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The Structure of Ammonium Heptafluozirconate and Potassium Heptafluozirconate and the Configuration of the Heptafluozirconate Group

BY G. C. HAMPSON AND LINUS PAULING

The only work which has been reported so far on the structure of the so-called intercalation compounds of composition M_xAB_7 is that of Hassel and Mark,[1] who carried out an X-ray investigation of the crystals of ammonium heptafluozirconate, $(NH_4)_3ZrF_7$, and ammonium heptafluohafniate, $(NH_4)_3HfF_7$. Both crystals are cubic, the cube edge being 9.35 and 9.40 Å., respectively, and both contain four molecules in the unit cell. From their data Hassel and Mark were unable to deduce the space group absolutely, but they considered that O_h^4 was the most probable and suggested a structure based on this. This structure was built up of NH_4^+ ions, $[ZrF_6]^=$ ions, and F^- ions. It is of considerable interest to know whether odd coördination complexes involving seven atoms surrounding a central atom can or cannot exist, and the work of Hassel and Mark has been quoted[2] as proving the latter contention. It must be remembered, however, that Hassel and Mark's structure was put forward only as a possibility, and it is now clear from our knowledge of atomic and ionic radii that this particular structure is highly improbable.

In the first place, large numbers of ions of the same charge (*e. g.*, six NH_4^+ ions) are grouped together, which is a very unlikely arrangement. Moreover, taking even the most favorable limits of their parameter values it is found that their structure places an ammonium ion only 1.54 Å. from a fluoride ion, whereas the nearest possible distance even assuming hydrogen bond formation is about 2.6 Å. (2.63 Å. is observed in NH_4F[3] and 2.76 Å. in NH_4HF_2[4]).

In view of these facts a reinvestigation of the problem seemed to be justified. We have carried out a study of the structure of ammonium heptafluozirconate and potassium heptafluozirconate, using data obtained from Laue, oscillation, and powder photographs, and have found that the substances do not contain $[ZrF_6]^=$ and F^- ions, but instead contain the complex ion $[ZrF_7]^{\equiv}$, in which zirconium has the coördination number seven. The structure of the crystals is similar to that of $(NH_4)_3AlF_6$, with the $[AlF_6]^{\equiv}$ complexes replaced by $[ZrF_7]^{\equiv}$; the orientation of these complexes is not uniquely determined, however, but shows some randomness, permitting the crystals to assume higher point-group and space-group symmetry than would be possible otherwise.

Crystals of $(NH_4)_3ZrF_7$ and K_3ZrF_7 were grown by dissolving zirconium fluoride in a hot solution containing a large excess of ammonium fluoride or potassium fluoride and allowing the solutions to crystallize slowly.[5] Small transparent optically isotropic octahedra were obtained, with faces which do not show very good reflections; the crystals deteriorate fairly rapidly on exposure to the atmosphere, and were usually protected during the preparation of the X-ray photographs with a thin film of oil or vaseline.

The Structure of $(NH_4)_3ZrF_7$.—Oscillation photographs about [110] (copper Kα radiation), Laue photographs with the X-ray beam parallel to [111], and powder photographs (copper Kα radiation) were prepared of $(NH_4)_3ZrF_7$. No reflections were found to occur from planes with mixed indices (*hkl* part odd and part even). This observation is in disagreement with the results of Hassel and Mark, who reported the presence of reflections of this type. The only such reflections recorded in their tables are (110) and (310). We prepared 5° oscillation photographs permitting reflection from these planes, using long exposure times, and were unable to detect the reflections on our films; there is also no sign of these reflections on our powder photographs, which show more lines than those reported by Hassel and Mark. It seems likely that these investigators were misled by the X-ray continuum, by β lines, or by some other feature of their photographs, and that their report of reflections from planes of mixed indices was due to misinterpretation of their data. Their choice of space group (O_h^4) and their suggested structure were based on

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[1] O. Hassel and H. Mark, *Z. Physik*, **27**, 89 (1924).

[2] For example, by W. G. Penney and J. S. Anderson, *Trans. Faraday Soc.*, **33**, 1363 (1937).

[3] W. H. Zachariasen, *Z. physik. Chem.*, **127**, 218 (1927).

[4] L. Pauling, *Z. Krist.*, **85**, 380 (1933).

