Supporting Information

$M_2Ba_2Sn_6$ (M = Yb, Ca): Metallic Zintl Phases with a Novel Tin Chain Substructure

Ming-Hui Ge and John D. Corbett*

Table S1 *Atomic parameters used for the extended Hückel calculations*

atom type	orbital	H_{ii} (eV)	ξ_{11}	ξ_{12}	c_1	c_2
Ba	6s	-4.760	1.263			
	6p	-2.640	1.263			
Yb	6s	-5.35	1.54			
	6p	-5.35	1.54			
	5d	-5.21	2.81	1.216	0.7063	0.4834
Ca	4s	-7.0	1.2			
	4p	-4.0	1.2			
	3d	-5.0	4.0	1.3	0.4000	0.7000
Sn	5s	-16.16	2.12			
	5p	-8.32	1.82			

[1] Brennan, T.D.; Burdett, J.K. *Inorg. Chem.* **1993**, 32, 746.

[2] Ren, J.; Liang, W.; Whangbo, M.-H. CAESAR, PrimeColor Software Inc., Raleigh, NC, USA, **1998**.

Table S2 *Overlap Population (OP) data for Sn–Sn interactions in $M_2Ba_2Sn_6$ (M = Yb, Ca)*

Bond	$Yb_2Ba_2Sn_6$		$Ca_2Ba_2Sn_6$	
	bond distance/Å	OP	bond distance/Å	OP
Sn3–Sn4	2.89	0.70	2.90	0.73
Sn3–Sn1	2.90	0.57	2.90	0.60
Sn2–Sn3	3.01	0.56	3.01	0.57
Sn1–Sn2	3.08	0.26	3.05	0.29
Sn4–Sn4	3.10	0.48	3.10	0.53
Sn2–Sn2	3.19	0.37	3.19	0.34

Figure S1. The coordination of Yb (a) and Ba (b) with atomic distances below 4.0 Å. Dotted and solid lines for Yb coordination differentiate the interatomic distance groups.

Figure S2. A single tin chain with Yb coordination marked for Yb–Sn distances below 3.4 Å

Figure S3. Density of States for Ca₂Ba₂Sn₆(left) and Yb₂Ba₂Sn₆(right) obtained from Extended Hückle calculations. Dashed line signifies the Fermi level.

a: $\text{Yb}_2\text{Ba}_2\text{Sn}_6$

Yb-d

Ba-d

Sn-p

b: $\text{Ca}_2\text{Ba}_2\text{Sn}_6$

Ca-d

Ba-d

Sn-p

Figure S4. Fatband representations for a) $\text{Yb}_2\text{Ba}_2\text{Sn}_6$ and b) $\text{Ca}_2\text{Ba}_2\text{Sn}_6$

Figure S5. Crystal orbital Hamiltonian population ($-\text{COHP}$) plot for separate Ba–Sn interactions in $\text{Yb}_2\text{Ba}_2\text{Sn}_6$.