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Molecular structure of *meso*-tetraphenylporphyrinatothallium(III) cyanide: Tl(tpp)(CN)

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Abstract

meso-Tetraphenylporphyrinatothallium(III) cyanide, Tl(tpp)(CN), was previously assumed to be monomeric and has been confirmed by X-ray analysis to exist as two independent molecules in one asymmetric unit. This unit displays two square-pyramidal coordination geometries for the thallium atoms with the cyano ligand coordinated to both Tl atoms. It crystallizes in the triclinic space group $P\bar{1}$, with a 10.003(3), b 16.231(7), c 21.277(8) Å, α 89.98(3), β 90.57(3), γ 90.31(3)° and $z = 4$. The structure was solved by direct methods. A total of 7995 unique reflections having $I > 3\sigma(I)$ was measured with an automated diffractometer and used to refine the crystal structure to a conventional R factor of 6.05%. The thallium–cyanide distances are 2.140(14) Å (for thallium(1)) and 2.277(14) Å (for thallium(2)) respectively, with thallium(1) situated 0.908 Å above the porphyrin ring and thallium(2) located 1.027 Å below the ring. IR and NMR spectroscopy provide complementary methods for investigation of the CN ligand. The characteristic band observed at 2160 cm^{-1} in the FTIR spectrum is assigned to the C≡N stretching in the Tl(tpp)(CN) complex. The ^{13}C resonance of axial cyano ligand is observed with a pulse delay of 3.5 s at 24°C at 139.2 ppm (with $^1J(^{205}\text{Tl}-^{13}\text{C})$ 5394 and $^1J(^{203}\text{Tl}-^{13}\text{C})$ 5344 Hz). This observation disagrees with the conclusion, drawn from previous work, in that an exchange process involving the apical ligand explains the invisibility due to line broadening at 35°C of the ^{13}C signal.

1. Introduction

Abraham *et al.* [1] first reported the synthesis and characterization of *meso*-tetraphenylporphyrinatothallium(III) cyanide, Tl(tpp)(CN), whose structure was assigned with the help of elemental analysis, mass spectrometry and ^1H and ^{13}C NMR measurements. The carbon resonance of the CN group was not observed at 35°C. However, all other ^{13}C signals in the porphyrin were clearly observed. Hence, they surmised that the lack of a peak at 35°C might be due to the

broadening of the ^{13}C signal through an exchange process involving the axial cyanide ligand. Our preliminary experiments showed that it is difficult to observe the C≡N stretching band by conventional IR spectroscopy. It seems that there are insufficient data to support the hypothesis of the cyano ligand being axially coordinated to the thallium atom. In this paper, X-ray diffraction and IR and NMR spectroscopic studies of the compound Tl(tpp)(CN) are reported which provide evidence for the cyano group being coordinated to the Tl atom. ^{13}C spectra in CDCl_3 solution at 24°C are examined with a long pulse delay in a search for new evidence concerning the intermolecular exchange of axial ligand.

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2. Experimental

2.1. Crystal data

$C_{90}H_{56}N_{10}Tl_2$ $M = 1686.2$, triclinic purple crystal, space group $P\bar{1}$, a 10.003(3), b 16.231(7), c 21.277(8) Å, α 89.98(3), β 90.57(3), γ 90.31(3)°, V 3454(2) Å³, D_c 1.621 g cm⁻³, μ 47.6 cm⁻¹, $F(000) = 1656$. There are four asymmetric units in one unit cell, *i.e.* $Z = 4$. Each asymmetric unit contains two independent molecules. Intensities were collected for a crystal of dimensions $0.4 \times 0.4 \times 0.5$ mm on a Siemens R 3m/v diffractometer using monochromatized Mo K α radiation (λ 0.71073 Å) *via* the θ - 2θ scan technique. Absorption correction was applied. The structure was solved by direct methods and each molecule was refined by blocked least-square refinement methods (see Table 1 for pertinent crystal information and details of data collection). All non-hydrogen atoms were refined with anisotropic thermal parameters, while all hydrogen atoms were added at the idealized position and included in the refinement. The final agreement factors R 6.05% and R_w 8.04% for 914 variables and 7595 unique reflections with $I > 3\sigma(I)$ were obtained. GOF was 1.42. A selection of bond distances and angles is given in Table 2.

