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# Coordination Properties of α-Hydroxy Carboxylic Acids. Part I. Binuclear Niobium(V) Complex Acids and some Salts

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*The conditions of dissolution of freshly precipitated niobium(V) oxide in α-hydroxy carboxylic acids glycolic, lactic, malic and tartaric were investigated. The dissolution is a function of the molar ratio α-hydroxy carboxylic acid/hydrated niobium(V) oxide, pH of the solution, temperature and time. From solutions of α-hydroxy monocarboxylic acids at* $2 < pH < 3$ *the binuclear complexes* $H_3O[Nb_2O_4(C_2H_2O_3)(C_2H_3O_3)]\cdot H_2O$ *and* $H_3O[Nb_2O_4(C_3H_4O_3)(C_3H_5O_3)]\cdot H_2O$ *were isolated. Colourless, poorly-crystalline complexes are 1:1 electrolytes and, according to i.r. spectral evidence, the binuclearity in their structures is achieved through oxygen bridges. With α-hydroxy dicarboxylic acids crystalline* $M[Nb_2O_3(C_4H_3O_5)(C_4H_4O_5)]\cdot nH_2O$ *and poorly crystalline complexes,* $M_2[Nb_2O_2(C_4H_2O_6)_2]\cdot nH_2O$, $M = H_3O^+, NH_4^+$, *were prepared as 1:1 electrolytes for the former and 1:2 electrolytes for the latter. Analytical, spectral, conductometric and potentiometric titration data give evidence for binuclear malatoniobate(V) and tartratoniobate(V) anions with bridging complex-forming agents.*

## Introduction

Aqueous solutions of oxalic [1] and tartaric [2] acids were found to be suitable solvents for dissolution of freshly precipitated niobium(V) and tantalum(V) oxides. Simple migration experiments of these solutions showed migration of the ions containing niobium(V) or tantalum(V) to the anode. Evaporation of a solution of freshly precipitated niobium(V) oxide in tartaric acid solution resulted in the precipitation of a complex described as $Nb(OH)(C_4H_4O_6)_2$. Potentiometric titrations [3] of alkali metal niobate(V) and tantalate(V) solutions with malic, tartaric and citric acids indicated that a complex was formed by the components. The conclusion was not the same for lactic acid. On addition of alcohol [4, 5] to the solution of freshly precipitated niobium(V) oxide in tartaric acid, the complex $Nb_2O_5(C_4H_4O_5)_2\cdot 10H_2O$ was isolated and described as heteropolyacid. Some alkali and alkaline earth metal salts [6], $M_2[Nb_2O_6(C_4H_4O_5)_2]\cdot nH_2O$, M = Li, Na, K, ½Ca, ½Sr, as well as some polynuclear compounds [7] were isolated. More detailed investigations of the dissolution of hydrated niobium(V) and tantalum(V) oxides in oxalic, glycolic, thioglycolic, lactic, malic, tartaric and citric acids and the isolation of water-soluble complexes were described [8].

Being particularly interested in the coordination properties of α-hydroxy carboxylic acids, in this paper we have extended our previous investigations of the crystalline binuclear malatoniobates(V) [9] to the other α-hydroxy carboxylic acids: glycolic, lactic, malic and tartaric. The results obtained for ammonium malato- and tartratoniobates(V) led us to prepare and re-investigate the earlier reported mononuclear complexes [8] of niobium(V) with the same ligands described as $Nb(OH)_3A$, $A = C_2H_2O_3^{2-}$, $C_3H_4O_3^{2-}$, $C_4H_4O_5^{2-}$, $C_4H_4O_6^{2-}$. Analytical, spectral, conductivity and potentiometric titration data reported here indicate the presence of binuclear oxygen-bridged anions for α-hydroxy monocarboxylic acid complexes and binuclear malato- and tartrato-bridged anions for α-hydroxy dicarboxylic acid complexes.

