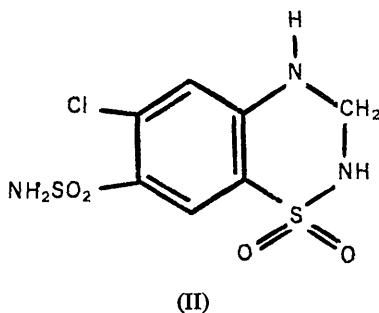Les faces planes triangulaires formant la plaquette sont du type (001).

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

(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 $P2_1$;

$a = 7,441 \pm 0,010$, $b = 8,463 \pm 0,010$, $c = 10,041 \pm 0,010$ Å
$\beta = 111,739 \pm 0,010°$

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

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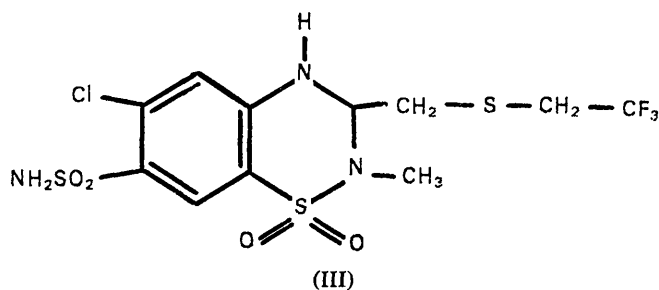
Les cristaux de polythiazide s'obtiennent d'une manière analogue à ceux d'hydrochlorothiazide, à partir d'une solution du dérivé dans le méthanol. Les cristaux sont incolores et se présentent sous forme de petites plaquettes.

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

Réseau monoclinique de groupe spatial Cc;

$a = 15,141 \pm 0,010$; $b = 9,616 \pm 0,010$; $c = 13,691 \pm 0,010$ Å
$\beta = 117,584 \pm 0,010°$

Volume de la maille, $V = 1766,8 \pm 4,3$ Å^3
Densité calculée, $D_c = 1,64 \pm 0,01$ g.cm^{-3}
Coefficient d'absorption linéaire,
$\mu = 55,8 \pm 0,2$ cm^{-1} (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.

Références

Cox, A. A. (1967). *A Program for Least-Squares Refinement of Unit-Cell Dimensions.* Univ. of London.
Gantt, C. L. & Synek, J. H. (1961). *Proc. Soc. Exp. Biol. Med.* **106**, 27.
Heinemann, H. O., Demartini, F. E. & Laragh, J. H. (1959). *Amer. J. Med.* **26**, 853.
Pignard, P. (1960). *Path. Biol.* **8**, 1381.

Refinement of the crystal structure of AmCl₃.* By John H. Burns and J.R. Peterson,† *Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.*

A refinement of the parameters of AmCl₃, which is of the UCl₃ structure type, was carried out using single-crystal X-ray diffraction data. An ionic radius of 0.984 ± 0.003 Å for Am^{3+} was derived.

The hexagonal UCl₃ structure type, to which AmCl₃ corresponds, was established by Zachariasen (1948) who used X-ray powder diffraction methods. He derived tentative

positional parameters for the atoms in UCl₃ and showed this structure to be characteristic for the series of trichlorides from La to Nd, for AcCl₃, and for the trichlorides from U to Am. Subsequent work by Templeton & Dauben (1954) showed that isotypism in the lanthanide series extends through GdCl₃. Further studies of isotypism among the actinide trichlorides have included AmCl₃ and CmCl₃ (Asprey, Keenan & Kruse, 1965), CmCl₃ (Wallmann, Fuger,

Peterson & Green, 1967), and EsCl₃ (Fujita, Cunningham & Parsons, 1969). The first single-crystal study of this structure type was on GdCl₃ 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 AmCl₃ 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 UCl₃ 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 UCl₃ atomic parameters are valid for all the actinides (Peterson & Cunningham, 1968).

