Inorg. Chem. **1997,** *36,* 4141−4146 **4141**

Synthesis and Spectroscopic and Structural Characterization of Two Novel Dilutetium Cofacial Porphyrin Dimers

Mohammed Lachkar,[†,‡] Alain Tabard,[§]
Stéphane Brandès,[§] Roger Guilard,*[,§] Aziz Atmani,[‡]
André De Cian,[‖] Jean Fischer,[‖] and Raymond Weiss*[,‖]

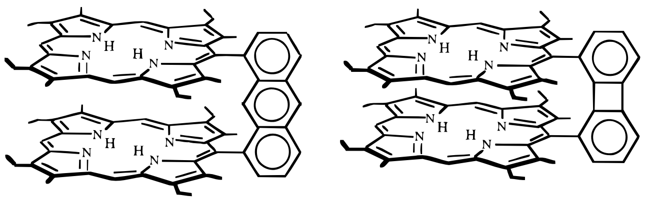
"LSEO" (UMR 5632), 6 boulevard Gabriel, 21100-Dijon, France, "LIMSAG" (UMR 5633), 6 boulevard Gabriel, 21100-Dijon, France, Faculté des Sciences, Dhar El Mahraz, 30000-Fès, Morocco, and Laboratoire de Cristallochimie et de Chimie Structurale (URA CNRS 424), 4 rue Blaise Pascal, 67070-Strasbourg, France

Received June 14, 1996

Introduction

During the last two decades, binuclear metal complexes have attracted considerable attention, since it was demonstrated that several heme and nonheme iron and copper-binding proteins possessing oxidase, oxygenase, or oxygen transport functions have binuclear active sites.[1−3] Numerous transition bimetallic complexes have now been synthesized.[4−11] Such derivatives usually exhibit properties in which the adjacent metals are involved in spin couplings and/or undergo multi-electron redox reactions.[12] Similar properties have been observed for many natural systems which are known to exhibit metal−metal interactions.

Although, lanthanide mono-, homoleptic and heteroleptic bis- and tris-, and expanded-porphyrin complexes have been known for several years,[13−19] to date, no studies have been devoted to binuclear lanthanide bis(porphyrin) complexes in which the two porphyrin ligands are covalently linked in a cofacial conformation. We report herein the synthesis, spectral properties and X-ray crystal structures of the bis(lutetium) derivatives of the anthracenyl- and biphenylenyl-bridged cofacial porphyrins (DPA)[Lu(OH)]$_2$·CH$_3$OH and (DPB)[Lu(OH)]$_2$·CH$_3$OH, DP^{4-} being either the anion of 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,-12,18-tetramethyl)porphyrin]anthracene, DPA^{4-}, or 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]biphenylene, DPB^{4-} (Figure 1).



(DPA)H$_4$ **(DPB)H$_4$**

Figure 1. Structure of the studied porphyrins.

Experimental Section

Chemicals. All chemicals were of reagent grade quality. 1,2,4-Trichlorobenzene (TCB) was distilled on CaH$_2$ under reduced pressure and stored over 4 Å molecular sieves. **Caution:** *Trichlorobenzene is toxic and should be handled under a hood!* Lu(acac)$_3$.3H$_2$O was prepared from LuCl$_3$.6H$_2$O according to a literature procedure.[20] Merck type 60 (230−400 mesh) silica gel was used for column chromatography.

Instrumentation. UV−visible spectra were recorded on a Varian Cary 1 spectrophotometer. IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Bruker IFS 66v spectrometer (Centre de Spectrométrie Moléculaire de l'Université de Bourgogne). NMR spectra were obtained on a 400 MHz Bruker WM spectrometer. Mass spectra were obtained with a Kratos Concept 32S spectrometer, and the data were collected and processed using a Sun 3/80 workstation.

Synthesis of (DPA)H$_4$ (1) and (DPB)H$_4$ (2). The free bases **1** and **2** were prepared as described in the literature.[21−25]

Synthesis of (DPA)[Lu(OH)]$_2$·CH$_3$OH (3). A TCB solution (25 mL) of free base (DPA)H$_4$ (0.22 mmol) and Lu(III)(acac)$_3$.3H$_2$O (0.57 mmol) was refluxed under argon for 17 h. After evaporation of TCB under reduced pressure, a red solid was obtained and chromatographed on a silica gel column (eluent: CH$_2$Cl$_2$). A bright red fraction was collected and evaporated. The crude product was recrystallized from CH$_2$Cl$_2$/CH$_3$OH to form dark blue needles (113.6 mg; yield 34%). Anal. Calcd for C$_{78}$H$_{80}$N$_8$Lu$_2$O$_2$·CH$_2$Cl$_2$**:** C, 59.44; H, 5.18; N, 7.02. Found: C, 59.86; H, 5.26; N, 7.10. DCIMS: $m/z = 1479$ ([M − 2OH + 1]$^+$). UV−vis (C$_6$H$_6$) [$\lambda_{\max}$, nm (ϵ, 10^{-3} M^{-1} cm^{-1})]: 336 (33.0), 402 (274.6), 501 (1.7), 538 (21.3), 575 (21.2). IR (KBr): 672 cm^{-1} [Lu−OH−Lu]. ^{1}H NMR (C$_6$D$_6$) (δ, ppm): 9.65 (s, 4H, meso-H), 9.21 (s, 2H, meso-H), 8.84 (s, 1H, 10-anth), 8.40 (d, 2H, 4,5-anth), 8.30 (s, 1H, 9-anth), 7.51 (t, 2H, 3,6-anth), 7.23 (t, 2H, 2,7-anth), 3.84 (m, 4H, Et), 3.74 (m, 4H, Et), 3.34 (q, 8H, Et), 2.74 (s, 12H, Me), 2.27 (s, 12H, Me), 1.64 (t, 12H, Et), 1.30 (t, 12H, Et), −0,68 (s, broad, OH).

Synthesis of (DPB)[Lu(OH)]$_2$·CH$_3$OH (4). Compound **4** was prepared starting from (DPB)H$_4$ (0.22 mmol) and Lu$^{\mathrm{III}}$(acac)$_3$.3H$_2$O

[†] Laboratoire de Synthèse et d'Electrosynthèse Organométalliques.

[‡] Laboratoire de Chimie Organique, Université Sidi Mohamed Ben Abdellah.

[§] Laboratoire d'Ingénierie Moléculaire pour la Séparation et les Applications des Gaz.

[‖] Laboratoire de Cristallochimie et de Chimie Structurale, Université Louis Pasteur de Strasbourg.

