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## ARTICLE TYPE

# Cobalt Corrole Catalyzed Hydrogen Evolution Reaction: Surprising Electronic Effects and Characterization of Key Reaction Intermediates

Atif Mahammed,[a] Biswajit Mondal,[b] Atanu Rana,[b] Abhishek Dey*[b] and Zeev Gross*[a]

**A surprising effect of halide substituents on reduction potentials and catalytic activity of halogenated cobalt corroles has been deduced by experimental and computational**
10 **methods; and the proton-activating cobalt(I) and the cobalt(II) corrole that is formed in the step during which hydrogen is formed were characterized by NMR spectroscopy.**

Facile electrochemical reduction of protons to hydrogen is a
15 major goal within the contemporary science devoted for the development of alternative energy sources.[1] The progress is slow on most electrodes, except of expensive and rare noble metals (mainly Pt).[2] The combination of standard and cheap electrode material with coordination complexes that are able to catalyze the
20 reaction at reasonable potentials has hence become an extensively investigated alternative.[3] We have contributed to this research area by introducing $Co-F_8$ (Scheme 1): immobilized on a graphite electrode it catalyzed the hydrogen evolution reaction (HER) very efficiently, even from water obtained from local sources without
25 requiring pre-treatment and also under aerobic conditions.[4,5] Disadvantages of $Co-F_8$ are the very expensive 3,4-difluoropyrrole, from which the corresponding corrole is prepared in quite low yields. This encouraged us to investigate the full series of $\beta$-pyrrole halogenated Co corroles ($Co-X_8$, X = H, Cl,
30 Br, F) for a systematic investigation on their utility as catalysts for HER. The comparison between the various complexes revealed surprising trends in redox potentials and catalytic activity, whose origin was addressed by experimental and computational investigations. We also report the spectroscopic
35 characterization of key intermediates involved in the reduction of protons to hydrogen.

Cyclic voltammetry (CV, Fig. 1) was used for deducing the effect of halogenation on the redox potentials of the bis-pyridine coordinated $Co-X_8$ complexes. Consistent with previous
40 knowledge,[6] the first reduction process was irreversible due to the increased lability of axial ligands upon the transformation from inert cobalt(III) to labile cobalt(II). The pyridine ligands in the $Co-X_8$ complexes could also be removed by pre-treatment with trifluoroacetic acid (TFA), upon which the first reduction became
45 reversible (Fig. 1b). The second and more important reduction progresses were reversible even in the absence of TFA, revealing

that all halogenated complexes were reduced at up to 600 mV less negative potentials than $Co-H_8$. However, the anticipated trend of $Co-F_8 > Co-Cl_8 > Co-Br_8$ regarding reduction facility
50 was not fulfilled: the first reduction potentials were practically identical (0.36 V) and the $E_{1/2}$ values for the second reduction were -1.39, -0.80, -0.78 and -0.97 V *vs.* Ag/AgCl for X = H, Cl, Br and F, respectively. Most surprising was that 2-electrons reduction of $Co-F_8$ occurs at a significantly more negative
55 potential than that of $Co-Br_8$ and $Co-Cl_8$. To address this puzzle, the series of analogous gallium corroles ($Ga-X_8$, where X = H, Cl, Br, or F) was prepared. The motivation was to check if the phenomenon is unique to cobalt or if it occurs even for post-transition metallocorroles wherein redox processes are limited to
60 the corrole macrocycle.



| | |
|---|---|
| | **Co-H$_8$: M= Co, X= H** |
| | **Co-F$_8$: M= Co, X= F** |
| | **Co-Cl$_8$: M= Co, X= Cl** |
| | **Co-Br$_8$: M= Co, X= Br** |
| | **Ga-H$_8$: M= Ga, X= H** |
| | **Ga-F$_8$: M= Ga, X= F** |
| | **Ga-Cl$_8$: M= Ga, X= Cl** |
| | **Ga-Br$_8$: M= Ga, X= Br** |

py= pyridine
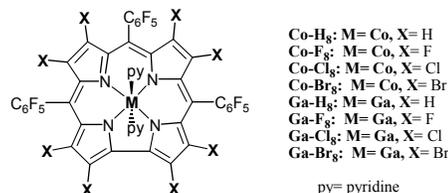
**Scheme 1** Chemical structures of the cobalt(III) and gallium(III) corroles.

