

427. *Water-soluble Complexes of Niobium (Columbium) and Tantalum. Part II.*¹ *The Dissolution of Niobic and Tantalic Acids in Amine Solutions.*

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Freshly precipitated niobic acid dissolves in dilute aqueous solutions of aliphatic amines, to form complexes which can be isolated by evaporation or by precipitation with organic solvents. Complexes of niobic acid with eleven amines have been isolated and its solubility in four others has been examined. The complexes vary somewhat in composition but generally contain from about one to three niobium atoms per molecule of amine. The complexes are diffusible through a dialysis membrane, but molecular-weight determinations show that the units are polynuclear.

The dissolution has some of the characteristics of a colloid dispersion and can be reversed by increasing the ionic strength by addition of neutral salts. The dissolution and ageing of the niobic acid are competitive processes and an aged precipitate does not dissolve. Dissolution is largely determined by the basic dissociation constant of the amine.

In spite of the complexing power of many basic nitrogen compounds, no water-soluble complexes of niobium or tantalum with nitrogen compounds appear to have been reported, apart from those with (2-hydroxyethyl)amines described in Part I.¹ Several non-aqueous solutions of amines have, however, been used in solvent-extraction processes² in which the niobium or tantalum, usually in the form of an inorganic acid complex, is extracted from an aqueous phase into an organic solution of an amine, though no definite complexes appear to have been isolated from such systems. Also, anhydrous complexes of amines with niobium pentachloride have been described.³ There is therefore experimental evidence that amines are able to attach themselves as ligands to the niobium atom.

We have now studied the dissolution of niobic and tantalic acid in aqueous solutions of a variety of amines. As in solutions of α -hydroxy-acids, tantalic acid was found in all cases examined to be very much less soluble than niobic acid, by a factor of as much as 10^3 under comparable conditions. The present paper therefore is concerned chiefly with the dissolution of niobic acid, the study of tantalic acid complexes being limited to a few experiments for comparison.

Freshly precipitated and washed niobic acid was found to be more or less easily soluble in dilute solutions of a number of primary, secondary, and tertiary aliphatic amines. From these solutions, by vacuum-evaporation, alone or combined with precipitation by alcohol and ether, solid complexes were obtained. Table 1 lists the amines used and

¹ Part I, Fairbrother and Taylor, *J.*, 1956, 4946.

² Leddicotte and Moore, *J. Amer. Chem. Soc.*, 1952, **74**, 1618; Ellenburg, Leddicotte, and Moore, *Analyt. Chem.*, 1954, **26**, 1045; Foss and Wilhelm, U.S.A.E.A. publ. ISC—694, 1954, 20.

³ Fowles and Pleass, *J.*, 1957, 2078.

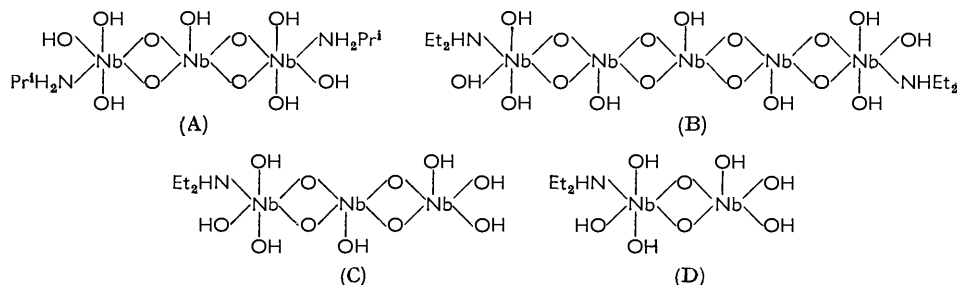
analyses of a number of the products isolated. From this can be seen the variable composition of the complexes, but in almost every case the ratio of atoms of niobium to molecules of amine lies between one and three. Niobic acid was also found to be soluble in aqueous solutions of trimethylamine, ethylamine, diisopropylamine, and cyclohexylamine. The products obtained by precipitation with alcohol and ether were white powders: those

TABLE I.

Amine	Found (%)			Amine	Found (%)		
	C	Nb ₂ O ₅	Ratio Nb/Amine		C	Nb ₂ O ₅	Ratio Nb/Amine
NH ₂ Me	5.6	64.6	1.04	NH ₂ Pr ¹	12.5	65.2	1.41
NHMe ₂	8.4	59.7	1.28	"	10.9	66.9	1.66
NHEt ₂	12.4	71.5	2.08	NH ₂ Bu	15.1	66.3	1.59
"	11.6	68.3	2.13	NH ₂ Bu ¹	11.9	71.0	2.16
"	11.5	68.4	2.15	NH ₂ Bu ¹	11.6	71.3	2.22
"	17.8	63.6	1.29	Piperidine	18.0	60.5	1.52
NEt ₃	13.1	68.3	2.82	"	17.6	57.4	1.47
NH ₂ Pr	16.3	56.5	0.94	(CH ₂ NH ₂) ₂	10.3	64.3	1.13

obtained by evaporation usually broke up into small glistening fragments which appeared isotropic under the microscope. In both cases the products gave ill-defined X-ray diffraction patterns. It is possible that some structure may exist, since the fracture on drying usually took place along straight lines, often parallel or nearly so.

