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Synthesis and spectroscopic characterization of planar binuclear nickel(II) hexa(*tert*-butyl)phthalocyaninate

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The title complex was synthesised using microwave irradiation and characterised by spectroscopic techniques.

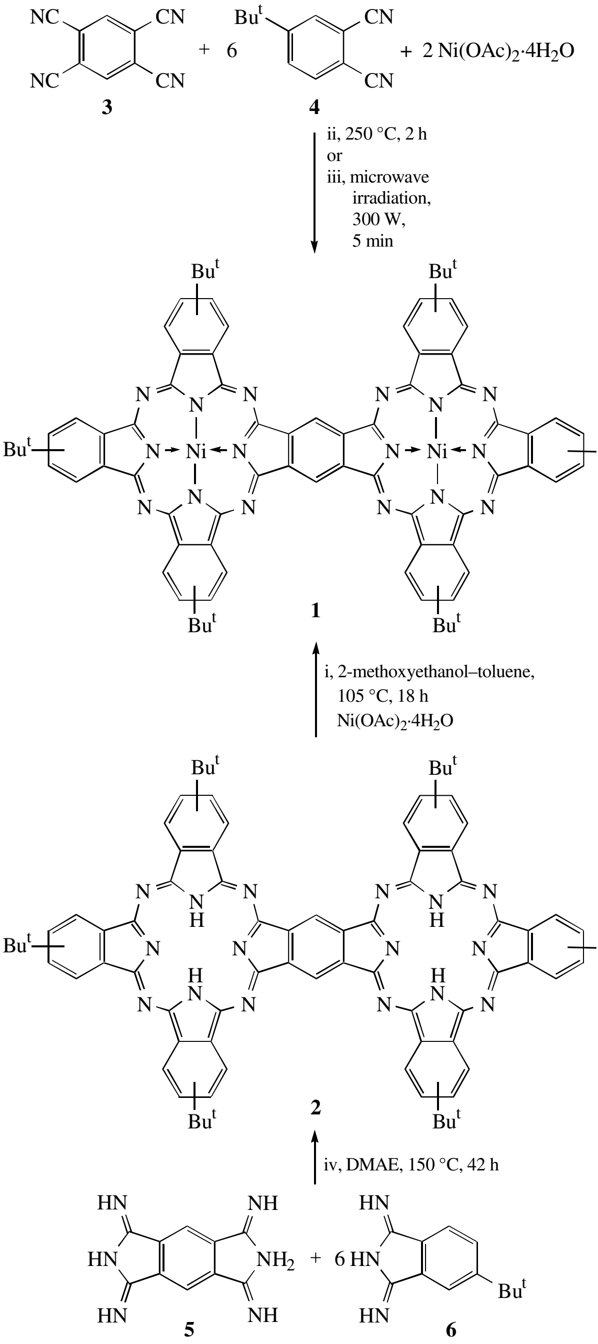
Binuclear porphyrins and phthalocyanines are of considerable current interest because of their applications in semiconductor technology, nonlinear optics and catalysis.[1–3] The use of binuclear phthalocyanine complexes as active membrane components in ion-selective electrodes for the rapid determination of bifunctional organic compounds is promising.[4]

We synthesised dinickel(II) bis{7(8)^2,12(13)^2,17(18)^2-tri-*tert*-butyltribenzo[*g*,*l*,*q*]-5,10,15,20-tetraazaporphyrino}[*b*,*e*]benzene **1** for the first time according to Scheme 1 with the use of the following approaches: (i) metallation of free ligand **2**; (ii) synthesis by the fusion of nitriles **3** or **4**; (iii) synthesis under microwave irradiation.

Planar binuclear phthalocyanine complexes are most frequently prepared from free ligands. To prepare bis{7(8)^2,12(13)^2,17(18)^2-tri-*tert*-butyltribenzo[*g*,*l*,*q*]-5,10,15,20-tetraazaporphyrino}[*b*,*e*]-benzene **2**, starting compounds bis(1,3-diiminoisoindoline) **5** and 5-*tert*-butyl-1,3-diiminoisoindoline **6** were synthesised in accordance with published procedures. They were obtained in almost quantitative yields from 1,2,4,5-tetracyanobenzene **3**, which was synthesised according to a standard procedure,[5] and 4-*tert*-butylphthalodinitrile **4**, respectively.

