Table III. Distances and Angles in $Pb_2Sb_2^{2-}$

atoms	dist, A	atoms	angles, deg	atoms	angles, deg
1-2	2.931 (3)	2-1-3	59.79 (6)	1-3-2	60.23 (6)
1-3	2.924 (2)	2-1-4	60.10 (10)	1-3-4	61.41 (7)
1-4	3.006 (4)	3-1-4	59.95 (10)	2-3-4	60.74 (11)
2-3	2.918 (3)	1-2-3	59.98 (6)	1-4-2	58.70 (9)
2-4	2.974 (5)	1-2-4	61.20 (7)	1-4-3	58.65 (9)
3-4	2.963 (5)	3-2-4	60.39 (11)	2-4-3	58.88 (10)

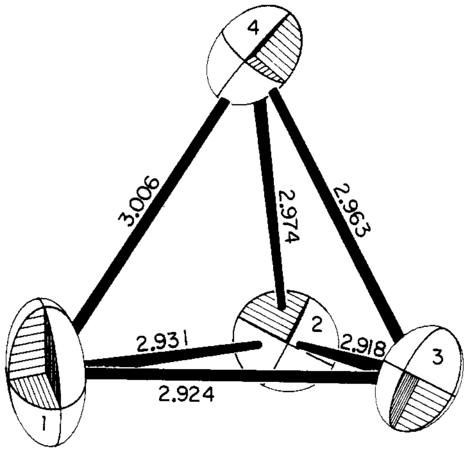

Figure 1. Partially disordered $Pb_2Sb_2^{2-}$ anion, with the *b* axis approximately vertical (50% thermal ellipsoids).

molecule appears to simply fill a cavity with no significant interaction with the anions. The shortest distance PbSb1-Nen1 at 3.87 (8) Å is not significantly less than distances to crypt carbons such as PbSb2-C12 at 3.96 (4) Å where hydrogen may also be important.

A view of the $Pb_2Sb_2^{2-}$ anion is shown in Figure 1. For complete disorder the observed cluster geometry would represent a mean tetrahedral configuration, each edge being an average of one Pb–Pb, one Sb–Sb, and four Pb–Sb distances. Although this was substantially the case in $Sn_2Bi_2^{2-}$, the present $Pb_2Sb_2^{2-}$ is only partially disordered. The refined occupancies (Table I) range from 27% lead at atom 3 to 66 and 67% lead at atoms 1 and 4. Correspondingly, the bond PbSb1–PbSb4 has the most Pb–Pb character and is significantly longer (3.006 Å) than the others while the bond with the most Sb–Sb character (PbSb2–PbSb3) is the shortest (2.918 Å) but not significantly so. The observed $Pb_2Sb_2^{2-}$ anion still exhibits a remarkable resemblance to $Sn_2Bi_2^{2-}$; both anions have longer distances to atom 4 and a very similar elongation of the thermal ellipsoid of atom 1. It is probable that these effects arise from the crystal packing with the crypt cations.

Appropriate bond lengths for Pb–Pb and Sb–Sb can be estimated from those in Sb_7^{3-}[10] and Pb_5^{2-}.[11] The averages of all distances in these are 3.081 and 2.782 Å, respectively, while use of only the axial–equatorial lengths in Pb_5^{2-} and the basal distances in Sb_7^{3-} gives 3.002 and 2.858 Å, respectively. The latter procedure provides somewhat better values with $Sn_2Bi_2^{2-}$,[7] probably because these distances involve similarly constrained and triply bonded atoms. Either way, the average Pb-Sb bond is 2.93 Å, which compares well with the observed average of 2.953 Å.

The difference estimated for Pb–Pb vs. Sb–Sb and Sn–Sn vs. Bi–Bi distances in these mixed species is not large, 0.14 and 0.11 Å (4–5%), respectively. This means the actual D_{2d} species has only a relatively small deviation from T_d symmetry, and this allows more or less complete disorder in the cavity between the crypt-K^+ cations. The partial order achieved with $Pb_2Sb_2^{2-}$ is consistent with the somewhat larger asymmetry estimated.

A pair of elements from different periods has been used throughout these studies of mixed anions so that these could be distinguished in the products by X-rays. In fact this proves to be of little value in these tetraatomic structures. We have not attempted the synthesis of $Sn_2Sb_2^{2-}$ or $Pb_2Bi_2^{2-}$ but are certain they are stable and well disordered in this structure. Stabilities of the mixed neutral species Sb_xBi_{4-x} are linear with composition,[12] and those of the mixed anions from different groups presumably behave quite similarly. However, the stabilities of alternate species (e.g., Sb_4^{2-}, $PbSb_3^{3-}$, Pb) are likely to be more important as far as the products found than just that of the ion of interest.

