Inorganic Chemistry

Crystal Structure and Electronic Properties of New Compound $Zr_{6.5}Pt_6Se_{19}$

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a part of effort to dope Zr into the layered transitional metal chalcogenide PtSe₂. With a new structure type (oC68), it is the first Pt-based ternary chalcogenide with group 4 elements (Ti, Zr, and Hf). The crystal structure adopts the orthorhombic space group *Cmmm* with lattice parameters of a = 15.637(6) Å, b = 26.541(10) Å, c = 3.6581(12) Å, and V = 1518.2(9) Å³. This unusual structure consists of several building units: chains of edge-sharing selenium trigonal prisms and octahedra centered by zirconium atoms, chains of corner-shared square pyramid, and square planar centered by Pt atoms. The condensation of these building blocks forms a unique structure with bilayered Zr_{5.54}Pt₆Se₁₉ slabs stacking along the *b* direction and large channels parallel to the *c* direction within the bilayered slabs. Band structure calculations suggest that partial occupancy of Zr atoms creates a pseudo gap at the Fermi level and is likely the main cause for the stability of this new phase.



Article

1. INTRODUCTION

The transition metal chalcogenide PtSe₂ recently has attracted interest after the discovery of type II Dirac semimetal behavior,¹ negative longitudinal magnetoresistance,² quantum oscillations,³ thickness and quantum confinement modulated semimetal to semiconductor transformation,^{4,5} and photocatalytic activity.⁶ First-principles calculations suggest that transition metal (TM) doped PtSe₂ exhibits versatile spintronic behavior depending on the nature of the dopant TM atoms and topological phase transition caused by broken inversion symmetry with Te substitution.⁸ Chemical doping has also been proven to be an effective tool to change carrier concentration⁹ and Fermi level¹⁰ and induce superconductivity in the transition metal chalcogenides.¹¹ However, the investigation of new materials and phase behavior in systems of the type TM–Pt–Se, where TM = group IVB–group VIIIB transition metals, has been largely neglected. Indeed, only a few reports on group VB ternary compounds, such as Nb_8PtSe_{20} , ¹² Ta₂PtSe₇, ¹³ and Ta₂Pt₃Se₈, ¹⁴ have been reported. Given the rich structural diversity and various bonding features in the Pt-based pnictide system,¹⁵⁻²¹ it is reasonable to speculate that phases in combinations of the electron-rich group IVB elements will form, with different structure features as the alkali and alkaline earth ternary Pt-based chalcogenides.²²⁻²⁶ During the course of doping studies of transition metal chalcogenide ZrSe2, we discovered a new ternary Ptbased layered chalcogenide, nonstoichiometric Zr_{6.5}Pt₆Se₁₉, with a new structure type (oC68). It is the first Pt-based ternary compound as a group IVB and chalcogenide, with

unique $PtSe_5$ square pyramids and layered stacking along the *b* axis and large channels parallel to the *c* directions in the structure. The detailed structural description, chemical bonding analysis, and band structure calculations are also described in this paper.

2. EXPERIMENTAL SECTION

2.1. Material Synthesis, Crystal Growth and Composition Analysis. The starting materials used were Zr pieces (99.9%, Alfa Aesar), Pt powder (99.95%, Alfa Aesar), and Se shots (99.999%, Alfa Aesar). The ZrSe₂ precursor was first synthesized through solid-state reaction by sealing stoichiometric Zr pieces and Se shots in a clean fused silica tube under a vacuum and then heated at 950 °C for 2 days. The obtained powders were ground and pressed into a pellet, followed by the same heat treatment two times to ensure homogeneity. The compound was initially found as impurities during the chemical doping studies for Pt_rZrSe_2 (0.1 $\leq x \leq$ 1.5) above 900 °C and later on was isolated successfully as small needle-shaped crystals on the wall of the alumina crucible container when the reaction temperature was above 1020 °C. Small crystals are selected for the X-ray single crystal diffraction. The refined chemical composition from single crystal diffraction is subsequently confirmed by both SEM energy-dispersive X-ray spectroscopy (SEM-EDX) and inductively coupled plasma mass spectrometry (ICP-MS) measure-

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ments. Since the characteristics of the X-ray energy spectra of Zr L α (2.044 keV) and Pt M α (2.048 keV) are nondistinguishable, the SEM-EDX is mainly used to check the presence of the chemical species, and ICP-MS is our main tool to precisely determine the chemical composition. The determined Zr/Pt/Se ratio is 6.1(5):5.72(7):19, very close to the refined chemical composition from X-ray single crystal diffraction.

