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Two-Dimensional Coordination Polymer {[Bi(Pyz)I_3]}: Structure and Analysis of the Packing Using the Hirshfeld Surface Method

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Abstract—The reaction of BiI_3 with pyrazine in tetrahydrofuran affords the two-dimensional coordination polymer {[Bi(Pyz)I_3]} (**I**), whose structure is determined by X-ray diffraction analysis (CIF file CCDC no. 1904990). The contributions of various interatomic contacts to the crystal packing of compound **I** are studied using the Hirshfeld surface analysis performed for the elementary unit of compound **I**. The interatomic distances I···H make the largest contribution to the crystal packing of compound **I**.

Keywords: bismuth, coordination polymers, pyrazine, crystal structure, analysis of Hirshfeld surfaces

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INTRODUCTION

Metal-organic frameworks (MOF) represent a broad class of complex compounds attracting attention of researchers due to a series of physicochemical properties [1–9]. Among the most intensively studied properties are luminescence and the possibility of conductivity using it in the development of sensors [10, 11], proton conductance [12], selective sorption of gases [13], etc. It should be mentioned that the most part of the known MOF are derivatives of transition metals, especially 3*d* elements. As compared to them, the MOF based on *p* elements (in particular, Bi(III), Pb(II)) are poorly studied [14–19]. The 2D pyrazine chlorobismuthate complex $[Bi_2Cl_6(Pyz)_4]$ has been described rather recently [20], and the related luminescent materials were obtained (by doping with lanthanide salts). It was earlier mentioned [21] that, under similar conditions (using a salt of the same cation as a precursor, an identical solvent, etc.), chloro-, bromo-, and iodobismuthates(III) often (although not always) turned out to be isostructural. Similar observations were made for some heteroligand halogenbismuthates(III) [22, 23]. Based on these facts, it seemed reasonable to continue the studies started in [20] by the synthesis of other pyrazine halide complexes of Bi(III), determination of their structures, and investigation of the properties.

In this work, we synthesized the 2D coordination polymer {[Bi(Pyz)I_3]} (**I**) and determined its structure by X-ray diffraction analysis. An analysis of the Hirshfeld surface was performed for compound **I** in order to establish the contributions of various interatomic contacts to the crystal packing.

EXPERIMENTAL

The initial reagents were purchased from commercial sources, and tetrahydrofuran was purified according to a standard procedure.

Synthesis of {[Bi(Pyz)I_3]} (I). Tetrahydrofuran (10 mL) was added to BiI_3 (100 mg, 0.17 mmol) and pyrazine (14 mg, 0.17 mmol), and the mixture was heated to 60°C. After the complete dissolution of the reagents (3 h), the solution was cooled down to room temperature. The gradual evaporation of the solvent (to ~1/5 of the initial volume) resulted in the formation of orange crystals of compound **I** suitable for X-ray diffraction analysis. The yield was 87%.

For $C_4H_4N_2I_3Bi$			
Anal. calcd., %	C, 7.2	H, 0.6	N, 4.2
Found, %	C, 7.6	H, 0.7	N, 4.4

X-ray diffraction analysis (XRD). The diffraction data for a single crystal of compound **I** were obtained

Table 1. Crystallographic data and experimental and structure refinement parameters for compound **I**

Parameter	Value
FW	669.77
Crystal system	Orthorhombic
Space group	*Pbca*
a, Å	12.6114(4)
b, Å	12.4677(4)
c, Å	14.2907(5)
V, Å^3	2247.00(13)
Z	8
ρ_{calc}, g/cm^3	3.960
μ, mm^{-1}	23.88
$F(000)$	2272
Crystal size, mm	0.25 × 0.20 × 0.17
Scan range over θ, deg	3.9–28.9
Range of indices *hkl*	$-16 \le h \le 17$, $-14 \le k \le 16$, $-19 \le l \le 17$
Number of measured/independent reflections	9962/2629
R_{int}	0.033
Number of reflections with $I > 2\sigma(I)$	2350
GOOF	1.09
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0255$, $wR_2 = 0.0512$
R factors (for all reflections)	$R_1 = 0.0309$, $wR_2 = 0.0531$
Residual electron density (max/min), e/Å^3	1.59/–1.50

at 130 K on an Agilent Xcalibur automated diffractometer equipped with an AtlasS2 two-coordinate detector (graphite monochromator, $\lambda(\text{Mo}K_\alpha) = 0.71073$ Å, ω scan mode). The integration, application of an absorption correction, and determination of the unit cell parameters were performed using the CrysAlisPro program package. The crystal structures were solved using the SHELXT program and refined by full-matrix least squares in the anisotropic (except for hydrogen atoms) approximation using the SHELXL program [24]. The positions of the hydrogen atoms of the organic ligands were calculated geometrically and refined in the riding model. The crystallographic data and details of XRD experiments are presented in Table 1.

