Journal of the University of Chemical Technology and Metallurgy, 45, 2, 2010, 195-200

INFRARED SPECTROSCOPIC STUDY OF TUTTON COMPOUNDS
II. VIBRATIONAL BEHAVIOUR OF NH_4^+ IONS INCLUDED IN $K_2'Me''(XO_4)_2 \cdot 6H_2O$ (Me'' = Mg, Co, Ni, Cu, Zn; X = S, Se)

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Received 22 February 2010
Accepted 25 March 2010

ABSTRACT

Infrared spectra of Tutton compounds $Me_2'Me''(XO_4)_2 \cdot 6H_2O$ (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 ν_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 ν_4 in good agreement with the low site symmetry C_1 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 ν_4 of the ammonium ions are observed in the spectra of the mixed crystals $K_{2-x}(NH_4)_xMe''(SeO_4)_2 \cdot 6H_2O$ (with exception of the magnesium compound) owing to the formation of polyfurcate 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 $K_{1.8}(NH_4)_{0.2}Me''(XO_4)_2 \cdot 6H_2O$ 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 $Me_2'Me''(XO_4)_2 \cdot 6H_2O$ (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 ν_4 of the ammonium ions and water librations. The spectral regions of ν_3, ν_1 and ν_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 $P2_1/c\,(C_{2h}^5)$ with two formula units in the unit-cell) are built up from isolated octahedra, [*Me*”$(H_2O)_6$] (three crystallographically different water molecules are coordinated to the *Me*” cations) and tetrahedra XO_4. The polyhedra are linked by hydrogen bonds and *Me*’ cations. All atoms and polyatomic units, except the divalent metal ions *Me*”, which lies at the centre of inversion C_i, are located at general positions C_1 [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, K_2SeO_4, $(NH_4)_2SeO_4$ and *Me*”$SeO_4 \cdot nH_2O$ (*Me*” = 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 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 NH_4^+ ions under perfect T_d symmetry exhibit four internal vibrations: $\nu_1(A_1)$, the symmetric N-H stretching modes, $\nu_2(E)$, the symmetric NH_4 bending modes, $\nu_3(F_2)$ and $\nu_4(F_2)$, 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: ν_1 = 3040 cm^{-1}, ν_2 = 1680 cm^{-1}, ν_3 = 3145 cm^{-1} and ν_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 NH_4^+ ions the degeneracy of both the doubly degenerate ν_2 modes and the triply degenerate ν_3 and ν_4 modes is lifted, thus resulting in the appearance of two bands for ν_2 (2A) and three bands for ν_3 and ν_4 (3A), respectively. The ν_1 mode is activated. The factor-group analysis (C_{2h} 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 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 NH_4^+ guest ions are presented in Figs. 2-5. The analysis of the infrared spectra reveals that three bands corresponding to ν_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 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 ν_4. One possible explanation of these spectroscopic findings is the pseudo-alkali character of the ammonium ions,

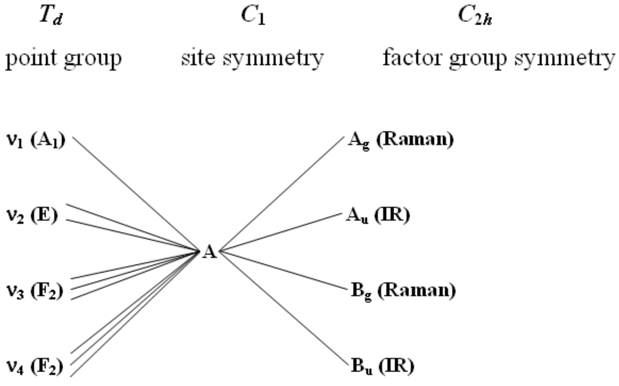

Fig. 1. Correlation diagram between T_d point symmetry, C_1 site-symmetry and C_{2h} factor-group symmetry (NH_4^+ ions in Tutton compounds).

