The Two Electron Oxidation of Cobalt Phthalocyanines by Thionyl Chloride: Implications for Lithium/Thionyl Chloride Batteries

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Introduction

The lithium/thionyl chloride (SOCl₂) cell is the highest energy density system known to date.¹ The battery consists of a lithium anode, a
carbon cathode, an inorganic electrolyte and thionyl chloride which functions both as the solvent and cathode active material. The most generally accepted cell reaction involves the formation of sulphur, sulphur dioxide and lithium chloride.

\[ 2\text{SOCl}_2 + 4\text{Li} \rightarrow \text{S} + \text{SO}_2 + 4\text{LiCl} \]

Intermediate species such as S\(_2\text{Cl}_2\), SCl\(_2\), SO, S\(_2\text{O}\), SO\(_2\) and SO\(_2\text{Cl}_2\) have been reported.\(^1\) The use of Li/\text{SOCl}_2\) batteries has been greatly restricted, however, because of the explosion hazard. Studies\(^9\) have shown that unstable intermediates from \text{SOCl}_2 reduction are responsible for spontaneous exothermic reactions in discharged cells. Safety vents can be installed in Li/\text{SOCl}_2\) batteries to release excessive pressure and have been successful in preventing explosions.\(^10\)-\(^12\)

Doping of the carbon cathode with iron or cobalt phthalocyanine complexes improves the cell voltage, the rate of discharge and the lifetime of Li/\text{SOCl}_2\) batteries.\(^13\)-\(^19\) Doddapaneni\(^13\)-\(^16\) reports that the electrode kinetics and the cell reaction are different at phthalocyanine-containing cathodes. His rotating disk electrode studies\(^16\) show that 1.36 times more electrons are transferred to each \text{SOCl}_2 molecule at an FePc treated carbon electrode than at a bare carbon electrode. For example, if \text{SOCl}_2 is reduced by two electrons at an FePc electrode then 1.47 electrons, on the average, are transferred to each \text{SOCl}_2 molecule at a bare carbon electrode. In this current work, the reaction of thionyl chloride with cobalt phthalocyanine was studied to understand the function of phthalocyanines in lithium/thionyl chloride cells.
Experimental

Cobalt tetraneopentoxyphthalocyanine (abbreviated CoTnPc) was used because of its increased solubility in organic solvents and was prepared by the method published by Leznoff and coworkers.\textsuperscript{20} Nitrogen (dried over drierite) was bubbled through thionyl chloride (reagent grade, BDH) for five hours prior to use to remove all traces of HCl and dissolved oxygen. 1,2-dichlorobenzene (DCB)(Gold Label, Aldrich), an inert solvent, was dried over 4Å molecular sieves (8-12 mesh, Aldrich) activated at 200°C under vacuum for two hours. Tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6})(98%, Aldrich) was recrystallized from absolute ethanol and dried at 140°C under vacuum for two hours. Tetrabutylammonium chloride (TBACl) (Eastman) was dried using molecular sieves as an 0.10M solution in DCB.

Electronic spectra were recorded with a Guided Wave Inc. Model 100-20 optical waveguide spectrum analyzer using a caliper fiber optic probe and a 0.100 or 0.200 cm quartz cell. Electrochemical data were obtained with either a Pine Model RDE3 double potentiostat, a Princeton Applied Research (PAR) Model 174A polarographic analyzer coupled to a PAR Model 175 universal programmer, or a PAR Model 173 potentiostat/galvanostat coupled to a PAR Model 179 digital coulometer. The PAR 174A analyzer, set in the differential-pulse mode, was used to perform differential-pulse voltammetry (DPV or DP voltammetry). Cyclic voltammetry (CV) and DPV were carried out under nitrogen using a conventional three-electrode cell. A platinum pseudo-micro disk described by the cross-sectional area of a 27-gauge wire (area 1.02 X 10\textsuperscript{-3} cm\textsuperscript{2}) sealed in soft glass or a platinum wire was used as the working electrode. A platinum wire served as the counter electrode, and a silver wire coated with silver chloride was used as a quasi-reference
electrode. The AgCl/Ag reference was isolated from the main solution by a medium glass frit. Potentials were referenced internally to the ferrocenium/ferrocene (Fc+/Fc) couple which occurred at +0.49V vs a platinum-tipped saturated calomel electrode (SCE) in DCB.

The bulk electrolysis cell consisted of a relatively large platinum-mesh working electrode, platinum-wire counter electrode and silver chloride/silver wire quasi-reference electrode. Both the counter and reference electrodes were separated from the working compartment by medium glass frits. All solutions used for electrochemistry contained ca. 10^{-4} \text{M} \text{CoTnPc} in DCB and 0.1M TBAPF$_6$ or TBACl as supporting electrolyte, and were deoxygenated by bubbling nitrogen for two hours prior to use.

Li/SOCl$_2$/C cells were prepared (in air) using a piece of ordinary pyrolytic graphite (OPG) as the cathode and lithium wire as the anode. The lithium was cut under the thionyl chloride solution to expose a fresh surface of metal. Rest potentials were measured using a Fluke 75 digital voltmeter and the potential of each electrode was measured versus a platinum-tipped SCE.

[Co(I)TnPc(2-)]$^-$ was prepared by bulk electrolysis (-1.00V vs AgCl/Ag, under N$_2$) of a Co(II)TnPc(2-) solution containing TBAPF$_6$. [Co(I)TnPc(2-)]$^-$ was also prepared chemically by reducing a 2.3 X 10^{-6} \text{M} solution of Co(II)TnPc(2-) in DCB containing 0.07M TBAPF$_6$ using a thin piece of graphite (0.5mm, HB pencil lead) inserted into a piece of lithium. This reaction was performed in a 0.100 cm quartz cell under nitrogen. [Co(III)TnPc(2-)]$^+$ was prepared by bulk electrolysis (+0.90V vs AgCl/Ag, under N$_2$) of a Co(II)TnPc(2-) solution containing TBACl.

In a typical experiment, 1 $\mu$l of SOCl$_2$ (1.4 X 10^{-5} moles, 140X excess) was added to a 1 ml DCB solution of CoTnPc (10^{-4}M) under nitrogen.
Rigorously dry conditions were used to prevent hydrolysis of SOCl₂ which would lead to protonation of the phthalocyanine by the HCl produced.

Results

Electronic Spectroscopy.- The oxidation and reduction processes on the cobalt phthalocyanine unit can take place either at the metal or at the organic ligand center. The electronic spectra of cobalt tetraneopentoxyphthalocyanine species in the [Co(I)TnPc(2-)]⁻, Co(II)TnPc(2-) and [Co(III)TnPc(2-)]+, as well as the oxidized TnPc(1-) and reduced TnPc(3-) oxidation states have been previously reported. Thus electronic spectroscopy provides a rapid and reliable method for assessing redox level changes occurring during the reactions described here between CoTnPc species and SOCl₂. The following chemistry is monitored by the electronic spectroscopic changes which occur when thionyl chloride, and other reagents where relevant, were added to a solution of CoTnPc in a specific oxidation state. The electronic spectra are usually sensitive to the nature of the axial groups, if any, attached to the central cobalt ion, and thus such axial groups can often be deduced.