(1) Kurtz, D. M.; Shriver, D. F.; Klotz, I. M. *Coord. Chem. Rev.* **1977**, *24*, 140.
(2) Beinert, H. *Coord. Chem. Rev.* **1980**, *23*, 55−85.
(3) Wilkins, R. G.; Harrington, P. C. *Adv. Inorg. Biochem.* **1983**, *5*, 51−85.
(4) Sheriff, S.; Hendrick, W. A.; Smith, J. L. *J. Mol. Biol.* **1987**, *197*, 273−296.
(5) Comarmond, J.; Plumeré, P.; Lehn, J.-M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330−6340.
(6) Gaykema, W. P. J.; Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1985**, *187*, 255−275.
(7) Drew, M. G. B.; McCan, M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1868−1878.
(8) Fenton, D. E.; Casellato, U.; Vigato, P. A.; Vidali, M. *Inorg. Chim. Acta* **1982**, *62*, 57−66.
(9) Cheng, B. S.; Cukiernik, F.; Fries, P. H.; Marchon, J. C.; Scheidt, W. R. *Inorg. Chem.* **1995**, *34*, 4627−4639.
(10) Vigato, P. A.; Tamburini, S.; Fenton, D. E. *Coord. Chem. Rev.* **1990**, *106*, 25−170.
(11) Guerriero, P.; Tamburini, S.; Vigato, P. A. *Coord. Chem. Rev.* **1995**, *139*, 17−243.
(12) Nelson, S. M. *Inorg. Chim. Acta* **1982**, *102*, 6027−6050.
(13) Wong, C.-P.; Venteicher, R. F.; Horrocks Jr., W. D. *J. Am. Chem. Soc.* **1974**, *96*, 7149−7150.
(14) Buchler, J. W.; De Cian, A.; Fischer, J.; Kihn-Botulinski, M.; Paulus, H.; Weiss, R. *J. Am. Chem. Soc* **1986**, *108*, 3652−3659.
(15) Girolami, G. S.; Milam, S. N.; Suslick, K. S. *J. Am. Chem. Soc.* **1988**, *110*, 2011−2012.
(16) Lachkar, M.; De Cian, A.; Fischer, J.; Weiss, R. *New J. Chem.* **1988**, *12*, 729−731.
(17) Duchowski, J. K.; Bocian, D. F. *J. Am. Chem. Soc.* **1990**, *112*, 3312−3318.
(18) Sessler, J. L.; Burrel, A. K. *Top. Curr. Chem.* **1991**, *161*, 177−273.
(19) Sessler, J. L.; Mody, T. D.; Hemmi, G. W.; Lynch, V. *Inorg. Chem.* **1993**, *32*, 3175−3187.
(20) Stites, J. G.; McCarty, C. N.; Quill, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 3142−3143.
(21) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388−5390.
(22) Chang, C. K.; Liu, H.-Y.; Abdalmuhdi, I. *J. Am. Chem. Soc.* **1984**, *106*, 2725−2726.
(23) Eaton, S. S.; Eaton, G. R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 3177−3184.
(24) Kim, K. Ph.D. Thesis, Stanford University, Stanford, CA, 1987.
(25) Guilard, R.; Lopez, M. A.; Tabard, A.; Richard, P.; Lecomte, C.; Brandès, S.; Hutchison, J. E.; Collman, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 9877−9889.

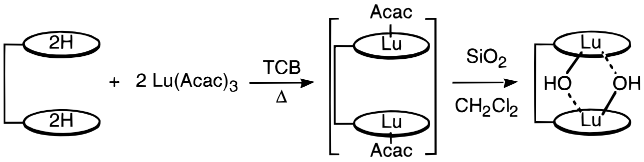
S0020-1669(96)00696-9 CCC: $14.00

Table 1. X-ray Experimental Parameters[a]

formula	$C_{162}H_{178}N_{16}O_7Cl_8Lu_4$ (**3′**)	$C_{158}H_{174}N_{16}O_7Cl_8Lu_4$ (**4′**)
M_r	3444.8	3392.8
a (Å)	18.913(5)	18.671(4)
b (Å)	14.447(4)	14.151(3)
c (Å)	28.666(8)	28.609(5)
β (deg)	91.07(2)	92.75(2)
V (Å^3)	7831.2	7550.2
data collcd	9447	8390
data obsd	6820	6254
$R(F)$	0.050	0.046
$R_w(F)$	0.075	0.073
GOF	1.625	1.665

[a] In common: color = dark blue, crystal system = monoclinic, $Z = 2$, space group = $P2_1/c$, diffractometer = Philips PW1100/16, temperature = −100 °C, radiation Cu Kα graphite monochromated.

Scheme 1



(0.57 mmol) using a similar procedure (65.6 mg; yield 27%). Anal. Calcd for $C_{76}H_{78}N_8Lu_2O_2\cdot CH_2Cl_2$**:** C, 58.89; H, 5.13; N, 7.14. Found: C, 59.18; H, 5.23; N, 7.20. DCIMS: $m/z = 1468$ ($[M - OH + 1]^+$). UV−vis (C_6H_6) [λ_{max}, nm (ϵ, 10^{-3} M^{-1} cm^{-1})]: 337 (31.2), 398 (298.7), 503 (1.4), 539 (17.3), 574 (16.5). IR (KBr): 670 cm^{-1} [Lu−OH−Lu]. ^{1}H NMR (C_6D_6) (δ, ppm): 9.66 (s, 4H, meso-H), 9.21 (s, 2H, meso-H), 7.10 (d, 2H, biphen), 6.77 (t, 2H, biphen), 6.49 (d, 2H, biphen), 4.10 (m, 4H, Et), 4.00 (m, 4H, Et), 3.60 (s, 12H, Me), 3.31 (m, 8H, Et), 2.72 (s, 12H, Me), 1.82 (t, 12H, Et), 1.24 (t, 12H, Me), 0.34 (s, broad, OH).

X-ray Experimental Section

Suitable single crystals of (DPA)[Lu(OH)]$_2\cdot$CH$_3$OH$\cdot$2CH$_2$Cl$_2\cdot$0.5H$_2$O (**3′**) and (DPB)[Lu(OH)]$_2\cdot$CH$_3$OH$\cdot$2CH$_2$Cl$_2\cdot$0.5H$_2$O (**4′**) were obtained as described in the previous section. Systematic searches in reciprocal spaces using a Philips PW1100/16 automatic diffractometer showed that the dark blue crystals of **3′** and **4′** belong to the monoclinic system.

The unit-cell dimensions and their standard deviations for both complexes were obtained and refined at −100 °C with Cu Kα radiation ($\lambda = 1.5405$ Å) by using 25 carefully selected reflections on a Philips PW1100/16 diffractometer. Table 1 reports X-ray experimental details and results.

