(*p*-Anisaldehyde thiosemicarbazonato)dimethylthallium(III): an Unusual Structure for a Co-ordinated Thiosemicarbazone

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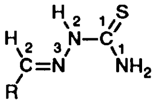
Reaction of an ethanolic solution of *p*-anisaldehyde thiosemicarbazone (HL) with an aqueous $[TlMe_2(OH)]$ solution afforded the compound $[TlMe_2L]$ in which the deprotonated thiosemicarbazone retains the typical structure of free thiosemicarbazones, an unusual arrangement of this type of ligand in a metallic complex.

In the solid state thiosemicarbazones, whose two main resonance forms are shown below, normally have (*i*) an approximately planar C^2–N^3–N^2–C^1(S)–N^1 chain; (*ii*) an *E*-configuration about the aldimine C^2–N^3 bond; and (*iii*) the thioamide S atom *trans* to the hydrazinic (NH–N) group.[1,†]



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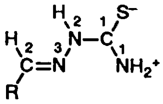
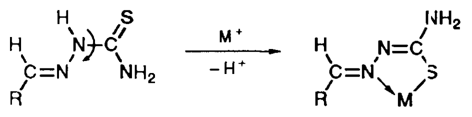


II

In spite of this ill suited structure, thiosemicarbazones generally co-ordinate *via* their N^3 and S atoms,[1] which is made possible by a 180° rotation about C^1–N^2. This switches the positions of S and N^1, giving an arrangement capable of forming a stable five-membered chelate ring with the metal.



Hitherto, the free-ligand structure has only been observed in the complexes of S-substituted thiosemicarbazones, in which co-ordination occurs *via* N^1 and N^3 (ref. 3). However, by reaction of *p*-anisaldehyde thiosemicarbazone (HL)‡ with $[TlMe_2(OH)]$ we have now obtained the complex $[TlMe_2L]$ **1**§ in which the deprotonated thiosemicarbazone retains the typical structure of free thiosemicarbazones and is co-ordinated to the thallium atom *via* N^2 and S (Fig. 1).¶

The Tl–C distances in **1** are normal for $TlMe_2$ compounds. The C–Tl–C angle is bent slightly back from the bite of the ligand. The Tl–N(2) distance is close to that observed in (cyclopentanone thiosemicarbazonato)dimethylthallium(III),[8] in which the sulfur atom is *cis* to the hydrazinic (NH–N) group. However, the intramolecular Tl–S distance is longer in **1**, showing the steric limitations imposed by the four-membered chelate ring and the preference of the dimethylthallium cation for co-ordination to N rather than S.[9] The Tl atom is 0.549(1) Å above the plane of the thiosemicarbazone fragment, which forms an angle of 22(1)° with the plane of the anisole ring. Weak intermolecular interaction between the metal and a second sulfur atom S′ links the $[TlMe_2L]$ molecules in the lattice, the Tl–S′ distance being less than the sum of the van der Waals radii (3.76 Å).[10]

The powder first isolated from the reaction mixture and monocrystals obtained from the mother-liquor after cooling have the same IR spectrum, in which the displacement of ν(N–H) toward higher wavenumbers (3520m, 3370m) than in the free ligand (3400s, 3260s) rules out co-ordination of the

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† At least one exception to the structural generalizations (*i*)–(*iii*) has been found among non-S-substituted thiosemicarbazones: in *N*′-[1-(2-pyridyl)ethylidene]-3-azabicyclo[3.2.2]nonane-3-carbothiohydrazide the sulfur atom is *cis* to the N^2–N^3 group.[2] Nevertheless, it should be noted that this thiosemicarbazone is also unusual in that (*a*) the hydrazinic hydrogen is located at N^3 instead of N^2, and (*b*) N^1 has no hydrogen atoms, which means that placing S *trans* to N^2–N^3 instead of *cis* no longer has the advantage of facilitating stabilization by an intramolecular N^1–H $\cdots$ N^3 hydrogen bond.