1. Solution reaction of [Co(I)TnPc(2-)]⁻ with SOCl₂

When a small excess of thionyl chloride (4 equivalents) was added to an electrochemically generated solution of [Co(I)TnPc(2-)]⁻ in DCB the cobalt phthalocyanine was rapidly oxidized (in seconds) by two electrons to [Co(III)TnPc(2-)]⁺ (Figure 1, Table 1,h). To within experimental error, the spectrum of the oxidized product is identical to that obtained when Co(II)TnPc(2-) is oxidized electrochemically in DCB/TBACl (Table 1,i). Since
a cobalt(III) centre strongly favours a six coordinate low spin configuration, this product must certainly be \([\text{Cl}_2\text{Co(III)TnPc(2-)}]^-\), the dichloride complex, analogous to the \([(\text{DMF})_2\text{Co(III)TnPc(2-)}]^+\) complex previously characterized.

If the thionyl chloride is added to a \([\text{Co(I)TnPc(2-)}]^-\) DCB solution and not mixed, then a blue layer (confirmed to be \(\text{Co(II)TnPc(2-)}\) by electronic spectroscopy) slowly forms (minutes) between the unreacted \([\text{Co(I)TnPc(2-)}]^-\) (yellow) and the newly created \([\text{Cl}_2\text{Co(III)TnPc(2-)}]^-\) (green). The \(\text{Co(II)TnPc(2-)}\) results from the reaction,

\[
[\text{Co(I)TnPc(2-)}]^- + [\text{Cl}_2\text{Co(III)TnPc(2-)}]^- \rightarrow 2 [\text{ClCo(II)TnPc(2-)}]^- \tag{1}
\]

when the \([\text{Co(I)TnPc(2-)}]^-\) and \([\text{Cl}_2\text{Co(III)TnPc(2-)}]^-\) layers come into contact with each other. This reaction is very favorable (Table 2,(i)).

Equation 1 indicates that the cobalt(II) phthalocyanine species is formed as a chloride adduct and this was confirmed by comparing the spectrum of the \(\text{Co(II)TnPc(2-)}\) product to that of \(\text{Co(II)TnPc(2-)}\) in DCB containing \(\text{TBACl}\) (Table 1,f). Binding of chloride ions to \(\text{Co(II)TnPc(2-)}\) affects the electronic spectrum by broadening and blue shifting the Q-band, and increasing the intensity of the Soret band at 347 nm (see Figure 2).

2. Solution reaction of \(\text{Co(II)TnPc(2-)}\) with \(\text{SOCl}_2\)

The reaction between thionyl chloride and \(\text{Co(II)TnPc(2-)}\) in DCB proceeds through several stages. There is a small shift and broadening of the Q band in the electronic spectrum immediately after the addition of \(\text{SOCl}_2\) (Figure 2, Table 1,g). The spectrum is still typical of a \(\text{Co(II)}\)
phthalocyanine species and thus the product is inferred to be the adduct \((\text{SOCl}_2)\text{Co(II)TnPc(2-)}\).

After the formation of the \((\text{SOCl}_2)\text{Co(II)TnPc(2-)}\) adduct, two-electron oxidation proceeded cleanly (isosbestic points), within minutes, to form \(\text{Cl}_2\text{Co(III)TnPc(1-)}\) (Figure 3, Table 1,k). Since the starting spectrum of \(\text{Co(II)TnPc(2-)}\) does not pass through the isosbestic points all of the \(\text{Co(II)TnPc(2-)}\) was converted to the \((\text{SOCl}_2)\text{Co(II)TnPc(2-)}\) adduct (perhaps some was directly oxidized to \(\text{Cl}_2\text{Co(III)TnPc(1-)}\) immediately after the addition of \(\text{SOCl}_2\). The identity of the phthalocyanine ring oxidized radical \(\text{TnPc(1-)}\) species is assured by its electronic spectrum and esr while the presence of the two chloride ions is assumed since they will be required by the six coordinate cobalt ion; moreover species of this type have been previously identified. Indeed further verification of this species was obtained when chlorine gas was used to generate it instead of thionyl chloride. The electronic spectra of the two \([\text{Co(III)TnPc(1-)}]^2+\) products (Table 1, k and l) were virtually the same except for a decrease in the extinction coefficients for the chlorine gas case due to slight decomposition of the cobalt phthalocyanine.

The comproportionation reaction,

\[
2\text{Cl}^- + \text{Co(II)TnPc(2-)} + \text{Cl}_2\text{Co(III)TnPc(1-)} \rightarrow 2 [\text{Cl}_2\text{Co(III)TnPc(2-)}]^- \quad (2)
\]

was also observed in DCB solution using electronic spectroscopy, but only in the presence of additional chloride ions. This indicates the importance of coordinating ligands, chloride in this case, for the production of \(\text{Co(III)Pc}\) species (\(\Delta E = +0.82\text{V}\), reaction (ii) in Table 2).
3. Solution reaction of [Co(III)TnPc(2-)]+ with SOCl₂

Addition of excess thionyl chloride (40 equivalents) to a solution of [Cl₂Co(III)TnPc(2-)]⁻ in DCB (prepared from the reaction of [Co(I)TnPc(2-)]- with a small excess of SOCl₂ (4 equivalents)) subsequently yielded Cl₂Co(III)TnPc(1-) as indicated by electronic spectroscopy. The reaction between [Cl₂Co(III)TnPc(2-)]⁻ and SOCl₂ was slow, taking about 30 minutes to go to completion. Thionyl chloride did not oxidize the Cl₂Co(III)TnPc(1-) further, even after adding more SOCl₂ (up to 9000 equivalents) and heating at 50°C for thirty minutes. Dissolution of Co(II)TnPc(2-) in neat thionyl chloride also yields Cl₂Co(III)TnPc(1-).

[Note, that at low SOCl₂ concentrations [Co(I)TnPc(2-)]- can be observed to stop at the [Co(III)TnPc(2-)]+ stage since oxidation to Cl₂Co(III)TnPc(1-) is very slow under such conditions.]

