DALTON

Molecular structure of [Tl(tpp)(O_2CCF_3)] and ^{19}F dynamic nuclear magnetic resonance of it and [Tl(tmpp)(O_2CCF_3)] [tpp = 5,10,15,20-tetraphenylporphyrinate, tmpp = 5,10,15,20-tetra(4-methoxyphenyl)-porphyrinate]

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The crystal structure of (*meso*-5,10,15,20-tetraphenylporphyrinato)(trifluoroacetato)thallium(III), [Tl(tpp)(O_2CCF_3)], was determined. The co-ordination sphere of the Tl^{3+} ion is an approximate square-based pyramid in which the apical site is occupied by an asymmetric bidentate $O_2CCF_3^-$ group. The average Tl–N bond distance is 2.200(5) Å and the Tl atom is displaced 0.741 Å from the porphyrin plane. The Tl–O(1) and Tl–O(2) distances are 2.309(7) and 2.64(1) Å, respectively. The extent of dissociation of [5,10,15,20-tetra(4-methoxyphenyl)porphyrinato](trifluoroacetato)thallium(III), [Tl(tmpp)(O_2CCF_3)], in CD_2Cl_2 was ≈4%. The free energy of activation at the coalescence temperature T_c was for the intermolecular trifluoroacetate exchange between ≈96 of [Tl(tmpp)(O_2CCF_3)] and ≈4% of CF_3CO_2H in CD_2Cl_2 solvent has been found to be $\Delta G_{238}^{\ddagger}$ 45.8 kJ mol^{-1} through ^{19}F NMR temperature-dependent measurements. However, [Tl(tmpp)(O_2CCF_3)] and its homologue [Tl(tpp)(O_2CCF_3)] do not dissociate in [$^2H_8$]tetrahydrofuran. They undergo intramolecular $CF_3CO_2^-$ exchange in this solvent and $\Delta G_{212}^{\ddagger}$ (or $\Delta G_{203}^{\ddagger}$) for this process was found to be 44.4 (or 42.0 kJ mol^{-1}) for [Tl(tpp)(O_2CCF_3)] {or [Tl(tmpp)(O_2CCF_3)]} from ^{19}F dynamic NMR spectroscopy. In the slow-exchange region the CF_3 and carbonyl (CO) carbons of the $CF_3CO_2^-$ group in [Tl(tpp)(O_2CCF_3)] are separately located at δ 115.9 [^1J(C–F) = 291, ^3J(Tl–^{13}C) = 239] and 156.5 [^2J(C–F) = 37, ^2J(Tl–^{13}C) = 128 Hz] at −100 °C.

Although the molecular stereochemistry of (*meso*-5,10,15,20-tetraphenylporphyrinato)(trifluoroacetato)iron(III), [Fe(tpp)(O_2CCF_3)],[1] the synthesis and ^1H NMR spectra of [Tl(tpp)(O_2CCF_3)] and [5,10,15,20-tetra(4-methoxyphenyl)-porphyrinato](trifluoroacetato)thallium(III), [Tl(tmpp)(O_2CCF_3)],[2] the ^{13}C NMR spectra of alkyl-substituted aryl thallium bis(trifluoroacetates), [TlR(O_2CCF_3)$_2$],[3–6] and the ^{19}F NMR spectra of [Tl(C_6H_4F-*p*)(O_2CCF_3)$_2$] and [Tl(C_6H_4F-*p*)$_2$(O_2CCF_3)] have been reported,[5] these studies disregarded the ^{19}F NMR spectra of the trifluoroacetate in the complexes. We were interested in the trifluoroacetate exchange in [Tl(tpp)(O_2CCF_3)] and [Tl(tmpp)(O_2CCF_3)]. The molecular structure and dynamic ^1H NMR studies of their acetato homologues [Tl(tpp)(O_2CMe)][7,8] and acetato[*meso*-5,10,15,20-tetra(4-pyridyl)porphyrinato]thallium(III), [Tl(tpyp)-(O_2CMe)],[9] have been reported by our group. It turned out that the acetate exchange in [Tl(tpp)(O_2CMe)] in CD_2Cl_2 was intramolecular,[7,8] whereas that in [Tl(tpyp)(O_2CMe)] in the same solvent was intermolecular.[9] The driving force for the intermolecular exchange might be hydrogen bonding between [Tl(tpyp)(O_2CMe)] and acetic acid. In the cases of [Tl(tpp)(O_2CCF_3)] and [Tl(tmpp)(O_2CCF_3)], in the presence of CF_3CO_2H, there might be a similar hydrogen bonding between the trifluoroacetate O of these two complexes and carboxy H of CF_3CO_2H. They could undergo intermolecular trifluoroacetate exchange in CD_2Cl_2 or [$^2H_8$]tetrahydrofuran ([$^2H_8$]thf). In the absence of CF_3CO_2H the intramolecular exchange might be the chief exchange mechanism for these two complexes in [$^2H_8$]thf.

In this paper ^1H and ^{13}C NMR spectroscopic studies of [Tl(tpp)(O_2CCF_3)] and [Tl(tmpp)(O_2CCF_3)] and an X-ray analysis of [Tl(tpp)(O_2CCF_3)] are reported. The ^{19}F NMR spectra of [Tl(tmpp)(O_2CCF_3)] in CD_2Cl_2 (or in [$^2H_8$]thf) and [Tl(tpp)(O_2CCF_3)] in [$^2H_8$]thf at low temperature were examined to infer the inter- and intra-molecular apical ligand exchange and to determine the free energy of activation at the coalescence temperature, $\Delta G_{Tc}^{\ddagger}$, for the exchange process.