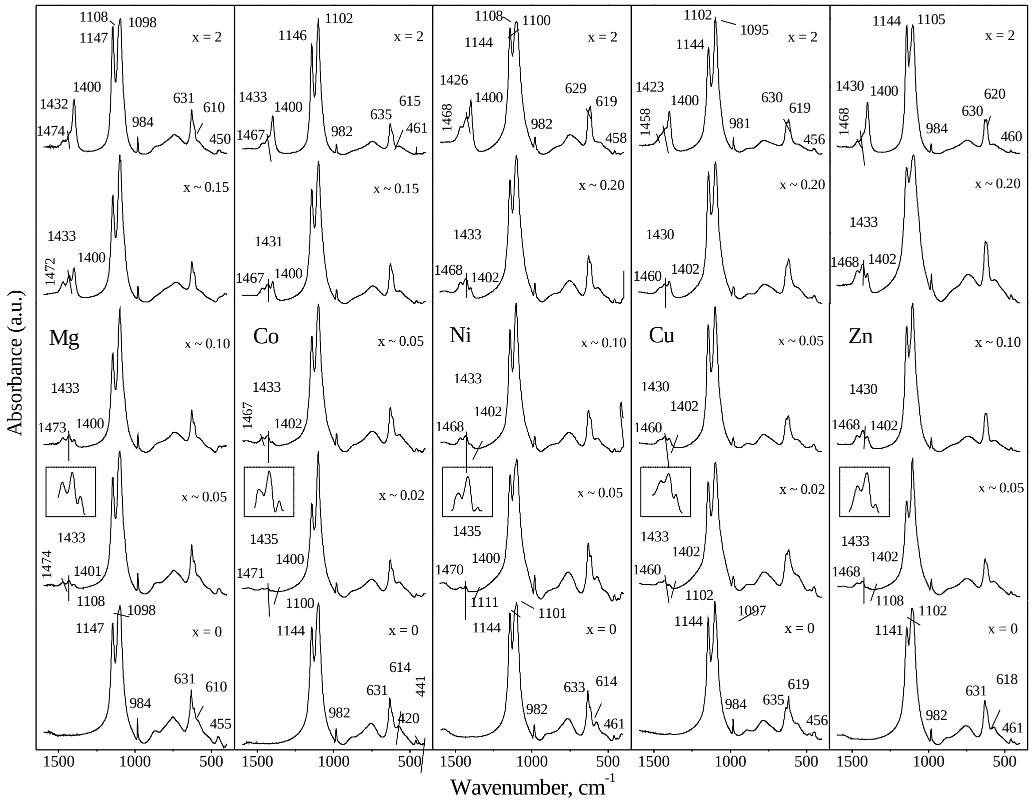

Fig. 2. Infrared spectra of the neat Tutton compouns and mixed crystals $K_{2-x}(NH_4)_xMe''(SO_4)_2\cdot 6H_2O$ (*Me*'' = Mg, Co, Ni, Cu, Zn) in the region of ν_4 of ammonium ions.

sometimes with some kind of disorder of the 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 NH_3D^+ 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 NH_4^+ guest ions in both potassium matrices (selenates and sulfates) is due to the different proton acceptor capability of the SO_4^{2-} and 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 *Me*'' ions via shorter *Me*'' – OH_2 bonds display water librations at higher frequencies as compared to those forming longer *Me*'' – OH_2 bonds (equatorial water molecules). The former *Me*'' – OH_2 bonds are much more polarized due to the stronger synergetic effect of the *Me*'' 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

