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X-Ray Diffraction and ^{35}Cl NQR Studies of Bis-2-picolinium Hexachlorostannate

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The crystal structure of bis-2-picolinium hexachlorostannate $(CH_3C_5H_4NH)_2SnCl_6$ was determined at room temperature by a single-crystal X-ray diffraction method. This crystal forms triclinic with space group C_i^1-$P\bar{1}$ and $Z=1$. The temperature dependence of the ^{35}Cl NQR spectrum was investigated at between 77 K and around 340 K, at which temperatures the signals faded out. Three signals with an equal intensity were observed with no anomaly in their temperature variation over the entire temperature region investigated. DTA measurements were carried out at between 140 and 430 K, and no heat anomaly was observed.

For the last thirty years many investigations have been carried out on A_2MCl_6 ionic crystals, where $[MCl_6]^{2-}$ is an octahedral ion, such as $[SnCl_6]^{2-}$ or $[TeCl_6]^{2-}$, and A is a mono-valent cation, as follows: (1) atomic or spherical-molecular ions, such as alkaline-metallic ions, NH_4^+ or $(CH_3)_4N^+$;[1—3] (2) long-chain ions, such as $C_nH_{2n+1}NH_3^+$ ($n \geq 2$);[4—6] (3) asymmetric alkyl-group-substituted ammonium ions, such as $CH_3NH_3^+$, $(CH_3)_2NH_2^+$ or $(CH_3)_3NH^+$;[7—10] and (4) planer ions, such as pyridinium ion $C_5H_5NH^+$ or guanidinium ion $(NH_2)_3C^+$.[11—13] This is because many of these compounds exhibit structural phase transitions and/or interesting molecular motions.

Nuclear quadrupole resonance (NQR) is very sensitive to structural phase transitions, because its frequencies sharply reflect any symmetry change in the charge distributions around the resonant nuclei.[1,2] Hence, measurements of the NQR frequencies and relaxation times give both static and dynamic information concerning phase transitions.[14—18] NQR has shown its usefulness in studying phase transitions, especially in A_2MCl_6 crystals.[1—3,14,17] Many of the phase transitions in A_2MCl_6 crystals 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. Anomalies in the temperature dependence of the NQR frequencies or relaxation times around the transition temperatures, which are due to the soft librational modes of the MCl_6, have frequently been observed, and much information concerning the transitions has been obtained by analyzing the anomalies (for example, see Ref. 19 and/or Ref. 20).

Bis-pyridinium hexachlorostannate, $(C_5H_5NH)_2SnCl_6$, and hexachlorotellurate, $(C_5H_5NH)_2TeCl_6$, undergo second-order structural phase transitions at 331 and 272 K, respectively, the transitions of which are interpreted as being driven by an orientational ordering of the pyridinium ion, $C_5H_5NH^+$.[21] However, unlike many A_2MCl_6 crystals, no displacive phase transition has been observed above 77 K in the two compounds, which are stable up to relatively high temperatures (the Sn and Te complexes decompose at 571 and 530 K, respectively).[22,23] Since the molecular structure of the pyridinium ion is a benzene-like planer ring, which has a pseudo-C_6 axis, it is easily understood that the pyridinium ring takes disordered orientations in crystals. In fact, the disorder of nitrogen sites has been reported for many pyridinium compounds.[24—32] However, if a methyl group is introduced in a pyridinium ion, it is expected that the group would hinder the ion (picolinium ion) from disordering in crystals. Therefore, a structural phase transition due to disordering of picolinium ions is not expected to undergo in the title compound. As expected, no order-disorder phase transition was found for the title compound between 77 and the melting point of 454 K in our previous work.[33] No displacive phase transition was observed either; this result was explained qualitatively in terms of hydrogen-bonding networks and a large primitive-cell volume.[33] In the present work, the crystal structure of bis-2-picolinium hexachlorostannate $(CH_3C_5H_4NH)_2SnCl_6$ was determined using a single-crystal X-ray diffraction technique in order to confirm the above explanation. Moreover, NQR and differential thermal analysis (DTA) measurements were carried out to verify that the title compound does not undergo a phase transition.

