

DYNAMICAL NMR STUDIES ON THALLIUM(III) MESO-TETRAPHENYLPORPHYRIN ACETATE

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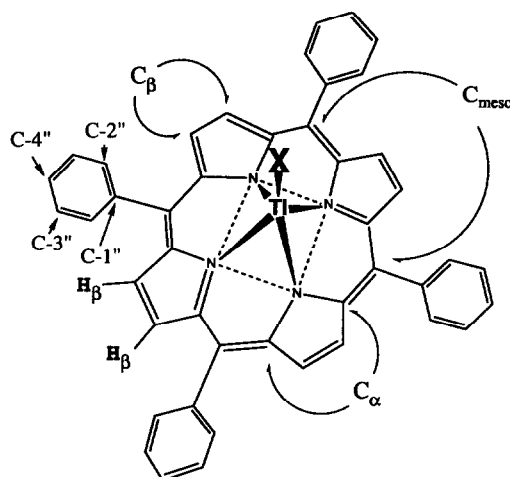
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Abstract—It is shown from the proton resonances spectra of thallium(III) meso-tetraphenylporphyrin acetate that the intermolecular exchange of the acetato group has an activation energy of 4.1 kcal mol⁻¹ in CD₂Cl₂. In the slow exchange region, the methyl and carbonyl carbons of the acetato group are observed at 18.8 ppm [with ³J(Tl—¹³C) coupling constant 280 Hz] and 174.9 ppm [with ²J(Tl—¹³C) coupling constant 235 Hz], respectively, at -90°C. The phenomenon of the rotation of phenyl groups in the complex from the angle 90–60° relative to the N₄ plane to approximately 0° was identified and examined by using ¹³C and ¹H NMR spectroscopy at various temperatures.

Thallium(III) meso-tetraphenylporphyrin acetate, Tl(tpp)(OAc), (shown in Fig. 1) is a compound suitable for dynamical NMR studies. It is believed that Tl(tpp)(OAc) has a coordination number of five, rather than six, because the thallium atom is displaced out of the porphyrin plane by about 0.9 Å.¹⁻⁴

In an NMR study of Tl(tpp)(OAc), Abraham *et al.*⁵⁻⁷ have reported that the methyl protons of the apical acetate ligand were observed as a sharp singlet at $\delta = -0.03$ ppm, with no evidence of coupling of the thallium nuclei with the acetate group. Neither the carbonyl nor methyl signals of the acetate ligand in the ¹³C NMR spectra was found. However, all other ¹³C signals in the porphyrin were clearly observed. Hence, they surmised that this effect might be due to the broadening of the ¹³C signal through an exchange process involving the apical ligand. In the present communication, the proton and ¹³C NMR spectra of Tl(tpp)(OAc) in solution at low temperatures are examined to confirm the previous inference and to determine the value of the



where X=OAc

Fig. 1. Structure of the Tl(tpp)(OAc) complex.

activation energy for the exchange process. Furthermore, an abnormal conformation change at low temperatures has been detected.

On cooling a 0.05 M solution of Tl(tpp)(OAc) in CD₂Cl₂ (Fig. 2), the methyl proton signal, which

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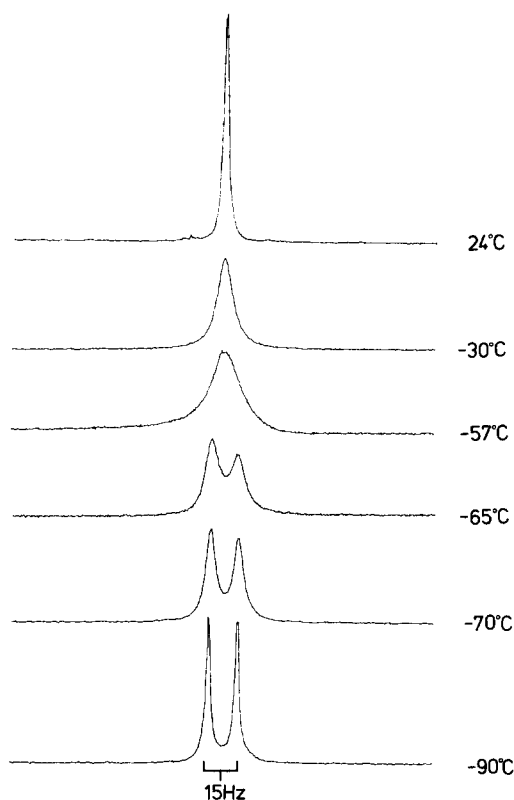


