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Synthesis and X-ray crystal structure of an unexpected neutral oxalate-bridged ytterbium(III) porphyrinate dimer

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Treatment of 5,10,15,20-tetraphenylporphyrin (H_2tpp) with an excess of $Yb^{III}[N(SiMe_3)_2]_3\cdot x[LiCl(THF)_3]$, generated *in situ*, in refluxing bis(2-methoxyethyl) ether solution, yielded the unexpected neutral oxalate-bridged dimer, $[Yb^{III}(tpp)(CH_3OCH_2CH_2OCH_3)]_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2CCO_2)$ 1, the structure of which was ascertained by X-ray crystallography.

Recently we reported the synthesis of cationic and neutral mono- and di-nuclear porphyrinate complexes *via* the protonolysis of lanthanide(III) amide complexes with porphyrin free base.[1,2] In this report, we further demonstrate that the propensity for the formation of lanthanide porphyrinate complexes is highly dependent on the nature of the porphyrin and the lanthanide precursor.

Treatment of an excess amount of $Yb^{III}[N(SiMe_3)_2]_3\cdot x[LiCl(THF)_3]$, generated *in situ*, with 5,10,15,20-tetraphenylporphyrin (H_2tpp) in refluxing bis(2-methoxyethyl) ether solution for 48 h, after work up in air, yielded the unexpected neutral oxalate-bridged dimer $[Yb^{III}(tpp)(CH_3OCH_2CH_2OCH_3)]_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2CCO_2)$ **1** in good yield (70%).† The dimeric nature of compound **1** was supported by its mass spectrum (FAB, positive-ion mode), which exhibited the highest mass peak at *m*/*z* 1660 corresponding to the $\{[Yb(tpp)]_2(O_2CCO_2)\}$ fragment for ^{174}Yb. Its structure was ascertained by X-ray crystallography (Fig. 1).‡ Crystals of $[Yb^{III}(tpp)(CH_3OCH_2CH_2OCH_3)]_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2CCO_2)\cdot 3C_4H_{10}O_2$ suitable for X-ray diffraction study were grown by slow evaporation of a saturated solution of compound **1** in 1,2-dimethoxyethane. Structural analysis revealed that the dimer is centrosymmetric with an oxalate dianion linking the two ytterbium centres *via* a $(\mu\text{-}\eta^2:\eta^2\text{-}O_2CCO_2)$ bridging mode. Each ytterbium(III) ion is eight-co-ordinate, being surrounded by four N atoms of the porphyrinate dianion and four O atoms of which two originated from the chelating 1,2-dimethoxyethane molecule and the other two from the oxalate ligand. The oxalate dianion co-ordinates as a bidentate ligand to both ytterbium atoms, forming five-membered YbOCCO rather than four-membered YbOCO rings. The Yb atom lies 1.176 Å above the N_4 mean plane. The average Yb–N and Yb–O (dimethoxyethane) distances are 2.364 and 2.511 Å, while the average distance of Yb–O (oxalate) is 2.353 Å. The dihedral angle formed between the mean plane defined by the four N atoms and the mean plane defined by the four O atoms [O(1), O(1A) and O(3), O(4)] is 1.3°. The porphyrin ring also 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.* 0.02, 0.14, 0.31 and 0.16 Å, respectively. The dihedral angles formed between the phenyl rings and the N_4 mean planes are 70.7° [C(21)–C(26)], 70.4° [C(27)–C(32)], 67.4° [C(33)–C(38)] and 64.2° [C(39)–C(44)]. The oxalate fragment is planar to within 0.006 Å. The three angles around C(45) are close to 120°. The C–O distances are practically the same [C(45)–O(1) 1.250(6) Å and C(45)–O(2) 1.248(6) Å] and lie between the normal ranges for C–O and C=O bonds. This suggests that there is significant π delocalization within the oxalate framework. There are two 1,2-dimethoxyethane solvate molecules in the asymmetric unit, one of which [C(53)–C(57)] is disordered and assigned a site occupancy of 0.5.

