

Intramolecular benzoate exchange in benzoato meso-tetra (4-methoxyphenylporphyrinato) thallium(III), Tl(tmpp)(C₆H₅CO₂)

Yeong-Horng Sheu,^a Tay-Ning Hong,^a Jyh-Horung Chen,^a* Feng-Ling Liao,^b Sue-Lein Wang,^b Shin-Shin Wang^c and Thomas C. Yang^d

^aDepartment of Chemistry, National Chung-Hsing University, Taichung 40227, Taiwan, R.O.C.

^bDepartment of Chemistry, National Tsing-Hua University, Hsin-Chu 30043, Taiwan, R.O.C.

^eUnion Chemical Laboratories, Hsin-Chu 30043, Taiwan, R.O.C.

^dDepartment of Chemistry, National Kaohsiung Normal University, Kaohsiung, Taiwan, R.O.C.

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Abstract --- The new compound benzoato meso-tetra(4-methoxyphenylporphyrinato)thallium(III). $Tl(tmpp)(C_6H_5CO_2)$, has been synthesized and its molecular structure determined by X-ray analysis. The coordination sphere of the Tl^{3+} ion is an approximate square-based pyramid in which the apical site is occupied by an asymmetric-bidentate $C_6H_5CO_2^-$ group. The average Tl-N bond distance is 2.24(1) Å and the Tl atom is displaced 0.811 Å from the porphyrin plane. The Tl(1)—O(5) and Tl(1)—O(6) distances are 2.57(2) and 2.27(2) Å, respectively. Variable temperature ¹³C NMR measurements show that the benzoato group of $Tl(tmpp)(C_6H_5CO_2)$ in CD₂Cl₂ solvent undergoes intramolecular exchange. In the slow exchange region, the carbonyl and C_{1^*} carbons of the benzoato group are separately located at 167.8 ppm [with ${}^{2}J$ (Tl- ${}^{13}C$) coupling constant 212 Hz] and 128.3 ppm [with ³J (Tl-¹³C) coupling constant 282 Hz] for Tl(tmpp)(C₆H₅CO₂) in CD₂Cl₂ at -90° C. In the fast exchange region, the C*OO and C₁ carbons of the C₆H₅CO₂ ligand in CD₂Cl₂ at 21 C are singlets at 168.4 and 130.3 ppm, respectively. The comparison of the ring current effect ($\Delta\delta$) for the benzoate ligand of $TI(tmpp)(C_6H_5CO_2)$ and benzoato meso-tetra(4-methoxyphenylporphyrinto)tin(IV), $Sn(tmpp)(C_6H_5CO_2)_2$, is also reported. C 1997 Elsevier Science Ltd. All rights reserved.

Keywords: crystal structure; thallium porphyrin complexes; intramolecular exchange; low temperature 13 C NMR; benzoato ligand; asymmetric bidentate ligand.

Previously, the synthesis, characterization and dynamic NMR studies of acetato meso-tetra(4methoxyphenylporphyrinto) thallium(III), Tl(tmpp) (OAc), were reported by our group [1]. It turned out that the acetato ligand exchange for Tl(tmpp)(OAc) in CD₂Cl₂ solvent was intramolecular. When the OAc of Tl(tmpp)(OAc) was replaced by a bulkier and heavier benzoate group, $C_6H_5CO_2^-$, the complex Tl(tmpp)(OAc) became benzoato meso-tetra(4methoxyphenylporphyrinto)thallium(III) Tl(tmpp) $(C_6H_5CO_2)$ (1). The acetato exchange of Tl(tmpp)(OAc) encouraged us to investigate a similar benzoato exchange for Tl(tmpp)(C₆H₅CO₂) in CD₂Cl₂ by ¹³C dynamic NMR method.

