

I wish to thank Professor R. H. Lyddane for some very helpful suggestions and discussion.

Appendix I

Derivation of Eq. 10.—Since no heat is lost or gained by a system in an adiabatic expansion, we may write

$$P = -(\partial E/\partial V)_S = -(\partial E_t/\partial V)_S - dE_p/dV - dE_p/dV$$

But as S is a function only of Θ/T , the latter does not change in an adiabatic process. And since E_t/T depends only on Θ/T , it is also true that $E_t/\Theta = (E_t/T)(T/\Theta)$ does not change in an adiabatic process. Hence

$$\left(\frac{\partial E_t}{\partial V}\right)_S = \left(\frac{\partial \Theta(E_t/\Theta)}{\partial V}\right)_S = \frac{E_t}{\Theta} \frac{d\Theta}{dV}$$

so that Eq. (10) follows immediately.

Appendix II

Calculation of Heat of Sublimation of Solid.—This calculation proceeds in a straightforward manner from the specific heats of solid, liquid, and vapor (assumed a perfect gas), the heat of fusion and the heat of vaporization of the liquid¹¹; but the latter must be corrected to give the heat of vaporization to form a perfect gas. This correction was made as follows. We assume all terms in Eq. (16) in p^2 , or higher powers, to be negligible, and then apply the thermodynamic equation

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p$$

Integrating $(\partial H/\partial p)_T$ from 1 atmosphere to zero pressure we find

$$\Delta H = - \left(B_p - T \frac{dB_p}{dT} \right) \frac{RT}{V}$$

where V is the volume of one mole of gas at T (the boiling point) and 1 atmosphere. We then use the data of Cath

and Onnes to evaluate B_p and dB_p/dT . This gives $\Delta H = 17.7$ cal.

For the heat of sublimation of the solid at 16.0°K. to give vapor at 0°K., we find 1840.6 cal. per mole; if the solid is at 11.0° it is 1848.9 cal. per mole.

§6. Summary

A detailed investigation has been made of the relation between the interatomic potential energy curve and the properties of solid argon. The characteristic temperature and the total energy of the solid have been expressed in a simple way in terms of the constants of the potential energy expression, and the condition for equilibrium has been set up and applied in the determination of the potential energy curve for argon from the experimental data. The effect of the setting in of disorder (premelting) in the solid has been considered. What is believed to be a good potential energy curve for argon has been found, and compared with some others which have been previously used. The effect of the distribution of the frequencies of the normal modes of vibration of the solid upon its physical properties has been considered, and the effect of possible deviations from the Debye theory estimated. Finally, it has been shown that the potential curve obtained reproduces, probably within the limits of error, the experimental values of the second virial coefficient of the gas.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Structures of Complex Fluorides.¹ The Stereochemistry of Some Fluocolumbate and Oxyfluocolumbate Complexes. The Crystal Structure of Potassium Oxyfluocolumbate-Potassium Bifluoride, $K_2CbOF_5 \cdot KHF_2$ *

By J. L. HOARD AND W. J. MARTIN

When columbium fluoride, potassium fluoride, and hydrofluoric acid are mixed in varying proportions in aqueous solution, six distinct crystalline compounds can be prepared.² Two of these, obtainable when columbium fluoride is added in excess, will not be discussed in detail. Empirical formulas of the remaining four compounds are

$K_2CbOF_5 \cdot H_2O$, K_3CbOF_6 , K_3HCbOF_7 , and K_2CbF_7 . An X-ray study of potassium heptafluocolumbate, K_2CbF_7 , demonstrating that it contains the seven-coördination complex, CbF_7^- , has been reported.^{1a} The purpose of the present paper is twofold: first, to point out the remarkable fact that three stereochemically distinct types of complex columbate ions are represented among the four compounds for which formulas are given above, and, secondly, to report in detail the determination from X-ray diffraction data of the crystal structure of potassium oxyfluocolumbate-

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(1) For earlier papers in this series see (a), THIS JOURNAL, **61**, 1252 (1939); (b), *ibid.*, **61**, 2849 (1939); (c), *ibid.*, **62**, 3126 (1940).

(2) C. W. Balke and E. F. Smith, *ibid.*, **30**, 1637 (1908).

potassium bifluoride, $K_2CbOF_5 \cdot KHF_2$ (or K_3HCbOF_7).

