found in the spectrum of **3** but with differences in relative intensities in the 1500–1400 region, very similar to those found in the spectra of $NaBPh_4$ and $TlBPh_4$ near 1280 (w, br) and 1235 (w);[28] 1200–1100 region very close to those of $CuBPh_4$ and $AgBPh_4$;[28] ν_{CH} 750 (s), 710 (vs).[28] NMR (DMF), ppm: ^{11}B, −6.5; ^{31}P, 209.7.

(c) From the Trimetallic Complex 4 and $NaBPh_4$. **4** (0.539 g, 0.528 mmol) was treated with $NaBPh_4$ (0.458 g, 1.43 mmol) in EtOH (30 mL) according to the same procedure as above. The crude orange-red product **2** (0.360 g) crystallized as orange-red needles (0.346 g, 16%) from CH_3CN/Et_2O (1:10).

Synthesis of the Iron Dinitrosyl Bis(phosphane amine–triphenylborane) 3 by Reversible Transformation of 2 or Directly from 1 and BPh_3. The only method that led to *crystalline* **3** was the decomposition of **2** in a CH_3CN/Et_2O solution. The compound dissolved only in DMF (slowly at room temperature); attempts to recrystallize **3** in this solvent resulted in its precipitation as an amorphous solid. Elemental analysis and IR spectra of ground single crystals of **3** were consistent with the presence of 0.5 CH_3CN/Fe. Anal. Calcd for $C_{57}H_{59.5}B_2FeN_{4.50}O_6P_2$ (**3**, 0.5 CH_3CN): C, 65.61; H, 5.71; N, 6.04. Found: C, 65.09; H, 5.63; N, 5.99. Mp: 179–180 °C. IR (KBr), cm^{-1}: ν_{NH} 3230 (w); ν_{NO} 1740 (s), 1690 (vs), 1200–1100 region similar to those of $CuBPh_4$ and $AgBPh_4$,[28] with an additional medium-intensity band at 1160; ν_{CH} 730 (s), 710 (vs).[28] NMR (DMF), ppm: ^{11}B, +7.4 (very broad); ^{31}P, see Discussion.

Interconversion of the Ammonium Tetraphenylborate 2 into the Amine–Triphenylborane 3. (a) Transformation 2 → 3. **2** can be converted into **3** by repeated crystallizations in CH_3CN/Et_2O (1:10). In a typical experiment, 0.720 g (0.533 mmol) of **2** was dissolved in 1 mL of CH_3CN; 10 mL of Et_2O was carefully added. The Et_2O layer was allowed to diffuse slowly into the CH_3CN solution at room temperature; the precipitate that formed overnight was filtered, washed twice with 15 mL of CH_3CN and then three times with 20 mL of Et_2O, and dried. The filtrate was evaporated, and the process was repeated twice to yield altogether 0.494 g (87%) of **3** as red parallelepipedic crystals. Benzene was detected by gas–liquid chromatography (SE 30, 80 °C) in the CH_3CN/Et_2O filtrate after transformation of **2** and identified by comparison with an authentic sample. The conversion of **2** into **3** was also observed to occur spontaneously (i) within $^1/_2$ h in pure CH_3CN, when solutions of **2** were concentrated under vacuum at ca. 40 °C, (ii) in CH_3CN or CH_2Cl_2 when solutions of **2** were left overnight at room temperature, and (iii) in the solid state; in one experiment, the decay could be monitored by IR spectroscopy as occurring within 2 h.

(b) Reverse Transformation of 3 to 2. Aqueous HCl (1.20 mmol) was added dropwise to a stirred suspension of **3** (0.64 g, 0.580 mmol) in CH_3CN (15 mL). The crystals slowly dissolved, and after 10 min at room temperature a homogeneous solution was obtained. The solvent was then evaporated under vacuum and the residue redissolved in EtOH (15 mL). The addition of $NaBPh_4$ (0.645 g, 1.88 mmol) in EtOH (15 mL) afforded a precipitate, which was filtered and washed with EtOH (3 × 10 mL) and Et_2O (5 × 15 mL), to yield 0.610 g (73%) of crystalline **2**.

