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Plutonium–Osmium η-$Pu_{19}Os$*

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Abstract. $Pu_{19}Os$, orthorhombic, *Cmca*, $Z = 2$, $a = 5{\cdot}345$ (5), $b = 14{\cdot}884$ (14), $c = 10{\cdot}898$ (15) Å, $Z = 2$, $\rho_c = 18{\cdot}12$ g cm^{-3}, $\mu = 954$ cm^{-1}. Data were collected on an automatic diffractometer. The structure was solved by direct methods and refined by full-matrix least squares. $R_w = 0{\cdot}0559$ for 361 observed reflections. The structure is disordered. Pu–Pu distances range from 2·55 to 3·64 Å.

Introduction. The Pu–Os phase diagram was first published 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 discovered that the ζ phase ($Pu_{19}Os$) is a high-temperature phase, stable between 195 and 434°C, which under most conditions would cool to room temperature without transforming. However, cold working the ζ phase at room temperature induced a change to a new, η phase.

In the present study a 5 at.% Os alloy was arc melted. This as-cast alloy was crushed and from among the fragments a single-crystal fragment was soon found. After the structure had been determined, comparison of a calculated powder pattern with the observed powder patterns of the ζ and η phases (Ellinger & Land, 1970) showed that it was the low-temperature η phase whose structure had been determined. Because of the relatively rapid cooling, we had expected to observe the quenched, ζ phase. Perhaps crushing the ingot induced the transformation. A side point of interest is that this is the first time that we have been able to find a usable single crystal of a very high-Pu-content alloy, as these alloys are usually soft and fine grained.

Preliminary precession photographs showed the crystal to be orthorhombic with space group *Cmca*, if centrosymmetric. Reflections *hkl* were present only if $h + k = 2n$, *h*0*l* were present only if $l = 2n$ and *hk*0 were present only if $h = 2n$. The structure determination subsequently confirmed *Cmca*.

Lattice constants were obtained from a least-squares refinement of 12 high-angle reflections measured on an automated Picker diffractometer. Intensity data were collected and processed in the manner described by Cromer & Larson (1977). A complete sphere of reflections was measured. Details of data collection are given in Table 1. Empirical absorption corrections were applied with the *CAMEL JOCKEY* program of Flack (1974, 1975) as well as a spherical absorption correction based on the mean radius of the crystal. This method, although much more rational in theory, in practice yielded results only a little better than the method of Furnas (1957) which has been used in this laboratory for many years.

Space groups *Cmca* and *C*2*ca* were both possible but statistical tests indicated the former. With a composition of about $Pu_{19}Os$ and 40 atoms per cell the structure has to be disordered in either of the above space groups. Application of direct methods easily found the structure which had four atoms in set 8(*f*) and 1 atom in set 8(*e*) of *Cmca*. A full-matrix least-squares refinement which minimized $\Sigma\, w(\Delta F)^2$ was made with anisotropic thermal parameters. All atoms

Table 1. *Data collection and reduction* (*Cromer & Larson*, 1977)

Radiation	Mo *Kα* (graphite monochromated)
$2\theta_{\max}$	50°
Take-off angle	3°
Step size	0·05°
Step time	2 s
Scan range	2°
$T_{\min}$ (threshold parameter)	2·0
Number of reflections	2906
Unique reflections	430
Unique reflections observed	361
Reflections measured twice	16
Reflections measured four times	107
Reflections measured seven times	3
Reflections measured eight times	303
Mean radius of crystal	0·002 cm
R_F (no corrections)	0·0588
R_F (corrected by *CAMEL JOCKEY*)	0·0460
Range of corrective factors from *CAMEL JOCKEY*	0·588–1·660
Range of corrective factors for spherical absorption	10·0–12·5

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Table 2. *Final least-squares parameters for* η-Pu$_{19}$Os

$R = 0\cdot0548$, $R_w = 0\cdot0559$, goodness of fit $= 2\cdot19$.

	x	y	z	Equivalent isotropic B
Pu(1)	0	0·1983 (1)	−0·0241 (2)	0·75 Å^2
Pu(2)	0	0·5043 (2)	0·3553 (2)	0·94
Pu(3)	0	0·3629 (2)	0·1810 (2)	1·06
Pu(4)	0	0·4234 (1)	−0·0526 (2)	1·35
Pu(5)	$\frac{1}{4}$	0·1848 (2)	$\frac{1}{4}$	1·45

were considered to be Pu and scattering factors f, $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography* (1974). Positional parameters are given in Table 2 along with the equivalent isotropic thermal parameters.* None of the thermal parameters was unusually large or very anisotropic.

