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138. **Kyoji Hayano and Sataro Imado** : Studies on Aluminum Complex Compound of PAS. IV.[*2] X-Ray Studies on the Structure of Calcium Alumino-*p*-aminosalicylate.

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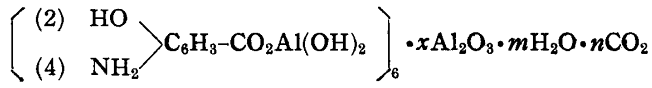
Crystallomorphological and optical properties of calcium alumino-*p*-aminosalicylate[*3] were reported in the preceding paper[*2] of this series. Further X-ray crystallographic studies on this compound were carried out in order to obtain some data in determining its chemical structure, which are described in the present paper.

Brown and others[1)] proposed the following formula for the compound of PAS and aluminum.



$$\left(\begin{matrix}(2)\ HO \\ (4)\ NH_2\end{matrix}\!\!>\!C_6H_3\text{-}CO_2Al(OH)_2\right)_6 \cdot xAl_2O_3 \cdot mH_2O \cdot nCO_2$$

$x = 3 \sim 6$; $m, n =$ not critical

This substance may be regarded as a double compound of basic aluminum *p*-aminosalicylate and alumina but its chemical composition was not clearly determined.

Burrows and others[2)] studied the compounds of salicylic acid and aluminum and forwarded the following formulae of complex compound :

$$H_2\left[(C_7H_4O_3)_2Al\genfrac{}{}{0pt}{}{OH}{OH_2}\right] \qquad M^{I}_2\left[(C_7H_4O_3)_2Al\genfrac{}{}{0pt}{}{OH}{OH_2}\right]$$

As described in previous papers, experiments carried out by the present authors using PAS afforded a substance giving analytical values agreeing with the following formulae :

$H_2[(C_7H_5O_3N)_2Al(OH)(H_2O)] \cdot 3H_2O$ (or $6H_2O$)	Al-PAS
$Ca[(C_7H_5O_3N)_2Al(OH)(H_2O)] \cdot 7H_2O$	Al-PAS-Ca

X-Ray crystal analysis was carried out with single crystal of Al–PAS–Ca.

1. Determination of the Size of Unit Cell and Space Group

As described in the preceding paper, the crystal of Al–PAS–Ca belongs to the triclinic holohedral class, *Ci*–$\bar{1}$.

Oscillation photographs around the three principal axes were taken with Cu–Kα radiation and the dimensions of a unit cell were evaluated. In order to presume its crystal structure, equatorial Weissenberg photographs around the *c* axis with the shortest period were prepared. In the preparation of Weissenberg photographs, three films were overlayed for exposure, the so-called multiple-film technique.

Intensities of reflections were determined visually, using a standard intensity scale. They were corrected for polarization and Lorentz factors, and the square of structure amplitudes, $|F(hko)|^2$, was calculated.

Dimensions of the unit cell were calculated from oscillation and Weissenberg photographs, and goniometric measurements of the crystal as follows :

[*1] Kashima-cho, Higashiyodogawa-ku, Osaka (早野恭二, 今戸佐太郎).

[*2] Part III : This Bulletin, 7, 766(1959).

[*3] See Part I of this series (p. 756) for chemical term of this designation.

1) P.M. Brown, Jr., M. Beekmann : C. A., 48, 14131(1954); U. S. Pat. 2,686,800(1954).

2) G. J. Burrows, I. William : J. Chem. Soc., **1928**, 222.