Fig. 2. 300 MHz ^1H NMR spectra of the axial acetato protons in $\text{Tl}(\text{tpp})(\text{OAc})$ in CD_2Cl_2 at various temperatures.

displays a single peak at room temperature ($\delta = 0.06$ ppm), broadens (temperature of coalescence, $T_c - 57^\circ\text{C}$) and finally splits into two peaks with a separation of 14.7 Hz. The process is completely reversible, and the results measured at 300 MHz confirm the separation as a coupling $^4J(\text{Tl}-\text{H})$ rather than a chemical-shift difference. The rate process is treated as a simple two-site exchange rate process and the use of the usual coalescence analysis yields the exchange rate of 32.65 s^{-1} at -57°C , which corresponds to an activation energy (E_a) of 4.1 kcal mol^{-1} .

^{13}C NMR data for $\text{Tl}(\text{tpp})(\text{OAc})$ at different temperatures is shown in Table 1. At -90°C (or -75°C), because the intermolecular exchange is extremely slow, methyl and carbonyl carbons of the acetato group are observed at 18.8 ppm [with $^3J(\text{Tl}-^{13}\text{C})$ coupling constant 280 Hz] and 174.9 ppm [with $^2J(\text{Tl}-^{13}\text{C})$ coupling constant 235 Hz], respectively. At 24°C , the rate of intermolecular exchange of the acetato ligand is 352 Hz. The exchange rate is comparable with the coupling frequency of $\text{Tl}-^{13}\text{C}$, i.e. 258 ± 23 Hz. In this intermediate exchange region, the signals are broadened beyond detection. Hence, no signal of the axial ^{13}C has been found at 24°C .

The abnormal conformation change due to the rotation of the phenyl group in the complex is also observed from the ^{13}C and ^1H NMR spectra at different temperatures. The temperature variation of the $c-2''$ carbon spectrum of $\text{Tl}(\text{tpp})(\text{OAc})$ is shown in Fig. 3 as from a doublet of doublets at 24°C to a triplet at -90°C . This indicates that the dihedral angles between the mean plane of the porphyrin skeleton and the planes of the four phenyl groups vary from a range of $90-60^\circ$ ^{3,8} to about 0° . Consequently, the two ortho carbons in the same phenyl group become more equivalent and the inner peaks of doublet of doublets merge together with decreasing temperature. Also, the steric hindrance between the phenyl groups and β -pyrrole increases. It causes the β -pyrrole proton to shift downfield by about 39 Hz from 9.07 ppm at 24°C to 9.20 ppm at -90°C . All other phenyl protons are shifted downfield about 16 ± 5 Hz (shown in Table 2). Furthermore, the chemical shift of C_α (and $c-1''$) shifts upfield about 53 Hz from 150.5 (or 142.4) ppm to 149.8 (or 141.7) ppm (shown in Table 1). Those effects are also evidenced from 2D NOESY at -90°C and 24°C as shown in Figs 4(a) and (b), respectively. Figure 4(a) indicates that there is a strong through space steric interaction between the protons of β -pyrrole and the phenyl protons, while in Fig. 4(b), there is only a weak through space interaction between the protons of β -pyrrole and *ortho* phenyl protons but no signal indicates the interaction between the protons of β -pyrrole and other phenyl protons. All these observations show that, as the temperature decreases, the phenyl groups rotate from the planes at the angle of $90-60^\circ$

