· been made at intervals of 5° over the temperature range, 5 to 40°. The molality of lead bromide was varied from 0.0015 to 0.018. The standard potentials of the cell were evaluated

with the use of the La Mer, Gronwall and Greiff extension of the Debye–Hückel equation. Activity coefficients were calculated.

Structures of Complex Fluorides.[1]   Potassium Oxyhexafluocolumbate, K₃CbOF₆

BY M. B. WILLIAMS AND J. L. HOARD

Hampson and Pauling[2] have reported X-ray data which indicate that $ZrF_7^=$ ions with the point group symmetry of C_{3v}-$3m$ exist within cubic crystals of potassium and ammonium heptafluozirconates. Cubic crystals of potassium oxyfluocolumbate, K₃CbOF₆, might be expected to have a structure like that of potassium heptafluozirconate and to contain $CbOF_6^=$ ions of symmetry C_{3v}. The fact that two compounds of similar formulas both crystallize in the cubic system is, however, by no means conclusive evidence that they belong to the same structural type (compare, for example, potassium and cesium chlorides). It has seemed of particular interest to investigate the structure of K₃CbOF₆ in detail since monoclinic crystals of potassium heptafluocolumbate, K₂CbF₇, have been shown[1b] to contain discrete $CbF_7^=$ ions with the point-group symmetry of C_{2v}-mm, entirely different from that found for $ZrF_7^=$. There are, moreover, certain features of the structure proposed by Hampson and Pauling[2] for the heptafluozirconates of potassium and ammonium which make it desirable to investigate other compounds that are presumably of a similar type. We find actually that crystals of K₃CbOF₆ and K₃ZrF₇ give rise to closely similar X-ray diffraction data.

Crystalline potassium oxyfluocolumbate, K₃CbOF₆, has been prepared in the form of small shining cubes by several investigators.[3] Marignac[3a] reported that his crystals were doubly refracting; Balke and Smith[3b] observed only a faint double refraction along the edges of their specimens, and Baker[3c] concluded that his preparation

was perfectly inactive in polarized light. The specimens of K₃CbOF₆ used in our work were small brilliant cubes which seemed to be perfectly isotropic under the polarizing microscope and entirely stable in air. They resulted from the isothermal evaporation of an aqueous solution prepared from freshly recrystallized K₂CbOF₆·H₂O and KF taken in the mole ratio one to four. It may be noted by way of comparison that crystals of K₅ZrF₇ commonly assume an octahedral habit.

Accurately oriented Laue and oscillation photographs from K₃CbOF₆ show no deviation from the point-group symmetry of O_h-$m3m$; the probable space-group of the crystal is thus limited to O_h, O, or T_d. The lattice constant a is 8.87 Å. as given by back reflection data, and the corresponding unit cell contains four stoichiometric molecules. The absence of reflections from planes with mixed indices points to a face-centered lattice.

Excepting that $a = 8.95$ Å. (instead of 8.87 Å.) all statements of the preceding paragraph apply equally well to K₃ZrF₇.[2] Indeed a further detailed comparison between the observed intensities of X-ray powder lines for K₃CbOF₆ (Table I) and the data reported[2] for K₃ZrF₇ makes it quite certain that the two substances crystallize with similar structures. Except for a few lines at large angles of scattering, the description of the intensity patterns is nearly identical for the two compounds. Such minor differences as appear are readily understood in terms of the small difference in lattice constant, the substitution of columbium for zirconium and of oxygen for fluorine, and possible variations in the effects of thermal vibrations on the scattering of X-rays by the crystals.

To establish the exact character of the structural type in which K₃CbOF₆ and K₃ZrF₇ (also

(1) For earlier papers in this series see (a), THIS JOURNAL, **57**, 1985 (1935); (b), *ibid.*, **61**, 1252 (1939); (c), **61**, 2849 (1939); (d), **62**, 3126 (1940); (e), **63**, 11 (1941); (f), **64**, 633 (1942).

(2) G. C. Hampson and L. Pauling, *ibid.*, **60**, 2702 (1938).

(3) See (a) Ch. de Marignac, *Bibl. univ., Arch. sc. phys. nat. Genève*, **23**, 259 (1865); (b) C. W. Balke and E. F. Smith, THIS JOURNAL, **30**, 1637 (1908); (c) H. Baker, *J. Chem. Soc.*, **35**, 760 (1879).

