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Ytterbium Diiodide Hydrates

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Harry A. Eick
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# SYNTHESIS AND CHARACTERIZATION OF YTTERBIUM DIIODIDE HYDRATES

By

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION
OF YTTERBIUM DIIODIDE HYDRATES

By

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The previously unreported ytterbium diiodide hydrates, $YbI_2.H_2O$ and $YbI_2.2H_2O$ have been prepared. Both hydrates possess orthorhombic symmetry; Lattice parameters for $YbI_2.H_2O$ and $YbI_2.2H_2O$ are: a = 16.012(5) Å, b = 8.140(2) Å, c = 4.5079(9) Å ; and a = 13.025(5) Å, b = 10.455(5) Å, c = 4.507(3) Å, respectively.

The monohydrate $YbI_2.H_2O$ was prepared by a solvent procedure, and the dihydrate $YbI_2.2H_2O$ by a solid-vapor procedure. These hydrates have been characterized by powder X-ray diffraction, IR, NMR, and elemental and water analyses. The ytterbium diiodide hydrates are compared and contrasted with analogous alkaline earth and lanthanide dihalide hydrates.

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# CHAPTER ONE: INTRODUCTION

## A. Preparatory and Structural Background

Lanthanide elements form a number of hydrates which belong to diverse structure types. Some methods for the preparation of lanthanide halide hydrates have been reported in the literature and are discussed below. The chloride and bromide halide hydrates have been studied extensively.

### 1. Lanthanide trihalide hydrates

The general preparatory procedure for hydrated lanthanide trichlorides ($MCl_3 \cdot xH_2O$; M = lanthanide) is dissolution of the lanthanide oxides in concentrated hydrochloric acid with subsequent precipitation of the hydrate upon removal of the acid.

The thermal decomposition of $MCl_3 \cdot xH_2O$ (x = 6,7) has been investigated with Differential Thermal Analysis (DTA) by numerous workers [1-5]. Wendlandt found that the heavier lanthanide (from Eu to Lu) trichloride hexahydrates begin to lose water of hydration in a slow stream of air in the temperature range 65°C to 95°C [2]. He also found that as

the basicity of the cation decreases, i.e., as the cationic radii decrease in size, the possibility of forming intermediate hydrates increases. When the trichloride hexahydrate was heated at 360°C - 425°C in air, the metal oxidechloride, the quantity of which increased as the basicity of the cation decreased, was found to be the product.

Ashcroft and Mortimer studied the thermal decomposition of the trichloride hydrates $MCl_3 \cdot xH_2O$ using a Differential Scanning Calorimeter (DSC) [6]. Decompositions carried out in a nitrogen atmosphere at relatively low temperatures, around 280°C, gave the anhydrous trichloride as the final product. They found three intermediate hydrates (x = 3, 2, 1) for M = La, Ce, Pr, Nd, Eu, and Gd, and two (x = 4, 1) for M = Sm, Tb, Er, Tm, Yb, and Lu.

The trichloride hexahydrate structures have been characterized by single crystal X-ray diffraction. Graeber, et al. demonstrated that $MCl_3 \cdot 6H_2O$ phases were describable with monoclinic symmetry ,space group P2/n and two molecules in a cell [8], as shown in Table I. The structure contains the 8-coordinate complexes $[MCl_2(OH_2)_6]$ that one third of the chlorine atoms form no bonds with metal atom.

The $MCl_3 \cdot 7H_2O$ structure was determined by Brouty and Herpin [7]. They reported for this heptahydrate triclinic symmetry, space group P1, z = 2, and a cell that contains the 9-coordinate complex $[MCl_2(OH_2)_7]$.

Table I. Lattice parameters, space groups and colors of lanthanide hexahydrates.

| Compound | Color | Space Group | Lattice Parameters a(Å) | b(Å) | c(Å) | ß(°) | Ref. |
|---|---|---|---|---|---|---|---|
| $SmCl_3 \cdot 6H_2O$ | Yellow | P2/n | 9.67 | 6.55 | 7.96 | 93.67 | [8] |
| $EuCl_3 \cdot 6H_2O$ | Colorless | P2/n | 9.68 | 6.63 | 7.96 | 93.67 | [8] |
| $GdCl_3 \cdot 6H_2O$ | Colorless | P2/n | 9.64 | 6.53 | 7.93 | 93.67 | [8] |
| $TbCl_3 \cdot 6H_2O$ | Colorless | P2/n | 9.63 | 6.51 | 7.89 | 93.67 | [8] |
| $DyCl_3 \cdot 6H_2O$ | Yellow | P2/n | 9.61 | 6.49 | 7.87 | 93.67 | [8] |
| $HoCl_3 \cdot 6H_2O$ | H. Y. | P2/n | 9.58 | 6.47 | 7.84 | 93.67 | [8] |
| $ErCl_3 \cdot 6H_2O$ | L. P. | P2/n | 9.57 | 6.47 | 7.84 | 93.67 | [8] |
| $TmCl_3 \cdot 6H_2O$ | Green | P2/n | 9.55 | 6.45 | 7.82 | 93.67 | [8] |
| $NdBr_3 \cdot 6H_2O$ | Blue | P2/n | 10.073 | 6.785 | 8.212 | 93.52 | [10] |
| $GdBr_3 \cdot 6H_2O$ | White | P2/n | 10.014 | 6.753 | 8.149 | 93.43 | [10] |
| $TbBr_3 \cdot 6H_2O$ | White | P2/n | 10.000 | 6.744 | 8.139 | 93.35 | [10] |
| $DyBr_3 \cdot 6H_2O$ | White | P2/n | 9.969 | 6.733 | 8.102 | 93.30 | [10] |
| $HoBr_3 \cdot 6H_2O$ | P. Y. | P2/n | 9.937 | 6.717 | 8.085 | 93.32 | [10] |
| $ErBr_3 \cdot 6H_2O$ | Pink | P2/n | 9.925 | 6.700 | 8.073 | 93.33 | [10] |
| $TmBr_3 \cdot 6H_2O$ | White | P2/n | 9.920 | 6.698 | 8.056 | 93.44 | [10] |
| $YbBr_3 \cdot 6H_2O$ | White | P2/n | 9.920 | 6.693 | 8.046 | 93.43 | [10] |
| $LuBr_3 \cdot 6H_2O$ | White | P2/n | 9.902 | 6.678 | 8.024 | 93.42 | [10] |

H. Y.= Honey Yellow L. P.= Light Pink P. Y. = Pale Yellow

The synthesis procedure for the lanthanide tribromide hydrates is similar to that for the trichloride hydrates. Mayer and Zolotov indicated [9] that tribromide monohydrates could be obtained as an intermediate phase during thermal decomposition of tribromide hexahydrates in air. They hypothesized that the decomposition proceeds according to the steps detailed in (1):

$$MBr_3 \cdot 6H_2O \rightarrow MBr_3 \cdot H_2O \rightarrow MBr_3 \rightarrow MOBr \rightarrow M_2O_3 \qquad (1)$$

M = Pr, Nd, Sm and Eu

Monohydrates were not observed with the heavier lanthanide elements; the hexahydrates decomposed directly through the oxidebromide according to (2):

$$MBr_3 \cdot 6H_2O \rightarrow MBr_3 + MOBr \rightarrow MOBr \rightarrow M_2O_3 \qquad (2)$$

M = Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu

In addition, it is interesting to note that the U, Np, and Am tribromide hexahydrates were prepared as evidenced by the mass increase of the appropriate anhydrous tribromide upon exposure to oxygen-free water vapor in an inert atmosphere.

The structural properties of lanthanide tribromide hexahydrates were discussed by Brown, et al. [10]. All of the tribromide hexahydrates are isostructural with the trichloride hexahydrates; they exhibit monoclinic symmetry, space group P2/n, with two molecules per unit cell. The

space group, lattice parameters, and colors of these hexahydrates are summarized in Table I.

Due to the intrinsic chemical instability of triiodide hydrates to undergo spontaneous decomposition to oxideiodides and HI, it is difficult to prepare the lanthanide triiodide hydrates. As a consequence they are only characterized to a limited degree.

