

the solid phase, whereas in most ternary systems of this type the solubility curves are concave. This indicates that the rate of decrease in solubility of calcium selenate increases with the addition of ammonium selenate. This may be due to a greater selenate ion activity in the solutions of low ammonium selenate concentration. However, the solubility of calcium selenate continuously decreases with increasing concentration of ammonium selenate, which would be expected from the common ion effect.

The corresponding sulfate system has been investigated thoroughly by Hill and Yanick.⁶ Isotherms at 25, 50, 75, and 100° were studied and results obtained by earlier investigators were shown to be incomplete in that several solid phases were not found because of their metastable nature. The solid phases were found to "differ from each other greatly in their rapidity of formation and in the time required to reach equilibrium," this time varying from a few minutes to several weeks. Hill and Yanick have pointed out that the formation of certain phases is very slow, particularly at the lower temperatures, which frequently makes it impossible to attain equilibrium.

If the sulfate and selenate systems be analogous, the eutectic mixture found in the present investigation would be in a metastable condition. It is

(6) Hill and Yanick, *THIS JOURNAL*, **57**, 645 (1935).

conceivable that because of persistence of metastable phases or because of lack of proper crystal nuclei, other solid phases may have been missed. However, samples which had been shaken occasionally over a period of three weeks and others which had been stirred continuously for as long as seven days showed no evidence of change in phase. Not a single instance was found in which a tie-line fell in the region of double salt formation except at the eutectic point. In view of this it would seem that analogous selenate solid phases are not formed at the temperature of this isotherm. However, correlation of the selenate and sulfate systems might be found at higher temperatures, although a few solubility determinations carried out at approximately 60° did not indicate such.

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Summary

1. The isotherm for the system calcium selenate-ammonium selenate-water has been determined at 30°.
2. Two solid phases, $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SeO}_4$, are present at this temperature.

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Structures of Complex Fluorides.¹ Potassium Heptafluocolumbate and Potassium Heptafluotantalate. The Configuration of the Heptafluocolumbate and Heptafluotantalate Ions

BY J. L. HOARD

Complex fluorides of quinquevalent tantalum of formulas RTaF_6 , R_2TaF_7 , and R_3TaF_8 have been described in the literature; those in which the atomic ratio of fluorine to tantalum is seven to one form the commonest and most characteristic class.² Columbium forms an extensive series of the type R_2CbF_7 , but, to a greater extent than tantalum, tends to form oxyfluorides such as $\text{K}_2\text{-CbOF}_5 \cdot \text{H}_2\text{O}$. The frequent occurrence of the seven to one ratio in the empirical formulas of so

(1) Studies of the structures of complex fluorides of tantalum, silicon, germanium, and other metals will be reported shortly from this Laboratory.

(2) Cf. Marks in J. N. Friend, "A Textbook of Inorganic Chemistry," J. B. Lippincott Co., Philadelphia, Pa., Vol. VI, Part III, p. 188.

many of these complex fluorides suggests strongly that TaF_7 and CbF_7 are stable coordination groups. It has been of interest to confirm this hypothesis through X-ray analysis of the structure of the isomorphous pair of crystals, potassium heptafluocolumbate and potassium heptafluotantalate, and to determine the configuration of the anions.

Recently published work³ indicates that ammonium and potassium heptafluozirconates contain ZrF_7 groups. As will be shown later, the configuration of ZrF_7^- is very different from that

(3) G. C. Hampson and L. Pauling, *THIS JOURNAL*, **60**, 2702 (1938).

of CbF_7^- and TaF_7^- . It is probable that the latter configuration is of more frequent occurrence.

Supplies of the common potassium heptafluotantalate and of potassium oxypentafluocolumbate monohydrate were available from earlier work in this Laboratory. Crystallization from hydrofluoric acid solutions yielded in each case the normal heptafluo compound, K_2MF_7 , in the form of small shining needles conforming closely to the description of Groth.⁴

Reported as orthorhombic, the needles do not show parallel extinction. The X-ray photographs show the symmetry of the monoclinic holohedry, departing slightly but definitely from the requirements of the orthorhombic system. There is no indication that the monoclinic angle, β , departs appreciably from 90° , but a careful comparison of intensities of corresponding reflections shows that of the axial planes only (010) is a true plane of symmetry.

In order to have agreement with the "International Tables"⁵ the a - and c -axes of the crystallographic description are interchanged in this paper. Within the estimated limit of error in measurement, 0.02–0.03 Å., there seems to be no significant difference in the lattice constants for potassium heptafluocolumbate and potassium heptafluotantalate. The values are $a_0 = 5.85$ Å., $b_0 = 12.67$ Å., $c_0 = 8.50$ Å., $a:b:c = 0.463:1:0.671$, $\beta = 90^\circ$. Groth⁴ gives $a:b:c = 0.4699:1:0.6682$ for the columbium salt and 0.4610:1:0.6682 for the tantalum compound. The short axis of the unit of structure, $a_0 = 5.85$ Å., is the needle axis of the macroscopic crystals. The virtual identity of the values of the lattice constants for corresponding columbium and tantalum compounds has been observed previously in a number of cases.