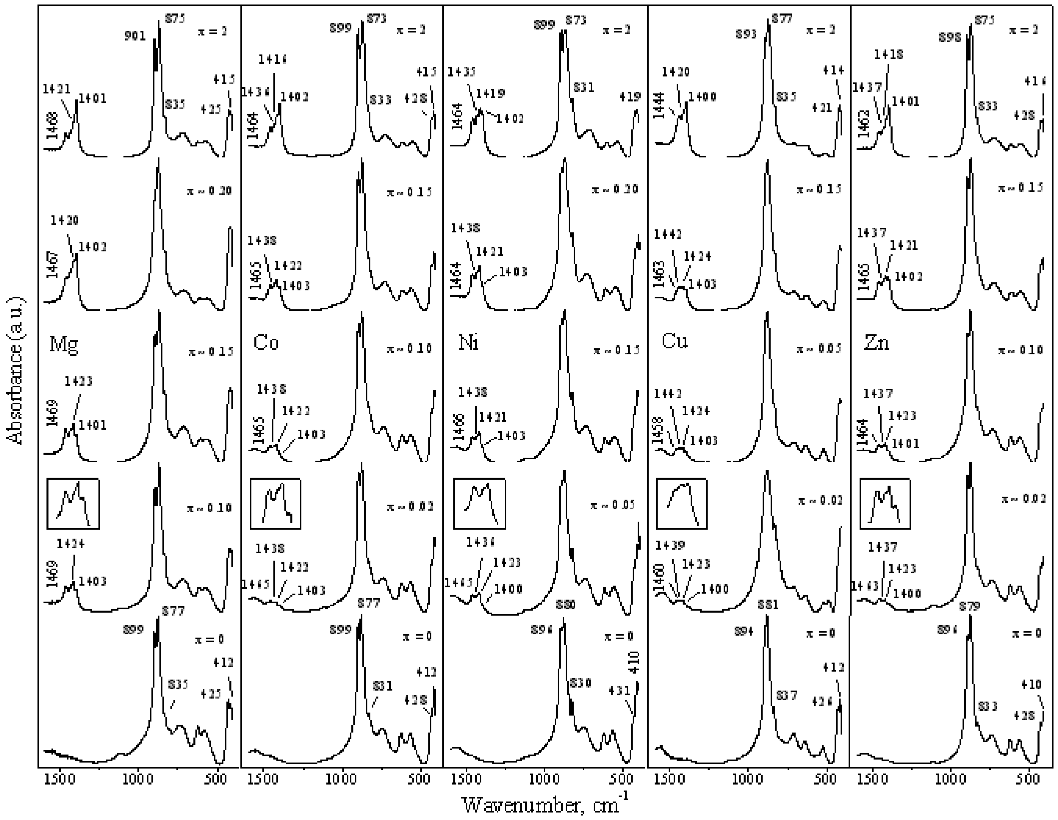

Fig. 3. Infrared spectra of the neat Tutton compouns and mixed crystals $K_{2-x}(NH_4)_xMe''(SeO_4)_2{\cdot}6H_2O$ (*Me*" = Mg, Co, Ni, Cu, Zn) in the region of ν_4 of ammonium ions.

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 $K_{1.8}(NH_4)_{0.2}Me''(XO_4)_2{\cdot}6H_2O$ 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 $K_{1.8}(NH_4)_{0.2}Me''(SO_4)_2{\cdot}6H_2O$ (*Me*" = Co, Ni, Cu, Zn) (band shifts 5-13 cm^{-1}), while those in $K_{1.8}(NH_4)_{0.2}Mg(SO_4)_2{\cdot}6H_2O$ 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*" (*Me*" = Co, Ni, Cu, Zn) and Mg^{2+} ions. The *Me*" ions form strong covalent bonds $Me''{-}OH_2$, while the magnesium ions form weaker bonds of electrostatic character $Mg{-}OH_2$, i.e. the *Me*" ions polarize the bonds O — 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*" ions, i.e. the proton acceptor strengths of the sulfate and selenate ions play smaller role. The opposite is probably true for the magnesium

