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

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

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Cyclic voltammetry, DPV and electronic spectroscopy are used to study the reaction between thionyl chloride and cobalt phthalocyanine. $SOCl_2$ reacts with $[Co(I)TnPc(2-)]^-$ and Co(II)TnPc(2-) to give two-electron oxidized species. Implications for $Li/SOCl_2$ batteries are discussed. Thionyl chloride also forms a mono $SOCl_2$ adduct with Co(II)TnPc(2-). Driving forces (ΔE values) have been calculated for CoTnPc comproportionation and CoTnPc + $SOCl_2$ reactions. Rest potential measurements of a $Li/SOCl_2$ cell show that addition of $AlCl_3$ stabilizes the LiCl product as $LiAlCl_4$. A catalytic two-electron mechanism is indicated for the reduction of thionyl chloride in a $Li/SOCl_2$/(CoTnPc,C) battery.

Introduction

The lithium/thionyl chloride ($SOCl_2$) 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]

$$2SOCl_2 + 4Li \longrightarrow S + SO_2 + 4LiCl$$

Intermediate species such as S_2Cl_2, SCl_2, SO, S_2O, SO_2 and SO_2Cl_2 have been reported.[1,3-8] The use of Li/$SOCl_2$ batteries has been greatly restricted, however, because of the explosion hazard. Studies[9] have shown that unstable intermediates from $SOCl_2$ reduction are responsible for spontaneous exothermic reactions in discharged cells. Safety vents can be installed in Li/$SOCl_2$ 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/$SOCl_2$ 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 $SOCl_2$ molecule at an FePc treated carbon electrode than at a bare carbon electrode. For example, if $SOCl_2$ is reduced by two electrons at an FePc electrode then 1.47 electrons, on the average, are transferred to each $SOCl_2$ 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.[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 ($TBAPF_6$)(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 1.02×10^{-3} cm^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[21] 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}M 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^{-4}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 µl 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 $SOCl_2$[22] 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.[23] 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.[23-25] (Table 1,c,e,j,m) Thus electronic spectroscopy provides a rapid and reliable method for assessing redox level changes occurring during the reactions described here between CoTnPc species and $SOCl_2$. 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 $SOCl_2$

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,[26] this product must certainly be $[Cl_2Co(III)TnPc(2-)]^-$, the dichloride complex, analogous to the $[(DMF)_2Co(III)TnPc(2-)]^+$ complex previously characterized.[23] (Table 1,j)

If the thionyl chloride is added to a $[Co(I)TnPc(2-)]^-$ DCB solution and not mixed, then a blue layer (confirmed to be Co(II)TnPc(2-) by electronic spectroscopy) slowly forms (minutes) between the unreacted $[Co(1)TnPc(2-)]^-$ (yellow) and the newly created $[Cl_2Co(III)TnPc(2-)]^-$ (green). The Co(II)TnPc(2-) results from the reaction,

$$[Co(I)TnPc(2-)]^- + [Cl_2Co(III)TnPc(2-)]^- \longrightarrow 2\,[ClCo(II)TnPc(2-)]^- \quad (1)$$

when the $[Co(I)TnPc(2-)]^-$ and $[Cl_2Co(III)TnPc(2-)]^-$ 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 was confirmed by comparing the spectrum of the Co(II)TnPc(2-) product to that of Co(II)TnPc(2-) in DCB containing TBACl (Table 1,f). Binding of chloride ions to 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 Co(II)TnPc(2-) with $SOCl_2$

The reaction between thionyl chloride and 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 $SOCl_2$ (Figure 2, Table 1,g). The spectrum is still typical of a Co(II) phthalocyanine species[23] and thus the product is inferred to be the adduct $(SOCl_2)Co(II)TnPc(2-)$.

After the formation of the $(SOCl_2)Co(II)TnPc(2-)$ adduct, two-electron oxidation proceeded cleanly (isosbestic points), within minutes, to form $Cl_2Co(III)TnPc(1-)$ (Figure 3, Table 1,k). Since the starting spectrum of Co(II)TnPc(2-) does not pass through the isosbestic points all of the Co(II)TnPc(2-) was converted to the $(SOCl_2)Co(II)TnPc(2-)$ adduct (perhaps some was directly oxidized to $Cl_2Co(III)TnPc(1-)$) immediately after the addition of $SOCl_2$. The identity of the phthalocyanine ring oxidized radical TnPc(1-) species is assured by its electronic spectrum[24,25] and esr[24] 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.[24] 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 $[Co(III)TnPc(1-)]^{2+}$ 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,

$$2Cl^- + Co(II)TnPc(2-) + Cl_2Co(III)TnPc(1-) \longrightarrow 2\,[Cl_2Co(III)TnPc(2-)]^- \quad (2)$$

was also observed in DCB solution using electronic spectroscopy, but <u>only</u> in the presence of additional chloride ions. This indicates the importance of coordinating ligands, chloride in this case, for the production of Co(III)Pc species (ΔE=+0.82V, reaction (ii) in Table 2).

3. Solution reaction of $[Co(III)TnPc(2-)]^+$ with $SOCl_2$

Addition of excess thionyl chloride (40 equivalents) to a solution of $[Cl_2Co(III)TnPc(2-)]^-$ in DCB (prepared from the reaction of $[Co(I)TnPc(2-)]^-$ with a small excess of $SOCl_2$ (4 equivalents)) subsequently yielded $Cl_2Co(III)TnPc(1-)$ as indicated by electronic spectroscopy. The reaction between $[Cl_2Co(III)TnPc(2-)]^-$ and $SOCl_2$ was slow, taking about 30 minutes to go to completion. Thionyl chloride did not oxidize the $Cl_2Co(III)TnPc(1-)$ further, even after adding more $SOCl_2$ (up to 9000 equivalents) and heating at 50°C for thirty minutes. Dissolution of Co(II)TnPc(2-) in neat thionyl chloride also yields $Cl_2Co(III)TnPc(1-)$.

