Thallium complexes of tetraphenylporphyrin: Tl(tpp-N-O)(OAc) and cis-acetato-N-p-tert-butylbenzensulfonylimido-meso-tetraphenylporphyrinatothallium(III) Tl(N-p-NSO₂C₆H₄'Bu-tpp)(OAc)

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Abstract

The crystal structures of Tl(tpp-N-O)(OAc) (3) and acetato-N-p-tert-butylbenzensulfonylimido-meso-tetraphenylporphyrinatothallium(III) Tl(N-p-NSO₂C₆H₄'Bu-tpp)(OAc) (5) have been determined. The coordination sphere around Tl³⁺ is a distorted square-based pyramid in which the apical site is occupied by a bidentate chelating OAc/C₀ group for 3 and 5. The plane of three pyrrole nitrogen atoms (i.e., N(1), N(2) and N(3)), strongly bonded to Tl³⁺ in 3 and 5, is adopted as a reference plane, 3N. The porphyrin ring is severely distorted and the pyrrole ring N(4) bonding to the oxygen and NSO₂C₆H₄'Bu group makes a dihedral angle of 46.5° and 46.7° with the 3N plane for 3 and 5, respectively. In 3, Tl³⁺ and O(1) are located on the same side at 1.11 and 1.34 Å from its 3N plane, and in 5, Tl³⁺ and N(5) are also located on the same side at 1.15 and 1.30 Å from its 3N plane. The free energy of activation at the coalescence Tc for the intermolecular acetate exchange process of 3 and 5 in CD₂Cl₂ is found to be ΔG₁₉₄ = 39.3 kJ/mol and ΔG₂⁰₈ = 44.1 kJ/mol, respectively, through ¹H NMR variable temperature measurements.

An electronegative substituent, O(1), bonded to Tl in 3 causes a significant negative contribution up to 145 Hz for Δ¹J(Tl-C, O) and 79 Hz for Δ¹J(Tl-C, O) for OAc⁻ in 3.

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Keywords: Thallium; X-ray diffraction; N-oxide; Torsion angle; Dynamic NMR

1. Introduction

Metalloporphyrins with a bridged structure between the central metal and one of the four pyrrole nitrogens have drawn much attention in recent times and so far bridged metalloporphyrins with a metal–O–N linkage (metal = Ni [1]), metal–N–N linkage (metal = Zn [2–4], Ni [5,6], Fe [3,7], Ti [5,8,9], Ga [8,9]) and metal–C–N linkage (metal = Fe [10]) have been reported. Balch and coworkers reported that the insertion of nickel(II) into H₃(OEP-N-O) (OEP = dianion of octaethylporphyrin) produced the complex Ni(OEP-N-O) (1), in which the metal ions are bound to a nearly planar set of three nitrogen atoms and one oxygen atom [1,11]. Upon replacing OEP²⁻ with tpp²⁻ (tpp = dianion of meso-tetraphenylporphyrin), the
complex 1 became Ni(tpp-N-O) (2) [12]. However, until now there has been no X-ray structural data available for the diamagnetic and bridged metal [M(III)] porphyrin complexes with an oxygen atom being inserted between one metal–N unit and with a coordination number (CN) above 4 (i.e., with CN ≥ 5).

In order to investigate the range of metal ions that can be inserted into H₂(tpp-N-O), we present the results upon replacing Ni(II) with Tl(III) in Ni(tpp-N-O) (2) forming a new complex Tl(tpp-N-O)(OAc) (3). This replacement increases the coordination number (CN) from four for 2 to six for Tl(tpp-N-O)(OAc) (3). The presence of acetate ligands in 3 plays a potential role in increasing the coordination number.

