961. *Water-soluble Complexes of Niobium (Columbium) and Tantalum. Part I. Complexes with α-Hydroxy-acids and (2-Hydroxyethyl)-amines.*

By Fred Fairbrother and John B. Taylor.

The solubility of niobic acid and tantalic acid in the α-hydroxy-acids glycollic, lactic, malic, and citric has been studied and solid 1 : 1 complexes isolated. The complexes are only stable in aqueous solution in the presence of excess of α-hydroxy-acid. No dissolution was observed in solutions of the dibasic acids malonic, succinic, adipic, or phthalic.

The solubility was also studied in the (2-hydroxyethyl)amines (" ethanolamines ") and polynuclear species were isolated.

Pure tantalic acid is much less soluble than pure niobic acid in all these complex-forming agents. Even where the solubility ratio is very great, however, there is no satisfactory separation by differential solubility of the coprecipitated acids.

The insolubility of the oxides of niobium (columbium) [1] and tantalum [2] in all common acids were among the first properties of these elements to be observed. In the 150 years since their discovery, few water-soluble compounds other than the complex fluorides [3] have been reported, and these mostly only in solution. The only ones that have received any measure of systematic examination have been the complexes with oxalic and tartaric acids, and of the composition and manner of formation of these there still exists some doubt. So far, no water-soluble cationic species of these elements, simple or complex, has been discovered. Russ [4] in 1902 reported that hydrated niobium oxide was soluble in oxalic acid and claimed to have prepared a complex oxalate $Nb(HC_2O_4)_5$ by the dissolution of the hydrated oxide in an excess of oxalic acid and also, by the reaction of oxalic acid with alkali niobates, a series of crystalline salts of the empirical formula $Nb_2O_5,3M^1{}_2O,6C_2O_3,xH_2O$. This formula would correspond to $M^1{}_3[Nb(C_2O_4)_3O],xH_2O$ implying a niobium co-ordination number of 7 but could equally well be written $M^1{}_3[Nb(C_2O_4)_3(OH)_2],(x-1)H_2O$ with a more symmetrical co-ordination number of eight.

In an appendix Russ stated that an attempt to prepare the corresponding oxalate–tantalum salts led to precipitation of the hydroxide, and solutions containing $Ta_2O_5,5M_2O,10C_2O_3$. The oxalate complex of tantalic acids was also found to be more easily decomposed by weak bases. Britton and Robinson [5] carried out conductometric and potentiometric titrations of alkali niobate and tantalate solutions with acids chosen chiefly for their varying strengths and found that, whilst strong and moderately strong acids precipitated the hydroxides readily, oxalic, lactic, tartaric, and malic acids retained the oxides in solution. They concluded from their experimental results that lactic acid does not appear to form complex lacto-niobic or -tantalic acids and that complex formation, as shown by the ability to hold these relatively insoluble oxides in clear solutions, is not confined to hydroxy-acids. In this connection oxalic acid was mentioned as a non-hydroxy-acid " in which the dissolution is probably of a colloidal nature." We shall show later that it is just this property of behaving as a hydroxy-acid which gives to oxalic acid its strong complex-forming power, and that the solutions therein of the hydroxides are not colloidal.

Edminster and Albritton,[6] by evaporation of a solution of freshly precipitated niobium hydroxide in tartaric acid, claimed to have obtained a crystalline compound $(C_4H_4O_6)_2NbOH$, *i.e.*, with two molecules of tartaric acid associated with each niobium atom, to which they ascribed the formula (I), the niobium having its normal co-valency of five. Such a formula would imply four replaceable hydrogen atoms.

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[1] Hatchett, *Phil. Trans.* 1802, 49.

[2] Ekeberg, *Svensk Vet. Akad. Handl.*, 1802, **23**, 180.

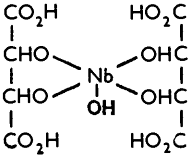
[3] Marignac, *Ann. Chim. Phys.*, 1866, **8**, 5.

[4] Russ, *Z. anorg. Chem.*, 1902, **31**, 42.

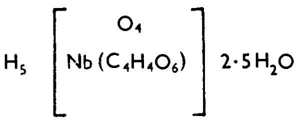
[5] Britton and Robinson, *J.*, 1933, 419.

[6] Edmister and Albritton, *J. Amer. Chem. Soc.*, 1932, **54**, 438.

