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The Crystal Structure of Rubidium Hexafluoroprotactinate(V), $RbPaF_6$*

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The crystal structure of $RbPaF_6$ has been determined from three-dimensional Ag $K\alpha$ X-ray data by Patterson and Fourier methods. Crystals are orthorhombic with $a = 8{\cdot}0483$ Å, $b = 12{\cdot}025$ Å, $c = 5{\cdot}8608$ Å, space group *Cmma*. After least-squares refinement of positions and anisotropic thermal parameters, the R index based on F was 0·048. Each Pa atom is bonded to eight F atoms in a dodecahedron having $D_{2d}-\bar{4}2m$ symmetry. Dodecahedra share edges to form chains along the a axis; in this feature, the structure resembles that of K_2ZrF_6. The Pa–F bond lengths are 2·34 Å and 2·09 Å for F atoms in the shared and unshared edges, respectively. The Rb atoms are between chains and have ten F neighbors at distances from 2·81 Å to 3·17 Å. The structure is contrasted with similar compounds of Nb and Ta.

Introduction

A method for determining ionic species in solution, based on a comparison of the frequencies and intensities of Raman lines characteristic of known complex ions in crystals, with those found in aqueous solutions was applied by Keller (1963) to identify $NbOF_5^{2-}$ and NbF_6^- ions in HF solutions. Keller & Chetham-Strode (1966*a*) studied TaF_6^- and TaF_7^{2-} ions in solution by the same method. In order to use this method to study fluoro complexes of protactinium (Keller & Chetham-Strode, 1966*b*) it was necessary to determine crystal structures of appropriate compounds.

It has been assumed that PaF_6^- ions exist in the crystal by Asprey & Penneman (1964) and by Bukhsh, Flegenheimer, Hall, Maddock & de Miranda (1966). The present study will show, for the case of $RbPaF_6$, as was previously shown for K_2PaF_7 (Brown & Smith, 1966; Brown, Kettle & Smith, 1967), that these crystals do not contain PaF_6^- or PaF_7^{2-} ions but that the Pa atoms are linked by F atoms into infinite chains in which the coordination number for Pa is 8 and 9, respectively. Since discrete PaF_6^- and PaF_7^{2-} ions do not exist in known crystals, the application of the spectroscopic method mentioned above will be more difficult for Pa than it was for Nb and Ta.

Experimental

The protactinium (^{231}Pa) used in the preparation of $RbPaF_6$ was part of a ~100 g batch obtained by workers at the Atomic Energy Research Establishment, Harwell, England and reported to contain 4% Nb (Walter, 1963). This impurity was removed by an ion exchange method described by Chetham-Strode & Keller (1966); a mass spectrographic analysis of the crystals used for the X-ray study showed them to contain less than 0·05% Nb. Synthesis and elemental analysis of $RbPaF_6$ were described by Keller & Chetham-Strode (1966*b*). The crystals formed were colorless needles having almost equidimensional cross section. It was more than a year after preparation of the crystals before the X-ray studies were begun, but no loss of crystallinity from α-radioactivity was detected other than possibly that represented by the large mosaic spread.

In order to minimize errors due to the large absorption coefficient of Pa, the sample was shaped by use of a race-track sphere grinder enclosed in a gloved box equipped for handling radioactive materials. A sphere, $0{\cdot}0213 \pm 0{\cdot}0005$ cm in diameter, was sealed in a thin walled glass capillary by a technique designed to limit contamination of the glass to the inside. Selection and mounting of the crystal were done in the box with micromanipulators observed through an external microscope with a long focal length. The capillary and crystal were removed from the box and transferred to tne X-ray devices for study.

Precession camera photographs of $RbPaF_6$ provided initial unit-cell dimensions and the diffraction symmetry. For more refined unit-cell values and the intensity data, the computer-controlled X-ray diffractometer of Busing, Ellison, Levy, King & Roseberry (1967) was used. Data from twelve reflections with 2θ values in the range 125–155° with Cu $K\alpha$ radiation (1·54051 Å) were used in a least-squares refinement of the unit-cell dimensions. The orthorhombic unit cell has $a = 8{\cdot}0483$ (0·0003), $b = 12{\cdot}0253$ (0·0005), and $c = 5{\cdot}8608$ (0·0002) Å at 24 ± 1 °C. The values in parentheses are the least-squares standard deviations and do not include any effect of absorption or instrument alignment on diffraction angles.

Systematic absences were of the type hkl for $h+k = 2n+1$ and $hk0$ for $h = 2n+1$, which are characteristic of space groups *Cmma* and *Cm2a*. In addition, hkl reflections with $h = 2n+1$ $(k = 2n+1)$ were relatively weak and diminished rapidly with increasing Bragg angle;

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this intensity pattern results from the arrangement of Pa atoms in special positions.

