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1 **Why Cobalt macrocyclic complexes are not efficient catalysts for the oxygen**
2 **reduction reaction, under acidic conditions.**

3

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8

9 **Abstract**

10 The activation of the oxygen reduction reaction (ORR) is of a primary importance for
11 the development of fuel cells. Cobalt macrocyclic complexes, *e.g.* those of
12 porphyrins, phthalocyanines, tetraazaannulenes (TAA), cyclam, have been tested in
13 order to replace platinum, the best catalyst but a rare and expensive metal. However
14 it has been noted in some studies that these complexes suffer from degradation in an
15 acidic environment. Suspicions have already been expressed that such degradation
16 are caused by hydrogen peroxide or demetallation, but the reason for the loss of
17 activity of these catalysts has never been experimentally established. In the present
18 work, it has been clearly demonstrated that cobalt complexes are stable in the
19 presence of acids when the metal centre is at the Co(III) oxidation state but are
20 demetallated when it is reduced to the Co(II) oxidation state, which occurs during the
21 oxygen reduction reaction. Co²⁺ is a borderline Lewis acid in Pearson's classification
22 and thus can be substituted by H⁺ in an acidic environment.

1 **Keywords** : Oxygen reduction reaction (ORR), cobalt macrocyclic complexes,
2 demetallation, aqueous acidic solution.

3

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1. Introduction

The oxygen reduction reaction (ORR) at electrodes is important for realizing efficient fuel cells. The reduction of dioxygen (O_2) is not easy, due to its electronic configuration and to its high activation energy barrier ; thus, ORR requires to be catalysed [1, 2]. The mediation of a catalyst is required in order to reduce the overpotential of ORR, which causes an important loss of potential in any electrochemical cell including an oxygen electrode, an issue of a primary importance for fuel cells [2]. Platinum is the best catalyst for ORR, a metal rare and of strategic importance and consequently expensive, which is an obstacle to the development of fuel cells. For that reason, the search for efficient substitutes to the precious metal has been intense. The importance of iron porphyrins in the transport and activation of oxygen in biological systems being well known and documented, the possibility to use iron porphyrins as catalysts has been tested, as well as cobalt complexes with porphyrins and other cyclic macrocycles [3-9]. The efficiency of metal complexes for ORR is known since a long time. The role of the metal centre has been scrutinized in many works from which it appears that iron and cobalt complexes are good candidates [10]. The overpotential is reduced when cobalt is the metal centre instead of iron. Accordingly, a huge number of works have been devoted to the study of the efficiency of cobalt(II) complexes. Fuel cells can be operated under various conditions, but for practical reasons, in particular due to the presence of CO_2 in air, the source of oxygen, it is advisable to work under acidic conditions. This of course requires that the complexes must be stable in acid media.

The intent of the present work is not to compare the respective properties of the various metal complexes, or those of their association with the electrodes, in order to orientate the selection of the most appropriate combination for ORR; this has already

1 been extensively documented in an incommensurable number of publications and
2 reviews [11-14]. The purpose of this report is to explain why the cobalt complexes,
3 despite their intrinsic promising qualities for the catalysis of ORR, cannot be efficient
4 catalysts for fuel cells working with acidic electrolytes. Among the huge number of
5 publications devoted to the ORR catalysis by cobalt complexes in acidic conditions,
6 from the 70's until now, only some of them noted that the intensity of the catalytic
7 current decreased with time along an electrolysis and mentioned the lack of stability
8 of the catalyst. Later on, thermal treatments of the catalysts associated with the
9 electrode material have been proposed in order to make them more stable [14-16].
10 Neither the improvement of the catalysts nor the result of their evolution under the
11 thermal treatment have however been clearly established [14].

12 The reason for the loss of efficiency of the cobalt macrocyclic complexes has never
13 been unequivocally demonstrated. Since the early beginning of the studies on N_4
14 chelates, various hypotheses have been proposed, such as leeching of the catalyst
15 from the electrode, destruction of the organic ligand through its reaction with
16 hydrogen peroxide (H_2O_2) generated at the electrode [14,17]. The loss of metal by
17 protonation of the ligand have been suspected to occur in acidic electrolytes [18]. In
18 the present study, by some experiments with various macrocyclic cobalt complexes,
19 it will be shown that demetallation is the reaction leading to the decrease of the
20 catalytic efficiency and the reason for this will be clarified.

21 **2. Experimental**

22 The cobalt porphyrin CoC_2diE and the cofacial bisporphyrin Co_2FTF_4 are gifts from Pr
23 Collman's group at Stanford University. $CoTAA$ has been synthesized by refluxing
24 dihydrodibenzo[5,9,14,18]tetraaza[14]annulene and $Co(OCOCH_3)_2$ in DMF under N_2

1 [19]. Sulfuric and trifluoroacetic acids are commercial products of analytical grade.
2 Ultra-pure water was obtained by reverse osmosis followed by ion exchange
3 (Millipore). N₂ (L'Air Liquide) used for flushing the solutions contains traces of O₂ (≤ 5
4 ppm).

