logna, Italy, with financial support from the University of Parma, Parma, Italy.

Registry No. I, 74436-25-2; II, 84802-26-6; III, 84802-27-7; $[(C_2\text{-}t\text{-}Bu)Ru_3(CO)_9HgI]_2$, 84802-25-5; $Ru_3(CO)_{12}$, 15243-33-1; $(CH_3)_3CC{\equiv}CH$, 917-92-0; HgI_2, 7774-29-0; $[As(C_6H_5)_4][Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)]$, 76741-75-8; $Na[Mo(CO)_3(C_5H_5)]$, 12107-35-6; $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2Hg$, 12194-13-7.

Supplementary Material Available: Listings of calculated coordinates of the hydrogen atoms for complex II and thermal parameters and observed and calculated structure factor amplitudes of complex II and complex III (30 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structure of Tetramercury Bis(hexafluoroarsenate), $Hg_4(AsF_6)_2$

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The preparation of $Hg_4(AsF_6)_2$ from Hg and AsF_5 in SO_2 solution is described. An X-ray crystallographic determination has shown that crystals of $Hg_4(AsF_6)_2$ are monoclinic, space group $P2_1/c$, with a = 5.489 (2) Å, b = 11.633 (4) Å, c = 9.850 (6) Å, β = 92.20 (4)°, V = 628.5 (5) Å^3, and d_{calcd} = 6.24 g cm^{-3} for Z = 2. To a first approximation the compound may be described as consisting of almost linear Hg_4^{2+} ions and octahedral AsF_6^- ions. However, there are relatively short interactions between the Hg_4^{2+} ions such that they form nonlinear chains running through the crystal.

Introduction

Oxidation of liquid mercury with a limited amount of arsenic pentafluoride in solution in liquid sulfur dioxide at room temperature leads to the formation of a deep red solution in equilibrium with the insoluble golden yellow metallic compound $Hg_{3-\delta}AsF_6$.[1] The deep red solution contains the Hg_4^{2+} and Hg_3^{2+} cations.[2] The overall reaction between the stoichiometric amounts of reactants needed to give the Hg_4^{2+} ion may be represented by

$$4Hg + 3AsF_5 \rightarrow Hg_4(AsF_6)_2 + AsF_3$$

However, it is probably not possible to obtain pure solutions of $Hg_4(AsF_6)_2$, which always appears to be in equilibrium with the insoluble compound $Hg_{3-\delta}AsF_6$ and $Hg_3(AsF_6)_2$ in solution

$$3Hg_4^{2+} + 2AsF_6^- \rightarrow 2Hg_3^{2+} + 2Hg_{3-\delta}AsF_6(s)$$

On crystallization, the deep red solution yielded crystals of $Hg_3(AsF_6)_2$ and red-black crystals of $Hg_4(AsF_6)_2$. The preparation and crystal structure of $Hg_3(AsF_6)_2$ have been previously described,[2] and a preliminary communication on the preparation, structure, and NMR and UV spectra of $Hg_4(AsF_6)_2$ has been published.[3] In this paper we give a full account of the determination of the structure of $Hg_4(AsF_6)_2$.

Experimental Section

Reactions were carried out under vacuum in flame-sealed double-bulb ampules fitted with medium glass frits. Sulfur dioxide (Matheson) was repeatedly distilled from, and stored over, phosphoric oxide before use. Arsenic pentafluoride was prepared directly from the elements.

Preparation of $Hg_4(AsF_6)_2$. Arsenic pentafluoride (2.96 g, 17.4 mmol) was condensed onto elemental mercury (4.658 g, 23.2 mmol) in ~10 mL of liquid sulfur dioxide at −196 °C, and the mixture was allowed to warm up to room temperature. A deep red solution containing the insoluble gold crystalline compound $Hg_{3-\delta}AsF_6$ was obtained after stirring for a few hours. The red solution was filtered, and the solvent was slowly distilled off under reduced pressure over a period of 1 week to give a mixture of yellow crystals $Hg_3(AsF_6)_2$ and red-black needle-shaped crystals $Hg_4(AsF_6)_2$.

