Synthesis and crystal structure of the first lanthanide complex of *N*-confused porphyrin with an η^2 agostic C–H interaction†

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Received (in Cambridge, UK) 11th October 2004, Accepted 25th November 2004
First published as an Advance Article on the web 5th January 2005
DOI: 10.1039/b415609a

The reaction of $Ln[N(SiMe_3)_2]_3{\cdot}[LiCl(THF)_3]_x$ (Ln = Yb and Er) with *N*-confused tetraphenylporphyrin (H_2NCTPP) followed by $Na(L_{OMe})$ (L_{OMe} = $(\eta^5\text{-}C_5H_5)Co[P(=O)(OMe)_2]$) gives (NCTPP)Ln($L_{OMe}$), whose X-ray structures exhibit an η^2 agostic interaction between the metal centre and the inner C–H bond of the NCTPP ligand.

The successful synthesis of *N*-confused porphyrin **1a** in 1994 by two independent research groups has generated a lot of curiosity due to the possible existence of new porphyrin isomers with unique properties.[1,2] *N*-Confused porphyrin (H_2NCP), an isomeric porphyrin, has an inverted pyrrole ring joined to the porphyrinic conjugated system through a β-carbon, and exhibits a peripheral pyrrolic nitrogen and an inner core carbon. Recently, Furuta and co-workers have succeeded in synthesizing "doubly *N*-confused porphyrins"[3] and "doubly *N*-confused hexaphyrin".[4] From the structural resemblance to the normal porphyrin, H_2NCP is expected to form complexes with a variety of metals. The unique coordination chemistry of H_2NCP towards transition metals has been demonstrated progressively. Important results include the non-traditional coordination modes of the NCP complexes,[5] the stabilization of abnormal metal oxidation states,[6] the formation of metal–carbon bonds,[7] and the formation of dinuclear or poly-nuclear complexes through nitrogen coordination on an inverted pyrrole ring.[7d,8] However, related studies on lanthanide complexes of H_2NCP have not yet been reported, possibly due to the instability of lanthanide NCP complexes. We are interested in the chemistry and luminescent property of lanthanide porphyrinate complexes. We[9] and others[10] have shown that the tripodal anion, L_{OMe}^- (L_{OMe}^- = $(\eta^5\text{-}C_5H_5)Co[P(=O)(OMe)_2]^-$), is capable of stabilizing labile normal porphyrinate lanthanide(III) complexes by effectively encapsulating the lanthanide ion, thereby shielding it from interactions with the environment. We have extended our study to *N*-confused porphyrins and herein report the first synthesis and characterization of novel lanthanide NCP complexes.

N-Confused tetraphenylporphyrin (H_2NCTPP) was prepared according to Lindsey's procedure with the synthetic yield up to about 35%.[11] H_2NCTPP can exist in various tautomeric forms (**1a**, **1b** or **1c**, see Fig. 1). The DFT calculations showed that **1a** was the most stable tautomer among **1a**–**1c**.[12] When **1a** was treated with excess $Ln[(N(SiMe_3)_2)_3{\cdot}[LiCl(THF)_3]_x$ (Ln = Yb or Er) under nitrogen in refluxing toluene for 12 h, followed by addition of excess NaL_{OMe} to the reaction mixture at room temperature, work up in air gave green crystals of [Ln(NCTPP)(L_{OMe})] (Ln = Yb **2**, or Er **3**) in 75% yield. The complexes are thermally and air stable and can be purified by column chromatography. However, when the same reaction was carried out without the subsequent addition of L_{OMe}^-, work up only led to the recovery of **1a**. This suggests that the lanthanide *N*-confused porphyrinate intermediate was rather unstable and could be stabilized by the tripodal anion, L_{OMe}^-. Complexes **2** and **3** were characterized by elemental analyses and spectroscopic techniques. The electrospray ionization high resolution mass spectrum (ESI-HRMS) of **2** and **3** exhibited the (M + 1) peak at *m*/*z* 1238.1591 and 1232.1593, which deviated less than 10 ppm from the theoretical values of 1238.1678 and 1232.1618, respectively, and their isotopic distribution patterns matched the theoretical distribution patterns as well. $^{31}P\{^1H\}$-NMR (*vs.* 85% H_3PO_4) of **2** and **3** displayed a single peak at δ 82.8 and −123.2 ppm, respectively. Each of the absorption spectra of **2** and **3** in CH_2Cl_2 shows a Soret band and a broad Q-band at 457 and 670 nm, respectively. These spectral features resemble those observed for related NCP complexes of nickel(II),[7a] but are in marked contrast to those of the planar [Ag^{III}(NCTPP)] complex,[6c] where the Soret band is observed at 447 nm and the Q-band appears with four peaks at 520, 554, 588, and 637 nm.