Using Cu $K\alpha$ radiation and oscillating about a_0 , a complete set of 15° (and several 5°) oscillation photographs was prepared from needle-like specimens 0.02–0.03 mm. in diameter of each compound. The reflections were recorded upon a cylindrical film of 5-cm. radius, the positions of the knife edges corresponding to $2 \sin \theta = 1.990$. Because of the small diameter of the specimens long exposures were required, but the resulting photographs were very clear and otherwise satisfactory for analysis.

(4) "Chemische Kristallographie," Engelmann, Leipzig, 1906. Erster Teil, pp. 574–575.

(5) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935, Erster Band, Gruppentheoretische Tafeln.

Examination of the photographs demonstrated the regular and complete absence of $\{h0l\}$ reflections with l odd and $\{0k0\}$ reflections with k odd. Among monoclinic space-groups only $C_{2h}^5 - P_{21/c}$ requires these absences; it is highly probable that the structure of these isomorphous crystals must be based upon this space-group.

During indexing, the intensities of all $\{0kl\}$ reflections were carefully estimated by visual comparison with an intensity scale prepared for this purpose. After correcting these intensities by the Lorentz and polarization factor, $(1 + \cos^2 2\theta)/2 \sin 2\theta$ to give the necessary relative values of $|F_{(0kl)}|^2$, a two-dimensional Patterson projection⁶ on (100) was made for each compound. The formula required is

$$P(Y,Z) = \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{(0kl)}|^2 \cos 2\pi(kY + lZ)$$

the projection possessing, of course, a center of symmetry. The largest numerical values of k and l are 16 and 10, respectively. The method of Lipson and Beevers⁷ is particularly convenient in carrying out the actual summations. Taking advantage of the fact that $|F_{(0\bar{k}l)}|^2 = |F_{(0kl)}|^2$, it is easily shown that

$$\begin{aligned} p(Y,Z) &= p(Y,0) + \sum_1^{10} p(Y,l) \cos 2\pi lZ, \text{ in which} \\ p(y,0) &= F_{(000)}^2 + 2\sum_1^{16} |F_{(0k0)}|^2 \cos 2\pi kY, \text{ and} \\ p(Y,l) &= 2|F_{(00l)}|^2 + 4\sum_1^{16} |F_{(0kl)}|^2 \cos 2\pi kY \end{aligned}$$

A set of the Lipson and Beevers strips was used in these and in the later summations.

On the resulting plot for the columbium salt large maxima are found at $Y = 1/2, Z = 0.067$; $Y = 0.243, Z = 1/2$; $Y = 0.257, Z = 0.450$, in addition to the identity maximum at 0,0. On the projection for the tantalum compound are found corresponding useful maxima at $1/2, 0.057$; $0.245, 1/2$; $0.255, 0.45$. It is apparent that neither columbium nor tantalum can lie in the centers of symmetry of the space group, but must be placed in the general positions: $x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x}, 1/2 + y, 1/2 - z; x, 1/2 - y, 1/2 + z$. Remembering that the coördinates of maxima in the Patterson projection represent components of interatomic distances in the projection upon (100) of the contents of the actual unit of structure, 4 Cb in the general position should lead to maxima in the YZ plot at 0,0; $\pm 2y, \pm 2z; 1/2, \pm(1/2 - 2z); \pm(1/2 - 2y), 1/2$. Upon solution, approximate values (for either columbium or tantalum) of $y = 0.128, z = 0.225$ are found. The positive values

(6) A. L. Patterson, *Z. Krist.*, **90**, 517 (1935).

(7) Lipson and Beevers, *Phys. Soc. London*, **48**, 772 (1936).

