38.2	2.7
74.6	0.4
229	.02

The method of graphical resolution is not very accurate and the distinction between a radius of 21.2 and 18.8 Å. cannot be considered as significant. It thus appears that about 90% by weight of the material consists of particles of radius 18.8 to 21.2 Å. Electron micrograph studies have revealed this carbon black to be particles of about 20 Å. radius clumped to form aggregates of about 120 Å. Surface and measurements carried out by gas adsorption indicate a particle size of 19 Å. radius.

Acknowledgment.—We wish to thank Dr. James Hillier of the R. C. A. Laboratory for the electron micrographs of colloidal gold and carbon black.

PRINCETON, N. J. RECEIVED NOVEMBER 25, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Chemistry of Scandium.[1] I

BY LEWIS POKRAS AND PETER M. BERNAYS[1a]

A new insoluble, non-volatile compound of scandium, $Sc(C_9H_6ON)_3 \cdot C_9H_7ON$, has been prepared by the reaction of 8-hydroxyquinoline (oxine) with an aqueous solution of $Sc(ClO_4)_3$ at pH 7.5. This lemon-yellow compound is unstable on prolonged heating. However, no indication of the formation of $Sc(C_9H_6ON)_3$ has been found. It is suggested that the extra molecule of oxine is held by molecular forces. A similarity in chemical behavior between thorium and scandium is suggested.

A rigorous classification of scandium ($Z = 21$) has never been given in the literature. Hopkins[2] includes scandium in the general term "rare earths," elements closely related chemically, which are placed in Division A of Group III. Yost[3] does not include scandium in the term rare earth, which he defines as a group of chemically similar elements, occurring between barium (Group II) and hafnium (Group IV). In the course of an investigation to determine the chemical nature of scandium ions in solution, it became necessary to devise a quantitative method having a small gravimetric factor, for the determination of scandium. (The analytical aspects of this problem will be described elsewhere.) In this connection an attempt was made to use 8-hydroxyquinoline (oxine) as a precipitant, since this compound had previously been used for several trivalent elements, including aluminum, gallium and indium.[4] The most frequently found compounds of oxine with transition elements are those in which each oxine satisfies one covalent and one coördination bond, *i. e.*, $Al(On)_3$ (HOn will be used as symbol for the free oxine, and On^- for the oxinate anion). In a few cases, an additional molecule of oxine may enter the compound, *i. e.*, $Th(On)_4 \cdot HOn$.[5]

Experimental

Materials.—All materials used herein were C. P. grade, and unless otherwise stated were used as commercially available with no further purification.

Scandium Perchlorate.—Scandium oxide purchased from the Var-Lac-Oid Corp., 116 Broad Street, New York, was dissolved in concd. $HClO_4$, and purified to remove rare earths and calcium by the buffered pyridine,[6] followed by the basic tartrate[7] method. A weighed amount of the purified oxide was then dissolved in a minimum of 0.5 N $HClO_4$ and diluted to volume.

Preparation of $ScOn_3 \cdot HOn$.—10.0 ml. of 0.02471 N $Sc(ClO_4)_3$ solution was diluted to 110 ml., 5 drops of 0.005% aerosol in water was added, and the solution was heated to 75°. Ten ml. of HOn in 2 N NH_4OAc was added, followed by the addition with stirring of 45 ml. of a buffer made by mixing 30 ml. of 2 N NH_4OAc with 15 ml. of 2 N NH_4OH. After standing, with occasional stirring, for 2 hours, the lemon-yellow precipitate was filtered through a sintered-glass crucible, washed with a minimum quantity of distilled water at room temperature, and heated to constant weight at 110° to remove free HOn which is always associated with the compound. When thus prepared the melting point is 195–197°.

Anal.[8] Calcd. for $Sc(C_9H_6NO)_3(C_9H_7NO)$: C, 69.43; H, 4.05; N, 9.00; Sc_2O_3 as ash, 11.09. Found: C, 69.47; H, 4.30; N, 8.74; Sc_2O_3 as ash, 11.36.

In order to establish the thermal stability of the new compound, a freshly prepared sample contaminated with excess HOn was heated at various temperatures up to 165° for a total of 898 hours. At intervals throughout this period the mass of the sample was determined. Results are indicated in Table I and in Fig. 1.

The solubility of the new compound $Sc(On)_3 \cdot HOn$ in H_2O is extremely low. This can be shown by testing for residual Sc^{+++} ions in solution after precipitation of $Sc(On)_3 \cdot HOn$ as described above. Using cochineal,[9] a reagent known to be sensitive to 1 part in 50,000, no Sc^{+++} ions could be found in the combined mother liquors of six precipitations, even on concentration of the filtrates to *ca.* 25 ml.

