Dalton Transactions

PAPER

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Cite this: DOI: 10.1039/c8dt04740e

Sulfur substitution in a Ni(cyclam) derivative results in lower overpotential for CO₂ reduction and enhanced proton reduction[†]

P. Gerschel,^a K. Warm,^b E. R. Farquhar,^c U. Englert, ^D^d M. L. Reback,^a D. Siegmund, ^D^e K. Ray ^D*^b and U.-P. Apfel ^D*^{a,e}

The replacement of the opposing nitrogen atoms in 1,4,8,11-tetraazacyclotetradecane (cyclam) with two sulfur atoms in 1,8-dithia-4,11-diazacyclotetradecane (dithiacyclam) enables the electrochemical reduction of protons and CO_2 via the corresponding nickel(II) complex at more positive potentials. In addition, a 10-fold enhancement in the proton reduction rate of [Ni(dithiacyclam)]²⁺ relative to [Ni(cylcam)]²⁺ was observed. The study provides vital insight into Nature's choice of employing predominantly sulfur based ligand platforms in achieving biological proton and CO_2 reductions.

Received 30th November 2018, Accepted 21st December 2018

DOI: 10.1039/c8dt04740e

rsc.li/dalton

Introduction

As part of the global industrialization era and its concomitant demand of fossil energies, the concentration of carbon dioxide (CO_2) in the atmosphere has dramatically risen to values over 400 parts per million.^{1,2} CO₂ is one of the major greenhouse gases and at such high concentrations it is detrimental to the environment. Therefore, it is of crucial importance to establish a "green" future utilizing the abundant CO_2 in the atmosphere as a feedstock for higher energy products and to establish post-fossil energy sources like hydrogen.^{3,4} In order to generate useful C1 building blocks such as carbon monoxide, formaldehyde, methanol and methane, one has to overcome the characteristic high energy demands associated with the conversion of CO_2 .⁵⁻⁷ Specifically, this tremendous energy demand originates from the initial one electron reduction step of the thermodynamically and kinetically inert linear CO₂ molecule to reorganize into the highly reactive bent CO₂ radical anion.8

^aRuhr-Universität Bochum, Anorganische Chemie I, Universitätsstraße 150, 44801 Bochum, Germany. E-mail: ulf.apfel@rub.de

^bHumboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Straße 2, 12489 Berlin, Germany. E-mail: kallol.ray@chemie.hu-berlin.de

^cCWRU Center for Synchrotron Biosciences, NSLS-II, Brookhaven National Laboratory, Upton, NY 11973, USA

^eFraunhofer UMSICHT, Osterfelder Straße 3, 46047 Oberhausen, Germany

Among the numerous methods to activate small molecules, e.g. H_2 and CO_2 , biomimetic electrocatalysis has been proven to be one of the most promising and sustainable strategies for the storage and release of energy in chemical bonds.9,10 Thereby the electrocatalyst serves to stabilize intermediary species, hence enabling a facilitated reduction at milder potentials.¹¹ However, finding suitable electrocatalysts with low overpotentials for the reduction of CO₂ as well as protons remains a challenge.^{12,13} Notably, one crucial problem in the electrochemical reduction of CO₂ is to suppress the formation of H₂ which is usually favored due to the inherent mass transport problem of CO₂ and its low solubility as compared to protons.¹⁴ In order to allow for new potential industrially-relevant electrocatalysts to arise, an understanding of the chemistry of such catalysts on a molecular level is of utmost importance to facilitate the CO2 reduction and hamper the H2 formation.15

Among the spectrum of homogeneous electrocatalysts that were reported to be highly selective for CO_2 reduction, a series of macrocyclic tetra-aza Co and Ni complexes was shown to be particularly promising.¹⁶ The most potent electrocatalyst for the selective CO_2 reduction in this series was $[Ni(cyclam)]^{2+}$ 1 (cyclam = 1,4,8,11-tetraaza-cyclotetradecane) (Scheme 1).^{8,16,17}



 $\mbox{Scheme 1}\ \mbox{Scheme 1}\ \mbo$



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^dRWTH Aachen, Institut für Anorganische Chemie, Landoltweg 1, 52056 Aachen, Germany

[†] Electronic supplementary information (ESI) available: Synthesis and characterization of compounds, UV/vis spectra, SEM images, EDX spectra, gas chromatograms, CO & H₂ quantification *via* GC and X-ray crystallographic analysis. CCDC 1539266. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt04740e

Published on 26 December 2018. Downloaded by Iowa State University on 1/20/2019 9:08:01 PM.

