Dedicated to Professor Ivan Petrov on the occasion of his 80th birthday

VIBRATIONAL SPECTRA OF HEXAAQUACOMPLEXES
XI. SPECTROSCOPIC CRITERIA FOR THE CLASSIFICATION OF THE ALUM TYPES

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The three existing (α, β and γ) alum types, may be clearly and unequivocally distinguished on the basis of their structural peculiarities. It is also possible to make a clear-cut distinction between the first two alum types on the basis of some details in their vibrational (IR and Raman spectra) as demonstrated in this paper. An attempt was made to relate the spectroscopic differences to the structural ones, thus putting forward spectroscopic criteria for distinguishing the alums on a more solid ground.

Key words: alums; alum types; IR spectra; Raman spectra

INTRODUCTION

For more than four decades the structural chemistry group within the Institute of Chemistry (Faculty of Natural Sciences and Mathematics in Skopje) makes significant research contributions, mostly through relevant publications in distinguished journals. The credit for this, one must say, goes to the founder of this group and our laureate, professor Ivan Petrov. The group was actually founded as a small spectroscopy group within the Division of Physical Chemistry and back in the 60s was dealing mainly with interpretation of IR spectra of various (mostly hydrogen-bonded) materials. Browsing through the very first publications one may find, however, papers where spectroscopy was used to extract some structural information [1, 2]. Later it was used in getting a deeper insight in crystal structures refined by conventional diffraction methods [3–5]. Indeed, both IR (lately, FT IR) and Raman methods appeared to be valuable complementary methods to the X-ray and neutron diffraction ones, this being demonstrated many times and is a well known fact nowadays.

In a series of papers under the same general title we studied several times the alum family of crystals. The compounds of this huge group (definitely one of the largest groups of isostructural compounds) show some interesting peculiarities:

- large number of atoms (192) in the unit cell, yet small number of atoms (11) in the asymmetric unit;
- three different alum types (α, β and γ);
- strong hydrogen bonding (at least strong, when crystalline hydrates are considered);
- large amplitudes of thermal motion for some oxygen atoms in the structure;
- disorder of the sulfate groups in the sulfate alums;
- multiple bands in the bending HOH region of the low-temperature vibrational spectra;
- ....

Many of the above points (i.e. those concerning the assignments in the spectra, or the appearance of multiple bands in the HOH bending region) were already discussed in our previous publications. Knowing, however, that the three types may be clearly distinguished from a structural point of view, we searched for relevant spectral differences between the α and β alums only (there is only one γ alum known so far) that would enable their positive classification. The idea was to identify spectral

parameters that are specific for a certain alum type and to interpret (or relate) the detected spectral differences in terms of the structural subtleties of the two types.

NOTATION AND RELEVANT CRYSTALLOGRAPHIC DATA

The alums, as mentioned, are a large class of isostructural double salts of the general formula $M^IM^{III}(RO_4)_2 \cdot 12H_2O$. M^I can be Na, K, Rb, Cs, Tl, NH_4, NH_3CH_3, N_2H_5, NH_3OH etc.; M^{III} can be Al, Ga, In, Sc, Ti, V, Cr, Mn, Fe, Co, Ru, Rh, Ir and Mo; R can be S or Se (some BeF_4 alums are also known to exist [6, 7]). Further information on the alum family of crystals may be found in the more than extensive literature (see [8–14] and the references therein). From now on, whenever we speak about a particular alum, we will adopt the $M^IM^{III}R$ system of abbreviations, where M^I, M^{III} and R are the chemical symbols (or other abbreviations like A for NH_4; Ha for NH_3OH; M for CH_3NH_3; Hy for N_2H_5). Thus, CsAlSe is simply $CsAl(SeO_4)_2 \cdot 12H_2O$; ACrS is $NH_4Cr(SO_4)_2 \cdot 12H_2O$ etc.

