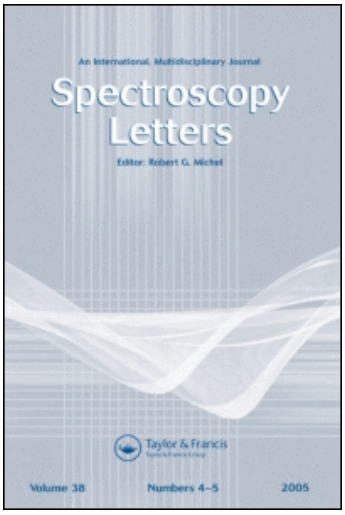

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IR SPECTRA OF $NiSO_4.nH_2O$ (n = 7,6,4,1,0) AND OF THEIR DEUTERATED ANALOGUES

Key words: nickel sulphates, IR-spectra

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Abstract

IR spectra were taken of $NiSO_4.nH_2O$ (n = 7,6,4,1,0) and of the fully and partially deuterated analogues of theirs in the region of 4000 cm^{-1} to 300 cm^{-1} in tablets of KBr, in Nujol in the region of 4000 cm^{-1} to 500 cm^{-1}, and in suspension of 1,3-hexachlorobutadiene from 4000 to 1000 cm^{-1}. They were interpreted in relation to the stretching and bending vibrations of the hydrate water, its symmetry, the types of H bonds in which it participates (H_2O - - - H - O - H - - - OSO_3 and H_2O - - H - O - H - - - OH_2) and their energy. The latter, calculated from spectroscopic data, varies within the interval of 32 - 22 kJ/mol for $NiSO_4.nH_2O$ (n = 7,6,4) and is 38.9 kJ/mol for $NiSO_4.H_2O$. Correlation has been established between the E of the H bond and d(Ni ← O). The librational vibrations were characterized mainly by the respective composite vibrations.

($\nu_L + \delta_{H_2O}$). The symmetry of the SO_4 group has been examined and compared in the various hydrates, as well as its bidentate coordination in the monohydrate.

The investigation of the hydrates of a given compound by the method of IR spectroscopy can provide useful information about the state of the hydrate water, about its participation in various H bonds with the surrounding groups, and about the symmetry of the oxoion in the crystalline structure of the investigated compounds. This is the aim of the investigation undertaken, which involves the taking and the interpretation of the IR spectra of $NiSO_4.nH_2O$ (n = 7,6,4,1,0) and of their fully or partially deuterated analogues.

There are data in pertinent literature about the IR spectra of $NiSO_4.nH_2O$ (n = 7,6,4,1), but they do not embrace the spectrum in its entire region and consistently for all hydrates. In some cases /1,2/ they involve examination only of the valency vibrations of H_2O in the region of 3700 to 2700 cm^{-1} for $NiSO_4.nH_2O$ (n = 7,6), while in /3/ they are related to all hydrates of $NiSO_4$ in the same region. The above publications do not comment on the bending vibration of the hydrate water. In /3/ there are also data about the SO_4 group in the hydrated sulphates (n = 7,6,4,1) in the region of 1200 - 900 cm^{-1}, the ν_2 and ν_4 vibrations of SO_4 remaining outside the investigated region. C. Rocchiccioli /4/ studied the stretching vibrations of hydrate water and the vibrations of the sulphate group for $NiSO_4.nH_2O$ (n = 7,1,0) and those of $NiSO_4.7D_2O$. There are also data /5/ about the stretching vibrations of the hydrate water in $NiSO_4.nH_2O$ (n = 7,6), and comparisons have been made with other data already published.

The structural data about the investigated compounds are the following: $NiSO_4.7H_2O$ - orthorhombic, a = 1186 pm, b = 1208 pm, c = 681 pm, z = 4, P 2_1 2_1 2_1 /6/; β-$NiSO_4.6H_2O$ - monoclinic, a = 987 pm, b = 721.4 pm, c = 2906.5 pm, β = 98°37', z = 8, C2/c /7/; $NiSO_4.4H_2O$ - monoclinic, a = 580 pm, b = 1320 pm, c = 765 pm, β = 91°04', z = 4 /3/; $NiSO_4.H_2O$ - monoclinic, a = 684 pm, b = 757 pm, c = 747 pm, β = 117°57' /8/; $NiSO_4$ - orthorhombic, a = 633.8 pm, b = 784.2 pm, c = 515.5 pm, z = 4 /9/.