$Ga-H_8$ and $Ga-Br_8$ were prepared according to published procedures,[7,8] while $Ga-F_8$ was synthesized by reaction of the fully $\beta$-pyrrole fluorinated tris-pentafluorophenylcorrole with
65 gallium chloride in pyridine under reflux, and $Ga-Cl_8$ was accessed via direct chlorination of $Ga-H_8$ (see ESI[†]). Both $Cl_2$ and N-chlorosuccinimid (NCS) were examined, in various solvents and at different temperatures, for identifying optimal conditions that would lead to full chlorination of all $\beta$-pyrrole positions. The
70 best results were obtained by reacting $Ga-H_8$ with NCS in *ortho*-dichlorobenzene at 150 °C for 30 min, followed by solvent evaporation and uptake of the solid material in benzene. Green solutions of $Ga-Cl_8$ were obtained upon treatment of the initially yellow reaction mixture with $NaBH_4$, whose role was to reduce
75 the oxidized macrocycle that was initially formed. The CV's of the $Ga-X_8$ complexes revealed almost identical reduction potentials (-0.86 V) for $Ga-Cl_8$ and $Ga-Br_8$, which are not only about 600 mV more positive relative to $Ga-H_8$, but also about 200

mV more positive than that of Ga-F$_8$ (Fig. S1, ESI†). As this trend is identical to that observed for the *second* reduction potential of the analogous cobalt complexes, *this result might suggest* that the reduction of the cobalt(II) corroles is corrole- and not metal-centred.
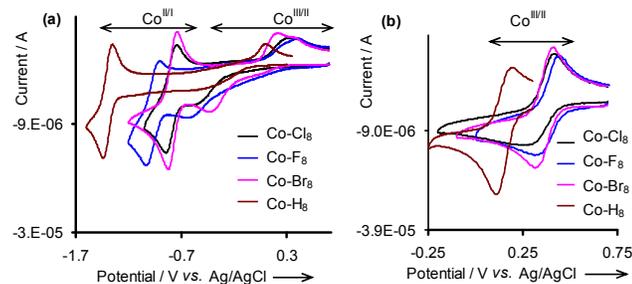


**Fig. 1** Cyclic voltammogram traces of the Co-X$_8$ complexes in acetonitrile solutions with 0.1 M TBAP as electrolyte, under a N$_2$ atmosphere, without (a) and in the presence of 0.13 M TFA (b). Scan rate: 100 mVs$^{-1}$; glassy carbon working electrode.

Further insight in how β-pyrrole halogenation affects the electrochemistry of the cobalt complexes was obtained from geometry optimized DFT calculations of the 1-e-reduced Co-X$_8$ complexes (Fig. S2, ESI†). The calculated ground state wave functions revealed low-spin Co(II) states with the d$_z^2$ orbital as the SOMO, consistent with previously reported evidence from EPR spectroscopy.[9] The comparison between [Co-F$_8$]$^-$ and [Co-Cl$_8$]$^-$ disclosed that the SOMO of the former complex is 0.137 eV higher in energy, which implies that further reduction of [Co-F$_8$]$^-$ (*i.e.,* the addition of another electron into d$_z^2$) should be less energetically favored than for [Co-Cl$_8$]$^-$. This finding is perfectly consistent with the 170 mV more negative second reduction potential of Co-F$_8$. The comparison of the DFT calculations on Co-F$_8$ and Co-Cl$_8$ also revealed why the halide substitution effect displays the same trend for reduction of the corrole (as in Ga-X$_8$) and the metal (as in [Co-X$_8$]$^-$). Both the metal's SOMO and the corrole's LUMO (π*) are much higher in energy for the F$_8$ complex. The stronger electron withdrawing effect of F *vs.* Cl is apparently more than outbalanced by the more effective π-donation of fluoride into the macrocycle's π system and through it to the metal as well.[10] Accordingly, addition of one electron to both the π* (as for Ga-X$_8$) and to the d$_z^2$ orbital of cobalt(II) (as for [Co-X$_8$]$^-$) occurs at more negative potentials for X= F.

Armed with the above insights, the full series of *β-pyrrole*-halogenated cobalt corroles was examined as catalysts for HER, with focus on kinetic reactivity ($i_{cat}/i_p$) and onset potentials. The addition of TFA to homogenous acetonitrile solutions induced catalytic waves, which for low TFA concentrations (*e.g.,* 2-4 mM TFA, Fig. 2a-c) were observed at potentials near to the Co$^{II/I}$ couple of the Co-X$_8$ complexes. The onset potentials were -0.4, -0.55, and -0.6 V for Co-Br$_8$, Co-Cl$_8$ and Co-F$_8$, respectively. The catalytic waves increased in amplitude in response to larger applied acid concentration (*e.g.,* 10 mM TFA), and for Co-Cl$_8$ and Co-Br$_8$, but not Co-F$_8$, progressively shifted to more negative potentials. Ultimately, the maxima of the two first mentioned complexes were actually positioned at more negative potentials (-1.33 and -1.23 V for Co-Cl$_8$ and Co-Br$_8$, respectively) than for Co-F$_8$ (-1.13 V). Various TFA concentrations were applied for

