Letters to the Editor

First example of structurally characterized double-decker sandwich rare-earth metal complex with crown-substituted phthalocyanine. Synthesis and structure of bis[tetra(15-crown-5)phthalocyaninato]ytterbium(III)

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Earlier,[1] we have demonstrated that the reaction of tetra-15-crown-5-phthalocyanine $H_2(R_4Pc)$ (R = 15-crown-5) with Yb^{III} acetate tetrahydrate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing 1-chloronaphthalene (2 h) afforded a series of sandwich complexes with the 1 : 2 and 2 : 3 metal—ligand ratios (Scheme 1).

Under analogous conditions, complexes of this type were also prepared for other lanthanides.[1] However, the triple-decker complex $(R_4Pc)_3Lu_2$ with 2 : 3 composition is the only structurally characterized representative of this series of compounds.[2]

We established for the first time the structure of a complex with 1 : 2 composition, *viz.*, $[(R_4Pc^{2-})Yb^{3+}(R_4Pc^{\bullet-})]$ (**1**). According to the results of X-ray diffraction analysis, molecule **1** (Fig. 1) is a double-decker sandwich in which the Yb^{III} atom is coordinated by eight nitrogen atoms (coordination polyhedron is a distorted tetragonal antiprism) of virtually coplanar phthalocyanine fragments of two tetra(15-crown-5)phthalocyanine ligands (Yb—N, 2.254(11)—2.410(13) Å). The macrocyclic ligands are twisted with respect to each other by 42.5°. The distance between the planes of the phthalocyanine fragments is 2.98 Å (rms deviations of the N atoms from the N(1)—N(2)—N(3)—N(4) and N(9)—N(10)—N(11)—N(12) planes are 0.02 and 0.01 Å, respectively; the angle between the planes is 0.6°).

The electronic absorption spectra were recorded on Varian Cary-100 and Specord NIR-61 instruments (Carl Zeiss Jena) in 1-cm quartz rectangular cells. The IR spectra were measured on a Nexus Fourier IR spectrometer (Nicolet) in Nujol mulls. The MALDI-TOF mass spectrum was obtained on a Kratos Kompact III spectrometer (N_2 laser, λ = 337 nm).

Synthesis of bis[4,5,4´,5´,4´´,5´´,4´´´,5´´´-tetrakis(1,4,7,10,13-pentaoxatridecamethylene)phthalocyaninato]ytterbium(III) (1). A mixture of tetra-15-crown-5-phthalocyanine (50 mg, 0.039 mmol), $Yb(OAc)_3 \cdot 4H_2O$ (9 mg, 0.026 mmol), and DBU (0.055 mL, 0.34 mmol) was refluxed (260 °C) in 1-chloronaphthalene (2 mL) in an inert atmosphere for 2 h. The reaction mixture was cooled, diluted with chloroform (20 mL), and filtered off from an insoluble precipitate. The resulting solution was chromatographed on a 30×2-cm column (neutral aluminum oxide), a green solution of complex **1** being separated by gradient elution with a chloroform—methanol mixture (99 : 1, v/v).

