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Hybrid iodobismuthates code: adapting the geometry of Bi polyhedra to weak interactions

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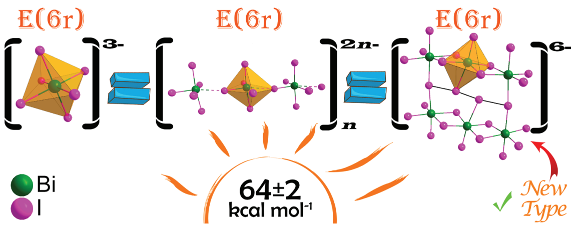
The crystal structure of the new iodobismuthate $(PyPy)_2(PyPyH)_2Bi_6I_{26}$ was found to consist of unusual hexanuclear $[Bi_6I_{26}]^{6-}$ anions containing the linear I_4^{2-} unit, and the experimental Bi–I bond lengths in this anion were used to obtain the relationship between bond length and bond energy. A statistical analysis of 229 crystal structures of iodobismuthates, based on the quantum chemically estimated strength of Bi–I bonds, revealed that the total energy of the Bi^{3+} polyhedron remains virtually constant at 64 ± 2 kcal mol^{-1}, regardless of its geometry within this family of materials. Thus, the polyhedron geometry flexibly adapts to the relatively weak interactions between iodobismuthate anions and embedded cations.



Keywords: iodobismuthates, Cambridge structural database, density functional theory, intermolecular interactions, bond length, bond energy, net energy conservation, bismuth–iodine polyhedron.

Currently, hybrid halometallate complexes comprising cations of organic bases are of high interest due to their valuable luminescent, thermochromic, photocatalytic and photogalvanic properties.[1–6] Among these, the compounds with a perovskite structure are under the most intensive study as promising candidates for application in high-efficiency photovoltaic systems, such as solar cells.[7–9] In this area, lead(II) derivatives are the most effective. Indeed, solar cells based on methylammonium and formamidinium iodoplumbates have been reported[10–13] to demonstrate an efficiency of more than 25%, comparable to that of Si-based cells.[14] However, the potential application of Pb-based perovskites as light-absorbers in solar cells is hindered by their high toxicity and low hydrolytic stability,[15] which inspires the search for alternative systems without these drawbacks.

Among such alternatives, hybrid halobismuthate complexes, mainly iodobismuthates, are the most promising due to their high stability to hydrolysis and low toxicity. Besides, these complexes have a considerable and still expanding structural diversity[16,17] comprising mono-, oligo- and polynuclear iodobismuthate anions of various dimensionality. On the one hand, this diversity hints at the possibility of fine-tuning the characteristics of these compounds, such as the optical band gap (E_g), essential for their practical application. Indeed, although the E_g value of most hybrid iodobismuthates exceeds that of methylammonium and formamidinium iodoplumbates (E_g = 1.51 eV),[18] there are several iodobismuthates with E_g close to that of the mentioned Pb derivatives, *e.g.*, compounds comprising methyl viologen[19–22] or 1,1′-(1,5-pentanediyl)-bis(4-methylpyridinium)[23] cations and linear 1D polynuclear $[BiX_5]_n^{2n-}$ anions.

On the other hand, the large structural diversity of hybrid iodobismuthates hinders the rational design of compounds with specific structural features and desired properties. Hence, the applicability of crystal engineering to create halobismuthates with a given structure and properties remains an important but unsolved task. The complexity of this task is due to the simultaneous action of several factors influencing the crystal formation. Among the most significant of these factors are the energetic benefits of the formation of the corresponding $[Bi_xHal_y]^{z-}$ polyhedra, as well as weak intermolecular interactions such as van der Waals forces, hydrogen and halogen bonds.[24–26]

Here, we report the possibility of narrowing the range of these factors for the family of hybrid iodobismuthate complexes. Namely, statistical analysis of a representative sample of 229 crystal structures of hybrid iodobismuthates available in the

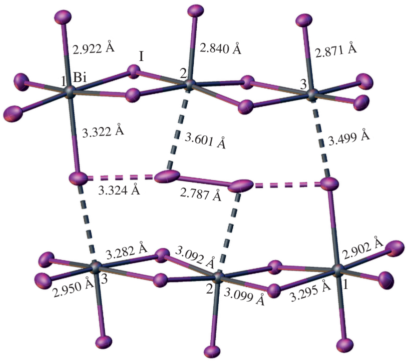


Figure 1 The structure of $[Bi_6I_{26}]^{6-}$ anion in complex **1**. The numbers of Bi atoms and the lengths of selected bonds are shown.

