

**<sup>205</sup>Tl(III)-NMR Study of Thallium(III) Metalloporphyrins**

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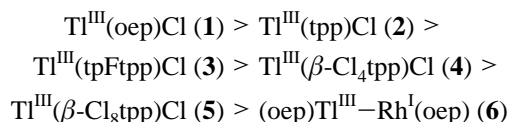
The first nuclear magnetic resonance spectra of porphyrins were published by Becker and Bradley in 1959.<sup>1</sup> Since that time NMR spectroscopy and related techniques have proven to be valuable in the study of porphyrins and metalloporphyrins.<sup>2</sup> On the contrary, there have been rather few reports of hetero-nuclear NMR studies with the readily accessible nuclei <sup>113</sup>Cd,<sup>3</sup> <sup>195</sup>Pt,<sup>4</sup> <sup>119</sup>Sn,<sup>5</sup> and <sup>31</sup>P.<sup>6</sup> Herein, we report on the first <sup>205</sup>Tl(III)-NMR study of five-coordinate thallium(III) porphyrins with chlorine as an axial ligand and a variety of different basicity macrocycles. The observed <sup>205</sup>Tl(III) chemical shifts are related to the distance of Tl(III) from the 4N<sub>p</sub>-mean plane.

Although a comprehensive presentation of <sup>205</sup>Tl-NMR spectroscopy has appeared in the literature<sup>7</sup> and *J*(Tl–H)<sup>8,9</sup> and *J*(Tl–C)<sup>10</sup> coupling constants have been measured in various porphyrin macrocycles, the <sup>205</sup>Tl nucleus has never been directly observed. The element thallium possesses two stable isotopes, <sup>203</sup>Tl (29.5%, natural abundance) and <sup>205</sup>Tl (70.5%, natural abundance), which have a nuclear spin 1/2 and hence are NMR-active. The relative receptivities of <sup>203</sup>Tl and <sup>205</sup>Tl nuclei are 0.055 and 0.1355, respectively, with the proton having an assigned value of 1. This makes the <sup>205</sup>Tl(III) nucleus one of the most receptive spin 1/2 nuclides. The very high receptivity

of both isotopes of thallium allows one to observe them directly with relatively little difficulty.

**Results.** Tl<sup>III</sup>(tpp)Cl,<sup>8</sup> Tl<sup>III</sup>(oep)Cl,<sup>8</sup> Tl<sup>III</sup>(tpFtpp)Cl,<sup>11</sup> Tl<sup>III</sup>(β-Cl<sub>4</sub>tpp)Cl,<sup>11</sup> Tl<sup>III</sup>(β-Cl<sub>8</sub>tpp)Cl,<sup>11</sup> and (oep)Tl<sup>III</sup>–Rh<sup>I</sup>(oep)<sup>12</sup> derivatives were prepared according to literature procedures.<sup>13</sup>

Their <sup>205</sup>Tl(III)-NMR spectra are presented in Figure 1. According to the observed chemical shifts of <sup>205</sup>Tl(III) signals (Table 1), the following order was derived:



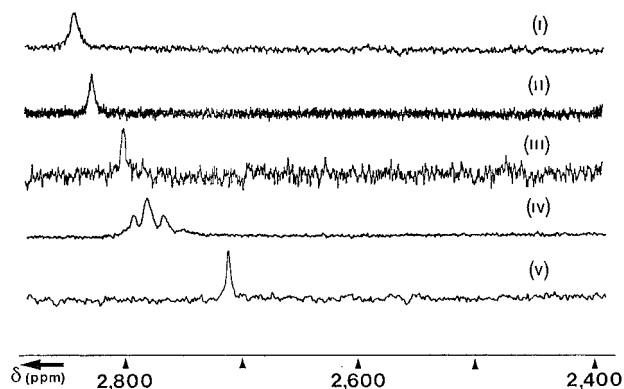
The above order reflects the decreasing basicity of the macrocycle among the five-coordinate complexes. The choice of the above derivatives in this study was based on the following criterion: Cl<sup>–</sup> was chosen as the axial ligand for all five coordinate derivatives. Consequently, all differences in the measured chemical shifts should be directly related to the nature of the porphyrin ring (electron density from the conjugated system) and/or the distance of the thallium atom from the mean plane of the four nitrogen atoms (deformation of the porphyrin ring due to the peripheral substituents or other structural deviations from ring planarity).<sup>14</sup> Tl<sup>III</sup>(oep)Cl and Tl<sup>III</sup>(tpp)Cl compounds possess different substituents at *meso* and pyrrolic positions, respectively. For **2** and **3** the fluoro-substitution in the phenyl groups seems to be the reason for the induced chemical shift from 2829 to 2804 ppm. For **2**, **4**, and **5** derivatives, chloro-substitution at the β-position produces similar differences in the chemical shifts. The electron-withdrawing ability of chlorine atoms, however, in association with the induced deviation from planarity of the porphyrin macrocycle, is a well-known factor for derivatives like **4** and **5**<sup>14,15</sup> and may be also play a role to the above mentioned influence on the chemical shifts.

The case of Tl<sup>III</sup>(β-Cl<sub>4</sub> tpp)Cl is equally interesting and indicative of the <sup>205</sup>Tl(III) shiftability. It displays high sensitivity to small differences in mixtures of different stereoisomers of this complex due to the different relative positions of the four chlorine atoms (one per pyrrole ring) on the porphyrin ring.<sup>11</sup> In the case of the (oep)Tl<sup>III</sup>–Rh<sup>I</sup>(oep) dimer the chemical shift is very different from all of the above mentioned complexes, and

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- (11) Tl<sup>III</sup>(tpFtpp)Cl: For the synthesis, a previous published procedure was followed.[8] Chromatographic column separation with SiO<sub>2</sub> (4 × 2 cm) was performed. With a mixture of solvents, CH<sub>2</sub>Cl<sub>2</sub>/hexane (4: 6–1:1) the free base, (tpFtpp)<sub>2</sub>, was eluted while Tl<sup>III</sup>(tpFtpp)Cl followed in the next fraction with CH<sub>2</sub>Cl<sub>2</sub> as eluent (70%). Tl<sup>III</sup>(β-Cl<sub>4</sub> tpp)Cl: The metalation was achieved by following the previously published procedure.<sup>8</sup> The reaction mixture was passed through a column of SiO<sub>2</sub> (5 × 4 cm). Using MeOH as a first eluent, four fractions with mixtures of complexes were collected. The desired complex was obtained with a mixture of solvents, toluene/hexane (1: 1–7:3) (55%). Tl<sup>III</sup>(β-Cl<sub>8</sub> tpp)Cl: The same procedure was also followed[8] for this synthesis. Again column chromatography of SiO<sub>2</sub> (7 × 4 cm) was performed. Toluene was used as the eluent, and Tl<sup>III</sup>(β-Cl<sub>8</sub> tpp)Cl was eluted in analytically pure form in the third fraction (60%).

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- (13) Abbreviations of the dianions: (oep)<sup>2–</sup> = 2,3,7,8,12,13,17,18-octaethylporphyrinate; (tpp)<sup>2–</sup> = 5,10,15,20-tetraphenylporphyrinate; (tpFtpp)<sup>2–</sup> = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinate; (β-Cl<sub>8</sub>tpp)<sup>2–</sup> = 2,3,7,8,12,13,17,18-octa-β-chloro-5,10,15,20-tetrakis(phenyl)porphyrinate; (β-Cl<sub>4</sub>tpp)<sup>2–</sup> = 2,7,12,17-tetra-β-chloro-5,10,15,20-tetraphenylporphyrinate.
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**Figure 1.**  $^{205}\text{Tl(III)}$ -NMR spectra of the five-coordinate thallium(III) porphyrins, (I–IV) in  $\text{CDCl}_3$  at room temperature.

