New Stannides $CaTSn_2$ (T = Rh, Pd, Ir) and $Ca_2Pt_3Sn_5$ – Synthesis, Structure and Chemical Bonding

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Intermetallic Calcium Compounds, Crystal Structure, Mössbauer Spectroscopy, Chemical Bonding

New stannides $CaTSn_2$ (T = Rh, Pd, Ir) and $Ca_2Pt_3Sn_5$ were prepared as single phase materials by a reaction of the elements in glassy carbon crucibles under flowing purified argon. The four compounds were investigated by X-ray diffraction both on powders and single crystals and their structures were refined from single crystal data. The stannides $CaTSn_2$ (T = Rh, Pd, Ir) adopt the $MgCuAl_2$ structure with space group *Cmcm*: a = 434.1(1), b = 1081.7(3), c = 748.8(2) pm, $wR2$ = 0.0400, 451 F^2 values for $CaRhSn_2$, a = 442.7(2), b = 1113.8(4), c = 745.6(2) pm, $wR2$ = 0.0318, 471 F^2 values for $CaPdSn_2$, and a = 429.5(1), b = 1079.5(3), c = 758.6(2) pm, $wR2$ = 0.0465, 455 F^2 values for $CaIrSn_2$ with 16 variables for each refinement. Chemical bonding analysis leads to the description of a distorted filled $CaSn_2$ substructure in which the tin-tin bonding is modified by the insertion of transition metal atoms into the planar calcium layers, favoring strong tin-transition metal bonding. ^{119}Sn Mössbauer spectra show single signals for $CaTSn_2$ (T = Rh, Pd, Ir) which are subjected to quadrupole splitting. The electron count of the $CaTSn_2$ compounds correlates with the ^{119}Sn isomer shift. $Ca_2Pt_3Sn_5$ crystallizes with the $Yb_2Pt_3Sn_5$ type structure: *Pnma*, a = 734.8(1), b = 445.50(7), c = 2634.8(5) pm, $wR2$ = 0.0636, 1406 F^2 values and 62 variables. The platinum and tin atoms in $Ca_2Pt_3Sn_5$ build a complex three-dimensional $[Pt_3Sn_5]$ polyanion in which the calcium cations fill distorted pentagonal and hexagonal channels. According to semi-empirical band structure calculations the strongest bonding interactions are found for the Pt-Sn contacts, followed by Sn-Sn bonding. The ^{119}Sn Mössbauer spectrum of $Ca_2Pt_3Sn_5$ shows two superimposed signals at δ = 2.10(3) and δ = 2.18(6) mm/s.