The Crystal Structure of the KF.2Al(C$_2$H$_5$)$_3$ Complex

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X-ray analysis of the KF.2 Al(C$_2$H$_5$)$_3$ complex shows that the space group is $R\bar{3}$, with cell parameters $a_r = b_r = c_r = 8\cdot95 \pm 0\cdot03$ Å, $\alpha_r = \beta_r = \gamma_r = 55°\ 20' \pm 0°\ 30'$, and only one formula unit in the cell. It follows that the complex is of an ionic type with K$^+$ cations and [(C$_2$H$_5$)$_3$Al–F–Al(C$_2$H$_5$)$_3$]$^-$ anions placed on crystallographic centres of symmetry. Each ion is surrounded by a not greatly distorted octahedron of ions of opposite kind. The new type of coordination around the fluorine atom, which is linked to two metal atoms by collinear bonds, is particularly emphasized; the hybridization type of the F atom is briefly discussed, taking into account the Al–F observed distance.

1. Introduction

In recent years Ziegler *et al.* (1960) and his collaborators have prepared and studied, from a physico-chemical viewpoint, a new class of organo-metallic compounds, whose general formula may be written:

$$MX.nAlR_3$$

where M is an alkali metal, X may be a halogen, hydrogen or a –CN group, and R is an alkyl radical. The stoichiometric index n may assume the two values 1 or 2.

Because of the very interesting structure of complexes containing alkyl–aluminum groups, and in view of their participation in the stereospecific catalysis of polymerization of alpha-olefins, we have undertaken a detailed X-ray structural study of the complex whose composition is KF.2 Al(C$_2$H$_5$)$_3$, belonging to the above class.

In a preceding communication to the editor (G. Natta, G. Allegra, G. Perego & A. Zambelli, 1961), we reported the lattice parameters and space group of this compound; moreover, we briefly discussed the ionic structure K$^+$[(C$_2$H$_5$)$_3$Al–F–Al(C$_2$H$_5$)$_3$]$^-$ and the surprising new coordination type of the fluorine atom, which appears to be bound to two aluminum atoms by collinear bonds.

In this note we wish to discuss in detail the crystal structure of this complex, as determined by two-dimensional Fourier refinement.

2. Unit cell dimensions. Application of the Patterson analysis to the determination of the space group

X-ray data show that the symmetry of the unit cell of KF.2 Al(C$_2$H$_5$)$_3$ is rhombohedral; the corresponding dimensions are:

$$a_r = b_r = c_r = 8\cdot95 \pm 0\cdot03 \text{ Å}; \quad \alpha_r = \beta_r = \gamma_r = 55°\ 20' \pm 0°\ 30'$$

Volume of the unit cell is: $V = (452 \pm 5)$ Å^3. From the value of the experimentally observed density (1·04 g.cm.$^{-3}$), we have deduced the presence of one formula unit in the cell; the value of the calculated density is in fact 1·05 g.cm.$^{-3}$.

In the following, for the sake of convenience we shall refer to the corresponding hexagonal non-primitive unit cell, containing three molecules, whose dimensions are:

$$a = b = 8\cdot31 \pm 0\cdot03 \text{ Å}; \quad c = 22\cdot65 \pm 0\cdot08 \text{ Å};$$
$$\gamma = 120°; \quad N = 3 .$$

In addition to the trivial systematic absence of the reflections whose indices satisfy the relationship: $-h + k + l \neq 3n$, no other systematic absence has been observed; moreover, since the following inequality among structure factors has been observed:

$$|F(hkl)| \neq |F(khl)|$$

(compare for instance the F_o values for the $[2\bar{2}1]$ zone, quoted in Table 3), all rhombohedral space groups other than $R3$ and $R\bar{3}$ are immediately excluded. In order to decide between $R3$ and $R\bar{3}$ we have studied the two-dimensional Patterson projections along [100] and $[2\bar{2}1]$.

The $a(=b)$ axis is the shortest rational axis that one may select in this structure: accordingly, the greatest resolution of interatomic vectors in the corresponding Patterson projection is to be expected. We have at first confined our attention to the four strongest Patterson maxima, apart from the maximum at the origin, whose approximate fractional coordinates are given in Table 1 (see Fig. 1, [100] projection).