5 A potentiostat EG&G-PAR (model 273) has been used for the electrochemical
6 studies. The working electrodes were platinum or vitreous carbon discs. All the
7 potentials in this publication are referred to the normal hydrogen electrode (NHE).
8 The UV-visible spectra were recorded using a Varian spectrophotometer (Cary 219).

9

10 **3. Results**

11 Co(II) macrocyclic complexes, with ligands such as cofacial bisporphyrins,
12 monoporphyrins, phthalocyanines, cyclams and tetraazaannulenes, have been
13 studied. These works provided valuable information about the behaviour of the cobalt
14 complexes towards the O₂ reduction to water or hydrogen peroxide but demonstrated
15 that the current of electrolysis decreases with time; the loss of efficiency of these
16 complexes must be attributed to their instability in contact with acidic media.

17 3.1 Tetraazaannulenes (TAA)

18 Some works have been devoted to Co(II)dibenzotetraaza[14]annulene (TAA)
19 (Scheme 1) and to related compounds.[5, 19, 20, 21] When this catalyst is adsorbed
20 on an edge plane pyrolytic graphite electrode (EPGE) in contact with an aqueous
21 acid solution (0.5 M H₂SO₄, P(O₂) = 1 atm), oxygen is reduced to hydrogen peroxide
22 at an onset potential of about 0.7 V [19]. However, upon a second potential scan with
23 the same electrode, the O₂ reduction wave is shifted towards more negative
24 potentials while simultaneously the limiting current decreases. Obviously, the

1 adsorbed catalyst is not really stable and this had already been noted earlier, as well
2 as for other catalysts. Heat treatment improves the stability but still a steady
3 decrease of the catalytic current is observed [14]. M(II)TAA, as well as other
4 substituted TAA complexes, can be electropolymerized, leaving a dense conductive
5 film deposited on the electrode [19, 21]. The formal redox potential for Co(III)/Co(II) is
6 close to 0.65 V for a film of CoTAA. The reduction wave for O₂ is clearly linked to the
7 metal redox system. From 0.75 V to the potential at which is positioned the peak
8 current for the reduction of Co(III), O₂ is reduced to H₂O₂. At more negative
9 potentials, oxygen is reduced to water through the 4-electron mechanism, which is
10 not observed with adsorbed CoTAA. Clearly, this can be attributed to the density of
11 the cobalt sites in the phase deposited by electropolymerization, allowing the
12 cooperation of vicinal metal centres. This has been demonstrated by the
13 copolymerization of CoTAA and other compounds inert for ORR, such as NiTAA and
14 H₂TAA. The more negative wave (4e) decreases with the amount of CoTAA in the
15 film and disappears completely for a mass ratio of CoTAA/H₂TAA = 1/5 (unpublished
16 results). This is an illustration of the importance of the cooperation between two
17 metal centres, the density of the Co centres being too low when CoTAA is
18 copolymerized with a large amount of H₂TAA. We have also previously reported that
19 for CoTAA electropolymerized on roughened GC and on porous electrodes (carbon
20 black powder in a Nafion® film) the number of electrons involved in the ORR
21 catalysis is significantly larger than two, which was ascribed to cooperation between
22 Co centres [21].

23 Thick poly-CoTAA films can be deposited on a graphite or a glassy carbon electrode
24 by electropolymerization of a saturated CoTAA solution in aqueous 2.25 M H₂SO₄, by
25 cycling between 0 V and 0.95 V [19]. When such a modified electrode is transferred

1 to an aqueous 0.5 M H₂SO₄ solution, cyclic voltammetry shows that both the Co(II)
2 oxidation and the Co(III) reduction peaks are present, superimposed on the important
3 capacitive current; the redox system is chemically reversible (Figure 1). The surface
4 concentrations of CoTAA, in the range of 1×10^{-9} mol cm⁻² to 7×10^{-9} mol cm⁻², have
5 been calculated by integration of the current under the peaks, after deduction of the
6 capacitive current.

7 Figure 1

8 The catalytic current of O₂ reduction at a rotating electrode decreases with time,
9 indicating that the catalyst is degraded. In order to investigate the reason for this loss
10 of activity, the poly-CoTAA film was cycled under a nitrogen atmosphere between 0 V
11 and 0.95 V. After 50 cycles, the loss of activity is 15 % and 45 % after 1000 cycles,
12 which demonstrates that the catalyst is degraded by potential cycling even under an
13 inert atmosphere. After immersion of the electrode in an aerated acidic aqueous
14 solution (H₂SO₄ 0.5 M) during 24 h, without polarization, the voltammogram recorded
15 under nitrogen is identical to the one of the electrode right after
16 electropolymerization. This latter observation suggests that no demetallation occurs
17 when cobalt is at the Co(III) oxidation state, the most compatible with the presence of
18 O₂. This assumption has been confirmed by cyclic voltammetry (Figure 1). After
19 polarization of the electrode at 0.95 V during 2h30mn (curve b), the peak current is
20 lower than on the voltammogram recorded right after the electropolymerization (curve
21 a). But, after a rest out of the solution the voltammogram recorded under nitrogen
22 proves that all the cobalt sites are still present (curve c). However, after setting the
23 potential of the electrode at 0 V for 2h30mn, in order to bring the metal centres to the
24 Co(II) state, the intensity of the peak is much lower and this loss of activity is
25 irreversible.

