

Low temperature vibrational spectroscopy. II. Evidence for order-disorder phase transitions due to weak C-H...Cl hydrogen bonding in tetramethylammonium hexachloroplatinate (IV), -tellurate (IV), and -stannate (IV) and the related perdeuterated compounds

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(Received 16 January 1978)

The low frequency infrared and Raman spectra of normal and perdeuterated $((\text{CH}_3)_4\text{N})_2[\text{MCl}_6]$ ($\text{M} = \text{Pt}$, Te , or Sn) have been measured at temperatures down to ~ 100 K and evidence for phase transitions was found. The spectra have been carefully assigned and it was shown that bands due to forbidden methyl torsions and other noncubic features play a role, especially in spectra at low temperatures. Possible site symmetries of the $[\text{PtCl}_6]^{2-}$ ion, which cannot have strictly O_h symmetry in either phase, have been deduced. The spectra of a mixed Pt:Te compound showed that the hexachlorometallate anions vibrate approximately independent of each other. The results have been compared with von der Ohe's recent extensive low temperature Raman study on protonated compounds with $\text{M} = \text{U}$, Sn , and Zr , and his conclusions are discussed. It is shown that crystals of this kind can be characterized by methyl-chlorine interaction and it is suggested that the phase transitions are caused by an ordering of rotationally disordered methyl groups via the formation of weak C-H...Cl hydrogen bonds at low temperatures. The transition temperatures and hence the interactions are shown to depend on both the kind of hydrogen isotope and metal present in the crystals.

I. INTRODUCTION

The tetramethylammonium cation, $(\text{CH}_3)_4\text{N}^+$, which is a convenient cation for the preparation of many salts of inorganic complex anions, has recently gained interest, because some of its compounds, among others the hexachlorometallates $((\text{CH}_3)_4\text{N})_2[\text{MCl}_6]$ ($\text{M} = \text{Sn}$, U , Zr , Te), exhibit first order phase transitions at lower temperatures; in the range of ~ 100 – 200 K.^{1,2} The origin of the transitions was not clear, as evidenced from the discussion in part I of this series.¹ The present work aims at a description of what happens during the transitions, and why they occur.

One way to study microscopic aspects of phase transitions is to record and compare the vibrational spectra of closely related compounds. It was anticipated^{1,2} that the transitions might occur quite generally in $((\text{CH}_3)_4\text{N})_2[\text{MCl}_6]$ compounds. To improve the conclusions obtainable from vibrational spectroscopy, which depend on correct assignment of bands, it was considered essential, (i) to apply infrared as well as Raman techniques, and (ii) to extend the measurements to cover also perdeuterated salts.

In this paper we report on the detailed spectral behavior down to temperatures of about 100 K, of the normal and perdeuterated $[\text{PtCl}_6]^{2-}$ salts. The previous results for normal $[\text{SnCl}_6]^{2-}$ and $[\text{TeCl}_6]^{2-}$ salts are improved and extended by addition of the missing infrared spectra (for $[\text{SnCl}_6]^{2-}$) and by the inclusion of deuterated salts.

The correctness of the well-known basic approximation of separating the crystal modes into internal molecular phonons and external lattice vibrations was tested and confirmed by measurements on $[\text{PtCl}_6]^{2-}$ in a host crystal of $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$. Furthermore, the in-

ternal vibrations of both normal and perdeuterated tetramethylammonium ions should be easily recognizable since they are known from a recent study in aqueous solution.³

Some bands around 300 cm^{-1} appearing in the low temperature phases, unassigned in our previous tellurium work,¹ can now be reliably assigned to methyl torsions by virtue of the results on the deuterated compounds. This is quite nice, because the bands appear in the metal-chlorine stretching range, which is of special interest in deducing the site symmetry of the $[\text{MCl}_6]^{2-}$ in the high and low temperature phases. The present results clearly demonstrate that spectroscopic transitions forbidden under cubic symmetry, e.g., involving methyl torsions, become allowed via small distortions in structure.

II. STRUCTURAL DETAILS

A. Platinum

The room temperature x-ray structure of $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ has been studied by Huggins⁴ using single crystal Laue examination, by others⁵⁻⁷ using powder methods, and recently by Berg and Sjøtofte⁸ using modern single crystal x-ray diffractometry. From these investigations, it is clear that the compound within a high degree of accuracy crystallizes in the $K_2[\text{PtCl}_6]$ type cubic face-centered antifluorite lattice of space group O_h^- - $Fm\bar{3}m$, with $Z = 4$ and $a = 10.72\text{ \AA}$. Optical isotropy of the compound was observed by Topsøe,⁹ Ries,¹⁰ and Staritzky and Singer ($n_D = 1.577 \pm 0.001$).¹¹ However, the presence of weak "forbidden" lines of high hkl indices in x-ray powder photographs⁷ and other noncubic features⁸ indicate a slight, yet unknown deviation from the strict antifluorite symmetry. The known atomic

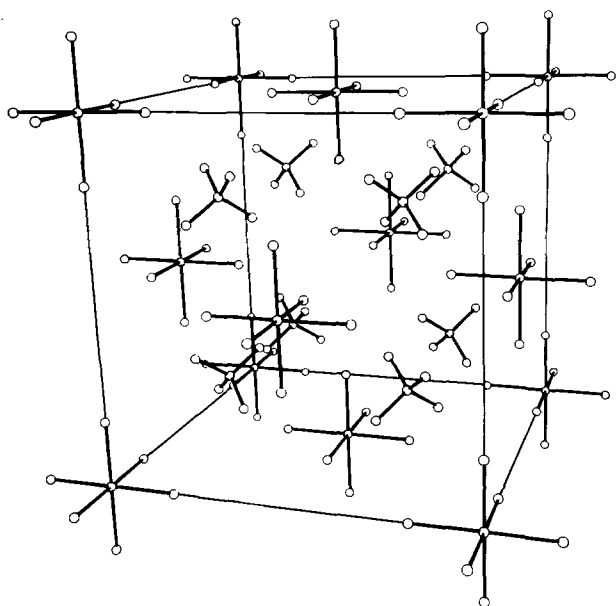


FIG. 1. Approximate structure of $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$. The positions of the hydrogen atoms are not known.⁸

positions⁸ are shown in Fig. 1, which clearly depicts octahedral $[\text{PtCl}_6]^{2-}$ and tetrahedral $(\text{C}_4\text{N})^+$ ions. The positions of hydrogen atoms are unknown.