Experimental

Material. The title compound was prepared by dissolving 2-picoline and $SnCl_4$ in 6 M hydrochloric acid ($1\ M = 1\ mol\ dm^{-3}$) with a stoichiometric ratio, and then by slowly evaporating water from the solution in a desiccator over P_2O_5. The thus-obtained crystal was recrystallized twice from dilute hydrochloric acid by a slow-evaporation method. The polycrystalline sample was pulverized and sealed in glass tubes for NQR and DTA measurements. A single crystal for X-ray measurement was obtained by recrystallizing the polycrystal once more. The density of the crystal (D_m) was measured by a flotation method in C_6H_5Cl–$BrCH_2CH_2Br$.

Measurements. The temperature dependence of the ^{35}Cl NQR frequencies (ν_Q) was measured with a home-made pulsed NQR spectrometer equipped with a home-made cryostat.[34] The sample temperature was controlled to within ±0.5 K with a temperature cotroller, and was determined within ±1 K with a copper–constantan thermocouple. DTA measurements were carried out using a home-made apparatus[35] at between 140 and 430 K with rates of about 4 K min^{-1} on heating and 2 K min^{-1} on cooling. The sample temperature was determined within ±1 K with a copper-constantan thermocouple.

Crystal Structure Determination. Crystal data and the experimental conditions are listed in Table 1. An X-ray measurement was made on a Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. The intensity data were corrected for both Lorentz-polarization and absorption effects. The result that no systematic absence was recognized indicates that the possible space groups are $P\bar{1}$ and $P1$. With the help of the NQR data, three ^{35}Cl NQR lines with an equal intensity being observed at room temperature, $P\bar{1}$ was adopted for the structural analysis. The structure was solved by direct methods, and refined by minimizing the function $\sum\omega||F_o|-|F_c||^2$ (ω=$4F_o^2/[\sigma^2(I)+(0.04F_o^2)^2]$) with the full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located by difference Fourier syntheses and refined isotropically. The atomic scattering factors were taken from Ref. 36. All of the calculations were carried out on a VAX station 4000 with the MolEN program package.[37] The fractional atomic coordinates and thermal displacement parameters are listed in Table 2. F_o-F_c tables were deposited as Document No. 69024 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Crystal Data, Data Collection, and Structure Refinement

Chemical formula		$C_{12}H_{16}Cl_6N_2Sn$
Formula weight		519.68
Crystal system		Triclinic
Space group		$P\bar{1}$
Lattice constants	a/Å	7.121(1)
	b/Å	8.237(1)
	c/Å	8.916(1)
	α/°	75.04(1)
	β/°	69.39(1)
	γ/°	83.61(1)
Volume of unit cell/Å^3		472.8
Formula unit per cell		1
D_x/g cm^{-3}		1.825
D_m/g cm^{-3}		1.824
Number of reflections for cell measurement		25
θ range/°		11.4—18.3
Linear absorption coefficient/mm^{-1}		2.192
Crystal shape		Plate
Crystal color		Colorless
Crystal size/mm^3		$0.50 \times 0.43 \times 0.40$
Data-collection method		ω–2θ scans
Absorption correction type		Empirical via ψ scans
Transmission factor		0.7483—0.9997
Number of reflections measured		6122
Number of independent reflections		5828
Number of observed reflections		5256
Criterion for observed reflections		$I \geq 3\sigma(I)$
Maximum value of θ/°		40.0
hkl range		$h=-12$—$+12$ $k=-14$—0 $l=-16$—$+15$
Number of standard reflections		3
Interval (Number of reflections)		200
Intensity decay/%		≤ 1.4
R[a]		0.036
wR[b]		0.076
S		2.66
Number of reflections used in refinement		5256
Number of parameters		130
$(\Delta/\sigma)_{max}$		0.55
$\Delta\rho_{max}$/eÅ^{-3}		0.93
$\Delta\rho_{min}$/eÅ^{-3}		0.00
Extinction coefficient		3.1×10^{-6}

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$. b) $wR=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Results and Discussion

