CONTRIBUTION NO. 1248 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE
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# Preparation of Metallic Thorium Diiodide[1a]

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Reaction of sublimed $ThI_4$ and excess, high purity thorium in sealed tantalum containers at about 800° results in the quantitative formation of the gold-colored $ThI_2$ on the surface of the metal. The compound is stable in tantalum up to 883°, where it decomposes incongruently to Th(s) and iodide-rich liquid of composition *ca.* $ThI_{3.4}$. The metallic character suggested by the appearance of the diiodide is confirmed by its very low electrical resistance and by its diamagnetism ($\chi_M = (-80 \pm 20) \times 10^{-6}$ e.m.u.). The compound is therefore not a true thorium(II) salt but probably should be formulated as $Th^{4+}(I^-)_2(e^-)_2$, with the electrons in a metal-like conduction band. There is no evidence for an analogous $ThBr_2$. Correlation of the results with earlier, contradictory studies of the $ThI_4$–Th system is substantially lacking, as these have claimed only dark colored thorium "dihalides." It is concluded that many prior reports of these compounds probably were vitiated by extensive side reactions with the glass containers. Similar container reactions have evidently also affected prior studies of the black, diamagnetic phase near or above $ThI_3$ in composition.

## Introduction

The literature relating to the existence, identity, and properties of intermediate phases in the $ThI_4$–Th system is both conflicting and incomplete. Prior investigations have been complicated by lack of equilibrium between phases, particularly with the metal, the poor quality of thorium metal available, side reactions with the glass containers, and the general characteristic that the lower iodide phases give little if any useful powder pattern diffraction data. As a result there is little clear evidence that any composition reported is physically or chemically characteristic of a pure phase; instead gross compositions frequently have been apportioned "à la mode" as mixtures of the simplest phases $ThI_3$, $ThI_2$, and ThI.

Specifically, Anderson and D'Eye[2] provided the first substantial evidence for dark colored, lower iodides of thorium. Reaction of $ThI_4$ with Th in proportions with over-all I/Th ratios of 3.0–3.4 at 450 to 555° gave water-soluble products of composition $ThI_{3.23}$ to $ThI_{3.5}$, interpreted as mixtures of $ThI_3$ and $ThI_4$. Hydrogen evolved on solution was found to be somewhat higher than theory. Similar reaction of mixtures with I/Th ratios of 1.3 to 2.4 gave dark products assigned as 50 to 90% $ThI_2$, the remainder $ThI_3$. Metal was recovered in all cases on solution of analytic samples in water. Both compounds were reported to disproportionate above 600°. The diffraction pattern obtained for the supposed $ThI_2$ was first assigned to that of a hexagonal, $CdI_2$-type structure, but this later was retracted.[3]

The reaction of 87 to 95% Th with $I_2$ in a 1:3 atom ratio at 550° gave, according to Hayek, *et al.*,[4,5] a reasonably homogeneous sample of $ThI_3$, described as black with a violet cast. Reaction with water gave a solution with the I/Th ratio of 2.94–3.03, a precipitate of 3 to 8% Th and $ThO_2$ plus a small amount of $ThSi_2$, and the roughly appropriate amount of $H_2$. Disproportionation of this $ThI_3$ at 550° through loss of the volatile $ThI_4$ yielded a similar, dark $ThI_2$ in 71 to 87% purity based on total I/Th. The corresponding lower bromides and chlorides were likewise prepared, according to these workers, with somewhat less satisfactory quantities of $H_2$ evolved (70 to 90% of that expected for $(X + H)/Th = 4.0$).

As a means of avoiding the use of impure Th metal for the reduction, Jantsch and co-workers[6] investigated the thermal decomposition of $ThI_4$ at 400°. The reducing strength of the product $ThI_{3.23}$ was determined only indirectly from the amount of $I_2$ evolved. Alternatively, reduction of $ThI_4$ by Al gave $ThI_{2.96-3.03}$, while further reduction of $ThI_3$ by excess Al was reported to be nil. Analogous reactions produced black $ThCl_{3.01}$ by Al reduction and, surprisingly, $ThCl_{3.27}$ by thermal decomposition of $ThCl_4$ at 450°.

