clusters showing loss of an iron atom. In the case of H^+ addition, the reaction produces H_2 via intermediate elimination of $H_2Fe(CO)_4$. The X-ray structural data show that compound I is a highly strained M–M framework, and this observation is supported by the fact that I readily produces $Fe(CO)_5$ upon reaction with CO. Studies are in progress to further establish the structure of II crystallograpically and to determine the nature of the products from the various reactions delineated herein.

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Registry No. I, 92786-73-7; II, 92763-37-6; $Fe(CO)_5$, 13463-40-6; $NaBiO_3$, 12232-99-4; $Na_2Fe(CO)_4$, 14878-31-0; Bi, 7440-69-9; Fe, 7439-89-6.

Supplementary Material Available: Listings of final positional and thermal parameters and observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Discrete Trigonal-Pyramidal Lead(II) Complexes: Syntheses and X-ray Structure Analyses of $[(C_6H_5)_4As][Pb(EC_6H_5)_3]$ (E = S, Se)

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Lead(II) nitrate, in solutions containing at least 3 mol equiv of $NaEC_6H_5$ (E = S, Se), forms triligated anions that crystallize readily as the tetraphenylarsonium salts $[(C_6H_5)_4As][Pb(SC_6H_5)_3]$ (**1**) and $[(C_6H_5)_4As][Pb(SeC_6H_5)_3]$ (**2**). The crystals so formed are isomorphous, and their structures have been determined by single-crystal X-ray diffractometry techniques. The salts crystallize in the monoclinic space group $P2_1/c$, with 4 formula units in unit cells of dimensions $a = 10.758$ (1) Å, $b = 17.561$ (1) Å, $c = 20.273$ (1) Å, and $\beta = 105.11$ (1)° for **1** and $a = 10.899$ (1) Å, $b = 17.638$ (2) Å, $c = 20.617$ (1) Å, and $\beta = 105.84$ (1)° for **2**. The structures have been refined by full-matrix least-squares techniques on F to agreement factors $R = 0.026$ (4866 observations with $F_o > 2\sigma(F_o)$) for **1** and $R = 0.034$ (3074 observations with $F_o > 3\sigma(F_o)$) for **2**. The discrete $[Pb(EC_6H_5)_3]^-$ anions are isostructural; the three S or Se atoms form the base of a trigonal pyramid whose apex is occupied by the Pb atom. The Pb–S distances in **1** are 2.619 (1), 2.647 (1), and 2.623 (1) Å, while in **2** the Pb–Se distances are 2.762 (1), 2.727 (1), and 2.733 (1) Å. Angles at the Pb atom range from 90.32 (4) to 96.14 (5)° in **1** and from 88.82 (4) to 96.57 (4)° in **2**. In both anions all three phenyl groups adopt a propeller-like conformation and are disposed in equatorial positions above the basal plane of chalcogen atoms. These salts represent the first unambiguous examples of the trigonal-pyramidal coordination geometry expected for isolated three-coordinated Pb(II). Lead-207 NMR spectra confirm that the $[Pb(EC_6H_5)_3]^-$ ions are the anionic lead(II) species recently prepared in situ in solution.

Introduction

Recently a multinuclear NMR study from one of our laboratories provided evidence for the existence of (benzenethiolato)- and (benzeneselenolato)plumbates(II) in solution.[1] These species could not be characterized completely by NMR as ligand exchange was fast on the NMR time scale, but it appeared they are probably triligated.

According to VSEPR theory, a $Pb^{II}S_3$ or $Pb^{II}Se_3$ kernel would be expected to adopt a trigonal-pyramidal geometry provided the lone pair is stereochemically active.[2] To the best of our knowledge this simple coordination geometry has not been established in the solid state for lead(II). In cases where it might have occurred, higher coordination numbers than 3 are in fact found. For instance, in the tris(*O*-ethyl xanthato)plumbate(II) ion, the ligand is disymmetrically bidentate, giving a PbS_6 kernel with irregular coordination geometry indicative of the presence of a stereochemically active lone pair; in addition, weak dimerization through sulfur atoms occurs.[3] Also, the structure of (penicillaminato)lead(II) is polymeric; the penicillaminato ligand is tridentate, but weaker bridging interactions, and again a stereochemically active lone pair, lead to an overall irregular $PbNO_2S_3$ coordination sphere.[4] In contrast, a more regular octahedral coordination about lead is found in $RbPbI_3$.[5]

The occurrence of bridging thiolato groups in the structures of (penicillaminato)lead(II) (see above) and (2-(morpholin-4-yl)ethanethiolato)lead(II) nitrate[6] raises the possibility that aggregation through sulfur might be a general feature of lead(II)–thiolate complexes in the solid state. We note that polynuclear species have also been detected in solutions containing Pb(II) and 2-mercaptoethanol.[7] On the other hand, $[(C_6H_5)_4As][Pb(SC_6F_5)_3]$ has been prepared and behaves as a simple 1:1 electrolyte in nitromethane solution, though the structure of this salt in the solid state is apparently unknown.[8]

We thought it desirable to characterize the (benzenethiolato)- and (benzeneselenolato)plumbates(II) in the solid state, anticipating that the coordination geometry about lead and the extent of aggregation would be of interest. Accordingly, we have now isolated in the solid state $[(C_6H_5)_4As][Pb(SC_6H_5)_3]$ (**1**) and $[(C_6H_5)_4As][Pb(SeC_6H_5)_3]$ (**2**) in forms suitable for X-ray analysis, and we report here the first well-documented examples of simple trigonal-pyramidal coordination for lead(II).