Experimental

The investigated hydrates and their fully or partially deuterated analogues were obtained in the following manner: The initial $NiSO_4.7H_2O$ was obtained by twofold recrystallization from water solution at 30°C. The lower hydrates $\beta NiSO_4.6H_2O$ and $NiSO_4.4H_2O$ were obtained by dehydration of the heptahydrate with ethyl alcohol under certain conditions /10/. The monohydrate - $NiSO_4.H_2O$ and the anhydrous salt were obtained by thermal dehydration under conditions defined in /3/.

The deuterated heptahydrate was isolated from solution of heavy water after severalfold recrystallization of $NiSO_4.7H_2O$ and the partially deuterated heptahydrate was isolated from a mixture of heavy and ordinary water. The deuterated and partially deuterated samples of $\beta NiSO_4.6H_2O$ and $NiSO_4.4H_2O$ were obtained by the methods already indicated, starting from $NiSO_4.7D_2O$, while the monohydrate and the anhydrous salt were obtained by thermal dehydration of $NiSO_4.4D_2O$ under the respective conditions /3/.

The compounds obtained were identified by the methods of quantitative analysis: Ni - complexometrically /11/, SO_4 - by weight analysis /12/ and water - after Fisher /13/.

The spectra of the samples were taken on a Perkin Elmer 983 in suspension of Nujol in a 4000 - 500 cm^{-1} range, in

1,3-hexachlorobutadiene in a 4000 - 1000 cm^{-1} range, and in KBr tablets from 4000 to 300 cm^{-1} .

Experimental Data and Discussion

Table 1 contains the values of the absorption bands observed in the IR spectra of $NiSO_4.nH_2O$ (n = 7,6,4,1,0) and of the respective fully and partially deuterated samples.

The spectra of $NiSO_4.nH_2O$ (n = 7,6,4) are very interesting from the point of view of the vibrations of the hydrate water, since they provide good information about the character of H bonds in which the water molecules participate with their surrounding structural groups, as well as about their symmetry.

In the spectrum of $NiSO_4.7H_2O$ in the region of the stretching vibrations of the hydrate water it is possible to record fairly well the two vibrations (ν_1 and ν_3) at 3375 and 3245 cm^{-1}, which are well identified with the isotope shift of the respective vibrations in the IR spectrum of the deuterated sample: ν_H/ν_D is 1.37 and 1.34, respectively. The position of these vibrations is indicative of the existence of strong hydrogen bonds in the crystalline structure, as confirmed also by the position of the flat bending vibration of the water, which is shifted toward the higher frequencies. The latter appears split into two components (1660 cm^{-1} and 1630 cm^{-1}) and bears confirmation for the structural data /1,5,6,14,15/ according to which the structure of $NiSO_4.7H_2O$ contains two crystallochemically unequivalent types of water molecules, namely: six molecules coordinated around the nickel and forming the octahedral aquacomplex $[Ni(H_2O)_6]^{2+}$ and one molecule not connected directly to it. This molecule is at a distance from the nickel of 440 pm, while in the case of the coordinated molecules the distance $Ni \leftarrow OH_2$ is 207 pm on the average. This determines considerable polarization of the OH bond of