The solid state structures of **2** and **3** were ascertained by X-ray crystallography‡ and shown to be isomorphous. A perspective drawing of **2** is depicted in Fig. 2. The good quality of the structural data enabled us to locate the hydrogen atom on C(20) from the Fourier difference maps. Consequently, the inner core C–H group in **2** can be assigned unambiguously. The overall structure of the NCTPP dianion adopts a nonplanar geometry with an inverted pyrrole ring tilted away from the metal and the porphyrin plane defined by N(2)–N(3)–N(4). The three regular pyrroles are slightly distorted, with a mean deviation of 0.0865 Å from the plane defined by 19 atoms on the pyrrole rings and methine carbons. The Yb^{3+} ion is eight-coordinate and is bonded to the $NCTPP^{2-}$ and the L_{OMe}^- ligands. Other than coordinating to the three O atoms of the L_{OMe} ligand, the Yb^{3+} ion is also

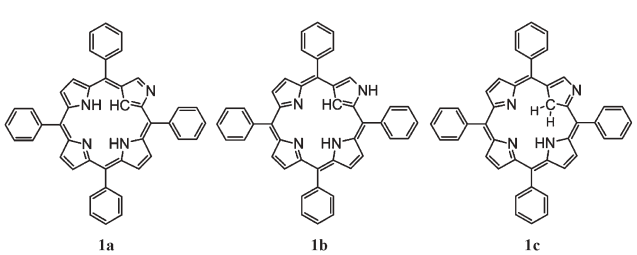

Fig. 1 The tautomers (**1a**, **1b**, **1c**) of *N*-confused porphyrin.

† Electronic supplementary information (ESI) available: experimental procedures and analytical data for all new compounds. See http://www.rsc.org/suppdata/cc/b4/b415609a/

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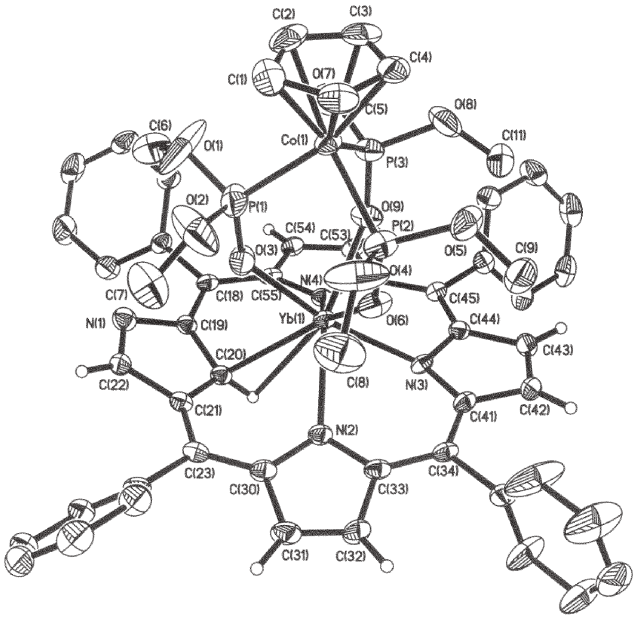

Fig. 2 A perspective drawing of compound **2**. Selected bond lengths (Å) and angles (°): Yb(1)–N(2) 2.395(5), Yb(1)–N(3) 2.314(5), Yb(1)–N(4) 2.393(4), Yb(1)–C(20) 2.601(6), C(19)–C(20) 1.409(8), C(20)–C(21) 1.405(8), C(21)–C(22) 1.430(8), C(22)–N(1) 1.320(8); N(1)–C(19)–C(20) 108.3(5), C(22)–N(1)–C(19) 107.2(5), N(3)–Yb(1)–N(2) 76.95(16), N(3)–Yb(1)–N(4) 77.12(15), N(4)–Yb(1)–N(2) 121.42(16).

bound to the three inner N atoms and forms an η^2 agostic bond with the inner C–H edge of the NCTPP ligand. The Yb centre sits 1.2464 Å above the mean plane. The Yb–N and Yb–O distances range over 2.314(5)–2.395(5) Å and 2.223(5)–2.250(4) Å, respectively, and are comparable to those reported for normal lanthanide monoporphyrinate complexes.[9] The Yb(1)···C(20) distance of 2.601(6) Å is much longer than the Yb–C bond distance [2.388(4) Å] reported in the literature.[13] In addition to the relatively short bond distance of C(19)–C(20) [1.409(8) Å] and C(20)–C(21) [1.405(8) Å], the bond angles of 108.3(5)° for N(1)–C(19)–C(20) and 107.2(5)° for C(22)–N(1)–C(19) are consistent with the tautomer form in **1a**.[14] Meanwhile, the distance from Yb(1) to the inner core hydrogen is only 2.57(6) Å with the inner C–H distance being 0.88(6) Å. Most interestingly, the solid-state geometry of C(20)–H···Yb(1) in **2** is within the bond distance of an agostic interaction. This seems to be in line with the effect due to the coordinatively unsaturated and electron-deficient Yb centre that results in a stronger three-centre two-electron C(20)–H···Yb(1) contact. Solid-state packing effects could be another factor that causes such interaction. The much shorter Yb(1)–N(3) distance *trans* to the inverted pyrrole ring suggests the stronger electron-donating ability of this pyrrolic N atom to the relatively electron-deficient lanthanide ion centre and further supports the agostic interaction between the metal and inner core C–H bond.[15] Similar agostic interaction between a transition metal ion and an inner C–H bond of NCP has been observed.[5a,5b] Moreover, when the same reaction was carried out with *C*-brominated NCTPP, no stable lanthanide complexes could be isolated. This suggests that the agostic interaction between C–H bond and Yb^{3+} ion may contribute to the stabilization of these lanthanide NCTPP complexes.