‡ Thiosemicarbazone HL was obtained by the general procedure described in ref. 4.

§ A solution of HL (0.58 g, 2.8 mmol) in ethanol (50 cm^3) was slowly added, with stirring, to an aqueous solution of $[TlMe_2(OH)]$ (2.8 mmol, *ca.* 50 cm^3) obtained by treating $TlMe_2I$[5] with freshly precipitated Ag_2O. A white powder formed which was filtered off. On cooling, the mother-liquor afforded white crystals that were dried *in vacuo* and used in the X-ray study. Correct elemental analysis. Yield (powder plus first batch of crystals) 0.71 g, 57%; m.p. 170 °C.

¶ X-ray diffraction measurements were performed twice, using monocrystals from different batches and identical results were obtained. Visual inspection afforded no evidence of there being more than one crystalline habit. Crystal data: $C_{11}H_{16}N_3OSTl$, M_r = 442.70, monoclinic, $P2_1/c$ (no. 14), a = 16.945(4), b = 7.454(5), c = 12.016(8) Å, β = 106.48(3)°, U = 1455.5 Å^3, Z = 4, D_c = 2.020 g cm^{-3}, μ(Mo-Kα) = 113.38 cm^{-1}, F(000) = 832. Measurement parameters: Enraf–Nonius CAD-4, T = 298 K, 3208 measured reflections ($1 < \theta < 26°$), 2418 unique, 1426 with $I_o > 3\sigma(I_o)$ used for refinement. Variation of intensity of standards during data collection, −0.3%, empirical absorption correction (0.855 < T < 1.131). Structure solution: Patterson (SHELX 86),[6] difference Fourier technique, 154 parameters; full-matrix least-squares refinement (SHELX 76),[7] $R = R'$ = 0.040, hydrogen atoms not found in difference maps and not included, all atoms refined anisotropically. Residual electron density +0.81, −1.15 e Å^{-3} (the largest peaks near the Tl atom). Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

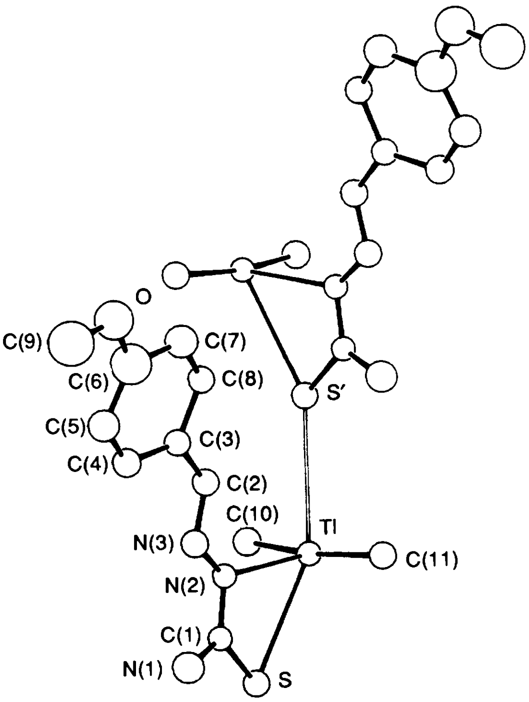

Fig. 1 Structure of (*p*-anisaldehyde thiosemicarbazonato)dimethylthallium(III), with numbering scheme. Selected bond lengths (Å) and angles (°): Tl–C(10) 2.14(2), Tl–C(11) 2.15(2), Tl–N(2) 2.56(1), Tl–S 2.991(4), Tl–S' 3.304(4), C(10)–Tl–C(11) 169.7(7), N(2)–Tl–S 55.7(3), N(2)–Tl–S' 99.2(3). Primed atoms related to unprimed equivalents by *x*, 0.5 − *y*, *z* − 0.5

$-NH_2$ group to the metal. As in other thiosemicarbazonates,[11] the C=S bands near 1000 cm^{-1} are less intense than in the free ligand, and the 835 cm^{-1} band is slightly shifted. However, the 1600 cm^{-1} band of the free ligand has not shifted toward higher wavenumbers as in thiosemicarbazonates in which the ligand is bound through the azomethine nitrogen. Strikingly, two new strong bands appear in **1** at 1550 and 1470 cm^{-1}, apparently due to the unusual electronic and structural characteristics of the thiosemicarbazone moiety in this complex.

