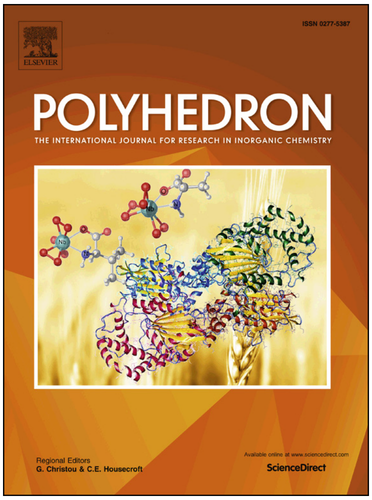

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Hexachloroethane reduction catalyzed by cobaloximes. Effect of the substituents on the equatorial ligands

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Abstract

The degradation of hexachloroethane using chloridobis(dimethylglyoximato)pyridinecobalt(III), chloridobis(methylphenylglyoximato)pyridinecobalt(III) and chloridobis(diphenylglyoximato)pyridinecobalt(III) is described. To achieve the degradation, the cobalt complexes were reduced to the Co(I) oxidation state by electrochemical means. The chemical catalysis was studied using cyclic voltammetry by monitoring the current increase near the Co(II)/Co(I) reduction potential as the concentration of organohalogen was increased in solution. Tetrachloroethene was found as the degradation product. The apparent rate constant for the dehalogenation of hexachloroethane was estimated for all cobaloximes, obtaining $2.54 \pm 0.08 \times 10^5$ for $[Co(dmgH)_2Cl(py)]$; $2.38 \pm 0.06 \times 10^5$ for $[Co(mpgH)_2Cl(py)]$ and $2.79 \pm 0.15 \times 10^5$ for $[Co(dpgH)_2Cl(py)]$.

Keywords: cobaloxime, cyclic voltammetry, electrochemistry, organohalides, catalysis

1. Introduction

Chlorinated organic compounds are listed among the most widely used pollutants on the planet mainly due to their versatility in various applications, such as solvents, plasticizers, and pesticides[1]. Some chlorinated polyethylenes such as tetrachloroethene[2] and hexachloroethane[3] are used as raw materials in the preparation of fungicides, insecticides, lubricants or plastics, and are often detected as contaminants in soils and wastewater[4]. The United States Environmental Protection Agency has classified these substances as possible carcinogens; consequently, their presence in the environment represents a risk to human health[5].

During the last years several technologies have been developed to degrade these type of substances. These processes comprehend bio-degradation[6], photocatalytic degradation[7], as well the use of molecular catalysts as cobalt porphyrins[8], cobinamides[9] and cobaloximes[10].

Gantzer and Wackett[11] reported the dehalogenation of polychlorinated ethenes using cobalamin as catalyst and titanium(III) citrate as a sacrifice reductant. The products observed by Gantzar and Wackett correspond to the hydrogenolysis of PCE (TCE, cis-1,2-dichloroethylene, vinyl chloride and ethene). These observations were complemented by the experiments of Schanke and Wackett[12] which demonstrated that catalytic reduction of chlorinated alkanes is possible by giving some alkenes as products. The main disadvantage of these cobalt-based systems is that a reducing agent must be added to the reaction medium in order to reach the Co (I) state[13].

In an alternative way to the addition of reducing agents McCauley et al. have electrochemically generated the reduced forms of cobalamin and cobinamide, and demonstrated that these compounds are efficient catalysts for the hydrogenolysis of aliphatic chloro-compounds[14].

Cobaloximes are a set of pseudo-macrocyclic bis(diglyoximato)cobalt complexes that show a pseudo-octahedral structure where the equatorial positions are occupied by two *vic*-dioximes forming a pseudo-macrocycle, and the axial positions are occupied by an anionic ligand and a nitrogenous base[15]. These structural characteristics make them good models of vitamin B12 and related compounds since they share many of their chemical properties, i.e. the nucleophilicity. Advantageously, it is easier to perform systematic structural changes on cobaloximes than in vitamin B12 related compounds[16].

It has been observed that the electron donor/withdrawal characteristics of substituent functional groups of the cobaloxime ligands have a variable influence on the reduction potential of cobalt, and therefore in the catalytic properties of those compounds[17–19]. Substitution on the nitrogenous axial base has a little impact on the electrochemical properties, while the groups on the dioxime backbone can exert a big influence on the Co (II/I) reduction potential.