$(NH_4)_3ZrF_7)$ crystallize is another matter, however, for, as pointed out by Hampson and Pauling, there is no space-group based upon a cubic face-centered lattice and leading to the observed holohedral Laue symmetry which provides atomic positions for four stoichiometric molecules of K_3ZrF_7 or K_3CbOF_6. Yet each of these apparently mutually incompatible data seems to be well-established. We shall assume, with Hampson and Pauling, that the structural type involves some randomness of atomic arrangement, and that the data given above for the size of the unit cell, type of lattice, and Laue symmetry are statistical results. Their choice of structure for K_3ZrF_7 and $(NH_4)_3ZrF_7$ is supported strongly by the resulting good agreement between calculated and observed intensities for X-ray powder lines.

The detailed arguments leading to the selection of the K_3ZrF_7 structural type have been reported[2] and we shall discuss only the data pertinent to K_3CbOF_6. The structure is based upon the space-group[4] O_h^5-$Fm3m$. The atomic distribution in K_3CbOF_6 is as follows

4Cb in 32(f); xxx, etc., with $x = 0.98$
4O in 32(f), with $x = 0.11$
8K_I, K_{II} in 32(f), with $x = 0.28$
4K_{III} in 32(f), with $x = 0.52$
12F in 192(l); xyz, etc., with $x = 0.19$, $y = 0.95$, $z = 0.90$
12F in 192(l), with $x' = 0.76$, $y' = 0.93$, $z' = 0.98$

These values for the atomic coördinates differ slightly from those given[2] for K_3ZrF_7 but in no case by more than 0.01. We find that the new parameters given above lead to a little better agreement in general between calculated and observed intensities, especially for {$hk0$} reflections appearing on oscillation photographs.

In Table I we present powder photographic data for K_3CbOF_6. Hartree's values for the form factors of potassium and fluorine, and the Thomas–Fermi values for columbium were used in the calculations, which otherwise followed the procedure reported[2] for K_3ZrF_7. Inspection of Table I shows that with the exception of a few reflections at large scattering angles (which are for the most part very weak) the calculated intensities parallel those visually estimated very closely. We have compared also calculated with observed intensities for seventeen {$hk0$} reflections (all that are observable with $CuK\alpha$ radiation) appearing on oscillation photographs and

(4) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935, Vol. 1.

again find fairly good agreement. These data provide considerable support for the correctness of the proposed structure and indicate that the atomic coördinates given above are not seriously in error.

TABLE I

Vvs = very very strong; Vs = very strong; S = strong; Ms = medium strong; M = medium; Wm = weak medium; W = weak; Vw = very weak; Vvw = very very weak; Abs = absent.

Indices hkl	Intensity Obsd.	Calcd.	Indices hkl	Intensity Obsd.	Calcd.
111	Vs	116	{751, 555}	Vw	2.0
200	Ms	56	662	Vvw	1.9
220	Vvs	197	840	Vw	2.0
113	Wm	8.8	{911, 753}	Vvw	0.5
222	Abs	0.4	842	Vw	3.5
400	Ms	44	664	Vw	2.3
133	W	6.1	931	Vvw	0.8
420	M	18	844	Vw	1.4
422	S	81	{771, 755, 933}	Vvw	2.9
{333, 511}	Wm	6.6	{10·0·0, 860}	Vvw	2.0
440	M	21	{10·2·0, 862}	W	3.9
531	Wm	11	{951, 773}	Vw	2.1
{442, 600}	Wm	7.5	{662, 10·2·2}	Vw	2.4
620	M	15	953	W	4.3
533	Vvw	0.7	{864, 10·4·0}	W	3.8
622	Vvw	4.7	10·4·2	M	0.2
444	Vw	2.7	{11·1·1, 775}	Vw	1.6
{551, 711}	Vw	1.0	880	Vvw	0.9
640	Vw	2.1			
642	M	14			
{731, 553}	Vw	2.4			
800	Vvw	0.7			
733	Vvw	1.6			
{820, 644}	Vw	3.3			
{660, 822}	W	4.7			

The probable structure of K_3CbOF_6 is very similar to that of $(NH_4)_3FeF_6$,[5] which, also based upon the space-group O_h^5, has the following atomic coördinates[4]

8N_I in 8(c): $1/4$ $1/4$ $1/4$, etc.
4N_{III} in 4(b): $1/2$ $1/2$ $1/2$, etc.
4Fe in 4(a): 000, etc.
24F in 24(e): $x00$, etc., with $x = 0.21$

