

Bis(2,3-naphthalocyaninato)lutetium(III) and (2,3-Naphthalocyaninato)(phthalocyaninato)lutetium(III) Complexes: Synthesis, Spectroscopic Characterization, and Electrochemistry

François Guyon,[†] Annig Pondaven,[†] Pierre Guenot,[‡] and Maurice L'Her^{*,†}

Université de Bretagne Occidentale, Centre National de la Recherche Scientifique, URA No. 322, Chimie, électrochimie moléculaires et chimie analytique, Faculté des Sciences et Techniques, 6 avenue Victor Le Gorgeu, B.P. 809, 29285 Brest Cedex, France, and Université de Rennes I, Centre Régional de Mesures Physiques de l'Ouest, Campus de Beaulieu, 35042 Rennes Cedex, France

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Bis(2,3-naphthalocyaninato)lutetium(III) and (2,3-naphthalocyaninato)(phthalocyaninato)lutetium(III) have been synthesized by condensation, with lutetium acetate, of 2 equiv of dilithium 2,3-naphthalocyaninate or with 1 equiv of dilithium phthalocyaninate and 1 equiv of the dilithium 2,3-naphthalocyaninate. These compounds were characterized by UV/visible, IR, ¹H NMR, and MS spectroscopies and electrochemical techniques. The unpaired electron is delocalized over the two macrocycles of the sandwich-type complexes. The HOMO-LUMO gap, 0.28 V, is the narrowest ever reported for compounds of this type.

Since their synthesis and characterization,¹⁻⁷ the bis(phthalocyaninates) of the lanthanides attracted the attention of many research groups by their numerous potential applications in various areas such as electrochromism, molecular electronics, and optronics.⁸⁻¹² The macroscopic characteristics of the molecular materials derive from those of their constitutive units; a possible way to induce modifications of the intrinsic properties of the molecules is to introduce substituents on their periphery or to extend the conjugation of the macrocycle, as in naphthalocyanines.^{13,14} The present work is focused on the lutetium complexes Lu(2,3-Nc)₂ and Lu(2,3-Nc)(Pc).¹⁵ Their synthesis, characterization, and physical properties have never been thoroughly described, even if the transition metal naphthalocyaninates are well-known.

Theoretical studies on the electronic properties of phthalocyaninates and naphthalocyaninates indicate that the energy gap between the HOMO and LUMO should be smaller for the latter compounds.¹⁶ As a consequence of the linear annelation of the benzene rings, the lutetium bis(2,3-naphthalocyaninate) would lead to a better intrinsic semiconductor than the bis(phthalocyaninate), with a lower thermal activation energy of the conduction process. The synthesis and the study of the lanthanide macrocyclic complexes having an extended aromatic character are thus challenging.

Our previous works have been focused on the synthesis and the characterization of symmetrically and unsymmetrically substituted lutetium bis(phthalocyaninates).¹⁷ Unsymmetrical complexes are interesting for many reasons. The delocalization of the unpaired electron and the polarizability could be different from what is generally observed for the symmetrical bis-(macrocycle) derivatives, inducing unusual electrical or optical properties.

Luk'yanets has described the synthesis and some physical properties of substituted lutetium bis(2,3-naphthalocyaninates); however, the substitution on each of the peripheral benzene ring generates many isomers.¹⁸ In a very short paper, the same author claims that he has prepared the lutetium tetra-*tert*-butyl-2,3-naphthalocyaninate phthalocyaninate; that is not clearly established from the very few reported data (λ_{\max}).¹⁹ More recently, Simon and Bouvet have studied the electrical properties of the lutetium mixed complex with the phthalocyaninate and 2,3-naphthalocyaninate ligands; they detailed neither the isolation nor the characterization of the hybrid complex.²⁰ In order to study the delocalization of the unpaired electron on such

[†] Université de Bretagne Occidentale.

[‡] Université de Rennes I.

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- (15) Abbreviations: Lu(Pc)₂ = bis(phthalocyaninato)lutetium(III); Lu(2,3-Nc)₂ = bis(2,3-naphthalocyaninato)lutetium(III); Lu(2,3-Nc)(Pc) = (2,3-naphthalocyaninato)(phthalocyaninato)lutetium(III).

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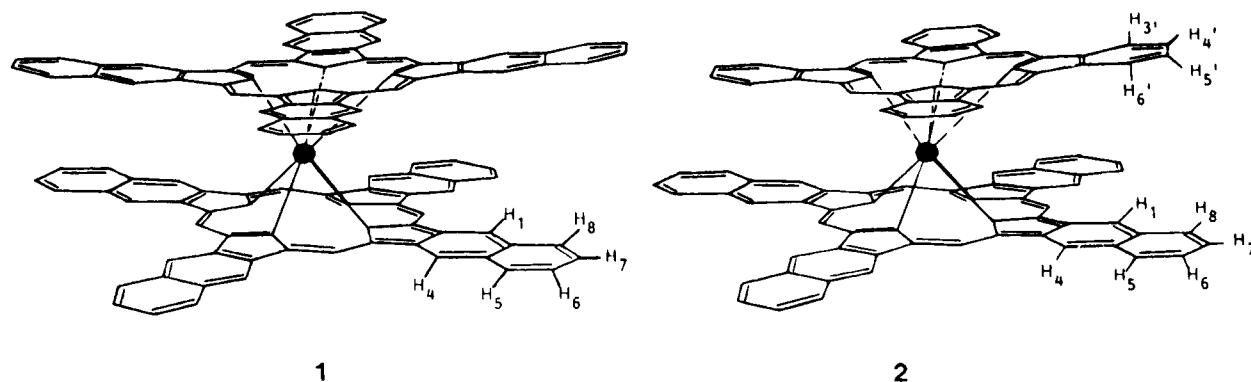


Figure 1. Representation of Lu(2,3-Nc)₂ (1) and Lu(2,3-Nc)(Pc) (2).

compounds, Ishikawa et al. have prepared the same unsymmetrical sandwich complex Lu(2,3-Nc)(Pc); they observed the formation of the bis(2,3-naphthalocyaninato)lutetium(III), but they identified the complex only by its UV/visible spectrum, without any further isolation and characterization.²¹

This article details the synthesis, the isolation, the purification, and the spectroscopic characterization (IR, NMR, MS) of the symmetrical bis(2,3-naphthalocyaninato)lutetium(III), Lu(2,3-Nc)₂; the mixed (2,3-naphthalocyaninato)(phthalocyaninato)lutetium(III), Lu(2,3-Nc)(Pc) (Figure 1), has also been prepared and fully characterized. The synthetic route is the one previously used for the preparation of the symmetrically and unsymmetrically substituted bis(phthalocyaninates).¹⁷ The electrochemical behavior of Lu(2,3-Nc)₂ and Lu(2,3-Nc)(Pc) has been studied as it provides precious informations on the electronic configuration; the UV/visible spectra of the oxidized and reduced species were recorded after exhaustive electrolysis or by spectroelectrochemistry.