## 2. Lanthanide dihalide hydrates

Several lanthanide dihalide hydrates ($MX_2 \cdot xH_2O$, X = Cl, Br, I) have also been reported. Their lattice parameters and symmetries are summarized in Table II. Although $SmI_2 \cdot H_2O$ is reported in the table to be orthorhombic, lattice parameters could not be found.

Europium dichloride dihydrate was characterized by Hasse and Brauer [11]. They prepared $EuCl_2 \cdot 2H_2O$ from a solution of $Eu_2O_3$ in dilute hydrochloric acid by employing amalgamated zinc for reduction of $Eu^{3+}$ followed by precipitation with concentrated hydrochloric acid.

They found that $EuCl_2 \cdot 2H_2O$ belongs to the monoclinic crystal system, space group C2/c, with z = 4 (see Table II). It is obvious that the atomic arrangement of $EuCl_2 \cdot 2H_2O$ is nearly the same as that of $SrCl_2 \cdot 2H_2O$ which has square antiprismatic coordination for the metal ions. They described that coordination shell of the $Eu^{2+}$ ion as probably consisting of two hemispheres, one of four chlorine

atoms and the other of four water molecules arranged to form the coordination number of 8.

Haschke and Eick prepared the dihalide monohydrates, $MX_2 \cdot H_2O$, (M = Sm, Eu; X = Br, I) for samarium and europium by vapor phase hydration of the anhydrous phase [12-14]. Powder X-ray data showed that the $SmBr_2 \cdot H_2O$ phase was indexable on orthorhombic symmetry with systematic extinctions consistent with space group Pnma. They also discovered an intermediate hydrate, $EuBr_2 \cdot H_2O$, when an anhydrous $EuBr_2$ specimen hydrolyzed in a powder X-ray diffraction camera [13]. This hydrated dibromide phase was isostructural with $SrBr_2 \cdot H_2O$ (and presumably with $SmBr_2 \cdot H_2O$), and was indexable on orthorhombic symmetry, space group Pnma.

The diiodide monohydrates, $SmI_2 \cdot H_2O$ and $EuI_2 \cdot H_2O$, have been identified [14,15]. Wang investigated the hydration of $SmI_2$ [15]. A hydrated anhydrous $SmI_2$ specimen was obtained with water absorbed on silica gel serving as the hydrating reagent. The powder X-ray diffraction pattern showed this $SmI_2 \cdot H_2O$ phase to be indexable as $\beta$-$SmI_2$ which is orthorhomic and isomorphous with $EuI_2$.

$EuI_2 \cdot H_2O$ was obtained by hydration of anhydrous $EuI_2$ with atmospheric moisture when a specimen was not rigorously isolated from the atmosphere. This monohydrate phase showed orthorhombic symmetry and is isostructural with $BaCl_2 \cdot H_2O$, space group Pbnm.

## 3. Alkaline earth halide hydrates

Lattice parameters and symmetries of selected alkaline earth dihalide hydrates are summarized in Table III. Because of their similar size and like charge the divalent lanthanide halides behave similarly to the alkaline earth halides. The crystallographic data presented in Tables II and III show the presence of structural similarities between $MX_2 \cdot H_2O$ (M = Sr, Ba, X = Cl, Br, I) and $LnX_2 \cdot H_2O$ (Ln = Sm, Eu, X = Br, I).

Table II. Lattice parameters and symmetries of selected lanthanide dihalide hydrates

| Compound | Symmetry | Lattice Parameters | | | | Ref. |
|---|---|---|---|---|---|---|
| | | a(Å) | b(Å) | c(Å) | ß(°) | |
| $EuCl_2.H_2O$ | Orthorhombic | 10.86 | 8.80 | 4.16 | | [19] |
| $EuCl_2.2H_2O$ | Monoclinic | 11.66 | 6.40 | 6.69 | 105.37 | [11] |
| $SmBr_2.H_2O$ | Orthorhombic | 11.43 | 9.18 | 4.32 | | [12] |
| $EuBr_2.H_2O$ | Orthorhombic | 11.46 | 9.20 | 4.29 | | [13] |
| $SmI_2.H_2O$ | Orthorhombic | | | | | [15] |
| $EuI_2 \cdot H_2O$ | Orthorhombic | 12.37 | 9.67 | 4.48 | | [14] |

Table III. Lattice parameters and symmetries of selected alkaline earth halide hydrates

| Compound | Symmetry | Lattice Parameters | | | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | a(Å) | b(Å) | c(Å) | ß(°) | V(Å$^3$) | |
| $BaCl_2 \cdot H_2O$ | Orthorhombic | 11.094 | 4.500 | 9.054 | | 452.0 | [18] |
| $BaBr_2 \cdot H_2O$ | Orthorhombic | 11.643 | 4.604 | 9.438 | | 505.9 | [18] |
| $BaI_2 \cdot H_2O$ | Orthorhombic | 12.494 | 4.772 | 10.014 | | 597.1 | [18] |
| $SrCl_2 \cdot H_2O$ | Orthorhombic | 10.881 | 4.162 | 8.864 | | 401.4 | [18] |
| $SrBr_2 \cdot H_2O$ | Orthorhombic | 11.464 | 4.295 | 9.229 | | 454.4 | [18] |
| $SrI_2 \cdot H_2O$ | Orthorhombic | 12.474 | 4.495 | 9.741 | | 546.2 | [18] |
| $CaCl_2 \cdot 2H_2O$ | Orthorhombic | 5.893 | 7.469 | 12.070 | | 531.3 | [16] |
| $CaI_2 \cdot 4H_2O$ | Monoclinic | 6.825 | 7.846 | 9.637 | 110.47 | 509.1 | [17] |
| $CaI_2 \cdot 6.5H_2O$ | Monoclinic | 6.755 | 8.162 | 17.878 | 107.76 | 2426.8 | [17] |

## 4. Spectroscopic studies

### Infrared spectrocopy

In general, lattice water exhibits vibrational frequencies at 3550 - 3200 $cm^{-1}$ (antisymmetric and symmetric -OH stretching) and at 1630 - 1600 $cm^{-1}$ (HOH bending). Lattice water also shows "libration modes" in the low-frequency region because of rotational oscillations of the water molecule. These rotations are restricted by interactions with neighboring atoms [23].

Lutz and Christian studied by infrared spectroscopy the isotypic alkaline earth halide monohydrates, $MX_2 \cdot H_2O$, with M = Sr and Ba and X = Cl, Br, and I [22]. They found that the water molecules are asymmetrically bonded in the chloride and bromide hydrates and symmetrically bonded in the case of the iodide hydrates.

### NMR spectroscopy

Nuclear magnetic resonance spectroscopy has become a useful tool for the study of the atomic arrangement and the electron charge distributions in a given specimen.

It is a highly characteristic feature of NMR that spectral lines of liquids are much narrower than those of solids. This substantial difference in line broadness arises from the static anisotropic interactions present in solids. In liquid specimens these interactions are averaged by the isotropic motions of the nuclei.

A good example to illustrate this difference in line broadness is the $^1$H-NMR linewith of water and ice. The resonance line of ice has a width of the order of $10^5$ Hz whereas that of liquid water is but a few Hz [43].

Line broadness in solids results from magnetic dipolar and quadrupolar interactions and from chemical shift anisotropy. Due to the restricted molecular motions present in solids, but not in liquids, the anisotropic interactions are not averaged out in time. In powdered samples these interactions give rise to NMR line broadening. To overcome this problem the Magic Angle Sample Spinning (MASS) technique was developed by Andrew, et al. [37] in 1959. It is capable of partially suppressing the anisotropic broadening.

Numerous NMR hydrate studies have been reported since Pake's first study in 1948 of the proton resonance absorption lines of the hydrated crystal, $CaSO_4 \cdot 2H_2O$ [24]. Pake determined the distance between hydrogen nuclei in the water molecules of hydration and the orientation of the line connecting the proton pair in the water molecule. The analysis of broad proton NMR absorption curve of the powder $CaSO_4 \cdot 2H_2O$, was also described to show that structural information about the water molecule could be obtained.

# CHAPTER TWO: EXPERIMENTAL

## A. Chemicals

Chemicals used in the synthesis experiments described in this work are listed in Table IV.

