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A new thallium–thiolate coordination environment as found in the polymer $[\{Tl_7(Sthff)_6\}_n][PF_6]_n$ (HSthff = tetrahydrofurfurylthiol)

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Received 19th March 1999, Accepted 9th April 1999

The crystal structure of the polymeric thallium–thiolate salt $[\{Tl_7(Sthff)_6\}_n][PF_6]_n$ (HSthff = tetrahydrofurfurylthiol) shows an unusual octahedrally coordinated thallium(I) atom linking novel Tl_6S_6 "prismane" units.

Homoleptic thiolate complexes of thallium(I) crystallise as monomers, oligomers and polymers and exhibit a large structural variety in the solid state. Structurally characterised complexes include: monomeric $[Tl(1,1\text{-}S_2PEt_2)]$[1] and dimeric $[Tl(1,1\text{-}S_2CNR_2)]_2$ (R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu or ^{i}Bu);[2,3] discrete molecules of $[Tl_8(S^tBu)_8]$;[4,5] polymeric TlSPh which consists of cage-like structural units $[Tl_5(SPh)_6]^-$ and $[Tl_7(SPh)_6]^+$;[4,5] linked 1,3-Tl_2S_2 ring two-dimensional polymers[5–8] for $TlSCH_2Ph$, $TlSC_7H_7$, $TlSC_6H_{11}$ and $Tl\{2,4,6\text{-}SC_6H_2(CF_3)_3\}\cdot 0.5diox$ (diox = 1,4-dioxane); dimeric $[Tl\{SSi(O^tBu)_3\}]_2$, which also contains a 1,3-Tl_2S_2 ring;[9] and $[\{Tl[1,2\text{-}(\mu\text{-}S)_2C_6H_4]\}_2]^{2-}$ which contains Tl_2S_4 cages.[10] Here we report a new structural motif for thallium(I) thiolates.

Although first reported in the 1950's[11–13] the use of tetrahydrofurfurylthiol † (HSthff), Fig. 1, as a proligand in coordination chemistry has not been explored. As part of a survey of the utility of the anion of HSthff as a ligand, we have studied its reaction with thallium hexafluorophosphate. Under anaerobic conditions, to a stirred solution of NaSthff ‡ (0.48 g, 3.4 mmol) in methanol (35 ml) was added thallium(I) hexafluorophosphate (1.19 g, 3.4 mmol) to form immediately a yellow solution. The mixture was stirred for 10 min after which time a yellow precipitate had begun to form. The precipitate redissolved on gentle warming and on cooling to room temperature gave the product as yellow needle-like crystals (0.52 g, 50% based on Tl).§

Crystallography¶ showed a structure of polymeric chain cations of $[Tl_7(Sthff)_6]^+$, Fig. 2; the novel Tl_6S_6 "prismane"-like units are linked through thallium(I) atoms on opposite faces. The resultant Tl_8S_6 unit consists of a cube of thallium atoms and each face of the cube is capped by the sulfur atom of a thiolate ligand; the unit shows pseudo-*m*3*m* symmetry. There is a crystallographic centre of symmetry at the centre of each cube and a pseudo-centre at each linking thallium. Two independent cube units alternate along the cation chain; there are only very small differences in orientation between the two units.

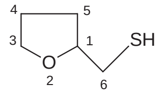

Fig. 1 Tetrahydrofurfurylthiol showing atom numbering.

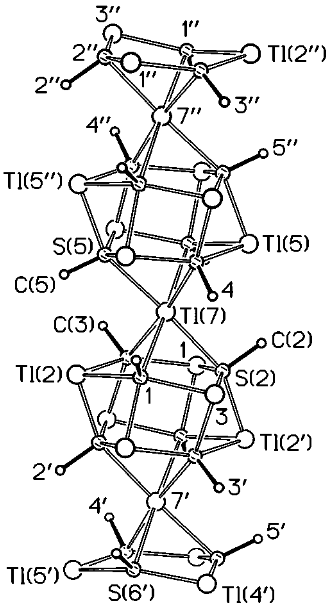

Fig. 2 Fragment of a cation chain showing the linking of Tl_8S_6 cube units through Tl(7) atoms at opposite corners of the cubes. Only the Tl, S and α-carbon atoms are shown; the sulfur atoms are hatched, the larger and smaller open circles represent the Tl and C atoms respectively, and the atom numbering scheme is indicated. The primed numbers indicate symmetry operations about inversion centres: ′ at $1 - x, -y, -z$ and ″ at $1 - x, -y, 1 - z$.