Srinivasan[7] systematically investigated tartratoniobic acid and obtained from a solution of niobic acid in tartaric acid, by precipitation with alcohol, a microcrystalline precipitate with the composition $Nb_2O_5(C_4H_4O_5)_2,10H_2O$, *i.e.*, with *one* tartaric acid molecule associated with each niobium atom, and to which he attributed a heteropoly-acid structure (II), although only one hydrogen atom in the molecule was replaceable by an alkali metal. Thus, a number of alkali salts of a tartaric–niobic acid complex, of the general formula $M^1_2O,Nb_2O_5(C_4H_4O_5)_2,xH_2O$, were prepared by the dissolution of the alkali niobate in tartaric acid.[8] Several salts of bivalent cations were also prepared by double decomposition of the potassium salt of this complex with the appropriate metal salt.[9] In all of these, only one hydrogen of the above formula was replaced.



(I)



$$H_5\left[\overset{O_4}{Nb(C_4H_4O_6)}\right]2{\cdot}5H_2O$$

(II)

Evidence of complex formation in solution between niobium hydroxide and citric, malic, lactic, gluconic, and tartronic acids is also given by the polarographic reduction of niobium in the presence of these acids.[10]

We have now examined the preparation, composition, and reactions of a number of water-soluble complexes of niobium, in a variety of α-hydroxy-acids and -amines. From the outset it may be stated that the work relates principally to the preparation of niobium complexes, since *pure* tantalic acid is markedly less soluble than *pure* niobic acid in all the complex-forming agents examined, and such complexes of tantalum as are formed are more easily decomposed. In this work we shall for brevity retain the names niobic or tantalic acid, respectively, for the hydrated oxides, although their acidic nature only becomes evident upon fusion with an alkali.

EXPERIMENTAL

Niobic and tantalic acids were prepared in batches by fusing 1—2 g. of the pentoxide (>99·9% purity) or alternatively in the case of niobium also the metal powder, with 5—10 g. of potassium pyrosulphate. The clear melt was cooled and dissolved with stirring in boiling 25% oxalic acid solution. The solution was filtered to remove insoluble matter, 2—3 g. of ammonium chloride were added and then 4N-ammonia solution, dropwise to the boiling solution, until precipitation was complete. Further ammonia was added until the pH was about 10. The heavy white precipitate, which settled rapidly on standing, was centrifuged hot, to avoid crystallisation of ammonium oxalate, washed five times on the centrifuge with about 3% ammonium chloride solution and then twice with hot distilled water.

Removal of the soluble salts by washing with water alone is, in the case of niobic acid, quite impracticable. As the washing proceeds the acid becomes more colloidal, so that centrifuging for 2 hr. at a relative centrifugal force value of 3000 may be insufficient to give a clear supernatant liquid. This tendency towards peptisation of the acid on washing is characteristic of the product of precipitation by the addition of ammonia solution to an acid oxalate solution. An alternative method of preparation, fusion of the pentoxide with alkali followed by decomposition of the niobate with mineral acid, gives a product which is much more granular and less easily peptised, but which is also less reactive towards complex-forming agents. Tantalic acid, in contrast to niobic acid, showed no tendency to peptisation on washing and gave a granular, relatively unreactive precipitate by whichever method it was prepared.

The reactivity of niobic acid towards complex-forming agents also varied greatly with its age. Freshly precipitated niobic acid prepared as described is the most reactive but the

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[7] Srinvasan, *Proc. Indian Acad. Sci.*, 1950, **31**, 194.

[8] *Idem, ibid.*, p. 300.

[9] *Idem, ibid.*, p. 381.

[10] Ferrett and Milner, A.E.R.E., C/R 1752, 1955.

reactivity rapidly falls on standing, even overnight, so that eventually it becomes comparable with that of niobic acid obtained by acidification of a niobate.

Solubility of Tantalic Acid.—Since tantalic acid showed no obvious tendency towards colloidality, attempts were made to measure its solubility in water by tracer methods. 0·231 g. of a mixed sodium potassium tantalate containing 0·1007 g. tantalum was neutron-irradiated in a Polythene tube until it had an activity of about 2·5 mc. of ^{182}Ta. After irradiation the contents of the tube were dissolved in 200 c.c. of distilled water and the tantalic acid precipitated by the addition of 10% perchloric acid to the hot solution. To reduce the possibility of adsorption of the activity on the glass surfaces, all vessels were treated with Silicone resin (Imperial Chemical Industries R.230 applied in 1% xylene solution and cured at 150—200°).

