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Monodentate and bidentate trifluoroacetato ligands in bis(trifluoroacetato)-(N-methyl-meso-tetraphenylporphyrinato)thallium(III)

—a new dynamic 4:3 piano stool seven-coordinate geometry

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Abstract

The crystal structure of bis(trifluoroacetato)-(*N*-methyl-*meso*-tetraphenylporphyrinato) thallium(III), Tl(N–Me–tpp)(CF₃CO₂)₂ (2), was established and the coordination sphere around the Tl³⁺ ion is described as 4:3 tetragonal base–trigonal base piano stool seven-coordinate geometry in which the two *cis* CF₃CO₂⁻ groups occupy two apical sites. The plane of the three pyrrole nitrogen atoms [i.e. N(2), N(3) and N(4)] strongly bonded to Tl³⁺ is adopted as the reference plane 3N. The pyrrole N(1) ring bearing the methyl group [i.e. C(45)H₃] is the most deviated one from the 3N plane making a dihedral angle of 23.3° whereas smaller angles of 9.9, 2.7 and 4.7° occur with pyrroles N(2), N(3), and N(4), respectively. Because of the larger size of the thallium(III) ion, Tl is considerably out of the 3N plane; its displacement of 1.02 Å is in the same direction as that of the two apical CF₃CO₂⁻ groups in **2** are separately located at δ 114.3 [¹*J*(C–F) = 290 Hz, ³*J*(Tl–C) = 411 Hz] and 155.1 [²*J*(C–F) = 37 Hz, ²*J*(Tl–C) = 204 Hz], respectively, at -106 °C. In the same slow-exchange region, the fluorine atoms of **2**, Tl(N–Me–tpp)(CF₃CO₂)⁺ and the free CF₃CO₂⁻ are located at δ -73.76 [⁴*J*(Tl–F) = 44 Hz], -73.30 [⁴*J*(Tl–F) = 22 Hz], and -76.15 ppm at -97 °C, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Piano stool; Intermolecular exchange; Seven-coordinate; Bidentate

1. Introduction

Several first-row transition metal complexes of *N*-substituted porphyrin $M^{II}(N-Me-tpp)Cl$ (M = Zn, Co, Mn, Fe and tpp = 5,10,15,20-tetraphenylporphyrinate) have been extensively studied by Anderson et al. [1–5]. The common feature in all these *N*-substituted metal-loporphyrins is that the metal atom is no longer coplanar with the four nitrogen atoms of the macrocycle and

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coordination geometry around the metal ion is a fivecoordinate distorted square-based pyramid. Iron(III) complexes of *N*-methylporphyrins, e.g. $[Fe^{III}(N-Me$ ttp)(CN)₂], $[Fe^{III}(N-Me-ttp)(5-MeIm)_2]^{2+}$ and $[Fe^{III-}(N-Me-ttmp)Im_2]^{2+}$ (with N-Me-ttp = *N*-methyltetra*p*-tolylporphyrin monoanion, N-Me-ttmp = *N*-methyltetramesitylporphyrin monoanion, Im = imidazole, 5-MeIm = 5-methylimidazole), are known as well [6]. We have recently reported the crystal structure of diacetato(*N* - methyl - *meso* - tetraphenylporphyrinato)thallium-(III), Tl(N-Me-tpp)(OAc)₂ (1), and the coordination sphere around the Tl³⁺ ion is described as an eight-

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co-ordinate square-based antiprism in which the two cis chelating bidentate OAc- groups occupy two apical sites [7]. The acetate and trifluoroacetate ions are known to be highly versatile in binding to metal ions. They can behave as mono- or bidentate donors to a single metal ion or give rise to a variety of more complicated patterns by acting as bridging groups [8]. When the OAc^- of 1 was replaced by a relatively bulkier trifluoroacetate group, CF₃CO₂⁻ the coordination number (CN) decreases from 8 for 1 to 7 for bis(trifluoroacetato) - (N - methyl - meso - tetraphenylporphyrinato)thallium(III), $Tl(N-Me-tpp)(CF_3CO_2)_2$ (2). Seven-coordinate complexes of the metal ion (M(III)) (M = Sc [9], Ti [10], V [11], Cr [12,13], Fe [13,14] and In [15–19]) have also been reported. However, until now there were no X-ray structural data available for M(III) complexes of porphyrin with seven-coordinate geometry and the stereochemistry for seven-coordination is not reported in mononuclear thallium(III) complexes.

