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Spectroscopic and X-ray studies of bis[dimethylthallium(III)]-1,3,4-thiodiazole-2,5-dithiolato

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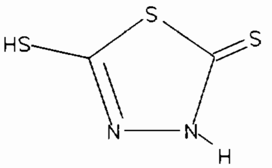
Abstract

The crystal structure of [$(TlMe_2)_2L$] (H_2L = 2,5-dimercapto-1,3,4-thiodiazole, bismuthiol I) has been determined. The compound crystallizes in the orthorhombic space group *Fdd*2 (No. 43) with $a = 17.003(2)$, $b = 32.810(9)$, $c = 9.543(7)$ Å and $Z = 16$ ($R = 0.049$, $R' = 0.045$). The ligand binds to the thallium atoms via an intricate net of weak Tl...N and Tl...S interactions, probably with a strong electrostatic contribution. The ^{13}C CPMAS spectra of H_2L and [$(TlMe_2)_2L$], and some other spectroscopic properties in the solid state and in solution, are also discussed.

Introduction

The reaction of bismuthiol I (2,5-dimercapto-1,3,4-thiodiazole, H_2L) with methylmercury(II) hydroxide



in aqueous/methanolic medium furnishes the compound [$(HgMe)_2L$] [1], in which four of the seven ligand atoms (the two N and the two exocyclic S atoms) behave as donor centres. Together, primary and secondary bonds make up a rather complicated coordination scheme, even though the methylmercury(II) cation, a 'soft' Lewis acid, usually exhibits simple lineal coordination [2]. We have now explored the bonding possibilities of L^{2-} further by preparing [$(TlMe_2)_2L$] and studying its properties in the solid state and in solution. Because the dimethylthallium cation has a wider range of coordination numbers, we expected significant differences from the methylmercury(II) compound.

Experimental

Bismuthiol I (EGA) was used as received. Analytical data were obtained using a Perkin-Elmer model 240B analyser. Conductivity measurements were made in Me_2SO solution with a WTW conductivity meter. Mass spectrum was recorded in a Kratos MS50TC spectrometer connected to a DS 90 data system, using electron impact (70 eV, *c.* 1.12×10^{-17} J) with the source at 250 °C and operating at an acceleration voltage of 8 kV. The sample was introduced via a direct injection probe, which was heated to 400 °C. ^1H and ^{13}C NMR spectra were recorded in $(CD_3)_2SO$ on a Bruker WM 250 instrument.

^{13}C CPMAS NMR spectra were obtained on a Bruker MSL-400 at 100.63 MHz, with single cross-polarization contacts of (typically) 3 ms with magic angle sample spinning at 4 kHz in 7 mm zirconia rotors. Spectral acquisition time was 16 ms and recycle time 6 s. Typically 1000 transients were collected prior to Fourier transformation. The TOSS pulse sequence [3] was used to eliminate spinning side bands. All chemical shifts were referred to an external glycine sample (δ 176.0 ppm).

Synthesis

The compound was obtained from dimethylthallium(III) iodide [4] following the procedure used for [$(HgMe)_2L$] [1]. *Anal.* Found: C, 11.91; H, 1.87; N, 3.58. Calc. $C_6H_{12}N_2S_3Tl_2$: C, 11.67; H, 1.95; N, 4.54%. m.p. 230 °C (decomposition). The EI mass spectrum

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exhibited the following important metallated fragmentations (normal values calculated using the most abundant isotope ^{205}Tl): m/z 205 (100, base, Tl^+), 220 (13.0, $TlMe^+$), 235 (59.1, $TlMe_2{}^+$), 368 [15.4, $(M-TlMe_2-Me)^+$], 383 [8.8, $(M-TlMe_2)^+$] and 398 [4.0, $(M-TlMe)^+$].

Determination of the crystal structure

A transparent, approximately prismatic crystal of $0.07 \times 0.13 \times 0.40$ mm was used.

