



SYNTHESIS AND MOLECULAR STRUCTURE OF MESO-TETRA(4-PYRIDYL) PORPHYRINATOTHALLIUM(III) CYANIDE: Tl(tpyp)(CN)

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Abstract—The new compound *meso*-tetra(4-pyridyl) porphyrinatothallium(III) cyanide, Tl(tpyp)(CN), has been synthesized and its molecular structure determined by X-ray analysis. The thallium–carbon(cyanide) distances are 2.163 (12) Å [for thallium (1)] and 2.121 (28) Å [for thallium (2)], respectively, with thallium(1) situated 0.825 Å above the porphyrin ring and thallium(2) located 0.900 Å below the ring. The characteristic band observed at 2163 cm⁻¹ in the FTIR spectrum confirms that the C≡N group is present in the Tl(tpyp)(CN) complex. The ¹³C resonance of the axial cyano ligand was observed at 137.7 ppm (24°C) (with ¹J(²⁰⁵Tl–¹³C) coupling constant 5852 Hz and ¹J(²⁰³Tl–¹³C) coupling constant 5795 Hz). The Correlation Spectroscopy *via* Long-Range Coupling technique (COLOC) was used to resolve two quaternary carbons *ie.* C_α and C-1 at 149.3 and 149.1 ppm, respectively.

Abraham *et al.*¹ first reported the synthesis and characterization of *meso*-tetraphenylporphyrinatothallium (III) cyanide, Tl(tpp)(CN) and its molecular structure was studied by our group.² As described in the previous paper,² with a pulse delay of 3.5 s (*ie.* longer than 3.0 s), the ¹³C signal of CN bonded to Tl(tpp)(CN) appeared 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. When the phenyl group was substituted by pyridine, it became *meso*-

tetra(4-pyridyl) porphyrinatothallium (III) cyanide, Tl(tpyp)(CN). The observation of the ¹³C resonance of the cyano ligand for this new complex is a challenging problem.

In this paper, the synthesis, X-ray diffraction, IR and NMR spectroscopic studies of the new complex, Tl(tpyp)(CN), are reported which provide evidence for the cyano group being coordinated to the Tl atom. Long pulse delay and COLOC (Correlation Spectroscopy *via* Long Range Coupling) technique were used to observe the ¹³C resonance of the cyano ligand and to identify the resonance of C_α and C-1, respectively.

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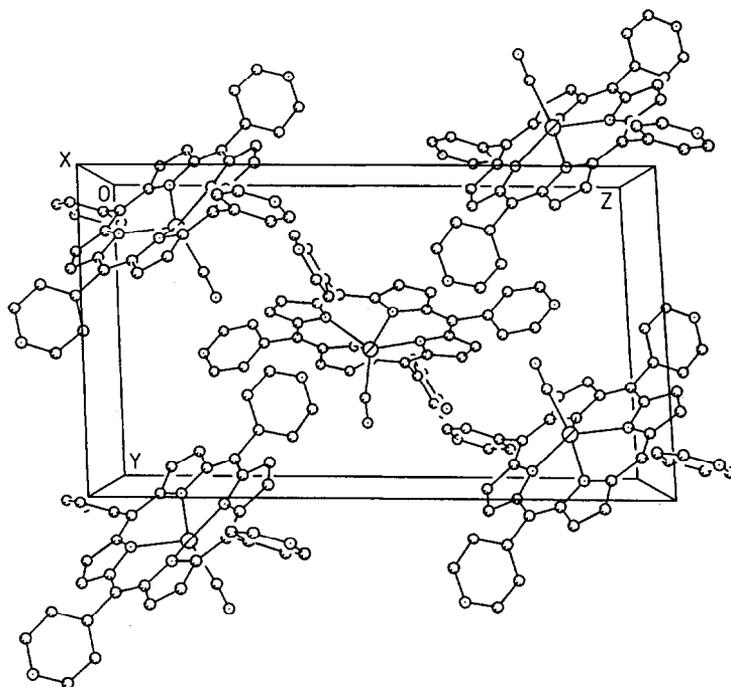


Fig. 1. Packing of Tl(tpyp)(CN) in the unit cell viewed down the *a* axis.

