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Authors

Morss, L.R.
Fuger, J.

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PREPARATION AND CRYSTAL STRUCTURES OF DICESIUM BERKELIUM HEXACHLORIDE AND DICESIUM SODIUM BERKELIUM HEXACHLORIDE[1a]

L. R. Morss and J. Fuger[1b]

Lawrence Radiation Laboratory
and Department of Chemistry
University of California
Berkeley, California

ABSTRACT

Cs_2BkCl_6 and $Cs_2NaBkCl_6$ have been prepared from aqueous solution on the scale of a few micrograms using the isotope ^{249}Bk. The crystal structures of these compounds have been determined. Cs_2BkCl_6 is not isomorphous with Cs_2PuCl_6 or Cs_2CeCl_6, which exhibit trigonal symmetry, but rather is hexagonal, space group $P6_3mc$ (C_{6v}^4), with two molecules per unit cell. Lattice parameters (95% confidence) are $a = 7.451 \pm 6$, $c = 12.097 \pm 9$ Å. $Cs_2NaBkCl_6$ is face-centered cubic ($Fm3m$ - O_h^5) and isomorphous with the corresponding americium compound. The lattice parameter is $a = 10.805 \pm 3$ Å. The crystal contains four molecules per unit cell.

Because of the comparatively short half-life and presently restricted availability of berkelium (as ^{249}Bk), the preparation and characterization of its compounds present an interesting challenge in inorganic synthesis. If these difficulties can be overcome, basic information can be obtained on the trivalent chemistry of this element and on its even more interesting tetravalent properties.

The frequently observed parallels in berkelium and cerium chemistry

focused our interest on a marginally stable compound of tetravalent cerium,

Cs_2CeCl_6. We had prepared this compound easily by precipitation from ice-

cold concentrated HCl, and with considerable difficulty by heating an intimate

mixture of $CeCl_3$ and CsCl for several days in several atmospheres pressure of

Cl_2. We selected the "wet" preparation as preferable, although it involved

more mechanical manipulations. (The major technical difficulty was the

quantitative removal of dried, centrifuged precipitate from the bottom of a

capillary microcone.)

EXPERIMENTAL

As a preliminary to the proposed synthesis of Cs_2BkCl_6, techniques

were first developed for the microgram-scale synthesis of Cs_2CeCl_6. Beginning

with a solution of 1 µg of Ce(III) in 1 µl of $2\underline{M}\ H_2SO_4$, methods of oxidation

and precipitation were investigated systematically; the procedure which gave

the optimum yield of Cs_2CeCl_6 was subsequently applied to the experiments

with Bk. In particular, the tetravalent hydroxide was selected as an

appropriate intermediate because the stability against reduction, ease of

precipitation, and speed of dissolution of Bk(IV) and Ce(IV) hydroxides were

expected to be similar.

Sources of berkelium.   Preliminary experiments utilized 4 µg of ^{249}Bk (which

had been recovered from ion-exchange beads used for magnetic susceptibility

measurements) without further purification. This material contained about

0.8 µg of the decay product ^{249}Cf. Later experiments were performed with 16 and

80 µg of ^{249}Bk freshly separated from daughter activity by an alpha-hydroxy-

isobutyric acid cation exchange column and finally purified using a leached

quartz cation-exchange "clean-up" column with high-purity reagents.[2] The resulting hydrochloric acid solutions were evaporated to dryness and taken up in $2\underline{M}$ H_2SO_4 to give a final Bk concentration of 1 µg/µl. Aliquots of Bk and appropriate reagent solutions were dispensed with a microburette of quartz capillary tubing of known internal diameter.

Preparation of Cs_2BkCl_6.   A 5-µg aliquot of Bk solution in $2\underline{M}$ H_2SO_4 was placed in a quartz microcone prepared by pulling quartz tubing to a capillary tip with a thin-walled, rounded bottom of internal diameter approximately 0.2 mm. To this solution was added 5 µl of saturated $NaBrO_3$ in $2\underline{M}$ H_2SO_4. After mixing and centrifuging, the solution was heated to 90° in a water bath for 3 minutes to accelerate oxidation of Bk(III) to Bk(IV). The cooled solution was then made basic by adding $5\underline{M}$ aqueous NH_4OH until precipitation was complete. About 25 µl of the NH_4OH solution was required to reduce excess bromate and neutralize the sulfuric acid. (This procedure was developed from the preliminary experiments with cerium. Hot $1\underline{M}$ BrO_3^- was required to achieve rapid oxidation; neutralization with gaseous NH_3 usually resulted in considerable precipitation of NH_4BrO_3.)

