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Synthesis, characterization and crystal structures of neutral mono- and di-nuclear lanthanide(III) porphyrinate complexes

Wai-Kwok Wong,*[a] Lilu Zhang,[a] Feng Xue[a] and Thomas C. W. Mak[a]

[a] *Department of Chemistry, Hong Kong Baptist University, Kowloon, Hong Kong*
[b] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong*

Received 20th April 1999, Accepted 9th July 1999

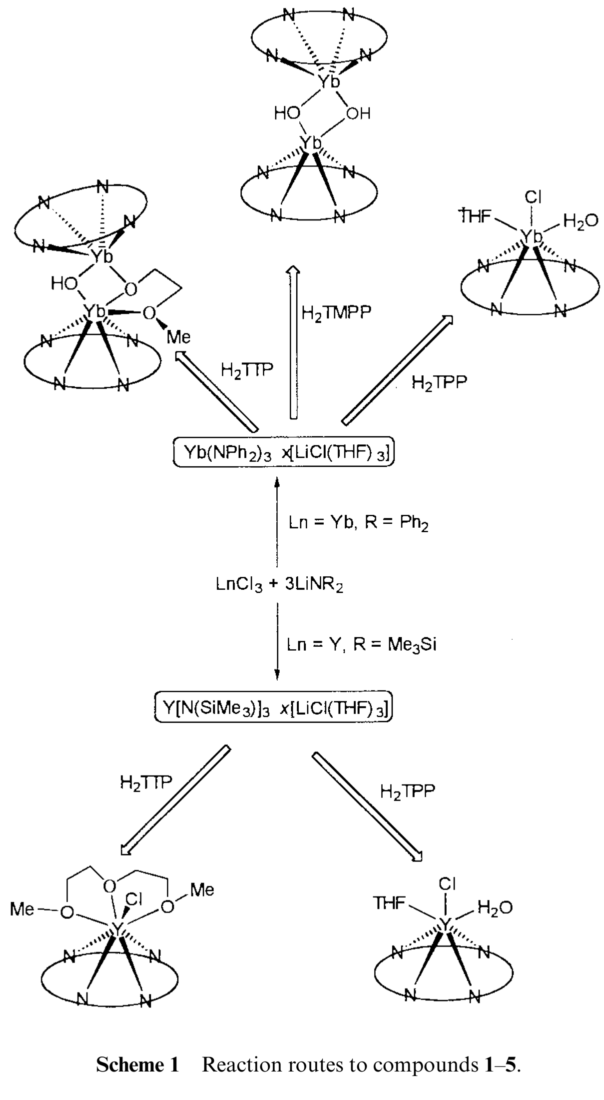
The interaction of 5,10,15,20-tetrakis(*p*-tolyl)porphyrin (H_2TTP) and 5,10,15,20-tetraphenylporphyrin (H_2TPP) with an excess of $Y^{III}[N(SiMe_3)_2]_3{\cdot}x[LiCl(THF)]_3$, generated *in situ*, in refluxing bis(2-methoxyethyl) ether gave the neutral monoporphyrinate complexes $[Y^{III}(TTP)(Cl)\{(CH_3OCH_2CH_2)_2O\}]$ **1** and $[Y^{III}(TPP)(Cl)(H_2O)(THF)]$ **2**, respectively. However, the interaction of 5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrin (H_2TMPP), H_2TTP and H_2TPP with an excess of $Yb^{III}(NPh_2)_3{\cdot}x[LiCl(THF)_3]$, generated *in situ*, in refluxing bis(2-methoxyethyl) ether gave the neutral hydroxide-bridged dinuclear porphyrinate complexes $[\{Yb^{III}(TMPP)(\mu\text{-}OH)\}_2]$ **3** and $[\{Yb^{III}(TTP)\}_2(\mu\text{-}OH)(\mu\text{-}OCH_2CH_2OCH_3)]$ **4**, and the neutral monoporphyrinate complex $[Yb^{III}(TPP)(Cl)(H_2O)(THF)]$ **5**, respectively. The structures of these five complexes have been established by X-ray crystallography.

Introduction

Spectroscopic evidence of the formation of lanthanide(III) monoporphyrinate complexes was first reported in 1974.[1] However, only a few studies were carried out on this system thenceforth, and most focused on lanthanide(III) bis(porphyrinates)[2] and porphyrin–phthalocyanine[3] heteroleptic sandwich complexes. Structural characterization of the neutral lanthanide(III) monoporphyrinate complexes of lutetium[4] and terbium[5] was accomplished only recently. Lanthanide amides are very reactive species and good precursor complexes for the preparation of organolanthanide complexes. Recently, we reported the synthesis of cationic lanthanide(III) monoporphyrinate complexes *via* the protonolysis of lanthanide amide with porphyrin free bases.[6] In this report we further demonstrate that, by varying the nature of the amides, porphyrins and lanthanide metal ions, one can prepare neutral mono- and di-nuclear porphyrinate complexes *via* the protonolysis reactions. Lachkar *et al.*[7] described the first neutral dinuclear lanthanide bis(porphyrin) complexes in which the two porphyrin ligands are covalently linked in a cofacial conformation and the two lanthanide(III) metal centers *via* two hydroxo-bridges. However, prior to this work, there was no report of hydroxy-bridged dinuclear lanthanide bis(porphyrin) complexes in which the two porphyrin ligands are unsupported.

Results and discussion

Recently we reported that the interaction of an excess of $Ln[N(SiMe_3)_2]_3{\cdot}x[LiCl(THF)_3]$ with the porphyrin free base H_2TMPP [5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrin] gave the cationic lanthanide(III) monoporphyrinate complexes $[Ln^{III}(TMPP)(H_2O)_3]Cl$ (Ln = Y, Er or Yb) in high yield.[6] We here report our investigation into the generality of this synthetic strategy and that the reaction product varied with the nature of the amide, porphyrin and lanthanide metals used in the protonolysis reaction. These results are summarized in Scheme 1. Compounds **1**–**5** were isolated as air-stable purple crystals in high yield. All gave satisfactory elemental analyses



Scheme 1 Reaction routes to compounds **1**–**5**.

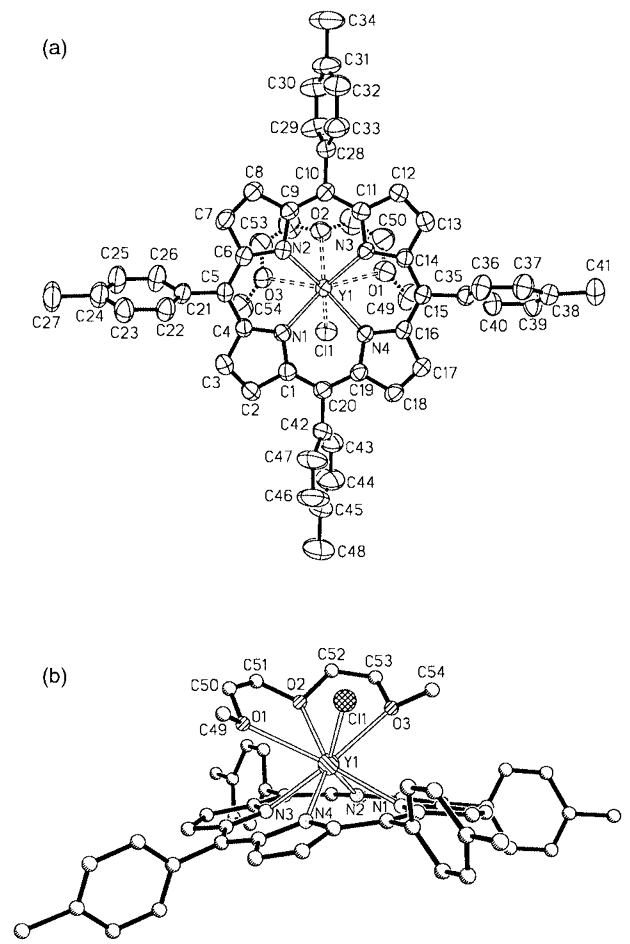


Fig. 1 The structure of compound **1**: (a) top view; (b) side view.

and exhibited electronic absorption spectra characteristic of normal metal porphyrin complexes.[8]

Preparation of neutral yttrium(III) monoporphyrinate complexes

Treatment of an excess of $Y^{III}[N(SiMe_3)_2]\cdot x[LiCl(THF)_3]$, generated *in situ* from the reaction of anhydrous YCl_3 with 3 equivalents of $Li[N(SiMe_3)_2]$ in tetrahydrofuran, with porphyrin free bases H_2TTP [5,10,15,20-tetrakis(*p*-tolyl)porphyrin] and H_2TPP [5,10,15,20-tetra(phenyl)porphyrin] in refluxing bis(2-methoxyethyl) ether solution for 48 h yielded the neutral yttrium(III) monoporphyrinate complexes $[Y^{III}(TTP)(Cl)\{(CH_3OCH_2CH_2)_2O\}]$ **1** and $[Y^{III}(TPP)(Cl)(H_2O)(THF)]$ **2**, respectively. This is in contrast to the reaction of an excess of $Y^{III}[N(SiMe_3)_2]\cdot x[LiCl(THF)_3]$ with H_2TMPP which gave the cationic porphyrin complex $[Y^{III}(TMPP)(H_2O)_3]^+$.[6] The low-resolution mass spectra (FAB, positive-ion mode) exhibited the highest mass peak at *m*/*z* 757 $[Y(TTP)^+]$ for **1** and 736 $[Y(TPP)Cl^+]$ for **2**. Their structures were established by X-ray crystallography.

