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Synthesis, Structure, Spectroscopic Properties, and Magnetic Properties of an Octakis(Alkylthio)-Substituted Lutetium(III) Bisphthalocyanine

Ayşe Gül Gürek,[†,⊥] Vefa Ahsen,*[,†,‡] Dominique Luneau,*[,§] and Jacques Pécaut[§]

TUBITAK, Marmara Research Center, Department of Chemistry, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey, Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, 41400 Gebze, Kocaeli, Turkey, and Laboratoire de Chimie Inorganique et Biologique (UMR 5046), DRFMC, CEA-Grenoble, 38054 Grenoble Cedex 9, France

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The synthesis of a new sandwich lutetium(III) bisphthalocyanine substituted with hexylthio groups (**1**), $[(C_6H_{13}S)_8\text{-}Pc]_2Lu$, is described. The compound is very soluble in most common organic solvents and has been fully characterized (elemental analysis, IR, ^1H and ^{13}C NMR, UV−vis spectroscopy, mass spectrometry). The chemically oxidized and reduced forms have been formed and characterized. The crystal structure of the compound (**1**) has been determined by X-ray diffraction on a single crystal. It crystallizes in the monoclinic space group $C2/c$ with $a = 31.558(2)$ Å, $b = 32.755(2)$ Å, $c = 20.489(1)$ Å, $\beta = 127.119(1)°$, and $Z = 4$. The temperature dependence of the magnetic susceptibility, measured on polycrystalline samples and in the range 6−300 K, is in agreement with one unpaired electron per molecular unit as found for the unsubstituted derivative. The magnetic results can be modeled assuming one-dimensional chain of spin $S = {}^1/_2$ with $g = 2.04$ and an antiferromagnetic coupling ($J = -11.83$ cm^{-1}, $H = -2J\sum S_iS_j$).

Introduction

Phthalocyanines (Pcs) have been used in industry for more than 50 years as pigments and dyes but also in many other areas because of their catalytic and photoconductive properties. Much attention has been paid to bis(phthalocyaninato)lanthanide complexes, especially the lutetium(III) derivative,[1,2] because they show electrochromic properties,[2,3] they yield intrinsic molecular semiconductors,[4,5] and they are attractive candidates for nonlinear optical applications.[6] Considerable efforts have been made to investigate their spectral, electrochromic, electrochemical,[2,7,8] magnetic,[9,10] and structural properties.

The structures of the rare earth diphthalocyanines, especially lutetium(III) complexes, have been studied. Several structures of the bis(phthalocyaninato)lanthanide complexes have been reported.[11−19] X-ray diffraction studies of bis(phthalocyaninato)lanthanide complexes show that they are sandwich-type compounds in which the lanthanide metal ion (M^{3+}) is eightfold coordinated to the isoindole nitrogens of phthalocyanine rings. The difference in the phthalocyanine ring distortions has been suggested to arise from the localization of the unpaired spin on the more distorted ring, and initial descriptions of the UV−vis absorption spectra of the bis(phthalocyaninato)lanthanide complexes appeared consistent with a localized model.[20−23]

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* To whom correspondence should be addressed. E-mail for V.A.: ahsen@penta.gyte.edu.tr. E-mail for D.L.: luneau@drfmc.ceng.cea.fr.

[†] TUBITAK.

[⊥] E-mail: ayse.gurek@posta.mam.gov.tr.

[‡] Gebze Institute of Technology.

[§] Laboratoire de Chimie Inorganique et Biologique.

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The substitution of the Pc_2Lu subunit with various types of chains[4,24−28] or macrocycles[29] has been already described. In particular, Pcs substituted with long alkoxymethyl,[4] alkoxy,[24,25] alkyl,[26,27] and poly(oxyethylene)[30] groups were synthesized to give Pc_2Lu complexes that are soluble in organic solvents. These complexes show discotic mesomorphism[4,23,24] and electrochromism.[31] A relationship between discotic mesomorphism and the electronic conductivities of the octa(alkoxy)-substituted Pcs was reported.[24,25,32]

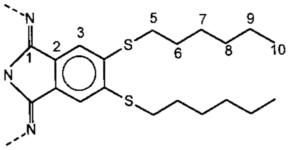
Early examples of octakis(alkylthio)-substituted Pcs have been described in the literature.[33−38] They exhibit columnar mesomorphism.[33−35,38−40] In this paper, we report the synthesis, the characterization, and the crystal structure of a lutetium(III) bisphthalocyanine substituted with hexylthio side chains, $[(C_6H_{13}S)_8Pc]_2Lu$ (derivative **1**).

