Synthesis, Structure, and Optical Characterization of Sandwich-type (2,3-Naphthalocyaninato)(octaethylporphyrinato)europium(III)

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The heteroleptic sandwich dimer of the title {Eu(OEP)(2,3-Nc)} has been synthesized, and its crystal structure, electronic absorption, and magnetic circular dichroism are discussed.

Heteroleptic rare-earth sandwich complexes containing 2,3-naphthalocyanine (2,3-Nc) are still very rare[1,2] and in particular, little is known on compounds containing both Nc and porphyrin,[2] while no X-ray data have been reported. Compounds containing both small and large macrocyclic ligands are important in elucidating the intrinsic properties of homoleptic sandwich complexes, such that without knowing the properties of compounds with slightly different structures, the understanding of even the simplest compounds is not necessarily correctly achieved. From this respect, we have synthesized the heteroleptic sandwich dimer of the title and examined its properties. In particular, we report here the first X-ray analysis of a compound containing both 2,3-Nc and another macrocycle.[3]

Eu(OEP)(2,3-Nc) was synthesized by refluxing a mixture of Eu(acac)$_3$·nH$_2$O (0.10 mmol), H$_2$OEP (0.05 mmol), naphthalonitrile (0.40 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (33 mmol) in *n*-octanol (4 ml) overnight under nitrogen. Subsequent silica gel chromatography using CH$_2$Cl$_2$–hexane as eluent, followed by recrystallization from CHCl$_3$–MeOH, gave 30 mg (43%) of the desired dimer as a dark green solid.[4] In the ^{1}H NMR spectrum in the presence of hydrazine hydrate, signals from OEP protons appeared at lower field compared with those of independent monomeric OEPs,[5] due perhaps to the effect of europium rather than the ring current effect of 2,3-Nc. In the IR spectrum, two bands are observed at 1323 and 1523 cm^{-1}, which are diagnostic bands for 2,3-Nc[6] and OEP[7] π radical monoanion, respectively. Thus, the co-existence of these two bands strongly suggests that the hole or unpaired electron resides on a delocalized orbital over the 2,3-Nc and OEP ligands.

The single crystals of Eu(OEP)(2,3-Nc) suitable for X-ray analysis were obtained by slow diffusion of hexane into a mixed CHCl$_3$–toluene solution.[8] Finally X-ray analysis revealed that the Eu(OEP)(2,3-Nc) molecules lie on the crystallographic mirror plane and crystallize as Eu(OEP)(2,3-Nc)·4CHCl$_3$. The CHCl$_3$ molecules are stuffed into crevices of the crystal lattice, which are made up by the large and folding Nc ligand. Probably, the inclusion solvent plays an important role to form mono crystals.[8] Figures 1 A and B illustrate the ORTEP drawing of Eu(OEP)(2,3-Nc) in two different views (top and side), along with the bond lengths and angles around Eu atom. Interestingly, only two of eight ethyl groups are tilted towards the Nc plane. This finding is revealed to be due to the intermolecular arrangement in the crystal packing, in which the above two pyrrole rings have face-to-face stacked by the Nc-naphthalene ring of another molecule with the interplanar distance of 3.22 Å. However, except for the ethyl group, the geometry of Eu(OEP)(2,3-Nc) can be said to keep approximately *mm* symmetry.