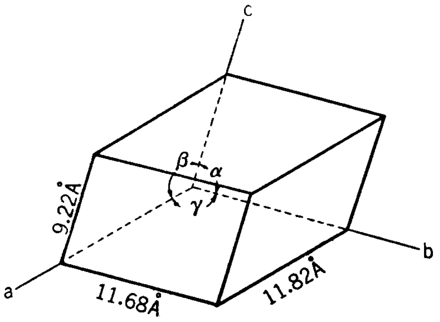


Fig. 1. The Unit Cell of $Ca\left[(C_7H_5O_8N)_2Al\begin{smallmatrix}OH\\OH_2\end{smallmatrix}\right]\cdot 7H_2O$

a = 11.82 Å	$\alpha = 92.5°\pm3°$
b = 11.68 Å	$\beta = 116.0°\pm3°$
c = 9.22 Å	$\gamma = 81.0°\pm3°$

From the foregoing results, volume V of the unit cell was calculated :

$$V = 1120.66\ \text{Å}^3$$

The number of formula units, Z, contained in a unit cell can be calulated from the following equation :

$$Z = \frac{\rho \cdot V}{M \cdot mH}$$

where ρ is the actual density of the crystal,^{*4} V is the volumer of the unit cell, mH is the mass (1.660×10^{-24} g.) corresponding to one atomic weight, and M is the molecular weight. Interpolation of the molecular weight for $Ca[(C_7H_5O_8N)_2Al(OH)(H_2O)]\cdot 7H_2O$ of $M=530.4$ into this formula gives the value of $Z=1.99$. Since the value of Z should be a positive integer, calculation of the X-ray molecular weight Mx from the obsereved density and the volume of the unit cell, taking $Z=2$, would give the value of $Mx=528.8$, which agrees well with the value calculated as heptahydrate, $Ca[(C_7H_5O_8N)_2Al(OH)(H_2O)]\cdot 7H_2O$.

Space group of the triclinic system would be either $C_1^1-P_i$ or $C_i^1-P\bar{1}$, and the following calculations were made in order to decide between these.

The values of $|F(hko)|^2$ were devided into several sets with ranges of suitable $\sin\theta/\lambda$ and the values of $|F(hko)|^2$ were averaged over each range. Then the fractions $N(z)$ of reflections whose intensities are equal to or less than a fraction z of the local average were evaluated and plotted in Fig. 2.

According to calculations by Howells and others,$^{4)}$ the value of $N(z)$ is theoretically given by the following formula :

When there is no center of symmetry in the crystal :

$$N_{(Z)} = 1 - \exp(-Z) \qquad \exp = \text{exponential function}^{a)}$$

When there is a center of symmetry in the crystal :

$$N_{(Z)} = \operatorname{erf}\left(\frac{1}{2}Z\right)^{1/2} \qquad \operatorname{erf} = \text{error function}^{b)}$$

Fig. 2 is a graph showing both determined values and theoretical curve, and the values determined clearly demonstrate the presence of the center of symmetry.

Therefore, space group is determined as $C_i^1-P\bar{1}$.

[*4] Part III. (*loc. cit.*). d_4^{13} 1.5665.

4) E. R. Howells, D. C. Phillips, D. Rogers : Acta Cryst., **3**, 210(1950).

(a) $\exp(-Z)=e^{-Z}$. (b) $\operatorname{erf}\left(\frac{1}{2}Z\right)^{1/2}=\frac{2}{\sqrt{\pi}}\int_0^{(\frac{1}{2}z)^{1/2}} e^{-y^2}dy$.

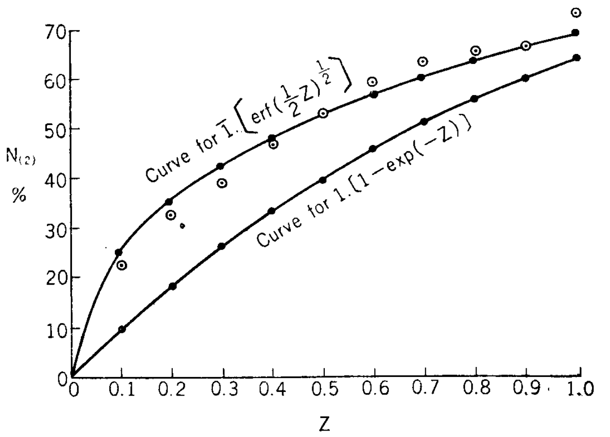


Fig. 2. Intensity Distribution for [*hko*] Zone

2. Calculation of Projection of Patterson Function

Equivalent positions of $C_i^1-P\bar{1}$ are as follows:

