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Preparation and Crystal Structures of Plutonium(III) Pentachloro Complexes, K_2PuCl_5 and Rb_2PuCl_5*

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K_2PuCl_5 and Rb_2PuCl_5 were prepared by heating mixtures of anhydrous $PuCl_3$ and respective alkali metal chlorides in vacuum-sealed quartz ampoules at 400–500°C. Their crystal structures are both orthorhombic with K_2PrCl_5-type structure (space group *Pnma*, $Z = 4$), determined by powder X-ray crystallography. K_2PuCl_5: lattice parameters $a = 12.674 \pm 0.003$, $b = 8.727 \pm 0.002$, $c = 7.969 \pm 0.002$ Å; cell volume 220.4 ± 0.2 Å^3; X-ray density 3.726 ± 0.004 g/cm^3. Rb_2PuCl_5: lattice parameters $a = 13.093 \pm 0.008$, $b = 8.909 \pm 0.005$, $c = 8.178 \pm 0.005$ Å; cell volume 238.5 ± 0.4 Å^3; X-ray density 4.088 ± 0.008 g/cm^3. Fourteen variable atom parameters of these complexes were obtained by electrostatic calculation with a program which maximizes the Madelung constant under the condition that the ion–ion separations in the crystal are all larger than respective critical distances. The measured Raman lines of Rb_2PuCl_5 are very close to those of hexachloride complexes. The bond lengths and stability of M_2PuCl_5 (M = K, Rb) are discussed. © 1988 Academic Press, Inc.

Introduction

As stated in a review by Meyer (*1*) on complex rare-earth halides, remarkable progress has been made in the last decade for the characterization of A_2RECl_5 compounds through synthesis and crystal structure studies, where *A* and *RE* stand for alkali metals and rare-earth elements, respectively. The complex chlorides crystallize either in an orthorhombic, *Pbnm*($Z = 4$) Cs_2DyCl_5 structure (*2*) or in an orthorhombic, *Pnma*($Z = 4$) K_2PrCl_5 (*3*) structure. The *Pbnm* structure appears with the alkali metal Rb or Cs in combination with the rare-earth elements of crystal radius small enough to adopt coordination number (CN) = 6 in ternary rare-earth trichlorides (*1*), while the *Pnma* structure is found with the alkali metal K or Rb and lighter rare-earth elements. In the former type of crystal structure, a trivalent rare-earth ion is coordinated by six chlorine atoms forming a slightly distorted octahedron. The two octahedra share a common edge, and the successive sharing results in formation of an infinite chain along the [001] direction, viz. $^1_\infty[RECl^t_{4/1}Cl^e_{2/2}]^{2-}$. On the other hand, the coordination number of chlorine atoms around a rare-earth ion is seven in the *Pnma* structure. These chlorine atoms form a monocapped trigonal prism. The two polyhedra share two common edges form-

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TABLE I

CRYSTAL DATA FOR K_2PuCl_5 AND Rb_2PuCl_5

	K_2PuCl_5	Rb_2PuCl_5
Crystal system:	Orthorhombic	
Space group	*Pnma* ($Z = 4$)	
a (Å)	12.674 ± 0.003	13.093 ± 0.008
b (Å)	8.727 ± 0.002	8.909 ± 0.005
c (Å)	7.969 ± 0.002	8.178 ± 0.005
Cell volume (Å^3) (per formula)	220.4 ± 0.2	238.5 ± 0.4
X-ray density (g/cm^3)	3.726 ± 0.004	4.088 ± 0.008

ing an infinite chain along the [010] direction, viz. ${}^{1}_{\infty}[RE\mathrm{Cl}^{t}_{3/1}\mathrm{Cl}^{e}_{4/2}]^{2-}$. For K_2PrCl_5, the Pr–Cl(4) bridging distance is slightly longer than the terminal distance (superscript *t*). The above information has been gained by single crystal X-ray diffraction analysis (*3*).

The actinide complexes A_2AnCl_5 (An = actinide elements) have not been systematically studied so far. The crystal structure of K_2UCl_5 and Rb_2UCl_5 had been reported to be orthorhombic and isostructural with Tl_2AlF_5 (*4*). Recently, however, Meyer *et al.* (*5*) showed that this is not the case: These are orthorhombic, but of K_2PrCl_5 type with space group *Pnma*. Very recently, the americium complexes K_2AmCl_5, $(NH_4)_2AmCl_5$, and Rb_2AmCl_5 have been prepared and their crystal structure analyzed (*6*). The crystal structure was found to be the same as that of K_2UCl_5 and Rb_2UCl_5, the lattice parameters being significantly different.