[5] C. Marignac, *Ann. chim.*, **60**, 257 (1860); H. Baker, *J. Chem. Soc.*, **35**, 760 (1879).

this presumably erroneous observation, and need not be discussed further.

The absence of any reflections from planes of mixed indices on our oscillation, Laue, and powder photographs makes it highly probable that the crystal lattice is face-centered.

Laue photographs taken with the X-ray beam parallel to [111] of thin crystal sections obtained by grinding octahedra on parallel octahedral faces were found to show a three-fold axis and three planes of symmetry, corresponding to the point groups T_d, O, and O_h. Since the Laue symmetry is of great importance in this investigation, the photographs were very carefully inspected, and were also studied by use of the α-ray integrating microphotometer.[6] Carbon prints were made of the photographs and the intensities of Laue spots due to planes of various holohedral forms were measured with the microphotometer, the intensity measurements being reproducible to within about 5%. No deviation from holohedry was found.

The powder photographic data for $(NH_4)_3ZrF_7$ (Table I) correspond to the value $a_0 = 9.365 \pm 0.010$ Å. for the edge of the unit cube, in good agreement with the value 9.353 Å. given by Hassel and Mark. With $4(NH_4)_3ZrF_7$ in the unit the density is calculated to be 2.32 g./cc.; the directly measured experimental value, 2.20 g./cc. (Hassel and Mark), is slightly smaller.

We have now to locate 4Zr, $12NH_4$, and 28F in the unit. The space groups compatible with the observed holohedral Laue symmetry and based on the face-centered cubic lattice are T_d^2, T_d^5, O^3, O^4, O_h^5, O_h^6, O_h^7, and O_h^8. Of these T_d^5, O^4, O_h^6, O_h^7, and O_h^8 provide no positions for the four zirconium atoms, and are accordingly ruled out of consideration.[7] T_d^2 provides four sets of no-parameter positions (4a, 4b, 4c, 4d) for four equivalent atoms, and sets of positions for 16, 24, 48, and 96 equivalent atoms; with 4Zr, $4(NH_4)_{I}$, $4(NH_4)_{II}$, and $4(NH_4)_{III}$ occupying 4a, 4b, 4c, and 4d, there is no way of placing all of the 28 fluorine atoms, so that this space group is also ruled out. O^3 and O_h^5 are ruled out in the same way; *there is no set of atomic positions for* $4(NH_4)_3ZrF_7$ *in the unit compatible with the observed holohedral Laue symmetry and face-centered lattice of the crystal.*

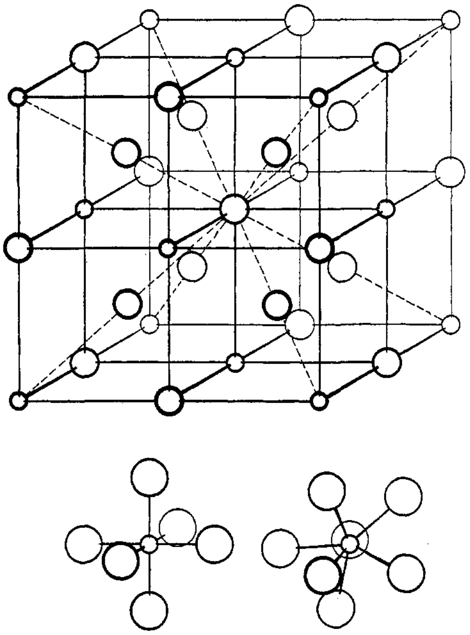

Fig. 1.—In the structure of $(NH_4)_3AlF_6$ each of the aluminum atoms (smallest circles) is surrounded by six fluorine atoms to form the octahedron shown below at the left side. In $(NH_4)_3ZrF_7$ and K_3ZrF_7 the $[AlF_6]^{\equiv}$ complexes are replaced by $[ZrF_7]^{\equiv}$ complexes such as that shown below at the right side.

The resolution of this difficulty might be achieved by assuming that the Laue symmetry is actually hemihedral or that the structure is actually based on a lattice with fewer lattice points than the face-centered lattice of the four-molecule unit, and that the intensities and intensity differences of X-ray reflections differentiating the actual Laue symmetry and lattice from those simulated are so small as to have been overlooked in our careful examination of the photographs. This is rendered improbable, however, by the fact that the crystal does not contain unlike atoms which resemble one another closely enough in stereochemical properties and X-ray reflecting power[8] to permit the simulation of a pseudo-unit in the usual way.