## Results and Discussion

### *Properties of the Solutions of Niobium(V) Oxide in α-Hydroxy Carboxylic Acids*

A complete dissolution of freshly precipitated niobium(V)- and tantalum(V) oxides [10] in α-hydroxy carboxylic acids: glycolic, lactic, malic and tartaric is possible. This dissolution is a function of the molar ration α-hydroxy carboxylic acid/hydrated niobium(V)-oxide, pH of the solution, temperature and time. It is possible to obtain clear, stable solutions of hydrated niobium(V) oxide in malic and tartaric acid aqueous solutions at a molar ratio acid/niobium of 3:1 (even 2:1), after heating the suspension at $pH > 2$ for two hours

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TABLE I. Analytical, I.r. Spectroscopic, and Physical Data for the Complexes.

| Complex | Analysis (%)[a] | | | | I.r. absorption bands (cm$^{-1}$) | | Dec. p. (°C) | $\lambda$[b] (S cm$^2$ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | C | H | Nb | N | $\nu_{asym.}(COO^-)$ | $\nu$(Nb–O–Nb) | | |
| $H_3O[Nb_2O_4(C_2H_2O_3)(C_2H_3O_3)]\cdot H_2O$ | 11.3<br>(11.0) | 2.7<br>(2.3) | 42.4<br>(42.6) | | 1660s | 850–650s,b | 25 | 142[c] |
| $H_3O[Nb_2O_4(C_3H_4O_3)(C_3H_5O_3)]\cdot H_2O$ | 15.7<br>(15.5) | 2.9<br>(3.0) | 40.3<br>(40.0) | | 1645s | 900–700s,b | 27 | 130[c] |
| $H_3O[Nb_2O_3(C_4H_3O_5)(C_4H_4O_5)]\cdot 4H_2O$ | 16.0<br>(16.3) | 3.1<br>(3.1) | 30.9<br>(30.5) | | 1650s | | 88 | d |
| $NH_4[Nb_2O_3(C_4H_3O_5)(C_4H_4O_5)]\cdot 4H_2O$ | 16.5<br>(16.3) | 3.5<br>(3.3) | 31.7<br>(31.5) | 2.6<br>(2.4) | 1630s | | 80 | 139 |
| $(H_3O)_2[Nb_2O_2(C_4H_2O_6)_2]\cdot 2H_2O$ | 16.5<br>(16.4) | 2.5<br>(2.4) | 31.7<br>(31.8) | | 1670s | 850–600s,b | 32 | 263 |
| $(NH_4)_2[Nb_2O_2(C_4H_2O_6)_2]\cdot 4H_2O$ | 15.2<br>(15.5) | 3.3<br>(3.3) | 29.8<br>(30.1) | 4.2<br>(4.5) | 1670s | | 32 | 238 |

[a] Calculated values are given in parentheses. [b] For $10^{-3}$ mol dm$^{-3}$ solutions in water at 25 °C. [c] For moist, freshly prepared substances. [d] Poorly soluble.

over a water bath. For a complete dissolution of hydrated niobium(V) oxide in glycolic and lactic acid aqueous solutions the same ratio is considerably higher, approx. 10:1 and 8:1 for glycolic and lactic acids, respectively. The time required to obtain a clear solution of hydrated niobium(V) oxide in α-hydroxy carboxylic acids is a function of the pH and the concentration of the acid present. It is shorter for higher pH and higher α-hydroxy carboxylic acid/hydrated niobium(V) oxide ratios. Freshly precipitated niobium(V) oxide can be dissolved in α-hydroxy carboxylic acids by refluxing the suspension without destroying the resulting complexes in the solutions.

### *Properties of the Complexes*

The binuclear complexes listed in Table I were prepared using the same general procedure by addition of acetone or ethanol to evaporated clear solutions of freshly precipitated niobium(V) oxide in the appropriate α-hydroxy carboxylic acids, with exception of malatoniobates(V). The latter were prepared by evaporation of the solutions at room temperature. For the preparation of all acids the solutions were run through a cation-exchange column before evaporation. Acetone was used for precipitation instead of ethanol where high solubility of complexes had been observed in mixtures of ethanol–water. Most of the complexes, according to their X-ray diffraction patterns, are poorly crystalline, except malatoniobates(V). A time-dependent change of colour from white to yellow-brown was observed for glycolato- and lactatoniobate(V) acids and to a lesser extent for tartratoniobate(V) acid. It was found that the origin of this change is not a function of the change in the chemical composition of the substances.

