2914 Russian Chemical Bulletin, International Edition, Vol. 65, No. 12, pp. 2914—2919, December, 2016

Coordination polymers with adjustable dimensionality based on Cu^{II} and bis-imidazolyl bridging ligand*

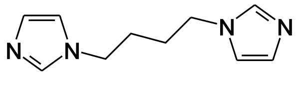
M. O. Barsukova,[a] D. G. Samsonenko,[a,b] T. V. Goncharova,[c] A. S. Potapov,[c,d]
S. A. Sapchenko,[a,b] D. N. Dybtsev,[a,b] and V. P. Fedin[a,b]★

[a]A. V. Nikolaev Institute of Inorganic Chemistry,
Siberian Branch of the Russian Academy of Sciences,
3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 330 9489. E-mail: cluster@niic.nsc.ru
[b]Novosibirsk State University, Department of Natural Sciences,
2 ul. Pirogova, 630090 Novosibirsk, Russian Federation
[c]I. I. Polzunov Altai State Technical University,
46 prosp. Lenina, 656038 Barnaul, Russian Federation
[d]National Research Tomsk Polytechnic University,
30 prosp. Lenina, 634050 Tomsk, Russian Federation

1,4-Bis(imidazol-1-yl)butane was synthesized from imidazole and 1,4-dibromobutane in an alkaline medium. A variation of the molar ratio of reagents in the system copper(II) chloride dihydrate and 1,4-bis(imidazol-1-yl)butane (bImB) upon heating in *N*,*N*-dimethylformamide resulted in the synthesis of two new coordination polymers [Cu(bImB)Cl$_2$] (**1**) and [Cu(bImB)$_2$Cl$_2$] (**2**), which were structurally characterized. Product **1** was found to possess a chain structure, while structure **2** is built of neutral layers, with the dimensionality of the extended coordination structures being determined by the reaction conditions. The new compounds were characterized by IR spectroscopy, elemental analysis, and powder X-ray diffraction data.

Key words: coordination polymer, copper, bis(imidazolyl)alkanes, X-ray diffraction.

Imidazole is a part of many biological molecules such as histidine. The chemistry of copper(II) imidazolyl complexes is closely related to the presence of such fragments in the nature as active sites of different enzymes.[1] From the point of view of coordination chemistry, copper(II) imidazolyl complexes are of interest due to the structural diversity, redox,[2] luminescent,[3] as well as magnetic properties,[4] which arouse from the paramagnetic nature of Cu^{2+} cations. An additional impulse to the studies of chemistry of copper imidazolyl complexes was given after discovery of their antitumor activity.[5,6] At the same time, organic bridging ligands with imidazolyl functional groups are actively used for the design of coordination polymers. Such compounds possess a number of unique properties, including ion-exchange, sensor, and sorption properties, which frequently are conjugated with the structural transformations of the metal-organic framework.[7] In this connection, the use of structurally flexible bis(imidazolyl)alkane bridging ligands in the synthesis of coordination polymers is promising for the studies of possible structural transitions and related functional properties. In the present work, we describe the synthesis of the organic ligand 1,4-bis(imidazol-1-yl)butane (bImB), as well as the preparation, crystal structure, and spectral analysis of two coordination polymers on its basis with copper(II) cations.


bImB

It was found that the dimensionality of coordination compounds can be varied on demand from one-dimensional (chain) to two-dimensional (network) depending on the conditions of the synthesis.

Results and Discussion

The organic ligand 1,4-bis(imidazol-1-yl)butane (bImB) was synthesized using a suggested by us new method, namely, by the reaction of imidazole with 1,4-dibromobutane in a superbasic medium DMSO—KOH. Earlier, this reaction was carried out either by using phase-transfer catalysis,[8] or generating an imidazolate anion upon treatment with sodium hydride.[9] Our method does not require expensive phase-transfer catalysts or metal hydrides and provides higher, nearly quantitative yield.

---

* Dedicated to Academician of the Russian Academy of Sciences R. Z. Sagdeev on the occasion of his 75th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2914—2919, December, 2016.