Experimental Section

All the chemicals were reagent grade and were used as received. Carbon and hydrogen analyses were performed by Guelph Chemical Laboratories Ltd., and Pb(II) was determined by EDTA titration using xylenol orange indicator.[9]

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Table I. Crystal Data and Experimental Conditions

compd	$PbAsS_3C_{42}H_{35}$ (**1**)	$PbAsS_3C_{42}H_{35}$ (**2**)
fw	918.05	1058.74
a, Å	10.758 (1)	10.899 (1)
b, Å	17.561 (1)	17.638 (1)
c, Å	20.273 (1)	20.617 (1)
β, deg	105.11 (1)	105.84 (1)
V, $Å^3$	3697.7	3812.7
temp, °C	25	
Z	4	
d(obsd), g cm^{-3}	1.654 (5)	1.856 (5)
d(calcd), g cm^{-3}	1.649	1.844
cryst dimens, mm	0.35 × 0.35 × 0.25	0.25 × 0.30 × 0.30
cryst faces	{100} {010} {001} {102} $(0\bar{1}1)$ $(01\bar{1})$	{100} {010} {001} {102} {011}
space group	$P2_1/c$ (C_{2h}^5-No.4)	
radiation (λ, Å)	Mo Kα (0.71073)	
abs coeff, cm^{-1}	56.77	81.80
transmissn factors		
max	0.323	0.336
min	0.191	0.160
detector aperture		
vert, mm	4	4
horiz, mm	3.0 + 1.0 tan θ	3.0 + 1.0 tan θ
cryst detector dist, mm	205	
takeoff angle, deg	6.5	
scan mode	θ–2θ	
scan width, deg	0.50 + 0.50 tan θ	0.80 + 0.35 tan θ
data collcd	$+h,-k,\pm l$ ($0 < 2\theta < 50$)	$-h,-k,\pm l$ ($0 < 2\theta < 50$)

Syntheses of the compounds were carried out under an argon atmosphere in a glovebag, using solvents that had been thoroughly deoxygenated with argon.

Synthesis. $[(C_6H_5)_4As][Pb(SC_6H_5)_3]$. A 1.6-g portion (14.5 mmol) of benzenethiol was added to 0.3 g (13.0 mmol) of sodium metal dissolved in 10 mL of methanol. The resultant solution of $NaSC_6H_5$ was added to a stirred solution of 1.42 g (4.3 mmol) of $Pb(NO_3)_2$ in 5 mL of water, producing a yellow precipitate. A solution containing 1.85 g (4.4 mmol) of tetraphenylarsonium chloride hydrate in 30 mL of methanol was added with stirring to the yellow precipitate followed by 60 mL of H_2O–MeCN (1/5 v/v). The mixture was warmed to 70 °C, giving a yellow solution, filtered hot, and left to crystallize. The light lemon yellow crystals of diffraction quality obtained in ca. 30 min were separated by decantation and dried in a stream of argon; yield 3.3 g (84%). Anal. Calcd for $C_{42}H_{35}AsPbS_3$: C, 54.95; H, 3.84; Pb, 22.57. Found: C, 55.07; H, 3.76; Pb, 22.45.

$[(C_6H_5)_4P][Pb(SC_6H_5)_3]$. The procedure was the same as for the tetraphenylarsonium derivative; yield 84%. Anal. Calcd for $C_{42}H_{35}PPbS_3$: C, 57.71; H, 4.04; Pb, 23.70. Found: C, 57.60; H, 4.03; Pb, 23.56.

$[(C_6H_5)_4As][Pb(SeC_6H_5)_3]$. The preparation of this yellow compound was very similar to that of the sulfur analogue, but C_6H_5SeH was used instead of C_6H_5SH; yield 26%. Anal. Calcd for $C_{42}H_{35}AsPbSe_3$: C, 47.65; H, 3.33. Found: C, 47.71; H, 3.32.

Physical Measurements. Lead-207 NMR Spectra. The 296 K 83.4-MHz ^{207}Pb NMR spectra were measured and referenced to $PbMe_4$ in toluene as described previously.[1] The samples were prepared in $CHCl_3$ and were saturated to 0.07 and 0.1 M for $[(C_6H_5)_4As][Pb(SC_6H_5)_3]$ and $[(C_6H_5)_4As][Pb(SeC_6H_5)_3]$, respectively.