The Stereochemistry of Some Fluocolumbate and Oxyfluocolumbate Complexes

Potassium oxypentafluocolumbate monohydrate, $K_2CbOF_5 \cdot H_2O$, is obtained from aqueous solutions (with no hydrofluoric acid) in which columbium fluoride and potassium fluoride have been dissolved in roughly equivalent proportions. It results also from the recrystallization from water of any of the four compounds of the group. Conceivably, this substance might contain the complex anion $Cb(OH)_2F_5^-$, but the fact that it is monoclinic and isomorphous with $K_2TiF_6 \cdot H_2O$ is strong evidence that we have to deal with octahedral $CbOF_5$ and TiF_6 groups. To confirm this conclusion and to determine if possible why the monohydrate is formed in preference to the anhydrous salt, for which the very stable cubic potassium chloroplatinate and hexagonal potassium fluogermanate structural types^{1b} are available, Mr. M. B. Williams of this Laboratory has undertaken an X-ray study of the isomorphous pair, $K_2CbOF_5 \cdot H_2O$ and $K_2TiF_6 \cdot H_2O$. (Under suitable conditions anhydrous K_2TiF_6 can be prepared with the K_2GeF_6 type of structure.³)

Potassium oxyhexafluocolumbate, K_3CbOF_6 , is obtained from aqueous solutions (with no hydrofluoric acid) in which columbium fluoride and potassium fluoride have been dissolved with the latter in large excess. The compound is cubic and may be expected to be isomorphous with potassium heptafluozirconate, K_3ZrF_7 , for which the structure is known.⁴ A nearly completed X-ray study⁵ of K_3CbOF_6 shows that this is indeed the case. The seven-coördination complexes ZrF_7^- and $CbOF_6^-$ have the point-group symmetry, C_3^v . It is interesting that K_3CbOF_6 develops only cube faces whereas K_3ZrF_7 is obtained with an octahedral habit.

The addition of a *limited* concentration of hydrofluoric acid to solutions which would normally furnish crystals of K_3CbOF_6 leads to the appearance of a new crystalline phase with the empirical composition K_3HCbOF_7 . The radius ratio of columbium to fluorine suggests that an eight-coördination group might be stable. In undertaking the X-ray study of this compound,

we thought it probable that either $CbOHF_7^-$ or $CbOF_6^-$ complexes would be found. Our results, described in detail later in this paper, show that the compound is actually an aggregate of K^+ , octahedral $CbOF_5^-$, and HF_2^- . The double salt formula, $K_2CbOF_5 \cdot KHF_2$, is appropriate therefore.

Potassium heptafluocolumbate, K_2CbF_7 , crystallizes from solutions containing columbium fluoride, potassium fluoride, and moderate or large concentrations of hydrofluoric acid. Of all the compounds listed, it is most easily prepared. As previously pointed out,^{1a} the point-group symmetry of CbF_7^- in K_2CbF_7 (also of TaF_7^- in K_2TaF_7 and in the tetragonal⁶ $(NH_4)_2TaF_7$) is that of C_2^v . The seven-coördination groups CbF_7^- (in K_2CbF_7) and $CbOF_6^-$ (in K_3CbOF_6) have, therefore, entirely distinct geometrical configurations. On an electrostatic basis the two types seem about equally stable. It would not be surprising if compounds could be prepared in which the CbF_7 group would show the point-group symmetry of C_3^v , or in which the $CbOF_6$ or ZrF_7 group would have the symmetry of C_2^v .

Some of the considerations of the preceding paragraphs are summarized in Table I. It seems remarkable indeed that rather small variations in the character of the solution phase should result in the production of four crystalline substances in which three completely distinct types of complex columbate ions are represented.