In order to figure out the structural features of oxygen and nitrogen inserted into the Tl–N bond, we also describe the synthesis and X-ray structural investigation on the metallation of 21-(4-tert-butyl-benzensulfonamido)-5,10,15,20-tetraphenylporphyrin [N-p-HNSO₂C₆H₄tBu-Htpp (4)], leading to the mononuclear complex cis-acetato-N-p-tert-butylbenzensulfonylimido-meso-tetraphenylporphyrinatothallium(III) Tl(N-p-NSO₂C₆H₄tBu-tpp)(OAc) (5). Because of the large size of Tl³⁺ (r离子 = 1.025 Å) [13] the relative position of acetate and the 4-tert-butylbenzensulfonyl ('BuBS) group coordinated to the Tl atom might lead to a cis configuration in 5 [5,8,9]. Prompted by earlier studies on the acetato exchange of Tl(tpp)(OAc) and Tl(N-NTs-tpp)-(OAc) in CD₂Cl₂ (NTs = tosylimido) [8,14,15], we investigated a similar intermolecular acetato exchange for 3 and 5 in CD₂Cl₂ by ¹H and ¹³C dynamic NMR methods. Thallium shows rich coupling patterns to the nuclei of the porphyrin core and to the porphyrin substituents and axial ligands. Many long-range Tl–C and Tl–H couplings to the porphyrin substituents and to the axial ligands are observed [16,17]. Moreover, there is no precedence in the literature that the magnitude of two- and three-bond thallium–carbon spin–spin coupling constants between the Tl atom and the OAc⁻ group of 3 and 5 depends on the electronegative substituents X (i.e., X = O in 3 and N in 5) attached to the thallium atom. Thus, the electronegative dependence of spin–spin coupling constants nJ(Tl–¹³C) (n = 2, 3) for the OAc⁻ ligand of 3 and 5 will be studied for the first time in the chemistry of thallium porphyrins. The compound 3 is the first thallium porphyrin complex with a Tl–O–N(Por) linkage and 5 represents the fourth thallium complex with a Tl–N(R)–N(Por) linkage reported in the literature [5,8,9].

2. Experimental

2.1. Tl((pp-N-O))(OAc) (3)

A mixture of H₂(tpp-N-O) (0.063 g, 0.1 mmol) in CH₂Cl₂ (20 cm³) and Tl(OAc)₃ (0.08 g, 0.2 mmol) in MeOH (10 cm³) was refluxed for 3 h (Scheme 1) [12]. After concentrating, the residue was redissolved in CH₂Cl₂, dried with anhydrous Na₂SO₄, and filtered. The filtrate was concentrated and recrystallized from CH₂Cl₂–MeOH [1:2 (v/v)] yielding the blue solid of 3 (0.062 g, 7 × 10⁻² mmol, 70%). Compound 3 was dissolved in toluene to crystallize out as blue crystals for single-crystal X-ray analysis. ¹H NMR (599.95 MHz, CDCl₃, 20 °C): δ 9.18 [dd, 2H, H₄]
2.2. $\text{TI}(N\text{-p-NSO}_2\text{C}_6\text{H}_4\text{Bu}-\text{tpp})(\text{OAc})$ (5)

