Acta Cryst. (1968). B**24**, 953

A Neutron and X-ray Diffraction Investigation of Aluminum Chloride Hexahydrate

BY D. R. BUCHANAN* AND P. M. HARRIS

Department of Chemistry, The Ohio State University, Columbus, Ohio, U.S.A.

(*Received* 24 *September* 1965 *and in revised form* 29 *September* 1967)

The structure of aluminum chloride hexahydrate, $AlCl_3.6H_2O$, has been studied with X-ray and neutron diffraction techniques. Precise values for the dimensions of the hexagonal unit cell have been obtained: $a=11{\cdot}827\pm0{\cdot}006$, $c=11{\cdot}895\pm0{\cdot}003$ Å. Single-crystal X-ray data have been used to confirm the space group, $R\bar{3}c$, and, by least-squares refinement with the intensity data, to determine more precise values for the coordinates of the oxygen atoms and the chlorine ions than had been obtained previously. The coefficients of the anisotropic temperature factors for these atoms and for the aluminum ion have been obtained and reduced to directed (r.m.s.) amplitudes of vibration. The coordinates of the atomic positions of the hydrogen atoms have been deduced from single-crystal neutron diffraction data; isotropic temperature factor coefficients for all of the atoms have also been obtained. The structure is shown to consist of chains of the type: $-Al(H_2O)_6^{3+}-3Cl^-{-}Al(H_2O)_6^{3+}-3Cl^-{-}$, proceeding parallel to the hexagonal c axis. The six water molecules surrounding a central aluminum ion form an essentially regular close-packed octahedron. The two hydrogen atoms associated with a given oxygen atom lie very nearly on the lines connecting the oxygen atom with the two nearest-neighbor chlorine ions, one of which is a member of the same chain as the oxygen atom, while the other is a member of a neighboring chain.

Introduction

The crystal structure of aluminum chloride hexahydrate, $AlCl_3.6H_2O$, has been determined previously by X-ray diffraction methods (Andress & Carpenter, 1934) from qualitative estimates of the intensities on rotation photographs. They found the crystal symmetry to be $R\bar{3}c$ (D_{3d}^6). The coordinates of the atomic positions of the oxygen atoms and of the chlorine and aluminum ions were determined, but neither the positions of the hydrogen atoms nor temperature factors for any of the atoms could be deduced from the data. A more extensive investigation employing both X-ray and neutron diffraction was therefore undertaken.

Sample preparation and crystal symmetry

Single crystals suitable for X-ray diffraction were readily grown from saturated aqueous solutions of $AlCl_3$. They are clear hexagonal prisms elongated along the c axis and are somewhat hygroscopic. A small single crystal, 0·67 mm × 3 mm, sealed in a glass capillary, was used for the single-crystal X-ray diffraction study. A larger single crystal was ground into nearly cylindrical shape (5·7 mm dia. × 11·8 mm high) for neutron diffraction measurement. It was protected from moisture by a thin-walled aluminum can sealed to a goniometer head.

Unit-cell dimensions were obtained from X-ray powder diffraction data obtained with Cu $K\alpha$ radiation, $\lambda=1{\cdot}5418$ Å. Cell dimensions were refined by a least-squares computer program after the methods of Cohen (1935) and Hess (1951). Eighty-five powder lines were used in the refinement; those which were resolved into α_1,α_2 doublets were replaced by their (hypothetical) α_{av} equivalents. The results of this process are: $a=11{\cdot}827\pm0{\cdot}006$, $c=11{\cdot}895\pm0{\cdot}003$ Å for the hexagonal unit cell.

The space group symmetry, $R\bar{3}c$, was confirmed from Weissenberg and precession photographs. In addition, the observed crystal density was 1·644 g.cm^{-3}; thus there are six molecules per hexagonal unit cell. In agreement with Andress & Carpenter (1934), the atoms are assigned to the following positions of $R\bar{3}c$ (in the triply-primitive hexagonal unit cell): 6 Al in (b), 18 Cl in (e), 36 O in (f). Steric considerations also indicate this to be the most reasonable assignment. The 72 H atoms were assigned in two sets to the general positions (f).

Intensity measurements: X-ray diffraction

Intensity data for 14 levels ($l=0$ to 13) of the hexagonal reciprocal lattice were obtained by the equi-inclination Weissenberg technique with Mo $K\alpha$ radiation. Intensities were estimated visually from multiple film packs with a calibrated exposure strip. The range of intensities measured was approximately 10,000 to 1. In order to correlate approximately the various levels, the intensities from precession photographs of the $h0.l$ and $h1.l$ reciprocal lattice levels were also estimated.

To test the reliability of the intensity estimation, the single crystal used to collect the photographic data was mounted on a diffractometer equipped with a proportional counter and pulse height analyzer. Intensity measurements were made for 19 equatorial reflections;

* Present address: Phillips Petroleum Company, Research and Development Department, Bartlesville, Oklahoma 74003, U.S.A.

Mo $K\alpha$ radiation and the ω-scan technique were used. The relationship between photographic and counter intensities was not quite linear, but was described by

$$I(\text{counter}) = kI^b(\text{film}) , \quad (1)$$

where $b = 0{\cdot}961$ from a least-squares fit of the data. Structure amplitudes, F_{hkl}, were obtained after correcting for 'photographic non-linearity' with equation (1), for 'spot extension' (Phillips, 1954, 1956), for Lorentz and polarization factors, and for absorption. The absorption corrections (with $\mu_{\text{calc}} = 10{\cdot}34$ cm^{-1} for Mo $K\alpha$) were made as if the crystal, actually a nearly regular hexagonal prism, were cylindrical. The maximum error in the relative intensities introduced by this approximation is estimated to be 2%.

