

INFRARED SPECTRA OF STRONTIUM FORMATE DIHYDRATE AND OF ITS DEUTERATED ANALOGUES

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ABSTRACT

The infrared spectra of strontium formate dihydrate and of isotopomers in which the formate and/or water protons are substituted with deuterons have been recorded and analyzed.

INTRODUCTION

Continuing our work on the vibrational spectra of various hydrated carboxylates [1-3], we now report data on the infrared spectra of $\text{Sr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, of a series of samples in which the water protons have been substituted, to a various degree, with deuterons and also of isotopomers containing deuteroformate ions. To the best of our knowledge, the infrared spectra of the dihydrate have not been reported, although the spectra of the anhydrous compound have been discussed [4,5]. The crystal structure of $\text{Sr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ has been determined by Osaki [6] and refined by Galigné [7].

EXPERIMENTAL

The studied compounds were prepared by dissolving the metal carbonate in aqueous (H_2O , D_2O or mixtures of the two) solutions of formic or deuteroformic acid. The infrared spectra were recorded, at room and liquid-nitrogen temperature (RT and LNT), on a Perkin-Elmer 580 infrared spectrophotometer. Raman spectra were also recorded (on a JEOL JRS-S1B and a Carry 80 instruments).

RESULTS AND DISCUSSION

The infrared spectra of $\text{Sr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ recorded at RT and LNT are given in Fig. 1. As can be seen, the lowering of the temperature produces significant changes, especially in the low-frequency region ($1000-400 \text{ cm}^{-1}$) where, except for the OCO in-plane bending, only the librational modes of water are expected to appear. The latter are known to have a noticeable negative temperature coefficient, i.e. to shift to higher frequencies on lowering the temperature and to become, at least apparently, stronger at LNT. On the grounds of such a behaviour it is easy to assign the bands at around 890, 860, 730, 720, 680 and 660 cm^{-1} (the frequencies are taken from the LNT spectrum) to librations of the two crystallographically non-equivalent types of water molecules. Two additional bands

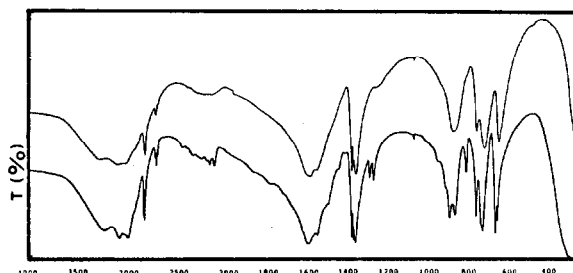


Fig. 1. Infrared spectra (RT and LNT) of $\text{Sr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$

(also temperature dependent) are present in the same region of the spectrum of the protiated compound (at around 810 and 760 cm^{-1}). However, they are sharper than the rest of the bands in this region and their shift to higher frequencies is less pronounced. In the spectrum of the deuterate, on the other hand, there is a single, rather intense band at around 790 cm^{-1} . Since this is the region where the OCO bending vibration is expected to appear, the 790 cm^{-1} band is a serious candidate for assignment to this mode. It is thus quite probable that in the protiated compound (as in the case of other hydrated carboxylates [2,8]) a mixing of the COO bending with water librations takes place. The appearance of a band at around 760 cm^{-1} in the Raman spectrum of the protiated compound and at around 780 cm^{-1} in that of the deuterate lends further support to such a conclusion.

The bands in the region of water stretching vibrations also become sharper at LNT, three maxima being clearly visible and a shoulder appearing at the high-frequency side of the lowest one (for two types of water molecules at least four bands would be expected under the site-group selection rules, each being split into three infrared active components if the correlation-field splitting is taken into account). The usual method of studying the spectra of samples with low deuterium content is not readily applicable here since in the region where the OD stretches of the HDO molecules are expected to appear, bands are already present in the spectra of the protiated compound. In any case, it seems that a single sharp band (at around 2430 cm^{-1}) and a complex feature consisting of at least three overlapping components (centered around 2300 cm^{-1}) are seen in the OD stretching region of samples with low deuterium content (Fig. 2a). The picture is similar in the OH stretching region, consistent with the existence of one longer (Ow...O distance 280.8 pm) and three shorter hydrogen bonds (the corresponding Ow...O distances being 273.6, 271.5 and 267.2 pm respectively) [7].

