

STUDIES ON NIOBIUM AND TANTALUM

Part III. Tartratonibates of Alkaline Earth and Other Metals

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INTRODUCTION

THE niobates of the alkaline earth and other metals have been found to be insoluble materials. The several niobates of the alkaline earth metals, got by fusion of the metal carbonates or oxides with niobium pentoxide, were insoluble as also the niobates of zinc, magnesium and other heavy metals (Jander, 1931). Pierre Sue (1937) found that, the alkaline earth niobates, obtained as precipitates by the double decomposition of a salt of the metal with a soluble niobate, were impure and colloidal. Balke and Smith (1908) prepared the insoluble metaniobates of the alkaline earth, aluminium, magnesium, cadmium and other metals. Many of the niobates were prepared during the present work and were found to be insoluble and unreactive towards tartaric acid solutions. Hence the tartratonibates of these metals were sought to be prepared in a different manner.

EXPERIMENTAL

Method of Preparation

Since many of the niobates of the heavy metals were found to be unreactive towards tartaric acid, attempts were made to prepare the compounds by other methods. When a solution of 2-potassium-2-tartrato-2-niobate was treated with soluble salts of metals, characteristic precipitates were obtained as indicated below:—

Potassium tartratonibate Soln.	+ CaCl ₂	Soln. → White ppt.
”	” + Sr (NO ₃) ₂	” → ”
”	” + Ba (NO ₃) ₂	” → ”
”	” + CuSO ₄	” → Light green ppt.
”	” + MgCl ₂	” → White ppt.
”	” + ZnCl ₂	” → ”
”	” + CdSO ₄	” → ”

Potassium tartratonioabate Soln.	+	$\text{Al}_2(\text{SO}_4)_3$ Soln.	→	White ppt.
„	„	+ PbCl_2	„ →	„
„	„	+ $\text{Th}(\text{NO}_3)_4$	„ →	„
„	„	+ $\text{Cr}(\text{NO}_3)_3$	„ →	Green ppt.
„	„	+ FeSO_4	„ →	Dirty white ppt. on standing.
„	„	+ $\text{Co}(\text{SO}_4)_2$	„ →	Light orange ppt. on standing.

In each case the precipitate was filtered and both the precipitate and the filtrate examined. The first case will serve as an illustration. In this case, the filtrate revealed the absence of both niobium and tartrate; the precipitate was found to contain calcium, niobium and tartrate. Hence it is possible that they exist together as a definite compound. The probability that the precipitate might be composed of a mixture of calcium niobate and calcium tartrate was eliminated by the following experiments:

(i) The precipitate was extracted with hot water, in which it was slightly soluble, and the extract answered all the tests for calcium, niobium and tartrate; calcium niobate was insoluble in water.

(ii) The precipitate was insoluble in cold acids, but dissolved to give clear solutions in hot concentrated hydrochloric acid. The solution precipitated niobic acid on dilution. Calcium niobate was insoluble in concentrated acids.

(iii) The precipitate was soluble in cold or hot dilute alkali hydroxides to clear solutions whereas calcium niobate was insoluble even in hot concentrated alkali hydroxides. Therefore it can be concluded that the compound obtained is the tartratonioabate of calcium; and by similar reasoning it can be seen that the characteristic precipitates that are obtained are the tartratonioabates of the various metals.

Calcium-2-tartrato-2-niobate

The preparation of this compound was undertaken by the double decomposition of potassium tartratonioabate and calcium chloride or calcium acetate. $\text{K}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10 \text{H}_2\text{O}$ was dissolved in warm water and a 10% solution of calcium chloride added drop by drop with vigorous stirring. A white precipitate was formed which settled down quickly; the solution was cooled in ice, filtered, washed with ice-cold water and dried. The analysis presented several difficulties and the final procedure adopted was the following:—

Analysis

(i) *Niobium*.—A weighed quantity of the finely ground substance (about 0.3 g.) was suspended in cold water (15 ml.) and about ten drops of a 10% solution of potassium hydroxide added; the substance dissolved to give a clear solution. A few more drops of the alkali hydroxide were added, the solution diluted (40 ml.), and heated to boiling when a turbidity appeared. The solution was treated with concentrated hydrochloric acid (1.5 ml.) when niobic acid was thrown down as a flocculent precipitate. The estimation was completed by filtering, washing, igniting and weighing it as Nb_2O_5 . To ensure the absence of any insoluble substance in it, it was fused with potassium hydrogen sulphate, taken up in ammonium oxalate solution, reprecipitated and finally weighed as Nb_2O_5 .

