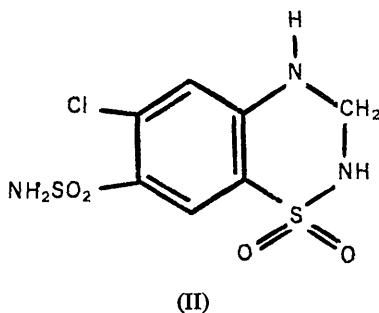


Les faces planes triangulaires formant la plaquette sont du type (001).

(b) *L'hydrochlorothiazide: dihydro-chloro-6-sulfamoyl-7, benzothiadiazine-1,2,4 dioxyde-1,1* (II).



Les cristaux d'hydrochlorothiazide se présentent également sous forme de petites plaquettes triangulaires incolores. Ils s'obtiennent par évaporation lente d'une solution du dérivé dans le méthanol.

Les données relatives à la maille cristalline déterminées comme précédemment, sont les suivantes:
Réseau monoclinique de groupe spatial $P2_1$;

$$a = 7,441 \pm 0,010, \quad b = 8,463 \pm 0,010, \quad c = 10,041 \pm 0,010 \text{ \AA}$$

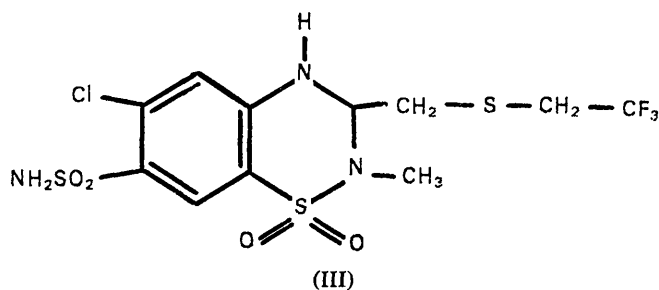
$$\beta = 111,739 \pm 0,010^\circ$$

Volume de la maille, $V = 587,4 \pm 2,1 \text{ \AA}^3$
Densité calculée, $D_c = 1,67 \pm 0,01 \text{ g.cm}^{-3}$
Coefficient d'absorption linéaire,
 $\mu = 61,2 \pm 0,2 \text{ cm}^{-1}$ (Cu $K\alpha$)

Nombre de molécules par maille, $Z = 2$.

Les faces planes triangulaires limitant le cristal sont des faces (001).

(c) *Le polythiazide: dihydro-chloro-6-sulfamoyl-7-méthyl-2-(trifluoro-2,2,2-éthyl-1)-thiométhyl-3-benzothiadiazine-1,2,4 dioxyde-1,1* (III).



Les cristaux de polythiazide s'obtiennent d'une manière analogue à ceux d'hydrochlorothiazide, à partir d'une solution du dérivé dans le méthanol. Les cristaux sont incolores et se présentent sous forme de petites plaquettes.

La maille cristalline a été déterminée comme celle des deux composés précédents:

Réseau monoclinique de groupe spatial Cc ;

$$a = 15,141 \pm 0,010; \quad b = 9,616 \pm 0,010; \quad c = 13,691 \pm 0,010 \text{ \AA}$$

$$\beta = 117,584 \pm 0,010^\circ$$

Volume de la maille, $V = 1766,8 \pm 4,3 \text{ \AA}^3$

Densité calculée, $D_c = 1,64 \pm 0,01 \text{ g.cm}^{-3}$

Coefficient d'absorption linéaire,

$$\mu = 55,8 \pm 0,2 \text{ cm}^{-1} \text{ (Cu } K\alpha)$$

Nombre de molécules par maille, $Z = 4$.

Le cristal plan est limité par les faces (101).

L'étude tridimensionnelle des structures de ces trois composés par diffraction des rayons X est actuellement en cours.

Nous remercions Messieurs les Professeurs H. Brasserur et J. Toussaint pour l'intérêt qu'ils portent à ce travail.

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Refinement of the crystal structure of AmCl_3 .* By JOHN H. BURNS and J. R. PETERSON,† *Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.*

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A refinement of the parameters of AmCl_3 , which is of the UCl_3 structure type, was carried out using single-crystal X-ray diffraction data. An ionic radius of $0.984 \pm 0.003 \text{ \AA}$ for Am^{3+} was derived.

The hexagonal UCl_3 structure type, to which AmCl_3 corresponds, was established by Zachariasen (1948) who used X-ray powder diffraction methods. He derived tentative

positional parameters for the atoms in UCl_3 and showed this structure to be characteristic for the series of trichlorides from La to Nd, for AcCl_3 , and for the trichlorides from U to Am. Subsequent work by Templeton & Dauben (1954) showed that isotypism in the lanthanide series extends through GdCl_3 . Further studies of isotypism among the actinide trichlorides have included AmCl_3 and CmCl_3 (Asprey, Keenan & Kruse, 1965), CmCl_3 (Wallmann, Fuger,

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† Present address: Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916, U.S.A.

