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Preparation and crystal structure of the actinoid ruthenium phosphides $ThRu_2P_2$ and URu_2P_2

R. Glaum*, J. H. Albering, W. Jeitschko and L. Boonk
Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-Klemm-Strasse 8, D-4400 Münster (Germany)

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Abstract

The new compounds $ThRu_2P_2$ and URu_2P_2 were prepared by the reaction between the powders of elemental thorium with RuP and a uranium–ruthenium alloy with elemental phosphorus, respectively, in a tin flux. The compounds crystallize in the orthorhombic space group *Pnma* with the lattice constants $a=753.15(5)$ pm [737.9(2) pm], $b=413.95(4)$ pm [406.7(1) pm], $c=1047.8(1)$ pm [1029.4(4) pm] for $ThRu_2P_2$ [URu_2P_2] and $Z=4$. The crystal structure was determined from single-crystal X-ray data; $R=0.049$ (352 structure factors, 26 variable parameters), $R=0.016$ (1109 F values, 27 variables) for the thorium and uranium compound respectively. One phosphorus position of URu_2P_{2-x} was found not to be fully occupied: $x=0.106(5)$. The structures of $ThRu_2P_2$ and URu_2P_2 are discussed together with several others of related compositions, for example, $BaZn_2As_2$ and $BaCu_2S_2$. While the bonding within the polyanions $[Zn_2As_2]^{2-}$ and $[Cu_2S_2]^{2-}$ may be rationalized on the basis of classical two-electron bonds, the structures of $ThRu_2P_2$ and URu_2P_2 show a tendency for higher coordination as it is typical for intermetallic phases.

1. Introduction

Of the almost 3000 structure types listed in *Pearson's Handbook* [1], the $ThCr_2Si_2$-type structure with more than 700 representatives occurs most frequently. Some 50 lanthanoid transition metal (T) phosphides with this structure are reported [2–5], including the series $LnRu_2P_2$ [6]. Of the corresponding actinoid transition metal phosphides, UFe_2P_2 [4, 7] and UNi_2P_2 [8, 9] have this body-centred tetragonal structure. $ThCo_2P_2$ and UCo_2P_2 [4] crystallize with the closely related primitive tetragonal $CaBe_2Ge_2$-type structure, and UCu_2P_2 [10] has the hexagonal Ce_2SO_2 ($CaAl_2Si_2$)-type structure. The structure reported here for $ThRu_2P_2$ and URu_2P_2 might be considered to be of a new type, although it is closely related to those of $BaZn_2As_2$ [11] and $BaCu_2S_2$ [12]. Preliminary accounts of this work have been reported previously [13, 14].

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*Present address: Institut für Anorganische und Analytische Chemie, Universität Giessen, Heinrich-Buff-Ring 58, D-6300 Giessen, Germany.

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2. Sample preparation

The starting materials were thorium ingots (nominal purity, 99.9%), small uranium platelets (Merck, 'nuklearrein'), ruthenium powder (Degussa, >99.9%), small pieces of red phosphorus (Hoechst-Knapsack, 'ultrapure') and tin (Merck, 99.9%). Thorium filings were prepared under dried paraffin oil. The uranium platelets were cleaned in diluted nitric acid prior to the reactions. The compound $ThRu_2P_2$ was synthesized by the reaction between elemental thorium and ruthenium–monophosphide RuP (prepared from the powders by annealing at 700 °C for 5 days) with a tin flux in evacuated silica tubes. The starting composition was Th:RuP:Sn = 1:2:10. After annealing for 8 days at 880 °C and slow cooling to 600 °C at a rate of 5 °C h^{-1}, the sample was quenched in air. The tin-rich matrix was dissolved in cold, slightly diluted (1:1) hydrochloric acid. $ThRu_2P_2$ was obtained in the form of small, needle-shaped crystals.

