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The Crystal Structure of ζ-$Pu_{19}Os$, a Structure Closely Related to β-Pu*

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Abstract

The structure of ζ-Pu–Os, the high-temperature phase of approximate composition $Pu_{19}Os$, has been solved by single-crystal methods and refined by full-matrix least squares. Data were collected with an automated Picker diffractometer. The crystals are orthorhombic, space group *Pnna*, with $a = 15{\cdot}839$ (5), $b = 7{\cdot}819$ (3), $c = 9{\cdot}151$ (3) Å and there are 52 atoms in the unit cell. The Os atoms substitute randomly in one or more of the Pu sites. The eight kinds of Pu atoms have from 12 to 15 neighbors at distances ranging from 2·51 to 3·85 Å. The structure is closely related to that of β-Pu and also has a feature in common with ζ-$Pu_{28}Zr$. The common features of these three structures are discussed. The average valence of Pu in the phase is 5·4, the same as that in β-Pu. For 1110 observed reflections $R = 0{\cdot}072$ and $R_w = 0{\cdot}068$.

Introduction

The Pu–Os phase diagram was first studied by Bochvar, Konobeevsky, Kutaitsev, Menshikova & Chebotarev (1958). They reported the intermediate phases $PuOs_2$, Pu_5Os_3, high- and low-temperature phases at about Pu_3Os and a phase at approximately $Pu_{19}Os$. Ellinger & Land (1970) have given a more detailed and accurate phase diagram of this system in the range 0 to 15 at.% Os. They found that at about 5 at.% Os there are both low- and high-temperature phases, designated η and ζ. The structure of the low-temperature, η phase was recently reported by Cromer (1978). In the present paper the structure of the high-temperature, ζ-$Pu_{19}Os$ phase is reported along with a description of features common to this phase, β-Pu (Zachariasen & Ellinger, 1963) and ζ-$Pu_{28}Zr$ (Cromer, 1979).

Experimental

A portion of the same alloy that was used for the η phase determination was heat treated at 573 K for 7 d and then cooled to room temperature at a rate of 25 K d^{-1}. The material was crushed and fragments were studied with a precession camera. Single crystals, different from the η phase, were easily found but none was completely free of small satellite crystals. The space group was uniquely determined to be *Pnna*. The $0kl$ reflections were absent except for $k + l = 2n$, $h0l$ were absent except for $h + l = 2n$ and $hk0$ were absent except for $h = 2n$.

Lattice constants were obtained from a least-squares refinement of 12 high-angle reflections measured on an automated Picker diffractometer. Intensity data were collected from a hemisphere of reciprocal space and processed in the manner described by Cromer & Larson (1977). Crystallographic data are given in Table 1 and details of data collection are given in Table 2. Empirical absorption corrections were based on the variation of intensities as a function of φ for a few reflections near $\chi = 90°$ (Furnas, 1957). In addition, spherical absorption corrections were applied based on the mean radius of the irregularly shaped crystal. Agreement between equivalent reflections (Table 2) was not as good as we usually find and not greatly improved by the absorption correction, probably because of diffraction from the satellite crystals adhering to the principal crystal. There were a number of Friedel pairs that agreed well with each other but not with another Friedel pair from the same form.

Structure determination and refinement

Comparison of the unit-cell volume with that of η-$Pu_{19}Os$ indicated that there are 52 atoms. There are only fourfold and eightfold positions in space group *Pnna*; thus no ordered structure is possible with the composition $Pu_{19}Os$. Assuming 52 equal atoms, direct methods quickly found the structure which has five

Table 1. *Crystallographic data for* ζ-$Pu_{19}Os$

Space group	*Pnna*	Z	52
a	15·839 (5) Å ($\lambda = 0{\cdot}70930$ Å)	d_c (5 at.% Os)	18·02 Mg m^{-3}
		μ	95·4 mm^{-1}
b	7·819 (3)		
c	9·151 (3)		

