

Cobalt-amine complexes as potential water oxidation catalysts

Degree project C in Chemistry

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Abstract:

The water oxidation (measured as oxygen evolution) activity of different cobalt complexes was measured, using different oxidation agents. Two cobalt complexes, based on a dinucleating ligand were synthesized. The ligand contained eight coordination groups in total, each of the two pockets having two amine and two pyridine electron pair donors. One of the synthesized complexes was a cobalt dimer with two bound chlorides, the structure of the other complex we have not managed to reveal. Both complexes were characterized using different spectroscopic methods. One of the complexes displayed moderate oxygen evolution in aqueous solution with added oxidant, but also changed structure when dissolved in water.

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1. Introduction

In the search for more durable sources of energy, solar energy is one of the more favourable candidates. Harvesting and storing photo-energy in efficient ways is a considerable challenge though, and a lot of research is being done on these topics. Many different energy carrying compounds are being investigated as alternative for fossil fuels, as storing electricity is as of yet far less efficient volumetrically and gravimetrically. For all of these alternative fuels (H₂, methanol etc.) one thing is required, electrons. One part of the puzzle is finding an efficient, abundant and durable source of electrons. As we have learned from nature, water seems to be a very good candidate, for obvious reasons. Electrolytic oxidation of water has been used for a long time for the production of H₂ gas, but has always required high over potentials, making the process expensive and inefficient. For efficient water oxidation in solar cells, catalyst have to be designed which work at low over potentials, have high turnover rates and numbers and good lifetime stability. Ideally the catalyst should not contain rare and expensive metals, as for example ruthenium, indium or platinum used in many other related issues^[1]. Preferably the used metals should not be toxic in use or when disposed of. In these senses both manganese and cobalt are much better candidates.

Photosynthesis is thought to have originated 3.4 billion years ago in cyanobacteria, and those billions of years of evolutionary pressure have led to an enzyme complex called photosystem II (PSII). A lot of effort has been focused on understanding this complex, and has resulted in a measure of understanding of the complex system. The active water oxidation site in the protein consists of a CaMn₄O₅ complex from which oxygen originates^[2]. The process is initiated by photon absorption by P680, a chromophore containing four chlorophyll molecules. When P680 gets reduced the 'reducing power' is transferred to be used in the 'dark reaction' (the light independent Calvin Cycle). The CaMn₄O₅ cluster serves P680 as an electron donor, where one could say the 'oxidation power' is build up, until it is strong enough to oxidize water, when it has lost four electrons. This CaMn₄O₅ complex is usually called the oxygen evolving complex (OEC). The complex catalyses the water oxidation reaction:



Mimicking this system is one of the efforts in the search for efficient water oxidation catalysts. Although the exact structure and reactions mechanism are still under debate, elements of the active sites are used as inspiration for artificial complexes.

The first reported molecular water oxidation complex was based on ruthenium^[3,4]. The complex was a dimer of two ruthenium(III) ions, each having two bipyridine and one water ligand, linked by an oxo-bridge. Reduction power was, as for most homogenous water oxidation complexes up to date, supplied by sacrificial oxidants in solution, in this case Ce(IV). The catalyst was able to perform oxygen evolution up to 4.2×10^{-3} molecules O₂ sec⁻¹ and had an average of 13 turnovers per molecule. Almost twenty years later the first manganese based complex was reported to catalyze water-oxidation. Since manganese is found the active site of PSII this is both for practical purposes and from a research view more much more interesting. Two terpyridine ligands coordinated two manganese ions, which were bridged by two oxygen atoms. The reported complex oxidized water using sodium hypochlorite as electron source.^[5] Oxygen evolution with NaOCl was lower than reported for the ruthenium complex, but using HSO₅⁻ as electron donor the reported activity was higher.

Even though the rates in the synthetic complexes were rather slow compared to the oxygen evolution complex (OEC) in PSII, which shows evolution up to 40 molecules per second and turnover numbers up to 600.000 in a sample of a membrane preparation^[6], these efforts pioneer part of human attempts to 'artificial photosynthesis', and bring us one step closer to solving our energy

problems, and besides that these studies also illuminated the reactivity and mechanism of the oxygen evolution, or electron harvesting complex in PSII.

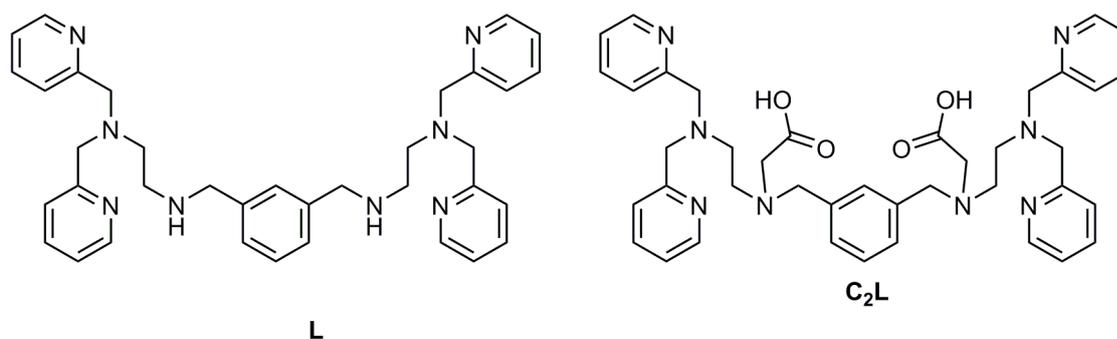
Another property of manganese complexes (and ions) is their reactivity towards peroxide compounds. Manganese is known to be present in hydrogen peroxide scavenging enzymes, and has even shown to catalyze peroxide disproportionation as unbound ion, in combination with inorganic salts^[7]. These enzymes are of major importance to all living beings, as the formation of oxygen radicals, originating from peroxides, is one of the main causes of cell aging, as they result in enzyme and DNA mutations and damage membranes. The enzymes catalyze the disproportionation reaction



Cobalt complexes have been known to be able to oxidize water since the 80's^[8,9,10]. Studies in that time regarding water oxidation assigned the activity to molecular complexes in solution (homogeneous catalysis), but it turned out that the formed cobalt oxide/hydroxide particles were in fact the active catalyst (heterogeneous catalysis). In a later study Co_3O_4 oxide proved to be the most successful catalyst in a study using different transition metal oxides (IrO_2 , Co_3O_4 , RuO_2 , RhO_2 and Mn_2O_3) as catalysts^[11]. In more recent work electrochemical water oxidation was studied, using a cobalt oxide/phosphate system^[12]. The active film was deposited on a conducting glass electrode and was shown to be an effective water oxidation catalyst.