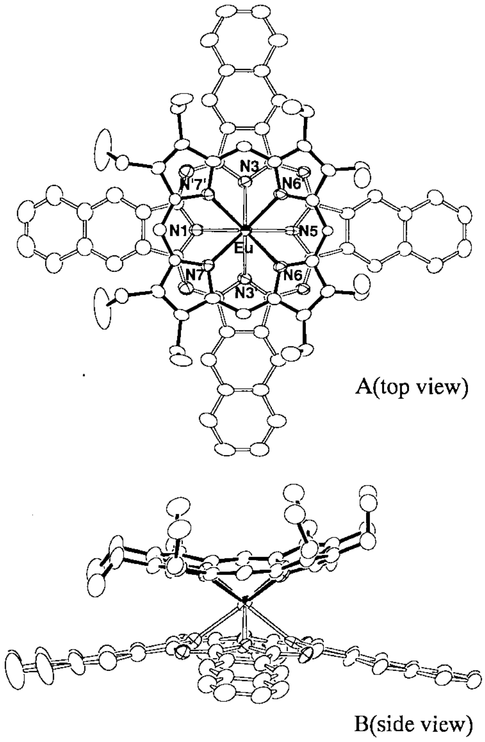

Figure 1 (A, B) ORTEP diagram of Eu^{III}(OEP)(Nc). The thermal ellipsoids are drawn 50% probability level. H atoms are omitted for clarity. Bond lengths and angles around Eu atom: for Nc ligand; Eu-N1=2.476(9), Eu-N3=2.493(5), Eu-N5=2.445(9), N1-Eu-N3=68.4(2), N3-Eu-N5=67.9(2), N1-Eu-N5=104.1(3), for OEP ligand; Eu-N6= 2.442(6), Eu-N7=2.438(5), N6-Eu-N7=74.5(2), N6-Eu-N6'=74.8(2), N7-Eu-N7'=73.5(2), N6-Eu-N7'=117.3(2).

The europium is octa-coordinated by eight pyrrole nitrogens forming a nearly square antiprismatic geometry, because the N(pyrrole)$_4$ mean planes are almost parallel and a twist angle is about 45°. The metal–N$_4$ mean plane center distances are 1.51(4) Å for 2,3-Nc and 1.27(4) Å for OEP, and therefore Eu lies further to the N$_4$ plane of 2,3-Nc by 0.24 Å. This is possibly due to the smaller central cavity of Nc (3.88(1) and 3.97(1) Å compared with 4.169(7) Å for OEP as diagnostic N–N distance). The mean distances between Eu and pyrrole nitrogen are 2.47 Å for Nc and 2.44 Å for OEP. The latter value is smaller than the 2.51 Å found in Eu(OEP)$_2$[9]. The two N$_4$ planes are almost parallel with a dihedral angle of 1(1)°, but substantial doming occurs for both the Nc and OEP ligands. The dihedral angles formed between the N$_4$ plane and the mean plane (NC$_4$ plane) of an individual pyrrole or isoindole ring are 10.4(10)°, 10.7(9)°, and 10.0(8)° for