Direct Synthesis of 3 by Reaction of $Fe(NO)_2[PhP(OCH_2CH_2)_2NH]_2$ (1) with BPh_3. Triphenylboron (0.37 g, 1.530 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of **1** (0.413 g, 0.766 mmol) in CH_2Cl_2 (30 mL). After 10 min, the solvent was removed and the ochre solid residue was washed (3 × 10 mL of CH_2Cl_2 and then 3 × 15 mL of Et_2O) and dried for several hours under vacuum, to yield 0.653 g (78%) of **3**, mp 175–180 °C. Anal. Calcd for $C_{57}H_{60}B_2FeN_4O_6P_2Cl_2$ (**3**, CH_2Cl_2): C, 61.80; H, 5.42; N, 5.05; P, 5.60. Found: C, 61.90; H, 5.46; N, 5.09; P, 5.66.

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Registry No. **1**, 84988-36-3; **2**, 92958-55-9; **3**, 92984-17-3; **4**, 84988-35-2; **6**, 15002-08-1; **7**, 57680-64-5; BPh_4^-, 4358-26-3.

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Preparation and Crystal Structure of Hg_3NbF_6 and Hg_3TaF_6: Mercury Layer Compounds

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The reaction of mercury with $Hg(MF_6)_2$ (M = Nb, Ta) dissolved in SO_2 gives rise to golden crystals of tetragonal $Hg_{3-\delta}MF_6$, which are subsequently transformed into silver crystals of trigonal Hg_3MF_6. The former are isostructural with the M = As, Sb analogues, but the latter have layer structures that are reported here for the first time. They consist of hexagonal sheets of Hg atoms that are separated by sheets of MF_6^- ions.

Introduction

In previous papers we have reported the preparation, structure and properties of the new homopolyatomic cations of mercury, Hg_3^{2+} and Hg_4^{2+}, formed by oxidation of mercury with SbF_5 and AsF_5. With excess oxidant the mercurous cation Hg_2^{2+} is formed, but with smaller amounts of oxidant the linear cations, Hg_3^{2+} and Hg_4^{2+}, are obtained.[1-4] With a still smaller amount of oxidant, the final product is the metal-like compound $Hg_{3-\delta}MF_6$ (M = As (δ = 0.18) and Sb (δ = 0.10)). Neutron and X-ray diffraction studies have shown that these compounds contain two nonintersecting mutually perpendicular sets of chains of mercury atoms that are incommensurate with the host lattice of MF_6^- anions.[5-7] Because of their unusual structure and anisotropic conductivity, these compounds have been of considerable interest to solid-state physicists. The extensive literature on the physical properties of these compounds has recently been reviewed.[8]

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Table I. Proposed Model for Hg_3NbF_6

Crystallographic Data

$M_r = 808.67$, trigonal, space group $P\bar{3}1m$, $Z = 1$, $a = 5.02\ (1)$ Å, $c = 7.68\ (7)$ Å, $D_x = 8.0\ (1)$ Mg m^{-3}

Atomic Coordinates

atom	site	*x*	*y*	*z*
Hg(1)	1b	0	0	$^1/_2$
Hg(2)	2d	$^1/_3$	$^2/_3$	$^1/_2$
Nb	1a^a	0	0	0
F	6k	0.309^b	0	0.143^b

^{a} In some samples the Nb atom is disordered over the three sites 1a and 3c ($^1/_3$, $^2/_3$, 0; $^2/_3$, $^1/_3$, 0). ^{b} Calculated by assuming an undistorted NbF_6 octahedron with Nb–F = 1.90 Å.

We have carried out many different reactions in attempts to obtain further examples of one-dimensional mercury chain compounds. In the case of the oxidation of mercury with $Hg(NbF_6)_2$ and $Hg(TaF_6)_2$ in SO_2 we were successful, but the golden crystals of $Hg_{3-\delta}NbF_6$ and $Hg_{3-\delta}TaF_6$ that were produced slowly transformed into silver metallic platelets. X-ray diffraction shows that these silver compounds have a composition similar to that of the golden ones, namely Hg_3NbF_6 and Hg_3TaF_6, but they contain sheets of mercury atoms in a close-packed layered structure rather than the chains of mercury atoms found in the golden compounds. The crystal structures of these compounds are described below. The structures of the golden compounds have been reported elsewhere.[9]