It is probable instead that ammonium heptafluozirconate is to be added to the list of crystals with structures involving some randomness of atomic arrangement, the treatment of which requires variation from the usual methods of application of the theory of space groups. We have found that a reasonable structure involving some randomness in orientation of $[ZrF_7]^{\equiv}$ complexes

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[6] W. T. Astbury, *Proc. Roy. Soc.* (London), **A123**, 575 (1929). We are indebted to Professor J. H. Sturdivant for the use of the microphotometer and to Dr. N. Elliott for assistance with the measurements.

[7] "International Crystal Structure Tables."

[8] As, for example, tetrahedrally coördinated aluminum and silicon atoms in sodalite, $Na_4Al_3Si_3O_{12}Cl$; L. Pauling, *Z. Krist.*, **74**, 213 (1930).

can be formulated which accounts satisfactorily for the X-ray data for $(NH_4)_3ZrF_7$, and that a similar structure can also be assigned to K_3ZrF_7.

The number of possible structures involving randomness of atomic arrangement of one type or another is so great that a straightforward structure determination cannot be carried out; it is necessary instead to apply the method of suggesting reasonable structures and testing them by comparison with the X-ray data. Now the X-ray photographs of $(NH_4)_3ZrF_7$ are closely similar to those of $(NH_4)_3AlF_6$, and it accordingly seems likely that the structure of $(NH_4)_3ZrF_7$ is to be obtained by the introduction of an additional fluorine ion in the $(NH_4)_3AlF_6$ arrangement.[9] This arrangement (Fig. 1) places 12 NH_4 at ${}^1/_2\,{}^1/_2\,{}^1/_2$, ${}^1/_4\,{}^1/_4\,{}^1/_4$, ${}^3/_4\,{}^3/_4\,{}^3/_4$, etc. (plus the positions obtained by application of the translational operations of the face-centered lattice), and 4 octahedral MF_6 groups at 000, etc. Additional fluorine ions might then be inserted at positions such as uuu with $u \cong {}^1/_8$. A fluorine ion here is about 1.9 Å. from three fluorine ions and an ammonium ion. This distance is too small, the minimum distance of approach expected for two fluorine ions (ionic radius 1.36 Å.) being about 2.4 Å. and for a fluorine ion and an ammonium ion about 2.6 Å. It is possible, however, to distort the arrangement of the adjacent ions in such a way, described below, as to give acceptable values to the interionic distances.

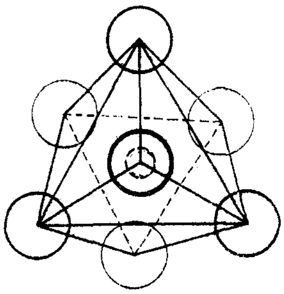

Fig. 2.—The $[ZrF_7]^{=}$ complex viewed along its three-fold axis.

The distance of the seventh fluorine ion at ${}^1/_8\,{}^1/_8\,{}^1/_8$ from the zirconium atom at 000 (1.9 Å.) is about the same as the zirconium-fluorine distance for the other six fluorine atoms—this way of inserting the seventh fluorine ion thus leads to the formation of a $[ZrF_7]^{=}$ complex. The existence of such a complex is to be expected. The ratio of univalent radii of zirconium and fluorine[10] is 0.80, which corresponds to stability of the coördination polyhedra[11] with coördination numbers 7, 8, or 9.

The distortion of the $[ZrF_6]^{=}$ octahedron accompanying insertion of the seventh fluoride ion will be such as to make the twelve small F–F distances equal, with the seven Zr–F distances also equal. The resulting polyhedron, shown in Fig. 2, has the angles F_3–Zr–F_7, F_3–Zr–F_6, F_4–Zr–F_6, etc., equal to 77°50′.

The sum of the crystal ionic radii for Zr^{4+} and F^- is 2.16 Å., and the sum of the octahedral covalent radius of zirconium and the covalent radius of fluorine is 2.15 Å. Oxygen and fluorine have nearly equal crystal radii, and the Zr–O distance in ZrP_2O_7 (octahedral coördination) is 2.02 Å.[12] These values suggest about 2.1 Å. for the Zr–F distance in the $[ZrF_7]^{=}$ complex. With Zr–F = 2.10 Å. the minimum F–F distance in the complex is 2.64 Å., which is only slightly less than twice the ionic radius of fluorine, 2.72 Å.