At temperatures below room temperature the $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ crystal has previously only been examined by microscopy: Ries¹⁰ found a phase transition to a highly optic anisotropic crystal at -58°C (215 K).

B. Tellurium

For $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$ few structural details are available. As discussed in Ref. 1, it is reasonable to assume a structure similar to that of the Pt salt. Accordingly, a lattice constant of $a = 12.902 \pm 0.003 \text{ \AA}$ can be calculated from the room temperature density ($1.508 \pm 0.003 \text{ g cm}^{-3}$ ¹¹).

C. Tin

The optical isotropy¹⁰⁻¹² and all structure parameters determined by Wyckoff and Corey¹² in their room temperature x-ray investigation on the Sn salt are in accordance with the assumption of Pt and Sn compounds being isostructural. Noncubic x-ray features were also observed in their single crystal Laue photographs,¹² but were explained as due to crystalline imperfections. According to the Raman spectroscopic investigations by von der Ohe,² the structure of $((\text{CH}_3)_4\text{N})_2[\text{SnCl}_6]$ is nearly but not fully compatible with the space group O_h^5 ; small splittings of some fundamental transitions being interpreted as due to small deviations from the antiferroite lattice, probably either in the form of a distortion or a doubling of the primitive volume.² At temperatures below $\sim 149 \pm 7 \text{ K}$, after transversing the phase transition, another kind of distortion was supposed. Ries¹¹ also observed a low temperature phase.

D. General

The Cl atoms in these salts are not approximately close packed as in $\text{K}_2[\text{PtCl}_6]$.¹³ The "ionic radius" of the tetramethylammonium ion, $\sim 3.60 \text{ \AA}$,^{14,15} is simply too large. In $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$, the result is a shortest interchlorine distance between adjacent octahedra of $5.751 \pm 0.004 \text{ \AA}$,⁸ which is much larger than the ~ 3.3 and 3.6 \AA Cl-Cl distances characteristic for the "closepacked" lattice in $\text{K}_2[\text{PtCl}_6]$.¹⁵

On the other hand, the size of the $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ cell (and certainly also of the other cells) is not determined by the methyl-methyl intercation repulsion, e.g., in the center of the cell (see Fig. 1). This is clearly proved by an x-ray investigation,¹⁶ showing that $((\text{CH}_3)_4\text{N})_2[\text{PtF}_6]$ has the same structure as $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ but a lattice constant of only 11.40 \AA and a shortest methyl-methyl contact distance of $\sim 4.0 \text{ \AA}$, in accordance with the 2.0 \AA van der Waals radius of the methyl group.¹⁷ In $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ the C-C distance was $4.65 \pm 0.01 \text{ \AA}$,⁸ i.e., appreciably larger than in the hexafluoride.

Presumably, the lattice constants of the tetramethylammonium hexachlorometallates are primarily determined by the metal-halogen bond length in combination with the closest possible contact between chlorine and methyl groups, as indicated in Table I. In the best investigated structure, $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ ⁸ the chlorine-carbon distance is rather short ($r_{\text{CCl}} = 3.72 \text{ \AA}$), compared to the van der Waals radii sum of 3.80 \AA .¹⁷ The lattice constants clearly increase in the order of increasing metal-chlorine distance, and the constancy of the N-Cl distance (Table I) might be taken as proof of the chlorine-methyl interaction. Each chlorine is "in touch" with four methyl groups from different neighboring cations, and each methyl group is "in touch" with three chlorines from different octahedra, in the cubic structure. It is not obvious what deformation of this structure might take place during the phase transitions, but presumably only one short C-H...Cl "bond" will be formed per methyl group.¹⁸

III. SPECTRAL EXPECTATIONS

The vibrational spectra of the tetramethylammonium and hexachlorometallate ions have been reported separately several times.

Tetramethylammonium. It is commonly found or assumed that the entire ion on the average has T_d symmetry [for a brief summary of some x-ray structural determinations on $(\text{CH}_3)_4\text{N}^+$ salts, see Ref. 1]. Within the T_d approximate symmetry, the vibrational freedom of the $(\text{CH}_3)_4\text{N}^+$ ion is distributed on the following symmetry species:

$$\Gamma_{\text{vib}} = 3a_1 + a_2 + 4e + 4t_1 + 7t_2.$$

Frequency assignments of the modes in $(\text{CH}_3)_4\text{N}^+$ and $(\text{CD}_3)_4\text{N}^+$ have recently been estimated.³ The modes expected to occur in the range below 600 cm^{-1} are given in Table IIA, where ν_n^+ refers to the standard Herzberg notation (ν_n) with addition of a cationic + to prevent confusion with anionic ν_n^- . Symmetry types and approximate normal coordinates are indicated in parantheses.

TABLE I. Lattice constants a and metal-chlorine bond lengths r_{MCl} (uncorrected for thermal vibration) of $((\text{CH}_3)_4\text{N})_2[\text{MCl}_6]$ salts. Also shown are the N-Cl distances which can be calculated as $a\sqrt{3/16 - x/2 + x^2}$, where $x = r_{\text{MCl}}/a$ (Å, units).

M	a	r_{MCl}	r_{NCl}	r_{CCl}	Reference
Mn	12.70 ± 0.02	~2.28 ^a	~4.58		19
Pt	12.720 ± 0.004	2.293 ± 0.004	4.584 ± 0.001	3.719 ± 0.005	8
Re	12.74 ± 0.01	2.36 ^b	4.58		20
Sn	12.87	2.44	4.62		12
Te	~12.902 ± 0.003 ^c	~2.53 ^d	~4.61	~3.8 ¹	
Ce	13.05 ± 0.03	2.55 ± 0.01	4.67	3.79 ± 0.05	22
U	13.06 ± 0.01 ^e	~2.75 ^f	~4.63		11
Th	13.12 ± 0.01	~2.81 ^f	~4.66		26

^aFrom $r_{\text{MCl}} = 2.276 \pm 0.04$ Å in $\text{K}_2[\text{MnCl}_6]$.¹⁹

^bFrom $r_{\text{MCl}} = 2.353 \pm 0.004$ Å in $\text{K}_2[\text{ReCl}_6]$.²¹

^cCalculated from density.

