P_1	T	T_2	T_3	Mean value
A	7.234	7.231	7.245	7.237

Summary

Crystal water and dissociation vapor pressure of the hydrates of alumino-*p*-aminosalicylic acid and calcium alumino-*p*-aminosalicylate were measured. Measurement of loss in weight showed that there are three moles of crystal water in Al-PAS and seven moles in Al-PAS-Ca. Thermobalance method showed that a pentahydrate of Al-PAS-Ca would be present besides the heptahydrate. Al-PAS is labile above 140° and undergoes decomposition but Al-PAS-Ca was found to be comparatively stable even at 180°.

Dissociation vapor pressure of the heptahydrate of Al-PAS-Ca was measured and heat of dissociation at around room temperature was calculated. Stability of these complex compounds in the air was also examined.

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137. **Kyoji Hayano and Sataro Imado**: Studies on Aluminum Complex Compound of PAS. III.[*2] On the Structure of Alumino-*p*-amimosalicylic Acid and its Calcium Salt.

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Syntheses and determination of crystal water in alumino-*p*-aminosalicylic acid[*3] (hereinafter abbreviated as Al-PAS) and its calcium salt (hereinafter abbreviated as Al-PAS-Ca) were described in the preceding two papers. Structural studies were then carried out on Al-PAS-Ca which are described herein.

Single crystal of Al-PAS-Ca of the size necessary for structural studies was successfully prepared and with this crystal, morphological and optical studies were carried out. Examination was then made for the presence of a center of symmetry in the molecule which would be necessary in finding the structure of Al-PAS-Ca. As one of the methods for examining the center of symmetry, infrared absorption spectrum and Raman effect of Al-PAS-Ca were meaured. Since all the Raman lines were found to be infrared active, it was concluded that there is no center of symmetry in the Al-PAS-Ca molecule.

1. Preparation of Single Crystal Sample

Al-PAS-Ca dissolves in water at room temperature at the rate of only 0.7~0.8 g. per 100 g. and heating of this mixture results in partial decomposition. Therefore, recrystallization from water is not desirable while the salt is extremely sparingly soluble in various organic solvents, and it is very difficult to obtain a well-developed, translucent single crystal suitable for crystallomorphological studies by the usual method. Various measures were tried and the following method gave the best result.

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

[*2] Part II : This Bulletin, 7, 761(1959).

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

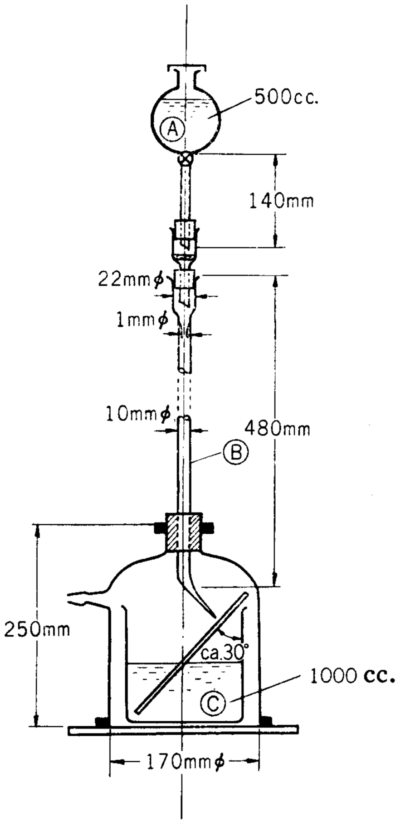

Fig. 1.
Apparatus for Preparation
of Single Crystal of
$Ca\left[(C_7H_5O_3N)_2Al{\genfrac{}{}{0pt}{}{OH}{OH_2}}\right]\cdot 7H_2O$

i) First Method: Rough diagram of the apparatus is shown in Fig. 1. A is a dropping funnel connected through a sintered glass filter to a glass tube B, whose tip is extended into a capillary. C is a beaker of ca. 1000-cc. capacity and a glass plate of ca. 70 mm. in width and ca. 200 mm. in length is placed in it, slanted at an angle of ca. 60° to the water level. In this C, 400 cc. of a 0.05% aqueous solution of ammonium alumino-*p*-aminosalicylate is placed and 400 cc. of 1.4% aqueous solution of calcium chloride is dropped from A, at the rate of one drop per 30 seconds, through the bottom capillary onto the glass plate. After about 3 days, translucent crystals will begin to separate out on the glass plate immersed in the solution. After one week, the crystals precipitaing out on the surface of solution, wall of the vessel, and on glass plate are all collected and stored in a glass bottle.