Cyclic Voltammetry and Differential-Pulse Voltammetry.—

1. Cyclic voltammetry of Thionyl Chloride

Thionyl chloride has been the subject of several electrochemical investigations which have revealed remarkable complexity. In summary, there is a two-electron reduction of thionyl chloride initially to form "SO" and 2Cl⁻ with the former reacting further to yield sulphur and SO₂. The voltammogram of SOCl₂ shows the initial two-electron reduction peak at ca -0.75V (vs AgCl/Ag) in organic solvents together with waves due to the reduction of the S and SO₂ which are generated. SO₂ reduction occurs at ca -0.95V while there are two reduction waves involving sulphur at about -0.7 and -1.5V. There is some variation in these values depending on the solvent used.
In our studies some control experiments were undertaken to evaluate which waves arose from thionyl chloride reduction, and which involved CoTnPc. Blank runs were performed in DCB/TBAPF₆ in which CoTnPc, SOCl₂, S and Cl⁻ were each studied individually. Under these solvent conditions, thionyl chloride exhibits its two-electron reduction peak at -0.69V but with some dependence upon thionyl chloride concentration, as previously observed. We observe sulphur reduction peaks (solution obtained by dissolving elemental sulphur in DCB) at -0.98 and -1.26V and chloride oxidation (1.8 X 10⁻³M solution of TBACl in DCB) at 0.75V vs AgCl/Ag.

The chloride which is generated in the thionyl chloride reduction process is oxidized at 0.77V vs AgCl/Ag, in DCB solution, ca 0.3V less positive than previously noted in other organic solvents. Chloride ion is probably destabilized in DCB, a very nonpolar solvent, making oxidation of chloride to chlorine gas more favorable.

2. Cyclic Voltammetry of CoTnPc/SOCl₂

The cyclic voltammogram of cobalt tetranepentoxypthalocyanine in DCB, has been previously reported and analyzed. The molecule undergoes quasi-reversible one-electron reductions and oxidations (i⁺=i₋, i≈ν>). The first reduction process (I) yields [Co(I)TnPc(2⁻)]⁻, while the first two oxidation processes, (II) and (III), generate [Co(II)TnPc(1⁻)]⁺ and [Co(III)TnPc(1⁻)]²⁺ respectively. To study the effect of thionyl chloride on the CoTnPc waves, microlitre amounts of SOCl₂ (oxygen and HCl free) were added to an electrochemical cell containing Co(II)TnPc(2⁻) in DCB.

When the thionyl chloride was added to the cell containing Co(II)TnPc(2⁻) in DCB/TBAPF₆, oxidation of the bulk solution to Cl₂Co(III)TnPc(1⁻) occurred over a period of about 10 minutes. The cyclic
voltammogram and DPV of CoTnPc in the presence of SOCl₂ is therefore the
currentmetry of Cl₂Co(III)TnPc(1⁻) and is shown in Figure 4; the results are
listed in Table 3. All of the SOCl₂ and CoTnPc waves were well separated
from each other except for the Co(II)TnPc(2⁻)/[Co(I)TnPc(2⁻)]⁻ wave (I)
which was obscured by SOCl₂ reduction in the CV experiment, but was
observable using DPV (Figure 4).

Recording the CV or DP voltammogram from +1.5 to +0.3V vs the AgCl/Ag
reference electrode eliminated the interference from the Cl⁻ oxidation
reaction, since chloride ions are not produced until SOCl₂ is reduced.

Before the addition of any SOCl₂, the [Co(II)TnPc(1⁻)]⁺/Co(II)TnPc(2⁻)
redox couple (II) appeared as a double wave probably due to aggregation
effects. After the addition of SOCl₂ only one such wave was observed in the
cyclic and DP voltammograms. Redox couples (I) and (III) in Table 3 shifted
negatively in the presence of SOCl₂. Current ratios (iₐ/iₙ) for all of the
cobalt phthalocyanine couples were equal to unity except for the
Co(II)TnPc(2⁻)/[Co(I)TnPc(2⁻)]⁻ couple (I) which was equal to 0.91 (measured
against a pure SOCl₂ background to correct for the SOCl₂ current) when SOCl₂
was present [DPV, scan rate 5mV/s, 1.5X free SOCl₂].

Two sets of data are listed in Table 3 for the electrochemistry of
CoTnPc in the presence of different concentrations of SOCl₂. The
Co(II)/Co(I) couple (I) could not be observed in the presence of a
significant excess of thionyl chloride but could be studied with a small
excess. Also listed in Table 3 are the half-wave potentials of CoTnPc in
the presence of chloride ions (TBACl). These will be used later to analyze
the redox couples of CoTnPc in the presence of SOCl₂.

Rest Potential Measurements.- The open circuit rest potentials of
various Li/SOCl₂/C cells are listed in Table 4. Eₐ represents the Li⁺/Li
couple in SOCl₂ vs SCE under the conditions stated in Table 4:

\[ \text{Li}^+ + e^- \rightarrow \text{Li}, \quad E = E_a \quad (3) \]

while \( E_c \) represents the liquid SOCl₂/C couple vs SCE:

\[ 2 \text{SOCl}_2 + 4 e^- \rightarrow \text{S} + \text{SO}_2 + 4 \text{Cl}^- \quad E = E_c \quad (4) \]

The difference between \( E_c \) and \( E_a \) should theoretically equal the potential of the cell \( (E_{cell}) \) and this was observed within a tenth of a volt.

**Discussion**

**Electronic Spectroscopy.** - The following two-electron redox reactions between thionyl chloride and CoTnPc, can be considered.

\[ [\text{Co(I)TnPc(2-)}^- + \text{SOCl}_2 \rightarrow [\text{Cl}_2\text{Co(III)TnPc(2-)}^- + "\text{SO}" \quad (5) \]

\[ \text{Co(II)TnPc(2-)} + \text{SOCl}_2 \rightarrow \text{Cl}_2\text{Co(III)TnPc(1-)} + "\text{SO}" \quad (6) \]

\[ [\text{Cl}_2\text{Co(III)TnPc(2-)}^- + \text{SOCl}_2 \rightarrow [\text{Cl}_2\text{Co(III)TnPc(0)})^+ + "\text{SO}" + 2 \text{Cl}^- \quad (7) \]

"SO" represents the initial reduction product of SOCl₂ but is likely to react further (see below). Reactions 5 (fast) and 6 (slow) are observed, but 7 is not. Oxidation process 5 involves the two-electron oxidation of
[Co(I)TnPc(2-)]- and not two sequential one-electron oxidations via Co(II)TnPc(2-) since the latter is not observed as a one electron oxidation intermediate. Similarly, no intermediate oxidation product is observed when reaction 6 is followed via electronic spectroscopy.