Cobaloximes have been widely studied because are good catalysts for the reduction of protons at low overpotentials in organic solvents[20]. However, we are interested in expanding the study of these compounds to the dehalogenation of organohalide compounds. In this context, we report the catalytic degradation of hexachloroethane, a compound environmentally persistent, bioaccumulative and toxic, by reaction with electrochemically generated Co(I) cobaloximes. The electrochemical potentials of the Co center have been systematically tuned by selecting the substituents of the equatorial in order to evaluate their influence on the catalytic process.

2. Experimental section

2.1. Materials and measurements

All the chemicals were commercially available and used as received. Complexes [Co(dmgH)$_2$Cl(py)][21] and [Co(dpgH)$_2$Cl(py)][22] were synthesized according to procedures reported in literature. The description of the synthetic procedures as well the instrumentation and characterization methods are described in the supporting information.

2.2. Electrochemistry

Cyclic voltammetry experiments were conducted on a Princeton Applied Research PG 580 potentiostat/galvanostat using a three-electrode single compartment cell including a glassy carbon working electrode, a Pt wire auxiliary electrode, and an Ag/AgCl reference electrode. Tetrabutylammonium hexafluorophosphate [NBu$_4$][PF$_6$] was used as the supporting electrolyte (0.1M). For all measurements, samples were degassed by purging with nitrogen.

2.3. Diffusion coefficient

The diffusion coefficients were determined using the Randles-Sevcik equation which assumes that mass transport occurs only by a diffusion process[23]:

$$i_p = (2{,}69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2} \qquad (1)$$

Where i_p is the peak current (A), n the number of electron equivalents exchanged during the oxidation/redox reversible process, A the active surface area of the working electrode (cm^2), D the diffusion coefficient ($cm^2 \cdot s^{-1}$), C the bulk concentration of the diffusing species ($mol \cdot cm^{-3}$) and ν the voltage scan rate ($V \cdot s^{-1}$).

3. Results and discussion

3.1 Synthesis

The cobaloximes used in this study are: $[Co(dmgH)_2Cl(py)]$ (where dmgH is dimethylglyoximato and py is pyridine), $[Co(mpgH)_2Cl(py)]$ (where mpgH is methylphenylglyoximato) and $[Co(dpgH)_2Cl(py)]$ (where dpgH is diphenylglyoximato). The structures of these complexes are presented in Fig. 1.

Cobaloximes (a) and (c) were previously reported. To obtain cobaloxime (b) we prepare *anti*-methylphenylglyoxime by condensation between 1-phenyl-1,2-propanedione and hydroxylamine hydrochloride in acidic ethanol solution. The cobaloxime $[Co(mpgH)_2Cl(py)]$ was prepared by coordination of the ligand $mpgH_2$ and pyridine to cobalt(II) chloride hexahydrate in a single step. The Fig. 2 shows the synthesis scheme followed to obtain this compound.

3.2. Electrochemistry in solution

3.2.1. Cobaloximes

The Fig. 3 shows the cyclic voltammograms of all the cobalt(III) complexes used in this study. The three of them show the same pattern which was described in the literature[24,25]. It consists of an irreversible cathodic wave attributed to the Co(III) to Co(II) reduction process, which is also associated to an equilibrium involving the loss of the chloride axial ligand[26]. To more negative potentials a quasi-reversible process is observed and assigned to the reduction process Co(II) to Co(I). Finally, at more positive potentials is observed an anodic irreversible wave which is assigned to the Co(II) to Co(III) oxidation process. The previously described cathodic, anodic and half wave potentials, as well the diffusion coefficients for each complex are summarized in Table 1.

There is a clear influence of the structure of the glyoxime equatorial ligands on the electrochemical behavior of the cobalt center. The substitution of a methyl group of the dimethylglyoxime ligand by a phenyl group results in a displacement of the Co(II) to Co(I) half-wave potential of 180 mV towards more positive potentials. In a similar way, the substitution of all the methyl groups by phenyl groups leads to a 320 mV positive displacement. It has been reported that substitution on the pyridine axial ligand exerts none or small influence on the Co(II/I) half-wave potential[27].

As our objective was to use these complexes to dehalogenate reductively hexachloroethane, we initially studied the electrochemical behavior of this compound in a cobaloxime free solution.