Crystals of complex **1** suitable for X-ray diffraction study were grown by slow evaporation of a saturated solution of it in toluene. A perspective view is shown in Fig. 1, and selected bond lengths and bond angles in Table 1. The yttrium(III) ion is eight-co-ordinated, surrounded by four N atoms of the porphyrinate dianion, one Cl atom and three O atoms of a chelating bis(2-methoxyethyl) ether molecule, and has a square antiprismatic co-ordination with an average dihedral angle between a pair of N–Y–N and O–Y–O (O–Y–Cl) planes of *ca.* 45.9°. The Y atom lies 1.237 Å above the N_4 mean plane. The average Y–N and Y–O distances are 2.39 and 2.57 Å, respectively. The Y–Cl distance is 2.6702(16) Å which is slightly longer than that of $[Y(C_5Me_5)_2Cl(THF)]$ [2.579(3) Å][9] and shorter than that of $[\{Y(C_5H_4SiMe_3)_2(\mu\text{-}Cl)\}_2]$ [2.704(1) and 2.684(1) Å].[10] The dihedral angle formed between the mean plane defined by the four N atoms and the mean plane defined by the Cl atom and the three O atoms is 5°. Fig. 6(a) gives the projections along the Ct–Y axes (Ct is the centroid of the N_4 mean plane) of this complex without the bis(2-methoxyethyl) ether and chloride ligands. The porphyrin ring exhibits a saddle like distortion with the average perpendicular distance for the nitrogens, pyrrole α-carbons, pyrrole β-carbons and *meso*-carbons from the N_4 mean plane being *ca.* 0.01, 0.15, 0.37 and 0.21 Å. The dihedral angles formed between the phenyl rings and the N_4 mean planes are 72.4 [C(21)–C(27)], 73.1 [C(28)–C(34)], 112.3 [C(35)–C(41)] and 106.6° [C(42)–C(48)].

Crystals of $[Y^{III}(TPP)(Cl)(H_2O)(THF)]\cdot[Y^{III}(TPP)(Cl)(H_2O)_2]\cdot 2C_4H_8O\cdot 0.5H_2O$ suitable for X-ray diffraction study were grown by slow evaporation of a saturated solution of compound **2** in tetrahydrofuran. A perspective view is shown in Fig. 2, with selected bond lengths and angles in Table 1. There are two independent Y–TPP moieties in the asymmetric unit. The yttrium(III) ions are seven-co-ordinated, with Y(1) surrounded by four N atoms of the porphyrinate dianion, one terminal Cl atom and two O atoms [O(1w) of the aqua ligand and O(1) of the THF molecule], and Y(2) by four N atoms of the porphyrinate dianion, one terminal Cl atom and two O atoms [O(2w) and O(3w) of the two aqua ligands]. The co-ordination polyhedron about the two Y atoms is best described as a monocapped trigonal prism. The displacement of the Y atoms above the mean plane defined by the four N atoms is 1.099 and 1.209 Å for Y(1) and Y(2), respectively, comparable to that of $[Y^{III}(TMPP)(H_2O)_3]^+$ (1.14 Å).[6] The average Y–N and Y–O bond lengths are 2.31 and 2.45 Å for Y(1) and 2.32 and 2.34 Å for Y(2). There is a large difference between the Y–Cl distance of Y(1) [2.829(5) Å] and Y(2) [2.531(5) Å]. The Y–Cl distance becomes longer as the vertical displacement of the metal from the N_4 mean plane becomes smaller. Electronic as well as steric effects may account for this observation. Intermolecular hydrogen bonds are observed between the aqua ligands and the chloride ligands. However, Cl(1) forms more extensive hydrogen bonding [Cl(1)···O(3w) 3.163, Cl(1)···O(2w) 3.200 Å] than Cl(2) [Cl(2)···O(1w) 3.046 Å]. Thus, Cl(1) will have less electron density available to interact with Y(1) than Cl(2) with Y(2). As a result, Y(1) will interact stronger with the N_4 ring than that of Y(2) resulting in a shorter average Y–N distance and a longer Y–Cl distance for Y(1) than for Y(2). Furthermore, Y(1) is also co-ordinated to a THF molecule, which is sterically more demanding than an aqua molecule. This will push the metal center closer to the N_4 ring.

The dihedral angle formed between the mean plane defined by the four N atoms and the mean plane defined by the Cl atom and the O atoms is 7.9° for the Y(1) moiety and 5.0° for the Y(2). The two porphyrin rings are approximately parallel with a dihedral angle of 3.4°. Fig. 6(b) and (c) give the projections along the Ct–Y of this complex without the aqua and the chloride ligands. Similar to **1**, the porphyrin rings exhibit a saddle like distortion with the average perpendicular distance for the nitrogens, pyrrole α-carbons, pyrrole β-carbons and *meso*-carbons from the N_4 mean plane being *ca.* 0.04, 0.15, 0.37 and 0.19 Å for Y(1) moiety, and 0.04, 0.20, 0.33 and 0.15 Å for Y(2). The dihedral angles formed between the phenyl rings and the N_4 mean planes are 67.4 [C(21)–C(26)], 56.9 [C(27)–C(32)], 98.9 [C(33)–C(38)] and 122.3° [C(39)–C(44)] for Y(1), and 104.6 [C(65)–C(70)], 61.3 [C(71)–C(76)], 68.8 [C(77)–C(82)] and 120.6° [C(83)–C(88)] for Y(2). Four THF molecules and one water [O(4w)] molecule of solvent of recrystallization were located; each has a site occupancy of 0.5. Intermolecular hydrogen bonds are also observed between the aqua ligands and the solvate THF molecules [O(1w)···O(4) 2.743, O(2w)···O(2) 2.749 Å] and the solvate aqua molecule [O(3w)···O(4w) 2.785 Å].

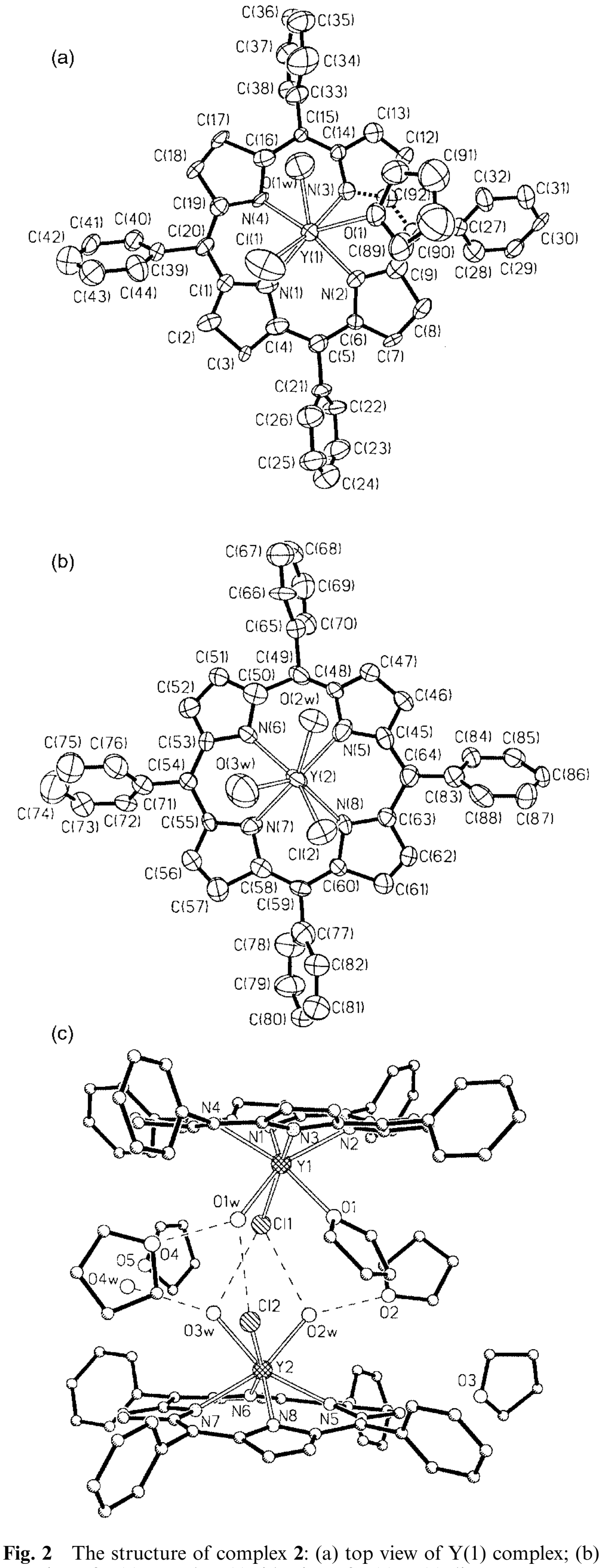


Fig. 2 The structure of complex **2**: (a) top view of Y(1) complex; (b) top view of Y(2) complex; (c) side view of Y(1)–Y(2) dimer.