According to the physical and spectral properties these complexes could be divided into two classes: i) with α-hydroxy monocarboxylic acids, glycolic and lactic; ii) with α-hydroxy dicarboxylic acids, malic and tartaric. It is interesting to follow the changes in the coordination sphere of niobium(V) starting with α-hydroxy monocarboxylic acids.

### *i) Glycolic and lactic acid complexes*

In comparison to malato- and tartratoniobates(V) these two compounds possess lower crystallinity and are thermally less stable. Freshly prepared, briefly air-dried glycolato- and lactatoniobate(V) acids are soluble in water. After drying for several hours in air or over silica they are only partially water-soluble. The preparations with a small excess of glycolic or lactic acid are soluble in water after drying. Recrystallisation from water removes the excess acid, but often gives a product of partially hydrolysed species. The water molecules present in these complexes could be constitutional, since

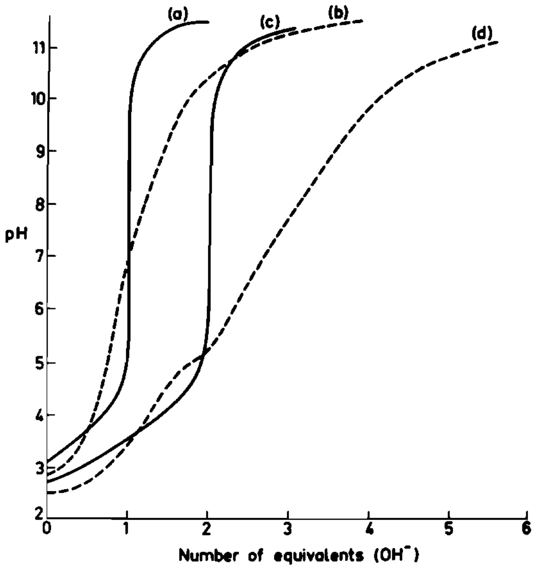

Fig. 1. Potentiometric titration curves. (a) glycolic acid, (b) $H_3O[Nb_2O_4(C_2H_2O_3)(C_2H_3O_3)]\cdot H_2O$, (c) *l*(+)-tartaric acid, (d) $(H_3O)_2[Nb_2O_2(C_4H_2O_6)_2]\cdot 2H_2O$.

unlike malato- and tartratoniobates(V), in the thermogravimetric decomposition curves there is no resolved step that could correspond to the loss of crystalline water molecules. Conductivity data in water obtained for moist glycolato- and lactatoniobate(V) acids are consistent with 1:1 electrolytes (Table I). Potentiometric titrations were carried out for glycolic acid, glycolato- and lactatoniobate(V) acids (moist), and the titration curves are represented in Fig. 1. From the titration curve of glycolatoniobate(V) acid it is evident that neutralisation of the free proton is followed by partial hydrolysis of the complex. These experiments are qualitative and additional experiments are necessary for determinations of acidity constant. The titration curve of lactatoniobate(V) acid is the same as that obtained for the glycolatoniobate(V) acid. Some information on the structure of these compounds can be obtained from the i.r. spectra. Broad absorption bands in the region 3500–3100 $cm^{-1}$ are due to the hydrogen bonded OH stretchings of water molecules present. The significant shift of the asymmetrical $COO^-$ stretching to lower wavenumbers in comparison to the position of this band in the i.r. spectra of the free ligands (Table I) indicates coordinated $COO^-$ groups [11]. The absence of absorption bands at 1242 and 1294 $cm^{-1}$, characteristic for the in-plane deformation of the hydroxyl group in zinc-glycolate and zinc-lactate [12], gives evidence for the coordination of the hydroxyl groups to the niobium. The assignment of a broad and strong absorption band in the region 900–650 $cm^{-1}$ to Nb–O–Nb stretchings instead to Nb–OH–Nb vibrations seems reasonable, since i.r. studies on some binuclear hydroxo-bridged complexes of Cr(II) [13], Cu(II) [14] and Pt(II) [15], always reveal the existence of a band in the region 900–1150 $cm^{-1}$ but not at lower wavenumbers. The absorption bands expected in the region 1700 and 1100 $cm^{-1}$, corresponding to the presence of $H_3O^+$ ions [16, 17] are not resolved, due to the strong ligand absorptions in these regions.

