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MOLECULAR STRUCTURE OF THALLIUM(III) MESO-TETRAPHENYLPORPHYRIN ACETATE: Tl(tpp)(OAc)

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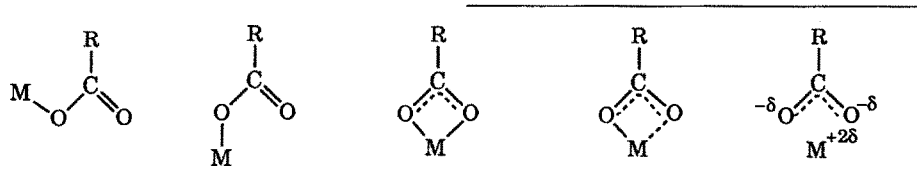
Abstract—X-ray diffraction data and solid-state ^{13}C CP/MAS spectra of thallium(III) meso-tetraphenylporphyrin acetate, Tl(tpp)(OAc), provide evidence for a chelating-bidentate acetato group coordinated to the thallium(III) atom. The displacement of the thallium atom from the porphyrin mean plane was 0.842 Å. The geometry around the thallium centre of the Tl(tpp)(OAc) molecule has Tl—O(1) = 2.361(9), Tl—O(2) = 2.229(10) and Tl—N = 2.219(7) Å. Fourier-transform IR spectra (400–4000 cm^{-1}) of Tl(tpp)(OAc) in KBr discs and in CH_2Cl_2 solvent are reported and assigned by comparison with the spectra of Tl(tpp)(CN). It is concluded that the intramolecular exchange of the acetato group between asymmetric pseudo-chelating **c** and **d** result in the adaptation of the chelating bidentate, **a** for the carboxylate at low temperature and that of the symmetric pseudo-chelating **b** at high temperature for Tl(tpp)(OAc) in CH_2Cl_2 solvent. This explains the resonances of ^{13}C and ^{1}H of the axial acetato group in low- and high-temperature solution NMR measurements.

Carboxylates serve as an important class of ligands in inorganic chemistry. In mononuclear complexes the carboxylate ion may coordinate to a metal in one of the following modes:



anti monodentate terminal (Ia) | *syn* monodentate terminal (Ib) | chelating-bidentate (II) | asymmetric (pseudo-chelating) (III) | free carboxylate (IV)

The most common forms are unidentate (**I**), chelating-bidentate (**II**), free carboxylate (**IV**) and asymmetric pseudo-chelating (**III**).[1–3]

In a previous paper,[4] we reported the dynamic

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NMR studies on the thallium(III) meso-tetraphenylporphyrin acetate Tl(tpp)(OAc). It was found that the intermolecular exchange of the acetato group had an activation energy of 4.1 kcal mol^{-1} in CD_2Cl_2. However, some ambiguities remain, because it is difficult to break two Tl—O bonds to undergo the intermolecular exchange with such a low activation energy. Due to the ring current effect, the ^1H chemical shifts of the axial acetato proton of Tl(tpp)(OAc) in CD_2Cl_2 at 24°C are shifted upfield *ca* 2.04 ppm from 2.1 (obtained on the acetic acid) to 0.06 ppm. The observation that the methyl protons of the apical acetate ligand appear as a sharp singlet at $\delta = 0.06$ ppm was an indication that the acetate ligand still remained in the axial position of the complex, even though the axial acetate exchange was a fast process compared with ^4J(Tl—H) = 14.7 Hz at 24°C. There is some argument about the validity of using intermolecular exchange to explain the NMR observation in the previous paper.[4] In order to elucidate the exchange mechanism, we now report the molecular structure of the crystalline Tl(tpp)(OAc) by X-ray analysis. On the NMR time-scale the X-ray structure of the solid at room temperature is a good simulation for the structure in solution at low temperature. The comparison of the Fourier transform spectra of Tl(tpp)(OAc) in crystals, expressed by Tl(tpp)(OAc)—S, and in CH_2Cl_2, expressed by Tl(tpp)(OAc)—L, will disclose that the intramolecular acetate exchange is the chief exchange mechanism.

