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Crystal Structure of Cobaltous Chloroaluminate, $Co(AlCl_4)_2$

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The bright blue crystals of empirical composition $CoCl_2.2\,AlCl_3$ formed when $CoCl_2$ and $AlCl_3$ are melted and then cooled together in a sealed system are shown, on the basis of a complete structure determination, to be cobaltous chloroaluminate, $Co(AlCl_4)_2$. There are four molecules of $Co(AlCl_4)_2$ in a monoclinic cell of dimensions

$$a = 12{\cdot}81,\ b = 7{\cdot}75,\ c = 11{\cdot}50\ \text{Å};\ \beta = 92{\cdot}2°,$$

space group C^6_{2h}–$I2/c$. The structure is most usefully described in terms of infinite chains of $Co(AlCl_4)_2$ parallel to the c axis. The cobalt atom is octahedrally coordinated, a surprising result in view of the color of the compound. Each $CoCl_6$ octahedron shares edges with two $AlCl_4$ tetrahedra and vertices with two others. Each $AlCl_4$ tetrahedron shares one edge with one $CoCl_6$ octahedron and a vertex with the next $CoCl_6$ octahedron along the chain. The $AlCl_4$ group is nearly regular. The $CoCl_6$ group is severely distorted, although the six Co–Cl distances are equal, within the limits of error of this study.

Introduction

When $AlCl_3$ and $CoCl_2$ are melted together at about 225 °C. in a sealed tube a blue solution is formed; at the same time, bright blue crystals can be condensed at the cool end of the tube. These crystals have the composition Co : Al : Cl = 1 : 2 : 8 ($CoCl_2.2\,AlCl_3$), as established from neutron activation analyses. The paucity of data on the structures of complex halides and current interest in the coordination of transition metal ions prompted the structure determination reported here. On the basis of this study $CoCl_2.2\,AlCl_3$ is in fact cobaltous chloroaluminate, $Co(AlCl_4)_2$, and will be referred to as such in this paper.

Unit cell and space group

Crystals of $Co(AlCl_4)_2$, as prepared from the melt, are bright blue in color and exhibit a needle-like habit. The crystals appear to be hexagonal in cross section. There is perfect cleavage along the needle axis. The crystals decompose rapidly in air, but are easily handled under mineral oil that has been pre-treated with $AlCl_3$ (Kumamoto, Ibers & Snyder, 1961).

A broken needle was selected for the X-ray photography. This crystal had dimensions of the order of $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}5$ mm. It was mounted directly in an oil-filled 0·2 mm. glass capillary tube, and the tube was sealed with Spectrovac wax. A series of Weissenberg and precession photographs was taken of the crystal mounted about its needle axis. From calibrated precession photographs we find the crystal to be monoclinic with

$$a = 12{\cdot}81 \pm 0{\cdot}02,\ b = 7{\cdot}75 \pm 0{\cdot}01,\ c = 11{\cdot}50 \pm 0{\cdot}02\ \text{Å};$$
$$\beta = 92{\cdot}2 \pm 0{\cdot}1°.†$$

The needle axis is [001]. The following systematic extinctions were noted: $h0l$ absent if either h or l is odd; $hk0$ absent if $h+k$ odd; $0kl$ absent if $k+l$ odd; hhl and $3h,h,l$ absent if l odd. These systematic extinctions are consistent only with the space groups C^4_s–Ic or C^6_{2h}–$I2/c$ (unique axis b). Both transformations from body-centered to possible C end-centered cells, namely

$$\bar{a}' = \bar{a} \pm \bar{c},\ \bar{b}' = \bar{b},\ \bar{c}' = \bar{c}\ ,$$

lead to a monoclinic angle near 130°. Such an angle is inconvenient if one wishes to produce directly as a computer print-out a semi-plottable form of a Fourier map. Moreover, the description adopted here of the cell as body centered, as we shall see, is convenient for it enables one to visualize readily the relation between this cell and a simpler hexagonal cell in which c is the unique axis and a and b the orthohexagonal axes ($a \approx \sqrt{(3)}b$). The realization that the monoclinic cell is a distortion of a simpler hexagonal cell contributed to the solution of the structure. Hence the advantages of maintaining the description of the monoclinic cell as body-centered completely outweigh any advantage that might be gained by redefining the cell to conform to the conventions of *International Tables for X-ray Crystallography* (1952).

