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THERMAL AND STRUCTURAL INVESTIGATION OF SOME OXALATO-NIOBIUM COMPLEXES

III. Strontium tris(oxalato)oxoniobate

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Strontium tris(oxalato)oxoniobate, $Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\,H_2O$ has been synthesized and characterized by elemental analysis, infrared spectroscopy and powder X-ray diffraction. A mechanism of thermal decomposition is suggested on the basis of differential thermal analysis. The conditions of strontium metaniobate formation, as final product of the thermal decomposition, have been established.

The carboxylato complexes are particularly important in niobium chemistry, especially for their current use in the solubilization of niobic acid and niobium pentoxide. The oxalato and tartrato complexes are mostly used for this purpose.

Among the oxalato complexes, first obtained by Russ [1], the alkali metal salts of the mono-, bis- and tris(oxalato)oxoniobate complexes have been most investigated. The same author observed the precipitation of tris(oxalato)niobate anion with some bivalent cations, but these complexes have not been investigated in any detail.

In two previous papers, [2, 3] we reported the synthesis, characterization and thermal decomposition mechanism of potassium and barium tris(oxalato)oxoniobates. These compounds were prepared with the aim of establishing new methods for the preparation of alkali metal and alkaline earth niobates. The thermal decomposition of some organic ligand complex compounds is an appropriate method for this purpose. This non-traditional procedure requires a lower temperature and yields compounds with the desired stoichiometry, with a definite degree of crystallinity, and of high purity.

In this paper, the synthesis of strontium tris(oxalato)oxoniobate is reported, with the same purpose of obtaining strontium metaniobate by a non-traditional method.

Results and discussion

The isolation of oxalato-niobato complexes in the solid state is quite difficult, when the preparation involves salts derived from cations which form insoluble oxalates, such as Sr or Ba. In this case the oxalato-niobato complex is often contamined by strontium oxalate, and it is practically impossible to separate these compounds.

Table 1 Infrared spectra

SrC_2O_4, cm^{-1}	$Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\,H_2O$, cm^{-1}	Assignment
510 w	490 ms	δ(O–C=O), ν(Nb–O_{ox})
	525 m	ν(C–C), δ(O–C=O)
600 w	560 w	ν(Nb–O_{ox}), ν(C–C)
	720 w	
	780 s	
795 m	810 m	δ(O–C=O)
	920 s	ν(Nb=O), ν(C–C), ν(C–O)
	955 s	
	1260 s	ν(C–O), δ(O–C=O)
1320 s	1325 s	ν(C–O), ν(C=C)
	1425 s	
1460 w		
1640 s	1660 vs, br	ν(C=O), (H_2O)
1670 s	1700 s	ν(C=O)
	1720 s	
	3480 m, br	(H_2O)

Abbreviations: vs – very strong, s – strong, m – medium, w – weak, br – broad

Strontium tris(oxalato)oxoniobate was prepared by treating tris(oxalato)oxoniobic acid, in excess of oxalic acid, with a strontium salt, at pH = 1. The complex is obtained as a crystalline white powder, insoluble in water, soluble in hydrochloric acid (1 : 1) and in oxalic acid. The strontium salt ismore soluble than the barium salt in HCl.

The strontium compound was characterized by chemical analysis, infrared spectra and X-ray diffraction powder diagrams and has the formula $Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\,H_2O$.

Infrared spectra

The infrared spectrum of strontium tris(oxalato)oxoniobate and the assignments of the absorption bands are given in Table 1, compared with the infrared spectrum of strontium oxalate.

The spectrum is very similar to that of barium tris(oxalato)oxoniobate [3]. The bands of free oxalate ions ($C_2O_4^{2-}$ or $HC_2O_4^-$) are not observed in the infrared spectrum of the complex. The bands due to oxalato groups coordinated to the niobium atom occur at wavenumbers close to those for the barium complex, at 490 and 560 cm^{-1} [3].

The characteristic Nb=O band occurs as a doublet at 920 cm^{-1}, close to the value found for the barium salt. This doublet indicates a lower molecular symmetry of the strontium complex as compared with the alkali metal salts, in which the Nb=O bond gives rise to a single band at 950 cm^{-1} [2].