Crystal data

$C_6H_{12}N_2S_3Tl_2$, $M = 617.11$, orthorhombic, $a = 17.003(2)$, $b = 32.810(9)$, $c = 9.543(7)$ Å, $U = 5324(6)$ Å^3 (by least-squares refinement on diffractometer angles for 15 automatically centred reflections, $10.8 > \theta < 17.6°$, λ(Mo Kα) = 0.71073 Å), space group $Fdd2$ (No. 43), $Z = 16$, $D_x = 3.079$ g cm^{-3}, $\mu = 24.85$ mm^{-1}, $F(000) = 4352$, $T = 296$ K, $R = 0.049$ for 768 observed reflections.

Data collection and processing

Enraf Nonius CAD-4 diffractometer, ω–2θ mode with ω scan width $[0.80 + 0.35 \tan\theta]$, max. scan speed 5.0° min^{-1}, graphite-monochromated Mo Kα radiation; 1398 unique reflections measured, ($0 < \theta < 25°$, $0 \leqslant h \leqslant 20$, $0 \leqslant k \leqslant 38$, $-2 \leqslant l \leqslant 11$; a standard reflection varied +3.1% of mean intensity over data collection), 768 with $I > 3\sigma(I)$; Lorentz and polarization corrections. Absorption corrections were applied at a later stage in refinement [5] (max., min. absorption corrections = 1.619, 0.696).

Structure analysis and refinement

The structure was solved by Patterson and Fourier techniques. In the final cycles of full-matrix least-squares refinement, only the Tl and S atoms were anisotropic, H atoms were not included in the model. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o)$; 74 parameters were refined. Correction for secondary extinction: $F_{corr} = F_c(1 - xF_c{}^2/\sin\theta)$, where x refined to 4×10^{-9} in the final run. Excluding unobserved reflections, R $[= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ and R' $\{= [\Sigma w(|F_o| - |F_c|)]^2/\Sigma w|F_o|^2\}$ values 0.049 and 0.045, respectively; maximum shift/estimated standard deviation (e.s.d.) = 0.02. Programs used: SHELX-76 [6] and ORTEP [7]; scattering factors from Cromer and Mann [8] with corrections for anomalous dispersion from Cromer and Liberman [9].

Discussion

Final atomic parameters are given in Table 1, intramolecular bond distances and angles in Table 2 and bond distances and angles around the thallium atoms in Table 3.

TABLE 1. Fractional atomic coordinates and isotropic temperature factors

Atom	x/a	y/b	z/c	B_{iso} (Å^2)
Tl(1)	0.2052(1)	0.1346(1)	0	4.85(8)
Tl(2)	0.1161(2)	0.2649(1)	0.5910(4)	7.7(1)
S(1)	0.2779(7)	0.0822(4)	0.230(2)	5.9(6)
S(2)	0.213(1)	0.1920(4)	0.697(2)	6.7(7)
S(3)	0.1922(7)	0.1297(3)	0.464(1)	4.1(6)
N(1)	0.333(2)	0.139(1)	0.412(4)	4.0(8)
N(2)	0.314(2)	0.165(1)	0.511(6)	6(1)
C(1)	0.266(3)	0.114(1)	0.360(5)	4(1)
C(2)	0.247(3)	0.164(1)	0.560(4)	2.9(9)
C(3)	0.205(2)	0.085(1)	−0.154(5)	4(1)
C(4)	0.234(3)	0.196(1)	0.115(6)	6(1)
C(5)	0.124(4)	0.246(1)	0.359(7)	7(1)
C(6)	0.083(4)	0.272(2)	0.806(7)	10(1)

TABLE 2. Intramolecular bond distances (Å) (excluding thallium) and interatomic bond angles (°) (excluding thallium as central atom)

S(1)–C(1)	1.63(5)
S(2)–C(2)	1.70(4)
S(3)–C(1)	1.68(5)
S(3)–C(2)	1.72(4)
N(1)–N(2)	1.31(6)
N(1)–C(1)	1.49(6)
N(2)–C(2)	1.23(6)
Tl(1)–S(1)–C(1)	98(1)
Tl(2)–S(2)–C(2)	110(1)
C(1)–S(3)–C(2)	96(1)
N(2)–N(1)–C(1)	114(1)
N(1)–N(2)–C(2)	119(1)
S(3)–C(1)–N(1)	102(1)
S(1)–C(1)–S(3)	137(1)
S(1)–C(1)–N(1)	121(1)
S(3)–C(2)–N(2)	108(1)
S(2)–C(2)–S(3)	125(1)
S(2)–C(2)–N(2)	126(1)