3.2.2. Hexachloroethane (HCA).

The Fig. 4 shows the cyclic voltammetry of HCA on DMF 0.1 M $[NBu_4][PF_6]$ between +0.5 V and –1.8 V on a carbon glass electrode working electrode. This voltammogram shows only one irreversible reduction wave at -1.58 V vs Ag/AgCl. According to literature, this wave is assigned to a concerted reductive cleavage which consists of the sum of two redox processes that results in the elimination of chloride [28]. The first one is a one electron reduction which leads to the break of a carbon chloride bond generating a radical. The second process consists of the reduction of the generated radical and the elimination of a second chlorine atom. The process may be written as follows:

$$C_2Cl_6 + e^- \rightarrow \cdot C_2Cl_5 + Cl^- \qquad (2)$$

$$\cdot C_2Cl_5 + e^- \rightarrow C_2Cl_4 + Cl^- \qquad (3)$$

Subsequent reductions process leading to dichloroethane are reported to occur at more negative potentials (> -1,8 V). It is important to note that the potential of the cathodic wave assigned to the hexachloroethane reduction is observed at a potential, at least, 500 mV more negative than the Co (II/I) half-wave potential of the cobaloximes used in this study.

3.3. Dehalogenation experiments

In the cyclic voltammetry experiments an increase of the cathodic current is observed after the addition of hexachloroethane to a cobaloxime solution, which is consistent with a chemical catalysis process. This behavior is depicted in Fig. 5, 6 and 7 which shows the cyclic voltammograms of the cobaloximes after the addition of 2 to 18 equivalents of the HCA. All these voltamograms were recorded at a scan rate of 100 mV s^{-1} using a concentration of 0.125 mM in 0.1M DMF $[NBu_4][PF_6]$ for all the complexes.

The catalytic currents were observed at a slightly more negative potential than the observed for the couple Co(II)/Co(I), but 500 mV to 900 mV more positive than the reduction potential observed for HCA. This behavior can be attributed to competing side processes such as substrate consumption (when the substrate concentration at the electrode surface is depleted relative to the bulk concentration) or catalyst deactivation[29].

The apparent rate constant for the degradation of HCA was estimated from the dependence between the current increase and the square root of the substrate concentration using the model of chemical catalysis described in the literature[30]. Hence, for a reaction of first order for both the catalyst and the organohalogen, the cathodic current is related to the concentration of the catalyst (mol cm^{-3}) and the square root of the concentration of the organohalogen (mol L^{-1}). The expression for this relation is represented by equation 1:

$$i_c = nFA[Cobaloxime]D^{1/2}{K_{app}}^{1/2}[RX]^{1/2} \qquad (4)$$

Where n is the number of electrons for the reaction (n=2), F is Faraday constant (96485 C mol^{-1}), A is the area of the electrode surface (0.072 cm^2), D is the diffusion coefficient (cm^2s^{-1}) and *k* is the apparent rate constant for the reaction ($M^{-1}s^{-1}$). The figures 5b, 6b and 7b shows the fitting of the cathodic current to this model. The apparent rate constants, as well the electrochemical parameters are resumed on table 1.

Head space gas-chromatography experiments were carried out after 60 minutes of electrolysis of cobaloxime hexachloroethane solutions of a 1:8 molar ratio. In each case, the potential employed for the electrolysis was slightly more negative than the potential observed for the catalytic waves. The only product found in these experiments was tetrachloroethylene (see Support Information).

In the literature, the processes of dehalogenation catalyzed by structurally similar cobalt complexes are described starting with a nucleophilic attack of the reduced cobalt complex to the organohalogen, eliminating a halogen anion and forming an organometallic bond[28].

This mechanism is plausible just if the halogenated derivative does not possess a great steric hindrance, since the reaction proceeds in a similar way as the SN2 type. In the case of HCA a reaction of this type is very unlikely to proceed due to the steric hindrance of the chlorine atoms present in the molecule.

We propose the reductive dehalogenation reaction for HCA to occur by an electron transfer associated with the formation of an intermolecular halide bridge between the substrate and the catalyst as is schematized in Fig. 8. The first step begins with a one electron reduction of the cobaloxime followed by the exchange of the chloride ligand with a solvent molecule. Subsequently, a second one electron reduction generates a Co (I) metallic center. The substrate interacts with the reduced Co through a chloride bridge causing a heterolytic cleavage of the C-Cl bond; the pentachloroethane radical can undergo a subsequent reductive elimination reaction generating tetrachloroethylene.

