

Relationship between the Skew Angle and Interplanar Distance in Four Bis(phthalocyaninato)lanthanide(III) Tetrabutylammonium Salts ([NBuⁿ]₄][Ln^{III}Pc₂]; Ln = Nd, Gd, Ho, Lu)

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Received February 14, 1996[⊗]

Four crystal structures of the title complexes have been analyzed by X-ray crystallography. **1:** C₈₀H₆₈N₁₇Nd, *a* = 17.0545(6) Å, *c* = 22.807(3) Å, tetragonal, *P4/ncc*, *Z* = 4. **2:** C₈₀H₆₈N₁₇Gd, *a* = 17.399(8) Å, *c* = 11.377(6) Å, tetragonal, *P42₁2*, *Z* = 2. **3:** C₈₀H₇₀N₁₇OHo, *a* = 18.096(5) Å, *c* = 11.079(6) Å, tetragonal, *P42₁2*, *Z* = 4. **4:** C₈₀H₇₀N₁₇OLu, *a* = 18.171(3) Å, *c* = 10.987(4) Å, tetragonal, *P4/nmm*, *Z* = 2. The [Ln^{III}Pc₂][−] and [NBuⁿ]₄⁺ ions in each crystal stack alternately in a column along the 4-fold axis. The Ln(III) cation of each [Ln^{III}Pc₂][−] is eight-coordinated by two phthalocyanato dianions (Pc). The interplanar distances between the two Pc rings have a linear relationship to the ionic radii of the central Ln(III) cations. The skew angles between the two Pc rings are 6.2, 34.4, 43.2, and 45.0° for the Nd, Gd, Ho, and Lu complexes, respectively. The skew angle seems to depend on the strength of the π–π interaction between the two Pc rings.

Introduction

Much attention has been paid to bis(phthalocyaninato)lanthanide complexes, [LnPc₂]^z (Pc = phthalocyanato dianion, [C₃₂N₈H₁₆]^{2−}), because they are considered as the most promising electrochromic display materials,² materials for molecular semiconductors,³ and attractive candidates for nonlinear optical applications.⁴ Considerable efforts have been made to investigate their spectral,⁵ electrochromic,⁶ electrochemical,⁷ magnetic,⁸ and structural⁹ properties. Theoretical treatments of electronic states of these complexes have also been attempted.¹⁰ Most of the interesting characteristics of the bis(phthalocyaninato)lanthanide complexes stem from their sandwich-type structure and the interplanar interaction between the π-electron

systems of the two Pc rings. Recently we found that they show six one-electron redox-reaction steps corresponding to *z* ranging from −4 to +2 in *o*-dichlorobenzene solution.¹¹ Besides lanthanoids, tin¹² and some actinoids^{13,14} have been reported to form sandwich-type complexes.

Weiss and co-workers have extensively studied the structures of lutetium complexes.⁹ And several structures of the [Ln^{III}Pc₂] complexes have been reported.¹⁵ From these structures, it is generally accepted that lanthanide ion occupies the central position with eight coordinated nitrogen atoms of the two phthalocyaninato moieties, which are parallel and are in a staggered conformation relative to each other (approximately 45°).

Recently several tetrabutylammonium salts of the [Ln^{III}Pc₂] complexes were prepared, and the crystal structures were analyzed in order to examine the electrochemical properties. The analyzed structures showed that the conformations of [Ln^{III}Pc₂][−] are not only staggered but also eclipsed if the Ln(III) ions are exchanged. The rotation angle of one Pc ring compared with another Pc ring, the skew angle, seems to be closely related to the ionic radius of the central Ln(III) ion. This paper reports a new relationship between the skew angle and the central Ln(III) ion.

Experimental Section

Materials. Lutetium(III), holmium(III), gadolinium(III), and neodymium(III) acetate hydrates and sodium methylate were obtained from Wako Pure Chemical Industries. *o*-Dicyanobenzene and tetrabutylam-

- [⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1996.
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Table 1. Crystallographic Data for [NBuⁿ][NdPc₂] (1), [NBuⁿ][GdPc₂] (2), [NBuⁿ][HoPc₂]·H₂O (3), and [NBuⁿ][LuPc₂]·H₂O (4)

	1	2	3	4
formula	C ₈₀ H ₆₈ N ₁₇ Nd	C ₈₀ H ₆₈ N ₁₇ Gd	C ₈₀ H ₇₀ N ₁₇ OHo	C ₈₀ H ₇₀ N ₁₇ OLu
<i>a</i> , Å	17.0545(6)	17.399(8)	18.096(5)	18.171(3)
<i>c</i> , Å	22.807(3)	11.377(6)	11.079(6)	10.987(4)
<i>V</i> , Å ³	6633.6(10)	3444.1(23)	3628.0(22)	3627.7(15)
<i>Z</i>	4	2	2	2
fw	1411.75	1424.76	1450.46	1458.48
space group	<i>P4/ncc</i>	<i>P4₂/2</i>	<i>P4₂/2</i>	<i>P4/nmm</i>
<i>T</i> , K	296	296	296	296
$\lambda(\text{Mo K}\alpha)$, Å	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calc} , g·cm ⁻³	1.414	1.374	1.328	1.335
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	8.44	10.22	11.48	14.18
<i>R</i> (<i>F</i>) ^b	0.048	0.077	0.060	0.054
<i>R</i> _w (<i>F</i> ²) ^c	0.105	0.209	0.142	0.145
<i>N</i> _{obs} ^a	2428	1932	1594	1713
<i>p</i> ₁ ^c	0.0649	0.1276	0.0991	0.0828
<i>p</i> ₂ ^c	9.0573	3.9707	0	0

