

Electrocatalytic Performance of Thiacalix[4]arene-based Co(II) Complex in Hydrogen Evolution Reaction

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The generic electron-rich thiacalix[4]arene bearing sulfur and oxygen coordinating donor atoms in the lower rim is underestimated as a pre-catalyst for the Hydrogen Evolution Reaction (HER). In addition, cobalt is a promising metal ion for many electrocatalytic applications, including HER. Herein, we report the electrocatalytic activity of a cobalt(II) compound based on thiacalix[4]arene that was characterized by cyclic voltammetry (CV). The CV using the glassy carbon as a working electrode *versus* Ag/AgCl, show two reduction peaks at -0.582 V and -1.270 V for the two redox couples Co²⁺/Co⁺ and Co⁺/Co, respectively. The two-electron proton reduction into hydrogen in the presence of the catalyst and 5 equivalents (12.5 mM) of acetic acid show a noticeable shift of about 780 mV compared to the catalyst-free reaction and 200 mV compared to the second wave observed for the acid-free solution. Moreover, a maximum anodic peak current of 32 μ A was observed upon adding 30 equivalents (75 mM) of acetic acid.

Keywords: Thiacalix[4]arene, Cobalt(II) complex, Electrocatalysis, proton reduction, cyclic voltammetry.

1. INTRODUCTION

The two-electron proton reduction into hydrogen is one of the most studied reactions because of many concerns related to its natural extraction, including economic and environmental ones. Natural gas reforming or gasification can produce the smallest diatomic gas (H₂). Still, the main problem remains in the emission of harmful CO₂ gas, in addition to the depletion of fossil fuels [1]. The electrochemical production of hydrogen by two-electron reduction of proton requires a catalyst to overcome the

overpotential. The electrocatalysts based on noble transition metals have shown great activities in HER [2].

Nevertheless, their high cost pushed the scientists to find alternatives based on cheap metals and electron-rich multidentate ligands. Therefore, supramolecular platforms such as the tetradentate electron-rich porphyrin displaying four nitrogen coordinating atoms in the internal ring of the molecule have been studied intensively [3, 4]. For example, Lei and co-workers studied the electrocatalytic activities of metal-based tetrakis(pentafluorophenyl)porphyrin. While the cyclic voltammetry of the free ligand showed two reversible redox couples at -1.17 and -1.61 V vs ferrocene and using the glassy carbon as working electrode, its complexes based on Co(II), Ni(II), Cu(II) and Zn(II) also presented two reversible reduction waves. For the cobalt complex, the first reduction wave ($E_{1/2} = -1.02$) appeared to be suitable for proton reduction and the maximum current was reached after adding 140 equivalents of trifluoroacetic acid [5]. The electrocatalysts based on S-containing counterparts have often shown better activities [6]. In this context, TC4A started attracting more attention for electrocatalytic reactions, including HER over C4A (Fig. 1).

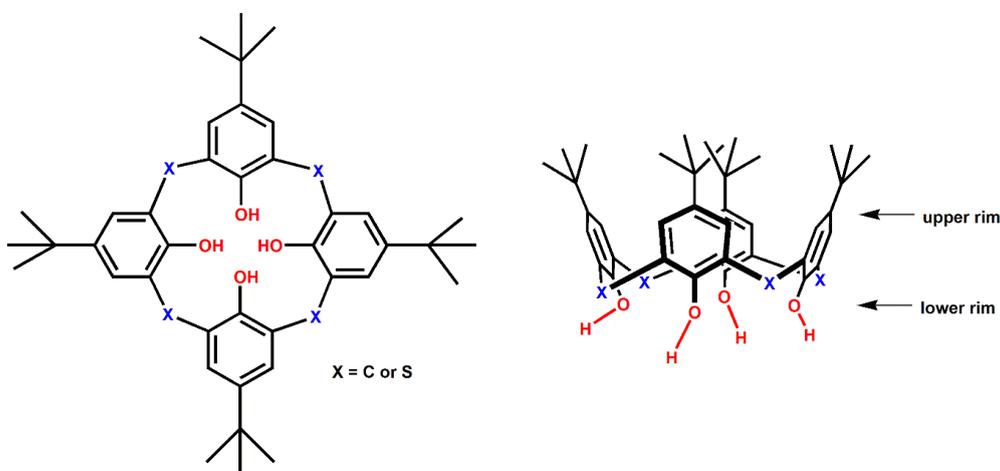


Figure 1. The chemical structure of calix[4]arene (C4A) and thiacalix[4]arene (TC4A)

