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Crystal Structure of the Compounds U_2N_2X and Th_2N_2X with X=Sb, Te, and Bi[*]

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The compounds U_2N_2Sb, U_2N_2Bi, U_2N_2Te, Th_2N_2Sb, Th_2N_2Bi, and Th_2N_2Te were prepared and found, from X-ray diffraction powder patterns, to form body-centered tetragonal crystals (space group $I4/mmm$) with the following unit-cell parameters:

	a_0 (Å)	c_0 (Å)	u
U_2N_2Sb	3·8937 ± 0·0002	12·3371 ± 0·0007	0·344 ± 0·003
U_2N_2Te	3·9631 ± 0·0002	12·561 ± 0·002	± 0·003
U_2N_2Bi	3·9292 ± 0·0005	12·548 ± 0·002	± 0·01
Th_2N_2Sb	4·049 ± 0·001	13·57 ± 0·01	± 0·003
Th_2N_2Te	4·0939 ± 0·0004	13·014 ± 0·001	± 0·003
Th_2N_2Bi	4·075 ± 0·001	13·62 ± 0·01	± 0·01

The atomic positions are 2Sb, 2Bi or 2Te in (000) $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and 4 metal atoms in (000) $(\frac{1}{2}\frac{1}{2}\frac{1}{2}) \pm (00u)$. The probable positions of the 4N atoms are (000) $(\frac{1}{2}\frac{1}{2}\frac{1}{2}) \pm (\frac{1}{2}0\frac{1}{4})$. Nitrogen in the Th_2N_2Sb crystal lattice can be replaced to an appreciable extent by oxygen. Saturated with oxygen, the compound has a composition given by the formula $Th_2(N_{1/2}O_{1/2})_2Sb$ and the lattice parameters $a_0 = 4{\cdot}041 \pm 0{\cdot}001$ and $c_0 = 12{\cdot}84 \pm 0{\cdot}01$ Å. Oxygen solubility and its effect on lattice parameters is considerably less in Th_2N_2Bi and is not at all perceptible in the remaining four compounds.

The crystal structures of thorium and uranium compounds with the general formula M_2Y_2X, where M= Th and U, Y= N or (N+O), and X= P, S, As, and Se, have been reported previously (Benz & Zachariasen, 1969). In what follows, the crystal structures of analogous compounds with X= Sb, Te, and Bi are reported.

Preparations were made in two ways as previously described (Benz & Zachariasen, 1969) with provisions for the lower stability with respect to vaporization of the X elements. In the first preparative method, cold-pressed powder mixtures of the binary compounds shown in column 1 of Table 1 were placed in a tungsten crucible covered with a lid and reacted in a nitrogen atmosphere for 2 hours at 1200° to produce the Sb and the Te compounds, and for 16 hours at 1000° for the Bi compounds. The U_2N_2Te and Th_2N_2Te compositions as formed by this method were determined from chemical analyses of samples by A. D. Hues in the Analytical Group of this Laboratory. The analyses, as listed in Table 1, are in reasonable agreement with the assumed formulas. In the second preparative method, stoichiometric mixtures of the mononitrides, MN, and the elements, X, were heated in a silica capsule for one

Table 1. *Preparations and chemical analyses of the compounds* U_2N_2X *and* $Th_2(N,O)_2X$, *with* X= Sb, Te *and* Bi

	Chemical analyses							
	Th		N		Te			
Reaction	anal. (±1%)	calc.	anal. (±0·5%)	calc.	anal. (±0·1%)	calc.	Material[*] balance (%)	Formula by analysis
$ThTe + ThN + \frac{1}{2}N_2 = Th_2N_2Te$	72·4	74·9	3·63	4·52	22·1	20·6	1·87	$Th_2N_{1{\cdot}66}Te_{1{\cdot}11}$
$UTe + UN + \frac{1}{2}N_2 = U_2N_2Te$	74·8	75·4	4·25	4·44	20·1	20·2	0·85	$U_2N_{1{\cdot}92}Te_{1{\cdot}00}$
$ThSb + ThN + \frac{1}{2}N_2 = Th_2N_2Sb$								
$ThSb + \frac{1}{2}ThN + \frac{1}{2}ThO_2 + \frac{1}{4}N_2 = Th_2NOSb$								
$USb + UN + \frac{1}{2}N_2 = U_2N_2Sb$								
$ThBi + ThN + \frac{1}{2}N_2 = Th_2N_2Bi$								
$UBi + UN + \frac{1}{2}N_2 = U_2N_2Bi$								

[*] 100 minus the weight per cent by analysis.

