BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1809—1815 (1968)

Nuclear Quadrupole Resonance Study of Antimony Pentachloride and Its Phase Transition

Hideaki CHIHARA, Nobuo NAKAMURA, Hideo ŌKUMA
and Syûuzô SEKI
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

(Received February 16, 1968)

A phase transition was found in solid antimony pentachloride at 212°K by the nuclear quadrupole resonance and the differential thermal analysis. In the high temperature solid phase, five resonance lines were observed that were all assigned to antimony resonances and that were dependent on temperature only slightly. The quadrupole coupling constant of ^{121}Sb was 84.54±0.01 MHz (asymmetry $\eta=1.0\pm0.3\%$). Chlorine resonances were not detected above the transition point. In the low temperature phase, many resonance lines were observed due both to chlorine and antimony; the latter gave the coupling constant for ^{121}Sb 186.43±0.03 MHz ($\eta=79.54\pm0.02\%$) and 172.8±0.3 MHz ($\eta=79.2\pm0.3\%$). There are two nonequivalent sites for antimony. The structure in the two solid phases was suggested as being trigonal bipyramidal above 212°K and a dimerized Sb_2Cl_{10} bridged by two chlorine atoms with hexa-coordinated antimony atoms below 212°K.

Pentahalides of phosphorus and its homologues are an interesting group of compounds in that they may exist in ionic or molecular form or in both forms in the solid state.[1] Other compound such as $NbCl_5$ exists in a dimeric molecular structure.[2a]

Phosphorus pentachloride dealt with in our previous paper exists in an ionic structure $PCl_4^+\cdot PCl_6^-$ though a molecular solid does form as a metastable modification.[3] On the other hand antimony pentachloride has been shown to assume the trigonal bipyramidal structure as shown in Fig. 1 by the X-ray diffraction study.[4] Since antimony is a quadrupolar nucleus, it was also hoped to detect antimony resonance by virtue of small distortion of the bipyramid. The result turned out that the solid exhibits an unusual phase transition by which molecules are dimerized at lower temperatures. The present paper describes the results of the nuclear quadrupole resonance (NQR) of chlorine and antimony in solid antimony pentachloride together with differential thermal study of the phase transition.

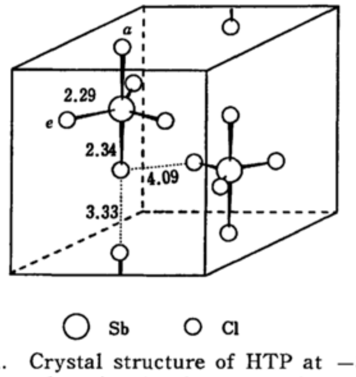


Fig. 1. Crystal structure of HTP at −30°C.[4] The numbers in the figure are internuclear distances in Å and *a* and *e* stand for axial and equatorial chlorine atoms.

In the rest of the present paper, we identify the chlorine atoms in the basal plane as 'equatorial' chlorines and the other two lying on the threefold axis of the molecule as 'axial' chlorines (see Fig. 1).

Experimental

Antimony pentachloride (Wakô Pure Chem. Ind., Ltd.) was distilled at 79°C under reduced pressure of 30 mmHg, condensed into the NQR cell and sealed off under reduced pressure. A small thermal anomaly caused by impurities, probably elementary chlorine, was observed at 170°K by the differential thermal analysis (DTA)[5] of the commercial speci-

---

[1] R. R. Holmes, *J. Chem. Education*, **40**, 125 (1963).

[2] a) R. W. G. Wyckoff, "Crystal Structures," 2nd ed., Vol. 2, Interscience, New York, N. Y. (1964), p. 171. b) *Ibid*., Vol. 3. c) *Ibid*., Vol. 1, p. 331.

[3] H. Chihara, N. Nakamura and S. Seki, This Bulletin, **40**, 50 (1967).

[4] S. M. Ohlberg, *J. Am. Chem. Soc.*, **81**, 811 (1959).

[5] H. Suga, H. Chihara and S. Seki, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **82**, 24 (1961).

men as obtained. Purification removed such a thermal anomaly and gave the melting point of 274.7±0.2°K. This is to be compared with 276.2°K found in the literature.⁶⁾ Both impure and purified specimens were used for NQR experiments for the reason to be described in the following section.