TABLE I
 AMPLITUDES IN ARBITRARY UNITS OF (0kl) REFLECTIONS

	$l \rightarrow$										
	0	1	2	3	4	5	6	7	8	9	10
0	7	0	-7.6	0	3.8	0	-1.2	0	0	0	0
1	0	0.8	-0.7	0	5.9	2.7	-2.2	-0.7	2.1	1.3	-1.2
2	-0.6	-4.4	-1.2	1.6	-1.3	-1.5	0.7	2.4	0	0	0
3	0	-1.6	-1.5	0.5	1.1	-2.7	-1.9	1.7	-0.5	-0.7	-0.7
$k \downarrow$ 4	-4.0	1.1	1.4	-3.3	-1.0	-0.7	1.6	0	-1.5	0	-0.5
5	0	1.7	-1.3	0	0.7	-2.1	1.2	0	-1.0	-1.7	1.3
6	-4.0	7.1	0.4	-2.1	0.8	3.2	0	0	0.7	0	
7	0	-0.5	0	-3.0	-1.9	3.2	2.4	-1.4	-1.0	1.6	
8	3.6	0	-3.6	0	2.2	-1.2	-2.0	0	0.9		
9	0	1.0	-0.7	-0.7	1.0	2.4	-1.9	-1.9	1.3		
10	-0.2	-2.2	2.4	2.5	-1.0	-0.3	-0.9	0.5	0.9		
11	0	0	1.5	0	0	-0.7	0	1.4			
12	-2.4	0	1.0	0	-1.4	0	0.9				
13	0	0	0	0	-1.8	-0.7	0.7				
14	0.2	0.9	0	-1.1	0	1.0					
15	0	0	0	0	-0.3						
16	1.0	0	-1.0								

for both y and z may be chosen arbitrarily provided that a consistent selection of potassium and fluorine positions is made thereafter.

The Patterson projection for the columbate shows sufficiently good resolution of the minor peaks to permit of the rather definite determination of the approximate values for the y and z potassium parameters. A careful analysis of the data indicates that both sets of potassium ions must lie in the general positions with $y_1 = 0.44$, $z_1 = 0.20$, $y_2 = 0.29$, $z_2 =$ about 0.445. Every possible Cb-K and K-K maximum which should appear on the Patterson plot as indicated by the various combinations of the parameter values thus far given is observed either as a resolved peak or, in a few cases, as part of a composite peak. No other non-equivalent assignment of columbium and potassium parameters could be found which would account for the Patterson data to even an approximately comparable degree.

Certain minor peaks indicative mainly of columbium-fluorine separations (since they correspond to distances of 1.5–2.0 Å.) remain unused upon the plot. These are of limited usefulness, although they prove to be in entire agreement with the final structure as determined.

A knowledge of the approximate positions of columbium (or tantalum) and potassium in the (100) projection of the contents of the unit cell should suffice to determine the phase of most of the (0kl) reflections, including virtually all of those of large amplitude. Proceeding from this assumption, phases were calculated and a Fourier

projection on (100) was made leaving out those few reflections for which the sign seemed seriously in doubt. With few exceptions the signs attached to the amplitudes in Table I, which are those of the final structure, are the same as those determined upon the basis of columbium and potassium parameters.

The structure factor for (0kl) reflections using only the general positions is

$$S_{(0kl)} = 4\sum_i f_i \cos 2\pi k y_i \cos 2\pi l z_i, \quad k + l \text{ even}$$

$$S_{(0kl)} = -4\sum_i f_i \sin 2\pi k y_i \sin 2\pi l z_i, \quad k + l \text{ odd}$$

The atomic f -values of Pauling and Sherman⁸ are used throughout this paper.

The reflection amplitudes used for calculation are proportional to the square roots of the observed relative intensities corrected by the Lorentz and polarization factor. The cross section of the needle-like specimens used was so small ($d \approx 0.03$ mm.) that the correction for absorption is practically constant throughout the angular range $0 < \theta < 90^\circ$. Since the scale of amplitudes is arbitrary, so is the resulting scale of electron density.

Inasmuch as the first somewhat incomplete Fourier projection for potassium fluocolumbate readily could be interpreted to give approximate values for all of the y and z parameters, it was immediately possible to make sure of the phase in the previously uncertain cases, and to include these in the final summation.

Since the origin is a center of symmetry, the general formula for the Fourier projection is

$$\rho(y, z) = \sum_k \sum_l F_{(0kl)} \cos 2\pi(ky + lz)$$

(8) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

It is, however, convenient to use summations of the Lipson and Beevers type. Since $F_{(0\bar{k}l)} = F_{(0kl)}$, $k + l$ even, and $F_{(0\bar{k}l)} = -F_{(0kl)$, $k + l$ odd ($y = 1/4$ is a glide plane), the projected electron density may be written as

$$\rho(y,z) = A(y,0) + \sum_1^{10} A(y,l) \cos 2\pi lz - \sum_1^{10} B(y,l) \sin 2\pi lz$$

in which

$$\begin{aligned} A(y,0) &= F_{(000)} + 2\sum_2^{16} F_{(0k0)} \cos 2\pi ky \\ A(y,l) &= 2F_{(00l)} + 4\sum_1^{16} F_{(0kl)} \cos 2\pi ky, \text{ and} \\ B(y,l) &= 4\sum_1^{16} F_{(0kl)} \sin 2\pi ky \end{aligned}$$

The A-series includes only reflections with $k + l$ even, the B-series includes only those with $k + l$ odd.