1 The stability of the Co(III) derivatives under acidic conditions has been
2 unambiguously established by the following experiment. A solution of $\text{CoTMTAA}(\text{Cl})_2$
3 in dichloromethane is brought in contact with an aqueous solution of H_2SO_4 (0.5 M)
4 and the complex partitions between the two phases. After a long contact of these
5 solutions with air, during a few hours, the UV-vis spectrum remained unchanged and
6 no $\text{H}_2\text{TMTAA}(\text{Cl})_2$ appears ; the formation of the protonated macrocycle would have
7 been detected through its intense absorption band at 348 nm.

8 When an electrode modified by the polymerization of $\text{Co}(\text{II})\text{TAA}$ is immersed for a
9 long time in an acidic aqueous solution of H_2O_2 ($3 \cdot 10^{-3}$ M), the voltammogram under
10 nitrogen is identical to the one obtained right after the film formation.

11 These observations suggest that the catalytic sites are stable when cobalt is at the
12 Co(III) state but readily degrade in the acidic aqueous solution when the metal centre
13 is at the Co(II) state. Moreover, hydrogen peroxide has no deleterious effect.

14 3.2 Monoporphyrin CoC_2diE

15 Porphyrins and phthalocyanines have attracted a lot of attention because of their
16 similarity with heme and other molecules involved in some biological processes. It
17 has been shown that cobalt complexes are worth more than the iron ones when the
18 catalysis of the electrochemical reduction of oxygen is the target. Cobalt
19 monoporphyrins, for example CoC_2diE (Scheme 1), catalyze the O_2 electroreduction
20 to hydrogen peroxide in an acidic environment.

21 Both CoC_2diE and Co_2FTF_4 can be dissolved in highly acidic aqueous solutions, but
22 the concentration of the cofacial derivative remains low, about 10^{-5} M. The
23 experiments described in the present study have been performed in 6 M aqueous
24 solutions of CF_3COOH . The voltammograms in Figure 2 have been obtained at a

1 stationary and at a rotating platinum disk electrode, for a saturated solution of
2 CoC_2diE obtained by dissolution under a constant flow of nitrogen, which takes about
3 2h.

4 Figure 2

5 Two redox systems appear at about 0.6 V and 0.3 V (curve a). The former is almost
6 reversible whereas the latter shows a sharp oxidation peak indicating that the re-
7 oxidation reaction is perturbed by a surface phenomenon. Two redox sites are
8 present in such a molecule, the Co centre and the macrocycle itself. It is known that
9 in the presence of water, Co(II) is oxidized to Co(III) before the oxidation of the
10 porphyrin ring to its radical cation. Moreover, a reduction current is detected below
11 0.6 V at the rotating electrode (curve b), showing that a mixture of the two redox
12 species of the second redox couple are present. This suggests that in the solution
13 the metal is present as Co(III), as shown by the reduction wave at 0.3 V, the
14 porphyrin being also partially oxidized as $\text{Co(III)C}_2\text{diE}^{\cdot 2+}$. The UV-vis spectrum of the
15 solution presents a Soret peak at 405 nm and two well separated bands at 520 nm
16 and 558 nm as well as a weak one at 645 nm, this latter band being typical of the
17 porphyrin radical cation. The presence of two well separated bands in the visible
18 region is an argument for the presence of Co(III) as the two bands are not so well
19 resolved for Co(II) solutions. That spectrum is almost identical with the spectrum of a
20 cobalt(III) octaethylporphyrin obtained by chemical oxidation. The ESR spectrum of
21 the solution obtained by dissolution of CoC_2diE , corresponding to the UV-vis
22 spectrum already described, consists in a unique line at $g = 2.004$ of a 27.96 G line
23 width; this is typical of the radical cation $\text{Co(III)C}_2\text{diE}^{\cdot 2+}$ and consistent with the fact
24 that Co(III) is diamagnetic; the presence of Co(II) in the solution would have been
25 revealed by a 8 lines spectrum, due to its $7/2$ spin. All these observations support the

1 conclusion that the result of the dissolution of CoC_2diE in 6 M CF_3COOH , under a
2 constant flow of N_2 , is a mixture of $\text{Co(III)C}_2\text{diE}^+$ and $\text{Co(III)C}_2\text{diE}^{\cdot 2+}$. Traces of O_2 in
3 the N_2 flux oxidize the Co(II) porphyrin in this acidic medium along its slow dissolution
4 process. The sharp oxidation peak observed on the voltammogram at 0.3 V results
5 more than probably from the re-oxidation of the insoluble $\text{Co(II)C}_2\text{diE}$ deposited
6 during the reduction scan.