Densities for $Co(AlCl_4)_2$ of 2·20 to 2·22 g.cm.$^{-3}$ were

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† Recently Corbett, Burkhard & Druding (1961) reported the preparation of a compound which they surmised to be $Cd(AlCl_4)_2$. On the basis of their X-ray powder data and the unit cell data above, it is unlikely that $Cd(AlCl_4)_2$ and $Co(AlCl_4)_2$ are isostructural.

obtained by the flotation method, when pre-dried CCl_4–CH_2Br_2 mixtures were used as flotation liquids. The density is not too reliable because of slow reaction of the crystals with the flotation liquid. (After about 10 minutes in such mixtures the crystals turn green.) Nevertheless, the density is satisfactorily close to that of 2·31 g.cm.$^{-3}$ predicted for four molecules of $Co(AlCl_4)_2$ in the unit cell.

Collection of intensities and their reduction to structure amplitudes

Intensity data were collected from the crystal with the use of Mo $K\alpha$ radiation filtered through Zr foil. The use of molybdenum radiation obviated the need for an absorption correction. (The linear absorption coefficient μ of $Co(AlCl_4)_2$ for Mo $K\alpha$ is about 35 cm.$^{-1}$ and hence μR, where R is the 'radius' of the crystal, is about 0·4.) Weissenberg data, obtained by the equi-inclination method, were collected from the $hk0$ to $hk6$ layers. Precession data were collected from the $hk0$, $0kl$, hhl, and $3h,h,l$ layers. Multiple films were used in the Weissenberg photography; multiple exposures in the precession photography.

Intensities were estimated by visual comparison with an intensity strip. This strip was made from timed exposures of the 220 reflection. The strip had a scale that ranged from a relative value of 1, this spot being barely visible, to 64. Ilford Industrial X-ray film type G was used for the photography.

Intensities were reduced to relative values of the structure amplitudes after account was taken of the appropriate Lorentz-polarization factors. The precession photographs provided sufficient data so that all structure amplitudes could be brought to a common scale, and only a single scale factor was carried in the ensuing calculations.

One advantage of combined Weissenberg-precession photography is that inter-layer correlations of intensities can be obtained without remounting the crystal. On the other hand not all data within the sphere of reflection can be obtained in this way. Because of this and because upper level data were not collected past $l=6$, the data obtained here are highly nonspherical. Nevertheless, of the approximately 1850 independent reflections within the sphere $\sin\theta_{Mo} \leq 0{\cdot}50$, we had access to about 1100. Of these only about 400 were sufficiently intense to be estimated.

Solution of the crystal structure

There were several important clues that led to the finding of a suitable trial structure. The volume per chlorine atom in $Co(AlCl_4)_2$ is about 35 Å^3, slightly greater than in $FeCl_3$ (33 Å^3), $CoCl_2$ (31 Å^3), or $AlCl_3$ (30 Å^3), all close-packed structures. Hence the chlorine atoms in $Co(AlCl_4)_2$ must be nearly close-packed. There is perfect cleavage along the c axis, and thus the cobalt and aluminum atoms probably fill holes in the close-packed chlorine lattice in such a way as to form chains parallel to c. The $hk0$ layer shows pseudotrigonal symmetry: the $[0k0]$ and $[3h,h,0]$ zones are approximately 60° from one another, and reflections at the same Bragg angle on these zones show similar intensities. Thus 020 resembles 310, 040 resembles 620 (both very intense), etc. A similar relation holds between the $[h00]$ and $[hh0]$ zones. Hence in projection onto the ab plane the atoms are probably approximately hexagonally packed. There must be a high density of atoms in the 040 and 620 planes to account for the high intensities of these reflections. Finally the intensities of reflections with l odd are generally much lower than those with l even. The cobalt atom is probably not contributing to reflections with l odd.

With these clues in mind various scale models (Cl radius, 1·80 Å) were constructed. The only one that satisfied all the available facts consisted of strings of cobalt atoms tied together by $AlCl_4$ tetrahedra in such a way that the cobalt atoms were in octahedral holes. The cobalt octahedra shared edges with two aluminum tetrahedra and vertices with two others. The $AlCl_4$ group was taken to be a perfect tetrahedron 3·5 Å on an edge, with the aluminum at the center. Then upon making the structure as symmetric as possible a set of trial parameters was obtained. This model, incidentally, had the cobalt atom at the origin and was consistent with the space group $I2/c$.