At an applied potential of *ca.* -1.0 V *vs.* NHE at pH 4 in water and utilizing a mercury working electrode, **1** allowed for a selective reduction of CO₂ to CO with a reaction rate of 32 h⁻¹ and high faradaic efficiencies of 96%. Furthermore, an excellent stability of compound **1** was reported allowing for more than 8000 turnovers over 8 hours without any notable decomposition.¹⁸ Although the reduced intermediate [Ni^I(cyclam)]⁺ species readily adsorbs on the Hg electrode and it was suggested that this adsorbate is responsible for the high activity of complex **1**, it is noteworthy that the CO₂ reduction is still observed when using glassy carbon working electrodes that did not reveal any interaction with the complexes.^{11,19}

While the electrocatalytic reduction processes are sufficiently well investigated and different variations of substitution patterns on the cyclam N-donor and C-framework atoms are reported (Scheme 1),¹⁹⁻²² incorporation of alternative donor atoms and their influence on the H^+ vs. CO_2 reduction are not yet investigated. Inspired by the sulfur-rich donor sets that nature has established in its powerful and efficient reductive enzymatic machineries, e.g. CO-dehydrogenase²³ or [FeFe]- and [NiFe]-hydrogenases,^{24,25} we became interested in investigating the CO₂ and proton reduction abilities of the nickel-cyclam complex upon partial replacement of its nitrogen atoms with sulfur. The potential advantage of using N,S-donor ligands was recently shown by Kojima et al., where a Ni^{II} complex bearing an S_2N_2 -type ligand (Ni^{II} - N_2S_2 , Scheme 2) allowed for photocatalytic reduction of CO2 with a TON of 713 and a high selectivity >99% for the formation of CO.²⁹

While the sulfur-containing cyclam derivatives shown in Scheme 2 and their corresponding first-row transition metal complexes have been reported,^{26–28} we herein outline for the first time their potential to act as electrocatalysts for the reduction of CO_2 to valuable C_1 building blocks.

Results and discussion

Synthesis and characterization

In order to better understand the importance of sulfur within the many known metalloenzymes and to allow for comparison with the electrocatalytic system **1**, we synthesized the sulfurcontaining cyclam derivative **1**,8-dithia-4,11-diazacyclotetradecane (dithiacyclam) **2** (Scheme 3 and Scheme S1†).³⁰ The reac-

 $\label{eq:scheme2} \begin{array}{l} \mbox{Scheme 2} & \mbox{Scheme 1} \\ \mbox{(left) and the photocatalyst Ni^{II}-N_2S2 (right).$^{26,29} \\ \end{array}$

Ni^{II}-N₂S₂



Scheme 3 Synthesis of [Ni(dithiacyclam)(NCCH₃)₂](ClO₄)₂ 3.

tion of the N₂S₂-donor ligand 2 with Ni(ClO₄)₂·6H₂O in acetonitrile subsequently afforded a dark purple crystalline solid in 87% yield (Scheme 3). The metalation of 2 was confirmed by electrospray-ionization mass spectrometry (ESI-MS), revealing two characteristic peaks at m/z = 292 and 391 for the [Ni(dithiacyclam)]⁺ and the [Ni(dithiacyclam)(ClO₄)]⁺ fragments. Moreover, the presence of two characteristic C=N stretching band at 2284 and 2309 cm⁻¹ in the IR spectrum of 3 indicated the additional binding of acetonitrile at the nickel center. According to single crystal X-ray analysis, the molecular composition of 3 can be best described as [Ni(dithiacyclam)(NCCH₃)₂] (ClO₄)₂ (Fig. 1 and Scheme 3).

Similar to the previously reported molecular structure of the $[Ni(cyclam)(NCCH_3)_2]^{2+}$ complex 1 that revealed the existence of two acetonitrile ligands in the axial positions,³¹ the Ni^{II} center in 3 is octahedrally surrounded by the dithiacyclam ligand and two additional acetonitrile molecules (Fig. 1). However, contrary to 1 and in line with the molecular structure of Ni^{II}-N₂S₂, the nitrogen atoms of the dithiacyclam and the acetonitrile ligands occupy equatorial positions with averaged Ni-N_{dithiacyclam} and Ni-N_{MeCN} distances of 2.13 and 2.07 Å, respectively. The sulfur donor atoms occupy the axial coordination sites and show averaged Ni-S_{dithiacyclam} distances of 2.39 Å, as defined by the local symmetry of the metal ion. Furthermore, a detailed analysis of the N/S-Ni-N/S bond angles of neighboring donor atoms showed angles between 83.5° and 97.4° revealing an overall distorted octahedral geometry for 3.

Solution behavior

Additional X-ray absorption near-edge spectroscopic studies (XANES) on a frozen acetonitrile solution of **3** at the Ni K-edge exhibits an edge inflection energy of *ca.* 8341.2 eV, with a

Fig. 1 Structural motif of $[Ni(dithiacyclam)(NCCH_3)_2](ClO_4)_2$ 3 drawn as balls and sticks (hydrogen atoms and ClO_4^- counter ions are omitted for clarity). Color code: C grey, N blue, S yellow and Ni turquoise.