Experimental Section

Synthesis. 1,2-Di(hexylthio)-4,5-dicyanobenzene (**2**) was synthesized according to a reported procedure.[36] All other reagents and solvents were obtained from commercial suppliers and were dried as described in the literature[41] before use. Elemental analysis was performed on a Carlo Erba elemental analyzer. Mass spectra were recorded using a VG Zab-Spec GC−MS spectrometer by fast atom bombardment technique using *m*-nitrobenzyl alcohol (MNBA) as the matrix.

Bis[4,5,4′,5′,4′′,5′′,4′′′,5′′′-octakis(hexylthio)phthalocyanine]lutetium(III) (1). A round-bottomed flask fitted with a condenser was degassed and flame-dried under dry argon. The flask was charged under argon with the dinitrile derivative **2** (2.68 g, 7.43 mmol), anhydrous $Lu(OAc)_3$ (0.4 g, 1.14 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (600 μL, 4 mmol), and 16 mL of hexan-1-ol. The mixture was refluxed under argon for 48 h. Evaporation of the hexan-1-ol under reduced pressure left a greenish-brown waxy residue. It was dissolved and heated under reflux in methanol (30 mL) and then separated by decantation. This purification step was repeated three times. Purification was further achieved by (i) a column chromatography over silica gel [CH_2Cl_2/*n*-hexane, 5:3 (v/v)] and (ii) two successive preparative thin layer chromatographies [silica gel; eluent CH_2Cl_2/*n*-hexane, 1:1 (v/v); $R_f = 0.5$]. Crystallization from a CH_2Cl_2/EtOH (5:1, v/v) mixture led to 300 mg (11%) of purple brown crystals. Anal. Calcd for $C_{160}H_{224}LuN_{16}S_{16}$, $M_w = 3059.7$: C, 62.86; H, 7.38; N, 7.32. Found: C, 62.62; H, 7.48; N, 7.12.

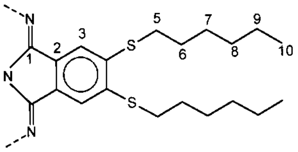
Table 1. ^{1}H Chemical Shifts (δ in ppm Downfield from TMS), Number of Protons, and Assignments for Oxidized, Neutral, and Reduced Forms of **1**



oxidized form[a]		neutral form[a]		reduced form[b]	
δ	atom	δ	atom	δ	atom
7.85 (16H)	3			8.89 (16H)	3
3.40 (32H)	5			3.59 (32H)	5
1.99 (32H)	6	2.13 (32H)	6	2.12 (32H)	6
1.71 (32H)	7	1.95 (32H)	7	1.88 (32H)	7
1.46 (64H)	8, 9	1.49 (64H)	8, 9	1.57 (64H)	8, 9
0.98 (48H)	10	0.99 (48H)	10	1.03 (48H)	10

[a] $CDCl_3$. [b] THF.

Table 2. ^{13}C Chemical Shifts (δ in ppm Downfield from TMS), Number of Carbons, and Assignments for Oxidized, Neutral, and Reduced Forms of **1**



oxidized form[a]		neutral form[a]		reduced form[b]	
δ	atom	δ	atom	δ	atom
163.84	1			159.71	1
140.93	4			138.86	4
138.14	2			136.87	2
119.82	3			122.85	3
36.35	5			35.06	5
31.95	6	34.15	6	32.06	6
29.39	7	29.43	7	30.02	7
22.85	8, 9	22.68	8, 9	23.54	8, 9
14.43	10	14.17	10	14.44	10

[a] $CDCl_3$. [b] THF.