Previous work

In the works of Berggren et al. activity was screened on several manganese based complexes, both in water oxidation and hydrogen peroxide disproportionation^[13]. To both complexes **L** and **C₂L** (amongst others) manganese ions were introduced, using manganese chloride (MnCl_2) and manganese acetate ($\text{Mn}(\text{OAc})_2$) for **L**, and manganese perchlorate for **C₂L**, as internal bridging groups are present in this ligand.



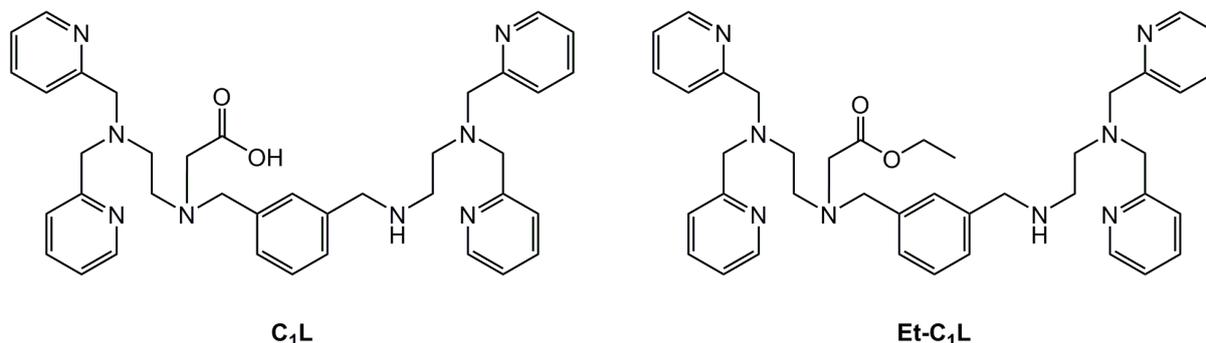
Scheme 1: Ligands L and C₂L

My work

L (scheme 1) was synthesized in five steps. In the first step a protective group was introduced on one of the functionalities of ethylene diamine, by using di-*t*-butyl dicarbonate, resulting in **1** (see also scheme 3). Thereafter two pyridylmethyl groups were introduced, forming **2**. After removing the protective group two of the synthesized amines (**3**) were linked together by isophthalaldehyde to give **4**. Finally the formed imines groups were reduced to amines, resulting in **L**.

To a different batch of the amine **L** (synthesized by Berggren), I attempted to introduce a single (protected) carboxylic group using ethyl bromoacetate (scheme 2), similar to the previously used route to synthesize **C₂L**^[14]. However, the product proved difficult to separate from the starting material, and I could not obtain **Et-C₁L**, the protected carboxylic acid, in purified form. As an

alternative procedure the unprotected carboxylic acid was introduced to **L**. Again LC-MS indicated **C₁L** was formed, but the yield of the reaction was too low and unspecific to obtain any useful product.



Scheme 2: C₁L and the protected Et-C₁L

Parallel to my attempts on synthesizing the ligands **L**, **C₁L** and **C₂L**; two cobalt complexes based on **L** were made. Two different methods were developed, both using cobalt perchlorate in dried methanol. One method produced a brown complex, the other, in which active carbon was used, a blue complex. Both products were screened for oxygen evolution activity using different oxidants and a Clark type electrode, and studied by cyclic voltammetry, electron spin resonance (EPR) spectroscopy, direct injection mass spectrometry (MS) and IR, visible and UV spectroscopy. Nuclear magnetic resonance (NMR) was attempted, but no peaks were observed using ¹H-NMR. This is not surprising since EPR indicated the presence of Co(II) in both complexes, which is paramagnetic, and the use of NMR spectroscopy on complexes containing paramagnetic centers is limited because of line broadening.

With these studies we hoped to illuminate the reactive and structural properties of the different cobalt complexes of **L**, **C₂L**.

Cobalt dimers are known to bind dioxygen, which can in some cases be reversible. We hoped to see if the synthesized complex had any of this kind of reactivity, and if so, shed light on properties of these reactions.

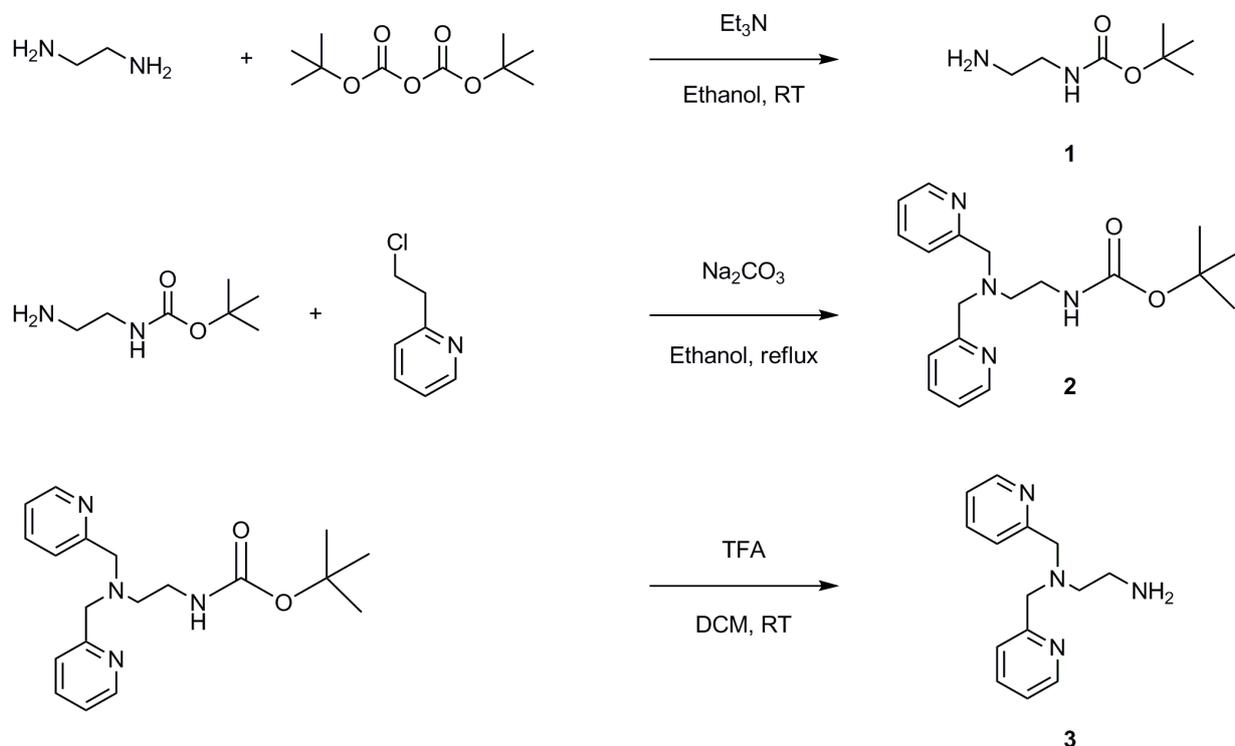
Overview

The blue cobalt complex, **[LCo₂Cl₂]²⁺**, showed moderate to low oxygen evolution using peroxide oxidants, possibly through disproportionation, no catalytic activity was seen using a single electron oxidant, but as the experiments were conducted in water this could have been an issue. The brown cobalt complex, **LCoX**, showed no catalytic activity under the tested conditions. Since the synthesis of ligands **C₁L** and **C₂L** were unsuccessful, there was no opportunity to synthesizing cobalt complexes containing these ligands.