X-ray Crystallography. The dark red needles of $Hg_4(AsF_6)_2$ were separated from the yellow crystals of $Hg_3(AsF_6)_2$ and were sealed in dry Lindemann capillaries under a dry nitrogen atmosphere in a dry box equipped with a microscope. Although visually the crystals appeared to be well-formed needles, many were not single. Preliminary precession photographs were used to give cell and symmetry information, and the following crystal data were then established with use of Mo K$\bar{\alpha}$ radiation on a Syntex P2$_1$ diffractometer (graphite monochromator).

Crystal Data for $Hg_4(AsF_6)_2$: fw = 1179.8; monoclinic; space group $P2_1/c$; a = 5.489 (2) Å, b = 11.633 (4) Å, c = 9.850 (6) Å, β = 92.20 (4)°, V = 628.5 (5) Å^3, and d_{calcd} = 6.24 g cm^{-3} for Z = 2; Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å); μ(Mo K$\bar{\alpha}$) = 553 cm^{-1}.

The crystal used throughout was a thin needle defined by the forms {011} and the approximate faces (301) and $(\bar{3}01)$, which were respectively 0.0033, 0.014, and 0.014 cm from an origin within the crystal. Unit cell dimensions for this crystal were obtained by using a least-squares fit of 2θ, ω, and χ for 14 high-angle (23 < 2θ < 30°) reflections on the diffractometer. Intensity data were measured by using θ–2θ scans over a scan range (Kα_1 − 1.2°) to (Kα_2 + 1.2°) with variable scan rates of 2.0–29.3° min^{-1} dependent on the intensity of a 2-s prescan. Stationary-background counts were recorded at each end of the scan, each for one-fourth of the scan time. Two standard reflections, which were monitored after every 48 reflections collected, showed no significant variations over the period of the data collection. A total of 1834 reflections (including standards) in the quadrants $(h,k,\pm l)$ with 2θ < 55° was eventually collected.

Lorentz and polarization corrections were applied to all reflections. At a later stage in the refinement several calculations of the absorption corrections were made so that the crystal shape and size were optimized. For the crystal dimensions above, the calculations using the program ABSORB[4] and a 10 × 7 × 7 Gaussian grid gave a range of A^* values from 26.42 to 9.93. After removing systematically absent and zero F_o data and averaging several equivalent reflections (R_{merge} = 0.039), we obtained a final data set of 1207 reflections; of these, 629 were considered observed ($I/\sigma(I)$ > 3.0).

Solution and Refinement of the Structure. With Z = 2 in the space group $P2_1/c$, the Hg_4^{2+} cation has crystallographic imposed inversion symmetry. The positions of the heavy atoms in the unit cell were found by inspection of the three-dimensional Patterson function. Least-

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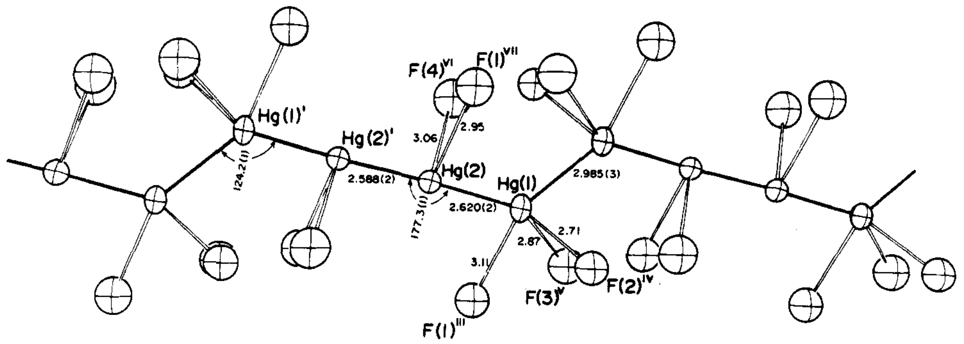

Figure 1. The $(Hg_4)_n^{2n+}$ polymeric cation and some short anion–cation Hg···F contacts <3.15 Å.

