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On the influence of the heterocyclic ring substituents on the structure of dimethylthallium pyrimidine-2-thionato complexes. Crystal structure of dimethyl-(4-trifluoromethylpyrimidine-2-thionate)thallium(III): a compound with intermolecular C–H $\cdots\pi$ interactions

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Abstract

The complex $[Me_2Tl(4\text{-}CF_3pymS)]$ has been prepared by reacting 4-trifluoromethylpyrimidine-2-thione (4-CF_3pymSH) with dimethylthallium(III) hydroxide in methanol. The resulting compound has a polymeric chain structure, with the thallium atom coordinated by two nitrogen and two sulfur atoms from two different ligands, which act as bridges between two metal atoms, as well as by two carbon atoms of the methyl groups. An intermolecular C–H $\cdots\pi$ interaction is observed between an H atom of each methyl group and one of the pyrimidine rings of the neighbouring chain. The structure of the complex is discussed in terms of the IR absorptions, the ^1H, ^{13}C and ^{205}Tl NMR spectra and FAB data.

Keywords: Crystal structure; Thallium(III) complex; Pyrimidine-2-thionate complex; Polymer complex; C–H $\cdots\pi$ interactions

1. Introduction

In recent years, interest has grown in the study of compounds with weak non-covalent interactions of the type X–H $\cdots\pi$ (X = N, O, C). This degree of interest is to a great extent due to the important role that these interactions seem to play in aggregation processes [1], molecular recognition phenomena [2], biological processes [3] and crystal engineering [4]. Among these attractive forces, the C–H $\cdots\pi$ interactions are the weakest but occur very frequently and are of particular importance in organic compounds [5] and biomolecules [3,6].

Metal complexes of heterocyclic thione ligands are of considerable interest since they are known to have relevance to biological systems [7] and exhibit great versatility in their coordination forms. Indeed, these ligands can act in the following ways: neutral monodentate systems through sulfur (η^1-S) [8]; through one of the nitrogen atoms (η^1-N) [9]; a neutral bridging ligand through sulfur (μ_2-S) [10]; a neutral –SN chelating ligand [11]; anion S-monodentate (η^1-S) [12]; an –N,S chelating ligand [13]; a binuclear bridging ligand μ_2-(S,N)(η^1-S, η^1-N) [14] or μ_2-(S,N)(η^2-S) [15]; a binuclear triple bridging ligand μ_2-(S,N)(η^2-S, η^1-N) [16] or μ_2-(S,N)(N, η^2-S; N′, η^2-S) [17] or a trinuclear triple bridging ligand μ_3-(S,N)(η^2-S, η^1-N) [18]. This versatility yields a variety of complexes with unusual geometries, variable nuclearities and great structural diversity. On the other hand, there is experimental evidence that the nature and location of the substituent on

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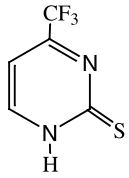

Scheme 1.

the heterocyclic ring is important in determining the structure of the metal heterocyclic thione complexes.

The structure of $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]$ was reported in a previous paper. The complex shows a tetranuclear structure with the pyrimidine ligand acting in an anionic μ_2-(S,N)(N, η^2-S; N′, η^2-S) manner [17]. In this paper, we report on the synthesis of the complex obtained by reaction of dimethylthallium(III) hydroxide and 4-trifluoromethylpyrimidine-2-thione (Scheme 1), which has the CF_3 group in position four of the pyrimidine ring but lacks the methyl group. The aim of this study was to assess the influence of the nature and position of the ring substituents on the structure of the thallium complex.

2. Results and discussion

The thionate complex $[Me_2Tl(4\text{-}CF_3pymS)]$ was obtained by simple stoichiometric reaction in a methanol/water medium between the thione precursor, 4-trifluoromethylpyrimidine-2-thione, and dimethylthallium(III) hydroxide.

