# Monodentate and bidentate trifluoroacetato ligands in bis(trifluoroacetato)-( $N$-methyl-meso-tetraphenylporphyrinato)thallium(III) <br> -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), $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2}$ (2), was established and the coordination sphere around the $\mathrm{Tl}^{3+}$ ion is described as $4: 3$ tetragonal base-trigonal base piano stool seven-coordinate geometry in which the two cis $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$groups occupy two apical sites. The plane of the three pyrrole nitrogen atoms [i.e. $\mathrm{N}(2), \mathrm{N}(3)$ and $\mathrm{N}(4)$ ] strongly bonded to $\mathrm{Tl}^{3+}$ is adopted as the reference plane 3 N . The pyrrole $\mathrm{N}(1)$ ring bearing the methyl group [i.e. $\mathrm{C}(45) \mathrm{H}_{3}$ ] is the most deviated one from the 3 N plane making a dihedral angle of $23.3^{\circ}$ whereas smaller angles of $9.9,2.7$ and $4.7^{\circ}$ occur with pyrroles $\mathrm{N}(2), \mathrm{N}(3)$, and $\mathrm{N}(4)$, respectively. Because of the larger size of the thallium(III) ion, Tl is considerably out of the 3 N plane; its displacement of $1.02 \AA$ is in the same direction as that of the two apical $\mathrm{CF}_{3} \mathrm{CO}_{2}{ }^{-}$ligands. The intermolecular trifluoroacetate exchange process for 2 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ solvent is examined through ${ }^{19} \mathrm{~F}$ and ${ }^{13} \mathrm{C}$ NMR temperature-dependent measurements. In the slow-exchange region, the $\mathrm{CF}_{3}$ and carbonyl (CO) carbons of the $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$groups in 2 are separately located at $\delta 114.3\left[{ }^{1} J(\mathrm{C}-\mathrm{F})=290 \mathrm{~Hz},{ }^{3} J(\mathrm{Tl}-\mathrm{C})=411 \mathrm{~Hz}\right]$ and $155.1\left[{ }^{2} J(\mathrm{C}-\mathrm{F})=37 \mathrm{~Hz},{ }^{2} J(\mathrm{Tl}-\mathrm{C})=204 \mathrm{~Hz}\right]$, respectively, at $-106{ }^{\circ} \mathrm{C}$. In the same slow-exchange region, the fluorine atoms of $\mathbf{2}, \mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)^{+}$and the free $\mathrm{CF}_{3} \mathrm{CO}_{2}{ }^{-}$are located at $\delta-73.76\left[{ }^{4} J(\mathrm{Tl}-\mathrm{F})=44 \mathrm{~Hz}\right],-73.30\left[{ }^{4} J(\mathrm{Tl}-\mathrm{F})=22 \mathrm{~Hz}\right]$, and -76.15 ppm at $-97{ }^{\circ} \mathrm{C}$, 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 $\mathrm{M}^{\mathrm{II}}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp}) \mathrm{Cl}(\mathrm{M}=\mathrm{Zn}, \mathrm{Co}$, $\mathrm{Mn}, \mathrm{Fe}$ and $\mathrm{tpp}=5,10,15,20$-tetraphenylporphyrinate) have been extensively studied by Anderson et al. [1-5]. The common feature in all these $N$-substituted metalloporphyrins is that the metal atom is no longer coplanar with the four nitrogen atoms of the macrocycle and

[^0]coordination geometry around the metal ion is a fivecoordinate distorted square-based pyramid. Iron(III) complexes of $N$-methylporphyrins, e.g. $\left[\mathrm{Fe}^{\text {III }}(\mathrm{N}-\mathrm{Me}-\right.$ $\left.\mathrm{ttp})(\mathrm{CN})_{2}\right],\left[\mathrm{Fe}^{\mathrm{III}}(\mathrm{N}-\mathrm{Me}-\mathrm{ttp})(5-\mathrm{MeIm})_{2}\right]^{2+}$ and $\left[\mathrm{Fe}^{\mathrm{III}}-\right.$ ( $\mathrm{N}-\mathrm{Me}-\mathrm{tmp}$ ) $\left.\mathrm{Im}_{2}\right]^{2+}$ (with $\mathrm{N}-\mathrm{Me}-\mathrm{ttp}=N$-methyltetra-$p$-tolylporphyrin monoanion, $\mathrm{N}-\mathrm{Me}-\mathrm{tmp}=N$-methyltetramesitylporphyrin monoanion, $\operatorname{Im}=$ 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), $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})(\mathrm{OAc})_{2}(\mathbf{1})$, and the coordination sphere around the $\mathrm{Tl}^{3+}$ ion is described as an eight-
co-ordinate square-based antiprism in which the two cis chelating bidentate $\mathrm{OAc}^{-}$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 $\mathrm{OAc}^{-}$of $\mathbf{1}$ was replaced by a relatively bulkier trifluoroacetate group, $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$the coordination number ( CN ) decreases from 8 for $\mathbf{1}$ to 7 for bis(trifluoroacetato) - ( $N$ - methyl - meso - tetraphenylporphyrinato)thallium(III), $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2}$ (2). Seven-coordinate complexes of the metal ion (M(III)) ( $\mathrm{M}=\mathrm{Sc}$ [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 $D_{5 h}$ pentagonal bipyramidal [21], the 1:4:2 $C_{2 v}$ capped trigonal prismatic [22], the $4: 3$ piano-stool $[23,24]$ and the $1: 3: 3 \quad C_{3 v}$ 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 $\mathbf{1}$ prompted us to investigate a similar trifluoroacetato exchange for $\mathbf{2}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ by a ${ }^{13} \mathrm{C}$ and ${ }^{19} \mathrm{~F}$ dynamic NMR method [7].

