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Heteroleptic protonated bis(phthalocyaninato) rare earth compounds containing 1,4,8,11,15,18,22,25-octa(butyloxy)-phthalocyanine ligand

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Abstract

Condensation between M(Pc)(acac) (M = Sm, Eu, Gd; Pc = phthalocyaninate; acac = acetylacetonate) and metal-free 1,4,8,11,15,18,22,25-octa(butyloxy)phthalocyanine in *n*-octanol afforded heteroleptic double-deckers H{M(Pc)[Pc(α-OC_4H_9)$_8$]} [Pc(α-OC_4H_9)$_8$ = 1,4,8,11,15,18,22,25-octa(butyloxy)phthalocyaninate]. The series of double-decker complexes were characterized by elemental analysis, mass spectra, electronic absorption spectra, and IR spectra. The molecular structure of the compound of Gd was determined by single-crystal X-ray diffraction analysis. It was found that it exists as a pair of enantiomers in the unit cell of the crystals. Furthermore, the complex of Sm reacted with NaOH producing a supramolecule in which two Na^+ ions connect two double-deckers together.

Keywords: Sandwich complexes; Rare earths; Bis(phthalocyaninato) complexes; Double-deckers; Supramolecule

1. Introduction

Bis(phthalocyaninato) rare earth complexes have been intensively studied as an important and useful class of advanced materials for gas sensors, electroluminescence, molecular magnet and molecular electronics [1]. In order to understand how the substituents affect the properties of this kind of complexes, heteroleptic phthalocyaninato metal complexes containing different phthalocyaninato ligands have aroused research interest in recent years [2–4]. We have recently reported the synthesis and spectroscopic properties of heteroleptic bis(phthalocyaninato) complexes of Eu, Gd, and Y [5]. As an extension of these researches, herein we describe the preparation of a novel series of heteroleptic bis(phthalocyaninato) rare earth double-deckers H{M(Pc)[Pc(α-OC_4H_9)$_8$]} (Scheme 1) containing 1,4,8,11,15,18,22,25-octa(butyloxy)-phthalocyanine ligand. It is noteworthy that all the works about bis(phthalocyaninato) rare earth complexes reported thus far dealt with unsubstituted or peripherally substituted phthalocyanines except M(Pc)[Pc(α-OC_4H_9)$_4$] and M[Pc(α-OC_4H_9)$_4$]$_2$ in which the 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine is contained [6,7]. The compounds described herein are the first example of bis(phthalocyaninato) rare earth(III) complexes containing phthalocyanines with eight substituents at non-peripheral positions. These complexes stably exit as protonated form. This is different from other bis(phthalocyaninato) rare earth complexes. Furthermore, when we dealt with H{Sm(Pc)[Pc(α-OC_4H_9)$_8$]} using NaOH, a slipped pseudo-quadruple-decker structure in which two anionic double-decker units were linked together by two sodium ions formed unexpectedly. And the linkage involved the coordination of the aza nitrogen atoms of phthalocyanine. The detail about the slipped pseudo-quadruple-decker supramolecular structure was published elsewhere [8].

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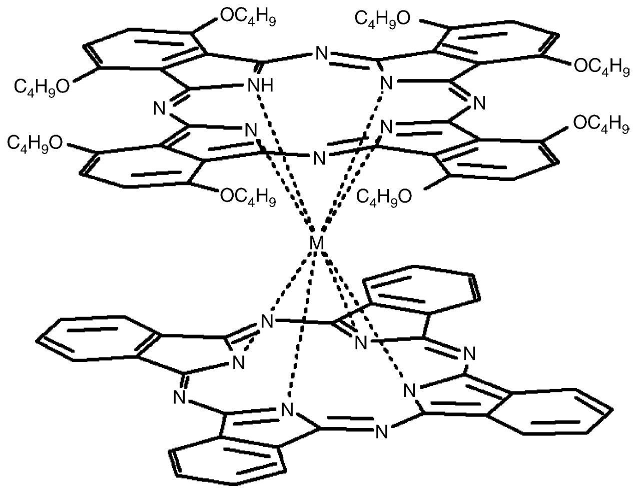

Scheme 1. Schematic structures of heteroleptic rare earth double-decker complexes H{M(Pc)[Pc(α-OC_4H_9)$_8$]} with 1,4,8,11,15,18,22,25-octa(butyloxy)-phthalocyanine and phthalocyanine ligands.