Table 1. *Fractional coordinates*

	y	z
(1)	$\frac{2}{3}$	0·088
(2)	$\frac{1}{3}$	0·176
(3)	$\frac{2}{3}$	0·167
(4)	0·000	0·076

Making the reasonable assumption that these maxima must be attributed principally to interatomic vectors connecting the heaviest atoms present in the structure (K, Al, F), we can see that arranging the atoms as in Table 2 will account fairly well both for the position and for the weight of the above-considered Patterson maxima.

Table 2.

	y	z
3 K	0·000	0·000
	$\frac{1}{3}$	$\frac{1}{3}$
	$\frac{2}{3}$	$\frac{2}{3}$
3 F	$\frac{2}{3}$	$\frac{1}{6}$
	0·000	$\frac{1}{2}$
	$\frac{1}{3}$	$\frac{5}{6}$
6 Al	$\pm$ ($\frac{2}{3}$	0·088)
	$\pm$ (0·000	0·421)
	$\pm$ ($\frac{1}{3}$	0·754)

Maximum (1) in Table 1 is explained as a K–Al vector (multiplicity $=2$); maximum (2) as an Al–Al vector (multiplicity $=1$); maximum (3) as a K–F vector (multiplicity $=2$), and finally maximum (4) as an Al–F vector (multiplicity $=2$).

Accepting the atomic disposition represented in Table 2, it is apparent that $R\bar{3}$ is strongly favoured; in fact the given coordinates are consistent with the centrosymmetrical $R\bar{3}$ space group, K and F atoms lying on two centres of symmetry, and the two Al atoms of every molecule on the same threefold axis.

Analysis of the [$2\bar{2}1$] Patterson projection (see Fig. 1) definitely confirms the said disposition, with regard to K, F and Al atoms. In fact, the most evident

Fig. 1. [100] (above) and [$2\bar{2}1$] (below) Patterson projections. Contours are drawn at arbitrary intervals.

feature of this projection, whose corresponding rational axis is 12·20 Å in length, is the existence of a maximum far stronger than any other (excepting the maximum at the origin); this is to be expected, because the above-discussed disposition of heavier atoms would result in the superposition of K and F atoms along this projection, and consequently only one outstanding interatomic vector (K + F)–Al would appear. It is also easy to see that the coordinates of the said Patterson maximum are consistent with the expected position of Al atoms.

This evidence led us to choose, for the KF.2 Al(C₂H₅)₃ complex, the space group $R\bar{3}$, accepting the centrosymmetrical array of heavier atoms described by the coordinates reported in Table 2, to which $(x_i = -y_i)$ coordinates are to be added. Subsequent calculations and refinement of the structure have confirmed these preliminary assumptions.

3. First structural considerations

Some very interesting structural conclusions may be drawn at this point, accepting the above deductions.

First of all, the approximate Al–F distance which results (about 1·80 Å, very near to the Al–F distance —1·81 Å—quoted for Na₃AlF₆), clearly indicates a bridge bonding of two Al atoms by a fluorine atom. The bridge bonds, which are centrosymmetrical, are necessarily collinear. Secondly, the crystal structure clearly appears to be ionic, with repeating units $K^+[(C_2H_5)_3Al–F–Al(C_2H_5)_3]^-$, the two ions being placed on crystallographic centres of symmetry; finally the Al–F–Al axis coincides with a threefold axis of the structure, so that the three ethyl groups linked to every aluminum atom are symmetrically related.

4. Fourier analysis and refinement of the structure

The number of independent positional parameters needed to describe, in the space group $R\bar{3}$, the crystal structure of KF.2 Al(C₂H₅)₃ complex, is particularly low; there are only seven, neglecting hydrogen atoms, since only one parameter is needed to fix the distance of the Al atoms from the F atom along the threefold axis, and six other parameters in order to locate the two independent carbon atoms. For this reason we have limited ourselves to Fourier analysis and subsequent refinement on two two-dimensional projections, corresponding to the Patterson projections of Fig. 1.