IR (KBr) ν_{max} (cm^{-1}): 3020, 2980, 2820, 1510, 1450, 1400, 1370, 1330, 1280, 1070, 940, 760. FAB MS (matrix; MNBA) *m*/*z*: 3060 (M^+), 1187 ($M - 16(SC_6H_{13})$), 1081, 995.

IR, NMR Measurements, and Thermogravimetric Analysis. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer (KBr pellet). NMR experiments were carried out using a Bruker 200 MHz spectrophotometer (ref: TMS). The reduction was carried out by dissolving under argon the derivative **1** (17 mg) in THF-d_7 (0.5 mL) in the presence of $NaBH_4$ (3 mg). Oxidation was achieved by adding bromine in $CDCl_3$ (60 μL, 0.58 M) to a solution of **1** (17 mg) in $CDCl_3$ (0.5 mL). ^{1}H NMR and ^{13}C NMR chemical shifts for compound **1** and its oxidized and reduced forms in $CDCl_3$ are summarized in Tables 1 and 2, respectively.

Thermogravimetric analysis was carried out on a DuPont differential thermoinstrument (type 990) at a rate of 10 °C min^{-1} in a nitrogen flow (100 mL min^{-1}).

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Table 3. Crystallographic Data and Structure Refinement Parameters for Pc_2Lu

formula	$C_{160}H_{224}N_{16}S_{16}Lu$
fw	3059.5
T (K)	298(2)
wavelength (Å)	0.710 73
cryst syst	monoclinic
space group	$C2/c$
a (Å)	31.558(2)
b (Å)	32.755(2)
c (Å)	20.489(1)
β (deg)	127.119(1)
V (Å^3)	16 888(1)
Z	4
D_c (g/cm^3)	1.203
μ_{abs} (mm^{-1})	0.834
R^a [$I > 2\sigma(I)$]	0.0508
$R_w{}^a$ (all data)	0.1466

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = \sum[w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$.

Table 4. Selected Bond Lengths (Å) and Angles (°) for Pc_2Lu^a

Lu−N1	2.383(3)	Lu−N2	2.394(4)
Lu−N3	2.379(4)	Lu−N4	2.377(4)
N1−Lu−N2	70.5(1)	N2−Lu−N2#1	82.5(2)
N3−Lu−N2	71.7(1)	N3−Lu−N3#1	140.3(2)
N3−Lu−N1#1	82.6(1)	N4−Lu−N3	70.9(1)
N4−Lu−N2	110.7(1)	N4−Lu−N4#1	82.0(2)
N4−Lu−N1#1	145.7(1)	N1#1−Lu−N1	140.2(2)
N1#1−Lu−N2	79.7(1)	N3#1−Lu−N2	145.6(1)
N3#1−Lu−N1#1	111.1(1)	N4#1−Lu−N3	79.3(1)
N4#1−Lu−N1#1	71.8(1)	N4#1−Lu−N2	141.5(1)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1$, y, $-z + {}^1/_2$.

X-ray Crystallography. Data were collected at room temperature (298 K) with a Bruker SMART CCD diffractometer equipped with a graphite monochromatized normal focus molybdenum-target X-ray tube. The data were processed through the SAINT reduction and absorption correction software[42] to give 54 387 collected reflections from which 20 361 were independent. The structures were solved and refined on F^2 using the SHELXTL[43] software. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement steps, in calculated position and with isotropic thermal parameters. Crystallographic data and structure refinement parameters are summarized in Table 3, and selected bond lengths and angles are given in Table 4.

Magnetic Susceptibility Measurements. The thermal dependence of the magnetic susceptibility was measured in the 6−300 K temperature range with a SHE SQUID magnetometer operating at a field strength of 0.5 T and on a polycrystalline sample from which was picked the single crystal used for the structure determination. The data were corrected for diamagnetism.

Absorption Spectroscopy. The UV−visible spectra in solution were recorded with a Schimadzu 2001 UV PC spectrophotometer at room temperature. The reduced form of **1** was prepared by adding 3 mg of $NaBH_4$ to 10 mL of a solution of **1** (10^{-5} M) in THF under argon atmosphere. The oxidized form of **1** was obtained by adding bromine in $CHCl_3$ (120 μL, 0.58 M) to 10 mL of a chloroformic solution of **1** (10^{-5} M). The visible spectra of the reduced, oxidized, and neutral forms of **1** are shown in Figure 4.

