175. Synthesis and Characterization of Crown-Ether-Containing Phthalocyanines with Group-IV-A Elements

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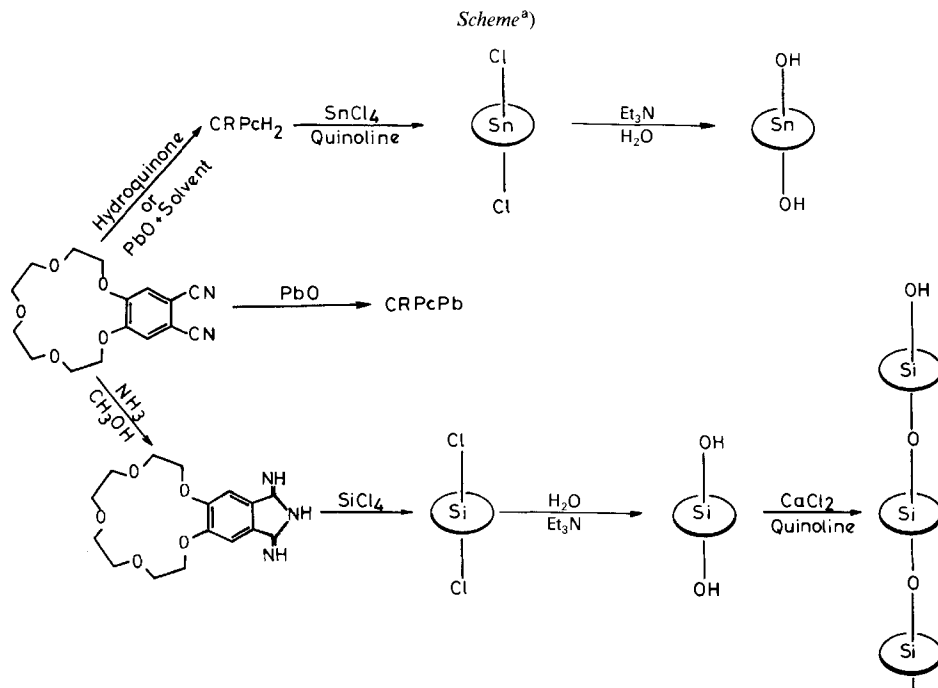
Group-IV-A phthalocyanines with four crown ether substituents have been prepared from 4',5'-dicyanobenzo(15-crown-5), 4',5'-diiminoisoindolino(15-crown-5), or metal-free phthalocyanine and the corresponding metal salts. The axial ligands of dichloro[tetra(15-crown-5)phthalocyaninato]silicon or -tin have been converted into dihydroxy derivatives by hydrolysis in aqueous Et_3N. The catalytic effect of H_2O-free $CaCl_2$ in quinoline is used for the polycondensation of dihydroxysilicon-phthalocyanine to cofacially arrayed polymers. The thermal stability of group-IV-A-metal phthalocyanines is confirmed by the higher initial decomposition points (290–440°) compared to those of the corresponding transition-metal phthalocyanines.

Introduction. – Phthalocyanines with crown ether substituents display a number of interesting properties which would make their incorporation with group-IV-A-metal ions of interest. In general, crown ether groups enhance the solubility of phthalocyanines. In addition, synthetic model systems of ion channels allowing the migration of alkali or alkali-earth cations have been reported to form by the 'piling up' of metal-free or copper phthalocyanines with four (15-crown-5) moieties [1]. Another distinct feature of phthalocyanines is the increase of conductivity after partial oxidation by halogen dopants [2–4].

Group-IV-A-metal phthalocyanines are capable of constructing more refined macrocycle stacking relationships *via* the condensation of axial ligands (*e.g.* OH, SH), consequently, the inclination of crown ether groups will be more appropriate for ion-channel formation, and the interplanar spacing of the phthalocyanine moieties will be more specific for halogen dopants than the ordinary stacking of planar monomeric phthalocyanine molecules.

Initial activity in our laboratory is focused upon synthesizing and understanding the properties of new types of crown-ether substituted metal-free and transition-metal phthalocyanines [1][5–7]. Ge-phthalocyanines were also investigated [8]. The objective of the present work is to devise syntheses of group-IV-A phthalocyanines with crown ether substituents.

Scheme[a])

[a])　The circle around Sn and Si denote the dianion of phthalocyanine with four (15-crown-5) moieties.

