Syntheses, characterization and crystal structures of 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine rare earth(III) complexes

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Rare earth(III) complexes of tmtaa, Ln(tmtaa)(Htmtaa)·0.6CH₂Cl₂ (Ln = Pr **1**, Nd **2**, Sm **3**, Gd **4**, Tb **5**, Er **6** and Yb **7**; H₂tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine) were prepared by reaction of Li₂tmtaa with LnCl₃(THF)₃ in tetrahydrofuran (THF). The complexes were characterized by infrared, mass and electronic spectra as well as DSC measurement. The crystal structures of Ln(tmtaa)(Htmtaa)·0.6CH₂Cl₂ (Ln = Sm **3**, Tb **5**, Er **6** and Yb **7**) were determined by X-ray crystal diffraction. The complexes are isomorphous and the crystals belong to a monoclinic crystal system with the space group of C2/m. The rare earth(III) ions in the complexes are coordinated by eight nitrogen atoms from tmtaa and Htmtaa to form eight-coordinate sandwich complexes. The average Ln–N bond lengths for tmtaa and Htmtaa are 2.463(7) and 2.543(7) Å for **3**, 2.438(7) and 2.540(7) Å for **5**, 2.406(9) and 2.474(9) Å for **6** and 2.388(8) and 2.495(8) Å for **7**, respectively. The tmtaa and Htmtaa in the complexes adopt markedly saddle conformations and coordinate to the rare earth(III) ions as delocalized conjugated π-electron systems. The acidic hydrogen in the complexes does not bind strongly to any of the nitrogen atoms of tmtaa or Htmtaa, but may belong to the four nitrogen atoms of Htmtaa. The influences of sandwich structures on the dihedral angles of the ligands were studied.

Coordination of small macrocycles such as tetraazaannulenes to transition metals is of current interest because these ligands complement other well-known N₄ macrocyclic derivatives such as porphyrins and phthalocyanines. Though 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetra-decine, abbreviated H₂tmtaa, has a structure and property resembling porphyrins and phthalocyanines (H₂pc), it shows important differences relative to the electronic delocalization, core size and framework flexibility. Since H₂tmtaa was first synthesized by Jaeger,[1] a lot of research into tmtaa transition metal complexes has been reported.[2–5] However, recent research has been mainly focused on the following three aspects. (a) Metal complexes of tmtaa are electron-rich compounds having strong functional groups to stabilize their derivatives. Thus metal complexes are used as starting materials for the preparation of metal–metal and metal–non-metal multiply bonded complexes.[6] The structures and properties of [(tmtaa)M]₂[6a–e] (M = Cr, Mo, W, Ru and Rh), [(tmtaa)M=E][6f–i] (M = V, Ti or Zr, E = O or S) and [(Me₈taa)M=E][6j,k] (M = Ti or V, E = O, S, Se or Te; M = Ge, E = Te; H₂Me₈taa = 5,14-dihydro-2,3,6,8,11,12,15,17-octamethyldibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecine) have been studied. (b) The 7,16-positions of the macrocycle are nucleophilic centers and many electrophilic reagents could react with these positions, through which many significant macrocyclic complexes could be prepared,[7] *e.g.* [Ni(tmtaa)HgBr]₂[Hg₂Br₆]·5C₂H₄Cl₂.[7a] (c) Owing to the flexibility of the macrocyclic framework, pseudo-planar [M(tmtaa)] (M = Pd[8a] or Pt[8b]) complexes have been synthesized.

Attention has been paid to the differences between H₂tmtaa and H₂pc, but the resemblances have been neglected. On account of the interesting electrochromic properties, the phthalocyanine rare earth complexes have been studied extensively.[9] The complexes of [Bu₄N][Ln(pc)₂],[9a] LnH(pc)₂,[9a–d] Ln(pc)₂[9e]
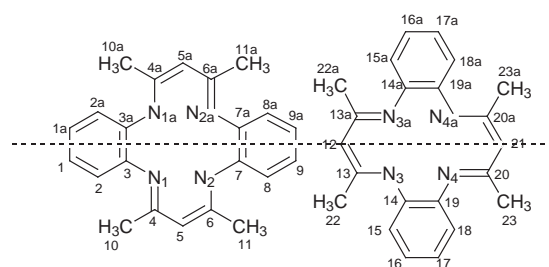

Fig. 1 The symmetric plane for tmtaa and Htmtaa in the complexes.

and Ln(pc)(OAc)[9c] have been synthesized and their crystal structures determined. However, there are few papers reporting on research into the rare earth complexes of H₂tmtaa.[10] The crystal structure of [Li(THF)][Ce(tmtaa)₂]·THF[10a] was determined by Magull and Simon. We synthesized the complex Y(tmtaa)(Htmtaa)·2THF[10b] and determined its crystal structure. The structure could not be discussed in detail because the quality of the crystal was not very high. In the current study, the complexes Ln(tmtaa)(Htmtaa)·0.6CH₂Cl₂ (Ln = Pr **1**, Nd **2**, Sm **3**, Gd **4**, Tb **5**, Er **6** and Yb **7**) have been synthesized and characterized, and the crystal structures of Ln(tmtaa)-(Htmtaa)·0.6CH₂Cl₂ (Ln = Sm **3**, Tb **5**, Er **6** and Yb **7**) determined. The rare earth(III) ions in the complexes are coordinated by eight nitrogen atoms of tmtaa and Htmtaa to form eight-coordinate sandwich complexes. The position of the acidic hydrogen, which has been the subject of a long debate on the complexes LnH(pc)₂ and Ln(pc)₂,[11] was determined by the crystal structure determination and XPS spectra in the complexes Ln(tmtaa)(Htmtaa)·0.6CH₂Cl₂ (see Fig. 1). The influences of the sandwich structure on the dihedral angles of the ligands were studied.