EXPERIMENTAL

Crystal data

$C_{46}H_{31}N_4O_2Tl$, $M = 876.1$, monoclinic, space group $P2_1/n$, $a = 10.276(2)$, $b = 16.610(4)$, $c = 21.148(6)$ Å, $\gamma = 90.86(2)°$, $V = 3609.2(1)$ Å^3, $D_c = 1.612$ g cm^{-3}, $\mu = 45.63$ cm^{-1}, $F(000) = 1728$, $Z = 4$ formula units/unit cell. Intensities were collected for a crystal of dimensions $0.2 \times 0.4 \times 0.5$ mm on a Siemens R 3m/V diffractometer using monochromatized Mo-K_α radiation ($\lambda = 0.7107$ Å), via the θ–2θ scan technique. The structure was solved by direct methods (see Table 1 for important crystal information and details on data collection). All the non-hydrogen atoms were defined with anisotropic thermal parameters, whereas all hydrogen atoms were refined isotropically and included in the structure factor calculation. The final agreement factors were $R = 0.056$ and $R_w = 0.0597$ for 478 variables and 5113 unique reflections with $I > 3\sigma(I)$. The GOF was 1.32. A selection of bond distances and angles is given in Table 2.

Table 1. Crystal data

Formula	$C_{46}H_{31}N_4O_2Tl$
Formula weight	876.1
a (Å)	10.276(2)
b (Å)	16.610(4)
c (Å)	21.148(6)
γ (°)	90.86(2)
V (Å^3)	3609.2(1)
Z	4
D_c (g cm^{-3})	1.612
Space group	$P2_1/n$
$F(000)$	1728
μ (cm^{-1})	45.63
R^a (%)	5.6
$R_w{}^b$ (%)	5.97
GOF	1.32
A^b	1
B^b	1.0×10^{-3}
Crystal size (mm)	$0.2 \times 0.4 \times 0.5$
Data collected	11,379
$2\theta_{max}$ (°)	60
Temperature (K)	293
Data used	5113
Discrimination	$I > 3\sigma(I)$

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

Preparation of the complex

This complex was prepared as previously reported[5] and crystals were grown by the diffusion of CH_2Cl_2 vapour into a toluene solution.

NMR spectra

CP/MAS ^{13}C solid-state NMR spectra were recorded at 26°C at 50.33 MHz using a Bruker MSL 200 solid-state NMR spectrometer.

IR spectra

IR spectra were recorded both in KBr discs and in CH_2Cl_2 solvent on BOMEM MB-100 and BOMEM DA-3.002 Fourier transform IR spectrometers.

RESULTS AND DISCUSSION

Description of the structure

The skeletal framework of the Tl(tpp)(OAc) molecule is illustrated in Fig. 1. It reveals the six-coordination of the thallium atom with four nitrogen atoms (Np) of the porphyrinato group and the chel-

Table 2. Selection of bond distances (Å) and angles (°)

Tl(1)—O(1)	2.361(9)	Tl(1)—N(4)	2.214(7)
Tl(1)—O(2)	2.299(10)	O(1)—C(1)	1.180(14)
Tl(1)—N(1)	2.204(7)	O(2)—C(1)	1.187(14)
Tl(1)—N(2)	2.237(7)	C(1)—C(1a)	1.508(15)
Tl(1)—N(3)	2.222(7)		
O(1)—Tl(1)—O(2)	51.6(4)	O(1)—Tl(1)—N(4)	90.7(3)
O(1)—Tl(1)—N(1)	90.2(3)	O(2)—Tl(1)—N(4)	130.2(3)
O(2)—Tl(1)—N(1)	121.5(3)	N(1)—Tl(1)—N(4)	83.9(2)
O(1)—Tl(1)—N(2)	127.5(3)	N(2)—Tl(1)—N(4)	139.4(3)
O(2)—Tl(1)—N(2)	88.8(3)	N(3)—Tl(1)—N(4)	82.6(3)
N(1)—Tl(1)—N(2)	83.1(2)	Tl(1)—O(1)—C(1)	93.6(7)
O(1)—Tl(1)—N(3)	127.3(3)	Tl(1)—O(2)—C(1)	96.6(7)
O(2)—Tl(1)—N(3)	95.5(3)	O(1)—C(1)—O(2)	118.1(10)
N(1)—Tl(1)—N(3)	140.1(2)	O(1)—C(1)—C(1a)	122.4(9)
N(2)—Tl(1)—N(3)	83.2(2)	O(2)—C(1)—C(1a)	119.5(10)

