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LETTER

Thiolate chemistry of the main group metals. The synthesis and structures of $[\text{Sn}(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_4]$ and $[\text{Pb}_3(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_6]$

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Although transition metal-thiolate coordination chemistry has witnessed a dramatic development as a consequence of its biological relevance [1-3], the chemistry of the main group metals with this fundamental ligand type remains largely undeveloped. Since the interaction of toxic main group metals with biological systems frequently involves bonding to enzyme sulfhydryl groups, main group metal-thiolate compounds are of some interest in the design of detoxification reagents [4]. While thiolate complexes of Group 14 metals have been known for many years [5], structural studies have been hampered by their generally poor solubility and lack of suitable crystallinity. As part of our extensive studies of metal-thiolate coordination chemistry [6], we have prepared several complexes of Group 14 metals with the thiolate ligand (2-HSC₅H₃N-3-SiMe₃) (1) whose triorganosilyl substituent confers enhanced solubility to the complexes and permits the isolation of discrete molecular species.

The reaction of Pb(NO₃)₂ with 2 equiv. of 1 in ethanol yields $[\text{Pb}_3(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_6]$ (2). Crystal data: monoclinic space group C2/c, $a = 23.596(4)$, $b = 14.228(2)$, $c = 20.185(3)$ Å, $\beta = 91.31(1)^\circ$, $V = 6774.8(12)$ Å³, $Z = 4$; structure solution and refinement based on 2744 reflections with $I_o \geq 3\sigma(I_o)$ converged at $R = 0.069$.

The structure of 2, shown in Fig. 1, consists of discrete trinuclear molecular species, with two distinct

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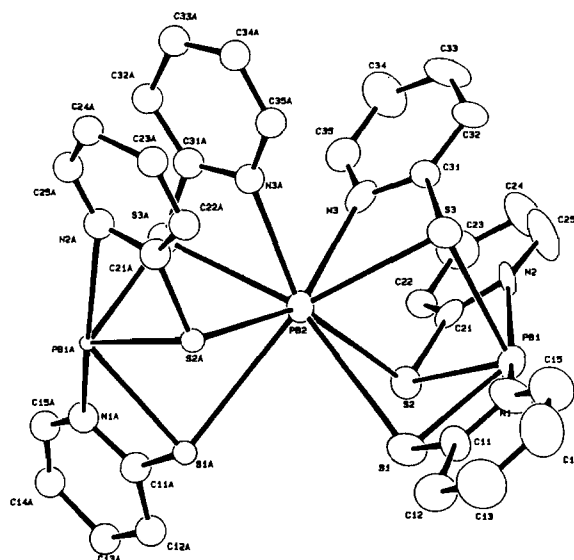


Fig. 1. ORTEP view of the structure of $[\text{Pb}_3(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_6]$ (2), showing the atom-labelling scheme. Selected bond lengths (Å) and angles ($^\circ$): Pb(1)-S(1), 2.707(9); Pb(1)-S(2), 2.737(7); Pb(1)-S(3), 2.782(8); Pb(1)-N(1), 2.81(3); Pb(1)-(2), 2.89(3); Pb(2)-S(3), 2.933(8); Pb(2)-N(3), 2.51(2); Pb(2)-S(1), 3.318(8); Pb(2)-S(2), 3.157(8); S(1)-Pb(1)-S(2), 77.0(2); S(1)-Pb(1)-S(3), 90.8(3); S(2)-Pb(1)-S(3), 94.8(2); N(1)-Pb(1)-N(2), 161.3(7); S(3)-Pb(2)-N(3), 56.2(6); N(3)-Pb(2)-N(3a), 65.5(9).