Table I. Structural Parameters for $Hg_4(AsF_6)_2$[a]

atom	x	y	z	U, Å^2
Hg(1)	22 (4)	834 (2)	3849 (2)	
Hg(2)	−1 (3)	241 (1)	1282 (2)	
As	5015 (6)	2940 (3)	1721 (4)	
F(1)	775 (7)	309 (3)	268 (4)	10 (1)
F(2)	246 (6)	281 (3)	68 (3)	8 (1)
F(3)	698 (7)	275 (4)	48 (4)	11 (1)
F(4)	317 (8)	319 (4)	300 (4)	12 (1)
F(5)	489 (7)	155 (3)	214 (4)	10 (1)
F(6)	481 (10)	423 (5)	139 (6)	17 (2)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	90.1 (15)	58.8 (12)	34.5 (9)	1.5 (11)	1.1 (9)	−3.6 (8)
Hg(2)	57.5 (11)	44.4 (9)	40.7 (9)	−1.3 (8)	1.9 (7)	−0.9 (7)
As	33 (2)	28 (2)	39 (2)	1 (2)	5 (1)	7 (2)

[a] Positional parameters ×10^4; thermal parameters ×10^3.

Table II. Interatomic Distances (Å) and Bond Angles (deg) (Hg···F < 3.35 Å)

Bond Lengths

Hg(1)-Hg(2)	2.620 (2)	Hg(2)-F(2)	3.34 (3)
Hg(2)-Hg(2)$^{\mathrm{I}}$	2.588 (2)	-F(5)	3.17 (4)
Hg(1)-Hg(1)$^{\mathrm{II}}$	2.985 (3)	-F(5)$^{\mathrm{III}}$	3.32 (4)
Hg(1)-F(5)	3.32 (4)	-F(1)$^{\mathrm{VII}}$	2.95 (4)
-F(1)$^{\mathrm{III}}$	3.11 (4)	-F(4)$^{\mathrm{VI}}$	3.06 (4)
-F(5)$^{\mathrm{III}}$	3.33 (4)	As-F(1)	1.75 (4)
-F(2)$^{\mathrm{IV}}$	2.71 (3)	-F(2)	1.71 (3)
-F(3)$^{\mathrm{V}}$	2.87 (4)	-F(3)	1.68 (4)
-F(6)$^{\mathrm{VI}}$	3.24 (6)	-F(4)	1.67 (4)
		-F(5)	1.67 (4)
		-F(6)	1.54 (6)

Bond Angles

Hg(1)-Hg(2)-Hg(2)$^{\mathrm{I}}$	177.27 (9)	F(2)-As-F(3)	95 (2)
Hg(2)-Hg(1)-Hg(1)$^{\mathrm{II}}$	124.21 (9)	-F(4)	88 (2)
Hg(2)-Hg(1)-F(5)	63.2 (7)	-F(5)	91 (2)
-F(1)$^{\mathrm{III}}$	83.0 (7)	-F(6)	85 (2)
-F(5)$^{\mathrm{III}}$	66.7 (7)	F(3)-As-F(4)	176 (2)
-F(2)$^{\mathrm{IV}}$	141.3 (2)	-F(5)	95 (2)
-F(3)$^{\mathrm{V}}$	135.1 (8)	-F(6)	91 (3)
-F(6)$^{\mathrm{VI}}$	78.8 (10)	F(4)-As-F(5)	87 (2)
Hg(1)$^{\mathrm{II}}$-Hg(1)-F(5)	125.4 (7)	-F(6)	87 (3)
-F(1)$^{\mathrm{III}}$	144.7 (7)	F(5)-As-F(6)	173 (2)
-F(5)$^{\mathrm{III}}$	121.0 (7)	As-F(1)-Hg(1)$^{\mathrm{VIII}}$	116 (2)
-F(2)$^{\mathrm{IV}}$	83.6 (7)	-Hg(2)$^{\mathrm{IX}}$	128 (2)
-F(3)$^{\mathrm{V}}$	85.7 (9)	Hg(1)-F(1)-Hg(2)$^{\mathrm{IX}}$	116 (1)
-F(6)$^{\mathrm{VI}}$	69.5 (10)	As-F(2)-Hg(2)	108 (1)
Hg(1)-Hg(2)-F(2)	87.0 (6)	-Hg(1)$^{\mathrm{X}}$	136 (2)
-F(5)	69.3 (7)	Hg(2)-F(2)-Hg(1)$^{\mathrm{X}}$	116 (1)
-F(5)$^{\mathrm{III}}$	89.0 (7)	As-F(3)-Hg(1)$^{\mathrm{XI}}$	138 (2)
-F(1)$^{\mathrm{VII}}$	84.4 (8)	As-F(4)-Hg(2)$^{\mathrm{XII}}$	132 (2)
-F(4)$^{\mathrm{VI}}$	88.0 (8)	As-F(5)-Hg(1)	114 (2)
Hg(2)$^{\mathrm{I}}$-Hg(2)-F(2)	90.4 (6)	-Hg(2)	116 (2)
-F(5)	109.3 (7)	-Hg(1)$^{\mathrm{VIII}}$	109 (2)
-F(5)$^{\mathrm{III}}$	112.2 (7)	-Hg(2)$^{\mathrm{VIII}}$	110 (2)
-F(1)$^{\mathrm{VII}}$	98.0 (8)	Hg(1)-F(5)-Hg(2)	47.5 (6)
-F(4)$^{\mathrm{VI}}$	94.4 (8)	-Hg(1)$^{\mathrm{VIII}}$	111 (1)
F(1)-As-F(2)	176 (2)	-Hg(2)$^{\mathrm{VIII}}$	136 (1)
-F(3)	81 (2)	Hg(2)-F(5)-Hg(1)$^{\mathrm{VIII}}$	135 (1)
-F(4)	96 (2)	-Hg(2)$^{\mathrm{VIII}}$	115 (1)
-F(5)	90 (2)	Hg(1)$^{\mathrm{I}}$-F(5)-Hg(2)$^{\mathrm{VIII}}$	46.4 (5)
-F(6)	94 (2)	As-F(6)-Hg(1)$^{\mathrm{XII}}$	129 (3)