* Work performed under the auspices of the Department of Energy.

atoms in the general position, two atoms in equipoint 4(*d*) and one in 4(*c*). A full-matrix least-squares refinement, which minimized $\sum w(\Delta F)^2$, was made with anisotropic thermal parameters. All atoms were considered to be Pu and scattering factors f, f' and f'' were taken from *International Tables for X-ray Crystallography* (1974). Positional parameters, along with the equivalent isotropic thermal parameters are given in Table 3.* None of the thermal parameters was unusually large or very anisotropic. No strong, direct evidence for the location of the Os atoms could be obtained from the behavior of the thermal parameters. After correction for f' the scattering amplitude of an Os atom is only about 10% less than Pu. Pu(1) does have the largest temperature factor and it will later be argued on other grounds that this is the most likely Os site.

* Listings of the final least-squares cycle containing the anisotropic thermal parameters, structure factors, thermal ellipsoid calculations, interatomic distance calculations and polyhedron calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34418 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Data collection and reduction* (*Cromer & Larson*, 1977)

Radiation	Mo $K\alpha$ (graphite monochromated)
2θ max	60°
Take-off angle	3°
Step size	0·05° 2θ
Step time	2 s
Scan range	2° (plus α_1–α_2 separation)
T_{min} (threshold parameter)	3·0
Number of reflections	6589
Unique reflections	1658
Unique reflections observed	1110
Reflections measured twice	13
Reflections measured three times	13
Reflections measured four times	1631
R_F (no corrections)	0·130
R_F (empirical corrections)	0·118
Range of corrective factors	0·026 to 0·182
Mean radius of crystal	0·022 mm

Table 3. *Least-squares parameters for* ζ-$Pu_{19}Os$

$R = 0{\cdot}072$, $R_w = 0{\cdot}068$, goodness of fit = 0·90.

	x	*y*	*z*	Equivalent isotropic *B* (Å²)
Pu(1)	¼	0	0·9147 (3)	2·15
Pu(2)	0·6599 (1)	¼	¼	1·96
Pu(3)	0·0174 (1)	¼	¼	1·72
Pu(4)	0·3223 (1)	0·6786 (2)	0·0856 (2)	2·09
Pu(5)	0·3441 (1)	0·0841 (2)	0·1907 (2)	2·01
Pu(6)	0·4925 (1)	0·3689 (2)	0·0981 (2)	1·98
Pu(7)	0·5627 (1)	0·0026 (2)	0·0839 (2)	2·13
Pu(8)	0·6638 (1)	0·6322 (2)	0·1094 (2)	1·92

It was earlier noted that the agreement between equivalent reflections was not as good as expected. In the hemisphere of data taken, the data could be divided into two sets, each set containing Friedel pairs. When this was done, in each set R_F was reduced by about a factor of two. Least-squares refinements, although giving essentially the same structural results, had a weighted sum of residuals a factor of 10 higher for these truncated data sets. This observation shows the value of having redundant data sets when systematic errors are present from absorption or satellite crystals.

