Crystal Structure of the Compounds U₂N₂X and Th₂(N,O)₂X, with X = P, S, As, and Se*

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The compounds Th_2NOAs, Th_2NOP, Th_2N_2S, Th_2N_2Se, U_2N_2As, U_2N_2P, U_2N_2S, and U_2N_2Se were prepared. From X-ray diffraction powder patterns, the compounds were found to have the Ce_2O_2S-type crystal structure (space group $P\bar{3}m1$) with the following lattice parameters:

	a (Å)	c (Å)
$Th_2(N,O)_2As$	$4\cdot041 \pm 0\cdot001$	$6\cdot979 \pm 0\cdot002$
Th_2N_2Se	$4\cdot0287 \pm 0\cdot0002$	$7\cdot156 \pm 0\cdot001$
$Th_2(N,O)_2P$	$4\cdot0285 \pm 0\cdot0003$	$6\cdot835 \pm 0\cdot001$
Th_2N_2S	$4\cdot008 \pm 0\cdot001$	$6\cdot920 \pm 0\cdot002$
U_2N_2As	$3\cdot833 \pm 0\cdot001$	$6\cdot737 \pm 0\cdot001$
Se	$3\cdot8622 \pm 0\cdot0005$	$6\cdot856 \pm 0\cdot001$
P	$3\cdot802 \pm 0\cdot001$	$6\cdot552 \pm 0\cdot002$
S	$3\cdot828 \pm 0\cdot001$	$6\cdot587 \pm 0\cdot002$

With the origin chosen at the X atom, where X = P, As, S or Se, the two metal atom (either Th or U) positions are $\pm(\frac{1}{3}, \frac{2}{3}, u_1)$ where $u_1 = 0\cdot293 \pm 0\cdot005$ for X = As or Se and $u_1 = 0\cdot278 \pm 0\cdot005$ for X = P or S. The probable locations of the two nitrogen (or nitrogen + oxygen) atoms are $\pm(\frac{1}{3}, \frac{2}{3}, u_2)$ with $u_2 \simeq 0\cdot63$. Apparent anomalous interatomic distances between the metal and different nonmetal atoms occur and these are attributed to different bond strengths.

Compounds were prepared with the general formula M_2Y_2X, where M is either thorium or uranium. The symbol Y represents nitrogen which, however, to a considerable extent may be replaced by oxygen. The symbol X denotes sulfur, selenium, phosphorus, or arsenic. Allbutt & Dell (1967) recently reported compounds U_2N_2P and U_2N_2S with lattice parameters virtually equal to those below. We used two different methods of preparation. In the first, mixtures of binary compounds as shown in column 1 of Table 1 were cold

pressed and reacted in a tungsten crucible under 1 atm N_2 at 1500 to 1700°C for $\frac{1}{2}$ to two hours. The thorium compounds with X = phosphorus and arsenic could not be obtained by heating the respective mixtures ThP + ThN and ThAs + ThN as had proved successful with the other analogous compounds, but, as shown in column 1 of Table 1, they were obtained when oxygen, as ThO_2, was added to the mixtures in amounts corresponding to the O/Th ratio of $\frac{1}{2}$. The chemical compositions of four products as given in an analytical report are listed in Table 1. Percentage weights unaccounted for by the chemical analyses range in value from 0·3 to 2·2 ± 1 % and are listed in column 8. Because

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Table 1. *Preparations and chemical analyses of the compounds* U_2N_2X *and* $Th_2(N,O)X$, *with* X = As, S, P, *and* Se