Smith *et al.* [2] reported the crystal structure of benzoato *meso*-tetra(4-methoxyphenylporphyrinto) tin(IV), Sn(tpp)(C₆H₅CO₂)₂. Sn(tpp)(C₆H₅CO₂)₂ is a tin(IV) complex with the benzoate, C₆H₅CO₂⁻, being unidentately coordinated to the Sn atom. When the tpp was substituted by *meso*-tetra-(4-methoxyphenyl)porphyrin (tmpp), it became benzoato*meso*-tetra-(4-methoxyphenylporphyrinato)tin(IV), Sn(tmpp)(C₆H₅CO₂)₂ (**2**). The synthesis, ¹³C and ¹H NMR spectroscopic studies of the new complex, Sn(tmpp)(C₆H₅CO₂)₂ (**2**), are also reported.

In this paper, ¹H and X-ray analysis of $Tl(tmpp)(C_6H_5CO_2)$ (1) are reported. The ¹³C NMR spectra at low temperature are examined to infer the intramolecular apical ligand, $C_6H_5CO_2$, exchange for $Tl(tmpp)(C_6H_5CO_2)$ in CD₂Cl₂. The comparison of

^{*}Author to whom correspondence should be addressed.

the ring current shielding effect for compounds (1), (2) is an interesting subject and is also investigated in this paper.

EXPERIMENTAL

Synthesis

Tl(tmpp)(C₆H₅CO₂) (1). Tl(tmpp)Cl (95.5 mg, 0.1 mmoles) [1] in CHCl₃ (20 cm³) was treated with sodium benzoate (155.8 mg) in CH₃OH (10 cm³) and stirred under reflux for ~13 h. After concentrating, it was dissolved in CH₂Cl₂ and extracted three times with distilled water to remove the excess C₆H₅CO₂Na. The CH₂Cl₂ layer was concentrated to dryness and gave purple prisms (91.8 mg, 87.9%). The crystals were grown by diffusion of ether vapour into a CHCl₃ solution. It was dissolved in CD₂Cl₂ (99.95% from Aldrich) for ¹H (Table 1, at 21°C) and ¹³C (Table 2, at 21 and -90° C) NMR measurement.

Sn(tmpp)($C_6H_5CO_2$)₂ (2). Free base (tmpp; 150 mg, 0.204 mmoles, from Aldrich) and powdered SnCl₂·2H₂O (92 mg, 0.408 mmoles) were stirred and refluxed in pyridine (30 cm³) for 3 h. The solution was

cooled to 50°C, then saturated $C_6H_3CO_2H$ (12 cm³, 32% in NH₃) was added, and heating and stirring were continued for another 3 h. After the solution was cooled, water (150 cm³) was added, and the solid collected by vacuum filtration, washed with water, and dried by suction. The filter cake was digested *in situ* with CH₂Cl₂, dried with anhydrous Na₂SO₄ and filtered. The filtrate was taken to dryness under reduced pressure by rotatory evaporation and the product obtained was recrystallized from CH₂Cl₂/*n*-hexane yielding blue crystals (181 mg, 81%). It was dissolved in CDCl₃ for NMR measurement at 21°C (shown in Tables 1 and 2).

Spectroscopy

¹H and ¹³C NMR spectra were recorded at 400.13 (or 600.20) and 100.61 (or 150.93) MHz, respectively, on a Bruker AM-400 spectrometer (or Bruker DMX-600) in CDCl₃ or CD₂Cl₂. ¹³C NMR data are relative to the centre line of CDCl₃ at 77.0 ppm (or CD₂Cl₂ at 53.6 ppm). ¹H NMR data are relative to CDCl₃ at 7.24 ppm (or CD₂Cl₂ at 5.30 ppm).

