TABLE III

COMPARATIVE DATA FOR THE ALUMINUM ALUMS AND $\Delta a_0$ FOR THE CHROME ALUMS

| | Structure type (Al alums) | Lattice constant (Al alums), Å. | References | $\Delta a_0$ for the chrome alums, Å. |
|---|---|---|---|---|
| $NH_4$ | $\alpha$ | 12.215 | (2) and (5) | 0.038 |
| K | $\alpha$ | 12.133 | (1) and (4) | .042 |
| Rb | $\alpha$ | 12.220 | (2) and (5) | .036 |
| Cs | $\beta$ | 12.330 | (2) and (5) | .045 |
| Tl | $\alpha$ | 12.207 | (2) and (5) | .031 |
| $NH_3CH_3$ | $\beta$ | 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, $\Delta a_0$, 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[3] has pointed out that similar reorientations probably occur as the size of the monovalent ion increases, eventually bringing about change in structure type from $\alpha$ to $\beta$ 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.

The author wishes to thank Mr. Leroy Alexander for assistance with part of the analyses and calculations. He also wishes to acknowledge the aid of a grant from the Graduate School of the University of Minnesota.

## 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 $\alpha$-structure, while the remaining alums possess the $\beta$ 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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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

# 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).

a different X-ray diffraction pattern. Thus data from samples 2B and 4B of the chrome alum series had to be rejected because of partial dehydration of the samples.

In the system thallium alum–potassium alum, only two solid solutions were available, so the data are incomplete at one end of the diagram (see Fig. 1). The chrome alum series required an abnormally long time to reach equilibrium during formation.[4] This was thought possibly to be tied up with the equilibrium between the violet and green forms in solution.[5,6] Accordingly, where possible, crystals of both the A and B duplicate series were photographed to check on the possibility of differences in the coördination of the chromium in the final mixed alum, inasmuch as the crystals in the A series were formed from the potassium, and those in the B series from the ammonium chrome alum as the initial solid.

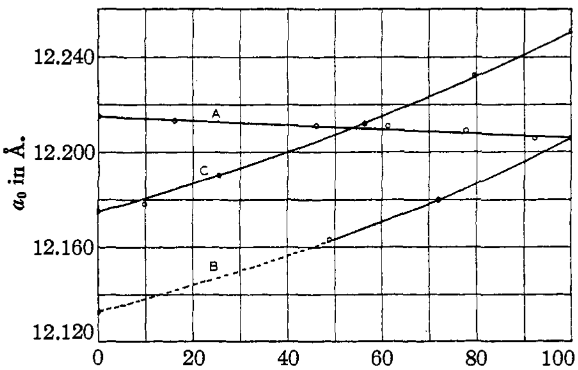

Fig. 1.—Lattice constants as a function of composition for solid solutions of alums; (A) thallium alum–ammonium alum, (B) thallium alum–potassium alum and (C) ammonium chrome alum–potassium chrome alum.

## Results

Data on the compositions of the pure alums and their solid solutions, and their lattice constants at 25°, are tabulated below for the various alum pairs. The results are also presented graphically in Fig. 1.

TABLE I

$TlAl(SO_4)_2 \cdot 12H_2O$–$NH_4Al(SO_4)_2 \cdot 12H_2O$

| Substance | Wt. % TlAl-$(SO_4)_2$[a] | Mole % $TlAl(SO_4)_2 \cdot 12H_2O$ | Lattice constant in Å. at 25 ± 0.1° |
|---|---|---|---|
| $NH_4Al(SO_4)_2 \cdot 12H_2O$ | 0 | 0 | 12.215 |
| 7A[a] | 14.17 | 16.18 | 12.213 |
| 5A | 36.27 | 46.20 | 12.211 |
| 4A | 45.62 | 61.11 | 12.211 |
| 3B | 55.03 | 77.74 | 12.209 |
| 2A | 62.53 | 92.35 | 12.206 |
| $TlAl(SO_4)_2 \cdot 12H_2O$ | 66.20 | 100.00 | 12.206 |

[a] Ref. 4.