Preparation of the neutral mono- and di-nuclear ytterbium(III) porphyrinate complexes

When an excess of $Yb^{III}(NPh_2)_3 \cdot x[LiCl(THF)_3]$, generated *in situ* from the reaction of anhydrous $YbCl_3$ with 3 equivalents of $LiNPh_2$ in tetrahydrofuran, was allowed to react with H_2TMPP and H_2TTP for 48 h in a refluxed bis(2-methoxyethyl) ether solution work-up gave air-stable purple crystals of the neutral dinuclear bis(porphyrin) complexes $[\{Yb^{III}(TMPP)(\mu\text{-}OH)\}_2]$ **3** and $[\{Yb^{III}(TTP)\}_2(\mu\text{-}OH)(\mu\text{-}OCH_2CH_2OCH_3)]$ **4** in 80 and 75% yield, respectively. This is in contrast to the reaction of an excess of $Yb^{III}[N(SiMe_3)_2]_3 \cdot x[LiCl(THF)_3]$ with H_2TMPP and H_2TTP which gave the cationic lanthanide complexes $[Yb^{III}(porp)(H_2O)_3]^+$ (porp = TMPP or TTP).[6] The mass spectra of compounds **3** and **4** showed similar fragmentation patterns and abundance, and revealed the dimeric nature of the compounds by exhibiting peaks at *m*/*z* corresponding to $[Yb_2(porp)_2(O)]^+$ (1828 for compound **3** and 1700 for **4**), $[Yb(porp)(OH)]^+$ (923 for **3** and 859 for **4**) and $[Yb(porp)]^+$ (906 for **3** and 842 for **4**) with the most abundant ion being $[Yb(porp)]^+$. The dimeric nature of compounds **3** and **4** was confirmed by X-ray crystallography.

Crystals of $[\{Yb^{III}(TMPP)(\mu\text{-}OH)\}_2] \cdot [\{Yb^{III}(TMPP)(H_2O)(\mu\text{-}OH)\}_2] \cdot 1.5C_6H_5Me$ suitable for X-ray analysis were grown by slow evaporation of a saturated solution of compound **3** in toluene at room temperature. A perspective view of the structure is shown in Fig. 3(a)–(e). Selected bond lengths and bond angles are shown in Table 1. The asymmetric unit consists of two independent halves of a centrosymmetric porphyrin dimer, and 3/2 disordered solvent toluene. In the Yb(1) dimer the seven-co-ordinated Yb(1) atom lies 1.140 Å below the mean plane defined by four N atoms of the porphyrin and 1.602 Å above the plane defined by three O atoms [O(9) and O(9a) of the two hydroxo-bridged ligands and O(10) of the aqua ligand], while the two mean planes form a dihedral angle of 1.5° with a separation of 2.726 Å. The two porphyrin planes are parallel but slide *ca.* 1.96° along the N(2)–Yb(1)–N(4) direction. The dihedral angle formed between the porphyrin rings and Yb–O mean plane [Yb(1)–O(9)–O(9a)–Yb(1a)] is 118.6°. The Yb(1)–N bond distances range from 2.271(6) to 2.357(9) Å, with an average value of 2.311 Å. The metal–hydroxide distance is 2.255(5) Å [Yb(1)–O(9)], the metal–aqua distance 2.389(6) Å [Yb(1)–O(10)], and the interatomic distance of Yb(1) ··· Yb(1a) is 3.724 Å. In the other independent dimer atom Yb(2) is eight-co-ordinated, surrounded by four N atoms of the porphyrinate dianion and four hydroxo-bridged ligands, in which all of them are disordered with site occupancy of 0.5, and has a square antiprismatic co-ordination geometry. The hydroxide groups are disordered into two almost perpendicular sets forming a dihedral angle of 89.0°. Each set has a dihedral angle of 90.4 and 87.2° relative to the porphyrin mean plane, respectively. The Yb(2)–N bond distances range from 2.274(6) to 2.335(9) Å, average 2.303 Å. The geometry of the $Yb_2(OH)_2$ core is distorted octahedral. The Yb(2) atom lies 1.050 Å below the N_4 mean plane defined by four N atoms of the porphyrin and 1.752 Å above the plane defined by four O atoms of the four hydroxo-bridged ligands, while the two mean planes form a dihedral angle of 0.9° with a separation of 2.804 Å. The two porphyrin planes are parallel, the interatomic distance of Yb(2) ··· Yb(2a) is 3.505 Å, and the metal–hydroxide distances are 2.370(8) [Yb(2)–O(11)] and 2.401(9) Å [Yb(2)–O(12)]. The O(11)–Yb(2)–O(12) bond angle is 56.5(4)°. The two independent porphyrin dimers in the unit cell form a dihedral angle of 143.9°. In these two dimers the two porphyrin macrocycles are almost perfectly eclipsed with the torsion angle of the Yb(1) dimer being 3.6° and that of the Yb(2) dimer nearly zero. Such an eclipsed geometry feature is also observed in $[\{Zr(TPP)\}_2(\mu\text{-}\eta^2\text{-}Q_2)_2]$ (Q = S or Se).[11] Fig. 7(a) and (b) give the projections along the Ct–Y of this complex without the aqua and hydroxo-bridging ligands. The porphyrin rings also exhibit a saddle like distortion with the average perpendicular distance for the nitrogens, pyrrole α-carbons, pyrrole β-carbons and *meso*-carbons from the N_4 mean plane being *ca.* 0.03, 0.13, 0.28 and 0.15 Å for Yb(1) dimer, and 0.02, 0.11, 0.25 and 0.11 Å for Yb(2). The dihedral angles formed between the phenyl rings and the N_4 mean planes are 70.5 [C(21)–C(26)], 65.2 [C(28)–C(33)], 59.5 [C(35)–C(40)] and 115.2° [C(42)–C(47)] for Yb(1), and 100.7

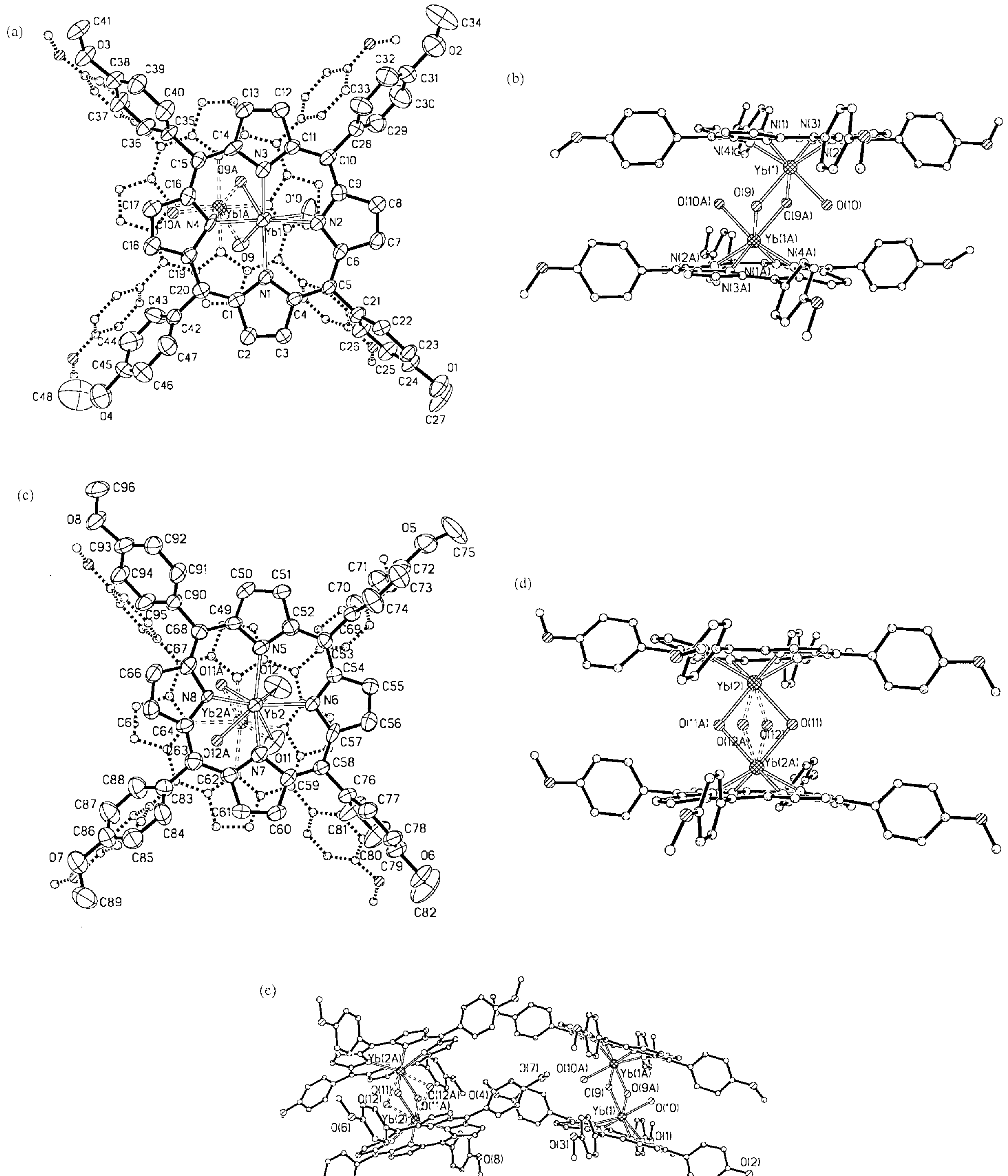


Fig. 3 The structure of compound **3**, in which there exists two independent centrosymmetric ytterbium dimers, for dimer Yb(1)–Yb(1a): (a) top view, (b) side view; for dimer Yb(2)–Yb(2a): (c) top view, (d) side view; (e) the conformation of the arrangement of the two dimers.

[C(69)–C(74)], 96.0 [C(76)–C(81)], 124.8 [C(83)–C(88)] and 61.6° [C(90)–C(95)] for Yb(2).

