Ternary Polar Intermetallics within the Pt/Sn/R Systems (R = La–Sm): Stannides or Platinides?

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**Recommended Citation**  
Rhodehouse, Melissa L.; Smetana, Volodymyr; Celania, Chris; Mudring, Anja-Verena; and Meyer, Gerd H., "Ternary Polar Intermetallics within the Pt/Sn/R Systems (R = La–Sm): Stannides or Platinides?" (2020). *Ames Laboratory Accepted Manuscripts*. 653.  
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Abstract
Starting generally with a 4:6:3 molar ratio of Pt, Sn, and R (where R = La–Sm), with or without the application of a NaCl flux, seven ternary compounds were obtained as single crystals. The platinides Pt₄Sn₆R₃ (R = La–Nd) crystallize with the Pt₄Ge₆Pr₃ type of structure (oP₅2, Pnma, a = 27.6–27.8 Å, b = 4.59–4.64 Å, c = 9.33–9.40 Å). With R = Pr, Pt₄Sn₆Pr₃–x (oP₅2, Pnma, a = 7.2863(3) Å, b = 4.4909(2) Å, c = 35.114(1) Å) is also obtained, which might be considered a high-temperature polymorph with disorder on the Sn- and Pr-sites. For R = Nd and Sm, a structurally related isostructural series with a slightly different composition Pt₃Sn₅R₂–x (oP₅2, Cmc2₁, a = 4.50–4.51 Å, b = 26.14–26.30 Å, c ≈ 7.29 Å) has been observed, together with Pt₇Sn₉Sm₅ (oS₄2, Amm2, a = 4.3289(5) Å, b = 28.798(4) Å, c = 7.2534(9) Å) under the same conditions. The latter exhibits the rare Zr₅Pd₉P₇-type structure, linking polar intermetallics to metal phosphides, in accord with P₇Pd₉Zr₅≡Pt₇Sn₉Sm₅. All structures may be described in terms of either negative Pt/Sn networks encapsulating positive R atoms, or {PtSnₓ} clusters (x = 5, 6, or rarely 7) sharing vertices and edges with R in the second coordination sphere and with considerable heterometallic Pt–R bonding contributions.

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Ternary Polar Intermetallics within the Pt/Sn/R Systems (R = La–Sm): Stannides or Platinides?

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ABSTRACT: Starting generally with a 4:6:3 molar ratio of Pt, Sn, and R (where R = La–Sm), with or without the application of a NaCl flux, seven ternary complexes were obtained as single crystals. The platinides Pt₅Sn₅R₂ (R = La–Nd) crystallize with the P₄Sr₅P₇ type of structure (Pnma, a = 27.6–27.8 Å, b = 4.59–4.64 Å, c = 9.33–9.40 Å). With R = Pr, Pt₅Sn₅Pr₃ (Pnma, a = 7.2863(3) Å, b = 4.4909(2) Å, c = 35.114(1) Å) is also obtained, which might be considered a high-temperature polymorph with disorder on the Sn- and Pr-sites. For R = Nd and Sm, a structurally related isostructural series with a slightly different composition PtₓSnᵧR₂₋ₓ (Pnma, Cmcm, a = 4.50–4.51 Å, b = 26.14–26.30 Å, c = 7.29 Å) has been observed, together with Pt₅Sn₅Sm (Amm₂, a = 4.3289(5) Å, b = 28.798(4) Å, c = 7.2534(9) Å) under the same conditions. The latter exhibits the rare Zr₅Pd₉P₇-type structure, linking polar intermetallics to metal phosphides, in accord with P₄Sr₅P₇.

Cluster complex halides such as {Pt₄Pr₃}₁₀ with isolated {Pt₄Pr₃} clusters or {Pt₄Pr₃}Br₃ with cluster chains constitute a symbiosis between intermetallic and salt. Subsequent elimination of the halide ligands, i.e., successive cluster under-occupation and/or disorder: monoclinic Pt₄Ge₃ (P2₁/m) and the disordered variant Pt₄Yb₃S₁₇ (P2₁/m), as well as five orthorhombic structures, slightly disordered Pt₄Ge₃Cₑ₃ (Cmcm), Pt₄Ge₃Pr₃ (Pnma, R = Pr–Dy), Td₂Sn₅Ce₃ (Pnma, R = La–Pr), Pt₄Al₃Ce₃ (Pnma), and Pt₄Sn₅Pr₃–ₓ (Pnma). The structures of this family are usually described as stacked pentagonal and hexagonal nets of mixed Sn and Pt encapsulating the R atoms, or {Pt₅Sn₅} clusters (x = 5, 6, or rarely 7) sharing vertices and edges with R in the second coordination sphere and with considerable heterometallic Pt–R bonding contributions.
Table 1. Crystallographic Details and Refinement Parameters for \( \text{Pt}_x \text{Sn}_y \text{R}_z \) (\( \text{R} = \text{La, Ce, Nd, Sm} \))

