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**Synthesis and Characterization of an Iron Carbonyl Cluster Containing Bismuth:
Crystal and Molecular Structure of Tetraethylammonium
(μ_3 -Bismuthido)nonacarbonyl(μ_3 -carbonyl)-triangulo-triferrate(1-),
[Et₄N][(μ_3 -Bi)Fe₃(CO)₉(μ_3 -CO)], a Cluso Cluster of the First Transition Series with a
Large Heteroatom**

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Sodium bismuthate, NaBiO₃, reacts with Fe(CO)₅ in methanol to generate [BiFe₃(CO)₁₀]⁻ (I) in good yield, and in the presence of hydroxide ion this reaction yields first [Bi[Fe(CO)₄]₄]³⁻ (II), which can be converted to I by oxidation. Production of CO₂ accounts for loss of oxygen from the bismuth atom. Compound I reacts with CO but not ethylene at room temperature. Complex II reacts with H⁺ to produce H₂ via intermediate formation of H₂Fe(CO)₄. [Et₄N⁺][Fe₃Bi(CO)₉(μ_3 -CO)]⁻ crystallizes in the centrosymmetric space group P2₁/n with *a* = 14.659 (5) Å, *b* = 12.126 (4) Å, *c* = 14.773 (6) Å, β = 109.10 (3)°, *V* = 2481.4 (15) Å³, *Z* = 4, and mol wt = 786.86. Diffraction data (2θ = 4.5–50.0°, Mo K α) were collected on a Syntex P2₁ automated four-circle diffractometer, and the structure was refined to *R_F* = 7.8% and *R_{wF}* = 4.9% for all 4401 reflections (*R_F* = 5.4% and *R_{wF}* = 4.7% for those 3446 reflections with $|F_o| > 3\sigma(|F_o|)$). The [Et₄N⁺] is disordered, and the [Fe₃Bi(CO)₉(μ_3 -CO)]⁻ anion has noncrystallographic C₃ (but not C_{3v}) symmetry. Iron–bismuth distances average 2.650 [2] Å, and iron–iron distances average 2.642 [7] Å.

Introduction

As part of the general scheme to study homogeneous systems that might become homogeneous catalysts, catalyst precursors, or catalyst models, we have been exploring the synthesis of some iron carbonyl clusters that contain bismuth. Bismuth is a large atom, and its inclusion in metal clusters is interesting from the standpoint of the steric demands it places on the cluster framework. Furthermore, the production of acrolein and acrylonitrile are industrially important reactions involving the use of a mixed bismuth–transition-metal oxide catalyst.¹

To date the number of well-characterized carbonyl clusters containing bismuth is limited to three: Bi[Co(CO)₄]₃,² Bi-Ir₃(CO)₉,³ and Bi₂[W(CO)₅]₃.⁴ They are generally prepared by addition of BiCl₃ to the metal carbonylate anions, or in some cases by the thermal addition of bismuth metal to the neutral carbonyl. The synthesis of Fe₃Bi₂(CO)₂₀ has been previously reported, but characterization was minimal.⁵ Prompted by this last work, we have investigated the reaction of NaBiO₃ with iron carbonyls and wish to report here our initial discoveries.

Experimental Section

All manipulations were carried out under dry nitrogen with use of standard Schlenk and vacuum line techniques. Methanol was distilled from magnesium activated with I₂. Infrared spectra were obtained on a Beckman 4820 spectrophotometer and the ¹³C spectra on a 360-MHz Nicolet NT-360 spectrometer. The ¹³C spectra were obtained on samples prepared from Fe(CO)₅ enriched to about 25% in ¹³CO. Analyses were performed by Galbraith Analytical Laboratories of Knoxville, TN. Visible spectra were obtained on a Cary 17 spectrophotometer.

Synthesis of [Et₄N][BiFe₃(CO)₁₀] (I) from Fe(CO)₅ and NaBiO₃. To a slurry of 4.0 g of NaBiO₃ (excess) in 80 mL of methanol was added 2.0 mL of Fe(CO)₅. The solution was heated to reflux for several hours with the color becoming brown. The gases were periodically flushed from the system into a saturated solution of Ba(OH)₂, precipitating the evolved CO₂ as BaCO₃ (yield 2.32 g, 0.0118 mol). The methanol solution was cooled and filtered and an aqueous solution of Et₄NBr added dropwise, precipitating the dark brown product. This was collected by filtration, washed with H₂O, and dried under vacuum. Recrystallization was effected by dissolving the product in CH₂Cl₂, filtering the solution, and precipitating the compound by addition of

hexane. Small single crystals suitable for X-ray diffraction were grown by slow cooling of a concentrated CH₂Cl₂ solution. The yield of this reaction was 3.36 g (86%). The yield of CO₂ (as BaCO₃) was 92% based on the cluster formed (79% based on Fe(CO)₅ consumed). If the gases were not periodically removed, lower yields result (35–40%) probably owing to reaction of the cluster with CO. Anal. Calcd for [Et₄N][BiFe₃(CO)₁₀]: C, 26.91; H, 2.66; N, 1.84; Fe, 22.08; Bi, 27.54. Found: C, 27.50; H, 2.63; N, 2.04; Fe, 21.03; Bi, 26.47. The IR ν_{CO} stretches were 2035 m, 1983 s, and 1946 m cm⁻¹ (CH₂Cl₂ solution); in a KBr pellet an additional weak band is observed at 1650 cm⁻¹. $\delta^{13}C$ = 317, 216 (ca. 1:9, -90 °C, CD₂Cl₂). The product is soluble in methanol, acetonitrile, acetone, and dichloromethane. In the visible spectrum a band is seen with λ_{max} = 550 nm, ϵ ca. 3900.