These chemically and thermally stable molecules possess four sulfur atoms arranged on a circular line and bridging four phenolic units. This arrangement made them strongly coordinate platforms for transition metals where the guests are logged on the cavity entrance. Therefore, they were widely used to extract metal ions from an aqueous medium [7, 8]. In addition, many scientists isolated coordination compounds based on TC4A with transition metals such as Cu(II), V(V), W(VI), Mn(II), Ni(II), Pd(II) and Fe(III) [9-11]. Most of these complexes were characterized by single-crystal X-ray diffraction and studied for their magnetic properties. In addition, Bilyk and co-workers prepared trinuclear species of Zn(II) and Co(II) based on TC4A ligand [12]. To the best of our knowledge, none of these reported complexes based on TC4A was studied for the Hydrogen Evolution Reaction (HER). However, only a few examples were reported, but all of them contain noble metals encapsulated in a pocket formed between TC4A. For example, Zhang and co-workers prepared an $\{Ni_{24}\}$ cluster forming a pocket between six TC4A. The authors encapsulated an ultrafine Pt nanocluster and suggested that the HER is carried close to the metal centre in a confined space [13]. In addition, the electrocatalytic activities of

other species were also studied in HER, Oxygen Evolution Reaction (OER), hydrogen oxidation, oxygen reduction, and Glucose Oxidation Reaction (GOR) [14-16].

In this paper, we report the electrochemical characterization of a reported Co(II) coordination complexes based on TC4A ligand and its electrochemical activities toward hydrogen production by two-electron reduction of protons.

2. EXPERIMENTAL SECTION

2.1. Materials

The starting materials were purchased from Merck and Acros Organics through Afaq Sada Trading Est and used as received (Table 1). The ligand TC4A was prepared using a microwave technique based on a reported procedure [17]. The complex (**1**) was synthesized according to a protocol described in the literature [12]. All analytical data were consistent with the literature data and confirmed the structure of the synthesized ligand and complex.

Table 1. The used chemical of the synthesis TC4A and complex 3

#	Chemical name	Source	Purity	CAS number
1	4-tert-butylphenol	Merck	99 %	98-54-4
2	Sulfur		99.98 %	7704-34-9
3	Tetraethylene glycol dimethyl ether		≥ 99 %	143-24-8
4	Sodium hydroxide		≥ 98 %	1310-73-2
5	Hydrochloric acid. 37 %		≥ 99.8 %	7647-01-0
6	Triethyl amine	Acros Organics	99.7 %	121-44-8
7	Solvent	Acros Organics	Analytical standard	

2.2. Electrochemical measurements

Electrochemical measurements are performed at 25 °C using a standard three-compartment cell with the working glassy carbon electrode (surface = 0.07 cm²), the reference Ag/AgCl electrode and platinum wire as the counter electrode. Before use, the working electrode is polished using emery papers of different grades, then washed with the used solvent and dried. Potentiostat (Autolab PGSTAT 128N) and NOVA 1.10 software are used for recording and processing the electrochemical data.

3. RESULTS AND DISCUSSION

Compound 1 was produced based on a reported reaction between TC4A (1.0 g, 1.19 mmol) and [Co(DMF)₆](ClO₄)₂ (2.12 g, 3.04 mmol) in dimethylformamide (DMF) in the presence of triethylamine (Et₃N) [12]. The recorded analytical data are coherent with the literature. The structure is a trinuclear

cluster of cobalt ions connected by one or two oxygens of the phenol groups. The three metal ions are sandwiched between two TC4A in cone conformation. The coordination sphere of the cobalt is CoO_4S_2 , and the geometry is nearly octahedral (Fig. 2). It is worth noting that one S atom of each TC4A is left uncoordinated. This would be of great interest for any catalytic reaction to stabilize the catalyst and recover. In addition, we believe that the metal centers close to the cavity give the chance of carrying the HER in confined space because of the small size of both H^+ and H_2 .

