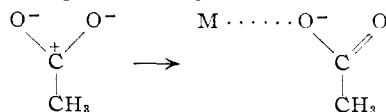


comes stronger, two C-O bonds of the acetate ion become uneven, and the separation of the two CO stretching frequencies may increase.



Thus we conclude that the effect of coordination is stronger in the Co^{3+} complex than in the Ni^{2+} complex. This result suggests the importance of the formal charge of the central metal in discussing the effect of coordination from the infrared spectra.

Table VI also indicates that the asymmetric CO stretching frequency is higher in the bidentate Cu^{2+} complex than in the unidentate Ni^{2+} complex.

TABLE VI
THE CO STRETCHING FREQUENCIES OF ACETATO COMPLEXES (CM.^{-1})

	Asym.	Sym.	Separation
Free CH_3COO^- ion	1578(s)	1425(s)	153
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	1530(s)	1418(s)	112
$\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$	1603(s)	1418(s)	185
$[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}](\text{ClO}_4)_2^a$	1603(s)	1380(s)	223

^a M. Linhard and B. Rau, *Z. anorg. Chem.*, 271, 121 (1953).

This fact may suggest that two Cu-O bondings in the former are responsible for higher frequency shift of the asymmetric CO stretching mode.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Iodides of Thorium(III), (II) and (I)¹

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The formation of iodides of thorium(III), (II) and (I) by the reduction of thorium(IV) iodide with excess elemental thorium at 550° is described. Procedures for the separation of the five components of the resulting reaction mixture have been devised; the resulting data confirm the existence of ThI_3 and provide evidence also for the existence of ThI_2 and ThI .

Earlier efforts to provide evidence for the existence of $\text{Th}^{<4+}$ as the fluoride,² chloride,³ bromide³ and iodide³⁻⁶ lead to the conclusions that (a) thorium(IV) fluoride is not reduced by thorium between 1175 and 1600°, (b) thorium(III) chloride, bromide and iodide are formed by direct union, and (c) the iodide of thorium(III) also results from the reduction of thorium(IV) iodide with either thorium or aluminum and probably from the thermal decomposition of thorium(IV) iodide. Most of the evidence for halides of $\text{Th}^{<3+}$ arises from the study of disproportionation of thorium(III) halides or reactions involving direct union at low halogen-thorium ratios and consists of marginal analytical data on unresolved mixtures of products that have not been characterized on the basis of either physical properties or selectivity of chemical reactions.

The experiments described below are concerned with the formation of at least four different iodides of thorium and with procedures for their separation.

Experimental

Materials.—Unless otherwise indicated, all materials employed in this work were reagent grade chemicals.

Elemental reagent grade thorium metal powder gave an X-ray pattern that was characteristic of the pure metal and did not include any lines attributable to oxide and/or other impurities. Furthermore, oxide contamination was not detectable in thorium residues from reactions in which thorium(IV) oxide does not participate (*e.g.*, with iodine) and therefore would be expected to concentrate if present. Iodine was resublimed, dried and stored over calcium chlo-

ride. Ammonia was dried and stored over sodium amide; that the gas was oxygen-free was ensured by passing it through a solution of potassium in ammonia prior to condensation in reaction vessels. Commercial *N,N*-dimethylformamide was successively dried over P_2O_5 , KOH and CaO , and finally distilled; only the fraction boiling at 150–151° at 750 mm. was used.

Methods.—X-Ray diffraction patterns were obtained with a Hayes unit, Cu $K\alpha$ radiation, a Ni filter, a tube voltage of 35 kv., and a filament current of 15 ma. Samples were diluted with starch, and the exposure time was 6 hr. Relative intensities were estimated visually.

Magnetic susceptibility measurements were made with a modified Curie-Cheneveau balance^{7,8}; Mohr salt was used for calibration. For samples of iodides that contained elemental thorium, susceptibilities were assumed to be additive and the susceptibility of the iodide(s) was obtained by subtracting the contribution of known thorium content from the total measured susceptibility.

Reactions between thorium or thorium iodides and iodine were carried out in Vycor tubes of 20 mm. i.d. that were degassed at 600°. After introduction of the reactants, the pressure was reduced to 10^{-3} mm. and the tubes were sealed.

Reactions in liquid ammonia were carried out in appropriate modifications of the equipment described elsewhere.⁹

Thorium was determined gravimetrically as ThO_2 (after complete removal of iodine), and iodine as AgI . Nitrogen was determined by the semimicro-Kjeldahl method.