TABLE II

$TlAl(SO_4)_2 \cdot 12H_2O$–$KAl(SO_4)_2 \cdot 12H_2O$

| Substance | Wt. % TlAl-$(SO_4)_2$[a] | Mole % $TlAl(SO_4)_2 \cdot 12H_2O$ | Lattice constant in Å. at 25 ± 0.1° |
|---|---|---|---|
| $KAl(SO_4)_2 \cdot 12H_2O$ | 0 | 0 | 12.133[b] |
| 3A[a] | 37.28 | 48.87 | 12.163 |
| 2A | 51.43 | 72.09 | 12.180 |
| $TlAl(SO_4)_2 \cdot 12H_2O$ | 66.20 | 100.00 | 12.206 |

[a] Ref. 4. [b] Ref. 3.

TABLE III

$NH_4Cr(SO_4)_2 \cdot 12H_2O$–$KCr(SO_4)_2 \cdot 12H_2O$

| Substance | Wt. % $NH_4Cr(SO_4)_2$[a] | Mole % $NH_4Cr(SO_4)_2 \cdot 12H_2O$ | Lattice constant in Å. at 25 ± 0.1° |
|---|---|---|---|
| $NH_4Cr(SO_4)_2 \cdot 12H_2O$ | 54.81 | 100.00 | 12.251[b] |
| 2A[a] | 43.18 | 79.50 | 12.232 |
| 3A | 30.21 | 56.24 | 12.2117 |
| 3B | 30.26 | | 12.2120 |
| 5A | 13.50 | 25.46 | 12.1899 |
| 5B | 13.52 | | 12.1898 |
| 6A | 5.226 | 9.91 | 12.178 |
| $KCr(SO_4)_2 \cdot 12H_2O$ | 0 | 0 | 12.175[b] |

[a] Ref. 4. [b] Ref. 1.

All lattice constants are believed to be accurate to ±0.001 Å. In Table III the values of the lattice constants for the members of a duplicate pair are given to four decimal places to indicate the accuracy with which separate determinations could be made. The value of the lattice constant reported for $NH_4Al(SO_4)_2 \cdot 12H_2O$, 12.215 Å. (Table I) is a revised value based on the previously reported value[3] and a redetermination in this study using CuK radiation. The value for the lattice constant of $TlAl(SO_4)_2 \cdot 12H_2O$, 12.206 Å. (Tables I and II), is the result of determinations using both CuK and FeK radiations. Lipson and Beevers[7] report for thallium alum 12.207 ± 0.002 Å.

It is seen from Fig. 1 that the system thallium alum–ammonium alum follows Vegard's law perfectly and that the deviations in the other two cases are very small, −0.005 Å. and −0.006 Å., respectively, for the chrome alum series and the thallium alum–potassium alum series in the vicinity of 50–50 mole per cent. It is interesting to note that a plot of the distribution of the alums between liquid solution (in water) and solid solution[4] for the two thallium alum pairs falls on the same line and the two pairs thus deviate equally from the ideal case of Roozeboom's Class I.[8] The chrome alum pair differs less from

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[5] Montemartini and Vernazza, *l'Ind. Chim.*, **7**, 857 (1932); **8**, 445 (1933); *cf. Brit. Chem. Abstracts*, **A**, 912 (1932); 562 (1933).

[6] Koppel, *Ber.*, **39**, 3738 (1906).

[7] Lipson and Beevers, *Proc. Roy. Soc.* (London), **A148**, 664 (1935).

[8] Roozeboom, *Z. physik. Chem.*, **8**, 504 (1891).

the ideal case. The ionic radii are as follows[9]: $NH_4^+ = 1.43$ Å., $Tl^+ = 1.44$ Å., and $K^+ = 1.33$ Å. Thus difference in size of the substituting ion is very important in determining deviations from ideality with respect to Vegard's law, but seems of little importance from the standpoint of the distribution ratios between liquid solutions and solid solutions. The data on the system potassium alum–ammonium alum,[3] where the maximum deviation from Vegard's law is $-0.003$ Å. for $a_0$ in the neighborhood of 50–50 mole per cent., bear this out.

