Electrode Adsorption Activates *trans*-[Cr(cyclam)Cl$_2$]$^+$ for Electrocatalytic Nitrate Reduction

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Electrode-Adsorption Activates *trans*-[Cr(cyclam)Cl$_2$]$^+$ for Electrocatalytic Nitrate Reduction

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Cyclic voltammetry reveals that aqueous *trans*-[Cr(cyclam)Cl$_2$]$^+$ is reversibly reduced at a mercury electrode, with a small prewave suggesting an adsorptive interaction between the complex and electrode surface. A catalytic current is observed in the presence of excess nitrate, with the onset potential for catalysis at the prewave. Nitrate is electrocatalytically reduced to nitrite, with preliminary mechanistic investigations implicating a chromium oxo intermediate.

Since being introduced over 100 years ago, industrial Haber-Bosch ammonia can be linked to over 4 billion births.[1] While over 100 Tg of fixed nitrogen are annually used as agricultural fertilizers, only 17% of this is actually ingested as protein by humans and livestock. The remainder of the fixed nitrogen is oxidized by soil organisms to a variety of nitrogenous compounds, including the nitrate anion.[2] This highly soluble anion is lost by runoff into waterways, leading to eutrophication and hypoxia and ultimately resulting in aquatic "dead zones".[3,4] Globally, eutrophication is estimated to cause over $2 billion damage each year.[5]

An appealing strategy for addressing this issue is the development of catalysts for nitrate reduction, which avoid some of the problems associated with existing biological denitrification and physical removal technologies.[6] In addition to eliminating these damaging waste streams, this strategy has the potential to convert nitrate to value-added products. However, selective nitrate reduction is difficult for two major reasons. First, it is a poor ligand due to its delocalized electronic structure, preventing effective binding to reduction catalysts. Nitrate is likely to be outcompeted by other ions present in aqueous media (e.g. X$^-$, CO$_3$$^{2-}$, PO$_4$$^{3-}$), most of which are better ligands. Second, multiple nitrate reduction products exist, many of which have similar reduction potentials,[7] making product selectivity challenging. The mechanistic control of appropriately designed molecular catalysts offers means to address these issues.

There are few examples of molecular catalysts for electrocatalytic nitrate reduction.[8-12] The most well-investigated is [Co(cyclam)Cl$_2$]$^+$, which produces hydroxylamine as the principal reduction product.[13-15] More recently, we have reported mechanistic investigations into the electrocatalytic reduction of nitrate (and nitrite) by Co(DIM)Br$_2$$^+$, where DIM = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene). In contrast to [Co(cyclam)Cl$_2$]$^+$, [Co(DIM)Br$_2$]$^+$, which features a redox-active macrocycle, operates at neutral pH and at a glassy carbon electrode, producing ammonia as the sole reduction product.[16,17] Despite these favorable properties, nitrate reduction is associated with a very large overpotential (*ca.* 1.2 V), prompting a search for other catalyst designs.

The metal ion offers an additional design parameter for tailoring both the product selectivity and the catalytic performance. In this regard, a report on the apparent electrocatalytic reduction of nitrate by *trans*-[Cr(cyclam)(H$_2$O)$_2$]$^{3+}$ drew our attention,[18] however this initial observation does not appear to have been investigated beyond a cursory note. Here, we report that the more readily accessed complex, *trans*-[Cr(cyclam)Cl$_2$]$^+$,[19] is an electrocatalyst for the reduction of aqueous nitrate, with the electrode material playing a critical role in catalytic performance. Preliminary investigations suggest that the nitrate reduction mechanism differs from that proposed for [Co(DIM)Br$_2$]$^+$.[16,17]
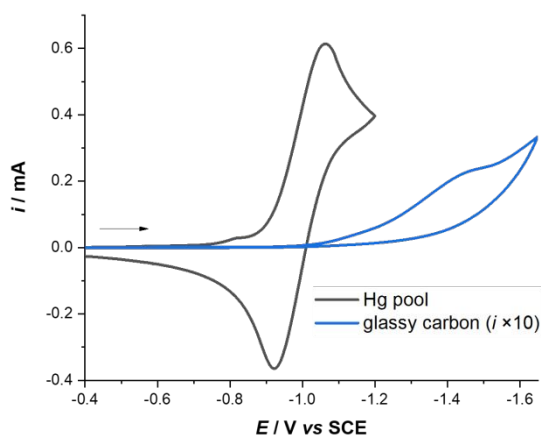
With a glassy carbon working electrode, the cyclic voltammogram (CV) of 5 mM *trans*-[Cr(cyclam)Cl$_2$]$^+$ in a non-coordinating diethylpiperazine (DEPP) aqueous buffer solution (0.1 M, pH 4.6)[20] reveals an irreversible reduction wave ($E_{p,c}$ = -1.47 V vs SCE), which we attribute to the Cr(III)/Cr(II) couple (Figure 1).[21] Interestingly, this wave becomes reversible when the measurement is repeated with a mercury pool working electrode ($E_{1/2}$ = -0.99 V vs SCE), with a remarkable anodic shift in the onset potential of over 200 mV (Figure 1). In addition to these changes, this couple is now associated with an irreversible prewave that has an onset potential of *ca.* -750 mV vs SCE.