For both [100] and [$2\bar{2}1$] projections we have obtained electron-density maps by the classical method of successive introduction of structure factors whose signs were deduced by successively refined atomic coordinates and thermal factors; on each projection, the starting point has consisted in the set of coordinates of K, F and Al atoms previously deduced by Patterson considerations (see section 2). Refinement for positional and thermal parameters has been
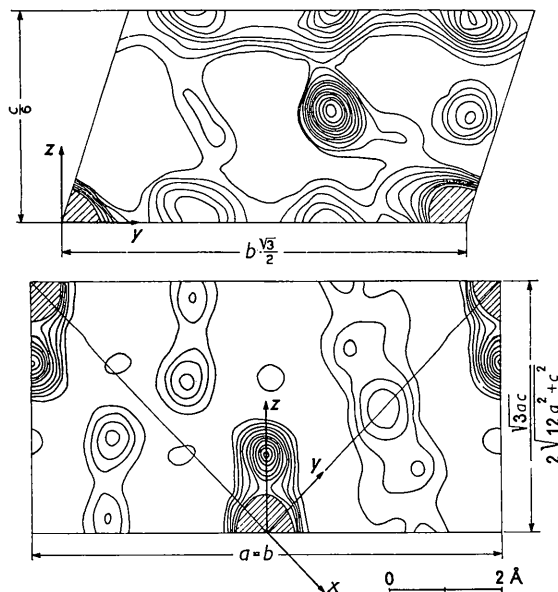
obtained at the end of every iteration by difference Fourier syntheses. Figs. 2 and 3 show the final Fourier syntheses of the electron density. The spots indicate the final atomic positions.

The mean value of the agreement factor R between observed and calculated structure factors, including non-observed reflections, is 0·123 for the two zones, the separate values for [100] (0·126) and [$2\bar{2}1$] (0·116)

Table 3

(100) Zone

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
0 0 3	29	23	0 2 20	18	20	0 4 17	24	25	0 6 21	11	11
0 0 6	117	-125	0 2 25	16	-14	0 4 20	<5	-1	0 6 $\overline{3}$	15	8
0 0 9	16	19	0 2 28	<3	4	0 4 23	6	-5	0 6 $\overline{6}$	<5	-5
0 0 12	109	122	0 2 $\overline{2}$	51	57	0 4 26	12	17	0 6 $\overline{9}$	18	16
0 0 15	12	4	0 2 $\overline{5}$	31	34	0 4 $\overline{1}$	26	-29	0 6 $\overline{12}$	29	31
0 0 18	6	-4	0 2 $\overline{8}$	27	26	0 4 $\overline{4}$	33	34	0 6 $\overline{15}$	7	-6
0 0 21	9	16	0 2 $\overline{11}$	10	4	0 4 $\overline{7}$	43	42	0 6 $\overline{18}$	<4	-2
0 0 24	14	16	0 2 $\overline{14}$	54	53	0 4 $\overline{10}$	35	31	0 6 21	11	13
0 0 27	6	-5	0 2 $\overline{17}$	8	10	0 4 $\overline{13}$	18	-13	0 7 2	27	20
0 1 2	83	117	0 2 $\overline{20}$	11	-6	0 4 $\overline{16}$	13	11	0 7 5	23	25
0 1 5	84	97	0 2 $\overline{23}$	<5	2	0 4 $\overline{19}$	20	19	0 7 8	<5	4
0 1 8	35	31	0 2 $\overline{26}$	22	24	0 4 $\overline{22}$	9	14	0 7 11	13	-13
0 1 11	40	-34	0 3 0	115	125	0 4 $\overline{25}$	9	-4	0 7 14	20	20
0 1 14	50	51	0 3 3	39	-32	0 5 1	16	-14	0 7 17	18	19
0 1 17	32	38	0 3 6	32	-26	0 5 4	11	7	0 7 $\overline{1}$	<5	-7
0 1 20	<5	6	0 3 9	60	53	0 5 7	38	35	0 7 $\overline{4}$	11	13
0 1 23	7	-7	0 3 12	81	83	0 5 10	28	28	0 7 $\overline{7}$	15	13
0 1 26	18	18	0 3 15	22	-19	0 5 13	16	-16	0 7 $\overline{10}$	11	11
0 1 29	<2	7	0 3 18	18	-15	0 5 16	17	14	0 7 $\overline{13}$	<4	—
0 1 $\overline{1}$	49	-55	0 3 21	17	21	0 5 19	19	22	0 7 $\overline{16}$	10	9
0 1 $\overline{4}$	17	22	0 3 24	24	25	0 5 22	<3	6	0 7 $\overline{19}$	8	7
0 1 $\overline{7}$	56	56	0 3 27	<3	-2	0 5 $\overline{2}$	58	57	0 8 1	5	-5
0 1 $\overline{10}$	76	71	0 3 $\overline{3}$	30	25	0 5 $\overline{5}$	37	32	0 8 4	<5	2
0 1 $\overline{13}$	21	-14	0 3 $\overline{6}$	<4	1	0 5 $\overline{8}$	<5	-6	0 8 7	19	14
0 1 $\overline{16}$	15	14	0 3 $\overline{9}$	34	28	0 5 $\overline{11}$	12	-10	0 8 10	11	11
0 1 $\overline{19}$	23	24	0 3 $\overline{12}$	53	59	0 5 $\overline{14}$	37	39	0 8 13	5	-6
0 1 $\overline{22}$	14	17	0 3 $\overline{15}$	19	-16	0 5 $\overline{17}$	16	17	0 8 $\overline{2}$	24	23
0 1 $\overline{25}$	10	-5	0 3 $\overline{18}$	<5	2	0 5 $\overline{20}$	<4	-3	0 8 $\overline{5}$	17	14
0 1 $\overline{28}$	9	9	0 3 $\overline{21}$	23	27	0 5 $\overline{23}$	<3	-4	0 8 $\overline{8}$	<4	-3
0 2 1	38	-44	0 3 $\overline{24}$	16	18	0 6 0	53	50	0 8 $\overline{11}$	<3	-4
0 2 4	66	65	0 3 $\overline{27}$	9	-10	0 6 3	6	-3	0 8 $\overline{14}$	15	17
0 2 7	89	91	0 4 2	38	38	0 6 6	10	-11	0 9 0	16	16
0 2 10	44	45	0 4 5	57	53	0 6 9	27	20	0 9 3	8	6
0 2 13	51	-46	0 4 8	30	23	0 6 12	40	38	0 9 6	<2	2
0 2 16	22	17	0 4 11	25	-20	0 6 15	10	-8	0 9 $\overline{3}$	<3	-4
0 2 19	43	46	0 4 14	33	33	0 6 18	8	-7	0 9 $\overline{6}$	4	-4