The attempts to synthesize an X-ray powder pure phase are also carried out with different starting ratios of Zr/Pt/Se = 6.5:6:19 (as refined Zr occupancy ratio) and Zr/Pt/Se = 9:6:19 (as Zr position fully occupied stoichiometric ratio) but unfortunately give poor yields. It is mainly due to the presence of the competing phases of $ZrSe_2$ and $PtSe_2$ in the powder during the synthesis. On the other hand, larger size crystals, up to 3 mm in length, were successfully synthesized when the assembly was heated at 1150 °C for 2 days and slowly cooled to 600 °C at a rate of 3 °C/h. Single crystal refinement from different batches of crystals with different starting Zr ($6.5 \le x \le 9$) ratios shows very similar Zr partial occupancies; therefore, we conclude the title compound is indeed a nonstoichiometric compound.

2.2. X-ray Crystallography. Phase identification and crystal structure were determined by single crystal X-ray diffraction. Single crystals were mounted on a Bruker D8 Quest Kappa single-crystal X-ray diffractometer equipped with a Mo K α I μ S microfocus source ($\lambda = 0.71073$ Å) operating at 50 kV and 1 mA with a HELIOS optics monochromator and a CPAD detector. The collected data set was integrated with Bruker SAINT and scaled with Bruker SADABS (multiscan absorption correction).²⁷ A starting model was obtained using the intrinsic phasing method in SHELXT,²⁸ and atomic sites were refined anisotropically using SHELXL2014.²⁹ Crystallographic parameters and refinement details for Zr_{6.5}Pt₆Se₁₉ are provided in Table 1. Atomic coordinates, equivalent anisotropic displacement

	Tabl	le 1.	Crystal	lographic	Details	for	$Zr_{6.5}Pt_6Se_{19}$
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temperature	298 K
wavelength	0.71073 Å
space group	<i>Cmmm</i> (No. 65)
unit cell dimensions	a = 15.637(6) Å, $b = 26.541(10)$ Å, c = 3.6581(12) Å
volume	1518.2 (9) Å ³
Ζ	2
absorption coefficient	52.422 mm ⁻¹
F(000)	2748
crystal size	$0.01 \times 0.02 \times 0.46 \text{ mm}^3$
θ range for data collection	3.02° to 30.51°
reflections collected	5916
independent reflections	1381 $[R(int) = 0.040]$
data/restraints/ parameters	1381/1/62
goodness-of-fit on F ²	1.094
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0256, wR_2 = 0.0604$
R indices (all data)	$R_1 = 0.0301, wR_2 = 0.0623$
largest diff. peak and hole	1.24 and $-1.60 \text{ e} \text{ Å}^{-3}$

parameters, occupancies, and some selected interatomic distances are included in Tables 2 and 3. More detailed selected interatomic angles are provided in Supporting Information Table S1. Integrated precession images along different planes are also shown in Figure S1, where the green circles indicate the indexed Bragg reflections. No indication of superstructure is observed in the title compound. Powder X-ray diffraction measurements were collected from $5^{\circ} < 2\theta < 90^{\circ}$ on a Rigaku Smartlab Diffractometer.

2.3. Electronic Band Structure Calculations. Electronic structure calculations were performed using two different methods: (1) the Stuttgart TB-LMTO-ASA program employing the tight-binding (TB) version of the linear muffin-tin orbital (LMTO)

method³⁰ in the atomic sphere approximation (ASA) and (2) the fullpotential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2K code.³¹ For the LMTO method, the Barth-Hedin local exchange correlation potential was implemented.³² Radii of the atomic spheres and interstitial empty spheres were obtained as implemented in the TB-LMTO-ASA program. The tetrahedron method was selected for the k-space integration.³³ The calculations utilized as basis sets Zr 5s/(5p)/4d/(4f), Pt 6s/6p/5d/(5f), and Se 5s/5p/(5d) (downfolded orbitals in parentheses).^{34,35} Reciprocal space integrations were performed using 305 irreducible kpoints. The chemical bonding analyses were investigated using the crystal orbital Hamilton population (COHP)³⁶ technique as implemented in the TB-LMTO-ASA 4.7 program package. For the WIEN2K method, the exchange and correlation energies were treated within the density functional theory (DFT) using the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA).³⁷ The self-consistencies were carried out using 1000 k-points ($10 \times 10 \times 10$ mesh) in the irreducible Brillouin zone. Spin orbit coupling effects are considered for the calculation. The computational results from both methods are compared and consistent with each other.