Symmetry Designations

I	$-x, -y, -z$	VII	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
II	$-x, -y, 1-z$	VIII	$1+x, y, z$
III	$-1+x, y, z$	IX	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
IV	$x, \frac{1}{2}-y, \frac{1}{2}+z$	X	$x, \frac{1}{2}-y, -\frac{1}{2}+z$
V	$-1+x, \frac{1}{2}-y, \frac{1}{2}+z$	XI	$1+x, \frac{1}{2}-y, -\frac{1}{2}+z$
VI	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$	XII	$-x, \frac{1}{2}+y, \frac{1}{2}-z$

squares refinement and a subsequent difference Fourier then located the missing fluorine atoms. Refinement of the positional and isotropic temperature factors of these atoms reduced R_1 to 0.135 for the observed reflections.[5] The introduction of anisotropic thermal motion for the three heavy atoms lowered R to 0.102. At this point the data were corrected for the effects of absorption. Subsequent least-squares refinement converged to give the residuals $R_1 = 0.070$ ($R_2 = 0.094$)[5] for the 629 observed ($F > 6\sigma(F)$) reflections and $R_1 = 0.121$ ($R_2 = 0.124$)[5] for 1207 nonzero reflections. In the final cycle of refinement no parameter shifted by more than 35% of its standard error and weights were calculated by using the expression $w = \sigma(F)^2 + 0.003F^2$. A comparison of the average $w||F_o| - |F_c||^2$ as a function of F_o and $\sin\theta$ after the application of this scheme showed no systematic trends. A final difference Fourier contained some residual peaks up to 3.9 e Å^{-3} in height close to the heavy atoms; the minimum trough was −2.8 e Å^{-3} near Hg(1). In all the refinements neutral-atom scattering curves were taken from ref 6. Computing was performed on a CDC 6400 computer using programs in the SHELX[7] and XRAY[8] systems as well as some local programs. The final atomic positional and thermal parameters are given in Table I. Bond lengths, bond angles, and some significant anion–cation contacts are given in Table II. A view of the $(Hg_4)_n^{2n+}$ polymeric chain showing some of the shorter Hg···F contacts is given in Figure 1, and the overall crystal packing is illustrated in Figure 2. A tabulation of the observed and calculated structure factors is available as supplementary material.

