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Spectroscopic Studies of Salts of 4-Methyl-benzenesulfonic acid. I. The Spectrum of Water in the Hexahydrates of Some Metal 4-Methyl-benzenesulfonates*

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Hexahydrates of the 4-methylbenzenesulfonates (*p*-toluenesulfonates) of magnesium, nickel, cobalt, and zinc were prepared and characterized by elemental and thermogravimetric analyses. The X-ray powder diffractograms were also recorded.

The main attention, however, was directed towards the study of the infrared spectra of these compounds and of their partially deuterated analogues. An analysis of the spectrum of water is presented in the present communication.

The spectra were recorded at room and liquid-nitrogen temperatures and, when necessary, at intermediate temperatures as well.

The spectra of the nickel, cobalt and magnesium compounds are quite similar, whereas those of the zinc analogue exhibit some differences.

Fewer bands than expected were found in all regions where the vibrations of the water molecules were expected to appear. The bands of water librational origin were located on the basis of their temperature sensitivity and shift on deuteration.

It was concluded that hydrogen bonding is not the only factor determining the position of the bands that originate from stretching and bending water vibrations.

INTRODUCTION

A number of metallic elements, among these some divalent transition metals, form salts (both anhydrous and hydrated) with 4-methylbenzenesulfonic acid.**

Such salts have been studied by various techniques, including X-ray diffraction,[1,2] infrared spectroscopy (see, for example, Refs. 2–4) and by thermal methods.[5]

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* Dedicated to Prof. Dušan Hadži on the occasion of his 70th birthday.

** The alternative (even more common) name for the acid is *p*-toluenesulfonic acid. This name (and the corresponding abbreviation H*p*TS) will be used in the present paper too.

The crystal structures of two members of the presently studied series, namely $Zn(pTS)_2 \cdot 6H_2O$ and $Co(pTS)_2 \cdot 6H_2O$, have been determined by X-ray diffraction[1,2], and only the unit cell parameters have been given for the magnesium salt.[1]

The infrared studies the results of which have been published[2-4] have a rather limited scope, the interest of the investigators being centered mainly on the assignment of the antisymmetric and symmetric stretching frequencies of the SO_3 group.

To the best of our knowledge, no complete vibrational assignment seems to have been published for either the studied metal salts or even for the 4-methylbenzenesulfonate (*p*-toluenesulfonate) ion. In fact, Uno *et al.*[6] only briefly mention the possibility of transferring the force constants calculated for the benzenesulfonate ion to the pTS^- one and state that, after some refinement, the calculated values reproduced well the frequencies observed for Na(*p*TS).

In the spectroscopic studies of the hexahydrates of $M(pTS)_2$ salts,[2] very little attention was paid to details concerning the vibrations of water molecules and only the frequencies of some of the modes were reported.

Being, for some time, interested in the study of the vibrational spectra of the hydrates of metal salts with anions of organic acids[7-10] and continuing our work on the spectra of *p*-toluenesulfonic acid monohydrate (this latter compound is, in fact, oxonium *p*-toluenesulfonate),[11] we decided to study in more detail the infrared spectrum of water in the case of the hexahydrates of four salts of *p*-toluenesulfonic acid and of their partially deuterated analogues. We plan to report, in due time, the results obtained for other salts of 4-methyl-benzenesulfonic acid as well.

EXPERIMENTAL

The studied compounds were prepared from the appropriate metal carbonates suspended in water and an aqueous solution of 4-methylbenzensulfonic acid, according to the method described in ref. 2. The products were recrystallized several times from water. The deuterated analogues were prepared accordingly, from suitable H_2O/D_2O mixtures.

For IR spectroscopic measurements, the samples were prepared as KBr pellets. A Perkin-Elmer 580 spectrophotometer was used to record the spectra. The low-temperature spectra were obtained using an RIIC VLT cell.

The compounds were identified by elemental analysis, using standard methods.