Experimental Section

Preparation of $Hg_{3-\delta}MF_6$ and Hg_3MF_6 (M = Nb, Ta). The general procedure and vessels for handling SO_2 solutions have been described elsewhere.[4] Niobium pentafluoride (Ozark-Mahoning) was purified by sublimation in a dry Kel-F tube under vacuum. This NbF_5 was then allowed to react with the stoichiometric amount of HgF_2 (Ozark-Mahoning) in dry SO_2 at room temperature to give a solution of $Hg(NbF_6)_2$ together with some solid. The solution was filtered off onto mercury at room temperature. Almost at once golden crystals were observed to grow on the surface of the mercury, and a fine white precipitate formed slowly. On standing for a few hours, the golden crystals were transformed into thin silver platelets, the solution became yellow in color, and some droplets of unreacted mercury remained. The white solid was removed by stirring the solution to give a suspension, which was then poured off through a filter, leaving the heavier silver-colored crystals and unreacted mercury behind. The white solid became yellow on removing the solvent under vacuum, and it was identified as $Hg_3(NbF_6)_2$ by Raman spectroscopy. The golden crystals have been shown by single-crystal X-ray diffraction[9] to be $Hg_{3-\delta}NbF_6$, isomorphous with $Hg_{3-\delta}AsF_6$.[5]

The reaction of $Hg(TaF_6)_2$ (Ozark-Mahoning) proceeded in the same way, giving golden crystals that were transformed into silver platelets and a white solid that became yellow on removal of the solvent and was identified as $Hg_3(TaF_6)_2$ by Raman spectroscopy. The golden crystals have been identified by X-ray diffraction as $Hg_{3-\delta}TaF_6$.[9]

Crystals of both the Hg_3MF_6 compounds are very thin soft platelets and have a silver metallic appearance very much like aluminum foil. A typical single crystal from these preparations had dimensions 2 × 2 × 0.05 mm.

X-ray Studies of Hg_3NbF_6 and Hg_3TaF_6. Precession photographs of the reciprocal plane parallel to the flat face of a well-developed crystal of Hg_3NbF_6 clearly show hexagonal symmetry but with orientational disorder of the crystal domains in the plane of approximately ±3°. The photographs can be indexed as *hk*0 projections by using the cell given in Table I. In addition to the *hk*0 reflections, some reflections from nearby higher layers also appear on these photographs. All such extra reflections are consistent with an additional orientational disorder of approximately ±10° about axes perpendicular to [001]. The *hk*0 reflections with $2h + k = 3n$ are generally much stronger than the other reflections and form a prominent hexagonal sublattice with $a = 2.90\ (1)$ Å. The relative intensities of the sublattice and superlattice vary from sample to sample, and in some cases the superlattice reflections are totally absent.

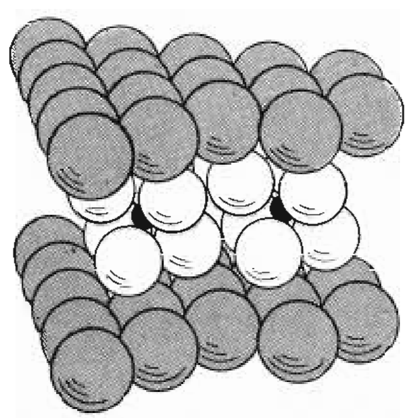

Figure 1. View of the layer structure of Hg_3NbF_6. The gray atoms are Hg, the white atoms are F, and the black atoms are Nb.

Photographs of the *h*0*l* projection show few reflections with $|l| > 1$ except for a complete series of weak 00*l* reflections. These are quite sharp in the 2θ direction but are spread into arcs by the orientational disorder. The quality of the crystals is too poor to permit an accurate measurement of the intensities of the Bragg peaks, but the principal features of the diffraction pattern can be explained by a model in space group $P31m$ in which layers of hexagonally close-packed NbF_6 octahedra alternate with hexagonally close-packed Hg layers as shown in Figure 1. All the atomic coordinates of the Nb and Hg atoms, and the *y* coordinate of the F atom, are determined by symmetry. The *x* and *y* coordinates of F, given in Table I, are calculated on the assumption that NbF_6 is a regular octahedron with Nb–F = 1.90 Å. The coordinates of F are close to the values $x = {}^1/_3$, $z = {}^1/_6$, which would correspond to the F and Hg atoms lying on a perfect cubic close-packed lattice.