The precipitated tantalic acid was well washed on the centrifuge and shaken in a thermostat at 25° with de-ionised water for 15 days. At intervals of 4, 7, 8, 9, 10, 11, and 15 days samples of the suspension were withdrawn and centrifuged and 10 c.c. of the clear liquid evaporated on a small planchet by infrared light. The radioactivity was determined in the usual way with a G.E.C. EHM2 thin mica-window counter. The reproducibility of the assay was carefully checked and was within ±4%. The results of the "solubility" measurements, however, were quite unreproducible, varying from 10^{-5} g. of Ta/100 c.c. to zero. Moreover, the greater the centrifugal force and the time of centrifuging, the smaller was the activity left in the liquid phase. One must conclude therefore that tantalic acid in pure water is, like niobic acid, also a colloid. This conclusion was confirmed by centrifuging a sample of the suspension for a short time to remove the larger particles and placing it in a "Kalle" dialysis tube. After 6 days no activity had diffused through the membrane, which readily passed such ions as $[(NH_3)_5ClCo]^{2+}$ and $[(NH_3)_6Co]^{3+}$.

In view of the fact that niobic acid passes even more easily into the colloidal state and indeed has been shown to be a radio-colloid [11] it is very unlikely that any "solubility" measurements in water of niobic acid would have much significance.

Preparation of the Complexes.—The same general method was used for all the complexes now described, with individual variations noted below. As a preliminary exploration, samples of niobic or tantalic acid were refluxed for 24 hr. with a fairly concentrated aqueous solution of the carboxylic acid under review, the suspension was cooled and centrifuged, and the clear liquid tested for the presence of niobium or tantalum by the tannin reaction. In cases where reaction occurred an amount of the freshly precipitated niobic or tantalic acid, containing about 1 g. of the metal, was refluxed for about 24 hr. with a 2—3% solution of the carboxylic acid, sufficient to dissolve the whole of the earth acid had reaction been complete. In practice, however, rarely more than one-third of the niobic acid, and only traces of pure tantalic acid, dissolved. Hardly any dissolution occurred in the cold. Previous workers have reported that a considerable excess of oxalic acid is required to dissolve niobic acid completely. It was found that in the case of the weaker complex-forming agents, glycollic and lactic acid, the continuous addition of ammonia so as to maintain the pH at 8—9 greatly increased the rate of dissolution of niobic acid. This clearly points to the α-hydroxy-acid anion being the effective complex-forming agent. After removal of undissolved hydroxide by centrifuging, the clear liquid was evaporated to a syrup under reduced pressure at 60° and the complex precipitated by the addition of an alcohol–ether mixture of a composition that would dissolve any uncombined hydroxy-acid. In this way the glycollic, lactic, malic, citric, and tartaric α-hydroxy-acids were found to form, with niobic acid, solid water-soluble complexes of definite composition. The precipitated acids were all non-crystalline and only gave very diffuse *X*-ray powder diagrams. They were so soluble in water that solubility measurements were impracticable with the amounts available, and attempts to crystallise by moistening or leaving in a moist atmosphere led, in the case of lactic, citric, and tartaric acids to the formation of straw-coloured hydrated scales which appeared crystalline but which in fact proved to be non-crystalline and glass-like.

All the solid α-hydroxy-acid complexes from which the excess of hydroxy-acid had been dissolved by the precipitant hydrolysed slowly on re-dissolution in water, this first becoming evident by a gradual clouding of the solution. It appears that α-hydroxy-acid complexes of niobic acid are only stable in the presence of an excess of complex-forming agent, usually at least three-fold but often much greater. There is much evidence for this. If a solution of an α-hydroxy-acid complex be placed in a dialysis tube suspended in running water, some niobic acid diffuses through as complex but most remains and is gradually precipitated as the hydroxy-acid is removed; a greater fraction of the niobium content can be dialysed away if

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[11] Schubert and Conn, *Nucleonics*, 1949, **4**, No. 6, 2; Schubert and Richter, *J. Colloid Sci.*, 1950, **5**, 376.

more complex-forming agent be added. In the same connection it was observed that sodium niobate, crystallised from alkaline solution, was hydrolysed with precipitation of niobic acid in a dialysis tube. This is in agreement with Hauser and Lewite's [12] observation that alkali niobate solutions can be dialysed through parchment membranes, yielding a stable niobium pentoxide sol practically free from alkali. Similarly, transport experiments with all complexes showed a net migration of niobic acid (as complex) to the anode with also, in the case of solutions containing more than about 1·5 g. of complex in 100 c.c., a precipitation of niobic acid gel at the cathode. In all preparations of the complexes, even after long refluxing the solution contained both excess of niobic acid and also free hydroxy-acid. The beginning of hydrolysis was not apparent to the eye and could only be followed quantitatively by a light-scattering photometer. Solutions which were clear to the eye gave a strong Tyndall scattering. It is to this sol formation that many of the conflicting statements in the literature are due. Clear solutions of many of the present α-hydroxy-complexes were precipitated on boiling by the addition of a neutral salt, *e.g.*, potassium chloride.