The X-ray powder diffractograms were obtained on a Carl Zeiss Universal X-ray Diffractometer HZG-4/C. The TGA and DTA curves were obtained with a Mettler Thermoanalyser in a flow of dry air, the heating rate being 5 K/minute and the temperature ranging from 290 to 520 K.

RESULTS AND DISCUSSION

Elemental and Thermal Analysis

The results of elemental and thermogravimetric analyses are given in Table I.

The dehydration of the hexahydrates of $Co(pTS)_2 \cdot 6H_2O$ and $Zn(pTS)_2 \cdot 6H_2O$ proceeds in a very similar way and takes place in one step between 360 and 430 K. Two closely lying endothermic peaks are seen on the DTA curve, the corresponding temperatures being 413 and 423 K.

TABLE I

Results of the elemental and TG analyses of the $M(pTS)_2 \cdot 6H_2O$ compounds

w(X) %	M=							
	Co		Ni		Zn		Mg	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found
C	33.01	33.46	33.02	33.45	32.60	31.48	35.42	35.23
H	5.10	4.93	5.15	5.81	5.08	4.79	5.52	6.16
M	11.59	11.41	11.53	11.23	12.67	12.53	5.12	5.09
H_2O	21.20	20.69	–	–	20.94	20.55	–	–

Crystal Structure Data

The X-ray powder diffraction patterns of Ni, Co, Zn and Mg 4-methylbenzenesulfonates hexahydrates are shown in Figure 1. As seen, they are quite similar, which is in agreement with the reported[1,2] isomorphism for three of the four presently studied compounds. On the basis of these diffractograms, it is safe to assume that the nickel compound is isomorphous with the remaining three analogues.

As mentioned earlier, the crystal structures of $Zn(pTS)_2 \cdot 6H_2O$ and $Co(pTS)_2 \cdot 6H_2O$ have been determined[1,2] and some data are available for the magnesium salt as well.[1]

All three compounds crystallize in the space group $P2_1/n$ with two formula units per unit cell. As anticipated, the parameters of the unit cell are very close to each other, the unit-cell volumes reflecting satisfactorily the differences in the metal-ion radii.

The metal ions are situated on inversion centres and are coordinated to six oxygen atoms from water molecules, these oxygen atoms forming an almost regular octahedron. The *p*TS-ions (excluding the methyl protons and SO_3 oxygens) are almost planar.

There are three crystallographically non-equivalent types of water molecules in the structure. All of them are trigonally coordinated : bonded to the metal ion and hydrogen-bonded to oxygen atoms from the sulfonate groups of two different *p*-toluenesulfonate (*p*TS–) ions. The angles around each water molecule add up to almost exactly 360°. The lengths of the hydrogen bonds in the structure of $Co(pTS)_2 \cdot 6H_2O$ are 279.6 and 277.0 pm for $H_2O(1)$, 274.4 and 276.1 pm for $H_2O(2)$ and 281.2 and 276.2 pm for $H_2O(3)$.[2] Due to the high unreliability factor *R* for the structure of the Zn analogue,[1] the reported lengths in this structure are less reliable. The local symmetry of the water molecules is C_1.

Infrared Spectra

The infrared spectra of the studied compounds recorded at the boiling temperature of liquid nitrogen (abbreviated henceforth as LNT) are shown in Figure 2.

As anticipated for isomorphous compounds, they are quite similar, although some differences are also present.

Not unexpectedly, the main differences are seen in the region of water absorptions. This is particularly true of the low-frequency region (1000–400 cm^{-1}), where the librational modes of water are expected to appear.

