Supporting Information

for

Bonding and oxidation state of a transition metal atom encapsulated in an isolated octahedral cluster cation of main group elements: Synthesis, crystal structure and electronic structure of $\text{Pt}_2\text{In}_{14}\text{Ga}_3\text{O}_8\text{F}_{15}$ containing highly positive 18-electron complex $[\text{PtIn}_6]^{10+}$ and low-valent In^+ ions

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Table S1. Crystallographic data and parameters of data collection and structure refinements of $\text{Pt}_2\text{In}_{14}\text{Ga}_3\text{O}_8\text{F}_{15}$

Empirical formula	$\text{Pt}_2\text{In}_{14}\text{Ga}_3\text{O}_8\text{F}_{15}$
Formula weight	2619.8
Space group; Z	$R\bar{3}m$ (No.166); 3
Temperature	298 K
Unit cell dimensions (pm) ^a : a, c	709.0(6), 4556.0(2)
Density (calculated)	6.58 g/cm ³
Crystal size [mm ³]	0.03x0.03x0.01
$\mu(\text{AgK}\alpha)$, λ (AgK α)	13.662 cm ⁻¹ , 56.051 pm
Diffractometer type, scan mode	Enraf-Nonius CAD4, ω -scan Graphite monochromator scintillation counter
Range for data collection	$4^\circ < 2\theta < 48^\circ$,
Limiting indices	$0 < h < 12$, $-12 < k < 0$, $0 < l < 49$
Scan-speed	variable, depending on I
Scan-width	1.1°
Reflections collected	2047
Independent reflections	1653
Reflections with $F < 2.0 \sigma(F)$	1210
Absorption correction	ψ -scan with 8 reflections
Refinement	Full-matrix least square method SHELX-97 ^{Error! Bookmark not defined.}
Number of free parameters	59
Goodness-of-fit on F^2	1.210
wR2	8.8 %
R1 (all 1653 Reflections)	5.4%

^a Powder diffraction data

Table S2. Anisotropic displacement factors for $\text{Pt}_2\text{In}_{14}\text{Ga}_3\text{O}_8\text{F}_{15}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	0.0061(2)	0.0061(2)	0.0054(3)	0	0	0.0031(1)
In(1)	0.0085(3)	0.0076(4)	0.0081(3)	-0.0018(3)	-0.0009(1)	0.0038(2)
In(2)	0.0072(4)	0.0214(3)	0.0092(3)	0.0009(1)	0.0019(3)	0.0036(1)
In(3)	0.0525(9)	0.0525(9)	0.0373(9)	0.000	0.000	0.0262(5)
Ga(1)	0.0096(9)	0.0096(9)	0.0040(9)	0.000	0.000	0.0048(4)
Ga(2)	0.0079(6)	0.0079(6)	0.0073(9)	0.000	0.000	0.0040(3)
O(1)	0.011(3)	0.007(4)	0.012(3)	-0.001(3)	-0.001(1)	0.0033(18)
O(2)	0.017(5)	0.017(5)	0.008(6)	0.000	0.000	0.008(2)
F(1)	0.029(3)	0.052(6)	0.032(4)	-0.031(4)	-0.016(2)	0.026(3)
F(2)	0.017(4)	0.017(4)	0.013(6)	0.000	0.000	0.0084(19)
F(3)	0.005(5)	0.005(5)	0.027(9)	0.000	0.000	0.002(2)
F(4)	0.025(9)	0.017(4)	0.018(4)	0.003(4)	-0.002(4)	-0.004(5)

Table S3. Exponents ζ_i and valence shell ionization potentials H_{ii} of Slater-type orbitals χ_i used for extended Hückel tight-binding calculation ^a

atom	χ_i	H_{ii} (eV)	ζ_i	C_1^b	ζ_i'	C_2^b
Ru	5s	-10.4	2.091	1.0		
Ru	5p	-6.90	1.420	1.0		
Ru	4d	-13.1	4.357	0.5225	2.265	0.5872
Ir	6s	-9.50	2.457	1.0		
Ir	6p	-4.50	1.810	1.0		
Ir	5d	-13.0	4.680	0.6009	2.490	0.5222
Pt	6s	-10.2	2.508	1.0		
Pt	6p	-4.00	1.840	1.0		
Pt	5d	-14.2	4.851	0.6105	2.588	0.5113
In	5s	-10.2	2.572	0.5823	1.477	0.5155
In	5p	-5.40	2.142	0.4828	1.149	0.6355
Sn	5s	-12.2	2.763	0.5995	1.625	0.4900
Sn	5p	-7.20	2.359	0.5222	1.320	0.5841
Bi	6s	-13.2	3.166	0.6501	1.898	0.4448
Bi	6p	-8.70	2.771	0.5789	1.604	0.5323

^a H_{ii} 's are the diagonal matrix elements $\langle \chi_i | H^{\text{eff}} | \chi_i \rangle$, where H^{eff} is the effective Hamiltonian. In our calculations of the off-diagonal matrix elements $H^{\text{eff}} = \langle \chi_i | H^{\text{eff}} | \chi_j \rangle$, the weighted formula was used (see: Ammeter, J.; Bürgi, H.-B.; Thibault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.).

^b Coefficients used in the double- ζ Slater-type orbital expansion.