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The first example of a carbon label for interpreting the ^{13}C NMR spectra of phthalocyanine metal complexes

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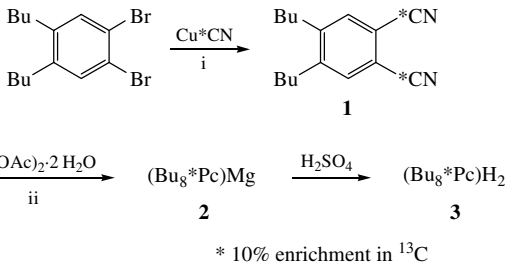
A carbon label has been introduced into phthalocyanine molecules in order to perform a correct assignment of signals in the ^{13}C NMR spectra of planar and sandwich-type metal complexes. With europium and lutetium as examples, the introduction of the label and the use of DEPT-135, GATED and ^{1}H–^{13}C COSY procedures enabled the recording and total assignment of signals in the ^{13}C NMR spectra of homo- and heteronuclear three-decked phthalocyanines of rare-earth elements.

Notwithstanding the limitations imposed by the low solubility and high molecular masses of phthalocyanines, NMR spectroscopy has recently become an efficient tool for determining the structures of these metal complexes.[1–4] By using substituted phthalocyanines and adjusting the recording conditions, it becomes possible to successfully record the ^{1}H NMR spectra of phthalocyanines and use them for identification and monitoring of the purity of resulting compounds.[5,6] It is more difficult to study phthalocyanine complexes by ^{13}C NMR spectroscopy because the ligands involve several types of quaternary carbon atoms,[7,8] which cannot be assigned exactly.

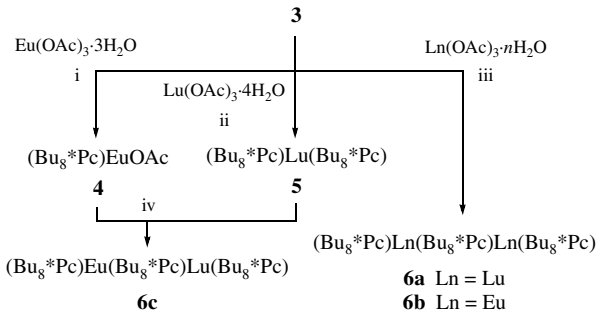
In this work aimed at a successful interpretation of ^{13}C NMR spectra of phthalocyanine complexes, we were the first to introduce a ^{13}C label to the α-pyrrole positions of the phthalocyanine macrocycle, which allowed us not only to observe an amplification of signals for these C atoms but also to assign the remaining signals in the spectrum using pulse techniques.

The carbon label was introduced at the stage of synthesis of 4,5-dibutylphthalodinitrile **1**. For this purpose, using the technique proposed previously,[5] 1,2-dibromo-4,5-dibutylbenzene was brought into the Rosenmund–von Braun reaction with a fivefold excess of copper cyanide containing ~10% ^{13}C (Scheme 1).

By performing the reaction in anhydrous DMF, we isolated phthalodinitrile **1** labeled with ^{13}C in 87% yield. The enrichment of the nitrile group with 10% ^{13}C is convenient not only for observing the signal intensities in ^{13}C NMR spectra (the signal of the CN group became two times more intense than that of the benzene ring CH) but also for saving the original Cu^{13}CN (99%, Merck). The subsequent reaction of phthalodinitrile **1** with magnesium acetate in isoamyl alcohol in the presence of MeOLi gave magnesium phthalocyanine **2** in 85% yield. Treatment of compound **2** with concentrated H_2SO_4 gave free phthalocyanine **3** in almost quantitative yield; using techniques developed previously,[6] the latter was converted to europium monophthalocyanine **4**, lutetium diphthalocyanine **5**, as well as homonuclear europium and lutetium triphthalocyanines **6a**,**b** containing the ^{13}C label at the 1-position of the macrocycle (Scheme 2). Furthermore, we carried out the reaction of europium monophthalocyanine **4** with lutetium diphthalocyanine **5** that gave new heteronuclear complex **6c** in a high yield; the three phthalocyanine ligands in this complex are magnetically non-equivalent.†



Scheme 1 *Reagents and conditions*: i, DMF, 4 h, reflux; ii, MeOLi, Am^{i}OH, reflux, 3 h.