Reactions.—The complexes gave the usual tannin precipitate, were decomposed with precipitation of niobic acid by cold 3N-sulphuric, -hydrochloric, or -nitric acid and 3N-sodium hydroxide, and by boiling 3N-acetic acid. Decomposition by hot 3N-sodium hydroxide gave, on cooling, crystals of the sparingly soluble sodium niobate.

Analysis.—The quantitative estimation of either niobium or tantalum in the absence of the other is relatively simple and a variety of gravimetric techniques are available, the metal usually being weighed as the ignited pentoxide. Niobic acid in the complexes now described was estimated partly by ignition of the tannin precipitates and partly by ashing and ignition of the compound itself.

Since, however, it was desired to investigate the possibility of using the differences in stabilities of the niobium and tantalum complexes as a means of separation, it was also necessary to explore the methods of estimating these two metals in the presence of one another. The difficulty of this has been commented upon by all who have worked in this field. Methods which have been used include fractional precipitation of the tannin complexes,[13] chromatography,[14] polarography,[15] *X*-ray fluorescence,[16] and colorimetry.[17] The chief difficulty of precipitation methods, as will be discussed further, lies in the fact that these elements lose much of their individuality when present together, and no precipitant yet known will clearly precipitate one without the other; at best, fractional precipitation becomes necessary.

In the present work, in addition to the gravimetric methods mentioned, niobium was estimated colorimetrically by the intensity in concentrated hydrochloric acid of the absorption peak at 282 mμ.[18] Control estimations by gravimetric methods showed this to be a rapid and reliable method and free from serious interference by tantalum, which also appears to form a complex with hydrochloric acid, with an absorption peak at 271 mμ. The optical density of the tantalum complex, however, is only about one-tenth that of the niobium complex in equivalent concentrations. Both complexes are destroyed by dilution with water or by boiling the concentrated acid solution.

Tantalum and niobium were also determined together by the pyrogallol colorimetric method [19] and thence tantalum by difference.

Perhaps the most direct method of estimating one of these metals when both are present, and which in this work proved the lack of separation from a mixed precipitate, was the use of radio-niobium and -tantalum. Tantalum-182 was obtained as already described. Niobium-95 (35 d.) was obtained as a carrier-free separated uranium-fission product in the form of the niobic acid–oxalate complex. This was radiochemically purified by dilution with a known weight of inactive niobic acid in oxalic acid solution, the oxalate complex destroyed by fuming with mixed perchloric and sulphuric acids under an infrared lamp, and the niobic acid re-precipitated with lithium hydroxide. During this work the previous observation [6] that niobic acid

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[12] Hauser and Lewite, *Z. angew. Chem.*, 1912, **25**, 100.

[13] Schoeller and Powell, "Analytical Chemistry of Tantalum and Niobium," Chapman and Hall, London, 1937.

[14] Burstall, Swain, Williams, and Wood, *J.*, 1952, 1497.

[15] Elving and Olson, *Analyt. Chem.*, 1956, **28**, 338, and ref. 10.

[16] Campbell and Carl, *Analyt. Chem.*, 1954, **26**, 800; 1956, **28**, 960; Mortimac, Romans, and Tews, *Appl. Spectroscopy*, 1954, **8**, 24.

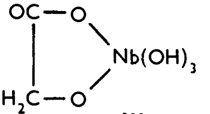
[17] Geld and Carroll, *Analyt. Chem.*, 1949, **21**, 1098; Telep and Boltz, *ibid.*, 1952, **24**, 163; Freund and Levitt, *ibid.*, 1951, **23**, 1813; Lauw-Zecha, Lord, and Hume, *ibid.*, 1952, **24**, 1169. See also refs. 18, 19, and 21.

[18] Kanzelmeyer and Freund, *Analyt. Chem.*, 1953, **25**, 1807.

[19] Dinnin, *ibid.*, p. 1803.

is not quantitatively precipitated from its oxalate solution by ammonia was confirmed. Mixtures of ^{182}Ta and inactive niobium or of ^{95}Nb and inactive tantalum enabled unambiguous determinations to be made of the composition of a precipitate.