Attempts were made to determine the molecular weights of the complexes cryoscopically in water. The results again showed some variability, probably because of slight hydrolysis during the experiment and because the complex was not composed of a single species. The results however showed unmistakably that the solid species, separated either by vacuum-evaporation or by precipitation with organic solvents, contained aggregates of from two to five, and exceptionally six, units of niobic acid co-ordinated to one or two molecules of amine. Typical structures suggested therefore are: For *iso*-



propylamine (A), which requires C, 12.4%; Nb, 48.1%; *M*, 580. A molecular weight of 600 for such a complex was found experimentally. Singly co-ordinated units may also be present or a mixture of singly and doubly complexed units, *e.g.*, for diethylamine a mixture of (B) (which requires C, 10.7%; Nb, 52.2%; *M*, 891; amine : Nb ratio = 1 : 2.5) with (C) (which requires C, 9.0%; Nb, 52.2%; *M*, 535; amine : Nb ratio = 1 : 3) or (D) (which requires C, 12.21%; Nb, 47.26; *M*, 393; amine : Nb ratio = 1 : 2). A molecular weight of 680 was found for one diethylamine complex.

The size of these units is also consistent with their diffusibility through a dialysis membrane. Migration of the niobium was to the anode. Similarly, electrophoretic experiments showed that the particles in a de-ionised suspension of niobic acid were negatively charged.

The dissolution of niobic acid in an aqueous amine solution has many of the features of a colloid-chemical process in which the amine acts as a peptising agent. Thus, precipitation of niobic acid by ammonia from a solution of the oxalic acid complex, as in the usual method of preparation, yields a product of very variable particle size, dependent

initially mainly upon the temperature of precipitation and the ionic strength of the solution. Immediately after its formation the precipitate starts to age, at a rate which is accelerated by rise of temperature and can be halted for many weeks by storage in a "deep-freeze" cabinet at -30° . This ageing is quite noticeable even overnight at room temperature.

Consequently, the dissolution of niobic acid in an aqueous amine solution depends, not only on the history of the niobic acid, but also on the manner in which the dissolution is carried out, the ageing and dissolution being competitive processes. For example, a given preparation of niobic acid was divided into several portions and these treated in different ways with the same volume of a dilute solution of diethylamine, insufficient in amount to dissolve all the niobic acid. After removal of the excess by centrifugation, the amount in solution was estimated gravimetrically. The results are shown in Table 2.

TABLE 2.

Treatment	g. of Nb_2O_5 in solution	Treatment	g. of Nb_2O_5 in solution
Shaken at room temp. $3\frac{1}{2}$ hr.	0.140	Boiled alone $3\frac{1}{2}$ hr.	} shaken with amine for 12 hr. 0.188
" " " 48 "	0.190	Stored at 18° 24 hr. ...	
Simmered gently $3\frac{1}{2}$ hr.	0.280	Stored at -30° 24 hr. }	
Refluxed vigorously $3\frac{1}{2}$ hr.	0.074		

It was found that the most effective method of dissolution was the heating at $70-80^{\circ}$ of a preparation of niobic acid which was freshly prepared or had been kept at a low temperature, with a solution of the appropriate amine.

It is a consequence of the heterogeneity of dispersion and the rapid ageing of the precipitate that no two batches of niobic acid are exactly alike and comparative experiments are only possible with different portions, treated, apart from the variable under consideration, in exactly the same manner. Within this limitation it was found that when an excess of niobic acid was shaken for 12 hours with dilute equimolar (0.01M) solutions of a series of amines the amount passing into solution increased, somewhat irregularly, with the dissociation constant of the amine (cf. Table 3). With the more basic amines in sufficient amounts and unaged preparations of niobic acid, dissolution occurs fairly readily at room temperature. In this it differs from the formation of

TABLE 3.