Single crystal neutron diffraction measurements*

Integrated intensities were measured by oscillating the crystal through the diffraction peak. Oscillation angles of 1 to 4·3° were used and the mean background at the extremes of the oscillation range was subtracted from the net count. The counter arm was maintained at a constant value of 2θ during the measurement of a reflection. The vertical aperture at the counter was limited by a Soller slit to approximately 0·5°; cadmium masks limited the horizontal aperture to about 5°. Intensity data were collected for 38 unique $hk.0$ and three $00.l$ reflections, comprising all reflections of these types accessible with a wavelength of 1·13 Å. In addition, the intensities of twelve $hk.1$ unique reflections were measured. The intensities for symmetry-equivalent reflections were averaged.

The intensity of each reflection was corrected for the Lorentz factor and for absorption ($\mu_{\text{calc}} = 0{\cdot}26$ cm^{-1}). Cylindrical absorption corrections were used for the $hk.0$ and $hk.1$ reflections; the crystal diameter for the latter set was taken as that of the vertical cylinder enclosing the slightly tilted crystal. Little error results from this assumption for the small tilt angles implied here, especially since μ is small. Cylindrical absorption corrections were also used for the set of $00.l$ reflections by analogy to the cylindrical absorption correction for (hypothetical) $\gamma = 0$ reflections for the n-level equi-inclination Weissenberg case.

An approximate secondary extinction correction was computed after one cycle of least-squares refinement using only those observed reflections with $|F_o| \leq 20$. Following Hamilton (1957), an 'extinction coefficient', E_s, was evaluated such that:

$$E_s = I(\text{obs})/I(\text{calc}) = \exp\left[-aI(\text{obs})\right] , \; E_s \geq 0{\cdot}70 . \quad (2)$$

For these data, $a = 1{\cdot}55 \times 10^{-4}$, corresponding to $E_s = 0{\cdot}67$ for the strongest reflection observed. This extinction correction was applied for the $hk.0$ and $hk.1$ reflections, but not for the $00.l$ reflections, since the crystal orientation was so different in this case.

Least-squares refinement: X-ray data

All least-squares refinements based on the intensity data were done on the IBM 709 computer at the University Numerical Computation Laboratory with Busing & Levy's (1959) program ORXLS. The computation of anisotropic temperature factors was restricted according to Levy's rules (Levy, 1956) for atoms in special positions. These restrictions are shown in Table 3.

The atomic scattering factors used throughout are those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for Al^{3+} and Cl^-, and those of Freeman (1959) for O^-. The input data for the first cycle of refinement were the atomic parameters determined by Andress & Carpenter (1934) (shown in Table 3), an estimated over-all temperature factor, and one scale factor. In later cycles, the overall scale factor was converted to 14 scale factors, one for each Weissenberg level, and individual isotropic temperature factors were computed. Finally anisotropic temperature factors were refined, holding the scale factors constant.

In all but the first few cycles of refinement, 355 unique reflections were used. These were weighted by:

$$w = 1/\sigma^2 ,$$

where

$$\sigma = (1/1{\cdot}75)\left[(|F_o|/|F_o|) + (|F_o|/|F_o|)\right] .$$

These weights were chosen because of our qualitative estimate that the measurement of medium intensities was more reliable than that of either very strong or of very weak intensities. The value of the constant term was empirically chosen to conform to this estimate. After each cycle two residuals were computed:

$$R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o| ,$$

and

$$R_w = [\Sigma \, (w^{1/2}||F_o| - |F_c||)^2]^{1/2} / [\Sigma \, (w^{1/2}|F_o|)^2]^{1/2} .$$

The refinement was terminated after 15 cycles, when the changes in all parameters were less than 20% of the standard deviations. The final values of R and R_w were, respectively, 0·087 and 0·103. Table 1 compares the observed values of the structure factors with the calculated values based on the final parameters; the final parameters and their standard deviations are shown in Table 3.

Least-squares refinement: neutron data

A calculation of bond lengths with the final values from the least-squares refinement based on the X-ray data showed that each oxygen atom has two nearest-neighbor chlorine ions at distances of 3·02–3·03 Å. These distances are within the range of O–H···Cl distances previously reported, 2·95–3·05 Å (*International Tables for X-ray Crystallography*, 1962). Structure factors cal-

* The neutron diffractometers and electronic circuitry used in this investigation were built by the Departments of Physics and Chemistry of The Ohio State University and are operated at the Battelle Memorial Institute Research Reactor.

culated for a model which placed a hydrogen atom 1 Å from the corresponding oxygen atom on the O–Cl vector agreed well with the observed magnitudes; this model was used as the basis for further refinement. The neutron scattering lengths used were (Bacon, 1955): $b_H = -0{\cdot}38 \times 10^{-12}$ cm, $b_O = 0{\cdot}58 \times 10^{-12}$ cm, $b_{Cl} = 0{\cdot}99 \times 10^{-12}$ cm, and $b_{Al} = 0{\cdot}35 \times 10^{-12}$ cm.

The first attempt at refinement was made allowing only the parameters for the hydrogen atoms, including individual isotropic temperature factors, to vary. The values of the other parameters were fixed at the X-ray values. The weighting scheme was an adaptation of that of Evans (1961). All of the unique *hk*.0, *hk*.1, and 00.*l* reflections observed (53) were used. Although the values of R and R_w reached 0·15 and 0·06, respectively, it was evident that the lack of data for reflections with large l led to large oscillations in the parameter values, especially the z coordinates of the hydrogen atoms. Thus it appeared that our best procedure was to obtain the x and y coordinates for the hydrogen atoms by refinement based on the *hk*.0 intensity data alone, and to obtain the z coordinates by another method.

