Diazaporphyrins: synthesis, characterization and X-ray crystal structure of (3,7,13,17-tetramethyl-2,8,12,18-tetrabutyl-5,15-diazaporphinato)chloroindium(III)

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The reaction of 3,7,13,17-tetramethyl-2,8,12,18-tetrabutyl-5,15-diazaporphine [H_2DAPMB] **1** with indium(III) acetate in acetic acid leads to the formation of acetatoindium(III) complex [In(OAc)DAPMB] **2**, which is easily converted to chloroindium(III) complex [In(Cl)DAPMB] **3**.

The size of the central coordination cavity in the porphyrin-type macrocycles, along with the operating specific electronic factors, has a large influence on the coordination properties of these ligands and on the structure of their metal complexes. Thus, the sterical correspondence between the radii of the coordination cavity (C_t–N_{pyr} distance) and the metal ion (r_M) often determines the location of the metal in respect to the plane of the macrocycle, conditions and strength of their σ- and π-bonding, and the stability of the complex to dissociation.[1] The numerous structural data which are available for complexes of common porphyrins, phthalocyanines (tetrabenzotetraazaporphyrins) and since recently for alkyl-substituted tetraazaporphyrins have shown that the replacement of four methine bridges in the porphyrin core with four *meso*-nitrogen atoms leads to a significant decrease in the central coordination cavity.[2] Complexes of azaporphyrins containing less than four *meso*-nitrogen atoms are very poorly investigated, and the structural data are available only for monoazaporphyrins.[3,4] In order to reveal the effect of diaza substitution of *meso*-methine bridges in the porphyrin macrocycle on the structure and coordination properties, we have started a systematic investigation of *trans*-diazaporphyrins.[5,6] Here we report the synthesis of (3,7,13,17-tetramethyl-2,8,12,18-tetrabutyl-5,15-diazaporphinato)chloroindium(III) [In(Cl)DAPMB] **3**, which is the first example of a diazaporphyrin characterised by X-ray crystallography.

