[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

Crystal-Chemical Studies of the Alums. II. The Purple Chrome Alums[1]

BY HAROLD P. KLUG

Up to the present about a dozen of the commoner alums, chiefly aluminum alums, have been studied by means of X-rays.[2-5] These studies have indicated that the various alums are not all isomorphous, but that at least three different alum structures exist. The structure of a particular alum is apparently dependent upon the size of the monovalent ion. The α structure is conditioned by medium-sized ions, the β structure by larger ones, and the γ structure by the smallest ions.[5]

In order to ascertain whether other alum structures exist, to gain more precise information concerning the conditions which determine the structure type, and to learn more of their crystal chemistry in general, a systematic study of the alums has been undertaken in this Laboratory. In this communication the results of a study of the lattice constants, densities (from X-ray data), and structure types of the purple chrome alums are reported.

Experimental

The potassium and ammonium chrome alums were the reagent grade salts of commerce, and were used without further purification. The remaining chrome alums were prepared by crystallization from solutions containing stoichiometric mixtures of the component simple sulfates. In the case of thallium alum an excess of chromic sulfate must be used to prevent the alum from being contaminated with excess thallous sulfate as observed in the preparation of thallium aluminum alum.[6] The crystals were removed from the mother liquor, washed successively with 50% aqueous alcohol, 95% alcohol, and ether, and then air dried. Except for the thallium alum their compositions were checked by analysis for chromium. The chromium was oxidized to chromate by ammonium persulfate, an excess of ferrous ammonium sulfate was then added, and the excess titrated with dichromate using diphenylamine sulfonate as an indicator according to the procedures of Hillebrand and Lundell,[7] and Kolthoff and Sandell.[8] In thallium alum the thallium content was checked by determination as thallous iodide according to the procedure of Hillebrand and Lundell.[9] Repeated attempts to prepare suitable crystals of the purple sodium chrome alum were all unsuccessful.

The X-ray technique was the same as described earlier,[1] except that CrK radiation was used. The densities were calculated in the usual way from the X-ray data on the basis of four molecules of the dodecahydrate formula per unit cell and the value 6.06×10^{23} for Avogadro's number.

The structure type was decided by calculating structure factors for the prism planes, (210), (230), (420), (610), and (620), first assuming the parameters of potassium aluminum alum[2] (α structure) and then assuming the parameters for cesium aluminum alum[5] (β structure), and finally comparing them with the observed intensities.[3]

Results

In Table I the structure types and lattice constants of the chrome alums are tabulated. The lattice constants are believed to be accurate to ±0.001 Å. Only the potassium alum has been measured previously, for which Lipson and Beevers[2] report 12.171 ± 0.002 Å., but, without indicating the temperature of their observation. Lipson,[5] likewise, reports it to have the α structure.

TABLE I

STRUCTURE TYPES AND LATTICE CONSTANTS OF THE PURPLE CHROME ALUMS

Alum	Structure type	Lattice constant in Å. at 25 ± 0.1°
$NH_4Cr(SO_4)_2 \cdot 12H_2O$	α	12.251 ± 0.001
$KCr(SO_4)_2 \cdot 12H_2O$	α	12.175 ± 0.001
$RbCr(SO_4)_2 \cdot 12H_2O$	β	12.256 ± 0.001
$CsCr(SO_4)_2 \cdot 12H_2O$	β	12.378 ± 0.001
$TlCr(SO_4)_2 \cdot 12H_2O$	β	12.238 ± 0.001
$NH_3CH_3Cr(SO_4)_2 \cdot 12H_2O$	β	12.516 ± 0.001

In Table II the densities of the chrome alums calculated from the X-ray data, together with previously reported density data, are tabulated.

TABLE II

DENSITY DATA FOR THE CHROME ALUMS

Alum	Density at 25° (from X-ray data)	Reported density 20°/4°[a]
NH_4	1.717	1.72
K	1.826	1.83
Rb	1.957	1.946
Cs	2.064	2.043
Tl	2.394	2.388
NH_3CH_3	1.658	...

[a] "International Critical Tables," Vol. I.

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(1) Paper I in this series appeared in THIS JOURNAL, **62**, 1492 (1940).

(2) Lipson and Beevers, *Proc. Roy. Soc.* (London), **148A**, 664 (1935).

(3) Lipson, *Phil. Mag.*, **19**, 887 (1935).

