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Crystallographic report

Supramolecular structure of 2-aminonicotinatodimethylthallium(III), $[TlMe_2(2anic)]_n$

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The title compound displays an overall two-dimensional supramolecular arrangement comprising $[TlMe_2(2anic)]$ units linked by Tl–N bonds and weak Tl···O interactions. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: dimethylthallium(III); diorganothallium complex; crystal structure; 2-aminonicotinic acid complex; supramolecular structure

COMMENT

The topology of the potential donor atoms in the anion 2-aminonicotinate ($2anic^-$) suggests that this ligand can form supramolecular assemblies. The tendency of the $[TlMe_2]^+$ cation to acquire high coordination numbers by intermolecular association[1] likewise favors supramolecularity. In the complex $[TlMe_2(2anic)]_n$, Fig. 1, each 2anic ligand bridges two $[TlMe_2]^+$ moieties, being strongly bound to one via the two oxygen atoms of the carboxylate group and less strongly to the other via the pyridine nitrogen atom. The polymeric chains so formed are associated through $Tl–O^{ii}$ secondary bonds in a two-dimensional supramolecular arrangement in which each $2anic^-$ ligand interacts with three metal centers. If the $Tl–O^{ii}$ secondary bond is taken into account, then the coordination polyhedron of the thallium atom may be described as a distorted pentagonal bipyramid with one vacant equatorial site and the methyl groups apical. The structural parameters of the $[TlMe_2]^+$ moiety are in the normal ranges found among similar complexes[1] and the $Tl–N(1)^i$ distance is similar to those reported for other pyridine derivatives of $[TlMe_2]^+$ [2.481(7)–2.744(4) Å].[1–3] The Tl–O bond lengths

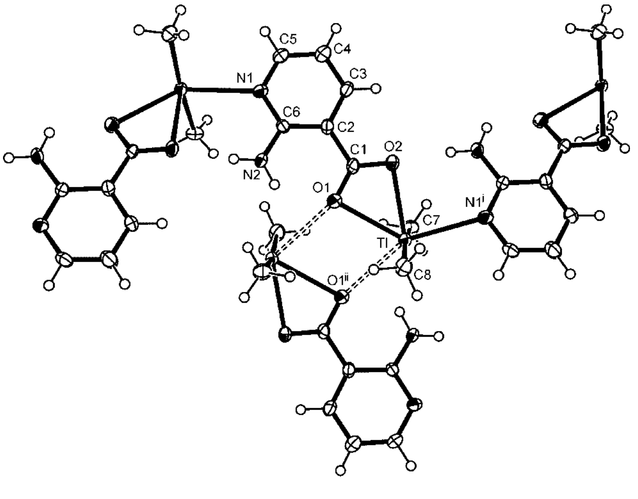

Figure 1. A fragment of the two-dimensional polymeric structure of $[TlMe_2(2anic)]_n$. Selected bond lengths (Å) and angles (°): Tl–C7 2.127(8), Tl–C8 2.114(8), Tl–O1 2.602(5), Tl–O2 2.533(5), $Tl–N1^i$ 2.696(6), $Tl–O1^{ii}$ 2.864(5); C7–Tl–C8 166.7(3), O1–Tl–O2 51.12(15), $O1–Tl–O1^{ii}$ 73.67(13), $O1–Tl–N1^i$ 132.89(17), $O2–Tl–N1^i$ 82.62(17), $O2–Tl–O1^{ii}$ 123.66(14), $N1^i–Tl–O1^{ii}$ 153.42(17). Symmetry code: $i = x, \frac{1}{2} - y, -\frac{1}{2} + z$; $ii = 1 - x, -y, 1 - z$.

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in the TlO_2C chelate ring also lie within the usual range of values [2.567(4)–2.644(9) Å], whereas the Tl–O(1)^{ii} distance [2.864(5) Å] is longer than those found in other $[TlMe_2]^+$ complexes of nicotinic acid derivatives[1,2] but shorter than the sum of the van der Waals radii (3.50 Å).[1,4]

EXPERIMENTAL

An aqueous solution of $TlMe_2OH$ (0.365 g, $TlMe_2I$, 1.01 mmol), prepared as described in the literature,[3] was added to a methanol solution (40 ml) of the ligand (0.140 g, 1.01 mmol) at room temperature. The mixture was stirred for about 8 h and then concentrated in a rotary evaporator until a solid product was formed (0.295 g, 79.51%). M.p. 218 °C. Anal. Found: C, 25.75; H, 2.85; N, 7.70. Required for $C_8H_{11}O_2N_2Tl$: C, 25.86; H, 3.00; N, 7.55%. Intensity data were collected at 120(2) K on a Bruker Nonius KappaCAD diffractometer for a crystal $0.04 \times 0.12 \times 0.14$ mm^3. Crystallographic data: $C_8H_{11}N_2O_2Tl$, $M = 371.56$, monoclinic, $P2_1/c$, $a = 6.7350(2)$, $b = 10.8050(4)$, $c = 14.0540(5)$ Å, $\beta = 103.240(2)°$, $V = 995.55$ Å^3, $Z = 4$, 1743 unique reflections, $R = 0.041$ (all data), $wR = 0.094$ (all data). Programs used: SHELXS-97, SHELXL-97 and ORTEP. CCDC reference number: 231528.

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