2.1. Structure of $[Me_2Tl(4\text{-}CF_3pymS)]$

An ORTEP view of $[Me_2Tl(4\text{-}CF_3pymS)]$, along with the atom labelling scheme, is shown in Fig. 1. Selected bond distances and angles, with estimated standard deviations, are given in Table 1.

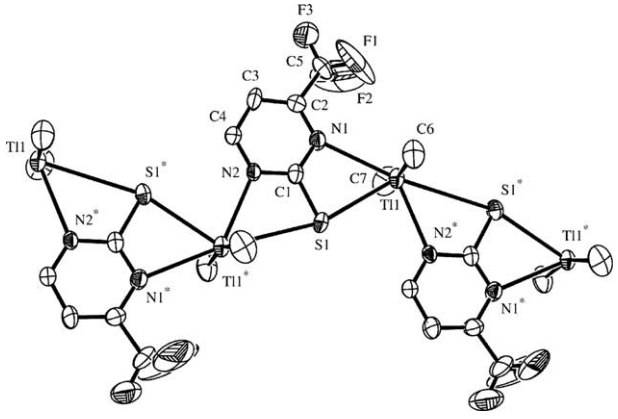

Fig. 1. A view of the polymeric chain structure of $[Me_2Tl(4\text{-}CF_3pymS)]_n$.

As can be seen, the complex has a polymeric structure in which each thallium atom is coordinated to the two methyl carbon atoms, the sulfur and nitrogen atoms of one chelating anionic ligand and the nitrogen atom of another neighboring thionate ligand. The coordination of the thallium atom is completed by a sulfur bridging atom of the vicinal ligand, as shown in Fig. 1. In this case, the Tl–S bridging distance is quite large at 3.331(4) Å, but is smaller than the sum of the van der Waals radii (3.76 Å) [19]. If the Tl–S interaction is included, the geometry around the thallium atom can be described as a highly distorted $[TlC_2N_2S_2]$ octahedron. Therefore, each ligand acts as a tridentate bridging μ(N,S,-η^2, N′, S-η^2) system between two adjacent thallium atoms of the polymer structure. As a result of the small bite angles of the chelating ligands, i.e., 55.4(3)° and 50.9(3)°, the bond angles involving the central atom and mutually *trans* donors, 172.2(3)–132.4(3)°, differ significantly from the theoretical value of 180°; the angles defined by two *cis* atoms of the different ligands and the thallium atom have values that deviate markedly from 90° [in the range 81.5(3)–98.9(7)°].

The sulfur bridging is asymmetrical, with one of the Tl–S bonds longer than the other [Tl(1)–S(1), 2.887(4); Tl(1)*–S(1), 3.331(4) Å]. Although the shorter bond distance is slightly longer than the average distance for terminal Tl–S bonds in other thallium(III) complexes (2.783 Å), it is within the normal range (2.832–3.141 Å) found in other thallium complexes having sulfur bridges [20].

The intermolecular Tl–N bond is significantly shorter [2.625(10) Å] than the intramolecular Tl–N attachments [2.792(12) Å]. Both distances are significantly shorter than the corresponding values found in the aforementioned tetranuclear $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]$ complex, which are in the range 2.804(7)–3.028(3) Å. Presumably this strengthening of the Tl–N bonding, 2.625(10) Å, compensates for the weaker Tl–S contacts made with the bridging ligand [21]. The Tl–C bond distances of 2.12(2) and 2.153(17) Å are similar to those observed in other thallium(III) complexes.

The average S–C [1.723(14) Å] and C–N [1.337(18) and 1.35(2) Å] bond distances are intermediate between the values observed in the free ligands 4,6-dimethylpyrimidin-2-thione [22] and 1-phenyl-4,6-dimethylpyrimidin-2-thione [11a] [1.692(2), 1.686(4) Å, respectively], which exist in the thione form in the solid state and the values of 1.781(2) and 1.782(3) Å found in the bis-pyrimidyl-2-2′-disulfide [23] and bis-4,6-dimethylpyrimidyl-2-2′-disulfide [24], which possess a simple C–S bond; this suggests that the ligand is coordinated in a form that is closer to the pyrimidine-2-thionato than to the thione form.