General equivalent position: $2i,\ x,\ y,\ z,\ \bar{x},\ \bar{y},\ \bar{z}$

Besides these, there are 8 sets of special positions like o, o, o. These sets are illustrated in Fig. 3.[5]

Therefore, taking the most common case and assuming that all atoms are present in the general positions, it would be necessary to determine a total of 99 parameters, even if the position of hydrogen atoms is to be disregarded.

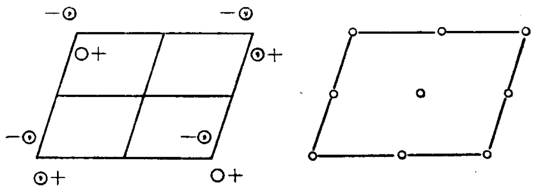


Fig. 3. Space Group $P\bar{1}(C_i^1)$

Such complete analysis is extremely difficult and, therefore, in order to obtain some information about the crystal structure, projection of Patterson function, $P(UV)$,[6] towards c axis of the shortest period was calculated according to the following formula:

$$P(UV)=\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}|F(hko)|^2\cos 2\pi(hU+kV)$$

For the calculation, Beevers–Lipson strips[7] were used, the period of unit cells was each divided into 60 equal parts, and calculation made with each part. Results are shown in Fig. 4.

As is well known, the Patterson map gives informations on the distribution of interatomic vectors in the crystal and the height of peaks in the Patterson function are proportional to the product of atomic numbers of atoms present at both ends of the corresponding interatomic vectors. Therefore, in substances like the present one in which the crystal consists of Ca, Al, C, N, and O(H), the main interatomic vectors would be vectors between Ca–Ca, Ca–Al, Ca–C(N,O), and Al–(C,N,O). The interatomic vectors appearing especially around the origin are known to give the arrangement of light atoms around Al or Ca atom.[8]

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[5] "International Tables for X-Ray Crystallography," 75(1952).

[6] A.L. Patterson: Z. Krist., **90**, 517(1935).

[7] H. Lipson, C.A. Beevers: Proc. Phys. Soc., **48**, 772(1936).

[8] Y. Saito, H. Kuroya: "Jikken Kagaku Koza" (Experimental Chemistry), **11**, 148(1956), Maruzen Co., Tokyo.

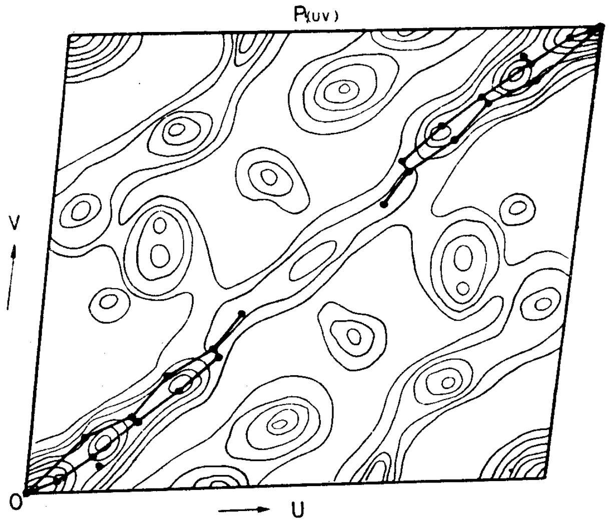

Fig. 4.
Patterson Projection P(UV)

The marked feature in Fig. 4 is the presence of several ranges of maxima parallel to the direction diagonal to the unit cell and passing through the origin. This suggests that a planar molecule is arranged approximately perpendicular to the plane of projection and parallel to each other. Based on these results, the shape of alumino-*p*-aminosalicylic acid complex ion that would explain the Patterson map to the best degree was presumed.