The large mosaic spread of the crystal made ω-scanning the most reliable technique for collection of intensities. In this mode no β-filter was used. The receiving slit width was adjusted so as to accept the entire peak at the Bragg angle and to allow measurement of the background by ω-scans at higher and lower 2θ values without including either the α or β lines. The proper slit width was calculated by taking into account the beam divergence, the doublet dispersion, and the crystal size. The data were collected for four ranges of Bragg angle with the following experimental conditions:

2θ-range	Take-off angle	Beam divergence	Slit width
< 10°	0·5°	0·13 mm	0·8 mm
10–15	0·5	0·13	1·2
15–20	2·5	0·65	3·0
> 20	2·5	0·65	4·0

Silver $K\alpha$ radiation was chosen because its absorption by $RbPaF_6$ is smaller than that of other useful radiations; Mo $K\alpha$ X-rays (0·71 Å) were deemed unsuitable because the L absorption edge of Pa is at 0·74 Å. All independent reflections were measured to a limit of $\sin\theta/\lambda = 0{\cdot}76$. At higher angles very few intensities were found greater than the estimated standard deviations of the measurements; these were not included in the refinement. For reflections with h and k odd the limit was $\sin\theta/\lambda = 0{\cdot}5$. Some 273 reflections were remeasured using Cu $K\alpha$ X-rays for the purpose of comparison.

Two problems arose from the use of Ag X-rays excited at 50 kV. The first was the observation of escape peaks from iodine in the scintillation counter produced by X-rays at the maximum of the continuous spectrum; the peaks appeared at the 2θ values of systematic absences, *viz.* (110) and (390). Once the source of these maxima was recognized, they were eliminated by reduction of the exciting voltage. The second problem was the effect of the Rb K absorption edge on the presence of an harmonic contribution from a strong reflection at lower Bragg angles whose indices are in the ratio of $\frac{2}{3}$ to the reflection being measured. (The ratio of wave lengths for Ag $K\alpha$ to Rb K edge is 0·685.) Although in ω-scanning harmonics are usually properly accounted for in the background measurement, in this case the background on the lower 2θ side of the peak is abnormally low. Nineteen reflections showed this effect, and were omitted from the refinement. Five other reflections at small Bragg angles were omitted because of difficulty in evaluating background levels.

Structure determination and refinement

Each observed intensity was converted to a relative structure factor, $|F_o|$, by application of a Lorentz–polarization factor and a normalization factor based on the value of a frequently measured reference reflection. An absorption correction for a spherical crystal with $\mu R = 3{\cdot}61$, obtained by linear interpolation between values from *International Tables* (1959), was applied. The mass absorption coefficient of Pa for Ag $K\alpha$ radiation was taken as 106 $cm^2\,g^{-1}$ from interpolation between values for Th and U (Roof, 1959). The data taken with Cu $K\alpha$ X-rays were similarly corrected for absorption, but the factors were very approximate because of the high value of μR, (~ 14).

A Patterson map made with the Ag data was interpreted to yield positions for Rb at 4 (g) and Pa at 4 (a) of space group *Cmma*. An electron density map with phases based on these heavy atoms revealed the F atoms in positions 8 (m) and 16 (o). The variable positional parameters and anisotropic temperature factors for each independent atom were adjusted by the method of least squares. The final values obtained and their standard errors are listed in Table 1. The atomic scattering factors used in structure-factor calculations were those of the neutral atoms given by Cromer & Waber (1965). For Rb and Pa atoms corrections for the real and imaginary components of anomalous dispersion (Cromer, 1965) were applied. A modification of the computer program by Busing, Martin & Levy (1962) was used for least-squares computations. The function minimized was

$$\Sigma\, w(s^2F_c^2 - F_o^2)^2\,,$$

where F_o and F_c are observed and calculated structure

Table 1. *Positional and thermal parameters* for* $RbPaF_6$

	Site	$x(10^4\sigma)$	$y(10^4\sigma)$	$z(10^4\sigma)$
Rb	4 g	0	$\frac{1}{4}$	0·4532 (6)
Pa	4 a	$\frac{1}{4}$	$\frac{1}{4}$	0
F(1)	8 m	0	0·4294 (16)	0·1459 (25)
F(2)	16 o	0·3059 (17)	0·3796 (11)	0·2476 (24)

	$\beta_{11}(10^4\sigma)$	$\beta_{22}(10^4\sigma)$	$\beta_{33}(10^4\sigma)$	$\beta_{12}(10^4\sigma)$	$\beta_{13}(10^4\sigma)$	$\beta_{23}(10^4\sigma)$
Rb	0·0069 (4)	0·0030 (2)	0·0171 (15)	0	0	0
Pa	0·0018 (2)	0·0021 (1)	0·0110 (3)	0	0	0
F(1)	0·0041 (20)	0·0067 (14)	0·0123 (43)	0	0	0·0056 (21)
F(2)	0·0068 (16)	0·0064 (11)	0·0303 (45)	0·0018 (12)	−0·0035 (24)	0·0042 (20)

