TIM})(\text{NO})]^+$.

Experimental mechanistic investigations reveal the critical role of the buffer for catalysis, with the conjugate acid likely acting as a proton shuttle. Intriguingly, the catalytic performance of $[\text{Co}(\text{TIM})\text{Br}_2]^+$ can be tuned by the buffer concentration. At pH 7, increasing phosphate buffer concentrations both increase the catalytic rate as well as decrease the onset potential, with optimal performance observed with ca. 500 mM of phosphate buffer. As supported by the results of DFT, higher buffer concentrations attenuate the catalytic performance, likely by competitive binding to cobalt.

While the impact of buffer on the mechanisms of water oxidation,^{33–35,37,38,62–65} HER,^{59,60,66} and CO_2 reduction have been previously reported, the role of buffer in nitrogen cycle electrocatalysis is largely unexplored.¹⁹ Importantly, the results herein demonstrate the critical role of buffer in nitrite reduction electrocatalysis, making an otherwise inactive complex active toward substrate reduction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c00909>.

Additional experimental details, materials, and methods (PDF)

Cartesian coordinates of computed structures (XYZ)

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Notes

The authors declare no competing financial interest.

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