

**INFRARED STUDY OF THE SPECTRUM OF WATER IN MAGNESIUM
MALONATE DIHYDRATE AND ITS PARTIALLY DEUTERATED ANALOGUES**

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Four bands are found in the O-D stretching region of the infrared spectra of the slightly deuterated analogue of the title compound. This fact and the existence of two bands in the D-O-D bending region of the spectra of samples containing isotopically isolated D_2O molecules show clearly that two types of water molecules forming non-equivalent hydrogen bonds exist in the structure of magnesium malonate dihydrate.

INTRODUCTION

Magnesium malonate dihydrate was first prepared by Finkelshtein as early as 1865 [1] along with other hydrates of magnesium malonate. A number of other metal salts with the same stoichiometry is known, some of them (those of Mg and Mn) being orthorhombic (space group $Pnab$) while others are monoclinic (e.g. the dihydrates of the malonates of Co, Ni and Zn) [2].

The crystal structure of the title compound has not been determined in detail (only the parameters of the unit cell are given in [2]) but it is reasonable to assume that it would be analogous to the structure [3] of $Mn(mal).2H_2O$ (hereafter mal denotes the malonate ion, $-OOC-CH_2-COO-$).

To the best of our knowledge, the only published infrared data for $Mg(mal).2H_2O$ are those of Farago and Amirhaeri [4], but they are limited to the carboxylic stretching region.

In view of our interest in the vibrational spectra of hydrates of metal carboxylates (e.g. [5-7]), we decided to study more closely the infrared spectrum of the title compound, paying special attention to the spectrum of water.

EXPERIMENTAL

The dihydrate of magnesium malonate was prepared from magnesium carbonate suspended in water and an aqueous solution of malonic acid [4].

The partially deuterated analogues were prepared by recrystallization of the protiated salt from H_2O/D_2O mixtures of appropriate composition.

The infrared spectra were recorded at room and liquid-nitrogen temperature (RT and LNT respectively) on a Perkin-Elmer 580 spectrophotometer. A VLT-2 cell was used for the low-temperature measurements.

RESULTS AND DISCUSSION

Stretching bands of isotopomers of water

The RT and LNT spectra of magnesium malonate dihydrate are shown in Fig. 1. As seen, two sharp bands (at 3520 and 3465 cm^{-1} at RT and 3520 and 3460 cm^{-1} at LNT) are present in the O-H stretching region of the spectra. They are followed by a rather broad feature composed of two broad and ill-resolved bands at RT (the frequencies of the observed maxima are 3345 and 3260 cm^{-1}) and of three components at LNT (3350 , 3290 and 3245 cm^{-1}). As can be seen, the wavenumber values of the components of the high-frequency doublet are practically temperature-independent, whereas the remaining bands on lowering the temperature shift considerably towards lower frequencies.

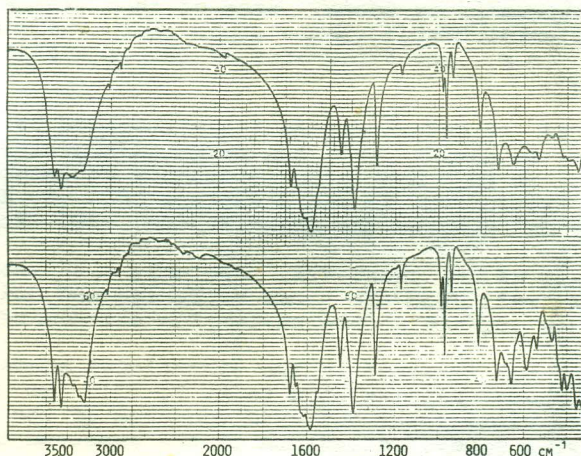


Fig. 1. RT and LNT spectra of $Mg(mal) \cdot 2H_2O$

The distribution of the frequencies is in agreement with the expectations based on the possible isomorphism between the isostructural magnesium and manganese compound. In the

structure of the latter, namely, two types of water molecules exist, each forming one weak and one stronger hydrogen bond. The corresponding O...O distances in the structure of $Mn(mal).2H_2O$, namely, are close to 294 and 280 pm and to 301 and 283 pm for the two non-equivalent types of H_2O molecules [3] (if the two compounds are indeed isomorphous, then a similar manner of bonding is expected for the magnesium compound as well). With such differences in the hydrogen-bond strengths, it is expected that the two stretching modes for each water type would be better represented as vibrations of the individual O-H oscillators than as antisymmetric and symmetric H_2O stretches.

Whereas the frequencies of the bands follow our expectations, their number is somewhat surprising. The group theory would, namely, predict splitting of each mode into three infrared active components, but no observable splitting of the two sharp bands exists. One is, then, inclined to believe that the three (or, perhaps, more) bands between 3400 and 3200 cm^{-1} are due to interactions of the fundamental stretches with second-order transitions (overtones and/or combinations) involving the water bending modes rather than to factor-group components of the fundamental modes themselves.

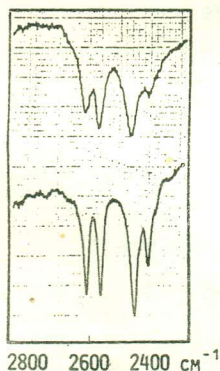


Fig. 2. The O-D stretching region in the RT and LNT spectra of $Mg(mal).2H_2O$

The situation in the O-D stretching region of the spectra of samples with a low deuterium content is considerably simpler. As seen in Fig. 2, namely, four bands are found (both at RT and LNT) in this region: two at higher (the LNT values are 2620 and 2550 cm^{-1}) and two at lower (2440 and 2390 cm^{-1}) frequencies. Somewhat confusing is the intensity of these four bands: that of the two high-frequency ones is almost equal, whereas the 2440 cm^{-1} band appears to be considerably stronger than that at 2390 cm^{-1} . The combined intensity of the two bands at higher frequencies, on the other hand, appears to be closer to the combined intensity of the two bands at lower frequencies. No completely satisfactory explanation of this rather curious fact can be given at this time although some sort of isotopic effect may be suspected.