TABLE I

Formula of crystalline phase	Crystal system	Formula of complex	Symmetry of complex
$K_2CbOF_5 \cdot H_2O$	Monoclinic	$CbOF_5^-$	Octahedral
K_3CbOF_6	Cubic	$CbOF_6^-$	C_3^v
$K_2CbOF_5 \cdot KHF_2$	Monoclinic	$CbOF_5^-$	Octahedral
K_2CbF_7	Monoclinic	CbF_7^-	C_2^v

Balke and Smith² assign the empirical formulas $5KF \cdot 3CbOF_3 \cdot H_2O$ and $4KF \cdot 3CbOF_3 \cdot 2H_2O$ to the two compounds which are obtained from solutions of potassium fluoride and columbium fluoride with the latter in excess. It is interesting that for both substances formulas can be written which would preserve discrete octahedral complexes, namely, $K_5[CbOF_5]_2[Cb(OH)_2F_4]$ and $K_4[CbOF_5][Cb(OH)_2F_4]_2$, respectively. If water of constitution be not present it is probable still that the coördination number of columbium is six; in this case there would be a limited sharing of elements, presumably of oxygen, between oc-

(3) Unpublished material.

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

(5) J. L. Hoard and M. B. Williams, unpublished material.

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

tahedra so as to preserve the correct stoichiometric relations.

Available evidence indicates that the octafluocolumbate ion, CbF_8^{\equiv} , is either non-existent or extremely unstable, whereas the analogous octafluotantalate ion, TaF_8^{\equiv} , may well exist as a stable complex. The most easily prepared fluotantalate of sodium, a compound which is stable in contact with warm air of high relative humidity, is the octafluotantalate, Na_3TaF_8 . Whenever crystalline compounds of columbium and tantalum of similar chemical formulas have been studied with X-rays, they have proved to be completely isomorphous with lattice constants differing by no more than a fraction of one per cent.^{1a} Nevertheless, all attempts to prepare sodium octafluocolumbate, Na_3CbF_8 , either from aqueous solution or from anhydrous hydrogen fluoride⁷ have proved unsuccessful. The tentative conclusion drawn from these facts is that Na_3TaF_8 contains a characteristic structural grouping, most probably the MF_8^{\equiv} complex, which is not accessible to columbium. We are studying the crystal structure of sodium octafluotantalate.

The Crystal Structure of Potassium Oxyfluocolumbate-Potassium Bifluoride, $\text{K}_2\text{CbOF}_5 \cdot \text{KHF}_2$

Crystals of potassium oxyfluocolumbate-potassium bifluoride, $\text{K}_2\text{CbOF}_5 \cdot \text{KHF}_2$, were prepared as small monoclinic needles in agreement with previous crystallographic descriptions. According to Balke and Smith,² crystals of this compound have $a:b:c::0.6304:1:0.4888$; $\beta = 86^\circ 41'$. From diffraction photographs taken with the needle axis, c , and the monoclinic axis, b , successively as axis of oscillation, we find the following values, accurate to within about 0.2%: $a = 8.82$, $b = 14.02$, $c = 6.82 \text{ \AA}$.; $a:b:c::0.629:1:0.486$; $\beta = 86^\circ 34'$. The X-ray patterns possess the required symmetry of the point-group, $\text{C}_2^h - 2/m$.

Reflections of the type $\{h k 0\}$ are not observed except for $h + k$ even; $\{h 0 l\}$ reflections are lacking except for both h and l even. These data point to either C_{2h}^6 or C_s^4 as the probable space-group.⁸ The assignment of the crystals to the monoclinic holohedry, and all other data which we shall present later support the choice of $\text{C}_{2h}^6 - \text{C}2/c$ as the correct space-group. The monoclinic unit is end-centered on (001) and contains four stoichiometric

molecules of K_2HCbOF_7 ; we must place 12 K, 4 Cb, 4 O, and 28 F from a consideration of the diffraction data.

Our most useful and comprehensive data were obtained from a series of 15° oscillation photographs taken with $\text{CuK}\alpha$ radiation from a specimen cylindrical along c about 0.11 mm. in diameter, c being used as the rotation axis. The specimen was small enough so that the correction for absorption of X-rays in the specimen varied only slightly with the angle of scattering for the equatorial $\{h k 0\}$ reflections, and could be neglected in considerations involving only relative intensities. Since the crystals are somewhat unstable in contact with the atmosphere, probably due to a tendency to lose hydrogen fluoride, our specimens were protected during exposure by a thin coating of shellac.