There are thus two types of thallium environment, one trigonal pyramidal (bonded to three S atoms) at the six corners of the "prismane", and one octahedral (bonded to six S atoms) at the bridging positions. This is the first example of a thallium thiolate containing octahedrally coordinated thallium atoms.|| The Tl–S bonds involving the trigonal pyramidal Tl atoms, *i.e.* within the prismane units, are in the range 2.880(11)–3.086(11) Å, mean 2.97(2) Å; about the linking, octahedral Tl(7) atoms, the Tl–S distances are rather longer, 3.138(11)–3.302(12) Å, mean 3.24(2) Å. Each sulfur atom is coordinated to four thallium atoms and the carbon atom of a tetrahydrofurfuryl group in a square-pyramidal pattern. There is extensive disorder in the thiolate ligands, which do not conform to the pseudo-*m*3*m* symmetry. There is a chiral centre in each ligand and we were not able to resolve clearly the two possible configurations in any of the ligands. We do note, however, that each tetrahydrofurfuryl group is oriented with the ring tilted towards a thallium atom so that there are interactions between the thallium atom and the atom (which we designated an oxygen atom) at the 2-position in the ring with distances of 3.03(9) to 3.36(7) Å.

There is also disorder in the positions of the fluorine atoms of the discrete PF_6^- anions. The cation chains lie parallel to the crystallographic *c* axis and the anions lie between pairs of chains. Each cation chain is linked to four others *via* the anions with close Tl · · · F interactions, the shortest five of which are in the range 3.05(8) to 3.39(5) Å.

The basic structural Tl–S motif in our complex, the capped cube, has similarities only, to our knowledge, in the two units that are bonded together in the complex polymer of Tl(SPh).[4,5] In our polymeric chain, two almost identical cubes, each with little distortion from regular cubes, are linked alternately through opposite corners of the cubes. The polymer of Tl(SPh) is a three-dimensional lattice of units described as $[Tl_7(SPh)_6]^+$

and $[Tl_5(SPh)_6]^-$; the crystal system is cubic and both units lie on three-fold symmetry axes. The cationic unit is a capped cube but with one Tl corner void. The anion is less regular, it is basically a completely capped cube but with three of the thallium atoms displaced considerably from the regular cube; these three atoms are in fact the atoms that link the cations with the anions and are not included in the formula of the anion units. If one starts with the array of sulfur atoms, as suggested by Krebs and Brömmelhaus,[4] the six sulfur atoms of the cation unit form an almost regular octahedron and seven of the eight faces of the octahedron are capped by thallium atoms. The octahedron of sulfur atoms in the anion is less regular, five of its faces are Tl-capped and the remaining three faces have rather offset capping thallium atoms. In our Tl(Sthff) polymer, the two S_6 octahedra are close to regular and each has all eight faces capped by thallium atoms.

Acknowledgements

We thank the Biotechnology and Biological Sciences Research Council for funding.

Notes and references

† IUPAC name: (tetrahydrofuran-2-yl)methanethiol.

‡ HSthff was prepared by a method similar to that reported previously.[13] Found: C, 51.0; H, 8.4; S, 27.2. $C_5H_{10}OS$ requires: C, 50.8; H, 8.5; S, 27.1%; ν_{max}/cm^{-1} (SH) 2555 (neat, KBr disc); δ_H(400 MHz; $CDCl_3$) 3.85 (m, 3H, CH_2{3} and CH{1}), 2.62 (m, 2H, CH_2{6}), 1.8 (mm, 4H, CH_2{4 + 5}), 1.47 (t, 1H, SH); δ_C(100 MHz, $CDCl_3$) 79.9 {C1}, 68.4 {C3}, 30.2 {C5}, 29.5 {C6}, 25.9 {C4}. NaSthff was prepared from HSthff and sodium metal in tetrahydrofuran.