^a Numbers of observed reflections with $I > 2\sigma(I)$. ^b $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (p_1P)^2 + p_2P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for [NBuⁿ][NdPc₂] (1)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Nd	0.2500	0.2500	0.04916(2)	0.0398
N1	0.2797(2)	0.1372(2)	-0.0179(2)	0.0446
N2	0.4216(2)	0.1509(2)	-0.0273(2)	0.0501
N3	0.2918(2)	0.1411(2)	0.1172(2)	0.0485
N4	0.1700(2)	0.0694(2)	0.1287(2)	0.0544
N5	0.2500	0.2500	0.3001(4)	0.105
C1	0.3547(3)	0.1093(3)	-0.0253(2)	0.0495
C2	0.3527(3)	0.0252(3)	-0.0354(2)	0.0507
C3	0.4113(3)	-0.0300(3)	-0.0451(3)	0.058
C4	0.3892(4)	-0.1062(3)	-0.0549(3)	0.070
C5	0.3102(4)	-0.1277(3)	-0.0562(3)	0.073
C6	0.2515(3)	-0.0729(3)	-0.0472(3)	0.063
C7	0.2738(3)	0.0037(3)	-0.0357(2)	0.0508
C8	0.2295(3)	0.0759(2)	-0.0259(2)	0.0467
C9	0.2479(3)	0.0747(3)	0.1261(2)	0.0504
C10	0.2993(3)	0.0086(3)	0.1387(3)	0.0589
C11	0.2840(4)	-0.0694(3)	0.1513(3)	0.073
C12	0.3478(4)	-0.1169(4)	0.1641(4)	0.089
C13	0.4227(5)	-0.0879(4)	0.1653(4)	0.092
C14	0.4389(4)	-0.0093(3)	0.1531(3)	0.075
C15	0.3752(3)	0.0388(3)	0.1395(2)	0.0564
C16	0.3684(3)	0.1220(3)	0.1266(2)	0.0502
C17	0.2301(14)	0.1806(9)	0.3388(8)	0.153
C17'	0.2252(19)	0.1802(8)	0.2631(9)	0.192
C18	0.1803(11)	0.1218(6)	0.3039(11)	0.182
C19	0.2245(9)	0.0459(9)	0.2988(10)	0.160
C18'	0.2373(12)	0.1048(6)	0.2971(12)	0.152
C19'	0.1587(11)	0.0642(8)	0.3019(13)	0.184
C20	0.1697(7)	-0.0226(5)	0.2897(5)	0.147

^a $U_{\text{eq}} = (1/3)\sum_i U_{ij}a_i^*a_j^*a_i^2$. The occupancies of C17 and C17' are 0.5. The occupancies of C18 and C19 are 0.54, and those of C18' and C19' are 0.46.

monium bromide were purchased from Tokyo Kasei Kogyo Co., and dimethyl formamide (DMF), methanol, and acetone were obtained from Kanto Chemical Co.

Synthesis of [NBuⁿ][Ln^{III}Pc₂]. Bis(phthalocyaninato)lanthanides were synthesized according to the method of Moskalev and Kirin¹⁶ with several modifications. A mixture of Ln(CH₃COO)₃·*n*H₂O (1.0 mmol), *o*-dicyanobenzene (0.8 mmol), and Na₂CO₃ (0.5 mmol) was introduced into a Pyrex test tube (4 cm in diameter and 20 cm in length) equipped with a glass tube and a thermocouple. The test tube was placed in a mantle heater equipped with a programmable temperature controller (Shimaden, RTC-5630). The mixture was heated from room temperature to 150 °C at a constant rate during 20 min, and then it was kept at 150 °C for 30 min. The mixture melted and changed from colorless to green. Then the temperature was raised to 280 °C within 15 min and was kept at 280 °C for 20 min. The melt became dark blue from green, and then the mixture solidified. The glass tube was connected to a vacuum pump, and under evacuation the temperature

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for [NBuⁿ][GdPc₂] (2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Gd	0.5000	0.0000	0.41007(6)	0.0886
N1	0.6007(6)	0.0504(6)	0.2827(8)	0.091
N2	0.5617(9)	0.1837(9)	0.2567(11)	0.111
N3	0.3882(7)	0.0156(9)	0.5365(8)	0.110
N4	0.3855(10)	0.1563(10)	0.5568(13)	0.111
N5	0.5000	0.0000	0.0941(13)	0.167
C1	0.6130(10)	0.1282(10)	0.2625(9)	0.097
C2	0.6931(8)	0.1422(8)	0.2298(10)	0.101
C3	0.7306(11)	0.2091(10)	0.1958(12)	0.126
C4	0.8048(12)	0.1988(12)	0.1653(18)	0.142
C5	0.8447(10)	0.1297(14)	0.1666(17)	0.133
C6	0.8077(10)	0.0621(11)	0.1997(13)	0.121
C7	0.7305(10)	0.0710(9)	0.2301(12)	0.102
C8	0.6701(8)	0.0128(13)	0.2627(11)	0.106
C9	0.3500(12)	0.0863(13)	0.5543(14)	0.107
C10	0.2710(10)	0.0785(14)	0.5793(12)	0.127
C11	0.2149(10)	0.1261(16)	0.6078(16)	0.153
C12	0.1443(18)	0.0993(20)	0.6282(26)	0.194
C13	0.1307(16)	0.0217(21)	0.6279(21)	0.202
C14	0.1841(13)	0.0327(14)	0.5973(17)	0.162
C15	0.2579(8)	0.0015(16)	0.5770(9)	0.123
C16	0.3347(11)	0.0372(12)	0.5533(13)	0.110
C17	0.4295(10)	0.0154(26)	0.1704(18)	0.187
C17'	0.4307(11)	0.0165(28)	0.0163(18)	0.197
C18	0.3725(12)	0.0594(21)	0.0931(37)	0.193
C19	0.3010(19)	0.0086(14)	0.0831(41)	0.201
C18'	0.3588(9)	0.0027(23)	0.0914(30)	0.194
C19'	0.3178(16)	0.0802(19)	0.0949(52)	0.195
C20	0.2345(12)	0.0642(15)	0.0616(26)	0.191

^a $U_{\text{eq}} = (1/3)\sum_i U_{ij}a_i^*a_j^*a_i^2$. The occupancies of C17 and C17' are 0.5. The occupancies of C18 and C19 are 0.47, and those of C18' and C19' are 0.53.