($2\bar{2}1$) Zone

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
0 1 2	83	117	2 2 0	89	89	3 $\overline{4}$ $\overline{14}$	31	27	5 $\overline{1}$ $\overline{12}$	58	56
0 2 4	66	65	2 3 2	75	71	3 $\overline{5}$ $\overline{16}$	<5	6	5 $\overline{2}$ $\overline{14}$	33	34
0 3 6	32	-26	2 4 4	7	8	3 $\overline{6}$ $\overline{18}$	<5	-6	5 $\overline{3}$ $\overline{16}$	4	4
0 4 8	30	23	2 5 6	4	2	3 $\overline{7}$ $\overline{20}$	4	-4	5 $\overline{4}$ $\overline{18}$	17	-19
0 5 10	28	28	2 6 8	7	-10	4 0 $\overline{8}$	30	23	5 $\overline{5}$ $\overline{20}$	<2	-4
0 6 12	40	38	2 7 10	15	14	4 1 $\overline{6}$	33	30	5 $\overline{6}$ $\overline{22}$	4	8
0 7 14	20	20	2 $\overline{1}$ $\overline{6}$	27	25	4 2 $\overline{4}$	20	6	6 0 $\overline{12}$	40	38
1 0 $\overline{2}$	83	117	2 $\overline{2}$ $\overline{8}$	29	26	4 3 $\overline{2}$	29	30	6 1 $\overline{10}$	26	21
1 1 0	55	58	2 $\overline{3}$ $\overline{10}$	54	54	4 4 0	33	29	6 2 $\overline{8}$	<5	5
1 2 2	92	80	2 $\overline{4}$ $\overline{12}$	60	72	4 5 2	23	21	6 3 $\overline{6}$	10	-7
1 3 4	5	7	2 $\overline{5}$ $\overline{14}$	35	30	4 6 4	<3	3	6 4 $\overline{4}$	5	6
1 4 6	27	-20	2 $\overline{6}$ $\overline{16}$	15	12	4 $\overline{1}$ $\overline{10}$	56	56	6 $\overline{1}$ $\overline{14}$	36	28
1 5 8	<5	-2	2 $\overline{7}$ $\overline{18}$	5	-3	4 $\overline{2}$ $\overline{12}$	40	43	6 $\overline{2}$ $\overline{16}$	9	11
1 6 10	12	14	3 0 $\overline{6}$	32	-26	4 $\overline{3}$ $\overline{14}$	46	45	6 $\overline{3}$ $\overline{18}$	<5	-2
1 7 12	24	24	3 1 $\overline{4}$	45	45	4 $\overline{4}$ $\overline{16}$	11	12	6 $\overline{4}$ $\overline{20}$	<4	-1
1 $\overline{1}$ $\overline{4}$	16	24	3 2 $\overline{2}$	53	50	4 $\overline{5}$ $\overline{18}$	<5	5	6 $\overline{5}$ $\overline{22}$	9	8
1 $\overline{2}$ $\overline{6}$	55	49	3 3 0	75	74	4 $\overline{6}$ $\overline{20}$	<4	-1	7 0 $\overline{14}$	20	20
1 $\overline{3}$ $\overline{8}$	34	-23	3 4 2	10	9	5 0 $\overline{10}$	28	28	7 1 $\overline{12}$	25	22
1 $\overline{4}$ $\overline{10}$	31	26	3 5 4	<5	—	5 1 $\overline{8}$	<5	1	7 2 $\overline{10}$	22	18
1 $\overline{5}$ $\overline{12}$	25	19	3 6 6	6	-10	5 2 $\overline{6}$	<5	-5	7 3 $\overline{8}$	<2	4
1 $\overline{6}$ $\overline{14}$	36	35	3 7 8	5	6	5 3 $\overline{4}$	5	5	7 $\overline{1}$ $\overline{16}$	4	5
1 $\overline{7}$ $\overline{16}$	<4	5	3 $\overline{1}$ $\overline{8}$	12	15	5 4 $\overline{2}$	18	19	7 $\overline{2}$ $\overline{18}$	<4	-2
2 0 $\overline{4}$	66	65	3 $\overline{2}$ $\overline{10}$	31	34	5 5 0	16	17	7 $\overline{3}$ $\overline{20}$	4	-4
2 1 $\overline{2}$	118	127	3 $\overline{3}$ $\overline{12}$	63	58						