Results and Discussion. – 4′,5′-Dicyanobenzo(15-crown-5) was obtained from the dibromo derivative by refluxing in DMF with 3 equiv. of CuCN [7] [9]. Group-IV-A-metal phthalocyanines were synthesized either from dicyanobenzo(15-crown-5) or metal-free phthalocyanine (CRPcH₂) and the corresponding metal salts *(Scheme* and *Fig. 1).*

In view of the routes previously found to be useful for the preparation of silicon phthalocyanines, the synthesis of dichloro[tetra(15-crown-5)phthalocyaninato]silicon
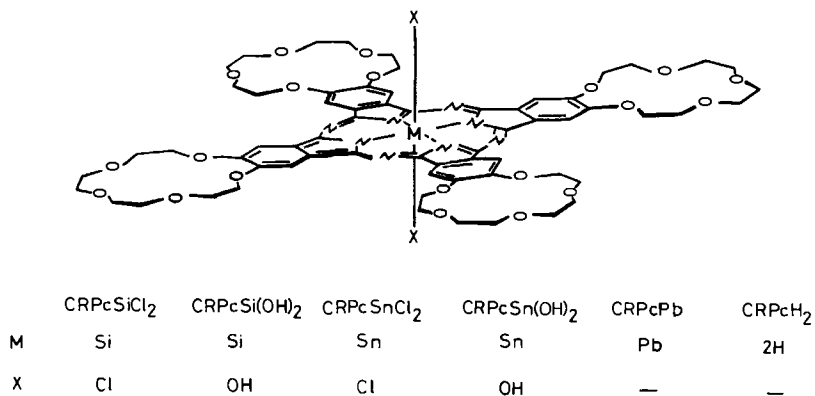

M	CRPcSiCl₂	CRPcSi(OH)₂	CRPcSnCl₂	CRPcSn(OH)₂	CRPcPb	CRPcH₂
M	Si	Si	Sn	Sn	Pb	2H
X	Cl	OH	Cl	OH	–	–

Fig. 1. *Group-IV-A-metal phthalocyanines*

Table 1. *Elemental Analysis of Phthalocyanines*

	Calc. [%]			Found [%]		
	C	H	N	C	H	N
CRPcSiCl$_2$	56.01	5.29	8.16	56.36	5.25	8.62
CRPcSi(OH)$_2$	57.56	5.58	8.39	57.39	5.20	8.64
HO(CRPcSi–O)$_n$–H[a])	58.35	5.50	8.50	58.57	5.05	8.12
CRPcSnCl$_2$	52.54	4.96	7.66	52.84	4.93	7.35
CRPcSn(OH)$_2$	53.90	5.23	7.85	53.70	4.81	7.44
CRPcPb	51.92	4.90	7.56	51.81	4.70	8.07
CRPcH$_2$	60.2	5.60	9.00	59.93	5.73	8.96

[a]) Calculated values correspond to the part shown in brackets.

(CRPcSiCl$_2$) from SiCl$_4$ and the dicyano compound could not be accomplished. To obtain CRPcSiCl$_2$, 4'5'-dicyanobenzo(15-crown-5) should be first converted into 4',5'-diiminoisoindolino(15-crown-5) which would then give the desired phthalocyanine when reacted with SiCl$_4$ under inert atmosphere [8][10–12]. Since CRPcSiCl$_2$ can be hydrolized to dihydroxy derivative CRPcSi(OH)$_2$ by treating with a suitable organic base (*e.g.* Et$_3$N), it appears that CRPcSiCl$_2$ will be a suitable intermediate for the synthesis of silicon phthalocyanines *(Table 1)*.

The polycondensation of dihydroxysilicon phthalocyanines to cofacially arrayed polymers has been usually carried out at high reaction temperatures of *ca.* 440° [2]. However, thermal degradation of crown-ether substituents occurs before this temperature was reached [7]. Consequently, catalytic effect of H$_2$O-free CaCl$_2$ in a high-boiling solvent should be employed to obtain polymers with reasonable number-average polymerization degree (HO[CRPcSi–O]$_n$–H) as indicated by *Orthmann* and *Wegner* [13] *(Fig. 2)*.