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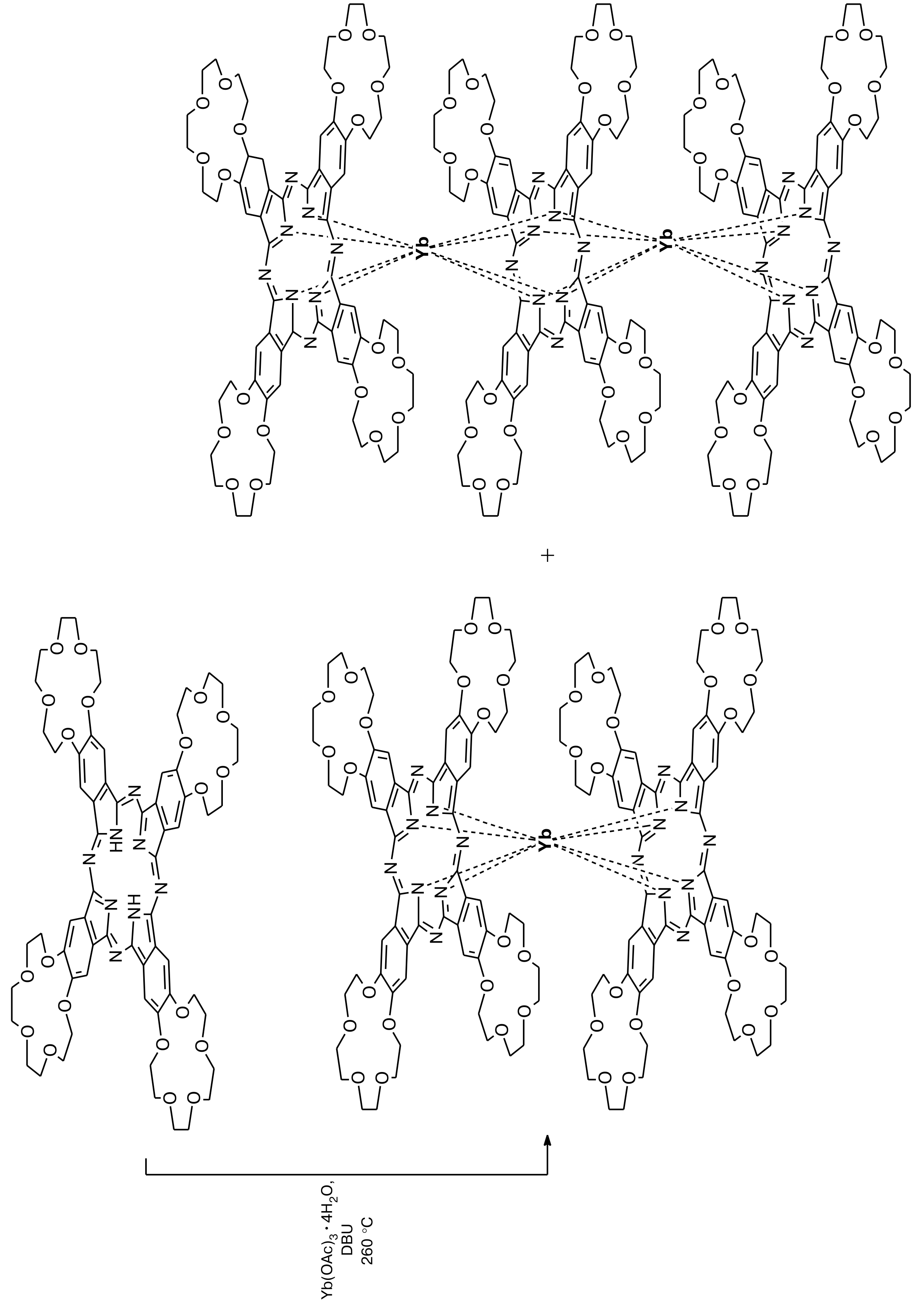
Scheme 1