Table 4. *Final atomic coordinates and thermal parameters*

		x	y	z	B ($Å^2$)	$\sigma(x)=\sigma(y)$ ($Å$)	$\sigma(z)$ ($Å$)
K	(3a)	0·000	0·000	0·000	2·85	—	—
F	(3b)	0·000	0·000	0·500	2·85	—	—
Al	(6c)	0·000	0·000	0·419	2·23	—	0·003
C^I	(18f)	0·266	0·180	0·400	3·80	0·015	0·017
C^{II}	(18f)	0·337	0·368	0·429	4·30	0·015	0·017
H^I	(18f)	0·276	0·201	0·349	6·00	not evaluat.	not evaluat.
H^{II}	(18f)	0·353	0·119	0·414	6·00	not evaluat.	not evaluat.
H^{III}	(18f)	0·328	0·348	0·480	6·00	not evaluat.	not evaluat.
H^{IV}	(18f)	0·250	0·432	0·416	6·00	not evaluat.	not evaluat.
H^V	(18f)	0·487	0·462	0·419	6·00	not evaluat.	not evaluat.
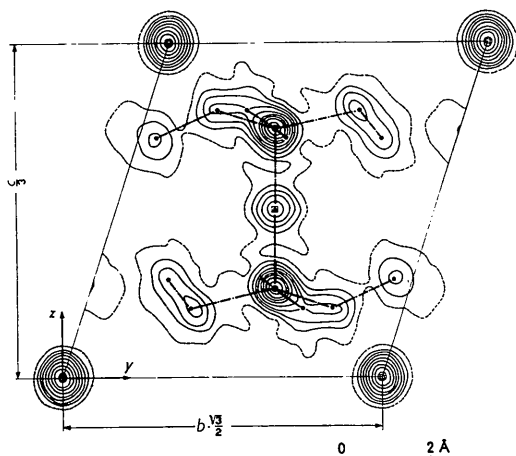
Fig. 2. Electron-density projection on (100). Contours are drawn at 2 (dotted line), 4, 6, 8, 10, 15, 20, 25... e.$Å^{-2}$. Smaller black dots correspond to the centres of carbon atoms; larger black dots aluminum atoms; black triangle a fluorine atom; white squares potassium atoms.
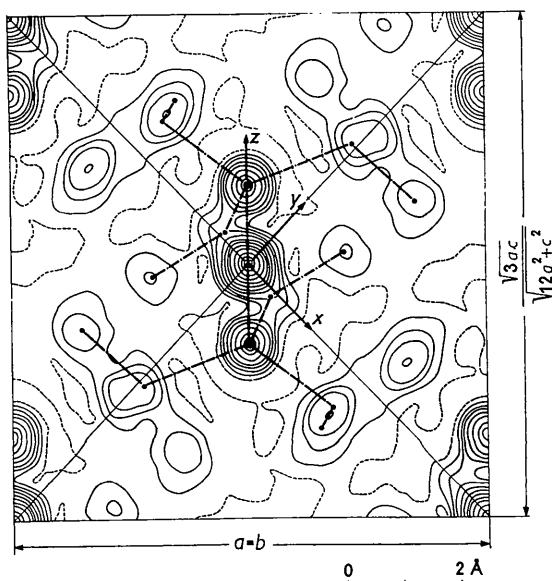
Fig. 3. Electron-density projection on [$2\bar{2}1$]. Contours and atomic centres are represented as in Fig. 3.

