

R_5Pt_4 Compounds ($R = Tb, Dy, Ho, Er, Tm, Lu$ and Y) Isotypic with Pu_5Rh_4

BY J. LE ROY, J.-M. MOREAU, D. PACCARD AND E. PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland and Centre Universitaire de Savoie, IUT Annecy and Laboratoire de Magnétisme, CNRS, Grenoble, France

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Abstract. Y_5Pt_4 , $Pnma$, $Z = 4$, $a = 7.458$ (5), $b = 14.546$ (7), $c = 7.519$ (4) Å, $D_x = 9.97$ g cm $^{-3}$, $\mu(\text{Ag } K_{\alpha}) = 593$ cm $^{-1}$. Data were collected on an automatic diffractometer and an empirical absorption correction was used. Starting positions for least-squares refinement were obtained from the Sm_5Ge_4 structure with which isotypism was suspected. $R = 0.069$ for 738 independent reflections. Tb_5Pt_4 , Dy_5Pt_4 , Ho_5Pt_4 , Er_5Pt_4 , Tm_5Pt_4 and Lu_5Pt_4 are isostructural with Y_5Pt_4 . Y_5Pt_4 is isotypic with Pu_5Rh_4 which itself is similar to Gd_5Si_4 and Sm_5Ge_4 . The structure can be described as a netting of Y_6Pt trigonal prisms and Y_8Y cubes. This construction principle is also found in the rhombohedral Er_3Ni_2 , the tetragonal U_3Si_2 and the tetragonal Zr_5Si_4 type where all atoms of the minority component are in the centres of the trigonal prisms. Y_5Pt_4 and Zr_5Si_4 can be built up of units similar to those found in FeB and U_3Si_2 .

Introduction. Structural data on R_7Pt_3 , R_2Pt , R_3Pt_3 and RPt compounds together with a compilation of earlier

work on R_xPt phases have recently been published in the course of experimental studies on the R_xPt ($x \geq 1$) intermetallic phases (Le Roy, Moreau, Paccard & Parthé, 1978). In the system $Yb-Pt$, Iandelli & Palenzona (1975) found a compound Yb_5Pt_4 with the Sm_5Ge_4 structure type. In this paper we report on the structure determination of other rare-earth-platinum compounds with the same stoichiometry.

Alloys of Y_5Pt_4 , Tb_5Pt_4 , Dy_5Pt_4 , Ho_5Pt_4 , Er_5Pt_4 , Tm_5Pt_4 and Lu_5Pt_4 were prepared from the elements by conventional arc melting techniques. The indentities of a single crystal of Y_5Pt_4 ($40 \times 35 \times 110$ μm) were collected with graphite-monochromated $\text{Ag } K_{\alpha}$ radiation on a computer-controlled four-circle Philips PW 1100 diffractometer. Data collection was carried out to a limit of 0.64 Å $^{-1}$ in $\sin \theta/\lambda$, yielding 1145 independent reflections, of which 578 with $I > 3\sigma(I)$ plus 160 with $I < 3\sigma(I)$ (but where $|F|_{\text{calc}} > |F|_{\text{obs}}$) were used in the structure refinement. The *CAMEL JOCKEY* experimental method for absorption correction (Flack, 1975, 1977) was used ($\mu R = 1.59$).

Table 1. Comparison of the parameters of slightly different M_5X_4 structures all having space group $Pnma$ and similar ratios of the cell parameters

The e.s.d.'s are given in parentheses. The Debye-Waller factor for Y_5Pt_4 is defined as $\exp[-2\pi^2 \times 10^{-2} U(2 \sin \theta/\lambda)^2]$. The numbering for Y_5Pt_4 is shown in brackets.