Experimental Section

Materials. Phthalonitrile is a commercial product purchased from Aldrich; the 2,3-dicyanonaphthalene has been synthesized following a procedure described in the literature.²²

Organic solvents were distilled before use, except 1-chloronaphthalene which was dried over 4 Å molecular sieves and percolated through a basic alumina column (Merck), just before use. Thin layer chromatography was performed on silica gel or alumina precoated aluminum foils (Merck). TLC has been used to monitor the preparations and to ascertain the purity of the products; the *R_f* values are given hereafter for each of the compounds. Column chromatography has been carried out using silica gel 60 (70–230 mesh) or activated basic aluminum oxide (50–200 micron) (Merck).

Physical Measurements. The UV/visible spectra were recorded on a Cary 219 spectrophotometer (Varian) or a HP-8452A diode-array spectrophotometer (Hewlett-Packard). A Perkin-Elmer 1430 spectrometer has been used for IR spectroscopy of solid samples, in KBr pellets. The ¹H NMR spectra were obtained using a Bruker AC 300 apparatus; to improve the solubility and also reduce the paramagnetic compounds, hydrazine monohydrate (Aldrich, 98%) was added to the solvent, DMSO-*d*₆ or DMF-*d*₇ (1% by volume). High resolution mass spectroscopy experiments (field desorption) were performed with a triple-sector VG Autospec spectrometer.

Voltammetry was carried out with a Princeton Applied Research potentiostat (Model 173) and a programmer (Model 175), on a platinum disk working electrode. The experiments have been performed under a purified nitrogen atmosphere (O₂ and H₂O concentration <5 ppm), in an inert atmosphere box (Jaram). A silver wire has been used as a pseudoreference electrode, but the ferrocene/ferrocenium couple is the

reference for all the reported potentials. For spectroelectrochemistry, the three electrode cell was filled and sealed in the drybox; the thickness of the quartz cuvette is approximately 0.4 mm, the working electrode being a platinum grid.

The solvents used for the electrochemical experiments were carefully purified before use. Methylene chloride was percolated through an activated neutral alumina column (Merck). Dimethylformamide, after contact with molecular sieves, was distilled twice under reduced pressure. Benzonitrile has been treated as described elsewhere.²³ The background electrolyte, tetrabutylammonium hexafluorophosphate, has been prepared from tetrabutylammonium hydroxide and hexafluorophosphoric acid (Aldrich), twice recrystallized in ethanol, and dried under vacuum at 100 °C.

Dilithium 2,3-Naphthalocyaninate, Li₂(2,3-Nc). Li₂(2,3-Nc) was synthesized according to Linstead's method, with some modifications.²⁴ Under N₂, clean lithium metal (0.17 g, 25 mmol) is placed in a round bottom flask with a solvent mixture of 3 mL of methanol and 17 mL of pentanol. The mixture is heated under nitrogen until reaction with lithium is complete. Then, 2,3-dicyanonaphthalene (2 g, 11 mmol) is added to the mixture which turns green-brown; the reaction mixture is refluxed for 3 h. The brown powder, obtained after cooling and removal of the solvent under reduced pressure, is dissolved in 20 mL of dry acetone; hexane (70 mL) is then added. The green precipitate is separated from the brown solution by filtration. This purification by precipitation is repeated twice. The green precipitate is placed in a Soxhlet extractor and extracted for 3 h with acetone (200 mL), in order to separate the dilithium naphthalocyaninate from the insoluble H₂(2,3-Nc) and LiOH. Acetone is evaporated down to a volume of 20 mL; Li₂(2,3-Nc) precipitates after the addition of hexane (70 mL). This latter purification step is performed several times. Formula: C₁₈H₂₄N₈Li₂. *M* = 726.24. Yield: 64%. IR (KBr): ν_{\max} = 1330, 1265, 895, 765, 470 cm⁻¹. UV/visible (in acetone): λ_{\max} = 318, 380, 660, 700, 736 nm. ¹H NMR (300 MHz, in CD₃COCD₃): 10 ppm (H₁ and H₄, 8H, s); 8.77 ppm (H₅ and H₈, AA'BB' multiplet, *J* = 3.22 and 6.35 Hz); 7.94 ppm (H₆ and H₇, 8H, AA'BB' multiplet).

Dilithium Phthalocyaninate, Li₂(Pc). Li₂(Pc) is synthesized as previously described.^{17,24}

Lutetium Bis(2,3-naphthalocyaninate), Lu(2,3-Nc)₂. Lutetium acetate (20 mg, 0.05 mmol) is added to a solution of the dilithium 2,3-naphthalocyaninate, (72 mg, 0.1 mmol) in 10 mL of quinoline, previously deaerated with N₂. The refluxing medium is stirred, under N₂, for 3 h. After cooling, the reaction mixture is poured on top of an alumina column (20g). The purple band, containing Lu(2,3-Nc)₂ associated with quinoline, is rapidly eluted with CH₂Cl₂. After complete removal of the solvents, the desired product is obtained as a dark solid. Formula: C₉₆H₄₈N₁₆Lu. *M* = 1599.37. Yield: 37.6 mg, 47%. *R_f* (neutral alumina, CH₂Cl₂) = 0.8. UV/visible/near-IR (CH₂Cl₂): λ_{\max} = 328, 572, 680, 760, 1089 nm. ¹H NMR (300 MHz, DMSO-*d*₆ + hydrazine monohydrate): 9.24 ppm (H₁ and H₄, 16H, s); 8.67 ppm (H₅ and H₈, 16H, mt); 7.95 ppm (H₆ and H₇, 16H, mt). ¹H NMR (300 MHz, DMF-*d*₇ + hydrazine monohydrate): 9.30 (H₁ and H₄, 16 H, s); 8.66 ppm (H₅ and H₈, 16 H, mt); H₆ and H₇ are masked by the solvent.

