Scandium Oxalate and its Ammine Complexes.

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The preparation and solubilities are given of scandium oxalate with 3, 6, and 18 mols. of water of crystallisation. Absorption by scandium oxalate of water vapour, carbon dioxide, and ammonia is described. Adsorption of ammonia leads to the formation of $[Sc(NH_3)_6]_2(C_2O_4)_3$ complexes by replacement of co-ordinated water. The formation of anionic scandium oxalate complexes in solution is described.

SCANDIUM OXALATE can be obtained from solutions of scandium salts by the addition of oxalic acid but precipitation is never complete. Although its solubility in water has been confirmed as *ca.* 60 mg./l. (Fischer and Bock, *Z. anorg. Chem.*, 1942, **249**, 146) scandium oxalate does not appear to be precipitated from solutions containing <1·5 g. of Sc^{3+} per litre. Supersaturation may be partly responsible, but the relatively great solubility of scandium oxalate in acid and alkaline media, and in those containing alkali or ammonium ions, must be attributed to the extensive formation of complexes.

No crystallographic observations have appeared on scandium oxalate, but isomorphism with lanthanon oxalates is to be expected and the numerous hydrates reported suggest the existence of " interstitial " forms similar to those observed by Wylie for the lanthanons (*J.*, 1947, 1687). Minor quantities of alien ions grossly affect the nature of the precipitated oxalate (Sterba-Bohm and Skramowsky, *Coll. Czech. Chem. Comm.*, 1929, **1**, 1) and these, together with adsorbed ammonia and carbon dioxide (see below), may in part account for the various degrees of hydration reported. Scandium oxalate hexahydrate is readily prepared by precipitation from 5% solutions of scandium at *ca.* 60° (Klein and Bernays, *J. Amer. Chem. Soc.*, 1951, **73**, 1364), but absorption of ammonia or carbon dioxide by the oxalate has to be avoided. Klein and Bernays, and Sterba-Bohm and Skramowsky (*locc. cit.*) took pains to avoid such contamination without apparently appreciating the extent to which these gases are absorbed by scandium oxalate (see below). In an inert atmosphere, at temperatures up to *ca.* 90°, the hexahydrated oxalate is normally precipitated. An 18-hydrate has, however, been obtained by prolonged boiling of an oxalate suspension, whilst a trihydrate has been obtained by precipitation at 8°. On an oxide basis, water solubilities of these hydrates show insignificant variations from the confirmed data for the hexahydrate of Fischer and Bock, and Sterba-Bohm and Skramowsky (*locc. cit.*).

Data on the solubility of scandium oxalate were variously reported by Meyer and his co-workers (*Z. anorg. Chem.*, 1910, **67**, 398; 1914, **86**, 9) and Wirth (*ibid.*, 1914, **87**, 9), but the scandium employed by these early workers was somewhat adulterated by thorium. Solubilities now obtained for pure scandium oxalate are presented in the Table.

Solubility of scandium oxalate.

Solvent	Temp.	Hexahydrate	G./l. (as oxide)	Solvent	Temp.	Hexahydrate	G./l. (as oxide)
Water ...	25°	0·20	0·060	10% HNO_3	25°	27·4	8·17
			(trihydrate) 0·060	20%	25	58·2	17·36
			(18-hydrate) 0·061	10%	50	110·0	32·8
1% HCl	25	1·39	0·413	5% H_2SO_4	25	2·88	0·861
10%	25	25·25	7·54	15%	25	32·5	9·73
20%	25	46·5	13·87	5%	50	23·6	7·05
15%	60	72·4	21·6				

The influence of pH, alkali, and ammonium ions upon precipitation of scandium oxalate from M-scandium chloride solution is shown in Fig. 1. The ultimate upward trend of the alkali curve is attributed less to the precipitation of oxalate than to the precipitation of hydroxide, basic salts, or alkali scandium oxalate.

FIG. 1. *Recovery of* $Sc_2(C_2O_4)_3$ *at* pH *values varied by addition of* (*A*) NaOH, (*B*) *aqueous ammonia.*

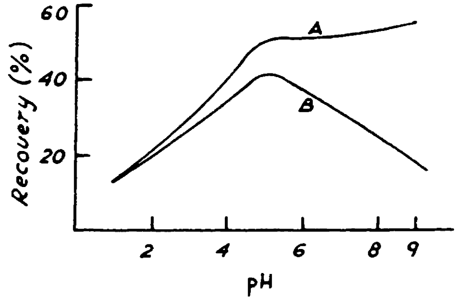
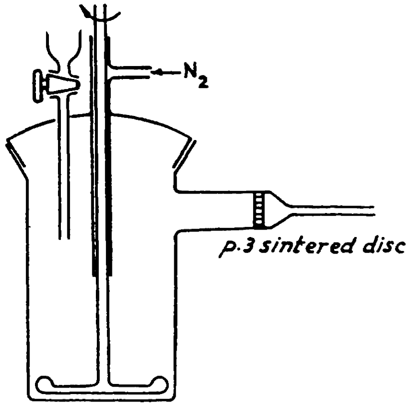