Reaction of [Et₄N][BiFe₃(CO)₁₀] with CO. About 1.0 g of [Et₄N][BiFe₃(CO)₁₀] was dissolved in 150 mL of CH₂Cl₂ and placed under flush of N₂ in a 300-mL Parr minireactor. The solution was purged twice with 750 psi of CO and then pressurized to 750 psi. The solution was stirred for 2 days, after which time the gases were vented and the solution was transferred to another flask. At that time small crystallites of a product only slightly soluble in CH₂Cl₂ had formed. IR (acetone, cm⁻¹): ν_{CO} stretch 2005 m, 1960 vs, 1922 sh, 1897 m, 1887 sh. Anal. Found: C, 18.62; H, 2.31; N, 1.70; Fe, 13.63; Bi, 50.12. The solvent and product Fe(CO)₅ were removed under vacuum into a trap and analyzed by IR.

Reaction of [Et₄N][BiFe₃(CO)₁₀] with C₂H₄. A solution of [Et₄N][BiFe₃(CO)₁₀] was prepared as in the reaction with CO and charged into the autoclave under N₂. The autoclave was purged twice with 250 psi of ethylene and then filled to 250 psi. At the end of 2 days the ethylene was vented and an infrared spectrum of the solution indicated that no change had occurred.

Synthesis of [Et₄N]₃[BiFe₄(CO)₁₆] (II) from NaBiO₃ and Fe(CO)₅/OH⁻. Pentacarbonyliron (0.5 mL) is quickly added to a solution of 0.5 g of KOH in 15 mL of methanol (degassed with N₂) cooled in an ice bath. A slurry of 0.42 g of NaBiO₃ in 15 mL of methanol continuously bubbled with N₂ is dropped slowly into the stirred carbonyl/KOH solution. The solution becomes deep green within about 15 min. After it is stirred for an additional 1 h, the solution is filtered and 0.6 g of [Et₄N]Br dissolved in methanol added. A fine, dark green-black precipitate results, which is washed several times with methanol. The yield is 1.05 g of crude material (88% yield based on iron for [Et₄N]₃[BiFe₄(CO)₁₆]). Purification is performed by

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dissolving the product in CH_3CN , filtering the solution, and precipitating the compound by addition of CH_2Cl_2 . The material reacts quickly with oxygen, resulting in I in variable yields. The synthesis may be conducted in aqueous solution.

The product is soluble in acetonitrile and insoluble in most other organic solvents. The PPN (PPN = bis(triphenylphosphine)nitrogen(1+)) salt can be prepared by use of [PPN]Cl in place of $[\text{Et}_4\text{N}]\text{Br}$. This salt is more soluble in organic solvents (e.g., CH_2Cl_2) but is difficult to purify. Anal. Calcd for $[\text{Et}_4\text{N}]_3[\text{BiFe}_4(\text{CO})_{16}]$: C, 37.79; H, 4.75; N, 3.30; Fe, 17.57; Bi, 16.43. Found: C, 37.14; H, 4.85; N, 3.20; Fe, 16.76; Bi, 16.96. IR (CH_3CN , cm^{-1}): 1962 s, 1906 m, 1867 m. No ^1H NMR signals were observed in concentrated CD_3CN solutions that could be attributed to metal hydrides. Visible spectra were obtained on 0.11 mM solutions of the $[\text{Et}_4\text{N}^+]$ salt in CH_3CN with $\lambda_{\text{max}} = 617$ nm and ϵ ca. 5000. ^{13}C NMR spectrum (-85°C , $\text{CD}_3\text{CN}/\text{C}_2\text{H}_5\text{CN}$): δ 225, 218 (ca. 1:3 intensity ratio).

Preparation of $[\text{Et}_4\text{N}]_3[\text{BiFe}_4(\text{CO})_{16}]$ (II) from BiCl_3 and $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 3/2$ diox (diox = Dioxane). To a 300-mL Schlenk flask containing 10.0 g of $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 3/2$ diox and 3.0 g of BiCl_3 is added 65 mL of dry tetrahydrofuran. The reaction ensues upon addition of the THF and is exothermic. After the solution is stirred overnight, the THF is removed under vacuum and the greenish brown residue dissolved in methanol and treated as above to yield 6.8 g of crude $[\text{Et}_4\text{N}]_3[\text{BiFe}_4(\text{CO})_{16}]$ (65%). Recrystallization was as before.

Protonation Reactions of II. A 100-mL gas bulb is charged with 0.10–0.20 g of the tetraethylammonium salt of II in a drybox. The gas bulb on a high-vacuum line is evacuated, and ca. 5–10 mL of CH_3CN or $\text{C}_2\text{H}_5\text{CN}$ is distilled in. After a known amount of $\text{HCl}(\text{g})$ is introduced, the flask is sealed and allowed to warm slowly to room temperature and remain there for 1–2 h. Holding the flasks in a slush bath at -78°C does not seem to affect the yield of H_2 . The H_2 is collected by Toepler pump into a gas buret by passing the permanent gases through a silica gel trap at -196°C . The residual nitrile solutions are brown after reaction. In the case where 2 equiv of H^+ is employed, an ionic iron carbonyl can be extracted by first removing the nitrile solvent in vacuo and then adding CH_2Cl_2 . When the solution is allowed to stand, needlelike crystals form, which redissolve in CH_3CN to give ν_{CO} stretches at 2000 s, 1985 sh, 1962 m and 1921 s, br cm^{-1} . The nature of this product is under further investigation.

It is noticed that when excess cold, gaseous HCl reacts with II, a deep red-violet complex is formed almost immediately. This material is very thermally unstable and decomposes above -78°C to yield a mixture of neutral brown products. Attempts to obtain the ^{13}C NMR spectrum of this purple material at low temperature did not succeed, probably owing to the low solubility of the complex in the $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ mixture employed. These brown products are unstable in solution.

In a variation on these protonation reactions, excess $\text{HCl}(\text{g})$ is distilled onto a 0.10-g sample of II followed by vacuum transfer of 30 mL of pentane into the reaction flask. The solution is then agitated, and while cold the volatiles are vacuum transferred to another Schlenk flask. This flask is transferred to a standard Schlenk line, where a sample is removed to obtain an infrared spectrum while still cold. The IR spectrum so obtained was in good agreement to that reported for $\text{H}_2\text{Fe}(\text{CO})_4$:⁶ 2117 w, 2049 m, 2039 s, 2023 m, 2005 m. The IR spectrum of an authentic sample of $\text{H}_2\text{Fe}(\text{CO})_4$ prepared similarly from $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 3/2$ diox and gaseous HCl /pentane was identical.

