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## The Crystal Structure of AlSeCl<sub>7</sub>

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Solid AlSeCl<sub>7</sub> 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<sub>4</sub> tetrahedra and SeCl<sub>6</sub> octahedra. The tetrahedra (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<sub>4</sub><sup>-</sup> and SeCl<sub>3</sub><sup>+</sup> ions.

### Introduction

A number of compounds with composition M<sup>n+</sup>Cl<sub>n</sub>.XCl<sub>4</sub> (X being S, Se or Te) were prepared and investigated by Groeneveld (1953). For the complex with M=Al and X=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<sub>4</sub> it can be anticipated that the title compound consists of AlCl<sub>4</sub><sup>-</sup> and SeCl<sub>3</sub><sup>+</sup> ions. Aluminum compounds AlBr<sub>3</sub>, Al(CH<sub>3</sub>)<sub>3</sub> and Al(CH<sub>3</sub>)<sub>2</sub>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<sub>3</sub> groups (Renes & MacGillavry, 1945; Palmer & Elliot, 1938; Brockway & Davidson, 1941). Gaseous aluminum trichloride also consists of double molecules, Al<sub>2</sub>Cl<sub>6</sub> (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<sub>7</sub>.

### Experimental

AlSeCl<sub>7</sub> was obtained by boiling a solution of 1.5 mol AlCl<sub>3</sub> and 1 mol SeCl<sub>4</sub> in SO<sub>2</sub>Cl<sub>2</sub>. After cooling, pale

yellow crystals appeared which were filtered in the absence of moisture. The product was washed with SO<sub>2</sub>Cl<sub>2</sub> 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-

tions in six quantities,  $a^*2$ ,  $b^*2$ ,  $a^*b^* \cos \gamma^*$ , etc. However, the repeat distances and angles of the real lattice are functions of the corresponding quantities in reciprocal space. For this reason it was impossible to calculate standard deviations with this program in the linear version.

Assuming a close-packed array of atoms, a chlorine atom with a radius of 1.8 Å occupies a volume of 33.05 Å<sup>3</sup>. Accordingly, the maximum number of chlorine atoms in the unit cell of AlSeCl<sub>7</sub> cannot be larger than  $V/33.05=15.2$ . There are clearly two units of AlSeCl<sub>7</sub> in the chosen cell. With  $Z=2$  the calculated density is 2.33 g.cm<sup>-3</sup>.

Non-integrated equi-inclination Weissenberg photographs (multiple-film technique) of the layers  $l=0, -1, \dots, -5$  and zero-layer photographs about [021] and [012] were taken at room temperature with Zr-filtered Mo radiation ( $\lambda=0.7107$  Å). The intensities of 1381 reflexions were estimated visually and reduced to structure factor moduli in the usual way. An absorption correction was applied assuming a cylindrical cross-section for the crystals used [ $\mu(\text{Mo } K\alpha)=57$  cm<sup>-1</sup>]. The structure factors of the various levels were put on a single scale by hand.

#### Determination of the structure and refinement

As a first step an unsharpened Patterson function was calculated which contained a large extended peak at a distance of 6.8 Å from the origin. It was anticipated that this peak, with a height about 0.4 times the value of the origin peak, should be attributed to several interactions of the kind Se–Se and Cl–Cl. The next class of peaks with heights about 0.1 times the value of the origin peak could be explained as being interactions of the mixed type Se–Cl. However, it was not possible to find a proper solution on the basis of the centric space group  $P\bar{1}$ .

The  $hk0$  reflexions were subjected to the  $N(z)$  test of Howells, Phillips & Rogers (1950). The computer-calculated and plotted curve (Fig. 1) clearly indicates that the structure is acentric and the space group is  $P1$ .

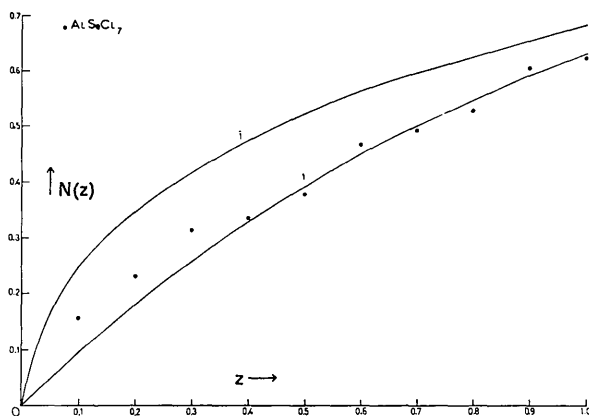


Fig. 1. The intensity distribution of reflexions  $hk0$  in AlSeCl<sub>7</sub>.

Taking into account the ionic radii of Se<sup>4+</sup> (0.5 Å) and of Cl<sup>-</sup> (1.8 Å) we arrive at a shortest Se–Cl distance of approximately 2.3 Å. A careful inspection of spheres with a radius of 2.3 Å about the origin and about the next-largest peak indicates that there are two candidates for single Se–Cl vectors representing a possible image of a part of the structure. A minimum function (Buerger, 1959) was therefore calculated by shifting over these two vectors. A model on spokes was constructed from the 31 highest peaks of this superposition function. We could distinguish two octahedra of chlorine atoms, the centres of which are separated by a vector of 6.8 Å (see Fig. 2) corresponding with the highest peak in the original Patterson function. The two octahedra are more or less oriented in the same direction, explaining why many overlapping interactions contribute to the predominant peak. At this stage two selenium and twelve chlorine atoms were located.