The resulting precipitate was centrifuged and washed three times with water. The precipitate, presumably $Bk(OH)_4$, was yellow-green and similar in physical appearance to $Ce(OH)_4$.

After centrifuging for one hour, excess water was removed by pipetting and the cone was cooled to the melting point of CCl_4 (-23°), freezing the hydroxide precipitate. A freshly prepared solution of $0.1\underline{M}$ CsCl in concentrated HCl containing dissolved Cl_2 was pipetted into the reaction cone to provide about 20 mole% excess of Cs over that required for Cs_2BkCl_6. In

rapid sequence, HCl gas was blown into the cone to replace most of the air

and to maintain the solution saturated in HCl, the cone was covered with

Parafilm and centrifuged briefly (in order to force all reagents into the

capillary tip) in a chilled centrifuge tube, and the reagents were stirred

to ensure complete dissolution of $Bk(OH)_4$.

It was possible to observe the stirring operation under the microscope.

The hydroxide dissovled to give a red solution, from which a red-orange pre-

cipitate formed immediately. The cone was recentrifuged and the supernatant

solution removed. The precipitate was then washed once with glacial acetic

acid (to remove water) and three times with diethyl ether. After the final

washing, the orange precipitate dried rapidly as the ether evaporated; the

reaction cone was immediately capped and mounted in toto as an X-ray

capillary. Gamma radioactivity monitoring showed that about one-half of

the Bk remained with the washed precipitate.

Preparation of $Cs_2NaBkCl_6$. The first two preparations of Cs_2BkCl_6 had been

carried out with one-microgram portions of Cf-contaminated berkelium. In

order to prove that the orange precipitate would not form under non-oxidizing

conditions, and therefore that it was a compound of Bk(IV); 1 μg of Bk

solution was carried through steps identical to those described above in a

reaction microcone with a somewhat smaller capillary-tip, except that sodium

sulfate was substituted for sodium bromate. In this way, oxidation of

Bk(III) was eliminated without altering other conditions. A white hydroxide

precipitate was observed. Upon dissolving this precipitate in CsCl-HCl

solution, no precipitate formed. However, upon blowing HCl gas over the

surface of the solution and cooling the cone, a yellow crystalline precipitate

appeared, first at the surface and then throughout the solution. This precipitate, very small in amount, survived washings as described above. Its X-ray powder pattern was remarkably similar to that reported for $Cs_2NaAmCl_6$, prepared recently by Bagnall et al.[3] We believe that under our experimental conditions sufficient sodium for a small yield of $Cs_2NaBkCl_6$ remained from the Na_2SO_4 solution. Similar experiments have shown very imperfect washing of microscale precipitates.

Encouraged by these results, we prepared $Cs_2NaBkCl_6$ twice, using 1-µg aliquots of recently purified Bk solution in capillary-tip microcones of 0.1 mm internal diameter. For the first preparation, Bk(III) hydroxide was precipitated with NaOH and the precipitate was washed three times with water. A solution of $0.1\underline{M}$ CsCl-$0.05\underline{M}$ NaCl in $6\underline{M}$ HCl was added in about 20% excess, the hydroxide was stirred until it dissolved, and HCl gas was then blown over the solution. In this first preparation, the hydroxide was faintly green in color but more flocculent than the Bk(IV) hydroxide. When HCl gas was blown into the microcone, a distinctly yellow precipitate formed, which was washed as above. Its X-ray powder pattern was again similar to that of face-centered cubic $Cs_2NaAmCl_6$.

The subsequent preparation was performed under reducing conditions by adding hydroxylamine to the Bk solution before precipitating the hydroxide. In this preparation both the hydroxide and the final precipitate were white. The powder pattern of the resulting substance was face-centered cubic, identical to that of the earlier (yellow) product. (An interpretation of these observations is offered in the Discussion.)

<u>X-ray Diffraction Equipment.</u> X-ray powder patterns were taken on Ilford G

Industrial X-ray film in a 57.3 mm diameter Debye-Scherrer Philips camera with

Straumanis mounting. (The camera chuck and cover were modified to accept the

long capillary-cones.) Copper radiation ($K\alpha_1$ = 1.54051Å), filtered through

0.01 mm nickel foil placed between sample and film, was generated by a Jarrell-

Ash 80-000 Microfocus X-ray unit. Exposure times were 2 to 8 hours. Most re-

flections for $2\theta < 20°$ and $> 160°$ were masked by the Ni filter support. Line

positions were measured visually to ±0.05 mm. Individual preparations were photo-

graphed twice and most films were read twice by independent observers on different

readers. Line intensities were measured with a Jarrell-Ash microphotometer.