In this model the Hg layers are in the form of a regular hexagonal net of Hg atoms rotated 30° about [001] from the axes of the NbF_6 hexagonal net. As a result, they contribute only to the sublattice reflections. If the F atoms were in their ideal positions ($^1/_3$, 0, $^1/_6$), they too would only contribute to the sublattice reflections. Apart from the small contribution caused by the displacement of the F atoms from these positions, the superlattice reflections result only from the ordering of the Nb atoms. Absence of superlattice reflections as found in some of the samples indicates that the Nb atoms randomly occupy different positions in different layers; i.e., the position of the Nb atom in the *n*th layer is not necessarily (0, 0, *n*) but might be ($^2/_3$, $^1/_3$, *n*) or ($^1/_3$, $^2/_3$, *n*).

Precession X-ray photographs of Hg_3TaF_6 show that it is isostructural with Hg_3NbF_6 and has a similar cell, with $a = 5.03\ (1)$ and $c = 7.4\ (4)$ Å. So far all the crystals of this compound studied show extensive disordering around [001].

Discussion

Unlike AsF_5 and SbF_5, NbF_5 and TaF_5 are not sufficiently strong oxidizing agents to oxidize elemental mercury. However, both compounds are good fluoride ion acceptors, and they react readily with HgF_2 to form $Hg(NbF_6)_2$ and $Hg(TaF_6)_2$. These salts can then be used to oxidize mercury in SO_2 to form the metallic compounds Hg_3NbF_6 and Hg_3TaF_6. The initial products of these reactions are golden crystals of $Hg_{3-\delta}NbF_6$ and $Hg_{3-\delta}TaF_6$, analogous to the previously reported $Hg_{3-\delta}AsF_6$ and $Hg_{3-\delta}SbF_6$. However, whereas $Hg_{3-\delta}AsF_6$ and $Hg_{3-\delta}SbF_6$ do not undergo any further reaction, the corresponding NbF_6 and TaF_6 compounds are transformed in the presence of liquid SO_2 into the silver platelets over a period of a few hours.

The structure of the Hg_3NbF_6 crystals is shown in Figure 1. It consists of hexagonal sheets of Hg atoms separated by two similar sheets of F atoms, the three sheets together forming a cubic close-packed array. The Nb atoms occupy one-third of the octahedral cavities between the F layers. Such a layer structure explains the morphology of the soft thin crystals whose metallic luster arises from the sheets of metallicly

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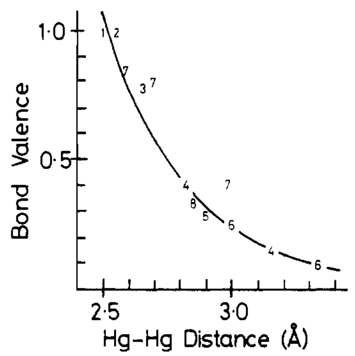

Figure 2. Relation between the bond valence (*y* axis) and bond length (*x* axis) in angstroms for Hg–Hg bonds. The line corresponds to the following equation: bond valence = exp((2.51 – distance)/0.35). The points correspond to (1) Hg_2^{2+},[15] (2) Hg_3^{2+},[1,2] (3) $Hg_{3-\delta}AsF_6$,[8] (4) β-Hg,[14] (5) Hg_3NbF_6, (6) α-Hg,[15] (7) $Hg_4^{2+}(AsF_6)_2$,[3] and (8) $KHgC_4$.[12]

bonded Hg atoms. In these sheets each Hg has six other Hg atoms as neighbors, at a distance of 2.90 (1) Å. Its coordination is completed by six F atoms from the two adjacent fluorine sheets, at distances of around 3.2 Å.

On being heated to 120 °C, the silver Hg_3NbF_6 crystals were transformed in about 30 min to the golden $Hg_{3-\delta}NbF_6$ crystals, as was confirmed by an X-ray powder photograph. Despite the apparent difference in the composition of these compounds, no mercury was observed to be formed in the transformation. When the golden crystals were cooled to room temperature and below, the silver crystals were not re-formed. Thus, it appears that this transformation is not reversible in the absence of the liquid SO_2 that was present during the formation of the silver crystals from the initially formed golden crystals.

Hg–Hg bonds occur in many compounds, but Hg_3NbF_6 and Hg_3TaF_6 are unusual in that this bonding occurs in sheets. In most cases the Hg atom has a strong tendency to form two collinear bonds as in Hg_3^{2+} and Hg_4^{2+}. Infinite linear chains are found in β-Hg and $Hg_{3-\delta}MF_6$ (M = As, Sb, Nb, Ta).

