

Solvent-free axial ligand substitution in octaphenoxypthalocyaninato silicon complexes using microwave irradiation[†]

M. David Maree and Tebello Nyokong*

Department of Chemistry, Rhodes University, Grahamstown, South Africa

Several axially substituted octaphenoxo silicon phthalocyanines were prepared by condensation of the complexes used as axial ligands with octaphenoxypthalocyaninato (dichloro) silicon under microwave irradiation.

Keywords: axial modification, silicon phthalocyanines

Axial modification of metallophthalocyanine (MPc) complexes induces changes in the properties of these complexes. Foremost is the increase in solubility. Axially ligated silicon phthalocyanines ((L)₂SiPc) complexes containing Si–O bonds have, in particular, received considerable attention.^{1–3} Axially ligated complexes are generally prepared by refluxing MPc in coordinating solvents or in the presence of the axial ligands for several hours.^{4–9} Solvent-free synthesis of MPc complexes under microwave irradiation has been reported,¹⁰ but there have been no reports of axial ligand substitution of MPc complexes using microwave radiation.

The synthesis of octaphenoxypthalocyaninato (dichloro) silicon ((OPh)₈PcSi(Cl)₂) will be reported elsewhere. In this work, microwave irradiation was used to effect the exchange of the axial chloro ligands in (OPh)₈PcSi(Cl)₂ for the ligands listed in Fig. 1.

Some of the starting materials utilized in this study as axial ligands to the (OPh)₈PcSi species, are not good microwave absorbers and thus straight reaction with the phthalocyanine did not deliver any product. In these cases an alumina bath was used which is claimed to be a good hyperfrequency beam absorber.¹¹

Typically, a homogenous solid mixture consisting of (OPh)₈PcSi(Cl)₂ and the compound to be used as an axial ligand (see Table 1 for quantities) was irradiated in the microwave oven for the times listed in Table 1. The yields were all in excess of 92%.

Table 1 Experimental details for the synthesis of the various axially ligated octaphenoxypthalocyaninato silicon

| Reagent | Reaction time/min | Alumina | Yield/% |
|---|-------------------|---------|---------|
| 2-Naphthol 1 | 3 | Yes | 93 |
| 1-Naphthol 2 | 3 | Yes | 94 |
| <i>p</i> -Nitrophenol 3 | 3.5 | Yes | 95 |
| <i>p</i> -Hydroxy benzaldehyde 4 | 3 | Yes | 94 |
| Dimethylaminoethanol 5 | 4 | No | 96 |
| Yriethanolamine 6 | 4 | No | 93 |
| Succinic anhydride 7 | 4.5 | Yes | 95 |

The complexes were characterized by ¹H-nuclear magnetic resonance (¹H-NMR) and UV/visible spectra and by elemental analysis. The ¹H-NMR peaks of the axial ligands showed considerable upfield shifts on coordination to (OPh)₈PcSi species.

Experimental

UV-visible spectra were recorded on a Varian 500 UV/visible/NIR spectrophotometer. ¹H-NMR (400 MHz) spectra were obtained in CDCl₃ using the Bruker EMX 400 NMR spectrometer. Microwave irradiations were carried out in a Defy DM206T microwave oven at a power of 800W.

General procedure: Solid (OPh)₈PcSi(Cl)₂ (0.01g, 7.42 μmol) was thoroughly mixed in a sample vial with 4 g of each of the solid or liquid compounds to be used as axial ligands using a spatula. The reagents for compounds **1**, **2**, **3**, **4** and **7** were placed in an alumina bath for irradiation while the reagents for compounds **5** and **6** were irradiated in the sample vials. The irradiation was done at 800W and the times are given in Table 1. The completeness of the reaction was determined using thin layer chromatography (TLC). After the reaction was complete, the mixtures were worked up as follows: compounds **1**, **2**, **3** and **4** were purified by washing with 10% NaOH until no more naphthol or phenol could be detected. The residual solids were washed with water (3 × 10ml) and extracted into chloroform. The chloroform extract was dried with anhydrous MgSO₄, filtered and the product was isolated by evaporation of the chloroform under reduced pressure. Compounds **5** and **6** were isolated by washing with water (3 × 20ml) to remove residual alcohols. The solid products were

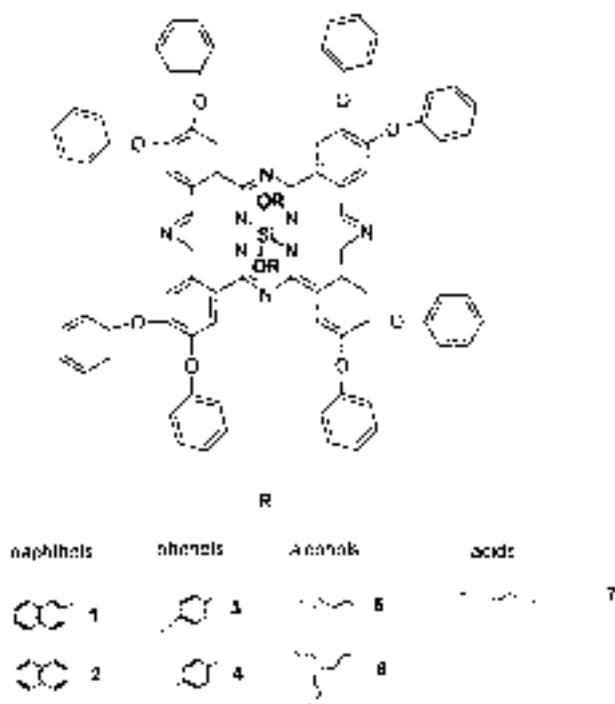


Fig. 1 Molecular structure of axially ligated octaphenoxypthalocyaninato silicon(IV).