Here, we report the preparation and crystal structure of K_2PuCl_5 and Rb_2PuCl_5. This paper refines and extends our preliminary result (*7*). Crystal system and lattice parameters were determined by X-ray powder diffraction analysis, while 14 variable atom parameters were obtained by use of an electrostatic method (*8, 9*) which was shown to give approximately correct values of the parameters for ionic crystals without intensity calculation of the diffraction peaks. Calculation of the atom parameters was carried out by coconverging all parameters on a computer program. The arrangement and separation of atoms in the crystals are examined as a function of crystal radius of alkali metals. With the aid of Raman spectra the coordination of chlorine atoms around plutonium is discussed. The change of molecular volume is compared for K_2AnCl_5, Rb_2AnCl_5, and $AnCl_3$ with An ranging from U to Am.

Experimental

All procedures followed those of Ref. (*9*) with the exception that trivalent complexes were not reacted with Cl_2. K_2PuCl_5 obtained was pale blue, while Rb_2PuCl_5 was yellow ochre.

Results and Discussion

Debye–Scherrer patterns of both K_2PuCl_5 and Rb_2PuCl_5 were essentially the same as that of K_2PrCl_5 (*3*) which is orthorhombic with space group *Pnma*. Unit cell dimensions were computed as in Ref. (*9*). All observed lines could be assigned to space group *Pnma*. Table I shows the crystal data. Due to the larger crystal radius of Rb^+ than K^+, the lattice parameters are larger in Rb_2PuCl_5. The observed and calculated $Q(=1/d^2)$ values for K_2PuCl_5 and Rb_2PuCl_5 are tabulated in columns 2 and 3 of Tables II and III, respectively. Q(calc) values were computed with the LAZY-PULVERIX program.

In the crystals A_2PuCl_5 (A = K, Rb) having the K_2PrCl_5 structure, there are 14 variable atom parameters to be determined. These are:

8A in (8d)	$x[A]$, $y[A]$, $z[A]$;
4Pu in (4c)	x[Pu], z[Pu];
4Cl(1) in (4c)	x[Cl(1)], z[Cl(1)];
4Cl(2) in (4c)	x[Cl(2)], z[Cl(2)];
4Cl(3) in (4c)	x[Cl(3)], z[Cl(3)];
4Cl(4) in (8d)	x[Cl(4)], y[Cl(4)], z[Cl(4)].

TABLE II

OBSERVED AND CALCULATED Q VALUES AND INTENSITIES FOR K_2PuCl_5

(*hkl*)	Q(obs)[a]	Q(calc)	I(obs)[b]	I(calc)	(*hkl*)	Q(obs)[a]	Q(calc)	I(obs)[b]	I(calc)
101	0.0215	0.0220	20	20	612	0.3025	0.3002	<1	0.3
200	0.0243	0.0249	8	8.4	440	0.3083	0.3097	2b	1.1
011	0.0284	0.0289	7	3.0	314	0.3195	0.3211	3	1.5
020	0.0518	0.0525	5	3.2	433	0.3576	0.3595	3	1.6
211	0.0531	0.0538	5	2.6	442	0.3708	0.3727	3	1.1
002	0.0621	0.0630	3	3.1	721		0.3733		0.7
301	0.0708	0.0718	8	6.5	134	0.3767	0.3763	3vb	0.7
121	0.0737	0.0745	9	8.3	613		0.3790		1.0
220	0.0765	0.0774	8	5.9	712	0.3794	0.3812	2vb	0.5
112	0.0814	0.0823	8	2.1	541		0.3815		0.4
202	0.0868	0.0879	2	1.8	015	0.4052	0.4068	1	1.0
400	0.0988	0.0996	2	2.5	343		0.4078		1.0
212	0.1007	0.1010	4	0.5	514	0.4195	0.4207	1	0.7
401	0.1143	0.1154	6	2.1	334	0.4247	0.4261	2b	1.2
022		0.1155		0.7	215	0.4313	0.4317	2vb	1.4
302	0.1180	0.1190	1	0.6	640		0.4342		1.1
122	0.1206	0.1217	5	1.5	820	0.4498	0.4510	2b	1.0
411	0.1274	0.1285	6	1.2	443		0.4514		0.3
312	0.1311	0.1321	6	1.8	524	0.4591	0.4601	2	0.2
031	0.1329	0.1339	3	1.3	802		0.4614		0.3
222	0.1393	0.1404	8	8.8	053	0.4685	0.4700	2vb	0.3
420	0.1510	0.1521	7	3.1	225		0.4711		0.5
013	0.1537	0.1549	5	1.8	060		0.4727		0.3
231	0.1576	0.1588	4	1.2	633	0.4823	0.4840	2vb	0.8
402	0.1616	0.1626	2	1.7	161	0.4933	0.4947	3vb	0.9
501	0.1705	0.1714	<1	0.4	253		0.4949		1.5
213	0.1784	0.1798	8	5.4	642		0.4972		0.8
132	0.1860	0.1874	5	1.7	260	0.4957	0.4976		0.6
303	0.1965	0.1978	<1	1.3	822	0.5121	0.5139	1	1.1
123	0.1991	0.2005	1	1.6	813	0.5509	0.5533	1	1.1
040	0.2086	0.2101	6	3.2	262	0.5586	0.5606	1	1.1
422	0.2137	0.2151	3	1.9	651	0.5676	0.5681	2vb	0.3
430	0.2183	0.2178	<1	0.6	453		0.5696		1.0
521	0.2227	0.2239	7	5.1	714		0.5701		0.5
512	0.2303	0.2318	4	0.8	460	0.5701	0.5722		0.5
141		0.2321		2.0	116	0.5849	0.5862	1	0.7
240	0.2334	0.2350	2	0.9	154		0.5864		1.0
332	0.2358	0.2372	3	1.3	206	0.5900	0.5918	1	0.2
610		0.2372		0.3	823		0.5927		0.2
403	0.2400	0.2413	3	0.4	462	0.6356	0.6353	2	0.5
413	0.2531	0.2545	6	2.6	10,1,0		0.6357		0.2
033	0.2581	0.2599	4	1.2	316		0.6360		0.2
114	0.2698	0.2713	6	1.7	354		0.6362		0.6
620	0.2753	0.2766	3	2.0	561	0.6432	0.6441	4	1.1
341	0.2804	0.2819	2	2.0	226		0.6443		0.7
233	0.2832	0.2848	6	2.6	743	0.6579	0.6569	1	0.5
602	0.2858	0.2871	2	0.9	833		0.6583		0.7
242	0.2965	0.2980	1	0.9					

