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Lattice stability in A_2MCl_6 ionic crystals ($A \equiv C_5H_5NH$ or $CH_3C_5H_4NH$; $M \equiv Sn$ or Te)

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Abstract. DSC and NQR measurements were carried out for $(CH_3C_5H_4NH)_2SnCl_6$ and $(CH_3C_5H_4NH)_2TeCl_6$. No structural phase transition was observed above 85 K and 130 K up to the melting points for the Sn and Te compounds, respectively. Many $A_2^I MCl_6$ ionic crystals, where $[MCl_6]^{2-}$ is an octahedral anion such as $[SnCl_6]^{2-}$ or $[TeCl_6]^{2-}$, exhibit structural phase transitions accompanied by rotations of the MCl_6 octahedra. However, $(C_5H_5NH)_2SnCl_6$ and $(C_5H_5NH)_2TeCl_6$ have been reported not to show such a displacive phase transition between 77 K and the decomposition temperature, although they undergo phase transitions driven by ordering of the pyridinium cations $C_5H_5NH^+$. The stable lattices in these four compounds are discussed and explained qualitatively in terms of N-H...Cl hydrogen-bonding networks and a large primitive-cell volume.

1. Introduction

Many A_2MCl_6 ionic crystals, where A is a monovalent cation and $[MCl_6]^{2-}$ is an octahedral ion such as $[SnCl_6]^{2-}$ or $[TeCl_6]^{2-}$, undergo structural phase transitions that are accompanied by rotations of the MCl_6 octahedra and are driven by soft rotatory lattice modes consisting of correlated rigid-body rotations of the octahedra themselves [1-3]. However, $(C_5H_5NH)_2SnCl_6$ (pyHSn) and $(C_5H_5NH)_2TeCl_6$ (pyHTe) do not show the displacive phase transition, although they undergo second-order phase transitions driven by orientational ordering of the pyridinium ions $C_5H_5NH^+$ [4, 5], which have a planar ring structure very similar to benzene, as shown in figure 1(a). The two compounds are isomorphous both below and above the transition temperatures [4]. The low-temperature phase (LTP) is triclinic with space group $P\bar{1}$ and $Z = 1$, and the high-temperature phase (HTP) is monoclinic with space group $B2/m$ and $Z = 2$ [4, 6].

It is easily understood that a pyridinium ring, which has a pseudo- C_6 axis, has disordered orientations in crystals. However, if a methyl group is introduced into a pyridinium ion, it is expected that the group will hinder the ion (picolinium ion) from disordering in crystals. Figure 1(b) shows a molecular structure of a 2-picolinium ion $CH_3C_5H_4NH^+$. In the present investigation, $(CH_3C_5H_4NH)_2SnCl_6$ (picHSn) and $(CH_3C_5H_4NH)_2TeCl_6$ (picHTe) were studied by differential scanning calorimetry (DSC) and nuclear quadrupole resonance

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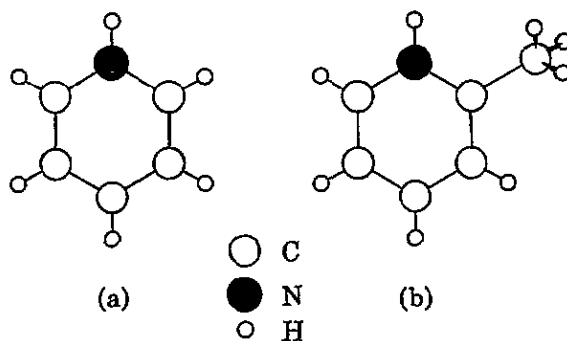


Figure 1. The molecular structures of (a) pyridinium ion $C_5H_5NH^+$ and (b) 2-picolinium ion $CH_3C_5H_4NH^+$.

(NQR). Since these compounds are not expected to show a phase transition driven by order-disorder of the nitrogen sites, our interest is in their lattice stabilities. That is, we would like to know whether they undergo the structural phase transitions driven by soft librational modes of the octahedral anions.

