with the flame spectrophotometric analyses for sodium, and Dr Torsten Lundström, Department of Chemistry, University of Uppsala, who made the piezo-electric tests. This work has been sponsored in part by the *Air Force Office of Scientific Research of the ARDC, USAF*, through its European Office on contract number AF 61(052)−162. The English text has been revised by Mr Donald Gillam.

1. Kohlschütter, H. W. and Hantelmann, P. *Z. anorg. allgem. Chem.* **248** (1941) 319.
2. Brosset, C., Biedermann, G. and Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 1917.
3. Shishniashvili, M. E., Kargin, V. A. and Batsanadze, A. L. *Zhur. fiz. Khim.* **21** (1947) 391.
4. Denk, G. and Bauer, L. *Z. anorg. allgem. Chem.* **267** (1951) 89.
5. Bassett, H. and Goodwin, T. H. *J. Chem. Soc.* **1949** 2239.
6. Denk, G. and Alt, J. *Z. anorg. allgem. Chem.* **269** (1952) 244.
7. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*, 3rd ed., Macmillan, New York 1952, p. 717.
8. *International Tables for X-ray Crystallography*, Vol. 1, The Kynoch Press, Birmingham 1952.
9. Johansson, G. *Acta Chem. Scand.* **14** (1960) 771.

Received March 28, 1960.

On the Crystal Structures of Some Basic Aluminium Salts

GEORG JOHANSSON

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A., Department of Inorganic Chemistry, The Royal Institute of Technology, Stockholm 70, Sweden

An aluminium chloride solution can be hydrolyzed by the addition of about 2.5 equivalents of alkali without the formation of a permanent precipitate of aluminium hydroxide. The addition of a suitable anion to this hydrolyzed solution precipitates basic salts, the structures of which are of a special interest since they might give some information about the polynuclear complexes that seem to exist in hydrolyzed aluminium salt solutions [1,2]. The structures of a number of them are being investigated and preliminary results of some of the structure determinations are given in this paper.

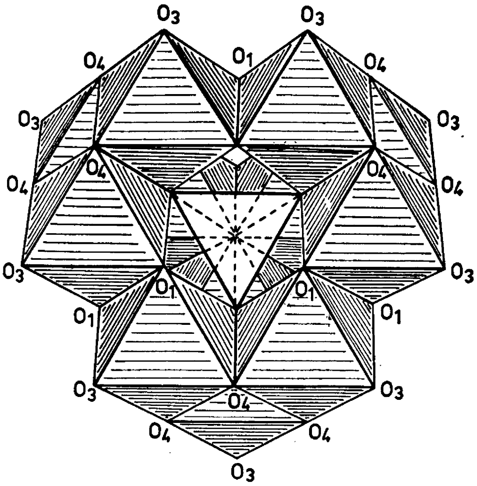

Fig. 1. The $Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$-ion. The drawing shows how the twelve AlO_6-octahedra are joined together by means of common edges. The tetrahedron of oxygen (O_2) atoms in the center of the group contains the 4-coordinated Al-atom.

If the aluminium chloride solution is hydrolyzed by sodium hydroxide and sodium selenate is added, tetrahedral crystals can be obtained, which, when dried in air, have the composition $Na_2O \cdot 13Al_2O_3 \cdot 8SeO_3 \cdot xH_2O$ (with x in this case equal to about 74, *cf.* Ref.[3]. The crystals are cubic, with $a_0 = 18.0$ Å and with two formula weights in the unit cell. The space group is $T_d^2 - F\bar{4}3m$. Three-dimensional intensity data have been collected with Cu*Kα*-radiation. The structure has been solved from the tree-dimensional Patterson function and refined by means of three-dimensional Fourier maps *. At the present stage of the refinement the reliability index, R, is 0.11 for the 245 observed reflections, but the positions of the sodium atoms are still uncertain. The parameters are:

---

* All calculations were carried out on a Burroughs 205 computer at the California Institute of Technology.

