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

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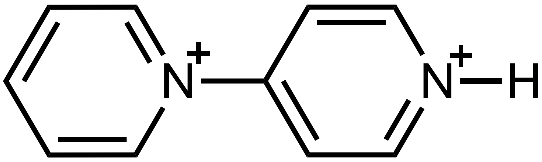
Content

Synthetic details

As part of a systematic study of hybrid halobismuthates, we have synthesized three new complexes with 1,4′-bipyridinium monocation (PyPy) and dication (PyPyH) as counterions (Scheme 1), 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**).



Scheme 1 Dication of 1,4′-bipyridinium, $[PyPyH]^{2+}$.

Synthesis of $[PyPy]_2[PyPyH]_2Bi_6I_{26}$ (1) and $[PyPyH]_2Bi_2I_{10}\cdot H_2O$ (2). An aqueous solution (10 ml) of $Bi(NO_3)_3\cdot 5H_2O$ (1.06 g, 2.2 mmol) and KI (2.90 g, 17.5 mmol) was added to an aqueous solution (10 ml) of 1,4′-bipyridinium chloride (0.50 g, 2.2 mmol) with stirring, then allowed to stand for a week. The resulting red crystalline precipitate containing crystals suitable for structural characterization was filtered under vacuum, washed with 96% ethanol and dried in air. Yield: 1.31 g. According to powder XRD (Figures S1 and S10), a mixture of **$[PyPyH]_2Bi_2I_{10}\cdot H_2O$** (62%) and **$[PyPy]_2[PyPyH]_2Bi_6I_{26}$** (38%) was formed. Details of the structure refinement by the Rietveld method:

complex **1,** space group $P2_1/n$, a = 19.7029(38), b = 10.8673(21) and c = 22.8604(40) Å, β = 108.561(15)°;

complex **2,** space group $P2_1/n$, a = 11.7691(9), b = 11.9211(9) and c = 14.9521(11) Å, β = 107.172(6)°;

R_{exp} = 3.20%, R_{wp} = 8.61%, R_p = 6.19%, GOF = 2.69.

Synthesis of $[PyPyH]_2Bi_2Br_{10}$ (3). An aqueous solution (10 ml) of $Bi(NO_3)_3\cdot 5H_2O$ (1.06 g, 2.2 mmol) and KBr (2.08 g, 17.5 mmol) was added to an aqueous solution (10 ml) of 1,4′-bipyridinium chloride (0.50 g, 2.2 mmol) with stirring, then allowed to stand for 1 day. The resulting colorless crystalline precipitate was filtered under vacuum, washed with 96% ethanol and dried in air. Yield: 1.13 g (67%). The single-phase state of the sample was confirmed by powder XRD (Figures S1 and S9). Details of the structure refinement by the Rietveld method: space group $P2_1/n$, a = 11.0361(3), b = 11.5865(6) and c = 14.1786(7) Å, β = 107.633(3)°, R_{exp} = 2.74%, R_{wp} = 9.16%, R_p = 6.42%, GOF = 3.35.

Details on XRD crystal structure determination

Experimental single crystal XRD data for compounds **1-3** were collected on a Bruker SMART APEX2 instrument (Table S1). 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.

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, β = 108.6870(10)°, V = 4565.53(16) Å^3, Z = 2, T = 150(2) K, d_{calc} = 3.771 g cm^{-3}. Total of 112612 reflections were collected (2.114° < θ <30.083°), μ = 20.345 mm^{-1}, 13402 independent reflections (R_{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, β = 107.2420(10)°, V = 1985.16(6) Å^3, Z = 2, T = 150(2) K, d_{calc} = 3.382 g cm^{-3}. Total of 50428 reflections were collected (2.237° < θ <30.541°), μ = 16.649 mm^{-1}, 6060 independent reflections (R_{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, β = 107.9990(10)°, V = 1694.67(14) Å^3, Z = 2, T = 120(2) K, d_{calc} = 3.005 g cm^{-3}. Total of 22971 reflections were collected (2.329° < θ <30.031°), μ = 22.178 mm^{-1}, 4954 independent reflections (R_{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.

CCDC 2017690–2017692 contain the supplementary crystallographic data for compounds **1**–**3**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:(+44) 1223-336-033; e-mail:deposit@ccdc.cam.ac.uk.

The crystal structure of complex **1** is formed by centrosymmetric hexanuclear $[Bi_6I_{26}]^{6-}$ anions (Figure 1) and crystallographically independent $[PyPyH]^{2+}$ and $[PyPy]^{+}$ cations connected by the hydrogen bond N–H…N, where the corresponding N…N distance is equal to 2.70 Å. At first glance, the ratio of the semiaxes of the I(3,7) atomic displacement ellipsoids suggests that the central I_4^{2-} moiety consists of I^- and I_3^- anions. However, our attempts to model the corresponding disorder were unsuccessful, while the interatomic distances in I_4^{2-} were found to be similar to those in the structurally characterized I_4^{2-} anions. The asymmetric geometry of I_4^{2-} in complex **1** is in accordance with the dissimilarity of Bi…I contacts between I_4^{2-} and $[Bi_3I_{11}]^{2-}$ fragments, which should support bismuth polyhedra. Among them, the most elongated Bi2…I7 contact (3.601 Å) is of particular interest, since it can significantly affect the stability of the Bi2 polyhedron.

The crystals of complexes **2** and **3** are formed by cations $[PyPyH]^{2+}$ and centrosymmetric anions $[Bi_2X_{10}]^{4-}$ [X = I (**2**) and Br (**3**)]. In the case of complex **2**, the crystals also contain lattice H_2O molecules (Figure S2). In general, the crystal structures of complexes **2** and **3** are similar (Figures S2–S5), and the theoretical powder XRD patterns of the corresponding 'normalized'[†] structures are identical [Figure S1(*b*)]. Instead of H_2O molecules in complex **2**, small voids (13 Å^3) are involved in the structure of complex **3** (Figure S5). The shortest X…X contacts are equal to 4.18 (**2**) and 4.02 (**3**) Å. An increase in the Bi–I bond lengths by ~ 0.2 Å and in the I…I distances in complex **2** (Table S2) as compared to the corresponding values of Bi–Br and Br…Br in complex **3** leads to an increase in the unoccupied volume. Besides, the absence of lattice H_2O molecules in structure **3** results in an even more significant change in cell parameters. In general, the addition of one non-hydrogen atom leads to an increase in the volume of the formula unit by 140 Å^3 (V/Z = 993 and 847 Å^3 for complexes **2** and **3**, respectively).

Details on quantum chemical calculations

All DFT calculations were performed with 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 at 900 eV).

Details on CSD search

The CSD (version 5.41, updated in March 2020) contains data on 10 structures with coordinated I_4^{2-} moiety (see pp. 15–18). Although in these cases the I_4^{2-} moiety also acts as a bridging ligand, the coordination was observed only through the two terminal I atoms. Thus, structure **1** can be reliably considered the first representative of both iodobismuthates containing unusual hexanuclear $[Bi_6I_{26}]^{6-}$ anions, and structures with the I_4^{2-} anion, in which all four I atoms are coordinated.

Since it was impossible to formalize the search unambiguously, the following main criteria were applied: (*a*) I…I…I…I moiety, (*b*) lengths of bonds and/or intra- and intermolecular contacts I…I in the range of 2.6–3.6 Å, (*c*) I…I…I angles in the range of 150–180° and (*d*) coordination of at least one I atom by any metal. The resulting sample, consisting of several dozen structures, was examined manually.

Bond energies reliabilities

Equation (1) (see main text) is also applicable to estimate binding energies from experimental Bi–I distances (Table 1). In this case, the energies of specific Bi–I bonds [$E(r)$],

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[†] Normalization implies removing the H_2O molecule from structure **2** and taking the unit cell parameters and scattering curves of structure **2** for both structures.

calculated from experimental distances, can be 13.3% higher (r_{exp}= 2.840) and 9.0% lower (r_{exp}= 3.601) than the corresponding values derived from the calculated bond lengths. Taking into account that the maximum difference between the Bi–I bond lengths occurs within one Bi polyhedron, we also calculated the total energy for a pair of Bi–I bonds inside the $\{\mathrm{I–Bi–I}\}^+$ moieties having the *trans* position of iodine atoms ($E_{trans\text{-pair}}$)[‡]. For 9 such pairs in the $[\mathrm{Bi_6I_{26}}]^{6-}$ anion, the energies calculated from the experimental Bi–I distances are 5.2–10.7% higher than those obtained from the calculated distances, *i.e.*, the systematic error in calculating the energy significantly decreases when the energies of *trans*-Bi–I bonds are summed up. The total energy of Bi–I bonds in $\mathrm{BiI_6}$ polyhedra is 6.9–8.2% higher than the corresponding values obtained from the calculated distances.

Thus, the calculation of the energy of a particular Bi–I bond from the experimental distances in the $[\mathrm{Bi_6I_{26}}]^{6-}$ anion is complicated by a significant systematic error with different signs. However, the corresponding calculations for the *trans*-{I–Bi–I} or $\{\mathrm{BiI_6}\}$ moieties give close and significantly smaller values of the systematic error, which also allows us to use equation (1) to estimate the total energies of the $\{\mathrm{BiI_6}\}$ octahedra.

[‡] Such a moiety was considered because distorted $\mathrm{BiI_6}$ octahedra with Bi atom displaced towards one of the vertices, edges or faces can be regarded as a structural unit in most known iodobismuthate anions. As a result, three pairs of Bi–I bonds with close sums of bond lengths within the I–Bi–I moiety can be considered in each structure.

Table S1 Crystal data and structure refinement for **1**–**3**.

Identification code	**1**	**2**	**3**
Empirical formula	$C_{40}H_{38}Bi_6I_{26}N_8$	$C_{20}H_{22}Bi_2I_{10}N_4O$	$C_{20}H_{20}Bi_2Br_{10}N_4$
Formula weight	5184.06	2021.37	1533.46
Temperature/K	150(2)	150(2)	120(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	19.6445(4)	11.7948(2)	10.9615(5)
b/Å	10.7663(2)	11.8919(2)	11.5477(5)
c/Å	22.7879(5)	14.8191(3)	14.0770(7)
β/deg	108.6870(10)	107.2420(10)	107.9990(10)
Volume/Å^3	4565.53(16)	1985.16(6)	1694.67(14)
Z	2	2	2
D (calc), Mg m^{-3}	3.771	3.382	3.005
μ/mm^{-1}	20.345	16.649	22.178
F(000)	4420	1748	1368
Crystal size/mm	0.24 × 0.24 × 0.08	0.12 × 0.08 × 0.06	0.24 × 0.16 × 0.12
θ range/deg	2.114–30.083	2.237–30.541	2.329–30.031
Index ranges	$-27 \le h \le 27$	$-16 \le h \le 16$	$-15 \le h \le 15$
	$-15 \le k \le 15$	$-16 \le k \le 16$	$-16 \le k \le 16$
	$-32 \le l \le 32$	$-21 \le l \le 21$	$-19 \le l \le 19$
Reflections collected	112612	50428	22971
Independent reflections, R_{int}	13402, 0.0671	6060, 0.0357	4954, 0.0583
Completeness to θ = 25.242° (%)	100.0	100.0	100.0
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max., min. transmission	0.0504, 0.0117	0.0998, 0.0511	0.7461, 0.2721
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	13402 / 0 / 362	6060 / 0 / 176	4954 / 0 / 163
Goodness-of-fit	1.132	1.035	1.027
$R1$, $wR2$ [I>2sigma(I)]	0.0443, 0.1028	0.0275, 0.0679	0.0291, 0.0664
$R1$, $wR2$ (all data)	0.0551, 0.1075	0.0328, 0.0701	0.0383, 0.0696
Largest diff. peak and hole/e Å^{-3}	2.195, -1.737	1.701, -1.363	2.466, -1.596

Table S2 Bond lengths (Å) in complexes **1**–**3**.