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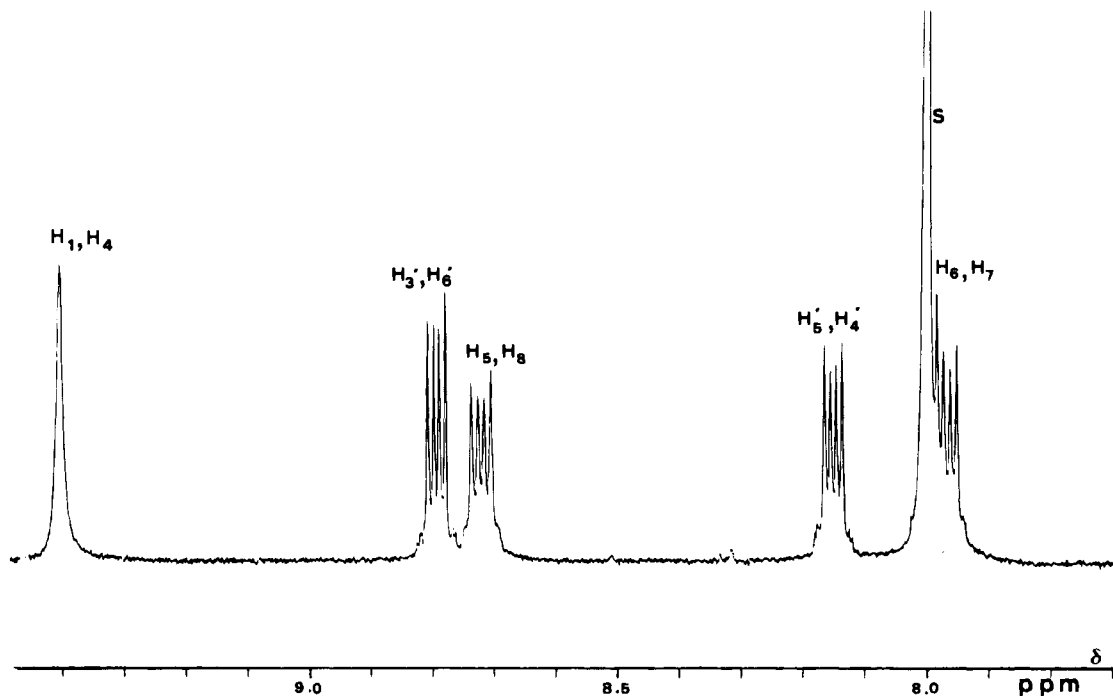


Figure 2. ^1H NMR spectrum of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ in dimethylformamide- d_7 + hydrazine hydrate (S = solvent).

Lutetium 2,3-Naphthalocyaninate Phthalocyaninate, $\text{Lu}(2,3\text{-Nc})(\text{Pc})$. Under N_2 , lutetium acetate (41 mg, 0.1 mmol) is added to a solution of $\text{Li}_2(\text{Pc})$ (52 mg, 0.1 mmol) and $\text{Li}_2(2,3\text{-Nc})$ (72 mg, 0.1 mmol) in 20 mL of 1-chloronaphthalene. The mixture is stirred at 245°C for 4 h. After cooling, the reaction mixture is poured on top of an alumina column. The small amount of $\text{Lu}(2,3\text{-Nc})_2$ produced during the synthesis is eluted with CHCl_3 and comes out with chloronaphthalene; the following blue band contains the expected compound, $\text{Lu}(2,3\text{-Nc})(\text{Pc})$. A green band which contains $\text{Lu}(\text{Pc})_2$ is finally eluted with CH_2Cl_2 . $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ is isolated as a dark-blue powder after evaporation of the solvent. Formula: $\text{C}_{80}\text{H}_{40}\text{N}_{16}\text{Lu}$. $M = 1399.30$. Yield: 23.8 mg, 17%. R_f (silica gel, CH_2Cl_2) = 0.6 ($R_f = 0.4$ for $\text{Lu}(\text{Pc})_2$ under the same conditions). UV/visible/near-IR (CH_2Cl_2): $\lambda_{\text{max}} = 326, 632, 706, 987$ nm. ^1H NMR (300MHz, $\text{DMSO}-d_6$ + hydrazine hydrate): 9.32 ppm (H_1 and H_4 , 8H, s); 8.72 ppm (H_3 and H_5 , H_3 and H_6 , 16H, mt); 8.13 ppm (H_4' and H_5' , 8H, mt); 7.94 ppm (H_6 and H_7 , 8H, mt). ^1H NMR (300 MHz, $\text{DMF}-d_7$ + hydrazine hydrate): 9.40 ppm (H_1 and H_4 , 8H, s); 8.79 ppm (H_3 and H_6 , 8H, AA'BB' multiplet, $J = 2.95$ and 5.60 Hz); 8.72 ppm (H_5 and H_8 , AA'BB' multiplet, $J = 3.17$ and 6.28 Hz); 8.15 ppm (H_4' and H_5' , 8H, AA'BB' multiplet); 7.97 ppm (H_6 and H_7 , 8H, AA'BB' multiplet). The spectrum is displayed in Figure 2.

Analysis of the Compounds. High resolution mass spectroscopy, described hereafter, clearly establishes that $\text{Lu}(2,3\text{-Nc})_2$ and $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ have been prepared. The spectra recorded down to $m/e = 40$ prove that the compounds are free of volatile impurities. The absence of organic matter, less than 5%, is also verified by 300-MHz ^1H NMR, from -0.5 to 12 ppm. However, some nonvolatile inorganic impurities could be present. Good elemental analysis were not obtained, even after repeated column chromatographies; this is quite usual for compounds of this family. Different samples of the same batches of the compounds were analyzed by two laboratories; the results are erratic and never really satisfying. Lu, C, and N contents are always less than the calculated values, especially for nitrogen and the metal: % of Lu for $\text{Lu}(2,3\text{-Nc})_2$, calcd = 10.9, 10.9 > found > 10.4; % of Lu for $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, calcd = 12.5, 12.5 > found > 11.6. As noted by one of the laboratories, refractory materials were left after analysis, which is not really surprising as the lanthanide nitrides (under reducing and anhydrous conditions), as well as the carbides and oxides, are easily formed and decompose only at very high temperatures.²⁵ The results for the elemental analysis of carbon are also low, but closer to the

theoretical values: % of C for $\text{Lu}(2,3\text{-Nc})_2$, calcd. = 72.0, found = 69.9; % of C for $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, calcd. = 68.6, found = 67.8. The difficulty in obtaining good elemental analysis, even for transition metal phthalocyanines, has recently been pointed out.²⁶ Although the results are not really satisfactory, the elemental analysis of carbon, as well as mass and NMR spectroscopies which prove the absence of organic impurities, lead us to the conclusion that the purity of the compounds is better than 95%.