zones being very similar. In Table 3 observed and calculated structure factors for each zone are compared.

Table 4 shows the final values of atomic coordinates and thermal factors, assumed isotropic for every atom; the values of the standard deviations for Al and C atoms, deduced by Cruickshank's method, modified for two-dimensional projections, are also given. Hydrogen atoms are not revealed by the electron-density maps, and only approximately by the difference Fourier syntheses built up with $F(hkl)$ values calculated without the contribution of the hydrogen atoms themselves; nevertheless, due to their large number, a definite improvement has been obtained in the R value by introducing them into the structure-factor calculations. Hydrogen atoms have been placed in tetrahedral sites around every carbon atom, assuming a staggered conformation for the [–CH_2–CH_3] group and the normally accepted value for the C–H distance (1·08 Å); their approximate thermal factor has been obtained by trial methods.

The values of atomic scattering factors introduced in our structure-factor calculations have been taken from the *Internationale Tabellen zur Bestimmung von Kristallstrukturen*; the scattering contribution by fluorine atoms has been evaluated on the basis of the scattering factor of the F^- ion.

5. Stereochemistry of the structure—Intra-ionic and inter-ionic distances. Probable electric charge distribution on the [($C_2H_5)_3$Al-F-Al($C_2H_5)_3$]$^-$ ion

Fig. 4 shows a steric picture of the relative position of the [($C_2H_5)_3$Al–F–Al($C_2H_5)_3$]$^-$ anion with respect to the surrounding K^+ cations. It may be seen that every ion is surrounded by a not greatly distorted octahedron of ions of the opposite kind; two opposite faces of this octahedron are equilateral triangles with edges of 8·31 Å, which are connected by six edges of 8·95 Å. This interesting structural feature is undoubtedly due to the rather retracted form of the anion, whose van der Waals shape may be considered as approximately spherical.

Bond lengths and angles which define the anion structure are also represented in Fig. 4, together with the corresponding standard deviations, deduced from the data given in Table 4. The dihedral angle between the (F–Al–C) and (Al–C–C) planes is 54° 45′ ± 1°.

Intra-ionic contacts between atoms separated by more than three bonds, and inter-ionic contacts are
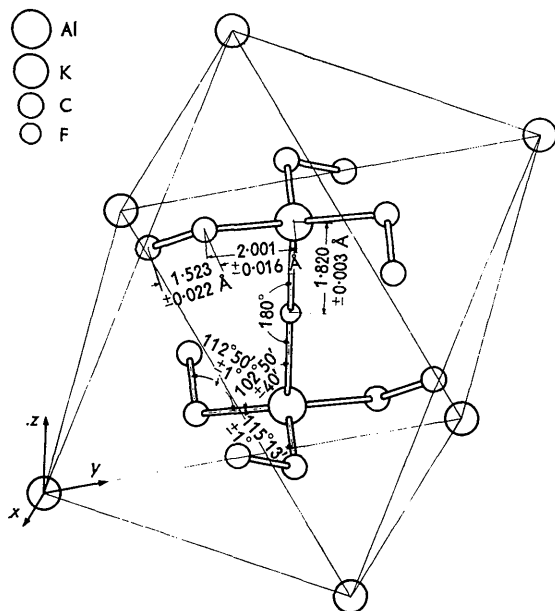
Fig. 4. Axonometric projection of the $[(C_2H_5)_6Al-F-Al(C_2H_5)_3]^-$ ion, and of the six nearest octahedrally disposed K^+ ions. Hydrogen atoms have been omitted. Bond lengths and valence angles have been also represented, together with the corresponding standard deviations.