[Note, that at low $SOCl_2$ concentrations $[Co(I)TnPc(2-)]^-$ can be observed to stop at the $[Co(III)TnPc(2-)]^+$ stage since oxidation to $Cl_2Co(III)TnPc(1-)$ 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[1,7,16,17,27,28] 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 SO_2. The voltammogram of $SOCl_2$ 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 SO_2 which are generated. SO_2 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/TBAPF$_6$ in which CoTnPc, SOCl$_2$, 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.[1] We observe sulphur reduction peaks (solution obtained by dissolving elemental sulphur in DCB) at -0.98 and -1.26V and chloride oxidation (1.8×10^{-3}M 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.[1,7] Chloride ion is probably destablized in DCB, a very nonpolar solvent, making oxidation of chloride to chlorine gas more favorable.

2. Cyclic Voltammetry of CoTnPc/SOCl$_2$

The cyclic voltammogram of cobalt tetraneopentoxyphthalocyanine in DCB, has been previously reported and analyzed.[23] The molecule undergoes quasi-reversible one-electron reductions and oxidations ($i_a = i_c$, $i \propto \nu^{1/2}$). 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 SOCl$_2$ (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/TBAPF$_6$, oxidation of the bulk solution to Cl$_2$Co(III)TnPc(1-) occurred over a period of about 10 minutes. The cyclic voltammogram and DPV of CoTnPc in the presence of $SOCl_2$ is therefore the voltammetry of $Cl_2Co(III)TnPc(1-)$ and is shown in Figure 4; the results are listed in Table 3. All of the $SOCl_2$ 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 $SOCl_2$ 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 $SOCl_2$ is reduced.

Before the addition of any $SOCl_2$, 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 $SOCl_2$ 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 $SOCl_2$. Current ratios (i_a/i_c) 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 $SOCl_2$ background to correct for the $SOCl_2$ current) when $SOCl_2$ was present [DPV, scan rate 5mV/s, 1.5X free $SOCl_2$].

Two sets of data are listed in Table 3 for the electrochemistry of CoTnPc in the presence of different concentrations of $SOCl_2$. 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 $SOCl_2$.

Rest Potential Measurements.- The open cicuit rest potentials of various $Li/SOCl_2/C$ cells are listed in Table 4. E_a represents the Li^+/Li

couple in $SOCl_2$ vs SCE under the conditions stated in Table 4:

$$Li^+ + e^- \longrightarrow Li \qquad E = E_a \qquad (3)$$

while E_c represents the liquid $SOCl_2/C$ couple vs SCE:

$$2\ SOCl_2 + 4\ e^- \longrightarrow S + SO_2 + 4\ Cl^- \qquad E = E_c \qquad (4)$$

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.

$$[Co(I)TnPc(2-)]^- + SOCl_2 \longrightarrow [Cl_2Co(III)TnPc(2-)]^- + \text{"SO"} \qquad (5)$$

$$Co(II)TnPc(2-) + SOCl_2 \longrightarrow Cl_2Co(III)TnPc(1-) + \text{"SO"} \qquad (6)$$

$$[Cl_2Co(III)TnPc(2-)]^- + SOCl_2 \longrightarrow [Cl_2Co(III)TnPc(0)]^+ + \text{"SO"} + 2\ Cl^- \qquad (7)$$

"SO" represents the initial reduction product of $SOCl_2$ 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-)]$^+$ 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.

A) $$[\mathrm{Co(I)TnPc(2-)}]^- + \mathrm{SOCl_2} \xrightarrow{\text{fast}} \mathrm{Co(II)TnPc(2-)}$$

$$\mathrm{Co(II)TnPc(2-)} + \mathrm{SOCl_2} \xrightarrow{\text{slow}} [\mathrm{Co(III)TnPc(1-)}]^{2+}$$

B) $$[\mathrm{Co(I)TnPc(2-)}]^- + \mathrm{SOCl_2} \xrightarrow{\text{fast}} \mathrm{Co(II)TnPc(2-)}$$

$$\mathrm{Co(II)TnPc(2-)} + \mathrm{SOCl_2} \xrightarrow{\text{fast}} [\mathrm{Co(III)TnPc(2-)}]^{+}$$

The reaction between [Co(I)TnPc(2-)]$^-$ and $SOCl_2$ must be fast because reaction 5 is fast. In case A the Co(II)TnPc(2-) reacts with thionyl chloride to give Cl_2Co(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 [Cl_2Co(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 [Cl_2Co(III)TnPc(2-)]$^-$ by thionyl chloride without stopping at the Co(II)TnPc(2-) stage.

Thionyl chloride oxidizes $[Cl_2Co(III)TnPc(2-)]^-$ to the one electron oxidation product $Cl_2Co(III)TnPc(1-)$ and not to the two-electron oxidation product $[Cl_2Co(III)TnPc(0)]^+$. It is possible that the $SOCl_2$ could have effected two-electron oxidation but then upon mixing,

$$[Cl_2Co(III)TnPc(2-)]^- + [Cl_2Co(III)TnPc(0)]^+ \longrightarrow 2\ Cl_2Co(III)TnPc(1-) \quad (8)$$

There was no electronic spectroscopic evidence, however, for the two-electron oxidation product. Indeed, the potential for the production of $[Co(III)TnPc(0)]^{3+}$ is very unfavorable.[23] Table 2 lists the driving forces (ΔE values) for many CoTnPc and $SOCl_2$ reactions. All of the reactions in Table 2 were observed in DCB solution, even reactions (iv) and (v) which have unfavorable ΔE values.

$(SOCl_2)$CoTnPc Adducts

Addition of thionyl chloride to Co(II)TnPc(2-) in DCB solution first yielded a $(SOCl_2)Co(II)TnPc(2-)$ adduct (Figures 2 and 3, Table 1,g). A 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 $SOCl_2$ to Co(II)TnPc(2-) was the same as that obtained when a fifty fold molar excess of $SOCl_2$ was added. This implies that not more than one molecule of $SOCl_2$ is coordinating to the Co(II)TnPc(2-).
- The cobalt phthalocyanine was still in the Co(II)Pc(2-) oxidation state as indicated by its electronic spectrum.[23]

- Co(II)Pc(2-) favors the formation of five coordinate complexes.[29] 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.[30-33] 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 $[Co(II)TnPc(1-)]^+/Co(II)TnPc(2-)$ redox couple (II) yielded a double wave. Co(II)TnPc species are known to aggregate[34] and such aggregation can cause splitting of waves in the cyclic voltammogram.[35] After adding $SOCl_2$, however, this couple yielded a single wave. The effect of $SOCl_2$ on the Co(II)TnPc(2-) redox couple can be explained in terms of the formation of a $(SOCl_2)$Co(II)TnPc(2-) adduct that was observed above using electronic spectroscopy. Axial coordination of $SOCl_2$ to Co(II)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 $SOCl_2$ binds much more strongly to Co(II)TnPc(2-) than Cl^-. A thousand times excess of chloride ions are needed to obtain a limiting spectrum of $[ClCo(II)TnPc(2-)]^-$ whereas Co(II)TnPc(2-) is completely converted to $(SOCl_2)$Co(II)TnPc(2-) after the addition of one equivalent of $SOCl_2$.

