It is also possible that the solutions with the $\delta_{Cd}$ fine structure contain nonadamantanoid species, also with $\{(\mu\text{-SPh})_3CdSPh\}$ and $\{(\mu\text{-SPh})_3CdX\}$ sites, such as the molecular species $[XCd_8(SPh)_{16}]^-$ with the structure already determined for $[ClZn_8(SPh)_{16}]^-$.[35] We find that DMF solutions of $Cd(SPh)_2$ containing $^1/_8X^-$ (X = Cl, Br, I) crystallize as structure **1a**, without halide incorporation, not as $[XCd_8(SPh)_{16}]^-$. Note that in $[XCd_8(SPh)_{16}]^-$ a single halide ion creates four $\{XCd(SPh)_3\}$ sites and thus could account for the high intensity of the halide-dependent resonance at $Q \leq 0.3$.

Addition of $SPh^-$ to DMF solutions of **1a** also causes changes in the $^{113}Cd$ NMR. Upon addition of even small amounts of $SPh^-$, the minor line at 130 ppm disappears, consistent with the DMF in its coordination sphere being replaced by $SPh^-$ ligands. With further addition of $SPh^-$, the NMR spectra are comprised of three major lines whose intensities vary with the solution composition ($Q = [SPh^-]/[Cd(SPh)_2]$). Up to $Q \approx 0.8$, the spectra are dominated by the line at 594 ppm. Subsequently, a line at 587 ppm becomes dominant, followed by a line at 606 ppm. By $Q = 4.0$, the only line observed is at 606 ppm.

Fuller details of the Cd NMR spectra of DMF solutions of $Cd(SPh)_2$ plus anionic ligands over the full range of $Q$ and of temperature will be published separately. Nevertheless, the pronounced spectral changes with anion addition signify the electrophile character of at least some of the sites in the species present in DMF solutions of $Cd(SPh)_2$ and are further evidence against the occurrence of **4** in these solutions.

There is some comparable iron arenethiolate chemistry: $[Fe_3(SPh)_6(CO)_6]$ dissolved in THF with a small amount of DMSO crystallizes (after removal of CO) as $[Fe(DMSO)_6][Fe_4(SPh)_{10}]$.[36] We note also the existence of $[Cd_4(SPh)_8(PPh_3)_2]$.[37]

## Summary

1. Crystalline compounds $_\infty[Cd(SAr)_2]$, which are structurally nonmolecular and comprised of vertex-linked adamantanoid cages, dissolve in DMF to form polycadmium macromolecules with extensive thiolate bridging.

2. These macromolecules appear to undergo rapid aggregation and deaggregation reactions, with an equilibrium distribution of large molecules at low temperature (ca. 225 K) and much smaller oligocadmium molecules at high temperature (ca. 340 K).

3. The $^{113}Cd$ and $^{13}C$ NMR spectra are consistent with vertex-linked adamantanoid cages as the structure type for the aggregates in solution. The postulated aggregate structures in solution are fragments of the known crystal structures.

4. The low ionic conductivity and the $^{113}Cd$ NMR data indicate that some ligand disproportionation occurs in solution, such that the larger oligoadamantanoid aggregates have small negative charges with SAr and DMF ligands distributed over peripheral terminal Cd coordination sites.

5. The aggregates in solution are electrophilic toward halide and thiolate ligands.

## Experimental Section

**Preparations and Crystallizations.** The compounds were prepared as previously described, and purified by recrystallization from DMF by addition of ethanol.[4]

**NMR.** The $^{113}Cd$ spectra were measured at natural abundance in DMF, at 66.6 MHz with a Bruker CXP300 spectrometer, using 10-mm tubes in a multinuclear probe locked to acetone-$d_6$ in an insert. Proton decoupling was not used. Typical spectra required 3000–6000 pulses (20 μs; tip angle ca. 75°) with recycle delays of ≤2 s. Relaxation times $T_1$ were estimated by tests with variable recycle delay periods, in order to ensure that the relative intensities of resonances were not significantly distorted by saturation. All solutions were deoxygenated by sparging with $N_2$. Temperatures in the sample tube were controlled to ±1° and were calibrated by replacement with a sample tube containing a platinum thermometer. Chemical shifts are referenced to external 0.1 M aqueous $Cd(NO_3)_2$ as zero: this reference resonates at −5 ppm relative to aqueous $Cd(ClO_4)_2$ at infinite dilution.

$^{13}C$ NMR spectra were measured on a JEOL FX-100 instrument at 25.05 MHz, with proton decoupling, and referenced to TMS. Small proportions of acetone were added to the DMF solutions for the lowest temperature measurements.

**Conductivity.** Conductivity measurements were obtained at 25 °C on solutions of $Cd(SPh)_2$, $(Me_4N)_2[Cd_4(SPh)_{10}]$, and $Bu_4NI$ in DMF. Concentrations were varied through the range 0.1 to $5 \times 10^{-5}$ M.

**Molecular Weight.** Because DMF is a very difficult solvent for molecular weight determinations by cryoscopic or osmometric methods (ebullioscopic data would not be relevant to the temperature range of the NMR data), cryoscopic measurements were made in HMPA. The low values of 290 ± 50 Da revealed that HMPA completely disrupted the aggregates and could not be regarded as comparable with DMF. Attempts to use the Signer isothermal distillation method in DMF are in progress.

**Acknowledgment.** Funding by the Australian Research Grants Scheme is gratefully acknowledged.

---

[35] Dance, I. G. *Aust. J. Chem.* **1985**, *38*, 1391.

[36] Walters, M. A.; Dewan, J. C. *Inorg. Chem.* **1986**, *25*, 4889.

[37] Black, S. J.; Einstein, F. W. B.; Hayes, P. C.; Kumar, R.; Tuck, D. G. *Inorg. Chem.* **1986**, *25*, 4181.

