Electronic Supplementary Material (ESI) for Dalton Transactions

$[PtBi_2I_{12}]^{2-}$: the first polyiodobismuthate containing octahedral heterometalic unit

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Computational details

Calculations of the electronic structure of anions $[PtBi_2I_{12}]^{2-}$, $[WBi_2I_{12}]^{2-}$ and $[HfBi_2I_{12}]^{2-}$ with D_{3d} symmetry have been analyzed on the basis of the spin-restricted ZORA method [1] implemented in the code ADF2012 [2]. We considered all relativistic effects (spin-orbit coupling and scalar effects) and used the local density approximation within the Vosko-Wilk-Nusair parametrization for local exchange correlations (LDA) [3] and generalized gradient approximation (GGA) functional BP86 [4,5]. The standard Slater type-orbital basis sets with triple-ξ quality plus one polarization function were employed for all atoms (TZP) [6]. The full geometry optimizations of the ground states were performed with the quasi-newtonian method [7]. Calculated vibrational spectra contain no imaginary frequencies. To study the effect of interactions between atoms of complex we used topological methods of quantum chemistry ELF (Electron Localization Function) and QTAIM (quantum theory of atoms in molecules) [8,9].

The ELF is assumed to approximate 1 in regions of space that are typical of the maximum localization of electron pairs with the antiparallel spins (colored blue in our drawings). The ELF is ~ 0.5 in regions where the electron density is close to that of the homogeneous electron gas (green) and ~0 in regions with delocalized electrons (red). The character of interatomic bonding can be inferred from the arrangement of the ELF basins, which consist of a set of all gradient lines of ELF that terminate at the local maximum point of the latter. Monosynaptic basins V(Y) are associated with the lone electron pairs; disynaptic basins V(Y1, Y2), with the two-center bonds; polysynaptic basins V(Y1, Y2…Yn), with many-center bonds and (where Yi are atoms).

According to the QTAIM, the structure of a many-electron system is completely determined by the set of the critical points of electron density $\rho(r, R)$ (r and R are the coordinates of electrons and nuclei), at which the electron density gradient $\nabla\rho$ (r, R) is zero. For non-degenerate states of system, only four types of the critical point of electron density are possible. These are as follows: *ncp* is the local maximum that corresponds to the positions of nuclei; *bcp* is the saddle bonding critical point; *rcp* is the saddle ring critical point; and *ccp* is cage critical point and the local minimum of $\rho(r, R)$. The numerical values of the parameters of the critical points such as the electron density $\rho(r, R)$, the Laplacian of electron density $\nabla^2\rho$(r,R), the ratio between the density kinetic energy G and the density potential energy U, the ratio between the density kinetic energy G, the density potential energy U and the electron density $\rho(r, R)$ at the critical points determine the character of interatomic interactions (covalence, ionicity, metallicity, etc.)

ELF of the anion $[PtBi_2I_{12}]^{2-}$ with optimized structure

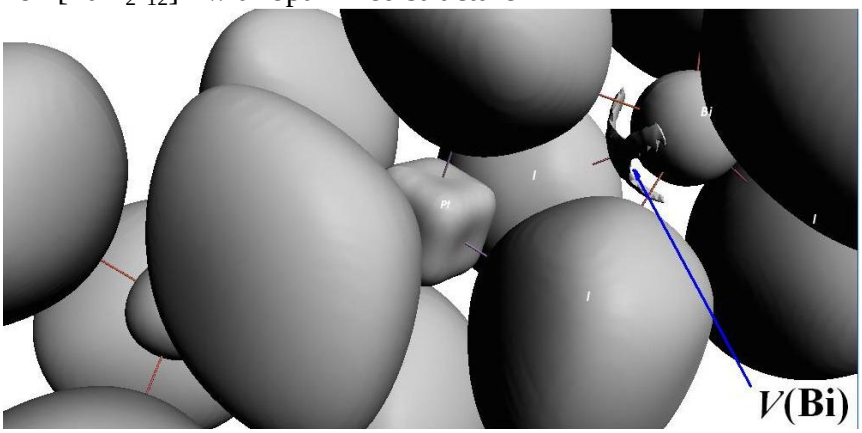

Figure 1S. The blue arrow points to the monosynaptic basin *V*(Bi) in anion $[PtBi_2I_9]^2$. Isosurface ELF is 0.385.