Among these silicon phthalocyanines, only CRPcSiCl$_2$ is sufficiently soluble in suitable solvents (*e.g.* DMSO) to obtain ^{1}H-NMR spectra. The signals of the aromatic
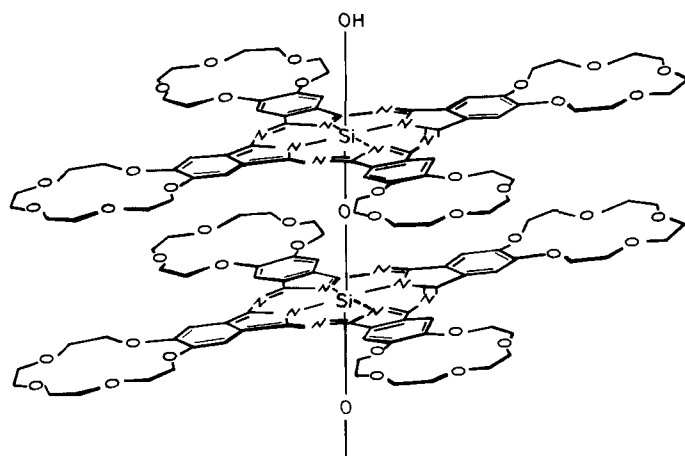

Fig. 2. *HO(CRPcSi–O)$_n$–H polymer (n ≈ 25)*

protons appear as a *singlet* at 8.06 ppm, while those of the aliphatic protons of crown ether moieties are observed between 3.85–3.51 ppm.

In the IR spectra of the three silicon phthalocyanines, the axial substituents can be clearly differentiated. For CRPcSiCl$_2$, the Si−Cl absorptions are observed at 520 cm^{-1} [12][14]. In the case of the dihydroxy derivative, this band disappears, while the absorptions at 870 cm^{-1} are attributed to O−Si−O antisymmetric stretching [2]. A weak band at the same frequency in the spectrum of CRPcSiCl$_2$ should be a consequence of partial hydrolysis. After the polymerization reaction, the 870-cm^{-1} band almost disappears, and a new Si−O-related broad band appears around 1100–1000 cm^{-1}, the region for aliphatic ether bands [2][7].

The average degree of polymerization was estimated by quantitatively determining the relative $\tilde{v}_{M-O} = 870$ cm^{-1} areas in the IR spectra of monomer and polymer relative to the well characterized invariant Ar−O−C modes of the crown ether moieties at 1210 cm^{-1} [2][15]. The average degree of polymerization was calculated according to the following reaction:

$$n \; CRPcSi(OH)_2 \rightarrow (HO)[CRPcSi-O]_n-H + (n-1) \; H_2O$$

The value of n was found to be around 25, and reproducible results within 10% deviations were obtained in subsequent reactions.

Sn is another group-IV-A element capable of forming extensive series of phthalocyanines [16–18]. Dichloro[tetra(15-crown-5)phthalocyaninato]tin (CRPcSnCl$_2$) was obtained only by reacting metal-free phthalocyanine (CRPcH$_2$) directly with SnCl$_4$ in quinoline. Other attempts to synthesize the same compound from dicyano or diiminoisoindoline derivative gave no defined products. *trans*-Chloro substituents can be hydrolyzed into dihydroxy derivative [CRPcSn(OH)$_2$], analog to the Si derivatives. Aqueous Et$_3$N solution has been proved to be the best medium for the hydrolysis.

Sn−Cl absorptions observed at 440 cm^{-1} in the IR spectrum of CRPcSnCl$_2$ disappeared after hydrolysis [2]. The Sn−O stretch and vibration bands of CRPcSn(OH)$_2$ can be assigned to peaks at 585 and 312–575 cm^{-1}, respectively [19]. The VIS spectra of the dichloro and dihydroxy derivatives can be easily distinguished by a relatively intense band at 760 nm for CRPcSnCl$_2$ which disappears for CRPcSn(OH)$_2$.

The reaction of 4′,5′-dicyanobenzo(15-crown-5) and PbO altogether in ethyleneglycol gave metal-free phthalocyanine (CRPcH$_2$) identified to be the same as the previously reported compound [7]. Similar phenomena were observed in the synthesis of phthalocyanine polymers from tetracyanodibenzo(18-crown-6) and PbO [20]. Probably, the oxidation of Pb(II) to Pb(IV) supplies the necessary two electrons to complete the 18-π electron system of the phthalocyanine moiety. To obtain lead phthalocyanine (CRPcPb), portionwise addition of PbO as described by *Linstead* and coworkers [21] was necessary.

CRPcPb is soluble in various organic solvents (*i.e.* CH$_2$Cl$_2$, CHCl$_3$, DMSO, *etc.*) as most of the other crown ethers containing transition-metal(II) complexes [7]. This property enabled us to obtain some spectra in solution.