During indexing, the intensities of all $\{h k 0\}$ reflections were carefully estimated by visual comparison with an intensity scale prepared for the purpose. Correction of these data by the appropriate values of the Lorentz and polarization factors furnished the relative values of $|F_{(h k 0)}|^2$ and of $|F_{(h k 0)}|$ which were used in the structure determination.

Following methods which have been described in some detail in connection with earlier work⁹ from this Laboratory, the $|F_{(h k 0)}|^2$ data were used to construct a Patterson¹⁰ projection on (001). Consideration of this projection leads to the assignment of columbiums to the fourfold positions⁸ $4(e):0y \frac{1}{4}$; $0\bar{y} \frac{3}{4}$, etc., with $y = 0.178$, of 4K_I to $4(e)$ with $y = 0.66$, and of 8K_{II} to $8(f):xyz$; $\bar{x}\bar{y}\bar{z}$; $\bar{x}, y, \frac{1}{2} - z$; $x, \bar{y}, \frac{1}{2} + z$; etc., with $x = 0.22$, $y = 0.10$.

A knowledge of the positions of columbium and potassium suffices for a determination of the phases of most of the reflections. The contribution of an atomic species in the general position of C_{2h}^6 to the structure factor for the plane $(h k 0)$ is: $A_i = 8f_i \cos 2\pi h x \cos 2\pi k y$. The f -values used in this paper are from the International Tables.¹¹

Leaving out those few reflections for which the assignment of phase seemed doubtful, the reflection amplitudes, $F_{(h k 0)}$, were used to calculate an approximate projection of relative electron den-

(7) A. W. Laubengayer and G. F. Polzer, private communication.

(8) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, Erster Band, p. 102.

(9) J. L. Hoard, THIS JOURNAL, 61, 1252 (1939); J. L. Hoard and H. H. Nordsieck, *ibid.*, 61, 2853 (1939).

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

(11) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, Zweiter Band, p. 571.

sity along c on (001). Using summations for which the Lipson and Beevers¹² strips can be used conveniently, we write for the projected electron density

$$\rho(x,y) = A(x,0) + \Sigma A(x,k) \cos 2\pi ky, \text{ in which}$$

$$A(x,0) = F_{(000)} + 2\Sigma F_{(h00)} \cos 2\pi hx, \text{ and}$$

$$A(x,k) = 2F_{(0k0)} + 4\Sigma F_{(hk0)} \cos 2\pi hx$$

The approximate Fourier projection confirms the assignment of parameter values to columbium and potassium previously given by the Patterson method. Positions of fluorine atoms are indicated in sufficient detail to make possible the complete assignment of phases to the $(hk0)$ reflection amplitudes. The final Fourier plot for (001) is shown in Fig. 1; a comparison of calculated with observed reflection amplitudes is given in Table II.

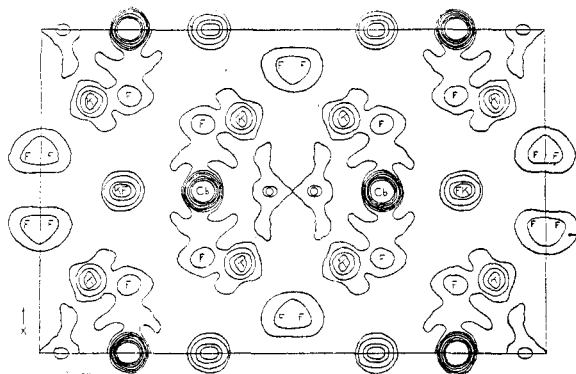


Fig. 1.—Fourier projection of relative electron density along c on (001).

A careful consideration of the Fourier projection shows that it is incompatible with the existence of either seven- or eight-coördination complexes within the crystal. The positions of the fluorine (or oxygen) peaks adjacent to columbium indicate rather that octahedral complexes lying along the two-fold axes are present, with two of the fluorine peaks not resolved from the main one due to columbium. That is, the pair of fluorine atoms above and below columbium define a line which is nearly parallel to c .