Single crystals of 0.22 × 0.28 × 0.32 and 0.21 × 0.27 × 0.32 mm^3 dimensions for **3′** and **4′**, respectively, were cut out from a cluster of crystals, glued at the end of a glass wire, and mounted on a rotation-free goniometer head. All quantitative data were obtained at −100 °C achieved with a local-build gas flow device on the same diffractometer using graphite monochromated radiation. Totals of 9447 $\pm h+k+l$ (**3′**) and 8390 $\pm h+k+l$ (**4′**) reflections were recorded (3° $< \theta <$ 52° (**3′**), 50° (**4′**)). The resulting data sets were transfered to a DEC-AXP3600S computer, and for all subsequent calculations the Nonius MolEN package[26] was used with the exception of a local data reduction program.

Three standard reflections measured every 1 h during the entire data collection period showed no significant trend. The raw step-scan data were converted to intensities using the Lehmann−Larsen[27] method and then corrected for Lorentz and polarization factors. A unique data set of 6820 (**3′**) and 6254 (**4′**) reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structures were solved using the heavy atom method. After refinements of the heavy atoms, difference-Fourier maps revealed maxima of residuals electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations as fixed contributors (C−H = 0.95 Å) and isotropic temperature factors such as $B(H) = 1.3B_{eqv}(C)$ Å^2. At this stage empirical absorption corrections were applied using the method of Walker and Stuart[28] since the face indexation was not possible under the cold gas stream. Full least-squares refinements against F converged to $R(F) = 0.050/0.046$ and $R_w(F) = 0.075/0.073$ for **3′** and **4′**, respectively ($w = 1/\sigma(F^2)$, $\sigma^2(F^2) = \sigma_{counts}{}^2 + (pI)^2$). Final difference maps revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come from ref 29.

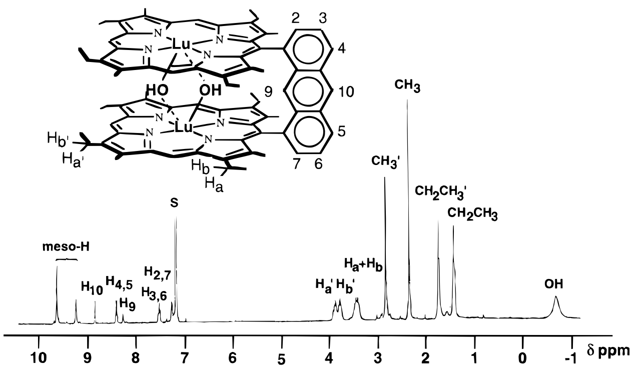


Figure 2. ^{1}H NMR spectrum of (DPA)[Lu(OH)]$_2\cdot$CH$_3$OH recorded at 294 K in C$_6$D$_6$.

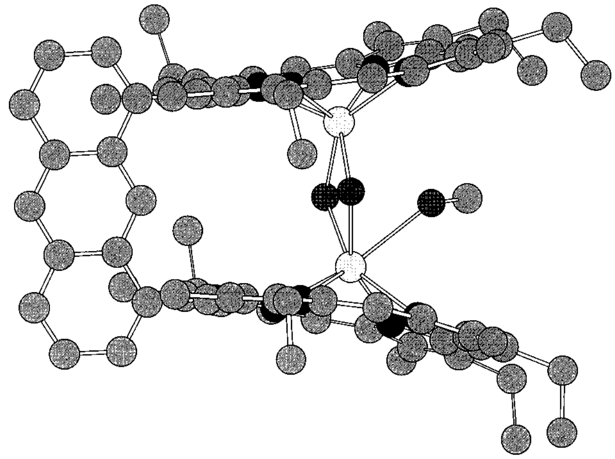


Figure 3. Stick and ball model for (DPA)[Lu(OH)]$_2\cdot$CH$_3$OH.

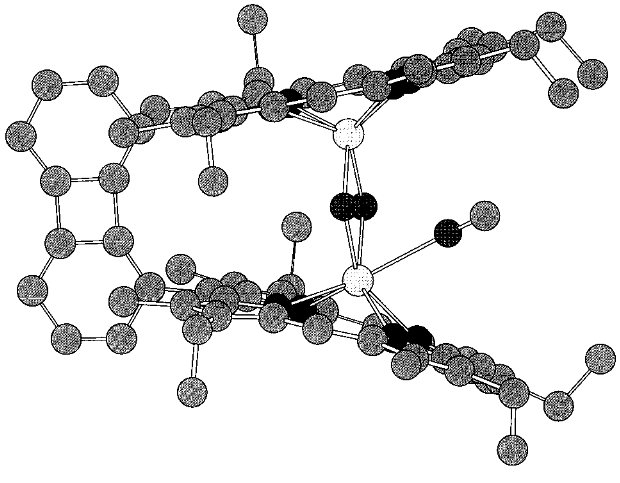


Figure 4. Stick and ball model for (DPB)[Lu(OH)]$_2\cdot$CH$_3$OH.

---

(26) Fair, C. K. *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*; Enraf-Nonius: Delft, The Netherlands, 1990.

(27) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr.* **1974**, *A30*, 580−584.

(28) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166.

(29) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, 2nd ed.; The Kynoch Press: Birmingham, U.K., 1974: (a) Table 2.2b; (b) Table 2.3.1.

Table 2. UV−Visible Data for the $(DP)H_4$ Free Bases and the $(DP)[Lu(OH)]_2{\cdot}CH_3OH$ Complexes in C_6H_6

	λ_{max}, nm (ϵ, 10^{-3} M^{-1} cm^{-1})				
	Soret region	*Q* bands			
compds		Q_y(1,0) band IV	Q_y(0,0) band III	Q_x(1,0) band II	Q_x(0,0) band I
$(DPA)H_4$	395 (190.5)	506 (14.1)	539 (5.1)	578 (6.0)	631 (3.3)
$(DPA)[Lu(OH)]_2{\cdot}CH_3OH$	402 (274.6)	501 (1.7)	538 (21.3)	575 (21.2)	
$(DPB)H_4$	379 (173.9)	511 (6.3)	540 (2.0)	580 (3.4)	632 (1.8)
$(DPB)[Lu(OH)]_2{\cdot}CH_3OH$	398 (298.7)	503 (1.4)	539 (17.3)	574 (16.5)	