All alums crystallize in the cubic space group $Pa3$ with $Z = 4$. The cell parameter spans the 1210–1270 pm range and is well within the "allowed" 10 % variation of the lattice parameters, for which one may expect true isomorphism in an isostructural series. This appears to be only partly true, however, since Lipson found that there are 3 structural types (or classes) designated as α, β and γ, following the order of their discovery [15, 16]. Irrespective of the alum type, both univalent and trivalent cations occupy four-fold positions of S_6 symmetry. If the former ions are put at ½,0.0 etc., the latter will occupy crystallographically distinct site of the same symmetry at 0,0,0 etc. All tetrahedral anions occupy C_3 positions (the central atom and one of the oxygen atoms lying along the body diagonal of the unit cell). In the γ alums (the only known example so far being NaAlS) the trigonal sulfate oxygens point towards the univalent (sodium) cations, while in α and β alums these oxygens point to the opposite direction. Half of the water molecules are coordinated to the univalent and the other half to the trivalent cations. The water molecules, therefore, occupy two 24-fold sets of positions of general symmetry.

Crystallographers argued for many decades about the best criterion for alum classification [16–20]. Morphologically it seemed to be an easy task, for the (210) faces appeared only in β alums [21]. The problem of the alum classification was successfully solved some 20 years ago by Beattie et al.

[19] who proved that the difference between the α and β alum types are best reflected through the geometry of the water molecules around the univalent cation. In α alums a distorted octahedron is formed (the $O_w–M^I–O_w$ angles are in the 64–66 ° range) whereas in β alums an almost regular hexagon exists (the angles being in the range from 60.0 to 60.2 °). Furthermore, in β alums the coordination of the univalent cation may be considered as 12-fold (the coordination polyhedron may be described as an elongated icosahedron), 6 oxygen atoms of the tetrahedral anions also being part of the coordination polyhedron. The polyhedron about the trivalent cation is in all cases an almost perfect octahedron. Due to the low site symmetry (C_1), all water molecules are asymmetric. A schematic illustration of the three alum types is given in Fig. 1. The water molecules in all alums are hydrogen bonded. According to a common practice, the water oxygens will be designated as Oa and Ob (for the water molecules coordinated to univalent and trivalent cations respectively). Further, O1 and O2 will be the sulfate oxygens on the threefold axes and at positions of general symmetry. Each water molecule coordinated to the univalent cation forms two hydrogen bonds of intermediate strength with the sulfate oxygens (one to O1 and the other to O2). The water molecules coordinated to M^{III} form two types of rather strong hydrogen bonds: one with the sulfate oxygen O2, and the other one with the Oa oxygen atom of the water molecules coordinated to the univalent cations. Table 1 contains the relevant information about the hydrogen bond strengths (due to the lack of reliable neutron diffraction data, O···O distances are considered as a crystallographic measure for the hydrogen bond strength).

As evident, in practically all α alums the hydrogen bonds in which the water molecules coordinated to the trivalent metal cations act as proton donors are basically equal (or are equal within one standard deviation). In β alums the corresponding two (rather strong) hydrogen bonds are definitely of different strength. This might be expected to have an impact on the spectral appearances of the α and β class alums.
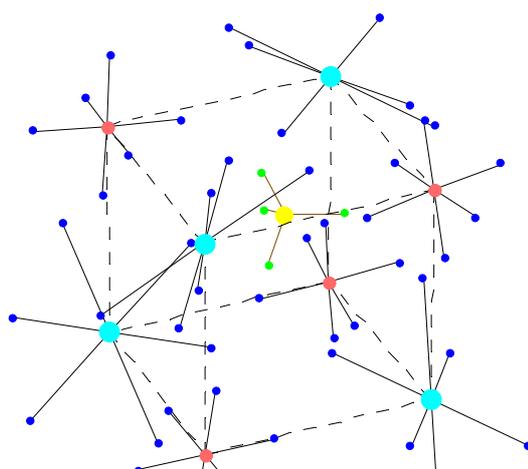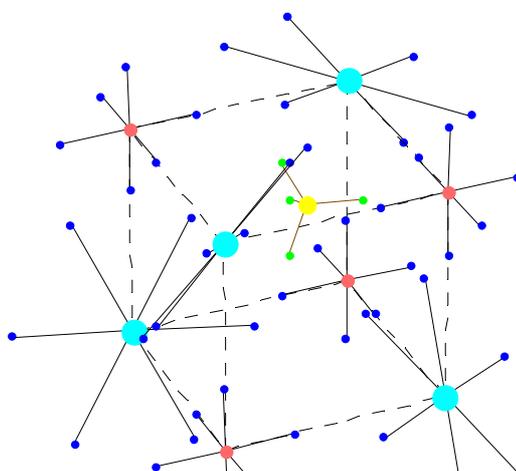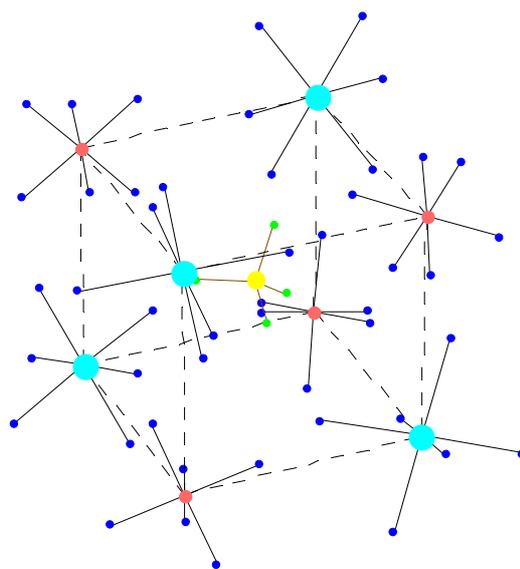
α – RbAlS