A particularly interesting aspect of the structure of $[Me_2Tl(4\text{-}CF_3pymS)]_n$ is the observation of intermolecular C–H $\cdots$ π interactions between one of the hydrogen

Table 1
Selected bond lengths (Å) and angles (°) of $[Me_2Tl(4\text{-}CF_3pymS)]$

Tl(1)–C(6)	2.12(2)	Tl(1)–C(7)	2.152(17)
Tl(1)–N(2)*	2.625(10)	Tl(1)–N(1)	2.792(12)
Tl(1)–S(1)	2.887(4)	Tl(1)–S(1)*	3.331(4)
S(1)–C(1)	1.723(14)	N(1)–C(1)	1.337(18)
N(1)–C(2)	1.341(19)	N(2)–C(4)	1.307(17)
N(2)–C(1)	1.35(2)	N(2)–Tl(1)*	2.625(10)
C(2)–C(3)	1.36(3)	C(2)–C(5)	1.52(2)
C(3)–C(4)	1.40(2)		
C(6)–Tl(1)–C(7)	161.2(11)	C(6)–Tl(1)–N(2)*	96.8(7)
C(7)–Tl(1)–N(2)*	97.9(7)	C(6)–Tl(1)–N(1)	87.2(5)
C(7)–Tl(1)–N(1)	90.2(7)	N(2)*–Tl(1)–N(1)	136.8(4)
C(6)–Tl(1)–S(1)	94.9(5)	C(7)–Tl(1)–S(1)	98.9(7)
N(2)*–Tl(1)–S(1)	81.5(3)	N(1)–Tl(1)–S(1)	55.4(3)
C(6)–Tl(1)–S(1)*	91.0(5)	C(7)–Tl(1)–S(1)*	89.1(6)
N(2)*–Tl(1)–S(1)*	50.9(3)	N(1)–Tl(1)–S(1)*	172.2(3)
S(1)–Tl(1)–S(1)*	132.34(3)		

atoms of each methyl group and the π cloud of the pyrimidine rings of the neighbouring chain. Such interactions lead to a situation where the polymeric chains in the packing arrangement of $[Me_2Tl(4\text{-}CF_3pymS)]_n$ (Fig. 2) lie along the crystallographic *b*-axis. The pyrimidine rings are essentially planar and are arranged parallel to the *ab* plane and the pyrimidine rings of other polymeric chains (angles between any two ring planes of different chains = 0.00°). The arrangement of these parallel chains is such that pyrimidine rings alternate with Me–Tl–Me units along the crystallographic *c*-axis, as shown in Fig. 2. Each of the Me–Tl–Me units interacts with the two adjacent pyrimidine rings. The C–H···π distances between C7 or C6 and the center of the pyrimidine ring are 3.608 (H···π 3.321 Å) and 3.641 Å (H···π 3.335 Å) and the C–H···π angles are in the expected range for C–H···π interactions (maximum C–H···π distance of 3.58 Å for intramolecular and 3.64 Å for intermolecular C–H···π interactions and a C–H···π angle of 100–180°).