Crystals of [{Yb^{III}(TTP)}$_2$(μ-OH)(μ-OCH$_2$CH$_2$OCH$_3$)]·0.25(C$_2$H$_5$)$_2$O suitable for X-ray diffraction study were grown by slow evaporation of a saturated solution of complex **4** in a tetrahydrofuran–diethyl ether mixture at room temperature. A perspective view is shown in Fig. 4. Selected bond lengths and bond angles are in Table 1. The structure reveals that the seven-co-ordinated Yb(1) atom and the six-co-ordinated Yb(2) atom are connected *via* a hydroxo-bridge and a (2-methoxy)-ethoxo-bridge. The hydroxide group forms a symmetrical bridge between the two Yb atoms with identical Yb–O distances being 2.182(5) [Yb(1)–O(3)] and 2.195(5) Å [Yb(2)–O(3)], whereas the (2-methoxy)ethoxy group forms an unsymmetrical bridge with Yb–O distances being 2.330(5) [Yb(1)–O(1)] and 2.189(5) Å [Yb(2)–O(1)]. Furthermore, this group also acts as a chelating ligand with the O atom of the methoxy group co-ordinated to the Yb(1) atom [Yb(1)–O(2) 2.472(6)] forming a five-membered ring. It is probably derived from cleavage of the bis(2-methoxy-ethyl) ether solvent molecule. The Yb–N bond distances range from 2.327(6) to 2.344(6) Å average 2.336 Å for Yb(1), and 2.288(6) to 2.324(6) Å average 2.304 Å for Yb(2). Atom Yb(1) is

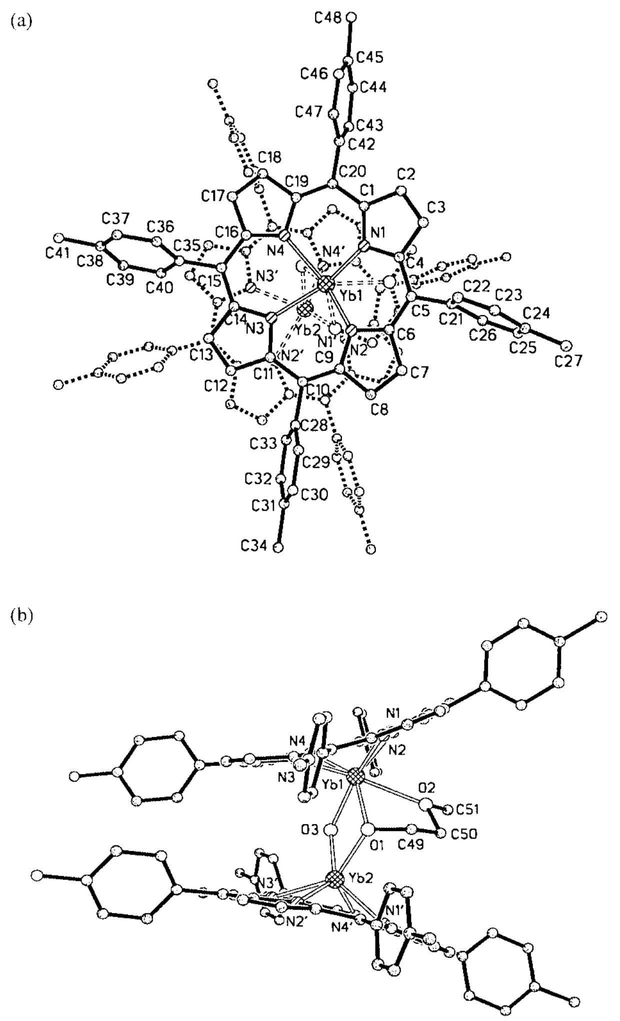


Fig. 4 The structure of compound **4**: (a) top view; (b) side view.

1.128 Å above the N_4 mean plane of the porphyrin ring, while Yb(2) is 1.057 Å from the corresponding porphyrin. The two porphyrins are not parallel, form a dihedral angle of 30.5°, and arranged approximately in a staggered conformation with the torsion angles ranging from 32.1 to 37°. Fig. 8(a) and (b) gives the projections along the Ct–Y of this complex without the O atoms of the bridging hydroxide and (2-methoxy)ethoxo groups. The porphyrin rings also exhibit a saddle like distortion with the average perpendicular distance for the nitrogens, pyrrole α-carbons, pyrrole β-carbons and *meso*-carbons from the N_4 mean plane being *ca.* 0.02, 0.14, 0.30 and 0.20 Å for Yb(1), and 0.02, 0.21, 0.13 and 0.29 Å for Yb(2). The dihedral angles formed between the phenyl rings and the N_4 mean planes are 77.4 [C(21)–C(26)], 116.6 [C(28)–C(33)], 63.1 [C(35)–C(40)] and 91.4° [C(42)–C(47)] for Yb(1), and 84.7 [C(21′)–C(26′)], 114.1 [C(28′)–C(33′)], 67.7 [C(35′)–C(40′)] and 82.7° [C(42′)–C(47′)] for Yb(2). There is a solvent diethyl ether molecule in the asymmetric unit, which is highly disordered with a site occupancy of 0.25.

However, interaction of an excess of $Yb^{III}(NPh_2)_3\cdot x[LiCl(THF)_3]$ with the porphyrin free base H_2TPP in refluxing bis(2-methoxyethyl) ether solution for 48 h gave the neutral monoporphyrinate complex $[Yb^{III}(TPP)(Cl)(H_2O)(THF)]$ **5** in moderate yield (45%) as violet crystals. Crystals of $[Yb^{III}(TPP)(Cl)(H_2O)(THF)]\cdot 1.5C_4H_8O\cdot 0.5CH_3OH$ suitable for X-ray analysis were grown by slow evaporation of a saturated solution of compound **5** in tetrahydrofuran at room temperature. A perspective view is shown in Fig. 5. Selected bond lengths and angles are in Table 1. The structure is similar to that of compound **2**. The Yb atom is seven-co-ordinated, surrounded by four N atoms of the TPP dianion, one terminal Cl atom and two O atoms [O(1w) of the aqua ligand and O(1) of the THF molecule] arranged in an antipyramidal conformation. The Yb atom lies 1.290 Å above the mean N_4 plane with an average Yb–N distance of 2.334 Å. Fig. 9 gives the projections along the Ct–Y of this complex without the aqua, THF and chloride ligands. The porphyrin ring displays a saddle like distortion with the average displacement of the nitrogens, pyrrole α-, pyrrole β- and *meso*-carbons from the N_4 mean plane being *ca.* 0.02, 0.12, 0.32 and 0.16 Å, respectively. The dihedral angles formed between the phenyl rings and the N_4 mean plane are 99.4 [C(21)–C(26)], 55.6 [C(27)–C(32)], 66.8 [C(33)–C(38)] and 122.1° [C(39)–C(44)]. There are two solvate THF and one

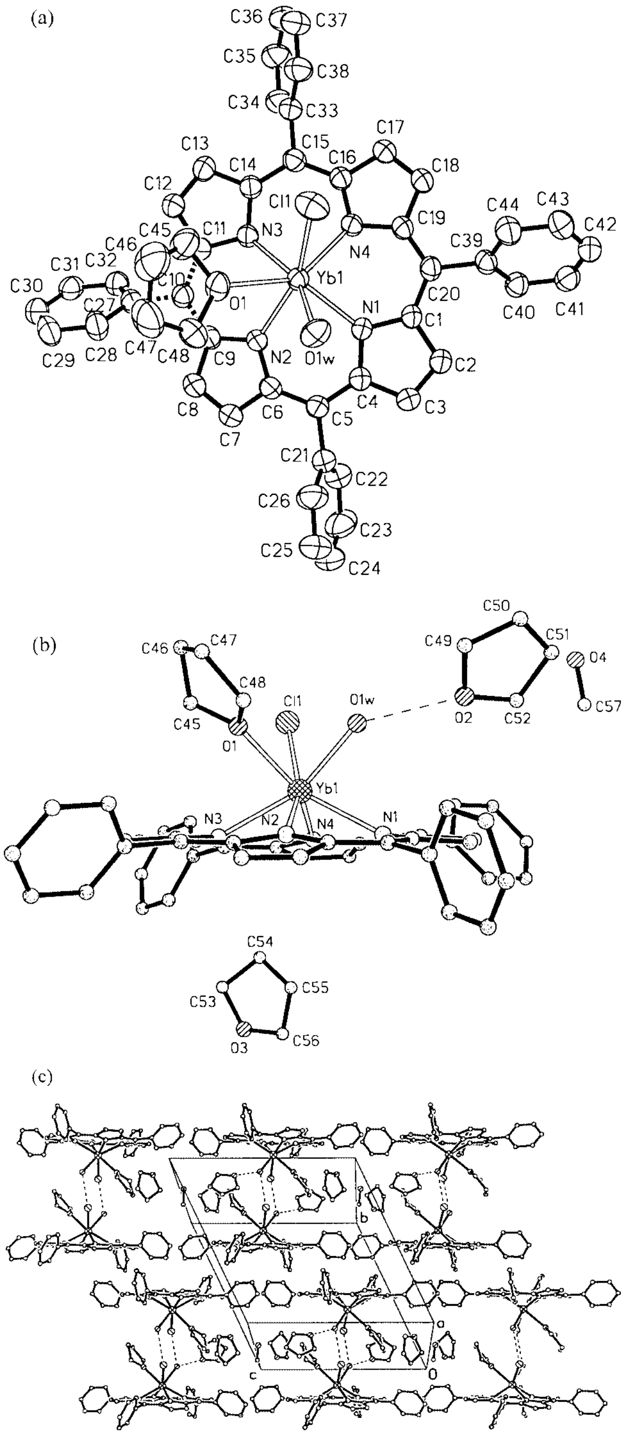


Fig. 5 The structure of compound **5**: (a) top view; (b) side view; (c) crystal packing viewed parallel to plane (100) showing the arrangement of hydrogen-bonded dimers into a two dimensional tape.