EXPERIMENTAL

Crystal data

$C_{123}H_{72}N_{27}Tl_3$, $M = 2541.2$, triclinic purple crystal, space group $P\bar{1}$, $a = 11.089(2)$, $b = 12.017(3)$, $c = 20.775(5)$ Å, $\alpha = 87.04(2)$, $\beta = 88.37(2)$, $\gamma = 84.25(2)^\circ$, $V = 2750.0(10)$ Å³, $D_c = 1.534$ g cm⁻³, $\mu = 44.47$ cm⁻¹ and $F(000) = 1242$. There is one asymmetric unit in the unit cell, *i.e.* $Z = 1$. Each asymmetric unit contains three molecules. These three molecules are shown in diagonal position in Fig. 1. Intensities were collected for a crystal of dimensions $0.2 \times 0.4 \times 0.4$ mm on a Siemens R 3m/v diffractometer using monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) via the θ - 2θ scan technique. Absorption corrections were applied. The structure was solved by direct methods and each molecule was refined by least-square refinement methods (see Table 1 for important crystal information and details on data collection). All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atoms were refined isotropically and included in the structure factor calculation. The final agreement factors were $R = 5.29\%$ and $R_w = 5.25\%$ for 693 variables and 8365 unique reflections with $I > 3\sigma(I)$. The GOF was 1.23. A selection of bond distances and angles is given in Table 2

Table 1. Crystal data

Formula	$C_{123}H_{72}N_{27}Tl_3$
Formula weight	2541.2
a (Å)	11.089(3)
b (Å)	12.017(3)
c (Å)	20.775(3)
α (°)	87.04(2)
β (°)	88.37(2)
γ (°)	84.25(2)
V (Å ³)	2750.0(11)
Z	1
D_c (g cm ⁻³)	1.534
Space group	triclinic, $P\bar{1}$
$F(000)$	1242
μ (cm ⁻¹)	44.47
R^a	5.29%
R_w^b	5.25%
GOF	1.23
A^b	1
B^b	7×10^{-4}
Crystal size(mm)	$0.2 \times 0.4 \times 0.4$
Data collected	9010
$2\theta_{max}$ (°)	55
Temperature(K)	293
Data used	8365
Discrimination	$I > 3\sigma(I)$

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

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

$$w = A/(\sigma^2 F_o + B F_o^2).$$

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

Tl(1)—C(41)	2.163 (12)	Tl(2)—N(10)	2.264 (7)
Tl(1)—N(1)	2.226 (7)	Tl(2)—N(12)	2.309 (7)
Tl(1)—N(3)	2.234 (6)	Tl(2)—N(10a)	2.269 (7)
Tl(1)—N(5)	2.240 (6)	Tl(2)—N(12a)	2.255 (8)
Tl(1)—N(7)	2.240 (6)	Tl(2)—C(62)	2.121 (28)
C(41)—N(9)	1.123 (20)	C(62)—N(14)	1.070 (56)
C(41)—Tl(1)—N(1)	116.0(4)	Tl(1)—N(5)—C(21)	122.2(5)
C(41)—Tl(1)—N(3)	114.8(4)	Tl(1)—N(5)—C(24)	123.7(5)
C(41)—Tl(1)—N(5)	105.4(4)	Tl(1)—N(7)—C(31)	122.5(6)
C(41)—Tl(1)—N(7)	107.4(4)	Tl(1)—N(7)—C(34)	123.3(5)
N(1)—Tl(1)—N(3)	82.8(2)	N(10)—Tl(2)—N(10a)	133.2(1)
N(1)—Tl(1)—N(5)	138.4(3)	N(10)—Tl(2)—N(12)	80.6(2)
N(1)—Tl(1)—N(7)	81.8(3)	N(10)—Tl(2)—N(12a)	81.5(3)
N(3)—Tl(1)—N(5)	83.4(2)	N(12)—Tl(2)—N(10a)	80.2(2)
N(3)—Tl(1)—N(7)	137.6(2)	N(12)—Tl(2)—N(12a)	133.5(1)
N(5)—Tl(1)—N(7)	82.6(2)	N(10a)—Tl(2)—N(12a)	81.6(3)
Tl(1)—C(41)—N(9)	171.4(12)	Tl(2)—N(10)—C(42)	119.3(5)
Tl(1)—N(1)—C(1)	122.8(6)	Tl(2)—N(10)—C(45)	121.7(6)
Tl(1)—N(1)—C(4)	123.9(6)	Tl(2)—N(12)—C(52)	122.1(5)
Tl(1)—N(3)—C(11)	125.7(5)	Tl(2)—N(12)—C(55)	124.1(5)
Tl(1)—N(3)—C(14)	124.7(5)	Tl(2)—C(62)—N(14)	168.7(31)
C(62)—Tl(2)—N(10a)	113.8(7)	C(62)—Tl(2)—N(10)	113.0(7)
C(62)—Tl(2)—N(12a)	113.2(7)	C(62)—Tl(2)—N(12)	113.2(7)