3. RESULTS AND DISCUSSION

3.1. Structural Description. The crystal structure of the title compound Zr_{6.5}Pt₆Se₁₉ is shown in Figure 1a. It crystallizes in a new structure type (oC68) in the centrosymmetric orthorhombic space Cmmm with lattice parameters a = 15.637(6) Å, b = 26.541(10) Å, and c =3.6581(12) Å. To the best of our knowledge, it is the only ternary, group 4 (Ti, Zr, and Hf), Pt-based chalcogenide. It is a bilayer structure composed of Zr and Pt polyhedra expanded along the ac plane and stacked along the b axis. The two slabs are related by inversion symmetry. However, within the bilayer slab, it appears to have stronger anisotropy along the *a* axis and thus is consistent with the quasi-1D morphology along the aaxis in the grown crystals. The local environments of the different Pt atoms [with two crystallographic sites Pt1 (8p) and Pt2 (4i)], Zr atoms [with two crystallographic sites Zr1 (4j) and Zr2 (8q)], and Se atoms are shown in Figure 1b-e, and their associated coordination and stacking are discussed below.

Pt1 atoms form a very unusual five coordinated PtSe₅ square pyramid with the connecting Se1, Se2, and Se5 atoms (Figure 2b). This is very different from square planar or octahedral coordination commonly observed in the Pt-related chalcoge-nides such as $PtSe_2$,³⁸ $Li_2Pt_3Se_4$,²³ $Na_2Pt_4Se_6$,²⁶ and Nb_8PtSe_{20} ¹² compounds. As far as we know, only one ternary transition metal Pt chalcogenide, $Ta_2Pt_3Se_8$,¹⁴ has similar PtSe₅ square pyramid coordination reported, and this is the first time the square pyramid coordination has been established in the group 10 platinum-group metal in an inorganic solid state compound. In the $Ta_2Pt_3Se_8^{14}$ compound, the PtSe₅ square pyramids are interconnected with the TaSe₆ trigonal prism forming a three-dimensional network. In our new compound Zr_{6.5}Pt₆Se₁₉, the PtSe₅ square pyramids are corner-shared through a common apical Se atom constructing the $Pt_2Se_{2/2}Se_8$ unit. The resulting Pt₂SeSe₈ units share edges along the basal Se atoms building the Pt₂SeSe_{8/2} chain. This Pt₂Se₅ chain (Figure 1b) grows along the crystallographic c axis. The Se5 atom is located at the apex of the PtSe₅ square pyramid with a slightly longer Pt–Se distance [2.693 (1) Å] than the basal plane Pt–Se bonding distances within the square nets [2.493] (1) Å for Pt1–Se1(\times 2) and 2.485 (1) Å for Pt1–Se2(\times 2)] and is reasonably comparable with the Pt-Se distances in the $Ta_2Pt_3Se_8$ compound [2.465(4)-2.583(5) Å]. The distortions of the basal plane are reflected by the angles Se1-Pt1-Se1, 94.39(4)°, and Se1– Pt1–Se2, 84.56(3)°.