The full tables of interatomic distances and bond angles, coordinates of atoms, and atomic shift parameters were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1904990; https://www.ccdc.cam.ac.uk/structures/).

RESULTS AND DISCUSSION

According to the CCDC data, the number of complexes of post-transition metals with pyrazines is fairly low. Only one compound $[(\text{SbF}_5)_2(\text{Pyz})]$ is described for Sb in which pyrazine acts as a linker connecting two $\{\text{SbF}_5\}$ fragments [25]. Heteroligand pyrazine halide complexes (X = Cl, Br, I) are known for Pb(II). The chloride [26] and iodide [27] complexes $\{[\text{Pb}_2(\text{Pyz})\text{X}_4]\}$ are isostructural. At the same time, the bromide complex differs in both composition ($\{[\text{Pb}(\text{Pyz})\text{Br}_2]\}$) and structure [28]. All these complexes are 2D coordination polymers. In the case of Sn(IV), the $\{[\text{Sn}(\text{Pyz})_2\text{Cl}_4]\}$ complex is one-dimensional [29].

The coordination environment of the Bi atoms in the structure of complex **I** is a distorted octahedron. Of four iodide ligands, two ligands are terminal (Bi–I_{term} 2.869–2.891 Å) and other two ligands are μ_2-bridging, whereas the Bi–I distance for one of them is significantly shorter than that for another (2.959 versus 3.371 Å). A similar elongation of bonds is typical of the bridging halide ligands [21]. Two coordination sites are occupied by pyrazine ligands (Bi–N 2.691–2.798 Å) acting as ligands. Thus, complex **I** is a 2D coordination polymer (Fig. 1), whose structure differs substantially from that of pyrazine chlorobismuthate(III) described earlier [20].

Although complex **I** exhibits no external properties of decomposition during isolation from the mother liquor, we found that the complex underwent decom-

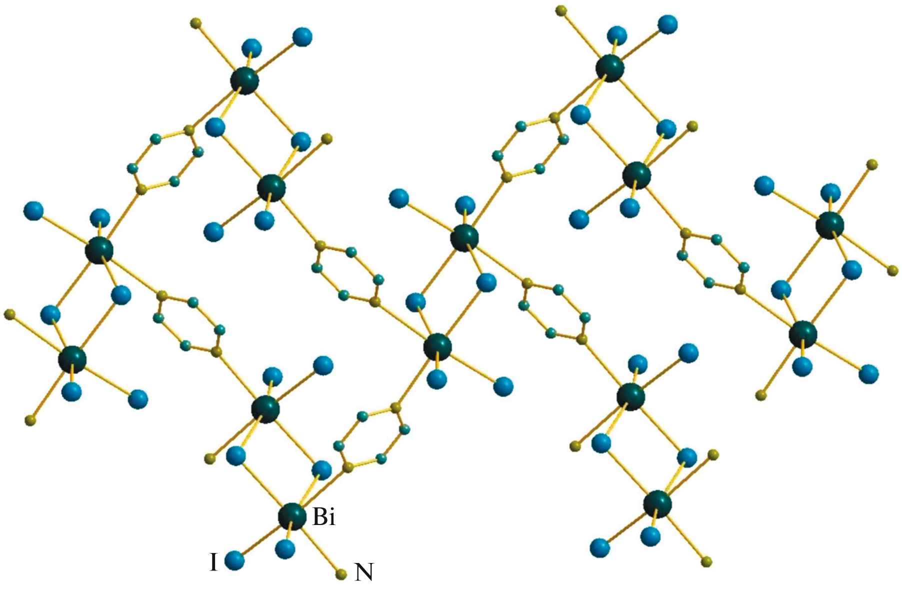

Fig. 1. Structure of the {[Bi(Pyz)I$_3$]} layer. Hydrogen atoms are omitted.

position under X-ray irradiation at room temperature. During XRD analysis, the color of a sample of compound **I** changes from light orange to gray-black. The obtained powder XRD patterns are not consistent with the calculated data for the structure of complex **I**: a new crystalline phase is formed, whose composition, according to the elemental analysis data, is similar to that of the initial phase (see Fig. 2). This effect is reproducible, and additional experiments make it possible to exclude the influence of other factors (hydrolysis, photo- or thermoinduced decomposition). The reasons for a low resistance of compound **I** to X-ray radiation are presently unobvious.