We went directly from this trial structure to a least-squares refinement. Since the least-squares technique was used extensively in this study we diverge here to indicate the form in which it was applied. Structure factors were computed with the use of individual, isotropic thermal parameters (initially guessed). The sources of the atomic scattering factors used are Al^{+3}, Freeman (1959); Cl^-, Boys (1958) (identical with Dawson (1960); Co^{+2}, Watson & Freeman (1961). No corrections for anomalous dispersion were made. In the least-squares calculations the function

$$\sum_{\text{reflections}} [|F_o| - s|F_c|]^2$$

was minimized, where s is the single scale factor which brings observed and calculated structure amplitudes to a common scale. Unit weights were used, except as indicated below. The goodness of fit between observed and calculated structure amplitudes was judged both from the conventional R factor, and from the error of fit function

$$(\text{error of fit})^2 = (m-n)^{-1}\Sigma[|F_o| - s|F_c|]^2$$

where m is the number of observations and n is the number of parameters adjusted (23 in the present case). Calculations were initially carried out on an IBM 704 and later on an IBM 7090.

With some optimism a least-squares refinement of the $l=0$ and $l=2$ data, based on the trial structure,

Table 1. *Final least-squares parameters for* $Co(AlCl_4)_2$

Atom	Position*	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Co	$4e$	0	—	0·0017	0·0012	$\frac{1}{4}$	—	2·15	0·13
Al	$8f$	0·0877	0·0008	0·2516	0·0018	0·5538	0·0010	2·80	0·21
Cl I	$8f$	0·1588	0·0007	0·4843	0·0019	0·6084	0·0009	3·66	0·21
Cl II	$8f$	0·1559	0·0006	0·0192	0·0016	0·6334	0·0007	2·69	0·18
Cl III	$8f$	0·0851	0·0007	0·2339	0·0015	0·3670	0·0008	2·56	0·19
Cl IV	$8f$	−0·0701	0·0007	0·2239	0·0014	0·6167	0·0009	2·88	0·21

* These equivalent positions for $I2/c$ are: $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$

$(4e)$ $\pm(0, y, \frac{1}{4})$ $(8f)$ $\pm(x, y, z)$; $\pm(\bar{x}, y, \frac{1}{2}-z)$

was first attempted. This refinement diverged: by the end of the second cycle the thermal parameter of the aluminum atom had increased from the initial guess of 3 Å^2 to 12·7 Å^2. It seemed likely that the aluminum position in the trial structure was incorrect; the high thermal parameter corresponds to an attempt to smear out the aluminum contributions to the structure amplitudes. However, the R factor of 0·39 for the structure before the refinement diverged was sufficiently low to foster faith in the rest of the trial structure.

The signs of the structure factors from the trial structure were assigned to the structure amplitudes for the layers $l=0$, 2, 4, and 6, and a three-dimensional Fourier series was computed. The Fourier map enabled us to confirm our suspicion that the aluminum atom was in an incorrect position and to derive the correct aluminum position. An improved scale factor and improved thermal and positional parameters for the other atoms were also obtained from this Fourier map.

A second least-squares refinement of the $l=0$, 2, 4, and 6 Weissenberg data and of the precession data, based on this new trial structure, was attempted. In this refinement zero weight was given to those close-in strong reflections believed to be weakened by extinction (200, 620, 040, 222, 004, $22\bar{2}$, and $20\bar{4}$). This refinement converged rapidly to parameters which gave an R factor of 0·13 and an error of fit of 4·2. Although these are satisfactory values for this type of structure, there were some serious difficulties. First, certain features of the structure were unreasonable; second, while the overall R factor was 0·13, the R factor for the 15 l-odd reflections (from the $0kl$ precession data) was 0·58. Since all of the calculations up to this point were based almost entirely on the relatively intense data for l even, it is only necessary that the derived structure, if correct, be so to within $\pm\frac{1}{4}$ in the z parameters. Seventeen close-in l-odd reflections were therefore selected and individual contributions of each atom to the structure factors of these reflections were calculated. A combination of $\pm\frac{1}{4}$ was sought which, when added to the z parameters, would substantially improve the agreement. Only one such combination was found. A final least-squares refinement of all of the data, including all of the available structure amplitudes for l odd, was based on this new model. This refinement converged rapidly to the parameters given in Table 1. The final error of fit is 3·45; this does not approach unity, for absolute weights were not employed. The final R factors (observed reflections only) are overall, 0·11; l-even, 0·10; l-odd, 0·13. The difference between the R factors for l-odd and l-even reflections is not significant, for the l-odd reflections are generally weaker and thus more difficult to estimate accurately, and also the limited l-odd data on the precession photographs make accurate scaling difficult. Table 2 lists the final values of F_c and the values of $|F_o|$. Not listed are the values of F_c for the 700 or so unobserved reflections. However, only about one dozen of these exceed the estimated maximum allowable values of $|F_o|$, and none by more than 30%. All in all the agreement is excellent; the assumption that the space group is $I2/c$, rather than Ic, thus seems justified.