(ii) *Calcium*.—From the acid filtrate obtained after the removal of niobic acid, calcium was precipitated as the oxalate and estimated by the volumetric method.

(iii) Tartaric acid was determined by the potassium iodate method (*vide* Part II).

(iv) H_2O by difference.

The following results were obtained:—

TABLE I

	Found %	Calculated for $\text{CaO} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10\text{H}_2\text{O}$
CaO ..	7.10	7.31
Nb_2O_5 ..	35.26	34.70
$\text{C}_4\text{H}_4\text{O}_5$..	34.31	34.46
H_2O ..	23.33	23.53

Therefore the compound prepared can be formulated as $\text{CaO} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10\text{H}_2\text{O}$ and named as calcium-2-tartrato-2-niobate 10-hydrate.

Strontium-2-tartrato-2-niobate

The preparation of this compound was undertaken by the double decomposition of potassium tartratonibate and strontium nitrate. A white precipitate was got, which after filtration and washing crumpled to a hard mass. It was finely ground in an agate mortar and analysed. The same procedure suggested for the calcium compound was used for the

determination of niobium, tartaric acid and water. Strontium was determined as the sulphate.

Results

TABLE II

	Found %	Calculated for $\text{SrO} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10\text{H}_2\text{O}$
SrO ..	12.28	12.70
Nb_2O_5 ..	33.22	32.70
$\text{C}_4\text{H}_4\text{O}_5$..	31.99	32.45
H_2O ..	22.51	22.15

The strontium-2-tartrato-2-niobate prepared corresponds to the formula $\text{SrO} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10\text{H}_2\text{O}$.

4-Barium-6-tartrato-6-niobate

This barium compound was similarly prepared by the double decomposition of potassium tartratonioabate and barium nitrate. The white precipitate obtained crumpled to a hard mass and was powdered. The analysis was conducted on the same lines as in the previous cases, barium being estimated as the sulphate.

Results

TABLE III

	Found %	Calculated for $4\text{BaO} \cdot 3\text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_6 \cdot 16\text{H}_2\text{O}$
BaO ..	24.60	24.64
Nb_2O_5 ..	31.91	32.02
$\text{C}_4\text{H}_4\text{O}_5$..	31.85	31.79
H_2O ..	11.64	11.56

In view of the higher barium content of this compound, the preparation was repeated several times and the analyses gave almost identical values: a thorough check up of the barium content was done and the values were unaltered. Therefore it is formulated as a basic salt having the composition $4 \cdot \text{BaO} \cdot 3 \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_6 \cdot 16\text{H}_2\text{O}$ and named as 4-barium-6-tartrato-6-niobate 16-hydrate.

5-Lead-6-tartrato-6-niobate

The lead compound was also prepared by the reaction of lead acetate on potassium tartratonibate in aqueous solution; it was obtained as a white precipitate which was filtered, washed with cold water, dried and analysed for lead, niobium, tartaric acid and water. The following results were obtained.

TABLE IV

	Found %	Calculated for $5\text{PbO} \cdot 3\text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_6 \cdot 20\text{H}_2\text{O}$
PbO ..	36.19	36.40
Nb ₂ O ₅ ..	25.90	26.02
C ₄ H ₄ O ₅ ..	26.20	25.89
H ₂ O ..	11.71	11.69

This was also constituted as a basic salt of the composition $5\text{PbO} \cdot 3\text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_6 \cdot 20\text{H}_2\text{O}$. It can be named as 5-lead-6-tartrato-6-niobate 20-hydrate.

Copper-2-tartrato-2-niobate

The copper compound was obtained as a light green precipitate, when a solution of copper sulphate was added to a solution of potassium tartratonibate. The precipitate on filtration and washing crumpled to a hard mass which was powdered and analysed for the various constituents, when the following results were obtained:

TABLE V

	Found %	Calculated for $\text{CuO} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10\text{H}_2\text{O}$
CuO ..	9.89	10.08
Nb ₂ O ₅ ..	33.92	33.67
C ₄ H ₄ O ₅ ..	33.20	33.45
H ₂ O ..	22.99	22.80

The copper-2-tartrato-2-niobate 10-hydrate has therefore the formula $\text{CuO} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10\text{H}_2\text{O}$.

The dehydration of the alkaline earth metal compounds was conducted in the same way as in the previous cases (*vide* Part I). The results are set out in the accompanying tables:—

Dehydration in air

(1) Calcium-2-tartrato-2-niobate 10-hydrate.