Collection and Reduction of X-ray Data. Well-developed, pale yellow crystals of equant habit were chosen for each salt. A preliminary photographic examination indicated the monoclinic space group $P2_1/c$,[10a] and a careful examination of the films showed that the salts were isomorphous and isostructural. Crystal densities were determined by flotation in mixtures of 1,2-dibromoethane and carbon tetrachloride.

The analyses were carried out on an Enraf-Nonius CAD4F diffractometer using an incident-beam monochromator and Mo radiation.[11] The thiolate structure **1** was undertaken first. Cell constants and an orientation matrix were determined from reflections recorded on a rotation photograph and refined with the angular settings for 24 high-angle reflections with $30 < 2\theta < 36°$. ω scans of intense, low-angle reflections had an average width at the base of 0.84°, a satisfactory value.[12] Crystal data for both salts are given in Table I. Intensity data were recorded at variable scan speeds ranging from 4.0 to 0.9° min^{-1}, values chosen to optimize counting statistics within a maximum time per datum of 75 s. Background estimates were made by extending the scan by 25% on each side. Standard reflections $6,0,\overline{16}$, $1,\overline{10},9$, $4,\bar{3},10$ and $0,\bar{9},\overline{11}$ were monitored every 166 min of X-ray exposure time and showed an average 5.5% decay over the total period of 127.8 h. In all, 6858 observations were recorded, of which 211 were standards. Corrections were applied for Lorentz, monochromator and crystal polarization, and background radiation effects, using the Structure Determination Package[13] running on a PDP 11/23+ computer. Standard deviations were assigned on the basis of counting statistics and a starting value chosen for *p* of 0.04.[14] Ten crystal faces were identified by optical goniometry and the crystal dimensions measured on a microscope equipped with a filar eyepiece. The data were corrected for absorption by the Gaussian method. A linear decay correction was applied, and the equivalent forms averaged, leaving 4869 unique data with $F_o > 2\sigma(F_o)$ for solution and refinement of the structure.

The same procedure was followed for the selenolate structure **2**. ω scans showed an average width at base of 0.73°. Variable scan speeds ranged from 4.0 to 1.4° min^{-1}, with a maximum time per datum of 60 s. A total of 117.0 h were required for recording intensity data. The crystal chosen had 12 faces, and an absorption correction was applied. A value of 0.05 was chosen for *p*. No decay correction was applied In all, 3079 unique data with $F_o > 3\sigma(F_o)$ were available. Details of experimental procedures are given in Table I for both **1** and **2**.

Solution and Refinement of the Structures. The thiolate structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares techniques on *F*. With all non-hydrogen atoms included, minimizing the function $\sum w(||F_o| - |F_c||)^2$, where F_o and F_c are the observed and calculated structure amplitudes, and the weight *w* defined as $4F_o^2/\sigma^2(F_o^2)$, refinement converged at agreement factors $R_1 = \sum(||F_o| - |F_c||)/\sum(|F_o|) = 0.048$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.098$. Scattering factors for neutral, non-hydrogen atoms were taken from ref 10b, and real dispersion corrections were included for all atoms.[15] A difference Fourier synthesis showed clear evidence for 25 of the 35 H atoms on the phenyl rings, so all were included in idealized positions (C–H = 0.90 Å; sp^2 hybridization) with fixed isotropic thermal parameters. The scattering factor values were taken from Stewart et al.[16] With non-hydrogen atoms assigned anisotropic thermal parameters and hydrogen atom positions recalculated to maintain ideal geometries, refinement converged at $R_1 = 0.0273$ and $R_2 = 0.0333$. An inspection of F_o and F_c suggested that an extinction parameter should be refined. Three reflections with asymmetric backgrounds were assigned zero weights, and then with use of 4866 observations with $F_o > 2\sigma(F_o)$ and a *p* factor of 0.04, refinement of 425 variables converged at agreement factors $R_1 = 0.026$ and $R_2 = 0.031$. In a total difference Fourier synthesis there were eight peaks with electron density greater than 0.3 (1) e $Å^{-3}$; of these, three were associated with the lead atom, and the remainder were of no chemical significance. The error in an observation of unit weight was 1.07 electrons, and the largest shift in the final cycle was 0.04σ. An analysis of R_2 in terms of F_o, λ^{-1} sin θ, and various combinations of Miller indices showed no unusual trends. The extinction parameter refined to 9.4 (5) × 10^{-8}.