In the discussion that follows, our attention will be focussed on the bands originating from the internal vibrations of the water molecules (and their deuterated

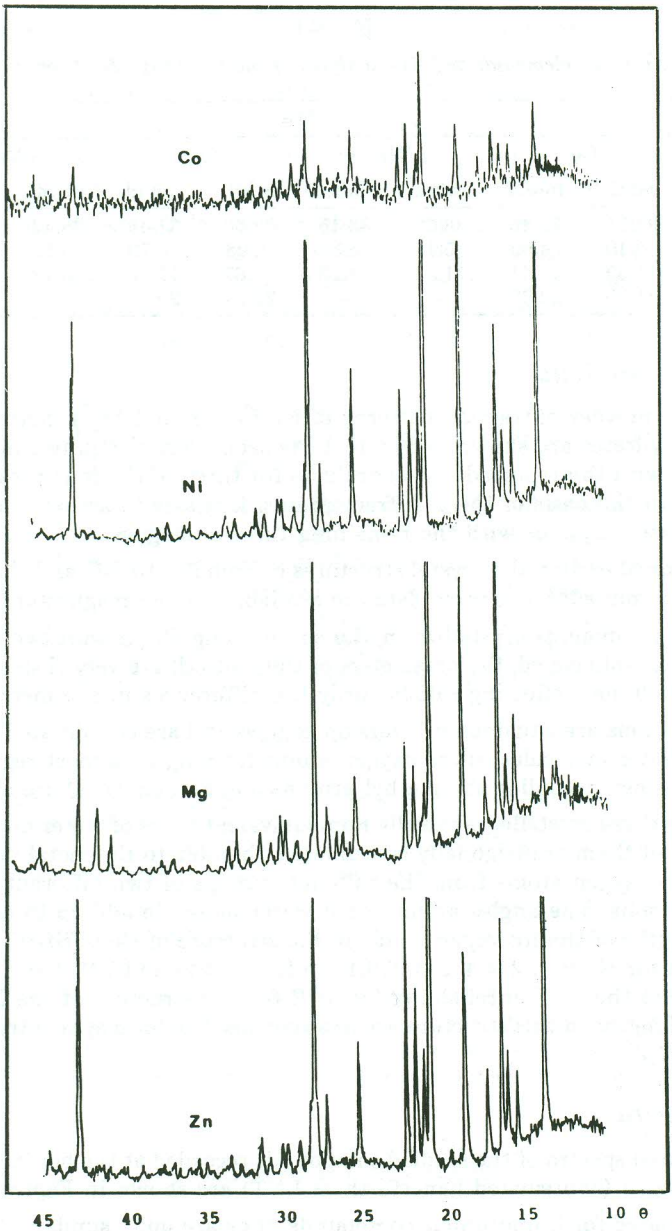

Figure 1. X-ray diffraction patterns for the four studied $M(pTS)_2 \cdot 6H_2O$ compounds.

analogues) and to those due to librations (hindered rotations) of these molecules. The frequencies of the bands which originate from vibrations of water isotopomers as well as their approximate descriptions are summarized in Table II.

Bands Due to Internal Water Vibrations

For three different types of water molecules, up to six water stretching and up to three water bending bands are expected to appear in the absence of correlation-field splitting. If a dynamic coupling between water vibrations is present, then the number of bands will increase correspondingly.

In the region of the stretching frequencies, a complex feature with several more or less resolved maxima is observed around 3400 cm^{-1} in the spectra of all the compounds studied (Figure 2). It is to be noted that the half-width of this feature does not exceed 200–300 cm^{-1} despite the fact that at least *six* bands should be found in this region. Somewhat surprising is also the rather high frequency of these bands in view of the *moderate* strength of the hydrogen bonds, deduced from the available crystallographic data.

