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INFRARED SPECTRA OF NICKEL FUMARATE AND ZINC FUMARATE

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Abstract: The infrared spectra of the crystallohydrates of nickel(II) fumarate and zinc(II) fumarate, as well as those of their partially deuterated analogues, were recorded at room temperature and at the boiling temperature of liquid nitrogen. The existence of more than two structurally different types of water molecules is stongly indicated.

Introduction

The diffraction studies of the fumarates of some divalent metals [1, 2] have indicated that the compounds are crystallohydrates with the general formula $M(C_4H_3O_4)_2 \cdot xH_2O$ where M = Mn, Ni, Co, Cu, Zn or Fe and the value of x was reported as either 2 [1] or 4 [2]. The thermal decomposition of some of the complexes of this type has also been studied [3]. It was shown that the water of crystallization is removed first and that on further heating a partial decomposition of the complexes themselves takes place.

The spectroscopic studies of this class of compounds are scarce and incomplete and this prompted us to record and study the infrared spectra of the fumarates of nickel(II) and zinc(II). Attention was paid particularly to the 3600–3000 cm^{-1} region where the appearance of the antisymmetric and symmetric stretching vibrations of the water molecules is expected, to the region of water bending frequencies (1700–1600 cm^{-1}) and to the low frequency region (below 900 cm^{-1}) in which the most interesting bands would be the bands originating from water librations and from metal-ligand stretching vibrations. Also deserving attention is the 1600–1400 cm^{-1} region where the antisymmetric ans symmetric COO^- stretches give rise to infrared bands which could be used to make structural inferences. In addition to the carboxylic stretching ones, bands due to modes which could be approximately described as C = C stretchings and CH_2 and CH bendings are expected to appear in the same spectral region.

Experimental

The studied compounds were prepared by a modification of the procedure described in the literature [1]. In fact, the initial step of the preparation was modified, in which the metal ions were precipitated as carbonates (rather than as hydroxides as suggested in Ref. 2) which were subsequently reacted with aqueous solutions of fumaric acid (the metal-to-fumaric acid mole ratio being 1 : 1). The main advantage of the modified procedure lies in the fact that the use of the insoluble metal hydroxides is avoided and thus the period necessary for the reaction to take place is considerably shortened. After the reaction with the acid, only the needed ions are present in the reaction system since the carbonate ions are removed (as carbon dioxide).

On standing for several days in a vacuum desiccator with phosphorus pentoxide and silica gel as drying agents, the nickel and zinc fumarates separated from the reaction mixture as crystallites which were almost insoluble in water.

The content of carbon, hydrogen and oxygen was determined by elemental microanalyss, and that of nickel (or zinc) by complexometric titration with a standard solution of EDTA.

The infrared measurements were performed on a Perkin-Elmer 580 infrared spectrophotmeter in the spectral range 4000–200 cm^{-1}. The standard KBr technique was utilized since the comparison with the spectra recorded from Nujol or hexachlorobutadiene mulls did not disclose any significant difference. The low-temperature spectra were recorded using a VLT-2 (RIIC, London) variable-temperature cell in which the coolant was liquid nitrogen. In the remaining text these spectra will be denoted by the abbreviation LNT (standing for *liquid-nitrogen temperature*).

The deuterated analogues were prepared by treating the crystalline compounds with deuterim oxide which was subsequently removed by drying in a vacuum desiccator over P_2O_5 and silica gel. Most probably because of their low solubility, the compounds could be only partly deuterated.

Results and discussion

The spectra of the hydrate of nickel fumarate and of its partially deuterated analogues are shown in Figs. 1–4, and those of the corresponding zinc compounds in Figs. 5–8.

Nickel fumarate

As expected, in the 3550–2900 cm^{-1} region of the room-temperature (RT) spectrum of the nickel compound (Figs. 1a and 2a) bands attributable to water stretching modes are indeed present. Such are the two sharp bands at 3460 cm^{-1} and 3400 cm^{-1}, the broad and intense one centered around 3000 cm^{-1} and a much weaker band (or, rather, a shoulder) appearing around 3040 cm^{-1}. A much weaker, broad and slightly structured band is observed below 2500 cm^{-1}. Although some of the bands may result from second-order transitions (overtones and/or combinations), their number is such that the existence of more than one type of water molecules is strongly indicated. Some of the water hydrons are, evidently, involved in the formation of very weak hydrogen bonds (the sharp, high-frequency bands are due to vibrations in which such hydrons take part), whereas the rest form much stronger hydrogen bonds. In fact, if the weak and broad band found below 2500 cm^{-1} is also due to fundamental water vibrations, it must be concluded that hydrogen bonds of quite considerable strength are formed.