Peterson & Green, 1967), and EsCl_3 (Fujita, Cunningham & Parsons, 1969). The first single-crystal study of this structure type was on GdCl_3 by Au & Au (1967). Morosin (1968) used single-crystal X-ray diffraction data to refine four lanthanide trichloride structures spanning the series from La to Gd and showed quantitatively the changes in bond lengths and angles which occur as the cations undergo the lanthanide contraction.

We have underway a similar study with transuranic trichlorides, and AmCl_3 is the first one for which have a completed refinement. We report it here because (1) no positional or thermal parameters for any of the actinide trichlorides has been determined from single-crystal data (not even for UCl_3 itself), and (2) the trichlorides provide an extensive isomorphous series of compounds of these heavy elements, from which the ionic radii may be derived to show the extent of the actinide contraction. Previous attempts to obtain radii from data on these compounds were limited by the assumption that the original UCl_3 atomic parameters are valid for all the actinides (Peterson & Cunningham, 1968).

The specimen was prepared from americium that was 99% ^{243}Am and 1% ^{241}Am . This Am was chemically purified by ion-exchange methods previously described by Peterson & Cunningham (1967) and absorbed in a single ion-exchange resin bead selected for its known capacity of approximately 1 μg . This bead was heated in air at 1265°C to remove the organic part and to convert the Am to AmO_2 , then inserted into a quartz capillary and attached to a vacuum line. Addition of HCl gas to the system at about 600°C converted the AmO_2 particle to pale yellow-pink AmCl_3 . From this substance a crystal was grown *in situ* by

heating to the melting point (determined to be $715 \pm 5^\circ\text{C}$) and carefully cooling while observing the sample with the aid of a microscope through the transparent walls of the quartz-tube microfurnace. The crystal was sealed off in 1/2 atm HCl and used for X-ray diffraction study. The sample was not entirely a single crystal, but a substantial portion was monolithic as determined by X-ray photographs and diffractometer scans.

Intensity data for 1490 reflections were obtained by a computer-controlled Picker X-ray diffractometer with $\text{Mo } K\alpha$ radiation ($\lambda = 0.70926 \text{ \AA}$) using a $\theta, 2\theta$ -scan technique. For twelve reflections the angles required to center each accurately were measured and used to refine, by the method of least-squares, the hexagonal unit-cell dimensions. The results were $a = 7.382(1)$ and $c = 4.214(1) \text{ \AA}$ at 23°C. The numbers in parentheses are the least-squares standard errors. Previous determinations from powder diffraction yielded $a = 7.390 \pm 0.003$, $c = 4.234 \pm 0.002 \text{ \AA}$ (Asprey, Keenan & Kruse, 1965) and $a = 7.384 \pm 0.004$, $c = 4.225 \pm 0.004 \text{ \AA}$ (Fuger, 1966). Corrections for absorption were calculated by the *ORABS* program of Wehe, Busing & Levy (1962) using an assumed value of $60 \text{ cm}^2 \cdot \text{g}^{-1}$ for the mass absorption coefficient of Am; transmission factors ranged from 0.15 to 0.30. Data reduction was followed by averaging of squared structure factors of equivalent reflections. The 328 independent observations obtained were used to refine the two positional and six anisotropic thermal parameters of the structure starting from the values for EuCl_3 given by Morosin (1968). The function minimized was $\sum \frac{1}{\sigma^2} (F_o^2 - S_o^2 F_c)$ with σ based on counting statistics and

Table 1. Refined positional and anisotropic thermal parameters of AmCl_3

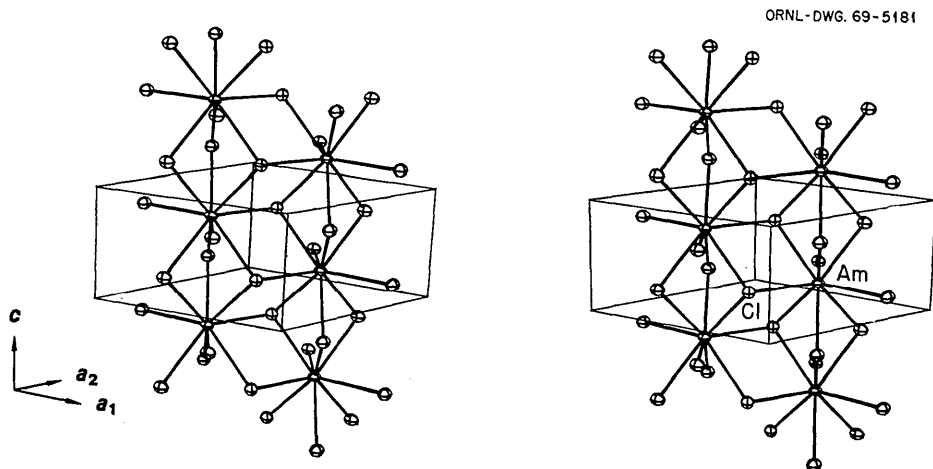
Atom	Site	x	y	z	β_{11}^\dagger	β_{22}	β_{33}	β_{12}
Am	2 (c)*	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.0049 (1)	—	0.0061 (2)	—
Cl	6 (h)*	0.3877 (4)	0.3019 (4)	$\frac{1}{4}$	0.0055 (4)	0.0057 (4)	0.0109 (8)	0.0032 (3)

