Structure, Electrochemistry, and Properties of Bis(ferrocenecarboxylato)(phthalocyaninato)silicon(IV) and Its Implications for (Si(Pc)O)$_n$ Polymer Chemistry[†]

Jack Silver,*[,‡] Jose L. Sosa-Sanchez,[§] and Christopher S. Frampton*[,||]

Department of Chemical and Life Sciences, The University of Greenwich, Woolwich Campus, Wellington Street, London SE18 9PF, U.K., Department of Biological and Chemical Sciences, Central Campus, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, U.K., and Roche Discovery Welwyn, P.O. Box 8, Welwyn Garden City, Herts Al7 2AY, U.K.

Received July 24, 1997

The crystal and molecular structure of bis(ferrocenecarboxylato)(phthalocyaninato)silicon(IV) (**1**) is reported. The structure is compared to the only other two fully solved Si(Pc) structures. The size of the Si atom is shown to vary with the nature of the axial ligands. The implications of this finding for the chemistry and structures of the [Si(Pc)O]$_n$ materials is discussed. The cyclic voltammograms of **1** manifest four couples. One of these is due to the ferrocenecarboxylato ligands; this indicates that both undergo oxidation and reduction at the same potentials. Here the first study of the electrochromic behavior of a complex that also contains a redox active ligand in addition to the electrochromic center (**1**) is also reported. The effect of the ligand redox properties on the electrochromic properties of the Si(Pc) center is discussed.

Introduction

The first silicon phthalocyanine was reported in 1960,[1] and within a few years a number of oligomeric silicon phthalocyanines containing silicon–oxygen backbones were reported.[2–7] Since then there has been considerable interest in such compounds and similar polymers in solution and in the solid state.[8–14]

Electronic and redox properties of both monomeric and oligomeric silicon phthalocyanines have been studied, and some have been successfully predicted from initial state molecular orbital energy levels.[15]

We have described the electrochromic properties of some silicon phthalocyanine thin films,[16] prepared from [Si(Pc)Cl$_2$], [Si(Pc)(OCH$_2$C$_6$H$_5$)$_2$], and [Si(Pc)(CH$_3$CO$_2$)$_2$]. Reversible color changes were observed for films of all three materials on cycling from neutral to negative voltages (to reduce the Si(Pc) entities) and back to neutral. As the Si(IV) does not easily reduce under the conditions used, the changes in color are ascribed to changes in the oxidation state of the phthalocyanine rings. It was demonstrated that the axial ligands have a major effect on the nature of the color change, and so it was thought worthwhile to investigate how a ligand capable of undergoing an oxidation change itself may modify the reduction colors of the Si(Pc) during electrochromic cycling. To attempt to address this point we have prepared bis(ferrocenecarboxylato)(phthalocyaninato)-silicon(IV), [Si(Pc)(FcCOO)$_2$], **1**. We report here the electro-chromic properties, electrochemistry, and crystal structure of **1** as well as the surprising solubility of this compound compared to its precursor [Si(Pc)Cl$_2$].

Experimental Section

2-Methoxyethyl ether (Aldrich) and ferrocenecarboxylic acid (Aldrich) were used without further purification. Quinoline (Aldrich) was vacuum distilled from BaO. Silicon tetrachloride (Aldrich) was used

---

* Authors to whom correspondence should be addressed: J.S., the chemistry work; C.S.F., the crystallographic work.

[†] Throughout this work Pc = the pthalocyaninato anion, [C$_{32}$H$_{16}$N$_8$]$^{2-}$, and cp = the cyclopentadienyl anion, [C$_5$H$_5$]$^-$.

[‡] The University of Greenwich.

[§] University of Essex.

[||] Roche Discovery Welwyn.

(1) Joyner, R. D.; Cekada, J., Jr.; Linck, R. G.; Kenney, M. E. *J. Inorg. Nucl. Chem.*, 1960, *15*, 387–388.

(2) Expositio, J. N.; Lloyd, J. E.; Kenney, M. E. *Inorg. Chem.* **1966**, *5*, 1979–1984.

(3) Janson, T. R.; Kane, A. R.; Sullivan, J. F.; Knox, K.; Kenney, M. E. *J. Am. Chem. Soc.* **1969**, *91*, 5210–5214.

(4) (a) Mooney, J. R.; Choy, C. K.; Knox, K.; Kenney, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 3033–3038. (b) Swift, D. R. Ph.D. Thesis, Case Western Reserve University, Cleveland, OH, 1970.

(5) Bernal Castillo, J.; Kenney, M. E. *Rev. Univ. Ind. San Tander, Invest.* **1978**, *8*, 5–15.

(6) Joyner, R. D.; Kenney, M. E. *Inorg. Chem.* **1962**, *1*, 717–718.

(7) Schoch, K. F., Jr.; Kundalkar, B. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 7071–7073.

(8) Dirk, C. W.; Inabe, T.; Schoch, K. F., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1539–1550.

(9) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1551–1567.

(10) Inabe, T.; Gaudiello, J. G.; Moquel, M. K.; Lyding, J. W.; Burton, R. L.; McCarthy, W. J.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7595–7608.

(11) Ciliberto, E.; Doris, K. A.; Pietro, W. J.; Reisner, G. M.; Ellis, D. E.; Fragalà, I.; Herbstein, F. H.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7748–7761.

(12) (a) Gaudiello, J. G.; Kellogg, G. E.; Tetrick, S. M.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 5259–5271. (b) Almeida, M.; Gaudiello, J. G.; Kellogg, G. E.; Tetrick, S. M.; Marcy, H. O.; McCarthy, W. J.; Butler, J. C.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 5271–5284 and references therein.