The input parameters for the refinement with *hk*.0 neutron data were the X-ray positions of the aluminum and chlorine ions and the oxygen atoms. The x and y coordinates of the hydrogen atoms, and individual isotropic temperature factors for all atoms were allowed to vary. After six cycles the refinement was terminated, at which time the values of R and R_w were, respectively, 0·163 and 0·060.

The values of the two hydrogen atom z parameters were determined in the following manner. The ratio of the observed structure factors for the 00.6 and 00.12 reflections was 1·41, while the structure factor observed for the 00.18 reflection was small. Both the 00.6 and 00.12 reflections are strong enough so that the counting statistics for both were quite good (<2%) and the only possibly larger error in the ratio $|F|(00.6)/|F|(00.12)$ is that introduced by an unknown extinction correction. Structure factor maps for these reflections were calculated to find that combination of z_H and $z_{H'}$ which made $|F|(00.18)$ smallest and gave that ratio for $|F|(00.6)/|F|(00.12)$ closest to 1·41. The values $z_H = 0{\cdot}083$ and $z_{H'} = 0{\cdot}144$ correspond to a ratio of 1·41 for $|F|(00.6)/|F|(00.12)$, with a near minimum value for $|F|(00.18)$. Although the structure factor maps are symmetric with respect to interchange of z_H and $z_{H'}$, and also symmetric about $z = 0{\cdot}25$, the requirement that the hydrogen atoms lie near the shorter O–Cl vectors allows this assignment without ambiguity. If the possible difference in extinction correction is taken to introduce a maximum error of 20% in this ratio, the maximum error is $\pm 0{\cdot}002$ for both z values. The residuals calculated from these z parameters, and the x and y parameters and isotropic temperature factors from the (*hk*.0) refinement are: $R = 0{\cdot}117$ and $R_w = 0{\cdot}033$ for the fifteen *hk*.1 and 00.*l* reflections. For all reflections the values are: $R = 0{\cdot}146$ and $R_w = 0{\cdot}048$. Observed and calculated values of F are compared in Table 2. A summary of the final values for the parameters appears in Table 3.

These results are further supported by comparison of the neutron diffraction pattern obtained from polycrystalline $AlCl_3.6D_2O$ with that pattern calculated from the atomic parameters determined above. In this case, $b_D = 0{\cdot}65 \times 10^{-12}$ cm was substituted for $b_H = -0{\cdot}38 \times 10^{-12}$ cm (Bacon, 1955). The semi-quantitative agreement between calculated and observed diffraction patterns is quite good.

Interatomic distances and angles

Table 4 shows a collection of nearest-neighbor distances. The standard deviation for each distance is calculated from the standard deviations of the atomic parameters as obtained from the least-squares refinements. Correlated errors are not taken into account. The standard deviations of the angles in Table 4 are