Seven-coordinated complexes of tungsten(II) and molybdenum(II) are known to adopt several different stereochemistries [20]: the 1:5:1 D_{5h} pentagonal bipyramidal [21], the 1:4:2 C_{2v} capped trigonal prismatic [22], the 4:3 piano-stool [23,24] and the 1:3:3 C_{3v} capped octahedral geometries. Generally these complexes are stereochemically non-rigid which is a consequence of the small energy difference between different forms and distortions exist from the idealized geometries which can lead to ambiguities whilst describing the structure. The acetato exchange process of 1 prompted us to investigate a similar trifluoroacetato exchange for 2 in CD_2Cl_2 by a ¹³C and ¹⁹F dynamic NMR method [7].

The structures of the two related heptacoordinated complexes $Mo(CO)_2(PMe_3)_2(CF_3CO_2)_2$ [25] and Mo(CO)₂(PEt₃)₂(CF₃CO₂)₂ [26] are similar capped trigonal prismatic geometries. The former contains two monodentate trifluoroacetate ligands whereas the latter contains one monodentate and one bidentate trifluoroacetate groups. No evidence of an intramolecular exchange between the two trifluoroacetate groups is observed for these complexes in dichloromethane at room temperature. Mo(CO)₂(PEt₃)₂(O₂CH)₂ [23] is yet another seven-coordinate d⁴ bis(formato) derivative adopting a 4:3 'piano stool' configuration with one monodentate and one bidentate O₂CH ligands that is fluxional on the NMR time scale. We report herein the preparation, structural characterization and dynamic behavior of an intra- and inter-molecular trifluoroacetate exchange process for a novel seven-coordinate mononuclear thallium(III) complex 2 having a 4:3 geometry with two differently coordinated CF₃CO₂ ligands. To the best of our knowledge, this is the first description of a seven-coordinate thallium N-methyl porphyrin complex with one bidentate and one monodentate coordinated CF₃CO₂ ligand.