In the infrared spectra of strontium and barium tris(oxalato)oxoniobates, the bands are generally shifted towards higher frequencies as compared with the related alkali metal salts. This is probably due to the influence of the heavier strontium or barium atom.

The same shift of the C=O bands of the oxalato groups towards higher values (from 1640 to 1700 cm^{-1}) and of the C–O band towards lower values (from 1320 to 1260 cm^{-1}) are observed in the infrared spectra of both the strontium and the barium salts, as compared with the infrared spectra of the pure oxalates. This fact indicates shortening of the C–O bond and lengthening of the C=O bond.

In the infrared spectrum of strontium tris(oxalato)oxoniobate the crystallization water molecules produce bands at 1660 and 3480 cm^{-1}, suggesting different types of bonding, in agreement with the observed stepwise elimination during heating, confirmed by thermogravimetry.

Table 2 X-ray diffraction lines of $Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\ H_2O$

d, Å	I/I_o	d, Å	I/I_o
7.7553	24	3.0972	24
7.4680	5	3.0193	27
7.0192	18	2.9760	24
6.6813	37	2.9567	20
6.4580	100	2.8950	63
6.1118	98	2.8184	39
5.8700	61	1.7944	27
5.7711	61	2.7411	69
5.4868	8	2.7168	31
5.0461	67	2.6390	33
5.0122	72	2.6106	25
4.8701	14	2.5786	51
4.7160	59	2.5390	24
4.5902	86	2.4766	22
4.4755	92	2.4351	24
4.4225	78	2.3803	61
4.1371	14	2.3563	20
3.9655	17	2.3304	16
3.8701	15	2.2984	49
3.8306	27	2.2159	22
3.6331	37	2.1953	18
3.5927	31	2.1591	22
3.5172	51	2.1319	20
3.4397	24	2.1016	20
3.3933	65	2.0624	27
3.2995	49	2.0076	31
3.2499	20	1.9802	18
3.1838	10	1.9371	22

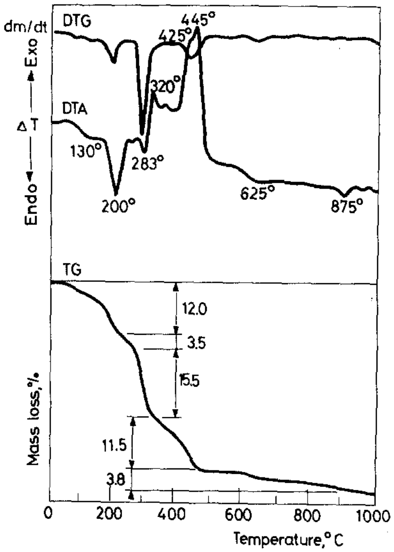

Fig. 1 Thermal curves of strontium tris(oxalato)oxoniobate

X-ray diffraction powder diagrams

The characteristic X-ray diffraction lines of strontium tris(oxalato)oxoniobate are shown in Table 2.

The presence of a large number of lines in the powder diagram (as in the case of potassium [2] and barium [3] tris(oxalato)oxoniobates) indicates a low symmetry structure of the complex, which may be either monoclinic or triclinic.

Thermogravimetry and differential thermal analysis

A scheme for the thermal decomposition of strontium tris(oxalato)oxoniobate, established from the TG and DTA curves (Fig. 1), is suggested in Table 3.

The strontium complex, $Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\,H_2O$, releases the crystallization water in two steps, as indicated by the weight losses at 140° and 210° (TG curve), associated with endothermal effects at 130° and 200°, respectively (DTA curve). Anhydrous strontium tris(oxalato)oxoniobate is formed above 210°.

Between 210 and 270°, the tris(oxalato)oxoniobate compex begins to decompose, with elimination of carbon monoxide and carbon dioxide. Under these conditions, the decomposition being carried out in the presence of air, the carbon monoxide formed during the first step of decomposition is probably partially oxidized to carbon dioxide, which is the main gaseous product finally evolved.

