Hydrogen bond study in the crystallohydrates of double phosphites $MCr(HPO_3)_2 \cdot nH_2O$

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It was found that in the crystallohydrates of double phosphites $MCr(HPO_3)_2 \cdot nH_2O$ ($M = Li$, Na, K, NH_4; $n = 8$—13) the hydrogen bonds between the water molecules mutually and between the water molecules and phosphite anions are formed. From the infrared molecular spectra the lengths and energies of these bonds were determined. The hydrogen bonds between the water molecules have a length 0.285—0.288 nm and the energy 19—21 kJ mol^{-1}, while those between the water molecules and anions have a length 0.263—0.265 nm and the energy 42—47 kJ mol^{-1}. According to these values, the phosphite anion belongs to the so-called positively hydrated anions and its influence is comparable with that of a phosphate anion. In the series of compounds $MCr(HPO_3)_2 \cdot nH_2O$ the energy of hydrogen bond between water molecule and anion increases with the decreasing size of cation of alkali metal.

Было найдено, что в кристаллогидратах двойных фосфитов $MCr(HPO_3)_2 \cdot nH_2O$ ($M = Li$, Na, K, NH_4; $n = 8$—13) имеются водородные связи между молекулами воды, а также между молекулами воды и фосфитными анионами. На основании инфракрасных молекулярных спектров были найдены длины и энергии этих связей. Между молекулами воды образуются связи длиной 0,285—0,288 нм и с энергией 19—21 кДж $моль^{-1}$, между молекулами воды и анионами имеют водородные связи длину 0,263—0,265 нм и энергию 42—47 кДж $моль^{-1}$ Фосфитный анион можно по этим значениям длины и энергии водородной связи включить в ряд так называемых положительно гидратирующихся анионов и его воздействие сопоставимо с фосфатным анионом. В ряду двойных хромо-щелочных фосфитов энергия водородной связи между молекулой воды и анионом повышается с уменьшением радиуса катиона щелочного металла.

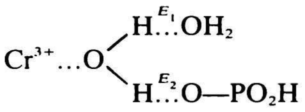
In crystal lattices of hydrates of inorganic salts the hydrogen bonds are formed both between the hydrate water molecules themselves and between the molecules of hydrate water and anions. These bonds affect not only the properties of crystallohydrate, but they can exert a direct influence upon the stability of crystal lattice itself [1—4]. The presence of a hydrogen bond in the lattice of crystallohydrate is manifested in the infrared molecular spectrum by a change of absorption bands caused by the vibration of water molecules [5] or eventually by the vibration of anion, if its symmetry is changed by the influence of the hydrogen bond [6—8]. From the infrared molecular spectra the length [2, 9—19] and energy [20—25] of a hydrogen bond be determined. The analysis of infrared spectra is concerned mostly with the stretching vibration of an OH group [1]. Also in this paper dealing with a study of the hydrogen bond in crystallohydrates of double phosphites $MCr(HPO_3)_2 \cdot nH_2O$ ($M = Li, Na, K, NH_4$; $n = 8$—13) the absorption bands of OH stretches were followed. The lengths of hydrogen bonds between the water molecules $^1R_{O\ldots O}$ and between the phosphite anion and water molecule $^2R_{O\ldots O}$ were determined from the correlation between $R_{O\ldots O}$ and $\nu(OH)$ [19]. The energies of hydrogen bonds between the water molecules, E_1, and between the phosphite anion and water molecule, E_2, were calculated according to following equations [25]

$$E_1 = \frac{3780-(\tilde{\nu}_1+\delta\tilde{\nu})}{14.8} - \exp\left[-\frac{3688-(\tilde{\nu}_1+\delta\tilde{\nu})}{120}\right],$$

$$E_2 = E_1 + 0.059\Delta\tilde{\nu} - \frac{7.5\times 10^5}{\Delta\tilde{\nu}^2},$$

where $\delta\tilde{\nu} = 45\left(1-\frac{10^4}{\Delta\tilde{\nu}^2}\right)$; $\Delta\tilde{\nu} = \tilde{\nu}_1 - \tilde{\nu}_2$ ($\tilde{\nu}_1$, $\tilde{\nu}_2$ are the wavenumbers of absorption bands $\nu(OH)$; see Table 1).