Table IV. Chemicals used for syntheses

| Compound or Element | Purity | Manufacturer |
|---|---|---|
| Ytterbium metal | 99.99% | Research Chemicals. Phoenix, AZ |
| Mercury iodide | Analytical reagent grade | Mallinckrodt St.Louis, MO |
| Methyl alcohol | 99.8% Anhydrous GR | EM Science Cherry Hill, NJ |
| Acetone | Analytical reagent grade | J.T. Baker Chemical Co Phillpsburg, NJ |
| Dimethyl ether | Analytical reagent grade | Matheson |
| Diethyl ether | Analytical reagent grade | Mallinckrodt St.Louis, MO |
| Calcium hydride | 95% | EM Science Cherry Hill, NJ |
| Benzo-phenone | | Fisher Scientific Springfield, NJ |
| Nitric acid | ACS/reagent grade | EM Science Cherry Hill, NJ |
| Silver nitrate | 99.9% | Sargent-Welch Skokie, IL |
| Ferric ammonium sulfate | Analytical reagent grade | Mallincrodt St.Louis, MO |
| Ammonium thiocaynide | Cerfified ACS grade | Fisher Scientific Springfield, NJ |

## B. Synthesis Equipment

A high vacuum line which can be pumped to $10^{-7}$ - $10^{-5}$ Torr must be used for the synthesis of ytterbium diiodide monohydrate. The liquid-nitrogen-trapped vacuum line used in this work consisted of a mercury diffusion pump, a CENCO roughing pump, and an all glass manifold as described by Shriver [26].

All manipulations of reactants and products were carried out in a glove box. The argon atmosphere of this box was continuously recirculated and purged of water with molecular sieves and of oxygen with heated BASF catalyst.

## C. Synthesis procedures

### 1. Anhydrous ytterbium diiodide

Metal chips were cut from a block of ytterbium kept in the glove box. Weighed pieces of Yb chips and $HgI_2$ in the molar ratio of 1:8 were placed in the lower bulb of a two bulb Pyrex reaction vessel.

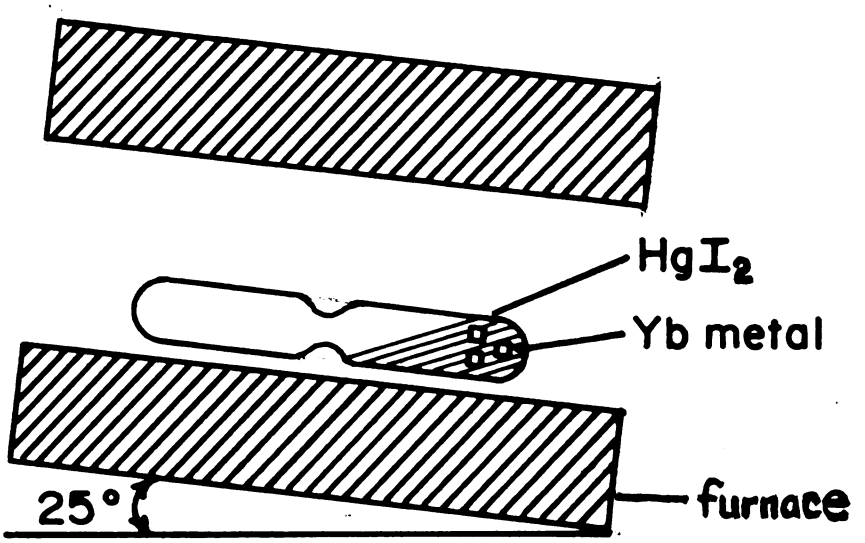
The Pyrex vessel was removed from the glove box, connected to the vacuum line, and evacuated to $10^{-3}$ Torr. The vessel was shaken gently to facilitate removal of trapped gases, sealed, and cut from the vacuum line at the end of second bulb with a hand torch.

The sealed Pyrex vessel was situated into a tubular

furnace for 7 days as is shown in Figure 1 and maintained at a temperature of 365$^{o}$C.

When mercuric iodide was removed from the reaction bulb by sublimation, the green anhydrous ytterbium diiodide remained. The absence of water was verified by infrared analysis.

Figure 1. Schematic representation of anhydrous ytterbium diiodide synthesis apparatus.



## 2. Ytterbium diiodide monohydrate

Ytterbium diiodide monohydrate was prepared in the apparatus shown in Figure 2. This H-shaped apparatus was cleaned before use in the following manner: It was first rinsed with an acid solution which contained 33% $HNO_3$, 5% HF, and 60% $H_2O$, then filled with aqua regia and allowed to sit overnight. The aqua regia was removed and the apparatus then rinsed with distilled water several times. It was then dried in an oven.

Ytterbium diiodide monohydrate synthesis experiments were attempted with three solvents: methyl alcohol, dimethyl ether, and acetone.

An elaborate purification procedure was developed for the solvent ultimately used. That procedure is described here.

About 75 ml of dimethyl ether was stirred for 24 h over 0.5 g of $CaH_2$ in a round flask situated in a dry ice bath to remove moisture, then distilled under high vacuum ($10^{-5}$ Torr), frozen with liquid nitrogen, and evacuated. It was necessary to repeat these stir-freeze-pump cycles several times, then distill the dimethyl ether into a pre-evacuated bottle which contained Na-K alloy (1:3) and benzophenone. When the color of the solution remained violet-blue, indicative of the absence of moisture, the ether was distilled into the H-shaped reaction vessel.

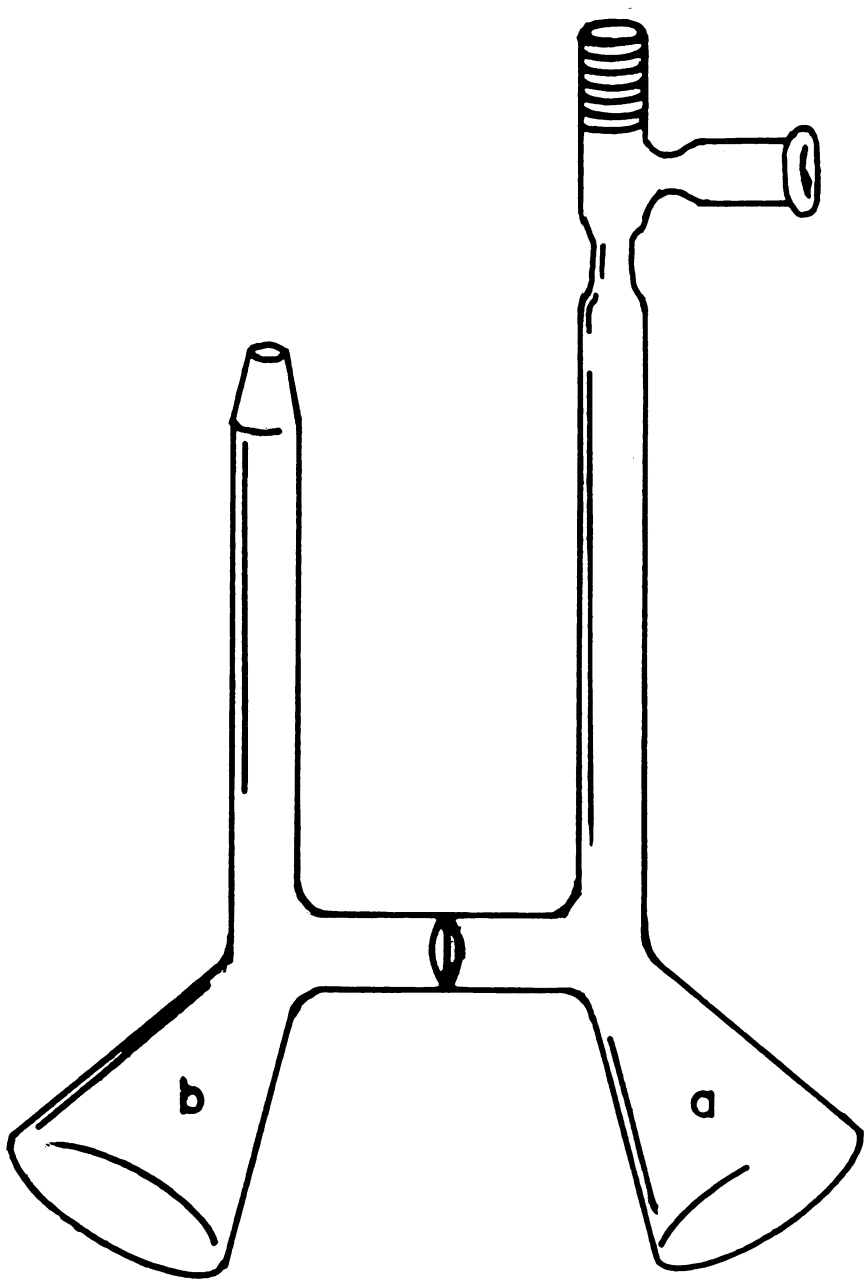
A weighed amount of powdered anhydrous ytterbium

diiodide was placed in chamber (a) [see Figure 2] through the Fisher-Porter stopcock. The same molar amount of water was purified by freeze and thaw cycles and distilled into a 5 mm o.d. glass ampoule which was then sealed. The sealed water ampoule was also introduced into chamber (a).