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month at 1000°. As revealed by the X-ray diffraction patterns of the products, pure compounds were obtained by both methods.

Additional preparations were made by the second method, with deviations from stoichiometric compositions. Changes in the N/M and the X/M ratios were thus found to have no significant effect on lattice parameters. Other preparations were made with the nitrogen partly replaced by oxygen which was added to the thorium and uranium compounds as ThO_2 and UO_2, respectively. The oxygen addition had a rather large effect on the lattice parameters of the compound Th_2N_2Sb, and reacted mixtures with bulk compositions represented by the formulas $Th_2(N_{3/4}O_{1/4})_2Sb$ and

Table 2. *X-ray diffraction data for* U_2N_2Sb(Cu *K*α, $\lambda = 1{\cdot}54051$ Å)

			$10^2 \times \sin^2 \theta$		Relative intensity	
h	*k*	*l*	Calculated	Observed	Calculated*	Observed
0	0	2	156	155	3·4	nil
1	0	1	430	431	11	*VW+*
0	0	4	624	626	2·7	*VVW−*
1	0	3	742	745	100·0	*VS*
1	1	0	783	783	43	*W+*
1	1	2	939		0·1	nil
1	0	5	1366		0·2	nil
0	0	6	1403	1407	8·1	*W*
1	1	4	1406		7·3	
2	0	0	1565	1570	20	*W*
2	0	2	1721	1724	0·7	*VVW−*
2	1	1	1996	1998	2·7	*VVW*
1	1	6	2186	2187	21	*M*
2	0	4	2189		1·9	
1	0	7	2301	2308	4·1	*M+*
2	1	3	2307		38	
0	0	8	2495	2489	0·3	*VVW−*
2	1	5	2931		0·1	nil
2	0	6	2969	2965	9·8	*W*
2	2	0	3131	3127	6·6	*VW+*
1	1	8	3277	3279	0·3	*VVW*
2	2	2	3287		0·3	
1	0	9	3549	3546	7·1	*W+*
3	0	1	3561		0·6	
2	2	4	3754	3755	0·8	*VW−*
2	1	7	3867	3865	3·6	*M−*
3	0	3	3873		8·2	
0	0	10	3898	3909	0·7	*W*
3	1	0	3913		7·3	
2	0	8	4060	4055	0·6	*VVW*
3	1	2	4069		0·0	
3	0	5	4496		0·0	nil
2	2	6	4534	4535	4·8	*W*
3	1	4	4537		2·5	
1	1	10	4681	4670	1·5	*VW−*
1	0	11	5108	5110	0·8	*M−*
2	1	9	5114		8·8	
3	2	1	5126		0·7	
3	1	6	5317	5331	10	*M−*
3	0	7	5432	5450	1·2	*M*
3	2	3	5438		11	
2	0	10	5463	5488†	2·0	*W+*
0	0	12	5613	5632	0·9	*VW−*
2	2	8	5625		0·4	
3	2	5	6062		0·0	nil
4	0	0	6261	6274	3·0	*VW+*
1	1	12	6396	6403	2·5	*W*
3	1	8	6408		0·2	
4	0	2	6417		0·1	
2	1	11	6673	6690	1·4	*W+*
3	0	9	6679		3·9	
4	1	1	6692		0·6	

Table 2 (*cont.*)

h	*k*	*l*	$10^4 \times \sin^2 \theta$ Calculated	$10^4 \times \sin^2 \theta$ Observed	Relative intensity Calculated*	Relative intensity Observed
4	0	4	6885	6893	0·5	*VVW*
1	0	13	6979	7015	1·9	*M*+
3	2	7	6997		2·4	
4	1	3	7003		6·4	
2	2	10	7029	7054†	2·0	*WM*
3	3	0	7044		2·4	
2	0	12	7178	7190	3·6	*VW*+
3	3	2	7200		0·0	
4	1	5	7627		0·0	nil
0	0	14	7640	7672	0·3	*W*+
4	0	6	7665		4·5	
3	3	4	7668		1·1	
3	1	10	7811	7831	2·9	*WM*
4	2	0	7827		6·8	
4	2	2	7983	7874†	0·4	*VVW*−
3	0	11	8239	8253	0·9	*M*
3	2	9	8245		9·8	
1	1	14	8423	8428	2·4	*W*
3	3	6	8447	8453	6·9	*WM*
4	2	4	8450		1·4	
2	1	13	8544	8553	5·1	*WM*
4	1	7	8563		3·3	
2	2	12	8744	8751	5·2	*W*
4	0	8	8756		0·6	
1	0	15	9162	9166	3·8	*W*
2	0	14	9205	9234	2·1	*MS*
4	2	6	9230		15	
3	1	12	9526	9529	17	*WM*
3	3	8	9539		0·9	
3	2	11	9804	9811	5·5	*MS*
4	1	9	9810		28	
5	0	1, 4 3 1	9822	9823	4·1	*VW*