β – CsAlS

γ – NaAlS

Fig. 1. Presentation (schematic) of the three alum types
(red circles – aluminum atoms; blue circles – water molecules; yellow circles – sulfur atoms; green circles – sulfate oxygens;
light blue circles – univalent cations; for purposes of clarity, hydrogen atoms were omitted)

Table 1

The O⋯O separations in selected α and β alums with more or less reliably refined structures
(the standard deviations given in parentheses refer to the rightmost digit; a – Nyburg et al. [14];
b – Figgis et al. [13]; c – Armstrong et al. [10]; d – Beattie et al. [19]; e – Beattie et al. [20];
*f – Brorson & Gajhede [9]; * – structure refined at low temperature).*

Alum	Type	Oa⋯O1/pm	Oa⋯O2/pm	Ob⋯O2/pm	Ob⋯Oa/pm
KAlS[a]	α	278.1(2)	275.6(2)	260.3(2)	262.6(2)
KCrS[a]	α	279.5(4)	275.0(4)	261.9(4)	261.1(3)
TlAlS[a]	α	280.4(4)	274.0(3)	262.3(4)	262.0(3)
TlGaS[a]	α	278.9(4)	274.9(3)	261.3(4)	261.1(4)
RbGaS[a]	α	280.8(5)	276.3(4)	262.1(4)	261.2(4)
RbCrS[b]	α	282.1(4)	276.3(4)	262.1(4)	262.0(4)
CsAlSe[c]	α	280.8(6)	275.2(6)	263.8(5)	262.5(5)
CsCrSe[b]	α	281.1(3)	275.3(3)	263.5(3)	262.0(3)
CsFeSe[c]	α	281.3(7)	276.3(7)	263.0(6)	263.0(6)
CsInSe[c]	α	280.9(14)	277.9(12)	262.2(12)	263.9(11)
CsAlS[d]	β	283.3(6)	277.8(6)	266.3(5)	260.2(5)
CsGaS[d]	β	285.4(4)	278.3(4)	265.3(4)	260.4(4)
CsInS[d]	β	286.1(6)	281.1(8)	263.2(7)	261.4(8)
RbVS[e]	β	287.1(7)	281.9(7)	263.0(6)	261.0(6)
CsVS[e]	β	284.3(1)	279.0(1)	264.2(1)	260.8(1)
CsCrS[d]	β	284.4(4)	278.4(5)	265.4(5)	259.2(5)
CsMnS[d]	β	284.5(8)	279.1(9)	265.9(8)	258.6(8)
CsFeS[d]	β	285.2(6)	278.1(6)	265.4(5)	260.4(6)
CsMoS[f,*]	β	282.4(2)	277.6(2)	263.8(2)	259.9(2)

Another important quantity may be the bond strength, calculated from the bond-length (following the procedure of Brown and Altermatt [22]). Table 2 comprises the bond strength values for the $M^I⋯O_w$ "bonds" in α and β alums, respectively.

Again, one can see that, due to the different environment in α and β alums, the bond strengths of $M^I⋯O_w$ separations differ significantly (on the average by more than 30 %) between α (stronger bonds) and β (weaker bonds) alums. This, also,

may be expected to have an important influence on the vibrational spectra of the two classes of compounds, particularly on the bands originating from the vibrations of the water molecules.