Determination of the Crystal Structure of $[\text{Et}_4\text{N}^+][\text{Fe}_3\text{Bi}(\text{CO})_9(\mu_3\text{-CO})^-]$. The crystal chosen for the crystallographic study was a brown parallelepiped with approximate dimensions of $0.2 \times 0.3 \times 0.4$ mm³. It was sealed into a thin-walled glass capillary tube under an inert atmosphere (N_2). The capillary was then mounted on a eucentric goniometer on the Syntex P₂ automated four-circle diffractometer at SUNY—Buffalo. All subsequent operations (Determination of unit cell parameters and the crystal's orientation matrix, data collection) were performed as described previously.⁷ Details appear in Table I.

A careful analysis of the data set revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent with the centrosymmetric monoclinic space group $P2_1/n$. Data were corrected for absorption and for Lorentz and polarization factors and were placed on an approximate absolute scale by means of Wilson plot.

Table I. Experimental Data for the X-ray Diffraction Study of $[\text{Et}_4\text{N}^+][\text{Fe}_3\text{Bi}(\text{CO})_9(\mu_3\text{-CO})^-]$

A. Crystal Parameters at 24 °C (297 K)	
cryst syst: monoclinic	$V = 2481.4 (15) \text{ \AA}^3$
space group: $P2_1/n$	$Z = 4$
$a = 14.659 (5) \text{ \AA}$	formula: $\text{C}_{18}\text{H}_{30}\text{NO}_{10}\text{BiFe}_3$
$b = 12.126 (4) \text{ \AA}$	mol wt = 786.86
$c = 14.773 (6) \text{ \AA}$	$D(\text{calcd}) = 2.106 \text{ g cm}^{-3}$
$\beta = 109.10 (3)^\circ$	

B. Measurement of Intensity Data
 diffractometer: Syntex P₂
 radiation: $\text{Mo K}\alpha$ ($\lambda = 0.710730 \text{ \AA}$)
 monochromator: pyrolytic graphite ($2\theta_m = 12.2^\circ$), equatorial mode; assumed 50% perfect
 reflns measd: $+h, +k, \pm l$ for $2\theta = 4.5\text{--}50.0^\circ$
 scan type: coupled $\theta(\text{cryst}) - 2\theta(\text{counter})$
 scan range: $[2\theta(K\alpha_1) - 0.9] - [2\theta(K\alpha_2) + 0.9]^\circ$
 bkgd: stationary cryst and counter, at each end of 2θ scan, each for $1/4$ of scan time
 total measmts: 4958 reflns, yielding 4402 unique data
 std reflns: 3 approx mutually orthogonal reflns collected after every 97 data points; no decay obsd
 abs coeff: $\mu = 88.2 \text{ cm}^{-1}$; corrected empirically by interpolation (in 2θ and ϕ) between 7 close-to-axial ψ scans

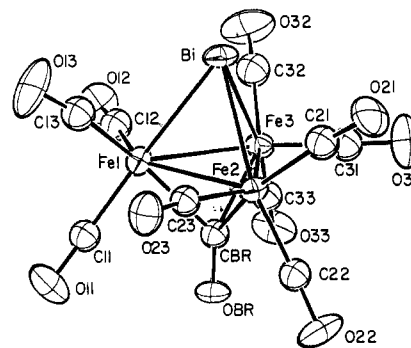


Figure 1. ORTEP-II diagram of the $[\text{Fe}_3\text{Bi}(\text{CO})_9(\mu_3\text{-CO})^-]$ anion.

The structure was solved by direct methods using the program MULTAN.⁸ The positions of the four heavy atoms (Bi + 3 Fe) were used to phase a difference Fourier, from which the positions of all atoms in the $[\text{BiFe}_3(\text{CO})_9(\mu_3\text{-CO})^-]$ anion were obtained. Subsequent difference-Fourier maps resulted in the location of all non-hydrogen atoms in the $[\text{Et}_4\text{N}^+]$ ion. This ion is disordered with two sites for each of the methylene carbons. This problem has been discussed previously in our structural study of $[\text{Et}_4\text{N}^+]_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$;⁹ in the present case, however, disorder is not required by crystallographic symmetry. All hydrogen atoms of the $[\text{Et}_4\text{N}^+]$ ion (40 in all, each with an occupancy of $1/2$) were input in idealized positions based upon $d(\text{C-H}) = 0.95 \text{ \AA}$ ¹⁰ and a perfectly staggered tetrahedral geometry; these positions were updated but were not refined.

Full-matrix least-squares refinement of positional parameters of all non-hydrogen atoms, anisotropic thermal parameters for Bi, Fe, and O atoms, and isotropic thermal parameters for all other non-hydrogen atoms led to convergence ($\Delta/\sigma < 0.01$ for all parameters) with $R_F = 7.8\%$, $R_{wF} = 4.9\%$, and $\text{GOF} = 1.48$ for all 4401 reflections.¹¹ For those 3446 data with $|F_o| > 3\sigma(|F_d|)$ discrepancy indices are $R_F = 5.4\%$, $R_{wF} = 4.7\%$, and $\text{GOF} = 1.62$. Final positional and thermal parameters are collected in Tables II and II-S (Table II-S is included in the supplementary material).

All calculations were performed on the SUNY—Buffalo-modified Syntex XTL system. The function $\sum w(|F_o| - |F_d|)^2$ was minimized during the least-squares process; here $w^{-1} = [\sigma(|F_o|)]^2 + [0.01|F_d|]^2$. The analytical scattering factors of the neutral atoms were corrected

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 (11) $R_F(\%) = 100 \sum |F_o| - |F_d| / \sum |F_d|$; $R_{wF}(\%) = 100 [\sum w(|F_o| - |F_d|)^2 / \sum w|F_d|^{2/3}]^{1/2}$; $\text{GOF} = [\sum w(|F_o| - |F_d|)^2 / (\text{NO} - \text{NV})]^{1/2}$, where NO = number of observations and NV = number of variables.