* The thermal parameters, β_{ij}, are coefficients in the temperature factor:

$$\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\,.$$

factors, s is a scale factor, and $w = 1/\sigma^2$. The variance was calculated from

$$\sigma^2(F_o^2) = [T + k^2B + \{0{\cdot}05(T-kB)\}^2] \, . \, [c/A(\mathrm{Lp})]^2 \, .$$

In this equation $c/A(\mathrm{Lp})$ is a factor which converts counts to squared structure factors (Lp = Lorentz–polarization, A = transmission factor), T = total counts, and kB = normalized background counts. The term $0{\cdot}05(T-kB)$ is included to allow for unknown systematic errors. After refinement to convergence, the index $R = \Sigma \,||F_o| - |F_c|| / \Sigma \,|F_o|$ was 0·048 for 351 reflections observed to be greater than 1σ. The standard deviation of an observation of unit weight,

$$\sigma_1 = \{ \, \Sigma \, w[F_o^2 - s^2F_c^2]^2/(m-n)\}^{1/2} \, ,$$

was 1·29. In this expression w is the weight of an observation and $m-n$ is the number of degrees of freedom, 324. A list of calculated and observed structure factors and standard deviations is presented in Table 2.

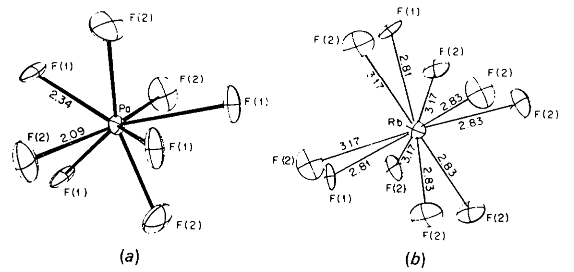

Fig. 1. Arrangement of F atoms around (*a*) the Pa atom (*b*) the Rb atom. Thermal motions are represented by 50% probability ellipsoids (Johnson, 1965).

Results and discussion

In $\mathrm{RbPaF_6}$ each Pa atom is bonded to eight F atoms which surround it in a dodecahedral arrangement having point symmetry D_{2d}–$\bar{4}2m$, within experimental error, although the crystallographic symmetry of the Pa site is only D_2–22. Two edges of each dodecahedron, on opposite sides of the Pa atom, are shared with adjacent dodecahedra, thereby forming chains along the crystallographic a axis. In each $\mathrm{PaF_8}$ polyhedron there are four F atoms which are in shared edges and four which are not; the Pa–F bond lengths are 2·34 Å and 2·09 Å, respectively. The longer bonds for the bridging F atoms are expected because of repulsion between the Pa atoms. Details of the $\mathrm{PaF_8}$ arrangement are given in Fig. 1(*a*) and in Table 3, which contains interatomic distances of interest. Fluorine atoms of successive $\mathrm{PaF_8}$ groups along the chains are related by the operations of the a-glide plane at $z=0$, in which the Pa atom lies. Fig. 2 shows a layer of the structure in and near such a plane.

Each Rb atom is surrounded by an approximately cubic array of eight $\mathrm{PaF_8}$ polyhedra belonging to four chains. This is shown in Fig. 3, which is a stereoscopic drawing of part of the structure. Between layers of

Table 2. *Observed and calculated structure factors and standard errors*

The column headings have the following meaning: L is the Miller index l, OBS and CAL are the observed and calculated structure factors on an absolute scale, S is the calculated sign, and ER is the standard error of the observation. Reflections having an X after the running index were omitted from the least-squares refinement for reasons given in the text.

