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.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 metal complexes, we were the first to introduce a $^{13}$C label to the spectra of phthalocyanine complexes, 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.

Reagents and conditions

Scheme 1

Reagents and conditions: i, DMF, 4 h, reflux; ii, MeOLi, AmiOH, reflux, 3 h.

Scheme 2

Reagents and conditions: i, α-$\text{C}_6\text{H}_4\text{Cl}_2$, DBU, reflux, 3–4 h; ii, Cu($\text{C}_6\text{H}_4\text{O})_2$, 230 °C, 1 h; iii, Cu($\text{C}_6\text{H}_4\text{O})_2$, 280 °C, 1 h; iv, 1,2,4-$\text{C}_6\text{H}_3\text{Cl}_3$, 154.79 ppm, 24.86 ppm, 15.27 ppm, 115.87 ppm, 134.00 ppm, 147.38 ppm, 32.49 ppm, 32.28 ppm, 22.61 ppm, 13.86 ppm.

Table 1

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^\alpha$C(1)</td>
<td>$^\beta$C(2)</td>
</tr>
<tr>
<td>1</td>
<td>115.87</td>
</tr>
<tr>
<td>2</td>
<td>154.79</td>
</tr>
<tr>
<td>5</td>
<td>160.37</td>
</tr>
<tr>
<td>6a</td>
<td>155.20</td>
</tr>
<tr>
<td>Inner</td>
<td>160.55</td>
</tr>
<tr>
<td>6b</td>
<td>188.75</td>
</tr>
<tr>
<td>Inner</td>
<td>213.05</td>
</tr>
<tr>
<td>6c</td>
<td>151.40</td>
</tr>
<tr>
<td>Outer</td>
<td>180.70</td>
</tr>
</tbody>
</table>

The spectra of compounds 1, 6a–c were recorded in CDCl$_3$, those of compound 2 – in [D$_6$]THF, and those of compound 5 – in [D$_8$]THF additionally containing 1–2 vol% N$_2$H$_4$·H$_2$O.
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 for non-labeled phthalonitrile 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 [D$_8$]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 the unpaired electron in the molecule, the expected set of weak-field signals appear (Table 1); they are especially well pronounced after a few hours.

The $^{13}$CNMR spectra of three-decked complexes 6a,b, similarly to their protonic spectra, contain two sets of signals 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 $\delta$ 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 $\delta$ 188.22 and 190.70 ppm) was non-obvious. In order to solve this problem, we synthesised trithiapthalocyanine 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$_8$Pc)$_2$Lu] 5. We found that labeled atoms manifested themselves as a signal at $\delta$ 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 $^1$H–$^{13}$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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References


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