Further evidence that [Co(I)TnPc(2-)]- is directly oxidized by two electrons to [Co(III)TnPc(2-)]2+ arises when reactions 5 and 6 are taken together. If, for example, [Co(I)TnPc(2-)]- is oxidized by one electron to Co(II)TnPc(2-) then one would observe either A or B below.

\[
\text{fast} \\
A) \quad [\text{Co(I)TnPc(2-)}^- + \text{SOCl}_2 \rightarrow \text{Co(II)TnPc(2-)}] \\
\text{slow} \\
\text{Co(II)TnPc(2-) + SOCl}_2 \rightarrow [\text{Co(III)TnPc(2-)}]^2+ \\
\]

\[
\text{fast} \\
B) \quad [\text{Co(I)TnPc(2-)}^- + \text{SOCl}_2 \rightarrow \text{Co(II)TnPc(2-)}] \\
\text{fast} \\
\text{Co(II)TnPc(2-) + SOCl}_2 \rightarrow [\text{Co(III)TnPc(2-)}]^+ \\
\]

The reaction between [Co(I)TnPc(2-)]- and SOCl2 must be fast because reaction 5 is fast. In case A the Co(II)TnPc(2-) reacts with thionyl chloride to give Cl2Co(III)TnPc(1-) according to reaction 6. This would result in a build up of Co(II)TnPc(2-) and the lack of production of [Cl2Co(III)TnPc(2-)]-, contrary to reaction 5. Case B, on the other hand, would satisfy reaction 5, but would contradict reaction 6. Hence, [Co(I)TnPc(2-)]- must be oxidized directly to [Cl2Co(III)TnPc(2-)]- by thionyl chloride without stopping at the Co(II)TnPc(2-) stage.
Thionyl chloride oxidizes \([\text{Cl}_2\text{Co}(\text{III})\text{TnPc}(2-)\])\(^-\) to the one electron oxidation product \(\text{Cl}_2\text{Co}(\text{III})\text{TnPc}(1-)\) and not to the two-electron oxidation product \([\text{Cl}_2\text{Co}(\text{III})\text{TnPc}(0)]^+\). It is possible that the \(\text{SOCl}_2\) could have effected two-electron oxidation but then upon mixing, 

\[\text{Cl}_2\text{Co}(\text{III})\text{TnPc}(2-)\]^- + \([\text{Cl}_2\text{Co}(\text{III})\text{TnPc}(0)]^+\] 

\[\rightarrow 2 \text{Cl}_2\text{Co}(\text{III})\text{TnPc}(1-) \quad (8)\]

There was no electronic spectroscopic evidence, however, for the two-electron oxidation product. Indeed, the potential for the production of \([\text{Co}(\text{III})\text{TnPc}(0)]^+\) is very unfavorable.\(^\text{23}\) Table 2 lists the driving forces (\(\Delta E\) values) for many \(\text{CoTnPc}\) and \(\text{SOCl}_2\) reactions. All of the reactions in Table 2 were observed in DCB solution, even reactions (iv) and (v) which have unfavorable \(\Delta E\) values.

\((\text{SOCl}_2)\text{CoTnPc}\) Adducts

Addition of thionyl chloride to \(\text{Co(II)TnPc}(2-)\) in DCB solution first yielded a \((\text{SOCl}_2)\text{Co(II)TnPc}(2-)\) adduct (Figures 2 and 3, Table 1g). A \(\text{Co(II)TnPc}(2-)\) mono thionyl chloride complex is proposed for the following reasons:

- The spectrum of the adduct after the addition of one equivalent of \(\text{SOCl}_2\) to \(\text{Co(II)TnPc}(2-)\) was the same as that obtained when a fifty fold molar excess of \(\text{SOCl}_2\) was added. This implies that not more than one molecule of \(\text{SOCl}_2\) is coordinating to the \(\text{Co(II)TnPc}(2-)\).
- The cobalt phthalocyanine was still in the \(\text{Co(II)Pc}(2-)\) oxidation state as indicated by its electronic spectrum.\(^\text{23}\)
Co(II)Pc(2-) favors the formation of five coordinate complexes.\(^2\) It is not certain at this time whether the oxygen or sulphur atom of SOCl\(_2\) is coordinating to the Co(II) metal center.

It is also possible that SOCl\(_2\) could coordinate to the phthalocyanine ligand. Brønsted acids, do indeed, protonate phthalocyanines and it is believed that the protons bind to the outer nitrogen atoms of the pc ring.\(^3\) When the phthalocyanine is protonated the Q band in the electronic spectrum shifts (ca 30 nm per bound proton) to longer wavelengths. Since shifts of this kind were not observed in the reactions with SOCl\(_2\), interactions between thionyl chloride (acting as a Lewis acid) and the phthalocyanine ring were minimal.

Cyclic Voltammetry and DPV of CoTnPc.- The electrochemistry of CoTnPc in the presence of thionyl chloride was complicated by the SOCl\(_2\) and chloride ions present. There are three potential sources of chloride ion:

1. Electrochemical reduction of SOCl\(_2\).
2. Reaction between CoTnPc species and SOCl\(_2\), and
3. Hydrolysis of thionyl chloride producing HCl.

Case 3 was eliminated by using anhydrous conditions and bubbling nitrogen through the SOCl\(_2\) prior to use to displace the HCl already present. In all of our studies, electronic spectroscopy showed that less than 5% of the CoTnPc was protonated due to the HCl from the thionyl chloride.

Before the addition of thionyl chloride to Co(II)TnPc(2-) in DCB the \([\text{Co(II)TnPc(1-)}]^+/\text{Co(II)TnPc(2-)}\) redox couple (II) yielded a double wave. Co(II)TnPc species are known to aggregate\(^4\) and such aggregation can cause splitting of waves in the cyclic voltammogram.\(^5\) After adding SOCl\(_2\).
however, this couple yielded a single wave. The effect of \( \text{SOCl}_2 \) on the 
\( \text{Co(II)}\text{TnPc(2\text{-})} \) redox couple can be explained in terms of the formation of a
\( \text{(SOCl}_2\text{)}\text{Co(II)}\text{TnPc(2\text{-})} \) adduct that was observed above using electronic
spectroscopy. Axial coordination of \( \text{SOCl}_2 \) to \( \text{Co(II)}\text{TnPc} \) will greatly reduce
aggregation and hence the first oxidation couple yields a single wave.

It is also possible that chloride ions could be responsible for the collapse
of the double wave. Electronic spectroscopy, however, has shown that \( \text{SOCl}_2 \)
binds much more strongly to \( \text{Co(II)}\text{TnPc(2\text{-})} \) than \( \text{Cl}^- \). A thousand times
excess of chloride ions are needed to obtain a limiting spectrum of 
\( \text{[ClCo(II)}\text{TnPc(2\text{-})]}^- \) whereas \( \text{Co(II)}\text{TnPc(2\text{-})} \) is completely converted to
\( \text{(SOCl}_2\text{)}\text{Co(II)}\text{TnPc(2\text{-})} \) after the addition of one equivalent of \( \text{SOCl}_2 \).

\( \text{[Co(I)}\text{TnPc(2\text{-})]}^- \) is not expected to bind axial ligands because of the
lower oxidation state of the cobalt and the \( \text{d}^8 \), square planar configuration
of the molecule. The shift of the \( \text{Co(II)}\text{TnPc(2\text{-})}/[\text{Co(I)}\text{TnPc(2\text{-})}^- \) couple (I)
in the presence of \( \text{SOCl}_2 \) (Table 3), therefore, reflects the preferential
binding of \( \text{SOCl}_2 \) to \( \text{Co(II)}\text{TnPc(2\text{-})} \) over \( \text{[Co(I)}\text{TnPc(2\text{-})]}^- \). If the thionyl
chloride is donating electron density to the \( \text{Co(II)} \) metal center,
\( \text{(SOCl}_2\text{)}\text{Co(II)}\text{TnPc(2\text{-})} \) will be more difficult to reduce than free
\( \text{Co(II)}\text{TnPc(2\text{-})} \) and the half wave potential of the \( \text{Co(II)}/\text{Co(I)} \) wave will
shift in the negative direction (as observed) due to the removal of
\( \text{Co(II)}\text{TnPc(2\text{-})} \) as the thionyl chloride adduct.