A more thorough but at the same time indirect characterization of the system has been provided by Watt, Sowards, and Malhotra.[7] The compositions $ThI_{2.39}$ to $ThI_{2.6}$ were prepared by heating the components in Vycor for three days at 550°, followed by sublimation of any small amounts of unreacted $ThI_4$ from the mixture. Unreacted Th was determined by solution of a portion of the sample in dilute $HClO_4$. The $ThI_3$ was separated by virtue of its oxidation by and subsequent solution in liquid $NH_3$ as the amidoiodides of Th(IV) plus $NH_4I$ (total I/Th = 2.98). The hydrogen recovery for the assigned composition $ThI_3$ was good. The ammonia-insoluble residue then was treated with anhydrous DMF to give a solution with I/Th = 1.97 to 2.09, *i.e.*, $ThI_2$. The residue at this point was found to consist of 76.3% metal and 20.7% $ThI_{1.12}$, suggestive of ThI. The ammonia-insoluble portion was shown to be readily oxidized to $ThI_3$ by $I_2$ at 105°. An increase in paramagnetism of the samples

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[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; (b) Department of Chemistry, Florida State University, Tallahassee, Florida.

[2] J. S. Anderson and R. W. M. D'Eye, *J. Chem. Soc. Suppl.*, 244 (1949).

[3] R. W. M. D'Eye, I. F. Ferguson, and E. J. McIver, *Congr. Intern. Chim. Pure Appl. 16e Paris 1957, Mem. Sect. Chim. Minerale*, 341 (1958).

[4] E. Hayek and Th. Rehner, *Experientia*, **5**, 114 (1949).

[5] E. Hayek, Th. Rener, and A. Frank, *Monatsh.*, **82**, 575 (1951).

[6] G. Jantsch, J. Homayr, and R. Zemek, *ibid.*, **85**, 526 (1954).

[7] G. W. Watt, D. M. Sowards, and S. C. Malhotra, *J. Am. Chem. Soc.*, **79**, 4908 (1957).

was noted as the apparent oxidation state decreased.

Although the foregoing results indicate some agreement on the existence of a phase near $ThI_3$ in composition, the supporting analytical data are in most cases relatively poor and the identification of its exact composition is not very substantial. Evidence for still lower iodides and their identity is conflicting and less well supported. The present work was undertaken in an attempt to clarify the system by use of substantially higher purity thorium metal as well as the far superior container material tantalum. The latter change is found to be of major consequence in that the alleged disproportionation reactions at or below 600° are now absent, and therefore may be presumed to have been due instead to the overwhelming reaction of the thorium iodides with the silica. The opportunity thus gained for study of the system at higher temperatures is also of marked aid though not a complete solution to overcoming the intrinsic difficulties of slow reaction of the metal and the poor quality of powder pattern data. More important, the considerable effect of impurities and side reactions even at 550° and below that must have been present in earlier studies in glass is evidenced by the isolation of pure, crystalline $ThI_2$, with properties such as to indicate that it is very unlikely that such has ever been prepared or recognized by previous workers. Although not a primary objective of this work, some additional verification and properties of an intermediate phase near $ThI_3$ have also been obtained.

## Experimental

**Materials.**—The thorium used only for the preparation of $ThI_4$ was cut from a billet of Ames thorium with a carborundum wheel; the listed impurity concentrations, in p.p.m., were N, 110; C, 770; Be, 115; Fe, 75; O, undetermined; other metals, below the limit of spectrographic detection. Reaction of this with sublimed iodine in excess was carried out in an evacuated Vycor tube in the shape of a shallow, inverted V, with the metal heated to 600° and the iodine to 120°. The product $ThI_4$ was dirty yellow in color, as expected from the quality of the starting metal, the contamination introduced by the cutting, and the use of a glass container. Canary yellow crystals, m.p. 566°, were obtained from two vacuum sublimations of the crude product in tantalum (in turn enclosed in glass) at 500°. A fair quantity of a somewhat pyrophoric residue remained from the first sublimation, but only a very small amount after the second.

