Les atomes de sodium se trouvent au centre de bipyramides triangulaires d'atomes de fluor et ont la coordinence 5. Ces polyèdres de fluor sont joints par les sommets, selon **c**, par les atomes F(7) qui ne sont donc reliés qu'à deux atomes de sodium. Cet écart à la loi de répartition électrostatique des charges (Pauling, 1929) dans un cristal ionique est à rapprocher des observations précédentes concernant les composés Li$_3$ThF$_7$ (Cousson, Pagès & Chevalier, 1978), Na$_7$Zr$_6$F$_{31}$ et K$_7$Th$_6$F$_{31}$ (Burns, Ellison & Levy, 1968; Brunton, 1971*b*; Zachariasen & Penneman, 1980) et (Na,Li)$_7$Th$_6$F$_3$ (Brunton & Sears, 1969) et demeure jusqu'à présent sans explication.

En conclusion, l'étude structurale de ce nouveau fluorure d'actinide obtenu par synthèse hydrothermale a permis de comprendre son isotypie avec le composé CsU$_6$F$_{25}$ et de déterminer sa formule – NaNp$_3$F$_{13}$ – *a priori* imprévisible.

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The Structure of Tribarium Undecaoxotetratellurate(IV), Ba$_3$Te$_4$O$_{11}$

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Abstract. $M_r = 1098{\cdot}4$, triclinic, $P\bar{1}$, $a = 9{\cdot}4245$ (5), $b = 9{\cdot}9759$ (9), $c = 7{\cdot}8877$ (4) Å, $\alpha = 110{\cdot}58$ (1), $\beta = 103{\cdot}27$ (1), $\gamma = 97{\cdot}80$ (1)°, $V = 658{\cdot}5$ Å^3, $Z = 2$, $D_c = 5{\cdot}54$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 176{\cdot}39$ cm^{-1}, $F(000) = 928$, $R = 0{\cdot}032$ for 3682 reflections. The structure consists of TeO$_3^{2-}$ and Te$_3$O$_8^{4-}$ ions which form Te$_8$O$_{22}^{12-}$ rings around a centre of symmetry with Te–O bonds of about 2·7 Å length. The Ba^{2+} ions couple these rings together. The TeO$_3^{2-}$ ion has the usual pyramidal shape, the Te$_3$O$_8^{4-}$ ion has a pseudo-twofold axis instead of the twofold axis found previously in Zn$_2$Te$_3$O$_8$ and Nb$_2$Te$_3$O$_{11}$.

Introduction. In the course of an investigation of the crystal structures of alkaline-earth tellurates and tellurites we found a barium compound which was present in all products resulting from solid-state reactions between BaCO$_3$ and TeO$_2$ in weight ratios from 1:1 to 1:2. Heating a 1:2 mixture at 1000 K over 8 d resulted in a single-phase product. Indexing of the Guinier powder pattern (Cu $K\alpha$, internal standard α-SiO$_2$) by means of the program *ITO* (Visser, 1969) led to the triclinic unit cell mentioned above. These cell dimensions differed from all known tellurates and tellurites of barium, BaTeO$_4$ (Sleight, Foris & Licis, 1972), BaTe$_2$O$_6$ (Kocak, Platte & Trömel, 1979*a*), BaTeO$_3$ I (Folger, 1975; Kocak, Platte & Trömel, 1979*b*), BaTeO$_3$ II (Kocak, Platte & Trömel, 1979*b*) and BaTeO$_3$.H$_2$O (Rottensten Nielsen, Grønbaek Hazell & Rasmussen, 1971). As we were able to isolate tiny crystals from the product we decided to undertake a structure determination of the compound, in spite of the fact that its formula was unknown.

