

THE FTIR SPECTRUM OF WATER IN AQUA(MALONATE)CADMIUM(II) HYDRATE**Mirjana Ristova¹, Panče Naumov¹, Bojan Šoptrajanov^{1,2}**¹*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, The "Sv. Kiril i Metodij" University, POB 162, MK-1001 Skopje, Republic of Macedonia*²*Macedonian Academy of Sciences and Arts, MK-1000 Skopje, Republic of Macedonia*

In view of our interest in the vibrational spectra of crystalline hydrates of metal(II) malonates, in the present communication we report the FT infrared spectra of the protiated and slightly deuterated analogue of aqua(malonate)cadmium(II) hydrate, recorded (in the 4000–400 cm⁻¹ region) at room temperature and the boiling temperature of liquid-nitrogen (RT and LNT, respectively). On the basis of the observed temperature effects and the spectral changes on deuteration, the bands originating from the internal and external vibrations of the water molecules (with the exception of the H–O–H bendings) were assigned.

Key words: malonate ion; cadmium(II) malonate dihydrate; rhombohedral polymorph; aqua(malonate)cadmium(II); FT infrared spectra

INTRODUCTION

In the recent years, crystalline hydrates of metal salts of organic acids such as acetic [1–6], formic [7], and malonic [8] have received much attention, especially in the field of crystal engineering [9]. In some cases, when the ligand possesses suitable properties, a spontaneous aggregation of small molecular building blocks in solution that recognize each other through multiple molecular recognition sites to form extended architectures may take place. Such a process is then suitable for use in the design of new materials.

The malonate ion (henceforth abbreviated as **mal**), the dianion of 1,3-propanedioic acid, is a dicarboxylic ligand with a unique behavior different from that of the oxalate ion and can exhibit diverse coordination modes. It is a versatile ligand, frequently used for designing complexes with desired magnetic properties [10] and in the design of molecular magnets [11]. Since the malonate ion has four potential proton-acceptor sites, ligands with proton-donor atoms may be introduced in order to create building blocks for self-assembling into metal-containing supramolecules by non-

covalent forces, such as hydrogen bonding [12–14] and aromatic π – π stacking interactions [15].

The latest literature data show that the malonate derivatives of divalent metals provide the framework for supramolecular crystal engineering [16–19] (when ligands such as 2,2'-bipyridine and 4,4'-bipyridine are used as spacers) and in the structure of the polymetallic active site in biological processes [20]. Thus, cadmium(II) malonates are suitable models for examining the coordination of metalloproteins in saccharide-specific lectin concanavalin A [21] and parvalbumin [22–23].

The structural diversity of divalent metal malonates arises from the low point-group symmetry of the compounds which leads to the formation of polymorphs. Thus, we focused on the synthesis of different metal(II) malonates and determined, by single crystal X-ray analysis, the crystal structures of the Cu(II) malonate trihydrate [24] and a novel rhombohedral polymorph cadmium(II) malonate formulated as aqua(malonate)cadmium(II) hydrate, [Cd(C₃H₂O₄)(H₂O)]·H₂O [25].

As a part of the spectroscopic studies of various crystalline hydrates of metal(II) carboxylate, we now report the results of our studies on the FTIR spectra of the rhombohedral polymorph.

Cadmium malonate, the starting material, exists as a monohydrate [26] whose Cd atom is seven-coordinate and as a dihydrate, whose structure was determined by Chung et al. [27] who characterized it as tetraaquobis(malonato)dicalcium(II). Unusual six- and eight-coordinated metal atoms are present in the structure. The mode of coordination of the carboxyl entity in the compound was established by ^{113}Cd NMR spectroscopy [27].

In the structure of the rhombohedral modification of $[\text{Cd}(\text{C}_3\text{H}_2\text{O}_4)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ the Cd atoms are seven-coordinated: chelated by the O atoms of two carboxyl entities, as well as by one malonate dianion through its two carboxyl ends. The seventh

coordination site is occupied by a water molecule. The Cd atom shows pentagonal bipyramidal coordination. The malonate dianion links the water coordinated cadmium ions into a three-dimensional network.

The studied compound has not been examined by infrared spectroscopy yet. To the best of our knowledge, only Bickly et al. [28] presented the result of a vibrational study of nickel(II) malonate dihydrate in the solid state and in aqueous solution. This work, however, has a rather limited scope and is mainly concerned with the assignment of the bands originating from the malonate ions and only briefly discusses some of the water modes. Our infrared study [29] published previously, referred to the spectra of water and its partially deuterated analogues in magnesium malonate dihydrate.

EXPERIMENTAL

Solid commercial cadmium carbonate was dissolved in a malonic acid–water mixture (1 : 2 molar ratio) and the cooled filtered aqueous solution was left to stand for one month when crystals of the title compound separated from the solution. The slightly deuterated analogue was prepared using vapor-phase exchange reaction with D_2O .

