Synthesis and Characterization of an Fe(I) Cage Complex with High Stability Towards Strong H-Acids

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The first synthesized and X-ray structurally characterized “classical” iron(I) dioximate showed an unrivaled stability towards strong acids; thus, calling for a reassessment of the origins of the electrocatalytic activity of similar low-valent cobalt and iron cage complexes with electron-withdrawing ribbed substituents, shown previously to be effective electrocatalysts of HER.

Molecular hydrogen is a potential alternative to carboniferous fossil fuels; if obtained from an appropriate source, such as water or aqueous solutions.¹ The use of cheaper and abundant non-platinum metal compounds in fuel cells, electrolyzers, and electrochemical hydrogen compressors/concentrators will make hydrogen energetics more available than ever. Among them, the most popular artificial electrocatalysts of HER are azomethine cobalt complexes, which mimic a natural cobalt-containing enzyme, cobalamin (vitamin B12);² however, the mechanism of the catalytic activity is still controversial.³ Since the early 1970s,⁴ cobalt hydrides, Co(III)-H, have been evoked as central intermediates of such HER.⁵ On the other hand, a recent re-investigation⁶ of the so-called “hydridocobaloxime” system,³ which has been used to support the plausible mechanism of the cobaloxime-catalyzed HERs in solution, showed no intermediate Co(III)-H species but an unsupported Co...Co dimer instead.

Cobalt clathrochelates represent another family of cobalt catalysts for hydrogen evolution. These macrobicyclic, aliphatic, aromatic, and hexahalogen-containing tris-dioximates have been proposed as efficient H₂-producing electrocatalysts.⁷ A plausible mechanism of their

electrocatalytic activity is proposed to be either a purely metal-centered activation of H⁺ ions or an intimate cooperation between the macrobicyclic ligand and the encapsulated cobalt ion for the formation of H₂.^{7a} Tris-dimethylglyoximate cobalt(I, II, and III) clathrochelates have been explored as catalytically active intermediates of clathrochelate-catalyzed HER;⁸ however, the exact catalytic mechanism remains an open question. Among the different scenarios discussed, the reaction mechanism might be similar to those proposed for the above-mentioned cobaloxime complexes. The reactive site might be localized on the polyazomethine quasi-aromatic caging ligands, or possibly possess an even more complex character; including both the encapsulated metallocenter and the caging ligand.⁹

On the other hand, it was unambiguously shown⁹ that the electrochemical reduction of the above-mentioned boron-capped aliphatic and aromatic cobalt(II) and cobalt(III) clathrochelates – in the presence of an acid – causes electro-deposition of cobalt-containing nanoparticles on the electrode surface, which then act as a very active catalysts for the production of H₂ from water.^{9,10} Such designed caging ligands have been used to decrease the potential of Co^{2+/+} reduction, aiming to minimize an overpotential of the clathrochelate-catalyzed 2H⁺/H₂ process.^{7c}

Iron cage complexes of this type can also potentially be used to electrocatalyze hydrogen production.^{7e, 11} Iron is one of the most abundant, ecologically friendly biometals. Hydrogenases, such as the iron-only [Fe], [FeFe], and the heterometallic [FeNi] hydrogenases, are recognized as incredibly efficient natural electrocatalysts; thus, initiating the search for their artificial mimics, diiron complexes¹² and their mononuclear analogs.¹³ In the latter case, all the proposed pathways of their electrocatalytic activity include the formation of iron(II) or iron(0) complexes as the intermediates. The iron(II) clathrochelates significantly outperform the cobalt ones, e.g., in terms of their stability in acidic conditions: while the latter decompose after prolonged exposure to strong acids in solutions, the former remain intact even in very strong acids, such as CF₃COOH, which is an appropriate solvent for their

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[†] Electronic supplementary information (ESI) available: the used materials, analytical, spectral, electrochemical, magnetometry and crystallographic methods and data. CCDC 1568417 and 1568418. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

synthesis.¹⁴ The system's robustness certainly is beneficial for the long-term stability of an electrocatalyst. The introduction of chlorine atoms as the ribbed substituents in the cobalt(II) clathrochelates¹⁵ led to the stabilization of low oxidation numbers of the encapsulated metal ion, potential intermediates. Here, we report an iron(I) cage complex with unprecedented chemical stability in acidic conditions.