Table 4. *Interatomic distances* (Å) *in* ζ-$Pu_{19}Os$

Pu(1)–2Pu(2)	2·851 (2)	Pu(6)–Pu(2)	3·136 (2)
–2Pu(4)	3·174 (2)	–Pu(3)	3·292)2)
–2Pu(5)	3·006 (3)	–Pu(3)	3·342 (2)
–2Pu(7)	2·967 (2)	–Pu(4)	3·402 (2)
–2Pu(8)	3·192 (2)	–Pu(4)	3·625 (2)
–2Pu(8)	3·277 (3)	–Pu(5)	3·065 (2)
		–Pu(5)	3·346 (2)
Pu(2)–2Pu(1)	2·851 (2)	–Pu(6)	2·735 (1)
–2Pu(4)	3·134 (2)	–Pu(6)	3·345 (1)
–2Pu(6)	3·136 (2)	–Pu(7)	3·075 (2)
–2Pu(7)	2·902 (2)	–Pu(7)	3·273 (3)
–2Pu(8)	3·210 (2)	–Pu(7)	3·460 (2)
–2Pu(8)	3·254 (2)	–Pu(8)	3·118 (3)
		–Pu(8)	3·407 (2)
Pu(3)–2Pu(4)	3·003 (2)		
–2Pu(5)	3·454 (2)	Pu(7)–Pu(1)	2·967 (2)
–2Pu(6)	3·292 (2)	–Pu(2)	2·902 (2)
–2Pu(6)	3·342 (2)	–Pu(3)	2·796 (3)
–2Pu(7)	2·796 (2)	–Pu(3)	3·687 (2)
–2Pu(7)	3·687 (2)	–Pu(4)	3·456 (2)
–2Pu(8)	3·277 (2)	–Pu(5)	2·993 (3)
		–Pu(5)	3·653 (2)
Pu(4)–Pu(1)	3·174 (2)	–Pu(6)	3·075 (2)
–Pu(2)	3·134 (2)	–Pu(6)	3·273 (3)
–Pu(3)	3·003 (2)	–Pu(6)	3·460 (2)
–Pu(4)	3·209 (1)	–Pu(7)	2·511 (1)
–Pu(4)	3·612 (1)	–Pu(8)	3·317 (2)
–Pu(5)	2·920 (2)	–Pu(8)	3·398 (3)
–Pu(5)	3·332 (2)		
–Pu(5)	3·364 (2)	Pu(8)–Pu(1)	3·192 (2)
–Pu(5)	3·418 (2)	–Pu(1)	3·277 (3)
–Pu(6)	3·402 (2)	–Pu(2)	3·210 (2)
–Pu(6)	3·625 (2)	–Pu(2)	3·254 (2)
–Pu(7)	3·456 (2)	–Pu(3)	3·277 (2)
–Pu(8)	3·023 (2)	–Pu(4)	3·023 (2)
–Pu(8)	3·102 (2)	–Pu(4)	3·102 (2)
		–Pu(5)	3·532 (3)
Pu(5)–Pu(1)	3·006 (3)	–Pu(5)	3·852 (3)
–Pu(3)	3·454 (2)	–Pu(6)	3·118 (3)
–Pu(4)	2·920 (2)	–Pu(6)	3·407 (2)
–Pu(4)	3·332 (2)	–Pu(7)	3·317 (2)
–Pu(4)	3·364 (2)	–Pu(7)	3·398 (3)
–Pu(4)	3·418 (2)	–Pu(8)	3·165 (1)
–Pu(5)	2·812 (1)	–Pu(8)	3·426 (1)
–Pu(5)	3·259 (1)		
–Pu(6)	3·065 (2)		
–Pu(6)	3·346 (2)		
–Pu(7)	2·993 (3)		
–Pu(7)	3·653 (2)		
–Pu(8)	3·532 (3)		
–Pu(8)	3·852 (3)		

Discussion

The interatomic distances to the neighbors, as defined in Cromer & Larson (1977), are given in Table 4. In the following discussion all atoms will be considered to be Pu. The notation β will refer to β-Pu, ζ will refer to ζ-$Pu_{19}Os$, η will refer to η-$Pu_{19}Os$, $\beta(n)$ will refer to atom type n in β, *etc.*

Before considering where the Os atoms might order, if indeed they do, it is desirable to consider the close relationship between the present structure and that of β (Zachariasen & Ellinger, 1963). The ζ-$Pu_{28}Zr$ structure (Cromer, 1979) also has some similarities to β. All three structures have one common axial length of about 7·8 Å. The c axis of the nearly orthogonal monoclinic cell of β is 7·859 Å, the b axis of ζ is 7·819 Å and the c axis of ζ-$Pu_{28}Zr$ is 7·858 Å.