			Sm_5Ge_4 (a)	Gd_5Si_4 (b)	Pu_5Rh_4 (c)	Y_5Pt_4 (d)	U (Å 2)
4M	Y(1) in 4(c)	x	0.2880 (8)	0.3560 (1)	0.3225 (1)	0.3180 (8)	1.3 (1)
		y	0.9976 (8)	0.0113 (1)	0.01077 (9)	0.0110 (8)	
		z	0.3795 (5)	0.3164 (1)	0.3424 (1)	0.3428 (5)	
8M	Y(2) in 8(d)	x	0.6157 (3)	0.6223 (0)	0.62196 (4)	0.6228 (3)	1.2 (1)
		y	0.1612 (5)	0.1795 (1)	0.16361 (6)	0.1667 (6)	
		z	0.9747 (5)	0.0289 (1)	0.0015 (1)	0.0009 (6)	
8M	Y(3) in 8(d)	x	0.3996 (3)	0.4028 (0)	0.40796 (4)	0.4085 (3)	1.4 (1)
		y	0.1781 (5)	0.1827 (1)	0.17796 (6)	0.1803 (6)	
		z	0.176 (2)	0.241 (1)	0.1898 (3)	0.1869 (4)	
4X	Pt(1) in 4(c)	x	0.367 (2)	0.375 (1)	0.3529 (2)	0.3590 (4)	1.8 (1)
		y	0.413 (2)	0.479 (1)	0.4602 (3)	0.4529 (4)	
		z	0.612 (2)	0.599 (1)	0.6114 (2)	0.6108 (4)	
4X	Pt(2) in 4(c)	x	0.221 (1)	0.1435 (6)	0.1845 (2)	0.1818 (2)	1.6 (1)
		y	0.5449 (6)	0.5395 (3)	0.5391 (1)	0.5411 (1)	
		z	0.469 (1)	0.4716 (7)	0.4609 (1)	0.4673 (2)	

References: (a) Smith, Johnson & Tharp (1967). (b) Iglesias & Steinfink (1972). (c) Cromer (1977). (d) This work.

Assuming isotypism with Sm_5Ge_4 (Smith, Johnson & Tharp, 1967) or Gd_5Si_4 (Iglesias & Steinfink, 1972) the parameters of both structures were used as starting points for the least-squares refinement by *CRYLSQ* (XRAY system, 1976). In both cases, the atomic parameters converged to the same values. The results are given in Table 1. The final R ($= \sum | \Delta F | / \sum | F_o |$) using isotropic thermal parameters and relativistic Hartree-Fock scattering factors (Cromer & Mann, 1968) and anomalous dispersion corrections from *International Tables for X-ray Crystallography* (1974) was 0.069.*

The isotypism of Tb_5Pt_4 , Dy_5Pt_4 , Ho_5Pt_4 , Er_5Pt_4 , Tm_5Pt_4 and Lu_5Pt_4 with Y_5Pt_4 was established by comparing observed and calculated powder diffraction intensities with the *LAZY PULVERIX* program (Yvon, Jeitschko & Parthé, 1977). The lattice parameters reported in Table 2 were obtained with *PARAM* (XRAY system, 1976). The reflexions were measured on films, calibrated with Si, taken with a Guinier-de Wolff camera and Cu $K\alpha$ radiation. The variation of the cell parameters is a consequence of the normal lanthanide contraction.

Discussion. A comparison of the point positions in Table 1 between Y_5Pt_4 , Sm_5Ge_4 , Gd_5Si_4 and Pu_5Rh_4 (Cromer, 1977) shows that Y_5Pt_4 is closer to Pu_5Rh_4 than the other two. As has already been noted by Cromer, the main differences are in the values of the x parameters, the extremes occurring for $M = Sm$ and Gd , with $M = Y$ or Pu being intermediate. The difference between the structure of the rare-earth silicide and germanide is unexpected and remains to be explained. We feel therefore that it is appropriate to state that Y_5Pt_4 is isotypic with Pu_5Rh_4 although the two other structures had been determined many years

* A list of structure factors has been deposited with the British Library Lending Division, as Supplementary Publication No. SUP 33695 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

before and normally the name of the type is taken from the compound whose structure is first determined.