In order to understand what interatomic contacts make the largest contribution to the crystal packing, we performed an analysis of the Hirshfeld surface (this approach is widely used for an analysis of packings of coordination compounds [30–37]) for the elementary unit of the polymer structure of compound **I** (Fig. 3) using the Crystal Explorer 3.1 program. The following

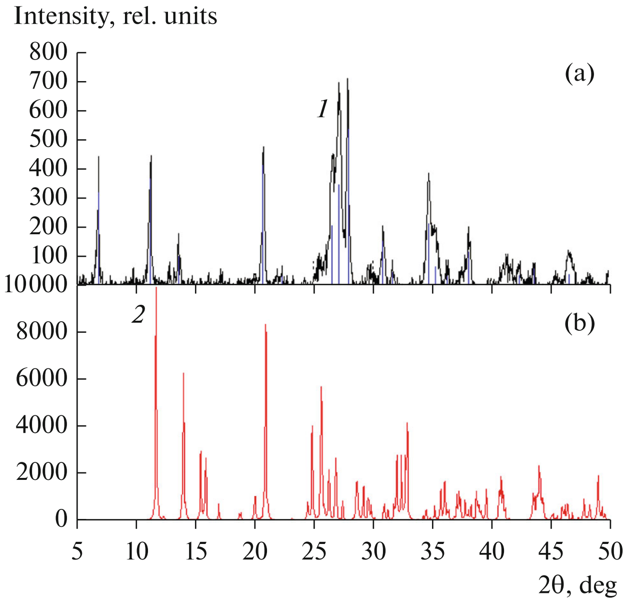

Fig. 2. (a) Experimental XRD pattern of the substance formed during the XRD experiment for the sample of compound **I** and (b) the calculated XRD pattern for compound **I**.

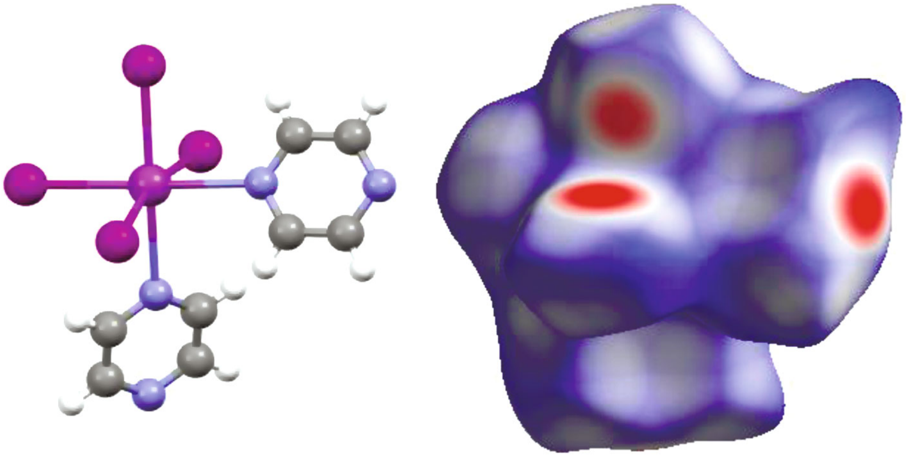

Fig. 3. Hirshfeld surface for the elementary unit of the structure of compound **I** obtained in the framework of the formalism of normalized contact lengths based on van der Waals radii according to Bondi [38] (d_{norm} [39]).

fractions of contributions of the interatomic contacts were found: I···H 50.9, C···I 15.2, I···I 8.5, I···N 7.3, H···H 5.2, Bi···I 4.1, N···H 3.5, Bi···N 3.5, C···H 0.9, and Bi···H 0.9%. Thus, the analysis of the Hirshfeld surface for the elementary unit of compound **I** showed that the I···H interatomic distances made the largest contribution to the crystal packing of this compound.