Fig. 1 shows β projected along its c axis. Note, in the center of the figure, the rectangular array of atoms made up of $\beta(1)$, $\beta(2)$, $\beta(5)$, $\beta(6)$ and $\beta(7)$. Fig. 2 shows ζ projected along the b axis. In the lower left of this figure there is a group of atoms similar to that in Fig. 1. Whereas in Fig. 1 the group is a double group, the two halves being related by a mirror at $y = \frac{1}{2}$, that in Fig. 2 is a triple group, its two halves related by a 2_1 axis parallel to y at $x = \frac{1}{4}$, $z = \frac{3}{4}$. To see the similarities fully add $\frac{1}{4}$ to the y coordinates of Fig. 2. For example, the coordinates of $\zeta(6)$, $\zeta(3)$ and $\zeta(6)$ at the lower left become 0·619, 0 and 0·381, virtually the same as those of $\beta(6)$, $\beta(5)$ and $\beta(6)$ in Fig. 1. $\beta(2)$, $\beta(1)$ and $\beta(2)$ lie on a true mirror and the analogous atoms $\zeta(8)$, $\zeta(2)$ and $\zeta(8)$ lie on a local, pseudo mirror.

Fig. 3 shows the network of atoms lying on the mirror plane of β. The Schäfli symbol for this network is $5353 + 3^3 5^2 + 3^4 5$ (1:2:2). For brevity it will be called a (3,5) net. $\beta(5)$ and $\beta(6)$, in Fig. 1, are nearly coplanar and the somewhat puckered network that they form is shown in projection in Fig. 4. The Schäfli symbol for this network is $3^2 6^2 + 3636$ (4:2) which for brevity will be called a (3,6) net. The β structure can be described as an alternating sequence of (3,5) and (3,6) nets. Pentagons fall over hexagons and the $\beta(7)$ atoms lie in the resulting holes.

Fig. 5 shows the network of atoms lying near the plane $x = 0{\cdot}16$ of ζ. This is a (3,5) network identical to that occurring in β. The network of atoms lying near the plane $x = \frac{1}{2}$ of ζ is shown in Fig. 6 and this (3,6) net is the same as that of β shown in Fig. 4. The ζ structure

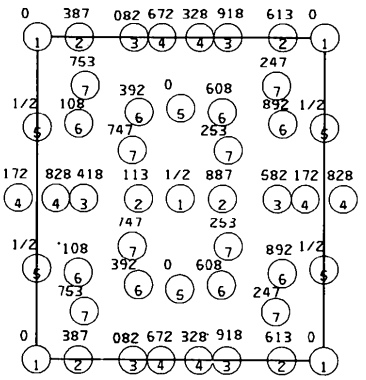

Fig. 1. The unit cell of β-Pu projected along the 7·8 Å c axis. The a axis is horizontal and the b axis is vertical, with the origin at the lower-left corner. Atom types are indicated inside the circles and z coordinates are given beside each circle.

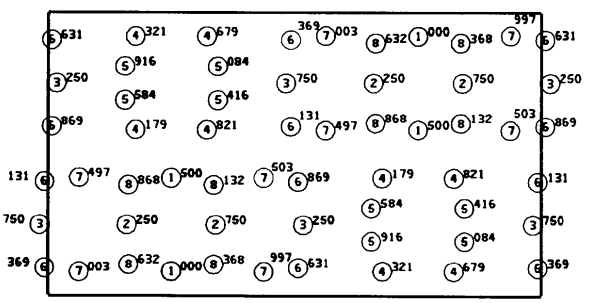

Fig. 2. The unit cell of ζ-$Pu_{19}Os$ projected along the 7·8 Å b axis. The a axis is horizontal and the c axis is vertical. The origin is at the upper-left corner. Atom types are indicated inside the circles and y coordinates are given beside each circle.