$[Co(I)TnPc(2-)]^-$ is not expected to bind axial ligands because of the lower oxidation state of the cobalt and the d^8, square planar configuration of the molecule. The shift of the Co(II)TnPc(2-)/$[Co(I)TnPc(2-)]^-$ couple (I) in the presence of $SOCl_2$ (Table 3), therefore, reflects the preferential binding of $SOCl_2$ to Co(II)TnPc(2-) over $[Co(I)TnPc(2-)]^-$. If the thionyl chloride is donating electron density to the Co(II) metal center, $(SOCl_2)$Co(II)TnPc(2-) will be more difficult to reduce than free Co(II)TnPc(2-) and the half wave potential of the Co(II)/Co(I) wave will shift in the negative direction (as observed) due to the removal of Co(II)TnPc(2-) as the thionyl chloride adduct.

The first oxidation couple of CoTnPc in the presence of $SOCl_2$ is more difficult to assign because oxidation could occur either at the Co(II) metal center or at the Pc(2-) ligand. Two different oxidized species are possible, $[Co(II)TnPc(1-)]^+$ or $[Co(III)TnPc(2-)]^+$, depending on the nature of the solvent and electrolyte present. Previous work[23] has shown that Co(II)TnPc(2-) is oxidized to $[Co(II)TnPc(1-)]^+$ in DCB/TBAP and to $[Co(III)TnPc(2-)]^{+}$ 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:

I	$Co(II)TnPc(2-)$ $[Co(I)TnPc(2-)]^{-}$
II	$[Co(II)TnPc(1-)]^{+}$ $Co(II)TnPc(2-)$
II'	$[Co(III)TnPc(2-)]^{+}$ $Co(II)TnPc(2-)$
III	$[Co(III)TnPc(1-)]^{2+}$ $[Co(II)TnPc(1-)]^{+}$
III'	$[Co(III)TnPc(1-)]^{2+}$ $[Co(III)TnPc(2-)]^{+}$

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 Co(II)TnPc(2-) by one electron yields $[Cl_2Co(III)TnPc(2-)]^{-}$. Hence, in DCB/TBACl and DCB/$SOCl_2$ the first oxidation couple is $[Co(III)TnPc(2-)]^{+}/Co(II)TnPc(2-)$ (couple II' in Table 3).

Chloride ions are needed over $SOCl_2$ for the production of $[Co(III)TnPc(2-)]^{+}$ 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 $Cl_2/2Cl^-$ couple is dramatically reduced (the anodic current due to $2Cl^- \longrightarrow Cl_2 + 2e^-$ 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} cm^2). The chloride ions result from the reduction of $SOCl_2$ and since $[ClCo(II)TnPc(2-)]^-$ is oxidized to $[Cl_2Co(III)TnPc(2-)]^-$ before chloride ions are oxidized to chlorine gas, one chloride ion is lost at the electrode surface for every $[Cl_2Co(III)TnPc(2-)]^-$ produced.

In summary, we propose the following redox couples for the cyclic voltammetry of CoTnPc in the presence of $SOCl_2$.

I $(SOCl_2)Co(II)TnPc(2-)/[Co(I)TnPc(2-)]^-$
II' $[Cl_2Co(III)TnPc(2-)]^-/(SOCl_2)Co(II)TnPc(2-)$
III' $Cl_2Co(III)TnPc(1-)/[Cl_2Co(III)TnPc(2-)]^-$

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

With an excess of $SOCl_2$ present, the various CoTnPc species, produced at the electrode surface, in lower oxidation states than $Cl_2Co(III)TnPc(1-)$ can be reoxidized by the thionyl chloride in solution. This is an example of a catalytic EC' mechanism:[36]

$$\begin{tikzcd}
O & + & ne^- & \rightleftharpoons & R & & \\
R & + & Z & \longrightarrow & O \arrow[ullll, dash] & + & Y
\end{tikzcd} \qquad (10)$$

O represents $[Co(III)TnPc(1-)]^{2+}$, Z is $SOCl_2$, Y represents the $SOCl_2$ 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 (i_a/i_c) 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_2Co(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 $SOCl_2$ where the reduction wave of $SOCl_2$ peaks at -0.69V vs AgCl/Ag. A large overpotential must, therefore, be required to overcome the activation energy barrier of adding an electron to $SOCl_2$. This implies the formation of a high energy intermediate, for example,

$$SOCl_2 + e^- \longrightarrow \underline{SOCl}\cdot + Cl^- \qquad (11)$$

A very recent paper[7] 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 $SOCl_2$. The $SOCl\cdot$ intermediate, formed after the transfer of one electron from CoTnPc to $SOCl_2$ (perhaps bound to the cobalt center), may drive the transfer of a second electron to produce SO and Cl^- in some kind of concerted reaction.

The addition of Co(II)TnPc(2-) (oxidized to Cl_2Co(III)TnPc(1-) by $SOCl_2$) to the thionyl chloride cells described in Table 4 had little effect on the lithium, thionyl chloride and overall cell potentials. Madou and coworkers[38,39] have also studied the effect of CoPc in a Li/$SOCl_2$ 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 $SOCl_2$ 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 $SOCl_2$.