2. Experimental

Synthetic procedures

All used solvents were dried before use.



Scheme 3: First part of the synthesis of ligand L, through intermediates 1, 2 and 3

Synthesis of N1,N1'-(1,3-phenylenebis(methylene))bis(N2,N2-bis(pyridin-2-ylmethyl)ethane-1,2-diamine) (**L**) (scheme 3 and scheme 4).

*Synthesis of tert-butyl 2-aminoethylcarbamate, **1** (scheme 3).*

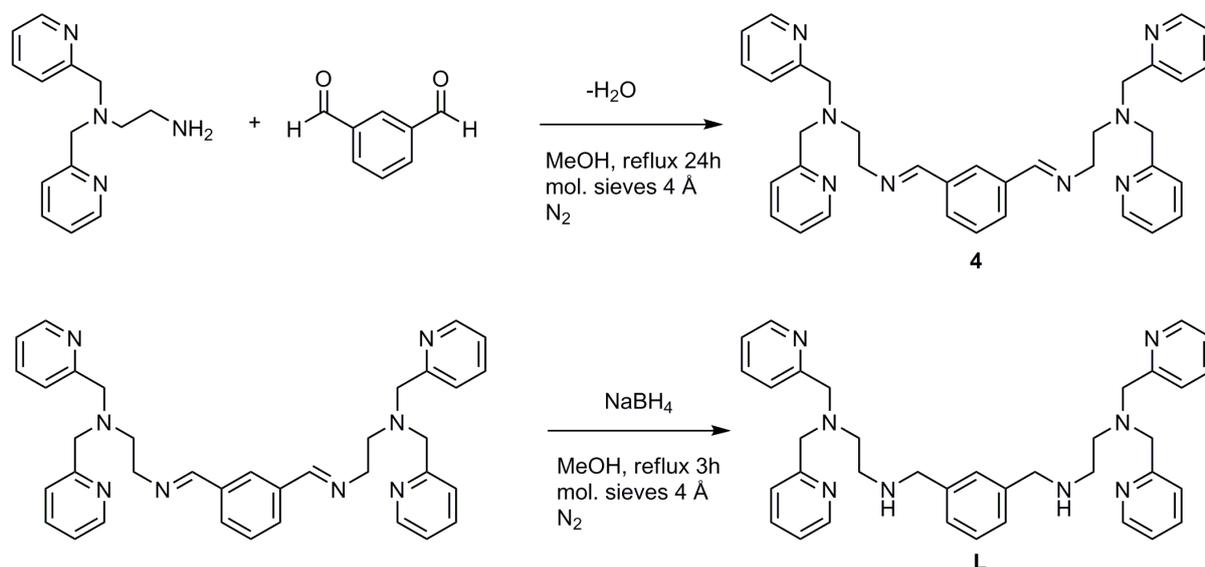
Diaminoethane (10 mL, 150 mmol) was mixed with triethylamine (0.8 mL, 5.8 mmol) in ethanol, and cooled on ice. Di-tert-butyl dicarbonate (boc_2O) was dissolved in ethanol (7.0 g boc_2O , 32.1 mmol in 10 mL ethanol), and added dropwise to the solution. The mixture was stirred for 2 hours after which the solvent was removed and the residue dissolved in dichloromethane. The amine was extracted from the organic layer with acetic acid (1M, 3 x 20 mL). The aqueous layer was alkalinized with a sodium hydroxide solution (2 M, 10 mL) and the product extracted to dichloromethane (5 x 5 mL). The combined organic layers were dried using anhydrous sodium sulfate, which was then filtered off and the solvent removed under reduced pressure. Yield: 41%, 380 mg.

*Synthesis of tert-butyl 2-(bis(pyridin-2-ylmethyl)amino)ethylcarbamate (**2**)*

In the second step pyridine groups were introduced on the unprotected amine **1** by adding 2.5 equivalents of 2-methylchloride pyridine-HCl (5.34 g, 30 mmol) and 4.5 equivalent Na_2CO_3 (5.8 g, 58 mmol) in ethanol. The solution was heated to reflux temperature for 6 hours under a protective atmosphere. The solvent was evaporated and the residue washed with an aqueous sodium hydroxide solution (2M, 20 mL), and the product was extracted with dichloromethane and subsequently purified by column chromatography (aluminium oxide, inactivated with 4% water, using 2% methanol in dichloromethane as eluent). **2** eluted as the second fraction. Yield: 81%, 650 mg.

*Synthesis of N1,N1-bis(pyridin-2-ylmethyl)ethane-1,2-diamine (**3**)*

The boc protecting group was removed from compound **2** (2.11 g, 6.16 mmol) by refluxing in trifluoroacetic acid (20 mL, concentrated) and 50 mL dichloromethane for one hour. The acid and the solvent were removed using an aspirator. Yield 71%, 1500 mg.



Scheme 4: Second part of the synthesis of ligand **L**, through intermediate **4**.

*Synthesis of N1,N3-bis(2-(bis(pyridin-2-ylmethyl)amino)ethyl)isophthalamide (**4**) and N1,N1'-(1,3-phenylenebis(methylene))bis(N2,N2-bis(pyridin-2-ylmethyl)ethane-1,2-diamine) (**L**)*

The primary amine **3** (650 mg, 2.7 mmol), was mixed with a half equivalent isophthalaldehyde (132 mg, 1.35 mmol) and the mixture refluxed for 24 hours in methanol under a protective atmosphere. After the reaction mixture had cooled to room temperature **4** was reduced to **L** by adding an excess sodium of borohydride (443 mg, 11.7 mmol), and again refluxing it for 3 hours. After the solvent was removed under reduced pressure the solid residue was extracted with DCM and characterized using NMR spectroscopy and mass spectrometry. The reduction appeared incomplete however, and subsequent reactions with sodium borohydride and later lithium aluminiumhydride did not improve the yield. Yield after first reduction: 600 mg, approximately 50% **L**. H-NMR (CDCl₃, 400 MHz), shift given in ppm relative to TMS: 8.48 4H d; 7.60 4H dt; 7.54 1H t; 7.43 2H d; 7.25-7.05 8H m; 7.25-7.05 3H m; 3.80 8H s; 3.7-3.5 4H m; 2.75 8H m. ESI-MS: (m/z) 587.5 (L+H⁺) and 609 (unknown).