A third important point is the difference in the geometry of the tetrahedral (sulfate) anion between the two types (cf. Table 3).

Two things become clear at first sight. First, the S–O distances in α alums are significantly shorter than in β, and second, the tetrahedron in β

alums is fairly regular (all distances being equal within one standard deviation). The first finding might be somewhat questionable in the light of the large temperature (displacement) factors for the oxygen atoms found in most α alums. The differences, therefore, may not be really that much pronounced. On the other hand, taking into account the fact that the sulfate group in β alums is coordinated to the univalent cations, this is what one would a priori expect (i.e. longer values of the S–O_2 distances for β as compared to α alums). Once again, this should also have some consequences on the vibrational spectra (particularly on the features due to the sulfate stretching vibrations).

Table 2

Bond strengths (s) calculated for the $M^I \cdots O_w$ separations in various α and β alums (an equation of the form $s = \exp[(r_0 - r)/B]$ was used, where $B = 37$ pm, r_0 is a constant characteristic for each pair of $M^I \cdots O_w$ separations and corresponding to a single bond distance [22], and r is the actual $M^I \cdots O_w$ separation; the meaning of other symbols is the same as in Table 1)

Alum	Type	$M^I \cdots O_w$/pm	$s(M^I \cdots O_w)$
KAlS[a]	α	295.4(1)	0.1084
KCrS[a]	α	301.0(2)	0.0932
RbGaS[a]	α	308.1(3)	0.1096
RbCrS[b]	α	308.2(3)	0.1093
CsAlSe[c]	α	322.5(4)	0.1126
CsCrSe[b]	α	323.2(2)	0.1105
CsFeSe[c]	α	322.7(5)	0.1120
CsInSe[c]	α	323.1(7)	0.1108
CsAlS[d]	β	331.4(5)	0.0885
CsGaS[d]	β	335.5(4)	0.0793
CsInS[d]	β	335.1(6)	0.0801
RbVS[e]	β	322.9(5)	0.0735
CsVS[e]	β	334.5(1)	0.0814
CsCrS[d]	β	334.9(4)	0.0805
CsMnS[d]	β	335.8(7)	0.0786
CsFeS[d]	β	335.9(5)	0.0784
CsMoS[f,*]	β	331.1(1)	0.0893

Table 3

*S–O1 and S–O2 distances for various sulfate alums of α and β type (standard deviations given in parentheses refer to the rightmost digit; a – Nyburg et al. [14]; b – Figgis et al. [13]; c – Armstrong et al. [10]; d – Beattie et al. [19]; e – Beattie et al. [20]; f – Brorson & Gajhede [9]; g – Sygusch [23]; * – structure refined at low temperature)*

Alum	Type	S–O1/pm	S–O2/pm
KAlS[a]	α	144.7(4)	147.2(2)
KCrS[a]	α	144.2(6)	147.0(3)
TlAlS[a]	α	143.9(5)	147.0(2)
TlGaS[a]	α	143.5(5)	146.8(3)
RbGaS[a]	α	143.9(5)	146.6(3)
RbCrS[b]	α	144.2(6)	146.5(3)
CsRhS[c]	α	145.0(2)	146.1(4)
CsIrS[c]	α	145.5(2)	146.5(5)
CsAlS[d]	β	148.0(2)	147.2(4)
CsGaS[d]	β	147.2(2)	147.3(3)
CsInS[d]	β	146.9(3)	147.2(4)
RbVS[e]	β	147.9(3)	147.0(5)
CsVS[d]	β	147.6(3)	148.2(6)
CsCrS[d]	β	146.0(2)	146.0(3)
CsMnS[d]	β	146.1(3)	146.2(6)
CsFeS[d]	β	146.8(2)	147.7(4)
CsMoS[f,*]	β	147.8(1)	147.8(1)
CsTiS[g]	β	147.5(9)	148.4(4)

EXPERIMENTAL PART

In order to obtain large single crystals of a good quality, sulfate alums were synthesized by slow evaporation from aqueous solutions of stoichiometric amounts of the corresponding salts. A parallel attempt to synthesize alums from chloride or nitrate salts in diluted sulfuric acid appeared to be completely successful and was used in the synthesis of some selenate alums (one recrystallization in the latter case appeared to be sufficient for obtaining single crystals free of the spectator ions).