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Table 2. Atomic Coordinates and	Equivalent	Isotropic Disp	lacement Parameters	(U_{ea})) of Zr _{6.5} Pt ₆ Se ₁₉
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atom	Wyckoff site	symm	x	у	z	occ.	$U_{\rm eq}^{\ a}$ (Å ²)
Zr1	4j	m2m	1/2	0.07771(7)	1/2	0.768(2)	0.0222(3)
Zr2	8q	<i>m</i>	0.17937(4)	0.13126(3)	1/2		0.0093(2)
Zr3	2d	mmm	0	0	1/2	0.354(3)	0.026(1)
Zr4	4j	m2m	1/2	0.24143(17)	1/2	0.305(2)	0.027(1)
Pt1	8p	<i>m</i>	0.33056(2)	0.13027(2)	0		0.00973(9)
Se1	8q	<i>m</i>	0.32143(5)	0.06667(3)	1/2		0.0129(2)
Se2	8q	<i>m</i>	0.31242(4)	0.19274(3)	1/2		0.0106(2)
Pt2	4i	m2m	0	0.13162(2)	0		0.0132(1)
Se3	8p	<i>m</i>	0.11283(4)	0.06710(3)	0		0.0119(2)
Se4	8p	<i>m</i>	0.11287(4)	0.19607(3)	0		0.0114(2)
Se5	4i	m2m	1/2	0.14847(5)	0		0.0144(2)
Se6	2b	mmm	1/2	0	0		0.0157(3)
U_{eq} is define	ed as one-third of th	e trace of the o	rthogonalized U_{ii} ten	sor.			

Table 3. Selected Interatomic Distances (Å) in Zr_{6.5}Pt₆Se₁₉

	Zr–Se	
Zr1–Se1	(×2)	2.808(1)
Zr1-Se5	(×2)	2.622(2)
Zr1–Se6	(×2)	2.757(2)
Zr2-Se1	(×1)	2.806(1)
Zr2–Se2	(×1)	2.644(1)
Zr2–Se3	(×2)	2.707(1)
Zr2–Se4	(×2)	2.718(1)
Zr3–Se3	(×8)	3.1032(9)
Zr4–Se2	(×2)	3.205(2)
Zr4–Se4	(×4)	3.035(3)
Zr4–Se5	(×2)	3.071(4)
	Pt-Pt	
Pt1-Pt1	(×2)	3.658(1)
Pt2-Pt2	(×2)	3.658(1)
	Pt-Se	
Pt1-Se1	(×2)	2.4930(9)
Pt1-Se2	(×2)	2.4849(8)
Pt1-Se5	(×1)	2.693(1)
Pt2-Se3	(×2)	2.459(1)
Pt2-Se4	(×2)	2.458(1)
	Zr–Zr	
Zr1–Zr1	(×2)	3.658(1)
Zr2–Zr2	(×2)	3.658(1)
Zr3–Zr3	(×2)	3.658(1)
Zr4–Zr4	(×2)	3.658(1)

The Pt2 atom forms a slightly distorted PtSe₄ square planar coordination with the Se3 and Se4 atoms (Figure 1c), as commonly observed in Pt-related compounds. These PtSe₄ units stack in an eclipsed manner along [001]. The bonding distances [2.459 Å for Pt2–Se3(×2) and 2.458 (1) Å for Pt2–Se4(×2)] are comparable to those in the basal plane with Pt1–Se distances. All the Pt–Se bond distances for both Pt1 and Pt2 atoms are generally smaller than the 6-coordinated Pt–Se distances such as in PtSe₂³⁸ and comparable to the 4-coordinated Pt–Se distances such as in Li₂Pt₃Se₄²³ and Na₂Pt₄Se₆.

Two of the Zr atoms [Zr1 (4*j*) and Zr2 (8*q*)] are found to be six-coordinated as expected. The Zr1 atoms form distorted octahedra with the neighboring Se1, Se5, and Se6 atoms, whereas the Zr2 atoms have trigonal prismatic coordination with the surrounding six Se1, Se2, Se3, and Se4 atoms. All the Zr–Se bond distances [2.622(2)–2.808(1) Å] are consistent with those reported Zr-Se distances in Cs₄Zr₃Te₁₆,³⁹ EuZrSe₃⁴⁰ and Ce₂ZrSe₅⁴¹ compounds. Each Zr1 atom is partially occupied (\sim 77%). Neighboring Zr_{0.77}Se₆ octahedra share edges along the equatorial Se atoms forming the Zr_{0.77}Se₄ chain (Figure 1d) that propagates along [001]. The octahedra formed by Zr1 atoms are highly distorted (see selected bond angles in Table S1) due to the neighboring Pt_2Se_5 chain. The geometric distortions about the metal atoms are consistent with the chemical inequivalence of the Se atoms. Each Se2, Se3, and Se4 atom is bound to three metal atoms. The Se1 and Se5 atoms bridge two Pt atoms and two Zr atoms, while the Se6 atom connects four Zr1 atoms. In contrast, the Zr2 atoms are fully occupied and are six-coordinated to the Se atoms in a trigonal prismatic fashion. The adjacent ZrSe₆ units are edgeshared along the basal Se atoms forming the ZrSe4 chain (Figure 1e) that expands along [001]. The Se–Se distances between the adjacent layers range from 3.539(2) to 3.663(2)Å. These values are slightly bigger than the Se–Se distance across the van der Waals' gap of PtSe2, 3.329(4) Å, but smaller than that of $ZrSe_2$, 3.782(3) Å.

