

THE WATER BENDING REGION IN THE SPECTRA OF THE HYDRATES
OF SOME METAL CARBOXYLATES

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In the infrared spectra of the dihydrates of nickel, cobalt, manganese and magnesium formates a band at around 1680 cm^{-1} , assignable to HOH bending is found, whereas in the spectra of the deuterated compounds the analogues of this band are accompanied by bands at lower frequencies (below 1200 cm^{-1}). Multiple bands are found also in the spectra of the deuterioanalogues of strontium formate dihydrate and of nickel and cobalt acetate tetrahydrate.

In the spectra of carboxylates (in our case formates and acetates), the HOH bending region is difficult to analyze since a strong band, due to the antisymmetric COO stretch, is present in the same region. It is, therefore, better to study the HOD and DOD bending regions in the spectra of the deuterioanalogues. In the spectra of the protiated compounds, namely, there are no strong bands in the corresponding regions and so it is easier to recognize new bands that appear when protium is gradually substituted by deuterium. As a part of our study of the vibrational spectra of formates and acetates /1-3/, we now report the results of the analysis of the HOH, HOD and DOD bending regions in the infrared spectra (recorded on a Perkin-Elmer 580 instrument) of the dihydrates of nickel, cobalt, manganese and magnesium formates (these compounds form an isomorphous series), of strontium formate dihydrate, of the tetrahydrates of nickel and cobalt acetates and of the partially deuterated analogues of all these compounds.

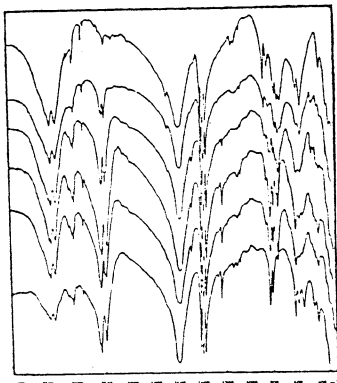


Fig. 1. IR spectra of cobalt formate dihydrate and of its partially deuterated analogues

RESULTS AND DISCUSSION

In the infrared spectra of the series of metal formates dihydrates (the divalent metal being, as pointed out earlier, Ni, Co, Mn or Mg), a band is found at around 1680 cm^{-1} (cf. Fig. 1 where, as an example, the spectra of cobalt formate dihydrate and of the series of its partially deuterated analogues are given). Since this band disappears on deuteration, it is assigned to the HOH bending, the frequency value being in the expected range /4/. Its DOD analogue is easy to identify around 1280 cm^{-1} , but at frequencies lower than 1200 cm^{-1} additional bands, absent in the spectra of the protiated species, appear in those

of the deuterates. Multiple bands are found also in the DOD bending region of the spectra of strontium formate dihydrate and of nickel and cobalt acetate tetrahydrate (Fig. 2). Their exact number in the latter case is difficult to determine, but it is obvious that there are a number of them and that they appear in a rather wide spectral region.

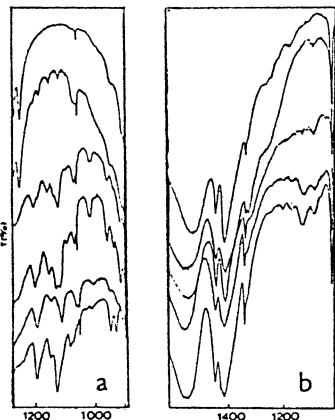


Fig. 2. The HOD/DOD bending region in the IR spectra of strontium formate dihydrate (a) and nickel acetate tetrahydrate (b) and of their partial¹; deuterated analogues

The spectra of the studied compounds are not unique in this respect since we have observed a similar spectral picture in a number of different crystallohydrates and have interpreted it /5/ by taking into account the geometry of the water molecules and their environment. The crystallographic data, namely, show that in all cases when multiple bands are encountered in the HOH, HOD and/or DOD bending region, the geometry of the water molecules is such as to imply the possibility of a pronounced anharmonicity of the corresponding vibrations. If this is indeed so, then interactions of various kinds become possible and it is then easy to understand the appearance of more bands (with frequencies spread out over a wider region) than would have been expected.

It should be pointed out that in the case of nickel acetate tetrahydrate, the COO antisymmetric stretch shifts towards higher frequencies on increase of the deuterium content in the sample (Fig. 2b), by all means because the much lower bending DOD frequency makes impossible the vibrational interaction which must exist in the case of the protiated compound.

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