RESULTS

Preliminary syntheses using 1-µg quantities of cerium under conditions

similar to those planned for berkelium gave powder patterns of Cs_2CeCl_6 whose

lattice parameters were in close agreement with those earlier reported for

macro-scale preparations, even when 1/5 as much lanthanum as cerium was in-

tentionally added as a trivalent impurity. Results of the Ce experiments are

shown in Table **I**.

Table I. Lattice Parameters of Trigonal Cs_2CeCl_6

Observer	a_o	c_o
Plumier[4]	7.484Å	6.034Å
Kaatz and Marcovich[5]	7.476	6.039
This work, 1 ug	7.480	6.046
This work, 1 ug with 20% La^{+3} in starting material	7.481	6.040

Six successful preparations of Cs_2BkCl_6 were achieved, two starting with 1 µg of Bk (contaminated with 20% Cf daughter), two using 5 µg of recently-purified Bk, and two using 40 µg of recently-purified Bk. (An attempted preparation using NaOH as precipitant for the hydroxide instead of NH_4OH (to avoid reduction of bromate by NH_3) resulted in a mixture of mostly $Cs_2NaBkCl_6$ with only a small amount of Cs_2BkCl_6.)

Least-squares fitting of lattice parameters to observed line positions was carried out using program LCR-2.[6] Theoretical line intensities were calculated by program POWD.[7]

All known complex compounds of the composition Cs_2MCl_6 exhibit either trigonal or cubic crystal structures. For the known actinide (IV) complexes of thorium through plutonium,[8] and for cerium,[5] the complexes are trigonal. Lead, zirconium, and smaller tetravalent cations form cubic complexes. Since the Bk^{4+} ion is believed to be only slightly smaller than Pu^{4+} but considerably larger than Pb^{4+}, it was anticipated that Cs_2BkCl_6 would be isostructural with the trigonal actinide (IV) hexachlorocomplexes. However, the powder patterns of Cs_2BkCl_6 showed that this compound is isostructural neither with Cs_2PuCl_6 nor with Cs_2PbCl_6. The powder patterns were indexable only in a hexagonal system typified by Rb_2MnF_6.[9] (It should be pointed out that some hexafluoro complex compounds are polymorphic, exhibiting two or even all three of these structures.)[10]

The systematic extinctions, namely (hhℓ) $\ell = 2n$, and special atomic positions establish the space group as $P6_3mc$ (C_{6v}^4), with atomic positions as follows: 2 Bk (b) 1/3, 2/3, 0.25; 2 Cs (b) 1/3, 2/3, 0.895; 2 Cs (a) 0, 0, 0.105; 6 Cl (c) 0.17, -0.17, 0.37; 6 Cl (c) 0.495, -0.495, 0.13. Atomic

positions not fixed by the space group were estimated by comparison with

Rb_2MnF_6. Unit cell dimensions were calculated by averaging 2θ values from

six films representing all four preparations. Program LCR-2 weighs each line

proportional to $1/\sin^2(2\theta)\sigma^2(\theta)$, where $\sigma(\theta)$ is the average error of a single

line reading from the mean. In many cases observed lines were considered to

be superpositions of two or more theoretically possible lines. In these

situations each of the theoretically possible lines was assigned to the

observed 2θ value and weighted with respect to its calculated intensity such

that the overall weight of the group remained $1/\sin^2(2\theta)\sigma^2(\theta)$, $\sigma(\theta)$ still

being the average error of the observed line reading from the mean of that

line on all films. This was accomplished by normalizing all the calculated

intensities for a group of superposed lines to $\Sigma I = 1$, and setting

$\sigma_i = \sigma_{net}/(I_i)^{1/2}$. Lattice parameters so calculated are a = 7.451 ± 1,

c = $12.097 \pm 2\overset{\circ}{A}$. Error limits are standard deviations representing only

internal consistency of averaged values of observed 2θ.

As an alternative method of calculating lattice parameters, 2θ

values from each film were used to calculate lattice parameters for that

film. The mean values, with error limits representing 95% confidence limits

for the four preparations (by applying the Student $\underline{t}$ value of 3.2 to standard

deviations generated from the four sets of lattice parameters), are a = 7.451

$\pm$ 6, c = $12.097 \pm 9\overset{\circ}{A}$.