A reasonable way of orienting the various $[ZrF_7]^{=}$ groups in a cubic unit can be suggested, based not on the space group O_h^5, as for $(NH_4)_3AlF_6$, but on T^4. With this structure there are sequences of groups $[ZrF_7]^{=}$, $(NH_4)^+$, $(NH_4)^+$, $(NH_4)^+$, $[ZrF_7]^{=}$, . . ., along the non-intersecting three-fold axes of T^4. With Zr, $(NH_4)_{I}$, $(NH_4)_{II}$, and $(NH_4)_{III}$ in the positions 4a ($x,x,x;\ {}^1/_2 + x,\ {}^1/_2 - x,\ \bar{x};\ {}^1/_2 - x,\ \bar{x},\ {}^1/_2 + x;\ \bar{x},\ {}^1/_2 + x,\ {}^1/_2 - x$) of this space group and parameter values $x_{Zr} = 0.99$, $x_{I} = 0.28$, $x_{II} = 0.50$, $x_{III} = 0.72$, and with the $[ZrF_7]^{=}$ group oriented with F_7 at about $x = 0.12$, the interatomic distances are satisfactory, the minimum NH_4–F distance being 2.6 Å. This structure based on T^4 cannot be accepted, however; it leads to calculated intensity values (deviation from Laue holohedry and from the face-centered lattice) which are incompatible with observation.

If it is assumed that the $[ZrF_7]^{=}$ complexes have some randomness of orientation, complete agreement with experiment is obtained. Each $[ZrF_7]^{=}$ group is considered to have its choice of orientation with its three-fold axis parallel to any one of the eight [111] directions, the zirconium

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(9) L. Pauling, This Journal, **46**, 2738 (1924); *Z. Krist.*, **74**, 104 (1930); G. Menzer, *ibid.*, **73**, 113 (1930).

(10) L. Pauling, This Journal, **49**, 765 (1927); **51**, 1010 (1929).

(11) The minimum radius ratio for stability of the seven-cornered polyhedron obtained by inserting a seventh atom at the center of a face of an octahedron (as in $[ZrF_7]^{=}$) is 0.592; those for stability of the square Archimedean antiprism and of the cube are 0.645 and 0.732, respectively; and that for stability of the nine-cornered polyhedron obtained by introducing three atoms at the centers of the vertical faces of a right triangular prism is 0.732.

Although Penney and Anderson[2] say that Li_4ZrF_8 and Na_3TaF_8 "are undoubtedly not examples of coördination number eight," it is probable that these substances do contain the complexes $[ZrF_8]^{4-}$ and $[TaF_8]^{=}$. The radius ratio for tantalum and fluorine, 0.85, is still larger than that for zirconium and fluorine. On the other hand, the radius ratio for silicon and fluorine is only 0.48, and it is accordingly highly probable that the tetragonal crystal $(NH_4)_3SiF_7$ contains $(NH_4)^+$ ions, F^- ions, and octahedral $[SiF_6]^{=}$ complex ions.

(12) G. R. Levi and G. Peyronel, *Z. Krist.*, **92**, 190 (1935).

atom near 000 assuming one of the corresponding positions uuu, $u\overline{uu}$, $\bar{u}u\bar{u}$, $\overline{uu}u$, $\overline{uuu}$, $\bar{u}uu$, $u\bar{u}u$, $uu\bar{u}$, with $u \cong 0.010$. The planes of symmetry of the complex are not preserved in the T^4 structure, the complex being rotated about its three-fold axis by about 10° from the symmetrical orientation relative to the crystal axes. In the random structure this rotation occurs in either the positive or the negative direction. It is thus assumed that there are sixteen orientations accessible to each $[ZrF_7]^{=}$ group. The ammonium ions I and III are similarly considered to be distributed at random among sets of four positions near $^1/_4\ ^1/_4\ ^1/_4$, $^3/_4\ ^3/_4\ ^3/_4$, etc.

It is probable that the randomness is not complete—the immediate environment of each $[ZrF_7]^{=}$ complex is expected to be like that for the T^4 structure. The random structure might be described as involving unit cubes of the T^4 type with different orientations in different small regions of the crystal. In order to account for the non-occurrence of reflections from planes with mixed indices these regions must be smaller than the regions giving coherent X-ray scattering; that is, they are of the maximum order of magnitude of 100 Å. in linear dimensions.