was raised to 340 °C within 20 min and was then kept at 340 °C for 30 min in order to remove any *o*-dicyanobenzene remained. The dark blue crude reaction products were cooled to room temperature, ground to powder, and dissolved in a small amount of DMF under sonication, and the resulting solution (ca. 15 cm³) was filtered to remove any insoluble residue. Since the electronic absorption spectra of the filtrates revealed that they were mixtures of [Ln^{III}Pc₂]⁻ and [Ln^{III}Pc₂]⁰, the filtrates were electrolyzed at a constant potential of -0.3 V vs Ag/AgCl in a two-compartment electrolysis cell divided with a frit. Both working and counter electrodes were stainless steel spiral wires (area of ca. 30 cm²). DMF solution almost saturated with sodium perchlorate was introduced into the counter electrode compartment. Electrolysis was carried out under nitrogen atmosphere for about 2 h until the current

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (\AA^2) for $[\text{NBu}^n_4][\text{HoPc}_2]$ (**3**)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Ho	0.5000	0.0000	0.09603(5)	0.0543
N1	0.3900(4)	0.0007(14)	0.0288(5)	0.067
N2	0.3721(11)	0.1347(9)	0.0503(7)	0.076
N3	0.4263(12)	0.0801(12)	0.2209(6)	0.073
N4	0.3170(8)	0.0204(9)	0.2469(15)	0.074
N5	0.5000	0.0000	0.4022(11)	0.116
C1	0.3459(14)	0.0705(13)	0.0464(22)	0.071
C2	0.2722(13)	0.0448(11)	0.0635(20)	0.076
C3	0.2076(12)	0.0877(13)	0.0875(34)	0.100
C4	0.1425(12)	0.0518(13)	0.1002(32)	0.120
C5	0.1433(11)	0.0269(15)	0.1095(30)	0.123
C6	0.2053(12)	0.0701(12)	0.0824(33)	0.097
C7	0.2693(11)	0.0314(14)	0.0676(19)	0.086
C8	0.3470(12)	0.0541(10)	0.0434(18)	0.053
C9	0.3524(14)	0.0754(12)	0.2462(17)	0.070
C10	0.3271(11)	0.1521(13)	0.2660(14)	0.084
C11	0.2546(10)	0.1784(10)	0.2991(15)	0.109
C12	0.2463(9)	0.2482(13)	0.3263(17)	0.134
C13	0.3030(12)	0.2972(9)	0.3291(17)	0.136
C14	0.3756(10)	0.2748(8)	0.2985(14)	0.095
C15	0.3858(10)	0.1997(9)	0.2712(12)	0.083
C16	0.4506(18)	0.1542(19)	0.2341(24)	0.107
C17	0.4305(7)	0.0023(37)	0.3245(14)	0.148
C17'	0.4324(8)	0.0001(47)	0.4832(15)	0.164
C18	0.3705(10)	0.0346(22)	0.4075(29)	0.194
C18'	0.3642(11)	0.0175(21)	0.4056(29)	0.192
C19	0.3061(10)	0.0197(16)	0.4077(36)	0.194
C19'	0.3145(12)	0.0505(15)	0.4098(40)	0.169
C20	0.2360(9)	0.0244(12)	0.4358(17)	0.159
O1	0.0000	0.0000	0.4403(100)	0.202
O2	0.0175(50)	0.0417(65)	0.4335(108)	0.139

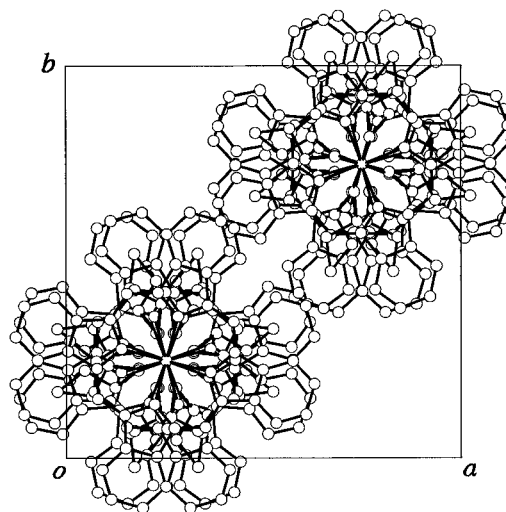
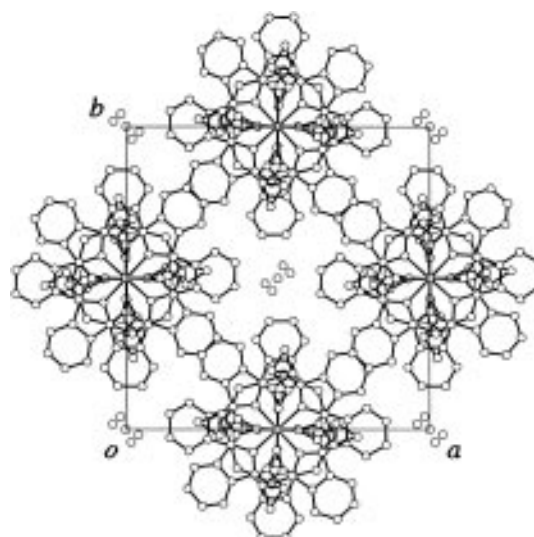
^a $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. The occupancies of C17 and C17' are 0.5. The occupancies of C18, C18', C19, and C19' are 0.5.

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (\AA^2) for $[\text{NBu}^n_4][\text{LuPc}_2]$ (**4**)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Lu	0.2500	0.2500	0.40265(5)	0.0476
N1	0.1729	0.1729	0.2788(4)	0.0524
N2	0.2500	0.0657(3)	0.2546(5)	0.064
N3	0.2500	0.1409(3)	0.5244(5)	0.0565
N4	0.1190(5)	0.1190	0.5472(5)	0.061
N5	0.2500	0.2500	0.8998(11)	0.110
C1	0.1853(3)	0.1005(3)	0.2591(4)	0.0582
C2	0.1167(3)	0.0628(3)	0.2328(4)	0.0665
C3	0.0996(5)	0.0097(4)	0.2048(7)	0.091
C4	0.0272(5)	0.0254(5)	0.1768(9)	0.119
C5	0.1890(3)	0.0980(3)	0.5428(4)	0.0569
C6	0.2113(3)	0.0214(3)	0.5650(5)	0.0672
C7	0.1714(4)	0.0417(4)	0.5861(6)	0.084
C8	0.2116(5)	0.1059(4)	0.6081(7)	0.099
C9	0.2500	0.1830(7)	0.8158(14)	0.111
C9'	0.2500	0.1793(8)	0.9751(16)	0.168
C10	0.2781(13)	0.1174(5)	0.8907(18)	0.197
C11	0.2167(10)	0.0610(10)	0.8964(20)	0.170
C12	0.2500	0.0133(7)	0.9300(14)	0.150
O1	0.2500	0.2204(43)	1.0500(61)	0.215
O2	0.2500	0.0947(24)	1.2946(38)	0.122
O3	0.2371(68)	0.2084(33)	1.1236(55)	0.151