*Synthesis of ethyl 2-((2-(bis(pyridin-2-ylmethyl)amino)ethyl)(3-((2-(bis(pyridin-2-ylmethyl)amino)ethylamino)methyl)benzyl)amino)acetate (**Et-C₁L**) and ethyl 2-((2-(bis(pyridin-2-ylmethyl)amino)ethyl)(3-((2-(bis(pyridin-2-ylmethyl)amino)ethylamino)methyl)benzyl)amino)acetic acid (**C₁L**)*

83 mg of **L** (0.14 mmol) was dissolved in 20 mL dichloromethane and cooled in an ice bath before 0.9 equivalent (0.13 mmol, 14 μL) ethyl bromoacetate and triethylamine (0.13 mmol, 18 μL) were added. The mixture was stirred overnight and the ice left to melt. The product was analyzed with LC-mass spectrometry. After 22 hours the conversion was still unsatisfactory, 13 μL (0.09 mmol) extra triethylamine was added and the mixture was again left overnight. The organic layer was then washed with a saturated K₂CO₃ (10mL) solution, and dried using Na₂SO₄. The K₂CO₃ solution was extracted with 3x 5 mL dichloromethane and from the combined organic layers a light brown oil was obtained after the solvent was removed. Purification was attempted using column chromatography

with deactivated aluminium oxide (5% H₂O) eluting with using different concentrations of methanol in dichloromethane (1-10%) and preparative high pressure liquid chromatography (HPLC), using mixtures of water in acetonitrile. The yield of **Et-C₁L** was too low (4 mg) after three unsuccessful purification attempts to continue our studies.

*Synthesis of 2,2'-(1,3-phenylenebis(methylene))bis((2-(bis(pyridin-2-ylmethyl)amino)ethyl)azanediyl) diacetic acid (**C₂L**)*

C₂L was synthesized according to the above synthesis of **C₁L** except an excess of ethyl bromoacetate and triethylamine was added. Yield 95 mg, 60%, but as this reaction was done with the crude mixture obtained after the unsuccessful reduction, the product was too impure to continue with it. Without further purification this product was too impure to synthesize metal complexes from and so this fraction was left for future work.

*Synthesis of **LCoX** (brown)*

54 mg (0.09 mmol) of **L** was dissolved in 5 mL methanol, and three equivalents cobalt perchlorate (33.6 mg) added. A few drops of water were added and the mixture aerated and stirred overnight. Yield 20 mg, we have not been able to determine the structure of this product, see later for further characterization. Direct injection MS: 454.1 was most intense, but a lot of other peaks were visible indicating a mixture of products.

*Synthesis of [**LCo₂Cl₂**](ClO₄)₂(blue)*

60 mg of **L** was dissolved in methanol, and 2 eqv. cobalt perchlorate added. The mixture was stirred for 30 minutes before half a gram of activated carbon was added. A stream of air was blown through the mixture and a large excess (10 mL) of concentrated HCl added following a modified literature procedure^[15]. Leaving it overnight, the solvent had evaporated and using sonication the solid was dissolved and partly suspended in acetonitrile. The carbon black was filtered off using celite, and a blue solution was collected. From the solution a light blue solid precipitated, which was collected as one fraction, and analyzed with IR spectroscopy (VK 12 (2)). The product [**LCo₂Cl₂**](ClO₄)₂ was obtained by slowly diffusing ether into the acetonitrile solution. Yield 31 mg (0.04 mmol, 40%). Direct injection MS in acetonitrile: 387.3 (LCo₂Cl₂²⁺ calc. 387.1), and 873.1 (LCo₂Cl₂²⁺ + ClO₄⁻, calc. 873.1).

Dissolving the complex in water changed the colour of the complex. In powder form, and in acetonitrile, the complex was blue. Dissolving it in water however, it turned pink. Direct mass injection of the complex was done both in acetonitrile (see above) and in water: 680.3 (LCoCl⁺, calc. 680.2 LCoCl⁺)

Oxygen evolution studies

Measurements performed using a standard Clark-type oxygraph electrode from Hansatech Instruments. Data was recorded in Oxygraph+ and analyzed in Mathematica 7.0.

Oxygen evolution (reaction 1) was measured using three different oxidation agents: hydrogen peroxide, oxone (potassium peroxymonosulfate) and cerium(IV) (as cerium ammonium nitrate). A Clark type electrode measures the current between a platinum and a silver electrode, which are connected by a potassium chloride salt bridge and separated from the reaction chamber by an oxygen permeable membrane. Oxygen gets reduced to water on the platinum surface, and on the silver electrode silver gets oxidized to silver(I) chloride. The reaction chamber can be sealed with an air tight plug to avoid atmospheric oxygen from getting into the solution.

Upon measurement the catalyst was brought in solution in the cavity, and degassed with argon until all oxygen was removed. Subsequently the degassed solution of the oxidant was added, and oxygen evolution measured for 10 minutes. The data was exported in Wolfram Mathematica 7.0 and a linear fit was made for the first 40 seconds of the measurement to obtain the turnover rate of the catalyst. For quantitative analysis, the turnover number, the total oxygen concentration was estimated looking at the shape of the graph. In each experiment the oxidant concentration was 10 mmol/L, the catalyst concentration was around 0.4 mmol/L. The results are summarized in table 1.

Table 1: Oxygen evolution rates

	$[\text{LCo}_2\text{Cl}_2]^{2+}$			LCoX		
	O ₂ evolution rate (nmol/sec)	O ₂ turnover rate (mol/mol catalyst)	O ₂ turnover number ¹	O ₂ evolution rate (nmol/sec)	O ₂ turnover rate (mol/mol catalyst) ¹	O ₂ turnover number
H ₂ O ₂	0.33	1.3×10^{-3}	0.2	n.d.	-	-
Oxone ²	0.28	1.0×10^{-3}	0.4	n.d.	-	-
Cerium(IV)	n.d.	-	-	n.d.	-	-

¹Estimated order of magnitude is given, in mol O₂ per mol catalyst. ² Corrected for spontaneous disproportionation.

Light absorption studies

Light absorption was measured on wide frequency range, using IR and UV/vis spectroscopy. IR transmission was measured in a Bruker IFS 66v/S spectrometer. The product was ground and pressed into KBr pellets.