Experimental

Preparation of the complexes

The complexes were prepared as previously reported.[2] Crystals of [Tl(tpp)(O_2CCF_3)], were grown by diffusion of diethyl ether vapour into a CH_2Cl_2 solution. Both complexes were dissolved in $CDCl_3$ (99.8% from Aldrich), in CD_2Cl_2 (99.95% from Aldrich) or in [$^2H_8$]thf (99.5% from Aldrich). The freshly prepared solutions were poured into several 5 mm NMR tubes. The tubes were then flame-sealed for ^1H, ^{13}C or ^{19}F NMR measurement.

NMR spectra

Proton and ^{13}C NMR spectra in $CDCl_3$, CD_2Cl_2 or [$^2H_8$]thf were recorded at 300.00 (400.13 or 600.20) and 75.47 (100.61 or 150.92) MHz, respectively, on a Bruker MSL-300 (AM-400 or DMX-600) spectrometer locked on solvent deuterium, and referenced to the solvent peak. The ^{19}F NMR spectra were measured in CD_2Cl_2 (or [$^2H_8$]thf) at 282.40, 376.50 or 564.71 MHz, respectively, on a Bruker MSL-300, AM-400 or DMX-600 spectrometer. Proton and ^{13}C NMR are relative to $CDCl_3$, CD_2Cl_2 or [$^2H_8$]thf at δ 7.24, 5.30 or 1.73 and the centre line of $CDCl_3$, CD_2Cl_2 or [$^2H_8$]thf at δ 77.0, 53.6 or 25.3; ^{19}F data are externally relative to $CFCl_3$. The temperature of the spectrometer probe was calibrated by the shift difference of the methanol resonance in the ^1H NMR spectrum.

Crystallography

Crystal data. [Tl(tpp)(O_2CCF_3)]·CH_2Cl_2, $C_{47}H_{30}Cl_2F_3N_4O_2Tl$, M = 1015.0, triclinic, space group $P\bar{1}$, a = 11.127(2),

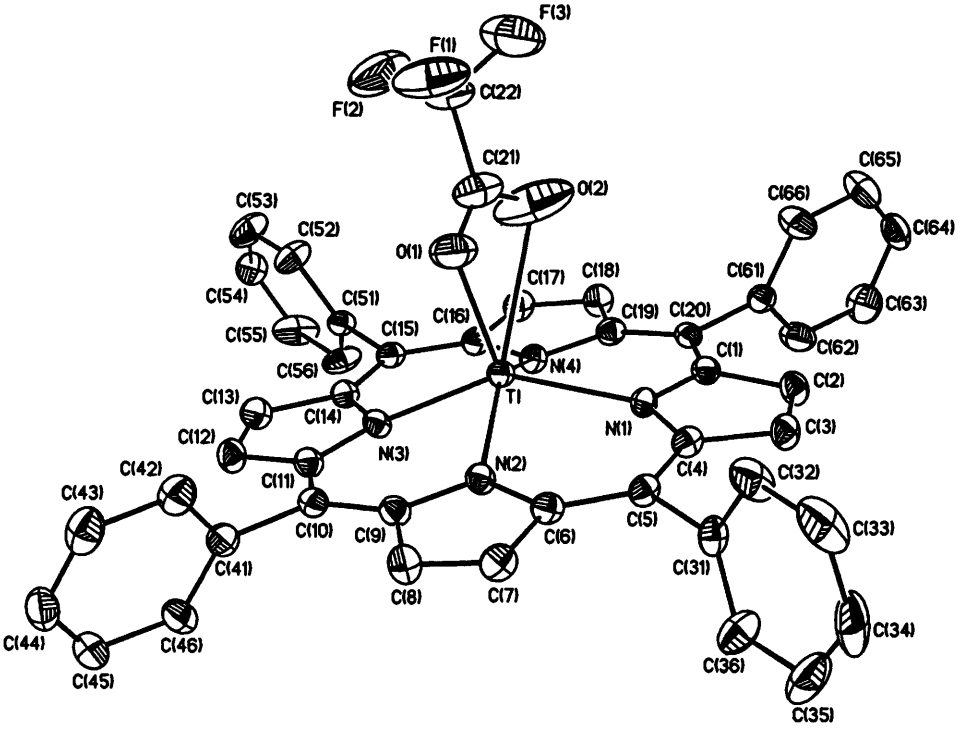


Fig. 1 Molecular configuration and atom labelling scheme for $[Tl(tpp)(O_2CCF_3)]\cdot CH_2Cl_2$. Hydrogen atoms and solvent C(71)H(71A)H(71B)-Cl(1)Cl(2) are omitted for clarity

b = 13.297(3), c = 14.706(3) Å, α = 97.51(2), β = 94.44(2), γ = 103.80(2)°, U = 2081.5(8) Å^3, Z = 2, D_c = 1.619 g cm^{-3}, $F(000)$ = 996, μ(Mo-Kα) = 40.66 cm^{-1}, 293 K.

Data collection, structure solution and refinement. X-Ray diffraction data were collected from a crystal of dimensions 0.3 × 0.5 × 0.7 mm on a Siemens R3m/V diffractometer by using crystal-monochromatized Mo-Kα radiation (λ = 0.710 73 Å). The θ–2θ scan technique was used. Of 7682 unique reflections collected up to $2\theta_{max}$ = 50°, 6434 with $F > 4\sigma(F)$ were considered observed and used in the structure analysis. Semiempirical absorption corrections were applied. The structure was solved by direct methods (SHELXTL PLUS).[10] Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms gave residuals R = 0.040 and R' = 0.054 {where $R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$ and $R' = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$}. The weighting scheme was $w = [\sigma^2(F) + 0.002F^2]^{-1}$. Hydrogen atom coordinates were calculated using a riding model and included in the refinement (based on F). Selected bond distances and angles are given in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/183.