The positions of these atoms were refined with a least-squares method (block-diagonal approximation). Dirac–Slater scattering factors calculated by Cromer & Waber (1965) were used for selenium and chlorine and afterwards also for aluminum atoms. This model refined to a conventional  $R$  index of 36.6% and resulted in a three-dimensional Fourier synthesis in which the two remaining chlorine atoms were found. It was now possible to distinguish more or less close-packed layers of halogen atoms.

Since the refinement with the block-diagonal approximation was slow, we shifted to a full-matrix refinement in which Se(1) was fixed at the origin. The justification for the application of this procedure to an acentric structure was the presence of strong interactions of the kind  $\frac{\delta F}{\delta x_i} \cdot \frac{\delta F}{\delta x_j}, \frac{\delta F}{\delta x_i} \cdot \frac{\delta F}{\delta y_j}$ , etc. contributing to the matrix of normal equations (Srinivasan, 1961). For example, we afterwards observed interactions  $\frac{\delta F}{\delta x_3} \cdot \frac{\delta F}{\delta x_7}, \frac{\delta F}{\delta y_3} \cdot \frac{\delta F}{\delta z_7}$  [Cl(3) and Cl(7)] amounting to  $-0.28 \times 10^3$  and  $-0.18 \times 10^3$ . The elements  $\left(\frac{\delta F}{\delta x_3}\right)^2$  and  $\left(\frac{\delta F}{\delta x_7}\right)^2$  were  $0.38 \times 10^4$  and  $0.36 \times 10^4$  respectively.

After four cycles with an overall temperature factor the reliability index dropped to 26.2%. Attempts to locate the aluminum atoms failed at this stage. The refinement was continued with individual isotropic  $B$  values and the  $R$  index decreased to 21.7%. It was decided to calculate a difference Fourier synthesis; the aluminum atoms could then be distinguished. After three more cycles with isotropic  $B$  values the agreement index dropped to 16.1%. Up to this stage unitary weights were used. Analysis of the residuals for different groupings of  $F$  values suggested the weighting scheme  $w=1/a+F_{\text{obs}}+bF_{\text{obs}}^2$  with  $a=2.0$  and  $b=0.0755$ ; for  $F_{\text{obs}} \leq 6.0$  the value  $F_{\text{obs}}=6.0$  was used. The smallest estimated intensity value (before reduction) was 1.0. The non-observed reflexions were given this intensity

values resulting in slightly varying  $F=(1 \times (Lp)^{-1} \times \text{absorption correction})^{1/2}$  after reduction. Only if  $F_{\text{calc}} > F_{\text{obs}}$  were these reflexions included in the refinement with an  $F_{\text{obs}}$  value of  $0.7 \times F$  and a constant weight of 0.05. The refinement with isotropic  $B$  values was continued over 4 cycles and  $R$  decreased to 12.3% (observed reflexions only). The largest errors, probably due to inefficient absorption correction and/or extinction effects, were observed for the 14 strongest reflexions (Table 1). These reflexions were discarded during the following calculations. A difference electron density map was computed, which gave a clear indication of the anisotropic thermal motion for nearly all the atoms. Since most difficulty was encountered in the location of the aluminum atom we checked that no disordering of these atoms was present in this map.

Table 1. Discarded structure factors

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>
2	0	0	83.7	102.4
-3	1	0	110.8	109.4
-6	2	0	114.2	96.7
3	-2	-1	107.8	153.4
0	-1	-1	76.1	107.8
-3	0	-1	110.1	169.4
2	3	-1	98.5	139.3
5	1	-2	125.4	147.5
2	2	-2	92.2	133.0
-1	3	-2	162.4	169.7
2	1	-3	139.1	162.5
-4	3	-3	118.0	146.7
4	3	-5	88.1	71.9
1	4	-5	106.5	122.6

The final anisotropic refinement was carried out over two cycles. The matrix to the normal equations was

Table 2. Calculated and observed structure factors on an absolute scale ( $\times 10$ ).