The positions for the thiolate structure were used as a starting point for refinement of the selenolate structure **2**. Of the 35 hydrogen atoms, 34 were found from a difference Fourier synthesis, at peak heights ranging from 0.8 (1) to 0.4 (1) e $Å^{-3}$, and included in idealized positions. Five reflections were dropped due to systematic errors, and refinement converged at agreement factors $R_1 = 0.034$ and $R_2 = 0.038$

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Table II. Atomic Positional (X10^4) and Thermal (X10^3) Parameters[a]

atom	x	y	z	U_{eq}, Å^2	atom	x	y	z	U_{eq}, Å^2
				Compound 1					
Pb	1542.6 (2)	2207.7 (1)	−961.5 (1)	518.0 (5)	C42	−491 (4)	6037 (3)	8241 (2)	53 (1)
As	1891.6 (4)	6066.0 (2)	7854.0 (2)	393 (1)	C43	−1357 (4)	5740 (3)	8569 (2)	60 (1)
S1	1070 (1)	2629.0 (9)	123.0 (6)	743 (4)	C44	−1030 (4)	5113 (3)	8975 (2)	60 (1)
S2	3157 (1)	3326.1 (7)	−1026.0 (6)	601 (4)	C45	154 (5)	4771 (2)	9062 (2)	56 (1)
S3	3268 (2)	1301.8 (8)	−196.5 (6)	750 (4)	C46	1021 (4)	5063 (2)	8737 (2)	47 (1)
C11	−595 (4)	2656 (2)	−23 (2)	48 (1)	C51	1594 (4)	5525 (2)	7007 (2)	42 (1)
C12	−1413 (5)	3254 (3)	21 (2)	58 (1)	C52	2618 (4)	5346 (3)	6743 (2)	58 (1)
C13	−2709 (5)	3136 (3)	−77 (2)	77 (2)	C53	2385 (5)	4947 (3)	6139 (2)	68 (2)
C14	−3236 (5)	2435 (4)	−219 (3)	91 (2)	C54	1165 (5)	4751 (3)	5805 (2)	66 (2)
C15	−2445 (6)	1844 (3)	−261 (3)	90 (2)	C55	143 (5)	4936 (3)	6061 (2)	64 (1)
C16	−1152 (5)	1946 (3)	−171 (3)	69 (2)	C56	360 (4)	5324 (3)	6669 (2)	51 (1)
C21	3268 (4)	3182 (2)	−1873 (2)	51 (1)	C61	1658 (4)	7129 (2)	7686 (2)	42 (1)
C22	4448 (5)	3056 (3)	−2009 (2)	69 (2)	C62	1413 (5)	7605 (3)	8182 (2)	53 (1)
C23	4543 (6)	2952 (4)	−2660 (3)	88 (2)	C63	1316 (5)	8378 (3)	8056 (2)	66 (2)
C24	3453 (6)	2955 (3)	−3200 (3)	84 (2)	C64	1421 (5)	8668 (3)	7445 (2)	67 (2)
C25	2291 (6)	3073 (3)	−3073 (2)	83 (2)	C65	1665 (5)	8200 (3)	6961 (2)	66 (2)
C26	2186 (5)	3197 (3)	−2427 (2)	67 (2)	C66	1791 (5)	7420 (3)	7077 (2)	53 (1)
C31	3606 (4)	771 (3)	−863 (2)	58 (1)	C71	3602 (4)	5906 (2)	8405 (2)	41 (1)
C32	3763 (5)	−16 (3)	−806 (3)	73 (2)	C72	4127 (4)	5179 (3)	8488 (2)	57 (1)
C33	4022 (6)	−438 (3)	−1321 (3)	91 (2)	C73	5291 (5)	5068 (3)	8948 (3)	70 (2)
C34	4109 (6)	−106 (4)	−1910 (3)	95 (2)	C74	5924 (4)	5663 (3)	9328 (2)	68 (2)
C35	3981 (5)	656 (4)	−1979 (3)	83 (2)	C75	5430 (5)	6383 (3)	9240 (2)	63 (1)
C36	3743 (5)	1095 (3)	−1462 (3)	71 (2)	C76	4267 (4)	6498 (3)	8777 (2)	52 (1)
C41	692 (4)	5700 (2)	8328 (2)	41 (1)					
				Compound **2**					
Pb	1521.7 (4)	2211.8 (3)	−982.0 (2)	56.9 (1)	C42	−505 (9)	6061 (6)	8211 (4)	53 (3)
As	1855.0 (9)	6101.3 (6)	7845.6 (5)	46.7 (3)	C43	−1343 (9)	5768 (6)	8536 (5)	72 (4)
Se1	1068 (1)	2850.7 (8)	134.3 (6)	79.1 (4)	C44	−1020 (9)	5165 (6)	8937 (5)	64 (3)
Se2	3212 (1)	3371.6 (7)	−999.6 (5)	63.8 (4)	C45	161 (9)	4820 (6)	9049 (5)	57 (3)
Se3	3255 (1)	1251.5 (7)	−181.5 (6)	75.2 (4)	C46	999 (9)	5132 (5)	8727 (5)	52 (3)
C11	−717 (8)	2658 (5)	−29 (4)	49 (3)	C51	1537 (8)	5564 (5)	7008 (4)	45 (3)
C12	−1516 (9)	3245 (6)	3 (5)	61 (3)	C52	2542 (9)	5396 (6)	6751 (5)	59 (3)
C13	−2812 (10)	3090 (7)	−106 (5)	82 (4)	C53	2317 (10)	4999 (7)	6159 (5)	72 (4)
C14	−3282 (10)	2396 (8)	−227 (6)	98 (5)	C54	1121 (11)	4788 (6)	5831 (5)	71 (4)
C15	−2498 (11)	1816 (8)	−253 (6)	103 (5)	C55	119 (10)	4969 (6)	6081 (5)	64 (4)
C16	−1224 (10)	1952 (6)	−163 (6)	77 (4)	C56	326 (9)	5349 (6)	6678 (5)	52 (3)
C21	3317 (9)	3199 (6)	−1888 (5)	57 (3)	C61	1614 (8)	7160 (5)	7684 (4)	50 (3)
C22	4458 (10)	3054 (6)	−2018 (5)	70 (4)	C62	1398 (10)	7636 (7)	8176 (5)	69 (4)
C23	4544 (10)	2949 (7)	−2683 (5)	87 (4)	C63	1277 (10)	8414 (6)	8040 (6)	77 (4)
C24	3487 (12)	2961 (8)	−3203 (5)	91 (5)	C64	1409 (12)	8689 (6)	7439 (6)	87 (5)
C25	2358 (12)	3100 (7)	−3082 (5)	86 (5)	C65	1631 (10)	8211 (7)	6976 (5)	69 (4)
C26	2275 (10)	3228 (7)	−2441 (5)	74 (4)	C66	1755 (10)	7436 (5)	7089 (5)	61 (4)
C31	3646 (9)	717 (6)	−907 (5)	59 (3)	C71	3560 (8)	5933 (5)	8336 (4)	43 (3)
C32	3840 (10)	−49 (6)	−875 (6)	75 (4)	C72	4090 (9)	5219 (6)	8453 (5)	62 (3)
C33	4075 (12)	−425 (6)	−1405 (6)	93 (5)	C73	5282 (10)	5104 (6)	8890 (6)	75 (4)
C34	4166 (11)	−59 (8)	−1984 (6)	93 (5)	C74	5918 (9)	5693 (7)	9263 (5)	70 (4)
C35	4017 (10)	679 (8)	−1999 (5)	88 (4)	C75	5413 (9)	6394 (6)	9200 (5)	66 (4)
C36	3771 (10)	1077 (6)	−1484 (5)	74 (4)	C76	4231 (9)	6529 (6)	8760 (5)	58 (3)
C41	685 (8)	5745 (5)	8316 (4)	41 (3)					