Table II. Atomic Coordinates for $[\text{Et}_4\text{N}^+][\text{Fe}_3\text{Bi}(\text{CO})_9(\mu_3\text{-CO})^-]$

atom	x	y	z	$B, \text{\AA}^2$
A. Atoms in the Tetranuclear Anion				
Bi	0.300 20 (3)	0.174 41 (3)	0.631 37 (3)	
Fe(1)	0.413 50 (10)	0.293 48 (11)	0.561 85 (10)	
Fe(2)	0.463 57 (9)	0.257 66 (11)	0.748 41 (10)	
Fe(3)	0.317 31 (9)	0.389 83 (12)	0.662 51 (10)	
C(11)	0.510 40 (79)	0.351 23 (88)	0.530 11 (75)	4.12 (22)
C(12)	0.320 02 (81)	0.357 71 (94)	0.467 11 (85)	4.61 (24)
C(13)	0.418 57 (80)	0.162 6 (10)	0.505 72 (85)	4.89 (24)
C(21)	0.426 69 (75)	0.174 9 (10)	0.830 90 (81)	4.37 (22)
C(22)	0.554 92 (75)	0.326 00 (93)	0.841 14 (78)	4.15 (21)
C(23)	0.541 11 (70)	0.164 76 (88)	0.714 38 (69)	3.48 (19)
C(31)	0.307 35 (82)	0.383 7 (10)	0.778 51 (90)	5.04 (25)
C(32)	0.191 89 (93)	0.382 1 (11)	0.588 85 (90)	5.56 (28)
C(33)	0.322 46 (74)	0.536 4 (10)	0.655 33 (76)	4.32 (23)
C(Br)	0.462 18 (67)	0.403 16 (86)	0.674 44 (69)	3.44 (19)
O(11)	0.573 23 (55)	0.386 07 (76)	0.509 82 (62)	
O(12)	0.262 65 (60)	0.396 00 (79)	0.403 36 (60)	
O(13)	0.427 97 (83)	0.086 50 (79)	0.463 83 (67)	
O(21)	0.410 75 (60)	0.124 49 (76)	0.889 46 (59)	
O(22)	0.615 31 (57)	0.369 00 (67)	0.899 58 (55)	
O(23)	0.597 21 (53)	0.104 41 (64)	0.704 72 (53)	
O(31)	0.295 90 (75)	0.383 79 (83)	0.852 12 (67)	
O(32)	0.113 72 (57)	0.388 08 (88)	0.539 01 (81)	
O(33)	0.322 87 (59)	0.630 29 (69)	0.652 89 (76)	
O(Br)	0.516 24 (44)	0.479 04 (53)	0.688 69 (49)	
B. Non-Hydrogen Atoms in the Disordered $[\text{Et}_4\text{N}^+]$ Cation				
N	0.374 28 (53)	0.246 66 (67)	0.159 43 (55)	3.41 (16)
C(1A)	0.308 9 (11)	0.144 5 (13)	0.152 0 (11)	2.11 (31)
C(1B)	0.336 9 (18)	0.245 6 (21)	0.237 3 (18)	5.67 (55)
C(2)	0.262 72 (91)	0.140 6 (11)	0.229 41 (93)	6.09 (30)
C(3A)	0.294 0 (18)	0.244 7 (23)	0.054 6 (19)	6.23 (61)
C(3B)	0.313 6 (13)	0.350 9 (15)	0.159 7 (13)	3.09 (37)
C(4)	0.232 0 (10)	0.359 9 (12)	0.056 7 (10)	7.05 (34)
C(5A)	0.416 5 (13)	0.246 1 (16)	0.085 3 (14)	3.31 (38)
C(5B)	0.441 2 (20)	0.342 6 (24)	0.157 8 (21)	7.12 (68)
C(6)	0.483 6 (10)	0.347 5 (12)	0.084 4 (10)	6.80 (33)
C(7A)	0.448 5 (12)	0.247 8 (15)	0.267 0 (13)	2.88 (35)
C(7B)	0.436 1 (19)	0.139 7 (22)	0.155 5 (19)	6.12 (59)
C(8)	0.520 3 (12)	0.142 1 (14)	0.269 6 (12)	9.28 (45)

for both the real and imaginary components of anomalous dispersion.¹²

Results and Discussion

Description of the Crystal Structure of $[\text{Et}_4\text{N}^+][\text{BiFe}_3(\text{CO})_9(\mu_3\text{-CO})^-]$. Crystals consist of equal numbers of discrete $[\text{BiFe}_3(\text{CO})_9(\mu_3\text{-CO})^-]$ anions and (disordered—vide supra) $[\text{Et}_4\text{N}^+]$ cations separated by normal van der Waals distances; there are no abnormally short interionic contacts. Interatomic distances are given in Table III; interatomic angles are collected in Table IV.

The geometry of the $[\text{BiFe}_3(\text{CO})_9(\mu_3\text{-CO})^-]$ ion is illustrated in Figure 1. This ion has approximate (noncrystallographic) C_3 symmetry but does not possess the theoretically possible higher C_{3v} symmetry.

Within the tetranuclear anion, the BiFe_3 core is tetrahedral. Individual bismuth-iron distances are $\text{Bi-Fe}(1) = 2.648$ (2) \AA , $\text{Bi-Fe}(2) = 2.652$ (1) \AA , and $\text{Bi-Fe}(3) = 2.650$ (2) \AA (average $\text{Bi-Fe} = 2.650$ [2] \AA),¹³ values remarkably similar to the internal iron-iron distances: $\text{Fe}(1)\text{-Fe}(2) = 2.646$ (2) \AA , $\text{Fe}(1)\text{-Fe}(3) = 2.634$ (2) \AA , $\text{Fe}(2)\text{-Fe}(3) = 2.645$ (2) \AA (average $\text{Fe-Fe} = 2.642$ [7] \AA).