In the synthesis of coordination polymers [Cu(bImB)Cl_2] (**1**) and [Cu$(bImB)_2Cl_2$] (**2**), we used copper(II) chloride dihydrate as a source of copper, which was involved in the reaction with different amounts of the organic bridging ligand bImB upon heating in a mixture of *N*,*N*-dimethylformamide (DMF) and methanol. Depending on the molar ratio of the starting reagents $CuCl_2 \cdot 2H_2O$: bImB = 1 : 1 or 1 : 3, we obtained single crystals of two coordination polymers, the structure of which was established by X-ray diffraction.

The single crystal X-ray diffraction data showed that the asymmetric unit of structure **1** contains one copper(II) cation, two chloride anions, and one molecule of 1,4-bis(imidazol-1-yl)butane, which occupy general positions. The coordination environment of copper(II) consists of two nitrogen atoms of the imidazole rings and two chloride anions (Fig. 1). The distances Cu—N are 1.950(3) and 1.952(3) Å, the distances Cu—Cl are 2.2600(10) and 2.2702(10) Å. The coordination polyhedron can be regarded as a strongly distorted (flattened along the axis C_2) tetrahedron. The angles N—Cu—N and Cl—Cu—Cl are 149.97(13)° and 142.84(4)°, respectively. The molecule of 1,4-bis(imidazol-1-yl)-butane acts as a bridging ligand coordinated to the two copper(II) cations. Each copper(II) cation coordinates two organic ligands, forming a zigzag-like polymeric chain (see Fig. 1). The polymeric chains are laid in layers parallel to the plane *ac*, which, in turn, form a double-layer packing. The polymeric chains are parallel inside the layer, the chains from the neighboring layers form crossed straight lines at an angle of ~74.4° (Fig. 2). The polymeric chains are linked to each other by the van der Waals interactions.

The asymmetric unit of structure **2** contains one copper(II) cation, one chloride anion, and one molecule of 1,4-bis(imidazol-1-yl)butane. The copper(II) cations occupy position 2*a* (one of the systems of inversion centers: 0, 0, 0; 0, 1/2, 1/2). The coordination environment of the copper(II) cation consists of four nitrogen atoms of the imidazole rings and two chloride anions. The coordination polyhedron is an octahedron elongated along the axis C_4, where the nitrogen atoms of the imidazole rings are located in the equatorial plane, while the axial positions are occupied by the chloride anions (Fig. 3). The distances Cu—N are 2.022(2) and 2.030(2) Å, the distance Cu—Cl is 2.9247(6) Å. The molecule of 1,4-bis(1-imidazolyl)butane acts as a bridging ligand coordinated to the two copper(II) cations. Each copper(II) cation, in turn, coordinates four organic ligands, forming