For this crystal structure, the formula weight is 727.60, the cell

volume is $581.6\overset{\circ}{A}^3$, and the calculated density is 4.155 g/cm^3. There are two

formula units per unit cell. Figure 1 is a projection of the unit cell upon

the $\underline{a}$ $\underline{b}$ plane.
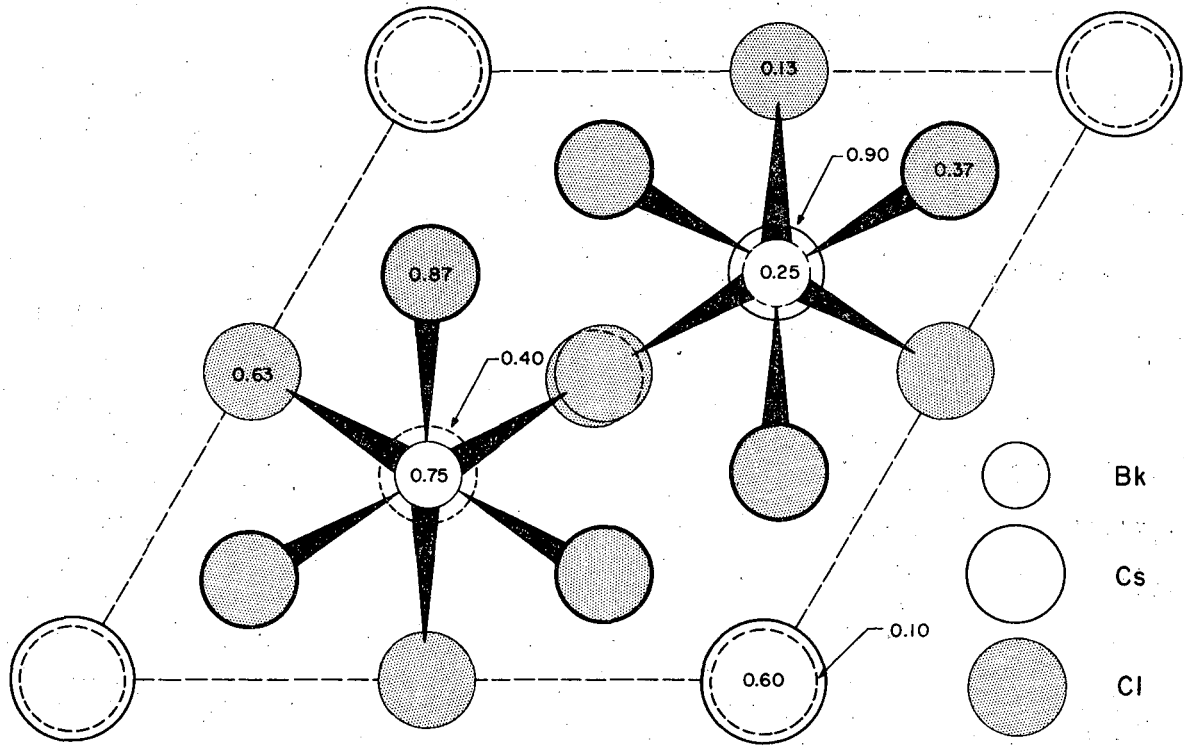
Fig. 1   Projection of unit cell of Cs_2BkCl_6 upon $\underline{a}\ \underline{b}$ plane.

Table II is a line list for averaged values from the six films. Table
III is a line list for unindexed lines; those attributable to known impurities
are so indicated. A measure of the rate of decomposition of Cs_2BkCl_6 due to
radioactivity and atmospheric moisture is the "growth" of unindexed lines:
one 5-μg sample with 61 indexable lines showed one unindexable line of trace
intensity four hours after preparation; 7 impurity lines after 18 hours; and
10 impurity lines after 96 hours (during 18 of which the sample had been exposed
to an X-ray beam), including two lines of medium intensity.

$Cs_2NaBkCl_6$ is isostructural with $Cs_2NaAmCl_6$[3] and with many other com-
pounds A_3BX_6 or A_2BCX_6.[11] The space group of these compounds is $Fm3m$ (O_h^5).
Atomic positions are as follows: 4 Bk (a) 0,0,0 + F.C.; 4 Na (b) 1/2, 1/2, 1/2
+ F.C.; 8 Cs (c) 1/4, 1/4, 1/4 + F.C. and 3/4, 3/4, 3/4 + F.C.; 24 Cl (e) 0,
0, ±0.24 + F.C.; 0, ±0.24, 0 + F.C.; ±0.24, 0, 0 + F.C. The lattice parameter,
calculated by averaging eight independently calculated lattice parameters
from four films obtained from two preparations, is 10.805 ± 3 (95% confidence).
Formula weight is 750.59; cell volume 1261.5 $\overset{\circ}{A}^3$; calculated density 3.952 g/cm^3;
4 formula units per unit cell. The Bk-Cl distance was fixed by finding the
best fit between observed and calculated intensities.