In the ^{13}C-NMR spectrum of CRPcPb in CDCl$_3$, absorptions of CH$_2$ C-atoms are between 70.50 and 68.39 ppm. The signals of the protonated aromatic C-atoms appear at 105.45 ppm; they split into two peaks at 107.21 and 104.0 ppm in the ^{1}H-coupled spectrum. The other three peaks can be assigned to aromatic C-atoms with alkoxy ($\delta = 150.15$ ppm) and alkyl substituents ($\delta = 132.04$ ppm), and the C-atoms in the inner

Table 2. *Thermal Properties of the Phthalocyanines*

	Initial decomp. temp. [°C]	Main decomp. temp. [°C]
CRPcSiCl$_2$	290	400
CRPcSi(OH)$_2$	350	550
OH(CRPcSi–O)$_n$–H	300	550
CRPcSnCl$_2$	410	500
CRPcSn(OH)$_2$	420	560
CRPcPb	440	520
CRPcH$_2$	290	410

core of phthalocyanine ring (δ = 153.91 ppm). In the ^{1}H-coupled spectrum, there is no considerable shift of these three peaks.

^{1}H-NMR spectrum of CRPcPb is also in agreement with the proposed structure. While aromatic H-atoms show a *singlet* at 8.72 ppm, the signals for the aliphatic ether H-atoms appear between 4.37 and 3.55 ppm [7].

Crown-ether-containing phthalocyanines can also be considered as crown ethers of high thermal stability [7][20]. This property is further confirmed with group-IV-A-metal phthalocyanines *(Table 2)*. The initial decomposition temperatures of the compounds synthesized during this work varies between 290 and 440°, and they decrease in the order of Pb > Sn(OH)$_2$ > SnCl$_2$ > Si(OH)$_2$ > SiCl$_2 \geqslant$ 2H. The thermal stability of group-IV-A-metal phthalocyanines is higher than that of the corresponding transition-metal phthalocyanines [7].

Experimental. – *General.* The UV/VIS spectra (λ_{max} [nm] (ε)) were obtained on a *Varian-DMS-90* spectrophotometer. IR spectra [cm^{-1}] were recorded on a *Perkin-Elmer-983* spectrophotometer (KBr pellets). ^{1}H- and ^{13}C-NMR spectra were taken on a *Bruker* 200-MHz spectrometer. Thermogravimetry and differential thermal analysis were run on a *DuPont* differential thermo-instrument type *990* at 10° min^{-1} (N$_2$ flow 20 cm^3·min^{-1}). Benzo(15-crown-5) [22], 4′,5′-dicyanobenzo(15-crown-5) [7], 4′,5′-diiminoisoindolino(15-crown-5) [8], and metal-free tetra(15-crown-5)-substituted phthalocyanine (CRPcH$_2$) [7] were synthesized according to the published procedures.

Synthesis of Dichloro[tetra(15-crown-5)phathalocyaninato]silicon (CRPCSiCl$_2$). SiCl$_4$ (3 ml, 26.2 mmol) was added to 19 ml of freshly distilled anh. quinoline under Ar and rapidly heated to 200°. At this temp., a suspension of 4 g (11.92 mmol) of 4′,5′-diiminoisoindolino(15-crown-5) in 15 ml of anh. quinoline was added to the soln. When the addition was completed, the colour became dark brown. The mixture was refluxed for 1 h and then cooled to 80°. The reaction medium was diluted with 20 ml of CHCl$_3$, refluxed for 1/2 h, and after cooling to r.t., it was filtered, washed first with CHCl$_3$ and then with EtOH and acetone. Well ground green product was stirred in 80 ml of conc. H$_2$SO$_4$ at r.t. over night, filtered, poured into ice-water, and the precipitate was separated by centrifugation. This product was treated with conc. HCl (20 ml) and then filtered, washed first with H$_2$O, until the filtrate became neutral, and successively with EtOH and Et$_2$O, dried *in vacuo* at 110°. Yield: 1.92 g (47%). UV/VIS (DMSO): 685 (39000), 658 (27200), 612 (15100), 451 (26400), 358 (51600), 338 (48800), 292 (60500). IR (KBr): 3400, 2920, 1600, 1480, 1390, 1290, 1210, 1090, 1040, 1020, 930, 870, 750, 615, 520. ^{1}H-NMR ((D$_6$)DMSO): 8.06 (*s*, 8 H); 3.85–3.51 (*m*, 64 H).

Hydrolysis of CRPcSiCl$_2$ to CRPcSi(OH)$_2$. CRPcSiCl$_2$ (0.38 g, 0.277 mmol) was stirred in a mixture of Et$_3$N/H$_2$O 1:1 (11 ml) at r.t. for 40 h and then evaporated to dryness under reduced pressure. The residue was treated with EtOH (3 ×) and then with Et$_2$O, and dried *in vacuo* at 110°. Yield: 0.35 g (95%). UV/VIS (DMSO): 685 (19200), 658 (15100), 448 (21600), 415 (21400), 357 (33100), 340 (33400), 285 (43200). IR (KBr): 3400, 2940, 1610, 1480, 1400, 1360, 1290, 1210, 1100, 1060, 1030, 940, 870, 760.

