

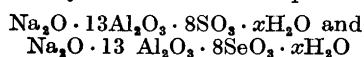
On the Crystal Structure of a Basic Aluminium Sulfate and the Corresponding Selenate

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Solutions of aluminium chloride can be hydrolyzed by the addition of about 2.5 equivalents of alkali before a permanent precipitate of aluminium hydroxide is formed. The pH of the solution is then still < 7 . Measurements of diffusion and freezing point depression seemed to indicate that such hydrolyzed solutions contain polynuclear complexes which may be built up from about six aluminium atoms¹. Similar conclusions have been drawn from results of pH-measurements in hydrolyzed aluminium perchlorate solutions².

Now, the addition of sulfate ions to aged solutions having an Al:OH ratio of about 1:2.5 results in a precipitation of basic aluminium sulfates³⁻⁵ which, under suitable conditions, can be obtained in a well-crystallized form⁶. Since the atomic arrangement in the crystals might give some information about the polynuclear complexes in the solution, an X-ray investigation on the structure of the crystals was initiated. This paper contains some preliminary results on the compounds



with x apparently varying between 76 and 68. The sulfate has previously been described by formulae which can be written as " $(\text{Al}_2(\text{OH})_6)_n\text{SO}_4$ "^{3,4,6} but the present

investigation has shown that alkali metal ions are an essential constituent of the salts.

The crystals were prepared in the following way: An aluminium chloride solution was heated to 80°C and hydrolyzed by adding about 2.5 equivalents of sodium hydroxide. The solution was then kept at 80°C for about 30 min, after which the basic salts could be precipitated by the addition of sodium sulfate or selenate solutions. If the aluminium concentration was low (approximately 0.01–0.1 M) and the sulfate or selenate was added in excess, then the crystallization was slow and tetrahedral crystals, large enough for single crystal X-ray work, were formed after a few days.

For the analyses, crystalline samples dried in air were dissolved in dilute hydrochloric acid. Aluminium was determined by precipitation with 8-hydroxyquinoline. Sodium was precipitated and weighed as sodium magnesium uranyl acetate. The amount of sodium was also determined independently with a flame spectrophotometer using solutions containing known amounts of sodium, aluminium and sulfate as standards. Sulfate was precipitated and weighed as BaSO₄ or titrated with standard sodium hydroxide after passing the solution through a hydrogen-saturated cation exchange column. The selenate ions were reduced with sulfur dioxide and weighed as Se. In the sulfate compound, the water was determined by Hartwig-Bendig's modification of Brush and Penfield's method as described by Kolthoff and Sandell⁷ but no independent analysis of the water content was made for the selenate compound.

A test for chloride in the crystals was negative ($< 0.01\%$).

The densities of the crystals were determined by a flotation method (for the sulfate) and by the displacement of benzene (for the sulfate) or of carbon tetrachloride (for the selenate).

The results of the analysis were as follows:

	$\text{Na}_2\text{O} \cdot 13\text{Al}_2\text{O}_3 \cdot 8\text{SO}_3 \cdot x\text{H}_2\text{O}$			$\text{Na}_2\text{O} \cdot 13\text{Al}_2\text{O}_3 \cdot 8\text{SeO}_3 \cdot x\text{H}_2\text{O}$		
	obs. %	$x = 76$ calc. %	$x = 68$ calc. %	obs. %	$x = 76$ calc. %	$x = 68$ calc. %
Al ₂ O ₃ :	38.7	39.02	40.75	35.8	35.14	36.53
SO ₃ (SeO ₃):	18.5	18.86	19.69	27.1	26.92	27.99
Na ₂ O:	1.6	1.82	1.90	1.5	1.64	1.71
H ₂ O:	40.5	40.30	37.66	35.6	36.30	33.77
				(diff).		
	1.97	1.97	1.88	2.11	2.15	2.07 g/ml

The water content of the sulfate crystals has been found to vary. When the crystals were dried in air at 25°C, the analyses (given above) indicated $x = 76$ but, when the crystals were dried, also at 25°C, in a desiccator over silica gel for a week, they gradually lost weight and attained a water content of 37.5 % corresponding to an x -value of 68 at the end of the drying period. Single crystals picked out from both products all gave apparently identical rotation (around [001]) and Weissenberg photographs ($hk0$, $hk1$). The crystal structure should consequently be the same for both products and some of the water molecules in the air-dried crystals must be zeolitic. When standing in moist air, the desiccator-dried product slowly took up water reversibly. The same phenomenon was also observed for the selenate.

When the preparations were dried over silica gel for a long period the water content continued to decrease slowly. After six weeks' drying, it corresponded to $x \approx 52$. However, the crystals broke and became opaque. The lines in the powder photographs were also broadened and indicated the formation of an X-ray amorphous product. This process seems to start in the neighbourhood of $x = 68$.

