Cesium Platinide Hydride $4Cs_2Pt\cdot CsH$: An Intermetallic Double Salt Featuring Metal Anions

Volodymyr Smetana and Anja-Verena Mudring*

Abstract: With Cs_9Pt_4H a new representative of ionic compounds featuring metal anions can be added to this rare-membered family. Cs_9Pt_4H exhibits a complex crystal structure containing Cs^+ cations, Pt^{2-} and H^- anions. Being a red, transparent compound its band gap is in the visible range of the electromagnetic spectrum and the ionic type of bonding is confirmed by quantum chemical calculations. This cesium platinide hydride can formally be considered as a double salt of the "alloy" cesium–platinum, or better cesium platinide, Cs_2Pt, and the salt cesium hydride CsH according to $Cs_9Pt_4H \equiv 4Cs_2Pt\cdot CsH$.

$\mathbf{G}$old and platinum are exceptional representatives of metals, whose absolute electronegativities[1] and first electron affinities[2] are similar to those of chalcogens and halogens, for example, sulfur, selenium, iodine, or astatine, suggesting the ability to form negatively charged ions in combination with electropositive bonding partners, as observed in CsAu,[3] which crystallizes isotypically with CsBr and CsI.[4] Halogens and gold compounds not only have crystal chemical similarities, but also similar chemical behavior, as gold shows the same tendency as halogens to disproportionate in a basic medium into the oxidation states $+I$ and $-I$.[5] Broad theoretical examinations revealed the importance of relativity for the chemistry of 6th row elements, such as gold and platinum, confirming the experimental observations, such as unusual oxidations states, higher electrochemical potentials, and the color of gold or the low melting point of mercury.[6] Since the relativistic orbital contraction, which is one part of the relativistic effect, affects mostly the states that can interact directly with the nucleus (the s-states), and is most apparent for elements with a high atomic number. Platinum and gold are the most prominent elements as a special combination of electronic shell structure ($5d^n6s^m$ valence levels) and relativity leads to unusual chemical behavior.

Both metals were reported to form salt-like compounds in combination with highly electropositive metals, such as cesium, for instance CsAu[3] and Cs_2Pt.[7] These compounds can be understood as relativistic analogues of metal halogenides and chalcogenides, respectively.[8] CsI and CsAu not only crystallize isotypically in the CsCl type of structure, it is even possible to dissolve CsAu (like CsI) in liquid ammonia. This has led to the discovery of a solvate, $CsAu\cdot NH_3$.[9] For CsAu also the formation of ternary oxides, such as Cs_3AuO[5a] (which formally can be written as a double salt according to $Cs_3AuO \equiv CsAu\cdot Cs_2O$) has been reported. The isotypic ternary oxide halides Cs_3XO ($X = Br, I$) are also known.[5] To date, no similar ionic ternary compounds are reported for platinides. It is expected that compounds featuring a charge separated Pt^{2-} anion are more difficult to obtain because of the lower electronegativity, lower first electron affinity, and the penalty that has to be paid through the second electron affinity to form a true Pt^{2-} anion. This situation is underpinned by the observation that only in combination with cesium, an ionic, transparent compound, Cs_2Pt, formed. The two characterized barium platinides, BaPt and Ba_2Pt,[8b,c] feature metallic conductivity and show just partial charge separation because barium is more electronegative than cesium. Our research aims at uncovering the possibility for Cs_2Pt to form double salts similar to CsAu ($Cs_3AuO \equiv CsAu\cdot Cs_2O$).

Herein we report on the synthesis and characterization of Cs_9Pt_4H, the first ionic double salt featuring Pt^{2-} anions. Reaction of platinum with cesium hydride in an excess of cesium yielded Cs_9Pt_4H as transparent cherry-red crystals (Figure 1). Cs_9Pt_4H is the first ternary compound containing platinum in the oxidation state $-II$ and exhibiting a maximum of charge separation. Ternary alkali-metal platinum hydrides, such as Na_2PtH_4, K_2PtH_4, Cs_2PtD_4, Cs_3PtD_5, Li_2PtH_6, Na_2PtH_6, and Cs_2PtD_6[10] have been reported, however, they are coordination compounds featuring either Pt^{2+} or Pt^{4+} coordinated by H^-. In contrast, Cs_9Pt_4H can be best described by the ionic formula $(Cs^+)_9(Pt^{2-})_4(H^-)$, in agreement with its red transparent appearance. The presence of hydride in the compounds was confirmed by 1H NMR spectroscopy (Supporting Information, Figure S2). This ionic formulation is supported by electronic structure calculations (see below).
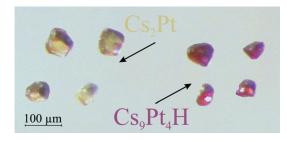
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Figure 1. Crystals of Cs_2Pt and Cs_9Pt_4H.

