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Bismuth porphyrin complexes: syntheses and structural studies

Bernard Boitrel,[a] Matthis Breede,[b] Penelope J. Brothers,*[b] Michael Hodgson,[b] Lydie Michaudet,[a] Clifton E. F. Rickard[b] and Najeh Al Salim[b]

[a] *Institut de Chimie, UMR CNRS 6509, Université Rennes 1, Campus de Beaulieu, Av. du Général Leclerc, 35042 Rennes Cedex, France*

[b] *Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand. E-mail: p.brothers@auckland.ac.nz*

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The synthesis of several new bismuth porphyrin complexes Bi(por)(X) containing the tpp or t*p*Clpp (t*p*Clpp = 5,10,15,20-tetra-*p*-chlorophenylporphyrin) porphyrin ligand and anions X = NO_3, Cl, Br, I are described. Molecular structures reported for Bi(t*p*Clpp)(X) for X = Cl, Br show that the complexes crystallise as centrosymmetric dimers doubly bridged through Cl or Br. Bi(t*p*Clpp)(NO_3) crystallises as a less symmetric dimer in which one NO_3 ligand bridges the two bismuth centres and the second NO_3 ligand interacts with only one bismuth atom. In all three structures the bismuth atoms are significantly displaced from the porphyrin N_4 planes and the Bi–halide or Bi–O distances are very long.

Introduction

One of the characteristics of the main group elements is the wide range in size from the lightest to the heaviest element in each group. For example, the covalent radii of the Group 15 elements range from 0.75 Å for nitrogen to 1.50 Å for bismuth. This is matched by the ability of the porphyrin ligand to form complexes with metals, and in some instances non-metals, from all regions of the periodic table. Despite this fact, porphyrin complexes in which there is a significant mismatch between the size of the coordinated element and the "hole" in the porphyrin (which has a radius close to 2.0 Å) remain the least well-characterised examples.

Porphyrin complexes of the Group 13, 14 and 15 elements are now well established, especially for the 3rd through 5th row elements (aluminium through antimony),[1] and the first example of a Group 16 porphyrin complex containing tellurium has recently been reported.[2] Among these groups, coordination to the lightest element boron has only recently been established. The boron atoms are too small to coordinate to all four porphyrin nitrogen atoms, and form 2 : 1 complexes containing two borons per porphyrin, with each boron interacting with only two porphyrin nitrogen atoms.[3] In porphyrin complexes containing the heaviest elements from Groups 13–15 (thallium, lead and bismuth), the very large sizes of the elements result in complexes with the coordinated element residing significantly out of the N_4 plane, as shown by X-ray structures of the Tl(III)[4] and Pb(II)[5] derivatives. Among these heavy elements, bismuth has received perhaps the least attention.

Bismuth porphyrin complexes were first reported in 1969 and 1974,[6] although the formulation of the complexes was later corrected in a review article.[7] In 1992 we published experimental details for the preparation of Bi(ttp)(NO_3) from H_2ttp and Bi(NO_3)$_3$ in pyridine.[8,9] We also investigated the variable temperature ^{1}H NMR temperature behaviour of Bi(ttp)(NO_3), which demonstrated the loss of symmetry in the plane containing the porphyrin ligand. We interpreted this as evidence for out-of-plane coordination of the bismuth atom.[8] This has recently been confirmed by an X-ray crystal structure determination of the triflato derivative Bi(oep)(SO_3CF_3). Preparative details and electrochemistry for Bi(por)(NO_3) and Bi(por)(SO_3CF_3) (por = tpp, oep, tmp, ttp) were also reported in this paper.[10] Another recent report described the structure of Bi(4ES)(NO_3)(H_2O) in which the porphyrin ligand 4ES is a derivative of tpp containing four amide pendant arms (derived from ethylsuccinyl chloride) linked to the *ortho* positions of the peripheral aryl groups.[11] The syntheses and spectroscopic characterisation of bismuth complexes of a water-soluble porphyrin have also been reported.[12]

In this study we report details of the preparation of new bismuth porphyrin complexes Bi(por)Cl, Bi(por)Br and Bi(por)I, and the X-ray crystal structures of Bi(t*p*Clpp)X, where X = Cl, Br, I or NO_3.

