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Preparation and Characterization of Ytterbium Diiodide Hydrates: $YbI_2 \cdot H_2O$ and $YbI_2 \cdot 2H_2O$

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The preparation of and X-ray powder diffraction data for the hydrates, $YbI_2 \cdot H_2O$ and $YbI_2 \cdot 2H_2O$, are reported. Orthorhombic lattice parameters for $YbI_2 \cdot H_2O$ are $a = 16.012(5)$, $b = 8.140(2)$, and $c = 4.5080(9)$ Å; those for $YbI_2 \cdot 2H_2O$ are $a = 13.037(3)$, $b = 10.467(2)$, and $c = 4.513(1)$ Å. Selected DTA–TGA and IR data are presented. These hydrates are contrasted with those of related lanthanoid(II) and alkaline earth halides.

Introduction

Even in the absence of literature reports of YbI_2 hydrates, it has long been assumed that upon exposure to the laboratory atmosphere YbI_2 would hydrate rapidly and subsequently decompose in a manner analogous to that of its lighter congeners and the alkaline earth halides (*1–7*). Thus, an uncharacterized X-ray powder diffraction pattern obtained from a YbI_2 specimen confined for an extended time under Ar in a vial capped with a paper-lined lid was assumed to be a hydrate. However, when its X-ray diffraction pattern was found to be indexable on orthorhombic symmetry with a cell larger than that of $EuI_2 \cdot H_2O$, it was apparent that this compound belonged to a different hydrate series (*3*). Since some of the X-ray reflections matched spurious reflections observed previously in YbI_2 specimens, the preparation and characterization of YbI_2 hydrates was undertaken. Data on two hydrates, $YbI_2 \cdot H_2O$ and $YbI_2 \cdot 2H_2O$, are reported herein.

Experimental

Preparatory Procedures

YbI_2. Ytterbium diiodide was prepared by reaction of Yb(s) with excess HgI_2 (*8*). Purity was verified by X-ray diffraction. All manipulations of anhydrous YbI_2 were performed in an argon-filled glove box whose atmosphere was continuously recirculated and purged of water (molecular sieves) and oxygen (heated BASF catalyst).

Hydration Procedures

YbI_2 hydrates. Two hydration procedures were utilized. In the first, which was utilized for dihydrate synthesis, YbI_2 and a hydrate, e.g., $CuSO_4 \cdot 5H_2O$, were confined in a closed Pyrex tube. In the glove box YbI_2 was weighed into a pyrolytic graphite boat and inserted into the tube. The capped tube was removed from the glove box and while Ar flowed over the specimen the hydrating agent was inserted. The tube was capped, evacuated quickly to ~10^{-1} Torr, backfilled with Ar to a pressure of ~300

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Torr, and set aside for 1 to 4 weeks. In some experiments the specimen was kept at ~5°C. When the mass of the YbI_2 specimen equaled or exceeded that expected for dihydrate formation, the product was examined by X-ray diffraction. If a higher hydrate was also present, the specimen was heated in a tube furnace under a 10^{-3} Torr vacuum at 70–80°C for 3 to 4 hr, then reexamined.

In the second procedure, which was used for monohydrate synthesis, hydration was effected in dimethylether (bp = −25°C) in an "H-vessel" modeled after one described elsewhere (*9*). This vessel consisted of two volumetric-like flasks whose necks were connected just above the flask with 12-mm glass tubing into which a coarse frit had been sealed. Standard taper joints allowed the necks of the H-vessel to be attached to a vacuum line or capped.

Approximately 75 ml of dimethylether (Matheson, anhydrous grade) was dried by condensing it with an isopropanol sludge bath into a thick-walled cylindrical glass tube fitted with a stopcock and a pressure gauge. The chilled ether was stirred with 0.4–0.5 g of CaH_2 for about 24 hr, then frozen with liquid nitrogen and evacuated to $<10^{-5}$ Torr. Stir–freeze–evacuate cycles were repeated several times until gas evolution ceased during the stirring cycle. The solvent was then distilled and stored over 1 : 3 Na–K alloy overnight.

