



Salicylate exchange in *meso*-tetraphenylporphyrinato salicylato thallium(III), Tl(tpp)(2-OH-C₆H₄CO₂) and ¹³C NMR investigation of its homolog thiocyanato (*meso*-tetra-*p*-tolylporphyrinato)thallium(III), Tl(tptp)(SCN)

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Abstract

This work determines the crystal structure of *meso*-tetraphenylporphyrinato salicylato thallium(III), Tl(tpp)(2-OH-C₆H₄CO₂) (or Tl(tpp)(SA)). The coordination sphere of the Tl³⁺ ion is an approximately square-based pyramid in which a chelating bidentate 2-OH-C₆H₄CO₂⁻ group occupies the apical site. The average Tl(1)–N bond distance is 2.221 Å and the Tl atom is displaced 0.76 Å from the porphyrin plane. The Tl(1)–O(1) and Tl(1)–O(2) distance are 2.36(1) and 2.47(1) Å, respectively. Variable temperature ¹³C NMR measurements reveal that the salicylato group of Tl(tpp)(SA) in CD₂Cl₂ solvent undergoes a ligand exchange. In the slow exchange region, the carbonyl and C_{1'} carbons of the salicylato group are separately located at 169.6 ppm [with a ²J(Tl–¹³C) coupling constant of 157 Hz] and 111.5 ppm [with a ³J(Tl–¹³C) coupling constant of 180 Hz] for Tl(tpp)(SA) in CD₂Cl₂ at –90°C. In the fast exchange region, the C*O and C_{1'} carbons of the 2-OH-C₆H₄CO₂⁻ ligand in CD₂Cl₂ at 24°C are singlets at 169.8 and 112.5 ppm, respectively. The ¹³C resonance of the axial isocyanato ligand in the compound thiocyanato (*meso*-tetra-*p*-tolylporphyrinato)thallium(III), Tl(tptp)(SCN), was observed at 110.7 ppm (24°C) with ²J(Tl–¹³C) coupling constant 253 Hz. This finding suggests that thiocyanato group is, as thiocyanate type, axially coordinated to the Tl atom in Tl(tptp)(SCN). In addition, there is no SCN⁻ exchange in the same compound. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Crystal structure; Thallium porphyrin complexes; *cis* geometries; Salicylato ligand; Low temperature ¹³C NMR analysis; Ligand exchange

1. Introduction

Our earlier work reported on the benzoate exchange in benzoato *meso*-tetra(4-methoxyphenylporphyrinato)thallium(III), Tl(tmpp)(C₆H₅CO₂) [1]. When replacing C₆H₅CO₂⁻ with the salicylate group, 2-OH-C₆H₄CO₂⁻, and replacing tmpp with tpp, the complex Tl(tmpp)(C₆H₅CO₂) became *meso*-tetraphenylporphyrinato salicylato thallium(III), Tl(tpp)(2-OH-C₆H₄CO₂) (**1**) [or Tl(tpp)(SA)]. The benzoate exchange of Tl(tmpp)(C₆H₅CO₂) encourages us to investigate a similar salicylato exchange for Tl(tpp)(SA).

In a related work, Senge *et al.* [2] reported on *meso*-tetraphenylporphyrinato thiocyanatothallium(III),

Tl(tpp)(SCN), and *meso*-tetra(4-methoxyphenylporphyrinato)thiocyanatothallium(III), Tl(tmpp)(SCN). Both complexes are thallium (III) complexes with the thiocyanate, SCN⁻, being unidentately coordinated to Tl atom. When replacing the tpp and tmpp with *meso*-tetra-*p*-tolylporphyrin (tptp), they became thiocyanato (*meso*-tetra-*p*-tolylporphyrinato) thallium(III), Tl(tptp)(SCN) (**2**). That investigation also reported on the synthesis, ¹³C and ¹H NMR spectroscopic studies of the new complex (**2**). The ¹³C signal of SCN⁻ unambiguously solve the dichotomy of thiocyanate vs isothiocyanate binding to the thallium centre.

In the light of above discussion, this work performs ¹H and X-ray analysis of **1**. The ¹³C NMR spectra at a low temperature are examined to infer the apical ligand, 2-OH-C₆H₄CO₂⁻, exchange for **1** in CD₂Cl₂. In addition, the exchange for *cis* bidentately 6-coordinate thal-

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lium(III) complex (**1**) is compared with the no exchangeable axial ligand for monodentately 5-coordinate thallium (III) complex (**2**).