Results and Discussion

Synthesis and General Properties. Octakis(alkylthio)-substituted lutetium bisphthalocyanine (**1**) was synthesized in one step (10% yield) using the chemical pathway[25] starting from 1,2-di(hexylthio)-4,5-dicyanobenzene (**2**). Purification was achieved by successive column chromatographies and recrystallization from a CH_2Cl_2/EtOH mixture. Compound **1** (Figure 1) is soluble in most organic solvents ($CHCl_3$, CH_2Cl_2, *n*-hexane, CCl_4, diethyl ether, DMF, DMSO, etc.) but insoluble in acetone, ethyl acetate, and alcohols.

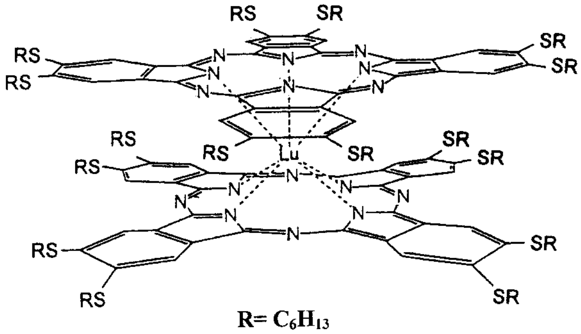

Figure 1. Schematic representation of the hexylthio-substituted lutetium diphthalocyanine (derivative **1**).

Mass spectrometry of compound **1** has been carried out showing a parent ion at $m/z = 3060$. The first fragment ion corresponds to the loss of all alkylthio moieties (see Experimental Section).

The thermal stability of the lutetium bisphthalocyanine derivative **1** was determined by thermogravimetric analysis; the decomposition starts significantly around 300 °C and becomes important around 400 °C.

NMR Studies. ^1H and ^{13}C NMR studies have been carried out to characterize the reduced and oxidized forms of **1**.

(i) ^{1}H NMR Spectroscopy. The chemical shifts, assignments, and spectra of the neutral and the different redox forms of **1** are detailed in Table 1. The assignments have been made by assuming that protons closer to the aromatic ring are shifted toward low fields. The results of the ^1H NMR are consistent with the results given in the literature.[4,30] Aromatic and $-SCH_2-$ protons (Table 1) are not observed distinctly in the neutral form because of their proximity to the paramagnetic center.

Derivative **1** was reduced and oxidized to suppress molecular paramagnetism, and the corresponding NMR spectra were recorded. Spectra data were analyzed and assignments were made by comparison with the corresponding dinitrile derivative (**2**) and the data given in the literature.[29,30,44]

In the ^1H NMR spectrum of the reduced form, a peak in the aromatic region at 8.89 ppm is visible which is not present in neutral **1**. For the methylene protons, four different peaks are observed. The integration (32H) and their chemical shifts allow the appropriate assignment of the 5, 6, 7, 8, and 9 positions.

Oxidation of **1** was carried out with bromine in $CDCl_3$. In the aromatic region, a peak at 7.85 ppm is detected, significantly shifted compare to the one of the reduced form (8.89 ppm).

(ii) ^{13}C NMR Spectroscopy. Spectral data and assignments for **1** are gathered in Table 2. 1,2-Di(hexylthio)-4,5-dicyano benzene (**2**) was used as a reference for the C atoms in the alkyl region.[36] The peaks in the aromatic region were assigned by using a conventional additivity law and a computer program named ACD Labs-NMR. These results were in agreement with those previously found for octa(hexylthio)-substituted monophthalocyanines.[36] The carbon atoms close to the central aromatic core are not observed in the neutral form. Oxidation and reduction restore the expected peaks.