In the chrome alum series both the A and B members of a duplicate pair gave the same diffraction pattern with identical lattice constants. The relative intensities were also alike indicating that the coördination of the chromium in the final mixed alum was the same regardless of the direction from which equilibrium was reached.

The authors wish to express their thanks and appreciation to Professor J. E. Ricci for his kindness in making the solid solution samples available. They also wish to acknowledge with gratitude a grant from the Graduate School of the University of Minnesota under which this study was carried out.

## Summary

1. Solid solutions of the following pairs of alums have been studied by means of X-rays: $TlAl(SO_4)_2 \cdot 12H_2O$–$NH_4Al(SO_4)_2 \cdot 12H_2O$, $TlAl(SO_4)_2 \cdot 12H_2O$–$KAl(SO_4)_2 \cdot 12H_2O$, and $NH_4Cr(SO_4)_2 \cdot 12H_2O$–$KCr(SO_4)_2 \cdot 12H_2O$.

2. The thallium–ammonium alum pair follows Vegard's law perfectly, while the other two pairs deviate slightly from the law.

3. The difference in size of the substituting ions is important in determining deviations from Vegard's law, but seems to have little bearing on the distribution ratios between liquid solutions and solid solutions and their deviation from the ideal case.

4. No change in the coördination of the chromium was noted in the chrome alum series for final mixed alums which approached equilibrium from opposite directions.

5. The following new values are reported for the lattice constants of the pure alums at 25 ± 0.1°:

$NH_4Al(SO_4)_2 \cdot 12H_2O$ $a_0 = 12.215 \pm 0.001$ Å.
$TlAl(SO_4)_2 \cdot 12H_2O$ $a_0 = 12.206 \pm 0.001$ Å.

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[9] Stillwell, "Crystal Chemistry," McGraw-Hill Book Co., New York, N. Y., 1938, p. 417.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

# The Steric Inhibition of Resonance. II.[1] Rates of Reaction of Nitro- and Cyano-aryl Halides

BY WILLIAM CARL SPITZER[2] AND GEORGE WILLARD WHELAND

Wheland and Danish[1] recently presented chemical evidence confirming the hypothesis[3] that resonance in aromatic nitro compounds could be partially inhibited by methyl substituents ortho to the nitro groups. However, the effect which they observed was rather small in magnitude, and its interpretation was made somewhat uncertain by the lack of quantitative data. For that reason, it seemed desirable to examine the problem in greater detail and in a more quantitative manner. The present paper describes the results of such an investigation.

As is well known, the reaction of an aromatic halide with an anionoid[4] or nucleophilic[5] reagent, such as hydroxide ion, alkoxide ion, ammonia, or the like, is greatly accelerated by the presence of one or more nitro groups ortho or para to the halogen atom. This activating effect of the nitro group is exerted also, but to a smaller extent, by a number of other meta-directing groups, including the carboxyl, aldehyde, and cyanide groups.[6] On the other hand, methyl substituents appear to exert the opposite effect and, especially when in the ortho and para positions, to make the reaction more difficult.[7] In accordance with the theory

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[1] For the first paper of this series, see G. W. Wheland and A. A. Danish, THIS JOURNAL, **62**, 1125 (1940).

[2] Abstract of a thesis presented by W. C. Spitzer to the Faculty of the Division of Physical Sciences of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1940.

[3] R. H. Birtles and G. C. Hampson, *J. Chem. Soc.*, 10 (1937); C. E. Ingham and G. C. Hampson, *ibid.*, 981 (1939).

[4] A. Lapworth, *Nature*, **115**, 625 (1925).

[5] C. K. Ingold, *J. Chem. Soc.*, 1120 (1933); *Chem. Rev.*, **15**, 225 (1934).

[6] M. Schöpff, *Ber.*, **22**, 3281 (1889); **23**, 3440 (1890); **24**, 3771 (1891).

[7] H. Lindemann and A. Pabst, *Ann.*, **462**, 24 (1928); N. Campbell, W. Anderson and J. Gilmore, *J. Chem. Soc.*, 446 (1940).