Notes

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Synthesis and Properties of ClF_6BF_4

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Received January 11, 1983

The only ClF_6^+ salts presently known are ClF_6PtF_6,[1-3] ClF_6SbF_6, and ClF_6AsF_6.[4] To improve the energy content of ClF_6^+ salts, replacement of these relatively heavy nonenergetic MF_6^- (M = Pt, Sb, As) anions by a lighter one such as BF_4^- is desirable. Attempts in our laboratory failed to synthesize ClF_6BF_4 by direct methods such as those used for the preparation of ClF_6MF_6 salts.[4] Consequently, indirect methods were sought to exchange the anion in $ClF_6^+MF_6^-$ for BF_4^-. Using low-temperature metathetical techniques, previously developed for NF_4^+ salts,[5] we have successfully converted ClF_6AsF_6 to ClF_6BF_4.

Experimental Section

Materials and Apparatus. ClF_6AsF_6[4] and $CsBF_4$[6] were prepared by known methods. The HF (Matheson Co.) was dried by storage over BiF_5.[5] Volatile materials were handled in a Teflon–FEP stainless steel vacuum line that was well passivated with ClF_3 and treated with HF prior to use. Nonvolatile materials were handled in the dry-nitrogen atmosphere of a glovebox. The metathesis was carried out in a previously described double-U-tube filter apparatus.[7] The thermal decomposition of ClF_6BF_4 was studied in a previously described sapphire apparatus.[8]

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer that was calibrated by comparison with standard gas calibration points.[9,10] Gas spectra were recorded with a Teflon cell of 5-cm path length equipped with AgCl windows. Spectra of solids were recorded as dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Cary Model 83 spectrophotometer with use of the 4880-Å exciting line of an Ar-ion laser and a Claassen filter[11] for the elimination of plasma lines. Sealed glass or quartz tubes were used as sample containers.

Synthesis of ClF_6BF_4. A mixture of ClF_6AsF_6 (0.5175 mmol) and $CsBF_4$ (0.5171 mmol) was loaded into the double-U-tube metathesis apparatus in the drybox. Dry HF (42 mmol) was condensed at −196 °C into the apparatus on the vacuum line, and the mixture was warmed for 30 min to 25 °C with stirring. The apparatus was cooled to −78 °C and inverted, and the solid and liquid phases were separated by filtration assisted by 2 atm of dry N_2 gas. The material volatile at 25 °C was pumped off for 1.5 h and separated by fractional condensation through a series of traps kept at −112, −142, and −196 °C. It consisted of BF_3 (~0.08 mmol), ClF_5 (~0.08 mmol), and the bulk of the HF solvent. The filter cake (199.6 mg, weight calculated for 0.517 mmol of $CsAsF_6$ 166.5 mg) was shown by vibrational spectroscopy to consist of mainly $CsAsF_6$ containing small amounts of ClF_6^+ and BF_4^-. The filtrate residue (67.4 mg, weight calculated for 0.517 mmol of ClF_6BF_4 122.1 mg, corresponding to a 55% yield) was shown by vibrational spectroscopy to consist mainly of ClF_6BF_4 containing a small amount of AsF_6^- salts as impurities. The losses of ClF_6BF_4 can be attributed to hang-up of ClF_6BF_4 on the filter cake (27%) and some reduction of ClF_6BF_4 (16%).

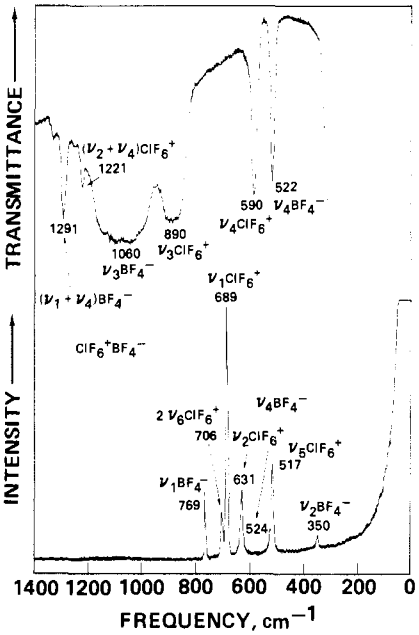

Figure 1. Infrared and Raman spectra of solid ClF_6BF_4 recorded at ambient temperature. The broken line in the infrared spectrum is due to absorption by the AgCl window material. The assignments for ClF_6^+ and BF_4^- are for point groups O_h and T_d, respectively.

