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Near-infrared spectroscopic study of basic aluminum sulfate and nitrate

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The tridecameric Al-polymer $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ was prepared by forced hydrolysis of Al^{3+} up to an OH/Al molar ratio of 2.2. Under slow evaporation crystals were formed of Al_{13}-nitrate. Upon addition of sulfate the tridecamer crystallised as the monoclinic Al_{13}-sulfate. These crystals have been studied using near-infrared spectroscopy and compared to $Al_2(SO_4)_3.16H_2O$. Although the near-infrared spectra of the Al_{13}-sulfate and nitrate are very similar indicating similar crystal structures, there are minor differences related to the strength with which the crystal water molecules are bonded to the salt groups. The interaction between crystal water and nitrate is stronger than with the sulfate as reflected by the shift of the crystal water band positions from 6213, 4874 and 4553 cm^{-1} for the Al_{13} sulfate towards 5925, 4848 and 4532 cm^{-1} for the nitrate. A reversed shift from 5079 and 5037 cm^{-1} for the sulfate towards 5238 and 5040 cm^{-1} for the nitrate for the water molecules in the Al_{13} indicate that the nitrate-Al_{13} bond is weakened due to the influence of the crystal water on the nitrate. The Al-OH bond in the Al_{13} complex is not influenced by changing the salt group due to the shielding by the water molecules of the Al_{13} complex.

1. Introduction

Although the hydrolysis of aluminium has been studied for more than 150 years, it is during the last 25 years that much attention has been paid to the Al_{13} complex. Al_{13} is a Keggin structure (Fig. 1) also known as the aluminium tridecameric complex with a general composition of $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ [1–3]. This complex is known to be formed by forced hydrolysis of Al^{3+} solutions by the addition of a basic solution like sodium hydroxide or carbonate. The structure of this complex was first studied by X-ray diffraction by Johansson and coworkers [4–7] after precipitation in the form of two different basic aluminium sulfates in which the Al_{13} structure is retained and are linked by H-bonding to the O-atoms of the SO_4-groups. The formation of this polymer has been extensively studied by ^{27}Al NMR (e.g. references in [1–3, 8]).

Kloprogge *et al.* [9, 10] described the precipitation of monoclinic basic aluminium sulphate $Na_{0.1}[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_{3.55}.9H_2O$. ^{27}Al Solid-state Magic-Angle Spinning Nuclear Magnetic Resonance spectroscopy showed that the tridecameric was preserved in the crystal structure. Kloprogge *et al.* [10] and Teagarden *et al.* [11] reported the infrared spectrum of Al_{13}-sulfate with typical adsorption bands of OH at 3440, 1085, and 980 cm^{-1}, H_2O at 3247 and 1640 cm^{-1}, and $SO_4{}^{2-}$ at 1135, 980, 715, 610, and 566 cm^{-1}. In addition, recently Kloprogge and Frost [12] have reported the Raman spectrum of the Al_{13}-nitrate. They observed two ν_1 symmetric NO_3^- stretching bands at 1048 and 1050 cm^{-1}, two ν_3 antisymmetric stretching bands at 1343 and 1358 cm^{-1}. Furthermore two bands at 712 and 714 cm^{-1} were ascribed to the ν_4 NO_3^- mode. Two small bands at 1027 and 1029 cm^{-1} were ascribed to nitrato bands formed after partial exchange of a minor amount of H_2O or OH-groups from the Al_{13} octahedra.

The Raman spectra of basic aluminium sulfate [13, 14] are dominated by two broad bands, which have been assigned to the ν_1 and ν_3 sulfate modes around 981 and 1051 cm^{-1}. In addition, the band around 724 cm^{-1} has been assigned to an Al-O mode of the polymerised Al-O-Al bonds in the Al_{13} structure. A sharp band at 1066 cm^{-1} and a minor band at 1384 cm^{-1} were assigned to minor NO_3^- impurities in the Al_{13}-sulfate crystals. These NO_3^- groups were thought to be on different positions than the nitrate groups in Al_{13}-nitrate based on the differences in the band positions.