The rather large peak at about 0.38, 0 must be interpreted as arising from the near superposition of two fluorine atoms in the general position not associated with columbium. The presence of this peak and of the closely associated one at about 0.62, 0 can have a reasonable interpretation only in case we assume that protons are situated in the centers of symmetry at $1/2, 0, 0$; $1/2, 0, 1/2$. With

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

TABLE II
COMPARISON OF CALCULATED WITH OBSERVED RELATIVE REFLECTION AMPLITUDES FOR $(hk0)$ REFLECTIONS

(hkl)	$F_{(hkl)}$ Obsd.	Calcd.	(hkl)	$F_{(hkl)}$ Obsd.	Calcd.
110	9	9	800	22	20
020	16	-15	820	4	-3
200	14	23	1·13·0	8	-11
130	25	-33	770	0	-1
220	18	-22	840	5	-2
040	24	-22	4·12·0	13	15
310	5	7	5·11·0	17	18
240	4	4	6·10·0	5	-6
150	11	10	3·13·0	5	-5
330	1	1	0·14·0	20	-28
060	42	32	860	15	14
400	32	42	910	7	8
420	18	-20	790	9	-10
260	36	30	2·14·0	7	-7
350	18	19	930	7	-8
170	10	-7	1·15·0	5	-4
440	26	-22	880	9	-9
510	19	21	950	2	-7
080	26	-25	5·13·0	7	-14
370	0	-1	6·12·0	10	9
530	11	-10	4·14·0	14	-20
280	24	-22	7·11·0	0	-2
460	15	16	3·15·0	0	4
190	16	-10	10·0·0	18	23
550	9	5	970	3	-9
600	18	20	0·16·0	0	-2
620	11	-13	10·2·0	7	-13
0·10·0	10	10	8·10·0	0	-2
390	7	-11	2·16·0	4	10
480	17	-19	10·4·0	5	-9
640	5	-2	6·14·0	4	-9
2·10·0	14	-13	5·15·0	9	-12
570	5	-5	990	0	-1
1·11·0	12	14	10·6·0	10	19
710	6	-9	1·17·0	7	14
660	25	22	7·13·0	2	-3
730	0	2	4·16·0	0	3
4·10·0	0	5	8·12·0	5	7
0·12·0	16	18	11·1·0	0	-2
590	0	-4	3·17·0	7	12
3·11·0	5	3	11·3·0	0	3
750	10	11	10·8·0	5	-17
2·12·0	10	8	0·18·0	4	8
680	15	-17	9·11·0	5	9

the z -parameter of fluorine about zero (or one-half), fluoride ions would be associated in pairs with protons to give HF_2^- groups lying approximately parallel to a .

If, in addition, potassium in 8(f) be assigned a z -parameter of about $3/4$, the structure as a whole will be dimensionally reasonable. Comparison of observed intensities of $\{h k 2\}$ reflections with those calculated on the basis of these approximate parameters provides strong support

for the correctness of the structure in its general outline.

To complete the structure determination in convincing fashion it is desirable to have a Fourier projection of relative electron density on (100), (010), or some other plane giving directly the z -parameters. The habit of the crystals, the apparent absence of a favorable cleavage, and the general prevalence of twinning on (100) combine to make difficult the experimental problem. We succeeded, however, in cutting from a comparatively large crystal a specimen which could be ground into a nearly cylindrical rod about 0.15 mm. in diameter along b as axis. This specimen proved to be a twin of the usual type, the two crystals being very nearly equal in size. To minimize the effects of this twinning the intensity data for the equatorial $\{h0l\}$ reflections were handled as follows: the observed intensities for the two planes of each form were averaged for each crystal; the sum of these averages was taken as the relative intensity for the given form from the specimen as a whole. The relative intensities obtained in this way for $\{h02\}$ and $\{h0\bar{2}\}$ reflections agreed satisfactorily with those observed on our earlier photographs taken with c as rotation axis. The reflection amplitudes, $F_{(h0l)}$, were taken proportional to the square roots of the quantities obtained by correction of these estimated intensities for absorption and for the effect of the Lorentz and polarization factors.

One columbium, one potassium, and two fluorine (or oxygen) atoms per stoichiometric molecule are exactly in phase and contribute their maximum scattering to $\{h0l\}$ reflections. The signs to be associated with the magnitudes, $|F_{(h0l)}|$, can be determined at once, therefore. The resulting Fourier projection is necessarily crude, and, at best, its precision is limited by the overlapping of peaks due to two potassium and two fluorine atoms in the region around $1/4, 3/4$. The plot is consistent nevertheless with our picture of the general character of the structure, and furnishes directly values for the z -parameters of potassium and fluorine leading to reasonable interatomic distances. The observed difference in intensity between corresponding planes, $(h0l)$ and $(h0\bar{l})$, is small in general; accordingly, the values of the variable z -parameters are near to those previously discussed in connection with the (001) projection.