^dFrom $r_{\text{MCl}} = 2.528 \pm 0.007$ Å in $(\text{NH}_4)_2[\text{TeCl}_6]$ and 2.525 ± 0.005 Å in $\text{Rb}_2[\text{TeCl}_6]$.²³

^eA value of $a = 12.96$ Å is quoted in Ref. 24.

^fFrom r_{MCl} in trigonal Cs salt.²⁵

Hexachlorometallate. In a regular octahedral symmetry one has

$$\Gamma_{\text{vib}} = a_{1g} + e_g + t_{2g} + 2t_{1u} + t_{2u},$$

and the frequencies of the first five modes are well established (Table II B); the ν_6 (t_{2u} , MCl_6 deformation) mode is inactive, but occurs near $\nu_5/\sqrt{2}$.

The compounds $((\text{CH}_3)_4\text{N})_2\text{MCl}_6$. In a cubic crystal, both ions maintain their high point group symmetries. The presence of two cations *per* primitive volume doubles the number of cationic modes, but at the same time the inversion center separates Raman and ir activity (Table III). Therefore, the only extra bands expected are the external lattice modes: cation translation $\nu_L^{\text{R}}(t_{2g})$ in Raman and anion-cation translation $\nu_L^{\text{IR}}(t_{1u})$ in infrared spectra.¹⁻² In a *noncubic* crystal, new bands may arise either due to a new (lower) symmetry splitting the modes already present, or because of an increased number of atoms in the primitive unit cell, giving rise to factor group (Davydov) splittings.

A note of caution should be added, however, when comparison is made between structural results derived from diffraction and spectroscopic methods. It must always be remembered that the x-ray structures represent time and space averaged structures, while the Raman and ir processes sample the domain crystal structure for time intervals in the order of 10^{-13} sec. The results based on ir and Raman spectra therefore reflect an "instantaneous" structure, provided that the correlation time of any random motion present is longer than this interaction time. This may very well be the case in our systems, yielding different structures depending on experimental method.

IV. EXPERIMENTAL

Equivalent amounts of $((\text{CH}_3)_4\text{N})\text{Cl}$ (Fluka, purum) or $((\text{CD}_3)_4\text{N})\text{Cl}$ (Merck, Sharp, & Dohme, 99 atomic % D) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, TeCl_4 , or SnCl_4 in excess hydro-

chloric solutions were mixed and concentrated in the heat (until crystals were formed) and then cooled. A mixed compound, consisting of Te doped with 25 atom % Pt was prepared similarly. Examination of the mixed crystals under a microscope of high magnifying power confirmed that the crystals were of uniform yellow color and thus homogeneous; the Pt and Te neat compounds are orange-red and yellow, respectively. (It is known that the Cs salts of $[\text{PtCl}_6]^{2-}$ and $[\text{TeCl}_6]^{2-}$ form complete solid solutions.³⁵)

TABLE II. Approximate frequencies (cm^{-1}) of internal modes based on the indicated recent literature.

A. Tetramethylammonium internal modes in the range below 600 cm^{-1} . ³			
Mode	H	D	
ν_4^* (a_2 , CH_3 torsion)	~301	213	
ν_8^* (e , C_4N deformation)	369	316	
ν_{12}^* (t_1 , CH_3 torsion)	~371	262	
ν_{19}^* (t_2 , C_4N deformation)	455	384	
B. Hexachlorometallate internals.			
MCl_6^{2-}	M = Pt ^a	M = Te ^b	M = Sn ^c
ν_1 (a_{1g} , MCl_6 str)	345	290	310
ν_2 (e_g , MCl_6 str)	320	250	235
ν_3^* (t_{1u} , MCl_6 str)	340	245	310
ν_4 (t_{1u} , MCl_6 def)	180	130	170
ν_5^* (t_{2g} , MCl_6 def)	160	130	170
ν_6^* (t_{2u} , MCl_6 def)	~115	~100	~115 ^d

^aReferences 7, 27-30.

^bSee Ref. 1.

^cReferences 2, 7, 27, 31-34.

^dAn ir band due to ν_6 has been observed in $\text{K}_2[\text{SnCl}_6]$ at 118 cm^{-1} at low temperature by the author.

TABLE III. Correlation of internal modes and unit cell modes.^a

2 isolated (CH ₃) ₄ N ⁺ ions of T _d Symmetry	Unit cell of O _h ⁵ space group			1 isolated MCl ₆ ²⁻ ion of O _h symmetry
	Internal (CH ₃) ₄ N ⁺	Externals	Internal MCl ₆ ²⁻	
a ₁ (ν ₁ ⁺ - ν ₃ ⁺)	a _{1g} (Ra) ν ₁ ⁺ - ν ₃ ⁺		ν ₁ ⁻	a _{1g} (ν ₁ ⁻)
a ₂ (ν ₄ ⁺)	a _{2g} (ia) ν ₄ ⁺			
	e _g (Ra) ν ₅ ⁺ - ν ₈ ⁺		ν ₂ ⁻	e _g (ν ₂ ⁻)
e(ν ₅ ⁺ - ν ₈ ⁺)	t _{1g} (ia) ν ₉ ⁺ - ν ₁₂ ⁺	{ ν _{libratory} ⁺ ν _{libratory} ⁻		
	t _{2g} (Ra) ν ₁₃ ⁺ - ν ₁₉ ⁺	ν _{translatory}	ν ₅ ⁻	t _{2g} (ν ₅ ⁻)
	a _{1u} (ia) ν ₄ ⁺			
t ₁ (ν ₉ ⁺ - ν ₁₂ ⁺)	a _{2u} (ia) ν ₁ ⁺ - ν ₃ ⁺			
	e _u (ia) ν ₅ ⁺ - ν ₈ ⁺			
t ₂ (ν ₁₃ ⁺ - ν ₁₉ ⁺)	t _{1u} (ir) ν ₁₃ ⁺ - ν ₁₉ ⁺	ν _{translatory}	ν ₃ ⁻ , ν ₄ ⁻	t _{1u} (ν ₃ ⁻ , ν ₄ ⁻)
	t _{2u} (ia) ν ₉ ⁺ - ν ₁₂ ⁺	ν _{libratory} [±]	ν ₆ ⁻	t _{2u} (ν ₆ ⁻)

^aThe notation of modes ν_n⁺ and ν_n⁻ differs from the one proposed by von der Ohe,² although the relation is obvious. Ra, ir, and ia denote Raman, infrared, and no activity.

