Acknowledgment. I wish to acknowledge the assistance of Professor O. Knop and Dr. W. J. Westerhaus for providing the samples and Professor R. J. Boyd for several useful discussions.

Registry No. $NaBPh_4$, 143-66-8; $KBPh_4$, 3244-41-5; $RbBPh_4$, 5971-93-7; $CsBPh_4$, 3087-82-9; NH_4BPh_4, 14637-34-4.

Contribution from the Materials Science Center and the
Department of Chemistry, Cornell University,
Ithaca, New York 14853

Electrochemistry in Liquid Sulfur Dioxide. A New Synthesis of Hg_3AsF_6 and Hg_3SbF_6

George E. Whitwell II, Douglas C. Miller,
and James M. Burlitch*

Received March 19, 1981

In a shared domain of chemistry and physics, low-dimensional synthetic metals such as TTF·TCNQ, Hg_3MF_6 (M = As, Sb), and $K_{1.75}Pt(CN)_4$ (KCP) have received considerable attention recently.[1-4] Redox-based synthetic procedures have generally been chemical in nature[5] although KCP has been prepared electrochemically;[6] an electrochemical preparation of a series of synthetic metals formed between an aromatic hydrocarbon (e.g., naphthalene, fluoroanthene, perylene) and a complex anion (MF_6; M = P, As, Sb, Bi) was recently reported,[7] and polyacetylene has been doped with AsF_6^- by an electrochemical method.[8] Although MF_6^- species are known for elements from many regions of the periodic chart,[9,10] further examples of mercury-chain compounds have not been forthcoming. With the goal of producing new mercury-chain compounds, we chose to employ the selectivity of electrochemical oxidation and hoped also to avoid the frequently intractable byproducts found in chemical preparations (e.g., SbF_3). We now report the synthesis of Hg_3AsF_6 and Hg_3SbF_6 at a mercury anode in liquid SO_2 solutions of the hexafluorometalates. Previous methods involve oxidation of Hg metal in liquid SO_2 by AsF_5 (or SbF_5) or $Hg_3(AsF_6)_2$ (or $Hg_3(Sb_2F_{11})_2$).[11,12] Another series of inorganic/organometallic mercury compounds, $Hg(M)_2$ (M = $Mn(CO)_5$, $Re(CO)_5$, $Fe(C_5H_5)(CO)_2$, or $Mo(C_5H_5)(CO)_3$) have also been prepared electrochemically.[13,14] The chemistry[15] and electrochemistry[16] of SO_2 solutions have been reviewed[17] and some recent voltammetric studies of $(CH_3)_4N^+$[18] and $(C_6H_5)_3C^+$[19] solutions indicate that trityl salts may have particular utility as electrolytes in SO_2.

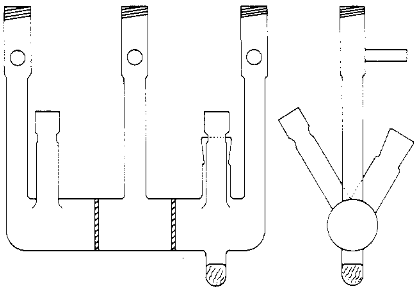

Figure 1. Front and end views of the electrochemical cell.

Experimental Section

Materials. SO_2 (Matheson) was drawn from the cylinder as a liquid and distilled from P_2O_5 under argon. Triple-distilled mercury (Merck) was used as received. $(CH_3)_4NAsF_6$ was prepared from $(CH_3)_4NOH$ (Aldrich) and $HAsF_6{\cdot}6H_2O$ (Ozark-Mahoning) in methanol and purified by a literature method.[20] $(C_6H_5)_3CSbF_6{\cdot}BF_3$ was prepared in situ from SbF_5 (Alfa) and $(C_6H_5)_3CBF_4$ (Alfa). $(CH_3)_4NPF_6$ was prepared by a method analogous to that for $(CH_3)_4NAsF_6$. $(CH_3)_4NMoF_6$ was prepared from $(CH_3)_4NI$ (Eastman) and MoF_6 (Pfaltz & Bauer) in SO_2 after the method of Hargreaves and Peacock;[21] the white solid was dissolved in SO_2 to afford a clear colorless solution which, upon saturation with BF_3, turned yellow. Except for the preparation and purification of $(CH_3)_4NAsF_6$ and $(CH_3)_4NPF_6$ (which are not hydrolyzed), all manipulations were performed in flame-dried glassware under purified argon atmospheres.[22] A PAR Model 173 potentiostat supplied the constant potential. Current was monitored with a Hewlett-Packard Model 7128A strip chart recorder.