(13) (a) Marks, T J. *Science*, **1985**, *227*, 881–889. (b) Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 857–879.

(14) Lever, A .B· P.; Minor, P. C. *Inorg. Chem.*, **1981**, *20*, 4015–4017.

(15) Anderson, A. B.; Gordon, T. L.; Kenney, M. E. *J. Am. Chem. Soc.* **1985**, *107*, 192–195.

(16) (a) U.K. P.A. 9109350.0, Oct 1994: Monophthalocyanine as reversible electrochromics (inventors J. Silver and P. J. Lukes). (b) Lukes, P. Ph.D. Thesis, University of Essex, 1989.

as supplied but transferred under N_2. 1,2-Dicyanobenzene (Aldrich) was dried under vacuum at 70 °C overnight but used without additional purification. In all cases any reaction requiring a nitrogen atmosphere was carried out in a glassware apparatus that was dried under vacuum (10^{-1} Torr) and heating the outside with a hot air gun.

1,3-Diiminoisoindoline. 1,3-Diiminoisoindoline was synthesized from 1,2-dicyanobenzene by a literature modification of the original procedure.[11]

Dichloro(phthalocyaninato)silicon(IV). $Si(Pc)Cl_2$ was prepared by the literature method,[8] but the product was isolated at 80 °C by filtration using a sintered-glass funnel. The product was rinsed with ethanol to remove the remaining quinoline and then Soxhlet extracted consecutively with methanol (12 h), acetone (12 h), and chloroform (12 h).

$C_{54}H_{34}N_8O_4Fe_2Si$ (1). A 400 mL volume of dry 2-methoxyethyl ether (dried first with NaOH pellets and then by distillation from Na metal under reduced pressure) was purged by bubbling N_2 for ∼10 min under a N_2 atmosphere. A 2 g amount of ferrocenecarboxylic acid was added and the solution brought to reflux. A 200 mg amount of [$Si(Pc)Cl_2$] was added and the mixture refluxed for 90 min. The solution was then cooled to room temperature and filtered. The blue-green filtrate was precipitated into 1000 mL of distilled water giving a blue solid that was filtered out and dried at ∼70 °C under vacuum. The product was purified by column chromatography (silica gel 60) using dichloromethane as eluent. A 96 mg amount of a dark-blue powder was obtained (yield 28.5%). IR (Nujol; ν in cm^{-1}; intensities ν = very, s = strong, m = medium, w = weak): 644 (w), 722 (vs), 735 (vs), 760 (m), 772 (w), 822 (w), 913 (m), 1021 (m), 1080 (s), 1336 (vs), 1521 (m), 1610 (w), 1673 (s). IR (KBr disk; ν in cm^{-1} (intensity): 428 (w), 470 (m), 506 (vw), 536 (m), 575 (w), 694 (m), 736 (vs), 761 (m), 781 (w), 822 (w), 915 (m), 1002 (w), 1024 (m), 1066 (m), 1083 (s), 1124 (vs), 1162 (s), 1290 (vs), 1336 (vs), 1376 (m), 1431 (s), 1455 (m), 1474 (w), 1528 (m), 1674 (vs). UV/vis (1-chloronaphthalene; λ_{max} in nm (absorbance normalized relative to Q-band at 690): 690 (1.00), 659 (0.17), 622 (0.18), 302 (0.28). UV/vis (chloroform; λ_{max} in nm (absorbance normalized relative to Q-band at 686): 686 (1.00), 656 (0.13), 616 (0.15), 360 (0.28). ^{1}H NMR (CDCl$_3$; δ in ppm (nCH (multiplicity bs = broad singlet, s = singlet, t = triplet, m = multiplet, qt = quartet), total H$_{type}$): 2.16 (2CH (bs), 4H$_{subs\ fc}$); 2.76 (5CH (s), 10H$_{unsubs\ Fc}$); 3.18 (2CH (t), 4H$_{subs\ Fc}$); 8.39 (8H$_A$ (m), 8H$_{Pc}$); 9.74 (8H$_B$ (qt); 8h$_{pc}$). FAB/MS (NOBA; m/z (relative abundance): 988 (13), 892 (4), 769 (20), 677 (15), 657 (5), 621 (6), 577 (6), 415 (10), 391 (30), 260 (33), 121 (100). Anal. Calcd (found): C, 64.94 (63.30); H, 3.43(3.44); N, 11.22(10.47). These results are not good, but the X-ray structure proves the composition of the compound.

Thin Film Preparation. For the electrochromic studies, thin films of **1** on indium-doped tin oxide (ITO) transparent glass electrodes were prepared by vacuum sublimation of the powdered material using an Edwards E306-A vacuum sublimator. Before deposition, the ITO plates were cleaned in an ultrasonic bath with isopropyl alcohol first and then rinsed with acetone and deionized water. Deposition was carried out at 10^{-5} Torr.

Infrared Spectroscopy. Infrared spectra were recorded on a FT-IR Perkin-Elmer 938 spectrophotometer. Polystyrene film was used as a reference for calibration. Samples were examined by reflectance as thin films on ITO glass or by transmission as Nujol mulls between KBr plates in the range 450−1800 cm^{-1}.

Mass Spectroscopy. Mass spectral data were obtained on a double-focusing KRATOS MS-50 mass spectrometer by the fast atom bombardment method (FAB) using o-nitrobenzyl alcohol (NOBA) as a matrix.

NMR Spectroscopy. The proton magnetic resonance spectrum was recorded on a Jeol EX-270 Fourier transform instrument. TMS was used as the reference. The solvent was deuterated chloroform. The spectrum gave accurate integration.