The structure of Y_5Pt_4 can be described as a netting of Y_6Pt trigonal prisms and Y_8Y cubes as shown in Fig. 1. Actually in Y_5Pt_4 , the Pt-centred trigonal prisms and the Y-centred cubes are slightly deformed as can be seen from the list of interatomic distances given in Table 3. The six Y atoms surrounding a given Pt atom in the form of a trigonal prism have been marked by asterisks. Y(1) which is in the centre of the cube has, however, also short bonds to Pt atoms in neighbouring trigonal prisms. As shown in Fig. 1 the Y_5Pt_4 structure can also be described as a stacking of U_3Si_2 -like and FeB-like layers which was first noted by Kripyakevich & Jartiss (1975).

In the Sm_5Ge_4 and Gd_5Si_4 structures one finds the same type of coordination polyhedra. However, due to the different values of the atomic parameters, an atom in the centre of a trigonal prism in one compound has a different number of equidistant neighbours from the other. These are presented graphically in Fig. 2. Thus a Ge atom has about seven Sm neighbours, only five

Table 2. Lattice constants of R_5Pt_4 compounds with the Pu_5Rh_4 structure type (space group $Pnma$)

E.s.d.'s are in parentheses; V = volume of the unit cell; n = number of atoms in the unit cell.

	a (Å)	b (Å)	c (Å)	$(V/n)^{1/3}$	Reference
Tb_5Pt_4	7.495 (5)	14.602 (8)	7.565 (5)	2.84	(a)
Dy_5Pt_4	7.452 (5)	14.533 (8)	7.526 (5)	2.83	(a)
Ho_5Pt_4	7.435 (6)	14.490 (9)	7.512 (7)	2.82	(a)
Er_5Pt_4	7.417 (5)	14.456 (7)	7.486 (6)	2.81	(a)
Tm_5Pt_4	7.385 (3)	14.378 (8)	7.460 (5)	2.80	(a)
Yb_5Pt_4	7.390	14.319	7.506	2.80	(b)*
Lu_5Pt_4	7.323 (3)	14.261 (7)	7.388 (3)	2.78	(a)
Y_5Pt_4	7.458 (5)	14.546 (7)	7.519 (4)	2.83	(a)

References: (a) This work. (b) Iandelli & Palenzona (1975).

* The point positions have not been determined for Yb_5Pt_4 . The compound was listed as having the Sm_5Ge_4 structure type; however, the point positions are probably closer to those of Pu_5Rh_4 .

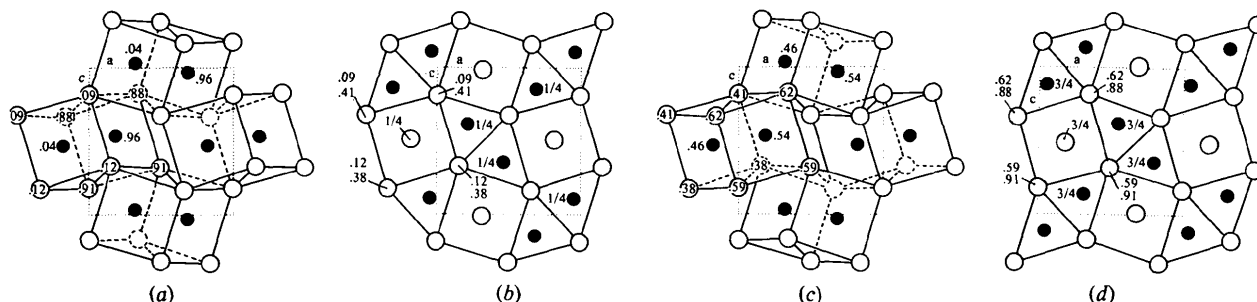


Fig. 1. Coordination polyhedra in Y_5Pt_4 which have their centres at (a) $y \approx 0$, (b) $y = \frac{1}{4}$, (c) $y \approx \frac{1}{2}$, (d) $y = \frac{3}{4}$. Open circles correspond to Y and filled circles to Pt atoms. At $y \approx 0$ and $y = \frac{1}{2}$ one finds a segment of the FeB type, while at $y = \frac{1}{4}$ and $\frac{3}{4}$ the arrangement is the same as in the U_3Si_2 type.