ating bidentate COO^-; the coordination polyhedra were: Tl(1)—O(1) = 2.361, Tl(1)—O(2) = 2.299, O(1)—C(1) = 1.180, O(2)—C(1) = 1.187 Å and the mean Tl(1)—Np = 2.219 Å. The thallium(I) atom lies 0.842 Å above the plane defined by the porphyrin ring system, and the O(1)—Tl(1)—O(2) bond angle is 51.6°. The dihedral angles between the mean plane of the porphine skeleton and the planes of the four phenyl groups are 70.0, 65.6, 86.3 and 78.3°, respectively. According to the X-ray analysis, the structure of Tl(tpp)(OAc)—S has type **II** acetate coordinations.

Solid-state NMR spectroscopy

Solid-state ^{13}C CP/MAS data of crystalline Tl(tpp)(OAc) at 26°C are shown in Table 3, with relevant literature values. Three major resonances with the methyl carbon at $\delta = 18.5$, carboxyl carbon at $\delta = 173.1$ and meso-carbons at $\delta = 122.8$ ppm were observed. Both the ^{13}C chemical shift and thallium–carbon coupling constant data for the crystalline are consistent with the low-temperature solution data of Tl(tpp)(OAc) in CD_2Cl_2 at −90°C. This provides further evidence that the carboxylate is chelating the thallium atom in the crystalline state. The structure of Tl(tpp)(OAc)-L at low temperature might be as in structure **II**.

IR spectroscopy

IR spectra of Tl(tpp)(OAc)-S and Tl(tpp)(OAc)-L are displayed in Figs 2(a) and (b), respectively. The IR spectrum of meso-tetraphenylporphyrinato

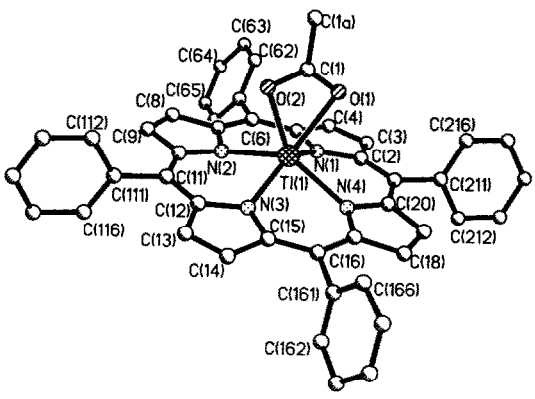


Fig. 1. Molecular configuration and labelling scheme of atoms (hydrogen atoms omitted) in Tl(tpp)(OAc).

Table 3. Comparison of ^{13}C shifts (δ) and thallium–carbon coupling constant (J) in Hz of Tl(tpp)(OAc) between solution and solid-state NMR measurements[a]

Temperature (°C)	C_{meso}	COC*H_3	C*OCH_3
26[b]	122.8	18.5	173.1
	(147)	(318)	(263)
−90[c]	122.5	18.8	174.9
	(148)	(280)	(235)

[a] Chemical shifts in ppm relative to TMS. Values in parentheses are J(Tl—^{13}C) coupling constants in Hz.
[b] CP/MAS ^{13}C solid-state NMR measurements.
[c] Solution NMR in CD_2Cl_2 from Ref. 4.