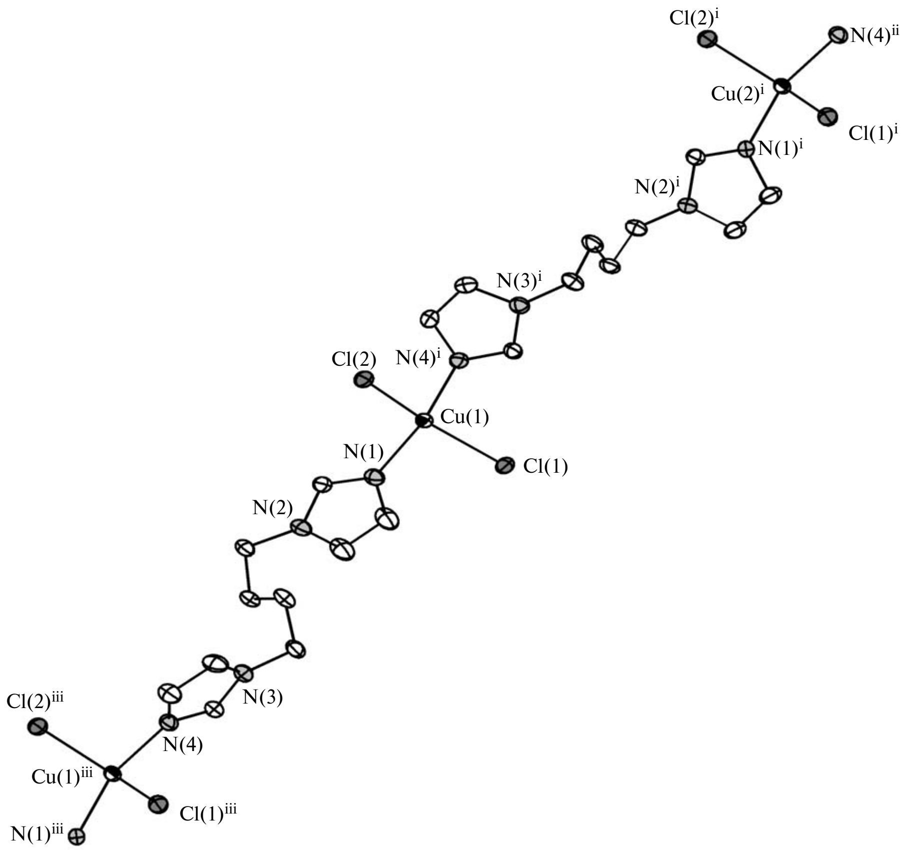


Fig. 1. A fragment of the polymeric chain in structure **1** (displacement ellipsoids at 50% probability). Hydrogen atoms are omitted. The coordinates of symmetrically equivalent atoms were obtained by the following symmetry operations: i) $1/2 + x$, $3/2 - y$, $1 + z$; ii) $1 + x$, y, $2 + z$; iii) $-1/2 + x$, $3/2 - y$, $-1 + z$.