ELF of the anion $[WBi_2I_{12}]^{2-}$ with optimized structure

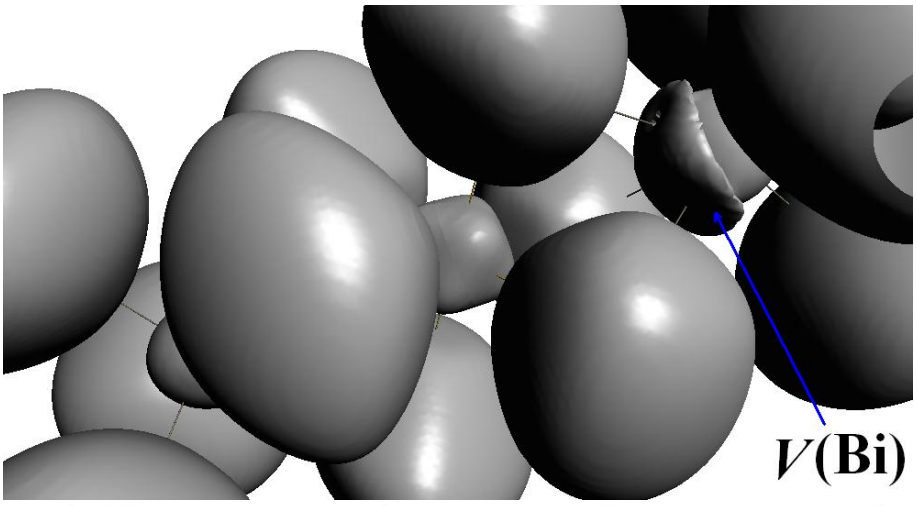

Figure 2S. The blue arrow points to the monosynaptic basin *V*(Bi) in anion $[WBi_2I_9]^2$. Isosurface ELF is 0.385.

ELF of the anion $[HfBi_2I_{12}]^{2-}$ with optimized structure

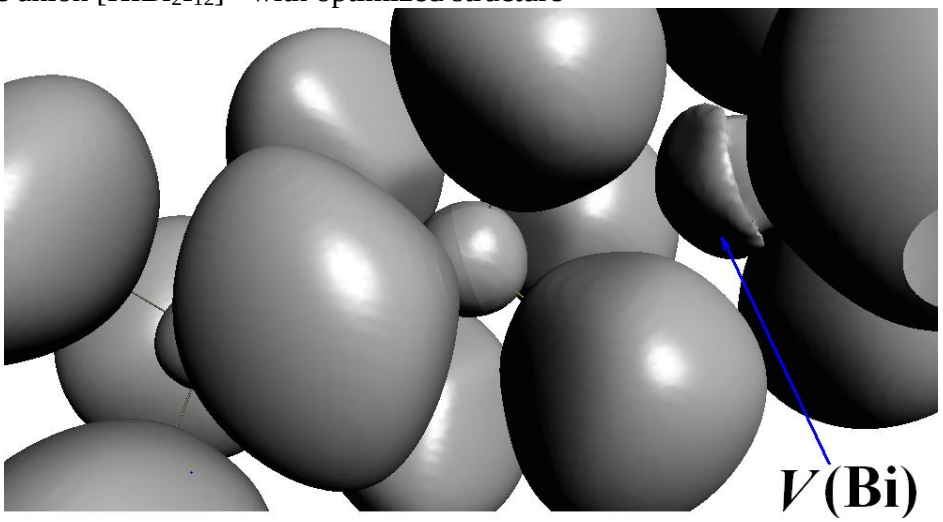

Figure 3S. The blue arrow points to the monosynaptic basin *V*(Bi) in anion $[HfBi_2I_9]^2$. Isosurface ELF is 0.385.

ELF of the anion $[WBi_2I_{12}]^{2-}$ with R(Bi-W)=3.600 Å.

