The lithium rhodium stannide LiRh$_3$Sn$_5$ was synthesized from the elements in a sealed tantalum tube and investigated via X-ray powder and single crystal diffraction: $Pbcn$, $a = 538.9(1)$, $b = 976.6(3)$, $c = 1278.5(3)$ pm, $wR_2 = 0.0383$, 1454 $F^2$ values, and 44 variables. Refinement of the occupancy parameters revealed a lithium content of 92(6)%. LiRh$_3$Sn$_5$ crystallizes with a new structure type. The structure is built up from a complex three-dimensional [Rh$_3$Sn$_5$] network, in which the lithium atoms fill channels in the $b$ direction. The [Rh$_3$Sn$_5$] network is governed by Rh–Rh (274 – 295 pm), Rh–Sn (262 – 287 pm), and Sn–Sn (289 – 376 pm) interactions. The lithium atoms have CN 13 (4 Rh + 9 Sn). Electronic band structure calculations and the COHP bond analysis reveal strong Rh–Sn bonds and also significant Rh–Rh bonding within the Rh$_3$Sn$_5$ network, which is additionally stabilized by weak but frequent Sn–Sn interactions.

Key words: Lithium Stannide, Crystal Chemistry, Chemical Bonding