The structures of the two related heptacoordinated complexes $\mathrm{Mo}(\mathrm{CO})_{2}\left(\mathrm{PMe}_{3}\right)_{2}\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2} \quad[25]$ and $\mathrm{Mo}(\mathrm{CO})_{2}\left(\mathrm{PEt}_{3}\right)_{2}\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2}[26]$ 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. $\mathrm{Mo}(\mathrm{CO})_{2}\left(\mathrm{PEt}_{3}\right)_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{2}$ [23] is yet another seven-coordinate $\mathrm{d}^{4}$ bis(formato) derivative adopting a $4: 3$ 'piano stool' configuration with one monodentate and one bidentate $\mathrm{O}_{2} \mathrm{CH}$ 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 $\mathrm{CF}_{3} \mathrm{CO}_{2}$ 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 $\mathrm{CF}_{3} \mathrm{CO}_{2}$ ligand.

## 2. Experimental

### 2.1. Preparation of $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2}$ (2)

The new compound $\mathbf{2}$ was synthesized by refluxing a mixture of $\mathrm{N}-\mathrm{Me}-\mathrm{Htpp}$ [7,27] $\left(0.15 \mathrm{~g}, 2.389 \times 10^{-4}\right.$ $\mathrm{mol})$ in dry $\mathrm{CHCl}_{3}\left(50 \mathrm{~cm}^{3}\right)$ and $\mathrm{Tl}\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{3}(0.26 \mathrm{~g}$, $\left.4.79 \times 10^{-4} \mathrm{~mol}\right)$ in dry $\mathrm{CH}_{3} \mathrm{OH}\left(2 \mathrm{~cm}^{3}\right)$ under $\mathrm{N}_{2}$ for 30 min . After concentrating, the residue was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and collected by filtration to remove any precipitate. The crystals of $2\left(0.13 \mathrm{~g}, 1.23 \times 10^{-4} \mathrm{~mol}\right.$, $86.6 \%$ ) were grown by removing $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and dissolving the residue in dry ether. The crystals were dissolved in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ for ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR measurements. ${ }^{1} \mathrm{H}$ NMR ( $600.25 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 20^{\circ} \mathrm{C}$ ): $\delta 9.09$ [dd, $\mathrm{H}_{\beta}(8,17)$, ${ }^{4} J(\mathrm{Tl}-\mathrm{H})=76 \mathrm{~Hz},{ }^{3} J(\mathrm{H}-\mathrm{H})=4.7 \mathrm{~Hz}$ ], where $\mathrm{H}_{\beta}(\mathrm{a}, \mathrm{b})$ represents the two equivalent $\beta$-pyrrole protons attached to carbons a and b, respectively; 9.09 [dd, $\left.\mathrm{H}_{\mathrm{B}}(7,18),{ }^{4} J(\mathrm{Tl}-\mathrm{H})=68 \mathrm{~Hz},{ }^{3} J(\mathrm{H}-\mathrm{H})=4.7 \mathrm{~Hz}\right] ; 9.00$ $\left[\mathrm{d}, \mathrm{H}_{\beta}(12,13),{ }^{4} J(\mathrm{Tl}-\mathrm{H})=61 \mathrm{~Hz}\right] ; 8.73$ [d, $\mathrm{H}_{\beta}(2,3)$, $\left.{ }^{4} J(\mathrm{Tl}-\mathrm{H})=7.1 \mathrm{~Hz}\right] ; 8.53(\mathrm{~s})$ and $8.24-8.27(\mathrm{~m})$ for phenyl ortho protons ( $o, o^{\prime}-\mathrm{H}$ ); 7.79-7.94 (m) for phenyl meta, para protons ( $m-, p-\mathrm{H}$ ); $-4.31\left[\mathrm{~d}, \mathrm{~N}-\mathrm{Me},{ }^{3} \mathrm{~J}(\mathrm{Tl}-\right.$ $\mathrm{H})=37 \mathrm{~Hz}$ ] for compound 2. ${ }^{1} \mathrm{H}$ NMR ( 600.25 MHz , $\left.\mathrm{CD}_{2} \mathrm{Cl}_{2},-73{ }^{\circ} \mathrm{C}\right): \delta 9.12\left[\mathrm{dd}, \mathrm{H}_{\beta}(8,17),{ }^{4} J(\mathrm{Tl}-\mathrm{H})=75\right.$ $\left.\mathrm{Hz},{ }^{3} J(\mathrm{H}-\mathrm{H})=4.4 \mathrm{~Hz}\right] ; 9.06\left[\mathrm{dd}, \mathrm{H}_{\beta}(7,18),{ }^{4} J(\mathrm{Tl}-\right.$ $\left.\mathrm{H})=69 \mathrm{~Hz},{ }^{3} J(\mathrm{H}-\mathrm{H})=4.4 \mathrm{~Hz}\right] ; 9.03\left[\mathrm{~d}, \mathrm{H}_{\mathrm{B}}(12,13)\right.$, $\left.{ }^{4} J(\mathrm{Tl}-\mathrm{H})=60 \mathrm{~Hz}\right] ; 8.76 \quad\left[\mathrm{~d}, \mathrm{H}_{\beta}(2,3),{ }^{4} J(\mathrm{Tl}-\mathrm{H})=7.2\right.$ $\mathrm{Hz}] ; 8.55(\mathrm{~s})$ and $8.24-8.28(\mathrm{~m})$ for phenyl ortho protons (o,o'-H); 7.78-7.95 (m) for phenyl meta, para protons $(m-, p-\mathrm{H}) ;-4.43\left[\mathrm{~d}, \mathrm{~N}-\mathrm{Me},{ }^{3} J(\mathrm{Tl}-\mathrm{H})=37\right.$ Hz ] for compound 2; $-4.61\left[\mathrm{~d}, \mathrm{~N}-\mathrm{Me},{ }^{3} J(\mathrm{Tl}-\mathrm{H})=21\right.$ Hz ] for compound $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{COO}\right)^{+} .{ }^{13} \mathrm{C}$ NMR ( $150.87 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 17{ }^{\circ} \mathrm{C}$ ): $\delta 157.1[\mathrm{~d}$, $\left.\mathrm{C}_{\alpha}(\mathrm{C} 1, \mathrm{C} 4),{ }^{2} J(\mathrm{Tl}-\mathrm{C})=90 \mathrm{~Hz}\right] ; 153.9\left[\mathrm{~d}, \mathrm{C}_{\alpha}(\mathrm{C} 9, \mathrm{C} 16)\right.