Electronic Absorption Spectroscopy. All UV−visible spectra were recorded in 1-chloronaphthalene or as thin films on a Perkin-Elmer Lambda 2 spectrophotometer. For the solution analysis, the same solvent was used in the reference cell. For electrochromic experiments the absorbance was taken *in situ* by placing the working electrode coated with **1** in a 1 cm path-length cuvette filled with approximately 2 mL

of electrolyte solution. A blank ITO plate immersed in electrolyte in a matched cuvette was placed in the reference compartment. A silver wire was placed opposite the working electrode and used as the counter electrode. The required potential for the redox (electrochromic) experiments was supplied manually using a voltage source coupled to a multimeter in a serial arrangement.

Microanalysis. Elemental analyses were performed in-house using a Carlo-Erba 1106 analyzer (C, H, N).

Cyclic Voltammetry. Measurements were made with an EG&G PAR model 362 scanning potentiostat with a Condeconn 310 interface and software. A three-electrode cell configuration was used, with a platinum wire working electrode, platinum wire secondary electrode, and a silver wire reference electrode. The solvent used was dichloromethane with 0.2 M tetrabutylammonium tetraflouroborate as the support electrolyte. Potentials were internally referenced to the ferrocene−ferrocenium couple which was set as +0.45 V to the standard calomel electrode.

X-ray Diffraction Study of [Si(Pc)(FcCOO)$_2$] (1). Crystals suitable for X-ray diffraction studies were grown from chloroform. The crystals rapidly lost CHCl$_3$ so they were freshly grown for the data collection and frozen to minimize solvent loss. Unit cell determination and data collection on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The crystal was cooled to 123 K with an Oxford Cryosystems Cryostream cooler.[17] [a] The structure was solved with direct methods, SHELXS-90,[17b] and refined with full-matrix least squares on F^2 with SHELXL-93.[17c] R-values: $R1 = ||F_o| - |F_c||/|F_o|$; $wR2 = w(F_o^2 - F_c^2)^2/w(F_o^2)^2)^{0.5}$. A disorder model was successfully refined for one of the two CHCl$_3$ solvent molecules.

Crystal Data for 1·2CHCl$_3$: $C_{56}H_{36}N_8O_4Si_1Cl_6Fe_2$, M = 1237.42, monoclinic, space group $P2_1/n$, a = 10.417(6) Å, b = 21.046(9) Å, c = 23.130(6) Å, β = 94.22(4)°, V = 5057(4) Å^3, Z = 4, D_c = 1.625 g cm^{-3}, $F(000)$ = 2512, μ(Mo Kα) = 0.974 mm^{-1}, T = 123 K. Intensities, ($h,k,\pm l$) of a blue-green needle dimensions 0.15 × 0.20 × 0.40 mm were collected by the $\omega−2\theta$ scan method to $2\theta_{max}$ of 54°. A total of 11 638 reflections were collected of which 11 032 were unique (R_{int} = 0.0212). Data were corrected for Lorentz, polarization, and decay (−4.7%) but not for absorption. All non-hydrogen atoms were refined anisotropically; hydrogen atoms located by difference synthesis were included in the model but not refined. Full-matrix least-squares refinement of 730 parameters gave $R1$ = 0.0326 and $wR2$ = 0.0845 for $I \geq 2\sigma(I)$ and $R1$ = 0.0471, $wR2$ = 0.0942, and S = 1.035 for all data. The largest difference peak and hole = 0.706 and −0.789 e Å^{-3}, respectively.

Further details of the crystal structure investigation can be obtained on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K., quoting the full journal citation.

Results and Discussion

Crystal and Molecular Structure of 1. The molecular structure of **1** (Figure 1) reveals that both the ferrocenecarboxylato units are orientated to the same side of the phthalocyanine (Pc) ring rather than to opposite sides as commonly found in structures where ferrocene molecules bind to metals in macrocyclic rings.[18] In **1** we believe this is caused by molecular packing (Figure 2) forces. Similar forces may also be responsible for the tilt of the free cyclopentadienyl ring of the ferrocenes toward the (Pc) ring.

The average bond angles within the Si(Pc) plane are very similar to those found in [Si(Pc)(OSi(CH$_3$)$_3$)$_2$][4a] (**2**) and in the

(17) (a) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105. (b) Sheldrick, G. M. SHELXS-90. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (c) Sheldrick, G. M. SHELXL-93. Program for crystal structure refinement, Göttingen, 1993.
(18) (a) Cesario, M.; Giannotti, C.; Guilhem, J.; Zakrzewski, J. *Acta Crystallograph.* **1992**, *C48*, 798−802. (b) Cesario M.; Giannotti, C.; Guilhem, Silver J.; Zakrzewski J. *J. Chem. Soc., Dalton Trans.* **1992**, 3059−3060. (c) *Ibid. J. Chem. Soc., Dalton Trans.* **1997**, 47−53.

Figure 1. Molecular structure of **1**, (ellipsoids drawn at 50% probability level, H's atoms omitted for clarity).