Implications for Li/SOCl$_2$ Batteries.- If the carbon cathode of a Li/SOCl$_2$ battery is coated or impregnated with cobalt phthalocyanine the thionyl chloride will oxidize the exposed CoTnPc to Cl$_2$Co(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/SOCl$_2$/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/SOCl$_2$/(CoTnPc,C) battery.

$$[\mathrm{Co(I)TnPc(2-)}]^- + \mathrm{SOCl_2} \longrightarrow [\mathrm{Cl_2Co(III)TnPc(2-)}]^- + \text{"SO"} \quad (12a)$$

$$2\mathrm{Li} + [\mathrm{Cl_2Co(III)TnPc(2-)}]^- \longrightarrow [\mathrm{Co(I)TnPc(2-)}]^- + 2\mathrm{LiCl} \quad (12b)$$

---

summing to:

$$2\mathrm{Li} + \mathrm{SOCl_2} \longrightarrow \text{"SO"} + 2\mathrm{LiCl} \quad (13)$$

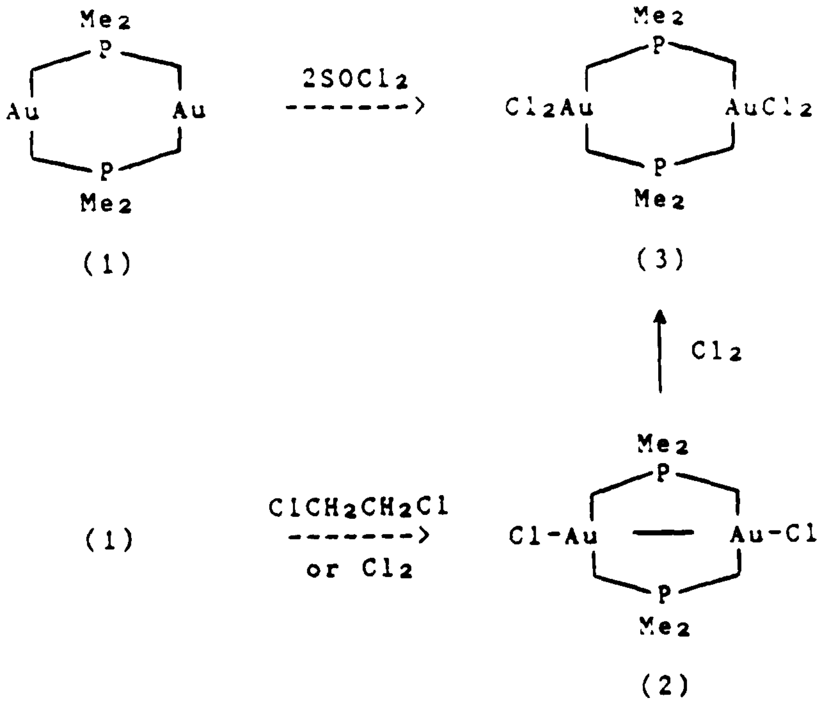
The CoTnPc will act as a mediator between the carbon cathode and the thionyl chloride. Assuming good electrical contact between the cobalt phthalocyanine catalyst and the carbon cathode, the oxidation state of the

CoTnPc will fluctuate, from $[Co(I)TnPc(2-)]^-$ (reduced by the cathode) to $Cl_2Co(III)TnPc(2-)$ (oxidized by $SOCl_2$). As a result, the $SOCl_2$ 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 $SOCl_2$. Riga[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 SO_2. Some evidence for the existence of SO has been recently reported.[7]

A two-electron reduction process could result in a safer $Li/SOCl_2$ battery by eliminating reactive intermediates that may form when $SOCl_2$ is reduced at a bare carbon cathode. The mechanism for the reduction of $SOCl_2$ 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.[1,3-6] Doddapaneni[13-15] proposes that the first step is the reduction of $SOCl_2$ to the $SOCl\cdot$ radical (Equation 11). The $SOCl\cdot$ 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 $SOCl\cdot$ radical (adsorbed on the MPc) can undergo a further one-electron reduction. Our work has shown this to be the case.

$SOCl_2$ 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[41] have also reported a two-electron oxidation using thionyl chloride. The gold(I)dimethylphosphonium-bis-methylide 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-methylide dimer parallels our observed reactions between CoTnPc species and $SOCl_2$. 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.



The kinetics of the reaction between CoTnPc and $SOCl_2$ are presently being studied to obtain more mechanistic information.[42]

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 mono thionyl chloride adduct and is then oxidized to $Cl_2Co(III)TnPc(1-)$.
2. A comproportionation reaction is observed between $[Co(I)TnPc(2-)]^-$ and its two-electron oxidized product $[Cl_2Co(III)TnPc(2-)]^-$ (Equation 1).
3. The lowest possible oxidation state of CoTnPc in a $Li/SOCl_2/C$ 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 $Li/SOCl_2/(CoTnPc,C)$ battery. A two-electron reduction process could result in a safer $Li/SOCl_2$ battery by eliminating reactive intermediates that may form when $SOCl_2$ is reduced by one electron at a carbon cathode not treated with cobalt phthalocyanine.

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Table 1. Electronic absorption maxima of cobalt tetraneopentoxyphthalocyanines.

Species[a]	Footnote	λ nm (ϵ, $M^{-1}cm^{-1}$)				
$[Co(I)TnPc(2-)]^-[TBA]^+$	b		356sh	472(38100)	645(16800)	710(54700)
	c	313(57900)	350sh	471(33300)	643(18400)	708(45000)
$[Co(I)TnPc(2-)]^-[Li/TBA]^+$	d		359sh	471(36600)	647(17200)	709(51300)
$Co(II)TnPc(2-)$			383(13800)		614(24200)	680(83800)
	e	330(40700)	380(13800)		612(25700)	678(72400)
$[ClCo(II)TnPc(2-)]^-[TBA]^+$	f	347			603(27400)	669(85000)
$(SOCl_2)Co(II)TnPc(2-)$	g	343	393(25900)		623(32000)	686(93900)
$[Cl_2Co(III)TnPc(2-)]^-[TBA]^+$	h		367(33500)		608(31200)	678(133000)
	i		369(30900)		607(31800)	677(134000)
$[(DMF)_2Co(III)TnPc(2-)]^+[ClO_4]^-$	j		355(63100)		610(37200)	676(148000)
$Cl_2Co(III)TnPc(1-)$	k		399(24800)	540(26500)	679(17100)sh	755(20600)br
	l	366sh	404(23000)	540(20600)	680(16700)sh	744(18900)br
$(ClO_4)_2Co(III)TnPc(1-)$	m	380(23600)	400(24000)	520(16600)	580sh	742(11500)