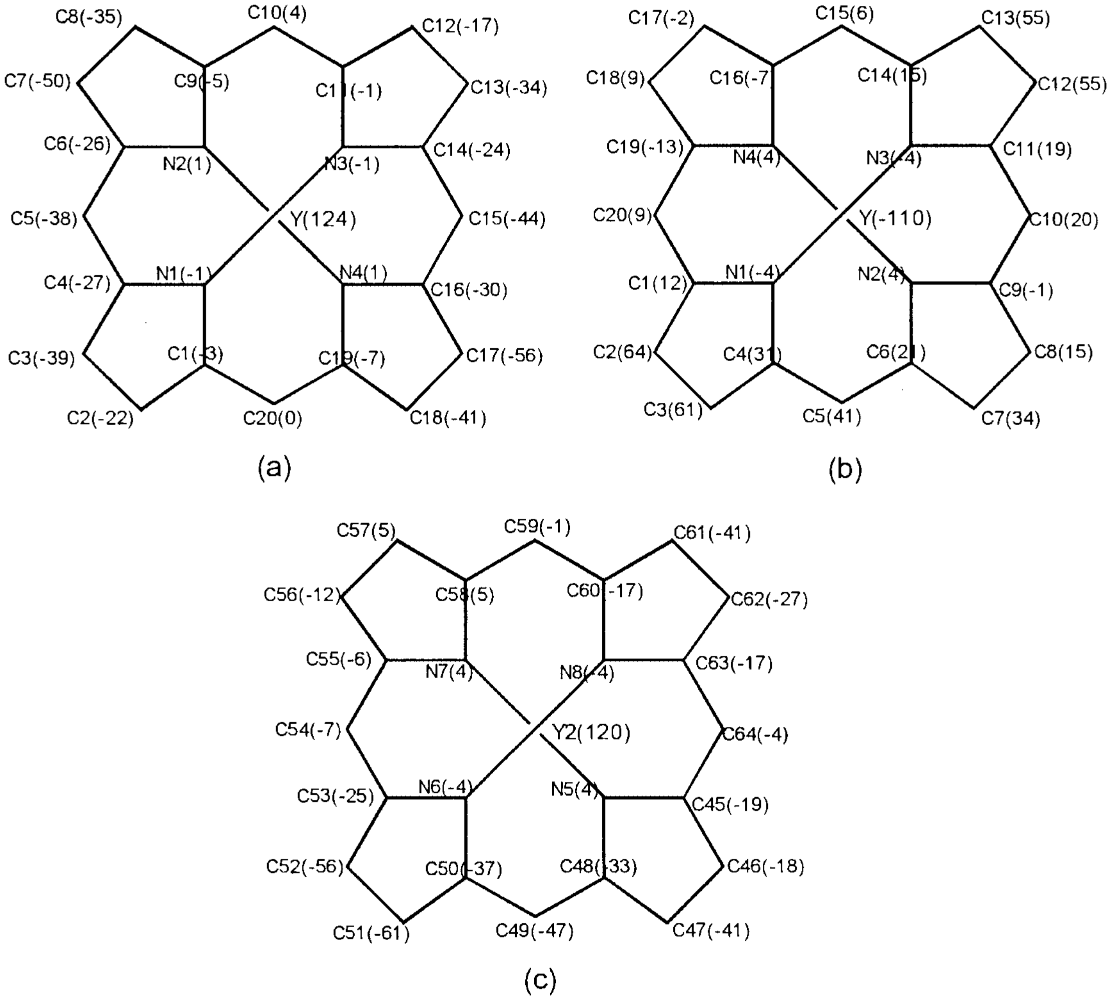


Fig. 6 Projections (a), (b) and (c) along the Ct–Y axes (Ct is the centroid of the N_4 mean plane) of compounds **1** [without the bis(2-methoxyethyl) ether and chloride ligands] and **2** (without the aqua ligands). The deviations of individual atoms from the N_4 mean plane are given in parentheses in units of 0.01 Å.

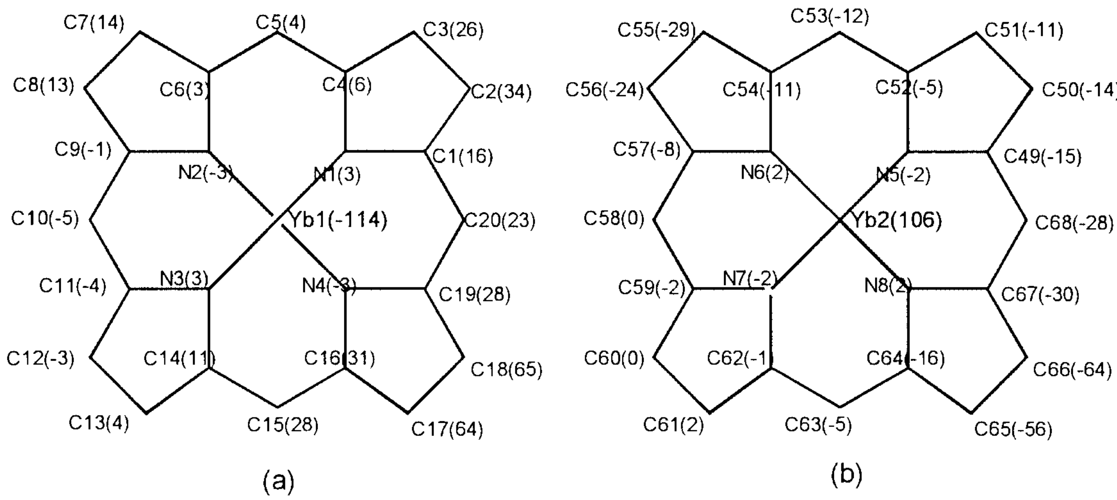


Fig. 7 Projections (a) and (b) along the Ct–Yb axes of compound **3** without the hydroxo bridging and aqua ligands. The deviations of atoms from the N_4 mean plane are given in parentheses in units of 0.01 Å.

solvate methanol molecules in the asymmetric unit. One of the solvate THF molecules [O(3)–C(56)] and the solvate methanol molecule are highly disordered and assigned with a site occupancy of 0.5. An intermolecular hydrogen bond is observed between the aqua ligand and a solvate THF molecule [O(1w) · · · O(2) 2.771 Å]. Fig. 5(c) gives the packing diagram of compound **5**. The mutual recognition of two adjacent Yb–TPP complexes, through a pair of centrosymmetrical O–H · · · Cl hydrogen bonds between the aqua and Cl ligands of different Yb atoms, generates a $(YbTPP)_2$ dimer (O · · · Cl being 3.085 Å), in which the two porphyrin rings are parallel and separated by 9.09 Å. The dimers are arranged side by side along the [100]

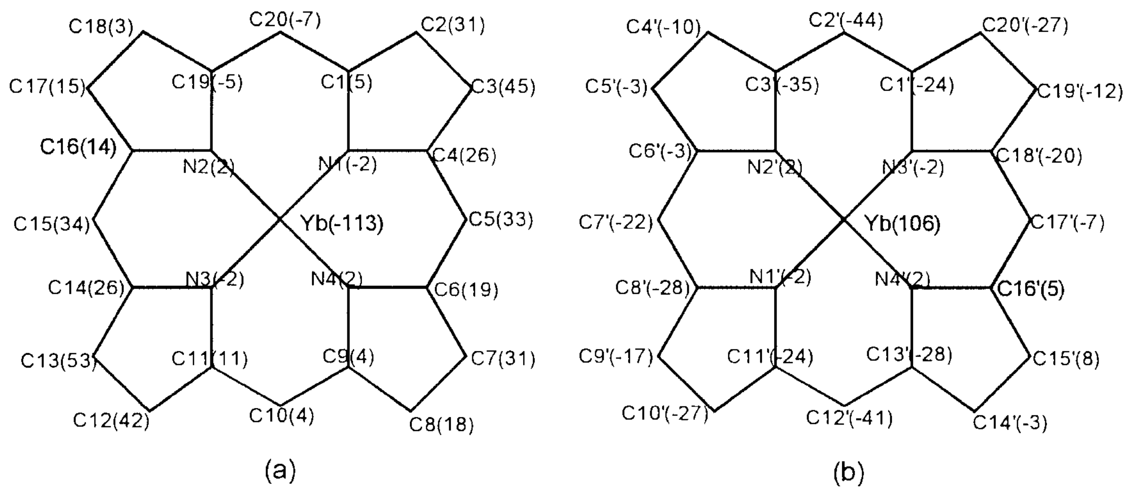


Fig. 8 Projections (a) and (b) along the Ct–Yb axes of compound **4** without the hydroxo-bridge and (2-methoxy)ethoxo-bridge ligands. The deviations of atoms from the N_4 mean plane are given in parentheses in units of 0.01 Å.