The 1−5 carbon atoms could not be observed because of the vicinity of the paramagnetic center in the neutral form. The other signals have been classified following their proximity to the aromatic core.[29,30] The NMR results of **1** indicate the diamagnetic states of the oxidized and reduced forms of Pc_2Lu, as described in the literature.[29,30]

Crystal Structure. The molecular structure of **1** is shown in Figure 2. The asymmetric unit contains one phthalocyanine ligand [$(C_6H_{13}S)_8$-Pc] and a half lutetium located on the twofold axis special position. The molecular central core has a structure close to those previously reported for unsubstituted bis(phthalocyaninato)lanthanide(III) com-

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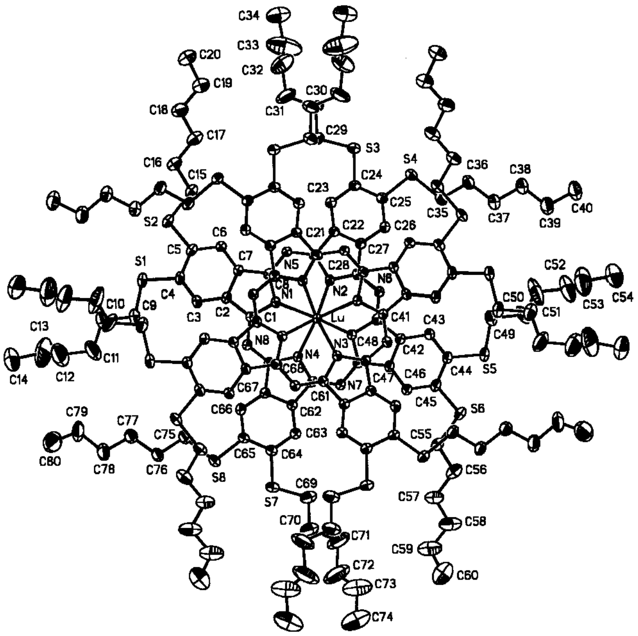

Figure 2. Molecular view of the bis(phthalocyaninato)lutetium(III) complex with atom labeling and ellipsoids at 30% probability.

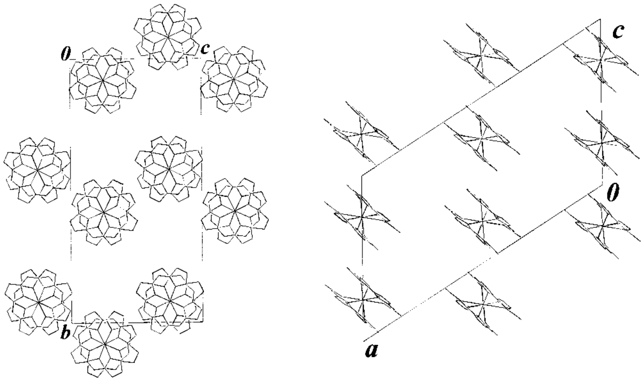

Figure 3. Crystal packing viewed along the *a* and *b* axes.

plexes.[13,14,45] The staggering angle between the two phthalocyanine macrocycle rings is α = 42°, which is comparable with those found for Pc_2Lu (α = 45°),[13] and the molecule is therefore chiral. The geometry of the coordination polyhedron around the lutetium ion is a slightly distorted antiprism. The four N_{iso} deviate by ± 0.04 Å from their mean plane.The $Lu-N_{iso}$ bond lengths range from 2.377(4) to 2.394(4) Å and compare well with those found for Pc_2Lu ($Lu-N_{mean}$ = 2.380(2) Å)[13] (Table 4). The interplanar distance between the two Pc, defined as the distance between the mean planes of the four N_{iso}, is 2.70 Å, which is in the range (2.67−2.70 Å) of the values reported for other Pc_2Lu or $[Pc_2Lu]^-$ complexes.[13,14,45] The Pc rings are distorted from planarity as generally observed[12,46] and have a saucer shape. Indeed, the dihedral angles between the mean plane of the four N_{iso} and the mean plane of each pyrrole ring are 7.38° (N1), 7.54° (N2), 2.52° (N3), and 12.66° (N4).

