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Synthesis and structure of europium(III) double- and triple-decker complexes with 2,3,9,10,16,17,23,24-octabutylphthalocyanine

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The reaction of 4,5-dibutylphthalodinitrile with $Eu(acac)_3\cdot 3H_2O$ at 130 °C results in sandwich-type bis[2,3,9,10,16,17,23,24-octabutylphthalocyaninato]europium(III) 1 and the reaction of free 2,3,9,10,16,17,23,24-octabutylphthalocyanine with $Eu(acac)_3\cdot 3H_2O$ at 196 °C gives tris[2,3,9,10,16,17,23,24-octabutylphthalocyaninato]dieuropium(III) 2. Structures of compounds 1 and 2 have been determined using X-ray diffraction analysis, electronic and NMR spectroscopy and mass spectrometry.

Compounds of transition metals containing coordinated natural porphyrins and their synthetic analogues, *viz*., phthalocyanines, draw a great deal of attention, primarily as metal complexes that possess unique structures and unusual physicochemical properties.[1–3] For example, phthalocyanine complexes of rare-earth elements are promising building blocks for cation-induced generation of supramolecular systems with various architectures that can be used to design chemical gas sensors and ion-selective sensors possessing high adjustable selectivity, materials for microelectronics and components of electrochromic devices, as well as to design unusual fragments for non-linear optics devices.[1,2]

It is well known that rare-earth elements can form complex compounds with various phthalocyanines.[4–7] In addition to planar and double-decker sandwich phthalocyanines, triple-decker complexes are known. However, it was only with crown-substituted lutetium phthalocyanine that the structure of $(L_4Pc)_3Lu_2$ (where L = 15-crown-5) was characterised.[8] Difficulties in the structural characterization of such objects are primarily due to problems in preparing single crystals suitable for X-ray diffraction analysis and due to their thermal instability owing to the presence of solvent molecules in the crystal.[8] Among phthalocyanine-containing europium(III) complexes, structurally characterised compounds are limited to non-substituted bis(phthalocyanine) Pc_2Eu,[9] heteroleptic bis(phthalocyanines) $(Et_2CHO)_4PcEuPc$[10] and $L_4PcEuPc$ (L = 15-crown-5),[11] as well as two mixed-ligand porphyrin-containing complexes.[12,13]

The aim of this work was to synthesise and study the structures of double- and triple-decker europium(III) complexes containing a coordinated 2,3,9,10,16,17,23,24-octabutylphthalocyaninate anion.

We found that the reaction of $Eu(acac)_3\cdot 3H_2O$ with 4,5-dibutylphthalodinitrile[14] in refluxing isoamyl alcohol in the presence of 1,4-diazabicycloundec-7-ene (DBU) for 6 h followed by chromatography of the resulting product on silica gel (with C_6H_6 as the eluent) results in double-decker complex bis[2,3,9,10,16,17,23,24-octabutylphthalocyaninato]europium(III) $[(Bu_8Pc)^{2-}Eu^{3+}(Bu_8Pc)^{-\cdot}]$ **1** in 46% yield.[†]

The reaction of free-base 2,3,9,10,16,17,23,24-octabutylphthalocyanine[14] and $Eu(OAc)_3\cdot 3H_2O$ in refluxing *n*-octanol for 1.5 h results in a product, the purification of which by chromatography (Bio-Beads S-X1, THF as the eluent) gives triple-decker complex tris[2,3,9,10,16,17,23,24-octabutylphthalocyaninato]dieuropium(III) $[(Bu_8Pc)^{2-}Eu^{3+}(Bu_8Pc)^{2-}Eu^{3+}(Bu_8Pc)^{2-}]$ **2** in 94% yield.[‡]

The structures of dark green single crystals of complex **1** obtained from a DMSO–$CHCl_3$ mixture (1:1) and dark blue single crystals of triple-decker complex **2** obtained from a MeOH–CH_2Cl_2 mixture (1:1) were established by X-ray diffraction analysis.[§]

According to X-ray diffraction data, the molecule of bis(phthalocyanine) **1** (Figure 1) has the structure of a double-decker sandwich, in which the Eu^{III} ion is bound to eight isoindole nitrogen atoms N_{iso} of two almost parallel phthalocyanine fragments (with a distorted tetragonal antiprism as the coordination polyhedron). The mean Eu–N_{iso} distance is 2.430(7)–2.453(7) Å. The phthalocyanine rings are concave with respect to the metal and are turned by 36.3° relative to

