INFRARED SPECTROSCOPIC STUDY OF TUTTON COMPOUNDS
II. VIBRATIONAL BEHAVIOUR OF NH$_4^+$ IONS INCLUDED IN K$_2$Me""(XO$_4$)$_2$:6H$_2$O (Me"" = Mg, Co, Ni, Cu, Zn; X = S, Se)

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ABSTRACT

Infrared spectra of Tutton compounds Me$_2$Me""(XO$_4$)$_2$:6H$_2$O (Me"" = K, NH$_4$; Me"" = Mg, Co, Ni, Cu, Zn; X = S, Se) as well as those of NH$_4^+$ ions included in the potassium matrices are presented and discussed in the region of the bending modes $v_4$ of the ammonium ions and water librations. The infrared spectroscopic experiments show that the ammonium ions incorporated in the potassium sulfates exhibit three bands corresponding to $v_4$ in good agreement with the low site symmetry C$_{2v}$ of the host potassium ions. However, when NH$_4^+$ ions replace K$^+$ ions in the respective selenate matrices four bands corresponding to the bending modes $v_4$ of the ammonium ions are observed in the spectra of the mixed crystals K$_{1.5}$(NH$_4$)$_1$Me""(SeO$_4$)$_2$:6H$_2$O (with exception of the magnesium compound) owing to the formation of polyfuranate hydrogen bonds between the ammonium cations and selenate anions due to the stronger proton acceptor capability of the selenate ions than that of the sulfate ones, thus leading to increasing of the coordination number of the ammonium ions. It has been established that the strength of the hydrogen bonds formed by the water molecules in the mixed crystals K$_{1.5}$(NH$_4$)$_1$Me""(SeO$_4$)$_2$:6H$_2$O decreases as compared to that of the hydrogen bonds in the respective neat potassium compounds due to the anti-cooperative effect, i.e. the proton acceptors in the mixed crystals are involved in hydrogen bonds with ammonium ions additionally to those with water molecules.

Keywords: Tutton compounds, crystal matrix-infrared spectroscopy, matrix-isolated NH$_4^+$ ions, hydrogen bond strength.

INTRODUCTION

The present paper continues our infrared spectroscopic studies on the Tutton salts Me$_2$Me""(XO$_4$)$_2$:6H$_2$O (Me"" = K, NH$_4$; Me"" = Mg, Mn, Co, Ni, Cu, Zn; X = S, Se) containing included NH$_4^+$ and SO$_4^{2-}$ ions. In the first part of these investigations the vibrational behavior of SO$_4^{2-}$ ions included in ammonium and potassium selenates are reported [1]. The infrared spectra of NH$_4^+$ and SO$_4^{2-}$ ions included in the structures of copper and magnesium Tutton salts are discussed in [2, 3]. Our interest in the Tutton salts is determined by the expectation that these compounds can be considered as potential proton conductors. Furthermore, it is well known that the inclusion of a small amount of NH$_4^+$ ions in the potassium selenates and phosphates leads to increasing of their proton conductivity. In this paper we report infrared spectra of NH$_4^+$ cations included in the structures of the respective potassium sulfates and selenates in the region of $v_4$ of the ammonium ions and water librations. The spectral regions of $v_3$, $v_1$, and $v_2$ of the NH$_4^+$ guest ions could not be analyzed precisely due to the overlapping of these motions with motions of other entities in the structures (normal modes of water molecules).
The crystal structures of Tutton compounds (they crystallize in the monoclinic space group $P2_1/a (C_{2v})$ with two formula units in the unit-cell) are built up from isolated octahedra, $[\text{Me}^+(\text{H}_2\text{O})_6]$ (three crystallographically different water molecules are coordinated to the $\text{Me}^+$ cations) and tetrahedra $\text{XO}_4^-$. The polyhedra are linked by hydrogen bonds and $\text{Me}^+$ cations. All atoms and polyatomic units, except the divalent metal ions $\text{Me}^+$, which lies at the centre of inversion $C_1$, are located at general positions $C_i$ [4-20]. Numerous papers are devoted to vibrational spectra (infrared and Raman) of Tutton salts (see, for example, Refs. [21-24] and Refs. therein).