Crystal Structure. Bis-2-picolinium hexachlorostannate $(CH_3C_5H_4NH)_2SnCl_6$ forms a triclinic crystal with space group C_i^1-$P\bar{1}$ and $Z=1$ at room temperature. The bond distances and bond angles are listed in Table 3, and the molecular structures of 2-picolinium and hexachlorostannate ions are depicted by ORTEP[38] in Fig. 1. H(2)–H(5) and H(n) denote the hydrogen atoms bonded to ring carbons C(2)–C(5) and nitrogen, respectively. H(6i) ($i=1$—3) express the methyl–hydrogen atoms. The crystal structure is shown as a projection onto the bc-plane in Fig. 2. The $[SnCl_6]^{2-}$ octahedra are located at the corners of the unit cell. Since the Sn atoms are on the center of symmetry (C_i), there are three crystallographically non-equivalent Cl atoms (Cl(1), Cl(2), and Cl(3)). The distortion of the octahedra is only slight, as can be seen from Table 3; the Sn–Cl distances are 2.43±0.01 Å, and the bond angles (Cl–Sn–Cl) are 90.0±0.7°. Two cations $(CH_3C_5H_4NH)^+$ fill the free space in the interior of the cell, and are connected by C_i at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$. The pyridinium rings are nearly planer, and the average C–C and C–N distances are 1.374 and 1.339 Å, respectively. These values compare favorably with the corresponding bond distances of 1.362 or 1.373 Å and 1.330 Å, respectively, in solid pyridine.[39] On the other hand, the C–H bond distances, the average value being 1.00 Å, and N–H distance of 0.95 Å were estimated to be somewhat shorter. The methyl group is slightly deformed and the C(1)–C(6)–H angles (105, 114, and 117°) deviate from a tetrahedral angle of 109° 28′.

Some important inter-molecular distances and angles are listed in Table 4. Since the van der Waals radii of H and Cl are 1.2 and 1.80 Å, respectively.[40,41] the hydrogen atoms located within 3.0 Å from chlorine atoms are given in the Table. We can see from Table 4 that two hydrogen atoms bonded to carbons are close to all chlorine atoms; Cl(2) and Cl(3) are approached by a single H(n), whereas Cl(1) is not (the N···Cl(1) and H(n)···Cl(1) distances are 3.467 (4) and 3.60 (6) Å, respectively).

^{35}Cl NQR Spectroscopy. Three ^{35}Cl NQR lines with an equal intensity were observed at room temperature, showing that there are three crystallographically non-equivalent chlo-

Table 2. Fractional Atomic Coordinates, Anisotropic Displacement Parameters (10^{-2} Å^2), Which Appear in Anisotropic Temperature Factor $T=\exp\{-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\}$, and Isotropic Displacement Parameters U_{iso} (10^{-2} Å^2) for H atoms

Atom	x	y	z	U_{11}, U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	0	0	0	2.685(6)	2.712(7)	2.743(6)	−0.183(6)	−0.643(5)	−0.372(5)
Cl(1)	−0.0616(1)	0.29894(8)	−0.09401(9)	4.24(3)	3.03(2)	4.34(3)	0.15(2)	−0.87(2)	−0.15(2)
Cl(2)	0.2884(1)	0.01198(9)	−0.25219(8)	4.14(3)	4.01(2)	3.76(2)	−0.61(2)	0.21(2)	−1.06(2)
Cl(3)	0.2181(1)	0.0668(1)	0.13220(9)	5.34(3)	4.31(3)	5.45(2)	−0.68(2)	−3.00(2)	−0.61(2)
N	0.5689(5)	0.3158(3)	0.7323(3)	6.05(11)	3.59(9)	4.86(10)	−1.39(8)	−2.37(8)	0.13(8)
C(1)	0.7098(4)	0.3686(4)	0.5853(3)	4.58(10)	4.56(11)	4.18(8)	0.08(9)	−2.12(7)	−1.20(8)
C(2)	0.7404(5)	0.5399(4)	0.5275(4)	4.19(11)	4.95(14)	3.62(10)	−0.58(11)	−0.73(9)	−0.05(10)
C(3)	0.6288(6)	0.6468(4)	0.6241(4)	5.69(16)	3.76(12)	4.90(14)	−0.17(12)	−1.07(12)	−0.04(11)
C(4)	0.4868(6)	0.5874(5)	0.7751(5)	5.19(15)	4.55(13)	4.85(13)	0.59(12)	−0.78(12)	−0.84(11)
C(5)	0.4587(6)	0.4188(5)	0.8264(4)	4.71(13)	6.18(18)	4.07(12)	−1.10(13)	−0.78(11)	0.22(13)
C(6)	0.8240(8)	0.2411(6)	0.4934(5)	9.37(26)	7.13(18)	7.43(15)	2.27(19)	−4.05(15)	−4.13(11)
H(*n*)	0.560(8)	0.200(6)	0.765(5)	8(1)					
H(2)	0.846(7)	0.580(6)	0.422(5)	6(1)					
H(3)	0.648(6)	0.761(5)	0.589(4)	5(1)					
H(4)	0.391(8)	0.658(7)	0.858(6)	7(1)					
H(5)	0.373(6)	0.364(5)	0.945(5)	5(1)					
H(61)	0.898(10)	0.167(8)	0.569(7)	12(1)					
H(62)	0.744(7)	0.174(5)	0.458(5)	7(1)					
H(63)	0.905(6)	0.288(5)	0.383(5)	5(1)					