There are three terminal carbonyl ligands associated with each iron atom. All geometric parameters are self-consistent

Table III. Interatomic Distances (\AA) for $[\text{Et}_4\text{N}^+][\text{Fe}_3\text{Bi}(\text{CO})_9(\mu_3\text{-CO})^-]$

A. Metal-Metal Distances			
Bi-Fe(1)	2.648 (2)	Fe(1)-Fe(2)	2.646 (2)
Bi-Fe(2)	2.652 (1)	Fe(1)-Fe(3)	2.634 (2)
Bi-Fe(3)	2.650 (2)	Fe(2)-Fe(3)	2.645 (2)
B. Iron-(μ_3 -Carbonyl) Distances			
Fe(1)-C(Br)	2.066 (10)	C(Br)-O(Br)	1.187 (12)
Fe(2)-C(Br)	2.072 (10)		
Fe(3)-C(Br)	2.079 (11)		
C. Terminal Fe-C and C-O Distances			
Fe(1)-C(11)	1.779 (12)	C(11)-O(11)	1.139 (15)
Fe(1)-C(12)	1.786 (12)	C(12)-O(12)	1.136 (15)
Fe(1)-C(13)	1.804 (12)	C(13)-O(13)	1.144 (16)
Fe(2)-C(21)	1.793 (12)	C(21)-O(21)	1.144 (14)
Fe(2)-C(22)	1.777 (11)	C(22)-O(22)	1.140 (14)
Fe(2)-C(23)	1.785 (11)	C(23)-O(23)	1.144 (13)
Fe(3)-C(31)	1.768 (13)	C(31)-O(31)	1.153 (16)
Fe(3)-C(32)	1.807 (14)	C(32)-O(32)	1.144 (17)
Fe(3)-C(33)	1.784 (13)	C(33)-O(33)	1.139 (15)
D. Distances in Disordered $[\text{Et}_4\text{N}^+]$ Ion			
N-C(1A)	1.548 (18)	C(1A)-C(2)	1.509 (21)
N-C(1B)	1.427 (27)	C(1B)-C(2)	1.653 (30)
N-C(3A)	1.609 (28)	C(3A)-C(4)	1.672 (32)
N-C(3B)	1.547 (21)	C(3B)-C(4)	1.603 (23)
N-C(5A)	1.423 (21)	C(5A)-C(6)	1.578 (25)
N-C(5B)	1.527 (31)	C(5B)-C(6)	1.416 (34)
N-C(7A)	1.605 (19)	C(7A)-C(8)	1.651 (26)
N-C(7B)	1.594 (29)	C(7B)-C(8)	1.733 (32)

Table IV. Interatomic Angles (deg) for $[\text{Et}_4\text{N}^+][\text{Fe}_3\text{Bi}(\text{CO})_9(\mu_3\text{-CO})^-]$

A. Angles within Fe_3Bi Cluster			
Fe(1)-Bi-Fe(2)	59.88 (4)	Bi-Fe(2)-Fe(1)	59.99 (4)
Fe(1)-Bi-Fe(3)	59.61 (4)	Bi-Fe(2)-Fe(3)	60.04 (4)
Fe(2)-Bi-Fe(3)	59.85 (4)	Fe(1)-Fe(2)-Fe(3)	59.71 (5)
Bi-Fe(1)-Fe(2)	60.13 (4)	Bi-Fe(3)-Fe(1)	60.16 (4)
Bi-Fe(1)-Fe(3)	60.22 (4)	Bi-Fe(3)-Fe(2)	60.12 (4)
Fe(2)-Fe(1)-Fe(3)	60.13 (5)	Fe(1)-Fe(3)-Fe(2)	60.16 (5)
B. Bi-Fe-CO Angles			
Bi-Fe(1)-C(11)	166.7 (4)	Bi-Fe(2)-C(21)	79.7 (4)
Bi-Fe(1)-C(12)	97.1 (4)	Bi-Fe(2)-C(22)	166.5 (4)
Bi-Fe(1)-C(13)	79.9 (4)	Bi-Fe(2)-C(23)	95.7 (3)
Bi-Fe(1)-C(Br)	97.7 (3)	Bi-Fe(2)-C(Br)	97.4 (3)
Bi-Fe(3)-C(31)	95.4 (4)	Bi-Fe(3)-C(33)	167.3 (4)
Bi-Fe(3)-C(32)	79.9 (4)	Bi-Fe(3)-C(Br)	97.3 (3)
C. Fe-Fe-CO Angles			
Fe(2)-Fe(1)-C(11)	111.5 (4)	Fe(1)-Fe(2)-C(21)	139.2 (4)
Fe(2)-Fe(1)-C(12)	140.2 (4)	Fe(1)-Fe(2)-C(22)	127.5 (4)
Fe(2)-Fe(1)-C(13)	107.2 (4)	Fe(1)-Fe(2)-C(23)	78.2 (4)
Fe(2)-Fe(1)-C(Br)	50.4 (3)	Fe(1)-Fe(2)-C(Br)	50.2 (3)
Fe(3)-Fe(1)-C(11)	126.6 (4)	Fe(3)-Fe(2)-C(21)	106.7 (4)
Fe(3)-Fe(1)-C(12)	80.4 (4)	Fe(3)-Fe(2)-C(22)	112.1 (4)
Fe(3)-Fe(1)-C(13)	139.5 (4)	Fe(3)-Fe(2)-C(23)	137.6 (3)
Fe(3)-Fe(1)-C(Br)	50.8 (3)	Fe(3)-Fe(2)-C(Br)	50.5 (3)
Fe(1)-Fe(3)-C(31)	139.3 (4)	Fe(2)-Fe(3)-C(31)	79.7 (4)
Fe(1)-Fe(3)-C(32)	105.3 (4)	Fe(2)-Fe(3)-C(32)	139.7 (4)
Fe(1)-Fe(3)-C(33)	111.6 (4)	Fe(2)-Fe(3)-C(33)	126.1 (4)
Fe(1)-Fe(3)-C(Br)	50.3 (3)	Fe(2)-Fe(3)-C(Br)	50.3 (3)
D. Terminal Fe-C-O Angles			
Fe(1)-C(11)-O(11)	178.6 (10)	Fe(2)-C(23)-O(23)	171.1 (9)
Fe(1)-C(12)-O(12)	176.2 (11)	Fe(3)-C(31)-O(31)	175.8 (12)
Fe(1)-C(13)-O(13)	171.4 (11)	Fe(3)-C(32)-O(32)	172.8 (12)
Fe(2)-C(21)-O(21)	174.0 (11)	Fe(3)-C(33)-O(33)	177.0 (11)
Fe(2)-C(22)-O(22)	178.2 (10)		
E. Angles Involving μ_3 -CO Ligand			
Fe(1)-C(Br)-O(Br)	132.6 (8)	Fe(1)-C(Br)-Fe(2)	79.5 (4)
Fe(2)-C(Br)-O(Br)	132.5 (8)	Fe(1)-C(Br)-Fe(3)	78.9 (4)
Fe(3)-C(Br)-O(Br)	132.8 (8)	Fe(2)-C(Br)-Fe(3)	79.2 (4)