Table 1. 10 $|F_c|$ *and* 10 $|F_o|$ *from X-ray diffraction data*

H	K	10 FC	10 FO
L = 0			
0	3	200	238
0	6	54	43
0	12	63	53
0	15	65	66
1	1	117	114
2	2	185	172
4	4	281	289
5	2	45	39
0	3	92	95
0	6	54	45
7	1	195	196
7	4	169	165
7	7	64	60
10	1	47	33
10	4	73	70
11	5	61	60
12	3	95	95
L = 1			
1	3	130	99
1	6	144	133
1	9	148	144
1	12	50	51
2	1	166	166
2	4	86	85
2	10	87	81
3	2	241	313
3	8	61	43
4	3	56	47
4	6	111	98
5	1	145	132
5	4	47	34
5	7	56	49
6	2	170	182
7	3	70	63
7	6	89	89
8	1	48	45
8	5	75	83
10	6	48	53
12	2	87	69
L = 2			
0	4	103	103
0	7	120	90
0	10	49	66
0	12	72	77
1	2	206	242
1	5	241	275
1	8	56	51
2	0	249	224
2	3	208	215
2	6	140	137
2	9	76	70
2	12	58	68
3	1	210	215
3	4	93	64
3	7	22	20
3	10	75	84
3	13	34	46
4	2	94	77
4	5	114	93
4	8	64	63
4	11	45	31
5	0	90	66
5	3	89	76
5	6	42	39
5	9	68	64
5	12	56	59
6	1	100	83
6	4	120	113
6	7	61	59
6	10	54	60
7	2	170	180
7	8	48	48
8	6	33	41
8	9	42	40
9	1	126	114
9	4	88	92
9	7	45	40
10	2	50	55
10	5	28	41
11	0	127	137
11	6	37	43
13	2	43	52
L = 3			
1	4	178	200
1	7	59	65
1	13	76	62
1	16	44	42
2	2	109	81
2	5	174	180
2	8	62	55
2	11	38	50
2	14	64	62
3	0	211	219
3	9	111	102
4	1	175	185
4	2	173	159
4	5	166	158
4	8	121	120
4	5	232	250
4	6	94	86
7	1	99	99
7	7	56	52
7	10	52	54
8	5	128	124
9	12	114	100
10	1	50	16
10	7	47	50
10	10	53	59
11	2	33	45
11	5	73	61
14	2	58	68
14	1	37	39
L = 4			
0	2	87	46
0	5	198	219
0	8	156	143
0	11	207	232
0	14	64	52
1	0	45	11
1	3	310	368
1	6	52	43
2	4	87	76
2	7	76	73
3	5	62	57
3	8	137	120
3	11	72	68
4	0	292	320
4	3	207	220
4	15	45	40
5	2	115	96
5	7	63	54
6	5	59	57
7	0	214	214
7	3	133	121
7	12	49	45
8	1	52	46
8	4	158	146
8	7	121	112
8	10	42	41
10	0	40	45
11	1	62	61
11	4	96	84
11	7	66	59
14	1	68	69
16	0	49	57
L = 5			
1	2	149	158
1	5	132	142
1	8	37	41
2	3	203	230
2	6	169	184
2	12	54	66
3	1	68	60
3	4	20	34
3	7	76	84
3	13	39	45
4	2	92	96
4	9	89	97
4	1	124	129
6	4	76	86
6	7	56	62
6	10	42	49
7	5	53	55
8	3	54	47
8	9	44	44
9	1	133	143
10	2	79	91
12	1	40	49
L = 6			
0	3	56	46
0	6	92	86
0	9	81	80
1	1	125	93
1	4	92	92
1	7	73	73
1	10	31	39
1	13	44	45
2	2	220	232
2	5	92	86
2	8	92	92
2	11	51	56
3	3	106	106
3	6	93	96
3	9	51	59
4	1	141	136
4	4	119	117
4	7	47	48
5	2	96	95
5	5	105	110
5	8	88	84
6	0	114	112
6	3	94	89
6	6	116	111
7	1	63	54
7	4	68	69
8	2	61	64
8	5	65	68
9	0	73	86
9	3	48	55
10	1	44	46
11	2	57	64
13	1	57	62
L = 7			
1	3	71	63
1	6	92	89
1	9	120	116
1	12	43	46
2	1	91	92
2	4	28	28
2	10	61	63
3	2	214	214
3	5	26	27
3	8	31	27
4	6	78	77
5	1	103	105
5	4	35	39
5	7	29	37
5	13	24	30
6	2	127	122
7	3	33	29
7	6	60	63
8	1	47	47
8	11	29	33
9	2	40	39
9	5	53	59
9	3	32	37
10	3	37	29
10	6	51	51
12	2	57	60
L = 8			
0	1	103	105
0	4	177	172
0	7	177	172
0	10	32	36
0	13	25	34
0	16	41	47
1	5	73	73
1	8	51	49
1	14	42	48
2	0	22	15
2	3	40	40
3	4	153	145
3	7	99	99
3	12	42	42
4	5	33	30
4	8	115	109
4	11	66	72
5	0	118	117
5	3	50	48
5	6	34	41
6	1	53	47
7	2	41	31
7	5	35	35
7	8	72	80
7	11	43	44
8	0	125	122
8	3	82	84
11	0	153	158
11	3	54	57
15	2	45	49
L = 9			
1	1	166	151
1	4	72	70
2	5	62	79
2	8	31	38
3	6	88	86
3	9	50	50
4	1	52	55
5	2	60	015
5	5	80	82
5	8	46	55
6	3	120	121
6	6	37	44
7	1	51	55
8	5	54	61
9	3	48	46
L = 10			
0	2	120	111
011		69	76
1	0	83	80
1	3	56	56
1	6	58	55
1	9	60	60
2	1	100	95
2	4	58	59
2	7	104	101
210		30	34
213		30	39
3	2	76	77
3	5	35	37
4	0	88	86
4	3	48	41
4	6	45	48
4	9	33	37
5	1	119	114
5	4	65	66
510		30	28
6	2	85	81
6	5	23	28
6	8	24	23
611		27	35
7	0	37	43
7	6	28	28
7	9	28	18
8	1	40	44
8	4	23	27
9	2	40	40
9	5	42	45
10	0	44	26
10	3	50	52
10	6	30	41
12	2	26	31
12	5	33	43
13	0	36	40
13	3	34	40
L = 11			
1	2	70	66
1	5	69	66
2	3	75	72
2	6	76	73
3	7	38	40
4	2	49	46
5	9	41	47
6	1	47	48
9	1	57	60
10	2	40	44
L = 12			
0	3	97	96
0	6	38	32
012		44	43
015		20	27
1	4	35	36
1	7	63	64
3	0	78	74
3	9	39	43
4	0	28	33
4	4	112	108
4	7	57	63
7	4	85	81
7	7	23	30
711		28	30
11	5	29	30
12	3	35	41
15	0	26	36
L = 13			
1	6	45	41
1	9	56	59
112		27	27
2	1	43	46
210		30	32
3	2	104	98
4	6	40	36
5	1	54	59
5	9	24	25
6	2	54	54
6	5	37	36
7	6	41	36
9	2	30	26
9	5	31	27
10	6	31	31
12	1	31	33
14	4	31	4

Table 2. $|F_c|$ *and* $|F_o|$ *from neutron diffraction data*

$|F_o|$ for *hk*.0 and *hk*.1 reflections is corrected for extinction.