In fact, there is some disagreement in the literature about the oxidation of CO to CO_2 in the thermal decomposition of simple and complex oxalates [4–6]. Gas-chromatographic analysis of the gaseous products of thermal decomposition of

Table 3 Thermal analysis data for $Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\,H_2O$

Weight loss, TG			Thermal effects		
Temperature, °C	Loss, %	Lost species	Endo	Exo	Compounds
					$Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\,H_2O$
20–140°	3.8	$3\,H_2O$	130°		$Sr_3[NbO(C_2O_4)_3]_2 \cdot 5\,H_2O$
140–210°	8.2	$5\,H_2O$	200°		$Sr_3[NbO(C_2O_4)_3]_2$
210–270°	3.5	$CO, (1-x)\,CO_2$	260°		$Sr[NbO_2(C_2O_4)_2] \cdot x\,CO_2 + SrC_2O_4$
270–330°	15.5	$2\,CO, 2\,CO_2$	285°		
330–460°	11.5	$3\,CO, CO_2$		320°	
				350°	
				445°	$2\,SrCO_3$ (orthorhombic)
460–980°	3.8	$x\,CO_2$		560°	
				625°	$SrNb_2O_6 \cdot x\,CO_2$
				875°	$2\,SrCO_3$ (hexagonal) + $SrNb_2O_6$

$Sr[NbO(C_2O_4)_3]_2$ at 350° demonstrated the presence of a CO and CO_2 mixture. The gaseous products remain partially adsorbed on the solid phase and the desorption occurs stepwise with increasing temperature [7].

The double endothermal effect at 260° and 285° reveals the decomposition of the tris(oxalato)oxoniobato complex (3:1) with the formation of the mono(oxalato)-oxoniobato complex (1:1) together with two strontium oxalate molecules.

The decomposition of the mono(oxalato)dioxoniobato complex begins at 320°, this reaction being revealed by a marked exothermal effect at 320° and a second weaker one at 350°. The decomposition is associated with a rapid weight loss between 270 and 330°, corresponding to a loss of $2\,CO_2$ and 2 CO molecules, and between 330 and 460° with the loss of another 3 CO and 1 CO_2 molecules. Some of the gaseous products remain adsorbed on the solid phase.

In the decomposition of the mono(oxalato)niobato complex, strontium metaniobate, $SrNb_2O_6$, is formed, with a weak exothermal effect at 560°.

Between 370 and 470° the decomposition of strontium oxalate occurs, with formation of strontium carbonate, associated with a double exothermal effect at 425 and 445° [5].

The last step of thermal decomposition indicates stepwise elimination of adsorbed CO and CO_2.

The endothermal effect at 875°, without weight loss, is due to a polymorphic transformation of strontium carbonate, from the orthorhombic to the hexagonal form.

The formation of strontium metaniobate occurs under these conditions at a lower temperature (560°) than is indicated in the literature (690°).

Finally, the thermal decomposition product of strontium tris(oxalato)oxoniobate is a mixture of strontium metaniobate and strontium carbonate, in 1:2 molar ratio

Table 4 X-ray diffraction data for the final product of thermal decomposition of $Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\,H_2O$

	Complex heated at 950°		Complex heated at 950° and washed with 1:1 HCl		
d, Å	I/I_0	Assignment	d, Å	I/I_0	Assignment
3.5365	97	$SrCO_3$			
3.4607	45	$SrCO_3$			
3.1684	20	$SrNb_2O_6$	3.1684	52	$SrNb_2O_6$
3.1015	39	$SrNb_2O_6$	3.0557	100	$SrNb_2O_6$
3.0273	100	$SrCO_3 + SrNb_2O_6$	3.0153	56	$SrNb_2O_6$
2.9625	15	$SrNb_2O_6$	2.9435	16	$SrNb_2O_6$
2.8341	10	$SrCO_3 + SrNb_2O_6$	2.8341	49	$SrNb_2O_6$
2.5516	13	$SrCO_3$			
2.4753	24	$SrCO_3 + SrNb_2O_6$	2.4753	26	$SrNb_2O_6$
2.4544	31	$SrCO_3$			
2.1661	19	$SrCO_3$			
2.0491	26	$SrCO_3 + SrNb_2O_6$	2.0491	9	$SrNb_2O_6$
1.9868	13	$SrCO_3 + SrNb_2O_6$	1.9868	15	$SrNb_2O_6$
1.9450	11	$SrCO_3$			
1.9087	19	$SrCO_3 + SrNb_2O_6$	1.9232	10	$SrNb_2O_6$
1.8732	16	$SrCO_3$			
1.7615	11	$SrCO_3$			
1.7458	14	$SrNb_2O_6$	1.7458	14	$SrNb_2O_6$
1.5105	11	$SrCO_3 + SrNb_2O_6$	1.5105	8	$SrNb_2O_6$

($SrNb_2O_6 + 2\,SrCO_3$). The strontium metaniobate can readily be separated from this mixture, by dissolving the strontium carbonate in 1:1 HCl the metaniobate being scarcely soluble.