URu_2P_{2-x} could be synthesized by the reaction of a heterogeneous uranium–ruthenium alloy $U_{1.3}Ru_2$ (prepared by the arc-melting of a cylindrical pellet of the elemental components under an argon atmosphere) with phosphorus in a tin flux (starting composition: $U_{1.3}Ru_2$:P:Sn = 1:2:10). After annealing at 900 °C for 10 days and cooling to 300 °C at a rate of 10 °C h^{-1}, the tin-rich matrix was removed with hot concentrated hydrochloric acid. The compound URu_2P_{2-x} crystallizes in the form of short, shiny black needles. With the starting composition given above, the ruthenium-stannide Ru_3Sn_7 [15] was obtained as a by-product.

Energy dispersive analyses in a scanning electron microscope showed no impurities such as silicon or tin in the crystals of the new compounds (detectability limits 1%). The samples were characterized by Guinier powder patterns using Cu $K\alpha_1$ radiation with α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. The lattice constants were obtained by least-squares fits.

3. Structure determination

The crystals of $ThRu_2P_2$ and URu_2P_2 were investigated using Laue and Buerger precession methods. The intensity data were recorded on a four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, a scintillation counter and a pulse-height discriminator. The background was determined at both ends of each $\theta/2\theta$ scan. Absorption corrections were made on the basis of psi scan data. The ratios of the highest to the lowest transmission were 1.63 and 1.31 for the thorium and the uranium compound respectively. In addition, a DIFABS correction [16] was made for the thorium compound. The crystallographic data are summarized in Table 1. The structure of $ThRu_2P_2$ was determined by direct methods [17] which resulted in the position of the thorium atom. The other atoms were located in difference Fourier syntheses. The uranium compound was found to be isotypic with

TABLE 1

Crystal data for $ThRu_2P_2$ and URu_2P_2

	$ThRu_2P_2$		$URu_2P_{1.894(5)}$	
Space group	*Pnma* (No. 62)		*Pnma* (No. 62)	
Lattice constants from Guinier powder [and single crystal] data[a]				
a (pm)	753.15(5)	[752.4(3)]	737.9(2)	[737.5(1)]
b (pm)	413.95(4)	[413.2(1)]	406.7(1)	[406.20(4)]
c (pm)	1047.8(1)	[1046.3(2)]	1029.4(4)	[1028.9(1)]
V (nm^3)	0.3267(1)	[0.3253(3)]	0.3089(3)	[0.3082(1)]
Formula units/cell, Z	4		4	
Formula weight	496.1		498.8	
Calculated density (g cm^{-3})	10.09		10.72	
Crystal dimensions (μm^3)	$2\times2\times45$		$30\times30\times70$	
$\theta/2\theta$ scans up to	$2\theta=80°$		$2\theta=90°$	
Range in *hkl*	±13 +7 +18		±14 +8 ±20	
Total number of reflections	4188		5517	
Absorption correction	From psi scans and DIFABS [16]		From psi scans	
Unique reflections	1213		1501	
R_i	0.074		0.021	
Reflections with $I>3\sigma(I)$	352		1109	
Number of variables	26		27	
R	0.049		0.016	
R_w	0.050		0.023	

[a] Lattice constants from single crystal data have systematic errors, especially for highly absorbing crystals, and therefore those from the powder data are considered more reliable. Standard deviations in the position of the last significant digit are listed in parentheses throughout the paper.

$ThRu_2P_2$. The structures were refined by full-matrix least-squares cycles with atomic scattering factors [18] corrected for anomalous dispersion [19]. A parameter accounting for secondary isotropic extinction was refined and applied to the calculated structure factors. Weights were assigned according to the counting statistics. In the final least-squares cycles the ideal occupancies were assumed, except for the significantly not fully occupied P2 position of the uranium compound. The metal atoms were refined with anisotropic thermal parameters. The atomic parameters and interatomic distances are given in Tables 2 and 3. Listings of the anisotropic thermal parameters and the structure factors are available from the authors.

