The 489° transformation in Na_2CO_3 makes its first appearance at 67.5 mole %. No level range is observed indicating that this transformation is not quite as spontaneous as its opposite member. The 361° transition in Na_2CO_3 is not detectable until approximately 92.5 mole % from which point its latent heat increases continuously. The X-ray data indicate that the upper and lower curves have approximately a 10 mole % separation at room temperature which explains the rapid decrease in the magnitude of the spontaneous latent heat. The consistency of the patterns in the δ–ϵ two phase region indicates that the X-ray sample preparation resulted in a fairly good approach to equilibrium and this also lends support to the validity of the entire diagram as constructed.

NOTE ADDED IN PROOF.—The author has hitherto been unable to offer any explanation for the heat effects at ca. 620° reported in ref. 2. Subsequent to the compilation of this manuscript, a probable explanation for the "anomalous heat effects" was forthcoming in a private communication from Drs. F. W. Wilburn, C. V. Thomasson and J. D. Mullen of Pilkington Brothers, Ltd., St. Helens, England which is abstracted herewith.

In the course of differential thermal analysis studies in the sodium carbonate–silica system we also have been unable to observe this peak (at ca. 600°) when using analytical reagent sodium carbonate. However, when using commercial sodium carbonate, which is known to contain up to 0.5% sodium chloride, a small peak at about 620° is observed. D. T. A. curves of sodium carbonate–sodium chloride mixtures (both of analytical reagent quality) show a small peak at about 620° which increases in area with increasing chloride content. Moreover Mellor[7] states that eutectic melting occurs between sodium carbonate–sodium chloride mixtures at 636°. Analytical reagent quality potassium carbonate shows no peak at about 620°, but a peak appears when analytical reagent quality potassium chloride is added as an impurity. Mellor again gives the eutectic melting temperature of these two substances at 636°.

NEW YORK, NEW YORK

The Crystal Structure of Antimony Pentachloride at −30°

BY STANLEY M. OHLBERG[1]

Antimony pentachloride belongs to the hexagonal system with $a = 7.49$ Å. and $c = 8.01$ Å. The space group is D^4_{6h}–$P6_3/mmc$ with two molecules to the unit cell. It forms a molecular crystal and the trigonal bipyramidal structure observed for the gaseous molecule is retained in the solid state. The bond distances between antimony and the three basal chlorine atoms is 2.29 Å. and that between antimony and the two apical chlorines is 2.34 Å.

Introduction

The crystal structures of a number of inorganic compounds in which a 1:5 stoichiometric ratio exists have been determined. Klug, Kummer and Alexander[2] have cited five different structural methods by which the 1:5 ratio is achieved in crystals, and none of them involves fivefold coordination. Byström and Wilhelmi[3] did observe fivefold coördination in K_2SbF_5. They describe a configuration of $SbF_5^=$ as an octahedron with a stereochemically active pair of s-electrons occupying the sixth corner. Another, and perhaps more obvious, method for achieving fivefold coördination would involve the formation of trigonal bipyramids. Although PCl_5[4] has a trigonal bipyramidal configuration in the gaseous state, it forms ionic crystals involving PCl_4^+ tetrahedra and PCl_6^- octahedra.[5] Antimony pentachloride also has a trigonal bipyramidal configuration in the gaseous state,[6] and moreover the low dielectric constant, 3.3, measured by Lowry and Jessop[7] at 0° suggests

that $SbCl_5$ forms a molecular type crystal. In addition, examination of the Raman spectra[8,9] points to the retention of the trigonal bipyramidal configuration in both the liquid and the solid state. In view of these facts the structure determination of solid $SbCl_5$ was undertaken in order to demonstrate its method for achieving a 1:5 stoichiometric ratio.

Experimental

The $SbCl_5$ was distilled under reduced pressure into thin-walled glass tubes of approximately 0.3 mm. in diameter. The samples were frozen with a Dry Ice slush and the tubes sealed off. Single crystals were grown by conventional low temperature techniques.[10,11] Both precession and Weissenberg photographs were taken at −30 ±2° with Zr-filtered MoK and Ni-filtered CuK radiation, respectively. Zero and first level photographs were taken about the [00·1], [10·0] and [11·0] axes. The hexagonal cell parameters determined from precession photographs are $a = 7.49$ Å. and $c = 8.01$ Å. The density calculated on the basis of 2 molecules per unit cell is 2.55 g./cm.³, in line with the density reported for the liquid, 2.378 g./cm.³ at 2.6°.[12]

The symmetry and systematic extinctions, $hh2\bar{h}l$ with l odd, limited the possible space groups to D^4_{6h}–$P6_3/mmc$. D^4_{3h}–$P\bar{6}2c$, and C^4_{6v}–$P6_3mc$. Subsequent interpretation

(1) Pittsburgh Plate Glass Research Center, P. O. Box 11472, Pittsburgh 38, Pa.