About 20 ml of purified dimethyl ether was then distilled into chamber (a) of the H-shaped reaction vessel which had been pre-evacuated to $10^{-6}$ Torr to dissolve the anhydrous ytterbium diiodide. The apparatus was removed from the vacuum line and kept at a temperature lower than the boiling point of dimethyl ether ($-25^{o}C$) in an isopropyl alcohol-dry ice bath ($-40^{o}C$).

The water ampoule was broken by several freeze-shake-thaw cycles. As the water reacted with the ytterbium diiodide, the color of the dimethyl ether solution changed from green to white. The solution was then filtered through the coarse frit in the H-vessel from chamber (a) into chamber (b). Finally, the white solution in chamber (b) was pumped to dryness by evacuating the H-vessel to $10^{-5}$ Torr on the high vacuum line. A bright greenish-yellow powder later demonstrated to be ytterbium diiodide monohydrate remained. Powder X-ray diffraction confirmed that the powder was a new phase.

Figure 2. Apparatus used for the synthesis of ytterbium diiodide monohydrate.



### 3. Ytterbium diiodide dihydrate

Ytterbium diiodide dihydrate was prepared by the hydration method described by Kwapisz [27]. A weighed amount of anhydrous ytterbium diiodide situated in a pyrolytic graphite boat was placed in a Pyrex tube in the glove box. The Pyrex tube was removed from the glove box, connected to the vacuum line, and evacuated. A quantity of cupric sulfate weighed according to equation (3) to give the appropriate molar ratio of water was inserted into a silica boat.

$$5YbI_2(s) + 2[CuSO_4 \cdot 5H_2O](s) \rightarrow 5[YbI_2 \cdot 2H_2O](s) + 2CuSO_4(s) \quad (3)$$

The tube was filled with argon, and as the gas flowed through the Pyrex tube, the silica boat was introduced. The tube was then evacuated to $10^{-3}$ Torr. During the hot weather in summer, the hydration reaction was conducted in a refrigerator ($4^{o}C$) over a period of 2 weeks.

As time passed, the color of the anhydrous ytterbium diiodide changed from green to dark green. The change of mass of each reagent indicated that anhydrous ytterbium diiodide was hydrated by the cupric sulfate, and that ytterbium diiodide dihydrate was produced. X-ray powder diffraction confirmed that the product was identical to that prepared by Kwapisz.

## C. Analysis

### 1. Ytterbium

Ytterbium metal content was determined by gravimetric procedures. A 6N $HNO_3$ solution was added to the sample confined in a platinum crucible to remove iodine, direct ignition at 950$^{o}$C produced the sesquioxide.

### 2. Iodine

The product was analyzed for iodine by the Volhald method [28] in acid medium. In this process an excess of standard silver nitrate was added to the solution and the excess $Ag^{+}$ was back-titrated with a standard potassium thiocyanate solution. A 40% ferricammonium sulfate solution served as indicator.

### 3. Water

Water analyses was conducted by Galbraith Laboratories, Inc., by the Karl Fisher water analysis method.

## D. Instruments

### 1. Powder X-ray Diffraction

The hydrated products were characterized by powder X-ray diffraction analysis. Interplanar d-spacings were determined with an evacuated Guinier camera (114.6 mm diameter) by using $CuK\alpha_1$ radiation ($\lambda\ \alpha_1$ = 1.54050 Å). Silicon powder ($\underline{a}$ = 5.43082(3) Å) was employed as an internal standard. Paraffin oil and Scotch$^R$ tape served to protect the silicon-sample mixture from further reaction with moisture.

For the anhydrous ytterbium diiodide specimens, powder X-ray diffraction was carried out with the sample confined in 0.3 mm o.d. sealed Lindemann glass capillaries.

### 2. Infrared

IR spectra were recorded with a BOMEM model DA3 Fourier-transform infrared spectrometer between 4000 $cm^{-1}$ and 800 $cm^{-1}$ at 3 $cm^{-1}$ resolution. The sample which was mixed with nujol and pressed between NaCl plates was maintained under vacuum during analysis.

### 3. NMR

NMR spectra were measured with the powdered sample in a sealed 5 mm o.d. NMR tube at 250 MHz on a Bruker WM-250

Spectrometer. The 16 step phase-cycled spin-echo [29] NMR procedure was used for removal of base line distortion due to ringing of the transmitter/probe circuits and dead time of the receiver. Two 90 degree pulses ($P_1$ = 9.5 and $P_2$ = 9.5 microsec), two delay times ($D_1$ = 50 and $D_2$ = 44 microsec) and recycle times (10 microsec) were used. Temperatures at which the measurements were taken varied in the range of $25^{o}C$ and $75^{o}C$.

# CHAPTER THREE: RESULTS

## A. Anhydrous ytterbium diiodide

The powder X-ray diffraction pattern of the anhydrous $YbI_2$ prepared by reaction with excess $HgI_2$ with Yb showed about 20 reflections which could be ascribed to a hexagonal cell with a = 4.504(3) Å and c = 6.970(5) Å.

Interplanar d-spacings and intensity values for anhydrous $YbI_2$ prepared in this study together with the values calculated by the program POWD12 [35] with the positional and thermal parameters reported for $CdI_2$ by Wyckoff [30] are given in Table V.

Table V. Observed and calculated interplanar d-spacings and intensities of anhydrous $YbI_2$

| h k l | $I_{obs}$* | $I_{calc}$ | $d_{obs}$(Å) | $d_{calc}$(Å) |
|---|---|---|---|---|
| 0 0 1 | M | 31.8 | 6.53 | 6.972 |
| 1 0 0 | VW | 1.9 | 4.037 | 3.900 |
| 0 0 2 | VW | 1.4 | 3.476 | 3.486 |
| 1 0 1 | VS | 100.0 | 3.343 | 3.404 |
| 1 0 2 | S | 59.0 | 2.597 | 2.599 |
| 1 1 0 | M | 40.0 | 2.228 | 2.252 |
| 1 1 1 | W | 12.1 | 2.138 | 2.143 |
| 1 0 3 | W | 24.2 | 1.997 | 1.996 |
| 2 0 1 | W | 20.2 | 1.878 | 1.877 |
| 2 0 2 | VW | 8.9 | 1.703 | 1.702 |
| 2 1 1 | W | 18.8 | 1.444 | 1.442 |
| 1 1 4 | VW | 18.2 | 1.379 | 1.378 |
| 3 0 0 | W | 7.5 | 1.301 | 1.300 |
| 2 0 4 | VW | 0.1 | 1.301 | 1.299 |
| 2 1 3 | VW | 0.1 | 1.247 | 1.245 |
| 2 2 0 | VW | 4.7 | 1.127 | 1.126 |
| 1 0 6 | VW | 2.3 | 1.110 | 1.114 |
| 2 2 1 | VW | 2.3 | 1.110 | 1.114 |
| 2 2 2 | W | | 1.069 | 1.111 |
| 3 1 1 | W | | 1.069 | 1.111 |

* VS, very strong; S, strong; M, medium; W; weak; VW, very weak.

