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Cluster Chemistry in Electron-Poor Ae−Pt−Cd Systems (Ae = Ca, Sr, Ba): (Sr,Ba)Pt_2Cd_4, $Ca_6Pt_8Cd_{16}$, and Its Known Antitype $Er_6Pd_{16}Sb_8$

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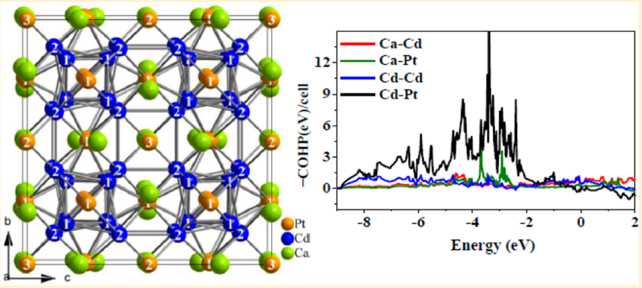
Supporting Information

ABSTRACT: Three new ternary polar intermetallic compounds, cubic $Ca_6Pt_8Cd_{16}$, and tetragonal (Sr, Ba)Pt_2Cd_4 have been discovered during explorations of the Ae−Pt−Cd systems. Cubic $Ca_6Pt_8Cd_{16}$ ($Fm\text{-}3m$, Z = 4, a = 13.513(1) Å) contains a 3D array of separate Cd_8 tetrahedral stars (*TS*) that are both face capped along the axes and diagonally bridged by Pt atoms to generate the 3D anionic network $Cd_8[Pt(1)]_{6/2}[Pt(2)]_{4/8}$. The complementary cationic surface of the cell consists of a face-centered cube of Pt(3)@Ca_6 octahedra. This structure is an ordered ternary variant of $Sc_{11}Ir_4$ ($Sc_6Ir_8Sc_{16}$), a stuffed version of the close relative $Na_6Au_7Cd_{16}$, and a network inverse of the recent $Er_6Sb_8Pd_{16}$ (compare $Ca_6Pt_8Cd_{16}$). The three groups of elements each occur in only one structural version. The new AePt_2Cd_4, Ae = Sr, Ba, are tetragonal ($P4_2/mnm$, Z = 2, $a \approx 8.30$ Å, $c \approx 4.47$ Å) and contain chains of edge-sharing Cd_4 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 $Ca_6Pt_8Cd_{16}$ and $Er_6Sb_8Pd_{16}$ come from polar Pt−Cd and Pd−Sb interactions, that Pt exhibits larger relativistic contributions than Pd, that characteristic size and orbital differences are most evident for Sb 5s, Pt_8, and Pd_{16}, and that some terms remain incomparable, Ca−Cd versus Er−Pd.



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 (triels) yield several novel binary polyanionic cluster compounds in which alkali (A) or alkaline-earth metals (Ae) act as electropositive counterions.[1,2] Additions of a third late transition metal to the systems, gold, in particular, have led to major gains in terms of new structures and bonding patterns and enhanced bonding. Several gold-based ternary compounds with fascinating structures and unusual bonding pattern have been discovered in A/Ae−Au−Tr/Di systems (Tr = Ga, In; Di = Zn, Cd).[3−15] For example, we recently isolated $Na_6Au_7Cd_{16}$ which contains tetrahedral star clusters of cadmium,[13] and several ternary compounds in K/Rb−Au−In systems with intriguing tunnel structures.[5,6] 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.[14] Switches to more tightly bound Ae metals generally produce substantial changes in products, particularly with higher symmetry and more uniform packing. Thus, the ternary $BaAu_xZn_{13-x}$ system ($1< x < 8$) contains a broad substitution derivative of cubic $BaZn_{13}$ as well as a closely related tetragonal phase.[15]

Relatively few studies have been carried out on the neighboring platinum-based ternary intermetallic systems,[16−23] although some amount of gold's relativistically enhanced bonding properties[24] would seem likely for Pt as well. The latter yields a 3D [$PtIn_2$] network in $CaPtIn_2$[16] with Ca in distorted pentagonal channels, whereas Ca_2Pt_2Cd[17] and Ca_2Pt_2In[18] feature planar [Pt_2Cd] and [Pt_2In] networks. The compound $Ca_6Pt_{2.33}Zn_{5.67}$ contains puckered networks of Pt and Zn.[21] The rare-earth-metal (R) rich $La_{23}Pt_7Cd_4$[22] and Gd_4PtCd[23] 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, $Ca_6Pt_8Cd_{16}$, a close relative of the unusual $Na_6Au_7Cd_{16}$[13] and (Sr/Ba)Pt_2Cd_4 which contain Cd tetrahedral stars in a closely knit cubic structure and chains of condensed cadmium tetrahedra, respectively. The report of $Er_6Pd_{16}Sb_8$ in the recent literature,[25] an antitype relative of the present network in$Ca_6Pt_8Cd_{16}$, 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 (99.995%, from Lonmin) were handled in dry N_2 (≤0.1 ppm H_2O by volume). The weighed reactants were weld 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 $Ca_6Pt_8Cd_{16}$ were initially picked from

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