Experimental

General procedures and materials

All chemicals were reagent grade and were used without further purification except as noted. All solvents were distilled from their sodium–benzophenone blue solutions (THF, benzene, hexane and diethyl ether) or from phosphorus pentaoxide (dichloromethane, acetonitrile) under a nitrogen atmosphere. All reaction operations were performed in a dry box under an argon atmosphere. The H_2tmtaa was prepared according to the literature.[12]

Infrared spectra in the 400–4000 cm^{-1} region were taken on a Hitachi 260-30 spectrophotometer at room temperature; KBr disc and Nujol mull techniques were employed. Ultraviolet and visible spectra covering the 14000–37000 cm^{-1} range were recorded on a Shimadzu UV-200S double beam spectrophotometer in dry THF solutions at room temperature. FAB mass spectra were carried out on a JEOL JMS-SX102A gas chromatograph–mass spectrometer in a magic bullet (M.B.). Nitrogen 1s photoelectron spectra were measured using a JEOL-JPS-90SX photoelectron spectrometer with a Mg-Kα X-ray target. The samples measured were prepared by pressing a mixed powder of the complex and KBr. Elemental analyses were determined with a Yanaco CHN Corder MT-3. DSC data were obtained using a Shimadzu DSC-50 differential calorimeter.

Preparation of LnCl$_3$(THF)$_3$ (Ln = Pr, Nd, Sm, Gd, Tb, Er or Yb)

LnCl$_3$(THF)$_3$ (Ln = Gd, Tb, Er or Yb) were prepared according to the literature[13] and recrystallized from dichloromethane–hexane, yield about 90%.

However, the preparation method mentioned above could not be used in the preparation of LnCl$_3$(THF)$_3$ (Ln = Pr, Nd or Sm) complexes because of their lower solubility in THF, hence the following method was developed. Suspensions of LnCl$_3$·6H$_2$O (Ln = Pr, Nd or Sm) (10 g, about 28 mmol) and THF (150 cm^3) were stirred at room temperature for 30 min, and then thionyl chloride (50 cm^3) (distilled twice from quinoline and linseed oil) was added slowly. The salt LnCl$_3$·6H$_2$O was dissolved in the resulting solution and the reaction solution refluxed with stirring at 75 °C for 10 h. The solvent and excess thionyl chloride were evaporated *in vacuo*. The residues were filtered off and washed with a mixture (200 cm^3) of diethyl ether and THF (v/v 10:1). The complexes were recrystallized from dichloromethane–diethyl ether, yield about 83%. In order to increase the solubility of LnCl$_3$(THF)$_3$ in THF, LnCl$_3$(THF)$_3$ were obtained from THF–dichloromethane (v/v 5:1) and used for the following reaction.

Preparation of Ln(tmtaa)(Htmtaa)·0.6CH$_2$Cl$_2$ (Ln = Pr, Nd, Sm, Gd, Tb, Er or Yb)

H_2tmtaa (0.344 g, 1.0 mmol) was added to a 25 cm^3 flask. The flask was filled with argon gas and covered with a rubber cap. THF (8 cm^3) was injected into the flask and H_2tmtaa was dissolved, and then the solution was cooled at 0 °C for 30 min. After that, *n*-butyllithium in hexane (1.2 cm^3 of 1.59 M, 1.9 mmol) was injected slowly into the reaction solution and a clear red solution formed instantaneously. A saturated THF–dichloromethane solution (11.0 cm^3) of ErCl$_3$(THF)$_3$ (about 0.5 mmol) was injected into the reaction solution, which was kept at 0 °C for 24 h. Red crystals of Er(tmtaa)(Htmtaa)·0.6CH$_2$Cl$_2$ **6** appeared. The products were collected by filtration and washed three times with cold THF, yield 0.270 g (59.8%) (Found: C, 59.50; H, 5.29; N, 12.32. C$_{44.6}$H$_{46.2}$N$_8$Cl$_{1.2}$Er requires C, 59.25; H, 5.15; N, 12.39%). IR(KBr): 1620, 1556, 1460, 1422, 1398, 1278, 1191, 740 cm^{-1}; UV (THF) λ_{max} (log ε): 379 (4.46), 419 (4.16) nm; FAB-MS (positive mode, M.B.): *m/z* 853 ([M + H]$^+$, ^{166}Er), 508 [M − Htmtaa]$^+$; DSC: dehydration tem-

perature of dichloromethane (T_1) 148.0 °C, decomposition temperature of the complex (T_2) 387.0 °C.