$a_0 = 3\cdot8937 \pm 0\cdot0002;\ c_0 = 12\cdot3371 \pm 0\cdot0007$.

* $(3\cdot28 \times 10^{-6})\ \{1+\cos^2 2\theta/\sin^2\theta \cos\theta\}\ p|F|^2$ where p = multiplicity and F = structure factor.

† Coincident with the α_2 component of the preceding line.

$Th_2(N_{1/2}O_{1/2})_2Sb$ were pure compounds, as evidenced by the X-ray diffraction powder patterns. A similar treatment carried out with Th_2N_2Bi resulted in considerably smaller changes in the lattice parameters. It seems, therefore, reasonable to assume that in the crystal lattice of this compound fewer nitrogen atoms are replaceable by oxygen than in the lattice of Th_2N_2Sb. The lower oxygen solubility is substantiated by phase identification. X-ray diffraction photographs of samples of reacted mixtures with the bulk composition $Th_2(N_{7/8}O_{1/8})_2Bi$, or with greater proportions of oxygen, contained lines corresponding to ThO_2 in addition to those of the principal phase, Th_2N_2Bi, indicating that the oxygen content of the preparations exceeded the solubility. In each reacted mixture containing one of the remaining four compounds a metal dioxide phase was present and the lattice parameters remained unchanged.

U_2N_2Sb was the first compound of the isostructural series to be prepared. The X-ray diffraction powder pattern, shown in Table 2, corresponds to a body-centered tetragonal cell of dimensions $a = 3\cdot894$, $c = 12\cdot337$ Å. The density, as calculated with two U_2N_2Sb formula weights per unit cell, is given in column 4 of Table 3.

If the origin is chosen at an Sb atom, the observed intensities (see Table 2) require the uranium atoms to in $\pm(00u)$ with $u = 0\cdot344 \pm 0\cdot003$. The only sites suitable for the nitrogen atoms are $\pm(\frac{1}{2}0\frac{1}{4})$. The structure of the compound is thus:

Space group, *I*4/*mmm* ;
Positions, (000) $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ + 2 Sb in (000) ;
4U in $\pm(00u)$, $u = 0\cdot344 \pm 0\cdot003$;
4N in $\pm(\frac{1}{2}0\frac{1}{4})$.

The existence of antimony vacancies in the structure is possible. No reliable evidence for the existence of vacancies was obtained, however, because of limitations in the accuracies of the chemical analyses and of the observed densities.

The structure is of the type first reported by Sillén (1939) for the disordered compound $(Na_{1/4}Bi_{3/4})_2O_2Cl$

Table 3. *Densities and crystal structure data for the M_2Y_2X compounds*

	a_0	c_0	Calc. density ($g.cm^{-3}$)
U_2N_2Sb	3·8937 ± 0·0002 Å	12·3371 ± 0·0007 Å	11·116 ± 0·002
U_2N_2Te	3·9631 ± 0·0002	12·561 ± 0·002	10·64
U_2N_2Bi	3·9292 ± 0·0005	12·548 ± 0·002	12·23
Th_2N_2Sb	4·049 ± 0·001	13·57 ± 0·01	9·17
$Th_2(N_{3/4}O_{1/4})_2Sb$	4·045 ± 0·003	13·18 ± 0·04	9·47
$Th(N_{1/2}O_{1/2})_2Sb$	4·041 ± 0·001	12·84 ± 0·01	9·76
Th_2N_2Te	4·0939 ± 0·0004	13·014 ± 0·001	9·44
Th_2N_2Bi	4·075 ± 0·001	13·620 ± 0·01	10·30
$Th_2(N,O)_2Bi$ (oxygen saturated)	4·074 ± 0·002	13·53 ± 0·03	10·37

and related oxyhalides. Recently, La_2O_2Te (Ballestracci, 1967) and Nd_2O_2Te (Raccah, Longo & Eick, 1967) crystals were reported to have this structure with u values of 0·346 and 0·341, respectively.