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Fig. 2 X-ray absorption near-edge spectroscopic studies (XANES) on a frozen acetonitrile solution of compound 1 (red) and 3 (black).

shoulder along the rising edge at 8336.3 eV corresponding to a 1s \rightarrow 4p shakedown transition, and a broad 1s \rightarrow 3d pre-edge peak at 8331.4 eV (Fig. 2). The data is well in accordance with the observed distorted octahedral structure of this complex in the solid state. The XANES spectrum of complex 1 shows a 0.6 eV blue shift of the edge inflection energy to 8340.6 eV, relative to 3, thereby supporting a more reduced Ni center in the latter. However, the 1s \rightarrow 3d pre-edge peak in 1 is observed at identical energy and comparable intensity relative to 3. Thus, the six coordinate geometry of 3 is also conserved in solution. Nevertheless, the 1s \rightarrow 4p shakedown transition shoulder is much less intense in 1 relative to 3, with a more symmetric Ni(N₆) core in 1 as compared to the asymmetric Ni(S₂N₄) core in 3 and is in good agreement to the structural observations.

Solvent dependency

Complex **3** is stable under argon, while under atmospheric conditions the color of the solid rapidly changes from purple to blue, suggesting a ligand exchange by reaction with air. Dissolving complex **3** in water also gives the same purple to blue transition yielding a blue solid after concentration. The obtained blue crystals were of poor quality thus not allowing for structural determination, although the ESI-MS revealed a similar pattern observed for **3** suggesting only the exchange of the acetonitrile ligands. Notably, if the blue solid was redissolved in dry acetonitrile, the color reverted back to purple and pure **3** was obtained. This experimental finding supports the assumption of a reversible ligand exchange between acetonitrile and water (Scheme 4). Furthermore, to determine the



Scheme 4 Schematic overview of the ligand exchange of 3 with water.



Fig. 3 UV/vis/NIR titration of 3 with water. The full black line corresponds to 3 in acetonitrile and the full red line to 3 in water.

equilibrium constant of the ligand exchange an UV/vis/NIR titration was carried out (Fig. 3). While complex **3** in acetonitrile absorbs light at 552 and 851 nm, the absorption in water is shifted to higher wavelengths at 591 and 962 nm generating two isosbestic points at 587 and 910 nm. Subsequently, the equilibrium constant was determined as $K = 4.3 \times 10^4$ and suggests that in water the formation of [Ni(dithiacyclam)(H₂O)₂](ClO₄)₂ is favored. However, no apparent UV/vis/NIR changes are visible for **1** up to the addition of 600 equivalents H₂O (Fig. S1†). This behavior is in line with previous reports showing no apparent electronic effects of water or acetonitrile ligands in axial position of **1**.^{31,32} The observed solvent exchange clearly suggests that, contrary to **1**, the electrochemical properties of **3** as well as any catalytic performance will strongly depend on the solvent used.

Electrochemistry

Complex 3 (1 mM) was characterized by cyclic voltammetry (CV) in dry acetonitrile with 0.1 M $[^{n}Bu_{4}N]^{+}PF_{6}^{-}$ as the supporting electrolyte. The CV of 3 reveals two distinct irreversible 1e⁻ reduction waves at -0.72 and -1.21 V vs. NHE for the $Ni^{II} \rightarrow Ni^{I}$ and $Ni^{I} \rightarrow Ni^{0}$ transitions (Fig. 4), which is in line with previous reports on Ni^{II}-N₂S₂.²⁹ In addition, a controlled potential coulometry held at -1.8 V vs. NHE revealed a total charge consumption equivalent to a two-electron reduction (Fig. S2[†]). The generated Ni⁰ species was found to adsorb on the surface of the working electrode where it gets oxidized to Ni^{II} at 0.80 V during the back scan of the CV, indicated by its strong non-diffusion-controlled oxidation signal. If the scan is reversed after the first reduction wave the stripping signal is avoided, which suggests an adsorption of the Ni⁰ species. In addition, the $Ni^{II/I}$ couple stays irreversible with increasing scan rate (Fig. S3[†]) suggesting a fast chemical reaction/structural reorganization after the electrochemical reduction. In contrast, 1 shows only a single reversible $Ni^{II} + e^- \leftrightarrow Ni^{I}$ reduction at a more cathodic potential (-1.16 V) under the same experimental conditions. Based on these results, it can be concluded that the incorporation of sulfur into the cyclam



Fig. 4 Cyclic voltammograms of 1 mM 1 (red) and 3 (black) in acetonitrile, with 0.1 M [7 Bu₄N]⁺PF₆⁻ at 100 mV s⁻¹.

framework enables a facilitated reduction of the complex and allows for the formation of a Ni⁰ species that is not observed for complex 1. Compared to our measurements in pure acetonitrile, cyclic voltammograms of 3 in mixtures of acetonitrile/ water (4:1) revealed a significantly altered behavior. Herein only the first reduction wave, above assigned as Ni^{II} \rightarrow Ni^I reduction, is observed at -0.79 V concomitant with a reoxidation wave at -0.16 V (Fig. 5 – black dashed line). Notably, while the reduction to Ni⁰ is not visible under such conditions, a strong catalytic current corresponding to water reduction can be observed and indicates a high affinity for H₂ evolution, which is confirmed by gas chromatographic analysis (section: solvent dependency of the HER activity). Similar solventdependent electrochemical changes were not observed for 1.