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In the synthesis, aside from cherry-red crystals of Cs_9Pt_4H, yellowish crystals were obtained. Single-crystal X-ray diffraction revealed them to be Cs_2Pt ($hP6$, Ni_2In type). Cs_2Pt has previously been described as a dark red compound.[7] The observed bathochromic shift might be due to a non-stoichiometric composition. For instance, CsAu can adopt colors from light yellow over orange to dark brown depending on the composition. Only stoichiometric CsAu is bright yellow. It is not possible to obtain Cs_9Pt_4H through interdiffusion of Cs_2Pt and CsH in analogy to the formation of Cs_3AuO from CsAu and Cs_2O owing to the low stability of CsH.

The new cesium platinide hydride Cs_9Pt_4H crystallizes in the tetragonal space group in its own type ($tI84$, $I4/m^{-1}$, $a = 14.071(1)$, $c = 18.494(2)$ Å, $V = 3661.4(8)$ Å^3, $Z = 6$, Table S1 and S2,[19] with seven crystallographically distinct cesium sites, two platinum and two hydrogen sites. It shows no direct structural relation to hexagonal Cs_2Pt. Its crystal structure contains 1D chains of corner-sharing $\{Cs_6H\}$ octahedra twisted at about 40° around the c axis with respect to each other and forming an **AAB** sequence of two distorted (**A**, squashed) and one regular (**B**) octahedral unit (Figure 2). Formally the structure can be described as an infinite chain $_\infty^1[CsH]_n$ surrounded by an intermetallic lattice of the composition $[Cs_2Pt]_{4n}$. Though the Cs–H separations within the chain are somewhat (1–7%) shorter, such a view describes solely the atom packing and not the bonding. The distribution of Cs and H atoms along the c axis is not uniform, which can be explained by the mutual orientation of the octahedra $\{HCs_6\}$ and the need to accommodate the neighboring platinum atoms. In the case of **A** pairs there is a different degree of distortion for both halves of the octahedron including minor deviations in the outer parts sharing vertices
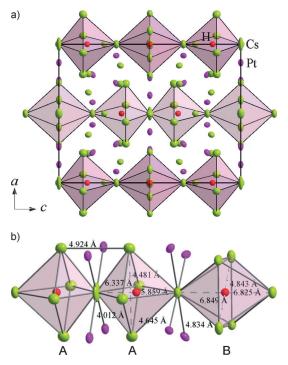
with **B** (Figure 2b). The highest grade of contraction within the $\{HCs_6\}$ octahedra is observed in the inner part around the Cs(9) position. With 4.012 Å the Cs−Cs interatomic distances are significantly shorter than in any other part of the structure and the central Cs(9) position is strongly polarized with a plate-like thermal ellipsoid. It is notable that Cs−Cs separation in the $\{HCs_6\}$ octahedra are longer than those in Cs_6O, comparable to the distances in CsAu and Cs_2Pt and definitely shorter than in pure Cs or unpolar Cs intermetallics (Table S3).[3b,5a,7,11] Cs(9) is coordinated by an octahedron formed by two hydrogen and four platinum atoms. All the faces of the octahedron are capped by cesium atoms, so that the central octahedron is embedded in a Cs_8 cube, which is the inverse Archimedean polyhedron. In such an atom packing, all the Cs−Cs contacts are surrounded by two Pt and one H increasing the (effective) positive charge of the cesium atoms and leading to a contraction of their interatomic distances. A somewhat different picture is observed for Cs3 having the same quantity and type of near-neighbors but definitely longer interatomic distances. Although the coordination polyhedron around Cs(3) is again the $\{Pt_4H_2\}$ octahedron, it is now covered by a Cs_8 tetragonal antiprism. The Cs−Cs bonds are less polarized having just one Pt and one H atom in direct proximity (Figure 2b and Figure S1). Cs(3) and Cs(9) feature a slightly distorted octahedral Pt_4H_2 coordination, Cs(4) is coordinated by a Pt_4 squashed tetrahedron, Cs(5) by a more regular Pt_4 tetrahedron, Cs(6) by a Pt_3H squashed tetrahedron, Cs(7) by a Pt_4H tetragonal pyramid, and Cs(8) is coordinated linearly by two H$^-$ ions. Pt(1) and Pt(2) are surrounded by slightly different, significantly distorted, square antiprisms of Cs atoms.