Complexes of Niobic Acid.—Glycollic acid. The crude product precipitated from a solution of niobic acid in ammonium glycollate contained ammonium ion. This was removed by passing the solution through a column of Amberlite-120 (H) in the acid cycle which removed the ammonium ion without decomposing the complex. The resulting solution, after concentration at 50—60° under reduced pressure gave a heavy white precipitate of the 1 : 1 glycollic-niobic acid *complex* (III). This was washed with ether and dried in a vacuum (Found : C, 11·0; Nb, 41·2%; C : Nb, 2·06 : 1. $C_2H_5O_6Nb$ requires C, 11·0; Nb, 42·7%; C : Nb, 2 : 1).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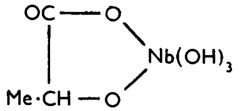
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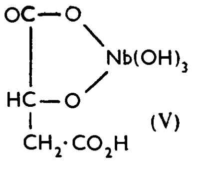
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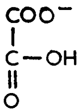

(VI)

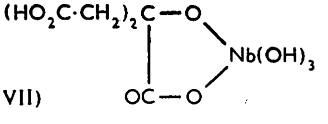
Thioglycollic acid. Sulphur-containing chelate rings are usually very stable, and thioglycollic acid forms stable chelates with several transition elements. This reagent or its ammonium salt, however, failed to dissolve niobic acid appreciably under conditions where the hydroxy-acid readily formed a complex. This is additional evidence of the importance of the hydroxyl group in the formation of the present series of complexes.

Lactic acid. Prepared and purified as described for glycollic acid, the *complex* (IV) in aqueous solution readily passed through a dialysis membrane [Found : C, 15·5; Nb, 40·9%; C : N, 2·94 : 1; *M* (cryoscopic, mean), 240. $C_3H_7O_6Nb$ requires C, 15·6; Nb, 40·3%; C : N, 2 : 1; *M*, 232].

Malic acid. Niobic acid was warmed to about 95° with a large excess of a solution of *rac.*-malic acid. In a few hours it almost completely dissolved. From the clear solution ether–alcohol precipitated a *complex* (V) of similar reactions to those described (Found : C, 17·5; Nb, 31·4%; C : Nb, 4·25 : 1. $C_4H_7O_8Nb$ requires C, 17·5; Nb, 33·8%; C : Nb, 4 : 1). It may be noted that the substance precipitated was a 1 : 1 complex although a large excess of hydroxy-acid was present. The complex was acid in reaction as would be expected from the presence of an uncomplexed carboxyl group.

Oxalic acid. Russ[4] prepared the oxalate complex by dissolving niobic acid in a large excess of oxalic acid from which he separated it by fractional crystallisation and obtained an oxalate : niobium ratio of 5 to 1. We refluxed an excess of niobic acid in 1·2 g. of oxalic acid and 70 c.c. of water for 20 hr. The amounts of niobic acid dissolved [as $Nb(OH)_5$] were 0·48 g., 0·39 g., and 0·56 g. in three experiments with different samples, the variation being due to differences in reactivity of the samples. Careful evaporation of one of these solutions over phosphoric oxide at room temperature gave a white amorphous powder with an oxalate : niobium ratio of 2·8 : 1 which is probably the parent acid of Russ's salts. It is unstable and on re-dissolution in water gradually precipitates niobic acid.

The oxalate complexes diffuse through a dialysis membrane. The solutions therefore are not collodial in character, but become so if the complex is decomposed by dilute acid or alkali, even though, as may happen in the cold and at low ionic strengths, a considerable time may elapse before visible flocculation occurs.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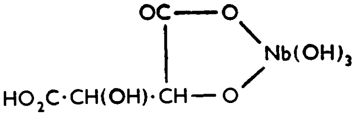
(VIII)

Oxalic acid is exceptional among the acids now discussed also in other ways. In the first place it is not obviously an α-hydroxy acid. It is, however, a fairly strong acid ($K_1^{25} = 6{\cdot}5 \times 10^{-2}$) so that in acid solution there is always an appreciable amount of the anion $HC_2O_4^-$ present which can be regarded as an α-hydroxy-anion (VI) which almost certainly behaves as the other α-hydroxy-anion groups.

Citric acid. The white *complex* (VII) was precipitated by alcohol–ether (Found : C, 20·3; Nb, 27·4%; C : Nb, 5·8 : 1; *M* (cryoscopic in water), 337. $C_6H_9O_{10}Nb$ requires C, 21·2; Nb, 27·4%; C : Nb, 6 : 1; *M*, 340). It is almost certain that only the central carboxyl group is involved in complex formation since inclusion of either of the terminal groups would require the formation of a 6-membered ring which the present work has shown to be unstable.