TABLE 1. Crystal data

Formula	$C_{90}H_{56}N_{10}Tl_2$
Formula weight	1686.2
a (Å)	10.003(3)
b (Å)	16.231(7)
c (Å)	21.277(8)
α (°)	89.98(3)
β (°)	90.57(3)
γ (°)	90.31(3)
V (Å ³)	3454(2)
Z	4
D_c (g cm ⁻³)	1.621
Space group	Triclinic, $P\bar{1}$
$F(000)$	1656
μ (cm ⁻¹)	47.6
R^a	6.05%
R_w^b	8.04%
GOF	1.42
A^b	1
B^b	2.0×10^{-3}
Crystal size (mm)	$0.4 \times 0.4 \times 0.5$
Data collected	14436
$2\theta_{max}$ (°)	60
Temperature (K)	293
Data used	7595
Discrimination	$I > 3\sigma(I)$

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

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

Tl(1)-C(1)	2.140(14)	Tl(2)-C(1')	2.277(14)
Tl(1)-N(1)	2.235(11)	Tl(2)-N(1')	2.240(11)
Tl(1)-N(2)	2.237(11)	Tl(2)-N(2')	2.237(11)
Tl(1)-N(3)	2.210(12)	Tl(2)-N(3')	2.211(11)
Tl(1)-N(4)	2.211(11)	Tl(2)-N(4')	2.218(11)
C(1)-N(1a)	1.016(29)	C(1')-N(1a')	1.009(22)
C(1)-Tl(1)-N(1)	107.7(6)	C(1')-Tl(2)-N(1')	106.9(4)
C(1)-Tl(1)-N(2)	108.8(5)	C(1')-Tl(2)-N(2')	108.9(4)
N(1)-Tl(1)-N(2)	82.8(4)	N(1')-Tl(2)-N(2')	84.0(4)
C(1)-Tl(1)-N(3)	112.1(6)	C(1')-Tl(2)-N(3')	112.5(5)
N(1)-Tl(1)-N(3)	140.1(4)	N(1')-Tl(2)-N(3')	140.6(4)
N(2)-Tl(1)-N(3)	81.9(4)	N(2')-Tl(2)-N(3')	82.6(4)
C(1)-Tl(1)-N(4)	112.4(6)	C(1')-Tl(2)-N(4')	113.5(4)
N(1)-Tl(1)-N(4)	83.6(4)	N(1')-Tl(2)-N(4')	81.7(4)
N(2)-Tl(1)-N(4)	138.8(4)	N(2')-Tl(2)-N(4')	137.6(4)
N(3)-Tl(1)-N(4)	84.1(4)	N(3')-Tl(2)-N(4')	83.7(4)
Tl(1)-C(1)-N(1a)	175.9(17)	Tl(2)-C(1')-N(1a')	178.6(16)

2.2. Preparation of complex

This complex was prepared as previously reported [1] and crystals were grown by diffusion of CH_2Cl_2 vapour into a toluene solution. It was dissolved in $CDCl_3$ to give a concentration of 5.7×10^{-2} M for NMR measurement. The ¹³C and ¹H NMR spectra in $CDCl_3$ solution are similar to those reported for this compound. ¹³C NMR: δ (ppm) 150.0 (C_α , $^2J(Tl-C) = 5$ Hz); 132.8 (C_β , $^3J(Tl-C) = 112$ Hz); 122.2 (C_{meso} , $^3J(Tl-C) = 117$ Hz); 141.8 (C-1", $^4J(Tl-C) = 17$ Hz); 135.3 (C-2", $^5J(Tl-C) = 9$ Hz) and 134.4 (C-2", $^5J(Tl-C) = 11$ Hz); 127.0 and 126.9 (C-3"); 128.2 (C-4"); 139.2 (C*N, $^2J(^{205}Tl-C) = 5394$, $^2J(^{203}Tl-C) = 5344$ Hz). ¹H NMR: δ (ppm) 9.06 (d, β -pyrrole, $^4J(Tl-H) = 59$ Hz); 8.39 (d, *ortho*-H, $^3J(H-meta-H) = 5$ Hz) and 8.10 (d, *ortho*-H, $^3J(H-meta-H) = 7$ Hz); 7.79 (m, *meta*-H); 7.73 (m, *para*-H).