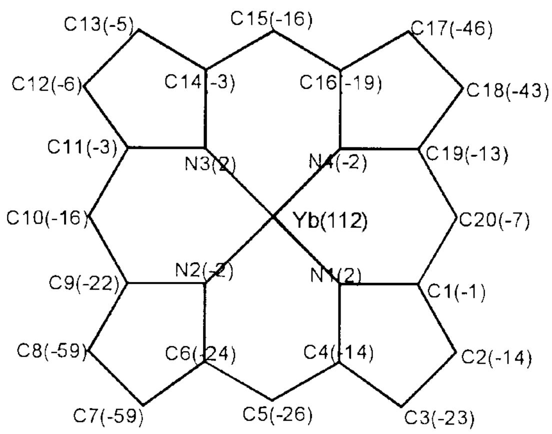
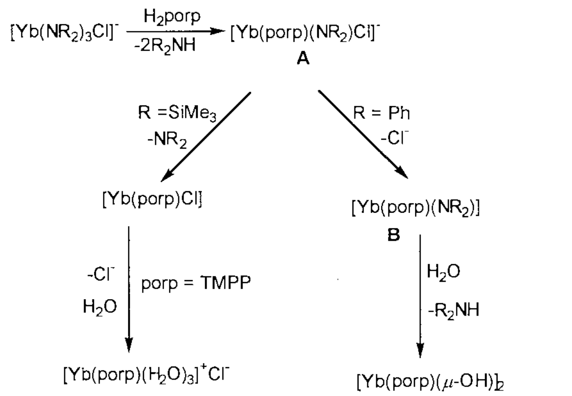


Fig. 9 The projection along the Ct–Yb axes of compound **5** without the aqua, THF and chloride ligands. The deviations of atoms from the N_4 mean plane are given in parentheses in units of 0.01 Å.



Scheme 2 Proposed mechanism for the formation of ytterbium(III) porphyrin complexes.

direction into a one-dimensional array, which is then extended along plane (100) to a two-dimensional tape; adjacent arrays are translated $\frac{1}{2}a$ along the [100] direction. The tapes are further packed along plane (010) to give a three-dimensional structure.

The propensity for the formation of lanthanide porphyrinate complexes is highly dependent on the nature of the porphyrin and the lanthanide precursor. The mechanism for their formation is not clear. However, it is very likely that the intermediate **A** $[Ln(porp)(NR_2)Cl]^-$ which arose from protonolysis of the lanthanide amide complex, $[Ln(NR_2)_3Cl]^-$ (generated *in situ* from the reaction of $LnCl_3$ with $LiNR_2$)[12] with porphyrin free base H_2porp is involved (Scheme 2). Then depending on the nature of the amide, lanthanide(III) metal ions and porphyrinate dianions, **A** could either lose a chloride group to give intermediate **B** $[Ln(porp)(NR_2)]$ or an amide group to give the neutral monoporphyrinate complex [Ln(porp)Cl]. A possible mechanism for the formation of the ytterbium(III) porphyrin complexes is shown in Scheme 2. With (diphenyl)amide, **A** lost the chloride group to give intermediate **B** $[Yb^{III}(porp)(NR_2)]$ which hydrolyzed to give the neutral dinuclear bis(porphyrin) complex. With bis(trimethysilyl)amide, **A** lost the amide group to give the neutral monoporphyrinate complex $[Yb^{III}(porp)Cl]$. With an electron donating methoxy or methyl group at the *para* position of the *meso*-aryls of the porphyrin, $[Yb^{III}(porp)Cl]$ underwent further dissociation of the chloride group to give the cationic lanthanide monoporphyrinate complex $[Yb^{III}(porp)(H_2O)_3]^+$. We are in the process of examining factors that affect and control the formation of lanthanide(III) porphyrin complexes.

In conclusion, we have synthesized and structurally characterized several neutral mono- and di-nuclear porphyrinate complexes. Notably complexes **3** and **4** are the first structurally characterized neutral hydroxo-bridged dinuclear lanthanide(III) bis(porphyrin) complexes in which the two porphyrin ligands are unsupported.

Experimental

Procedures

All reactions were carried out in an atmosphere of dry nitrogen or *in vacuo*. Solvents were dried by standard procedures, distilled and deaerated prior to use. All chemicals used were of reagent grade, obtained from the Aldrich Chemical Company and, where appropriate, degassed before use. 5,10,15,20-Tetrakis(*p*-methoxyphenyl)porphyrin (H_2TMPP), tetrakis(*p*-tolyl)porphyrin (H_2TTP) and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (H_2TPP) were prepared according to literature methods.[13] The compound $Ln(NR_2)_3 \cdot x[LiCl(THF)_3]$ ($R = Ph$ or $SiMe_3$) was generated *in situ* according to the literature procedure.[12] Microanalyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The IR spectra (KBr pellets) were recorded on a Nicolet Nagna-IR 550 spectrometer, electronic absorption spectra in the UV–VIS region on a Hewlett-Packard 8453 UV Visible spectrophotometer and NMR spectra on a JEOL EX270 spectrometer. Chemical shifts of ^1H NMR spectra

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1**–**5**

Compound **1**							
Y(1)–Cl(1)	2.6702(16)	Y(1)–O(1)	2.690(5)	Y(1)–N(1)	2.368(4)	Y(1)–N(2)	2.411(5)
Y(1)–O(2)	2.478(4)	Y(1)–O(3)	2.539(4)	Y(1)–N(3)	2.414(4)	Y(1)–N(4)	2.380(4)
Cl(1)–Y(1)–O(1)	72.11(10)	Cl(1)–Y(1)–O(2)	93.52(11)	O(2)–Y(1)–O(3)	65.02(13)	N(1)–Y(1)–N(2)	74.96(15)
Cl(1)–Y(1)–O(3)	74.77(10)	Cl(1)–Y(1)–N(1)	89.26(11)	N(1)–Y(1)–N(3)	116.83(14)	N(1)–Y(1)–N(4)	74.95(15)
Cl(1)–Y(1)–N(2)	146.18(11)	Cl(1)–Y(1)–N(3)	140.09(12)	N(2)–Y(1)–N(3)	73.06(15)	N(2)–Y(1)–N(4)	118.61(14)
Cl(1)–Y(1)–N(4)	84.40(10)	O(1)–Y(1)–O(2)	64.34(15)	N(3)–Y(1)–N(4)	75.01(14)		
Compound **2**							
Y(1)–Cl(1)	2.829(5)	Y(2)–Cl(2)	2.531(5)	Y(1)–N(4)	2.326(7)	Y(2)–N(8)	2.431(6)
Y(1)–N(1)	2.299(5)	Y(2)–N(5)	2.407(8)	Y(1)–O(1)	2.483(7)	Y(2)–O(2w)	2.344(5)
Y(1)–N(2)	2.342(5)	Y(2)–N(6)	2.452(6)	Y(1)–O(1w)	2.419(5)	Y(2)–O(3w)	2.334(9)
Y(1)–N(3)	2.286(6)	Y(2)–N(7)	2.381(5)				
Cl(1)–Y(1)–O(1)	93.0(2)	Cl(2)–Y(2)–O(2w)	86.0(2)	Cl(1)–Y(1)–N(4)	105.7(2)	Cl(2)–Y(2)–N(8)	78.5(2)
Cl(1)–Y(1)–O(1w)	78.7(2)	Cl(2)–Y(2)–O(3w)	66.4(2)	N(1)–Y(1)–N(2)	77.7(2)	N(5)–Y(2)–N(6)	76.8(2)
O(1w)–Y(1)–O(1)	69.7(2)	O(2w)–Y(2)–O(3w)	79.1(2)	N(1)–Y(1)–N(3)	124.8(2)	N(5)–Y(2)–N(7)	121.5(2)
Cl(1)–Y(1)–N(1)	72.3(2)	Cl(2)–Y(2)–N(5)	124.3(2)	N(1)–Y(1)–N(4)	75.8(2)	N(5)–Y(2)–N(8)	76.1(2)
Cl(1)–Y(1)–N(2)	113.9(2)	Cl(2)–Y(2)–N(6)	157.2(2)	N(2)–Y(1)–N(4)	121.7(2)	N(6)–Y(2)–N(8)	118.5(2)
Cl(1)–Y(1)–N(3)	162.1(1)	Cl(2)–Y(2)–N(7)	98.2(2)	N(3)–Y(1)–N(4)	76.4(2)	N(7)–Y(2)–N(8)	75.5(2)
Compound **3**							
Yb(1)–Yb(1A)	3.724(1)	Yb(2)···Yb(2A)	3.505(1)	Yb(1)–N(1)	2.357(9)	Yb(2)–O(12A)	2.430(9)
Yb(1)–O(9)	2.255(5)	Yb(2)–O(11)	2.370(8)	Yb(1)–N(2)	2.273(6)	Yb(2)–N(5)	2.301(8)
Yb(1)–O(9A)	2.247(7)	Yb(2)–O(11A)	2.318(8)	Yb(1)–N(3)	2.343(7)	Yb(2)–N(6)	2.302(6)
Yb(1)–O(10)	2.389(6)	Yb(2)–O(12)	2.401(9)	Yb(1)–N(4)	2.271(6)	Yb(2)–N(7)	2.335(9)
						Yb(2)–N(8)	2.274(6)
O(9)–Yb(1)–Yb(9A)	68.3(3)	O(11)–Yb(2)–Yb(11A)	83.2(3)	N(1)–Yb(1)–N(2)	74.8(3)	N(5)–Yb(2)–N(6)	78.8(2)
O(9)–Yb(1)–O(10)	80.3(2)	O(11)–Yb(2)–O(12)	56.5(4)	N(1)–Yb(1)–N(3)	120.2(3)	N(5)–Yb(2)–N(7)	124.6(2)
O(9)–Yb(1)–N(1)	84.3(2)	O(11)–Yb(2)–N(5)	140.5(3)	N(1)–Yb(1)–N(4)	78.7(3)	N(5)–Yb(2)–N(8)	76.3(3)
O(9)–Yb(1)–N(2)	136.8(2)	O(11)–Yb(2)–N(6)	84.8(2)	N(2)–Yb(1)–N(3)	75.0(2)	N(6)–Yb(2)–N(7)	77.3(3)
O(9)–Yb(1)–N(3)	146.7(2)	O(11)–Yb(2)–N(7)	85.4(3)	N(2)–Yb(1)–N(4)	122.6(2)	N(6)–Yb(2)–N(8)	126.6(2)
O(9)–Yb(1)–N(4)	88.5(2)	O(11)–Yb(2)–N(8)	139.8(3)	N(3)–Yb(1)–N(4)	76.1(2)	N(7)–Yb(2)–N(8)	79.3(2)
Compound **4**							
Yb(1)···Yb(2)	3.6260(5)			Yb(1)–N(1)	2.340(6)	Yb(2)–N(1′)	2.324(6)
Yb(1)–O(1)	2.330(5)	Yb(2)–O(1)	2.189(5)	Yb(1)–N(2)	2.334(5)	Yb(2)–N(2′)	2.300(6)
Yb(1)–O(2)	2.472(6)			Yb(1)–N(3)	2.327(6)	Yb(2)–N(3′)	2.303(6)
Yb(1)–O(3)	2.182(5)	Yb(2)–O(3)	2.195(5)	Yb(1)–N(4)	2.344(6)	Yb(2)–N(4′)	2.288(6)
O(1)–Yb(1)–O(2)	66.56(19)			N(1)–Yb(1)–N(2)	77.8(2)	N(1′)–Yb(2)–N(2′)	78.3(2)
O(2)–Yb(1)–O(3)	89.4(2)			N(1)–Yb(1)–N(3)	123.0(2)	N(1′)–Yb(2)–N(3′)	124.3(2)
O(1)–Yb(1)–O(3)	69.20(18)	O(1)–Yb(2)–O(3)	71.61(18)	N(1)–Yb(1)–N(4)	74.8(2)	N(1′)–Yb(2)–N(4′)	77.0(2)
O(1)–Yb(1)–N(1)	138.3(2)	O(1)–Yb(2)–N(1′)	90.12(19)	N(2)–Yb(1)–N(3)	76.7(2)	N(2′)–Yb(2)–N(3′)	76.7(2)
O(1)–Yb(1)–N(2)	85.72(19)	O(1)–Yb(1)–N(2′)	98.93(19)	N(2)–Yb(1)–N(4)	121.5(2)	N(2′)–Yb(2)–N(4′)	126.5(2)
O(1)–Yb(1)–N(3)	88.9(2)	O(1)–Yb(1)–N(3′)	142.5(2)	N(3)–Yb(1)–N(4)	76.8(2)	N(3′)–Yb(2)–N(4′)	79.4(2)
O(1)–Yb(1)–N(4)	144.09(19)	O(1)–Yb(1)–N(4′)	127.6(2)				
Compound **5**							
Yb(1)–Cl(1)	2.6388(18)	Yb(1)–O(1)	2.428(4)	Yb(1)–N(2)	2.344(4)	Yb(1)–N(3)	2.339(4)
Yb(1)–O(1w)	2.331(4)	Yb(1)–N(1)	2.320(4)	Yb(1)–N(4)	2.333(4)		
Cl(1)–Yb(1)–O(1)	79.86(12)	Cl(1)–Yb(1)–O(1w)	81.89(13)	O(1)–Yb(1)–O(1w)	74.46(16)	N(1)–Yb(1)–N(2)	77.52(16)
Cl(1)–Yb(1)–N(1)	121.64(12)	Cl(1)–Yb(1)–N(2)	157.57(13)	N(1)–Yb(1)–N(3)	123.48(16)	N(1)–Yb(1)–N(4)	76.09(15)
Cl(1)–Yb(1)–N(3)	98.67(13)	Cl(1)–Yb(1)–N(4)	76.94(12)	N(2)–Yb(1)–N(3)	76.52(15)	N(2)–Yb(1)–N(4)	122.00(16)
				N(3)–Yb(1)–N(4)	76.79(15)		