Figure 2. Packing diagram of **1** showing the position of the ferrocenecarboxylato ligands.

two rings of $[((CH_3)_3SiO)_2Si(CH_3)OSi(Pc)OSi(Pc)OSi(Pc)OSi-(CH_3(OSi(CH_3)_3)_2]^{4b}$ (**2a**), though the bond lengths manifest some significant differences (Table 1). First, the Si—N bond lengths are significantly shorter in compound **1** and this must be a consequence of the longer Si—O axial bonds (Table 1) that leave the Si atom needing more electron density. This need is compensated by the Si atom bonding more strongly to the ligating N atoms in the Pc ring. Second, the shortening of the Si—N bonds causes a slight lengthening of the adjacent N—C bonds. The other bond lengths in the arene rings are similar to those in **2** and in **2a**. So overall we see that a contraction away from the center in the phthalocyanine core takes place in **2** to accommodate what must be a "larger" Si atom. The effective size of the Si atom in the Pc plane thus depends on the nature and distance of the axial ligands. In **1** the Si—O bond lengths of 1.749(2) and 1,751(2) Å are obviously weaker than those of **2** (1.678(2) and 1.680(2) Å) and provide evidence that the C

atom of the carboxylate group is more able to compete for the oxygen than the Si atom.

The possibility of the variation of the Si—N bond lengths in Si(Pc) structures is pertinent to both oxidized and nonoxidized $[Si(Pc)O]_n$ polymers such as those studied by Marks and co-workers.[9-13] Studies on such polymers[9-13] made extensive use of X-ray diffraction powder data to establish the positions of the Si(Pc) molecules. The interplanar distances[10,12a] along the *c* axes suggest Si—O bonds between the rings range from 1.615 to 1.618 Å (but the errors would be around 0.01 Å). Hence changes in the Si—O bond lengths that may occur on oxidation of the polymer were not detectable or taken into account. Similarly, Pc core contraction changes were also not detectable. The only full structural investigation reported in the literature for a $[(RSi(Pc))_2O]$ system was highly disordered on the axial ligands and only refined to $R = 12.7\%$.[11] The errors quoted in that work are around 0.020 Å so the authors could not actually make in-depth analysis of the bond lengths in the Pc plane.[11]

The Fe—C and C—C bond lengths in the ferrocencarboxylato ligands of **1** are within the usual range found in other structures containing this ligand.[19] The cp rings in each ligand in **1** are eclipsed. The fact that only one oxygen bond to the Si atom from each ligand makes the nonbonding C=O bond lengths worthy of note. The C=O lengths (1.211(3) and 1.214(3) Å) are very small for such ligands and are comparable to those found in diacetylferrocene (1.217 Å)[20] a but are much smaller than those reported for ferrocenedicarboxylic acid[20b] (though in the latter hydrogen bonding to the acidic H of the neighboring molecule lengthens the bond to around 1.26 Å). In contrast, the C—O bonding is much longer. In other compounds containing ferrocenecarboxylato bonds to metals[21,22] the C—O bond lengths are close to those found in ferrocenedicarboxylic acid,[20] so no previous structure shows a C—O bond from a ferrocenecarboxylate bound to a semimetal or metal as long as 1.333(3) or 1.337(3) Å as found in **1**. The carboxylate moieties are nearly coplanar with the cp rings to which they bond (at angles of 7.51(12) and 6.00(13)° to the cp planes).

Electrochromic Properties. Thin films of **1** were prepared by sublimation onto ITO transparent glass electrodes. On reduction using aqueous KCl (0.1 M) electrolyte the blue-green (neutral) films changed to blue (Figure 3), but this change was irreversible and usually resulted in film peeling from the electrode. The final reduced spectrum had five bands at 378, 500, 612, 688, and 865 nm, respectively. When the potential was no longer applied, the spectrum changed and had three main broad bands at 378, 624, and 867 nm. This final species gives an IR spectrum that identified it as $[Si(Pc)(OH)_2]$; it gave no evidence for the presence of a carbonyl stretch (Figure 4) . Thus, during reduction of the film the axial ferrocenecarboxylato ligands are replaced.

On oxidation in the same electrolyte some loss of color was detected (Figure 5) which was not reversed when the potential was no longer applied. The electronic spectrum of the returned neutral film was less intense than the original one and manifested a slight broadening of the bands. No major new band appeared in the 350–1100 nm region. No changes in the infrared were observed after the oxidation showing that the ferrocenecarboxy-

(19) Roberts, R. M. G.; Silver, J.; Yamin, B. M.; Drew, M .G. B.; Eberhardt, U. *J. Chem. Soc., Dalton Trans.* **1988**, 1549–1556.
(20) (a) Palenik, G. J. *Inorg. Chem.* **1970**, *9*, 2424–2430. (b) Palenik, G. J. *Inorg. Chem.* **1969**, *8*, 2744–2749.
(21) Churchill, M. R.; Li, Y.-J.; Nalewajek, D.; Schaber, P. M.; Dorfman, J. *Inorg. Chem.* **1985**, *24*, 2684–2687.
(22) Cotton, F. A.; Falvello, L. R.; Reid, A. H.; Tacher, J. H. *J. Organomet. Chem.* **1987**, *319*, 87–97.

Table 1. Selected Bond Lengths (in Å) around the Si Centers in the Three [Si(Pc)] Structures

	1	[SiPc(OSi(CH$_3$)$_3$)$_2$] (**2**)	cent of Pc ring	outer Pc ring
Si—O	1.749(2)	1.678(2)	1.666(4)	1.657(4)
Si—O	1.752(2)	1.680(2)	1.666(4)	1.706(5)
Si—N	1.900(2)	1.924(2)	1.926(5)	1.928(3)
Si—N	1.905(2)	1.922(2)	1.926(5)	1.914(6)
Si—N	1.907(2)	1.918(2)	1.924(5)	1.924(4)
Si—N	1.911(2)	1.915(2)	1.924(5)	1.921(6)
N—C$_1$ (av)	1.385(2)	1.375(4)	1.377(8)	1.379(7)
N$_1$—C$_1$ (av)	1.319(2)	1.32(4)	1.316(7)	1.320(8)
C$_1$—C$_2$ (av)	1.448(3)	1.449(4)	1.448(8)	1.441(7)
C$_2$—C$_2$ (av)	1.391(3)	1.386(5)	1.381(9)	1.383(7)
C$_2$—C$_3$ (av)	1.399(3)	1.391(3)	1.390(9)	1.386(7)
C$_3$—C$_4$ (av)	1.388(3)	1.380(6)	1.376(10)	1.376(8)
C$_4$—C$_4$ (av)	1.400(3)	1.385(2)	1.382(11)	1.387(8)