The Cell (Figure 1). The electrolysis cell employed in these reactions consisted of a horizontal 140-mm (25-mm o.d.) Pyrex tube divided into three chambers (50, 40, and 50 mm) by two 20-mm sintered glass frits (M porosity). Three 75-mm stems (10-mm o.d.) emerged vertically from the top (one from each end, one from the center) and were capped by Rotaflo TF2/18 (0-8 mm) Teflon stopcocks, from which parallel 20-mm stems (7-mm o.d.) extended to the rear. The anode chamber had a 12-mm i.d. × 20-mm deep well and also two 10-mm o.d. necks 50 mm long tilting 30° from vertical (one forward, one back) which terminated with O-ring adapters. The cathode chamber had one similar tube tilting forward. The three 7-mm stems were connected by short pieces of butyl tubing to a yoke possessing a male 10/30 ₸ joint. Its mate had a glass-to-metal seal which was connected by Swagelock fitting to $^1/_4$-in. copper tubing leading to a T-bore stopcock atop a 90-cm capillary tube Hg bubble/manometer. The third stopcock arm was connected via butyl tubing to the argon/vacuum manifold.[22]

The working electrode consisted of 20 g of Hg in the well into which was immersed a glass-sealed platinum-wire electrode. The Ag/AgCl reference electrode was a coiled 0.020-in. Ag wire shielded in a 7-mm glass tube plugged with glass wool and possessing a small vent 2 cm from the end. The wire was oxidized by a $1^1/_2$ V dry cell in 1 M HCl for 1 min. The wire was sealed at the external end in a 5-10 mm thick epoxy plug (Torr-seal). The counterelectrode was a 5 mm × 20 mm × 0.025 mm Pt foil welded to a glass sealed 0.030-in. Pt wire. All three electrodes were sealed with Viton O-rings.

Electrochemical Syntheses. The electrolysis cell was set up as described above and carefully vacuum tested (<0.003 T) and then flamed dry. The stopcocks were replaced by septa under argon flush,

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and a CCl_4 dry ice (chunks) slush bath (−23 °C) was raised to immerse the horizontal section. The three-way stopcock was set to isolate the system from the no-air line while maintaining connection with the bubble/manometer.

A 100-mL modified Schlenk tube (MST) equipped with a magnetic stir bar was charged with $(CH_3)_4NAsF_6$ (3.5 g, 13.3 mmol). Under positive argon flow, the tube was attached to the SO_2 still, and 75 mL was collected with a dry ice/methanol slush. The Dewar was removed and the MST detached from the still and fitted with a septum. A mercury-filled bubbler was attached via a needle for venting, and the mixture was stirred to produce a clear, colorless solution which was allowed to warm to its boiling point. The bubbler needle was then removed and replaced by a $^1/_{16}$-in. o.d. stainless-steel cannula, which was purged with SO_2 vapors and then used to transfer the solution into the cell, filling each chamber in turn. The current varied positively with voltage, and the Hg pool was polarized at +1.300 V relative to the Ag/AgCl reference electrode. The initial current was 17 mA and dropped to 10 mA over the first 10 min. In $^1/_2$ h, the counterelectrode chamber solution was deep red (SO_2 reduction product) and the working chamber solution was yellow (Hg_3^{2+}) with a 2 mm deep red layer (Hg_4^{2+}) on the Hg surface. After 2 h (~60 C), the current fluctuated up and down, while golden crystals began to form on the Hg surface and the red color above it began to disappear. The completion of that process required about 20 min and the current steadied at 8 mA with the Hg surface completely covered by golden crystals. After $3^3/_4$ h the electrolysis was stopped (total charge passed 123 C). The counterelectrode chamber was first emptied by means of a cannula and then with a second cannula rinsed with fresh SO_2 (2 × 10 mL) and left empty. Next, the middle chamber was emptied and rinsed (2 × 10 mL). Finally, the working chamber was emptied and rinsed until the rinsings were colorless. The cooling bath was lowered to allow the residual SO_2 to evaporate through the bubbler. The septa were individually replaced by the Teflon stopcocks (argon flush) and the cell briefly and cautiously evacuated before closure for removal to the drybox (Vacuum Atmosphere Corp.). The total yield of bright golden crystals was 0.93 g or 92% on the basis of 1 mol of Hg_3AsF_6/faraday. The presence of Hg in solution was confirmed by precipitation of Hg upon addition of the SO_2 solution to aqueous NH_4OH and ice. Characterization of the product was by direct comparison of Ni-filtered Cu X-ray powder pattern with that of an authentic sample.[11] The powder diffraction data has been submitted to the Powder Diffraction File.