A mixture of $\text{TI(OAc)}_3$ (0.05 g, 1.31 $\times$ 10$^{-4}$ mol) in MeOH (20 cm$^3$) and $\text{N}_2\text{p-NSO}_2\text{C}_6\text{H}_4\text{H}_3\text{Bu}-\text{tpp}$ (0.05 g, 6.06 $\times$ 10$^{-5}$ mol) in $\text{CH}_2\text{Cl}_2$ (50 cm$^3$) was refluxed for 3 h (Scheme 1) [9]. After concentrating, the residue was dissolved in $\text{CH}_2\text{Cl}_2$, dried with anhydrous Na$_2$SO$_4$, and filtered. The filtrate was concentrated and recrystallized from $\text{CH}_2\text{Cl}_2$–MeOH [1:3 (v/v)] yielding the bluish-purple solid of 5 (0.046 g, 4.23 $\times$ 10$^{-5}$ mol) which was then dissolved in $\text{CH}_2\text{Cl}_2$ and layered with MeOH to get purple crystals for single crystal X-ray analysis. $^1\text{H}$ NMR (299.95 MHz, $\text{CD}_2\text{Cl}_2$, 20 °C): $\delta$ 9.05 [dd, 2H, $\text{H}_b$ (10, 19), $^3\text{J}(\text{TI–H}) = 17.1$ Hz and $^3\text{J}(\text{H–H}) = 4.8$ Hz]; 8.92 [dd, 2H, $\text{H}_b$ (9, 20), $^4\text{J}(\text{TI–H}) = 10.4$ Hz and $^3\text{J}(\text{H–H}) = 4.8$ Hz]; 8.69 [dd, 2H, $\text{H}_b$ (4, 5), $^4\text{J}(\text{TI–H}) = 76.5$ Hz]; 8.38 [dd, 2H, $^3\text{J}(\text{H–H}) = 7$ Hz] and 8.10 [dd, 2H, $^3\text{J}(\text{H–H}) = 7$ Hz] for ortho protons; 7.85–7.76 (m, 12H, for meta and para protons); 7.07 [dd, 2H, $^1\text{BuBS}_3\text{H}_5$ or $\text{H}$(49, 51), $^3\text{J}(\text{H–H}) = 8$ Hz]; 6.94 [s, 2H, $\text{H}_b$ (14, 15)], 6.09 [dd, 2H, $^1\text{BuBS}_2\_8$ or H (48, 52), $^3\text{J}(\text{H–H}) = 8$ Hz]; 1.15 (s, 9H, tert-butyl protons); 0.62 (s, 3H, OAc). ESI–MS, m/z (assignment, rel. intensity): 154 ([NBA + H]$^+$, 100), 614 ([H$_2$tpp]$^+$, 36.31), 630 ([H$_2$tpp-N$^-$O]$^+$, 40.13), 631 ([H$_2$tpp-N$^-$O + H]$^+$, 42.67), 833 ([Tl(tpp-N-O)]$^+$, 64.31), UV/Vis spectrum, $\lambda_{max}$ [cm$^{-1}$ (M$^{-1}$ cm$^{-1}$)] in $\text{CH}_2\text{Cl}_2$: 333.2 (17.1), 477.2 (173.0), 584.4 (9.1), 626.0 (10.9).

2.3. Spectroscopy

Proton and $^{13}$C NMR spectra were recorded at 299.95 (or 599.95) and 75.43 (or 150.87) MHz, respectively, on Varian VXR-300 (or Varian Unity Inova-600) spectrometers locked on deuterated solvent, and referenced to the solvent peak. Proton NMR is relative to $\text{CD}_2\text{Cl}_2$ or $\text{CDCl}_3$ at $\delta$ = 5.30 or 7.24 and $^{13}$C NMR to the center line of $\text{CD}_2\text{Cl}_2$ or $\text{CDCl}_3$ at $\delta$ = 53.6 or 77.0. HMOC (heteronuclear multiple quantum coherence) was used to correlate protons and carbon through one-bond coupling and HMBC (heteronuclear multiple bond coherence) for two- and three-bond proton–carbon coupling. Nuclear Overhauser effect (NOE) difference spectroscopy was employed to determine the $^1\text{H}$$-^1\text{H}$ proximity through space over a distance of up to about 4 À.

Positive ion mode ESI mass spectra were acquired at room temperature on a ThermoFinnigan LCQ Advantage mass spectrometer. The positive-ion fast atom bombardment mass spectrum (FAB MS) was obtained in a nitrobenzyl alcohol (NBA) matrix using a JEOL JMS-SX/SX 102A mass spectrometer. UV/Vis spectra were recorded at 20 °C on a HITACHI U-3210 spectrophotometer.

Table 1 presents the crystal data as well as other information for 3 and 5. Measurements for 3 were taken on a Nonius Kappa CCD diffractometer using monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.71073 À) at a temperature of 100(1) K. Measurements for 5 were taken on a Bruker AXS SMART-1000 diffractometer using monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.71073 À) at a temperature of 100(2) K. Multi-scan absorption corrections were made for 3 and empirical absorption corrections were made for 5. The structures were solved by direct methods (SHELXL-97) [18] and refined by the full-matrix least-squares method. The OAc group within 3 is disordered with an occupancy factor of 0.6 for O(2)O(3)(C4)(C45) and 0.4 for O(2)O(3)(C45)(C46). These four atoms (i.e., O(2), O(3), C(45) and C(46)) were refined with isotropic displacement parameters. All non-hydrogen atoms, except the

Table 1

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<th>Crystal data for 3 - $\text{CH}_2\text{Cl}_2$ and 5</th>
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<tr>
<td>$R_p$</td>
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<td>$wR_2$</td>
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$^a$ $R_p = |\sum F_O | - |\sum F_E | / |\sum F_O |$; $^b$ $wR_2 = (\sum [w(F^2_O - F^2_E)^2] / \sum [w(F^2_E)^2])^{1/2}$.
above four atoms, were refined with anisotropic thermal parameters, whereas all hydrogen atoms were placed in calculated positions and refined with a riding model. Table 2 lists selected bond distances and bond angles for complexes 3 and 5.