REFERENCES

1. Barsukova, M.O., Samsonenko, D.G., Sapianik, A.A., et al., *Polyhedron*, 2018, vol. 144, p. 219.
2. Demakov, P.A., Sapchenko, S.A., Samsonenko, D.G., et al., *Russ. Chem. Bull.*, 2018, vol. 67, p. 490.
3. Litvinova, Y.M., Gayfulin, Y.M., Kovalenko, K.A., et al., *Inorg. Chem.*, 2018, vol. 57, p. 2072.
4. Cheplakova, A.M., Kovalenko, K.A., Samsonenko, D.G., et al., *Dalton Trans.*, 2018, vol. 47, p. 3283.
5. Sidorov, A.A., Kiskin, M.A., Aleksandrov, G.G., et al., *Russ. J. Coord. Chem.,* 2016, vol. 42, p. 621. https://doi.org/10/1134/S003602361808020X
6. Sapianik, A.A., Zorina-Tikhonova, E.N., Kiskin, M.A., et al., *Inorg. Chem.*, 2017, vol. 56, p. 1599.
7. Zorina-Tikhonova, E.N., Gogoleva, N.V., Aleksandrov, E.V., et al., *Russ. Chem. Bull.*, 2016, vol. 65, p. 759.
8. Bazhina, E.S., Aleksandrov, G.G., Kiskin, M.A., et al., *Russ. Chem. Bull.*, 2016, vol. 65, p. 249.
9. Bazhina, E.S., Aleksandrov, G.G., Bogomyakov, A.S., et al., *Polyhedron*, 2014, vol. 77, p. 47.
10. Sapianik, A.A., Kiskin, M.A., Samsonenko, D.G., et al., *Polyhedron*, 2018, vol. 145, p. 147.
11. Khan, I.S., Samsonenko, D.G., Irgashev, R.A., et al., *Polyhedron*, 2018, vol. 141, p. 337.
12. Ponomareva, V.G., Aliev, S.B., Shutova, E.S., et al., *RSC Adv.*, 2017, vol. 7, p. 403.
13. Bolotov, V.A., Kovalenko, K.A., Samsonenko, D.G., et al., *Inorg. Chem.*, 2018, vol. 57, p. 5074.
14. Gschwind, F., Jansen, M., Gschwind, F., et al., *Crystals*, 2012, vol. 2, p. 1374.
15. Ouyang, H., Chen, N., Chang, G., et al., *Angew. Chem., Int. Ed. Engl.*, 2018, vol. 57, p. 13197.
16. Köppen, M., Beyer, O., Wuttke, S., et al., *Dalton Trans.*, 2017, vol. 46, p. 8658.
17. Köppen, M., Meyer, V., Ångström, J., et al., *Cryst. Growth Des.*, 2018, vol. 18, p. 4060.
18. Koppen, M., Dhakshinamoorthy, A., Inge, A.K., et al., *Eur. J. Inorg. Chem.*, 2018, p. 3503.
19. de Lima, G.M., Walton, R.I., Clarkson, G.J., et al., *Dalton Trans.*, 2018, vol. 47, p. 8013.
20. Sorg, J.R., Wehner, T., Matthes, P.R., et al., *Dalton Trans.*, 2018, vol. 47, p. 7669.
21. Adonin, S.A., Sokolov, M.N., and Fedin, V.P., *Coord. Chem. Rev.*, 2016, vol. 312, p. 1.
22. Bowmaker, G.A., Junk, P.C., Lee, A.M., et al., *Aust. J. Chem.*, 1998, vol. 51, p. 293.
23. Bowmaker, G.A., Harrowfield, J.M., Junk, P.C., et al., *Aust. J. Chem.*, 1998, vol. 51, p. 285.
24. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.
25. Sham, I.H.T., Patrick, B.O., von Ahsen, B., et al., *Solid State Sci.*, 2002, vol. 4, p. 1457.
26. Liao, Q.-X., Zhang, J., Qin, Y.-Y., et al., *Jiegou Huaxue*, 2006, vol. 25, p. 789.
27. Aslani, A. and Morsali, A., *Inorg. Chim. Acta*, 2009, vol. 362, p. 5012.
28. Mrad, M.L., Feddaoui, I., Abdelbaky, M.S.M., et al., *Inorg. Chim. Acta*, 2018, vol. 476, p. 38.
29. Grigsby, W.A., Morien, T.S., Raston, C.L., et al., *Aust. J. Chem.*, 2004, vol. 57, p. 507.
30. Katkova, S.A., Mikherdov, A.S., Kinzhalov, M.A., et al., *Chem.-Eur. J.*, 2019, vol. 25, p. 8590.

31. Semyonov, O., Lyssenko, K.A., and Safin, D.A., *Inorg. Chim. Acta*, 2019, vol. 488, p. 238.
32. Kinzhalov, M.A., Baykov, S.V., Novikov, A.S., et al., *Z. Kristallogr—Cryst. Mater.*, 2019, vol. 234, p. 155.
33. Afkhami, F.A., Mahmoudi, G., Khandar, A.A., et al., *J. Mol. Struct.*, 2019, vol. 1176, p. 743.
34. Novikov, A.S., Ivanov, D.M., Bikbaeva, Z.M., et al., *Cryst. Growth Des.*, 2018, vol. 18, p. 7641.
35. Kinzhalov, M.A., Novikov, A.S., Khoroshilova, O.V., et al., *J. Struct. Chem.*, 2018, vol. 59, p. 1302.
36. Bikbaeva, Z.M., Ivanov, D.M., Novikov, A.S., et al., *Inorg. Chem.*, 2017, vol. 56, p. 13562.
37. Mahmoudi, G., Zangrando, E., Mitoraj, M.P., et al., *New J. Chem.*, 2018, vol. 42, p. 4959.
38. Bondi, A., *J. Phys. Chem.*, 1966, vol. 70, p. 3006.
39. McKinnon, J.J., Jayatilaka, D., and Spackman, M.A., *Chem. Commun.*, 2007, p. 3814.

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