(4) Lipson, *Nature*, **135**, 912 (1935).

(5) Lipson, *Proc. Roy. Soc.* (London), **151A**, 347 (1935).

(6) Hill, Smith and Ricci, THIS JOURNAL, **62**, 858 (1940).

(7) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 410.

(8) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1936, p. 579.

(9) Ref. 7, p. 378.

TABLE III

COMPARATIVE DATA FOR THE ALUMINUM ALUMS AND Δa_0 FOR THE CHROME ALUMS

	Structure type (Al alums)	Lattice constant (Al alums), Å.	References	Δa_0 for the chrome alums, Å.
NH_4	α	12.215	(2) and (5)	0.038
K	α	12.133	(1) and (4)	.042
Rb	α	12.220	(2) and (5)	.036
Cs	β	12.330	(2) and (5)	.045
Tl	α	12.207	(2) and (5)	.031
NH_3CH_3	β	12.479	(3) and (4)	.037
			Average =	.038

In Table III are the lattice constants and structure types of the corresponding aluminum alums for comparison with the chrome alum data of Table I. It is interesting to note that the rubidium and thallium alums change structure type in passing from the aluminum alum to the chrome alum. Also the increase in lattice constant, Δa_0, is practically constant for the series in passing to the chrome alums, as might be expected. Pauling[10] reports for the radii of Cr^{+3} and Al^{+3}, 0.64 and 0.50 Å., respectively. This increase, therefore, is only about one-seventh of the difference in diameter, 0.28 Å., of a Cr^{+3} and an Al^{+3} ion, despite the fact that one Cr^{+3} ion is substituted for an Al^{+3} ion in the distance, a_0. In a purely ionic lattice, such as NaCl, the interionic distances are additive and substitution of a larger cation will bring about a corresponding increase in lattice constant. In complex structures, such as the alums, slight reorientations of the coördinated water molecules and of the sulfate groups apparently occur, resulting in a much smaller increase in lattice constant. Lipson[8] has pointed out that similar reorientations probably occur as the size of the monovalent ion increases, eventually bringing about change in structure type from α to β form. In the present case the reorientations brought about a change in structure type for the rubidium and thallium alums. Further discussion of this problem must await the accumulation of data for more of the alums.

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Summary

1. Lattice constants for a series of chrome alums have been determined at 25 ± 0.1°.

2. The densities of these alums at 25° have been calculated from the X-ray data.

3. The structure types of the alums have been determined. The ammonium and potassium chrome alums have the α-structure, while the remaining alums possess the β structure.

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[10] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1st ed., 1939, pp. 326, 330.

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Crystal-Chemical Studies of the Alums. III. Further Solid Solution Studies[1]

BY HAROLD P. KLUG AND LEROY ALEXANDER

In the systematic study of the crystal chemistry of the alums now in progress in this Laboratory, solid solution formation and conformity to Vegard's law[2] are being investigated. The results of a study of solid solutions of potassium and ammonium alums have already been presented.[3] Recently Hill, Smith and Ricci[4] reported their results of a chemical study of solid solution formation among some alum pairs. Through the kindness of Professor J. E. Ricci samples of their solid solutions were made available for this study. This communication presents such studies of the following alum pairs: $TlAl(SO_4)_2 \cdot 12H_2O$–$NH_4Al(SO_4)_2 \cdot 12H_2O$, $TlAl(SO_4)_2 \cdot 12H_2O$–$KAl(SO_4)_2 \cdot 12H_2O$, and $NH_4Cr(SO_4)_2 \cdot 12H_2O$–$KCr(SO_4)_2 \cdot 12H_2O$.

Experimental

For the preparation and chemical analysis of these solid solutions see reference 4. They were used without further analysis or treatment, and are referred to in this communication by the numbers given in the paper by Hill, Smith and Ricci.[4] The X-ray technique has been described earlier.[3] In addition to FeK radiation, CuK, and CrK radiations were used in this study, the latter for the chrome alum series. The appearance of the X-ray photographs served as a check on the composition of the solid solutions, dehydration resulting in the appearance of

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[1] Paper II in this series appeared in THIS JOURNAL, **62**, 2992 (1940).

[2] Vegard, *Z. Physik*, **5**, 17 (1921).

[3] Klug and Alexander, THIS JOURNAL, **62**, 1492 (1940).

[4] Hill, Smith and Ricci, *ibid.*, **62**, 858 (1940).