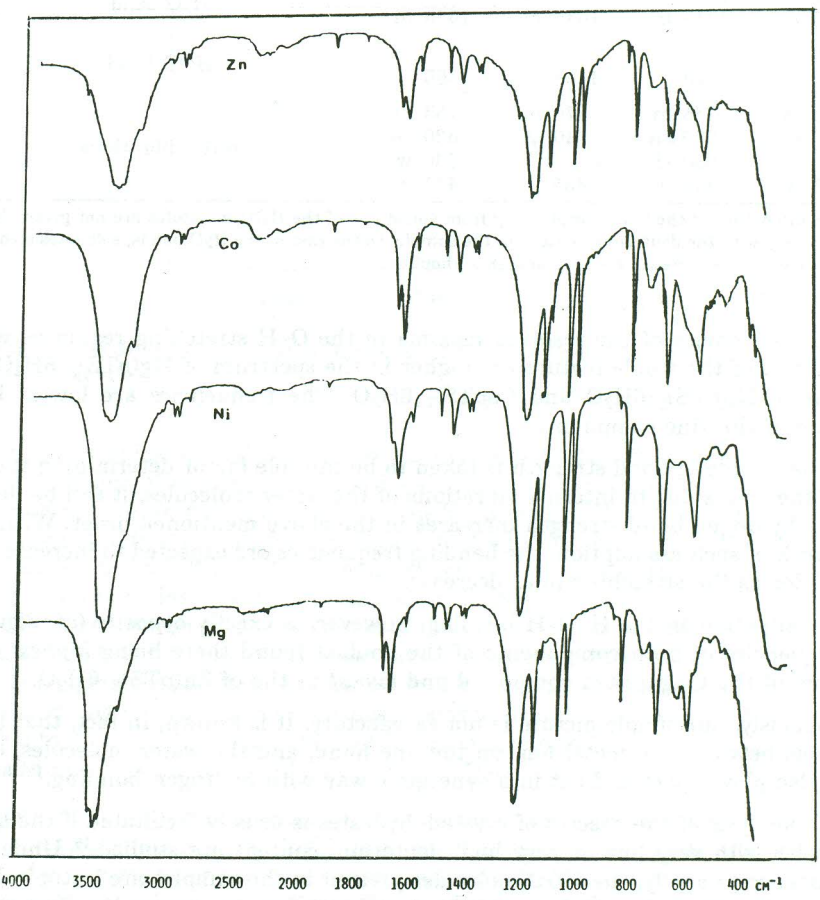

Figure 2. LNT infrared spectra of the $M(pTS)_2 \cdot 6H_2O$ compounds.

TABLE II

Observed wavenumbers (at LNT) and assignments of H_2O and HDO bands in the spectra of the studied $M(pTS)_2 \cdot 6H_2O$ type compounds and their partially deuterated analogues

M=				Assignment
Mg	Co	Ni	Zn	
3470 vs	3450 vs	3450 vs	3445 vs	
3430 vs	3405 vs	3410 vs	3410 vs	H_2O stretch
3400 vs	3375 vs	3375 vs	3365 vs	
3290 w	3265 w	3270 w	3255 w	bands due tosecond-order transitions
2580	2580	2580	2580	
2550	2545	2548	2545	OD stretches from
2525	2530	2530	2530	isotopically isolated HDO
2519	2510	2505	2500	
1685 m	1670 m	1670 m	1665 m	H_2O bend
1655 m	1645 m	1645 m	1640 m	
1475				HOD bend
1465	1470	1468	1465	
735 m	755 m	770 m	755 m	
610 sh	620 sh	640 sh	620 sh	water librations
	580 sh		530 w	
445 w	440 w	485 w	475 w	

* The intensities of the bands originating from vibrations of the HDO molecules are not given since they vary with the deuterium content in the sample. In the case of the H_2O bands, s denotes strong, m – medium, w – weak, v – very and sh – shoulder.

The frequencies of the resolved maxima in the O–H stretching region as well as the centroid of the whole feature are higher in the spectrum of $Mg(pTS)_2 \cdot 6H_2O$ than in those of $Ni(pTS)_2 \cdot 6H_2O$ and $CopTS)_2 \cdot 6H_2O$. The frequencies are lowest in the spectrum of the zinc compound.

If the hydrogen-bond strength is taken to be the sole factor determining the position of the bands due to internal vibrations of the water molecules, it can be deduced that the hydrogen bond strength increases in the above mentioned order. Within the framework of such assumption, the bending frequencies are expected to increase in the same order as the stretching ones decrease.

The situation in the H–O–H bending, however, is exactly *opposite* (*cf.* Figure 2), the frequencies of both components of the doublet found there being *highest* in the spectrum of the magnesium compound and *lowest* in the of $Zn(pTS)_2 \cdot 6H_2O$.