Results and Discussion

Synthesis. It was estimated that starting from the dilithium salts of the naphthalo- and phthalocyanine macrocycles, $\text{Li}_2(2,3\text{-Nc})$ and $\text{Li}_2(\text{Pc})$, would be a good path for the synthesis of the lutetium bis(naphthalocyaninate) and particularly for the preparation of the hybrid sandwich complex $\text{Lu}(2,3\text{-Nc})(\text{Pc})$. However, $\text{Li}_2(2,3\text{-Nc})$ is not as easily prepared as its phthalocyanine analog, $\text{Li}_2(\text{Pc})$, its purification being a difficult operation.

$\text{Lu}(2,3\text{-Nc})_2$, has been prepared by addition of 2 mol of $\text{Li}_2(2,3\text{-Nc})$ to 1 mol of lutetium acetate in refluxing quinoline. Like its starting material, $\text{Li}_2(2,3\text{-Nc})$, $\text{Lu}(2,3\text{-Nc})_2$ is much more difficult to prepare than the corresponding phthalocyanine complexes. After the first attempts of synthesis in chloronaphthalene, under air, brown solids were isolated from the reaction medium; their solution UV/visible spectra indicate that they are mixtures of the oxidized and neutral forms of $\text{Lu}(2,3\text{-Nc})_2$ and of organic impurities. In solution, 2,3-naphthalocyanines are readily oxidized by atmospheric dioxygen.¹⁸ This is not surprising as it appears from the electrochemical study described hereafter, that the first oxidation step of the compounds bearing naphthalocyanine rings occurs at lower potentials than for $\text{Lu}(\text{Pc})_2$. When the reaction is performed under a nitrogen atmosphere and without the addition of a base, $\text{Lu}(2,3\text{-Nc})_2$ is obtained at a very poor yield; the major product is an insoluble species, probably a salt of its oxidized form, $\text{Lu}(2,3\text{-Nc})_2^+$, produced by the action of the traces of dioxygen in the N_2 stream. The neutral molecular form of $\text{Lu}(2,3\text{-Nc})_2$ has been

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isolated from experiments done under nitrogen in the presence of quinoline. Under such experimental conditions the molecular compound, $\text{Lu}(2,3\text{-Nc})_2$, is the main product of the reaction as shown by the UV/visible spectrum. The yield of the synthesis (47%) is rather high.

For the synthesis of $\text{Lu}(\text{Pc})(2,3\text{-Nc})$, an equimolar mixture of $\text{Li}_2(2,3\text{-Nc})$ and of $\text{Li}_2(\text{Pc})$ is added to lutetium acetate in refluxing chloronaphthalene; the reaction leads to the three complexes— $\text{Lu}(2,3\text{-Nc})_2$, $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, and $\text{Lu}(\text{Pc})_2$ —while $\text{Lu}(2,3\text{-Nc})_2$ is not abundant. The two complexes $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ and $\text{Lu}(\text{Pc})_2$ are separated from the reaction mixture by column chromatography on alumina. The yield for the preparation of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ is 17%.

$\text{Lu}(2,3\text{-Nc})_2$ and $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ have been characterized by UV/visible, IR, NMR, and mass spectroscopies. Spectrophotometry and FD-MS ascertain, unambiguously, the formation of the lutetium sandwich complexes.

IR, NMR, and FD-MS Spectroscopies. Lanthanide bisphthalocyanines have been extensively studied by IR spectroscopy.²⁷ However, results have never been reported for the $\text{Lu}(2,3\text{-Nc})_2$ or for the heterocomplex $\text{Lu}(2,3\text{-Nc})(\text{Pc})$. The IR spectra of these compounds have some intense bands and many weak ones. $\text{Lu}(2,3\text{-Nc})_2$ and $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ strongly absorb at 1330 cm^{-1} ; that strong band corresponds to the stretching vibration of the pyrrole. Another band at 760 cm^{-1} , less intense, is common to $\text{Lu}(2,3\text{-Nc})_2$ and $\text{Lu}(2,3\text{-Nc})(\text{Pc})$; this absorption is attributed to the $\gamma\text{-CH}$ vibration of the naphthalene. Two other bands, at 1115 and 730 cm^{-1} , are observed in the spectrum of the unsymmetrical sandwich $\text{Lu}(2,3\text{-Nc})(\text{Pc})$; they are characteristic of the phthalocyanine cycle.

$\text{Lu}(2,3\text{-Nc})_2$ and $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ have an unpaired electron. Obtaining NMR spectra of the molecular compounds is impossible, due to their paramagnetism and also to their poor solubility; these difficulties have been overcome by dissolving the compounds in deuterated dimethylformamide (DMF-*d*₇) or dimethylsulfoxide (DMSO-*d*₆), in the presence of hydrazine hydrate which reduces the paramagnetic molecule to its more soluble monoanionic form.

The ¹H NMR spectrum of $\text{Lu}(2,3\text{-Nc})_2$ obtained in DMF is unsatisfactory as the signal of two protons of the naphthalene ring (H_6 and H_7) (Figure 1) is masked by the proton of the amide function of the solvent, at 8 ppm. These two protons of the naphthalene ring are apparent when deuterated dimethyl sulfoxide is used, but with a poorer resolution. $\text{Lu}(2,3\text{-Nc})_2$ has no isomeric forms; consequently, the assignment of the various signals is straightforward. The inner protons (H_1 and H_4) are shifted downfield, at 9.24 ppm, more than the corresponding protons of $\text{Lu}(\text{Pc})_2$ (H_3' and H_6' at 8.90 ppm). One also notices that the signals of the outer protons of $\text{Lu}(2,3\text{-Nc})_2$ (H_5 , H_8 and H_6 , H_7) are positioned respectively at 8.67 and 7.95 ppm, when the outer protons of the bis(phthalocyaninate) (H_4' and H_5') appear at 8.17 ppm. This is not surprising as the naphthalocyanine ring current is spread over a more extended conjugated system.^{28,29} The extension of the conjugation affects the H_1 , H_4 , H_5 , and H_8 protons and apparently not the outer protons H_6 and H_7 , the shift of which is identical to that of the corresponding protons of 2,3-dicyanonaphthalene. When comparing a mono-(naphthalocyaninate), $\text{Li}_2(2,3\text{-Nc})$ for example, to $\text{Lu}(2,3\text{-Nc})_2$, one observes that the resonance frequency of the H_1 and H_4 protons is shifted upfield, from 10 to 9.24 ppm; this effect,

comparable with the shift observed in the phthalocyanine series,¹⁷ can be attributed to the additivity of the shielding effects of the ring-currents in the sandwich complex.³⁰ The H_5 and H_8 proton signals are only very slightly shifted downfield.