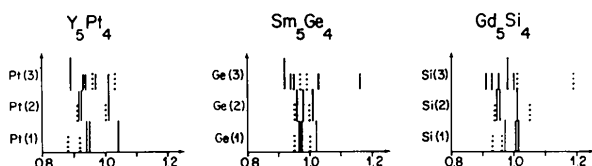


Fig. 2. Number of closest neighbours surrounding an atom in the trigonal prism centres *versus* normalized distances for the Y_5Pt_4 , Sm_5Ge_4 and Gd_5Si_4 structures. Atoms forming the surrounding trigonal prism are indicated with full lines, those which do not belong to that prism with broken lines. The height of the line indicates the number of neighbours at a given distance (either one or two). The distances are normalized to the sum of the atomic radii for coordination number 12 ($r_Y + r_{Pt} = 3.17$, $r_{Sm} + r_{Ge} = 3.18$, $r_{Gd} + r_{Si} = 3.11$ Å).

Table 3. Interatomic distances in Y_5Pt_4 up to 4.1 Å

The Y atoms forming the surrounding trigonal prism are marked with asterisks.

$Y(1)-Y(2^{xiv,xv})$	3.401 (7)	$Pt(1)-Y(1^i)$	2.793 (7)
$-2Y(2^{xvi,xvii})$	3.407 (7)	$-Y(1^{ii})$	2.920 (7)
$-2Y(3^{i,v})$	3.539 (7)	$-2Y(2^{iii,iv})^*$	2.970 (5)
$-2Y(3^{vi,vii})$	3.544 (7)	$-2Y(3^{i,v})^*$	3.007 (5)
$-Pt(1^i)$	2.793 (7)	$-2Y(3^{vi,vii})^*$	3.300 (5)
$-Pt(1^{vii})$	2.920 (7)	$-2Pt(1^{ii,vii})$	4.074 (5)
$-Pt(2^{ii})$	2.873 (7)	$-Pt(2^i)$	2.742 (4)
$-Pt(2^{xviii})$	3.173 (7)	$-Pt(2^{ii})$	3.940 (5)
$-2Pt(3^{xiv,xv})$	3.057 (2)	$Pt(2)-Y(1^{vii})$	2.873 (7)
$Y(2)-Y(1^{xi})$	3.401 (7)	$-Y(1^{viii})$	3.173 (7)
$-Y(1^{xviii})$	3.407 (7)	$-2Y(2^{iii,iv})^*$	2.909 (5)
$-Y(2^{xix})$	3.700 (6)	$-2Y(2^{ix,x})^*$	2.923 (5)
$-2Y(2^{vi,xii})$	3.934 (6)	$-2Y(3^{vi,vii})^*$	3.199 (5)
$-Y(3^{vi})$	3.526 (6)	$-Pt(1^i)$	2.742 (4)
$-Y(3^{xx})$	3.686 (6)	$-Pt(1^{vii})$	3.940 (5)
$-Y(3^{xxv})$	3.865 (6)	$Pt(3)-Y(1^{xi})$	3.057 (2)
$-Y(3^i)$	4.029 (6)	$-Y(2^i)^*$	2.822 (5)
$-Y(3^{iv})$	4.060 (6)	$-Y(2^{iv})^*$	2.822 (4)
$-Pt(1^{xxi})$	2.970 (5)	$-Y(2^{xii})^*$	2.970 (5)
$-Pt(2^{xxii})$	2.909 (5)	$-Y(3^{iv})^*$	2.951 (5)
$-Pt(2^{ix})$	2.923 (5)	$-Y(3^{xiii})^*$	3.069 (5)
$-Pt(3^i)$	2.822 (5)	$-Y(3^i)^*$	3.193 (5)
$-Pt(3^{xxv})$	2.822 (5)	$-Y(3^{vi})$	3.258 (5)
$-Pt(3^{xxii})$	2.970 (5)	$-Pt(3^{xiii})$	3.003 (3)
$Y(3)-Y(1^i)$	3.539 (7)		
$-Y(1^{ii})$	3.544 (7)	Symmetry code	
$-Y(2^{xii})$	3.526 (6)	(i) x, y, z	
$-Y(2^{xx})$	3.686 (6)	(ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$	
$-Y(2^{iv})$	3.865 (6)	(iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$	
$-Y(2^i)$	4.029 (6)	(iv) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$	
$-Y(2^{xxv})$	4.060 (6)	(v) $x, \frac{1}{2} - y, z$	
$-Y(3^{xx})$	3.800 (6)	(vi) $\frac{1}{2} + x, y, \frac{1}{2} - z$	
$-2Y(3^{vi,xii})$	3.873 (7)	(vii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$	
$-Pt(1^i)$	3.007 (5)	(viii) $x, y, 1 + z$	
$-Pt(1^{ii})$	3.300 (5)	(ix) $1 - x, 1 - y, 1 - z$	
$-Pt(2^{ii})$	3.199 (5)	(x) $1 - x, y - \frac{1}{2}, 1 - z$	
$-Pt(3^{xxv})$	2.951 (5)	(xi) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$	
$-Pt(3^{xiii})$	3.069 (5)	(xii) $x - \frac{1}{2}, y, \frac{1}{2} - z$	
$-Pt(3^i)$	3.193 (5)	(xiii) $x, 1 - y, 1 - z$	
$-Pt(3^{xii})$	3.258 (5)	(xiv) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$	
		(xv) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$	
		(xvi) $1 - x, y - \frac{1}{2}, z$	
		(xvii) $1 - x, 1 - y, z$	
		(xviii) $x, y, z - 1$	
		(xix) $x, \frac{3}{2} - y, z$	
		(xx) $\bar{x}, 1 - y, z$	
		(xxi) $\frac{1}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$	