Obviously, our simple picture is not satisfactory. It is known, in fact, that the interactions between the metal ion, on the one hand, and the water molecules, on the other, also play a part and act in a synergetic way with hydrogen bonding.[12-15]

The analysis of the spectra of crystallohydrates is usually facilitated if the spectra of samples with very low or very high deuterium content are studied.[16] Under such circumstances, namely, the HDO molecules present in the samples are isotopically isolated and, moreover, the O–H and O–D stretchings become uncoupled. The number of O–D stretching bands in the former or O–H bands in the latter case reflects then the number of non-equivalent protons in the structure.

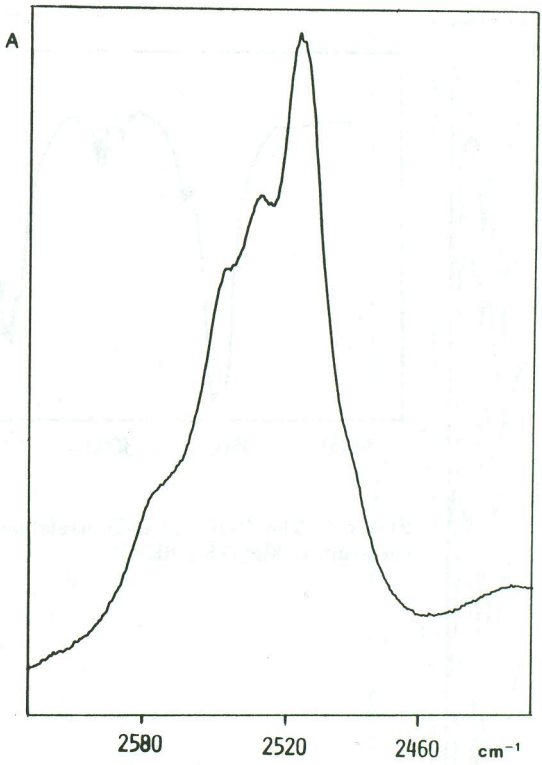

Figure 3. The O–D stretching region in the spectrum of a $Co(pTS)_2 \cdot 6H_2O$ sample with a low deuterium content.

For our samples, in which there are *six* crystallographically different protons, the expected number of bands would also be six, each of approximately equal intensity. Unfortunately, we were unable to observe such a number of bands in our spectra. Even at LNT, the bands are strongly overlapped and what is seen *e.g.* in the spectrum of the cobalt compound (Figure 3) is a band which is appreciably stronger than those appearing as more or less resolved shoulders on its high-frequency side. The reason for such extensive overlapping lies, obviously, in the fact that the strengths of the hydrogen bonds formed by water molecules are not very different and, consequently, the O–D frequencies are close to each other. In order to have a clearer picture, a reliable band deconvolution or curve-fitting procedure could be of help but they were unavailable to us at the time when the work was in progress. Thus, the infrared frequencies could not be correlated with the reported O–H···O distances.

Apart from the exact frequencies, the appearance of the spectra in the H–O–H bending region is similar for all the compounds studied. Two bands are, namely, observed, the one at lower frequency being appreciably more intense. The intensity of the feature is not, however, entirely due to the bands originating from the H–O–H bendings, since in the spectra of samples with relatively high deuterium content bands are still visible in this region, their intensity being much lower than in the spectra of

Figure 4. The H–O–H and H–O–D bending region in the LNT spectra of protiated and partially deuterated $Mg(pTS)_2 \cdot 6H_2O$ (the deuterium content increases from top to bottom).