The (100) projection for potassium heptafluocolumbate is shown in Fig. 1. Columbium and potassium positions are very nearly those derived from the Patterson projection, and nearly identical values (about 17 in arbitrary units) for the maximum density are found for the structurally non-equivalent potassium ions. Table II gives data on the approximate maximum density for each peak together with the y and z parameter values. It appears that the peaks at $y = 0.250$, $z = 0.203$ and $y = 0.102$, $z = 0.403$ are each to be interpreted as the projection of two fluorine atoms, each member of a pair having nearly the values of y and z given by the map. The smaller and nearly equal peaks at $y = -0.023$, $z = 0.216$; $y = 0.108$, $z = 0.005$; and $y = 0.076$, $z = 0.128$ are without doubt the projections of individual fluorine atoms. The last of these is least well defined and some allowance is made in the parameter values given for overlapping with the columbium peak.

Because of fluctuations from the average in the regions far removed from the peaks the contour line of lowest density, representing about one unit, is drawn in somewhat arbitrarily in parts of the projection. It is intended to provide a common base line for the various peaks. There are fluctuations in the background of as much as about ± 2 units from the average, although the average absolute deviation is considerably smaller than this.

It is possible in a similarly direct manner to calculate the phase of each reflection for potassium heptafluotantalate. The Fourier projection for the tantalate is not reproduced since it is generally quite similar although considerably inferior in detail to that of the isomorphous columbate.

TABLE II
DATA FROM THE FOURIER PROJECTIONS ON (100)

Peak	Maximum density	Coördinates y	Coördinates z
Potassium fluocolumbate			
Cb	45	0.128	0.223
K _I	17	.440	.188
K _{II}	16.5	.285	.445
F _I + F _{II}	15	.250	.203
F _{III} + F _{IV}	14	.102	.403
F _V	9	-.023	.216
F _{VI}	8	.108	.005
F _{VII}	8	.076	.128
Potassium fluotantalate			
Ta	72	0.128	0.223
K _I	17	.440	.187
K _{II}	17	.285	.443
F _I + F _{II}	13	.255	.210
F _{III} + F _{IV}	16	.125	.375
F _V	9	-.025	.207
F _{VI}	9	.120	.008
F _{VII}	11	.095	.110

Data giving the positions and maximum values in arbitrary units of the various peaks are included in Table II. A more accurate estimate of intensities is needed for the tantalum than for the co-

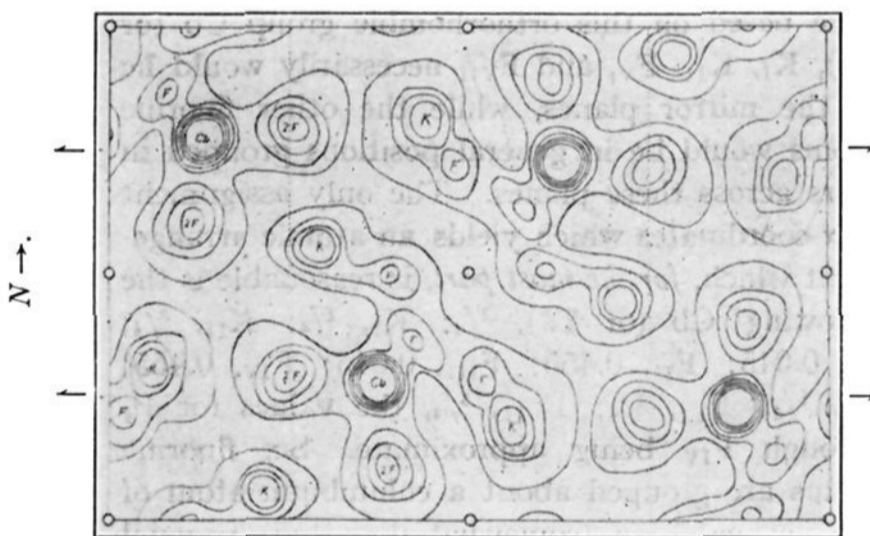


Fig. 1.—Fourier projection on (100) of relative electron density in potassium fluocolumbate.

lumbium compound in order to get equally precise information about the positions of fluorine and potassium. The atomic coördinates derived from the columbate projection probably form the more satisfactory set for the tantalate as well.

Consideration of the relative intensities of $(0kl)$, $(\neq 1kl)$, and $(\neq 2kl)$ reflections, particularly the observation that $(hk0)$ reflections with $h + k$ odd are either weak or absent altogether, results in approximate values of the x -parameters of columbium or tantalum and potassium as follows: Cb or Ta: $x = 0.25$; K_I: $x = 0.25$; K_{II}: $x = 0.75$.