TABLE I

DATA FROM THE IR SPECTRA OF $NiSO_4.nH_2O$

Table 1

$NiSO_4.7H_2O$				β-$NiSO_4.6H_2O$				$NiSO_4.4H_2O$				$NiSO_4.H_2O$		$NiSO_4$	
H_2O	D_2O	HDO	ν_H/ν_D	H_2O	D_2O	HDO	ν_H/ν_D	H_2O	D_2O	HDO	ν_H/ν_D	H_2O	D_2O		
3375	2460	3200	1.37	3435	2540		1.35	3495 3440 3350	2585 2540		1.35 1.35	3200	2350		$\nu_{3(OH)}$
3245	2460		1.34	3280 3200	2450		1.34	3280							$\nu_{1(OH)}$
		2420 2345				2400 2350				2520 2450					$\nu_{1(OD)}$ HDO
2410 2320 2265 2080				2445 2405 2320 2080				2145 2063							$\delta_{H_2O}+\nu_L$
														1975 1840	$2\nu_{1,SO_4}$
1660 1630				1670 1630				1655 1630				1530			δ_{H_2O}
		1465 1445				1470 1440				1450 1425					δ_{HDO}
1098	1094			1097 1140	1097 1140			1150 1105 1080	1155 1105 1080			1150 1100 1022	1150 1100 1022	1235 1155 1045	ν_{3,SO_4}
983	983			985	980	980		985				980 920		985	ν_{1,SO_4}
760	580		1.32	780											ν_{R,H_2O}
620	615			660 630	660 635	660 625		620	620			630 604		685 613 595	ν_{4,SO_4}
					470				470		1.3				ν_{ω,H_2O}
442	442			455		455		455						485	ν_{2,SO_4}
390	390			385		385		370	370	370		365			ν_{6,NiO_6}

the coordinated water, and its possibilities for the realization of strong H bonds with the structural groups surrounding it in the crystal. Depending on their surroundings, part of the water molecules have three approximately planar neighbours, while another part are in a tetrahetral coordination.

δ_{D_2O} is not to be observed due to overlapping with the intensive asymmetric stretching vibration of SO_4, but δ_{HDO} is recorded very well, moreover split, $\Delta\nu = 20\ cm^{-1}$. This fact is related to the presence of unsymmetrical water molecules in the structure, i.e. such as are participating in various types of H bonds as $O_3SO - - - H \text{——} O \text{——} H - - - H_2O$. One confirmation of that is also the character of the absorption band corresponding to the symmetric stretching vibration (ν_1) of NDO, which is split also ($\nu_1 = 2420, 2345\ cm^{-1}$) i.e. $\Delta\nu = 75\ cm^{-1}$.

The spectrum of the monoclinic β-$NiSO_4.6H_2O$, of the deuterated sample respectively, does not differ essentially from the spectrum of the heptahydrate in the region of the stretching and bending vibrations of the hydrate water. This is in accordance with the crystalline structure of $NiSO_4.6H_2O$ /7,14,16/, whereby it also has the octahedral aquacomplex $[Ni(H_2O)_6]^{2+}$, though here five of the six water molecules coordinated around Ni have trigonal surroundings and only one has tetrahedral surrounding. This fact may serve to explain the great difference in the intensity of the two components to which δ_{H_2O} is split.

In the structure of $NiSO_4.4H_2O$, unlike the heptahydrate and the hexahydrate, according to /3,17,18/, two of the sites in the octahedron of the Ni ion are held by oxygen atoms from two different sulphate groups participating in the formation of another octahedron. The basic structural group is

TABLE II

ENERGY OF H-BONDS IN $NiSO_4.nH_2O$, n= 7,6,4.

Type of H bonds	$NiSO_4.7H_2O$		$NiSO_4.6H_2O$		$NiSO_4.4H_2O$	
	$\Delta\nu$	E,kJ	$\Delta\nu$	E,kJ	$\Delta\nu$	E,kJ
Ni ← OH_2 - - - OH_2	412	29.6	377	27.1	307	22.1
Ni ← OH_2 - - - OSO_3	-	-	457	32.9	377	27.1