It is interesting that relative to the cobalt at the origin, three of the chlorine atoms were initially in correct positions and the fourth was correct to within $\frac{1}{2}$ in its z parameter. This led to the placement of the aluminum atom in the wrong tetrahedral hole. The correct structure might have been found sooner had the data for the l-odd reflections been included in the calculation of the Fourier map. Yet the omission of these data from the initial least-squares refinements was fortunate, for convergence to a structure correct to within $\pm\frac{1}{4}$ in the z parameters was thus assured.

Description of the structure

Data on the structures of complex halides are limited, and no structures of comparable stoichiometry have been described in the literature. The structure of $Co(AlCl_4)_2$ may be described in terms of the placement of cobalt and aluminum atoms in octahedral and tetrahedral holes, respectively, of a nearly close-packed chlorine lattice. The chlorine atoms lie approximately in planes parallel to the ab plane of the unit cell. In each unit cell there are four such chlorine planes, which we label A, B, A' and B' (Fig. 1), whose fractional heights along c (z parameters) are approximately 0·12, 0·37, 0·63, and 0·88. The chlorine atoms within a given plane are approximately hexagonally arranged. The A' plane superimposes almost exactly onto the A plane, as does the B' plane onto the B plane. This is not required by the symmetry of the space group.

Table 2. *Observed and calculated structure factors for* $Co(AlCl_4)_2$

H	K	L	OBS	CAL
00	00	00		756
02	00	00	193	173
04	00	00	181	-174
08	00	00	044	-039
12	00	00	149	153
14	00	00	063	072
01	01	00	158	128
03	01	00	089	092
05	01	00	041	053
07	01	00	057	055
09	01	00	038	043
13	01	00	032	041
02	02	00	146	-140
04	02	00	057	060
06	02	00	314	358
08	02	00	117	126
10	02	00	070	-061
03	03	00	063	063
05	03	00	092	093
07	03	00	086	095
09	03	00	057	052
00	04	00	304	363
02	04	00	101	106
04	04	00	086	-078
12	04	00	101	109
14	04	00	051	051
01	05	00	108	111
03	05	00	048	058
13	05	00	035	043
02	06	00	019	-030
04	06	00	044	041
06	06	00	149	155
08	06	00	073	059
05	07	00	063	060
07	07	00	073	065
09	07	00	025	032
00	08	00	092	105
02	08	00	032	037
01	09	00	057	053
00	01	01	038	034
02	01	01	073	094
04	01	01	019	028
06	01	01	035	-038
08	01	01	067	-073
10	01	01	032	-043
12	01	01	029	024
14	01	01	038	047
02	01	-01	063	072
06	01	-01	041	-044
00	03	01	029	029
02	03	01	051	-051
04	03	01	089	-091
06	03	01	057	044
08	03	01	073	083
02	03	-01	019	008
04	03	-01	019	-028
08	03	-01	057	059
12	03	-01	035	-045
03	04	-01	025	030
05	04	-01	022	015
00	05	01	029	038
02	05	01	060	066
08	05	01	035	-024
10	05	01	048	-052
02	05	-01	089	090
04	05	-01	016	027
06	05	-01	048	-051
00	07	01	029	030
04	07	01	070	-069
08	07	01	038	045
08	07	-01	038	047
02	09	-01	038	051
02	00	02	136	-128
04	00	02	155	167
08	00	02	206	-210
10	00	02	041	-052
14	00	02	044	-049
04	00	-02	349	-401
06	00	-02	200	-189
08	00	-02	079	075
16	00	-02	032	-046
01	01	02	111	-098
03	01	02	032	-032
05	01	02	057	-057