---

Contribution from the Department of Chemistry,
York University, North York, Ontario, Canada M3J 1P3

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

P. A. Bernstein and A. B. P. Lever*

*Received July 14, 1989*

Cyclic voltammetry, DPV, and electronic spectroscopy are used to study the reaction between thionyl chloride and cobalt phthalocyanine. $SOCl_2$ reacts with $[Co^ITnPc(2-)]^-$ and $Co^{II}TnPc(2-)$ to give two-electron-oxidized species. Implications for $Li/SOCl_2$ batteries are discussed. Thionyl chloride also forms a $SOCl_2$ monoadduct with $Co^{II}TnPc(2-)$. Driving forces ($\Delta E$ 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 sulfur, sulfur dioxide, and lithium chloride.[2]

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

---

[1] Bowden, W. L.; Dey, A. N. *J. Electrochem. Soc.* **1980**, *127*, 1419.

0020-1669/90/1329-0608$02.50/0

**Table I.** Electronic Absorption Maxima of Cobalt Tetraneopentoxyphthalocyanines

| species[a] | footnote | λ, nm (ε, $M^{-1}$ $cm^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| $[Co^{I}TnPc(2-)]^{-}[TBA]^{+}$ | *b* | | 356 sh | 472 (38100) | 645 (16800) | 710 (54700) |
| | *c* | 313 (57900) | 350 sh | 471 (33300) | 643 (18400) | 708 (45000) |
| $[Co^{I}TnPc(2-)]^{-}[Li/TBA]^{+}$ | *d* | | 359 sh | 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* | 366 sh | 404 (23000) | 540 (20600) | 680 (16700) sh | 744 (18900) br |
| $(ClO_4)_2Co^{III}TnPc(1-)$ | *m* | 380 (23600) | 400 (24000) | 520 (16600) | 580 sh | 742 (11500) |

[a] [CoTnPc] ≈ $10^{-4}$ M in DCB solution except as otherwise noted. TBAP = tetrabutylammonium perchlorate, DMF = dimethylformamide, br = broad and sh = shoulder. [b] Electrochemical reduction of $Co^{II}TnPc(2-)$; $[(TBA)PF_6]$ = 0.048 M. [c] Electrochemical reduction of $Co^{II}TnPc(2-)$; [TBAP] = 0.3 M.[23] [d] Reduction of $Co^{II}TnPc(2-)$ using Li/C with 0.07 M $(TBA)PF_6$. [e] With 0.3 M TBAP.[23] [f] With 0.10 M (TBA)Cl. [g] $[SOCl_2]$ = $2.7 \times 10^{-3}$ M. [h] From the oxidation of $Co^{I}TnPc(2-)$ containing 0.07 M $(TBA)PF_6$ with $4 \times 10^{-4}$ M $SOCl_2$. [i] Electrochemical oxidation of $Co^{II}TnPc(2-)$; [(TBA)Cl] = 0.10 M. [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 0.013 M $SOCl_2$. [l] Oxidation of $Co^{II}TnPc(2-)$ by chlorine gas. [m] Electrochemical oxidation of $Co^{II}TnPc(2-)$; [TBAP] = 0.3 M.[23]

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 Section

Cobalt tetraneopentoxyphthalocyanine (abbreviated CoTnPc) was used because of its increased solubility in organic solvents and was prepared by the method published by Leznoff and co-workers.[20] Nitrogen (dried over drierite) was bubbled through thionyl chloride (reagent grade, BDH) for 5 h 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 4-Å molecular sieves (8-12 mesh, Aldrich) activated at 200 °C under vacuum for 2 h. Tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$) (98%, Aldrich) was recrystallized from absolute ethanol and dried at 140 °C under vacuum for 2 h. Tetrabutylammonium chloride ((TBA)Cl) (Eastman) was dried by using molecular sieves as an 0.10 M 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 Model 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 with a conventional three-electrode cell. A platinum pseudo micro disk described by the cross-sectional area of a 27-gauge wire (area $1.02 \times 10^{-3}$ $cm^2$) 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 +0.49 V 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 0.1 M $(TBA)PF_6$ or (TBA)Cl as supporting electrolyte, and were deoxygenated by bubbling nitrogen for 2 h prior to use.

$Li/SOCl_2/C$ cells were prepared (in air) by 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 with a Fluke 75 digital voltmeter, and the potential of each electrode was measured versus a platinum-tipped SCE.

---

(2) Dey, A. N.; Schlaikjer, C. R. *Proc. 26th Power Sources Symp.* **1974**, U.S. Pat. 4,020,240, 1977.

(3) Carter, B. J.; Subba Rao, S.; Williams, R.; Evans, M.; Kim, S.; Tsay, F. D. *Proc. 31st Power Sources Symp.* **1984**, 400.

(4) Behl, W. K.; Christopulos, J. A.; Ramirez, M.; Gilman, S. *J. Electrochem. Soc.* **1973**, *120*, 1619.

(5) Attia, A. I.; Sarrazin, C.; Gabriel, K. A.; Burns, R. P. *J. Electrochem. Soc.* **1984**, *131*, 2523.

(6) Carter, B. J.; Evans, M.; Williams, R. M.; Kim, S.; Tsay, F. D.; Subba Rao, S.; Frank, H.; Szpak, S. *Proc. 31st Power Sources Symp.* **1984**, 493.

(7) Sakai, M.; Osteryoung, J.; Osteryoung, R. A. *J. Electrochem. Soc.* **1988**, *135*, 3001.

(8) Istone, W. K.; Brodd, R. J. *J. Electrochem. Soc.* **1982**, *129*, 1853.

(9) Bowden, W. L.; Dey, A. N. *J. Electrochem. Soc.* **1980**, *127*, 1419 and references therein.

(10) Zak, U.; Reshef, D.; Kreinin, H. *Proc. 31st Power Sources Symp.* **1984**, 427.

(11) Hall, J. C. *Proc. 31st Power Sources Symp.* **1984**, 443.

(12) Bailey, J. C. *Proc. 32nd Int. Power Sources Symp.* **1986**, 508.

