Structural studies of the whole series of lanthanide double-decker compounds with mixed 2,3-naphthalocyaninato and octaethylporphyrinato ligands

Yongzhong Bian,[a] Daqi Wang,[b] Rongming Wang,[a] Linhong Weng,[c] Jianmin Dou,[b] Dongyuan Zhao,[c] Dennis K. P. Ng*[d] and Jianzhuang Jiang*[a]

[a] *Department of Chemistry, Shandong University, Jinan 250100, China. E-mail: jzjiang@sdu.edu.cn*
[b] *Department of Chemistry, Liaocheng University, Liaocheng 252000, China*
[c] *Department of Chemistry, Fudan University, Shanghai 200433, China*
[d] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China. E-mail: dkpn@cuhk.edu.hk*

Received (in Montpellier, France) 7th October 2002, Accepted 10th January 2003
First published as an Advance Article on the web 8th April 2003

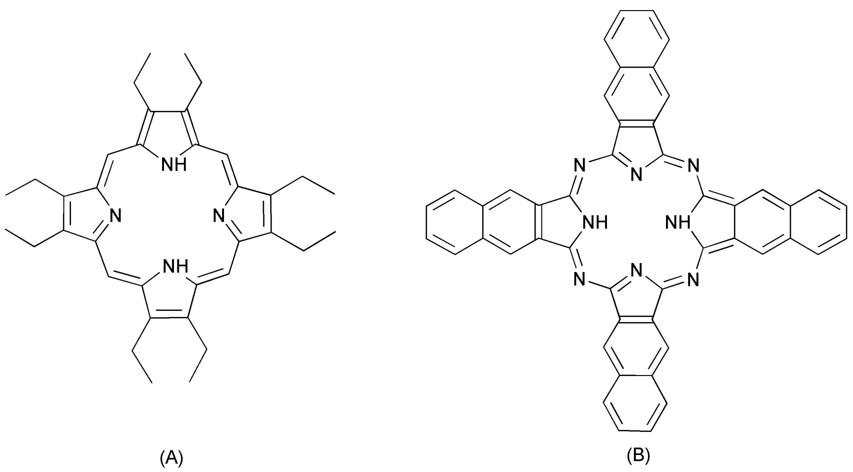
The molecular structures of a series of nine mixed (2,3-naphthalocyaninato)(octaethylporphyrinato) double-decker complexes of lanthanide(III), M(Nc)(OEP) (M = La, Pr, Nd, Tb, Dy, Ho, Er, Tm, Yb), have been determined by single-crystal X-ray diffraction analysis. All these compounds together with the Sm, Eu, Gd, Y, Lu and Ce analogues, whose structures have been solved previously, crystallize in the same orthorhombic system, *Pnma*, $Z = 4$. The molecular structures of all these compounds are isostructural, exhibiting a slightly distorted square antiprismatic geometry with two domed ligands. The metal centre of M(Nc)(OEP) is coordinated by eight nitrogen atoms from the isoindole and pyrrole of the Nc and OEP rings, respectively. The ring-to-ring separation between the two domed ligands, as defined by the two N_4 mean planes, decreases monotonically from 3.056 to 2.652 Å along the series of La to Lu as a result of lanthanide contraction. This interplanar distance as well as the average M–N(Nc) and M–N(OEP) bond lengths of M(Nc)(OEP) (except M = Ce) show a linear relationship with the ionic radius of the metal centre. The skew/twist angle between the two macrocyclic rings remains almost unchanged, *ca.* 45°, for the whole series of lanthanide complexes, regardless of the size of the metal centre.

Introduction

Phthalocyanines and porphyrins are two important classes of tetrapyrrole pigments.[1] They can form complexes with almost the complete Periodic Table of elements. In particular, sandwich-type complexes of phthalocyanines and/or porphyrins with large metal ions such as rare earth, actinide, early transition and main group metals have been obtained. There has been a growing interest in sandwich-type rare earth complexes with tetrapyrrole ligands.[2] Owing to the large π systems and the intrinsic nature of the metal centres, these compounds exhibit intriguing properties that enable them to be used in many areas such as electrochromic displays,[3] field-effect transistors,[4] gas sensors[5] and receptors for saccharides.[6] The triple-decker complexes $Eu_2(Pc^*)_2(Por)$ (Pc* = general phthalocyaninate, Por = general porphyrinate) are also potentially useful in multibit molecular information storage.[7] Extensive studies have been conducted to examine various aspects of their physicochemical properties such as spectroscopy, electrochemistry and the extent of π-π interactions. Comparatively, structural data are not so abundant, in particular for a whole series of lanthanide complexes with identical tetrapyrrole ligands.[2] Ohashi and co-workers have recently reported the molecular structures of a series of bis(phthalocyaninato)lanthanide(III) complexes $[n\mathrm{Bu_4N}][\mathrm{M(Pc)_2}]$ (M = Nd, Gd, Ho, Lu; Pc = phthalocyaninate).[8] It has been found that the skew/twist angle, defined as the rotation angle of one ring away from the eclipsed conformation of the two rings, increases from 6.2° to 45.0° as the size of the metal centre decreases along the series, suggesting an increase in π-π interactions. Such a trend, however, has not been observed for the 14 $[\mathrm{M(Pc)_2}]^-$ structures determined by Homborg and co-workers.[9] It has been suggested that other factors such as cation-anion interactions and the effects of solvated molecules may also play important role in determining the lattice energy of crystals and then the molecular structure of these complexes. These inconsistencies suggest that further investigation is needed to elucidate the effects of the metal centre on the structural properties of these sandwich-type complexes.