2.3. NMR spectra

¹H and ¹³C NMR spectra were recorded at 400 and 100.614 MHz, respectively, using a Bruker AM-400 spectrometer. ¹³C NMR spectra were also obtained at 75.46 and 50.31 MHz on Varian VXR-300 and Gemini-200 spectrometers, respectively. Chemical shifts are reported in ppm downfield from internal Me_4Si .

2.4. IR spectra

IR spectra were recorded in KBr discs on a Bomem MB-100 FTIR spectrometer.

3. Results and discussion

The skeletal framework of the *Tl(tpp)(CN)* molecule, with $P\bar{1}$ symmetry in the crystal is illustrated in Fig. 1. This reveals the five-coordination geometry of the thallium atom with the four nitrogen atoms (Np) of the

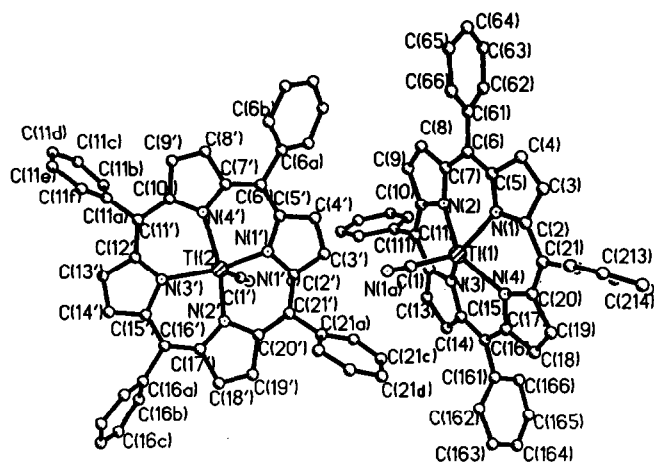


Fig. 1. Molecular configuration and scheme of labelling atoms (hydrogen atoms omitted) of two independent $Tl(tpp)(CN)$ molecules in one asymmetric unit.

porphyrinato group and the CN for each monomer; the coordination polyhedron is very close to a square pyramid with a $Tl(1)-CN$ (or $Tl(2)-CN$) bond distance of 2.140 Å (or 2.277 Å), a $C\equiv N$ bond of 1.016 Å (1.009 Å) for $Tl(1)$ (or $Tl(2)$) and a mean $Tl(1)-Np$ (or $Tl(2)-Np$) bond of 2.223 Å (or 2.227 Å); the thallium(1) atom (or $Tl(2)$) lies 0.908 Å (or 1.027 Å) above (or below) the plane defined by the porphyrin ring system, resulting in

a mean $C(1)-Tl(1)-Np$ (or $C(1')-Tl(2)-Np$) bond angle of 110.3° (or 110.5°). The dihedral angles between the mean plane of the porphyrin skeleton and the planes of the four phenyl groups are 70.1 (or 70.1), 85.2 (or 81.8), 82.0 (or 81.1), 63.5 (or 69.5°) for $Tl(1)$ (or $Tl(2)$), respectively. The axial $Tl(1)-C(1)N(1)$ (or $Tl(2)-C(1')N(1')$) bond is tilted 4.1° (or 1.4°) from the normal to the mean skeletal plane. The distance between $Tl(1)$ and $Tl(2)$ is 9.266 Å.

