

# First X-ray crystal structure of a lanthanide(III) monoporphyrinic complex using non-planar porphyrin rings

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Twenty-three years after the first synthesis of lanthanide(III) porphyrins the X-ray crystal structure of [Tb<sup>III</sup>(β-Cl<sub>8</sub>tpp)(O<sub>2</sub>CMe)(Me<sub>2</sub>SO<sub>2</sub>)] is reported; the synthetic route to four halogenated porphyrins H<sub>2</sub>(β-X<sub>n</sub>tpp) (X = Cl or Br, n = 4 or 8) is described and compared with the corresponding [Tb<sup>III</sup>(β-X<sub>n</sub>tpp)(O<sub>2</sub>CMe)]; the highly distorted structure of the Tb<sup>III</sup> complex is compared with similar perhalogenated porphyrinic complexes; the X-ray structure of the brominated free base is also reported.

Since the first reported synthesis of lanthanide monoporphyrinates in 1974,<sup>1a</sup> several studies on these systems have appeared in the literature.<sup>1,2</sup> Here, we report on the first X-ray structure of a lanthanide monoporphyrinate, [Tb<sup>III</sup>(β-Cl<sub>8</sub>tpp)(O<sub>2</sub>CMe)(Me<sub>2</sub>SO<sub>2</sub>)], and the structure of the inherently non-planar free base H<sub>2</sub>(β-Br<sub>8</sub>tpp). The synthesis of the [Tb<sup>III</sup>(β-X<sub>n</sub>tpp)(O<sub>2</sub>CMe)] and H<sub>2</sub>(β-X<sub>n</sub>tpp) derivatives, is also described (X = Cl or Br, n = 4 or 8). This new family of lanthanide(III) monoporphyrinates is promising both for the synthesis of novel homo- and hetero-leptic bisporphyrinates, formally analogous to the photosynthetic reaction centre special pair,<sup>3</sup> and for their photochemical<sup>1b</sup> and magnetic properties.<sup>1d</sup>

According to a previously reported chlorination procedure,<sup>4</sup> stirring an *o*-dichlorobenzene solution of [Ni<sup>II</sup>(tpp)] (1 equiv.) at 150 °C for 2–3 h with 4.2 or 12 equiv. of bromo (or chloro) succinimide affords [2,7,12,17-tetra- or 2,3,7,8,12,13,17,18-octahalogeno-5,10,15,20-tetraphenylporphyrinato]nickel(II) respectively.†‡ The chromatographically pure (Al<sub>2</sub>O<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>) nickel(II) derivatives were then demetallated in concentrated H<sub>2</sub>SO<sub>4</sub> (95%). The analytically pure free bases were obtained after extraction with CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O, drying over MgSO<sub>4</sub>, and chromatography (once or twice) on Al<sub>2</sub>O<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>.§ Reaction of tris(pentane-2,4-dionato)terbium(III) (15 equiv.) with H<sub>2</sub>(β-X<sub>n</sub>tpp) (1 equiv.) in refluxing 1,2,4-trichlorobenzene (tcb),<sup>5</sup> for 3 h affords the corresponding terbium monoporphyrinate complexes.¶|| The terbium(III) complexes were purified by column chromatography on Al<sub>2</sub>O<sub>3</sub> using, in order, toluene (elimination of tcb), CH<sub>2</sub>Cl<sub>2</sub> (the unreacted free base is separated), MeOH–dmf (3 : 1 v/v) (part of the desired derivative) and Me<sub>2</sub>SO (the major quantity of the desired complex) as eluents. The last two fractions were collected, evaporated to dryness, and the solid residue was recrystallized by slow evaporation in a saturated toluene solution.

The ORTEP diagram of the complex [Tb<sup>III</sup>(β-Cl<sub>8</sub>tpp)(O<sub>2</sub>CMe)(Me<sub>2</sub>SO<sub>2</sub>)] shown in Fig. 1,\*\* sheds light on the molecular structure of lanthanide monoporphyrinates. The coordination sphere of terbium consists of the four nitrogen atoms of the substituted porphyrin, the oxygen atoms of a bidentate acetate and the oxygen atoms of two Me<sub>2</sub>SO solvent molecules. The coordination geometry of the terbium(III) ion is square antiprismatic, the average dihedral angle between a pair of N–Tb–N and O–Tb–O planes being 46.74°. The mean Tb–N and Tb–O bond distances are 2.427 and 2.445 Å, respectively. The