$, $\left.{ }^{2} J(\mathrm{Tl}-\mathrm{C})=29 \mathrm{~Hz}\right] ; 153.5\left[\mathrm{~d}, \mathrm{C}_{\alpha}(\mathrm{C} 11, \mathrm{C} 14),{ }^{2} J(\mathrm{Tl}-\mathrm{C})=\right.$ $70 \mathrm{~Hz}] ; 151.9$ [d, C $\left.{ }_{\alpha}(\mathrm{C} 6, \mathrm{C} 19),{ }^{2} J(\mathrm{Tl}-\mathrm{C})=17 \mathrm{~Hz}\right] ; 141.5$ $\left(\mathrm{d},{ }^{4} J(\mathrm{Tl}-\mathrm{C})=42 \mathrm{~Hz}\right)$ and $141.3\left(\mathrm{~d},{ }^{4} J(\mathrm{Tl}-\mathrm{C})=41 \mathrm{~Hz}\right)$ for phenyl-C ${ }_{1}$; $137.1\left(\mathrm{~d},{ }^{3} J(\mathrm{Tl}-\mathrm{C})=37 \mathrm{~Hz}\right), 136.0(\mathrm{~s})$, 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- $\mathrm{C}_{2,6}$, phenyl- $\mathrm{C}_{3,5}$ and phenyl-C4; 134.5 [d, $\mathrm{C}_{\beta}(\mathrm{C} 7, \mathrm{C} 18)$, $\left.{ }^{3} J(\mathrm{Tl}-\mathrm{C})=109 \mathrm{~Hz}\right] ; 134.4$ [d, C ${ }_{\beta}(\mathrm{C} 12, \mathrm{C} 13),{ }^{3} J(\mathrm{Tl}-$ $\mathrm{C})=111 \mathrm{~Hz}] ; 132.8\left[\mathrm{~d}, \mathrm{C}_{\beta}(\mathrm{C} 8, \mathrm{C} 17),{ }^{3} \mathrm{~J}(\mathrm{Tl}-\mathrm{C})=114\right.$ $\mathrm{Hz}] ; 129.6$ [d, $\mathrm{C}_{\beta}(\mathrm{C} 2, \mathrm{C} 3),{ }^{3} J(\mathrm{Tl}-\mathrm{C})=10 \mathrm{~Hz}$ ]; 126.8 [d, $\left.\mathrm{C}_{m}(\mathrm{C} 10, \mathrm{C} 15),{ }^{3} \mathrm{~J}(\mathrm{Tl}-\mathrm{C})=171 \mathrm{~Hz}\right] ; 124.9\left[\mathrm{~d}, \mathrm{C}_{m}(\mathrm{C} 5\right.$, C20), $\left.{ }^{3} J(\mathrm{Tl}-\mathrm{C})=141 \mathrm{~Hz}\right] ; 32.1\left[\mathrm{~s}, \mathrm{~N}-\mathrm{Me},{ }^{2} J(\mathrm{Tl}-\mathrm{C})=\right.$ $32.1 \mathrm{~Hz}] ;{ }^{13} \mathrm{C}$ NMR ( $150.87 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2},-106{ }^{\circ} \mathrm{C}$ ): $\delta 156.0\left[\mathrm{~d}, \mathrm{C}_{\alpha}(\mathrm{C} 1, \mathrm{C} 4),{ }^{2} J(\mathrm{Tl}-\mathrm{C})=89 \mathrm{~Hz}\right] ; 152.5[\mathrm{~d}$, $\left.\mathrm{C}_{\alpha}(\mathrm{C} 9, \mathrm{C} 16),{ }^{2} J(\mathrm{Tl}-\mathrm{C})=23 \mathrm{~Hz}\right] ; 152.3 \quad\left[\mathrm{~d}, \mathrm{C}_{\alpha}(\mathrm{C} 11\right.$, C14), $\left.{ }^{2} J(\mathrm{Tl}-\mathrm{C})=61 \mathrm{~Hz}\right] ; 150.1$ [s, C ${ }_{\alpha}(\mathrm{C} 6, \mathrm{C} 19)$ ]; 140.5 $\left(\mathrm{d},{ }^{4} J(\mathrm{Tl}-\mathrm{C})=40 \mathrm{~Hz}\right)$ and $140.9\left(\mathrm{~d},{ }^{4} J(\mathrm{Tl}-\mathrm{C})=39 \mathrm{~Hz}\right)$ for phenyl- $\mathrm{C}_{1} ; 137.1\left(\mathrm{~d},{ }^{3} J(\mathrm{Tl}-\mathrm{C})=31 \mathrm{~Hz}\right), 136.4(\mathrm{~d}$, $\left.{ }^{3} J(\mathrm{Tl}-\mathrm{C})=34 \mathrm{~Hz}\right), 135.2\left(\mathrm{~d},{ }^{3} J(\mathrm{Tl}-\mathrm{C})=37 \mathrm{~Hz}\right), 133.3$ (s), 128.3 (s), 127.7 (s), 127.6 (s), 127.2 (s), 126.6 (s), 126.3 (s) for phenyl- $\mathrm{C}_{2,6}$, phenyl- $\mathrm{C}_{3,5}$ and phenyl-C4;
$134.0\left[\mathrm{~d}, \mathrm{C}_{\beta}(\mathrm{C} 7, \mathrm{C} 18),{ }^{3} J(\mathrm{Tl}-\mathrm{C})=107 \mathrm{~Hz}\right] ; 133.8$ [d, $\mathrm{C}_{\beta}(\mathrm{C} 12, \mathrm{C} 13),{ }^{3} J(\mathrm{Tl}-\mathrm{C})=95 \mathrm{~Hz} ; 132.0 \quad\left[\mathrm{~d}, \mathrm{C}_{\beta}(\mathrm{C} 8\right.$, C17), $\left.{ }^{3} J(\mathrm{Tl}-\mathrm{C})=129 \mathrm{~Hz}\right] ; 129.2\left[\mathrm{~d}, \mathrm{C}_{\beta}(\mathrm{C} 2, \mathrm{C} 3),{ }^{3} J(\mathrm{Tl}-\right.$ $\mathrm{C})=8.3 \mathrm{~Hz}] ; 125.4\left[\mathrm{~d}, \mathrm{C}_{m}(\mathrm{C} 10, \mathrm{C} 15),{ }^{3} J(\mathrm{Tl}-\mathrm{C})=168\right.$ $\mathrm{Hz}] ; 123.9$ [d, $\left.\mathrm{C}_{m}(\mathrm{C} 5, \mathrm{C} 20),{ }^{3} J(\mathrm{Tl}-\mathrm{C})=134 \mathrm{~Hz}\right] ; 30.7$ $\left[\mathrm{s}, ~ \mathrm{~N}-\mathrm{Me},{ }^{2} J(\mathrm{Tl}-\mathrm{C})=20 \mathrm{~Hz}\right] ; 155.1\left(\mathrm{~m}, \mathrm{CF}_{3} \mathbf{C O O}\right.$, ${ }^{2} J(\mathrm{C}-\mathrm{F})=37 \mathrm{~Hz}$ and $\left.{ }^{2} J(\mathrm{Tl}-\mathrm{C})=204 \mathrm{~Hz}\right) ; 114.3(\mathrm{~m}$, $\mathrm{CF}_{3} \mathrm{COO},{ }^{1} J(\mathrm{C}-\mathrm{F})=290 \mathrm{~Hz}$ and $\left.{ }^{3} J(\mathrm{Tl}-\mathrm{C})=411 \mathrm{~Hz}\right)$. MS; m/z (assignment, relative intensity): 1058 $\left(\left[\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2}\right]^{+}\right.$, 1.94$), 945 \quad([\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-$ $\left.\left.\operatorname{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)\right]^{+}, 4.96\right), 832\left([\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})]^{+}, 10.76\right)$,

