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Homoleptic Lanthanide Triple-Deckers of 5,15-Diazaporphyrin with D_{2h} Symmetry

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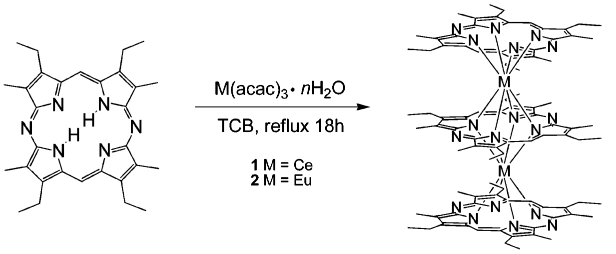
Two novel homoleptic diazaporphyrinato lanthanide sandwich complexes $M_2(DAP)_3$ [M = Ce (**1**), Eu (**2**); DAP= 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15-diazaporphyrinate] were synthesized by a one-pot reaction of the corresponding $M(acac)_3 \cdot nH_2O$ (acac = acetylacetonate) with metal-free D_{2h} type diazaporphyrin, H_2DAP. The spectroscopic and electrochemical properties are compared with those of complexes based on D_{4h} symmetry porphyrin ligands.

Sandwich-type metal complexes of tetrapyrrolic macrocycles were first reported by Linstead as far back as 1936 with the first synthesis of a tin bis(phthalocyanine), $Sn(Pc)_2$.[1] In recent years, lanthanide tetrapyrrole "sandwich-complexes" have been the subject of considerable research interest due to potential applications as advanced materials.[2,3] Modifications have been made to the porphyrin (Por) and phthalocyanine (Pc) ligands to enhance the properties of sandwich complex materials and facilitate their fabrication process. Although a large number of double decker, and several triple decker complexes, have been reported to date, the complexes have always been based on D_{4h} symmetry Por or Pc monomers. Recent studies of low symmetry Pc complexes have revealed that the heteroaromatic π-system is affected significantly by the reduction in molecular symmetry. Marked changes are observed in the $\pi \rightarrow \pi^*$ absorption bands of the monomer complexes in the UV−vis region.[4] It therefore seems reasonable to assume that if sandwich-type complexes can be prepared based on a reduced symmetry ligand, then the current understanding of the electronic structure of sandwich complexes could be enhanced considerably. We selected opposite-diazaporphyrins (DAPs) for study since they can be readily synthesized in high yield and are known to have an electronic structure that is markedly different from those of the D_{4h} type porphyrin congeners.[5,6] In this Communication, we report the synthesis and characterization of the first triple-decker Por analogues, $M_2(DAP)_3$ [M = Ce (**1**), Eu (**2**)] (Scheme 1). The structure of **2** is analyzed by X-ray crystallography. This is only the second X-ray structure to be reported for a triple decker Por analogue. The results obtained can be readily compared to those obtained for the higher symmetry $Ce_2(OEP)_3$ complex by Buchler et al. in 1986.[7]

Scheme 1. Synthesis of Rare Earth Diazaporphyrinato Triple-Deckers



Metal-free diazaporphyrin, H_2DAP[6] (60 mg, 0.12 mmol), was reacted with $M(acac)_3 \cdot nH_2O$ (0.4 mmol, M = Ce and Eu for **1** and **2**, respectively) in refluxing 1,2,4-trichlorobenzene for 18 h. After removing the solvent by evaporation, the residue was purified on an alumina column using toluene

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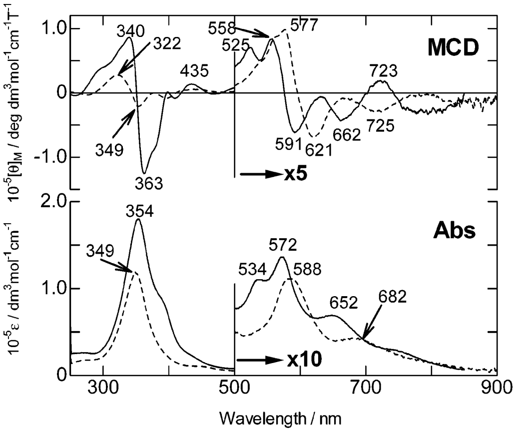

Figure 1. MCD (top) and electronic absorption spectra (bottom) of **1** (—) and **2** (···) in $CHCl_3$.

as the eluent. The first fraction (brown for **1** and green for **2**) contained the triple-decker sandwich target complex, while a second blue-purple fraction contained a small amount of unreacted metal-free DAP which was eluted from the column with chloroform. Compounds **1** and **2** were further purified by recrystallization from a mixture of chloroform and methanol and then characterized by elemental analysis and various spectroscopic methods.[8,9] No homoleptic double-decker complex was isolated or detected.

