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Abstract

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INFRARED ABSORPTION SPECTRA OF TITANIUM AND NIOBIUM OXALATES

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It is known that elements of Groups IV and V of the periodic system form complex compounds with oxalic acid. Titanium oxalates in aqueous solutions were thoroughly studied by A. K. Babko and co-workers (^{1}), and niobium oxalate solutions have for many years been used for separating it from tantalum (^{2}). Titanium and niobium oxalates have also been isolated in the solid state ($^{3-5}$). However, until recently there was no convincing evidence for the complex character of the synthesized oxalates, especially in the case of niobium. Usually the authors gave only the gross composition, which is far from sufficient for recognizing them as complex compounds.

One of the most promising methods for establishing the complex character of crystalline salts at present is the method of studying their absorption spectra in the infrared region. In particular, the work of J. Lecomte and co-workers (^{6}) showed that the number of absorption bands increases on going from simple oxalates to complex ones. They found that in the region between 1100 and 1600 cm^{-1} three bands are observed for complex oxalates instead of two in the spectrum of simple oxalates, and between 750 and 900 cm^{-1} two bands instead of one. This phenomenon was explained by the loss, by oxalate groups in complex salts, of their high symmetry owing to the formation of a coordination bond with the complex-forming agent. The authors of these works came to the conclusion that the method of studying IR spectra can be used to establish the complex character of a given oxalate.

As a result of a number of studies, we synthesized in the solid state various oxalic-acid derivatives of titanium and niobium ($^{7-12}$), whose composition corresponds to the following formulas: $Na_3[NbO(C_2O_4)_3] \cdot 2H_2O$, $K_3[NbO(C_2O_4)_3] \cdot 2H_2O$, $(NH_4)_3[NbO(C_2O_4)_3] \cdot 2H_2O$, $Ca[TiO(C_2O_4)_2] \cdot 4H_2O$, $Sr[TiO(C_2O_4)_2] \cdot 5.5\ H_2O$, $Ba[TiO(C_2O_4)_2] \cdot 4H_2O$. Since there was no direct evidence that the oxalate group is complex-bound to titanium and niobium in these compounds, we decided to record their infrared spectra. At the same time, we recorded spectra in the same wavelength regions also for the corresponding simple oxalates of sodium, potassium, ammonium, calcium, strontium, and barium. All compounds were examined on an IKS-14 double-beam spectrometer. Titanyl oxalates, as well as oxalates of alkaline-earth elements, were recorded by the powder method. The procedure for preparing samples for recording spectra was as follows. 800 mg of chemically pure sodium bromide, which had been recrystallized from the melt and thoroughly dried, and 4 mg of the substance under investigation (0.5% by weight) were carefully mixed and ground in a vibratory mill. From the resulting powder, passing through a sieve with 10,000 openings/cm^2, disks 20 mm in diameter were pressed under vacuum and at a pressure of 8000 kg/cm^2; these disks were used for carrying out the experiment.

Oxaloniobates, as well as simple oxalates of alkali metals and ammonium, were recorded in the form of a paste. Hexachlorobutadiene was used as the filler for wavelengths in the region 4000-2000 cm^{-1}, and Vaseline oil in the other regions.

The results obtained by us are shown in Figs. 1 and 2. As is evident from the figures, the infrared spectra of all the salts studied contain a number of quite clearly expressed maxima. In full agreement with the literature data (^{6}), in the spectra of simple oxalates we obtained, in the wavelength region 900-750 cm^{-1}, one absorption maximum, and in the region 1600-1100 cm^{-1}, two sharp absorption maxima. The spectra of compounds containing titanium and niobium, however, have in the indicated regions, respectively, two and three absorption bands. This gives us grounds to assert that the titanium and niobium derivatives are complex compounds. In all spectra, except for the spectrum of simple sodium oxalate, in the wavelength region 3700-3200 cm^{-1}, absorption bands are observed that are attributable to vibrations of water molecules contained in the salts. The presence of another absorption maximum in the region 1690-1760 cm^{-1} apparently indicates that this water is water of crystallization and not constitutional water (^{13}). Since the titanium derivatives have practically no additional absorption bands, it may be concluded that both oxalate groups are coordinated to titanium. However, the spectra of the niobium derivatives contain a number of additional bands. In particular, for the ammonium derivative, intense bands at 3174, 3028, and 2850 cm^{-1} are observed, which may be assigned to stretching vibrations of the N—H bond. In addition, all niobium derivatives contain an intense band at 1720 cm^{-1}, which may be assigned to an undissociated carboxyl group, and a band near 1620 cm^{-1}, attributable to the dissociated form of the carboxyl group. The presence of these absorption bands led us to carry out additional studies of the thermal stability of the oxalate derivatives. It was found that two oxalate groups in the niobium compound are bound less strongly than another one, i.e., upon thermal decomposition at about 200-220° two oxalate groups decompose, while the third oxalate group decomposes only at 320-350°. At the same time, in the titanium derivatives both oxalate groups decompose simultaneously. To this it must be added that, in studying the interaction of potassium niobate with oxalic acid in aqueous solutions, in all cases we observed the formation of a compound in which only one oxalate group corresponds to one niobium atom (^{14}-^{19}). Summarizing the experimental results given above, it may be concluded that in the niobium derivative only one oxalate group is coordinated to niobium.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 1. Infrared absorption spectra of oxalates and titanyloxalates of alkaline-earth metals:
a –calcium oxalate, *b* –calcium titanyloxalate, *v* –strontium oxalate, *g* –strontium titanyloxalate, *d* –barium oxalate, *e* –barium titanyloxalate

Fig. 2. Infrared absorption spectra of oxalates and oxaloniobates of alkali metals and ammonium:
a –sodium oxalate, *b* –sodium oxaloniobate, *v* –potassium oxalate, *g* –potassium oxaloniobate, *d* –ammonium oxalate, *e* –ammonium oxaloniobate

Thus, for the titanium and niobium compounds studied by us, the following general formulas may be proposed:

$$\mathrm{Me^{II}[TiO(C_2O_4)_2]} \cdot n\,\mathrm{H_2O} \quad \text{and} \quad \mathrm{Me^{I}[NbO_2C_2O_4]} \cdot \mathrm{2Me^{I}HC_2O_4} \cdot m\,\mathrm{H_2O},$$

where $\mathrm{Me^{II}}$ is a divalent metal, and $\mathrm{Me^{I}}$ is a monovalent metal.

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Note: Figure translations are in progress. See original paper for figures.