Table 3. Selected Geometric Parameters (Å, degree)

Sn–Cl(1)	2.4313(6)	Cl(1)–Sn–Cl(2)	89.26(2)
Sn–Cl(2)	2.4420(6)	Cl(1)–Sn–Cl(3)	89.28(3)
Sn–Cl(3)	2.4330(9)	Cl(2)–Sn–Cl(3)	89.32(3)
C(1)–C(2)	1.385(5)	C(1)–C(2)–C(3)	119.1(2)
C(2)–C(3)	1.379(5)	C(2)–C(3)–C(4)	121.5(3)
C(3)–C(4)	1.374(4)	C(3)–C(4)–C(5)	117.7(3)
C(4)–C(5)	1.359(5)	C(4)–C(5)–N	120.4(3)
N–C(5)	1.340(5)	C(5)–N–C(1)	123.7(3)
N–C(1)	1.338(3)	N–C(1)–C(2)	117.6(3)
C(1)–C(6)	1.490(6)	C(2)–C(1)–C(6)	123.8(3)
N–H(*n*)	0.93(5)	N–C(1)–C(6)	118.6(3)
C(2)–H(2)	0.98(3)		
C(3)–H(3)	0.92(4)		
C(4)–H(4)	1.06(5)		
C(5)–H(5)	1.03(3)		
C(6)–H(61)	1.04(7)	C(1)–C(6)–H(61)	105(4)
C(6)–H(62)	1.01(6)	C(1)–C(6)–H(62)	117(3)
C(6)–H(63)	0.95(3)	C(1)–C(6)–H(63)	114(3)

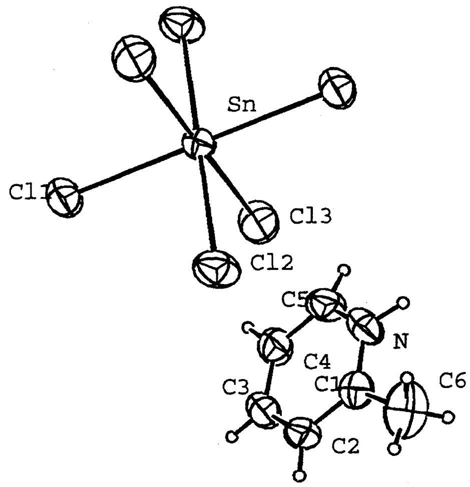

Fig. 1. The molecular structures of $[CH_3C_5H_4NH]^+$ and $[SnCl_6]^{2-}$ drawing by ORTEP with 50%-probability-displacement ellipsoids.

rine atoms in the crystal. The temperature dependence of the NQR frequencies (ν_Q) is shown in Fig. 3, and some ν_Q values determined at several temperatures along with temperature coefficients $\Delta\nu_Q/\Delta T$ are listed in Table 5. Three signals, named as listed in Fig. 3, were observed over the entire temperature region investigated. The frequencies of all of the lines decreased monotonously with increasing temperature from 77 K, and ν_{Qh}, ν_{Qm}, and ν_{Ql} faded out at 345, 333, and 339 K, respectively. This fade-out phenomenon was caused by reorientational motions of the $[SnCl_6]^{2-}$ octahedra.[42—45] DTA measurements were carried out between 140 and 430 K, and no heat anomaly was observed. These results show that there is no structural phase transition above 77 K in the title compound.

The temperature variations of ν_{Qh} and ν_{Ql} are nearly the same, and more gentle than that of ν_{Qm}, as can be seen from both Fig. 3 and $\Delta\nu_Q/\Delta T$ in Table 5. In general, NQR frequency decreases with increasing temperature. This was explained by Bayer et al. as being due to an averaging effect of the molecular vibrations, such as librations or rotational oscillations on the electric field gradient (EFG) at the resonant nuclei.[46—48] A factor group analysis[49] of this crystal has revealed that there are three librational modes of the anions (A_g modes), each of which is a rotational vibration about one of the crystal axes. Since these librations are considered to be responsible for the temperature dependence of the NQR frequencies, their $\Delta\nu_Q/\Delta T$ should be nearly the same. This is because three crystallographically non-equivalent Cl atoms