Scheme 1. Synthesis of (K18-cw6THF₂)(Fe⁺)@L

Chemical reversibility of the reduction of the clathrochelate (Fe²⁺)@L (Scheme 1) was recognized from the cyclic voltammetry (CV) experiments, recorded in dichloromethane. The reversible reduction wave is observed at $E_{1/2} = -0.95$ V vs. the Fc/Fc⁺ couple (to which all potentials are referenced here, Fig. S1) with a peak-to-peak separation of 100 mV and diffusional control, as its peak current depends linearly on the square root of the scan rate (Fig. S2). Adding trifluoroacetic acid to the solution altered the CV response only slightly; however, no electrocatalytic enhancement of the current or changes in the reversibility were observed (Fig. S3). The preparative electrolyses of 1 mM THF solution of (Fe²⁺)@L at -0.95 V – in the presence of the acid – did not result in hydrogen evolution, as controlled by gas chromatography. Thus, this clathrochelate is not an electrocatalyst of HER under these conditions. Even more surprising, the product of its electrochemical reduction is immune to the presence of strong acids. While previous data on similar iron(II)-containing systems suggested a metal-centered Fe^{2+/1+} process, our finding inspired us to perform UV-vis spectroelectrochemistry to further study the composition of the reduction product.

Figure 1. UV-vis spectroelectrochemistry of 1 mM THF solution of (Fe²⁺)@L during electrochemical reduction (a) and subsequent re-oxidation (b) with the acquisition time of 1 min.

The electrolysis of (Fe²⁺)@L at -1.2 V, inside an UV-vis spectroelectrochemical cell in THF solution, led to a steady decrease in intensity of the characteristic absorption band of

the iron(II) species at 450 nm and a simultaneous generation of new bands at 580 and 460 nm, which are assigned to the corresponding iron(I) species. Switching the potential to 0.1 V resulted in the reversal of this process (Fig. 1). Notably, in the absence of the oxidizing potential, the signal of the reduced species was constant over 3 h, implying its chemical stability.

Figure 2. Absorption UV-vis spectra of the equimolar THF solutions of (Fe²⁺)@L (in red) and (K18C6THF₂)(Fe⁺)@L (in black) (a) and general view of clathrochelate (Fe⁺)@L anion with non-hydrogen atoms shown as thermal ellipsoids at 50% probability level (b).

Thus, we attempted to reduce the hexachloroclathrochelate (Fe²⁺)@L chemically, and to isolate the product for further characterization. The reaction of (Fe²⁺)@L with potassium(I) graphite, KC₈, in the presence of 18-crown-6 in THF (Scheme 1), gave brown crystals of (K18C6THF₂)(Fe⁺)@L, suitable for single-crystal X-ray diffraction analysis.¹⁶ The UV-vis spectrum of this product in THF solution (Fig. 2, a) is identical to the one collected under spectroelectrochemical conditions, suggesting that (K18C6THF₂)(Fe⁺)@L is identical to the compound obtained by electrochemical reduction of (Fe²⁺)@L at -1.2 V.

Single-crystal X-ray diffraction analysis confirmed the formation of an iron(I) clathrochelate anion (Fig. 2, b) with a well separated (18-crown-6, 18C6) potassium counter-cation, where the latter additionally coordinates two molecules of THF (Fig. 1, a). At 120 K, [(Fe⁺)@L][−] adopts a trigonal-prismatic geometry (the distortion angle $\varphi = 0.9^\circ$) with Fe–N bond distances (1.900(2) – 2.012(2) Å); slightly longer compared to the parent iron(II) complex (Fe²⁺)@L (1.898 – 1.904 Å at r.t.),¹⁷ as characteristic of the iron(I) ion. It is worth mentioning that the thermal ellipsoid of the iron ion is shifted from the center of its FeN₆-coordination polyhedron, and elongated towards one of the ribbed fragments of the caging ligand. This observation is indicative of the low-spin iron(I) ion undergoing a Jahn–Teller distortion. Accordingly, modelling the disorder resulted in the iron ion occupying three positions around the molecular B...B C₃-pseudoaxis (with the refined occupations of 0.52, 0.38, and 0.10, see SI).