Results and discussion

We previously reported the preparation of Bi(ttp)(NO_3), containing tetra-*p*-tolylporphyrin, but this compound defied attempts to produce X-ray quality crystals.[8] We have subsequently found that use of tetra-*p*-chlorophenylporphyrin affords compounds which crystallise more readily, and as a result we prepared the analogous compound Bi(t*p*Clpp)(NO_3) by the same method, the reaction of Bi(NO_3)$_3$·5H_2O with the free base porphyrin in refluxing pyridine. Slow evaporation of a dichloromethane solution of the compound was successful in producing crystals of Bi(t*p*Clpp)(NO_3)·CH_2Cl_2 suitable for an X-ray determination.

Bismuth porphyrin complexes containing a halide anion have not previously been reported. The reaction of $BiCl_3$ or BiI_3 with H_2(por) in refluxing pyridine yielded the corresponding bismuth porphyrin chloride and iodide complexes, Bi(t*p*Clpp)Cl and Bi(por)I (por = ttp, t*p*Clpp). The chloride complex Bi(tpp)Cl also resulted unexpectedly from the reaction of $BiPh_3$ with H_2tpp in refluxing benzonitrile, followed by chromatography on silica using CH_2Cl_2 as eluent.

To date, all well-characterised bismuth porphyrin complexes contain bismuth(III). In an attempt to prepare a complex containing bismuth(V) we investigated the reaction of Ph_3BiBr_2 with H_2t*p*Clpp in refluxing pyridine. Although the reaction was successful in producing a bismuth porphyrin, Bi(t*p*Clpp)Br, the product contained bismuth(III) resulting from reduction of the bismuth under the reaction conditions. The nature or fate of the reductant was not investigated. All three of the chloride, bromide and iodide complexes were characterised by X-ray crystallography.

The syntheses of the bismuth porphyrin complexes were carried out under nitrogen in order to protect the reactants and products from air and moisture at the elevated temperatures of the reactions in refluxing solvent. However the products are stable in the solid state, inert towards air and moisture, but are sensitive to demetallation under acidic conditions. For example, the chloro complexes Bi(por)Cl will slowly demetallate in

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CH_2Cl_2 solution. Chromatography on silica gel was used to purify the complexes, although this does cause decomposition of minor amounts of the complexes.

All of the bismuth porphyrin complexes reported here show "hyper" type UV-Vis spectra typical of bismuth(III) porphyrins.[7] Similarly, all show broadened doublets for the *ortho* and *meta* protons of the *p*-tolyl or *p*-chlorophenyl groups on the periphery of the porphyrin rings. We previously observed this phenomenon for Bi(ttp)NO$_3$, and a variable temperature ^{1}H NMR study indicated that the energy of activation for this process was in the range observed for rotation of the peripheral aryl ring.[8] At low temperature, rotation of the aryl rings is slow on the NMR time scale and the two chemically different faces of the porphyrin ligand are reflected in the chemically different H_o, H_o' and H_m, H_m' protons.

The recently published molecular structures of Bi(oep)(SO$_3$CF$_3$) and Bi(4ES)(NO$_3$)(H$_2$O) show that both exist in the solid state as dinuclear complexes, the former bridged through two triflato ligands and the latter through carbonyl oxygen donors on the pendant ester groups. This trend is continued in all four of the structurally characterised complexes Bi(t*p*Clpp)X (X = NO$_3$, Cl, Br, I) reported here, which exist in the solid state as dinuclear species. {Bi(t*p*Clpp)(NO$_3$)}$_2$ is bridged in an asymmetric fashion by one of the two nitrate ions, and the two bismuth atoms in the dinuclear assembly have different coordination environments. However, the ^{1}H NMR spectra of Bi(por)NO$_3$ (por = ttp,[8] t*p*Clpp) show only one type of bismuth porphyrin, suggesting either that the dinuclear structure is not retained in solution or that the molecule is fluxional on the NMR time scale. Similarly, the presence of the bridging halide ligands in the structures of {Bi(t*p*Clpp)X}$_2$ (X = Cl, Br, I) lowers the symmetry within each porphyrin ligand in the solid state. The fact that the porphyrins retain their four-fold symmetry in solution, as evidenced by the ^{1}H NMR spectra, again can be interpreted as evidence that the complexes are monomeric in solution. A further possibility is rapid rotation (on the NMR time scale) of the porphyrins about the Bi $\cdots$ Bi axis if the dinuclear structure does persist in solution.