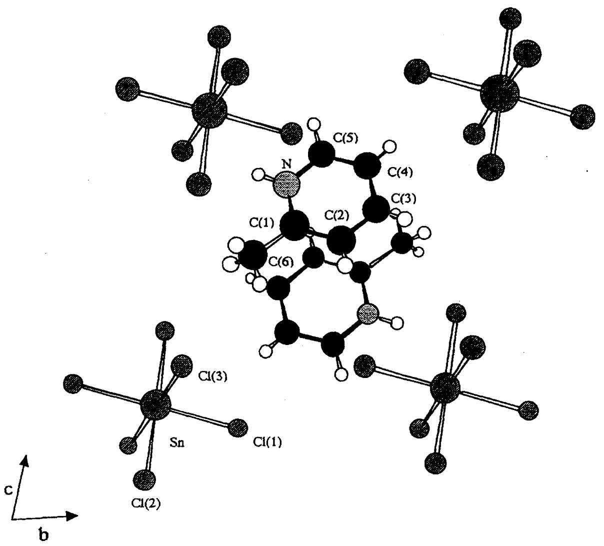

Fig. 2. Projection of the unit cell onto the *ac*-plane.

Table 4. Selected Inter-Molecular Distances and Angles (Å, degree)

C(2)···Cl(1)	3.707(3)	C(2)–H(2)···Cl(1)	165(4)
C(4)···Cl(1)	3.579(4)	C(4)–H(4)···Cl(1)	153(4)
N···Cl(2)	3.318(3)	N–H(*n*)···Cl(2)	128(4)
C(4)···Cl(2)	3.604(4)	C(4)–H(4)···Cl(2)	122(3)
C(6)···Cl(2)	3.676(6)	C(6)–H(62)···Cl(2)	152(3)
N···Cl(3)	3.457(3)	N–H(*n*)···Cl(3)	137(5)
C(5)···Cl(3)	3.537(3)	C(5)–H(5)···Cl(3)	141(3)
C(6)···Cl(3)	3.572(4)	C(6)–H(61)···Cl(3)	135(5)
H(2)···Cl(1)	2.76(4)	Sn–Cl(1)···H(2)	112.1(9)
H(4)···Cl(1)	2.60(5)	Sn–Cl(1)···H(4)	100(1)
H(*n*)···Cl(2)	2.67(6)	Sn–Cl(2)···H(*n*)	106.4(9)
H(4)···Cl(2)	2.93(4)	Sn–Cl(2)···H(4)	91.5(9)
H(62)···Cl(2)	2.76(5)	Sn–Cl(2)···H(62)	115.0(9)
H(*n*)···Cl(3)	2.72(5)	Sn–Cl(3)···H(*n*)	114(1)
H(5)···Cl(3)	2.68(4)	Sn–Cl(3)···H(5)	105(1)
H(61)···Cl(3)	2.76(6)	Sn–Cl(3)···H(2)	101(2)

Table 5. ^{35}Cl NQR Frequencies ν_Q Determined at Several Temperatures and Temperature Coefficients $\Delta\nu_Q/\Delta T$ Evaluated between 77 and 333 K

	ν_Q (MHz)		
T (K)	ν_{Qh}	ν_{Qm}	ν_{Ql}
77	17.492	17.068	16.522
100	17.485	17.035	16.514
200	17.446	16.877	16.462
293	17.380	16.713	16.387
333	17.342	16.632	16.348
$\Delta\nu_Q/\Delta T$ (kHz K^{-1})	−0.586	−1.70	−0.680

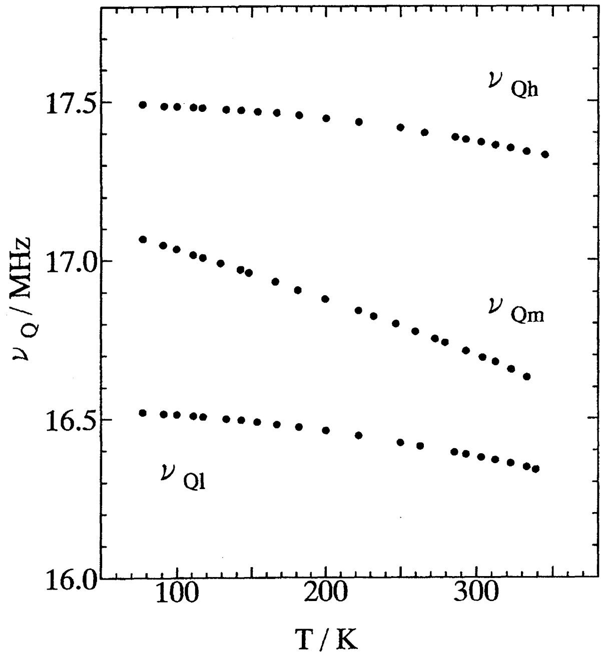

Fig. 3. Temperature dependence of ^{35}Cl NQR frequencies.