Among the tetrapyrrole ligands, 2,3-naphthalocyaninates (Fig. 1) are of particular interest because of their more extended π systems. Rare earth complexes of these ligands, however, have been little studied.[10] Recently, we have employed a one-pot base-promoted tetramerization method to prepare a series of heteroleptic double-deckers M(Nc)(OEP) (M = Y, La–Lu except Ce and Pm) and first determined the molecular structures of Nc containing sandwich compounds, including M(Nc)(OEP) (M = Sm, Eu, Gd, Y, Lu),[11] Ce(Nc)(OEP)[12] and $Nd_2(Nc)(OEP)_2$.[11] We report herein an extension of this work, which involves a systematic analysis and comparison of the structural parameters of the whole rare earth series of M(Nc)(OEP) (M = Y, La–Lu except Pm).[13]

DOI: 10.1039/b209882m



(A) (B)

Fig. 1 Structural formulae of (A) octaethylporphyrin (H_2OEP) and (B) 2,3-naphthalocyanine [$H_2(Nc)$].

Results and discussion

Crystal structures

All the mixed double-deckers M(Nc)(OEP) (M = Y, La–Lu except Pm) crystallize in the same orthorhombic system with a *Pnma* space group. Fig. 2 shows the molecular packing diagram of La(Nc)(OEP), which is typical for the other rare earth double-deckers. The structures for the Ce, Pr, Sm and Y analogues also contain solvated THF (for M = Pr) or cyclohexane (for M = Ce, Sm, Y), which may come from the solvents used for recrystallization. The solvent molecule has half-site occupancy with an internal mirror plane.

Molecular structures

The ORTEP drawings of the molecular structures of La(Nc)(OEP) and Ho(Nc)(OEP) viewed from two different perspectives are shown in Fig. 3. All the newly determined structures resemble those of the Sm, Eu, Gd, Y, Lu and Ce analogues reported elsewhere.[11,12] For all these double-deckers, the metal centre is octa-coordinated by the four isoindole and four pyrrole nitrogen atoms of the Nc and OEP rings, respectively, forming a nearly perfect square antiprism. A comparison of their structural parameters is given in Table 1. The average M–N(Nc) bond lengths of these double-deckers are longer than those of the corresponding $M(Pc)_2$ (M = La,[14] Ce,[15] Pr,[16] Nd,[17] Y,[18] Er,[19] Lu[20]) by *ca.* 0.06–0.08 Å, while the average M–N(OEP) bond lengths of M(Nc)(OEP) [M = Ce (2.442 Å), Eu (2.440 Å)] are shorter than those in $M(OEP)_2$ [M = Ce (2.475 Å),[21] Eu (2.510 Å)].[22] As shown in Table 1, the mean M–N(Nc) bond distance is longer than the mean M–N(OEP) bond distance for all these complexes, probably due to the smaller cavity size of Nc. Similar results have also been found for other heteroleptic (phthalocyaninato)(porphyrinato)lanthanide complexes,[23] in which the metal centre also lies closer to the N_4 mean plane of Por than the N_4 plane of Pc*.

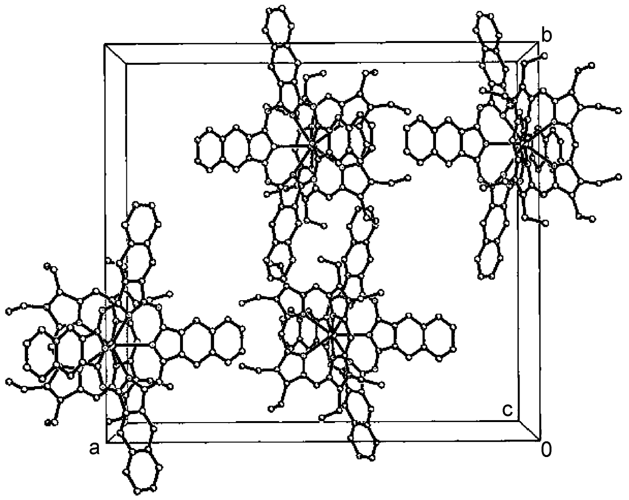


Fig. 2 Crystal structure of La(Nc)(OEP) viewed along the *c* axis.