A far better grade of electron-beam-melted thorium metal was used for all subsequent studies of the system. Vacuum fusion indicated this had an oxygen content of 230 p.p.m. while emission spectrograph examination showed only a faint trace of Si (~50 p.p.m.), with Al, Be, Ca, Cr, Fe, Mg, Mn, Ni, and Zr below the limit of detection (20 p.p.m. except Fe, 100; Zr, 200). This material was used either as $^1/_8$ in. slabs with the surface cleaned by filing or as rolled to 5 to 8 mil foil so it could be cut with shears. The metal and all iodide samples were stored in evacuated containers and all transfers were carried out in an inert atmosphere glove box.

**Reactions.**—The $ThI_4$–Th system was studied entirely in sealed tantalum containers. The prefabricated container was filled in the drybox, crimped shut and arc-welded under $\sim ^1/_3$ atm. of He. This was in turn enclosed in an evacuated Vycor container before being heated; in thermal analysis and equilibration experiments an internally sealed thermocouple was either in a built-in well or in contact with the Ta wall, respectively. In some of the latter studies the samples were quenched by dropping them into a silicone oil reservoir at the bottom of the glass enclosure.

The direct synthesis of $ThI_2$ readily results when thorium metal, preferably as foil with a large surface, is heated with $ThI_4$ at between about 700 and 850°. A capped cylinder of 0.75 in. Ta 1 to 2 in. long was half-filled with 0.5 in. square Th sheets, the cap with a 2 by 0.25 in. filling tube welded on, about an equal weight of $ThI_4$ loaded in the drybox, and the apparatus welded shut. The container was positioned in the furnace so that the metal was near the hottest point of the furnace. On a small scale the $ThI_4$ was completely converted to $ThI_2$ in 12 hr. at 800°; for the quantities as described above (10 to 15 g. of $ThI_2$) the vessel was heated for 6–8 days at 800°, although a shorter time may have been adequate. On cutting the crucible open in the drybox, the $ThI_2$ is found on the surface of the metal, from which it can be cleanly separated by flexing the latter. Use of metal containing appreciable amounts of oxygen results in slight to moderate contamination by the voluminous, acicular $ThOI_2$.

**Analyses.**—Iodide was determined gravimetrically as AgI and thorium, to $\leqslant 0.3\%$ by titration at pH 3 with standard EDTA using sodium alizarinsulfonate as the indicator.

## Results and Discussion

Thorium diiodide prepared as above is found as well formed, lustrous gold-colored crystals on the surface of the metal. The material reacts rapidly with dilute aqueous acid to give $H_2$ and a clear solution. The stoichiometry determined for such a solution is clearly that due to $ThI_2$; on two separate preparations, obsd.: Th, 47.40, 47.53; I, 52.30, 52.16; I/Th, 2.018, 2.007; theor.: Th, 47.76; I, 52.24; I/Th, 2.000. The identity of the compound was further confirmed by measurement of the $H_2$ evolved on solution of two different preparations in dilute HCl, giving 38.1 and 22.0 ml. STP compared to 38.8 and 21.4 ml., respectively, calculated for $ThI_2 + 2H^+ \rightarrow Th^{4+} + 2I^- + H_2$. In addition, an oxygen content of only 135 p.p.m. was obtained for one sample by the inert gas fusion method.

Microscopically, $ThI_2$ crystals occur as thin plates with pseudohexagonal but probably at best only monoclinic symmetry. This classification is compatible with the relatively simple powder pattern[8] to the extent that three of the weaker lines defy hexagonal indexing with a reasonable unit cell and yet cannot be assigned to either metal, $ThOI_2$ or "$ThI_3$." The thermal stability assigned to $ThI_2$ necessarily depends on the conditions. When heated under dynamic vacuum in an open tantalum crucible $ThI_2$ begins to lose $ThI_4$ by sublimation from the heated portion at 550–600°, and the residue is thorium metal if the disproportionation is carried to completion at 800°. Under less drastic, isothermal conditions the only transformation observed by direct and differential thermal analysis on heating to 1005° is at ~880°, where $ThI_2$ melts incongruently to thorium and a liquid with $I/Th \approx 3.4$. The metal product in this case was identified by the powder pattern of the black product obtained on quenching a $ThI_2$ composition from 930°, while the liquid composition was roughly bracketed between I/Th values of 3.24 and 3.56 by thermal