L	OBS	CAL	S	ER
0 0 L				
1	231	238	+	6
2	248	265	+	6
3x	138	146	+	4
4	241	251	+	7
5	139	163	+	6
6x	131	124	+	7
7	133	132	+	6
8	107	78	+	7
0 2 L				
0x	267	242	+	7
1x	400	457	+	10
2	157	165	+	4
3	258	277	+	7
4	160	164	+	6
5	154	170	+	6
6	135	149	+	6
7	119	100	+	6
8	111	130	+	7
0 4 L				
0	307	297	+	8
1	141	163	+	4
2	373	415	+	9
3	169	179	+	5
4	180	187	+	6
5	147	157	+	6
6	138	135	+	6
7	119	115	+	6
8	65	61	+	10
0 6 L				
0x	121	103	+	4
1	327	321	+	8
2	167	175	+	5
3x	318	262	+	9
4	154	162	+	6
5	158	160	+	6
6x	138	125	+	6
7	83	75	+	8
8	86	93	+	8
0 8 L				
0	317	321	+	8
1	133	125	+	6
2	227	229	+	7
3	157	152	+	4
4	215	205	+	7
5	136	130	+	6
6	96	92	+	7
7	95	91	+	7
0 10 L				
0	120	125	+	8
1	244	237	+	7
2	127	115	+	6
3	203	156	+	6
4	130	125	+	6
5	102	110	+	7
6	105	54	+	7
7	66	65	+	11
8	76	75	+	10
9	52	43	+	14
10	27	44	+	28
0 12 L				
0x	155	155	+	7
1	91	105	+	5
2	206	156	+	6
3x	122	102	+	7
4	123	114	+	6
5	87	50	+	9
0 14 L				
0	85	86	+	9
1	170	147	+	7
2	65	50	+	11
3	115	121	+	7
4	50	76	+	9
5	90	86	+	9
0 16 L				
0	150	141	+	7
1	66	73	+	12
2	111	113	+	8
3	70	68	+	12
4	54	95	+	9
0 18 L				
0x	68	61	+	12
1 1 L				
1	44	30	-	2
2	40	43	+	4
3	92	55	-	3
4	85	69	+	7
5	46	41	-	12
6	52	46	+	11
1 3 L				
1	36	23	+	5
2	59	102	-	3
3	33	35	+	6
4	61	52	-	9
5	74	77	+	9
1 5 L				
1	65	72	-	4
2	14	21	+	14
3	58	58	-	4
4	65	72	+	8
5	30	38	-	20
1 7 L				
1	0	5	+	0
2	54	43	-	10
3	63	68	+	9
4	42	45	-	12
1 9 L				
1	0	5	-	0
2	30	52	+	19
3	24	39	-	25
1 11 L				
1	45	35	+	13
2	18	18	-	16
2 0 L				
0x	240	217	-	6
1x	415	383	-	11
2	141	129	-	4
3	321	325	-	8
4	230	229	-	7
5	179	174	-	6
6	126	123	-	6
7	81	84	-	10
8	113	97	-	7
2 2 L				
0x	401	396	-	10
1	178	158	-	5
2	364	355	-	9
3	200	201	-	5
4	237	237	-	7
5	149	156	-	6
6	122	117	-	6
7	123	114	-	6
8	60	67	-	11
2 4 L				
0	115	108	-	4
1	350	375	-	10
2	228	222	-	6
3	260	263	-	7
4	133	130	-	6
5	151	154	-	6
6	141	142	-	6
7	100	91	-	7
8	104	93	-	7
2 6 L				
0	358	357	-	9
1	173	173	-	5
2	274	290	-	7
3	122	130	-	6
4	165	171	-	6
5	126	128	-	6
6	117	117	-	6
7	111	112	-	6
8	69	66	-	9
2 8 L				
0	193	187	-	6
1	263	289	-	7
2	97	104	-	6
3	182	194	-	6
4	133	136	-	6
5	138	134	-	6
6	115	114	-	6
7	103	82	-	7
2 10 L				
0	258	252	-	7
1	113	116	-	6
2	194	202	-	6
3	121	118	-	6
4	152	151	-	6
5	105	111	-	7
6	78	92	-	8
7	86	88	-	8
2 12 L				
0	71	82	-	9
1	191	198	-	6
2	118	111	-	6
3	156	157	-	6
4	102	99	-	7
5	108	103	-	7
6	57	89	-	7
2 14 L				
0	156	153	-	6
1	90	82	-	9
2	146	149	-	6
3	90	89	-	7
4	109	107	-	7
5	80	83	-	8
2 16 L				
0	73	72	-	9
1	137	126	-	6
2	69	70	-	9
3	112	104	-	7
3 1 L				
1	117	105	-	4
2	37	32	+	5
3	36	36	-	6
4	68	67	+	9
5	67	55	-	9
3 3 L				
1	71	64	-	4
2	59	87	-	3
3x	196	81	+	6
4	60	47	-	10
5	48	49	+	12
3 5 L				
1	0	19	-	0
2	12	27	+	17
3	85	77	-	7
4	62	57	+	10
3 7 L				
1	51	57	+	11
2	27	39	-	21
3	32	27	+	18
4	44	41	-	13
3 9 L				
1	24	19	-	23
2	32	41	+	18
3x	114	26	-	7
3 11 L				
1	44	8	+	14
4 0 L				
0	421	423	+	11
1	205	191	+	5
2	307	291	+	8
3	149	144	+	6
4	195	191	+	6
5	156	144	+	6
6	119	125	+	6
7	117	123	+	6
8	80	71	+	8
4 2 L				
0	202	189	+	5
1	361	356	+	9