These positions correspond to a highly symmetrical arrangement of NH_4^+ and regular octahedral $FeF_6^=$ ions. With the substitution of K^+ for NH_4^+ and $CbOF_6^=$ for $FeF_6^=$ ions the symmetry of a single cell is necessarily lowered,

(5) R. W. G. Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, N. Y., 2nd ed., 1931, p. 307.

although a dimensionally satisfactory arrangement[2] can be based upon the cubic space-group T^4-$P2_13$. In K_3CbOF_6 the randomness of atomic arrangement is as follows: a columbium atom may occupy any one of the eight vertices of a small cube (ca 0.04 a on an edge) circumscribed about a lattice point, which, in $(NH_4)_3FeF_6$, is occupied by an iron atom. A similar statement holds for the substitution of K^+ for NH_4^+ ions. The $CbOF_6^{\equiv}$ ion of symmetry C_{3v} may be oriented with its unique three-fold axis pointing in either sense along any one of the four cube diagonals. In addition the complex may be rotated about its three-fold axis in either sense through about $10°$ from the symmetrical orientation relative to the cube axes. This description corresponds to sixteen equally probable orientations accessible to each $CbOF_6^{\equiv}$, and leads statistically to the observed results for the size of the unit cell, type of lattice, and Laue symmetry. A full discussion of this subject is given by Hampson and Pauling.[2]

The configuration of the $CbOF_6^{\equiv}$ ion may be regarded as derived from an octahedral CbF_6^- group by adding an oxygen ion along one of the three-fold axes accompanied by some distortions so as to minimize the effects of steric hindrance. The resulting group has a unique three-fold axis. Our assignment of parameters places oxygen on this unique axis of the complex but it is evident that the diffraction data are not adequate to decide this point.

The parameter data correspond to a Cb–F or Cb–O separation of about 2.0 Å. and F–F or O–F separations of adjacent pairs of atoms of about 2.52 Å. In K_2CbF_7[1b] the more accurately known parameters lead to an average Cb–F distance of 1.97 Å. within the $CbF_7^{\equiv}$ ion of symmetry C_{2v}-mm.

It is rather surprising that quinquevalent columbium should form seven-coördination complexes with two entirely different configurations, namely, that of $CbOF_6^{\equiv}$ (C_{3v}) and that of $CbF_7^{\equiv}$ (C_{2v}). There is, however, some evidence which indicates that these alternative arrangements of seven bonds may be of comparable stability.

It has been shown[6] that the set of atomic orbitals expected to be primarily concerned in bond formation for Cb^V (and Zr^{IV}), namely, $4d^55sp$, can lead to either of the observed configurations. This conclusion is based only upon symmetry considerations and explicit forms for the bond orbitals have not been given. It is true also that the alternative arrangements are about equally satisfactory in a steric sense,[1b] and that electrostatic contributions to the bonds should be about equally important in the two cases. Although these tentative statements are not a reflection of any precise knowledge regarding the actual electron distributions within these complexes it seems plausible to assume that the alternative configurations do not differ greatly in stability. Upon this basis it would be the packing relations between the given cations and the complex anions which would determine the configuration to be assumed by $CbF_7^{\equiv}$ or $CbOF_6^{\equiv}$ in the formation of a crystalline phase.

Summary

X-Ray photographs of crystalline potassium oxyhexafluocolumbate, K_3CbOF_6, show cubic holohedral symmetry, and indicate a face-centered unit of structure with $a = 8.87$ Å. containing four stoichiometric molecules. As in the case of the heptafluozirconates,[2] K_3ZrF_7 and $(NH_4)_3ZrF_7$, these data are incompatible with the usual rigorous application of the theory of space-groups, and it is necessary to assume that they are statistical results for a structure in which there is some randomness in the atomic arrangement. Our X-ray data for K_3CbOF_6 are accounted for satisfactorily by the structural type proposed for the heptafluozirconates. Crystalline K_3CbOF_6 is then an aggregate of K^+ and $CbOF_6^{\equiv}$ ions of point-group symmetry C_{3v}. The $CbF_7^{\equiv}$ ion in crystalline potassium heptafluocolumbate[1b] possesses the symmetry of C_{2v}, entirely different from that of $CbOF_6^{\equiv}$ or $ZrF_7^{\equiv}$. There is some reason to believe that the alternative configurations may be of comparable stability.

(6) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).