belong to the same octahedron, and each of the librations has a similar effect on three kinds of Cl atoms, judging from the crystal structure. However, when hydrogen atoms approach a chlorine atom from the direction perpendicular to the principal axis of EFG at the chlorine nucleus, the temperature variation of the NQR line arising from the chlorine nucleus could be more gentle than that expected for the non-hydrogen bonding system, or negligibly small or positive, depending on the strength of the hydrogen bonds.[50,51)] In the $[SnCl_6]^{2-}$ octahedron, the principal axes of EFG at the chlorine nuclei almost coincide with the Sn–Cl bond axes in general, and in the title compound, the Sn–Cl···H angles make nearly a right angle, as can be seen from Table 4. Among the hydrogen atoms located within 3.0 Å from the chlorine atoms, H(*n*) seems to be responsible for the mild temperature variations of ν_{Qh} and ν_{Ql}. This is because H(*n*) is expected to be more positively charged than the hydrogen atoms bonded to carbons, and because only one of three kinds of chlorine atoms is away from H(*n*), whereas the hydrogen atoms bonded to carbons are close to all of the chlorine atoms.

Table 3 shows that the Sn–Cl(1) and Sn–Cl(3) distances are nearly equal, and are slightly shorter than Sn–Cl(2) length. An increasing bond-distance can be related to an increasing ionic-character of the bond, which leads to a decrease in the ^{35}Cl NQR frequencies within the framework of the Townes & Dailey theory.[52)] Thus, the lowest-frequency signal (ν_{Ql}) is assigned to Cl(2). Furthermore, the temperature variation of ν_{Qm} is rather steeper than those of the other two lines. The above discussion leads to the fact that the resonance line with the largest temperature variation (ν_{Qm}) can be assigned to the chlorine atoms away from H(*n*), i.e., Cl(1). As a result, the rest line (ν_{Qh}) is assignable to Cl(3). The assignments proposed here, $\nu_{Qh}\leftrightarrow$Cl(3), $\nu_{Qm}\leftrightarrow$Cl(1), and $\nu_{Ql}\leftrightarrow$Cl(2), are based on qualitative arguments. Single-crystal-Zeeman-split NQR spectroscopy, see e.g. Ref. 53, would give a unique assignment.

Figure 4 shows that each picolinium ion is connected by a bifurcated N–H···Cl hydrogen bond to the two neighboring octahedra. It appears from the figure that a single octahedron makes four hydrogen bonds. However, since this figure is

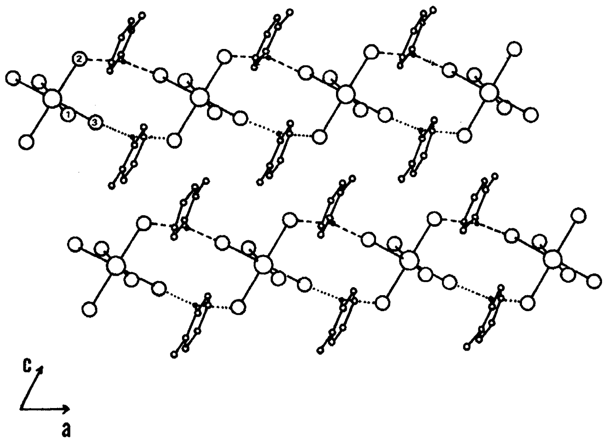

Fig. 4. Projection of the crystal lattice along *b*-axis with emphasizing N–H···Cl hydrogen-bonding networks. In this figure, the hydrogen atoms bonded to carbon atoms are omitted.

a projection, for example, the octahedron centered at 0, 0, 0 overlaps with that at 0, 1, 0. Therefore, a single anion has two N–H···Cl hydrogen bonds. These differences in the hydrogen bonds are shown by the dotted and dashed lines.