2. Experimental

2.1. Preparation of $Tl(N-Me-tpp)(CF_3CO_2)_2$ (2)

The new compound 2 was synthesized by refluxing a mixture of N–Me–Htpp [7,27] (0.15 g, 2.389×10^{-4} mol) in dry CHCl₃ (50 cm³) and Tl(CF₃CO₂)₃ (0.26 g, 4.79×10^{-4} mol) in dry CH₃OH (2 cm³) under N₂ for 30 min. After concentrating, the residue was dissolved in CH₂Cl₂ and collected by filtration to remove any precipitate. The crystals of 2 (0.13 g, 1.23×10^{-4} mol, 86.6%) were grown by removing CH₂Cl₂ and dissolving the residue in dry ether. The crystals were dissolved in CD₂Cl₂ for ¹H and ¹³C NMR measurements. ¹H NMR (600.25 MHz, CD₂Cl₂, 20 °C): δ 9.09 [dd, H_β(8,17), ${}^{4}J(\text{Tl}-\text{H}) = 76 \text{ Hz}, {}^{3}J(\text{H}-\text{H}) = 4.7 \text{ Hz}$, where $H_{\beta}(a,b)$ represents the two equivalent β-pyrrole protons attached to carbons a and b, respectively; 9.09 [dd, $H_{B}(7,18), {}^{4}J(T1-H) = 68 Hz, {}^{3}J(H-H) = 4.7 Hz]; 9.00$ [d, $H_{B}(12,13)$, ${}^{4}J(Tl-H) = 61$ Hz]; 8.73 [d, $H_{B}(2, 3)$, ${}^{4}J(\text{Tl}-\text{H}) = 7.1$ Hz]; 8.53 (s) and 8.24–8.27 (m) for phenyl *ortho* protons (o, o'-H); 7.79–7.94 (m) for phenyl meta, para protons (m-, p-H); -4.31 [d, N–Me, ${}^{3}J(TI-$ H) = 37 Hz] for compound 2. ¹H NMR (600.25 MHz, CD₂Cl₂, -73 °C): δ 9.12 [dd, H₈(8,17), ⁴J(Tl-H) = 75 Hz, ${}^{3}J(H-H) = 4.4$ Hz]; 9.06 [dd, H₈(7,18), ${}^{4}J(T)$ H) = 69 Hz, ${}^{3}J(H-H) = 4.4$ Hz]; 9.03 [d, H₆(12,13), ${}^{4}J(\text{Tl}-\text{H}) = 60 \text{ Hz}]; 8.76 \text{ [d, } H_{B}(2,3), {}^{4}J(\text{Tl}-\text{H}) = 7.2$ Hz]; 8.55 (s) and 8.24-8.28 (m) for phenyl ortho protons (o,o'-H); 7.78-7.95 (m) for phenyl meta, para protons (*m*-, *p*-H); -4.43 [d, N–Me, ${}^{3}J(TI-H) = 37$ Hz] for compound 2; -4.61 [d, N–Me, ${}^{3}J(TI-H) = 21$ Hz] for compound $Tl(N-Me-tpp)(CF_3COO)^+$. ¹³C NMR (150.87 MHz, CD₂Cl₂, 17 °C): δ 157.1 [d, $C_{\alpha}(C1, C4)$, ²J(T1-C) = 90 Hz]; 153.9 [d, $C_{\alpha}(C9, C16)$, ${}^{2}J(\text{Tl}-\text{C}) = 29 \text{ Hz}]; 153.5 \text{ [d, } C_{\alpha}(\text{C11, C14}), {}^{2}J(\text{Tl}-\text{C}) =$ 70 Hz]; 151.9 [d, $C_{\alpha}(C6, C19)$, ${}^{2}J(T1-C) = 17$ Hz]; 141.5 $(d, {}^{4}J(Tl-C) = 42 Hz)$ and 141.3 $(d, {}^{4}J(Tl-C) = 41 Hz)$ for phenyl-C₁; 137.1 (d, ${}^{3}J(TI-C) = 37$ Hz), 136.0 (s), 135.7 (s), 133.4 (s), 133.2 (s), 129.1 (s), 128.5 (s), 128.3 (s), 127.7 (s), 127.2 (s) and 126.9 (s) for phenyl- C_{26} , phenyl-C_{3,5} and phenyl-C4; 134.5 [d, $C_{\beta}(C7, C18)$, ${}^{3}J(TI-C) = 109$ Hz]; 134.4 [d, C_B(C12, C13), ${}^{3}J(TI-$ C) = 111 Hz]; 132.8 [d, C_{β}(C8, C17), ³*J*(T1-C) = 114 Hz]; 129.6 [d, $C_{\beta}(C2, C3)$, ${}^{3}J(T1-C) = 10$ Hz]; 126.8 [d, $C_m(C10, C15), {}^{3}J(T1-C) = 171$ Hz]; 124.9 [d, $C_m(C5, C5)$ C20), ${}^{3}J(TI-C) = 141$ Hz]; 32.1 [s, N-Me, ${}^{2}J(TI-C) =$ 32.1 Hz]; ¹³C NMR (150.87 MHz, CD_2Cl_2 , -106 °C): δ 156.0 [d, C_α(C1, C4), ²J(T1-C) = 89 Hz]; 152.5 [d, $C_{\alpha}(C9, C16), {}^{2}J(T1-C) = 23 Hz]; 152.3 [d, C_{\alpha}(C11, C)]$ C14), ${}^{2}J(TI-C) = 61$ Hz]; 150.1 [s, C_a(C6, C19)]; 140.5 $(d, {}^{4}J(Tl-C) = 40 \text{ Hz})$ and 140.9 $(d, {}^{4}J(Tl-C) = 39 \text{ Hz})$ for phenyl-C₁; 137.1 (d, ${}^{3}J(Tl-C) = 31$ Hz), 136.4 (d, ${}^{3}J(Tl-C) = 34$ Hz), 135.2 (d, ${}^{3}J(Tl-C) = 37$ Hz), 133.3 (s), 128.3 (s), 127.7 (s), 127.6 (s), 127.2 (s), 126.6 (s), 126.3 (s) for phenyl-C_{2.6}, phenyl-C_{3.5} and phenyl-C4;

134.0 [d, $C_{\beta}(C7, C18)$, ${}^{3}J(T1-C) = 107$ Hz]; 133.8 [d, $C_{\beta}(C12, C13)$, ${}^{3}J(T1-C) = 95$ Hz]; 132.0 [d, $C_{\beta}(C8, C17)$, ${}^{3}J(T1-C) = 129$ Hz]; 129.2 [d, $C_{\beta}(C2, C3)$, ${}^{3}J(T1-C) = 8.3$ Hz]; 125.4 [d, $C_{m}(C10, C15)$, ${}^{3}J(T1-C) = 168$ Hz]; 123.9 [d, $C_{m}(C5, C20)$, ${}^{3}J(T1-C) = 134$ Hz]; 30.7 [s, N-Me, ${}^{2}J(T1-C) = 20$ Hz]; 155.1 (m, CF₃COO, ${}^{2}J(C-F) = 37$ Hz and ${}^{2}J(T1-C) = 204$ Hz); 114.3 (m, CF₃COO, ${}^{1}J(C-F) = 290$ Hz and ${}^{3}J(T1-C) = 411$ Hz). MS; m/z (assignment, relative intensity): 1058 ([T1(N-Me-tpp)(CF₃CO₂)]⁺, 1.94), 945 ([T1(N-Me-tpp)](-F, CO)]^{+}, 10.76), 832 ([T1(N-Me-tpp)]^{+}, 10.76), 832 ([