Pb environments. The irregular geometries associated with the Pb centers are characteristic of distortions produced by the presence of the stereochemically active lone pair [7]. The Pb(1) site exhibits trigonal pyramidal coordination to three thiolate donors with additional secondary interactions to two pyridyl nitrogen donors [8]. While the Pb(1)-N distances are longer than anticipated for a single bond interaction, they are well within the sum of van der Waals radii for Pb and N, 3.55 Å. The Pb(2) atom coordinates to the S(3) and N(3) donors of two chelating ligands in a square pyramidal arrangement with Pb(2) at the apex. Significant secondary interactions with S(1) and S(2) are evident to produce overall distorted eight coordination about the Pb(2) center. The influence of the lone pair on the coordination geometry of Pb(2) is again evident. The overall geometry of 2 is similar to that reported for $[\text{Pb}_3(\text{SC}_6\text{H}_2\text{-2,4,6-Pr}_3)_6]$ [9].

The reaction of SnCl₂ with 2 equiv. of 1 in acetonitrile yields a yellow solution from which microcrystals of $[\text{Sn}(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_2]$ (3) can be isolated upon addition of diethyl ether. Upon dissolution in acetonitrile, 3 slowly disproportionates to give a black residue of Sn metal and $[\text{Sn}(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_4]$ (4). Crystal data for C₃₂H₄₈N₄Si₄S₄Sn (4): tetragonal I4₁, $a = 14.863(2)$, $c = 18.798(3)$ Å, $V =$

4152.6(8) Å³, $Z = 4$; structure solution and refinement based on 2349 reflections with $I_o \geq 3\sigma(I_o)$ converged at $R = 0.041$.

The structure of **4**, illustrated in Fig. 2, consists of discrete mononuclear units with the Sn atom in a distorted dodecahedral arrangement of ligand donors, with the S groups in the B positions or the expanded bisphenoidal loci and the N groups in the A positions of the contracted bisphenoid [10]. Curiously, the structure of the complex of the under-

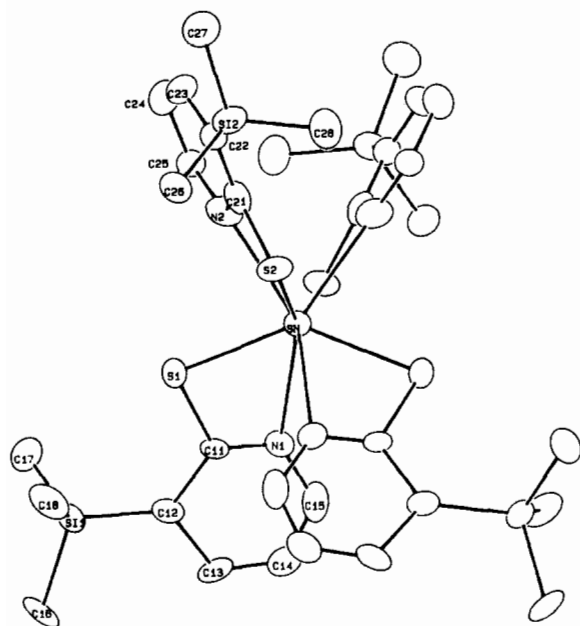


Fig. 2. ORTEP view of the structure of $[\text{Sn}(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_4]$ (**3**). Selected bond lengths (Å) and angles (°): Sn–S(1), 2.482(4); Sn–S(2), 2.510(4); Sn–N(1), 2.60(1); Sn–N(2), 2.52(1); S(1)–Sn–S(1a), 137.2(2); S(2)–Sn–S(2a), 138.7(2); N(1)–Sn–N(1a), 67.8(4); N(2)–Sn–N(2a), 67.2(5).

ivatized 2-pyridinethiol with Sn(IV), $[\text{Sn}(2\text{-SC}_5\text{H}_4\text{N})_4]$ [11], exhibits distorted octahedral $[\text{SnS}_4\text{N}_2]$ coordination, such that the nitrogen donors of two ligands are non-coordinating. The fluxional behaviour reported for $[\text{Sn}(2\text{-SC}_5\text{H}_4\text{N})_4]$ may thus involve an eight coordinate species of the type reported here. We are currently investigating the influence of the identity and the location of the substituents on the pyridinethiol moiety in dictating stereochemistry, both in solution using multinuclear NMR and in the solid state by X-ray crystallography.

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