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[8] The powder pattern data for $ThI_2$, with relative intensities in parentheses, are: 7.83 (8), 3.41 (2), 3.14 (2), 3.01 (2), 2.883 (10), 2.643 (8), 2.328 (6), 2.208 (2), 1.982 (10), 1.638 (2), 1.592 (4), 1.567 (2), 1.404 (8), 1.329 (8), 1.131 (4), 1.103 (2), 0.984 (6), 0.901 (6). $ThOI_2$ gives a very complex pattern.

analysis of such mixtures. Cooling $ThI_2$ compositions from ~900° gives, in addition to the (more precise) peritectic halt at 883°, an additional arrest at 752°, which is assigned to the incongruent melting point of the black "$ThI_3$" phase (*vide infra*). The latter arises from the substantial decomposition of $ThI_2$ at the melting point and the fact that it re-forms only slowly at normal cooling rates. However, equilibration of the mixture for 20 to 30 min. at 800° is sufficient to regenerate the $ThI_2$ and thereby cause the complete disappearance of the 752° arrest.

The compound $ThI_2$ resembles a metal in appearance very much, and indeed, it has many of the other appropriate properties. The golden crystals are soft enough that they may be readily pressed into a strong, hard pellet in an evacuable, "KBr" press at 26,000 p.s.i. The density calculated from the dimensions is 7.205 g. cm.$^{-3}$. Resistance measurements made on the pellet in the glove box with a VTVM gave 3 to 5 ohms across the 0.50 in. diameter and less than 1 ohm between the faces (0.116 in.). This result suggests all or part of the two extra electrons per thorium necessitated by the stoichiometry are delocalized in a metal-like conduction band. The possible extent of this process is clarified by the magnetic susceptibility measured by the Gouy method, for the compound is *diamagnetic*, with $\chi_M$ only $(-80 \pm 20) \times 10^{-6}$ e.m.u. The most plausible interpretation of these facts is that only the diamagnetic cores $Th^{4+}$ and $I^-$ are present and that both electrons are metallic in character, *i.e.*, $Th^{4+}(I^-)_2(e^-)_2$. The compound is thus a further example of the behavior recently recognized in the diiodides of lanthanum, cerium, and praseodymium, $M^{3+}(I^-)_2e^-$,[9] but with twice as many metal-like electrons in the present case. Approximation of (only) the diamagnetic core corrections for $Th^{4+}$ and $2I^-$[10] gives $\chi_M \sim 50 \times 10^{-6}$ e.m.u. mole$^{-1}$ as a rough measure of the net Pauli paramagnetism of the conduction electrons, compared to a similarly corrected value of $\sim 115 \times 10^{-6}$ e.m.u. g.-atom$^{-1}$ for thorium metal[11] and the equivalent quantity of $\sim 125 \times 10^{-6}$ e.m.u. mole$^{-1}$ for $La^{3+}(I^-)_2e^-$.[12] The metal-like conductivity and diamagnetism of $ThI_2$ certainly seem to rule out a conventional thorium(II) salt. A possible alternative to the above might be with one electron "metallic" and the other in covalent bonds to form a dimeric thorium cation, *i.e.*, $(^1/_2Th_2{}^{6+})(I^-)_2e^-$. This would be even more unusual and is considered less likely although it cannot be eliminated by present information.