Mercury atoms can be found in sheets in the graphite intercalate $KHgC_4$.[10] Although the Hg–Hg distances are similar in both the intercalate and Hg_3NbF_6 (2.85 and 2.90 Å, respectively), the sheets differ in that in the Nb compound each Hg has six nearest Hg neighbors and a formal charge of $^1/_3$ +, while in the intercalate each Hg has only three Hg neighbors and a formal charge of 0.

Following the approaches of Pauling[11] and Brown and Shannon,[12] it is possible to correlate the lengths of Hg–Hg bonds with their bond strength (or bond valence) as shown in Figure 2. The bond valences have been assigned as follows: For Hg_2^{2+} and Hg_3^{2+} a bond valence of 1.00 is assumed. For Hg_4^{2+} the terminal Hg atoms are assumed to form bonds to F of 0.58 valence unit (vu) and to the inner Hg of 0.36 vu, giving bond valences of about 0.85 for the central bond, 0.80 for the terminal bond, and 0.40 for the weak bridging bond between Hg_4^{2+} ions. For $Hg_{3-\delta}AsF_6$ the atomic valence of the Hg atom (2.00) is diminished by its formal charge (0.36 vu, being the valence of the bonds formed to F) and by a further 0.10 to allow for the bonding to the adjacent perpendicular chains (because of the incommensurate nature of this structure, bond lengths vary from one atom to another). In β-Hg there are two short bonds and eight longer bonds, and the valences of these have been chosen so that they sum to 2.0 at each Hg atom. A similar method of assigning valences has been used for α-Hg, where there are six short and six longer bonds. The bond valence expected for Hg_3NbF_6 is the atomic valence of Hg (2.00) less the valence of the bonds to F (0.33 = formal charge on each Hg) divided by the number of Hg–Hg bonds (6). The solid curve in Figure 2 corresponds to the expression

$$\text{bond valence} = \exp((2.51 - \text{distance})/0.35)$$

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Registry No. $Hg(NbF_6)_2$, 93255-71-1; $Hg(TaF_6)_2$, 93255-75-5; Hg_3NbF_6, 93255-73-3; Hg_3TaF_6, 93255-74-4; Hg, 7439-97-6.

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Reactivity of the Monodentate Dithiocarbamate Ligand in $CpFe(CO)_2(\eta^1\text{-}SC(S)NR_2)$

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The most convenient route to $CpFe(CO)_2(\eta^1\text{-}SC(S)NR_2)$ (**1**) is the reaction between $CpFe(CO)_3{}^+PF_6{}^-$ (**2**) and Na^+dtc^- in acetone. Chelation of **1**, which proceeds in very low yield thermally, is induced by PPh_3 + CS_2, $Mo(CO)_6$, or Cp_2TiCl_2. Reaction of **1** with $NO^+PF_6{}^-$ leads to replacement of both carbonyls in **1** by NO^+ together with chelation of the dtc ligand, giving $[CpFe(NO)(\eta^2\text{-dtc})]^+PF_6{}^-$ (**3**). Transmetalation of the dtc ligand in **1** is obtained upon heating with $Fe_2(CO)_9$ or $[CpMo(CO)_3]_2$, giving the known complexes $Fe(CO)_2(\eta^2\text{-dtc})_2$ (**4**) and $CpMo(CO)_2(\eta^2\text{-dtc})$ (**5**), respectively. Reaction of **1** with KCN in methanol gives the new anionic metallacycle $K^+[CpFe(CO)(SC(NR_2)(SCN))]^-$ (**6**), which can be acylated by PhCOCl to give $CpFe(CO)(SC(NR_2)SCNCOPh)$ (**7**). The reaction of **1** with electrophiles gives different products depending on whether the counteranion of the electrophilic reagent is a potential ligand: the action of CH_3I leads to $CpFe(CO)_2I$ and $MeSC(S)NMe_2$ whereas that of $Me_3O^+BF_4{}^-$ gives $[CpFe(CO)_2(\eta^1\text{-}SC(SMe)(NMe_2))]^+BF_4{}^-$ (**8**). This reaction also demonstrates the nucleophilic properties of the uncoordinated sulfur atom in a monodentate dtc complex.

Dithiocarbamate complexes (dtc = dimethyl- or diethyldithiocarbamate) are one of the most extensively used and studied families in inorganic chemistry, and their various aspects have been thoroughly reviewed.[2] However, it is