The intensity calculations were made with the usual formula

$$I_{hkl} = C\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\,p\,F^2_{hkl} \qquad (1)$$

in which C is a constant, p is the frequency factor of the form, and F_{hkl} is the structure factor

$$F_{hkl} = \Sigma_j f_j\, e^{2\pi i(hx_j + ky_j + lz_j)} \qquad (2)$$

the summation being over all of the atoms in the unit cell. Screening-constant f-factors[13] were used. The atomic distribution corresponding to the random structure is the following, based on the space group O_h^5:

4 Zr in 32 f: xxx, etc., with $x = 0.99$;
8 N_I, N_{III} in 32 f, with $x_{I,III} = 0.28$;
4 N_{II} in 4b: $^1/_2{}^1/_2{}^1/_2$, etc.;
4 F (F_7) in 32 f, with $x_F = 0.12$;
12 F (F_1, F_2, F_3) in 192 l: xyz, etc., with $x' = 0.20$, $y' = 0.96$, $z' = 0.91$;
12 F (F_4, F_5, F_6) in 192 l, with $x'' = 0.77$, $y'' = 0.94$, $z'' = 0.99$.

In Table I there are given the results of the powder photographic measurements. The indices which are bracketed together are those for planes whose reflections are superimposed on the powder photograph.

TABLE I

POWDER PHOTOGRAPHIC DATA FOR $(NH_4)_3ZrF_7$

Indices	$\theta_{\text{measd.}}$	a_0, Å.	I_{visual}	$I_{\text{calcd.}}$
111	8°7′	9.430	V. v. strong	215
200	9°27′	9.374	Strong	108
220	13°26′	9.367	V. strong	124
311	15°52′	9.335	Weak-medium	24
222	....	....	Absent	0.4
400	19°12′	9.361	Medium-strong	40.7
331	21°1′	9.353	V. weak	9.2
420	21°30′	9.389	Medium	34.7
422	23°45′	9.361	Medium-strong	43.4
511 333	25°14′	9.380	Medium	25.4
440	27°41′	9.367	Weak-medium	22.4
531	29°3′	9.374	Medium	30.4
600 442	29°28′	9.387	Weak-medium	19.0
620	31°20′	9.358	Weak-medium	18.2
533	32°34′	9.374	V. weak	6.1
622	33°10′	9.328	V. weak	9.5
444	34°43′	9.361	V. v. weak	3.6
551 711	35°57′	9.361	Weak	9.4
640	36°23′	9.354	V. weak	7.3
642	37°58′	9.361	Weak-medium	18.2
731 553	39°6′	9.371	Weak	9.3
800	....	....	Absent	1.3
820 644	42°35′	9.376	V. weak	8.7
660 822	44°7′	9.378	V. weak	6.7
751 555	45°16′	9.380	V. v. weak	5.3
840	47°1′	9.406	V. v. weak	3.3
911 753	48°25′	9.371	V. weak	8.2
842	48°49′	9.369	V. weak	8.2
664	50°40′	9.333	V. v. weak	3.9
931	51°37′	9.363	V. v. weak	5.8
844	53°41′	9.356	V. v. weak	4.9
771 755 933	54°56′	9.354	V. weak	8.3
1000 860	55°14′	9.367	V. v. weak	4.8
1020 862	56°48′	9.378	Weak	13.6
951 773	58°10′	9.369	V. weak	7.6
Mean		9.365 Å.		

The agreement between the visually estimated intensity values and the calculated values is satisfactory. It is felt that the parameter values are reliable to within about 0.01 or 0.02; satisfactory agreement was not obtained with the zirconium parameter x equal to 0.00 instead of 0.99, nor with the N_I, N_{III} parameter $x_{I,III}$ equal to 0.25,

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[13] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

nor with the $[ZrF_7]^{=}$ complex rotated about its three-fold axis through an angle much greater than or less than 10°.[14]

The Structure of K_3ZrF_7.—The powder photographic data for K_3ZrF_7 (Table II) are closely similar to those for $(NH_4)_3ZrF_7$, and indicate a similar structure. The value of a_0, 8.951 ± 0.010 Å., is nearly 5% less than for the ammonium salt. No reflections incompatible with a face-centered lattice were observed. The intensity values calculated for a random structure based on O_h^5 with the same parameter values as for $(NH_4)_3ZrF_7$ agree well with the estimated values. A small improvement is obtained by placing 4 K_{II} in 32 f with $x_{II} = 0.52$ instead of in 4b (corresponding to $x_{II} = 0.500$), and increasing $x_{I,III}$ from 0.28 to 0.29. Values of $I_{calcd.}$ for this arrangement are given in Table II.

