INFRARED SPECTRA AND THERMAL BEHAVIOUR OF SALTS OF THE BIS(MALONATO) OXOVANADIAM(IV) ANION

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Infrared spectra of a series of anhydrous (Rb, Cs) and hydrated (Na, K, Ca, Sr, Ba, Pb, Ag, Ti) salts of the complex anion \([\text{VO(C}_2\text{H}_2\text{O}_4)_2]^{2-}\) were recorded and briefly discussed. The thermal behaviour of these compounds, as well as that of the corresponding diprotonated ethylenediamine cation, were investigated by TG- and DTA-methods in N\(_2\)-atmosphere and complemented with studies carried out in crucible furnaces in air. Pyrolysis intermediates and residues were characterized by IR spectroscopy and overall stoichiometries for the degradation processes were proposed. In most cases orthovanadate/VO\(_2\) mixtures were obtained as final residues in N\(_2\), whereas the corresponding divanadates were produced in air.

The vanadyl(IV) cation, VO\(^{2+}\), is the most stable vanadium(IV) species and it dominates to a great extent the chemistry of this oxidation state [1–3]. This cation is also the most important vanadium species appearing in living systems [4, 5].

As it is known, the VO\(^{2+}\) cation prefers oxygen donor ligands [6] and a great number of complexes with carboxylate anions have been prepared and investigated in the last decades.

An interesting series of salts of the complex anion bis(malonato)oxovanadate(IV), \([\text{VO(C}_2\text{H}_2\text{O}_4)_2]^{2-}\), were prepared and characterized sixty years ago by Schramm [7] but they have not been subsequently studied by modern physicochemical methods.

As part of our present studies devoted to the synthesis and characterization of vanadyl complexes and salts of different types [8–14] we have now investigated the vibrational and thermal behaviour of a great number of salts of the above mentioned complex anion.

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Experimental

Preparation of samples

The starting material for most of the preparations was the ammonium salt of the complex anion: \((\text{NH}_4)_2[\text{VO(C}_3\text{H}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O}\). This salt was obtained by treating \(\text{NH}_4\text{VO}_3\) with malonic acid in the presence of ammonium carbonate [7]. The most insoluble dimalonatovanadyl salts (Ag, Tl, Pb, Ca, Sr, Ba) could be obtained by double decomposition of the ammonium salt and the corresponding nitrates or chlorides of the respective cation [7]. Other salts were obtained by treating \(\text{Ba[VO(C}_3\text{H}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}\) with the respective metal sulfate. After the separation of the precipitated \(\text{BaSO}_4\) and concentration of the solution, crystals were obtained by slow evaporation at room temperature.

A general overview of these experimental procedures, which also shows the stoichiometries of the investigated salts, is presented in Table 1.

Table 1 Summary of the synthetic procedures and the stoichiometries of the prepared compounds.

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\begin{align*}
(\text{NH}_4)_2[\text{VO(C}_3\text{H}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O} & \rightarrow + \text{AgNO}_3 \rightarrow \text{Ag[VO(C}_3\text{H}_2\text{O}_4)_2]\cdot \text{H}_2\text{O} \\
& \rightarrow + \text{TINO}_3 \rightarrow \text{Tl[VO(C}_3\text{H}_2\text{O}_4)_2]\cdot \text{H}_2\text{O} \\
& \rightarrow + \text{Pb(NO}_3)_2 \rightarrow \text{Pb[VO(C}_3\text{H}_2\text{O}_4)_2]\cdot 6\text{H}_2\text{O} \\
& \rightarrow + \text{Ca(NO}_3)_2 \rightarrow \text{Ca[VO(C}_3\text{H}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O} \\
& \rightarrow + \text{SrCl}_2 \rightarrow \text{Sr[VO(C}_3\text{H}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O} \\
& \rightarrow + \text{BaCl}_2 \rightarrow \text{Ba[VO(C}_3\text{H}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O} \\
& \rightarrow + \text{Cs}_2\text{SO}_4 \rightarrow \text{Cs}_2[\text{VO(C}_3\text{H}_2\text{O}_4)_2] \\
& \rightarrow + \text{Rb}_2\text{SO}_4 \rightarrow \text{Rb}_2[\text{VO(C}_3\text{H}_2\text{O}_4)_2] \\
& \rightarrow + \text{K}_2\text{SO}_4 \rightarrow \text{K}_2[\text{VO(C}_3\text{H}_2\text{O}_4)_2]\cdot 4\text{H}_2\text{O} \\
& \rightarrow + \text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2[\text{VO(C}_3\text{H}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}
\end{align*}
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