Results and Discussion

Molecular structure of $[Tl(tpp)(O_2CCF_3)]$

The skeletal framework of the complex $[Tl(tpp)(O_2CCF_3)]\cdot CH_2Cl_2$, with $P\bar{1}$ symmetry, is illustrated in Fig. 1. It reveals the six-co-ordination of the thallium atom with four nitrogen atoms of the porphyrinato group and the asymmetric bidentate $O_2CCF_3^-$ ligand. Bond distances (Table 1) are: Tl–O(1) 2.309(7), Tl–O(2) 2.64(1), O(1)–C(21) 1.14(2), O(2)–C(21) 1.21(2), C(21)–C(22) 1.51(2), C(22)–F(1) 1.27(1), C(22)–F(2) 1.28(1), C(22)–F(3) 1.30(2) and mean Tl–N 2.200(5) Å.

Table 1 Selected bond distances (Å) and angles (°) for $[Tl(tpp)(O_2CCF_3)]$

Tl–O(1)	2.309(7)	C(22)–F(2)	1.28(1)
Tl–O(2)	2.64(1)	C(22)–F(3)	1.30(2)
O(1)–C(21)	1.14(2)	Tl–N(1)	2.184(5)
O(2)–C(21)	1.21(2)	Tl–N(2)	2.212(5)
C(21)–C(22)	1.51(2)	Tl–N(3)	2.197(5)
C(22)–F(1)	1.27(1)	Tl–N(4)	2.206(5)
Tl–O(1)–C(21)	104.7(8)	O(1)–Tl–N(1)	112.5(2)
Tl–O(2)–C(21)	85.9(9)	O(1)–Tl–N(2)	94.9(2)
O(1)–C(21)–O(2)	120(1)	O(1)–Tl–N(3)	101.8(2)
O(1)–C(21)–C(22)	120(1)	O(1)–Tl–N(4)	121.9(2)
O(2)–C(21)–C(22)	120(1)	O(2)–Tl–N(1)	91.3(3)
C(21)–C(22)–F(1)	114.3(8)	O(2)–Tl–N(2)	137.1(3)
C(21)–C(22)–F(2)	110(1)	O(2)–Tl–N(3)	119.1(3)
C(21)–C(22)–F(3)	111(1)	O(2)–Tl–N(4)	78.6(3)
F(1)–C(22)–F(2)	109(1)	N(1)–Tl–N(2)	84.7(2)
F(1)–C(22)–F(3)	104(1)	N(1)–Tl–N(3)	144.7(2)
F(2)–C(22)–F(3)	107.8(9)	N(1)–Tl–N(4)	84.8(2)
O(1)–Tl–O(2)	47.8(3)	N(2)–Tl–N(3)	84.2(2)
N(3)–Tl–N(4)	84.2(2)	N(2)–Tl–N(4)	143.0(2)

The thallium atom lies 0.683 and 0.741 Å from the four porphyrin nitrogens and the 24-atom porphyrin plane ($C_{20}N_4$), respectively. The dihedral angles between the mean planes of the skeleton ($C_{20}N_4$) and the planes of the phenyl groups are 82.4 [C(34)], 70.2 [C(44)], 73.8 [C(54)] and 76.3° [C(64)].

The radius of the central 'hole' ($C_t \cdots N$, distance from the geometrical centre of the mean plane of the 24-atom core to the porphyrinato-core N atoms) in $[Tl(tpp)(O_2CCF_3)]$ is 2.092 Å which is larger than 2.01 Å suggested by Collins and Hoard.[11] The thallium(III) is bonded in a highly expanded porphyrinato core ($C_{20}N_4$) and the porphyrin ($C_{20}N_4$ and Tl) can be regarded as dome shaped. The net doming is ≈0.06 Å (=0.741 − 0.683). Fig. 2 shows the displacement (in Å) of each atom of the porphyrin ($C_{20}N_4$ and Tl) from the porphyrin mean plane ($C_{20}N_4$). The structure of $[Tl(tpp)(O_2CCF_3)]$ is quite different from that of $[Fe(tpp)(O_2CCF_3)]$. The core of the

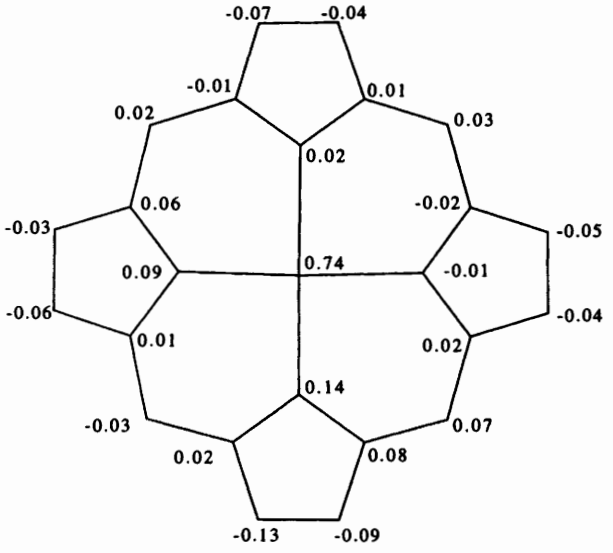
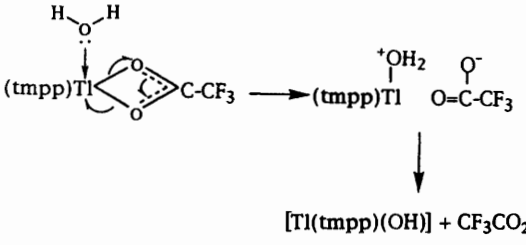