Cs_9Pt_4H is a direct-bonding analogue of the auride oxide Cs_3AuO (($(Cs^+)_3(Au^-)(O^{2-})$).[5a] Cs_9Pt_4H has a salt-like character and contains platinum in the oxidation state −II, in analogy with Cs_2Pt, and hydride ions in analogy with CsH. On the other hand it makes sense to compare the platinide hydride with Ba_9In_4H[12] which crystallizes similarly but not isotypically with Cs_9Pt_4H. In spite of an analogous formula, Ba_9In_4H has an excess of electrons which are responsible for its metallic characteristics. The high density of states (DOS) and a deep, but narrow pseudo gap above the Fermi level ($+3e^-$) confirms that assumption. Ba_9In_4H exhibits the same structural motifs as Cs_9Pt_4H and even the space group but crystallizes with a much smaller cell ca. 1/3 of Cs_9Pt_4H arising from the c axis being 1/3 shorter). All the $\{HBa_6\}$ octahedra have an identical orientation resulting in the smaller c axis. Owing to different orientation of the $\{Ba_6H\}$ and $\{HCs_6\}$ octahedra, the coordination number of both In atoms is ten, while the equivalent Pt atoms in Cs_9Pt_4H have a coordination of eight near neighbors. The most reasonable explanation for these structural differences is the chemical bonding being influenced by relativistic effects and resulting in different charge redistribution within the structure. In Cs_9Pt_4H, five out of eight Cs atoms in the coordination sphere of Pt2 have close contacts to H and are strongly polarized. On the other hand, in spite of longer distances, negatively charged Pt ions exhibit repulsive interactions. To compensate the charge loss, reduce the repulsion, and stabilize the structure, $(Pt1)_4$ squares twist moving closer to Cs atoms in the outer shell. As a result, the

Figure 2. a) Crystal structure of Cs_9Pt_4H, b) local environment and interatomic distances within the $(Cs_6H)_n$ chain.

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Cs–Pt distance spectrum splits into two regions, 3.34–3.76 Å and 4.05–4.15 Å.

To gain more insight into the bonding nature of Cs_9Pt_4H and to compare it with Cs_2Pt, density functional theory (DFT)-based band-structure calculations have been performed for both compounds using VASP.[13] The electronic DOS curves (Figure 3) exhibit similar features for both
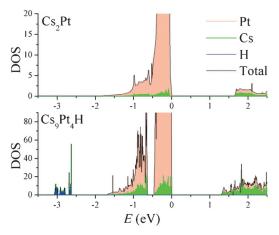

Figure 3. Density of state (DOS) curves for Cs_2Pt and Cs_9Pt_4H.

platinides including large mostly Pt 5d contributions found at 0–0.5 eV below the Fermi level and visible band gaps of 1.3 and 1.7 eV, respectively. Pt 6s are located mostly at 0.6–1 eV below the Fermi level. Hydrogen contributions can be found at 3 eV below the Fermi level and show a minor overlap with Cs. Pt and H contributions are completely separated in agreement with the separation of the elements in the crystal structure. DFT methods usually underestimate the magnitude of the band gap but these values fit perfectly with the observed transparency of the compounds and align with the color change from dark red for Cs_9Pt_4H to yellow for Cs_2Pt.