Amine	10^4K	g. of Nb_2O_5 in 100 c.c.	Amine	10^4K	g. of Nb_2O_5 in 100 c.c.
NH_2Bu	4.1	0.201	NH_2Pr^1	5.3	0.494
NH_2Bu^1	2.3	0.295	Piperidine	15.8	0.520
NEt_3	6.4	0.422	NH_2Et_2	12.6	0.617

Niobic acid is insoluble in ammonia ($K = 1.8 \times 10^{-6}$) and in pyridine ($K = 2.3 \times 10^{-9}$) solutions.

complexes with α -hydroxy-acids, undoubtedly as a consequence of the different nature of the two processes. Amine dissolution involves co-ordination of nitrogen to the niobium followed by increased hydration and dispersion of the precipitate, whereas complexing with α -hydroxy-acids involves chelate formation by the elimination of water from two adjacent hydroxyl groups.

The attachment of the amine molecules, to the finer particles at least, appears to take place very rapidly and to be succeeded, as a slower secondary process, by the dispersion of the complex to give a clear solution. Larger particles, though they may take up some amine, are not dispersed even after a long time.

These matters could be followed by observing the change in electrical conductivity (at 25°) on mixing a de-ionised suspension of niobic acid with a solution of an amine. For example, 50 c.c. portions of 1% (v/v) piperidine ($\sim M/10$) were mixed separately at 25° with (a) 50 c.c. of de-ionised water, (b) 50 c.c. of a de-ionised suspension of niobic acid, freshly prepared as described on p. 2078, and containing 0.2008 g. of Nb_2O_5 , and (c) 50 c.c. of the same suspension which had been heated to $125^{\circ} \pm 5^{\circ}$ for 2 hours in an autoclave. The

specific conductivity of the de-ionised suspension was negligible compared with those of the mixtures, which were as follows: (a) 1.80×10^{-3} mho; (b) at 15 min. after mixing 1.66 mho, but within 4 hr. 1.63×10^{-3} mho, and in 3 days, by which time the solution had become quite clear, 1.58×10^{-3} mho where it remained for a further two days. If it is assumed that the complex is relatively non-conducting, the last figure indicates a consumption of amine corresponding to an amine : niobium ratio of about 1 : 1.2, which is within the range of compositions of many of the solid amine complexes. Of the total amount of amine taken up however, nearly two-thirds was taken up in the first few minutes, without any obvious clearing of the solution. This could be due in part to an unobserved dissolution of the finer particles or more probably to co-ordination of amine molecules on the periphery of most of the particles, followed by their slower break up and dispersion.

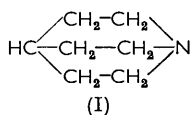
In contrast, the immediate fall in conductivity of the aged mixture (c) was much less, to 1.75×10^{-3} mho, and only to 1.71×10^{-3} mho after one week. This corresponds to an absorption of amine about 40% of that by the unaged sample. Longer heating would undoubtedly have decreased the absorption still further. The aged mixture did not become clear even when kept for many weeks.

It is well known that, in many cases, aliphatic monoamines co-ordinate less readily than does ammonia, that secondary amines do so even less, and that, with a number of metal ions, tertiary amines have little tendency to co-ordinate at all. On the other hand, it is known that the stability of the ferric amines, with which perhaps the present series has more in common, is in the reverse direction.⁴ As already mentioned, the dissolution of niobic acid in aqueous amine solutions of equimolar concentration appears to depend partly on the basic dissociation constant of the amine. There can be no question however of the dissolution's being due to an increase in the charge : size ratio of the particles due to de-protonation by the base. Both the acid dissociation of the niobic acid (as shown by the low conductivity of a purified suspension) and the proton affinity of the bases are much too small. It is only at very high hydroxyl-ion concentrations, in solutions of strong alkalis, that de-protonation occurs, with the resulting break up of the niobic acid into anions that can subsequently crystallise as alkaline niobates. Even here, as shown by Hauser and Lewite,⁵ the process can be reversed, and practically the whole of the alkali removed by dialysis. Also, with a given amine and excess of niobic acid, the amount passing into solution decreases with increasing concentration of amine and the complexes are insoluble in pure amine. In fact, with many amines a convenient alternative to concentration of the solution or precipitation with alcohol and ether was to precipitate the complexes by addition of excess of amine. Thus, a sample of freshly precipitated and washed niobic acid was divided into several equal parts each of which was made up to 100 c.c. with a different volume of amine. The mixtures were shaken for 12 hours in a water-thermostat at 70° and the niobic acid passing into solution estimated. The results were:

Amine solution (% v/v)	2.5	5.0	7.5	10.0	15.0	20.0	60.0
Mg. of Nb ₂ O ₅ dissolved per c.c. of amine ...	237	144	142	84	65	34	5

Bailar⁴ has suggested that the instability of tertiary amine complexes of many metal ions may be due to steric factors. A consideration of space models of the various amines used in the present work and the irregular dependence of the dissolution on the basic

dissociation constants also suggested that steric factors might play a part. The rôle of steric factors in determining the stabilities of amine addition compounds of trimethylboron has been discussed by Brown,⁶ who found that the addition compound of quinuclidine (I) with trimethylboron was much more stable than that between its "open" analogue triethylamine and trimethylboron. Through the kindness of Professor Brown in



⁴ Sidgwick, *J.*, 1941, 433; Bailar, "The Chemistry of the Co-ordination Compounds," Reinhold, New York, 1956, p. 62.