2	148	160	+	5
3	247	237	+	7
4	156	146	+	6
5	162	155	+	6
6	130	137	+	6
7	99	93	+	7
8	56	92	+	7
4 4 L				
0	320	312	+	8
1	158	151	+	4
2	300	291	+	8
3	162	155	+	6
4	191	192	+	6
5	147	146	+	6
6	116	115	+	6
7	96	104	+	7
8	64	41	+	10
4 6 L				
0	124	120	+	6
1	277	271	+	7
2	147	145	+	6
3	231	232	+	7
4	154	154	+	6
5	140	143	+	6
6	109	112	+	6
7	69	72	+	9
4 8 L				
0	252	246	+	7
1	120	117	+	6
2	227	226	+	7
3	142	143	+	6
4	170	170	+	6
5	117	116	+	6
6	92	88	+	7
7	92	86	+	8
4 10 L				
0	110	106	+	6
1	223	211	+	7
2	124	118	+	6
3	174	173	+	6
4	111	109	+	6
5	100	104	+	7
6	102	90	+	7
4 12 L				
0	179	186	+	6
1	107	101	+	6
2	170	167	+	6
3	74	94	+	8
4	111	111	+	6
5	85	87	+	8
4 14 L				
0	74	98	+	9
1	136	150	+	6
2	74	91	+	8
3	107	112	+	7
4	70	77	+	5
4 16 L				
0	134	125	+	6
1	92	70	+	10
2	102	107	+	7
5 1 L				
1	20	8	+	10
2	25	30	+	21
3	87	81	-	7
4	50	51	+	11
5 3 L				
1	43	42	+	13
2	56	67	-	10
4	45	38	-	13
5 5 L				
1	56	63	-	10
4	54	55	+	11
5 7 L				
3	40	61	+	15
5 9 L				
2	46	40	+	13
3	16	35	-	37
6 0 L				
0x	122	54	-	7
1	272	265	-	7
2	175	179	-	6
3x	274	243	-	8
4	141	146	-	6
5	144	140	-	6
6x	128	118	-	6
7	70	77	-	11
6 2 L				
0	246	267	-	7
1	135	138	-	6
2	261	261	-	7
3	152	159	-	6
4	194	182	-	6
5	141	133	-	6
6	103	103	-	7
7	101	56	-	7
6 4 L				
0	176	168	-	6
1	273	269	-	7
2	125	125	-	6
3	158	199	-	6
4	135	141	-	6
5	138	133	-	6
6	102	109	-	7
7	73	78	-	9
6 6 L				
0x	298	274	-	8
1	136	141	-	6
2	215	210	-	6
3x	153	120	-	6
4	150	150	-	6
5	116	114	-	6
6x	55	97	-	8
7	50	96	-	9
6 8 L				
0	128	119	-	6
1	219	220	-	6
2	122	124	-	6
3	165	163	-	6
4	109	102	-	6
5	108	110	-	7
6	114	104	-	7
6 10 L				
0	184	187	-	6
1	106	106	-	7
2	168	173	-	6
3	56	101	-	7
4	122	120	-	6
5	87	99	-	8
6 12 L				
0x	107	91	-	7
1	164	155	-	6
2	87	98	-	9
3x	145	127	-	6
4	95	96	-	7
6 14 L				
0	127	133	-	6
1	71	75	-	9
2	121	118	-	6
3	86	82	-	9
7 1 L				
2	29	23	+	20
7 3 L				
2	66	44	-	13
7 5 L				
2	35	16	+	18
8 0 L				
0	224	224	+	7
1	148	144	+	6
2	235	231	+	7
3	120	121	+	6
4	147	127	+	6
5	109	114	+	8
6	105	107	+	7
8 2 L				
0	143	140	+	6
1	236	232	+	7
2	129	131	+	6
3	172	171	+	6
4	111	117	+	6
5	122	122	+	6
6	111	107	+	7
8 4 L				
0	240	243	+	7
1	136	125	+	6
2	187	176	+	6
3	115	124	+	6
4	154	159	+	6
5	110	115	+	7
6	76	86	+	9
8 6 L				
0	108	113	+	7
1	195	190	+	6
2	120	115	+	6
3	173	170	+	6
4	118	123	+	6
5	102	109	+	7
8 8 L				
0	176	159	+	6
1	109	102	+	7
2	183	180	+	6
3	127	116	+	6
4	124	119	+	6
5	87	97	+	8
8 10 L				
0	93	89	+	7
1	148	157	+	6
2	111	103	+	7
3	124	128	+	6
4	52	88	+	8
8 12 L				
0	146	147	+	6
1	87	88	+	8
2	113	119	+	7
3	76	79	+	9
10 0 L				
0	73	90	-	9
1	171	175	-	6
2	135	134	-	6
3	157	157	-	6
4	107	107	-	7
10 2 L				
0	167	176	-	6
1	105	113	-	7
2	165	169	-	6
3	108	117	-	7
4	125	128	-	6
10 4 L				
0	123	130	-	6
1	173	173	-	6
2	56	59	-	7
3	133	140	-	6
4	106	110	-	7
10 6 L				
0	170	174	-	6
1	104	110	-	7
2	139	146	-	6
3	91	58	-	8
4	114	108	-	7
10 8 L				
0	79	54	-	9
1	154	149	-	6
2	106	103	-	7
3	113	115	-	7
10 10 L				
0	121	131	-	7
1	96	89	-	9
12 0 L				
0x	147	150	+	6
1	110	109	+	9
12 2 L				
0	106	108	+	7