The header spanning columns 3–5: [((CH$_3$)$_3$SiO)$_2$Si(CH$_3$)OSi(Pc)OSi(Pc)-OSi(Pc)OSi(CH$_3$(OSi(CH$_3$)$_3$)$_2$] (**2a**)

^{a} Av = average of the distances.
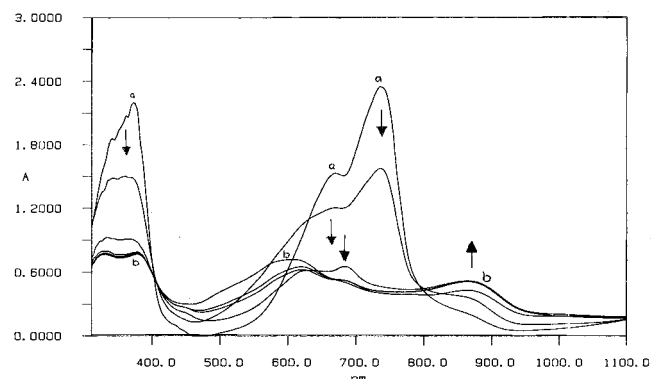
Figure 3. Electronic absorption spectra of a thin film of **1** on an ITO transparent glass electrode during the process of reduction using a 0.1 M KCl aqueous electrolyte. The original blue green film (labelled a) changes to blue (labeled b). Arrows indicate the direction of the band changes under negative potentials (up to −1.0 V) in the penultimate spectrum. The final spectrum obtained after cessation of the negative potential shows three broad bands labelled b.

Figure 4. Infrared spectrum taken from a film of **1** that underwent reduction (used for the experiment in Figure 3).
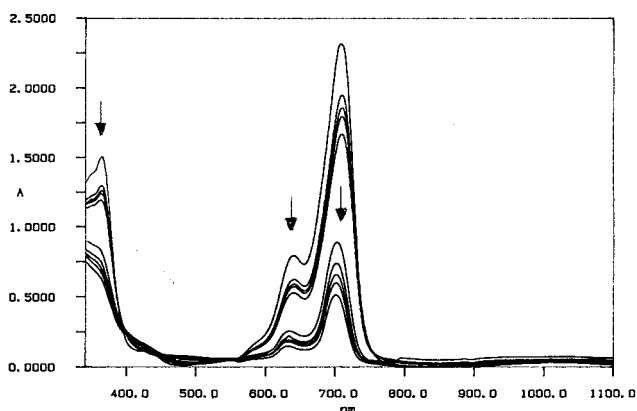
Figure 5. Electronic absorption spectra of a thin fim of **1** on an ITO transparent glass electrode under positive potentials up to +1.2 V for the final spectrum (oxidation) in 0.1 M KCl aqueous elecrolyte showing a loss of color. Arrows indicate the direction of change.
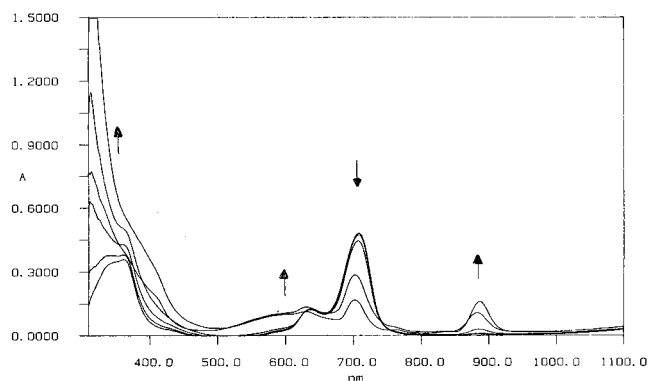
Figure 6. Electronic absorption spectra of a thin film of **1** on an ITO transparent glass electrode under oxidation (potentials up to +1.2 V for the final spectrum) in a 0.1 M KBr aqueous electrolyte. Arrows indicate the direction of change.

lato ligands remained on the complex. There were some very minor changes around 400−500 nm in the oxidized spectrum (Figure 5) that may be due to the oxidized ligand. These then disappeared when the potential no longer applied. It seems that the presence of the ferrocenylcarboxylato ligands affects the stability (on reduction) and properties of the films. More evidence for this was found from the cyclic voltammetry analysis carried out on compound **1**. The films could be voltage cycled between the oxidized and neutral state around 10^2 times before the films manifest obvious fading.