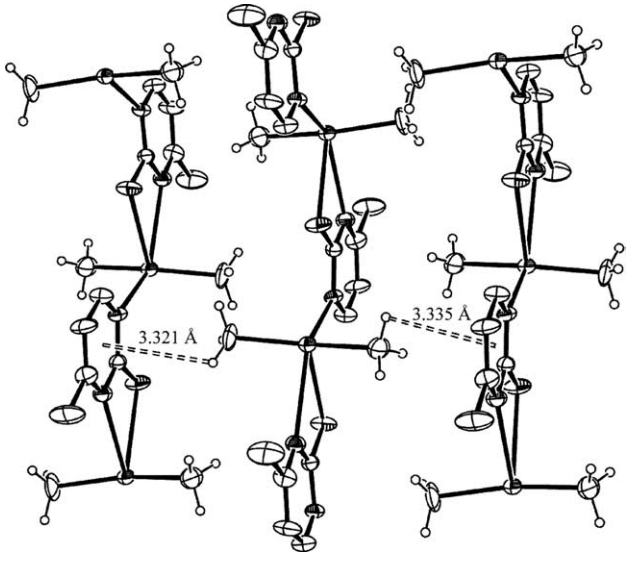

Fig. 2. Crystal packing diagram of $[Me_2Tl(4\text{-}CF_3pymS)]_n$; intermolecular C–H···π interactions are represented by a dashed line (fluorine atoms are omitted for clarity).

This type of interaction also exists in the tetranuclear compound $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$ (Fig. 3). In this case, however, the intermolecular C–H···π interaction is stronger; the C7–H···π/H···π distances are 3.630/3.314 Å, C15–H···π = 3.385/2.583 Å and the C7–H···π and C15–H···π angles are 101.56 and 141.18°, respectively.

2.2. Vibrational spectrum

The IR spectrum of the complex does not contain bands due to *ν*(N–H) (3180–3100 cm^{-1} for the free ligand), suggesting that deprotonation of the NH group has occurred and that the ligand is therefore coordinated in the thionato form.

The strong bands for *ν*(C=C) and *ν*(C=N) at 1604–1545 and 1570–1512 cm^{-1} in the free ligand spectrum are shifted to lower wavenumbers in the complex. This shift provides further evidence that the ligand is coordinated in the thionato form. In addition, the complex shows a band at 550 cm^{-1}, which can be attributed to ν_{asym} (C–Tl–C).

2.3. NMR spectra

The ^1H NMR spectrum of the complex does not show the signal attributable to the NH proton of the free ligand, which appears as a broad singlet at 14.6 ppm. The absence of this signal indicates that in the complex the ligands are deprotonated. The spectrum of the complex shows the signals of all the hydrogen atoms of the pyrimidine ring and the signals are shifted with respect to

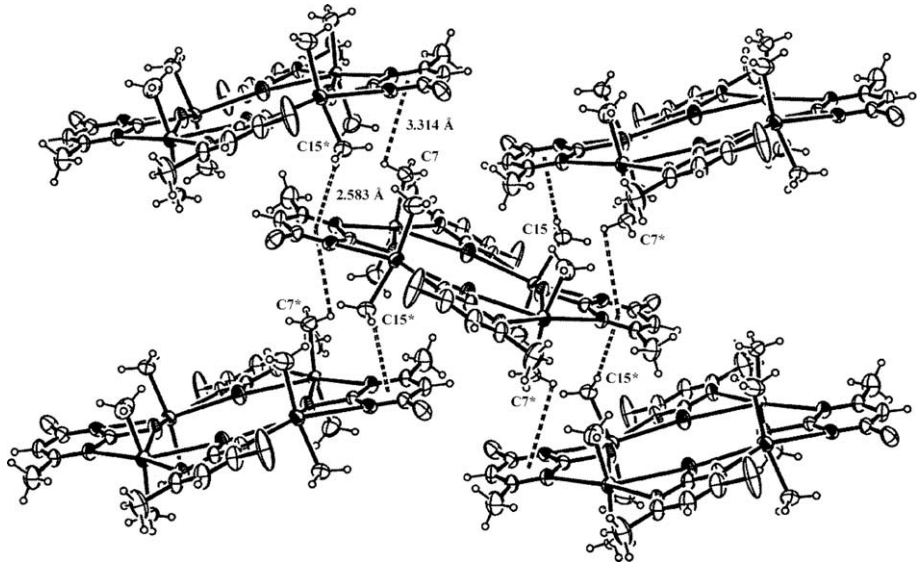

Fig. 3. Crystal packing diagram of $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$; intermolecular C–H $\cdots$ π interactions are represented by a dashed line.

the corresponding signals in the free ligand spectrum. The ^{13}C NMR spectrum of the complex shows all the expected signals and the main change observed is the shift in the C_2 signal, probably due to the reduction in the order of the C–S bond. This situation again provides evidence that the thionato form of the ligand predominates in the complex.