A Dean type super-regenerative spectrometer was used for measurements of chlorine and antimony resonances. The resonance was searched between 7.5 and 60 MHz, the maximum sensitivity of the spectrometer being in the range 25 to 45 MHz.

Digital frequency determinations and the cryostat have been described elsewhere.³⁾ The accuracy of the frequency determination was within 0.001 MHz.

Results and Discussion

General Features of Phase Transition. A thermal anomaly in solid phase was found at 211.8±0.4°K by the DTA as shown in Fig. 2. It is convenient to denote the phase below the transition as the low temperature phase (LTP) and that above as the high temperature phase (HTP).

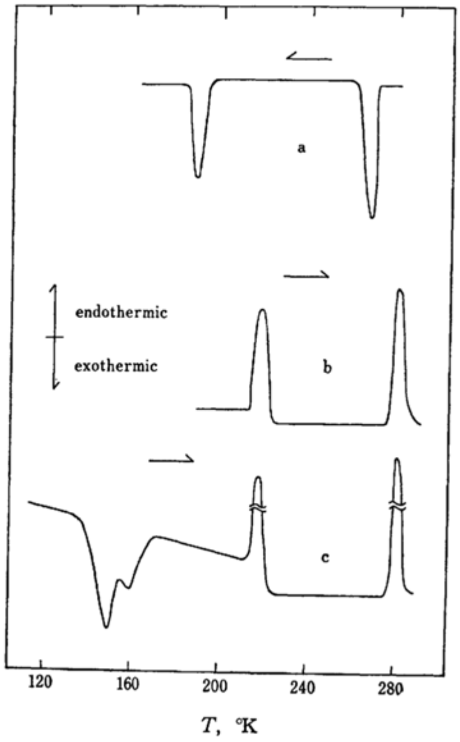


Fig. 2. The DTA curves of $SbCl_5$.
a : slow cooling curve
b : heating curve of slowly cooled sample
c : heating curve of rapidly cooled sample. The ordinate scale is enlarged 5 times of that for curve b. The transition and the melting point coincide with those of curve b.

A typical DTA curve in the cooling direction is shown in Fig. 2a, where the HTP is supercooled down to about 190°K for an impure sample, and to still lower temperature for a pure one. The LTP is superheated only by about 1°.

The area of the transition peak under the DTA curve b in Fig. 2 was about half of that of the melting peak where 2.4 kcal/mol is absorbed.⁶⁾ This phase transition is probably of the first order or of the isothermal type because there is a marked hysteresis in transition temperature⁷⁾ and also because NQR frequencies change abruptly at the transition as discussed later in this paper.

Figure 2c is the DTA curve (at the heating rate 10°/min) of $SbCl_5$ quenched by immersion of the liquid into liquid nitrogen (several minutes to reach 77°K); here exothermic peaks were observed before the phase transition took place. The exotherm occurred in two stages, one peak at 150°K and the other at 160°K. These peaks were displaced to lower temperatures by about 10° respectively at a slower rate of heating (1°/min) and the second peak became a shoulder of the first.

It is probable that $SbCl_5$ forms a glass by rapid cooling of the liquid to 77°K although a search for a glass transition was not successful. The exothermic peaks may be attributed to the crystallization of the glass into the LTP. This crystallization is likely to occur in the sequence

$$\text{glass} \longrightarrow \text{HTP (supercooled)} \longrightarrow \text{LTP}$$

in accordance with law of successive transformation.⁸⁾ In support of this view, the relative area under the exothermic peaks in Fig. 2c was found to be 1 : 2.1 in comparison with 1 : 2.3 for the ratio of the areas of transition and fusion. There is an indication that a quenched specimen also contains a certain amount of LTP because the exothermic peak area is much smaller than the endothermic peak area. A quantitative estimate of that amount, however, did not seem meaningful.

The phase transition appeared to be sluggish particularly in the cooling direction. Thus the resonance lines of LTP were broad and weak after first cooling through the transition point although the HTP resonances

---

6) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," circular of NBS 500, NBS, U. S. Government Printing, Washington (1952).

7) D. G. Thomas and L. A. K. Staveley, *J. Chem. Soc.*, **1951**, 2572.