The Pt_2Se_5 unit formed by Pt1 atoms is edge-shared with the neighboring $ZrSe_6$ octahedra by Zr1 atoms and condenses to construct the $Zr_{0.77}Pt_2Se_6$ chain (Figure 2a). The stacking and condensation of the $Zr_{0.77}Pt_2Se_6$ chains, $PtSe_4$ units, and two $ZrSe_4$ chains build a unique $Zr_{2.77}Pt_3Se_{10}$ monolayered slab (Figure 2b) along the *a* direction. The $Zr_{0.77}Pt_2Se_6$ chains are edge-shared to the apical Se atoms of the $ZrSe_4$ chains. The two and opposite sides of the distorted $PtSe_4$ square planar units are shared with the two $ZrSe_4$ chains along the basal Se atoms. These two $ZrSe_4$ chains are related by a mirror-plane symmetry. Two $Zr_{2.77}Pt_3Se_{10}$ monolayered slabs join through edge-sharing of the equatorial Se atoms of the $Zr_{0.77}Se_6$ octahedra. Thus, the $Zr_{5.54}Pt_6Se_{19}$ bilayered slab is constructed.

Two different Zr atoms, Zr3(2d) and Zr4(4j), lie in between the Zr_{5.54}Pt₆Se₁₉ bilayered slabs. Both Zr3 and Zr4 atoms are not fully occupied, with occupancy only 0.354(3) for Zr3 and 0.305(2) for Zr4, respectively. The Zr3 atoms are located within the channels of the bilayered slabs. On the other hand, the Zr4 atoms are sandwiched between the neighboring bilayered slabs. Although the Zr–Se contacts outside the slabs are long (between ~3 and 3.2 Å), the corresponding Zr–Se interactions are not to be neglected based on band structure calculations. Consequently, $Zr_{6.5}Pt_6Se_{19}$ can be viewed as a pseudo-two-dimensional structure. If all of the Zr sites are fully occupied, one would expect a stoichiometric $Zr_9Pt_6Se_{19}$



Figure 1. (a) The crystal structure of $Zr_{6.5}Pt_6Se_{19}$ projected along the *c* axis. Different building units by Zr and Pt coordination polyhedra are highlighted for clarity. (b) Pt_2Se_5 chain formed by corner and edge-shared $Pt(1)Se_5$ square pyramid for Pt1 atoms. (c) $PtSe_4$ square planar units for Pt2 atoms surrounded by four Se atoms. (d) $Zr_{0.77}Se_4$ chain formed by edge-shared $ZrSe_6$ octahedra for Zr1 atoms, and Zr1 has a partial occupancy of 0.768(2). (e) $ZrSe_4$ chain formed by edge-shared $ZrSe_6$ trigonal prisms for Zr2 atoms.



Figure 2. (a) The $Zr_{0.77}Pt_2Se_6$ chain formed by the condensation of the Pt_2Se_5 and the $Zr_{0.77}Se_4$ chains. (b) The stacking sequence in the $Zr_{2.77}Pt_3Se_{10}$ monolayered slab displayed in two different isometric views.



Figure 3. (a) Density of states (DOS) of the hypothetical $Zr_9Pt_6Se_{19}$ phase (210*e*–) with fully occupied Zr sites. Weighted average crystal orbital Hamilton population (–COHP) of the (b) Zr–Se and (c) Pt–Se interactions. The Fermi level (EF) is set at 0 eV. The total electron count of 200*e*[–] is denoted by dashed lines. Qualitative molecular orbital diagrams of the main d-block in the idealized (d) PtSe₄ (*D*4*h*) and (e) PtSe₅ (*C*4*v*) units with a d⁸ electronic configuration.

for the compound $Zr_{6.5}Pt_6Se_{19}$ is Zr^{4+} , Pt^{2+} , and Se^{2-} and yielded a net charge balance of the compound of $[6.5 \times 4 + 6 \times 2 + 19 \times (-2) = 0]$.