(2) H. P. Klug, E. Kummer and L. E. Alexander, THIS JOURNAL, **70**, 3064 (1948).

(3) A. Byström and K. Wilhelmi, *Arkiv för Kemi*, **3**, 461 (1951).

(4) M. Roualt, *C. R. Acad. Sci. Paris*, **206**, 51 (1938).

(5) H. M. Powell, D. Clark and A. F. Wells, *J. Chem. Soc.*, **642** (1942).

(6) M. Roualt, *Ann. Phys., Lpz.*, **14**, 78 (1940).

(7) T. M. Lowry and G. Jessop, *J. Chem. Soc.*, 782 (1930)

(8) H. Moureau, M. Magat and G. Wetroff, *Proc. Ind. Acad. Sci.,* *Raman Jubilee Vol.*, 361 (1938).

(9) K. A. Jensen, *Z. anorg. Chem.*, **250**, 264 (1943).

(10) H. Kaufman and I. Fankuchen, *Rev. Sci. Instr.*, **20**, 735 (1949).

(11) S. C. Abrahams, R. L. Collins, W. N. Lipscomb and T. B. Reed, *ibid.*, **21**, 396 (1950).

(12) J. H. Simons and G. Jessop, THIS JOURNAL, **53**, 1265 (1931).

of the Patterson projection on (00·1) established that 2 Sb and 4 Cl atoms are at $(^1/_3, {}^2/_3)$ and $(^2/_3, {}^1/_3)$. In space group C^4_{6v}, the 4 Cl atoms would be placed in two sets of (b) $^1/_3, {}^2/_3, z$; $^2/_3, {}^1/_3, {}^1/_2 + z$. The requirement that two sets of coördinates be used implies that the 2 Cl atoms are placed at different distances from an Sb atom. A condition of this kind is extremely unlikely for physical reasons and C^4_{6v} was consequently abandoned as a possible space group. Of the two remaining possibilities, D^4_{6h} was tentatively taken as the correct space group and retained as such on the basis of subsequent structure factor calculations described below.

The intensities of the $hk \cdot 0$ reflections were obtained by visual comparison with calibrated intensity strips on triple Weissenberg photographs and converted to values of $|F|^2$ by division by the Lorentz and polarization factors. Since the crystals were grown in glass capillaries, hence perfect cylinders, and the reflections were on the equatorial layer line, an absorption correction for $\mu r = 4.9$ was applied using the method of Bradley.[13]

The intensities of the $hh \cdot l$ reflections were obtained from triple precession photographs and corrected for the Lorentz and polarization factors in the manner described by Waser.[14] Satisfactory values were obtained without absorption corrections since μr was only 0.5 for Mo Kα radiation.

Structure Determination.—The heights and locations of the peaks observed on a Patterson projection on the (00·1) axis strongly suggested these atomic coördinates[15]

$$2 \text{ Sb in 2(c)}: \frac{1}{3}, \frac{2}{3}, \frac{1}{4}; \frac{2}{3}, \frac{1}{3}, \frac{3}{4}; \quad 4 \text{ Cl in 4(f)}: \frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, \bar{z};$$

$$\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z; \frac{1}{3}, \frac{2}{3}, \frac{1}{2} - z; \quad 6 \text{ Cl in 6(h)}: x, 2x, \frac{1}{4}; 2\bar{x}, \bar{x}, \frac{1}{4};$$

$$x, \bar{x}, \frac{1}{4}; \bar{x}, 2\bar{x}, \frac{3}{4}; 2\bar{x}, x, \frac{3}{4}; \bar{x}, x, \frac{3}{4}$$

Thus it was only necessary to determine two atomic coördinates. A value for x in 6(h) was obtained readily from the $hk \cdot 0$ Patterson projection. Structure factors were then calculated and their signs were used to calculate the Fourier projection on (00·1), (Fig. 1). A least squares calculation[16]
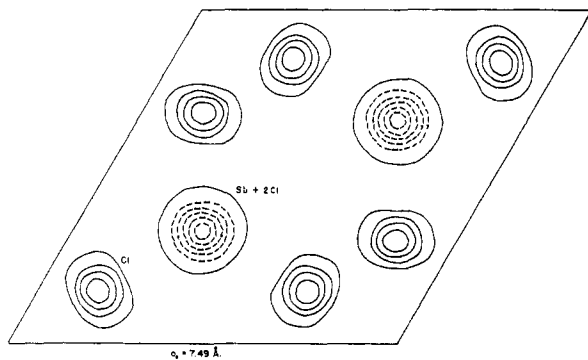