(13) Doddapaneni, N. *Proc. 30th Power Sources Symp.* **1982**, 169.

(14) Doddapaneni, N. *Proc. 31st Power Sources Symp.* **1984**, 411.

(15) Doddapaneni, N. *Proc. Electrochem. Soc.* **1984**, *84-12*, 630.

(16) Doddapaneni, N. Report DELET-TR-81-0381-F; Order No. AD-A118696; 97 pp; available from NTIS, Springfield, VA; *Gov. Rep. Announce. Index(U.S.)* **1982**, *82* (26), 5431; *Chem. Abstr.* **1982**, *98*, 61979w.

(17) Zagal, J. H.; Pãez, C.; Barbato, S. *Proc. Electrochem. Soc.* **1987**, *87-12*, 211.

(18) Venkatasetty, H. V. U.S. Pat. 4,252,875, 1981; *Chem. Abstr.* **1981**, *94*, 195032h.

(19) Doddapaneni, N. *Proc. 32nd Int. Power Sources Symp.* **1986**, 525.

(20) Leznoff, C. C.; Marcuccio, S. M.; Greenberg, S.; Lever, A. B. P.; Tomer, K. B. *Can. J. Chem.* **1985**, *63*, 623.

(21) Sahami, S.; Weaver, M. J. *J. Solution Chem.* **1981**, *10*, 199.

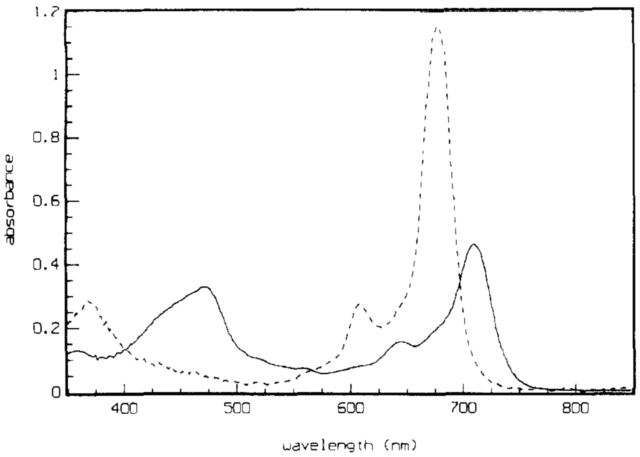


**Figure 1.** Electronic absorption spectra of $Co^{I}TnPc(2-)(TBA)$ (—) and its two-electron-oxidation product $Cl_2Co^{III}TnPc(2-)(TBA)$ (- - -) with $SOCl_2$ in DCB. [CoTnPc] = $8.65 \times 10^{-5}$ M, $[(TBA)PF_6]$ = 0.07 M, and $[SOCl_2]$ = $4 \times 10^{-4}$ M.

$[Co^{I}TnPc(2-)]^-$ was prepared by bulk electrolysis (−1.00 V vs AgCl/Ag, under $N_2$) of a $Co^{II}TnPc(2-)$ solution containing $(TBA)PF_6$. $[Co^{I}TnPc(2-)]^-$ was also prepared chemically by reducing a $2.3 \times 10^{-4}$ M solution of $Co^{II}TnPc(2-)$ in DCB containing 0.07 M $(TBA)PF_6$ using a thin piece of graphite (0.5 mm, 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 (+0.90 V vs AgCl/Ag, under $N_2$) of a $Co^{II}TnPc(2-)$ solution containing (TBA)Cl.

In a typical experiment, 1 μL of $SOCl_2$ ($1.4 \times 10^{-5}$ mol, 140X excess) was added to 1 mL of a 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 I*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 that 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 equiv) 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 I*h*). To within experimental error, the spectrum of the oxidized product is identical with that obtained when $Co^{II}TnPc(2-)$ is oxidized electrochemically in DCB/(TBA)Cl (Table I*i*). Since a cobalt(III) center strongly favors 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 I*j*).

**Table II.** Driving Forces (Δ*E* Values) for CoTnPc and $SOCl_2$ Reactions in DCB *Calculated* by Using the Half-Wave Potentials of CoTnPc in Table III and Using 0.15 V vs $Fc^+/Fc$ (0.64 V vs SCE, Table IV) for the Reduction Potential of $SOCl_2$

| reacn no. | reactions | Δ*E*, V |
|---|---|---|
| | CoTnPc Comproportionation Reactions | |
| i | $Co^{I}TnPc(2-)(TBA) + Cl_2Co^{III}TnPc(2-)(TBA) \rightarrow 2ClCo^{II}TnPc(2-)(TBA)$ | +1.06[a] |
| ii | $Co^{II}TnPc(2-) + Cl_2Co^{III}TnPc(1-) + 2(TBA)Cl \rightarrow 2Cl_2Co^{III}TnPc(2-)(TBA)$ | +0.82[a] |
| | CoTnPc + $SOCl_2$ Reactions[b] | |
| iii | $Co^{I}TnPc(2-)(TBA) + SOCl_2 \rightarrow Cl_2Co^{III}TnPc(2-)(TBA) + \text{“SO”}$ | +0.74 |
| iv | $Co^{II}TnPc(2-) + SOCl_2 \rightarrow Cl_2Co^{III}TnPc(1-) + \text{“SO”}$ | −0.09 |
| v | $2Cl_2Co^{III}TnPc(2-)(TBA) + SOCl_2 \rightarrow 2Cl_2Co^{III}TnPc(1-) + \text{“SO”} + 2(TBA)Cl$ | −0.50 |