2. Experimental

2.1. General

2,3-Dicyanohydroquinone was purchased from Aldrich. $CHCl_3$, CH_3OH, and toluene were used as received from Beijing Chemical Reagents. The compounds of metal free 1,4,8,11,15,18,22,25-octa(butyloxy)-phthalocyanine H_2[Pc(α-OC_4H_9)$_8$] and M(Pc)(acac) were prepared according to the literature procedures [9,10]. The electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. IR spectra were recorded in KBr pellets using a BIORAD FTS-165 spectrometer with 2 cm^{-1} resolutions. Crystal data were collected on a Bruker SMART CCD diffractometer.

2.2. *Synthesis of heteroleptic double-deckers H{M(Pc)[Pc(α-OC_4H_9)$_8$]} (**1**–**3**)*

A mixture of M(Pc)(acac) (0.05 mmol) and H_2[Pc(α-OC_4H_9)$_8$] (0.05 mmol) in *n*-octanol (5 mL) was refluxed for 8 h under nitrogen to give a dark-blue solution. The reaction solution was cooled to room temperature and ca. forty milliliters methanol was added. The obtained precipitate was filtered off and washed with methanol. The residue was chromatographed on a silica gel column with $CHCl_3$ to remove some amounts of unsubstituted M(Pc)$_2$ as the first fraction. The column was then eluted with $CHCl_3$/MeOH (100:2-3) to elute the desired double-decker H{M(Pc)[Pc(α-OC_4H_9)$_8$]} as the second fraction. The crude product was repeatedly purified by the same chromatographic procedure, followed by recrystallization from a mixture of $CHCl_3$ and MeOH to afford dark blue microcrystals. The data of reaction yield, mass spectra and elemental analysis were given in Table 1.

3. Results and discussion

3.1. Synthesis

Several synthetic pathways have been developed to heteroleptic bis(phthalocyaninato) rare earth(III) double-decker complexes having two different phthalocyanine ligands $M^{III}(Pc')(Pc'')$ ($Pc' \neq Pc''$ = general phthalocyaninate) [2–5]. In the present work, the so-called raise-by-one-story method [3] has been employed to prepare the non-peripherally substituted phthalocyanine-containing heteroleptic bis(phthalocyaninato) rare earth complexes. Treatment of M(Pc)(acac) with metal-free 1,4,8,11,15,18,22,25-octa(butyloxy)-phthalocyanine gives the heteroleptic double-decker compounds in relatively high yields. Surprisingly, although the protonated reduced species have been demonstrated to be the intermediate, all the reported bis(phthalocyaninato) rare earth(III) compounds obtained thus far according to the above-described preparation and isolation procedure have been isolated in the neutral form [1]. However, heteroleptic bis(phthalocyaninato) rare earth compounds were isolated in the protonated form H{M(Pc)[Pc(α-OC_4H_9)$_8$]} in the present case. Obviously, the incorporation of 1,4,8,11,15,18,22,25-octa(butyloxy)-phthalocyanine ligand into the double-decker molecules stabilized the protonated form of bis(phthalocyaninato) rare earth. These protonated double-deckers can be considered as a kind of weak acid. So, they are expected to react with strong base such as NaOH to form salt. In order to prove this point, the protonated compound of Sm was treated with NaOH methanol solution and a new compound formed. Unexpectedly, in this new compound, two hetero-double-deckers were connected

Table 1

Elemental analytical and mass spectroscopic data for the heteroleptic rare earth double-decker complexes H{M^{III}(Pc)[Pc(α-OC_4H_9)$_8$]} (**1**–**3**)

	Yield (%)	M^+/MH^+ (*m*/*z*)[a,b]	Elemental analysis[a] (%)		
			C	N	H
H{Sm(Pc)[Pc(α-OC_4H_9)$_8$]} (**1**)	14	1753.5 (1753.7)[c]	65.58 (65.77)	12.12 (12.78)	5.85 (5.58)
H{Eu(Pc)[Pc(α-OC_4H_9)$_8$]} (**2**)	21	1755.9 (1755.9)[c]	66.16 (65.71)	12.06 (12.77)	5.95 (5.57)
H{Gd(Pc)[Pc(α-OC_4H_9)$_8$]} (**3**)	32	1759.8 (1759.7)[d]	65.76 (65.51)	12.32 (12.73)	5.79 (5.55)

[a] Calculated values given in parentheses.