**Table 1.**  $^{205}\text{Tl(III)}$  Data and  $T_1$  Measurements for the Complexes  $\text{Tl}^{\text{III}}(\text{Por})\text{Cl}$  in  $\text{CDCl}_3$  at Room Temperature, versus  $\text{Tl}^{\text{III}}(\text{NO}_3)_3$ , and  $\text{Tl(III)}-4\text{N}_p$  Distances

complex	$\delta$ (ppm) <sup>a</sup>	$T_1$ (s)	$\text{Tl(III)}-4\text{N}_p$ (Å)
$\text{Tl}^{\text{III}}(\text{oep})\text{Cl}$	2844	$0.3668 \pm 0.0518$	0.69 <sup>17</sup>
$\text{Tl}^{\text{III}}(\text{tpp})\text{Cl}$	2829	$0.3116 \pm 0.0362$	0.62 <sup>9</sup>
$\text{Tl}^{\text{III}}(\text{tpFtp})\text{Cl}$	2804	$0.113 \pm 0.009$	
$\text{Tl}^{\text{III}}(\beta\text{-Cl}_4\text{tpp})\text{Cl}$	2787	$0.1081 \pm 0.0125$	0.71 <sup>16</sup>
$\text{Tl}^{\text{III}}(\beta\text{-Cl}_8\text{stpp})\text{Cl}$	2722	$0.0965 \pm 0.0125$	

<sup>a</sup> The chemical shifts are given in ppm toward higher frequency with respect to  $\text{Tl}^{\text{III}}(\text{NO}_3)_3$ .

it appears at 128.11 ppm.<sup>12</sup> It should be noted that the “axial” ligand  $[\text{Rh}^{\text{I}}(\text{oep})]^-$  (in the case of  $(\text{oep})\text{Tl}^{\text{III}}-\text{Rh}^{\text{I}}(\text{oep})$ ), present in the coordination sphere of thallium, introduces several important changes in relation to the monomer complexes (due to the M–M bond and the “nature” of the whole complex).

In order to complete and examine the behavior of the thallium nucleus in the porphyrin rings, preliminary  $T_1$  measurements were carried out at room temperature (except for the dimer (VI)). These values are summarized in Table 1. We observe that  $T_1$  values also follow the same order as  $^{205}\text{Tl(III)}$  chemical shifts do. Therefore, as a preliminary conclusion, it appears that

relaxation times depend on the electronic environment of the porphyrin ring with similar coordination (five coordinate) but not directly on the thallium– $4\text{N}_p$  distance.

Over the past years  $^{205}\text{Tl(III)}$ -NMR spectroscopy has become a valuable tool in inorganic and bioinorganic chemistry,<sup>17</sup> owing to the sensitivity of the  $^{205}\text{Tl(III)}$  signal to structural differences and different coordination sites. Taking into account the relatively easy synthesis of thallium(III) porphyrin derivatives and the easily detectable  $^{205}\text{Tl(III)}$  nuclei (in only 1–2 h),  $^{205}\text{Tl(III)}$ -NMR could be used as a probe for the study and the elucidation of electronic properties and structural changes of the porphyrinic ring.

Further  $^{205}\text{Tl(III)}$ -NMR studies and determination of  $J(^{205}\text{Tl(III)}-\text{H})$  and  $J(^{205}\text{Tl(III)}-^{13}\text{C})$  coupling constants of thallium(III) derivatives are two intriguing questions currently under investigation in our laboratory.

**NMR Instrumentation.** All NMR experiments,  $^{205}\text{Tl(III)}$ -NMR spectra, and  $T_1$  measurements were carried out in  $\text{CDCl}_3$  solutions of  $1 \times 10^{-5}$  mol, on a Varian Unity Plus 300 MHz instrument. Chemical shifts are given versus irradiation frequency of a solution  $\text{Tl}^{\text{III}}(\text{NO}_3)_3$  in  $\text{D}_2\text{O}$ , set at 173 019 179.9 Hz (irradiation frequency) for  $^{205}\text{Tl(III)}$ -NMR signal, spectral width 80 kHz and number of data points 64 k. All experiments and  $T_1$  measurements were performed at room temperature for the selected derivatives.

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