FT IR spectra were recorded using a specular reflection accessory, on a Perkin Elmer System 2000 instrument. Typically, depending on the sample size, 16 or 32 scans were used for the background spectrum and 32, 64 or 128 spectra for the sample spectrum. The resolution (4 cm^{-1}) and the OPD velocity of the mirror (0.2 cm/s) were the same in all cases. The Kramers–Kronig transformation [24] was employed to calculate the absorption spectra from the reflection ones. The spectra obtained in this way were almost identical to the transmission spectra obtained from pressed KBr disks or mulls in Nujol between KBr plates.

The Raman spectra were recorded on a Jobin Yvon T64000 Raman system. The excitation source was INNOVA 300 FRED Ar$^+$ laser operating at either 514.3 or 488 nm. For colorless systems the power was adjusted to $\approx$ 1 W. The resolution was about 3 cm^{-1} and the wavenumber accuracy was about 1 cm^{-1}.

Grams 2000 and Grams/32 software packages [25,26] were used for spectra acquisition and manipulation.

SPECTROSCOPIC RESULTS AND THEIR INTERPRETATION

We shall first discuss the spectral region of the stretching vibrations of tetrahedral anions. Since all studied selenate alums are of the α type, the attention was focused only on sulfate alums.

A close inspection of the Raman spectra reveals that significant differences exist in the region of the bands due to the sulfate stretching (both symmetric and antisymmetric) of α and β alums. The results are given in Figure 2 and Figure 3.

The spectral features are consistent with the structural differences (cf. Table 3), even (as discussed earlier) if the true geometry differences are not really as pronounced as would appear if the literature data are taken at face value. Indeed, the consistently lower frequencies of the symmetric SO$_4$ vibrations in β alums (cf. Fig. 2) point to a small but significant expansion of the S–O distances in this class. The possible reason might be the coordination of the sulfate O2 oxygens to the univalent cations.

Differences exist in the shapes of the bands due to the antisymmetric SO$_4$ stretchings as well (cf. Fig. 3). A doublet is found in all α alums, compared to a singlet band in β ones. This is, again, consistent with the geometry of the tetrahedral ions, that of the β sulfate groups being closer to the ideal one. If this is the true reason for the encountered spectral differences, one must conclude that the doublet in the Raman spectra of α alums must be due to site group splitting of the ν$_3$(SO$_4$) modes. This finding is somewhat questionable from the viewpoint of the results obtained from sulfate doped selenate alums [27], where it appears that the observed splitting in the IR spectra results from interaction of identical oscillators in the unit cell. However, a possibility should be kept in mind that the host lattice "imposes" the effective symmetry of the host ions (selenates) on the sulfate guests and therefore, the results may not be the same as in pure sulfate compounds.

The feature due to the OH stretching vibrations resulting from the water molecules that are strongly hydrogen bonded, is also different in α and β alums (cf. Fig. 4). Two bands (at ≈3000 and at ≈ 2750 cm^{-1}) can be detected in β alums, compared to one band (at ≈ 2900 cm^{-1}) in the compounds of the α type. This could easily be explained as a result of the pronounced differences in the hydrogen bond strength in β alums (cf. Table 1), unlike those in α alums where both hydrogen bonds are of practically equal strength.
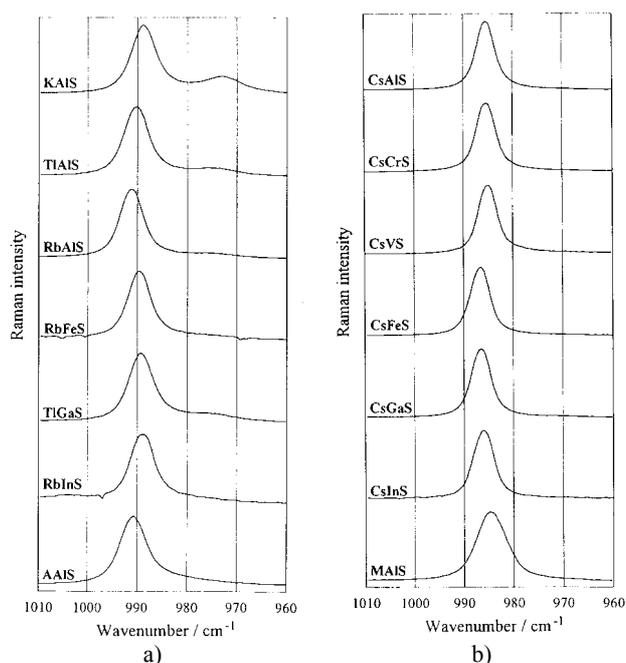