The purity of ((CH₃)₄N)₂[PtCl₆] was checked by analysis. Found (calculated) percentages were, C = 17.15 (17.28); H = 4.28 (4.35); N = 5.21 (5.04); Cl = 38.05 (38.25).

The experimental methods used in obtaining spectra at room and lower temperatures have been described in detail.¹ However, the far ir interferometric technique was improved in two ways.

(i) The rather poor heat conductivity of pressed disks of polyethylene was overcome by covering the disk surface with nujol and pressing it onto a pure wedged silicon plate (obtainable from Topsis, Inc., Frederikssund, Denmark) in good contact along the whole periphery with the variably cold junction of the cryostat. The temperature was determined by an iron-constantan thermocouple.

(ii) The double sided interferograms were corrected for drift and apodized using a squared sinus function prior to Cooley-Tukey fast Fourier transformation, done in a large computer with plotting facilities.

The true temperatures in the Raman experiments were estimated by recording the ν₅⁻ mode on both sides of the exciting line and calculating the temperature T from the ratio of integrated intensity. The formula used was

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = \left(\frac{\nu_0 + \nu}{\nu_0 - \nu} \right)^4 \exp\left(\frac{-h\nu}{kT} \right),$$

where ν₀ and ν are the laser and ν₅⁻ frequency, h and k are Planck's and Boltzmann's constant, respectively. The estimated error limit (± 10 K) was mainly caused by uncertainties in determining the baselines. The temperature determined in this way was generally a few degrees higher than that of the copper block surrounding the same ampul, due to the heating effect of the laser beam.

V. RESULTS AND DISCUSSION

A. General

The low frequency Raman and ir spectra are shown in Figs. 2-4. The ir spectra are averages of two or several recordings. The bands are given in Tables IV and V. The Raman region above 500 cm⁻¹ looked much like Fig. 11 of von der Ohe's first paper² and Fig. 1 of Ref. 3 and is not depicted.

A comparison of the spectra at room and liquid-nitrogen temperatures (Figs. 2-4) clearly shows the expected presence of phase transformations, independently of which kind of metal is present. The usual improvement in resolution and minor shifts in frequency and intensity are seen as well. All the observed changes in spectra with temperature were reversible and gradual, probably with some small hysteresis.

The measurements are generally in accordance with the previous results at room temperature: Adams and Morris⁷ found for M = Pt(Sn): ν₁⁻ = 339(307), ν₂⁻ = 315(-), ν₃⁻ = 326(298), ν₄⁻ = 182(172), ν₅⁻ = 166(-), ν₆⁻(calculated) = 77(-), and ν₇⁻ = 90(76) cm⁻¹; Wharf and Shriver³¹ found for M = Sn: ν₁⁻ = 312, ν₂⁻ = 235, ν₃⁻ = 309, ν₄⁻ = 168, ν₅⁻ = 165, and ν₆⁻(calculated) = 112 cm⁻¹. The consistency in the case of tellurium was also good.² Test runs showed that the room and low temperature Raman results of von der Ohe for ((CH₃)₄N)₂[SnCl₆] were reproducible as well, and therefore his results are incorporated in Table IV, and reference is made to figures in his papers.²

B. Assignments

The importance of correct assignments in understanding the nature of the crystals and their transformations clearly cannot be over emphasized (cf. the Introduction).

The spectra of the mixed Te:Pt compound (Table V) show that the compound spectroscopically behaved very