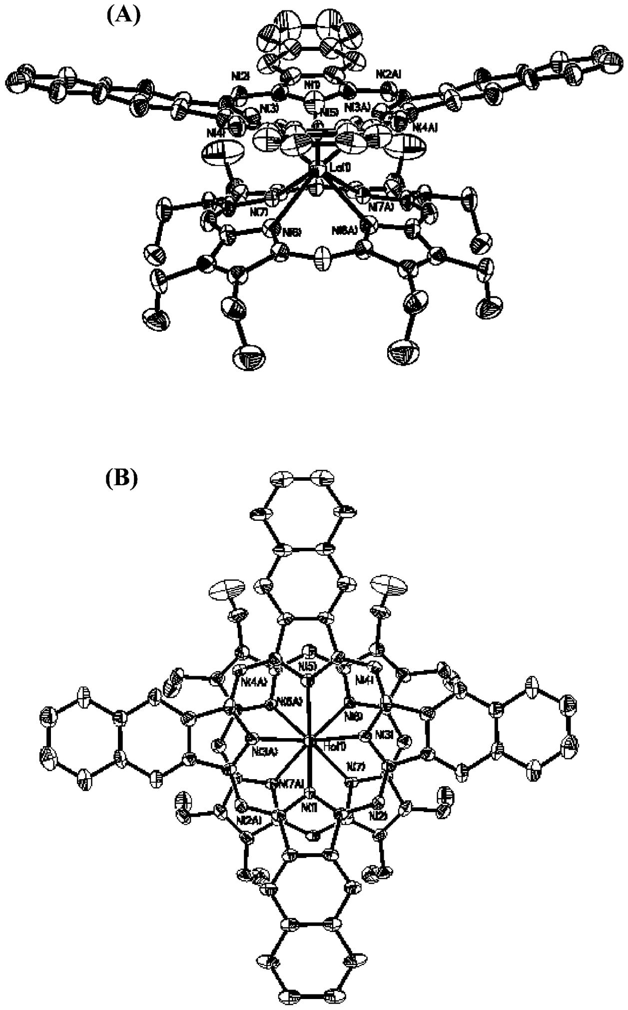


Fig. 3 Molecular structure of (A) La(Nc)(OEP) in side view and (B) Ho(Nc)(OEP) in top view. Hydrogen atoms are omitted for clarity and the ellipsoids are drawn at the 30% probability level.

Table 1 Comparison of the structural data for M(Nc)(OEP) (M = Y, La–Lu except Pm)

	La	Ce[a]	Pr	Nd	Sm[b]	Eu[c]	Gd[b]	Tb
Ave. M–N(Nc) bond distance/Å	2.598	2.483	2.551	2.550	2.515	2.477	2.488	2.477
Ave. M–N(OEP) bond distance/Å	2.509	2.442	2.478	2.468	2.457	2.440	2.440	2.426
M–N_4(Nc) plane distance/Å	1.665	1.479	1.603	1.591	1.547	1.510	1.499	1.499
M–N_4(OEP) plane distance/Å	1.392	1.291	1.337	1.302	1.287	1.270	1.256	1.256
Interplanar distance between the two N_4 planes/Å	3.056	2.770	2.941	2.893	2.834	2.780	2.754	2.755
Dihedral angle between the Nc and OEP N_4 planes/°	2.5	0.4	1.1	1.1	0.7	1.0	0.7	0.9
Ave. dihedral angle φ for the Nc ring/°	11.8	13.5	11.7	12.4	12.7	10.4	13.6	12.8
Ave. dihedral angle φ for the OEP ring/°	15.0	15.0	14.2	15.4	15.0	16.1	15.6	15.4
Ave. twist angle/°	44.9	45.0	44.7	44.5	45.0	45.0	45.0	44.8

	Dy	Y[b]	Ho	Er	Tm	Yb	Lu[b]
Ave. M–N(Nc) bond distance/Å	2.441	2.460	2.459	2.465	2.448	2.432	2.446
Ave. M–N(OEP) bond distance/Å	2.425	2.410	2.411	2.414	2.407	2.382	2.388
M–N_4(Nc) plane distance/Å	1.454	1.465	1.460	1.459	1.447	1.463	1.442
M–N_4(OEP) plane distance/Å	1.252	1.233	1.233	1.232	1.223	1.225	1.210
Interplanar distance between the two N_4 planes/Å	2.705	2.698	2.693	2.691	2.670	2.688	2.652
Dihedral angle between the Nc and OEP N_4 planes/°	1.4	0.9	1.1	0.8	0.1	0.7	0.1
Ave. dihedral angle φ for the Nc ring/°	13.9	13.7	13.1	12.9	12.8	11.8	13.1
Ave. dihedral angle φ for the OEP ring/°	15.1	15.3	15.5	15.2	15.5	14.9	14.9
Ave. twist angle/°	44.8	45.0	44.7	44.6	45.0	44.8	45.0

[a] Cited from ref. 12. [b] Cited from ref. 11*a* (after correction). [c] Cited from ref. 11*b*.