[b] By MALDI-TOF.

[c] Mass corresponding to the most abundant isotopic peak of the protonated molecular ion (MH^+).

[d] Mass corresponding to the most abundant isotopic peak of the molecular ion (M^+).

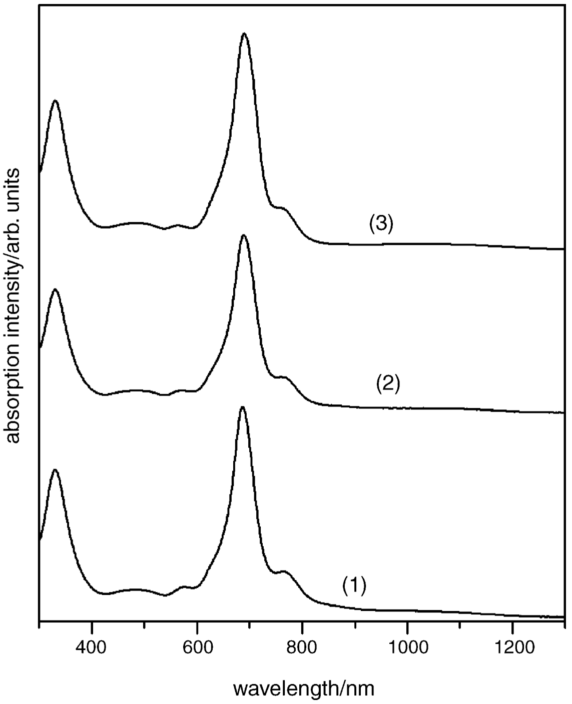

Fig. 1. Electronic absorption spectra of H{M(Pc)[Pc(α-OC_4H_9)$_8$]}: M = Sm (**1**), Eu (**2**) and Gd (**3**) in $CHCl_3$.

together by two Na^+ ions [8]. This proved that the protonated form of bis(phthalocyaninato) rare earth compounds does act as a kind of weak acid and alkoxy substituent at non-peripheral positions provided new coordinating atoms for bis(phthalocyaninato) rare earth compounds.

3.2. Electronic absorption spectra

The electronic absorption spectra of rare earth compounds H{M(Pc)[Pc(α-OC_4H_9)$_8$]} for M = Sm, Eu, Gd were shown in Fig. 1. Their spectra show a typical Soret band at ca. 330 nm and two Q bands at 686–690 and 755–765 nm (Table 2) just like those of reduced double-decker $[M^{III}(Pc)_2]^-$ [11] and $[M^{III}(Pc^*)_2]^-$ [12]. But the typical near IR band with wavelength larger than 1380 nm in the near IR region which is highly characteristic for the neutral single-hole bis(phthalocyaninato) rare earth(III) compounds due to an electron transition from the second occupied HOMO to the first semi-occupied HOMO was not observed. These indicate that the present compounds exist as protonated form. Along with the lanthanide contraction from Sm to Gd, the intense Q band at 686–690 of these compounds is red-shifted and the weak one at lower energy around 755–765 nm blue-shifted, leading to a decreased separation in the order from Sm to Gd. This trend is contrary to the electronic absorption spectra of reduced unsubstituted and peripherally substituted bis(phthalocyaninato) analogues. In those cases the separation of two Q bands increases monotonically when the size of the central metal decreases [11,12]. This difference is perhaps due to the weaker π–π interaction between two phthalocyanine units in the present compounds. In general, the short wavelength Q band and long wavelength Q band were assigned to the transitions of second HOMO to LUMO and HOMO to second LUMO, respectively. However, in present case it seems that the weaker π–π interaction between two phthalocyanine rings results in a diminished energy separation between the HOMO and second HOMO, which induces larger transition energy from the HOMO to second LUMO in comparison with that from second HOMO to LUMO. This in turn leads to a reverse trend in the splitting of two Q bands of H{M(Pc)[Pc(α-OC_4H_9)$_8$]} along with lanthanide contraction compared with $[M^{III}(Pc)_2]^-$ and $[M^{III}(Pc^*)_2]^-$.