Table 1. ¹H (400.13) MHz NMR data for compounds Tl(tmpp)(C₆H₅CO₂) (1) in CD₂Cl₂ and Sn(tmpp)(C₆H₅CO₂)₂ (2) in CDCl₃ at 21°C,^a and the ring current effect ($\Delta\delta$) in ppm for the benzoate ligand in the complex^b

| Compound | <i>β</i> -Η | H (orth | 2,6 10 H) | H (met | (_{3,5} ta H) | $H_{4^{\prime\prime}}$ | $H_{3^{\prime\prime},5^{\prime\prime}}$ | $H_{2^{\circ},6^{\circ}}$ | <i>p</i> -O-CH ₃ |
|----------------------------------------------------|----------------------------|------------|--------------|---------------|---------------------------|-------------------------------------------|-------------------------------------------|-------------------------------------------|-----------------------------|
| $Tl(tmpp)(C_6H_5CO_2)$ | 9.09 | 8.25 | 8.06 | 7.32 | 7.27 | 6.93 | 6.69 t(7.9) | 6.39 d(7.6) | 4.06 |
| (1) In CD_2CI_2 | (04.5) | (7.5) | (7.7) | (7.0) | (0.2) | $\Delta \delta = -0.68$ | $\Delta \delta = -0.78$ | $\Delta \delta = -1.73$ | |
| $Sn(tmpp)(C_6H_5CO_2)_2$ (2) in CD Cl ₃ | 9.23 (7.5) ^e | 8. (8 | 16 .9) | 7.32 (8.9) | | 6.67 t(7.2) $\Delta \delta = -0.94$ | 6.33 t(7.8) $\Delta \delta = -1.14$ | 4.91 d(7.4) $\Delta \delta = -3.21$ | 4.11 |

^a Chemical shifts are reported in ppm relative to $CHCl_3$ at 7.24 ppm or to CH_2Cl_2 at 5.30 ppm. Values in parentheses beneath were ${}^{3}J(H-H)$ coupling constants in Hz unless it was specified.

 ${}^{b}\Delta\delta = \delta(\text{coord}) - \delta(\text{free})$, ^IH chemical shift difference between the coordination and the free benzoic acid.

 ^{c4}J (Tl—H) coupling constants.

^d Key: d = doublet, t = triplet.

 $e^{4}J$ (Sn—H) coupling constants.

Table 2. ¹³C NMR data for compound Tl(tmpp)(C₆H₅CO₂) (1) in CD₂Cl₂ at 21 and -90°C and compound Sn(tmpp)(C₆H₅CO₂)₂ (2) in CDCl₃ at 21°C. Values in parentheses beneath are J (Tl--¹³C) coupling constant in Hz

| Compound | Temp (°C) | соо | C4 | C _a | C (C | 2.6 2.2') | Ci | C _β | C _{4"} | C _{1"} | C _{2*,6*} | C _{3",5"} | C _m | C _{3,5} (C _{3,3'}) | O—Me |
|--------------------------------------------------------------------------------|--------------|----------------|-------|----------------|---------------|---------------|---------------|----------------|-----------------|-----------------|--------------------|--------------------|----------------|------------------------------------------|------|
| $\frac{1}{\text{Tl(tmpp)}(C_6H_5CO_2)}$ (1) in CD ₂ Cl ₂ | 21 | 168.4 | 160.0 | 150.6 (20) | 136.4 (24) | 135.6 (24) | 134.5 (29) | 132.6 (121) | 131.3 | 130.3 | 129.1 | 127.2 | 122.2 (150) | 112.6 112.5 | 55.8 |
| | - 90 | 167.8 (212) | 158.1 | 149.1 (18) | 135.6 (18) | 135.2 (18) | 132.7 (29) | 132.1 (122) | 130.9 | 128.3 (282) | 128.0 | 126.6 | 121.4 (150) | 111.4 111.0 | 55.3 |
| Sn(tmpp)($C_6H_5CO_2$ (2) in CDCl ₃ |)2 21 | 162.9 | 159.9 | 147.5 | 13 | 5.9 | 133.4 | 132.6 | 129.5 | 128.1 | 127.3 | 126.2 | 121.4 | 112.5 | 55.6 |

Crystallography

Crystal data and other information for $[Tl(tmpp)(C_6H_5CO_2) \cdot CHCl_3]$ are given in Table 3. Measurements were made on a Siemens SMART CCD diffractometer using monochromatized Mo- K_{α} radiation ($\lambda = 0.71073$ Å) via the $\omega : 2\theta$ scan technique. Absorption correction was based on 3516 symmetry-equivalent reflections using the SHELXTL-PC program package ($T_{min.max} = 0.482, 0.906$). The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares. All nonhydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atom positions were calculated using a riding model and included in the structure factor calculation. Selected bond distances and angles for $[Tl(tmpp)(C_6H_5CO_2) \cdot CHCl_3]$ are given in Table 4.