The two N_4 planes are virtually parallel with a dihedral angle of 0.1–2.5°. The two ligands, however, are significantly domed. The average dihedral angle φ of the NC_4 mean plane of an individual isoindole or pyrrole ring with respect to the corresponding N_4 mean plane shows the degree of nonplanarity and is thus a measure of doming. For this series of complexes, the value of φ varies in the range of 10.4–13.9° for the Nc ring and 14.2–16.1° for OEP, showing that the latter is slightly more deformed. It should be pointed out that the four dihedral angles for a particular ligand are not equivalent due to the packing forces in the crystal, which also affect the orientation of the ethyl groups in OEP. As shown in Fig. 3(A), two of the ethyl groups are tilted towards the Nc plane, while the remaining six are away from the Nc plane.

Relationship between the interplanar distance and the size of the metal centre

Studies of the relationship between interplanar distance and the metal size for these sandwich-type complexes are rare.[2] By examining the structures of [nBu$_4$N][M(Pc)$_2$] (M = Nd, Gd, Ho, Lu) and other double-deckers including $M^{III}(Pc)_2$ (M = Pr, Nd, Y, Er, Lu), $HLu^{III}(Pc)_2$, $M^{IV}(Pc)_2$ (M = Zr, Sn, Ce, Th, U) and $[Ti^{IV}(Pc)_2]^{0.66+}$, Ohashi and co-workers have found an approximately linear relationship between the interplanar distance and the ionic radius of the metal centre for these complexes.[8] A similar trend has also been reported by Homborg and co-workers and the following relationships have been derived for bis(phthalocyaninato) metal complexes: $D_{av}[\text{M–N(Pc)}] = 0.648 \cdot R_8 + 177$ and $D_{ip} = 1.76 \cdot R_8 + 102$, in which $D_{av}[\text{M–N(Pc)}]$ = average M–N(Pc) bond length, D_{ip} = interplanar distance and R_8 = ionic radius of octa-coordinated metal centre (all in pm).[9] Since factors such as the valence of the metal centre, crystal system, the counter cation/anion, *etc.*, will exert a significant influence on the structural parameters, a more logical comparison should be made on a whole series of complexes with identical ligands, oxidation state, counter cation/anion (for complex salts) and molecular packing environment. The mixed double-deckers M(Nc)(OEP) (M = Y, La–Lu except Pm), which fulfill all these conditions, are excellent candidates for a detailed study of the effects of metal centre on the structural parameters.

For this series of complexes, the ring-to-ring separation as defined by the two N_4 mean planes decreases from 3.056 Å(for M = La) to 2.652 Å(for M = Lu). The average M–N(Nc) and M–N(OEP) bond distances also decrease monotonically with the ionic radius of the rare earth centre. These relationships are shown graphically in Figs. 4 and 5, from which the following equations can be derived: $D_{ip} = 2.09 \cdot R_8 + 58$; $D_{av}[\text{M–N(Nc)}] = 0.86 \cdot R_8 + 158$; $D_{av}[\text{M–N(OEP)}] = 0.61 \cdot R_8 + 180$ (all in pm).[24] The cerium analogue Ce(Nc)(OEP) is the only exception. As shown in Figs. 4 and 5, all the lines are flanked by two hypothetical points generated by taking the ionic radii of cerium(III) and cerium(IV) ions. The unique behaviour of this cerium compound can be attributed to the fact that the cerium centre adopts an valence intermediate between +3 and +4, which has been supported by a range of spectroscopic and electrochemical methods.[12]

Relationship between the skew/twist angle and the size of the metal centre

The skew/twist angle, which is defined as the average dihedral angle of N(Nc)–centre(Nc N_4 plane)–centre(OEP N_4 plane)–N(OEP) in this case, ranges from 44.5° to 45.0° for all these

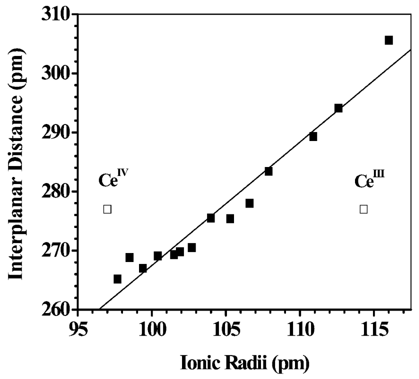


Fig. 4 Plot of ring-to-ring distance of M^{III}(Nc)(OEP) as a function of the rare earth radii of M^{III}; the open squares show the positions for hypothetical Ce^{III}(Nc)(OEP) and Ce^{IV}(Nc)(OEP).