Crystal structures were obtained for four complexes, {Bi(t*p*Clpp)(NO$_3$)}$_2$ and {Bi(t*p*Clpp)X}$_2$ (X = Cl, Br, I). The data for the iodo complex {Bi(t*p*Clpp)I}$_2$ were of poor quality and the structure did not refine well. However, the structure obtained was sufficient to determine that the iodo and bromo complexes are isostructural,[13] and the discussion below relating to the bromo complex also applies to the iodo complex.

All four structurally characterised complexes are distinguished by large displacements (>1.1 Å) of the bismuth atoms from the porphyrin N$_4$ planes, 1.133(4) and 1.090(4) Å for Bi1 and Bi2 in {Bi(t*p*Clpp)(NO$_3$)}$_2$, 1.126(1) Å in {Bi(t*p*Clpp)Cl}$_2$ and 1.114(2) Å in the bromo analog. These distances compare with the displacements of 1.07 Å in {Bi(oep)(OSO$_2$CF$_3$)}$_2$, 1.125 Å in {Bi(4ES)(NO$_3$)(H$_2$O)}$_2$, 1.174 Å in the lead complex Pb(t*n*Prp)[5] and 0.69 Å in Tl(oep)Cl.[14] Of the lead and thallium complexes, the lead complex is more directly comparable as the Pb(II) and Bi(III) centres share the 6s^2 electron configuration. Bi(III) would be expected to be slightly smaller than Pb(II), and this is borne out by the smaller magnitude of the displacements from the N$_4$ plane.

The Bi–N(porphyrin) distances among the three new complexes span the range 2.302(8) to 2.393(7) Å, with no significant differences between the Bi–N(av) distances around each bismuth centre, which are 2.347 and 2.328 Å for {Bi(t*p*Clpp)(NO$_3$)}$_2$, 2.344 Å for {Bi(t*p*Clpp)Cl}$_2$ and 2.331 Å for {Bi(t*p*Clpp)Br}$_2$. The recently reported structures of {Bi(oep)(SO$_3$CF$_3$)}$_2$ and {Bi(4ES)(NO$_3$)(H$_2$O)}$_2$ show similar Bi–N(av) distances of 2.305 and 2.34 Å.[10,11]

Important bond lengths and angles for {Bi(t*p*Clpp)(NO$_3$)}$_2$ (Fig. 1) are given in Table 1. The coordination geometry about the two bismuth centres is very asymmetric. One of the nitrato groups (N(9)) coordinates to Bi(1) in a bidentate fashion through O(1) and O(2). The second nitrato group (N(10)) bridges between Bi(1) and Bi(2) through two oxygen atoms (O(6) and O(5)). These four Bi–O bond lengths are similar (2.692(7)–2.858(6) Å). In addition, the remaining oxygen atom on the second nitrato group, O(4) interacts with both Bi(1) and Bi(2) with longer Bi–O distances (2.981(7), 2.907(7) Å). Thus Bi(1) is formally eight coordinate, while Bi(2) is six-coordinate, as shown in Fig. 2. The Bi–O distances are all very long when compared to other bismuth complexes containing nitrato ligands. For example, the Bi–O distances (2.725(7)–2.981(7) Å) are as long or longer than those in a series of [Bi(NO$_3$)(polyethyleneglycolate)]$_2$ complexes, in which they span the range 2.38–2.85 Å.[15] The bismuth porphyrin complex Bi(4ES)(NO$_3$)(H$_2$O) contains a bidentate nitrato ligand with Bi–O distances of 2.706(5) and 2.789(4) Å.[11]