Complex **1**

Bi(1)-I(6)	2.9024(6)
Bi(1)-I(4)	2.9055(7)
Bi(1)-I(5)	2.9222(6)
Bi(1)-I(1)	3.2950(6)
Bi(1)-I(2)	3.2994(6)
Bi(1)-I(3)	3.3216(6)
Bi(2)-I(10)	2.8397(6)
Bi(2)-I(8)	3.0788(6)
Bi(2)-I(2)	3.0812(6)
Bi(2)-I(9)	3.0917(6)
Bi(2)-I(1)	3.0991(6)
Bi(3)-I(12)	2.8710(6)
Bi(3)-I(11)	2.9298(7)
Bi(3)-I(13)	2.9501(6)
Bi(3)-I(9)	3.2820(6)
Bi(3)-I(8)	3.3177(7)
Bi(3)-I(3)	3.499
I(3)-I(7)	3.3239(12)
I(7)-I(7) (-x,-y,-z)	2.7864(18)

Complex **2**

Bi(1)-I(5)	2.9504(3)
Bi(1)-I(2)	3.0012(4)
Bi(1)-I(3)	3.0284(4)
Bi(1)-I(4)	3.1104(4)
Bi(1)-I(1)	3.1698(3)
Bi(1)-I(1) (-x+1, -y+2, -z+2)	3.2583(4)

Complex **3**

Bi(1)-Br(3)	2.7223(5)
Bi(1)-Br(5)	2.7653(5)
Bi(1)-Br(2)	2.8062(5)
Bi(1)-Br(4)	2.8955(5)
Bi(1)-Br(1)	2.9901(5)
Bi(1)-Br(1) (-x+1, -y+2, -z)	3.0605(5)

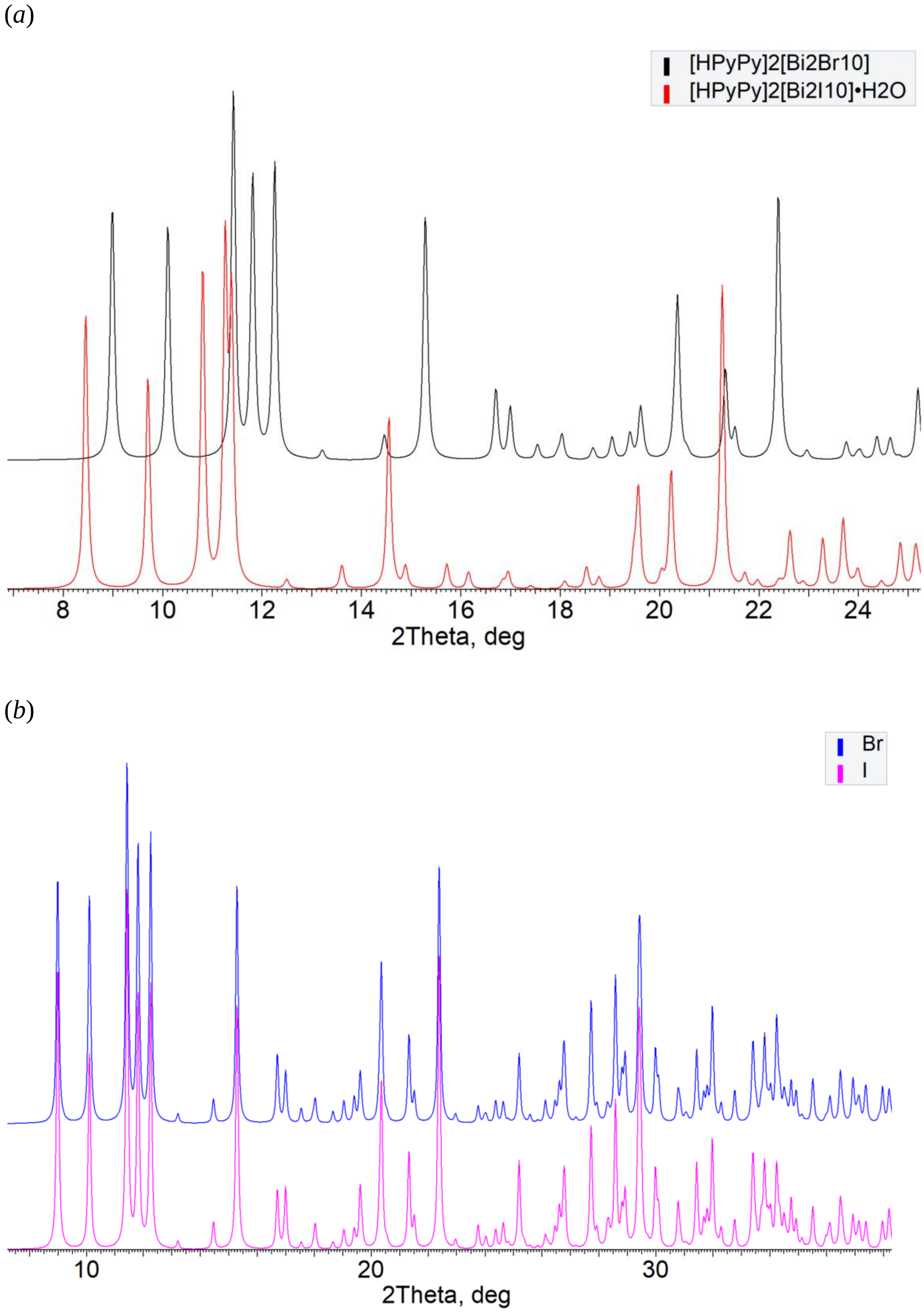


Figure S1 (*a*) ‘Non-normalized’and (*b*) ‘normalized’[§] calculated powder XRD patterns for $(PyPyH)_2Bi_2I_{10}\cdot H_2O$ (**2**) and $(PyPyH)_2Bi_2Br_{10}$ (**3**).

[§] ‘Normalization’ implies artificial equality of unit cell parameters for **2** and **3** and deletion of H_2O molecule from **2**.

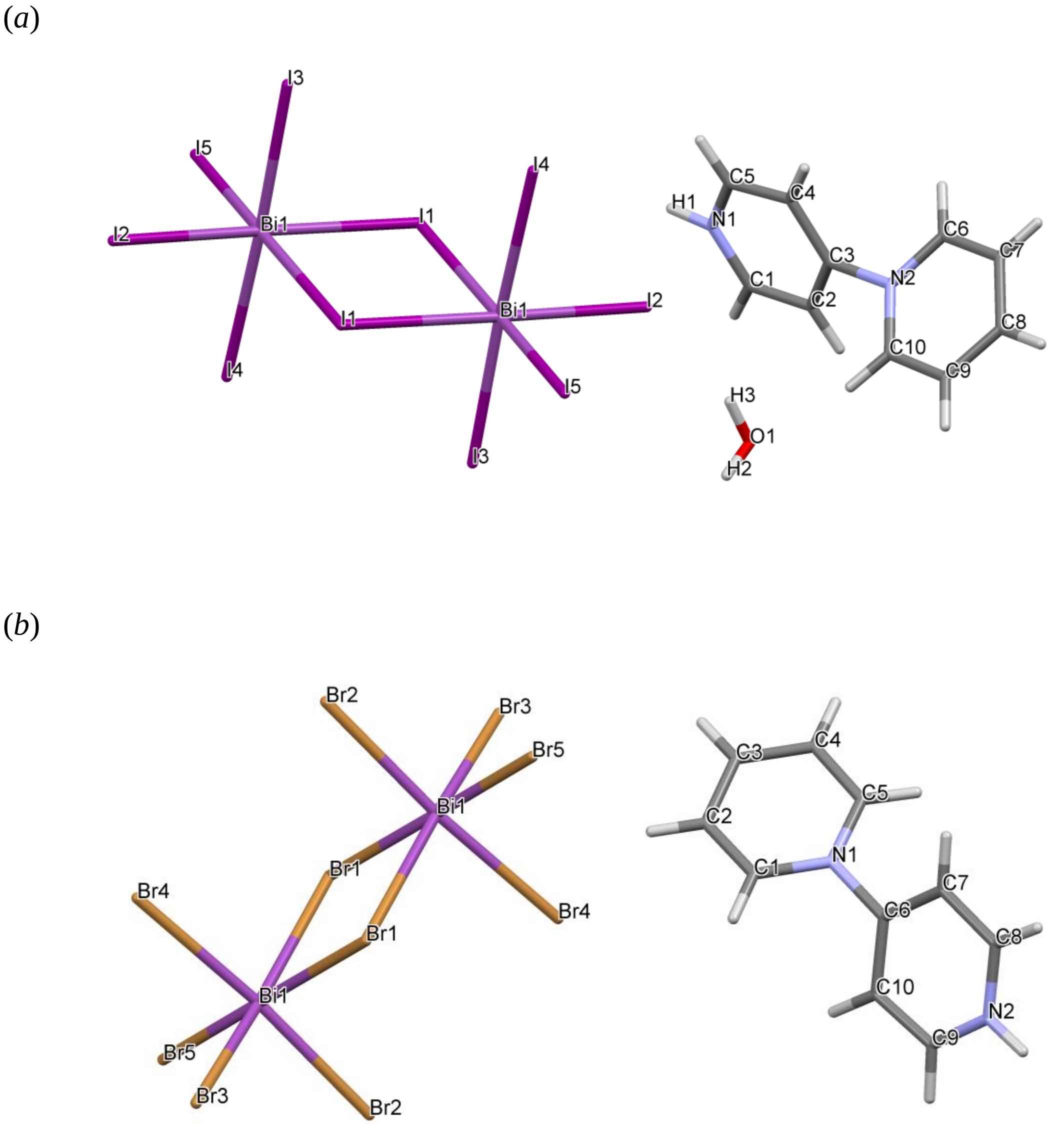
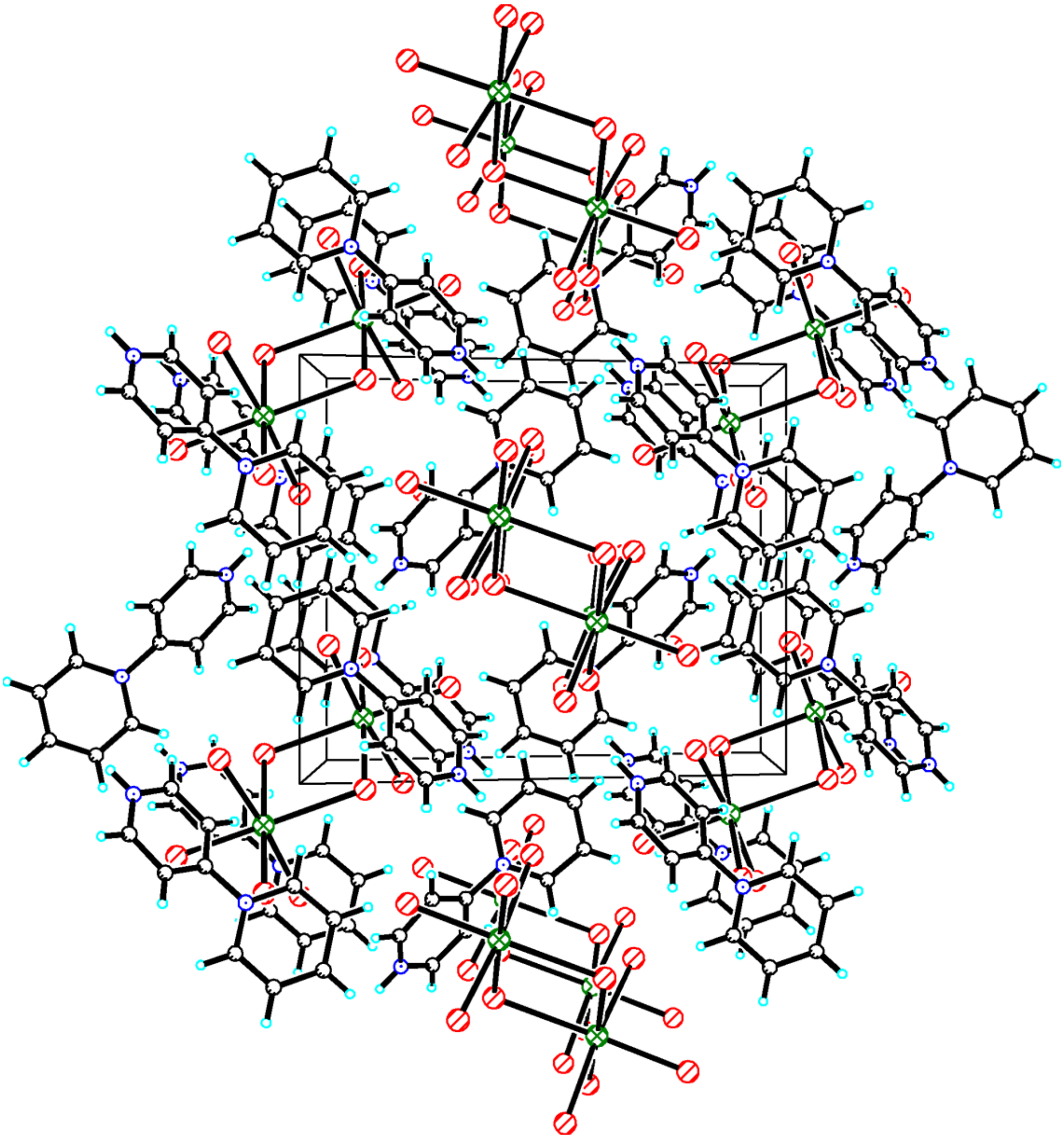
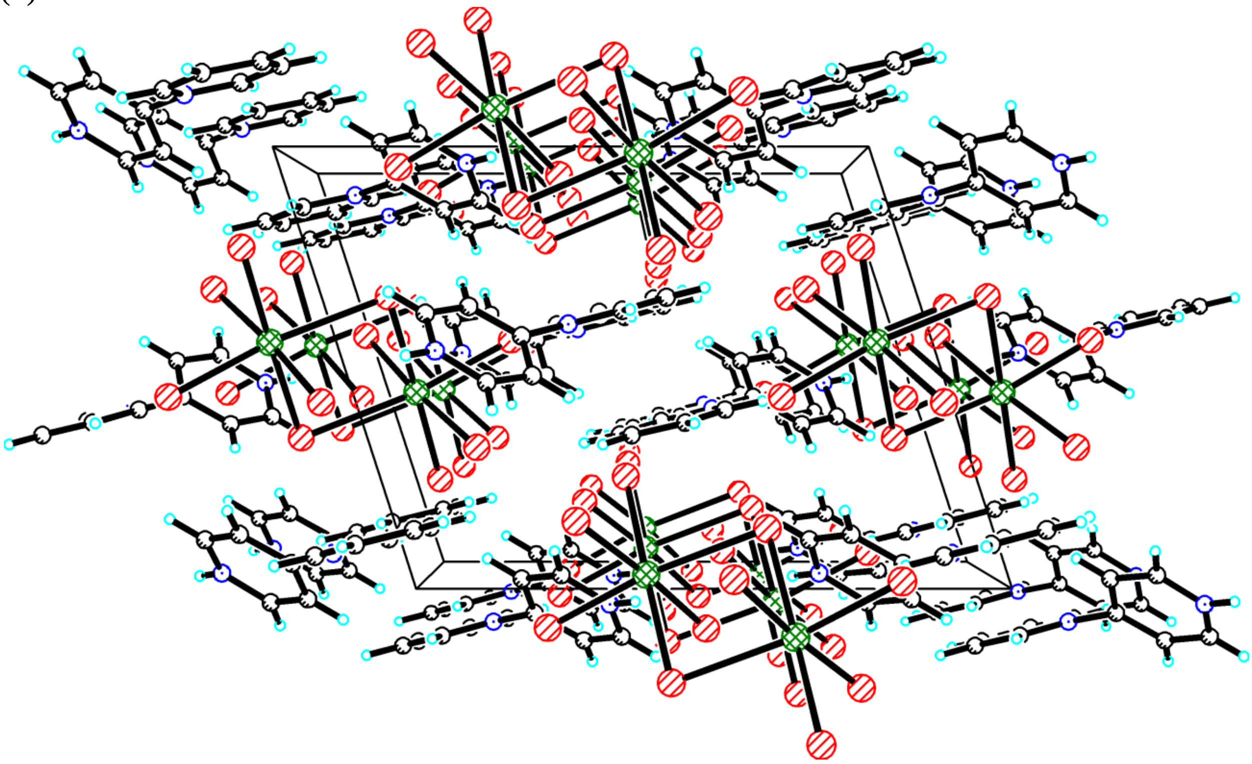