**EXPERIMENTAL.**

The simple metal selenates, $\text{K}_2\text{SeO}_4$, $(\text{NH}_4)_2\text{SeO}_4$ and $\text{Me}''\text{SeO}_4\cdot 3\text{H}_2\text{O}$ ($\text{Me}'' = \text{Mg, Co, Ni, Cu, Zn}$) were prepared according to the crystallization procedure described in [1-3]. Commercial sulfates were used. The reagents used were 'p.a.' (Merck). The Tutton salts were obtained by crystallization from the saturated solutions of the respective simple sulfates and selenates. The samples containing included $\text{NH}_4^+$ ions were prepared using the same crystallization procedure in the presence of the guest ions. The infrared spectra were recorded on a Bruker model IFS 25 Fourier transform interferometers (resolution $< 2$ cm$^{-1}$) at ambient temperature using KBr discs as matrices. Ion exchange or other reactions with KBr have not been observed (infrared spectra using Nujol mulls were also measured).

**RESULTS AND DISCUSSION.**

The free tetrahedral $\text{NH}_4^+$ ions under perfect $T_d$ symmetry exhibit four internal vibrations: $v_1(A_g)$, the symmetric N-H stretching modes, $v_3(E)$, the symmetric NH$_4$ bending modes, $v_4(F_g)$ and $v_5(F_g)$, the asymmetric N-H stretching and NH$_4$ bending modes, respectively. The normal vibrations of the free ammonium ions in aqueous solutions are reported to appear at: $v_1 = 3040$ cm$^{-1}$, $v_2 = 1680$ cm$^{-1}$, $v_3 = 3145$ cm$^{-1}$ and $v_4 = 1400$ cm$^{-1}$ [25]. On going into solid state the normal modes are expected to shift to higher or lower frequencies due to different intra- and intermolecular interactions.

Due to the low site-symmetry $C_1$ of the tetrahedral $\text{NH}_4^+$ ions the degeneracy of both the doubly degenerate $v_2$ modes and the triply degenerate $v_3$ and $v_4$ modes is lifted, thus resulting in the appearance of two bands for $v_2 (2A)$ and three bands for $v_3$ and $v_4 (3A)$, respectively. The $v_1$ mode is activated. The factor-group analysis ($C_{2v}$ factor-group symmetry) predicts a splitting of each species of A symmetry into four components $-A_u + A_g + B_u + B_g$ (related to interactions of identical oscillators, correlation field effects). The species $A_u$ and $B_u$ are infrared active, while $A_g$ and $B_g$ are Raman active (mutual exclusion principle). Consequently, 18 infrared bands $(9A_u + 9B_u)$ and 18 Raman bands $(9A_g + 9B_g)$ will correspond to the normal motions of the ammonium ions. The correlation diagram between the $T_d$ point group, site-symmetry of the $\text{NH}_4^+$ ions and factor-group symmetry is shown in Fig. 1.