Complete parameter data for $K_2CbOF_5 \cdot KHF_2$ are given in Table III.

TABLE III
PARAMETER DATA FOR $K_2CbOF_5 \cdot KHF_2$

Atom	Position	Atomic coordinates		
		x	y	z
Cb	4(e)	0	0.178	$1/4$
K	4(e)	0	.660	$1/4$
K	8(f)	0.217	.100	0.79
O	4(e)	0	.044	$1/4$
F	4(e)	0	.31	$1/4$
F	8(f)	.205	.178	0.17
F	8(f)	.05	.178	.51
F	8(f)	.380	.03	.48
H	4(b)	0	$1/2$	0

TABLE IV
COMPARISON OF CALCULATED WITH OBSERVED RELATIVE REFLECTION AMPLITUDES FOR $(hk2)$ AND $(hk\bar{2})$ REFLECTIONS

(hkl)	$ F_{(hkl)} $ Obsd.	Calcd.	(hkl)	$ F_{(hkl)} $ Obsd.	Calcd.
112	5	5	192	3	6
11 $\bar{2}$	5	11	19 $\bar{2}$	0	3
022	8	11	552	2	5
202	4	10	55 $\bar{2}$	0	0
20 $\bar{2}$	2	6	602	6	15
132	0	1	60 $\bar{2}$	6	17
13 $\bar{2}$	6	9	622	5	12
222	6	10	62 $\bar{2}$	0	1
22 $\bar{2}$	5	7	0·10·2	0	5
042	13	13	392	3	2
312	3	4	39 $\bar{2}$	5	8
31 $\bar{2}$	4	7	482	3	7
242	3	5	48 $\bar{2}$	4	12
24 $\bar{2}$	0	1	642	0	2
152	8	28	64 $\bar{2}$	0	4
15 $\bar{2}$	0	1	2·10·2	6	9
332	0	1	2·10· $\bar{2}$	5	6
33 $\bar{2}$	0	2	572	0	0
062	8	7	57 $\bar{2}$	0	1
402	13	30	662	8	19
40 $\bar{2}$	13	31	66 $\bar{2}$	6	10
422	0	0	4·10·2	2	4
42 $\bar{2}$	5	5	4·10· $\bar{2}$	0	1
262	12	13	0·12·2	7	10
26 $\bar{2}$	8	6	592	0	3
352	0	1	59 $\bar{2}$	0	2
35 $\bar{2}$	11	8	2·12·2	4	4
172	0	4	2·12· $\bar{2}$	4	4
17 $\bar{2}$	0	1	682	6	14
442	6	7	68 $\bar{2}$	3	5
44 $\bar{2}$	4	5	802	9	14
512	3	6	80 $\bar{2}$	7	10
51 $\bar{2}$	3	6	822	4	8
082	8	10	82 $\bar{2}$	4	11
372	0	3	4·12·2	5	6
37 $\bar{2}$	0	1	4·12· $\bar{2}$	4	7
532	5	9	5·11·2	5	11
53 $\bar{2}$	4	6	5·11· $\bar{2}$	4	10
282	9	13	6·10·2	2	5
28 $\bar{2}$	7	8	6·10· $\bar{2}$	0	1
462	6	7			
46 $\bar{2}$	8	14			

Calculated and observed amplitudes for certain general classes of reflections appearing on photographs taken with c as rotation axis are compared in Table IV. The agreement is good in general, and indicates that the parameter data are reasonably satisfactory.

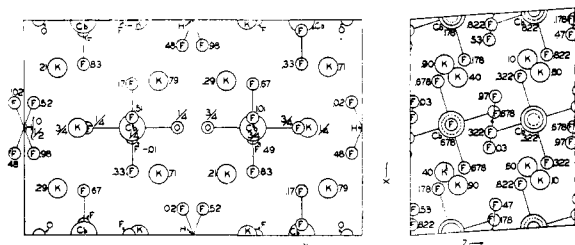


Fig. 2.—Diagrammatic projections of the unit of structure along c on (001) and on (010). The distance of each atom above the plane of projection is indicated.