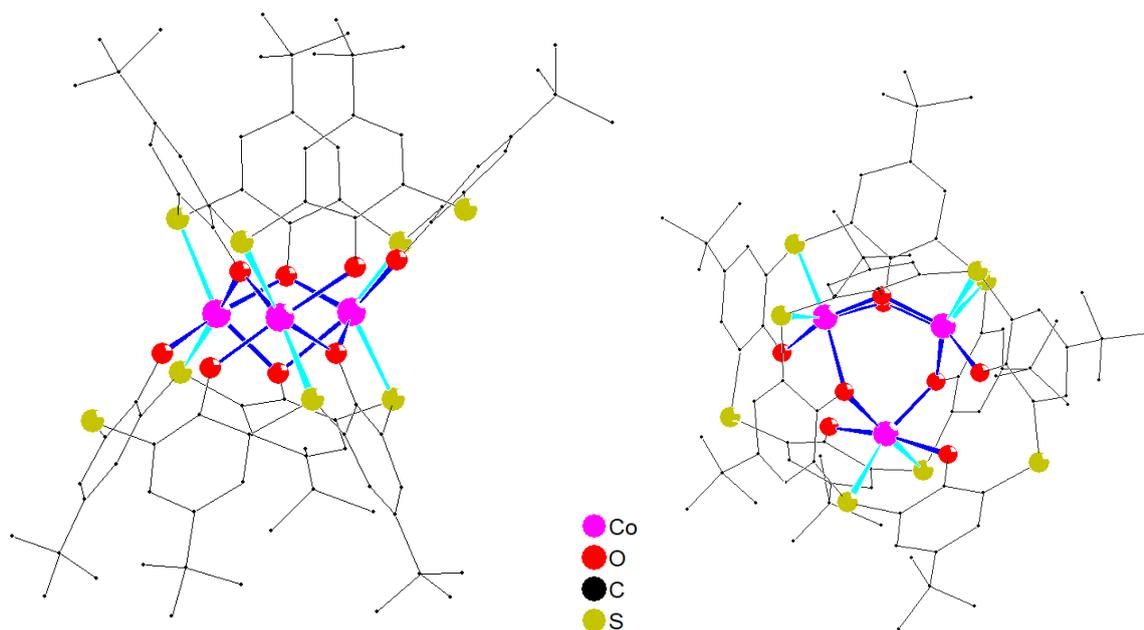


Figure 2. Side and top views of the structure of **1**. The hydrogen atoms are omitted for more clarity.

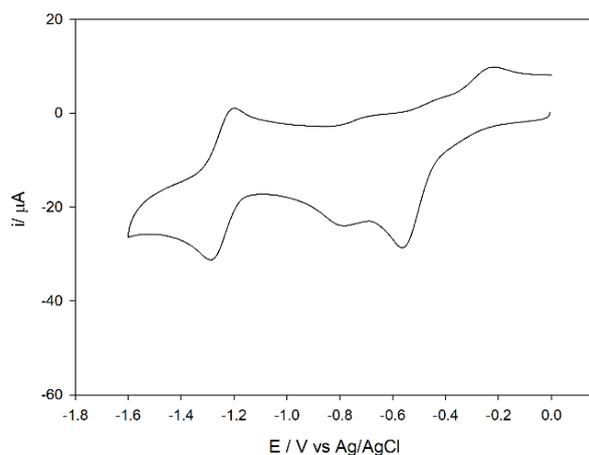


Figure 3. Cyclic voltammetry of Co(II) complex in DMF solution (2.5 mM) containing 0.2 M $[\text{NBu}_4][\text{BF}_4]$ at carbon electrode vs Ag/AgCl at a scan rate of 100 mVs^{-1} .