[a] $Q = 1/d^2$ in Å^{-2}.

[b] Visually estimated.

TABLE III

OBSERVED AND CALCULATED Q VALUES AND INTENSITIES FOR Rb_2PuCl_5

(*hkl*)	Q(obs)[a]	Q(calc)	I(obs)[b]	I(calc)	(*hkl*)	Q(obs)[a]	Q(calc)	I(obs)[b]	I(calc)
101	0.0203	0.0208	9	10	033	0.2477	0.2480	1b	1.1
200	0.0228	0.0233	5	3.2	114	0.2560	0.2577	2	1.3
011	0.0278	0.0276	7	2.5	042	0.2591	0.2614	2b	1.2
211	0.0502	0.0509	1	2.2	341	0.2685	0.2690	4vb	2.7
002	0.0591	0.0598	3	4.1	602		0.2698		1.0
102	0.0646	0.0656	1	0.1	233		0.2713		2.1
301	0.0668	0.0675	9	9.4	440	0.2938	0.2949	4b	0.8
121	0.0703	0.0712	9	8.1	314	—	0.3043	—	1.2
220	0.0730	0.0737	10	7.1	433	0.3395	0.3413	2b	1.4
112	0.0772	0.0782	3	1.9	721	0.3503	0.3512	2vb	0.4
400	0.0925	0.0933	1	1.7	613	0.3562	0.3572	2	0.8
401	0.1073	0.1083	2	1.6	343	—	0.3887	—	1.1
122	0.1149	0.1160	4	1.4	623	0.3949	0.3950	1b	0.4
411	0.1200	0.1209	3	1.1	514		0.3977		0.6
312	0.1242	0.1249	3b	1.6	334	0.4030	0.4051	1	1.0
031	0.1273	0.1283	3	1.1	640	0.4097	0.4116	1b	1.2
222	0.1325	0.1335	8	7.9	820	—	0.4237	—	1.3
420	0.1426	0.1437	7	2.0	642	0.4712	0.4714	1vb	0.9
013	0.1460	0.1472	5	1.4	253		0.4729		1.1
213	0.1692	0.1705	7	4.2	161		0.4744		0.9
132	0.1776	0.1790	5	1.5	822	—	0.4835	—	1.4
303	—	0.1871	—	1.5	505	0.5180	0.5196	1vb	0.2
123	—	0.1908	—	1.1	813		0.5205		0.9
040	0.1998	0.2016	6	3.1	552		0.5206		0.5
422	0.2019	0.2035	4	1.2	453	0.5432	0.5429	1	0.8
600	—	0.2100	—	1.4	116	0.5584	0.5567	1	0.4
521	0.2100	0.2112	6	5.7	823		0.5583		0.2
512	0.2174	0.2182	1	0.8	154		0.5600		0.7
431	0.2199	0.2217	4	0.4	226	0.6115	0.6120	1vb	0.5
141		0.2224		1.0	561		0.6144		1.3
332	—	0.2257	—	1.2	653	0.6597	0.6596	1	0.4
413	0.2393	0.2405	2b	2.2	752		0.6606		0.3

[a] $Q = 1/d^2$ in Å^{-2}.