| parameter | \( \text{Pt}_4 \text{Sn}_6 \text{La}_3 \) | \( \text{Pt}_4 \text{Sn}_6 \text{Ce}_3 \) | \( \text{Pt}_4 \text{Sn}_6 \text{Pr}_3 \) | \( \text{Pt}_4 \text{Sn}_6 \text{Nd}_3 \) | \( \text{Pt}_4 \text{Sn}_6 \text{Nd}_1.84 \) | \( \text{Pt}_3 \text{Sn}_5 \text{Nd}_1.89 \) | \( \text{Pt}_3 \text{Sn}_5 \text{Sm}_5 \) |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| CCDC No.  | 1833492        | 1833495        | 1833516        | 1833494        | 1833493        | 1732670        | 1833491        |
| structure type | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) |
| formula weight, \( \text{fw} \) [g/mol] | 1909.23        | 1912.86        | 1915.23        | 1925.22        | 1443.95        | 1462.51        | 1482.64        |
| space group | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) | \( \text{Pnma} \) (No. 62) |
| \( a \) [Å] | 27.787(5)     | 27.7018(7)    | 27.623(1)      | 27.647(3)      | 4.515(3)       | 4.4978(5)      | 4.5330(4)      |
| \( b \) [Å] | 4.6380(9)     | 4.6149(1)     | 4.5958(2)      | 4.5858(9)      | 26.14(2)       | 26.298(4)      | 28.798(4)      |
| \( c \) [Å] | 9.399(2)      | 9.3712(2)     | 9.3499(5)      | 9.326(1)       | 7.291(5)       | 7.2925(8)      | 7.291(5)       |
| \( V \) [Å\(^3\)] | 1211.3(4)    | 1198.02(5)    | 1187.0(1)      | 1182.4(8)      | 860.4(9)       | 862.6(2)       | 883.35(2)      |
| density (calculated) [g/cm\(^3\)] | 10.47         | 10.61          | 10.72          | 10.80          | 11.15          | 11.15          | 11.70          |
| \( \mu \) [mm\(^{-1}\)] | 68.4          | 69.8           | 71.3           | 72.2           | 73.6           | 75.2           | 75.1           |
| \( F(000) \) | 3132          | 3144           | 3156           | 3168           | 2377           | 2404           | 2440           |
| \( \theta \) range [°] | 1.5 to 35.0   | 2.0 to 29.1    | 2.3 to 33.2    | 3.1 to 30.6    | 3.1 to 30.6    | 2.8 to 30.0    | 2.8 to 30.0    |
| index ranges | \( -44 \leq h \leq 43 \) | \( -38 \leq h \leq 38 \) | \( -40 \leq h \leq 40 \) | \( -6 \leq h \leq 6 \) | \( -4 \leq h \leq 6 \) | \( -6 \leq h \leq 6 \) | \( -6 \leq h \leq 6 \) |
| \( -7 \leq k \leq 7 \) | \( -6 \leq k \leq 6 \) | \( -7 \leq k \leq 7 \) | \( -37 \leq k \leq 32 \) | \( -36 \leq k \leq 37 \) | \( -40 \leq k \leq 35 \) | \( -9 \leq k \leq 10 \) | \( -9 \leq k \leq 10 \) |
| \( -15 \leq l \leq 15 \) | \( -13 \leq l \leq 13 \) | \( -13 \leq l \leq 14 \) | \( -10 \leq l \leq 9 \) | \( -10 \leq l \leq 8 \) | \( -9 \leq l \leq 10 \) | \( -9 \leq l \leq 10 \) | \( -9 \leq l \leq 10 \) |
| intensity data/independent | 22068/2942 | 13338/1956 | 22029/2380 | 2952/1418 | 3221/1364 | 4663/1956 |
| \( R_{w}/R_2 \) | 0.0649/0.0527 | 0.0714/0.0660 | 0.0757/0.0492 | 0.0912/0.0912 | 0.0319/0.0493 | 0.0388/0.0454 |
| refinement method | Full-matrix least-squares on \( F^2 \) | Full-matrix least-squares on \( F^2 \) | Full-matrix least-squares on \( F^2 \) | Full-matrix least-squares on \( F^2 \) | Full-matrix least-squares on \( F^2 \) | Full-matrix least-squares on \( F^2 \) | Full-matrix least-squares on \( F^2 \) |
| data/parameters | 2942/80 | 1956/80 | 2380/80 | 14186/64 | 1364/64 | 1394/68 |
| goodness of fit, \( \text{GOF (} F^2 \) | 1.032 | 1.025 | 1.050 | 1.09 | 1.02 | 1.043 |
| Flack parameter | - | - | - | 0.48(2) | 0.29(1) | 0.036(13) |
| R1 or R2, \( [I_o > 2\sigma(I)] \) | 0.389; 0.0812 | 0.0405; 0.0984 | 0.0373; 0.0545 | 0.0484; 0.1053 | 0.0246; 0.0458 | 0.0224; 0.0438 |
| R1 or R2, (all data) | 0.0610; 0.0875 | 0.0593; 0.1057 | 0.0843; 0.0634 | 0.0615; 0.1098 | 0.0269; 0.0645 | 0.0243; 0.0441 |
| largest diff. peak and hole [e Å\(^-3\)] | 4.31 and −4.34 | 4.38 and −7.15 | 3.58 and −4.41 | 5.31 and −4.42 | 3.06 and −2.49 | 2.20 and −2.58 |