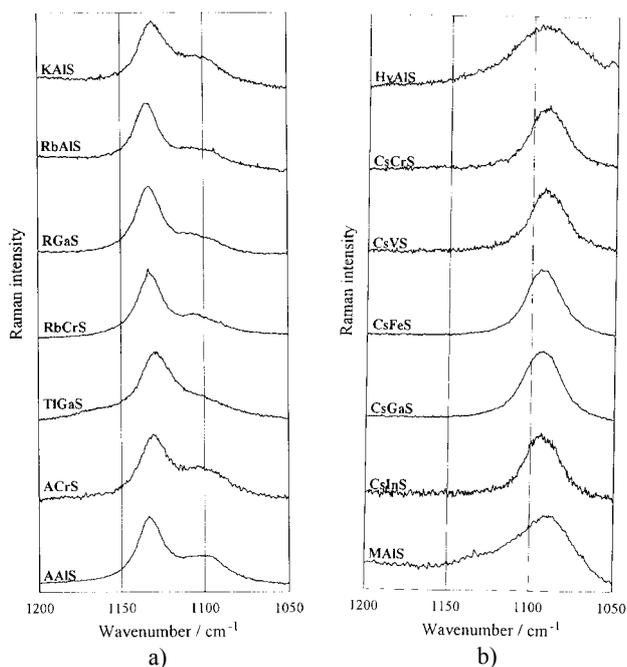**Fig. 2.** The symmetric SO$_4$ stretching region in the Raman spectra of some α (a) and β (b) alums

Fig. 3. The antisymmetric SO_4 stretching region in the Raman spectra of some α (a) and β (b) alums
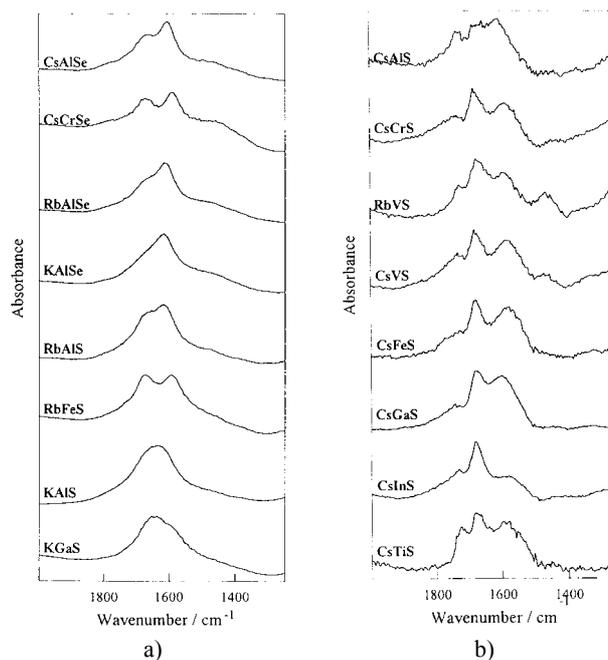

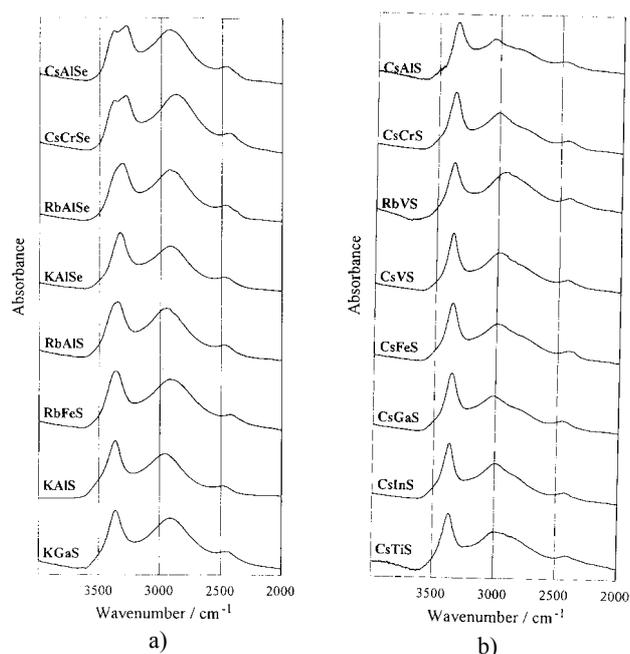**Fig. 5.** The region of the HOH bending vibrations in the FT IR spectra of some α (a) and β (b) alums