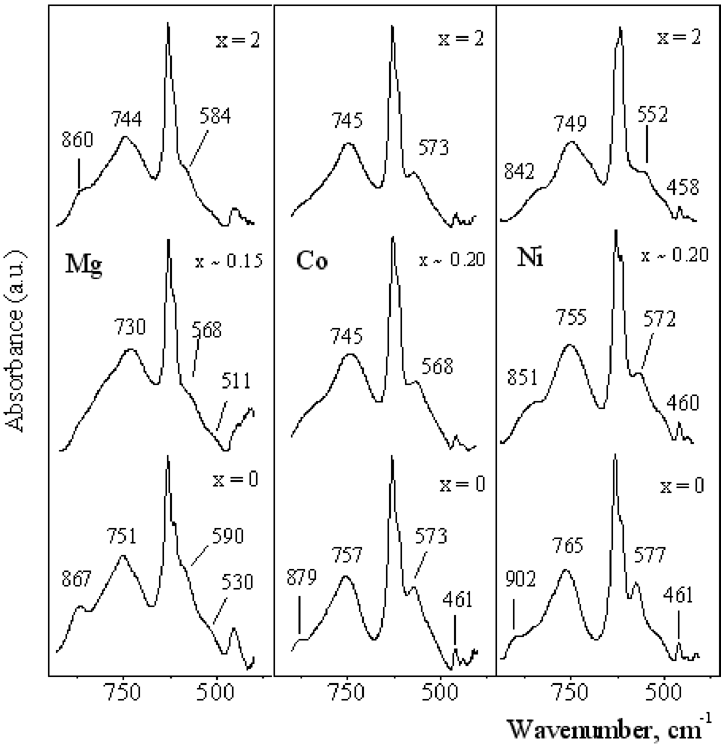

Fig. 4. Infrared spectra of the neat Tutton compouns and mixed crystals $K_{2-x}(NH_4)_xMe''(SO_4)_2 \cdot 6H_2O$ (*Me''* = Mg, Co, Ni, Cu, Zn) in the region of water librations.

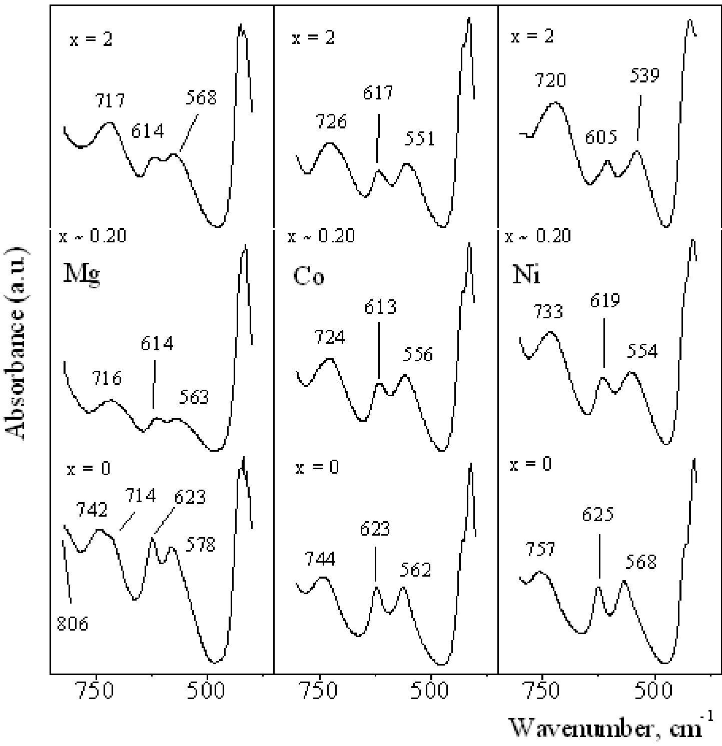

Fig. 5. Infrared spectra of the neat Tutton compouns and mixed crystals $K_{2-x}(NH_4)_xMe''(SeO_4)_2 \cdot 6H_2O$ (*Me''* = Mg, Co, Ni, Cu, Zn) in the region of water librations.

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 ν_4 in good agreement with the low site symmetry C_1 of the host potassium ions. (ii) The ammonium guest ions included in the potassium selenates exhibit four bands corresponding to ν_4 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 NH_4^+ guest ions and the XO_4^{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 $K_{1.8}(NH_4)_{0.2}$*Me*"$(SO_4)_2{\cdot}6H_2O$ and $K_{1.8}(NH_4)_{0.2}$*Me*"$(SeO_4)_2{\cdot}6H_2O$ (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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