If the above-mentioned unusual distribution of the intensities in the case of the magnesium compound is ignored, then the frequencies of the bands in this region may be used to estimate the Ow...O distances in the structure. To do this,

one may use the relationship between the O-D frequencies of isotopically isolated HDO molecules and the $Ow...O$ distances derived by Berglund, Lindgren and Tegenfeldt [8]. The values thus derived are 299.3, 291.2, 277.4 and 273.9 pm for the four $Ow...O$ separations, corresponding to O-D frequencies equal to 2620, 2550, 2440 and 2390 cm^{-1} .

As far as the O-D stretching region is concerned, one further point should be mentioned. As seen in Fig. 3, namely, the increase in the deuterium content does not produce any significant shift in the position of the bands in this region or, for that matter, appearance of new bands. This,

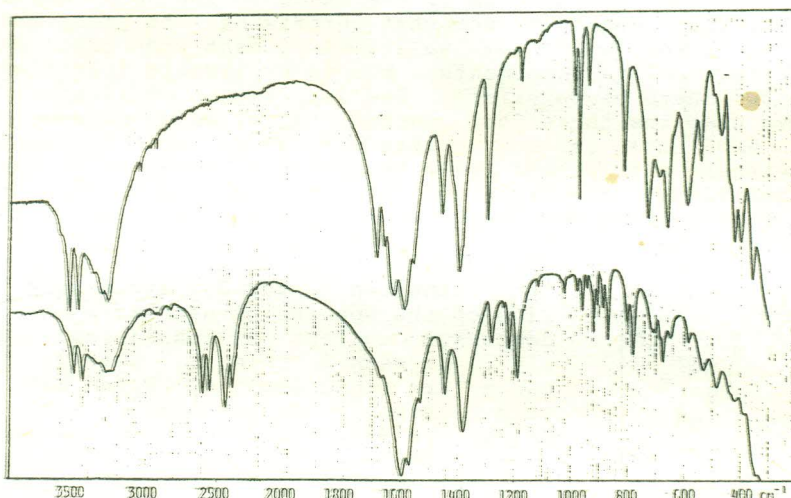


Fig. 3. LNT spectra of protiated and partially deuterated $Mg(mal).2H_2O$

of course, means that not only the O-H and O-D oscillators within the HDO molecules but also the two O-D oscillators of the D_2O molecules are practically completely decoupled. A similar conclusion, it should be recalled, was made on the basis of the analysis of the O-H stretching region as well. Even in the spectra of samples with high deuterium content the 2440 cm^{-1} band remains the strongest one in the whole region but the differences in the intensity are much less than in the case of the slightly deuterated analogues.

Regions of H-O-H, H-O-D and D-O-D bending vibrations

The analysis of the H-O-H bendings of the two non-equivalent types of water molecules is complicated by the fact that in the region where the corresponding bands are expected to

appear, intense bands due to the antisymmetric COO stretchings of the malonate ions are present. Still, the parallel analysis of the spectra of the protiated compound and those of the deuterated samples (Fig. 3) shows that the intensity of the band whose frequency is close to 1680 cm^{-1} decreases on deuteration. The whole feature centered around 1600 cm^{-1} , furthermore, is much narrower in the spectra of the deuterated samples so that one or more further H-O-H bending band(s) must be hidden here.

The region of H-O-D bendings provides very little information. This region, namely, is dominated by the rather strong and broad bands due to vibrations of the malonate ions and there is no detectable difference between the spectra of samples with varying deuterium content.

The situation the D-O-D bending region, on the other hand, is much simpler. Two deuteration-sensitive bands are, namely, found here (their frequencies being close to 1230 and 1200 cm^{-1}), in agreement with the existence of two types of water molecules.

Water librations

Under the selection rules of the site-groups of the two non-equivalent types of water molecules (assuming complete isomorphism with the manganese compound), three infrared active librations are expected for each such type. As in other hydrates, these bands are expected to be temperature-sensitive, their intensity and frequency increasing with the decrease of temperature.

As seen (Fig. 3), it is impossible to locate all expected librational bands. In fact, the comparison of the RT and LNT spectra of the protiated compound, on the one hand, and the parallel analysis of the spectra of the protiated and deuterated compound, on the other, makes it possible to attribute with certainty to water librations only the bands appearing around 690 and 590 cm^{-1} (LNT values) and, perhaps, also the band around 465 cm^{-1} . Since the effective symmetry of both water molecules must be low, it is quite probable that *mixing* of librational modes is present [9]. Under such circumstances, it is better to refrain from a precise assignment of the librational bands.

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ИЗУЧУВАЊЕ, СО ПОМОШ НА ИНФРАЦРВЕНА СПЕКТРОСКОПИЈА, НА СПЕКТРОТ НА ВОДА КАЈ МАГНЕЗИУМ МАЛОНАТ ДИХИДРАТ И КАЈ НЕГОВИТЕ ДЕЛУМНО ДЕУТЕРИРАНИ АНАЛОЗИ

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Во O-D валентната област на инфрацрвените спектри на магнезиум малонат дихидрат со ниска содржина на деутериум во образецот најдени се четири ленти што покажува дека во структурата постојат два типа молекули вода од кои секоја образува нееквивалентни водородни врски. До истиот заклучок може да се дојде врз основа на постоењето на две ленти во областа на деформационите D-O-D вибрации во спектрите на обрасци што содржат изотопски изолирани D₂O молекули.