[a] $[CoTnPc] \approx 10^{-4}M$ in DCB solution except as otherwise noted. [b] Electrochemical reduction of $Co(II)TnPc(2-)$, $[TBAPF_6]=0.048M$. [c] Electrochemical reduction of $Co(II)TnPc(2-)$, $[TBAP]=0.3M$.[23] [d] Reduction of $Co(II)TnPc(2-)$ using Li/C with 0.07M $TBAPF_6$. [e] With 0.3M TBAP.[23] [f] With 0.10M TBACl. [g] $[SOCl_2]=2.7 \times 10^{-3}M$. [h] From the oxidation of $Co(I)TnPc(2-)$ containing 0.07M $TBAPF_6$ with $4 \times 10^{-4}M$ $SOCl_2$. [i] Electrochemical oxidation of $Co(II)TnPc(2-)$, $[TBACl]=0.10M$. [j] Electrochemical oxidation of $Co(II)TnPc(2-)$ in DMF solution containing 0.3 M TBAP.[23] [k] From the oxidation of $Co(II)TnPc(2-)$ with 0.013M $SOCl_2$. [l] Oxidation of $Co(II)TnPc(2-)$ by chlorine gas. [m] Electrochemical oxidation of $Co(II)TnPc(2-)$, $[TBAP]=0.3M$.[23] TBAP=tetrabutylammonium perchlorate, DMF=dimethylformamide, br=broad and sh=shoulder.

Table 2. Driving forces (ΔE values) for CoTnPc and $SOCl_2$ reactions in DCB <u>calculated</u> 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 $SOCl_2$.

CoTnPc Comproportionation Reactions	ΔE(V)
i) Co(I)TnPc(2-)(TBA) + Cl_2Co(III)TnPc(2-)(TBA) ---> 2ClCo(II)TnPc(2-)(TBA)	+1.06[a]
ii) Co(II)TnPc(2-) + Cl_2Co(III)TnPc(1-) + 2TBACl ---> $2Cl_2$Co(III)TnPc(2-)(TBA)	+0.82[a]

CoTnPc + $SOCl_2$ Reactions[b]	ΔE(V)
iii) Co(I)TnPc(2-)(TBA) + $SOCl_2$ ---> Cl_2Co(III)TnPc(2-)(TBA) + "SO"	+0.74
iv) Co(II)TnPc(2-) + $SOCl_2$ ---> Cl_2Co(III)TnPc(1-) + "SO"	-0.09
v) $2Cl_2$Co(III)TnPc(2-)(TBA) + $SOCl_2$ ---> $2Cl_2$Co(III)TnPc(1-) + "SO" + 2TBACl	-0.50

[a] These potential differences are approximately equal to ΔE°.[36] Using $RT\ln K = nF\Delta E^\circ$, where $n = 1$ and $T = 294°K$, yields $K = 1.5 \times 10^{18}$ for (i) and $K = 1.1 \times 10^{14}$ for (ii). [b] For these calculations it was assumed that $SOCl_2$ is reduced by two electrons at 0.15V vs Fc^+/Fc in DCB.

Table 3. Electrochemical data for cobalt tetraneopentoxyphthalocyanine in DCB.

	$E_{1/2}$,V (ΔE_p,mV)[a]				
	Oxidation				Reduction
	III	III'	II	II'	I
In DCB/TBAP[b]	+0.59 (90)		+0.03 (89)		-0.91 (70)
In DCB/$TBAPF_6$:[c]	+0.69 (63)		+0.17[d] -0.06		-1.01 (104)
with 6 equiv Cl^- [e]		+0.65 (122)		-0.06(115)	-1.12
In the presence of $SOCl_2$:					
1.5X free $SOCl_2$[f]		+0.68 (63)		+0.01 (100)	-1.11
28 equiv $SOCl_2$[g]		+0.65 (75)		-0.04 (117)	
In DMF/TBAP[b]		+0.38		-0.02	-0.85 (85)

[a] Potentials are reported with respect to the ferrocenium/ferrocene couple. $E_{1/2}=(E_{pa}+E_{pc})/2$ and $E_p=E_{pa}-E_{pc}$. See text for definition of couples. [b] These literature half-wave potentials and peak separations are for a 1 X 10^{-4}M CoTnPc solution in DCB or DMF containing 0.1M TBAP at a scan rate (ν) of 20mV/s. $i_a=i_c$ and $i \propto \nu^{1/2}$.[23] [c] [CoTnPc]=1.62 X 10^{-4}M in DCB, [$TBAPF_6$]=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. $i_a=i_c$ for the three redox couples. [d] A 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^{-4}M in DCB, [$TBAPF_6$]=0.07M, [TBACl]=1.8 X 10^{-3}M, ν=100 mV/s. [f] Same conditions as in (c) except with 2.5 X 10^{-4}M free $SOCl_2$ (est. from the $SOCl_2$ reduction current). $i_a=i_c$ for couples II' and III'. i_a=0.91 i_c for couple I. [g] [CoTNPc]=1.22 X 10^{-4}M, [$SOCl_2$]= 3.4 X 10^{-3}M, [$TBAPF_6$]=0.058M in DCB, ν=50 mV/s. $i_a=i_c$ for couples II' and III'.

Table 4. Open circuit rest potentials in volts of Li/$SOCl_2$/C cells.