Cambridge Structural Database (CSD), based on the quantum-chemically obtained relationship between bond length and bond strength, allowed us to reveal the 'conservation' of the net interaction energy of bismuth polyhedra at 64 ± 2 kcal mol^{-1}, despite their diversity. Such conservation makes the difficultly predictable cation–iodobismuthate and anion–anion interactions the main factors that determine the structure of the iodobismuthate anion and, therefore, the properties of the compound in each particular case.

As part of a systematic study of hybrid halobismuthates, we have synthesized three new complexes with 1,4′-bipyridinium monocation $[PyPy]^+$ and dication $[PyPyH]^{2+}$ as counterions, namely iodobismuthates $(PyPy)_2(PyPyH)_2Bi_6I_{26}$ **1** and $(PyPyH)_2Bi_2I_{10}{\cdot}H_2O$ **2** together with bromobismuthate $(PyPyH)_2Bi_2Br_{10}$ **3**.[†] The iodobismuthate anion in complex **1** has an unprecedented structure (Figure 1),[‡] with the I_4^{2-} moiety clutched between two $Bi_3I_{11}^{2-}$ fragments.

Quantum chemical calculations of the crystal structure of complex **1** were carried out by the density functional theory (DFT) method in VASP[27] using the PBE functional[28] with the D3 empirical dispersion correction[29] and a plane-wave basis set.[§] Since the crystal structure of complex **1** includes symmetry-induced disordering of 1,4′-bipyridinium cations, which consists in disordering the H atom involved in the N–H···N bond, DFT calculations were performed for the model system obtained by reducing the symmetry of the experimentally established structure, namely $P2_1/n \rightarrow P1$. The mentioned model was optimized so that the geometry of the cation and anion was in good agreement with the experiment.[†] The electron density distribution in it was analyzed within the QTAIM framework,[30,31] which makes it possible to identify the bonding interatomic interactions.[32] QTAIM analysis has shown that each Bi atom in complex **1** is bonded to six iodine atoms (see Figure 1), making this structure the first example of an I_4^{2-} anion in which all four I atoms are coordinated.[†]

Besides identifying bonding interactions, QTAIM is also capable of estimating their energies using the Espinosa–Mollins–Lecomte correlation scheme: $E_{\text{bond}} \approx -0.5V(r)$, where $V(r)$ is electron potential energy density at the so-called bond critical point.[31] Although this relation is commonly used for non-covalent interactions, it can be reliably applied to estimate the bond strength of other bond types.[33] Using this relation, we have calculated the energies of all 72 independent (due to the symmetry reduction) Bi–I bonds in complex **1**, whose lengths after optimization varied from 2.893 to 3.569 Å. The considerable range of Bi–I bond lengths allowed us to construct an equation relating the Bi–I bond length to its energy.[†] This dependency can be perfectly ($R^2 = 0.9993$) described by an exponential function:

$$E(r) = 40352e^{-2.683r} \qquad (1)$$

Notably, the stronger (shorter) Bi–I bonds in the BiI_6 octahedron are opposed by the weaker (longer) ones (see Figure 1). Application of equation (1) to the experimental bond lengths in complex **1** revealed that all linear I–Bi–I fragments have an almost constant net energy of the two Bi–I bonds (Table 1). That is, each pair of *trans*-Bi–I bonds has a total energy in the range of 20.0–22.6 kcal mol^{-1}, despite the fact that the energies of individual bonds vary from 2.6 to 19.8 kcal mol^{-1}. This result agrees well with the known[25] constancy of the *trans*-{I···I} distances in these compounds. Since each BiI_6 octahedron consists of three linear I–Bi–I fragments, the energies of the BiI_6 octahedra in complex **1** are also almost constant and amount to 63.1–66.3 kcal mol^{-1} (see Tables 1 and S3[†]).