8) See *e.g.* R. S. Bradley, *Quart. Revs.*, **5**, 315 (1951).

disappeared abruptly. It was therefore necessary to anneal the LTP, before the measurements on the LTP were started, by subjecting it to heating and cooling cycles across the transition point. Thus, the sample was first cooled to just below the transition temperature while watching for the disappearance of an HTP signal and then warmed up so that the signals from both phases could be seen. The temperature was then lowered slightly to aid in crystallization of LTP. Such cycle was repeated several times until the resonance lines of LTP were observed distinctly. This procedure enhanced the intensity of the chlorine resonances, but the antimony resonances were generally much broader and weaker than the chlorine resonances.

Although the resonance frequencies were independent of the purity of the sample, the line intensity of unpurified sample was stronger than that of pure one probably because the rate of the transition was faster. Annealing was more effective for an impure sample. Therefore, the frequencies were determined by use of unpurified specimen.

One outstanding feature of the transition is the large abrupt change in the antimony resonance frequencies at the transition point; in fact it is so large that it could hardly be accounted for merely by a change in the crystal structure.

All available evidences are consistent with a possibility that the transition is accompanied with a change in the valence state of the antimony atom. It is perhaps significant to note that one of the HTP resonance lines (ν_5') was observed in supercooled HTP, even at 180°K, about 30° below the transition point. Its frequency was practically independent of the temperature, remaining the same as that at the transition point (25.391 MHz). Similarly, the intensity did not change until the transition started. The intensity decrease was used to monitor the progress of phase transition.

High Temperature Phase. Five strong NQR lines were observed in HTP between 7.5 and 40 MHz as listed in Table 1a together with their assignments. The frequency values agree well with those reported by Schneider and DiLorenzo[9] within experimental errors. All of these lines were ascribed toantimony nuclei. The quadrupole coupling constants e^2Qq/h and asymmetry parameters η are calculated[10,11] and listed in Table 1b.

TABLE 1 a. RESONANCE FREQUENCIES IN HTP AND THEIR ASSIGNMENTS

Resonance line	Frequency (MHz) 215°K	Frequency (MHz) 274°K	Assignment
ν_1'	——	7.71*	$^{123}Sb(3/2 \leftrightarrow 1/2)$
ν_2'	——	12.682	$^{121}Sb(3/2 \leftrightarrow 1/2)$
ν_3'	15.415	15.396	$^{123}Sb(5/2 \leftrightarrow 3/2)$
ν_4'	23.130	23.096	$^{123}Sb(7/2 \leftrightarrow 5/2)$
ν_5'	25.389	25.361	$^{121}Sb(5/2 \leftrightarrow 3/2)$

* Accurate to within 0.01 MHz

TABLE 1 b. QUADRUPOLE COUPLING CONSTANTS AND ASYMMETRY PARAMETER OF ANTIMONY IN HTP AT 274°K

	$\left\lvert \frac{e^2Qq}{h} \right\rvert$ (MHz)	η(%)
^{121}Sb	84.54 ± 0.01	1.0 ± 0.3
^{123}Sb*	107.78 ± 0.01	1.4 ± 0.4

* Calculated from ν_3' and ν_4'. The calculated value of ν_1' lies at 7.704 ± 0.004 MHz and agrees well with the observed value in Table 1a.

As expected from the trigonal bipyramidal molecular structure of the HTP (Fig. 1), the coupling constants of central atoms (antimony nuclei) are small but they do not vanish be-

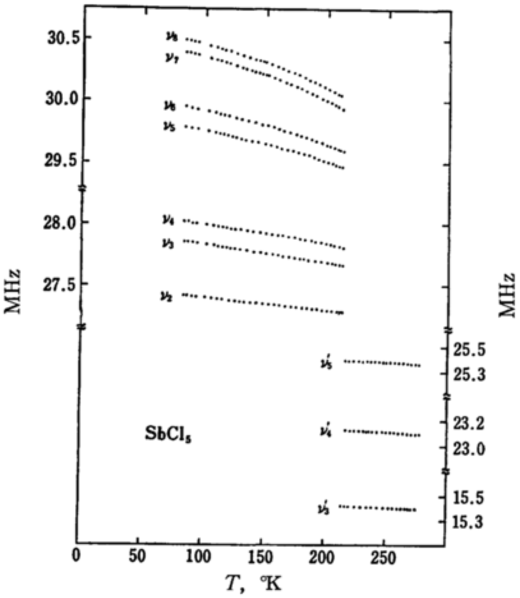


Fig. 3. Temperature dependence of the NQR frequency in both phase. The resonances of LTP are due to ^{35}Cl, and those of the HTP are due to ^{121}Sb and ^{123}Sb.