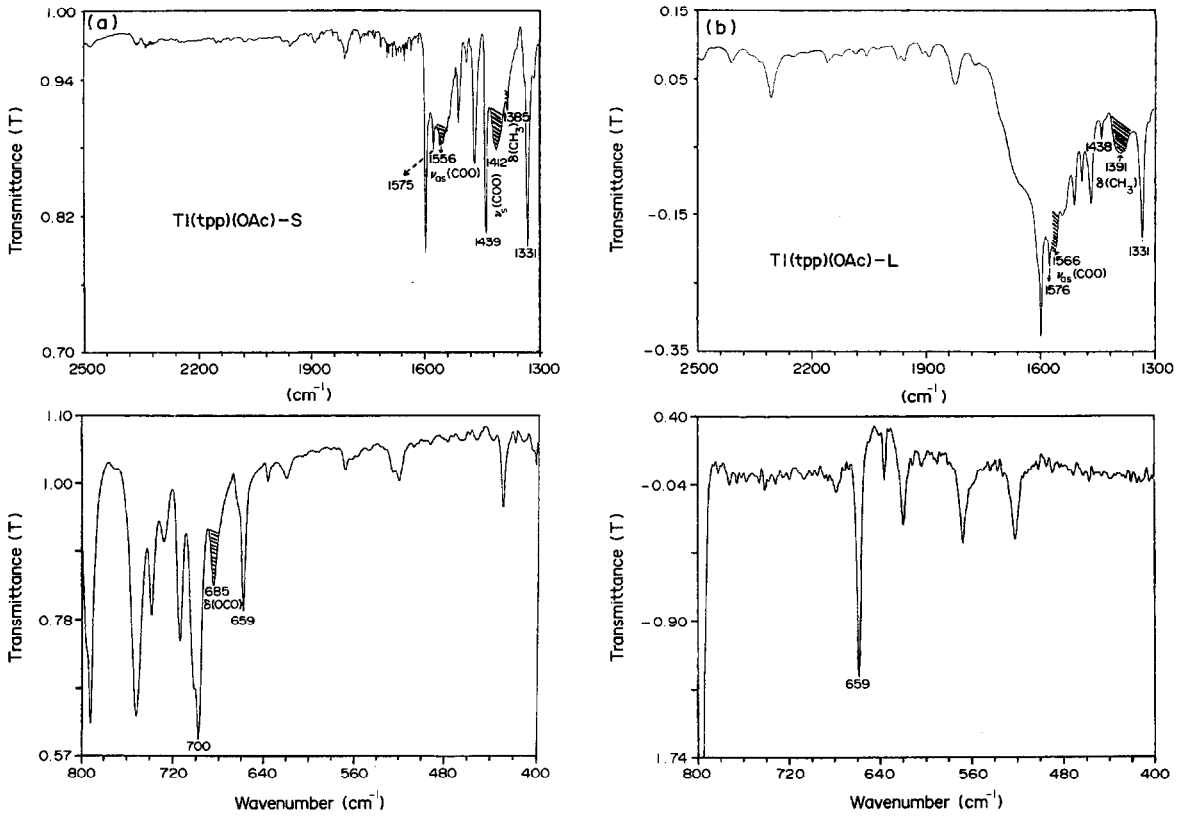


Fig. 2. IR spectra of (a) solid Tl(tpp)(OAc) and (b) Tl(tpp)(OAc) in CH_2Cl_2. Both spectra were recorded at 24°C. The hatched bands were assigned to the vibrations of the coordinated acetate molecules.

thallium(III) cyanide,[6] Tl(tpp)(CN), is shown in Fig. 3. A comparison of the vibrational frequencies of Tl(tpp)(OAc)-S [shown in Fig. 2(a)] with those of Tl(tpp)(CN) (shown in Fig. 3) enable assignment of the bands at 1556 [$\nu_{asym}(CO_2)$], 1412 [$\nu_{sym}(CO_2)$], 1385 [$\delta(CH_3)$, CH_3 symmetric deformation] and 685 cm^{-1} [δ(OCO), symmetric O—C—O deformation] as due to the chelating-bidentate acetates in Tl(tpp)(OAc)-S. On the basis of comparisons with the IR spectra of Tl(tpp)(OAc)-S [shown in