The non-volatility of scandium oxinate and its insolubility in water was proven as follows: $Sc(On)_3 \cdot HOn$ was prepared as described above, utilizing a known quantity of Sc_2O_3. The scandium content of the oxinate was then determined using the basic tartrate method[7]: taken as Sc_2O_3, 0.0684 g.; found as Sc_2O_3, 0.0687 g. Since the amount of scandium oxide recovered is equal to that taken,

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[1] Part of a paper presented at the Detroit Meeting of the American Chemical Society, April 18, 1950.

[1a] Southwestern Louisiana Institute, Lafayette, La.

[2] B. S. Hopkins, "Chapters in the Chemistry of the Less Familiar Elements," Stipes Publishing Co., Champaign, Ill., 1938, Chapter 6, p. 2.

[3] D. M. Yost, H. Russell, Jr., and C. S. Garner, "The Rare-Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 1.

[4] R. Berg, "Die analytische Verwendung von o-Oxychinolin (Oxin) und Seiner Derivate," 2nd revised edition, F. Enke, Stuttgart, 1938, p. 3.

[5] F. J. Frere, THIS JOURNAL, **55**, 4362 (1933).

[6] E. A. Ostroumov, *Zhur. Anal. Khim.*, **3**, 153 (1948). See also *C. A.*, **42**, 7655[e] (1948).

[7] R. Fresenius and G. Jander, "Handbuch der Analytischen Chemie," Springer, Berlin, 1940–1942, Part III, p. 734.

[8] Performed by the Micro-Tech Laboratory, Skokie, Illinois.

[9] P. E. Wenger and R. Duckert, *Helv. Chim. Acta*, **28**, 872 (1945).

TABLE I

LOSS OF WEIGHT OF $Sc(On)_3 \cdot HOn$ ON HEATING (MEAN OF THREE DETERMINATIONS)

Time of heating, hr.	Time, hr.	Temp., °C.	Sample wt., g.[a]
16.5	16.5	Room, desicc.	0.1586
46.5	63.0	Room, desicc.	.1588
5.5	68.5	110	.1543
17.5	86.0	110	.1536
23.25	109.3	135	.1462
8.0	117.3	135	.1449
15.5	132.8	165	.1315
4.5	137.3	165	.1302
18.5	155.8	165	.1187
25.5	181.3	165	.1060
45.25	226.5	165	.0931
23.75	250.3	165	.0871
23.75	274.0	165	.0829
23.25	297.3	165	.0797
23.5	320.8	165	.0752
26.25	347.0	165	.0736
44.75	391.8	165	.0691
30.5	422.3	165	.0661
66.25	488.5	165	.0629
74.5	563.0	165	.0612
335.0	898.0	165	.0531

Mean deviation three samples 2.1%

[a] Theoretical weight for $ScOn_3 \cdot HOn$, 0.1543 g.; for $ScOn_3$, 0.1183 g.; for Sc_2O_3, 0.01712 g.

no material could have been lost by solubility in water or by volatilization.

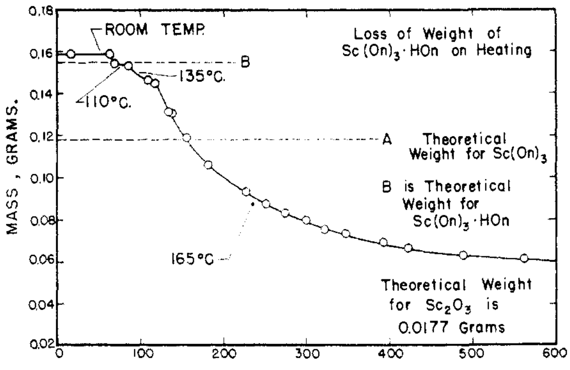

Fig. 1.

Scandium oxinate is very soluble in 2 *N* HCl, 6 *N* HOAc and the common organic solvents such as benzene, toluene, chloroform, carbon tetrachloride, dioxane, acetone, methanol and ethanol. The absorption spectrum of the compound in $CHCl_3$ and toluene has been studied, using a Beckman ultraviolet spectrophotometer and quartz absorption cells. Absorption maxima are found at 373 and 320 mμ in both solvents. However, the 320 mμ maximum appears to coincide with the absorption maximum of pure HOn in these solvents.

X-Ray powder diffraction examination, using a G. E. powder camera, and CuK_α radiation, of a number of preparations of the new compound made under slightly different conditions show that there is no free HOn nor any Sc_2O_3 detectable in any preparation studied.