Table IV is a line list for averaged $\underline{d}$ spacings from each of the four
films. All lines are included for calculated intensities greater than 3. The
stability of $Cs_2NaBkCl_6$ when stored in air is indicated by a calculated lattice
parameter of 10.810 $\overset{\circ}{A}$ and the presence of only two impurity lines in the powder
pattern of a three-month-old sample.

Table V lists the powder pattern impurities in $Cs_2NaBkCl_6$.

Table II. Powder Pattern Line List for Ca_2BkCl_6 (hexagonal)

No. Obs.	I_{obs}	d_{obs}	h k l	d_{calc}	I_{calc}[a]
1	60[b]	5.93	0 0 2	6.05	20
1	52[b]	5.74	1 0 1	5.69	97
6	40[b]	4.411	1 0 2	4.413	61
6	100[b]	3.729α 3.732β	1 1 0	3.726	100
6	40[b]	3.422	1 0 3	3.420	75
6	32	3.173	1 1 2	3.172	22
4	5[b]	3.116	2 0 1	3.117	21
5	5[b]	3.018	0 0 4	3.024	5
6	55	2.846	2 0 2	2.847	83
5	22	2.735	1 0 4	2.738	18
6	46	2.519	2 0 3	2.519	62
3	2[b]	2.430	2 1 0	2.439	2
6	18	2.392	2 1 1	2.391	20
6	52	2.260	1 0 5 / 2 1 2	2.265 / 2.262	36
6	27	2.202	2 0 4	2.206	16
6	37	2.150	3 0 0	2.151	13
6	47	2.087	2 1 3	2.087	43
6	23	2.025	3 0 2	2.027	7
6	60	1.934	2 0 5	1.936	22
5	37	1.895	2 1 4	1.898	13
6	70	1.861	2 2 0	1.863	41
6	58	1.774	1 1 6 / 3 1 1	1.773 / 1.771	36
6	70	1.714	2 1 5 / 3 1 2 / 2 0 6	1.718 / 1.716 / 1.710	35
6	7	1.668	1 0 7	1.669	2
6	24	1.636	3 1 3	1.636	19
2	4	1.600	4 0 1	1.599	3
5	6	1.588	2 2 4	1.586	3
6	20	1.557	4 0 2 / 2 1 6	1.559 / 1.554	14
2	6	1.540	3 1 4	1.540	7
4	20	1.512	0 0 8	1.512	5
4	20	1.4966	4 0 3	1.4978	12
6	24	1.4704	1 0 8 / 3 0 6 / 3 2 1	1.4722 / 1.4710 / 1.4694	24
6	25	1.4375	3 1 5 / 3 2 2	1.4388 / 1.4379	13
2	39	1.4105	2 1 7 / 4 1 0	1.4100 / 1.4081	15
6	24[b]	1.4042	1 1 8	1.4011	7
3	10[b]	1.3890	3 2 3	1.3897	11
6	26	1.3694	4 1 2 / 2 0 8 / 2 2 6	1.3714 / 1.3692 / 1.3682	14
5	17	1.3419	4 0 5 / 3 1 6	1.3422 / 1.3384	8
2	2[b]	1.3287	3 2 4	1.3296	4
6	16[b]	1.2616	3 2 5 / 5 0 2 / 4 0 6	1.2627 / 1.2621 / 1.2596	10