7 The UV-vis spectrum recorded after dissolution of $\text{Co(II)C}_2\text{diE}$ under rigorous
8 exclusion of oxygen, in an N_2 atmosphere box, is totally different. The complete
9 dissolution lasts 12h instead of 2h for the dissolution on the bench, under a constant
10 flow of N_2 . The UV-visible spectrum is fully identical to the spectrum of $\text{H}_2\text{C}_2\text{diE}$,
11 which dissolves instantaneously in 6 M CF_3COOH . These observations suggest that
12 $\text{Co(II)C}_2\text{diE}$ is demetallated by contact with the acidic aqueous solution, a rather slow
13 reaction, while, when the dissolution is operated on the bench under a constant flow
14 of N_2 , the macrocyclic complex is oxidized to $\text{Co(III)C}_2\text{diE}^+$ and $\text{Co(III)C}_2\text{diE}^{\cdot 2+}$,
15 certainly because of the traces of O_2 present in the gas flow.

16 3.3 Cofacial bisporphyrins Co_2FTF_4

17 It has been demonstrated that cofacial bisporphyrins (FTF = face-to-face), *e.g.*
18 Co_2FTF_4 (Scheme 1), drive the reduction to water through the $4e^-$ mechanism, due to
19 the cooperation of the two metal centres, Co(II) being essential for O_2 binding, the
20 second, Co(III) or another Lewis acid, being needed for the rupture of the O–O
21 bond.[22-25]

22 The dissolution of the cofacial bisporphyrin Co_2FTF_4 in aqueous 6 M CF_3COOH , on
23 the bench under a flow of N_2 takes about 2h. The voltammograms of the solution is
24 presented in Figure 3.

Figure 3

1
2 The cyclic voltammogram is typical of the bisporphyrin, identical to the one observed
3 in benzonitrile; the two Co(III)/Co(II) reversible redox systems are visible at about 0.5
4 V (curve a), the domain of stability of the mixed-valence compound Co(III)Co(II)FTF₄
5 being about 0.34 V. As already observed for Co(II)C₂diE, the hydrodynamic
6 voltammogram (curve b) shows that Co(II) has been oxidized to Co(III), the porphyrin
7 moieties being partially oxidized. The dissolution of Co₂FTF₄ in aqueous 6 M
8 CF₃COOH in an N₂ atmosphere box is a very slow process. After neutralization by
9 NaHCO₃ of the acidic solution thus obtained, the cofacial bisporphyrin is extracted by
10 CH₂Cl₂. Its UV-vis spectrum (Figure 4) is identical in all respects to the characteristic
11 one of H₄FTF₄.

Figure 4

12
13 It can be concluded that under acidic conditions Co(II)₂FTF₄, as well as Co(II)C₂diE,
14 is oxidized to its Co(III) derivatives in the presence of traces of O₂. However, under
15 complete exclusion of O₂, these Co(II) porphyrins are demetallated.

16 4. Discussion

17 On view of these experimental observations, under acidic conditions, it is evident that
18 the macrocyclic complexes are stable when the metal is Co(III) but are demetallated
19 when it is as present Co(II). The Co³⁺ ion is a much harder Lewis acid than Co²⁺ and
20 for that reason will bind more strongly to the nitrogen hard bases of the macrocycles.
21 From the works already published and from calculations, it is possible to evaluate the
22 difference of stability between the two complexes of cobalt in their redox state. This
23 can be evaluated from the relative values of E°(Co³⁺/Co²⁺) and E°(Co^{III}L/Co^{II}L), the
24 formal redox potential of the complex:

$$\text{Log}_{10}[\text{K}(\text{Co}^{\text{III}}\text{L})/\text{K}(\text{Co}^{\text{II}}\text{L})] = [E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+}) - E^{\circ}(\text{Co}^{\text{III}}\text{L}/\text{Co}^{\text{II}}\text{L})]/0.059 \quad (1)$$

$E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+})$ has been evaluated to be 1.92 V [26], but 1.81 V is a value proposed by some authors [27]. From $E^{\circ}(\text{Co}^{\text{III}}\text{L}/\text{Co}^{\text{II}}\text{L})$ values reported in publications and evaluated in the present work, $\text{Log}_{10}[\text{K}(\text{Co}^{\text{III}}\text{L})/\text{K}(\text{Co}^{\text{II}}\text{L})]$ has been calculated and reported in Table 1, assuming that $E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+}) = 1.92$ V.

Table 1

From the experimental data in Table 1 it is clear that, whatever is the nature of the ligand, the Co(III) complexes are much more stable than those of Co(II). In the case of CoTAA, as well as that of CoCyclam, which catalytic properties towards ORR have also been examined [28], DFT calculations confirm the much higher stability of the Co(III) complexes by a factor of 10^{27} and 10^{17} , respectively (Table 1, Supplementary material).

It is not really easy to unambiguously conclude whether the reduction wave of O_2 coincides with the reduction wave of Co(III) to Co(II), as observed with polymerized CoTAA, or occurs at more negative potentials, as reported in some cases [7, 29]. However, in both cases, when ORR occurs the redox state of cobalt in the catalyst is Co(II), which can be easily replaced by two hard acid ions such as H^+ . This also should occur in the case of Co(II)Cyclam, which binding constant is $\text{K}(\text{Co}(\text{II})\text{Cyclam}) = 10^{14}$. [30] The affinity of Cyclam for the proton is high, $\text{K}(\text{H}_2\text{Cyclam}) = 10^{22}$ [31], the consequence being that even a rather concentrated Co(II)Cyclam solution (0.01 M) would be completely demetallated below pH = 4.