\(^{27}\)Data taken from ref 27.
Table 2. Atomic Positions and Equivalent Thermal Parameters of Pt$_4$Sn$_6$La$_3$, Pt$_3$Sn$_5$Nd$_{1.84}$, and Pt$_7$Sn$_9$Sm$_5$

| atom  | Wyckoff | x        | y        | z        | $U_{eq}$ |
|-------|----------|----------|----------|----------|----------|
| Pt1   | 4c       | 0.54367(2) | 1/4      | 0.62889(8) | 0.00461(9) |
| Pt2   | 4c       | 0.68688(2) | 1/4      | 0.37954(8) | 0.00369(9) |
| Pt3   | 4c       | 0.45061(2) | 3/4      | 0.87904(9) | 0.00561(1) |
| Pt4   | 4c       | 0.68668(2) | 1/4      | 0.86909(9) | 0.00362(9) |
| Sn1   | 4c       | 0.49845(3) | 1/4      | 0.87771(1) | 0.00441(1) |
| Sn2   | 4c       | 0.49713(3) | 3/4      | 0.6281(1)  | 0.0043(1)  |
| Sn3   | 4c       | 0.35691(3) | 3/4      | 0.8749(1)  | 0.0083(1)  |
| Sn4   | 4c       | 0.63739(3) | 1/4      | 0.6244(1)  | 0.0050(1)  |
| Sn5   | 4c       | 0.71562(3) | 3/4      | 0.27941(9) | 0.0045(2)  |
| Sn6   | 4c       | 0.71757(3) | 3/4      | 0.96389(9) | 0.0045(2)  |
| Nd1   | 4c       | 0.59312(2) | 3/4      | 0.8666(1)  | 0.0060(1)  |
| Nd2   | 4c       | 0.40707(2) | 1/4      | 0.6171(1)  | 0.0060(1)  |
| Nd3   | 4c       | 0.72051(2) | 3/4      | 0.6243(8)  | 0.0042(1)  |
| Pt1   | 4a       | 0.47763(8) | 1/2      | −0.5012(4) | 0.0028(4)  |
| Pt2   | 4a       | 0.32537(10)| 1        | −0.0184(5) | 0.0028(4)  |
| Pt3   | 4a       | 0.44899(7) | 0        | 0.2158(2)  | 0.0016(4)  |
| Sn1   | 4a       | 0.39387(7) | 1/2      | −0.2426(2) | 0.0031(4)  |
| Sn2   | 4a       | 0.27753(6) | 0        | 0.4671(3)  | 0.0100(4)  |
| Sn3   | 4a       | 0.54906(12)| 3/4      | 0.3335(5)  | 0.0017(6)  |
| Sn4   | 4a       | 0.37976(11)| 1/2      | 0.5024(4)  | 0.0036(6)  |
| Sn5   | 4a       | 0.40123(12)| 1/2      | 0.1306(5)  | 0.0035(6)  |
| Pt1   | 1a       | 0.28934(13)| 1/2      | 0.2586(4)  | 0.0044(6)  |
| Pt2   | 1a       | 0.29479(15)| 1/2      | −0.3157(5) | 0.0121(8)  |
| Pt3   | 1a       | 0.3157(5)  | 0        | 0.3897(2)  | 0.0048(2)  |
| Sn1   | 4b       | 0.92479(3) | 1/2      | 0.3938(1)  | 0.0081(2)  |
| Sn2   | 4b       | 0.64679(3) | 1/2      | 0.4415(1)  | 0.0063(2)  |
| Sn3   | 4b       | 0.79125(3) | 1/2      | 0.4856(1)  | 0.0051(2)  |
| Sn4   | 4b       | 0.55566(6) | 1/2      | 0.5252(2)  | 0.0049(3)  |
| Sn5   | 4b       | 0.83999(6) | 1/2      | 0.6327(3)  | 0.0052(4)  |
| Pt1   | 1a       | 0.70123(6) | 0        | 0.5624(2)  | 0.0046(3)  |
| Pt2   | 1a       | 0.86855(6) | 1/2      | 0.3701(2)  | 0.0049(3)  |
| Pt3   | 1a       | 0.72089(6) | 1/2      | 0.2296(2)  | 0.0076(3)  |
| Sn1   | 1a       | 0.41027(4) | 1/2      | 0.2013(2)  | 0.0059(2)  |
| Sn2   | 1a       | 0.72874(4) | 1/2      | 0.6957(1)  | 0.0051(2)  |
| Sn3   | 1a       | 0.72874(4) | 1/2      | 0.6957(1)  | 0.0051(2)  |

*SOF = 0.839(8).*

The resulting product was identified via powder X-ray diffraction (XRD) to be multiphase, containing Pt$_4$Sn$_6$Sm$_3$ as the main product with further unknown phases. Small crystals of Pt$_7$Sn$_9$Sm$_5$ were selected and characterized by single-crystal XRD.

Pt$_4$Sn$_6$La$_3$, Pt$_3$Sn$_5$Nd$_{1.84}$, and Pt$_7$Sn$_9$Sm$_5$. The stoichiometric composition (Pt$_4$Sn$_6$La$_3$) has been loaded inside a tantalum tube and sealed under the same conditions. Following the same initial heating, the sample was slowly cooled and annealed for 3 days at 600 °C. The resulting products contained Pt$_4$Sn$_6$La$_3$ together with the pseudobinary solid solution Pt$_7$Sn$_9$Sm$_5$ in multiphase samples with unidentified phases (most likely, ternaries).

Structure Analysis. Powder and single-crystal XRD were used to characterize products. Samples were crushed in air and a portion was ground to a fine powder for phase analysis. Powders were sandwiched between greased Mylar sheets housed by an aluminum holder. Data were collected on a STOE STADI P image plate diffractometer (Cu Kα radiation, λ = 0.71073 Å; Si external standard, a = 5.4308(1) Å) and analyzed using WinXPOW software. Single-crystal XRD was performed on a Bruker APEX CCD and Bruker VENTURE diffractometer (both Mo Kα radiation, λ = 0.71073 Å, respectively). The raw frame data were collected using the Bruker APEX3 program, while the frames were integrated with the Bruker

overnight before being placed inside an argon-filled glovebox. All samples, masses of which were between 250 mg and 500 mg, were weighed and loaded into tantalum ampules inside an argon-filled glovebox. Ampules were sealed under argon, followed by sealing in evacuated silica tubes. Samples were placed in a furnace at 1000 °C for 24 h, followed by slow cooling (−20 °C h$^{-1}$) to 850 °C or 700 °C and annealed for 72 h. The NaCl flux was removed with water after the end of the reaction.