Table 4. Tables for the calculation of the trigonal prism linkage coefficients for the Pu_5Rh_4 and Zr_5Si_4 structure types

For details see Parthé & Moreau (1977).

	Pu_5Rh_4		$Pnma$		Number
	Pu(1) in 4(c)	Pu(2) in 8(d)	Pu(3) in 8(d)		
Rh(1) in 4(c)	0	4	2		= 6
Rh(2) in 4(c)	0	2	4		= 6
Rh(3) in 8(d)	0	3	3		= 6
p	0	$\frac{4}{8}(4 + 2) + 3$ = 6	$\frac{4}{8}(2 + 4) + 3$ = 6		

$$LC = (8 \times 6 + 8 \times 6)/16 = 6$$

$$R_{6(1+E/P)} T_{LC} = R_{6(1+4/16)} T_6 = R_5 T_4$$

	Zr_5Si_4		$P4_12_2$		Number
	Zr(1) in 4(a)	Zr(2) in 8(b)	Zr(3) in 8(b)		
Si(1) in 8(b)	0	3	3		= 6
Si(2) in 8(b)	0	3	3		= 6
p	0	6	6		

$$LC = (8 \times 6 + 8 \times 6)/16 = 6$$

$$R_{6(1+E/P)} T_{LC} = R_{6(1+4/16)} T_6 = R_5 T_4$$

from the surrounding trigonal prism, the sixth being too far away, and two from outside the prism. A Si atom has seven nearly equidistant Gd neighbours, that is six from the trigonal prism and one from outside, while Pt has nearly eight neighbours, six from the prism and two from outside.