According to the method described above, Ln(tmtaa)(Htmtaa)·0.6CH$_2$Cl$_2$ (Ln = Pr **1**, Nd **2**, Sm **3**, Gd **4**, Tb **5** or Yb **7**) were prepared. The complexes were characterized by element analyses, IR spectra, UV spectra, mass spectra and DSC measurement. For **1** (yield 50.7%) (Found: C, 60.11; H, 5.63; N, 12.26. C$_{44.6}$H$_{46.2}$N$_8$Cl$_{1.2}$Pr requires C, 61.03; H, 5.31; N, 12.77%). IR(KBr): 1622, 1558, 1462, 1421, 1395, 1280, 1185, 740 cm^{-1}; UV (THF) λ_{max} (log ε): 379 (4.40), 419 (4.11) nm; FAB$^+$(M.B.): *m/z* 827 [M + H]$^+$, 483 [M − Htmtaa]$^+$; DSC: T_1 170.1 °C, T_2 427.0 °C. For **2** (yield 46.8%) (Found: C, 59.97; H, 5.59; N, 12.51. C$_{44.6}$H$_{46.2}$N$_8$Cl$_{1.2}$Nd requires C, 60.80; H, 5.29; N, 12.72%). IR(KBr): 1618, 1554, 1460, 1418, 1392, 1276, 1184, 740 cm^{-1}; UV (THF) λ_{max} (log ε): 379 (4.44), 419 (4.14) nm; FAB$^+$(M.B.): *m/z* 830 ([M + H]$^+$, ^{144}Nd), 486 [M − Htmtaa]$^+$; DSC: T_1 163.0 °C, T_2 343.0 °C. For **3** (yield 46.8%) (Found: C, 59.65; H, 5.62; N, 12.06. C$_{44.6}$H$_{46.2}$N$_8$Cl$_{1.2}$Sm requires C, 60.38; H, 5.25; N, 12.63%). IR(KBr): 1620, 1550, 1455, 1418, 1396, 1285, 1182, 740 cm^{-1}; UV (THF) λ_{max} (log ε): 379 (4.43), 419 (4.13) nm; FAB$^+$(M.B.): *m/z* 838 ([M + H]$^+$, ^{152}Sm), 494 [M − Htmtaa]$^+$; DSC: T_1 162.7 °C, T_2 424.0 °C. For **4** (yield 47.7%) (Found: C, 59.39; H, 5.01; N, 12.47. C$_{44.6}$H$_{46.2}$N$_8$Cl$_{1.2}$Gd requires C, 59.91; H, 5.25; N, 12.53%). IR(KBr): 1618, 1550, 1458, 1419, 1399, 1282, 1183, 740 cm^{-1}; UV (THF) λ_{max} (log ε): 379 (4.45), 419 (4.15) nm; FAB$^+$(M.B.): *m/z* 844 ([M + H]$^+$, ^{158}Gd), 500 [M − Htmtaa]$^+$; DSC: T_1 173.9 °C, T_2 430.3 °C. For **5** (yield 46.8%) (Found: C, 60.00; H, 5.50; N, 12.15. C$_{44.6}$H$_{46.2}$N$_8$Cl$_{1.2}$Tb requires C, 59.80; H, 5.21; N, 12.51%). IR(KBr): 1622, 1550, 1453, 1417, 1399, 1276, 1190, 740 cm^{-1}; UV (THF) λ_{max} (log ε): 379 (4.42), 419 (4.12) nm; FAB$^+$(M.B.): *m/z* 845 [M + H]$^+$, 501 [M − Htmtaa]$^+$; DSC: T_1 165.6 °C, T_2 429.0 °C. For **7** (yield 46.8%) (Found: C, 59.04; H, 5.32; N, 12.63. C$_{44.6}$H$_{46.2}$N$_8$Cl$_{1.2}$Yb requires C, 58.81; H, 5.12; N, 12.31%). IR(KBr): 1620, 1550, 1455, 1418, 1396, 1285, 1182, 740 cm^{-1}; UV (THF) λ_{max} (log ε): 379 (4.44), 419 (4.15) nm; FAB$^+$(M.B.): *m/z* 860 ([M + H]$^+$, ^{174}Yb), 516 [M − Htmtaa]$^+$; DSC: T_1 178.0 °C, T_2 422.0 °C.

X-Ray crystallography

Red crystals were selected from the products and were mounted on glass fibers. X-Ray data for complexes **3**, **5** and **7** were collected on a Siemens P4 four-circle diffractometer by means of an ω–2θ scan mode and Mo-Kα radiation at room temperature. The cell parameters and an orientation matrix for data collection were obtained through the least-squares method for the diffraction data from 25 reflections. The three check reflections measured every 100 reflections showed no decay in intensities. The data were corrected by Lorentz-polarization and a semi-empirical method from ψ-scans absorption corrections. The structures were solved by a heavy-atom method and refined by full-matrix least-squares methods using SHELXTL.[14] All non-hydrogen atoms of the complexes were refined anisotropically. The occupancy factor of the CH$_2$Cl$_2$ molecule was estimated according to the electron density. All hydrogen atoms were added to the structures at their ideal positions, except one disordered atom associated with the N atoms in the Htmtaa ligand and those attached to the disordered solvent molecule.