When the aqueous electrolyte was changed to 0.1 M KBr, the reduction process was identical to that in the KCl case. This was expected as the same K$^+$ ions would enter the film for charge balance in each case. However, on oxidation the results were different (Figure 6). New bands were observed at 580 and 884 nm, and the band in the Soret region increased significantly in intensity. (We believe this latter band grows due to the formation of bromine). There was a smaller change in the 400−500 nm region which may again be associated with the ferrocenecarboxylato ligand being oxidized or may be part of the tail of the bromine spectrum. These changes in oxidation were also found when a film of **1** was exposed to bromine vapor
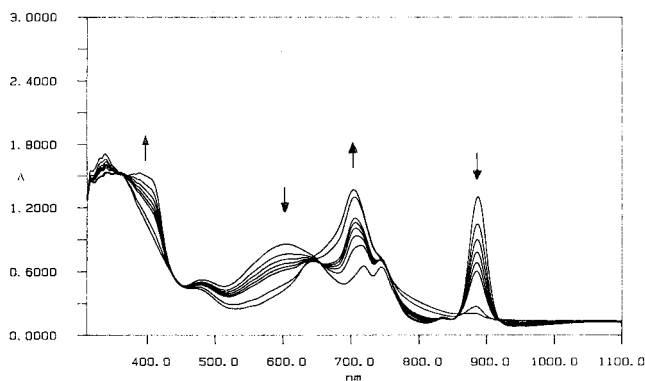
Figure 7. Electronic absorption spectra of a thin film of **1** on glass. The film was oxidized by Br_2 vapor, and then removed from the vapor. Spectra were then taken at 100 min intervals. They show the changes occurring as the Br_2 vapor is released from the film.

(see time scans taken every 100 min showing release of vapor (Figure 7) and further discussion after the following paragraph).

Infrared spectra of the species obtained after releasing the oxidation potential in the KBr electrolyte had a number of changes compared to the original neutral film; particularly, the C=O stretch moved to 1684 cm^{-1} from 1670 cm^{-1} and several other changes were apparent, with several bands changing position or relative intensity. However, this neutral to oxidized species can be cycled. Thus we suggest that the changes in the infrared of the returned to neutral species that occur through release of the oxidation potential are likely to be the result of either a phase change caused by the Br$^-$ ions entering the films when they oxidize, or at least they indicate more porous films. Such phase changes generated by electrochromic cycling have been observed previously.[13b,23 a–c] In addition the ferrocenecarboxylato ligands which are also oxidized during this process will remain oxidized on release of the potential and some Br$^-$ ions will remain in the film to balance this charge. On oxidation the Br$^-$ ions in the lattice (not associated with the oxidized ferrocenecarboxylato entities) near the electrode lose electrons to generate bromine. When the potential is no longer applied, then the oxidized species are slowly reduced by the surrounding chemical environment in solution. The Br$^-$ ions flow out of the film during this process, and the Br_2 molecules probably first reoxidize some of the molecules of **1** becoming Br$^-$ ions. These ions then flow out as the reoxidized molecules of **1** are in turn reduced. However, the Br$^-$ ions balancing the charge on the oxidized ferrocenecarboxylato ions remain.

The infrared spectrum obtained after the chemical oxidation process has had time to reverse is also different to that of the original neutral film (Figure 8a) though the electronic spectrum is very similar. The C=O band in this case is at 1689 cm^{-1}, and other changes are apparent (Figure 8b). The Br_2 molecules instantaneously oxidize the exposed films of **1** as they enter becoming Br$^-$ ions and then on removal of the films from the Br_2 environment the process slowly reverses. Thus on oxidation the films expand to accommodate the Br$^-$ ions. Again, as seen from the C=O stretch in the final infrared spectrum, the ferrocenecarboxylato ligands are still oxidized.

From the changes in the final infrared spectra and the lack of change in the final electronic spectra of both the electrochemical and chemically oxidized films when returned to their neutral states, we conclude that the films are more porous. This
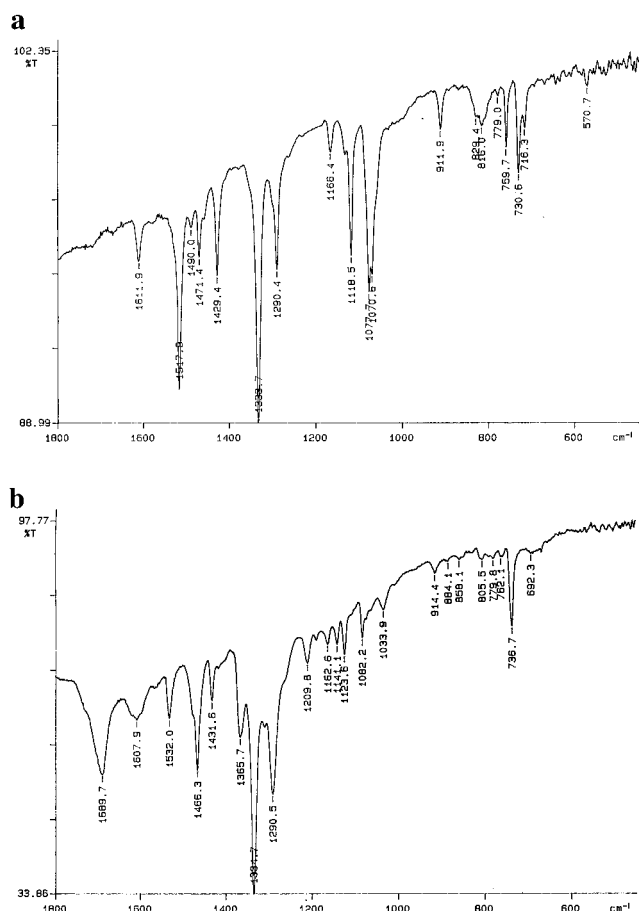
(23) (a) Silver, J.; Lukes, P.; Hey, P.; Ahmet, M. T. *J. Mater. Chem.* **1991**, *1*, 881–888. (b) *Ibid.* **1991**, *2*, 841–847. (c) Silver, J.; Lukes, P.; Houlton, A.; Howe, S.; Hey, P.; Ahmet, M. T. *J. Mater. Chem.* **1992**, *2*, 849–855.