⁵ Hauser and Lewite, *Z. angew. Chem.*, 1912, 25, 100.

⁶ Brown, *J.*, 1956, 1248.

supplying a sample of quinuclidine hydrochloride we were able to carry out a similar experiment with niobic acid.

0.2959 g. of quinuclidine hydrochloride was distilled with sodium hydroxide to give 0.002 mole of quinuclidine. A freshly prepared sample of niobic acid was divided into two parts which were shaken, for 12 hours at room temperature, respectively with 100 c.c. of 0.02M-triethylamine and of 0.02M-quinuclidine. After removal of excess of niobic acid by centrifugation, the Nb_2O_5 in solution was found to be, for triethylamine 0.030 g. and for quinuclidine 0.050 g. Since triethylamine and quinuclidine have almost the same basic dissociation constant,⁷ it must be concluded that also in the case of the dissolution of niobic acid steric considerations play a part.

A number of experiments were carried out with samples of niobic and tantalic acid prepared under similar conditions in order to compare their reactivities with given amines. In some cases, for example, in diethylamine, a "solubility" ratio approaching 1000 : 1 in favour of niobium was found. When the two acids were individually precipitated and then mixed, good separation could be achieved by using this difference in solubility in amines. On the other hand, when the niobic and tantalic acids were co-precipitated from the mixed solutions of a complex or prepared from mixed oxides, the dissolved niobium always contained considerable amounts of tantalum. This is clearly a consequence of the polynuclear character of the amine complexes and of the replacement of niobium by tantalum in the oxygen-bridged groups.

EXPERIMENTAL

Niobic and tantalic acid were precipitated by ammonia from a solution in oxalic acid of a melt with pyrosulphate. The cooled fused mass was dissolved in 4% oxalic acid instead of the more concentrated solutions used in Part I. This avoided much of the difficulty with crystallisation of ammonium oxalate from the neutralised solutions and the consequent necessity of keeping the solutions hot during the initial stages of purification. In turn this led to a more active product. The precipitates were washed on the centrifuge, three times with 2% ammonium chloride solution and twice with distilled water. As the washing with water proceeded, the niobic acid showed a tendency to become dispersed. "De-ionised" suspensions were prepared by passing a well-washed reactive suspension four times through a column of Amberlite Monobed Resin (MB3). This effectively removed soluble ions whilst very little niobic acid adhered to the resin: most of this could be removed by distilled water. Such a de-ionised suspension remained stable for many days.

The amines used were purified by fractionation, and solutions of the complexes generally prepared by warming a suspension of about 0.5 g. of Nb_2O_5 in 150 c.c. of 10% v/v amine solution. Complete dissolution required 10—30 min. The volume of solution was then reduced, by evaporation in a vacuum at $>40^\circ$, to a syrup, which was either allowed to dry over silica gel in a vacuum-desiccator or precipitated with alcohol and ether or excess of parent amine. Precipitation with excess of amine, followed by washing with acetone and ether, was especially valuable for the isolation of complexes with the less volatile amines, such as ethylenediamine, where the excess of amine was difficult to remove by evaporation without decomposition of some of the complex.

The complexes were all insoluble in common organic solvents and in the parent amine, but very soluble in water to give solutions with a faint alkaline reaction. In most cases hydrolysis was slow and solutions could be boiled without decomposition. The triethylamine, ethylenediamine, and cyclohexylamine complexes, however, were decomposed in boiling water with precipitation of niobic acid. 3N-Mineral acids and acetic acid precipitated niobic acid from aqueous solutions of the complexes. A quantitative measurement of the stability of the niobic acid-isopropylamine complex as a function of pH on addition of dilute hydrochloric acid or sodium hydroxide, indicated a fairly sharply defined region of stability between pH 2.2 and 11.9; outside these limits niobic acid was rapidly precipitated.

The formation and decomposition of the isopropylamine complex was found to be particularly

⁷ Pearson, *J. Amer. Chem. Soc.*, 1954, **76**, 258.

useful as an analytical tool in another work. Niobium halides or oxyhalides dissolved immediately in 5—10% *isopropylamine* solution with complete hydrolysis without loss. Addition of 3*N*-acetic acid precipitated niobic acid from the solution in an easily filterable form.

When the solutions of the complexes were warmed with 3*N*-sodium hydroxide, the niobate was formed and deposited as crystals on cooling.

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