Transport experiments showed a migration of the niobium to the anode.

In view of the two uncomplexed carboxyl groups, it was thought that it should be possible to prepare salts of this complex by direct neutralisation. This aspect of the problem has not been fully explored. Hot sodium hydroxide solution decomposes the complex, depositing crystals of the sparingly soluble sodium niobate on cooling.

Tartaric acid. The complex formed between niobic acid and tartaric acid has already received much attention. The composition has been described both as a 1 : 1 and 1 : 2 complex. We prepared the complex (VIII) by the general methods described above, and isolated it by precipitation with alcohol (Found : C, 13·9; Nb, 31·5%; C : Nb, 3·5 : 1. Calc. for $C_4H_7O_9Nb$: C, 16·4; Nb, 31·8%; C : Nb, 4 : 1).

DISCUSSION

In contrast to the foregoing results, no dissolution of niobic acid was found to occur with the dibasic acids malonic, succinic, adipic, or phthalic, or with potassium hydrogen phthalate, and of the acid ammonium salts only in the case of malonic acid and that to a barely detectable extent. Similarly the amounts dissolved by sodium β-hydroxybutyrate or thenoyltrifluoroacetone in benzene, water, or alcohol solution or by acetylacetone in alcohol or water were so small as to leave some uncertainty as to whether they were in true solution.

The results leave no doubt that the present series of α-hydroxy-acid niobium complexes are formed by the co-ordination of the acid anion to the niobium and the completion of a five-membered ring by elimination of water.

Since the niobic acid as such is invariably present as a hydrated suspension or a colloid, whether as a starting material or as the product of decomposition, it is more profitable to regard the formation of these complexes as heterogeneous reactions. Throughout, we have found that rate processes and the history or mode of preparation of the earth acid are of more significance than ionic equilibria involving complex niobium species. The effect of rapid ageing on the reactivity of the precipitated niobic acid has already been noted. Many of the conflicting statements in the literature regarding non-precipitation by various reagents can be attributed to hysteresis. Attempts were made to accelerate the attainment of a steady state (" equilibrium " would be incorrect since this would imply the possibility of approach from either side) by ultrasonic radiation at a frequency of 1 megacycle/sec. and a power of 250 w. The results were disappointing. The solutions became heated but the rate of reaction was no greater than that produced by boiling.

The coagulation, precipitation, or dissolution of niobic or tantalic acids appears to take place through a reversible condensation of neighbouring hydroxyl groups, whether of adjacent earth acid units or of earth acid and a complex-forming agent. For the latter, either two hydroxyl groups, or one hydroxy-group and a carboxylic anion, in the α-position are necessary to make possible the formation of a 5-membered chelate ring. Examples of the condensation involving two hydroxyl groups are given by the catechol complexes.[20]

The actual process of dissolution can be visualised as the attachment of a molecule of complex-forming agent in this way to one of the peripheral hydrated niobium atoms of a particle or colloid micelle, with the subsequent breaking of the metal–oxygen bonds which hold it to the rest of the particle. The lower solubility of tantalic acid must be attributed to the greater stability of the Ta–O–Ta bonds relative to the stability of the complexes.

Experience with malonic and β-hydroxybutyric acids indicates that six-membered rings, though not impossible, are much less stable. This is not surprising, for the ***average*** bond angle in a five-membered ring is 108° compared with 120° in a six-membered ring. Since the Nb–O bonds are probably largely covalent the smaller ring would involve much less strain.

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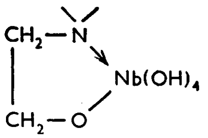
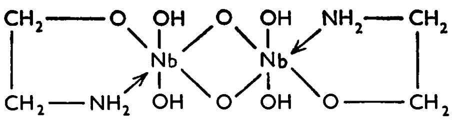
[20] Rosenheim and Roehrich, *Z. anorg. Chem.*, 1932, **204**, 342.