The near-infrared (NIR) spectral region has been defined by Kaye [15, 16] to extend from 700 to 3500 nm (14285 to 2860 cm^{-1}). The only fundamental vibrations in the NIR region between 4000 and 10000 cm^{-1} are those associated with hydrogen atoms associated with hydroxyl groups or water in the case of minerals and inorganic compounds like aluminium sulfates. Rossman [17] reported average band positions for hydroxyl and

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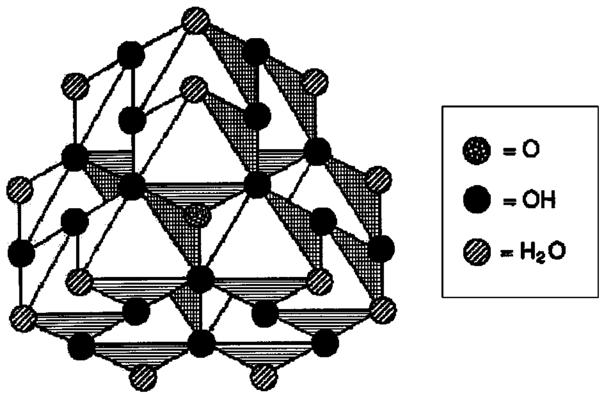

Figure 1 Model of the Al_{13} Keggin structure.

water in the NIR region around 4200 cm^{-1} as being due to M-OH motions, 5200 cm^{-1} as the H_2O combination mode (bend + stretch) and around 7100 cm^{-1} as the first OH stretch overtone. This means that NIR spectroscopy is a very suitable technique to study compounds as the Al_{13} salts, which contains both water and OH groups in the Al_{13} Keggin structure combined with additional crystal water in the structure, and obtain more information about the local environments involved.

This paper forms a continuation of our study of the vibrational spectroscopy of basic aluminium sulfate and nitrate. To date the near-infrared spectra of basic aluminium salts have not been studied or published. Therefore, the objective of this paper is to extensively report the near-infrared (NIR) spectra obtained at 298 K of basic aluminium sulfate and to compare them to basic aluminium nitrate and hydrated aluminium sulfate, $Al_2(SO_4)_3.16H_2O$.

2. Experimental

2.1. Basic aluminium sulfate and nitrate

The synthesis and characterisation of the monoclinic basic aluminium sulfate used in this study has been extensively described by Kloprogge *et al.* [2, 8, 9, 18, 19]. The tridecameric aluminium polymer was obtained by forced hydrolysis of a 0.5 M aluminium nitrate solution with a 0.5 M sodium hydroxide solution until an OH/Al molar ratio of 2.2 was reached. Next, the basic aluminium sulfate was precipitated by the addition of the appropriate amount of 0.5 M sodium sulfate and aged for 42 days before removal from the solution. Crystals collected from the wall of the container were shown to be phase pure by X-ray diffraction, ^{27}Al solid state nuclear magnetic resonance spectroscopy and chemical analysis. The basic aluminium nitrate was prepared from the same hydrolysed aluminium solution followed by very slow evaporation of the excess water at room temperature.

2.2. Infrared and near-infrared spectroscopy (NIR)

The samples were dried to remove any adsorbed water and stored in a desiccator before measurement in the FT-IR spectrometer. The sample (1 mg) was finely ground for one minute, combined with oven dried spectroscopic grade KBr having a refractive index of 1.559 and a particle size of 5–20 mm (250 mg) and pressed into a disc using 8 tonnes of pressure for five minutes under vacuum. The spectrum of each sample was recorded in triplicate by accumulating 64 scans at 4 cm^{-1} resolution between 400 cm^{-1} and 4000 cm^{-1} using the Perkin-Elmer 1600 series Fourier transform infrared spectrometer equipped with a LITA detector.