Fig. 1.—Fourier projection of SbCl₅ on (00·1). Solid lines are at intervals of 4 electrons/Å.² Dashed lines are at intervals of 20 electrons/Å.²

was subsequently made to further refine the x parameter for chlorine and an isotropic temperature factor. The final parameters were $x = 0.157$ and $B = 4.89$. An initial value for z in 4(f) was selected on the basis of the bond distance between antimony and the apical chlorines (2.43 Å.) determined by Raoult.[6] Structure factors were calculated for the $hh \cdot l$ reflections and the signs of these used to calculate a Fourier projection on ($\bar{1}1 \cdot 0$), (Fig. 2). An experimental value for the z coördinate of the apical chlorine atoms was then taken from the ($hh \cdot l$) Fourier. Final values of z and an isotropic temperature factor were again obtained from a least squares calculation,[16] which yielded $z = 0.542$ and $B = 3.90$.

(13) A. J. Bradley, Proc. Phys. Soc. (London), **47**, 879 (1935).

(14) J. Waser, Rev. Sci. Instr., **22**, 567 (1951).

(15) "International Tables for X-Ray Crystallography," Vol. I, the Kynoch Press, Birmingham, England, 1952, p. 304.
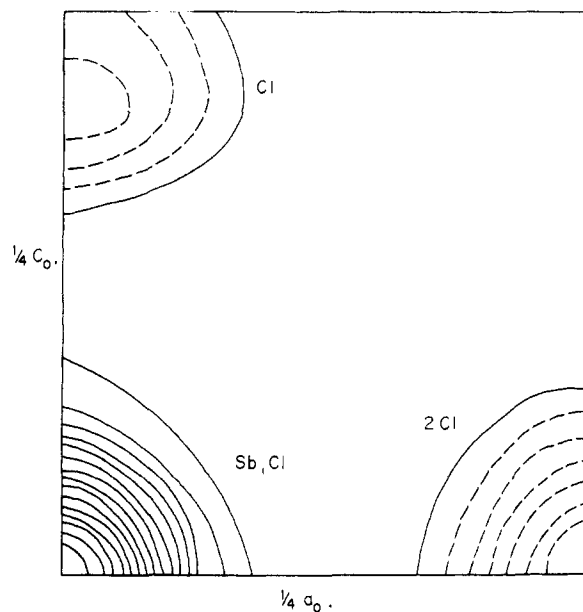
(16) E. W. Hughes, THIS JOURNAL, **63**, 1737 (1941).

Fig. 2.—Fourier projection of SbCl₅ on ($\bar{1}1 \cdot 0$). The data depicted are actually the contents of the orthohexagonal cell projected on the equivalent plane (100). Solid lines are at intervals of 4 electrons/Å.² Dashed lines are at intervals of 2 electrons/Å.²

For the final structure, $R = \Sigma(|F_{obsd.}| - |F_{calcd.}|)/\Sigma|F_{obsd.}| = 0.08$ for the ($hk \cdot 0$) reflections and 0.14 for the ($hh \cdot l$) reflections. The observed and calculated structure factors are given in Table I.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS

($hk \cdot 0$) Reflections

hkl	$|F_0|$	F_c	hkl	$|F_0|$	F_c
100	42	−55	610	7	−7
200	100	−94	710	13	13
300	85	74	220	111	117
400	49	−48	320	14	−15
500	29	−26	420	29	−29
600	39	42	520	23	21
700	0	−3	620	11	−12
800	9	−7	720	4	−6
110	99	107	330	31	35
210	51	−49	430	17	−16
310	31	−29	530	7	−8
410	45	43	630	10	9
510	17	−18	440	23	27

($hh \cdot l$) Reflections

| hkl	$|F_0|$	F_c	hkl	$|F_0|$	F_c
110	107	109	334	28	24
220	120	127	444	24	24
330	46	43	006	60	−64
440	36	37	116	33	−24
550	14	11	226	37	−43
002	118	−118	336	22	−12
112	22	−17	446	14	−14
222	77	−65	008	21	31
332	24	−9	118	13	8
442	31	−19	228	16	21
552	14	−3	338	11	5
004	128	122	0,0,10	20	−23
114	62	52	1,1,10	19	−11
224	72	75	2,2,10	12	−16

Discussion

The trigonal bipyramidal structure found for SbCl₅ in the gaseous state[8] persists in the crystalline state as shown in Fig. 3. This makes a seventh structural design for achieving the 1:5 stoichiometric ratio and the second one wherein the coördination number is five. Examples of each of the seven types are given in Table II.