3. Results and discussion

3.1. Molecular structures of 3 and 5

The X-ray molecules are depicted in Fig. 1a for the complex Tl(tpp-N-O)(OAc) (3) and in Fig. 1b for Tl(N-p-NSO₂C₆H₄t-Bu-tpp)(OAc) (5). The complex 3 co-recrystallizes with 1 equiv. of CH₂Cl₂ solvent molecule in the triclinic space group P1, and complex 5 recrystallizes in the monoclinic space group P2₁/n. In both 3 and 5, it is obvious that the oxygen and NSO₂C₆H₄t-Bu moieties have been inserted into the Tl–N bond of acetato(meso-tetraphenylporphyrinato)thallium(III) Tl(tpp)(OAc) (see Scheme 1) [15].

The metal–ligand bond distances and the bond angles are summarized in Table 2. The bond distance (Å) are Tl–O(2) = 2.357(9), Tl–O(3) = 2.348(8) and Tl–O(1) = 2.126(4) and the mean Tl–N(p) = 2.264(4) for 3; for 5 the values are Tl(1)–O(1) = 2.337(2) and Tl(1)–O(2) = 2.350(2) and the mean Tl(1)–N(p) = 2.241(2). Since the acetate of 3 was disordered, data reported involving O(2) and O(3) refer to the acetate at the higher occupancy factor of 0.6.

The geometry around Tl³⁺ is described as a distorted square-based pyramid in which the apical site is occupied by a bidentate chelating OAc⁻ group for 3 and 5. Fig. 2 shows the actual porphyrin skeleton of 3 and 5. The pyrrole nitrogens N(4) (in 3 and 5) are no longer bonded to the thallium as indicated by their longer internuclear distances, 2.831(4) Å for N(4)–Tl(1) (in 3) and 2.899(2) Å for N(4)–Tl(1) (in 5). The plane of three strongly bound pyrrole nitrogen atoms (i.e., N(1)–N(3) for 3 and 5) is adopted as a reference plane 3N. It is noted that the ionic radius increases from 0.63 Å for Ni²⁺ to 1.025 Å for Tl³⁺ [1,13]. Because of the larger size of Tl³⁺, Tl and O(1) lie 1.11 Å and 1.34 Å, respectively, above the 3N plane in 3, compared to 1.15 Å for Tl(1) and 1.30 Å for N(5) in 5 (cf. 0.05 Å for Ni(II) in Ni(OEP-N-O)) (Fig. 2) [1].

### Table 2

Selected bond distances (Å) and bond angles (°) for compounds 3·CH₂Cl₂ and 5

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<th>Bond lengths</th>
<th>3·CH₂Cl₂</th>
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<td>Tl–O(2)</td>
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<td>Tl–O(3)</td>
<td>2.348(8)</td>
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<th>Bond angles</th>
<th>3·CH₂Cl₂</th>
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<td>O(2)–Tl–O(3)</td>
<td>55.2(4)</td>
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<tr>
<td>O(2)–Tl–N(1)</td>
<td>92.6(3)</td>
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</tr>
<tr>
<td>O(2)–Tl–N(2)</td>
<td>100.0(3)</td>
<td></td>
</tr>
<tr>
<td>O(2)–Tl–N(3)</td>
<td>145.9(3)</td>
<td></td>
</tr>
<tr>
<td>O(2)–Tl–O(1)</td>
<td>103.1(2)</td>
<td></td>
</tr>
<tr>
<td>N(1)–Tl–O(1)</td>
<td>87.51(14)</td>
<td></td>
</tr>
<tr>
<td>N(1)–Tl–N(2)</td>
<td>83.41(16)</td>
<td></td>
</tr>
<tr>
<td>N(3)–Tl–N(2)</td>
<td>81.53(16)</td>
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The porphyrin macrocycle is indeed distorted because of the presence of the oxygen [O(1)] and the NSO$_2$C$_6$H$_4$tBu group in 3 and 5, respectively (Fig. 2). Thus, N(4) in the 3 and 5 pyrrole rings bearing the oxygen and the NSO$_2$C$_6$H$_4$tBu group is deviated most from the 3N plane and oriented separately with a dihedral angle of 47.3° and of 46.7°, whereas small angles of 7.0°, 13.1° and 9.0° occur with N(1), N(2) and N(3) pyrroles for compound 3 and 6.8°, 10.8° and 7.9° with N(1), N(2) and N(3) pyrroles for compound 5. The dihedral angles between the mean plane of the skeleton (3N) and the plane of the phenyl group are 49.8° [C(24)], 53.1° [C(30)], 44.7° [C(36)] and 44.0° [C(42)] for 3 and the corresponding angles are 49.4°, 57.4°, 45.0° and 53.1° for 5.