3.3. Band Structure Analysis. To examine the role of the partial occupancies of the Zr atoms in the stability of $Zr_{6.5}Pt_6Se_{19}$, electronic structure calculations have been

performed. The calculations are based on the hypothetical $Zr_9Pt_6Se_{19}$ compound with all the Zr atoms fully occupied. As shown in the density of states (DOS) plot (Figure 3a), the Fermi level of the hypothetical 210-electron phase lies along the shoulder of a high-DOS peak. In contrast, there is a pseudogap with an ultralow-DOS corresponding to a total

electron value of $200e^-$. The removal of $10e^-$, such as in the partial occupancies of Zr atoms, provides a great electronic stability. Thus, the $200e^ Zr_{6.5}Pt_6Se_{19}$ is more favorable than the $210e^ Zr_9Pt_6Se_{19}$ phase. The crystal orbital Hamilton populations (COHP) also provide a rationale for the partial occupancies of the Zr atoms. As shown in Figure 3b, the Zr–Se interactions are optimal in $Zr_{6.5}Pt_6Se_{19}$; the antibonding states are empty while the bonding states are fully occupied. This is not the case for $Zr_9Pt_6Se_{19}$, where the Fermi level lies in antibonding Zr–Se states. The integrated -COHP (-ICOHP) up to the Fermi level ($200e^-$) of the nearestneighbor Zr–Se and Pt–Se interactions in $Zr_{6.5}Pt_6Se_{19}$ is enumerated in Table 4. The Zr–Se interactions are the major

Table 4. Integrated Crystal Orbital Hamilton Population (-ICOHP) up to Total Electron Count of $200e^-$

interaction	d (Å)	–ICOHP (eV/ bond)	N per unit cell	% contribution
Pt1-Se1	2.493	2.65	2	8.2
Pt1-Se2	2.485	2.70	2	8.4
Pt1-Se5	2.693	1.26	1	2.0
Pt2-Se3	2.459	2.86	2	8.9
Pt2-Se4	2.458	3.03	2	9.4
Zr1-Se1	2.808	1.41	2	4.4
Zr1-Se5	2.622	2.14	2	6.6
Zr1–Se6	2.757	1.53	2	4.7
Zr2-Se1	2.806	1.82	1	2.8
Zr2-Se2	2.644	2.47	1	3.8
Zr2-Se3	2.707	2.08	2	6.4
Zr2–Se4	2.717	2.18	2	6.8
Zr3–Se3	3.103	1.10	8	13.6
Zr4–Se2	3.206	0.85	2	2.6
Zr4–Se4	3.035	1.28	4	7.9
Zr4–Se5	3.071	1.13	2	3.5

contributors (~63%) to the –ICOHP values due to their frequency. As such, the Zr atoms have a vital part to play in the chemical bonding in $Zr_{6.5}Pt_6Se_{19}$. The significant Zr–Se interactions are also reflected in the DOS plot where the Zr atoms effectively mix with the Se atoms below the Fermi level (–1.7 to –8 eV). Thus, the partial occupancy of the Zr atoms plays a crucial role in the electronic stability of $Zr_{6.5}Pt_6Se_{19}$.

To shed light on role of the Zr atoms in the chemical bonding in $Zr_{6.5}Pt_6Se_{19}$, COHP has been calculated, with results shown in Figure 3b and Supporting Information. As can be seen in Figure 3b, if all the Zr sites are fully occupied, the Fermi level will fill part of the antibonding states, which will destabilize the PtSe chains. Once Zr sites follow experimental occupancies, all the Pt–Se bonds and Zr–Se bonds are optimal; i.e., the antibonding states are unfilled while bonding states stay below the Fermi level. The –ICOHP up to the Fermi level for the respective nearest-neighbor interactions in $Zr_{6.5}Pt_6Se_{19}$ have been computed (Table 4).

