Synthesis and Characterisation of Porphyrazinoctamine Derivatives: X-Ray Crystallographic Studies of [2,3,7,8,12,13,17,18-Octakis(dibenzylamino)-porphyrazinato]magnesium(II) and {2,3,7,8,12,13,17,18-Octakis[allyl(benzyl)amino]-porphyrazinato}nickel(II)

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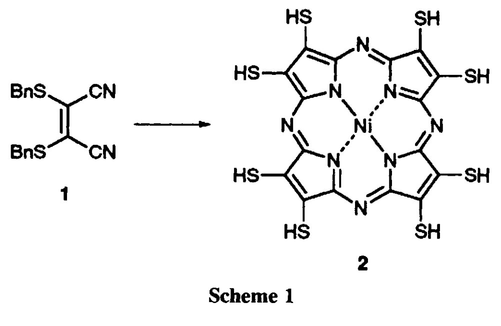
2,3-Bis(dibenzylamino)- and 2,3-bis[allyl(benzyl)amino]-2Z-butene-1,4-dinitriles are macrocyclised by reaction with magnesium propoxide in propanol to provide the corresponding (porphyrazinato)magnesium(II) derivatives, the structures of which are confirmed by X-ray crystallographic studies of the title magnesium and nickel(II) complexes; cyclisation of alternative diaminomaleonitrile derivatives gives the corresponding porphyrazinoctamines.

Recently, we described the synthesis of the porphyrazine octathiolate derivative **2** by macrocyclisation of 2,3-bis(benzylthio)maleonitrile **1** using magnesium propoxide in propanol, transmetallation and reductive debenzylation (Scheme 1).[1] The octathiolate **2** exhibited unusual coordination chemistry. Complexes were isolated with four metal cations peripherally bonded to the eight thiolate residues either *via* quadruple bidentate (*S–S*)[2] or tridentate (*S–meso-N–S*)[1] coordination. This peripheral multimetallation is in addition to metal–ion complexation within the porphyrazine cavity and thus provides novel pentametallic arrays. These complexes, denoted star porphyrazines, are of considerable interest for the study of indirect metal–metal interactions *via* the porphyrazine π-system. Herein, we report the synthesis of the analogous porphyrazinoctaamine derivatives. This novel† class of ligands is also expected to show rich and varied multimetallic complexation.

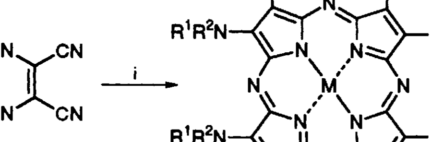
Commercial, inexpensive diaminomaleonitrile **3** was converted into the *N,N,N′,N′*-tetraalkyl derivatives **4a**, **4b** and **5a–5c** following the methods reported by Sheppard and coworkers. Thus, tetramethylation and benzylation of diamine **3** gave adducts **4a**[3] and **4b**‡ (53%). Dimethylation and diallylation of *N,N′*-dibenzyldiaminomaleonitrile[3] (**5**, R^1 = Bn, R^2 = H) gave diamines **5a** (64%) and **5c** (80%) respectively. Finally, sequential double reductive alkylation[3] of **3** using pyridine-2-carboxaldehyde and methylation gave dinitrile **5b** (51%) (Scheme 2). All five dinitriles **4a**, **4b** and **5a–5c** were readily cyclised using the magnesium propoxide method introduced by Linstead.[4] Heating under reflux of propanol solutions of the dinitriles with magnesium propoxide gave the porphyrazines **6a–6e** (Scheme 3, Table 1). In each case, the porphyrazines were isolated and purified by chromatography on neutral alumina. All five porphyrazines were isolated as blue–black solids with purple reflections.