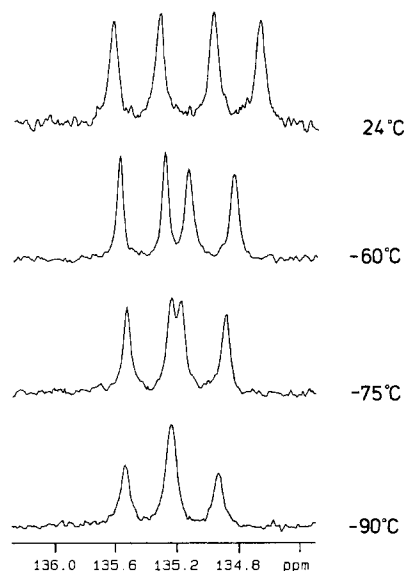


Fig. 3. Temperature dependence of chemical shifts for the $\text{C}-2''$ carbons of $\text{Tl}(\text{tpp})(\text{OAc})$ in CD_2Cl_2 .

Table 1. ^{13}C chemical shifts (δ) and thallium-carbon coupling constant (J) in Hertz of $\text{Tl}(\text{tpp})(\text{OAc})$ in CD_2Cl_2^a

Temperature ($^{\circ}\text{C}$)	C_α	C_β	C_{meso}	$\text{C-1}''$	$\text{C-2}''$	$\text{C-3}''$	$\text{C-4}''$	COC^*H_3	C^*OCH_3
Room temperature ^b	149.3 (17)	131.8 (120)	121.6 (147)	141.1 (27)	133.8 (22) 134.6 (18)	126.1	127.3	—	—
24	150.5 (18)	132.9 (118)	122.7 (148)	142.4 (27)	134.8 (25) 135.5 (23)	127.2	128.4	—	—
-60	150.1 (18)	133.1 (118)	122.7 (148)	142.0 (28)	135.0 (22) 135.4 (22)	127.4	128.4	—	—
-75	149.9 (17)	133.1 (118)	122.5 (148)	141.8 (28)	135.0 (22) 135.4 (22)	127.3	128.3	18.8 (279)	174.8 (234)
-90	149.8 (17)	133.1 (118)	122.5 (148)	141.7 (28)	135.1 (23) 135.4 (23)	127.3	128.3	18.8 (280)	174.9 (235)

^aChemical shifts in ppm relative to TMS. Values in parentheses beneath are $J(\text{Tl}-^{13}\text{C})$ coupling constants in Hertz.

^bFrom ref. 6.

relative to the N_4 plane to the planes approximately parallel to it.

EXPERIMENTAL

Dynamic NMR spectroscopy

Proton and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer in dichloromethane- d_2 , locked on solvent deuterium, and referenced to

the residual solvent peak. The temperature of the spectrometer probe was calibrated by the shift difference of methanol resonance in the ^1H NMR spectrum.

Preparation of $\text{Tl}(\text{tpp})(\text{OAc})$

$\text{Tl}(\text{tpp})(\text{OAc})$ was prepared as described elsewhere.^{5,9} It was dissolved in CD_2Cl_2 to give a concentration of 0.05 M for the NMR measurement.

Table 2. Proton chemical shifts (δ) and thallium-proton coupling constant J in Hertz for the $\text{Tl}(\text{tpp})(\text{OAc})$ complex in CD_2Cl_2 in the absence of the axial ligand^a

Temperature ($^{\circ}\text{C}$)	$\text{H}_\beta(\beta\text{-pyrrole})$	<i>o</i> -phenyl	<i>m,p</i> -phenyl
Room temperature ^b	9.02 (64 Hz)	8.31, 8.08	7.73
24	9.07 (63 Hz)	8.35, 8.18	7.82
-90	9.20 (64 Hz)	8.38, 8.25	7.88

^aChemical shifts in ppm relative to TMS. Values in parentheses beneath are $J(\text{Tl}-\text{H})$ coupling constants in Hertz.

^bFrom ref. 5.