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

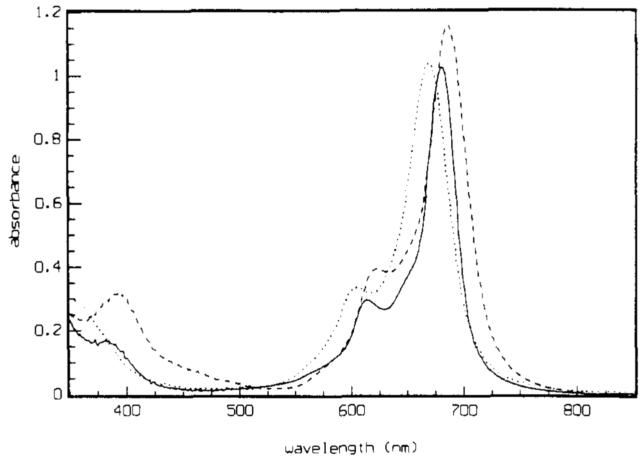


**Figure 2.** Electronic absorption spectra of $Co^{II}TnPc(2-)$ (—), $(SOCl_2)Co^{II}TnPc(2-)$ (- - -), and $[ClCo^{II}TnPc(2-)]^-$ (···) in DCB. [CoTnPc] = $6.12 \times 10^{-5}$ M, $[SOCl_2]$ = $2.8 \times 10^{-3}$ M for the thionyl chloride adduct, and [(TBA)Cl] = 0.10 M for the chloro complex.

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 $[Co^{I}TnPc(2-)]^-$ (yellow) and the newly created $[Cl_2Co^{III}TnPc(2-)]^-$ (green). The $Co^{II}TnPc(2-)$ results from the reaction

$$[Co^{I}TnPc(2-)]^- + [Cl_2Co^{III}TnPc(2-)]^- \rightarrow 2[ClCo^{II}TnPc(2-)]^- \quad (1)$$

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 II, reaction 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 $Co^{II}TnPc(2-)$ product to that of $Co^{II}TnPc(2-)$ in DCB containing (TBA)Cl (Table I*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 I*g*). The spectrum is still typical of a cobalt(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

---

(22) Staniewicz, R. J.; Gary, R. A. *J. Electrochem. Soc.* **1979**, *126*, 981.

(23) Nevin, W. A.; Hempstead, M. R.; Liu, W.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1987**, *26*, 570.

(24) Myers, J. F.; Rayner Canham, G. W.; Lever, A. B. P. *Inorg. Chem.* **1975**, *14*, 461.

(25) Rayner Canham, G. W.; Myers, J.; Lever, A. B. P. *J. Chem. Soc., Chem. Commun.* **1973**, 483.

(26) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980.

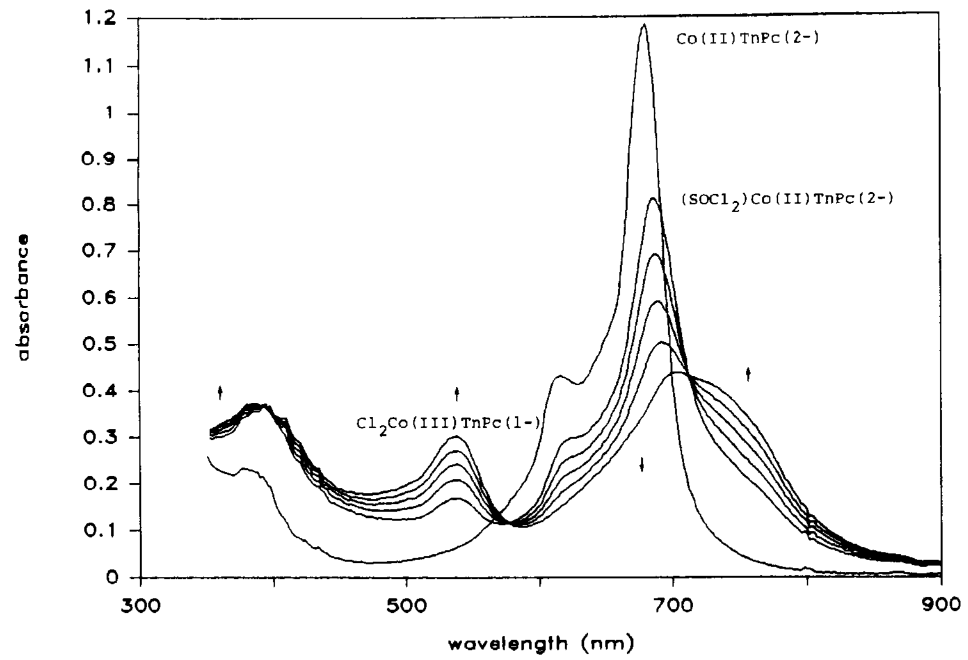


**Figure 3.** Spectra for the oxidation of $Co^{II}TnPc(2-)$ to $Cl_2Co^{III}TnPc(1-)$ by thionyl chloride in DCB. [CoTnPc] = $1.14 \times 10^{-4}$ M, and [$SOCl_2$] = $5.5 \times 10^{-3}$ M. These spectra were recorded over a period of 11 min at room temperature.

minutes, to form $Cl_2Co^{III}TnPc(1-)$ (Figure 3, Table I*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] spectrum 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 I*k*,*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

$$2Cl^- + Co^{II}TnPc(2-) + Cl_2Co^{III}TnPc(1-) \rightarrow 2[Cl_2Co^{III}TnPc(2-)]^- \quad (2)$$

was also observed in DCB solution by 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 $Co^{III}Pc$ species ($\Delta E = +0.82$ V; reaction ii in Table II).

**3. Solution Reaction of $[Co^{III}TnPc(2-)]^+$ with $SOCl_2$.** Addition of excess thionyl chloride (40 equiv) 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 equiv)) 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 min 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 equiv) and heating at 50 °C for 30 min. 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 sulfur and $SO_2$. The voltammogram of $SOCl_2$ shows the initial two-electron-reduction peak at ca −0.75 V (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. −0.95 V while there are two reduction waves involving sulfur at about −0.7 and −1.5 V. 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/$(TBA)PF_6$ 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 −0.69 V but with some dependence upon thionyl chloride concentration, as previously observed.[1] We observe sulfur reduction peaks (solution obtained by dissolving elemental sulfur in DCB) at −0.98 and −1.26 V and chloride oxidation ($1.8 \times 10^{-3}$ M solution of (TBA)Cl in DCB) at 0.75 V vs AgCl/Ag.