comparing the catalytic activity of the halogenated cobalt corrole in terms of onset potentials and kinetic reactivity (Fig. 2d,e). The conclusions from these results were that: a) the most reactive catalyst is Co-F$_8$, followed by Co-Cl$_8$ and the least reactive Co-Br$_8$; and b) that the onset potential is earliest for Co-Br$_8$, followed by Co-Cl$_8$ and Co-F$_8$ (similar results obtained also under heterogeneous conditions, see Fig. S4-S6, ESI†). The trend in onset potential is opposite to intuition, but fully consistent with that observed for the redox potentials and the computational results. Taken together, all the results point toward cobalt(I) corrole as the proton-reducing reaction intermediate.
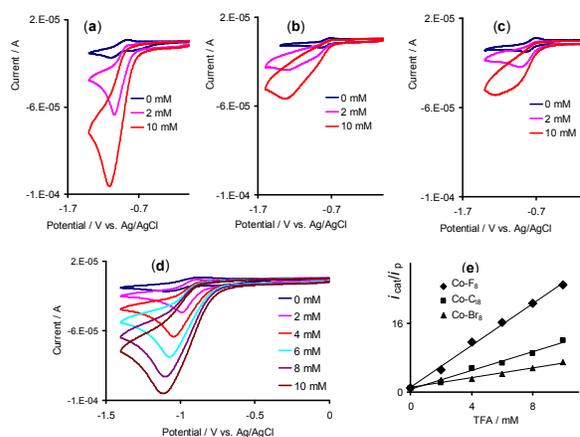


**Fig. 2** Cyclic voltammograms of 1 mM (a) Co-F$_8$, (b) Co-Cl$_8$, and (c) Co-Br$_8$ in acetonitrile solutions containing 0.1 M TBAP in the presence of 0, 4, and 10 mM TFA. (d) Cyclic voltammograms of Co-F$_8$ in the presence of 0, 2, 4, 6, 8 and 10 mM TFA. (e) Dependence of $i_{cat}/i_p$ for Co-F$_8$, Co-Cl$_8$, and Co-Br$_8$ on the concentration of TFA in acetonitrile. Scan rate: 100 mV/s; glassy carbon working electrode.

Spectroscopic characterizations of Co-Cl$_8$ in the various oxidation and coordination states that are relevant to HER were performed for gaining additional insight into the multistep and potentially multiple pathways involved in the overall process. The $^{19}$F NMR spectrum of the $C_{2v}$ symmetry 6-coordinate Co(III) complex (Fig. 3a) displayed two kinds of C$_6$F$_5$ rings in a 2:1 ratio, each of which with only one type of *ortho*-F resonances. Its $^1$H NMR spectrum (Fig. S10, ESI†) disclosed the high field shifted resonances (at 1.22, 5.40, and 6.36 ppm) of the coordinated pyridine molecules that complete the coordination sphere.[11] The suspected proton-reducing reaction intermediate [Co-X$_8$]$^{2-}$ was prepared by adding 2 equiv amount of Co(Cp*)$_2$ to a THF-d$_8$ solution of Co-Cl$_8$ under a N$_2$ atmosphere. The $^{19}$F NMR spectrum, recorded after the solution color changed from green to red, was characterized by very narrow resonances (Fig. 3b). This implies the formation of a diamagnetic complex, consistent with d$^8$ Co$^I$ in a square planar geometry. The 2:1 ratio of both the *ortho*-F and *meta*-F resonances were also supportive of that conclusion, consistent with the DFT calculations that point towards metal-centred reduction. The low affinity of [Co-X$_8$]$^{2-}$ to axial ligands, already deduced from the earlier described electrochemical results, is also reflected in the $^1$H NMR spectrum of the reaction mixture that displayed only resonances of non-coordinated pyridine (Fig. S11, ESI†). The subsequent addition of TFA to [Co-Cl$_8$]$^{2-}$ induced a color change from red to brown and