A similar mechanism was proposed by Payne for the reductive degradation of 2,6-dibromophenol by vitamin B12 as a catalyst[32].

Fontecave, Artero, and others have studied extensively these systems for proton reduction from acid sources in organic solvents[33–36]. They have reported a marked dependence of the reduction activity, expressed on the apparent rate constant, with the electron-withdrawal characteristics of the glyoxime substituents, whereas the half-wave potential of the Co(II)/Co(I) process turns more positive, the hydrogen evolution decreases[37].

In a clear difference with those observations, the apparent rate constants for the hexachloroethane catalytic reduction found in this study (Table 1) do not show extended differences. In an opposite direction, the higher magnitude rate constant was observed for the cobaloxime displaying the better electron-withdrawal substituent. This behavior could be explained since the latter reaction should be independent on the basicity of the cobalt center, and probably driven by conformational halogen effects[38,39].

4. Conclusions

In cyclic voltammetry experiments, the addition of HCA to electrochemically generated Co(I) cobaloximes produces catalytic waves which are consistent with a chemical catalysis process.

Although the Co complexes employed show substantial differences on the Co (II/I) reduction potential, the observed rate constant do not show significant differences. Under the experimental conditions employed in this study, only tetrachloroethene was observed as a degradation product.

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Table 1: Reduction potentials, diffusion coefficients and apparent rate constants of the cobaloximes used in this study.

	E_{PC} (V) Co(III/II)	E_{PA} (V) Co(III/II)	$E_{1/2}$ (V) Co(II/I)	D (cm^2/s)	k_{app} ($M^{-1}s^{-1}$) HCA
$Co^{(III)}(dmgH)_2Cl(py)$	-0.54	0.13	-0.95	5.36×10^{-6}	$2.54 \pm 0.08 \times 10^5$
$Co^{(III)}(mpgH)_2Cl(py)$	-0.45	0.17	-0.77	4.81×10^{-6}	$2.38 \pm 0.06 \times 10^5$
$Co^{(III)}(dpgH)_2Cl(py)$	-0.37	0.23	-0.63	3.23×10^{-6}	$2.79 \pm 0.15 \times 10^5$

Figure captions

Fig. 1: Structure of the cobaloximes used in this study: (a) [Co(dmgH)$_2$Cl(py)]; (b) [Co(mpgH)$_2$Cl(py)]; (c) [Co(dpgH)$_2$Cl(py)].

Fig. 2: Scheme of the synthesis. i) NH$_2$OH*HCl, HCl, MeOH. ii) Cobalt(II) chloride hexahydrate, pyridine, MeOH.

Fig. 3: Overlapping of cyclic voltammograms of the cobaloximes: [Co(dmgH)$_2$Cl(py)] black line, [Co(mpgH)$_2$Cl(py)] red line and [Co(dpgH)$_2$Cl(py)] blue line. All were recorded at a concentration of 1.5 mM in DMF 0.1 M [NBu$_4$][PF$_6$].

Fig. 4: Cyclic voltammogram of a 2.3 mM HCA recorded in DMF 0.1 M [NBu$_4$][PF$_6$].

Fig. 5: a) Cyclic voltammogram of Co$^{(III)}$(dmgH)$_2$Cl(py) 0.125 mM in 0.1M [NBU$_4$][PF$_6$]. Registered at a scanning speed of 100 mV s^{-1} (black) in the presence of 2, to 16 equivalents of HCA (blue). b) Dependence of the current on the square root of HCA concentration. The data was adjusted to I$_C$=m[HCA]$^{1/2}$ + c, m = -2.03x10^{-3}, c = 1.68x10^{-5}, R^2 = 0.9929.

Fig. 6: a) Cyclic voltammogram of Co$^{(III)}$(mpgH)$_2$Cl(py) 0.125 mM in 0.1M [NBU$_4$][PF$_6$]. Registered at a scanning speed of 100 mV s^{-1} (black) in the presence of additions of 2 to 16 equivalents of HCA (blue). b) Dependence of the current increase on the HCA concentration. The data was adjusted to I$_C$=m[HCA]$^{1/2}$ + c, m = -1.73x10^{-3}, c = 1.31x10^{-5}, R^2 = 0.9949.