Discussion

From elementary analysis and the further considerations described below no other formula than $ScOn_3 \cdot HOn$ can be written for the newly prepared compound, unless one considers extremely complicated polynuclear coördination compounds. One other possibility is that the compound should be written $H[Sc(On)_4]$. Berg[10] has shown that a mercury oxinate compound exists, in which the metal is in the anion. The compound $HgOn \cdot 2H_2O$ forms a silver salt $Ag_2[Hg(On)(OH)_2]$. To accept such a suggestion for the scandium compound would require that the coördination number of scandium be taken as 8. Since the ionic radius of scandium is 0.81 Å.,[11] such a coördination number is unlikely. In addition, many compounds of scandium can be explained on the assumption of a coördination number of 6, but these compounds do not fit an assumed coördination number of 8. Further, since $H[Sc(On)_4]$ is an acid, one would expect it to be considerably more soluble in water and less soluble in organic solvents than is the case.

The data on loss of weight on heating show no discontinuity at the point corresponding to a composition $Sc(On)_3$. This composition is what one would expect by an analogy with indium, gallium or aluminum. It can be concluded, therefore, that $Sc(On)_3 \cdot HOn$ is a molecular addition compound which is stable with respect to decomposition into $Sc(On)_3$ and HOn. In fact continued heating of $Sc(On)_3 \cdot HOn$ at 100° does not bring about a change in weight of the sample, therefore there is no decomposition of the sample.

It has been shown that the extra molecule of HOn is firmly held in the newly prepared molecular addition compound. It has also been demonstrated that such HOn is probably not in the coördination sphere of the scandium atom. It must therefore be held by as yet unexplained forces, as is the case in the analogous thorium,[5] uranium[5] and plutonium[12] compounds. A survey[4] of those elements which form precipitates with 8-hydroxyquinoline shows that the three elements just listed, and no other (except antimony, which forms a very unusual oxinate: $SbOOn \cdot HOn$) add a molecule of HOn in this way.

Of the three elements, thorium, uranium or plutonium, which give molecular addition compounds with oxine, thorium is the most common and most readily available. It might be fruitful therefore to compare in detail the reactions of Sc^{III} and Th^{IV} toward the various reagents which have been suggested for the qualitative and quantitative detection of scandium. While it must be admitted that many other ions exhibit close similarities to Sc^{III} in some properties, it is to be noted that the similarities in chemical properties between scandium and thorium are especially striking.

With cochineal,[13] and with carminic acid, which is the active agent in cochineal, Th^{IV} and Sc^{III} give essentially identical reactions. It is interesting to note that tests in this Laboratory have shown that, under similar conditions, the cerite earths La^{III} and Nd^{III} do not interfere.

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(10) R. Berg, *J. prakt. Chem.*, **115**, 181 (1927); *cf.* ref. 4.

(11) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1945, p. 346.

(12) B. G. Harvey, H. G. Heal, A. G. Maddock and E. B. Rowley, *J. Chem. Soc.*, 1010 (1947).

(13) G. Charlot, *Anal. Chim. Acta*, **1**, 218 (1947).

The microcrystalline test employing $[Co(NH_3)_6](NO_3)_3$ and sodium fluoride[9] is also given by both Sc^{III} and Th^{IV}.

The reagent suggested by Kuznetsov[14]—the Schiff base of *o*-aminophenylarsonic acid and salicylaldehyde—which gives a yellow color in the presence of Sc^{III} is just as satisfactory as a test for Th^{IV}.

With Morin[15] Sc^{III} gives a green fluorescence in ultraviolet light. Th^{IV} is also reported to give fluorescence, but weaker than that of Sc^{III}. Beck[15] also recommended sodium alizarin sulfonate as a reagent for Sc^{III} but did not mention Th^{IV} in this connection. Tests have shown that Th^{IV} gives the same crimson to violet color, and (on standing) violet precipitate, as does Sc^{III}.

With murexide[16] (ammonium purpurate) Sc^{III} gives a purple to yellow color change. Th^{IV} gives the same test, except in the presence of sulfate ion. However the addition of nitrilotriacetate, $N(CH_2COOH)_3$, to the Sc^{III} system regenerates the color of the reagent, indicating that the $Sc–N(CH_2COOH)_3$ complex is more stable than the murexide complex. The latter reaction does not occur for Th^{IV}.

Acknowledgment.—The work described herein was supported in part by a Frederick Gardner Cottrell Grant from the Research Corporation, whose financial assistance is gratefully acknowledged.

[14] V. I. Kuznetsov, *J. Gen. Chem.* (*U. S. S. R.*), **14**, 897 (1944).

[15] G. Beck, *Mikrochim. Acta*, **2**, 9 (1937).