The NIR spectroscopy analyses were performed on a Perkin Elmer System 2000 NIR-FT Raman spectrometer equipped with a Spectron Laser Systems SL301 Nd : YAG laser operating a wavelength of 1064 nm. For the samples 32 scans were accumulated at a spectral resolution of 16 cm^{-1} using a mirror velocity of 0.2 cm^{-1}/s to get an acceptable signal/noise ratio.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

3. Results and discussion

Fig. 2 depicts the IR spectra of the Al_{13}-sulfate and nitrate samples used in this NIR study in comparison to

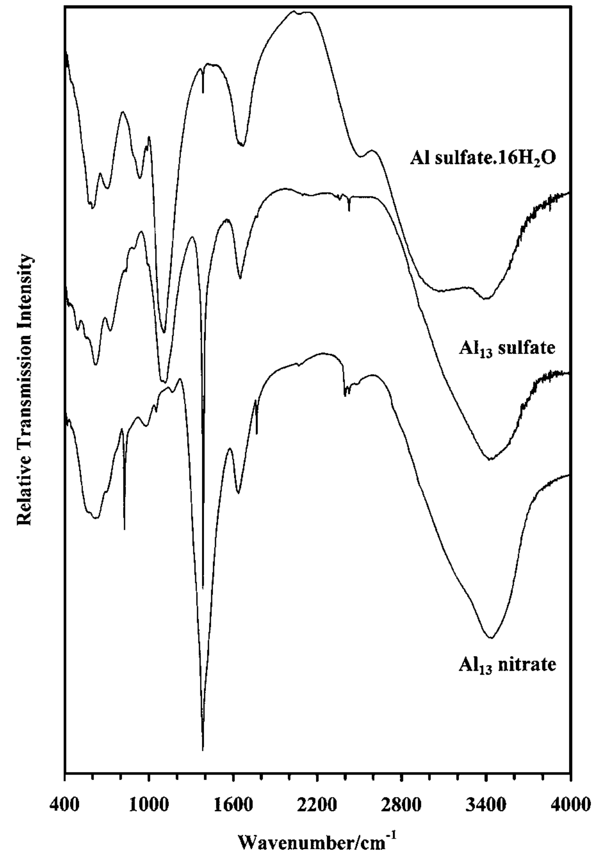

Figure 2 Infrared spectra of hydrated aluminium sulfate and Al_{13}-sulfate and nitrate in the region 400–4000 cm^{-1}.

TABLE I Band component analysis of the infrared spectra of aluminium sulfate, Al_{13} sulfate and Al_{13} nitrate in the region between 400 and 4000 cm^{-1}

$Al_2(SO_4)_3.16H_2O$ (cm^{-1})	Al_{13} sulfate (cm^{-1})	Al_{13} nitrate (cm^{-1})	Assignment
3400	3434	3433	OH-stretch (1)
3063	3068	3192	H_2O OH-stretch (2)
2512			Combination band
		1764	NO_3 combination band ($\nu_1 + \nu_4$)
1679	1688	1670	H_2O bend (1)
1623	1639	1629	H_2O bend (2)
	1384	1387	ν_3 NO_3
		1163	Al-OH_2 bend (1)
1097	1113		ν_3 SO_4
	1089		ν_3 SO_4/Al-OH_2 bend (2)
		1050	ν_1 NO_3
987	990 shoulder		ν_1 SO_4/Al-OH_2 bend (3)
934		981	Al-OH_2 bend (4)
892 shoulder	895		
	838	823	ν_2 NO_3
		776	ν_4 NO_3
704	723	702	Al-O antisymmetric stretch
		620	
597	620		ν_4 SO_4
576	552		ν_4 SO_4
		561	
	491		

normal hydrated aluminium sulfate. The assignment of the bands is reported in Table I. Both the Al_{13}-sulfate and nitrate are characterised by two OH-stretching modes around 3430–3435 cm^{-1} and 3065–3200 cm^{-1}. Associated OH-deformation bands are observed around 1089 cm^{-1} and 1163 cm^{-1} for the Al_{13}- sulfate and nitrate, respectively. In the case of Al_{13}-sulfate the 1089 cm^{-1} band is probably overlapping with the ν_3 mode of the sulfate group. In addition a band around 990 cm^{-1} and 981 cm^{-1} may also represent OH-deformation modes, although in the case of Al_{13}-sulfate this band is more likely to be a complex of the ν_1 of the sulfate group and the OH-deformation vibration.

Band component analysis of the asymmetric band around 1635 cm^{-1} indicate the presence of two different water bending modes around 1630–1640 cm^{-1} and 1670–1690 cm^{-1}, respectively, with intensity ratios of approximately 45 and 55 % for both the Al_{13}-sulfate and nitrate (Fig. 3). This shows the similarity in the crystal structures of both Al_{13}-salts. Based on the chemical analysis of the Al_{13}-sulfate [9, 10], where 12 H_2O molecules are associated with the Keggin structure and 9 H_2O molecules are present as crystal water, one would expect a ratio of approximately 57 and 43 % which is very close to the observed intensities. This means that the band around 1630–1640 cm^{-1} is associated with the crystal water and the higher wavenumber band with the water in the Keggin structure.