Conditions	E_{cell}	E_{anode} (E_a) vs SCE	$E_{cathode}$ (E_c) vs SCE	E_c-E_a
Using $SOCl_2$:[a]	3.24	-2.57	0.58	3.15
CoTnPc(3×10^{-4}M)	3.25	-2.63	0.58	3.21
1.6M $AlCl_3$	3.88	-3.20	0.63	3.83
1.0M $AlCl_3$,0.6M $LiAlCl_4$	3.81	-3.10	0.72	3.82
1.0M $AlCl_3$,0.6M $LiAlCl_4$,CoTnPc(3×10^{-4}M)	3.81	-3.01	0.72	3.73
Using DCB, 0.07M $TBAPF_6$:				
0.14M $SOCl_2$	3.54	-2.87	0.64	3.51
1.4M $SOCl_2$	3.72	-2.96	0.74	3.70
3.1M $SOCl_2$	3.76	-2.96	0.79	3.75
1.4M $SOCl_2$,CoTnPc(3×10^{-4}M)	3.67	-2.96	0.67	3.63
Literature values in $SOCl_2$:[39]				
1.6M $LiAlCl_4$	3.6			
1.6M $LiAlCl_4$,CoPc	3.7			
1.6M $LiAlCl_4$,$AlCl_3$	3.9			
1.6M $LiAlCl_4$,$AlCl_3$,CoPc	4			
	3.72 (calc for $4Li+2SOCl_2 \rightarrow 4LiCl+S+SO_2$)[43]			

[a] 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 $SOCl_2$) is 0.28M.[22] The HCl acted as the electrolyte when measuring the electrode potentials in neat $SOCl_2$.

LEGENDS

Figure 1. Electronic absorption spectra of Co(I)TnPc(2-)(TBA) (——) and its two electron oxidation product Cl_2Co(III)TnPc(2-)(TBA) (---) with $SOCl_2$ in DCB. [CoTnPc] = 8.65 X 10^{-5} M, [$TBAPF_6$] = 0.07 M and [$SOCl_2$] = 4 X 10^{-4} M.

Figure 2. Electronic absorption spectra of Co(II)TnPc(2-) (——), ($SOCl_2$)Co(II)TnPc(2-) (---) and [ClCo(II)TnPc(2-)]$^-$ (···) in DCB. [CoTnPc] = 6.12 X 10^{-5} M, [$SOCl_2$] = 2.8 X 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 Cl_2Co(III)TnPc(1-) by thionyl chloride in DCB. [CoTnPc] = 1.14 X 10^{-4} M, [$SOCl_2$] = 5.5 X 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 $SOCl_2$. [CoTnPc] = 1.62 X 10^{-4} M, [$SOCl_2$] ≈ 2.5 X 10^{-4} M and [$TBAPF_6$] = 0.067 M. The ferrocenium/ferrocene couple occurred at +0.43V vs AgCl/Ag.

Fig

--- 32 ---

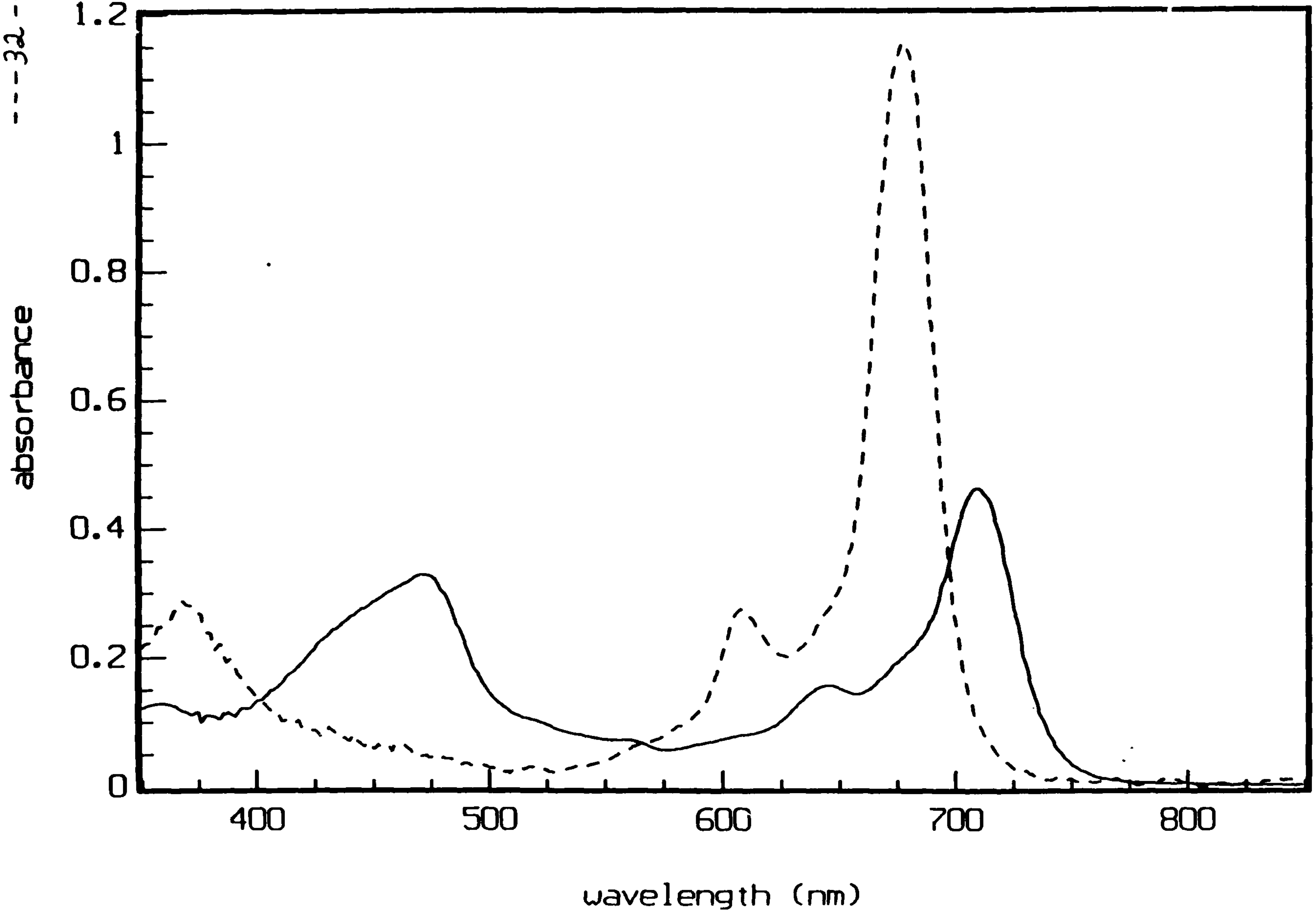
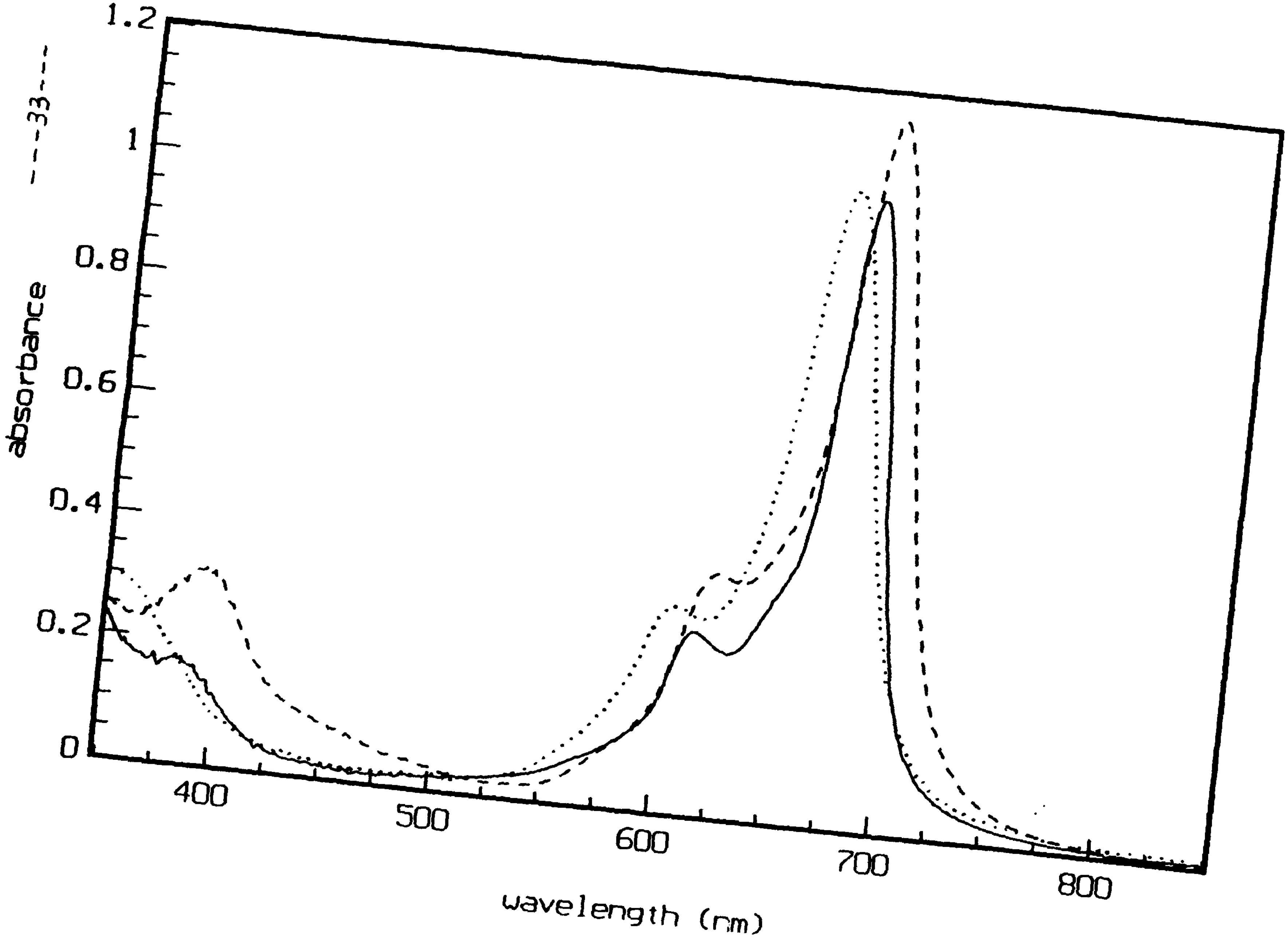