The structure of Y_5Pt_4 can be compared with the other structures which are built up of transition-metal-centred trigonal prisms of Y or rare-earth atoms (Parthé & Moreau, 1977). Y_5Pt_4 belongs to the special

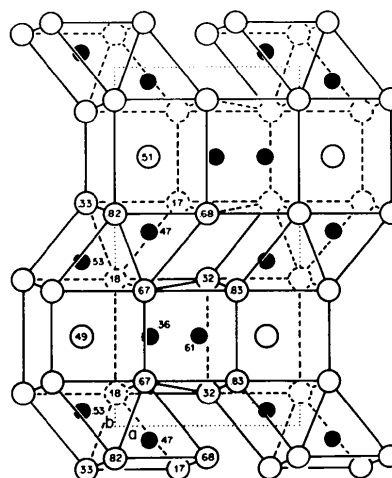


Fig. 3. Arrangement of polyhedra in Y_5Pt_4 with their centres at $z \approx \frac{1}{2}$.

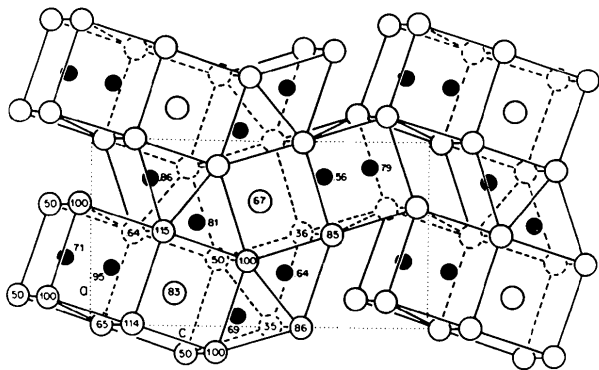


Fig. 4. Arrangement of polyhedra in Zr_5Si_4 with their centres at $y \approx \frac{3}{4}$.

group of structures where there are two construction elements: trigonal prisms and tungsten-like cubes of Y or rare-earth atoms. For composition R_3T_2 , two structure types of this special group are known: rhombohedral Er_3Ni_2 and tetragonal U_3Si_2 (Le Roy, Moreau, Paccard & Parthé, 1977). Y_5Pt_4 is an example of the composition R_5T_4 . Kripyakevich & Jartiss (1975) have shown that there also exists a second structure with the same composition and the same structural features, namely tetragonal Zr_5Si_4 (Pfeifer & Schubert, 1966). All these structures with centred trigonal prisms may be classified according to the value of the trigonal prism linkage coefficient (Parthé & Moreau, 1977). The trigonal prism linkage coefficient (LC) for the Pu_5Rh_4 and the Zr_5Si_4 structures can be obtained from Table 4.

The essential difference between the Y_5Pt_4 and the Zr_5Si_4 structure may be seen by comparing the (001) projection of Y_5Pt_4 (Fig. 3) with the (010) projection of Zr_5Si_4 (Fig. 4). In Y_5Pt_4 there are infinite slabs similar

to those found in FeB and U_3Si_2 stacked alternately, while in Zr_5Si_4 only fragments of these slabs are arranged alternately in herring-bone fashion.

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Structure du Chrome Pentacarbonyle Thiocarbonyle*

PAR J. Y. SAILLARD ET D. GRANDJEAN

Laboratoire de Cristallogénie, associé au CNRS n° 254, Université de Rennes, avenue du Maréchal Leclerc, 35042 Rennes CEDEX, France

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Abstract. $Cr(CO)_5(CS)$, orthorhombic, $Pnma$, $a = 12.374$ (3), $b = 11.528$ (2), $c = 6.629$ (1) Å, $Z = 4$. The structure was solved by both Fourier and direct methods. Full-matrix least-squares refinement con-

verged at $R = 0.054$ and $R'' = 0.054$ for 846 independent reflexions. Structural disorder between the CS and the five CO groups is observed.

Introduction. La résolution de la structure cristalline de $Cr(CO)_5(CS)$ a été entreprise dans le cadre de l'étude

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