Complex $[\text{LCo}_2\text{Cl}_2]^{2+}$ displayed a colour change when dissolved in water (from blue to pink). The complex seemed to have the same colour as cobalt perchlorate, so the absorption of the former in acetonitrile was measured as well.

The peaks in the acetonitrile spectrum around 600 nm (590, 629, 666 and 690 nm) are likely to be d-d transitions (Figure 1).

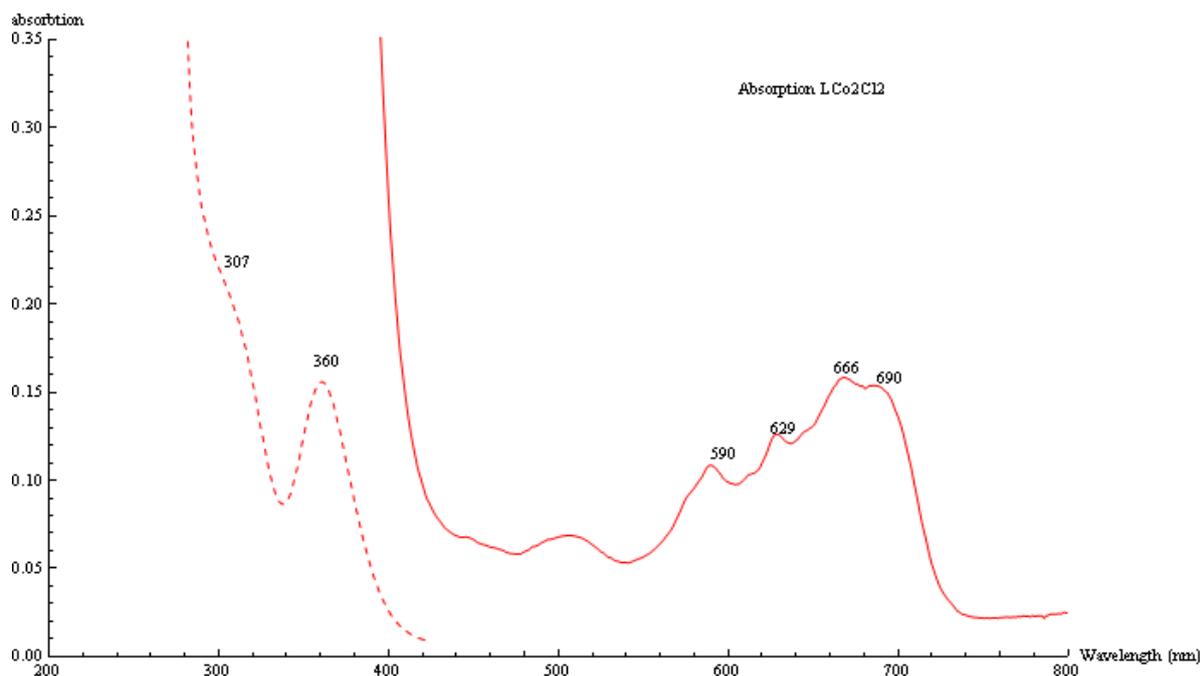


Figure 1. light absorption of $[LCo_2Cl_2]^{2+}$ in water, for the dashed line the intensity was divided by 10.

The UV/vis spectrum of **LCoX**, figure 2, did not provide much information. It showed three peaks: at 592, 383 and 254, but they were not well defined and this hinted an unspecific structure (Figure 2).

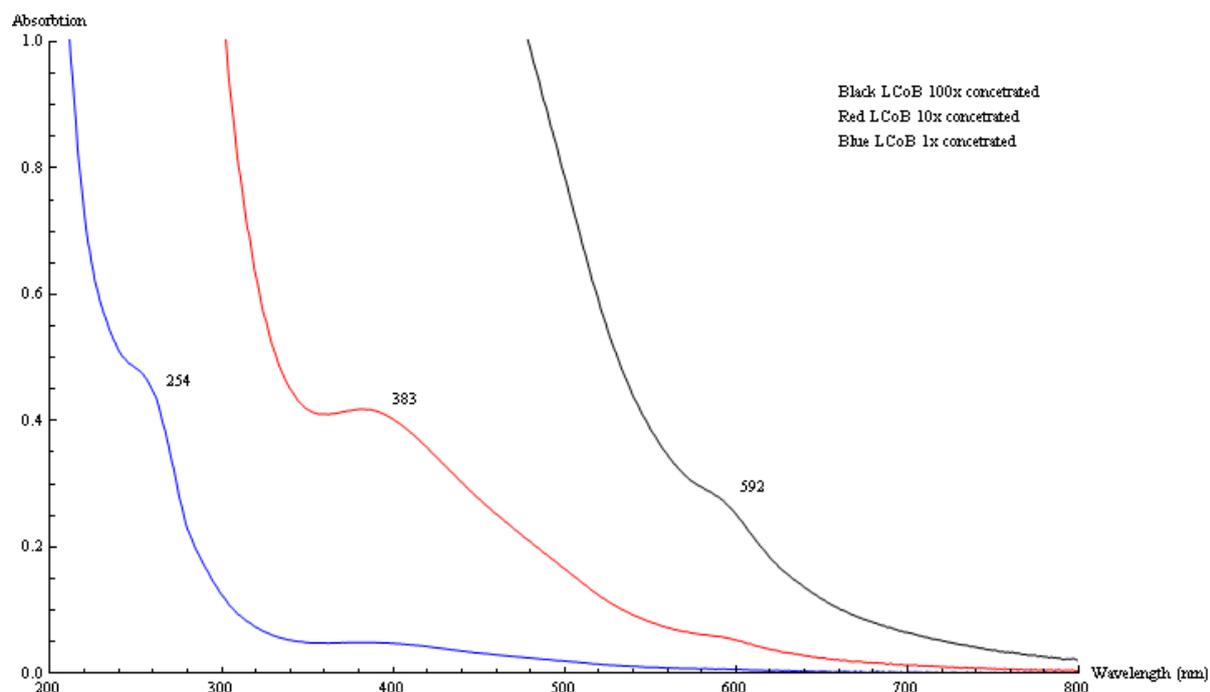


Figure 2. light absorption of **LCoX** in water, measured at three different concentrations.

The IR-spectroscopy showed the presence of ligand in the coloured complexes, for example by the presence of bands from the pyridines around 1600 cm^{-1} (Figure 3).