X-Ray data for complex **6** were collected on a Rigaku RASA-7R four-circle diffractometer by means of an ω–2θ scan mode and Mo-Kα radiation at room temperature. The crystal structure was solved by heavy-atom methods and refined by block-diagonal least-squares. The non-hydrogen atoms were assigned to anisotropic thermal parameters. The solvent CH$_2$Cl$_2$ molecule was disordered and was refined isotropically and its occupancy factor estimated according to the electron density. All hydrogen atoms were added to the structure at their ideal positions, except one disordered atom associated with the N atoms in the Htmtaa ligand and those attached to the

Table 1 Crystal and refinement data of complexes

	3	5	6	7
Formula	$C_{44}H_{45}N_8Sm \cdot 0.6CH_2Cl_2$	$C_{44}H_{45}N_8Tb \cdot 0.6CH_2Cl_2$	$C_{44}H_{45}N_8Er \cdot 0.6CH_2Cl_2$	$C_{44}H_{45}N_8Yb \cdot 0.6CH_2Cl_2$
M	886.18	894.74	904.11	908.87
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$	$C2/m$	$C2/m$
a/Å	17.647(4)	17.510(4)	17.372(2)	17.143(3)
b/Å	16.102(3)	16.151(3)	16.120(2)	16.135(3)
c/Å	16.183(3)	16.206(3)	16.219(2)	16.339(3)
β/°	96.63(2)	94.39(2)	94.31(1)	93.95(3)
V/Å^3	4583(3)	4570(2)	4529(1)	4481(2)
Z	4	4	4	4
D_c/g cm^{-3}	1.284	1.301	1.326	1.347
$F(000)$	1804	1817		1837
Crystal size/mm	$0.46 \times 0.38 \times 0.38$	$0.48 \times 0.36 \times 0.24$	$0.40 \times 0.30 \times 0.25$	$0.40 \times 0.16 \times 0.12$
θ range for data collection/°	1.71 to 25.01	1.72 to 25.02	2.5 to 27.5	1.74 to 24.99
Reflections collected	5135	5124	5699	5034
Independent reflections (R_{int})	4193 (0.0264)	4182 (0.0748)	4187	4094 (0.0303)
Max., min. transmission	0.9082, 0.8180	0.8990, 0.6980		0.9041, 0.7925
Variables	263	263	252	263
R	0.0694	0.0695	0.0670	0.0705
Rw	0.1910	0.1902	0.097	0.1856

disordered solvent molecule. The H atoms were fixed in the final refinements. Absorption correction was made for the intensity data. All calculations were performed using the UNICS III program system.[15]

The crystal data, experimental details and refinement results for the four complexes are summarized in Table 1.
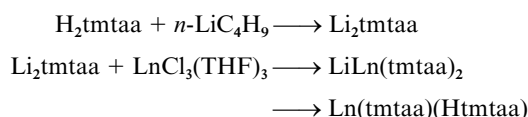
CCDC reference number 186/1391.

See http://www.rsc.org/suppdata/dt/1999/1695/ for crystallographic files in .cif format.

Results and discussion

Syntheses and characterization of macrocyclic rare earth complexes

Reaction of H_2tmtaa in THF solution with 2 equiv. of LiC_4H_9 in hexane gave a clear red solution and Li_2tmtaa was produced. When Li_2tmtaa reacted with 1/2 or 1 equiv. of $LnCl_3(THF)_3$, the red products, Ln(tmtaa)(Htmtaa)·0.6CH_2Cl_2, were crystallized out from the reaction solution. The three reactions may occur in solution as follows (Ln = Pr, Nd, Sm, Gd, Tb, Er or Yb):

$$H_2\text{tmtaa} + n\text{-}LiC_4H_9 \longrightarrow Li_2\text{tmtaa}$$

$$Li_2\text{tmtaa} + LnCl_3(THF)_3 \longrightarrow LiLn(\text{tmtaa})_2$$

$$\longrightarrow Ln(\text{tmtaa})(H\text{tmtaa})$$

Though all reaction operations were performed in a dry box under an argon atmosphere, there were trace amounts of water in the reaction solution which reacted with $LiLn(tmtaa)_2$ to produce Ln(tmtaa)(Htmtaa). When a solution of H_2tmtaa treated with 2.4 equiv. of LiC_4H_9 was added to $LnCl_3(THF)_3$ (0.5 equiv.), crystals did not appear in the reaction solution kept at 0 °C for 4 days. Since the coordination number of a rare earth(III) ion in $LiLn(tmtaa)_2$ and Ln(tmtaa)(Htmtaa) is eight, the solubility of them in THF is different. Ln(tmtaa)(Htmtaa) has a lower solubility in THF than that of $LiLn(tmtaa)_2$ and is easier to separate from the reaction solution. Consequently, Ln(tmtaa)(Htmtaa)·0.6CH_2Cl_2 were obtained from the reaction solution. Under anhydrous conditions, the complex [Li(THF)]-[Ce(tmtaa)$_2$]·THF[10a] was obtained by reaction of Li_2tmtaa with $CeBr_3$ under excess LiC_4H_9 in THF solution. We attempted to prepare $LiLn(tmtaa)_2$ complexes by adding dry diethyl ether to the red reaction solution of H_2tmtaa : LiC_4H_9 : $LnCl_3(THF)_3$ = 2 : 4.8 : 1. Unfortunately, pure complexes were not obtained.