07	01	02	073	-074
09	01	02	051	-055
11	01	02	035	-036
01	01	-02	139	-125
03	01	-02	063	-074
05	01	-02	105	-101
07	01	-02	073	-074
11	01	-02	035	-034
13	01	-02	038	-037
00	02	02	127	-130
02	02	02	358	-404
04	02	02	051	-053
08	02	02	105	-091
14	02	02	070	-069
02	02	-02	193	183
04	02	-02	057	-052
10	02	-02	130	-138
12	02	-02	089	-101
01	03	02	124	-121
03	03	02	108	-110
05	03	02	092	-092
07	03	02	048	-051
01	03	-02	060	-056
03	03	-02	022	012
05	03	-02	041	-040
07	03	-02	067	-071
09	03	-02	044	-048
11	03	-02	054	-053
13	03	-02	029	-033
02	04	02	086	-085
04	04	02	060	053
08	04	02	146	-139
10	04	02	038	-035
04	04	-02	222	-212
06	04	-02	124	-122
08	04	-02	041	042
01	05	02	029	-032
07	05	02	057	-053
09	05	02	054	-063
01	05	-02	089	-087
03	05	-02	082	-092
05	05	-02	082	-084
07	05	-02	035	-036
00	06	02	054	-065
02	06	02	139	-136
08	06	02	048	-047
10	06	-02	054	-068
12	06	-02	057	-050
01	07	02	060	-062
03	07	02	076	-077
05	07	02	054	-058
04	08	-02	054	-063
06	08	-02	044	-042
03	09	-02	048	-050
00	01	03	101	100
02	01	03	032	036
08	01	03	032	-036
02	01	-03	041	-051
04	01	-03	041	051
06	01	-03	048	062
08	01	-03	032	033
12	01	-03	029	-028
01	02	-03	019	-021
03	02	-03	013	-011
05	02	-03	019	014
02	03	03	070	-080
06	03	03	051	059
06	03	-03	070	-068
08	03	-03	038	-049
00	05	03	070	074
08	05	03	035	-032
02	05	-03	029	-035
04	05	-03	051	057
02	07	03	035	-042
06	07	03	029	041
06	07	-03	029	-030
00	09	03	029	028
00	00	04	203	-285
02	00	04	029	-022
04	00	04	174	182
06	00	04	073	073
08	00	04	162	146
10	00	04	120	112
12	00	04	060	-060
14	00	04	032	-039
02	00	-04	127	127
04	00	-04	257	257
06	00	-04	035	041
08	00	-04	063	078
10	00	-04	063	068
16	00	-04	029	046
01	01	04	117	100
03	01	04	095	088
05	01	04	044	043
07	01	04	076	073
09	01	04	054	060
03	01	-04	063	069
05	01	-04	117	118
07	01	-04	035	038
09	01	-04	035	040
11	01	-04	057	055
00	02	04	057	068
02	02	04	266	246
04	02	04	165	156
06	02	04	101	-133
08	02	04	060	-050
10	02	04	076	079
12	02	04	041	040
14	02	04	051	050
16	02	04	057	045
02	02	-04	165	167
04	02	-04	060	058
06	02	-04	117	-114
08	02	-04	044	042
10	02	-04	108	114
01	03	04	127	137
03	03	04	070	075
09	03	04	041	040
01	03	-04	070	077
03	03	-04	057	073
05	03	-04	060	060
11	03	-04	060	057
00	04	04	111	-120
04	04	04	111	103
06	04	04	044	049
08	04	04	095	102
10	04	04	086	079
12	04	04	041	-039
02	04	-04	098	095
04	04	-04	139	160
08	04	-04	054	050
10	04	-04	044	046
03	05	04	051	049
05	05	04	048	059
07	05	04	076	075
09	05	04	041	046
01	05	-04	032	-026
03	05	-04	032	034
05	05	-04	076	090
07	05	-04	057	055
09	05	-04	044	038
00	06	04	029	030
02	06	04	105	106
04	06	04	089	077
06	06	04	048	-049
02	06	-04	051	057
06	06	-04	038	-039
10	06	-04	079	062
01	07	04	076	079
03	07	04	041	036
01	07	-04	060	061
03	07	-04	041	038
08	08	04	044	037
02	08	-04	044	043
04	08	-04	057	059
00	01	05	067	079
02	01	05	041	036
04	01	05	016	-022
06	01	05	041	-047
10	01	05	029	038
12	01	05	029	014
02	01	-05	041	-039
04	01	-05	082	080
06	01	-05	105	104
10	01	-05	060	-057
12	01	-05	057	-054
01	02	-05	025	017
00	03	05	098	-100
02	03	05	057	-049
04	03	05	070	061
04	03	-05	057	-055