Further phase characterization of the intermediate $ThI_4$–$ThI_2$ system has been limited primarily to that necessary to establish the phase relationships previously given for $ThI_2$. As noted, the black "$ThI_3$" melts at 752° to give $ThI_2$ and a liquid considerably richer in $ThI_4$, the latter being evident from thermal analysis of intermediate mixtures and from the sharp increase in I/Th of the dark phases obtained in samples equilibrated above 752° and quenched. There is also a distinct transition to an olive-green product under the latter circumstances; this has been taken to be a $ThI_4$–$ThI_2$ mixture principally because of the lack of thermal or X-ray evidence for solid iodides other than $ThI_2$ above the melting point of "$ThI_3$." Further, the 566° melting point of $ThI_4$ is lowered to only 560° at the eutectic with "$ThI_3$," indicative of a tetraiodide-rich liquid composition over "$ThI_3$" in this region. Although not investigated directly, the composition of the black phase is probably at I/Th $\leqslant$ 3.4 on the basis of thermal results. If the true composition is materially lower in iodide than this, the rate of formation must be very slow, since products of this limiting composition were obtained on reaction of $ThI_4$ and excess metal for 16 hr. at ~630 to 670° where the equilibrium phase $ThI_2$ forms only very slowly. Powder patterns of this composition are useable though not of high quality, showing a dozen or more unique lines and none due to $ThI_4$. Finally, the black $ThI_{3.39}$ is qualitatively diamagnetic, and, in some contrast to $ThI_2$, shows very high resistances ($>10^7$ ohms) in pellet form. Although the composition of the pure intermediate phase here is not clear, experience with polycrystalline $GdI_2$–$GdI_3$[13] mixtures and with a 1:1 $ThI_2$–$ThI_4$ composition indicates that a much lower resistance ($10^2$–$10^3$ ohms) would be observed if in this case $ThI_4$ were admixed with a metallic salt with I/Th $\geqslant$ 3.0.

Comparison of the foregoing findings with the earlier and somewhat contradictory literature regarding particularly the compound $ThI_2$ is primarily negative, since there is no mention of other than dark compounds of this composition. Reported diiodide products prepared *via* either further reduction of "$ThI_3$" by metal[2] or disproportionation with sublimation of $ThI_4$[5] probably were instead primarily the result of further reaction with the inappropriate glass container. The fact that about one-half of the powder pattern data reported for black "$ThI_2$"[3] are in rough agreement with those obtained here is probably fortuitous, and these might be equally well assigned to $ThSi_2$ or to the very complex $ThOI_2$ pattern. The existence of black $ThBr_2$ and $ThCl_2$[5] seems similarly suspect; in the present study, reaction of $ThBr_4$ and Th at 700 to 890° gave no evidence for a thorium dibromide, although a "$ThBr_3$" phase similar to the iodide (Br/Th $\leqslant$ 3.4) was suggested by limited thermal analysis and equilibration studies.[14]

Since $ThI_2$ is found to grow directly on the surface of the metal it is difficult to imagine that a still lower iodide such as ThI[7] could be stable under these conditions. Also, it appears doubtful that the system investigated by Watt and co-workers[7] contained the same diiodide as reported herein. Although the previous preparation was separated by means of its solution in dimethylformamide (DMF), the present, golden $ThI_2$ exhibits no

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(9) J. D. Corbett, L. F. Druding, W. J. Burkhard, and C. B. Lindahl, *Discussions Faraday Soc.*, **32**, 79 (1961).

(10) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 78.

(11) J. F. Smith and J. D. Greiner, *Phys. Rev.*, **115**, 884 (1959).

(12) R. A. Sallach and J. D. Corbett, to be published.

(13) J. E. Mee and J. D. Corbett, to be published.

(14) Melting incongruently at 748°. Reaction with metal lowers the 680° melting point of $ThBr_4$ to a eutectic at 666°.

noticeable solubility in dry DMF at room temperature. On warming, a reaction begins at 70 to 80° to give unknown products both in solution and as a precipitate; neither phase then reduces water as does $ThI_2$. Satisfactory, alternate explanations for the solid, paramagnetic mono- and diiodide products obtained in the previous study are not apparent. The formation of mono- and diiodides of thorium amides in unknown oxidation states from treatment of the $ThI_x$ with liquid $NH_3$ would also allow for the observation that these two products could be reconverted to $ThI_4$ by excess $I_2$ at 105°; however, this is not consistent with the (unreported) low nitrogen content.[15] Although the purity of the metal employed earlier was unspecified, it may be significant that the reported susceptibility is 4.7 times that accepted for high quality metal.[11]

