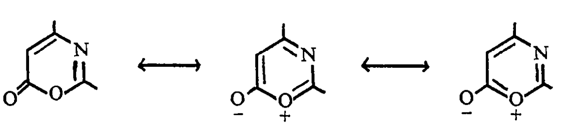
O(1)–C(2) bond shortening and concomitant C=N lengthening from normal values (compare O(1)–C(2) with O(1)–C(6); C=N = 1·28 Å) are probably responsible for the extremely low $\bar{\nu}_{C=O}$ in the infrared (1550 cm^{-1}) and Raman (1548 cm^{-1}) spectra. The acetoxy, oxazinone and phenyl groups are individually coplanar; the angles between the acetoxy–oxazinone and phenyl–oxazinone planes are 8·40 and 2·9°, respectively. The conformation of the acetoxy group [C(7) and N(3) are *anti* with respect to the C(4)–O(4) bond] is undoubtedly influenced by a stabilizing O(7)···H(5) interaction (2·30 Å, Fig. 1). The conformation of the *m*-bromophenyl moiety is set by intermolecular packing interactions which prevent the Br from trading places with H(13) (see Fig. 1). The unequal pairs of exocyclic angles at C(2), C(4) and C(6) in the oxazinone ring arise from the different electronegativities of the attached atoms and, in the case of C(2) and C(4), to participation in double bonds.


(VI*a*) (VI*b*) (VI*c*)

This work establishes unequivocally for the first time the constitution of a 1,3-oxazin-6-one system. In a recent paper (Martin, Burpitt, Gott, Harris & Meen, 1971) it was claimed that benzoylisocyanate and ketene reacted to give a compound whose chemical and spectral properties were nearly identical to those reported here for I*a*. However, the authors gave the structure as II, an assignment which must now be considered erroneous.

This work was supported at the University of Maryland by the National Science Foundation and the University of Maryland's Computer Science Center, and at Catholic University by the Petroleum Research Fund of the ACS and the Research Corporation (New York).

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The Crystal Structure of Ammonium Hexachloroantimonate(V) Monohydrate and the Crystal Data of the Anhydrous Compound

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(*Received* 29 *May* 1973; *accepted* 12 *June* 1973)

Abstract. $NH_4SbCl_6.H_2O$ crystallizes in the orthorhombic space group *Immm* (No. 71) with the lattice dimensions $a=7{\cdot}113$ (2), $b=9{\cdot}049$ (3), and $c=8{\cdot}049$ (3) Å. The unit cell contains 2 formula units giving a density D_x of 2·375 g cm^{-3}. The structure is built up from $SbCl_6^-$ octahedra and $(NH_4.OH_2)^+$ groups which involve hydrogen bonding. Single-crystal photographs of NH_4SbCl_6 show monoclinic symmetry, possible space groups *Cc* (No. 9) or *C*2/*c* (No. 15). The lattice parameters are $a=12{\cdot}062$ (6), $b=6{\cdot}310$ (3), $c=15{\cdot}220$ (6) Å, and $\beta=129{\cdot}11$ (9)°. With 4 formula units per cell the density D_x is 2·605 g cm^{-3}.

Structure determination of $NH_4SbCl_6.H_2O$. Suitable crystals of $NH_4SbCl_6.H_2O$ were grown from aqueous solutions of the acid $HSbCl_6$ and an excess of NH_4Cl (Weinland & Feige, 1903). The 'octahedral' crystal that we actually used was bounded by the faces {110} and {011}. The average edge length was 0·4 mm. Intensity data for all 429 unique reflexions in the range $4° < 2\theta < 60°$ were collected on an automatic Picker-FACSI diffractometer. Using monochromatic Mo $K\alpha$ radiation and the technique of an ω–2θ scan the intensity of each reflexion (hkl) with $h+k+l=$even was measured twice in different octants. Apart from the usual data-reduction process, an absorption correction ($\mu = 41{\cdot}7\ \mathrm{cm}^{-1}$) was applied. During the structure refinement allowances were also made for secondary extinction (Larson, 1970) and for anomalous dispersion.

As suggested by the interpretation of the Patterson function, the refinement was carried out in the centrosymmetric space group *Immm* (No. 71) assuming the following symmetry positions (Wyckoff notation): Sb in 2(a), Cl(1) in 4(i) and Cl(2) in 8(n). Since the Patterson vectors Sb → O, Sb → N were not resolved from one another, we placed O and N at the same site 4(j) using the scattering factor of oxygen. The atomic scattering factors f employed in the calculations were those of Cromer & Mann (1968). The additional correction terms $\Delta f'$ and $\Delta f''$, accounting for anomalous dispersion exhibited by Sb and Cl, were taken from Dauben & Templeton (1955). Full matrix least-squares refinement by means of *CRYLSQ* (Stewart, Kundell & Baldwin, 1970) with weights w adjusted so that $w(|F_o|-|F_c|)^2$ was independent of F_o resulted in the final residual of 2·6% (429 reflexions) and the structure parameters listed in Table 1. Relevant interatomic distances and bond angles are given in Table 2. A list of structure factors is available.*