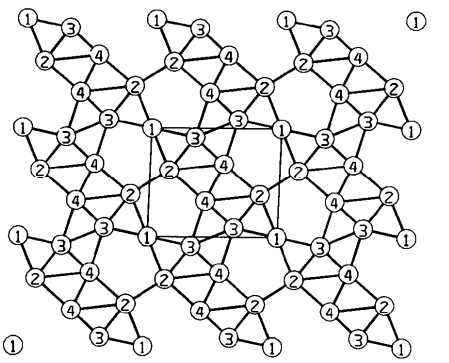

Fig. 3. Network of atoms lying in the $y = \frac{1}{2}$ plane of β-Pu. The a axis is horizontal and the 7·8 Å c axis is vertical.

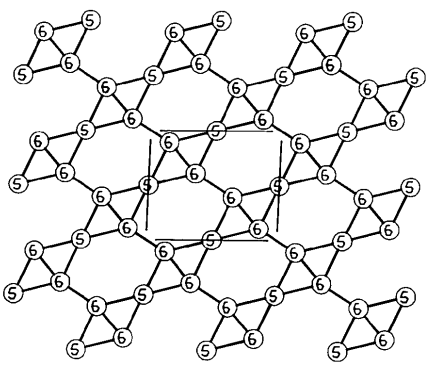

Fig. 4. Network of atoms lying near the $y = \frac{1}{4}$ or $\frac{3}{4}$ plane of β-Pu. The a axis is horizontal and the 7·8 Å c axis is vertical.

can be described as (3,6) layers alternating with *two* (3,5) layers. Pentagons lie over hexagons and $\zeta(7)$ atoms fill the holes. Pentagons lie over pentagons in the double (3,5) layers and $\zeta(1)$ atoms lie in these holes.

In the paper on the structure of η it was argued that Os might be concentrated in the site of $\eta(5)$ which has the closest neighbors and has icosahedral surroundings which are different from those of all the other atoms. In the ζ structure $\zeta(1)$ and $\zeta(2)$ both have icosahedral surroundings and both have average neighbor distances distinctly smaller than the other sites. For two reasons it is suggested that the Os atoms are more likely to be concentrated in $\zeta(1)$ rather than in $\zeta(2)$. $\zeta(1)$ has a distinctly larger thermal parameter than $\zeta(2)$ (Table 3). Secondly, $\zeta(1)$ is the only site that does not have a direct counterpart in the β structure.

The relation between β and ζ-$Pu_{28}Zr$ can be seen in Fig. 7. There is a group of atoms made up of types 2, 3, 4, 6 and 8 surrounding Pu(1) at $\frac{1}{2}$, $\frac{1}{4}$, 0·875. This group is similar to the group in Fig. 1 but twice the size. The doubling results from a twofold axis passing through Pu(1). The z coordinates closely match those in Fig. 1. There is also a local, pseudo mirror passing through atoms 4, 6, 1, 6 and 4. Fig. 8 shows the network of atoms in this structure. The net is complicated but has features similar to the nets shown earlier.

Figs. 9–11 show stereo drawings of the polyhedra found in ζ. Table 5 gives the correspondence between the atoms and polyhedra in ζ and β. Only for $\zeta(2)$, $\zeta(7)$ and $\zeta(8)$ are the polyhedra identical in the two structures. For the other atoms, save $\zeta(1)$ for which there is no counterpart, although positions within the nets are equivalent, the surroundings on either side of the nets are not.