[b] Visually estimated.

Since it seemed difficult to obtain diffraction data with precise enough intensities to be able to determine the above variable parameters from the Guinier films, and since the present compounds are essentially ionic, these parameters were determined by an electrostatic method (*8, 9*). The basis of the method is that the atom parameters are to be those which bring about the maximum Madelung constant (condition 1) under the restriction that the ion–ion separations of any pairs of ions in the crystals are larger than the respective critical distances (condition 2). In doing the calculation, when the number of these parameters is more than two, the parameters should be separated into groups; otherwise it is practically impossible to follow the change of the Madelung constant as a function of these parameters. The parameters in a group are those which can explicitly be calculated together. For example, the parameters which define the atom position of one atom are to be grouped. In a preceding paper (*8*), the six variable atom parameters of β-Rb_2GeF_6, were obtained for u(Rb1), u(Rb2), and two explicit pairs of atom parameters, i.e., u(F1)–v(F1) and u(F2)–v(F2) by converging from initially guessed parameters. The maximization of the Madelung constant was performed successively for each above parameter or parameter pair using newly determined values, and then this cycle was repeated (*8*). Through this process, electrostatic interactions between atoms of the different groups are reflected in the atom parameters. In order to do the calculation with smaller correction values, the parameters related to the strong interactions (bonds), in other words those which have a large effect on the Madelung constant, should be calculated first. The interactions were classified according to their magnitude (*9*): (1) the largest interaction between a higher valency cation and anions coordinated to it; (2) medium strength interaction between a lower valency cation and the coordinated anions; (3) smaller repulsion between anions.

It remained difficult to determine the parameters of the present compounds with the above subsidiary means since the number of the parameters is too large. Then, a program to obtain directly the parameters which give rise to the maximum Madelung constant without utilizing any extra hypothesis as above was written. In the program, calculation starts also from a set of initially guessed variable atom parameters. The Madelung constant was first calculated for three cases $x[A] - W$, $x[A]$, and $x[A] + W$ with regard to the atom parameter $x[A]$, where W is a specified small positive number by which the change of the Madelung constant around $x[A]$ can be obtained under the condition that the other parameters are held constant. First, W was taken to be 0.005 (for refinement calculation 0.0001). One of the three $x[A]$ parameter values gives the maximum Madelung constant. The selected parameter needs to satisfy condition 2 (*8*). If not, this value is abandoned, and the parameter value which gives the second largest Madelung constant is taken from the remaining two. A satellite program provides a set of initial atom parameters which meet condition 2. Therefore, at least one of three such values satisfies the condition.

Similarly, the Madelung constant was calculated for $y[A] - W$, $y[A]$, and $y[A] + W$ using the obtained value of the $x[A]$ parameter (the other parameters held unchanged), which gives two parameter values of $x[A]$ and $y[A]$. This process was continued until the 14th value of the parameter, z[Cl(4)], was obtained. Then, this cycle was repeated for parameters $x[A]$, $y[A]$, · · · , z[Cl(4)]. Computation was terminated when the Madelung constant did not increase throughout two cycles of computation. For the Madelung constants, the method of Bertaut (*10, 11*) was used. The correctness of the program to calculate the constants was checked by comparing the obtained constants for several crystal structures with those of Johnson and Templeton (*12*). Another check was made by calculating CsCl constants with six different descriptions (*13*). These were well in accord with the literature value.

Condition 2 states that the ion–ion separations should be equal or longer than the critical distances. We use as the critical distances values 0.1 Å smaller than the sum of the crystal radii of Shannon (*14*).