The absorption and magnetic circular dichroism (MCD) spectra of **1** and **2** were recorded in $CHCl_3$, Figure 1. The spectrum of **1** is dominated by a B-band at 354 nm, which contains a marked shoulder on the lower energy side, and a Q-band at 652 nm. The B-band is significantly blue-shifted when compared with that of $Ce_2(OEP)_3$, while the Q-band in contrast is red-shifted.[5] The corresponding monomer species show similar spectral shifts.[6] Recent time-dependent DFT calculations of ZnDAP[6] predict that the introduction of nitrogen atoms at the *meso* positions causes a blue-shift of the B-band and a red-shift of the Q-band with a concomitant decrease and increase, respectively, of the absorption intensity. Although calculations have not been carried out for **1** and **2**, the spectral properties would be expected to broadly reflect those of the DAP monomer. The MCD spectra of **1** and **2** show pseudo-Faraday *A*-terms in the Q and B spectral regions due to the presence of closely lying *B*-terms of opposite sign,[10] despite the fact that the MCD spectrum of H_2DAP monomer contains resolved MCD peaks corresponding to absorption peaks and shoulders (Faraday *B*-terms).[6] For example, in the MCD spectrum of **1**, one dispersion type curve appears in the B-band region between 340 and 363 nm and is associated with an absorption peak at 354 nm, while another in the Q-band region lies between 558 and 662 nm corresponding to the absorption peak at 572 nm. This suggests that the absorption and MCD spectra of lanthanide triple-deckers do not reflect the D_{2h} symmetry of the DAP ligand, as has been observed previously for cation-induced cofacial crown ether dimers and μ-oxo dimers of ligands of C_{2v} symmetry.[11,12]

Table 1. Redox Potential Data (vs Fc^+/Fc) for the $M_2(DAP)_3$ (M = Ce (**1**), Eu (**2**)) Complexes in *o*-DCB Containing 0.1 M TBAP

	O_3	O_2	O_1	R_1	R_2	R_3	ΔE
1	0.89[a]	0.30	−0.26	−1.73	−2.17	−2.43[a]	1.47
2	0.85	0.33	−0.05	−1.64	−2.05	−2.43[a]	1.59

[a] Data from differential pulse voltammogram.

The electrochemical properties of compounds **1** and **2** were investigated through cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in *o*-DCB. The potentials obtained for ring-centered oxidation and reduction are summarized in Table 1. Both **1** and **2** exhibit three reversible one-electron oxidation and one-electron reduction processes. The potential differences between the first oxidation and reduction potentials of $Ce_2(OEP)_3$ and $Eu_2(OEP)_3$ have been reported previously to be 1.86 and 1.81 V,[13] respectively, while the corresponding values for **1** and **2** were found to be 1.47 and 1.59 V. The electrochemical data therefore correspond well with the red-shifts observed for the lowest energy $\pi \rightarrow \pi^*$ bands of **1** and **2** relative to those of $Ce_2(OEP)_3$ and $Eu_2(OEP)_3$. The first oxidations for **1** and **2** occur at −0.26 and −0.05 V (vs Fc^+/Fc), respectively. These potentials are considerably more negative than those exhibited by monomeric DAP complexes, for example at ca. 0.45 V in the case of CuDAP,[6] reflecting the effect of the strong $\pi-\pi$ interactions between the ligands within sandwich complexes. Interestingly, **1** shows an additional, irreversible oxidation couple at 0.61 V. This process can be attributed to the Ce^{III}/Ce^{IV} redox couple and has been observed previously for other cerium sandwich complexes.[13−15]

Crystals of **2** were obtained for X-ray crystallography by slowly diffusing methanol into a chloroform solution.[16] The structure was found to have a triclinic unit cell containing a sandwich complex solvated by a water molecule, Figure 2, in which both of the europium ions have approximately square-antiprism coordination environments based on the

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(8) Selected data for **1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 2H, meso-inner DAP), 1.88 (s, 4H, meso-outer DAP), 1.54 (s, 24H, $-CH_3$-*o*), 0.88 (s, 12H, $-CH_3$-*i*), 0.65, −0.19 (m, 16H, CH_2-*o*), 0.20 (s, 12H, CH_3-DAP-*i*), −0.35, −1.23 (br, 8H, CH_2-*i*), −5.83 to −5.98, −6.70 to −6.83 (m, 24H, $-CH_3$-DAP-*o*); ESI-TOF mass (*m*/*z*): 1716 (M^+ + 1); UV−vis($CHCl_3$) [λ_{max}/nm (log ϵ)] 349 (5.07), 445 (4.03), 587 (4.05), 682 (3.63). Anal. Calcd for $C_{90}H_{102}N_{18}Ce_2{\cdot}2C_7H_8{\cdot}2H_2O$: C, 64.51; H, 6.35; N, 13.02. Found: C, 64.68; H, 6.34; N, 12.25.