4. Discussion

The crystal structures of $ThRu_2P_2$ and URu_2P_2 (Fig. 1) are similar to the structures of $BaZn_2As_2$ [11] and $BaCu_2S_2$ [12]. They have the same space group and similar atomic positions. However, the coordination polyhedra are

TABLE 2

Atom parameters of $ThRu_2P_2$ and $URu_2P_{1.894(5)}$[a]

Atom	Occupancy	x	y	z	B
$ThRu_2P_2$					
Th	0.996(4)	0.2666(2)	1/4	0.3308(1)	0.53(1)
Ru1	1.01(1)	0.3680(4)	1/4	0.6323(3)	0.57(4)
Ru2	0.99(1)	0.3895(4)	1/4	0.0485(3)	0.61(4)
P1	1.14(2)	0.030(1)	1/4	0.659(1)	0.8(1)
P2	1.06(4)	0.096(1)	1/4	0.027(1)	1.0(1)
URu_2P_2					
U	1.002(1)	0.27132(3)	1/4	0.33190(2)	0.296(2)
Ru1	0.993(2)	0.36394(5)	1/4	0.63626(4)	0.287(4)
Ru2	0.995(1)	0.38978(5)	1/4	0.04955(4)	0.316(4)
P1	0.972(5)	0.0279(2)	1/4	0.6629(1)	0.36(1)
P2	0.894(5)	0.0911(2)	1/4	0.0287(1)	0.42(2)

[a] All atoms are in position 4c of the *Pnma* space group. The positional parameters are given in the standardized form proposed by Gelato and Parthé [20]. The occupancy parameters (second column) were assumed to be ideal in the final least-square cycles, except for the significantly different occupancy parameter of the P2 atom in the uranium compound. The presently reported value of 0.894(5) was obtained in a refinement, where the thermal parameter of the P2 position was also refined and the occupancy parameters of the other atoms were assumed to be 100%. The last column contains the isotropic thermal parameters of the phosphorus atoms and the equivalent isotropic thermal parameters of the metal atoms (× 100, in units of nm^2).

different. Gelato and Parthé [20, 21] have proposed to call such a relationship 'isopointal', while the term 'isotypic' should be reserved for structures which have similar atomic environments, in addition to the requirements for 'isopointal' structures. Figure 2 shows a comparison of the $ThRu_2P_2$ and $BaZn_2As_2$-type structures. These structures are discussed in more detail below.

The thorium atoms (the corresponding values for the uranium atoms are given in parentheses) are surrounded by eight phosphorus atoms forming a bicapped trigonal prism at distances ranging from 289.0 to 343.0 pm (276.2 to 339.3 pm). This coordination is augmented by nine ruthenium neighbours at distances between 309.9 and 346.5 pm (303.6 and 338.9 pm) which might still be considered as weakly bonding. There are no bonding Th–Th (U–U) interactions. The ruthenium atoms occupy two different sites. The Ru1 atoms have five phosphorus neighbours at an average distance of 243.5 pm (239.1 pm) forming a distorted square pyramid, while the Ru2 atoms have four phosphorus neighbours in tetrahedral coordination with the (expected) shorter average distance of 238.7 pm (236.8 pm). At first sight, it is surprising that the Ru–P distances in the uranium compound are shorter than in the thorium compound. However, this is readily rationalized by considering that the P2 site in the uranium compound is occupied to only 89.4%. The P1 atoms have five ruthenium neighbours at an average distance of 247.7 pm (243.0 pm) forming a square pyramid with four Th (U) atoms

TABLE 3

Interatomic distances (pm) in the structures of $AnRu_2P_2$ (An≡Th, U)[a]