	Product chemical composition						
Reaction	U or Th anal ±1%	calc	N anal ±0·5%	calc	As or S anal ±0·1%	calc	Mat. bal.*	Formula by analyses
ThAs + $\frac{1}{3}$ThN + $\frac{1}{3}$ThO₂ + $\frac{1}{3}$N₂ = Th₂NOAs	81·4	81·6	3·3	2·5	14·0	13·2	1·3	$Th_2N_{1\cdot3}O_{0\cdot5}As_{1\cdot1}$†
UAs + UN + $\frac{1}{2}$N₂ = U₂N₂As	82·5	82·2	4·12	4·8	13·1	12·9	0·3	$U_2N_{1\cdot7}As_{1\cdot0}$
ThS + ThN + $\frac{1}{2}$N₂ = Th₂N₂S	87·7	88·5	4·7	5·3	5·38	6·1	2·2	$Th_2N_{1\cdot8}S_{0\cdot9}$
US + UN + $\frac{1}{2}$N₂ = U₂N₂S	87·5	88·8	4·76	5·3	5·53	6·0	2·2	$U_2N_{1\cdot9}S_{0\cdot9}$
ThP + $\frac{1}{3}$ThN + $\frac{1}{3}$ThO₂ + $\frac{1}{3}$N₂ = Th₂NOP								
UP + UN + $\frac{1}{2}$N₂ = U₂N₂P								
ThSe + ThN + $\frac{1}{2}$N₂ = Th₂N₂Se								
USe + UN + $\frac{1}{2}$N₂ = U₂N₂Se								

* Percentage weight required for material balance as calculated from the difference, 100 minus the percentage by analysis.
† The oxygen was added in the preparation (see column 1) and, therefore, the material balance was assumed to be oxygen.

oxygen had been added, the unanalyzed weight in the Th₂NOAs preparation as listed in row 1 of Table 1 is attributed to oxygen and is written explicitly in the formula given in the last column of Table 1. The weight required for material balance in the remaining three analyzed preparations may be dissolved oxygen too. Apart from the oxygen contents which, as inferred above, have a large uncertainty, the chemical analyses are in fair agreement with the assumed formulas as listed in column 1 of Table 1 if allowances are made for the uncertainties in the chemical analyses and in purity as based upon absence of foreign lines in X-ray diffraction powder patterns. The second method of preparation was investigated as a check on chemical compositions. In this method, weighed quantities of binary compounds and the elements X, as required to give the formulas listed in column 1 of Table 1, were reacted for 30 days at 1000 °C in a sealed evacuated silica tube. In all eight cases the products were found by X-ray diffraction powder patterns, to be pure compounds although the diffraction lines were less sharp than those obtained with the method-one preparations.

The X-ray diffraction patterns of the various preparations are all similar. As illustrated in Table 2, which gives the diffraction data for U₂N₂Se, the patterns correspond to hexagonal symmetry. The cell dimensions obtained for the various preparations are listed in Table 3. The calculated and pycnometric densities (as determined by immersion of samples in bromobenzene) are listed in columns 4 and 5 respectively of Table 3. The densities require one stoichiometric molecule per unit cell. The pycnometric values are somewhat lower than the calculated ones presumably due to the porous nature of the preparations.

Table 2. *X-ray diffraction data for* U₂N₂Se (Cu, Kα; λ = 1·54050 Å)

h	k	l	10⁴ × sin² θ Calculated	Observed	Relative intensities Calculated*	Observed
0	0	1	126	127	2·9	vw
0	0	2	505	509	14·6	m−
1	0	0	530	536	11·1	m−
1	0	1	657	661	100	vvs
1	0	2	1035	1040	37·2	s
0	0	3	1136	1142	9·2	w+
1	1	0	1591	1600	27·5	m+
1	0	3	1666	1674	14·8	m
1	1	1	1717	1720	0·6	vvw−
0	0	4	2019	2026	1·4	vvw
1	1	2	2096	2103	10·9	w+
2	0	0	2121	2124	1·4	vvw
2	0	1	2248	2254	15·2	m
1	0	4	2550	2554	9·4	w+
2	0	2	2626	2633	8·0	vw
1	1	3	2727	2731	12·3	m−
0	0	5	3155	3163	1·1	vvw
2	0	3	3257	3263	4·4	vw
1	1	4	3610	3618	3·0	vw−
1	0	5	3686	3695	3·8	vw
2	1	0	3712	3720	1·0	vvw
2	1	1	3839	3845	11·5	m
2	0	4	4141	4148	3·9	vw
2	1	2	4217	4226	6·8	vw+