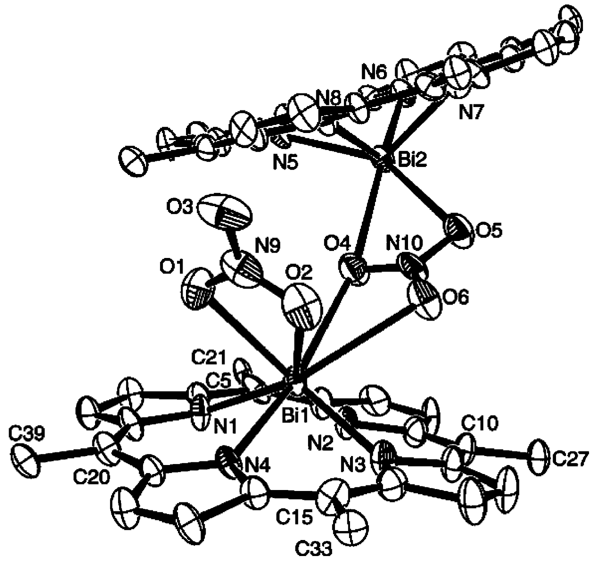

Fig. 1 Molecular structure of Bi(t*p*Clpp)NO$_3$. Aryl rings omitted for clarity.

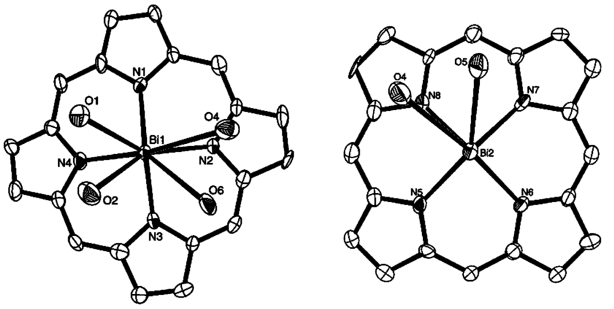

Fig. 2 Coordination geometry around the bismuth atoms in Bi(t*p*Clpp)NO$_3$.

The halide complexes {Bi(t*p*Clpp)Cl}$_2$, {Bi(t*p*Clpp)Br}$_2$ and {Bi(t*p*Clpp)I}$_2$ all crystallise as centrosymmetric dimers with bridging halide ions. The chloro and bromo structures are similar, and only that of the bromo complex is shown in Fig. 3. In each complex the bismuth atoms are six-coordinate. The bridges are almost symmetric, with the difference between the two unique Bi–X bonds within each complex less than 0.03 Å. The bridging halide groups are staggered with respect to the porphyrin nitrogen atoms, giving distorted trigonal prismatic geometry around each bismuth atom (shown for the chloro complex in Fig. 4). The bismuth halide distances in {Bi(t*p*Clpp)Cl}$_2$ are 3.0425(8) and 3.0638(8) Å and in {Bi(t*p*Clpp)Br}$_2$ are 3.2048(6) and 3.2319(6) Å. Suitable comparisons are the doubly chloro-bridged anions [Bi$_2$Cl$_{10}$]$^{4-}$ and

Table 1 Important bond lengths (Å) and angles (°) for Bi(t*p*Clpp)NO$_3$, Bi(t*p*Clpp)Cl and Bi(t*p*Clpp)Br[a]