---

9) R.F. Schneider and J.V. DiLorenzo, *J. Chem. Phys.*, **47**, 2343 (1967).

10) R. Livingston and H. Zeldes, "Table of Eigenvalues for Pure Quadrupole Spectra, Spin 5/2," ORNL Report 1913, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1955).

11) See the appendix of H. Chihara, N. Nakamura and H. Ōkuma, *J. Phys. Soc. Japan*, **24**, 306 (1968).

cause the bond lengths from antimony to equatorial chlorines are different from those to axial chlorines. Furthermore the field gradient is almost axially symmetric.

As is seen from Fig. 3, all the resonance frequencies are only slightly dependent on temperature in HTP (*e.g.* 0.5 kHz/deg for ν_5') in comparison with those of LTP. This behavior is rather extraordinary though there are examples of this sort (for instance ν_1 of ionic solid PCl_5[3]). If the molecules are undergoing librational motion, it should cause much greater decrease in frequency as the temperature is raised.[12]

Another experimental fact to be noted is that chlorine resonances are entirely missing in the range of 7.5 to 40 MHz[*1] whereas antimony resonances are observable.

An off-hand approach to a plausible interpretation for these experimental results is to assume a reorientational motion about the threefold axis of the $SbCl_5$ molecule. X-ray diffraction study[4] shows a deformed chlorine electron density suggesting a large angular amplitude perpendicular to the molecular axis. Disappearance of resonance due to equatorial chlorine atoms may be explained by such reorientation. Similar situation has been found in the case of *trans*-1, 2-dichloroethane which undergoes reorientation about the Cl…Cl axis.[13] However, the disappearance of resonances of axial chlorine atoms must be due to some additional effect. Now, if one examines the molecular packing in the crystal, the intermolecular approach of axial chlorine atoms are found considerably shorter (3.33 Å) than the sum of van der Waals radii (3.60 Å). Since it is difficult to imagine a special type of interaction between these chlorine atoms, we assume that the distance found is actually the one between the average positions of the chlorine atoms and that the molecule precesses about its figure axis. Nutation is very likely to be superposed upon the precession. Actual instantaneous separation between the intermolecular chlorines would then be longer than 3.33 Å and the field gradient at the axial chlorine nucleus would be disturbed severely to the extent that its resonance frequency falls below 7.5 MHz. The effect of the precession upon the resonance frequency may be evaluated by the formula[14]

$$\nu = \nu_Q(3\cos^2\theta - 1)/2,$$

where ν_Q is the resonance frequency corresponding to the static lattice and θ is the angle of precession. If the chlorine frequency is reduced greatly by precession, the same factor must apply to the antimony frequency.

Therefore, using the relation

$$\frac{\nu^{Cl}}{\nu^{Sb}} = \frac{\nu_Q{}^{Cl}}{\nu_Q{}^{Sb}}$$

and substituting $\nu_Q{}^{Cl} = 35$ MHz, $\nu^{Cl} \leq 10$ MHz, and $\nu^{Sb(121)} = 12.682$ MHz ($3/2 \longleftrightarrow 1/2$), we obtain $\nu_Q{}^{Sb} = 44.38$ MHz which corresponds to $|e^2Qq(^{121}Sb)/h| = 295$ MHz. While this is not of unconceivable magnitude in comparison with the atomic $|e^2Qq(^{121}Sb)/h| = 410$ MHz, we get more or less embarassed with a large angle of precession (43°) necessary to give rise to the reduction of the resonance frequency. In the present instance of $SbCl_5$, X-ray diffraction does not indicate a possibility of such a large angle of precession.

Very short relaxation time associated with chlorines can also explain the disappearance of their resonances by virtue of extremebroadening of the resonance lines as suggested by Schneider, *et al.* However the reason for shortening of chlorine relaxation time and not for antimony relaxation time is rather difficult to find.