A weighed quantity of degassed, frozen water sealed in an evacuated, easily fractured Pyrex ampoule was brought into the glove box. The mass of YbI_2 required by stoichiometry and the water ampoule were inserted into one side of the H-vessel which was subsequently evacuated to $<10^{-5}$ Torr. This side was immersed in liquid nitrogen and about 25 ml of $(CH_3)_2O$ was condensed into it. The anhydrous YbI_2 dispersed in the solvent—it did not appear to dissolve. The apparatus was then removed from the vacuum line and placed in a dry ice–isopropanol bath (−40°C), and the water ampoule was broken by vigorous shaking and freeze–thaw cycles. The solvent immediately became opaque (milky-colored). The mixture was poured through the coarse frit into the other side of the H-vessel to remove glass particles. After ~3 hr at −40°C the $(CH_3)_2O$ was distilled from the vessel. The bright greenish-yellow solid monohydrate remained.

Analysis

Reaction products were characterized by chemical, powder X-ray diffraction, and IR analysis. X-ray diffraction data were obtained in a 114.59-mm evacuated Guinier camera with monochromatized Cu$K\alpha_1$ ($\lambda\alpha$ = 1.54050 Å) radiation. NBS certified Si (a = 5.430821(3) Å) served as the internal standard. Samples of YbI_2 were covered first with Na-dried paraffin oil and then with Scotch tape to minimize hydration or hydrolysis during transfer to the camera. Observed interplanar d-spacings were indexed with either the program ITO9 or the program TREOR (*10, 11*).

The IR spectrum of the monohydrates was recorded with a Bomem Model DA3 FTIR spectrometer. The sample, mixed with Nujol and confined between NaCl plates, was blanketed with dry N_2 during analysis. The IR spectrum of the dihydrate was obtained on a Nicolet Model 740 FTIR instrument by the KBr pellet procedure. DTA–TGA data were collected on a Mettler thermoanalyzer under an Ar flow of ~4 liters hr^{-1} at a scan rate of 5°C min^{-1} with previously heated Al_2O_3 as reference.

Ytterbium content was determined gravimetrically by thermally decomposing weighed quantities of the hydrate specimens. Iodine content was determined by the Volhard (*12*) back-titration procedure. Water content was determined by Galbraith Laboratories, Inc., by Karl Fisher water analysis.

TABLE I

MILLER INDICES, OBSERVED AND CALCULATED INTERPLANAR *d*-SPACINGS, AND OBSERVED INTENSITIES FOR ORTHORHOMBIC $YbI_2 \cdot H_2O$

$h\ k\ l$	I_{obs}[a]	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
2 3 0	vw	2.570	2.570
5 1 1	m	2.486	2.485

[a] v, very; m, medium; s, strong; w, weak.

Results

YbI_2

Interplanar *d*-spacings and intensities of YbI_2 agreed well with those reported for hexagonal CdI_2-type YbI_2 (*13*). Spurious reflections observed on occasion corresponded to dihydrate reflections and probably formed during transfer of the specimen to the Guinier camera.

$YbI_2 \cdot H_2O$

This hydrate could be prepared only by the second $[(CH_3)_2O]$ procedure. All observed *d*-spacings were indexed by the program TREOR with a figure-of-merit of 29.0 to a cell of orthorhombic symmetry (*14*). Refined cell parameters are $a = 16.012(5)$, $b = 8.140(2)$, and $c = 4.5080(9)$ Å. Calculated and observed interplanar *d*-spacings, Miller indices, and observed intensities are presented in Table I. Extinctions are consistent with space group $P2_12_12_1$ (*15*). The IR spectrum is presented in Fig. 1.