{Bi(t*p*Clpp)(NO$_3$)}$_2$		{Bi(t*p*Clpp)Cl}$_2$		{Bi(t*p*Clpp)Br}$_2$	
Bi(1)–N(1)	2.368(7)	Bi(1)–N(1)	2.337(3)	Bi–N(1)	2.326(4)
Bi(1)–N(2)	2.393(7)	Bi(1)–N(2)	2.339(3)	Bi–N(2)	2.338(4)
Bi(1)–N(3)	2.302(8)	Bi(1)–N(3)	2.351(3)	Bi–N(3)	2.333(4)
Bi(1)–N(4)	2.325(7)	Bi(1)–N(4)	2.350(3)	Bi–N(4)	2.327(4)
Bi(2)–N(5)	2.367(8)				
Bi(2)–N(6)	2.344(7)				
Bi(2)–N(7)	2.299(8)				
Bi(2)–N(8)	2.303(7)				
Bi(1)–O(1)	2.725(7)	Bi–Cl(1)	3.0638(8)	Bi–Br	3.2048(6)
Bi(1)–O(2)	2.692(7)	Bi–Cl(1)#1	3.0425(8)	Bi–Br#1	3.2319(6)
Bi(1)–O(4)	2.981(7)	Cl(1)–Bi#1	3.0424(8)		
Bi(1)–O(6)	2.858(6)				
Bi(2)–O(4)	2.907(7)				
Bi(2)–O(5)	2.754(7)				
		Cl(1)–Bi–Cl(1)#1	89.93(2)	Br–Bi–Br#1	92.294(14)
		Bi–Cl(1)–Bi#1	90.07(2)	Bi–Br–Bi#1	87.705(14)
Bi(1)–N(av)	2.347(8)	Bi–N(av)	2.344(3)	Bi–N(av)	2.331(4)
Bi(2)–N(av)	2.328(8)				
Bi(1)–N$_4$	1.133(4)	Bi–N$_4$	1.126(1)	Bi–N$_4$	1.114(2)
Bi(2)–N$_4$	1.090(4)				

[a] Bi–N$_4$ distance is the displacement of the Bi atom from the mean porphyrin N$_4$ plane.

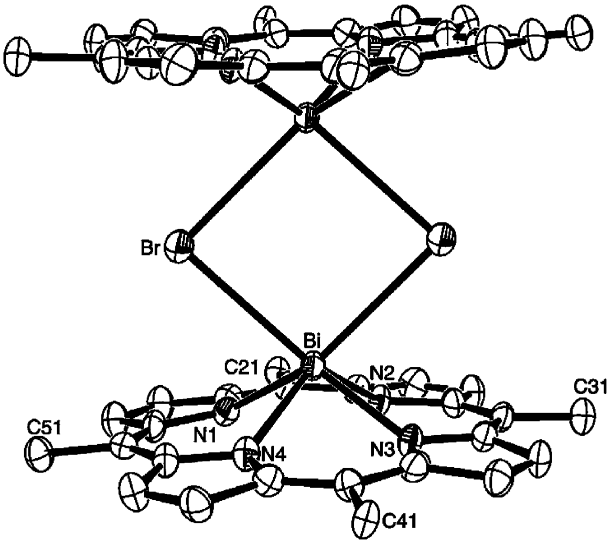

Fig. 3 Molecular structure of Bi(t*p*Clpp)Br. Aryl rings omitted for clarity.

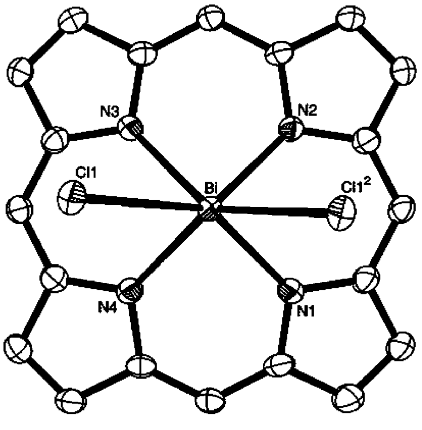

Fig. 4 Coordination geometry around the bismuth atom in Bi(t*p*Clpp)Cl.

[Bi$_2$Cl$_8$(THF)$_2$]$^{2-}$ in which the Bi–Cl distances span the range 2.49–2.72 Å (terminal) and 2.84–2.92 Å (bridging).[16] One of the Bi–Cl bridging distances (2.60, 3.14 Å) in the neutral bis(2-methoxyethyl) ether (L) complex {Bi(L)Cl$_3$}$_2$ is even longer.[17] In [BiBr$_2$(18-crown-6)]$^+$[BiBr$_4$]$^-$ the Bi–Br distances span the range 2.66–2.69 Å (terminal) and 2.87–3.22 Å (bridging).[18] In the two porphyrin complexes the bismuth halide distances are similar to or longer than the longest distances in the complexes selected for comparison.