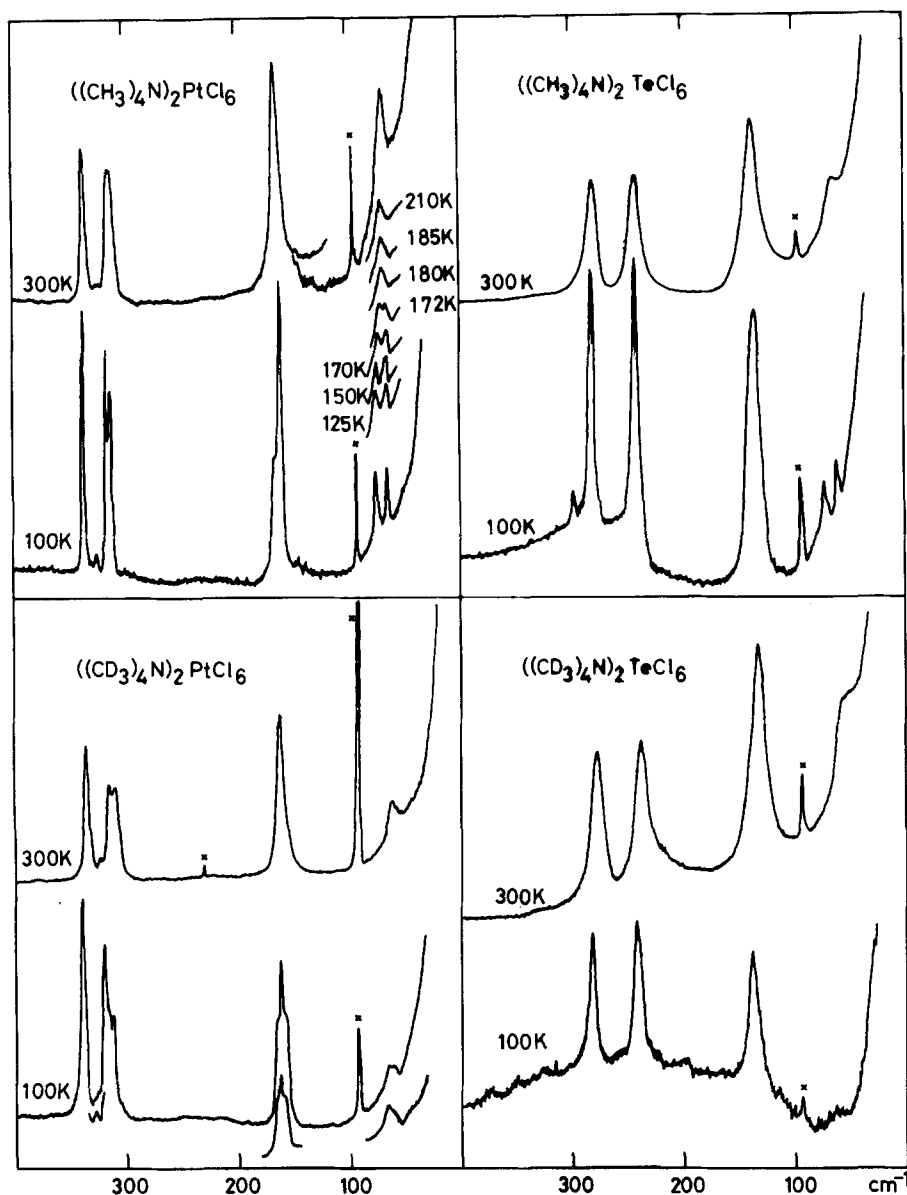


FIG. 2. Temperature dependency of Raman scattering spectra. Powdered samples in glass ampuls. Excitation: ~ 50 mW Kr^+ laser line of 647.1 nm wavelength. Plasma lines escaping filtration are indicated with χ . Resolution 2 cm^{-1} .

nearly like a physical mixture. Therefore, the approximation of dividing the crystal normal modes into internal cationic modes, anionic modes, and external ionic modes (translations and librations) as expected is a good one in these compounds.

In this fortunate situation the assignments of the cationic internal vibrations above 350 cm^{-1} can be transferred directly from the investigation of the normal and deuterated tetramethylammonium ion in aqueous solution,³ and hence need no further discussion. Also for most of the anionic internals there is little doubt about their position (Table II B). Problems arise in the region near 300 cm^{-1} , which was difficult to interpret. The modes expected close to 300 cm^{-1} were: $\nu_2^-(M = \text{Pt})$, $\nu_1^-(M = \text{Sn})$, $\nu_8^+(\text{CD}_3)_4\text{N}$ and $\nu_4^+(\text{CH}_3)_4\text{N}$. The bands near 300 cm^{-1} in $(\text{CH}_3)_4\text{N}_2[\text{TeCl}_6]$ must therefore be assigned to ν_4^+ and those of $(\text{CD}_3)_4\text{N}_2[\text{TeCl}_6]$ to ν_8^+ . This shows unequivocally that methyl torsional modes can indeed be observed in infrared and Raman in these kinds of compounds, as was supposed in Ref. 1. In itself, this is an

interesting observation because relatively little is known³ about the inactive methyl torsions in neopentane-type molecules $(\text{CH}_3)_4\text{X}$; $\text{X} = \text{C}, \text{Si}, \text{Pb}, \text{N}^+, \text{As}^+$, etc.

With these results in mind, a probable assignment for the platinates and stannates was worked out (Table IV), based on the criterion that $[\text{MCl}_6]^{2-}$ modes should be unaffected by deuteration and have frequencies near values known for closely related crystals (Table II B). Note that the clear situation in the tellurates made it easy to separate ν_4^+ or ν_8^+ from ν_2^- in $[\text{PtCl}_6]^{2-}$ or ν_1^- in $[\text{SnCl}_6]^{2-}$. A similar situation possibly occurred in $(\text{CH}_3)_4\text{N}_2[\text{UCl}_6]$, in which ν_1^- is near 300 cm^{-1} : The presence² of two Raman bands at 297 and 303 cm^{-1} below T_c can be nicely explained as due to ν_1^- and ν_4^+ . Although this interpretation was mentioned, von der Ohe considered these two bands as caused by ν_1^- via cell doubling.

The assignment of ν_4^+ to low temperature ir bands at $\sim 215 \text{ cm}^{-1}$ in deuterated compounds (not observable in