RESULTS AND DISCUSSION

Molecular structure of [Tl(tmpp)(C₆H₅CO₂) · CHCl₃]

The skeletal framework of the complex $[Tl(tmpp)(C_6H_5CO_2) \cdot CHCl_3]$, with $P2_1/C$ symmetry, is illustrated in Fig. 1. It reveals the six-coordination of the thallium atom with four nitrogen atoms of the porphyrinato group and the asymmetric bidentate $C_6H_5CO_2^-$ ligand; bond distances (shown in Table 4) are: Tl(1)-O(5) = 2.57(2), Tl(1)

O(6) = 2.27(2), O(5) - C(49) = 1.31(3), O(6) - C(49) = 1.17(2), C(49) - C(50) = 1.50(3) and the mean Tl(1) - N = 2.24(1) Å. The CHCl₃ molecule C(56)H(56a)Cl(1)Cl(2)Cl(3), in [Tl(tmp))(C₆H₅ CO₂) · CHCl₃] arose from the solvent trapped during the crystal growth.

The thallium atom lies 0.789 and 0.811 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 group are 63.1 [C(24)], 80.7 [C(31)], 70.6 [C(38)] and 71.1^o [C(45)].

The radius of the central "hole" ($C_1 \cdots N$, the distance from the geometrical centre of the mean plane of the 24-atom core to the porphyrinato-core N atoms) in [Tl(tmpp)($C_6H_5CO_2$) · CHCl₃] is 2.096 Å which is larger than 2.01 Å suggested by Collins *et al.* [3]. The thallium(III) atom is bonded in a highly expanded porphyrinato core ($C_{20}N_4$) in [Tl(tmpp) ($C_6H_5CO_2$) · CHCl₃] and the porphyrin ($C_{20}N_4$ and Tl) can be viewed as a domed shape. The net doming is 0.02 Å (= 0.811–0.789). Figure 2 shows the displacement (in Å) of each atom of the porphyrin ($C_{20}N_4$).

¹³C and ¹H NMR for Tl(tmpp)($C_6H_5CO_2$) (1) in CD₂Cl₂ and Sn(tmpp)($C_6H_5CO_2$)₂ (2) in CDCl₃ solution

Figure 3 shows the representative broad band ${}^{13}C$ spectra of Tl(tmpp)(C₆H₅CO₂) (1) in CD₂Cl₂ solvent

| Formula | $C_{56}H_{42}Cl_3N_4O_6Tl$ | |
|---------------------------------|--------------------------------------------|--|
| Formula weight | 1177.7 | |
| a (Å) | 12.4443(4) | |
| b (Å) | 33.313(1) | |
| c (Å) | 12.0870(4) | |
| $\beta(^{\circ})$ | 99.853(1) | |
| $V(\text{\AA}^3)$ | 4937(1) | |
| Ζ | 4 | |
| $D_{\rm c}({\rm g~cm^{-3}})$ | 1.584 | |
| Space group | $P2_1/C$ | |
| F(000) | 2344 | |
| $\mu(cm^{-1})$ | 34.90 | |
| R ^a | 7.79% | |
| Rw^{b} | 10.68% | |
| GOF | 0.87 | |
| A^{b} | 1 | |
| $B^{ m b}$ | 3.19×10^{-2} | |
| Crystal size (mm ³) | $0.45 \times 0.31 \times 0.21$ | |
| Data collected | 17980 | |
| $2\theta_{\max}(\gamma)$ | 51.4 | |
| Temperature (K) | 296 | |
| Data used | 6511 ($R_{int} = 0.0345$ after abs. cor.) | |
| Discrimination | $I > 3.0\sigma(I)$ | |
| | | |