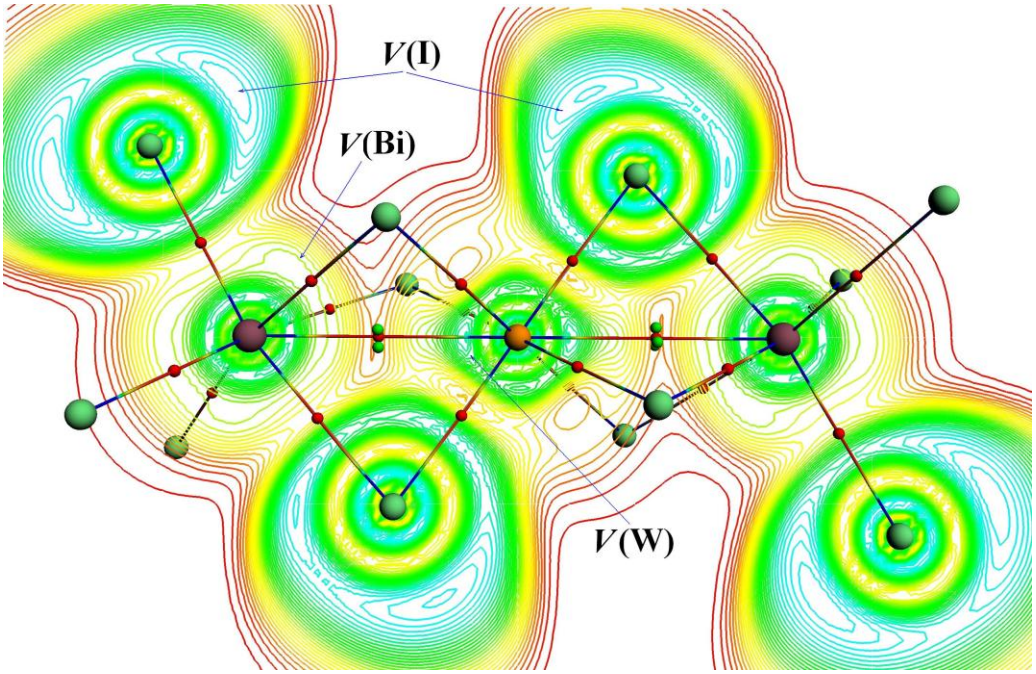

Figure 6S. Map of ELF and critical points in the $[Bi_2WI_{12}]^{2-}$ anion: *V*(Yi)-monosynaptic basin and critical points: bcp-red balls, ccp - blue balls and rcp - green balls. R(Bi-W)=3.600 Å.

ELF of the anion $[HfBi_2I_{12}]^{2-}$ with R(Bi-Hf)=3.000 Å.

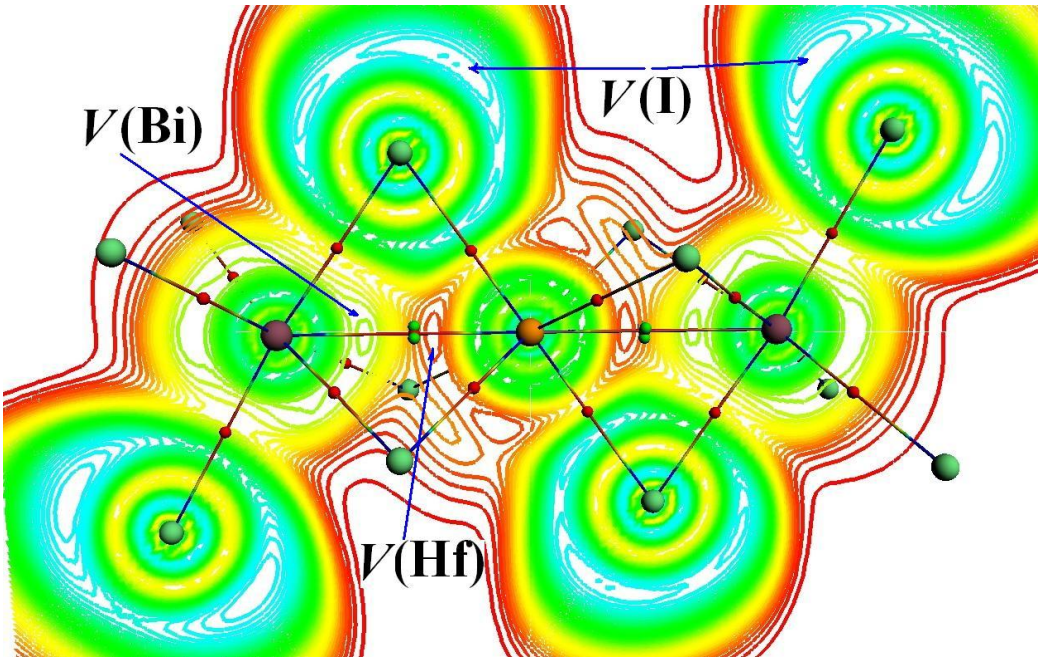

Figure 5S. Map of ELF and critical points in the $[Bi_2HfI_{12}]^{2-}$ anion: *V*(Yi)-monosynaptic basin and critical points: bcp-red balls, ccp - blue balls and rcp - green balls. R(Bi-Hf)=3.000 Å. *V*(Hf) - not filled monosynaptic basin.