Table 1. *The positional and thermal parameters of* $NH_4SbCl_6.H_2O$

Estimated standard deviations in units of the last quoted figure are given in parentheses. The parameters U_{ij} of the anisotropic temperature factor correspond to the expression:

$$\exp\,[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*)]\,.$$

	x	y	z
Sb	0	0	0
Cl(1)	0	0	0·29321 (15)
Cl(2)	0·23733 (12)	0·18370 (9)	0
O,N	0	$\frac{1}{2}$	0·16887 (69)

	U_{11}	U_{22}	U_{33}	U_{12}
Sb	0·0278 (2)	0·0275 (3)	0·0320 (2)	0
Cl(1)	0·0538 (6)	0·0840 (10)	0·0335 (5)	0
Cl(2)	0·0404 (4)	0·0383 (5)	0·0756 (6)	−0·0111 (3)
O,N	0·0633 (27)	0·0822 (36)	0·0640 (26)	0

Table 2. *Interatomic distances* (Å) *and angles* (°) *of* $NH_4SbCl_6.H_2O$

Estimates of the standard deviations are given in parentheses. The superscripts refer to the following equivalent positions:

i $\bar{x}, y, 0$; ii $x, \bar{y}, 0$; iii $0, \frac{1}{2}, \bar{z}$;
iv $0, 0, 1-z$; v $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-z$; vi $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}$.

Sb–Cl(1)	2·360 (2)
Sb–Cl(2)	2·369 (2)
Cl(2)–Sb–Cl(2$^{\mathrm{i}}$)	90·88 (5)
Cl(2)–Sb–Cl(2$^{\mathrm{ii}}$)	89·12 (5)
(O,N)···(O,N)$^{\mathrm{iii}}$	2·718 (11)*
O ···N	2·75 (3)†
Cl(2) ···Cl(2$^{\mathrm{ii}}$)	3·325 (3)
Cl(1) ···Cl(1$^{\mathrm{iv}}$)	3·329 (4)
Cl(1) ···Cl(2)	3·344 (3)
Cl(2) ···Cl(2$^{\mathrm{i}}$)	3·376 (3)
(O,N)···Cl(1$^{\mathrm{v}}$)	3·570 (3)
(O,N)···Cl(2)	3·590 (5)
(O,N)···Cl(2$^{\mathrm{vi}}$)	3·655 (6)

* From centrosymmetric model.
† From non-centrosymmetric model (see text).

We also attempted refinement in the non-centrosymmetric space group *Imm*2 (No. 44) which implies a non-statistical distribution of the O and N atoms. This resulted in poorly conditioned normal equations, causing slight fluctuations of the $(NH_4\ OH_2)^+$ group, independent of whether the geometry of the $SbCl_6^-$ ion was constrained or not. Despite this instability the O–N distance itself remained astonishingly constant: the mean value is given in Table 2 for the sake of comparison.

Crystal data of NH_4SbCl_6. Single crystals of NH_4SbCl_6 were obtained by the reaction of $SbCl_5$ and NH_4Cl in liquid sulphur dioxide and subsequent evaporation of the solvent at −10°C (Jander & Immig, 1937). As the crystals are rather unstable in the presence of moisture, they were sealed into thin-walled glass capillaries. Powder specimens were more easily prepared by pumping off the water from a sample of the monohydrate at room temperature.

The monoclinic symmetry of NH_4SbCl_6 and preliminary values of the lattice dimensions were derived from precession photographs of the layers ($h0l$) and (hkn) with n ranging from 0 to 4. According to the systematic absence of the reflexions hkl with $h+k$ odd and $h0l$ with l odd, the space groups *Cc* (No. 9) or *C*2/*c* (No. 15) are possible. An earlier attempt to index a Guinier film of NH_4SbCl_6 by the method of de Wolff (1957) had led to a different result: a smaller pseudo-orthorhombic body-centred unit cell with the lattice dimensions $a' = 6{\cdot}310$ (3), $b' = 9{\cdot}359$ (3), and $c' = 7{\cdot}610$ (3) Å. In this context it is interesting to note that the axial ratio for this subcell, 0·6742:1:0·8131, is very similar to that of $RbSbCl_6$, 0·6719:1:0·8136, reported by Steinmetz (see Weinland & Feige, 1903). The subcell is also easily recognized from the single-crystal photographs, since the intensities of the layers ($hk1$), ($hk3$) *etc.*, which require a doubling of the cell, are comparatively weak. The transformation between the subcell and the actual monoclinic unit cell is given by the vector equations $\mathbf{a}=\mathbf{b}'+\mathbf{c}'$, $\mathbf{b}=\mathbf{a}'$, and $\mathbf{c}=-2\mathbf{c}'$.