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Figure 1. Cyclic voltammograms of 5 mM *trans*-[Cr(cyclam)Cl$_2$]$^+$ in 0.1 M DEPP buffer pH 4.62 at Hg pool working electrode (black) and glassy carbon working electrode (blue), scan rate 50 mV/s.

The presence of the prewave indicates the adsorption of an electroactive species onto the electrode surface.[22,23] Indeed, the current for this prewave is directly proportional to the scanning rate (Figure S5), as expected for a surface-adsorbed species. It is notable that the prewave for *trans*-[Cr(cyclam)Cl$_2$]$^+$ is not observed when the CV experiment is conducted in non-protic solvents, suggesting that hydrogen-bonding interactions from the solvent may be important for stabilizing the adsorbed species (Figure S9).

It is worth noting that a prewave is also observed in the reduction of [Ni(cyclam)]$^{2+}$ at a mercury electrode,[24, 25] which is proposed to be due to adsorption of the reduction product [Ni^I(cyclam)]$^+$ on the electrode surface.[26] A computational study suggested that [Ni^I(cyclam)]$^+$ is attracted to the mercury surface by dispersion interactions between the cyclam amine hydrogens and the electron-rich surface.[27-29] However, since the prewave is also not observed in the aqueous phase CV of *trans*-[Cr(cyclam)(NO$_3$)$_2$]$^+$,[30] interactions with the chloride ligands in -[Cr(cyclam)Cl$_2$]$^+$ may also be important to stabilizing the adsorbed species (Figure S10).

Density functional theory (DFT) calculations were performed to help provide insight into these electrochemical processes. DFT has been used successfully in the past to calculate reduction potentials of inorganic complexes, often achieving errors on the order of ~0.15-0.3 eV.[16, 31-33] Despite these past successes, it is still prudent to continuously evaluate computational methodology before drawing conclusions from it, and as such a small but thorough benchmarking study was performed, as is detailed in the ESI. This was done by evaluating a standard DFT methodology's ability to reproduce experimentally known reduction potentials of Cr(III) complexes with amine and polypyridine ligands. The methodology performed reasonably well, with errors on the order of ~0.2 eV. Of note, however, was that in every case the DFT calculations overestimated the unfavorability of the reduction process, i.e. the calculated potentials were always more negative than the experimental results (these results are further detailed in the ESI). Figure 2

shows calculated square schemes for [Cr(cyclam)Cl$_2$]$^+$ that consider pure reductions (vs. SCE) as horizontal pathways and chloride dissociation as vertical pathways. Reactions that involve a simultaneous reduction of Cr and loss of chloride are the sum of horizontal and vertical pathways and are given as the diagonals in volts. The reduction of [Cr(cyclam)Cl$_2$]$^+$ is calculated to occur at -1.23 V. Note that this is more negative than the measured potential for the reversible wave at -0.99 V by approximately 0.2 V, which is what would be predicted from the methodology benchmarking. Dissociation of each of the chloride ligands from the resulting Cr(II) complex is calculated as being favorable at -5.6 and -4.9 kcal/mol, respectively. These calculations do not provide information on the rate of ligand loss, so it is not clear how long-lived these Cr(II)-chloro species would be, however, the reversible Cr(III)/Cr(II) wave (Figure 1) suggests that ligand loss in solution is slow on the electrochemical time scale.
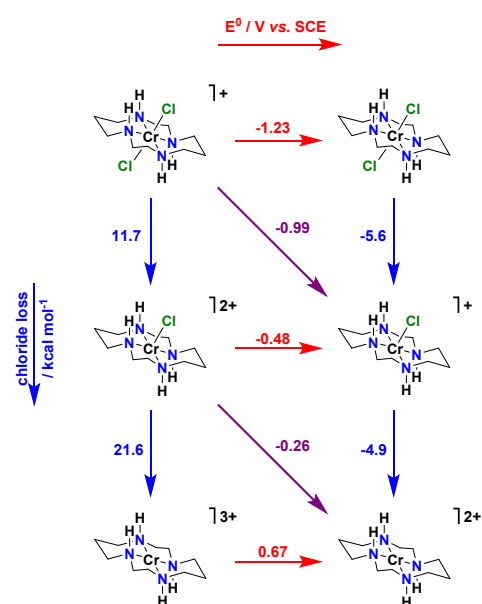

Figure 2. Square schemes calculated using DFT for [Cr(cyclam)Cl$_2$]$^+$. Diagonal values in purple represent the calculated reduction potentials with simultaneous loss of chloride included and are given in V.