2.4. Mass spectrum

The FAB spectrum of the complex shows peaks due to different fragments of the polymeric compound $[Me_2Tl(4\text{-}CF_3pymS)]_n$, with the appropriate isotope distribution, along with peaks due to $[Me_3Tl_6(4\text{-}CF_3pymS)_5]$, $[MeTl_5(4\text{-}CF_3pymS)_5]$, $[Me_3Tl_4(4\text{-}CF_3pymS)_4]$, $[Me_3Tl_2(4\text{-}CF_3pymS)_2]$, $[Me_2Tl_2(4\text{-}CF_3pymS)_2]$ and $[Me_4Tl_2(4\text{-}CF_3pymS)]$, at $m/z = 2168$, 1931, 1580, 814, 798 and 648, respectively.

3. Conclusion

Comparison of the structures of $[Me_2Tl(4\text{-}CF_3pymS)]_n$ and $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$ (Fig. 4) [17] shows that there are some similarities between the two complexes (Table 2). In both cases, all nitrogen and exocyclic sulfur atoms are coordinated to the metal and in each complex there are asymmetric sulfur bridges between thallium metal centers. Nevertheless, there are clear differences between the two compounds. In $[Me_2Tl(4\text{-}CF_3pymS)]_n$ the interval for the Tl–S bond distances is greater [2.887(4)–3.331(4) Å] and Tl–N smaller [2.625(12)–2.792(12) Å] than in $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$. Moreover, in $[Me_2Tl(4\text{-}CF_3pymS)]_n$ all thallium atoms form asymmetric bridges, whereas in $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$ one thallium is symmetrical and the other one asymmetrical.

The greater length of one of the Tl–S bonds in the polymer [3.331(4) Å] means that the chelate angle containing the sulfur atom is smaller [50.9(3)°] than those found in the tetranuclear complex [55.25(14)–53.03(13)°]. In addition, the disposition of the ligands in the polymer is such that the S–Tl–S angle is 132.34(3)°, whereas in the tetramer the corresponding angles are only 87.12(6) and 85.60(6)°.

The reason for the differences in the structures of the two complexes probably lies in the greater steric hindrance introduced into the ligand $4\text{-}CF_3\text{-}6\text{-}CH_3pymSH$ by the presence of the methyl and trifluoromethyl groups. The presence of these groups forces the ligands in the tetrameric complex to have different dispositions, a situation that makes the thallium centers inequivalent,

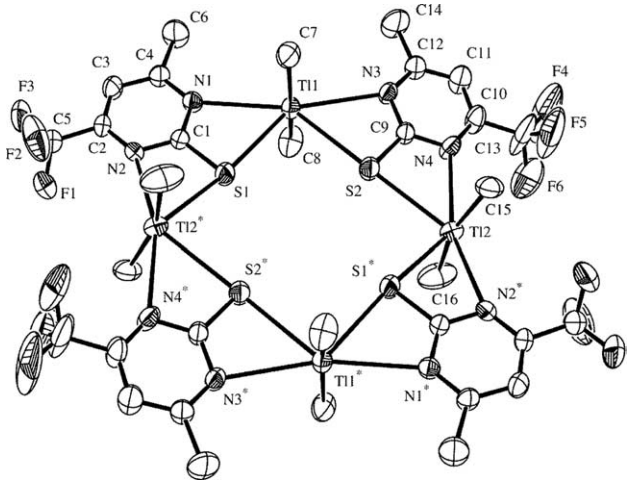

Fig. 4. ORTEP drawing of $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$.