FIG. 2. *Apparatus for preparation of scandium oxalate in an inert atmosphere.*



Although earlier workers have been unable to agree upon the composition of various alkali scandium oxalates, available data support Wirth's suggestion (*ibid.*, p. 1) that in oxalate solution scandium forms an anionic complex of the type $[Sc(C_2O_4)_3]^{3-}$. Iron and aluminium form similar complexes, but Crouthamel and Martin (*J. Amer. Chem. Soc.*, 1950, **72**, 1382), in studying ytterbium oxalate complexes, decided that, whilst $[Yb(C_2O_4)_3]^{3-}$ was not formed in significant quantities, the complex necessarily carried a negative charge. Apart from variation of valency, many of the properties of scandium and ytterbium are closely analogous and it is to be expected that this may extend somewhat to the oxalates and their complexes. Experiments with ion-exchange resins give evidence for the formation of complex anions containing scandium and oxalate ions in the ratios 1 : 2·8 at pH 6·1 and 1 : 1·32 at pH 8·6, but insufficient additional results are available for further characterisation of the complexes.

Little attention appears to have been paid hitherto to the affinity of scandium oxalate for water vapour, ammonia, and carbon dioxide. Anhydrous scandium oxalate absorbs moisture quite readily, to form the trihydrate, but then, as with the 6- and the 18-hydrate, the oxalate is no longer deliquescent. Adsorption of carbon dioxide occurs only when the oxalate is moist; no definite composition levels appear to be reached, but 6% of carbon dioxide appeared to be the limit of adsorption, *i.e.*, $Sc^{3+} : C_2O_4^{2-} : CO_2 = 6 : 9 : 1$. Fischer and Bock (*loc. cit.*) attributed the solubility of scandium oxalate in various solutions to the presence of carbonate ions; carbonated oxalates show a slight increase in solubility over normal oxalates, but the effect is much less than that with ammoniated oxalates.

When a small quantity of moist scandium oxalate hexahydrate, freshly precipitated in an inert atmosphere, is exposed to a large volume of ammonia vapour at *ca.* 25°, an anhydrous ammino-compound is formed containing scandium, ammonia, and oxalate ions in the ratio 2 : 12 : 3, *i.e.*, equivalent to $[Sc(NH_3)_6]_2(C_2O_4)_3$. This has close analogy to the ammino-compounds reported in the preceding paper, and can be construed as replacement of co-ordinated water by ammonia molecules.

Dry ammonia vapour is not absorbed by dry scandium oxalate, but the introduction of water vapour into the system immediately initiates exothermic reaction. Anhydrous oxalate in moist ammonia vapour absorbs 12 mols. of ammonia per mol. of oxalate. The 3- and the 18-hydrate, either moist or in a moist atmosphere, absorb ammonia up to the same level giving respectively anhydrous and 12-hydrated ammines.

Adequate determination of heat of ammination was prevented by lack of facilities, but, apart from qualitative tactile indications, a temperature rise of 10° was noted in one case of ammination of the anhydrous oxalate.

The great influence of ammonium ions upon the solubility of scandium oxalate (see above) was paralleled by the solubility of the solid ammine oxalates in water. Hexahydrated scandium oxalate, precipitated in an inert atmosphere and ammoniated whilst still moist on the filter, was readily soluble in cold water, giving a neutral solution. When heated, the solution decomposed with evolution of ammonia and precipitation of hexahydrated scandium oxalate. Similar decomposition occurred on the addition of sodium hydroxide.

The affinity of scandium oxalate for ammonia diminishes somewhat with age. This is particularly so with the anhydrous and hexahydrated salts, but rejuvenation is easily affected by boiling the oxalate in water for a short time.

Ammination of scandium oxalate throws additional light on the nature of its hydrates. Co-ordination of six ammonia molecules to one scandium ion by the obvious displacement of 6 mols. of water can only mean that the latter were previously co-ordinated to the scandium and were neither interstitial in nature nor mere attributes of crystal formation. No displacement of unco-ordinated water occurs, as shown by ammination of the 18-hydrate, so the probability is increased that twelve water molecules in the 18-hydrate are present interstitially.

The presence of moisture as a prerequisite to ammination even of the hydrated oxalate represents but a further example of aquo-catalysis.

EXPERIMENTAL

The scandium was that derived from wolframite residues and thortveitite as described by Vickery (*J.*, 1954, 245). "AnalaR" oxalic acid was recrystallised once before use. Other reagents were of similar standard. Nitrogen, carbon dioxide, and ammonia were all of normal cylinder quality and were dried before use.

Precipitation and filtration of scandium oxalate in an inert atmosphere was effected in the apparatus shown in Fig. 2. Early attempts to influence the degree of hydration by variation of concentration of reagents were unsuccessful but did show the minimum concentration of scandium which could be precipitated by oxalic acid to be 1·5 g./l.