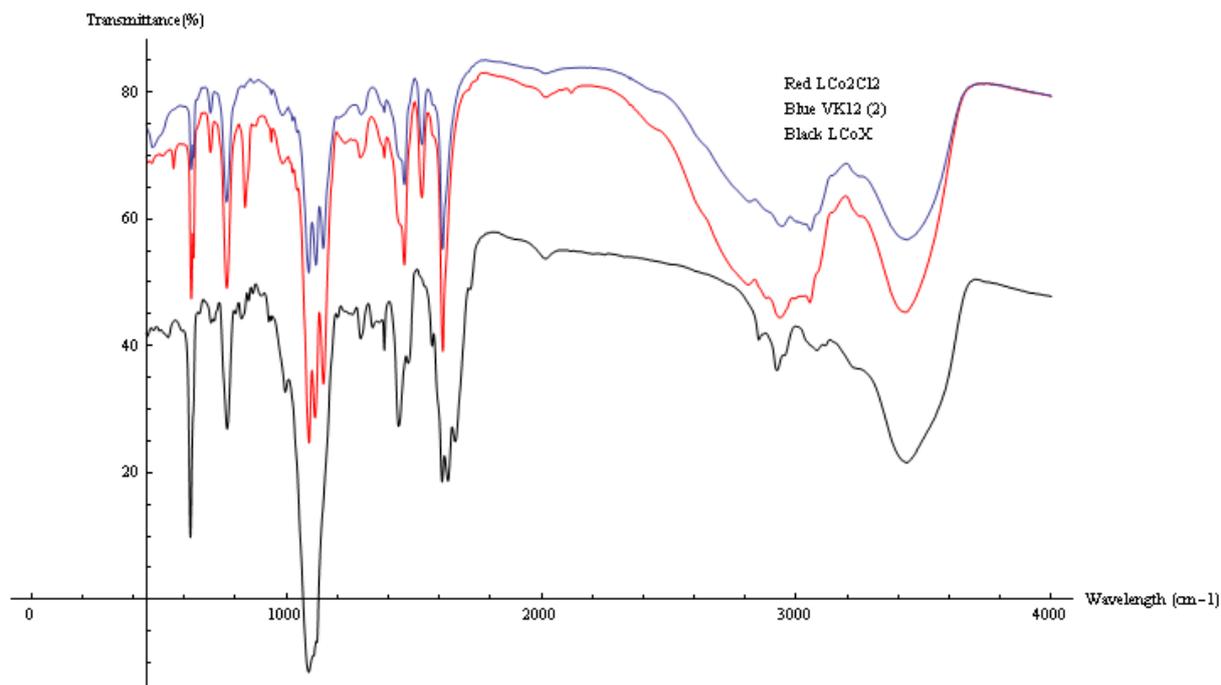


Figure 3. Infrared absorption of $[\text{LCo}_2\text{Cl}_2]^{2+}$, VK12 (2) and LCoX in KBr pellets, for clarity the black line, belonging to LCoX was moved down by 27. The complexes $[\text{LCo}_2\text{Cl}_2]^{2+}$, VK12 (2) appear similar, except for two peaks, missing in VK 12 (2) but present in $[\text{LCo}_2\text{Cl}_2]^{2+}$.

Electron paramagnetic resonance studies

EPR studies were performed on both complexes. Measurements were made in frozen acetonitrile at 4, 11 and 21 K; EPR spectra were recorded at X-band range using Bruker ELEXSYS-E500 spectrometer. Quantification of cobalt(II) EPR signals were made by double integration of the signals recorded at 5 K using 0.20 mW microwave power and compared with the EPR spectrum of a cobalt perchlorate solution in a phosphate buffer.

Cobalt(III) in the low spin state (which is the most common form) does not have any unpaired electrons, as is it a d^6 transition metal ion, and is thus EPR silent. Cobalt(II) however has unpaired electrons both in high spin and low spin state. The cobalt nucleus itself has a spin momentum of $S=7/2$, so the EPR signals could have a hyperfine structure, split up in 8 lines.

Both complexes appeared to have high spin cobalt(II), a significant signal was visible around 1475 G or $g \approx 4.5$ in both samples, see figure 4 and 5. The $[\text{LCo}_2\text{Cl}_2]^{2+}$ complex showed hyperfine coupling at ≈ 3300 G, or $g \approx 2$; at least 8 peaks were visible, indicating the presence of low spin cobalt(II) (Figure 4).

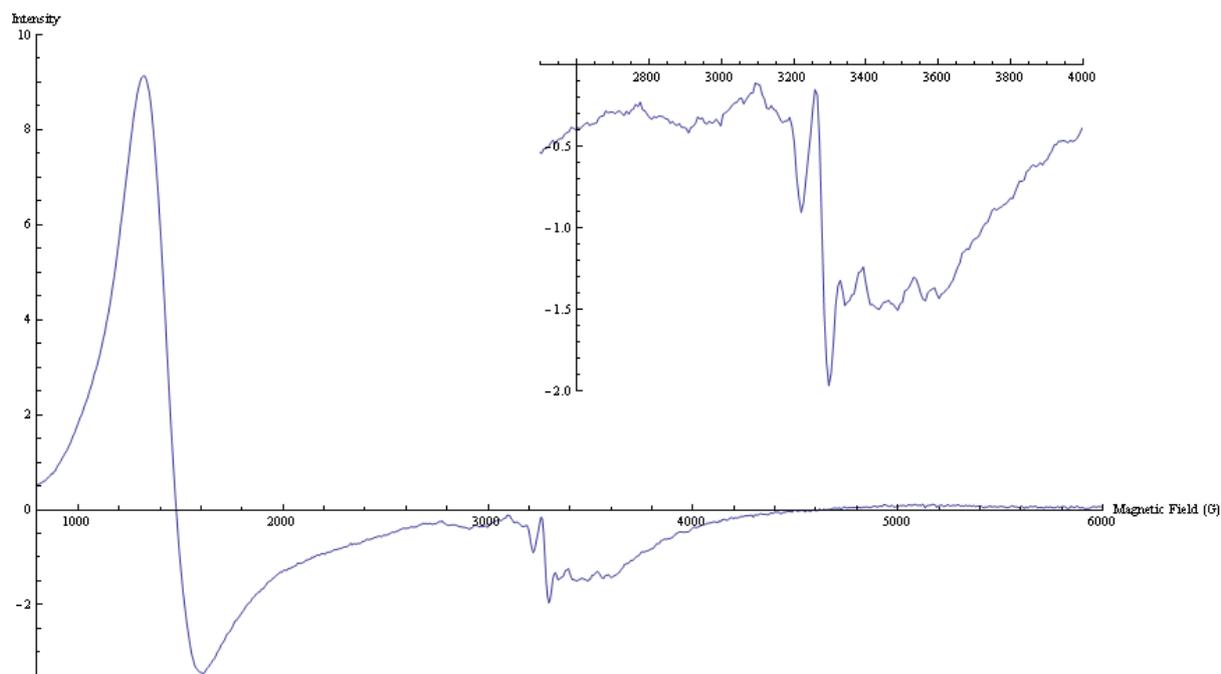


Figure 4. EPR spectrum of complex $[LCo_2Cl_2]^{2+}$, close-up is made from the hyperfine structure around 3300 G.

