

Table 2 (cont.)

<i>l</i>	Obs.	Calc.
-20	<i>vs</i>	39.58
-23	<i>vw</i>	0.20
-26	<i>vs</i> (-26 > -20)	61.62
-29	<i>w</i> (-29 > -8)	4.12
-32	<i>m</i>	8.64
-35	<i>m</i>	10.59
72 <i>R</i> (8 6 3 2 2 3) ₃		
1	<i>vw</i>	2.31
4	<i>vw</i>	1.50
7	<i>s</i>	11.86
10	<i>vvw</i>	0.41
13	<i>w</i>	3.05
16	<i>vs</i>	31.93
19	<i>vvw</i>	0.57
22	<i>vvs</i>	74.96
25	<i>s</i> (25 > 7)	18.24
28	<i>vs</i>	32.57
31	<i>vvw</i>	0.74
34	<i>vs</i>	24.52
-2	<i>vvw</i>	0.31
-5	<i>m</i>	7.36
-8	<i>w</i> (-8 > -11)	5.82
-11	<i>w</i> (-11 > 13)	3.38
-14	<i>m</i>	7.49
-17	<i>vs</i>	29.53
-20	<i>m</i> (-20 > -14)	10.36
-23	<i>vvs</i> (-23 > 22)	100.00
-26	<i>vs</i>	34.03
-29	<i>s</i>	13.56
-32	<i>s</i>	15.04
-35	<i>s</i>	15.42

One of the polytypic regions of specimen 232/51 is 36*R*(7 5)₃ with 12 layers in its elementary stacking sequence while those of all the other polytypes in the same specimen contain 24 layers. At first sight this seems to be a case where there is a change in the Burgers vector of the screw dislocation around which the crystal grew (Mardix & Kiflawi, 1970). However, since the polytypic region 36*R*(7 5)₃ is located between regions of the family 24*L* it follows that during the growth of the crystal two changes in the dimension of

the Burgers vector *b* of the screw dislocation must have occurred – a change from 24 *C*₀ to 12 *C*₀ and back to 24 *C*₀, where *C*₀ is the interplanar distance between the (00.1) planes. Such a change (by 75 Å) is unlikely to occur, and still more unlikely to occur twice. Thus we may presume that this is a case of ‘degeneracy’ where the stacking sequence of 24 consecutive layers is 7 5 7 5. The unit cell of such a sequence happens to be 36*R*(7 5)₃. Similar cases have already been found (Mardix & Kiflawi, 1970).

Two peculiarities of the 24-layer polytypes should be noted:

(a) The number of known 24*L* polytypes is greater than the known number of any other family. 33 different 24-layer polytypes are now known in comparison with 25 and 13 polytypes respectively of the next most frequent families 20*L* and 16*L*.

(b) Each specimen that was found to belong to the family 24*L* contains a relatively large number of different polytypes in wide regions. All 33 known 24*L* polytypes were found in only 4 specimens: 232/51 and 232/56 which are reported here; 220/58 (Mardix & Brafman, 1968) and 106/34 (Kiflawi & Mardix, 1969). No other specimens investigated in this laboratory were found to contain 24-layer polytypes.

A ZnS crystal containing several kinds of 24-layer polytypes was reported by Farkas-Jahnke (1965).

It is clear that property (a) might be a consequence of property (b).

References

- FARKAS-JAHNKE, M. (1965). *Acta Cryst.* **18**, 571.
 KIFLAWI, I. & MARDIX, S. (1969). *Acta Cryst.* **B25**, 2415.
 MARDIX, S. & BRAFMAN, O. (1968). *Acta Cryst.* **B24**, 258.
 MARDIX, S., KALMAN, Z. H. & STEINBERGER, I. T. (1970). *Acta Cryst.* **A26**, 599.
 MARDIX, S. & KIFLAWI, I. (1970). *Crystal Lattice Defects*, **2**, 129.
 MARDIX, S., KIFLAWI, I. & KALMAN, Z. H. (1969). *Acta Cryst.* **B25**, 1586.