The proximity of the fluorine positions to that of columbium on the (100) projection together with the comparatively short (5.85 Å.) a -axis indicates that all fluorine atoms are coordinated by columbium. The a -axis is, however, too long to permit of sharing of fluorine between two columbium atoms since the Cb-F (or Ta-F) separation as estimated from empirical data or from the sum of either the ionic or covalent radii is only about 2.0 Å.; discrete complexes must exist within the structure.

In considering possible values for the other parameters along the a -axis it is illuminating to make use of the pseudo-orthorhombic character of these crystals. The orthorhombic space group which would require the complete absence of ($hk0$) reflections, $h + k$ odd, in addition to the regular absences of C_{2h}^6 , and which possesses also a center of symmetry is $D_{2h}^{16} - Pnma$. (In order to agree with the description of the "International Tables"⁵ it is necessary to carry out a cyclic permutation of axes in going from C_{2h}^5 to D_{2h}^{16} .) In addition to the symmetry of C_{2h}^5 , D_{2h}^{16} has mirror planes at $x = 1/4$ and $x = 3/4$. If the structure were based on this orthorhombic group Cb (or Ta), K_I , K_{II} , F_V , and F_{VII} necessarily would lie in the mirror planes, while the other fluorine atoms would be in general positions grouped in pairs across these planes. The only assignment of x -coordinates which yields an atomic arrangement which, for the most part, is reasonable is the following: Cb (or Ta), $1/4$; K_I , $1/4$; K_{II} , $3/4$; F_I , 0.045; F_{II} , 0.455; F_{III} , 0.045; F_{IV} , 0.455; F_V , $1/4$; F_{VI} , $1/4$; F_{VII} , $3/4$, the values for F_I through F_{IV} being approximate. Six fluorine atoms are grouped about a columbium atom of the vertices of a (somewhat distorted) trigonal prism; the seventh fluorine atom (F_{VII} , with $x = 3/4$, $y = 0.075$, $z = 0.125$) is placed just halfway between two such anions. It is, however, immediately apparent that this structure cannot be entirely correct, and that F_{VII} must have a value of x much less than $3/4$ (about 0.54–0.56); this being true, the symmetry becomes that of C_{2h}^5 and F_{VII} becomes a part of a CbF_7 (or TaF_7) coordination group.

Crowding an uncoordinated fluoride ion into the space between two complex anions gives what is *a priori* an unreasonable type of structure which has never been shown to exist. With $x = 3/4$, F_{VII} would be surrounded by nine fluorine atoms at distances ranging from 2.60 to

3.15 Å., columbium at 3.1 Å., and two potassium ions (lying in the plane $x = 3/4$) at only 2.30–2.35 Å. These last are 0.30–0.35 Å. less than the well established minimum of about 2.66 Å. for the K-F separation (coordination number six). A large component of 1.1–1.3 Å. along a is required to bring these two $K-F_{VII}$ separations up to about 2.66 Å.; it is provided if the x -coordinate of F_{VII} is put equal to about 0.55, in which case this fluorine atom must be considered as part of the coordination complex.

In order to demonstrate conclusively from experimental data alone that the structure does contain CbF_7 complexes, it is desirable to make a Fourier analysis of ($hk0$) data, since the fluorine atom in question, F_{VII} , should be resolved in the (001) projection. By cutting a section from a needle-like crystal it was possible to obtain a specimen, of rather irregular shape with a maximum diameter of about 0.20–0.25 mm. along both the a and b axes. A set of oscillation photographs was prepared and the equatorial ($hk0$) reflections were subjected to the same sort of analysis as previously outlined for the ($0kl$) data. An additional correction, that for absorption in the crystal, was required in this case. In spite of the irregular shape of the specimen its small size permitted of an estimate of the average absorption correction which is sufficiently good for the present purpose.

A Patterson projection on (001) shows that columbium and potassium are indeed very nearly in the planes $x = 1/4$ and $x = 3/4$ but gives no indication of any departure from them. The plot has a symmetry plane at $X = 1/2$; unless the components of interatomic distances depart considerably from one half the peaks at $1/2 + \delta$ and $1/2 - \delta$ will not be resolved, as in the present case.

For the larger values of h , the intensities of ($hk0$) reflections, $h + k$ odd, become large enough to require that the x -coordinate of columbium depart quite appreciably from one-fourth. There are in addition certain observed regularities in the ($hk0$) intensities which lead to the conclusion that for columbium, $x \leq 0.26$; for potassium, $x_I \geq 0.24$, $x_{II} \leq 0.75$. By taking into account the approximate positions of fluorine it is possible to calculate reflection amplitudes which agree well enough in magnitude with those observed as to allow the definite selection of the signs to be associated with the latter in making the Fourier analysis.