Scheme 2 *Reagents and conditions*: i, *o*-$C_6H_4Cl_2$, DBU, reflux, 3–4 h; ii, $C_{16}H_{33}OH$, 230 °C, 1 h; iii, $C_{16}H_{33}OH$, 280 °C, 1 h; iv, 1,2,4-$C_6H_3Cl_3$, $C_{16}H_{33}OH$, 220 °C, 20 min.

Table 1 ^{13}C NMR spectra of the compounds synthesised.

Compound[a]		δ/ppm							
		*C(1)	C(2)	C(3)	C(4)	α-CH_2	β-CH_2	γ-CH_2	Me
1		115.87	112.83	134.00	147.38	32.49	32.28	22.61	13.86
2		154.79	139.49	124.76	143.68	36.30	35.33	24.86	15.27
5		160.37	138.03	123.90	141.64	36.47	35.62	25.09	15.60
6a	Outer	155.20	122.28	134.50	141.84	35.15	33.95	23.52	14.54
	Inner	160.55	124.52	136.62	143.73	35.88	34.15	23.86	14.99
6b	Outer	188.75	86.63	119.25	140.82	35.34	34.23	24.11	15.06
	Inner	213.05	114.85	130.15	143.99	38.46	34.98	24.82	15.81
6c	Outer Lu	151.40	127.78	121.67	141.70	35.26	33.95	23.66	14.62
	Outer Eu	190.70	87.42	119.69	140.97	35.35	34.18	23.91	14.90
	Inner	188.22	132.88	127.78	144.07	36.88	34.23	24.36	15.38

[a]The spectra of compounds **1**, **6a–c** were recorded in $CDCl_3$, those of compound **2** – in [$^{2}H_8$]THF, and those of compound **5** – in [$^{2}H_8$]THF additionally containing 1–2 vol% $N_2H_4·H_2O$.

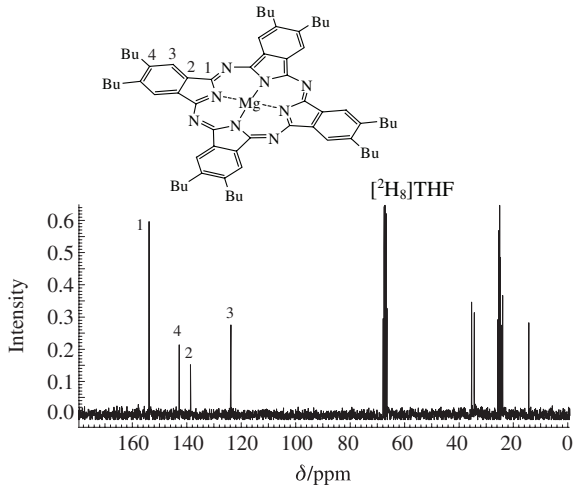


Figure 1 The ^{13}C NMR spectrum of complex **2** ([$^2H_8$]THF).

The spectroscopic data and signal assignments in the ^{13}C NMR spectra of the compounds synthesised are presented in Table 1. The ^{13}C NMR data[5] for non-labeled phthalonitrile **1** are given for comparison. In the case of magnesium complex **2**, cyclic tetramerisation of compound **1** to the phthalocyanine macrocycle results in a downfield shift of the signal of labeled C(1) by 38.92 ppm (Table 1, Figure 1). The spectrum of lutetium diphthalocyanine **5** recorded in [$^2H_8$]THF displays no signals of C atoms in the aromatic region owing to the presence of an unpaired electron in the molecule. However, after addition of a three- to five-fold molar excess of hydrazine hydrate, which reduces diphthalocyanine **5** to the diamagnetic anion $[(Bu_8Pc)_2Lu]^-$, the expected set of weak-field signals appear (Table 1); they are especially well pronounced after a few hours.

The ^{13}C NMR spectra of three-decked complexes **6a**,**b**, similarly to their protonic spectra,[6] contain two sets of signals

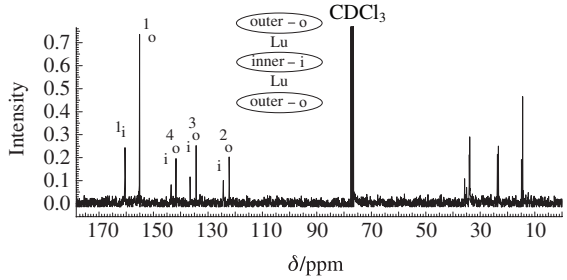


Figure 2 The ^{13}C NMR spectrum of complex **6a** ($CDCl_3$).