6	16[b]	1.2393	3 1 7 / 3 3 0 / 2 0 9 / 3 0 8	1.2432 / 1.2418 / 1.2408 / 1.2370	13
3	8[b]	1.2144	3 3 2 / 4 2 1	1.2165 / 1.2133	4
5	6[b]	1.1948	4 2 2 / 3 2 6	1.1954 / 1.1932	11
3	6[b]	1.1892	1 0 10 / 5 0 4	1.1890 / 1.1870	3
6	12[b]	1.1738	2 1 9 / 2 2 8	1.1772 / 1.1740	18
3	8[b]	1.1687	4 2 3	1.1672	11
5	12[b]	1.1538	3 1 8 / 4 1 6 / 5 1 1	1.1550 / 1.1544 / 1.1537	19
3	5[b]	1.1316	2 0 10 / 4 2 4	1.1327 / 1.1310	6
2	5[b]	1.0901	4 2 5	1.0890	7
4	15[b]	1.0869	5 0 6	1.0869	0.4
2	6[b]	1.0842	1 0 11 / 2 1 10	1.0841 / 1.0837	5
5	12[b]	1.0757	6 0 0 / 3 1 9	1.0755 / 1.0748	13
5	12[b]	1.0570	6 0 2 / 3 2 8 / 3 3 6 / 4 3 1	1.0588 / 1.0578 / 1.0574 / 1.0568	11
6	12[b]	1.0433	5 1 5 / 4 3 2 / 4 2 6	1.0452 / 1.0449 / 1.0434	10
6	16[b]	1.0306	5 2 0 / 4 0 9 / 4 1 8	1.0333 / 1.0326 / 1.0305	13
4	12[b]	1.0012	2 1 11 / 3 1 10 / 4 3 4	1.0025 / 1.0022 / 1.0010	10
3	8[b]	0.9958	4 2 7 / 1 0 12 / 3 2 9	0.9964 / 0.9960 / 0.9951	7
2	6[b]	0.9695	4 0 10	0.9678	2
3	2[b]	0.9595	3 3 8	0.9597	3
4	10[b]	0.9369	3 1 11 / 3 2 10 / 6 1 4	0.9370 / 0.9367 / 0.9358	9
5	10[b]	0.9312	2 1 12 / 4 4 0 / 5 0 9	0.9316 / 0.9314 / 0.9309	12
5	12[b]	0.9198	4 4 2 / 5 1 8 / 5 2 6 / 7 0 1 / 5 3 1	0.9205 / 0.9198 / 0.9195 / 0.9192 / 0.9192	17
2	4[b]	0.9123	3 0 12 / 6 1 5 / 7 0 2 / 5 3 2	0.9128 / 0.9115 / 0.9113 / 0.9113	9
3	6[b]	0.9092	4 0 11	0.9087	3
2	2[b]	0.8984	7 0 3 / 5 3 3	0.8986 / 0.8986	7
2	4[b]	0.8936	2 0 13 / 6 2 1	0.8941 / 0.8924	3
2	< 2[b]	0.8830	3 2 11	0.8828	5
3	6[b]	0.8752	6 0 8 / 6 2 3	0.8764 / 0.8736	20
5	12[b]	0.8539	6 1 7 / 4 0 12 / 7 1 0 / 5 2 8	0.8551 / 0.8549 / 0.8547 / 0.8531	17
2	8[b]	0.8390	6 2 5	0.8393	8
2	2[b]	$0.8242α_1$	6 1 8 / 5 4 1	0.8248 / 0.8243	7
2	4[b]	$0.8168α_1$	4 2 10	0.8167	10
1	< 2[b]	$0.8127α_1$	6 3 0	0.8130	9
1	< 2[b]	$0.8064α_1$	4 0 13	0.8060	3
2	2[b]	$0.7976α_1$	5 1 11 / 4 3 10 / 5 4 4	0.7977 / 0.7976 / 0.7970	19
1	6[b]	$0.7928α_1$ $0.7928α_2$	4 4 8	0.7930	20
1	4[b]	$0.7909α_1$	8 0 3	0.7909	10