[a] Estimated standard deviations are given in parentheses and correspond to the least significant digit(s). $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*a_ia_j$.

for 425 variables using 3074 observations with $F_o > 3\sigma(F_o)$ and a p factor of 0.05. Again, an analysis of R_2 in terms of F_o, $\lambda^{-1}\sin\theta$, and Miller indices combinations indicated a satisfactory weighting scheme. The error in an observation of unit weight is 1.005 electrons. In a final difference Fourier synthesis there were seven peaks with electron density greater than 0.4 (1) Å^{-3}, and all were associated with the lead atom.

Positional and U(equiv) thermal parameters are given for the refined atoms of both structures in Table II. Tables of hydrogen atom parameters, anisotropic thermal parameters, root-mean-square amplitudes of vibration, supplementary dimensions, weighted least-squares planes, torsion angles, and structure amplitudes have been deposited as supplementary material.[17]

Results and Discussion

General Procedures. The anions $[Pb(EC_6H_5)_3]^-$ (E = S, Se) produced by the reaction

$$Pb^{2+} + 3EC_6H_5^- \rightarrow [Pb(EC_6H_5)_3]^-$$

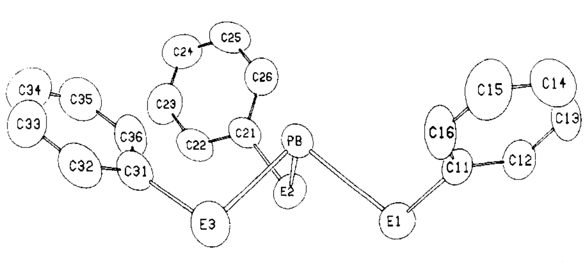

Figure 1. Perspective view of the anion, showing the atom-numbering scheme.

were isolated as their $[(C_6H_5)_4As]^+$ (and, for E = S, $[(C_6H_5)_4P]^+$) salts. The ^{207}Pb NMR chemical shifts for $[(C_6H_5)_4As][Pb(SC_6H_5)_3]$ and $[(C_6H_5)_4As][Pb(SeC_6H_5)_3]$ in $CHCl_3$ are 2868 and 3214 ppm, respectively, at 295 K. These values can be regarded as identical with those previously attributed to $[Pb(SC_6H_5)_3]^-$ and $[Pb(SeC_6H_5)_3]^-$ prepared in situ in methanol from excess $EC_6H_5^-$ (2818 and 3188 ppm, respectively), making allowance for solvent effects on δ_{Pb},

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(17) Supplementary material.