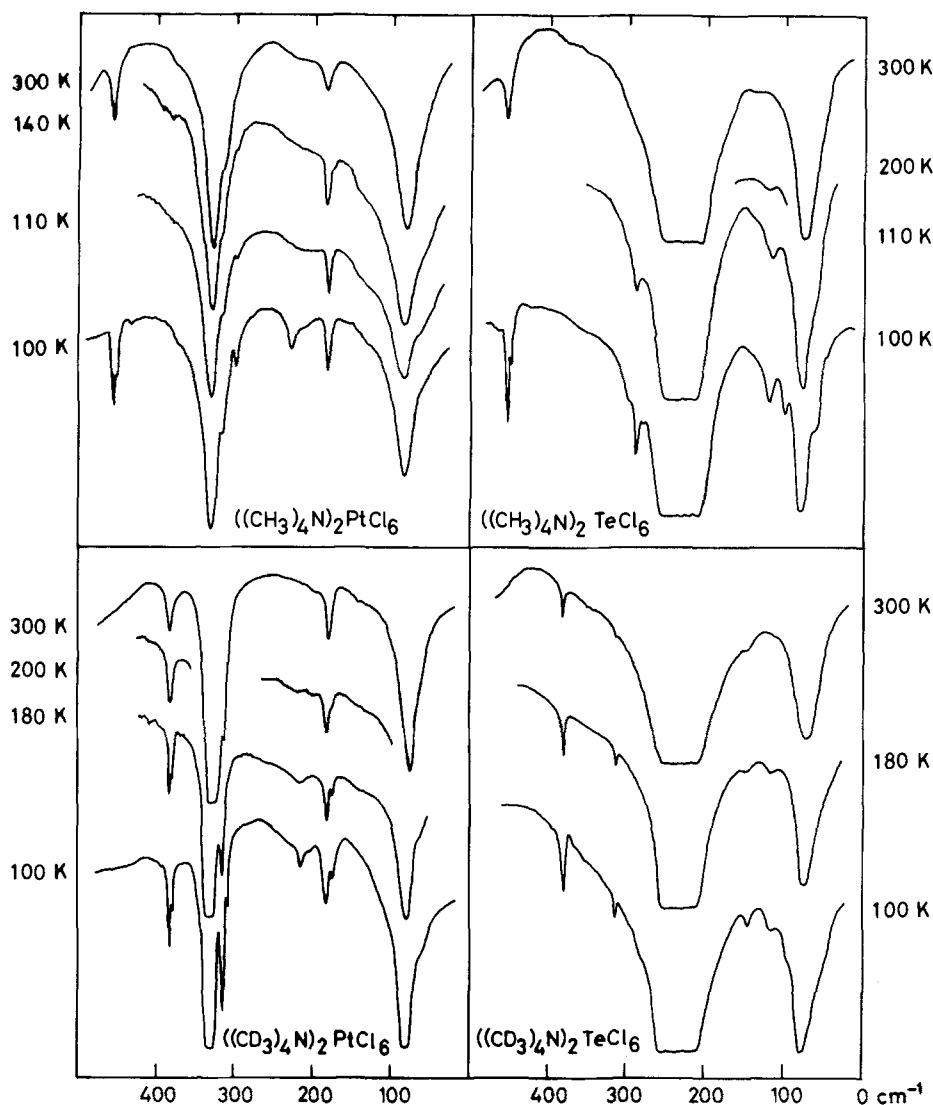


FIG. 3. Temperature dependency of interferometric far infrared absorption spectra. Powder samples in pressed polyethylene disks (see Experimental). Resolution 2 cm^{-1} .

tellurate due to ν_3^+) is in accordance with the expected value.³ The hydrogen compounds, wherein ν_4^+ is expected at $\sim 300 \text{ cm}^{-1}$,³ also had a somewhat similar band at $\sim 230 \text{ cm}^{-1}$, where no band is expected. This band is probably a component of ν_4^+ , although the frequency is rather low. Both the ~ 215 and $\sim 230 \text{ cm}^{-1}$ bands showed a considerable variation in intensity and position. A similar behavior was found for a strong translatory ir band near 229 cm^{-1} in ordinary disordered H_2O -ice condensed on a window at $\sim 100 \text{ K}$.³⁶ We exclude our bands from being due to ice, because of the vacuum in the instrument and because the frequency of H_2O -ice should not depend on the deuteration or the kind of metal in the examined compound. Internal zeolitic water (which might be suspected to be present in the empty space in the center of the unit cell) might have similar frequencies as in ice, modified slightly by different couplings to CH_3 and CD_3 groups, but chemical analyses showed that $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ contained less than 0.3% water, and the compounds have not been reported to crystallize as hydrates. Therefore, the bands are most likely due to ν_4^+ (a_{2g} or a_{2u}), in spite of the low frequency.

At 300 K, the assignment of bands below 100 cm^{-1} is clear: There is one lattice mode in ir, $\nu_L^{\text{ir}}(t_{1u})$, and one

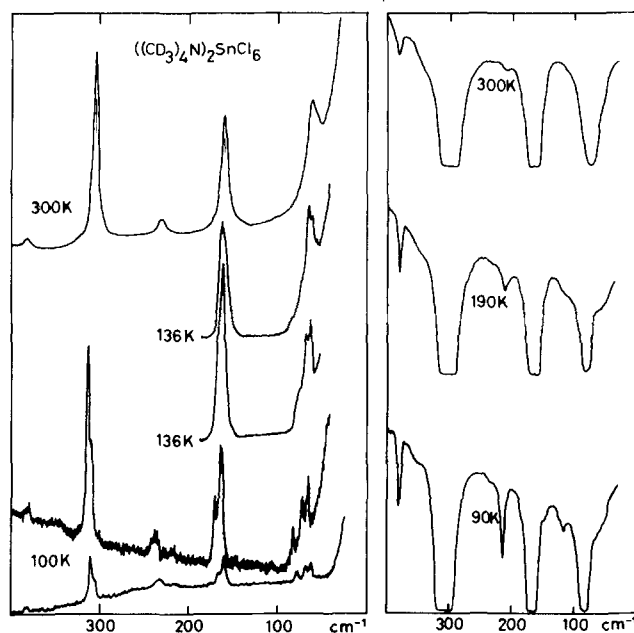


FIG. 4. Raman spectra (left) obtained with $\sim 50 \text{ mW}$ of Ar^+ laser line of 514.5 nm wavelength. Note the hysteresis at 136 K . Conditions explained in Fig. 2. For hydrogen compound consult Ref. 2. Infrared spectra (right) as in Fig. 3.

TABLE V. Frequencies (cm^{-1}) and qualitative intensities of bands observed in 25 atom% platinum-doped $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$, showing lack of excessive external couplings, cf. Table 4.^a

Mode	300 K		100 K	
	Pt	Te	Pt	Te
ν_1^r	338m	280s	338m	282s
ν_3^r	<u>~ 327sbr</u>	<u>~ 234sbr</u>	<u>~ 331sbr</u>	<u>~ 238sbr</u>
ν_2^r	313m	<u>312w</u>	315m	<u>314w</u>
ν_4^r		<u>182wsh</u>		<u>182w</u>
ν_5^r	162w	139s	163w	136s
ν_4^t				292m
ν_L^{tr}		<u>77sbr</u>		<u>81sbr</u> <u>~ 64sh</u>

^aBands underlined were observed in ir. Intensity codes: s = strong, m = medium, w = weak, sh = shoulder, br = broad.

in Raman spectra, $\nu_L^{\text{ra}}(t_{2g})$. At low temperatures, the situation is complicated by the appearance of new bands which probably also are lattice modes, – and in tellurates and stannates ν_5^r is seen around 100 cm^{-1} in the infrared.

The deuteration shift in frequency for a ν_L^{ra} translatory mode, assuming harmonic isotope-independent restoring forces, should follow $(\nu^{\text{D}}/\nu^{\text{H}})_{\text{translation}} = \sqrt{M^{\text{H}}/M^{\text{D}}} = 0.928$ (where M^{H} stands for mass of $((\text{CH}_3)_4\text{N})^+$ and analogously for M^{D}). This ratio is in close agreement with the values observed at room temperature. The frequency shift of a cation librational mode on deuteration can be approximately given, noting that the ratio $I^{\text{H}}/I^{\text{D}}$ (where I is the moment of inertia of the cation around one of its S_4 axes) is relatively insensitive to geometry. Then, assuming standard staggered conformation and a harmonic isotope-independent approximation to the librational potential barrier, one has $(\nu^{\text{D}}/\nu^{\text{H}})_{\text{libration}} = \sqrt{I^{\text{H}}/I^{\text{D}}} = 0.86$. No modes showing such large shifts were observed and hence cation librational modes must be inactive.