Calculation of the energies E_1, E_2 is based on an assumption of double excitation of water molecule by a neighbouring water molecule and the anion with the corresponding two values for wavenumber of stretching vibration of the OH group, $\tilde{\nu}_1$ and $\tilde{\nu}_2$. This model, the validity of which we have proved in other publication dealing with the coordination sphere of a chromium central atom in the studied compounds [26], can be formally depicted in the following way [27, 28]



According to the E_2 values, the anions can be divided into the negatively hydrated ($E_2 < E_1$) and the positively hydrated ($E_2 > E_1$) [1, 29]. The oxygen acids anions are mostly positively hydrated (exceptions being *e.g.* ClO_4^- and NO_3^-) and they can be arranged into series according to the increasing E_2 values, *e.g.* [1, 28]

$$WO_4^{2-}\ (25\text{—}26) < CO_3^{2-}\ (30\text{—}31) < SO_4^{2-}\ (31\text{—}34) < PO_4^{3-}\ (36\text{—}38).$$

(Numbers in brackets are the E_2 values in kJ mol^{-1} which slightly depend on the cation properties.)

Table 1

Infrared molecular spectra of studied double phosphites in the region of $\nu(\mathrm{OH})$, $\nu(\mathrm{OD})$
$\bar{\nu}_1$, $\bar{\nu}_2$ ... wavenumbers of absorption bands $\nu(\mathrm{OH})$, $\nu(\mathrm{OD})$

Compound	$\bar{\nu}_1(\nu(\mathrm{OH}))$ cm^{-1}	$\bar{\nu}_1(\nu(\mathrm{OD}))$ cm^{-1}	$\bar{\nu}_1(\nu(\mathrm{OH}))/\bar{\nu}_1(\nu(\mathrm{OD}))$	$\bar{\nu}_2(\nu(\mathrm{OH}))$ cm^{-1}	$\bar{\nu}_2(\nu(\mathrm{OD}))$ cm^{-1}	$\bar{\nu}_2(\nu(\mathrm{OH}))/\bar{\nu}_2(\nu(\mathrm{OD}))$
$LiCr(HPO_3)_2 \cdot 8H_2O$	3440	2500	1.376	3000	2300	1.304
$NaCr(HPO_3)_2 \cdot 13H_2O$	3450	2550	1.353	2950	2250	1.311
$KCr(HPO_3)_2 \cdot 12H_2O$	3420	2550	1.341	2930	2260	1.296
$NH_4Cr(HPO_3)_2 \cdot 8H_2O$	3440	—	—	2950	—	—

The aim of this work is to study the hydrogen bonds in above-mentioned double phosphites, to estimate the distortion effect of the phosphite anion on water molecules and explain the effect of the size of cation M on energies and lengths of hydrogen bonds.

Experimental

The preparation of double phosphites $MCr(HPO_3)_2 \cdot nH_2O$ has been already reported several times [26, 30, 31]. Sodium and potassium salts were prepared by mixing the water solutions of chromium trichloride and corresponding alkali phosphite in the ratio 1:2. The lithium salt was prepared by precipitation of a mixture of the aqueous solutions of LiH_2PO_3 and $CrCl_3$ (2:1) with methanol. The ammonium salt was prepared by precipitation of a mixture of the aqueous solutions of H_3PO_3 and $CrCl_3$ (2:1) with ammonium. The grey-violet crystalline precipitates were always collected, washed several times by ethanol and ether, and air-dried at room temperature. Preparation of fully deuterated analogs of chromium(III) alkali double phosphites started from hydrolysis of phosphorus trichloride with heavy water. In this way prepared D_3PO_3 acid was neutralized with solid anhydrous carbonate of the corresponding alkali metal and through the resulting solution was bubbled for 20 min with dry nitrogen in order to remove CO_2. Further the solution of anhydrous $CrCl_3$ in D_2O was prepared by addition of a few crystals of chromium(II) sulfate to the suspension of $CrCl_3$ in D_2O. Otherwise, the preparations were carried out as described above, this time, however, in dry atmosphere.