Characteristic sulfate bands are ν_1 around 990 cm^{-1}, ν_3 around 1113 and 1089 cm^{-1} and ν4 around 620 and 552 cm^{-1}. These vibrations agree well with earlier results reported by Kloprogge *et al.* [10] and Teagarden *et al.* [11], who observed typical adsorption bands of

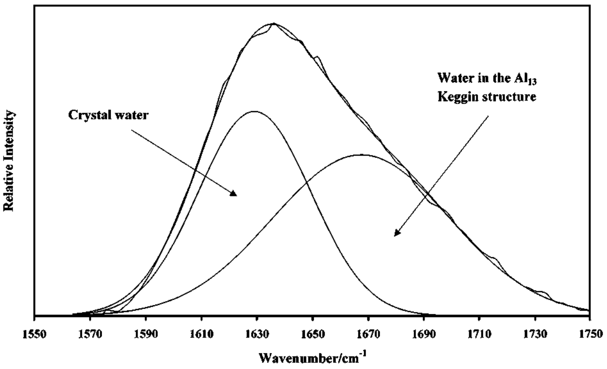

Figure 3 Band component analysis of the water-bending region of Al_{13}-sulfate.

OH at 3440, 1085, and 980 cm^{-1}, H_2O at 3247 and 1640 cm^{-1}, and sulfate (SO_4) at 1135, 980, 610, and 566 cm^{-1} for Al_{13} sulfate. The nitrate group in the Al_{13}-nitrate is represented by ν_1 around 1050 cm^{-1}, ν_2 around 823 cm^{-1}, ν_3 around 1387 cm^{-1} and ν_4 around 776 cm^{-1}. Although the IR spectrum of Al_{13}-nitrate has not been published before, these vibrations agree well with vibrations observed in the Raman spectrum [12].

Fig. 4 shows the NIR spectra in the region between 4000 and 8000 cm^{-1} of the aluminium sulfate and the Al_{13}-sulfate and nitrate. All three depict multiple overlapping bands in this region requiring band component

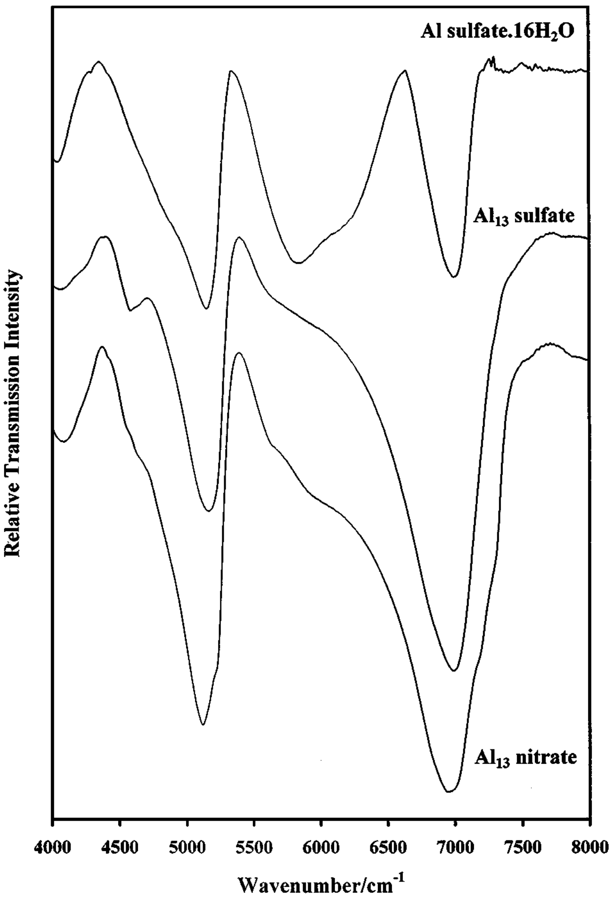

Figure 4 Near-infrared transmission spectra (true intensities) of hydrated aluminium sulfate and Al_{13}-sulfate and nitrate in the region 4000–8000 cm^{-1}.