Crystals were set with [001] and [110] as rotation axes and rotation and Weissenberg photographs ($hk0-hk7$ (sulfate), $hk0-hk8$ (selenate) and $hhl-h, h+6, l$ (selenate)) were taken with CuK radiation. The crystals were found to be cubic with $a = 17.9 \pm 0.1 \text{ \AA}$ (sulfate) and $a = 18.0 \pm 0.1 \text{ \AA}$ (selenate). There are two formula weights in the unit cell, *i.e.* 4 Na, 52 Al, 16 S(Se) and about 264 to 280 O (as O, OH and H_2O).

Piezo-electric tests on the crystals were positive, indicating that the atomic arrangement lacks a centre of symmetry. This is also suggested by the tetrahedral shape of the crystals.

The crystals were found to be optically isotropic with a refractive index n_D^{20} of 1.495 (sulfate) and 1.514 (selenate).

The Laue symmetry is $m3m$. For the sulfate crystals, the reflections systematically absent are $h00$ with h odd which is characteristic⁸ only for the space group No. 208— $P4_232$. Moreover, all reflections with $h+k$, $h+l$, and $k+l = \text{odd}$ are weak. For the selenate crystals, these weak reflections could not be detected even on heavily exposed photographs and may be systematically absent. The selenate compound would then belong to one of the

space groups No. 209— $F432$, No. 216— $F43m$ or No. 225— $Fm3m$.⁹

Of these, No. 225 is not in accordance with the piezo-electric tests and No. 216 is the only one offering point positions that would allow the aluminium and selenium atoms to be situated in completely occupied, definite point positions.

The Patterson projections along [001] have been calculated and a survey of possible arrangements of AlO_4 -octahedra in accordance both with the Patterson projections and the space groups $P4_232$ (for the sulfate) and $F43m$ (for the selenate) has been made. However, using this information alone, the number of possible Al—O—frameworks is quite large. On the other hand, if we assume that the structure contains only one kind of discrete Al—O—OH— H_2O group, which the solution data seem to suggest, the number of possibilities can be reduced considerably. Thus, there are 52 aluminium atoms in the unit cell and the symmetry (pseudo-symmetry for the sulfate) of the atomic arrangement corresponds to a face-centered cubic cell. Since there are at least four crystallographically equivalent groups in an F -centered cell, there are at most $52/4 = 13$ aluminium atoms in each Al—O—OH— H_2O complex in the structure. But, with the assumption made, the number of aluminium atoms per complex ion could not be less than 13 since this is a prime number. The complexes with six aluminium atoms which have been proposed for perchlorate solutions^{1,2} do not thus seem to be present in these crystals which, instead, should contain $Al_{13}O_x(OH)_y(H_2O)_z$ groups.

A complete structure determination of one of the compounds thus seemed to be of interest and a determination of the structure of the selenate has been carried out by one of us (G.J.). The results of that investigation confirm our assumption of discrete groups with 13 aluminium atoms. The groups are, however, built up from twelve AlO_4 octahedra and one AlO_4 tetrahedron instead of 13 AlO_4 octahedra as was at first expected. The formula of the complex ions in the crystals seems to be $Al_{13}O_{40}H_{48}^{7+}$ or $[Al_{13}O_4(OH)_{24}(H_2O)_{13}]^{7+}$.

A detailed account of the results of the structure determination of the selenate will be published later⁹. Further studies on the sulfate are in progress (R.S.).

The authors wish to thank Dr Staffan Tengnér, Department of Analytical Chemistry, Royal Institute of Technology, for his help

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

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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

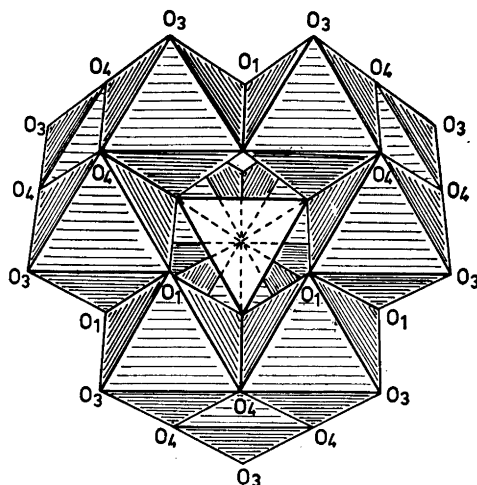


Fig. 1. The $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ -ion. The drawing shows how the twelve AlO_6 -octahedra are joined together by means of common edges. The tetrahedron of oxygen (O_2) atoms in the center of the group contains the 4-coordinated Al-atom.

of a number of them are being investigated and preliminary results of some of the structure determinations are given in this paper.

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 $\text{Na}_2\text{O} \cdot 13\text{Al}_2\text{O}_3 \cdot 8\text{SeO}_3 \cdot x\text{H}_2\text{O}$ (with x in this case equal to about 74, cf. Ref.³). The crystals are cubic, with $a_0 = 18.0 \text{ \AA}$ 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 $\text{CuK}\alpha$ -radiation. The structure has been solved from the three-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.