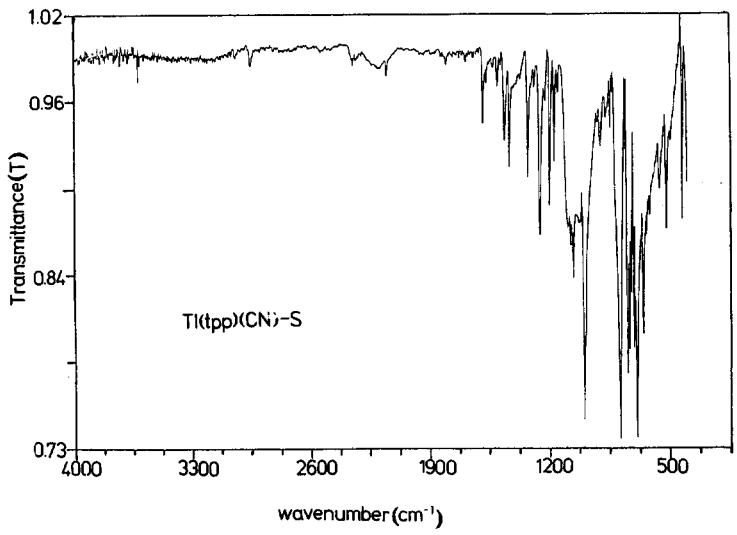


Fig. 3. IR spectrum of solid Tl(tpp)(CN) at 24°C.

Table 4. Selected IR frequencies and band assignment for acetate ions (cm^{-1}) and Tl(tpp)(OAc) in the crystalline state (cm^{-1}) and in liquid CH_2Cl_2

Band assignment	CH_3COO^- [7] solid	CH_3COO^- [7] aqueous solution	Tl(tpp)(OAc)-S[a] (chelating, bidentate)	Tl(tpp)(OAc)-L[a] (pseudo-chelating)
ν_{as}(COO)	1578	1556	1556	1566
ν_s(COO)	1414	1413	1412	—
$\delta(CH_3)$	1430	1344	1385	1391
δ(OCO)	646	650	685	—
ρ_r(COO)	460	471	—	—

[a] S = solid and L = liquid in CH_2Cl_2. Both data are recorded at 24°C.

Fig. 2(a)], the bands at 1566 [$\nu_{asym}(CO_2)$] and 1391 cm^{-1} [$\delta(CH_3)$] shown in Fig. 2(b) have been assigned to modes of vibrational frequencies due to the asymmetric pseudo-chelating acetate in Tl(tpp)(OAc)-L. Bond frequencies and assignments of the coordinated acetate molecules are listed in Table 4. On going from Tl(tpp)(OAc)-S to Tl(tpp)(OAc)-L at 24°C, bands of $\nu_s(CO_2)$ and δ(COC), which are symmetric modes of COO, disappear and only the antisymmetric CO_2 stretching mode at 1566 cm^{-1} exists.

