Synthesis and Characterization of a Novel Lutetium(III) Triple-decker Sandwich Compound: a Tris(1,2-naphthalocyaninato) Complex

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The triple-decker sandwich complex tris(1,2-naphthalocyaninato)dilutetium(III) has been prepared in good yield, and characterized by mass spectroscopy, UV-VIS spectroscopy and electrochemistry.

Bisphthalocyanines, sandwich type complexes of phthalocyaninato ligands with lanthanide ions and some other metals, are promising compounds for various applications. Their conducting, electrochromic and optoelectronic properties,¹ being due to the π -electrons, should be modified by extension of the conjugation of the macrocyclic ligands.² 1,2- and 2,3-Naphthalocyanines are the first targets of such a study.³

À new compound, the tris(1,2-naphthalocyaninato) complex of lutetium, $[Lu_2(nc)_3]$ 1, was formed during the synthesis of the lutetium bis(1,2-naphthalocyanine), 2. Triple-decker sandwiches, also called 'super complexes,' have been mentioned recently in the literature. Compounds of three porphyrin⁴ units or of mixed porphyrin-phthalocyanine (1-2 or 2-1) macrocycles⁵ have been isolated and well characterized. Mentions of the existence of the trisphthalocyanines (pc) are scarce; their possible formation during the synthesis of the bisphthalocyanines has been suggested.^{6,7} The formation of $[Y_2(pc)_3]$ was established by mass spectrometry, but the yield and the purity of the product were not reported.8 No more results have been published since. Here is described the synthesis and characterization of the novel lutetium tripledecker sandwich molecule; 1 (Fig. 1) is the first compound of this type with naphthalocyanine macrocycles. The complex has been studied by electrochemistry and UV-VIS spectrophotometry, in order to obtain information on the electronic configuration.

A method for the synthesis of the bisphthalocyanines of lutetium(III) has been elaborated, starting from the lithium derivatives.⁹ This pathway was used for the preparation of $[Lu(nc)_2]$ 2. $[Li_2(nc)]$ could theoretically exist as a mixture of four isomers;¹⁰ consequently, 2 has 13 possible isomers and 1, the triple-decker sandwich, many more. As the different forms of $[Li_2(nc)]$ were not isolated, 1 is certainly a mixture of isomers.

During the overnight reflux of $[Li_2(nc)]$ with lutetium acetate in 1-chloronaphthalene, a mixture of 1 and 2 is formed [eqn. (1)].

$$3[Li_2(nc)] + 2 Lu[OAc]_3 \rightarrow x [Lu_2(nc)_3] + y [Lu(nc)_2]$$
 (1)

The reaction mixture was poured on the top of a silica gel



Fig. 1 One possible representation of 1, $[Lu^{11}_2(nc)_3]$

column. Only one fraction was eluted with dichloromethane: 1 and 2, together with 1-chloronaphthalene. A complete separation of the two compounds by column chromatography is not possible, even after removal of 1-chloronaphthalene. Thus, the solid residue was dissolved in DMSO, with addition of hydrazine hydrate; under such conditions, only the lutetium bis(1,2-naphthalocyanine) 2 is reduced. The mixture was chromatographed on silica gel with CH_2Cl_2 ; the anionic reduced form of 2 does not move under such conditions. Compound 1 was isolated (final yield 55%) and characterized. Compound 2 was recovered by elution with methanol.

Satisfactory elemental analysis for $C_{144}H_{72}N_{24}Lu_2$ was obtained: found, C, 69.5; H, 3.0; N, 12.9. Calc. C, 69.45; H, 2.9; N, 13.5%. Unfortunately, ¹H NMR spectroscopy was not possible because of the very low solubility of 1. In the present case, it is not possible to increase the solubility by reduction as has been done for lutetium bisphthalocyanines, the three macrocyclic rings being in their dianionic form (nc²⁻). The high resolution mass spectrum (FAB+) showed the molecular ion at m/z = 2488. The mass spectrum (Fig. 2) showed the good purity of compound 1, and the high resolution molecular mass, (m/z 2487.502) agreed with the calculated value (2487.524), confirming the identity of the prepared derivative. The species at m/z = 1244 is the doubly charged ion of 1. MS-MS experiments proved that 1 is not produced by an internal recombination, that the monophthalocyanine of Lu observed at m/z = 887 is a daughter ion of 1, and that 2 is the only impurity (m/z = 1601, <5%).

Electrochemical studies of 1 were performed at a platinum electrode in CH₂Cl₂ (electrolyte: 0.1 mol dm⁻³ Bu₄NPF₆). Two reversible one-electron processes appear on the cyclic voltammogram of Fig. 3, between -0.8 and 1 V. Voltammetry at a rotating disk electrode shows that both are oxidation steps occurring at 0.03 and 0.29 V (νs . Fc⁺/Fc) [eqn. (2)].

$$[Lu_2(nc)_3] \stackrel{e}{\longleftrightarrow} [Lu_2(nc)_3]^+ \stackrel{e}{\longleftrightarrow} [Lu_2(nc)]^{2+}$$
 (2)

Electrochemical studies at a platinum disk ultramicroelectrode (diameter 10 μ m) were performed with and without addition of a supporting electrolyte. The wave heights are identical in both experiments, indicating that the electroactive species does not contribute by migration, to the mass transfer



Fig. 2 FAB+ mass spectrum of 1

from the solution to the electrode; that means that it is uncharged.¹¹ This observation establishes that **1** is obtained as its molecular form, which is in agreement with the fact that no reduction wave of an oxidized macrocycle (nc⁻) is detected in the domain. Bisphthalocyanines and bisnaphthalocyanines show one reduction wave and one oxidation wave; at -0.42and -0.02 V for [Lu(pc)₂]; at -0.26 and 0.07 V for **2**;^{12,3} in these complexes, one reduced and one oxidized form of the ligand are associated with the lanthanide cation. For com-



Fig. 3 Voltammetry of 1, in CH₂Cl₂: cyclic voltammetry ($\nu = 0.1$ V s⁻¹) and RDE voltammetry (n = 500 rpm, $\nu = 5$ mV s⁻¹)



Fig. 4 UV-VIS spectrum of 1 and 2 in CH₂Cl₂

pound 1, no reduction process occurs as the three ligand moieties are in their reduced form. But, surprisingly, only two steps are observable. Extending the conjugation over a third macrocyclic ring stabilizes the HOMO, as it is much more difficult to oxidize the triple-decker sandwich than the reduced form of the bisnaphthalocyanine (where the two ligands are in their reduced state, as in 1).

The UV-VIS spectrum of 1 (Fig. 4) is different from that of 2. The Soret region (300-400 nm) is almost the same for the two compounds. The λ_{max} for the Q bands are identical; however, for 1, the band is larger and complex, due to shoulders at about 620 and 720 nm. An important feature is the absence of the weak band at 500 nm, visible in the spectrum of 2. Such a transition is usually present in bismacrocyclic complexes when one of the macrocycles is oxidized. This also confirms that the triple-decker associates two Lu³⁺ cations and three macrocycles in their anionic form (nc²⁻).

Efforts to obtain single crystals of the compound are in progress.

This work was supported by funds from the CNRS, the Université de Bretagne Occidentale and a grant from the Région de Bretagne (F. Guyon). Dr P. Guenot (Université de Rennes I) is thanked for his help in mass spectroscopy.

Received, 26th January 1994; Com. 4/00506F

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