Results and Discussion

Synthesis and Properties of ClF_6BF_4. The successful synthesis of ClF_6BF_4 according to

$$ClF_6AsF_6 + CsBF_4 \xrightarrow[-78\ °C]{\text{HF solution}} CsAsF_6\downarrow + ClF_6BF_4$$

demonstrates that the metathetical process previously developed for the indirect synthesis of NF_4^+ salts[5] is transferable to ClF_6^+ salts. The yield of only 55% for ClF_6BF_4 can be attributed to the following factors: (i) hang-up of some mother liquor on the filter cake; (ii) possibly, the use of an insufficient amount of solvent causing precipitation of some ClF_6BF_4; (iii) reduction of some ClF_6BF_4 to ClF_5 and BF_3 by attack of metal parts of the apparatus by this strongly oxidizing HF solution. No attempts have been made as yet to maximize the yield by varying or eliminating any of these conditions.

ClF_6BF_4 is a white crystalline solid that is highly soluble in anhydrous HF. It is stable at room temperature and starts to slowly decompose under a dynamic vacuum at about 70 °C according to

$$ClF_6BF_4 \rightarrow ClF_5 + F_2 + BF_3$$

The nature of the decomposition products was established by their infrared spectra, which showed only the absorptions characteristic for BF_3 and ClF_5. An exhaustive vacuum py-

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0020-1669/83/1322-1950$01.50/0

rolysis of ClF_6BF_4 was carried out at 110 °C and resulted in only a small amount of a solid residue, which was identified by Raman spectroscopy as $CsAsF_6$.

The presence of octahedral ClF_6^+ and tetrahedral BF_4^- ions in ClF_6BF_4 was established by infrared and Raman spectroscopy. The spectra together with the observed frequencies and assignments for ClF_6^+ and BF_4^- in point groups O_h and T_d, respectively, are shown in Figure 1. The spectra confirm our previous assignments for ClF_6AsF_6, where ν_1 of ClF_6^+ and ν_1 of AsF_6^- had almost identical frequencies and had to be assigned on the basis of their relative intensities.[4] The frequencies and assignments for BF_4^- in ClF_6BF_4 closely correspond to those in NF_4BF_4.[12]

Conclusion. The successful synthesis of ClF_6BF_4 and its relatively good thermal stability confirm the previous prediction of unusual stability for salts containing coordinatively saturated cations.[4] However, as expected, the thermal stability of ClF_6^+ salts is inferior to that of NF_4^+ salts.[8]

Acknowledgment. The authors are grateful to C. J. Schack, L. R. Grant, and R. D. Wilson for their help and to the Office of Naval Research and the Army Research Office for financial support.

Registry No. ClF_6BF_4, 85662-38-0.

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Direct Electrochemical Synthesis of Thorium Diiodide and Some Derivatives

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Received April 20, 1982

Thorium diiodide has been the subject of a number of preparative and structural investigations, prompted in part by the problem of the correct formulation of the compound.[1,2] The synthesis involves the reduction of thorium tetraiodide with thorium metal at elevated temperature (~800 °C), and the phase that is obtained is dependent in part on the thermal history.[2,3] It has been argued[2] that the structure should be written as $Th^{4+}(e)_2I_2$, in order to emphasize that this is not a simple Th^{2+} species. No addition compounds have been reported, but the oxy compound $ThOI_2$ is known; again, the preparation involves a protracted high-temperature (>750 °C) reaction between ThO_2 and ThI_4, followed by sublimation to remove impurities.[5]

As part of a general investigation of the direct synthesis of metal halides by the electrochemical oxidation of the metal in nonaqueous media,[6-10] we have now found that thorium diiodide can be easily prepared at room temperature. The oxidation of thorium into a solution of iodine in acetonitrile yields $ThI_2{\cdot}2CH_3CN$, which loses the neutral ligand on heating to give ThI_2. Complexes with bidentate nitrogen donor ligands have been obtained by similar methods. Attempts to prepare adducts with dimethyl sulfoxide were unsuccessful because of an oxygen-transfer reaction, which produces dimethyl sulfide and a quantitative yield of $ThOI_2$.