Table 3. Atomic Coordinates and Thermal Equivalent Parameters for $(DPA)[Lu(OH)]_2{\cdot}CH_3OH{\cdot}2CH_2Cl_2{\cdot}0.5H_2O$ (**3′**)

atom	*x*	*y*	*z*	B^a (Å^2)	atom	*x*	*y*	*z*	B^a (Å^2)
Lu1	0.31439(2)	0.19350(3)	0.12435(2)	3.58(1)	C53	0.1031(6)	0.4661(8)	−0.0141(3)	6.2(3)
Lu2	0.16907(2)	0.34593(3)	0.12622(2)	3.47(1)	C54	0.1379(5)	0.4748(7)	0.0309(3)	5.0(2)
C1	0.3853(5)	0.1982(7)	0.2291(3)	4.5(2)	C55	0.1835(6)	0.5454(8)	0.0456(4)	6.0(3)
C2	0.3694(5)	0.1767(7)	0.2776(3)	4.6(2)	C56	0.2094(5)	0.5601(6)	0.0904(4)	4.9(2)
C3	0.3185(5)	0.1113(7)	0.2776(3)	3.9(2)	C57	0.2475(6)	0.6394(7)	0.1050(4)	5.9(3)
C4	0.3008(4)	0.0900(6)	0.2280(3)	3.6(2)	C58	0.2598(5)	0.6291(7)	0.1538(4)	5.6(3)
C5	0.2531(4)	0.0252(6)	0.2109(3)	3.5(2)	C59	0.2261(5)	0.5419(6)	0.1665(4)	4.4(2)
C6	0.2378(4)	0.0042(6)	0.1636(3)	3.4(2)	C60	0.2182(5)	0.5106(7)	0.2108(4)	4.6(2)
C7	0.1830(5)	−0.0557(6)	0.1451(3)	3.8(2)	N61	0.1366(4)	0.3799(5)	0.2009(2)	3.6(2)
C8	0.1871(5)	−0.0551(6)	0.0982(3)	3.8(2)	N62	0.0585(4)	0.2801(5)	0.1332(2)	3.4(2)
C9	0.2462(5)	0.0043(7)	0.0867(3)	4.1(2)	N63	0.1145(4)	0.4029(6)	0.0595(3)	4.6(2)
C10	0.2714(5)	0.0198(6)	0.0414(3)	4.2(2)	N64	0.1956(4)	0.5012(5)	0.1279(3)	4.6(2)
C11	0.3271(5)	0.0736(7)	0.0283(3)	4.3(2)	C65	0.2156(6)	0.4566(8)	0.3154(4)	6.1(3)
C12	0.3590(6)	0.0744(7)	−0.0177(3)	5.6(2)	C66	0.2874(6)	0.411(1)	0.3189(4)	8.8(4)
C13	0.4163(5)	0.1327(7)	−0.0152(4)	5.1(2)	C67	0.1038(6)	0.3012(8)	0.3255(4)	5.6(3)
C14	0.4180(5)	0.1666(6)	0.0308(3)	4.5(2)	C69	−0.0565(6)	0.0912(8)	0.1823(4)	5.7(3)
C15	0.4716(6)	0.2256(7)	0.0489(4)	5.3(2)	C71	−0.0756(5)	0.1248(8)	0.0760(4)	5.4(3)
C16	0.4806(5)	0.2547(7)	0.0955(4)	5.4(3)	C72	−0.1498(6)	0.1661(9)	0.0763(4)	6.9(3)
C17	0.5388(5)	0.3056(8)	0.1134(5)	6.4(3)	C73	0.0129(7)	0.356(1)	−0.0527(4)	7.7(4)
C18	0.5288(6)	0.3146(9)	0.1607(4)	6.4(3)	C75	0.1189(7)	0.533(1)	−0.0538(4)	8.2(3)
C19	0.4655(5)	0.2687(7)	0.1690(3)	4.9(2)	C76	0.1867(9)	0.512(1)	−0.0781(5)	10.5(4)
C20	0.4388(5)	0.2560(8)	0.2139(4)	5.9(3)	C77	0.2730(7)	0.7184(8)	0.0752(4)	7.3(3)
N21	0.3422(4)	0.1452(5)	0.1997(3)	4.0(2)	C78	0.3448(8)	0.702(1)	0.0557(5)	9.6(4)
N22	0.2750(4)	0.0431(5)	0.1272(2)	3.8(2)	C79	0.2970(8)	0.6906(9)	0.1865(5)	8.9(4)
N23	0.3640(4)	0.1325(5)	0.0580(3)	4.0(2)	C81	0.2160(4)	−0.0342(6)	0.2462(3)	3.5(2)
N24	0.4337(4)	0.2343(6)	0.1302(3)	4.4(2)	C82	0.2445(5)	−0.1158(6)	0.2603(3)	3.5(2)
C25	0.4081(6)	0.2200(9)	0.3177(4)	6.0(3)	C83	0.2097(5)	−0.1718(6)	0.2927(3)	4.4(2)
C26	0.4744(7)	0.168(1)	0.3313(5)	8.7(4)	C84	0.1484(5)	−0.1451(6)	0.3114(3)	3.7(2)
C27	0.2874(5)	0.0734(8)	0.3216(3)	5.1(2)	C85	0.1165(4)	−0.0610(6)	0.2984(3)	3.3(2)
C29	0.1280(6)	−0.1105(8)	0.1698(4)	5.4(2)	C86	0.1514(4)	−0.0038(6)	0.2651(3)	3.2(2)
C31	0.1386(5)	−0.1005(7)	0.0641(4)	4.9(2)	C87	0.1196(4)	0.0788(6)	0.2520(3)	3.4(2)
C32	0.0688(6)	−0.0452(9)	0.0586(4)	6.8(3)	C88	0.0554(4)	0.1082(6)	0.2688(3)	3.2(2)
C33	0.3334(7)	0.011(1)	−0.0583(4)	7.0(3)	C89	0.0213(4)	0.0519(6)	0.3024(3)	3.7(2)
C35	0.4684(6)	0.1483(8)	−0.0524(4)	6.1(3)	C90	0.0525(5)	−0.0311(6)	0.3161(3)	3.9(2)
C36	0.5321(6)	0.0877(8)	−0.0481(4)	7.3(3)	C91	−0.0431(5)	0.0834(7)	0.3216(3)	4.2(2)
C37	0.6027(7)	0.3373(9)	0.0837(5)	7.6(3)	C92	−0.0722(5)	0.1636(7)	0.3081(3)	4.3(2)
C38	0.6598(7)	0.265(2)	0.0844(6)	12.7(6)	C93	−0.0398(5)	0.2182(6)	0.2734(3)	3.9(2)
C39	0.5768(7)	0.362(1)	0.1951(5)	10.3(4)	C94	0.0223(4)	0.1932(6)	0.2545(3)	3.3(2)
C41	0.1781(5)	0.4388(6)	0.2279(3)	4.0(2)	O1	0.2043(4)	0.2155(5)	0.0958(3)	6.1(2)
C42	0.1717(5)	0.4147(7)	0.2765(3)	4.3(2)	O2	0.2701(4)	0.3113(5)	0.1631(3)	6.2(2)
C43	0.1249(5)	0.3441(6)	0.2795(3)	4.2(2)	C95	0.1911(8)	0.214(1)	−0.0267(5)	8.5(4)
C44	0.1027(4)	0.3216(6)	0.2316(3)	3.2(2)	Cl1	0.1336(3)	0.1233(3)	−0.0406(2)	10.6(1)
C45	0.0554(4)	0.2516(6)	0.2168(3)	3.3(2)	Cl2	0.2395(3)	0.2451(3)	−0.0771(2)	11.0(1)
C46	0.0350(4)	0.2324(6)	0.1703(3)	3.6(2)	C96	0.456(1)	0.003(1)	0.1679(9)	7.2(6)
C47	−0.0171(5)	0.1634(6)	0.1545(3)	3.8(2)	Cl3	0.4323(3)	−0.1137(4)	0.1730(2)	13.7(2)
C48	−0.0256(5)	0.1753(6)	0.1081(3)	4.3(2)	Cl4	0.5405(4)	0.0124(7)	0.1795(4)	13.4(3)
C49	0.0220(5)	0.2473(6)	0.0950(3)	3.7(2)	O3	0.3086(6)	0.3431(8)	0.0784(4)	7.3(3)
C50	0.0271(5)	0.2822(7)	0.0492(4)	5.1(2)	C97	0.312(1)	0.363(2)	0.033(1)	8.4(7)
C51	0.0655(5)	0.3544(7)	0.0324(3)	4.6(2)	OW	0.486(1)	0.445(2)	−0.0297(7)	10.9(6)
C52	0.0585(6)	0.3917(8)	−0.0137(4)	5.8(3)					