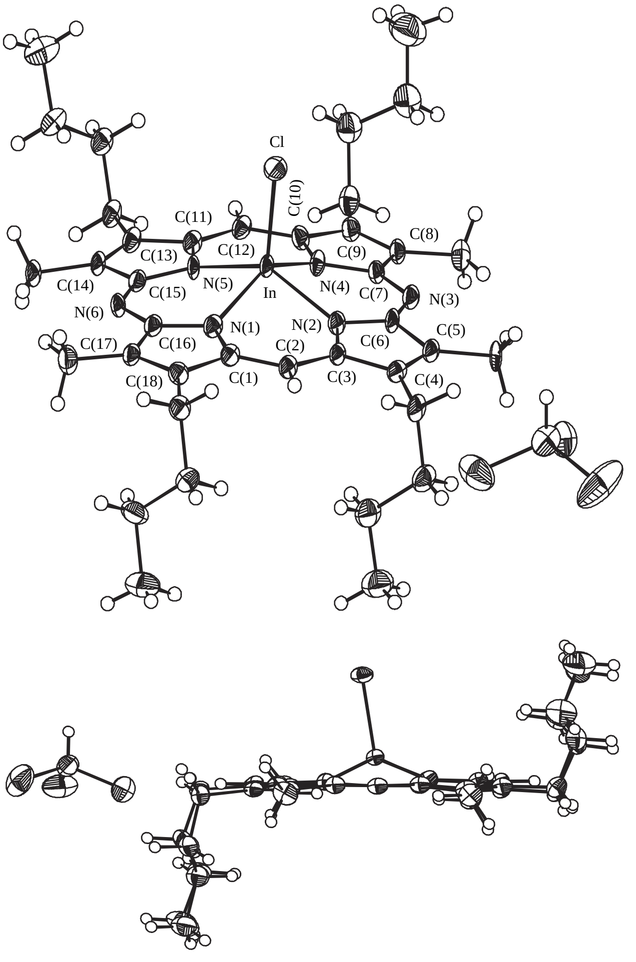

Figure 1 Molecular structure of [In(Cl)DAPMB]·$CHCl_3$; with 50% probability, thermal ellipsoids show all non-hydrogen atoms: (top) a perspective view and (bottom) a side view along the axis through the *meso*-nitrogen atoms. Selected average bond lengths (Å): In–Cl 2.376(2), In–N_{pyr} 2.135, N_{pyr}–C_α(C_{meso}) 1.377, N_{pyr}–C_α(N_{meso}) 1.367, C_α–C_{meso} 1.396, C_α–N_{meso} 1.337, C_β–C_α(C_{meso}) 1.459, C_β–C_α(N_{meso}) 1.448, C_β–C_β 1.361; selected average bond angles (°): C_α–N_{pyr}–C_α 107.7, N_{pyr}–C_α–C_{meso} 124.1, N_{pyr}–C_α–N_{meso} 127.7, C_α–C_{meso}–C_α 127.6, C_α–N_{meso}–C_α 124.4, N_{pyr}–In–N_{pyr} 85.0 (C_{meso}), 83.3 (N_{meso}) and 142.9 (opposite). N_{pyr}: N(1), N(2), N(4), N(5); N_{meso}: N(3), N(6); C_α: C(1), C(3), C(6), C(7), C(10), C(12), C(15), C(16); C_β: C(4), C(5), C(8), C(9), C(13), C(14), C(17), C(18); C_{meso}: C(2), C(11).

Refluxing 3,7,13,17-tetramethyl-2,8,12,18-tetrabutyl-5,15-diazaporphine [H_2DAPMB][6] **1** (0.17 mmol) with indium(III) acetate (1.7 mmol) in glacial acetic acid (50 ml) yielded intermediate acetatoindium(III) complex [In(OAc)DAPMB] **2**, which was extracted with CH_2Cl_2 and washed thoroughly with water. A solution of **2** was then treated with aqueous HCl and, after washing with water and drying over $MgSO_4$, chromatographed on alumina (III grade, eluent: CH_2Cl_2–MeOH, 100:1). Pink-violet complex **3** was precipitated after the addition of *n*-hexane to the partly evaporated eluate (60% yield).[†] Slow diffusion of methanol into the chloroform solution of **3** gave violet crystals of the chloroform solvate **3**·$CHCl_3$. One of these crystals with dimensions of 0.2×0.3×0.7 mm was suitable for an X-ray diffraction study.[‡] Perspective and side views of **3** are displayed in Figure 1.

The indium atom is located outside the mean plane of the four-coordinating pyrrole-type nitrogen atoms N_{pyr}, and the diazaporphyrin skeleton has a slight ‘doming’ in the opposite direction (the average displacement of its atoms increased from the centre to the periphery: *ca.* 0.09, 0.06, 0.15 and 0.22 Å for C_α, C_{meso}, N_{meso} and C_β atoms, respectively). It is noteworthy that in **3** the displacement of the In atom from the $(N_{pyr})_4$ mean plane (0.68 Å) is larger and the average In–N_{pyr} bond length [2.135(6) Å] is slightly shorter than that in *meso*-tetraphenylporphinatochloroindium(III) [In(Cl)TPP], having a similar

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[†] Analysis for **3**. ^{1}H NMR (300 MHz, $CDCl_3$, 297 K) δ: 10.21 (s, 2H, *meso*-CH), 4.05 (m, 8H, α-CH_2), 3.66 (s, 12H, α-Me), 2.28 (q, 8H, β-CH_2), 1.80 (s, 8H, γ-CH_2), 1.15 (t, 12H, δ-Me). UV–Vis [benzene, λ_{max}/nm (lg ε)]: 379 (4.94), 399sh, 536sh, 550 (4.14), 558 (4.15), 571sh, 583 (4.49), 595 (4.96). IR (KBr, ν/cm^{-1}): 524w, 672w, 718m, 748s, 769m, 860m, 927m, 940vw, 986s, 1104m, 1159vs, 1194w, 1300w, 1381s, 1460s, 2860s, 2935s, 2960m. Found (%): C, 61.46; H, 6.86; N, 11.25. Calc. for $C_{38}H_{50}ClInN_6$ (%): C, 61.58; H, 6.80; N, 11.34.