Compound **2** was prepared according to Scheme 1 (iv).[†] In contrast to published data,[6] the use of a simple chloroform–ethanol (50:1, by volume) chromatographic system allowed us to separate the target compound. Compound **2** was identified by TLC; its structure was confirmed by MALDI-TOF mass spectrometry. The peak of the molecular ion (*m*/*z* 1288) exactly corresponds to the calculated value. The use of a 30-fold excess of a nickel salt allowed us to reach 100% conversion of compound **2** in the metallation reaction.[‡]

The use of fundamentally new approaches (such as fusion and microwave irradiation) to the synthesis of the planar binuclear phthalocyaninate from nitriles allowed us not only to shorten considerably the reaction time but also to improve the yield of the target complex.



The synthesis by the fusion of corresponding nitriles **3** and **4** [Scheme 1, (ii)][§] gave compound **1** in 9% yield, whereas a structurally similar complex was obtained[7] in only 0.7% yield by boiling in quinoline. In the course of reaction, 1,2,4,5-tetracyanobenzene and 4-*tert*-butylphthalodinitrile oligomers were formed in considerable amounts; this considerably decreased

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[†] *Synthesis procedure* (iv): bis(diiminoisoindoline) **5** (0.12 g, 0.56 mmol) and 5-*tert*-butyl-1,3-diiminoisoindoline **6** (0.67 g, 3.37 mmol) were dissolved in 40 cm^3 of *N*,*N*-dimethylaminoethanol. The solution was refluxed at 150 °C in an argon atmosphere for 42 h. The reaction mixture was cooled to room temperature and added to 200 cm^3 of water. The precipitate formed was filtered off and washed sequentially with 3% HCl and 3% NaOH. The resulting compound was dried and chromatographed (30×3 column, Lancaster Silica Gel 60/230). Benzene and then chloroform–ethanol (50:1, v/v; R_f 0.8) was used as an eluent. 215 mg (8.3%) of compound **2** was obtained. MS (MALDI-TOF): bis($\mathrm{PcBu^tH_2}$)$^+$: *m*/*z* 1288; UV-VIS/CHCl$_3$, λ_{max} 686 nm ($\varepsilon\times10^{-4}$ = 4.4).

[‡] *Synthesis procedure* (i): compound **2** (0.15 g, 0.116 mmol) was mixed with 0.87 g (3.49 mmol) of nickel(II) acetate tetrahydrate, and the mixture was dissolved in 30 cm^3 of toluene-2-methoxyethanol (4:1, v/v). The resulting mixture was refluxed with stirring at 105 °C in an argon flow for 18 h. The reaction was monitored by TLC (toluene–chloroform, 1:1, v/v). The reaction mixture was filtered; the filtrate was evaporated on a rotary evaporator; 100 cm^3 of ethanol was added, and the solution was refluxed for 10 min. For the complete precipitation of compound **1**, 50 cm^3 of water were added. The resulting precipitate was filtered off on a glass filter and washed with ethanol. R_f 0.3 in chloroform–ethanol (50:1, v/v). 0.10 g (60%) of compound **1** was isolated. MS (MALDI-TOF): bis($\mathrm{PcBu^tNi}$)$^+$: *m*/*z* 1401; UV-VIS/CHCl$_3$, λ_{max} 662 nm ($\varepsilon\times10^{-4}$ = 3.0), 706 nm ($\varepsilon\times10^{-4}$ = 3.5).

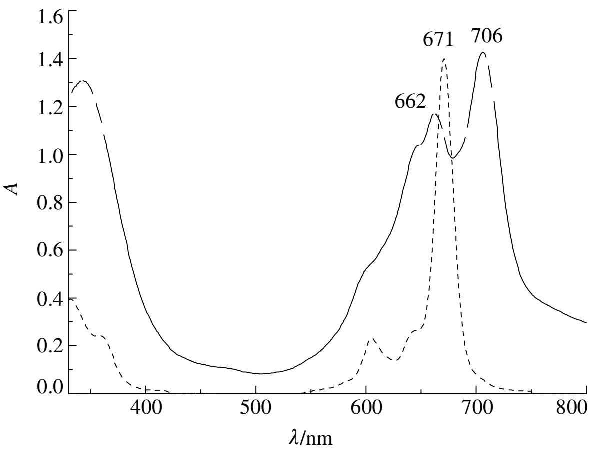

Figure 1 Electronic absorption spectra of nickel(II) tetra-*tert*-butylphthalocyaninate (dashed line) and compound **1** (solid line).

the yield of compound **1** and made the purification difficult to perform. We proposed to extract compound **1** with benzene in a Soxhlet apparatus.