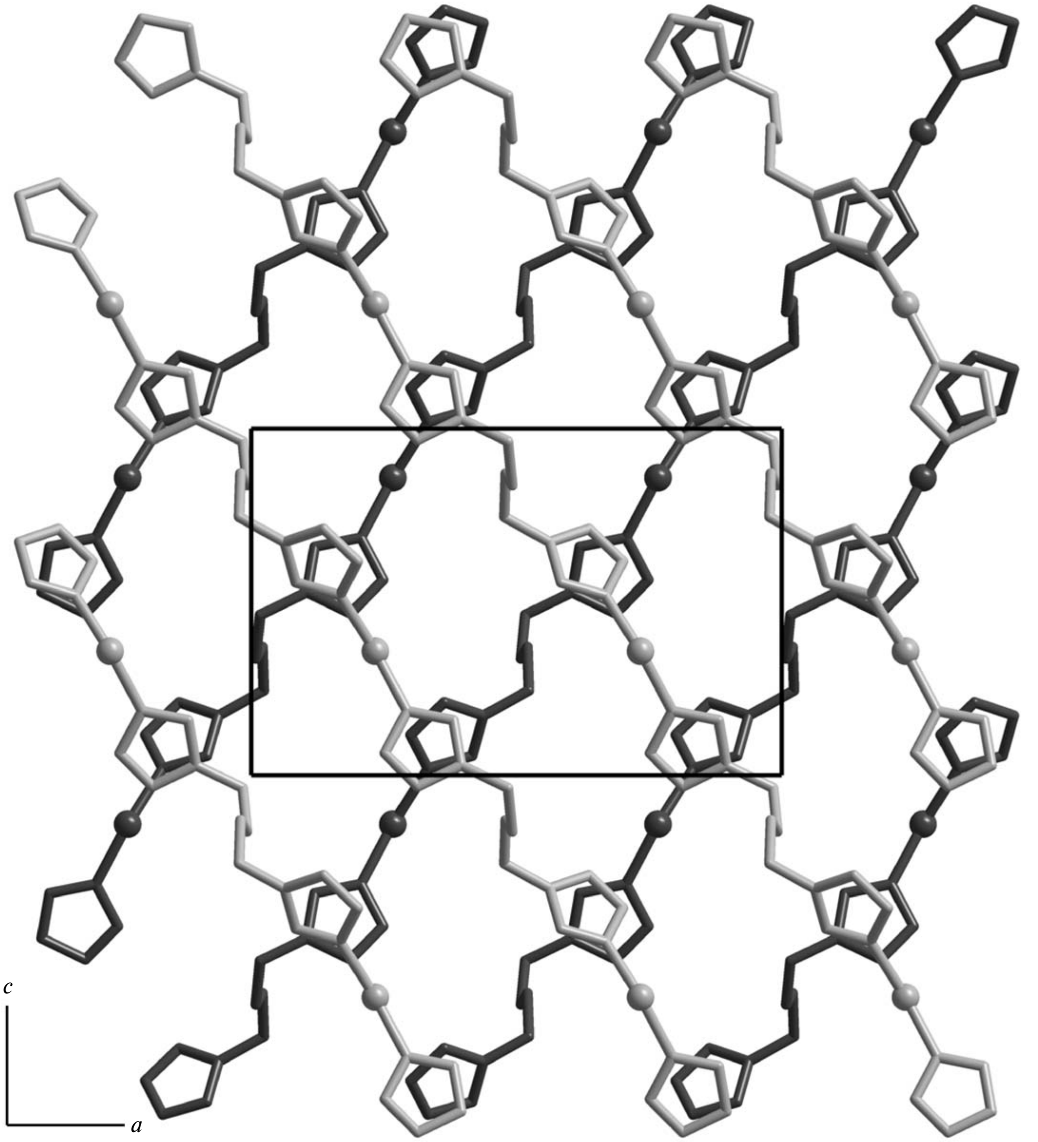


Fig. 2. The packing of the polymeric chains in structure **1**. Hydrogen and chlorine atoms are omitted. Positions of copper(II) cations are shown as spheres. The chains of the neighboring layers are shown in different shades of grey.

a polymeric layer of the **sql** topology (Fig. 4). The layers form a three-layer close packing, being placed on the system of (102) planes. The polymeric layers are linked to each other by the van der Waals interactions.

The phase purity of the samples of compounds **1** and **2** was confirmed by powder X-ray diffraction. The experimental diffractograms of compounds **1** and **2** are in good agreement with those calculated from the single crystal X-ray diffraction data (Fig. 5). The IR spectra of compounds **1** and **2** showed absorption bands attributed to the stretching vibrations ν(O—H) of the adsorbed water molecules at 3467 and 3424 cm^{-1}, respectively. The vibrations in the region of 2950—3124 cm^{-1} correspond to the asymmetric and symmetric vibrations of the ligand fragments C—C. The C—N stretching vibrations of the imidazolyl ring were found at 1093 and 1110 cm^{-1} for compounds **1** and **2**, respectively.

Note that the formation of the chain structure **1** or the layered structure **2** takes place under absolutely identical reaction conditions, except the concentration of the organic ligand bImB. The use of the lower concentration (the molar ratio metal : ligand = 1 : 1) leads to the formation of the chain product **1** with a similar formula ratio Cu : bImB = 1. When an excess of the ligand is used (metal : ligand = 1 : 3), product **2** with the layered structure and a formula ratio Cu : bImB = 0.5 crystallizes from the reaction mixture. The literature data show that the formation of the chain coordination polymers similar to