§ Found: C, 15.8; H, 2.3; S, 8.2. $C_{30}H_{54}F_6O_6PS_6Tl_7$ requires: C, 15.8; H, 2.4; S, 8.4%; λ_{max}/nm (CH_3OH) 224 (ε/dm^3 mol^{-1} cm^{-1} 47600), 256 (sh) (13600) and 292 (8700); δ_H(400 MHz, CD_3OD) 4.18 (m, 1H, CH{1}), 3.80 (mm, 2H, CH_2{3}), 3.29 (m, 2H, CH_2{6}), 1.60–2.14 (mm, 4H, CH_2{4 + 5}); δ_C(100 MHz, $CDCl_3$): 80.0 {C1}, 68.0 {C3}, 30.5 {C5}, 29.7 {C6}, 26.0 {C4}.

¶ Crystal data: $C_{30}H_{54}O_6S_6Tl_7PF_6$, $M = 2278.7$, monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a = 14.401(2)$, $b = 23.661(2)$, $c = 15.2958(12)$ Å, $\beta = 97.404(9)°$, $V = 5168.4(10)$ Å^3, $Z = 4$, $D_c = 2.93$ g cm^{-3}, $F(000) = 4056$, $T = 293(1)$ K, μ(Mo-Kα) = 220.7 cm^{-1}, λ(Mo-Kα) = 0.71069 Å, 5054 reflections measured, 4819 unique, $R_{int} = 0.053$, $wR_2 = 0.133$, $R_1 = 0.161$ for all the data;[14] $R_1 = 0.052$ for the 1683 "observed" data. In the refinement, the Tl, S and P atoms were refined anisotropically, while the C, O and F atoms (most of which were disordered with partial site occupancy) were refined with isotropic thermal parameters. CCDC reference number 186/1419. See http://www.rsc.org/suppdata/dt/1999/1533/ for crystallographic files in .cif format.

|| It has been suggested,[6] though not fully reported, that a similar coordination environment is seen in polymeric $[Tl_5(SC_3H_7)_5]$.

1 S. Esperas and S. Husebye, *Acta Chem. Scand.*, *Ser. A*, 1974, **28**, 1015.

2 L. Nilson and R. Hesse, *Acta Chem. Scand.*, 1969, **23**, 1951; P. Jennische, A. Olin and R. Hesse, *Acta Chem. Scand.*, 1972, **26**, 2799; P. Jennische and R. Hesse, *Acta Chem. Scand.*, 1973, **27**, 3531; H. Anacker-Eickhoff, P. Jennische and R. Hesse, *Acta Chem. Scand.*, *Ser. A*, 1975, **29**, 51; H. Pritzkow and P. Jennische, *Acta Chem. Scand.*, *Ser. A*, 1975, **29**, 60; E. Efwing, H. Anacker-Eickhoff, P. Jennische and R. Hesse, *Acta Chem. Scand.*, *Ser. A*, 1976, **30**, 335.

3 D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301.

4 B. Krebs and A. Brömmelhaus, *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 1682.

5 B. Krebs and A. Brömmelhaus, *Z. Anorg. Allg. Chem.*, 1991, **595**, 167.

6 A. Brömmelhaus, A. Pinkerton and B. Krebs, *Annual Meeting of the American Crystallographic Association*, Toledo, OH, 1991, abstract p. 123.

7 B. Krebs, A. Brömmelhaus, B. Kersting and M. Nienhaus, *Eur. J. Solid State Inorg. Chem.*, 1992, **t29**, 167.

8 D. Labahn, E. Pohl, R. Herbst-Irmer, D. Stalke, H. W. Roesky and G. M. Sheldrick, *Chem. Ber.*, 1991, **124**, 1127.

9 W. Wojnowski, K. Peters, E.-M. Peters and H. G. v. Schnering, *Z. Anorg. Allg. Chem.*, 1985, **531**, 147.

10 B. E. Bosch, M. Eisenhawer, B. Kersting, K. Kirschbaum, B. Krebs and D. M. Giolando, *Inorg. Chem.*, 1996, **35**, 6599.

11 J. H. Chapman and L. N. Owen, *J. Chem. Soc.*, 1950, 579.

12 Y. K. Yuryev and E. G. Vendelshtein, *Zh. Obshch. Khim.*, 1952, **22**, 687; *J. Gen. Chem. USSR (Engl. Transl.)*, 1952, **22**, 751.

13 V. C. Barry and J. E. McCormick, *Proc. R. Irish Acad.*, *Sect. B*, 1958, **59**, 345.

14 G. M. Sheldrick, SHELXL, Program for Crystal Structure Refinement, University of Göttingen, 1993.

Communication 9/02193K