H	K	FC	FO
L = 0			
1	1	5.6	6.6
3	0	38.5	37.5
2	2	3.0	4.1
4	1	21.5	22.5
3	3	9.5	11.2
6	0	10.1	11.6
5	2	2.8	4.2
4	4	34.5	33.8
7	1	50.4	50.5
6	3	5.1	3.8
5	5	22.3	29.2
9	0	13.6	12.8
8	2	1.9	4.1
7	4	33.0	34.8
6	6	16.5	16.4
10	1	19.5	15.9
9	3	1.1	1.5
8	5	11.9	11.3
12	0	8.4	5.2
7	7	8.8	5.7
11	2	1.5	1.5
10	4	10.2	8.3
9	6	9.0	6.9
13	1	4.7	4.5
12	3	29.0	30.5
8	8	7.2	8.3
11	5	15.9	16.0
10	7	1.4	7.2
15	0	3.0	5.2
14	2	3.0	3.5
13	4	13.4	9.5
9	9	8.8	4.7
12	6	7.6	9.5
15	1	13.6	8.0
11	8	6.6	3.5
15	3	11.3	5.6
14	5	0.4	0.0
10	10	11.8	6.4
L = 1			
8	1	21.9	23.2
4	6	18.4	27.0
7	3	12.3	12.2
1	9	45.9	42.5
3	8	10.1	13.7
5	7	13.1	18.0
2	10	27.0	26.9
7	6	21.8	21.0
9	5	24.2	19.2
1	12	13.4	8.8
12	2	24.7	25.1
10	6	17.6	13.1
L = 6			
0	0	48.8	47.8
L = 12			
0	0	33.1	33.8
L = 18			
0	0	10.6	3.5

computed from Cruickshank & Robertson's (1953) equation with the substitution of the r.m.s. errors in atomic position for the standard deviations originally used by these authors. We have estimated the error introduced by this assumption to be less than 0·2° in the standard deviation of the angle.

The $Al(H_2O)_6^{3+}$ octahedron is almost regular with an Al–O distance of 1·88 Å. This distance agrees well with the sum of the Pauling (1960) crystal radii for Al^{3+} and 0: 1·90 Å, and also falls within the range of values for Al–O distances reported for an aluminum coordination number of 6: 1·85–1·98 Å (*International Tables for X-ray Crystallography*, 1962). Specific examples of mean Al–O distances are: topaz ($Al_2SiO_4F_2$) (Alston & West, 1928), 1·92 Å; diaspore (AlOOH) (Ewing, 1935), 1·92 Å and (Busing & Levy, 1958*a*,*b*), 1·851–1·980 Å; and β-alum ($CsAl(SO_4)_2.12H_2O$) (Cromer, Kay & Larsen, 1966), 1·882 Å. The mean value of the O–Al–O angle is 90°0′, indicating a regular octahedron within experimental error. This symmetrical arrangement is also indicated by the almost identical values for the two distinct O–O distances, between the two nearest-neighbor oxygen atoms related by the threefold axis, and between the two nearest neighbors related by the threefold inversion axis.

Each water molecule is hydrogen-bonded to two chlorine ions through the two hydrogen atoms, each hydrogen atom participating in an O–H···Cl bond. The O–Cl distances are 3·02 and 3·03 Å; the difference is not significant. The two O–H distance, 0·99 and 1·04 Å, are similar to the values reported, for example, for: heavy ice (Peterson & Levy, 1957*a*), 1·01 Å; $Na_2CO_3NaHCO_3.2H_2O$ (Bacon & Curry, 1956), 1·01 Å; $CaSO_4.2H_2O$ (Atoji & Rundle, 1958), 0·99 Å; $FeSiF_6.6H_2O$ (Hamilton, 1962), 0·92 Å; $CuF_2.2H_2O$ (Abrahams & Prince, 1962), 0·980 Å; $MgSO_4.4H_2O$ (Baur, 1964), 0·967 Å; β-alum (Cromer *et al.*, 1966), 0·941–0·984 Å; and $NiSO_4.6H_2O$ (O'Connor & Dale, 1966), 0·93–1·00 Å. The two O–H–Cl angles differ by 12° although this difference, when compared with the standard deviations of the angles, may not be significant. These angles of 180° and 168°, with the former more reliably determined, suggest that the O–H···Cl bonds are very nearly linear. The H–O–H angle of 113°

Table 4. *Interatomic distances and angles in* $AlCl_3.6H_2O$

(*a*) Bonded distances	
Al–O	1·88 ± 0·02 Å
O –H	1·04 ± 0·04
O –H′	0·99 ± 0·06
(*b*) Distances involved in hydrogen bonds	
O –Cl	3·02 ± 0·02
O –Cl′	3·03 ± 0·01
H –Cl	1·98 ± 0·03
H′–Cl′	2·05 ± 0·06
(*c*) Other distances	
O–O related by 3	2·68 ± 0·02
O–O related by $\bar{3}$	2·65 ± 0·01
H–H′	1·70 ± 0·07
(*d*) Bond angles	
H—O –H′	113 ± 4°
Cl –H –O	180 ± 3
Cl′–H′–O	168 ± 6
O—Al–O	90 ± 1
O—Al–O′	90 ± 1

Table 3. *Parameter values for* $AlCl_3.6H_2O$: *hexagonal coordinates*

A. Position coordinates

	x	*y*	*z*
Al^{3+}	0	0	0
Cl^-	0·2684 ± 0·0004 (0·26)*	0	0·25
O	0·1070 ± 0·0008 (0·12)	0·1455 ± 0·0008 (0·14)	0·0906 ± 0·0008 (0·10)
H	0·070 ± 0·001	0·188 ± 0·002	0·145 ± 0·002
H′	0·203 ± 0·004	0·197 ± 0·004	0·084 ± 0·002

B. Temperature factor coefficients

1. Isotropic

	X-ray *B*	Neutron *B*
Al^{3+}	0·86 ± 0·11 Å²	0·76 ± 0·59 Å²
Cl^-	1·65 ± 0·06	1·40 ± 0·20
O	1·59 ± 0·11	1·15 ± 0·25
H	—	2·07 ± 0·45
H′	—	1·98 ± 0·44