This unexpected observation led us to hypothesize the conservation of the net energy of the $\{I\text{–}Bi\text{–}I\}^+$ and $\{BiI_6\}^{3-}$ moieties in various $[Bi_xI_y]^{z-}$ structures, similar to the previously reported net energy conservation of alkali metal cations[34] (Na^+ and K^+) and small anions[35] (CN^-, NCO^- and $MeCOO^-$). To test this hypothesis, we analyzed all 229 structures of hybrid iodobismuthates available in the CSD[36] (ver. 09.2019) that do not contain disordered $\{BiI_6\}^{3-}$ moieties or other halide anions. As a result, 262 $[Bi_xI_y]^{z-}$ anions were found. Analysis of these crystal structures revealed (Tables 2 and S4–S9[†]) that the average net energies of Bi polyhedra are, indeed, nearly unchanged at 64.4 ± 1.6 kcal mol^{-1}. The mean value and standard deviation

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[†] See details in Online Supplementary Materials.

[‡] *Crystal data for* **1**. $C_{40}H_{38}Bi_6I_{26}N_8$ ($M = 5184.06$), monoclinic, space group $P2_1/n$, $a = 19.6445(4)$, $b = 10.7663(2)$ and $c = 22.7879(5)$ Å, $\beta = 108.6870(10)°$, $V = 4565.53(16)$ Å^3, $Z = 2$, $T = 150(2)$ K, $d_{\text{calc}} = 3.771$ g cm^{-3}. Total of 112612 reflections were collected ($2.114° < \theta < 30.083°$), $\mu = 20.345$ mm^{-1}, 13402 independent reflections ($R_{\text{int}} = 0.0671$). Data / restraints / parameters: 13402 / 0 / 362. The final refinement parameters were: $R_1 = 0.0551$, $wR_2 = 0.1075$ for reflections with $I > 2\sigma(I)$; $R_1 = 0.0443$, $wR_2 = 0.1028$ for all reflections; largest diff. peak/hole 2.195, –1.737 e Å^{-3}. GOF = 1.132.

Crystal data for **2**. $C_{20}H_{22}Bi_2I_{10}N_4O$ ($M = 2021.37$), monoclinic, space group $P2_1/n$, $a = 11.7948(2)$, $b = 11.8919(2)$ and $c = 14.8191(3)$ Å, $\beta = 107.2420(10)°$, $V = 1985.16(6)$ Å^3, $Z = 2$, $T = 150(2)$ K, $d_{\text{calc}} = 3.382$ g cm^{-3}. Total of 50428 reflections were collected ($2.237° < \theta < 30.541°$), $\mu = 16.649$ mm^{-1}, 6060 independent reflections ($R_{\text{int}} = 0.0357$). Data / restraints / parameters: 6060 / 0 / 176. The final refinement parameters were: $R_1 = 0.0328$, $wR_2 = 0.0701$ for reflections with $I > 2\sigma(I)$; $R_1 = 0.0275$, $wR_2 = 0.0679$ for all reflections; largest diff. peak/hole 1.701, –1.363 e Å^{-3}. GOF = 1.035.

Crystal data for **3**. $C_{20}H_{20}Bi_2Br_{10}N_4$ ($M = 1533.46$), monoclinic, space group $P2_1/n$, $a = 10.9615(5)$, $b = 11.5477(5)$ and $c = 14.0770(7)$ Å, $\beta = 107.9990(10)°$, $V = 1694.67(14)$ Å^3, $Z = 2$, $T = 120(2)$ K, $d_{\text{calc}} = 3.005$ g cm^{-3}. Total of 22971 reflections were collected ($2.329° < \theta < 30.031°$), $\mu = 22.178$ mm^{-1}, 4954 independent reflections ($R_{\text{int}} = 0.0583$). Data / restraints / parameters: 4954 / 0 / 163. The final refinement parameters were: $R_1 = 0.0383$, $wR_2 = 0.0696$ for reflections with $I > 2\sigma(I)$; $R_1 = 0.0291$, $wR_2 = 0.0664$ for all reflections; largest diff. peak/hole 2.466, –1.596 e Å^{-3}. GOF = 1.027.