Atom	Position	Positional parameters
48 Al_1	48(h)	$x = 0.057$ $z = 0.328$
4 Al_2	4(b)	—
48 O_1	48(h)	$x = 0.047$ $z = 0.677$
16 O_2	16(e)	$x = 0.441$
48 O_3	48(h)	$x = 0.069$ $z = 0.223$
48 O_4	48(h)	$x = 0.158$ $z = 0.447$
16 Se	16(e)	$x = 0.882$
48 O_5	48(h)	$x = 0.138$ $z = 0.968$
16 O_6	16(e)	$x = 0.828$
16 O_7	16(e)	$x = 0.663$
12 O_8	16(e)	$x = 0.190$
24 O_9	24(g)	$z = 0.960$

The structure is built up from discrete aluminium-oxygen groups (Fig. 1) each containing 12 AlO_6 octahedra sharing O_1-O_1 and O_2-O_4 edges, and with an additional aluminium atom in the center of a tetrahedron of O_2 atoms. These large groups,which have the composition $Al_{13}O_{40}$, are not directly connected but are joined to the selenate groups by means of hydrogen bonds between O_3 of an aluminium-oxygen group and O_5 of a SeO_4 group. If the hydrogen atoms are located from the positions of hydrogen bonds and from Pauling's rule for the sum of the electrostatic bond strengths, the formula for the discrete aluminium-oxygen complexes seems to be $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. The formula for the basic salt now being considered should then be written $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SeO_4)_4 \cdot 13H_2O$. It is interesting to note that both the rings of six AlO_6 octahedra, that can be distinguished in the hydrargillite structure, and the groups of three octahedra which, linked together by common edges and corners, build up the diaspore and boehmite structures, can also be seen in the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$-groups (Fig. 1).

If the aluminium chloride solution is hydrolyzed with ammonia and ammonium sulfate is added to a high concentration, tetrahedral crystals of another kind can be obtained. They were first described by Bassett and Goodwin[4] who gave them the formula $6(NH_4)_2SO_4 . 11Al_2O_3 . 6SO_3 . xH_2O$ (x = ca 72). The crystals are tetragonal with Laue symmetry $4/m$ and have the same kind of reflections systematically absent as the basic selenate. If a face centered unit cell is chosen the cell dimensions are $a = b = 19.8$ Å and $c = 19.6$ Å as determined from precession and Weissenberg photographs. The density is 1.86 g/cm³. According to these results and the analysis data given by Bassett and Goodwin[4] the following number of atoms should be present in the unit cell: Al: 52 (51.4), S: 28 (27.9), NH_4^+: 28 (28.0). The formula may therefore be written $(NH_4)_7[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_7 . xH_2O$. The similarities to the basic selenate seem to be an indication that the same kind of discrete aluminium-oxygen groups are present in both compounds.

A monoclinic basic aluminium sulfate forming plate-like crystals also seems to be built up from the same kind of aluminium-oxygen complexes. It can be obtained from dilute hydrolyzed aluminium chloride solutions by the addition of sodium sulfate (for example from solutions that are about 0.01 M in Al^{3+} and 0.03 M in SO_4^{2-}). The composition is $13Al_2O_3 \cdot 6SO_3 \cdot xH_2O$ (x = ca 79) and the crystals seem to be identical with the compound $13Al_2O_3 \cdot 6SO_3 \cdot xH_2O$ described by Bassett and Goodwin[4]. The space group is C_{2h}^4 or C_s^2, with the intensity distribution favouring the centrosymmetric C_{2h}^4. The unit cell dimensions are: $a = 20.2$ Å, $b = 11.5$ Å, $c = 25.0$ Å, $\beta = 103°$ (symmetry $P2/a$ or Pa) but the crystals can also occur in a form with a unit cell of only half this size, with $a = 14.2$ Å, $b = 11.5$ Å, $c = 17.7$ Å, $\beta = 102.3°$ (symmetry $P2/n$ or Pn). This, however, can spontaneously switch over to the larger unit cell without any noticeable changes in the appearance of the crystal or of the sharpness of the spots on the Weissenberg photographs. Three-dimensional intensity data have been collected with Cu*Ka* radiation from the crystals containing the smaller unit cell. About 3 200 reflections were observed. The three-dimensional Patterson function could be interpreted by assuming two aluminium-oxygen complexes similar to those in the basic selenate to be present in the unit cell according to the symmetry *P*2/*n*. Three dimensional Fourier maps seem to confirm this assumption and also reveal the positions of four of the sulfate groups in a fourfold position; the remaining two sulfate groups, however, are apparently statistically distributed over two positions close to a center of symmetry in the unit cell. This result in connection with the fact that for some of the zonal data, for example the *h*3*l*-reflections, the intensity distribution is closer to one expected for a noncentrosymmetric space group seems to indicate the presence of small deviations from a centrosymmetric arrangement. The space group should then be *Pn* rather than *P*2/*n*. The refinement of the structure will be continued according to this space group.