Overall, the crystal structures show Bi–N(porphyrin) distances which are less than the sum of either the ionic or covalent radii for bismuth and nitrogen,[19] and longer distances between bismuth and the bridging anions (NO$_3^-$, Cl$^-$ or Br$^-$) or neutral ligands (MeCN). The structures can be interpreted in terms of [Bi(t*p*Clpp)]$^+$ cations with a reasonable degree of Bi–N covalent bonding within the cations but predominantly ionic interactions between the bismuth atoms and the bridging anions. The dinuclear arrangement observed for all the crystal structures of bismuth porphyrin complexes reported to date can be attributed to a combination of electrostatic effects arising from the out-of-plane bismuth atom in the ionic fragment [Bi(por)]$^+$ and the tendency for the large Bi(III) ion to increase its coordination number. An X-ray crystal structure of a second chloro complex, {Bi(ttp)Cl}$_2$ did not give publishable data, but nevertheless showed a different structure in which the two porphyrin ligands were oriented at an angle, with the Bi$_2$Cl$_2$ four-membered ring folded along the Cl ··· Cl axis. This indicates that additional structural possibilities for bismuth porphyrin complexes beyond those reported to date may yet come to light.

Experimental

All preparations were carried out under nitrogen using Schlenk techniques and dried, distilled and degassed solvents. BiNO$_3$·5H$_2$O, BiCl$_3$ and BiI$_3$ were commercially available. Ph$_3$BiBr$_2$ was prepared by the stoichiometric reaction of BiPh$_3$ with Br$_2$ in CH$_2$Cl$_2$ at room temperature. ^{1}H NMR spectra were recorded on either Bruker AM 400 or AM 200 spectrometers using CDCl$_3$ as solvent. UV-Vis spectra were recorded on a Shimadzu UV-2101 PC instrument. Mass spectra were recorded on a VG 70-SE spectrometer. Elemental analyses were carried out by the Microanalytical Laboratory, University of Otago.

Syntheses

Bi(t*p*Clpp)NO$_3$. Bi(NO$_3$)$_3$5·H$_2$O (5.7 g, 10.7 mmol) and H$_2$t*p*Clpp (0.75 g, 1.0 mmol) were dissolved in dry pyridine (50 mL), and the resulting dark purple solution was heated at reflux temperature for 6 h. During the course of the reaction the solution changed colour from the initial dark purple to a deep green. After this time the pyridine was removed under reduced

Table 2 Crystal data for Bi(t*p*Clpp)$NO_3\cdot CH_2Cl_2$, Bi(t*p*Clpp)$Cl\cdot 2CH_2Cl_2$ and Bi(t*p*Clpp)$Br\cdot 2CH_2Cl_2$

	Bi(t*p*Clpp)$NO_3\cdot CH_2Cl_2$	Bi(t*p*Clpp)$Cl\cdot 2CH_2Cl_2$	Bi(t*p*Clpp)$Br\cdot 2CH_2Cl_2$
Formula	$C_{45}H_{26}BiCl_6N_5O_3$	$C_{46}H_{28}BiCl_9N_4$	$C_{46}H_{28}BiBrCl_8N_4$
M/g mol^{-1}	1106.39	1164.75	1209.21
Crystal system	Triclinic	Triclinic	Triclinic
a/Å	13.8620(2)	13.6069(3)	14.6444(4)
b/Å	17.1885(2)	14.7244(4)	14.6228(4)
c/Å	21.1094(2)	15.3454(3)	15.2375(4)
α/°	93.0970(10)	107.4020(10)	70.7520(10)
β/°	102.180(10)	95.4200(10)	63.5130(10)
γ/°	91.5710(10)	111.6610(10)	75.9100(10)
V/Å^3	4905.30(10)	2652.87(11)	2739.23(13)
T/K	150(2)	293(2)	203(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
μ/mm^{-1}	3.963	3.809	4.370
Reflections collected	43902	23176	25806
Independent reflections, R(int)	18256, 0.0586	9384, 0.0251	11123, 0.0484
Final R indices [$I>2\sigma(I)$] $R1$, $wR2$	0.0606, 0.1629	0.0252, 0.0652	0.0419, 0.0873
R indices (all data) $R1$, $wR2$	0.0805, 0.1730	0.0279, 0.0662	0.0618, 0.0941

