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Preparation and Mechanism of Formation of Anhydrous Scandium(III) Chloride and Bromide

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During the past few years, interest in the chemistry of scandium has increased, with emphasis being placed on its coordination chemistry¹ and on phase studies of scandium halide-scandium systems.² For many studies, anhydrous scandium compounds, particularly the halides, are very desirable starting materials. Hydrated scandium(III) halides are readily formed by dissolving scandium oxide, Sc_2O_3 , in the corresponding acid and evaporating the resulting solution to dryness. However, with the exception of the fluoride, these compounds cannot be dehydrated by heating without hydrolysis taking place.

As part of our investigation into the coordination chemistry of scandium,^{3,4} a method for the synthesis of anhydrous halides using inexpensive materials and relatively simple apparatus was desirable. We now report procedures for the synthesis of anhydrous scandium(III) chloride and bromide from aqueous solution, starting from the oxide Sc_2O_3 .

Experimental Section

Reagents.—Scandium(III) oxide, Sc_2O_3 (99.9%), was purchased from Research Organic/Inorganic Corp. All other chemicals were of reagent grade or equivalent. Methanol was dried over molecular sieves, Type 5A.

Apparatus.—The quartz sublimator consisted of two portions, a lower flat-bottomed portion, 15 cm long \times 44 mm in diameter fitted with a 24/25 female joint, and an upper portion, 10 cm long \times 30 mm in diameter with a 24/25 male joint on one end and a high-vacuum stopcock joined through a graded seal at the other end. The sublimator containing the solid in the lower portion was connected through the stopcock to a vacuum pump and positioned vertically with the lower portion in a tube furnace. Temperatures were monitored by a thermocouple positioned at the base of the sublimator.

Anhydrous Scandium(III) Chloride.— Sc_2O_3 (1.0 g) was dissolved in 28 ml of 1:1 hydrochloric acid (19% HCl) by refluxing for at least 1 hr. The solution was allowed to cool to room temperature and 9.0 ml of concentrated (29%) ammonium hydroxide solution added with stirring. A clear solution with pH \approx 3 was obtained. The solution was transferred to a beaker which was placed on a hot plate, and the water was removed by boiling until a moist solid was obtained. The solid was dried under vacuum over P_2O_5 at room temperature overnight and then transferred to the sublimator. The remaining water was removed by heating under vacuum at 150° for 3 hr. A sealing tube containing a coarse fritted disk was inserted in the vacuum line. The temperature was then increased to 300°, maintained at this temperature for 4 hr, and then raised to 500° for 30 min. The ammonium chloride sublimed on the walls of the upper portion of the sublimator. Final heating at 850° resulted in sublimation of white crystals of anhydrous scandium(III) chloride onto the walls of the lower portion, yield 64%.

Anhydrous Scandium(III) Bromide.—The above procedure was used except that 1.0 g of Sc_2O_3 was dissolved in 19 ml of 48% hydrobromic acid, and 10.0 ml of concentrated ammonium hydroxide was added to the resulting cooled solution, yield 61%.

Cesium Hexachloroscandate(III).—Cesium chloride (1.68 g, 0.01 mol) was added with stirring to a filtered solution of 0.5 g (0.0033 mol) of scandium(III) chloride in 50 ml of anhydrous methanol. The clear solution obtained was concentrated under vacuum to approximately 10 ml before a crystalline product began to appear. This was removed by filtration, washed with anhydrous ether, and dried under vacuum over P_2O_5 at room temperature. *Anal.* Calcd for Cs_3ScCl_6 : Sc, 6.85. Found: Sc, 6.9.

Physical Measurements.—Infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer (4000–250 cm^{-1}) and on a Digilab FTS-16 Fourier transform spectrometer (400–80 cm^{-1}), using Nujol mulls; 1500 scans of the sample were usually sufficient to produce satisfactory spectra on the latter instrument.

Analyses.—Scandium was determined by ignition to the oxide Sc_2O_3 at 900°.