Table 1

Crystal data and structure refinement parameters for $Tl(N-Me-tpp)-(CF_3CO_2)_2 \cdot Et_2O$ (2·Et₂O)

Empirical formula ^a Formula weight Space group Z	$\begin{array}{l} C_{53}H_{41}F_{6}N_{4}O_{5}Tl \ (\textbf{2}{\cdot}Et_{2}O) \\ 1132.27 \\ P\bar{1} \\ 2 \end{array}$
Unit cell dimensions	
a (Å)	9.5350(11)
b (Å)	13.4138(15)
<i>c</i> (Å)	19.308(2)
α (°)	96.865(2)
β (°)	101.223(2)
γ (°)	94.785(2)
$V(Å^3)$	2390.4(4)
$D_{\rm calc} \ ({\rm g \ cm^{-3}})$	1.573
Radiation, λ (Å)	Mo, 0.71073
Temperature (K)	293(2)
Absorption coefficient (mm ⁻¹)	3.454
R ^b (%)	3.61
R _w ^c (%)	11.27
Goodness-of-fit	0.885

^a Including solvate molecules.

^b
$$R = [\Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|].$$

 $^{c}R_{w} = [\Sigma w(||F_{o}| - |F_{c}||)^{2} / \Sigma w(|F_{o}|)^{2}]^{1/2}; w = A/(\sigma^{2}F_{o} + BF_{o}^{2}).$

Table 2

Selected bond distances (Å) and bond angles (°) for compound $2 \cdot \text{Et}_2\text{O}$

Bond lengths			
Tl-N(1)	2.700(4)	Tl-O(1)	2.235(5)
Tl-N(2)	2.276(4)	T1-O(3)	2.462(7)
Tl-N(3)	2.243(4)	Tl-O(4)	2.514(7)
Tl-N(4)	2.278(4)	O(1)-C(46)	1.250(8)
C(46)-C(47)	1.51(1)	O(2)–C(46)	1.220(9)
C(48)-C(49)	1.52(1)	O(3)–C(48)	1.226(9)
		O(4)–C(48)	1.21(1)
Bond angles			
O(3)–T1–O(4)	51.3(2)	O(4)-Tl- $N(1)$	140.2(2)
O(1)–T1–N(1)	75.3(2)	O(4)-Tl-N(2)	83.0(2)
O(1)-Tl-N(2)	101(2)	O(4)-Tl-N(3)	86.5(2)
O(1)–T1–N(3)	165.2(2)	O(4)-Tl-N(4)	144.4(2)
O(1)-Tl-N(4)	109.2(2)	O(2)-C(46)-O(1)	129.7(7)
O(3)–T1–N(1)	153.4(2)	O(3)-C(48)-O(4)	124.5(8)
O(3)-Tl-N(2)	131.4(2)	C(46)-O(1)-T1	115.0(5)
O(3)–T1–N(3)	80.8(2)	C(48)-O(3)-T1	93.0(6)
O(3)-Tl-N(4)	93.8(2)	C(48)-O(4)-T1	91.0(6)

628 ([N–Me–tpp]⁺, 58.24), 627 ([N–Me–tpp–H]⁺, 100.00), 205 (²⁰⁵Tl⁺, 23.22), 203 (²⁰³Tl⁺, 9.63). UV–Vis spectrum: λ (nm) ($\varepsilon \times 10^{-3}$ (M⁻¹ cm⁻¹)] (CHCl₃): 440 (253), 452 (202), 556 (10.8), 601 (14.1), 648 (8.5).