(9) Selected data for **2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.95 (s, 2H, meso-*i*), 14.11 (s, 4H, meso-*o*), 6.89−6.92 (m, 8H, CH_2-*i*), 5.59−5.64 (m, 12H, $-CH_3$-*i*), 4.39 (s, 12H, CH_3-DAP-*i*), 3.36~3.47 (m, 16H, CH_2-*o*), 3.13 (s, 24H, CH_3-DAP-*o*), 0.98−1.01 (m, 24H, $-CH_3$-*o*); ESI-TOF mass (*m*/*z*): 1740 (M^+ + 2); UV−vis($CHCl_3$) [λ_{max}/nm (log ϵ)] 354 (5.25), 534 (4.04), 572 (4.13), 652 (3.84). Anal. Calcd for $C_{90}H_{102}N_{18}Eu_2$: C, 62.13; H, 5.91; N, 14.49. Found: C, 62.77; H, 6.16; N, 13.79.

(10) If the ground state is orbitally degenerate, Faraday *B* and *C* terms would be present rather than Faraday *A* and *C* terms (Stillman, M. J.; Nyokong, T. In *Phthalocyanines. Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Vol. I, Chapter 3, pp 133−290).

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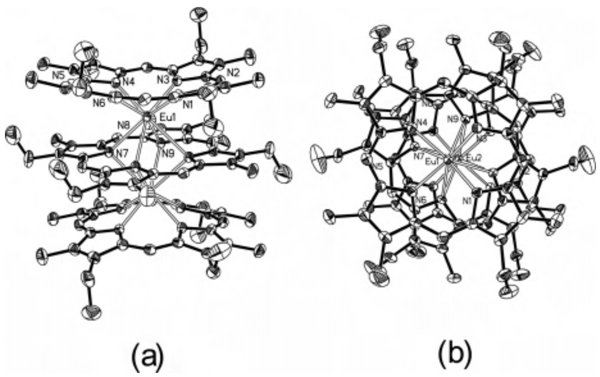

Figure 2. View of the molecular structure of **2**: (a) side view, (b) top view. Displacement ellipsoids are shown in the 30% probability level. Hydrogens in both parts a and b are omitted for clarity.

eight pyrrole nitrogens of neighboring DAP ligands. The Eu−Eu distance is 3.61 Å, and the Eu−$N_{pyrrole}$ distances are 1.31 and 1.80 Å for the external and internal DAPs, respectively. These distances are slightly shorter than those observed in the case of $Ce_2(OEP)_3$.[7] The external and internal DAPs rotate by ca. 62° with respect to the Eu→N_{meso} vectors (i.e., dihedral angle N_2−Eu_1−Eu_2−N_8), which means that the pyrroles rotate by ca. 28°. The macrocyclic rotations are therefore significantly smaller than the ca. 40° rotations observed by Buchler et al. in the case of $Ce_2(OEP)_3$.[7]

In summary, we have prepared the first examples of lanthanide triple-decker sandwich complexes comprised of D_{2h} symmetry monomer units, $M_2(DAP)_3$ (M = Ce, Eu). The structure of $M_2(DAP)_3$ has been verified by X-ray crystallography, and the electrochemical and spectroscopic properties of both complexes have been examined in detail.

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Supporting Information Available: Crystallographic data in CIF format. ^{1}H NMR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal data for **2**: $C_{90}H_{104}Eu_2N_{18}O$, M_w= 1757.83, triclinic, space group $P\bar{1}$ with a = 12.795(4) Å, b = 13.124(4) Å, c = 14.338(4) Å, α = 89.559(4)°, β = 77.806(4)°, γ = 68.619(4)°, V = 2185.0(11) Å^3, D_c = 1.336 g cm^{-3}, Z = 1. The structure was solved based on heavy-atom Patterson methods and refined by a full-matrix least-squares procedure using 7539 data to a conventional R_1 (gt) value of 0.0535 (wR_2 = 0.1412). All computations were carried out using the SHELXS-97 software.