	$ThRu_2P_2$	URu_2P_2		$ThRu_2P_2$	URu_2P_2
An: 1P2	289.0(10)	276.2(3)	Ru2: 1P2	222.4(11)	221.5(3)
2P1	304.9(7)	300.2(2)	1P1	242.4(11)	241.3(2)
2P2	309.9(7)	304.5(2)	2P1	245.0(6)	242.2(2)
2P1	313.8(8)	305.9(2)	2Ru2	284.4(3)	279.7(1)
1P2	343.0(10)	339.3(3)	2Ru1	296.9(3)	290.5(1)
1Ru2	309.9(3)	303.6(1)	1An	309.9(3)	303.6(1)
2Ru1	310.4(2)	303.1(1)	1An	310.9(3)	306.9(1)
1Ru2	310.9(3)	306.9(1)	2An	329.7(3)	325.1(1)
1Ru1	325.0(3)	320.7(1)			
2Ru2	329.7(2)	325.1(1)	P1: 2An	304.9(7)	300.2(2)
2Ru1	346.5(3)	338.9(1)	2An	313.8(8)	305.9(2)
2An	412.9(2)	405.7(1)	1Ru2	242.4(11)	241.3(2)
2An	414.0(1)	406.7(1)	2Ru2	245.0(6)	242.2(2)
			1Ru1	250.1(11)	239.6(2)
Ru1: 2P2	236.0(5)	233.9(2)	1Ru1	256.0(10)	249.5(2)
1P2	239.6(10)	238.6(3)			
1P1	250.1(11)	239.6(2)	P2: 1An	289.0(10)	276.2(3)
1P1	256.0(10)	249.5(2)	2An	309.9(7)	304.5(2)
2Ru2	296.9(3)	290.5(1)	1An	343.0(10)	339.3(3)
2An	310.4(2)	303.1(1)	1Ru2	222.4(11)	221.5(3)
1An	325.0(3)	320.7(1)	2Ru1	236.0(5)	233.9(2)
2An	346.5(3)	338.9(1)	1Ru1	239.6(10)	238.6(3)
			2P2	258.7(9)	250.8(2)

[a] All distances shorter than 520 pm (An–An), 390 pm (An–Ru, Ru–Ru, Ru–P), 385 pm (An–P) and 370 pm (P–P) are listed. Thus, all distances shown in the coordination polyhedra of Fig. 1 can be found in this table.

outside the triangular faces of the pyramid. The P2 atoms have four ruthenium neighbours at the much shorter average distance of 233.5 pm (232.0 pm). In addition they have three Th (U) neighbours and they form two weak bonds to two other P2 atoms at 258.7 pm (250.8 pm).

Both phosphorus atoms might also be described as nine coordinated with six neighbours forming a trigonal prism, which is augmented by three neighbours outside the rectangular faces of the prism. Such phosphorus environments are frequently encountered in phosphides with a metal:phosphorus ratio of 2:1 [22–24]. In these phosphides the nine neighbours of each phosphorus atom are solely metal atoms, while here two metal neighbours of the P2 atoms are replaced by phosphorus atoms. This is a consequence of the higher phosphorus content of the $ThRu_2P_2$-type compounds. Since the arrangement of the trigonal prisms around the phosphorus atoms is frequently outlined to visualize such structures, we show this arrangement in Fig. 3. In contrast to the phosphides with a metal:phosphorus ratio of 2:1, where the trigonal prisms share edges, the trigonal prisms in the $ThRu_2P_2$-type compounds interpenetrate each other.