The chloride that is generated in the thionyl chloride reduction process is oxidized at 0.77 V vs AgCl/Ag, in DCB solution, ca. 0.3 V 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 ($i_a = i_c$), $i \propto v^{1/2}$). 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, microliter 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/$(TBA)PF_6$, oxidation of the bulk solution to $Cl_2Co^{III}TnPc(1-)$ occurred over a period of about 10 min. 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

---

(27) Abraham, K. M.; Mank, R. M. *J. Electrochem. Soc.* **1980**, *127*, 2091.

(28) Dampier, F. W.; Cole, T. A. *J. Electrochem. Soc.* **1986**, *133*, 938.

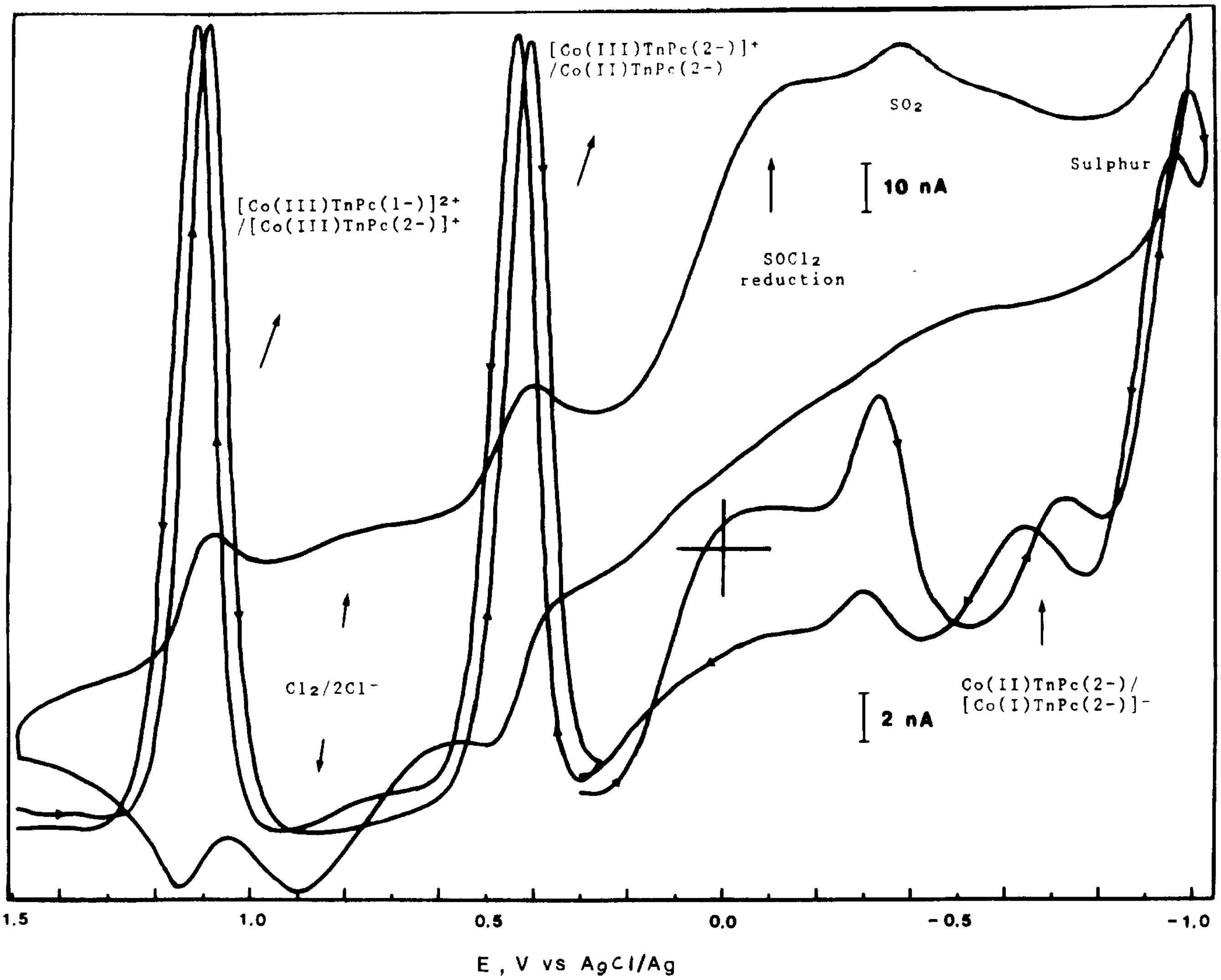


**Figure 4.** Cyclic voltammogram (—, $v$ = 100 mV/s) and DPV (→—, $v$ = 5 mV/s, 5 mV modulation amplitude) of a DCB solution of CoTnPc and $SOCl_2$. [CoTnPc] = 1.62 × $10^{-4}$ M, [$SOCl_2$] ≈ 2.5 × $10^{-4}$ M, and [$(TBA)PF_6$] = 0.067 M. The ferrocenium/ferrocene couple occurred at +0.43 V vs AgCl/Ag.