The low-spin nature of the Fe(I) ion in (K18C6THF₂)(Fe⁺)@L was also confirmed by DC-SQUID magnetometry of a microcrystalline powder sample. Its effective magnetic moment is slightly temperature-dependent, varying from 1.74

μ_B at 2 K to $1.85 \mu_B$ at r.t. (Fig. S4), which is close to the spin-only value for a low-spin d^7 ion ($S = \frac{1}{2}$). The $S = \frac{1}{2}$ spin-state is further confirmed by X-band EPR spectroscopy. An EPR spectrum of $(K18C6THF_2)(Fe^+)@L$ recorded in frozen solution at 50 K (Fig. 3) is characterized by a rhombic g -tensor with well-resolved hyperfine structure due to electron coupling to two of the six donor nitrogen atoms (^{14}N , 99.6% nat. abundance, $I = 1$) of the caging ligand, resulting in hyperfine lines on the baseline crossing g_y magnetic field positions and the characteristic five-line pattern at g_x and g_z . The same values of the magnetic tensors were reported previously for the isoelectronic low-spin d^7 cobalt(II) clathrochelate,¹⁷ the only difference being no hyperfine coupling to the encapsulated metal ion in the case of the non-magnetic ^{56}Fe nucleus (in contrast to the ^{59}Co nucleus, $I = 7/2$). To further corroborate that the unpaired electron is mostly localized on the encapsulated metal ion, the ^{57}Fe enriched (approx. 97%) isotopomer $(K18C6THF_2)(^{57}Fe^+)@L$ was prepared, which resulted in additional hyperfine splitting to the $I = \frac{1}{2}$ nucleus of ^{57}Fe .

Figure 3. CW X-band EPR spectra of a 1 mM solution of the iron(II) clathrochelate $(K18C6THF_2)(Fe^+)@L$ with natural abundance of ^{56}Fe (blue line) and its ^{57}Fe -enriched isotopomer (green line), recorded in frozen 2-methyltetrahydrofuran solution at 50 K. The corresponding best-fit spectra calculated with using numerical solutions of the spin Hamiltonian are shown with black lines. The principal components of the magnetic interaction tensors from the simulation are: g -tensor: $[g_x, g_y, g_z] = [2.000, 2.027, 2.121]$; hyperfine tensors: $[A_x, A_y, A_z] = [34, 39, 35]$ MHz for two ^{14}N nucleus and $[60, 12, 29]$ MHz for ^{57}Fe .

The 10% ^{57}Fe -enriched solid sample of $(K18C6THF_2)(Fe^+)@L$ was also used for the acquisition of a zero-field ^{57}Fe Mössbauer spectrum. This spectrum shows an asymmetric quadrupole doublet with an isomer shift, δ , of $0.43(1) \text{ mm s}^{-1}$ (Fig. 4, a). As expected for ^{57}Fe Mössbauer spectroscopy, δ increases upon the metal-centered reduction of $(Fe^{2+})@L$ ($\delta = 0.20(1) \text{ mm s}^{-1}$, Fig. 4, b) to $(K18C6THF_2)(Fe^+)@L$. The quadrupole splitting parameter, $|\Delta E_Q| = 0.94(1) \text{ mm s}^{-1}$, for $(K18C6THF_2)(Fe^+)@L$ also is characteristic of low-spin iron complexes with trigonal-prismatic FeN_6 -polyhedra.^{14a}