Diagrammatic projections of the derived structure on (001) and (010) are shown in Fig. 2. The data do not permit us to distinguish between oxygen and fluorine. If the structure conforms exactly to the requirements of the space-group, oxygen atoms would lie on the two-fold axes, occupying one of the sets of positions starting either in 0, 0.044, $1/4$ or in 0, 0.312, $1/4$. In Fig. 2, oxygen atoms are placed arbitrarily in the first set. It is highly probable in any case that oxygen is bonded to columbium to give octahedral CbOF_6 groups, and that the maximum degree of random character, if any be present, could involve nothing more than failure to distinguish between oxygen and fluorine in defining the orientation of the complex. On this basis, the structure can be described briefly as a salt-like aggregate of K^+ , HF_2^- , and CbOF_5^- .

The octahedral complex is nearly regular with an average Cb-F or Cb-O distance of 1.88 Å., and F-F separations between adjacent neighbors of about 2.65 Å. In the seven-coördination complex, CbF_7^- , the corresponding average distances were found^{1a} to be Cb-F, 1.97 Å.; F-F, 2.47 Å. The dimensions of these complexes are mutually consistent, and are in agreement with published data on ionic radii.¹³

The separation of the fluorine ions in the bifluoride group is found to be about 2.30 Å., to be compared with the accurately determined value, 2.26 Å., in potassium bifluoride.¹⁴

Each potassium ion in 4(e) has as nearest

neighbors six fluorine atoms at distances varying from about 2.60 to 2.82 Å., the average being 2.71 Å. The sum of the ionic radii for coördination number six is 2.66 Å. Each potassium ion of this kind has also as near neighbors four fluorine atoms at 3.4 Å., and two protons at 2.82 Å. This rather small K^+-H^+ separation must have a destabilizing effect upon the structure, and helps to account for the slow decomposition of the crystals when exposed to the atmosphere.

Each potassium ion in the general position has as nearest neighbors seven fluorine atoms at distances varying from about 2.67 to 2.86 Å., the average being 2.76 Å. Three other fluorine atoms are situated 3.2, 3.7, and 3.9 Å., respectively, from a potassium ion of this kind.

The minimum separation between fluorine atoms of adjacent complexes is about 3.1 Å.

At least two other compounds, namely, $\text{K}_2\text{SnF}_6 \cdot \text{KHF}_2$ and $\text{K}_2\text{PbF}_6 \cdot \text{KHF}_2$, have been reported¹⁵ as completely isomorphous with $\text{K}_2\text{CbOF}_5 \cdot \text{KHF}_2$.

Summary

In the first section of this paper we point out that X-ray diffraction data prove the existence of three stereochemically distinct types of fluorocolumbate and oxyfluorocolumbate complexes: namely, the octahedral CbOF_6^- ion, and two seven-coördination groups, CbOF_7^- and CbF_7^- , which possess the point-group symmetries C_3^v and C_2^v , respectively. Data on four crystalline compounds containing these complex anions are summarized in Table I.

In the second section we use X-ray data to show that crystals of potassium oxypentafluorocolumbate-potassium bifluoride, $\text{K}_2\text{CbOF}_5 \cdot \text{KHF}_2$ or K_3HCbOF_7 , possess a monoclinic unit cell with $a = 8.82$, $b = 14.02$, $c = 6.82$ Å., $\beta = 86^\circ 34'$, space-group $\text{C}_{2h}^6 - \text{C}2/c$, containing four stoichiometric molecules. A Patterson projection on (001) calculated from visually estimated $\{hk0\}$ intensities is used to fix x and y coördinates of columbium and potassium. This simplifies the calculation of a Fourier projection (Fig. 1) of relative electron density on (001), which yields x and y coördinates for all atoms (Table III). A Fourier analysis of $\{h0l\}$ data furnishes approximate values of the four variable z -parameters. The parameter data of Table III account satisfactorily for the observed intensities of X-ray

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(14) L. Helmholz and M. Rogers, THIS JOURNAL, 61, 2590 (1939).