If one of the chloride ligand losses occurs simultaneously with reduction, the estimated potential is -0.99 V, and if both chlorides are lost the estimated potential is -0.77 V. Note that any chloride loss will result in an irreversible wave in the CV, such as what is seen for the adsorption prewave at -0.75 V. Taken together, the experimental and computational results suggest that while reversible reduction to [Cr(cyclam)Cl$_2$] occurs in solution, reduction of the electrode-adsorbed complex is coupled to loss of chloride ligand(s). Importantly, either process would eventually give rise to the same complex after the chlorides finally dissociate, [Cr(cyclam)]$^{2+}$, which is considered as the active species for nitrate reduction (*vide infra*).

In the presence of excess nitrate, *trans*-[Cr(cyclam)Cl$_2$]$^+$ is an electrocatalyst for nitrate reduction in aqueous solution. As with the CV experiments described above, the electrocatalytic performance is also dependent on the nature of the working

electrode. At a glassy carbon electrode, the CV of *trans*-[Cr(cyclam)Cl$_2$]$^+$ in the presence of 50 mM NaNO$_3$ reveals a catalytic current with onset potential of *ca.* -0.92 V vs SCE, which corresponds to the irreversible Cr(III)/Cr(II) wave observed in the absence of nitrate (Figure S6). Constant potential electrolysis (-1.1 V vs SCE, 1 h) provides a mixture of nitrite and ammonia, with Faradaic efficiencies of 24 % and 17 %, respectively. No hydroxylamine is observed.

Superior electrocatalytic nitrate reduction is observed for the mercury pool working electrode, with the onset potential for nitrate reduction on mercury anodically shifted by over 150 mV. The observed onset potential for electrocatalysis is the same as the onset potential of the prewave in the absence of nitrate (Figure 3), indicating that the adsorbed species is responsible for nitrate reduction. This is reminiscent of electrocatalytic CO$_2$ reduction by [Ni(cyclam)]$^{2+}$, where the onset potential for CO$_2$ reduction coincides with that of the prewave.[24, 25]
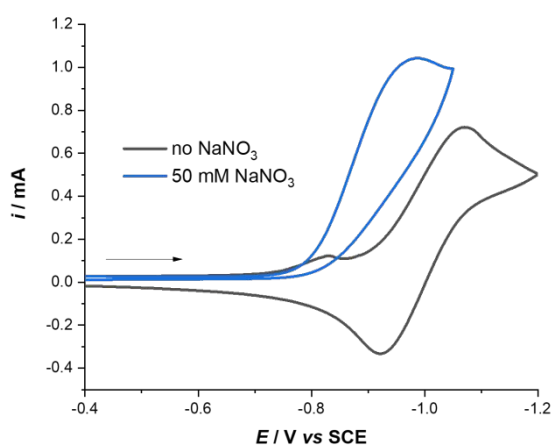

Figure 3. Cyclic voltammograms of 5 mM *trans*-[Cr(cyclam)Cl$_2$]$^+$ in 0.1 M DEPP buffer pH 4.62, Hg pool working electrode (black) and with 50 mM NaNO$_3$ (blue), scan rate 50 mV/s.

In addition to the decreased overpotential, improved product selectivity is observed for electrocatalysis at the mercury pool working electrode. Constant potential electrolysis (-0.98 V vs SCE, 12 h) produces nitrite as the sole nitrogen-containing product of electroreduction in quantitative Faradaic efficiency.[34] No ammonia or hydroxylamine are detected.