Table 2
Comparison of bond lengths (Å) and angles (°) for $[Me_2Tl(4\text{-}CF_3pymS)]_n$ and $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$

Complex	Tl–C		Tl–N		Tl–S		C–N	C–S
$[Me_2Tl(4\text{-}CF_3pymS)]_n$	Tl(1)–C(6)	Tl(1)–C(7)	Tl(1)–N(1)	Tl(1)–N(2)*	Tl(1)–S(1)	T(1)–S(1)*		
	2.12(2)	2.152(17)	2.792(12)	2.625(10)	2.887(4)	3.331(4)	1.337(18)	1.723(14)
							1.35(2)	
$[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$	Tl(1)–C(8)	Tl(1)–C(7)	Tl(1)–N(1)	Tl(1)–N(3)	Tl(1)–S(1)	Tl(1)–S(2)	C–N	C–S
	2.135(9)	2.153(9)	2.804(7)	2.882(2)	2.848(7)	2.966(2)	1.344(9)	1.731(8)
	Tl(2)–C(15)	Tl(2)–C(16)	Tl(2)–N(4)	Tl(2)–N(2)*	Tl(2)–S(2)	Tl(2)–S(1)*	C–N	C–S
	2.123(8)	2.129(10)	2.858(7)	2.905(2)	3.028(7)	2.889(3)	1. 334(10)	1.722(8)
$[Me_2Tl(4\text{-}CF_3pymS)]_n$	C(7)–Tl(1)–C(6)	N(1)–Tl(1)–S(1)	N(2)*–Tl(1)–S(1)		N(1)–Tl(1)–S(1)*		N(1)–Tl(1)–N(2)*	S(1)–Tl(1)–S(1)*
	161.2(11)	55.4(3)	50.9(3)		172.2(3)		136.8(4)	132.34(3)
$[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$	C(7)–Tl(1)–C(8)	N(1)–Tl(1)–S(1)	N(3)–Tl(1)–S(2)		N(3)–Tl(1)–S(1)*		N(1)–Tl(1)–N(3)	S(1)–Tl(1)–S(2)
	164.6(4)	55.25(14)	54.24(14)		141.33(14)		163.12(19)	87.12(6)
	C(15)–Tl(2)–C(16)	N(4)–Tl(2)–S(2)	S(1)*–Tl(2)–N(2)*		N(4)–Tl(2)–S(1)*		N(4)–Tl(2)–N(2)*	S(2)–Tl(1)–S(1)*
	162.4(5)	54.81(15)	53.03(13)		140.20(15)		160.5(2)	85.60(6)

despite the fact that they are all in a TlC2N2S2 environment. At two of these centers, Tl1 and Tl1*, the coordinated nitrogen atoms are those adjacent to the methyl groups, whereas for the other two metal centers the coordinated nitrogen atoms are those nearest to the trifluoromethyl groups. In the polymer, on the other hand, all of the thallium centers are coordinated by one nitrogen adjacent to the trifluoromethyl group and another nitrogen atom.

In both compounds weak intermolecular C–H $\cdots\pi$ interactions exist between an H atom of each methyl group and one of the pyrimidine rings. These interactions are strongest in the tetranuclear compound $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$. The intermolecular C–H $\cdots\pi$ interactions give rise to a situation in which the polymeric chains are arranged as shown in the packing diagram of $[Me_2Tl(4\text{-}CF_3pymS)]_n$ (Fig. 2). In this arrangement the pyrimidine rings are parallel, while in the tetranuclear complex $[Me_2Tl(4\text{-}CF_3\text{-}6\text{-}CH_3pymS)]_4$ (Fig. 3) these interactions give rise to a different packing in which not all of the pyrimidine rings are parallel with one another.

4. Experimental

4.1. General considerations

4-Trifluoromethylpyrimidine-2-thione (4-CF_3pymSH) was obtained commercially and was used as supplied. Dimethylthallium hydroxide was obtained from the corresponding iodide by treatment with freshly prepared Ag_2O.