pressure, giving a dark green solid. This was then dissolved in the minimum amount of dichloromethane and chromatographed on silica gel (4 × 15 cm). Using dichloromethane as the eluent the free-base porphyrin was removed first followed closely by the title compound. Repeat chromatography always yielded a small amount of the free-base porphyrin in the product band by UV-Vis analyses. Green crystals of the title compound were obtained by slow evaporation of the dichloromethane solution. Yield 0.94 g, 92%. Anal. Found: C, 50.84; H, 2.52; N, 6.74. $C_{44}H_{24}N_5BiCl_4O_3\cdot H_2O$ requires C, 50.79; H, 2.24; N, 6.95%. HR-MS Found: 959.05484. Calcd for $C_{44}H_{24}N_4BiCl_4$ [M^+]: 959.05295. UV-Vis (CH_2Cl_2): λ_{max}/nm (log ε) 352.5 (4.69), 469.5 (5.28), 600.5 (3.99), 647.5 (4.08). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.13 (s, 8H, H_β), 8.06 (br s, 8H, H_o), 7.75 (d, 8H, J = 8.2 Hz, H_m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.0, 139.2, 135.0, 132.7, 127.3, 122.1.

Bi(ttp)Cl. H_2ttp (0.60 g, 0.9 mmol) was dissolved in benzonitrile (5 mL) and the mixture was heated at 130 °C. A solution of $BiPh_3$ (0.40 g, 9.0 mmol) in benzonitrile (1 mL) was then added and the mixture was refluxed for 48 h before being dried under vacuum. The resulting compound was redissolved in dichloromethane and purified on a silica gel column. The desired compound was obtained as a green solid. Yield 0.24 g, 30%. HR-MS (LSIMS): Found: 877.2773. Calcd for $C_{48}H_{36}BiN_4$ [M]$^+$: 877.2744. UV-Vis (CH_2Cl_2): λ_{max}/nm (log ε): 360 (4.71), 472 (5.25), 602 (3.97), 651 (4.13). IR (KBr, cm^{-1}): 993 ν(Bi–N). ^{1}H NMR (500 MHz, $CDCl_3$, 300K): δ 9.01 (s, 8H, H_β); 8.14 (br s, 4H, H_o); 7.96 (br s, 4H, H_o'); 7.58 (s, 8H, H_m); 2.75 (s, 12H, CH_3).

Bi(t*p*Clpp)Cl. $BiCl_3$ (2.34 g, 7.42 mmol) and H_2t*p*Clpp (0.50 g, 0.66 mmol) were dissolved in dry pyridine (50 mL) and the resulting dark purple solution was heated at reflux temperature for 12 h. During the course of the reaction the solution changed colour from the initial dark purple to a deep green. After this time the pyridine was removed under reduced pressure, giving a dark green solid. This was then dissolved in the minimum amount of dichloromethane and chromatographed on silica gel (4 × 15 cm). Dichloromethane was used to elute the free-base porphyrin first, followed by dichloromethane/acetone (4 : 1) which eluted the title compound as a green band. Repeat chromatography always yielded a small amount of the free-base porphyrin in the product band by UV-Vis analyses. Green crystals of the title compound were obtained by slow evaporation of the dichloromethane/acetone solution. Yield 0.58 g, 88%. Anal. Found: C, 55.18; H, 2.70; N, 6.28. $C_{44}H_{24}N_4BiCl_5\cdot C_6H_5N$ requires C, 55.30; H, 2.69; N, 6.45%. HR-MS Found: 959.05546. Calcd for $C_{44}H_{24}N_4BiCl_4$ [M^+]: 959.05295. UV-Vis (CH_2Cl_2): λ_{max}/nm (log ε) 362.5 (4.30), 474.5 (5.83), 605.0 (3.55), 652.0 (3.75). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (s, 8H, H_β), 7.83 (br s, 8H, H_o), 7.68 (br s, 8H, H_m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.7, 139.6, 134.6, 131.7, 127.0, 121.9.