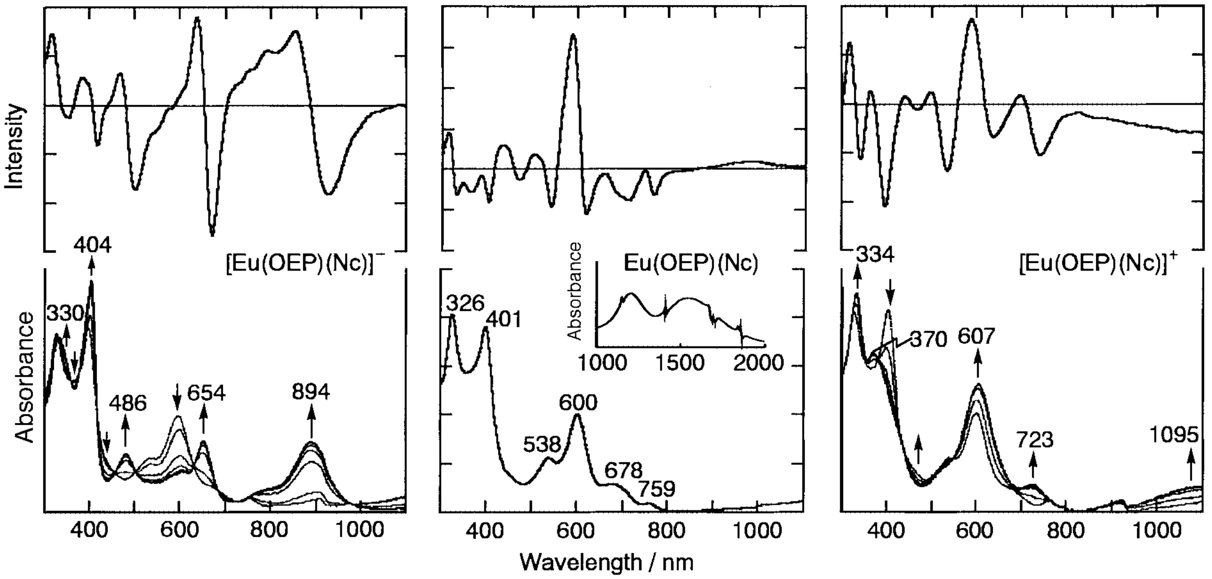

Figure 2 MCD (top) and absorption (bottom) spectra of Eu(OEP)(Nc)$^-$, Eu(OEP)(Nc), and Eu(OEP)(Nc)$^+$. The spectra of Eu(OEP)(Nc) were measured in chloroform, while those of Eu(OEP)(Nc)$^-$ and Eu(OEP)(Nc)$^+$ were collected in *o*-dichlorobenzene containing 0.1 M TBAP during one-electron reduction or oxidation processes.

the Nc and 19.8(3)° and 12.4(3)° for the OEP ring, showing that the latter is more domed.

Figure 2 shows the electronic absorption and magnetic circular dichroism (MCD) of Eu(OEP)(2,3-Nc) in chloroform. Two intense bands seen at 326 and 401 nm may be assigned to the Soret bands of 2,3-Nc and OEP, respectively, in relation to similar systems consisting of Pc, porphyrins and rare-earth metals.[10] Several peaks are observed in the 500–800 nm region, with the most intense peak being seen at 600 nm, which is about 100 nm to longer wavelength than that in Y(Pc)(TPP)[10b] (TPP:tetraphenyl-porphyrinato) in the same solvent. In the near-IR region, two bands of comparative intensity are observed at 1206 and 1550 nm, which are at much longer wavelength than those of Y(Pc)(TPP) (1002 and 1350 nm).[10b] In general, the Q and near-IR bands of homoleptic rare-earth sandwich complexes shift to longer wavelength with increasing molecular size of the constituting macrocycles, i.e., in the order of OEP or TPP to Pc and further to Nc, and Ishikawa et al. have succeeded in reproducing the spectra nicely using molecular orbital calculations.[11] However, the assignments of the bands of heteroleptic double-decker compounds are still not yet firmly established. Our data, in consideration of those of one-electron oxidised and reduced species, support the following assignments in D_{4d} symmetry.[12] (i) The near-IR bands at 1206 and 1550 nm are intervalence transitions from $b_1(\pi)$ HOMO to $a_2(\pi)$ SOMO, since the one-electron reduced species does not show bands beyond 1000 nm. (ii) The bands between ca. 480 and 800 nm are Q band in origin, since the MCD intensity per unit absorption intensity in this region is much larger than that in the Soret band region (this tendency is more pronounced in the MCD spectra of the reduced species, Figure 2, left).

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8 Crystal data for Eu(OEP)(2,3-Nc)·4CHCl$_3$: $C_{84}H_{68}N_{12}Eu{\cdot}4CHCl_3$. MW = 1875.01, orthorhombic space group *Pnma (#62)*, a = 27.9422(8), b = 26.124(1), c = 10.9643(7) Å, V = 8003(1) Å^3, Z = 4, d_{calc} = 1.556 g/cm^3, μ(Mo Kα) = 12.39 cm^{-1}. T = –123°C, crystal size = 0.20 × 0.20 × 0.10 mm, Rigaku/MSC Mercury CCD. A total of 58354 reflections were measured in which 9864 were independent (R_{int} = 0.042). Final R_1 = 0.055, R_w = 0.063 for observed 4364 reflections($I > 3.00\,\sigma(I)$).

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