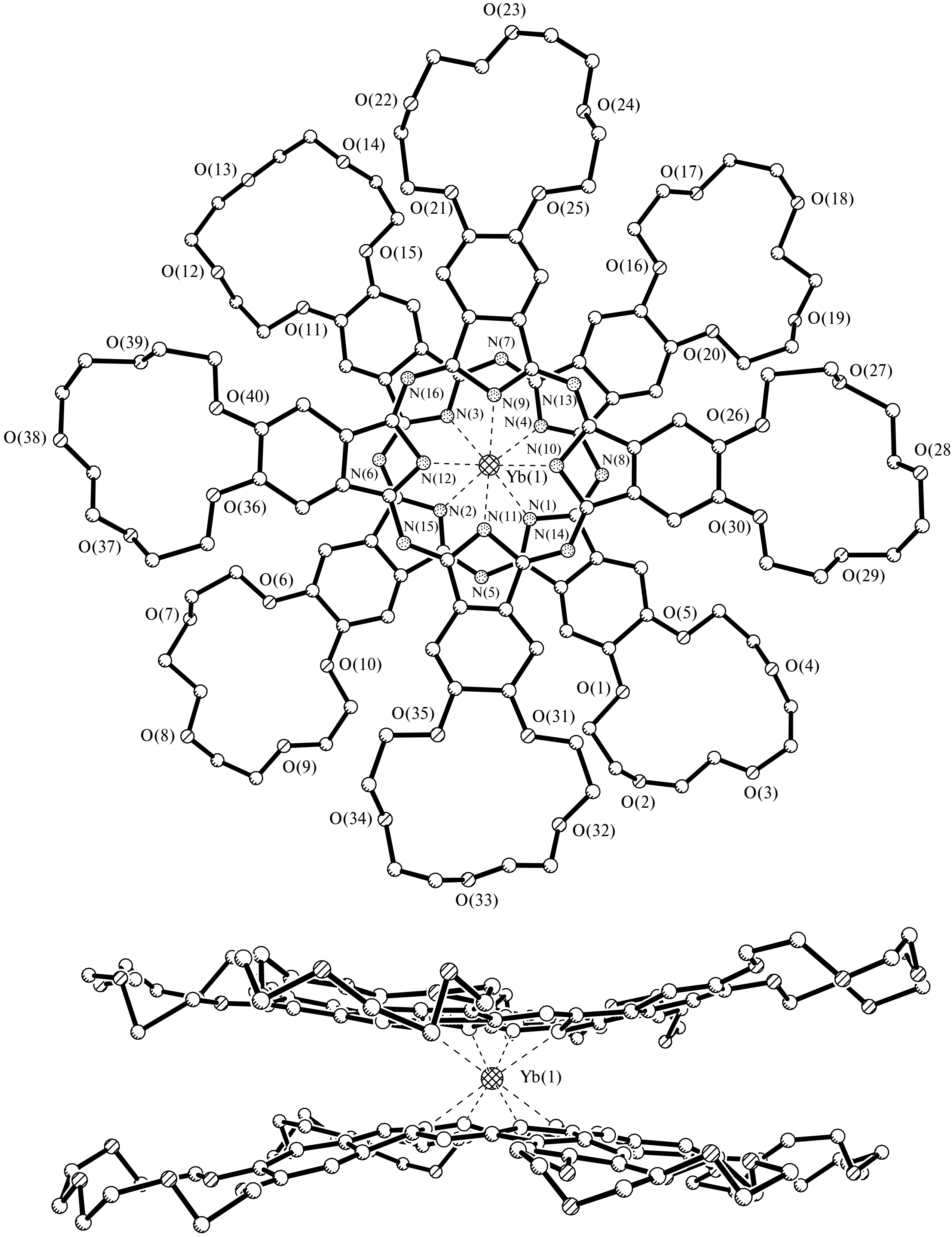


Fig. 1. Structure of complex **1**: *a*, frontal projection; *b*, horizontal projection.

The yield of [$(R_4Pc^{2-})Yb^{3+}(R_4Pc^{\bullet -})$] (**1**) was 24.74 mg (35%). The electronic absorption spectrum, λ_{max}/nm (logε): 292 (5.06), 369 (5.12), 479 (4.60), 670 (5.18), 1410 (4.08) (band of the donor-acceptor exchange interaction between the Pc^{2-} dianion and $Pc^{\bullet -}$ radical anion). IR (main bands of the phthalocyanine and crown fragments, cm^{-1}): 1600, 1500 (C—C, benzene ring), 1320 (radical anion), 1280, 1130, 1100, 1060, and 940 (crown substituents). MS MALDI-TOF: m/z = 2714 (experimental), 2718.9 (calculated).

Dark-green single crystals of **1** with eight molecules of diphenyl ether of solvation, which were suitable for X-ray diffraction analysis, were prepared by slow evaporation of a solution of complex **1** in a 1 : 1 : 1 chloroform—methanol—diphenyl ether mixture.

X-ray diffraction data were collected at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, the Russian Academy of Sciences) according to standard procedures[3] on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λ-Mo-Kα radiation, graphite monochromator, φ and ω scan techniques, scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max} = 50°$). For complex $\mathbf{1}\cdot 8Ph_2O$: $C_{256}H_{224}N_{16}O_{48}Yb$, M = 4465.55, monoclinic system, space group *Cc*, at 293 K a = 36.227(6), b = 23.727(6), c = 25.454(6) Å, β = 113.810(2)° V = 20017.2(8) Å^3, Z = 4; 29286 measured reflections of which 8171 independent reflections were with $F^2 > 2\sigma(I)$, ρ_{calc} = 1.482 g cm^{-3}, μ = 5.61 cm^{-1}, R_1 = 0.0697, wR_2 = 0.1919.

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