with narrow ranges, vis., $\text{Fe-CO} = 1.768$ (13)– 1.807 (14) \AA (average 1.787 [13] \AA), $\text{C-O} = 1.136$ (15)– 1.153 (16) \AA (average 1.143 [5] \AA), and $\angle\text{Fe-C-O} = 171.3$ (9)– 178.6 (10)°.

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(13) Esd's of average values are calculated via the scatter formula

$$\sigma = \left[\frac{\sum_{i=1}^{i=N} (d_i - \bar{d})^2}{(N-1)} \right]^{1/2}$$

They are thus external estimates on the esd on an individual measurement.

The μ_3 -carbonyl ligand is linked symmetrically to all three iron atoms and is associated with lengthened Fe–C and C–O distances (as compared to those of the terminal Fe–C–O systems discussed above); individual Fe–(μ_3 -CO) distances are Fe(1)–C(Br) = 2.066 (10) Å, Fe(2)–C(Br) = 2.072 (10) Å, and Fe(3)–C(Br) = 2.079 (11) Å (average 2.072 [6] Å), while the carbon–oxygen bond length is C(Br)–O(Br) = 1.187 (12) Å.

Each iron atom possesses one carbonyl ligand that is essentially trans to the bismuth atom (angles of relevance are Bi–Fe(1)–C(11) = 166.7 (4)°, Bi–Fe(2)–C(22) = 166.5 (4)°, and Bi–Fe(3)–C(33) = 167.3 (4)°). The remaining Bi–Fe–CO angles are, however, not equivalent and suggest that the three Fe(CO)₃ moieties each rotate in a similar sense, so as to avoid interligand repulsions. Thus, three of the remaining Bi–Fe–CO angles are acute (Bi–Fe(1)–C(13) = 79.9 (4)°, Bi–Fe(2)–C(21) = 79.7 (4)°, and Bi–Fe(3)–C(32) = 79.9 (4)°) while the remaining three are obtuse (Bi–Fe(1)–C(12) = 97.1 (4)°, Bi–Fe(2)–C(23) = 95.7 (3)°, and Bi–Fe(3)–C(31) = 95.4 (4)°). It is this rotation of Fe(CO)₃ groups that destroys the possible C_{3v} symmetry of the anion, reducing it to C_3 .

The Structure of [BiFe₃(CO)₁₀][−]. The observed molecular structure of [BiFe₃(CO)₁₀][−] is consistent with the analytical and spectroscopic data available for the complex. The low-field ¹³C signal at 317 ppm and the infrared band at 1650 cm^{−1} can be assigned to the triply bridging carbonyl. Bridging carbonyl ¹³C NMR signals have been generally found at low field ([HFe₃(CO)₁₁][−] $\delta_{\mu\text{-CO}}$ = 284.0),¹⁴ and the ν_{CO} can be compared to that found for [Fe₄(CO)₁₃]^{2−} at 1685 cm^{−1} in the solid state (this molecule is highly fluxional on the NMR time scale even at −100 °C and a ¹³C signal for μ_3 -CO has not been observed).¹⁵ The other ¹³C signal at 218 ppm is roughly 9 times the size of that at 317 ppm and is characteristic of terminal carbonyls.

The structure of the [BiFe₃(CO)₁₀][−] ion is interesting when compared to that of the known isoelectronic cobalt and iridium clusters. In the case of cobalt,² an open structure is formed where the Co(CO)₄ unit may be viewed as a pseudohalide in a BiX₃ type complex with no Co–Co interactions. The bismuth–cobalt bonds appear to be long (average 2.766 Å). In fact, the Bi–Co distances are longer than the Bi–Ir distances found in BiIr₃(CO)₉ (average 2.734 Å).³ The iridium complex, on the other hand, is a closo cluster containing three Ir–Ir bonds as well as the three Bi–Ir bonds. Both of these are electron-precise complexes. In the case of Bi[Co(CO)₄]₃, the trigonal-pyramidally coordinated bismuth would retain one electron pair and have three shared pairs of electrons with cobalts, giving it a stable eight-electron configuration. The 18-electron rule is obeyed about each cobalt. The BiIr₃(CO)₉ cluster obeys Lauher's predictions¹⁶ and can be viewed as a 48-electron closed three-metal cluster with bismuth donating three electrons to the cluster count. The 18-electron rule is also obeyed about each iridium and the octet rule about bismuth. The authors who synthesized the Co₃[−] and Ir₃–Bi clusters believed that the distinguishing feature between the formation of the closo and open structures was primarily steric with Co being too small to form M–M bonds when also bonded to Bi. These constraints, of course, do not apply when the larger iridium is bonded to bismuth. In related Co₃MR (M = group 4 atom, R = Ph, alkyl, halide, etc.), this steric effect on forming closo clusters is also seen. For M = Ge, R = Ph complexes of the formulations PhGeCo₃(CO)₁₁ and PhGeCo₃(CO)₉ containing one and three metal–metal bonds respectively have been observed, but when M = Sn, the observed structure is the open species RSn[Co(CO)₄]₃.¹⁷

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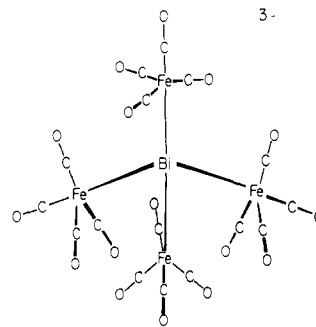


Figure 2. Proposed structure of [BiFe₄(CO)₁₆]^{3−}.