Figure S2 Fragments of crystal structures of complexes (a) **2** and (b) **3**.

(*a*)



(*b*)



(*c*)

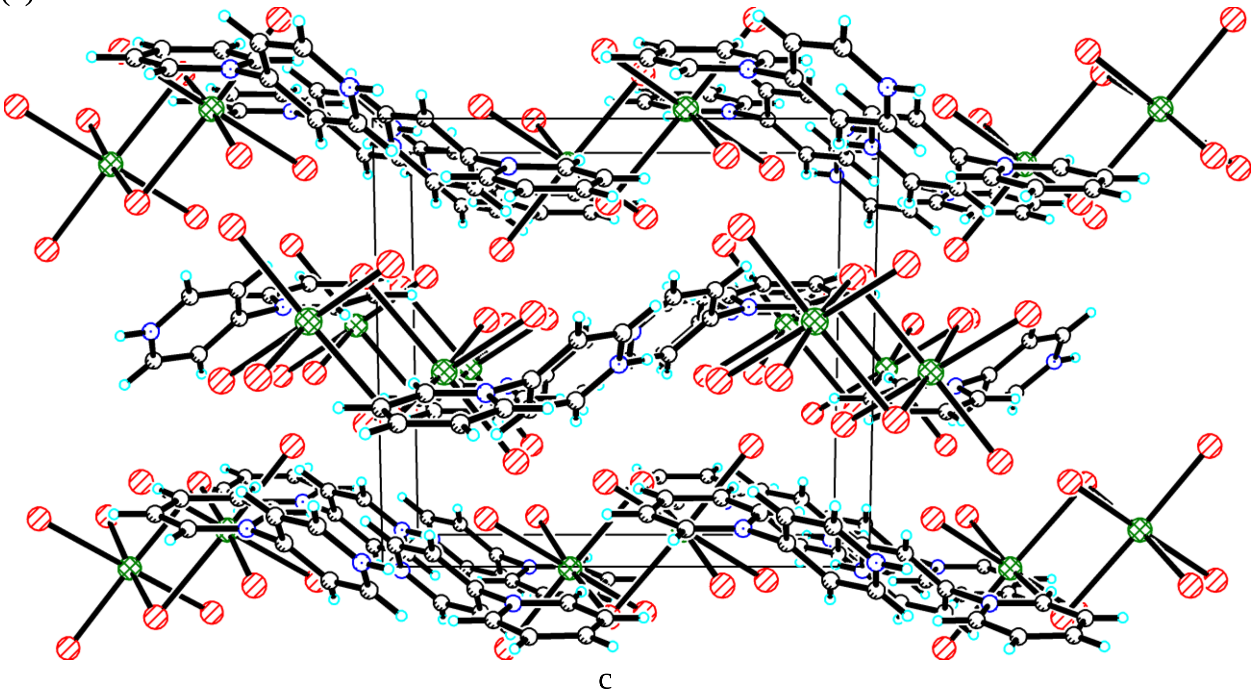
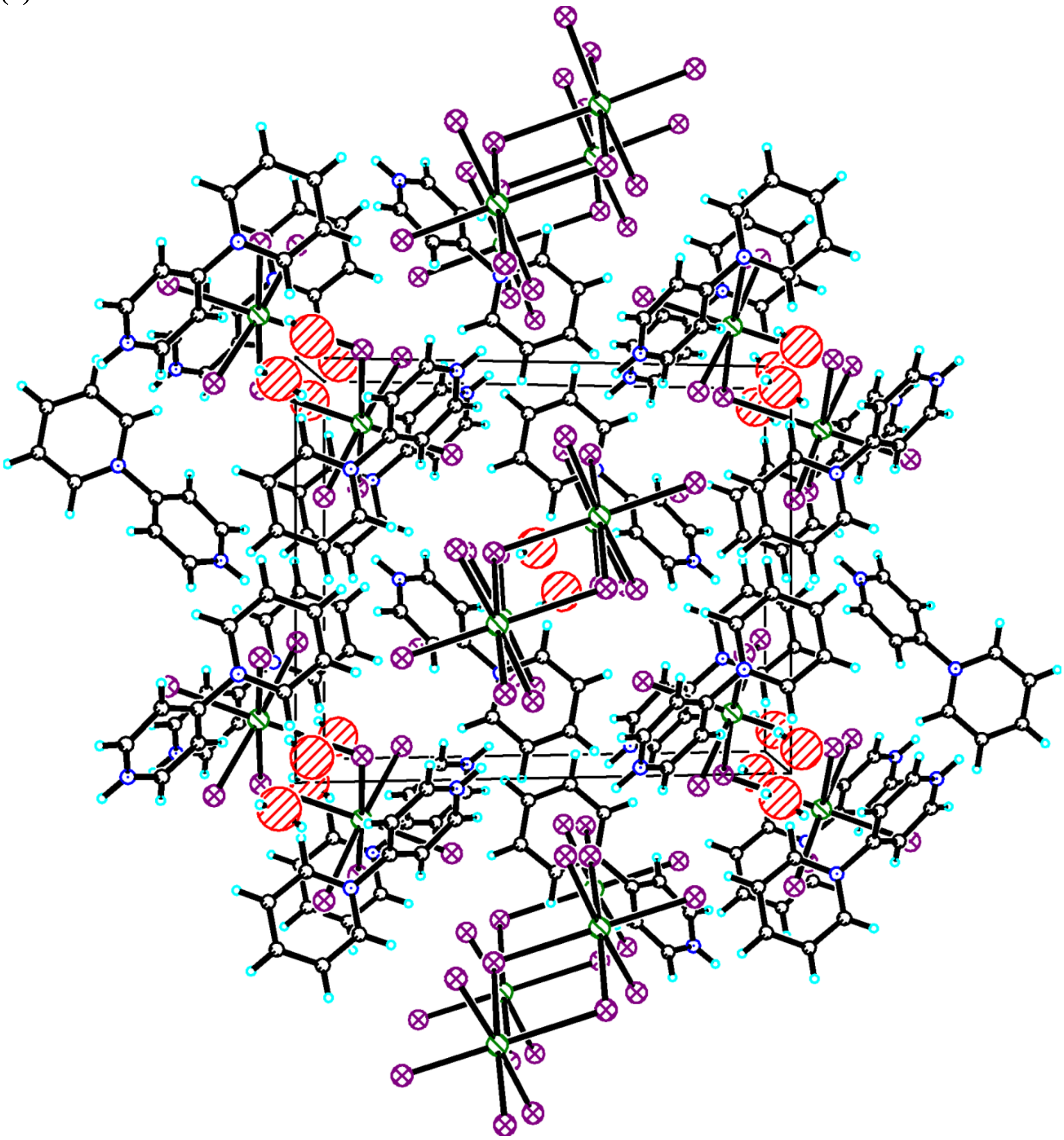
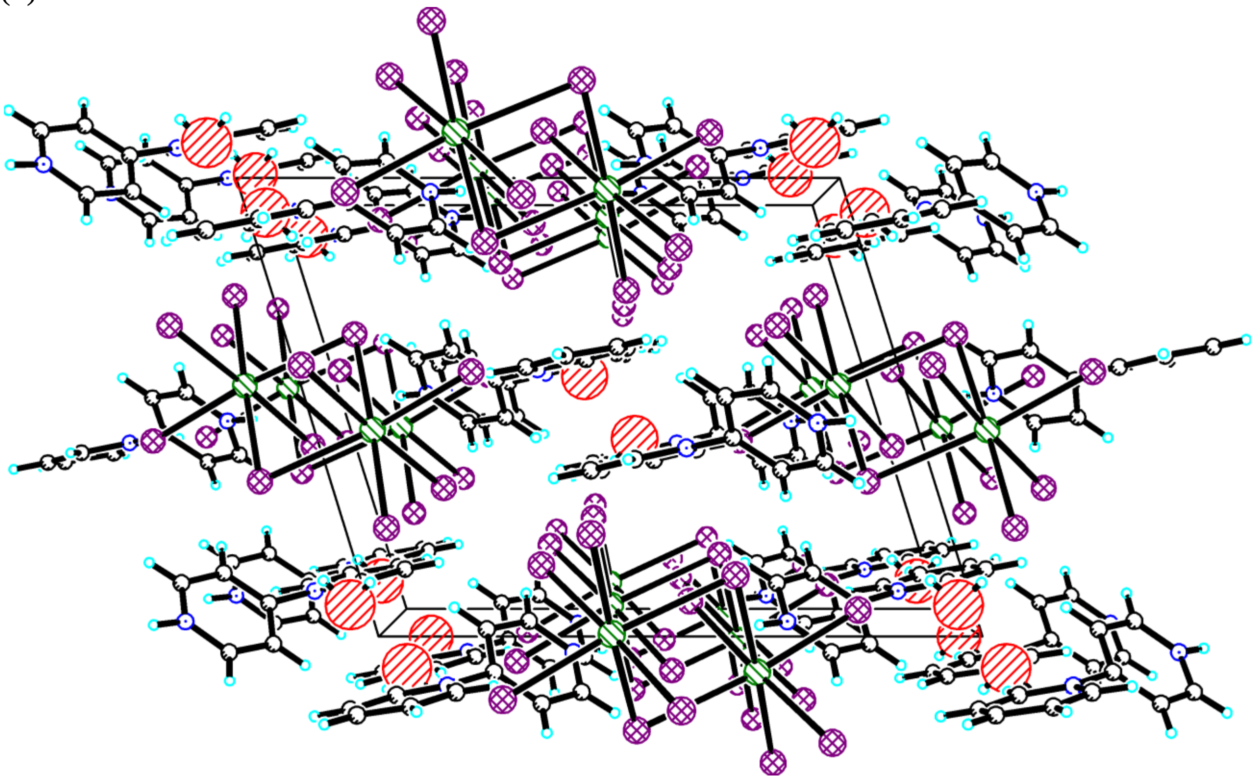


Figure S3 Projections of structure of complex **3** along (*a*) *x*, (*b*) *y* and (*c*) *z* axes.