The first oxidation couple of \( \text{CoTnPc} \) in the presence of \( \text{SOCl}_2 \)
is more difficult to assign because oxidation could occur either at the
\( \text{Co(II)} \) metal center or at the \( \text{Pc(2\text{-})} \) ligand. Two different oxidized
species are possible, \( \text{[Co(II)}\text{TnPc(1\text{-})]}^+ \) or \( \text{[Co(III)}\text{TnPc(2\text{-})]}^+ \), depending on
the nature of the solvent and electrolyte present. Previous work\( ^2 \) has
shown that \( \text{Co(II)}\text{TnPc(2\text{-})} \) is oxidized to \( \text{[Co(II)}\text{TnPc(1\text{-})]}^+ \) in DCB/TBAP and
to \([\text{Co(III)TnPc}(2-)\]^+\) in DMF TBAP. In DMF solution, coordination of the solvent to the Co center favors the formation of the Co(III) species. The different redox couples of CoTnPc have been defined as follows:

\[
\begin{align*}
I & : \text{Co(II)TnPc}(2-) \rightarrow [\text{Co(II)TnPc}(2-)\]^+ \\
II & : [\text{Co(II)TnPc}(1-)\]^+ \rightarrow \text{Co(II)TnPc}(2-) \\
II' & : [\text{Co(III)TnPc}(2-)\]^+ \rightarrow \text{Co(II)TnPc}(2-) \\
III & : [\text{Co(III)TnPc}(1-)\]^2+ \rightarrow [\text{Co(II)TnPc}(1-)\]^+ \\
III' & : [\text{Co(III)TnPc}(1-)\]^2+ \rightarrow [\text{Co(III)TnPc}(2-)\]^+ \\
\end{align*}
\]

As can be seen in Table 3, the half-wave potentials for couples II and II' only differ by 50 mV, making it difficult to determine the chemistry involved from the potential alone.

The oxidation potentials of CoTnPc in the presence of chloride ion (TBACl) are identical, within experimental error, to those in the presence of 28 equivalents of thionyl chloride. This suggests that the redox processes are the same for both systems. In the presence of TBACl it was shown by spectroelectrochemistry (Table 1.i) that oxidation of \(\text{Co(II)TnPc}(2-)\) by one electron yields \([\text{Cl}_2\text{Co(II)TnPc}(2-)\]^+\). Hence, in DCB/TBACl and DCB/SOCl\(_2\) the first oxidation couple is \([\text{Co(III)TnPc}(2-)\]^+/\text{Co(II)TnPc}(2-)\) (couple II' in Table 3).

Chloride ions are needed over SOCl\(_2\) for the production of \([\text{Co(III)TnPc}(2-)\]^+\) because reaction 2 does not proceed in the presence of excess SOCl\(_2\), but only proceeds in the presence of additional chloride ions. Cyclic voltammetry has also shown that Co(III)TnPc species preferentially bind Cl\(^-\) over SOCl\(_2\). When CoTnPc is added to an electrochemical cell containing SOCl\(_2\) ([SOCl\(_2\)]=2.8 \times 10^{-3}M and [CoTnPc]=2.2 \times 10^{-4}M) the current
associated with the Cl₂/2Cl⁻ couple is dramatically reduced (the anodic current due to 2Cl⁻ → Cl₂ + 2e⁻ was 1.16 µA before the addition of CoTnPc and 0.26 µA afterwards using a Pt disk electrode of area 1.02 × 10⁻³ cm²).

The chloride ions result from the reduction of SOC₁₂ and since [ClCo(II)TnPc(2⁻)]⁻ is oxidized to [Cl₂Co(III)TnPc(2⁻)]⁻ before chloride ions are oxidized to chlorine gas, one chloride ion is lost at the electrode surface for every [Cl₂Co(III)TnPc(2⁻)]⁻ produced.

In summary, we propose the following redox couples for the cyclic voltammetry of CoTnPc in the presence of SOC₃₂.

I  (SOC₁₂)Co(II)TnPc(2⁻)/[Co(I)TnPc(2⁻)]⁻

II'  [Cl₂Co(III)TnPc(2⁻)]⁻/(SOC₁₂)Co(II)TnPc(2⁻)

III'  Cl₂Co(III)TnPc(3⁻)/[Cl₂Co(III)TnPc(2⁻)]⁻

The identity of the waves could be further complicated, however, depending upon the kinetics of the equilibria reactions involved.

With an excess of SOC₃₂ present, the various CoTnPc species, produced at the electrode surface, in lower oxidation states than Cl₂Co(III)TnPc(1⁻) can be reoxidized by the thionyl chloride in solution. This is an example of a catalytic EC' mechanism:³⁶

\[
0 + n \text{e}^- \rightleftharpoons R
\]

\[
R + Z \rightarrow 0 + Y
\]  \hspace{1cm} (10)

O represents [Co(III)TnPc(1⁻)]²⁺, Z is SOC₃₂, Y represents the SOC₃₂ reduction products and R is either [Co(I)TnPc(2⁻)]⁻, Co(II)TnPc(2⁻) or [Co(III)TnPc(2⁻)]⁺. An important feature in the differential-pulse voltammogram of CoTnPc is that the current ratio (iₐ/iₖ) for the
Co(II)TnPc(2-) / [Co(I)TnPc(2-)]$^-\$ redox couple changed from unity to 0.91 in the presence of 1.5 equivalents of thionyl chloride. The cathodic current is larger than the anodic current because of the oxidation of [Co(I)TnPc(2-)]$^-$ by SOCl$_2$. Reaction 5 will increase $i_c$ due to reduction of the [Cl$_2$Co(III)TnPc(2-)]$^-$ produced, and decrease $i_a$ due to removal of [Co(I)TnPc(2-)]$^-\$. There is, in effect, a catalytic current due to the conversion of the reduced species to an oxidized species by the SOCl$_2$. This was only observed for the redox couple involving [Co(I)TnPc(2-)]$^-\$. While [Co(I)TnPc(2-)]$^-\$ reacts rapidly with thionyl chloride catalytic currents were not observed for the other CoTnPc redox couples because the reaction of SOCl$_2$ with Co(II)TnPc(2-) and [Co(III)TnPc(2-)]$^+$ was too slow to be observed on the time scale of the DPV experiment (5mV/s).