Table 1
Crystal data and structure refinement parameters for $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})$ $\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2} \cdot \mathrm{Et}_{2} \mathrm{O}\left(2 \cdot \mathrm{Et}_{2} \mathrm{O}\right)$

| Empirical formula $^{\mathrm{a}}$ | $\mathrm{C}_{53} \mathrm{H}_{41} \mathrm{~F}_{6} \mathrm{~N}_{4} \mathrm{O}_{5} \mathrm{Tl}\left(2 \cdot \mathrm{Et}_{2} \mathrm{O}\right)$ |
| :--- | :--- |
| Formula weight | 1132.27 |
| Space group | $P \overline{1}$ |
| $Z$ | 2 |
| Unit cell dimensions |  |
| $a(\AA)$ | $9.5350(11)$ |
| $b(\AA)$ | $13.4138(15)$ |
| $c(\AA)$ | $19.308(2)$ |
| $\alpha\left({ }^{\circ}\right)$ | $96.865(2)$ |
| $\beta\left({ }^{\circ}\right)$ | $101.223(2)$ |
| $\gamma\left({ }^{\circ}\right)$ | $94.785(2)$ |
| $V\left(\AA^{3}\right)$ | $2390.4(4)$ |
| $D_{\text {calc }}\left(\mathrm{g} \mathrm{cm}{ }^{-3}\right)$ | 1.573 |
| $\mathrm{Radiation}, \lambda(\AA)$ | $\mathrm{Mo}, 0.71073$ |
| Temperature $(\mathrm{K})$ | $293(2)$ |
| Absorption coefficient $\left(\mathrm{mm}^{-1}\right)$ | 3.454 |
| $R{ }^{\mathrm{b}}(\%)$ | 3.61 |
| $R_{\mathrm{w}}{ }^{\text {c }}$ (\%) | 11.27 |
| Goodness-of-fit | 0.885 |

[^1]Table 2
Selected bond distances ( $\AA$ ) and bond angles ( ${ }^{\circ}$ ) for compound $2 \cdot \mathrm{Et}_{2} \mathrm{O}$

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

$628\left([\mathrm{~N}-\mathrm{Me}-\mathrm{tpp}]^{+}, \quad 58.24\right), 627$ ([N-Me-tpp-H]${ }^{+}$, 100.00), $205\left({ }^{205} \mathrm{Tl}^{+}, 23.22\right), 203\left({ }^{203} \mathrm{Tl}^{+}, ~ 9.63\right) . \mathrm{UV}-\mathrm{V}$ is spectrum: $\lambda(\mathrm{nm})\left(\varepsilon \times 10^{-3}\left(\mathrm{M}^{-1} \mathrm{~cm}^{-1}\right)\right]\left(\mathrm{CHCl}_{3}\right): 440$ (253), 452 (202), 556 (10.8), 601 (14.1), 648 (8.5).

### 2.2. Spectroscopy

Proton and ${ }^{13} \mathrm{C}$ NMR spectra in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(99.6 \%$ 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 $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $\delta=5.30\left({ }^{1} \mathrm{H} \mathrm{NMR}\right)$ and the center line of $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $\delta=53.6\left({ }^{13} \mathrm{C} \mathrm{NMR}\right)$. The ${ }^{19} \mathrm{~F}$ spectra were measured in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at 564.49 MHz in a Varian Unity Inova-600 spectrometer. ${ }^{19} \mathrm{~F}$ NMR data are internally referenced to $\mathrm{CFCl}_{3}$. The temperature of the spectrometer probe was calibrated by the shift difference of the methanol resonance in the ${ }^{1} \mathrm{H}$ NMR spectrum. ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ 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 $24{ }^{\circ} \mathrm{C}$ in a Hitachi U-3210 spectrophotometer.