The reliability index, *R*, assuming the space group to be *P*2/*n*, is at the present stage of the refinement 0.24 for all observed reflections. The parameters for the aluminium atoms in the aluminium-oxygen complexes are:

Atom	Parameters		
	x	*y*	*z*
4 Al_1:	0.338	0.980	0.220
4 Al_2:	0.482	0.796	0.267
4 Al_3:	0.137	0.795	0.390
4 Al_4:	0.307	0.437	0.329
4 Al_5:	0.276	0.620	0.437
4 Al_6:	0.453	0.619	0.375
2 Al_7:	1/4	0.705	1/4

Fellowships from the *Corning Glass Works Foundation* and from the *Sweden-America Foundation* in support of part of this work is gratefully acknowledged.

1. Brosset, C., Biedermann, G. and Sillén, L. G. *Acta Chem. Scand.* **8** (1954) 1917.
2. Kohlschütter, H. W. and Hantelmann, P. *Z. anorg. allgem. Chem.* **248** (1941) 319.
3. Johansson, G., Lundgren, G., Sillén, L. G. and Söderquist, R. *Acta Chem. Scand.* **14** (1960) 769.
4. Bassett, H. and Goodwin, T. H. *J. Chem. Soc.* **1949** 2239.

Received March 28, 1960.

On Observable Discontinuities and Coherence in the Kinetics of Enzymically Reacting Systems. A Misprint

J. A. CHRISTIANSEN

Sundvænget 9, Hellerup, Denmark

The following misprint in my paper in this volume p. 107 should be corrected: The sequence (A) should read

$$\begin{array}{lll} B_1 + X_1 \rightleftharpoons X_2 + A_2 & (\pm 1) & \\ B_2 + X_2 \rightleftharpoons X_3 + A_3 & (\pm 2) & (A) \\ B_3 + X_3 \rightleftharpoons X_1 + A_1 & (\pm 3) & \end{array}$$

X_1, X_2 and X_3 being three different forms, or compounds with the substrates (B_i, A_i), of the enzyme. The plus signs mean the reactions in the direction from left to right, the minus signs indicating reactions in the opposite direction.

Received March 30, 1960.

Free Butyric Acid as a Possible Source of Off-Flavour of the Cow's Milk After Administration of Oestrogens

TORLEIV LUNAAS

Department of Sexual Physiology and Sexual Pathology, Veterinary College of Norway, Oslo, Norway

During investigations on the metabolism of oestrogens in the cow undertaken at this department[1] peculiar alterations of the milk after parenteral administration of the hormones were repeatedly observed [2]. To further explore the nature of these alterations 10 mg oestradiol-17β in 5 ml propyleneglycol was injected intramusculary to a non-pregnant cow producing 8 liters milk a day. Daily milk samples were frozen on the day of drawing and analysed in series immediately after thawing.

On the week after injection the milk produced per day gradually decreased to