Discussion

In the ionic approximation the crystal structure consists of Hg_4^{2+} cations and AsF_6^- anions. The Hg_4^{2+} cation has crystallographic inversion symmetry with terminal bond lengths of 2.620 (2) Å and a central bond length of 2.588 (2) Å. Although not constrained by symmetry to be so, the Hg_4^{2+} ion is very nearly linear with Hg–Hg–Hg bond angles of 177.3 (1)° and a trans configuration. Both Hg–Hg bond lengths are significantly longer than the analogous distances in the Hg_3^{2+} and the Hg_2^{2+} cations (Table III). In the compounds $Hg_{2.86}AsF_6$ and $Hg_{2.91}SbF_6$, there are infinite chains along the a and b directions, which are noncommensurate with the anion lattice. The average charge on the mercury atoms in these chains is 0.3+ and Hg–Hg distances have been found to be 2.64 (1)[1] or 2.670 (5) Å.[9] From the data given in Table III,

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(5) $R_1 = \sum||F_o| - |F_c||/\sum F_o$; $R_2 = [\sum w|F_o - F_c|^2/\sum wF_o^2]^{1/2}$.

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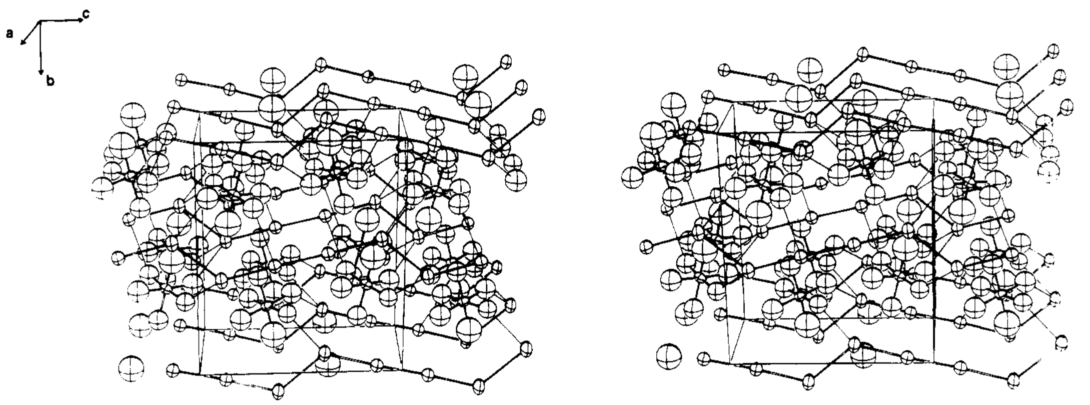

Figure 2. Crystal packing of the compound $(Hg_4)(AsF_6)_2$. The view has been rotated about the *c* direction to reduce overlap. Some of the shorter Hg···F interactions are indicated.

Table III. Mercury-Mercury Bond Lengths and Mercury Contact Distances

compd	Hg-Hg [Hg···Hg], Å	shortest Hg···X, Å
Hg_2F_2[a]	2.507 (1)	2.14 (Hg···F)
Hg_2Cl_2[a]	2.526 (6)	2.43, 3.21 (Hg···Cl)
Hg_2Br_2[a]	2.49 (1)	
$Hg_2(NO_3)_2 2H_2O$[b]	2.54	
$Hg_2(AsF_6)_2SO_2$[c]	2.45 (1)	
$[Hg_2(C_6H_4N_2)_2](ClO_4)_2$[d]	2.498 (2)	2.16 (3), 2.94 (4) (Hg···N) 2.86 (3), 2.89 (4), 3.04 (3) (Hg···O)
$[Hg_2\{Se(C_6H_5)_2\}_4](ClO_4)_2$[e]	2.553 (1)	2.653 (2), 2.919 (2) (Hg···Se) 2.626 (16) (Hg···O)
	2.558 (1)	2.70, 2.80 (Hg···Se)
$Hg_3(AsF_6)_2$[f]	2.552 (5)	2.38 (5), 2.83 (8), 2.92 (9), 2.96 (7) (Hg···F)
$Hg_3(AlCl_4)_2$[g]	2.551 (1), 2.562 (1)	2.517 (3), 2.562 (4), 3.21 → 4.00 (Hg···Cl)
$(Hg_4^{2+})(AsF_6)_2$[i]	2.583 (6), 2.619 (4) [2.992 (6)]	2.71 (3), 2.87 (4), 2.95 (4), 3.06 (4) → 3.33 (4) (Hg···F)
$(Hg_{2.86})(AsF_6)$[h-j]	2.64 (1)	2.99 (4) (Hg···F)
	2.64 (2) (neutron) [3.24 (2)]	2.87 (1), 2.981 (5) (Hg···F)
	2.665 (5)	
$(Hg_{2.91})(SbF_6)$[k]	2.65 (3) [3.23 (1)]	

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it may be seen that the Hg–Hg bond length increases with decreasing formal charge on the Hg atoms.