$Ni_2(SO_4)_2.8H_2O$. However, this structure, essentially different from the structure of the higher hydrates, is responsible for the existence also in this case of two types of crystallochemical water molecules, as well as of asymmetrically structured water molecules participating in hydrogen bonds of the O_3SO - - - H ——— O ——— H - - - H_2O. However, the difference in the length of the Ni ← OH_2 bonds in the three hydrates, which is accordingly 203 pm for the heptahydrate /6/, 205 pm for the hexahydrate /7/ and 209 pm for the tetrahydrate /17,18/, determines the different polarization of the coordinate water molecules and hence the difference in the energies of the H bonds in which they participate. On the basis of spectroscopic data obtained by us it is possible to calculate the approximate values of these bonds according to Sokolova's equation /19/. The values obtained $\Delta\nu/\nu_o = 3.8xEx10^{-3}$ kJ/mol for H bonds calculated in relation to the recorded symmetrical stretching vibration (ν_1) and the same about the free molecule in a gas state ($\nu_1 = 3657\ cm^{-1}$) are presented in Table 2.

The values found for the energies of the hydrogen bonds are in good correlation with the roentgenostructural data about

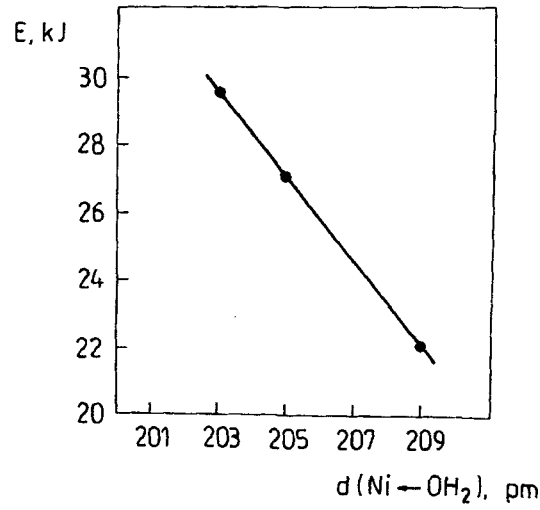

FIG. I

ENERGY OF H-BONDS IN $NiSO_4.nH_2O$, n= 7,6,4 .

the distance d(Ni ← OH_2) in the different hydrates (Fig. 1) and also with the recorded T_{max} of the endoeffects observed in their DTA curves /10/.

The spectrum of the monohydrate in the region of the stretching and bending vibrations of the water is essentially different from those examined so far. The strong and relatively narrow absorption curve found, which corresponds to the ν_3 stretching vibration, is drawn to a considerable extent to the lower frequencies, to 3200 cm^{-1}. If we calculate E of a H bond with this vibration, we shall obtain for it a value of about 38.9 kJ/mol, which is considerably higher than that of the H bonds in the remaining hydrates of $NiSO_4$. These data have been confirmed by the roentgenostructural and spectroscopic investigations of H. Oswald /8, 20/ on $MeSO_4.H_2O$ (Me = Mg, Ni, Cu, Co, Fe and Zn) and are explained by the particular position

of the water molecule in the crystalline structure of $NiSO_4.H_2O$. It participates in the building of the highly deformed octahedron around Ni and forms strong H bonds with the adjacent SO_4 groups. According to the roentgenostructural data /8/ the length of the H bonds is 271.8 pm, i.e. considerably smaller than the average value of H bridges in many other hydrates. The energy of this H bond correlates also with the high temperature of the thermal dehydration of $NiSO_4.H_2O$ /10/.

The presence of the octahedral NiO_6 group is proved first of all by the absorption observed in the spectra of the investigated hydrates in the 390-370 cm^{-1} interval and, according to /21,22,23/it may be ascribed to the coordination bond $Ni \leftarrow O(H_2)$ or $Ni \leftarrow O(SO_3)$.