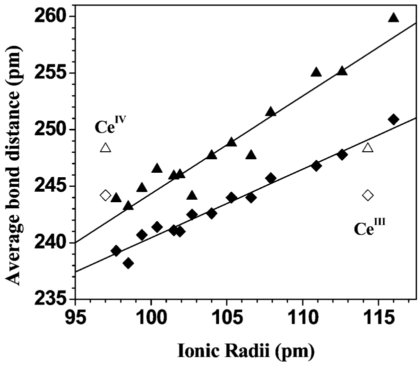


Fig. 5 Plot of the average bond lengths of M–N(Nc) (▲) and M–N(OEP) (◆) of M^{III}(Nc)(OEP) as a function of the rare earth radii of M^{III}; the open triangles and rhombuses show the positions for hypothetical Ce^{III}(Nc)(OEP) and Ce^{IV}(Nc)(OEP).

complexes, showing that the two ligands are almost fully staggered. This is in contrast to the trend observed for [nBu$_4$N][M(Pc)$_2$] (M = Nd, Gd, Ho, Lu), in which the skew/twist angle increases (from 6.2° to 45.0°) as the size of the metal centre decreases.[8] It has been suggested that the eclipsed conformer is favoured for double-deckers with a large ring-to-ring separation. The skew/twist angle could reach 0° if the interplanar distance is longer than the van der Waals distance. The actual situation, however, is much more complicated. Crystal packing forces induced by the counter cation/anion (for complex salts) and the solvent of crystallization may also play an important role. The former, in particular, greatly affects the lattice energy and is therefore one of the decisive factors.

For neutral double-deckers, which do not have counter cations or anions in the crystal lattice, the ligand-ligand repulsive force seems to be the key factor controlling the relative orientation of the two macrocyclic ligands. For many bis(phthalocyaninato) complexes of tervalent (*e.g.*, In, Bi, La, Pr, Nd, Y, Er, Lu) and tetravalent (*e.g.*, Ti, Zr, Sn, Ce, Th, U) metals, the skew/twist angle does not vary linearly with the ionic radius of the metal centre. The values normally lie between 38° and 45°, and also do not depend on the crystal system that they adopt.[2b] Structurally characterized mixed (phthalocyaninato)(porphyrinato) metal complexes are still very rare. The skew/twist angles for Ce(Pc)(TMPP) [TMPP = *meso*-tetra(4-methoxyphenyl)porphyrinate],[23a] La(Pc)(TPP) (TPP = *meso*-tetraphenylporphyrin-ate)[23b] and [Gd(Pc)(TPP)][SbCl$_6$][23b] were found to be 43.4°, 45.7° and 37.1°, respectively. Again no linear relationship exists between the skew/twist angle and the ionic size for these three complexes. In fact, to the best of our knowledge, there are only four known examples of double-deckers, namely [nBu$_4$N][MPc$_2$] (M = Bi, La, Ce, Nd), with a small skew/twist angle (between 4.1° to 6.2°). The ionic radii R_8 of these metal centres are all greater than 1.11 Å. The situation for bis(porphyrinato) metal complexes is a bit complicated due to the different substituents at the *meso* and β positions of the porphyrin rings. In many cases, the skew/twist angles lie between 30° and 45°.[2,25]

The fact that the skew/twist angles for all the M(Nc)(OEP) in this study are virtually identical at 45°, regardless of the size of the metal centre, seems to suggest that ligand-ligand repulsion is a determining factor. By assuming a staggered orientation, the non-bonding interactions between the fused benzene rings of Nc and the β-ethyl groups of OEP can be minimized. It is expected that when the ring-to-ring separation increases, the repulsion between the two macrocyclic ligands can be

Table 2 Crystallographic data for M(Nc)(OEP) (M = Y, La–Lu except Pm)

	La	Ce[a]	Pr	Nd	Sm[b]	Eu[c]	Gd[b]
Formula	$C_{84}H_{68}LaN_{12}$	$C_{87}H_{74}CeN_{12}$	$C_{86}H_{72}N_{12}O_{0.5}Pr$	$C_{84}H_{68}N_{12}Nd$	$C_{87}H_{74}N_{12}Sm$	$C_{84}H_{68}EuN_{12}$	$C_{84}H_{68}GdN_{12}$
M_r	1384.41	1427.70	1422.47	1389.74	1437.9	1875.01	1402.8
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a/Å	28.368 (5)	29.048 (7)	29.062 (8)	28.618 (8)	28.8000 (12)	27.9422 (8)	28.708 (6)
b/Å	26.078 (4)	26.642 (6)	26.502 (7)	26.329 (8)	26.5153 (11)	26.124 (1)	26.524 (5)
c/Å	11.0950 (18)	10.888 (2)	10.962 (3)	10.987 (3)	10.9682 (4)	10.9643 (7)	10.951 (2)
U/Å^3	8208 (2)	8426 (6)	8443 (4)	8278 (4)	8375.8 (6)	8003 (1)	8339 (3)
Z	4	4	4	4	4	4	4
μ/mm^{-1}	0.567	0.588	0.624	0.674	0.749	1.239	0.842
Reflections collected	39 136	40 515	33 375	32 527	41 430	58 354	16 651
Independent reflections	6900	10 852	7571	7434	10 958	9864	5864
R_{int}	0.2155	0.1545	0.1202	0.1147	0.0918	0.042	0.1477
$R1$ [$I > 2\sigma(I)$]	0.0605	0.0690	0.0706	0.0837	0.0556	0.055	0.0839
$wR2$ [$I > 2\sigma(I)$]	0.1152	0.1619	0.1607	0.2018	0.1343	0.063	0.1972