Discussion. This is the first reported crystal structure determination of a very high-Pu-content intermediate phase. Ellinger & Land (1970) state that Pu$_{19}$Ru is isostructural with η-Pu$_{19}$Os. Interatomic distances are given in Table 3 and a drawing of the structure in projection along **x** is shown in Fig. 1.

Table 3. *Interatomic distances* (Å) *in* η-Pu$_{19}$Os

Pu(1)–2Pu(1)	3·129 (3)	Pu(3)—Pu(1)	3·341 (5)
–Pu(2)	3·289 (4)	–Pu(2)	2·835 (4)
–Pu(2)	3·423 (4)	–2Pu(2)	3·425 (3)
–2Pu(3)	3·301 (3)	–2Pu(3)	3·067 (3)
–Pu(3)	3·317 (4)	–Pu(4)	2·700 (5)
–Pu(3)	3·341 (5)	–Pu(4)	3·474 (4)
–2Pu(4)	3·335 (3)	–2Pu(5)	3·063 (4)
–Pu(4)	3·365 (4)	Pu(4)–2Pu(1)	3·335 (3)
–2Pu(5)	3·279 (4)	–Pu(1)	3·365 (4)
–2Pu(5)	3·298 (4)	–2Pu(2)	3·051 (3)
Pu(2)—Pu(1)	3·289 (4)	–Pu(2)	3·469 (6)
–Pu(1)	3·423 (4)	–2Pu(2)	3·636 (3)
–Pu(2)	3·156 (6)	–Pu(3)	2·700 (5)
–2Pu(2)	3·523 (4)	–Pu(3)	3·474 (4)
–Pu(3)	2·835 (4)	–Pu(4)	2·552 (5)
–2Pu(3)	3·425 (3)	–2Pu(5)	3·001 (3)
–2Pu(4)	3·051 (3)	Pu(5)–2Pu(1)	3·279 (4)
–Pu(4)	3·469 (6)	–2Pu(1)	3·298 (4)
–2Pu(4)	3·636 (3)	–2Pu(2)	3·212 (4)
–2Pu(5)	3·212 (4)	–2Pu(3)	3·063 (4)
Pu(3)–2Pu(1)	3·301 (3)	–2Pu(4)	3·001 (3)
–Pu(1)	3·317 (4)	–2Pu(5)	2·673 (3)

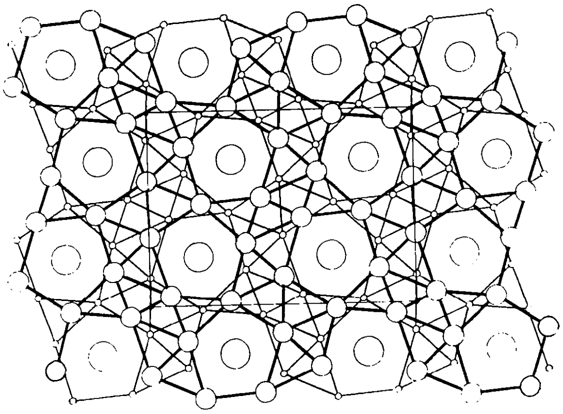

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the η-Pu$_{19}$Os structure projected along **x**. The origin is at the lower left; **y** is horizontal and **z** is vertical. The large circles are Pu(5) at $x = \frac{1}{4}$. The medium circles are at $x = \frac{1}{2}$ and the small circles at $x = 0$.

With such a small amount of Os it seems reasonable that the Os atoms would order or the phase would not form at all. The average interatomic distance found for Pu(5) is smaller than for the other atoms, so the Os atoms, being considerably smaller than Pu, would most likely be in this site. The scattering factor of Os is only about 10% smaller than that of Pu after correction for $\Delta f'$. If only about two out of the eight atoms in the Pu(5) site are Os, the effect on the thermal parameter would not be large. Nevertheless, the thermal parameter of Pu(5) is largest in spite of its being closer to its neighbors than the other atoms. It is thus probable that the Os atoms are in the Pu(5) site.