Lithium cell: Rest Potential Measurements. - The addition of AlCl$_3$ to a Li/SOCl$_2$/C cell had a large effect (0.63V shift) on the Li$^+$/Li redox couple; it became much more favorable to produce Li$^+$. This was reflected in an increase of the cell potential by the same amount (0.64V). Hence, the AlCl$_3$ must be stabilizing the LiCl product as the LiAlCl$_4$ complex salt. Theoretical calculations$^{37}$ predict a change in potential between 530 and 630 mV, depending upon the value of the equilibrium constant for the reaction.

Previous work by Madou et al.$^{38,39}$ indicated that the potential of the lithium electrode is not affected by AlCl$_3$. They added AlCl$_3$ to a cell already containing LiAlCl$_4$ electrolyte. Since LiAlCl$_4$ can dissociate to LiCl and AlCl$_3$, their experiment was not as sensitive to the addition of AlCl$_3$ as the one performed above in which AlCl$_3$ was added to neat SOCl$_2$.

Rest potential measurements of the carbon cathode in a Li/SOCl$_2$/C cell revealed that thionyl chloride is a strong oxidizing agent ($E=0.58$ to 0.79V
vs SCE in Table 4). This is not obvious, however, from the cyclic voltammogram of \( \text{SOCl}_2 \) where the reduction wave of \( \text{SOCl}_2 \) peaks at \(-0.69\) V vs AgCl/Ag. A large overpotential must, therefore, be required to overcome the activation energy barrier of adding an electron to \( \text{SOCl}_2 \). This implies the formation of a high energy intermediate, for example,

\[
\text{SOCl}_2 + e^- \rightarrow \text{SOCl}^- + \text{Cl}^- \quad (11)
\]

A very recent paper reports evidence that the first charge transfer step is rate determining. The formation of a high energy intermediate could explain the two-electron reactions observed between CoTnPc and \( \text{SOCl}_2 \). The \( \text{SOCl}^- \) intermediate, formed after the transfer of one electron from CoTnPc to \( \text{SOCl}_2 \) (perhaps bound to the cobalt center), may drive the transfer of a second electron to produce SO and \( \text{Cl}^- \) in some kind of concerted reaction.

The addition of Co(II)TnPc(2-) (oxidized to \( \text{Cl}_2\text{Co(III)TnPc}^- \)) by \( \text{SOCl}_2 \) to the thionyl chloride cells described in Table 4 had little effect on the lithium, thionyl chloride and overall cell potentials. Madou and coworkers have also studied the effect of CoPc in a Li/\( \text{SOCl}_2 \) cell. Addition of CoPc increased the rest potential of the cell, but only by 100 mV. Because the changes in electrochemical potentials are small, one could infer that the thermodynamics of the reaction between \( \text{SOCl}_2 \) and Li are unchanged in the presence of CoPc, i.e., the products of the reaction are the same. This, however, would be premature since the concentration of CoPc dissolved in the thionyl chloride is very small, many orders of magnitude less than the amount of \( \text{SOCl}_2 \).
Implications for Li/SOCl₂ Batteries. - If the carbon cathode of a Li/SOCl₂ battery is coated or impregnated with cobalt phthalocyanine the thionyl chloride will oxidize the exposed CoTnPc to Cl₂Co(III)TnPc(1⁻) under open circuit conditions. In closed circuit, however, the carbon cathode will reduce the oxidized cobalt phthalocyanine. To determine the lowest oxidation state of CoTnPc in a Li/SOCl₂/C battery the electronic spectrum of Co(II)TnPc(2⁻) in DCB was monitored in the presence of a piece of graphite inserted into a lump of lithium (see expt. section). The Co(II)TnPc(2⁻) was reduced to [Co(I)TnPc(2⁻)]⁻ (Table 1,d). The [Co(I)TnPc(2⁻)]⁻ solution was allowed to stand in contact with the Li/C for two days to ensure that this was indeed the lowest oxidation state of CoTnPc achievable under these conditions.

The following mechanism is, therefore, evident for the reduction of thionyl chloride in a Li/SOCl₂/(CoTnPc,C) battery.

\[
[\text{Co(I)TnPc(2⁻)]}⁻ + \text{SOCl}_2 \rightarrow [\text{Cl}_2\text{Co(III)TnPc(2⁻)]}⁻ + "\text{SO}"
\]

\[
2\text{Li} + [\text{Cl}_2\text{Co(III)TnPc(2⁻)]}⁻ \rightarrow [\text{Co(I)TnPc(2⁻)]}⁻ + 2\text{LiCl}
\]

summing to:

\[
2\text{Li} + \text{SOCl}_2 \rightarrow "\text{SO}" + 2\text{LiCl}
\]

The CoTnPc will act as a mediator between the carbon cathode and the thionyl chloride. Assuming good electrical contact between the cobalt phthalocyanine catalyst and the carbon cathode, the oxidation state of the
CoTnPc will fluctuate, from $[\text{Co}(I)\text{TnPc}(2-)^-]$ (reduced by the cathode) to $\text{Cl}_2\text{Co}(\text{III})\text{TnPc}(2^-)$ (oxidized by $\text{SOCl}_2$). As a result, the $\text{SOCl}_2$ will be catalytically reduced by two electrons. "SO" and chloride ions may not be the actual products of the thionyl chloride reduction. These species have been chosen only because they are the simplest two-electron reduction products of $\text{SOCl}_2$. Riga\textsuperscript{40} however, does report that sulphur and chloride ions are products of thionyl chloride reduction by iron and molybdenum phthalocyanines. The sulphur probably results from the disproportionation reaction of SO to yield $S$ and $\text{SO}_2$. Some evidence for the existence of SO has been recently reported.\textsuperscript{7}

A two-electron reduction process could result in a safer Li/$\text{SOCl}_2$ battery by eliminating reactive intermediates that may form when $\text{SOCl}_2$ is reduced at a bare carbon cathode. The mechanism for the reduction of $\text{SOCl}_2$ at a carbon electrode is not well understood. The generally accepted cell reaction is the two-electron reduction of thionyl chloride to sulphur, sulphur dioxide and chloride ion. Many other species, however, have been identified.\textsuperscript{1,3-6} Doddapaneni\textsuperscript{13-15} proposes that the first step is the reduction of $\text{SOCl}_2$ to the SOCl\textsuperscript{·} radical (Equation 11). The SOCl\textsuperscript{·} radical dimerizes and then decomposes to several intermediate species, some of which are known to cause safety hazards. When metal phthalocyanines are present, Doddapaneni proposes that the SOCl\textsuperscript{·} radical (adsorbed on the YPc) can undergo a further one-electron reduction. Our work has shown this to be the case.