2.2. Spectroscopy

Proton and ¹³C NMR spectra in CD₂Cl₂ (99.6% from Aldrich) were recorded at 299.95 (or 600.25) and 75.43 (or 150.87) MHz, respectively, on Varian VXR-300 (or Varian Unity Inova-600) spectrometers locked on deuteriated solvent and referenced to the solvent peak CD₂Cl₂ at $\delta = 5.30$ (¹H NMR) and the center line of CD_2Cl_2 at $\delta = 53.6$ (¹³C NMR). The ¹⁹F spectra were measured in CD₂Cl₂ at 564.49 MHz in a Varian Unity Inova-600 spectrometer. ¹⁹F NMR data are internally referenced to CFCl₃. The temperature of the spectrometer probe was calibrated by the shift difference of the methanol resonance in the ¹H NMR spectrum. ¹H-¹³C COSY technique was employed to correlate protons and carbon through one-bond coupling and heteronuclear multiple bond coherence (HMBC) for two- and three-bond proton-carbon coupling.

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 24 °C in a Hitachi U-3210 spectrophotometer.

2.3. Crystallography

Table 1 contains the crystal data and other information for Tl(N–Me–tpp)(CF₃CO₂)₂·Et₂O. Measurements were taken in a Siemens SMART CCD diffractometer for **2**·Et₂O using monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). SADABS absorption corrections were made for **2**·Et₂O. The structures were solved by direct methods (SHELXTL PLUS) and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atom positions were calculated using a riding model and were included in the structure factor calculation. Table 2 lists selected bond distances and angles.

3. Results and discussion

3.1. Molecular structure of 2

Fig. 1 illustrates the skeletal framework of complex **2**·Et₂O. It is a seven-coordinate *N*-methylporphyrin complex of the porphyrin N₄ with two oxygen atoms of the chelating bidentate $CF_3CO_2^-$ ligand from first trifluoroacetate [O(3), O(4), C(48), C(49)], and one oxygen



Fig. 1. Molecular configuration and atom-labeling scheme for $Tl(N-Me-tpp)(CF_3CO_2)_2 \cdot Et_2O$ (or $2 \cdot Et_2O$), with ellipsoids drawn at 30% probability. Hydrogen atoms and solvent Et_2O are omitted for clarity. F(1)F(2)F(3) in $2 \cdot Et_2O$ is disordered with an occupancy factor 0.7 for F(1)F(2)F(3) and 0.3 for F(1)F(2')F(3').

atom of the monodentate $CF_3CO_2^-$ ligand from second trifluoroacetate [O(1), O(2), C(46), C(47)]. Visual inspection as well as other stereo drawings suggested that the geometrical configuration around Tl³⁺ could be classified as either a 4:3 piano stool or a highly distorted capped trigonal prism. To determine the stereochemistry of 2, we have utilized the δ parameters of Porai-Koshits and Aslanov [28], as calculated by Muetterties and Guggenberger [29]. Upon viewing 2 as a 4:3 system, [N(1)N(2)N(3)N(4):O(1)O(3)O(4)], the observed angle between the two planes of the ligating atom is 0.6°. Normalization of metal-ligand bond lengths by projecting onto a sphere of unit radius results in an angle (δ_1) of 1.1° between the two planes of the 4:3 geometry (Table 3), nearly identical with the ideal value of 0° [30–33]. With 0° as the criteria both for the angle between the two planes and for the dihedral angle across the diagonal of the quadrilateral face, the corresponding values of 1.1 and 8.4° (Table 3) which characterize 2 indicate the compatibility of the observed structure with the 4:3 tetragonal base-trigonal base geometry. Alternatively, the observed structure of 2 could be described as a highly distorted capped trigonal prismatic arrangement with N(3) capping the quadrilateral face generated by O(3), O(4), N(2), N(4) and the remaining O(1), N(1) atoms being on the unique edge. Comparison of the parameter δ values (76.5, 44.6, 41.5°), to that of the idealized monocapped trigonal prism $(41.5, 0, 0^\circ)$, the geometry is not indicative of the monocapped trigonal prism (Table 3). The δ values listed in Table 3 are strongly suggestive of the observed structure having a 4:3 tetragonal base-trigonal base geometry. Earlier this kind of 4:3 piano stool geometry observed for $Mo(CO)_2(PEt_3)_2(O_2CH)_2$ [23], was $MoBr(O_2CCF_3)(CO)_2(PPh_3)_2$ [24], $W(t-C_4H_9NC)_3$ - $W(CO)_3(S_2CN(CH_3)_2)_2$ $(CO)_{2}I_{2}$ [31], [32] and $W(CO)_2(PPh_3)(S_2CNEt_2)_2$ [33] in the literature. Selected bond distances and angles are summarized in Table 2. The interaction of the first trifluoroacetate ligand with thallium is bidentate chelation. This kind of bidentate interaction was previously observed for Tl(N-Me-tpp) $(OAc)_2$ with Tl(1)-O(1) = 2.517(6) and Tl(1)-O(2) =2.330(6) Å. The second trifluoroacetate oxygen O(2) is 3.167(6) Å distanced from thallium which is considerably longer than that of the Tl-O(1) distance and the ligand's interaction with thallium is classified as monodentate. Hence only three oxygen atoms [i.e. O(1), O(3), O(4)] are coordinated to the thallium atom.

