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Preparation and Structure of a Methylthallium(III) Complex of a Quinquedentate Ligand Resulting from a Ring-opening Reaction of 2,6-Bis(2-methyl-2-benzothiazolinyl)pyridine

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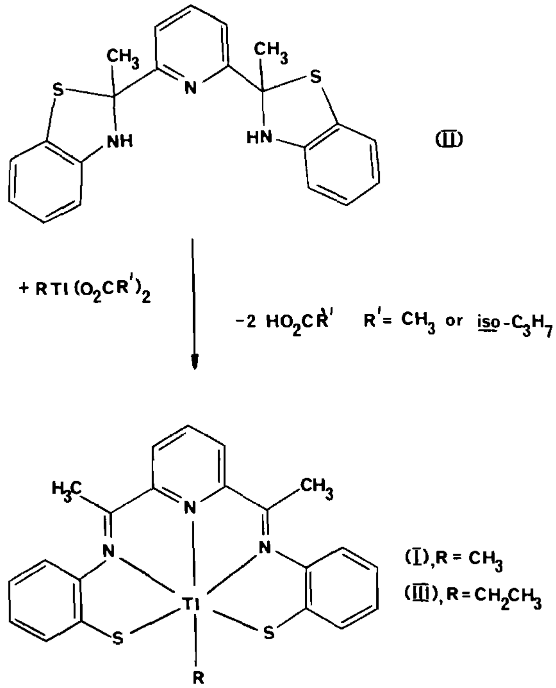
The reported chemistry of mono-organothallium(III) moieties involving potentially multidentate ligands is restricted to the five coordinate methylthallium(III) porphyrin complexes [1] and some phenylthallium(III) complexes with tri-and tetradentate shift bases [2]. We report here the preparation and crystal structure of {2,6-bis[1-methyl-2-(2-thiolophenyl)-2-azaethene] pyridine} methylthallium(III), $CH_3Tl(L - H_2)$, (I), which is the first example of a five-coordinate CH_3Tl^{2+} ion.

Preparation and Characterisation

Ready rearrangement and deprotonation of 2,6-bis(2-methyl-2-benzothiazolinyl)pyridine, (II), occurred on reaction with an equimolar amount of diacetatomethylthallium(III) [3] in chloroform at 25 °C, and orange crystals of (I) were obtained on standing (Reaction (1)).



A similar reaction was observed for di-iso-butyratoethylthallium(III) [3]. The composition of the products was established by elemental analysis [4]. The i.r. spectrum of (I) showed bands at 1665, 1660, 1650, 1640, 1600 and 1580 cm^{-1} characteristic of the imine and aromatic groups in this ligand system [5]. The band at 3350 cm^{-1} [ν(NH)] present in (II) is absent in the spectrum of (I).

The mass spectrum (200 °C) of the methyl complex gave a molecular ion at m/e 593, 595 while the spectrum of the ethyl compound showed a $[M - 15]^+$ peak at m/e 592, 594. The mass spectra of (I) at the lower temperature of 120 °C showed no trace of Tl containing ions. Peaks corresponding to $(CH_3)_2^-(L - H_2)$, $(CH_3)(L - H_2)$ and $(L - H)$ (m/e 405, 390, 376) were present. Similarly the mass spectrum of the ethyl compound showed only organic ions with masses of m/e 433, 418, 404, 390 corresponding to $(CH_3CH_2)_2(L - H_2)$, $CH_3CH_2(CH_2)(L - H_2)$, $CH_3\cdot CH_2(L - H_2)$ and $CH_3(L - H_2)$ respectively.

Low solubilities prevented determination of useful ^1H n.m.r. spectra (CW). The ^1H PFT n.m.r. spectrum at 27 °C of (I) ($DMSO_{d6}$) showed aromatic protons, a signal at –2.90(δ/ppm; relative to TMS) assigned to part of the CH_3–Tl doublet, and signals in the region 0.81 to 5.11δ, possibly due to decomposition products. A 220 MHz spectrum ($DMSO_{d6}$) at 101 °C showed no evidence of a doublet which could be assigned to the CH_3–Tl group ($^1J(^{205}T-^1H)$ expected ~950 Hz [6]). A four-line multiplet in the region 2.05 to 2.48δ (CH_3–C=N and CH_3–S) and aromatic multiplets centered at 7.1 and 8.0 were present and on integration gave ratios of 9.1:8.1:2.8 respectively.

The apparent decomposition of (I) both on the probe in the mass spectrometer and in hot DMSO solution suggests that the thallium–methyl group is transferred to a sulphur atom, presumably accompanied by reduction of the Tl(III) to Tl(I). In view of the less than satisfactory n.m.r. and mass spectroscopy measurements and X-ray study was undertaken on (I) to complete the characterisation.

Crystal Data

$C_{22}H_{20}N_3S_2Tl$: M = 594.3, orthorhombic, a = 13.498(2), b = 16.350(2), c = 19.193(4) Å; U = 4235 Å^3, Z = 8, Space group P_{bca}. The crystals diffracted only weakly and the X-ray structure determination was undertaken using 694 data with $I > 3\sigma(I)$ obtained on a Philips PW1100 4-circle diffractometer equipped with graphite monochromatised MoK_α radiation (λ = 0.71069 Å). Refinement [7] of positional and temperature parameters (Tl anisotropic; owing to the shortage of data, the phenyl and pyridyl groups in the chelating ligand were treated as