B. Ytterbium diiodide monohydrate

It was indicated previously (Chapter two,sec 2.) that several synthesis attempts were made with methyl alcohol, acetone, and dimethyl ether. The results obtained with each solvent are presented here.

The green $YbI_2$ powder produced bubbles when it contacted the water-methanol solvent. As it reacted gas evolution persisted and a green solution resulted. When diethyl ether was added to the methyl alcohol solvent to precipitate $YbI_2 \cdot H_2O$, a yellow precipitate formed; its color changed to white.

When acetone was used as solvent, the $YbI_2$ dissolved readily at room temperature to form a dark violet solution. The violet color probably results from ionization of the iodide ion in the acetone solution and its subsequent complexation with acetone. When the acetone was removed under vacuum by heating about 20 minutes with a heat gun, the green powder appeared again. By powder X-ray diffraction it was verified that the green powder was anhydrous $YbI_2$.

In other experiments with the $YbI_2$-acetone solution the acetone solvent was removed slowly by inserting into liquid nitrogen the end of the chamber of the H-shaped vessel that did not contain the specimen. As the acetone was removed slowly, the violet color disappeared and the yellow powder again formed. Prof. Dr. Hodorowicz determined the water of hydration by DTA-TGA and demonstrated that the yellow powder

was $YbI_2 \cdot 10H_2O$. This DTA-TGA result shows that it is possible to form higher hydrates of divalent ytterbium iodide.

The powder X-ray pattern of $YbI_2 \cdot H_2O$ was characteristic of an orthorhombic cell with the lattice parameters; a = 16.012(5) Å, b = 8.140(2) Å, and c = 4.5080(9) Å. The interplanar d-spacings were indexed and the parameters refined by the programs ITO9 [33] or TREOR [34]. In Table VI the observed interplanar d-spacings and corresponding intensities and the calculated d-spacings of $YbI_2 \cdot H_2O$ are presented. Every reflection is indexed and the figure-of-merit is 29.0 [46]. Extinctions are consistent with space group $P2_12_12_1$ [40].

Table VI. Observed and calculated interplanar d-spacings and observed intensities of $YbI_2.H_2O$

| h k l | $I_{obs}$ | $d_{calc}$(Å) | $d_{exp}$(Å) |
|---|---|---|---|
| 2 0 0 | VS | 8.006 | 8.018 |
| 1 1 0 | VS | 7.256 | 7.247 |
| 2 1 0 | M | 5.708 | 5.722 |
| 3 1 0 | W | 4.463 | 4.474 |
| 0 2 0 | VW | 4.070 | 4.080 |
| 4 0 0 | VW | 4.003 | 4.007 |
| 0 1 1 | VW | 3.945 | 3.944 |
| 1 1 1 | W | 3.829 | 3.833 |
| 4 1 0 | M | 3.592 | 3.594 |
| 2 1 1 | VS | 3.537 | 3.535 |
| 3 2 0 | W | 3.236 | 3.238 |
| 3 1 1 | W | 3.172 | 3.173 |
| 0 2 1 | S | 3.021 | 3.021 |
| 4 0 1 | S | 2.993 | 2.993 |
| 1 2 1 | VW | 2.969 | 2.971 |
| 4 2 0 | S | 2.854 | 2.855 |
| 2 2 1 | S | 2.826 | 2.826 |
| 4 1 1 | M | 2.809 | 2.809 |
| 1 3 0 | VW | 2.675 | 2.675 |
| 3 2 1 | W | 2.629 | 2.631 |

The infrared spectrum of $YbI_2 \cdot H_2O$ was recorded to help characterize the environment of the water molecule. $YbI_2 \cdot H_2O$ exhibits the infrared spectrum shown in Figure 3. The principal features of this infrared spectrum are the bands between 1600 $cm^{-1}$ and 3600 $cm^{-1}$. Figure 3 shows bands at 3430 $cm^{-1}$ and 1610 $cm^{-1}$ which result from the O-H asymmetric stretching and HOH bending modes of the water molecule, respectively.

Solid-state powder static proton NMR spectra of $YbI_2 \cdot H_2O$ are shown in Figure 4. Spectra from 25°C and 75°C are compared, and the effects of temperature on the appearance of the NMR spectra are illustrated in Figure 4.

The results of the elemental and water analyses are tabulated in Table VIII.

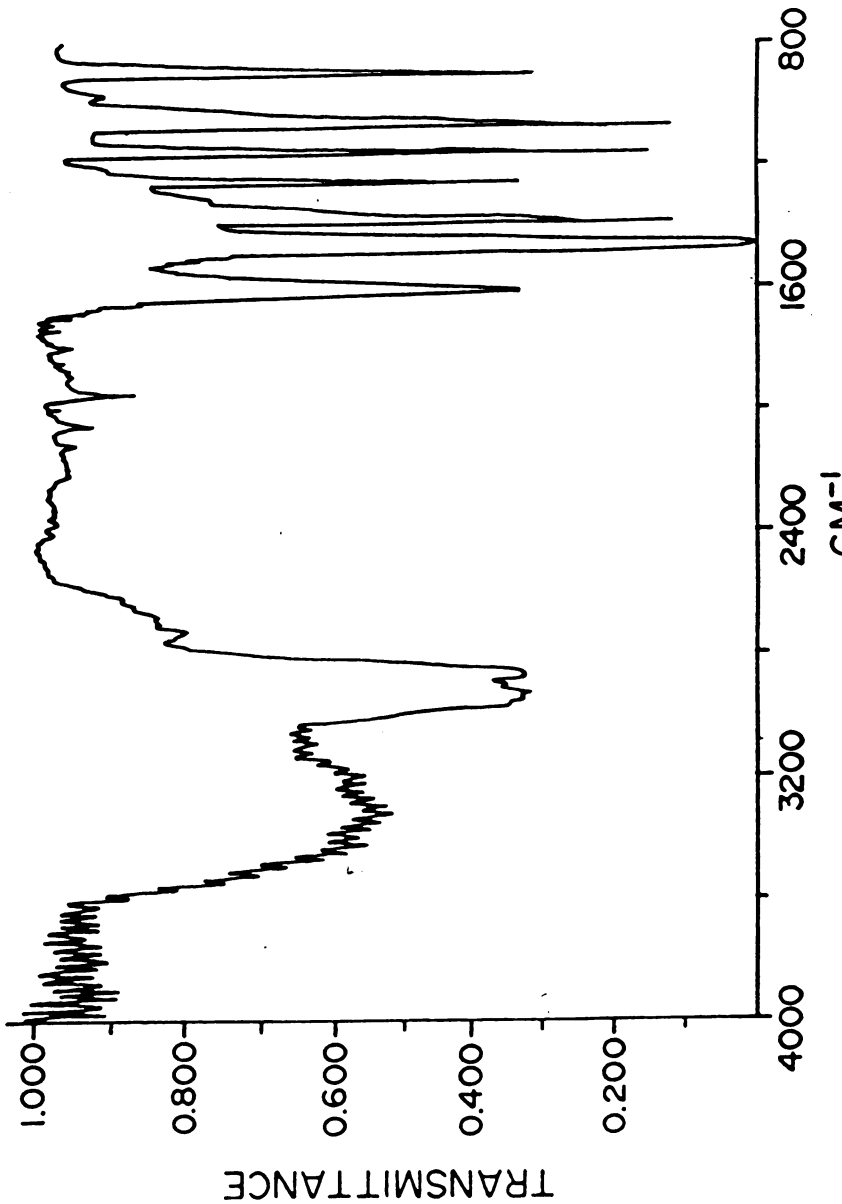
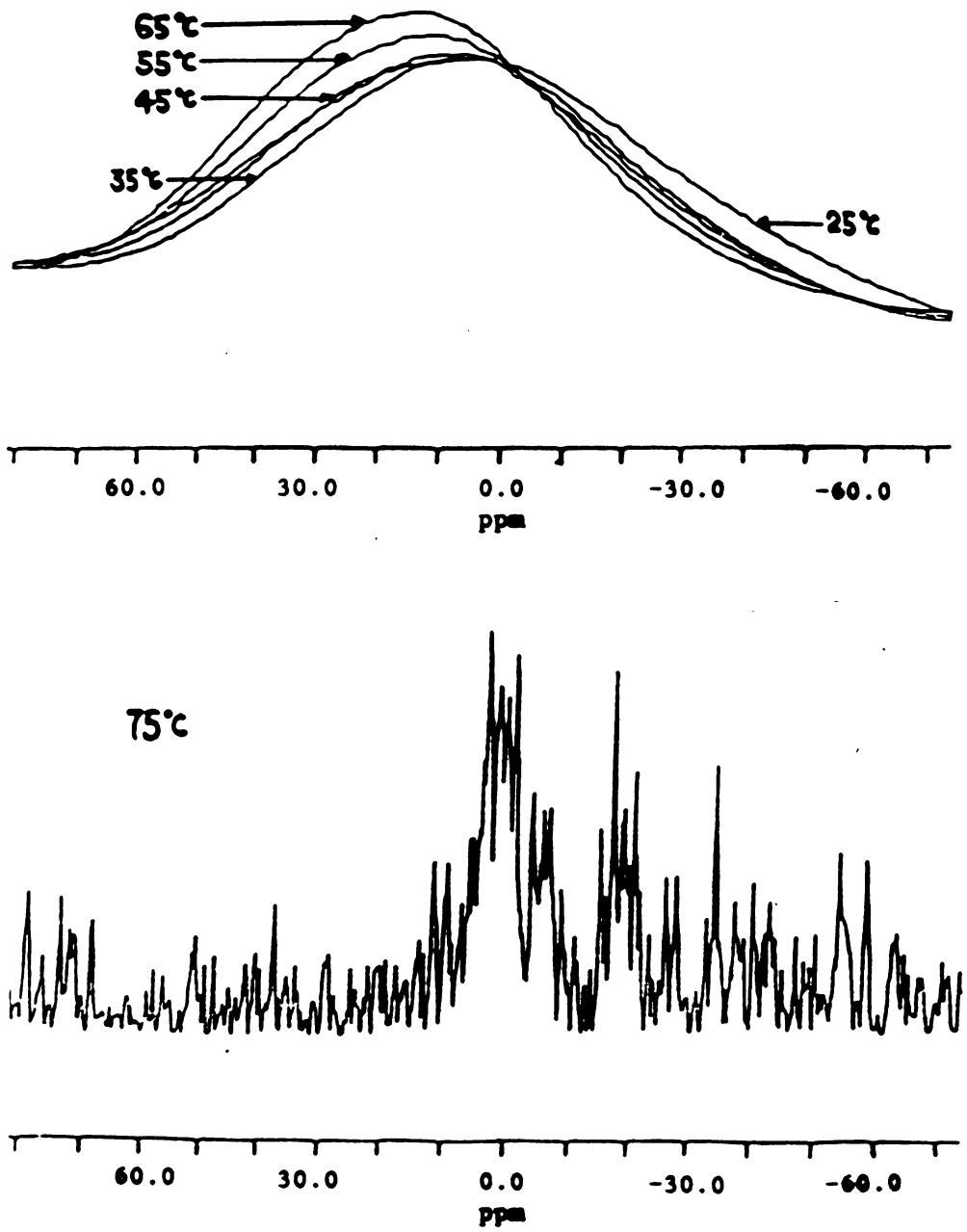