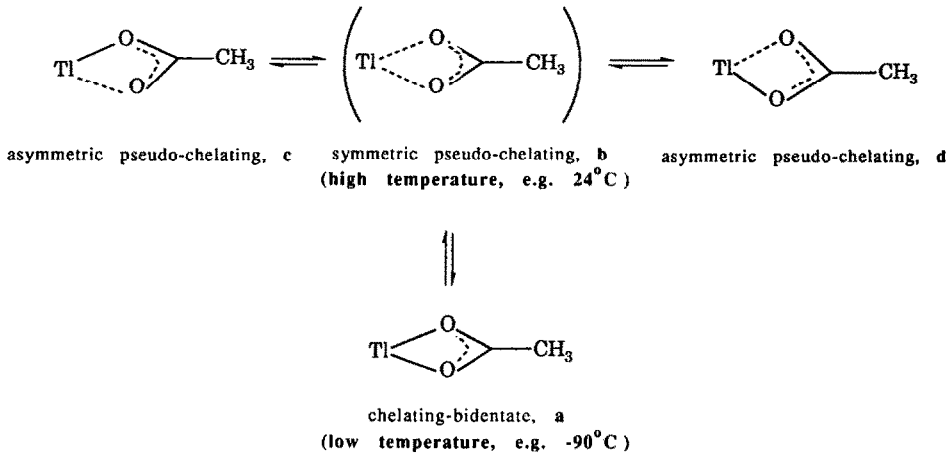
If the intermolecular acetato exchange (shown in Scheme I) proceeds in Tl(tpp)(OAc)-L, we should see the "free" CH_3COO^- ion, with structure **IV**, at 24°C. This ion has symmetric and antisymmetric COO stretching modes at 1415 and 1570 cm^{-1}. It has been examined in solution and in the solid state of sodium acetate by Ito and Bernstein,[7] which is also depicted in Table 4. The IR data of Tl(tpp)(OAc)-L at 24°C were different from those of free acetate, as shown in Table 4. Second, instead of observing the proton resonance of methyl at 2.1 ppm, it was observed at 0.06 pm. Both results indicate that structure **IV** should not exist in Tl(tpp)(OAc)-L at 24°C. This rules out the intermolecular ligand exchange mechanism.

If the carboxyl group is unidentate, one of the C—O bonds should have enhanced the double-bond character and should give rise to a high-frequency band. Such bands are observed in the 1590–1650 cm^{-1} region.[8] However, the ν_{asym}(COO) band of Tl(tpp)(OAc)-L observed at 1566 cm^{-1} (shown in Table 4) was inconsistent with unidentate coordination. Furthermore, according to Stoilova *et al.*[9] unidentate acetates exhibit three bands (COO deformation) at 920–720 cm^{-1} and a strong band [$\pi(CO_2)$] at 540 cm^{-1}. All these four bands are absent in Tl(tpp)(OAc)-L at 24°C. The two facts described above indicate that in CH_2Cl_2 at 24°C Tl(tpp)(OAc) should not be a monodentate acetate complex (structure **I**). Thus, the acetate coordination of Tl(tpp)(OAc)-L at 24°C turns out to be asymmetric pseudo-chelating (**III**).

We propose the intramolecular acetato exchange mechanism (shown in Scheme II) to explain the observations of the IR and NMR measurements. The complex Tl(tpp)(OAc)-L is chelating-bidentate (**a**) at low temperature (e.g. −90°C), which explains why the methyl and carbonyl carbons of the acetato group in CD_2Cl_2 are observed at 18.8 [with $^3J(Tl—^{13}C) = 280$ Hz] and 174.9 ppm [with $^2J(Tl—^{13}C) = 235$ Hz], respectively. It also explains that the methyl proton signal is observed as a doublet at *ca* 0.06 ppm [with $^4J(Tl—H) = 14.7$ Hz] at the same temperature.[4] As the temperature increases from −90 to 24°C, it becomes symmetrically pseudo-chelating **b**, an intermediate of asymmetric pseudo-chelating **c** and **d**. The $\nu_{as}(CO_2)$ band at 1566 cm^{-1} and $\delta(CH_3)$ at 1391 cm^{-1} correspond to the structures **c** and **d**. The rate of interchange between **c** and **d** is *ca* 10^{12}–10^{13} s^{-1}. It is much faster than the NMR time-scale at 24°C. On the NMR instrument only structure **b** was detected at high temperature. This explains our previous report that the methyl protons of the apical acetate ligand were observed at 24°C as a sharp singlet at

(II), **a** (IV)

Scheme I



Scheme II

$\delta = 0.06$ ppm, with no evidence of coupling of the thallium nuclei with the acetate group.[4] It also explains the disappearance of the symmetric modes of COO, i.e. $\nu_s(CO_2)$ and δ(COC) and the enhancement of $\nu_{as}(CO_2)$ for Tl(tpp)(OAc)—L at high temperatures.

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