Fig. 2 Diagram of the porphyrin core ($C_{20}N_4$ and Tl) of [Tl(tpp)(O_2CCF_3)] showing the displacement (in Å) of the atoms from the mean plane of the porphyrin ($C_{20}N_4$)



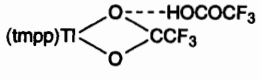
Scheme 1

former complex is domed whereas that of the latter complex is a pronounced S_4 ('sad') ruffling.[1] In [Tl(tpp)(O_2CCF_3)] the $O_2CCF_3^-$ is asymmetrically and bidentately co-ordinated to the Tl atom whereas in [Fe(tpp)(O_2CCF_3)] it is unidentate.[1]

^{19}F Dynamic NMR investigation

***(i)* [Tl(tmpp)(O_2CCF_3)] in CD_2Cl_2.** The results of the ^{19}F dynamic NMR studies of [Tl(tmpp)(O_2CCF_3)] in CD_2Cl_2 revealed two stages. The first stage is possibly comprised of hydrolysis of [Tl(tmpp)(O_2CCF_3)] [equation (1)] and

$$[Tl(tmpp)(O_2CCF_3)] + H_2O \longrightarrow [Tl(tmpp)(OH)] + CF_3CO_2H \quad (1)$$



(2)

hydrogen bonding between trifluoroacetate O and CF_3CO_2H [equation (2)] where water comes from the CD_2Cl_2 solvent. The production of CF_3CO_2H upon hydrolysis is supported by several reproducible observations of 4% dissociation of [Tl(tmpp)(O_2CCF_3)] in a CD_2Cl_2-saturated solution at −70 °C. A hydration constant of (2.31 ± 0.06) × 10^{-4} mol dm^{-3} is evaluated at this temperature. The second stage involves reversible intermolecular chemical exchange of the $CF_3CO_2^-$ ligand between [Tl(tmpp)(O_2CCF_3)] and CF_3CO_2H. The mechanism of reaction (1) is given in Scheme 1.

When a 0.02 mol dm^{-3} solution of [Tl(tmpp)(O_2CCF_3)] in CD_2Cl_2 (Fig. 3) was cooled the ^{19}F signal of $CF_3CO_2^-$, a single peak at 20 °C (δ −75.35), first broadened (coalescence temperature T_c = 238 K) and then split into two sets of peaks (singlet at δ −78.07 and doublet at −75.09) of separation 842 Hz at a frequency of 282.40 MHz. At −70 °C the single peak at δ −78.07 corresponds to the trifluoroacetic acid (CF_3CO_2H);

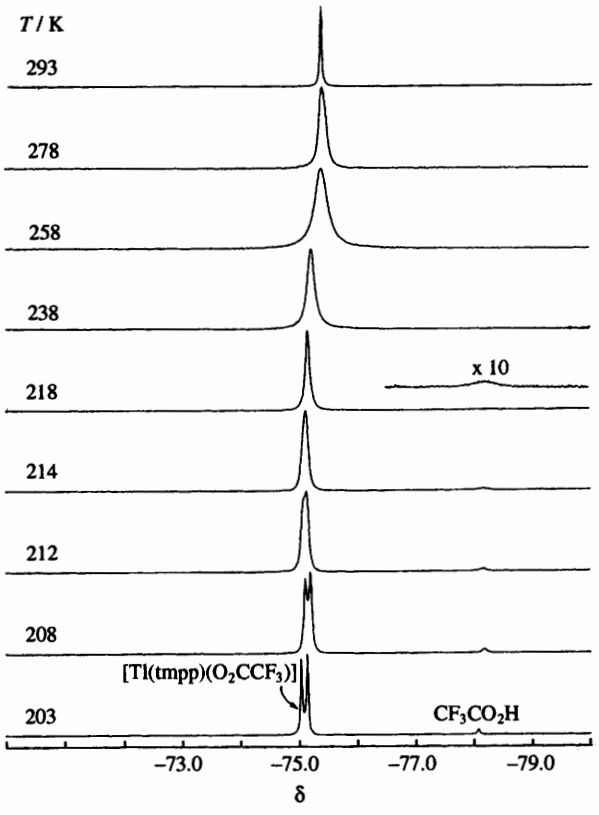


Fig. 3 The 282.40 MHz ^{19}F NMR spectra for the axial $CF_3CO_2^-$ of [Tl(tmpp)(O_2CCF_3)] and for CF_3 of CF_3CO_2H in CD_2Cl_2 at various temperatures

the other doublet peak at δ −75.09, with a separation of 29.8 Hz, is due to a ^4J(Tl–^{19}F) coupling of [Tl(tmpp)(O_2CCF_3)]. As the exchange of $CF_3CO_2^-$ between [Tl(tmpp)(O_2CCF_3)] and CF_3CO_2H is reversible, this intermolecular process can be treated as a two-site exchange;[12] by taking into account the unequal populations of the two sites, *i.e.* ≈96% of [Tl(tmpp)(O_2CCF_3)] and ≈4% of CF_3CO_2H, a comparison of observed and computed spectra yields $\Delta G_{238}^{\ddagger}$ = 45.8 kJ mol^{-1}.