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Results and Discussion

The bis(lutetium) porphyrins **3** and **4** were synthesized by reacting the free bases **1** and **2**, respectively, with lutetium tris(acetylacetonate) in TCB according to Scheme 1.

The reaction progress was monitored by recording the UV−visible absorption spectra. Completion of the reaction, which generally occured within 16−17 h, was indicated by the complete disappearance of the absorption at 630 nm and the intensity increase of the bands at 538 and 575 nm. Simultaneously the Soret band was slightly shifted.

The bis(lutetium(III)) complexes were isolated as red stable powders, which present the following $(DP)[Lu(OH)]_2{\cdot}CH_3OH$ formulation on the basis of mass spectral data. In DCI ionization mode, the molecular peak for the DPB complex is observed at $m/z = 1485$ (50%). The observed base peak at $m/z = 1468$ corresponds to the $[M - OH + 1]^+$ fragment for

Table 4. Atomic Coordinates and Thermal Equivalent Parameters for (DPB)[Lu(OH)]$_2$·CH$_3$OH·2CH$_2$Cl$_2$·0.5H$_2$O (**4′**)

atom	*x*	*y*	*z*	B^a (Å^2)	atom	*x*	*y*	*z*	B^a (Å^2)
Lu1	0.31565(2)	0.17914(3)	0.13134(2)	2.76(1)	C48	0.0524(5)	0.3758(7)	−0.0067(3)	3.9(2)
Lu2	0.16828(2)	0.33461(3)	0.13352(2)	2.83(1)	C49	0.0947(5)	0.4545(6)	−0.0076(3)	4.0(2)
C1	0.3813(5)	0.1777(6)	0.2393(3)	4.1(2)	C50	0.1286(5)	0.4635(6)	0.0385(3)	3.4(2)
C2	0.3645(5)	0.1548(7)	0.2866(3)	4.0(2)	C51	0.1735(5)	0.5361(6)	0.0533(3)	3.7(2)
C3	0.3070(5)	0.0974(6)	0.2851(3)	3.7(2)	C52	0.2017(4)	0.5529(6)	0.0982(3)	3.6(2)
C4	0.2878(4)	0.0816(6)	0.2347(3)	3.0(2)	C53	0.2446(5)	0.6334(6)	0.1146(3)	4.0(2)
C5	0.2334(4)	0.0226(6)	0.2164(3)	2.9(2)	C54	0.2573(5)	0.6227(6)	0.1613(4)	4.8(2)
C6	0.2203(4)	−0.0018(6)	0.1681(3)	2.9(2)	C55	0.2225(5)	0.5351(6)	0.1737(3)	4.1(2)
C7	0.1650(4)	−0.0599(6)	0.1478(3)	3.2(2)	C56	0.2187(5)	0.4999(7)	0.2200(3)	4.6(2)
C8	0.1745(4)	−0.0649(5)	0.1010(3)	2.7(2)	N57	0.1409(4)	0.3604(5)	0.2097(2)	3.4(2)
C9	0.2385(5)	−0.0103(6)	0.0928(3)	3.2(2)	N58	0.0614(4)	0.2561(5)	0.1399(2)	3.1(2)
C10	0.2708(5)	−0.0037(6)	0.0495(3)	3.6(2)	N59	0.1088(3)	0.3912(5)	0.0663(2)	3.1(2)
C11	0.3317(4)	0.0471(6)	0.0390(3)	3.2(2)	N60	0.1904(4)	0.4932(5)	0.1359(3)	3.4(2)
C12	0.3681(5)	0.0393(6)	−0.0058(3)	3.9(2)	C61	0.2250(5)	0.4402(8)	0.3251(3)	5.1(2)
C13	0.4250(5)	0.0947(7)	−0.0012(3)	4.4(2)	C62	0.2975(7)	0.395(1)	0.3306(4)	8.5(4)
C14	0.4252(5)	0.1374(7)	0.0450(3)	4.1(2)	C63	0.1250(5)	0.2664(8)	0.3328(3)	5.1(2)
C15	0.4789(5)	0.1998(7)	0.0640(3)	4.0(2)	C64	−0.0549(5)	0.0659(7)	0.1903(3)	4.5(2)
C16	0.4858(4)	0.2317(6)	0.1096(3)	3.7(2)	C65	−0.0813(5)	0.1029(7)	0.0843(3)	3.9(2)
C17	0.5444(5)	0.2865(7)	0.1290(4)	4.8(2)	C66	−0.1536(6)	0.1569(8)	0.0814(4)	6.0(3)
C18	0.5327(5)	0.2987(7)	0.1755(3)	4.6(2)	C67	0.0052(5)	0.3368(7)	−0.0460(4)	4.3(2)
C19	0.4669(5)	0.2479(6)	0.1834(3)	4.0(2)	C68	0.1038(6)	0.5215(7)	−0.0476(4)	5.2(3)
C20	0.4390(5)	0.2340(7)	0.2271(3)	4.3(2)	C69	0.1702(6)	0.4996(9)	−0.0742(4)	6.9(3)
N21	0.3338(3)	0.1321(5)	0.2081(2)	3.1(2)	C70	0.2686(6)	0.7115(7)	0.0827(4)	5.9(3)
N22	0.2644(3)	0.0302(5)	0.1333(2)	3.2(2)	C71	0.3354(7)	0.6877(8)	0.0582(5)	7.0(3)
N23	0.3672(4)	0.1064(5)	0.0684(2)	3.2(2)	C72	0.2976(7)	0.6873(8)	0.1949(5)	7.9(3)
N24	0.4370(4)	0.2118(5)	0.1431(2)	3.4(2)	C73	0.1887(4)	−0.0306(6)	0.2499(3)	2.9(2)
C25	0.4100(5)	0.1852(8)	0.3291(4)	5.3(3)	C74	0.2134(5)	−0.1235(6)	0.2631(3)	3.8(2)
C26	0.4739(6)	0.119(1)	0.3383(4)	7.5(3)	C75	0.1785(5)	−0.1768(6)	0.2944(3)	4.1(2)
C27	0.2748(5)	0.0576(7)	0.3278(3)	4.5(2)	C76	0.1156(5)	−0.1478(6)	0.3158(3)	3.7(2)
C28	0.1025(5)	−0.1072(8)	0.1704(3)	5.0(2)	C77	0.0940(5)	−0.0598(6)	0.3033(3)	3.4(2)