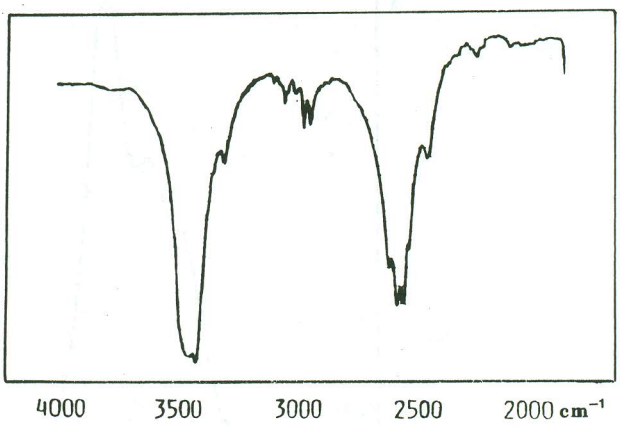

Figure 5. The O–H and O–D stretching region in the LNT spectrum of $Mg(pTS)_2 \cdot 6H_2O$.

the protiated compounds (*cf.* Figure 4 where the corresponding region of the LNT spectra of the partially deuterated analogues of $Mg(pTS)_2 \cdot 6H_2O$ is shown). Frequencies of the maxima observed in the spectra of the deuterated analogues do not coincide with those of the bands found in the spectra of the protiated compounds.

In the spectra of the partly deuterated samples, bands are found above 1450 cm^{-1}, but their number and exact assignment are complicated by the fact that, in the same region, bands due to vibrations of the anion are present. The situation is even worse in the D–O–D bending region, where only shoulders appear (around 1200 cm^{-1}) on the high-frequency side of the intense band which is due to SO_3 stretches. The bands that are assigned to the bending modes of water isotopomers are marked with arrows in Figure 4.

It should be noted that, at the low-frequency side of the feature, due to water stretching vibrations, at least one weak additional band consistently appears (in the 3290–3255 cm^{-1} region). The picture is quite similar in the O–D stretching region of the spectra of the partially deuterated analogues with high deuterium content (Figure 5). Both of these facts make the assignment of weak bands straightforward and we

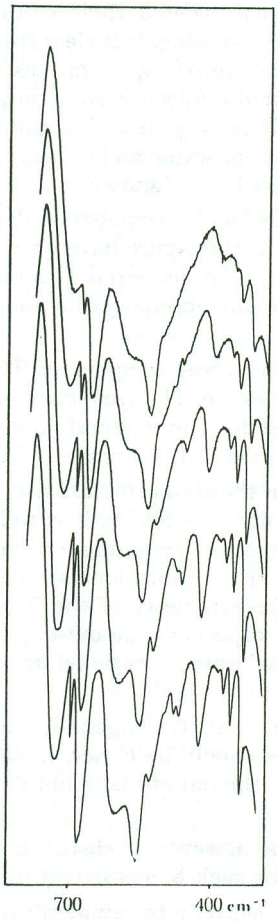

Figure 6. The water librational region in the spectra of $Mg(pTS)_2 \cdot 6H_2O$ recorded at different temperatures (the temperature decreases from top to bottom).

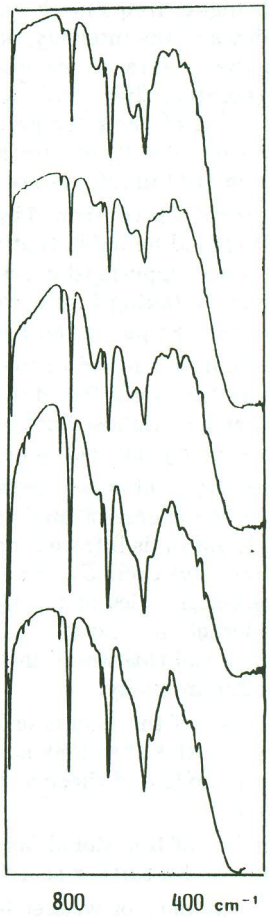

Figure 7. The water librational region in the LNT spectra of partially deuterated $Mg(pTS)_2 \cdot 6H_2O$ (the deuterium content increases from top to bottom).

assign them to second-order transitions involving the H–O–H or D–O–D bendings, respectively.