### *ii) Malic and tartaric acid complexes*

The malatoniobate(V) acid $H_3O[Nb_2O_3(C_4H_3O_5)(C_4H_4O_5)]\cdot 4H_2O$, and its ammonium salt are exceptions among the complexes discussed here. These highly crystalline, poorly soluble but thermally stable (Table I) substances were prepared without the addition of ethanol or acetone to the malic acid aqueous solution of hydrated niobium(V) oxide. Crystallisation of the acid starts immediately after passage of the clear solution through the cation exchange column and is completed by letting the solution evaporate at ambient temperature. Due to the low solubility in water neither conductivity nor potentiometric titration data are available. The acid is isostructural with its ammonium salt. The corresponding tartratoniobates(V) are water-soluble, less crystalline and thermally less stable. Conductivity data are consistent with 1:2 electrolytes (Table I). The potentiometric titration curve is represented in Fig. 1. The curve for $(H_3O)_2[Nb_2O_2(C_4H_2O_6)_2]\cdot 2H_2O$ exhibits two steps and, similarly to glycolatoniobate(V) acid, a partial hydrolysis of the complex occurs as a simultaneous process. The protons released in aqueous solution of glycolato-, lactato-, and tartratoniobate(V) acids indicate the presence of moderately strong acids. According to the existing evidence the origin of these protons is not common, as they could be present in the form of hydronium ions or could dissociate from carboxylato ligands as already discussed for copper(II) tartrato trihydrate elsewhere [18].

The interpretation of the i.r. spectra of malatoniobates(V) is very similar to that made earlier [9] for the binuclear malatoniobates(V). Sharp and strong absorption bands in the region 1650 and 1670 $cm^{-1}$ for malato- and tartratoniobates(V) respectively indicate the coordination of both carboxyl groups, since there is no evidence for the presence of uncoordinated COOH groups, as has been found in malato- and tartrato(phenanthroline)cobalt(II) complexes [19]. Significant changes in the spectra in the region 1200–1000 $cm^{-1}$ indicate the involvement of all hydroxyl groups [9, 20], in the coordination sphere of niobium(V). The absence of the strong absorption band in the 850–700 $cm^{-1}$ region in the spectra of malatoniobates(V) excludes the presence of oxygen bridges in these highly crystalline complexes. The i.r. spectra give evidence for the presence of oxygen bridges in the tartratoniobate(V) acid, due to the broad absorption present in the 850–650 cm$^{-1}$ region (Table I). Their presence in the ammonium salt, according to the i.r. spectra, is not so explicit. The appearance of this band in the spectrum of the tartratoniobate(V) acid could indicate the presence of intramolecular oxygen bridges or a polynuclear anion similar to that found in the $Mo_4O_{11}(C_4H_3O_5)_2^{4-}$ ions [21].

In the chemistry of complex compounds of niobium(V) no marked tendency for the formation of binuclear complexes [22] has been observed. In this paper this tendency is confirmed in the reactions of freshly precipitated niobium(V) oxide with α-hydroxy carboxylic acids. In complexes with glycolic and lactic acids the binuclearity seems to be achieved through oxygen bridges. The molecules of α-hydroxy dicarboxylic acids, malic and tartaric, are bridges between two niobium atoms in malato- and tartratoniobates(V). Examples of bridging malato [9, 21] and tartrato [23–26] anions in transition metal complexes are numerous. The prepared compounds represent new binuclear complexes of niobium(V) with biologically interesting α-hydroxy carboxylic acids with appreciable versatility of binding to different metal atoms. In addition, it is to be expected that some water molecules are coordinated to the niobium atoms, stabilising the structure and increasing the coordination number of niobium(V).