Polymerization of CRPcSi(OH)$_2$. CRPcSi(OH)$_2$ (50 mg, 0.0374 mmol) and CaCl$_2$ (10 mg, 0.09 mmol) was refluxed in anh. quinoline (5 ml) for 5 h. After filtration, the precipitate was washed successively with abs. EtOH, hot H$_2$O, EtOH again, and Et$_2$O, and dried *in vacuo* at 110°. Yield: 30 mg (61%). IR (KBr): 3420, 2920, 1600, 1470, 1350, 1280, 1210, 1100, 1040, 870, 760.

Synthesis of CRPcSnCl₂. Anh. SnCl₄ (0.1 ml, 0.85 mmol) was added into anh. quinoline under Ar, and then metal-free phthalocyanine (CRPcH₂; 0.250 g, 0.196 mmol) was charged into this mixture rapidly with vigorous stirring. After the reaction mixture was held at 220° for 2.5 h, it was cooled to r.t., and diluted with quinoline/EtOH 1:2 (6 ml), and filtered. The purplish green precipitate was treated with conc. HCl (15 ml) twice and centrifugated with H₂O, until the centrifugate was neutral, then washed with CHCl₃ and Et₂O, and dried *in vacuo* at 110°. Yield: 0.1 g (35%) UV/VIS (DMSO): 760 (35000), 711 (60400), 674 (22000), 640 (15100), 506 (22800), 364 (36200), 327 (25200), 287 (22300). IR (KBr): 3430, 2920, 1600, 1500, 1480, 1440, 1400, 1380, 1350, 1280, 1210, 1110, 1055, 940, 875, 735, 440.

Hydrolysis of CRPcSnCl₂ to CRPcSn(OH)₂. This hydrolysis reaction was carried out starting from 0.07 g (0.05 mmol) CRPcSnCl₂ as in the case of the Si analog. Yield: 0.05 g (73%). UV/VIS (DMSO): 712 (45300), 676 (15000), 642 (8800), 470 (10300), 362 (20400), 305 (13900), 287 (12800). IR (KBr): 3420, 2920, 1600, 1490, 1480, 1450, 1400, 1380, 1350, 1280, 1210, 1100, 1055, 940, 870, 740, 585.

Synthesis of CRPcPb. 4′,5′-Dicyanobenzo(15-crown-5) (0.25 g, 0.786 mmol) was heated to 200° in 20 min, and PbO (0.053 g, 0.237 mmol) was added in 6 portions. The reaction was continued at 220° for 3 h. After cooling to r.t. the green precipitate was dissolved in CH₂Cl₂/EtOH 3:1 (90 ml) and filtered. The filtrate was evaporated to dryness, and the green phthalocyanine was separated by column chromatography (CH₂Cl₂/MeOH 20:1). Yield: 0.050 g (18%). UV/VIS (DMSO): 748 (13600), 700 (23200), 667 (27200), 642 (25700), 602 (21500), 403 (23000), 338 (49300), 289 (50700). IR (KBr): 3440, 2920, 1600, 1490, 1450, 1400, 1380, 1360, 1280, 1210, 1130, 1100, 1050, 940, 860, 740, 585. ¹H-NMR (CDCl₃): 8.72 (*s*, 8 H); 4.37–3.55 (*m*, 64 H). ¹³C-NMR (CDCl₃): ¹H-coupled: 153.99; 150.35; 132.26; 107.21; 104.00; 73.43–66.07 (*m*). ¹H-decoupled ¹³C-NMR: 153.91; 150.15; 132.04; 105.45; 70.50; 69.46; 68.83; 68.39.

Synthesis of Metal-Free Phthalocyanine (CRPcH₂) via PbO and Ethyleneglycol. A mixture of dicyanobenzo(15-crown-5) (0.25 g, 0.786 mmol), PbO (0.133 g, 0.595 mmol), and ethyleneglycol (1 ml) was heated to 220° for 4 h. After cooling, the green precipitate was treated with acetone (10 ml) and filtered. The crude product was stirred with AcOH (3 × 15 ml) at 45°, filtered, washed with H₂O, EtOH, and Et₂O, and then dried *in vacuo*. Yield: 0.040 g (16%). This product was identical with the previously reported CRPcH₂ [7].

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