2. Anisotropic (X-ray)

β_{ij}	O	Cl^-	Al^{3+}
β_{11}	0·0038 ± 0·0005	0·0046 ± 0·0002	0·0034 ± 0·0004
β_{22}	0·0042 ± 0·0007	0·0053 ± 0·0005	β_{11}
β_{33}	0·0030 ± 0·0003	0·0026 ± 0·0001	0·0017 ± 0·0002
β_{12}	0·0014 ± 0·0010	$\frac{1}{2}\beta_{22}$	$\frac{1}{2}\beta_{11}$
β_{13}	0·0000 ± 0·0001	$\frac{1}{2}\beta_{23}$	0
β_{23}	−0·0011 ± 0·0030	−0·0008 ± 0·0007	0

* The values in parentheses are those obtained by Andress & Carpenter (1934).

is somewhat larger than the almost tetrahedral angle reported for heavy ice, 109°33′ (Peterson & Levy, 1957*a*), but well within the range of other H–O–H angles reported: 115·5° for $CuF_2.2H_2O$ (Abrahams & Prince, 1962) and 109°–116° for β-alum (Cromer *et al.*, 1966). The interproton distance, H–H, is somewhat larger (1·70 Å) than that usually reported. Table 5 compares the O–Cl, H–H, and O–H distances and the H–O–H angles for this and for other crystalline hydrates with O–H···Cl bonds.

Discussion of the structure

Fig. 1 shows a portion of the triply primitive hexagonal unit cell. In the interest of clarity, not all atoms are shown but several characteristics are exhibited. The

Table 5.* *Bond distances and angles in some hydrated chlorides*

Crystal	Distance O–Cl	Distance H–H	Distance† O–H	Angle H–O–H	Method of measurement‡
$CuCl_2.2H_2O$ [a]	3·00 Å	1·553 Å	0·95 Å	108°	N.D.
$K_2HgCl_4.H_2O$	3·26 [b]	1·60 [c]–1·61 [d]	(0·98)	110	P.M.R.
$K_2CuCl_4.2H_2O$	3·04 [e]	1·61 [c]–1·62 [d]	(1·02)	105	P.M.R.
$(NH_4)_2CuCl_4.2H_2O$	3·09 [e]	1·59 [c]–1·61 [d]	(1·01)	105	P.M.R.
$BaCl_2.2H_2O$ [f]	—	1·496, 1·548	0·968, 0·974 0·965, 0·953	102·5, 105·8	N.D.
$AlCl_3.6H_2O$ [g]	3·03	1·70	0·99, 1·04	113	N.D.

* Adapted in part from Chidambaram (1962).
† The values in parentheses were assumed, *a priori*.
‡ N.D. Neutron diffraction; P.M.R. Proton magnetic resonance.

References: (*a*) Peterson & Levy (1957*b*)
(*b*) Wyckoff (1957)
(*c*) Itoh, Kusaka, Yamagata, Kiriyama & Ibamoto (1953*b*)
(*d*) McGrath & Silvidi (1961)
(*e*) Itoh, Kusaka, Yamagata, Kiriyama & Ibamoto (1953*a*)
(*f*) Padmanabhan, Busing & Levy (1963)
(*g*) This work

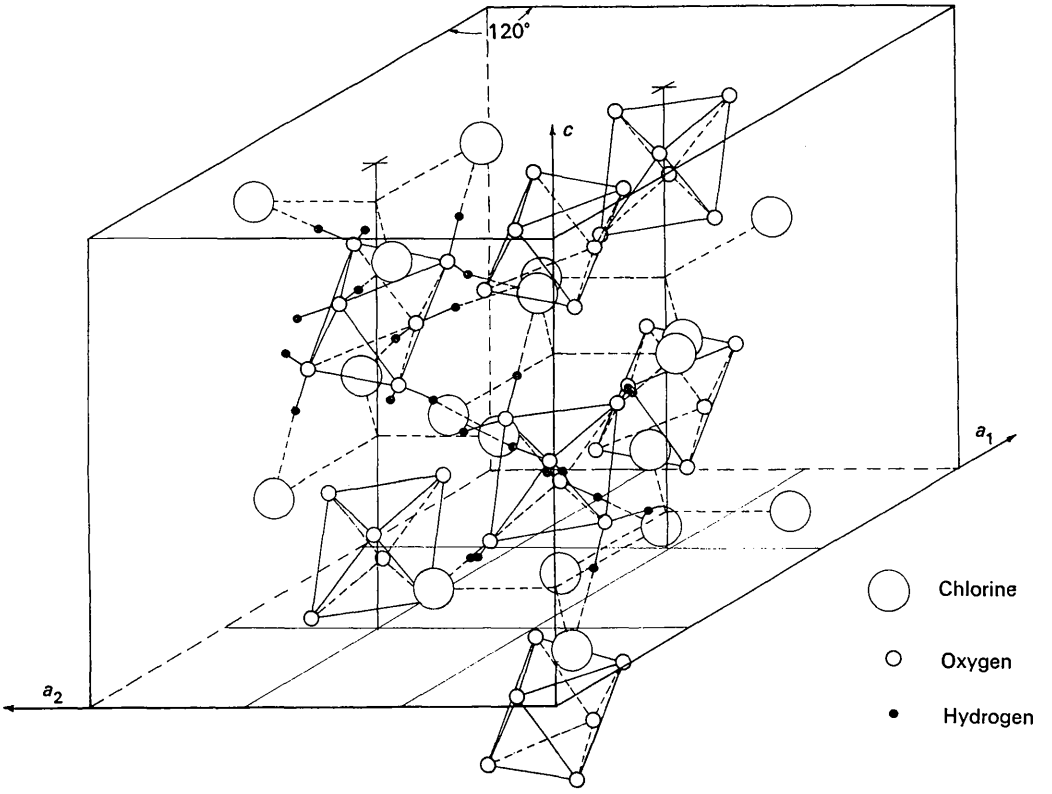


Fig. 1. The unit cell of $AlCl_3.6H_2O$. Al^{3+} at the centers of the O octahedra are not shown. Not all H are shown.