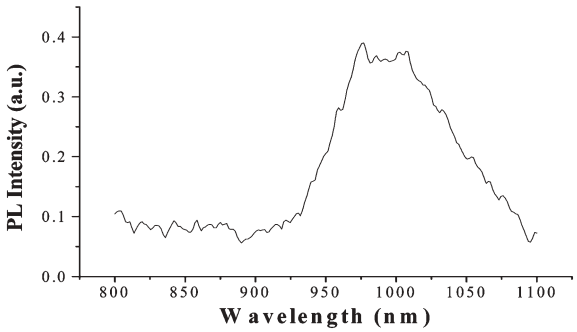

Fig. 3 NIR luminescence spectrum of **2** in toluene upon excitation at 600 nm at room temperature.

The agostic interaction was further confirmed by ^{1}H NMR data for **2**. Based on 2-D COSY ^{1}H NMR data, the resonance at δ 37.85 ppm, which is substantially downfield shifted, can be unambiguously assigned to the inner C–H proton of NCP. Since the magnitude of the pseudocontact shift is inversely proportional to the cube of the average distance from the metal ion to the nucleus of interest,[16] a large downfield shift of the inner C–H proton indicates a strong interaction between the Yb^{3+} ion and the inner C–H bond. Complex **2** also exhibited an emission band corresponding to the Yb^{3+} ion in the NIR region. The solution NIR emission spectrum of **2** upon excitation at 600 nm is shown in Fig. 3. The emission peaks centred at *ca.* 992 nm can be assigned to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{3+}. It has been shown that the C–H vibration may quench NIR emission of Ln^{3+} ions.[17] The NIR emission of [Yb(NCTPP)(L_{OMe})] is at least an order of magnitude weaker than the corresponding porphyrinate complex [Yb(TPP)(L_{OMe})] (TPP^{2-} = 5,10,15,20-tetraphenylporphyrinate dianion).[9] This provides further evidence for the presence of an η^2 agostic interaction between the Yb^{3+} ion and the inner C–H bond of the $NCTPP^{2-}$ ligand.

In summary, we have synthesized and fully characterized the first lanthanide *N*-confused porphyrinate complexes. Structural and spectroscopic data provide evidence for an η^2 agostic interaction between the Ln^{3+} ion and the inner C–H bond.

We thank Hong Kong Baptist University (FRG/03-04/II-52) and Hong Kong Research Grants Council (HKBU 2038/02P) for financial support.

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Notes and references

‡ *Crystal data for* **2**·H_2O: $C_{55}H_{53}CoN_4O_{10}P_3Yb$, M = 1254.89, monoclinic, $P2_1/n$, a = 13.7713(8), b = 28.6597(18), c = 14.9785(9) Å, β = 114.942(1)°, V = 5360.4(6) Å^3, T = 273(2) K, Z = 4, μ(Mo-Kα) = 21.95 cm^{-1}, 26345 reflections measured, 9439 unique (R_{int} = 0.0302), $R1$ = 0.0415, $wR2$ = 0.1029 for 7304 [$I > 2\sigma(I)$] observed reflections. *Crystal data for* **3**·H_2O: $C_{55}H_{53}CoN_4O_{10}P_3Er$, M = 1249.11, monoclinic, $P2_1/n$, a = 13.7562(9), b = 28.5604(19), c = 15.0423(10) Å, β = 115.514(1)°, V = 5333.5(6) Å^3, T = 273(2) K, Z = 4, μ(Mo-Kα) = 20.26 cm^{-1}, 26205 reflections measured, 9350 unique (R_{int} = 0.0312), $R1$ = 0.0482, $wR2$ = 0.1265 for 7307 [$I > 2\sigma(I)$] observed reflections. CCDC 253410 and 253411. See http://www.rsc.org/suppdata/cc/b4/b415609a/ for crystallographic data in .cif or other electronic format.

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