The units $[(TlMe_2)_2L]$ are held together by an intricate network of Tl...N and Tl...S interactions, probably with a large ionic component. In Fig. 1, the $[(TlMe_2)_2L]$ unit whose coordinates are given in Table 1 is shown in bold lines, together with four other units (in single lines), obtained from the first one by application of one of the symmetry operations given in Table 3. This five-unit arrangement is necessary to display the coordination around the two independent thallium atoms in the 'bold' unit. The relevant distances and angles around these thallium atoms are those given in Table 3.

Figure 2 is a stereoscopic projection showing all the crystallographically independent interactions involving the bismuthiol I ligand of the 'bold' $[(TlMe_2)_2L]$ unit.

TABLE 3. Distances (Å) and angles (°) around the thallium atoms

Tl(1)–S(2)	3.45(2)^{ii}
Tl(1)–S(1)	3.21(1)^{iv}
Tl(1)–N(1)	2.70(4)^{iv}
Tl(1)–S(1)	3.05(2)
Tl(1)–C(3)	2.19(4)
Tl(1)–C(4)	2.35(5)
Tl(2)–S(1)	3.46(1)^{i}
Tl(2)–S(2)	3.39(2)^{iii}
Tl(2)–N(2)	2.70(4)^{iii}
Tl(2)–S(2)	3.08(1)
Tl(2)–C(5)	2.30(7)
Tl(2)–C(6)	2.14(7)
S(1)–Tl(1)–C(3)	94(1)
S(1)–Tl(1)–C(4)	94(1)
S(1)–Tl(1)–S(2)^{ii}	153.4(4)
S(1)–Tl(1)–S(1)^{iv}	127.9(4)
S(1)–Tl(1)–N(1)^{iv}	74.8(8)
C(3)–Tl(1)–C(4)	162(1)
C(3)–Tl(1)–S(2)^{i}	81(1)
C(3)–Tl(1)–S(1)^{iv}	102(1)
C(3)–Tl(1)–N(1)^{iv}	100(1)
C(4)–Tl(1)–S(2)^{i}	85(1)
C(4)–Tl(1)–S(1)^{iv}	86(1)
C(4)–Tl(1)–N(1)^{iv}	98(1)
S(2)^{ii}–Tl(1)–S(1)^{iv}	78.5(4)
S(2)^{ii}–Tl(1)–N(1)	131.7(8)
S(1)^{iv}–Tl(1)–N(1)	53.8(8)
S(2)–Tl(2)–C(5)	94(1)
S(2)–Tl(2)–C(6)	85(1)
S(2)–Tl(2)–S(1)^{i}	167.2(4)
S(2)–Tl(2)–S(2)^{iii}	76.5(4)
S(2)–Tl(2)–N(2)^{iii}	121.3(9)
C(5)–Tl(2)–C(6)	165(1)
C(5)–Tl(2)–S(1)^{i}	85(1)
C(5)–Tl(2)–S(2)^{iii}	110(1)
C(5)–Tl(2)–N(2)^{iii}	86(1)
C(6)–Tl(2)–S(1)^{i}	92(1)
C(6)–Tl(2)–S(2)^{iii}	84(1)
C(6)–Tl(2)–N(2)^{iii}	107(1)
S(1)^{i}–Tl(2)–S(2)^{iii}	115.6(4)
S(1)^{i}–Tl(2)–N(2)^{iii}	71.4(9)
S(2)^{iii}–Tl(2)–N(2)^{iii}	49.5(9)

Symmetry operations: $^{i}\,\frac{1}{4}-x,\ \frac{1}{4}+y,\ \frac{1}{4}+z$; $^{ii}\,x,\ y,\ -1+z$; $^{iii}\,\frac{1}{2}-x,\ \frac{1}{2}-y,\ z$; $^{iv}\,-\frac{1}{4}+x,\ \frac{1}{4}-y,\ -\frac{1}{4}+z$.