Table 3. Crystal data for $[Tl(tmpp)(C_6H_5CO_2) \cdot CHCl_3]$

^a $R = [\Sigma ||F_0| - |F_c|| / \Sigma |F_0|]$

^b $R_w = [\Sigma w(||F_0| - |F_c||)^2 / \Sigma w(|F_0|)^2]^{1/2}; w = A/(\sigma^2 F_0 + BF_0^2)$

| Tl(1)—O(5) | 2.57(2) | $Tl(1) \rightarrow N(1)$ | 2.24(1) |
|---------------------|----------|--------------------------|----------|
| Tl(1)-O(6) | 2.27(2) | Tl(1)— $N(2)$ | 2.28(1) |
| O(5)—C(49) | 1.31(3) | Tl(1) - N(3) | 2.20(1) |
| O(6)—C(49) | 1.17(2) | Tl(1)-N(4) | 2.24(1) |
| C(49)—C(50) | 1.50(3) | | |
| O(5) - Tl(1) - N(1) | 122.1(5) | O(6) - Tl(1) - N(1) | 103.5(5) |
| O(5) - Tl(1) - N(2) | 80.7(6) | O(6) - Tl(1) - N(2) | 129.2(5) |
| O(5) - Tl(1) - N(3) | 90.7(5) | O(6) - Tl(1) - N(3) | 113.9(5) |
| O(5) - Tl(1) - N(4) | 140.3(6) | O(6) - TI(1) - N(4) | 93.9(5) |
| N(1) - TI(1) - N(2) | 82.4(4) | N(2) - Tl(1) - N(3) | 82.6(4) |
| N(1) - Tl(1) - N(3) | 140.9(5) | N(2) - Tl(1) - N(4) | 136.6(5) |
| N(1) - Tl(1) - N(4) | 83.1(4) | N(3) - Tl(1) - N(4) | 83.3(4) |
| O(5)—Tl(1)—O(6) | 53.1(6) | C(50)C(49)O(5) | 116(2) |
| C(49)—O(5)—Tl(1) | 83(1) | C(50)C(49)O(6) | 120(2) |
| C(49)—O(6)—Tl(1) | 100(1) | O(5)-C(49)-O(6) | 123(2) |
| | | | |

Table 4. Selected bond distance (Å) and angle (°) for $[Tl(tmpp)(C_5H_5CO_2) \cdot CHCl_3]$



Fig. 1. Molecular configuration and atom labelling scheme for $[Tl(tmpp)(C_6H_5CO_2) \cdot CHCl_3]$. Hydrogen atoms and solvent C(56)H(56a)Cl(1)Cl(2)Cl(3) are omitted for clarity.

at 21°C and -90° C, respectively, and their ¹³C data appear in Table 2. At 21°C, intramolecular exchange of the C₆H₅CO₂⁻ group is rapid, indicated by singlet signals due to carbonyl carbons at 168.4 ppm and C_{1"} carbons at 130.3 ppm shown in Fig. 3(a). At -90° C, the rate of the intramolecular exchange of C₆H₅CO₂⁻ for Tl(tmpp)(C₆H₅CO₂) (1) in CD₂Cl₂ is slow comparable with the coupling frequency of Tl-¹³C, i.e. 247 ± 35 Hz. Hence, C*O and C_{1°} carbons of C₆H₅CO₂⁻ shown in Fig. 3(b) are observed at 167.8 ppm [with ²J (Tl-¹³C) = 212 Hz] and 128.3 ppm [with ³J (Tl-¹³C) = 282 Hz], respectively.