Pt$_4$Sn$_6$La$_3$, Pt$_3$Sn$_5$Pr$_{1.8}$, and Pt$_3$Sn$_5$Ce$_{2.8}$. Loadings of rare-earth metals (R = La–Sm) with Pt and Sn pieces in Pt:Sn:R molar ratios of 4:6:3 were weighed and placed inside tantalum tubes, along with ~250 mg of NaCl. Samples were sealed under the same conditions and placed in a tube furnace, following the heating profile described above. The somewhat disordered Pt$_4$Sn$_6$R$_{1.8}$, has been detected in the samples annealed at higher temperatures. No disordered variants have been detected in the samples with R = La and Ce. Isostructural Pt$_4$Sn$_6$Nd$_{1.8}$ has been observed to form directly after arc melting but transforms eutectoidally after 5 days of annealing at temperatures of <900 °C.

Pt$_7$Sn$_9$Sm$_5$. The starting composition for Pt$_7$Sn$_9$Sm$_5$ was weighed and loaded according to the above indicated method, with NaCl as a flux. The sample was sealed and heated according to the same scheme.
SAINT\textsuperscript{21} software package, using a narrow-frame algorithm integration of the data and were corrected for absorption effects using the multiscan technique (SADABS).\textsuperscript{22} All positions were refined anisotropically. Initial models of the crystal structures were obtained with the SHELXT-2014 program\textsuperscript{23} and refined using the SHELXL-2014 program\textsuperscript{24} within the APEX3 software package. All Pt\textsubscript{4}Sn\textsubscript{6}Pr\textsubscript{3} show signs of twinning or potential incommensurate modulation (see Figure S2 in the Supporting Information). Pt\textsubscript{4}Sn\textsubscript{6}Pr\textsubscript{3} and Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3} have been refined as inversion twins of which Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3} is enantiomorphically pure while Pt\textsubscript{4}Sn\textsubscript{6}Nd\textsubscript{2−} has been found to be a racemate. This fact correlates well with somewhat higher residual electron density peaks, compared to the isostructural Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3} structures. In the present case, one can either start with, or use a method, single crystals of Pt\textsubscript{4}Sn\textsubscript{6}La\textsubscript{3}, Pt\textsubscript{3}Sn\textsubscript{5}Nd\textsubscript{1.84} and of Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3}. Further data have been deposited (see the Supporting Information).

### RESULTS AND DISCUSSION

It is surprising that, until recently, the ternary intermetallic compounds known in the Pt/Sn/Pr systems have been the isocompositional PtSnR with R throughout the entire lanthanide series, including yttrium.\textsuperscript{3,25} The ambient pressure forms of PtSnR with R = Tb−Lu and Y,\textsuperscript{1} crystallize with the HoPtSn/ZeNiAl type, which is an anti-derivative of Fe\textsubscript{3}P, with the MgSrSi type, which is an anti-derivative of cotunnite (PtCl\textsubscript{3}), R = La−Eu.\textsuperscript{25} In PtSnPr, R has 12 nearest neighbors from 3.130 Å to 3.596 Å, as heterometallic {PrPt\textsubscript{6}Sn\textsubscript{6}} clusters, and Pt, the most electronegative of the three atom types, has four Sn atoms (2.729−2.897 Å) and six Pr atoms (3.130−3.596 Å) as nearest and second-nearest neighbors.

The reaction of binary Pt/Pr alloys, such as Pt\textsubscript{3}Pr\textsubscript{10}, with an obviously reactive tin flux yielded two new ternary intermetallics in the Pt/Sn/Pr system: Pt\textsubscript{1}Sn\textsubscript{3}Pr\textsubscript{2} with 29.2 mol % Pt, and Pt\textsubscript{3}Sn\textsubscript{10}Pr\textsubscript{3} with 30.8 mol % Pt.\textsuperscript{2} Subsequent stoichiometric loadings of PtSnPr\textsubscript{3} with and without an reactive NaCl flux resulted in two different products: stoichiometric Pt\textsubscript{4}Sn\textsubscript{6}Pr\textsubscript{3} isostructural with the Pt\textsubscript{4}GePr\textsubscript{3} structure type,\textsuperscript{17} as well as slightly substoichiometric Pt\textsubscript{4}Sn\textsubscript{6}Pr\textsubscript{3} with a new structure type. Utilizing the same flux method, single crystals of Pt\textsubscript{4}Sn\textsubscript{6}R\textsubscript{3} were grown for R = La, Ce, Pr, and Nd, all of which adopt the reported Pt\textsubscript{4}GePr\textsubscript{3} type. However, note that an alternative description model in a (3 + 1)D superspace group has been recently proposed for Pt\textsubscript{4}GeCe\textsubscript{3}\textsuperscript{26} that is representative of the same Pt\textsubscript{4}GePr\textsubscript{3} structure type. Although the same model might be applied to other Ge and Sn representatives, the initial structural description in the Pnma space group can be considered as a commensurately modulated three-dimensional (3D) approximant. The new Pt\textsubscript{4}Sn\textsubscript{6}Pr\textsubscript{3} type is obtained only with R = Pr (x = 0.09). These slightly substoichiometric ternary intermetallics appear to be a high-temperature “modification” of the Pt\textsubscript{4}GePr\textsubscript{3} type. All attempts to produce the isocompositional Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3} or Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3} have failed, resulting in a compositional split into Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3} and Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3} (51 mol % Sn and 43 mol % Sn, respectively, vs 47 mol % in the hypothetical Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3}).