In another experiment, the Hg pool was first seeded with three 10-mg pieces of Hg_3AsF_6. In this case, the current passage remained steady throughout and the production of golden solid was similarly steady. The solution was yellow with some red at the surface in this case as well. The yield, however, dropped to 55%. Electrolyses in $(CH_3)_4NPF_6$ were also performed, with and without seeds, but no solid material was produced. The solution became yellow and deep red at the Hg surface.

Discussion

The electrochemical synthesis of Hg_3AsF_6 is a convenient preparation of this material. Freedom from undesirable byproducts and the on–off control of electrolysis are particular advantages. While we did not attempt to produce large single crystals, it is to be expected that with a suitably constructed Hg electrode such crystals would be produced. The time of reaction is less than that required for previously published methods, which take several days to 1 week. On the other hand, the reaction setup is somewhat more complex and demanding.

Analogous syntheses of Hg_3SbF_6 were also performed, although $(CH_3)_4NSbF_6$ was found to be an unsuitable electrolyte, as the anion (presumably as a fluoride donor) decomposed the intended product and electrolyses with this salt gave small amounts of Hg_3SbF_6 with a large quantity of a flaky gray solid. $(CH_3)_4NSb_2F_{11}$ was effective except that as SbF_5 was released during electrolysis direct chemical reaction ensued and complicated the system. A substantial quantity of Hg_3SbF_6 formed on the frit in the working chamber, and the material in the well was contaminated by an insoluble grayish white material thought to be SbF_3. An alternative system of $(C_6H_5)_3CBF_4{\cdot}SbF_5$ was less complex, but the liberated BF_3 tended to attack O-rings, making it difficult to maintain an air-tight seal. Also in this system and in the $(C_6H_5)_3CAsF_6$ system, unidentified reduction byproducts caused difficulties during workup, frequently destroying the product. We anticipate, then, that with a suitable vessel, $(CH_3)_4NSbF_6{\cdot}BF_3$ would be the best electrolyte for the preparation of Hg_3SbF_6.

A similar electrolysis was performed in $(CH_3)_4NMoF_6{\cdot}BF_3$ solution. This reaction produced a substantial quanity of red and yellow solid in the working chamber and spongy red solid in the counterelectrode chamber as well. No golden or other metallic solid was evident and the products that did form were not isolated.

Comparison of the results for syntheses of Hg_3AsF_6 with and without added crystals of the product suggests that initial formation of the chain compound is a critical aspect. Apparently in the absence of the chain compound, the concentration of Hg_4^{2+} at the mercury surface must build to a considerable level before synproportionation occurs to form the chain compound. Evidence for the equilibrium

$$3Hg^0 + Hg_3^{2+} + 2AsF_6^- \rightleftharpoons 2Hg^0 + Hg_4^{2+} + 2AsF_6^- \rightleftharpoons 2Hg_3AsF_6$$

has been obtained in previous chemical syntheses; both Hg_3^{2+} and Hg_3AsF_6 were necessary for the isolation of $Hg_4(AsF_6)_2$,[23] and also the reaction of Hg and $Hg_3(AsF_6)_2$ to form Hg_3AsF_6[11] was incomplete. The equilibrium is manifested in our system in the transient red color in solution. The delayed formation of Hg_3AsF_6 is unusual for an electrochemical reaction, as the final oxidation state is apparently skipped at first and only reached by subsequent chemical reaction.

The failure to form a chain compound with PF_6^- is probably associated with the smaller size of the anion.[10] Thus MoF_6^- (which falls between AsF_6^- and SbF_6^- in size)[10] was chosen for the subsequent experiment. This system was complicated with byproduct precipitation, with the reactions taking a course other than the desired one. Direct reaction of MoF_6 with Hg produces only $Hg_2(MoF_6)_2$.[24]

Sulfur dioxide has not received much attention as a solvent for inorganic electrosynthesis although it has been employed for electrochemical organic preparations.[17] Our experience indicates that it should be useful in other systems requiring a nonreactive, aprotic solvent offering high solubility to a large range of compounds.

Acknowledgment. Financial support of this work by the Cornell University Materials Science Center is gratefully acknowledged.

Registry No. Hg_3AsF_6, 59539-90-1; Hg_3SbF_6, 59539-91-2; SO_2, 7446-09-5.

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Contribution from the Department of Chemistry,
University of California, Berkeley, California 94720

Reduction of Nitric Oxide by Tin(II)[1]

Dan E. Hendriksen* and Richard E. Powell[2]

Received August 17, 1981

We have reported earlier from this laboratory[3a] the kinetics of the very fast copper(I)-catalyzed reduction of nitric oxide

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* To whom correspondence should be addressed at Corporate Research, Exxon Research and Engineering Co., Linden, NJ 07036

0020-1669/82/1321-1693$01.25/0