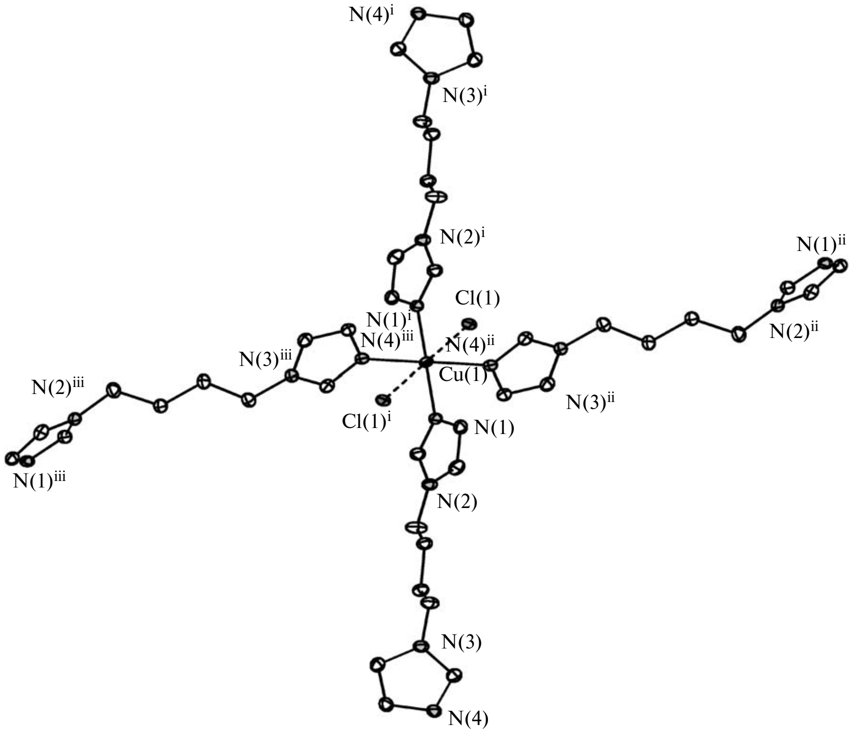


Fig. 3. Coordination environment of the copper(II) cation in structure **2** (displacement ellipsoids at 50% probability). Hydrogen atoms are omitted. The coordinates of symmetrically equivalent atoms were obtained by the following symmetry operations: i) $-x$, $1-y$, $1-z$; ii) $-1+x$, $3/2-y$, $1/2+z$; iii) $1-x$, $-1/2+y$, $1/2-z$.

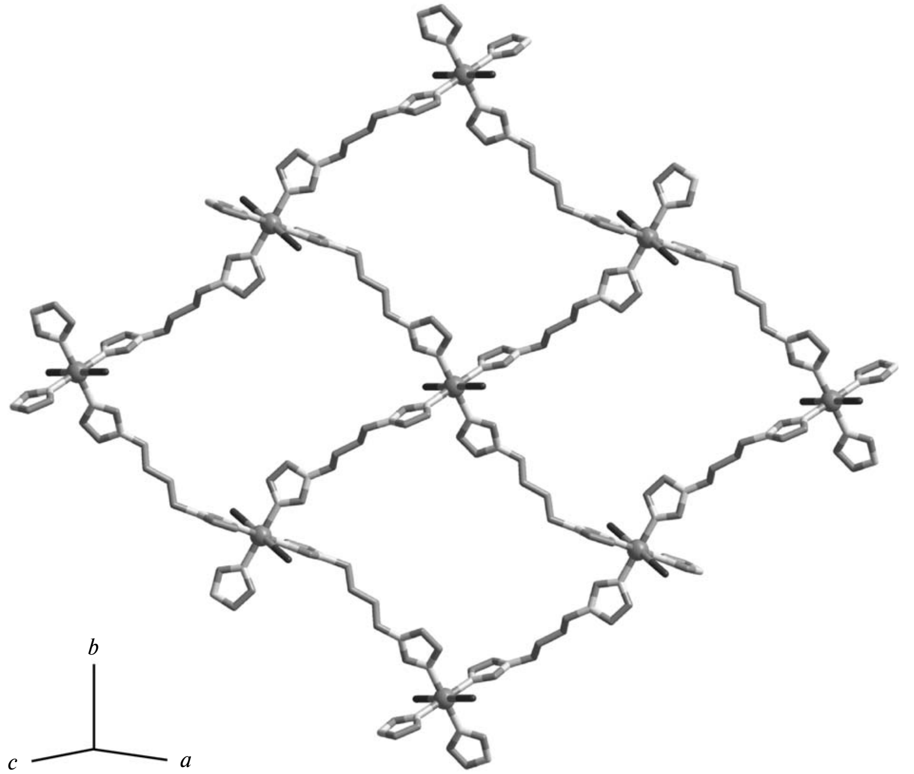


Fig. 4. A fragment of the polymeric layer in structure **2**. Hydrogen atoms are omitted. Positions of copper(II) cations are shown as spheres.