**Table III.** Electrochemical Data for Cobalt Tetraneopentoxyphthalocyanine in DCB

| | $E_{1/2}$, V ($\Delta E_p$, mV)[a] | | | | |
|---|---|---|---|---|---|
| | oxidn | | | | redn |
| | III | III′ | II | II′ | I |
| in DCB/TBAP[b] | +0.59 (90) | | +0.03 (89) | | −0.91 (70) |
| in DCB/$(TBA)PF_6$[c] | +0.69 (63) | | +0.17[d]<br>−0.06 | | −1.01 (104) |
| with 6 equiv of $Cl^-$[e] | | +0.65 (122) | | −0.06 (115) | −1.12 |
| in the presence of $SOCl_2$ | | | | | |
| 1.5× free $SOCl_2$[f] | | +0.68 (63) | | +0.01 (100) | −1.11 |
| 28 equiv of $SOCl_2$[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 $\Delta E_p = E_{pa} - E_{pc}$. See text for definition of couples. [b] These literature half-wave potentials and peak separations are for a 1 × $10^{-4}$ M CoTnPc solution in DCB or DMF containing 0.1 M TBAP at a scan rate ($v$) of 20 mV/s. $i_a = i_c$, and $i \propto v^{1/2}$.[23] [c] [CoTnPc] = 1.62 × $10^{-4}$ M in DCB. [$(TBA)PF_6$] = 0.067 M. 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 +0.17 V was approximately twice as large as the one at −0.06 V. [e] [CoTnPc] = 3 × $10^{-4}$ M in DCB, [$(TBA)PF_6$] = 0.07 M. [(TBA)Cl] = 1.8 × $10^{-3}$ M, $v$ = 100 mV/s. [f] Same conditions as in footnote *c* except with 2.5 × $10^{-4}$ M free $SOCl_2$ (estimated 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 × $10^{-4}$ M, [$SOCl_2$] = 3.4 × $10^{-3}$ M. [$(TBA)PF_6$] = 0.058 M in DCB, $v$ = 50 mV/s. $i_a = i_c$ for couples II′ and III′.

shown in Figure 4; the results are listed in Table III. 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 with DPV (Figure 4).

Recording the CV or DP voltammogram from +1.5 to −0.3 V 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 III shifted negatively

**Table IV.** Open Circuit Rest Potentials (V) 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 ($3 \times 10^{-4}$ M) | 3.25 | −2.63 | 0.58 | 3.21 |
| 1.6 M $AlCl_3$ | 3.88 | −3.20 | 0.63 | 3.83 |
| 1.0 M $AlCl_3$, 0.6 M $LiAlCl_4$ | 3.81 | −3.10 | 0.72 | 3.82 |
| 1.0 M $AlCl_3$, 0.6 M $LiAlCl_4$, CoTnPc ($3 \times 10^{-4}$ M) | 3.81 | −3.01 | 0.72 | 3.73 |
| using DCB, 0.07 M $(TBA)PF_6$ | | | | |
| 0.14 M $SOCl_2$ | 3.54 | −2.87 | 0.64 | 3.51 |
| 1.4 M $SOCl_2$ | 3.72 | −2.96 | 0.74 | 3.70 |
| 3.1 M $SOCl_2$ | 3.76 | −2.96 | 0.79 | 3.75 |
| 1.4 M $SOCl_2$, CoTnPc ($3 \times 10^{-4}$ M) | 3.67 | −2.96 | 0.67 | 3.63 |
| lit. values in $SOCl_2$[39] | | | | |
| 1.6 M $LiAlCl_4$ | 3.6 | | | |
| 1.6 M $LiAlCl_4$, CoPc | 3.7 | | | |
| 1.6 M $LiAlCl_4$, $AlCl_3$ | 3.9 | | | |
| 1.6 M $LiAlCl_4$, $AlCl_3$, CoPc | 4 | | | |
| | 3.72[b] | | | |

[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 0.28 M.[22] The HCl acted as the electrolyte when measuring the electrode potentials in neat $SOCl_2$. [b] Calculated for $4Li + 2SOCl_2 \rightarrow 4LiCl + S + SO_2$.[43]

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 5 mV/s, 1.5× free $SOCl_2$].

Two sets of data are listed in Table III 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 III are the half-wave potentials of CoTnPc in the presence of chloride ions ((TBA)Cl). 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 IV. $E_a$ represents the $Li^+$/Li couple in $SOCl_2$ vs SCE under the conditions stated in Table IV

$$Li^+ + e^- \rightarrow Li \qquad E = E_a \tag{3}$$

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

$$2SOCl_2 + 4e^- \rightarrow S + SO_2 + 4Cl^- \qquad E = E_c \tag{4}$$

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.

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

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

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

"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. The oxidation process in eq 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 path A or path B.

path A

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

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

path B

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

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

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 buildup 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

$$[Cl_2Co^{III}TnPc(2-)]^- + [Cl_2Co^{III}TnPc(0)]^+ \rightarrow 2Cl_2Co^{III}TnPc(1-) \tag{8}$$

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 II lists the driving forces ($\Delta E$ values) for many CoTnPc and $SOCl_2$ reactions. All of the reactions in Table II were observed in DCB solution, even reactions iv and v, which have unfavorable $\Delta E$ 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 Ig). A $Co^{II}TnPc(2-)$ mono thionyl chloride complex is proposed for the following reasons:

The spectrum of the adduct after the addition of 1 equiv of $SOCl_2$ to $Co^{II}TnPc(2-)$ was the same as that obtained when a 50-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 sulfur 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 $SOCl_2$; (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 addition of $SOCl_2$, 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 by 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 1 equiv 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 III), 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:

$$Co^{II}TnPc(2-)/[Co^{I}TnPc(2-)]^- \text{ (I)}$$

$$[Co^{II}TnPc(1-)]^+/Co^{II}TnPc(2-) \text{ (II)}$$

$$[Co^{III}TnPc(2-)]^+/Co^{II}TnPc(2-) \text{ (II')}$$

$$[Co^{III}TnPc(1-)]^{2+}/[Co^{II}TnPc(1-)]^+ \text{ (III)}$$

$$[Co^{III}TnPc(1-)]^{2+}/[Co^{III}TnPc(2-)]^+ \text{ (III')}$$

As can be seen in Table III, 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 ((TBA)Cl) are identical, within experimental error, to those in the presence of 28 equiv of thionyl chloride. This suggests that the redox processes are the same for both systems. In the presence of (TBA)Cl, it was shown by spectroelectrochemistry (Table I*i*) that oxidation of $Co^{II}TnPc(2-)$ by one electron yields $[Cl_2Co^{III}TnPc(2-)]^-$. Hence, in DCB/(TBA)Cl and DCB/$SOCl_2$ the first oxidation couple is $[Co^{III}TnPc(2-)]^+/Co^{II}TnPc(2-)$ (couple II' in Table III).