The magnesium complexes **6a**, **6c** and **6e** were demetallated by reaction with trifluoroacetic acid to produce porphyrazines **7a**, **7c** and **7e**. Subsequent reaction with nickel(II) acetate[5] resulted in selective metallation within the macrocyclic cavity to provide the corresponding nickel complexes **8a**, **8c** and **8e**. Spectroscopic data were in full agreement with the proposed formulations and the data for the octakis-dibenzylamino derivative **6c** are representative.§ Compound **6c** showed an electronic absorption spectrum with the Q band at 707 nm, a less intense peak at 574 nm and the Soret band[6] at 368 nm. As the definitive confirmation of the structures, single crystal X-ray determinations were carried out on the magnesium porphyrazine **6c**¶ (Fig. 1) and the nickel porphyrazine **8e**‖ (Fig. 2), recrystallised from chlorobenzene–methanol and ethyl acetate–hexanes, respectively.

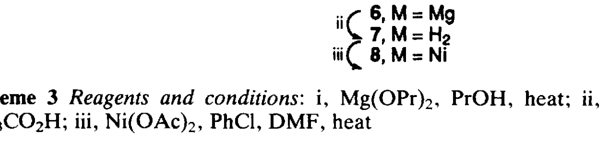
In this work we have outlined our initial studies on the synthesis of characterisation of a structurally novel class of macrocycles: 2,3,7,8,12,13,17,18-porphyrazineoctaamines.



Scheme 1



Scheme 2 *Reagents and conditions*: i, R^1CHO, MeOH; $NaBH_4$, THF, MeOH; R^1CHO, MeOH; $NaBH_4$, THF, MeOH; R^2X, NaH, THF; ii, R^1X (R^1 = R^2), NaH, THF



Scheme 3 *Reagents and conditions*: i, $Mg(OPr)_2$, PrOH, heat; ii, CF_3CO_2H; iii, $Ni(OAc)_2$, PhCl, DMF, heat

Table 1[a] Preparation of porphyrazines **6**, **7** and **8**

Entry	R^1, R^2	4 or 5 (%)	6 (%)	7 (%)	8 (%)
1	Me, Me	**4a** (ref. 3)	**6a** (29, 48)	**7a** (21)	**8a** (43)
2	Bn, Me	**5a** (64)	**6b** (25)	—	—
3	Bn, Bn	**4b** (53)	**6c** (31)	**7c** (86)	**8c** (59)
4	2-pyr, Me	**5b** (51)	**6d** (25)	—	—
5	Bn, allyl	**5c** (80)	**6e** (20)	**7e** (82)	**8e** (92)

[a] 2-pyr = 2-pyridylmethyl, yields of **5a** and **5c** based upon the known **5** (R^1 = Bn, R^2 = H, see ref. 3).

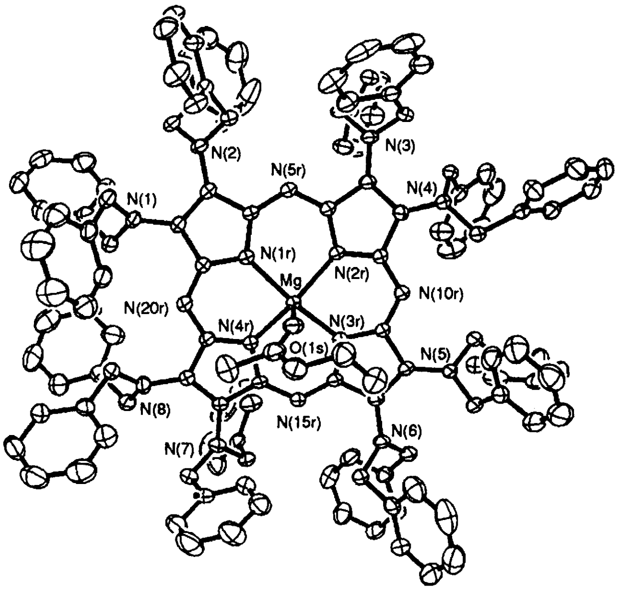


Fig. 1 X-ray crystal structure of [2,3,7,8,12,13,17,18-octakis(dibenzylamino)porphyrazinato]magnesium(II)