## Experimental

### *Preparation of the Solutions of Niobium(V) Oxide in α-Hydroxy Carboxylic Acids*

A mixture of 2 g $Nb_2O_5$ and 20 g $KHSO_4$ was heated in a Pt-crucible over a red flame until a clear melt was obtained. After cooling the melt was dissolved in 150 cm$^3$ of $H_2C_2O_4 \cdot 2H_2O$ (10%) on a water bath. The hydrated niobium(V) oxide as precipitated by addition of concentrated $NH_4OH$, centrifuged off and washed with a hot aqueous solution of $NH_4Cl$ (2%). The white precipitate was dissolved in 100 cm$^3$ of $H_2C_2O_4 \cdot 2H_2O$ (10%) and precipitated again, centrifuged off and washed as already described. The obtained moist precipitate of hydrated niobium(V) oxide was added to a 100 cm$^3$ of water containing glycolic (12 g), or lactic (10 g), or *dl*-malic (6 g) or *l*-tartaric (7 g) acids. Conc. $NH_4OH$ (1–2 .cm$^3$) was added to the mixtures increasing pH to the range 2–3. The resulting mixtures were warmed in a water bath for two hours (for glycolic and lactic acids 4–6 hours). The pH value of the resulting clear solutions was in the same range. These solutions were used for the preparation of all complexes discussed in this work.

### *Preparation of the Complexes*

For the preparation of glycolato-, lactato-, malato-, and tartratoniobate(V) acids the solutions were slowly passed through a cation-exchange column containing Dowex 50-X resin in order to remove ammonium ions. Some differences in preparation of acids and their ammonium salts are noted below.

### *Glycolato- and Lactatoniobates(V)*

Glycolic and lactic acid solutions of hydrated niobium(V) oxide were evaporated at 40 °C until a volume of 10 cm$^3$ was reached. After cooling, acetone was added (120 cm$^3$) to the solutions. White precipitates formed which were left to settle down, filtered off, washed with acetone and dried over silica; yield *ca.* 70%.

### *Malatoniobates(V)*

The precipitation of malatoniobate(V) acid was observed immediately after passing the malic acid solution of hydrated niobium(V) oxide through the cation-exchange column. The precipitation was continuous during the evaporation of the solution at ambient temperature for several days. The same procedure was applied for the ammonium salt. The compounds formed were filtered off, washed with water and dried over silica; yield 80% for both compounds.

### *Tartratoniobates(V)*

Tartaric acid solutions of niobium(V) oxide were evaporated at 40 °C until a volume of 20 cm$^3$ was obtained. The clear solutions were left in a refrigerator overnight in order to crystallise out the excess ammonium tartrate or tartaric acid in the case of the tartratoniobate(V) acid preparation. After removal of these compounds, the solutions were further evaporated to a volume of *ca.* 10 cm$^3$. The separated ammonium tartrate, or tartaric acid, was removed again and the clear solutions precipitated with ethanol (80 cm$^3$), or acetone in the case of tartratoniobate(V) acid. Both compounds were filtered off, washed with ethanol or acetone and dried over silica; yield 60% for both complexes.

### *Analysis*

Niobium was determined as $Nb_2O_5$ after destroying the compounds in a Pt-crucible over a small flame. Microanalytical determinations of carbon, hydrogen and nitrogen were performed by the Microanalytical Laboratory of the 'Rudjer Bošković' Institute, Zagreb. Analytical data are summarized in Table I.

### *Physical Measurements*

Infrared spectra were recorded on a Perkin Elmer 580B (4000–180 cm$^{-1}$) spectrophotometer as Nujol mulls and KBr pellets. Electrolytic conductance measurements were carried out for $10^{-3}$ mol dm$^{-3}$ solutions using a Tacusell Electronique conductivity bridge with a cell equipped with 1 cm$^2$ platinum electrodes at 25 ± 0.2 °C. Thermogravimetric measurements were carried out on a Cahn RG electromicroanalytical balance with a heating rate of 2 °C/min in air. X-ray diffraction patterns were recorded on a Philips X-ray diffractometer with a proportional counter, using graphite monochromatized CuK$\alpha$ radiation. Potentiometric titrations were performed with a Metrohm potentiograph (automat) Model E 436 at 25 °C under nitrogen atmosphere. The concentrations were $5 \times 10^{-3}$ and 0.1 mol dm$^{-3}$ for the complexes and sodium hydroxide, respectively. Changes in pH were followed using a glass electrode calibrated before each measurement. An attempt to perform the titrations at constant ionic strength failed because the acids were not soluble in 0.1 mol dm$^{-3}$ $KNO_3$ solution.

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