These experimental results are in complete opposition to the conclusions previously drawn from DFT calculations about the stability of metalloporphyrins and

1 metallophthalocyanines in acidic media, stating that the metal ions are not replaced
2 by protons at pH = 1 [32].

3 Reviews on the catalysis of ORR have mentioned that the instability of the non-
4 precious metal catalysts in acidic media could result from the deleterious influence of
5 H₂O₂ or from the replacement of the metal ion by protons [14, 17]. From this work it
6 appears clearly that hydrogen peroxide does not have a major impact on the stability
7 but that Co²⁺ is easily substituted by protons.

8 **5. Conclusion**

9 Co³⁺, a much harder Lewis acid than Co²⁺, will bind more strongly to the nitrogen
10 hard bases of the macrocycles and remains bound under acidic conditions. However,
11 H⁺ will have a higher affinity than Co²⁺ for the hard base sites of the ligand. It is more
12 than probable that Fe²⁺, another borderline acid in the classification of Lewis acids,
13 will behave similarly to Co²⁺, and consequently, what has been observed for the
14 cobalt complexes should also be true for Fe catalysts in an acidic environment. What
15 occurs to the catalysts after an heat-treatment is not really clear but, whether they
16 have been transformed to metallic particles or to any other form, the redox state of
17 the metal compatible with the potential of the oxygen reduction reaction is the M(II)
18 redox state, which explains why these modified catalysts are also prone to
19 demetallation under acidic conditions.

20

1 6. Figure captions

2 Figure 1 Cyclic voltammetry at a graphite electrode covered by a CoTAA film
3 (H_2SO_4 0.5 M, $v = 200 \text{ mV}\cdot\text{s}^{-1}$, under N_2). a: right after the film formation; b: after a
4 2h30mn polarization at 0.95 V ; c: after b and 4 days stay in air ; d: after 2h30 min at
5 0 V.

6

7 Figure 2 Voltammetry of CoC_2diE ($\sim 10^{-5} \text{ M}$) in an aqueous solution of 6 M
8 CF_3COOH , at a platinum disk electrode. a: cyclic voltammetry ($u = 1 \mu\text{A}$, $v = 100$
9 $\text{mV}\cdot\text{s}^{-1}$); b: voltammetry at a rotating electrode ($u = 2.5 \mu\text{A}$, $v = 2 \text{ mV}\cdot\text{s}^{-1}$, $\omega = 400$
10 rpm).

11

12 Figure 3 Voltammetry of Co_2FTF_4 ($\sim 10^{-5} \text{ M}$) in an aqueous solution of 6 M
13 CF_3COOH , at a platinum disk electrode. a: cyclic voltammetry ($u = 0.4 \mu\text{A}$, $v = 100$
14 $\text{mV}\cdot\text{s}^{-1}$); b: voltammetry at a rotating electrode ($u = 1 \mu\text{A}$, $v = 2 \text{ mV}\cdot\text{s}^{-1}$, $\omega = 400 \text{ rpm}$).

15

16 Figure 4 UV-vis spectrum of Co_2FTF_4 after extraction with CH_2Cl_2 of a solution
17 obtained by dissolution in an aqueous solution of 6 M CF_3COOH , under a rigorous
18 exclusion of oxygen.

19

20

7. Bibliography

- 1 [1] M. L'Her, Redox Properties, Electrochemistry of Oxygen, in: A.J. Bard (Ed.)
2 Encyclopedia of Electrochemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim,
3 Germany, 2007, pp. bard070005.
4
- 5 [2] M.R. Tarasevich, A. Sadkowsky, E. Yeager, Oxygen Electrochemistry, in: B.E.
6 Conway, J.O.M. Bockris, E. Yeager, S.U.M. Khan, R.E. White (Eds.) Comprehensive
7 Treatise of Electrochemistry, Springer US, Boston, MA, 1983, pp. 301-398.
- 8 [3] F. Beck, The redox mechanism of the chelate-catalysed oxygen cathode, Journal
9 of Applied Electrochemistry, 7 (1977) 239-245.
- 10 [4] A. Bettelheim, R.J.H. Chan, T. Kuwana, Electrocatalysis of oxygen reduction. Part
11 II. Adsorbed cobalt(III) tetrapyrrolylporphyrin on glassy carbon electrode, Journal of
12 Electroanalytical Chemistry, 99 (1979) 391-397.
- 13 [5] I. Bhugun, F.C. Anson, Adsorption on graphite and catalytic reduction of O₂ by the
14 macrocyclic complex of cobalt(II) with 2,3,9,10-tetraphenyl-1,4,8,11-
15 tetraazacyclotetradeca-1,3,8,10-tetraene, Journal of Electroanalytical Chemistry, 430
16 (1997) 155-161.
- 17 [6] J.P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, F.C. Anson,
18 Electrode Catalysis of the Four-Electron Reduction of Oxygen to Water by Dicobalt
19 Face-to-Face Porphyrins, Journal of the American Chemical Society, 102 (1980)
20 6027-6036.