C. Phase transitions

The phase transformation in $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ occurs at 175 ± 5 K, clearly characterized by the sudden (first order) appearance of a new band in the low frequency Raman region (Fig. 2). In a polarizing petrographic microscope, with a low-temperature stage equipped with a thermoelement accurately calibrated by using a number of substances with known transformation points, the compound transformed at 173.6 ± 1 K, indicating that Ries's result¹⁰ was 41° too high. An orange-red large single crystal, which allowed a 6471 Å laser beam to pass without appreciable loss of polarization, lost its transparency (irreversibly) and turned bright lemon-yellow (reversibly) by passing the transformation. It was impossible to measure clean polarized Raman spectra of the low temperature phase, probably due to the formation of microcrystalline domains and internal fractures. The attempts showed that some orientation of the domains was preserved and that the Raman bands

at 340, 168, and 67 cm^{-1} were distinctly polarized. The intensity of the bands at 319 and 315 cm^{-1} did not depend on polarization and hence must belong to a symmetry different from that of the former bands and the bands at 164 and 77 cm^{-1} , which changed somewhat with the setting of the analyzer.

The phase transition also seemed to occur in $((\text{CD}_3)_4\text{N})_2[\text{PtCl}_6]$, but unfortunately the effect on the spectra was so small that it was impossible to estimate the transition temperature accurately. It might not be much different from 190 K, according to the ir results. In the tellurates the transition was difficult to introduce, probably because of low equilibrium points (~ 110 K), and the deuterated salt did not transform during any Raman experiment (at low temperature fluorescence was a problem). The bright yellow tellurates turned faintly yellow to white at 100 K.

The transformation temperatures given by von der Ohe² for $((\text{CH}_3)_4\text{N})_2[\text{SnCl}_6]$ (142 K upon cooling and 156 K upon heating) are in accordance with our average result which was $T_c = 145 \pm 10$ K. The deuterated salt behaved qualitatively similar to the hydrogen compound, but has a lower transformation point $T_c = 136 \pm 10$ K, as determined in several runs besides the two shown in Fig. 4.

Hence, the deuterated hexachlorostannate seems to require cooling to a lower temperature than the protonated compound to introduce the transformation into the low temperature modification. This feature is the opposite of what was expected and hence is quite interesting. The protonated tellurate compound likewise seems to transform more easily needing less cooling than the deuterium one.

The dependence of the transformation temperature (or ease of transition) on deuteration shows that the methyl groups are involved in the transition, a conclusion also reached by von der Ohe.² The discussion in Sec. II.D showed the methyl groups to be "in touch" with the chlorine atoms. Normally, methyl protons are not known to have any tendency to form what is loosely

defined as "hydrogen bonds,"^{37,38} but the protons on a $(\text{CH}_3)_4\text{N}^+$ ion might have some slight C-H...Cl hydrogen bonding ability^{15,39} at low temperatures due to delocalization of the positive charge. Depending on the system, deuterium is known to form weaker or stronger "hydrogen bonds" than hydrogen under "similar" conditions.³⁸ Therefore, in our compounds more or less thermal energy (higher or lower temperature) might be required to stabilize C-D...Cl bonds relative to hydrogen.

It is therefore suggested that the transitions occur due to the formation of weak hydrogen bonds at low temperatures, probably at the same time "freezing out" relatively free methyl rotation. These hydrogen bonds might be the cause of the distortion of the cubic structure of the compounds. Within this hypothesis the transitions should be of order-disorder type, with methyl rotational disorder in the high temperature phase. This disordering might not be completely random at room temperature, thus causing the small deviations from cubic symmetry, discussed in the next section.

D. Symmetry distortions

Having established the assignments of the bands, it can be concluded, as previously done for Te and Sn,¹⁻² that the features of the room temperature spectra are closely but not fully compatible with the O_h^5 structure. For the platinates, the small deviation present at 300 K which was also evident in x-ray and other experiments⁸ causes (i) ν_2 to be broad or split, (ii) weakly ir active, and (iii) ν_3 to be weakly Raman active. These features are preserved and reinforced below T_c . The room temperature x-ray Weissenberg photographs⁸ indicated that a weak superstructure with two or more formula units in the unit cell might be present. Therefore, it is difficult to use these splittings for a reliable deduction of the structural symmetry.

Nevertheless, it can be argued that the absence of couplings in the mixed Te:Pt crystal (where the $[\text{TeCl}_6]^{2-}$ and $[\text{PtCl}_6]^{2-}$ internal mode frequencies, band shapes, and splittings seemed virtually independent of doping, even at ~ 100 K), indicates that the breakdown of the cubic selection rules most probably corresponds to a lowering of the local $[\text{MCl}_6]^{2-}$ site symmetry, rather than an increase in the number of $[\text{MCl}_6]^{2-}$ octahedra in the primitive unit cell.

Following this idea, we investigated, one by one, for all the well-known subgroups of O_h ,^{40,41} whether (i) $\nu_2(e_g)$ was split and (ii) had an ir active component, and (iii) whether $\nu_3(t_{1u})$ was allowed in Raman. The possibility of LO-TO splitting⁴² of ν_2 was not considered because the weak ir activity of ν_2 indicates a small polarizing field and hence a small LO-TO splitting. Other complications might be present too, as discussed in Ref. 43, but are not considered important.

In this way, the following site symmetry point groups were found for $[\text{PtCl}_6]^{2-}$ at room temperature:

D_{2d} , C_{4v} , S_4 , C_4 , D_2 , C_{2v} , C_2 , C_s , and C_1 .

The absence of any cubic or rhombohedral group in the

list is in accordance with the weak tetragonal distortion in lattice parameters indicated by the x-ray results.⁸

In the low temperature phase, further $\nu_{19}(t_{2g})$, $\nu_4^-(t_{1u})$, and $\nu_5^-(t_{2g})$ were split into doublets or triplets, $\nu_4^-(a_{1u}$ or $t_{2u})$ appeared in ir and a new Raman band was seen below 100 cm^{-1} . The most useful observations were (i) the three components of ν_5^- in $((\text{CD}_3)_4\text{N})_2[\text{PtCl}_6]$ and (ii) the strongly polarized behavior characteristic of totally symmetric modes which was observed for the 168 cm^{-1} component of ν_5^- in the hydrogen compound. These two mutually consistent observations exclude any tetragonal site symmetry, hence indicating that the Pt site symmetry in both isotopic low temperature phases is D_2 , C_{2v} , C_2 , C_s , or C_1 .

