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# Formation and Structure of the Oxygen-Centered Lead Thiolate Cluster $Pb_5O(SR_F)_8 \cdot 2C_7H_8$ [$R_F$ = 2,4,6-Tris(trifluoromethyl)phenyl]

**Frank T. Edelmann,**[*,†] **Jan-Karel F. Buijink,**[‡]
**Sally A. Brooker,**[§] **Regine Herbst-Irmer,**[‖]
**Ulrike Kilimann,**[‖] **and Frank M. Bohnen**[‖]

Department of Chemistry, Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany, Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand, Groningen Center for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands, and Institute of Inorganic Chemistry of the Georg-August-Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

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## Introduction

In 1991 we reported the first preparation of a σ-bonded diarylplumbylene, namely, $Pb(R_F)_2$ (**1**),[1] where $R_F$ denotes the sterically and electronically stabilizing 2,4,6-tris(trifluoromethyl)phenyl (or "nonafluoromesityl") substituent.[2,3] More recently other diarylplumbylenes of the type $PbAr_2$ without intra- or intermolecular donor stabilization have been prepared and structurally characterized.[4] Due to their limited accessibility, very little is known about the reactivity of these highest diaryl carbene homologues. Initial studies on the derivative chemistry of $Pb(R_F)_2$ showed that this compound is far less reactive than the corresponding diaryl stannylene $Sn(R_F)_2$. It was found that, in marked contrast to $Sn(R_F)_2$,[3c,5] **1** does not undergo oxidative addition reactions leading to organolead(IV) compounds containing the $Pb(R_F)_2$ unit.[6] Thus far the only well-behaved reaction of **1** is the elimination of the two σ-bonded aryl groups upon treatment with 2 equiv of 2,4,6-tris(trifluoromethyl)thiophenol which affords the unsolvated lead(II) thiolate $Pb(SR_F)_2$ (**2**) (eq 1).[1]

$$\underset{\mathbf{1}}{Pb(R_F)_2} + 2R_FSH \rightarrow \underset{\mathbf{2}}{Pb(R_F)_2} + 2R_FH \qquad (1)$$

Lead(II) thiolates, derived both from simple alkanethiols[7] and from sterically encumbered arenethiols,[8] have received some attention in the past. However, studies concerning their reactivity remain very limited to date.[8a,9] We report here the reaction of **2** with molecular oxygen leading to the unusual pentanuclear lead thiolate cluster $Pb_5O(SR_F)_8 \cdot 2C_7H_8$ (**3**) ($C_7H_8$ = toluene).

## Experimental Section

**General Procedures and Characterization.** Solvents were dried over sodium−benzophenone and freshly distilled under $N_2$ prior to use. A Braun MB 150-GI glovebox was used for storage of the compounds and to prepare samples for spectroscopic studies. The starting material $Pb(SR_F)_2$ (**2**) was prepared as described previously.[1] Elemental analyses were performed by the Analytical Laboratory of the Institute for Inorganic Chemistry at the University of Göttingen. NMR spectra were recorded on a Bruker AM 250 spectrometer and were externally referenced to TMS. FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates in the range of 4000−380 $cm^{-1}$.

**Synthesis.** A sample of 1.0 g (1.2 mmol) of **2** was repeatedly (2 or 3 times) recrystallized from a minimum amount of hot toluene (ca. 30 mL) under an atmosphere of dry air, until the habit of the resulting crystals had completely changed from very fine needles to compact, bright yellow cubes. The crystals were washed with pentane (15 mL) and dried under vacuum to give 0.67 g (75%) of **3**. Mp: 116−118 °C (dec). $^1H$ NMR ($C_6D_6$): δ 7.95 (br s, 16 H, $C_6H_2$); 7.16 (m, 10 H, $C_6H_5Me$), 2.33 (s, 6 H, $C_6H_5Me$). $^{19}F$ NMR ($C_6D_6/CFCl_3$): δ −60.7 (m, 48 F, *o*-$CF_3$), −63.8 (m, 24 F, *p*-$CF_3$). Anal. Calcd for $C_{86}H_{32}F_{72}OPb_5S_8$ (3741.55): C, 27.61; H, 0.86; Pb; 27.69. Found: C, 27.98; H, 1.01; Pb, 27.25.