The librational vibrations characteristic of the coordinated water molecules in the investigated hydrates can be observed only partially, since some of them overlap with the normal vibrations of the sulphate groups (ν_1, ν_4, ν_2), moreover not only in the ordinary spectra but in their deuterated analogues as well. However, they are characterized by the corresponding composite vibrations ($\delta_{H_2O} + \nu_L$) appearing in the region of 2400 - 2100 cm^{-1}. For instance, in $NiSO_4.7H_2O$ there appears only rocking vibration (ν_R) at 760 cm^{-1} which corresponds to that at 580 cm^{-1} in the deuterated spectrum (ν_H/ν_D = 1.32). Also manifested is the composite vibration at 2410 cm^{-1} which corresponds to it. However, according to the roentgenostructural data and the results of the investigations by Elsken /24/, there must be not one but a total of four librational vibrations (two ν_R and two ν_ω) in this spectrum. Actually, four composite ones are to be observed, from which it is possible to calculate the values of the respective librational vibrations (Table 1).

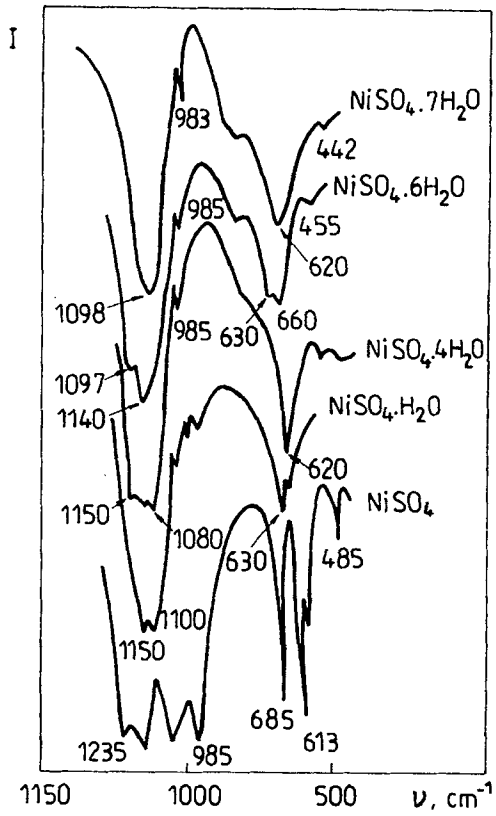

FIG. II

NORMAL OSCILLATIONS OF THE SO_4 GROUP

The absorption bands of the SO_4 groups participating in the structure of the examined hydrates indicate disruption of their regular tetrahedral symmetry, at different degrees for the different hydrates (Fig. 2, a, b, c, d). Infrared active at the heptahydrate become the symmetrically stretching (ν_1) and the symmetrically bending (ν_2) vibrations, but the respective threefold degenerated asymmetric (ν_3 and ν_4) vibrations appear as simple ones. These data are indicative of light

deformation of the octahedron, this being due to participation of the SO_4 groups in hydrogen bonds with the water molecules coordinated around the nickel. The sulphate groups from the hexahydrate also participate in such type of H bonds. Its spectrum shows also its four normal vibrations, ν_3 and ν_4 being twofold split. This is indicative of lowering of its tetrahedral symmetry (T_d) C_s, corresponding to a pyramid with isosceles triangle as its base, which is in full accord with the structural data /7,16/. According to them, only one of the four S—O bonds is shorter than the rest. In the tetrahydrate the symmetry of the sulphate group is different from that in the hexahydrate. In it also the four normal vibrations are to be observed in the IR spectrum, but the absorption band corresponding to the ν_3 vibration is threefold split, while ν_1 is simple. This is to be expected, having in mind the fact that in $NiSO_4.4H_2O$ two of the oxygen atoms of one sulphate group are connected with nickel atoms from two different nickel octahedrons /3,17,18/.

Besides the ν_1 and ν_2 vibrations of SO_4 the spectrum of the monohydrate shows complete reading of the degeneration of ν_3, i.e. its corresponding absorption is of the threefold split type, while that corresponding to ν_4 is of the twofold split type.

Fig 2 presents, for the purpose of comparison, the normal vibrations of the SO_4 groups in the hydrates examined and of the anhydrous $NiSO_4$. Clearly to be seen is the lowering of their symmetry in the direction of the lower hydrates and the reaching of C_{2V} symmetry in $NiSO_4$, corresponding to bidentate coordination of the SO_4 group /25/.

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