represented in Fig. 5, in which a picture of the ionic packing is also given. Hydrogen atoms have been omitted; only the most significant interatomic-contact distances have been represented. All C–C distances
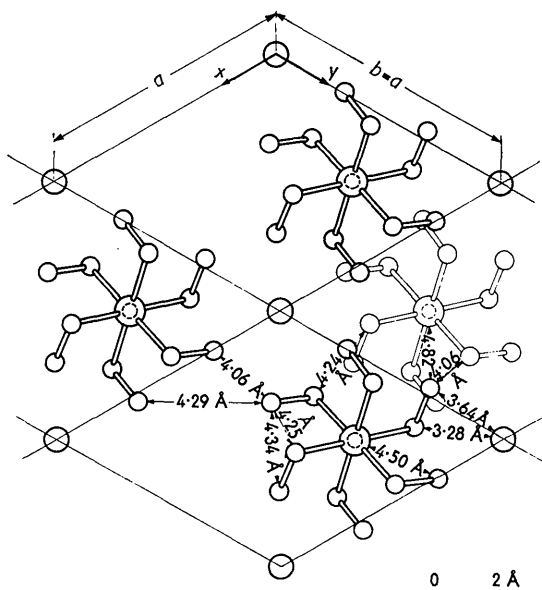

Fig. 5. Projection of a part of the structure along the z axis. K^+ ions at $z=0$ have been represented by heavy lines; $[(C_2H_5)_3Al-F-Al(C_2H_5)_3]^-$ ions at $z = \frac{1}{4}$ have been represented by heavy lines, and at $z = -\frac{1}{4}$ by thin lines. The most remarkable intra-ionic and inter-ionic contact distances have been represented. Hydrogen atoms omitted.

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appear to be greater than the value of 4·0 Å, usually quoted as the van der Waals contact distance for methyl or methylenic groups; C–Al distances are equal or greater to 4·5 Å, a value which may also be considered as close to the van der Waals contact distance.

It seems interesting to emphasize the rather short value found for the C(methylenic)–K distance (3·28 Å). We have calculated the approximate charge distribution on the $[(C_2H_5)_3Al-F-Al(C_2H_5)_3]^-$ ion, by using Pauling's criterion of electronegativities: the result which we obtained shows that methylenic groups are affected by a definite amount of negative charge, thus leading us to conclude that a certain electrostatic attraction is a reasonable explanation for the short C–K distance.

We started by writing the following formula for the anion, which, in a formal way, allows us to consider at first all the bonds as simply covalent:

$$(CH_3-CH_2-)_3Al^--F^+-Al^--(-CH_2-CH_3)_3 \ .$$
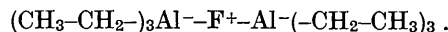
By using the following approximate formula, proposed by Pauling, which gives the amount of ionic character of a single bond between atoms A and B, with electronegativities x_A and x_B:

$$\% \text{ ionic character} = (1 - \exp{[-\tfrac{1}{4}(x_A-x_B)^2]}) \times 100$$

and attributing the values reported in Pauling's *The Nature of the Chemical Bond* (1960) to the various x_i, we have obtained the following charge distribution, in electrons:

F	$+0\cdot58e$	C(methylic)	$+0\cdot12e$
Al	$-0\cdot45e$	H	$-0\cdot04e$
C(methylenic)	$+0\cdot30e$		

From these data methyl groups may be considered as uncharged, but a negative charge of 0·22 electrons affects every methylenic group.

6. Discussion of the structure

The most interesting structural feature of the $KF.2 Al(C_2H_5)_3$ complex is undoubtedly the presence of collinear bridge bonds between a fluorine atom and the two adjacent aluminum atoms; this is a completely new and surprising coordination type. The resulting Al–F distance (1·82 Å) is almost the same as the corresponding distance observed in the Na_3AlF_6 complex (1·81 Å), in which six coordinated Al–F bonds are present. It might be expected that, in the coordination of one fluorine atom to two aluminum atoms, a larger Al–F distance would result; in fact, a number of observed bridge-bond distances are longer than the corresponding single-bond distances: compare for instance the two different Al–C bridge and non-bridge distances observed in the $[Al(CH_3)_3]_2$ crystal structure (2·23 and 2·00 Å respectively).