^a $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. The occupancies of C9 and C9' are 0.25. The occupancies of C10, C11, and C12 are 0.5.

dropped to almost zero. The solution was placed on the alumina column and eluted with methanol containing 2% sodium methylate. A deep blue band that was eluted after the green band for $[\text{Ln}^{\text{III}}\text{Pc}_2]^0$ was collected, an excess amount of tetrabutylammonium bromide was added, and the resulting solution was concentrated to a volume of 30 cm^3 on a rotary evaporator and then was cooled in a refrigerator. Dark purple crude crystals were obtained by filtration. After recrystallization from acetone, yields were between 36.4% and 41.3%. Products were identified from UV/visible absorption and IR spectra and elemental

**Figure 1.** Crystal structure of $[\text{NBu}^n_4][\text{Nd}^{\text{III}}\text{Pc}_2]$ viewed along the *c* axis.**Figure 2.** Crystal structure of $[\text{NBu}^n_4][\text{Ho}^{\text{III}}\text{Pc}_2] \cdot \text{H}_2\text{O}$ viewed along the *c* axis.

analyses. Anal. Calcd for $\text{LuC}_{80}\text{N}_{17}\text{H}_{70}\text{O}$: C, 65.79; H, 4.83; N, 16.30. Found: C, 66.25; H, 4.86; N, 16.43. Calcd for $\text{HoC}_{80}\text{N}_{17}\text{H}_{70}\text{O}$: C, 66.25; H, 4.86; N, 16.42. Found: C, 66.94; H, 4.61; N, 15.58. Calcd for $\text{GdC}_{80}\text{N}_{17}\text{H}_{68}$: C, 67.44; H, 4.81; N, 16.71. Found: C, 67.22; H, 4.76; N, 16.27. Calcd for $\text{NdC}_{80}\text{N}_{17}\text{H}_{68}$: C, 68.06; H, 4.86; N, 16.87. Found: C, 68.02; H, 4.81; N, 16.65.

Preparation of Single Crystals. Needle-like crystals of $[\text{NBu}^n_4][\text{Ln}^{\text{III}}\text{Pc}_2]$ (20 mg) were dissolved in 200 cm^3 of acetone under sonication, and the resulting solution was filtered. To the filtrate placed in a 200 cm^3 flask was added 5 cm^3 of distilled water. The mouth of the flask was covered with a plastic film having some small holes, and the flask was allowed to stand for about 1 week at room temperature until the volume of the solution decreased to about 30 cm^3 . Dark purple crystals thus obtained were filtered off and dried *in vacuo* at 80 $^\circ\text{C}$.

X-ray Crystal Structure Determinations. X-ray intensity data for $[\text{NBu}^n_4][\text{Nd}^{\text{III}}\text{Pc}_2]$ (**1**) and $[\text{NBu}^n_4][\text{Gd}^{\text{III}}\text{Pc}_2]$ (**2**) were collected on a Weissenberg type FIXD diffractometer with imaging plates (Rigaku Catg. R-Axis Iics), which was developed in our laboratory. The details of data collection with the new diffractometer have been described.¹⁷ Intensity data were corrected for Lorentz and polarization factors but not for absorption. The intensity data for $[\text{NBu}^n_4][\text{Ho}^{\text{III}}\text{Pc}_2] \cdot \text{H}_2\text{O}$ (**3**) and $[\text{NBu}^n_4][\text{LuPc}_2] \cdot \text{H}_2\text{O}$ (**4**) were collected on AFC-5R and AFC-7S four-circle diffractometers, respectively. A brief summary of crystal data and data collection parameters is given in Table 1, and the complete

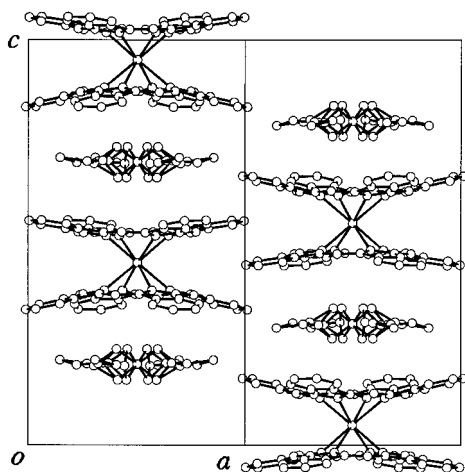


Figure 3. Crystal structure of [NBuⁿ][Nd^{III}Pc₂] viewed along [110]. The disordered [NBuⁿ]⁺ ions are sandwiched between the [Nd^{III}Pc₂]⁻ ions.

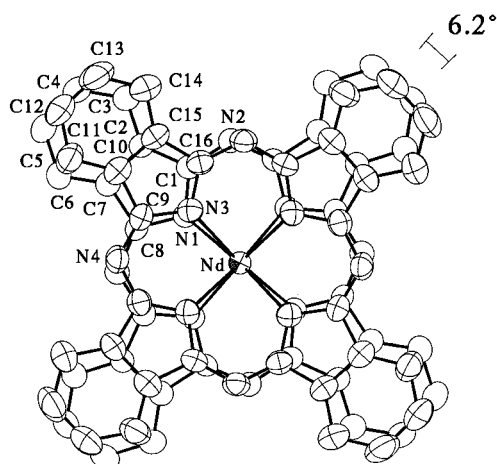


Figure 4. Molecular structure of [Nd^{III}Pc₂]⁻ and numbering scheme of the atoms. The thermal ellipsoids, at the 50% probability level, of the atoms of the upper Pc ring show the principal-axis planes. The skew angle between the upper and lower Pc rings is 6.2°.

