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The structure of triphenyl(1-phenyl-5-mercapto-*1H*-1,2,3,4-tetrazolato)lead(IV): towards the first example of a π-coordinated metallotetrazole?

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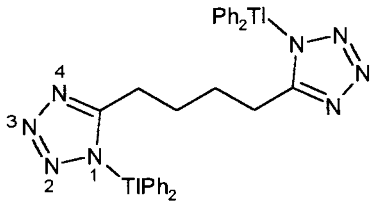
Abstract

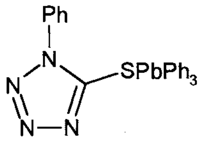
The structure of the organolead thiotetrazolate 5-(Ph_3PbS)CN_4Ph-1 has been determined and incorporates intermolecular N–Pb interactions that are suggestive of the onset of π-coordination. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lead; Tetrazole; Structure

There is considerable interest in the supramolecular structures that are adopted when metals are coordinatively linked by ligands containing suitably disposed combinations of donor atoms. In this respect, the coordination chemistry of metallotetrazoles presents a number of opportunities, and examples are available that utilise the full spectrum of nitrogen combinations for metal binding. This is particularly true among the derivatives of poly-functionalised ligands (i.e. which contain two or more tetrazole units) [1] culminating in the solvated diphenylthallium derivative (**I**·2MeOH) in which all four available nitrogen centres are involved in bonding, either directly to the metal (N^1, N^3, N^4) or in hydrogen bonds (N^2) [2]. However, all the known metallotetrazoles incorporate σ-M–N linkages and, despite the fact that the tetrazolate anion is formally a 6π-electron ring system isoelectronic with $C_5H_5^-$, no examples of facially coordinated tetrazoles are known [3]. $R_fCN_4Mn(CO)_5$ has been claimed to contain an η^5-π tetrazolate on the basis of a similarity in ν(CO) with those of $CpMn(CO)_3$, but this structure only persists in solution; in the solid state, rearrangement to $[(R_fCN_4)_3Mn_2(CO)_6]Mn(CO)_3$ occurs incorporating bridging σ-tetrazolate donors [4]. We now wish to report the synthesis and structural characterisation of Ph_3PbSCN_4Ph (**1**) whose 1-D polymeric structure incorporates intermolecular N–Pb interactions suggestive of the onset of π-M–N bonding and which contrasts sharply with those of analogous organotin systems.



(I)



(1)

Compound **1** was prepared from Ph_3PbCl and the ammonium salt $[NH_4][SCN_4Ph\text{-}1]$ and its crystal structure is shown in Fig. 1. As expected from other studies, lead is bonded to the thio-tetrazole through sulphur with the ligand adopting its thio- rather than thione form. The Pb–S distance (2.607(4) Å) is comparable to that in other structures e.g. Ph_3PbSPh 2.515(2) Å [5]. In addition, the molecules stack along *b* such that N(2) approaches an adjacent metal centre at a distance (3.339 Å) that can be considered bonding [Σ(van der Waals radii for Pb, N): 3.82 Å]. This bond is weak in comparison with the intermolecular N:→Pb of 2.58(5) Å in Me_3PbN_3 [6] and the chelating interaction of 2.685 Å in $(4\text{-}MeC_6H_4)(4\text{-}MeOC_6H_4)(2\text{-}Me_2NCH_2C_6H_4)PbI$, [7] although in general data for N-coordinated

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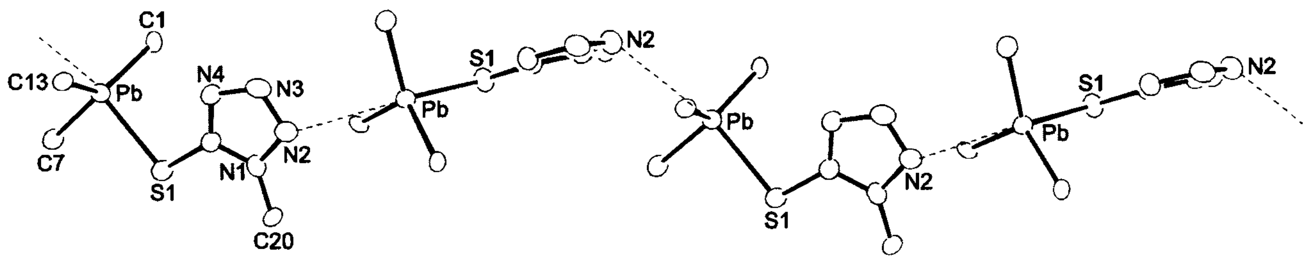