The specimen was prepared from americium that was 99% ²⁴³Am and 1% ²⁴¹Am. 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 AmO₂, 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 AmO₂ particle to pale yellow-pink AmCl₃. From this substance a crystal was grown in situ by

heating to the melting point (determined to be 715±5°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 Mo $K\alpha$ radiation ($\lambda = 0.70926$ Å) using a θ, 2θ-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) Å at 23°C. The numbers in parentheses are the least-squares standard errors. Previous determinations from powder diffraction yielded $a = 7.390 \pm 0.003$, $c = 4.234 \pm 0.002$ Å (Asprey, Keenan & Kruse, 1965) and $a = 7.384 \pm 0.004$, $c = 4.225 \pm 0.004$ Å (Fuger, 1966). Corrections for absorption were calculated by the ORABS program of Wehe, Busing & Levy (1962) using an assumed value of 60 cm².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 EuCl₃ given by Morosin (1968). The function minimized was $\sum \dfrac{1}{\sigma^2} (F_o^2 - S_c^2 F_o)$ with σ based on counting statistics and

Table 1. Refined positional and anisotropic thermal parameters of AmCl₃

Atom	Site	x	y	z	β_{11}†	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 P6₃/m (International Tables for X-ray Crystallography, 1952).
† The β values are coefficients in the expression

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

because of site symmetry, $\beta_{11} = \beta_{22} = 2\beta_{12}$ for Am and $\beta_{23} = \beta_{13} = 0$ for both atoms.
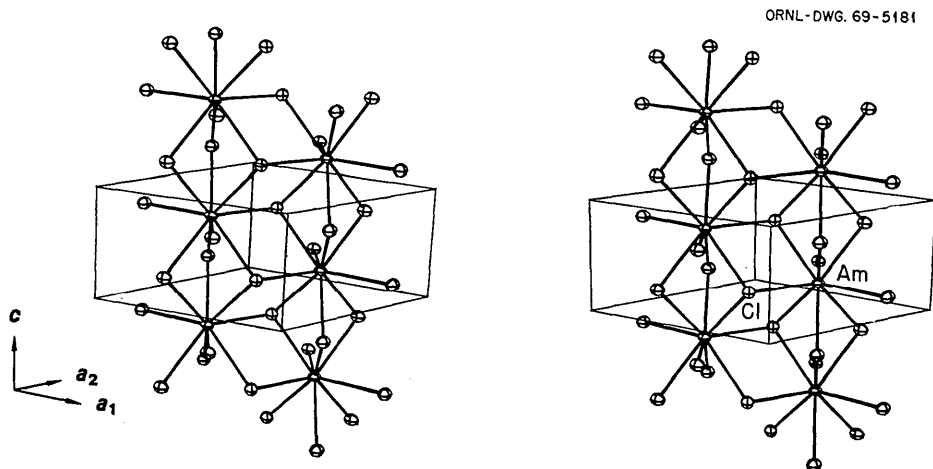
ORNL-DWG. 69-5181

Fig. 1. Stereoscopic view of the structure of AmCl₃. 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*

[Table of structure factors with columns repeated: L OBS CAL]

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

A stereoscopic view of the structure of AmCl₃ 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 AmCl₃ 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 EsCl₃, derivation of ionic radii for the actinides other than Am³⁺ 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).

References

ASPREY, L. B., KEENAN, T. K. & KRUSE, F. H. (1965). *Inorg. Chem.* **4**, 985.

AU, C. & AU, R. (1967). *Acta Cryst.* **23**, 1112.

FUGER, J. (1966). *J. Inorg. Nucl. Chem.* **28**, 3066.

FUJITA, D. K., CUNNINGHAM, B. B. & PEARSONS, T. C. (1969). *Inorg. Nucl. Chem. Letters,* **5**, 307.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal-Structure Illustrations.* ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

MOROSIN, B. (1968). *J. Chem. Phys.* **49**, 3007.

PETERSON, J. R. & CUNNINGHAM, B. B. (1967). *Inorg. Nucl. Chem. Letters,* **3**, 327.

PETERSON, J. R. & CUNNINGHAM, B. B. (1968). *J. Inorg. Nucl. Chem.* **30**, 823.

TEMPLETON, D. H. & DAUBEN, C. H. (1954). *J. Amer. Chem. Soc.* **76**, 5237.

WALLMANN, J. C., FUGER, J., PETERSON, J. R. & GREEN, J. L. (1967). *J. Inorg. Nucl. Chem.* **29**, 2745.

WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS, A Fortran Program for Calculating Single Crystal Absorption Corrections.* ORNL-TM-229, Oak Ridge National Laboratory, Tennessee.

ZACHARIASEN, W. H. (1948). *J. Chem. Phys.* **16**, 254; *Acta Cryst.* **1**, 265.