ii) Second Method: In a 500-cc. beaker, 400 cc. of a 0.05% aqueous solution of ammonium alumino-*p*-aminosalicylate is placed and a bag of fish skin containing calcium chloride solution (7.4 g. of $CaCl_2 \cdot 2H_2O$ dissolved in 50 cc. of water) is suspended in this solution. This is allowed to stand for 1~2 weeks by which crystals will precipitate out on the internal and outer surfaces of the fish-skin bag.

A single crystal, obtained by either of these methods, will have grown to the size of 2 mm. in length and 0.5 mm. in both width and thickness. These crystals become opaque by losing a part of crystal water when left in a dry room for a long time but can be maintained in a stable state if stored in a closely stoppered glass bottle or painted with a small amount of vaselin on the crystal surface.

2. Crystallomorphological and Optical Characteristics

The single crystal obtained by the foregoing methods was examined for crystallomorphological and optical characteristics. A single crystal of Al-PAS-Ca is shown in Fig. 2, and Fig. 3 shows the ideal form of crystal obtained from microscopic measurement.

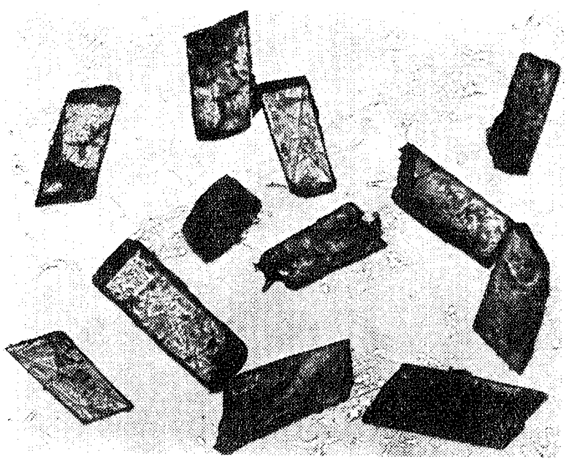

Fig. 2. Single Crystal of (×25)
$Ca\left\{(C_7H_5O_3N)_2Al\begin{matrix}OH\\OH_2\end{matrix}\right\}\cdot 7H_2O$

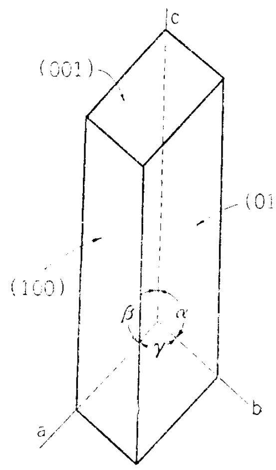

Fig. 3. Single Crystal of
$Ca\left\{(C_7H_5O_3N)_2Al\begin{matrix}OH\\OH_2\end{matrix}\right\}\cdot 7H_2O$

This crystal belongs to the triclinic system and possesses a center of symmetry, so that it is in the triclinic holohedral class (*Ci*-i).

The facial angles were measured and the principal axes were selected as indicated in Fig. 3. Axial angles were : $\alpha=92.5^\circ\pm3^\circ$, $\beta=116.0^\circ\pm3^\circ$, $\gamma=81.0^\circ\pm3^\circ$.

The direction of optical elastic axis in this crystal is a rectangular extinction to the outer surface. Cleavage is well developed and cleaved surface is perfect. After cleavage, the crystal becomes flat.