Electrocatalytic CO₂ reduction

 $[Ni(cyclam)]^{2+}$ **1** is reported to show a high selectivity towards CO_2 reduction over H_2 formation in acetonitrile/water (4:1) mixtures.^{18,19} To see if the dithiacyclam 2 ligand provided any benefit, we looked at the CO_2 reduction ability of complexes **3**



Fig. 5 Cyclic voltammograms of 1 mM 1 (red) and 3 (black) with 0.1 M [$^{\prime\prime}$ Bu₄N] $^{+}$ PF₆⁻ in acetonitrile/water (4 : 1) at 100 mV s⁻¹. The solutions are either purged with argon (dashed lines) or saturated with CO₂ (solid lines).

and **1** under similar conditions. Upon addition of CO_2 to an acetonitrile/water (4:1) solution of 3, the shape of the catalytic current changed drastically in comparison to the measurements without CO_2 (Fig. 5). Here, the catalytic current is shifted to more cathodic potentials and the H₂ formation seems to be hampered by the addition of CO₂. Furthermore, a diffusion limitation, indicated by a wave shape, can be observed at -1.30 V, suggesting a preferable CO₂ reduction followed by an additional catalytic current below -1.50 V for the evolution of hydrogen. Notably, 3 enables a facilitated CO_2 reduction at a potential ~200 mV more anodic compared to complex 1. In an effort to verify the CO₂ reduction and to identify the nickel carbonyl species generated during the CO₂ reduction, IR spectroelectrochemical (SEC-IR) experiments of 1 and 3 were carried out in an electrochemical cell with a threeelectrode setup (WE: glassy carbon electrode, RE: Ag wire, CE: Pt wire) attached to the ATR unit of an IR spectrometer. All measurements were performed under catalytic conditions in a CO_2 saturated acetonitrile/water mixture (4:1) containing 20 mM of the Ni^{II} complex **1** or **3** with 0.1 M $[^{n}Bu_{4}N]^{+}PF_{6}^{-}$ as the electrolyte. The working electrode was placed 200 µm above the ATR crystal and the potential was held for 800 s before the IR scan was initiated. The SEC-IR 3D-spectrum of 3 shows the generation of a low-valent Ni-CO species with a distinct IR band at 2065 cm⁻¹ for a broad potential range below -1.0 V, confirming the catalytic reduction of CO₂ (Fig. 6A). The frequency observed for the Ni-CO species is in the same range as the stretching frequency observed for $Ni(CO)_4$ (2056 cm⁻¹), suggesting the formation of a Ni⁰-CO species.^{33,34} However, based on these experiments no statement about the exact nature of the reduced species can be made. Furthermore, this band is not observed when the experiments were performed in pure acetonitrile (non-catalytic conditions) or pure water (only H₂ formation). $[Ni(cyclam)]^{2+}$ (1) also shows catalytic CO₂ reduction, but within a more narrow potential range between -1.1 to -1.4 V with a characteristic IR band at 1944 cm⁻¹, which corresponds to a Ni^I-CO species (Fig. 6B).¹¹ Notably, at more cathodic potentials the Ni^I-CO species disappears and H₂ formation is dominant, which is in line with previous literature reports on complex 1.¹⁹ Contrary to the reported experiments in pure acetonitrile (noncatalytic conditions),¹¹ an additional band in the IR spectrum can be observed at 1780 cm^{-1} for 1 in CO₂ saturated acetonitrile/ water mixtures (4:1) indicating the formation of formic acid/ formate, which is in line with earlier reports for the formation of formic acid by 1 upon CO₂ reduction.³⁵ The most striking result of the presented measurements is the small potential window (from ca. -1.1 V to ca. -1.4 V) necessary for achieving the Ni^I-CO species and for CO₂ reduction when using complex 1. In contrast, more positive potentials (<-1.0 V) are required for 3, consequently revealing an improved catalytic performance towards CO2 reduction of 3 compared to 1.

Homogenous vs. heterogenous nature of the catalytic CO₂ reducing species

Admittedly, based on these experiments, no information about the nature of the catalytic active species (homogeneous



Fig. 6 Spectroelectrochemical-IR spectra of a 20 mM solution of complex 3 (A) or complex 1 (B) in acetonitrile/water (4:1), saturated with CO_2 , recorded during chronoamperometry at different potentials.

complex vs. deposited material on the electrode surface) and its corresponding electronic state is obtained. Thus, an initial rinse-test was performed. A 1 mM solution of complex 3 in acetonitrile was subjected to controlled potential coulometry (CPC). While holding a reducing potential during CPC at either the $Ni^{II} \rightarrow Ni^{I}$ or $Ni^{I} \rightarrow Ni^{0}$ couple, an enrichment of the Ni^I or Ni⁰ oxidation state will occur and will eventually affect the catalysis. The electrochemical cell was then refurbished with fresh CO_2 saturated acetonitrile/water (4:1) electrolyte without manipulation of the working electrode followed by linear sweep (LSV) experiments to provide insight into the nature of the active species that is present. The results of these experiments show that the LSV after generation of the Ni⁰ species is similar to the LSV in presence of complex 3 under catalytic conditions (Fig. 7). Hence, a deposited Ni⁰ species seems to significantly contribute to the overall CO₂ reduction as a catalytic active species (Fig. S4[†]). If the active species was in solution, the LSV would have been identical to those measured in acetonitrile/water (4:1) with CO_2 in the absence of any complex 3. In addition, this experiment shed some light on the nature of the electronic state of the active species.