Acta Cryst. (1971). **B27**, 381

Refinement of the Structure of (-)-Ephedrine Hydrochloride

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A previous structure determination from two projections of ephedrine hydrochloride has now been refined to *R* = 0.054 using a full set of three-dimensional diffractometer data. The mean standard deviation in bond length has been improved from 0.033 to 0.006 Å.

Introduction

Previous work by Phillips (1954) on the crystal and molecular structure of ephedrine hydrochloride was

carried out in projection on (010) and (001) with Weissenberg data. The mean standard deviation of the bond lengths was estimated to be 0.033 Å. The positional atomic coordinates given by Phillips were used for a

calculation of bond lengths and bond angles: the parameters obtained were found to differ from those published by Phillips by up to 0.2 Å and 14° respectively. These discrepancies have already been pointed out in the form of editorial comments in *Structure Reports* (1954). Phillips has since informed us that there was a misprint in his original paper: the *z/c* coordinate for the C(4) atom was quoted as 0.6390 instead of 0.6930 as it ought to have been.

In order to make a critical comparison between the ephedrine molecule on the one hand and catecholamines and related compounds on the other it was found necessary to obtain more accurate parameters than those given by Phillips. Ephedrine and the other aminoalcohols being studied in our research programme are all biologically active and are of great interest in molecular pharmacology.

Experimental

Reagent pure (–)-ephedrine hydrochloride was recrystallized in water. The unit-cell dimensions were determined from Weissenberg photographs and from diffractometer measurements. The density of single crystals was measured by flotation in mixed organic solvents.

Crystal data

(–)-ephedrine hydrochloride, monoclinic
 $C_{10}H_{15}ON \cdot HCl$ M.W. 201.70
 $a = 12.671 \pm 0.003$ Å $V = 550.85$ Å³
 $b = 6.090 \pm 0.004$ Å $D_m = 1.208 \pm 0.002$ g.cm⁻³
 $c = 7.301 \pm 0.002$ Å $D_x (Z=2) = 1.216$ g.cm⁻³
 $\beta = 102.11 \pm 0.08^\circ$ $\mu_{Mo K\alpha} = 3.13$ cm⁻¹

Absent reflexions: $0k0$ when k is odd.

Space group: $P2_1$.

All data agree well with those given by Phillips (1954). The intensities of the reflexions were collected with an automatic diffractometer (PAILRED) using strictly monochromatic Mo $K\alpha$ radiation. The crystal selected for the intensity measurements was trimmed to a nearly spherical shape (largest and smallest radii 0.21 and 0.20 mm respectively) and was oriented about the b axis. In order that the measurement of intensities should be as accurate as possible the fainter reflexions were scanned up to 7 times and the background was counted for one minute on each side of every peak. In all, 1965 independent reflexions were recorded corresponding to the Cu sphere. The integrated intensities were corrected for background and for Lorentz and polarization factors but not for extinction or absorption. The latter was negligible anyway because of the shape of the crystal and the low μ value. The corrected relative structure amplitudes were put on an absolute scale by Wilson statistics. The $|F_{obs}| \leq 0.7$, comprising 7.4 per cent of the entire set of reflexions, were regarded as 'unobserved' in the following refinement procedure. All calculations up to this stage were performed with

our program system *CRYSTAL* on an IBM 360/75 computer (Bergin & Ringertz, 1969). The rest of the calculations were carried out on an IBM 7090 with the program system *X-RAY-63* by Stewart & High (1965) with the exception of the plot program *ORTEP* by Johnson (1965) which was executed on an IBM 360/75.

Refinement procedure

The coordinates for the non-hydrogen atoms given by Phillips (1954) were applied initially. The atomic scattering factors for the neutral atoms and Cl⁻ were those listed in *International Tables for X-ray Crystallography* (1962) and that for N⁺ was interpolated from the scattering factors of O⁺ and B⁺. Because of the method of counting, which approached fixed-count measurement, the structure amplitudes were given unit weight. Several weighting schemes were tried but did not result in any noticeable improvement compared with the unit weighting adopted. The first cycles of full-matrix least-squares refinement involving non-hydrogen atoms only and isotropic temperature factors yielded an R value of 12.1%. With anisotropic temperature factors the discrepancy index dropped to 7.5 per cent. In a three-dimensional difference Fourier synthesis all the 16 hydrogen atoms were easily located. The hydrogen atoms were now included in a block-diagonal least-squares refinement with coordinates from the difference map and with isotropic temperature factors, equal to those of the atoms to which they were covalently bound. The least-squares refinement was continued until the shifts in the positional coordinates for the non-hydrogen atoms were less than 15% of their estimated standard deviations and those for the hydrogen atoms less than their e.s.d. values, resulting in a final R value of 5.4% for all reflexions and 5.2% with the 'unobserved' reflexions excluded. A table of final observed and calculated structure factors has been deposited in the library of the Royal Swedish Academy of Science, 104 05 Stockholm 50, from where copies can be obtained. The final positional and thermal parameters are given in Tables 1 and 2 respectively.