	Tb	Dy	Y[b]	Ho	Er	Tm	Yb	Lu[b]
Formula	$C_{84}H_{68}N_{12}Tb$	$C_{84}H_{68}DyN_{12}$	$C_{87}H_{74}N_{12}Y$	$C_{84}H_{68}HoN_{12}$	$C_{84}H_{68}ErN_{12}$	$C_{84}H_{68}N_{12}Tm$	$C_{84}H_{68}N_{12}Yb$	$C_{84}H_{68}LuN_{12}$
M_r	1404.42	1408.00	1376.5	1410.43	1412.76	1418.47	1418.54	1420.5
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a/Å	28.550 (4)	28.589 (13)	28.7098 (12)	28.546 (5)	28.617 (5)	28.632 (14)	28.739 (6)	28.9566 (12)
b/Å	26.489 (3)	26.655 (13)	26.5642 (12)	26.529 (5)	26.626 (5)	26.669 (13)	26.832 (5)	26.9686 (11)
c/Å	10.9353 (14)	10.922 (5)	10.9279 (5)	10.915 (2)	10.918 (2)	10.938 (5)	10.866 (2)	10.9212 (4)
U/Å^3	8269.7 (18)	8323 (7)	8334.2 (6)	8266 (3)	8319 (3)	8352 (7)	8379 (3)	8528.6 (6)
Z	4	4	4	4	4	4	4	4
μ/mm^{-1}	0.902	0.944	0.748	1.004	1.055	1.109	1.162	1.203
Reflections collected	40 241	33 102	40 782	35 753	27 634	32 525	31 602	41 766
Independent reflections	7097	5676	12 514	6077	5904	7487	5449	12 748
R_{int}	0.1071	0.3429	0.1347	0.1111	0.0122	0.0834	0.2362	0.0570
$R1$ [$I > 2\sigma(I)$]	0.0521	0.0475	0.0633	0.0622	0.0500	0.0689	0.0422	0.0426
$wR2$ [$I > 2\sigma(I)$]	0.1153	0.0552	0.1508	0.1553	0.0848	0.1625	0.0440	0.1079

[a] Cited from ref. 12. [b] Cited from ref. 11*a* (after correction). [c] Cited from ref. 11*b*.

reduced, leading to a smaller skew/twist angle. In fact, this has been found for the triple-decker $Nd_2(Nc)(OEP)_2$, which has a ring-to-ring separation of 3.155 Å and a skew/twist angle of 30.8°.[11a]

Experimental

Preparation and characterization of M(Nc)(OEP)

Experimental details concerning the preparation and characterization of these complexes were previously described.[11] The details for the cerium analogue Ce(Nc)(OEP) will be published elsewhere.[12]

Growth of single crystals

Small cubic single crystals of M(Nc)(OEP) suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a mixed $CHCl_3$–toluene or $CHCl_3$–toluene–THF solution. Typically, 10 mg of M(Nc)(OEP) was dissolved in 10 cm^3 of $CHCl_3$–toluene (1:1) or $CHCl_3$–toluene–THF (10:9:1) under sonication. The solution was then filtered and the filtrate was placed in a test tube, on top of which was added slowly a layer of hexane (10 cm^3). The opening of the tube was covered with a plastic film, then the solution was allowed to stand for several days at ambient temperature. Dark crystals thus obtained were used directly for X-ray diffraction analyses.

X-Ray crystal structure determinations for M(Nc)(OEP)

Crystal data and details of data collection and structure refinement are given in Table 2. Data were collected on a Bruker SMART CCD diffractometer with an $Mo_{K\alpha}$ sealed tube ($\lambda = 0.71073$ Å) at 293 K, using an ω scan mode with an increment of 0.3°. Preliminary unit cell parameters were obtained from 45 frames. Final unit cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling;[26] SADABS for absorption correction;[27] and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.[28] All the H atoms in these compounds were obtained geometrically. These H atoms were included in the subsequent least-squares refinement as fixed contributors. The final refinement with anisotropic temperature factors for non-H atoms led to R values of 0.0422–0.0839 for these compounds as listed in Table 2. CCDC reference numbers 194117–194125. See http://www.rsc.org/suppdata/nj/b2/b209882m/ for crystallographic files in CIF or other electronic format.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Grant No. 20171028), National Ministry of Science and Technology of China (Grant No. 2001CB6105–04), The Science Committee of Shandong Province (Grant No. Z99B03), National Educational Ministry of China, Shandong University and The Chinese University of Hong Kong for support.