We think that the actual shortening of the Al–F

distance with respect to the expected value may be explained by the analysis of the most probable co-ordination type between fluorine and aluminum atoms. It seems very reasonable to conclude that an (sp) hybridization on the fluorine atom gives rise to two σ-bonds; a certain overlap of π-type between the filled $2p_y$ and $2p_z$ fluorine orbitals with $3d$ empty aluminum orbitals could be responsible for the stabilization of the (sp) σ-bonding. The (sp) hybridization itself may be responsible for the shortening of the Al–F distance: compare for instance the value quoted for the C–C single-bond distance (1·47 Å) in dimethylacetylene, where the two central C atoms are (sp) hybridized, with the normal value (1·54 A). On the other hand, it has been demonstrated that the fluorine atom has a strong activity in decreasing the size of the $3d$ orbitals of second row elements (Craig, private communication); this fact would allow an efficient π-overlap with $2p$ fluorine orbitals. It seems probable that a similar coordination type takes place in the two compounds $K_4Ru_2Cl_{10}O.H_2O$ and $Ti_2Cl_4(C_5H_5)_2O$. From the X-ray structural description either of the former (Mathieson, Mellor & Stephenson, 1952) or of the latter compound (P. Corradini & G. Allegra, 1959), collinear bridge bonds between the central oxygen atom and the two adjacent metal atoms result, and in every case the Me–O distance appears to be shorter than the expected single-bond distance.

The distortion of the tetrahedral coordination around aluminum atoms may be explained on the basis of the classical theory of electrostatic repulsion between pairs of bonding electrons: owing to the larger electronegativity of fluorine with respect to carbon atom, the Al–C bonding electron pairs are nearer to the aluminum atom than the Al–F⁻ strongly polarized electron pair, so that $\angle$ C–Al–C angles become larger (115° 13') and $\angle$ F–Al–C angles smaller (102° 50') than the tetrahedral value. The Al–C distance (2·00 Å) is practically equal to the value quoted for Al–C non-bridge distance in aluminum trimethyl dimer (1·99–2·00 Å). The $\angle$ Al–C–C bond angle (112° 50') and the C–C distance (1·52 Å) appear to be close to the normal values.

Finally it is interesting to note that the value of the dihedral angle between the (C–C–Al) and (C–Al–F) planes (54° 45') results to be rather close to the value (60°) corresponding to exact staggering between two tetrahedrally coordinated atoms.

7. Experimental

A KF.2 Al(C₂H₅)₃ (I) solution was obtained by reaction of finely ground KF with a stoichiometric quantity of Al(C₂H₅)₃ dissolved in toluene, at about 60 °C., in inert atmosphere. We then carried out the crystallization of (I) by slow evaporation of toluene from the solution at room temperature; by lowering the evaporation rate, we succeeded in obtaining colourless crystals whose greatest dimension was comprised between 30 and 40 mm. Their density has been evaluated by suspending them in a mixture of anhydrous heptane and chloroform.

Rotation and Weissenberg photographs were taken with small crystals fitted in Lindemann capillary tubes, in inert atmosphere; the greatest linear dimension of the crystals was approximately 0·4 mm.

References

CORRADINI, P. & ALLEGRA, G. (1959). *J. Amer. Chem. Soc.* **81**, 5510.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.

GILLESPIE, R. J. & NYHOLM, R. S. (1957). *Quart. Rev. Chem. Soc. London*, **11**, 339.

International Tables for X-ray Crystallography (1952). Birmingham: The Kynoch Press.

Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.

LEWIS, P. H. & RUNDLE, R. E. (1953). *J. Chem. Phys.* **21**, 986.

MATHIESON, A. McL., MELLOR, D. P. & STEPHENSON, N. C. (1952). *Acta Cryst.* **5**, 185.

MENZER, G. (1929). *Fortsch. Min. Kryst. Petrog.* **13**, 56.

NATTA, G., ALLEGRA, G., PEREGO, G. & ZAMBELLI, A. (1961). *J. Amer. Chem. Soc.* **83**, 5033.

PAULING, L., SPRINGALL, H. D. & PALMER, K. J. (1939). *J. Amer. Chem. Soc.* **61**, 927.

PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.

WHELAND, G. W. (1955). *Resonance in Organic Chemistry.* New York: Wiley.

ZIEGLER, K., KÖSTER, R., LEHMKUHL, H. & REINERT, K. (1960). *Liebigs Ann. Chem.* **629**, 33.