- 1 [7] R.R. Durand, F.C. Anson, Catalysis of dioxygen reduction at graphite electrodes
2 by an adsorbed cobalt(II) porphyrin, *Journal of Electroanalytical Chemistry and*
3 *Interfacial Electrochemistry*, 134 (1982) 273-289.
- 4 [8] R. Jasinski, Cobalt Phthalocyanine as a Fuel Cell Cathode, *J. Electrochem. Soc.*,
5 112 (1965) 526-528.
- 6 [9] P. Gouérec, M. Savy, Oxygen reduction electrocatalysis: ageing of pyrolyzed
7 cobalt macrocycles dispersed on an active carbon, *Electrochimica Acta*, 44 (1999)
8 2653-2661.
- 9 [10] J.H. Zagal, M.A. Páez, J.F. Silva, Fundamental Aspects on the Catalytic Activity
10 of Metallomacrocyclics for the Electrochemical Reduction of O₂, in: J.H. Zagal, F.
11 Bedioui, J.-P. Dodelet (Eds.) *N₄-Macrocyclic Metal Complexes*, Springer New York,
12 New York, NY, 2006, pp. 41-82.
- 13 [11] J.H. Zagal, S. Griveau, J.F. Silva, T. Nyokong, F. Bedioui,
14 Metallophthalocyanine-based molecular materials as catalysts for electrochemical
15 reactions, *Coordination Chemistry Reviews*, 254 (2010) 2755-2791.
- 16 [12] Y.M. Zhao, G.Q. Yu, F.F. Wang, P.J. Wei, J.G. Liu, Bioinspired Transition-Metal
17 Complexes as Electrocatalysts for the Oxygen Reduction Reaction, *Chem. Eur. J.*,
18 25 (2019) 3726-3739.
- 19 [13] Z.P. Li, B.H. Liu, The use of macrocyclic compounds as electrocatalysts in fuel
20 cells, *Journal of Applied Electrochemistry*, 40 (2010) 475-483.
- 21 [14] J.-P. Dodelet, Oxygen Reduction in PEM Fuel Cell Conditions: Heat-Treated
22 Non-Precious Metal-N₄ Macrocycles and Beyond, in: J.H. Zagal, F. Bedioui, J.-P.

- 1 Dodelet (Eds.) N4-Macrocyclic Metal Complexes, Springer New York, New York, NY,
2 2006, pp. 83-147.
- 3 [15] V.S. Bagotsky, M.R. Tarasevitch, K.A. Radyushkina, O.E. Levina, S.I.
4 Andrusyova, Electrocatalysis of the oxygen reduction process on metal chelates in
5 acid electrolyte, *Journal of Power Sources*, 1977, pp. 233-240.
- 6 [16] A. Van der Putten, A. Elzing, W. Visscher, E. Barendrecht, Oxygen reduction on
7 pyrolysed carbon supported metal chelates, *Journal of Electroanalytical Chemistry*,
8 1986, pp. 233-244.
- 9 [17] F. Jaouen, J.-P. Dodelet, Non-Noble Electrocatalysts for O₂ Reduction: How
10 Does Heat Treatment Affect Their Activity and Structure? Part I. Model for Carbon
11 Black Gasification by NH₃: Parametric Calibration and Electrochemical Validation, *J.*
12 *Phys. Chem. C*, 111 (2007) 5963-5970.
- 13 [18] R.R. Durand, J.P. Collman, F.C. Anson, Dissolution of insoluble dicobalt cofacial
14 porphyrins in concentrated acids to produce increased stability in their catalysis of
15 the reduction of dioxygen, *Journal of Electroanalytical Chemistry*, 151 (1983) 289-
16 294.
- 17 [19] C. Miry, D. Le Brun, J.-M. Kerbaol, M. L'Her, Cobalt(II)-
18 dibenzotetraaza[14]annulene complex electropolymerization for electrode
19 modification, *Journal of Electroanalytical Chemistry*, 494 (2000) 53-59.
- 20 [20] I. Bhugun, F.C. Anson, Enhancement of the Catalytic Activity of a Macrocyclic
21 Cobalt(II) Complex for the Electroreduction of O₂ by Adsorption on Graphite,
22 *Inorganic Chemistry*, 35 (1996) 7253-7259.