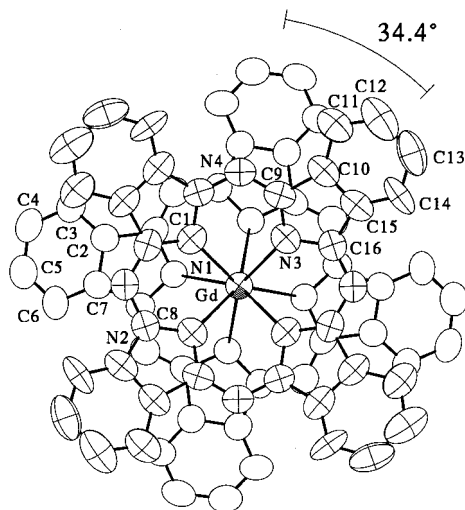


Figure 5. Molecular structure of [Gd^{III}Pc₂]⁻ and numbering scheme of the atoms. The thermal ellipsoids, at the 30% probability level, of the atoms of the upper Pc ring show the principal-axis planes. The skew angle between the upper and lower Pc rings is 34.4°.

crystallographic details are included in the Supporting Information. All the crystal structures were solved by direct methods using the SAPI91 program package¹⁸ and refined by full-matrix least-squares procedures using SHELXL93.¹⁹ All the butyl groups are disordered in two sites.

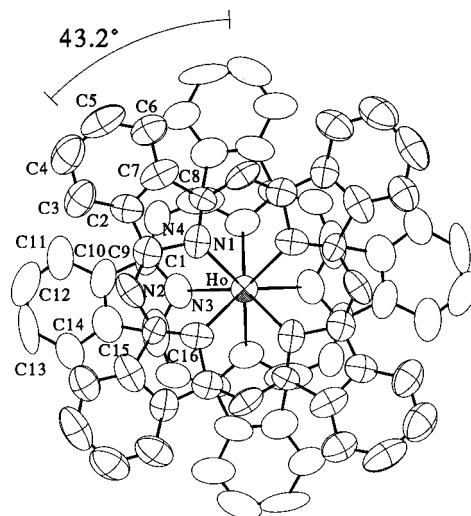


Figure 6. Molecular structure of [Ho^{III}Pc₂]⁻ and numbering scheme of the atoms. The thermal ellipsoids, at the 50% probability level, of the atoms of the upper Pc ring show the principal-axis planes. The skew angle between the upper and lower Pc rings is 43.2°.

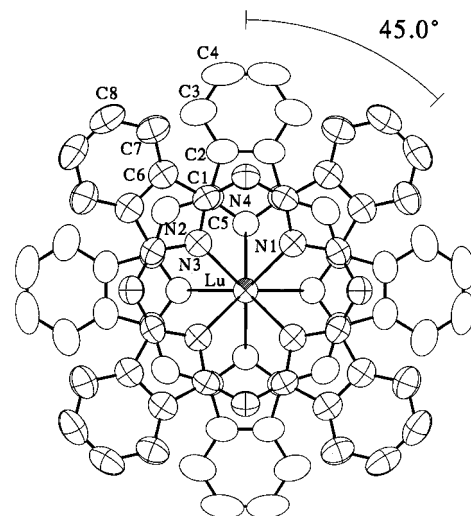


Figure 7. Molecular structure of [Lu^{III}Pc₂]⁻ and numbering scheme of the atoms. The thermal ellipsoids, at the 50% probability level, of the atoms of the upper Pc ring show the principal-axis planes. The skew angle between the upper and lower Pc rings is 45.0° from the symmetry of this molecule.

All the H atoms of the Pc ligands in **1** and **4** were located on the difference Fourier maps and those in **2** and **3** were obtained geometrically. These H atoms were included in the subsequent least-squares refinement as fixed contributors. The H atoms of the butyl groups were not included. The final refinement with anisotropic temperature factors for non-H atoms except for the disordered butyl atoms, which were refined isotropically, led to *R* values of 0.048, 0.077, 0.060, and 0.054 for **1–4**, respectively. Atomic coordinates for the four crystals are given in Tables 2 to 5. Anisotropic temperature factors and the parameters of the H atoms are included in the Supporting Information. Atomic scattering factors including anomalous terms were taken from ref 20. The calculations were carried out on the Sparc 10 computer in our laboratory.

Results

Crystal Structures. The crystal structures of **1** and **3** are shown in Figures 1 and 2, respectively. The crystal structures

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Table 6. Selected Bond Distances (Å) for [NBuⁿ][NdPc₂] (**1**), [NBuⁿ][GdPc₂] (**2**), [NBuⁿ][HoPc₂] (**3**), and [NBuⁿ][LuPc₂] (**4**)^a

	1	2	3	4			
Nd–N1	2.509(4)	Gd–N1	2.437(10)	Ho–N1	2.423(7)	Lu–N1	2.404(3)
Nd–N3	2.523(4)	Gd–N3	2.434(11)	Ho–N3	2.407(8)	Lu–N3	2.392(6)
N1–C1	1.376(6)	N1–C1	1.39(2)	N1–C1	1.51(3)	N1–C1	1.352(5)
N1–C8	1.363(6)	N1–C8	1.39(2)	N1–C8	1.27(3)		
N2–C1	1.345(6)	N2–C1	1.32(2)	N2–C1	1.25(3)	N2–C1	1.336(6)
N2–C8 ⁱ	1.341(6)	N2 ⁱⁱ –C8	1.32(3)	N2–C8 ⁱⁱ	1.38(3)	N2–C1 ⁱⁱⁱ	1.336(6)
N3–C9	1.374(6)	N3–C9	1.41(2)	N3–C9	1.37(3)	N3–C5	1.370(6)
N3–C16	1.363(6)	N3–C16	1.32(2)	N3–C16	1.42(4)		
N4–C9	1.333(6)	N4–C9	1.37(2)	N4–C9	1.18(3)	N4–C5	1.329(10)
N4 ⁱ –C16	1.341(6)	N4–C16 ⁱⁱ	1.36(2)	N4 ⁱⁱ –C16	1.37(4)	N4–C5 ^{iv}	1.328(6)
C1–C2	1.452(6)	C1–C2	1.46(2)	C1–C2	1.43(3)	C1–C2	1.452(7)
C2–C7	1.395(7)	C2–C7	1.40(2)	C2–C7	1.38(2)	C2–C2 ^{iv}	1.385(11)
C7–C8	1.462(6)	C7–C8	1.51(2)	C7–C8	1.49(3)		
C9–C10	1.456(7)	C9–C10	1.41(3)	C9–C10	1.48(3)	C5–C6	1.470(8)
C10–C15	1.393(7)	C10–C15	1.41(3)	C10–C15	1.37(3)	C6–C6 ⁱⁱⁱ	1.406(12)
C15–C16	1.452(6)	C15–C16	1.50(2)	C15–C16	1.49(3)		

^a Symmetry codes: (i) $1/2 - y, x, z$; (ii) $1/2 + y, 1/2 - x, z$; (iii) $1/2 - x, y, z$; (iv) y, x, z .