The FTIR spectra were recorded, from pressed KBr pellets, at RT and LNT, using a Perkin–Elmer System 2000 FTIR spectrometer. All together 16 background and 32 sample scans were averaged for each spectrum. The resolution was 4 cm^{-1} . A P/N 21525 variable temperature cell (Graseby Specac) with KBr windows was employed to record the LNT spectra.

RESULTS AND DISCUSSION

The O–H stretching region in the FTIR spectra of a $[\text{Cd}(\text{C}_3\text{H}_2\text{O}_4)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ recorded at RT and LNT is presented in Fig. 1.

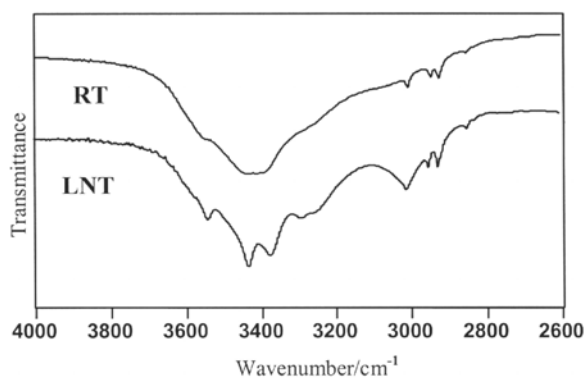


Fig. 1. The O–H stretching region in the spectra of $[\text{Cd}(\text{C}_3\text{H}_2\text{O}_4)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ recorded at RT (upper curve) and LNT (lower curve)

A very broad and irregularly shaped feature centered around 3415 cm^{-1} is immediately apparent in the RT spectrum. A noticeable substructure clearly develops at low temperature and at least five well-resolved components (at 3540 , 3429 , 3371 , 3290 and 3009 cm^{-1}) appear. The increased intensity of the bands below 3100 cm^{-1} is worth mentioning.

The position of the bands suggest that the hydrogen bonds in which some of the water protons take part are of quite considerable strength, in line with the structural data. Namely, two types of water molecules exist in the structure [25], the coordinated water molecule being hydrogen bonded to the uncoordinated water molecule and also to an adjacent carboxyl O2 atom with different strengths (the $\text{O} \cdots \text{O}$ distances are 266.9 and 275.4 pm , respectively). The uncoordinated water molecule consolidates the structure by forming weaker hy-

drogen bonds to another coordinated water molecule (the $O\cdots O$ distance is 289 pm) and also to an adjacent carboxyl O4 atom (the corresponding distance is 286.7 pm). The pertinent details of the structure are shown in Fig. 2.

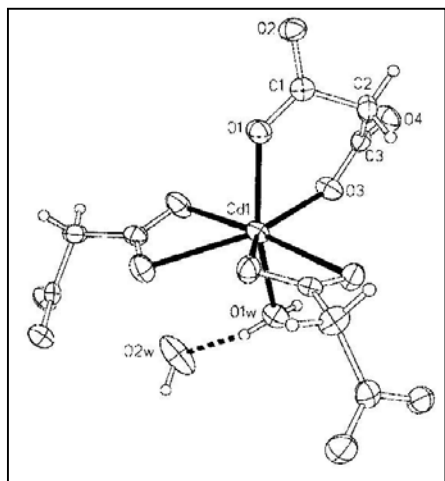


Fig. 2. ORTEP diagram (50 % probability level) of the coordination in the structure of $[Cd(C_3H_2O_4)(H_2O)] \cdot H_2O$

The comparison of the spectra of the protiated and deuterated compounds makes it easier to locate the bands that originate from vibrations in which the exchangeable hydrogens play a significant part. Particularly useful for the interpretation of the region of the water stretching vibrations are the spectra of the slightly deuterated analogues in which the HOD molecules are isotopically isolated with H_2O molecules. The appearance of the LNT spectrum of such a sample in the $\nu(O-D)$ region is shown in Fig. 3.

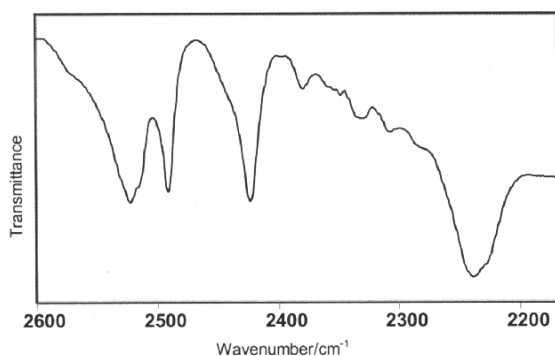


Fig. 3. The O-D stretching region in the LNT spectrum of slightly deuterated $[Cd(C_3H_2O_4)(H_2O)] \cdot H_2O$