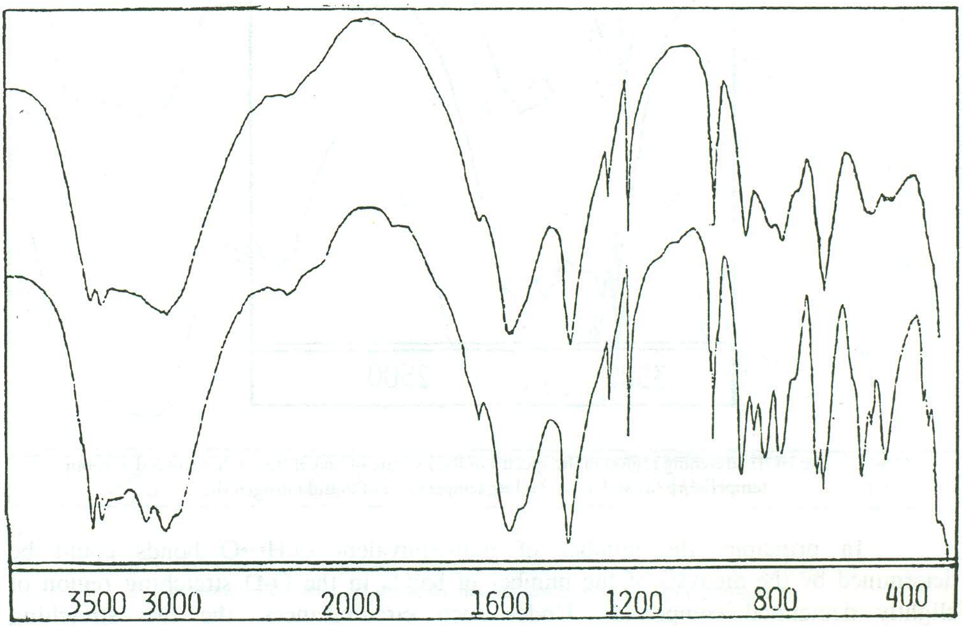

Fig. 1 - Infrared spectra of the hydrate of nickel fumarate recorded at room temperature (a) and at the boiling temperature of liquid nitrogen (b)

At least six bands are seen above 2900 cm^{-1} at LNT (Figs. 1b and 2b) and the band below 2500 cm^{-1} is also split. This confirms the conclusion about the existence of crystallographically different water molecules but it is not possible to prove unequivocally that the compound is a *dihydrate* as suggested by the results of the microelemental analysis (the calculated values for the mass fractions, assuming the compound to be a dihydrate, are C – 29.56 %, H – 3.08 %, O – 49.28 %, whereas the experimental values are C – 30.31 %, H – 3.15 %, O – 48.77 %). If all the above-mentioned bands are, namely, due to fundamental water vibrations and no complications related to correlation-field effects are present, then the number of observed bands rules out the possibility of the compound being a dihydrate.

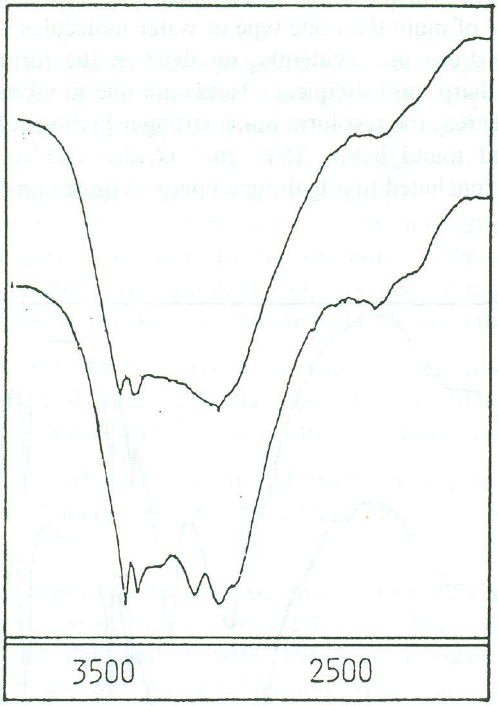

Fig. 2 – The HOH stretching region in the spectra of the hydrate of nickel fumarate recorded at room temperature (a) and at the boiling temperature of liquid nitrogen (b)