### 2.3. Crystallography

Table 1 contains the crystal data and other information for $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2} \cdot \mathrm{Et}_{2} \mathrm{O}$. Measurements were taken in a Siemens SMART CCD diffractometer for $2 \cdot \mathrm{Et}_{2} \mathrm{O}$ using monochromatized $\mathrm{Mo} \mathrm{K} \alpha$ radiation ( $\lambda=0.71073 \AA$ ). SADABS absorption corrections were made for $\mathbf{2} \cdot \mathrm{Et}_{2} \mathrm{O}$. 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 $\mathbf{2}$

Fig. 1 illustrates the skeletal framework of complex $2 \cdot \mathrm{Et}_{2} \mathrm{O}$. It is a seven-coordinate $N$-methylporphyrin complex of the porphyrin $\mathrm{N}_{4}$ with two oxygen atoms of the chelating bidentate $\mathrm{CF}_{3} \mathrm{CO}_{2}{ }^{-}$ligand from first trifluoroacetate $[\mathrm{O}(3), \mathrm{O}(4), \mathrm{C}(48), \mathrm{C}(49)]$, and one oxygen


Fig. 1. Molecular configuration and atom-labeling scheme for $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2} \cdot \mathrm{Et}_{2} \mathrm{O}$ (or $\mathbf{2} \cdot \mathrm{Et}_{2} \mathrm{O}$ ), with ellipsoids drawn at $30 \%$ probability. Hydrogen atoms and solvent $\mathrm{Et}_{2} \mathrm{O}$ are omitted for clarity. $\mathrm{F}(1) \mathrm{F}(2) \mathrm{F}(3)$ in $\mathbf{2} \cdot \mathrm{Et}_{2} \mathrm{O}$ is disordered with an occupancy factor 0.7 for $\mathrm{F}(1) \mathrm{F}(2) \mathrm{F}(3)$ and 0.3 for $\mathrm{F}\left(1^{\prime}\right) \mathrm{F}\left(2^{\prime}\right) \mathrm{F}\left(3^{\prime}\right)$.
atom of the monodentate $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$ligand from second trifluoroacetate $[\mathrm{O}(1), \mathrm{O}(2), \mathrm{C}(46), \mathrm{C}(47)]$. Visual inspection as well as other stereo drawings suggested that the geometrical configuration around $\mathrm{Tl}^{3+}$ 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 $\delta$ parameters of Porai-Koshits and Aslanov [28], as calculated by Muetterties and Guggenberger [29]. Upon viewing 2 as a 4:3 system, $[\mathrm{N}(1) \mathrm{N}(2) \mathrm{N}(3) \mathrm{N}(4): \mathrm{O}(1) \mathrm{O}(3) \mathrm{O}(4)]$, the observed angle between the two planes of the ligating atom is $0.6^{\circ}$. Normalization of metal-ligand bond lengths by projecting onto a sphere of unit radius results in an angle $\left(\delta_{1}\right)$ of $1.1^{\circ}$ between the two planes of the $4: 3$ geometry (Table 3 ), nearly identical with the ideal value of $0^{\circ}$ [30-33]. With $0^{\circ}$ 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 $8.4^{\circ}$ (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 $\mathrm{N}(3)$ capping the quadrilateral face generated by $\mathrm{O}(3), \mathrm{O}(4), \mathrm{N}(2), \mathrm{N}(4)$ and the remaining $\mathrm{O}(1), \mathrm{N}(1)$ atoms being on the unique edge. Comparison of the parameter $\delta$ values (76.5, 44.6, $41.5^{\circ}$ ), 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 $\delta$ 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 was observed for $\mathrm{Mo}(\mathrm{CO})_{2}\left(\mathrm{PEt}_{3}\right)_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{2}$ [23], $\operatorname{MoBr}\left(\mathrm{O}_{2} \mathrm{CCF}_{3}\right)(\mathrm{CO})_{2}\left(\mathrm{PPh}_{3}\right)_{2} \quad[24], \quad \mathrm{W}\left(t-\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{NC}\right)_{3}-$ $(\mathrm{CO})_{2} \mathrm{I}_{2} \quad[31], \quad \mathrm{W}(\mathrm{CO})_{3}\left(\mathrm{~S}_{2} \mathrm{CN}\left(\mathrm{CH}_{3}\right)_{2}\right)_{2} \quad[32] \quad$ and $\mathrm{W}(\mathrm{CO})_{2}\left(\mathrm{PPh}_{3}\right)\left(\mathrm{S}_{2} \mathrm{CNEt}_{2}\right)_{2}[33]$ 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 $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})$ $(\mathrm{OAc})_{2}$ with $\mathrm{Tl}(1)-\mathrm{O}(1)=2.517(6)$ and $\mathrm{Tl}(1)-\mathrm{O}(2)=$ $2.330(6) \AA$. The second trifluoroacetate oxygen $\mathrm{O}(2)$ is $3.167(6) \AA$ distanced from thallium which is considerably longer than that of the $\mathrm{Tl}-\mathrm{O}(1)$ distance and the ligand's interaction with thallium is classified as monodentate. Hence only three oxygen atoms [i.e. $\mathrm{O}(1)$, $\mathrm{O}(3), \mathrm{O}(4)]$ are coordinated to the thallium atom.

The nitrogen atom bearing the methyl group is much farther from the $\mathrm{Tl}^{3+}[\mathrm{Tl}-\mathrm{N}(1) 2.700(4) \AA]$ compared to the other three nitrogen atoms [T1-N(2) 2.276(4), $\mathrm{Tl}-\mathrm{N}(3) \quad 2.243(4)$, $\mathrm{Tl}-\mathrm{N}(4)$ 2.278(4) A]. Since the $\mathrm{Tl}-\mathrm{N}(1)$ distance is quite large, the nitrogen atom $\mathrm{N}(1)$ is probably not coordinated to the thallium. However, in ${ }^{1} \mathrm{H}$ NMR [599.95 MHz, Fig. 2(a)] at $20{ }^{\circ} \mathrm{C}$ the $\mathrm{H}_{\beta}(2,3)$ and $\mathrm{N}-\mathrm{Me}$ protons are observed at 8.73 ppm [with ${ }^{4} J(\mathrm{Tl}-\mathrm{H})=7.1 \mathrm{~Hz}$ ] and at -4.31 ppm [with $\left.{ }^{3} J(\mathrm{Tl}-\mathrm{H})=70 \mathrm{~Hz}\right]$, respectively. Furthermore, ${ }^{13} \mathrm{C}$ NMR data [ 150.87 MHz ] at $17{ }^{\circ} \mathrm{C}$ show $\mathrm{C}_{\beta}(\mathrm{C} 2, \mathrm{C} 3)$ and $\mathrm{C}_{\alpha}(\mathrm{Cl}, \mathrm{C} 4)$ resonances at 129.5 ppm [with ${ }^{3} J(\mathrm{Tl}-$ $\mathrm{C})=10 \mathrm{~Hz}$ ] and 157.1 ppm [with ${ }^{2} J(\mathrm{Tl}-\mathrm{C})=90 \mathrm{~Hz}$ ],