Additionally, to elucidate if the deposited Ni^0 species is solely elemental nickel, a rinse-test was performed with $[Ni(NCCH_3)_6](BF_4)_2$. Although we observed nickel deposition upon reduction at the same experimental conditions as shown before, the deposited species showed no activity for the CO_2 reduction (Fig. S5[†]).

Catalyst performance and nature of the active CO₂ reduction catalyst

Additional long-term electrolysis was performed in order to determine the formed products, the turnover numbers (TONs), turnover frequencies (TOFs) and faradaic efficiencies (FEs) for the catalytic reduction of CO_2 . For the long-term measurement, a 1 mM solution of 3 in CO_2 saturated acetonitrile/water (4:1) with 0.1 M [ⁿBu₄N]⁺PF₆⁻ as electrolyte was used in a two-



Fig. 7 Linear sweep voltammograms measured in the presence of CO_2 in acetonitrile/water (4 : 1), with 0.1 M [ⁿBu₄N]⁺PF₆⁻ at 100 mV s⁻¹. LSV of a solution without 3 (dashed black); LSV of a solution with 1 mM 3 (black); LSV of a solution without 3, after previous CPC of a solution with 1 mM 3 held at -0.72 V (1st reduction wave, red); LSV of a solution without 3, after previous CPC of a 1 mM solution of 3 held at -1.21 V (2nd reduction wave, blue).

compartment cell where the working and reference electrodes are separated from the counter electrode *via* a Nafion membrane. During CPC at -1.5 V *vs.* NHE for 32 h, the quantity of produced CO and H₂ was measured after 1 h and subsequently after every 2 h *via* an online GC (Table S1 and Fig. S6†). At the beginning of the experiment, CO was observed as the main product of the electrolysis with 70% CO and 30% H₂. Notably, in course of the experiment, H₂ became the main product and after 6 h an equilibrium-ratio of ~24% CO and ~76% H₂ was reached. During the electrolysis, the FE continuously increased and converged to a maximum of 97% after 30 h. The steady increase of the FE can be attributed to the continuous co-deposition of the catalytic active species throughout the experiment. Based on the GC data after 30 h a TON of 23 with a TOF

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of $2.1 \times 10^{-4} \text{ s}^{-1}$ and a faradaic efficiency of 23% for the CO generation was obtained and a TON of 740 with a TOF of 6.9 × 10^{-3} s^{-1} and a faradaic efficiency of 74% for the hydrogen evolution was obtained.

Electrocatalytic H₂ evolution

While both complexes were capable of electrochemically reducing CO₂ at moderate potentials, the observed electrocatalytic behavior of 3 in the presence of water (Fig. 5) highlights the persistent problem of competing proton and CO₂ reductions. Thus, we likewise pointed our attention towards the use of complex 1 and 3 as potential electrocatalyst for the hydrogen evolution reaction (HER). Titration experiments were carried out in the presence of equimolar amounts of acetic acid to a 1 mM solution of 3 in acetonitrile. Upon addition of 1-10 equivalents acetic acid, a continuous increase of the current for both reduction waves is observed (Fig. 8). This increase indicates that the H₂ formation already starts from the Ni^I state of complex 3. Both reduction waves are, however, shifted to more anodic potentials upon the addition of 1 equiv. acid indicating a protonation of complex 3. Adding further equivalents of acetic acid leads to a shift of the onset values towards more anodic potentials and finally resulting in an onset potential of -0.61 V at -0.1 mA in the presence of an excess acid (>1000 equiv.). It is worth mentioning that for the same excess amounts of acetic acid without 3, H₂ formation starts at potentials below -1.15 V. Hence, complex 3 significantly lowers the overpotential by 540 mV for HER.

Nature of the catalytic HER species

In order to determine the nature of the catalytic active species, again a rinse test was performed. The results of these experiments show that both LSVs either after CPC for the generation of Ni¹ and after CPC for the generation of Ni⁰ are similar to the LSV in presence of 3 under catalytic HER conditions (Fig. 9). Consequently, 3 seems to be a precursor for the generation of a deposited catalytic active Ni¹ species for HER. The deposited Ni species was further confirmed by SEM images and EDX



Fig. 8 Cyclic voltammograms of 1 mM 3 with increasing equivalents of acetic acid (HOAc) in acetonitrile, with 0.1 M $[^{7}Bu_{4}N]^{+}PF_{6}^{-}$ at 100 mV s⁻¹.

