Synthesis of metal phthalocyanines with cyclopropyl substituents

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Based on 4-cyclopropylphthalodinitrile, cyclopropyl-substituted phthalocyanine complexes of zinc and lutetium were synthesised and spectroscopically characterised.

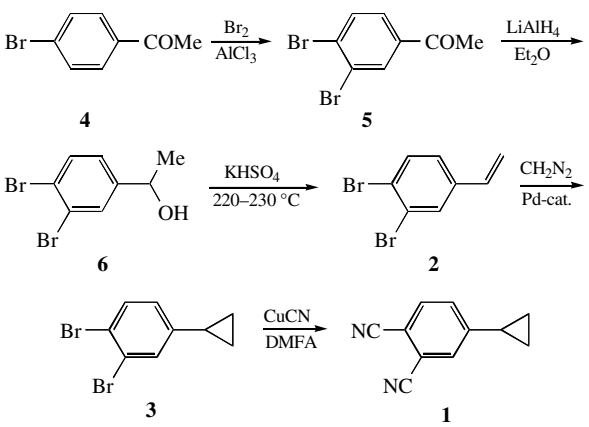
Phthalocyanine complexes with unsaturated substituents or functional groups are of particular interest because of their unique physico-chemical properties. Thus, phthalocyanines containing vinyl[1] or acetylenic[2] substituents were synthesised. However, we failed to find data on phthalocyanine complexes with cyclopropyl substituents.

A conceivable procedure for preparing cyclopropyl-substituted phthalocyanines can be based on the use of an appropriate phthalogen such as 4-cyclopropylphthalodinitrile **1**. The aim of this work was to obtain this dinitrile and to synthesise mono- and diphthalocyanine metal complexes on this basis. As examples, zinc and lutetium acetates were chosen because zinc can give only monophthalocyanine complexes with no axial ligands, whereas lutetium can form sandwich diphthalocyanines along with monophthalocyanine complexes.

The cyclopropanation of 3,4-dibromostyrene **2** followed by the cyanation of resulting 1,2-dibromo-4-cyclopropylbenzene **3** by the Rosenmund–von Braun reaction is a convenient and selective method for the synthesis of compound **1**. Starting dibromostyrene **2** was prepared from *p*-bromoacetophenone **4** according to well-known procedures. The bromination of compound **4** resulted in 3,4-dibromoacetophenone[3] **5** in 65% yield; the reduction of this latter with $NaBH_4$ or $LiAlH_4$ afforded 1-(3,4-dibromophenyl)ethanol[4] **6** in 88% yield. According to published data,[1] alcohol **6** was dehydrated at 220 °C by adding it to $KHSO_4$ in the presence of a small amount of hydroquinone for 45 min followed by the distillation of the resulting olefin. However, a considerable portion of the olefin was found to undergo polymerisation under these conditions. To prevent polymerisation, we changed the dehydration procedure as follows: a mixture of compound **6** and $KHSO_4$ (molar ratio of 5:1) in the presence of a small amount of hydroquinone was evacuated at 0.5 Torr and heated in an oil bath at 220 °C; the dehydration product was distilled off at 70–90 °C for 10 min. The reaction mixture was diluted with diethyl ether (in the presence of hydroquinone) and dried with Na_2SO_4. The yield of 3,4-dibromostyrene was ~65% (99% purity).

The cyclopropanation of olefin **2** was performed under conditions of simultaneous generation and catalytic decomposition of diazomethane using $(PhCN)_2PdCl_2$ (0.5 mol%) as a catalyst. 1,2-Dibromo-4-cyclopropylbenzene **3** was obtained in ~90% yield.†

The reaction of compound **3** with CuCN in boiling DMF for 3 h resulted in almost complete conversion of the starting dibromide. The treatment of the reaction mixture with $FeCl_3$ followed by the chromatographic separation on SiO_2 afforded previously uncharacterised 4-cyclopropylphthalodinitrile **1** in ~40% yield.‡



The refluxing of compound **1** in isoamyl alcohol with $Zn(OAc)_2 \cdot H_2O$ (molar ratio of 2.5:1) in the presence of DBU in an argon atmosphere for 2 h resulted in the formation of zinc 2,9(10),16(17),23(24)-tetracyclopropylphthalocyanine **7** as an isomer mixture.§ After cooling, the solvent was evaporated in a vacuum, and the residue was purified by column chromatography (SiO_2, ethyl acetate as an eluent). Phthalocyanine **7** was obtained as dark blue crystals in ~55% yield.