$\zeta(1)$ and $\zeta(2)$ each have 12 neighbors at an average distance of 3·08 Å forming somewhat distorted icosahedra. $\zeta(3)$ has 14 neighbors at an average distance of 3·26 Å. This atom has a ring of five atoms on one side capped by a single atom and a ring of six atoms on the other side with a double cap. $\zeta(4)$ has 14 neighbors at

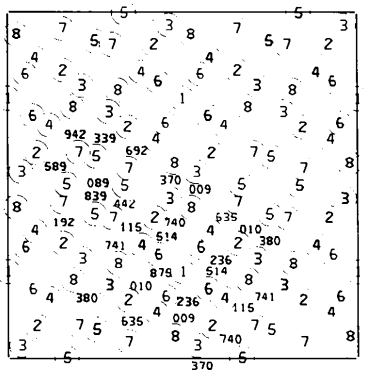

Fig. 7. ζ-$Pu_{28}Zr$ projected along the 7·8 Å c axis. The a axis is horizontal and the b axis is vertical. The origin is at the lower-left corner. Atom types are indicated in the circles. The z coordinates of some of the atoms are shown near the circles.

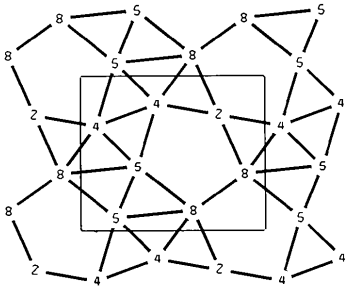

Fig. 5. Network of atoms lying near the plane $x = 0{\cdot}16$ of ζ-$Pu_{19}Os$. The 7·8 Å b axis is vertical and the c axis is horizontal.

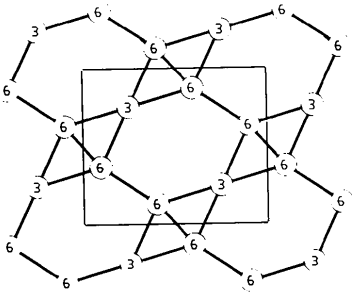

Fig. 6. Network of atoms lying near the plane $x = \frac{1}{2}$ of ζ-$Pu_{19}Os$. The 7·8 Å b axis is vertical and the c axis is horizontal.

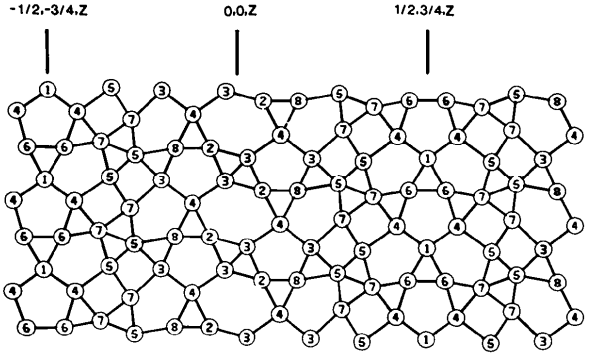

Fig. 8. Network of atoms lying in the plane containing the origin and type 1 atoms of ζ-$Pu_{28}Zr$. The 7·8 Å c axis is vertical.

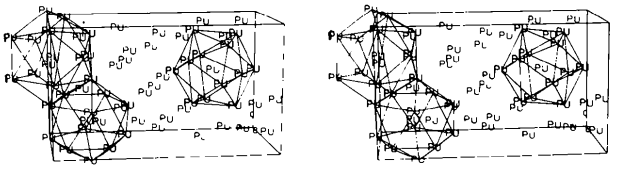

Fig. 9. Stereodrawing showing polyhedra for Pu(1), Pu(2), and Pu(3) in ζ-$Pu_{19}Os$. The origin is at the lower-right rear. The view direction is approximately along y. Pu(1) is on the right at $\frac{1}{4}$, $\frac{1}{2}$, 0·585. Pu(2) is at 0·840, $\frac{3}{4}$, $\frac{1}{4}$, lower left and Pu(3) is at 0·983, $\frac{3}{4}$, $\frac{3}{4}$, upper left.

Table 5. *Correspondence between atoms and polyhedra in β-Pu and ζ-$Pu_{19}Os$*

N is the number of neighbors, f_n is the number of n-sided faces and v_n is the number of n-fold vertices.