To further elucidate the electronic structure of Cs_9Pt_4H, the electron localization function (ELF) was calculated. The large value of the ELF at the H site indicates strongly paired electrons. The ELF value between the nearest Cs and Pt as well as Cs and H is incredibly low, indicating a very small contribution of covalent bonding and, what is more important, the same type of Cs/H and Cs/Pt interactions. The −ICOHP values for Cs–Pt and Cs–H pairs range from 0.14 to 0.21 and 0.09 to 0.14 eV/bond, respectively, being comparable to those found in Cs_2Pt and CsH. This scenario is very similar to CaH_2 with its strong ionic character.[14] It is worth noting that polarization interactions are very important for the bonding in the Cs_2Pt case and strong polarization of all positions have been observed also in the platinide hydride. H and Pt contours deviate from spherical shape being strongly distorted towards the Cs atoms (Figure 4).

Cs_9Pt_4H is an advanced illustration for the relativistic stabilization of the $6s^2$ state serving as an extra proof for full charge separation in Cs_2Pt and close relationship of platinum to the chalcogens. The formulation $(Cs^+)_9(Pt^{2−})_4(H^−)$ is compatible with its dark red color and 1.3 eV band gap obtained from the band structure calculations. The discovery
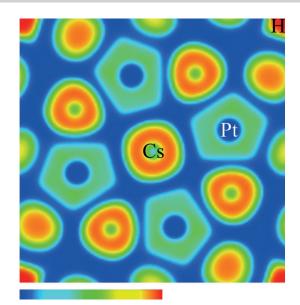

Figure 4. Electron localization function of a layer perpendicular to the c axis ($z=0.5$) in the structure of Cs_9Pt_4H.

of the ionic platinide hydride opens up the question of the boundaries between polar intermetallics and salts. Following gold, which can exhibit a stable negatively charged anion and coexist with other strong oxidizers, platinum joins the family opening wider horizons of possible combinations. Following the same principle, Cs_2Pt could combine with other active metal salts, especially real chalcogenides.

Experimental Section

All sample preparation and handling was carried out under inert conditions using standard Schlenk and glove box techniques. CsH was prepared by ball-milling metallic cesium under 2 bar of hydrogen at 50 °C.

Platinum black (or pieces), cesium metal, and cesium hydride powder with the stoichiometric ratio $Cs_{12}Pt_4H$ were arc-welded into Ta tubes under Ar and jacketed with an evacuated fused silica ampule. The ampule was heated at 200–400 °C for 3–4 days, slowly cooled to 100 °C at a rate of 2 °Ch$^{−1}$ and quenched in water. The reaction products were multiphase and contained an excess of Cs, which could be removed through distillation at 150 °C in a dynamic vacuum. A platinum richer loading according to a composition of $Cs_{11}Pt_7H$ resulted in a mixture of Cs_9Pt_4H and a second phase, which is known but not completely understood, of the composition Cs_xPt ($x <$ 0.5, Figure S3). Yellow and dark red transparent crystals were mechanically separated from the Cs melt. ^1H MAS NMR spectroscopy was used to confirm the presence of H$^−$ in the final products (Figure S2).

Full structural optimizations and band structure calculations on Cs_9Pt_4H were carried out with the projector-augmented wave (PAW) method of Blöchl[15] as implemented in the Vienna ab initio Simulation Package (VASP) by Kresse and Joubert.[13,16] Correlation and exchange were described by the Perdew-Burke-Enzerhof general gradient approximation (GGA-PBE).[17] Starting meshes of $4 \times 4 \times 4$ up to $7 \times 7 \times 7$ k-points were used to sample the first Brillouin zones for reciprocal space integrations, while the energy cutoffs of the plane-wave basis sets were set to 500 eV. With these settings the calculations converged until the energy difference between two iterative steps fell below $10^{−5}$ eV/cell. The −ICOHP data were subtracted from the VASP calculations using the LOBSTER code.[18]

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[19] CCDC 431183 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via The Cambridge Crystallographic Data Centre.

Communications

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Cesium Platinide Hydride 4Cs₂Pt·CsH:
An Intermetallic Double Salt Featuring
Metal Anions

Metal anions: The first cesium platinide hydride has been obtained and characterized. Cs_9Pt_4H contains Cs^+ cations, Pt^{2-}, and H^- anions and demonstrates the ability of Cs_2Pt to combine with salts into more complex formations. Transparency, band gap in the visible range of the electromagnetic spectrum, and ionic bonding confirm the relativistic stabilization of the Pt $6s^2$ state.

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