Index of refraction was measured with a cleaved piece, under the microscope, using a mixture of bromoform and bromonaphthalene for immesion. The observed index of refraction : $\alpha'=1.648$, $\gamma'=1.656$, $\gamma'-\alpha'=0.008$.

3. Specific Gravity of Al-PAS-Ca Crystal

Specific gravity of Al-PAS-Ca crystal was measured by a pycnometer with xylene and the value obtained was d_4^{13} 1.5665.

4. Infrared Absorption Spectrum of Al-PAS-Ca*4

In order to study the chemical structure of Al-PAS-Ca, infrared spectral measurement was carried out. It seemed significant to make comparative examination of infrared spectra of other PAS compounds and, therefore, the spectra of PAS-Na (I), basic PAS-Ca (II), and Al-PAS (IV and V) were measured for comparative discussion with the chemical structure of Al-PAS-Ca (III), which are shown in Fig. 4. The assignment for these compounds are listed in Table I.

It will be seen from Table I that there is no fundamental difference in the infrared absorptions of PAS-Na, basic PAS-Ca, Al-PAS-Ca, and Al-PAS, each absorption being in the same position. However, intensity of each absorption is not constant, ν_{C-O} of $CO-O^-$ being the strongest in PAS-Na and weakest in the aluminum salt.

These facts suggest that there is no structural change in PAS-Na, basic PAS-Ca, Al-PAS-Ca, and Al-PAS from that of PAS, and structural difference is limited to their salts.

All compounds exhibit absorptions due to crystal water and hydroxyl in the 3-μ region but these could not be assigned and are omitted from this discussion.

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*4 The infrared spectra were measured by Perking-Elmer Model-21 spectrometer.

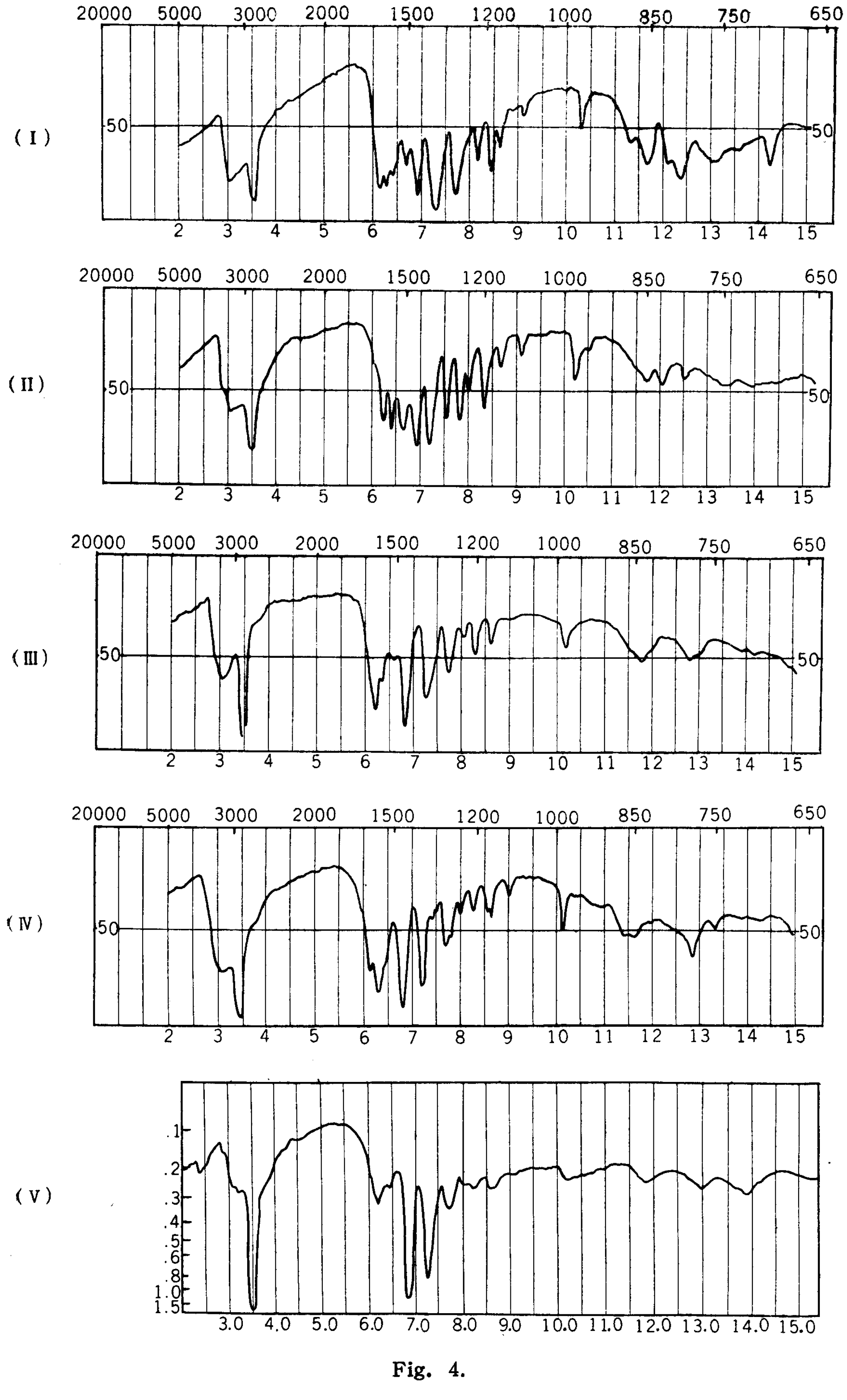
(I)
20000
5000
3000
2000
1500
1200
1000
850
750
650
50
2
3
4
5
6
7
8
9
10
11
12
13
14
15
(II)
(III)
(IV)
(V)
.1
.2
.3
.4
.5
.6
.8
1.0
1.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0