	ζ-$Pu_{19}Os$							β-Pu							
	N	f_3	f_4	v_3	v_4	v_5	v_6		N	f_3	f_4	v_3	v_4	v_5	v_6
Pu(1)	12	20				12									
Pu(2)	12	20				12		Pu(1)	12	20				12	
Pu(3)	14	20	2		6	4	4	Pu(5)	14	18	3		6	6	2
Pu(4)	14	24				12	2	Pu(3)	13	22			1	10	2
Pu(5)	14	20	2		3	10	1	Pu(4)	15	20	3	1	4	7	3
Pu(6)	14	22	1		2	10	2	Pu(6)	14	22	1		2	10	2
Pu(7)	13	22		1		9	3	Pu(7)	13	22		1		9	6
Pu(8)	15	26			1	10	4	Pu(2)	15	26			1	10	4

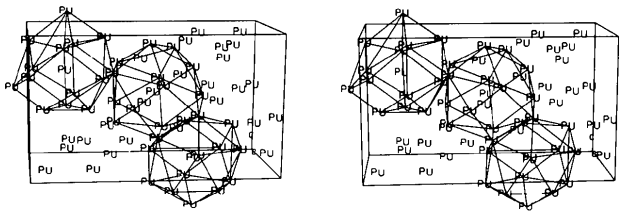

Fig. 10. As Fig. 9, but showing Pu(4) on the right at 0·322, 0·679, 0·086, Pu(5) on the left at 0·844, 0·416, 0·691 and Pu(6) at 0·508, 0·869, 0·598 in the middle.

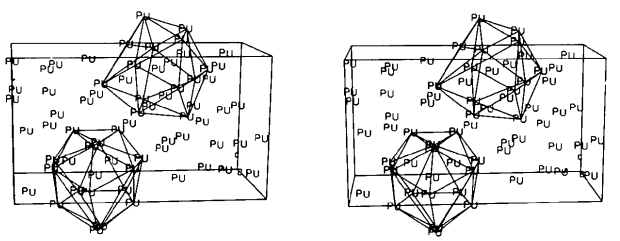

Fig. 11. As Fig. 9, but showing Pu(7) on the right at 0·437, 0·997, 0·916 and Pu(8) on the left at 0·664, 0·632, 0·109.

an average distance of 3·27 Å which form a rather distorted Frank & Kasper (1958) CN 14-type polyhedron. ζ(5) has 14 neighbors at an average distance of 3·29 Å. There are six neighbors in a ring approximately coplanar with the central atom and four atoms on either side of the ring. ζ(6) has 14 neighbors at an average distance of 3·26 Å and the polyhedron can be described as was that of ζ(5). ζ(7) has 13 neighbors at an average distance of 3·19 Å. The neighbors form rings of five atoms on either side, one ring capped by one atom and the other ring capped by two atoms. This atom lies between the two kinds of nets. In both structures this atom has a close contact through a center of symmetry: 2·51 Å for ζ(7) and 2·60 Å for β(7). There is also one short distance of 2·55 Å in η. ζ(8) has 15 neighbors at an average distance of 3·30 Å. This polyhedron (in Fig. 11) lies on a pseudo mirror in the $x = 0{\cdot}66$ plane. There are five neighbors approximately coplanar with ζ(8) in the pseudo mirror. Five atoms lie on either side of this plane. In the β structure, β(2) lies on a true mirror.

Zachariasen (1973) has discussed the radii of Pu in its various phases and deduced the number of valence electrons. He defines the mean radius as $r = V_a^{1/3}/2^{5/6}$ where V_a is the mean atomic volume. For the present ζ structure $V_a = 21{\cdot}8$ Å^3 and $r = 1{\cdot}568$ Å. The mean valence, using Zachariasen's relation, is therefore 5·4 electrons, the same value as for β-Pu. The mean valence for η-$Pu_{19}Os$ is also 5·4 and that of ζ-$Pu_{28}Zr$ is 5·2, the same as for γ-Pu.

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