Formation of Thorium Iodides.—Known weights of iodine and thorium corresponding to different reaction ratios were intimately mixed and heated at 100° for *ca.* 50 min. (*i.e.*, until the color of iodine vapor was no longer evident). The resulting mixtures (ThI_4 and Th) were then heated at 550° for 3 days. Over this period, ThI_4 that sublimed into the cool end of the tubes was returned to the main body of the reaction mixtures at regular intervals. Finally, the small quantities of ThI_4 that remained were separated from the non-volatile fraction by sublimation. The tubes were cooled, transferred to a dry-box and opened in an oxygen-free helium atmosphere.

The ends of the tubes containing ThI_4 were removed

(1) This work was supported in part by The U. S. Atomic Energy Commission, Contract AT-(40-1)-1639.

(2) J. C. Warf, *THIS JOURNAL*, 74, 1864 (1952).

(3) E. Hayek, T. Rehner and A. Frank, *Monatsh.*, 82, 575 (1951).

(4) J. S. Anderson and R. W. M. D'Eye, *J. Chem. Soc.*, S244 (1949).

(5) E. Hayek and T. Rehner, *Experientia*, 5, 114 (1949).

(6) G. Jantsch, T. Homayr and F. Zemek, *Monatsh.*, 85, 526 (1954).

(7) F. W. Gray and J. Farquharson, *J. Sci. Instr.*, 9, 1 (1932).

(8) W. K. Witherspoon, Thesis, Tulane University, New Orleans, La., 1949.

(9) G. W. Watt and C. W. Keenan, *THIS JOURNAL*, 71, 3833 (1949).

separately. *Anal.* Calcd. for ThI_4 : Th, 31.4; I, 68.6. Found: Th, 31.4; I, 68.6. X-Ray diffraction data for this substance are included in Table I.

TABLE I
X-RAY DIFFRACTION DATA FOR THORIUM(IV) IODIDE AND THORIUM(IV) AMIDOTRIIODIDE 4-AMMONIATE

ThI_4		$\text{Th}(\text{NH}_2)_3 \cdot 4\text{NH}_3$	
d , Å.	I/I_0	d , Å.	I/I_0
7.03	1.0	4.14	1.0
4.08	0.3	3.60	1.0
3.25	.9	2.56	0.9
2.70	.9	2.19	.8
2.45	.6	2.09	.5
2.33	.2	1.81	.1 ^a
2.25	.2	1.67	.5
2.11	.2	1.63	.5
1.87	.2	1.49	.4
1.78	.2 ^a	1.40	.4

^a Less intense lines not included here.

The non-volatile products were removed from the tubes, ground intimately to ensure uniformity of sampling, and treated in the manner described below.

Separation of Thorium.—In order to establish the I/Th ratios in the lower thorium iodides that comprised the major portion of the non-volatile products, the unreacted thorium present was removed as follows. In a typical case, a 1.2372-g. sample of the non-volatile product (from a reaction involving I/Th = 1) was stirred with *ca.* 20 ml. of perchloric acid solution at pH 1 for 6 hr. at 25° and the insoluble elemental thorium was removed by filtration, washed with water and dried. Thus there was separated 0.4477 g. of thorium (36.2% of sample) that gave a negative test for iodide and an X-ray diffraction pattern characteristic of thorium and including no extraneous lines. In independent experiments, samples of thorium of different origin and particle size were shown to be substantially insoluble in perchloric acid under the above conditions. For example, 0.0583 g. of finely divided thorium was treated as described above and 0.0579 g. or 99.3% was recovered unchanged.

The perchloric acid solution was analyzed for thorium and iodine. Found: Th, 0.3430 g. or 27.7% of the original sample; I, 0.4485 g. or 36.3% of the sample. Thus, 100.2% of the sample was accounted for, and the I/Th ratio in the perchloric acid-soluble fraction was 2.39. In strictly analogous experiments involving *initial* I/Th ratios of 2.0 and 3.0, the I/Th ratios found in the acid-soluble fractions were 2.42 and 2.60, respectively.

Separation of Thorium(III) Iodide.—Without prior separation of unreacted thorium, thorium(III) iodide was separated from the non-volatile reaction product as follows. Samples were treated with excess anhydrous liquid ammonia for 8 hr. at -33.5°, whereupon part of the solid dissolved and hydrogen was liberated. Following filtration, the ammonia-insoluble fraction was washed with ammonia and the solvent was evaporated.

In a representative experiment, the combined filtrate and washings yielded 2.33 g. of a white crystalline and *diamagnetic* solid; the recovery was substantially quantitative. *Anal.* Calcd. for $\text{Th}(\text{NH}_2)_3 \cdot 4\text{NH}_3$: Th, 33.9; I, 55.3; N, 9.3. Found: Th, 33.3; I, 54.7; N, 10.1. X-Ray diffraction data for this compound are given in Table I. On the basis of the weight of this product found, 37.4 cc. of hydrogen should have been liberated during the reaction of thorium(III) iodide with the solvent; found, 37.3 cc.