Although two independent molecules exist in one asymmetric unit in crystalline $Tl(tpp)(CN)$ only monomeric peaks are observed from the 1H and ^{13}C NMR solution spectra. Figure 2 shows the representative broad band ^{13}C spectrum of $Tl(tpp)(CN)$ in $CDCl_3$ solution at $24^\circ C$. The ^{13}C signal of CN bonded to $Tl(tpp)(CN)$ appears as two pairs of doublets at 166.01 and 112.40 ppm and 165.76 and 112.65 ppm for the outer and inner pairs, respectively. The outer pair arises from $^{205}Tl-^{13}C$ coupling (5394 Hz) and the inner one from $J(^{203}Tl-^{13}C)$ (5344 Hz), with relative intensities of $7/3$ ($= 2.4$), approximately equal to the receptivity ratio ($= 2.5$) of ^{205}Tl and ^{203}Tl . This is also confirmed by noting that $^1J(^{205}Tl-^{13}C)/^1J(^{203}Tl-^{13}C) = 1.0094$, which is quite close to the theoretical value calculated from $\gamma(^{205}Tl)/\gamma(^{203}Tl) = 1.0098$. Due to the ring current effect, the ^{13}C chemical shifts of axial CN received upfield shift by about 29.3 ppm from 168.5

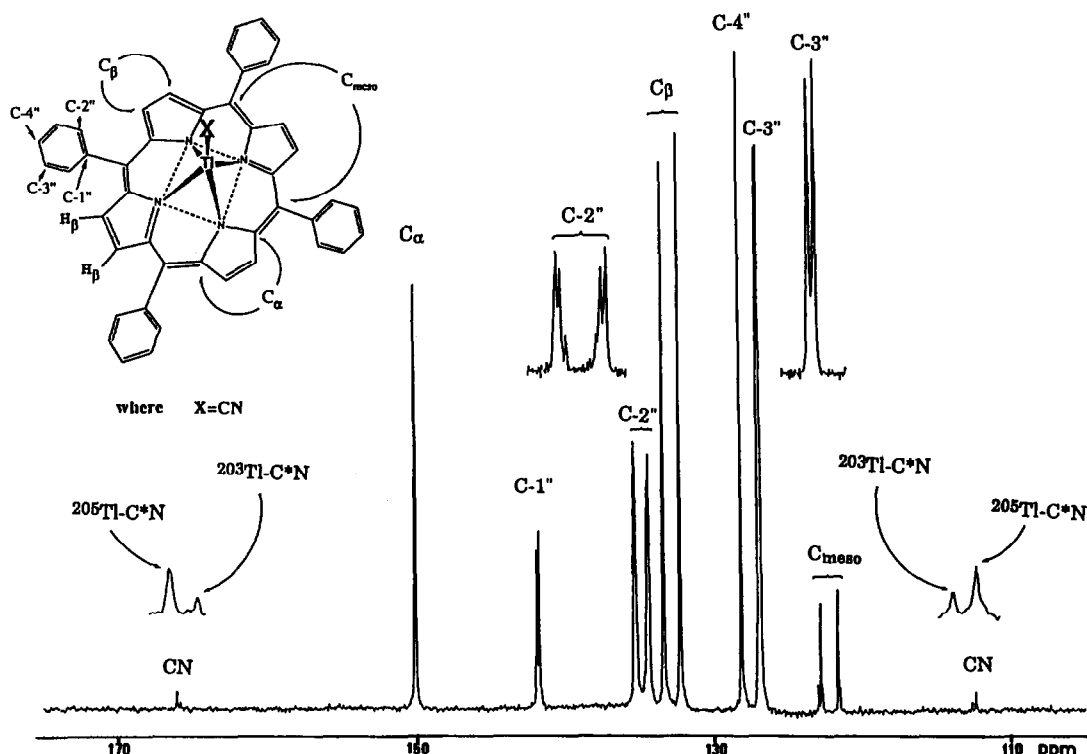


Fig. 2. 100.614 MHz ^{13}C broad band NMR spectrum of $Tl(tpp)(CN)$ in $CDCl_3$ at $24^\circ C$ with a pulse delay of 3.5 s.

ppm (obtained from saturated aqueous solution of the KCN salts) [2] to 139.2 ppm. The value of $^1J(^{203,205}Tl-^{13}C)$ obtained for $Tl(tpp)(CN)$ is consistent with those obtained (5645 [$^1J(^{205}Tl-^{13}C)$], 5593 Hz [$^1J(^{203}Tl-^{13}C)$]) from benzonorbornadiene-thallium(III) acetate and (5750 [$^1J(^{205}Tl-^{13}C)$], 5696 Hz [$^1J(^{203}Tl-^{13}C)$]) from 3-acetoxy-2-norbornyl thallium diacetate [3].