All complexes were characterized by UV, IR and mass spectra as well as DSC measurement. The UV and IR spectra of the complexes were similar to each other, but were different from those of the ligand. IR bands of H_2tmtaa at 1620s, 1600m, 1554s and 1512s cm^{-1} were assigned to C=N and C=C stretching modes.[16] After formation of the complexes, the IR bands shifted to lower frequencies and the bands appeared about 1620s, 1551s, 1456s, 1420s and 1390s cm^{-1}. The UV and visible spectra of the complexes were measured at room temperature in THF solutions. Two absorption peaks at 379 nm (log $\varepsilon = 4.49$) and 419 nm (log $\varepsilon = 4.17$) appeared. Comparison with a maximum absorption band (348 nm) of H_2tmtaa showed a 31 nm shift to a longer wavelength upon complex formation. The crystalline complexes are stable in dry air, but decompose readily in moist conditions. The DCS curves of complexes show strong exothermic peaks at about 160 °C. In the same temperature range, the TG-DTA curves reveal weight loss processes and the percentage of weight lost agrees with loss of 0.6CH_2Cl_2 in complexes. The complexes decomposed about 420 °C.

All molecular ion peaks of the complexes, $[M + 1]^+$, appear in the FAB mass spectra. The intensities of the molecular ion peaks for the complexes are in agreement with the isotopic abundance of the rare earth elements. The fraction peaks of the complexes are peaks of $[M - H\text{tmtaa}]^+$ and of $[H_2\text{tmtaa}]^+$.

The crystal structures of Ln(tmtaa)(Htmtaa)·0.6CH_2Cl_2 (Ln = Sm, Tb, Er or Yb)

The crystal structures of Ln(tmtaa)(Htmtaa)·0.6CH_2Cl_2 (Ln = Sm **3**, Tb **5**, Er **6** and Yb **7**) are isomorphous and are similar to each other. There is only half of a formula unit in the asymmetric cell. Figs. 2 and 3 display the molecular structures of Sm(tmtaa)(Htmtaa) and Yb(tmtaa)(Htmtaa) without the acidic hydrogen which could not be located. Selected bond distances and angles are listed in Table 2.

All complexes are constituted of a rare earth(III) ion, tmtaa, Htmtaa and 0.6CH_2Cl_2. As expected, tmtaa and Htmtaa in the complexes adopt markedly saddle conformations as is usually employed because of steric interactions between the methyl groups and benzene rings. The rare earth(III) ions in the complexes are coordinated by eight nitrogen atoms of tmtaa and Htmtaa to form eight-coordinate sandwich complexes. The coordination polyhedrons are square prisms (see Fig. 4). The average Ln–N bond lengths for tmtaa and Htmtaa are 2.463(7) and 2.543(7) Å for **3**, 2.438(7) Å and 2.540(7) Å for **5**, 2.406(9) Å and 2.474(9) Å for **6** and 2.388(8) Å and 2.495(8) Å for **7**, respectively. It is clear that the average Ln–N bond lengths for Htmtaa are longer than those for tmtaa in the complexes. The average Ln–N bond lengths decrease with an increase in atomic number and the differences in Ln–N distances are consistent
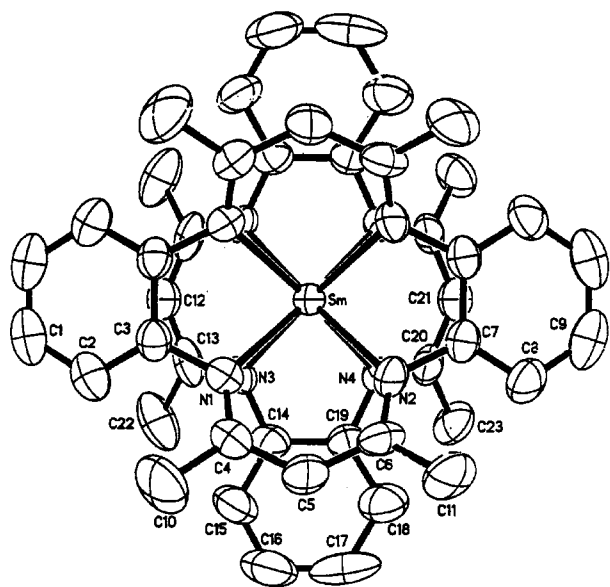
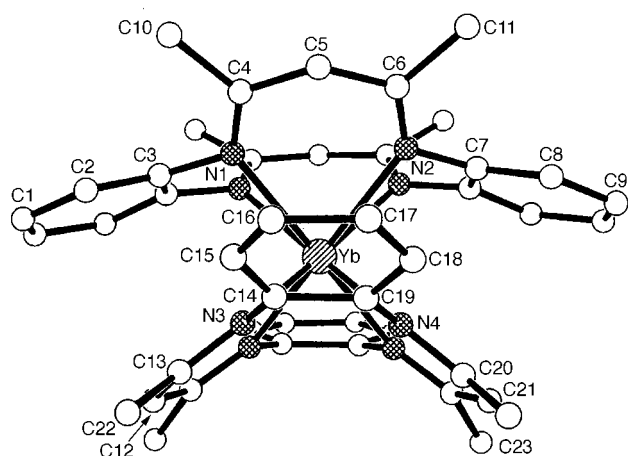**Fig. 2** The molecular structure of Sm(tmtaa)(Htmtaa).