3.3. IR spectra

The IR spectra of all these compounds **1**–**3** showed a relatively strong band at ca. 1328 cm^{-1}. Meanwhile another absorption with medium intensity appears at about 1380 cm^{-1}. They are attributed to the marker IR band for both unsubstituted and substituted phthalocyanine dianions [13]. The intense characteristic phthalocyanine π-radical anion band at 1310–1320 cm^{-1} was not observed. These results provided further evidence for the full dianion nature of both phthalocyanines in these double-decker compounds.

3.4. Structural studies

Structural data of homoleptic bis(phthalocyaninato) compounds for most rare earth metals in neutral or reduced forms have been reported in a number of scattered reports [1,14]. But, structurally characterized heteroleptic bis(phthalocyaninato) rare earth double-decker complexes are still rare and limited to the neutral species M(Pc)[Pc(α-OC_5H_{11})$_4$] (M = Sm, Eu, Gd, Er, Yb) [6]. The crystal and molecular structure of protonated double-decker H{Gd(Pc)[Pc(α-OC_4H_9)$_8$]} (**3**) described herein is the first report about the structure of reduced heteroleptic bis(phthalocyaninato) rare earth complexes. Single crystals of H{Gd(Pc)[Pc(α-OC_4H_9)$_8$]} suitable for X-ray diffraction analysis were obtained by slow diffusion of MeOH into

Table 2
Electronic absorption data for **1**–**3** in $CHCl_3$

1	330 (4.99)	484 (4.26)	577 (4.30)	686 (5.14)	765 (4.48)	951 (3.66)[a]
2	331 (4.96)	484 (4.23)	572 (4.23)	688 (5.12)	760 (4.43)	989 (3.59)[a]
3	330 (5.00)	484 (4.26)	564 (4.21)	690 (5.16)	755 (4.45)	1023 (3.57)

Values are λ_{max} (nm) (log ε).

[a] Shoulder band and it is very difficult to determine the exact peak position.

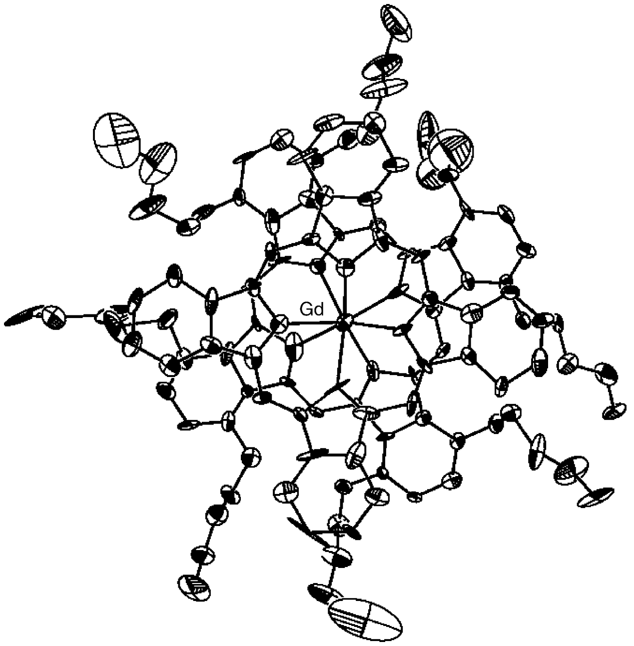

Fig. 2. Molecular structures of H{Gd(Pc)[Pc(α-OC_4H_9)$_8$]} (**3**) in the top view showing the 30% probability thermal ellipsoids for all non-hydrogen atoms.