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Selected interatomic distances (Å) and bond angles (deg) for **1**.

Bi(1)–I(1)	2.863(2)	Bi(2)···Pt(1)	4.101(2)
Bi(1)–I(2)	3.488(2)	Na(1)–O(1)	2.40(2)
Bi(2)–I(3)	3.338(2)	Na(1)–O(2)	2.40(2)
Bi(2)–I(4)	2.887(2)	Na(2)–O(2)	2.41(2)
Pt(1)–I(2)	2.6750(15)	Na(2)–O(3)	2.31(2)
Pt(1)–I(3)	2.6763(16)	Na(1)···Na(2)	3.27(2)
Bi(1)···Pt(1)	4.286(2)	Na(1)···Na(1)^{iii}	3.44(2)
I(1)–Bi(1)–I(1)^{i}	97.35(6)	I(2)–Pt(1)–I(3)^{i}	179.21(5)
I(1)–Bi(1)–I(2)	85.36(4)	I(3)–Pt(1)–I(3)^{i}	89.26(5)
I(1)–Bi(1)–I(2)^{i}	113.21(5)	Na(1)–O(1)–Na(1)^{iii}	91.6(8)
I(1)–Bi(1)–I(2)^{ii}	148.79(5)	Na(1)–O(2)–Na(2)	85.6(6)
I(2)–Bi(1)–I(2)^{i}	65.35(4)	O(1)–Na(1)–O(1)^{iv}	74.3(6)
I(3)–Bi(2)–I(3)^{i}	68.56(5)	O(1)–Na(1)–O(2)	105.5(5)
I(3)–Bi(2)–I(4)	91.93(6)	O(1)–Na(1)–O(2)^{iv}	175.4(5)
I(4)–Bi(2)–I(3)^{i}	96.97(6)	O(1)–Na(1)–O(2)^{v}	101.1(5)
I(4)–Bi(2)–I(3)^{ii}	158.69(6)	O(2)–Na(2)–O(2)^{iv}	78.7(7)
I(4)–Bi(2)–I(4)^{i}	99.15(7)	O(2)–Na(2)–O(3)	89.0(8)

I(2)–Pt(1)–I(2)^{i}	89.49(5)	O(2)–Na(2)–O(3)^{iv}	163.9(9)
I(2)–Pt(1)–I(3)	90.08(5)	O(2)–Na(2)–O(3)^{v}	88.9(7)
I(2)^{i}–Pt(1)–I(3)	91.17(5)	O(3)–Na(2)–O(3)^{iv}	101.2(9)

Symmetry operations to generate equivalent atoms: (i) $1 - x + y, 1 - x, z$; (ii) $1 - y, x - y, z$; (iii) $x - y, - y, - z$; (iv) $- y, x -$ y, z; (v) $- x + y, - x, z$.

Table 3. Selected topological parameters of electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), density of total energy (E), and ratio E/ρ (degree of binding) in a.u. at bcp in the $[WBi_2I_{12}]^{2-}$ anion with interatomic distance R_{Bi-W} = 3.6 00 Å.

	R	ρ	$\nabla^2\rho$	E	E/ρ
Bi-W	3.600	0.019	0.035	-0.001	-0.051
Bi-I_t	3.007	0.041	0.054	-0.010	-0.232
I_{br}-Bi	2.997	0.040	0.066	-0.008	-0.198
I_{br}-W	2.793	0.055	0.081	-0.016	-0.293

Table 4. Selected topological parameters of electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), density of total energy (E), and ratio E/ρ (degree of binding) in a.u. at bcp in the $[HfBi_2I_{12}]^{2-}$ anion with interatomic distance R_{Bi-Hf} = 3.3 Å.

	R	ρ	$\nabla^2\rho$	E	E/ρ
Bi-Hf	3.300	0.022	0.040	-0.002	-0.074
Bi-I_t	2.997	0.042	0.056	-0.010	-0.236
I_{br}-Bi	2.848	0.051	0.085	-0.013	-0.256
I_{br}-Hf	2.866	0.049	0.069	-0.013	-0.267