In principle, the number of non-equivalent O-H•••O bonds could be determined by the analysis of the number of bands in the O-D stretching region of slightly deuterated compounds. Under such circumstances, the two stretching vibrations of any given HOD molecule become decoupled – one is an almost pure O-H and the other an almost pure O-D stretch. Assuming an approximately equal probability for each proton to be replaced by a deuteron, the number of O-D stretching bands would reflect the number of non-equivalent hydrons. If all hydrons are crystallographically different, the ν(O-D) bands would have practically the same intensity. On the other hand, if two or more hydrons are equivalent, the intensity of the corresponding band would reflect this fact. Furthermore, since practically all nearest neighbors are H_2O molecules, the existence of structurally equivalent molecules does not have any observable effect (when identical oscillators are present, correlation-field splitting effects complicate the spectral picture).

Unifortunately, in the present case such an analysis is difficult if not impossible. In the region below 2500 cm^{-1} where the ν(O-D) bands appear, bands are present in the spectra of the protiated compound (see above) and it is impossible to discriminate between these bands and those originating from the O-D stretching vibrations of the isotopically isolated HOD molecules. On closer examination, five or six new bands seem to be present in the above-mentioned region (Fig. 3) but it is not possible to exactly determine either their exact number or their intensity.

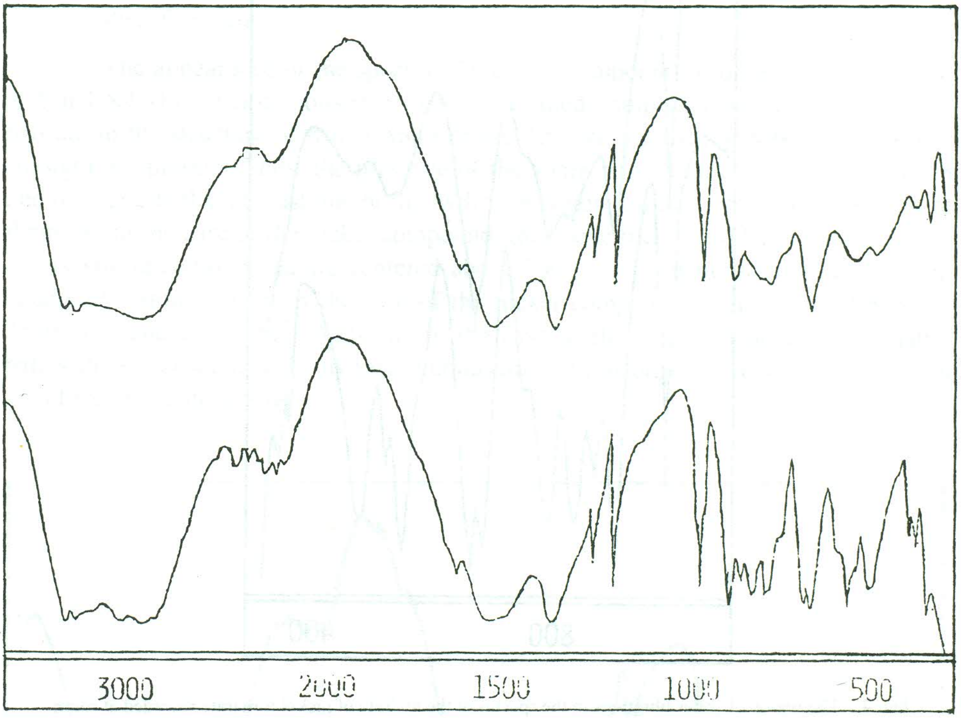

Fig. 3 Infrared spectra of partially deuterated analogue of the hydrate of nickel fumarate at room temperature (a) and at the boiling temperature of liquid nitrogen (b)