Results and Discussion

Dehydration of hydrated lanthanide halides has been used successfully in many cases to produce anhydrous species in high yield.⁵ The scandium(III) ion, however, is considerably smaller than any of the lanthanide ions and thus has a much greater tendency to hydrolyze, making it more difficult to obtain anhydrous halides of scandium.

When scandium(III) oxide, Sc_2O_3 , is dissolved in an excess of a hydrohalic acid (HCl, HBr, HI) and the resulting solution evaporated to dryness, the hydrated scandium(III) halide, $\text{ScX}_3 \cdot n\text{H}_2\text{O}$ (X = Cl, Br, I), is obtained. The infrared spectra of these compounds all exhibit a strong broad absorption band at 3200–3500 cm^{-1} assigned to $\nu(\text{O-H})$, a strong band at 1610–1620 cm^{-1} ($\delta(\text{H}_2\text{O})$), and a strong broad band in the region of 480 cm^{-1} . This last band is assigned to $\nu(\text{Sc-O})$ ^{4,6} indicating that the scandium ion is surrounded by coordinated water molecules, probably as $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$. No halogen-sensitive bands are observed in the spectra, signifying that coordination of the halide ions does not take place in these hydrated scandium halides. If these compounds are heated, either at atmospheric pressure or under vacuum, hydrolysis takes place and Sc_2O_3 is produced.

The presence of the coordinated water molecules in the hydrated scandium halides obviously facilitates the hydrolysis of the scandium ion. Thus, in order to prepare anhydrous scandium halides by a procedure involving the use of water as a solvent at some stage, the coordination of water molecules to the scandium(III) ion must be prevented.

When scandium oxide is dissolved in an excess of hydrohalic acid and ammonium hydroxide added to the resulting cooled solution to produce an ammonium halide to scandium halide ratio of 9:1, the final pH of the solution is approximately 3. Evaporation of these solutions to dryness on a hot plate, followed by further drying under vacuum over P_2O_5 at room temperature overnight, results in a white solid. The infrared spectra of the solids obtained for the three halides are listed in Table I. For the chloride and bromide products, three bands of medium intensity are observed between 400 and 650 cm^{-1} . These are assigned to librational

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(5) M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962).

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modes of lattice water.⁷ Bands assigned to $\nu(\text{OH})$ and $\delta(\text{H}_2\text{O})$ from the water are also present. The chloride product also exhibits a strong band at 310 cm^{-1} whereas the bromide product has a strong band at 280 cm^{-1} . This halogen-sensitive band and the lack of a strong broad absorption in the region of 480 cm^{-1} previously shown to be characteristic of $\nu(\text{Sc-O})$ suggests that in these products the scandium(III) ion is coordinated by halide ions and not by water molecules as in $\text{ScX}_3 \cdot n\text{H}_2\text{O}$. The positions of the halogen-sensitive bands are

TABLE I
INFRARED SPECTRA^a OF SOLIDS OBTAINED AFTER DRYING
AT ROOM TEMPERATURE

Chloride	Bromide	Iodide	Assignment
3800 m, br	3300 m, br	3500-3200 s	$\nu(\text{O-H})$ $\nu(\text{N-H})$ $\delta(\text{H}_2\text{O})$
1600 m	1600 m	1580 m	
580 } m	640 }		Lattice water
520 }	540 }		
420 }	460 }		
310 s	280 s	~480 s, br	$\nu(\text{Sc-O})$ $\nu(\text{Sc-X})$

^a Values in cm^{-1} . All spectra showed additional strong bands in the region of 200 cm^{-1} associated with the ammonium ions.

similar to those observed for $\nu(\text{Sc-Cl})$ ^{8,9} and $\nu(\text{Sc-Br})$,^{8,9} in compounds containing coordinated halide ions. For the iodide product, however, the spectrum does not possess any bands that may be assigned to $\nu(\text{Sc-I})$ but does show the strong broad absorption at 480 cm^{-1} . Thus, it is concluded that in this product coordination of water rather than iodide ion occurs.