Our isolation and characterization of [BiFe₃(CO)₁₀][−] represents the first isolation of a closo cluster of the first transition series containing bismuth. It is obvious that, while steric effects may inhibit bond formation between metal atoms attached to bismuth, they are not forbidden entirely.

The Fe–Fe vectors in this cluster average 2.642 Å. For comparison, the Fe–Fe bond length in Fe₂(CO)₉ is 2.52 Å¹⁸ and the average Fe–Fe bond length in [Fe₄(CO)₁₃]^{2−} is 2.54 Å.¹⁹ The [BiFe₃(CO)₁₀][−] cluster is structurally similar to the Fe₄ species with the apical iron tricarbonyl unit being replaced with bismuth and the semibridging carbonyls becoming terminal. The lack of bridging character to the carbonyl can arise from two effects: (1) the lower charge on [BiFe₃(CO)₁₀][−] or (2) the longer Fe–Fe bonds.

The [BiFe₃(CO)₁₀][−] anion might be more logically compared to Fe₃As₂(CO)₉²⁰ and Fe₃(CO)₁₀(NSiMe₃)₂₁ whose structures have been reported. In the arsenic complex a triangle of irons each containing three terminal carbonyls is triply bridged on both sides by arsenic atoms. The average bond distance in that case was 2.623 Å, which is not significantly different from that in [BiFe₃(CO)₁₀][−].

In the case of Fe₃(CO)₁₀(NSiMe₃)₂₁, which is isoelectronic and isostructural with [BiFe₃(CO)₁₀][−], the average Fe–Fe bond distance is 2.535 Å and is 0.11 Å shorter than for our BiFe₃ cluster. The lengthening of the Fe–Fe bonds in [BiFe₃(CO)₁₀][−] is not unexpected considering the steric requirements of Bi vs. those of As and N. The Fe–N distances range from 1.870 to 1.920 Å and the Fe–As distances from 2.331 to 2.376 Å, while for the Fe–Bi bonds we have distances of 2.648–2.652 Å. The parameters involving the μ_3 -CO ligand, however, are quite normal and almost identical with those of the μ_3 -CO ligand in [Fe₄(CO)₁₃]^{2−} in which the Fe–C distances are 1.99–2.02 Å, the Fe–Fe–C angles are 51.0–52.0°, and the Fe–C–O angles are 132.2–135.5°. The μ_3 -C–O distances are also the same within experimental error (1.20 vs. 1.187 Å). Similar parameters are observed for μ_3 -CO in Fe₃(CO)₁₀(NSiMe₃)₂₁.

One of the more striking structural features is the acuteness of the angles at bismuth, which average 59.78° and is the same as that seen for the Ir–Bi cluster (59.7°). This makes the metal framework for BiFe₃ almost a perfect tetrahedron with all angles very close to 60° and the Fe–Fe distances very close to the Fe–Bi values. The orientation of ligands about bismuth makes it very exposed. In other BiX₃ complexes, X–Bi–X angles are 102.9° (av) for Bi[CH(SiMe₃)₂]₃,²² 94° (av) for

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Table V. Representative Data from Protonation Reactions of II with HCl(g)

amt of II used, g	10 ⁴ × (amt of II used), mol	10 ⁴ × (amt of HCl(g) added), mol	mol of HCl(g) added/mol of cluster	10 ⁴ × (amt of H ₂ produced), mol	mol of H ₂ produced/mol of cluster
0.1555	1.41	0.47	0.33	0.0	0.00
0.1725	1.56	0.48	0.31	0.0	0.00
0.4017	3.64	3.52	0.97	0.0	0.00
0.2026	1.84	1.98	1.08	0.08	0.04
0.4022	3.65	5.60	1.53	1.61	0.44
0.1987	1.80	3.36	1.87	1.15	0.64
0.1579	1.43	2.81	1.96	0.917	0.64
0.0891	0.807	1.93	2.38	0.712	0.88
0.1810	1.64	4.11	2.51	1.50	0.91
0.1509	1.187	3.60	3.01	1.27	1.07
0.0847	0.666	2.06	3.10	0.73	1.09
0.1040	0.943	3.65	3.86	1.10	1.16

BiPh₃,²³ and 106.8° (av) for [Bi[Co(CO)₄]₃]²⁻

In keeping with the postulate that the Fe-Fe bonds are very strained, [BiFe₃(CO)₁₀]⁻ is observed to react with pressures of CO (750 psi, room temperature, 2 days) to produce a new metal carbonyl cluster and Fe(CO)₅ ≥ 1 mol/mol of cluster. Crystals of this material form very easily and precipitate as the reaction proceeds when performed in CH₂Cl₂, and a structural investigation is in progress. On the other hand, ethylene was not observed to react with [BiFe₃(CO)₁₀]⁻ and this may be due to steric effects.

Spectroscopic and Chemical Characterization of [BiFe₄(CO)₁₆]³⁻. The green material formulated as [BiFe₄(CO)₁₆]³⁻ (Figure 2) has not given suitable crystals for an X-ray determination. The [Me₄N⁺] salt of the complex appears to give readily large well-shaped crystals upon cooling of its CH₃CN solutions, but these give only powder patterns in an X-ray beam (possibly as a result of solvent loss).