For [Tl(tmpp)(O_2CCF_3)] in CD_2Cl_2 the rate-determining step for stage 1 could either be a bimolecular exchange as in equation (1) or a unimolecular dissociation of the complex [equation (3)] followed by protonation of $O_2CCF_3^-$ [equation (4)]. Since the equilibrium constant for protonation of

$$[Tl(tmpp)(O_2CCF_3)] \longrightarrow [Tl(tmpp)]^+ + CF_3CO_2^- \quad (3)$$

$$CF_3CO_2^- + H_2O \rightleftharpoons CF_3CO_2H + OH^- \quad (4)$$

$CF_3CO_2^-$ with free water molecules in solution [equation (4)] is ≈3.85 × 10^{-14} mol dm^{-3} at 25 °C the forward reaction is a difficult process. If the unimolecular dissociation [equation (3)] and protonation of $O_2CCF_3^-$ [equation (4)] is the chief mechanism, then we cannot explain the observation of CF_3CO_2H originating from the hydrolysis of [Tl(tmpp)(O_2CCF_3)] in CD_2Cl_2 solvent. Obviously the mechanism of unimolecular dissociation is inconsistent with the experimental result.

***(ii)* [Tl(tpp)(O_2CCF_3)] in [$^2H_8$]thf.** When a 3 × 10^{-2} mol dm^{-3} solution of [Tl(tpp)(O_2CCF_3)] in CD_2Cl_2 was cooled at a spectral frequency of 564.71 MHz, the ^{19}F signal of $CF_3CO_2^-$, a sharp single peak at 20 °C (δ −75.52, $\Delta\nu_{\frac{1}{2}}$ = 2 Hz), became a broad singlet at −90 °C with $\Delta\nu_{\frac{1}{2}}$ = 66 Hz. It appears that the coalescence temperature (T_c) for the $CF_3CO_2^-$ exchange of [Tl(tpp)(O_2CCF_3)] in CD_2Cl_2 is considerably lower than

−90 °C. Hence, [Tl(tpp)(O_2CCF_3)] was dissolved in [$^2H_8$]thf for a much lower temperature measurement. When a 0.025 mol dm^{-3} solution of [Tl(tpp)(O_2CCF_3)] in [$^2H_8$]thf (Fig. 4) was cooled the ^{19}F signal of $CF_3CO_2^-$, a single peak at 20 °C, first broadened (T_c = 212 K) then split into two peaks with a separation of 28.6 Hz at −100 °C. As the exchange of $CF_3CO_2^-$ within [Tl(tpp)(O_2CCF_3)] is reversible, the results at 376.50 MHz confirm the separation as a coupling $^4J(Tl-^{19}F)$ rather than a chemical shift difference. The only fluorine species observed by ^{19}F NMR spectroscopy is [Tl(tpp)(O_2CCF_3)] and the chemical shifts in fast exchange at temperatures above T_c are between two resonances in slow exchange at −100 °C. This is an intramolecular exchange process. A comparison of observed and computed spectra yields $\Delta G_{212}^{\ddagger}$ = 44.4 kJ mol^{-1}.[12]

The complex [Tl(tpp)(O_2CCF_3)] does not hydrolyse in [$^2H_8$]thf or CD_2Cl_2. Hence, the exchange of $CF_3CO_2^-$ for [Tl(tpp)(O_2CCF_3)] in [$^2H_8$]thf (or CD_2Cl_2) solvent is intramolecular. If ≈0.05 cm^3 CF_3CO_2H is intentionally added to the solution of [Tl(tpp)(O_2CCF_3)] in [$^2H_8$]thf (or CD_2Cl_2) the $CF_3CO_2^-$ exchange switches from intra- to inter-molecular (Fig. 5). At −100 °C the singlet peak with a population of 90% at δ −76.70 corresponds to the added CF_3CO_2H and the other doublet peak with population 10% at δ −75.13 and a separation of 27.2 Hz shown in Fig. 5(*b*) is due to [Tl(tpp)(O_2CCF_3)]. These two peaks arise from slow exchange of $CF_3CO_2^-$ between [Tl(tpp)(O_2CCF_3)] and CF_3CO_2H. The slow-exchange limit should be at temperatures below −100 °C. At 20 °C the sharp singlet in Fig. 5(*a*) is due to fast exchange of $CF_3CO_2^-$ between the former two compounds. The key step for the occurrence of intermolecular $CF_3CO_2^-$ exchange in the complexes [Tl(tpp)(O_2CCF_3)] and [Tl(tmpp)(O_2CCF_3)] is the existence of CF_3CO_2H either externally added or initially present or from hydrolysis.

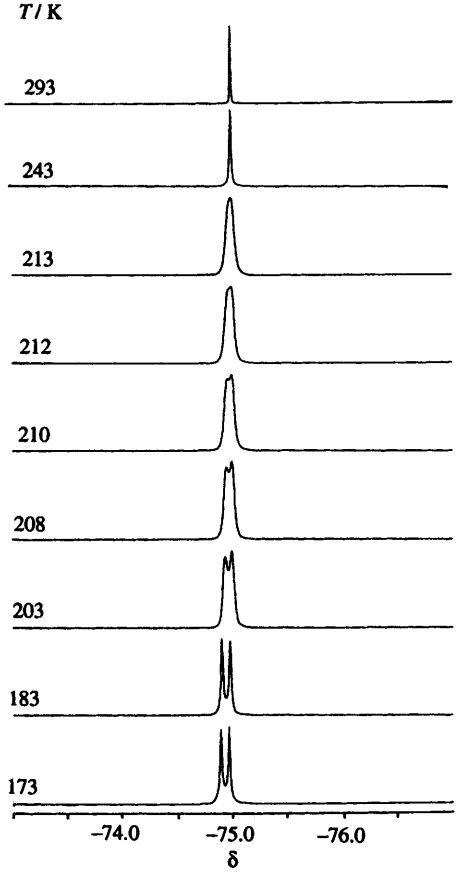
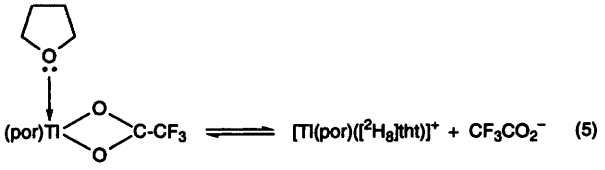