Another possibility is to take account of a special intermolecular effect. Thus, if an axial chlorine atom forms a charge transfer bond to an equatorial chlorine atom on the neighboring molecule and if such bonds are switched owing to reorientation about the threefold axis, the effect would be seen not in antimony resonances but only in chlorine resonances. The effect could be so large as to cause a broadening of chlorine resonance by, say, 1 MHz. However, quantitative explanation based on this mechanism does not seem feasible with our present knowledge on the nature of Sb–Cl bond and the electronic structure of chlorine atom.

Low Temperature Phase. After the first cooling, a number of spurious signals appeared in addition to the LTP resonances and supercooled HTP resonances. The extraneous absorptions may have been due to a piezoelectric effect and could be sorted out by application of weak magnetic field to the specimen. Annealing did eliminate many of them but several lines persisted even after annealing. Altogether sixteen resonance absorption lines were observed at liquid nitrogen temperature and seven of them are shown in Fig. 3. They are also listed in Tables 2 and 3 indicating

---

[12] H. Bayer, *Z. Phys.*, **130**, 227 (1951).

[*1] This is in agreement with the results of Schneider and DiLorezo.[9]

[13] J. L. Ragle and A. P. Caron, *J. Chem. Phys.*, **40**, 3497 (1964); T. Tokuhiro, *ibid.*, **41**, 438 (1964).

[14] T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press, New York (1958).

our assignments. An independent study of this material by Schneider *et al.* was helpful in making these assignments.

Generally, antimony resonances were broader (width being 30—40 kHz) than chlorine resonances (2—3 kHz). It is seen that chlorine resonances appear in pairs (ν_3 and ν_4; ν_5 and ν_6; ν_7 and ν_8); ν_1 of ^{35}Cl also seems to have a doublet structure above 100°K though it was not made definite because the intensities were very weak and their separation was about twice the quench frequency of the spectrometer. The corresponding ^{37}Cl resonances were not obrerved in the frequency range covered. All the chlorine resonances observed are in agreement with the result by Schneider *et al.* With regard to antimony resonances, we did not detect two absorptions, which Schneider *et al.* reported at 27.93 and 54.22 MHz, but instead were able to observe absorptions at 47.3±0.1 (ν_{16}), 49.8±0.1 (ν_{17}), and 51.00±0.01 (ν_{18}) MHz. Extremely weak ν_{17} was not assigned; this may have been a spurious signal but the effect of magnetic field was not evident.

TABLE 2. RESONANCE FREQUENCIES OF ^{35}Cl IN LTP AT SELECTED TEMPERATURES AND THEIR ASSIGNMENTS BASED ON THE DIMER STRUCTURE

Resonance line	Frequency (MHz)			Assignment[a)]
	77°K	124.7°K	211.7°K	
ν_1	18.718	18.646[b)] 18.700	——	*b*
ν_2	27.417	27.370	27.283	*a*
ν_3	27.860	27.796	27.665	*a*
ν_4	28.013	27.958	27.815	*a*
ν_5	29.789	29.704	29.465	*t*
ν_6	29.953	29.860	29.599	*t*
ν_7	30.396	30.281	29.937	*t*
ν_8	30.494[c)]	30.385	30.047[d)]	*t*

a) *b*, *a* and *t* stand for bridging, axial, and terminal chlorines.
b) Doublet structure is dubious, see in text.
c) at 83.3°K.
d) at 210.4°K; this line faded out at 211.7°K.

TABLE 3 a. RESONANCE FREQUENCIES, APPARENT INTENSITIES AND ASSIGNMENTS OF ANTIMONY IN LTP AT LIQUID NITROGEN TEMPERATURE

Resonance line	Frequency (MHz)	intensity[a)]	assignment[b)]
ν_{11}	28.71 ±0.05	W	^{123}Sb′ (5/2↔3/2)
ν_{12}	31.02 ±0.01	W	^{123}Sb (5/2↔3/2)
ν_{13}	38.42 ±0.01	M	^{123}Sb (3/2↔1/2)
ν_{14}	39.68 ±0.01	W	^{121}Sb′ (3/2↔1/2)
ν_{15}	42.893±0.001	S	^{121}Sb (3/2↔1/2)
ν_{16}	47.3 ±0.1	V.W	^{121}Sb′ (5/2↔3/2)
ν_{17}	49.8 ±0.1	V.W	——[c)]
ν_{18}	51.00 ±0.01	M	^{121}Sb (5/2↔3/2)
ν_{19}[d)]	35.6		^{123}Sb′ (3/2↔1/2)
ν_{20}[d)]	44.1		^{123}Sb′ (7/2↔5/2)
ν_{21}[d)]	47.6		^{123}Sb (7/2↔5/2)

a) V.W; very weak, W; weak, M; medium, S; strong.
b) Two sites for antimony are distinguished by the primed and the unprimed.
c) Unassignable.
d) ν_{19}, ν_{20} and ν_{21} are not observed but calculated values.