Figure 8. (a) Infrared spectrum of a thin film of **1** on glass before exposure to Br_2 vapor. (b) As in (a) except after exposure to Br_2 vapor. Note change in position of the C=O stretch to 1689 cm^{-1} compared to that in (a).

change is due to film expansion and manifests itself in the infrared spectra more than the electronic spectra. If it had been a full phase change, we would have expected more change in the electronic spectra as seen for instance in α and β-[Fe(Pc)].[23c] It should be noted that oxidized ferrocenecarboxylato groups would not be expected to alter the electronic spectra of the complex much as the extinction coefficients of the ferrocene type molecules are very small. From these observations we conclude that when an oxidizable ligand is present on Si(Pc) it takes part in the oxidation cycle and if stable in its oxidized form remains in that state causing changes in the film structure if the potential is released. However if it is cycled back to neutral under an applied potential, it will be reduced.

Cyclic Voltametry. Four redox processes were observed for **1** (Table 2). By comparison to ferrocenecarboxylic acid itself, the redox process due to the latter ligand in compound **1** is at 0.69(2) V relative to the S.C.E. Hence, the other three redox processes are due to the macrocyclic ring.

In the main group pthalocyanines the first oxidation potential is separated from the first reduction by around 1.5 V which is said to correspond to the magnitude of the energy difference between the HOMO and LUMO (except for the cases where the metal ions are not in the macrocyclic plane, for example Pb^{2+} or Cd^{2+}).[14] However, it has been established that the individual potentials for the first ring reduction and first ring oxidation do vary and are functions of the polarizing potential of the central metal ion (taken as charge/radius (ze/r)). It has been shown that the more polarizing the central metal ion, the more difficult it is to oxidize and the easier it is to reduce the

Table 2. Main Group Element Pthalocyanines Exhibiting Redox Processes Occurring at the Ring Alone, the Metal or Metalloid Center Remaining Invariant (All in V versus SCE)

compd	oxidn potentials			redn potentials		solvent	ref
	2nd	1st	other oxidn[a]	1st	2nd		
1		1.23(2)	0.69(2)	−0.55(2)	−1.02(2)	CH_2Cl_2	this work
4				−0.54	−1.14	DMF	14
3		1.00		−0.90	−1.48	CH_2Cl_2	24
$ClGa^{III}Pc$		0.86		−0.74	−1.14	DMF	14
$ClIn^{III}Pc$		0.83		−0.72	−0.95	DMF	14
$Cd^{II}Pc$	0.88	0.54		−1.17		DMF	14
$Hg^{II}Pc$		0.25		−1.30		DMF	14
$Mg^{II}Pc$	1.26	0.65		−0.92	−1.26	DMF	14

[a] Oxidation potential of the ferrocenecarboxylato groups in **1**.

macrocyclic ring.[14] Linear plots of ze/r against the first oxidation and first reduction potentials have been obtained for many M(Pc) species.[14] On the reduction plot [(O-^{t}Am)$_2$Si(Pc)] (O-^{t}Am = *tert*-amyloxy) with a reduction potential of −0.540 V fitted very well, though no oxidation potential was given for the compound.[14]

Compound **1** has a first reduction potential of −0.55(2) V, which is in keeping with the above, and its first oxidation potential of 1.23(2) V is not too far from the straight line established for the first oxidation potentials.[14] However for compound **1** the separation between the first reduction and oxidation potential is 1.79(4) V. This separation value is close to that of [((n-C_6H_{13})$_3$SiO)$_2$Si(Pc)] (**3**) which has a value of 1.90 V.[24] It is worth noting that such separations of 1.79 and 1.90 V match well the splitting of 1.86 eV between the a_{1u} and e_g levels seen in ref 26 and of 1.80 eV (see discussion of the electronic spectrum) in this work for **1**. We note in agreement with Lever *et al.*[14,25] that the first reduction potential for **3** does not fit the polarization plot, whereas those of **1** do. It might be expected that compound **3** has a geometry around the Si atom very similar to that of **2**, whereas we expect the Si−O bond length in [(O-^{t}Am)$_2$Si(Pc)] (**4**) is more likely to be similar to that found in **1** as in **4** the O atom bonds to a C atom. Compounds **1** and **4** would then be expected to have oxidation and reduction potentials that are close to each other, and we would expect compound **3** to have different values. The shorter Si−O bonds in **3** would mean the polarizing power of the Si atom in this compound is less great in the Pc ring and hence it is more difficult to reduce.

The oxidation potential of the ferrocenecarboxylato groups in **1** is 0.69(2) V; they apparently undergo simultaneous rather than sequential oxidation and reduction. By the cycling of **1** between 0 and + 1.2 V, it was established that the ferrocenecarboxylato ligand could be reversibly oxidized without decomposing the complex. This is in keeping with the oxidation of the thin films which were also reversible. The oxidation potential of the ligand is close to that of ferrocenecarboxylic acid, 0.65(2) V, in the same solvent. It is therefore just harder to oxidize this moiety when it is complexed to Si(Pc) than it is uncomplexed. In CH_2Cl_2 the ferrocenecarboxylic acid is likely to be partially deprotonated, but it has not been established whether it is a monomer or not. The second reduction potential of **1** is at −1.02(2) V. It was not possible to verify the behavior

of **1** in aqueous media (due to its insolubility) so it could not be compared to the thin film on reduction. In CH_2Cl_2 **1** could be reversibly cycled between −1.5 and 1.0 V without serious change to the cyclic voltammogram. So in the absence of water no evidence was found for the replacement of the ferrocenecarboxylato ligands. This was quite different from the thin films.