(*a*)



(*b*)



(*c*)

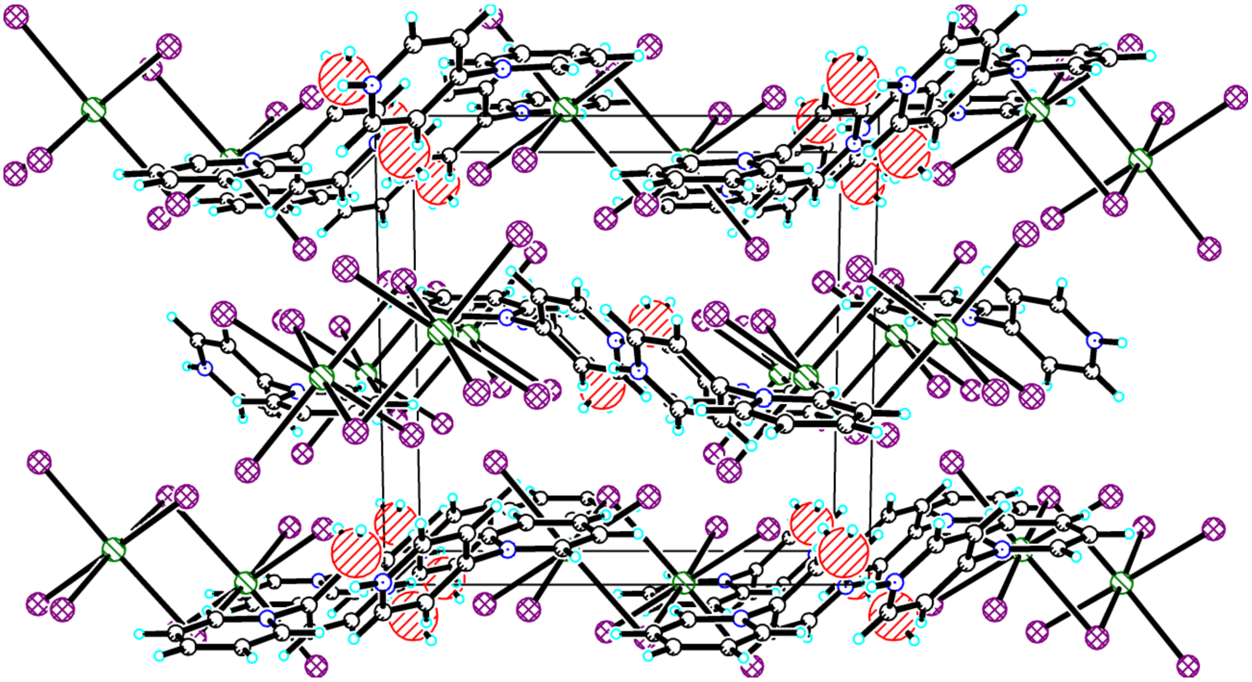
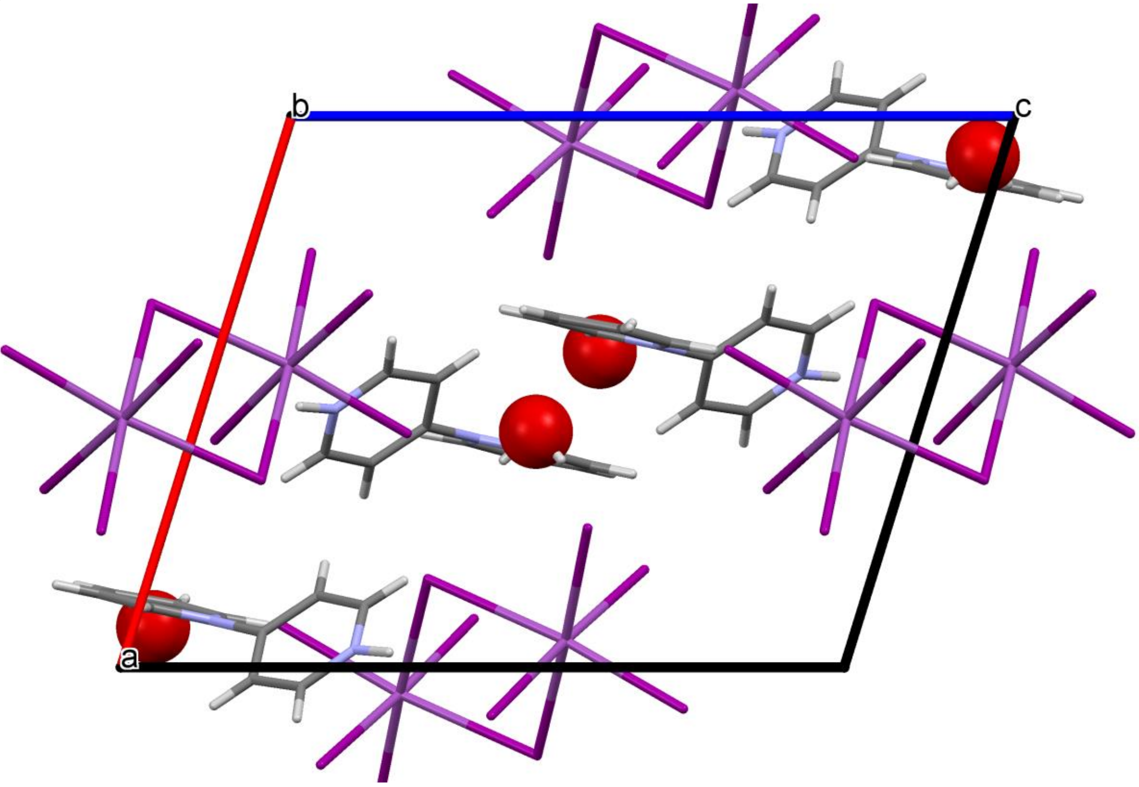


Figure S4 Projections of the structure of complex **2** along (*a*) *x*, (*b*) *y* and (*c*) *z* axes with H_2O molecules depicted as red spheres.

(*a*)



(*b*)

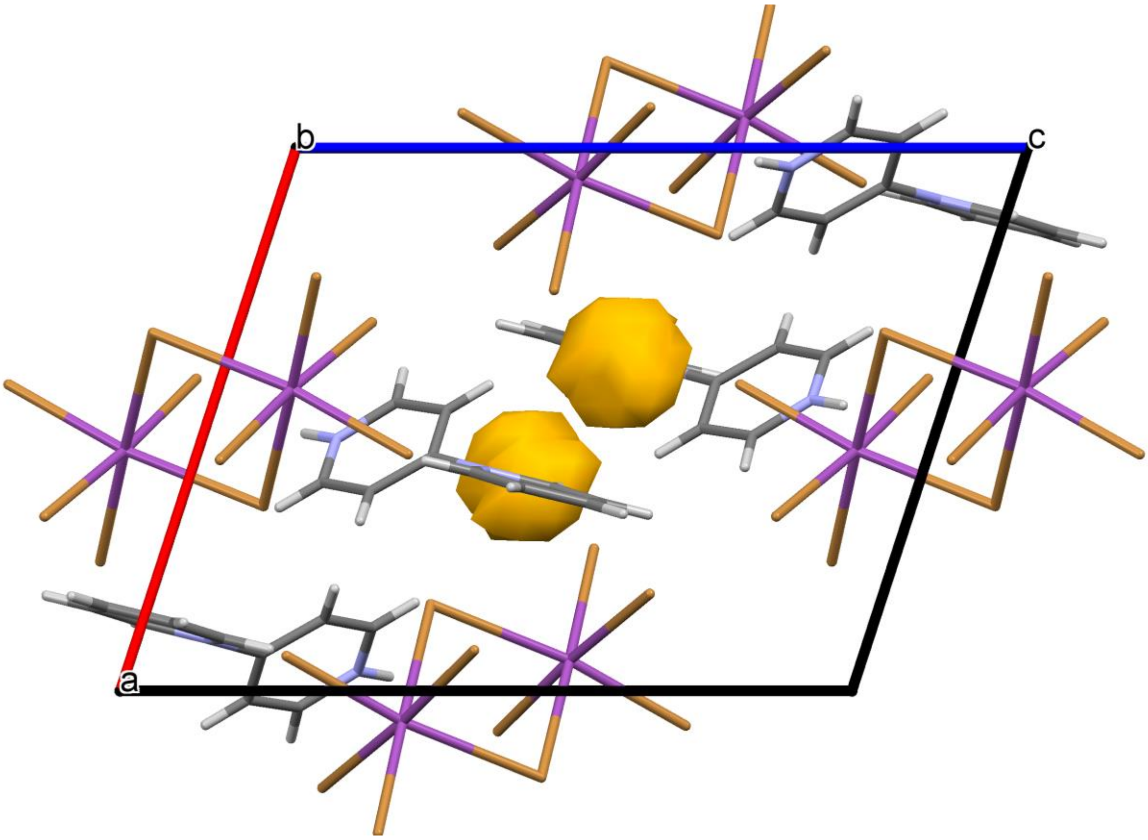


Figure S5 Projections of structures of complexes (*a*) **2** and (*b*) **3** along the *y* axis. The yellow shapes in the structure of complex **3** represent pores (13 Å^3).

Known structures containing a coordinated {I_4} moiety according to CCSD (v. 5.41, March 2020)

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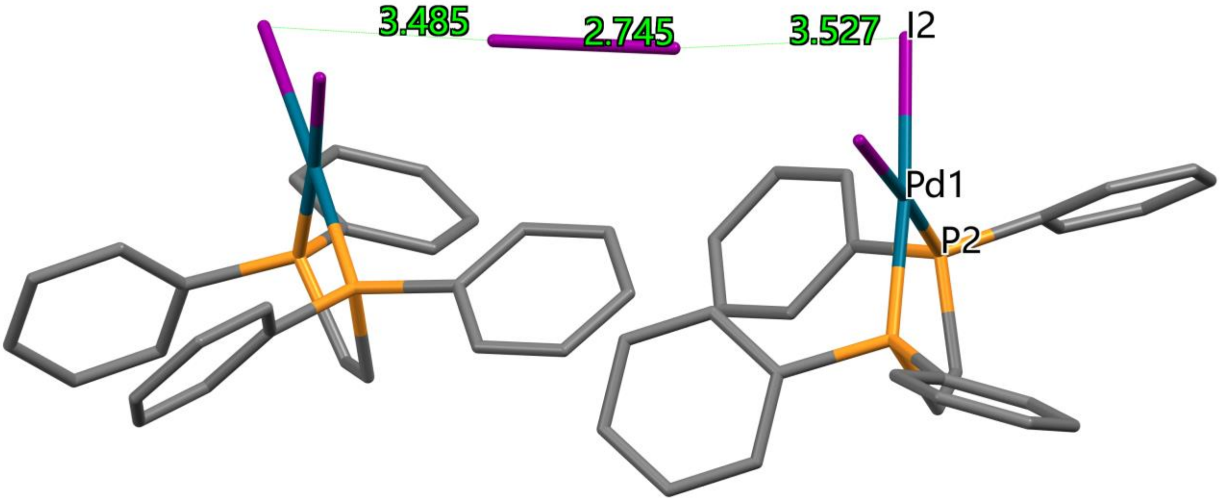

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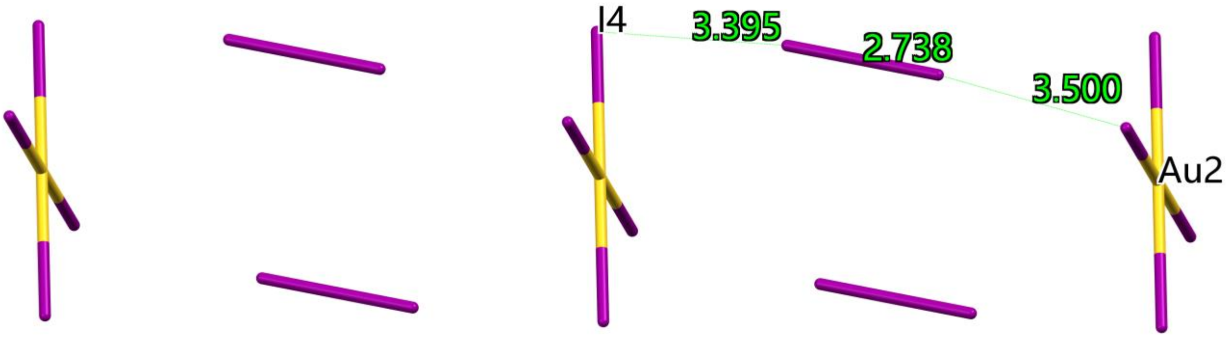