The local symmetries of all possible sites in all space groups are well known^{40,41,44} and therefore all space groups which contain the site symmetries deduced above can in principle be listed (a quite long list). Within the reasonable further assumption that the $[\text{PtCl}_6]^{2-}$ site symmetry is isomorphous with the Laue class symmetry (= the point group of the factor group), the number of space groups is quite limited. For a C_{4v} site symmetry, e.g., two space groups C_{4v}^1 ($P4mm$) and C_{4v}^2 ($I4mm$) are found,⁴⁴ the former cell containing four formulas and the latter being one of the equal cell ($Z_{\text{primitive}} = 1$) subgroups of the antifluorite lattice, all of which have been listed by von der Ohe.²

Unfortunately, it is impossible to deduce that much information about the tellurate and stannate site symmetries. It seems as if a center of symmetry is present and that they are more nearly cubic O_h^5 than the platinates at room temperature, consistent with their lower transformation tendency. Yet, the totally symmetric (a_{1g} in T_d) skeletal CN stretching band (at 752 cm^{-1}) was split into a doublet in the Raman spectrum² of the high temperature phase of $((\text{CH}_3)_4\text{N})_2[\text{SnCl}_6]$ (at 200 K), and a weak Raman band at 86 cm^{-1} was seen (ν_2^{ir} ?), indicating cell doubling or loss of centrosymmetry.² The low temperature phases of the tellurates might be tetragonal according to observed splittings while the low temperature stannate phases probably are of orthorhombic or lower symmetry, because of the presence of three nearby components of the Raman active (cubic t_{2g}) cationic translatory mode ν_L^{Ra} . Von der Ohe² did not assign the Raman band of lowest frequency to a ν_L^{Ra} component (due to the lack of "deuterated" results) and therefore did not exclude tetragonal symmetry. The compound $((\text{CH}_3)_4\text{N})_2[\text{ZrCl}_6]$ behaved² qualitatively like the stannate in both phases, whereas $((\text{CH}_3)_4\text{N})_2[\text{UCl}_6]$ had a detailed behavior of its own.

Generally, the number of splittings for the majority of the cubic degenerate modes were lower than predicted from the site symmetries. This is not unexpected, because of the limited resolution and the possibility of "accidental" degeneracy. The doubling or quadrupling of the cell, which probably takes place in some of the phases, does not split the mode frequencies (by Davydov splitting) to any great extent.

The implication is that the bonding in and geometry of the $[\text{MCl}_6]^{2-}$ "octahedra" is influenced somewhat (hydro-

gen bonding?) by the methyl groups of the surrounding cations and vice versa, but there is no evidence of interaction between neighboring $[MCl_6]^{2-}$ ions. In conclusion, all examined tetramethylammoniumhexachlorometallates seem to be able to perform phase transformations at low temperatures. The transition temperatures and detailed symmetries of the phases depend on the metal M.

VI. CONCLUSIONS

The experiments performed during this work have been analyzed in order to unravel the phase transformations of tetramethylammoniumhexachlorometallates. As a first step towards this, the spectra have been carefully assigned. This revealed the presence of methyl torsional bands in the vibrational spectra at low temperatures; estimations of possible site symmetries of $[MCl_6]^{2-}$ was deduced. Reasons for our belief, that the transitions might be of the order-disorder category via the presence of weak C-H...Cl hydrogen bonding at low temperature, have been presented. It is hoped that certain neutron diffraction experiments presently in progress may clarify this situation.

VII. SUMMARY

During recent years the research activity concerning phase transitions in $A_2[MX_6]$ crystals has been steadily growing. The $A_2[MX_6]$ family of crystals is a very large one,⁴⁵⁻⁴⁸ allowing for wide substitution in A (alkali and other monovalent metals, ammonium and substituted ammonium ions of increasing complexity) and in MX_6 (many hexahalides of tetravalent metals exist, in most cases comprising all halogens).^{45,46} Examples of phase transitions in alkali metal hexachlorometallates are discussed in Refs. 1, 34, 49 and references therein. Many substituted ammonium compounds have been known for a long time, see, e.g., Ref. 10, and their phase transitions are recently becoming well characterized.

Most notable is perhaps the work⁵⁰⁻⁵⁴ on the rhombohedral methylammonium hexachlorostannate and platinite, $(CH_3NH_3)_2[MCl_6]$, $M = Sn, Pt$, which transform at 156 and 125 K, respectively. The experimental methods used were ³⁵Cl NQR spectroscopy, DTA, PMR,⁵⁰⁻⁵² electronic absorption, Raman⁵³⁻⁵⁴ and infrared spectroscopy,⁵⁵ and x-ray diffraction.⁵²⁻⁵³ It was concluded that rigid methylammonium ions performed very free rotation around the C_3 axis in both phases,⁵⁰⁻⁵² that hydrogen bonding was weak,^{51,55} that the low-temperature x-ray space group symmetry and structure was unchanged ($R3m$) within experimental accuracy⁵² and that the phase transitions probably are related to soft modes involving small rotations of $[MCl_6]^{2-}$ octahedra, preserving the center of symmetry.⁵⁰⁻⁵² The Raman spectra of both phases of $(CH_3NH_3)_2[SnCl_6]$ have been measured⁵⁴ and showed splittings at low temperature, analogous to our results.

Interesting is also the peculiar Raman spectra⁵⁴ of the compound $((CH_3)_3CNH_3)_2[SnCl_6]$, both at room and low temperature. The tertiary butylammonium ion is isomeric with the tetramethylammonium ion (exchange of

C and N atoms). Apparently, the hexachlorostannate salt of $((CH_3)_3CNH_3)^+$ also seems to have a phase transition (judging from the Raman spectra, Fig. 2 of Ref 54, but most remarkably both phases had no obvious ν_1 band at all.

ACKNOWLEDGMENT

The author is very grateful to the Technical University of Denmark for the economic support received and to NATO for the research grant No. 1245. Professor David M. Adams, Department of Chemistry, The University, Leicester, England, is thanked for helpful discussions, and Dr. J. Rose-Hansen, University of Copenhagen, for the low temperature microscopic examination.

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