4.2. Synthesis of $[TlMe_2(4\text{-}CF_3pymS)]$

An aqueous solution containing $Me_2Tl(OH)$, obtained by treating Me_2TlI (100.1 mg, 0.277 mmol) with freshly precipitated Ag_2O for 24 h in darkness, was slowly added with stirring to a solution of 4-CF_3pymSH (50 mg, 0.277 mmol) in methanol. The reaction mixture was stirred for 24 h in darkness at room temperature. After a few days crystals suitable for X-ray diffraction were obtained. Yield: 0.825 g (72%). *Anal.* Calc. for $C_7H_8F_3N_2$ STl: C, 20.3; N, 6.8; H, 1.9; S, 7.7%. Found: C, 20.3; N, 6.6; H, 1.9; S, 7.6%. I.R. (KBr/cm^{-1}): 1580vs, 1540vs, 1430vs, 1350vs, 1210m, 1190s, 1150m, 1135m, 1115m, 1085w, 1000w, 990w, 845m, 825m, 815m, 780w, 730s, 675sS, 550m, 475m. ^{1}H-NMR (DMSO-d^6, ppm): δ 8.49 (H_6, d); 7.16 (H_5, d); 1.58 (Tl–CH_3, s broad). ^{13}C-NMR (DMSO-d^6, ppm): δ 186.10 (s, C_2); 158.28 (s, C_6); 153.36 (q, C_4); 123.07 (q, CF_3); 108.17 (s, C_5); 23.47 [s, $(CH_3)_2Tl$]. ^{205}Tl NMR (DMSO-d^6, ppm): 3580.

4.3. Physical measurements

Elemental analysis was performed using a Carlo–Erba EA microanalyser. IR spectra were recorded as KBr mulls on a Bruker IFS-66V spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 MHz instrument using DMSO-d^6 as solvent. Chemical shifts were recorded against TMS as the internal standard. ^{205}Tl NMR spectra were obtained on a Bruker AMX500 spectrometer using DMSO-d^6 as solvent. The mass spectra (FAB) were recorded on a Micromass Autospec spectrometer, with 3-nitrobenzyl alcohol as the matrix material.

4.4. X-ray crystallography

Crystal data: $C_7H_8F_3N_2$ STl, $M = 413.58$, yellow plate with dimensions $0.46 \times 0.29 \times 0.06$ mm, monoclinic, space group $P2_1/c$, $a = 9.5567(6)$ Å, $b = 11.3061(8)$ Å, $c = 11.2561(8)$ Å, $\alpha = 90.000°$, $\beta = 105.692(5)°$, $\gamma = 90.000°$, $V = 1170.88(14)$ Å^3, $Z = 4$, $D_c = 2.346$ g cm^{-3}, $F(000) = 752$, μ(Mo Kα) = 13.976 mm^{-1}.

Data collection and processing. X-ray data were collected on a Smart-CCD-1000 Bruker diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 293 K. The ω scan technique was employed to measure intensities in all crystals up to a maximum Bragg angle of 26.47°. No decomposition of the crystals occurred during data collection. Corrections were applied for Lorentz and polarization effects. Absorption corrections were carried out using SADABS [25]. A total of 2397 reflections were collected, of which 2397 were unique ($R_{int} = 0.000$) and 1804 satisfied the $I > 2\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Structure analysis and refinement. The structure was solved by direct methods, missing atoms were located in the difference Fourier map and included in subsequent refinement cycles. The structure was refined by full-matrix least-squares refinement on F^2, using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were included using a riding model with C–H distances of 0.93–0.97 Å and fixed isotropic thermal parameters. The weighting scheme of the form $\omega = 1/\sigma^2(F)$ was introduced and the refinement proceeded smoothly to convergence with a maximum $\delta/\sigma = 0.000$ when $R = 0.0836$, $R_w = 0.2070$ and GOF = 1.014 (goodness-of-fit) for 127 variables.

Crystallographic programs used for the structure solutions and refinement were those included in SHELX-97 [26]. Atomic scattering factors and anomalous-dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography [27]. An Ortep3 drawing [28], along with the numbering scheme used, is shown in Fig. 1.

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-215980. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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