The homoatomic tetrahedra clusters of the elements from silicon through lead are known in the 1:1 intermetallic phases with sodium through cesium.[5,13] Doubtless, these do not contain ions with the full 4– charge, rather some electron density is instead delocalized onto the cations. No polyatomic ions with this high a charge density have been isolated from molecular solvents with cryptated cations. The related $(M^{IV}{}_3M^{V})^{3-}$ or $(M^{IV}M^{V}{}_3)^{1-}$ ions have not been identified either, the latter perhaps because inadequate anion separation that would be provided by a single cation (no 1– ions are known). However, many more of these cations probably exist in solution, and it may be only that the correct cation, solvent, alloy phase, reaction parameters, and isolation techniques have not yet been found.

Acknowledgment. We are indebted to Professor R. A. Jacobson for continued use of the diffraction facilities and programs.

Supplementary Material Available: Listings of additional bond distances, observed and calculated structure factors, and anisotropic thermal parameters in the crypt cations (Tables IV–VI) (10 pages). Ordering information is given on any current masthead page.

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Convenient, High-Yield Synthesis of $(Et_4N)_2[Fe_2OCl_6]$

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Much attention has been focused recently upon oxo-bridged diiron(III) complexes. In addition to being a common hydrolysis product of ferric salts and an oxidation product of ferrous compounds, $\{Fe_2O\}^{4+}$ units are known or believed to comprise the active centers of various metalloproteins. Included here are the dioxygen binding site in hemerythrins[1] and the functional cores of *Escherichia Coli* ribonucleotide reductase,[2] beef spleen purple acid phosphatase, and porcine uteroferrin.[3] Recently we reported[4] the synthesis and properties of several oxo- and hydroxo-bridged diiron(III) compounds as models for the diiron sites in these proteins. During the course of this work, $(Et_4N)_2[Fe_2OCl_6]$ was found to be a useful starting material, particularly for the synthesis

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of $[Fe_2O(O_2CC_6H_5)_2(HB(pz)_3)_2]$,[4b] where $HB(pz)_3$ is the hydrotris(1-pyrazolyl)borate anion. Although several preparations of $[Fe_2OCl_6]^{2-}$ ([**1**]) with a variety of counterions are available, we were interested in a straightforward route that would allow large-scale synthesis utilizing readily available starting materials. Here, we report a convenient, high-yield method for preparing the tetraethylammonium salt of anion [**1**].

Experimental Section

All reagents were purchased from commercial sources and used as received. No precautions were taken with respect to the drying of solvents or starting materials, and exclusion of oxygen was unnecessary. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta GA.

Tetraethylammonium (μ-Oxo)bis[trichloroferrate(III)], $(Et_4N)_2[Fe_2OCl_6]$ ($(Et_4N)_2$[1]). A solution of $NaOCH_3$, prepared by allowing 1.20 g (0.0522 mol) of metallic Na to react with 250 mL of CH_3OH, was added dropwise over a period of 2.5 h to a solution of 14.2 g (0.0525 mol) of $FeCl_3{\cdot}6H_2O$ in 350 mL of CH_3OH with rapid stirring. During the addition the reaction mixture changed from a light yellow color to deep brown. After the addition was complete, the reaction mixture was stirred for 1 h and then 9.50 g (0.0573 mol) of solid Et_4NCl was added. After ~10 min CH_3OH was stripped off by a rotary evaporator (the heating bath was maintained at ≤35 °C) until a thick slurry was obtained. It is important not to take the mixture completely to dryness, a step that markedly decreases the final yield. To the slurry of crude product was added 200 mL of CH_3CN. The resulting cloudy brown suspension was stirred for 15 min and filtered through a pad of Celite to remove NaCl. After the Celite cake was washed with 50–100 mL of CH_3CN, the combined filtrates were concentrated to a thick brown oil. This material was dissolved in 20 mL of CH_3CN, and 300 mL of $CHCl_3$ was added over several minutes. The product separated as a brown oil, leaving unreacted Et_4NCl to remain in solution and thus effecting an important purification step. The product was separated from the $CHCl_3$ layer by using a separatory funnel and diluted to 55–60 mL with CH_3CN. After addition of ~100 mL of THF to this deep red-brown solution, a small amount of precipitate formed that was filtered off. To the filtrate was added another ~150 mL of THF, and the slightly cloudy solution was cooled to −20 °C. After approximately 1 day the first crop of brown crystals was filtered off and washed with THF. More THF was added to the filtrate until it became cloudy, and then the mixture was stored at −20 °C for another day. A second crop was obtained and washed with THF. The two crops were separately ground to a powder and dried under vacuum to remove lattice solvent. The yield for the first crop was 10.93 g (69.7%) and for the second crop was 2.63 g (16.8%), giving a combined yield of 13.56 g (86.5%) of a golden brown powder. Anal. Calcd for $C_{16}H_{40}Cl_6Fe_2N_2O$: C, 31.98; H, 6.71; Cl, 35.40, N, 4.66. Found: C, 31.89; H, 6.66; Cl, 35.19; N, 4.67. UV–Vis (CH_3CN, 0.9 mM): λ 375 nm (sh, ϵ_{Fe} 2540 cm^{-1} M^{-1}), 316 (sh, 8450), 302 (sh, 9040), 293 (9410), 244 (6280). IR (KBr, cm^{-1}): 857 (vs, ν_{as}(FeOFe)), 365 (s, $\nu_{as}(FeCl_3)$), 318 (m, $\nu_s(FeCl_3)$). These spectroscopic values are in good agreement with those in the literature.[5-10] As noted in ref 5, solutions of **1** in CH_3CN decompose upon standing for several hours at room temperature.