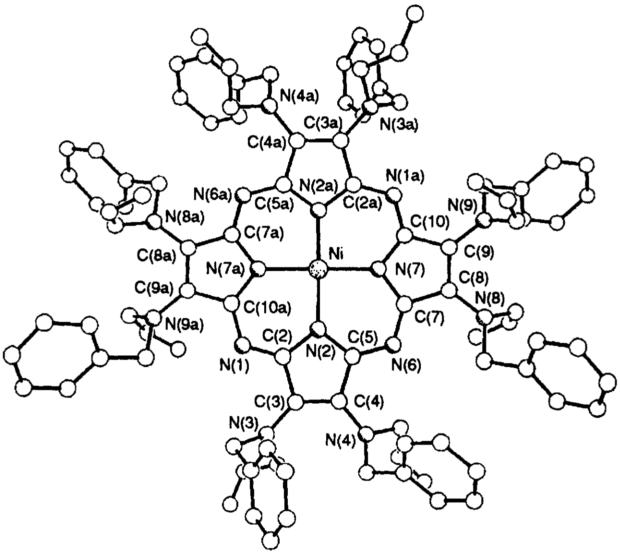


Fig. 2 X-ray crystal structure of {2,3,7,8,12,13,17,18-octakis[allyl-(benzyl)amino]porphyrazinato}nickel(II)

Clearly, the synthetic strategy is flexible and should be suitable for the synthesis of diverse analogues. Further studies on the preparation of related molecules and multimetallic complexation will be reported in due course.

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Footnotes

† Kopranenkov *et al.* have reported the preparation of [2,3,7,8,12,13,17,18-octakis(*tert*-butylamino)porphyrazinato]magnesium(II). However, these authors do not provide convincing data in support of their structural assignment. See ref. 7.

‡ All new compounds were fully characterised by spectroscopic data and microanalysis and/or HRMS. Porphyrazine was directly converted into the nickel complex **8c** for characterisation.

§ *Selected data* for **6c**: mp 185–190 °C (EtOAc–hexanes); TLC 0.86 (EtOAc: hexanes 2:3); IR (CH_2Cl_2) v/cm^{-1} 2957, 1450, 1430, 1314, 1285, 1233, 944, 881, 711, 675, 655; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 368 (4.75), 574 (4.45), 707 (4.51); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (m, 32H), 7.1 (m, 48H), 5.25 (s, 32H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 140.3, 137.7, 129.1, 128.4, 126.9, 55.3; HRMS (FAB) *m/z* calc. for $C_{128}H_{112}MgN_{16}$: (M + H$^+$), 1897.9185. Found: (M + H$^+$), 1897.9124. Satisfactory elemental analysis was obtained.

¶ *Crystal data* for **6c**: $C_{138}H_{134}N_{16}O_2Mg$, M = 2072.92, monoclinic, a = 18.939(4), b = 27.813(6), c = 22.582(5) Å, β = 99.56(3)°, V = 11730(4) Å^3, space group $P2_1/n$, Z = 4, D_c = 1.17 g cm^{-3}, μ(Cu-Kα) = 0.60 mm^{-1}, F(000) = 4408. Data were measured on a Siemens rotating anode crystallographic system at the University of California, Davis, with Cu-Kα radiation (Ni filter). The structure was solved with the direct methods program SHELXS-90[8] and refined (all non-H atoms anisotropic) by full-matrix least-squares analysis on F^2 (all data) by using the program SHELXL-93,[9] to give R = 0.074 (all data, on F) and wR = 0.229 (all data, on F^2) for the 14359 unique reflections measured. A disordered molecule of solvent was situated about the origin, but the disorder was so severe that a chemically sensible model for this occluded molecule could not be obtained.

|| *Crystal data* for **8e**: $C_{96}H_{96}N_{16}Ni{\cdot}C_6H_5Cl$, M = 1645.1, monoclinic, a = 17.453(2), b = 10.634(2), c = 25.256(3) Å, β = 109.11(2)°, V = 4429 Å^3, space group $P2_1/n$, Z = 2 (the molecule has crystallographic C_i symmetry), D_c = 1.23 g cm^{-3}, μ (Cu-Kα) = 10.4 cm^{-1}, F(000) = 1740. A clear prism of dimensions 0.07 × 0.40 × 0.60 mm was used. Data were measured on a Siemens P4/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically to give R = 0.062, R_w = 0.065 for 4759 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$]. The structure contains two pairs of disordered and partially overlapping 0.25 occupancy C_6H_5Cl molecules per porphyrazine unit.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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