The spectrum of the unsymmetrical compound $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, has been obtained from solutions in DMSO-*d*₆ and in DMF-*d*₇ (Figure 2). It appears that the two different macrocycles are present: the AA'BB' multiplets of the H_3 , H_6' and H_4' , H_5' protons of the phthalocyanine, as the multiplets of the H_5 , H_8 and H_6 , H_7 protons of the naphthalocyanine are well separated. The H_3 , H_4' , H_5' , and H_6' protons are unaffected by the replacement of one phthalocyaninate of $\text{Lu}(\text{Pc})_2$ by a naphthalocyanine ring.¹⁷ The protons of the naphthalene ring of this unsymmetrical sandwich complex are slightly shifted when compared to those of $\text{Lu}(2,3\text{-Nc})_2$ ($\Delta\delta \leq 0.1$ ppm). NMR spectroscopy unambiguously proves the formation of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, as the protons of the phthalocyaninate and of the naphthalocyaninate ligands are fully distinguishable.

Fast atom bombardment mass spectrometry (FAB-MS) has been used to characterize labile compounds such as porphyrins and phthalocyanines.^{31–33} The studies on the bis(phthalocyaninates) are not well documented: a previous work on the *tert*-butyl-substituted bis(phthalocyaninates) revealed that the molecular ion is not as abundant as the fragment ions.¹⁷ The spectra of the lutetium sandwich complexes vary dramatically with the matrix used for FAB-MS. High resolution mass spectra were obtained by field desorption technique (FD). The molecular ion peaks are observed at $m/z = 1600$ and 1400 for $\text{Lu}(2,3\text{-Nc})_2$ and $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ respectively. The FD technique is more appropriate for the sandwich compounds than the chemical ionization and leads to the determination of the gross formulas of the prepared compounds. Exact mass measurement for the molecular ion of $\text{Lu}(2,3\text{-Nc})_2$, corresponding to $\text{C}_{96}\text{H}_{48}\text{N}_{16}^{175}\text{Lu}$, gives 1599.370 (theoretical: 1599.366). For the molecular ion of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, $\text{C}_{80}\text{H}_{40}\text{N}_{16}^{175}\text{Lu}$, the value is 1399.307 (theoretical: 1399.303). The measured masses are close enough to the theoretical values (0.4 ppm) to ascertain, undoubtedly, the nature of the prepared derivatives. Figure 3 illustrates that the experimental spectra of the molecular ion of $\text{Lu}(2,3\text{-Nc})_2$ and of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ match perfectly the theoretical distribution of masses expected from the isotopic distribution (inserts). The peaks visible only on the experimental spectra, respectively at $m/z = 1598$ and 1398 , are due to the $(M - \text{H})^+$ ions. The conventional mass spectrum of $\text{Lu}(2,3\text{-Nc})_2$ (Figure 4) shows the good purity of the corresponding vapor; the small peaks at masses higher than 1600 are due to recombinations of the molecular ion with oxygen or iodine from the traces of CsI left after calibration of the spectrometer. From MS/MS experiments it appears that the peaks at $m/z < 1600$ are due to the fragmentation of $\text{Lu}(2,3\text{-Nc})_2$.

Electrochemistry. The electrochemical behavior of $\text{Lu}(\text{Pc})_2$ has been extensively studied, but only few results on the substituted bis(phthalocyaninates) and bis(naphthalocyaninates) have appeared in the literature.^{6,17,18,34,35} Bouvet and Simon reported only ΔE° , the difference between the oxidation and the reduction potentials of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$.²⁰ The electrochemi-

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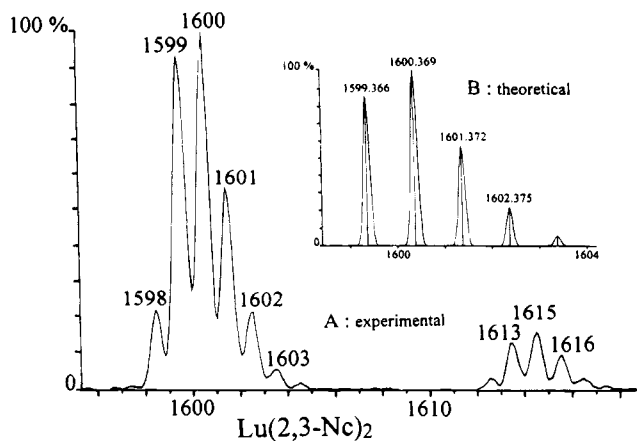


Figure 3. Field desorption mass spectra of Lu(2,3-Nc)₂ and Lu(2,3-Nc)(Pc): (A) experimental; (B) theoretical (natural isotopic abundance).

