Contribution from the Department of Chemistry, Shivaji College (University of Delhi), New Delhi-15, India

Organic Compounds of Niobium and Tantalum
Reactions of Niobium and Tantalum Pentaethoxides with α-Hydroxy Carboxylic Acids

S. Prakash and R. N. Kapoor[*]

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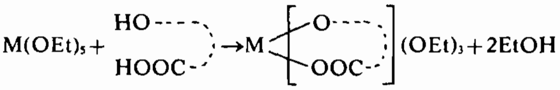
Reactions of niobium and tantalum pentaethoxides with various α–hydroxy carboxylic acids (lactic, mandelic, and salicylic acid) have been studied in different stoichiometric ratios and compounds having the composition, $M(OEt)_3(C_3H_4O_3)$, $M(OEt)(C_3H_4O_3)_2$, $M(C_3H_5O_3)(C_3H_4O_3)_2$, $M(OEt)_3(C_8H_6O_3)$, $M(OEt)(C_8H_6O_3)_2$, $M(C_8H_7O_3)(C_8H_6O_3)_2$, $M(OEt)_3(C_7H_4O_3)$, $M(OEt)(C_7H_4O_3)_2$ *and* $M(C_7H_4O_3)_2(C_7H_5O_3)$ *(where M is niobium or tantalum) have been quantitatively isolated. These products are either viscous liquids or crystalline solids. The above mono-substituted derivatives are monomeric in boiling benzene.*

Introduction

During the last two decades considerable interest has been shown in the coordination compounds of niobium and tantalum. Recently quite interesting results have been reported as a result of investigations on the reactions of niobium and tantalum pentalkoxides with β–diketones,[1-3] β–Ketoesters,[4,5] acyl halides,[6-8] glycols[9] and catechol[10] by the authors and other workers. Very little work has, however, been carried out on the α–hydroxy carboxylic acid derivatives of these elements. Funk and coworkers[11] carried out some preliminary work on the reactions of nobium and tantalum pentachlorides with salicylic and mandelic acids. Rosenheim and Roehrich[12] synthesised internal complexes of pentavalent niobium and tantalum with salicylic acid.

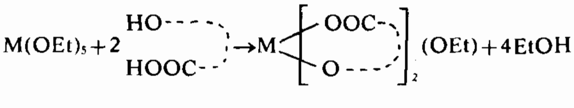
In view of the interesting results obtained earlier it was considered worthwhile to extend the investigations by carrying out a systematic study of the reactions of niobium and tantalum pentaethoxides with various α–hydroxy carboxylic acids. During the course of the investigations the reactions of pentaethoxides of these two elements with lactic, mandelic, and salicylic acid in different stoichiometric ratios have been investigated in anhydous benzene medium. The ethanol produced during the course of these reactions was removed azeotropically with benzene, its amount could be used to check the progress of the reaction. It was found that two moles of ethanol could be replaced when the reactions were carried out in the molar ratio of 1:1 indicating that both the hydroxyl as well as carboxyl groups were effective in replacing ethanol as shown below:



$$\mathrm{M(OEt)_5} + \begin{matrix}\mathrm{HO}\\ \mathrm{HOOC}\end{matrix} \rightarrow \mathrm{M}\left[\begin{matrix}\mathrm{O}\\ \mathrm{OOC}\end{matrix}\right]\mathrm{(OEt)_3} + 2\mathrm{EtOH}$$

(where M is niobium or tantalum).

In another set of reactions niobium and tantalum pentaethoxides were made to react with the above α–hydroxy carboxylic acids in the molar ratio of 1:2. The product in each case was found to be a disubstituted derivative. On the basis of the amounts of alcohol liberated during the reactions and the analytical data of the products obtained, these reactions can be represented by the following equation:



$$\mathrm{M(OEt)_5} + 2\begin{matrix}\mathrm{HO}\\ \mathrm{HOOC}\end{matrix} \rightarrow \mathrm{M}\left[\begin{matrix}\mathrm{OOC}\\ \mathrm{O}\end{matrix}\right]_2\mathrm{(OEt)} + 4\mathrm{EtOH}$$

(where M is niobium or tantalum).