Fig. 3 The molecular structure of Yb(tmtaa)(Htmtaa).

Fig. 4 The coordinate polyhedron of Sm(III) in Sm(tmtaa)(Htmtaa)·0.6CH$_2$Cl$_2$.

Table 2 Selected bond distances (Å) and angles (°)

	3	**5**	**6**	**7**
Ln–N1	2.530(7)	2.530(7)	2.472(8)	2.481(8)
Ln–N2	2.556(8)	2.551(8)	2.478(9)	2.509(9)
Ln–N3	2.443(7)	2.415(7)	2.394(9)	2.362(8)
Ln–N4	2.483(7)	2.460(7)	2.417(9)	2.413(8)
N1–C3	1.430(11)	1.428(11)	1.421(14)	1.424(13)
N1–C4	1.321(13)	1.318(12)	1.301(16)	1.301(14)
N2–C6	1.321(13)	1.303(13)	1.293(16)	1.278(14)
N2–C7	1.414(13)	1.395(11)	1.430(15)	1.381(13)
N3–C13	1.339(12)	1.318(11)	1.342(14)	1.304(14)
N3–C14	1.412(13)	1.406(13)	1.408(15)	1.386(14)
N4–C19	1.416(12)	1.420(12)	1.410(15)	1.404(14)
N4–C20	1.297(12)	1.300(11)	1.305(14)	1.313(13)
C4–C5	1.431(14)	1.410(14)	1.455(19)	1.43(2)
C5–C6	1.411(13)	1.425(14)	1.397(18)	1.42(2)
C12–C13	1.351(14)	1.375(13)	1.369(15)	1.42(2)
C20–C21	1.415(14)	1.418(12)	1.402(14)	1.411(13)
N3#–Ln–N3	71.5(4)	72.2(4)		74.9(5)
N3–Ln–N4	64.7(2)	65.5(2)	66.0(3)	65.8(3)
N3–Ln–N4#	104.2(3)	105.7(3)		108.2(3)
N4–Ln–N4#	70.3(4)	71.2(4)		72.9(4)
N4–Ln–N1#	175.5(3)	175.7(2)		175.2(3)
N3#–Ln–N1	111.2(2)	110.9(2)		110.7(3)
N3–Ln–N1	75.6(2)	74.8(2)	74.0(3)	73.3(3)
N4–Ln–N1	113.3(3)	112.6(3)	112.0(3)	111.7(3)
N1#–Ln–N1	63.0(4)	63.5(4)		63.7(4)
N3–Ln–N2	112.7(3)	112.4(3)	111.1(3)	110.6(3)
N4–Ln–N2	78.7(3)	77.2(3)	75.1(3)	74.8(3)
N4#–Ln–N2	114.0(4)	112.8(3)		111.5(3)
N1–Ln–N2	69.9(3)	70.6(3)	71.2(3)	71.7(3)
N3–Ln–N2#	175.7(2)	175.4(3)		174.5(3)
N1–Ln–N2#	101.7(3)	102.6(2)		104.2(3)
N2–Ln–N2#	63.1(4)	63.0(4)		63.9(4)

Symmetry operation: # $x, -y, z$.