Table 3 contains some comparative data. The N(4)=O(1) distance of 1.369(5) Å in 3 is comparable to that in Ni(II)-OEP-N(O) [1.363(6) Å] [1]. The trans O(1)-Tl-N(2) and N(1)-Tl-N(3) angles [155.45(16)° and 121.28(15)°] in 3 and the corresponding N(5)-Tl-1-N(2) and N(1)-Tl(1)-N(3) angles [151.74(9)° and 118.84(8)°] in 5 indicate that both complexes are severely distorted from linearity.

In compound 3, such a large deviation from planarity for the N(4) pyrrole is also reflected by observing a 19–22 ppm upfield shift of the C$_\beta$ (C17, C18) at 112.9 ppm compared to 135.2 ppm for C$_\beta$ (C2, C13), 133.7 ppm for C$_\beta$ (C3, C12) and 131.8 ppm for C$_\beta$ (C7, C8). In compound 5, a similar deviation is also found for the N(4) pyrrole by observing a 16–21 ppm upfield shift of the C$_\beta$ (C14, C15) at 115.7 ppm compared to 136.4 for C$_\beta$ (C10, C19), 133.7 ppm for C$_\beta$ (C9, C20) and 132.2 ppm for C$_\beta$ (C4, C5). Similarly, the non-planarity of the porphyrins causing upfield shifts of C$_\beta$ resonances were also observed with a magnitude of 16–21 ppm for Tl(N-NTs-tpp)(OAc) [8].

### 3.2. $^1$H and $^{13}$C NMR for 3 and 5 in CD$_2$Cl$_2$ and CDCl$_3$

Complexes 3 and 5 were characterized by $^1$H (Fig. 3) and $^{13}$C NMR analysis. In solution, the molecules have effective C$_s$ symmetry with a mirror plane running through the N(2)-Tl-O(1)-N(4) unit for 3 and the N(2)-Tl(1)-N(4)-N(5) unit for 5. There are four distinct $\beta$-pyrrole protons H$_\beta$, four $\beta$-pyrrole carbons C$_\beta$, four $\alpha$-pyrrole carbons C$_\alpha$, two different meso carbons C$_{meso}$ and two phenyl-C$_1$ carbons for both the complexes.

The NMR study of 3 showed four different types of Tl–H coupling constants for H$_\beta$ in CD$_2$Cl$_2$ at 20 °C (Fig. 3a). The doublet at 8.70 ppm is due to H$_\beta$ (7, 8) with $^3$J(Tl–H) = 78 Hz and the singlet at 6.64 ppm is due to H$_\beta$ (17, 18). The doublet of a doublets at 9.18 ppm is due to H$_\beta$ (2, 13) with $^3$J(Tl–H) = 14 Hz and $^3$J(H–H) = 4.2 Hz and the doublet of a doublets at 8.93 ppm is due to H$_\beta$ (5, 14).