Figure 3. Infrared spectrum of $YbI_2.H_2O$.

Figure 4. NMR spectra of $YbI_2.H_2O$ at $25^oC$ -- $75^oC$.



C. Ytterbium diiodide dihydrate

Several attempts were made in summer months to prepare $YbI_2 \cdot 2H_2O$ with $CuSO_4 \cdot 5H_2O$ as the hydrating agents in anticipation that $YbI_2 \cdot 2H_2O$ would be the product. However, anhydrous $YbI_2$ formed a different hydrate at room temperature in the Pyrex reaction vessel. When the reaction was carried out for two weeks in the refrigerator ($4^oC$) in summer, the $YbI_2$ surface became dark green, but a yellow-colored solid had formed beneath it. X-ray powder diffraction showed the surface to be $YbI_2 \cdot 2H_2O$, with other unidentified compounds present in the lower part of the product. This inhomogeneous product apparently results from the differential absorption of water by the anhydrous $YbI_2$. As might be expected, $YbI_2 \cdot 2H_2O$ was produced on the surface with a lower hydrate beneath the surface.

According to the program ITO9 [33] the d-spacings of this dark-green colored hydrate are indexable on orthorhombic symmetry with a figure-of-merit of 22.9. The observed and calculated d-spacings and the observed intensity data for $YbI_2 \cdot 2H_2O$ are presented in Table VII. The lattice parameters were refined by program APPLEMAN [36]: a = 13.024(5) Å, b = 10.455(5) Å, and c = 4.507(3) Å.

Metal and iodine analysis data of the dihydrate are presented in Table VIII.

Table VII. Observed and calculated interplanar d-spacings and observed intensities of $YbI_2.2H_2O$

| h k l | $I_{obs}$ | $d_{calc}$(Å) | $d_{obs}$(Å) |
|---|---|---|---|
| 1 1 0 | S | 8.153 | 8.160 |
| 2 0 0 | S | 6.512 | 6.496 |
| 0 2 0 | VW | 5.228 | 5.228 |
| 1 2 0 | S | 4.851 | 4.846 |
| 2 2 0 | S | 4.077 | 4.075 |
| 3 1 0 | VW | 4.010 | 4.010 |
| 1 1 1 | VW | 3.945 | 3.948 |
| 0 3 0 | VS | 3.485 | 3.488 |
| 0 2 1 | W | 3.414 | 3.413 |
| 3 2 0 | M | 3.340 | 3.347 |
| 1 2 1 | M | 3.302 | 3.299 |
| 4 0 0 | VW | 3.256 | 3.255 |
| 2 2 1 | VS | 3.023 | 3.022 |
| 3 1 1 | W | 2.996 | 2.997 |
| 4 2 0 | VW | 2.764 | 2.766 |
| 3 3 0 | S | 2.718 | 2.718 |
| 1 3 1 | VW | 2.697 | 2.699 |
| 3 2 1 | S | 2.684 | 2.683 |
| 4 3 0 | VW | 2.397 | 2.383 |
| 4 2 1 | VW | 2.359 | 2.359 |

Table VIII. Elemental and water analysis results

| compound | | Yb(%) | I(%) | water(%) |
|---|---|---|---|---|
| $YbI_2 \cdot H_2O$ | cal. | 38.90 | 57.05 | 4.05 |
| | exp. | 38.95(4) | 58.85(7) | 4.05(29) |
| $YbI_2 \cdot 2H_2O$ | cal. | 37.38 | 54.83 | 7.78 |
| | exp. | 38.33(3) | 53.90(8) | |

# CHAPTER FOUR: DISCUSSION

## A. Synthesis

### Anhydrous ytterbium diiodide

Anhydrous $YbI_2$ was prepared by chemical reaction (4) in an excess of $HgI_2$.

$$Yb(s) + HgI_2(l) \longrightarrow YbI_2(s) + Hg(l) \qquad (4)$$

$Hg_2I_2$ was also a probable product. No effort was made to separate the Hg from either the excess of $HgI_2$ or from $Hg_2I_2$ that may have formed. The vapor pressure data of each reaction component as shown in Table IX substantiate that $HgI_2$ should be separable quantitatively by sublimation from $YbI_2$.

Oxidation of ytterbium by $HgI_2$ took place easily: ytterbium metal is a powerful reducing agent, ($Yb^{+3} + 3e^- \longrightarrow Yb$, $E^o = -2.27$ V ) ($Yb^{+3} + e^- \longrightarrow Yb^{+2}$, $E^o = -1.21$ V) This large reduction potential coupled with the large vapor pressure difference between Hg and $HgI_2$ and $YbI_2$ assured quantative reduction [47]

Table IX. Vapor pressure of selected compounds at various temperatures

| Compound | Vapor Pressure | | Temp. | Ref. |
|---|---|---|---|---|
| $CaSO_4 \cdot 2H_2O$ | 0.005 | mg/l | 25°C | [41] |
| $CuSO_4$ | 1.4 | mg/l | 25°C | [41] |
| $HgI_2$ | 100 | Torr | 262°C | [41] |
| Hg | 100 | Torr | 262°C | [41] |
| $YbI_2$ | $1.9 \times 10^{-16}$ | Torr | 260°C | [47] |
| | 2 | Torr | 790°C | |

Ytterbium diiodide monohydrate

Although methyl alcohol, ethyl alcohol, acetone, dimethyl ether, and diethyl ether were considered as solvents for the synthesis reaction, dimethyl ether proved to be the solvent of choice.