Experimental. Platelet, 0·025 × 0·025 × 0·005 cm, Nonius CAD-4, graphite-monochromated Mo $K\alpha$, θ–2θ scan, 3781 measured, 99 with $I < 3\sigma(I)$, 3682 unique. From the intensities it was obvious that a subcell was present with $a = 3{\cdot}8658$, $b = 3{\cdot}9683$, $c = 3{\cdot}8563$ Å, $\alpha = 109{\cdot}65$, $\beta = 104{\cdot}73$, $\gamma = 110{\cdot}77$°, and a volume 1/14 of the true cell, containing one heavy atom. It is related to the true cell by the transformation 4/14, −2/14, 4/14; 2/14, 6/14, 2/14; −5/14, −1/14, 2/14. In accordance with this a Patterson synthesis revealed per unit cell fourteen maxima of approximately equal weight. All of these can be transformed to lie on one straight line through the origin with coordinates $x = n/14$, $y = 8n/14$, $z = 8n/14$

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(n=1,...,14). In addition, the Patterson peaks indicated that these coordinates are very nearly correct in the x and y directions, but much less so along z. Assuming a centre of symmetry, the fact that the atoms are on a straight line leaves a choice between two possible origin positions: either at a heavy atom or between two heavy atoms. The latter choice led to convergence in least-squares refinement, based on F. In the starting model the coordinates of the nth heavy atom were represented by: $0{\cdot}071n{-}0{\cdot}036$, $0{\cdot}214n{-}0{\cdot}107$, $0{\cdot}571n{-}0{\cdot}286$ (n=1,...,14). In the initial least-squares refinement for all seven atoms, Te scattering factors were used (Cromer & Mann, 1968). Refinement based on the full reflection set gave poor results. It was then decided to start refinement with a reflection set with $l \leq 2$, to reduce the influence of the lack of precision of the z coordinates. This refinement led to convergence (R = 0·24). The resulting coordinate set showed considerable shifts in the z positions of atoms 2, 4, and 5. Subsequent refinement using all reflections gave an R of 0·13. Fourier difference maps revealed the positions of the oxygen atoms which enabled us to decide that the atoms 1, 6, and 7 are Ba atoms. As we clearly found eleven oxygen atoms the formula of the compound is $Ba_3Te_4O_{11}$. Maximum LS shift to error = 0·027, maximum/minimum height = 2·2–2·8 e Å^{-3}. Final refinement (165 parameters) with anisotropic temperature factors, absorption and extinction corrections [transmission factors 0·08–0·423, secondary-extinction parameter (Larson, 1967) 5·68 $\times 10^{-6}$] yielded an R of 0·032.* Atomic dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). Corrections for Lorentz and polarization effects were applied. All computations were carried out with XRAY (Stewart, 1976).

Discussion. Final coordinates are given in Table 1, selected bond lengths and angles in Table 2. A projection of the unit-cell contents along **b** is depicted in Fig. 1, which also gives the numbering of the atoms.

As can be seen in Fig. 2 and Table 1, the structure contains $Te_3O_8^{4-}$ ions and TeO_3^{2-} ions. Co-existence of these two ions has not previously been found. The TeO_3^{2-} ion has the usual pyramidal shape. A comparison with other barium tellurites is given in Table 3. The $Te_3O_8^{4-}$ ion has previously only been found in $Zn_2Te_3O_8$ (Hanke, 1966) and $Nb_2Te_3O_{11}$ (Galy & Lindqvist, 1979). In both cases the structure had a crystallographic twofold axis through the central Te atom of the Te_3O_8 group. In $Ba_3Te_4O_{11}$ this is not the case, and hence the Te_3O_8 group is more irregular, but Fig. 2 shows that a pseudo-twofold axis is still present. Te(2) has two equatorial oxygens at 1·85 (1) Å. A similar arrangement is found in $Zn_2Te_3O_8$ [Te—O$_{eq}$ = 1·83 (3) Å] and in $Nb_2Te_3O_{11}$ [Te—O$_{eq}$ =