Fig. 7: a) Cyclic voltammogram of Co$^{(III)}$(dpgH)$_2$Cl(py) 0.125 mM in 0.1M [NBU$_4$][PF$_6$]. Registered at a scanning speed of 100 mV s^{-1} (black) in the presence of additions of 2 to 16 equivalents of HCA (blue). b) Dependence of the current increase on the HCA concentration. The data was adjusted to I$_C$=m[HCA]$^{1/2}$ + c, m = -1.57x10^{-3}, c = 1.33x10^{-5}, R^2 = 0.9991.

Fig. 8: General reductive dehalogenation mechanism of hexachloroethane using electrochemically generated Co(I) cobaloximes.

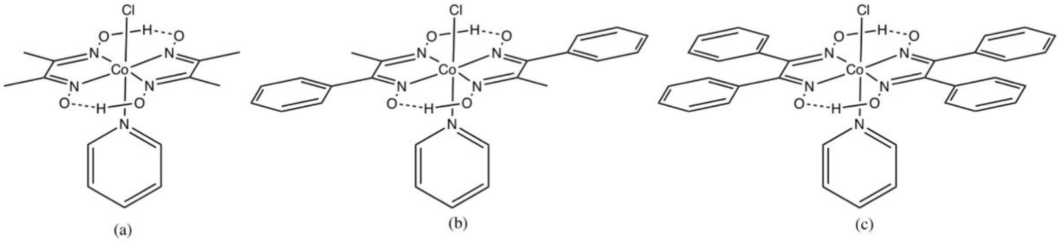


Fig. 1

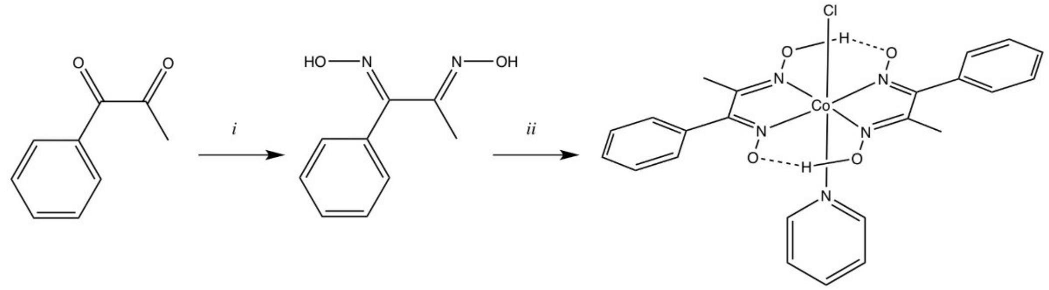


Fig. 2

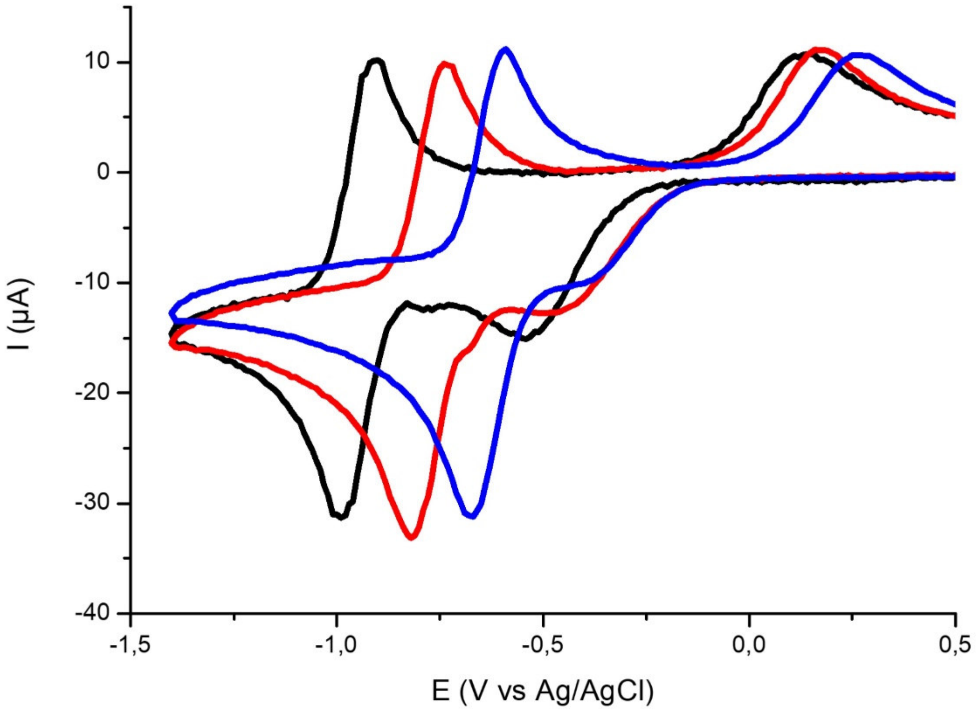


Fig. 3

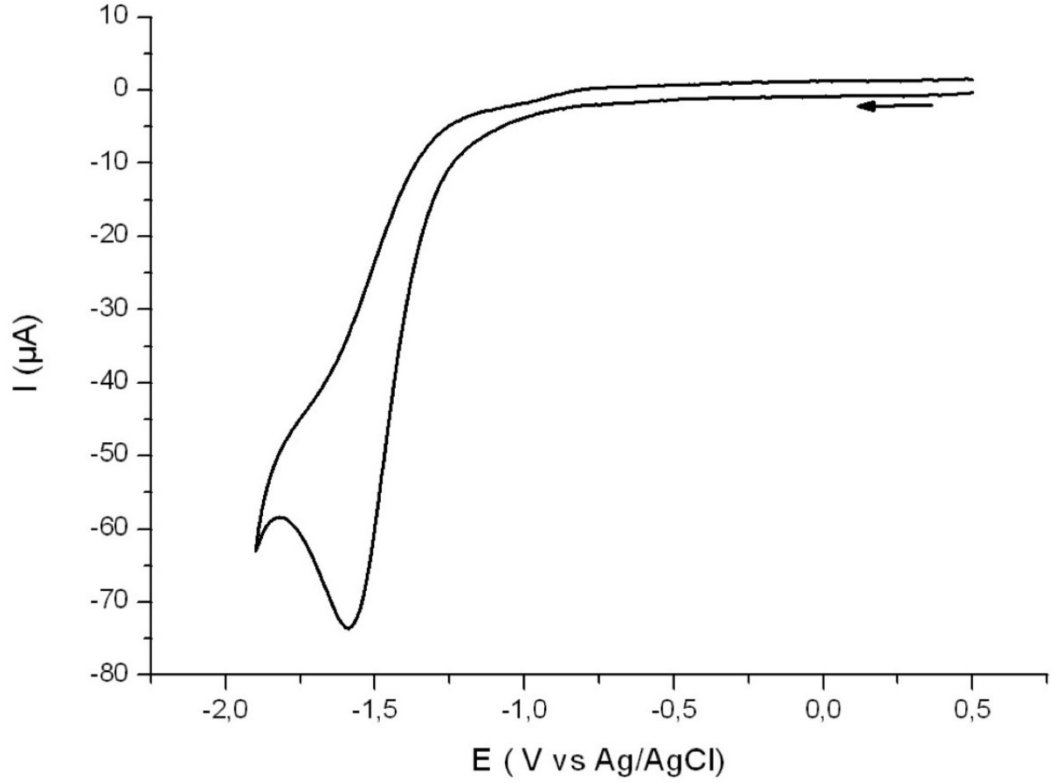


Fig. 4

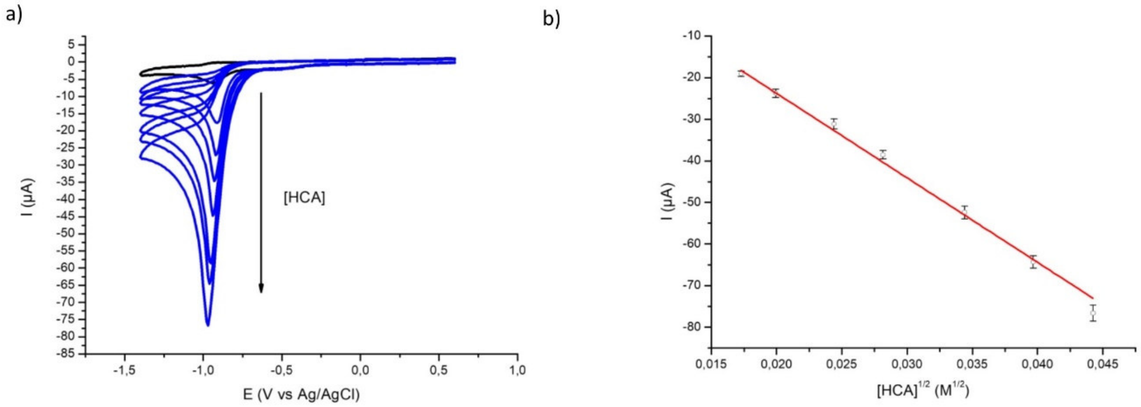

a)
I (μA)
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
[HCA]
-1,5
-1,0
-0,5
0,0
0,5
1,0
E (V vs Ag/AgCl)
b)
I (μA)
-10
-20
-30
-40
-50
-60
-70
-80
0,015
0,020
0,025
0,030
0,035
0,040
0,045
[HCA]^1/2 (M^1/2)

Fig. 5