- 1 [21] P. Convert, C. Coutanceau, P. Crouigneau, F. Gloaguen, C. Lamy, Electrodes
2 modified by electrodeposition of CoTAA complexes as selective oxygen cathodes in
3 a direct methanol fuel cell, *J. Appl. Electrochem.*, 31 (2001) 945-952.
- 4 [22] R. Guillard, S. Brandes, C. Tardieux, A. Tabard, M. L'Her, C. Miry, P. Guerec, Y.
5 Knop, J.P. Collman, Synthesis and Characterization of Cofacial Metallodiporphyrins
6 Involving Cobalt and Lewis Acid Metals: New Dinuclear Multielectron Redox
7 Catalysts of Dioxygen Reduction, *J. Am. Chem. Soc.*, 117 (1995) 11721-11729.
- 8 [23] Y. Le Mest, C. Inisan, A. Laouénan, M. L'Her, J. Talarmin, M. El Khalifa, J.-Y.
9 Saillard, Reactivity toward Dioxygen of Dicobalt Face-to-Face Diporphyrins in Aprotic
10 Media. Experimental and Theoretical Aspects. Possible Mechanistic Implication in
11 the Reduction of Dioxygen, *J. Am. Chem. Soc.*, 119 (1997) 6095-6106.
- 12 [24] Y. Le Mest, M. L'Her, J.P. Collman, N.H. Hendricks, L. McElwee-White,
13 Remarkable oxygen affinity of a mixed valence dicobalt cofacial porphyrin
14 $\text{Co}^{\text{III}}\text{Co}^{\text{II}}\text{FTF}_4$, *J. Am. Chem. Soc.*, 108 (1986) 533-535.
- 15 [25] Y. Le Mest, M. L'Her, J. Courtot-Coupez, J.P. Collman, E.R. Evitt, C.S.
16 Bencosme, Electrochemical behaviour of a binary cofacial dicobalt porphyrin in
17 aprotic media under a nitrogen atmosphere, *Journal of Electroanalytical Chemistry*
18 *and Interfacial Electrochemistry*, 184 (1985) 331-346.
- 19 [26] N. Maki, T. Tanaka, Cobalt, in : A. J. Bard, R. Parsons, J. Jordan, IUPAC (Eds)
20 Standard potentials in aqueous solution, M. Dekker, New York, 1985, pp 367-381.
- 21 [27] S.G. Bratsch, Standard Electrode Potentials and Temperature Coefficients in
22 Water at 298.15 K, *Journal of Physical and Chemical Reference Data*, 18 (1989) 1-
23 21.

- 1 [28] T. Geiger, F.C. Anson, Homogeneous catalysis of the electrochemical reduction
2 of dioxygen by a macrocyclic cobalt(III) complex, *J. Am. Chem. Soc.*, 103 (1981)
3 7489-7496.
- 4 [29] C.L. Ni, F.C. Anson, Relation between the Reduction Potentials of Adsorbed and
5 Unabsorbed Cobalt(III) Tetrakis(N-methylpyridinium-4-yl)porphyrin and Those Where
6 It Catalyzes the Electroreduction of Dioxygen, *Inorganic Chemistry*, 24 (1985) 4754-
7 4756.
- 8 [30] S. Cabani, N. Ceccanti, G. Conti, Enthalpy Changes in the Binding of O₂ to Co(II)
9 Complexes with 1,4,8,11-Tetraazacyclotetradecane, *Inorganica Chimica Acta*, 1984.
- 10 [31] M. Micheloni, A. Sabatini, P. Paoletti, Solution chemistry of macrocycles. Part 1.
11 Basicity constants of 1,4,8,11-tetra-azacyclotetradecane, 1,4,8,12-tetra-
12 azacyclopentadecane, and 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane,
13 *J. Chem. Soc., Perkin Trans. 2*, (1978) 828-830.
- 14 [32] Y. Chen, X. Hua, S. Chen, Theoretical study of stability of metal-N₄ macrocyclic
15 compounds in acidic media, *Chinese Journal of Catalysis*, 37 (2016) 1166-1171.

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Ms. Ref. No.: EA20-02870

Title: Why Cobalt macrocyclic complexes are not efficient catalysts for the oxygen reduction reaction, under acidic conditions.

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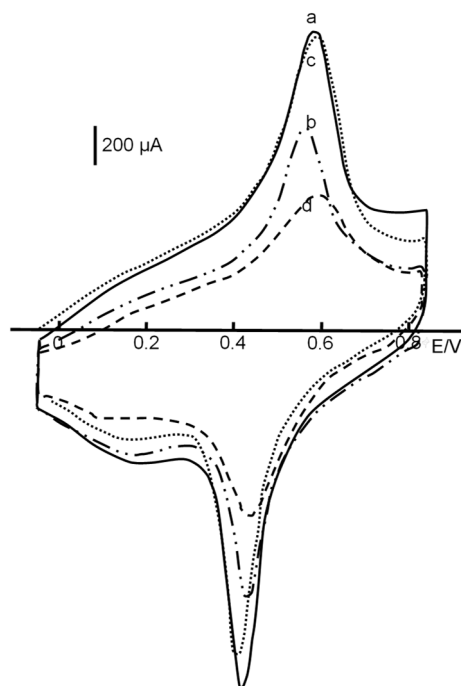


Figure 1 Cyclic voltammetry at a graphite electrode covered by a CoTAA film (H_2SO_4 0.5 M, $v = 200 \text{ mV}\cdot\text{s}^{-1}$, under N_2). a : right after the film formation ; b : after a 2h30mn polarization at 0.95 V ; c : after b and 4 days stay in air ; d : after 2h30 mn at 0 V.