### Crystal Structures

Polar intermetallics of the composition Pt\textsubscript{4}Sn\textsubscript{6}R (1, 23.1 mol % R) exist with R = La−Nd (oPS2, Pnma, a = 27.6−27.8 Å, b = 4.59−4.64 Å, c = 9.33−9.40 Å). With R = Pr, a closely related composition, Pt\textsubscript{3}Sn\textsubscript{5}Pr\textsubscript{3}, has been uncovered with a previously unreported crystal structure (2, oPS2, Pnma, a = 7.286(3) Å, b = 4.4909(2) Å, c = 35.114(1) Å). Unexpectedly, Nd and Sm, under the same reaction conditions, formed compositionally related Pt\textsubscript{4}Sn\textsubscript{6}Sm\textsubscript{2−} (3a, oPS2, Cmc\textsubscript{2}1, a = 4.515(3) Å, b = 26.14(2) Å, c = 7.291(5) Å), Pt\textsubscript{3}Sn\textsubscript{5}Sm\textsubscript{1} (3b, oPS2, Cmc\textsubscript{2}1, a = 4.533 Å, b = 26.629 Å, c = 7.318 Å), and Pt\textsubscript{4}Sn\textsubscript{6}Sm\textsubscript{3} (4, 23.8 mol % Sm, oS42, Ammm, a = 4.3289(5) Å, b = 28.798(4) Å, c = 7.2534(9) Å). The closely related Pt\textsubscript{4}Sn\textsubscript{6}Eu\textsubscript{2} (20 mol % Eu) had already been reported and is isostructural with Pt\textsubscript{4}Sn\textsubscript{6}R (R = Nd and Sm; 3c, oPS2, Cmc\textsubscript{2}1, a = 4.533 Å, b = 26.629 Å, c = 7.318 Å).\textsuperscript{27} Table 1 summarizes crystallographic details for all structures of the compounds just mentioned, except for Pt\textsubscript{4}Sn\textsubscript{6}Pr\textsubscript{3} which has been reported in a preceding article.\textsuperscript{2} Table 2 gives atomic parameters for Pt\textsubscript{4}Sn\textsubscript{6}La\textsubscript{3}, Pt\textsubscript{3}Sn\textsubscript{5}Nd\textsubscript{1.84}, and Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3}.

Although the full picture of all phases that might exist in the ternary systems Pt/Sn/R is certainly not known to date, the close compositions of 1 = PtSn\textsubscript{15.0}R\textsubscript{4.75}, 2 = PtSn\textsubscript{15.0}Pr\textsubscript{1.25}, 3 = PtSn\textsubscript{15.0}R\textsubscript{1.67}−0.61 = Nd (R = Nd, Sm, and Eu), and 4 = PtSn\textsubscript{15.0}Sm\textsubscript{1.29}−0.71, and strong structural similarities may make a point for the strong influence of geometric factors in the variation within the greater structural family. Although being not directly related, Pt\textsubscript{4}Sn\textsubscript{6}La\textsubscript{3} and Pt\textsubscript{4}Sn\textsubscript{6}M\textsubscript{3} both show some correlation of unit-cell parameters to Pt\textsubscript{4}Sn\textsubscript{6}Nd\textsubscript{1.84} (Pt\textsubscript{4}Sn\textsubscript{6}Eu\textsubscript{2}). The new ternary intermetallics Pt\textsubscript{4}Sn\textsubscript{6}R (R = La−Pr, 1) are isostructural with the analogous “germanides”, Pt\textsubscript{4}GeR\textsubscript{3} which include R = Pr, Nd, Sm, Gd, Tb, and Dy,\textsuperscript{17} while Pt\textsubscript{4}GeLa\textsubscript{3} has not been reported and those with R = Ce\textsuperscript{16} and Y\textsuperscript{18} belong to closely related structural derivatives.

There are usually alternative ways to describe crystal structures. In the present case, one can either start with, first, heteroatomic Pt and Sn clusters encapsulating endohedral R

