Inorg. Chem. **2004**, *43*, 4740–4742

Inorganic Chemistry

Article

The First Slipped Pseudo-Quadruple-Decker Complex of Phthalocyanines

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Received March 7, 2004

The first slipped pseudo-quadruple-decker complex of phthalocyanines was formed unexpectedly upon treatment of the protonated double-decker $Sm^{III}H(Pc)[Pc(\alpha\text{-}OC_4H_9)_8]$ with NaOH. The supramolecular structure contains two double-decker units linked by two sodium ions by an extremely rare coordination mode of phthalocyanines in which an aza nitrogen atom and two oxygen atoms from neighboring alkoxy substituents form a tridentate ligand.

Sandwich-type phthalocyaninato rare-earth-metal complexes have been studied extensively since the first report of bis(phthalocyaninato)lanthanide(III) in the 1960s.[1] The intense interest of this class of compounds stems from their intriguing optical and electrical properties, arising mainly from the $\pi-\pi$ interactions, leading to a wide range of applications in the fields of molecular electronics and photonics.[2] Theoretical calculations have predicted that an extended array of phthalocyanine rings will exhibit enhanced conductivity properties.[3] Compounds with such a structure may also function as molecular-based magnets.[4] Due to the bonding nature of rare-earth-metal(III/IV) ions, this class of compounds, however, is limited to double- and triple-decker complexes. To extend this system, Ishikawa et al. have prepared bis(phthalocyaninato)lutetium(III) in which one of the phthalocyaninato ligands is linked to one or four 15-crown-5 units on the periphery. These compounds form supramolecular structures in the presence of K^+ or NH_4^+ ions, exhibiting distinct electronic and magnetic properties.[5] Such supramolecular assemblies remain extremely rare despite their great intrinsic interests and potential applications.[6] In this Article, we describe an unprecedented manner to link up two bis(phthalocyaninato) double-decker complexes, forming a slipped pseudo-quadruple-decker complex. The linkage involves the coordination of the aza nitrogen atoms of phthalocyanine.[7]

During the course of our exploration of new synthetic pathways to heteroleptic bis(phthalocyaninato) rare-earth-metal complexes,[8] we found that the reaction of $Sm^{III}(Pc)(acac)$ (Pc = phthalocyaninate; acac = acetylacetonate), prepared from $Sm(acac)_3 \cdot nH_2O$ and $Li_2(Pc)$, with 1,4,8,11,15,18,22,25-octa(butyloxy)phthalocyanine $[H_2Pc(\alpha\text{-}OC_4H_9)_8]$ in 1-octanol gave the protonated double-decker $Sm^{III}H(Pc)[Pc(\alpha\text{-}OC_4H_9)_8]$ (**1**) in 14% yield (see the Supporting Information). This kind of protonated species usually exists as an intermediate which is oxidized readily in air, giving

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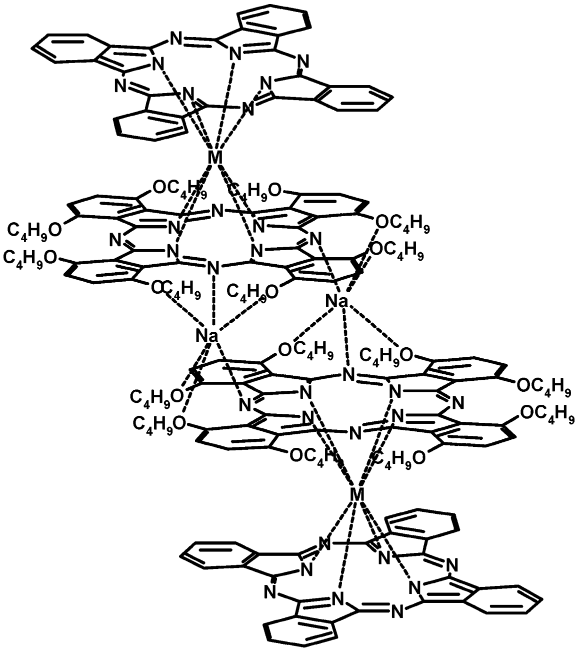
10.1021/ic049705i CCC: $27.50

Chart 1



the normal double-decker $M^{III}(\text{ring-1}^{2-})(\text{ring-2}^{\bullet-})$.[9] It seems that this octa-α-substituted phthalocyaninato ligand can stabilize the protonated form, allowing it to be isolated in this reaction. Compound **1** did not show the characteristic π-radical near-IR electronic absorption and the IR marker band for phthalocyanine radical anions at ca. 1310 cm^{-1}.[2] This observation together with the elemental analysis and mass spectral data supports the formulation of this compound.