**X-ray Crystallography**. A bright yellow crystal of **3** was mounted on a Siemens-Stoe AED2 diffractometer with monochromated Mo Kα radiation. A semiempirical absorption correction was applied. The structure was solved by direct methods using SHELXS-90.[10] The structure was refined against $F^2$ with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (0.027P)^2 + 44.76P$ with $P = (F_o^2 + 2F_c^2)/3$ (Program SHELXL-97).[11] The *R* values are defined as $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically positioned and treated as riding. Some of the *p*-$CF_3$ groups are disordered over two positions. They were refined with distance restraints. The anisotropic displacement parameters of the fluorine atoms lying opposite to each other were fixed to the same values. Also one complete $SR_F$ group is disordered and refined with distance restraints and restraints for the anisotropic displacement parameters. The toluene molecules show relatively high displacement parameters, but a possible disorder was not resolved. Again restraints were used. Crystal and refinement data are summarized in Table 1.

## Results and Discussion

Bright yellow $Pb(SR_F)_2$ (**2**), as prepared according to eq 1, notoriously crystallizes in the form of very fine thin needles

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[†] Otto-von-Guericke-Universität Magdeburg.
[‡] University of Groningen.
[§] University of Otago.
[‖] Georg-August-Universität Göttingen.

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**Table 1.** Crystallographic Data for $Pb_5O(SR_F)_8 \cdot C_7H_8$ (**3**)

| | |
|---|---|
| formula: $C_{86}H_{32}F_{72}OPb_5S_8$ | fw: 3741.55 |
| $a = 17.385(4)$ Å | space group: $P\bar{1}$ (No. 2) |
| $b = 18.104(5)$ Å | $T = -120$ °C |
| $c = 20.073(5)$ Å | $\lambda = 0.71073$ Å |
| $\alpha = 68.20(1)°$ | $\rho_{calcd} = 2.253$ g cm$^{-3}$ |
| $\beta = 78.21(1)°$ | $\mu = 7.923$ mm$^{-1}$ |
| $\gamma = 70.81(1)°$ | R1$^a$ $[I > 2\sigma(I)] = 0.0453$ |
| $V = 5516(2)$ Å$^3$ | wR2$^b$ (all data) $= 0.0957$ |
| $Z = 2$ | |

$^a$ $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b$ $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$.

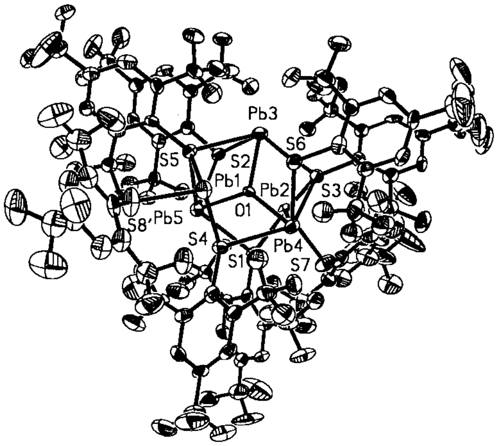

**Figure 1.** ORTEP diagram of $Pb_5O(SR_F)_8 \cdot 2C_7H_8$ (**3**).

unsuitable for X-ray diffraction. However, during repeated attempts to obtain single crystals by recrystallization from hot toluene, occasionally the formation of well-formed dark yellow cubes was observed. An X-ray crystal structure determination (vide infra) showed that this material was the unusual oxygen-centered lead thiolate cluster $Pb_5O(SR_F)_8 \cdot 2C_7H_8$ (**3**). The serendipitous formation of **3** can easily be traced back to oxygen contamination during the recrystallization process. Later in the course of the investigation it was discovered that high yields (ca. 75%) of **3** can be obtained in a more straightforward manner by repeatedly recrystallizing **2** from hot toluene under an atmosphere of dry air. Small amounts of the known disulfide $R_FSSR_F$ (**4**)[2] have been detected by TLC in the mother liquid, so that a plausible reaction pathway can be formulated as follows:

$$\underset{\mathbf{1}}{5Pb(SR_F)_2} + {}^1/_2O_2 \rightarrow \underset{\mathbf{3}}{Pb_5O(SR_F)_8} + \underset{\mathbf{4}}{R_FSSR_F} \qquad (2)$$

Elemental analyses are in agreement with the formulation of **3** as $Pb_5O(SR_F)_8 \cdot 2C_7H_8$, whereas very little further information was gained from the usual combination of spectroscopic methods. The true nature of the product was revealed only by the X-ray analysis. The molecular structure of **3** is depicted in Figure 1; selected interatomic distances and angles are listed in Table 2.