$\text{SOCl}_2$ as a Two-electron Oxidizing Agent.—Thionyl chloride has been shown to oxidize CoTnPc by two electrons. Whether the reaction represents a true two-electron transfer or two step-wise, but concerted, one-electron transfers remains to be solved. Schmidbaur and Jandik\textsuperscript{41} have also reported
a two-electron oxidation using thionyl chloride. The gold(I)dimethylphosphonium-bis-methyldide dimer 1 is oxidized to the gold(III) complex 3, without any gold(II) intermediate being observed. Using 1,2-dichloro or 1,2-dibromo-ethane, on the other hand, the gold(I) dimer is converted into the Au-Au bonded gold(II) complex. Ethylene is eliminated in this oxidative addition process. Compound 2 can also be prepared using chlorine or bromine. Excess halogen will convert either 1 or 2 into the Au(III) complex 3.

The two-electron reaction between thionyl chloride and the gold(I)dimethylphosphonium-bis-methyldide dimer parallels our observed reactions between CoTnPc species and SOCl₂. The similarity between these two systems is remarkable: two-electron oxidations are observed with no sign of the one-electron intermediate being formed, and, in each case, the one-electron oxidation product is stable and can be prepared using alternative methods.

\[
\begin{align*}
(1) & \quad \text{Me}_2\text{P} \quad \text{Au} \quad \text{P} \quad \text{Me}_2 \\
& \quad \text{Cl}_2 \text{Au} \quad \text{Cl}_2 \\
(2) & \quad \text{Cl}-\text{Au} \quad \text{Au-Cl} \\
& \quad \text{Cl}\text{Me}_2\text{P} \quad \text{Me}_2 \quad \text{P} \quad \text{Me}_2 \\
& \quad \text{Cl}-\text{Me}_2\text{P} \quad \text{Me}_2 \quad \text{P} \quad \text{Me}_2
\end{align*}
\]
The kinetics of the reaction between CoTnPc and SOCl₂ are presently being studied to obtain more mechanistic information.

Conclusions

1. Thionyl chloride reacts with [Co(I)TnPc(2-)]⁻ and Co(II)TnPc(2-) to give two-electron oxidized species (Equations 5 and 6). [Co(III)TnPc(2-)]⁺ is oxidized by one electron to [Co(III)TnPc(1-)]²⁺. Co(II)TnPc(2-) first forms a monothionyl chloride adduct and is then oxidized to Cl₂Co(III)TnPc(1-).
2. A comproportionation reaction is observed between [Co(I)TnPc(2-)]⁻ and its two-electron oxidized product [Cl₂Co(III)TnPc(2-)²⁻]⁻ (Equation 1).
3. The lowest possible oxidation state of CoTnPc in a Li/SOCl₂/C battery is [Co(I)TnPc(2-)]⁻ due to reduction at the carbon cathode.
4. A two-electron catalytic cycle is indicated for the reduction of thionyl chloride in a Li/SOCl₂/(CoTnPc,C) battery. A two-electron reduction process could result in a safer Li/SOCl₂ battery by eliminating reactive intermediates that may form when SOCl₂ is reduced by one electron at a carbon cathode not treated with cobalt phthalocyanine.

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References


42. Bernstein, P. A.; Lever, A. B. P., to be submitted for publication.
### Table 1. Electronic absorption maxima of cobalt tetraneopentoxyphthalocyanines.

<table>
<thead>
<tr>
<th>Species &amp; Footnote</th>
<th>λ nm (ε, M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(I)TnPc(2-)][TBA]+</td>
<td>a 356sh 472(38100) 645(16800) 710(54700)</td>
</tr>
<tr>
<td>b 313(57900) 350sh 471(33300) 643(18400) 708(51300)</td>
<td></td>
</tr>
<tr>
<td>[Co(I)TnPc(2-)][Li/TBA]+</td>
<td>c 359sh 471(36600) 647(17200) 709(51300)</td>
</tr>
<tr>
<td>d 356sh 472(38100) 645(16800) 710(54700)</td>
<td></td>
</tr>
<tr>
<td>Co(II)TnPc(2-)</td>
<td>e 383(13800) 614(24200) 680(83800)</td>
</tr>
<tr>
<td>f 330(40700) 380(13800) 612(25700) 678(72400)</td>
<td></td>
</tr>
<tr>
<td>[C1Co(II)TnPc(2-)][TBA]+</td>
<td>g 347</td>
</tr>
<tr>
<td>367(33500) 608(31200) 678(133000)</td>
<td></td>
</tr>
<tr>
<td>(SOC12)Co(II)TnPc(2-)</td>
<td>h 343</td>
</tr>
<tr>
<td>393(25900) 623(32000) 686(93900)</td>
<td></td>
</tr>
<tr>
<td>[Cl2Co(III)TnPc(2-)][TBA]+</td>
<td>i 343</td>
</tr>
<tr>
<td>369(30900) 607(31800) 677(134000)</td>
<td></td>
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<tr>
<td>[(DMF)2Co(III)TnPc(2-)][ClO4]-</td>
<td>j 355(63100) 610(37200) 676(148000)</td>
</tr>
<tr>
<td>k 399(24800) 540(26500) 679(171000)sh 755(20600)br</td>
<td></td>
</tr>
<tr>
<td>l 366sh 404(23000) 540(20600) 680(167000)sh 744(18900)br</td>
<td></td>
</tr>
<tr>
<td>(Cl04)2Co(II)TnPc(1-)</td>
<td>m 380(23600) 400(24000) 520(16600) 580sh 742(11500)</td>
</tr>
</tbody>
</table>

*<sup>a</sup>[CoTnPc]⁺10⁻⁴M in DCB solution except as otherwise noted.  ^<sup>b</sup>Electrochemical reduction of Co(II)TnPc(2-). [TBAPf]=0.048M.  ^<sup>c</sup>Electrochemical reduction of Co(II)TnPc(2-), [TBAP]=0.3M.  ^<sup>d</sup>Reduction of Co(II)TnPc(2-) using Li/C with 0.07M TBAPf.  ^<sup>e</sup>With 0.3M TBAP.  ^<sup>f</sup>With 0.10M TBACl.  ^<sup>g</sup>[SOC12]=2.7 X 10⁻³M.  ^<sup>h</sup>From the oxidation of Co(I)TnPc(2-) containing 0.07M TBAPf with 4 X 10⁻⁴M SOC12.  ^<sup>i</sup>Electrochemical oxidation of Co(II)TnPc(2-), [TBACl]=0.10M.  ^<sup>j</sup>Electrochemical oxidation of Co(II)TnPc(2-) in DMP solution containing 0.3 M TBAP.  ^<sup>k</sup>From the oxidation of Co(II)TnPc(2-) with 0.013M SOC12.  ^<sup>l</sup>Oxidation of Co(II)TnPc(2-) by chlorine gas.  ^<sup>m</sup>Electrochemical oxidation of Co(II)TnPc(2-). [TBAP]=0.3M.  ^<sup>n</sup>TBAP=tetrabutylammonium perchlorate. DMF=dimethylformamide.  br=broad and sh=shoulder.
Table 2. Driving forces (ΔE values) for CoTnPc and SOCl₂ reactions in DCB calculated using the half-wave potentials of CoTnPc in Table 3 and using 0.15V vs Fc⁺/Fc (0.64V vs SCE. Table 4) for the reduction potential of SOCl₂.