It appears, however, that six-membered rings can be formed in solution with strong inorganic polyhydroxy-acids. Niobic acid is also appreciably soluble in chromic and ortho- and poly-phosphoric acids, all of which form oxygen-bridged condensed acids with hydroxyl groups in the required position, and also, as is well known, in concentrated sulphuric acid. The last, in conjunction with alkali pyrosulphate fusion, has long been the principal reagent for the dissolution of niobic or tantalic oxides. Freshly precipitated and centrifuged, but still moist, niobic or tantalic acid will dissolve slowly in 10% oleum from which, as from the product of pyrosulphate fusion, it is precipitated on dilution with water and boiling. The dissolution probably occurs through chelation with the disulphuric (pyrosulphuric) anion, which is decomposed by water. The hysteresis in the precipitation of niobic acid from sulphuric acid solution is most marked. The solution can be diluted to about half-molar strength in the cold and only begins to become cloudy after 1—2 hr. On the other hand it is rapidly precipitated on boiling from a 5M-solution. Selenic acid is particularly interesting for comparison. Niobic acid dissolves rapidly to give a clear solution in 15M-selenic acid but is precipitated in the cold on dilution to about 7M, at which concentration it is not precipitated from sulphuric acid even on boiling.

It should be pointed out that although in the present series of α-hydroxy-acid complexes the molecular ratio of niobic to α-hydroxy-acid was, with the exception of oxalic acid, always 1 : 1, this does not entirely exclude the formation of complexes containing additional molecules of α-hydroxy-acid which might be removed by the alcohol or ether used as precipitant.

Following the foregoing results with α-hydroxy-acids and the observation—which will form the subject of a later communication—that niobic acid and, to a less extent tantalic acid, form water-soluble complexes with a variety of nitrogen bases, we also studied the complex-forming action of the (2-hydroxyethyl)amines ("ethanolamines"), since these contain both a hydroxyl group and a basic nitrogen atom in such a position that the formation of a five-membered chelate ring seemed possible (cf. IX).

(IX) 

 (X)

The only previous indication of the formation with niobium of a chelate ring of this type is that implied in the formation of a water-insoluble complex with 8-hydroxyquinoline.[21]

(2-Hydroxyethyl)amines used were commercial products and were fractionated under reduced pressure at least three times; they had b. p.: (2-hydroxyethyl)amine, 100°/53 mm.; di-(2-hydroxyethyl)amine, 160°/18 mm.; tri-(2-hydroxyethyl)amine, 210—212°/16 mm.

Complex formation was followed in the same way as for the α-hydroxy-acids. The three hydroxyethylamines showed a considerable difference both in rate and amount of dissolution, those in (2-hydroxyethyl)amine being the greatest and in tri-(2-hydroxyethyl)amine the least. For example, excess of freshly precipitated niobic acid, from the same preparation, was refluxed for 20 hr. under the same conditions with 70 c.c. of 0·0095M-solutions of each of the amines. This concentration was the same as used in the α-hydroxy-acid experiments and corresponds to a concentration of 2 g. of citric acid in 70 c.c. of water, which was found to be a convenient standard for comparison.

After removal of excess of solid by centrifuging, solid complexes were isolated by vacuum evaporation below 50° followed by alcohol–ether precipitation, or the "solubility" measured by evaporation to dryness and ignition. The amounts dissolved (g. per 100 c.c. of 0·0095M-amine) were as follows, the first figure in parentheses referring to Nb_2O_5, and the second to Ta_2O_5: (2-Hydroxyethyl)amine (0·148, 0·016); di-(2-hydroxyethyl)amine (0·104, 0·003); tri-(2-hydroxyethyl)amine (0·045, 0·004). Reaction is much the most extensive with the first amine. The weight of tantalic acid dissolved was in each case very much less than that of the niobic acid.

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[21] Kasner, Garcia-Porrata, and Grove, *Analyt. Chem.*, 1955, **27**, 492.

The complexes were white powders, soluble in water except in the case of tri-(2-hydroxyethyl)amine where rapid hydrolysis gave an immediate cloudy solution : 3N-mineral acids and 3N-acetic acid precipitated niobic acid : 2N-ammonia solution had no effect. Sodium hydroxide gave the niobate as with the α-hydroxy-acid complexes.

Analysis and molecular weight determination pointed to no simple formula but rather to polynuclear species.