TABLE 3 b. QUADRUPOLE COUPLING CONSTANTS AND ASYMMETRY PARAMETERS OF ^{121}Sb AND ^{123}Sb AT LIQUID NITROGEN TEMPERATURE

	$\lvert e^2Qq/\boldsymbol{h}\rvert$ (MHz)	η(%)	calculated from
Site I			
^{121}Sb	186.43±0.03	79.54±0.02	ν_{15}, ν_{18}
^{123}Sb	238.22±0.08	79.26±0.04	ν_{12}, ν_{13}
Site II			
^{121}Sb′	172.8 ±0.3	79.2 ±0.3	ν_{14}, ν_{16}
^{123}Sb′*	221	79	——

* These values were derived by taking 1.278 times the coupling constant of ^{121}Sb's and assuming the same η as ^{121}Sb.

From the observed frequencies and the assignments given in Table 3a for antimony nuclei, the quadrupole coupling constants and the asymmetry parameters were calculated by help of the tables of eigenvalues for spins 5/2[10] and 7/2[11]. They are listed in Table 3b. ν_{19}, ν_{20}, and ν_{21} were not detected, either because the intensities were weak or because of the noise disturbance from external sources between 34 and 36 MHz.

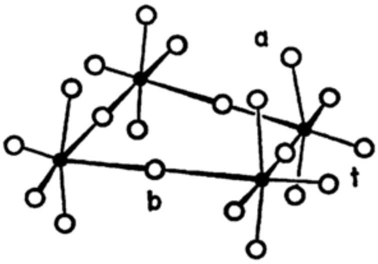
There are two nonequivalent antimony sites, one having slightly lower coupling constant than the other and both having about 79% asymmetry. We ascribe the small difference in the coupling constant between the two sites to crystallographic nonequivalence.

Structure of the Low Temperature Phase. We shall now consider what structure of the low temperature phase would be consistent with the experimental results. A drastic change in the antimony resonances, particularly its asymmetry parameter, across the transition point strongly suggests that the transition is related to a change in molecular structure. There are several possibilities, ionic $SbCl_4^+\cdot SbCl_6^-$ structure, dimerized structure Sb_2Cl_{10}, and tetramer or higher polymer structure. In the following these different structural models will be separately examined.

a) Ionic Structure, $SbCl_4^+\cdot SbCl_6^-$. Since phosphorus pentachloride exists in this structure in the stable solid phase, there is a good reason to assume this type of ionic units. We previously measured[3] the chlorine resonance frequencies in $PCl_4^+ \cdot SbCl_6^-$ to aid in the assignment for PCl_5 and found them at 24.03 and 24.96 MHz at 77°K. A comparison with the frequencies in Table 2 implies that $SbCl_6^-$ is not a likely species in LTP. Also large asymmetry in the electric field gradient at Sb is not compatible with the symmetric chlorine arrangements in $SbCl_4^+$ or $SbCl_6^-$.

b) *Dimer Structure, Sb_2Cl_{10}, and Higher Polymars.* Dimerized form of molecules are not rare although few compounds possess corresponding monomers as stable species. Examples are $NbCl_5$, $NbBr_5$, $TaCl_5$, $MoCl_5$,[2a] $NbOCl_3$,[2b] UCl_5,[15] $AlBr_3$, $AuCl_3$, ICl_3[2a] and others. Some pentahalides take a molecular shape shown in Fig. 4a. It is interesting to note that the niobium resonance frequencies in $(NbCl_5)_2$ give a rather small coupling constant 78 MHz and a large asymmetry parameter 32%[16] as in the present case of $SbCl_5$.

a. Dimer.



b. Tetramer.