(3, 12) with $^4J(^{203}Tl-H) = 20$ Hz and $^3J(H-H) = 4.2$ Hz. Likewise, there were also four different types of $^{13}C$-Tl coupling constants for C$_\beta$ 3 in CD$_2$Cl$_2$ at 20 °C. The doublet at 131.8 ppm is due to C$_\beta$ (C7, C8) with $^3J(^{13}C-^{203}Tl) = 156$ Hz and the singlet at 133.7 ppm is due to C$_\beta$ (C3, C12). The doublet at 135.2 ppm is due to C$_\beta$ (C2, C13) with $^3J(^{13}C-^{203}Tl) = 44$ Hz and the doublet at 112.9 ppm is due to C$_\beta$ (C17, C18) with $^3J(^{13}C-^{203}Tl) = 80$ Hz.

The NMR study of 5 showed four different types of $^{1}H$-Tl coupling constants for H$_\beta$ in CD$_2$Cl$_2$ at 20 °C. The doublet at 8.69 ppm is assigned as H$_\beta$ (4, 5) with $^4J(1H-^{203}Tl) = 76.5$ Hz and the singlet at 6.94 ppm is due to H$_\beta$ (14, 15). The doublet of a doublet at 9.05 ppm is due to H$_\beta$ (10, 19) with $^4J(^{203}Tl-H) = 17.1$ Hz and $^3J(H-H) = 4.8$ Hz and the doublet of a doublet at 8.92 ppm is due to H$_\beta$ (9, 20) with $^3J(^{203}Tl-H) = 10.4$ Hz and $^3J(H-H) = 4.8$ Hz. Likewise, there were also four different types of $^{13}C$-Tl coupling constants for C$_\beta$ 5 in CD$_2$Cl$_2$ at 20 °C. The doublet at 132.2 ppm is due to C$_\beta$ (C4, C5) with $^3J(^{13}C-^{203}Tl) = 165$ Hz and the doublet at 136.4 ppm is due to C$_\beta$ (C10, C19) with $^3J(^{13}C-^{203}Tl) = 37$ Hz. The singlet at 133.7 ppm supposedly due to C$_\beta$ (C9, C20) with $^3J(^{13}C-^{203}Tl)$ is not observed and the doublet at 115.7 ppm is due to C$_\beta$ (C14, C15) with $^3J(^{13}C-^{203}Tl) = 78$ Hz. The $^1H$ NMR spectra reveal that the aromatic protons of the 'BuBS group appear as a doublet at 6.94 ppm (‘BuBS-H$_3$) and a doublet at 6.09 ppm (‘BuBS-H$_2$) for 5. Due to the porphyrin ring current effect, all NSO$_2$C$_6$H$_4$Bu and acetato protons are shifted upfield compared to their counterparts in free NSO$_2$C$_6$H$_4$Bu and OAc$^-$. The above ring current effect indicates that both the NSO$_2$C$_6$H$_4$Bu and acetate ligands are bonded to Tl in 5 in the solution phase.

The interpretation of these data was confirmed by NOE difference spectroscopy for 3 in CD$_2$Cl$_2$ at 20 °C (Fig. 3a). At 20 °C, this rotation is extremely slow. Hence, the rate of intramolecular exchange of the ortho protons for 3 in CD$_2$Cl$_2$ is also extremely slow. The singlet at 8.85 ppm is assigned to ortho protons o-H (38, 40) (Fig. 3b). The other singlet at 8.05 ppm is due to ortho protons o-H (34, 44) and has been found at 20 °C (Fig. 3a). At −90 °C, this rotation is extremely slow. Hence, the rate of intramolecular exchange of the ortho protons for 3 in CD$_2$Cl$_2$ is also extremely slow. The singlet at 8.55 ppm is assigned to ortho protons o-H (38, 40) (Fig. 3b).

In a similar way, the meta and para protons appearing as multiplet (7.76–7.84 ppm) at 20 °C (Fig. 3a) changed to 7.94 [t, m'-H (37, 41)], 7.86 [t, m-H (25, 29)], 7.82 [m, m'-H (35, 43)], 7.81 [m, p'-H (36, 42)] and 7.80 [m, m-H (23, 31) and p-H (24, 30)] ppm at −90 °C (Fig. 3b).