The (001) projection of electron density (in arbitrary units) is shown in Fig. 2. The columbium, potassium, and six of the seven fluorine atoms are resolved, with coordinates along the *b*-axis which are nearly identical with those obtained from the (100) projection. Table III lists the origin, position, and approximate magnitude of each observed peak. One fluorine atom, F_{VI}, expected to appear at approximately $x = 0.18, y = 0.108$, is not resolved from the outer portion of the nearby columbium peak; this peak shows, however, the type of asymmetry expected in case the fluorine atom be present in the required region. As a detailed map of the relative electron density, the projection does not appear to be very satisfactory, however.

The atomic coordinates read from the (001) map of electron density are those expected for the structure with a seven-coördination complex. The fluorine atom F_{VII} is clearly resolved with $x = 0.56, y = 0.075$, values which definitely make it a part of the coördination group of columbium. The region around $x = 0.75, y = 0.075$ is one of low electron density and the possibility of having present a fluoride ion uncoördinated by columbium is excluded.

TABLE III

DATA FROM THE (001) PROJECTION OF POTASSIUM HEPTAFLUOCOLUMBATE

Peak	Maximum density	Coördinates	
		<i>x</i>	<i>y</i>
Cb	47	0.266	0.128
K _I	18	.236	.445
K _{II}	21	.757	.280
F _{I(2)}	16	.055	.250
F _{II(2)}	18	.447	.250
F _{III}	11	.090	.105
F _{IV}	11	.450	.105
F _V	12	.225	-.024
F _{VII}	11	.560	.072

In view of the approximate character of the intensity data, the parameters of fluorine obtained from the (001) projection, particularly along the short *a*-axis, are not presumed to be very accurate. The agreement between the values of the parameters along *b* as derived from the (001) and the more satisfactory (100) projection does indicate that a fair approximation to all atomic positions has been obtained. Table IV contains a complete set of parameter values which are believed to represent as satisfactory results as are obtainable from the data at hand.

In some cases the positions given for fluorine are not exactly those read from the projections, but

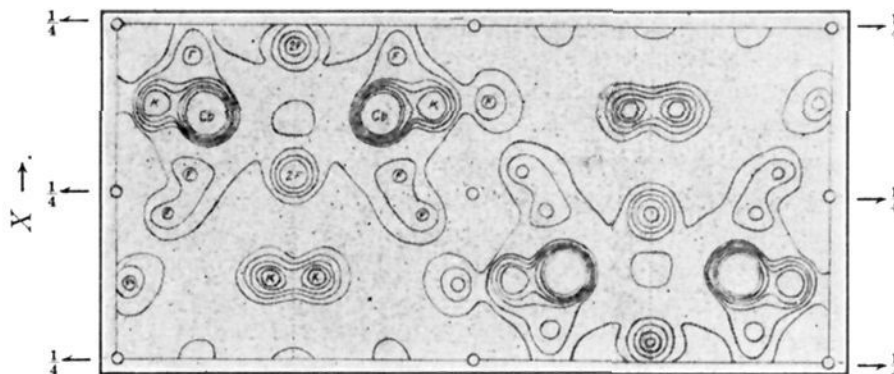


Fig. 2.—Fourier projection on (001) of relative electron density in potassium fluocolumbate.

are well within the probable limits of error. Some consideration has been given to the possibility of having the interatomic distances entirely self-consistent. In cases of imperfect resolution of fluorine atoms the particular choice of parameter values has been based upon the general character of the structure.

This structure accounts satisfactorily for the observed intensities of (*hk*0), (0*kl*), and the more general (2*kl*) and ($\bar{2}$ *kl*) reflections. Very accurate parameter values for fluorine are not required in order to achieve reasonably detailed agreement between observed and calculated intensities.

TABLE IV

COMPLETE PARAMETER DATA FOR POTASSIUM FLUOCOLUMBATE

Atom	Atomic coördinates		
	<i>x</i>	<i>y</i>	<i>z</i>
Cb	0.266	0.128	0.223
K _I	.236	.440	.188
K _{II}	.757	.280	.445
F _I	.045	.245	.200
F _{II}	.455	.255	.205
F _{III}	.045	.105	.400
F _{IV}	.455	.110	.410
F _V	.225	-.025	.215
F _{VI}	.180	.110	.005
F _{VII}	.550	.075	.125

Although no Fourier projection on (001) was attempted for potassium heptafluotantalate, the data already presented together with the generally close similarity between corresponding ($\neq kl$) and ($\neq 2kl$) reflections from the columbate and tantalate (with due allowance for the difference in scattering power of columbium and tantalum) make it quite certain that *x*-parameter values are nearly identical in the two cases. There is no indication that the structures of this iso-

morphous pair of crystals differ appreciably either as to configuration or in actual dimensions.