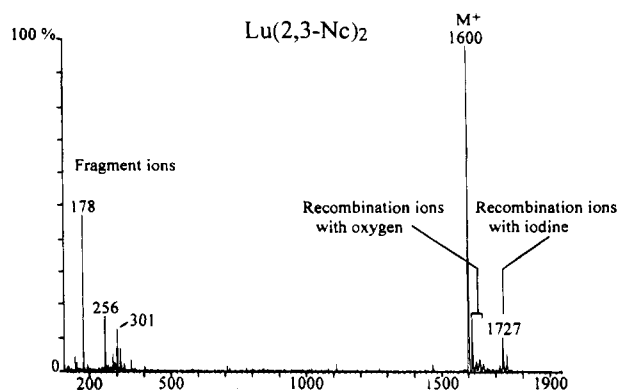


Figure 4. Field desorption mass spectrum of Lu(2,3-Nc)₂.

cal study of Lu(2,3-Nc)₂ and Lu(2,3-Nc)(Pc) is important for various reasons. First of all, the behavior of the sandwich complexes is typical and useful for their characterization. Second, ΔE° , the difference between the oxidation and reduction potentials, allows the prediction of some electrical properties of the condensed phases derived from these molecular precursors; ΔE° leads to a good estimate of the thermal activation energy for the conduction process.^{20,36}

The redox properties of Lu(2,3-Nc)₂ and Lu(2,3-Nc)(Pc) were studied by cyclic voltammetry and hydrodynamic voltammetry, using a glassy carbon or a platinum electrode, in various solvents. As it appears from Figure 5, the voltammograms of Lu(2,3-Nc)₂ are very similar to those of the symmetrical and

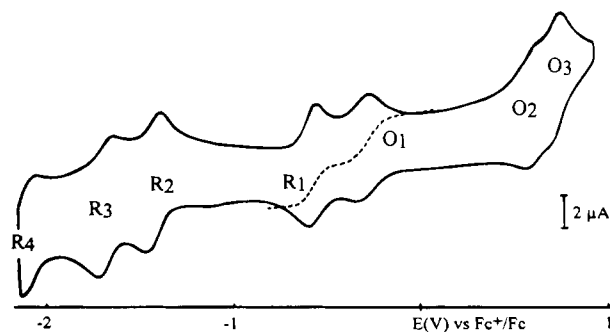


Figure 5. Voltammetry of Lu(2,3-Nc)₂ in benzonitrile ([Bu₄NPF₆] = 0.1 M; platinum electrode): (—) cyclic voltammetry (scan rate 100 mV s⁻¹); (---) rotating disk electrode (scan rate 2 mV s⁻¹).

unsymmetrical bis(phthalocyaninates); they only differ by the potential values.^{6,13,17} Two perfectly reversible waves are observed in the region of -0.5 V: the neutral form of the sandwich complex undergoes one oxidation and one reduction steps, as shown by the rotating disk experiment. In benzonitrile, two other oxidation steps occur at about 0.7 V, separated by only 0.15 V. Three reduction processes are observed before the limitation of the domain. The electrochemical behavior of Lu(2,3-Nc)(Pc) is very similar. As shown by comparison with LuPc₂ solutions and by coulometry on the O₁ or R₁ steps, these redox steps are monoelectronic and reversible at the time scale of cyclic voltammetry.⁶ The solutions of the monooxidized and reduced species prepared by electrolysis are stable. The species generated on the O₂, O₃, R₂, R₃ and R₄ processes are unstable and regenerate the O₁ and R₁ states. The potential values measured in benzonitrile and methylene chloride are listed in Table 1, the ferrocene/ferrocenium couple being the common reference for all the reported potentials. ΔE° is the difference ($E^\circ_{O1} - E^\circ_{R1}$).

In the case of the lanthanide bis(phthalocyaninates) and related complexes, all the redox exchanges occur on π -orbitals of the conjugated macrocyclic ligands; except for the case of the cerium bis(phthalocyaninate), the redox state of the lanthanide cation does not change.¹³

For Lu(Pc)₂ in CH₂Cl₂, the reduction and the oxidation potentials are respectively -0.42 and -0.02 V, ΔE° being 0.40 V.⁶ The first observation is that the replacement of one of the two phthalocyaninates of Lu(Pc)₂ by a 2,3-naphthalocyanine ring shifts the redox systems by 0.2 V toward more negative potentials. When both the ligands are 2,3-naphthalocyaninates, the potentials are more negative, but the reduction potential is only slightly shifted by the second substitution, from -0.60 to -0.62 V; the oxidation is more affected, as its potential is reduced by 0.1 V. Bredas and his co-workers, from the study of the electronic structure of the phthalocyanine-like compounds, have concluded that the linear annelation of the outer benzene ring of H₂(Pc), which leads to the 2,3-naphthalocyaninate, destabilizes the HOMO of H₂(2,3-Nc) ($\Delta E_i = 0.39$ eV) and the LUMO ($\Delta E_i = 0.22$ eV).¹⁶ The same general trend is also observed for the lanthanide bis(macrocycle) complexes; however, the situation is more complex.

The lutetium bis(phthalocyaninates) and bis(naphthalocyaninates) are neutral radicals, the HOMO being semioccupied (SOMO). The X-ray crystallographic study of Lu(Pc)₂ by De Cian et al. has shown that the distance between the two N₄ planes is 2.69 Å; the two macrocyclic ligands being domed, the distance between the two phthalocyaninates is certainly larger but difficult to evaluate.⁷ The close proximity of the two π -systems in a face-to-face configuration induces the splitting

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Table 1. Standard Potentials for Lu(2,3-Nc)₂, Lu(2,3-Nc)(Pc), Lu(Pc)₂^a

	solvents	R ₄	R ₃	R ₂	R ₁	O ₁	O ₂	O ₃	ΔE°
Lu(2,3-Nc) ₂	BN	-2.26	-1.82	-1.52	-0.61	-0.32	0.63	0.77	0.29
	CH ₂ Cl ₂				-0.625	-0.34			0.285
Lu(Pc)(2,3-Nc)	BN		-1.89	-1.56	-0.54	-0.15	0.85		0.39
	CH ₂ Cl ₂				-0.60	-0.24			0.36
Lu(Pc) ₂	BN	-2.40	-1.92	-1.54	-0.46	-0.05	1.05	1.43	0.41
	CH ₂ Cl ₂				-0.41	-0.02			0.40

^a Key: R, reduction; O, oxidation; ΔE° = (E°_{O1} - E°_{R1}); reference, E°(Fc⁺/Fc).

of the molecular orbitals;³⁷ a very similar situation is observed for dimeric face-to-face porphyrins.³⁸ The splitting of the orbitals of the lanthanide sandwich complex is clearly illustrated by the extensive study of the redox behavior of Lu(Pc)₂: the voltammogram consists of sets of two monoelectronic steps separated by approximately 0.4 V.⁶ One could reasonably expect a very similar behavior for the naphthalocyanine complex. The cyclic voltammogram of Figure 5 illustrates the splitting of the energy levels, as two electrons can be successively removed from Lu(2,3-Nc)₂⁻.