Applicability of this method for determining the variable atom parameters of this crystal structure was examined first for K_2 $PrCl_5$ for which the atom parameters had been determined by single crystal X-ray diffraction analysis (*3*). The coordination number of Cl^- around Pr^{3+} is 7 in this structure. Since a crystal radius of Pr^{3+} (CN = 7) was not listed in the table of Shannon, it was estimated to be 1.198 Å from the Pr^{3+}

TABLE IV

ATOM PARAMETERS FOR K_2PuCl_5 AND Rb_2PuCl_5

		K_2PuCl_5	Rb_2PuCl_5
8K or 8Rb: (8d)	x	0.6904	0.6888
	y	0.4820	0.4867
	z	0.5336	0.5279
4Pu: (4c)	x	0.5102	0.5094
	z	0.0587	0.0658
4Cl(1): (4c)	x	0.0128	0.0127
	z	0.0759	0.0817
4Cl(2): (4c)	x	0.8146	0.8189
	z	0.3039	0.3046
4Cl(3): (4c)	x	0.6838	0.6734
	z	0.8601	0.8636
4Cl(4): (8d)	x	0.5687	0.5673
	y	0.5364	0.5407
	z	0.1559	0.1495

(CN = 6) crystal radius and the difference of La^{3+} (CN = 7) and La^{3+} (CN = 6) crystal radii in the table. The coordination number of Cl^- around K^+ is 9. However, the ninth chlorine atom is considerably more distant from K^+ than the other eight atoms. We took 1.65 Å for K^+ (CN = 8) in this calculation. As Cl^- crystal radius, 1.67 Å was taken.

Calculation of the initial set of the parameters for K_2PrCl_5 with lattice constants $a = 12.631$, $b = 8.756$, and $c = 7.973$ Å (*3*) with the satellite program showed that no parameter set could produce K–Cl, Pr–Cl, and Cl–Cl distances all larger than the critical distances. The condition was not satisfied until the crystal radius of Cl^- was diminished to 1.63 Å. Therefore, calculation of the atom parameters by maximization of the Madelung constant was carried out with this Cl^- value, which corresponds to the critical distances of K–Cl = 3.18, Pr–Cl = 2.728, and Cl–Cl = 3.16 Å. Calculation of the Madelung constant was made first for h, k, and l's each from −4 to +4, and then with refined values of the parameters for h, k, and l's each from −12 to +12. The atom parameters obtained are: $x[K] = 0.6731$, $y[K] = 0.4914$, $z[K] = 0.5441$, $x[Pr] = 0.5086$, $z[Pr] = 0.0773$, $x[Cl(1)] = 0.0022$, $z[Cl(1)] = 0.0806$, $x[Cl(2)] = 0.8014$, $z[Cl(2)] = 0.3261$, $x[Cl(3)] = 0.6815$, $z[Cl(3)] = 0.8722$, $x[Cl(4)] = 0.5729$, $y[Cl(4)] = 0.5388$, and $z[Cl(4)] = 0.1555$. The values are in reasonable agreement with those of Meyer and Hüttl (*3*) except for a relatively large difference in the values of Cl(2) and Cl(4). Regarding this, we consider that there might remain some problems in the estimation of anion–anion critical distances (crystal radius sum minus 0.1 Å) under the circumstances that the crystal radii of anions have not been defined clearly and no values have been presented as a function of coordination number (*14*). In other words, it is possible that to treat the anion–anion repulsions as interactions based on the semihard sphere model is inappropriate. Further studies on this issue are required for more refined calculations. Anyway, all the parameters above obtained are consistent with those of Meyer and Hüttl (*3*) within the errors of parameter values ~0.01.

Calculation of the atom parameters for K_2PuCl_5 was performed for a Cl^- crystal radius of 1.60 Å which was the largest radius that satisfied condition 2 for all pairs of K–Cl, Pu–Cl, and Cl–Cl critical values, i.e., 3.15, 2.71, and 3.10 Å, respectively. As the Pu^{3+} (CN = 7) crystal radius, 1.21 Å, which was obtained in the same manner as in the case of Pr^{3+} (CN = 7), was used. The results are shown in Table IV. Calculation of these parameters involves Madelung constant computation for $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, and $-12 \leq l \leq 12$. The Madelung constant, Madelung energy (per mol), and half the shortest atom distance obtained are 16.5732, −2033.52 kcal/mol, and 1.35504 Å, respectively.

In the rightmost column of Table II are shown the calculated intensities using the above parameter values with LAZY-PULVERIX, which are reasonably in agreement with the observed ones.