Table 3
Dihedral angle calculations ${ }^{\text {a }}$ for comparison of molecule 2 with two trial geometries

| Trial geometry | Defining planes | $\delta_{i}$ | $\delta_{i}$ Dihedral angles $\left({ }^{\circ}\right)$ |  |
| :--- | :--- | :--- | :--- | :--- |
|  |  |  | Observed | Idealized |
| $4: 3$ (piano stool), $\mathrm{N}(1) \mathrm{N}(2) \mathrm{N}(3) \mathrm{N}(4): \mathrm{O}(1) \mathrm{O}(3) \mathrm{O}(4)$ | $\mathrm{N}(1) \mathrm{N}(2) \mathrm{N}(3) \mathrm{N}(4) / \mathrm{O}(1) \mathrm{O}(3) \mathrm{O}(4)$ | $\delta_{1}$ | 1.1 | 0.0 |
|  | $\mathrm{~N}(1) \mathrm{N}(3) \mathrm{N}(4) / \mathrm{N}(1) \mathrm{N}(3) \mathrm{N}(2)$ | $\delta_{2}$ | 8.4 | 0.0 |
| $1: 4: 2$ (capped trigonal prism), $\mathrm{N}(3): \mathrm{O}(3) \mathrm{O}(4) \mathrm{N}(2) \mathrm{N}(4): \mathrm{O}(1) \mathrm{N}(1)$ | $\mathrm{O}(3) \mathrm{O}(4) \mathrm{N}(3) / \mathrm{O}(3) \mathrm{O}(4) \mathrm{O}(1)$ | $\delta_{1}$ | 76.5 | 41.5 |
|  | $\mathrm{O}(3) \mathrm{N}(1) \mathrm{N}(4) / \mathrm{O}(3) \mathrm{N}(1) \mathrm{O}(1)$ | $\delta_{2}$ | 44.6 | 0.0 |
|  | $\mathrm{~N}(1) \mathrm{O}(4) \mathrm{N}(2) / \mathrm{N}(1) \mathrm{O}(4) \mathrm{O}(1)$ | $\delta_{3}$ | 41.5 | 0.0 |

[^2]

Fig. 2. ${ }^{1} \mathrm{H}(600.25 \mathrm{MHz})$ NMR spectra for $\mathbf{2}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ showing four different $\beta$-pyrrole protons $\mathrm{H}_{\beta}$, phenyl protons ( $o-\mathrm{H}, m, p-\mathrm{H}$ ) and the $\mathrm{N}-\mathrm{Me}$ protons at: (a) 20 and (b) $-73^{\circ} \mathrm{C}$.
respectively. These two results confirm that the thal-lium-N(1) distance of 2.700(4) $\AA$ is long enough, but it does fall within the sum of the van der Waals radii of thallium and nitrogen, $\sim 3.55 \AA$. This longer $\mathrm{T} 1 \cdots \mathrm{~N}(1)$ contact is described as a weak (secondary) bond [3436]. The Tl- $\mathrm{N}(1)$ bond length of $2.700(4) \AA$ for 2 is slightly shorter than the $\mathrm{Tl}-\mathrm{N}$ bond length of 2.71(3) $\AA$ for $\mathrm{Tl}\left[\mathrm{Tp}^{\left(\mathrm{CF}_{3}\right)^{2}}\right]$ [37] and 2.74(7) $\AA$ for $\mathrm{Tl}\left[\mathrm{Tp}^{\mathrm{Trip}}\right]$ [38].

The other three non-alkylated pyrrole nitrogen atoms $[\mathrm{N}(2), \mathrm{N}(3), \mathrm{N}(4)]$ bind strongly to the $\mathrm{Tl}(\mathrm{III})$ ion. We adopt the plane of the three strongly bound pyrrole nitrogen atoms [i.e. $\mathrm{N}(2), \mathrm{N}(3), \mathrm{N}(4)$ ] as a reference plane 3 N . Fig. 3 illustrates the displacement (in $\AA$ ) of various atoms $\left(\mathrm{C}_{20} \mathrm{~N}_{4}, \mathrm{Tl}, \mathrm{N}-\mathrm{Me}\right.$, and $\left.2 \mathrm{CF}_{3} \mathrm{CO}_{2}^{-}\right)$from the 3 N plane. Because of its larger size, the thalliu-
$\mathrm{m}(\mathrm{III})$ ion is pushed away from the 3 N plane; its displacement of $1.02 \AA$ is in the same direction as that of the two apical $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$ligands [cf. $1.17 \AA$ for $\mathrm{Tl}(\mathrm{III})$ in $\left.\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})(\mathrm{OAc})_{2}\right][7]$. The two approximately perpendicular trifluoroacetates with an angle of $81.0^{\circ}$ are bound cis to Tl and lie above the macrocycle making a dihedral angle of 56.2 and $43.0^{\circ}$ with the 3 N plane for the two trifluoroacetates. The porphyrin macrocycle is indeed distorted (Fig. 3) as a result of the $\mathrm{N}-$ Me group. Thus, pyrrole $\mathrm{N}(1)$ [i.e. the plane of $\mathrm{N}(1)$, $\mathrm{C}(1)-\mathrm{C}(4)$ ] bearing the methyl group [i.e. $\mathrm{C}(45) \mathrm{H}_{3}$ ] is the most deviated from the 3 N plane, making a dihedral angle of $23.3^{\circ}$, whereas smaller angles of 9.9, 2.7 and $4.7^{\circ}$ occur with pyrroles $\mathrm{N}(2), \mathrm{N}(3)$ and $\mathrm{N}(4)$, respectively. Such a large deviation from planarity is
also reflected in the NMR data for pyrrole $\mathrm{N}(1)$ by observing a 3.2-4.9 ppm upfield shift of $\mathrm{C}_{\beta}(\mathrm{C} 2, \mathrm{C} 3)$ at 129.6 ppm , compared to 134.5 ppm for $\mathrm{C}_{\beta}(\mathrm{C} 7, \mathrm{C} 18)$,

$\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{COO}\right)_{2}$
Fig. 3. Diagram of the porphyrin core $\left(\mathrm{C}_{20} \mathrm{~N}_{4}, \mathrm{Tl}, \mathrm{N}-\mathrm{Me}\right.$, and $2 \mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$) of compound 2 showing the displacement (in $\AA$ ) of the atoms from the mean plane of 3 N .