C29	0.1294(5)	−0.1131(7)	0.0649(3)	4.1(2)	C78	0.1281(4)	−0.0034(5)	0.2697(3)	2.8(2)
C30	0.0622(5)	−0.0543(8)	0.0516(4)	5.1(3)	C79	0.0705(4)	0.0729(6)	0.2752(3)	3.0(2)
C31	0.3438(6)	−0.0204(8)	−0.0463(4)	5.9(3)	C80	0.0375(5)	0.0154(6)	0.3089(3)	3.5(2)
C32	0.4823(6)	0.1126(8)	−0.0378(4)	5.9(3)	C81	−0.0224(5)	0.0411(7)	0.3316(3)	3.9(2)
C33	0.4639(7)	0.207(1)	−0.0622(5)	7.6(3)	C82	−0.0511(5)	0.1297(8)	0.3184(3)	4.4(2)
C34	0.6078(5)	0.3236(9)	0.1034(4)	6.2(3)	C83	−0.0212(5)	0.1848(6)	0.2852(3)	3.9(2)
C35	0.6679(8)	0.267(1)	0.1097(7)	12.3(5)	C84	0.0414(5)	0.1572(6)	0.2611(3)	3.4(2)
C36	0.5789(6)	0.3488(9)	0.2114(4)	6.8(3)	O1	0.2069(3)	0.2083(4)	0.0979(2)	3.7(1)
C37	0.1833(5)	0.4224(6)	0.2373(3)	3.9(2)	O2	0.2760(3)	0.3059(5)	0.1658(3)	5.8(2)
C38	0.1819(5)	0.3963(6)	0.2850(3)	3.8(2)	Cl1	0.1494(2)	0.1283(3)	−0.0366(1)	8.17(9)
C39	0.1398(5)	0.3184(6)	0.2879(3)	3.9(2)	Cl2	0.2687(2)	0.2492(3)	−0.0542(2)	12.0(1)
C40	0.1152(4)	0.2957(6)	0.2392(3)	3.1(2)	Cl3	0.5790(3)	0.3644(3)	0.3420(2)	10.2(1)
C41	0.0681(4)	0.2199(6)	0.2242(3)	3.1(2)	Cl4	0.4670(2)	0.4908(4)	0.3188(3)	14.9(2)
C42	0.0419(4)	0.2065(6)	0.1782(3)	3.0(2)	C85	0.2008(6)	0.2258(9)	−0.0183(4)	6.8(3)
C43	−0.0143(5)	0.1362(6)	0.1624(3)	3.5(2)	C86	0.5530(7)	0.4789(8)	0.3366(5)	7.7(3)
C44	−0.0248(5)	0.1508(6)	0.1164(3)	3.4(2)	O3	0.3259(5)	0.3160(6)	0.0774(4)	10.9(3)
C45	0.0212(4)	0.2253(6)	0.1024(3)	3.1(2)	C87	0.3441(9)	0.388(1)	0.0640(8)	28.2(6)
C46	0.0224(5)	0.2620(6)	0.0567(3)	3.6(2)	OW	0.508(1)	0.541(1)	0.0149(6)	11.0(5)
C47	0.0611(5)	0.3391(6)	0.0405(3)	3.2(2)					

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

the DPB complex while the base peak at $m/z = 1479$ is the $[M - 2(OH) + 1]^+$ fragment for the DPA derivative.

UV−visible data of the free bases (DPA)H$_4$ and (DPB)H$_4$ and the bis(lutetium) bis(porphyrins) (DPA)[Lu(OH)]$_2$·CH$_3$OH and (DPB)[Lu(OH)]$_2$·CH$_3$OH are given in Table 2. A typical UV−visible spectrum of the porphyrin metal-free base (DP)H$_4$ exhibits an intense absorption Soret band close to 400 nm due to a $\pi-\pi^*$ transition[30,31] and four satellite bands, labeled I−IV, located between 500 and 700 nm. These four bands have optical density values according to the sequence IV > II > III > I which corresponds to a so-called "phyllo" type spectrum.[32] The coordination of a metal ion to the porphyrin core induces significant changes in the electronic spectra. These are disappearance of the band at 630 nm and increase of the intensity of the two middle bands at 538 and 575 nm as well as a large bathochromic shift for the Soret band (7 nm for **3** and 19 nm for **4**).[33] These two latter different shifts are attributable to the inter-ring distance; the larger shift is observed for the DPB derivative where the $\pi-\pi$ system interaction is stronger due to a smaller interplanar distance.[34−37]

Characteristic IR spectra of bimetallic species are observed. Bands at ≈1510 and ≈1595 cm^{-1} which are typical of acetylacetonato complexes are not observed.[38] In contrast the

---

(30) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138−163.

(31) Abdalmuhdi, I. O. Ph.D. Thesis, Michigan State University, East Lansing, MI, 1986.

(32) Smith, K. M. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific: Amsterdam, 1975; p 3.

(33) Wong, C.-P. *Inorg. Synth.* **1983**, *22*, 156−162.

(34) Collman, J. P.; Chong, A. O.; Jamieson, G. B.; Oakley, R. T.; Rose, E.; Schmittou, E. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 516−533.

(35) Chang, C. K.; Kuo, M.-S.; Wang, C.-B. *J. Heterocycl. Chem.* **1977**, *14*, 943−945.