Fig 2


---33---
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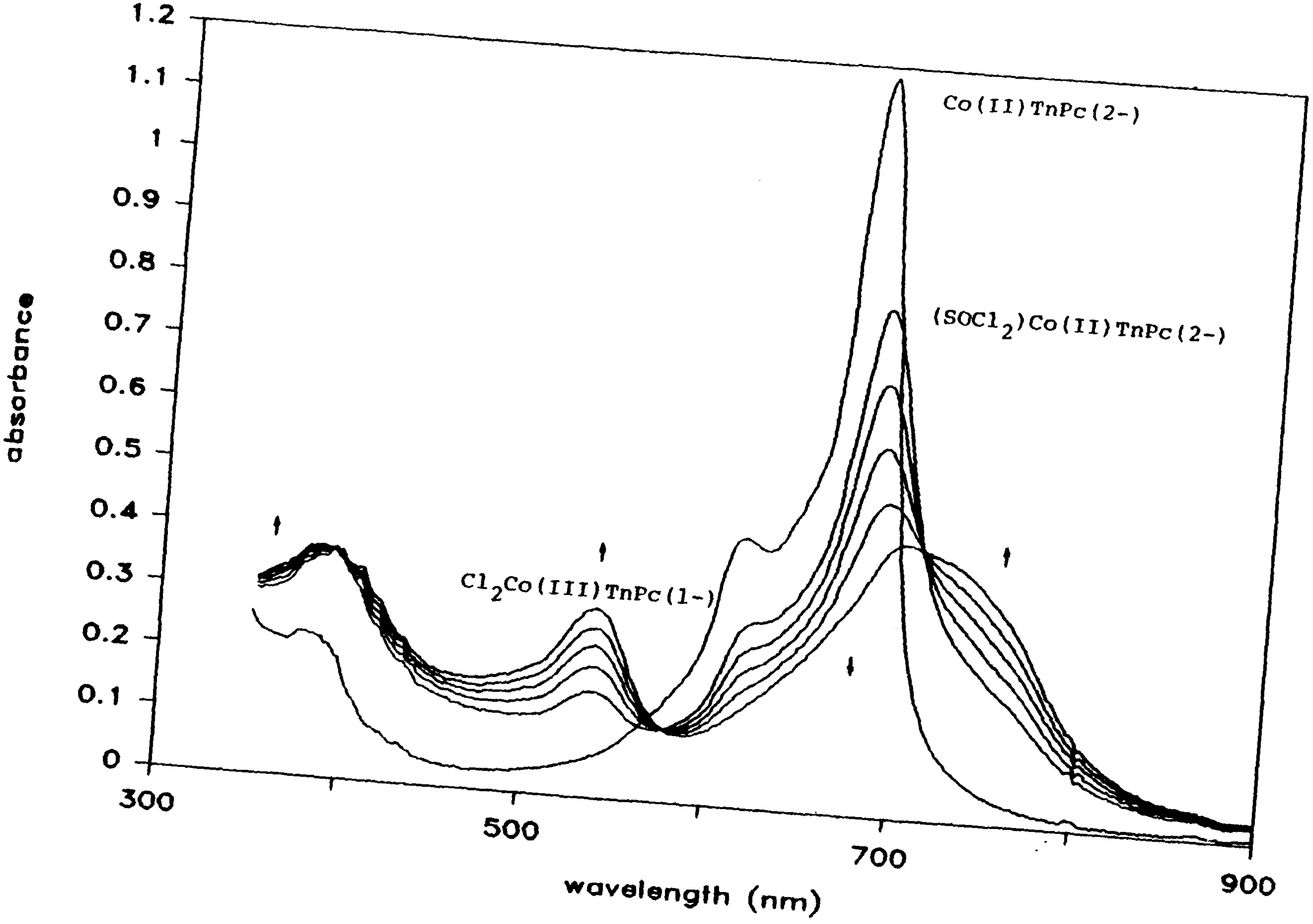
0.4
0.2
0
400
500
600
700
800
wavelength (nm)