The intramolecular exchange of the $C_6H_5CO_2^$ group is rapid for $Tl(tmpp)(C_6H_5CO_2)$ (1) in CD_2Cl_2



Fig. 2. Formal diagram of the porphyrin core $(C_{20}N_4 \text{ and }Tl)$ of $[Tl(tmpp)(C_6H_5CO_2) \cdot CHCl_3]$ in which each atom symbol is replaced by a number showing the displacement (in Å) of that atom from the mean plane of porphyrin $(C_{20}N_4)$.

at 21 C, whereas the rotation of anisole group along $C_1 - C_{meso}$ bond is slow at the same temperature on the NMR time-scale. It is supported by both the assignment of 136.4, 135.6 ppm to the $C_{2.6}$ carbons and 112.6, 112.5 ppm due to the $C_{3.5}$ carbons (shown in Table 2) and by the assignment of 8.25, 8.06 ppm to $H_{2.6}$ protons (or *ortho*-H) and 7.32, 7.27 ppm due to $H_{3.5}$ protons (or *meta*-H, shown in Table 1).

The singlet signals for carbonyl carbons at 162.9 ppm and $C_{1^{-}}$ carbons at 128.1 ppm (shown in Table 2) for Sn(tmpp)($C_6H_5CO_2$)₂ (2) in CDCl₃ at 21 and -50 C indicates no $C_6H_5CO_2^-$ exchange in compound (2). The benzoate might be, as in the case of Sn(tpp)($C_6H_5CO_2$)₂ [2], unidentately coordinated to the Sn atom for compound (2), and the tin(IV) atom is centered in an expanded porphyrinato core ($C_{20}N_4$).

Compared with compound (1), the rotation of the anisole group along $C_1 - C_{meso}$ for compound (2) is fast at 21°C on the NMR time-scale. It is supported by both the assignment of 135.9 ppm to $C_{2.6}$ carbons and 112.5 ppm due to the $C_{3.5}$ carbons (shown in Table 2) and by the assignment of 8.16 ppm to $H_{2.6}$ protons and 7.32 ppm due to $H_{3.5}$ protons (shown in Table 1).

Due to the ring current effect, upfield shifts for the ${}^{1}H$ resonances of $H_{4^{\circ}}$, $H_{3^{\circ},5^{\circ}}$ and $H_{2^{\circ},6^{\circ}}$ in

Tl(tmpp)(C₆H₅CO₂) (1) are $\Delta \delta = -0.68$ [from 7.6] (obtained from C_6H_5COOH) to 6.93 ppm], -0.78 (from 7.47 to 6.69 ppm) and -1.73 ppm (from 8.12 to 6.39 ppm), respectively (shown in Table 1). From the same effect, upfield shifts for the ¹H resonances of $H_{4''}$, $H_{3'',5''}$ and $H_{2'',6''}$ in Sn(tmpp)(C₆H₅CO₂)₂ (2) are $\Delta \delta = -0.94$ (from 7.61 to 6.67 ppm), -1.14 (from 7.47 to 6.33 ppm) and -3.21 ppm (from 8.12 to 4.91 ppm), respectively (shown in Table 1). All indicate that as the protons of the benzoate ligand become closer to the C_{ℓ} , the shielding gets larger. The porphyrin ($C_{20}N_4$ and Tl) of compound (1) is viewed as domed shape whereas that (C₂₀N₄ and Sn) of compound (2) is planar. C_{ℓ} (1.3391, 0.14134, 0.13389), of compound (1) is different from Tl(1), (1.38291, 0.14291, 0.09151, atom whereas C_r of compound (2) is Sn atom. The distances between $H_{4^{\circ}}$, $H_{3^{\circ},5^{\circ}}$, $H_{2^{\circ},6^{\circ}}$ and C_{ℓ} are longer in compound (1) than in compound (2). Hence the ring-current effect $\Delta \delta$ is larger in compound (2) than in compound (1) with (-0.94 vs)-0.68 ppm) for H_{4"}, (-1.14 vs -0.78 ppm) for H_{3",5} and (-3.21 vs - 1.73 ppm) for $H_{2^{\circ},6^{\circ}}$.

In summary, although the bulky benzoate group is asymmetrically and bidentately coordinated to the thallium atom in compound (1), it still undergoes the







intramolecular $C_6H_5CO_2^-$ exchange in CD_2Cl_2 solvent.

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