A feature of considerable interest in the structure of $Hg_4(AsF_6)_2$ is the significant interaction of 2.985 (3) Å between terminal atoms of neighboring Hg_4^{2+} cations across the center of symmetry at (0, 0, $^1/_2$). This interaction has no parallel in Hg_2^{2+} and Hg_3^{2+} compounds and results in infinite zigzag chains of mercury atoms parallel to *b* in the *bc* plane (Figure 2). In these chains the Hg(2)–Hg(1)–Hg(1)′ angle is 124.2 (1)°. The Hg–Hg distance between Hg_4^{2+} ions is comparable to the shortest interatomic distance (3.0 Å) in metallic mercury. It is slightly shorter than the interchain contacts (3.085 (2),[2] 3.099 (2) Å[9]) in the compound $Hg_{2.86}AsF_6$, and it is considerably shorter than the van der Waals contact distance between two mercury atoms. This latter distance is not well-defined, but both Grdenic[10] and Glidewell[11] have suggested 3.4 Å as a reasonable estimate. If it is accepted that there is a bonding interaction between the Hg_4^{2+} cations, then the structure of $Hg_4(AsF_6)_2$ is intermediate between that of $Hg_3(AsF_6)_2$,[2] which has an ionic structure with no short contacts between the Hg_3^{2+} ions, and the infinite-chain structure of $Hg_{3-\delta}AsF_6$,[1,9] in which there are infinite chains of mercury atoms and no small discrete cations can be distinguished. In view of the high electrical conductivity of the infinite-chain compounds,[12] it seems reasonable to predict that some conductivity might be observed along the zigzag chains of the present compound.

The hexafluoroarsenate anion, within the estimated standard deviations, is approximately octahedral with As–F bond lengths in the range 1.54 (6)–1.75 (4) Å. These values may be compared to the As–F bond length in $KAsF_6$ of 1.719 (3) Å.[13] Bond angles are close to the expected values.

Apart from the Hg···Hg contact between terminal atoms of the Hg_4^{2+} cations, the present structure also contains several Hg···F contacts, which may be of significance. These contacts are as short as 2.71 (3) Å, and the arrangement of the shorter contacts with respect to the $(Hg_4)_n^{2n+}$ chain is illustrated in Figure 1. Comparable interactions are also common in "ionic" mercurous compounds and the compounds $Hg_3(AsF_6)_2$ and $Hg_3(AlCl_4)_2$. The strongest of the interactions between the "ions" in these compounds makes angles of approximately 180° with Hg–Hg bonds in the Hg_2^{2+} and Hg_3^{2+} cations so that these compounds are perhaps better described as complexes of the type X–Hg–Hg–X (X = F, Cl, Br, H_2O, SO_4, AsF_6) and X–Hg–Hg–Hg–X (X = $AlCl_4$, AsF_6). The distances

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Inorg. Chem. **1983**, *22*, 1347-1355

involved are summarized in Table III. In $Hg_4(AsF_6)_2$, however, the interaction of the Hg_4^{2+} ion with the AsF_6^- anion in a direction approximately collinear with the terminal Hg–Hg bonds is replaced by the intercation Hg···Hg interaction at 124° to the terminal Hg–Hg bond and several weak Hg···F contacts with the anions. These latter Hg···F interactions are considerably longer than the short interactions (2.38 Å) in $Hg_3(AsF_6)_2$,[2] which are collinear with the Hg–Hg bonds. They resemble in length the interactions in other compounds that are not collinear with the Hg–Hg bonds. For example, the closest Hg···F contacts in $Hg_{2.86}AsF_6$ are 2.87 (1) or 2.98 (1) Å.[1,15]