The gap between the two energy levels is much narrower than for the phthalocyanine complex. As a consequence of the effect of the annelation, which influences differently the oxidation and the reduction processes, ΔE° is much smaller for Lu(2,3-Nc)₂ (0.28 V) than for Lu(Pc)₂ (0.40 V) or Lu(2,3-Nc)(Pc) (0.36 V). Bouvet and Simon reported the same value, ΔE° = 0.36 V, for the hybrid sandwich complex but did not mention the value of ΔE° for Lu(2,3-Nc)₂.²⁰

The very low ΔE° value for Lu(2,3-Nc)₂ is a really important observation; this is the narrowest gap between the oxidation and reduction processes ever reported for the compounds of the lutetium phthalocyanine series. As a matter of fact, ΔE° represents the energy for putting a second electron on the semioccupied HOMO of the neutral radical or to remove one of the two electrons of the HOMO in Lu(2,3-Nc)₂⁻: that is the energy for pairing the two electrons on the HOMO. As mentioned by Simon and co-workers, ΔE° is a good estimate for the thermal activation energy for the conduction of electric charges in the solid material.³⁶ One can reasonably expect the electrical properties of Lu(2,3-Nc)₂ thin films or crystals to be different from those of Lu(Pc)₂ and Lu(2,3-Nc)(Pc).

UV/Visible Spectrophotometry. The UV/visible spectra of the oxidized and reduced forms of Lu(2,3-Nc)₂ (Figures 6 and 7) and of Lu(2,3-Nc)(Pc) (Figure 8) were recorded after exhaustive electrolysis. Spectroelectrochemistry is the only way to obtain the spectra of some of the highly reactive reduced or oxidized species. When the redox state of Lu(2,3-Nc)₂ is modified, the evolution of the spectra is very similar to what is observed for Lu(Pc)₂.⁶ Upon the monoelectronic reduction, the Q band at 760 nm disappears and is replaced by a peak at shorter wavelengths (λ_{max} = 706 nm); the less intense transition usually observed at longer wavelengths for the monoreduced species is located above 820 nm, out of the range experimentally available for the spectroelectrochemical measurements (Figure 6). The band characteristic of the electronic transition to the SOMO (ca. 475 nm) disappears. Further reductions to the di- and trianionic forms lead to spectra with less intense bands in the 600–750 nm range. The Soret band for the neutral and reduced species is not greatly affected by the uptake of electrons. This, which is also true for the oxidized forms of Lu(2,3-Nc)₂ (Figure 7), is not really surprising as they correspond to transitions from deeper occupied to unoccupied levels. After

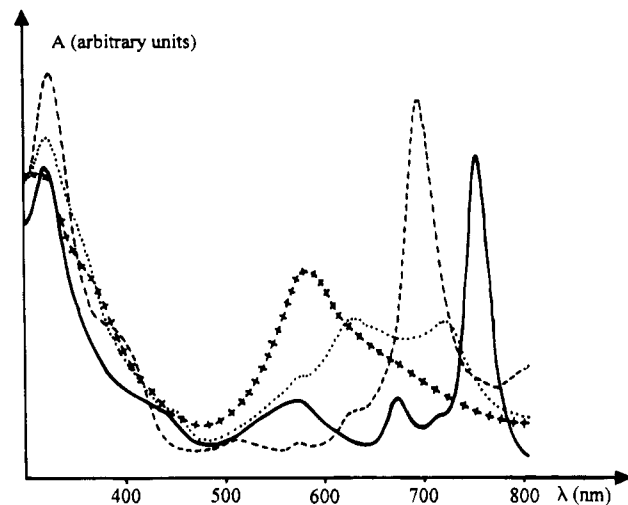


Figure 6. Absorption spectra of the reduced forms of Lu(2,3-Nc)₂ in benzonitrile: (—) Lu(2,3-Nc)₂, (---) Lu(2,3-Nc)₂⁻, (· · ·) Lu(2,3-Nc)₂²⁻, (- · -) Lu(2,3-Nc)₂³⁻.

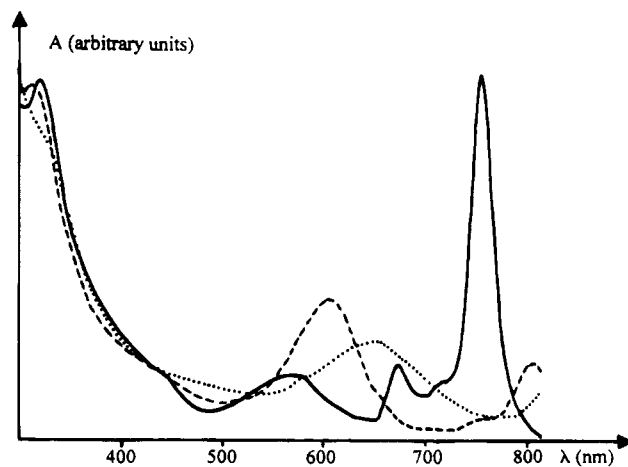


Figure 7. Absorption spectra of the oxidized forms of Lu(2,3-Nc)₂ in benzonitrile: (—) Lu(2,3-Nc)₂, (---) Lu(2,3-Nc)₂⁺, (· · ·) Lu(2,3-Nc)₂²⁺.

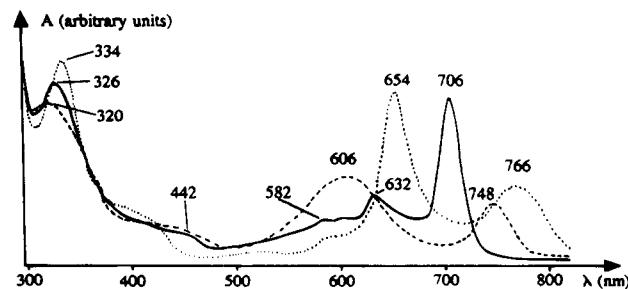


Figure 8. Absorption spectra of Lu(2,3-Nc)(Pc) (—), Lu(2,3-Nc)(Pc)⁺ (---), and Lu(2,3-Nc)(Pc)⁻ (· · ·) in CH₂Cl₂.

oxidation, the intense Q band of Lu(2,3-Nc)₂ vanishes; broad peaks appear at 600 nm for the monocationic species and at 650 nm for the dication.