In a similar fashion, the rotation for the phenyl group of 5 in CD$_2$Cl$_2$ at 20 °C along the C(2)–C(21) or C(7)–C(27) bond is slow and that rotation along C(12)–C(33) or C(17)–C(39) is at the intermediate region. Hence, the $^1H$ resonances for the ortho protons of 5 were observed with two sets of doublets: one doublet at 8.38 ppm is assigned...
to ortho protons o-H (26, 28) with $^3J$(H–H) = 7 Hz and the other doublet at 8.10 ppm is due to ortho protons o-H (22, 32) with $^3J$(H–H) = 7 Hz. Moreover, no signals of o’-H (38, 40) and o’-H (34, 44) of 5 have been detected at 20 °C.

3.3. Dynamic NMR of 3 and 5 in CD$_2$Cl$_2$

Upon cooling of a 0.02 M CD$_2$Cl$_2$ solution of 3, the methyl proton signal of OAc$^-$, being a single peak at 20 °C ($\delta = 0.45$ ppm), first broadened (coalescence temperature $T_c = -89$ °C) and then split into two peaks with a separation of 12 Hz at $\delta = 0.35$ ppm at -100 °C. As the exchange of OAc$^-$ within 3 is reversible, the results at 599.95 MHz confirm the separation as a coupling of $^4J$(Tl–H) rather than a chemical shift difference. The most likely cause of loss of coupling is due to the reversible dissociation of acetate with a small dissociation constant.

$$\text{OAc}^- + \text{CD}_2\text{Cl}_2 \rightarrow \text{Tl(tpp-N-O)}^+ + \text{OAc}^- \quad (1)$$

Such a scenario would lead to the change in the chemical shift with temperature and no detectable free OAc$^-$ and Tl(tpp-N-O)$^+$ at low temperature, but would lead to the loss of coupling between acetate and thallium at higher temperature [20]. The chemical shift in the high-temperature limit is the average of the two species (i.e., Tl(tpp-N-O)(OAc) and OAc$^-$) in Eq. (1) weighted by their concentration. The free energy of activation $\Delta G^\text{184}$ = 39.3 kJ/mol is therefore determined for the intermolecular exchange of OAc$^-$ in 3. The free energy of activation at the coalescence temperature $T_c$ for a similar OAc$^-$ exchange of 5 in CD$_2$Cl$_2$ is determined to be $\Delta G^\text{285}$ = 44.1 kJ/mol. At 20 °C, intermolecular exchange of the OAc$^-$ group for 3 is rapid as indicated by the appearance of singlet signals due to carbonyl carbons at 175.8 ppm and methyl carbons at 18.9 ppm. At -100 °C, the rate of intermolecular exchange of OAc$^-$ for 3 in CD$_2$Cl$_2$ is slow. Hence, at this temperature, the methyl and carbonyl carbons of OAc$^-$ are observed at $\delta = 18.5$ ppm [with $^3J$(Tl–C) = 135 Hz] and 176.0 ppm [with $^2J$(Tl–C) = 156 Hz] as doublets, respectively. These $^{13}$C resonances are quite close to that of 5 in which the two corresponding carbons were observed in CD$_2$Cl$_2$ at $\delta = 18.6$ ppm [with $^3J$(Tl–C) = 221 Hz] and 176.4 ppm [with $^2J$(Tl–C) = 205 Hz] as doublets at -90 °C, but with different $^2J$(Tl–C) coupling constants. The bulky ‘Bu group in 5 increases the free energy of activation for the intermolecular OAc$^-$ exchange in CD$_2$Cl$_2$ from $\Delta G^\text{171} = 36.0$ kJ/mol for Tl(N-NTs-tpp)(OAc) to $\Delta G^\text{208} = 44.1$ kJ/mol for 5 [8].