(36) Chang, C. K. *J. Heterocycl. Chem.* **1977**, *14*, 1285−1288.

(37) Kagan, N. E.; Mauzerall, D.; Merrifield, R. B. *J. Am. Chem. Soc.* **1977**, *99*, 5484−5486.

(38) Buchler, J. W.; Eikelmann, G.; Puppe, L.; Rohbock, K.; Schneehage, H. H.; Weck, D. *Liebigs Ann. Chem.* **1971**, *745*, 135−151.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for $\mathrm{(DPA)[Lu(OH)]_2 \cdot CH_3OH \cdot 2CH_2Cl_2 \cdot 0.5H_2O}$ (**3′**) and $\mathrm{(DPB)[Lu(OH)]_2 \cdot CH_3OH \cdot 2CH_2Cl_2 \cdot 0.5H_2O}$ (**4′**)

distances			angles		
	3′	**4′**		**3′**	**4′**
Lu1-Np	2.316(5)	2.316(5)	Lu1−O1−Lu2	105.3(1)	105.2(1)
Lu2−Np	2.301(5)	2.298(5)	Lu1−O2−Lu2	105.4(1)	106.4(1)
Lu1−O1	2.245(4)	2.241(4)	O1−Lu1−O2	73.5(2)	73.9(1)
Lu2−O1	2.186(4)	2.196(3)	O1−Lu2−O2	74.3(2)	74.4(1)
Lu1−O2	2.206(4)	2.193(4)	Cα−Np−Cα	105.6(8)	106.2(8)
Lu2−O2	2.223(4)	2.211(4)	Np−Cα−C*β*	110.4(8)	110.1(8)
N−Cα	1.381(7)	1.367(7)	Np−Cα−Cm	123.8(8)	124.4(8)
Cα−C*β*	1.441(8)	1.453(8)	Cα−C*β*−C*β*	106.7(8)	106.7(9)
C*β*−C*β*	1.367(8)	1.351(8)	Cα−Cm−Cα	128.3(8)	127.7(8)
Cα−Cm	1.394(8)	1.402(8)			

IR spectra of **3** and **4** exhibit an OH stretching absorption at 3678 $\mathrm{cm^{-1}}$ and a characteristic vibration located at 672 $\mathrm{cm^{-1}}$ for **3** and 670 $\mathrm{cm^{-1}}$ for **4**, indicating the presence of a μ-hydroxo bridging group. Similar infrared frequencies have been already reported for the tetraphenylporphyrin dimer $\mathrm{[(TPP)Lu(OH)]_2 \cdot H_2O}$[39] and agree well with a $\mathrm{[Lu{-}(OH)_2{-}Lu]}$ coordination scheme.

Figure 2 shows the ^{1}H NMR spectrum of $\mathrm{(DPA)[Lu(OH)]_2 \cdot CH_3OH}$. The chemical shift spectral range is characteristic of a diamagnetic complex. The disappearence of the pyrrole NH resonance at high field unambiguously demonstrates the coordination of the two macrocycles. In the positive chemical shift region, no significant change is observed when the bis(lutetium) complex spectra and those of the starting free-base macrocycles are compared. Only the relative positions of the two meso proton signals are reversed compared to those of the corresponding free bases. The suggested $\mathrm{(DP)[Lu(OH)]_2 \cdot CH_3OH}$ formula is confirmed by the X-ray crystal structure.

Crystal Structures of $\mathrm{(DPA)[Lu(OH)]_2 \cdot CH_3OH \cdot 2CH_2Cl_2 \cdot 0.5H_2O}$ (3′) and $\mathrm{(DPB)[Lu(OH)]_2 \cdot CH_3OH \cdot 2CH_2Cl_2 \cdot 0.5H_2O}$ (4′). Figures 3 and 4 display stick and ball models of the cofacial porphyrin complexes $\mathrm{(DPA)[Lu(OH)]_2 \cdot CH_3OH}$ (**3**) and $\mathrm{(DPB)[Lu(OH)]_2 \cdot CH_3OH}$ (**4**) as found in the crystals of **3′** and **4′**. Tables 3 and 4 list the coordinates of all independent non-hydrogen atoms present in the unit cells of **3′** and **4′**, respectively. Table 5 gives selected bond lengths, bond angles, and means. The crystal structures of **3′** and **4′** consist of packings of four bis(porphyrin) complexes **3** and **4** with eight $\mathrm{CH_2Cl_2}$ and two water molecules of solvation. The overall geometries of the bis(porphyrin) ligands are similar to those already known for $\mathrm{(DPB)Co_2}$,[40] $\mathrm{(DPB)CoAl(OC_2H_5)}$,[25] $\mathrm{(DPA)M_2}$ and $\mathrm{(DPB)M_2}$ (M = Cu, Ni),[41] (DPB)CuMnCl,[42] and $\mathrm{[(DPA')Fe_2(\mu\text{-}im)(Him)_2]Cl}$.[43] In **3** and **4**, the two lutetium atoms are bridged by two $\mathrm{OH^-}$ anions. A molecule of methanol is also weakly bonded to one of the metal atoms. Thus, one lutetium atom is hexacoordinated whereas the other is heptacoordinated. A second alternative concerning the proton distributions in **3** and **4** has also been examined. Indeed, the overall charge of **3** and **4** would remain unchanged if one of the bridging groups would be a water molecule and the seventh ligand of Lu1 would be a methoxy anion. This alternative has been excluded on the basis of the Lu−O bond distances: The four Lu−O distances which range from 2.186(4) to 2.245(4) Å in **3** and from 2.193(4) to 2.241(4) Å in **4** are very similar, despite the different coordination numbers of the two metal atoms. Furthermore, the mean values of these distances, 2.215(9) Å in **3** and 2.210(7) Å in **4**, are clearly shorter than the mean value of the two $\mathrm{Lu{-}OH_2}$ distances present in $\mathrm{(Pc)Lu(OAc)(H_2O)_2}$[44] (2.331(7) Å). Moreover, the Lu1−O bond distance of 2.531(11) Å in **3** and 2.489(9) Å in **4** is quite long, a fact which is not in favor of a methoxy anion as a ligand bound to Lu1.