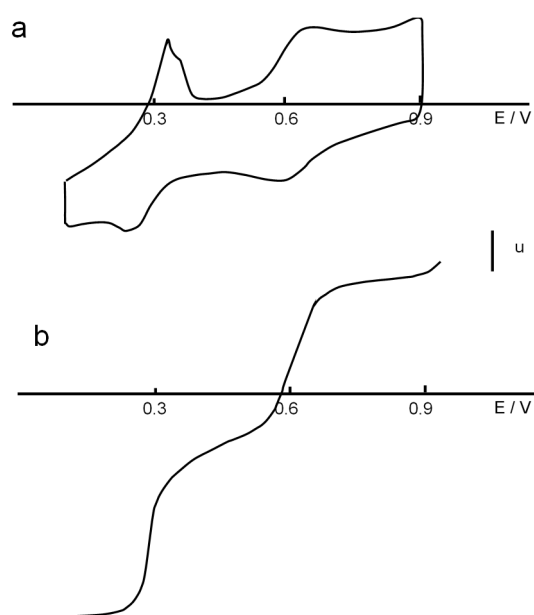


Figure 2 Voltammetry of CoC_2diE ($\sim 10^{-5}$ M) in an aqueous solution of 6 M CF_3COOH , at a platinum disk electrode. a : cyclic voltammetry ($u = 1 \mu\text{A}$, $v = 100 \text{ mV}\cdot\text{s}^{-1}$); b : voltammetry at a rotating electrode ($u = 2.5 \mu\text{A}$, $v = 2 \text{ mV}\cdot\text{s}^{-1}$, $\omega = 400 \text{ rpm}$).

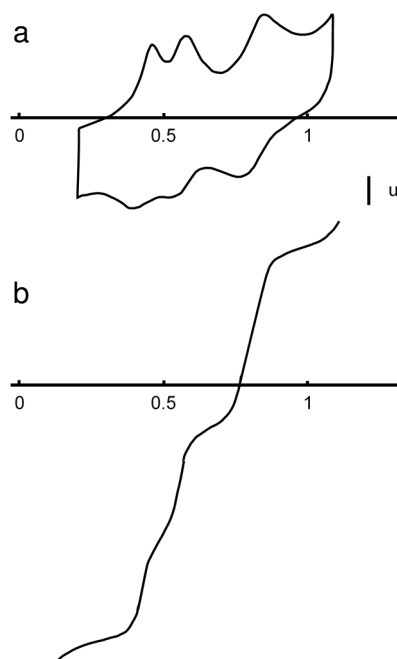


Figure 3 Voltammetry of Co_2FTF_4 ($\sim 10^{-5}$ M) in an aqueous solution of 6 M CF_3COOH , at a platinum disk electrode. a : cyclic voltammetry ($u = 0.4 \mu\text{A}$, $v = 100 \text{ mV}\cdot\text{s}^{-1}$); b : voltammetry at a rotating electrode ($u = 1 \mu\text{A}$, $v = 2 \text{ mV}\cdot\text{s}^{-1}$, $\omega = 400 \text{ rpm}$).

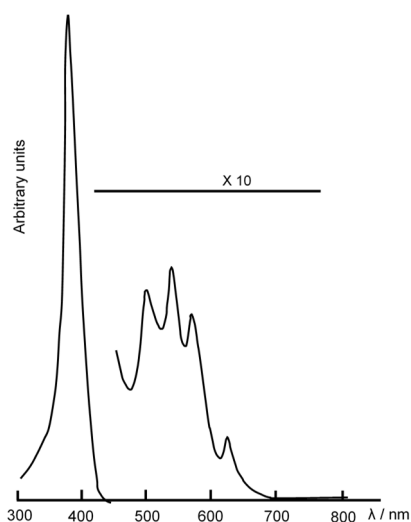


Figure 4 UV-vis spectrum of Co_2FTF_4 after extraction with CH_2Cl_2 of a solution obtained by dissolution in an aqueous solution of 6 M CF_3COOH , under a rigorous exclusion of oxygen.

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Table 1: Relative stabilities of some Co(III) and Co(II) complexes.

Ligand ^a	$E^{\circ}(\text{Co}^{3+}\text{L}/\text{Co}^{2+}\text{L}) / \text{V}$	$\text{Log}_{10}[\text{K}(\text{Co}^{3+}\text{L})/\text{K}(\text{Co}^{2+}\text{L})]$	$\text{Log}_{10}[\text{K}(\text{Co}^{3+}\text{L})/\text{K}(\text{Co}^{2+}\text{L})]$	Ref.
		(exp.) ^b	(DFT) ^c	
ox ₃	0.57	22.9		[26]
edta ₂	0.38	26.1		[26]
terpy ₂	0.31	27.3		[26]
cyclam	0.40	25.8	17.1	[26]
TAA	0.58 a	22.7	27.1	this work
C ₂ diE	0.29 a	27.7		this work
FTF ₄	0.55 a	23.2		this work

^a Ox, oxalate ion ; edta, ethylenediaminetetraacetate ion ; terpy, 2,2',2''-terpyridine ; cyclam, 1,4,8,11-tetraazacyclotetradecane ; TAA, (benzo)₂[14]tetraeneN₄ ; C₂diE, diethylester mesoporphyrin ; FTF₄, face-to-face bisporphyrin. ^b Calculated from the experimental values of $E^{\circ}(\text{Co}^{3+}\text{L}/\text{Co}^{2+}\text{L})$ due to the rather poor solubility of the compound in the aqueous acid solution, the uncertainty on these redox potential is not less than ± 0.02 V. ^c Calculated from the DFT values of $E^{\circ}(\text{Co}^{3+}/\text{Co}^{2+})$.