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]

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Direct Electrochemical Synthesis of Thorium Diiodide and Some Derivatives

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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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a factor which has been emphasized in the electrochemical syntheses of other metal halides.[8,9,11] We have noted elsewhere that the electrochemical oxidation of metals favors the formation of compounds in which the metal is in a low oxidation state,[8,12,13] and such a situation obviously applies for the thorium/iodine system. An added advantage is that adducts of ThI_2 can be prepared in situ, and of course the uncomplexed compound is easily obtained by thermal decomposition of $ThI_2\cdot 2CH_3CN$.

The infrared spectrum of solid $ThI_2\cdot 2CH_3CN$ has two medium-intensity absorptions at 2270 and 2300 cm^{-1}, confirming the presence of acetonitrile; the reason for the presence of this doublet is not obvious at present. The UV–visible spectrum of $ThI_2\cdot 2CH_3CN$ in acetonitrile at 25 °C shows two strong absorptions at 285 and 325 nm (35 100 cm^{-1}, $\epsilon_{max} = 4.22 \times 10^3$, and 30 800 cm^{-1}, $\epsilon_{max} = 2.94 \times 10^3$).

Electrochemical Efficiency. As in previous work, we have measured the electrochemical yield (E_F), defined as moles of metal dissolved per faraday of electricity. Such experiments are typically carried out at a constant current of 20 mA over 2 h. For the CH_3CN/I_2 systems, we find $E_F = 0.48$ mol faraday^{-1}, implying the anode reaction

$$Th + 2I^- \rightarrow ThI_2 + 2e^- \qquad (1)$$

in keeping with the thorium(II) obtained from acetonitrile solution. This E_F value is equal within experimental error to that required for Faradaic behavior. It is worth noting that this result casts no light on the question of the structure and formulation of ThI_2, although the formation of adducts which are stable at room temperature establishes that the molecule is a Lewis acid. Any discussion of the electronic structure of thorium in these compounds is beyond the scope of the present paper.

Anionic Halogen Complexes. The electrochemical oxidation of a metal into a nonaqueous solution of $R_4NX + X_2$ represents a simple one-step route to the tetraalkylammonium salts of MX_n^{m-} anions.[14] We therefore investigated the oxidation of thorium into a solution of $(C_2H_5)_4NI$ and I_2 in acetonitrile. As the reaction proceeded, an insoluble material was precipitated. Analysis showed an unreasonably high iodine content, and after a number of similarly unsuccessful attempts, we concluded that anionic iodine complexes of thorium cannot be prepared by this method. A similar situation pertains for titanium, zirconium, and hafnium,[7] although anionic chloro and bromo complexes of these elements can be prepared electrochemically, as is the case for thorium(IV).[15]

Reaction of $ThI_2\cdot 2CH_3CN$ with Dimethyl Sulfoxide. As noted in the Experimental Section, the attempted preparation of a Me_2SO adduct of ThI_2 was foiled by the subsequently demonstrated reaction

$$ThI_2\cdot 2CH_3CN + (CH_3)_2SO \rightarrow ThOI_2 + (CH_3)_2S + 2CH_3CN$$

The use of low-oxidation-state metal halides (e.g., titanium(III) and vanadium(II)) to reduce organic compounds is well established, and it seems that thorium(II) can now be added to the list. More importantly, the reaction is a very convenient procedure, following electrochemical synthesis, to $ThOI_2$, otherwise only obtained by high-temperature reaction.

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Registry No. $ThI_2\cdot 2CH_3CN$, 85613-74-7; $ThI_2\cdot$bpy, 85613-75-8; $ThI_2\cdot$phen, 85613-76-9; ThI_2, 13779-95-3; $ThOI_2$, 13841-21-9; Th, 7440-29-1; $(CH_3)_2SO$, 67-68-5; $(CH_3)_2S$, 75-18-3.

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Inner-Sphere Coordination of Cl^- by Ni^{2+} As Determined by ^{35}Cl NMR

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Recently the inner- and outer-sphere coordination of Cl^- by Ni^{2+} in aqueous solutions has been studied by NMR, X-ray diffraction, neutron diffraction, Raman spectroscopy, optical spectroscopy, XAFS, and thermodynamic measurements. Values reported for $\bar{n}$, the average number of chloride ions in the inner sphere per nickel ion, range from near zero to 0.4 in a 1 M $NiCl_2$ solution. The problem of determining $\bar{n}$ is difficult because of its small value and the difficulty of interpretation of data due to the indirect nature of some of the methods used. We have attempted to determine $\bar{n}$ by measuring the area of the ^{35}Cl NMR signal since this is a direct method that essentially requires no detailed theory for interpretation. It is based on the fact that in the slow-exchange region the NMR signal arises from free Cl^- only while that due to Cl^- in the inner sphere is unobservable due to shifting and broadening by the contact interaction and quadrupole interaction. Thus measurement of the area of the observed ^{35}Cl resonance will give the concentration of free Cl^- in the solution. The main disadvantages of the method are the need to make rather precise area measurements when $\bar{n}$ is small and the need to go to low temperatures in order to achieve slow exchange.

Experimental Section

The chloride salts were dried in an oven, cooled in a desiccator, weighed, transferred to volumetric flasks, and diluted to volume with deionized water. Aliquots of the chloride solutions were taken and titrated with $AgNO_3$ according to the Mohr method. There was good agreement between concentrations calculated from the weights and the value obtained from titration. In cases where a difference existed, it was assumed to be due to samples gaining water during weighing. The concentrations obtained from titration were used and were known to be better than 1%.

The NMR apparatus has been previously described.[1] Measurements of the ^{35}Cl resonance were made at 8.31 MHz with 10-kHz magnetic field modulation. The modulation frequency was raised from 5 kHz in order to assure no overlap of sidebands even though experiments showed this would not be a problem at the lower modulation frequency. Samples were placed in precision 12-mm NMR tubes and filled with identical volumes of solutions in order to have a constant filling factor. Spectra were taken at four or five rf amplitudes, which were measured with a linear rf voltmeter and fit with digitally computed Lorentzian dispersion curves to obtain the width and the amplitude of the resonance. The line shapes were accurately Lorentzian. Since a linear rf detection method was used, a number proportional to the number of nuclei at resonance was calculated by multiplying the width by the amplitude of the resonance and dividing by the rf amplitude. This number is referred to as the area of the resonance. An average of the areas measured at different rf levels was computed and generally had a standard deviation of about 1% except for the very broad lines.

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