first is that there are two distinct orientations for the $Al(H_2O)_6^{3+}$ octahedron; examples of these are to be found at 0,0,0 and at $0,0,\frac{1}{2}$. Their relative orientations differ by about 28° in the xy plane. The structure may be thought of as being composed of parallel chains of the type:

$$-Al(H_2O)_6^{3+}-3Cl^-\text{–}Al(H_2O)_6^{3+}-3Cl^-\text{–},$$

The chains advancing parallel to the c axis of the unit cell. The octahedra in a chain are each surrounded by twelve chlorine ions, all at distances of 3·03 Å from a corner of an octahedron (oxygen atom) but at different distances from the center of the octahedron (the aluminum ion). Of these twelve chlorine ions, six belong to the chain of which the octahedron is a member, the other six to other chains. The two hydrogen atoms bonded to a given oxygen atom are also hydrogen-bonded to two chlorine ions, hydrogen atom H to a chlorine ion of the same chain as that of which it is a member, and hydrogen atom H′ to a chlorine ion in a different chain. Each chlorine ion participates in four hydrogen bonds, two through hydrogen atoms on two octahedra in the same chain as the chlorine ion, and two through hydrogen atoms on octahedra in two other chains. The O–Cl–O angles about a chlorine ion occur in pairs and are, approximately, 75°, 109°, and 138°.

Thermal motion

Table 6 presents the values of $(\overline{u_\perp^2})^{1/2}$ (as given by $B=8\pi^2\overline{u_\perp^2}$) derived from the isotropic temperature factors calculated in the X-ray and neutron least-squares refinements. The estimate of error shown is based on the standard deviations in the isotropic temperature factors calculated during refinement.

Table 6. *Isotropic thermal amplitudes in* $AlCl_3.6H_2O$

	X-ray $(u_\perp{}^2)^{1/2}$	Neutron $(u_\perp{}^2)^{1/2}$
H	–	0·162 ± 0·017 Å
H′	–	0·148 ± 0·017
O	0·142 ± 0·005 Å	0·121 ± 0·012
Cl^-	0·145 ± 0·003	0·133 ± 0·009
Al^{3+}	0·105 ± 0·006	0·098 ± 0·038

The magnitudes and orientations of the principle axes of the r.m.s. thermal vibration ellipsoids of each type of atom have been computed from the anisotropic coefficients β_{ij} (Busing & Levy, 1958*a*,*b*). Table 7 shows the lengths of the semi-principal axes, $(\overline{u_i^2})^{1/2}$, together with the angles for each principal axis with respect to the hexagonal crystallographic axes. The errors in the directions angles are estimated to be less than 10°, and those for $(\overline{u_i^2})^{1/2}$ less than 0·03 Å. These estimates are also based on the standard deviations calculated during refinement.

Table 7. *Anisotropic thermal amplitudes in* $AlCl_3.6H_2O$

	ij*	Angle ij	$(\overline{u_i^2})^{1/2}$
O	11	56°	0·18 Å
	12	143	
	13	55	
	21	91	0·12
	22	46	
	23	31	
	31	34	0·14
	32	93	
	33	112	
Cl^-	11	90	0·17
	12	37	
	13	113	
	21	90	0·13
	22	71	
	23	23	
	31	0	0·15
	32	120	
	33	90	
Al^{3+}†	11	—	0·13
	12	—	
	13	90	
	21	—	0·13
	22	—	
	23	90	
	31	90	0·11
	32	90	
	33	0	

* i refers to the ith axis of the thermal ellipsoid. j refers to the jth axis of the hexagonal unit cell.

† The angles of axes 1 and 2 of the thermal ellipsoid are indeterminate since the ellipsoid has a circular cross-section in the plane defined by $\mathbf{a}_1$ and $\mathbf{a}_2$.

This work was supported in part under contract with the Air Force Office of Scientific Research. The authors wish to thank Dr W. R. Busing and Dr H. A. Levy for the use of their excellent computer program, Dr R. A. Erickson for his aid in some of the experimental phases of this work, Dr J. M. Stewart for his aid and advice with respect to various aspects of digital computation, and the referees for their helpful comments and criticisms.

References

ABRAHAMS, S. C. & PRINCE, E. (1962). *J. Chem. Phys.* **36**, 50.
ALSTON, N. A. & WEST, J. (1928). *Z. Kristallogr.* **69**, 149.
ANDRESS, K. R. & CARPENTER, C. (1934). *Z. Kristallogr.* **87**, 446.
ATOJI, M. & RUNDLE, R. E. (1948). *J. Chem. Phys.* **29**, 1306.
BACON, G. E. (1955). *Neutron Diffraction.* Oxford: Clarendon Press.
BACON, G. E. & CURRY, N. A. (1956). *Acta Cryst.* **9**, 82
BAUR, W. H. (1964). *Acta Cryst.* **17**, 863.
BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
BUSING, W. R. & LEVY, H. A. (1958*a*). *Acta Cryst.* **11**, 450.
BUSING, W. R. & LEVY, H. A. (1958*b*). *Acta Cryst.* **11**, 798.
BUSING, W. R. & LEVY, H. A. (1959). U.S. Atomic Energy Commission Publication ORNL 59-4-37.
CHIDAMBARAM, R. J. (1962). *J. Chem. Phys.* **36**, 2361.
COHEN, M. V. (1935). *Rev. Sci. Instrum.* **6**, 68.