Experimental single-crystal X-ray diffraction (XRD) data for compounds **1**–**3** were collected on a Bruker SMART APEX2 instrument. Due to the absence of well-faceted crystals, the absorption was taken into account by a semiempirical method based on equivalents using SADABS. The structures were determined using a combination of the direct method and Fourier syntheses. The structures were refined by the full-matrix anisotropic least squares method. All the calculations were carried out using SHELXS and SHELXL software.

CCDC 2017690–2017692 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[§] All DFT calculations were performed within the framework of the PBE exchange-correlation functional using VASP 5.4.1. Atomic cores were described using PAW potentials. Valence electrons (2*s* and 2*p* for N atoms; 5*d*, 6*p*, and 6*s* for Bi; 4*s* and 4*p* for Br; 1*s* for H) were described in terms of a plane-wave basis set (the kinetic energy cutoff was 900 eV).

Table 1 Bi–I binding energies calculated from the experimental lengths of Bi–I bonds in the crystal structure of complex **1**.

Polyhedron	r(Bi–I)/Å	Energy/kcal mol^{-1}		
		$E(r)^a$	$E_{trans\text{-pair}}{}^b$	$E_{\text{polyhedron}}{}^c$
Bi1^d	2.902	16.77	22.61	66.34
	3.295	5.84		
	2.905	16.63	22.41	
	3.299	5.78		
	2.922	15.89	21.32	
	3.322	5.43		
Bi2	2.840	19.80	22.37	63.12
	3.601	2.57		
	3.079	10.43	20.80	
	3.081	10.37		
	3.092	10.07	19.95	
	3.099	9.88		
Bi3	2.871	18.22	21.60	63.43
	3.499	3.38		
	2.930	15.55	21.04	
	3.318	5.49		
	2.950	14.74	20.79	
	3.282	6.05		
Average	3.127	10.72	21.43	64.30

[a] $E(r)$ is the energy of a single Bi–I bond. [b] $E_{trans\text{-pair}}$ is the net energy of two Bi–I bonds in the linear I–Bi–I moiety. [c] $E_{\text{polyhedron}}$ is the net energy of six Bi–I bonds in the BiI_6 moiety. [d] See the numbering of Bi atoms in Figure 1.

Table 2 Mean, standard deviation, minimum and maximum values of the $E_{\text{polyhedron}}$ energy for crystal structures containing different $[Bi_xI_y]^{z-}$ moiety and determined at different temperatures.^{a}

Subset of structures	$<E>$	σ	min	max	Total count
All structures	64.4	1.6	55.6	72.9	262
$[BiI_4]_n^{n-}$	64.7	0.7	62.5	66.1	33
$[BiI_6]^{3-}$	63.1	2.2	55.6	68.1	31
$[Bi_2I_9]^{3-}$	64.2	1.5	59.3	69.2	53
$[Bi_2I_{10}]^{4-}$	63.9	1.1	61.5	66.2	25
trans-$[Bi_3I_{12}]^{3-\ b}$	65.1	1.2	62.5	67.2	24
α-$[Bi_4I_{16}]^{4-\ b}$	65.3	1.8	63.2	72.9	23
All structures (150 K)	64.3	1.2	60.2	66.1	51
All structures (295 K)	64.1	1.6	55.6	69.2	128
trans-bond pairs^c	21.5	1.1	12.0	27.0	1479

[a] All energy values are given in kcal mol^{-1}. [b] Structures containing α-$[Bi_4I_{16}]^{4-}$ and *trans*-$[Bi_3I_{12}]^{3-}$ were determined according to the published data.[16] [c] Values for $E_{trans\text{-pair}}$ energy.

also hardly differ among crystal structures from different subsets corresponding to specific structural motifs or XRD measurement temperatures. Thus, we observe almost complete indifference of the $E_{\text{polyhedron}}$ value to the structure of the polyhedron. Moreover, despite the well-known dependence of bond lengths on temperature, we see no differences (exceeding the accuracy of the evaluation) in the conserved net energies when comparing compounds studied at 150 ± 5 and 295 ± 5 K (see Tables 2, S10 and S11[†]).