As seen, four bands of unequal intensity are found. The highest-frequency one (its LNT value is 2522 cm^{-1} with shoulders on it) is broader than the two middle bands (at 2424 and 2491 cm^{-1}) and the asymmetric band at 2239 cm^{-1} . If the deuteration factor of 1.34 is employed, the lowest-

frequency band at 2239 cm^{-1} would place the corresponding $\nu(OH)$ frequency around 3000 cm^{-1} , close to the observed value of 3009 cm^{-1} . The above-mentioned bands are apparently due to the O-H or O-D stretching modes that correspond to the more strongly hydrogen bonded water molecule – the coordinated one [$d(O\cdots O) = 266.9\text{ pm}$]. The $\nu(OH)$ bands of the uncoordinated water molecules appear in the $3500\text{--}3200\text{ cm}^{-1}$ region.

The location of the H-O-H bending bands is practically impossible since in the region above 1600 cm^{-1} the very strong bands (originating from the antisymmetric COO stretches) appear in this region. The spectrum of the slightly deuterated analogue is of little help – the weak $\delta(H-O-D)$ bands are practically indistinguishable among those originating from vibrations of the anion (see Fig. 4).

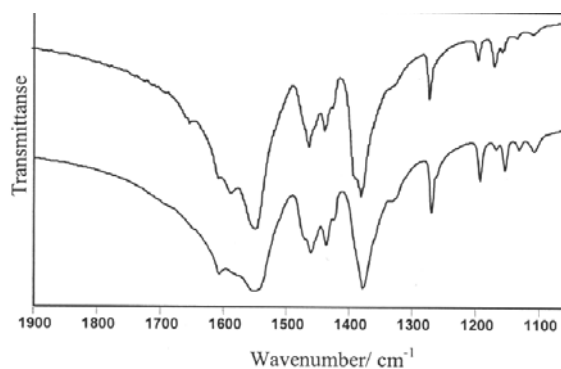


Fig. 4. The $1900\text{--}1050\text{ cm}^{-1}$ region in the spectra recorded at LNT (upper curve) and at RT (lower curve)

On the other hand, the location of the librational bands is facilitated if spectra recorded at various temperatures are available. As the temperature is lowered, namely, the bands which are due to water librations shift towards higher frequencies and gain, at least apparently, in intensity (Fig. 5).

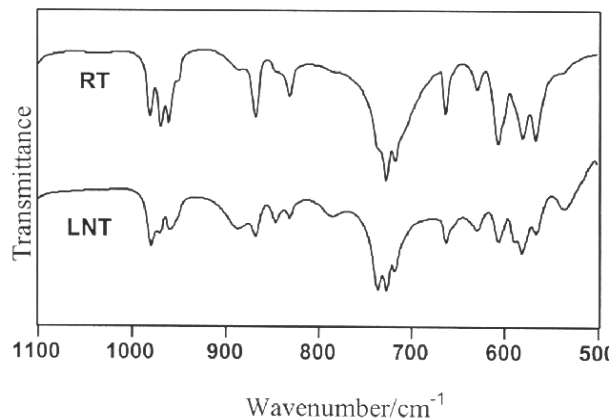


Fig. 5. The $1100\text{--}500\text{ cm}^{-1}$ region in the spectra recorded at RT (upper curve) and at LNT (lower curve)

As seen, the above-described behavior is characteristic for a number of bands in this region. Such are the bands at 979, 957, 580, 560 and 520 cm^{-1} that gain in intensity, while new bands appear at 885, 783 and 629 cm^{-1} . The number of temperature-sensitive bands is the higher than that

expected for two types of water molecules. In the case of a rich spectrum such as that presently studied it is not unconceivable that interactions between water librations and modes of the anion may take place as already encountered by us [4].

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Резиме

ФУРИЕ ТРАНСФОРМЕН ИНФРАЦРВЕН СПЕКТАР НА ВОДАТА ВО АКВА(МАЛОНАТО)КАДМИУМ(II) ХИДРАТ

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Клучни зборови: малонатен јон; кадмиум(II)малонат дихидрат; ромбоедарски полиморфизам; аква(малонато)кадмиум(II) хидрат; Фурије трансформни инфрацрвени спектри

Продолжувајќи ги нашите испитувања на вибрационите спектри на кристалохидратите на метал(II) малонати, во овој труд се обработени Фурије трансформните инфрацрвени спектри на протираниот аква(малонато)кадмиум(II) хидрат и на неговиот малку деутериран аналог. Спектрите се снимени (во подрачјето од 4000 до 400 cm^{-1}) на собна температура и на

температурата на вриење на течен азот (RT и LNT соодветно). Врз основа на температурните ефекти и на промените при деутерирање, асигнирани се лентите што потекнуваат од внатрешните и надворешните модови на молекулите вода (со исклучок на деформационите Н–О–Н вибрации).