Experimental Section

General Procedures. Thorium (Alfa Inorganics) was cut in the form of disks, ca. 8 mm in diameter and 1 mm thick. Acetonitrile (BDH Ltd.) was dried over phosphorus pentoxide and distilled under nitrogen before use. The ligands 2,2′-bipyridine and 1,10-phenanthroline were dried for 3–4 h at 105 °C.

Thorium was determined by dissolving the compound before titrating the resultant solution at pH 2.1 against EDTA, with Alizarin S as indicator.[4] Halogen analysis was by the Volhard technique.

Infrared spectra, recorded as Nujol mulls on a Perkin-Elmer IR-18 instrument, served to confirm the presence of neutral ligands. The UV–visible spectrum was obtained with a Beckman ACTA MVI spectrophotometer.

Electrochemical Methods. The electrochemical syntheses followed methods described in earlier publications.[6-10] The solution phase, typically 50 mL in volume, was contained in a 100-mL tall-form beaker; the cathode was a platinum foil (1 × 1 cm) while a disk of thorium suspended on a platinum wire formed the anode. All preparations were carried out under an atmosphere of dry nitrogen.

Preparation of $ThI_2{\cdot}2CH_3CN$ and Related Adducts. The electrolysis of thorium metal (applied voltage 15 V, initial current 30 mA) into a solution of iodine (1.6 g) plus 15 mg of tetraethylammonium perchlorate in acetonitrile (40 mL) for 6 h resulted in the dissolution of 0.70 g of metal. The addition of diethyl ether (60 mL) to the final dark yellow solution resulted in the precipitation of yellow $ThI_2{\cdot}2CH_3CN$, which was collected, washed with more ether, and dried in vacuo at room temperature; yield 86%, based on thorium dissolved. Anal. Calcd for $ThI_2C_4H_6N_2$: Th, 40.9; I, 44.7. Found: Th, 40.3; I, 45.1.

The preparation of adducts of ThI_2 by direct synthesis met with mixed success. With 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), yellow 1:1 adducts were prepared by electrolyzing thorium into an acetonitrile (50 mL) solution of iodine (1.5 g) plus ligand. The products $ThI_2{\cdot}bpy$ (or $ThI_2{\cdot}phen$) are soluble in the reaction mixture, but were easily precipitated by the addition of diethyl ether; the precipitate was washed with ether and dried in vacuo; yield 90%, for both compounds. Anal. Calcd for $ThI_2C_{10}H_8N_2$: Th, 36.2; I, 39.5. Found: Th, 35.7; I, 38.2. Calcd for $ThI_2C_{12}H_6N_2$: Th, 34.8; I, 38.1. Found: Th, 34.2; I, 37.0.

Attempts to prepare adducts with Ph_3P, Ph_3PO, and Me_2SO gave products with inconsistent and unreasonable analyses; in the case of Me_2SO (see below) and possibly Ph_3PO, this must be due in part to the reaction between ThI_2 and ligand.

Thorium Diiodide. When a sample of $ThI_2{\cdot}2CH_3CN$ was heated at 90 °C for 3 h in vacuo, the weight loss corresponded to a 96 ± 2% loss of acetonitrile and the final yellow product was analyzed to be ThI_2. Anal. Calcd for ThI_2: Th, 47.8; I, 52.2. Found: Th, 46.9; I, 52.2. Acetonitrile driven off by heating was collected in $CDCl_3$ in vacuo; the ^1H NMR spectrum of the resultant solution consisted of a singlet at 2.0 ppm from Me_4Si.

Reaction of ThI_2 with Dimethyl Sulfoxide. In view of the problems noted above hindering the preparation of ThI_2/Me_2SO complexes, we investigated this system in some detail. A sample of Me_2SO (3 mL, 4.4 g, 57 mmol) was shaken with a suspension of ThI_2 (200 mg, 0.41 mmol) for 3 h at room temperature. At the end of this time, the recovered solid was shown to be $ThOI_2$, formed in quantitative yield (208 mg, 0.41 mmol). Anal. Calcd for $ThOI_2$: Th, 46.2; I, 50.6. Found: Th, 46.1; I, 50.4. The presence of dimethyl sulfide in the reaction mixture was suggested by the odor and confirmed by GLC (retention time identical with that of an authentic sample).

Discussion

The direct electrochemical room-temperature synthesis of $ThI_2{\cdot}2CH_3CN$ and the ready conversion of this into ThI_2 represent a simple and efficient synthetic route into the chemistry of thorium(II). The method appears to have many advantages over the high-temperature methods used previously,

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