Table 1. Final fractional atomic coordinates and their estimated standard deviations (in parentheses)

	x/a	y/b	z/c
C(1)	0.3983 (3)	0.3216 (8)	0.7830 (5)
C(2)	0.5102 (4)	0.2961 (9)	0.8309 (6)
C(3)	0.5779 (3)	0.4558 (11)	0.7852 (6)
C(4)	0.5341 (3)	0.6441 (10)	0.6915 (6)
C(5)	0.4217 (3)	0.6689 (8)	0.6439 (5)
C(6)	0.3542 (2)	0.5074 (9)	0.6899 (4)
C(7)	0.2331 (3)	0.5464 (7)	0.6378 (4)
C(8)	0.1971 (3)	0.6971 (7)	0.7822 (4)
C(9)	0.1969 (3)	0.5826 (7)	0.9681 (5)
C(10)	0.0458 (3)	0.9565 (8)	0.8041 (6)
O	0.1688 (2)	0.3546 (6)	0.6296 (4)
N	0.0858 (2)	0.7798 (6)	0.6976 (4)
Cl	0.1250 (1)	0.0	0.3254 (1)
H(1)	0.346 (4)	0.199 (10)	0.821 (6)
H(2)	0.547 (4)	0.131 (10)	0.892 (6)

Table 1 (*cont.*)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(3)	0.660 (3)	0.411 (9)	0.825 (6)
H(4)	0.589 (4)	0.822 (9)	0.623 (6)
H(5)	0.382 (3)	0.802 (9)	0.555 (6)
H(7)	0.217 (3)	0.642 (9)	0.507 (6)
H(8)	0.247 (3)	0.830 (9)	0.805 (5)
H(91)	0.136 (3)	0.497 (11)	0.969 (5)
H(92)	0.271 (3)	0.536 (9)	1.024 (5)
H(93)	0.183 (3)	0.663 (9)	1.055 (6)
H(101)	0.088 (4)	1.038 (10)	0.840 (6)
H(102)	0.035 (4)	0.878 (10)	0.950 (7)
H(103)	-0.023 (3)	0.994 (12)	0.740 (6)
H(11)	0.176 (4)	0.275 (10)	0.559 (7)
H(121)	0.075 (3)	0.833 (8)	0.575 (5)
H(122)	0.044 (3)	0.713 (8)	0.675 (5)

Description and discussion of the structure

Geometry of the molecule

The configuration of the molecule is illustrated in Fig. 1 which also shows the ellipsoids of thermal motion scaled to include 50 per cent probability. The configuration shown is that assigned to (-)-ephedrine. The overall shape conforms nicely with those of related compounds, that is, the molecule is in its most extended form, the C(8)-N bond being nearly parallel to the C(6)-C(7) bond. This general conformation of the molecule is not only found in the bis-(+)-pseudoephedrine complex of copper(II) (Bailey, Harrison & Mason, 1968) but also in (-)-noradrenaline (Carlström & Bergin, 1967) and dopamine (Bergin & Carlström, 1968). However, this arrangement is not in agreement with that predicted for ephedrine by Close (1950) who, from chemical evidence, proposed that the C(8)-C(9) bond rather than the C(8)-N bond should be parallel to C(6)-C(7) and hence the hydroxyl and methylamino groups would be quite far apart. In such an arrangement the nitrogen atom would be shielded by carbon

atoms on three sides and only one of its hydrogen atoms would be readily available for hydrogen bonding.