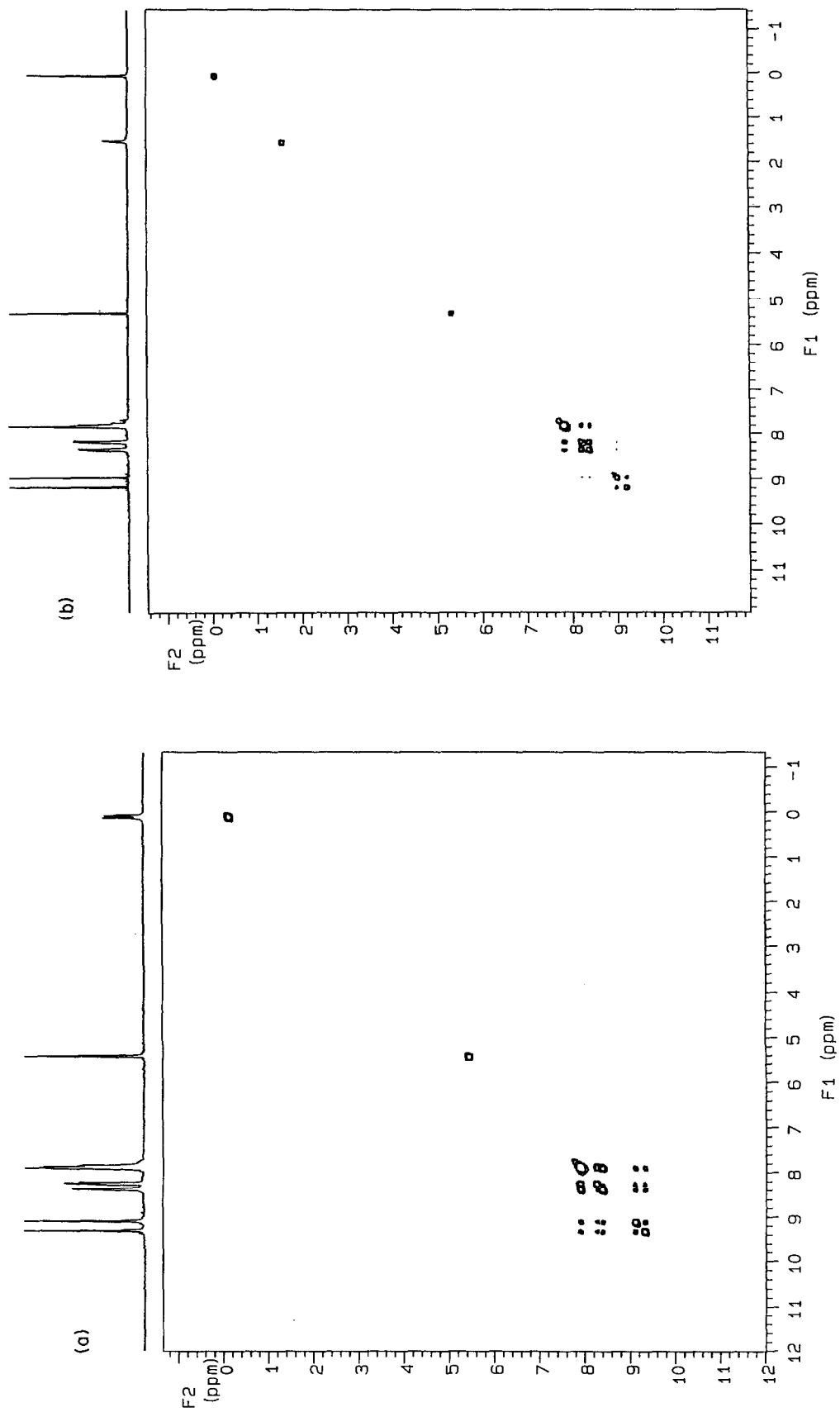


Fig. 4. ²H NOESY spectra for Ti(tpp)(OAc) in CD₂Cl₂ at temperatures of (a) -90°C and (b) 24°C.

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