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 $2Cl^- \rightarrow Cl_2 + 2e^-$ was 1.16 μA before the addition of CoTnPc and 0.26 μA afterward when a Pt disk electrode of area $1.02 \times 10^{-3}$ cm² was used). 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 $SOCl_2$:

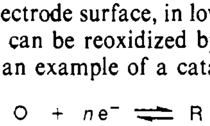
$$(SOCl_2)Co^{II}TnPc(2-)/[Co^{I}TnPc(2-)]^- \text{ (I)}$$

$$[Cl_2Co^{III}TnPc(2-)]^-/(SOCl_2)Co^{II}TnPc(2-) \text{ (II')}$$

$$Cl_2Co^{III}TnPc(1-)/[Cl_2Co^{III}TnPc(2-)]^- \text{ (III')}$$

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]



(9)

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 equiv 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 $[Cl_2Co^{III}TnPc(2-)]^-$

---

(29) Minor, P. C. Ph.D. Thesis, York University, North York, Ont., Canada, 1983.

(30) Gaspard, S.; Verdaguer, M.; Viovy, R. *J. Chem. Res. Miniprint* **1979**, 3072.

(31) Iodko, S. S.; Kaliya, O. L.; Lebedev, O. L.; Luk'yanets, E. A. *Koord. Khim.* **1979**, *5*, 611.

(32) Gaspard, S.; Verdaguer, M.; Viovy, R. *J. Chim. Phys. Physicochim. Biol.* **1972**, *69*, 1740.

(33) Borovkov, N. Yu.; Akopov, A. S. *Russ. J. Phys. Chem.* **1986**, *60*, 448.

(34) Nevin, W. A.; Liu, Wei; Lever, A. B. P. *Can. J. Chem.* **1987**, *65*, 855.

(35) Hempstead, M. R.; Lever, A. B. P.; Leznoff, C. C. *Can. J. Chem.* **1987**, *65*, 2677.

(36) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons, Inc.: New York, 1980.

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 (5 mV/s).

**Lithium Cell: Rest Potential Measurements.** The addition of $AlCl_3$ to a $Li/SOCl_2/C$ cell had a large effect (0.63 V 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 (0.64 V). 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 ($E$ = 0.58–0.79 V vs SCE in Table IV). This is not obvious, however, from the cyclic voltammogram of $SOCl_2$ where the reduction wave of $SOCl_2$ 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 $SOCl_2$. This implies the formation of a high-energy intermediate, for example

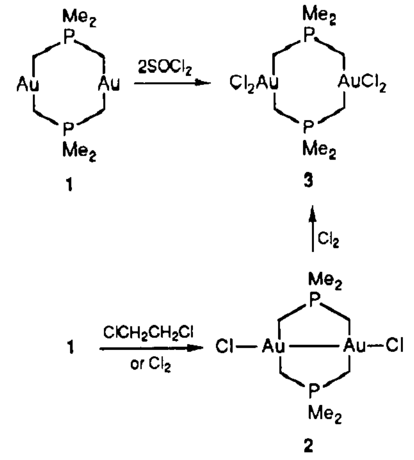
$$SOCl_2 + e^- \rightarrow SOCl^\bullet + Cl^- \qquad (10)$$

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 $SOCl^\bullet$ 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 IV had little effect on the lithium, thionyl chloride, and overall cell potentials. Madou and co-workers[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 $Cl_2Co^{III}TnPc(1-)$ under open circuit conditions. In a 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 Experimental Section). The $Co^{II}TnPc(2-)$ was reduced to $[Co^{I}TnPc(2-)]^-$ (Table I*d*). The $[Co^{I}TnPc(2-)]^-$ solution was allowed to stand in contact with the Li/C for 2 days to ensure that this was indeed the lowest oxidation state of CoTnPc achievable under these conditions.

**Scheme I**



The following mechanism is, therefore, evident for the reduction of thionyl chloride in a $Li/SOCl_2/(CoTnPc,C)$ battery.

$$[Co^{I}TnPc(2-)]^- + SOCl_2 \rightarrow [Cl_2Co^{III}TnPc(2-)]^- + \text{“SO”} \qquad (11)$$

$$2Li + [Cl_2Co^{III}TnPc(2-)]^- \rightarrow [Co^{I}TnPc(2-)]^- + 2LiCl \qquad (12)$$

summing to

$$2Li + SOCl_2 \rightarrow \text{“SO”} + 2LiCl \qquad (13)$$

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 sulfur and chloride ions are products of thionyl chloride reduction by iron and molybdenum phthalocyanines. The sulfur 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 sulfur, sulfur 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 $SOCl^\bullet$ radical (eq 10). The $SOCl^\bullet$ 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 $SOCl^\bullet$ 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 stepwise, 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** (Scheme I) is oxidized to the gold(III) complex **3**, without any gold(II) intermediate being observed.

---

(37) Devynk, J.; Petit, A.; Brage, M. C.; Descroix, J. P. Presented at the Electrochemistry Society, Fall Meeting, Detroit, MI, 1982; Paper No. 263.

(38) Madou, M. J.; Smith, J. J.; Szpak, S. *J. Electrochem. Soc.* **1987**, *134*, 2794.

(39) Madou, M.; Kinoshita, K.; McKubre, M. C. H.; Szpak, S. *Proc. Electrochem. Soc.* **1984**, *84–12*, 618.

(40) Riga, J.; Savy, M.; Verbist, J. J. *Bull. Soc. Chim. Belg.* **1985**, *94*, 267.

(41) Schmidbaur, H.; Jandik, P. *Inorg. Chim. Acta* **1983**, *74*, 97.