† *Synthetic procedure*. A mixture of europium acetate octabutylphthalocyanine **4** (165 mg, 0.141 mmol) and lutetium hexadecabutyldiphthalocyanine **3** (145 mg, 0.069 mmol) was heated for 20 min at 200 °C in 1,2,4-trichlorobenzene (2 ml) containing a catalytic amount of hexadecan-1-ol. After the reaction was completed, the resulting mixture was diluted with THF (25 ml), insoluble admixtures were filtered off, and the solvent was removed *in vacuo*. The residue was washed with boiling 80% aqueous MeOH (3×50 ml) and dried *in vacuo*. The resulting powder was dissolved in THF and purified by chromatography in a 2.5×40 cm column (Bio-Beads S X1, THF as the eluent); the dark blue fraction was collected. The yield of compound **6c** was 83%. Additional purification of compound **6c** from traces of homonuclear triphthalocyanine complexes **6a**,**b** was carried out by preparative TLC (Merck Silica Gel 60, 40×63 μm using benzene–hexane 2:1 as the eluent). Electronic spectroscopy (C_6H_6, λ_{max}/nm): 347, 659. ^1H NMR ($CDCl_3$) δ: 10.74 (s, 8H, H_{Ar}), 9.87 (s, 8H, H_{Ar}), 7.81 (s, 8H, H_{Ar}), 4.23–4.33 (m, 16H, α-CH_2), 3.96 (t, 16H, α-CH_2), 3.40 (m, 16H, β-CH_2), 3.16–3.26 (m, 16H, α-CH_2), 2.85–2.90 (m, 16H, γ-CH_2), 2.57–2.65 (m, 16H, β-CH_2), 2.27–2.37 (m, 16H, γ-CH_2), 2.04–2.10 (m, 16H, β-CH_2), 1.86–1.96 (m, 40H, γ-CH_2 and Me), 1.64 (t, 24H, Me), 1.40 (t, 24H, Me). MS (MALDI-TOF), *m*/*z*: 3210 (MH^+). The ^{13}C NMR spectrum is presented in Table 1.

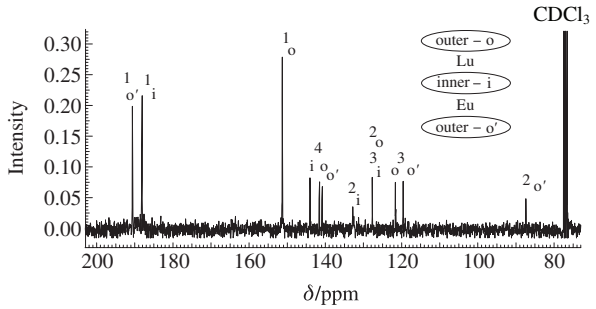


Figure 3 The aromatic region of the ^{13}C NMR spectrum of complex **6c** ($CDCl_3$).

corresponding to the C atoms of the inner and outer decks (Table 1, Figure 2). The paramagnetic properties of the europium ion result in deshielding of C(1) signals in complex **6b** in comparison with **6a** by ~33 and 53 ppm for the outer and inner decks, respectively. In this case, the adjacent C(2) atoms are shielded by 10–35 ppm and the C(3) atoms are shielded by 6–15 ppm. In heteronuclear complex **6c**, the magnetic non-equivalence of the three phthalocyanine ligands results in a triple set of signals, of which the three signals corresponding to the labeled C(1) atoms have the highest intensities (Figure 3). A comparison of the spectra of compounds **6a** and **6c** shows that the signal at δ 151.40 ppm corresponds to the C atoms of the outer deck coordinated with a lutetium ion. The assignment of the two other neighbouring signals (at δ 188.22 and 190.70 ppm) was non-obvious. In order to solve this problem, we synthesised triphthalocyanine **6c** containing a ^{13}C label in the outer deck coordinated with an europium ion, from labeled europium phthalocyanine **4** and non-labeled lutetium phthalocyanine $[(Bu_8Pc)_2Lu]$ **5**. We found that labeled atoms manifested themselves as a signal at δ 190.70 ppm; that is, the C(1) atoms of the outer deck in this compound are deshielded more strongly on the europium side than the C(1) atoms of the inner deck, which is untypical of homonuclear analogues. The signals of C(2)–C(4) atoms in the spectrum of compound **6c** were assigned using DEPT-135, GATED and ^1H–^{13}C COSY techniques.

Thus, the introduction of a ^{13}C label to the 1-position of the phthalocyanine ring and the use of additional techniques allowed us to perform a correct assignment of signals in the ^{13}C spectra of lanthanide sandwich complexes.

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