With the absence of any Zr–Zr and Se–Se bonds, the zirconium and selenium atoms adopt their usual oxidation states: Zr(+4) and Se(-2). The oxidation state of the Pt2 atom is +2, following the typical d⁸ electronic configuration for a transition metal in a square planar coordination environment. For a square-based pyramidal geometry (as in the case of the Pt1 atom), both the d⁶ and d⁸ electronic configurations are common. As such, Pt1 can either be in +2 or +4 oxidation states. Although transition metals with five-coordination

geometry are frequent in solid-state compounds, as we discussed before, it is quite uncommon in Pt-based selenides. Typically, the Pt atoms in these compounds are coordinated in either square-planar or octahedral fashion. In organometallics, there are only a few Pt-based molecules with square pyramidal configuration and are based on Pt(+4).⁴²⁻⁴⁴ However, the Pt1(+4) oxidation state leads to a highly electron-deficient (Zr⁴⁺)_{6.5}(Pt1⁴⁺)₄(Pt2²⁺)₂(Se²⁻)₁₉ phase. In contrast, the Pt1(+2) assignment points to an electron-precise compound, consistent with the Fermi level lying in a pseudogap with ultralow DOS. Hence, $Zr_{6.5}Pt_6Se_{19}$ can be formulated as $(Zr^{4+})_{6.5}(Pt^2)_6(Se^{2-})_{19}$.

Qualitative orbital analysis of square planar PtSe4 and square-based pyramidal PtSe5 units coupled with the electronic structure calculations of the solid-state compound also offer a rationale for the stability of $(Zr^{4+})_{6.5}(Pt^{2+})_6(Se^{2-})_{19}$. Figure 3d and e illustrate the main d-block orbitals of the idealized units of $PtSe_4(D_{4h})$ and $PtSe_5(C_{4\nu})$, respectively, with d⁸ electronic configuration. In both cases, the ordering of the energy levels of the MOs are the same: $x^2 - y^2 > z^2 > xz = yz = xy$. Strong σ antibonding states (based from the $x^2 - y^2$ orbitals) are present in the lowest unoccupied molecular orbitals of both the PtSe4 and PtSe₅ units. In the solid-state compound, these strong Pt-Se σ -antibonding interactions are located above -0.2 eV (Figure 3c). These are unoccupied in Zr_{6.5}Pt₆Se₁₉ but partially filled in the hypothetical Zr₉Pt₆Se₁₉ phase. As such, the absence of strong Pt–Se σ -antibonding interactions favors the formation of Zr_{6.5}Pt₆Se₁₉. Meanwhile, only weak antibonding Pt-Se states (based from the z^2 orbitals) are involved in the highest occupied molecular orbitals of both the PtSe4 and PtSe₅ units. Due to the polarized z^2 orbital, the antibonding interaction between Pt and the apical Se orbitals in the PtSe5 unit is rather weak. Compared with the Pt1-Se distances involving the basal Se atoms (2.485 to 2.493 Å), Pt1-Se5 separation along the apical Se position is longer (2.693 Å), which further weakens the antibonding interaction along these orbitals. In the solid-state material, these weak antibonding Pt-Se interactions based on the z^2 orbitals are located just below the Fermi level of $Zr_{6.5}Pt_6Se_{19}$ (-1.7 to -4.2 eV). Thus, the partial occupancies of the Zr atoms enhance the electronic stability of Zr_{6.5}Pt₆Se₁₉ by preventing the filling up of strong Pt–Se σ -antibonding states.

4. CONCLUSIONS

In summary, a new ternary chalcogenide $Zr_{6.5}Pt_6Se_{19}$, with a new structure type is reported with a nonstoichiometric ratio. It consists of $PtSe_5$ square pyramid, $PtSe_4$ plane, and $ZrSe_6$ octahedra/trigonal prism building blocks and forms a unique layered structure along the *b* direction. Band structure calculations show that the partial occupancies of the Zr atoms create a pseudogap at the Fermi level, optimize the Pt–Se bonding state, and thus enhance the electronic stability for the compound.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00522.

The selected interatomic angles, integrated precession images along different planes and COHP plot for Zr-Se, Pt-Se, and Zr-Pt interactions for $Zr_{6.5}Pt_6Se_{19}$ model (PDF)

Accession Codes

CCDC 1981675 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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