To facilitate a comparative study with other nonprotonated double-decker complexes, NaOH was used to remove the proton of this compound with a view to preparing the anionic double-decker $\{Sm^{III}(Pc)[Pc(\alpha\text{-}OC_4H_9)_8]\}^-$. After a mixture of **1** and NaOH in $CHCl_3$/MeOH (1:1) was stirred at ambient temperature for 1 h followed by recrystallization of the crude product, dark green single crystals suitable for X-ray diffraction analysis were obtained (see the Supporting Information). Unexpectedly, the compound was found to be a slipped pseudo-quadruple-decker structure in which two anionic double-decker units are linked together by two sodium ions (Chart 1).

The molecular structure of the slipped pseudo-quadruple-decker **2** was determined by X-ray diffraction analysis at −100 °C. The compound crystallizes in the monoclinic system with a $P2_1/a$ space group.[10] Each unit cell contains two molecules of **2** and four molecules of solvated MeOH. As shown in Figure 1, this supramolecular structure is composed of two heteroleptic bis(phthalocyaninato)samarium(III) units connected by two sodium atoms through the $Pc(\alpha\text{-}OC_4H_9)_8$ rings. Each sodium atom is hexacoordinated by two aza nitrogen atoms and four adjacent butyloxy oxygen atoms, all from the two $Pc(\alpha\text{-}OC_4H_9)_8$ rings, forming a distorted trigonal antiprism. The ring-to-ring separation of the two $N(\text{isoindole})_4$ mean planes of $Pc(\alpha\text{-}OC_4H_9)_8$ is 4.23 Å, while the separation between the two C_4 axes for each $Sm^{III}(Pc)[Pc(\alpha\text{-}OC_4H_9)_8]$ unit is 6.97 Å.

Each double-decker unit retains typical structural features of bis(phthalocyaninato) complexes.[8b] The samarium center is octacoordinated by the isoindole nitrogen atoms of the two phthalocyaninato ligands, forming a distorted antiprism. The average skew angle, defined as the rotation angle of one ring away from the eclipsed conformation of the two rings, is 33.3°. The nonfully staggered orientation of the Pc and $Pc(\alpha\text{-}OC_4H_9)_8$ rings makes the sandwich structure adopt a lower C_4 symmetry. The two $N(\text{isoindole})_4$ mean planes are virtually parallel with a dihedral angle of 2.6°, but the two ligands are significantly domed. The average dihedral angles of the individual isoindole NC_4 rings with respect to the corresponding $N(\text{isoindole})_4$ mean plane are 23.4° and 22.3° for Pc and $Pc(\alpha\text{-}OC_4H_9)_8$ ligands, respectively. This deformation adjusts the orientation of the aza nitrogens' lone-pair electrons, facilitating the complexation with sodium ions. The separation between the two $N(\text{isoindole})_4$ planes is 2.91 Å, with the samarium atom lying almost in the center {1.462 Å [from $Pc(\alpha\text{-}OC_4H_9)_8$] vs 1.445 Å (from Pc)}.

The electronic absorption spectra of the protonated double-decker **1** in $CHCl_3$ and the slipped pseudo-quadruple-decker **2** in $CHCl_3$/MeOH are given in Figure 2. It can be seen that all the major bands are shifted slightly to the blue upon formation of the supramolecular structure.

The ^1H NMR spectrum of **1** in $CDCl_3$ did not show the expected signals. The actual reason is not clear at this stage. We suspect that the proton is weakly linked to one of the isoindole nitrogen atoms, preferentially at the more electron rich $Pc(\alpha\text{-}OC_4H_9)_8$ ring, and undergoes a tautomerization as in the case of $M^{III}H(\text{Por-1}^{2-})(\text{Por-2}^{2-})$ (M = La, Lu; Por = general porphyrinate).[11] The extensive exchange process precludes the acquisition of a satisfactory NMR spectrum. However, when the spectrum was recorded in $CDCl_3$/DMSO-d_6 (1:2) in the presence of 3 equiv of NaOD (40% in D_2O), the signals corresponded well with the double-decker structure. The spectrum showed two rather broad signals at δ 8.21 (masked by the residual $CHCl_3$ signal) and 7.60 for the α- and β-ring protons of Pc, respectively, a broad band at δ 6.9 assignable to the $Pc(\alpha\text{-}OC_4H_9)_8$ ring protons, two multiplets at δ 4.28−4.34 and 3.78−3.88 for the diastereotopic OCH_2 protons, two partially overlapped multiplets at δ 1.45−1.78 for the remaining CH_2 protons, and a triplet at δ 1.05 for the terminal methyl groups. The assignments were confirmed by a $^1H-^1H$ COSY experiment (see the Supporting Information). On the basis of these data, however, it cannot be concluded whether these signals are due to the nonassociated $Na\{Sm^{III}(Pc)[Pc(\alpha\text{-}OC_4H_9)_8]\}$, the slipped pseudo-quadruple-decker **2**, or a mixture of these two species.