Table 1. *Final coordinates*

	x	y	z	B^*_{eq}(Å^2)
Te(1)	0·19165 (6)	0·53934 (5)	0·43778 (7)	1·12
Te(2)	0·24024 (6)	0·71695 (6)	0·94893 (7)	1·25
Te(3)	0·31022 (6)	0·94054 (5)	0·47237 (6)	1·04
Te(4)	0·11974 (6)	0·29851 (5)	0·91801 (7)	1·21
Ba(1)	0·01376 (6)	0·11169 (5)	0·30976 (6)	1·42
Ba(2)	0·40609 (6)	0·17711 (5)	0·14442 (6)	1·39
Ba(3)	0·45597 (5)	0·37276 (5)	0·71766 (6)	0·96
O(1)	0·2093 (8)	0·3710 (7)	0·4761 (10)	2·55
O(2)	0·3891 (8)	0·6426 (8)	0·5358 (9)	2·21
O(3)	0·1307 (7)	0·6358 (8)	0·6644 (8)	1·86
O(4)	0·3163 (9)	0·8927 (7)	0·9370 (9)	2·47
O(5)	0·4008 (7)	0·6312 (7)	0·9329 (8)	1·50
O(6)	0·3559 (8)	0·8126 (7)	0·2633 (8)	1·95
O(7)	0·1041 (7)	0·8736 (7)	0·4052 (8)	1·86
O(8)	0·3153 (7)	0·0993 (6)	0·4025 (8)	1·80
O(9)	0·0548 (8)	0·1569 (7)	0·0040 (9)	2·41
O(10)	0·2317 (8)	0·1919 (8)	0·7819 (10)	2·86
O(11)	0·2783 (8)	0·4142 (7)	0·1381 (9)	2·05

* Defined according to Willis & Pryor (1975).

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Te(1)–O(1)	1·830 (8)	O(1)–Te(1)–O(2)	100·2 (4)
Te(1)–O(2)	1·844 (7)	O(1)–Te(1)–O(3)	96·4 (3)
Te(1)–O(3)	1·967 (7)	O(2)–Te(1)–O(3)	96·9 (3)
Te(1)–O(11)	2·629 (7)		
Te(2)–O(3)	2·048 (6)	O(3)–Te(2)–O(4)	88·8 (3)
Te(2)–O(4)	1·845 (8)	O(3)–Te(2)–O(5)	97·7 (3)
Te(2)–O(5)	1·849 (7)	O(3)–Te(2)–O(6)	177·9 (3)
Te(2)–O(6)	2·250 (6)	O(4)–Te(2)–O(5)	99·6 (3)
		O(4)–Te(2)–O(6)	90·1 (3)
		O(5)–Te(2)–O(6)	84·2 (3)
Te(3)–O(6)	1·880 (7)	O(6)–Te(3)–O(7)	102·0 (3)
Te(3)–O(7)	1·857 (6)	O(6)–Te(3)–O(8)	97·2 (3)
Te(3)–O(8)	1·849 (7)	O(7)–Te(3)–O(8)	98·6 (3)
Te(4)–O(9)	1·861 (8)	O(9)–Te(4)–O(10)	96·0 (4)
Te(4)–O(10)	1·851 (8)	O(9)–Te(4)–O(11)	96·4 (3)
Te(4)–O(11)	1·876 (6)	O(10)–Te(4)–O(11)	97·0 (3)
Te(4)–O(7′)	2·718 (5)		