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 interaction by the long-range Coulombic interaction.[54)] In a previous paper, on the basis of this Cochran's theory, the lattice stability of the title compound was explained by assuming that there are hydrogen-bonding networks, and that the primitive-cell volume is very large.[33)] This assumption was confirmed by the present investigation. As described above, there are hydrogen-bonding networks and the volume of unit cell is 472.8 Å^3. This value is considerably large compared with 326 Å^3 for $(CH_3NH_3)_2SnCl_6$ at 293 K,[55)] or 380 Å^3 for $[(CH_3)_2NH_2]_2SnCl_6$ at room temperature.[56)] These crystals undergo a displacive phase transition.[57,58)]

Conclusions

Bis-2-picolinium hexachlorostannate $(CH_3C_5H_4NH)_2$-$SnCl_6$ forms a triclinic crystal with space group C_i^1-$P\bar{1}$ and $Z=1$ at room temperature. This crystal is stable from 77 K up to a melting point of 454 K. This lattice stability can be explained qualitatively in terms of hydrogen-bonding networks and a large primitive-cell volume.[33)] Three ^{35}Cl NQR lines were assigned to three crystallographically non-equivalent chlorine atoms as follows: $\nu_{Qh}\leftrightarrow$Cl(3), $\nu_{Qm}\leftrightarrow$Cl(1), and $\nu_{Ql}\leftrightarrow$Cl(2).

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References

1) M. Kubo and D. Nakamura, "Advances in Inorganic and Radiochemistry," Academic Press, New York (1966), Vol. 8, p. 257.

2) D. Nakamura, R. Ikeda, and M. Kubo, *Coord. Chem. Rev.*, **17**, 281 (1975).

3) R. L. Armstrong and H. M. Van Driel, "Advances in Nuclear Quadrupole Resonance," Heyden, London (1975), Vol. 2, p. 179.

4) T. Okuda, K. Inui, A. Nakata, M. Katada, H. Terao, and K. Yamada, *J. Mol. Struct.*, **296**, 103 (1993).

5) M. Cermak, A. Fuith, P. Vanek, J. Silha, and Z. Malkova, *Phys. Status Solidi B*, **182**, 289 (1994).

6) J. Kroupa, A. Fuith, K. J. Schenk, H. Warhanek, and M. Cermak, *Ferroelectrics*, **159**, 3251 (1994).

7) Y. Kume, R. Ikeda, and D. Nakamura, *J. Magn. Reson.*, **33**, 331 (1979).

8) A. Ishikawa, K. Horiuchi, R. Ikeda, and D. Nakamura, *J. Mol. Struct.*, **192**, 237 (1989).

9) K. Horiuchi, *Phys. Status Solidi B*, **178**, 127 (1993).

10) R. Ikeda, R. Kadel, Al. Weiss, N. Ishida, and D. Nakamura, *Ber. Bunsenges. Phys. Chem.*, **86**, 685 (1982).

11) Y. Tai, A. Ishikawa, K. Horiuchi, T. Asaji, and D. Nakamura, *Z. Naturforsch., A*, **43A**, 1002 (1988).

12) Y. Tai, T. Asaji, D. Nakamura, and R. Ikeda, *Z. Naturforsch., A*, **45A**, 477 (1990).

13) Y. Furukawa and D. Nakamura, *Bull. Chem. Soc. Jpn.*, **59**, 2642 (1986).

14) F. Borsa and A. Rigamonti, "Magnetic Resonance of Phase Transitions," ed by F. J. Owens, C. P. Poole, Jr., and H. A. Farach, Academic Press, New York (1979), p. 79.

15) H. Chihara and N. Nakamura, "Advances in Nuclear Quadrupole Resonance," Heyden, London (1980), Vol. 4, p. 1.

16) R. Blinc, *Phys. Rep.*, **79**, 331 (1981).

17) A. Rigamonti, *Adv. Phys.*, **33**, 115 (1984).

18) F. Borsa and A. Rigamonti, "Structural Phase Transitions II," ed by K. A. Muller and H. Thomas, Springer-Verlag, Berlin (1991), p. 83.

19) G. P. O'Leary, *Phys. Rev. Lett.*, **23**, 782 (1969).

20) C. A. Martin and R. L. Armstrong, *J. Magn. Reson.*, **20**, 411 (1975).

21) Y. Tai, T. Asaji, R. Ikeda, and D. Nakamura, *Z. Naturforsch., A*, **44A**, 300 (1989).

22) D. Borchers and Al. Weiss, *Z. Naturforsch., A*, **42A**, 739 (1987).