<table>
<thead>
<tr>
<th>CoTnPc Comproportionation Reactions</th>
<th>ΔE(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Co(I)TnPc(2-)(TBA) + Cl₂Co(III)TnPc(2-)(TBA)</td>
<td>1.06</td>
</tr>
<tr>
<td>--&gt; 2ClCo(II)TnPc(2-)(TBA)</td>
<td></td>
</tr>
<tr>
<td>ii) Co(II)TnPc(2-) + Cl₂Co(III)TnPc(1-) + 2TBACl</td>
<td>0.82</td>
</tr>
<tr>
<td>--&gt; 2Cl₂Co(III)TnPc(2-)(TBA)</td>
<td></td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>CoTnPc + SOCl₂ Reactions(^b)</th>
<th>ΔE(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iii) Co(I)TnPc(2-)(TBA) + SOCl₂ --&gt; Cl₂Co(III)TnPc(2-)(TBA) + &quot;SO&quot;</td>
<td>0.74</td>
</tr>
<tr>
<td>iv) Co(II)TnPc(2-) + SOCl₂ --&gt; Cl₂Co(III)TnPc(1-) + &quot;SO&quot;</td>
<td>-0.09</td>
</tr>
<tr>
<td>v) 2Cl₂Co(III)TnPc(2-)(TBA) + SOCl₂ --&gt; 2Cl₂Co(III)TnPc(1-) + &quot;SO&quot; + 2TBACl</td>
<td>-0.50</td>
</tr>
</tbody>
</table>

*These potential differences are approximately equal to ΔE\(^\circ\). Using RTlnK = nFΔE\(^\circ\), where n = 1 and T = 294 K. yields K = 1.5 x 10\(^{18}\) for (i) and K = 1.1 x 10\(^{14}\) for (ii). \(^b\)For these calculations it was assumed that SOCl₂ is reduced by two electrons at 0.15V vs Fc⁺/Fc in DCB.
Table 3. Electrochemical data for cobalt tetraneopentoxyphthalocyanine in DCB.

<table>
<thead>
<tr>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>III'</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>E+ V (ΔE_p mV)</th>
<th>Oxidation Event</th>
<th>Reduction Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>In DCB/TBAPb</td>
<td>+0.39 (90)</td>
<td>+0.03 (89)</td>
<td>-0.91 (70)</td>
</tr>
<tr>
<td>In DCB/TBAPF6c</td>
<td>+0.69 (63)</td>
<td>+0.17d</td>
<td>-1.01 (104)</td>
</tr>
<tr>
<td></td>
<td>-0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>with 6 equiv Cl-</td>
<td>+0.65 (122)</td>
<td>-0.06 (115)</td>
<td>-1.12</td>
</tr>
<tr>
<td>In the presence of SOCl2:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5X free SOCl2f</td>
<td>+0.68 (63)</td>
<td>+0.01 (100)</td>
<td>-1.11</td>
</tr>
<tr>
<td>28 equiv SOCl2g</td>
<td>+0.65 (75)</td>
<td>-0.04 (117)</td>
<td></td>
</tr>
<tr>
<td>In DMF/TBAPb</td>
<td>+0.38</td>
<td>-0.02</td>
<td>-0.85 (83)</td>
</tr>
</tbody>
</table>

*Potentials are reported with respect to the ferrocenium/ferrocene couple. $E_+=(E_{pa}+E_{pc})/2$ and $E_p=E_{pa}-E_{pc}$. See text for definition of couples. bThese literature half-wave potentials and peak separations are for a 1 X 10^-4M CoTnPc solution in DCB or DMF containing 0.1M TBAP at a scan rate (v) of 20mV/s. i_i=i_c and i_i=v v 1/2. c[CoTnPc]=1.62 X 10^-4M in DCB, [TBAPF6]=0.067M. Peak separations were measured by cyclic voltammetry at 100 mV/s. DPV at 5 mV/s was used to determine the half-wave potentials and current ratios. i_i=i_c for the three redox couples. dA double wave was observed. The wave at +0.17V was approximately twice as large as the one at -0.06V. e[CoTnPc]=3 X 10^-4M in DCB, [TBAPF6]=0.07M. [TBACl]=1.8 X 10^-3M, v=100 mV/s. fSame conditions as in (c) except with 2.5 X 10^-4M free SOCl2 (est. from the SOCl2 reduction current). i_i=i_c for couples II' and III'. i_i=0.91 i_c for couple I. g[CoTnPc]=1.22 X 10^-4M, [SOCl2]= 3.4 X 10^-3M. [TBAPF6]=0.058M in DCB, v=50 mV/s. i_i=i_c for couples II' and III'.
Table 4. Open circuit rest potentials in volts of Li/SOCl₂/C cells.

<table>
<thead>
<tr>
<th>Conditions</th>
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<td>3.81</td>
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<td>-2.96</td>
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<td>1.6M LiAlCl₄,AlCl₃,CoPc</td>
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*Thionyl chloride was the only solvent used and was exposed to the air. At room temperature, the maximum solubility of HCl (from the hydrolysis of SOCl₂) is 0.28M.²² The HCl acted as the electrolyte when measuring the electrode potentials in neat SOCl₂.
LEGENDS

**Figure 1.** Electronic absorption spectra of Co(I)TnPc(2-)(TBA) (---) and its two electron oxidation product Cl₂Co(III)TnPc(2-)(TBA) (----) with SOCl₂ in DCB. [CoTnPc] = 8.65 × 10⁻⁵ M, [TBAPF₆] = 0.07 M and [SOCl₂] = 4 × 10⁻⁴ M.

**Figure 2.** Electronic absorption spectra of Co(II)TnPc(2-) (---), (SOCl₂)Co(II)TnPc(2-) (----) and [ClCo(II)TnPc(2-)]⁻ (· · ·) in DCB. [CoTnPc] = 6.12 × 10⁻⁵ M, [SOCl₂] = 2.8 × 10⁻³ M for the thionyl chloride adduct, and [TBACl] = 0.10 M for the chloro complex.

**Figure 3.** Oxidation of Co(II)TnPc(2-) to Cl₂Co(III)TnPc(1-) by thionyl chloride in DCB. [CoTnPc] = 1.14 × 10⁻⁴ M, [SOCl₂] = 5.5 × 10⁻³ M. These spectra were recorded over a period of 11 minutes at room temperature.

**Figure 4.** Cyclic voltammogram (---, ν=100 mV/s) and DPV (—, ν=5 mV/s, 5 mV modulation amplitude) of a DCB solution of CoTnPc and SOCl₂. [CoTnPc] = 1.62 × 10⁻⁴ M, [SOCl₂] = 2.5 × 10⁻⁴ M and [TBAPF₆] = 0.087 M. The ferrocenium/ferrocene couple occurred at +0.43 V vs AgCl/Ag.
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