

Intermediate-valent $Ce_{23}Ru_7Mg_4$ and $RE_{23}Ru_7Mg_4$ ($RE = La, Pr, Nd$) with $Pr_{23}Ir_7Mg_4$ -type Structure

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The rare earth-rich magnesium compounds $RE_{23}Ru_7Mg_4$ ($RE = La, Ce, Pr, Nd$) were synthesized from the elements in sealed tantalum ampoules in an induction furnace. They crystallize with the hexagonal non-centrosymmetric $Pr_{23}Ir_7Mg_4$ -type structure, space group $P6_3mc$. The structures of $La_{23}Ru_{6.88(1)}Mg_4$ ($a = 1017.7(4)$, $c = 2286.5(5)$ pm, $wR2 = 0.0277$, $2708 F^2$, 71 variables), $Ce_{23}Ru_7Mg_4$ ($a = 993.5(3)$, $c = 2243.9(8)$ pm, $wR2 = 0.0573$, $2268 F^2$, 70 variables), and $Pr_{23}Ru_7Mg_4$ ($a = 996.8(3)$, $c = 2241.5(6)$ pm, $wR2 = 0.0492$, $2565 F^2$, 70 variables) have been refined from single-crystal diffractometer data. The structures are built up from complex three-dimensional networks of edge- and corner-sharing RE_6Ru trigonal prisms. Cavities within these networks are filled by slightly elongated Mg_4 tetrahedra (311 – 315 pm in $Pr_{23}Ru_7Mg_4$) and RE_6 octahedra. The cerium compound has an a parameter which is even smaller than that of $Nd_{23}Ru_7Mg_4$, indicating intermediate-valent cerium. This was confirmed by magnetic susceptibility measurements. $Ce_{23}Ru_7Mg_4$ shows an average, reduced magnetic moment of $2.01 \mu_B/Ce$ atom. $Pr_{23}Ru_7Mg_4$ contains stable trivalent praseodymium ($3.64 \mu_B/Pr$ atom).

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