with the change of effective ionic radii of the eight-coordinate rare earth complexes (Sm 1.079 Å; Tb 1.040 Å; Er 1.004 Å and Yb 0.985 Å).[17] The average Ln–N lengths in the complexes are compared with those of the structurally characterized rare earth complexes of H$_2$tmtaa, Y(tmtaa)(Htmtaa)·2THF[10b] and [Li(THF)][Ce(tmtaa)$_2$]·THF,[10a] in which the average M–N bond lengths (tmtaa and Htmtaa) (A ring and B ring) are 2.40(2), 2.47(2) Å (M = Y) and 2.478(6), 2.666(6) Å (M = Ce), respectively. For phthalocyanine rare earth complexes, the average Ln–N bond lengths are similar to those of the rare earth complexes of H$_2$tmtaa reported here, the average Ln–N bond lengths in [NBu$_4$][Lu(pc)$_2$]·2DMF[9a] being 2.374(2) Å for ring A and 2.393(2) Å for ring B, in LuH(pc)$_2$·CH$_2$Cl$_2$[9c] being 2.372(3) Å for ring A and 2.387(2) Å for ring B and in Er(pc)$_2$[9e] being 2.42(2) Å, respectively. The four nitrogen atoms of tmtaa and Htmtaa in the complexes are coplanar, and the corresponding mean planes are almost parallel. The dihedral angles of the corresponding mean planes in the complexes are 3.1° for **3**, 2.8° for **5**, 1.2° for **6** and 2.2° for **7**, respectively. In the complexes, the rare earth(III) ions deviate from the 4N mean plane of Htmtaa [1.605(9) Å for **3**, 1.583(9) Å for **5**, 1.535(10) Å for **6** and 1.532(9) Å for **7**] and lie away from the 4N mean plane of tmtaa [1.513(9) Å for **3**, 1.472(9) Å for **5**, 1.422(10) Å for **6** and 1.400(9) Å for **7**]. The displacement of the rare earth(III) ions from the plane of the four nitrogen atoms in the complexes is much larger than those of transition metal complexes because of the bigger ionic radii of rare earth metals. Compared with phth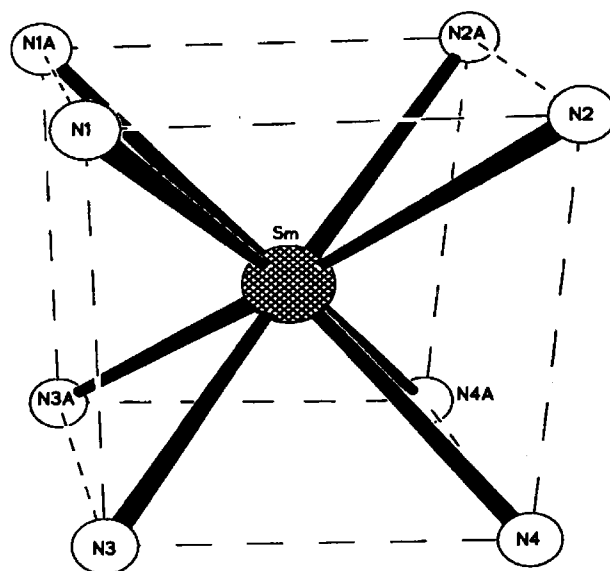alocyanine rare earth complexes, the distances of the rare earth(III) ions to the plane of the four nitrogen atoms in the tmtaa complexes are significantly shorter, [NBu$_4$][Lu(pc)$_2$]·2DMF[9a] 1.334 Å for ring A and 1.367 Å for ring B, LuH(pc)$_2$[9a] 1.337 Å for ring A and 1.339 Å for ring B, Lu(pc)$_2$·CH$_2$Cl$_2$[9c] 1.35 Å for ring A and 1.34 Å for ring B, Er(pc)$_2$ 1.37 Å. This may be attributed to the fact that the core size of phthalocyanine is larger than that of H$_2$tmtaa and that the steric interactions of two macrocyclic ligands in rare earth complexes of H$_2$tmtaa are stronger than those in the phthalocyanine rare earth complexes. It was suggested that tmtaa and Htmtaa in the complexes adopt markedly saddle conformations and that

Table 3 Average bond angles (°), comparison of average dihedral angles (°) and selected average distances (Å)
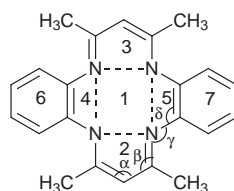
	3		5		6		7		H₂tmtaa
	tmtaa	Htmtaa	tmtaa	Htmtaa	tmtaa	Htmtaa	tmtaa	Htmtaa	
Ln–N	2.463(7)	2.543(7)	2.438(7)	2.540(7)	2.406(9)	2.474(9)	2.388(8)	2.495(8)	
Ln–N₄	1.513	1.605	1.472	1.583	1.422	1.535	1.400	1.532	
C–N[a]	1.318(7)	1.321(13)	1.309(11)	1.301(12)	1.323(13)	1.297(15)	1.308(11)	1.290(13)	1.330
C–N[b]	1.383(12)	1.422(11)	1.396(13)	1.412(11)	1.409(15)	1.426(16)	1.395(14)	1.402(14)	1.404
C–C[a]	1.383(12)	1.421(13)	1.396(11)	1.418(14)	1.386(15)	1.426(18)	1.42(2)	1.42(2)	1.387
1–2	42.4	35.5	43.5	33.9	44.1	34.6	43.5	33.7	36.5
1–3	36.3	33.5	36.1	33.9	38.6	34.6	35.5	33.7	32.0
1–4	11.9	10.3	11.2	9.4	10.9	10.3	10.6	8.7	19.5
1–5	11.9	12.2	11.2	12.6	10.9	9.6	10.6	11.1	20.6
1–6	19.4	16.1	19.1	16.6	18.0	17.0	18.2	15.9	24.1
1–7	19.4	18.8	19.1	18.2	18.0	16.6	18.2	16.0	25.1
1–1ₕ[c]	3.1		2.8		1.2		2.2		
α	128.0(13)	128.2(10)	128.8(12)	128.6(10)		127.1(12)	128.4(13)	128.0(11)	127.3
β	123.6(11)	122.2(10)	122.7(10)	122.8(10)	124.1(11)	124.8(11)	122.6(10)	122.1(10)	120.1
γ	124.3(9)	124.4(8)	123.4(5)	124.7(9)	123.8(10)	122.6(10)	122.2(10)	123.4(10)	127.4
δ	114.8(9)	115.5(5)	114.9(8)	115.6(5)	115.3(10)		114.3(10)	115.2(6)	117.2