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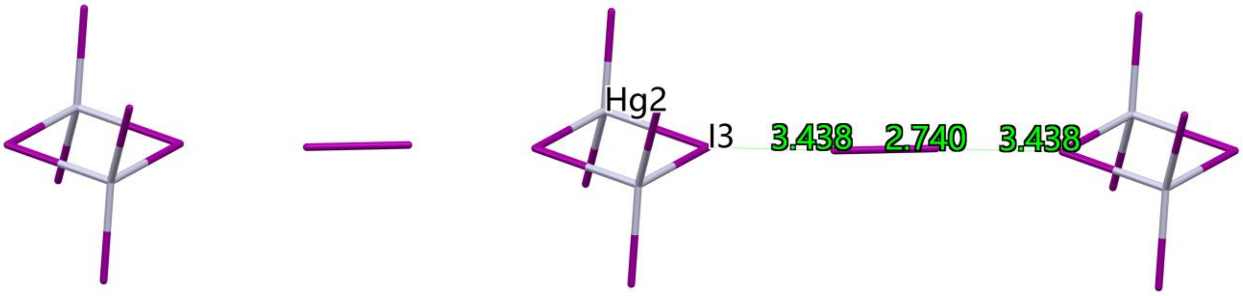

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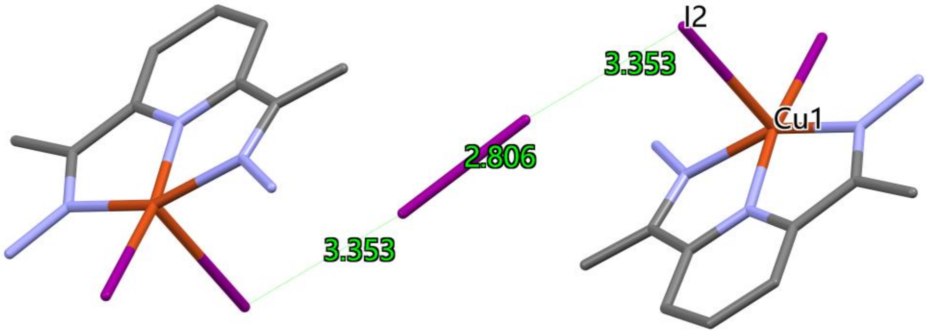

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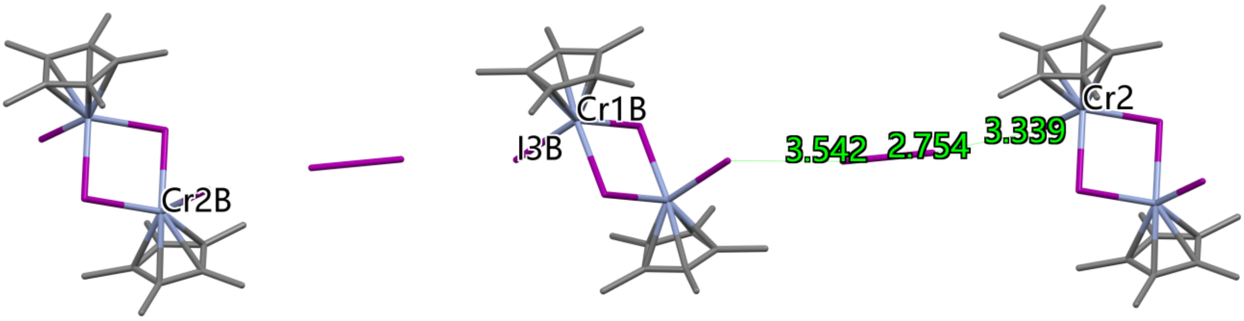

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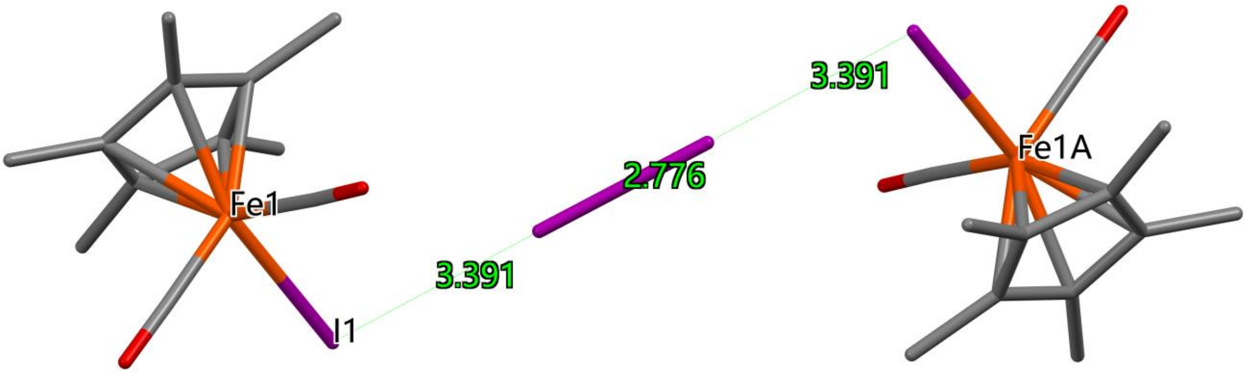

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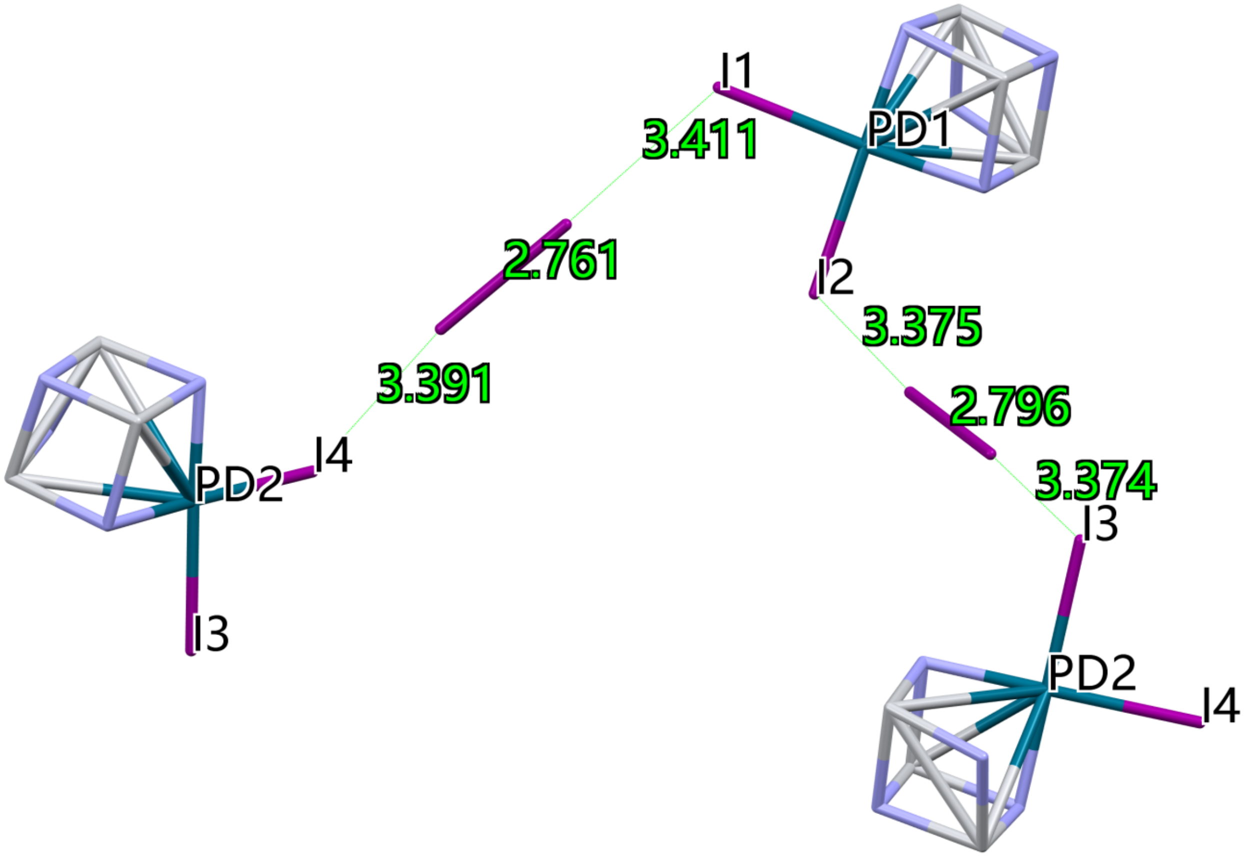

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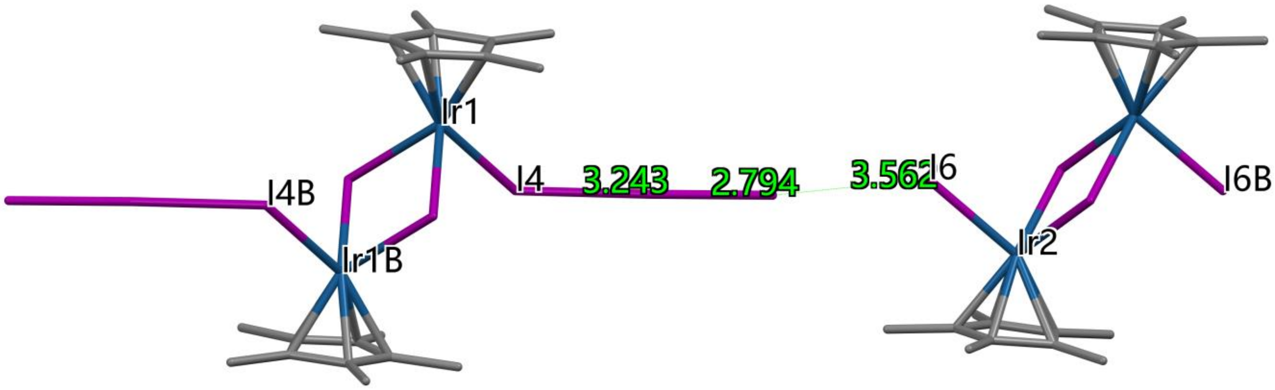

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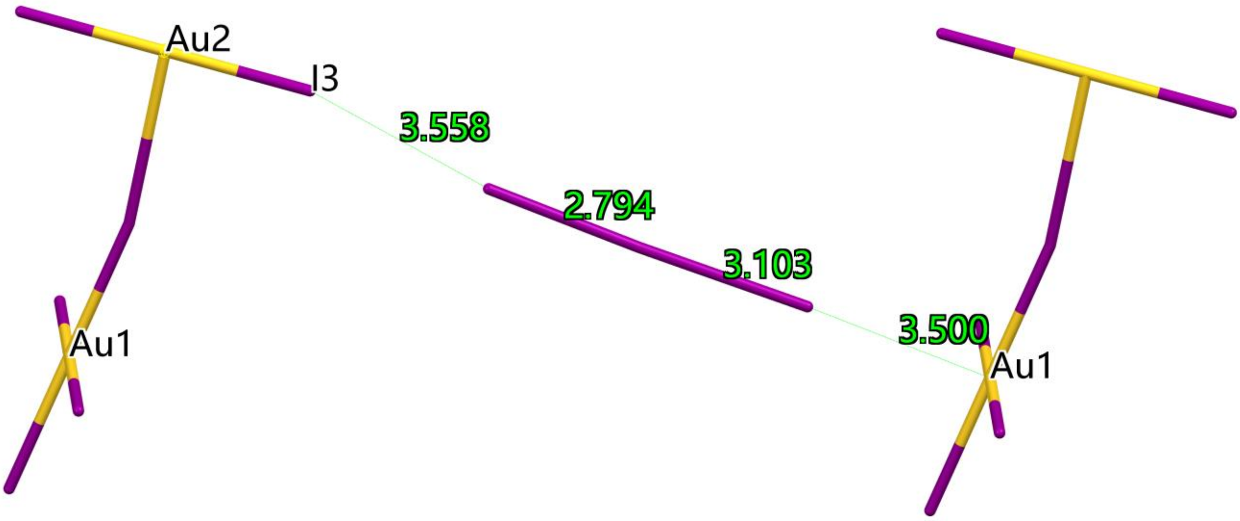

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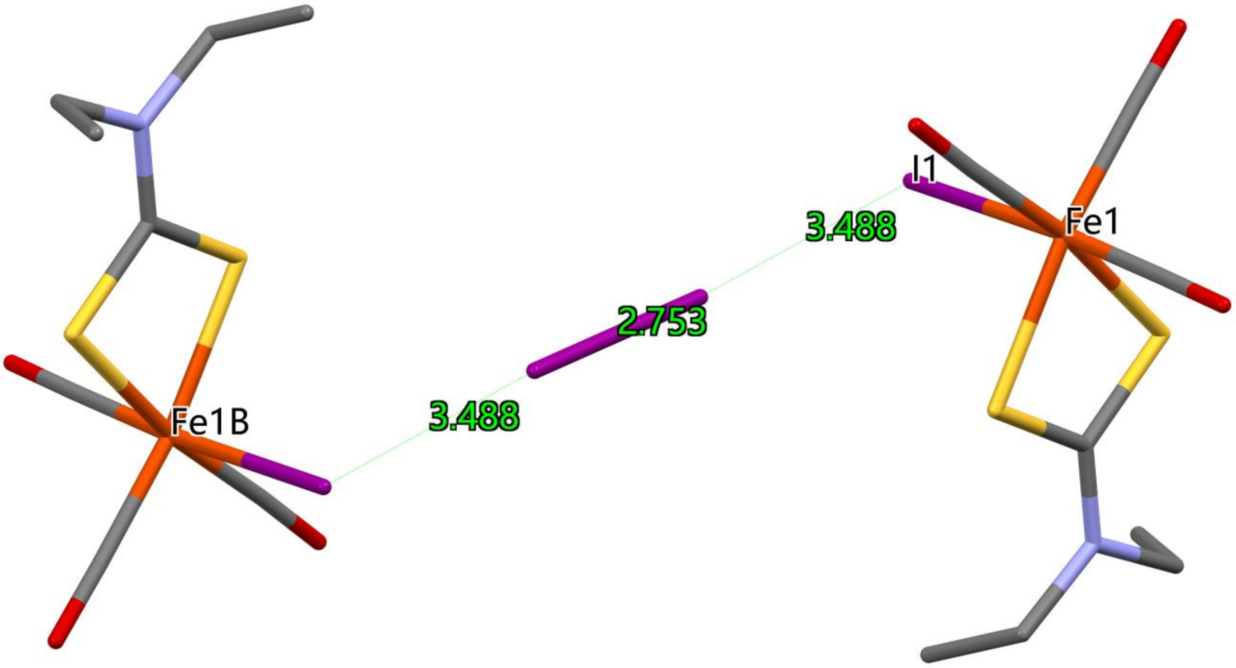

[S9] L. M. Castro-Castro and A. M. Guloy, *Angew. Chem.*, 2003, **115**, 2877.