The difference in product selectivity with the [Co(DIM)Br$_2$]$^+$ electrocatalyst is striking, where ammonia is the sole reduction product, and species with intermediate nitrogen oxidation states are not observed. This suggests that the electrocatalytic nitrate reduction by *trans*-[Cr(cyclam)Cl$_2$]$^+$ follows a different mechanism. The observation of nitrite as a reduction product when electrolysis was conducted at the Hg electrode led us to hypothesize that nitrate reduction occurs via N-O bond heterolysis at chromium, releasing nitrite with the concomitant formation of a chromium oxo intermediate. The analogous transformation occurs in nitrate reductase[35] and related bioinspired complexes.[36-40] In light of the ability of chromium oxo complexes to facilitate two-electron oxygen atom transfer to a number of substrates, we further hypothesized that a suitable phosphine might intercept this intermediate, yielding

the corresponding phosphine oxide. To test this, we conducted a constant potential electrolysis experiment in the presence of 25 mM triphenylphosphine-3,3',3''-trisulfonate, a water-soluble phosphine. Following 12 h electrolysis at neutral pH and under anaerobic conditions, the ^{31}P{^{1}H} NMR spectrum of the electrolysis solution reveals that 30 % of the starting phosphine is converted to the corresponding phosphine oxide. Control experiments reveal that both chromium complex and nitrate must be present for electrolytic phosphine oxidation.
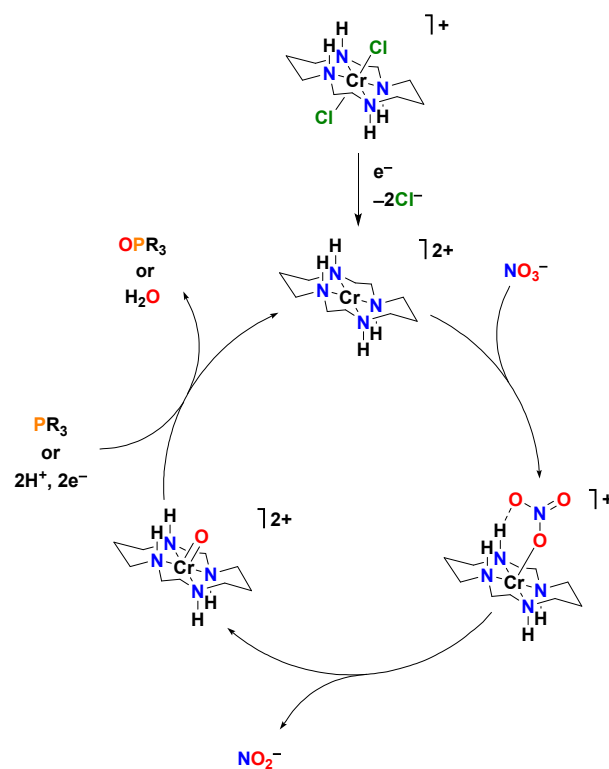
Figure 4. Minimalist catalytic cycle for nitrate reduction by *trans*-[Cr(cyclam)Cl$_2$]$^+$. The possible binding of ancillary ligands during the catalytic cycle is not shown.

Taken together, these results suggest a plausible mechanism for electrocatalytic nitrate reduction by *trans*-[Cr(cyclam)Cl$_2$]$^+$ (Figure 4) at the Hg pool electrode, which is supported by DFT-calculated thermodynamics. One electron reduction of the Cr(III) complex provides the entry point into the catalytic cycle. Since our results strongly suggest that interactions with the mercury electrode surface stabilize this intermediate, the precise structure of this Cr(II) species may be surface dependent. Following binding of nitrate to reduced chromium, a two-electron N-O bond cleavage step affords the corresponding Cr(IV) oxo while releasing nitrite. It is likely that bond cleavage is assisted by hydrogen bonding interactions from the cyclam amine protons, similarly to our proposal for N-O bond cleavage by Co(DIM)$^+$.[16, 17] DFT calculates nitrate binding to [Cr(cyclam)]$^{2+}$ and the subsequent Cr(IV) oxo formation as both being thermodynamically viable and potentially reversible with calculated ΔG values of 1.1 and 0.0 kcal/mol, respectively, consistent with nitrate reduction catalysis by [Cr(cyclam)]$^{2+}$. A sequence of proton and electron transfer steps leads to the liberation of water and regenerates the Cr(II) species. In the

presence of the phosphine, the Cr(IV) oxo can intercepted by the phosphine, resulting in phosphine oxidation and regeneration of the catalytically active Cr(II) species.

In conclusion, we have demonstrated that *trans*-[Cr(cyclam)Cl$_2$]Cl is an electrocatalyst for nitrate reduction in aqueous media at both glassy carbon and mercury pool electrodes. Surface adsorption of the catalyst onto mercury promotes its reduction, as evidenced by the adsorption prewave in the cyclic voltammogram. This anodically shifts the onset potential for nitrate reduction by 200 mV from that at glassy carbon. The mechanism of nitrate reduction likely differs from that proposed for [Co(DIM)Br$_2$]$^+$, with preliminary mechanistic experiments implicating a chromium-oxo intermediate capable of oxygen atom transfer.

Conflicts of interest

There are no conflicts to declare.

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