References

1 (*a*) *Phthalocyanines - Properties and Applications*, eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, vol. 1; 1993, vols. 2 and 3; 1996, vol. 4; N. B. McKeown, *Phthalocyanine Materials – Synthesis, Structure and Function*, Cambridge University Press, New York, 1998; (*c*) *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vols. 1–10.

2 (*a*) J. Jiang, K. Kasuga and D. P. Arnold, in *Supramolecular Photo-sensitive and Electro-active Materials*, ed. H. S. Nalwa, Academic Press, New York, 2001, pp. 113–210; (*b*) J. W. Buchler and D. K. P. Ng, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 3, ch. 20; (*c*) D. K. P. Ng and J. Jiang, *Chem. Soc. Rev.*, 1997, **26**, 433.

3 M. M. Nicholson, in *Phthalocyanines - Properties and Applications*, eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1993, vol. 3, pp. 71–117.

4 (*a*) M. Madru, G. Guillaud, M. Al Sadoun, M. Maitrot, C. Clarisse, M. Le Contellec, J.-J. André and J. Simon, *Chem. Phys. Lett.*, 1987, **142**, 103; (*b*) R. Madru, G. Guillaud, M. Al Sadoun, M. Maitrot, J. -J. André, J. Simon and R. Even, *Chem. Phys. Lett.*, 1988, **145**, 343; (*c*) C. Clarisse, M. T. Riou, M. Gauneau and M. Le Contellec, *Electron. Lett.*, 1988, **24**, 674; (*d*) G. Guillaud, M. Al Sadoun, M. Maitrot, J. Simon and M. Bouvet, *Chem. Phys. Lett.*, 1990, **167**, 503.

5 (*a*) J. Souto, M. L. Rodríguez, J. A. de Saja and R. Aroca, *Int. J. Electron.*, 1994, **76**, 763; (*b*) P. Bassoul, T. Toupance and J. Simon, *Sens. Actuators B*, 1995, **26–27**, 150; (*c*) K. R. Rickwood, D. R. Lovett, B. Lukas and J. Silver, *J. Mater. Chem.*, 1995, **5**, 725; (*d*) B. Liang, C. Yuan, Y. Wei, Y. Zhang, D. Jiang, S. Zhang and A. Lu, *Synth. Met.*, 1997, **88**, 219; (*e*) J. Álvarez, J. Souto, M. L. Rodríguez-Méndez and J. A. de Saja, *Sens. Actuators B*, 1998, **48**, 339.

6 (*a*) A. Sugasaki, M. Ikeda, M. Takeuchi and S. Shinkai, *Angew. Chem. Int. Ed.*, 2000, **39**, 3839; (*b*) A. Sugasaki, M. Ikeda, M. Takeuchi, K. Koumoto and S. Shinkai, *Tetrahedron*, 2000, **56**, 4717.

7 (*a*) J. Li, D. Gryko, R. B. Dabke, J. R. Diers, D. F. Bocian, W. G. Kuhr and J. S. Lindsey, *J. Org. Chem.*, 2000, **65**, 7379; (*b*) D. Gryko, J. Li, J. R. Diers, K. M. Roth, D. F. Bocian, W. G. Kuhr and J. S. Lindsey, *J. Mater. Chem.*, 2001, **11**, 1162.

8 N. Koike, H. Uekusa, Y. Ohashi, C. Harnoode, F. Kitamura, T. Ohsaka and K. Tokuda, *Inorg. Chem.*, 1996, **35**, 5798.

9 H. Hückstädt, A. Tutaβ, M. Göldner, U. Cornelissen and H. Homborg, *Z. Anorg. Allg. Chem.*, 2001, **627**, 485.

10 See, for example: (*a*) J. Jiang, W. Liu, K.-L. Cheng, K.-W. Poon and D. K. P. Ng, *Eur. J. Inorg. Chem.*, 2001, 413; (*b*) J. Jiang, W. Liu, K.-W. Poon, D. P. Arnold and D. K. P. Ng, *Eur. J. Inorg. Chem.*, 2000, 205; (*c*) T. Nyokong, F. Furuya, N. Kobayashi, W. Liu, D. Du and J. Jiang, *Inorg. Chem.*, 2000, **39**, 128; (*d*) T. Gross, F. Chevalier and J. S. Lindsey, *Inorg. Chem.*, 2001, **40**, 4762; (*e*) M. Bouvet, P. Bassoul and J. Simon, *Mol. Cryst. Liq. Cryst.*, 1994, **252**, 31; (*f*) Ishikawa, O. Ohno and Y. Kaizu, *J. Phys. Chem.*, 1993, **97**, 1004; (*g*) F. Guyon, A. Pondaven, P. Guenot and M. L'Her, *Inorg. Chem.*, 1994, **33**, 4787; (*h*) M. Passard, A. Pauly, J. P. Germain and C. Maleysson, *Synth. Met.*, 1996, **80**, 25; (*i*) F. Guyon, A. Pondaven, J.-M. Kerbaol and M. L'Her, *Inorg. Chem.*, 1998, **37**, 569; (*j*) V. M. Negrimovskii, M. Bouvet, E. A. Luk'yanets and J. Simon, *J. Porphyrins Phthalocyanines*, 2001, **5**, 423.