Finally, the preparation of $ThI_3$ and $ThCl_3$ by thermal decomposition of the respective tetrahalides at 400 to 450° *in vacuo*[6] is very questionable. Since $ThI_4$ can be readily sublimed at 500–600° without any trace of decomposition and is quite stable in tantalum at lower temperatures, the prior observation to the contrary must instead have been a result of reaction with the oxide containers or with gaseous impurities. The absence of decomposition of $ThI_4$ in $Al_2O_3$ containers at 380–500° also has been established by Scaife and Wylie.[16]

The present $ThI_2$ example also brings to attention an important consideration involved in the characterization of simple salts in apparent, lower oxidation states. Although the composition $ThI_2$ suggests a divalent state for the metal, the electrical and magnetic properties indicate that the compound probably should be instead formulated in terms of the normal Th(IV) state with the two electrons necessary for charge conservation delocalized much as in the metal. It therefore seems advisable to include at least a qualitative check for a salt-like resistance in the characterization of any supposed subhalide, particularly an iodide, that shows negligible magnetic evidence for a simple reduced cation before the presence of localized, metal–metal bonding, for example, can be distinguished from the metallic possibility. With lower resistance results, or where magnetic measurements do not clearly distinguish between possible choices of paramagnetic cores, a measurement of the temperature dependence of resistivity would of course be necessary.

With regard to thorium compounds with other anions that are analogous to the diiodide, the refractory sulfides also are so constituted. Eastman, *et al.*,[17] have shown that ThS, and perhaps $Th_2S_3$, are appropriately diamagnetic and have high electronic conductivities. In fact BaS, CeS, US, and ThS, all of which occur in the NaCl structure, apparently have 0, 1, 2, and 2 electrons per metal atom so involved, respectively. It does not seem appropriate to refer to the last three and $Th_2S_3$ as examples of lower oxidation states in the specific sense, however, as the electrons in question do not appear to be localized or shielding as would be the case with the reduced cations. In fact, the metal–sulfide distances reported[17] for the above series are in close agreement with the sums of the radii for $S^{2-}$ and $Ba^{2+}$, $Ce^{3+}$, $U^{4+}$, or $Th^{4+}$, respectively, the stability in these cases being considerably increased by the extra Madelung energy derived from the higher charged cations.

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[15] G. W. Watt, private communication.

[16] D. E. Scaife and A. W. Wylie, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy*, **IV**, 215 (1959).

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CONTRIBUTION FROM THE CHEMICAL LABORATORY OF
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# Complexes in the Rhodium(III)-Chloride System in Acid Solution

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The following species have been isolated and characterized in the rhodium(III)-chloride system in acid solution by means of ion exchange techniques: $RhCl^{2+}$ (coördinated water molecules not shown); $RhCl_2^+$; *cis*- and *trans*-$RhCl_3$; $RhCl_4^-$; $RhCl_5^{2-}$; and $RhCl_6^{3-}$. By utilization of the molar absorptivities of these species at appropriate wave lengths, approximate successive formation constants at 120° for the various members of the series have been determined. The constants at an ionic strength of 6.0 *M* are: $k_1 > 10^3$; $k_2 > 10^3$; $k_3 \sim 10^3$; $k_4 = 250 \pm 120$; $k_5 = 28 \pm 8$; and $k_6 = 0.56 \pm 0.18$.

The color of aqueous solutions of rhodium(III) chloride varies from yellow to various shades of red depending upon the nature and history of the solution. For example, a solution of hydrous rhodium(III) oxide in dilute hydrochloric acid is yellow; on heating to boiling, the solution becomes cherry-red. Dissolution of hydrated rhodium(III) chloride in water yields a red-brown solution, which turns yellow on boiling,[1,2] or red if an excess of hydrochloric acid is present during the heating process. These color changes, coupled with

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