When these products are heated under vacuum at 150° for 3 hr in the sublimator, the remaining water is removed. This is confirmed by comparison of the infrared spectra of the solids before and after heating (Tables I and II). It can also readily be seen that the

TABLE II
INFRARED SPECTRA^a OF PRODUCTS OBTAINED AFTER
HEATING AT 150° FOR 3 HR

Chloride	Bromide	Iodide	Assignment
3150 s	3150 s	3150 s	$\nu(\text{N-H})$
		400-500 s, br	$\nu(\text{Sc-O})$
310 s	280 s		$\nu(\text{Sc-X})$

^a Values in cm^{-1} . All spectra showed additional strong bands in the region of 200 cm^{-1} associated with the ammonium ion.

positions of the bands assigned to $\nu(\text{Sc-Cl})$ and $\nu(\text{Sc-Br})$ remain unchanged on dehydration. For the iodide, however, the very broad absorption between 400 and 500 cm^{-1} is identical with that observed for Sc_2O_3 . Thus it was concluded that hydrolysis had taken place for the iodide but not for the chloride or bromide. Further heating at 300° caused the ammonium halide to sublime onto the walls of the sublimator. In early experiments it was found that a large percentage of the anhydrous scandium(III) halide was lost during the sublimation of the ammonium halide. (Taylor and

Carter⁵ made a similar observation in their paper on the preparation of anhydrous lanthanide halides.) This loss became negligible when a sealing tube containing a coarse fritted disk was inserted in the vacuum line. Although no solid was collected on the disk, the cosublimation of the scandium halide with the ammonium halide was eliminated. Final heating at 850° resulted in white crystalline sublimes of anhydrous scandium(III) chloride and bromide in good yield. The infrared spectra of anhydrous ScCl_3 and ScBr_3 are identical with those reported by Greenwood and Tranter.⁸ Thus, when coordination of chloride and bromide ions occurs, rather than water molecules, hydrolysis of the scandium(III) ion is prevented.

It was found by a series of experiments that the optimum ammonium halide to scandium halide ratio necessary to prevent hydrolysis was 9 to 1. In view of this high ratio and the tendency of scandium(III) to be six-coordinate, the species present is probably the $[\text{ScX}_6]^{3-}$ ion ($\text{X}^- = \text{Cl}^-, \text{Br}^-$). For Cs_3ScCl_6 two strong absorption bands are observed in the far-infrared, one in the region of 310 cm^{-1} ($\nu(\text{Sc-Cl})$, F_{1u}) and the other in the region of $150-100\text{ cm}^{-1}$ ($\delta(\text{Cl-Sc-Cl})$, F_{1u}).¹⁰ The broadness of these bands suggests that they are probably composite in nature, indicating some deviation from O_h symmetry. The strong band observed in the chloride sample both after drying under vacuum at room temperature (Table I) and after complete removal of the water by heating (Table II) is in the same position as that assigned to $\nu(\text{Sc-Cl})$ in Cs_3ScCl_6 . Other bands in the region of 200 cm^{-1} are due to the ammonium ion, with $\delta(\text{Cl-Sc-Cl})$ being observed in a similar position to that in Cs_3ScCl_6 .

Although we were unable to isolate Cs_3ScBr_6 by a number of approaches, on the basis of the position of $\nu(\text{Sc-Cl})$ and simple mass considerations, the strong band at 280 cm^{-1} in the spectra of the bromide samples is assigned to $\nu(\text{Sc-Br})$ from the $[\text{ScBr}_6]^{3-}$ ion.

Conclusions

A simple procedure has been developed for the synthesis of anhydrous ScCl_3 and ScBr_3 , from aqueous media, hydrolysis of the scandium(III) ion being prevented by the formation of the $[\text{ScX}_6]^{3-}$ ion ($\text{X}^- = \text{Cl}^-, \text{Br}^-$) during the preparation. For the iodide, no evidence for the formation of a corresponding species was obtained, coordination of water occurring preferentially. On dehydration of the iodide sample, hydrolysis takes place and no ScI_3 is isolated. Presumably the scandium(III) ion is too small to accommodate six iodide ions whereas the lanthanide(III) ions, all of which are larger than the scandium(III) ion, are apparently able to, since anhydrous lanthanide iodides can be obtained by a similar procedure⁵ to that outlined above.

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