If the intercation Hg···Hg contact and one or two of the shortest Hg···F contacts to Hg(1) are considered, then the environment of Hg(1) in $Hg_4(AsF_6)_2$ is similar to that of the Hg atoms in the two modifications of tetrakis(diphenylseleno)dimercury(I) perchlorate, $[(C_6H_5)_2Se]_4Hg_2(ClO_4)_2$.[16] Other interionic interactions of comparable strength in other Hg(I) and Hg(II) compounds have been observed, and many of these are discussed elsewhere.[17] However, the nature of these additional interactions is still unclear. A recent calculation[18] on the mercurous halides Hg_2F_2 and Hg_2Cl_2 indicated that the closest next-neighbor fluorine and chlorine atoms might be close enough to transfer charge into the LUMO of the Hg_2Cl_2 (or Hg_2F_2) molecule, strengthening the Hg–Hg bond and weakening the Hg–Cl bond. However, in $Hg_3(AlCl_4)_2$ there is no correlation between the Hg–Hg bond lengths and the adjacent collinear Hg···Cl interactions, since the long Hg–Hg bond (2.562 Å) is collinear with the long Hg···Cl interaction (2.562 Å) and the short Hg–Hg bond (2.551 Å) is collinear with a short Hg···Cl interaction (2.517 Å) (Table III). However evidence of the charge-transfer interaction in this case can certainly be seen in terms of a lengthening of the two Al–Cl bonds involved.[14] The lengths of the remaining longer intermolecular Hg···Cl contacts in this and other structures may then be of importance in explaining these observed bond length trends. The standard deviations on the distances generally precludes a similar observation in the present compound although we may note that the longer As–F bonds (1.75 (4) and 1.71 (3) Å) are to the fluorine atoms involved in the shortest Hg···F contacts. The crystal packing indicated in Figure 2 consists of layers of mercury chains interspersed with layers of hexafluoroarsenate anions along *a*.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Registry No. $Hg_4(AsF_6)_2$, 51383-33-6; AsF_5, 7784-36-3; Hg, 7439-97-6.

Supplementary Material Available: A listing of structure factor amplitudes for $Hg_4(AsF_6)_2$ (7 pages). Ordering information is given on any current masthead page.

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Electrochemistry of the Trinuclear Aquo $Mo^{IV}{}_3$ and $Mo^{III}{}_3$ Ions in Acidic Media

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The trinuclear ions containing Mo(IV), $Mo_3O_4(H_2O)_9^{4+}$ ($Mo^{IV}{}_3$) and the oxalato derivative $Mo_3O_4(C_2O_4)_3(H_2O)_3^{2-}$, can be reversibly reduced in acidic media to trinuclear Mo(III) species. The reductions involve two sequential electron-transfer steps with formal potentials that are pH dependent:

$$Mo^{IV}{}_3 + 2e^- \overset{E^f_1}{\rightleftharpoons} Mo^{III}{}_2Mo^{IV} \qquad Mo^{III}{}_2Mo^{IV} + 1e^- \overset{E^f_2}{\rightleftharpoons} Mo^{III}{}_3$$

Two waves are evident in voltammograms and polarograms of $Mo_3O_4(C_2O_4)_3(H_2O)_3^{2-}$, but with $Mo^{IV}{}_3$ the two formal potentials are too close together to observe separate waves. However, logarithmic analysis of the shapes of normal-pulse polarograms allowed the two formal potentials to be evaluated. The reductions of both complexes are believed to be accompanied by protonation of the bridging and capping oxo ligands. The new, trinuclear $Mo^{III}{}_3$ species resulting from the three-electron reduction of $Mo^{IV}{}_3$ exhibits a characteristic ESR spectrum. The mixed-valent intermediate, $Mo^{III}{}_2Mo^{IV}$, is diamagnetic. Possible structural changes that accompany the addition of electrons and protons to $Mo^{IV}{}_3$ are discussed.

The crystal structures of ions containing molybdenum in oxidation state IV have been determined for anionic complexes containing oxalate[1] and edta[2] (edta = ethylenediaminetetraacetate) as ligands. In both of these cases the structures are based upon a trimeric core of composition $Mo_3O_4^{4+}$ (Figure 1). In addition, the structure of an isothiocyanato complex has been surmised.[3] Earlier studies[4] had suggested a dimeric structure for the aquo Mo(IV) ion, which was the assumption made in a previous report from this laboratory.[6] Since more recent structural studies seem to show conclusively that aquo Mo(IV) is trimeric,[3,7] we have reexamined the electrochemistry of this ion in greater detail to see whether it is consistent with the presence of three reducible centers in the ion. While this study was in progress, Richens and Sykes reported the results of experiments on aquo Mo(IV) that included some electrochemical measurements.[8,9] Where they overlapped, our ex-

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