That the studied compound is indeed a crystalline hydrate is further confirmed by the existence of bands due to the H-O-H bending and to water librational modes. Thus, a relatively weak band seen around 1650 cm^{-1} in the RT spectrum, gains intensity on lowering the temperature (see Fig. 1b), a feature typical of the water bending bands. The frequency shifts and the increase in intensities make it much easier to assign the bands which are due to water librations. Among these are the bands which, in the RT spectrum (Fig. 4a), appear around 890 cm^{-1} and 670 cm^{-1} and become appreciably stronger in the LNT spectrum. Even more pronounced is the increase in intensity of the bands which, in the LNT spectrum, are found around 875 cm^{-1} and 825 cm^{-1} (in the RT spectrum they appear as ill-resolved components of the complex feature between 860 and 730 cm^{-1}) as well as those which are seen around 525 cm^{-1} and 490 cm^{-1}. It is quite possible that additional bands may also be due to water librations, but even the enumerated bands could serve as a proof that two (and probably more) types of water molecules are present in the structure of the nickel compound.

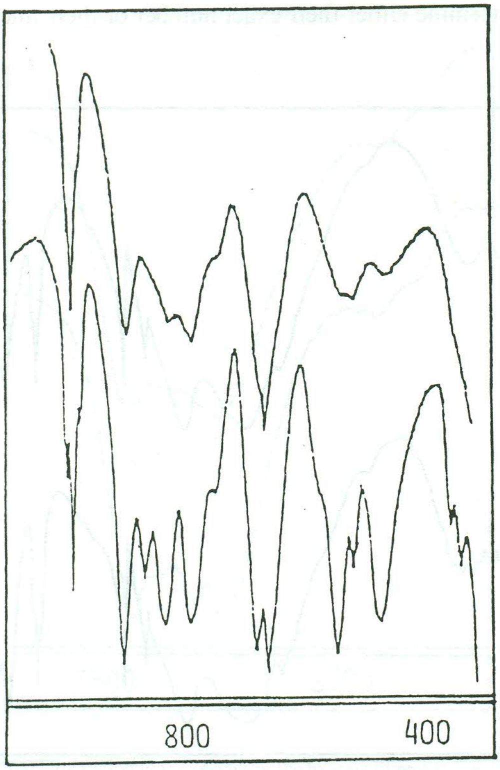

Fig. 4 – The region of water librations in the spectra of the hydrate of nickel fumarate recorded at room temperature (a) and at the boiling temperature of liquid nitrogen (b)

The bands due to the metal-to-ligand stretching vibrations are expected below 600 cm^{-1}. To one of these modes (in the present case they are of the M-O type) the weak band around 350 cm^{-1} (cf. Fig. 1) could be attributed. It experiences no appreciable shift and does not change its intensity on lowering the temperature. This (as well as its low frequency) rules out the possibility that it could belong to a mode with a predominantly H_2O librational character.

The antisymmetric and symmetric COO^- stretching vibrations are expected, as mentioned above, to give rise to bands in the 1600–1350 cm^{-1} region of which those due to $\nu_{as}(COO)$ should be much more intense and easier to detect. A very strong (and probably complex) temperature-independent band is indeed found around 1560 cm^{-1} and there is little doubt that its constituents originate from the antisymmetric carboxylic stretches. The components (practically unresolved) of the slightly less intense band found around 1380 cm^{-1} undoubtedly originate from the symmetric COO^- stretches. On the basis of the frequency difference $\Delta\nu$ between the antisymmetric and symmetric carboxylic stretching bands, it should be concluded that the fumarate ions serve as bridging ligands connecting neighboring nickel atoms. Such a role of the fumarate groups is expected (the two carboxylate groups are in a *trans* position) and is further confirmed by the low solubility in water of the studied compound. If, namely, nickel fumarate were *ionic*, a much higher solubility would be anticipated.

Zinc fumarate

The appearance of the spectra of the zinc compound recorded at RT (Fig. 5a) and at LNT (Fig. 5b) demonstrates that the studied compound is again a crystalline hydrate in the structure of which water molecules forming hydrogen bonds of various strength are present. Thus, the presence of the sharp band around 3500 cm^{-1} (Figs. 5 and 6) suggests that at least one of the hydrogen bonds is much weaker than the rest of them. As in the case of the nickel compound, the above-mentioned band is followed by a very strong complex feature centered above 3000 cm^{-1} and by the less intense (but apparently stronger than in the case of the nickel compound) multiple band between 2500 cm^{-1} and 2200 cm^{-1}. Again as in the case of the nickel analogue, these latter bands show that some of the hydrogen bonds are quite strong, whereas the rest of them are of intermediate strength.