terbium(III) ion lies 1.282 and 1.469 Å out of the mean N<sub>4</sub> and mean O<sub>4</sub> plane, respectively, while the N<sub>4</sub> and O<sub>4</sub> mean planes manifest a dihedral tilt angle of 1.71°. Scheidt and Lee<sup>6</sup> have shown that the mean absolute perpendicular displacements of the β-carbons from the porphyrin mean plane (C<sub>β</sub>) increase with decreasing dihedral angles between the phenyl rings and porphyrin core in saddled [M(tpp)]<sup>n+</sup> derivatives. The porphyrin ring of the Tb<sup>III</sup> complex also manifests a marked saddle distortion with a mean absolute perpendicular displacement for the β-carbons from the N<sub>4</sub> mean plane of 0.89 Å. Relative to [Fe<sup>III</sup>(β-Cl<sub>8</sub>tpp)Cl] (C<sub>β</sub> = 0.87 Å),<sup>7</sup> [Zn(β-Cl<sub>8</sub>tpp)] (C<sub>β</sub> = 0.79 Å),<sup>8a</sup> and [Ru(β-Cl<sub>8</sub>tpp)] (C<sub>β</sub> = 0.48 Å),<sup>8b</sup> this magnitude of distortion is the largest yet observed for a β-halogeno metalloporphyrin. The displacement of the individual chlorine atoms from the N<sub>4</sub> mean plane is in the range 1.03–2.18 Å, which is considerably larger than that found in [Zn(β-Cl<sub>8</sub>tpp)] (1.17–1.48 Å)<sup>8a</sup> and [Ru(β-Cl<sub>8</sub>tpp)] (0.68–1.11 Å).<sup>8b</sup> Finally, as in the following structure of the free base, rotation of the phenyl rings with respect to the porphyrin mean plane minimizes unfavourable steric interactions with the flanking chloride substituents. The dihedral angles formed between the phenyl rings and the N<sub>4</sub> mean plane are: 49.03° [C(21)–C(26)], 49.36° [C(27)–C(32)], 49.38° [C(33)–C(38)] and 49.74° [C(39)–C(44)].

The saddle distortion of H<sub>2</sub>(β-Br<sub>8</sub>tpp) is particularly severe (Fig. 2). Thus, the C<sub>β</sub> are canted well above the N<sub>4</sub> mean plane (C<sub>β</sub> = 1.263 Å) relative to that observed in the related species

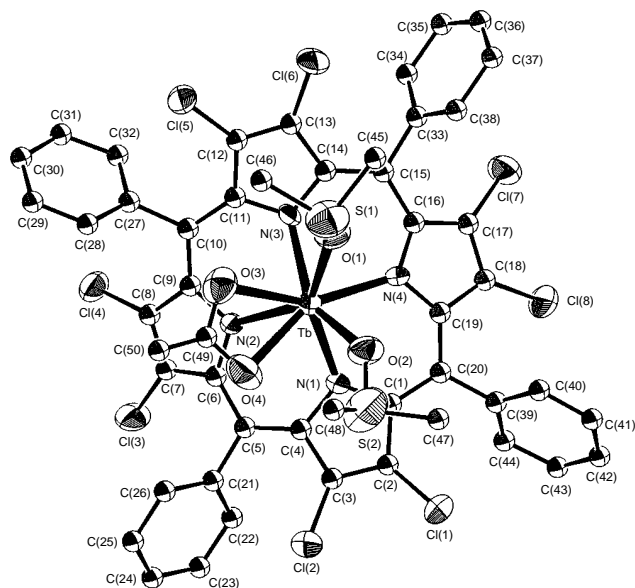
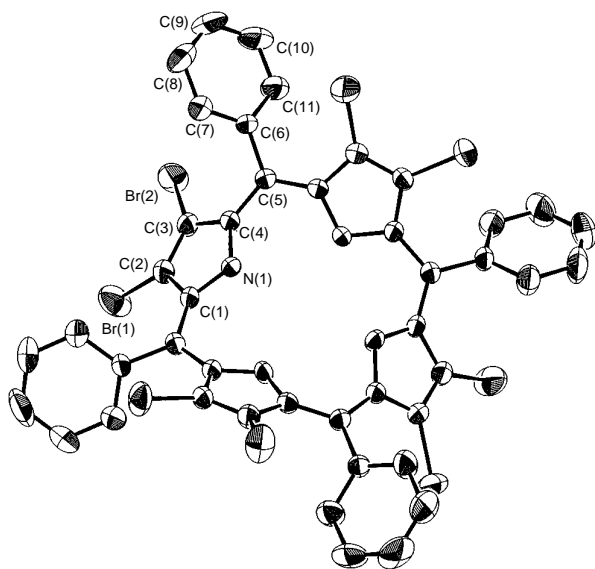


Fig. 1 ORTEP diagram of [Tb<sup>III</sup>(β-Cl<sub>8</sub>tpp)(O<sub>2</sub>CMe)(Me<sub>2</sub>SO<sub>2</sub>)]. All carbon atoms are shown isotropic for clarity, and heteroatoms are anisotropic with 30% probability thermal ellipsoids.