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(10) Crystal data for **2**·2MeOH: $C_{194}H_{200}N_{32}Na_2O_{18}Sm_2$, M_w = 3614.54 g/mol, monoclinic, space group $P2_1/a$ (No. 14), with a = 15.6327(8) Å, b = 31.577(2) Å, c = 19.6687(10) Å, β = 111.392(1)°, V = 9040.2(8) Å^3, D_c = 1.328 g cm^{-3}, and Z = 2. The structure was solved by direct methods and refined by a full-matrix least-squares procedure using 15615 data to a conventional R value of 0.0761 (R_w = 0.1081). CCDC reference number 223763.

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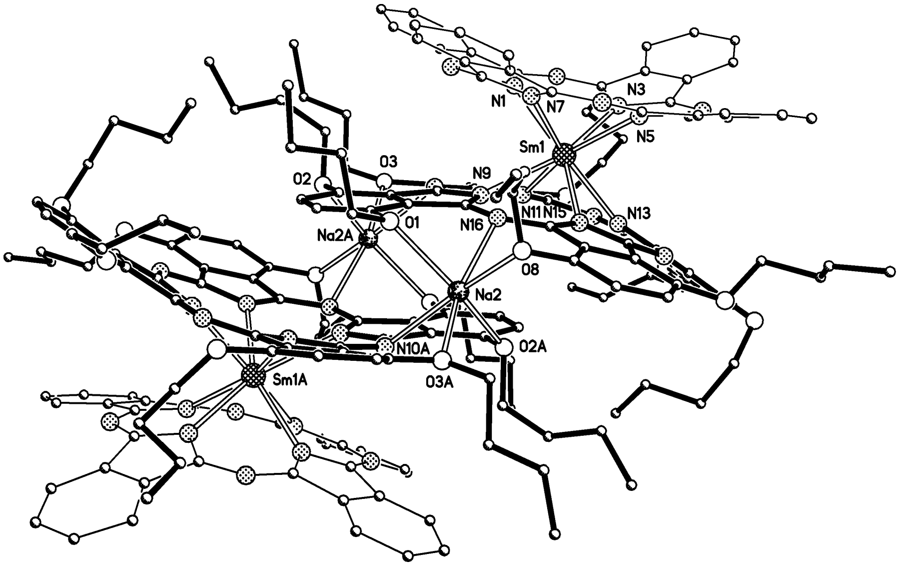

Figure 1. Molecular structure of the slipped pseudo-quadruple-decker **2**. Hydrogen atoms are omitted for clarity.

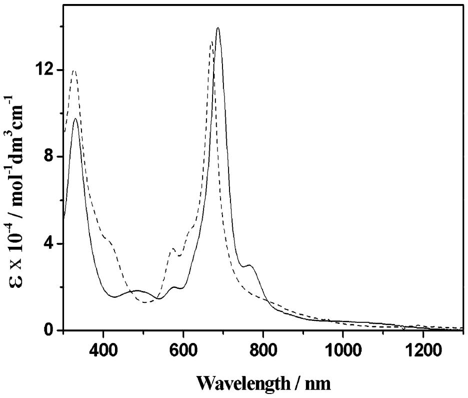

Figure 2. Electronic absorption spectra of **1** in $CHCl_3$ (solid line) and **2** in $CHCl_3$/MeOH (95:5) (dashed line).

The redox behavior of **2** was studied by cyclic voltammetry and differential pulse voltammetry in CH_2Cl_2. Four quasi-reversible one-electron oxidations at +1.39, +0.88, +0.36, and +0.01 V and four quasi-reversible one-electron reductions at −0.86, −1.23, −1.59, and −1.85 V were revealed. The potential difference between the first oxidation and the first reduction, which reflects the HOMO−LUMO gap, was found to be 0.87 V. The value is slightly smaller than that for **1** (1.02 V) measured under the same conditions.

In conclusion, we have reported the unexpected formation of an unprecedented pseudo-quadruple-decker complex of phthalocyanines, the molecular structure of which has been determined. The supramolecular structure is held by a rare coordination mode of phthalocyanines in which an aza nitrogen atom and two oxygen atoms from neighboring alkoxy substituents form a tridentate ligand. It is envisaged that this new binding mode can be utilized to construct different supramolecular structures of phthalocyanines through manipulation of the metal ions. This work is under investigation.

Acknowledgment. We thank Profs. Xiaoming Chen and Daqi Wang for solving the molecular structure of **2**. Financial support from the National Science Foundation of China (Grant Nos. 20171028 and 20325105), Ministry of Science and Technology of China (Grant No. 2001CB6105-04), Ministry of Education of China, The Science Foundation of Shandong Province (Grant No. Z99B03), and The Chinese University of Hong Kong is gratefully acknowledged.

Supporting Information Available: Synthesis and characterization data of compounds **1** and **2** and $^1H-^1H$ COSY spectrum of **1** in $CDCl_3$/DMSO-d_6 (1:2) in the presence of 3 equiv of NaOD (40% in D_2O) (Figure S1) (PDF) and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049705I