2. Experimental

2.1. Preparation of $Tl(tpp)(SA)$ (**1**)

$Tl(tpp)Cl$ (144.3 mg, 0.15 mmol) in $CHCl_3$ (30 cm^3) was treated with sodium salicylate (90.1 mg, 0.56 mmol) in CH_3OH (25 cm^3) and stirred under reflux for 12 h. After concentration, the mixture was dissolved in CH_2Cl_2 and extracted four times with distilled water to remove excess sodium salicylate. The CH_2Cl_2 layer was then concentrated to dryness, producing a purple prism (148.2 mg, 91.5%). Next, the crystals were grown by diffusion of ether vapour into a CH_2Cl_2 solution. This crystal was dissolved in $CDCl_3$ (or CD_2Cl_2) for 1H and ^{13}C NMR Table 3 measurements at 24°C. 1H NMR δ (ppm): 9.07 (d, $^4J(Tl-H)=67$ Hz, β -pyrrole H), 8.38 (s) and 8.16 (s) for $H_{2,6}$, 7.80 (s) and 7.79 (s) for $H_{3,5}$, 7.76 (s) for H_4 , 6.78 (t, $^3J(H-H)=7.6$ Hz, $H_{4'}$), 6.21 (d, $^3J(H-H)=8.2$ Hz, $H_{3'}$), 6.16 (d, $^3J(H-H)=8.0$ Hz, $H_{6'}$), 6.08 (t, $^3J(H-H)=7.5$ Hz, $H_{5'}$).

2.2. Preparation of $Tl(tptp)(SCN)$ (**2**)

Compound **2** was prepared by substituting sodium salicylate with KSCN (61.2 mg, 0.63 mmol) and $Tl(tpp)Cl$ with $Tl(tptp)Cl$ (167.4 mg, 0.18 mmol) in the preparation of **1**. Purple crystals (**2**) (143.9 mg, 85.6%) were obtained. This crystal was dissolved in $CDCl_3$ for 1H and ^{13}C NMR Table 3 measurements at 24°C. 1H NMR δ (ppm): 9.17 (d, $^4J(Tl-H)=60$ Hz, β -pyrrole H), 8.32 (d, $^3J(H-H)=7.4$ Hz) and 8.06 (d, $^3J(H-H)=7.2$ Hz) for $H_{2,6}$, 7.64 (d, $^3J(H-H)=7.6$ Hz) and 7.55 (d, $^3J(H-H)=7.6$ Hz) for $H_{3,5}$, 2.71 (s, CH_3).

2.3. NMR spectra

1H and ^{13}C spectra in $CDCl_3$ (or CD_2Cl_2) were recorded at 400.13 (or 600.16) and 100.61 (or 150.92) MHz, respectively, on a Bruker AM-400 (or Bruker DMX-600) spectrometers at 24 and $-90^\circ C$. 1H and ^{13}C NMR relative to $CDCl_3$ (or CD_2Cl_2) at 7.24 (or 5.30 ppm) and the central line of $CDCl_3$ (or CD_2Cl_2) at 77.0 (or 53.6 ppm), respectively.

2.4. Crystallography

Table 1 lists the crystal data and other information for $Tl(tpp)(SA)\cdot H_2O$. Measurements were taken on a Siemens SMART CCD diffractometer using monochromatic $MoK\alpha$ radiation ($\lambda=0.71073$ Å). Next, absorption corrections were based on 7027 symmetry-

Table 1
Crystal data for $Tl(tpp)(SA)\cdot H_2O$

Formula	$C_{51}H_{35}N_4O_4Tl$
Formula weight	972.2
a (Å)	11.1192(3)
b (Å)	13.4847(3)
c (Å)	15.6027(4)
α (°)	68.990(1)
β (°)	71.386(1)
γ (°)	83.794(1)
V (Å ³)	2069.6(6)
Z	2
D_c (g cm^{-3})	1.560
Space group	$P\bar{1}$
$F(000)$	964
μ (cm ⁻¹)	39.54
R^a	5.19%
R_w^b	5.32%
GOF	1.05
A^b	1
B^b	1.5×10^{-3}
Crystal size (mm ³)	$0.32 \times 0.40 \times 0.50$
Data collected	20690
$2\theta_{max}$ (°)	57.7
Temperature (K)	296
Data used	6170 ($R_{int}=0.0726$)
Discrimination	$I > 3\sigma(I)$

$$^a R = [\sum ||F_o| - |F_c|| / \sum |F_o|].$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}; w = A / (\sigma^2 F_o + BF_o^2).$$

equivalent reflections using the SHELXTL-PC program package with ($T_{min,max}=0.374, 0.928$). The structures were solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen-atom positions were located on a difference map and included in the structure factor calculation. Table 2 lists selected bond distances and angles for $Tl(tpp)(SA)\cdot H_2O$.