The ammonia-insoluble products were found to consist of elemental thorium and iodides of $\text{Th}^{<3+}$ and without exception to be paramagnetic. Thus for a typical sample, the susceptibility ($\chi_g = 4.54 \times 10^{-6}$) was found to be significantly greater than that of pure elemental thorium ($\chi_g = 1.92 \times 10^{-6}$). The elemental thorium was separated from a 2.0464-g. sample of this same product by the perchloric acid treatment described above. Found: Th, 1.7653 g. or 86.3% of sample. The perchloric acid solution was analyzed for thorium and iodine; found: Th, 0.1365 g. or 6.67%; I, 0.1218 g. or 5.95%; I/Th, 1.63; ammonia-insoluble product accounted for, 98.9%. In a series of experiments employing samples that correspond to *initial* I/Th ratios that were varied from 3 to 1, the I/Th ratios

found in the perchloric acid fractions from the ammonia-insoluble product ranged from 1.80 to 1.05.

Separation of Thorium(II) and Thorium(I) Iodides.—In a typical case, 0.8980 g. of the ammonia-insoluble portion (I/Th = 1.8) of the initial non-volatile reaction product was stirred with 5 ml. of *anhydrous* N,N-dimethylformamide for 1 hr.,¹⁰ filtered, and washed with 3-ml. portions of fresh solvent. The combined filtrate and washings was evaporated and the residue was dissolved in dilute nitric acid for analysis. *Anal.* Found: Th, 0.0605 g.; I, 0.0677 g.; I/Th = 2.04. In strictly analogous experiments, ratios of 1.97 and 2.09 were found.

For the analysis of the dimethylformamide-insoluble portion, a 0.6001-g. sample was treated with perchloric acid in order to separate elemental thorium by the procedure outlined above. Found: Th, 0.4576 g. or 76.3% of the sample. The perchloric acid solution was analyzed for thorium and iodine. Found: Th, 0.4576 g. or 12.8%; I, 0.0475 g. or 7.9%. I/Th = 1.13; dimethylformamide-insoluble product accounted for, 97.0%. Data obtained in independent experiments showed equally favorable material balances and I/Th = 1.09 and 1.13. The magnetic susceptibility of this product ($\chi_g = 3.01 \times 10^{-6}$) was found to be significantly greater than that of the parent ammonia-insoluble product ($\chi_g = 2.55 \times 10^{-6}$).

Oxidation of Iodides of $\text{Th}^{<3+}$ to Thorium(IV) Iodide.—By the methods outlined above, the ammonia-insoluble portion of a non-volatile initial reaction product was found to contain 77.9% elemental thorium, 10.8% thorium as iodides of $\text{Th}^{<3+}$, and 10.2% iodine. Accordingly, 0.9714 g. of this material was heated at 105° for 48 hr. with 2.2 g. of iodine (*i.e.*, 23% in excess of the weight required for complete conversion of the mixture to thorium(IV) iodide). The unreacted iodine was removed by fractional sublimation, the remaining yellow solid product¹¹ was treated with excess anhydrous liquid ammonia for 1 hr. at -33.5°, and the insoluble fraction was washed with liquid ammonia. The black ammonia-insoluble material was found to consist of *iodine-free* elemental thorium that was identified by means of its X-ray diffraction pattern. The ammonia-soluble product consisted of (only) white ammoniated thorium(IV) iodide that did not give a satisfactory X-ray diffraction pattern. Since other experiments showed that thorium(IV) iodide forms a series of ammoniates apparently analogous to the ammoniates of thorium(IV) bromide,¹² it was necessary to establish conditions leading to a reproducible composition. Thus, after 14 hr. at 10⁻³ mm., the 7-ammoniate was found to be the stable phase. *Anal.* Calcd. for $\text{ThI}_4 \cdot 7\text{NH}_3$: Th, 27.0; I, 59.1; NH₃, 13.9. Found: Th, 27.4; I, 59.1; NH₃, 13.9.

Properties of Thorium(IV) Amidotriiodide 4-Ammoniate.—This ammonobasic iodide is slightly soluble in water at room temperature and appreciably soluble in dilute acids. When heated or exposed to the atmosphere, the color of the salt changes from white to pale yellow, presumably owing to deammoniation. The stability of the 4-ammoniate at room temperature was demonstrated by measuring the loss of ammonia at 10⁻³ mm. over a period of 15 hr.; analysis of the residual solid showed that only 10% of the ammonia was lost.