Table 2 (*cont.*)

h	k	l	10⁴ × sin² θ Calculated	Observed	Relative intensities Calculated*	Observed
0	0	6	4544	—	0·0	nil
1	1	5	4746	4747	3·3	vw
3	0	0	4773	4778	3·8	vw
2	1	3	4848	4852	4·4	vw
3	0	1	4899†		0·1	
1	0	6	5074	5075	4·0	vw
2	0	5	5277	5276	2·1	vw
3	0	2	5278†		2·2	
2	1	4	5732	5730	4·9	w
3	0	3	5909	5906	3·4	vw
1	1	6	6135	6133	0·2	trace
0	0	7	6185	6182	0·8	vvw−
2	2	0	6364	6362	2·8	vw
2	2	1	6490	—	0·1	nil
2	0	6	6665	6665	3·1	vw+
1	0	7	6715	6715	0·7	vvw−
3	0	4	6792	6789	1·3	vvw−
2	1	5	6868 }	6866	3·4 }	vw
2	2	2	6869 }		1·9 }	
3	1	0	6894†		0·5	
3	1	1	7021	7019	5·7	vw+
3	1	2	7399	7395	4·0	vw
2	2	3	7500	7500	3·2	vw
1	1	7	7776	7774	4·6	w+
3	0	5	7928	7926	2·6	vw
3	1	3	8030	8030	3·5	vw+
0	0	8	8078†		0·1	
2	1	6	8256	8254	7·0	m
2	0	7	8306†		0·8	
2	2	4	8383	8379	1·5	vvw−
4	0	0	8485	8481	0·3	vvw−
1	0	8	8608 }	8609	3·2 }	m
4	0	1	8611 }		3·5 }	
3	1	4	8914	8912	6·0	m
4	0	2	8990	8988	2·7	vvw
3	0	6	9317	—	0·3	trace
2	2	5	9519	9519	4·8	w+
4	0	3	9621	9620	3·6	w−
1	1	8	9669	9669	1·2	vvw
2	1	7	9897	9896	5·7	w+

$a_0 = 3·8622 \pm 0·0002$ Å; $c_0 = 6·8560 \pm 0·0005$ Å.

* $(1·65 \times 10^{-5}) \dfrac{1+\cos^2 2\theta}{\sin^2 \theta \cos \theta} p|F|^2$ where p = multiplicity and F = structure factor.

† Coincident with the $K_{\alpha 2}$ component of the preceding line.

If the origin is chosen at the X atom, the metal atoms are at $\pm(\frac{1}{3},\frac{2}{3},u_1)$ with $u_1 \simeq 0·28$. The Y atoms have too small a scattering effect to be located by intensity considerations. However, the only positions which can accommodate the Y atoms are $\pm(\frac{1}{3},\frac{2}{3},u_2)$ with $u_2 \simeq 0·63$.

Thus it is concluded that the compounds have the Ce₂O₂S type of structure:

Space group: $P\bar{3}m1$ (D^3_{3d})
2M in $\pm(\frac{1}{3},\frac{2}{3},u_1)$
2Y in $\pm(\frac{1}{3},\frac{2}{3},u_2)$
1X in (000)

The observed intensities give the same value, $u_1 = 0·293 \pm 0·005$, for each of the arsenic and selenium compounds, and $u_1 = 0·278 \pm 0·005$ for each of the phosphorus and sulfur compounds. It is reason-

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

	a (Å)	c (Å)	Density, g.cm^{-3} Calc	Pycn	u_1	u_2
$Th_2(N,O)_2As$	$4{\cdot}041 \pm 0{\cdot}001$	$6{\cdot}979 \pm 0{\cdot}002$	$9{\cdot}58$	$9{\cdot}3$	$0{\cdot}293 \pm 0{\cdot}005$	$0{\cdot}635$
Th_2N_2Se	$4{\cdot}0287 \pm 0{\cdot}0002$	$7{\cdot}156 \pm 0{\cdot}001$	$9{\cdot}43$	$7{\cdot}9$	$0{\cdot}293$	$0{\cdot}628$
$Th_2(N,O)_2P$	$4{\cdot}0285 \pm 0{\cdot}0003$	$6{\cdot}835 \pm 0{\cdot}001$	$9{\cdot}08$	$8{\cdot}5$	$0{\cdot}278$	$0{\cdot}630$
Th_2N_2S	$4{\cdot}008 \pm 0{\cdot}001$	$6{\cdot}920 \pm 0{\cdot}002$	$9{\cdot}04$	$8{\cdot}1$	$0{\cdot}278$	$0{\cdot}626$
U_2N_2As	$3{\cdot}833 \pm 0{\cdot}001$	$6{\cdot}737 \pm 0{\cdot}001$	$11{\cdot}22$	–	$0{\cdot}293$	$0{\cdot}630$
Se	$3{\cdot}8622 \pm 0{\cdot}0005$	$6{\cdot}856 \pm 0{\cdot}001$	$10{\cdot}94$	$9{\cdot}0$	$0{\cdot}293$	$0{\cdot}628$
P	$3{\cdot}802 \pm 0{\cdot}001$	$6{\cdot}552 \pm 0{\cdot}002$	$10{\cdot}84$	$8{\cdot}7$	$0{\cdot}278$	$0{\cdot}626$
S	$3{\cdot}828 \pm 0{\cdot}001$	$6{\cdot}587 \pm 0{\cdot}002$	$10{\cdot}65$	$9{\cdot}83$	$0{\cdot}278$	$0{\cdot}627$