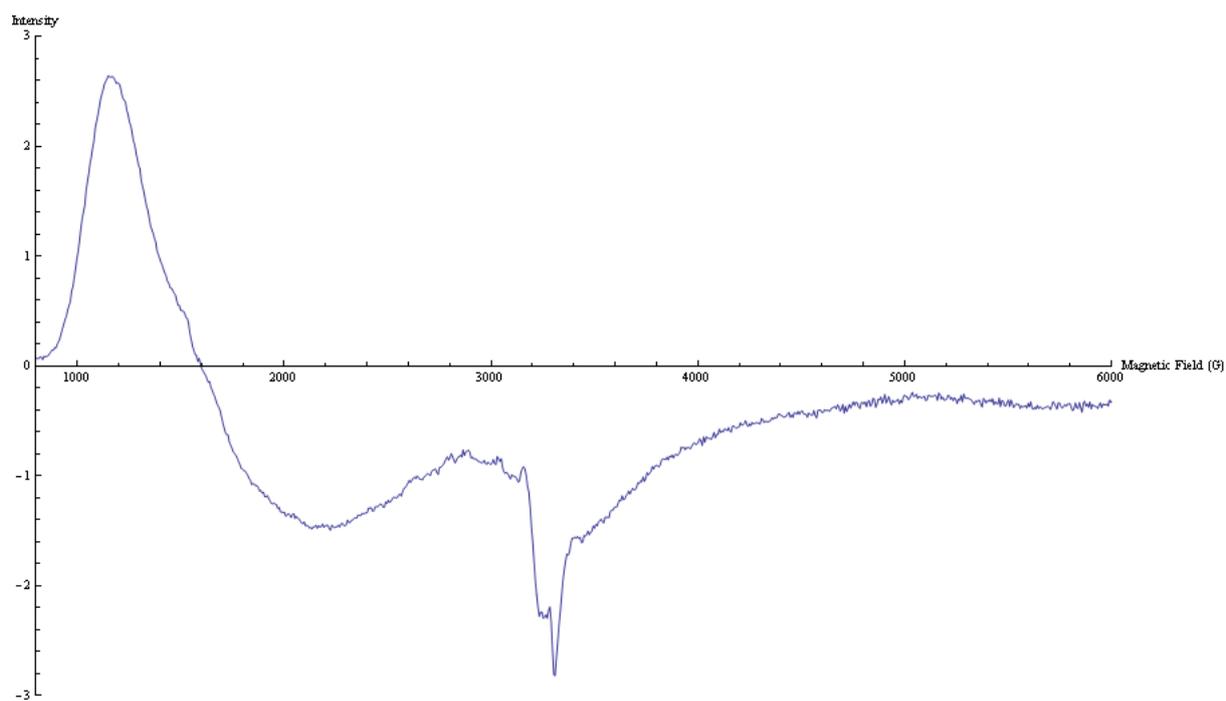


Figure 5. EPR spectrum of complex $LCoX$. As the signal from the complex is less intense, the background noise and the signals from the cavity are more visible.

Cyclic voltammetry

For electrochemical analysis of **LCoX** and $[\text{LCo}_2\text{Cl}_2]^{2+}$ an Autolab potentiostat, equipped with GPES electrochemical interface Eco Chemie was used. Solutions were prepared in 4 mL 0.1 M TBAPF₆ (tetrabutylammonium hexafluorophosphate) in dried acetonitrile (Fluka, electrochemical quality). The working electrode was a glassy carbon electrode, 3 mm diameter, the counter electrode was a glassy carbon rod and the reference electrode was an Ag/Ag⁺ electrode. The counter and reference electrodes were separated from the bulk solution by fritted glass. Oxygen was removed prior to the experiments by bubbling argon through the solution.

The voltammograms of **LCoX** did not show any well defined oxidation or reduction peaks. In the $[\text{LCo}_2\text{Cl}_2]^{2+}$ solution displayed one strong reduction peak at 1.15 V, and upon lowering the voltage after that two distinct oxidations were visible at 0.45 V and -0.3 V (Figure 6). Upon lowering the scan rate the oxidation peak at 0.45 V disappeared, indication the lower oxidation state was only moderately stable.