The non-observed reflexions are indicated by a minus sign.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>
1	0	0	70	112	3	4	0	119	150	10	-4	0	-75	30
4	0	0	455	537	1	4	0	114	112	11	-4	0	122	151
4	0	0	700	705	4	0	0	705	700	12	-4	0	124	154
6	0	0	545	625	3	4	0	257	278	13	-4	0	134	158
7	0	0	369	406	4	0	0	186	156	14	-4	0	139	161
8	0	0	285	317	5	0	0	149	126	15	-4	0	143	164
9	0	0	310	259	4	0	0	275	216	16	-4	0	147	167
10	0	0	268	263	7	4	0	213	177	17	-4	0	151	170
11	0	0	190	194	4	0	0	120	104	18	-4	0	155	173
12	0	0	130	117	9	4	0	95	96	19	-4	0	159	176
-11	0	0	204	210	17	4	0	90	160	20	-4	0	163	179
-10	0	0	80	60	11	5	0	96	104	21	-4	0	167	182
-9	0	0	100	158	10	5	0	184	199	22	-4	0	171	185
-8	0	0	156	168	9	5	0	80	30	23	-4	0	175	188
-7	0	0	683	636	8	4	0	709	265	24	-4	0	179	191
-6	0	0	148	150	7	4	0	83	45	25	-4	0	183	194
-5	0	0	226	207	6	4	0	227	250	26	-4	0	187	197
-4	0	0	100	100	5	4	0	176	148	27	-4	0	191	200
-3	0	0	279	273	4	4	0	243	275	28	-4	0	195	203
-2	0	0	728	674	3	4	0	209	187	29	-4	0	199	206
-1	0	0	384	442	2	5	0	392	378	30	-4	0	203	209
1	1	0	726	748	-1	5	0	455	401	31	-4	0	207	212
2	1	0	607	620	0	5	0	188	168	32	-4	0	211	215
3	1	0	398	409	1	5	0	199	186	33	-4	0	215	218
4	1	0	500	451	2	5	0	194	179	34	-4	0	219	221
5	1	0	451	377	3	5	0	167	173	35	-4	0	223	224
6	1	0	331	316	4	5	0	199	196	36	-4	0	227	227
7	1	0	88	42	5	5	0	278	242	37	-4	0	231	230
8	1	0	707	747	6	5	0	81	87	38	-4	0	235	233
9	1	0	156	169	7	5	0	67	197	39	-4	0	239	236
10	1	0	177	181	8	5	0	107	151	40	-4	0	243	239
11	1	0	554	577	9	5	0	115	150	41	-4	0	247	242
12	1	0	112	115	10	5	0	114	141	42	-4	0	251	245
13	1	0	100	105	11	5	0	159	155	43	-4	0	255	248
14	1	0	156	158	12	5	0	198	216	44	-4	0	259	251
-11	2	0	-86	87	-25	6	0	87	114	-2	5	0	407	412
-10	2	0	114	114	-24	6	0	172	208	-3	5	0	411	416
-9	2	0	213	203	-13	6	0	121	116	-4	5	0	415	420
-8	2	0	418	380	-2	6	0	341	353	-5	5	0	419	424
-7	2	0	132	111	-11	6	0	88	12	-6	5	0	423	428
-6	2	0	176	176	0	6	0	368	358	-7	5	0	427	432
-5	2	0	51	41	1	6	0	-87	98	-8	5	0	431	436
-4	2	0	350	297	2	6	0	237	274	-9	5	0	435	440
-3	2	0	70	247	3	6	0	41	67	-10	5	0	439	444
-2	2	0	681	615	4	6	0	163	189	-11	5	0	443	448
-1	2	0	430	410	5	6	0	97	57	-12	5	0	447	452
1	2	0	508	462	6	6	0	109	78	-13	5	0	451	456
2	2	0	102	60	7	6	0	140	148	-14	5	0	455	460
3	2	0	719	680	8	6	0	97	146	-15	5	0	459	464
4	2	0	288	252	9	6	0	88	97	-16	5	0	463	468
5	2	0	500	429	10	6	0	-94	41	-17	5	0	467	472
6	2	0	152	111	-7	6	0	-84	81	-18	5	0	471	476
7	2	0	242	207	-2	6	0	-86	63	-19	5	0	475	480
8	2	0	291	284	-1	6	0	135	146	-20	5	0	479	484
9	2	0	262	253	0	6	0	86	96	-21	5	0	483	488
10	2	0	124	108	7	6	0	99	128	-22	5	0	487	492
11	2	0	-83	107	2	6	0	171	119	-23	5	0	491	496
12	2	0	130	138	3	6	0	143	146	-24	5	0	495	500
13	2	0	-103	103	-3	6	0	149	143	-25	5	0	499	504
14	2	0	107	44	-2	6	0	107	104	-26	5	0	503	508
-13	3	0	164	171	-1	6	0	-80	106	-2	6	0	507	512
-12	3	0	-83	63	0	6	0	149	141	-3	6	0	511	516
-11	3	0	-87	51	1	6	0	-87	81	-4	6	0	515	520
-10	3	0	293	191	2	6	0	94	122	-5	6	0	519	524
-9	3	0	215	192	3	6	0	-97	95	-6	6	0	523	528
-8	3	0	210	215	4	6	0	139	147	-7	6	0	527	532
-7	3	0	368	364	5	6	0	-87	82	-8	6	0	531	536
-6	3	0	296	273	6	6	0	142	146	-9	6	0	535	540
-5	3	0	177	152	7	6	0	200	180	-10	6	0	539	544
-4	3	0	130	109	8	6	0	-87	85	-11	6	0	543	548
-3	3	0	163	163	9	6	0	145	145	-12	6	0	547	552
-2	3	0	402	314	10	6	0	97	106	-13	6	0	551	556
-1	3	0	237	174	11	6	0	284	246	-14	6	0	555	560
0	3	0	253	253	0	6	0	109	109	-15	6	0	559	564
1	3	0	58	54	1	6	0	175	178	-16	6	0	563	568
2	3	0	738	107	2	6	0	-87	97	-17	6	0	567	572
3	3	0	102	115	3	6	0	88	110	-18	6	0	571	576
4	3	0	525	467	4	6	0	-80	90	-19	6	0	575	580
5	3	0	476	374	5	6	0	189	176	-20	6	0	579	584
6	3	0	167	243	6	6	0	141	146	-21	6	0	583	588
7	3	0	113	172	7	6	0	91	113	-22	6	0	587	592
8	3	0	375	281	8	6	0	124	124	-23	6	0	591	596
9	3	0	138	138	9	6	0	191	185	-24	6	0	595	600
10	3	0	-93	107	10	6	0	211	217	-25	6	0	599	604
11	3	0	139	136	11	6	0	128	127	-26	6	0	603	608
12	3	0	167	167	12	6	0	175	170	-27	6	0	607	612
-13	4	0	-210	63	-7	6	0	-84	41	-2	7	0	611	616
-12	4	0	213	192	-2	6	0	317	316	-3	7	0	615	620
-11	4	0	176	176	-3	6	0	191	191	-4	7	0	619	624
-10	4	0	86	88	0	6	0	134	134	-5	7	0	623	628
-9	4	0	275	278	1	6	0	118	119	-6	7	0	627	632
-8	4	0	291	215	2	6	0	149	149	-7	7	0	631	636
-7	4	0	347	314	3	6	0	245	240	-8	7	0	635	640
-6	4	0	311	313	4	6	0	236	236	-9	7	0	639	644
-5	4	0	403	403	5	6	0	241	241	-10	7	0	643	648
-4	4	0	477	477	6	6	0	185	176	-11	7	0	647	652
-3	4	0	677	676	7	6	0	-86	97	-12	7	0	651	656
-2	4	0	288	288	8	6	0	147	147	-13	7	0	655	660
-1	4	0	295	260	9	6	0	319	280	-14	7	0	659	664