Oxalate solubilities in the media given in Table 1 were obtained by sealing 0·5 g. of oxalate in a glass tube with 15—20 ml. of solvent. The sealed tubes were shaken continuously in a thermostat for 3½ days, then left stationary in the thermostat for 1½ days. Before the tubes were opened the residual oxalate was centrifuged at high speed for 30 min. 10 ml. of solution were cautiously evaporated to dryness in a weighed platinum dish under infra-red lamps, and the residue was moistened with 1—2 drops of sulphuric acid, re-evaporated, ignited at 1200° for 30 min., and weighed. Oxide weights were converted back into the appropriate oxalate hydrate.

Data for the curves in Fig. 1 were obtained by igniting and weighing as oxide the scandium oxalate precipitated from solutions containing quantities of scandium under the conditions given.

The anionic nature of the oxalate complex in solution was observed by equilibrating portions (50 ml.) of scandium oxalate solution with 10 g. each of Dowex-50 resin (hydrogen form) and Amberlite IRA-400 resin (chloride form). Negligible adsorption of scandium occurred on the cation-exchange but 82% was taken up by the anionic-exchange resin. A short series of experiments was then made in which 200-ml. portions of scandium oxalate solution each containing 200 mg. of Sc_2O_3 [668 mg. of $Sc_2(C_2O_4)_3,6H_2O$] were adjusted, by addition of sodium hydroxide solution, to pH 6—8. These were then shaken for 24 hr. with Amberlite IR-100 resin (50 g.); the resin was filtered off and washed with cold distilled water, and the scandium oxalate complex leached out with 5% sulphuric acid (200 ml.). The scandium content of this eluate was determined by direct evaporation and ignition; oxalate was determined by permanganate titration. Results (mg./200 ml. of eluate) were:

pH	6·1	6·9	7·5	8·0	8·6
Sc_2O_3	164	153	174	163	182
$H_2C_2O_4$	306	231	218	165	160
$Sc_3^+ : C_2O_4^{2-}$	1 : 2·8	1 : 2·25	1 : 1·87	1 : 1·51	1 : 1·32

Adsorption of ammonia by moist scandium oxalate was first observed during metathesis by sodium hydroxide of a scandium oxalate precipitate which had remained for several hours on a filter paper in the laboratory atmosphere. When the oxalate was reconstituted with water and the alkali added, an odour of ammonia was noticed. Subsequently ammination of the oxalate was effected by passing ammonia gas through a slurry of the oxalate or over a thin layer of moist oxalate held in a flat Vitreosil dish.

For the preparation of the anhydrous ammine *oxalate*, the hexahydrated oxalate was first precipitated and filtered off under nitrogen (apparatus: Fig. 2). The nitrogen flow was then replaced by ammonia. Dehydration of the scandium oxalate filter cake was rapid and obvious. After 15 minutes' ammoniation, nitrogen was passed through the apparatus which was then opened and the solid ammino-oxalate extracted. Ammonia in the solid was determined by treatment with alkali and absorption of the liberated ammonia in standard acid. Scandium was determined by direct ignition to oxide, and oxalate by permanganate titration in acid solution {Found: Sc_2O_3, 25·2; $(C_2O_4)^{2-}$, 47·0; NH_3, 36·1. $[Sc(NH_3)_6]_2(C_2O_4)_3$ requires Sc_2O_3, 24·6; $(C_2O_4)^{2-}$, 47·3; NH_3, 36·6%}. The 3- and the 18-oxalate hydrates prepared as indicated above were ammoniated by passing ammonia over samples of these hydrates in Petri dishes in a larger glass container. After 4 hours' exposure, samples gave analyses: 3-*Hydrate:* Sc_2O_3, 24·9; $(C_2O_4)^{2-}$, 47·0; NH_3, 36·2. $[Sc(NH_3)_6]_2(C_2O_4)_3$ requires Sc_2O_3, 24·6; $(C_2O_4)^{2-}$, 47·3; NH_3, 36·6. 18-*Hydrate:* Sc_2O_3, 17·5; $(C_2O_4)^{2-}$, 34·0; NH_3, 26·7; loss on ign., 82·5. $[Sc(NH_3)_6]_2(C_2O_4)_3,12H_2O$ requires Sc_2O_3, 17·8; $(C_2O_4)^{2-}$, 34·1; NH_3, 26·4; loss on ign., 82·2%.

Ammination of anhydrous scandium oxalate was effected by first dehydrating the trihydrate at 150° for 18 hr. and then passing over the solid a stream of ammonia obtained by blowing carbon dioxide-free air through carbon dioxide-free ammonia solution and then over the oxalate. A thermometer in the body of the anhydrous oxalate showed a rapid rise in temperature of the solid (20 g.) from 18° to 28° in the first five minutes of ammoniation; thereafter the temperature decreased throughout the ammination.

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