[S10] L. Hewison, S. H. Crook, B. E. Mann, A. J. H. M. Meijer, H. Adams, P. Sawle and R. A. Motterlini, *Organometallics*, 2012, **31**, 5823.

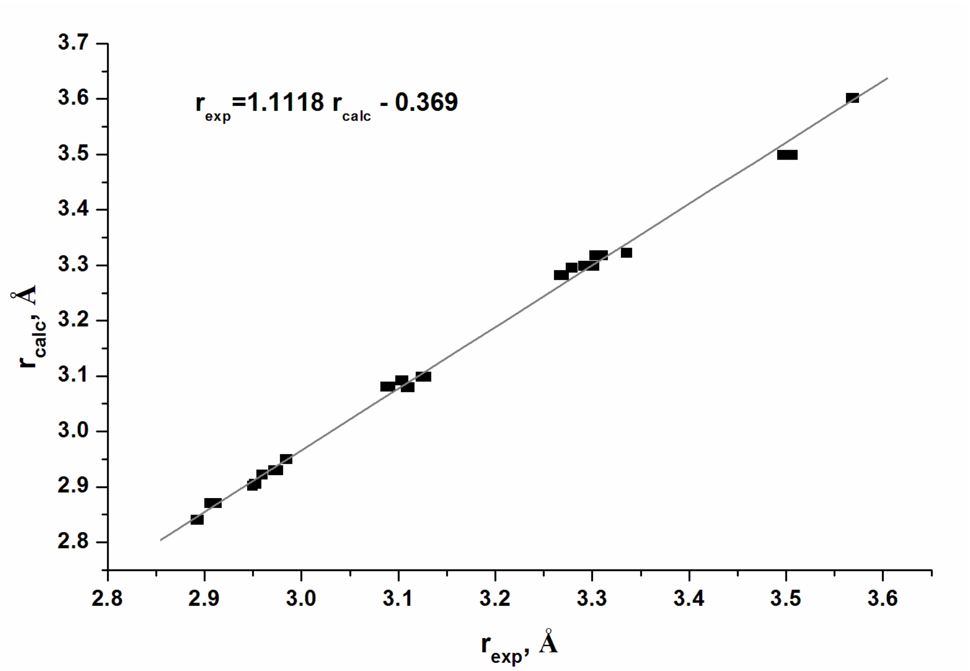

Figure S6 Correlation between the calculated and experimental values of the Bi–I bond lengths, R^2 = 0.997. The largest discrepancy between the calculated and experimental bond lengths is observed for the shortest (+0.054 Å) and longest (-0.031 Å) Bi–I distances.

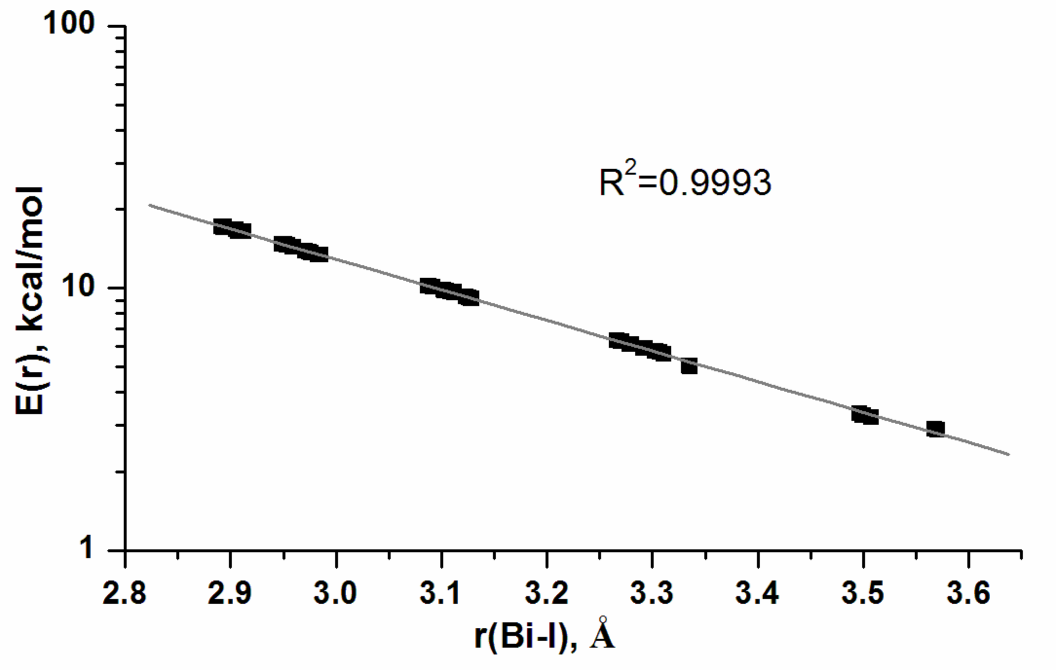

Figure S7 Dependence of the calculated energies on the calculated lengths of Bi–I bonds in the $[Bi_6I_{26}]^{6-}$ anion (in semilogarithmic coordinates).

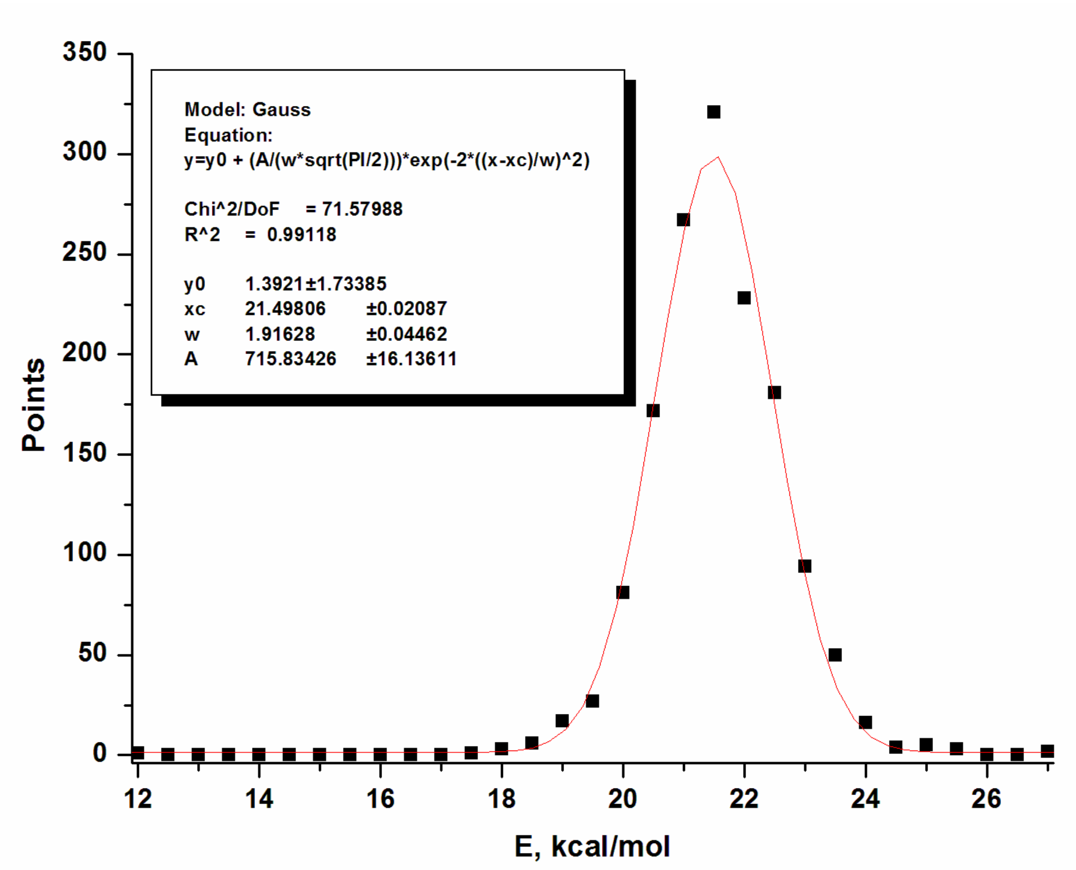

Figure S8 Normal distribution of $E_{trans\text{-pair}}$ energies for Bi–I bonds.

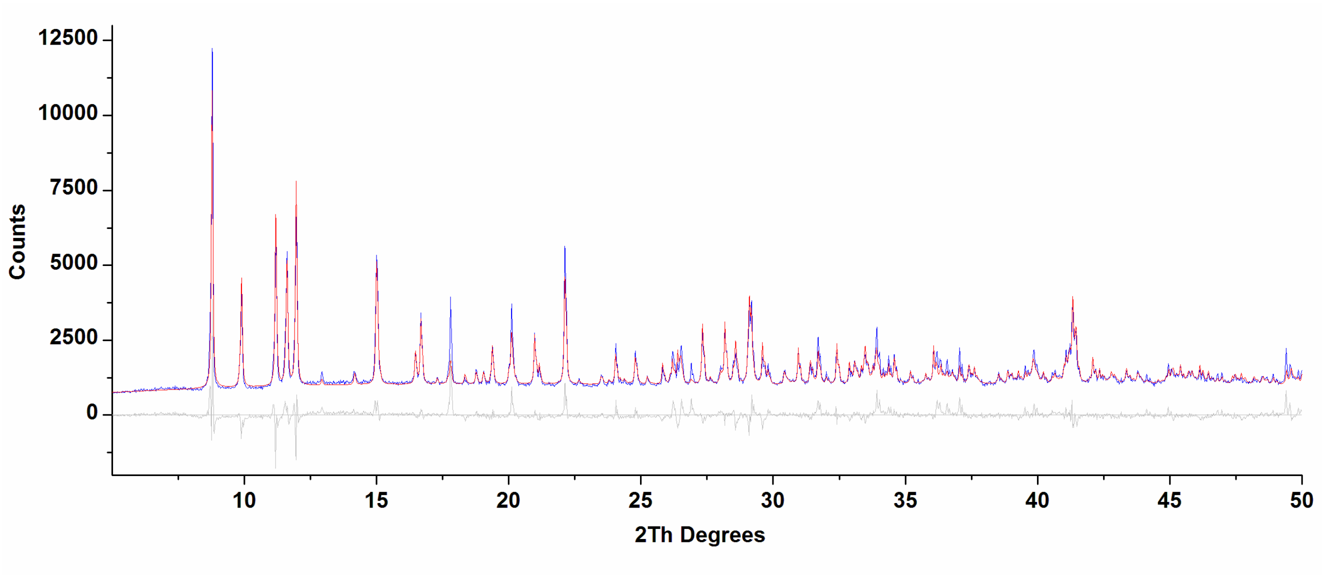

Figure S9 Rietveld refinement profiles of room-temperature powder XRD data for $[PyPyH]_2Bi_2Br_{10}$ (**3**). Red and blue lines correspond to the calculated profile and experimental pattern, respectively. The bottom trace shows the difference curve.