a toluene/$CHCl_3$ (1:1) solution. This heteroleptic double-decker compound crystallizes in the triclinic system with two molecules per unit cell. Fig. 2 shows a perspective view of the structure of H{Gd(Pc)[Pc(α-OC_4H_9)$_8$]} (**3**). The data describing the deformation and relative position of two phthalocyanine rings in the whole molecule of this compound were listed in Table 3. It is noteworthy that the metal ion lies closer to the N_4 mean plane of Pc ring than to Pc(α-OC_4H_9)$_8$ and the deformation of Pc is a bit of larger than Pc(α-OC_4H_9)$_8$ ring (Table 3). This result is obviously different from those reported for neutral heteroleptic M(Pc)[Pc(α-OC_5H_{11})$_4$] [6], in which the rare earth atom lies almost in the center of Pc and tetra-substituted Pc(α-OC_5H_{11})$_4$ rings and the latter ligand is more deformed compared with the unsubstituted Pc ring. Comparison of these significantly different structural results between H{Gd(Pc)[Pc(α-OC_4H_9)$_8$]} and M(Pc)[Pc(α-OC_5H_{11})$_4$] seems to suggest that the acidic proton might locate in the ring of Pc(α-OC_4H_9)$_8$ in the protonated heteroleptic double-deckers. This proposition is rationalized by the fact that Pc(α-OC_4H_9)$_8$ is much electron-richer than Pc ligand due to the eight electron-donating butyloxy groups attached to the non-peripheral positions of Pc(α-OC_4H_9)$_8$. The interaction between the proton and Pc(α-OC_4H_9)$_8$ ring leads to longer M-N_4[Pc(α-OC_4H_9)$_8$] plane distance with respect to that of M-N_4(Pc) and a slightly less deformation degree of Pc(α-OC_4H_9)$_8$ ring than Pc.

Table 3
The structural data for **3**

Compound	H{Gd(Pc)[Pc (α-OC_4H_9)$_8$]}
Average M-N(Pc) bond distance (Å)	2.359
Average M-N[Pc(α-OC_4H_9)$_8$] bond distance (Å)	2.459
M-N_4(Pc) plane distance (Å)	1.368
M-N_4[Pc(α-OC_4H_9)$_8$] plane distance (Å)	1.468
Interplanar distance (Å)	2.836
Dihedral angle between the two N_4 planes (°)	0.6
Average dihedral angle for the Pc ring (°)[a]	13.6
Average dihedral angle for the Pc(α-OC_4H_9)$_8$ ring (°)[a]	11.3
Average twist angle (°)[b]	31.2

[a] The average dihedral angle of the individual isoindole rings with respect to the corresponding N_4 mean plane.

[b] Defined as the rotation angle of one ring away from the eclipsed conformation of the two rings.

The average twist angle, which is defined as the rotation angle of one ring away from the eclipsed conformation of the two rings, is 31.2° for H{Gd(Pc)[Pc(α-OC_4H_9)$_8$]}. It is likely that the non-fully staggered orientation with a skew angle about 31° can minimize the non-bonding interactions between the unsubstituted Pc and 1,4,8,11,15,18,22,25-octa(butyloxy)phthalocyanine rings. Due to the non-fully staggered orientation of the Pc and Pc(α-OC_4H_9)$_8$ rings and the sandwich-like structure of HGd(Pc)[Pc(α-OC_4H_9)$_8$], this heteroleptic double-decker takes relatively lower symmetry, C_4, existing as a pair of enantiomers of chiral molecules in a unit cell of crystals. This paper thus reports the first structural characterization of a series of novel chiral sandwich bis(tetrapyrrole) molecules induced by tuning the skew angles between the two phthalocyanine rings of a heteroleptic double-decker molecules.

4. Conclusion

Briefly summarizing above, 1,4,8,11,15,18,22,25-octa (butyloxy)-phthalocyanine-containing heteroleptic bis (phthalocyaninato) rare earth complexes H{M(Pc)[Pc(α-OC_4H_9)$_8$]} have been prepared and spectroscopically characterized. Significant change was induced by the eight butyloxy substituents at the 1,4,8,11,15,18,22,25 non-peripheral positions of the Pc(α-OC_4H_9)$_8$ ring in these heteroleptic double-decker complexes. Moreover, X-ray single crystal molecular structural studies demonstrate that these heteroleptic double-decker molecules are chiral in nature due to the two non-fully staggered phthalocyanine rings. This offers a new concept for inducing sandwich bis(tetrapyrrole) molecular chirality. We believe that further elaboration of the present system should lead to a more generalized concept for designing chiral bis(tetrapyrrole) compounds, which will attract attention in view of the design of molecular machines, devices, and recognition systems.

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