3. Results and discussion

3.1. Molecular structure of $[Tl(tpp)(SA)\cdot H_2O]$

Figure 1 illustrates the skeletal framework of complex $Tl(tpp)(SA)\cdot H_2O$ with $P\bar{1}$ symmetry. This framework has a *cis* six-coordinate thallium with four nitrogen atoms of the porphyrinato group and the asymmetric bidentate 2-OH- $C_6H_4CO_2^-$ ligand. Bond distances (Å) are $Tl(1)-O(1)=2.36(1)$, $Tl(1)-O(2)=2.47(1)$, $O(2)-C(51)=1.30(2)$, $O(1)-C(51)=1.15(2)$, $C(50)-C(51)=1.57(2)$ Å and the mean $Tl(1)-N=2.221(8)$ Å. The geometrical configuration around the Tl^{3+} ion is an approximately square-based pyramid in which an asymmetric (chelating) bidentate 2-OH- $C_6H_4CO_2^-$ group occupies the apical site. The dihedral angles between the mean plane of the skeleton ($C_{20}N_4$) and the planes of the phenyl group

Table 2
Selected bond distance (Å) and angle (°) for Tl(tpp)(SA)·H₂O

Tl(1)–O(1)	2.36(1)	Tl(1)–N(1)	2.225(6)
Tl(1)–O(2)	2.47(1)	Tl(1)–N(2)	2.230(6)
O(2)–C(51)	1.30(2)	Tl(1)–N(3)	2.213(7)
O(1)–C(51)	1.15(2)	Tl(1)–N(4)	2.217(8)
C(50)–C(51)	1.57(2)	C(49)–O(3)	1.47(2)
O(1)–Tl(1)–N(1)	87.4(3)	O(2)–Tl(1)–N(1)	128.6(3)
O(1)–Tl(1)–N(2)	113.9(3)	O(2)–Tl(1)–N(2)	84.7(3)
O(1)–Tl(1)–N(3)	131.8(3)	O(2)–Tl(1)–N(3)	86.9(3)
O(1)–Tl(1)–N(4)	101.6(3)	O(2)–Tl(1)–N(4)	130.7(3)
N(1)–Tl(1)–N(2)	83.1(2)	N(2)–Tl(1)–N(3)	84.1(2)
N(1)–Tl(1)–N(3)	140.5(3)	N(2)–Tl(1)–N(4)	141.4(3)
N(1)–Tl(1)–N(4)	83.8(3)	N(3)–Tl(1)–N(4)	83.4(3)
O(1)–Tl(1)–O(2)	53.4(3)	O(2)–C(51)–O(1)	126(1)