were referenced to internal deuteriated solvents and then recalculated to TMS (δ 0.00). Low-resolution mass spectra were obtained on a Finnigan MAT SSQ-710 or MAT 95 spectrometer in FAB (positive ion) mode.

Preparations

Compounds **1**–**5** were prepared by similar procedures. A typical procedure is given for **1**.

[Y(TTP)(Cl){($CH_3OCH_2CH_2)_2$O}] 1. A solution of *n*-BuLi (1.6 M, 3.0 cm^3, 4.8 mmol) in hexane was added dropwise over a period of 10 min to a solution of $(Me_3Si)_2NH$ (0.78 g, 4.8 mmol) in tetrahydrofuran (20 cm^3), and allowed to stir at room temperature for 2 h, then transferred to a suspension of YCl_3 (0.31 g, 1.6 mmol) in tetrahydrofuran (20 cm^3). After stirring at room temperature for 24 h the mixture was centrifuged and filtered. The solvent of the filtrate was removed *in vacuo*, and the residue redissolved in bis(2-methoxyethyl) ether (10 cm^3) and filtered. The filtrate was then added to a solution of H_2TTP (0.20 g, 0.3 mmol) in bis(2-methoxyethyl) ether (20 cm^3) and refluxed. The progress of the reaction was monitored by UV–VIS spectroscopy. After refluxing for 36 h the solution was cooled to room temperature and filtered, and the residue extracted with dichloromethane (3 × 10 cm^3). The solvent of the combined filtrate was removed *in vacuo* to give a purple residue. This was washed with diethyl ether (2 × 10 cm^3), extracted with toluene (3 × 10 cm^3) and filtered. The filtrate was concentrated *in vacuo* to *ca.* 15 cm^3 and then allowed to evaporate slowly in air to give purple crystals, which were filtered off and dried *in vacuo*, yield 0.22 g (74%), mp >300 °C [Found: C, 66.4; H, 5.2; N, 5.7. Calc for $C_{54}H_{50}ClN_4O_3Y\cdot 0.5CH_2Cl_2$: C, 66.4; H, 5.2; N, 5.7%]. IR (cm^{-1}, in KBr): 3348w, 3019w, 2920w, 1520w, 1480w, 1450w, 1328m, 1260w, 1182w, 1107w, 1036w, 991s, 868w, 799vs, 726m, 524w and 419w. ^1H NMR [$(CD_3)_2CO$, 25 °C]: δ 8.78 (8 H, s), 8.10 (4 H, br s), 7.92 (4 H, br s), 7.58 (8 H, br m), 2.82 (6 H, s), 2.80 (4 H, br s) and 2.68 (4 H, br s). UV–VIS data in $CHCl_3$, 20 °C, λ/nm [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 423(6.12), 552(4.75) and 593(4.29). Positive-ion FAB mass spectrum: *m*/*z* 757, $[Y(TPP)]^+$ for ^{89}Y.

[Y(TTP)(Cl)(H$_2$O)(THF)] 2. *n*-Butyllithium (1.6 M, 3.6 cm^3, 5.76 mmol), $(Me_3Si)_2NH$ (0.93 g, 5.77 mmol), YCl_3 (0.37 g, 1.89 mmol) and H_2TPP (0.20 g, 0.33 mmol) were used. After refluxing for 36 h the solution was cooled to room temperature and filtered, and the residue extracted with tetrahydrofuran (3 × 10 cm^3). The solvent of the combined filtrate was removed *in vacuo* to give a purple residue. This was washed with diethyl ether (2 × 10 cm^3), extracted with dichloromethane (3 × 10 cm^3) and filtered. The filtrate was concentrated *in vacuo* to *ca.* 15 cm^3 and then allowed to evaporate slowly in air to give purple crystals, which were filtered off and dried *in vacuo*, yield 0.26 g (81%), mp >300 °C [Found: C, 66.9; H, 5.4; N, 5.7. Calc. for $C_{100}H_{86}Cl_2N_8O_6Y_2\cdot 2C_4H_8O\cdot 0.75CH_2Cl_2$: C, 66.9; H, 5.3; N, 5.7%]. IR (cm^{-1}, in KBr): 3060w, 2968w, 2360s, 1812w, 1698s, 1595m, 1541w, 1476m, 1439m, 1329m, 1260m, 1177m, 1006s, 988vs, 966w, 917w, 880w, 799vs, 753s, 723s, 710vs, 695m, 582w, 526w and 420w. ^1H NMR ($CDCl_3$, 25 °C): δ 8.51 (8 H, s), 7.72 (20 H, m), 3.56 (14 H, m), 1.77 (14 H, m) and 0.76 (2 H, br s). UV–VIS data in $CHCl_3$, 20 °C, λ/nm [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 422(5.75), 515(4.02) and 551(4.38). Positive-ion FAB mass spectrum: *m*/*z* 736, Y(TPP)Cl; 710, $[Y(TPP)]^+$ for ^{89}Y and ^{35}Cl.