When one mole of niobium or tantalum pentaethoxide was made to react with three moles of α–hydroxy carboxylic acid (lactic, mandelic, or salicylic acid), the replacement of only four moles of ethanol was possible and a disubstituted derivative was obtained. The replacement of the fith ethoxy group could, however, be possible when the alkoxide was refluxed with 3.5 moles of acid for several hours when a trisubstituted derivative was obtained. The excess acids were removed from the products by washing with ether or chloroform.

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[*] Department of Chemistry, University of Jodhpur, Jodhpur, India.

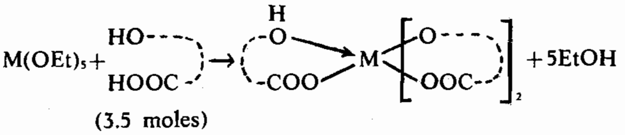
(1) R.N. Kapoor, S Prakash, and P.N. Kapoor, *Bull. Chem. Soc. Japan*, *40*, 1384 (1967).
(2) R. Gut, H. Buser and E. Schmid, *Helv. Chim. Acta*, *48*, 878 (1965).
(3) P.N. Kapoor and R.C. Mehrotra, *J. Less-Common Metals*, *8*, 339 (1965).
(4) R.C. Mehrotra and P.N. Kapoor, *J. Less-Common Metals*, *7*, 176, 453 (1964).
(5) R.C. Mehrotra, R.N. Kapoor, S. Prakash, and P.N. Kapoor, *Australian J. Chem.*, *19*, 2079 (1966).
(6) R.N. Kapoor, S. Prakash, and P.N. Kapoor, *Ind. J. Chem.*, 5 (6), 442 (1967).
(7) S. Prakash., P.N. Kapoor, and R.N. Napoor, *J. Prakt. Chem.*, *4*, (36), 24 (1967).
(8) R.C. Mehrotra and P.N. Kapoor, *J. Less-Common Metals* (1960).
(9) R.N. Kapoor, S. Prakash, and P.N. Kapoor, *Z. Anorg. Allgem. Chem.*, *351*, 219 (1967).
(10) R.N. Kapoor, S. Prakash, and P.N. Kapoor, *Z. Anorg. Allgem. Chem.*, *353*, 109 (1967).
(11) H. Funk, W. Weiss, and K.H. Roethe, *Z. Anorg. Allgem. Chem.*, *301*, 271 (1959).
(12) V.A. Rosenheim and E. Roehrich, *Z. Anorg. Allgem. Chem.*, *204*, 342 (1932).

Table I. Reactions of niobium and tantalum pentaethoxides with lactic acid.

S.N.	Alkoxide (g)	Lactic acid (g)	Molar ratio	Products and their Physical characteristics	Amount of alcohol in azeotrope Found (g)	Amount of alcohol in azeotrope Calc. (g)	Analysis Found % Metal	Analysis Calc. % Metal
1.	NB(OEt)$_5$ (1.75)	0.49	1:1	Nb(OEt)$_3$(C$_3$H$_4$O$_3$) . light yellow solid, soluble in benzene. .Mol. wt.: 350.	0.50	0.52	29.8	29.4
2.	Nb(OEt)$_5$ (1.58)	0.89	1:2	Nb(OEt)(C$_3$H$_4$O$_3$)$_2$. white crystalline solid, sparingly soluble in benzene.	0.88	0.89	29.2	29.8
3.	Nb(OEt)$_5$ (1.55)	1.32	1:3.5	Nb(C$_3$H$_5$O$_3$)(C$_3$H$_4$O$_3$)$_2$. white crystalline solid, sparingly soluble in benzene.	1.04	1.09	25.0	25.5
4.	Ta(OEt)$_5$ (1.49)	0.33	1:1	Ta(OEt)$_3$(C$_3$H$_4$O$_3$) . white viscous liquid, soluble in benzene . Mol. wt.: 410.	0.33	0.32	44.8	44.8
5.	Ta(OEt)$_5$ (2.64)	1.17	1:2	Ta(OEt)(C$_3$H$_4$O$_3$)$_2$. white crystalline solid, sparingly soluble in benzene.	1.18	1.19	44.1	45.1
6.	Ta(OEt)$_5$ (2.25)	1.50	1:3.5	Ta(C$_3$H$_5$O$_3$)(C$_3$H$_4$O$_3$)$_2$. white crystalline solid, sparingly soluble in benzene.	1.25	1.27	41.5	41.5

Table II. Reactions of niobium and tantalum pentaethoxides with mandelic acid.