Fig. 4. The suggested molecular structure in LTP. Filled circles are antimony and open circles are chlorine atoms; *a*, *b*, and *t* denote axial, bridging and terminal chlorines.

Many investigators also observed bridging and terminal halogen resonances of dimerized trihalogen compounds as summerized in Fig. 5. The figure shows the frequency ratio of the terminal and bridge halogen *vs.* the electronegativity difference between the halogen and the central atom. It is seen that different ligands lead to different but parallel straight lines on each of which various central atoms are arranged according to their electronegativity. This empirical relationship may be useful in making assignments. Now, the four higher frequencies (ν_5 to ν_8 in Table 2) can be assigned to the terminal chlorines (identified with *t* in Fig. 4a), the three medium frequencies (ν_2 to ν_4) to the axial chlorines (*a* in Fig. 4a), and the remaining ν_1 to the bridge chlorine (*b* in Fig. 4a). The ratio of the average of ν_5 through ν_8 to ν_1 is then 1.6 and is included in Fig. 5; the point lies close to the chloride line. We agree with Schneider *et al.* on this assignment.

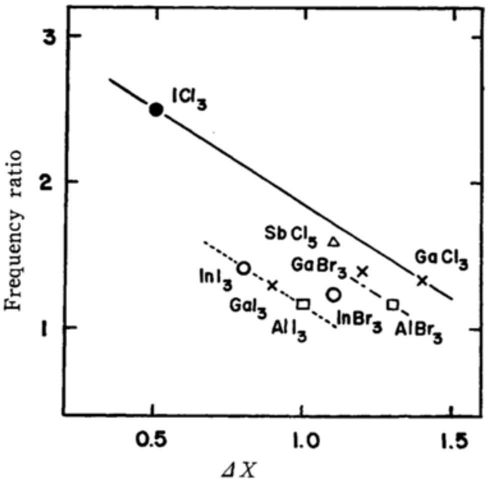


Fig. 5. Ratio of the resonance frequencies for terminal and bridging halogen atoms *vs.* electronegativity difference of central atom and halogen. The resonance frequencies were taken from É. I. Fedin and G. K. Semin, 'Use of Nuclear Quadrupole Resonance in Chemical Crystallography II', in 'The Mössbauer Effect and its Applications in Chemistry,' Consultants Bureau Enterprises, Inc., New York (1964).

The differential thermal analysis experiments also support dimerization model or any type of polymerization model. Thus, the slow transition in the cooling direction can be explained by the difficulty in perfect pairing of monomers; annealing does help to grow dimer nuclei larger. The reverse reaction, the decomposition, can proceed quickly upon heating.

Tetramer structure as shown in Fig. 4b is known for $TaCl_4F$[17a] and $SbCl_4F$.[17b] However bridge atoms are not chlorine but fluorine.

---

[15] G. S. Smith, Q. Johnson and R. E. Elson, *Acta Cryst.*, **22**, 300 (1967).

[16] A. H. Reddoch, *J. Chem. Phys.*, **35**, 1085 (1961).

[17] a) H. Preiss, *Z. Anorg. Allg. Chem.*, **346**, 272 (1966). b) H. Preiss, *Z. Chem.*, **6**, 350 (1966).

Similarly, polymer chains are known for $BeCl_2$.[2c)] We consider that tetramer or higher polymers are rather unlikely for $SbCl_5$ for two reasons; (a) chlorine polyhedra usually share edges rather than corners or faces in forming polymer chains and if $SbCl_5$ should form a polymer chain, the six-coordinated polyhedra must share corners and (b) the number and distribution of chlorine resonances are not readily reconciled with such a polymer structure while keeping the number of nonequivalent antimony sites two.

We are inclined to think that the dimer structure is the most probable structure for the low temperature phase of antimony pentachloride. Crystal structure determination of the low temperature phase is very desirable in order to correlate the asymmetry parameter and the coupling constant of antimony with the geometry of the dimer. It would also be interesting to study kinetics and detailed mechanism of the phase transition since this is one of very few phase transitions which accompany a change in the valence state, perhaps to our knowledge the sole example for a molecular crystal.

When the measurements of the present study were completed, Professor R. F. Schneider of New York State University at Stony Brook drew our attention to that he and his colleague were also studying the same compound. We were benefited in making some of the assignments through his courtesy of showing us his results prior to publication for which we extend our gratitude.