Probably the most remarkable feature in the studied spectra is the appearance of a number of new bands in the DOD bending region of the spectra of samples containing

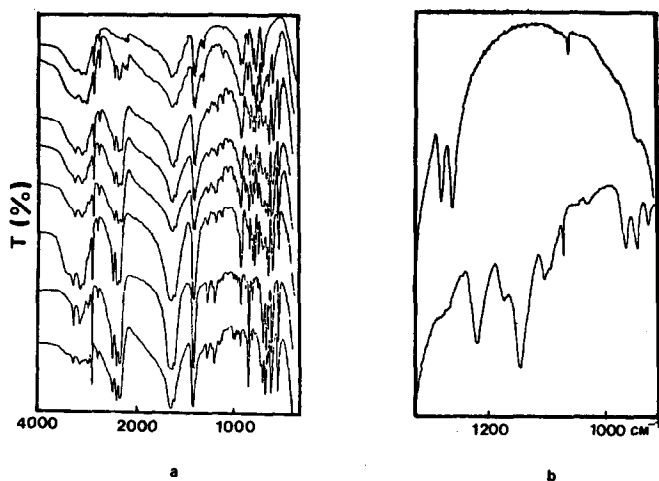


Fig. 2. The spectra of the series of partially deuterated samples (a) and the DOD bending region in the spectra of the protiated and perdeuterated strontium formate dihydrate (b)

mainly D_2O molecules (such bands are not present, as can be seen in Fig. 2b, in the spectrum of the protiated compound). These bands are spread from around 1200 cm^{-1} (the expected frequency region for the DOD bending vibrations) to around 1000 cm^{-1} or even below. This is similar to what has been observed by us earlier in a number of crystallohydrates [9] and also in other XH_n -containing species [10] and interpreted as being due to coupling of the fundamental bending mode with some second-order transition and/or low-lying fundamental. The precondition for such a coupling to take place is, we believe, the anharmonicity of the fundamental vibration. The surrounding of the two water molecules is such [7] that the vibrations may indeed be anharmonic. Thus, around one of the water oxygens there are three potential proton-acceptors, one of them being discarded by Galigné [7] on the basis of its inconvenient disposition with regard to the water molecule $\text{Ow}(1)$, whereas in the case of the other water molecule a strontium ion and a proton-donating water molecule are located in the general direction of the lone-pair region. Without knowing the position of the hydrogen atoms it is difficult to see whether the conditions for formation of bifurcated hydrogen bonds are favorable in the former case (this would certainly be a considerable factor leading to anharmonicity) but it is certain that the force field around the second of the water molecules is indeed asymmetric.

As in other formates, in the region below 1400 cm^{-1} a complex feature of closely lying bands (originating from COO symmetric stretching and CH bending vibrations) is found. The interpretation of the origin of these bands is somewhat simplified by the availability of spectra of the

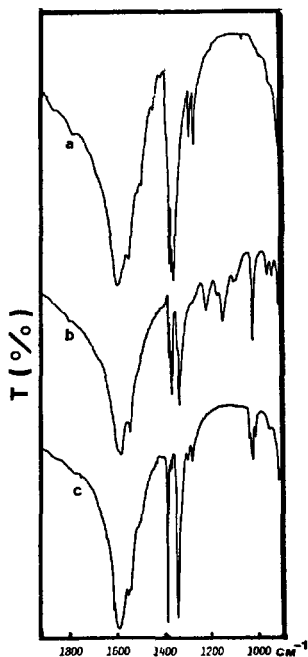


Fig. 3. The 1450 - 1200 cm^{-1} region in the spectra of $\text{Sr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Sr}(\text{DCOO})_2 \cdot 2\text{D}_2\text{O}$ and $\text{Sr}(\text{DCOO})_2 \cdot 2\text{H}_2\text{O}$ (a, b and c respectively)

deuterated isotopomers. As can be seen in Fig. 3, namely, by far the simplest picture is found in the spectra of $\text{Sr}(\text{DCOO})_2 \cdot 2\text{H}_2\text{O}$. The bands which in the spectra of the fully protiated isotopomer originate from CH bendings are now being shifted to slightly above 1000 cm^{-1} and only two bands remain in the 1350 cm^{-1} region. These two bands then must be due to the expected, in absence of an appreciable correlation-field splitting, two COO symmetric stretchings. Somewhat surprisingly, the situation in the $\text{Sr}(\text{DCOO})_2 \cdot 2\text{D}_2\text{O}$ spectrum is not at all simple, probably because of the appearance in this region of some of the high-frequency components of the above-mentioned progression of bands. The fact that the frequencies of the remaining bands in the spectrum of the perdeuterated compound are not identical with any of those found in the $\text{Sr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ spectrum seems to indicate that the form of the normal modes which are predominantly COO bending in character is not the same in the two cases.

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