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Fig. 9 Linear sweep voltammograms measured in the presence of acetic acid (HOAc) in acetonitrile, with 0.1 M $[^{n}Bu_{4}N]^{+}PF_{6}^{-}$ at 100 mV s⁻¹. LSV of a solution without **3** (dashed black); LSV of a solution with 1 mM **3** (black); LSV of a solution without **3**, after previous CPC of a solution with 1 mM **3** held at -0.72 V (1st reduction wave, red); LSV of a solution of **3** held at -1.21 V (2nd reduction wave, blue).

spectra. During CPC of a solution of 3 (5 μ M) in acetonitrile with 0.1 M [${}^{n}Bu_{4}N$] ${}^{+}PF_{6}^{-}$ for 15 h at -1.1 V vs. NHE, a light yellowish tan colored solid was observed to be deposited on the glassy carbon working electrode (Fig. S7 and S8†). Subsequent EDX analysis of the deposited species revealed not only the presence of nickel but also a significant amount of sulfur and nitrogen with a ratio ranging from a formal Ni_{1.3}S₁N_{1.2} to Ni_{3.6}S₁N_{2.3} composition (Fig. S9 and Table S2†). Thus, it seems that nickel is not solely present as a pure metal but rather as a hitherto unknown amorphous, heterogeneous film. Moreover, these experimental findings are in line with earlier reports which showed that [Ni(tetrathiacyclam)]²⁺ (tetrathiacyclam = 1,4,8,11-tetrathia-cyclotetradecane) also generates a deposited Ni species on the working electrode upon reduction.²⁸

Solvent dependency of the HER activity

While the previous experiments were performed in acetonitrile, the apparent reaction of 3 with water (Scheme 4) drew our attention to the influence of the solvent on the catalytic hydrogen evolution. Electrochemical measurements revealed that 3 enables H₂ evolution in a mixture of acetonitrile/water (4:1) at -1.00 V and in pure water at more cathodic potentials (-1.23 V), but with a significantly enhanced current vs. potential slope (Fig. 10A). Further addition of acetic acid showed the expected shift of the catalytic current towards more anodic potentials revealing an onset potential of -0.73 V in case of acetonitrile/water (4:1) and -0.58 V in case of water (Fig. 10A). Catalyst precursor 3 showed the best performance for H₂ evolution in water (-0.58 V), followed by acetonitrile (-0.61 V) and a mixture of acetonitrile/water (4:1) (-0.73 V). These results were further supported by GC quantification of the generated H_2 gas during CPC at -1.1 V in different solvents in the presence of acetic acid (Fig. 10B). Compound 3 in water shows by far the highest production of H_2 with 4.86 mmol g^{-1} h^{-1} ,



Fig. 10 (A) Cyclic voltammograms of 1 mM 3 in acetonitrile (black), acetonitrile/water (4:1) (blue) and water (red) in absence (dashed lines) and presence (solid lines) of acetic acid (HOAc) at 100 mV s⁻¹. (B) Solvent-dependent GC quantification of the amounts of H₂ generated by 1 and 3 during controlled potential coulometry for 3 minutes at -1.1 V vs. NHE in the presence of acetic acid.

10 times higher compared to the production of H₂ in acetonitrile (0.47 mmol $g^{-1} h^{-1}$) and 40 times higher than in acetonitrile/water (4:1) (0.12 mmol g⁻¹ h⁻¹). While the amounts of H_2 generated by 1 in acetonitrile (0.08 mmol g⁻¹ h⁻¹) and acetonitrile/water (4:1) (0.18 mmol g⁻¹ h⁻¹) are comparable to with compound 3, an 18-times lower H₂ amount for 1 is found in water (0.27 mmol g^{-1} h^{-1}). Overall, complex 3 serves as a catalyst precursor to a heterogeneous electrocatalyst for the H₂ evolution reaction that is significantly more active compared to 1. The strong solvent dependency of the HER furthermore suggests that the catalytic activity most likely stems from a molecular catalyst adsorbed on the surface of the glassy carbon electrode. Since 3 showed the best catalytic performance in water, this system was chosen for a long-term measurement in order to determine the TON, TOF and FE. For the long-term measurement, a 0.5 mM solution of 3 with 350 mM acetic acid and 1 M KCl as electrolyte was used in a twocompartment cell, where the working and reference electrodes are separated from the counter electrode via a Nafion membrane. During CPC at -0.9 V vs. NHE for 20 h, the quantity of produced H₂ was measured every 30 minutes via an online GC (Fig. S10[†]). Notably, the H₂ production decreases with time and via linear convergence, a catalytic collapse after roughly 40 h is anticipated (Fig. S11[†]). Based on the GC data a TON of 613 with a TOF of $4.3 \times 10^{-3} \text{ s}^{-1}$ and a faradaic efficiency of 75% for the proton reduction catalyzed by 3 at -0.9 V vs. NHE in water was obtained.

Conclusions

In conclusion, we herein describe the synthesis and molecular structure of $[Ni(dithiacyclam)(NCCH_3)_2]^{2+}$ 3 and compare its performance for the electrocatalytic reduction of protons and CO₂ relative to the intensively investigated $[Ni(cyclam)]^{2+}$ complex 1. The replacement of the two nitrogen atoms opposite to each other in cyclam with sulfur atoms to form dithiacyclam, induces a significantly altered electrochemical behavior

and enables the CO_2 reduction at a more positive potential and an 18-fold increase in the H_2 evolution capability of $[Ni(dithiacyclam)]^{2+}$ 3 relative to $[Ni(cyclam)]^{2+}$ 1. Based on CV studies, the improved catalytic performance of 3 can be attributed to the access of a thermodynamically facilitated lowvalent deposited catalytic active Ni^I species, which is hitherto present as an unknown amorphous, heterogeneous film on the electrode surface. The results reported herein thus clearly indicate the importance of sulfur due to tuning of the coordination environment and with this, the catalytic and electronic properties of the active sites.