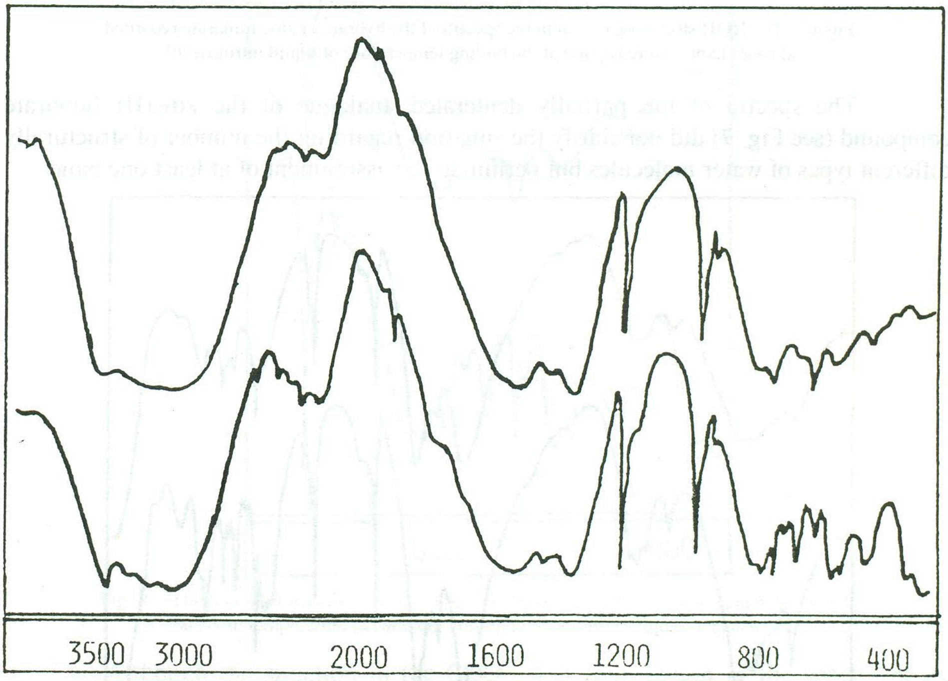

Fig. 5 – Infrared spectra of the hydrate of zinc fumarate recorded at room temperature (a) and at the boiling temperature of liquid nitrogen (b)

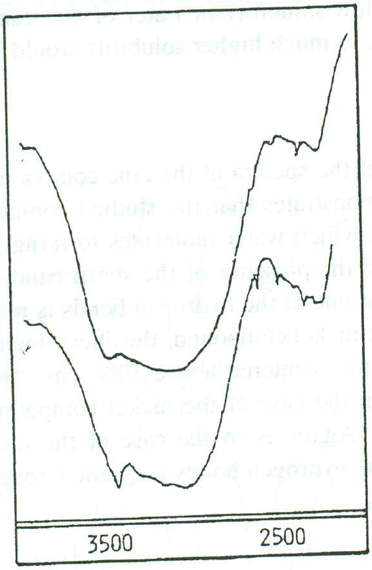

Fig. 6 The HOH stretching region in the spectra of the hydrate of zinc fumarate recorded at room temperature (a) and at the boiling temperature of liquid nitrogen (b)

The spectra of the partially deuterated analogue of the zinc(II) fumarate compound (see Fig. 7) did not clarify the situation regarding the number of structurally different types of water molecules but permitted the assignment of at least one band