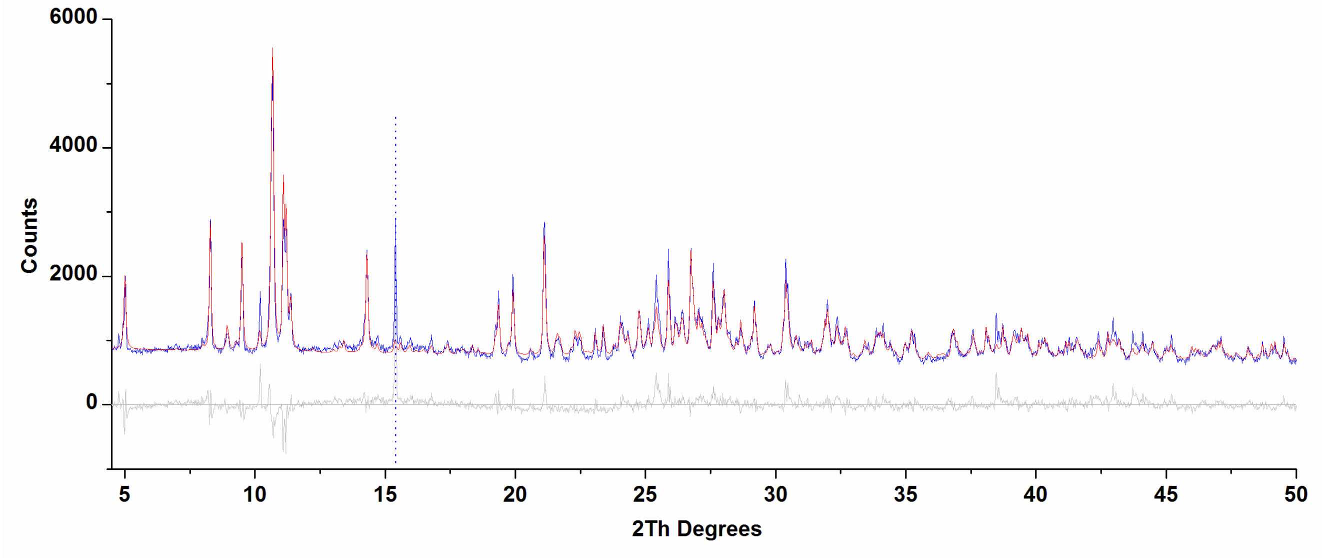

Figure S10 Rietveld refinement profiles of room-temperature powder XRD data for a mixture of $[PyPyH]_2Bi_2I_{10}\cdot H_2O$ **(2)** (62 ± 1%) and **$[PyPy]_2[PyPyH]_2Bi_6I_{26}$ (1)** (38 ± 1%). Red and blue lines correspond to the calculated profile and experimental pattern, respectively. The bottom trace shows the difference curve. The vertical dashed line indicates an unidentified peak.

Table S3 Bi–I binding energies calculated from the experimental and DFT-optimized lengths of Bi–I bonds in the structure of complex **1**.

Polyhedron	$\boldsymbol{r}_{\mathrm{calc}}$**(Bi–I)**/Å	$\boldsymbol{r}_{\mathrm{exp}}$**(Bi–I)**/Å	$\boldsymbol{E}$/kcal mol^{-1}		
			$\boldsymbol{E(r)}^{a}$	$\boldsymbol{E}_{\boldsymbol{trans}\text{-}\mathbf{pair}}^{b}$	$\boldsymbol{E}_{\mathbf{polyhedron}}^{c}$
Bi1	2.950	2.902	16.77 (14.74)[d]	22.61 (20.84)	66.34(60.88)
	3.279	3.295	5.84 (6.10)		
	2.953	2.905	16.63 (14.62)	22.41 (20.46)	
	3.295	3.299	5.78 (5.84)		
	2.960	2.922	15.89 (14.35)	21.32 (19.58)	
	3.336	3.322	5.43 (5.23)		
Bi2	2.893	2.840	19.80 (17.18)	22.37 (19.98)	63.12 (58.62)
	3.569	3.601	2.57 (2.80)		
	3.111	3.079	10.43 (9.57)	20.80 (19.72)	
	3.089	3.081	10.37 (10.15)		
	3.104	3.092	10.07 (9.75)	19.95 (18.92)	
	3.127	3.099	9.88 (9.17)		
Bi3	2.908	2.871	18.22 (16.50)	21.60 (19.86)	63.43 (59.07)
	3.501	3.499	3.38 (3.36)		
	2.974	2.930	15.55 (13.82)	21.04 (19.49)	
	3.306	3.318	5.49 (5.67)		
	2.984	2.950	14.74 (13.45)	20.79 (19.72)	
	3.269	3.282	6.05 (6.26)		
Average	**3.145**	**3.127**	**10.72 (8.74)**	**21.43 (19.84)**	**64.30 (59.52)**

[a] $E(r)$ is the corresponding Bi–I bond energy. [b] $E_{trans\text{-pair}}$ is the energy of *trans*-Bi–I bond pairs. [c] $E_{\mathrm{polyhedra}}$ is the total energy of BiI_6 polyhedron. [d] In parentheses are the energy values obtained from the calculated Bi–I distances, averaged from 4 symmetrically equivalent distances.

Table S4 Calculated $E_{\text{polyhedron}}$ energies for compounds containing $[BiI_4]^-$.

Refcode	***T*/K**	***E*_polyhedron_ /kcal mol^{-1}**	**Deviation from the mean E_polyhedron_ value (%)**
AGODIM	150	64.696	+1
AGODEI	150	64.292	0
AGODOS	150	65.582	+2
ZINZII	150	65.115	+1
TOVGAP	100	63.700	-1
AYENEZ	292	65.100	+1
AYENOJ	292	65.234	+1
AYEPAX	286	64.753	+1
CENMIU	150	64.254	0
CENQIY	150	64.578	0
COPWEK	293	62.530	-3
DEBHUP	293	63.900	-1
HIYMAG	300	64.899	+1
HOJNIG	296	64.481	0
IMEKES	296	65.026	+1
KEZJOO	295	64.377	0
LEWKEG	120	65.238	+1
LEYHEC	295	64.277	0
PAQLAX	150	65.429 64.407	+2 0
PAQLEB	120	63.867	-1
POVYUU	295	64.936	+1
PURMIY	295	64.803	+1
QINCOI	293	65.468	+2
SIWGUD	130	66.060	-3
SIWHAK	130	64.597	0
VIPLUC	296	64.269	0
VUXLAD	293	64.978	+1
ZEWPUP	100	64.392	0
ZUCSOH	330	65.420	+2
$Li[BiI_4]\cdot 5H_2O$	295	63.183	-2
$Mg[BiI_4]_2\cdot 8H_2O$	293	65.360	+2
$Mn[BiI_4]_2\cdot 8H_2O$	293	64.921	+1

Table S5 Calculated $E_{\mathrm{polyhedron}}$ energies for compounds containing $[\mathrm{BiI_6}]^{3-}$.

Refcode	***T*/K**	$E_{\mathrm{polyhedron}}$ /kcal mol^{-1}	**Deviation from the mean $E_{\mathrm{polyhedron}}$ value** (%)
BARZOM	150	62.234	-3
ZINZOO	150	64.704	+1
GOHLEX	150	63.535	-1
IMEKIW	296	62.358	-3
IYIVIX	293	61.841	-4
		63.481	-1
JANGAJ	296	55.614	-14
KIBSAQ	293	62.747	-3
KIBSEU	293	62.054	-4
KIBSIY	293	63.086	-2
KIBSOE	293	63.435	-1
KIZZOL	153	62.465	-3
		61.992	-4
		64.027	-1
		63.162	-2
KIZZUR	296	65.018	+1
KOQCAU	295	61.901	-4
MISBAU	100	64.393	0
MISBAU01	300	62.066	-4
POPJUC	293	66.250	+3
QAPLOJ	296	65.424	+2
		63.922	-1
QOJMEI	293	63.270	-2
RETFII	293	61.422	-5
UQOMIY	293	63.420	-1
		65.416	+2
VEXSEZ	290	62.579	-3
YEZZOV	293	60.754	-6
		59.956	-7
417538-ICS	-	68.136	+6
		66.323	+3

Table S6 Calculated $E_{\text{polyhedron}}$ energies for compounds containing $[Bi_2I_9]^{3-}$.

Refcode	***T*/K**	**$E_{\text{polyhedron}}$** /kcal mol^{-1}	**Deviation from the mean $E_{\text{polyhedron}}$ value** (%)
ZINZEE	150	62.796 64.075	-2 0
BAYHIT	293	65.468	+2
BIQCIQ	296	69.158	+7
BOWFEB	293	63.067	-2
DEJMOU01	295	62.451	-3
EGEGUV	150	64.568	0
ESOQUZ	150	64.217	0
ESORAG	150	64.575	0
ESOROU	294	59.258	-8
FIPLAR	295	63.456	-1
HEBSOY	293	65.365	+2
HEGRUJ	150	63.895	-1
IZANON	223	63.455 63.746	-1 -1
JEFFIM	173	63.752	-1
JOMGEA	190	65.814	+2
LEWKIK	250	62.693	-3
LODHIY	190	64.363	0
LODHOE	220	64.509	0
LOFROO	293	63.709	-1
MAVHUO	293	64.567	0
MNBISB01	293	63.257	-2
MOCRIF	173	62.186	-3
NATPEF	173	61.192	-5
PARCIW	150	63.925	-1
PARCOC	150	63.346	-2
PUFCUP	100	64.236	0
PURLAP	295	63.979	-1
RETFII	293	63.015	-2
SATKEE	150	65.674	+2
SAVMUY	150	63.870	-1
SIWGEN	130	64.070	0
SIWGOX	130	62.893	-2
SUWKAY	295	62.554	-3
SUWKAY01	296	64.783	+1
SUWKAY06	100	66.491 67.995	+3 +6
TARWIV	293	63.510	-1
TELLEE	298	63.617	-1
TUHDEH	293	63.789	-1
UJUPAS	100	65.459	+2
UVIJIU	300	63.881	-1
UVIJIU01	350	65.059	+1

VEXJOA	293	64.470	0
XAXGOU	293	64.039	-1
XAXGUA	293	64.450	0
XIHPEM	120	64.442	0
XIHPIQ	200	65.769	+2
ZICVEP	293	64.926	+1
ZICVIT	293	63.508	-1
ZICWUG	296	65.327	+1
1448-ICSD	-	66.738	+4

Table S7 Calculated $E_{\mathrm{polyhedron}}$ energies for compounds containing $[\mathrm{Bi_2I_{10}}]^{4-}$.

Refcode	T/K	$E_{\mathrm{polyhedron}}$ /kcal mol^{-1}	**Deviation from the mean $E_{\mathrm{polyhedron}}$ value** (%)
FEVNEC01	298	64.085	0
2 (this work)	150	63.765	-1
EFEREP	293	63.220	-2
EVINUT	293	64.419	0
HAYZIT	293	63.807	-1
NIXNAM	293	63.719	-1
OZEROC	153	64.726	+1
PAQXIQ	293	63.844	-1
PAQXIQ01	150	64.124	0
PURMEU	295	63.924	-1
QOJMIM	293	62.368	-3
TEPRAK	296	63.977	-1
TEPREO	296	64.566	0
UTIKAK	223	61.479	-4
YAXXAZ	296	62.968	-2
YAXXED	296	62.896	-2
YAYZII	291	65.971	+2
YEZZUB	293	62.891	-2
YIBTOV	293	65.432	+2
		62.936	-2
YIBTUB	100	66.176	+3
		63.733	-1
414593-ICSD	-	65.919	+2
417538-ICSD	-	63.526	-1
		63.565	-1

Table S8 Calculated $E_{\text{polyhedron}}$ energies for compounds containing $[Bi_3I_{12}]^{3-}$.

Refcode	***T*/K**	$E_{\text{polyhedron}}$ /kcal mol^{-1}	**Deviation from the mean $E_{\text{polyhedron}}$ value** (%)
AYODAU	293	64.126	0
AZOMUZ	296	64.575	0
		64.748	+1
AZONUA	296	66.957	+4
		66.110	+3
AZUDUW	296	64.039	-1
		64.156	0
FASHIT	150	65.226	+1
IVAPAY	100	64.376	0
		64.556	0
KEPMEX	295	64.801	+1
KEPMEX01	150	65.376	+2
		64.638	0
LEWDUP	130	65.424	+2
NAJMOC	100	67.176	+4
		66.571	+3
QAHFEN	100	65.749	+2
		62.477	-3
QAPLUP	296	67.176	+4
		66.571	+3
TEZKEQ	173	63.574	-1
YOGPAL	295	63.815	-1
YOGPOZ	295	65.615	+2
YOWZAN	173	63.868	-1

Table S9 Calculated $E_{\mathrm{polyhedron}}$ energies for compounds containing $[\mathrm{Bi_4I_{16}}]^{4-}$ anions.