06	03	-05	048	-054
08	03	-05	029	-033
10	03	-05	048	041
12	03	-05	060	064
05	04	05	022	-017
01	04	-05	019	009
03	04	-05	035	-031
05	04	-05	022	-018
00	05	05	029	027
06	05	05	051	-045
10	05	05	041	042
02	05	-05	060	-058
04	05	-05	038	042
06	05	-05	082	085
10	05	-05	029	-035
01	06	-05	025	019
00	07	05	057	-061
02	07	05	019	-026
04	07	05	051	052
02	09	-05	022	-036
06	09	-05	035	018
00	00	06	092	-107
02	00	06	130	-113
04	00	06	257	-247
06	00	06	095	-083
08	00	06	130	115
10	00	06	035	020
12	00	06	044	-047
16	00	06	041	-040
04	00	-06	168	167
08	00	-06	177	-177
10	00	-06	067	-078
01	01	06	035	-031
03	01	06	117	-119
05	01	06	060	-062
09	01	06	041	-042
01	01	-06	035	-037
03	01	-06	111	-103
09	01	-06	073	-078
00	02	06	048	-052
02	02	06	206	175
06	02	06	095	-083
08	02	06	057	-055
10	02	06	120	-109
12	02	06	057	-055
02	02	-06	276	-260
04	02	-06	117	-112
06	02	-06	051	-056
08	02	-06	032	-034
10	02	-06	057	060
14	02	-06	070	-067
03	03	06	051	-049
05	03	06	032	-025
09	03	06	070	-064
11	03	06	041	-048
01	03	-06	054	-054
03	03	-06	098	-128
05	03	-06	051	-048
09	03	-06	054	-045
00	04	06	057	-072
02	04	06	086	-079
04	04	06	149	-162
06	04	06	057	-057
08	04	06	076	077
04	04	-06	086	101
08	04	-06	127	-126
10	04	-06	054	-056
01	05	06	041	-041
03	05	06	108	-102
05	05	06	057	-060
09	05	-06	057	-064
00	06	06	019	-029
02	06	06	073	069
06	06	06	048	-044
10	06	06	044	-055
02	06	-06	117	-119
04	06	-06	060	-055
01	07	-06	038	-038
03	07	-06	067	-075
04	08	06	054	-055
08	08	-06	041	-048
03	09	06	048	-048
00	03	07	025	-028
00	07	07	029	-030
00	00	08	162	178
02	00	08	048	049
04	00	08	041	-034
06	00	08	029	046
12	00	08	060	064
14	00	08	038	043
02	00	-08	048	056
06	00	-08	067	063
12	00	-08	044	056
14	00	-08	041	038
01	01	-08	111	112
03	01	-08	054	043
00	02	08	060	068
06	02	08	146	122
02	02	-08	041	-031
06	02	-08	114	118
09	03	-08	035	038
00	04	08	098	118
12	04	08	041	045
00	06	08	035	040
06	06	08	044	058
06	06	-08	044	057
07	07	08	041	039
00	08	08	019	038
00	01	09	019	-021
00	03	09	035	032
00	00	10	067	-059
02	00	10	029	-034
04	00	10	073	073
08	00	10	098	-090
10	00	10	073	-062
02	00	-10	073	-066
04	00	-10	114	-107
12	00	-10	029	-035
01	01	10	092	-068
01	01	-10	051	-050
02	02	10	158	-118
06	02	10	057	-040
02	02	-10	076	066
06	02	-10	057	-051
03	03	10	029	-020
00	04	10	041	-046
04	04	10	041	048
04	04	-10	079	-074
12	04	-10	035	-029
05	05	-10	041	-051
06	06	-10	041	-034
00	00	12	070	-059
04	00	12	086	078
06	00	12	041	046
08	00	12	041	036
04	00	-12	054	049
06	00	-12	041	041
08	00	-12	044	049
01	01	12	063	041
03	01	12	057	044
03	01	-12	048	032
00	02	12	054	050
02	02	12	070	047
06	02	12	063	-043
02	02	-12	101	075
06	02	-12	044	-036
03	03	12	051	038
03	03	-12	041	033
00	04	12	041	-039
04	04	12	051	056
04	04	-12	041	038
05	05	-12	051	041
00	06	12	035	027
06	06	-12	022	-015
00	00	14	032	-017
04	00	14	048	-046
03	01	14	057	-042
03	01	-14	044	-042
00	02	14	025	-019
06	02	14	022	-011
02	02	-14	054	-040
03	03	14	025	-022
03	03	-14	073	-046
04	04	14	022	-033
00	01	15	029	-024
00	03	15	019	018
00	00	16	054	043
02	00	16	041	025
01	01	-16	044	034