Methyl alcohol whose boiling point is 64.5°C was chosen initially for the preparation. It was thought that this solvent could be removed easily and that it would not react with $YbI_2$. However, with dimethyl ether as solvent significantly more pure $YbI_2 \cdot H_2O$ could be prepared than was obtained with either methyl alcohol or acetone. Accordingly, this solvent has proved to be the best found to date for the preparation of $YbI_2 \cdot H_2O$. The fact that dimethyl ether must be kept at a temperature below its boiling point, -25°C, somewhat complicates the synthesis procedure. From the IR spectrum it is clear that dimethyl ether did not form complex with $YbI_2$. Some of the problems encountered in this $YbI_2 \cdot H_2O$ synthesis procedure are decomposition of the solutions during synthesis because of impurities not removed or leakage in the high vacuum system, air sensitivity of the components, the length of time required for the synthesis procedure, and purification of the solvent.

However this method also has some advantages. The exceedingly high vapor pressure of dimethyl ether allows very easy solvent removal and its low dielectric constant tends to increase the $YbI_2 \cdot H_2O$ yield.

Ytterbium diiodide dihydrate

This preparation was attempted first via a solid-vapor procedure in a Pyrex reaction vessel by Kwapisz [27]. He prepared a ytterbium diiodide hydrate specimen which he thought was the monohydrate, but which was later demonstrated to be the dihydrate, $YbI_2 \cdot 2H_2O$.

Some of the problems encountered in this synthesis procedure were selection of a suitable hydrating agent, variable reaction time with respect to the environment, low thermodynamic stability of the product, and production of an inhomogeneous layered product.

Kwapisz prepared $YbI_2 \cdot 2H_2O$ according to equation (5).

$$5YbI_2(s) + 2[CuSO_4 \cdot 5H_2O](s) \rightarrow 5[YbI_2 \cdot 2H_2O](s) + 2CuSO_4(s) \quad (5)$$

He found that with $CuSO_4 \cdot 5H_2O$ as a hydrating agent one or two water molecules could readily be donated for this $YbI_2 \cdot 2H_2O$ synthesis. $CaSO_4 \cdot 2H_2O$ was initially used as a hydrating agent by Kwapisz, but with it the $YbI_2$ did not evidence any hydration whatsoever. Since the residual $H_2O$ vapor in dried air for $CaSO_4$ is 0.005 mg/liter and that for anhydrous $CuSO_4$ is 1.4 mg/liter [41], the absence of hydration with $CaSO_4 \cdot 2H_2O$ is readily understandable. The partial pressure of $H_2O$ in the reaction environment must be controlled carefully to avoid production of higher $YbI_2$ hydratesprior to completion of the desired hydration

reaction.

Several generalizations of $YbI_2 \cdot 2H_2O$ synthesis experiments made by the solid - vapor method indicate the following:

First, the formation of $YbI_2 \cdot 2H_2O$ was complete within 7 days at room temperature. Since the $H_2O$ tensimetric pressure of the hydrating agent is greater in summer than in winter, the hydration reaction proceeds more rapidly in summer than in winter.

Second, the vapor pressure of water required for hydration must either equal or be slightly less than that of $CuSO_4 \cdot 5H_2O$ since hydration can be achieved.

Third, $YbI_2 \cdot 2H_2O$ must possess greater thermodynamic stability than does the monohydrate since monohydrate was never observed in a product prepared by this procedure. However, this dihydrate may be metastable toward either further hydration or hemihydration.

B. Powder X-ray diffraction

Anhydrous ytterbium diiodide

The standard deviations of the parameters derived from the observed reflections by locally written programs were very small, typically less than ± 0.005 Å an indication that the parameters are well determined. This good fit is considered evidence that $YbI_2$ exhibits the hexagonal symmetry $CdI_2$-type structure. The $CdI_2$-type structure is the

only reported structural form for $YbI_2$. This structure consists of a layer-like atomic arrangement and exhibits in its physical properties the characteristics of layered compounds [38].

The $CdI_2$ layered structure in the crystal can be viewed as hexagonal close-packing of iodine ions with the small cadmium ions nested in the octahedral holes between every two layers of iodine ions. To maintain stoichiometry half of the octahedral holes must be vacant. These vacancies result in the two adjacent layers of iodine atoms being held together by van der Waal's forces.

According to Asprey and Kruse [38] $YbI_2$ does not exibit the polytypism so characteristic of the $CdI_2$-type structure. With the atomic positional and thermal parameters reported by Asprey and Kruse, the reflection intensities could be calculated by the program POWD12. The agreement between calculated and observed intensities for $YbI_2$ as shown in Table V substantiates that the metal ions occupy the 1a positions and the iodide ions the 2d positions in the space group.

Ytterbium diiodide monohydrate

The symmetry of $YbI_2 \cdot H_2O$ is the same as those of $SrCl_2 \cdot H_2O$, $MBr_2 \cdot H_2O$ (M = Sm, Eu,and Sr), and $EuI_2 \cdot H_2O$. The lattice parameters observed for the $YbI_2.H_2O$ are: a can be as big as by a factor of approximately 1.5 of the above related divalent halide monohydrates, and b and c are

consistent with those reported previously for the divalent halide monohydrates, as is illustrated in Table II and Table III.

The $YbI_2 \cdot H_2O$ unit cell volume of 587.63 $Å^3$ can be regarded as the summation of the volume of anhydrous $YbI_2$, 61.2 $Å^3$, and that of $H_2O$, 36.74 $Å^3$, derived from the structure of solid water [30]. This summation would imply that the cell contains six $YbI_2 \cdot H_2O$ moieties, or that z = 6.

It was thought initially that $EuI_2.H_2O$ structure (z=4) expected to be the structure type for $YbI_2.H_2O$ with Yb atom substituted for Eu atom. The lattice parameter a which is calculated from the hypothetical cell containing six $EuI_2.H_2O$ moieties is 18.05 Å. The $EuBr_2.H_2O$ structure (z = 4) was also considered. The lattice parameter a, 17.19 Å, is calculated from the hypothetical large cell containing six $EuBr_2.H_2O$ moieties. On the basis of these above calculations it is clear that the calculated lattice parameter a, 17.19 Å, from the $EuBr_2.H_2O$ structure is closer to the lattice parameter a, 16.012 Å, of the observed present investigation, $YbI_2.H_2O$. Thus it is suggested that the best structurral model for the $YbI_2.H_2O$ would entail, probably, $EuBr_2.H_2O$ with positional coordinates transformed to the large cell.

Numerous attempts were made to calculate a theoretical powder pattern for $YbI_2 \cdot H_2O$ by using positional parameters of related hydrates which have the same space group, $P2_12_12_1$, and reasonably similar values of z, with estimated

thermal parameters. For example, $CeOSO_4 \cdot H_2O$ and $TiOSO_4 \cdot H_2O$ were used as model structures. For these calculations the ytterbium atom was situated in the cation site, one X occupied the O atom site, and the second X occupied the S atom site. The water molecule occupied its established position. Lattice parameters for $YbI_2 \cdot H_2O$ were used for the calculation. None of the theoretical intensities matched the observed pattern. The CRYSTDAT data base was also searched for an appropriate structural model for $YbI_2 \cdot H_2O$; this search was not fruitful [42].

As was discussed earlier (Chapter one, sec 3) the lanthanide(II) and the alkaline earth halides form similar hydrates. Since the radius of $Ca^{2+}$ with coordination number 8 is 1.26 Å and that of $Yb^{2+}$ 1.28 Å [32], there should be structual similarities between $CaX_2$ and $LnX_2$ (Ln = Yb and adjacent elements, Tm and Lu; X= Cl, Br, I). Thus, their halide hydrates would be expected to show some similar structure types as is evident in Table X.