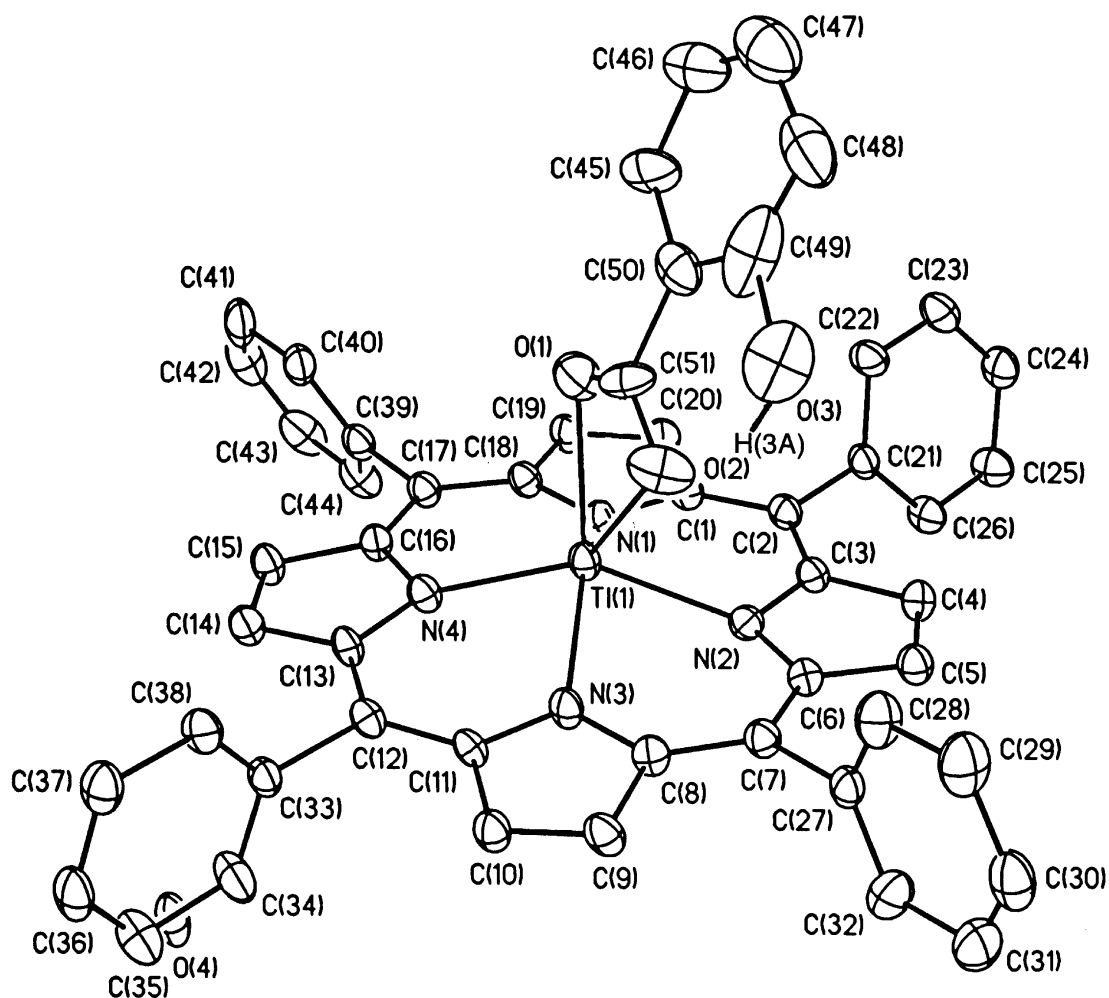


Fig. 1. Molecular configuration and atom-labeling scheme for Tl(tpp)(SA)·H₂O, with ellipsoids drawn at 30% probability. Hydrogen atoms except H(3A) are omitted for clarity. Solvent is O(4)H(4A)H(4B).

are 66.3° [C(24)], 89.6° [C(30)], 89.2° [C(36)], and 68.1° [C(42)]. The Tl atom lies 0.76 Å from the 24-atom porphyrin plane (C₂₀N₄). The central hole's radii (C_v–N). The distance from the geometrical centre (C_v) of the mean

plane of the 24-atom core to the porphyrinato-core N atoms) is 2.094 Å which is larger than 2.01 Å suggested by Collin *et al.* [3]. The thallium(III) atom is bonded in a highly expanded porphyrinato core (C₂₀N₄) and the

distortion of the porphyrin (C₂₀N₄ and Tl) can be viewed as a domed shape.

The observed H(3A)⋯O(2) and O(2)⋯O(3) distances are 1.803 and 2.627 Å, respectively. These distances are shorter than those expected from the van der Waals distances (2.60 and 2.80 Å, respectively). The O(3)–H(3A)–O(2) angle is 153.7° and its deviation from linearity is not too severe. Therefore, an intramolecular hydrogen bond exists between H(3A) and the O(2) atom.

3.2. ¹³C and ¹H NMR for Tl(tpp)(SA) (**1**) in CD₂Cl₂ and Tl(tptp)(SCN) (**2**) in CDCl₃ solution

Figure 2 depicts the representative broad band ¹³C spectra of **1** in CD₂Cl₂ solvent at 24 and –90°C, respectively. Table 3 summarizes their ¹³C data. At 24°C, the exchange of the 2-OH-C₆H₄CO₂[–] group is rapid, indicated by singlet signals arising from carbonyl carbons at 169.8 ppm and C_{1'} carbons at 112.5 ppm shown in Fig. 2(a). At –90°C, the rate of the exchange of 2-OH-C₆H₄CO₂[–] for **1** in CD₂Cl₂ is slower than the coupling frequency of Tl–¹³C, i.e. 169 ± 12 Hz. Hence, C*O and C_{1'} carbons of 2-OH-C₆H₄CO₂[–] [Fig. 2(b)] are observed at 169.6 ppm [with ²J(Tl–¹³C) = 157 Hz] and 111.5 ppm [with ³J(Tl–¹³C) = 180 Hz], respectively.