Fig 3


Co(II)TnPc(2-)
(SOCl$_2$)Co(II)TnPc(2-)
Cl$_2$Co(III)TnPc(1-)
absorbance
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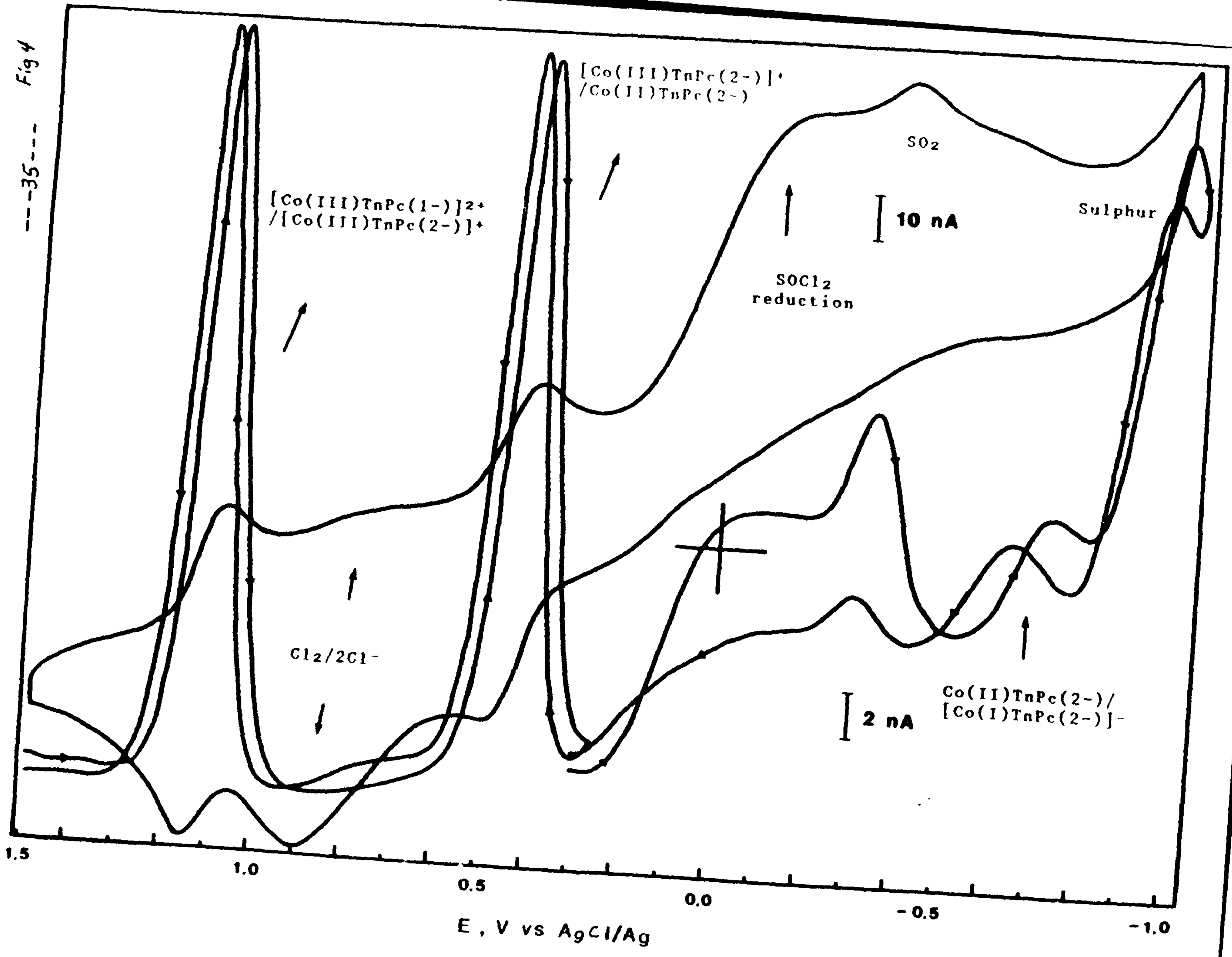
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
300
500
700
900
wavelength (nm)

Fig 4


[Co(III)TnPc(1-)]2+
/[Co(III)TnPc(2-)]+
[Co(III)TnPc(2-)]+
/Co(II)TnPc(2-)
SO2
Sulphur
10 nA
SOCl2
reduction
Cl2/2Cl-
2 nA
Co(II)TnPc(2-)/
[Co(I)TnPc(2-)]-
1.5
1.0
0.5
0.0
-0.5
-1.0
E, V vs AgCl/Ag

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