The Metal-rich Phosphide Ce$_4$Ir$_{13.55}$P$_9$

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Needle-shaped crystals of the metal-rich phosphide Ce$_4$Ir$_{13.55}$P$_9$ were synthesized from the elements in a lead flux (starting composition 1:2:2:60) at 1370 K followed by slow cooling. Ce$_4$Ir$_{13.55}$P$_9$ crystallizes with a new orthorhombic structure type: $Pnma$, $a = 1269.1(2)$, $b = 399.1(1)$, $c = 3349.9(7)$ pm, $wR^2 = 0.0722$, 2025 $F^2$ values and 139 variables. Two of the 14 crystallographic iridium sites show small defects. All phosphorus atoms have slightly distorted trigonal prismatic metal coordination by cerium and iridium. The iridium and phosphorus atoms build up a three-dimensional [Ir$_{13.55}$P$_9$]$^{6-}$ polyanion in which the cerium atoms fill distorted hexagonal cavities. Within the polyanion the phosphide anions are isolated, and one additionally observes a broad range of Ir–Ir bonding (Ir–Ir distances 278–298 pm). From a geometrical point of view the Ce$_4$Ir$_{13.55}$P$_9$ structure can be considered as an intergrowth structure of distorted ThCr$_2$Si$_2$- and SrPtSb-related slabs.

Key words: Phosphide, Cerium, Crystal Chemistry