**Fig. 2** ORTEP diagram of  $H_2(\beta\text{-Br}_8\text{tpp})\cdot 2\text{dmf}$  labelling the crystallographically independent atoms with 50% probability thermal ellipsoids

$H_2(\beta\text{-Br}_8\text{tpp})$  ( $C_\beta = 0.903 \text{ \AA}$ )<sup>7</sup> and  $H_2(\beta\text{-Br}_8\text{tmp})$  ( $C_\beta = 0.95 \text{ \AA}$ )<sup>7,8b</sup>. The pronounced non-planarity of  $H_2(\beta\text{-Br}_8\text{tpp})$  is also reflected by the large average perpendicular displacement of the *meso* carbons ( $C_m = 0.317 \text{ \AA}$ ) from the  $N_4$  mean plane relative to that observed for  $H_2(\beta\text{-Br}_8\text{tmp})$  ( $C_m = 0.30 \text{ \AA}$ )<sup>7,8b</sup> and  $H_2(\beta\text{-Br}_8\text{tpp})$ <sup>8a</sup> ( $C_m = 0.091 \text{ \AA}$ ). The marked saddle distortion of  $H_2(\beta\text{-Br}_8\text{tpp})$ , and hence tipping of the pyrrole rings, results in particularly acute dihedral angles for the phenyl rings relative to the  $N_4$  mean plane ( $29.7^\circ$ ). The pyrrole rings themselves are alternately canted above and below the  $N_4$  mean plane with an average value of  $44.6^\circ$ .

The role played by non-planar porphyrin ligands in the coordination chemistry of rare-earth elements, and the unusual spectroscopic properties (UV–VIS, NMR data and electrochemical potentials) of their mono- or bis-porphyrinate complexes are two intriguing questions currently under investigation in our laboratory.

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### Footnotes

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† This lack of regioselectivity is justified by the predominant absence of localized double-bond character in the metalloporphyrin (see also ref. 4) which results in the introduction of one halogen atom in each pyrrolic/pyrrolic ring; H. J. Callot, *Tetrahedron Lett.*, 1973, **50**, 4987.

‡ A detailed description of the synthesis, purification and the complete spectroscopic data of the nickel(ii)  $\beta$ -tetra- and  $\beta$ -octa-halogenated tpp complexes as well as the X-ray study of  $[\text{Ni}(\beta\text{-Br}_8\text{tpp})]$  will be published elsewhere, work in progress.

§ UV–VIS data in  $\text{CH}_2\text{Cl}_2$ , 20 °C,  $\lambda_{\text{max}}/\text{nm}$ ,  $[\log(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})]$  in parentheses:  $H_2(\beta\text{-Cl}_4\text{tpp})$ , 426 (5.44), 523 (4.35), 599 (3.56), 667 (3.54);  $H_2(\beta\text{-Cl}_8\text{tpp})$ , 453 (5.38), 551 (4.04), 601 (4.03), 719 (3.85);  $H_2(\beta\text{-Br}_4\text{tpp})$ , 430 (5.40), 527 (4.29), 598 (3.51), 673 (3.49);  $H_2(\beta\text{-Br}_8\text{tpp})$ , 469 (5.31), 569

(4.02), 625 (4.14), 745 (3.88). All complexes gave satisfactory elemental analysis data.

¶ The pyrolysis of  $\text{Tb}^{\text{III}}(\text{acac})_3$  during the course of this high temperature synthesis provides a reasonable explanation for the unexpected presence of the acetate ligand on the coordination sphere of terbium. For all the investigated complexes characteristic IR bands were observed at the regions 1440–1446 and 1490–1496  $\text{cm}^{-1}$ , representative of the bidentate coordination of the  $\text{O}_2\text{CMe}$  ligand (see also: K. Nakamoto, in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, 3rd edn., 1978).

|| UV–VIS data in  $\text{CH}_2\text{Cl}_2$ , 20 °C,  $\lambda_{\text{max}}/\text{nm}$ ,  $[\log(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})]$  in parentheses:  $[\text{Tb}^{\text{III}}(\beta\text{-Cl}_4\text{tpp})(\text{O}_2\text{CMe})]$ , 432 (5.25), 563 (4.20), 596 (3.76);  $[\text{Tb}^{\text{III}}(\beta\text{-Cl}_8\text{tpp})(\text{O}_2\text{CMe})]$ , 460 (4.77), 553 (3.69), 598 (3.85), 652 (3.89);  $[\text{Tb}^{\text{III}}(\beta\text{-Br}_4\text{tpp})(\text{O}_2\text{CMe})]$ , 432 (5.20), 569 (4.15), 596 (3.64);  $[\text{Tb}^{\text{III}}(\beta\text{-Br}_8\text{tpp})(\text{O}_2\text{CMe})]$ , 474 (4.65), 552 (3.48), 612 (3.42), 669 (3.50). All complexes gave satisfactory elemental analysis data.

\*\* *Crystal data*:  $[\text{Tb}^{\text{III}}(\beta\text{-Cl}_8\text{tpp})(\text{MeCO}_2)(\text{Me}_2\text{SO})_2]$ ,  $\text{C}_{72}\text{H}_{63}\text{Cl}_8\text{N}_4\text{O}_5\text{S}_2\text{Tb}$ ,  $M = 1570.91$ ; monoclinic, space group  $P2_1/c$ ;  $a = 19.775(5)$ ,  $b = 13.516(3)$ ,  $c = 30.015(6) \text{ \AA}$ ,  $\beta = 108.409(7)^\circ$ ,  $U = 7612(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c(D_m) = 1.371(1.36) \text{ g cm}^{-3}$ ,  $T = 298 \text{ K}$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/407.

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