Electronic Spectrum. The UV−visible absorbance spectrum of **1** in 1-chloronaphthalene shows the Q band at 690 nm which corresponds to 1.80 eV. This corresponds to the difference between the HOMO and the LUMO orbitals and therefore to the difference between first oxidation and first reduction potential of **1**.[25,26] The spectrum in the thin films (Figure 3) show that in the solid state the Q band is centered at 710 nm.

NMR Spectra. The positions of the ^{1}H resonance's in **1** are in keeping with the presence of large ring-current effects.[27 a,b] The resonances of the ferrocene carboxylate groups all show substantial high-field shifts compared to the positions of such moieties in the absence of a macrocyclic ring current. It is worth comparing the ^{1}H resonances of the ferrocenecarboxylate group with those reported for the related [GeTPP(Fc)$_2$] (**5**). The inner cyclopentadienyl rings in **1** give rise to an AA′BB′ multiplet that arises as the ring is fixed as in **5**, though in **1** the overall the shifts caused by the macrocyclic rings currents are less as the cyclopentadienyl ring is further from the macrocycle. The outer cp ring protons of **1** give rise to a singlet showing the rings rotate freely in solution just as found in **5**.[17a]

Mössbauer Spectroscopy. Compound **1** manifests a quadrupole splitting (ΔE_Q) of 2.33(1) mm s^{-1}, which is closer to that of ferrocene itself (2.37(1) mms^{-1}) than it is to ferrocenecarboxylic acid (2.23(1) mms^{-1}). These data, which while showing that in **1** the ferrocenecarboxylato ligands are electron deficient at the iron center compared to ferrocene itself,[28−31] also show that the deficiency is only small. This shows that the [Si(Pc)] moiety in **1** is not pulling as much electron density from the ferrocenecarboxylato ligands as the proton does in the parent acid. This finding is in keeping with the long Si−O

(24) De Wulf, D. W.; Leland, J. K.; Wheeler, B. L.; Bard, A. J.; Batzel, D. A.; Dininny, D. R.; Kenney, M. E. *Inorg. Chem.* **1987**, *26*, 266−270.

(25) Lever, A. B. P.; Milaeva, E. R.; Speier, G. In *Phthalocyanines, Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, **1993**, Vol. 3, pp 1−69.

(26) Hush, N. S.; Woolsey, I. S. *Mol. Phys.* **1971**, *21*, 465−474.

(27) (a) Maskasky, J. E.; Kenney, M. E. *J. Am. Chem. Soc.* **1971**, *93*, 2060−2062. (b) Wheeler, B. L.; Nagasubramanian, G.; Bard, A. J.; Schechtman, L. A.; Dininny, D. R.; Kenney, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7404−7410.

(28) Houlton, A.; Miller, J. R.; Roberts, R. M. G.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1990**, 2181−2184.

(29) Houlton, A.; Miller, J. R.; Roberts, R. M. G.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1991**, 467−470.

(30) Houlton, A.; Brown, R. A.; Roberts, R. M. G.; Silver, J.; Slade, E. *J. Chem. Soc., Dalton Trans.* **1993**, 1519−1523.

(31) Brown, R. A.; Houlton, A.; Howe, S. D.; Roberts, R. M. G.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1993**, 3329−3332.

bond and the resulting Si−N bonds found in the structure. Thus the carboxylate groups need little electron density from their ferrocenes.

We have previously found a linear relationship between oxidation potential and ΔE_Q [32] for substituted ferrocenes. The oxidation potential and ΔE_Q for **1** does not fit this relationship, and indeed the oxidation potential is close to that of the parent ferrocenecarboxylic acid. We believe this is due to the fact that on oxidation there will be a total change in the bond lengths of the Si−O(C═O)C$_{ferrocene}$ areas of the molecule. We note that a similar oxidation potential for the ferrocenecarboxylates was found in the Cu salts;[21] we found that the latter compound also has a ΔE_Q value close to that of ferrocene itself.[33] Thus it appears that when oxidation potentials are affected by bonding remote from the iron atom in the ferrocene, then the relationship we previously found breaks down.[32]

Conclusions

The structure of **1** has yielded some useful insight into the ability of the Pc ring to change its structure to accommodate Si atoms that manifest different effective atomic radii when bound to different axial ligands. This finding has important ramifica-

tions as the influence of such an effect has not been considered in the structure of [Si(Pc)O]$_n$ polymers when partially oxidized.

The electrochromic properties of **1** are very different from our previous findings due to the presence of the ferrocenecarboxylato ligands. During reduction of the films of **1** this ligand becomes electron rich and is replaced on the the Si(Pc) by OH$^-$ ions. The fate of the ferrocencarboxylato species when the replacement takes place was beyond the scope of this work. On oxidation of the films of **1** in aqueous solution the ferrocenecarboxylato ligands become oxidized and appear to remain oxidized when the potential is released. However if the films are reduced from the oxidized state to the neutral state, the ligands are also reduced. The latter observation is in keeping with the cyclic voltammetry results in CH$_2$Cl$_2$. In CH$_2$Cl$_2$ **1** could be cycled between the oxidized and reduced states reversibly.

Supporting Information Available: One X-ray crystallographic file, in CIF format, is available for [Si(Pc)(FcCOO)$_2$]. Access information is given on any current masthead page.

IC970934X

(32) Roberts, R. M. G.; Silver, J. *J. Organomet. Chem.* **1984**, *263*, 235−241.
(33) Jassim, Q. A. A. Ph.D. Thesis, University of Essex, 1987.