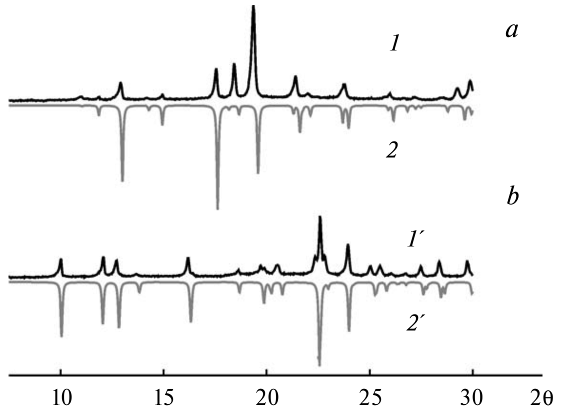


Fig. 5. Comparison of experimental (*1*, *1´*) and simulated (*2*, *2´*) X-ray diffraction patterns for compound **1** (*a*) and compound **2** (*b*).

structure **1** in the system copper—bis(imidazol-1-yl)butane was observed when copper(I) chloride and bromide were used in the solvothermal synthesis,[10,11] as well as under conditions of slow diffusion from the methanolic solution of the ligand to the aqueous solution of copper(II) chloride,[12] with the halide ions being included in the coordination environment of copper cations. The formation of the layered coordination polymer with a square-type topology of the polymeric layer was observed in the case of a slow diffusion from a methanolic solution of 1,4-bis(imidazol-1-yl)butane to the aqueous solution of copper(II) bromide.[12] Apart from that, the formation of layered coordination polymers was observed upon standing of aqueous solutions containing copper(II) chloride, nitrate, or sulfate, with the indicated counterions not being included in the coordination sphere of the copper(II) cation.[13] To sum up, according to the analysis of the published data, the formation of either one-dimensional or two-dimensional structure of a given coordination polymer depends simultaneously on many difficult-to-systematize parameters, which include the nature of anion used in the synthesis of copper salts, the metal oxidation state, solvent, and method of synthesis. In the present work, we showed that a controlled formation of a layered or a chain coordination polymer can occur depending on only one parameter of the reaction mixture, namely, the ratio of reagents.

In conclusion, we optimized a procedure for the synthesis of the flexible bridging ligand 1,4-bis(imidazol-1-yl)butane and obtained two coordination polymers on its basis with copper(II) chloride. The composition, the structure, and the phase purity of the products were established by single-crystal X-ray diffraction and confirmed by elemental analysis, IR spectroscopy, and powder X-ray diffraction. The ratio of the reagents in the reaction mixture was found to influence the dimensionality of the coordination compound, that leads to the formation of chain or layered structure.

Experimental

The starting compounds, *i.e.*, copper(II) chloride dihydrate, *N*,*N*-dimethylformamide, and methanol, were at least of reagent grade and used without additional purification. IR spectra were recorded on a Scimitar FTS 2000 Fourier-transform spectrometer in the 4000—400 cm^{-1} range in KBr pellets. NMR spectra were recorded on a Bruker AV-300 spectrometer (300 MHz for protons, 75 MHz for ^{13}C). Elemental analysis was carried out on a Euro EA 3000 analyzer in the Analytical Laboratory of the A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences. Powder X-ray diffraction data were recorded on a Shimadzu XRD 7000S powder diffractometer (Cu-Kα radiation).