Refcode	***T*/K**	$\boldsymbol{E}_{\mathbf{polyhedron}}$ /kcal mol^{-1}	**Deviation from the mean** $\mathbf{E}_{\mathbf{polyhedron}}$ **value** (%)
FEVNUS	150	65.556	+2
BOWFIF	293	63.239	-2
CENMUG	150	64.951	+1
CENPIX	150	65.745	+2
DISLEZ	298	64.818	+1
HUJCIZ	296	65.277	+1
IBADEX	150	65.677	+2
KANDOT	243	65.377	+2
LOFJUO	130	65.185	+1
LOKSAF	295	65.857	+2
LUMPUG	293	64.590	0
NOFLOM	296	64.430	0
PUFCOJ	100	72.910	+13
SAVNAF	150	64.932	+1
UTIKEO	223	63.895	-1
		64.225	0
VIPLOW01	296	64.301	0
WULXEI	293	64.613	0
XASZIB	100	64.771	+1
XOLKAL	296	64.719	+1
YIJZEZ	293	64.629	0
ZODPUD	295	65.936	+2
		66.344	+3

Table S10 Calculated $E_{\mathrm{polyhedron}}$ energies for compounds based on single crystal XRD data measured at 150 ± 5 K.

Refcode	***T*/K**	$\boldsymbol{E}_{\mathbf{polyhedron}}$ /kcal mol^{-1}	**Deviation from the mean E$_{\mathbf{polyhedron}}$ value** (%)	**Anion**
AGODIM	150	64.696	+1	BiI_4
AGODEI	150	64.292	0	BiI_4
ZINZAA	150	63.389 63.342	-2 -2	Bi_2I_{11}
BARZOM	150	62.234	-3	BiI_6
2 (this work)	150	63.765	-1	Bi_2I_{10}
1 (this work)	150	64.297	0	Bi_6I_{26}
FEVNUS	150	65.556	+2	Bi_4I_{16}
ZINZII	150	65.115	+1	BiI_4
ZINZOO	150	64.704 61.846	+1 -4	BiI_6 Bi_2I_{11}
TOVGAP	150	63.700	-1	BiI_4
ZINZEE	150	62.796 64.075	-2 0	Bi_2I_9
CENMIU	150	64.254	0	BiI_4
CENMUG	150	64.951	+1	Bi_4I_{16}
CENPIX	150	65.745	+2	Bi_4I_{16}
CENQIY	150	64.578	0	BiI_4
DEKNEN	153	64.516	0	Bi_6I_{22}
DEKNIR	153	65.477	+2	Bi_6I_{22}
EGEHAC	150	64.568	0	Bi_2I_9
EGISUK	150	65.421	+2	Bi_8I_{28}
ESOQUZ	150	64.217	0	Bi_2I_9
ESORAG	150	64.575	0	Bi_2I_9
FASHIT	150	65.226	+1	Bi_3I_{12}
GAYRIK	150	62.238	-3	BiI_5
GOHLEX	150	63.535	-1	BiI_6
HEGRUJ	150	63.895	-1	Bi_2I_9
IBADEX	150	65.677	+2	Bi_4I_{16}
KEPMEX01	150	65.376 64.638	+2 0	Bi_3I_{12}
KIZZOL	153	62.465 61.992 64.027 63.161	-3 -4 -1 -2	BiI_6
OZEROC	153	64.726	+1	Bi_2I_{10}
PAQLAX	150	65.429 64.407	+2 +1	BiI_4
PAQXIQ01	150	64.124	0	Bi_2I_{10}
PARCIW	150	63.925	-1	Bi_2I_9
PARCOC	150	63.346	-2	Bi_2I_9
PELSOP	150	66.070	+3	Bi_6I_{22}

PELSUV	150	65.359	+2	γ-Bi_6I_{22}
SATKEE	150	65.674	+2	Bi_2I_9
SAVMUY	150	63.869	-1	Bi_2I_9
SAVNAF	150	64.932	+1	Bi_4I_{16}
SAVNEJ	150	65.487	+2	Bi_6I_{22}
SAVNIN	150	65.293	+1	Bi_6I_{22}
VERWAR	150	65.424	+2	Bi_6I_{22}
VIPMOX	150	64.503	0	Bi_2I_8
VIPMUD	150	64.562	0	Bi_2I_8

Table S11 Calculated $E_{\text{polyhedron}}$ energies for compounds based on single crystal XRD data measured at 295 ± 5 K.

Refcode	***T*/K**	$E_{\text{polyhedron}}$ /kcal mol^{-1}	**Deviation from the mean $E_{\text{polyhedron}}$ value** (%)	**Anion**
FEVNEC01	298	64.085	0	Bi_2I_{10}
ALINOY	293	64.043	-1	Bi_8I_{30}
AYENEZ	292	65.100	+1	BiI_4
AYENOJ	292	65.234	+1	BiI_4
AYODAU	293	64.126	0	Bi_3I_{12}
AZOBUO	296	64.640	0	Bi_2I_7
AZOFOM	296	64.748	+1	Bi_2I_7
AZOGIH	296	64.796	+1	Bi_5I_{18}
AZOMUZ	296	64.575 64.748	0 +1	Bi_3I_{12}
AZONUA	296	66.957 66.110	+4 +3	Bi_3I_{12}
AZUBII	296	66.004	+3	Bi_2I_7
AZUDUW	296	64.039 64.156	-1 0	Bi_3I_{12}
BAYHIT	293	65.468	+2	Bi_2I_9
BIQCIQ	296	69.158	+7	Bi_2I_9
BOWFEB	293	63.066	-2	Bi_2I_9
BOWFIF	293	63.239	-2	Bi_4I_{16}
BOWFOL	293	62.968	-2	Bi_4I_{14}
COPVUZ	293	64.376	0	BiI_5
COPWEK	293	62.530	-3	BiI_4
DEBHUP	293	63.900	-1	BiI_4
DEJMOU01	295	62.451	-3	Bi_2I_9
DISLEZ	298	64.818	+1	Bi_4I_{16}
DOMKOI	293	66.861	+4	Bi_6I_{24}
EFEREP	293	63.220	-2	Bi_2I_{10}
ESOROU	294	59.258	-8	Bi_2I_9
EVINUT	293	64.419	0	Bi_2I_{10}
FIPLAR	295	63.456	-1	Bi_2I_9
FIPQAW	295	66.556	+3	Bi_6I_{22}
HAYZIT	293	63.807	-1	Bi_2I_{10}
HEBSOY	293	65.365	+2	Bi_2I_9
HIYMAG	300	64.899	+1	BiI_4
HOJNIG	296	64.481	0	BiI_4
HUJCIZ	296	65.277	+1	Bi_4I_{16}
IMEKES	296	65.026	+1	BiI_4
IMEKIW	296	62.358	-3	BiI_6
IYIVIX	293	61.841	-4	BiI_6
JANFOW	296	64.652	0	Bi_2I_8
JANGAJ	296	55.614	-14	BiI_6

KANDUZ	296	64.691	+1	Bi_5I_{18}
KEPMEX	295	64.801	+1	Bi_3I_{12}
KEZJOO	295	64.377	0	BiI_4
KIBSAQ	293	62.747	-3	BiI_6
KIBSEU	293	62.054	-4	BiI_6
KIBSIY	293	63.086	-2	BiI_6
KIBSOE	293	63.435	-1	BiI_6
KIZZUR	296	65.018	+1	BiI_6
KOQCAU	295	61.901	-4	BiI_6
KOZNAO	295	64.105	0	Bi_2I_7
LEYHEC	295	64.277	0	BiI_4
LOFROO	293	63.708	-1	Bi_2I_9
LOKSAF	295	65.857	+2	Bi_4I_{16}
LUMPUG	293	64.590	0	Bi_4I_{16}
MAVHUO	293	64.567	0	Bi_2I_9
MIKZOV	295	65.072	+1	BiI_5
MIKZUB	295	65.465	+2	BiI_5
MISBAU01	300	62.066	-4	BiI_6
MNBISB01	293	63.257	-2	Bi_2I_9
NAJMIW	295	65.750	+2	Bi_3I_{12}
NAJMUI	295	65.229	+1	Bi_5I_{18}
NIXNAM	293	63.719	-1	Bi_2I_{10}
NOFLOM	296	64.430	0	Bi_4I_{16}
PAQXIQ	293	63.844	-1	Bi_2I_{10}
PIXJUC01	293	63.778	-1	BiI_5
POPJUC	293	66.250	+3	BiI_6
POVYUU	295	64.936	+1	BiI_4
PURLAP	295	63.979	-1	Bi_2I_9
PURMEU	295	63.924	-1	Bi_2I_{10}
PURMIY	295	64.803	+1	BiI_4
QAPLOJ	296	65.424 63.922	+2 -1	BiI_6
QAPLUP	296	67.176 66.571	+4 +3	Bi_3I_{12}
QINCOI	293	65.468	+2	BiI_4
QOJMEI	293	63.270	-2	BiI_6
QOJMIM	293	62.368	-3	Bi_2I_{10}
RETFII	293	61.422 63.015	-5 -2	BiI_6 Bi_2I_9
SASFUQ	293	63.609 64.922	-1 +1	BiI_5
SAVNOT	293	63.863	-1	Bi_3I_{11}
SIBXAC	295	62.363	-3	Bi_2I_8
SOWNUN	295	63.658	-1	BiI_5
SUWKAY	295	62.554	-3	Bi_2I_9
SUWKAY01	296	64.783	+1	Bi_2I_9
TARWIV	293	63.510	-1	Bi_2I_9
TELLEE	298	63.617	-1	Bi_2I_9

TEPRAK	296	63.977	-1	Bi_2I_{10}
TEPREO	296	64.566	0	Bi_2I_{10}
TUHDEH	293	63.789	-1	Bi_2I_9
UQOMIY	293	63.420	-1	BiI_6
UVIJIU	300	63.881	-1	Bi_2I_9
VEXJOA	293	64.470	0	Bi_2I_9
VEXSEZ	290	62.579	-3	BiI_6
VIPLOW01	296	64.301	0	Bi_4I_{16}
VIPLUC	296	64.269	0	BiI_4
VUXLAD	293	64.978	+1	BiI_4
WULXEI	293	64.613	0	Bi_4I_{16}
XAXGOU	293	64.039	-1	Bi_2I_9
XAXGUA	293	64.450	0	Bi_2I_9
XOLJUE	296	64.156	0	Bi_2I_8
XOLKAL	296	64.719	+1	Bi_4I_{16}
YAXXAZ	296	62.968	-2	Bi_2I_{10}
YAXXED	296	62.896	-2	Bi_2I_{10}
YAYZII	291	65.971	+2	Bi_2I_{10}
YEGTEJ	295	64.499	0	Bi_5I_{18}
YEZZIP	293	62.976 62.205	-2 -3	BiI_5
YEZZOV	293	60.754 59.956	-6 -7	BiI_6
YEZZUB	293	62.891	-2	Bi_2I_{10}
YIBTOV	293	65.432 62.936	+2 -2	Bi_2I_{10}
YIJZEZ	293	64.629	0	Bi_4I_{16}
YOGPAL	295	63.815	-1	Bi_3I_{12}
YOGPOZ	295	65.615	+2	Bi_3I_{12}
ZICVEP	293	64.926	+1	Bi_2I_9
ZICVIT	293	63.508	-1	Bi_2I_9
ZICWUG	296	65.326	+1	Bi_2I_9
ZIYBAK01	293	62.990	-2	Bi_2I_7
ZODPOX	295	64.657	0	Bi_4I_{14}
ZODPUD	295	65.936 66.344	+2 +3	Bi_4I_{16}
$LiBiI_4 \cdot 5H_2O$	295	63.183	-2	BiI_4
$Mg[BiI_4]_2 \cdot 8H_2O$	293	65.360	+2	BiI_4
$Mn[BiI_4]_2 \cdot 8H_2O$	293	64.921	+1	BiI_4

Refinement of the value of the numerical coefficient in the Pauling equation for the multiplicity of the Bi–I bond based on the data of this work

Earlier, an attempt was made to estimate the multiplicity of Bi–I bonds by their length using the Pauling equation.[S11] For the corresponding calculations, the following assumptions were made: the total multiplicity of bonds in the $\{BiI_6\}$ moieties was set equal to 3, and the Bi–I distance of 3.07Å corresponds to a bond with a multiplicity of 0.5. The empirical multiplier in the equation was set to 0.6, as for the C-C bonds.

Based on the published results,[S12] taking into account the fact that each Bi–I bond has a multiplicity calculated as $3\frac{E(r)}{E(6r)}$, and the total multiplicity of Bi–I bonds in the I–Bi–I moiety with a total energy of 21.5 kcal mol^{-1} is 1, the empirical coefficient for the calculation of the multiplicity of the Bi–I bond using the Pauling equation was refined as 0.3744 for iodobismuthates:

$$n = 0.5\exp\left(\frac{3.07-r}{0.3744}\right) \tag{S1}$$

In equation (S1), n is the bond multiplicity; 3.07 is the length (Å) of the Bi–I bond, corresponding to a multiplicity of 0.5; r is the length of the Bi–I bond.

The total value of the multiplicity of the Bi–I bond per one $\{BiI_6\}$ polyhedron, calculated according to equation (S1), is 3.01 and 2.98 for complexes **1** and **2**, respectively.

[S11] L. Paulung, *J. Am. Chem. Soc.*, 1947, **69**, 542

[S12] A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, 1984.