Fig. 4.

Table I. Infrared Absorption Data (μ)

Compd. / Assignment	PAS-Na (I)	Basic PAS-Ca (I)	Al-PAS-Ca (III)	Al-PAS·$6H_2O$ (VI)	Al-PAS·$3H_2O$ (V)
ν_{C-C} of aromatic ring	6.15	6.05	6.15	6.13	6.11
δ_{NH_2}	6.27	6.25	6.24	6.30	6.20
ν_{C-O} of carboxylate ion	6.45	6.39	6.37	6.42	6.35 6.45
Aromatic ring	6.69	6.65	6.66		
Nujol and aromatic ring	6.92	6.93	6.85	6.80	6.85
Nujol and aromatic ring	7.28	7.13	7.27	7.20	7.20
δOH of phenol	7.35	7.55	7.40	7.40 7.50	7.44
ν_{C-O} of carboxylate ion	7.70	7.82	7.75	7.70	7.68
ν_{C-N} of aromatic NH_2	8.16	8.00	8.05	8.00	8.00
ν_{C-O} of phenolic OH	8.44	8.34	8.30	8.27	8.20
Aromatic ring	8.61	8.67	8.63	8.55	8.55
Aromatic ring	9.11	9.07	9.05	9.02	9.05

6.0～9.0 μ region, NaCl prism. Sample : Nujol mull.

5. Raman Spectrum of Al-PAS Complex Ion*[5]

As stated in Section 2, the crystal of Al-PAS-Ca belongs to the triclinic system, *Ci*-i, and possesses a center of symmetry, but it is not possible to conclude from these facts alone whether the molecular structure has a center of symmetry or not. Therefore, examination of this point was made through Raman effect and infrared absorption spectrum.