Table 3. *Interatomic distances less than* 4 Å

	Number at this distance	Distance (Å)	σ (Å)
Rb–F(1)	2	2·812	0·017
Rb–F(2)	4	2·828	0·013
Rb–F(2)	4	3·167	0·014
Pa –F(2)	4	2·086	0·014
Pa –F(1)	4	2·344	0·008
F(1)–F(1)*	2	2·40	0·03
F(1)–F(2)	2	2·60	0·02
F(1)–F(2)	2	2·82	0·02
F(1)–F(2)	2	2·84	0·03
F(2)–F(2)	2	3·00	0·03
F(2)–F(2)	2	3·04	0·03
F(2)–F(2)	2	3·10	0·03
F(2)–F(2)	2	3·11	0·03
F(2)–F(2)	2	3·16	0·03

* The F–F distances are those of the PaF_8 polyhedron.

chains there is an *a*-glide plane at $z=\frac{1}{2}$; the Rb atoms are near, but not in, this plane. Thus successive Rb atoms along the *a* axis are displaced alternately toward layers on opposite sides of the plane. On the side toward which the Rb atom is displaced, it has six near F atom neighbors, four at 3·16 Å and two at 2·81 Å. On the opposite side, it has four at 2·83 Å. These contacts are shown in Figs. 1(*b*) and 2 and are listed in Table 3.

From an overall view, the structure of $RbPaF_6$ is quite similar to that of K_2ZrF_6 (Bode & Teufer, 1956) which has chains of ZrF_8 dodecahedra with shared edges. In the latter structure, however, there is a different accommodation for the alkali ions, since there are twice as many, and the point symmetry of the dodecahedra is C_{2v}–*mm*.