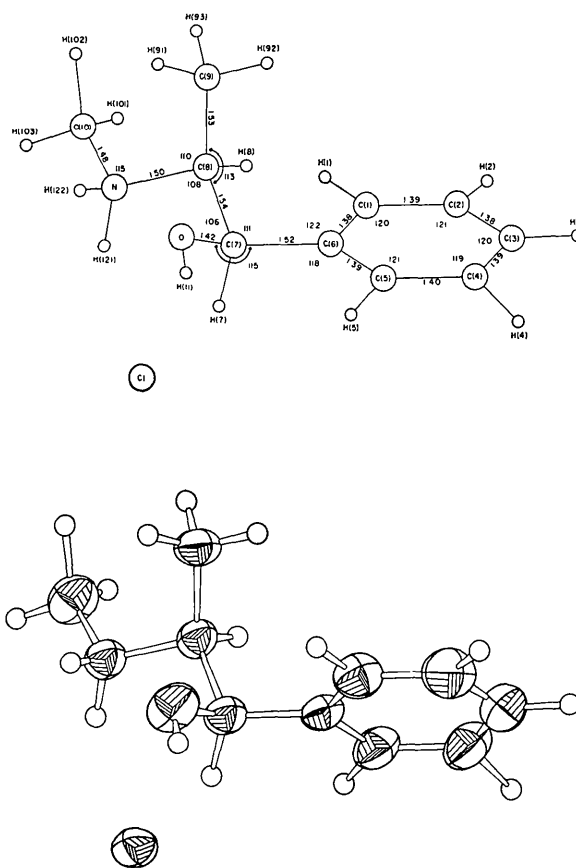


Fig. 1. The numbering of the atoms and major bond lengths and bond angles in the ephedrine molecule (top). Thermal ellipsoids of non-hydrogen atoms scaled to 50 per cent probability. The hydrogen atoms are only shown as small equally-sized spheres (bottom).

Table 2. *Thermal parameters and their standard deviations (in parentheses)*

β_{ij} are the coefficients in the expression: $\exp \{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0080 (3)	0.0245 (12)	0.0200 (8)	0.0016 (5)	0.0040 (4)	0.0032 (8)
C(2)	0.0091 (4)	0.0351 (16)	0.0232 (9)	0.0061 (7)	0.0032 (5)	0.0018 (11)
C(3)	0.0068 (3)	0.0498 (24)	0.0215 (8)	0.0029 (7)	0.0035 (4)	-0.0023 (12)
C(4)	0.0072 (3)	0.0420 (19)	0.0239 (9)	-0.0022 (7)	0.0064 (4)	-0.0009 (12)
C(5)	0.0069 (3)	0.0286 (13)	0.0192 (7)	0.0003 (5)	0.0051 (4)	0.0041 (8)
C(6)	0.0061 (2)	0.0223 (8)	0.0130 (5)	0.0011 (5)	0.0036 (2)	-0.0003 (8)
C(7)	0.0058 (2)	0.0262 (12)	0.0142 (5)	-0.0008 (4)	0.0030 (3)	-0.0038 (7)
C(8)	0.0051 (2)	0.0219 (9)	0.0148 (6)	-0.0013 (4)	0.0028 (3)	-0.0031 (6)
C(9)	0.0071 (2)	0.0307 (13)	0.0128 (6)	-0.0009 (5)	0.0033 (3)	-0.0020 (7)
C(10)	0.0078 (3)	0.0271 (15)	0.0228 (8)	0.0015 (5)	0.0045 (4)	-0.0047 (9)
O	0.0084 (2)	0.0298 (10)	0.0241 (6)	-0.0048 (4)	0.0056 (3)	-0.0125 (7)
N	0.0054 (2)	0.0237 (9)	0.0150 (5)	-0.0009 (3)	0.0027 (2)	-0.0030 (6)
Cl	0.0065 (0)	0.0272 (2)	0.0146 (1)	0.0012 (1)	0.0027 (1)	-0.0034 (2)

	<i>B</i>		<i>B</i>		<i>B</i>		<i>B</i>
H(1)	4.1 (1.2)	H(5)	3.1 (1.0)	H(92)	1.8 (0.9)	H(103)	3.8 (1.0)
H(2)	6.1 (1.5)	H(7)	1.8 (0.9)	H(93)	1.8 (0.9)	H(11)	3.4 (1.2)
H(3)	3.2 (1.1)	H(8)	1.4 (0.8)	H(101)	3.7 (1.2)	H(121)	1.8 (0.9)
H(4)	5.5 (1.3)	H(91)	3.0 (0.9)	H(102)	3.7 (1.2)	H(122)	1.6 (0.9)

From the pharmacological point of view this is a very improbable situation as the nitrogen atom carrying the positive charge which is essential for the biological activity should be as accessible as possible.