Table III. Bond Distances and Bond Angles[a]

		dist, Å				dist, Å	
atom 1	atom 2	**1**	**2**	atom 1	atom 2	**1**	**2**
Pb	E1	2.619 (1)	2.727 (1)	C34	C35	1.352 (9)	1.31 (2)
Pb	E2	2.647 (1)	2.762 (1)	C35	C36	1.367 (8)	1.36 (2)
Pb	E3	2.623 (1)	2.733 (1)	C41	C42	1.372 (6)	1.375 (13)
E1	C11	1.763 (5)	1.913 (10)	C41	C46	1.381 (6)	1.359 (13)
E2	C21	1.771 (5)	1.891 (11)	C42	C43	1.380 (6)	1.374 (15)
E3	C31	1.755 (5)	1.912 (11)	C43	C44	1.364 (7)	1.33 (2)
As	C41	1.910 (4)	1.908 (10)	C44	C45	1.377 (7)	1.386 (15)
As	C51	1.915 (4)	1.917 (10)	C45	C46	1.375 (6)	1.382 (14)
As	C61	1.903 (4)	1.906 (11)	C51	C52	1.380 (6)	1.374 (13)
As	C71	1.907 (4)	1.912 (10)	C51	C56	1.372 (6)	1.365 (13)
C11	C12	1.389 (6)	1.367 (14)	C52	C53	1.376 (6)	1.371 (14)
C11	C16	1.381 (7)	1.361 (15)	C53	C54	1.354 (7)	1.35 (2)
C12	C13	1.372 (8)	1.40 (2)	C54	C55	1.373 (7)	1.37 (2)
C13	C14	1.355 (9)	1.33 (2)	C55	C56	1.373 (7)	1.366 (14)
C14	C15	1.358 (9)	1.35 (2)	C61	C62	1.383 (6)	1.386 (15)
C15	C16	1.367 (8)	1.37 (2)	C61	C66	1.378 (6)	1.368 (14)
C21	C22	1.385 (7)	1.366 (15)	C62	C63	1.380 (7)	1.40 (2)
C21	C26	1.391 (6)	1.374 (15)	C63	C64	1.371 (7)	1.37 (2)
C22	C23	1.361 (7)	1.41 (2)	C64	C65	1.355 (7)	1.34 (2)
C23	C24	1.380 (8)	1.34 (2)	C65	C66	1.391 (7)	1.39 (2)
C24	C25	1.356 (9)	1.34 (2)	C71	C72	1.389 (6)	1.380 (14)
C25	C26	1.359 (7)	1.37 (2)	C71	C76	1.370 (6)	1.389 (14)
C31	C32	1.382 (6)	1.37 (2)	C72	C73	1.367 (6)	1.38 (2)
C31	C36	1.393 (7)	1.388 (15)	C73	C74	1.369 (7)	1.36 (2)
C32	C33	1.376 (7)	1.36 (2)	C74	C75	1.365 (7)	1.35 (2)
C33	C34	1.349 (9)	1.39 (2)	C75	C76	1.369 (6)	1.379 (14)

