Cluster Chemistry in Electron-Poor Ae—Pt—Cd Systems (Ae = Ca, Sr, Ba): (Sr,Ba)Pt₂Cd₄, Ca₆Pt₈Cd₁₆, and Its Known Antitype Er₆Pd₁₆Sb₈

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Supporting Information

ABSTRACT: Three new ternary polar intermetallic compounds, cubic Ca₆Pt₈Cd₁₆, and tetragonal (Sr,Ba)Pt₂Cd₄, have been discovered during explorations of the Ae—Pt—Cd systems. Cubic Ca₆Pt₈Cd₁₆ (Fm-3m, Z = 4, a = 13.513(1) Å) contains a 3D array of separate Cd₄ tetrahedral stars (TS) that are both face capped along the axes and diagonally bridged by Pt atoms to generate the 3D anionic network Cd₄[Pt- (1)]₄/Pt(2)]₄. The complementary cationic surface of the cell consists of a face-centered cube of Pt(3)/@Ca₆ octahedra. This structure is an ordered ternary variant of Sc₁₁Ir₄ (Sc,Ir,Sc₁₁), a stuffed version of the close relative Na₆Au₇Cd₁₆, and a network inverse of the recent Er₆Sb₈Pd₁₆ (compare Ca₆Pt₈Cd₁₆). The three groups of elements each occur in only one structural version. The new AePt₂Cd₄, Ae = Sr, Ba, are tetragonal (Pt₄/mmm, Z = 2, a ≈ 8.30 Å, c ≈ 4.47 Å) and contain chains of edge-sharing Cd₄ tetrahedra along c that are bridged by four-bonded Ba/Sr. LMTO-ASA and ICOHP calculation results and comparisons show that the major bonding (Hamilton) populations in Ca₆Pt₈Cd₁₆ and Er₆Sb₈Pd₁₆ come from polar Pt−Cd and Pt−Pd interactions, that Pt exhibits larger relativistic contributions than Pd, that characteristic size and orbital differences are most evident for Sb 5s, Pt₈, and Pd₁₆, and that some terms remain incomparable, Ca₆Pt₈Cd₁₆.

INTRODUCTION

Exploratory syntheses have played significant roles in solid-state and materials chemistry in the discovery of new compounds and the revelation of their chemical and physical properties. The heavy group 13 elements (trilens) yield several novel binary polyanionic cluster compounds in which alkali (A) or alkaline-earth metals (Ae) act as electropositive counterions. Addition of a third late transition metal to the systems, gold, and bonding patterns and enhanced bonding. Several gold-based ternary compounds with fascinating structures and unusual bonding patterns have been discovered in A/Ae−Au−Tr/Di systems (Tr = Ga, In; Di = Zn, Cd). For example, recently isolated Na₆Au₇Cd₁₆, which contains tetrahedral star clusters of cadmium, and several ternary compounds in K/Rb−Au−In systems with intriguing tunnel structures. The Na−Au−Zn system contains two new compounds with linear tunnels that are populated by new examples of somewhat diffuse but locally ordered Na cation distributions. Switches to more tightly bound Ae metals generally produce substantial changes in products, particularly with higher symmetry and more uniform packing. Thus, the ternary Ba₄Au₃Zn₁₃−x system (1 < x < 8) contains a broad substitution derivative of cubic BaZn₁₃ as well as a closely related tetragonal phase. Relatively few studies have been carried out on the neighboring platinum-based ternary intermetallic systems although some amount of gold’s relativistically enhanced bonding properties would seem likely for Pt as well. The latter yields a 3D [PtIn₃] network in CaPtIn₁₆ with Ca in distorted pentagonal channels, whereas Ca₆Pt₈Cd₁₆ and Ca₆PtIn₁₆ feature planar [Pt₄Cd] and [Pt₄In] networks. The compound Ca₆Pt₃Zn₁₃−x, which contains puckered networks of Pt and Zn, contains the rare-earth-metal (R) rich La₃Pt₇Cd₄, and Gd₄PtCd₂₃ contain transition-metal-centered trigonal prisms of rare-earth-metal atoms and isolated cadmium tetrahedra. Here we report the synthesis, structure, and bonding of two new compound types, Ca₆Pt₈Cd₁₆, a close relative of the unusual Na₆Au₇Cd₁₆, and (Sr/Ba)Pt₂Cd₄, which contain Cd tetrahedral stars in a closely knit cubic structure and chains of condensed cadmium tetrahedra, respectively. The report of Er₆Sb₈Pd₁₆ in the recent literature, an antitype relative of the present network in Ca₆Pt₈Cd₁₆, raises more interesting questions about relationships between similar but reordered elements in this relatively unusual structure type.

EXPERIMENTAL SECTION

Syntheses. The starting materials dendritic calcium, strontium, barium (99.9%), and cadmium (99.999%, all from Alfa Aesar) and platinum (99.99%, from Lonmin) were handled in dry N₂ (≤0.1 ppm H₂O by volume). The weighed reactants were welded sealed in tantalum containers and subsequently enclosed in an evacuated silica jacket to protect Ta from air when heated. A series of Ae−Pt−Cd compositions was reacted at 950 °C for 12 h, quenched in cold water, and annealed at 650 °C for 4 days. Crystals of Ca₆Pt₈Cd₁₆ were initially picked from...