Discussion. A paper concerning the crystal structure of $CH_3CO^+SbCl_6^-$ (Le Carpentier & Weiss, 1972) has

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* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30159 (6 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

given rise to the present paper as it was realized that $CH_3CO^+SbCl_6^-$ and $NH_4^+SbCl_6^-.H_2O$ form homoeotypic arrangements. In other words, the methyloxocarbonium ion, CH_3CO^+, and the $(NH_4.OH_2)^+$ group behave as equivalent structural units when packed together with $SbCl_6^-$ ions. In addition, we were able to establish from Guinier photographs that $NH_4^+SbCl_6^-.NH_3$ belongs to the same series of homoeotypic structures (Gruner, 1973). The lattice parameters of all three compounds are the following:

	a (Å)	b (Å)	c (Å)
$CH_3CO^+SbCl_6^-$	7·144 (3)	9·091 (5)	7·974 (4)
$(NH_4.OH_2)^+SbCl_6^-$	7·113 (2)	9·049 (3)	8·049 (3)
$(NH_4.NH_3)^+SbCl_6^-$	7·218 (3)	9·131 (4)	8·104 (3)

The crystal structure of $NH_4SbCl_6.H_2O$ is related to the well-known structure type of K_2PtCl_6, since the arrangements of the $PtCl_6^{2-}$ and the $SbCl_6^-$ ions are topologically equivalent, and the sites of the potassium ions are occupied by H_2O and NH_4^+ in turn. This similarity can be illustrated more precisely by the following group/subgroup relation (Neubüser & Wondratschek, 1966): in going from the space group of K_2PtCl_6 (*Fm*3*m*) to that of $NH_4SbCl_6.H_2O$ (*Immm*) the threefold and the fourfold axes are lost, but apart from a topological distortion the translation lattice remains unchanged, *i.e. Immm* is a 'zellengleiche' subgroup of *Fm*3*m*. The observed reduction of symmetry results from the formation of pairs between H_2O and NH_4^+. Although direct evidence is missing, the comparatively short O–N distance (see Table 2) clearly indicates some interaction *via* hydrogen bonds leading to the discrete group $(NH_4.OH_2)^+$. There are two possibilities for the orientation of this polar group with respect to the direction of the *c* axis. As the X-ray structure determination does not enable one to distinguish between the parallel alignment of the cations $(NH_4.OH_2)^+$–which would imply the space group *Imm*2 – and the statistical distribution – which implies the centrosymmetric space group *Immm* – preference is given to the latter.

From the viewpoint of crystal chemistry the dehydration of $NH_4SbCl_6.H_2O$ is of interest. *In vacuo* this process takes place very easily even at room temperature; upon exposure to the atmosphere at normal humidity, however, the anhydrous salt reverts to the monohydrate just as easily. Therefore one may expect that the reaction involves only small structural changes, an assumption which is corroborated by the metrical relations between the unit-cell dimensions and by group theoretical considerations like those mentioned above. This will be shown in some detail.

The symmetry reduction while going from the space group *Immm* ($NH_4SbCl_6.H_2O$) to the space group *C*2/*c* (NH_4SbCl_6) can be visualized by the following scheme:

Immm
↓
*I*2/*m* [*i.e. C*2/*m*] (Maximal subgroup of index 2, 'zellengleich'.)
↓
*C*2/*c* (Maximal subgroup of index 2, 'klassengleich'.)

In the first step the twofold symmetry along the direction [001] is lost. Formally one obtains the space group *C*2/*m* (No. 12) in the unconventional setting *I*2/*m*. This setting, however, corresponds to the pseudocell of NH_4SbCl_6, the lattice dimensions a',b',c' of which (see *Crystal data* of NH_4SbCl_6) are similar to those of the monohydrate. In the second step the symmetry of the crystal class is retained, but along the direction [001] every other translation is lost, *i.e.* the lattice constant c' of the pseudocell must be doubled in order to obtain the true unit cell of NH_4SbCl_6.

With the given outline of the group-theoretical relation between $NH_4SbCl_6.H_2O$ and NH_4SbCl_6 it was possible to deduce the principal arrangement of the $SbCl_6^-$ ions in NH_4SbCl_6. A single-crystal structure determination is now in progress. For the sake of completeness it should be mentioned that several compounds exhibit quite similar X-ray powder patterns to that of NH_4SbCl_6, *e.g.* $KSbCl_6$, $NOSbCl_6$, NH_4TaCl_6 (Burgard & MacCordick, 1970), and NH_4NbCl_6 (Weishaupt, 1973).

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