Calcd for $YbI_2 \cdot H_2O$: Yb, 38.90; I, 57.05; H_2O, 4.05%. Found: Yb, 38.95; I, 58.85; H_2O, 4.05 ± 0.20%.

$YbI_2 \cdot 2H_2O$

Initial attempts to hydrate YbI_2 by the first procedure with $CaSO_4 \cdot 2H_2O$ were unsuccessful. With $CuSO_4 \cdot 5H_2O$ the dihydrate and $CuSO_4 \cdot {\sim}3H_2O$ resulted. For example, a 1.0811-g YbI_2 specimen increased in mass to 1.1681 g and appeared homogeneous, indicative of dihydrate formation. In many instances a homogeneous reaction product was not obtained; the product was layered with hydrate on the top and YbI_2 on the bottom. In other instances, particularly during summer, a higher hydrate formed. Impure hydrate also formed upon direct addition of water from a syringe to a specimen of YbI_2 confined in a septum-covered flask.

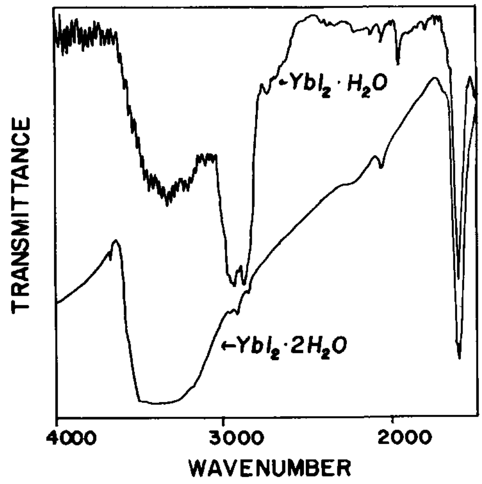

FIG. 1. The IR Nujol mull spectrum of $YbI_2 \cdot H_2O$ confined between NaCl plates and that of $YbI_2 \cdot 2H_2O$ mixed with KBr.

TABLE II

MILLER INDICES, OBSERVED AND CALCULATED INTERPLANAR *d*-SPACINGS, AND OBSERVED INTENSITIES FOR ORTHORHOMBIC $YbI_2 \cdot 2H_2O$

h k l	I_{obs}[a]	d_{calc} (Å)	d_{obs} (Å)
1 1 0	s	8.162	8.176
2 0 0	vs	6.519	6.518
0 2 0	x	5.233	5.247
1 2 0	m	4.857	4.856
2 2 0	s	4.081	4.084
3 1 0	w	4.014	4.013
1 1 1	w	3.949	3.954
2 1 1	vvs	3.497	3.494
0 2 1	w	3.418	3.418[b]
3 2 0	s	3.343	3.345
1 2 1	s	3.306	3.303
4 0 0	x	3.259	3.263
2 2 1	m	3.0269	3.0260
3 1 1	mw	2.9991	2.9984
4 2 0	w	2.7666	2.7671
3 3 0	m	2.7206	2.7179
1 3 1	ms	2.7004	2.7009
3 2 1	ms	2.6864	2.6868
1 4 0	x	2.5655	2.5662
5 1 0	x	2.5301	2.5255
4 3 0	vvw	2.3817	2.3803
4 2 1	vvw	2.3587	2.3576
5 2 0	vw	2.3338	2.3345
5 0 1	vvsb	2.2577	2.2574
0 0 2		2.2565	
3 4 0	vw	2.2417	2.2432
1 4 1	vw	2.2303	2.2308
5 1 1	w	2.2070	2.2087
1 1 2	x	2.1749	2.1750
2 4 1	mb	2.1384	2.1381
6 1 0	mb	2.1275	2.1297
5 3 0	w	2.0886	2.0880
1 5 0	x	2.0669	2.0661
1 2 2	x	2.0464	2.0460
6 2 0	w	2.0068	2.0071
2 5 0	w	1.9931	1.9926
6 1 1	w	1.9244	1.9261
3 2 2	mwb	1.8704	1.8699
5 4 0	w	1.8470	1.8469
6 2 1	vw	1.8337	1.8341
3 3 2	mw	1.7368	1.7366
5 4 1	vvw	1.7094	1.7098
7 1 1	vvw	1.6988	1.6982
2 6 0	vvw	1.6851	1.6861
6 4 0	vvw	1.6717	1.6696

[a] v, very; m, medium; s, strong; w, weak; b, broad; x, barely visible.