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[†] *Synthetic procedure*. A mixture of 4,5-dibutylphthalodinitrile (200 mg, 0.83 mmol), $Eu(acac)_3\cdot 3H_2O$ (47 mg, 0.09 mmol) and DBU (70 mg, 0.42 mmol) was heated under an inert atmosphere in 2 ml of isoamyl alcohol and kept for 6 h under reflux conditions (130 °C). After the reaction was completed, the resulting mixture was diluted with $CHCl_3$ (25 ml) and insoluble admixtures were filtered off. The solvent was distilled off from the mother liquor using a rotary evaporator. The residue was refluxed in 80% aqueous MeOH (3×50 ml) followed by filtering and drying in a vacuum (100 °C). The powder formed was dissolved in C_6H_6 and chromatographed on a 35×3.5 cm column (Merck Silica Gel 40, 63×200 mm, C_6H_6 as the eluent). Preparative purification was performed by TLC (Merck Aluminium Oxide F_{254} neutral, C_6H_6 as the eluent). The yield of compound **1** was 89 mg (46%). ^1H NMR ($[^2H_8]THF + N_2H_4\cdot H_2O$) δ: 10.94 (s, 16H, H_{Ar}), 4.27 (t, 32H, α-CH_2), 2.57–3.09 (m, 64H, β,γ-CH_2), 1.77 (t, 48H, Me). Electronic absorption spectrum [(C_6H_6, λ_{max}/nm (log ε)]: 330 (5.14), 355 (5.06), 486 (4.62), 615 (4.67), 684 (5.17). MS (MALDI-TOF), *m/z*: 2075 (MH^+).

[‡] *Synthetic procedure*. A mixture of 2,3,9,10,16,17,23,24-octabutylphthalocyanine (50 mg, 0.052 mmol) and $Eu(OAc)_3\cdot 3H_2O$ (16 mg, 0.042 mmol) was heated under Ar in *n*-octanol (1 ml) and kept for 1.5 h under reflux conditions (196 °C). After the synthesis was completed, MeOH (30 ml) was added to the reaction mixture. The precipitate was filtered off, washed with MeOH (3×10 ml) and dried in a vacuum (100 °C). The resulting powder was dissolved in THF and chromatographed on a 40×2.5 cm column (Bio-Beads S X1, THF as the eluent); the first dark blue fraction was collected. The yield of compound **2** was 52 mg (94%). ^1H NMR ($CDCl_3$) δ: 12.72 (s, 8 H, H_{Ar} inner), 9.52 (s, 16H, H_{Ar} outer), 4.85 (t, 16H, α-CH_2 inner), 4.09–4.02 (overlapping multiplets, 48H, β-CH_2 inner, α-CH_2 outer), 3.47 (m, 16H, γ-CH_2 inner), 2.71 (m, 32H, β-CH_2 outer), 2.45 (m, 32H, γ-CH_2 outer), 2.28 (t, 24H, Me inner), 1.78 (t, 48H, Me outer). Electronic absorption spectrum [(C_6H_6, λ_{max}/nm (log ε)]: 346 (5.28), 662 (5.19). MS (MALDI-TOF), *m/z*: 3189 (MH^+).

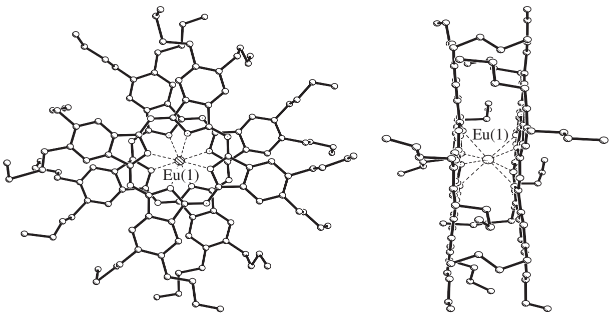

Figure 1 Structure of complex **1**: frontal and vertical projections.

each other. The distance between the $4N_{iso}$ planes of the phthalocyanine fragments equals 3.013 Å, which is shorter than the van der Waals distance (3.34 Å) for aromatic systems, suggesting the existence of π–π interactions between the phthalocyanine ligands in compound **1** [the root-mean-square deviation of nitrogen atoms from the plane N(1)N(2)N(3)N(4) does not exceed 0.02 Å and their deviation from the N(9)N(10)N(11)N(12) plane does not exceed 0.01 Å; the angle between the planes is 0.9°].