TABLE II Band component analysis of the NIR spectra of aluminium sulfate, Al_{13} sulfate and Al_{13} nitrate in the region 4300–7600 cm^{-1}

$Al_2(SO_4)_3.16H_2O$/ cm^{-1}	Calculated/ cm^{-1}	Al_{13} sulfate/ cm^{-1}	Calculated/ cm^{-1}	Al_{13} nitrate/ cm^{-1}	Calculated/ cm^{-1}	Assignment
7038	6800	7018	6868	6996	6866	Overtone OH-stretch (1) (2x) Al-OH
6891	6463	6777	6502	6543	6625	Combination OH-stretch (1 + 2) Al-OH + crystal H_2O
6219	6126	6213	6136	5925	6384	Overtone OH-stretch (2) (2x) crystal H_2O
5795	5604	5703	5940	5624	5886	Overtone Al-OH(3/4) (6x)
5229	5079	5236	5122	5238	5103	H_2O combination (bend 1 + stretch 1) Al_{13}
5163	5023	5158	5073	5153	5062	H_2O combination (bend 2 + stretch 1) crystal H_2O + Al_{13}
5070	5037	5047	5064	5040	5010	Overtone H_2O bend (1) (3x) Al13
4907	4869	4874	4917	4848	4887	Overtone H_2O bend (2) (3x) crystal H_2O
4707	4742	4641	4752	4631	4862	Combination H_2O (bend 1 + stretch 2) Al_{13} + crystal H_2O
4563	4686	4553	4703	4532	4821	Combination H_2O (bend 2 + stretch 2) crystal H_2O

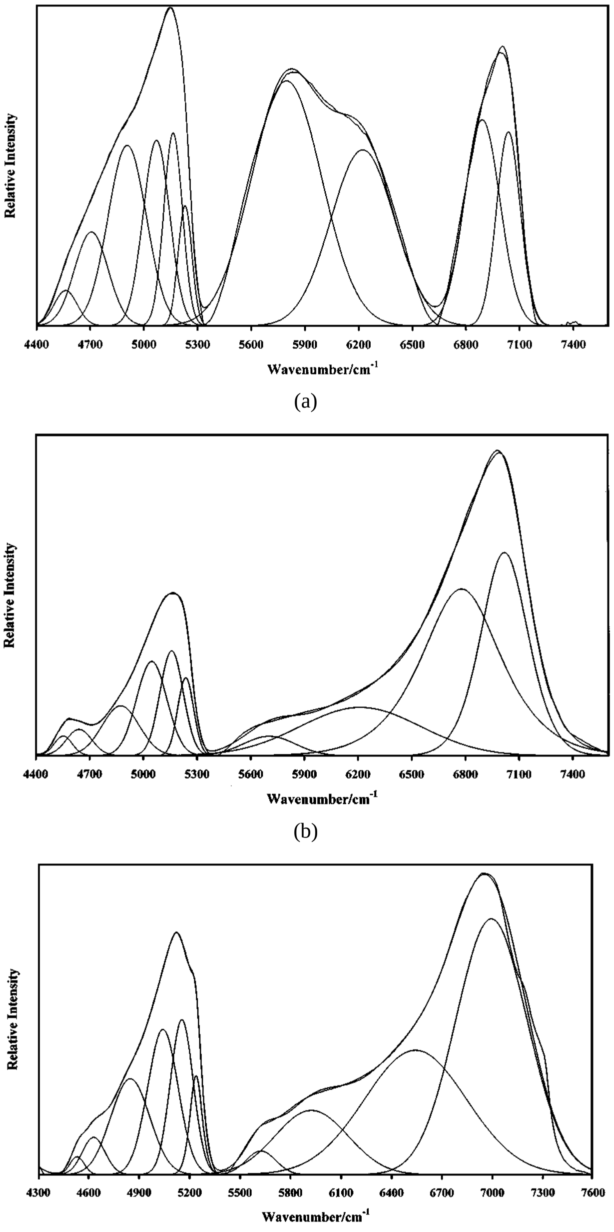

Figure 5 Band component analysis of the near-infrared transmission spectra between 4400 and 7600 cm^{-1} of hydrated aluminium sulfate (a), Al_{13}-sulfate (b) and Al_{13}-nitrate (c).