TABLE II

POWDER PHOTOGRAPHIC DATA FOR K_3ZrF_7

Indices	$\theta_{measd.}$	a_0, Å.	I_{visual}	$I_{calcd.}$
111	8°35′	8.923	Medium-strong	112.0
200	9°56′	8.916	Medium	45.2
220	14°7′	8.917	V. v. strong	217.6
311	16°35′	8.935	V. weak	7.4
222	....	.....	Absent	1.9
400	20°8′	8.940	Strong	46.7
331	22°5′	8.917	V. weak	6.7
420	22°39′	8.930	Weak	12.9
422	24°54′	8.948	V. strong	86.2
511 333	26°33′	8.939	Medium	19.4
440	29°7′	8.939	Medium-strong	27.2
531	30°31′	8.958	Weak-medium	17.9
600 442	31°1′	8.954	Weak	12.0
620	32°55′	8.952	Medium-strong	24.6
533	34°20′	8.941	V. v. weak	4.0
444	36°31′	8.954	V. weak	5.8
551 711	37°48′	8.960	V. v. weak	6.1
640	38°22′	8.933	Extremely weak	2.2
642	39°56′	8.964	Medium-strong	28.6
731 553	41°10′	8.973	V. weak	7.3
800	43°20′	8.964	V. v. weak	2.4
820 644	44°56′	8.976	V. v. weak	3.9
660 822	46°42′	8.964	Medium	10.1
751 555	48°5′	8.950	V. v. weak	6.5
840	50°14′	8.950	Weak	8.0
911 753	51°31′	8.950	V. weak	7.6
842	51°58′	8.950	V. v. weak	5.7
664	53°46′	8.941	V. v. weak	5.9
931	54°56′	8.962	V. v. weak	5.5
844	57°8′	8.969	V. weak	8.2
771 755 933	58°37′	8.962	V. weak	9.8
1020 862	61°3′	8.962	Medium-strong	20.1
	Mean	8.951 Å.		

Discussion.—The interatomic distances in the crystals, Zr–F = 2.1 Å., F–F ≥ 2.6 Å., NH_4–F ≥ 2.6 Å., and K–F ≥ 2.6 Å., have the magnitudes expected from comparison with other crystals. The parameter values cannot be determined with great accuracy, and the atomic positions are uncertain to about ±0.10 Å.

The existence of discrete MX_7 complexes has not been verified hitherto by structural investigation. It is probable that the configuration found for the $[ZrF_7]^{=}$ ion is possessed also by IF_7 and by other complexes in which seven atoms are coördinated about a central atom. A similar coördination polyhedron is found[15] in the A-modification of La_2O_3 and other rare-earth sesquioxides, in which each rare-earth ion is surrounded by seven oxygen ions; in these crystals the neighboring MO_7 groups share oxygen ions.

It is of interest to note that whereas usually replacement of potassium ion by ammonium ion causes an increase in the dimensions of the crystal unit, a decrease is observed[16] from KHF_2 to NH_4HF_2, presumably as a result of the formation of strong N–H–F hydrogen bonds in the latter crystal. The observation that a_0 is larger for $(NH_4)_3ZrF_7$ than for K_3ZrF_7 indicates that there are not many strong N–H–F hydrogen bonds in the fluozirconate.[17]

Summary

X-Ray photographs of ammonium heptafluozirconate indicate a Laue holohedral face-centered cubic unit of structure with $a_0 = 9.365$ Å., containing 4 $(NH_4)_3ZrF_7$. The theory of space-groups provides no way of placing all of the atoms in definite positions in the unit. A structure involving some randomness of distribution among positions provided by the space group O_h^5

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[14] Satisfactory calculated intensity values were also not obtained with use of the structure factor $\left(\sin \frac{2\pi r_0}{d}\right) \Big/ \frac{2\pi r_0}{d}$ for the fluorine atoms, corresponding to random distribution over the surface of a sphere.

[15] L. Pauling, *Z. Krist.*, **69**, 415 (1929).

[16] L. Pauling, *ibid.*, **85**, 380 (1933).