Infrared spectra of the neat Tutton compounds as well as those of mixed crystals containing included $\text{NH}_4^+$ guest ions are presented in Figs. 2-5. The analysis of the infrared spectra reveals that three bands corresponding to $v_4$ of the ammonium ions included in sulfate matrices are observed in the spectra in agreement with the low site-symmetry $C_1$ of the host potassium ions (Fig. 2). The increase in the concentrations of the $\text{NH}_4^+$ ions changes the spectra shape of the ammonium ions in the case of magnesium, cobalt and copper sulfate matrices – the lowest frequency bands at around 1400 cm$^{-1}$ increase in intensity with the increasing ammonium ion concentrations. However, Fig. 4 shows that the inclusion of ammonium ions in selenate matrices (with exception of the magnesium compound) leads to the appearance of four bands in the region of $v_4$. One possible explanation of these spectroscopic findings is the pseudo-alkali character of the ammonium ions.
sometimes with some kind of disorder of the \( \text{NH}_4^+ \) ions. This phenomenon is observed in some ammonium salts when the coordination number of the ammonium group is higher than 5 as a result of the formation of di- or trifurcate hydrogen bonds [26, 27]. Thus, the appearance of four bands corresponding to bending modes of \( \text{NH}_3 \text{D}^+ \) ions instead of three expected in struvite type compounds is commented in terms of disorder of the ammonium ions [28-30]. In our opinion the observed difference in the vibrational behavior of the \( \text{NH}_4^+ \) guest ions in both potassium matrices (selenates and sulfates) is due to the different proton acceptor capability of the \( \text{SO}_4^{2-} \) and \( \text{SeO}_4^{2-} \) ions. The latter ions are known to exhibit a stronger proton acceptor ability [31, 32]. This fact will facilitate the formation of polyfurcate hydrogen bonds in the selenate matrices, thus leading to an increase in the coordination number of the ammonium ions, i.e. to a disorder of the guest ions.

Interesting spectroscopic findings are revealed when the spectra of the neat potassium sulfates and selenates and those the mixed crystals containing isomorphously included ammonium ions are compared in the region below 800 cm\(^{-1}\) where water librations occur (Figs. 4 and 5). Two types of water librations for the sulfates are discussed briefly in the literature – rocking and wagging, the former observed at higher frequencies. Each type is characterized with two broad bands. The water molecules bonded to the \( \text{Me}^{2+} \) ions via shorter \( \text{Me}^{2+} - \text{OH}_2 \) bonds display water librations at higher frequencies as compared to those forming longer \( \text{Me}^{2+} - \text{OH}_2 \) bonds (equatorial water molecules). The former \( \text{Me}^{2+} - \text{OH}_2 \) bonds are much more polarized due to the stronger synergetic effect of the \( \text{Me}^{2+} \) ions (stronger metal water interactions). The mean values of the wavenumbers for the rocking librations are 855 and 740 cm\(^{-1}\), and 770 and 680 cm\(^{-1}\) in the potassium and ammonium sulfates, respectively. The respective wagging modes appear at 570 and 441 cm\(^{-1}\) in the potassium compounds and at 544 and 425 cm\(^{-1}\) in the ammonium ones [22].

Water molecules involved in stronger hydrogen bonds are reported to exhibit water librations at larger wavenumbers [28 and Refs. therein]. Thus, the commented above mean wavenumbers for the water vibrations indicate that stronger hydrogen bonds are formed in the neat potassium compounds as compared to the ammonium
ones. The $XO_4^{2-}$ ions in the ammonium salts are expected to act as weaker proton acceptors than in the respective potassium ones, since these ions are involved in hydrogen bonds with both the $NH_4^+$ ions and the water molecules (anti-cooperative effect or proton acceptor competitive effect) [32 and Refs. therein].

When the spectra of the neat potassium compounds and those of the mixed crystals $K_{1-x}(NH_4)_{x}Me^{+}(XO_4)_{2}\cdot6H_2O$ are compared, it is readily seen that the bands corresponding to water librations in the mixed crystals broaden and shift to lower frequencies, thus indicating that weaker hydrogen bonds are formed in the mixed crystals. These spectroscopic findings are owing to the decrease in the proton acceptor capacity of the $SO_4^{2-}$ and $SeO_4^{2-}$ ions due to the formation of hydrogen bonds between the anions and the ammonium cations. The analysis of the spectra in the case of sulfate matrices (see Fig. 4) reveals that the bands corresponding to water librations are slightly shifted to lower frequencies in $K_{1-x}(NH_4)_{x}Me^{+}(SO_4)_{2}\cdot6H_2O$ ($Me^{+} = Co, Ni, Cu, Zn$) (band shifts 5-13 cm$^{-1}$), while those in $K_{1-x}(NH_4)_{x}Mg(SO_4)_{2}\cdot6H_2O$ are considerably shifted to smaller wavenumbers (band shifts 21-22 cm$^{-1}$).