With 1,2-dichloro or 1,2-dibromoethane, 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 by 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 (eqs 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 $[Cl_2Co^{III}TnPc(2-)]^-$ (eq 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.

**Acknowledgment.** We are indebted to the Natural Sciences and Engineering Research Council (NSERC, Ottawa) and the Office of Naval Research (Washington, DC) for financial support and to the Province of Ontario for a graduate scholarship (P.B.). We are very grateful to S. Greenberg for supplying the CoTnPc and to Dr. Elaine Dodsworth for helpful suggestions in the preparation of the manuscript.

---

[42] Bernstein, P. A.; Lever, A. B. P. To be submitted for publication.
[43] Madou, M. J.; Szpak, S. *J. Electrochem. Soc.* **1984**, *131*, 2471.

---

Contribution from the Chemistry Departments, The Ohio State University,
Columbus, Ohio 43210, and University of Warwick, Coventry CV4 7AL, England

# Lacunar Cyclidene Complexes of Nickel(II) and Cobalt(II) Containing a Misoriented Pendant Base: Synthesis and Characterization of a New T-Form Hemoglobin Model

Harrell E. Tweedy,[†] Nathaniel W. Alcock,[‡] Naohide Matsumoto,[†] Peter A. Padolik,[†]
Neil A. Stephenson,[†] and Daryle H. Busch*[,†,1]

*Received February 24, 1989*

A new model for the T-form of hemoglobin has been developed; it consists of a cobalt(II) complex with a pentadentate ligand in which the binding of the axial ligand is inhibited by a steric device. The compounds reported here are isomeric lacunar cyclidene complexes containing a pyridyl group covalently attached to the macrocycle. One isomer possesses a stereochemistry suitable for the intramolecular coordination of the pyridine nitrogen, as demonstrated by ESR experiments on the cobalt(II) complex. The separation of the isomeric components is described together with their characterization. A crystal structure is reported for one of the isomers: (2,3,10,11,13,19-hexamethyl-23-[2-(1-methylpyridiniumyl)]-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-$\kappa^4 N$)nickel(II) iodide, $C_{32}H_5I_3N_7NiH_2O$, orthorhombic, $Pna2_1$, $a = 12.247$ (2) Å, $b = 25.236$ (6) Å, $c = 12.260$ (2) Å, $V = 3789$ (1) Å$^3$, $Z = 4$, and $R = 0.056$ and $R_w = 0.063$ for 3534 reflections with $I > 2.5\sigma(I)$. The dioxygen binding ability of the pentadentate isomer of the cobalt(II) complex has been studied, and the observed steric and electronic effects are evaluated as a basis for the control of dioxygen affinity.

## Introduction

The study of transition-metal complexes that bind dioxygen reversibly is of interest due to their potential use in dioxygen enrichment/separation and as models for the dioxygen-carrying heme proteins.[2] Complexes derived from pentadentate ligands are particularly attractive since they avoid the need for an exogenous Lewis base. Further, attention to the steric relationships associated with coordination of the appended base can be used to exert unusual control over ligand binding and, thereby, the dioxygen affinity of the complex. Here we report the synthesis and characterization of an unusual pentadentate cyclidene that exhibits impaired dioxygen affinity. This system joins the 2-methyl- and 1,2-dimethylimidazole complexes of various superstructured iron(II) porphyrins[3] as models for the T-form of hemoglobin.[4] In hemoglobin, it is believed that the conformational change associated with cooperative $O_2$ binding produces the observed reduction in dioxygen affinity by impairment of the axial ligand binding.

Several approaches have been adopted for the incorporation of an additional Lewis base to give a pentadentate ligand, as shown schematically in Figure 1 for complexes of various macrocyclic ligands possessing four other nitrogen donors. Cobalt(II) and iron(II) complexes formed from such pentadentate ligands reversibly bind dioxygen in the absence of added base.[4,5] Very few such complexes have sufficient autoxidation protection of the

---

* To whom correspondence should be addressed.
[†] The Ohio State University.
[‡] University of Warwick.

[1] Current address: Department of Chemistry, University of Kansas, Lawrence, KS 66045.
[2] (a) Traylor, T. G.; Traylor, P. S. *Annu. Rev. Biophys. Bioeng.* **1982**, *11*, 105. (b) Collman, J. P.; Halbert, T. R.; Suslick, K. S. In *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed.; Wiley & Sons: New York, 1980; p 1. (c) Busch, D. H. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1988; pp 61–85G. (d) Busch, D. H. *Trasfus. Sangue* **1988**, *33* (1), 57.
[3] (a) Collman, J. P.; Brauman, J. I.; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3333. (b) Geibel, J.; Cannon, J.; Campbell, D.; Traylor, T. G. *J. Am. Chem. Soc.* **1978**, *100*, 3525.
[4] Traylor, T. G. *Acc. Chem. Res.* **1981**, *14*, 102.
[5] (a) Niswander, R. H.; Taylor, L. T. *J. Am. Chem. Soc.* **1977**, *99*, 5935. (b) Zanello, P.; Cini, R.; Cinquantini, A.; Orioli, P. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2159. (c) Cini, R.; Zanello, P.; Cinquantini, A.; Colligiani, A.; Piazino, C.; Valentini, G. *Inorg. Chim. Acta* **1983**, *79*, 203. (d) Cini, R.; Zanello, P.; Cinquantini, A.; Colligiani, A.; Pinzino, C.; Valentini, G. *Inorg. Chim. Acta* **1984**, *88*, 105. (e) Colligiani, A.; Pinzino, C.; Valentini, G.; Cini, R.; Zanello, P.; Cinquantini, A. *Inorg. Chim. Acta* **1985**, *103*, 105. (f) Braydich, M. D.; Fortman, J. J.; Cummings, S. C. *Inorg. Chem.* **1983**, *22*, 484. (g) Delgado, R.; Glogowski, M. W.; Busch, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 6855.

0020-1669/90/1329-0616$02.50/0 © 1990 American Chemical Society