Notes:
(a) Scaled from POWD Program to I_{110} = 100. Entries refer to h k l values in center column and are for overall $(α_1+α_2)$ intensities.

(b) Estimated visually because film saturation on high background precluded accurate densitometer reading.

Table III.   Powder Pattern Impurities in Cs_2BkCl_6

d	Intensity[a]	No. Obs.	Identification
4.240	8	1	
3.870	10	2	$Cs_2NaBkCl_6$ 220
3.317	4	1	
3.052	4	1	
2.919	8	2	CsCl 100
2.639	8	4	
2.328	2	2	
1.519	4	1	
1.506	4	1	

a)   Estimated visually. Scale same as for Table II.

Table IV. Powder Pattern Line List for $Cs_2NaBkCl_6$ (cubic)

I_{obs}	d_{obs}	h k l	d_{calc}	I_{calc}[a]	I_{obs}	d_{obs}	h k l	d_{calc}	I_{calc}[a]
70[b]	6.20	1 1 1	6.238	188	25	0.9863	10 4 2	0.9864	25.0
20[b]	5.38	2 0 0	5.403	13.8	5[b]	0.9739	{11 1 1 / 7 7 5}	0.9743	5.9
220[b]	{3.822α / 3.818β}	2 2 0	3.820	343	13	0.9545α₁	8 8 0	0.9550	13.2
74	3.268	3 1 1	3.258	105	20	0.9438α₁	{11 3 1 / 9 7 1 / 9 5 5}	0.9440	20.4
36	3.114	2 2 2	3.119	33.8	23	0.9265α₁	{10 6 0 / 8 6 6}	0.9265	24.1
150[b]	{2.699α / 2.702β}	4 0 0	2.701	193	14	0.9169α₁	{11 3 3 / 9 7 3}	0.9165	10.0
43	2.478	3 3 1	2.479	41.9	30	0.9002α₁	{12 0 0 / 8 8 4}	0.9004	33.1
7	2.417	4 2 0	2.416	7.9	3[b]	0.8913α₁	{11 5 1 / 7 7 7}	0.8912	8.1
120[b]	2.204	4 2 2	2.206	156	29	0.8765α₁ / 0.8764α₂	{10 6 4 / 12 2 2}	0.8764	37.1
47	2.080	{5 1 1 / 3 3 3}	2.079	49.3	10[b]	0.8680α₁	{9 7 5 / 11 5 3}	0.8679	17.9
103	1.910	4 4 0	1.910	124	25[b]	0.8547α₁ / 0.8546α₂	12 4 0	0.8542	29.2
51	1.826	5 3 1	1.826	48.5	3[b]	0.8465α₂	9 9 1	0.8463	8.2
---	-----	{6 0 0 / 4 4 2}	1.801	4.3		0.8444α₁	{12 4 2 / 10 8 0 / 8 8 6}	0.8437	6.0
65	1.709	6 2 0	1.708	71.0	12[b]	0.8336α₁ / 0.8341α₂	10 8 2	0.8336	28.9
23	1.649	5 3 3	1.648	15.1	15[b]	0.8263α₁ / 0.8256α₂	{11 7 1 / 11 5 5 / 9 9 3 / 13 1 1}	0.8263	28.8
8	1.628	6 2 2	1.629	6.3	10[b]	0.8145α₁ / 0.8143α₂	12 4 4	0.8145	36.8
47	1.558	4 4 4	1.560	39.8	15[b]	0.8078α₁ / 0.8074α₂	{11 7 3 / 13 3 1 / 9 7 7}	0.8076	30.4
31	1.512	{7 1 1 / 5 5 1}	1.513	37.0	10[b]	0.8054α₁	{12 6 0 / 10 8 4}	0.8054	7.6
---	-----	6 4 0	1.498	2.3	25[b]	0.7967α₁ / 0.7964α₂	12 6 2	0.7966	38.8
75	1.443	6 4 2	1.444	77.6	5[b]	0.7904α₁ / 0.7902α₂	{13 3 3 / 9 9 5}	0.7902	27.5
37	1.406	{7 3 1 / 5 5 3}	1.407	25.3					
21	1.3494	8 0 0	1.3506	17.1					
11	1.3204	7 3 3	1.3200	4.6					
37	1.2725	{8 2 2 / 6 6 0}	1.2734	36.1					
21	1.2472	{7 5 1 / 5 5 5}	1.2477	15.9					
38	1.2072	8 4 0	1.2080	46.3					
8	1.1848	{7 5 3 / 9 1 1}	1.1860	17.2					
18	1.1520	6 6 4	1.1518	17.9					
12	1.1312	9 3 1	1.1327	12.2					
34	1.1025	8 4 4	1.1028	35.0					
16	1.0846	{7 7 1 / 9 3 3 / 7 5 5}	1.0860	12.7					
45	1.0590	{10 2 0 / 8 6 2}	1.0595	41.6					
22	1.0443	{9 5 1 / 7 7 3}	1.0446	15.2					
13	1.0056	9 5 3	1.0076	11.0					

Notes: (a) Scaled from POWD program to mean of measured intensities. Entries refer to h k l values in center column and are for overall ($\alpha_1 + \alpha_2$) intensities.

(b) Estimated visually because film saturation or high background precluded accurate densitometer reading.

Table V. Powder Pattern Impurities in $Cs_2NaBkCl_6$

d	Intensity[a]	No. Obs.	Identification
2.824	10	2	NaCl 200
2.356	< 5	1	
1.993	< 5	1	NaCl 220
1.864	< 5	2	

a) Estimated visually. Scale same as Table IV.