The spectroscopic characterization and elemental analyses as well as chemical reactivity favor the formulation given in which bismuth is tetrahedrally coordinated to four Fe(CO)₄ units (no Fe-Fe bonds). Formally, one could view bismuth as Bi³⁻ with four tetrahedrally displaced electron pairs which are donated to each of the Fe(CO)₄ species. This makes the environment around iron a trigonal bipyramid with the substituted ligand in an axial position as seen for other Fe(CO)₄L complexes.²⁴ The infrared spectrum is consistent with this analysis as the nearly perfect T_d symmetry possible would predict three IR-active bands as observed. Furthermore, the low-temperature ¹³C spectrum shows two signals in an approximate intensity ratio of 1:3, which coalesce around -45 °C into one band. This is also consistent with the trigonal-bipyramidal geometry about each iron (all of which are equivalent). A difficulty lies in the observation that no Fe-(CO)₄L complexes show resolution of the axial and equatorial carbonyls under similar circumstances.²⁵ We believe that our observation arises from the steric bulk of bismuth and crowding of carbonyls in this complex. Attempts were made to test this hypothesis by preparing Fe(CO)₄BiPh₃ and studying its ¹³C behavior, but simple substitution does not occur; rather, cluster formation is observed with the production of deeply colored solutions whose infrared spectra showed the presence of bands assignable to bridging carbonyls. Evidently the

photochemical processes that dissociate Fe-CO also cause cleavage of Bi-Ph to generate higher nuclearity species. Chemical evidence for the presence of Fe(CO)₄ units in II is that the protonation of the green material eliminates H₂ gas (Table V) via the intermediate formation of H₂Fe(CO)₄, which is known to decompose in this manner.²⁶ The release of H₂Fe(CO)₄ indicates the presence of at least one active Fe(CO)₄ unit. Since the ¹³C NMR shows only one signal at room temperature, this Fe(CO)₄ unit must be either equivalent to the other Fe-CO moieties or accidentally degenerate with the average signal of the other carbonyls. It is unlikely that the carbonyls of an Fe(CO)₄ unit not directly bonded to another iron would exchange with those on the other metal since bridged intermediates postulated in exchange mechanisms of this type are not possible between the nonbonded metal centers. Accidental degeneracy also appears unlikely here, and we favor the interpretation where all the irons are equivalent tetra-carbonyl-containing moieties.

Mechanism for the Synthesis of the Bi-Fe Clusters. The addition of NaBiO₃ to Fe(CO)₅ at elevated temperatures produces cluster I, in which no Bi-O bonds remain. In this process the bismuth is formally reduced. In order for this to occur, something must be oxidized, and one obvious choice is CO. To test this hypothesis, the off-gases of the reaction were passed through concentrated aqueous Ba(OH)₂, which precipitated the evolved CO₂ as BaCO₃.

The yield of CO₂ observed is 79% based on Fe(CO)₅ used or 92% based on [BiFe₃(CO)₁₀]⁻ formed. This process is similar to that observed by Gladfelter and co-workers for the reaction of NO₂⁻ with Fe(CO)₅ to yield [Fe(CO)₃NO]⁻, CO₂, and CO.²⁷ The iron carbonyl nitrosyl complex is then observed to react with Fe₃(CO)₁₂ to produce [Fe₄(CO)₁₂N]⁻ with evolution of CO₂.²⁸

The synthesis in the presence of base may proceed via the same mechanism with oxidation of CO, but testing this hypothesis is more difficult than for complex I as here CO₂ (as carbonate) is also a product of the reaction of Fe(CO)₅ and OH⁻. This process may be compared to the reaction of XO₃²⁻ (X = S, Se, Te) with Ru₃(CO)₁₂ in alkaline media ([HRu₃(CO)₁₁]⁻ presumably being the cluster present), which produces in low yield (<5%) H₂Ru₃(CO)₉X upon workup.²⁹ The reaction with BiO₃⁻ is much cleaner, and higher yields are obtained. Furthermore, the reactions with XO₃²⁻ were subjected to acidification before isolation and it is unclear if formation of the Ru₃X species resulted prior to or subsequent to this step. In the case of BiO₃⁻, the isolation of the metal carbonyl bismuth-containing product before any type of protonation step indicates that M-Bi bond formation occurs first. While the normal yields of the synthesis of [BiFe₃(CO)₁₀]⁻ are on the order of 35-40%, when the system was purged with N₂ as the reaction progressed the yield was higher (ca. 86%). This can be attributed to the reaction of this cluster with adventitious CO. Indeed, when CO was bubbled through a reaction solution, the yield was reduced to 20%.

Final Remarks

Sodium bismuthate, NaBiO₃, reacts with iron carbonyls to reduce the Bi-O bonds and form Fe-Bi bonds. Oxidation of CO to CO₂ is the likely means by which the Bi-O reduction occurs. The presence of base dramatically alters the product type observed: with OH⁻ Bi[Fe(CO)₄]₄³⁻ (II) is produced, while in the absence of hydroxide, [BiFe₃(CO)₁₀]⁻ (I) results. Complex II is readily oxidized by oxygen or H⁺ to yield

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clusters showing loss of an iron atom. In the case of H⁺ addition, the reaction produces H₂ via intermediate elimination of H₂Fe(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 crystallographically 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; NaBiO₃, 12232-99-4; Na₂Fe(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 [(C₆H₅)₄As][Pb(EC₆H₅)₃] (E = S, Se)

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Lead(II) nitrate, in solutions containing at least 3 mol equiv of NaEC₆H₅ (E = S, Se), forms triligated anions that crystallize readily as the tetraphenylarsonium salts [(C₆H₅)₄As][Pb(SC₆H₅)₃] (**1**) and [(C₆H₅)₄As][Pb(SeC₆H₅)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 *P*2₁/*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 β = 105.11 (1)° for **1** and *a* = 10.899 (1) Å, *b* = 17.638 (2) Å, *c* = 20.617 (1) Å, and β = 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 > 2σ(*F*_o)) for **1** and *R* = 0.034 (3074 observations with *F*_o > 3σ(*F*_o)) for **2**. The discrete [Pb(EC₆H₅)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(EC₆H₅)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}S₃ or Pb^{II}Se₃ 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 xantho)plumbate(II) ion, the ligand is disymmetrically bidentate, giving a PbS₆ 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 PbNO₂S₃ coordination sphere.⁴ In contrast, a more regular octahedral coordination about lead is found in RbPbI₃.⁵

The occurrence of bridging thiolato groups in the structures of (penicillaminato)lead(II) (see above) and (2-(morpholin-4-yl)ethanethiolato)lead(II) nitrate⁶ 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, [(C₆H₅)₄As][Pb(SC₆F₅)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 [(C₆H₅)₄As][Pb(SC₆H₅)₃] (**1**) and [(C₆H₅)₄As][Pb(SeC₆H₅)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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