Fig. 1. The structure of **1** showing the labelling used in the text. Thermal ellipsoids are illustrated at the 30% probability level. Selected metric data: Pb–S 2.607(4), Pb–C(1) 2.19(1), Pb–C(7) 2.21(1), Pb–C(13) 2.22(1), Pb–N(2′) 3.339 Å; C(1)–Pb–C(7) 113.2(5), C(1)–Pb–C(13) 126.5(5), C(7)–Pb–C(13) 114.6(5), C(1)–Pb–S 102.0(3), C(7)–Pb–S 89.8(3), C(13)–Pb–S 100.9(3), S–Pb–N(2) 165.0(2)°. Only the α-carbons of the phenyl rings are shown for clarity.

organolead compounds are scarce. Furthermore, ^{207}Pb-NMR (172.2 ppm) indicates a tetrahedral geometry about lead in solution. However, the N(2)–Pb intermolecular interaction in the solid state does manifest itself in a flattening of the C_3Pb moiety [Σ(∠C–Pb–C) = 354.3°] from tetrahedral towards a trigonal bipyramidal geometry such that the overall stereochemistry about lead can be described as *trans*-$NSPbC_3$ [N(2′)–Pb–S: 165.0(2)°]. Interestingly, in both $[Me_3SnSCN_4Ph]_3$ [8] and $[Bz_3SnSCN_4Ph]_\infty$ [9] it is the less sterically hindered N(3), not N(2), which is involved in intermolecular coordination to tin.

The intermolecular orientation of the tetrazole with respect to lead in **1** is unique. In a σ-bonded arrangement the metal and the intermolecularly coordinated tetrazole ring would be expected to be co-planar, so that coordination is achieved via the lone pair on nitrogen. Indeed, this expectation is fulfilled in, for example, the structure of $[Bz_3SnSCN_4Ph]_\infty$ [9], which otherwise has the same 1D arrangement of molecules as **1**. Thus, in the tin compound the metal lies only 0.265 Å out of the CN_4 plane, and the dihedral Sn–N(3)–N(2)–N(1) angle (numbering equivalent to Fig. 1) is 173° [9]. Further dihedral M–N(3)–N(2)–N(1) angles (M = Sn, Tl) are collated in Table 1 to show the uniformity of σ-bridging in metallotetrazolates. In **1**, however, lead lies 2.632 Å below the tetrazole plane and the analogous dihedral angle involving the metal and the tetrazole [Pb–N(2)–N(3)–N(4)] is 126.1°. Moreover, slippage of the lead below the CN_4 plane accommodates close approach of the hindered donor N(2). Thus, although the N(2) → Pb interaction is weak it is more in keeping directionally with the π-orbitals of the azole ring than the σ-oriented nitrogen lone pair. Clearly, the length of the Pb···N interaction makes an unambiguous interpretation of the bonding contentious, and the fact that the lead interacts essentially in an η^1 manner with only one ring nitrogen is inconsistent with conventional ideas of π-bond formation. Indeed, an alternative description of the interaction is that of a very weak, directionally-challenged σ-bond. However, some distinction between these two interpretations can be made using the ideas of Dunitz [12], in which crystal structures are seen as mimicking points along a reaction pathway. For example, a collective analysis of five-coordinate $XYSnR_3$ structures has been used to describe the pathway of an S_N2 displacement reaction, in which the incoming (intermolecular) Y···Sn interaction gets shorter as the intramolecular bond Sn–X (X is now considered as the leaving group) lengthens. In such cases the Sn–Y···Sn–X arrangement is linear, and a similar situation would be anticipated if a weak σ-bond existed between N(2) and Pb. No such arrangement is observed. Indeed, if, in a thought experiment, two neighbouring molecules were translated towards each other along the Pb···Pb vector, the lead would pass under N(2) towards the centre of the adjacent tetrazole ring, ultimately generating an η^5-CN_4–Pb interaction. Thus, we believe that **1** represents a coordinate at the initial stages of a reaction pathway that would ultimately generate an unambiguous example of the long sought-after η^5-bonded tetrazole and is unique in that respect. The soft nature of the metal involved, lead, is clearly important, and the structure of **1** is reminiscent of those of $Ba[Ge(py^*)_3]_2$ (py* = 3,5-