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**Figure 1.** Projections of the crystal structures of (a) Pt\textsubscript{4}Sn\textsubscript{6}Pr\textsubscript{3} (1), (b) Pt\textsubscript{3}Sn\textsubscript{5}Pr\textsubscript{3}, (c) Pt\textsubscript{3}Sn\textsubscript{5}Nd\textsubscript{2−} (3), and (d) Pt\textsubscript{4}Sn\textsubscript{6}Sm\textsubscript{3} (4) onto equivalent planes. [Color legend for atoms: green, R, orange, Pt, and blue, Sn.]
atoms, or second, with Pt-centered Sn clusters that are surrounded, in the second coordination sphere, by R atoms. Either way, these building units, \{R\textsubscript{Pt6Sn8}\} or \{Pt\textsubscript{Sn}R\textsubscript{7}\} (Figures 1 and 2), are connected to 3D structures. In the first description, a 3D heteroatomic network of atoms with high electronegativities, 2.28 (Pt) and 1.96 (Sn) in the Pauling scale,\textsuperscript{28} encompasses electropositive lanthanide atoms R (EN = 1.13 for Pr). In the second description, the atom with the highest electron affinity, EA(Pt) = 205.3 kJ/mol, is surrounded by five to seven Sn atoms, EA(Sn) = 116 kJ/mol, and additional R atoms at larger distances. Philosophically, we treat the structures of these polar ternary intermetallics as either Werner-type coordination complexes, with the positive central atom (R) surrounded by negative ligands (Pt, Sn), or we consider them as anti-Werner-type cluster complexes\textsuperscript{29} with less electron-affine Sn/R clusters with Pt as the central atom. The latter description paves a way to a better understanding of the condensation of clusters from cluster complexes such as \{Pr\textsubscript{Pt}x\textsubscript{H}y\textsubscript{Pr}\} via binary Pt\textsubscript{Pr} (with \{Pr\textsubscript{Pr}\} clusters) to ternaries such as Pt\textsubscript{Sn}R\textsubscript{Pr}. Let us start with the perhaps more classical description. The crystal structures of all compounds in this Article may be described in terms of network structures where the electronegative Pt and Sn atoms form tunnels along certain directions, including the large R atoms which, viewed alone, form straight or zigzag chains (Figure 1). Thus, the stoichiometric Pt\textsubscript{Sn}R\textsubscript{3} (1) with the Pt\textsubscript{Ge}\textsubscript{R}-type structure exhibits linear one-side branched channels along the b- and c-axes. The structure is then formed of R-centered heteroatomic clusters \{R\textsubscript{Pt}Sn\} forming the stem and \{R\textsubscript{Pt}Sn\}, which is responsible for the branches (Figure 1). The latter consist of three parallel 6-4-6 and 5-5-5 membered rings, respectively (see Figure 2a). On the other hand, these clusters can be represented as randomly equatorially capped hexagonal and pentagonal prismatic polyhedra. Each branch polyhedron has common pentagonal faces with two stem polyhedra and shares pentagonal faces with identical units along the b-axis, forming a parallel tunnel.

Although Pt\textsubscript{Sn}R\textsubscript{Pr} \textsubscript{3} \textsubscript{2} (2) has the same space group symmetry, as well as almost identical compositions and unit-cell volumes, the compound shows distinct differences in atomic packing (Figure 1b) and exhibits disorder of both cationic (R) and anionic (Sn) sites. From the cationic point of view, the structure contains three building units: 4-7-4 \{R\textsubscript{Pt}Sn\}, 5-7-5 \{R\textsubscript{Pt}Sn\}, and 5-4-5 \{R\textsubscript{Pt}Sn\}. The 4-7-4 units form two-sided branched octagonal tunnels along the b-axis (Figure 1b), having large hexagonal faces shared with the 5-7-5 units forming the branches. Similar tunnels were frequently observed for the A/Au/Tr intermetallics (A = active metal, Tr = triel),\textsuperscript{30} including cationic zigzag chains and large positional disorders. A separate set of pentagonal tunnels along the b-direction is observed in between, forming cationic zigzag chains along the a-axis through bigger shared hexagonal faces (see Figures 1b and 2c, shown in violet). The packing of green, yellow, and violet polyhedra (Figure 2c) results in smaller voids in the form of tetrahedral stars, which are, again, reminiscent of the active metal polar intermetallics (e.g., A\textsubscript{Ga}Au\textsubscript{Ga})).\textsuperscript{31,32}

Pt\textsubscript{Sn}R\textsubscript{Pr} \textsubscript{3} \textsubscript{2} (R = Nd, Sm, and Eu (3)) exhibits its own set of coordination polyhedra and their packing (Figure 1c) and, because of multiple structural aspects, can be considered as a more ordered replacement variant for 2 with Nd and also a transition structure from 2 to 4. The compound contains only two symmetrically inequivalent Nd sites with a minor occupational disorder in one of them. One coordination polyhedron, \{Nd\textsubscript{Pt}Sn\} (Figure 2e), is common for 2, 3, and also 4 (see below) forming a set of pentagonal tunnels along the a-axis through the shared distorted hexagonal faces, while \{Nd\textsubscript{Pt}Sn\} is an average version for the two remaining polyhedra in 2. The latter form two sets of tunnels along the a-axis, sharing pentagonal Pt\textsubscript{Sn} faces and smaller trigonal Pt\textsubscript{Sn} faces, forming zigzags. The packing of these polyhedra is not dense and similar to 2, which leads to the formation of distorted cubic voids. Interestingly, unit-cell volumes in the row increase from Nd to Eu, pointing toward at least partial change of the oxidation state of those elements being consistent with the change of stoichiometry as a compensation mechanism. For the latter, this is not something extraordinary, since +2 is the most common oxidation number of Eu in intermetallics, particularly with group 11 metals,\textsuperscript{33,34} while a mixed valent state is also not rare.\textsuperscript{35}

Pt\textsubscript{Sn}Sm\textsubscript{3} \textsubscript{4} (4) crystallizes with a slightly lower symmetric, well-ordered representative of the series, although with slightly