3.4. O(1) and N(5) atoms connected to α-thallium

The effect of a different electronegative atom O(1) [or N(5)] attached to the thallium(III) in 3 (or 5) on $^2J$(Tl–C) and $^3J$(Tl–C) of the OAc$^-$ ligand was studied. The importance of the thallium carbon coupling comes mainly from the Karplus-type dependence of $^3J$(Tl–C) on the torsion angle $\Phi$(Tl–O–P–C$^-$) [21–23]. Hence, the complexity of the $^3J$(Tl–C) coupling is primarily due to the angular dependence on $\Phi$ and also due to the substituent effects arising from the nature, position and orientation. The substituents (X) bonded to the coupled Tl atoms induce an additional angular dependence on the torsion angle $\Psi$(X–C–Tl–X) = $^\nu$(Tl–C, X)$^\nu$(Tl–C, P), where $^\nu$(Tl–C, X) and $^\nu$(Tl–C, P) are the $^\nu$(Tl–C) coupling for the X-monosubstituted Tl(tpp)(OAc) and for the parent molecule of Tl(tp)(OAc), respectively [21]. In Table 4, the coupling constants from our study and the published ones for thallium porphyrin derivatives are provided for a comparison of the experimental $^\Delta^\nu J$(Tl–C, X) values [5,8,14]. A maximum positive contribution to $^\Delta^\nu J$(Tl–C, X) is expected in the transoid arrangement ($\Phi = 180^\circ$ and $\Psi = 180^\circ$). The absolute values of $\Phi$ and $\Psi$ are observed to be approximately constant around 180° and 80.1 6.8° for complexes 3, 5 and their homologue, respectively (Table 4), therefore the magnitude of $^\Delta^\nu J$(Tl–C) in the system X–Tl(O–P–C$^-$) shows a strong dependence on the electronegativity (\(\chi\)) of the substituent X. A large negative value of $^\Delta^\nu J$(Tl–C, O) = -145 Hz is observed for 3 while a small negative values of $^\Delta^\nu J$(Tl–C, N) = -57 ± 3 Hz are assessed for 5, 6 and 7 (Table 4) [5,8]. Likewise, the magnitude of the geminal thallium–carbon coupling constant, $^2J$(Tl–C), for the OAc$^-$ of 3 and 5 in the system X–Tl(O–P–C$^-$) depends on the electronegativity (\(\chi\)) of the substituent X (Table 4). Experimentally, a large negative value of $^\Delta^\nu J$(Tl–C, O) = -79 Hz is observed for 3 while a small negative value of $^\Delta^\nu J$(Tl–C, N) = -28 ± 3 Hz is calculated for 5, 6 and 7 (Table 4) [5,8]. Owing to the magnitude of $^\Delta^\nu J$(Tl–C, X) (n = 2, 3) increasing with increasing electronegativity of X, the smaller electronegativity of N(5)–SO$_2$C$_6$H$_4$/Bu (with \(\chi[N(5)] = 2.98\)) for 5 than the O(1) atom (with \(\chi[O(1)] = 3.44\)) for 3 [24,25] results in the magnitude of $|^\Delta^\nu J$(Tl–C, N)| = 59 Hz in 5 being smaller than that of $|^\Delta^\nu J$(Tl–C, O)| = 145 Hz in 3 (Table 4). In a similar case, the absolute value of $|^\Delta^\nu J$(Tl–C, N)| = 30 Hz in 5 is smaller than that of $|^\Delta^\nu J$(Tl–C, O)| = 79 Hz in 3 (Table 4).

4. Conclusions

We have investigated two new diamagnetic and mononuclear thallium(III) porphyrin complexes 3 and 5 and their X-ray structures are established. NOE difference spectroscopies, HMQC and HMBC were employed for the unambiguous assignment of the $^1$H and $^{13}$C NMR resonances of 3 and 5 in CDCl$_3$ at 20 °C and in CD$_2$Cl$_2$ at 20 and -90 °C. In brief, the electronegativity ($\chi$) of the X atom attached to the α-thallium nucleus correlates to the
magnitude of the $\Delta^{3,5}J$ (Ti-C, X) coupling for the Ti(O$_2$CCH$_3$)$_2$ fragment in the thallium porphyrin system. The two compounds, despite different electronic and steric properties for O(1) in 3, and for the N-imido-benzensulfonyl group in 5, the structural deformations occurring in the tetrapyrrole macrocycles are similar.

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Appendix A. Supplementary data

Fig. S1 shows the $_1^H$ NMR spectrum of 5 in CD$_2$Cl$_2$ at 20 °C. Figs. S2 and S3 show the HMQC and HMBC spectra of 3 in CD$_2$Cl$_2$ at 20 °C. CCDC 288278 (for 3) and CCDC 261305 (for 5) contain the supplementary crystallographic data for this paper. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK on request (fax: +44 1223 336 033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.poly.2006.01.020.

References