Bi(t*p*Clpp)Br. Ph_3BiBr_2 (0.36 g, 0.06 mmol) and H_2t*p*Clpp (0.225 g, 0.30 mmol) were dissolved in dry pyridine (30 mL) and the resulting solution was heated at reflux temperature for 12 h. The solvent was removed from the green solution and the residue was dissolved in CH_2Cl_2 and chromatographed on Florisil, using CH_2Cl_2 to elute the free base porphyrin and CH_2Cl_2/EtOH (19 : 1) to elute the product. The solvent was removed from the fraction containing the product, and the microcrystalline green residue was recrystallised from CH_2Cl_2/hexane at −10 °C. Yield 0.15 g, 48%. Anal. Found: C, 52.15; H, 2.70; N, 5.16. $C_{44}H_{24}N_4Cl_4BiBr\cdot 0.5(C_6H_{14})$ requires C, 52.15; H, 2.89; N, 5.18%. UV-Vis (CH_2Cl_2): λ_{max}/nm 400 (sh), 476.5 (Soret), 553, 604, 653.

Bi(ttp)I. BiI_3 (2.00 g, 3.4 mmol) and H_2ttp (0.40 g, 0.6 mmol) were dissolved in dry pyridine (50 mL), and the resulting solution was heated at reflux temperature for 6 h. The pyridine was evaporated under reduced pressure, and the residue was redissolved in CH_2Cl_2 and chromatographed twice on silica gel. Dichloromethane was used to elute free base porphyrin, followed by CH_2Cl_2/EtOH (19 : 1) which eluted the product as a green band. The volume of the solution was reduced, resulting in dark green crystals of the product. Anal. Found: C, 56.28; H, 3.80; N, 5.28. $C_{48}H_{36}N_4BiI\cdot H_2O$ requires C, 56.37; H, 3.75; N, 5.48%. UV-Vis (CH_2Cl_2): λ_{max}/nm 405, 486.5 (Soret), 562, 612, 661. ^{1}H NMR ($CDCl_3$): δ 9.12 (s, 8 H, H_β), 8.00 (br, 8 H, H_o), 7.55 (d, 8 H, ^3J = 7.6 Hz, H_m), 2.72 (s, 12 H, CH_3).

Bi(t*p*Clpp)I. This compound was prepared as described above using BiI_3 (1.06 g, 1.8 mmol) and H_2t*p*Clpp (0.225 g, 0.3 mmol) in dry pyridine (50 mL). The product was chromatographed on Florisil, and eluted using CH_2Cl_2/EtOH to yield dark green microcrystals. Yield 0.30 g, 92%. UV-Vis (CH_2Cl_2): λ_{max}/nm 391, 476.5 (Soret), 559, 606, 655. ^{1}H NMR ($CDCl_3$): δ 8.91 (s, 8 H, H_β), 7.91 (br, 8 H, H_o), 7.68 (d, 8 H, ^3J = 8.6 Hz, H_m).

X-Ray crystallography

Suitable single crystals of Bi(t*p*Clpp)(NO_3), Bi(t*p*Clpp)Br and Bi(t*p*Clpp)Cl were obtained from CH_2Cl_2, CH_2Cl_2/hexane and CH_2Cl_2 solutions, respectively. The crystals were mounted under paratone oil and data were collected on a Siemens SMART diffractometer using Mo-Kα radiation (λ = 0.71073 Å) at 150 K. The SMART software was used for data collection and determination of lattice parameters, SAINT for integration of reflections[20] and SADABS[21] for absorption corrections. SHELXTL[22] was used for structure solution, refinement and graphics. A summary of crystallographic data is given in Table 2.

All three crystals of Bi(t*p*Clpp)(X) contain solvent of crystallization and one (X = NO_3) or two (X = Br, Cl) molecules of dichloromethane were clearly resolved. Residual electron density corresponding to additional disordered solvent was present and this has been removed using the Squeeze function of PLATON.[23] Selected interatomic distances and angles are given in Table 1.

CCDC reference numbers 195728–195730.

See http://www.rsc.org/suppdata/dt/b2/b210318d/ for crystallographic data in CIF or other electronic format.

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