Experimental

General techniques

All reactions were performed under a dry Ar or N_2 atmosphere using standard Schlenk techniques or by working in a glovebox. Starting materials and chemicals were obtained from commercial suppliers and used without further purification. Prior to their use, all solvents were dried and degassed according to standard methods. 1,8-Dithia-4,11-diazacyclotetradecane (dithiacyclam) 2 was synthesized according to a literatureknown procedure with minor alterations.³⁰ A synthetic description is provided within the SI part. Mass spectra were obtained with a *Bruker* Daltonics Esquire 6000 instrument. UV/Vis/NIR spectra were recorded with a *JASCO* V-670 at 25 °C and are reported in [nm]. IR spectra were recorded with a *Bruker* Tensor 27 FT-IR attached with a *Pike* Miracle ATR unit and are reported in [cm⁻¹]. CHN-analyses were measured with an *Elementar* vario MICRO cube.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled with care and prepared only in small quantities.

Synthesis of [Ni(dithiacyclam)(NCCH₃)₂](ClO₄)₂ (3)

Dithiacyclam (200 mg, 0.84 mmol) was suspended in 10 mL toluene and $Ni(ClO_4)_2$ ·6H₂O (312 mg, 0.84 mmol) dissolved in

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10 mL acetonitrile was added. First, the color of the reaction mixture changed to purple and subsequently a purple precipitate was formed. The mixture was stirred for 24 h. Afterwards, the mixture was filtered, the remaining solid was washed with toluene and dried in vacuum to afford 3 (360 mg, 87%) as a purple solid. **IR**: $\tilde{\nu} = 3264$, 2922, 2874, 2309, 2284, 1473, 1419, 1366, 1309, 1083 cm⁻¹. **UV/Vis/NIR** (MeCN): $\lambda = 352$, 552, 851, 925 (shoulder) nm. **ESI-MS**: calcd for $[C_{10}H_{22}N_2NiS_2]^+$: 292.1 and $[C_{10}H_{22}ClN_2NiO_4S_2]^+$: 391.0; found: 292 and 391. **EA**: calcd for $[C_{14}H_{28}Cl_2N_4NiO_8S_2 + 0.2 CH_3CN]$: C, 29.70%; H, 4.95%; N, 10.10%; found: C, 29.85%; H, 5.16%; N, 9.78%.

Generation of [Ni(dithiacyclam)(H₂O)₂](ClO₄)₂

A sample of complex 3 was dissolved in 5 mL water. After 5 min stirring at room temperature, the solvent was removed in vacuum to afford a dark blue solid. The solid was used without further purification. **UV/Vis/NIR** (H₂O): λ = 371, 591, 847 (shoulder), 962 nm. **ESI-MS**: calcd for [C₁₀H₂₂ClN₂NiO₄S₂]⁺: 391.0; found: 391. **EA**: calcd for [C₁₀H₂₆Cl₂N₂NiS₂O₁₀ + 0.15 CH₃CN]: C, 23.16%; H, 4.99%; N, 5.64%; found: C, 23.24%; H, 4.76%; N, 5.74%.

Electrochemistry

The electrochemical studies were performed using a GAMRY Reference 600 or a PalmSens3 potentiostat in a standard threeelectrode setup. A glassy carbon electrode was used as working electrode (WE), a Ag wire as pseudo-reference or a conc. Ag/AgCl as reference electrode (RE) and a Pt wire as counter electrode (CE). The working electrode was prepared by successive polishing with 1.0 and 0.3 µm alumina pastes and subsequent sonication. Tetrabutylammonium hexafluorophosphate $([^{n}Bu_{4}N]^{+}PF_{6}^{-}, 0.1 \text{ M})$ was used as electrolyte in all electrochemical measurements either in anhydrous acetonitrile or a mixture of acetonitrile/water (4:1). For measurements in pure water KCl (1 M) was used as electrolyte. Prior to each experiment, the electrochemical cell was degassed with Ar for 10 min and an Ar atmosphere was maintained throughout the measurement. All cyclic voltammograms were recorded at a scan rate of 100 mV s⁻¹ and all pseudo-referenced potentials were referenced against the ferrocene/ferrocenium couple (Fc/Fc⁺). Controlled potential coulometry (CPC) were performed at defined potentials under otherwise identical conditions as reported above.

Quantification of the reduction products³⁶

Quantification of the headspace gas composition within the H-type cell was performed using an Agilent Technologies 7820A gas chromatograph equipped with a thermal conductivity (TCD) and a flame ionization detector (FID) as well as a methanizer. Gas separation was performed using a two-column separation system (HP-PLOT Q 30 m \times 0.53 mm \times 40 μ m column & HP-Molesieve 5 Å 30 m \times 0.53 mm \times 25 μ m) using argon as the carrier gas.