Table 1
Intermolecular dihedral M–N(3)–N(2)–N(1) angles for selected metallotetrazoles [a]

Compound	M–N(3)–N(2)–N(1) (°)	Ref.
1,6-$(Bu_3SnN_4C)_2(CH_2)_6$	176.3, 172.8	[10]
$(Bu_3SnN_4CCH_2CH_2)_3CNO_2$	168.0, 170.6, 170.6, 173.6, 175.4, 176.9	[11]
1,3,5-$(Bu_3SnN_4C)_3C_6H_3$	163.2, 169.5, 171.8, 175.7, 177.9, 179.9	[11]
$[Ph_2TlN_4CPh\cdot MeOH]_2$	162.3	[2]
1,4-$(Ph_2TlN_4C)_2(CH_2)_4\cdot 2MeOH$	166.0	[2]
Ph_3PbSCN_4Ph	126.1	This work

[a] Atom numbering follows the format of Fig. 1.

dimethylpyrazol-1-yl) [13] and $Ba_2(DAP)_3[N(SiMe_3)_2]$ (DAP = diazapentadienyl) [14] which also incorporate π-interactions with cyclic or acyclic conjugated C, N ligands.

1. Experimental

Spectra were recorded on the following instruments: Jeol GX270 (^{1}H-, ^{13}C-NMR), GX400 (^{209}Pb-NMR), Perkin–Elmer 599B (IR; Nujol mull on KBr plates).

1.1. Synthesis of **1**

Ph_3PbCl (0.95 g, 2.0 mmol) in methanol (240 ml) was added dropwise to a well-stirred solution of $[NH_4][SCN_4Ph]$ (0.48 g, 2.4 mmol) also in methanol (30 ml). The solution was then refluxed for 3 h, the solvent removed in vacuo and the residue extracted into acetone. After separation of insolubles, the acetone was evaporated and the remaining solid recrystallised from hot methanol to yield 1 (0.84 g, 68%; m.p. 156–8°C). Anal. Calc. for $C_{25}H_{20}N_4PbS$: C, 48.8 (48.8); H, 3.27 (3.25), N, 8.89 (9.10)%. ^{1}H-NMR ($CDCl_3$): 7.40–7.86 (m, 20H, C_6H_5); ^{13}C-NMR: 159.0 (CN_4), 136.3, 134.7, 129.9, 129.3, 129.2, 124.5 (C_6H_5); ^{207}Pb-NMR (100°C; relation to Et_4Pb): 172.2 ppm.

1.2. Crystallography

A colourless crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm was used for data collection.

Crystal data: $C_{25}H_{20}N_4PbS$, $M = 615.70$, monoclinic, $a = 11.116(2)$, $b = 16.270(3)$, $c = 13.055(2)$ Å, $\beta = 100.49(2)°$, $U = 2321.6(7)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_{calc.} = 1.762$ g cm^{-3}, μ(Mo–K$_\alpha$) = 7.376 mm^{-1}. Crystallographic measurements were made at 293(2) K on a CAD4 automatic four-circle diffractometer in the range $2.02 < \theta < 23.92°$ ($\lambda = 0.71069$ Å). Data (3634 independent reflections) were corrected for Lorentz and polarisation and also for absorption [15]. (Max. and min. absorption corrections; 1.000, 0.336, respectively). In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. The solution of the structure (SHELX86) and refinement (SHELX93) [16,17] converged to a conventional [i.e. based on 2532 F^2 data with $F_o > 4\sigma(F_o)$, 281 parameters] $R_1 = 0.0487$ and $wR_2 = 0.1276$. Goodness of fit = 1.046. The max. and min. residual densities were 1.211 and −1.171 e Å^{-3}, respectively. The asymmetric unit (shown in Fig. 1, along with the labelling scheme used) was produced using ORTEX [18].

2. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 118701 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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