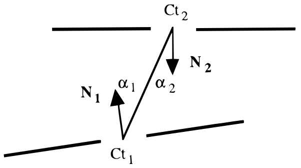
Table 6. Conformational Parameters for Cofacial Metalloporphyrins[a]

compds	Ct−Ct (Å)	tilt (deg)	α (deg)	Sr (Å)	Sp (Å)	ref
$\mathrm{(DPA)Ni_2}$	4.56	2.4	31.7	3.87	2.39	41
$\mathrm{(DPA)[Lu(OH)]_2 \cdot CH_3OH}$	5.67	19.7	14.1	5.49	1.39	this work
$\mathrm{(DPB)Cu_2}$	3.86	4.4	25.0	3.50	1.63	41
(DPB)CuMnCl	3.94	5.2	25.8	3.54	1.71	42
(DPB)CoAl(OEt)	4.08	7.4	29.8	3.54	2.03	25
$\mathrm{(DPB)[Lu(OH)]_2 \cdot CH_3OH}$	5.54	27.1	13.9	5.38	1.33	this work
$\mathrm{[(DPA')Fe_2(\mu\text{-}im)(Him)_2]Cl}$	5.96	28.4	14.2	5.78	1.46	43

[a] If $\mathbf{N}_i$ (i = 1, 2) is the unit vector normal to the 24-atom average plane and $\mathbf{Ct_1Ct_2}$ is the vector joining the two four nitrogen centers then

$$\cos(\alpha_i) = \frac{\mathbf{N_i} \cdot \mathbf{Ct_1Ct_2}}{|\mathbf{Ct_1Ct_2}|}$$

The slip angle α is calculated as the average of α_1 and α_2, the slip parameter being $\mathrm{Sp} = |\mathbf{Ct_1Ct_2}| \sin(\alpha)$. The inter-ring separation is defined by $\mathrm{Sr} = |\mathbf{Ct_1Ct_2}| \cos(\alpha)$.[25]



With the exception of the $\mathrm{[(DPA')Fe_2(\mu\text{-}im)(Him)_2]Cl}$ derivative, the structures of **3** and **4** are the only yet known structures having one or several bridging ligands bonded to metals which are bonded to cofacial porphyrins. The angles between the two 24-atom core mean planes of the porphyrin macrocycles are 19.7(2) and 27.1(1)° in **3** and **4**, respectively. These angles are, as expected, larger than those found in $\mathrm{(DPA)Ni_2}$ (2.4°) and (DPB)CuAl(OEt) (7.4°) which contain no bridging ligands and are similar to that found in $\mathrm{[(DPA')Fe_2(\mu\text{-}im)(Him)_2]Cl}$ (28.4°; see Table 6). Other conformational parameters are also affected as seen from Table 6. For instance, the openings of the cofacial porphyrins defined as the distances between the methine carbon atoms of the two macrocycles which are directly linked to the spacers and their trans methine carbon atoms are 4.97 and 7.14 Å in **3** and 4.17 and 7.42 Å in **4**. The anthracenyl and biphenylenyl connectors are planar within experimental errors: Maximum deviations from planarity are 0.026(8) and 0.057(8) Å in **3** and **4**, respectively. As in $\mathrm{[(DPA')Fe_2(\mu\text{-}im)(Him)_2]Cl}$, and in contrast to the nonbridged derivatives, the mean planes of the connector units are nearly orthogonal to the porphyrin core mean planes: The dihedral angles between these mean planes deviate from 90° by 1.7(1) and 1.7(1)° in **3** and 6.1(1) and 2.9(1)° in **4**. The metal−metal distances are 3.523(6) and 3.526(6) Å in **3** and **4**, respectively. The different coordination numbers of the metals lead to slightly different $\mathrm{Lu{-}N_p}$ distances: $\mathrm{Lu1{-}N_p}$ has a mean value of 2.316(5) Å, and Lu2−

---

(39) Unpublished results.

(40) Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Tabard, A.; Guilard, R.; Seok, W. K.; Ibers, J. A.; L'Her, M. *J. Am. Chem. Soc.* **1992**, *114*, 9869−9877.

(41) Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417−424.

(42) Guilard, R.; Brandès, S.; Tabard, A.; Bouhmaida, N.; Lecomte, C.; Richard, P.; Latour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 10202−10211.

(43) Naruta, Y.; Sawada, N.; Tadokoro, M. *Chem. Lett.* **1994**, 1713−1716. $\mathrm{(DPA')^{4-}}$ = the anion of 1,8-bis[5-(2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-15-phenyl)porphyrin]anthracene; im = imidazolate.

(44) De Cian, A.; Moussavi, M.; Fisher, J.; Weiss, R. *Inorg. Chem.* **1985**, *24*, 3162−3167.

N_p, a mean value of 2.301(7) Å in **3**. These values are equal to 2.316(5) and 2.298(5) Å in **4**. The average Lu−N_p distances are in **3** and **4** slightly shorter than those present in the phthalocyanine derivatives (Pc)Lu(OAc)$(H_2O)_2$ (2.345(2) Å) and $(Pc)_2Lu{\cdot}CH_2Cl_2$ (2.380(2) Å) in which the metals are octacoordinated.[44] The out-of-plane displacements of the metal atoms of 1.35 and 1.26 Å away from the $4N_{iso}$ mean planes are also larger in these phthalocyanine complexes.[44] The porphyrin macrocycles have a convex shape in both complexes, the metal atoms being out of the 24-atom core mean planes of the rings by 1.236(5), 1.196(5) (**3**) and 1.224(1), 1.123(4) Å (**4**). These macrocycles are domed with some ruffling. Within experimental errors, the pyrrole rings are planar (largest deviations are 0.019(7) Å in **3** and 0.025(7) Å in **4**). The dihedral angles of the pyrrole rings with the 24 atom core mean planes of the rings range from 3.9 to 10.0° (Lu1 macrocycle) and from 4.4 to 9.6° (Lu2 macrocycle) in **3.** They range from 1.8 to 11.5° (Lu1 macrocycle) and from 3.6 to 7.1° (Lu2 macrocycle) in **4**. The bond distances and bond angles in the ligands and the solvate molecules have the normal expected values (see Table 5). There are no unusual intermolecular contacts.

Supporting Information Available: For **3′** and **4′**, ORTEP plots with labeling schemes, X-ray experimental data (Tables SI and SII), temperature factors for anisotropic atoms (Tables SIII and SIV), hydrogen atoms positional parameters (Tables SV and SVI), complete bond distances and bond angles (Tables SVII and SVIII), an IR spectrum of (DPA)$[Lu(OH)]_2{\cdot}CH_3OH$ (Figure SIX), and deviations of the porphyrinic core atoms from the 24 core atoms mean planes for (DPA)$[Lu(OH)]_2{\cdot}CH_3OH$ and (DPB)$[Lu(OH)]_2{\cdot}CH_3OH$ (Figures SX and SXI) (36 pages). Ordering information is given on any current masthead page. Tables SI−SVIII have been deposited on the CCDC and are available on request from the Director of Cambridge Crystallographic Data Center, 12 Union Road, GB-Cambridge CB2 1EZ, U.K., on quoting the full journal citation.

IC960696Q