[b] May contain contribution from strongest YbI_2 reflection.

However, heating a specimen which contained both di- and a higher hydrate in a high vacuum at 70–80°C produced the pure dihydrate.

Calcd for $YbI_2 \cdot 2H_2O$: Yb, 37.38; I, 54.83; H_2O, 7.78%. Found: Yb, 38.33; I, 53.90.

All observed *d*-spacings were indexed by the program ITO9 with a figure-of-merit of 24 to a cell of orthorhombic symmetry (*10,14*). Refined cell parameters calculated with the program APPLEMAN are: a = 13.037(3), b = 10.467(2), and c = 4.513(1) Å (*16*). Calculated and observed interplanar *d*-spacings, Miller indices, and observed intensities are presented in Table II. Although no YbI_2 reflection was apparent in an overexposed Guinier film, the d = 3.41 Å value overlaps the most intense YbI_2 reflection.

The DTA–TGA results presented in Fig. 2 and obtained from a specimen prepared by the first hydration procedure indicate it to be a dihydrate; the IR spectrum is presented in Fig. 1. The mass loss determined from the TG data agrees well with the 7.78% value expected for the dihydrate.

Discussion

Analytical Results

Experimental analysis results for ytterbium agreed well with the formula expected on the basis of mono- and dihydrate compositions. Elemental iodine analyses were slightly lower than the expected theoretical values. Two Karl Fisher water analyses on the monohydrate deviated significantly from each other even though the average is close to the expected value. One set of duplicate analyses obtained on a dihydrate specimen yielded results consistent with a tetrahydrate formulation, an indication that the specimen had hydrated further either prior to or during analysis. Additional Karl Fisher analyses were not sought on the dihydrate since by difference the H_2O con-

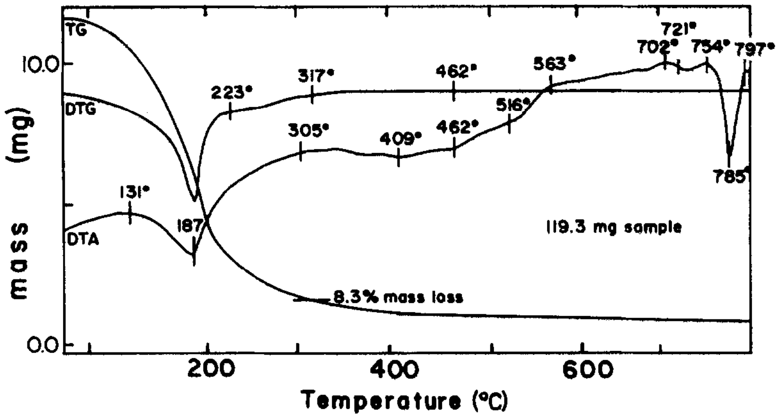

FIG. 2. The DTA–TGA curve of argon-blanketed $YbI_2 \cdot 2H_2O$ obtained with previously heated Al_2O_3 as reference at a scan rate of 5°C min^{-1}.

tent, 7.77%, agrees well with the theoretical value, and the TG data indicated the compound to be a dihydrate. Both IR spectra confirm the presence of H_2O.

Synthesis and Structure

As expected, direct addition of water to a septum-covered vial containing powdered YbI_2 produced impure dihydrate, probably because the exterior of the particles formed higher hydrates before the interior could react.