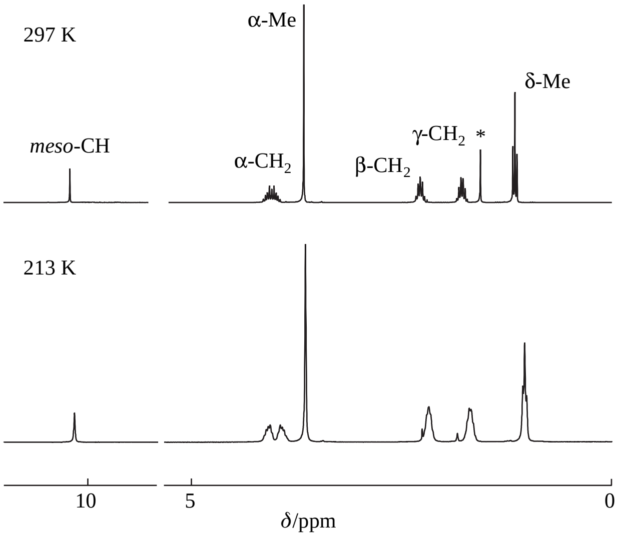

Figure 2 ^{1}H NMR spectra of [In(Cl)DAPMB] in $CDCl_3$ at 297 and 213 K.

'doming' of the macrocyclic skeleton (0.61 and 2.156 Å, respectively).[7] These changes in the coordination geometry of the In atom are a consequence of the *trans*-diaza substitution, decreasing the diameter of the core of the macrocyclic ligand from 4.134 Å in [In(Cl)TPP] to 4.049 Å in **3**. Whereas the four pyrrole N atoms in [In(Cl)TPP] form a square with sides of 2.923 Å, the distance between the pyrrole-type N atoms adjacent to the *meso*-N bridge (2.839 Å) in **3** is shorter than that between N atoms adjacent to the *meso*-CH bridge (2.887 Å). The contraction of the coordination cavity and its square distortion result mainly from the changes in the bond lengths and bond angles of the *meso*-atom bridges. Indeed, the N_{meso}–C_{α} bond (1.337 Å) in **3** is shorter than the C_{meso}–C_{α} bond {1.396 Å; 1.402 Å in [In(Cl)TPP][7]} and $\angle(C_{\alpha}$–N_{meso}–$C_{\alpha})$ of 124.4° is smaller than $\angle(C_{\alpha}$–C_{meso}–$C_{\alpha})$ {127.6°; 126.2° in [In(Cl)TPP][7]}. Shortening of the N_{pyr}–C_{α} bonds (1.37 Å) and elongation of the C_{α}–C_{β} bonds (1.45 Å), which were observed for **3** in comparison with [In(Cl)TPP] (1.38 and 1.43 Å, respectively), may indicate an increase of the conjugation in the internal 16-membered ring due to diaza substitution. A further interesting aspect is the conformation of the *n*-butyl groups in respect to the mean plane of the macrocycle: two of them neighbouring to one *meso*-CH bridge are stretched below, and the two other, above the mean plane of the macrocycle. As can be seen from the side view in Figure 1, the *n*-butyl groups positioned at the same side as the In–Cl moiety cause a deviation of the In–Cl bond from a normal to the mean plane by *ca*. 4.5°. The In–Cl bond in **3** [2.376(2) Å] is longer than in [In(Cl)TPP][7] (2.369 Å).

The ^{1}H NMR spectra of **3** in $CDCl_3$, displayed in Figure 2, reveal two diastereotopic α-CH_2 protons of the butyl groups. Their inequivalence, arising from a slow rotation of the butyl groups, already seen at 297 K, is clearly discernible at 213 K by splitting of the α-CH_2 signal.