Fig. 4. The region of the HOH stretching vibrations in the FT IR spectra of some α (a) and β (b) alums
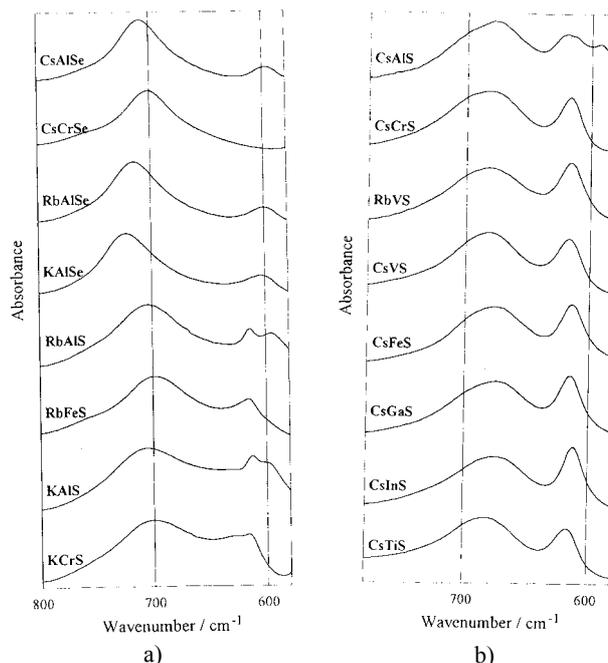

Fig. 6. One of the librational HOH bands of the water molecules coordinated to M^I, in the FT IR spectra of some α (a) and β (b) alums

Differences between the two structural types are found in the HOH bending region as well (cf. Fig. 5), but these could not be explained straightforwardly. One could still speculate that the force field for the δ(HOH) vibrations of the six water molecules coordinated to M^I must be substantially different for the regular hexagonal geometry (in β alums) compared to the distorted octahedral (in α alums).

The last difference between the two alum classes that we are referring to appears in the region of the librational modes of the water molecules. The water librational bands at ≈ 700 cm^{-1} (these bands were earlier attributed to the wagging librations of the water molecules coordinated to the univalent cation) are consistently lower in the case of β alums (cf. Fig. 6). On the other hand, both theoretical and experimental studies show that an important

factor that affects the librational frequencies is the M–O$_w$ bond strength. This has been shown to be by some 30 % (on the average) lower in β alums, as a result of the extended (12-fold) coordination of the MI ions. The result is the trend we observe

It should perhaps be noted that for pairs of α and β alums with the **same anion and M^{III} cation**, the frequencies of the librational bands above 900 cm^{-1} (these were assigned to the wagging librations of the water molecules coordinated to M^{III}) are

consistently **higher** in β alums. However, since these frequencies are at the same time M^{III} cation sensitive, they can not be used as a criterion for distinguishing the alum class.

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Р е з и м е

ВИБРАЦИОНИ СПЕКТРИ НА ХЕКСААКВА-КОМПЛЕКСИ
XI. СПЕКТРОСКОПСКИ КРИТЕРИУМИ ЗА КЛАСИФИКАЦИЈА НА СТИПСИТЕ

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Клучни зборови: стипси; типови на стипси; инфрацрвени спектри; Раманови спектри

Трите постоечки типови на стипси (α, β и γ) можат еднозначно да се разликуваат врз основа на нивните структурни специфичности. Исто така е можно да се направи разлика помеѓу првите два типа на стипси врз основа на некои детали во нивните вибрациони (инфрацрвени и Раманови) спектри, како што е покажано во овој труд. Направен е обид да се поврзат спектроскопските разлики со структурните и на таков начин да се формулираат спектроскопски критериуми за разликување на стипсите базирани на поцврсти основи.