[{Yb(TMPP)(μ-OH)}$_2$] 3. *n*-Butyllithium (1.6 M, 3.0 cm^3, 4.8 mmol), Ph_2NH (0.81 g, 4.8 mmol), $YbCl_3$ (0.45 g, 1.6 mmol) and H_2TMPP (0.22 g, 0.3 mmol) were used. After refluxing for 48 h the solution was cooled to room temperature and filtered, and the residue extracted with dichloromethane (3 × 10 cm^3). The solvent of the combined filtrate was removed *in vacuo* to give a purple residue. This was washed with diethyl ether (2 × 10 cm^3), extracted with toluene (3 × 10 cm^3) and filtered. The filtrate was concentrated *in vacuo* to *ca.* 15 cm^3 and then allowed to evaporate slowly in air to give purple crystals, which were filtered off and dried *in vacuo*, yield 0.50 g (80%), mp >300 °C [Found: C, 60.7; H, 4.3; N, 5.6. Calc. for $C_{96}H_{74}N_8O_{10}Yb_2\cdot 3H_2O$: C, 60.7; H, 4.2; N, 5.9%]. IR (cm^{-1} in KBr): 2841w, 2360w, 1606m, 1518s, 1506s, 1480w, 1462w, 1438w, 1328m, 1289m, 1248vs, 1200w, 1174s, 1035m, 990s, 846w, 801m, 730w, 599w and 538w. UV–VIS data in $CHCl_3$, 20 °C, λ/nm [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 422(5.41), 555(4.41) and 596(4.02). Positive-ion FAB mass spectrum: *m*/*z* 1828, $[Yb_2(TMPP)_2(O)]^+$; 923, $[Yb(TMPP)(OH)]^+$; 906, $[Yb(TMPP)]^+$ for ^{174}Yb.

[{Yb(TPP)}$_2$(μ-OH)(μ-OCH$_2$CH$_2$OCH$_3$)] 4. *n*-Butyllithium (1.6 M, 3.0 cm^3, 4.8 mmol), Ph_2NH (0.81 g, 4.8 mmol), $YbCl_3$ (0.45 g, 1.6 mmol) and H_2TTP (0.22 g, 0.3 mmol) were used. After refluxing for 48 h the solution was cooled to room temperature and filtered, and the residue extracted with dichloromethane (3 × 10 cm^3). The solvent of the combined filtrate was removed *in vacuo* to give a purple residue. This was washed with diethyl ether (2 × 10 cm^3), extracted with toluene (3 × 10 cm^3) and filtered. The filtrate was concentrated *in vacuo* to *ca.* 15 cm^3 and then allowed to evaporate slowly in air to give purple crystals, which were filtered off and dried *in vacuo*, yield 75%, mp >300 °C (Found: C, 66.6; H, 4.7; N, 5.9. Calc. for $C_{99}H_{80}N_8O_3Yb_2\cdot 0.25C_4H_{10}O$: C, 66.9; H, 4.6; N, 6.2%). IR (cm^{-1}, in KBr): 3026w, 2918m, 2360m, 1653s, 1592s, 1495m, 1384m, 1417m, 1201w, 1182w, 1107w, 1068w, 991vs, 797vs, 748m, 725m, 692m, 578w, 524w, 509w and 419w. UV–VIS data in $CHCl_3$, 20 °C, λ/nm [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 419(5.42), 552(4.09) and 591(3.35). Positive-ion FAB mass spectrum: *m*/*z* 1700, $[Yb_2(TTP)_2(O)]^+$; 859, $[Yb(TTP)(OH)]^+$; 842, $[Yb(TTP)]^+$ for ^{174}Yb.

[Yb(TPP)(Cl)(H$_2$O)(THF)] 5. *n*-Butyllithium (1.6 M, 2.3 cm^3, 3.7 mmol), Ph_2NH (0.62 g, 3.7 mmol), $YbCl_3$ (0.34 g, 1.2 mmol) and H_2TPP (0.12 g, 0.2 mmol) were used. After refluxing for 48 h the solution was cooled to room temperature and filtered, and the residue extracted with dichloromethane (3 × 10 cm^3). The solvent of the combined filtrate was removed *in vacuo* to give a purple residue. This was redissolved in the minimum volume of chloroform and chromatographed on a dry silica gel column (2 × 12 cm^3). Two purple bands, one eluted with chloroform and the other with methanol, were obtained. The solvent of the chloroform band was identified as the free porphyrin by UV–VIS spectroscopy. The solvent of the methanol band was removed *in vacuo* to give a purple residue. This was extracted with tetrahydrofuran (2 × 10 cm^3), filtered, concentrated *in vacuo* to *ca.* 10 cm^3 and then allowed to evaporate slowly in air to give purple crystals, which were filtered off and dried *in vacuo*, yield 0.1 g (45%), mp >300 °C [Found: C, 60.1; H, 4.3; N, 5.4. Calc. for $C_{48}H_{38}ClN_4O_2Yb\cdot 0.5(CH_3OH\cdot C_4H_8O\cdot CHCl_3)$: C, 59.9; H, 4.4; N, 5.5%]. IR (cm^{-1}, in KBr): 3400vs, 1596s, 1549m, 1480w, 1440m, 1261s, 1201w, 1177w, 1069s, 1019s, 989vs, 800vs, 753m, 701s, 659w, 578w and 426w. UV–VIS data in $CHCl_3$, 20 °C, λ/nm [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 421(5.85), 551(4.59) and 588(4.31). Positive-ion FAB mass spectrum: *m*/*z* 786, $[Yb(TPP)]^+$ for ^{174}Yb.

X-Ray crystallography

The crystals were all wrapped in epoxy glue to prevent them from losing solvent, and attached on a thin glass stem. They were stable during the data collection. The intensity data of compounds **1**–**5** were collected to 0.82 Å at 294 K on an MSC/Rigaku RAXIS IIc imaging-plate diffractometer using Mo-Kα radiation (λ = 0.71073 Å) from a Rigaku RU-200 rotating-anode generator operating at 50 kV and 90 mA.[14] A self-consistent semiempirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR program.[15] Structure refinements of compounds **1**, **4** and **5** were performed against F^2 with the SHELX 97 package,[16] while **2** and **3** were refined against *F* with SHELXTL PC.[17] Pertinent crystallographic data and other experimental detailed are summarized in Table 2. For compound **2** the refinement against *F* is based on observed reflections [$F > 6\sigma(F)$], and the structure was divided into two blocks for refinement, the number of parameters and data-to-parameter ratio of each block being 516 (6.8 : 1) and 564 (6.3 : 1), respectively. The *meso*-phenyl groups [C(21) to C(44) and C(65) to C(88)] were refined with a fixed rigid model (hexagon), only the parameters of the pivot atoms being allowed to vary; therefore there are no estimated standard deviations for those of the subsequent atoms and all bond lengths. Non-co-ordinated solvent molecules, four THF [O(2) to C(96), O(3) to C(100), O(4) to C(104) and O(5) to C(108)] and one water molecule [O(4w)] were found disordered and assigned half site occupancy. Compound **3** was refined against *F* based on observed reflections [$F > 6\sigma(F)$]; three solvent toluene molecules were found disordered in the asymmetric unit and each assigned half site occupancy. One of the toluene molecules [C(101) to C(106)] was refined with a fixed rigid model. The largest difference peak of 3.88 e Å^3 at 1.897 Å from Yb(2) and 1.376 Å from N(6) was regarded as a ghost peak and

Table 2 Crystallographic data for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{54}H_{50}ClN_4O_3Y$	$C_{100}H_{87}Cl_2N_8O_{6.5}Y_2$	$C_{106.5}H_{88}N_8O_{11}Yb_2$	$C_{100}H_{82.5}N_8O_{3.25}Yb_2$	$C_{54.5}H_{52}ClN_4O_4Yb$
Formula weight	927.34	1753.5	2001.9	1794.32	1035.49
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P1$ (no. 1)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	15.276(1)	13.607(2)	15.807(2)	16.758(2)	13.680(1)
b/Å	28.313(2)	14.732(2)	18.212(2)	27.758(2)	14.740(2)
c/Å	13.846(1)	14.933(2)	18.864(2)	20.303(2)	14.969(1)
α/°	—	63.95(2)	70.26(2)	—	64.59(1)
β/°	109.43(1)	87.14(2)	72.93(2)	108.09(2)	87.25(1)
γ/°	—	71.12(2)	68.06(2)	—	70.34(1)
V/Å^3	5647.5(6)	2529.6(6)	4653.3(9)	8977.5(8)	2550.9(3)
Z	4	1	2	4	2
μ/mm^{-1}	1.120	1.246	2.063	2.124	1.932
Unique reflections (R_{int})	8138 (0.00)	6225 (0.00)	13644 (0.00)	12384 (0.00)	8136 (0.00)
Observed reflections, n	6262 [$I > 2\sigma(I)$]	3532 [$F > 6\sigma(F)$]	9883 [$F > 6\sigma(F)$]	11177 [$F > 4\sigma(F)$]	7802 [$I > 2\sigma(I)$]
No. of parameters, p	569	1071 (516/564)	1173	1055	615
R_F	0.0833	0.0779	0.0683	0.0888	0.0555
R'	0.2098	0.1027	0.0893	0.1809	0.1539

cannot be further reduced due to poor data quality. A highly disordered solvent diethyl ether molecule was found in compound **4** and assigned $\frac{1}{4}$ site occupancy; carbon atoms [C(52) to C(54)] were refined isotropically. In compound **5** one of the solvent THF molecules [O(3) to C(56)] and the methanol molecule [O(4) to C(57)] are disordered and were assigned half site occupancy.

CCDC reference number 186/1568.

See http://www.rsc.org/suppdata/dt/1999/3053/ for crystallographic files in .cif format.

Acknowledgements

Thanks are due to the Hong Kong Baptist University and the Hong Kong research Grants Council (HKBU 142/95P and CUHK 303/96P) for financial support.

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