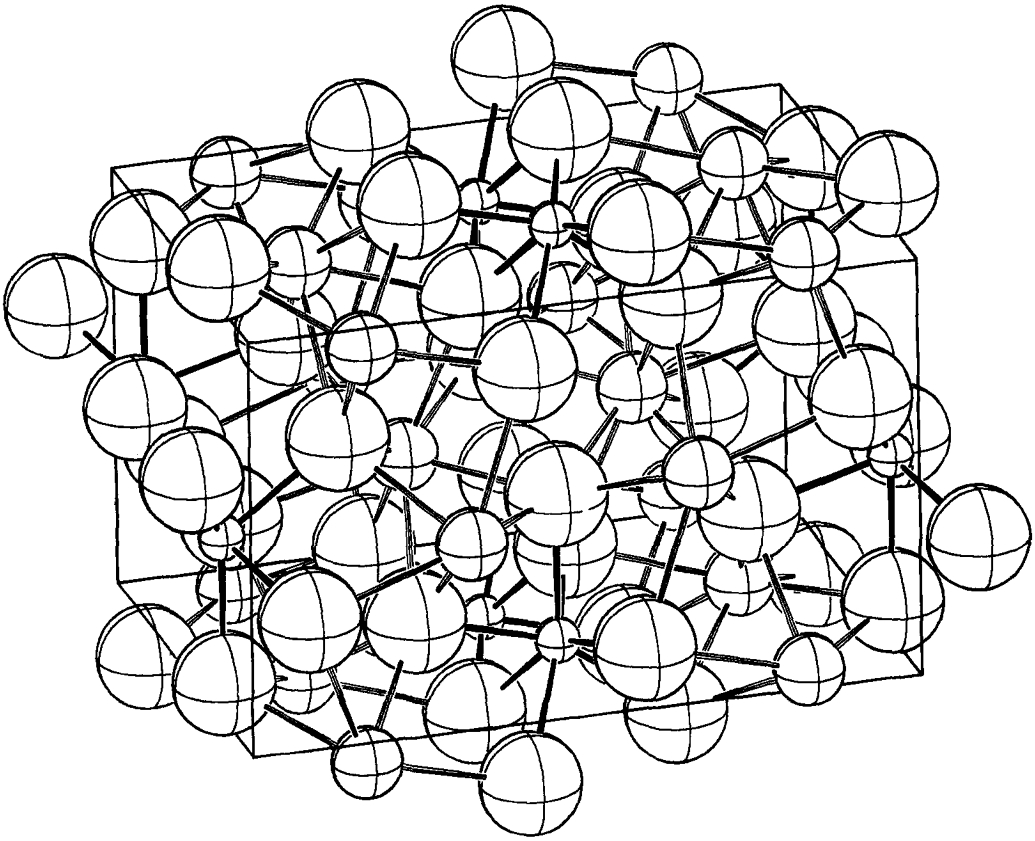

FIG. 1. Perspective view of K_2PuCl_5 and Rb_2PuCl_5. Smallest spheres, Pu; middle-sized spheres, K or Rb; largest spheres, Cl.

Figure 1 illustrates a perspective view of this crystal obtained with the ORTEP2 program. The smallest, middle, and largest circles denote plutonium(III), alkali metal, and chlorine atoms, respectively. As shown by Meyer and Hüttl (*3*), the numbers of coordination of chlorine atoms around a Pu^{3+} atom and around an alkali metal are seen to be 7 and 8 (+1), respectively. The chlorine atoms around the Pu^{3+} atom form a monocapped trigonal prism. This polyhedron links with another one via a common edge forming an infinite chain along the *b* axis, i.e., ${}^{1}_{\infty}[PuCl^{t}_{3/1}Cl^{e}_{4/2}]^{2-}$ where *e* and *t* stand for edge sharing and terminal chlorine atoms, respectively. Four Cl(4) atoms coordinated to one plutonium atom participate in the edge sharing. Bond distances for K_2PuCl_5 calculated by using the obtained atom parameters are tabulated in Table V.

Calculation of the atom parameters for Rb_2PuCl_5 was carried out in the same manner as that for K_2PuCl_5. As the crystal radius of Rb^+, the eight coordination value, 1.75 Å (*14*), was adopted for the same reason as in K_2PuCl_5. Because the satellite program calculation revealed that there can be no atom parameter set which satisfied condition 2 with the Cl^- crystal radius of 1.67 Å (literature value), it was reduced to 1.60 Å, which is the maximum value in agreement with condition 2. The critical distances for Rb–Cl, Pu–Cl, and Cl–Cl are then 3.25, 2.71, and 3.10 Å, respectively.

TABLE V

BOND DISTANCES (Å) FOR K_2PuCl_5 AND Rb_2PuCl_5[a]

K_2PuCl_5			
Pu–Cl(2)	2.710	K–Cl(3)	3.150
Pu–Cl(3)	2.710	K–Cl(2)	3.151
Pu–Cl(4)	2.720(4×)	K–Cl(1)	3.151
Pu–Cl(1)	2.912	K–Cl(2)	3.180
		K–Cl(4)	3.209
		K–Cl(3)	3.298
		K–Cl(4)	3.415
		K–Cl(1)	3.495
		K–Cl(4)	4.115
Rb_2PuCl_5			
Pu–Cl(2)	2.710	Rb–Cl(3)	3.250
Pu–Cl(3)	2.710	Rb–Cl(1)	3.251
Pu–Cl(4)	2.754(2×)	Rb–Cl(2)	3.261
Pu–Cl(4)	2.784(2×)	Rb–Cl(2)	3.269
Pu–Cl(1)	2.883	Rb–Cl(4)	3.354
		Rb–Cl(3)	3.468
		Rb–Cl(4)	3.513
		Rb–Cl(1)	3.558
		Rb–Cl(4)	4.274

[a] Final significant figures are given for comparative purposes; precision is ca. ± 0.01 Å.