			angle, deg					angle, deg	
atom 1	atom 2	atom 3	**1**	**2**	atom 1	atom 2	atom 3	**1**	**2**
E1	Pb	E2	90.32 (4)	88.82 (4)	C34	C35	C36	120.9 (6)	123 (1)
E1	Pb	E3	91.08 (5)	90.11 (4)	C31	C36	C35	121.3 (6)	121 (1)
E2	Pb	E3	96.14 (5)	96.57 (4)	As	C41	C42	121.0 (3)	121.2 (8)
Pb	E1	C11	101.4 (1)	100.8 (3)	As	C41	C46	118.2 (3)	119.3 (8)
Pb	E2	C21	98.8 (2)	96.3 (4)	C42	C41	C46	120.7 (4)	119 (1)
Pb	E3	C31	97.1 (2)	95.7 (4)	C41	C42	C43	119.6 (4)	120 (1)
C41	As	C51	107.9 (2)	108.2 (4)	C42	C43	C44	119.7 (4)	120 (1)
C41	As	C61	110.2 (2)	109.5 (5)	C43	C44	C45	120.9 (4)	122 (1)
C41	As	C71	109.3 (2)	109.3 (4)	C44	C45	C46	119.7 (4)	117 (1)
C51	As	C61	110.1 (2)	110.2 (5)	C41	C46	C45	119.3 (4)	122 (1)
C51	As	C71	111.2 (2)	110.9 (5)	As	C51	C52	119.8 (3)	119.2 (8)
C61	As	C71	108.1 (2)	108.7 (5)	As	C51	C56	119.3 (3)	120.0 (8)
E1	C11	C12	119.4 (4)	119.2 (9)	C52	C51	C56	121.0 (4)	120.8 (9)
E1	C11	C16	123.8 (4)	122.4 (9)	C51	C52	C53	118.8 (4)	119 (1)
C12	C11	C16	116.8 (5)	118 (1)	C52	C53	C54	120.2 (5)	120 (1)
C11	C12	C13	120.8 (5)	118 (1)	C53	C54	C55	121.2 (4)	121 (1)
C12	C13	C14	121.4 (6)	122 (1)	C54	C55	C56	119.5 (5)	120 (1)
C13	C14	C15	118.3 (6)	120 (1)	C51	C56	C55	119.4 (4)	119 (1)
C14	C15	C16	121.6 (6)	120 (1)	As	C61	C62	120.3 (3)	120.6 (9)
C11	C16	C15	121.1 (5)	122 (1)	As	C61	C66	118.9 (3)	117.6 (9)
E2	C21	C22	120.8 (4)	121 (1)	C62	C61	C66	120.7 (4)	122 (1)
E2	C21	C26	121.8 (4)	122.9 (9)	C61	C62	C63	118.6 (4)	118 (1)
C22	C21	C26	117.4 (4)	116 (1)	C62	C63	C64	120.8 (5)	120 (1)
C21	C22	C23	121.1 (5)	121 (1)	C63	C64	C65	120.4 (5)	120 (1)
C22	C23	C24	120.4 (6)	120 (1)	C64	C65	C66	120.2 (4)	122 (1)
C23	C24	C25	118.9 (5)	119 (1)	C61	C66	C65	119.2 (4)	118 (1)
C24	C25	C26	121.3 (5)	121 (1)	As	C71	C72	120.4 (3)	121.0 (9)
C21	C26	C25	120.8 (5)	123 (1)	As	C71	C76	119.7 (3)	119.2 (8)
E3	C31	C32	123.2 (4)	121 (1)	C72	C71	C76	119.5 (4)	120 (1)
E3	C31	C36	120.5 (4)	123 (2)	C71	C72	C73	119.0 (5)	120 (1)
C32	C31	C36	116.3 (5)	116 (1)	C72	C73	C74	120.5 (5)	120 (1)
C31	C32	C33	121.4 (5)	120 (1)	C73	C74	C75	120.9 (4)	121 (1)
C32	C33	C34	120.7 (6)	122 (1)	C74	C75	C76	118.8 (5)	120 (1)
C33	C34	C35	119.4 (6)	116 (2)	C71	C76	C75	121.2 (4)	119 (1)

[a] Estimated standard deviations are given in parentheses and correspond to the least significant digit(s).

which are expected to be sizeable.[18] Hence, the earlier formulation is confirmed.

Description of the Structures. The crystal structure of each compound consists of discrete cations and anions, the shortest cation···anion As···Pb distances being 4.945 (1) and 4.999 (1) Å in **1** and **2**, respectively. The shortest interionic distances are 2.636 and 2.680 Å between H16 and H54 in **1** and H35 and H43 in **2**, respectively. We note particularly that there are no interanionic interactions, the shortest Pb–Pb distances being 9.647 (1) and 9.788 (1) Å in **1** and **2**, respectively. Figure 1 gives the atom-numbering scheme used and shows a perspective view of a $[Pb(EC_6H_5)_3]^-$ anion. Figure 2 shows a stereoview of the anion in **1**, with atoms plotted as 50%

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(18) Harris, R. K.; Kidd, R. G. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 8.

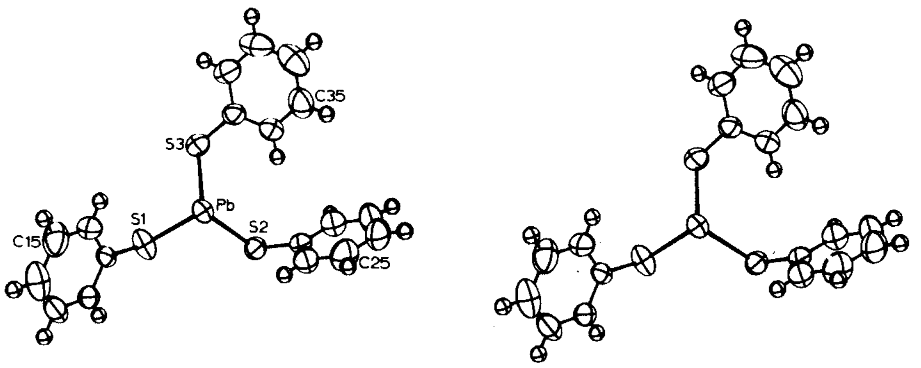

Figure 2. Stereoview of the $[Pb(SC_6H_5)_3]^-$ anion.

probability thermal ellipsoids; the anion in **2** is isostructural, and a stereoview is included in the deposited material. Selected bond distances and bond angles in the two compounds are listed in Table III.