Fig. 4 The 376.50 MHz ^{19}F NMR spectra for [Tl(tpp)(O_2CCF_3)] in [$^2H_8$]thf at various temperatures

***(iii)* [Tl(tmpp)(O_2CCF_3)] in [$^2H_8$]thf.** The complex [Tl(tmpp)(O_2CCF_3)] does not hydrolyse in [$^2H_8$]thf. It undergoes intramolecular $CF_3CO_2^-$ exchange in this solvent; $\Delta G_{203}^{\ddagger}$ = 42.0 kJ mol^{-1} from ^{19}F dynamic NMR at a frequency of 282.40 MHz {the ^{19}F NMR spectra of [Tl(tmpp)(O_2CCF_3)] in [$^2H_8$]thf at various temperatures are available from the authors on request}.

In [$^2H_8$]thf solvent [Tl(por)(O_2CCF_3)] (por = tpp or tmpp) is solvated by a better nucleophile as in equations (5) and (4). As



described above, the forward reaction of equation (4) is a forbidden process, therefore the $CF_3CO_2^-$ formed in (5) recombines with [Tl(por)([$^2H_8$]thf)]$^+$. This explains why the exchange of $CF_3CO_2^-$ with [Tl(por)(O_2CCF_3)] in [$^2H_8$]thf is intramolecular. Overall, the mechanism of bimolecular exchange [shown in equations (1) and (5)] explains not only the presence of CF_3CO_2H and [Tl(tmpp)(O_2CCF_3)] in CD_2Cl_2 but also the absence of CF_3CO_2H in solutions of [Tl(por)(O_2CCF_3)] in [$^2H_8$]thf.

^{13}C and ^1H NMR spectra

The ^{13}C NMR data for [Tl(tmpp)(O_2CCF_3)] and [Tl(tpp)(O_2CCF_3)] in CD_2Cl_2, $CDCl_3$ or [$^2H_8$]thf at two temperatures appear in Table 2. At 20 °C intermolecular exchange of the $CF_3CO_2^-$ group is rapid, indicated by quartet signals due to carbonyl carbons at δ 157.4 with $^2J(^{13}C-F)$ = 37 Hz and CF_3 carbons at δ 115.2 with $^1J(^{13}C-F)$ = 290 Hz for [Tl(tmpp)(O_2CCF_3)] in CD_2Cl_2, but no $Tl-^{13}C$ splitting was observed. Likewise, at 20 °C, intramolecular exchange of the $CF_3CO_2^-$ group is rapid, indicated by quartet signals due to both carbonyl carbons [δ 157.5, $^2J(^{13}C-F)$ = 38 Hz] and CF_3 carbons [δ 115.0, $^1J(^{13}C-F)$ = 290 Hz] for [Tl(tpp)(O_2CCF_3)] in $CDCl_3$ shown in Fig. 6(*a*), but still no $Tl-^{13}C$ splitting was

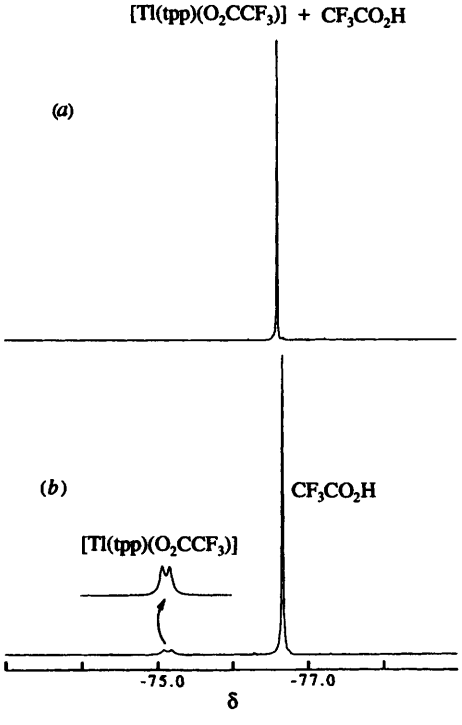


Fig. 5 The 282.40 MHz ^{19}F NMR spectra for [Tl(tpp)(O_2CCF_3)] + ≈0.05 cm^3 CF_3CO_2H in [$^2H_8$]thf at (*a*) 20 and (*b*) −100 °C