		Found :			Required :		
Amine	Formula	C (%)	Nb (%)	*M*	C (%)	Nb (%)	*M*
2-Hydroxyethylamine ...	$(HO\cdot C_2H_4\cdot NH_2)_2[Nb(OH)_4]_2$	10·8	45·9	430	11·8	45·8	406
Di(-2-hydroxyethyl)amine	$[(HO\cdot C_2H_4)NH]_2[Nb(OH)_4]_4$	11·2	47·6	880	12·2	47·7	796
Tri-(2-hydroxyethyl)amine	$[(HO\cdot C_2H_4)_3N]_2[Nb(OH)_4]_5$	14·0	45·0	—	13·9	44·9	1059

The formation of these complexes from niobic acid probably takes place in the same way as with α-hydroxy-acids, by the attachment of the ligand to the periphery of the hydrated particle followed by detachment of the complex from the parent micelle. In the case of the hydroxyethylamines the fragments detached appear to be larger than in the case of the hydroxy-acids. One possible structure for the mono-(2-hydroxyethyl)amine complex is (X) with similar structures for the di- and the tri-(2-hydroxyethyl)amine complex, containing respectively four and five niobium atoms bridged by oxygen atoms.

In all the foregoing experiments, the most outstanding feature was the much smaller solubility in solutions of all the complex-forming agents of freshly precipitated tantalic acid, than of niobic acid; even greater difference was found for dissolution by amines. In a solution of diethylamine almost 1000 times more niobic acid than tantalic acid was dissolved under the same conditions. In the hydroxyethylamines the ratio was only about 10 to 30 times and in citric acid about 50 times.

In view of these wide differences it was hoped that a satisfactory method of separation of the metals might be devised, based on their differential solubility, which would avoid the use of the hydrofluoric acid associated with the only successful commercial separations devised in 100 years. No satisfactory separation of the co-precipitated acids, however, has yet been achieved, owing to the fact that each of these two elements appears to lose its identity when intimately mixed with the other. This fact has been commented upon from various angles by several workers. In the present work niobic oxide and tantalic oxide in about equal proportions were (*a*) fused separately with pyrosulphate, dissolved in oxalic acid precipitated as the hydroxides washed and then mixed; (*b*) fused with pyrosulphate and dissolved in oxalic acid separately, but the hydroxides simultaneously precipitated from the mixed oxalic acid solutions; (*c*) mixed before fusion, etc. The products of (*a*), (*b*), and (*c*) were then treated in the same way with solutions of complex-forming agents. In (*a*) the niobic and tantalic acids behaved quite independently and very little tantalic acid passed into solution. In (*b*) and (*c*) no separation was achieved and far more tantalic acid passed into the aqueous phase that would have done so under the same experimental conditions but in the absence of niobic acid.

Many experiments were carried out along these lines but four will suffice to illustrate this point.

(*a*) Approximately equal weights of niobium pentoxide and tantalum pentoxide were converted into the hydroxides, mixed, and refluxed with a 5% solution of diethylamine in water for ¾ hr. The ratio Nb : Ta in the aqueous phase was 200 to 1. (*b*) A similar experiment but the oxides were first fused together : The ratio Nb : Ta in aqueous phase was 6·7 to 1. (*c*) With 2 g. citric acid in 70 c.c. water and a reflux time of 22 hr. the niobium extracted from separately precipitated mixed hydroxides contained less than 2% of tantalum, in close agreement with individual experiments on the separated oxides. (*d*) When the hydroxides were co-precipitated the niobium contained 16% of tantalum, whilst on doubling the citric acid concentration the tantalum content rose to 25%. This enhanced solubility of tantalic acid in the presence of niobic acid could be due to either or both of two causes : (i) a separation of the tantalum atoms and breaking of the strong Ta–O–Ta bonds in the mixed micelle (since it is neither solid nor crystalline, " solid solution " or " mixed crystal " seems inappropriate) in a somewhat similar manner to the increased speed of dissolution of some metals when alloyed, or (ii) the formation of polynuclear species in the aqueous phase.

We are of the opinion that the latter is probably the major cause of the observed effect. That it is not simply due to a greater slowness of dissolution of tantalic acid with the formation of a complex of comparable stability to that of niobium is shown by the fact that the reverse process, that of hydrolysis, takes place more readily with tantalum.

In the case of the present α-hydroxy-acid complexes, although freezing-point determinations gave values approximately those of the monomeric species, the precision was not sufficient to exclude polynuclear units. Moreover, although the solutions were clear, some hydrolysis undoubtedly occurred.

In the case of the hydroxyethylamines the evidence was much clearer that the oxides passed into the aqueous phase as polynuclear units. In such a unit the tantalic acid molecules can be condensed with niobic acid molecules as in the mixed micelle.

It follows therefore that it is unlikely that a successful separation process can be devised which does not involve the metals as single atoms unconnected through oxygen bonds or other bridges. The success of the separation processes involving the complex fluorides may be attributed to the monomeric character of these complexes.

We are indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of us (J. B. T.).

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