23) P. P. Khodadad, B. Viossat, P. Toffoli, and N. Rodier, *Acta Crystallogr., Sect. B*, **B35**, 2896 (1979).

24) R. F. Copeland, S. H. Conner, and E. A. Mayers, *J. Phys. Chem.*, **70**, 1288 (1966).

25) S. K. Porter and R. A. Jacobson, *J. Chem. Soc. A*, **1970**, 1356.

26) P. A. Tucker and P. A. Kroon, *Acta Crystallogr., Sect. B*, **B29**, 2967 (1973).

27) S. Geller, P. M. Skarstad, and S. A. Wilber, *J. Electrochim. Soc.*, **122**, 332 (1975).

28) H. Hartl, *Acta Crystallogr., Sect. B*, **B31**, 1781 (1975).

29) C. Brassy, R. Robert, B. Bachet, and R. Chevalier, *Acta Crystallogr., Sect. B*, **B32**, 1371 (1976).

30) H.-N. Adams and J. Strahle, *Z. Anorg. Allg. Chem.*, **485**, 65 (1982).

31) F. Calderazzo, G. Pampalori, M. Lanfanchi, and G. Pelizzi, *J. Organomet. Chem.*, **296**, 1 (1985).

32) A. El-Kholi, A. Muller, R. Christophersen, and K. Dehnicke, *Acta Crystallogr., Sect. C*, **C44**, 1233 (1988).

33) K. Horiuchi, H. Iwafune, T. Asaji, and D. Nakamura, *J. Phys.; Condens. Matter*, **6**, 9075 (1994).

34) K. Horiuchi, R. Ikeda, and D. Nakamura, *Ber. Bunsenges.*

Phys. Chem., **91**, 1351 (1987).

35) Y. Kume, R. Ikeda, and D. Nakamura, *J. Magn. Reson.*, **33**, 331 (1979).

36) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England (1974), Vol. IV.

37) C. K. Fair, "MolEN. An Interactive Intelligent System for Crystal Structure Analysis," Enraf–Nonius, Delft, The Netherland (1990).

38) C. K. Johnson, "ORTEPII. Report ORNL-5138," Oak Ridge National Laboratory, Tennessee, USA (1976).

39) "Kagaku Binran," (in Japanese), revised 4th ed, ed by Chemical Society of Japan, Maruzen, Tokyo (1993).

40) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, New York (1960).

41) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding," W. A. Benjamin, New York (1968).

42) K. Horiuchi, T. Shimizu, H. Iwafune, T. Asaji, and D. Nakamura, *Z. Naturforsch.*, *A*, **45A**, 485 (1990).

43) K. Horiuchi and D. Nakamura, *Z. Naturforsch.*, *A*, **47A**, 277 (1992).

44) K. Horiuchi, *Z. Naturforsch.*, *A*, **49A**, 286 (1994).

45) K. Horiuchi and Al. Weiss, *J. Mol. Struct.*, **345**, 97 (1995).

46) H. Bayer, *Z. Phys.*, **130**, 227 (1951).

47) T. Kushida, *J. Sci. Hiroshima Univ. Ser. A*, **19**, 327 (1955).

48) T. C. Wang, *Phys. Rev.*, **99**, 566 (1955).

49) G. Turrell, "Infrared and Raman Spectra of Crystals," Academic Press, London (1972).

50) K. Horiuchi, A. Sasane, Y. Mori, T. Asaji, and D. Nakamura, *Bull. Chem. Soc. Jpn.*, **59**, 2639 (1986).

51) K. Horiuchi, *J. Chem. Soc.*, *Faraday Trans.*, **89**, 3359 (1993).

52) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

53) V. Nagarajan, H. Paulus, N. Weiden, and Al. Weiss, *J. Chem. Soc.*, *Faraday Trans. 2*, **82**, 1499 (1986).

54) W. Cochran, *Adv. Phys.*, **9**, 387 (1960).

55) K. Kitahara, H. Kiriyama, and Y. Baba, *Bull. Chem. Soc. Jpn.*, **52**, 324 (1979).

56) O. Knop, T. S. Cameron, M. A. James, and M. Falk, *Can. J. Chem.*, **61**, 1620 (1983).

57) Y. Furukawa, H. Kiriyama, and R. Ikeda, *Bull. Chem. Soc. Jpn.*, **50**, 1927 (1977).

58) K. Horiuchi, H. Ishida, and D. Nakamura, *Bull. Chem. Soc. Jpn.*, **58**, 2590 (1985).