CROMER, D. T., KAY, M. I. & LARSEN, A. C. (1966). *Acta Cryst.* **21**, 383.
CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.
EVANS, H. T. (1961). *Acta Cryst.* **14**, 689.
EWING, F. J. (1935). *J. Chem. Phys.* **3**, 203.
FREEMAN, A. J. (1959). *Acta Cryst.* **12**, 261.
HAMILTON, W. C. (1957). *Acta Cryst.* **10**, 629.
HAMILTON, W. C. (1962). *Acta Cryst.* **15**, 353.
HESS, J. B. (1951). *Acta Cryst.* **4**, 212.
International Tables for X-ray Crystallography (1962). Vol. 3. Birmingham: Kynoch Press.
ITOH, J., KUSAKA, R., YAMAGATA, Y., KIRIYAMA, R. & IBAMOTO, H. (1953*a*). *Physica*, **19**, 415.
ITOH, J., KUSAKA, R., YAMAGATA, Y., KIRIYAMA, R. & IBAMOTO, H. (1953*b*). *J. Phys. Soc. Japan*, **8**, 293.
LEVY, H. A. (1956). *Acta Cryst.* **9**, 679.
MCGRATH, J. W. & SILVIDI, A. A. (1961). *J. Chem. Phys.* **34**, 322.
O'CONNOR, B. H. & DALE, D. H. (1966). *Acta Cryst.* **21**, 705.
PADMANABHAN, V. M., BUSING, W. R. & LEVY, H. A. (1963). *Acta Cryst.* **16**, A26.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
PETERSON, S. W. & LEVY, H. A. (1957*a*). *Acta Cryst.* **10**, 70.
PETERSON, S. W. & LEVY, H. A. (1957*b*). *J. Chem. Phys.* **26**, 220.
PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746.
PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 819.
WYCKOFF, R. W. G. (1957). *Crystal Structures*, Vol. 2. New York: Interscience.

Acta Cryst. (1968). B**24**, 960

The Crystal Structure of Lead n-butylxanthate. I. Disordered Structure

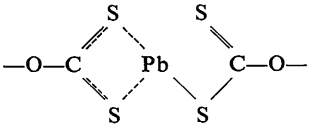
BY HITOSI HAGIHARA AND YASUNARI WATANABE
The Institute of Physical and Chemical Research, Yamato-machi, Kita-Adachi-gun, Saitama-ken, Japan

AND SHUJI YAMASHITA
Tokyo Metropolitan Isotope Research Center, Fukazawa-cho, Setagaya-ku, Tokyo, Japan

(*Received* 8 *September* 1967)

Lead n-butylxanthate, $Pb(SSCOC_4H_9)_2$, crystallizes into ordered and disordered structures. The disordered crystal is monoclinic with $a=36{\cdot}87\pm0{\cdot}25$, $b=4{\cdot}58\pm0{\cdot}11$, $c=10{\cdot}71\pm0{\cdot}09$ Å; $\beta=112{\cdot}0\pm0{\cdot}6°$; the space group is $C2/c$ and $Z=4$. The ordered crystal is also monoclinic. Its cell dimensions are the same as those of the disordered crystal except that the b axis is quadruplicated. A three-dimensional X-ray structure analysis was carried out with the disordered crystal by the split atom method. The asymmetric molecule of $Pb(SSCOC_4H_9)_2$ is found to distribute about the twofold rotation axis with the multiplicity 0·5, satisfying the conditions of the space group $C2/c$.

The lead atom is bonded to one xanthate group with Pb–S distances of $2{\cdot}82\pm0{\cdot}04$ and $2{\cdot}77\pm0{\cdot}09$ Å and to the other with $2{\cdot}76\pm0{\cdot}06$ and $3{\cdot}03\ \pm0{\cdot}08$ Å. The two xanthate groups are bonded to the lead atom with S–Pb–S bond angles $91{\cdot}7\pm1{\cdot}5°$ and $93{\cdot}7\pm2{\cdot}2°$. These results suggest the following type of bonding between lead atom and the dithiocarbonic ends of the xanthate groups:



Introduction

In an analysis of lead ethylxanthate crystal by X-ray diffraction (Hagihara & Yamashita, 1966) a molecule of lead ethylxanthate, $Pb(SSCOC_2H_5)_2$, has been found to form an asymmetric unit of the structure. The four sulphur atoms of the dithiocarbonic ends of the two ethylxanthate groups are coordinated to the lead atom without any symmetry relations. The Pb–S distances have been found to be 2·74 and 2·84 Å for one xanthate group and 2·79 and 2·95 Å for the other, all $\pm0{\cdot}03$ Å. Within each branch of the molecule consisting of a lead atom and one xanthate group, the difference between the Pb–S distances was concluded to be significant. In order to ascertain whether such a type of bonding of the lead atom with the dithiocarbonic sulphur atoms exists also in the other alkylxanthates, the structure analysis of lead n-butylxanthate crystal has been carried out.

Experimental

Preparation of the crystals

Lead n-butylxanthate powder was obtained as a white precipitate when an aqueous solution of purified potassium n-butylxanthate was added slowly to an