Table 2 (cont.)

H	K	L	FD	FE	H	K	L	FD	FE	H	K	L	FD	FE	H	K	L	FD	FE	H	K	L	FD	FE					
6	2	-2	577	587	4	7	-2	169	167	7	0	-3	378	312	4	5	-3	562	499	5	0	-4	216	199	2	4	-4	-80	57
7	2	-2	90	85	-3	7	-2	-74	68	8	0	-3	158	143	5	5	-3	303	277	6	0	-4	137	143	4	4	-4	256	252
8	2	-2	736	755	-7	7	-2	276	268	6	6	-3	751	764	6	6	-3	766	767	7	0	-4	176	122	4	4	-4	-87	63
9	2	-2	170	181	7	0	-3	350	350	7	0	-3	353	353	7	0	-3	354	352	7	0	-4	112	112	7	0	-4	168	173
10	2	-2	220	217	0	7	-2	301	297	11	7	-2	197	138	8	5	-3	104	787	0	0	-4	-81	47	6	4	-4	107	96
11	2	-2	130	124	1	7	-2	264	262	-2	7	-2	194	184	0	8	-3	104	41	10	0	-4	86	114	7	4	-4	156	167
12	2	-2	157	158	7	1	-2	391	391	7	1	-2	383	383	7	1	-2	384	384	7	1	-4	143	150	-1	3	-4	105	101
13	2	-2	113	86	3	7	-2	238	251	-7	7	-2	215	270	-12	4	-3	121	110	12	0	-4	-94	55	0	3	-4	-104	176
-17	3	-2	86	170	6	7	-2	197	116	-4	7	-2	337	318	-11	4	-3	-90	65	13	0	-4	161	156	1	-3	-4	-103	91
-11	3	-2	300	236	4	7	-2	189	215	-4	7	-2	186	163	-10	6	-3	184	205	0	3	-4	487	497	2	-3	-4	164	191
-10	3	-2	133	165	1	-5	-3	115	83	-4	7	-2	307	466	0	4	-3	99	86	1	-4	-4	352	335	1	-4	-5	-103	23
-9	3	-2	178	184	7	-5	-3	197	150	-3	7	-2	177	167	-8	4	-3	160	162	7	1	-4	464	413	4	-3	-5	204	250
-8	3	-2	139	140	-1	-4	-3	103	71	-7	7	-2	383	386	-7	6	-3	88	90	3	1	-4	231	231	-3	-7	-4	200	218
-7	3	-2	323	316	-7	-4	-3	108	97	-1	7	-2	-44	51	-6	4	-3	154	123	4	1	-4	524	587	-7	-7	-4	-96	53
-6	3	-2	137	117	-1	-4	-3	150	163	0	7	-2	387	269	-7	4	-3	94	89	4	1	-4	104	104	-1	-2	-4	-94	90
-5	3	-2	276	214	0	-4	-3	128	148	1	7	-2	330	318	-4	6	-3	-84	8	4	-4	428	423	0	-2	-4	93	122	
-4	3	-2	111	107	1	-4	-3	103	124	3	7	-2	370	354	-7	6	-3	148	166	7	1	-4	69	84	-7	-7	-4	184	167
-3	3	-2	167	167	7	-4	-3	168	161	4	7	-2	465	491	-7	6	-3	140	130	8	1	-4	266	266	2	-2	-4	102	103
-2	3	-2	93	93	7	-4	-3	164	161	4	7	-2	161	161	0	-4	-3	89	89	4	-4	-4	177	176	9	-7	-4	168	167
0	3	-2	73	52	4	-4	-3	164	148	4	7	-2	370	311	0	4	-3	260	227	10	1	-4	133	128	-4	-1	-5	336	350
1	3	-2	308	333	-4	-3	-3	136	169	7	7	-2	377	317	1	6	-3	430	306	11	1	-4	126	127	-3	-1	-5	-89	75
2	3	-2	204	196	-5	-3	-3	107	187	8	7	-2	411	388	7	6	-3	194	122	4	-4	-4	118	136	-2	-1	-5	300	365
3	3	-2	345	334	-4	-3	-3	237	210	0	7	-2	238	224	3	4	-3	111	140	-9	2	-4	206	226	-1	-1	-5	189	171
4	3	-2	261	231	-3	7	-2	167	133	10	7	-2	166	173	4	6	-3	109	199	-8	2	-4	288	265	0	-1	-5	300	291
5	3	-2	386	426	-7	-3	-3	160	131	11	7	-2	176	167	5	6	-3	24	747	-7	2	-4	141	144	-1	-1	-5	334	332
6	3	-2	179	161	-1	-3	-3	213	142	12	7	-2	132	160	6	6	-3	-87	57	-6	2	-4	265	222	2	-1	-5	397	421
7	3	-2	165	169	0	-3	-3	209	160	13	7	-2	114	109	7	4	-3	210	205	-5	2	-4	237	205	3	-1	-5	348	370
8	3	-2	360	254	-3	-3	-3	160	167	14	7	-2	167	167	4	-4	-3	167	167	4	-4	-4	488	481	3	-1	-5	318	317