Spectroelectrochemistry (SEC)

Infrared spectroelectrochemistry (IR-SEC) measurements were carried out on a SP-02 cell (*Spectroelectrochemistry Partners*)

attached to a *Bruker* Tensor 27 FT-IR spectrometer with a *Pike* Miracle ATR unit. A *PalmSens3* was used as potentiostat with a standard three-electrode setup (WE: glassy carbon electrode, RE: Ag wire, CE: Pt wire). All measurements were carried out in CO_2 saturated acetonitrile/water (4:1) mixtures containing 20 mM of the Ni^{II} species and 0.1 M [n Bu₄N]⁺PF₆⁻ as electrolyte. Prior to each experiment, the electrochemical cell was degassed with Ar for 10 min and an Ar atmosphere was maintained throughout the measurement. Furthermore, the working electrode was prepared by successive polishing with 1.0 and 0.3 µm alumina pastes and subsequent sonication. The WE was placed 200 µm above the ATR crystal and the potential was held for 800 s before the IR scan was initiated. The IR measurement (128 scans) was completed in roughly 260 s.

X-ray absorption spectroscopy (XAS)

XAS measurements were carried out on beamline 9-3 of the Stanford Synchrotron Radiation Lightsource (SLAC National Accelerator Laboratory, Menlo Park, CA, USA). The SPEAR3 storage ring was operated at 3.0 GeV and 500 mA with top-off injection. A cryogenically cooled Si(220) ($\varphi = 0^{\circ}$) double crystal monochromator was used for energy selection. A Rh-coated collimating mirror upstream of the monochromator set to a 13 keV cutoff rejected higher order harmonics, while a Rh-coated toroidal mirror downstream of the monochromator focused the beam in both vertical and horizontal planes. The beamline was operated in a fully-tuned configuration. Sample temperatures were maintained at 10 K using an Oxford Instruments CF1208 continuous flow liquid helium cryostat. A Ni metal foil was used for internal energy calibration, with the first inflection point of the reference foil edge set to 8333.0 eV. XAS data were collected as fluorescence spectra using a 100 pixel monolithic germanium detector (Canberra). A Co filter of six absorption lengths and Soller slits were used to reduce scatter and maintain detector linearity. Samples were monitored for photoreduction during data collection, and new spots exposed as required. Tandem Mossbauer/XAS cups with a sample window of 6 mm × 10 mm were used to provide 2-3 independent beam spots on each sample. Averaging and normalization of the XAS data was performed using Athena, a graphical implementation of the IFEFFIT package.

Electron dispersive X-ray (EDX) spectroscopy

SEM images and EDX spectra of the deposited species were obtained using a *ZEISS* Gemini 2 Merlin HR-FESEM. The sample was placed on a conductive carbon-based carrier inside the vacuum chamber of the instrument. The SEM images were recorded with an operating voltage of 20 keV and the EDX spectra were recorded with an operation voltage in the 0 to 20 keV range. In order to identify the elements and obtain their mass fractions, the spectra were correlated to a data base. The spot size during the EDX measurements amounted up to 2.5 μ m in diameter and depth with an operating voltage of 20 keV.

X-ray data collection and structure solution refinement

Single crystals suitable for X-ray structure analysis were coated with Paratone N oil, mounted on a fiber loop and placed in a cold N₂ stream on the diffractometer. A Bruker D8 Venture diffractometer performing φ and ω scans at 100(2) K was used to collect diffraction data for 3. Intensities were measured using graphite-monochromatic Mo K_{α} radiation ($\lambda = 0.71073$ Å). The crystal used in the diffraction experiment was a pseudo-merohedral twin with relative domain volumes of 0.576(4): 0.424(4). The structure was solved by intrinsic phasing;³⁷ a difference Fourier synthesis revealed disorder for the cationic complex, a counter anion and the solvent region. The final structure model was refined on $F^{2,37}$ Two conformations of the macrocyclic ligand involve disorder of the ethylene versus propylene bridges. A perchlorate anion was treated as disordered over two edge-sharing alternative orientations. The sum of the occupancies for three mutually exclusive sites of the solvent water molecule was restrained to unity. All hydrogen atoms were introduced at their idealized positions and refined using a riding model. Crystallographic data as well as refinement parameters are presented in Table S2 in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Fonds of the Chemical Industry (Liebig grant to U.-P. A. and Kekulé fellowship to P. G.) and the Deutsche Forschungsgemeinschaft (Emmy Noether grant to U.-P. A., AP242/2-1 and AP242/5-1). K.R. thanks financial support from the DFG (Cluster of Excellence "Unifying Concepts in Catalysis"; EXC 314-2, and the Heisenberg-Program). XAS studies at SSRL BL 9-3 were made possible by the US DOE Office of Science (Contract No. DE-AC02-76SF00515) and US NIH (P41-GM-103393 to SSRL SMB Program and P30-EB-009998 to CWRU Center for Synchrotron Biosciences). This work was supported by the Fraunhofer Internal Programs under Grant No. Attract 097-602175.

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