Table 7. Selected Bond Angles (deg) for [NBuⁿ][NdPc₂] (**1**), [NBuⁿ][GdPc₂] (**2**), [NBuⁿ][HoPc₂] (**3**), and [NBuⁿ][LuPc₂] (**4**)^a

	1	2	3	4			
N1–Nd–N1 ⁱⁱ	68.20(9)	N1–Gd–N1 ^{iv}	69.3(2)	N1–Ho–N1 ^{iv}	70.99(14)	N1–Lu–N1 ^{ix}	71.32(10)
N1–Nd–N1 ⁱⁱⁱ	104.9(2)	N1–Gd–N1 ^v	107.0(5)	N1–Ho–N1 ^v	110.4(3)	N1–Lu–N1 ^x	111.1(2)
N1–Nd–N3	75.74(13)	N1 ^v –Gd–N3	79.5(4)	N1–Ho–N3 ^{vi}	80.6(5)	N1–Lu–N3	80.41(13)
N3–Nd–N3 ⁱⁱ	67.75(9)	N3–Gd–N3 ^{iv}	69.6(3)	N3–Ho–N3 ^{iv}	70.7(2)	N3–Lu–N3 ^{ix}	71.76(13)
N3–Nd–N3 ⁱⁱⁱ	104.0(2)	N3–Gd–N3 ^v	107.6(5)	N3–Ho–N3 ^v	109.9(4)	N3–Lu–N3 ^x	112.0(3)
C1–N1–C8	107.5(4)	C1–N1–C8	107.3(13)	C1–N1–C8	108.2(9)	C1–N1–C1 ^{viii}	107.4(5)
C1–N2–C8 ⁱ	123.6(4)	C1–N2–C8 ^{vi}	122.1(15)	C1–N2–C8 ^{iv}	126.0(12)	C1–N2–C1 ^{vii}	123.4(6)
C9–N3–C16	107.5(4)	C9–N3–C16	104.6(15)	C9–N3–C16	110.0(14)	C5–N3–C5 ^{vii}	108.0(6)
C9–N4–C16 ⁱⁱ	123.7(4)	C9–N4–C16 ^{iv}	123.5(18)	C9–N4–C16 ^{vi}	124.5(18)	C5–N4–C5 ^{viii}	123.2(6)
N1–C1–N2	127.6(4)	N1–C1–N2	128.2(15)	N1–C1–N2	125.4(21)	N1–C1–N2	127.8(5)
N1–C1–C2	109.9(4)	N1–C1–C2	110.6(14)	N1–C1–C2	103.8(18)	N1–C1–C2	110.3(4)
C1–C2–C7	106.4(4)	C1–C2–C7	107.1(13)	C1–C2–C7	111.4(24)	C1–C2–C2 ^{viii}	105.9(3)
C2–C7–C8	106.0(4)	C2–C7–C8	105.8(14)	C2–C7–C8	103.6(21)		
N1–C8–N2 ⁱⁱ	127.3(4)	N1–C8–N2 ^{iv}	128.7(15)	N1–C8–N2 ^{vi}	128.0(19)		
N1–C8–C7	110.0(4)	N1–C8–C7	109.2(17)	N1–C8–C7	112.7(17)		
N3–C9–N4	127.2(4)	N3–C9–N4	124.5(19)	N3–C9–N4	125.7(23)	N3–C5–N4	128.1(5)
N3–C9–C10	109.9(4)	N3–C9–C10	113.8(19)	N3–C9–C10	105.9(18)	N3–C5–C6	109.9(5)
C9–C10–C15	106.0(4)	C9–C10–C15	104.4(17)	C9–C10–C15	111.0(18)	C5–C6–C6 ^{vii}	106.0(3)
C10–C15–C16	106.5(4)	C10–C15–C16	105.5(16)	C10–C15–C16	104.5(21)		
N3–C16–N4 ⁱ	128.1(4)	N3–C16–N4 ^{vi}	127.7(17)	N3–C16–N4 ^{vi}	130.9(23)		
N3–C16–C15	110.0(4)	N3–C16–C15	111.5(18)	N3–C16–C15	107.8(24)		

^a Symmetry codes: (i) $1/2 - y, x, z$; (ii) $y, 1/2 - x, z$; (iii) $1/2 - x, 1/2 - y, z$; (iv) $1/2 + y, 1/2 - x, z$; (v) $1 - x, -y, z$; (vi) $1/2 - y, x - 1/2, z$; (vii) $1/2 - x, y, z$; (viii) y, x, z ; (ix) $y, 1/2 - x, z$; (x) $1/2 - x, 1/2 - y, z$.

of **2** and **4** are similar to those of **1** and **3**, respectively. In all the crystals, the [Ln^{III}Pc₂][−] and [NBuⁿ]⁺ ions stack alternately along the 4-fold axes. The solvent water molecules in **3** and **4** are situated on the 4-fold axes between the above columns. In order to show the packing mode, the projection of **1** viewed along the diagonal axis in the *ab* plane is shown in Figure 3. The [NBuⁿ]⁺ ion assumes a disordered structure to occupy the wide space between the anions in the column. There are no unusually short contacts between the molecules.

Molecular Structures. The ORTEP drawings of the molecular structures of **1–4** viewed along the 4-fold axis are shown in Figures 4–7, respectively. Selected bond distances and angles are given in Tables 6 and 7, respectively. The Ln–N distances are in good agreement with the corresponding ones determined so far. Other distances and angles are not significantly different from the usual ones.