In the crystal, the molecules of $[(C_6H_{13}S)_8Pc]_2Lu$ are staked in columns along the direction of the *a* axis with a brickstone arrangement. The separation length between the molecules in these columns is equal to the *a* axis length [31.558(2) Å] (Figure 3). However, the shortest intermolecular distances are found along the *c* axis direction where the molecules' arrangement may be described as slipped-stacked columns (Figure 3) in which the lutetium(III) ions make a zigzag chain with an intermetallic Lu−Lu distance of 11.539(2) Å and a Lu−Lu−Lu angle of 125.20°. Along the columns (*c* axis direction), the shortest intermolecular distance between the macrocycle cores is 3.58(1) Å. Shorter intermolecular distances (3 Å) are found between the peripheral chains ($C_6H_{13}S$).

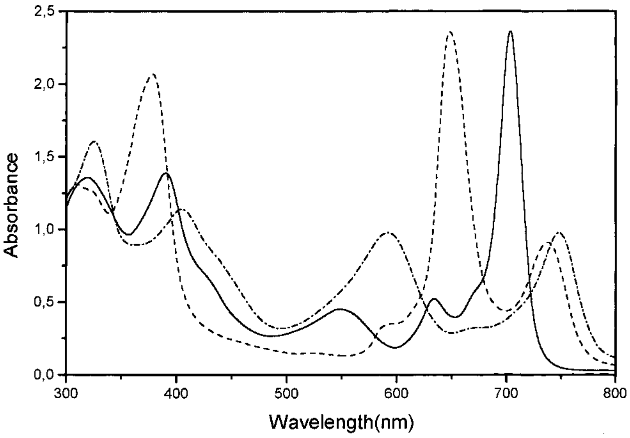

Figure 4. UV−visible spectra of the neutral form, $[(C_6H_{13}S)_8Pc]_2Lu$ (**1**) (—), in $CHCl_3$, oxidized form $[(C_6H_{13}S)_8Pc]_2Lu^+$(-.-) in $CHCl_3$ and reduced form $[(C_6H_{13}S)_8Pc]_2Lu^-$ (- - -) in THF ($c = 10^{-5}$ M).

Absorption Spectroscopy. Several redox states are known for the Pc_2Lu molecule, discovered by Moskalev and Kirin[2,47] 30 years ago, but the most important ones for practical purpose are the green neutral molecule Pc_2Lu, the oxidized cation Pc_2Lu^+, which is orange, and the one-electron reduced anion Pc_2Lu^-, which is blue:[7,48]

$$\mathrm{Pc_2Lu^-} \overset{-e^-}{\rightleftharpoons} \mathrm{Pc_2Lu} \overset{-e^-}{\rightleftharpoons} \mathrm{Pc_2Lu^+}$$

Figure 4 shows the UV−visible spectrum of the neutral, oxidized, and reduced forms of **1**. The neutral complex (**1**) is oxidized and reduced using solution of Br_2 in $CHCl_3$ and a solution of $NaBH_4$ in THF, respectively. The Q-band absorption of neutral unsubstituted Pc_2Lu in dichlorobenzene was found to be at 658 nm, and it was proposed that effects on the peak position λ_{max} due to the various substituents were relatively small.[24−27,29−31,48] In contrast, the bulkier hexylthio chains have rather large effects on the spectra. In the present case, the intense long-wave absorption appears at 704 nm in chloroform for **1**. The neutral species is brownish purple as compared to the green unsubstituted Pc_2Lu complex, the alkoxy-substituted $[C_{12}OPc]_2Lu$[24,25] derivative and the alkyl-substituted $[C_nPc]_2Lu$[26,27] complexes (n = 8, 12, and 18). Both the absorption coefficient and wavelength of the maximum of the Q-band are increased with thioether side chains instead of alkyloxy,[24] alkyl,[26,27] and alkyloxymethyl[4,31,48] groups. The position of the Soret band is, however, unaffected. The Soret bands appear at 390 and 319 nm as two broad absorptions.