(15) P. Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1906, Erster Teil, p. 464.

reflections (Tables II and IV), and lead to reasonable interatomic distances. The structure (Fig. 2) is an aggregate of K^+ , octahedral $CbOF_6^-$,

and HF_2^- ions; the double salt formula, $K_2CbOF_6 \cdot KHF_2$, is appropriate, therefore.

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Studies in the Physical Chemistry of Insulin. II. Crystallization of Radioactive Zinc Insulin Containing Two or More Zinc Atoms*

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I. Introduction

The molecular weight of insulin as estimated by the equilibrium ultracentrifuge is reported as 35,100,¹ and from results with the sedimentation ultracentrifuge¹ in combination with those from diffusion measurements² as 40,900. The molecular weight of insulin calculated from the dimensions of the unit cell revealed by X-ray measurements is 38,500 and as corrected for residual water, 37,400.³⁻⁶

The zinc content of insulin was given by Scott and Fisher⁷ as 0.52% by weight for crystalline zinc insulin. The minimal molecular weight, assuming one atom of zinc, would thus be 12,570, or three atoms of zinc 37,710, a value in good agreement with that derived from X-ray or ultracentrifugal measurements.

Cohn, Ferry, Livingood and Blanchard⁸ succeeded in crystallizing radioactive zinc insulin. Beginning with crystalline zinc insulin⁹ they electrolyzed the insulin free of zinc from acid solution. Amorphous, isoelectric insulin prepared in this manner has since been shown to contain a negligible amount of zinc, namely, less than 0.01%.¹⁰ When they substituted the radioactive zinc (Zn^{65} isotope of half-life 250 days) for ordinary

zinc, taking precautions to maintain the excess of zinc in solution at a low level, the radioactive zinc insulin crystals that separated rarely contained more than 0.31% although one preparation was obtained which contained 0.36% radioactive zinc.¹¹ If the radioactive zinc insulin that was crystallized contained but 2 atoms of zinc, which was assumed, the molecular weight on the basis of the lower zinc content reported would have been 42,200, and of the higher, 37,300, results which are also in good agreement with the molecular weights estimated from X-ray and ultracentrifuge studies.

Preparation of Radioactive Zinc.—The radioactive zinc that was available when these earlier measurements were carried out had been prepared by the cyclotron at the University of California and was supplied us by Dr. Livingood. Radioactive zinc has now been prepared by the Harvard cyclotron for the newer experiments that are here reported. Zinc was bombarded with 11-million volt deuterons for a total exposure of 500 microampere hours during January, February and March, 1940. The proportion of radioactive zinc atoms in the final product was of the order of one in ten billion; this was sufficiently concentrated so that analyses for radioactive zinc content could be carried out with reasonable accuracy on samples of 1 mg. of zinc, corresponding to zinc insulin samples of the order of 0.2 g. The bombarded zinc was treated chemically¹² to remove gallium and copper, and the zinc was prepared as the sulfide.

The zinc sulfide was transformed into the chloride for the crystallization of the zinc insulin.^{13,7} Radioactivity, and therefore zinc content, was determined upon dried samples with a Lauritzen-type quartz fiber electroscop, using 2.3 mm. of aluminum filtration, so that only gamma rays were recorded. Comparison was made in each case with a weighed standard sample of the radioactive zinc sulfide. As a further analytical check, zinc sulfide was transformed into zinc ammonium phosphate¹⁴ and then

* Presented at the Fifth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Columbia University, New York, December 30, 1940, to January 1, 1941.

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(8) Cohn, Ferry, Livingood and Blanchard, *Science*, **90**, 183 (1939).

(9) Furnished through the kindness of Eli Lilly and Co., Indianapolis, Indiana.

(10) We are indebted to Dr. Vincent du Vigneaud and to Dr. Julian Rachele of the Department of Biochemistry of the Cornell University Medical College for proving that our amorphous insulin was zinc-free on the basis of polarigraphic measurements; and for the results of analysis of the ordinary zinc insulin crystals.

(11) In a paper presented to the 100th meeting of the American Chemical Society, September 12, 1940, L. C. Maxwell and R. F. Feldkamp reported that they had confirmed these results by obtaining insulin crystals with a zinc content of 0.355%.

(12) We are indebted to Dr. A. K. Solomon for carrying out this chemical separation.

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