It can be seen from the figures that the coordination about lead is trigonal pyramidal in both anions. As discussed above, this is the expected coordination geometry for an isolated three-coordinate lead(II) complex with a stereochemically active lone pair, but these $[Pb(EC_6H_5)_3]^-$ anions seem to be the first clear-cut examples of such species.

The $[Pb(SC_6H_5)_3]^-$ Anion. In the thiolato complex the three sulfur atoms form the base of a trigonal pyramid with the lead atom at the apex. The idealized symmetry of the PbS_3 kernel is C_{3v}, but two of the Pb–S distances are nearly equal at 2.619 (1) and 2.623 (1) Å and significantly shorter than the third distance of 2.647 (1) Å, while the S–Pb–S angles are 90.32 (4), 91.08 (5), and 96.14 (5)°. The largest S–Pb–S angle, involving S2 and S3, we tentatively attribute to repulsive steric interaction between the phenyl substituents in the solid state. There are short intramolecular nonbonded distances between H36 and both C21 and C22: 2.87 and 2.93 Å, respectively, in **1**; 2.95 and 3.00 Å, respectively, in **2**. The Pb–S distances, especially the largest, are comparable to the intrachelate Pb–S distance of 2.646 (4) Å found in the structure of (2-morpholin-4-yl)ethanethiolato)lead(II) nitrate[6] but shorter than the intrachelate distance of 2.716 Å reported for (penicillaminato)lead(II).[4]

As can be seen from Figure 1, the phenyl groups all occupy equatorial positions above the three basal sulfur atoms. The dihedral angles Pb–S–C*X*1–C*X*6 are 52.1, 57.7, and 42.2°[17] so that the phenyl rings are twisted into a propeller-like arrangement. Within the phenyl rings the C–C–C angles are in the range found in other phenylthiolates[19] and also in triphenylphosphines.[20] The S–C*X*1–C*X*6 angles of 123.8 (4), 121.8 (4), and 123.2 (4)° are systematically larger than the related S–C*X*1–C*X*2 angles of 119.4 (4), 120.8 (4), and 120.5 (4)°; similar canting of the phenyl rings relative to the corresponding S–C vectors has been found in other arylthiolate complexes (e.g., ref 19). At sulfur, Pb–S–C*X*1 angles of 101.4 (1), 98.8 (2), and 97.1 (2)° are smaller than values found for terminal ligands in other arylthiolate complexes (e.g., 107.2 (2) and 107.9 (2)° in $[(CH_3)_4N]_2[Hg(S(4\text{-}C_6H_4Cl))_4]$;[19a] 107.8 (4), 110.2 (5), and 114.4 (4)° in $[(C_6H_5)_4P]_2[Cu(SC_6H_5)_3]$[19b]).

The $[Pb(SeC_6H_5)_3]^-$ Anion. This anion is isostructural with its sulfur analogue; a perspective view is shown in Figure 3 (supplementary material).[17] The Pb–Se distances are 2.727 (1), 2.762 (1), and 2.733 (1) Å and the Se–Pb–Se angles 88.82 (4), 90.11 (4), and 96.57 (4)°. Again, one angle is significantly larger than the other two. Few structural data are available for Pb(II)–Se species; reported Pb–Se distances are in the range 2.80–3.30 Å,[21] all longer than the distances found here and for higher coordination numbers at the lead atom.

Regarding the structures of the two $[Pb(EC_6H_5)_3]^-$ anions, several generalizations can be made. First, they are both discrete and have the trigonal-pyramidal coordination geometry expected for species of the VSEPR type AX_3E. Earlier, this same geometry was ascribed to the related $M(SC_6F_5)_3$ species (M = Sb, Bi) on the basis of a vibrational and ^{19}F NMR study.[8] Second, they both have all three phenyl groups in equatorial positions; this conformation is expected to minimize interactions between the stereochemically active lone pair on lead and those at the sulfur atoms, but its adoption could also be a packing effect. Third, they both have one Pb–E bond significantly longer than the other two, with no apparent correlation with the angles at sulfur or at lead; we are inclined at present to attribute the variation in bond angles to packing forces, but there seems no obvious explanation for the disparity in bond lengths. Finally, we note that one E–Pb–E angle is significantly greater than the other two, a fact we attribute to steric repulsions.

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Registry No. $[(C_6H_5)_4As][Pb(SC_6H_5)_3]$, 92055-38-4; $[(C_6H_5)_4As][Pb(SeC_6H_5)_3]$, 92055-39-5; $[(C_6H_5)_4P][Pb(SC_6H_5)_3]$, 92055-40-8.

Supplementary Material Available: Listings of root-mean-square amplitudes of vibration, selected torsion angles, hydrogen atom parameters, additional bond angles, anisotropic thermal parameters, weighted least-squares planes, and observed and calculated structure amplitudes and Figure 3, showing a stereoview of the $[Pb(SeC_6H_5)_3]^-$ anion (59 pages). Ordering information is given on any current masthead page.

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