[a] Six-membered chelate ring. [b] Five-membered chelate ring. [c] 1 shows the 4N mean plane of tmtaa and 1ₕ shows the 4N mean plane of Htmtaa in the complexes.
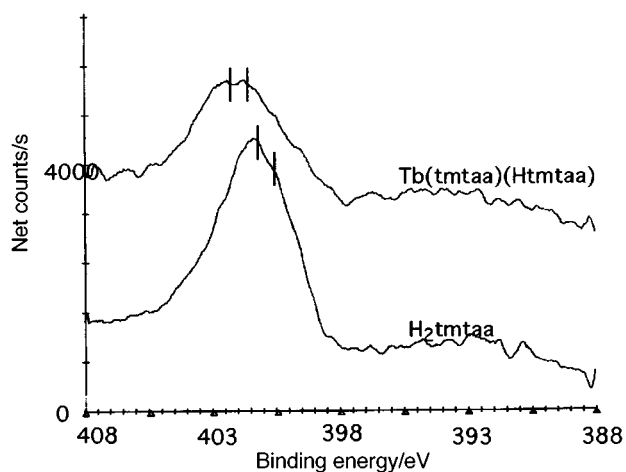

Fig. 5 The nitrogen 1s X-ray photoelectron spectra for Tb(tmtaa)-(Htmtaa) and H₂tmtaa.

phthalocyanine in analogous complexes adopts nearly planar conformations.

The positions of the acidic hydrogens in the complexes

The acidic hydrogens in phthalocyanine rare earth complexes are known to play important roles in the electrochromic properties. However, the positions of the acidic hydrogens in the complexes have not been clearly determined. The eight central nitrogen atoms are chemically equivalent to each other and the acidic hydrogen does not bind strongly to any of the nitrogen atoms in LnH(pc)₂ and Ln(pc)₂. In the Ln(tmtaa)(Htmtaa)·0.6CH₂Cl₂ (Ln = Sm, Tb, Er or Yb) complexes, there is a symmetric plane in the crystal. The position of the symmetric surface for tmtaa and Htmtaa in the complex is different (see Fig. 1), and so there are two types of nitrogen atoms for tmtaa or Htmtaa in the complexes. The average C–N bond lengths in

the five-membered chelate rings are about 1.410 Å and show single bond characteristics. The average C–N and C–C bond lengths in the six-membered chelate rings are about 1.300 Å and 1.410 Å, respectively, and show double bond characterstics, and so tmtaa and Htmtaa coordinate the rare earth(III) ions as delocalized conjugated-electron systems. Hence, the four nitrogen atoms in tmtaa or Htmtaa are chemically equivalent to each other, respectively. We think that the acidic hydrogens in the complexes do not bind strongly to any of the nitrogen atoms of tmtaa and Htmtaa and that they may belong to the four nitrogen atoms of Htmtaa. (a) The average Ln–N bond lengths in Htmtaa are significantly longer (about 0.08 Å) than those of tmtaa in the complexes. (b) We obtained N 1s X-ray photoelectron spectra of Tb(tmtaa)(Htmtaa)·0.6CH₂Cl₂ and H₂tmtaa (see Fig. 5). The spectra show that there are two equal peaks in Tb(tmtaa)(Htmtaa)·0.6CH₂Cl₂. The data imply that there are two types of nitrogen atom in the complex and the quantity of each is almost equal.[18]

The positions of the acidic hydrogens in the complexes are also different from those in Y(tmtaa)(Htmtaa)·2THF, in which the acidic hydrogen has been located and binds to one of the nitrogen atoms in Htmtaa.

The influence of sandwich structures on the dihedral angles of the ligands

The unequal flexing of the two types of chelate ring, the *o*-phenylenediamine chelate rings and the 2,4-pentanediiminato rings, causes the lone pair electrons of the nitrogen atoms of the dianionic form of the ligand to point slightly out of the plane, to the side containing the benzenoid rings. In order to maximize the overlap of the ligand and metal orbitals, the metals must be displaced to one side of the plane of the four nitrogens, and so all benzenoid rings are directed to the inner molecules when the sandwich rare earth complexes are formed. Though tmtaa and Htmtaa are rotated by 90° to each other in the structures of the complexes, the interactions between the methyl groups and the

benzene rings of the two ligands are very strong. Some important parameters for Ln(tmtaa)(Htmtaa)·0.6CH$_2$Cl$_2$ (Ln = Sm, Tb, Er or Yb) are compiled in Table 3. When compared with the ligand, it is found that the dihedral angles of plane 1 to plane 4 and plane 1 to plane 5 in the complexes are decreased (about 7.6–10.8°) and the dihedrals of plane 1 to plane 2 and plane 1 to plane 3 are increased about 1.0–6.6°. This may be attributed to the interactions between the methyl groups or the benzene rings of one ligand and the benzene rings or the methyl groups of another ligand. The extent of the dihedral angles of plane 1 to plane 2 and plane 1 to plane 4 is different, which may explain why plane 2 and plane 3 connect plane 1 with a N=C double bond. Plane 4 and plane 5 connect plane 1 with a N–C single bond and are easily distorted. With an increase of atomic number, the distances of the two N$_4$ planes of tmtaa and Htmtaa are decreased and the intensities of the interactions between the methyl groups or the benzene rings of one ligand and the benzene rings or the methyl groups of another ligand are increased. Consequently, the dihedral angles of plane 1 to plane 2 show a decrease and the dihedral angles of plane 1 to plane 4 show an increase.

Acknowledgements

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