SYNTHESIS AND MOLECULAR STRUCTURE OF MESO-TETRA(4-PYRIDYL) PORPHYRINATOOTHALLIUM(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 J(²⁰⁵Tl-¹³C) coupling constant 5852 Hz and J(²⁰³Tl-¹³C) coupling constant 5795 Hz). The Correlation Spectroscopy via Long-Range Coupling technique (COLOC) was used to resolve two quaternary carbons ie. C₆ 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 (i.e. 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 C₆ and C-1, respectively.
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, \(a = 87.04(2), \beta = 88.37(2), r = 84.25(2)\), \(V = 2750.0(10) Å^3\), \(D_\text{c} = 1.534 \text{ g cm}^{-3}\), \(\mu = 44.47 \text{ cm}^{-1}\) 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 × 0.4 × 0.4 mm on a Siemens R 3m/v diffractometer using monochromatized Mo-K\(\alpha\) radiation (\(\lambda = 0.71073\) Å) via the \(\theta-2\theta\) 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

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<tr>
<th>Formula</th>
<th>C_{123}H_{72}N_{27}Tl_{3}</th>
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<tr>
<td>Formula weight</td>
<td>2541.2</td>
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<tr>
<td>(a(Å))</td>
<td>11.089(3)</td>
</tr>
<tr>
<td>(b(Å))</td>
<td>12.017(3)</td>
</tr>
<tr>
<td>(c(Å))</td>
<td>20.775(5)</td>
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<tr>
<td>(\alpha(°))</td>
<td>87.04(2)</td>
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<tr>
<td>(\beta(°))</td>
<td>88.37(2)</td>
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<tr>
<td>(\gamma(°))</td>
<td>84.25(2)</td>
</tr>
<tr>
<td>(V(Å)^3)</td>
<td>2750.0(11)</td>
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<tr>
<td>(Z)</td>
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</tr>
<tr>
<td>(D_\text{c}(\text{g cm}^{-3}))</td>
<td>1.534</td>
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<tr>
<td>Space group</td>
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<tr>
<td>(F(000))</td>
<td>1242</td>
</tr>
<tr>
<td>(\mu(\text{cm}^{-1}))</td>
<td>44.47</td>
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<tr>
<td>(R^a)</td>
<td>5.29%</td>
</tr>
<tr>
<td>(R_w^a)</td>
<td>5.25%</td>
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<td>GOF</td>
<td>1.23</td>
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<tr>
<td>(A^a)</td>
<td>1</td>
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<tr>
<td>(B^a)</td>
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<td>Discrimination</td>
<td>(I &gt; 3\sigma(I))</td>
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\(^aR = \sqrt{\left[\sum F_o^2 - \left|F_c\right|^2\right]/\left|F_o\right|^2}.\)

\(^bR_w = \sqrt{\left[\sum w(F_o^2 - \left|F_c\right|^2)^2\right]/\left(\sum w(F_o^2)^2\right)};\)

\(w = A/(\sigma^2F_o + BF_o^2)\).
Preparation of the complex

Tppy (100 mg) in boiling chloroform (50 cm$^3$) was treated with thallium(II) acetate (280 mg) in dry methanol (5 cm$^3$) and heating was continued for a further 2 h. After cooling, it was extracted with distilled water twice (50 x 2 cm$^3$), 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 cm$^3$). The whole reaction bottle was wrapped with aluminum foil. After the addition of a solution of NaCN (400 mg) in dry methanol (10 cm$^3$), the mixture was stirred at room temperature for 3 days, then extracted with distilled water twice (50 x 2 cm$^3$). The purple crystals, Tl(tppy)(CN), (99.7 mg, 72.6%) were collected by vacuum filtration and dried. The crystals were grown by diffusion of CH$_2$Cl$_2$ vapour into a toluene solution. It was dissolved in CDCl$_3$ (99.8% from Aldrich) to give a concentration of 8.6 x 10$^{-2}$ M for NMR measurement at 24°C.\textsuperscript{13}C NMR: $\delta$(ppm) 149.3 [C$_8$], 2J(Tl$-$C) = 7 Hz; 133.0 [C$_6$], 3J(Tl$-$C) = 108 Hz; 119.8 [C$_{max}$, 4J(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$, 2J($^{205}$Tl$-$C) = 5852 Hz, 2J($^{203}$Tl$-$C) = 5795 Hz). \textsuperscript{1}H NMR: $\delta$(ppm) 9.06 (d, $\beta$-pyrrole, 4J(Tl$-$'H) = 58 Hz); 8.37 and 8.07 (2 and 2$''$-H); 9.16 and 9.09 (3 and 3$''$-H).
Fig. 2. Molecular configuration and scheme of labelling atoms (hydrogen atom omitted) of 1.5 independent Tl(tpyp)(CN) molecules in one asymmetric unit. An atom denoted * in the right subscript has been derived according to inversion symmetry.