The atom parameter values obtained are shown in Table IV. The values are seen to be slightly changed from those for K_2PuCl_5. The Madelung constant, Madelung energy (per mol), and half the shortest atom distance obtained are 16.4102, −2013.53 kcal/mol, and 1.35503 Å, respectively. It is interesting that the Madelung constant of Rb_2PuCl_5 is smaller than that of K_2PuCl_5 by 0.163 for the same shortest atom distance which corresponds to one of the Pu–Cl distances. The difference in the Madelung constant results in lower Madelung energy for K_2PuCl_5. The calculated intensities, I(calc), for Rb_2PuCl_5 are shown in the rightmost column of Table III. These are seen to be in reasonable agreement with the observed intensities (column 4). The arrangement and coordination of atoms in Rb_2PuCl_5 is essentially the same as in K_2PuCl_5. Bond distances calculated by using the obtained atom parameters are listed in Table V.

Figure 2 shows the arrangement of chlorine atoms around Pu^{3+}. The bond distances given in the figure are those for K_2PuCl_5. One each of Cl(1), Cl(2), and Cl(3) atoms together with four Cl(4) atoms surround the plutonium atom. The Cl(1) atom is right over the plutonium along the direction of the *c* axis.

As the chlorine positions change, the Pu–Cl distances also change. The bond distances are the same or elongated for the case of the rubidium compound. The reverse is seen only for Pu–Cl(1) where 2.912 Å decreases to 2.883 Å. The Pu–Cl(2) and Pu–Cl(3) distances, 2.710 Å, do not change. Two Pu–Cl(4) bonds with the lower (along *c* axis) Cl(4) atoms increase their distance from 2.720 Å of K_2PuCl_5 to 2.754 Å of Rb_2PuCl_5. With the higher Cl(4) atoms the bond distance increases to a larger degree. In this case, 2.720 increases to 2.784 Å. Such general trends of increase in the Pu–Cl and *A*–Cl bond distances may be understood as associated with weaker bonds and higher lattice energy. The smaller Madelung constant for Rb_2PuCl_5, though the constant corresponds to a geometrical

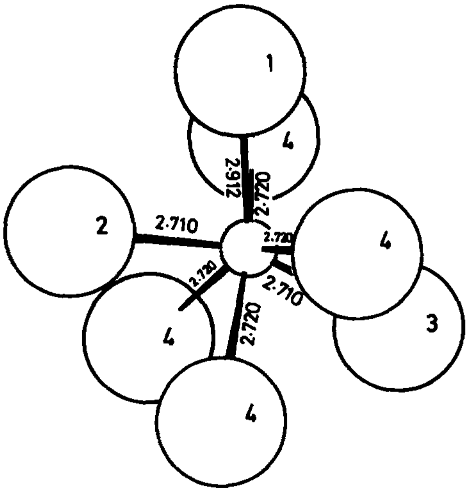

FIG. 2. Arrangement of chlorine atoms around Pu^{3+} atom in K_2PuCl_5 and Rb_2PuCl_5. Center atom, Pu^{3+}. Bond distances are for K_2PuCl_5.

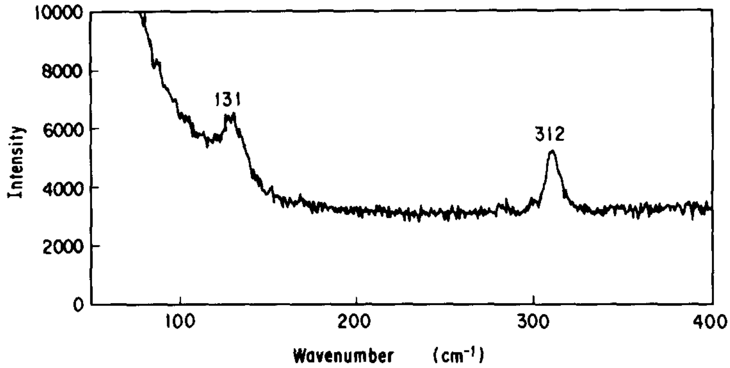

FIG. 3. Raman spectra for Rb_2PuCl_5.

arrangement and not to the bonding distance, suggests a marginal stability for Rb_2PuCl_5.