9	3	-2	203	205	7	-3	-3	130	141	-12	2	-3	-113	67	0	6	-3	170	117	-3	2	-4	444	430	5	-1	-5	200	267
10	3	-2	215	221	3	7	-2	264	246	-11	2	-3	-106	74	7	7	-3	236	276	-2	2	-4	369	354	6	-1	-5	-87	84
11	3	-2	86	67	2	7	-2	244	198	7	7	-2	211	201	10	4	-3	164	164	10	4	-4	630	615	0	-1	-5	348	332
12	3	-2	190	124	5	-3	-3	268	249	-9	2	-3	325	297	4	7	-3	231	230	2	4	-4	76	70	8	-1	-5	-93	14
13	3	-2	95	57	6	-3	-3	97	48	-8	2	-3	-87	50	5	7	-3	-176	86	1	7	-4	457	450	9	-1	-5	237	282
-11	4	-2	148	144	7	0	-3	244	198	7	2	-3	211	201	10	4	-3	164	164	10	4	-4	24	24	3	4	-4	137	137
-10	4	-2	81	37	8	0	-3	-103	20	-2	2	-3	131	127	-3	-4	-4	73	150	3	7	-4	514	544	-5	0	-5	-87	44
-9	4	-2	180	191	8	0	-3	157	145	-5	2	-3	445	494	-7	-4	-4	77	88	4	7	-4	100	134	-6	0	-5	179	171
-8	4	-2	277	277	7	0	-3	119	149	-7	2	-3	163	163	-7	1	-3	163	163	7	0	-4	324	324	3	4	-4	164	164
-7	4	-2	300	346	11	0	-3	140	154	-3	2	-3	404	412	0	-4	-4	98	80	6	2	-4	392	371	-2	0	-5	164	149
-6	4	-2	284	284	11	0	-3	164	176	-7	2	-3	464	461	1	-4	-4	104	186	7	2	-4	414	412	-1	0	-5	158	168
-5	4	-2	164	171	-7	-7	-3	-106	75	7	2	-3	464	436	3	-4	-4	134	141	9	2	-4	233	237	1	0	-5	72	96
-4	4	-2	511	427	-6	7	-2	227	250	7	2	-3	426	393	4	-4	-4	-94	47	10	2	-4	278	273	7	0	-5	321	367
-3	4	-2	378	367	7	0	-3	164	177	2	7	-2	464	464	7	0	-3	164	164	7	0	-4	153	153	7	0	-4	317	317
-2	4	-2	502	498	-4	7	-2	355	378	5	7	-2	153	149	4	-4	-4	98	111	12	2	-4	184	182	4	0	-5	-77	247
-1	4	-2	360	341	-3	7	-2	180	167	6	7	-2	252	212	7	-4	-4	141	173	17	2	-4	171	117	5	0	-5	266	27
0	4	-2	425	425	7	0	-3	164	164	7	0	-3	248	248	7	0	-3	248	248	7	0	-4	271	262	4	0	-5	178	178
1	4	-2	374	360	-1	7	-2	101	88	8	7	-2	259	236	-3	-3	-4	94	129	2	3	-4	431	422	7	0	-5	116	109
2	4	-2	280	266	0	7	-2	491	495	0	7	-2	-91	33	-2	-3	-4	-91	86	3	4	-4	248	246	8	0	-5	276	277
3	4	-2	276	267	7	0	-3	181	171	-1	7	-2	211	214	-1	7	-2	211	211	7	0	-4	32	32	8	0	-5	104	104
4	4	-2	334	309	7	0	-3	164	190	11	7	-2	179	166	0	-4	-4	153	172	5	3	-4	464	524	10	0	-5	235	240
5	4	-2	149	107	3	7	-2	264	199	17	2	-3	165	177	1	-3	-4	124	147	6	4	-4	251	268	-7	1	-5	271	254
6	4	-2	116	87	7	0	-3	164	411	-10	7	-2	377	292	7	0	-3	181	187	5	10	-4	574	574	10	0	-5	486	486
7	4	-2	147	144	5	7	-2	171	140	-9	7	-2	137	137	1	-3	-4	104	101	8	4	-4	213	232	-5	1	-5	360	355
8	4	-2	137	166	6	-2	-3	265	231	-9	7	-2	194	205	4	-3	-4	-141	163	9	4	-4	267	237	-4	1	-5	331	297
9	4	-2	265	267	7	-2	-3	265	217	2	7	-2	256	218	5	6	-3	217	208	10	3	-4	106	106	-3	1	-5	163	176
10	4	-2	87	74	8	7	-2	165	171	-6	7	-2	447	519	6	-3	-4	156	148	11	7	-4	182	204	-2	1	-5	224	184
11	4	-2	90	131	0	-2	-3	282	241	-6	7	-2	410	381	7	0	-3	305	338	12	-4	-4	-96	85	-1	1	-5	265	248
-9	5	-2	388	311	-1	-1	-1	164	154	-3	7	-2	464	448	8	-3	-4	164	183	3	7	-4	701	701	0	0	-5	183	183
-8	5	-2	71	99	-1	-1	-1	-114	54	0	3	-3	754	240	0	-3	-4	168	180	0	4	-4	371	287	1	1	-5	534	546