[or Tl(2)—CN] bond distance of 2.163 Å (or 2.121 Å), a C≡N bond of 1.123 Å (or 0.70 Å) for Tl(1) [or Tl(2)] and a mean Tl(1)—Nₚ (or Tl(2)—Nₚ) bond of 2.235 Å (or 2.27 Å); the thallium(1) atom [or 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 C(41)—Tl(l)—Nₚ (or C(62)—Tl(2)—Nₚ) 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° (Cₘₛ, C₇₆, C₈₇, N₈₈, C₉₉, C₁₁₀), 112.1° (C₁₆, C₇, C₈, N₂₄, C₁₃₀, C₁₄₀), 66.1° (C₁₉₉, C₁₇₉, C₁₈₉, N₄₉, C₁₉₉, C₂₇₉), 110.2° (C₂₈₀, C₂₇₀, N₅₀, C₂₉₀, C₃₀₀) for Tl(1) and 117.4° (C₄₇₉, C₄₈₉, C₄₉₉, N₁₁₉, C₂₀₀, C₁₁₀), 105.9° (C₅₇₉, C₅₈₉, C₅₉₉, N₁₃₀, C₆₀₀, C₁₁₀), 117.4° (C₄₇₉, C₄₈₉, C₄₉₉, N₁₁₉, C₅₀₀, C₅₁₀), 105.9° (C₅₇₉, C₅₈₉, C₅₉₉, N₁₃₀, C₆₀₀, C₁₁₀) for Tl(2). The axial Tl(l)—C(41)N₉ (or Tl(2)—C(62)N(14)) bond is tilted 8.6° (or 11.3°) from the normal to the mean skeletal plane. The distance between Tl(1) and Tl(2) is 11.774 Å.

Figure 3 shows the representative broad band ¹³C spectrum of Tl(tpyp)(CN) in CDCl₃ solvent at 24°C with a pulse delay of 3.5 s. The ¹³C signal of CN bonded to Tl(tpyp)(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 ²⁰⁵Tl—¹³C coupling (5852 Hz) and the inner one from ²⁰³Tl—¹³C (5795 Hz), with relative intensity 7 : 3 (2.4), approximately equal to the receptivity ratio ( = 2.5) of ²⁰⁵Tl and ²⁰³Tl. This is also confirmed by noting that ¹J(²⁰⁵Tl—¹³C)/¹J(²⁰³Tl—¹³C) = 1.0098 which is the same as the theoretical value calculated from ¹J(²⁰⁵Tl)/¹J(²⁰³Tl) = 1.0098. Due to the ring current effect, the ¹³C chemical shifts of axial CN are upfield shifted 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(²⁰³,²⁰⁵Tl—¹³C) obtained from Tl(tpyp)(CN) are agreeable to those obtained [5645 [¹J(²⁰⁵Tl—¹³C)], 5593 Hz [¹J(²⁰³Tl—¹³C)]] from benzonorbornadiene thallium(III) acetate, [5750 [¹J(²⁰⁵Tl—¹³C)], 5696 Hz [¹J(²⁰³Tl—¹³C)]] from 3-acetoxy-2-norboryl thallium diacetate⁴ and [5394 [¹J(²⁰⁵Tl—¹³C)], 5344 Hz [¹J(²⁰³Tl—¹³C)]] from meso-tetraphenylporphyrinatothallium(III) cyanide.² Two ¹⁴N carbons i.e. C₂ and C₁ are resolved by COLOC technique. It turns out that two resonances at C₂₄ due to coupling with ²⁰³,²⁰⁵Tl with coupling constant 7 Hz, correlates with protons of β-pyrrole being shown in Fig. 4.

The FTIR spectrum of the Tl(tpyp)(CN) complex shows a band at 2163 cm⁻¹, assigned to the Tl—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, ¹³C NMR spectroscopies and from X-ray
Fig. 3. 100.614 MHz $^1$C broad band NMR spectrum of Tl(tpyp)(CN) in CDCl$_3$ at 24°C with a pulse delay of 3.5 s.

Fig. 4. The COLOC spectrum of Tl(tpyp)(CN) in CDCl$_3$ at 24°C.
crystal structure collectively provide unambiguous evidence that Tl(tpyp)(CN) is thallium(II) 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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REFERENCES