The thermal decomposition of the amidoiodide *in vacuo* was studied as follows. For example, 2.1570 g. of the salt was heated at 10⁻³ mm. from 25 to 700° at the rate of 0.5°/min. Evolution of ammonia was first observed at 50°, nitrogen at 150°, and ammonium iodide sublimed out of the tube at 270°. Tests for hydrogen were negative. The solid residue consisted of a gray-green crystalline and paramagnetic solid ($\chi_g = 1.34 \times 10^{-6}$). *Anal.* Found: Th, 71.8; I, 24.4; qualitative tests for nitrogen were negative. Although the foregoing composition is reproducible, X-ray diffraction patterns for this and several similar products were both ill-defined and not strictly reproducible, but gave no evidence for the presence of thorium(IV) oxide.

Discussion

The results given above show that the formation of thorium(IV) iodide by direct union¹³ at 100° fol-

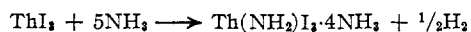
(10) The results obtained in this separation were uninfluenced by varying the contact time from 1 to 6 hr.

(11) In preliminary experiments it was found that the conversion of thorium to thorium(IV) iodide was incomplete under these conditions.)

(12) R. C. Young, *THIS JOURNAL*, **57**, 997 (1935).

lowed by reduction of the iodide with thorium at 550° results in a reaction mixture that contains unreacted thorium, ThI₄, ThI₃, and probably both ThI₂ and ThI. After removal of ThI₄ by sublimation, the successful separation of the remaining iodides from thorium by dissolution in perchloric acid solution permitted the direct establishment of I/Th ratios in the mixture of the three lower iodides. Thus, as the original I/Th ratio was progressively decreased from 3 to 1, the ratios found for the corresponding lower iodides decreased from 2.60 to 2.39. At the same time, the magnetic susceptibility increased and this is strongly suggestive of increasing ThI content since this component is the only one likely to contribute to enhanced paramagnetism. Further evidence for the progressively increasing lower iodide content (and decreasing ThI₃ content) resulted from the study of the reactions employed to separate ThI₃.

Without prior separation of thorium from the initial non-volatile reaction product, ThI₃ was separated by virtue of its reaction with liquid ammonia



As the I/Th ratio in the initial reactions was decreased, the volumes of hydrogen liberated when the non-volatile products were treated with liquid ammonia also decreased, thus indicating a decreased ThI₃ content and increased quantities of the iodides of Th^{<3+}. The fact that ThI₃ was found only in the non-volatile product does not support either the statement by Anderson and D'Eye⁴ that this iodide is appreciably volatile or the report by Hayek, *et al.*,³ that this iodide disproportionates over the temperature range 500–600°. Although the properties of thorium(IV) amidotriiodide 4-ammoniate were not studied extensively, it was found that its thermal decomposition yields ammonia, nitrogen, ammonium iodide, and a paramagnetic non-volatile residue that did not contain nitrogen. While reproducible, the

composition of this non-volatile residue does not correspond satisfactorily to any simple iodide of thorium but most nearly approximates Th₃I₂. In view of the fact that the paramagnetism of thorium and thorium compounds cannot be interpreted simply on a spin-only basis,¹³ it is probably entirely fortuitous that, assuming the formula Th₃I₂, the measured moment corresponds to 1.74 B.M.

The ammonia-insoluble fraction of the non-volatile reaction product was found to consist of unreacted thorium and iodides of Th^{<3+}, as evidenced by I/Th ratios determined after dissolving the lower iodides in perchloric acid. Again, the paramagnetism of these ammonia-insoluble solids increased as the I/Th ratio in the perchloric acid-soluble fraction approached unity. It was also demonstrated that these lower iodides are completely oxidized to ThI₄ upon reaction with iodine. In view of the numerical values for I/Th ratios and the trend that they exhibit as a function of the I/Th ratios in the original reactions, it must be concluded that ThI₂ and ThI are both present, although the possibility of the presence of structurally more complex iodides is not precluded. This conclusion is supported strongly by the I/Th ratios found for the two iodide fractions isolated by means of the dimethylformamide separation described above. For three independent experiments for which data on both fractions and satisfactory material balances were obtained, the respective compositions were ThI_{2.03} and ThI_{1.12}.

Finally, it should be noted that the importance of the lower oxidation states of thorium in relation to its status as a member of the actinide series has been discussed by Warf.²

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(13) For example, although the thorium atom presumably contains two unpaired electrons, the measured moment of the thorium used in these experiments amounts to only 1.03 B.M. In agreement with expectations, the thorium(IV) halides are diamagnetic, but the only lower halide likely to be diamagnetic would be a covalent thorium(II) halide. See also: P. W. Selwood, "Magnetochemistry," Second Edition, Interscience Publishers, Inc., New York, N. Y., 1956.