1,4-Bis(imidazol-1-yl)butane (bImB). A mixture of imidazole (1.36 g, 20 mmol), powdered KOH (1.68 g, 30 mmol), and DMSO (5 mL) was stirred at 80 °C for 30 min and cooled, then 1,4-dibromobutane (2.16 g, 10 mmol) in DMSO (5 mL) was added dropwise and the stirring was continued for another 8 h at 80 °C. Then, the reaction mixture was diluted with water (200 mL) and a mixture of water and DMSO was removed *in vacuo*. A solid residue was treated with boiling ethyl acetate to extract an organic product, the extract was distilled *in vacuo*. The yield was 95%, colorless crystals, m.p. 81—83 °C. Found (%): C, 63.2; H, 7.5; N, 29.5. $C_{10}H_{14}N_4$. Calculated (%): C, 63.3; H, 7.4; N, 29.5. IR, ν/cm^{-1}: 1577, 1461, 1431 (Im). ^1H NMR (DMSO-d_6), δ: 1.33 (t, 2 H, $ImCH_2\underline{CH_2}$, J = 8 Hz); 3.95 (t, 4 H, $Im\underline{CH_2}CH_2$, J = 8 Hz); 6.85 (d, 2 H, $H_{Im}(4)$, J = 2 Hz); 7.01 (d, 2 H, $H_{Im}(5)$, J = 2 Hz); 7.61 (s, 2 H, $H_{Im}(2)$). ^{13}C NMR (DMSO-d_6), δ: 27.7 ($ImCH_2\underline{CH_2}$); 45.3 ($Im\underline{CH_2}CH_2$); 119.3 ($C_{Im}(5)$); 128.4 ($C_{Im}(4)$); 137.2 ($C_{Im}(2)$).

***catena*-Dichloro-1,4-bis[(imidazol-1-yl)butane]copper [$Cu(bImB)Cl_2$] (1).** A mixture of $CuCl_2 \cdot 2H_2O$ (17 mg, 0.1 mmol), 1,4-bis(imidazol-1-yl)butane (19 mg, 0.1 mmol), *N*,*N*-dimethylformamide (2 mL), and methanol (2 mL) was heated in a glass vial with a screw cap at 100 °C for 24 h. The crystals formed were washed with *N*,*N*-dimethylformamide (5×1 mL) and dried in air. The yield was 26 mg (80% calculated on Cu). Found (%): C, 36.5; H, 4.7; N, 17.0. $C_{10}H_{14}Cl_2CuN_4$. Calculated (%): C, 37.0; H, 4.4; N, 17.3. IR (KBr), ν/cm^{-1}: 3468 (w), 3124 (s), 2932 (m), 1638 (m), 1520 (s), 1448 (s), 1409 (m), 1369 (m), 1279 (m), 1236 (s), 1093 (s), 956 (m), 863 (m), 757 (m), 656 (s), 629 (m), 572 (w), 438 (w).

***catena*-Dichloro-bis[1,4-bis(imidazol-1-yl)butane]copper [$Cu(bImB)_2Cl_2$] (2).** A mixture of $CuCl_2 \cdot 2H_2O$ (17 mg, 0.1 mmol), 1,4-bis(imidazol-1-yl)butane (57 mg, 0.3 mmol), *N*,*N*-dimethylformamide (2 mL), and methanol (2 mL) was heated in a glass vial with a screw cap at 100 °C for 24 h. The crystals formed were washed with *N*,*N*-dimethylformamide (5×1 mL) and dried in air. The yield was 37 mg (72% calculated on Cu). Found (%): C, 46.0; H, 5.8; N, 21.4. $C_{20}H_{28}Cl_2CuN_8$. Calculated (%): C, 46.6; H, 5.5; N, 21.8. IR (KBr), ν/cm^{-1}: 3424 (w), 3122 (s), 2941 (m), 1639 (m), 1518 (s), 1467 (m), 1441 (m), 1380 (m), 1271 (s), 1237 (s), 1110 (s), 1036 (m), 943 (s), 886 (s), 846 (s), 738 (s), 660 (s), 624 (m), 452 (w).

X-ray diffraction study. Single crystal X-ray diffraction data for **1** and **2** were measured at 130 K on an Agilent Xcalibur automated diffractometer equipped with an AtlasS2 2D detector (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ω-scan technique). The integration, correction for absorption, and determination of the unit cell parameters were carried out using the CrysAlisPro software.[14] The structure was solved by direct methods and refined by the full-