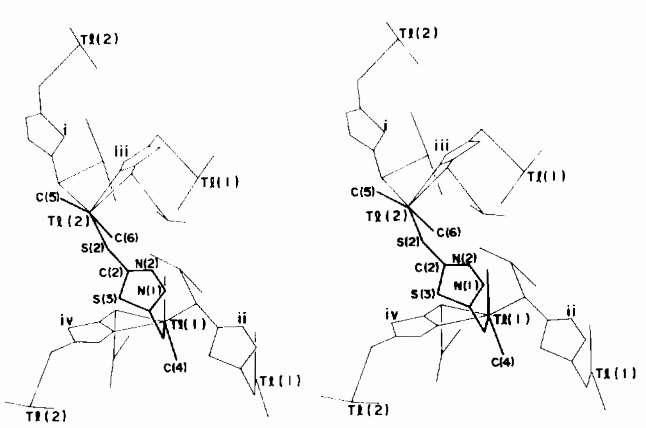

Fig. 1. Stereoscopic projection showing coordination around the two independent thallium atoms and the numbering scheme. Superscripts i, ii, iii and iv indicate that the $[(TlMe_2)_2L]$ unit so labelled was obtained from the one in bold lines by the symmetry operation given the same number in Table 3.

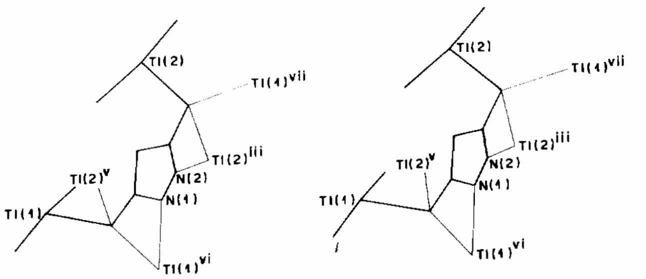

Fig. 2. Stereoscopic view of the structure, showing all the crystallographically independent interactions of the bismuthiol I ligand. Superscripts v, vi and vii have meanings analogous to i–iv (see Fig. 1) for the following symmetry operations: $^{v}\,\frac{1}{4}-x,\ -\frac{1}{4}+y,\ -\frac{1}{4}+z$; $^{vi}\,\frac{1}{4}+x,\ \frac{1}{4}-y,\ \frac{1}{4}+z$; $^{vii}\,x,\ y,\ 1+z$.

The thallium atoms are bound axially to two methyl groups, and have four equatorial atoms (one S from each of three ligand molecules and one N belonging to one of these ligands) at distances that are rather long but still shorter than the sums of the van der Waals radii ($r_{Tl}+r_s=3.76$ Å and $r_{Tl}+r_N=3.51$ Å) [10]. The importance of these equatorial interactions can be assessed by comparing their interatomic distances with those found for thallium–sulfur and thallium–nitrogen in dimethyl(4-amino-5-mercapto-3-trifluoromethyl-1,2,4-triazolato)thallium(III) (Tl–S = 2.85(1) Å and Tl–N = 2.61(2) Å) [11] the pentagonal ligand of which has coordination properties somewhat similar to those of bismuthiol I.

Tl(1) and Tl(2) differ as regards the order of their equatorial atoms (Fig. 1). In the equatorial plane of Tl(1), the sulfur atom subtending the shortest Tl–S bond length, S(1), lies between a sulfur and a nitrogen atom (S(2)^{ii} and N(1)^{iv}) whereas in the equatorial plane of Tl(2), S(2) lies between two sulfur atoms (S(1)^{i} and S(2)^{iii}). Moreover, these 'planes' have very different degrees of planarity; χ^2 for the least-squares plane through Tl(1), S(1), S(2)^{ii}, S(1)^{iv} and N(1)^{iv} is 202, as against 2585 for the least square-planes through Tl(2), S(2), S(1)^{i}, N(2)^{iii} and S(2)^{iii}. The poor planarity around Tl(2) can be ascribed to a twist in the plane of ligand 3 that seems also to place S(2)^{iii} farther from Tl(2) than S(1)^{iv} is from Tl(1).