The synthesis[¶] of compound **1** under microwave irradiation[8] allowed us not only shorten the reaction time to 5 min but also considerably simplify the separation of planar binuclear nickel(II) hexa(*tert*-butyl)phthalocyaninate, as compared with the synthesis by fusion, because the reaction mixture contained oligomer impurities in smaller amounts. Compound **1** was identified by TLC; its structure was confirmed by MALDI-TOF mass spectrometry. The peak of the molecular ion (*m/z* 1401) exactly corresponds to the calculated value. The yield of compound **1** was 18%, which is a maximum yield for complexes of this structure.

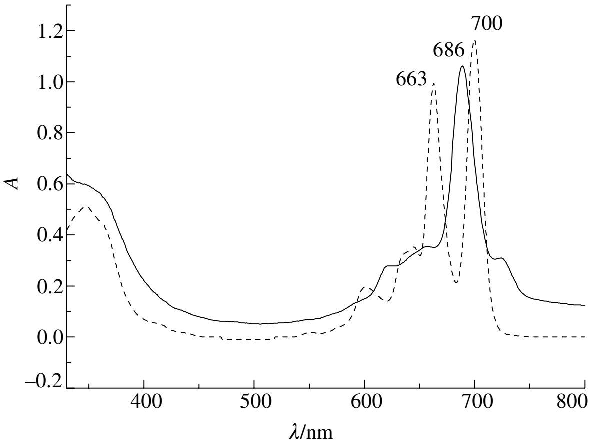

Figure 2 Electronic absorption spectra of tetra-*tert*-butylphthalocyanine (dashed line) and compound **2** (solid line).

We studied the electronic absorption spectra of compounds **1** and **2** (Figures 1 and 2, respectively). As compared with nickel(II) monophthalocyaninate, *Q*-band splitting in the electronic absorption spectrum is typical of planar binuclear nickel(II) phthalocyaninate; this is likely due to a decrease in the symmetry from D_{4h} to D_{2h}. The absorption spectrum of the metal-free binuclear phthalocyanine is also different from that of its mono analogue. Such spectral changes are characteristic of other planar binuclear phthalocyanines.[7] The molar absorption coefficients of compounds **1** (662 nm: $\varepsilon \times 10^{-4} = 3.0$; 706 nm: $\varepsilon \times 10^{-4} = 3.5$) and **2** (686 nm: $\varepsilon \times 10^{-4} = 4.4$) are lower than those of a monophthalocyaninate [nickel(II) tetra(*tert*-butyl)phthalocyaninate] (671 nm: $\varepsilon \times 10^{-5} = 1.4$) and a monophthalocyanine [tetra(*tert*-butyl)phthalocyanine] (663 nm: $\varepsilon \times 10^{-4} = 9.9$; 700 nm: $\varepsilon \times 10^{-5} = 1.1$), respectively.

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[§] *Synthesis procedure* (ii): 1,2,4,5-tetracyanobenzene **3** (0.10 g, 0.56 mmol), 4-*tert*-butyl-*o*-phthalodinitrile **4** (0.62 g, 3.37 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.21 g, 1.12 mmol) were placed in a 50 cm^3 flask equipped with a reflux condenser, and the mixture was fused for 2 h. The target product was extracted from the reaction mixture in a Soxhlet apparatus. The extract was chromatographed on a column (30×3 cm, 70-230 Lancaster Silica Gel). Benzene and then chloroform was used as an eluent. Compound **1** (80 mg) was isolated using preparative TLC [Al_2O_3; chloroform–ethanol (50:1, v/v)]. MS (MALDI-TOF): bis($Pc^{Bu^t}Ni$)$^+$: *m/z* 1401; UV-VIS/$CHCl_3$, λ_{max} 662 nm ($\varepsilon \times 10^{-4} = 3.0$), 706 nm ($\varepsilon \times 10^{-4} = 3.5$).

[¶] *Synthesis procedure* (iii): 1,2,4,5-tetracyanobenzene **3** (0.10 g, 0.56 mmol), 4-*tert*-butyl-*o*-phthalodinitrile **4** (0.62 g, 3.37 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.21 g, 1.12 mmol) were placed in a 50 cm^3 flask, and the mixture was fused under microwave irradiation (300 W). The reaction mixture was cooled to room temperature and dissolved in benzene; the solution was chromatographed (30×3 cm column with 70-230 Lancaster Silica Gel; eluent: benzene). Next, 160 mg (18%) of compound **1** was separated using preparative TLC.