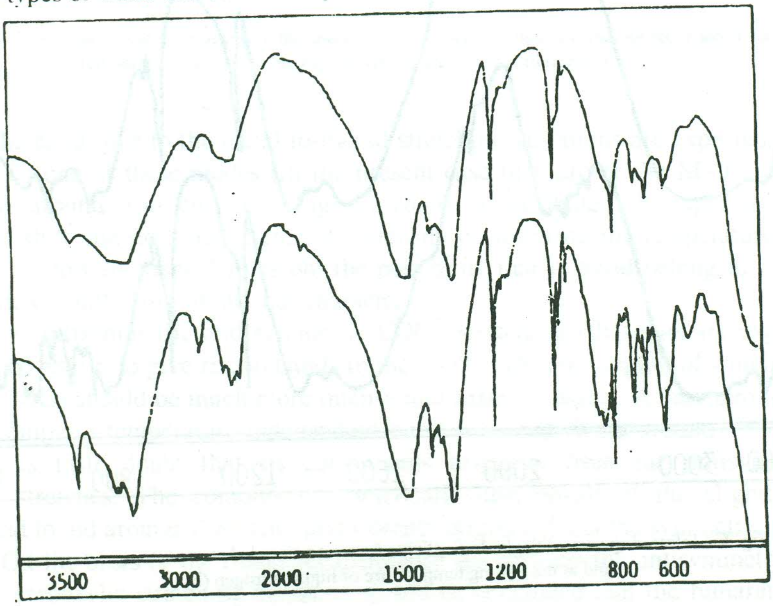

Fig. 7 Infrared spectra of partially deuterated analogue of the hydrate of zinc fumarate at room temperature (a) and at the boiling temperature of liquid nitrogen (b)

originating from the water bending modes. Thus, the band which has a frequency of $\approx$1620 cm^{-1} in the spectrum of the protiated compound disappears on deuteration and a new band (attributable to some of the D-O-D bendings) occurs around 1200 cm^{-1}.

As in the case of the nickel compound, the location of the bands arising from water librations can be placed with little difficulty since most of the bands appearing in the region below 900 cm^{-1} are temperature-sensitive. The sharp and temperature-independent bands are certainly due to fumarate vibrations, whereas those which are broader and shift to higher frequencies on lowering the temperature must be attributed to water librations. As in the case of the nickel compound, the number of water librational bands shows that, most probably, there are more than two structurally distinct types of water molecules.

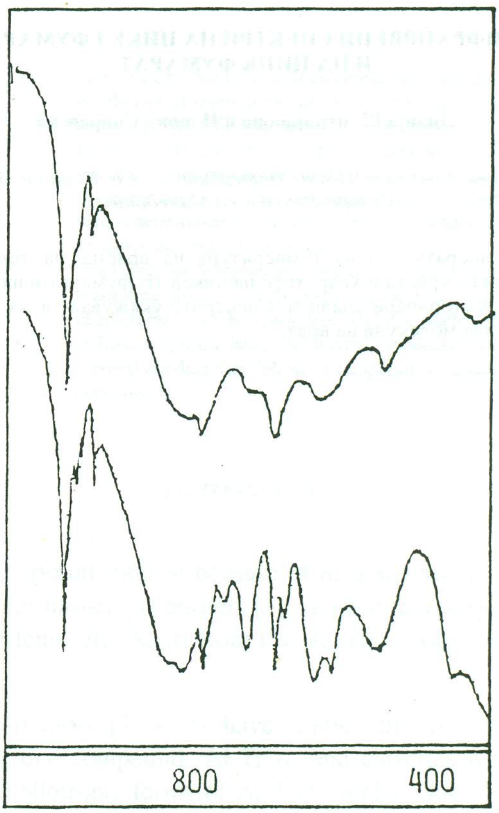

Fig. 8 The region of water librations in the spectra of the hydrate of zinc fumarate recorded at room temperature (a) and the boiling temperature of liquid nitrogen (b)

Although the situation in the COO^- stretching region in the spectra of the zinc compound is not as simple as that in the case of the nickel analogue, the strong and complex bands around 1600 cm^{-1} and 1400 cm^{-1} certainly belong to the antisymmetric and the symmetric COO^- stretchings respectively. The less intense and sharper bands in the same region are, then, due to the modes which are predominantly C=C stretching and CH_2 and CH bending in character.

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Резиме

ИНФРАЦРВЕНИ СПЕКТРИ НА НИКЕЛ ФУМАРАТ И НА ЦИНК ФУМАРАТ

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На собна температура и на температура на вриење на течниот азот снимени се инфрацрвените спектри на кристалохидратите на никел(II) фумарат и на цинк(II) фумарат, како и на нивните делумно деутерирани аналози. Спектрите укажуваат дека постојат повеќе од два структурно различни типа молекули на вода.