The molecular structure of **3** consists of a pentanuclear, oxygen-centered lead thiolate cluster (see Figure 2). The central $Pb_3O$ unit is essentially planar (Pb3−O1−Pb4 116.8(3)°, Pb3−O1−Pb5 116.5(3)°, Pb4−O1−Pb5 126.6(3)°). With an average of 2.205 Å the Pb−O distances are comparable to those in the tetragonal rutile structure of $PbO_2$ but significantly shorter than those in PbO (2.30 Å).[12] Six sulfur atoms above and below the $Pb_3O$ plane form a trigonal prismatic array with each sulfur atom bridging two lead atoms of the central unit. Each one of the central lead atoms (Pb3, Pb4, Pb5) is weakly bonded to two upper and two lower sulfur atoms. These Pb−S distances fall in the range between 2.854(3) and 3.180(3) Å (av 3.008 Å). Two distances are in the range of weak bonds (Pb1−S4 2.834(3) Å, Pb1−S5 2.852(3) Å, Pb2−S1 2.784(3) Å, Pb2−S3 2.909(3) Å), while the others are much longer (Pb1−S6 3.633(3) Å, Pb2−S2 3.625(3) Å). Pb1 and Pb2 are further coordinated to an $SR_F$ ligand with a mean Pb−S distance of 2.617 Å. Additionally there is coordination to the toluene molecules. The distances from Pb to the centers of the toluene rings are 3.548 and 3.705 Å, respectively. Weak coordination of arene ligands to lead is fairly common, and a small number of such complexes have been structurally characterized.[3e,13−17] Typical examples include monomeric $(1,2\text{-}C_6H_4Me_2)_2Pb(AlCl_4)_2$,[16] polymeric $\{[(C_6H_6)Pb(AlCl_4)_2]C_6H_6\}_\infty$,[13] and the mixed-metal fluoroalkoxide derivative $Pb_2Li_2[OCH(CF_3)_2]_6(C_6H_6)$.[17]

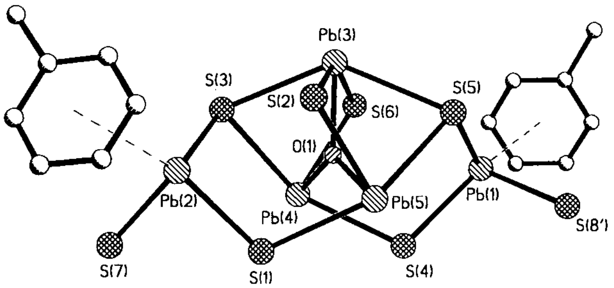

**Figure 2.** ORTEP diagram of the cluster core in $Pb_5O(SR_F)_8 \cdot 2C_7H_8$ (**3**).

**Table 2.** Selected Distances (Å) and Angles (deg) for **3**

| | | | |
|---|---|---|---|
| Pb(1)−S(8′) | 2.598(6) | Pb(3)−S(6) | 3.042(3) |
| Pb(1)−S(8″) | 2.642(11) | Pb(3)−S(5) | 3.062(3) |
| Pb(1)−S(4) | 2.834(3) | Pb(4)−O(1) | 2.206(6) |
| Pb(1)−S(5) | 2.852(3) | Pb(4)−S(6) | 2.854(3) |
| Pb(1)−S(6) | 3.633(3) | Pb(4)−S(4) | 2.954(3) |
| Pb(2)−S(7) | 2.614(3) | Pb(4)−S(3) | 3.040(3) |
| Pb(2)−S(1) | 2.784(3) | Pb(4)−S(1) | 3.180(3) |
| Pb(2)−S(3) | 2.909(3) | Pb(5)−O(1) | 2.215(6) |
| Pb(2)−S(2) | 3.625(3) | Pb(5)−S(2) | 2.860(3) |
| Pb(3)−O(1) | 2.193(6) | Pb(5)−S(1) | 2.950(3) |
| Pb(3)−S(3) | 2.979(3) | Pb(5)−S(5) | 3.024(3) |
| Pb(3)−S(2) | 2.991(3) | Pb(5)−S(4) | 3.164(3) |
| | | | |
| Pb(3)−O(1)−Pb(4) | 116.8(3) | Pb(4)−O(1)−Pb(5) | 126.6(3) |
| Pb(3)−O(1)−Pb(5) | 116.5(3) | | |

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determination of $Pb_5O(SR_F)_8 \cdot C_7H_8$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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