TABLE II

STRUCTURAL TYPES HAVING A 1:5 STOICHIOMETRIC RATIO

PCl₅	PCl₄⁺, PCl₆⁻ (CsCl type)[5]
PBr₅	PBr₄⁺, Br⁻[17]
Tl₂AlF₅	AlF₆ (infinite octahedral chains)[18]
(NH₄)₃ZnCl₅	ZnCl₄⁻, Cl⁻[19]
(NH₄)₂InCl₅·H₂O	(InCl₅H₂O)(octahedra)[2]
K₂SbF₅	SbF₅⁻ (octahedra)[3]
SbCl₅	SbCl₅ (trigonal bipyramid)

The bond distance between the antimony and the three basal chlorine atoms, 2.29 Å., is in good agreement with that found for the gas, 2.31 Å. The distance between the antimony and the apical chlorine atoms is 2.34 Å., which is 0.09 Å. less than that found for the gas. The packing of the molecules is such that the closest intermolecular distance is 3.33 Å. between apical chlorine atoms. The next closest intermolecular approach is 4.09 Å. between a basal chlorine and an apical chlorine and hardly seems sufficient to hold the crystal together. If the space group is changed to D_3^4h –P6̄2c, this permits rotation of the three basal chlorine atoms about the molecular Cl–Sb–Cl axis and thereby the van der Waals distance between basal chlorine atoms and apical chlorines could be brought within the range normally observed. However, structure factor calculations based on the space group D_3^4h–P6̄2c with a range of coördinates chosen to yield more reasonable van der Waals distances did not agree with the observed

(17) H. M. Powell and D. Clark, *Nature*, **145**, 971 (1940).

(18) C. Brosset, *Z. anorg. allgem. Chem.*, **235**, 139 (1937).

(19) H. P. Klug and L. Alexander, THIS JOURNAL, **66**, 1056 (1944).
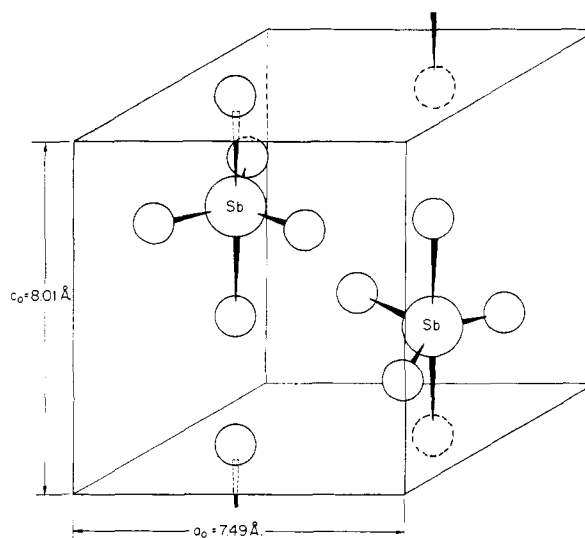
Fig. 3.—The crystal structure of SbCl₅.

data as well as did those based on D_6^4h–P6₃/mmc. (This was taken as a further confirmation of the original choice of space group). Inspection of the Fourier projection on the (00·1) face (Fig. 1) suggests a more likely explanation for the large intermolecular Cl–Cl distance. It is seen that the chlorine atoms are somewhat elliptical with their major axes perpendicular to the Sb–Cl bond. This could indicate a torsional vibration of the three basal chlorine atoms about the Cl–Sb–Cl molecular axis. Thus, although the van der Waals distance between the basal chlorine atoms and the apical chlorines of neighboring molecules is large for the atoms at rest, the aforementioned type of thermal vibrations could bring these atoms within the normal van der Waals range.

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PITTSBURGH 13, PA.

The Chemistry of the Solvated Metal Chelates. I. Thermochemical and Kinetic Studies[1,2]

BY JAMES H. VAN TASSEL AND WESLEY W. WENDLANDT

The heats of solvation and the kinetics of the thermal decomposition of the thorium and uranium(VI) 8-quinolinol chelates were determined. The heats of solvation, represented by the reaction $M(C_9H_6NO)_n(s) + C_9H_6NOH(s) = M(C_9H_6NO)_n·C_9H_6NOH(s)$, were found to be 6.5 ± 0.2 and 4.9 ± 0.2 kcal./mole for the thorium and uranium chelates, respectively. The thermal decomposition was found to be first order with activation energies for the thorium and uranium chelates of 42 ± 4 and 26 ± 2 kcal./mole, respectively. A new mechanism for the thermal decomposition of the thorium chelate is proposed. From the heats of solvation and kinetic studies, the nature of the interaction between the solvate molecule and the metal chelate is discussed.

Introduction

8-Quinolinol (oxine) forms five-membered ring chelates with a large number of metal ions having

(1) Taken in part from the M.S. thesis of J. H. Van Tassel, August, 1957.

the general formula $M(Ox)_n$, where M is a metal ion of charge n, and Ox is the 8-quinolinol ion.

(2) Presented at the 13th Southwest Regional Meeting of the American Chemical Society, Tulsa, Oklahoma, December 5–7, 1957.