The interatomic distances in U_2N_2Sb are U – 4N = 2·27 ± 0·02 Å, U – 4Sb = 3·36 ± 0·03 Å.

The configuration of the four uranium atoms about a nitrogen atom is tetrahedral. Four of the edges of each NU_4 tetrahedron are shared with other tetrahedra so as to produce endless layers normal to the c axis of composition U_2N_2 per area a^2. The shared edges of the tetrahedron are appreciably shorter (3·60 Å) than the unshared edges (3·894 Å). Each antimony atom is bonded to eight uranium atoms which form a nearly perfect cube, the edges being 3·894 Å normal to the c axis and 3·859 Å parallel to it.

The structure can be described as a stack of tetrahedral layers U_2N_2 with alternating Sb-layers in the sequence $[U_2N_2]Sb[U_2N_2]^*Sb^*[U_2N_2]Sb$---, where the asterisk denotes a horizontal displacement of $\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2)$.

The compounds U_2N_2Bi and U_2N_2Te have the same structure as the antimony compound while U_2N_2P, U_2N_2As, U_2N_2S and U_2N_2Se, recently reported (Benz & Zachariasen, 1969), have the Ce_2O_2S type of structure.

In the U_2N_2P structure the uranium atoms are also in tetrahedral configuration about nitrogen and again endless layers $[U_2N_2]$ are formed. However, in this case three edges of each NU_4 tetrahedron are shared with other tetrahedra, and the layers $[U_2N_2]$ are hexagonal. The stacking sequence of $[U_2N_2]$ and P layers in the U_2N_2P structure is $[U_2N_2]$ P $[U_2N_2]$ P---, and each P atom is bonded to six uranium atoms, forming a nearly perfect octahedron.

For the compounds U_2N_2X the structure type is thus determined by the size of the X atom. When X = Sb, Bi, or Te it is possible to have a coordination number of eight for atom X with respect to uranium without bringing the uranium atoms into too close contact, and the tetragonal structure is found. However, for the smaller atoms, X = P, As, S or Se, the coordination number for atom X must be reduced from eight to six to avoid too short U–U separations, and the Ce_2O_2S type of structure results.

The observed U–N distance of 2·27 ± 0·02 Å in U_2N_2Sb is considerably smaller than one would anticipate, while the value U–Sb = 3·36 ± 0·03 Å is much larger than expected. For comparison, U–Sb = 3·10 Å in USb (Ferro, 1952). The apparently anomalous distances in U_2N_2Sb can be understood in terms of the bond strengths, and the unequal distribution of strength between the U–N and the U–Sb bonds. Since each nitrogen atom forms four bonds to uranium, the strength of each bond must be 0·75 in order to satisfy the valence of three for nitrogen. Thus one should expect the same U–N distance as in UN_2 where the bond strength is also 0·75, and where the observed U–N distance is 2·30 Å. Similarly, the bond strength of each U–Sb bond is only 0·375 in U_2N_2Sb, and hence one should except an appreciably larger U–Sb bond length than in USb where the bond strength is 0·50.

U_2N_2Sb is a representative of a whole series of isostructural compounds, the lattice constants of which are listed in Table 3. The u values were determined as those values giving the best fit between calculated ($\{[1+\cos^2 2\theta]/\sin^2\theta \cos\theta\}pF^2$ values) and the observed high angle line intensities. The values thus deduced are 0·344 with the uncertainty of ± 0·003 for the compounds U_2N_2Sb, U_2N_2Te, Th_2N_2Sb, and Th_2N_2Te while, because of poorer quality diffraction lines, the limits of uncertainties were somewhat greater for the other compounds, being ± 0·005 for Th_2NOSb and ± 0·01 for Th_2N_2Bi and U_2N_2Bi. The cell dimensions of U_2N_2Sb, U_2N_2Bi, U_2N_2Te and Th_2N_2Te show no significant variation from one preparation to another. However, as shown in Table 4, the length of the c axis decreases considerably with increasing oxygen content in the preparations $Th_2(N,O)_2Sb$ and $Th_2(N,O)_2Bi$. This is a startling observation since the bond length to an oxygen atom is usually greater than to a nitrogen atom. However, the result makes sense in terms of bond strength analysis. At the composition $Th_2(N_{1/2}O_{1/2})_2Sb$ the strength of each Th–Sb bond is 0·375; but in the compound Th_2N_2Sb the strength of the Th–Sb bond has decreased to only 0·25.