* Symmetry position in space group $P6_3/m$ (*International Tables for X-ray Crystallography*, 1952).

† The β values are coefficients in the expression

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

because of site symmetry, $\beta_{11} = \beta_{22} = 2\beta_{12}$ for Am and $\beta_{23} = \beta_{13} = 0$ for both atoms.



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Fig. 1. Stereoscopic view of the structure of AmCl_3 . Atoms are represented by 90% probability ellipsoids of thermal motion.

an allowance of 5% of the intensity to account for unknown, systematic errors. The discrepancy index, $R = \sum(|F_o| - S|F_c|) / \sum|F_o|$, reached 0.035 and the standard deviation of an observation of unit weight was 1.00. The refined parameter values are given in Table 1, and the observed and calculated structure amplitudes are listed in Table 2.

Table 2. Observed and calculated structure factors on an absolute scale

hkl	Obs	Calc	hkl	Obs	Calc
100	100	100	100	100	100
110	110	110	110	110	110
111	111	111	111	111	111
200	200	200	200	200	200
210	210	210	210	210	210
211	211	211	211	211	211
300	300	300	300	300	300
310	310	310	310	310	310
311	311	311	311	311	311
400	400	400	400	400	400
410	410	410	410	410	410
411	411	411	411	411	411
500	500	500	500	500	500
510	510	510	510	510	510
511	511	511	511	511	511
600	600	600	600	600	600
610	610	610	610	610	610
611	611	611	611	611	611
700	700	700	700	700	700
710	710	710	710	710	710
711	711	711	711	711	711
800	800	800	800	800	800
810	810	810	810	810	810
811	811	811	811	811	811
900	900	900	900	900	900
910	910	910	910	910	910
911	911	911	911	911	911
1000	1000	1000	1000	1000	1000
1010	1010	1010	1010	1010	1010
1011	1011	1011	1011	1011	1011
1100	1100	1100	1100	1100	1100
1110	1110	1110	1110	1110	1110
1111	1111	1111	1111	1111	1111
1200	1200	1200	1200	1200	1200
1210	1210	1210	1210	1210	1210
1211	1211	1211	1211	1211	1211
1300	1300	1300	1300	1300	1300
1310	1310	1310	1310	1310	1310
1311	1311	1311	1311	1311	1311
1400	1400	1400	1400	1400	1400
1410	1410	1410	1410	1410	1410
1411	1411	1411	1411	1411	1411
1500	1500	1500	1500	1500	1500
1510	1510	1510	1510	1510	1510
1511	1511	1511	1511	1511	1511
1600	1600	1600	1600	1600	1600
1610	1610	1610	1610	1610	1610
1611	1611	1611	1611	1611	1611
1700	1700	1700	1700	1700	1700
1710	1710	1710	1710	1710	1710
1711	1711	1711	1711	1711	1711
1800	1800	1800	1800	1800	1800
1810	1810	1810	1810	1810	1810
1811	1811	1811	1811	1811	1811
1900	1900	1900	1900	1900	1900
1910	1910	1910	1910	1910	1910
1911	1911	1911	1911	1911	1911
2000	2000	2000	2000	2000	2000
2010	2010	2010	2010	2010	2010
2011	2011	2011	2011	2011	2011
2100	2100	2100	2100	2100	2100
2110	2110	2110	2110	2110	2110
2111	2111	2111	2111	2111	2111
2200	2200	2200	2200	2200	2200
2210	2210	2210	2210	2210	2210
2211	2211	2211	2211	2211	2211
2300	2300	2300	2300	2300	2300
2310	2310	2310	2310	2310	2310
2311	2311	2311	2311	2311	2311
2400	2400	2400	2400	2400	2400
2410	2410	2410	2410	2410	2410
2411	2411	2411	2411	2411	2411
2500	2500	2500	2500	2500	2500
2510	2510	2510	2510	2510	2510
2511	2511	2511	2511	2511	2511
2600	2600	2600	2600	2600	2600
2610	2610	2610	2610	2610	2610
2611	2611	2611	2611	2611	2611
2700	2700	2700	2700	2700	2700
2710	2710	2710	2710	2710	2710
2711	2711	2711	2711	2711	2711
2800	2800	2800	2800	2800	2800
2810	2810	2810	2810	2810	2810
2811	2811	2811	2811	2811	2811
2900	2900	2900	2900	2900	2900
2910	2910	2910	2910	2910	2910
2911	2911	2911	2911	2911	2911
3000	3000	3000	3000	3000	3000
3010	3010	3010	3010	3010	3010