In the case of selenate matrices the band shifts vary in wider intervals - 2-24 cm$^{-1}$ for the cobalt, nickel, copper and zinc compounds and 9-30 cm$^{-1}$ for the magnesium compound. These band shifts are calculated for both the rocking modes in the regions of 751-782 cm$^{-1}$ and 713-757 cm$^{-1}$, and the wagging modes in the region of 590-574 cm$^{-1}$ and 523-578 cm$^{-1}$ (neat potassium sulfates and selenate, respectively). We believe that these differences in the vibrational behaviour of the water librations are due to the remarkably different synergetic effect of $Me^{n+}$ ($Me^{n+} = Co, Ni, Cu, Zn$) and Mg$^{2+}$ ions. The $Me^{n+}$ ions form strong covalent bonds $Me^{n+} \cdot \cdot OH_2$, while the magnesium ions form weaker bonds of electrostatic character Mg$\cdot\cdot OH_2$, i.e. the $Me^{n+}$ ions polarize the bonds O$\cdot\cdot$H much stronger than the magnesium ions. Thus, one can consider that the strength of the hydrogen bonds in the cobalt, nickel, copper and zinc compounds depends predominantly on the synergetic effect of the $Me^{n+}$ ions, i.e. the proton acceptor strengths of the sulfate and selenate ions play smaller role. The opposite is probably true for the magnesium

Fig. 3. Infrared spectra of the neat Tutton compounds and mixed crystals $K_{2a}(NH_4)_{x}Me^{n+}(SeO_4)_{2}\cdot6H_2O$ ($Me^{n+} = Mg, Co, Ni, Cu, Zn$) in the region of $v_o$ of ammonium ions.
Fig. 4. Infrared spectra of the neat Tutton compounds and mixed crystals $K_{\frac{x}{2}}(NH_4)_{\frac{x}{2}}Me''(SO_4)_{2} \cdot 6H_2O$ ($Me'' = Mg, Co, Ni, Cu, Zn$) in the region of water librations.

Fig. 5. Infrared spectra of the neat Tutton compounds and mixed crystals $K_{\frac{x}{2}}(NH_4)_{\frac{x}{2}}Me''(SeO_4)_{2} \cdot 6H_2O$ ($Me'' = Mg, Co, Ni, Cu, Zn$) in the region of water librations.
ions - the strength of the hydrogen bonds in the magnesium matrices is governed by the proton acceptor ability of the proton acceptors. Furthermore, when the band shifts in the selenate and sulfate matrices are compared, it is seen that these shifts are generally larger in the spectra of the former compounds than those in the spectra of the respective sulfates due to the stronger proton acceptor ability of the selenate ions.

CONCLUSIONS

The spectroscopic experiments reveal: (i) The ammonium ions included in the potassium sulfates exhibit three bands corresponding to νd in good agreement with the low site symmetry C1 of the host potassium ions. (ii) The ammonium guest ions included in the potassium selenates exhibit four bands corresponding to νd due probably to some kind of disorder of the guest ions (with exception of the magnesium selenate). (iii) The formation of hydrogen bonds between the NH4+ guest ions and the SO4 2- host ions leads to a decrease in the proton acceptor capabilities of the anions (anti-cooperative or proton acceptor competitive effect) and as a result the hydrogen bonds formed by the water molecules show a tendency to weaken on going from the neat potassium compounds to mixed crystals K13(NH4)10Me2(SO4)2·6H2O and K19(NH4)16Me2(SO4)2·6H2O (the bands corresponding to water librations broaden and shift slightly to lower frequencies). This effect is much more pronounced in the case of cations with a weaker synergetic effect (magnesium, cobalt and nickel).

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