The nitrogen atom bearing the methyl group is much farther from the Tl³⁺ [Tl–N(1) 2.700(4) Å] compared to the other three nitrogen atoms [Tl–N(2) 2.276(4), Tl–N(3) 2.243(4), Tl–N(4) 2.278(4) Å]. Since the Tl–N(1) distance is quite large, the nitrogen atom N(1) is probably not coordinated to the thallium. However, in ¹H NMR [599.95 MHz, Fig. 2(a)] at 20 °C the H_β(2,3) and N–Me protons are observed at 8.73 ppm [with ⁴J(Tl–H) = 7.1 Hz] and at – 4.31 ppm [with ³J(Tl–H) = 70 Hz], respectively. Furthermore, ¹³C NMR data [150.87 MHz] at 17 °C show C_β(C2,C3) and C_α(C1,C4) resonances at 129.5 ppm [with ³J(Tl–C) = 10 Hz] and 157.1 ppm [with ²J(Tl–C) = 90 Hz],

Table 3

Dihedral angle calculations ^a for comparison of molecule **2** with two trial geometries

Trial geometry	Defining planes	δ_i	δ_i Dihedral angles (°)	
			Observed	Idealized
4:3 (piano stool), N(1)N(2)N(3)N(4):O(1)O(3)O(4)	N(1)N(2)N(3)N(4)/O(1)O(3)O(4)	δ_1	1.1	0.0
	N(1)N(3)N(4)/N(1)N(3)N(2)	δ_2	8.4	0.0
1:4:2 (capped trigonal prism), N(3):O(3)O(4)N(2)N(4):O(1)N(1)	O(3)O(4)N(3)/O(3)O(4)O(1)	δ_1	76.5	41.5
	O(3)N(1)N(4)/O(3)N(1)O(1)	δ_2	44.6	0.0
	N(1)O(4)N(2)/N(1)O(4)O(1)	δ_3	41.5	0.0

^a The published coordinates were used to project the structure onto a sphere [30] after which the usual dihedral angles (δ) between planes [29,31] were calculated.



Fig. 2. ¹H (600.25 MHz) NMR spectra for **2** in CD₂Cl₂ showing four different β -pyrrole protons H_{β}, phenyl protons (*o*-H, *m*, *p*-H) and the N–Me protons at: (a) 20 and (b) -73 °C.

respectively. These two results confirm that the thallium–N(1) distance of 2.700(4) Å is long enough, but it does fall within the sum of the van der Waals radii of thallium and nitrogen, ~ 3.55 Å. This longer Tl···N(1) contact is described as a weak (secondary) bond [34– 36]. The Tl–N(1) bond length of 2.700(4) Å for **2** is slightly shorter than the Tl–N bond length of 2.71(3) Å for Tl[Tp^{(CF₃)2}] [37] and 2.74(7) Å for Tl[Tp^{Trip}] [38].

The other three non-alkylated pyrrole nitrogen atoms [N(2), N(3), N(4)] bind strongly to the Tl(III) ion. We adopt the plane of the three strongly bound pyrrole nitrogen atoms [i.e. N(2), N(3), N(4)] as a reference plane 3N. Fig. 3 illustrates the displacement (in Å) of various atoms ($C_{20}N_4$, Tl, N–Me, and $2CF_3CO_2^-$) from the 3N plane. Because of its larger size, the thalliu-