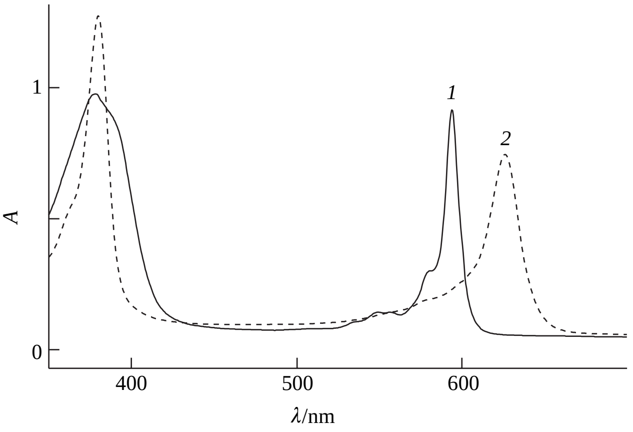

Figure 3 UV–Vis spectra of [In(Cl)DAPMB] in (*1*) CH_2Cl_2 and (*2*) CF_3COOH.

The UV–Vis spectrum of **3** in CH_2Cl_2 (Figure 3) is typical of metal complexes of azaporphyrins. As a result of diaza substitution, the symmetry of the macrocyclic chromophore is lowered from D_{4h} in porphyrins and tetraazaporphyrins to D_{2h} (or even C_{2v}, if the out-of-plane position of the In atom is taken into account). There is no splitting of the $\pi \rightarrow \pi^*$ transition band in the long-wave region. This correlates with the theoretical work,[8] which predicted a very large difference in the intensities of the Q_1 ($f_r = 0.100$) and Q_2 ($f_r = 0.0006$) transitions and a small energy gap between both of the transitions (310 cm^{-1}) for complexes of diazaporphyrins. Addition of CF_3COOH to a solution of **3** in CH_2Cl_2 results in a bathochromic shift of the *Q*-band (860 cm^{-1}), which is consistent with the complete acid–base interaction with one of two *meso*-nitrogen atoms.[9] Complex **3** is stable in CF_3COOH, but dissolving it in conc. H_2SO_4 is followed by rapid demetallation. Under comparable conditions (*ca*. 17.6 M H_2SO_4), **3** is 100 times less stable to dissociation than [In(Cl)TPP][10] (k_{obs}^{298} = 4.394×10^{-4} and 0.065×10^{-4} s^{-1}, respectively). It was found previously[5] that the corresponding Cu complex of **1** [CuDAPMB] exibits a much higher stability in conc. H_2SO_4 than the Cu complexes of common porphyrins. Evidently, the opposite effect of the diaza substitution on the stability of Cu^{II} and In^{III} complexes is connected with differences in the steric correspondence of these ions to the coordination cavities of porphyrins and diazaporphyrins. The smaller size of the diazaporphyrin core determines its stronger σ- and π-bonding with the Cu^{II} cation (r_M = 0.72 Å), located in the plane of the macrocyclic ring, and weaker bonding with the larger In^{III} cation (r_M = 0.81 Å), which is located outside the plane of the macrocyclic ring.

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[‡] *Crystal data for* **3**·$CHCl_3$: $C_{39}H_{51}Cl_4InN_6$, *M* = 860.48, triclinic, space group *P*1, *a* = 12.582(2) Å, *b* = 13.217(2) Å, *c* = 13.268(3) Å, *α* = = 112.47(1)°, *β* = 90.19(2)°, *γ* = 103.64(1)°, *V* = 1970.7(6) Å^3, *Z* = 2, D_c = 1.450 g cm^{-3}, *μ* = 0.907 mm^{-1}, *F*(000) = 888. Data were measured using a CAD4 Enraf Nonius diffractometer {*T* = 170 K, graphite-monochromated MoKα radiation, *λ* = 0.71069 Å, *θ* = 2.07–29.96°, *θ*/2*θ* scan mode, 7522 reflections were collected of which 7179 were unique [*R*(int) = 0.0617]}. The structure was solved by direct methods using the SHELXS-86 and SHELXL-93 programs. Refinement on F^2 in an anisotropic approximation for all non-hydrogen atoms (hydrogen atoms isotropic) by a full-matrix least-squares method converged to R_1 = = 0.0675 [$I > 2\sigma(I)$], wR_2 = 0.1972 (all data) and *S* = 1.020 based on 451 parameters and 7179 unique reflections. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 1999. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/49.

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