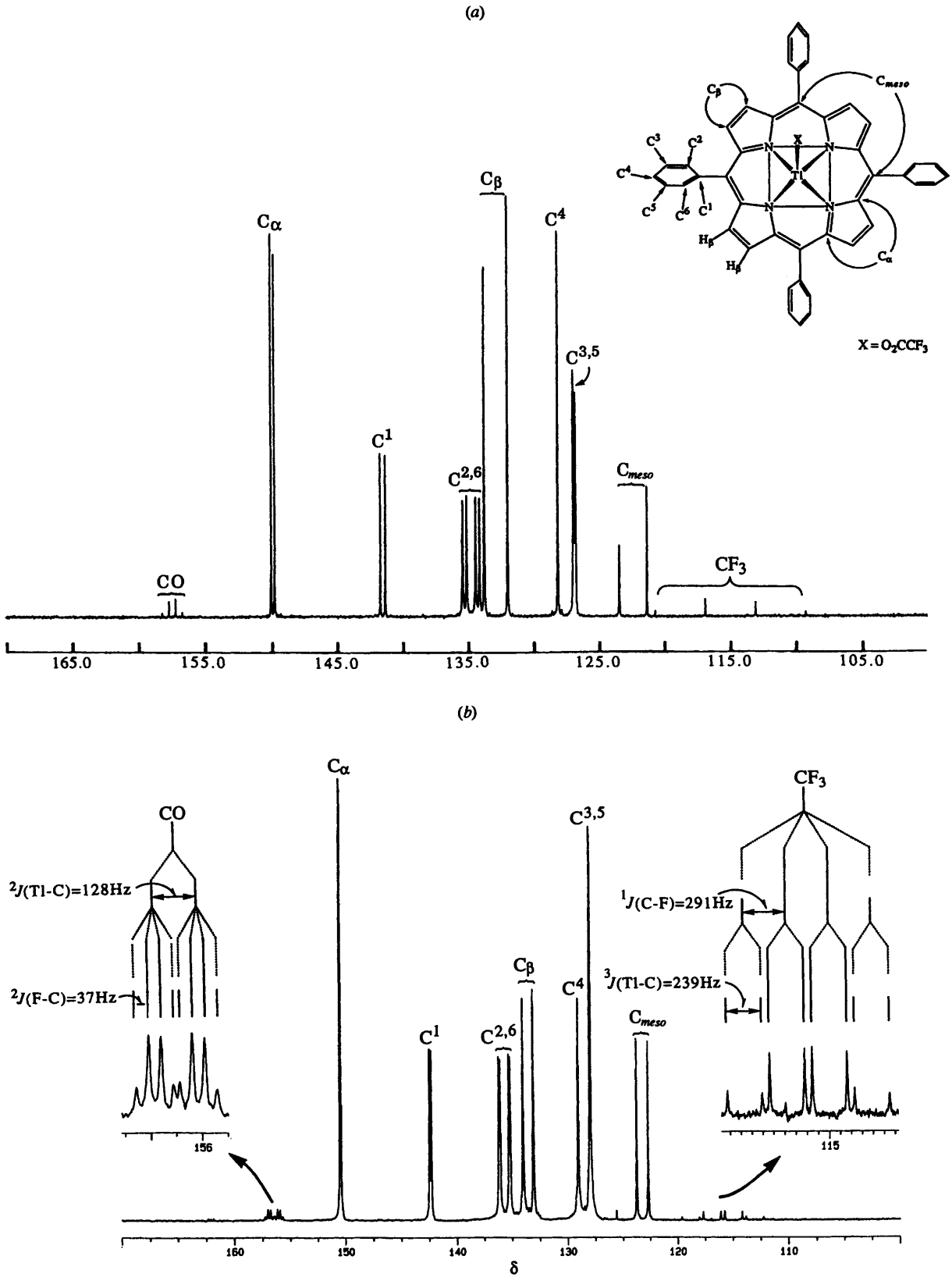


Fig. 6 The ^{13}C broad-band NMR spectra for [Tl(tpp)(O_2CCF_3)]: (*a*) in $CDCl_3$ at 20 °C (75.47 MHz), (*b*) in [$^2H_8$]thf at −100 °C (150.92 MHz)

observed. The $^1J(^{13}C–F)$ and $^2J(^{13}C–F)$ coupling constants of CF_3 and CO for [Tl(tpp)(O_2CCF_3)] and [Tl(tmpp)(O_2CCF_3)] at 20 °C are quite similar to those of [TlR(O_2CCF_3)$_2$] (R = aryl) whereas the resonances of CF_3 and CO for the former complexes are upfield compared with those of the latter complex [δ 118.5 ± 0.2, $^1J(^{13}C–F)$ 289.3 ± 2.3 Hz for CF_3; δ 161.2 ± 1.3, $^2J(^{13}C–F)$ = 38.5 ± 2.6 Hz for CO].[4,5]

At −100 °C the rate of intramolecular exchange of $CF_3CO_2^-$ for [Tl(tpp)(O_2CCF_3)] in [$^2H_8$]thf is 1 Hz. This is slow comparable with the coupling frequency of Tl–^{13}C, *i.e.* 184 ± 56 Hz. Hence, the CO and CF_3 carbons of $CF_3CO_2^-$ in [Tl(tpp)(O_2CCF_3)] shown in Fig. 6(*b*) are observed at δ 156.5 [$^2J(^{13}C–F)$ = 37 and $^2J(Tl–^{13}C)$ = 128 Hz] and 115.9 [$^1J(^{13}C–F)$ = 291 and $^3J(Tl–^{13}C)$ = 239 Hz], respectively.