S.N.	Alkoxide (g)	Mandelic acid (g)	Molar ratio	Products and their Physical characteristics	Amount of alcohol in azeotrope Found (g)	Amount of alcohol in azeotrope Calc. (g)	Analysis Found % Metal	Analysis Found % Mandelate	Analysis Calc. % Metal	Analysis Calc. % Mandelate
1.	Nb(OEt)$_5$ (1.91)	0.91	1:1	Nb(OEt)$_3$(C$_8$H$_6$O$_3$). Yellowish white crystalline solid, soluble in benzene. Mol. wt.: 414.	0.54	0.54	25.4	39.3	24.6	39.6
2.	Nb(OEt)$_5$ (1.82)	1.74	1:2	Nb(OEt)(C$_8$H$_6$O$_3$)$_2$. Yelowish white cryst. solid, soluble in benzene.	0.98	1.02	20.4	68.0	21.2	68.4
3.	Nb(OEt)$_5$ (1.74)	2.49	1:3.5	Nb(C$_8$H$_7$O$_3$)(C$_8$H$_6$O$_3$)$_2$. Yellowish white cryst. solid, soluble in benzene.	1.20	1.24	17.8	83.2	17.1	82.9
4.	Ta(OEt)$_5$ (1.96)	0.74	1:1	Ta(OEt)$_3$C$_8$H$_6$O$_3$). Yellowish white cryst. solid, soluble in benzene. Mol. wt.: 482.	0.43	0.43	37.8	32.9	38.8	32.1
5.	Ta(OEt)$_5$ (1.76)	1.32	1:2	Ta(OEt)(C$_8$H$_6$O$_3$)$_2$. Yellowish white cryst. solid, soluble in benzene.	0.79	0.78	34.0	56.1	34.2	57.0
6.	Ta(OEt)$_5$ (1.98)	2.22	1:3.5	Ta(C$_8$H$_7$O$_3$)(C$_8$H$_6$O$_3$)$_2$. Yellowish white cryst. solid, soluble in benzene.	1.06	1.12	29.3	71.5	28.6	71.3



(where M is niobium or tantalum).

The above results seem to indicate that the primary pentavalency of both niobium and tantalum is satisfied by a combination of carboxylic and phenoxy oxygen atoms of the salicylic acid molecule. In earlier literature describing the salts of salicylic acid with metals like beryllium,[13] iron,[14] and titanium,[15] only the phenoxy oxygen has been shown to form a primary valency bond. However, in view of the comparative acidic character of the carboxyl and the phenoxyl hydrogen atoms (Dissociation constants of the order of 10^{-3} and $10^{-7.5}$ respectively) in salicylic acid molecule, it is to be expected that the carboxyl group should be more reactive. It is for this reason that the fifth primary valency of niobium or tantalum, in the trisubstituted derivatives, is satisfied by the combination of a carboxylic oxygen atom of the salicylic acid molecule.

The above derivatives are either viscous liquids or crystalline solids soluble in benzene, the mono- and disubstituted derivatives being more so. Molecular weight determination studies show that the monosubstituted derivatives of niobium and tantalum are monomeric in benzene. All these derivatives were found to undergo decomposition on heating even under reduced pressure.

Experimental Section

Experimental techniques, reagents and analytical methods were similar to those described in earlier communications.[1,6,7,9,10] Mandelic and salicylic acids B.D.H./Analar were dried under reduced pressure before use. Lactic acid was purified by distillation before use. Mandelic acid was estimated by exidation with ceric sulfate.[16] Salicylic acid was estimated by

(13) V.A. Rosenheim and Lehmann, *Ann.*, *153*, 440 (1924).

(14) R.W. Asmussen and E.R. Medsen, *Z. Anorg. Allgem. Chem.*, *212*, 321 (1933).

(15) O. Hauser and A. Leavite, *Ber.*, *4B*, 213 (1965).