Atoms Pu(1) through Pu(4) lie on the mirror at $x = 0, \frac{1}{2}$ (see Fig. 1) and form nets with the Schläfli symbol $3^45 + 3^2535$ (3:2). Pu(5) lies in between pentagonal holes in these nets. The polyhedron surrounding Pu(5) is a distorted icosahedron with distances ranging from 2·673 to 3·298 Å. Pu(1) and Pu(2) have 15 neighbors while Pu(3) and Pu(4) have 13 neighbors. Each of these four atoms lies on a mirror and has five neighbors in the mirror. Pu(1) and Pu(2) have five additional neighbors on each side of the mirror while Pu(3) and Pu(4) have four other neighbors on each side of the mirror.

Pu(4) has a short distance of 2·55 Å to itself through a center of symmetry. In β-Pu (Zachariasen & Ellinger, 1963) Pu(7) has a similar short distance of 2·59 Å through a center of symmetry. These two polyhedra are identical in shape in both substances. There is a ring of five atoms on either side of the central atom and each ring is capped by a single atom. The 13th, very close atom is at the edge, in the plane between the two rings.

Thanks are due to R. E. Tate for preparation of the alloy. All calculations were done on a CDC-7600 with

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* 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 33175 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the *LASL* system of crystallographic programs developed primarily by A. C. Larson.

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Hexaamminecobalt(III) Chloride

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Abstract. $Co(NH_3)_6Cl_3$, M_r = 267·5, monoclinic, $C2/m$, a = 12·46 (1), b = 21·30 (2), c = 12·74 (1) Å, β = 112·96 (8)°, Z = 12, D_m = 1·74 (flotation), D_c = 1·75 g cm^{-3}, 20°C. The four independent and very regular $Co(NH_3)_6^{3+}$ octahedra are each surrounded by 14 nearest-neighbour Cl atoms. Only one of the Cl polyhedra is severely distorted.

Introduction. Gimènez-Huguet (1961) reported the cell dimensions of $Co(NH_3)_6Cl_3$ as a = 12·50, b = 12·29, c = 21·68 Å, γ = 113·63°, and the space group as $P2_1/m$. The twelve Co atoms were distributed at two 4(f) and two 2(e) sites and six N atoms surrounding each Co atom occupied four positions in a plane parallel to (001) and two other positions above and below this plane such that the remaining two Co–N bonds were perpendicular to (001).

A great deal of interest in hexaamminecobalt(III) complexes was initiated amongst workers in NMR (Reynhardt, 1974*a*,*b*; Kim, 1960; Ito & Chiba, 1969) by the reportedly unusual broad linewidth transitions (Murray & Waugh, 1958) and the phase transitions observed in specific-heat experiments (Ziegler, 1941; Matsuo, Tatsumi, Suga & Seki, 1973). A recent NMR investigation of the ^{59}Co quadrupole parameters (Reynhardt, 1974*a*) revealed a marked difference between the quadrupole coupling constant at one Co site and those at the other three sites. The quadrupole coupling constant, which is expected to be mainly of intramolecular origin, is 17 MHz at one Co site while the corresponding values at the other sites vary from 1 to 3 MHz.

Although the ratio of the number of Co atoms occupying twofold and fourfold positions is in agreement with the results of an NMR study of $Co(ND_3)Cl_3$ by Ito & Chiba (1969), the Co–N bond directions obtained from the experimental deuteron electric field gradient tensors do not agree with those reported by Gimènez-Huguet (1961).

Crystals were obtained by slow evaporation of a saturated aqueous solution. Rotation, Weissenberg and precession photographs showed that the crystals belong to the monoclinic system and systematic absences were observed for general reflections hkl: $h + k = 2n + 1$, allowing three possible space groups, *viz* $C2$, Cm or $C2/m$. No trace could be found of the 13 weak reflections among $0kl$, $hk0$ and $h0l$ which, according to Gimènez-Huguet (1961), indicated a primitive lattice.