Note that the 'three sigma rule' applied to the $E_{\text{polyhedron}}$ values of all 262 structures also results in a rather small change in the stabilization energy of the $\{BiI_6\}^{3-}$ fragment, which is in the range of 59.6–69.2 kcal mol^{-1} for > 99% of the structures. This change has the same order of magnitude as the energy of intermolecular interactions in organic and organoelement crystals. Moreover, it is important to note that the stabilization energy of the $\{BiI_6\}^{3-}$ polyhedron does not depend on the formal coordination number of the Bi atom. For example, analysis of the QEPXIS[37] and SOXXUZ[38] from CSD demonstrated that distorted tetragonal-pyramidal and trigonal-bipyramidal $\{BiI_5\}^{2-}$ polyhedra have stabilization energy very close to that for $\{BiI_6\}^{3-}$ fragments (66.3 and 61.1 kcal mol^{-1}, respectively).

Then, our statistical analysis confirms the conservation of the net energy of *trans*-{I–Bi–I} bond pairs at the level of 21.5 ± 1.1 kcal mol^{-1}, which corresponds to 1/3 of the total energy of Bi–I bonds in the $\{BiI_6\}$ octahedron. The obtained distribution of the $E_{trans\text{-pair}}$ values is undoubtedly Gaussian-like with $R^2 = 0.991$ (Figure S8[†]). Thus, the results of statistical analysis performed on a sufficiently large and representative sample of iodobismuthate complexes show that the total energy of the main structural units, namely *trans*-{I–Bi–I} and $\{BiI_x\}$ moieties, remains virtually constant regardless of the anion structure. This means that Bi polyhedra flexibly adapt to weak intermolecular interactions, such as electrostatic, van der Waals, hydrogen bonds and Hal···Hal interactions. These findings affect the design of the crystal structures of iodobismuthates in several ways: (1) the discovered conservation of net energy of the *trans*-$\{I–Bi–I\}^+$ and $\{BiI_6\}^{3-}$ moieties should be explicitly incorporated into the force field to allow proper flexibility of these moieties, and (2) electrostatic and other intermolecular interactions should receive particular attention as the main forces determining the crystal structure of iodobismuthates.

In summary, we have synthesized compound **1,** which includes unusual hexanuclear anions, $[Bi_6I_{26}]^{6-}$, containing the first example of I_4^{2-} with all iodine atoms being coordinated. The presence of 72 independent Bi–I interactions in this compound allowed us, with the help of DFT calculations, to derive equation (1), relating the length of the Bi–I bond to its energy. Using this equation, we have analyzed the energy state of all 229 iodobismuthate structures available in the CSD and found that although the strength of individual Bi–I bonds varies in the range of 2–20 kcal mol^{-1}, the net interaction energy in *trans*-{I–Bi–I} bond pairs and $\{BiI_x\}$ polyhedra are highly unchanged, being 21.5 ± 1.1 and 64.4 ± 1.6 kcal mol^{-1}, respectively. This result allows us to consider bismuth–iodine polyhedra as a new example of 'net energy conservation of weak interactions', which was found earlier for alkali metal cations (Na^+ and K^+) and small anions (CN^-, NCO^- and $MeCOO^-$). This conservation occurs regardless of geometry of a particular $[Bi_xI_y]^{z-}$ anion, crystal packing, anionic or cationic composition. Thus, we conclude that the energy of the crystal structure of iodobismuthate weakly depends on the stability of the Bi polyhedron. The order of magnitude of the energy variations upon changing the Bi polyhedra corresponds to that of weak non-covalent interactions in the second coordination sphere, such as electrostatic, van der Waals, intermolecular hydrogen and halogen bonds, which should receive particular attention in future modeling of these compounds. Besides, our results suggest that some coordination polyhedra may play a less significant role in determining the crystal structures of corresponding compounds, with inevitable consequences for their crystal engineering.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.03.007.

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