The cobalt atoms are approximately hexagonally arranged in planes parallel to the chlorine planes at heights of $\frac{1}{4}$ and $\frac{3}{4}$. The cobalt atoms occupy one-quarter of the octahedral holes.

Aluminum atoms connect chlorine planes B and A' and chlorine planes B' and $A+1$. The aluminum atoms do not lie in planes, and those between B and A' cannot be superimposed onto those between B' and $A+1$. Rather the aluminum atoms occupy particular tetrahedral holes and are not hexagonally arranged.

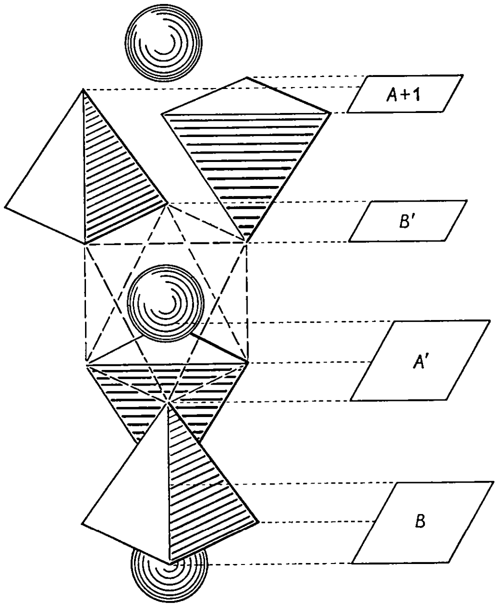

Fig. 1. Part of an infinite $Co(AlCl_4)_2$ chain parallel to c. The view is down along [110]. Aluminum atoms at the centers of the solid tetrahedra are not shown. A $CoCl_6$ octahedron is shown in dashed lines.

An alternate, more useful description of the structure in terms of infinite chains of $Co(AlCl_4)_2$ parallel to the c axis is possible. Each $AlCl_4$ tetrahedron shares one edge with a $CoCl_6$ octahedron and a vertex with the next cobalt octahedron along the chain. Each $CoCl_6$ octahedron shares edges with two $AlCl_4$ tetrahedra and vertices with two others. This arrangement is shown in Fig. 1. It differs from our initial guess mainly in the arrangement relative to one another of the four $AlCl_4$ tetrahedra associated with each cobalt. The chains of $Co(AlCl_4)_2$ are separate from one another; only van der Waals chlorine–chlorine contacts exist between them. This is the justification for deciding that $CoCl_2 . 2\,AlCl_3$ is cobaltous chloroaluminate.

Table 3. *Interatomic distances in* $Co(AlCl_4)_2$

$AlCl_4$ group

(Al, 0)	(I, 0)*	2·105 ± 0·019 Å
	(III, 0)	2·151 ± 0·016
	(IV, 0)	2·183 ± 0·014
	(II, 0)	2·188 ± 0·018
(II, 0) (IV, 0)		3·300 ± 0·013
(I, 0) (III, 0)		3·488 ± 0·016
(III, 0) (IV, 0)		3·555 ± 0·014
(I, 0) (IV, 0)		3·564 ± 0·016
(II, 0) (III, 0)		3·573 ± 0·015
(I, 0) (II, 0)		3·616 ± 0·015

$CoCl_6$ group

(Co, 0) (II, 4)	= (Co, 0) (II, 5)	2·453 ± 0·009 Å
(Co, 0) (IV, 4)	= (Co, 0) (IV, 5)	2·472 ± 0·012
(Co, 0) (III, 0)	= (Co, 0) (III, 2)	2·475 ± 0·013
(II, 4) (IV, 4)	= (II, 5) (IV, 5)	3·300 ± 0·013
(III, 0) (III, 2)		3·399 ± 0·020
(II, 4) (III, 2)	= (II, 5) (III, 0)	3·474 ± 0·014
(IV, 4) (IV, 5)		3·494 ± 0·021
(II, 4) (IV, 5)	= (II, 5) (IV, 4)	3·497 ± 0·014
(IV, 4) (III, 0)	= (IV, 5) (III, 2)	3·559 ± 0·014
(II, 4) (III, 0)	= (II, 5) (III, 2)	3·659 ± 0·014

Non-bonded Cl–Cl distances within a chain (< 4 Å)

(IV, 0) (II, 4)	= (II, 0) (IV, 4)	3·576 ± 0·015 Å
(IV, 6) (I, 0)		3·954 ± 0·016

Al · · · Co distances

(Co, 0) (Al, 0)	4·113 ± 0·014 Å
(Co, 0) (Al, 4)	3·225 ± 0·014

All interchain Cl · · · Cl distances are 3·73 Å or greater.

* The number following the designation of the atom signifies the following symmetry transformation of the coordinates given in Table 1.