2. Experimental details

The crystals of picHSn or picHTe were prepared by dissolving 2-picoline and $SnCl_4$ or TeO_2 in 6 N hydrochloric acid with a stoichiometric ratio, and then by slow evaporation of water from the solution in a desiccator over P_2O_5 . All reagents were obtained from Kanto Chemical Co. The crystals thus obtained were recrystallized twice from dilute hydrochloric acid by the slow evaporation method. The polycrystalline sample was sealed in a glass tube for NQR measurement and was pulverized for DSC measurement.

DSC measurements were carried out between about 130 K and the melting point with a DSC220 and SSC5200 differential scanning calorimeter from Seiko Instruments Inc. Detection of the ^{35}Cl NQR signals in picHSn and picHTe was attempted with a modified Dean-type superregenerative spectrometer over a frequency range 14.0–18.0 MHz. The NQR signals detected were confirmed by observing the disappearance of the signals when applying a static magnetic field. The temperature dependence of the ^{35}Cl NQR frequency ν_Q was measured with a home-made pulsed NQR spectrometer equipped with a home-made cryostat [7].

3. Results and discussion

DSC measurements were repeated several times; however, no heat anomaly was detected for both picHSn and picHTe above about 130 K except at the melting points T_m . Table 1 gives the values obtained for an enthalpy change ΔH_m and an entropy change ΔS_m at T_m . The melting points of both compounds are about 120 K lower than the decomposition temperatures T_d [4] of the corresponding pyridinium compounds. The picolinium compounds have almost the same ΔS_m , which suggests that solid phases below T_m of both compounds have similar degrees of order. This is well understood by postulating that they have similar crystal structures; in general, A_2SnCl_6 and A_2TeCl_6 have the same

Table I. Values of ΔH_m and ΔS_m .

Compound	T_m (K)	ΔH_m (kJ mol ⁻¹)	ΔS_m (J K ⁻¹ mol ⁻¹)	T_d (K)
picHSn	454	37	81	571 (pyHSn)
picHTe	417	36	86	530 (pyHTe)

or very similar structures [4, 6, 8]. In the following discussion, we shall assume that they have similar crystal structures.

Three ^{35}Cl NQR signals were detected for picHSn; however, no signal was obtained for picHTe. Since the same number of ^{35}Cl NQR lines as detected in picHSn has been observed in the LTP of the pyridinium compounds [4], the crystal structure of picHSn seems similar to that of the LTP, where three crystallographically inequivalent chlorine atoms exist [4]. The temperature dependence of ν_Q was measured between 85 K and the temperature at which the signals faded. ν_Q decreased gradually on heating and no anomaly was recognized. From the DSC and NQR results it is concluded that no structural phase transition exists above 85 K in picHSn nor above 130 K in picHTe.

$(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$ (MASn) [9, 10] and $[(\text{CH}_3)_2\text{NH}_2]_2\text{SnCl}_6$ (DMASn) [7, 8] undergo second-order structural phase transitions that are interpreted as driven by soft rotatory lattice modes of the $[\text{SnCl}_6]^{2-}$ ions. MASn [11], DMASn [12], pyHSn [4] and pyHTe [6] have similar crystal structures, i.e. they have N-H...Cl hydrogen-bonding networks. In figure 2 the crystal structures of DMASn [12] and pyHSn [4] are shown schematically, emphasizing the hydrogen-bonding networks. In spite of their similar crystal structures, pyHSn and pyHTe do not show the displacive phase transition. On the other hand, librational modes of the MCl_6 octahedra in $A_2\text{MCl}_6$ crystals become soft also in non-hydrogen-bonding systems such as K_2ReCl_6 [13], K_2OsCl_6 [14] or K_2SnCl_6 [15, 16]. Therefore, the hydrogen-bonding networks may be insignificant for the phase transitions in MASn and DMASn, or rather they may work so as to hinder the crystals from undergoing the displacive transitions. Let us discuss this point further using Cochran's [17] theory.