TABLE VI

Temp. °C.	H ₂ O lost %	Molecules of H ₂ O Removed	Molecules of H ₂ O Retained
50	5.97	2.45	7.55
110	11.41	4.86	5.14
130	15.85	6.75	3.25

(2) Strontium-2-tartrato-2-niobate 10-hydrate.

TABLE VII

Temp. °C.	H ₂ O lost %	Molecules of H ₂ O Removed	Molecules of H ₂ O Retained
50	5.59	2.53	7.47
110	10.44	4.72	5.28
130	15.26	6.89	3.11

(3) 4-Barium-6-tartrato-6-niobate 16-hydrate.

TABLE VIII

Temp. °C.	H ₂ O lost %	Molecules of H ₂ O Removed	Molecules of H ₂ O Retained
50	3.01	4.16	11.84
110	7.77	10.75	5.25
130	10.61	14.68	1.32

It is found from the dehydration studies in air that greater number of molecules of water is removed from the alkaline earth metal salts than in the alkali metal compounds and it is interesting to note that only in the

barium compound dehydration has taken place to such an extent as to leave behind only one molecule of water.

The following salts were dehydrated in vacuum at 135° C.

TABLE IX

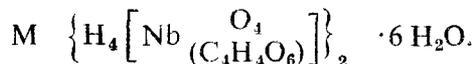
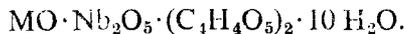
	Temp. °C	H ₂ O lost %	Molecules of H ₂ O Removed	Molecules of H ₂ O Retained
Ca Salt ..	135	20.68	8.79	1.21
Sr „ ..	135	20.41	9.21	0.79
Ba „ ..	135	11.40	15.78	0.22

Thus it can be seen that these salts lose a greater number of molecules of water by dehydration in vacuum and in the barium salt the dehydration is almost complete leaving behind nearly an anhydrous product.

DISCUSSION

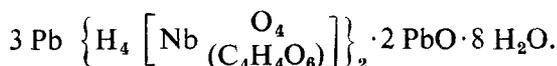
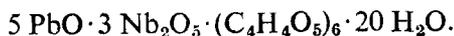
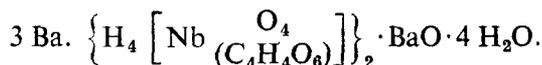
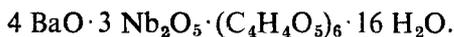
The tartratonibates of the alkaline earth and other metals have been prepared by double decomposition of the potassium complex with a soluble salt of the metal. They can be considered to be salts of 2-tartrato-2-niobic acid (*vide* Part I).

The calcium, strontium and copper compounds are normal salts whereas those of barium and lead are found to be basic salts. Examples of basic salts among heteropoly compounds are numerous. It has been found that with an increase in the atomic weight of the cation, there is also an increase in the amount of water removed from the compound by dehydration. This can be illustrated by the alkaline earth metal salts, where the number of molecules of water removed is significant particularly in the barium salt. On the assumption that these compounds are salts of 2-tartrato-2-niobic acid, the following structures can be assigned to the various compounds:



where M = Ca, Sr or Cu.

The basic barium and lead salts may be assigned the following structures:—



SUMMARY

The niobates of the alkaline earth and other metals are insoluble and hence the tartratonibates of these metals are prepared by double decomposition of soluble metal salts with potassium tartratonibate. The calcium-2-tartrato-2-niobate 10-hydrate of the formula $\text{CaO} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10 \text{ H}_2\text{O}$ has been prepared and studied. The strontium tartratonibate prepared has the formula $\text{SrO} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10 \text{ H}_2\text{O}$. A copper compound of the formula $\text{CuO} \cdot \text{Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 10 \text{ H}_2\text{O}$ has been prepared in a similar manner.

The barium and lead tartratonibate are also prepared by the above method of double decomposition but they are obtained as basic salts of the formulæ $4 \text{ BaO} \cdot 3 \text{ Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_6 \cdot 16 \text{ H}_2\text{O}$ and $5 \text{ PbO} \cdot 3 \text{ Nb}_2\text{O}_5 \cdot (\text{C}_4\text{H}_4\text{O}_5)_6 \cdot 20 \text{ H}_2\text{O}$. It is significant that the dehydration of the barium salt gives a practically anhydrous compound. The calcium, strontium and copper compounds obtained are considered as the normal salts of the 2-tartrato-2-niobic acid whereas those of barium and lead are regarded as basic salts. Suitable heteropoly acid structures are assigned to these compounds.

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