The central lanthanoid(III) ions are sandwiched by the two Pc ligands and are 8-fold coordinated by the isoindole nitrogen atoms (N_{iso}) of two Pc rings which form a saucer shape, as

shown in Figure 3. The plane composed of the four N_{iso} atoms of the Pc ligand is at a right angle to the 4-fold axis. The bent angle is defined as the angle between the plane composed of the N_{iso} atoms and the vector connecting the N_{iso} atom and the center of the central C–C bond of the isoindole moiety. The calculated bent angles listed in Table 8 clearly indicate that the two Pc ligands have different conformations. Figure 8 shows the two modes of contacts between the [Ln^{III}Pc₂][−] and [NBuⁿ]⁺ ions, A and B, observed in both sides of the [Ln^{III}Pc₂][−] ion. Mode A is a closer contact than mode B. This indicates that the closer contacts cause the smaller bent angles of the Pc rings in the four crystals.

It has been reported that the interplanar distance between the two Pc ligands is defined as the distance between the upper and lower planes composed of four N_{iso} atoms.²¹ The calculated interplanar distances are 3.08, 2.89, 2.76, and 2.67 Å for **1–4**, respectively.

The four molecules are very similar to each other except for the skew angles of the two ligands around the 4-fold axis. We define the skew angle of the two Pc rings as the projected angle of N(1)–Ln–N(4) onto the plane composed of the four N_{iso}

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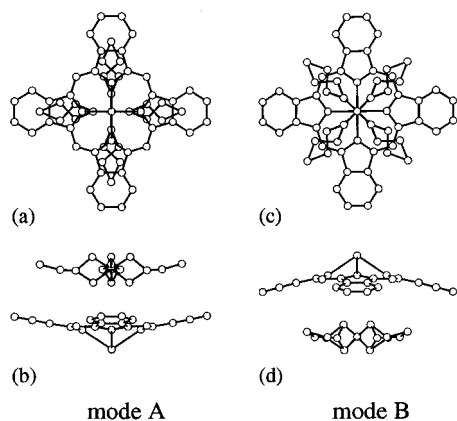


Figure 8. Two contact modes between the [NBu₄]⁺ and [Nd^{III}Pc₂]⁻ ions: (a) view along the 4-fold axis of mode A and (b) its side view; (c) view along the 4-fold axis of mode B and (d) its side view.

Table 8. Bent Angles (deg) for [NBu₄][NdPc₂] (1), [NBu₄][GdPc₂] (2), [NBu₄][HoPc₂] (3), and [NBu₄][LuPc₂] (4)

	1	2	3	4
mode A	10.51	12.15	10.72	11.59
mode B	13.07	15.64	13.81	13.31

atoms. The calculated skew angles are 6.2, 34.4, 43.2, and 45.0° for 1–4, respectively.

Discussion

Relationship between the Interplanar Distance and the Ionic Radius. Table 9 shows the ionic radii,²² and interplanar distances observed in the MPC₂ or MPcPc_{ox} complexes determined so far, where Pc_{ox} is the phthalocyanato anion compared with phthalocyanato dianion, Pc. The interplanar distance, d_N , was calculated from the distance between the upper and lower planes composed of the four N_{iso} atoms. Figure 9 shows the relationship between the ionic radii and the interplanar distances. The interplanar distances are linearly dependent on the ionic radii. If the N_{iso}–M–N'_{iso} angles, N_{iso} and N'_{iso} belonging to the upper and lower Pc rings, respectively, are approximately the same among these complexes, the interplanar distance should linearly depend on the M–N_{iso} distance, which has a linear relationship to the ionic radius of the M ion. This may be why such a linearship relation can be obtained.

Relationship between the Skew Angle and the Interplanar Distance. Table 9 also shows the skew angles. There seems to be no relationship between the skew angle and the interplanar

Table 9. Comparison of Ionic Radius, d_N ,^a d_{int} ,^b and Skew Angle Values in MPC₂ and MPcPc_{ox}^c Structures

complex	ionic radius, Å	d_N , Å	d_{int} , Å	skew angle, deg	ref
[Ti ^{IV} Pc ₂] ^{0.66+}	0.88	2.42	... ^d	41.1	33
Y ^{III} PcPc _{ox}	1.159	2.760	3.07 ^e	45	29
Zr ^{IV} Pc ₂	0.98	2.52 ^f	3.10 ^e	39.7 ^e	30
Sn ^{IV} Pc ₂	0.95	2.61 ^e	3.01 ^e	42	23
Ce ^{IV} Pc ₂	1.11	2.79 ^e	3.27 ^e	38.8 ^e	32
Pr ^{III} PcPc _{ox}	1.266	3.0	3.25 ^e	42	31
Pr ^{III} Pc _{ox2}	1.266	3.08 ^e	3.21 ^e	41 ^e	34
Nd ^{III} PcPc _{ox}	1.249	2.96 ^e	3.29 ^e	38	26
Nd ^{III} Pc ₂	1.249	3.0	...	42.3	28
[Nd ^{III} Pc ₂] ⁻	1.249	3.08	3.59	6.2	this work
[Gd ^{III} Pc ₂] ⁻	1.193	2.89	3.48	34.5	this work
[Ho ^{III} Pc ₂] ⁻	1.155	2.76	3.30	43.2	this work
Er ^{III} PcPc _{ox}	1.144	2.74	3.06 ^e	41.4	35
[Lu ^{III} Pc ₂] ⁻	1.117	2.701	3.21 ^e	43	9c
Lu ^{III} HPc ₂	1.117	2.676	3.05 ^e	41	9c
Lu ^{III} PcPc _{ox}	1.117	2.69	3.06 ^e	45	9b
Lu ^{III} PcPc _{ox}	1.117	2.68	3.08 ^e	41	15
[Lu ^{III} Pc ₂] ⁻	1.117	2.67	3.24	45	this work
Th ^{IV} Pc ₂	1.19	2.87 ^e	3.32 ^e	39.8 ^e	24
Th ^{IV} Pc ₂	1.19	2.98	3.30 ^e	38	25
Th ^{IV} Pc ₂	1.19	2.96	3.39 ^e	37.4	27
U ^{IV} Pc ₂	1.14	2.81	...	37	21
U ^{IV} Pc ₂	1.14	2.84 ^e	3.28 ^e	39.1 ^e	24

^a Distance between the upper and lower planes composed of four N_{iso} atoms. ^b Distance between the upper and lower average planes of Pc ligands. ^c Phthalocyaninato anion, C₃₂H₁₆N₈⁻. ^d Not calculated owing to the lack of the atomic parameters. ^e Value calculated using reported atomic coordinates. ^f This distance was given as 2.20 Å in ref 30.