viations. The final  $R$  value is 10.9% (including all reflexions) and 10.1% (excluding non-observed reflexions).

The structure factors are listed in Table 2, the positional parameters and their standard deviations in Table 3, and the vibrational parameters  $U_{ij}$  in Table 4.

Structures with space group  $P1$  are quite rare and have three degrees of freedom, *i.e.* one atom can be fixed at will in the unit cell on  $x_0y_0z_0$ . As a result of the least-squares refinement this atom has zero standard deviations in its positional parameters if one refines with a full matrix. This situation is less paradoxical if one remembers that the reflexion intensities are functions of distances and not of positions. The standard deviations in the distance are independent of the choice of origin.

### Discussion of the structure

A projection of the structure along the direction  $\mathbf{a}^*$  on (100) is presented in Fig. 2. The average values of machine-calculated standard deviations are 0.013 Å for Se-Cl, 0.016 Å for Al-Cl and 0.018 Å for Cl-Cl dis-

tances, the influence of errors in the unit-cell parameters being negligible. However, no estimate of systematic errors is incorporated in these standard deviations.

A careful study of adjoining unit cells (not shown in Fig. 2) reveals that the chlorine atoms are stacked in cubic close-packed layers, and suggests a partial ionic character for the structure. The selenium atoms are coordinated octahedrally by six chlorine atoms. The octahedra are distorted in such a way (Table 5) that there are three short Se-Cl distances (average value  $\sim 2.1$  Å) and three large Se-Cl distances (average value  $\sim 3.0$  Å). The symmetry is approximately  $C_{3v}$ . The selenium atom is located on the line connecting the centres of gravity of the two kinds of chlorine atoms (Fig. 3). The interatomic Cl-Cl distances are approximately 3.2 Å in the small triangle and approximately 4.0 Å in the large triangle of chlorine atoms.

Each Al atom is surrounded tetrahedrally by 4 Cl atoms at distances of 2.1 Å. These tetrahedra are quite regular (Table 5). The atoms Cl(13) and Cl(14) are only coordinated to Al, the atoms Cl(1), Cl(4), Cl(5), Cl(7), Cl(8) and Cl(11) only to Se; Cl(2), Cl(3), Cl(6), Cl(9),

Table 3. Atomic parameters (in fractions of cell edges) and their standard deviations (Å)

	$x$	$\sigma(x)$	$y$	$\sigma(y)$	$z$	$\sigma(z)$
Se(1)	0.0	0.0	0.0	0.0	0.0	0.0
Se(2)	0.4763	0.0037	0.3436	0.0060	0.7871	0.0076
Cl(1)	0.0480	0.0131	0.6668	0.0187	0.8784	0.0236
Cl(2)	0.1320	0.0107	0.8490	0.0174	0.6557	0.0194
Cl(3)	0.9963	0.0129	0.4714	0.0170	0.1280	0.0192
Cl(4)	0.9270	0.0119	0.1580	0.0201	0.2658	0.0232
Cl(5)	0.8059	0.0119	0.8348	0.0214	0.7848	0.0257
Cl(6)	0.2965	0.0097	0.3041	0.0165	0.2878	0.0206
Cl(7)	0.4905	0.0116	0.9846	0.0160	0.6428	0.0222
Cl(8)	0.3671	0.0115	0.4890	0.0188	0.0278	0.0226
Cl(9)	0.5768	0.0108	0.1601	0.0174	0.4109	0.0194
Cl(10)	0.4418	0.0121	0.7835	0.0146	0.8794	0.0173
Cl(11)	0.6807	0.0098	0.5491	0.0165	0.9802	0.0195
Cl(12)	0.2040	0.0097	0.0746	0.0194	0.4805	0.0233
Cl(13)	0.8713	0.0097	0.0237	0.0160	0.5443	0.0212
Cl(14)	0.6278	0.0109	0.4212	0.0179	0.2595	0.0218
Al(1)	0.0460	0.0095	0.8565	0.0162	0.4558	0.0200
Al(2)	0.4838	0.0104	0.1670	0.0168	0.2080	0.0205