The FTIR spectrum of the $Tl(tpp)(CN)$ complex shows a band at 2160 cm^{-1} , assigned to CN stretching. This characteristic band is found between $2260\text{--}2210\text{ cm}^{-1}$ for the nitriles in organic compound [4]. FTIR provides additional evidence for the existence of the CN ligand in the complex.

At 24°C , the coupling frequency of $Tl-^{13}C$ was observed at $5396 \pm 25\text{ Hz}$ indicating that the ligand exchange rate should be small compared to the $Tl-C$ coupling constant. This disagrees with the previous surmise that broadening of the signal due to the intermolecular exchange of the ligand, which could occur at a rate comparable with the $Tl-^{13}C$ couplings, accounts for the unobserved ^{13}C resonance of cyano ligand [1]. Some ambiguities remain, because a 25 MHz (carbon) frequency was used in the earlier study and the temperature was 35°C [1]. The present work utilized a 100 MHz frequency at 24°C . The differing NMR "timescales" and temperatures must be taken into account in discussion as to why the coordinated cyanide signal was not seen earlier. Meanwhile, we have repeated the previous work by using a 100 MHz (carbon) frequency in $CDCl_3$ solvent at 48, 35 and 24°C with a pulse delay of 2.5 s (*i.e.* shorter than 3 s); the coordinated cyanide signal was not observed at these three temperatures. Temperature was the only variable in this experiment. Hence, the temperature difference is not a major cause for the CN signals not being observed. With pulse delay of 3.5 s (*i.e.* longer than 3.0 s), the coordinated cyanide signal was always seen when using any NMR instrument with a carbon frequency of 100, 75 or 50 MHz. It seemed that the NMR "timescales" were still not the major factor for detecting coordinated cyanide resonance. Furthermore, when the pulse delay was increased from 3.5 to 4.0 s, the ratios of the peak integral of the CN signal to the 4° carbons of C_a , $C-1''$ and C_{meso} increased by a factor of about 2–2.5 from 0.02, (0.04 and 0.06) to 0.05, (0.08 and 0.12), respectively. This indicated that the spin-lattice relaxation

time (T_1) of the CN carbon should be very long and suggested that the long pulse delay be used in observing the CN signal. This explained why the coordinated cyanide signal was not seen earlier because the previous workers did not use a suitable pulse delay. When the phenyl group of $Tl(tpp)(CN)$ was replaced by pyridine, it became *meso*-tetra(4-pyridyl)porphyrinatathallium(III) cyanide, $Tl(tpyp)(CN)$. With a pulse delay of 3.5 s, the ^{13}C of CN bonded to $Tl(tpyp)(CN)$ shows similar behaviour and appears as two pairs of doublets at 166.77 and 108.61 ppm and 166.50 and 108.90 ppm for the outer and inner pairs, respectively [5].

FTIR, ^{13}C NMR spectroscopies and X-ray crystal structure collectively provide unambiguous evidence that $Tl(tpp)(CN)$ is thallium(III) porphyrin complex with the cyano group axially coordinated to the Tl atom. The previous report indicated that the carbon resonance of CN group was not observed at 35°C for $Tl(tpp)(CN)$ [1]. However, its resonance was clearly observed at 24°C in $CDCl_3$ for compounds $Tl(tpp)(CN)$ and $Tl(tpyp)(CN)$ with a pulse delay of 3.5 s. All these results suggest that the cyano ligand of $Tl(tpp)(CN)$ does not undergo the intermolecular ligand exchange reaction at 24°C .

4. Supplementary material available

Tables of atomic coordinates and thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates for $Tl(tpp)(CN)$.

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