Table 1. Crystallographic parameters and details of X-ray diffraction experiment

Parameter	**1**	**2**
Empirical formula	$C_{10}H_{14}Cl_2CuN_4$	$C_{20}H_{28}Cl_2CuN_8$
M/g mol^{-1}	324.69	514.94
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/c$
a/Å	14.9245(4)	7.6061(5)
b/Å	9.5062(3)	17.6047(6)
c/Å	9.7578(3)	8.9119(5)
β/deg		114.965(7)
V/Å^3	1384.39(7)	1081.83(11)
Z	4	2
d_{calc}/g cm^{-3}	1.558	1.581
μ/mm^{-1}	1.947	1.283
F(000)	660	534
Crystal size/mm	0.20×0.12×0.09	0.39×0.16×0.07
θ Range for data collection	3.29—28.99	3.42—28.43
Range of indices hkl	$-21 < h < 13$, $-12 < k < 13$, $-13 < l < 9$	$-8 < h < 11$, $-23 < k < 16$, $-7 < l < 12$
Number of reflections collected/unique	4284/2433	3205/1988
R_{int}	0.0176	0.0180
N_{hkl} c $I > 2\sigma(I)$	2312	1749
Goodness of fit on F^2	1.090	1.066
R-factors ($I > 2\sigma(I)$)		
R_1	0.0264	0.0342
wR_2	0.0636	0.0956
R-factors (based on all reflections)		
R_1	0.0289	0.0395
wR_2	0.0650	0.0995
Residual electron density (max/min), e/Å^3	0.592/–0.359	0.532/–0.602

matrix least squares method with anisotropic displacement parameters (except hydrogen atoms) using the SHELX-2014 software.[15] The hydrogen atoms of the organic ligands were positioned geometrically and refined using a riding model. The crystallographic data and the details of diffraction experiments are given in Table 1. The full tables of interatomic distances and bond angles, atomic coordinates, and atomic displacement parameters were deposited with the Cambridge Crystallographic Data Center (CCDC 1482782 and 1482783), as well as can be requested from the authors.

This work was financially supported by the Russian Science Foundation (Project No. 15-13-10023).

References

1. S. Godlewska, J. Jezierska, K. Baranowska, E. Augustin, A. Dolega, *Polyhedron*, 2013, **65**, 288.
2. G. T. Musia, X. Li, D. R. Powell, *Inorg. Chim. Acta*, 2003, **348**, 69.
3. W. Wu, J. Xie, D. Xie, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 2010, **55**, 384 [*Zh. Inorg. Khim.,* 2010, **55**, 429].
4. M. V. Fedin, S. L. Veber, E. G. Bagryanskaya, V. I. Ovcharenko, *Coord. Chem. Rev.*, 2015, **289—290**, 341.
5. H. Tamura, H. Imai, J. Kuwahara, Y. Sugiura, *J. Am. Chem. Soc.*, 1987, **109**, 6870.
6. C. Marzano, M. Pellei, F. Tisato, C. Santini, *Anti. Canc. Agents Med. Chem.*, 2009, **9**, 185.
7. A. Karmakar, A. V. Desai, S. K. Ghosh, *Coord. Chem. Rev.*, 2016, **307**, 313.
8. J. S. Parent, A. M. J. Porter, M. R. Kleczek, R. A. Whitney, *Polymer*, 2011, **52**, 5410.
9. I. Kammakakam, S. Nam, T.-H. Kim, *RSC Adv.*, 2015, **5**, 69907.
10. Y. Qi, F. Luo, S. R. Batten, Y.-X. Che, J. M. Zheng, *Cryst. Growth. Des.*, 2008, **8**, 2806.
11. M. Dai, Z. Yang, C. Ni, H. Yu, Y. Chen, H. Li, Z. Ren, J. Lang, *Inorg. Chem. Commun.*, 2014, **40**, 205.
12. X. Li, Y. Gu, X. Deng, K. Zhao, L. Jin, *Cryst. Eng. Comm.*, 2011, **13**, 6665.
13. J.-F. Ma, J. Yang, G.-L. Zheng, L. Li, Y.-M. Zhang, F.-F. Li, J. F. Liu, *Polyhedron*, 2004, **23**, 553.
14. CrysAlisPro 1.171.38.41. Rigaku Oxford Diffraction. 2015.
15. G. M. Shedrick, *Acta Crystallogr., Section A*, 2008, **64**, 112.

Received June 3, 21016;
in revised form July 15, 2016