Five samples of Cs_2BkCl_6 were weighed and assayed for ^{249}Bk and ^{249}Cf by growth of α-activity[12] in measured aliquots, taking the ^{249}Bk half-life as 314 days and that of ^{249}Cf as 345 years.[13] Three samples (weighing from 8 to 16 µg) were analyzed by potentiometric ultramicro-titration for Bk^{4+} with standard Fe^{++} solution and subsequently for Cl^- with standard Ag^+. Anal. Calcd for Cs_2BkCl_6: Bk, 34.2; Cl, 29.24. Found: total Bk, 31.6±3.5; Bk(IV), 29.9±0.9; Cl, 27.8±1.5. Error limits represent 95% confidence intervals, and for total Bk include half-life uncertainties. The low Bk and Cl analyses, and the Cl:Bk atom ratio of 6.2:1, indicate the presence of about 7 weight percent of CsCl. The most troublesome sources of potential errors were transfer losses, chloride contamination, and dust particles.

Since the lattice parameters of Cs_2CeCl_6 did not change significantly when La^{3+} was present in the Ce^{4+} reagent (Table I), it was expected that trivalent impurities would not coprecipitate with Cs_2BkCl_6. Most of the assayed samples were taken from a single synthesis; the Bk reagent used in this synthesis contained 3.3% ^{249}Cf (due to ^{249}Bk decay during the 15 days since the Bk-Cf separation column). The α assays showed 0.1% Cf in the Cs_2BkCl_6 (extrapolated back to the date of synthesis). The failure of Cf(III) to coprecipitate represents further evidence of the preparation of a Bk(IV) compound.

It is to be expected that Cf will coprecipitate with $Cs_2NaBkCl_6$. On this assumption the average Cf:Bk ratio in $Cs_2NaBkCl_6$ samples when X-rayed was 0.018.

Table VI gives interatomic distances in both compounds.

Table VI.   Interatomic Distances

	Cs_2BkCl_6[a]	$Cs_2NaBkCl_6$
Bk-Cl	6 at 2.55 Å	6 at 2.58 Å
Na-Cl	--	6 at 2.82
Bk-Bk	6 at 7.40	8 at 7.64
	6 at 7.45	
Cs(a)-Cl	6 at 3.74	12 at 3.82
	3 at 3.88	
	3 at 3.59	
Cs(b)-Cl	6 at 3.74	
	3 at 3.90	
	3 at 3.53	

a) For Cs_2BkCl_6 distances not determined by space group were estimated

from ionic radii and by comparison with Rb_2MnF_6.

DISCUSSION

The berkelium hydroxide precipitated after bromate oxidation invariably was green (actually yellowish-green) in color. We believe this species to be $Bk(OH)_4$, or, more properly, a hydrous oxide of Bk(IV). The intense orange color of Cs_2BkCl_6 is probably caused by a strong Bk^{4+}-Cl electron transfer band.

The experiment performed with Bk(III) under reducing conditions (using hydroxylamine) indicated that both $Bk(OH)_3$ and $Cs_2NaBkCl_6$ are white. However, we observed a green hydroxide and a yellow $Cs_2NaBkCl_6$ when neither oxidizing nor reducing reagents were added to the original solution. We conclude that $Bk(OH)_3$, like $Ce(OH)_3$, is slowly oxidized to Bk(IV) hydroxide by air and/or solution radiolysis products. The yellow color of $Cs_2NaBkCl_6$ precipitated from this hydroxide is most likely due to a small amount of the intensely colored tetravalent chlorocomplex $BkCl_6^{2-}$.

The ease of precipitation of Cs_2BkCl_6 from chloride solution demonstrates the thermodynamic stability of aqueous Bk(IV) chlorocomplexes, since Bk(IV) (uncomplexed) is a stronger oxidant than Cl_2 by about 0.26 volt.[14,15] We believe that Bk(IV) chlorocomplex ions are at least as thermodynamically stable (toward dissociation or reduction) as corresponding Ce(IV) ions in aqueous HCl, because Cs_2BkCl_6 can be prepared easily from aqueous HCl solution despite the presence of chloride and radiolytically produced reducing agents.

Some qualitative conclusions may be inferred from observations made during the preparation of these chlorocomplexes. It is possible to precipitate $Cs_2NaBkCl_6$ from HCl solution at room temperature. Similar precipitation of $Cs_2NaAmCl_6$ in this laboratory required high HCl concentration and cooling; furthermore, no such compound of plutonium could be precipitated even from

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