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**Figure 2.** R- and Pt-centered clusters in the crystal structures of Pt\textsubscript{Sn}R\textsubscript{3} \textsubscript{1} (1), Pt\textsubscript{Sn}R\textsubscript{3} \textsubscript{2} \textsubscript{x} (2), Pt\textsubscript{Sn}R\textsubscript{Nd} \textsubscript{2} \textsubscript{x} (3), and Pt\textsubscript{Sn}Sm\textsubscript{3} \textsubscript{4} (4).
different atomic ratios (i.e., PtSn_{1.29}Sm_{0.71} instead of PtSn_{1.89}Sm_{0.18}). The new Pt_{5}Sn_{8}Sm_{3} belongs to the very rare Zr_{5}Pd_{9}P_{7} structure type linking polar intermetallics to metal phosphides, in accord with the formulation P_{5}Pd_{9}Zr_{5} = Pt_{5}Sn_{8}Sm_{3}. Similar to 2, three types of \{SmPt_{5}Pr_{2}\} polyhedra of similar architectures (Figure 2g) build the entire structure. They are connected to form pentagonal channels along the a-axis with a different degree of fusion with the neighboring units. 5–3–5 \{SmPt_{5}Sn_{3}\} polyhedra are responsible for the zigzag chains along the b-axis sharing larger pentagonal faces with two identical polyhedra (see Figures 1d and 2g, shown in violet). 5–4–5 \{SmPt_{5}Sn_{3}\} (red) together with 5–3–5 \{SmPt_{5}Sn_{3}\} (green), form fly-shaped trimers formally separated in the bc-plane. Green polyhedra share pentagonal faces with two red ones, while the latter have only a small trigonal face in common. The selected packing results in a limited number of small empty trigonal channels along the c-axis.

In summary, the electropositive rare-earth element atoms R in Pt_{5}Sn_{8}R_{1} (R = La–Nd), Pt_{5}Sn_{8}Pr_{2–x} (2), Pt_{5}Sn_{8}R_{2–x} (3, R = Nd–Eu), and Pt_{5}Sn_{8}Sm_{3} (4) have high coordination numbers of 15 and 16 (for 1), 14, 15, and 17 (for 2), 14 and 16 (for 3), and 13 (for 4), with heteroatomic “ligand” spheres of Pt and Sn atoms. Since the atomic radii of Sn (1.45 Å) and Pt (1.35 Å) are very similar, a mixed-ligand PtSn_{1.5} axis with a dihedral angle of 15 and 16 (for a small lanthanide-contraction effect) is neglected by the change of composition and perhaps oxidation state of Sn and Eu, leading to practically identical values for the Nd and Sm compounds and a more significant increase for the Eu one. The average Sn–Sn/Pt distance in Pt_{5}Sn_{8}Sm_{3} is much smaller (3.290 Å), which might be attributed to a coordination number of only 13 for all three Sm positions in the structure.

In the second, the anti-Werner way to describe the crystal structures of these ternary phases, we take the atom with the highest electronegativity, or electron affinity (Pt) as the central atom. Then, in all of the structures discussed in this Article, Pt is the central atom of a Sn polyhedral/cluster, \{PtSn_{5}\} with x = 5, 6, 7 (see Figures 2b, 2d, 2f, and 2h). All structures, Pt_{5}Sn_{8}R_{3} (1, R = La–Nd), Pt_{5}Sn_{8}Pr_{3–x} (2), Pt_{5}Sn_{8}R_{2–x} (3, R = Nd–Eu), and Pt_{5}Sn_{8}Sm_{3} (4) exhibit \{PtSn_{5}\} square pyramids, whereas their proportion is changing from 100% in 1, to 50% in 2 and 4, to 33% in 3. 2, 3, and 4 exhibit polyhedra close to trigonal prisms but have slopes of up to 30° between the horizontal faces. Finally, each of the latter contains one \{PtSn_{5}\} polyhedron atypical for any other structure, \{PtSn_{6}\} octahedra in 2, regular trigonal prisms in 4, and monocapped trigonal prisms in 3. From this point of view, it becomes clear that the structure of 2 is at a transition point between those with R = La–Pr and R = Sm–Eu, the latter of which have not yet been obtained with Pt_{5}Sn_{8}R_{2} stoichiometry. However, all of the structures do exhibit identical building principles, forming chains through the edge and vertex sharing of the common \{PtSn_{5}\} pyramids and \{PtSn_{6}\} prisms.

The polyhedra are mostly square pyramids but there are also prisms, distorted octahedra, and others. Average Pt–Sn distances in Pt_{5}Sn_{8}R_{3} are close to 2.66 Å (Table 3) and reflect somewhat the lanthanide contraction, which seems surprising. Since Pt has a higher electronegativity/electron affinity than Sn, we are, strictly speaking, dealing with platinides, not stannides, and thus, may remove the question mark from the title! The \{PtSn_{5−}R\} clusters must be connected via common Sn atoms, in accord with the compositions of 1 = PtSn_{1.89}La_{0.75}, 2 = PtSn_{1.89}Pr_{0.75}, 3 = PtSn_{1.89}Nd_{0.67}–0.69, and 4 = PtSn_{1.89}Sm_{0.71}, which happens in rather different ways (see Figure 3).

In the second coordination sphere, Pt is surrounded by R atoms with average distances of ~3.5 Å with a stronger reflection of the lanthanide contraction. This is only surprising when one considers whether there is Pt–R bonding. The sum of the atomic radii of Pt (1.35 Å) and Pr (1.85 Å) (i.e., 3.20 Å) suggests that there are no significant bonding interactions. The obvious influence of the lanthanide contraction on the Pt–R distances then would simply be a packing effect. However, integrated crystal orbital Hamilton populations show a value of ~0.80 eV/bond for Pt–Pr bonding, which is much less than the 2.28 eV/bond for Pt–Sn bonding, but it adds up to 18% of the overall bonding for Pt_{5}Sn_{8}Pr_{3}.