The exchange of the 2-OH-C₆H₄CO₂[–] group is rapid for (**1**) in CD₂Cl₂ at 24°C. Whereas the rotation of phenyl group along C₁–C_{meso} bond is slow at the same temperature on the NMR time-scale. This slow rotation is supported by assigning 134.9, 134.2 ppm to the C_{2,6} carbons Table 3 and by assigning 8.38, 8.16 ppm to H_{2,6} protons (or *ortho*-H).

Owing to the ring current effect, upfield shifts for the ¹H resonances of H_{6'}, H_{5'}, H_{3'} and H_{4'} in (**1**) are –1.59 [from 7.75 (obtained from salicylic acid) to 6.16 ppm], –0.80 (from 6.88 to 6.08 ppm), –0.67 (from 6.88 to 6.21 ppm) and –0.68 (from 7.46 to 6.78 ppm), respectively. As the H_{6'} proton approaches the C_{1'}, the shielding becomes larger.

Isothiocyanate (–N*≡C=S) carbon nuclei resonate between 120 and 130 ppm. Typical nitrile shift values (110–115 ppm) are characteristic of thiocyanates (–S*–C≡N) [4]. The doublet signals for the SCN[–] carbons at 110.7 ppm with ²J(Tl–¹³C) = 253 Hz for Tl(tptp)(SCN)(**2**) in CDCl₃ at 24°C (Table 3) indicate that S*CN[–] exchange does not occur in compound (**2**). The thiocyanate might be, as in the case of Tl(tpp)(SCN) and Tl(tmpp)(SCN), unidentately coordinated to the Tl atom for compound (**2**). Interestingly, ligands (X) such as CN[–] [5–7], SCN[–], CH₃[–] [8] that are unidentately and *cis* 5-coordinate bonded to Tl atom in Tl(por)X turn out not to be exchangeable. However, the chelating bidentate ligands (L) such as OAc[–] [7,9,10], C₆H₅COO[–] [1,11], CF₃COO[–] [12], SA[–] in Tl(por)L undergo either intramolecular or intermolecular ligand exchange.

Table 3
¹³C NMR data for compound Tl(tpp)(SA)(**1**) in CD₂Cl₂ at 24 and –90°C and compound Tl(tptp)(SCN)(**2**) in CDCl₃ at 24°C. Values in parentheses beneath are J(Tl–¹³C) coupling constant in Hz

Compound	Temperature (°C)	COO	C ₉	C ₁	C _{2,6}	C _β	C ₄	C _{3,5}	C _m	C _{2'}	C _{6'}	C _{1'}	C _{3'}	C _{4'}	<i>p</i> -CH ₃	SCN
Tl(tpp)(SA)(1)	24	169.8	149.9 (19)	141.6 (27)	134.9 (23)	132.2 (123)	127.6	126.6	122.2 (151)	159.4	129.8	112.5	117.3	115.7	133.6	–
	–90	169.6 (157)	148.9 (20)	140.7 (29)	134.8 (21)	132.4 (127)	127.4	126.5	121.8 (156)	158.1	128.8	111.5 (180)	117.2	115.2	133.4	–
Tl(tptp)(SCN)(2)	24	–	150.1 (17)	138.7 (25)	135.2 (23)	132.7 (110)	137.7	127.7, 127.4	122.4 (135)	–	–	–	–	–	21.5	110.7 (253)