The prepared products were analyzed gravimetrically [31, 32]. After oxidation by conc. HNO_3 and a subsequent oxidation by peroxodisulfate catalyzed by Ag^+ the phosphorus content was determined as $Mg_2P_2O_7$. In the filtrate which was reduced by ethanol the chromium content was determined as Cr_2O_3 and in the filtrate after the phosphorus and chromium determination the contents of alkali metals were determined: lithium as Li_2SO_4, sodium as $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ and potassium as K_2SO_4. The ammonium content was determined separately by a distillation method proposed by Parnas and Wagner [33].

The infrared molecular spectra were recorded using a UR-20 spectrophotometer (Zeiss, Jena) and KBr pellets (1—3 mg of sample per 1 g of KBr). In spite of certain drawbacks [34—36], the KBr pellets technique is better suited to the studies of hydrogen bond than the suspension technique in various derivatives of paraffine hydrocarbons [1, 37].

Results and discussion

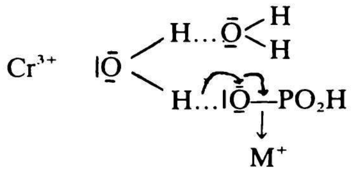
In Table 1 the wavenumbers $\tilde{\nu}_1$ and $\tilde{\nu}_2$ of $\nu(\text{OH})$ and $\nu(\text{OD})$ vibrations and their ratios are collected. According to *Novak* [19] the values of ratio $\tilde{\nu}(\nu(\text{OH}))/\tilde{\nu}(\nu(\text{OD}))$ confirm that the hydrogen bonds between the water molecules are weak and those between the phosphite anion and water molecule are medium strong. In Table 2 the obtained values E_1, E_2, $^1\text{R}_{\text{O...O}}$ and $^2\text{R}_{\text{O...O}}$ are presented. The energies of hydrogen bonds between the water molecules in the crystal lattice of double phosphite are close to the energies of hydrogen bonds in liquid water. All energies of hydrogen bonds between the water molecules and phosphite anions are higher than those between the water molecules alone, so the phosphite anion can be classified as a typical positively hydrated anion exhibiting a strong distortion effect on water molecules comparable with the distortion effect of the phosphate anion [1].

Table 2

The energies and lengths of the hydrogen bonds "water—water" (E_1, $^1\text{R}_{\text{O...O}}$) and "anion—water" ($E_2$, $^2\text{R}_{\text{O...O}}$) in double phosphites studied

Compound	E_1 kJ mol^{-1}	E_2 kJ mol^{-1}	$^1\text{R}_{\text{O...O}}$ nm	$^2\text{R}_{\text{O...O}}$ nm
$\text{LiCr(HPO}_3)_2\cdot 8\text{H}_2\text{O}$	20	42	0.287	0.265
$\text{NaCr(HPO}_3)_2\cdot 13\text{H}_2\text{O}$	19	46	0.288	0.264
$\text{KCr(HPO}_3)_2\cdot 12\text{H}_2\text{O}$	21	47	0.285	0.263
$\text{NH}_4\text{Cr(HPO}_3)_2\cdot 8\text{H}_2\text{O}$	20	46	0.287	0.264

In the series of chromium(III) alkali double phosphites a gradual decrease of energies and an increase of the length of phosphite—water hydrogen bonds with the increasing polarization power of alkali metal cation can be observed. This effect can be explained by the following scheme



The larger the polarization power of the M$^+$ cation, the more decreases the electron density on the oxygen atom of an anion and the more difficult becomes the donation of a free electron pair to the hydrogen bond. In the ammonium salt, the electron density on the oxygen atom is most probably still more reduced by a formation of hydrogen bond N—H...O which is indicated also by the observed increase of wavenumber of the $\delta(\text{NH})$ vibration by 35 cm^{-1} compared to 1400 cm^{-1} for the free cation NH_4^+ [38, 39].

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