

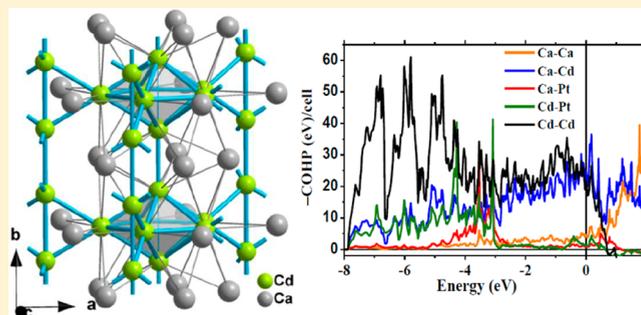
# Substantial Cd–Cd Bonding in $\text{Ca}_6\text{PtCd}_{11}$ : A Condensed Intermetallic Phase Built of Pentagonal $\text{Cd}_7$ and Rectangular $\text{Cd}_{4/2}\text{Pt}$ Pyramids

Fakhili Gulo,<sup>†</sup> Saroj L. Samal, and John D. Corbett\*

Ames Laboratory, DOE and Department of Chemistry, Iowa State University, Ames, Iowa 50010, United States

## Supporting Information

**ABSTRACT:** The novel intermetallic  $\text{Ca}_6\text{PtCd}_{11}$  is orthorhombic,  $Pnma$ ,  $Z = 4$ , with  $a = 18.799(2)$  Å,  $b = 5.986(1)$  Å,  $c = 15.585(3)$  Å. The heavily condensed network contains three types of parallel cadmium chains: apically strongly interbonded  $\text{Cd}_7$  pentagonal bipyramids, linear Cd arrays, and rectangular  $\text{Cd}_{4/2}\text{Pt}$  pyramids. All of the atoms have 11–13 neighbors. Calculations by means of the linear muffin-tin orbitals method in the atomic spheres approximation indicate that some Cd–Cd interactions correspond to notably high Hamilton populations (1.07 eV per average bond) whereas the Ca–Ca covalent interactions (integrated crystal orbital Hamiltonian population) are particularly small (0.17 eV/bond). (Pt–Cd interactions are individually greater but much less in aggregate.) The Ca–Ca separations are small, appreciably less than the single bond metallic diameters, and unusually uniform ( $\Delta = 0.14$  Å). The Cd atoms make major contributions to the stability of the phase via substantial 5s and 5p bonding, which include back-donation of Cd 5s, 5p and Pt 5d into Ca 3d states in the principal bonding modes for Ca–Cd and Ca–Pt. Bonding Ca–Ca, Ca–Cd, and Cd–Cd states remain above  $E_F$ , and some relative oxidation of Ca in this structure seems probable.  $\text{Ca}_6\text{PtCd}_{11}$  joins a small group of other phases in which Cd clustering and Cd–Cd bonding are important.



## INTRODUCTION

Exploratory syntheses in intermetallic systems have led to numerous novel compounds with unprecedented structures and unusual bonding features.<sup>1</sup> To understand and rationalize this rich chemistry and its associated complex bonding remains extremely challenging. Polar intermetallic phases formed between alkali metals or alkaline-earth metals and multiple heavy p-block elements often qualify as Zintl (valence) phases, which attain closed-shell electron configurations through formal electron transfer and covalent closed-shell bond formation.<sup>2–5</sup> The more recent utilization of earlier p-metals and, often, late transition metals as well has led to many new electron-poorer yet strongly bonded products with new structural features. Such compounds are electronically situated between Zintl and Hume–Rothery phases and often entail more highly condensed structures and fewer valence electrons per atom (e/a). Gold in particular has been very effective in affording new and unusual clusters, networks, or tunnel constructions with a range of cations, evidently because of substantial relativistic effects<sup>6</sup> that enhance gold's bonding to itself and later metals, for example, in many A/Ae–Au–Tr/Tt systems (A = alkali metal, Ae = alkaline earth metal, Tr = triel (Ga, In, Tl), Tt = tetrel (Ge, Sn)).<sup>7–15</sup> Introduction of late transition metals such as Cd and Zn in place of Tr leads to larger clusters and more networks. For example, we recently discovered gold-based ternary compounds such as  $\text{Na}_6\text{Au}_7\text{Cd}_{16}$  built on cadmium tetrahedral stars<sup>16</sup> and a greatly contrasting Na–Au–Zn system with

tunnel structures populated by somewhat diffuse but locally ordered cation distributions.<sup>17</sup> Switching the electropositive component to the more tightly bound alkaline-earth or rare-earth (R) metals generally produces higher symmetry phases and more uniform packing.<sup>18</sup>

Relatively few studies have been carried out on the neighboring platinum-based ternary intermetallic systems<sup>19–22</sup> although some amount of gold's novel relativistic enhancement of bonding would seem likely for Pt. Most studies have pertained mainly either to higher cation or Pt proportions or to products unrelated to those in the present study.

Enhancements of the cadmium proportions in such ternaries have been found to yield phases with new and novel aggregations of this component. Recently, we reported  $\text{Ca}_6\text{Pt}_8\text{Cd}_{16}$ ,<sup>23</sup> which contains strongly bonded Pt-centered calcium octahedra ( $\text{Pt}@Ca_6$ ) and a network of  $\text{Cd}_8$  tetrahedral stars that are face-capped by Pt. Nearly the same arrangement is also found in the close Na–Au analogue  $\text{Na}_6\text{Au}_7\text{Cd}_{16}$ <sup>16</sup> as well as in  $\text{Er}_6\text{Sb}_8\text{Pd}_{16}$ , a provocative *inverse* relative of the first analogue.<sup>24</sup> These structures seem to be dominated by strongly interbonded T–Cd aggregates in which T refers to a late, heavy transition metal Au, Pt, Pd, etc., whereas Cd seemingly lacks a competitive condensed cluster chemistry of its own in the

Received: June 8, 2013