analysis to distinguish various bands (Fig. 5). Table II reports the observed bands and calculated bands based on information from the infrared spectra presented in Table I. The hydrated aluminium sulfate is characterised by basically three broad bands each containing two or more overlapping modes. Band component analysis indicates that the band around 6900 cm^{-1} consists of the first overtone of the OH-stretch (1) plus the combination band of OH-stretch (1) and (2). The first overtone of OH-stretch (2) is observed as a relatively broad band around 6219 cm^{-1}. The broad band around 5795 cm^{-1} can be assigned to the third overtone of Al-OH_2 (3). In roughly the 4500–5500 cm^{-1} region six bands are observed related to the second overtones of the bending modes and combination bands of the bending and stretching modes of the crystal water. All observed bands are located about 100 cm^{-1} higher than expected from the theoretical calculations. That fact that there are two water modes recognisable in the normal infrared, which is reflected in the NIR spectra, indicate that hydrated aluminium sulfate contains two clearly different sites for its crystal water.

The two spectra of the Al_{13}-sulfate and nitrate are very similar although minor differences can be observed in the intensities. In comparison to the normal hydrated aluminium sulfate the strong double band around 6000 cm^{-1} is much weaker and broader for both the Al_{13}-salts. Also the complex band with a maximum around 5200 cm^{-1} is relatively weaker than for the normal sulfate salt. A clear second band can be recognised around 4600 cm^{-1} for the Al_{13}-sulfate, which is present as a shoulder in the Al_{13}-nitrate spectrum. The assignment of various bands based on band component analysis and the theoretically calculated band positions of various overtone and combination bands are all in reasonable agreement as shown in Table II. Based on this assignment the bands around 6213 and 4874 and 4553 cm^{-1} are purely related to crystal water outside the Al_{13} Keggin structure in the sulfate. Similar bands are observed for the Al_{13}-nitrate around 5925, 4848 and 4532 cm^{-1} revealing a slight shift towards lower wavenumbers due to the stronger influence of the nitrate compared to the sulfate. Al_{13} related water bands are found around 5079 and 5037 cm^{-1} for the sulfate and around 5238 and 5040 cm^{-1} for the nitrate. This reversed shift compared to the crystal water bands indicate that the crystal water molecules are relative strongly influencing the nitrate groups thereby weakening the bonding of the nitrate to the Al_{13} Keggin structure. This effect is much smaller for the sulfate as the crystal water molecules are less strongly bonded to the sulfate groups. The two high wavenumber bands are associated with OH-stretching modes of either only the Al-OH of the Al_{13} Keggin structure around approximately 7000 cm^{-1} and with a combination of the Al-OH of the Al_{13} with the OH-stretch of the crystal water around approximately 6550–6700 cm^{-1}. The overtone Al-OH does not differ significantly for the sulfate and nitrate as these hydroxyl groups in the Keggin structure are relatively shielded from the salt groups by the outer water molecules. The effect of the nitrate and sulfate however does reflect in the OH-stretch combination band where a difference of more than 200 cm^{-1} can be observed.

4. Conclusions

Near-infrared spectroscopy forms a strong tool in addition to the conventional infrared and Raman spectroscopy to get a better understanding of the structure of Al_{13}-salts and especially of the hydroxyl groups and various water molecules in the Al_{13} Keggin structure and in the structure outside the Al_{13} complex. Although the near-infrared spectra of the Al_{13}-sulfate and nitrate are very similar indicating similar crystal structure, there are minor differences related to the strength with which the crystal water molecules are bonded to the salt groups. The interaction between the crystal water molecules and nitrate are stronger than with the sulfate. This is reflected in a shift towards lower wavenumbers of the bands associated with the crystal water. On the other hand, this stronger interaction with the nitrate results in a weaker interaction with the water molecules in the Al_{13} complex compared to the Al_{13}-sulfate. The hydroxyl groups in the Al_{13} complex are relatively shielded by the water molecules and therefore do not reflect the influence of the nitrate or sulfate in their band positions.

Acknowledgments

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