The benzene ring is planar within the limits of error and the deviations of the atoms from the plane defined by the equation $-0.2148 X + 0.2757 Y + 0.6517 Z = 0.5134$ are given in Table 3. The fully extended side chain is not far from being planar with respect to the atoms C(6)-C(7)-C(8)-N-C(10). The equation of this plane is $0.4777 X + 0.4421 Y - 0.4690 Z = 0.5707$ and the deviations of the atoms from the plane are also given in Table 3. The acute angle between the normals to the two planes is 76.2° . This configuration is in agreement with those of other phenethylamines (Chotia & Pauling, 1969).

Table 3. Deviations from the best planes through the benzene ring (A) and the side chain (B)

	A		B
C(1)	+0.0002 Å	C(6)	-0.129 Å
C(2)	-0.0012	C(7)	+0.033
C(3)	+0.0015	C(8)	+0.216
C(4)	-0.0009	N	-0.015
C(5)	-0.0001	C(10)	-0.105
C(6)	+0.0004		

The bond angles and bond lengths and their e.s.d. values are listed in Tables 4 and 5 and the more important ones are also illustrated in Fig. 1. The mean aromatic C-C distance, 1.388 Å, and the mean paraffinic C-C distance, 1.525 Å, agree well with standard bond lengths. The two C-N bonds, 1.478 and 1.501 Å, have

Table 4. Interatomic distances and standard deviations (in parentheses)

C(1)-C(2)	1.394 (6) Å	C(5)-H(5)	1.09 (5) Å
C(2)-C(3)	1.382 (8)	C(7)-H(7)	1.10 (4)
C(3)-C(4)	1.390 (8)	C(8)-H(8)	1.02 (5)
C(4)-C(5)	1.399 (6)	C(9)-H(91)	0.93 (5)
C(5)-C(6)	1.390 (6)	C(9)-H(92)	0.98 (4)
C(6)-C(1)	1.376 (5)	C(9)-H(93)	0.85 (5)
C(6)-C(7)	1.518 (5)	C(10)-H(101)	0.74 (5)
C(7)-C(8)	1.538 (5)	C(10)-H(102)	1.20 (5)
C(8)-C(9)	1.528 (5)	C(10)-H(103)	0.93 (4)
C(7)-O	1.418 (5)	O-H(11)	0.73 (6)
C(8)-N	1.501 (4)	N-H(121)	0.93 (4)
N-C(10)	1.478 (6)	N-H(122)	0.66 (4)
C(1)-H(1)	1.08 (5)	O...Cl	3.066 (3)
C(2)-H(2)	1.16 (6)	N...Cl'	3.164 (3)
C(3)-H(3)	1.05 (4)	N...Cl''	3.139 (3)
C(4)-H(4)	1.43 (5)		