The Q-band of the neutral species of the alkylthio-substituted complex **1** is red-shifted by around 40 nm compared with those of alkyl-substituted $[C_nPc]_2Lu$, alkoxy-substituted $[C_{12}OPc]_2Lu$ complex, and the alkoxymethyl-substituted $[C_{12}OCH_2Pc]_2Lu$ complexes.[4,24−27,31,48] The shifts observed in the Q-bands of the oxidized and reduced forms of **1** are similar to that of the neutral form of **1** and those obtained for oxidized dark green form, λ_{max} = 748 nm, and for the reduced blue form, λ_{max} = 648 nm. The Soret band for the reduced and oxidized species is not significantly affected by the uptake of electrons.

Magnetism. The temperature dependence of the magnetic susceptibility (χ) for the molecular unit and its product with the temperature (χT) are shown in Figure 5. At 300 K, χT is 0.368 cm^3 K mol^{-1} which confirms, if necessary, the presence of one spin $S = {}^1/_2$ per molecule (χT = 0.375 cm^3 K mol^{-1} for $g = 2$ and $S = {}^1/_2$).[5,13,25,49−51] When the

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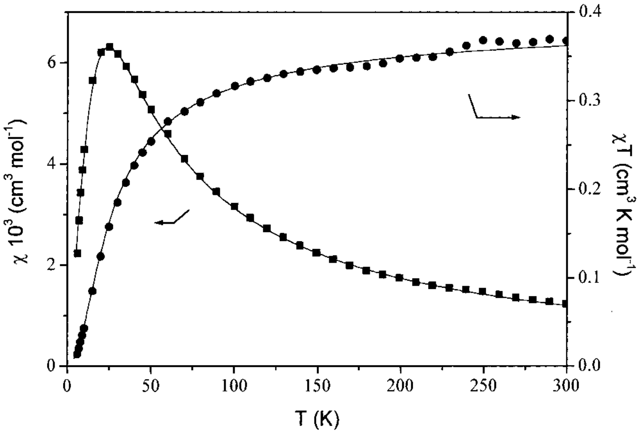

Figure 5. Thermal dependence of χ and χT product for Pc_2Lu. The solid lines are the best fit obtained assuming an infinite chain of spin $S = {}^1/_2$.

complex is cooled, χT decreases continuously and tends toward a value close to zero at 6 K (0.014 cm^3 K mol^{-1}), while χ exhibits a maximum at 24 K. The thermal dependence of χ and χT indicates clearly that significant antiferromagnetic intermolecular interactions occur between the molecules. In the temperature range 80−300 K, the magnetic susceptibility has been fit to a Curie−Weiss law, $\chi = C/T - \theta$, for comparison with previously reported results. The Curie constant, $C = 0.40$, corresponds to the one expected for a spin of $S = {}^1/_2$ ($g = 2.07$), and the θ value ($\theta = -28$ K) is in the range of a previous one reported for Pc_2Lu.[4,13,50] However, our measurement down to 6 K allows a deeper insight of the magnetic properties than a simple Curie−Weiss description, which cannot account for the maximum of χ vs T. Indeed, such a maximum indicates a low dimension. Thus, the data were fitted (Figure 5) using an analytical expression for a $S = {}^1/_2$ infinite chain,[52] with $g = 2.04$ and an antiferromagnetic exchange coupling of $J = -11.8$ cm^{-1}, close to the one estimated from EPR for Pc_2Lu.[53] From the magnetic point of view, our result shows that this compound is mainly one-dimensional (1D), as it was also found for Pc_2Lu[54] and in accordance with the crystal structure. Indeed, taking into account only the Pc_2Lu central cores which carry most of the spin density,[10] the shortest intermolecular contacts (<3.25 Å) are observed in columns running parallel to the *c* axis (Figure 3). They are well isolated from each other, and the magnetic couplings should occur mainly in these columns. The short contacts between the peripheral atoms (3 Å) should have negligible contribution to the magnetism behavior because of the weak propensity of the σ bond for spin delocalization. Thus, the magnetic interactions between the columns should be negligible. Our results also suggest that the unpaired electron is delocalized on both Pc macrocycles, and the magnetic interactions arise through a mechanism of the McConnell type.[55] If not, this would mean a dilution of the spin carriers on half of the Pc rings, which should result in a smaller interaction.

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Supporting Information Available: Crystallographic data for the title compound in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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