Table 4. *Bond distances in M_2Y_2X compounds with M = U or Th, Y = N or (N,O) and X = Sb, Te, or Sb*

Compound	Bond distances M–4Y	M–4X
U_2N_2Sb	2·27 ± 0·02 Å	3·36 ± 0·03 Å
U_2N_2Te	2·31	3·42
U_2N_2Bi	2·29*	3·40*

Table 4 (*cont.*)

Th_2N_2Sb	2·39*	3·56*
$Th_2(N_{1/2}O_{1/2})_2Sb$	2·35*	3·49*
Th_2N_2Te	2·38	3·54
Th_2N_2Bi	2·41*	3·58*
$Th_2(N,O)_2Bi$ (oxygen saturated)	2·40*	3·57*

* Limits of uncertainties in bond distances are of the order of two to three times that of the compound U_2N_2Sb.

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Neutron Diffraction Refinement of the Crystal Structure of Potassium Copper Chloride Dihydrate, $K_2CuCl_4.2H_2O$

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A refinement of the crystal structure of $K_2CuCl_4.2H_2O$ (space group $P4_2/mnm$; $a=7{\cdot}477$, $c=7{\cdot}935$ Å) has been carried out using the intensities of 201 independent three-dimensional single-crystal neutron reflexions with $\sin\theta/\lambda \le 0{\cdot}57$ Å^{-1}. The final R index on F is 0·039. The copper atom has a distorted octahedral coordination consisting of two H_2O molecules at 1·971 Å, two Cl atoms at 2·285 Å and two Cl atoms at 2·895 Å. The water molecule is trigonally coordinated and forms two equivalent O–H---Cl bonds at distances of 3·116 Å with H–O---Cl angles of 4·7°. The O–H distance in the water molecule is 0·955 Å (uncorrected for thermal motion) and the H–O–H angle is 109·7°.

Introduction

The crystal structure of $K_2CuCl_4.2H_2O$ has been studied using X-rays by Hendricks & Dickinson (1927) and Chrobak (1934) (see also Wyckoff, 1965). The heavy-atom positions have been determined approximately in these investigations. The proton magnetic resonance in a single crystal of this compound has been studied by Itoh, Kusaka, Yamagata, Kiriyama & Ibamoto (1953) and by McGrath & Silvidi (1961); the length and orientation of the interproton vector determined by the latter have also been used recently by El Saffar (1968) to predict the hydrogen positions.

Experimental

The preliminary analysis of the crystal structure was carried out on the basis of 53 *hll* intensities collected at 1·17 Å from a cylindrical sample with its axis parallel to $[01\bar{1}]$ in the neutron diffractometer at the Philippine Research Reactor (PRR-1) near Manila. The final refinement was based on three-dimensional data collected in the neutron diffractometer 3D-FAD (Momin, Sequeira & Chidambaram, 1969) at the CIRUS reactor in Trombay. The crystal used was a rectangular parallelepiped (weight = 46 mg) with its longest edge of 3·7 mm parallel to $[11\bar{1}]$. A total of 201 independent reflexions were measured at 1·406 Å up to $\sin\theta/\lambda = 0{\cdot}57$ Å^{-1}.

The space group extinctions for $P4_2/mnm$ were confirmed.[*] Using the 2θ values of 26 reflexions, the unit-cell constants were refined and found to be $a = 7{\cdot}477(13)$

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[*] The systematic extinctions are also consistent with the non-centrosymmetric space groups $P\bar{4}n2$ and $P4_2nm$, in view of which one of the referees has suggested that the authors should re-examine the space group determination. In anisotropic least-squares refinements these space groups would involve 8 and 17 additional parameters respectively. To reject $P4_2/mnm$ in favour of either of these at a significance level of 0·005 would require an improvement in the R index by ratios of 1·08 and 1·12 respectively (Hamilton, 1964). In view of the fact that (*a*) the structure refined in the space group $P4_2/mnm$ to an R index of 0·039, (*b*) there were no anomalous thermal parameters or bond lengths in this refinement and (*c*) since at worst only small deviations from this are likely to arise in the refinements in the non-centrosymmetric space groups which would become highly non-linear in consequence, we have not considered it worth while to attempt such refinements in the space groups $P\bar{4}n2$ and $P4_2nm$.