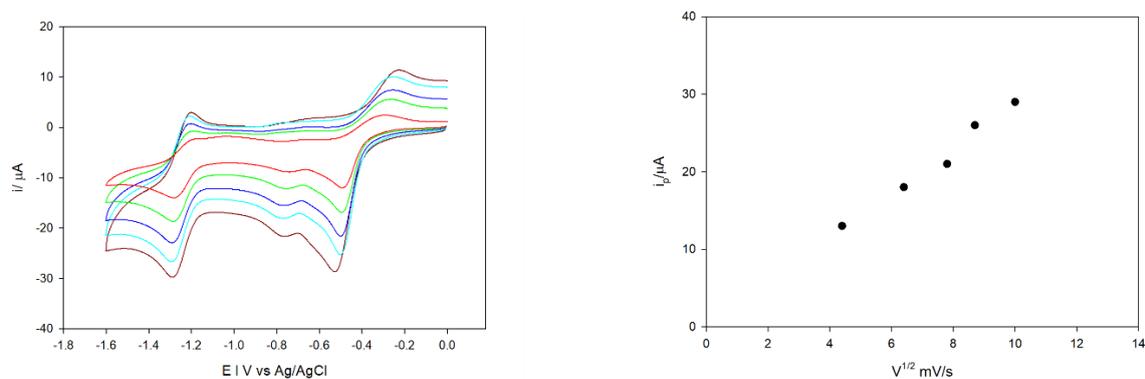


Figure 4. Left: Cyclic voltammetry of a solution of DMF containing 2.5 mM of Co(II) complex and 0.2 M of $[\text{NBu}_4][\text{BF}_4]$ at carbon electrode vs Ag/AgCl at different scan rates. Right : The root square of the peak potential vs the peak current. The different scan rate of the CVs is as following: brown: 100 mVs^{-1} , magenta: 80 mVs^{-1} , blue: 60 mVs^{-1} , green, 40 mVs^{-1} and red: 20 mVs^{-1} .

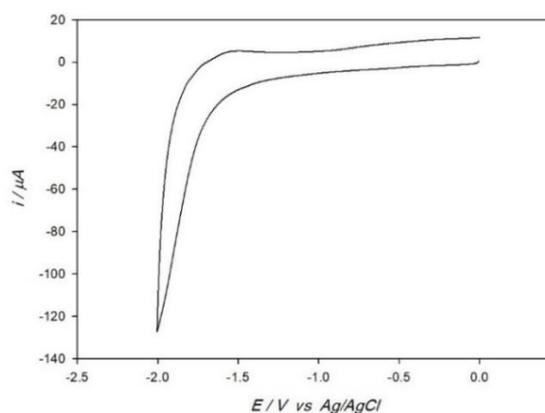


Figure 5. Cyclic voltammetry of the catalyst-free solution of DMF contained 20 mM CH_3COOH and 0.2 M $[\text{Bu}_4\text{N}][\text{BF}_4]$, scan rate 100 mVs^{-1} at glassy carbon electrode vs Ag/AgCl

Cyclic voltammetry of a DMF solution containing 2.5 mM complex **1** and 0.2 M tetrabutylammonium tetrafluoroborate, $[\text{NBu}_4][\text{BF}_4]$ (electrolyte) was recorded on glassy carbon using platinum wire as counter electrode vs Ag/AgCl. Figure 3 shows two reduction peaks of the redox couples $\text{Co}^{2+}/\text{Co}^+$ and Co^+/Co at -0.582 V and -1.270 V , respectively. The CV at different scan rates ranging from 20 mV to 100 mV show a proportional increase of the height of the peak current. This is reflected in a linear dependence of the root square of the scan rate versus the anodic peak current at constant temperature (Fig. 4). In accordance with the work of Dylla and co-workers, this indicates the non-absorption process at the electrode [18].

The activity of complex **1** was further evaluated in the two-electron reduction of a proton into hydrogen in the presence of acetic acid. The proton reduction in the above-mentioned solution occurs at -1.070 V in the presence of 5 equivalents (12.5 mM) of acetic acid, with a shift of about 200 mV to the more positive potentials compared to the second wave of the acid-free solution (Fig. 7A). This shift increases with the acetic acid equivalent until the saturation, 360 mV with 35 equivalents (87.5 mM) of acids (Fig. 7B). Notably, a considerable shift of about 780 mV is observed compared to the proton's direct reduction in a catalyst-free solution (Fig. 5). Similarly, the peak current increases with the number of acetic acids from an original value of $14 \mu\text{A}$ for the acid-free solution until a maximum of $33 \mu\text{A}$ with 35 equivalents (87.5 mM) of acetic acid (Fig. 7C). In the literature, other cobalt(II) coordination