* To receive any correspondence. Email: t.nyokong@ru.ac.za

[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

dried at 60 °C under vacuum. For compound **7** it was necessary to separate the chloroform extract of the reaction mixture on preparative TLC plates with chloroform as eluent.

Octaphenoxyphthalocyaninato (bis(1-naphthol)) silicon (OPh)₈PcSi(C₁₀H₇O)₂ **1**: yield 93%; (Found: C, 76.94; H, 4.33; N, 6.89. Calc. for C₁₀₀H₆₂N₈O₁₀Si; C, 76.78; H, 4.01; N, 7.19); δ_H (CDCl₃) 8.98 (s, 8H, phenyl), 7.47 (t, 16H, phenoxy), 7.30 (m, 24H, phenoxy), 7.04 (t, 4H, axial naphthol), 6.92 (m, 4H, axial naphthol), 6.44 (d, 2H, axial naphthol), 6.18 (d, 2H, axial naphthol)

Octaphenoxyphthalocyaninato (bis(2-naphthol)) silicon (OPh)₈PcSi(C₁₀H₇O)₂ **2**: yield 94%; (Found: C, 76.22; H, 3.77; N, 7.24. Calc. for C₁₀₀H₆₂N₈O₁₀Si; C, 76.81; H, 4.05; N, 7.24); δ_H (CDCl₃) 9.00 (s, 8H, phenyl), 7.51 (t, 16H, phenoxy), 7.29 (m, 24H, phenoxy), 7.05 (d, 2H, axial naphthol), 6.93 (m, 4H, axial naphthol), 6.43 (d, 2H, axial naphthol), 6.21 (d, 2H, axial naphthol), 2.79 (s, 2H, axial naphthol)

Octaphenoxyphthalocyaninato (bis(p-nitrophenol)) silicon (OPh)₈PcSi(C₆H₄O₃N)₂ **3**: yield 95%; (Found: C, 71.82; H, 4.06; N, 9.04. Calc. for C₉₂H₅₆N₁₀O₁₄Si; C, 71.13; H, 3.63; N, 9.02); δ_H (CDCl₃) 8.94 (s, 8H, phenyl), 7.53 (t, 16H, phenoxy), 7.32 (m, 24H, phenoxy), 6.59 (d, 4H, axial phenyl), 2.44 (d, 4H, axial phenyl)

Octaphenoxyphthalocyaninato (bis(p-hydroxybenzaldehyde)) silicon (OPh)₈PcSi(C₇H₅O₂)₂ **4**: yield 94%; (Found: C, 74.12; H, 3.49; N, 7.88. Calc. for C₉₂H₅₆N₈O₁₂Si; C, 74.08; H, 3.76; N, 7.54); δ_H (CDCl₃) 9.14 (s, 2H, axial formyl), 8.96 (s, 8H, phenyl), 7.50 (t, 16H, phenoxy), 7.32 (m, 24H, phenoxy), 6.26 (d, 4H, axial phenyl), 2.54 (d, 4H, axial phenyl)

Octaphenoxyphthalocyaninato (bis(dimethylaminoethanol)) silicon (OPh)₈PcSi(C₄H₁₀ON)₂ **5**: yield 96%; (Found: C, 70.53; H, 4.81; N, 8.77. Calc. for C₈₈H₆₈N₁₀O₁₀Si; C, 72.71; H, 4.71; N, 9.64); δ_H (CDCl₃) 9.00 (s, 8H, phenyl), 7.48 (t, 16H, phenoxy), 7.28 (m, 24H, phenoxy), 0.58 (s, 12H, axial methyl), -0.85 (t, 4H, axial β-methine), -2.00 (t, 4H, axial α-methine)

Octaphenoxyphthalocyaninato (bis(triethanolamine)) silicon (OPh)₈PcSi(C₆H₁₄O₃N)₂ **6**: yield 93%; (Found: C, 69.94; H, 4.55; N, 8.78. Calc. for C₉₂H₇₆N₁₀O₁₄Si; C, 70.17; H, 4.86; N, 8.92); δ_H (CDCl₃) 9.04 (s, 8H, phenyl), 7.53 (t, 16H, phenoxy), 7.30 (m, 24H,

phenoxy), 0.95 (t, 8H, axial δ-methine), 0.50 (s, 8H, axial γ-methine), -1.21 (t, 4H, axial β-methine), -2.20 (t, 4H, axial α-methine)

Octaphenoxyphthalocyaninato (bis(succinicanhydride)) silicon (OPh)₈PcSi(C₄H₅O₄)₂ **7**: yield 95%; (Found: C, 70.11; H, 3.58; N, 7.15. Calc. for C₈₈H₅₈N₈O₁₆Si; C, 69.86; H, 3.91; N, 7.37); δ_H (CDCl₃) 9.05 (s, 8H, phenyl), 7.51 (t, 16H, phenoxy), 7.32 (m, 24H, phenoxy), -0.91 (t, 4H, axial β-methine), -2.10 (t, 4H, axial α-methine)

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