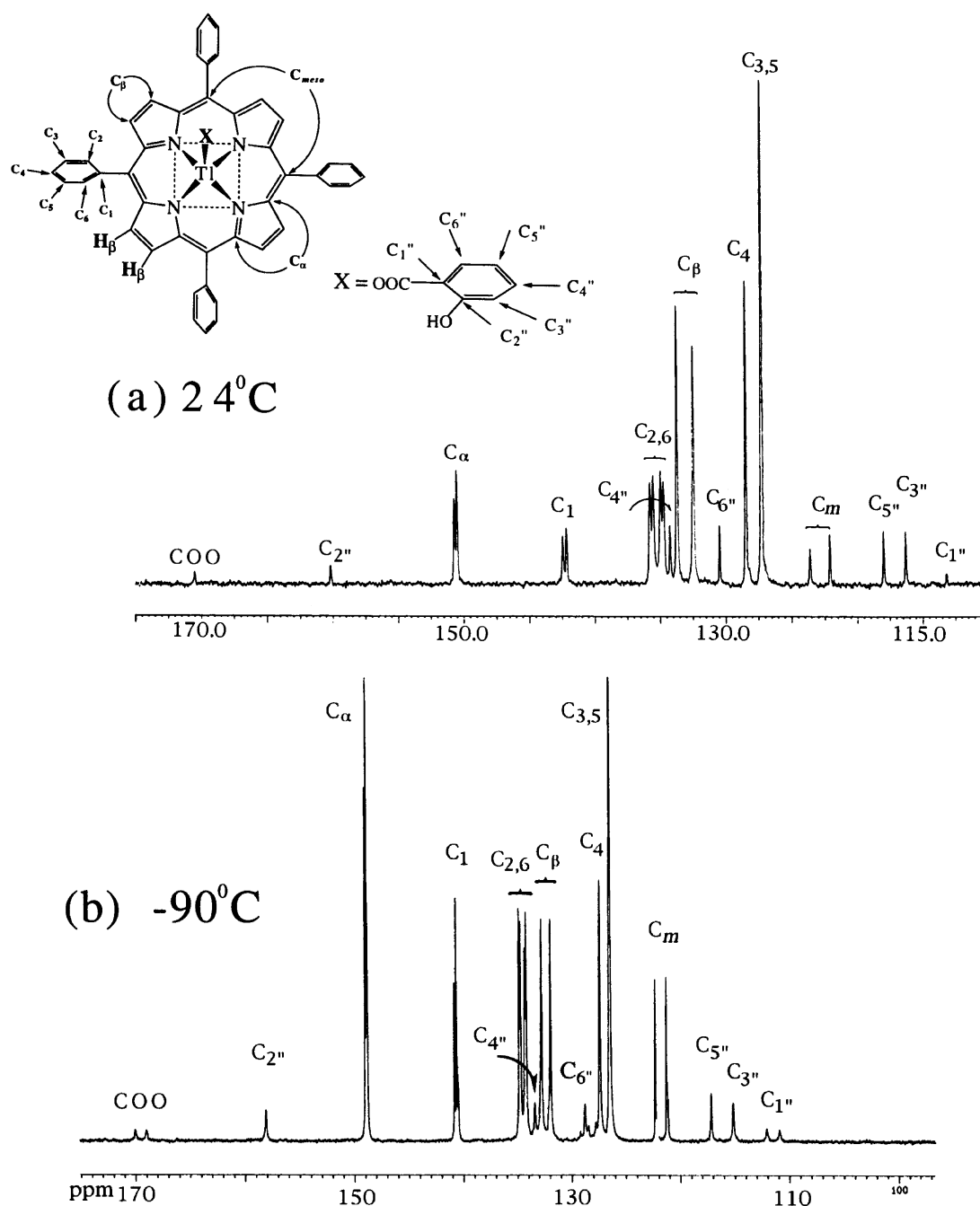


Fig. 2. ^{13}C broad band NMR spectra for $\text{Tl}(\text{tp})\text{(SA)}$ in CD_2Cl_2 (a) at 24°C (100.61 MHz) and (b) at -90°C (150.92 MHz).

3.3. The relative magnitude of mesomeric, inductive and intramolecular hydrogen bond effects on chelating bidentate and cis 6-coordinate complex, $\text{Tl}(\text{tp})\text{L}$, with $\text{L} = \text{OAc}^-$, $\text{C}_6\text{H}_5\text{COO}^-$, CF_3COO^- , and SA^-

The mesomeric effect can account for the upfield shift of -6.4 ppm for carbonyl carbons from $\text{Tl}(\text{tp})\text{(OAc)}$ (at 174.9 ppm) [9] to $\text{Tl}(\text{tp})\text{(C}_6\text{H}_5\text{COO)}$ (at 168.5 ppm) [11]. This is owing to the fact that the mesomeric inter-

action decreases electron deficiency at the carbonyl carbon in $\text{Tl}(\text{tp})\text{(C}_6\text{H}_5\text{COO)}$. The upfield shift of -17.4 ppm for carbonyl carbons from $\text{Tl}(\text{tp})\text{(OAc)}$ [9] to $\text{Tl}(\text{tp})\text{(CF}_3\text{COO)}$ (at 157.5 ppm) [12] is ascribed to the inductive effect originating from the electronegative fluorine atoms. Moreover, the downfield shift of 1.3 ppm for the same carbons from $\text{Tl}(\text{tp})\text{(C}_6\text{H}_5\text{COO)}$ [11] to $\text{Tl}(\text{tp})\text{(SA)}$ (at 169.8 ppm) is attributed to the intramolecular hydrogen bond in **1**.

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