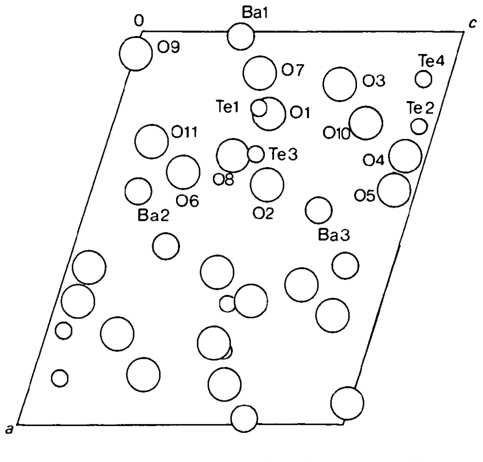

Fig. 1. A projection of the unit-cell contents along **b**.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38251 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·84 (2) Å].Compared with these latter compounds the bond lengths for the non-equatorial oxygens of the central Te differ substantially in length, Te(2)—O(3) being 2·048 (6) Å and Te(2)—O(6) 2·250 (6) Å. The Te(3)—O(6) distance, 1·880 (7) Å, is considerably shorter than Te(1)—O(3), 1·967 (7) Å. In Table 4, using the numbering given in Fig. 3, a comparison is given with the bond lengths and angles around the central Te atom in known Te_3O_8 units (angle 12 means the angle between bond numbers 1 and 2). The atoms Te(1) and Te(3) have normal threefold coordination as shown in Table 4. The TeO_3 and Te_3O_8 units are linked to form a Te_8O_{22} ring by bonds Te(4)—O(7′), 2·718 (5) Å, and Te(1)—O(11), 2·629 (7) Å. These rings lie around a centre of symmetry on the *c* axis. Fig. 2 gives a view of the ring. The barium atoms are situated between these rings. Ba(1) and Ba(2) are 7 coordinated and have a mean Ba—O distance of 2·79 (1) Å, Ba(3) is 8 coordinated with a mean Ba—O distance of 2·76 (1) Å.

Table 3. *Threefold coordinated* Te^{IV} *in barium tellurites*

		Distances (Å)			Angles (°)*		
		(1)	(2)	(3)	(12)	(13)	(23)
$BaTeO_3$ (I)		1·86	1·86	1·87	98	100	89
$BaTeO_3$ (II)	Te(1)	1·83	1·83	1·88	105	105	97
	Te(2)	1·86	1·86	1·88	95	95	99
	Te(3)	1·82	1·85	1·85	96	96	98
$BaTeO_3.H_2O$		1·85	1·86	1·86	103	99	97
$Ba_3Te_4O_{11}$	Te(1)	1·83	1·84	1·97	100	96	97
	Te(3)	1·85	1·86	1·88	99	97	102
	Te(4)	1·85	1·86	1·88	96	97	97
$Ba_3Te_2O_6Cl_2$[a]		1·86	1·86	1·86	96	96	96

Reference: (*a*) Hottentot & Loopstra (1983).

* Angle (12) means the angle between bonds 1 and 2.

Table 4. *Bond lengths and angles around the central* Te^{IV} *atom in* Te_3O_8 *units*

Bond number	$Zn_2Te_3O_8$ ($\sigma = 0{\cdot}03$ Å)	$Nb_2Te_3O_{11}$ ($\sigma = 0{\cdot}02$ Å)	$Ba_3Te_4O_{11}$ ($\sigma = 0{\cdot}01$ Å)
1, 6	1·98	1·84	1·84, 1·84
2, 5	2·10	2·10	2·05, 2·25
3, 4	1·83	1·84	1·85, 1·85
Bond angle	($\sigma = 2°$)	($\sigma = 1°$)	($\sigma = 0{\cdot}3°$)
12, 56	123	137	132·6, 132·7
23, 35	84	90	88·8, 90·1
24, 45	93	92	97·7, 84·2
25	175	183	177·9
34	106	88	99·7

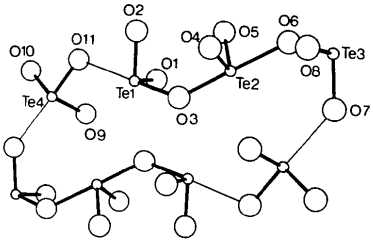

Fig. 2. A view of the Te_8O_{22} ring projected along **b**.

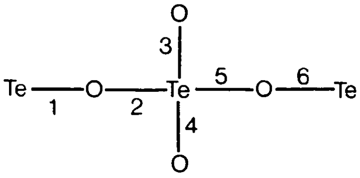

Fig. 3. Bond numbering as used in Table 4.

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