Fig. 4. The $564.49 \mathrm{MHz}{ }^{19} \mathrm{~F}$ NMR spectra for the axial trifluoroacetato fluorines of $\mathbf{2}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $20,-59\left(=T_{\mathrm{c}}\right)$ and $-97{ }^{\circ} \mathrm{C}$.
134.4 ppm for $\mathrm{C}_{\beta}(\mathrm{C} 12, \mathrm{C} 13)$, and 132.8 ppm for $\mathrm{C}_{\beta}(\mathrm{C} 8$, C 17 ). Similarly the non-planarity of porphyrin causing upfield shifts of $\mathrm{C}_{\beta}$ resonances was also observed with a magnitude of $5.6-7.0 \mathrm{ppm}$ for $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})(\mathrm{OAc})_{2}$ [7]. The dihedral angles between the mean plane of the skeleton 3 N and the planes of the phenyl groups are $54.0^{\circ}[C(24)], 69.1^{\circ}[C(30)], 68.1^{\circ}[C(36)]$ and $56.5^{\circ}$ [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 $\AA$ for pyrrole $\mathrm{N}(1), 0.65 \AA$ for pyrrole $\mathrm{N}(2), 0.98 \AA$ for pyrrole $\mathrm{N}(3)$ and $0.95 \AA$ for pyrrole $\mathrm{N}(4)$. The angles between the Tl-N vector and the corresponding pyrrole ring are $58.0^{\circ}$ for pyrrole $\mathrm{N}(1), 17.3^{\circ}$ for pyrrole $\mathrm{N}(2)$, $26.5^{\circ}$ for pyrrole $\mathrm{N}(3)$ and $24.8^{\circ}$ for pyrrole $\mathrm{N}(4)$.

### 3.2. Dynamic NMR of 2 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$

The trifluoroacetate ligands engage in different binding modes in the solid state. These ligands exchange monodentate and bidentate coordination modes rapidly in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$, even at $-90^{\circ} \mathrm{C}$, with an activation barrier too small to be readily measured by a variable-temperature NMR technique. The intramolecular exchange of two different $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$groups attains equivalency in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ solution on the ${ }^{13} \mathrm{C}$ (or ${ }^{19} \mathrm{~F}$ ) NMR time scale. Hence, only one kind of $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$in $\mathbf{2}$ is observed. A similar rapid exchange between the mono- and bidentate coordination modes of the carboxyate ligand has been observed in solution of $\left[\mathrm{Mo}(\mathrm{CO})_{2}\left(\mathrm{PEt}_{3}\right)_{2}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{2}\right]$, even at $-90{ }^{\circ} \mathrm{C}$ [23], and an analogous exchange process has been described for carboxylate ligands in the related compounds $\left[\mathrm{Ru}\left(\mathrm{O}_{2} \mathrm{CR}^{\prime}\right)_{2}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2}\right]\left(\mathrm{R}^{\prime}=\right.$ $\mathrm{Me}, \mathrm{CF}_{3}, \mathrm{C}_{2} \mathrm{~F}_{5}$ or $\mathrm{C}_{6} \mathrm{~F}_{5}$ ) [39]. When a $1.22 \times 10^{-2} \mathrm{M}$ solution of 2 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ was cooled, the ${ }^{19} \mathrm{~F}$ signals of two $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$being a single peak at $20^{\circ} \mathrm{C}(\delta=$ -74.57 ppm ), first broadened (coalescence temperature $T_{\mathrm{c}=}=-59^{\circ} \mathrm{C}$ ) 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 $-97^{\circ} \mathrm{C}$ at a frequency of 564.49 MHz (Fig. 4). The singlet at -76.15 ppm is assigned as $\mathrm{CF}_{3} \mathrm{CO}_{2}{ }^{-}$. The doublet at -73.30 ppm is due to $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)^{+}$with ${ }^{4} J(\mathrm{Tl}-\mathrm{F})=22 \mathrm{~Hz}$. The other doublet at -73.76 ppm is due to 2 with ${ }^{4} J(\mathrm{Tl}-\mathrm{F})=44 \mathrm{~Hz}$. The relative concentration of $2 / \mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)^{+} / \mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$is 1:0.11:0.09 at $-97{ }^{\circ} \mathrm{C}$. This assignment is also supported by the observations of ${ }^{1} \mathrm{H}$ NMR for $\mathbf{2}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $-97{ }^{\circ} \mathrm{C}$ showing two doublets in $0.12: 1$ ratio for the $\mathrm{N}-\mathrm{Me}$ resonances at $\delta-4.68 \mathrm{ppm}\left[{ }^{3} J(\mathrm{Tl}-\mathrm{H})=30 \mathrm{~Hz}\right]$ due to $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)^{+}$and -4.51 ppm $\left[{ }^{3} J(\mathrm{Tl}-\mathrm{H})=72 \mathrm{~Hz}\right]$ due to 2 . This ratio is quite close to 0.11 calculated from ${ }^{19} \mathrm{~F}$ NMR data. As a result of this observation, the most likely cause for the loss of cou-
pling should be due to reversible dissociation of trifluoroacetate