Complex **1** dissolves in chloroform and in dimethyl sulfoxide.* In the latter solvent it is a non-electrolyte. The main changes in the ^{1}H NMR spectrum ($CDCl_3$, room temperature) with respect to the free ligand are the loss of the N^2H signal due to deprotonation, the deshielding of the C^2 proton (*ca.* 0.1 ppm), the slight shielding of the phenyl protons and the practically total loss of the two signals due to the non-equivalent protons of the $-NH_2$ group of L (a very broad signal at δ *ca.* 5.8 can be observed only at very high concentrations). A number of weak signals are tentatively attributed to the presence of small concentrations of other isomer(s) of the complex.†

The ^{1}H NMR spectrum is sensitive to temperature changes. Besides the expected[12] broadening of the signals from the $TlMe_2$ fragment on cooling, at −20 °C the $-NH_2$ group signal becomes observable as two bands (one of them split) at δ 5.17 and 6.65, each of which integrates for one proton as in the free ligand at room temperature. Although this change may indicate that at room temperature the ligand in **1** co-ordinates, as usual, *via* N^3 and S, and that it is only upon cooling that it evolves toward N^2, S-co-ordination and the free-ligand configuration, another explanation is also possible. If the C(1)–N(1) bond retains some degree of multiplicity after metallation, then on cooling, a temperature should be reached at which the hindrance of rotation about this bond will split the $-NH_2$ signal. At present this second explanation seems to be the more likely, since (pyridine-2-carbaldehyde thiosemicarbazonato)dimethylthallium(III), a compound with a 'normal' N^3,S co-ordination scheme in the solid state,[13] behaves like **1** when its ^{1}H NMR spectrum is recorded at low temperatures.

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* $\Lambda_M[10^{-3} mol dm^{-3}, (CH_3)_2SO]$ = 4 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (250.13 MHz, $CDCl_3$) at room temperature: δ 7.87 (1 H, s, methyne), 7.59 (2 H, d, $C-H_{ring}$), 6.89 (2 H, d, $C-H_{ring}$), 3.83 (3 H, s, CH_3O) and 1.27 [6 H, d, $^2J(^1H-^{205}Tl)$ 353.7 Hz, $TlMe_2$]; minor signals (integration *ca.* 9% of the main signals) δ 8.48(s), 7.59 (d), 6.89 (d), 5.04 (br s) and 3.86 (s). At −20 °C: δ 7.88 (1 H, s, methyne), 7.60 (2 H, d, $C-H_{ring}$), 6.90 (2 H, d, $C-H_{ring}$), 6.65 (1 H, br s, NH_2), 5.17 (1 H, br s, NH_2), 3.85 (3 H, s, CH_3O), 1.27 [6 H, d, $^2J(^1H-^{205}Tl)$ 352.1 Hz, $TlMe_2$]; minor signals (integration *ca.* 11% of the main signals) δ 8.48 (s), 7.39 (d), 6.97 (d), 5.13 (s) and 3.86 (s).

† Some work has been done on the spectroscopic differences between the *E*- and *Z*-isomers about the aldimine C^2-N^3 bond. In non-deprotonated ligands, the C^2–H proton is more deshielded and the N^2–H proton more shielded in the *E*-isomer than the *Z*-isomer (ref. 1).

Acknowledgements

We are grateful to the Dirección General de Investigación Científica y Técnica del Ministerio de Educación y Ciencia, Spain, for financial support (project PB87-0482).

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Received 16*th September* 1992; *Communication* 2/04969D