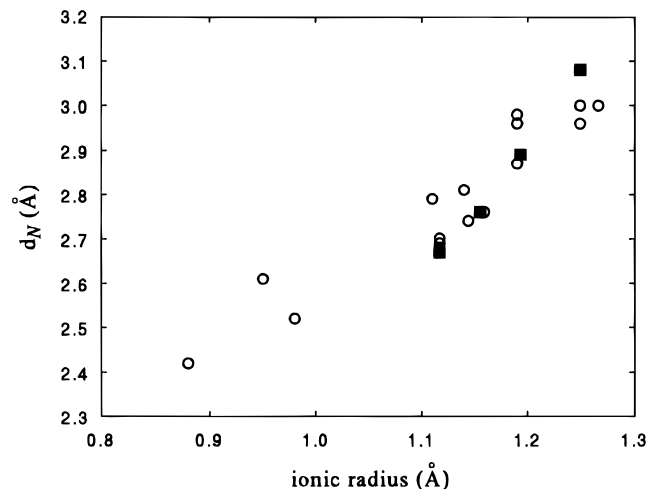


Figure 9. Plots of the interplanar distances, d_N , against the ionic radii of the central atoms. The black squares indicates the four [Ln^{III}Pc₂]⁻ ions in this work.

distance. This may be due to the fact that the calculated interplanar distances are too small, considering the van der Waals radius of the aromatic carbon atom.³⁶

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Table 10. Comparison of Interplanar Distances and Staggered Angles in MPc Structures

complex	interplanar dist, Å	staggered angle, deg	ref
H ₂ (Pc)I	3.251(3)	40.0	43
H ₂ (Pc)I	3.205 ^a	40	44
Li(Pc _{ox}) ^b	3.245(2)	38.7(3)	45
Fe(Pc)I	3.38	38.3 ^a	40
Co(Pc)I	3.123(1)	40	41
Ni(Pc)I	3.244 ^a	39.5	37
Ni(Pc)Br	3.216 ^a	39.1(6)	38
Ni(Pc)ClO ₄ ⁻	3.233(1)	39.5	39
Cu(Pc)I	3.195 ^a	39.2(3)	42

^a Values calculated using reported atomic coordinates. ^b Phthalocyaninato anion, C₃₂H₁₆N₈⁻.

Table 10 lists the interplanar distances and skew angles observed in the metallophthalocyanines, MPc (M = H₂, Li, Fe, Co, Ni, Cu), which have the tetragonal crystal system. The structure of MPc is almost planar, and M is 4-fold-coordinated by the N_{iso} atoms of the Pc ring. The MPc complexes are stacked in a column parallel to the 4-fold axis in the tetragonal cell. The interplanar distances are 3.123–3.251 Å, and the skew angles are 38.7–40°. This indicates that the minimum value of the interplanar distance may be 3.1 Å. The short interplanar distances in Table 8 are due to the saucer shape of the Pc rings.

We defined the π – π interaction distance as the distance between the average planes of the upper and lower Pc moieties. Each average plane is calculated from the atoms of four five-membered rings and the nitrogen atoms connecting the five-membered rings, since these atoms overlap with those of another Pc moiety. The π – π interaction distances calculated, d_{int} , are also given in Table 9. Most of the distances are greater than 3.1 Å. This suggests that the d_{int} value is more appropriate for the interplanar distance than d_{N} if the π – π interaction is taken into account.

Figure 10 plots the skew angles against the π – π interplanar distances. As the d_{int} value increases, the skew angle

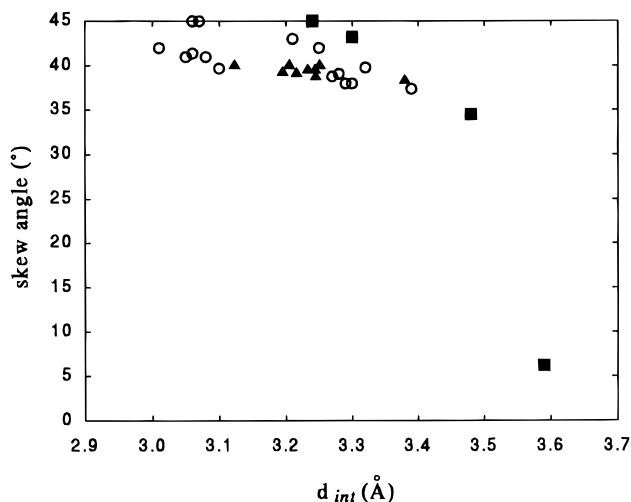


Figure 10. Plots of the skew angles against the π – π interaction distances, d_{int} . The black squares indicates the four [Ln^{III}Pc₂]⁻ ions in this work, and the black triangles are plots of the MPc complexes.

gradually decreases. The d_{int} distances for the MPc complexes, which are the same as d_{N} , appear to have the same relationship. The linear relationship is changed when the d_{int} value is greater than 3.5 Å, which is the sum of the van der Waals radii of the aromatic carbon atoms. This may suggest that, as the π – π interaction decreases, the skew angle decreases and approaches zero if the π – π interaction becomes sufficiently small. This is why the skew angles of **1** and **2** are so small.

It was believed that the two Pc rings of the MPc₂ complexes have a skew angle of about 45°. However, this is caused by the fairly strong π – π interaction between the two Pc rings. When the interplanar distance is greater than the usual van der Waals contacts, the skew angle is small.

Acknowledgment. This work was partly supported by Grants-in-Aid on the Priority-Area Research (Rare Earth Metal Complexes) from the Ministry of Education, Science, and Culture, Japan (Nos. 06241221 and 07230220).

Supporting Information Available: Four X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

IC960158D

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