Discussion

The reaction used here to prepare the tetraethylammonium salt of [**1**] is shown in eq 1. The yields given in this and the following equations are for isolated, pure product. The order of addition in the first step of the procedure is quite important. When solid $FeCl_3{\cdot}6H_2O$ was added to a methanolic solution of NaOMe followed by Et_4NCl, a large quantity of $(Et_4N)(FeCl_4)$ precipitated and the yield of $(Et_4N)_2$[**1**] was substantially diminished. Another key point is that the methanol reaction mixture must not be taken to complete dryness, a step that apparently causes formation of an insoluble product, decreasing the yield markedly (~60% for two trials). Removal of excess Et_4NCl was achieved in the $CHCl_3$ precipitation step. This step proved to be important because crystallization of $(Et_4N)_2$[**1**] is retarded by the presence of excess Et_4NCl. Also, Et_4NCl contaminates the product if it is not removed prior to the CH_3CN/THF crystallization step.

$$2FeCl_3{\cdot}6H_2O + 2NaOMe \xrightarrow[2Et_4NCl]{MeOH} \rightarrow \rightarrow \underset{86.5\%}{(Et_4N)_2[Fe_2OCl_6]} + 2NaCl \quad (1)$$

Several recent papers have described alternative procedures for preparing [**1**] with a variety of counterions.[5-11] The procedure[5] most similar to ours is shown in eq 2. This route requires preparation of one of the starting materials and gives a lower purified yield than the one described here. Three additional methods for preparing [**1**] are shown in eq 3,[6] 4,[7,12] and 5.[9] The yield for eq 4 was not reported;[7,8] in our hands, a 13% yield was obtained by using this procedure as described in ref 7. Finally, in two reports[10,11] [**1**] was prepared as a side product of the reaction of interest, one of which is given in eq 6.[10] The structure of $[Fe(phen)_3]$[**1**]·DMF, obtained as a trace byproduct in the synthesis of *mer*-$[Fe(phen)Cl_3{\cdot}DMF]$, has been described.[11] The procedure given here has the following advantages over these alternative methods: only inexpensive, commerical reagents are required; there is no need to regulate the amount of water present in the reaction mixture; aerobic conditions may be used; the reaction is clean, affording large quantities of pure crystalline product in better than 85% yield.

$$2(Me_4N)(FeCl_4) + 3.0NaOH(aq) \xrightarrow[EtOH]{MeCN} \rightarrow \rightarrow \underset{41\%}{(Me_4N)_2[Fe_2OCl_6]} + 2NaCl \quad (2)$$

$$2(Et_4N)(FeCl_4) + 2NaOSiMe_3 \xrightarrow{MeCN} \underset{66\%}{(Et_4N)_2[Fe_2OCl_6]} + (Me_3Si)_2O + 2NaCl \quad (3)$$

$$2FeCl_3 + 3py + H_2O \xrightarrow{EtOH} (Hpy)_2[Fe_2OCl_6]{\cdot}py \quad (4)$$

$$2(NO)[FeOCl_2] \xrightarrow[CH_2Cl_2]{2PPh_4Cl} \underset{38.7\%}{(PPh_4)_2[Fe_2OCl_6]} \quad (5)$$

$$2(C_6H_5)_3PC(Se)P(C_6H_5)_3 + 4FeCl_3 \xrightarrow[CH_2Cl_2]{H_2O} [((C_6H_5)_3P]_2C(Se)]_2[Fe_2OCl_6] + 2FeCl_2 + 2HCl \quad (6)$$

In conclusion, a straightforward, inexpensive, high-yield route to $(Et_4N)_2[Fe_2OCl_6]$ has been discovered. This route offers some advantages over those previously reported and allows large-scale preparation of an important starting material for several interesting binuclear iron(III) complexes.

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Note Added in Proof. The high-yield synthesis of $[Fe(bpy)_3][Fe_2OCl_6]$ has just been reported: Weiss, H.; Strähle, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1453–1455.

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