[17] Weak hydrogen bonds, as in NH_4N_3 [L. K. Frevel, *ibid.*, **94**, 197 (1936)], do not lead to decrease in dimensions of crystals of ammonium compounds relative to the corresponding potassium compounds.

is found to account satisfactorily for the X-ray data. This structure is closely related to that of $(NH_4)_3AlF_6$; the $[AlF_6]^{\equiv}$ complex ions are replaced by $[ZrF_7]^{\equiv}$ complex ions in which zirconium has coördination number seven. Potassium heptafluozirconate is found to have a similar structure, with a_0 = 8.95 Å.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Binary System Cadmium Nitrate–Water: Vapor Pressure–Temperature Relations

BY WARREN W. EWING AND WALTER R. F. GUYER

This article presents the vapor pressure data for the binary system cadmium nitrate–water, and is a continuation of the series of studies being made on the alkaline earth nitrates in this Laboratory. Results for calcium nitrate, magnesium nitrate, and zinc nitrate already have been published. The alkaline earth nitrates are a particularly fruitful group for these investigations for several reasons: the water–nitrate system is quite stable; various hydrates exist, making crystalline mixture studies possible. The salts are very soluble in water, yielding solutions which can be supercooled. Vapor pressures have been obtained for a concentration as high as 86% cadmium nitrate (26 molal).

In addition to the anhydride, three hydrates of cadmium nitrate are mentioned in the literature: the dihydrate, which melts incongruently at 56.8°; the tetrahydrate, which melts congruently at 59.5°; and the enneahydrate which melts incongruently at 3.5°. Although the tetrahydrate was observed as early as 1855, by v. Hauer,[1] the existence of the dihydrate was not satisfactorily demonstrated until the work of G. Malquori[2] was published.

Sieverts and Petzold,[3] in their work on the nitrates of the second group in the periodic system, recently determined the solubility curve of the cadmium nitrate–water system. In the "I. C. T." very fragmentary data of vapor pressure for cadmium nitrate are found.

Preparation of Materials.—C. P. cadmium nitrate tetrahydrate was recrystallized three times as the tetrahydrate. The tetrahydrate was dried by putting it over 55% sulfuric acid in a vacuum desiccator. The single phase solutions were analyzed after the vapor pressure had been determined by ignition in porcelain crucibles to the oxide at 600° for two hours. These solutions had been concentrated almost to dryness in a rapid drier before ignition.

Experimental.—The vapor pressure measurements were made in the modified Smith–Menzies apparatus.[4–6] The dibutyl phthalate trap, having two capillaries, introduced by Ewing and Fisher in their work on zinc nitrate,[7] was used for all of the vapor pressure measurements.

TABLE I

THE VAPOR PRESSURES OF SATURATED SOLUTIONS OF CADMIUM NITRATE (m = metastable)

Temp., °C.	V. p., mm.	Temp., °C.	V. p., mm.
Solid phase: Tetrahydrate		Solid phase: Dihydrate	
0.00	2.93	30.00	5.26m
4.99	4.09	40.03	7.95m
9.97	5.56	49.02	10.59
15.00	7.34	49.93	10.81
19.94	9.81	51.04	11.05
24.88	12.76	52.00	11.26
29.87	16.36	52.42	11.33
35.03	20.68	53.04	11.31
40.18	25.77	54.02	11.48
45.18	30.95	55.03	11.34
50.03	36.09	55.91	11.20
55.06	39.97	56.02	11.00
56.13	40.22	56.60	10.92
57.13	40.14	Solid phase: Anhydride	
58.00	39.39	20.01	1.18m
58.96	32.88	25.00	1.56m
58.00	27.91	30.00	2.13m
57.75	26.10	35.00	2.84m
55.01	18.73	39.98	3.71m
54.86	18.56	50.03	6.45m
49.99	11.58	55.02	8.35m
44.98	7.42m	60.00	10.86
44.62	7.42m	61.43	11.58
39.97	4.80m	61.60	11.70
34.98	3.06m	70.13	17.37

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(3) Sieverts and Petzold, *Z. anorg. allgem. Chem.*, **212**, 49 (1933).

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(5) Ewing, *ibid.*, **49**, 1963 (1927).

(6) Ewing, Klinger and Brandner, *ibid.*, **56**, 1053 (1934).

(7) Ewing and Fisher, *ibid.*, **59**, 1046 (1937).