$$\text{Cl}' = x, 1 + y, z$$

$$\text{Cl}'' = -x, \frac{1}{2} + y, 1 - z$$

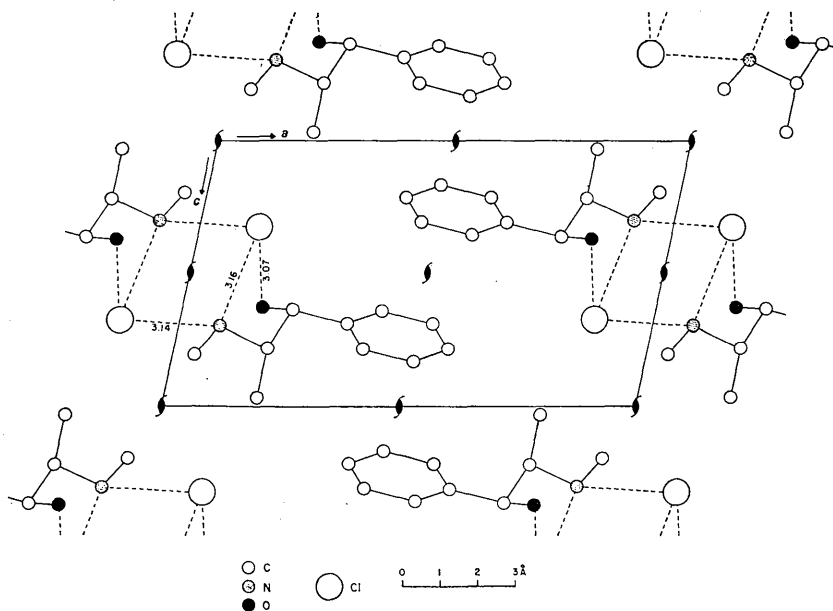


Fig. 2. The packing of the ephedrine molecules in the unit cell and the hydrogen bonding system to the chlorine ions. Distances in Å.

significantly different lengths according to the test suggested by Cruickshank (1966). The C(8)–N–C(10) angle (115.0°) is also much larger than a tetrahedral angle. These differences have already been observed by Phillips (1954). The mean C–N bond length, 1.490 Å, moreover is longer than the standard C–N bond but agrees well with the average value for a C–N⁺ single bond (Hahn, 1957). The mean C–H and N–H bond length, 0.99 Å is quite acceptable but the deviation from this value is considerable (0.66 to 1.43 Å). This is certainly due to the fact that no efforts were made to restrict the positional coordinates or *B* values of the hydrogen atoms during the least-squares refinement procedure. The positions of some of the hydrogen atoms is thus not as accurate as might be implied by their e.s.d. values. There is one short intramolecular distance, O···N = 2.877 Å, indicative of a hydrogen bond. However, neither the hydrogen atoms on the N atom nor that on the O atom have orientations suitable for the formation of such a bond, the closest approach (2.76 Å) being that between H(122) and O. In pseudoephedrine there is a similar situation with a short O···N distance (2.70 Å) which was interpreted by Bailey, Harrison & Mason (1968) as a genuine intramolecular hydrogen bond. However, the positions of the hydrogen atoms were not determined in this case.

Hydrogen bonds and packing of the molecule

The mutual arrangement of the ephedrine molecules and the hydrogen bonding system shown in Fig. 2 have already been elegantly described in the previous structure determination of ephedrine hydrochloride by Phillips (1954). There is accordingly not much to add. The two N···Cl distances of 3.12 and 3.20 Å reported

by Phillips are now found to be nearly equidimensional, 3.14 and 3.16 Å respectively. These values are slightly shorter than the N···Cl distances in the closely related compounds dopamine hydrochloride, 3.18, 3.26, 3.32 Å (Bergin & Carlström, 1968) and noradrenaline hydrochloride, 3.20 and 3.21 Å (Carlström & Bergin, 1967). Each of the two hydrogen atoms of the nitrogen atom are directed towards a chlorine atom; the angle N–H(121)···Cl' ($x, 1+y, z$) is 156° while the angle N–H(122)···Cl'' ($-x, \frac{1}{2}+y, 1-z$) is 164° , resulting in H···Cl distances appreciably shorter than the sum of van der Waals radii. In the third hydrogen bond, O···Cl (3.07 Å), the O–H···Cl angle (158°) is likewise quite favourable and also in this case the H···Cl distance is short, 2.38 Å. Apart from the hydrogen bonding system the structure is held together by van der Waals forces.

The temperature factor

The thermal parameters of the atoms given in Table 2 and of the non-hydrogen atoms also illustrated in Fig. 1 are all acceptable. It should be mentioned here that the direction of the largest thermal vector of the chlorine atom suggested by Phillips (1954) is nearly that now actually observed.

It is a pleasure to thank D. Carlström for his help and interest in this study and Ingrid Hacksell for producing the figures. The work was supported by the Swedish Medical Research Council (Project No B70-11X-144-06A).