Preparation of the complex

Tpyp (100 mg) in boiling chloroform (50 cm³) was treated with thallium(III) acetate (280 mg) in dry methanol (5 cm³) and heating was continued for a further 2 h. After cooling, it was extracted with distilled water twice (50 × 2 cm³), then concentrated and passed down a column of alumina (50 g, basic, activity V). The major purple band eluting with chloroform was collected and concentrated and then dissolved in chloroform (60 cm³). The whole reaction bottle was wrapped with aluminum foil. After the addition of a solution of NaCN (400 mg) in dry methanol (10 cm³), the mixture was stirred at room temperature for 3 days, then extracted with distilled water twice (50 × 2 cm³). The purple crystals, Tl(tpyp)(CN), (99.7 mg, 72.6%) were collected by vacuum filtration and dried. The crystals were grown by diffusion of CH₂Cl₂ vapour into a toluene solution. It was dissolved in CDCl₃ (99.8% from Aldrich) to give a concentration of 8.6 × 10⁻² M for NMR measurement at 24°C. ¹³C NMR: δ(ppm) 149.3 [C_α, ²J(Tl—C) = 7 Hz]; 133.0 [C_β, ³J(Tl—C) = 108 Hz]; 119.8 [C_{meso}, ³J(Tl—C) = 113 Hz]; 149.1 (C—1); 129.8 and 129.0 (C—2, C—2''); 148.6 (C—3, C—3''); 137.7 (C*N, ²J(²⁰⁵Tl—C) = 5852 Hz, ²J(²⁰³Tl—C) = 5795 Hz). ¹H NMR: δ(ppm) 9.06 (d, β-pyrrole, ⁴J(Tl—¹H) = 58 Hz); 8.37 and 8.07 (2 and 2''—H); 9.16 and 9.09 (3 and 3''—H).

NMR spectra

¹H and ¹³C NMR spectra were recorded at 400.13 and 100.61 MHz, respectively, using Bruker AM-400 Spectrometer at 24°C. COLOC (Correlation Spectroscopy via Long-Range Coupling) was used to correlate protons and carbon through two or three-bond coupling. Chemical shifts are reported in ppm downfield from internal Me₄Si

IR spectra

IR spectra were recorded in KBr discs on a BOMEM DA-3.002 FTIR spectrometer.

RESULTS AND DISCUSSION

The packing of Tl(tpyp)(CN) in the unit cell viewed down the a axis is shown in Fig. 1. Three molecules are located diagonally in one asymmetric unit. The approximate inversion was Tl(2). Hence only 1.5 independent molecules are enough to generate one asymmetric unit. The skeletal framework of these 1.5 independent molecules with *P* $\bar{1}$ symmetry in the crystal is illustrated in Fig. 2. This reveals the five-coordination geometry of the thallium atom with the four nitrogen atoms (N_p) of the porphyrinato group and the CN for each independent molecule; the coordination polyhedron is very close to a square-pyramid with a Tl(1)—CN