Table 2 Carbon-13 NMR chemical shifts (δ) and thallium–carbon coupling constants (J in Hz) of [Tl(tmpp)(O_2CCF_3)] and [Tl(tpp)(O_2CCF_3)] in CD_2Cl_2, $CDCl_3$ or [$^2H_8$]thf *

Compound	T/°C	C^4	C_α	$C^{2,6}$ ($C^{2,2'}$)		C^1	C_β	C_{meso}	$C^{3,5}$ ($C^{3,3'}$)	p-OCH_3	$COCF_3$	$COCF_3$
[Tl(tpp)(O_2CCF_3)]	20	128.1	149.9	135.2	134.2	141.5	132.8	122.4	126.9	—	115.0	157.5
in $CDCl_3$			(20)	(24)	(23)	(29)	(135)	(161)	126.8		^1J(C–F) = 290	^2J(C–F) = 38
in [$^2H_8$]thf	−100	129.1	150.5	136.1	135.2	142.4	133.6	123.2	128.0	—	115.9	156.5
			(9)	(19)	(19)	(26)	(140)	(159)	127.9		^1J(C–F) = 291	^2J(C–F) = 37
											^3J(Tl–C) = 239	^2J(Tl–C) = 128
[Tl(tmpp)(O_2CCF_3)]	20	160.1	150.4	136.5	135.7	134.0	132.9	122.4	112.7	55.8	115.2	157.4
in CD_2Cl_2			(20)	(23)	(23)	(29)	(134)	(159)	112.5		^1J(C–F) = 290	^2J(C–F) = 37
	−90	158.5	149.0	135.8	135.3	132.6	132.3	121.5	111.6	55.0	—	—
			(17)	(21)	(21)	(28)	(139)	(160)	111.4			

* Chemical shifts in ppm relative to the centre line of CD_2Cl_2 at δ 53.6, to the centre line of $CDCl_3$ at δ 77.0 or to the centre line of the upfield resonance of [$^2H_8$]thf at δ 25.3. Values in parentheses beneath are J(Tl–^{13}C) coupling constants in Hz unless specified.

Table 3 Proton chemical shifts (δ) and thallium–proton coupling constants (J in Hz) for [Tl(tmpp)(O_2CCF_3)] and [Tl(tpp)(O_2CCF_3)] in CD_2Cl_2 [a]

Compound	T/°C	H_β (β-pyrrole)	$H^{2,6}$ (*o*-H)		$H^{3,5}$ (*m*-H)		H^4 (*p*-H)	p-OCH_3
[Tl(tmpp)(O_2CCF_3)]	20	9.14 (72)	8.25 (7) [b]	8.05 (7)	7.34 (6) [b]	7.28 (7)	—	4.06
in CD_2Cl_2	−70	9.13 (76)	8.19 (7)	7.93 (8)	7.27 (7)	7.13 (8)	—	3.93
	r.t. [c]	9.10 (67)	8.15 (m)		7.27 (m)		—	4.18
[Tl(tpp)(O_2CCF_3)]	20	9.17 (73)	8.39 (s) [d]	8.20 (s)	7.82 (m) [d]			—
in CD_2Cl_2	−70	9.21 (76)	8.37 (5)	8.15 (7)	7.79 (m)		7.72 (6)	—
	r.t. [c]	9.09 (73)	8.26 (m)		7.82 (m)			—

[a] Chemical shifts in ppm relative to CD_2Cl_2 at δ 5.3. Values in parentheses are J(Tl–H) coupling constants in Hz. [b] ^3J(H–H)/Hz. [c] Room temperature; from ref. 2. [d] s = Singlet, m = multiplet.

Low solubility precluded observation of these ^{13}C resonances at −90 °C for [Tl(tmpp)(O_2CCF_3)] in [$^2H_8$]thf or CD_2Cl_2.

The intermolecular (or intramolecular) exchange of the $CF_3CO_2^-$ group is rapid for [Tl(tmpp)(O_2CCF_3)] {or [Tl(tpp)(O_2CCF_3)]} in CD_2Cl_2 (or $CDCl_3$) at 20 °C, whereas rotation of the anisole (or phenyl) group along C^1–C_{meso} bond is slow at the same temperature on the NMR time-scale for both compounds. This is supported either by the assignment of the peaks at δ 135.2, 134.2 (or 136.5, 135.7) to the $C^{2,6}$ carbons and 126.9, 126.8 (or 112.7, 112.5) due to the $C^{3,5}$ carbons (shown in Table 2) or by the assignment of the peaks of δ 8.25, 8.05 (or 8.39, 8.20) to the $H^{2,6}$ protons and 7.34, 7.28 (or 7.82) due to $H^{3,5}$ protons (in Table 3) for [Tl(tmpp)(O_2CCF_3)] {or [Tl(tpp)(O_2CCF_3)]}. Inequivalent *o*- and *m*-H protons at 20 °C (Table 3) are observed for [Tl(tpp)(O_2CCF_3)] and [Tl(tmpp)(O_2CCF_3)] in this work while the literature data appear to show average values at room temperature.[2]

Conclusion

Trifluoroacetic acid results from the hydrolysis of [Tl(tmpp)(O_2CCF_3)] in CD_2Cl_2, and both compounds, CF_3CO_2H and [Tl(tmpp)(O_2CCF_3)], undergo intermolecular $CF_3CO_2^-$ exchange. Neither complex [Tl(tpp)(O_2CCF_3)] nor [Tl(tmpp)(O_2CCF_3)] hydrolyse in [$^2H_8$]thf and they undergo intramolecular $CF_3CO_2^-$ exchange in this solvent. It is unclear why [Tl(tmpp)(O_2CCF_3)] hydrolyses to CF_3CO_2H in CD_2Cl_2 but [Tl(tpp)(O_2CCF_3)] doesn't. Nevertheless this may be related to electron donation from the methoxy group in [Tl(tmpp)(O_2CCF_3)] to the Tl^{3+} atom through the conjugated π system. This disperses the positive charge on Tl, weakens the Tl–O bond, and enhances the production of CF_3CO_2H in CD_2Cl_2 solvent through equation (1). Furthermore, this is the first report of the observation of ^{13}C NMR data at low temperature for the intramolecular $CF_3CO_2^-$ exchange of [Tl(tpp)(O_2CCF_3)].

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