$$
\begin{align*}
& \mathrm{Tl}(\mathrm{~N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2} \\
& \quad \rightleftharpoons \mathrm{Tl}(\mathrm{~N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)^{+}+\mathrm{CF}_{3} \mathrm{CO}_{2}^{-} \tag{1}
\end{align*}
$$

with a moderate dissociation constant and reasonable rate at room temperature [40]. The dissociation constant of $(1.86 \pm 0.39) \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$ is evaluated at $-97{ }^{\circ} \mathrm{C}$ for reaction (1). Such a scenario would not only lead to the change in the chemical shift with temperature and detectable free $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$and $\mathrm{Tl}\left(\mathrm{N}-\mathrm{CH}_{3}-\mathrm{tpp}\right)\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)^{+}$at low temperature, but also would lead to the loss of coupling between triffuoroacetate 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 $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $17^{\circ} \mathrm{C}$ than $-106^{\circ} \mathrm{C}$. Due to poor solubility, no signals of carbonyl and $\mathrm{CF}_{3}$ carbons at $17^{\circ} \mathrm{C}$ have been found. At $-106{ }^{\circ} \mathrm{C}$, the rate of intermolecular exchange of $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$for $\mathbf{2}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ is slow. Hence, at this temperature the CO and $\mathrm{CF}_{3}$ carbons of $\mathrm{CF}_{3} \mathrm{CO}_{2}^{-}$ in 2 are observed at 155.1 ppm [with ${ }^{2} J(\mathrm{C}-\mathrm{F})=37$ and $\left.{ }^{2} J(\mathrm{Tl}-\mathrm{C})=204 \mathrm{~Hz}\right]$ and 114.3 ppm [with ${ }^{1} J(\mathrm{C}-\mathrm{F})=$ 290 and ${ }^{3} J(\mathrm{Tl}-\mathrm{C})=411 \mathrm{~Hz}$ ], respectively. These ${ }^{13} \mathrm{C}$ resonance values are quite close to that of $\mathrm{Tl}(\operatorname{tpp})\left(\mathrm{O}_{2} \mathrm{CCF}_{3}\right)$, in THF- $d_{8}$ at $-100{ }^{\circ} \mathrm{C}$, i.e. 156.5 ppm $\left[\right.$ with ${ }^{2} J(\mathrm{C}-\mathrm{F})=37$ and $\left.{ }^{2} J(\mathrm{Tl}-\mathrm{C})=128 \mathrm{~Hz}\right]$ and 115.9 ppm [with ${ }^{1} J(\mathrm{C}-\mathrm{F})=291$ and ${ }^{3} J(\mathrm{Tl}-\mathrm{C})=239$ Hz [41]. The increase in the $J(\mathrm{Tl}-\mathrm{C})$ coupling constant from 128 to 204 Hz for CO and from 239 to 411 Hz for $\mathrm{CF}_{3}$ might be in correlation to the increase in the effective nuclear charge $Z_{\text {eff }}$ of the Tl atom from $\mathrm{Tl}(\operatorname{tpp})\left(\mathrm{O}_{2} \mathrm{CCF}_{3}\right)$ to 2 and the estimated value of $Z_{\text {eff }}$ [ Tl in 2$] / Z_{\text {eff }}\left[\mathrm{Tl}\right.$ in $\left(\mathrm{Tl}(\operatorname{tpp})\left(\mathrm{O}_{2} \mathrm{CCF}_{3}\right)\right]$ is $1.18 \pm 0.02$.

In contrast, no intramolecular exchange between the two trifluoroacetate groups is observed for the related seven-coordinate bis(trifluoroacetato) complexes $\mathrm{Mo}(\mathrm{CO})_{2}\left(\mathrm{PMe}_{3}\right)_{3}\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2}[25]$ and $\mathrm{Mo}(\mathrm{CO})_{2}\left(\mathrm{PEt}_{3}\right)_{2}-$ $\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)_{2}$ [26] in dichloromethane at $27{ }^{\circ} \mathrm{C}$. Moreover, the dynamic processes involving not only intramolecular exchange between mono- and bidentate trifluoroacetate groups but also intermolecular exchange among 2, $\mathrm{Tl}(\mathrm{N}-\mathrm{Me}-\mathrm{tpp})\left(\mathrm{CF}_{3} \mathrm{CO}_{2}\right)^{+}$and $\mathrm{CF}_{3} \mathrm{CO}_{2}{ }^{-}$for 2 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ are observed. Interestingly, the dynamic properties for the exchange of trifluoroacetate in $\mathbf{2}$ is found to be very similar to the exchange of acetate group in $\mathbf{1}$ as reflected by variable temperature ${ }^{13} \mathrm{C},{ }^{1} \mathrm{H}$ and ${ }^{19} \mathrm{~F}$ NMR studies.

## 4. Conclusions

This work describes a new compound $\mathbf{2}$ being characterized by spectroscopic and crystallographic method.

The seven-coordinate thallium complex $\mathbf{2}$ is the first of its kind with a $4: 3$ 'piano stool' geometry. Dynamic ${ }^{13} \mathrm{C}$ and ${ }^{19} \mathrm{~F}$ 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 $\left(\mathrm{Tl}^{3+}\right)$ 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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[^1]:    ${ }^{\text {a }}$ Including solvate molecules
    ${ }^{\mathrm{b}} R=\left[\Sigma| | F_{\mathrm{o}}\left|-\left|F_{\mathrm{c}}\right|\right| / \Sigma\left|F_{\mathrm{o}}\right|\right]$.
    ${ }^{\mathrm{c}} R_{\mathrm{w}}=\left[\Sigma w\left(| | F_{\mathrm{o}}\left|-\left|F_{\mathrm{c}}\right|\right|\right)^{2} / \Sigma w\left(\mid F_{\mathrm{o}}\right)^{2}\right]^{1 / 2} ; w=A /\left(\sigma^{2} F_{\mathrm{o}}+B F_{\mathrm{o}}^{2}\right)$.

[^2]:    ${ }^{\text {a }}$ The published coordinates were used to project the structure onto a sphere [30] after which the usual dihedral angles $(\delta)$ between planes $[29,31]$ were calculated.