0	x, y, z	4	$x, y, 1+z$
1	$\bar{x}, \bar{y}, \bar{z}$	5	$x, \bar{y}, z-1/2$
2	$\bar{x}, y, 1/2-z$	6	$\bar{x}, y, 3/2-z$

In Table 3 the principal interatomic distances and their standard deviations are listed. All Al–Cl distances are significantly shorter than 2·3 Å, the sum of the tetrahedral radii of Al and Cl (Pauling, 1960). The Al–Cl I distance is significantly shorter than the other three; this is reasonable for Cl I is the only chlorine atom not bonded to cobalt. Chlorine I undergoes significantly more thermal motion (Table 1), as would also be expected. The Cl–Cl distances of the tetrahedron are for the most part shorter than 3·60 Å, twice the ionic radius of chlorine. The II–IV distance of 3·30 Å is very short indeed. The II–IV edge is the common one between the $AlCl_4$ tetrahedron and the $CoCl_6$ octahedron, and so such a contraction is perhaps not too unexpected. The only other chloroaluminate reported in the structure literature is $NaAlCl_4$, which Baenziger (1951) studied. He found Al–Cl distances of from 2·11 to 2·16 Å, and Cl–Cl distances of from 3·39 to 3·54 Å. (Baenziger does not give limits of error for these distances, but they are probably about 0·03 to 0·05 Å.) Thus the dimensions of the $AlCl_4$ tetrahedron in $Co(AlCl_4)_2$ and in $NaAlCl_4$ are essentially the same, although the $AlCl_4$ group is packed very differently in the two structures.

The Co–Cl distances in the $CoCl_6$ octahedron are not significantly different from one another, but the octahedron is severely distorted. Such a distortion explains the appearance of an electron spin resonance spectrum at room temperature (Swalen, 1960), for such a spectrum would not be observed if the octahedron were perfect. The Co–Cl distance of 2·47 Å is somewhat longer than would be expected on the basis of the sum (2·3 Å) of the cobalt octahedral radius and the chlorine radius (Pauling, 1960), but agrees well with the value of 2·49 Å found by Dunitz (1957) in α-cobalt dipyridine dichloride. The bonding along the $Co(AlCl_4)_2$ chains is very compact; the inter-chain bonding is loose, the shortest Cl–Cl interchain contacts being 3·73 Å.

$Co(AlCl_4)_2$ is another of the few exceptions to the rule that octahedral complexes of divalent cobalt are red or pink and tetrahedral complexes blue. However, the symmetry of the structure is sufficiently low so that the degeneracies of the excited energy levels of Co^{+2} are removed, and large shifts in the characteristic absorption bands can occur.

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Refinement of the Structure of $BaTiO_3$ and other Ferroelectrics

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The structure of $BaTiO_3$ as determined by Evans (1961) is reliable, provided it is recognized that the thermal parameters, which are all rather small, are not very accurately known. The large standard deviations obtained by use of a least-squares program (Evans, 1961; Geller, 1961) are inconsistent with the terms in which the model is defined; this internal contradiction means that the application of the program to this type of structure is suspect, and cannot be used to discredit the empirical agreement between three independent determinations. The evidence suggests that position parameters may be found with fair confidence, by suitable methods of refinement, even when thermal parameters are doubtful.

Refinement of the structure of $BaTiO_3$ and other ferroelectrics

It would be a great pity if all the outstandingly careful work of Evans (1961) on the structure of $BaTiO_3$ led only to the conclusion that 'the structure is essentially indeterminate'. The evidence quoted by Evans himself is against such a conclusion, though it is true that a satisfactory statistical method of estimating the errors in the parameters has not yet been found.

The parameters have been determined in three independent investigations, by Evans (1961), Frazer, Danner & Pepinsky (1955) and Känzig (1951). Evans refined the structure in terms of four different non-cubic models. The results of all six models are recorded in Evans's Table 2. The mean values and mean deviations of the parameters are shown here in Table 1; the extreme range of the thermal parameters is also shown. It can be seen that there is very reasonable agreement in the position parameters (that for O_2 being least accurate) and that there is order-of-magnitude agreement in the thermal parameters, none of which are abnormally large. It is well known that thermal parameters are particularly sensitive to any disregarded or inadequately corrected systematic errors, such as effects of extinction, absorption, or incorrect scaling; hence it is not really surprising (though it may be disappointing) that agreement between them is not closer. The empirical agreement between position parameters obtained in quite independent investigations, and by refinement of different models, shows that these are not very sensitive to variations in the thermal parameters—a fact also noted by Danner, Frazer & Pepinsky (1960), and