In triple-decker complex **2** (Figure 2), Eu^{III} ions are also localised between the planes of phthalocyanine ligands; the Eu–Eu distance is 3.569(1) Å. The coordination polyhedron of each Eu^{III} ion is a distorted tetragonal antiprism, like compound **1**. The two outer rings have the same orientation with respect to the inner ring. The twist angle is 27.9°, which is somewhat smaller than that in bis(phthalocyanine) **1**. The adjacent macrocycles are not equidistant from Eu; the distances between the metal and the N_{iso} atoms of the outer ligands are 2.368(9)–2.409(9) Å, whereas the mean Eu–N_{iso} distance for the inner ligand is somewhat larger, *viz*., 2.601(8)–2.664(9) Å. This may be explained by the fact that the internal macrocycle forming bonds with two metal atoms at once cannot be bound as strongly as the outer ligands. The intramolecular interplanar distance of two adjacent ligands is 3.121 Å, which is somewhat larger than in bis(phthalocyanine) **1** [the root-mean-square deviation of nitrogen atoms from the N(1)N(2)N(5)N(7) plane does not exceed 0.06 Å; the N(9)N(11)N(13)N(11a) atoms are arranged in the same plane; the interplanar angle is 4°].

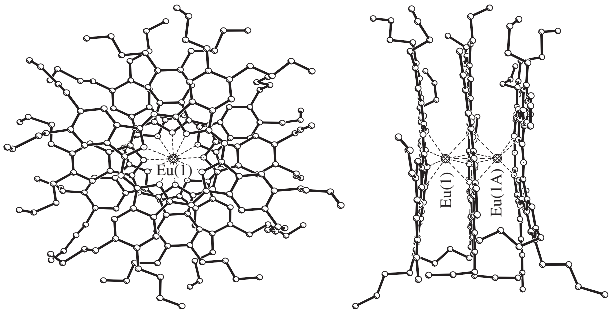

Figure 2 Structure of complex **2**: frontal and vertical projections.

X-ray diffraction data are in good agreement with the results obtained by ^1H NMR and mass spectrometry, as well as electronic absorption spectroscopy. In fact, the MALDI-TOF spectra of phthalocyanines **1** and **2** show molecular ion peaks with masses corresponding to theoretically calculated values, whereas electronic absorption spectra contain absorption bands characteristic of each type of complexes.[†,‡]

A specific feature of bis(phthalocyanines) is that their molecules contain a radical fragment $Pc^{\cdot-}$, which does not allow satisfactory NMR spectra to be obtained in common solvents. Therefore, the ^1H NMR spectra of compound **1** were recorded in $[^2H_8]$THF in the presence of 1–2 vol% hydrazine hydrate that allowed the $Pc^{\cdot-}$ fragment to be reduced into the Pc^{2-} dianion. The paramagnetic nature of europium(III) results in an insignificant broadening of resonance signals in the spectrum and their downfield shift[†] with respect to complexes of diamagnetic lanthanides.[1]

A characteristic feature of proton spectra of tris(phthalocyanines) is that they contain two sets of single-type signals with an integral intensity ratio of 1:2, which is due to higher deshielding of internal ligand protons in comparison with the two external protons. The resonance proton signals of the internal ligand in tris(phthalocyanine) **2** are shifted downfield with respect to the signals of bis(phthalocyanine) **1**, which suggests that protons in this compound are deshielded more strongly than in the other compounds studied.

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[§] *X-ray diffraction study.* X-ray diffraction experiments were carried out at the Centre for Structural Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) using standard procedures[15] on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo, graphite monochromator, ω-scanning, scanning step 0.3°, frame measurement time 10 s, $2\theta_{max} = 50°$).

For compound **1**: $C_{129.5}H_{159.5}Cl_{1.5}EuN_{16}O_{1.5}$, $M = 2169.3$, space group $P\bar{1}$, $a = 10.801(2)$, $b = 21.346(4)$ and $c = 27.8956(4)$ Å, $\alpha = 80.82(3)°$, $\beta = 89.62(3)°$, $\gamma = 81.03(3)°$ (112 K), $V = 0.6270(1)$ Å^3, $Z = 2$, 28451 measured reflections including 10260 independent reflections with $F^2 > 2\sigma(I)$, $d_{calc} = 1.149$ g cm^{-3}, $\mu = 1.250$ cm^{-1}, $R_1 = 0.0912$, $wR_2 = 0.177$.

For compound **2**: $C_{196.5}H_{253}Cl_5Eu_2N_{24}O_2$, $M = 3464.4$, space group $C2/c$, $a = 17.289(6)$, $b = 40.084(13)$ and $c = 25.819(9)(4)$ Å, $\beta = 93.367(1)°$ (112 K), $V = 17857(10)$ Å^3, $Z = 8$, 19421 measured reflections including 6091 independent reflections with $F^2 > 2\sigma(I)$, $d_{calc} = 1.289$ g cm^{-3}, $\mu = 0.831$ cm^{-1}, $R_1 = 0.0807$, $wR_2 = 0.189$.

CCDC 649629 and 649630 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2007.