## CONCLUSIONS

The series Pt_{5}Sn_{8}R_{3} has been observed for the light rare-earth elements (R = La–Nd). They are isostructural with Pt_{5}Ge_{3}R_{3} (R = Pr–Dy), the so-called “germanides”. These, which are, in fact, platinides, similar to the corresponding “stannides”, are subject to the higher electronegativity/electron affinity of Pt than Sn. The Pr compound could be considered to be dimorphic with Pt_{5}Sn_{8}Pr_{2–x} because of the high-temperature modification with a slight under-occupation of the correspond-

| Average Distances (Å) | Molar Volumes, V_{m} (cm^{3}/mol) |
|------------------------|-----------------------------------|
| R@PtSn_{5} | d(R–(Sn–Pt)) | d(Pt–Sn) | d(Pt–R) | PtSn_{8}R_{3} | PtGe_{3} |
| Pt_{5}Sn_{8}La_{3} | 3.489 | 2.675 | 3.536 | 182.4 | – |
| Pt_{5}Sn_{8}Ce_{3} | 3.477 | 2.666 | 3.523 | 180.4 | 153.5 |
| Pt_{5}Sn_{8}Pr_{3} | 3.467 | 2.660 | 3.489 | 178.7 | 152.5 |
| Pt_{5}Sn_{8}Nd_{3} | 3.463 | 2.658 | 3.482 | 178.3 | – |
| Pt_{5}Sn_{8}Pr_{2–0.91} | 3.445 | 2.735 | 3.389 | 173.0 | – |
| Pt_{5}Sn_{8}Nd_{3–0.14} | 3.397 | 2.753 | 3.383 | 129.5 | – |
| Pt_{5}Sn_{8}Sm_{3–0.06} | 3.401 | 2.737 | 3.387 | 129.9 | – |
| Pt_{5}Sn_{8}Sm_{3} | 3.290 | 2.816 | 3.122 | 272.3 | – |
| Pt_{5}Sn_{8}Pr_{3} | – | – | – | – | 149.0 |
| Pt_{5}Sn_{8}Eu_{2} | 3.454 | 2.781 | 3.473 | 130.0 | – |

"The molar volume, V_{m}, is calculated from the cell volume, V_{0}, via the expression V_{m} = (V_{0} × N_{A})/Z or V_{m} = M/ρ (where N_{A} is Avogadro’s number, M is the molar weight, and ρ is the density)."

3.224 Å and 3.780 Å, as well as Pt–Pt distances ranging from 3.370 Å to 3.961 Å. Therefore, the shortest distances are close to the sum of the atomic radii of Pr (1.85 Å) and the average of Pt and Sn (1.40 Å) (1.85 Å + 1.40 Å = 3.25 Å). With the large coordination numbers of R (16 and 15), the average distances must be considerably longer. For the \{RSn_{5}Pt_{x}\} clusters, they vary only little with the size of the rare-earth atoms, but there is a small lanthanide-contraction effect through the Pt_{5}Sn_{8}R_{3} (R = La–Pr) series: 3.489 (La) to 3.467 Å (Pr). A practically opposite trend is observed for the Pt_{5}Sn_{8}R_{x} (3, R = Nd–Eu) series, because of multiple factors: the lanthanide-contraction effect is neglected by the change of composition and perhaps oxidation state of Sn and Eu, leading to practically identical values for the Nd and Sm compounds and a more significant increase for the Eu one. The average Sn–Sn/Pt distance in Pt_{5}Sn_{8}Sm_{3} is much smaller (3.290 Å), which might be attributed to a coordination number of only 13 for all three Sm positions in the structure.
ing R sites ($x = 0.09$). Pt$_3$Sn$_6$Pr$_{3-x}$ crystallizes in the same space group (Pnma) and has an almost identical unit-cell volume. However, the crystal structures of Pt$_3$Sn$_6$Pr$_3$ and Pt$_3$Sn$_6$Pr$_{3-x}$ are distinctly different and show, besides under-occupation of Pr sites, disorder of both Sn and Pr sites. None of these phases has been observed for the heavier rare-earth elements (i.e., Sm or Eu). Instead, Pt$_3$Sn$_5$Nd$_2$$_{3-x}$, $x = 0.16$ (Nd) and 0.11 (Sm) surprisingly crystallize isostructurally with Pt$_3$Sn$_5$Eu$_2$. All attempts to synthesize Pt$_3$Sn$_5$Nd$_3$ and Pt$_3$Sn$_5$Pr$_3$ with Nd or Sm have failed. Instead, compositionally related Pt$_7$Sn$_9$Sm$_5$ was obtained, a new example for the rare Zr$_5$Pd$_9$P$_7$-type structure linking polar intermetallics to metal phosphides, in accordance with the formulation P$_7$Pd$_9$Zr$_5$ = Pt$_7$Sn$_9$Sm$_5$.

Bonding in all of these compounds is predominantly heterometallic with Pt−Sn, Sn−R, and Pt−R bonding contributions decreasing in this sequence.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00884.

Supplemental graphic information (Figure S1–S3); supplemental tabular information (Table S1) (PDF)

**Accession Codes**
CCDC 1833491–1833495, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
Research at the Ames Laboratory was supported in part by the Office of the Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy (DOE), and the Department of Chemistry at Iowa State University (ISU). Ames Laboratory is operated for DOE by ISU, under Contract No. DE-AC02-07CH11358. Research at Stockholms Universitets was supported by the Kungl. Vetenskapsakademien, through the Göran Gustafsson Prize to A.V.M. and Energimyndigheten (Grant No. 46595).

Figure 3. Packing/connection of {PtSn$_x$} polyhedra in the crystal structures of Pt$_3$Sn$_6$R$_3$ (1), Pt$_3$Sn$_6$R$_{3-x}$ (2), Pt$_3$Sn$_6$R$_{2-x}$ (3), and Pt$_3$Sn$_6$Sm$_5$ (4). [Color legend: green, R; orange, Pt; and blue, Sn.]
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