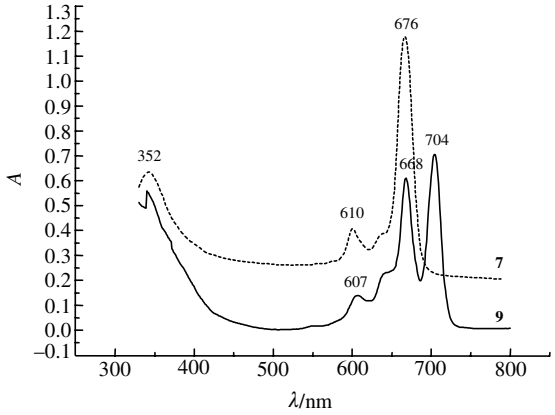


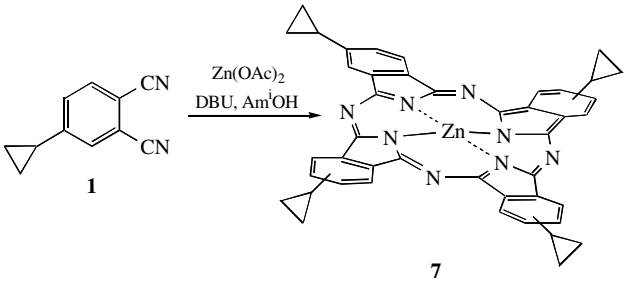
Figure 1 Electronic absorption spectra of compounds **7** and $^{\Delta}PcH_2$ (ethyl acetate).

† Compound **3**: bp 120–122 °C (0.5 Torr). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.46 (d, 1H, H-6, J_{ortho} 8.2 Hz), 7.32 (d, 1H, H-3, J_{meta} 2.1 Hz), 6.34 (dd, 1H, H-5, J_{meta} 2.1 Hz, J_{ortho} 8.2 Hz), 1.82 (tt, 1H, CH, J_{trans} 4.9 Hz, J_{cis} 8.4 Hz), 0.98 and 0.64 (2m, 2×2H, CH_2CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 145.4 (C-4), 133.3 (C-6), 131.0 (C-3), 126.1 (C-5), 124.6 (C-2), 120.9 (C-1), 14.9 (CH), 9.6 (CH_2CH_2). MS, *m*/*z*: 278 (4), 276 (9) and 274 (5) $[M]^+$, 116 (100).

‡ Compound **1**: mp 62–63 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.69 (d, 1H, H-6, J_{ortho} 8.2 Hz), 7.44 (d, 1H, H-3, J_{meta} 2.1 Hz), 7.38 (dd, 1H, H-5, J_{meta} 2.1 Hz, J_{ortho} 8.2 Hz), 1.99 (tt, 1H, CH, J_{trans} 4.9 Hz, J_{cis} 8.4 Hz), 1.21 and 0.83 (2m, 2×2H, CH_2CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 151.6 (C-4), 133.1 (C-5), 130.2 (C-6), 130.0 (C-3), 115.6 and 115.4 (2CN), 115.1 (C-2), 111.5 (C-1), 15.6 (CH), 11.3 (CH_2CH_2). MS, *m*/*z*: 168 (100) $[M]^+$, 167 (84) $[M - H]^+$, 141 (81) $[M - HCN]^+$, 114 (42) $[M - 2HCN]^+$, 39 (55) $[C_3H_3]^+$.

§ Compound **7**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.0–1.6 (br. m, cyclopropyl), 7.5–8.0 and 8.7–9.2 (2br. m, arom.). MS, *m*/*z*: 737 and 738 $[M]^+$. Found (%): C, 70.98; H, 4.57; N, 14.93. Calc. for $C_{44}H_{32}N_8Zn$ (%): C, 71.59; H, 4.37; N, 15.19.

The ^{1}H NMR spectrum of compound **7** exhibited broad signals at δ 1.0–1.6, 7.5–8.0 and 8.7–9.2 ppm. The broadening of signals is likely due to the occurrence of several isomers with different arrangements of cyclopropyl substituents at the periphery of a phthalocyanine ring, which weakly affect the positions of signals because the substituents are at a considerable distance from each other.