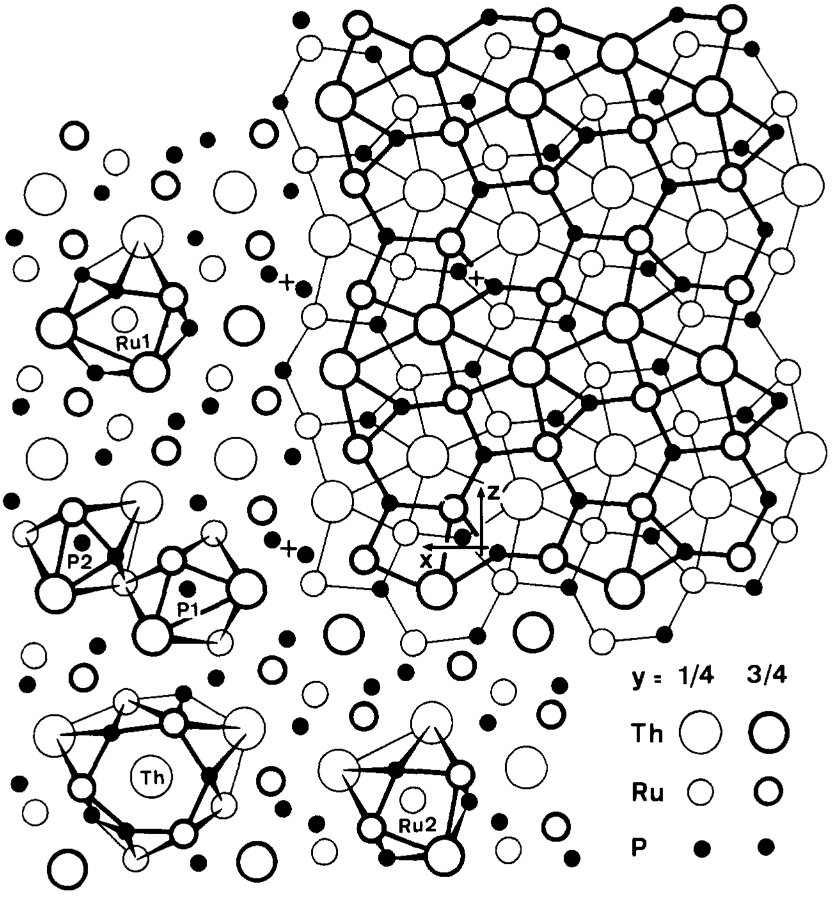
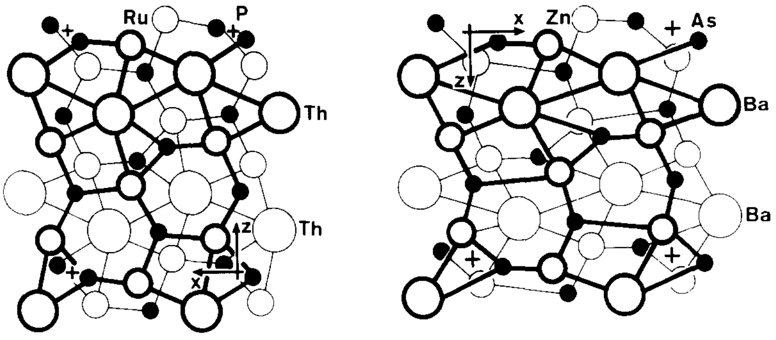


Fig. 1. Crystal structure and coordination polyhedra of $ThRu_2P_2$. The atoms connected by the thick and thin lines are at $y=\frac{3}{4}$ and $\frac{1}{4}$ respectively.

Several structure types exist for compounds of similar composition with an atomic ratio of A:T:X = 1:2:2. The $ThCr_2Si_2$-type structure is the most common [1], even though one might distinguish between the two branches with and without X–X bonds. This structure occurs with all transition and post-transition elements from chromium to zinc. The $CaBe_2Ge_2$-type structure (*e.g.* the series $LnRh_2P_2$ [25]) and the Ce_2SO_2-type structure (*e.g.* $EuMn_2P_2$ [26]) also have several representatives, while only one or two compounds are known with each of the following structure types: $LaRe_2Si_2$ [27], $HfFe_2Si_2$ [28], $BaCu_2S_2$ [12] and the currently reported $ThRu_2P_2$.

It is instructive to compare the isopointal structures of $ThRu_2P_2$, $BaZn_2As_2$ [11] and $BaCu_2S_2$ [12] with some of the structures of related compositions. In $BaCu_2S_2$ and $BaZn_2As_2$ the copper and the zinc as well as the sulphur and arsenic atoms have four nearest neighbours in (distorted) tetrahedral arrangement. The chemical bonding within the $[Cu_2S_2]^{2-}$ and $[Zn_2As_2]^{2-}$



$ThRu_2P_2$
(a)

$BaZn_2As_2$
(b)

Fig. 2. Comparison of the structures of (a) $ThRu_2P_2$ and (b) $BaZn_2As_2$. The structures are closely related although the atomic coordinations are different. The atoms connected by thick and thin lines are at $y=\frac{3}{4}$ and $\frac{1}{4}$ respectively. These lines also emphasize the similarity of the two structures and do not necessarily represent bonding interactions; this is especially true for the $BaZn_2As_2$ structure.