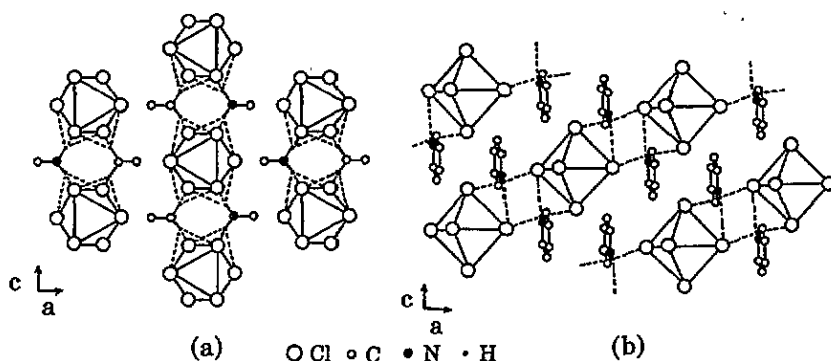


Figure 2. The crystal structures of (a) $[(\text{CH}_3)_2\text{NH}_2]_2\text{SnCl}_6$ (orthorhombic $Pnmm$; $Z = 2$) and (b) $(\text{C}_5\text{H}_5\text{NH})_2\text{SnCl}_6$ (monoclinic $B2/m$; $Z = 2$) projected on the a - c plane. Atomic arrangements are schematically shown and N-H...Cl hydrogen bonds are depicted by the broken lines. The hydrogen atoms bonded to the carbon atoms are omitted.

According to Cochran's theory, the lattice instability that leads to structural phase transitions in ionic crystals occurs via a subtle cancellation of the short-range (SR) interaction

by the long-range (LR) Coulombic interaction. This can be written schematically as follows:

$$\omega_s^2 \propto (\text{SR interaction}) - (\text{LR interaction}) \quad (1)$$

where ω_s is a soft phonon frequency. In the present case we are interested in the stability of the rotatory lattice vibrations of the SnCl_6 octahedra. For simplicity, we regard the molecular ions as point charges for the Coulombic interaction. Since the LR interaction is inversely proportional to a primitive-cell volume V , it is more difficult for a crystal with a larger V to undergo the displacive phase transition. The primitive-cell volume of pyHSn is 423 \AA^3 at 297 K [4] and that of pyHTe is 434 \AA^3 at room temperature [6], the values of which are larger than those of MASn (326 \AA^3 at 298 K [11]) and DMASn (380 \AA^3 at room temperature [12]). Furthermore, for a small displacement of ions the SR force works more effectively in the crystals having interionic hydrogen bondings than in the non-hydrogen-bonding system, because cations can exist closer to anions in the former system. Since pyridine has a fairly strong base character and the average $\text{N} \cdots \text{Cl}$ bond distance in pyHSn (3.148 \AA [4]) is shorter than those in MASn (3.523 \AA [11]) and DMASn (3.519 \AA [12]) by about 0.1 \AA , the $\text{N-H} \cdots \text{Cl}$ hydrogen bonds in pyHSn and pyHTe crystals must be relatively strong. Thus, it is inferred that the crystal lattices in pyHSn and pyHTe have stronger SR forces and weaker LR forces than those in MASn and DMASn. On the basis of Cochran's theory, therefore, the lattice stabilities of pyHSn and pyHTe are explained qualitatively in terms of their $\text{N-H} \cdots \text{Cl}$ hydrogen-bonding networks and large primitive-cell volumes.

It has been concluded from the present experimental results that the crystal structures of picHSn and picHTe are similar to those of pyHSn and pyHTe. Thus a considerable number of $\text{N-H} \cdots \text{Cl}$ hydrogen bonds are expected to exist in the picolinium compounds. Moreover, the picolinium crystals are considered to have larger primitive-cell volumes than the pyridinium crystals, because the picolinium ions have a larger molecular volume than the pyridinium ions. Hence, it is also explained using Cochran's theory that no displacive phase transition was observed in the picolinium compounds.

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