Drawings of the structure and of the complex anion are shown in Figs. 3a and 3b. Table V lists

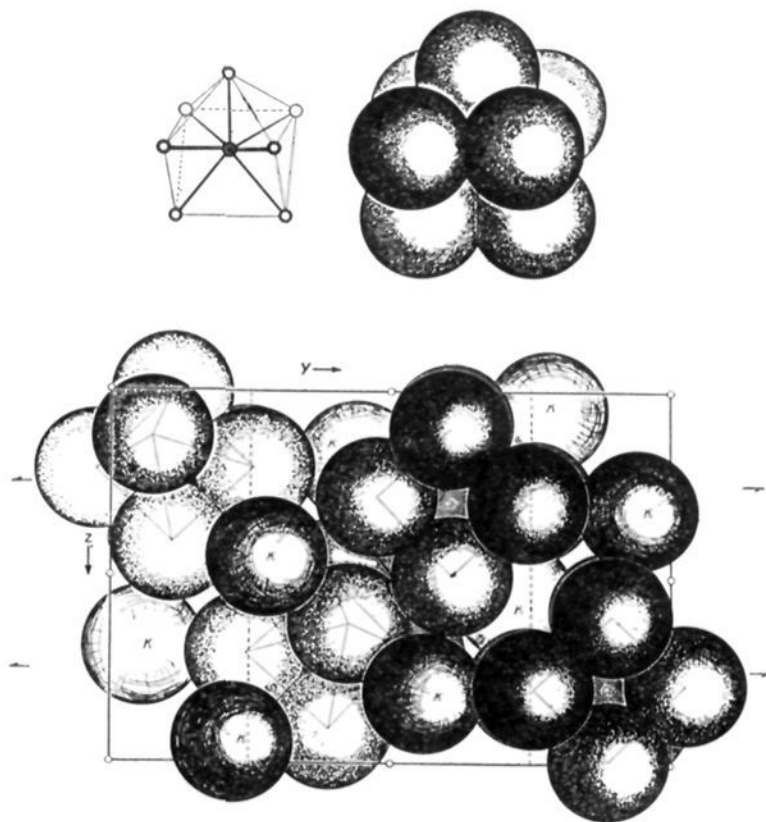


Fig. 3a.—Drawing of the complex anion with the two-fold axis vertical.

Fig. 3b.—Packing drawing along the short a axis of the structure of potassium fluocolumbate. Both cations and complex anions are very nearly centered in the planes $x = 1/4$ and $x = 3/4$.

all pertinent interatomic distances as calculated from the parameter data of Table IV. Cb-F separations lie between 1.94 and 2.01 Å., the average being 1.97 Å. The F-F separations of adjacent pairs of atoms within the anion vary between 2.41 and 2.98 Å., the average of all thirteen quantities being 2.53 Å. Leaving out the two comparatively large values, the average of eleven distances lying between 2.41 and 2.54 Å. is 2.47 Å. These values, which indicate a considerable degree of interpenetration of the closed valence shells of adjacent fluorine atoms within the complex, are probably a little smaller than would have been anticipated. The data are consistent, however, in requiring a complex anion of about these dimensions, even though the fluorine atoms be assigned coordinates which, while still within the probable limits of error of the Fourier projections, would make the F-F separations as large as possible. These considerations have already been given some weight in the selection of the parameter data of Table IV.

TABLE V

INTERATOMIC DISTANCES IN POTASSIUM FLUOCOLUMBATE

Atom pair (Inside the anion)	Separation, Å.	Atom pair (Outside the anion)	Separation, Å.
Cb-F _I	1.98	K _I -F _I	2.72
Cb-F _{II}	1.96	K _I -F _{II}	2.68
Cb-F _{III}	2.01	(K _I -F _{III}) ₁	2.75
Cb-F _{IV}	1.96	(K _I -F _{IV}) ₁	2.76
Cb-F _V	1.95	(K _I -F _{III}) ₂	2.76
Cb-F _{VI}	1.94	(K _I -F _{IV}) ₂	2.94
Cb-F _{VII}	1.98	K _I -F _V	2.86
F _I -F _{II}	2.41	K _I -F _{VI}	2.79
F _I -F _{III}	2.46	K _I -F _{VII}	2.65
F _I -F _{VI}	2.52	(K _{II} -F _I) ₁	2.72
F _{II} -F _{IV}	2.54	(K _{II} -F _{II}) ₁	2.72
F _{II} -F _{VI}	2.98	(K _{II} -F _I) ₂	2.77
F _{II} -F _{VII}	2.44	(K _{II} -F _{II}) ₂	2.86
F _{III} -F _{IV}	2.41	K _{II} -F _{III}	2.77
F _{III} -F _V	2.52	K _{II} -F _{IV}	2.81
F _{IV} -F _V	2.74	K _{II} -F _V	2.84
F _{IV} -F _{VII}	2.53	K _{II} -F _{VI}	2.89
F _V -F _{VI}	2.49	K _{II} -F _{VII}	2.68
F _V -F _{VII}	2.41	F _{VII} -F _{VII}	2.91
F _{VI} -F _{VII}	2.44		