References

BAILEY, N. A., HARRISON, P. M. & MASON, R. (1968). *Chem. Comm.* **10**, 559.

Table 5. *Interatomic angles and standard deviations (in parentheses)*

C(6)–C(1)–C(2)	120.1 (4)°	C(8)–C(7)–H(7)	105 (3)°
C(1)–C(2)–C(3)	120.6 (5)	O–C(7)–H(7)	114 (2)
C(2)–C(3)–C(4)	119.8 (4)	C(7)–C(8)–H(8)	109 (3)
C(3)–C(4)–C(5)	119.4 (5)	C(9)–C(8)–H(8)	109 (2)
C(4)–C(5)–C(6)	120.5 (4)	N–C(8)–H(8)	107 (2)
C(5)–C(6)–C(1)	119.7 (3)	C(8)–C(9)–H(91)	115 (2)
C(5)–C(6)–C(7)	117.9 (4)	C(8)–C(9)–H(92)	109 (3)
C(1)–C(6)–C(7)	122.4 (4)	C(8)–C(9)–H(93)	116 (3)
C(6)–C(7)–C(8)	110.5 (3)	H(91)–C(9)–H(92)	123 (4)
C(6)–C(7)–O	114.9 (3)	H(91)–C(9)–H(93)	91 (4)
O–C(7)–C(8)	105.7 (3)	H(92)–C(9)–H(93)	101 (4)
C(7)–C(8)–C(9)	113.2 (3)	N–C(10)–H(101)	112 (4)
C(7)–C(8)–N	107.8 (2)	N–C(10)–H(102)	107 (3)
C(9)–C(8)–N	110.1 (3)	N–C(10)–H(103)	108 (4)
C(8)–N–C(10)	115.0 (3)	H(101)–C(10)–H(102)	99 (4)
C(6)–C(1)–H(1)	120.0 (3)	H(101)–C(10)–H(103)	123 (6)
C(2)–C(1)–H(1)	120.0 (3)	H(102)–C(10)–H(103)	106 (4)
C(1)–C(2)–H(2)	120.0 (2)	C(8)–N–H(121)	116 (3)
C(3)–C(2)–H(2)	119.0 (3)	C(8)–N–H(122)	122 (4)
C(2)–C(3)–H(3)	112.0 (3)	C(10)–N–H(121)	105 (3)
C(4)–C(3)–H(3)	128.0 (3)	C(10)–N–H(122)	104 (4)
C(3)–C(4)–H(4)	129.0 (2)	H(121)–N–H(122)	92 (4)
C(5)–C(4)–H(4)	112.0 (2)	C(7)–O–H(11)	116 (4)
C(4)–C(5)–H(5)	123.0 (2)	O–H(11)···Cl	158 (5)
C(6)–C(5)–H(5)	116.0 (2)	N–H(121)···Cl'	156 (3)
C(6)–C(7)–H(7)	107.0 (2)	N–H(122)···Cl''	164 (5)

- BERGIN, R. & CARLSTRÖM, D. (1968). *Acta Cryst.* B24, 1506.
 BERGIN, R. & RINGERTZ, H. (1969). In RINGERTZ, H. *Stereochemical Aspects of Purine Degradation*. Thesis. Stockholm 1969.
 CARLSTRÖM, D. & BERGIN, R. (1967). *Acta Cryst.* 23, 313.
 CHOTIA, C. & PAULING, P. (1969). *Proc. Nat. Acad. Sci. Wash.* 63, 1063.
 CLOSE, W. J. (1950). *J. Org. Chem.* 15, 1131.
 CRUICKSHANK, D. W. J. (1966). In LIPSON, H. & COCHRAN, W. *The Crystalline State*, Vol. III, *The Determination of Crystal Structures*, p. 356. London: Bell.
 HAHN, T. (1957). *Z. Kristallogr.* 109, 438.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*. ORNL-3794, Oak Ridge National Laboratory, Tennessee.
 PHILLIPS, D. C. (1954). *Acta Cryst.* 7, 159.
 STEWART, J. M. & HIGH, D. (1965). *X-RAY-63, Program System for X-ray Crystallography for the IBM 709-7090-7094*. Depts. of Chemistry, Univ. of Washington, Seattle and Univ. of Maryland, College Park, U.S.A.
Structure Reports (1954). 18, 769. Utrecht: Oosthoek.