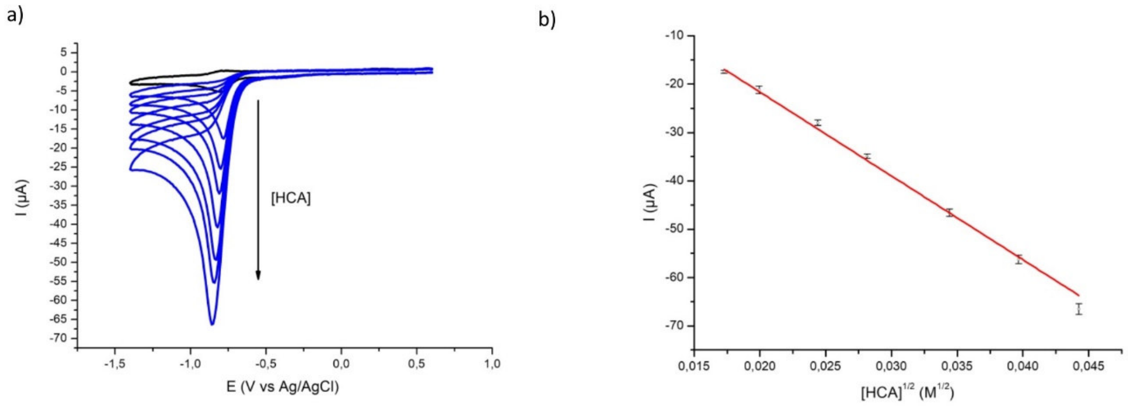

a)
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
I (µA)
[HCA]
-1,5
-1,0
-0,5
0,0
0,5
1,0
E (V vs Ag/AgCl)
b)
-10
-20
-30
-40
-50
-60
-70
I (µA)
0,015
0,020
0,025
0,030
0,035
0,040
0,045
[HCA]^1/2 (M^1/2)

Fig. 6

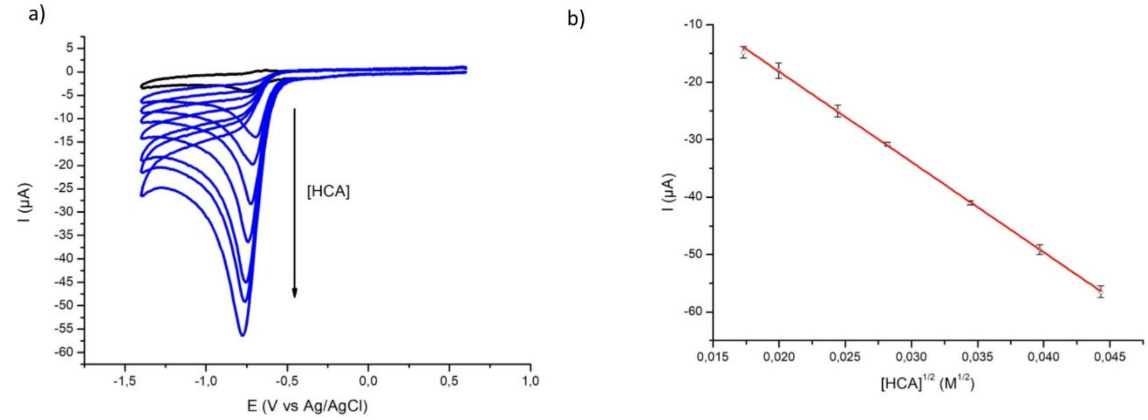

a)
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
I (μA)
[HCA]
-1,5
-1,0
-0,5
0,0
0,5
1,0
E (V vs Ag/AgCl)
b)
-10
-20
-30
-40
-50
-60
I (μA)
0,015
0,020
0,025
0,030
0,035
0,040
0,045
[HCA]^1/2 (M^1/2)