3011	3011	3011	3011	3011	3011
3100	3100	3100	3100	3100	3100
3110	3110	3110	3110	3110	3110
3111	3111	3111	3111	3111	3111
3200	3200	3200	3200	3200	3200
3210	3210	3210	3210	3210	3210
3211	3211	3211	3211	3211	3211
3300	3300	3300	3300	3300	3300
3310	3310	3310	3310	3310	3310
3311	3311	3311	3311	3311	3311
3400	3400	3400	3400	3400	3400
3410	3410	3410	3410	3410	3410
3411	3411	3411	3411	3411	3411
3500	3500	3500	3500	3500	3500
3510	3510	3510	3510	3510	3510
3511	3511	3511	3511	3511	3511
3600	3600	3600	3600	3600	3600
3610	3610	3610	3610	3610	3610
3611	3611	3611	3611	3611	3611
3700	3700	3700	3700	3700	3700
3710	3710	3710	3710	3710	3710
3711	3711	3711	3711	3711	3711
3800	3800	3800	3800	3800	3800
3810	3810	3810	3810	3810	3810
3811	3811	3811	3811	3811	3811
3900	3900	3900	3900	3900	3900
3910	3910	3910	3910	3910	3910
3911	3911	3911	3911	3911	3911
4000	4000	4000	4000	4000	4000
4010	4010	4010	4010	4010	4010
4011	4011	4011	4011	4011	4011
4100	4100	4100	4100	4100	4100
4110	4110	4110	4110	4110	4110
4111	4111	4111	4111	4111	4111
4200	4200	4200	4200	4200	4200
4210	4210	4210	4210	4210	4210
4211	4211	4211	4211	4211	4211
4300	4300	4300	4300	4300	4300
4310	4310	4310	4310	4310	4310
4311	4311	4311	4311	4311	4311
4400	4400	4400	4400	4400	4400
4410	4410	4410	4410	4410	4410
4411	4411	4411	4411	4411	4411
4500	4500	4500	4500	4500	4500
4510	4510	4510	4510	4510	4510
4511	4511	4511	4511	4511	4511
4600	4600	4600	4600	4600	4600
4610	4610	4610	4610	4610	4610
4611	4611	4611	4611	4611	4611
4700	4700	4700	4700	4700	4700
4710	4710	4710	4710	4710	4710
4711	4711	4711	4711	4711	4711
4800	4800	4800	4800	4800	4800
4810	4810	4810	4810	4810	4810
4811	4811	4811	4811	4811	4811
4900	4900	4900	4900	4900	4900
4910	4910	4910	4910	4910	4910
4911	4911	4911	4911	4911	4911
5000	5000	5000	5000	5000	5000

Values of $|F_{obs}|$ and F_{calc} are listed under the headings OBS and CAL, respectively. The reflection marked with an \times was omitted from the refinement.

A stereoscopic view of the structure of AmCl_3 is shown in Fig. 1. The atoms are represented by 90% probability ellipsoids of thermal motion (Johnson, 1965). Each Am atom is bonded to nine Cl atoms: six form a trigonal prism with the Am atom at its center, and three are situated just outside the vertical prism faces.

Bond distances of 2.874 (2) Å, apical, and 2.915 (2) Å, equatorial, were calculated from the refined structural parameters. The equatorial atoms of one prism form the apical atoms of adjacent prisms, connecting the structure in three dimensions. When the metal-chlorine bond distances

for the four lanthanide compounds reported by Morosin (1968) are plotted *vs.* the radii of six-coordinated trivalent lanthanide ions derived by Templeton & Dauben (1954), the distances in AmCl_3 are found at the radius of 0.984 ± 0.003 Å. This value differs from the 1.006 Å obtained by Peterson & Cunningham (1968) who made several assumptions not required by the present treatment using single-crystal data, but agrees with the 0.985 Å which they derived from lattice parameters of the cubic sesquioxide (Peterson & Cunningham, 1967).

Although unit-cell dimensions are available for all the actinide trichlorides up to EsCl_3 , derivation of ionic radii for the actinides other than Am^{3+} should await the determination of structural parameters also, because these probably change with cation radius, as was found in the case of the lanthanide trichlorides (Morosin, 1968).

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