	M–4Y	M–3X
$Th_2(N,O)_2As$	$2{\cdot}39 \pm 0{\cdot}02$ Å	$3{\cdot}10 \pm 0{\cdot}03$ Å
Th_2N_2Se	$2{\cdot}39$	$3{\cdot}13$
$Th_2(N,O)_2P$	$2{\cdot}41$	$3{\cdot}00$
Th_2N_2S	$2{\cdot}41$	$3{\cdot}01$
U_2N_2As	$2{\cdot}27$	$2{\cdot}97$
Se	$2{\cdot}29$	$3{\cdot}00$
P	$2{\cdot}29$	$2{\cdot}85$
S	$2{\cdot}28$	$2{\cdot}87$

able to adjust the u_2 value such that the Y atom is placed equidistantly from the four nearest M atoms.

Table 3 gives the parameter values and the bond lengths M $-$ 4Y and M $-$ 3X for the various compounds. As reported in the paper describing the Ce_2O_2S structure (Zachariasen, 1949), the M $-$ 4Y distances are shorter, and the M $-$ 3X distances longer, than would be anticipated from the atomic radii. This apparent anomaly can be attributed to the fact that the M $-$ Y and M $-$ X bonds do not have the same strength (Pauling, 1929; Zachariasen, 1963). Thus, in Ce_2O_2S the bond strengths are 0·50 for the Ce–O and 0·33 for the Ce–S bonds.

Chemical analyses were done by R. D. Gardner in the Analytical Group of the Los Alamos Scientific Laboratory.

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Crystal Structure of DL-Valine*

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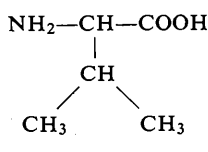*Centre of Advanced Study in Physics, University of Madras, Madras 25, India*

The crystal structure of DL-valine has been determined by the use of the symbolic addition phase determination method of Karle & Karle. DL-valine crystallizes in the space group $P2_1/c$ with cell dimensions $a = 5{\cdot}21 + 0{\cdot}02$; $b = 22{\cdot}10 + 0{\cdot}04$; $c = 5{\cdot}41 + 0{\cdot}02$ Å and $\beta = 109{\cdot}2°$ with $Z = 4$. The molecules are held together by a series of hydrogen bonds in a three-dimensional network. The conformation of the valine molecule is found to be similar to that found in the hydrohalide derivatives of valine. A comparative account of the molecular features of the valine molecule as found here and in the other structures is briefly given at the end.

Introduction

Valine is an essential amino acid whose chemical formula is

$$NH_2—CH—COOH$$
$$|$$
$$CH$$
$$/ \quad \backslash$$
$$CH_3 \qquad CH_3$$

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The crystal structures of L-valine hydrochloride monohydrate (Rao, 1967) and L-valine hydrochloride (Parthasarathy, 1966; Ando, Ashida, Sasada & Kakudo, 1967) have been recently determined. In these two structures the conformation of the valine molecule is similar except for the orientation of the methyl pair at the terminal end of the valine residue. Three different orientations are possible for the methyl pair and two of these have been found to occur, one in each of the above two structures. Recent conformational studies on poly-L-valine have indicated (C. M. Venkatachalam,