Table 4. Vibrational parameters  $U_{ij}$  (Å<sup>2</sup>) in the temperature factor  $\exp[-2\pi^2\sum_{ij}U_{ij}a_i^*a_j^*h_ih_j]$

	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{23}$	$2U_{13}$
Se(1)	0.0200	0.0206	0.0228	0.0051	0.0334	0.0058
Se(2)	0.0209	0.0182	0.0274	0.0047	0.0315	0.0071
Cl(1)	0.0635	0.0372	0.0659	0.0330	0.0697	0.0277
Cl(2)	0.0450	0.0508	0.0316	0.0411	0.0692	0.0369
Cl(3)	0.0677	0.0322	0.0199	0.0345	0.0265	0.0016
Cl(4)	0.0494	0.0570	0.0553	0.0413	0.0799	0.0515
Cl(5)	0.0332	0.0592	0.0710	-0.0069	0.0901	-0.0111
Cl(6)	0.0221	0.0356	0.0472	0.0172	0.0511	0.0129
Cl(7)	0.0505	0.0283	0.0634	0.0232	0.0575	0.0193
Cl(8)	0.0403	0.0529	0.0589	0.0240	0.0768	0.0392
Cl(9)	0.0419	0.0446	0.0331	0.0429	0.0568	0.0276
Cl(10)	0.0652	0.0258	0.0127	0.0129	0.0206	0.0002
Cl(11)	0.0284	0.0394	0.0394	-0.0085	0.0601	-0.0124
Cl(12)	0.0253	0.0617	0.0658	-0.0270	0.1097	-0.0150
Cl(13)	0.0309	0.0325	0.0598	0.0337	0.0576	0.0278
Cl(14)	0.0385	0.0435	0.0552	-0.0005	0.0813	0.0073
Al(1)	0.0199	0.0245	0.0373	0.0102	0.0462	-0.0021
Al(2)	0.0238	0.0272	0.0282	0.0153	0.0436	0.0164

Cl(10) and Cl(12) are shared by tetrahedra and octahedra. It can be seen that the shared chlorine atoms are at larger distances from the selenium atoms.

In view of the observed coordination and distances we may conclude that the structure is composed of  $\text{AlCl}_4^-$  ions and  $\text{SeCl}_3^+$  ions, in agreement with the do-

Table 5. Bond lengths ( $\text{\AA}$ ) and decimal angles in  $\text{AlSeCl}_7$

Se(1) octahedron		Se(2) octahedron	
Se(1)—Cl(1)	2.11	Se(2)—Cl(7)	2.12
—Cl(2)	3.03	—Cl(8)	2.11
—Cl(3)	3.05	—Cl(9)	3.03
—Cl(4)	2.07	—Cl(10)	3.05
—Cl(5)	2.13	—Cl(11)	2.13
—Cl(6)	3.11	—Cl(12)	2.97
Cl(1)—Se(1)—Cl(2)	86.7	Cl(7)—Se(2)—Cl(8)	100.0
—Cl(3)	165.0	—Cl(9)	88.1
—Cl(4)	99.3	—Cl(10)	165.8
—Cl(5)	99.4	—Cl(11)	98.9
—Cl(6)	90.2	—Cl(12)	85.9
Cl(2)—Se(1)—Cl(3)	79.8	Cl(8)—Se(2)—Cl(9)	166.3
—Cl(4)	171.4	—Cl(10)	90.9
—Cl(5)	85.9	—Cl(11)	99.3
—Cl(6)	84.8	—Cl(12)	88.1
Cl(3)—Se(1)—Cl(4)	93.3	Cl(9)—Se(2)—Cl(10)	79.5
—Cl(5)	86.6	—Cl(11)	90.3
—Cl(6)	81.8	—Cl(12)	81.4
Cl(4)—Se(1)—Cl(5)	99.1	Cl(10)—Se(2)—Cl(11)	88.2
—Cl(6)	89.0	—Cl(12)	85.4
Cl(5)—Se(1)—Cl(6)	166.3	Cl(11)—Se(2)—Cl(12)	170.2
Al(1) tetrahedron		Al(2) tetrahedron	
Al(1)—Cl(2)	2.12	Al(2)—Cl(6)	2.12
—Cl(3)	2.14	—Cl(9)	2.17
—Cl(12)	2.15	—Cl(10)	2.14
—Cl(13)	2.09	—Cl(14)	2.13
Cl(2)—Al(1)—Cl(3)	108.3	Cl(6)—Al(2)—Cl(9)	112.0
—Cl(12)	107.5	—Cl(10)	109.2
—Cl(13)	113.1	—Cl(14)	108.3
Cl(3)—Al(1)—Cl(12)	108.2	Cl(9)—Al(2)—Cl(10)	107.9
—Cl(13)	110.6	—Cl(14)	107.5
Cl(12)—Al(1)—Cl(13)	109.0	Cl(10)—Al(2)—Cl(14)	112.0