Thus, all the experimental data collected for complex $(K18C6THF_2)(Fe^+)@L$ prove that it is indeed a low-spin iron(II) compound, confirming the assignment of the first electrochemical reduction of the iron(II) clathrochelate to an $Fe^{2+/+}$ process. To test the stability of the iron(II) complex in acidic conditions, suggested by the observations from CV, we followed the response of the addition of trifluoroacetic acid to a solution of $(K18C6THF_2)(Fe^+)@L$ in THF by UV-vis spectroscopy. The titration of up to 20 equivalents of this acid under anaerobic conditions did not cause a significant decrease in the signal intensity of the iron(II) species. However, conducting the same experiment in the presence of air resulted in its quick oxidation to the parent clathrochelate $(Fe^{2+})@L$. GC analysis of the headspace showed that no H_2 is produced, confirming that the formation of a stable metal(II) intermediate is not a sufficient condition for the electrocatalytic activity in HER.

Figure 4. Zero-field ^{57}Fe Mössbauer spectra of $(K18C6THF_2)(Fe^+)@L$ (a) and $(Fe^{2+})@L$ (10% ^{57}Fe) (b), recorded at 77 K. The circles represent the experimental data; the black line depicts the best fit to the experimental data.

The same result (the absence of H_2 evolution) was obtained for the reaction of the previously described cobalt(II) clathrochelate $((n-Bu)_4N)(Co^+)@L$ with trifluoroacetic acid.^[15a] However, the parent complex $(Co^{2+})@L$ was electrocatalytically active in HER.^{7c} Therefore, the inertness of the cobalt(II) compound towards protonation excludes the possibility that the electrocatalysis occurs *via* a homogenous molecular mechanism and, instead, suggests the formation of catalytically active cobalt nanoparticles under the harsh electrocatalytic conditions.¹⁰

Conclusions

In summary, a remarkably robust iron(II) clathrochelate demonstrated an unrivaled stability under strongly acidic conditions. The observed resistance of this compound to decomposition in the presence of strong acids may be the reason for its lack of electrocatalytic activity, both under

homogenous conditions and as a precursor of electrocatalytically active iron nanoparticles. The same chemical behavior was found for its cobalt(I)-encapsulating clathrochelate analog,^{15a} the cobalt(II)-containing macrobicyclic precursor of which is known to efficiently catalyze hydrogen evolution from acidic media, including aqueous solutions. This calls for a reassessment of the origins of the electrocatalytic activity of similar cobalt and iron(II) complexes with electron-withdrawing ribbed substituents, shown previously to be effective electrocatalysts for hydrogen evolution, including those in water electrolyzers. Moreover, the main paradigm in the design of macrobicyclic ligands for electrocatalytic $2\text{H}^+/\text{H}_2$ conversion using cage metal complexes should be shifted from attempts of stabilizing the +1 oxidation state of an encapsulated metal ion, which eventually leads to the absence of electrocatalytic activity. Instead, the optimization of clathrochelates with a proven HER activity^[7,15] should become a priority with a focus on external functionalization that allows their strong chemical or physical adsorption on working electrodes.

This work was supported by Russian Science Foundation (project 17-73-20369). The spectral characterizations were performed with the financial support of the EU Research and Innovation Staff Exchange (RISE) (H2020-MSCA-RISE-2017, Project 778245 'CLATHROPROBES'). KM acknowledges the generous support by the Friedrich-Alexander University Erlangen–Nürnberg (FAU). The contribution of the Center for molecular composition studies of INEOS RAS is also gratefully acknowledged. MALDI-TOF mass spectrometric measurements were performed using an equipment of CKP FMI IPCE RAS.

Conflicts of interest

There are no conflicts to declare.

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- Synthesis of (K18cw6THF₂)(Fe⁺)@L*. Complex (Fe²⁺)@L (0.30 g, 0.46 mmol), and 18-crown-6 (0.12 g, 0.46 mmol), were dissolved in dry THF (20 ml) under purified argon and potassium graphite C₈K (0.113 g, 0.48 mmol) was added under intensive stirring. The reaction mixture was stirred at r.t. for 24 h. Then the precipitate formed was separated by centrifugation and the solution obtained precipitated with dry hexane (20 ml) for 7 days. The yield of the brown crystals of (K18cw6THF₂)(Fe⁺)@L was 0.372 g (73%).
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