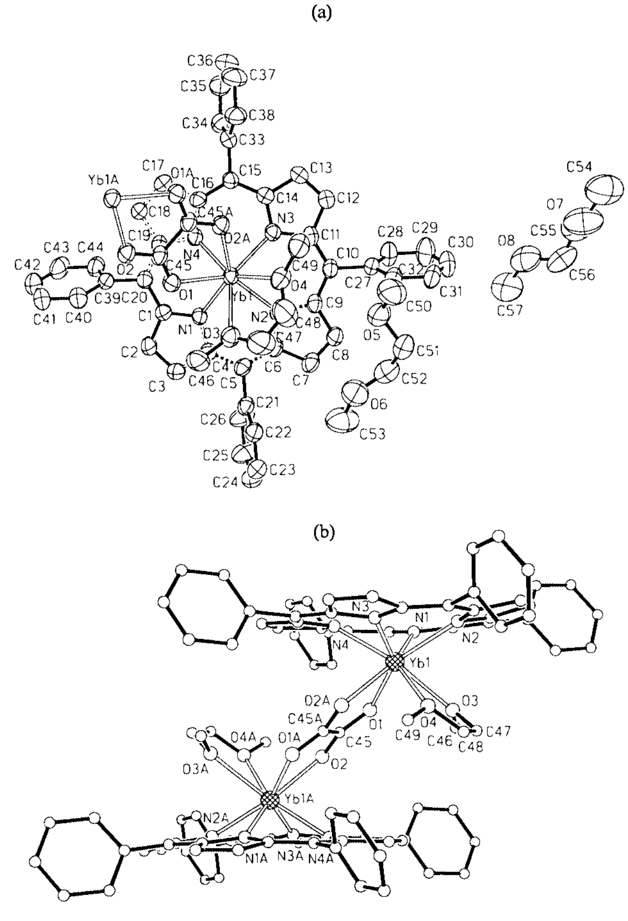

Fig. 1 A perspective drawing of the molecular structure of compound **1**: (a) top view, (b) side view. Selected bond lengths (Å) and angles (°): Yb(1)–O(1) 2.355(3), Yb(1)–O(2A) 2.350(3), Yb(1)–O(3) 2.522(5), Yb(1)–O(4) 2.499(4), Yb(1)–N(1) 2.365(4), Yb(1)–N(2) 2.374(4), Yb(1)–N(3) 2.359(4), Yb(1)–N(4) 2.357(4), C(45)–O(1) 1.250(6), C(45)–O(2) 1.248(6), C(45)–C(45A) 1.537(11), O(1)–Yb(1)–O(2A) 68.59(13), O(1)–Yb(1)–O(3) 69.84(14), O(2A)–Yb(1)–O(3) 106.00(14), O(1)–Yb(1)–O(4) 105.29(13), O(2A)–Yb(1)–O(4) 70.47(13), N(1)–Yb(1)–N(2) 75.70(13), N(1)–Yb(1)–N(3) 121.27(15), N(1)–Yb(1)–N(4) 75.83(16), N(2)–Yb(1)–N(3) 75.60(15), N(2)–Yb(1)–N(4) 119.40(14), N(3)–Yb(1)–N(4) 75.57(15).

When the above reaction and work up were carried out under nitrogen atmosphere with complete exclusion of carbon

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dioxide, a purple compound whose mass spectrum (FAB, +ve) was neither that of compound **1** nor that of [Yb^{III}(tpp)(H_2O)$_3$]Cl was isolated. We are still in the process of characterizing this compound. However, when the same reaction mixture was refluxed for 36 h under nitrogen and then bubbled with carbon dioxide at room temperature for 2 h, a purple compound whose mass spectrum (FAB, +ve) was identical to that of compound **1** was isolated. Although the origin of the oxalate dianion is not clear yet the above results suggest that it may be possible that the oxalate dianion is derived from the coupling of carbon dioxide from air during the work up.

The present result is in contrast to the reaction of 5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrin (H_2tmpp) or 5,10,15,20-tetrakis(*p*-tolyl)porphyrin (H_2ttp) with Yb^{III}[N(SiMe$_3$)$_2$]$_3$·*x*[LiCl(THF)$_3$] and H_2tpp with Yb^{III}(NPh$_2$)$_3$·*x*[LiCl(THF)$_3$], which gave the cationic complex [Yb^{III}(por)(H_2O)$_3$][Cl][1] (por = tmpp or ttp) and the neutral mononuclear porphyrinate complex [Yb^{III}(tpp)Cl(H_2O)(THF)],[2] respectively. This shows that the type of product obtained from lanthanide–amide protonolysis with porphyrin free base is influenced by the nature of the lanthanide–amide complexes and the porphyrin free bases. Notably compound **1** is the first neutral oxalate-bridged lanthanide porphyrinate dimer to be characterized structurally.

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Notes and references

† Synthetic procedures for compound **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$_3$Si)$_2$NH (0.78 g, 4.8 mmol) in tetrahydrofuran (20 cm^3). The reaction mixture was allowed to stir at room temperature for 2 h, and then transferred to a suspension of YbCl$_3$ (0.45 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 was redissolved in bis(2-methoxyethyl) ether (10 cm^3) and filtered. The filtrate was then added to a solution of H_2tpp (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 was first washed with hexane (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3) to remove any remaining lithium amide, and then extracted with dichloromethane (3 × 10 cm^3) and filtered. The solvent of the combined filtrate was removed *in vacuo* to give a purple residue, which was redissolved in 1,2-dimethoxyethane and filtered. The filtrate was concentrated to *ca.* 15 cm^3 and then allowed to evaporate slowly in air to give purple crystals of **1**·3($CH_3OCH_2CH_2OCH_3$), which were filtered off and dried *in vacuo*. Yield: 0.13 g, 40%, violet crystal; mp > 300 °C. IR (cm^{-1}, in KBr): 3383s, 1595s, 1478m, 1439m, 1384w, 1331m, 1263w, 1200w, 1177s, 1070m, 1006m, 990vs, 799vs, 754m, 723m, 702s, 659m, 578w, 426w. UV–VIS data in CHCl$_3$, 20 °C, λ_{max}/nm [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 422(5.20), 551(4.01), 630(3.35). MS (FAB, +ve) *m*/*z*: 1660 {[Yb(tpp)]$_2$(O_2CCO_2)} for ^{174}Yb.

‡ *Crystal data* for **1**·3($CH_3OCH_2CH_2OCH_3$): $C_{55}H_{53}YbN_4O_7$, dark red prism, 0.12 × 0.20 × 0.40 mm, $M = 1055.05$, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.646(1)$, $b = 23.715(3)$, $c = 17.944(2)$ Å, $\beta = 103.2(1)°$, $V = 5329.2(10)$ Å^3, $Z = 4$, $T = 294$ K, μ(Mo-Kα) = 18.38 cm^{-1}, 15046 reflections measured, final $R_1 = 0.063$ for 7715 [$I > 2.0\sigma(I)$] observed reflections, $wR_2 = 0.155$ (based on F^2) for 8594 unique reflections using the SHELXL-97 program package.[3] Intensity data of compound **1** was collected at 294 K on a MSC/Rigaku RAXIS IIC imaging-plate system[4] using Mo-Kα radiation ($\lambda = 0.71073$ Å) from a Rigaku RU-200 rotating-anode generator operating at 50 kV and 90 mA.

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See http://www.rsc.org/suppdata/dt/b0/b003434g/ for crystallographic files in .cif format.

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