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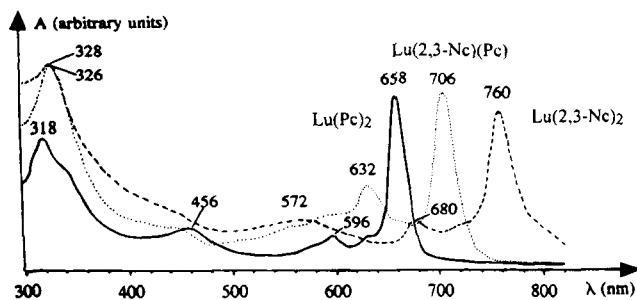


Figure 9. Absorption spectra of $\text{Lu}(\text{Pc})_2$ (—), $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ (···), and $\text{Lu}(2,3\text{-Nc})_2$ (- - -).

Table 2. Characteristics of the UV/visible and Near-IR Spectra for $\text{Lu}(2,3\text{-Nc})_2$, $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, and $\text{Lu}(\text{Pc})_2$ in CH_2Cl_2

	λ_{max} , nm (log ϵ)				
$\text{Lu}(2,3\text{-Nc})_2$	1089 (4.48)	760 (5.07)	680 (4.48)	572 (4.47)	328 (5.03)
$\text{Lu}(\text{Pc})(2,3\text{-Nc})$	987 (3.91)	706 (4.96)	632 (4.63)		326 (5.05)
$\text{Lu}(\text{Pc})_2$	914 (3.72)	658 (5.12)	596 (4.36)	456 (4.45)	318 (5.04)

The evolution of the spectra of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ (Figure 8) after reduction or oxidation is similar to what is observed for $\text{Lu}(\text{Pc})_2$ or $\text{Lu}(2,3\text{-Nc})_2$. The maximum of the Q band of this hybrid sandwich complex is at 706 nm, a wavelength shorter than for $\text{Lu}(2,3\text{-Nc})_2$ and higher than for $\text{Lu}(\text{Pc})_2$.

An interesting feature of the UV/vis spectra of the bis-(naphthalocyaninates), when compared to the bis(phthalocyaninates), is the shift of the Q band toward higher wavelengths. Such a shift can be explained by the extension of the conjugated system, particularly in the case of the linear annelation (2,3-Nc); the π -electrons of the naphthalene fragments participate in the conjugated system. Figure 9 shows the spectra of compounds $\text{Lu}(2,3\text{-Nc})_2$, $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, and $\text{Lu}(\text{Pc})_2$; the wavelengths of the maxima (λ_{max}) and the corresponding molar absorption coefficients (ϵ) appear in Table 2. Our measurements agree with those reported by Ishikawa et al. and by Simon and Bouvet.^{21,39} $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ has two different macrocycles; however, as observed for unsymmetrically substituted bisphthalocyanines, its Q band lies in the middle of the corresponding absorption bands of $\text{Lu}(\text{Pc})_2$ and $\text{Lu}(2,3\text{-Nc})_2$.¹⁷

The localization of the unpaired electron on one of the macrocycles or its delocalization over the two units is an important issue. From the ground-state and excited-state absorption, fluorescence and phosphorescence spectra, Holten and co-workers concluded that bis(porphyrinato)thorium(IV) sandwich complexes are strongly-coupled π systems, supermolecules, with delocalized molecular orbitals.⁴⁰ Konami et al. have shown that the overlap of the orbitals of cofacial dimers of porphyrins or phthalocyanines is influenced by the ring-to-ring distance (r) and by the rotation angle between the two rings (θ).⁴¹ They concluded that for $\text{Lu}(\text{Pc})_2$ ($r = 2.69 \text{ \AA}$, $\theta = 45^\circ$)⁷ the overlap is significant and that the two moieties of the molecule interact. In a closely related compound, the oxidized cerium bis(porphyrinate) where the two macrocycles are sepa-

rated by 3.4 Å , the hole is delocalized on the time scale of Raman resonance spectroscopy.⁴² For the cerium and yttrium bis(octaethylporphyrinates), Buchler concluded from NMR and ENDOR experiments that the two macrocyclic units of the dimers are identical.⁴³ From an IR study of the oxidized actinide(IV) homo- or heterosandwich complexes with porphyrins and phthalocyanines, Kadish, Guillard, and co-workers reach the conclusion that the positive charge is delocalized over both the macrocycles.⁴⁴

One would reasonably expect the delocalization also to occur for $\text{Lu}(\text{Pc})_2$ and related compounds. However, from the comparison of the ESR spectra of $\text{Lu}(\text{Pc})_2$ and $\text{Lu}(\text{Pc})$, Petit states that the unpaired electron is localized on one of the rings of the sandwich lutetium complex.⁴⁵ In the case of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, the naphthalocyanine ring would be electron deficient, as expected from the energy levels of the molecular orbitals and of course from the redox potentials reported herein.¹⁶ From the absorption and MCD spectra of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$, Ishikawa et al. came to the conclusion that the electron is delocalized over the two different moieties of the unsymmetrical molecule.²¹ We fully agree with their argument based on the observation that the Q band of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ lies in the middle of the ones of $\text{Lu}(\text{Pc})_2$ and $\text{Lu}(2,3\text{-Nc})_2$. Figure 9 allows the comparison of the spectra of $\text{Lu}(\text{Pc})_2$ and $\text{Lu}(2,3\text{-Nc})_2$ with the one of their hybrid, $\text{Lu}(2,3\text{-Nc})(\text{Pc})$. The wavelength of the maximum of the Q band of this latter compound is right in between the maxima of the symmetrical complexes. Moreover, the spectrum of $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ in this region does not show any evidence for the presence of bands belonging to the parent macrocycles. This is a more general observation as the UV/visible spectra of unsymmetrically substituted lutetium bisphthalocyanines are all very similar to the one of $\text{Lu}(\text{Pc})_2$: the bands are shifted, according to the electronic properties of the substituents. However, the dissymmetry of the molecule does not induce any significant modification of the structure of the spectra that could be ascribed to the transitions characteristic of each of the macrocyclic rings.¹⁷ It is obvious that the unpaired electron of the semioccupied HOMO is delocalized over the two π -macrocycles. Whether this electron is unequally shared by the two macrocycles of a molecule like $\text{Lu}(2,3\text{-Nc})(\text{Pc})$ or other unsymmetrical complexes that we have prepared, is now under study by IR and Raman spectroscopies of the different redox states of a series of complexes.

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