complexes based on ligands such as porphyrin or pyridoxal thiosemicarbazone have been used in HER (Table 2). Comparing the onset potential shift *versus* the catalyst-free proton reduction reaction, the complex 9 formed of divalent cobalt ion and pyridoxal thiosemicarbazone ligand show the lower shift estimated to 270 mV under the same conditions of our catalytic studies [19]. However, compared to the well-known pre-catalysts porphyrin ligand, Beyene and co-workers prepared and studied seven cobalt(II) complexes of porphyrin substituted on the *meso*-positions by *para*-substituted phenyl with electron-donating or electron-withdrawing groups (Fig. 6). Even though the electrocatalytic studies are performed in DMSO using the glassy carbon working electrode and the standard hydrogen electrode (NHE) as a reference, only complex 4 shows better results than our complex in terms of onset potential shift *versus* the catalyst-free reaction. The authors relate the best results of the complex bearing $-\text{SO}_3\text{H}$ groups to the higher acidity. The other complexes, including those bearing acid groups, show a lower shift than the studied complex 1 [20].

Table 2. Onset potential shift compared to the catalyst-free reaction

#	Complex	Shift / mV more positive values <i>vs.</i> Ag/AgCl in DMF	Shift / mV more positive values <i>vs.</i> NHE in DMSO	Reference
1	[Co ₃ (TC4A) ₂] (1)	780	-	This work
2	[Co(TPP-COOMe)] (2)	-	620	[20]
3	[Co(TPP-COOH)] (3)	-	720	
4	[Co(TPP-SO ₃ H)] (4)	-	890	
5	[Co(TPP)] (5)	-	560	
6	[Co(TPP-NH ₂)] (6)	-	630	
7	[Co(TPP-OH)] (7)	-	470	
8	[Co(TPP-OMe)] (8)	-	490	
9	[Co(PLSC)(SO ₄)(H ₂ O) ₂] (9)	270	-	

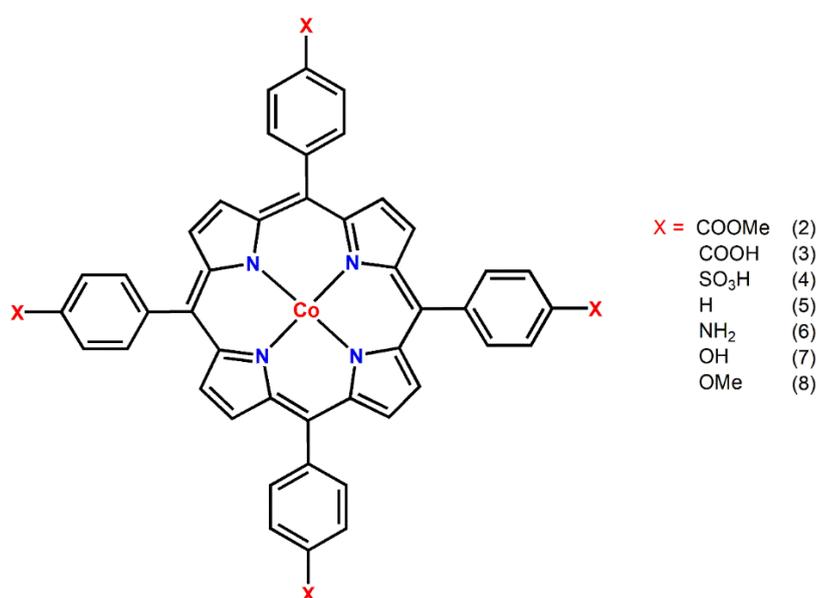


Figure 6. Cobalt(II) porphyrins used in HER in the presence of acetic acid as a source of proton