Bands Due to Water Librations

The location of these bands in the studied compounds is not easy because of the presence, in the same spectral region, of bands due to vibrations localized mainly in the six-membered aromatic ring and in the SO_3 group.

The assignment of water librational bands is, however, facilitated if the temperature sensitivity of the bands is examined. Water librational bands are, namely, known[17] to

shift towards higher frequencies when the temperature is lowered, their width decreasing appreciably and the intensity, at least apparently, increasing. It is clear from Figure 6 (in which the spectra of the magnesium compound, recorded at various temperatures, are presented) that bands with such behaviour do indeed exist in our case. In fact, on the basis of their temperature sensitivity, it is easy to assign the bands at around 730, 610 and 450 cm^{-1} to the librational modes of water molecules. The bands that arise from H_2O librations are marked with asterisks in Figure 6.

The assignment is confirmed by the fact that these bands disappear on deuteration (Figure 7). It should be noted that all spectra shown in this figure have been recorded at LNT and so the uppermost curve in this figure should be compared with the bottom curve in Figure 6, taking into account the change in the abscissa scale and the concentration of the sample in the KBr pellets.

Similar bands are found in the spectra of the other three compounds. The easiest to compare are the bands found in the 800–700 cm^{-1} range. The frequency of the corresponding band is highest for the nickel and lowest for the magnesium compound. This is approximately (but not quite) in line with the order of the stretching frequencies.

For three types of water molecules, six to nine librational bands are expected, depending on the degree of mixing of the corresponding modes. As it is well known, the twisting libration is infrared inactive for water molecules retaining (crystallographically or effectively) their C_{2v} symmetry, but the other two librations are active even under the selection rules of the C_{2v} group. When the symmetry of the force field is low, a considerable mixing of the librational modes (especially the out-of-plane ones) may take place and this would increase the number of water librational bands having a non-negligible intensity.

On the basis of the results of Eriksson and Lindgren[18] for trigonally coordinated water molecules, the librations at higher frequencies should be closer, in their form, to the rocking mode and those at lower frequency to the out-of-plane librations (wagging and twisting).

The number of librational bands assigned above, however, is clearly much lower than expected and a further search for candidates for such bands is required.

In fact, a number of weaker bands also show sensitivity to temperature changes (see Figure 6). Among these, in the spectrum of the magnesium compound, the bands at 550, 520 and 500 cm^{-1} can be mentioned. It should be added that, even at LNT, the whole region from 800 to 450 cm^{-1} is considerably broadened, indicating that additional non-resolved bands and/or bands due to accidentally degenerate modes may be present in this region.

The assignment of the librational modes can be made more exact if a normal-coordinate analysis, based on a reliable force field, is carried out.

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SAŽETAK

Spektroskopska studija soli 4-metilbenzensulfonske kiseline. I. Spektar vode u heksahidratima nekih metalnih 4-metilbenzensulfonata

Mirjana Ristova, Bojan Šoptrajanov i Kiro Stojanoski

Priređeni su heksahidrati 4-metilbenzensulfonata (*p*-toluensulfonati) magnezija, nikla, kobalta i cinka, te karakterizirani elementnom i termogravimetrijskom analizom. Snimljeni su i rendgenski difraktogrami prašaka. Međutim, glavna je pažnja usmjerena na infracrvene spektre ovih spojeva i njihovih djelomično deuteriranih analoga. U ovom prilogu prikazana je analiza spektra vode.

Spektri su snimljeni pri sobnoj i temperaturi tekućeg dušika, a ako je bilo potrebno i na temperaturama između toga. Spektri spojeva nikla, kobalta i magnezija pokazuju neke razlike. Utvrđeno je manje vrpci nego se očekivalo u svim područjima gdje se očekuju vibracije molekula vode. Vrpce uslijed libracija vode utvrđene su na temelju temperaturne osjetljivosti i pomaka deuteriranjem. Zaključeno je, da vodikova veza nije jedini faktor koji određuje položaj vrpci koje proizlaze iz vibracija istezanja i svijanja molekule vode.