m(III) ion is pushed away from the 3N plane; its displacement of 1.02 Å is in the same direction as that of the two apical CF₃CO₂⁻ ligands [cf. 1.17 Å for Tl(III) in Tl(N–Me–tpp)(OAc)₂] [7]. The two approximately perpendicular trifluoroacetates with an angle of 81.0° are bound *cis* to Tl and lie above the macrocycle making a dihedral angle of 56.2 and 43.0° with the 3N plane for the two trifluoroacetates. The porphyrin macrocycle is indeed distorted (Fig. 3) as a result of the N–Me group. Thus, pyrrole N(1) [i.e. the plane of N(1), C(1)–C(4)] bearing the methyl group [i.e. C(45)H₃] is the most deviated from the 3N plane, making a dihedral angle of 23.3°, whereas smaller angles of 9.9, 2.7 and 4.7° occur with pyrroles N(2), N(3) and N(4), respectively. Such a large deviation from planarity is

also reflected in the NMR data for pyrrole N(1) by observing a 3.2–4.9 ppm upfield shift of $C_{\beta}(C2,C3)$ at 129.6 ppm, compared to 134.5 ppm for $C_{\beta}(C7, C18)$,



Tl(N-Me-tpp)(CF3COO)2

Fig. 3. Diagram of the porphyrin core $(C_{20}N_4, Tl, N-Me, and 2CF_3CO_2^-)$ of compound **2** showing the displacement (in Å) of the atoms from the mean plane of 3N.



Fig. 4. The 564.49 MHz 19 F NMR spectra for the axial trifluoroacetato fluorines of **2** in CD₂Cl₂ at 20, $-59 (= T_c)$ and $-97 \, ^{\circ}$ C.

134.4 ppm for $C_{\beta}(C12, C13)$, and 132.8 ppm for $C_{\beta}(C8, C17)$. Similarly the non-planarity of porphyrin causing upfield shifts of C_{β} resonances was also observed with a magnitude of 5.6–7.0 ppm for Tl(N–Me–tpp)(OAc)₂ [7]. The dihedral angles between the mean plane of the skeleton 3N and the planes of the phenyl groups are 54.0° [C(24)], 69.1° [C(30)], 68.1° [C(36)] and 56.5° [C(42)].

The Tl ion is displaced from the plane of the three individual pyrrole groups which suggests that the pyrrole nitrogen lone pairs are not optimally situated for covalent bonding to the metal. The displacements of the Tl ion from the plane of each pyrrole ring are 2.26 Å for pyrrole N(1), 0.65 Å for pyrrole N(2), 0.98 Å for pyrrole N(3) and 0.95 Å for pyrrole N(4). The angles between the Tl–N vector and the corresponding pyrrole ring are 58.0° for pyrrole N(1), 17.3° for pyrrole N(2), 26.5° for pyrrole N(3) and 24.8° for pyrrole N(4).

3.2. Dynamic NMR of 2 in CD_2Cl_2

The trifluoroacetate ligands engage in different binding modes in the solid state. These ligands exchange monodentate and bidentate coordination modes rapidly in CD_2Cl_2 , even at -90 °C, with an activation barrier too small to be readily measured by a variable-temperature NMR technique. The intramolecular exchange of two different $CF_3CO_2^-$ groups attains equivalency in CD_2Cl_2 solution on the ¹³C (or ¹⁹F) NMR time scale. Hence, only one kind of $CF_3CO_2^-$ in 2 is observed. A similar rapid exchange between the mono- and bidentate coordination modes of the carboxyate ligand has been observed in solution of $[Mo(CO)_2(PEt_3)_2(O_2CH)_2]$, even at -90 °C [23], and an analogous exchange process has been described for carboxylate ligands in the related compounds $[Ru(O_2CR')_2(CO)(PPh_3)_2]$ (R' = Me, CF₃, C₂F₅ or C₆F₅) [39]. When a 1.22×10^{-2} M solution of 2 in CD₂Cl₂ was cooled, the ¹⁹F signals of two $CF_3CO_2^-$ being a single peak at 20 °C ($\delta =$ -74.57 ppm), first broadened (coalescence temperature $T_{\rm c} = -59$ °C) and then split into three set of peaks (singlet at -76.15 ppm, one doublet at -73.30 ppm and the other doublet at -73.76 ppm) at -97 °C at a frequency of 564.49 MHz (Fig. 4). The singlet at -76.15 ppm is assigned as CF₃CO₂⁻. The doublet at -73.30 ppm is due to Tl(N-Me-tpp)(CF₃CO₂)⁺ with ${}^{4}J(\text{Tl}-\text{F}) = 22$ Hz. The other doublet at -73.76 ppm is due to 2 with ${}^{4}J(Tl-F) = 44$ Hz. The relative concentration of $2/Tl(N-Me-tpp)(CF_3CO_2)^+/CF_3CO_2^$ is 1:0.11:0.09 at -97 °C. This assignment is also supported by the observations of ¹H NMR for **2** in CD₂Cl₂ at -97 °C showing two doublets in 0.12:1 ratio for the N–Me resonances at δ – 4.68 ppm [³J(Tl–H) = 30 Hz] due to $Tl(N-Me-tpp)(CF_3CO_2)^+$ and -4.51 ppm $[{}^{3}J(TI-H) = 72 \text{ Hz}]$ due to 2. This ratio is quite close to 0.11 calculated from ¹⁹F NMR data. As a result of this observation, the most likely cause for the loss of coupling should be due to reversible dissociation of trifluoroacetate