The $TlMe_2$ unit is almost linear for both Tl(1) and Tl(2). The large e.s.d.s prevent interpretation of the differences between Tl(1)–C(3) and Tl(1)–C(4) and between Tl(2)–C(5) and Tl(2)–C(6). The values of B_{iso}

indicate some disorder for the methyl groups, especially $C(5)H_3$ and $C(6)H_3$.

There are some similarities between this structure and that found for $[(HgMe)_2L]$ [1]. In both, all nitrogen atoms and exocyclic sulfur atoms are coordinated to the metal, and in both there are asymmetric sulfur bridges between metal centres. Nevertheless there are also clear differences. In the thallium compound M–S is longer and M–N shorter than in the mercury derivative; as in other systems [12], the Tl–N bond is probably stronger than the Tl–S interaction, an assumption supported by the bond length values. Moreover, in $[(TlMe_2)_2L]$ both the exocyclic sulfur atoms form asymmetric bridges, whereas only S(1) does in the mercury compound. As a result, thallium has a larger coordination number in $[(TlMe_2)_2L]$ than mercury in $[(HgMe)_2L]$, even counting the very weak Hg...N interactions in $[(HgMe)_2L]$.

The changes in the ligand molecule with respect to its geometry in H_2L [13] or $[(HgMe)_2L]$ [1] are difficult to assess, due again to large e.s.d.s. There does, however, seem to be a significant difference with respect to H_2L [13] as regards the C(1)–N(1) and C(2)–N(2) distances. Also, in $[(TlMe_2)_2L]$ the bond angles at S(1) and S(2) are different (e.g. Tl(1)–S(1)–C(1) = 98(2)°; Tl(2)–S(2)–C(2) = 110(1)°), increasing the asymmetry of the two halves of the bismuthiol I ring.

The ^{13}C CPMAS NMR spectrum of H_2L is in keeping with the X-ray diffraction results for the crystalline solid [13]. Although the signals are weak due to there being no hydrogens directly bound to carbons, two clear peaks at 188.5 and 158.8 ppm can be assigned to thione and thiol carbons, respectively. The spectrum of $[(TlMe_2)_2L]$ shows the low frequency doublet typical of the splitting of the thallium methyl resonance by coupling with ^{203}Tl and ^{205}Tl nuclides. Each band of this doublet is further split, probably due to magnetic differences arising from the differences in coordination between Tl(1) and Tl(2) and from the lattice disorder of the CH_3 groups (*vide supra*). The chemical shift of these carbons (referred to the more strong peak of each multiplet) is 25.0 ppm, while the coupling constant $^1J(^{203/205}Tl–^{13}C)$ is 2644 Hz. In the high frequency part of the spectrum there appears a strong band at 175.9 ppm suggesting that the two thioamide groups of the bismuthiolato anion share a common electronic distribution intermediate between those of thiol and thione groups. Other weak signals occur at 185.2, 177.3 and 170.4 ppm.

$[(TlMe_2)_2L]$ is insoluble in organic solvents of low dielectric constant, but is soluble in dimethyl sulfoxide. In this medium its molar conductivity (26 ohm^{-1} cm^2 mol^{-1} for a 10^{-3} M solution) is at the lower end of the range reported for 1:1 electrolytes [14]. In keeping with this, the values of $^2J(^{203/205}Tl–^1H)$ (232 Hz) and $^1J(^{203/205}Tl–^{13}C)$ (2915 Hz) are very close to those observed for $(TlMe_2)ClO_4$ in this solvent (438 and 2918 Hz, respectively [15]). The ^{13}C NMR signals of H_2L at 188.5 and 151.5 ppm show that the free ligand has the same structure in $(CD_3)_2SO$ solution as in the solid state [13]. The ligand part of the spectrum of $[(TlMe_2)_2L]$ (one band at 178.5 ppm) is also almost the same in the solid state as in $(CD_3)_2SO$ solution, in keeping with the idea that ionic forces are important in the lattice.

Acknowledgements

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