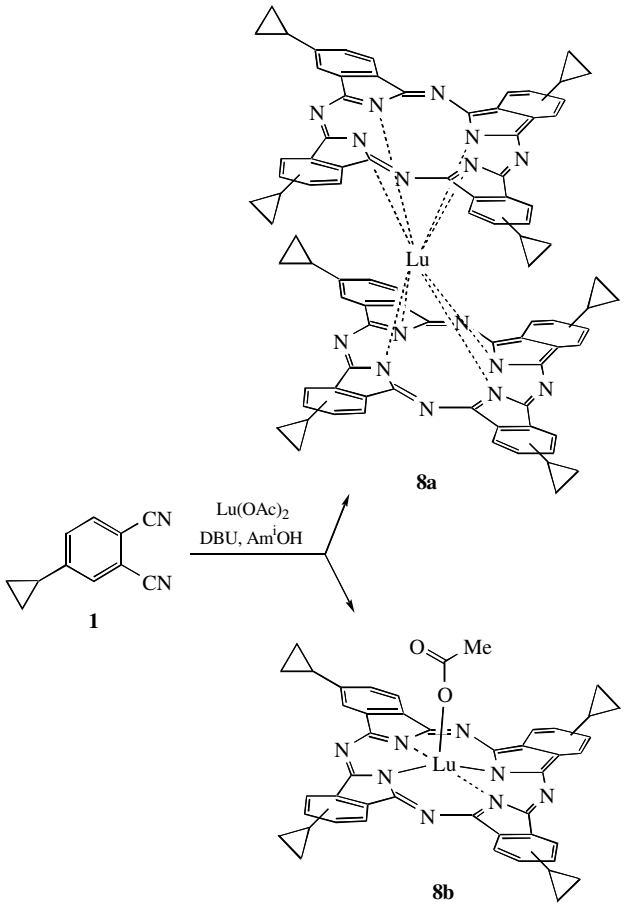


1 **7**

The reaction of compound **1** with lutetium acetate at a salt-to-nitrile ratio of 1:10 under analogous conditions resulted in a mixture of lutetium mono- and diphthalocyanines **8a** and **8b** (in a ratio of ~8:1) in ~25% total yield.¶

Moreover, a minor amount of metal-free 2,9(10),16(17),23(24)-tetracyclopropylphthalocyanine ($^{\Delta}PcH_2$) was separated from the reaction mixture by chromatography and characterised by a visible spectrum.

Figure 1 shows the electronic absorption spectra of compounds **7** and $^{\Delta}PcH_2$ in $CHCl_3$. The absorption maximum of compound **7** (Q-band) occurs at 676 nm, which is consistent with published data for alkyl-substituted phthalocyanines.[6,7] The absorption spectrum of $^{\Delta}PcH_2$ exhibits Q-band splitting because



8a **1** **8b**

¶ Compound **8a**: MS, *m/z*: 906 $[M]^+$. Found (%): C, 61.19; H, 3.94; N, 12.19. Calc. for $C_{46}H_{35}O_2N_8Lu$ (%): C, 60.93; H, 3.86; N, 12.36.

Compound **8b**: MS, *m/z*: 1520 $[M]^+$. Found (%): C, 67.32; H, 4.38; N, 14.89. Calc. for $C_{88}H_{64}N_{16}Lu$ (%): C, 67.69; H, 4.21; N, 14.74.

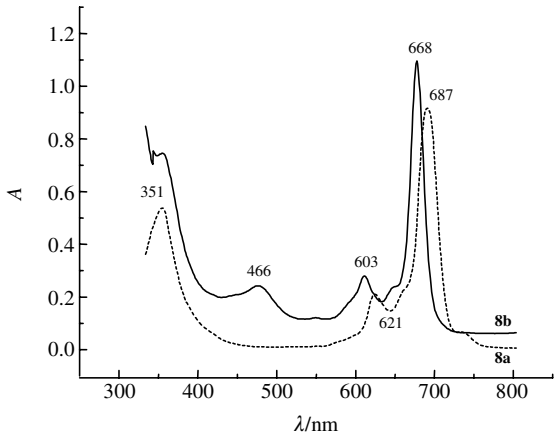


Figure 2 Electronic absorption spectra of compounds **8a** and **8b** (ethyl acetate).

of the lowered symmetry of this phthalocyanine (D_{2h} symmetry group).

The absorption spectra of complexes **8a** and **8b** (Figure 2) exhibit Q-bands at 687 and 668 nm, respectively. The spectrum of **8b** also contains an absorption band in the region 400–500 nm with λ_{max} = 466 nm, which is typical of diphthalocyanines.

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