 $Tl(N-Me-tpp)(CF_3CO_2)_2$

$$\rightleftharpoons Tl(N-Me-tpp)(CF_3CO_2)^+ + CF_3CO_2^-$$
(1)

with a moderate dissociation constant and reasonable rate at room temperature [40]. The dissociation constant of $(1.86 \pm 0.39) \times 10^{-4}$ mol dm⁻³ is evaluated at -97 °C for reaction (1). Such a scenario would not only lead to the change in the chemical shift with temperature and detectable free CF₃CO₂⁻ and Tl(N-CH₃-tpp)(CF₃CO₂)⁺ at low temperature, but also would lead to the loss of coupling between trifluoroacetate and thallium at higher temperatures. The chemical shift in the high-temperature limit is the average for all the three species in Eq. (1) weighted by their concentration.

Compound 2 is unusually less soluble in CD_2Cl_2 at 17 °C than -106 °C. Due to poor solubility, no signals of carbonyl and CF₃ carbons at 17 °C have been found. At -106 °C, the rate of intermolecular exchange of $CF_3CO_2^-$ for 2 in CD_2Cl_2 is slow. Hence, at this temperature the CO and CF₃ carbons of CF₃CO₂⁻ in 2 are observed at 155.1 ppm [with ${}^{2}J(C-F) = 37$ and $^{2}J(TI-C) = 204$ Hz] and 114.3 ppm [with $^{1}J(C-F) =$ 290 and ${}^{3}J(TI-C) = 411$ Hz], respectively. These ${}^{13}C$ resonance values are quite close to that of $Tl(tpp)(O_2CCF_3)$, in THF- d_8 at -100 °C, i.e. 156.5 ppm [with ${}^{2}J(C-F) = 37$ and ${}^{2}J(TI-C) = 128$ Hz] and 115.9 ppm [with ${}^{1}J(C-F) = 291$ and ${}^{3}J(TI-C) = 239$ Hz] [41]. The increase in the J(TI-C) coupling constant from 128 to 204 Hz for CO and from 239 to 411 Hz for CF₃ might be in correlation to the increase in the effective nuclear charge $Z_{\rm eff}$ of the Tl atom from $Tl(tpp)(O_2CCF_3)$ to 2 and the estimated value of Z_{eff} [T1 in 2]/ Z_{eff} [T1 in (Tl(tpp)(O₂CCF₃)] is 1.18 ± 0.02.

In contrast, no intramolecular exchange between the two trifluoroacetate groups is observed for the related bis(trifluoroacetato) seven-coordinate complexes Mo(CO)₂(PMe₃)₃(CF₃CO₂)₂ [25] and Mo(CO)₂(PEt₃)₂-(CF₃CO₂)₂ [26] in dichloromethane at 27 °C. Moreover, the dynamic processes involving not only intramolecular exchange between mono- and bidentate trifluoroacetate groups but also intermolecular exchange among 2, $Tl(N-Me-tpp)(CF_3CO_2)^+$ and $CF_3CO_2^-$ for 2 in CD_2Cl_2 are observed. Interestingly, the dynamic properties for the exchange of trifluoroacetate in 2 is found to be very similar to the exchange of acetate group in 1 as reflected by variable temperature ¹³C, ¹H and ¹⁹F NMR studies.

4. Conclusions

This work describes a new compound 2 being characterized by spectroscopic and crystallographic method. The seven-coordinate thallium complex **2** is the first of its kind with a 4:3 'piano stool' geometry. Dynamic ¹³C and ¹⁹F NMR spectra for the trifluoroacetato group of **2** reveal that this group undergoes an intermolecular exchange. We have also shown that one large metal ion (Tl^{3+}) coordinates well away from the plane of the four pyrrole nitrogen atoms and that in this location the thallium can accommodate additional ligation.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 162986 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

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