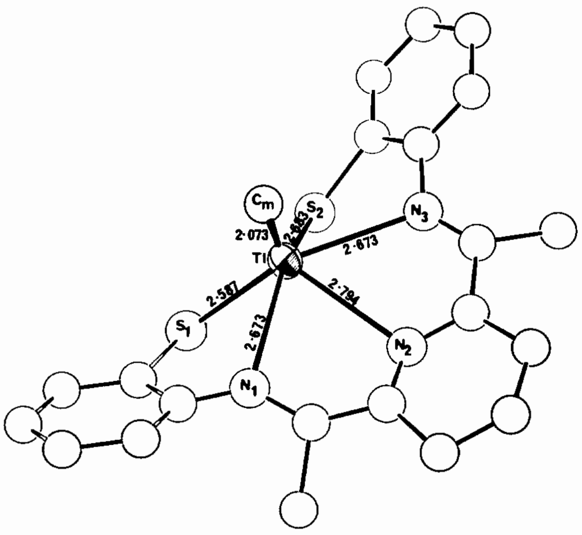


Figure 1. The methylthallium(III) complex, showing bond lengths in the co-ordination sphere. Estimated standard deviations on the bond lengths shown vary from 0.008 to 0.012 Å.

rigid bodies, C–C 1.395 and C–N 1.340 Å) by full matrix least squares has given a conventional R factor of 0.104.

The complex (Figure 1) has a highly distorted pentagonal pyramidal coordination geometry with the methyl carbon occupying the axial position. The two *ortho*-C_6H_4 (N, S) groups are twisted away from the S(1)S(2)N(1)N(3) least squares plane (maximum deviation from planarity ±0.06 Å) and are inclined to each other at 40° (Figure 2). The conformation of the ligand is such that the pyridine ring is bent away from the S_2N_2 plane at an angle of 25°. The degree of folding about the N(1)...N(3) line is less than the corresponding angle of 49° found in [Cd(3,2,3-N_5)-Br]$^+$ [8] where the seventh coordination site is sterically crowded. The ligand conformation is unlike the helical arrangement found for Zn(L – H_2) [9] and the arrangement in the Cd(II) complexes of the analogous oxygen containing benzoxazoline ligands [10].

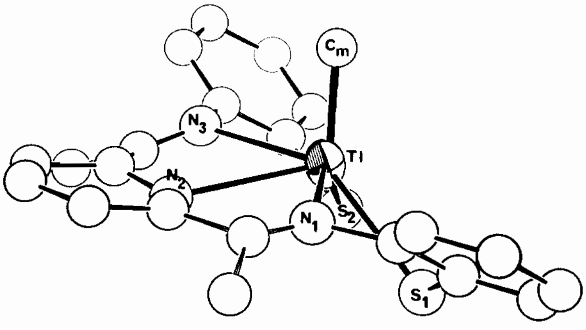


Figure 2. A view of the methylthallium(III) complex showing the nonplanarity adopted by the (L – H_2) system. The molecule exhibits an approximate mirror plane (N_2TlCm) whereas in Zn(L – H_2) the corresponding two halves are related by an approximate two-fold axis [9].

Although the N(2)–Tl distance of 2.79(6) Å is within the sum of the covalent radii of Tl(III), 1.45 Å [11] and nitrogen, the interaction must be weak because the idealised lone pair on the nitrogen is not directed towards the Tl atom. The N(2)–Tl bond makes an angle of 18° with the plane defined by the rigid body pyridyl group.

The N–Tl distances found here are significantly longer than similar values reported for pyridyl [12], 2.57(4), 2.46(3) Å and 1,10-phenanthroline [13], 2.57(3), 2.37(1) Å, complexes of Tl(III). The bonding of the 'N_3S_2' ligand system to thallium may be attributed to strong Tl–S interactions with the peripheral nitrogen atoms acting as a complicated but largely irrelevant part of the 'S_2^{2-}' donor set.

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References

1 K. Enrick, R. W. Matthews and P. A. Tasker, *Inorg. Chem.*, in press.
2 L. Pellerito, R. Cefatu and C. Ruisi, *J. Organometal. Chem., 44,* 243 (1972).
3 H. Kurosawa and R. Okawara, *Inorg. Nucl. Chem. Lett., 3,* 93 (1967).
4 Calcd. for $C_{22}H_{20}N_3S_2Tl$: C 44.4; H 3.4; N 7.1; S 10.8%. Found: C 44.4; H 3.6; N 6.9; S 10.9%. Calcd. for $C_{23}H_{22}N_3S_2Tl$: C 45.4; H 3.6; N 6.9; S 10.5% . Found: C 45.3; H 3.7; N 6.6; S 10.3%.
5 L. F. Lindoy and D. H. Busch, *Inorg. Chem., 13,* 2495 (1974).
6 C. S. Hoad, R. W. Matthews, M. M. Thakur and D. G. Gillies, *J. Organometal. Chem., 124,* C31 (1977).
7 "SHELX-76", G. M. Sheldrick, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.
8 S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. B. Othman and N. B. Mason, *Chem. Comm.*, 167 (1977), where (3,2,3-N_5) ≡ 2,15-dimethyl-3,7,10,14,20-penta-azabicyclo-[14.3.1]eicosa-1(20),2,14,16,18-pentaene.
9 V. L. Goedken and G. G. Christoph, *Inorg. Chem., 12,* 2316 (1973).
10 D. C. Liles, M. McPartlin, P. A. Tasker, H. C. Lip and L. F. Lindoy, *Chem. Comm.*, 549 (1976).
11 G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. A,* 648 (1967).
12 G. B. Deacon, S. J. Faulks, B. M. Gatehouse and A. J. Jozsa, *Inorg. Chim. Acta, 21,* L1 (1977).
13 T. L. Blundell and H. M. Powell, *Proc. Roy. Soc. (Lond.), A331,* 161 (1972) and W. J. Baxter and G. Gafner, *Inorg. Chem., 11,* 176 (1972).