[16] G. Beck, *Anal. Chim. Acta*, **1**, 69 (1947).

CHICAGO 16, ILL. RECEIVED APRIL 26, 1950

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Anion Exchange Studies. I. Separation of Zirconium and Niobium in HCl–HF Mixtures[1]

BY KURT A. KRAUS AND GEORGE E. MOORE

The specificity of anion exchange resins for negatively charged ions suggests their use for studies of negatively charged complexes of metal ions and for separations of metals which form such complexes. Anion exchange resins should be particularly useful with metal ions which would precipitate if not complexed (*e. g.*, 4th and 5th group elements), where cation exchange resins could not be used to full advantage. This paper, which deals with the separation of zirconium and niobium, is the first one of a series[2] dealing with these two groups of elements. Although the studies were restricted to HF–HCl mixtures it is expected that similarly effective separations could be attained with other complexing agents.

Experimental

Columns, Column Operation, Materials.—The adsorption columns were constructed of "Transflex" tubing with cross-sectional area *ca.* 0.03 sq. cm., as determined by weighing a column of water of known length. The resin used was Dowex-1, a "strong-base," quaternary amine polymer of mesh size 200–230 as obtained by wet screening. Only the chloride form of the resin was used. The eluent was contained in 50-ml. bakelite burets and the height of the liquid column was occasionally adjusted to maintain approximately the desired flow rate. It was not attempted to maintain constant flow rates. Instead, the volume of eluent which had passed was determined from the buret readings at frequent intervals.

In most cases the zirconium and niobium were added in a small volume to a column which had previously been equilibrated with the desired acid mixture. The added solution was of approximately the same composition as the solution in the column and the eluent. In a few cases the additions were carried out with the column liquid at a composition to cause strong adsorption, and the material was then eluted by changing the composition of the eluent.

The experiments were carried out with tracer zirconium (Zr^{95}, β-emitter $T_{1/2}$ = 65 d.)[3] and tracer niobium (Nb^{95}, β-emitter, $T_{1/2}$ = 35 d.),[3] which were obtained by neutron bombardment of spectroscopically pure zirconium metal[4] in the ORNL reactor.[5] The metal was dissolved in HF–HCl mixtures. Since Nb^{95} is the daughter of Zr^{95}, it was "carrier-free" while by necessity some inactive zirconium was present (*ca.* 0.5 mg. per experiment). The experiments were carried out in a thermostated room at 25 ± 1°. C. P. chemicals were used throughout.

Analytical Procedures. Direct Scanning of Columns.—The data were obtained through continuous monitoring of the activity of the effluent,[6] and through direct scanning of the columns with a detector to locate the activities (bands) and determine their elution rates. After elution identity of the tracers was established through standard radiochemical assays.

The determination of elution rates by scanning offers a number of advantages over the method of continuous monitoring of the effluent. Thus the elution of a previously identified activity can be determined rapidly and with relatively high precision, since the bands in general are quite sharp. Except in the most unfavorable cases a precision of better than 10% is attainable with the band moving through less than 1 cm. of column. Thus considerable time can be saved particularly when the elution rate of a material is unknown and when the optimum length of the column cannot be predicted. It is possible to measure elution rates of several activities at the same time and under identical conditions. Furthermore, the same band (or series of bands) can be studied under a variety of eluting conditions by changing the composition of the

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[1] This document is based on work performed for the Atomic Energy Commission at Oak Ridge National Laboratory.

[2] In two earlier communications (K. A. Kraus and G. E. Moore, THIS JOURNAL, **71**, 3263, 3855 (1949)) the method was shown to be successful for the separation of zirconium and hafnium, and niobium and tantalum. Since then the zirconium-hafnium separation was confirmed by E. H. Huffman and R. C. Lilly (*ibid.*, **71**, 4147 (1949)).

[3] Information from "Table of Isotopes," by G. T. Seaborg and I. Perlman, *Rev. Mod. Phys.*, **20**, 585 (1948).

[4] The only appreciable impurity was hafnium. It yields Hf^{181} (β-emitter, $T_{1/2}$ = 46 d.[3]) on bombardment. In most cases its behavior was very similar to zirconium and, as a first approximation, all results for zirconium also apply for hafnium. Details for their separation will be given in a later paper. Since in most cases discussed here relative enrichment of zirconium and hafnium was not determined, the uncertainty in the reported elution constants for Zr is relatively high.

[5] For some of the earlier work fission product Nb^{95} was used which was kindly furnished us by W. H. Baldwin and co-workers who isolated it from fission product mixtures.

[6] K. A. Kraus and G. E. Moore, THIS JOURNAL, **72**, 4293 (1950).