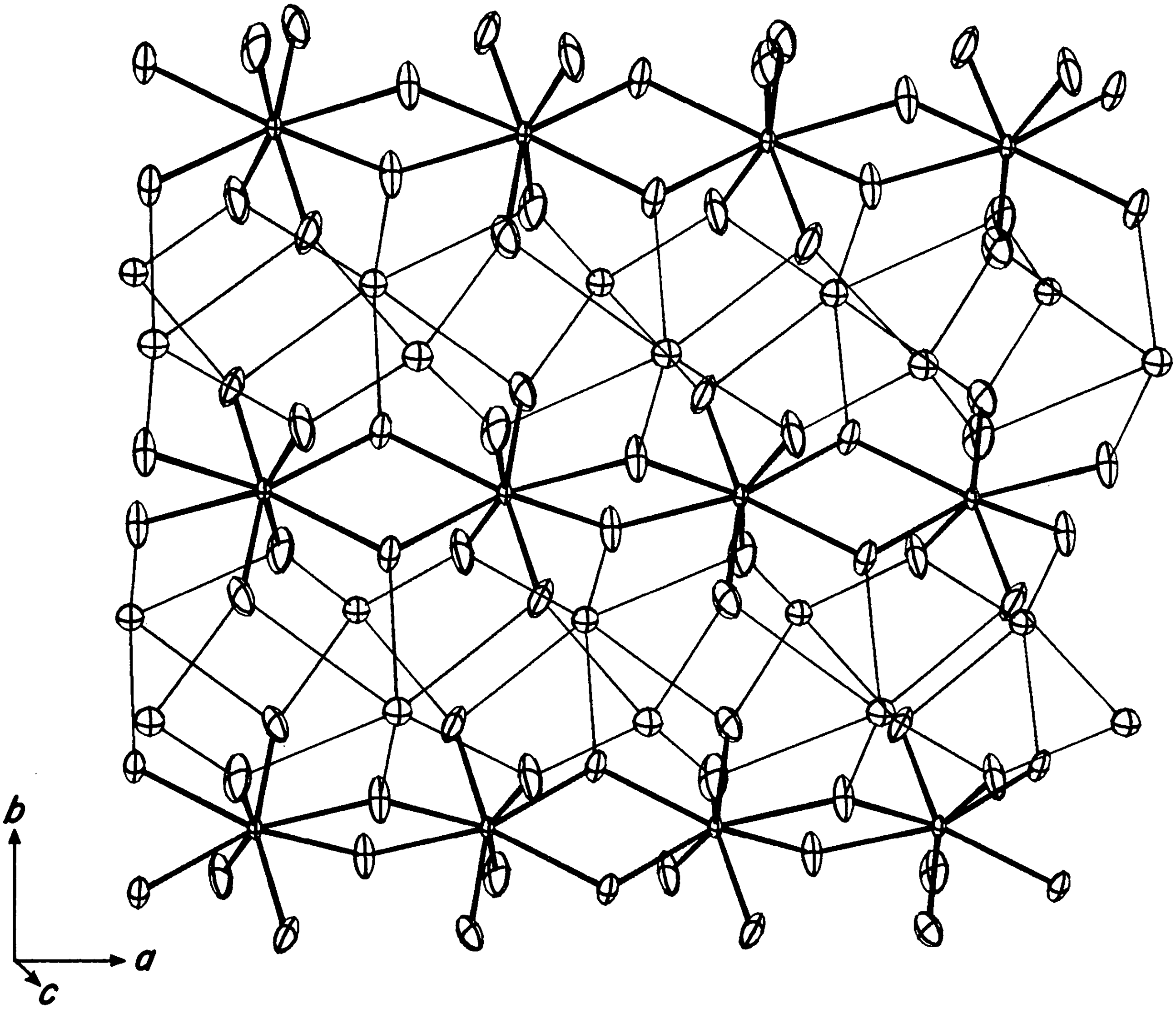

Fig. 2. A layer of the $RbPaF_6$ structure parallel to (001). Heavy lines indicate Pa–F bonds and light lines connect Rb atoms and F atoms. The complete ten-coordination of each Rb atom is not shown, but successive Rb atoms along **a** are shown with the complementary six and four linkages.

The thermal motions of the atoms all appear reasonable in view of the atomic masses, the geometry and the bonding. As may be seen in Fig. 2, two F(1) atoms in a shared edge of the dodecahedron are each bonded to two Pa atoms, forming a rhombus. Motion of the F atoms within the plane of the rhombus is restricted by F–F contacts or by Pa–F bond stretching, but motion out of this plane results mainly in bending of bonds. In agreement with this description, the observed thermal ellipsoid is prolate and has its long axis perpendicular to the plane mentioned above. Atom F(2) is unshared, and its thermal motion is described by an oblate ellipsoid with its short axis (to a rough approximation) along the Pa–F(2) bond direction. Ellipsoids for the heavy atoms are much smaller: Rb is nearly isotropic, while Pa shows a smaller amplitude along the chain direction than perpendicular to it.

The results of previous studies related to the structure of $RbPaF_6$ can now be clarified. Asprey, Kruse, Rosenzweig & Penneman (1966) synthesized a number of ABF_6 compounds in which A was NH_4^+, K^+, Rb^+, or Cs^+ and B was U^{5+} or Pa^{5+}, and found by X-ray powder diffraction that all except $CsUF_6$ (Rosenzweig & Cromer, 1967) were isostructural with $RbPaF_6$. Using the unit cell and space group for $RbPaF_6$ from the present study, they indexed the patterns of these substances and obtained unit-cell dimensions. Since the list of compounds includes $KPaF_6$, the earlier report of its unit cell and space group by Brown & Easey (1966) is seen to be incorrect. These latter workers had based their indexing on an erroneous interpretation by Charpin (1965) of the powder pattern of isostructural KUF_6.

It is interesting to summarize the currently known structures involving Pa^{v} halides and to compare them with the corresponding Nb^{v} and Ta^{v} compounds. In contrast to $RbPaF_6$, both $RbNbF_6$ and $RbTaF_6$ (Cox, 1956) have a CsCl-like arrangement of Rb^+ and MF_6^- ions, the $KOsF_6$ structure. The only other complex fluoride of Pa which has been reported in detail is K_2PaF_7 (Brown, Kettle & Smith, 1967). In it the Pa atoms are nine-coordinated by a trigonal prism plus an equatorial triangle of F atoms. Two edges are shared in each polyhedron to form chains with the K atoms between them. In K_2NbF_7 and K_2TaF_7 the heavy metal has the well-known seven coordination of a trigonal prism with one face capped (Hoard, 1939; Brown & Walker, 1966). Recently $PaCl_5$ was found to crystallize with infinite chains of $PaCl_7$ pentagonal bipyramids sharing apices (Dodge, Smith, Johnson & Elson, 1967), while $NbCl_5$ and $TaCl_5$ form octahedrally coordinated dimeric units (Zalkin & Sands, 1958). The structure of PaF_5 has not been reported, but NbF_5 and TaF_5 have tetrameric units with the metal atoms octahedrally coordinated (Edwards, 1964). According to Brown & Easey (1966) Na_3PaF_8 is isostructural with Na_3UF_8 which Rüdorff & Leutner (1960) showed to have uranium in cubic coordination. The corresponding compound, Na_3TaF_8 (Hoard, Martin, Smith & Whitney, 1954), has antiprismatic TaF_8^{3-} ions.