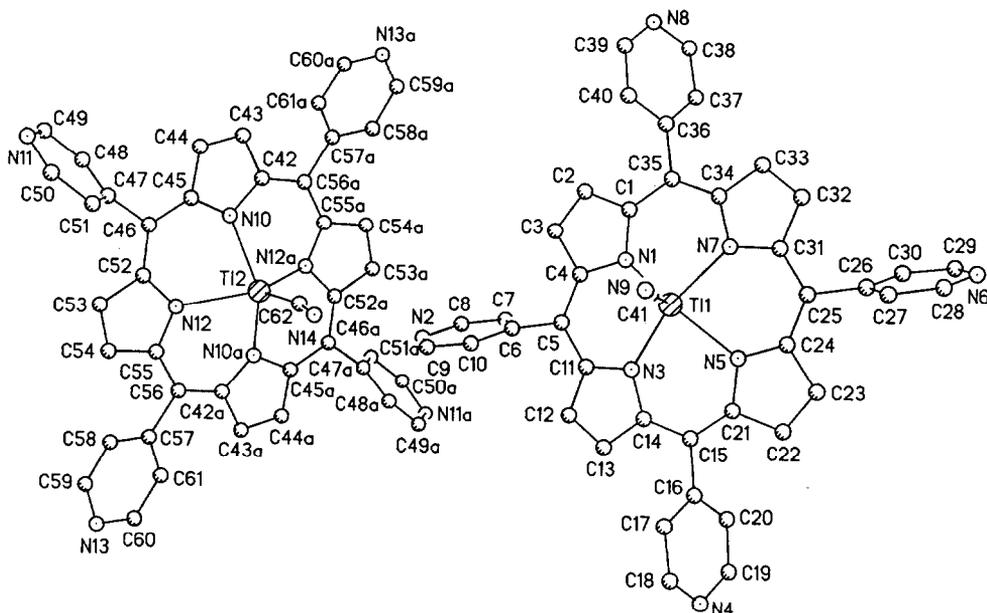


Fig. 2. Molecular configuration and scheme of labelling atoms (hydrogen atom omitted) of 1.5 independent $\text{Tl}(\text{tpyp})(\text{CN})$ molecules in one asymmetric unit. An atom denoted *a* in the right subscript has been derived according to inversion symmetry.

[or $\text{Tl}(2)-\text{CN}$] bond distance of 2.163 Å (or 2.121 Å), a $\text{C}\equiv\text{N}$ bond of 1.123 Å (or 1.070 Å) for $\text{Tl}(1)$ [or $\text{Tl}(2)$] and a mean $\text{Tl}(1)-\text{N}_p$ (or $\text{Tl}(2)-\text{N}_p$) bond of 2.235 Å (or 2.274 Å); the thallium(1) atom [or $\text{Tl}(2)$] lies 0.825 Å (or 0.900 Å) above (or below) the plane defined by the porphyrin ring system, resulting in a mean $\text{C}(41)-\text{Tl}(1)-\text{N}_p$ (or $\text{C}(62)-\text{Tl}(2)-\text{N}_p$) bond angle of 110.9° (or 113.5°). The dihedral angles between the mean plane of the porphyrin skeleton and the plane of four pyridine groups are 61.6 (C_{36} , C_{37} , C_{38} , N_8 , C_{39} , C_{40}), 112.1 (C_6 , C_7 , C_8 , N_2 , C_9 , C_{10}), 66.1 (C_{16} , C_{17} , C_{18} , N_4 , C_{19} , C_{20}), 110.2° (C_{26} , C_{27} , C_{28} , N_6 , C_{29} , C_{30}) for $\text{Tl}(1)$ and 117.4 (C_{47} , C_{48} , C_{49} , N_{11} , C_{50} , C_{51}), 105.9 (C_{57} , C_{58} , C_{59} , N_{13} , C_{60} , C_{61}), 117.4 (C_{47a} , C_{48a} , C_{49a} , N_{11a} , C_{50a} , C_{51a}), 105.9° (C_{57a} , C_{58a} , C_{59a} , N_{13a} , C_{60a} , C_{61a}) for $\text{Tl}(2)$. The axial $\text{Tl}(1)-\text{C}(41)\text{N}(9)$ [or $\text{Tl}(2)-\text{C}(62)\text{N}(14)$] bond is tilted 8.6° (or 11.3°) from the normal to the mean skeletal plane. The distance between $\text{Tl}(1)$ and $\text{Tl}(2)$ is 11.774 Å.