The K-F separations range between 2.65 and 2.94 Å. for eighteen quantities (nine for each potassium), the average being 2.78 Å. The coordination polyhedra formed by the fluorine atoms which are nearest neighbors of potassium are quite irregular in shape, but correspond to a reasonably uniform distribution of negative charge about each univalent cation. The closest distance of approach of two fluorine atoms not coordinated by the same columbium atom is about 2.91 Å. (F_{VII}-F_{VII}); excepting this pair, separations of this type are well over 3.0 Å.

The complex anion, CbF₇⁻, which is shown to exist within crystals of potassium heptafluocolumbate is not required by the space group to possess any symmetry whatever. It seems very likely, however, that the isolated ion, undistorted by less symmetrical surroundings, would have the symmetry of the point-group C₂^v - mm; that is, a two-fold axis in which two mutually perpendicular mirror planes intersect. An independent study⁹ of the tetragonal ammonium heptafluotantalate provides convincing evidence for the existence of a TaF₇ group *required* to possess the symmetry of C₂^v.

The CbF₇ or TaF₇ polyhedron is conveniently visualized as derived from an MF₆ group in the form of a trigonal prism by the addition of a seventh fluorine atom through the center of one square face, followed by the appropriate distortion.

(9) J. L. Hoard and John S. Shell, unpublished material.

The configuration for ZrF_7^{-3} recently reported⁸ to exist within crystals of the cubic ammonium and potassium heptafluozirconates possesses the symmetry of $C_3^v - 3m$, and is, therefore, entirely different from that of CbF_7^- or TaF_7^- . On the basis of a purely ionic model there does not seem to be much to choose between these two possibilities since, for a given M-F distance, the number and magnitude of the important separations of adjacent pairs of fluorine atoms are about equal. No quantum mechanical treatment of seven-coordinated covalent complexes has been reported; hence, considered as covalent complexes, no convincing reason can be given for preferring either configuration to the other. If it be assumed that the extensive and characteristic series of stable fluotantalates of type formula R_2TaF_7 contains in all cases TaF_7^- ions similar to that found in the present study, it follows that this configuration is usually preferred.

The investigation of the structures of crystals of the hexagonal $CsTaF_6$ and the orthorhombic Na_3TaF_8 is being undertaken in this Laboratory. With the use of an integrating photometer patterned after the one described by Robinson,¹⁰ which should soon be in operation, it is hoped to obtain intensity data of sufficient accuracy to make possible detailed structural determinations. The ratio of the univalent radii indicates the probable existence of TaF_8 complexes. The possibility of the TaF_6 group having the trigonal prism configuration should be investigated also.

Summary

It is shown from X-ray data that the isomor-

(10) B. W. Robinson, *J. Sci. Instruments*, **10**, 233 (1933).

phous crystals potassium heptafluocolumbate and potassium heptafluotantalate possess nearly identical monoclinic (pseudo-orthorhombic) units of structure with $a_0 = 5.85 \text{ \AA}$., $b_0 = 12.67 \text{ \AA}$., $c_0 = 8.50 \text{ \AA}$., $\beta = 90^\circ$, space group $C_{2h}^6 - P2_{21/c}$, containing four molecules. A Patterson projection on (100) utilizing visually estimated intensities from excellent photographs is interpreted unambiguously to give approximate values of y and z parameters for columbium or tantalum and potassium atoms (all atoms are in general positions). These data suffice to determine the phase of all important $(0kl)$ amplitudes (Table I); a Fourier projection (Fig. 1) on (100) of relative electron density for each compound yields y and z coordinates for all atoms (Table II). A Fourier analysis of the less satisfactory $(hk0)$ data (Fig. 2) gives x coordinates of all atoms (Table III) and checks rather closely the y parameter values of the (100) projection. The parameter data of Table IV account satisfactorily for the intensities of X-ray reflections, and lead to generally reasonable interatomic distances (Table V).

The structure (Fig. 3b) is an aggregate of K^+ and CbF_7^- or TaF_7^- ions. Although not required by the space group to possess any symmetry, the undistorted heptafluocolumbate (Fig. 3a) or heptafluotantalate ion would show apparently the symmetry of $C_2^v - mm$. This configuration is entirely different from that recently reported⁸ for the ZrF_7^- ion of symmetry $C_3^v - 3m$. It is probable that the extensive series of stable fluotantalates having the atomic ratio $7F/Ta$ contains TaF_7^- ions with the configuration established in this paper.

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