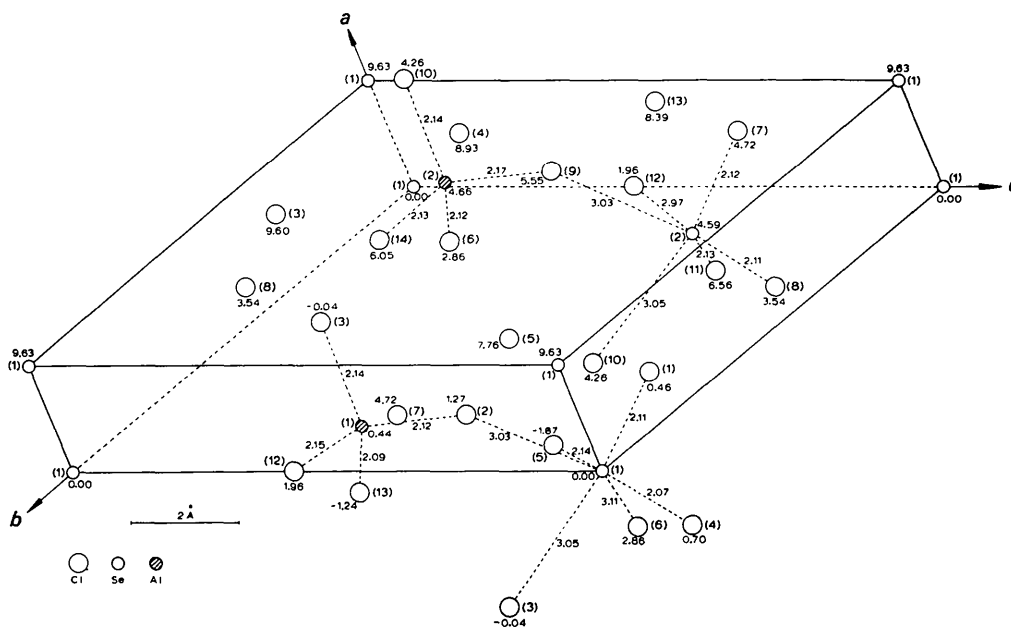


Fig. 2. Projection of the structure of  $\text{AlSeCl}_7$  along the direction  $\mathbf{a}^*$  on a plane parallel to (100). The heights ( $\text{\AA}$ ) of the atoms above this plane are indicated. The numbers in brackets indicate the atoms. The remaining numbers ( $\text{\AA}$ ) refer to bond lengths.

nating properties of  $\text{SeCl}_4$  (Groeneveld, 1953). The observed Al-Cl distances (average 2.13 Å) in this structure agree very well with those ( $\sim 2.14$  Å) found in  $\text{AlCl}_4^-$  ions in the compound  $\text{Mg}(\text{CH}_3\text{CN})_6(\text{AlCl}_4)_2$  (Stork-Blaisse & Romers, 1971). Al is coordinated octahedrally in  $\text{AlCl}_3$  and accordingly the Al-Cl distances are larger ( $\sim 2.31$  Å) (Ketelaar *et al.* 1947).

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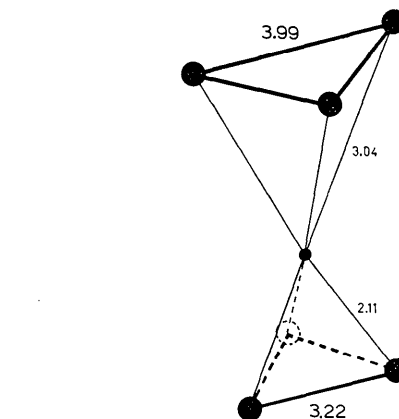


Fig. 3. Idealized deformed octahedron with  $C_{3v}$  symmetry. The distances shown (Å) are mean values of the two octahedra.

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## The Crystal and Molecular Structure of a Sulphur-Containing Antibiotic, 'vD844', 5-Oxo-6-N-methylformylamino-4,5-dihydro-1,2-dithiolo[4,3-b] pyrrole

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The antibiotic 5-oxo-6-N-methylformylamino-4,5-dihydro-1,2-dithiolo[4,3-b]pyrrole,  $\text{C}_7\text{H}_6\text{N}_2\text{O}_2\text{S}_2$ , crystallizes in the monoclinic space group  $P2_1/c$  with four molecules in a unit cell of dimensions  $a = 14.22$ ,  $b = 3.788$ ,  $c = 19.06$  Å;  $\beta = 116.4^\circ$ . The unit cell also contains about 3 molecules of water. The structure was solved from two- and three-dimensional Patterson syntheses and refined by the full-matrix least-squares method, producing a final  $R$  value of 0.105. It shows some disorder, caused partly by the water molecules and partly by the presence of two different conformations of the vD844 molecule in the crystal. The ring system is approximately planar and the side chain is twisted about  $42^\circ$  out of this plane, the angle being approximately the same in both of the conformations of the vD844 molecule. N-H...O hydrogen bonds of length 2.83 Å connect the vD844 molecules in pairs. The positions of the water molecules are not well defined; the molecular packing is very compact and leaves sufficient space for only about three of any four equivalent positions to be occupied. The average distance found between the oxygen atoms of two water molecules is 2.34 Å.

### Introduction

A compound with anti-bacterial activity, and called vD844, has been separated from the culture fluid of an

unidentified *Streptomyces* species isolated from a soil sample collected near Copenhagen. It is strongly active against *Neisseria* and certain other gram-negative organisms, but it is rather toxic. Chemical investiga-