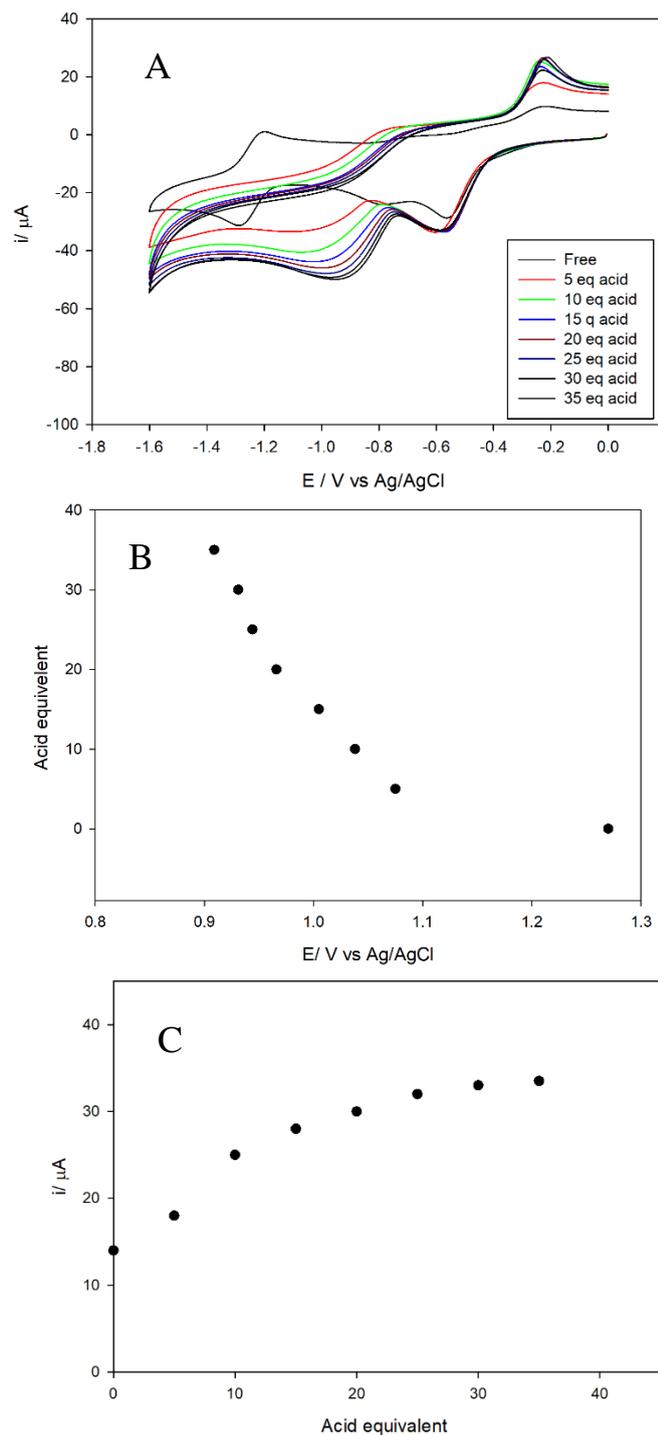


Figure 7. A: Cyclic voltammogram obtained from the solution of DMF contained 2.5 mM Co(II) complex, different equivalents of CH_3COOH and 0.2 M $[\text{Bu}_4\text{N}][\text{BF}_4]$, scan rate 100mVs^{-1} at glassy carbon electrode under N_2 . B: The peak potential shift vs the number of acetic acid equivalent. C: The number of acetic acid equivalent vs the peak current.

4. CONCLUSION

A cobalt complex based on the generic electron-rich TC4A ligand has been prepared and characterized by cyclic voltammetry. The second reduction wave at -1.274 V appears suitable for the

HER. However, in the presence of 5 equivalents (12.5 mM) of acetic acid, the potential shift of about 200 mV to reach a maximum of 360 mV with 35 equivalents (87.5 mM) of acids. The peak current reaches its maximum value at 33 μ A. Based on the complex structure where three cobalt(II) are sandwiched between two TC4A ligands that possess an interior small empty space, we suggest that the catalytic reaction occurs in a confined space close to metal centres. Our compound shows better onset potential activity than other reported cobalt(II) complexes with ligands such as porphyrin or pyridoxal thiosemicarbazone.

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