In the second hydration procedure with acetone and methanol as solvents erratic results were obtained. Reproducible results were obtained only with $(CH_3)_2O$. The possibility of methyletherate formation was considered unlikely, and absorptions expected for $(CH_3)_2O$ are not apparent in the monohydrate IR spectrum. The volatile dimethylether is probably removed relatively easily under the high vacuum to which the product was subjected. Additionally, if both hydrate cells are assumed to contain the same number of YbI_2 molecules, the monohydrate volume, which is ~30 Å^3 less than that of the dihydrate, argues against etherate formation (*3*).

The $YbI_2 \cdot 2H_2O$ lattice parameters are similar to those of the related divalent halide monohydrates $SrCl_2 \cdot H_2O$; $MBr_2 \cdot H_2O$, M = Sm, Eu, Sr; and $EuI_2 \cdot H_2O$. $EuCl_2 \cdot 2H_2O$ and $SrCl_2 \cdot 2H_2O$, on the other hand, exhibit monoclinic symmetry (*17*). As would be expected for a higher hydrate, the unit cell volume of $YbI_2 \cdot 2H_2O$ is 79.45 Å^3 larger than that of the related $EuI_2 \cdot H_2O$ cell (*3*). While Eu^{3+} typically exhibits a coordination of 8 or 9, Yb^{3+} is normally 6-coordinate. Thus the atomic arrangement in these YbI_2 hydrates must differ significantly from those of the lighter (and larger) halides. To substantiate further that this $YbI_2 \cdot 2H_2O$ is not structurally related to $EuI_2 \cdot H_2O$, a theoretical powder diffraction pattern was calculated for $YbI_2 \cdot H_2O$ with the program POWD12 (*18*) by using the positional and thermal parameters of $SrBr_2 \cdot H_2O$, which also crystallizes with orthorhombic symmetry (*4*). As expected, the intensity mismatch was severe. Even though the X-ray reflections of the dihydrate are consistent with space group *Pnnm* (No. 58), the structure cannot be definitively assigned to this space group because a model structure from which the observed intensities may be calculated could not be found (*15*). A search of the CRYSTDAT data base for orthorhombic symmetry dihydrate structures did not yield any entries which could serve as a model system (*19*).

The DTA–TGA results on the dihydrate

are of particular interest. They indicate that in an inert atmosphere both H_2O molecules can be removed completely at about 185°C without conversion to oxideiodide, hydrogen, and water. Diiodide melting occurs at 785°C, very close to the reported 780°C value (*20*).

Numerous attempts to prepare a single crystal of the monohydrate by slow evaporation of the solvent were unsuccessful, possibly because true solution was never achieved. The IR spectra clearly establish the presence of H_2O in the specimens, but attempts to assign peaks by comparing them with those in related halide hydrates (*7*) were unsuccessful. While no attempt was made to prepare the dihydrate by the methylether solvent procedure, the monohydrate clearly could not be prepared by the first hydration procedure. If the quantity of $CuSO_4 \cdot 5H_2O$ were insufficient to produce the dihydrate, a mixture of dihydrate and unreacted YbI_2 remained. Since upon hydration dihydrate is the initial phase observed, it must be thermodynamically more stable than the monohydrate, and therefore should be preparable by either procedure.

Since the CN VIII ionic radii of Ca^{2+} and Yb^{2+} differ by only 0.02 Å (*21*), their hydrate chemistry might be expected to be similar. Indeed, a $CaI_2 \cdot 4H_2O$ structure has been reported (*6*). The H_2O analysis results obtained on the two "$YbI_2 \cdot 2H_2O$" specimens provide evidence that a tetrahydrate can probably be formed. Evidence for a lower calcium halide hydrate could not be found. However, in view of the many differences observed between the mixed halide systems of calcium and ytterbium, a similarity between their hydrate behavior need not be expected (*22, 23*).

Acknowledgments

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