Selection rules are entirely different for Raman effect and infrared absorption. The vibration that changes the dipole moment of the molecule becomes active to infrared ray and the vibration that changes polarizability becomes active to Raman effect. In

Table II. Raman and Infrared Spectra of $(NH_4)_2\left[(C_7H_5O_3N)_2Al_{OH_2}^{OH}\right]$ and $Ca\left[(C_7H_5O_3N)_2Al_{OH_2}^{OH}\right]\cdot 7H_2O$

Raman spectrum of ammonium salt		Infrared spectrum of calcium salt	
Wave no. (cm^{-1})	Relative intensity	Wave no. (cm^{-1})	Relative intensity
627	vw, S	669	vw,
661	vw, S	720	w,
769	w, B	768	w, sh
870	w, B	781	s, B
990	vw, B	850	s, B
1042	vw, B	863	w, sh
1151	vw, B	986	s,
1210	w, S	1113	vw,
1250	m, S	1160	s,
1293	m, S	1204	s,
1345	s, S	1242	m,
1369	s, S	1288	s,
1390	s, S	1363	s,
1460	m, S	1513	w,
1495	m, S	1570	w,
1570	m, S	1605	s,
1615	m, S	1652	w, sh
1667	w, S	1660	w, sh
3475	m, S	2873	s,
		3250	s, B

Exciting line=Hg 4358 Å; w=weak; m=medium; s=strong; v=very; S=sharp; B=broad; sh=shoulder.

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*[5] The Raman spectra were measured by Yukigosei Raman spectrograph Type RL-II.

a molecule with center of symmetry, vibration symmetrical to the center would be Raman active but inactive to infrared ray, while antisymmetric vibration would be Raman inactive but active to infrared ray. Inversely, if the same frequency was observed in both Raman and infrared spectra, it may be concluded that the molecule does not possess a center of symmetry. The Raman and infrared absorption spectra of Al-PAS complex ion are shown in Table II. It will be clear from this table that the same frequency is detected in these spectra and this fact indicates that there is no center of symmetry in this complex ion.

In the Al-PAS complex ion, PAS molecules would take either the *cis* or *trans* configuration. In a *cis*-configuration, the PAS molecules would be coordinated to the central aluminum atom in such a way to have no center of symmetry, as indicated in Fig. 5(I), while a *trans*-configuration would give the PAS molecules coordinated to the central atom in perfect symmetry. Even in the latter case, there would be no center of symmetry since the ligands OH and H_2O would be coordinated above and below the central atom.

It is therefore impossible to determine whether this complex ion takes the *cis*- or *trans*-configuration but the fact that it does not possess a center of symmetry in either case agrees with the result of Raman and infrared spectral measurements. Molecular structure of Al-PAS-Ca and the fact that it has a plane structure will be described in a subsequent paper.

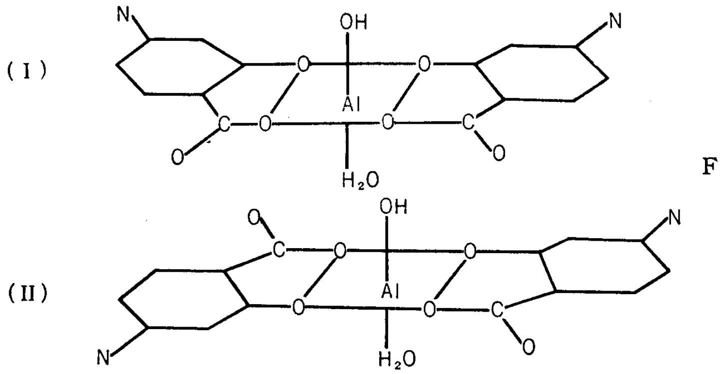

Fig. 5.

Since Al-PAS-Ca is sparingly soluble in water, 40~50% aqueous solution of ammonium salt, freshly prepared from Al-PAS, was used as a sample in taking the Raman spectrum. This solution had a faint browish tint and, therefore, saturated aqueous solution of sodium nitrite was used as a filter to eliminate the line of mercury. The width of the slit was 0.05 mm. and exposure was 10 hours.

Summary

In order to elucidate chemical structure of alumino-*p*-aminosalicylic acid, single crystal of calcium alumino-*p*-aminosalicylate was prepared and its crystallomorphological and optical characteristics were examined. Examination of the presence or absence of the center of symmetry in this salt molecule was made through infrared absorption spectrum and Raman effect. Presence of the spectra with the same frequency in the Raman and infrared spectral measurements indicated the absence of a center of symmetry in the molecule of alumino-*p*-aminosalicylic acid.

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