Figure 3 shows the representative broad band ^{13}C spectrum of $\text{Tl}(\text{tpyp})(\text{CN})$ in CDCl_3 solvent at 24°C with a pulse delay of 3.5 s. The ^{13}C signal of CN bonded to $\text{Tl}(\text{tpyp})(\text{CN})$ 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. The outer pair arises from $^{205}\text{Tl}-^{13}\text{C}$ coupling (5852 Hz) and the inner one from $J(^{203}\text{Tl}-^{13}\text{C})$ (5795 Hz), with relative intensity 7 : 3 (2.4), approxi-

mately equal to the receptivity ratio (= 2.5) of ^{205}Tl and ^{203}Tl . This is also confirmed by noting that $^1J(^{205}\text{Tl}-^{13}\text{C})/^1J(^{203}\text{Tl}-^{13}\text{C}) = 1.0098$ which is the same as the theoretical value calculated from $\gamma(^{205}\text{Tl})/\gamma(^{203}\text{Tl}) = 1.0098$. Due to the ring current effect, the ^{13}C chemical shifts of axial CN are upfield shift about 30.8 ppm from 168.5 ppm (obtained on saturated aqueous solution of the KCN salts)³ to 137.7 ppm. The value of $^1J(^{203,205}\text{Tl}-^{13}\text{C})$ obtained from $\text{Tl}(\text{tpyp})(\text{CN})$ are agreeable to those obtained {5645 [$^1J(^{205}\text{Tl}-^{13}\text{C})$], 5593 Hz [$^1J(^{203}\text{Tl}-^{13}\text{C})$]} from benzonorbornadiene thallium(III) acetate, {5750 [$^1J(^{205}\text{Tl}-^{13}\text{C})$], 5696 Hz [$^1J(^{203}\text{Tl}-^{13}\text{C})$]} from 3-acetoxy-2-norbornyl thallium diacetate⁴ and {5394 [$^1J(^{205}\text{Tl}-^{13}\text{C})$], 5344 Hz [$^1J(^{203}\text{Tl}-^{13}\text{C})$]} from *meso*-tetraphenylporphyrinatothallium(III) cyanide.² Two 4° carbons i.e. C_α and $\text{C}-1$ are resolved by COLOC technique. It turns out that two resonances at C_α due to coupling with $^{203,205}\text{Tl}$ with coupling constant 7 Hz, correlates with protons of β -pyrrole being shown in Fig. 4.

The FTIR spectrum of the $\text{Tl}(\text{tpyp})(\text{CN})$ complex shows a band at 2163 cm^{-1} , assigned to the $\text{Tl}-\text{CN}$ stretching. This characteristic band is found between 2200–2000 cm^{-1} for the cyano complexes in organometallic compounds.⁵ FTIR provides an alternative evidence for the existence of the CN ligand in the complex.

FTIR, ^{13}C NMR spectroscopies and from X-ray

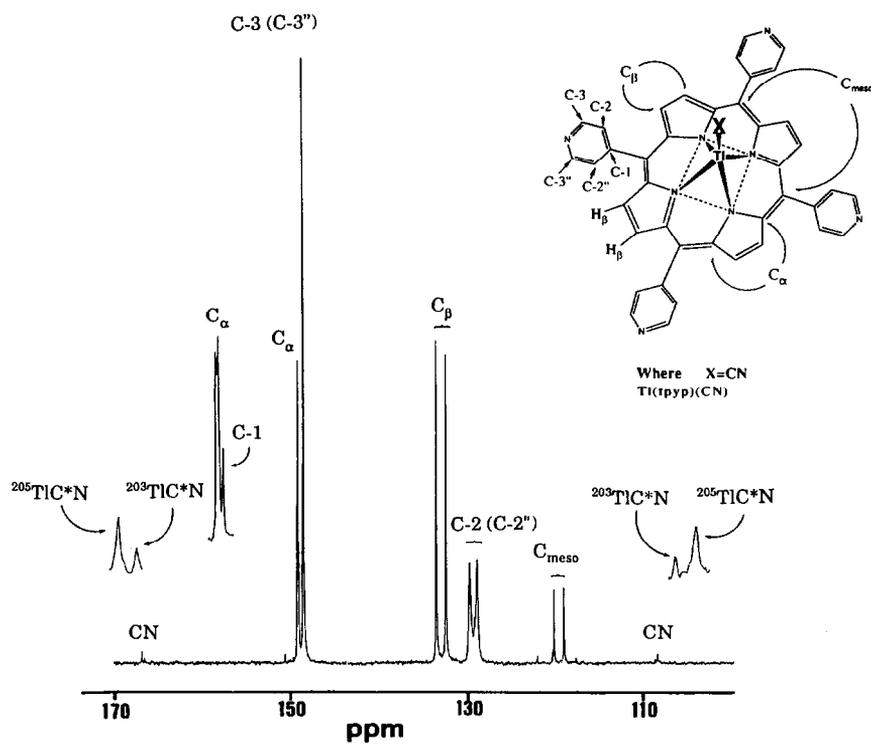


Fig. 3. 100.614 MHz ^{13}C broad band NMR spectrum of $\text{Tl}(\text{tpyp})(\text{CN})$ in CDCl_3 at 24°C with a pulse delay of 3.5 s.