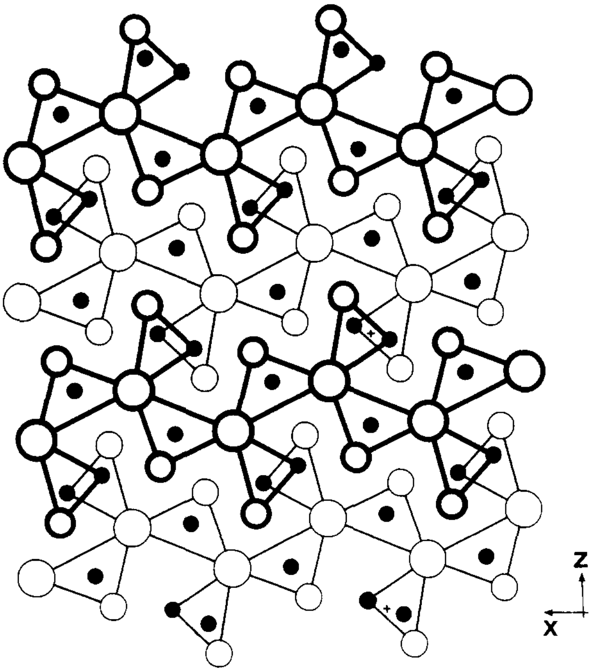


Fig. 3. Trigonal prismatic environments of the phosphorus atoms in $ThRu_2P_2$.

polyanions can be readily rationalized (at least roughly) on the basis of classical two-electron bonds by counting two electrons for each of the short distances within the polyanions. In this way all atoms within the polyanions obtain eight (or eighteen, depending on how one counts) electrons. Assigning oxidation numbers (where the bonding electrons are counted at the more electronegative partner) the formulas $Ba^{2+}[Cu^{1+}Cu^{1+}S^{2-}S^{2-}]^{2-}$ and $Ba^{2+}[Zn^{2+}Zn^{2+}As^{3-}As^{3-}]^{2-}$ are obtained. The near-neighbour environments in the Ce_2SO_2-type compounds $ZrCu_2P_2$ [29], $HfCu_2P_2$ [30], $ThCu_2P_2$ [31] and UCu_2P_2 [10], where the copper atoms have four phosphorus neighbours and the phosphorus atoms have four copper neighbours, can be rationalized in the same manner. Accordingly the zirconium, hafnium, thorium and uranium atoms obtain the reasonable oxidation number +4, for example, $U^{4+}[Cu^{1+}Cu^{1+}P^{3-}P^{3-}]^{4-}$.

However, this simple rationalization on the basis of two-electron bonds breaks down in $ThRu_2P_2$ as well as in $LaRe_2Si_2$ [27], $HfFe_2Si_2$ [28] and UFe_2P_2 [4, 7]. In these structures the late transition metal and the metalloid atoms all have higher coordination numbers. All of these structures contain some metalloid–metalloid bonds and in addition, in most of them there are indications for bonding between the late transition metal atoms, for example, in $LaRe_2Si_2$ the shortest Re–Re distance is 259 pm and in $HfFe_2Si_2$ and UFe_2P_2 the shortest Fe–Fe distances are 252.9 pm and 271.9 pm respectively. Similarily, the shortest Ru–Ru interactions of 284.4 pm and 279.9 pm in $ThRu_2P_2$ and URu_2P_2 respectively might still be considered as weakly bonding. This tendency for high coordination numbers is indicative for the bonding in intermetallic compounds with broad bands.

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