11 (*a*) J. Jiang, Y. Bian, F. Furuya, W. Liu, M. T. M. Choi, N. Kobayashi, H.-W. Li, Q. Yang, T. C. W. Mak and D. K. P. Ng, *Chem.-Eur. J.*, 2001, **7**, 5059 and a corrigendum appeared in 2002, **8**, 2214; (*b*) F. Furuya, N. Kobayashi, Y. Bian and J. Jiang, *Chem. Lett.*, 2001, 944.

12 J. Jiang, Y. Bian, Y. Tao, M. T. M. Choi, M. Bai, C. Ma, A. C. H. Ng, N. Pan, X. Sun, D. P. Arnold, Z. -Y. Zhou, T. C. W. Mak and D. K. P. Ng, manuscript in preparation.

13 The promethium analogue is not included because of the absence of stable isotopes for this element.

14 G. Ostendorp and H. Homborg, *Z. Naturforsch., B: Chem. Sci.*, 1995, **50**, 1200.

15 M. S. Haghighi, C. L. Teske and H. Homborg, *Z. Anorg. Allg. Chem.*, 1992, **608**, 73.

16 A. Darovsky, L. Y. Wu, P. Lee and H. S. Sheu, *Acta Crystallogr., Sect. C*, 1991, **47**, 1836.

17 (*a*) A. N. Darovskikh, A. K. Tsytsenko, O. V. Frank-Kamenetskaya, V. S. Fundamenskii and P. N. Moskalev, *Kristallografiya*, 1984, **29**, 455 (*Chem. Abstr.*, 1984, **101**, 46753e); (*b*) A. N. Darovskikh, O. V. Frank-Kamenetskaya and V. S. Fundamenskii, *Kristallografiya*, 1986, **31**, 901 (*Chem. Abstr.*, 1986, **105**, 236208m).

18 J. L. Paillaud, M. Drillon, A. Decian, J. Fischer, R. Weiss, R. Poinsot and A. Herr, *Physica B (Amsterdam)*, 1991, **175**, 337.

19 G. Ostendorp, J. -P. Werner and H. Homborg, *Acta Crystallogr., Sect. C*, 1995, **51**, 1125.

20 A. De Cian, M. Moussavi, J. Fischer and R. Weiss, *Inorg. Chem.*, 1985, **24**, 3162.

21 J. W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski, H. Paulus and R. Weiss, *J. Am. Chem. Soc.*, 1986, **108**, 3652.

22 J. W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski and R. Weiss, *Inorg. Chem.*, 1988, **27**, 339.

23 (*a*) M. Lachkar, A. De Cian, J. Fischer and R. Weiss, *New J. Chem.*, 1988, **12**, 729; (*b*) D. Chabach, M. Tahiri, A. De Cian, J. Fischer, R. Weiss and M. El Malouli Bibout, *J. Am. Chem. Soc.*, 1995, **117**, 8548; (*c*) M. Tahiri, D. Chabach, M. El Malouli Bibout, A. De Cian, J. Fischer and R. Weiss, *Ann. Chim. (Paris)*, 1995, **20**, 81.

24 The values of R_8 (the effective ionic radii of the octa-coordinated metal ions) were taken from: R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

25 See, for examples: (*a*) J. W. Buchler, A. De Cian, J. Fischer, P. Hammerschmitt, J. Löffler, B. Scharbert and R. Weiss, *Chem. Ber.*, 1989, **122**, 2219 B9; (*b*) G. A. Spyroulias, A. G. Coutsolelos, C. P. Raptopoulou and A. Terzis, *Inorg. Chem.*, 1995, **34**, 2476; (*c*) G. A. Spyroulias, C. P. Raptopoulou, D. de Montauzon, A. Mari, R. Poilblanc, A. Terzis and A. G. Coutsolelos, *Inorg. Chem.*, 1999, **38**, 1683.

26 *SMART and SAINT for Windows NT Software Reference Manuals*, v. 5.0, Bruker Analytical X-Ray Systems, Madison, WI, USA, 1997.

27 G. M. Sheldrick, SADABS–A Software for Empirical Absorption Correction, University of Göttingen, Germany, 1997.

28 *SHELXL Reference Manual*, v5.1, Bruker Analytical X-Ray Systems, Madison, WI, USA, 1997.