(16) M.R. Verma and S.D. Paul, *J. Sci. Industr. Res.*, *13B*, 347 (1954).

Table III. Reactions of niobium and tatalum pentaethoxides with salicylic acid.

S.N.	Alkoxide	Salicylic acid (g)	Molar ratio (g)	Products and their physical characteristics	Amount of alcohol in azeotrope		Analysis			
							Found %		Calculated %	
					Found	Calc. (g)	Metal (g)	Salicylate	Metal	Salicylate
1.	$Nb(OEt)_5$ 2.13	0.92	1:1	$Nb(OEt)_3(C_7H_4O_3)$. Yellowish white cryst. solid, soluble in benzene. mol. wt.: 377.	0.63	0.60	24.8	37.9	25.5	37.4
2.	$Nb(OEt)_5$ 2.36	2.05	1:2	$Nb(OEt)(C_7H_4O_3)_2$. Pale yellow cryst. solid, Soluble in benzene.	1.27	1.34	21.9	66.0	22.6	66.3
3.	$Nb(OEt)_5$ 2.09	2.72	1:3.5	$Nb(C_7H_5O_3(C_7H_4O_3)_2$. Pale yellow cryst. solid, sparingly soluble in benzene.	1.51	1.51	18.3	81.8	18.5	81.5
4.	$Ta(OEt)_5$ 1.78	0.61	1:1	$Ta(OEt)_3(C_7H_4O_3)$. White cryst. solid, soluble in benzene. mol. wt.: 466.	0.40	0.39	39.2	31.0	39.8	30.0
5.	$Ta(OEt)_5$ 1.78	1.22	1:2	$Ta(OEt)(C_7H_4O_3)_2$. Yellowish white cryst. solid, soluble in benzene.	0.76	0.73	35.9	53.8	36.3	54.3
6.	$Ta(OEt)_5$ 1.74	1.77	1:3.5	$Ta(C_7H_5O_3)(C_7H_4O_3)_2$. Yellowish white cryst. solid, sparingly soluble in benzene.	0.88	0.98	29.9	70.2	30.8	69.2

alkaline potassium permanganate oxidation method.[17] Molecular weights were determined by a gallenkemp semimicro ebulliometer.

As the synthetic procedures used in all the reactions were the same, details are given in two cases only and the rest of the reactions are summarised in Table I, II, and III.

Reaction Between Niobium Pentaethoxide and Salicylic Acid (Molar ratio 1:1). Salicylic acid (0.92 g) was added to a benzene (50 g) solution of niobium pentaethoxide (2.13 g). A clear yellow solution was obtained. It was refluxed at 120-30°C and the binary azeotrope of ethanol-benzene was slowly fractionated over 5 hours. The excess solvent was distilled out under reduced pressure. The residue when dried at 55°C/0.1 mm for an hour yielded a yellowish white crystalline solid. (Ethanol in azeotrope, 0.63 g: replacement of one equivalent requires 0.60 g).

Found: Nb, 24.8; Salicylate, 37.9%; mol. wt., 377.

Calculated for $Nb(OEt)_3(C_7H_4O_3)$: Nb, 25.51; Salicylate, 37.4%; mol. wt., 364.

Reaction Between Tantalum Pentaethoxide and Mandelic Acid (Molar Ratio 1:1). To a benzene (50 g) solution of tantalum pentaethoxide ,1.96 g), mandelic acid (0.74 g) was added. The light yellow solution so obtained was refluxed under a fractionating column and the liberated ethanol was separated azeotropically with benzene at 68-80°C. Excess of benzene was distilled out at 80°C. A yellow solution was obtained which was concentrated under reduced pressure. A yellowish white crystalline solid was obtained which was dried at 50°C/0.4 mm. (Ethanol in azeotrope, 0.43 g: replacement of one equivalent requires, 0.43 g).

Found: Ta, 37.8; Mandelate, 32.9%; mol. wt. 482.

Calculated for $Ta(OEt)_3(C_8H_6O_3)$: Ta, 38.8; Mandelate, 32.1%; mol. wt., 466.

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(17) W. Bottger, « Newer methods of Volumetric Chemical Analysis », p. 61 (1938).