In making this presumption, the use was made of the shape of *p*-aminosalicylic acid molecule which had already been clarified by Bertinotti and others[9] from crystal-structure analysis.

Accordingly, the shape of the complex ion shown in Fig. 5 was postulated in which the two molecules of *p*-aminosalicylic acid are co-ordinated in a coplanar position to aluminum, and water molecule and oxygen atom of OH are coordinated above and below the aluminum atom.

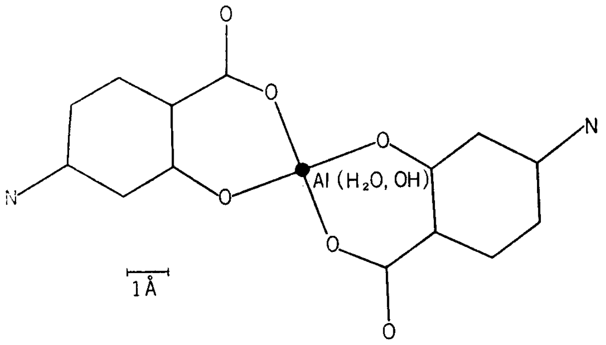

Fig. 5. A Schematic Drawing of the Complex Ion $[Al(OH)(OH_2)(C_7H_5O_3N)_2]^{2-}$

The shape of molecule indicated in Fig. 5 seems as if it had a center of symmetry, but because OH and H_2O are coordinated to aluminum, the molecule as a whole lacks the center of symmetry, and this shape would not in any way be inconsistent with the conclusion drawn from examination of the Raman effect and the infrared spectrum. Possibility of a *cis*-type was also examined but it was found that a *trans*-type more rationally explained the Patterson map and, therefore, the *trans*-type was adopted. However, this does not entirely exclude the possibility of a *cis*-type since the analysis was not made completely.

If this complex ion were to be assumed, as indicated in Fig. 4, to take the position with molecular plane inclined approximately 82~83° to the plane of projection and with

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[9] F. Bertinotti, G. Giacomello, A. M. Liquori: Acta Cryst., **7**, 808(1954).

its long axis parallel to the plane of the paper, it would be possible to make a rational explanation of interatomic vectors from aluminum to other atoms to a fair extent.

Moreover, such an arrangement was found to be plausible if the Van der Waals radius of each atom is taken into consideration.

The foregoing conclusion is not strictly final, since a complete analysis of the crystal structure has not been made as yet but it is considered to give approximate features of the crystal structure. It is therefore presumed that the molecule has a plane structure, the crystal is ionic, and is composed of Ca^{2+} ion and the above-mentioned complex ion, $\left[(C_7H_5O_3N)_2Al\genfrac{}{}{0pt}{}{OH}{OH_2}\right]^{2-}$. The calcium ion is present between the complex ion layers distributed in the direction diagonal to the unit cell and the crystal is constituted by their mutual static force of attraction. Crystal water would be distributed among these ions and are stabilizing the crystal.

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Summary

Structural determination of the newly synthesized calcium alumino-*p*-aminosalicylate was not sufficiently made through chemical means and X-ray crystallographic studies were carried out. By taking oscillation and Weissenberg photographs, size of unit cells and space groups were determined. X-Ray method of calculating the molecular weight from unit cells gave values agreeing with a heptahydrate. Space group was $C_i^1-P\bar{1}$, which indicated the presence of a center of symmetry in the crystal but complete analysis of crystal structure was extremely difficult and, therefore, in order to obtain some information of atomic arrangement in the crystal, projection of Patterson function towards the *c* axis (the shortest period) was made.

Closer examination of the Patterson map, combined with packing considerations, revealed that a planar complex ion is possibly arranged parallel in the direction diagonal to the projected unit cell and inclined approximately 82~83° from the plane of projection.

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