The larger radius of Pa^{5+} (0·9 Å) compared with Nb^{5+} and Ta^{5+} ($\sim$0·7 Å) makes it able to have higher coordination numbers. An obvious way of achieving this, while maintaining electroneutrality, is the sharing of polyhedral edges in a chain; examples of this type are seen above. The six and seven coordination found for the chlorides above can be explained on the basis of radius ratio, but on this basis coordinations up to 9 for fluorides around Ta and Nb should be allowed, while usually only six or seven and, in one case, 8 are found. Protactinium, however, has *f*-orbitals available and these may contribute to the formation of a larger number of bonds.

Structural data currently available indicate that U^{v} shows a behavior similar to Pa^{v}, but that the *d*-

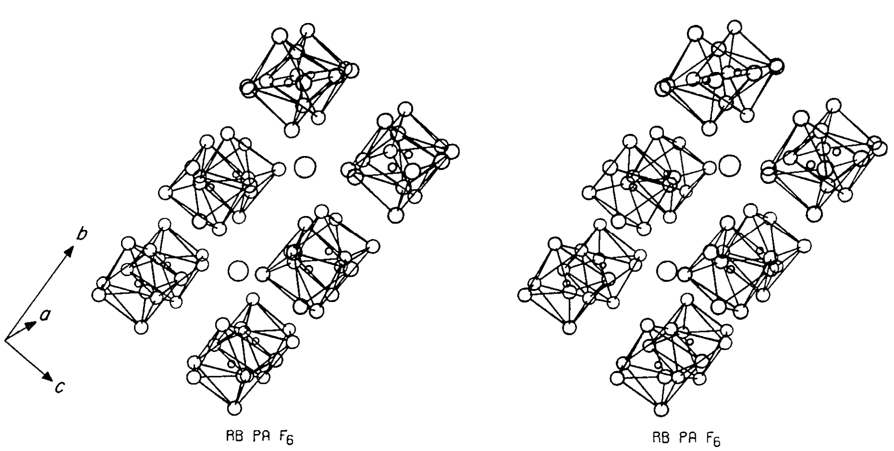

Fig. 3. A stereoscopic drawing of a portion of the $RbPaF_6$ structure, viewed nearly along the chain direction. Small, medium, and large circles represent Pa, F, and Rb atoms, respectively. Two dodecahedra of each chain are shown.

transition metal analogues, Nb^V and Ta^V, do not. Iyer & Smith (1967) have noted similarly that there is no structural resemblance between the rare-earth double oxides of Pa^V and the analogous compounds of Nb^V and Ta^V.

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The Crystal Structure of 8,16-Oxido-*cis*-[2.2]metacyclophane

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The crystal structure of 8,16-oxido-*cis*-[2.2]metacyclophane, $C_{16}H_{14}O$, is orthorhombic, space group probably $Cmc2_1$, with $a=8{\cdot}78$, $b=16{\cdot}04$, $c=8{\cdot}42$ Å, $Z=4$. The structure was deduced from the three-dimensional Patterson synthesis and refined by block-diagonal least squares to a final agreement residual of 0·057. The molecule has nearly *mm* symmetry, and is folded to a dihedral form so that the angle between the slightly boat-shaped six-membered rings is 99·6°. The bond angle subtended by the oxygen atom is 101·4°, while the mean value of those in the methylene bridges is 119·0°. The strain implied by these values is consistent with the tendency of the compound to transform into the corresponding pyrene derivative, with ejection of the hetero atom.

Introduction

Although several *trans*-[2.2]metacyclophanes have been reported (Lindsay, Stokes, Humber & Boekelheide, 1961), the title compound (I) is the first reported example of a *cis*-[2.2]metacyclophane (Hess, Bailey & Boekelheide, 1967; Renfroe, Gurney & Hall, 1967). Steric strain is inferred for such compounds from their known tendency (on heating, or treatment with acid) to transform into the corresponding pyrene derivatives, with ejection of the hetero atoms (Boekelheide, 1967). The crystal structure analysis was undertaken in order to determine the geometrical characteristics of such strain. It was realized from the beginning that the ac-

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