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The Crystal Structure of AlSeCl_7

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Solid AlSeCl_7 appears as irregular blocks of yellow triclinic crystals. The space group is $P1$. The lattice constants are $a=9.87$, $b=8.27$, $c=9.83$ Å, $\alpha=139.9^\circ$, $\beta=94.8^\circ$, $\gamma=93.8^\circ$ and $Z=2$. The structure, solved by minimum functions applied to photographic data (Mo radiation), is built up from AlCl_4 tetrahedra and SeCl_6 octahedra. The tetrahedra ($\text{Al-Cl}=2.13$ Å) are quite regular but the octahedra are distorted and contain three long and three short Se-Cl distances (3.04 and 2.11 Å). The chlorine atoms contributing to the long Se-Cl distances are shared between Al and Se. The structure consists approximately of AlCl_4^- and SeCl_3^+ ions.

Introduction

A number of compounds with composition $\text{M}^{n+}\text{Cl}_n \cdot \text{XCl}_4$ (X being S, Se or Te) were prepared and investigated by Groeneveld (1953). For the complex with $\text{M}=\text{Al}$ and $\text{X}=\text{Se}$ he found an Al/Se ratio of 1:1 and not a ratio of 2:1 as reported by Weber (1858) and Lenher & Kao (1926). In view of the chlorine donating properties of SeCl_4 it can be anticipated that the title compound consists of AlCl_4^- and SeCl_3^+ ions. Aluminum compounds AlBr_3 , $\text{Al}(\text{CH}_3)_3$ and $\text{Al}(\text{CH}_3)_2\text{X}$, X being Br or Cl, form dimeric molecules in the solid and vapour state, in which the aluminum atoms are tetrahedrally coordinated by Br, Cl or CH_3 groups (Renes & MacGillavry, 1945; Palmer & Elliot, 1938; Brockway & Davidson, 1941). Gaseous aluminum trichloride also consists of double molecules, Al_2Cl_6 (Palmer & Elliot, 1938). In the solid state, however, it forms cubic close-packed layers of Cl ions with Al ions in octahedral coordination (Ketelaar, MacGillavry & Renes, 1947). In view of the fluctuating coordinating properties of aluminum with respect to chlorine it was deemed necessary to investigate the crystal structure of AlSeCl_7 .

Experimental

AlSeCl_7 was obtained by boiling a solution of 1.5 mol AlCl_3 and 1 mol SeCl_4 in SO_2Cl_2 . After cooling, pale

yellow crystals appeared which were filtered in the absence of moisture. The product was washed with SO_2Cl_2 and dried *in vacuo*. The crystals were of irregular shape. Owing to their extreme sensitivity to moisture several crystals were used during the investigation.

Unit-cell dimensions were derived from equi-inclination Weissenberg photographs about axes a' (zero, first and second layer) and c' (zero layer) using unfiltered copper radiation ($\lambda_{K\alpha_1}=1.54051$, $\lambda_{K\alpha_2}=1.54433$, $\lambda_{K\beta}=1.39217$ Å). The photographs were superposed with aluminum powder lines ($a=4.0492$ Å at 20°C). The measured interplanar spacings $d(hkl)$ were determined with a linear least-squares program resulting in the following parameters:

$$\begin{array}{ll} a' = 14.50 \text{ \AA} & \alpha' = 123.4^\circ \\ b' = 6.37 & \beta' = 42.7 \\ c' = 9.83 & \gamma' = 121.3 \end{array}$$

The Delaunay reduced cell (*International Tables for X-ray Crystallography*, 1952) was obtained by the transformation $1\ 0\ \bar{1}/0\ 1\ 1/0\ 0\ \bar{1}$ resulting in a unit cell with

$$\begin{array}{ll} a = 9.87 \text{ \AA} & \alpha = 139.9^\circ \\ b = 8.27 & \beta = 94.8 \\ c = 9.83 & \gamma = 93.8 \end{array}$$

This cell is identical with the Bravais reduced cell (Kennard, Speakman & Donnay, 1967). The least-squares program produces estimated standard devia-