According to Meyer (*1*), rare-earth complex chlorides, A_2RECl_5, crystallize in the K_2PrCl_5-type structure (space group *Pnma*) if A^+ is either K^+ or Rb^+ and RE^{3+} has CN = 9 in binary chlorides provided that the polarization of RE^{3+} is not too large. The present compounds, though not rare-earth complexes, accord with his classification since the chlorine atom coordination around Pu^{3+} is 9 in $PuCl_3$ (*15*).

Figure 3 shows the Raman spectrum of Rb_2PuCl_5 taken at room temperature. It is interesting that the figure shows two peaks at 131 and 312 cm^{-1} which are very close to 132 and 312 cm^{-1} for Rb_2PuCl_6 (9). In the case of Rb_2PuCl_6, the Raman lines could be interpreted in terms of $PuCl_6^{2-}$ which are slightly distorted from O_h symmetry. The angles Cl–Pu–Cl in Rb_2PuCl_6 are 101.04, 86.27, and 85.15° (if O_h, the angles should be 90° and the bond distances should all be the same). The 132 and 312 cm^{-1} lines could be assigned to threefold degenerate $\nu_5(F_{2g})$ and nondegenerate $\nu_1(A_{1g})$ normal modes of the O_h symmetry. The Raman spectra for α-Cs_2UCl_6, Cs_2NpCl_6, and Cs_2PuCl_6 (*16, 17*), which are also of distorted O_h, have shown the ν_5 and ν_1 lines near those of Rb_2PuCl_6.

For Rb_2PuCl_5, the chlorine coordination around plutonium can be regarded as distorted O_h if Cl(1) is neglected. The bond angles are between 68.08 and 98.89°, and the bond distances Pu–Cl between 2.710 and 2.784 Å. The coincidence of the Raman lines of Rb_2PuCl_5 with those of Rb_2PuCl_6 could thus be explained by this fact. Broadness of the present peaks may be attributed to the distortion of the crystal. Berringer *et al.* (*18*) have pointed out the insensitivity of the Raman and infrared spectra of these kinds of compounds. K_2PuCl_5 did not exhibit any Raman bands. The reason is unclear, but it is possible that the compound was decomposed under the laser light on exposure.

Combination of the present lattice parameters for K_2PuCl_5 and Rb_2PuCl_5 with the available lattice parameter data for K_2UCl_5 and Rb_2UCl_5 (*5*) as well as K_2AmCl_5 and Rb_2AmCl_5 (*6*) enables us to trace the change of molecular volume with increasing atomic number of the actinides. Curves 1 and 2 in Fig. 4 show the change of the molecular volume ratios $V(K_2AnCl_5)/V(K_2UCl_5)$ and $V(Rb_2AnCl_5)/V(Rb_2UCl_5)$, respectively, where *An* denotes the actinides. Both curves are seen to decrease with the increase of the atomic number. Curve 3 represents the molecular volume change of $AnCl_3$ expressed as $V(AnCl_3)/$

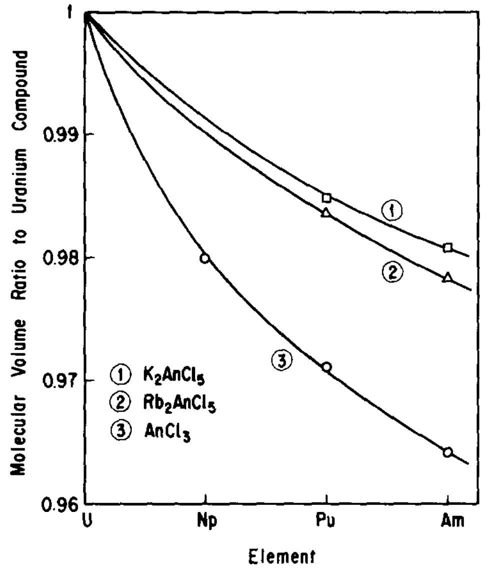

FIG. 4. Change of molecular volume ratio with the actinide elements from uranium to americium.

$V(UCl_3)$. To obtain these values, the literature lattice parameters of UCl_3 (*5*), $NpCl_3$ (*19*), $PuCl_3$ (*20*), and $AmCl_3$ (*6, 21*) were used. It is seen from curve 3 that the volume decreases with increasing atomic number or decreasing crystal radius of the actinides. The slopes of the K_2AnCl_5 and/or Rb_2AnCl_5 curves are smaller than that of $AnCl_3$, which can be ascribed to the larger number of the other atoms to one actinide atom in the formula of the complex chlorides.

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