the thus resulting $^{19}F$ NMR spectrum (Fig. 3c) displayed paramagnetic shifts and broadening of all resonances. A practically identical NMR spectrum was obtained via reduction of Co-Cl$_8$ by excess NaBH$_4$, which points towards the formation of [Co-Cl$_8$]$^-$ in both cases. Supporting evidence for the Co(II) oxidation state in [Co-Cl$_8$]$^-$ was obtained by comparing its UV-vis and EPR spectra (Fig. S12, ESI†) with previous reports.[9,12]
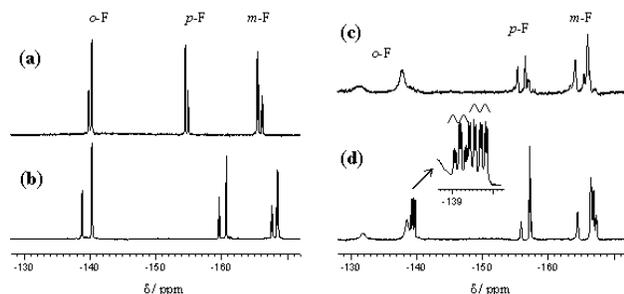


**Fig. 3** $^{19}F$ NMR spectra of Co-Cl$_8$ before (a) and after (b) reduction by Co(Cp*)$_2$, and after successive addition of TFA (c).  (d) The $^{19}F$ NMR spectrum of Co-Cl$_8$ treated with NaBH(OAc)$_3$. All manipulations were performed in a N$_2$-purged glove box at ambient temperature, and THF-d$_8$ was the common solvent for all the experiments.
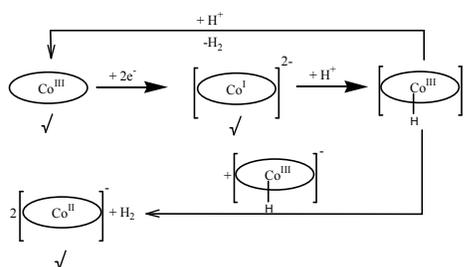


**Scheme 2** Mechanism for H$_2$ evolution catalyzed cobalt corroles. The represents cyrcles and √ symbolises (corrole)$^{3-}$ and the fully identified complexes, respectively.

The results presented so far are fully consistent with the doubly reduced Co(I) complexes, [Co-X$_8$]$^{2-}$, as the active species that react with H$^+$. The putative Co(III) intermediate [(Co-X$_8$)-H]$^-$ could not be trapped under the reaction conditions, apparently because it subsequent reactions are too fast. The two accepted pathways for the decay of [(Co-X$_8$)-H]$^-$ are via the reaction of two such intermediates as to form H$_2$ and two equivalents of [(Co-X$_8$)]$^-$ or via reaction with H$^+$ and release of H$_2$ and the initial Co(III) complex (Scheme 2).[13] Attempts to produce [(Co-X$_8$)-H]$^-$ have hence focused on reaction conditions under which the second scenario cannot take place. For that purpose, the reaction of Co-Cl$_8$ with two hydride donors, NaBH$_4$ and NaBH(OAc)$_3$, were examined. Practically identical $^{19}F$ NMR spectra were obtained in both cases, consisting of an about 1:1 ratio of the already characterized paramagnetic Co(II) complex [(Co-X$_8$)]$^-$ and a new diamagnetic complex of $C_s$ rather than $C_{2v}$ symmetry. This conclusion was deduced from the 2:2:1:1 ratio of the *ortho*-F atoms (Fig. 3d, inset), implying a 5-coordinate square pyramidal Co(III) complex. Formulation of the product as [(Co-X$_8$)-H]$^-$ would be consistent with that data, but the resonance of the cobalt

hydride could not be identified in the $^1H$ NMR spectrum of the reaction product.

Examination of the CoX$_8$ series revealed a surprising effect of halide substituents on reduction potentials and catalytic activity regarding HER. DFT calculations revealed π-donation by F into the corrole system and through it to the metal center as the dominant factor of both phenomena. Two important reaction intermediates were characterized by NMR spectroscopy, the proton-activating cobalt(I) complexes and the product resulting from the step during which hydrogen is formed. The bimolecular reaction between the putative cobalt(III) hydrides is apparently dominant[4,13] at the conditions used for spectroscopic characterizations, albeit the alternative pathway could not be ruled out. The improved insight into the reaction details is an important asset for the design of even more effective cobalt-based catalysts for HER.

## Notes and references

*$^a$Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel; E-mail: chr10zg@tx.technion.ac.il*
*$^b$Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700032, India; E-mail: icad@iacs.res.in*
†Electronic Supplementary Information (ESI) available: Detailed experimental procedures and data. See DOI: 10.1039/b000000x/

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