Strontium metaniobate and carbonate formation was confirmed by the infrared spectra and X-ray diffraction powder diagrams.

In the infrared spectra of the mixture (strontium metaniobate and carbonate), the characteristic bands of the CO_3^{2-} ion are present at 700, 865, 1075 and 1435 cm^{-1} [8], and a weak band at 660 cm^{-1}, due to the presence of metaniobate, is also observed.

The X-ray diffraction pattern (Table 4) of the mixture contains the characteristic lines of strontium metaniobate [9].

After washing with hydrochloric acid, the X-ray diffraction patterns confirms the presence of strontium metaniobate.

In order to obtain a well-crystallized strontium metaniobate, longer thermal treatment at 950° is necessary.

Experimental

Synthesis of strontium tris(oxalato)oxoniobate

The synthesis is carried out with hydrated niobic acid, obtained by a previously-described procedure [3].

1 g dried niobic acid is dissolved in a hot solution containing 2.46 g oxalic acid in 100 ml water (1:3 molar ratio). For complete dissolution of the niobic acid, a few drops of conc. HCl are added, and the solution is boiled. After filtration, the solution is treated with 2.77 g $Sr(NO_3)_2$ dissolved in water. The solution is maintained at ca. 80° for 1 hr, and then at room temperature for 8–10 hrs. The strontium complex deposits gradually as a white crystalline precipitate, which is filtered off, washed with hot water, then with alcohol, and dried. The precipitation is not quantitative.

For analysis the complex was dissolved in oxalic acid solution or in 1:1 hydrochloric acid. Strontium was determined gravimetrically, by precipitation as sulfate. Alternatively, strontium was determined by atomic absorption spectroscopy. Niobium was determined gravimetrically, by precipitation as niobic acid in the filtrate left after strontium separation, by adding ammonia to pH 7, and calcination to Nb_2O_5. Alternatively, niobium was determined by precipitation with 8-hydroxyquinoline and decomposition to Nb_2O_5. The oxalate content was determined by permanganometric titration after solubilization of the complex in 1:1 hydrochloric acid. The carbon content was determined by microcombustion.

The results of the elemental analysis are as follows:

	Nb	Sr	C_2O_4	C	H_2O
Found (%):	15.88	22.39	46.20	12.20	12.00
Calcd. (%):	16.12	22.80	45.80	12.49	12.50

These data are in agreement with the composition $Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\ H_2O$.

The infrared spectra were recorded with an UR 20 Carl Zeiss Jena (DDR) spectrophotometer in KBr pellets, in the range 4000–400 cm^{-1}. The X-ray powder diagrams were recorded with a TUR-M 62 diffractometer, using Cu K_α radiation.

The TG, DTG and DTA curves were recorded with a derivatograph, in air, with a rate of temperature increase of 5 deg/min.

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Zusammenfassung — Strontium-tris(oxalato)oxoniobate, $Sr_3[NbO(C_2O_4)_3]_2 \cdot 8\,H_2O$, wurde synthetisiert und durch Elementaranalyse, Infrarotspektroskopie und Röntgenpulverdiffraktometrie charakterisiert. Basierend auf differentialthermoanalytischen Ergebnissen wird ein Mechanismus für die thermische Zersetzung vorgeschlagen. Die Bedingungen für die Bildung von Strontiummetaniobat, dem Endprodukt der thermischen Zersetzung, wurden ermittelt.

Резюме — Синтезирован триоксалатоксониобат стронция — $Sr_3[NbO(C_2O_4)_3]_2 \cdot 8H_2O$ — и охарактеризован элементарным анализом, инфракрасной спектроскопией и порошковой рентгегографией. На основании дифференциального термического анализа предложен механизм термического разложения. Определены условия образования метаниобата стронция, как конечного продукта термического разложения.