Table X. Comparison of the structure types of some lanthanide dihalide with those of alkaline earth halides

| M\X | Cl | Br | I | Ref. |
|---|---|---|---|---|
| Sm | $PbCl_2(9)^a$<br>$CaF_2(8)$ | $PbCl_2(9)^a$<br>$SrBr_2(8)$ | $m\text{-}EuI_2(7)^a$<br>$PbCl_2(7)$ | [3] |
| Eu | $PbCl_2(9)$<br>$CaF_2(8)$ | $SrBr_2(8)$<br>$PbCl_2(9)$ | $m\text{-}EuI_2(7)$<br>$PbCl_2(9)$ $SrI_2(7)$ | [39] |
| Tm | $SrI_2(7)$ | $SrI_2(7)$ $\alpha\text{-}PbO_2(6)$<br>$CaCl_2(6)$ $TiO_2(6)$ | $CdI_2(6)$ | [39] |
| Yb | $SrI_2(7)$ | $CaCl_2(6)$ | $CdI_2(6)$ | [39] |
| Ba | $PbCl_2(9)$<br>$Fe_2P(9)$<br>$CaF_2(8)$ | $PbCl_2(9)$ | $PbCl_2(9)$<br>$Fe_2P(9)$ | [39] |
| Sr | $PbCl_2(9)$<br>$CaF_2(8)$ | $PbCl_2(9)$<br>$SrBr_2(8)$ | $PbCl_2(9)$<br>$SrI_2(7)$ | [39] |
| Ca | $SrI_2(7)$<br>$CaCl_2(6)$<br>$\alpha\text{-}PbO_2(6)$ | $CaCl_2(6)$<br>$\alpha\text{-}PbO_2(6)$<br>$TiO_2(6)$ | $CdI_2(6)$ | [39] |

$(\ )^a$ = coordination number of the cation

Ytterbium diiodide dihydrate

The symmetry of $YbI_2 \cdot 2H_2O$, orthorhombic by the program ITO9, is the same as those of $SrCl_2 \cdot H_2O$, $MBr_2 \cdot H_2O$ (M = Sm, Eu, Sr). The unit cell volume of 613.81 $Å^3$ can be regarded as the summation of the volume of $YbI_2$, 61.2 $Å^3$, derived from the unit cell volume of anhydrous $YbI_2$, and that of $H_2O$, 35.8 $Å^3$, derived from the structure of solid water. When these volumes are compared to that of the dihydrate, it is apparent that the unit cell contains four $YbI_2 \cdot 2H_2O$ moieties, or that z = 4.

Several attempts were made to calculate theoretical X-ray powder diffraction patterns of $YbI_2 \cdot 2H_2O$ by using positional and thermal parameters of related hydrates which have the same space group, Pbnm. None of the theoretical intensities matched the observed pattern. The CRYSTDAT data base was also searched for an appropriate structural model for $YbI_2 \cdot 2H_2O$; this search was not successful.

## C. Infrared spectra

$YbI_2 \cdot H_2O$ exhibited the infrared spectra shown in Figure 3. The O-H stretching frequency of the water observed at 3325 $cm^{-1}$ is shifted to a lower wavenumber than that of free water because the rigidity of the crystalline lattice constrains the $H_2O$ molecule. This observation suggests that the hydroxy group is probably weakly hydrogen-bonded to the anion. However, if only weak hydrogen-anion bonds are

present, the shifting of the O-H stretching modes is more influenced by the nature of the metal ions than by the strength of hydrogen bridges [22]. In general, lattice water molecules are trapped in the crystalline lattice either by weak hydrogen-bonds to anions or by weak ionic bonds to the metal ions. On the basis of literature data, the structures of the iodide monohydrates are more symmetric with respect to the H-bonds than those of the bromide and chloride monohydrates. This behavior was predicted previously [22]. For example, iodide monohydrates possess $C_{2V}$ symmetry, whereas bromide and chloride monohydrates do not. From the appearance of two uncoupled O-H stretching modes, the water molecules in the latter two monohydrates are unsymmetrically bonded, with a symmetry lower than $C_{2V}$. These modes are also shifted to lower wavenumbers because the rigidity of the crystalline lattice constrains the $H_2O$ molecule.

Table XI. Comparison of IR absorption frequency of water with that in $YbI_2 \cdot H_2O$.

| Free $H_2O(cm^{-1})$ | Crystal $H_2O(cm^{-1})$ | Assignment |
|---|---|---|
| 3430 | 3435 | $\nu_{asym}$ stretch |
| 3325 | 3330 | $\nu_{sym}$ stretch |
| 1610 | 1620 | $\nu_{bend}$ |

D. NMR

In this work the available MASS-NMR instrument could not be used because of a malfunctioning contact and its relatively slow spinning speed (2-5 kHz). In order to achieve line narrowing of very wide homogeneous proton NMR lines, a very high spinning speed (about 20 kHz) is required. Also, if the line shape is Gaussian, the static NMR line width is directly related to the second moment, M, according to the Van Vleck equation (6):

$$M = 0.180 \left( \Delta\nu_{1/2} \right)^2 \qquad (6)$$

where $\Delta\nu_{1/2}$ is full width at half-height [44]. Therefore, the STATIC NMR technique had to be utilzed.

The line width and the second moment can be used to characterize the broad featureless absorptions obtained in solid-state proton NMR studies. The second moment, M, of nuclear spin, I, is the sum of M(hetero) and M(homo) as follows:

$$M(\text{hetero}) = (1/3)\gamma_I^2\gamma_S^2\hbar^2 S(S+1) \sum_{j,k}[(1-3\cos^2\theta_{j,k})^2/r_{j,k}^6] \qquad (7)$$

$$M(\text{homo}) = (3/4)\gamma_I^4\hbar^2 I(I+1) \sum_{j,k}[(1-3\cos^2\theta_{j,k})^2/r_{j,k}^6] \qquad (8)$$

where I and S are nuclear spins, $\gamma$ is the magnetogyric ratio of spin I or S, $\theta$ is the angle between the field direction and the internuclear vector, r, and $\hbar$ is $h/2\pi$ (h = Plank's

constant). Any rapid molecular motion will tend to partially average the dipolar interactions (i.e., the angular parts of the above equations), so that the second moment will appear to be decreased below its rigid lattice value. spin-spin relaxation time ($T_2$) will then increase. In particular, at the melting point or above the onset of molecular motion,thesecond moment drops to a relatively small value.

The hydrate spectra shown in figure 5 are markedly temperature - dependent. There is a large decrease in the second moment parameters at 75°C, an indication that water molecular motion is taking place. As the temperature is raised from 25°C, hindered rotational and vibrational motion of water molecules increases and free rotational motion of water probably occurs between 65°C and 75°C.

## E. Elemental and water analysis

### Ytterbium diiodide monohydrate

The standard deviation of duplicate Karl Fisher water analyses of $YbI_2 \cdot H_2O$ indicated that the average water content agreed well with the theoretical value. Elemental ytterbium and iodide analyses agreed with the expected formula, $YbI_2 \cdot H_2O$.

### Ytterbium diiodide dihydrate

Metal and iodine analyses indicate that the ytterbium

and iodine content exhibit good agreement with values calculated for a dihydrate. However, water analysis by the Karl Fisher method was inconsistent with that expected for a dihydrate product. It is presumed that the product became hydrated further either during analysis or transfer.

## SUGGESTIONS FOR FUTURE WORK

The single crystal of $YbI_2 \cdot H_2O$ should be prepared by the solvent procedure for a better understanding of the properties of hydrates by single crystal X-ray diffraction procedures. It is necessary that high quality crystal be used, therefore the crystallization techniques must be improved.

A thermal decomposition study of $YbI_2 \cdot H_2O$ by TGA-DTA is needed for qualitative identification. TGA-DTA has become a useful analytical tool that enables one to determine phase transitions of hydrates.

Solid-state NMR studies of $YbI_2 \cdot H_2O$ should be achieved by the Magic Angle Spinning technique to obtain structural information.

The $YbI_2 \cdot 2H_2O$, which was prepared by only the solid-vapor procedure, might be synthesized by the solvent procedure. By varing the water stoichiometry, various other hydration numbers might be determined and a phase diagram constructed.

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