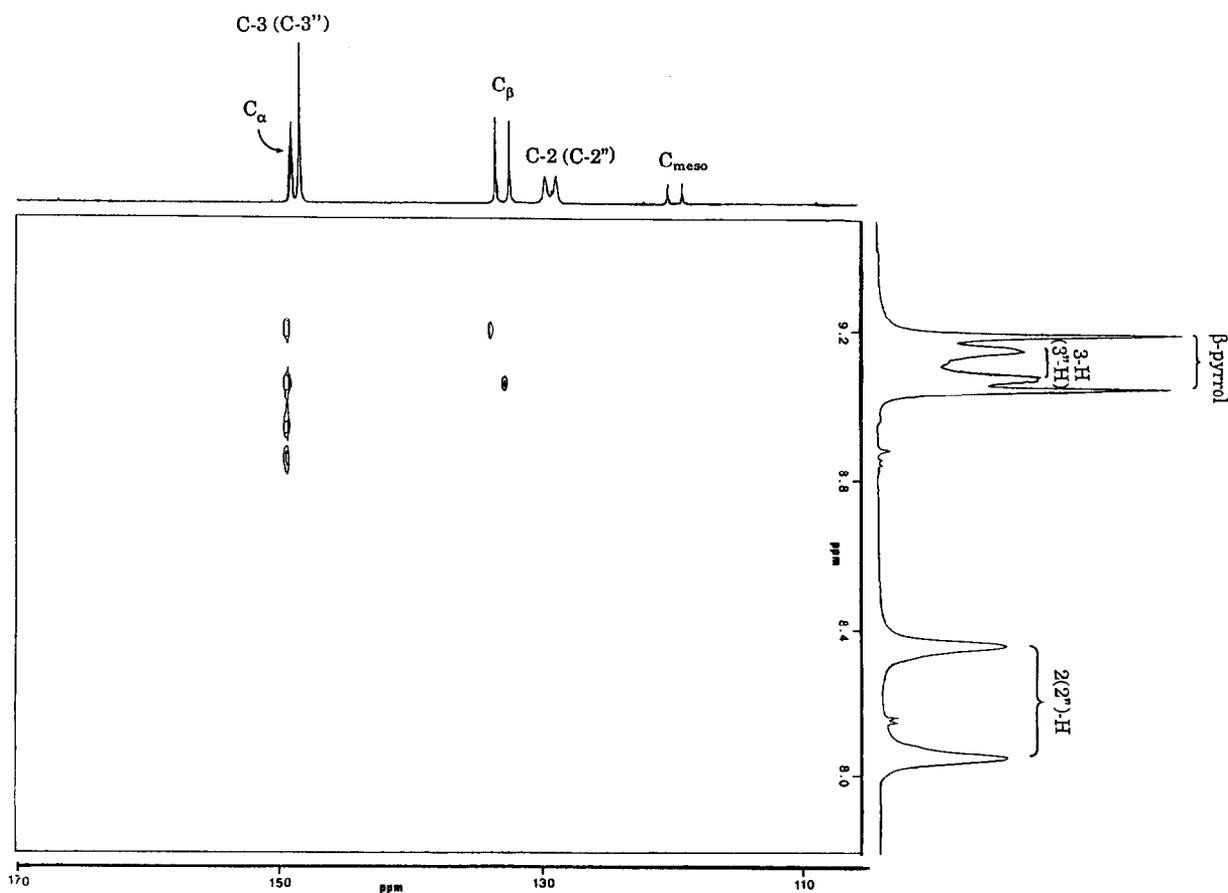


Fig. 4. The COLOC spectrum of $\text{Tl}(\text{tpyp})(\text{CN})$ in CDCl_3 at 24°C .

crystal structure collectively provide unambiguous evidence that Tl(tpyp)(CN) is thallium(III) porphyrin complex with the cyano group axially coordinated to the Tl atom. The spin-lattice relaxation time (T_1) of CN carbon should be very long and suggested that the long pulse delay be used in observing the CN signal.

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