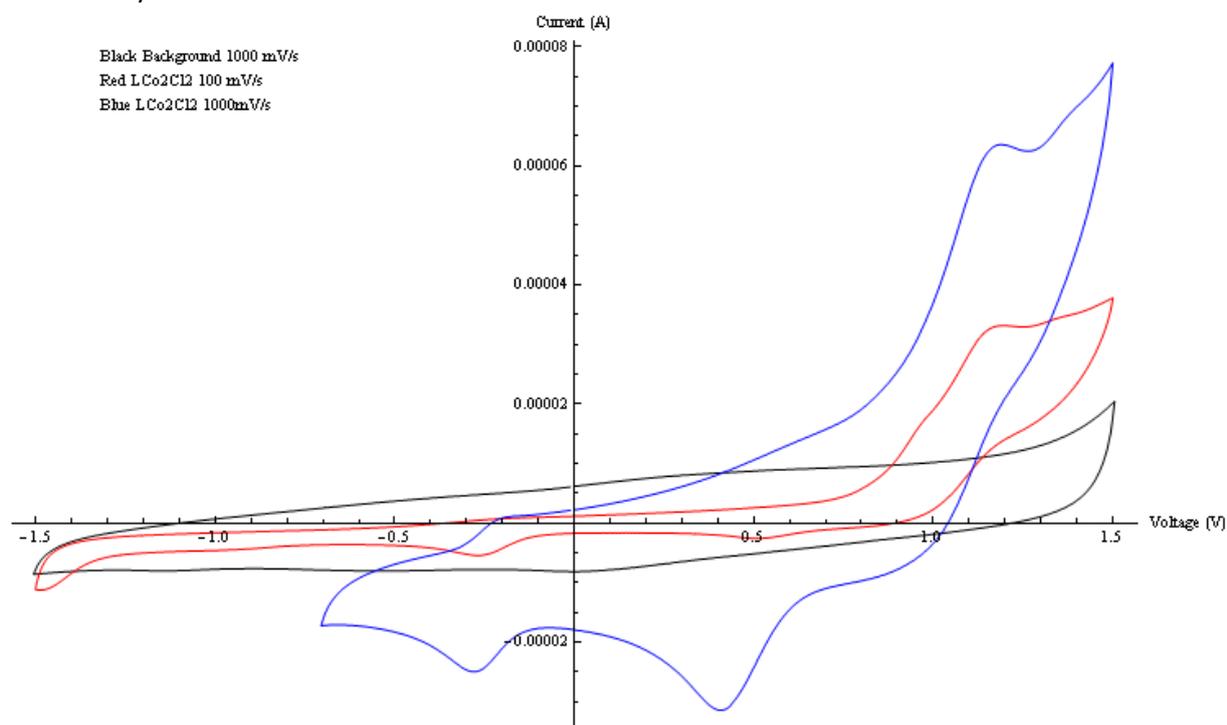
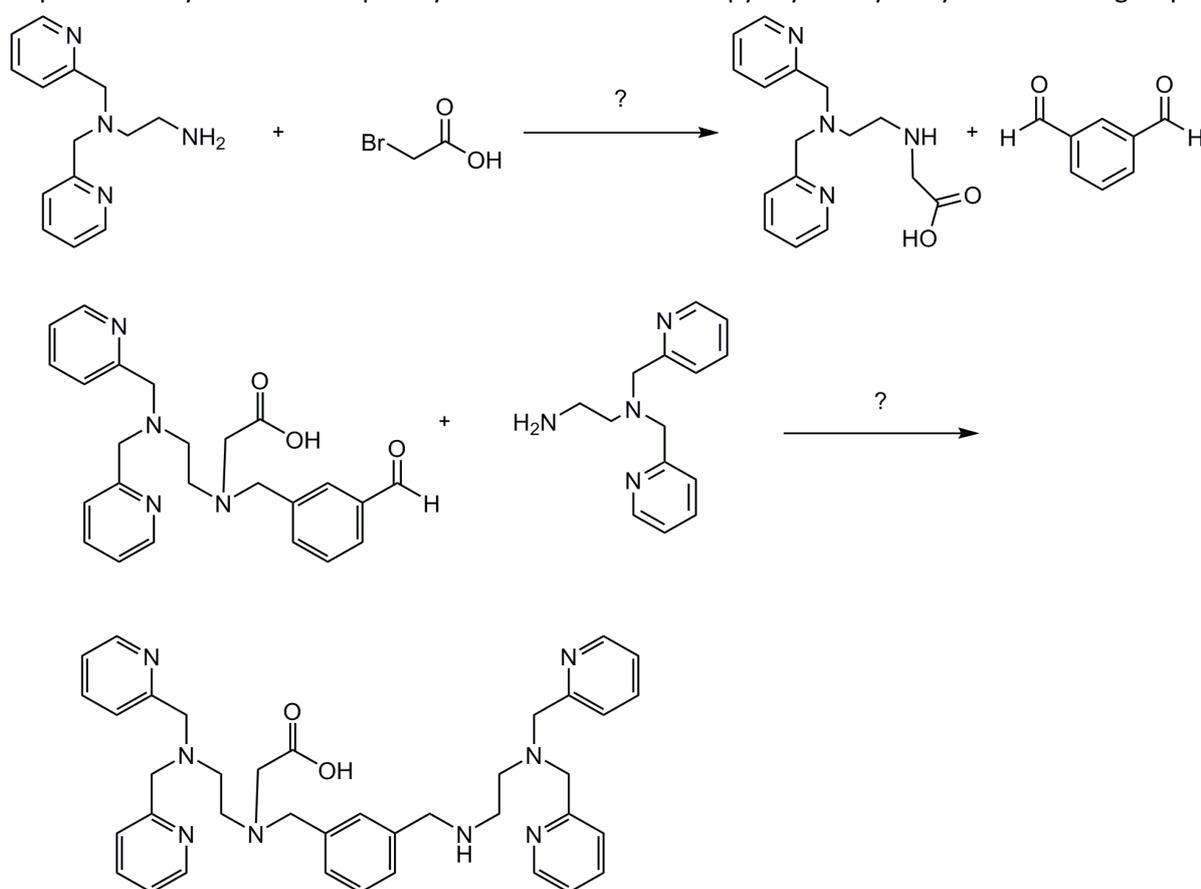


Figure 6. Cyclic voltammograms of $[\text{LCo}_2\text{Cl}_2](\text{ClO}_4)_2$.

3. Result analysis and discussion

The synthesis of ligand L was unsuccessful; the last step, the reduction seemed at first incomplete, and later, possibly using a too strong reductant the mixture was too impure. Introducing the carboxylic functionality (both single and double) was successful, but the purification using deactivated aluminium oxide and preparative high pressure liquid chromatography was unsuccessful. However, from analytical liquid chromatography mass spectrometry presence of the product was observed. For future work the purification procedures should be optimized and performed on higher quantities of material. Especially for synthesizing the asymmetric complex, it might be feasible to use an asymmetric synthesis as well. Introducing one dipyriddylmethyl functionality at a time could mean the reaction equilibria can be pushed instead of adding half equivalent and getting mixtures of product. For example the following synthesis could be tried (Scheme 5). First introducing the carboxylic acid functionality on one of the dipyriddylmethyl ethylene diamine, introducing this group to isophthalaldehyde and subsequently the unfunctionalized dipyriddylmethyl ethylene diamine group.



Scheme 5. alternative synthesis of C₁L.

Synthesizing and characterizing the cobalt complexes was successful. Although the structure of the brown cobalt complex **LCoX** could not be clarified, the blue complex **[LCo₂Cl₂](ClO₄)₂** was identified as such by direct injection mass spectrometry. It was assumed that the two chlorides were bridging the cobalt(II) ions so that both metal ions are hexacoordinated. Recrystallizing and analyzing the complex by X-ray crystallography may illuminate this. Also further analyzing the light absorption characteristics of a recrystallized complex could give more information about the ligand environment of the cobalt ions.

It would be interesting to further investigate the water oxidation properties of $[\text{LCo}_2\text{Cl}_2](\text{ClO}_4)_2$. As the complex appeared to be unstable in water, in which the oxygen evolution measurements were taken, this would of course drastically affect the results. More insight in the stability of the complex towards water could be obtained by light absorption studies in different water:acetonitrile mixtures. The complex may be stable in mixtures containing only a small amount of water and we could perform oxygen evolution studies on the intact complex.

If the blue complex could be purified further, more EPR measurements can be taken to see if the complex is high or low spin or both; in the EPR spectra we made either of the signals might have been arising from other cobalt complexes or ions.

In the future it would be useful to make KBr pellet IR spectra of the ligand L. With these data it would be possible to assign ligand-metal absorption bands and this may shed more light on the structure of the complex.

4. References

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