Fig. 7

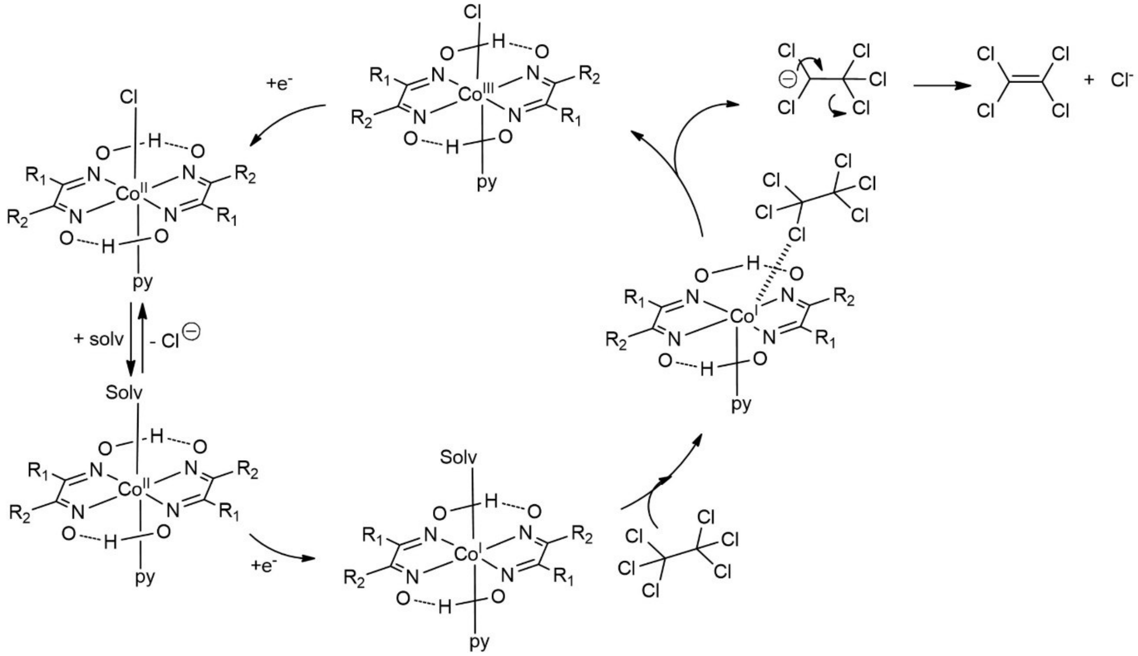
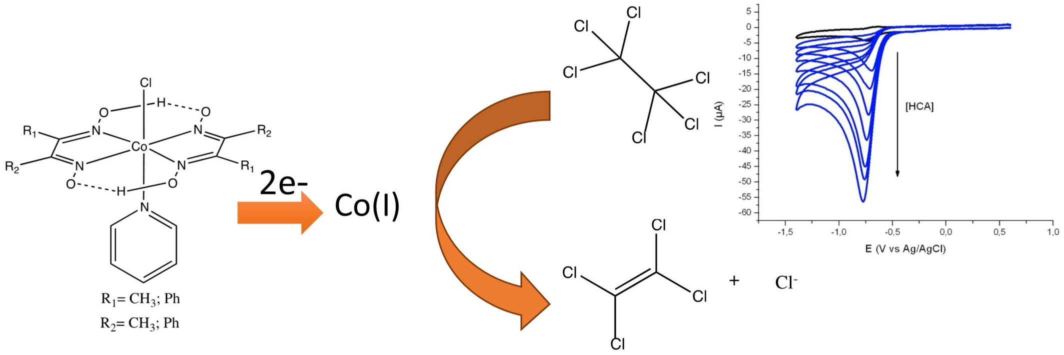


Fig. 8



Graphical abstract-synopsis

Three cobaloximes were used as catalysts for the reductive degradation of hexacloroethane. Tetrachloroethane was found as the degradation product. Although the Co complexes employed show substantial differences on the Co (II/I) reduction potential, the observed rate constant do not show significant differences