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Synthesis and Structure of Zn(II) Complexes with Cyclobutane-1,1-dicarboxylic Acid Anions and Calcium and Barium Cations

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Abstract—New zinc(II) compounds with cyclobutane-1,1-dicarboxylic acid (H_2Cbdc) anions and calcium $[CaZn(Cbdc)_2(H_2O)_3]_n$ (**I**) and barium $[BaZn(Cbdc)_2(H_2O)_2]_n$ (**II**) cations were obtained. According to X-ray diffraction data (CIF files CCDC nos. 2055176 (**I**), 2055177 (**II**)), compounds **I** and **II** are coordination polymers in which zinc atoms are connected by bridging and chelating-bridging acid dianions to form 2D architectures with a square lattice topology. Alkaline earth metal atoms do not affect the dimensionality of compound packing.

Keywords: coordination polymers, zinc, dicarboxylic acids, cyclobutane-1,1-dicarboxylic acid, X-ray diffraction

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INTRODUCTION

The design and synthesis of zinc-based coordination polymers is a relevant area of scientific research [1]. The composition and structure of these compounds determine their physicochemical properties and applicability for the sorption and separation of gases and organic and inorganic substrates [2–5], for heterogeneous catalysis [6, 7], and for development of luminescent materials and sensors [8–10]. The structure of zinc polymers can be changed post-synthetically, e.g., on exposure of crystals to UV radiation, which induces a solid-phase [2 + 2]-cycloaddition reaction [11–13]. The synthesis of heterometallic coordination polymers containing both zinc atoms and atoms of other transition metals or s-elements expands the structural diversity of polymers and allows for the targeted synthesis of compounds with specified properties, e.g., luminescent [14, 15] or magnetic [16, 17] properties. Heterometallic polymers can be synthesized using both the conventional method of synthesis from simple salts and the stepwise synthesis from low-molecular-weight initial complexes [15, 18–20]. Dicarboxylic acid anions of various nature are widely used as ligands for the construction of coordination polymers of different dimensionality [1, 20, 21]. The nature of the dicarboxylic acid used is a key factor determining the polymer structure. For example, bridging coordination, promoting the formation of frameworks, is typical of terephthalate anions [1, 22, 23]. The use of more conformationally flexible ligands, in particular malonate anions and their substituted analogues, opens up additional coordination opportunities and increase the structural diversity of the obtained polymers [21, 24, 25]. The heterometallic M–M' malonate systems, where M is a 3d metal atom, M' is an alkali or alkaline earth metal atom, generally tend to form coordination polymers in which 3d metals form the bis-chelate dianions {M(R1R2Mal)2-(H2O)x}2– (x = 0–2), while main group metal cations bind these dianions to one another via coordination of oxygen atoms of carboxyl groups and water molecules [18, 21]. An increase in the s-cation radius usually leads to higher dimensionality of the polymer packing [21].

In this study we describe the synthesis and structure of two 2D zinc coordination polymers with cyclobutane-1,1-dicarboxylate anions and calcium $[CaZn(Cbdc)_2(H_2O)_3]_n$ (**I**) and barium $[BaZn(Cbdc)_2(H_2O)_2]_n$ (**II**) cations in which the carboxylate anions occupy only bridging position with respect to zinc atoms. It was shown that for compounds **I** and **II**, a change in the radius of alkaline earth metal cation does not affect the polymer packing dimensionality.

EXPERIMENTAL

The syntheses of all compounds were performed in air using distilled water, $ZnSO_4 \cdot 7H_2O$ (Reachim, pure grade), $Ca(OH)_2$ (Reachim, pure grade), $Ba(OH)_2 \cdot$

H_2O (Sigma Aldrich, 98%), and cyclobutane-1,1-dicarboxylic acid (H_2Cbdc, Sigma Aldrich, 99%).

Infrared spectra were measured on a Perkin Elmer Spectrum 65 spectrophotometer equipped with a Quest ATR Accessory (Specac) attachment in the attenuated total reflectance (ATR) mode in the 400–4000 cm^{-1} range. Elemental analysis was carried out on an automated EuroEA-3000 C, H, N, S-analyzer (EuroVector).

Synthesis of $[CaZn(Cbdc)_2(H_2O)_3]_n$ (I). Weighed portions of $Ca(OH)_2$ (0.026 g, 0.35 mmol) and H_2Cbdc (0.050 g, 0.35 mmol) were dissolved in water (30 mL), and a solution of $ZnSO_4 \cdot 7H_2O$ (0.049 g, 0.17 mmol) in water (10 mL) was added. The reaction mixture was stirred for 1 h and filtered. The resulting colorless solution was kept in air at room temperature. The colorless crystals of **I** suitable for X-ray diffraction, which formed after a week, were isolated, washed with cold acetonitrile ($T = -5°C$), and dried in air at $T = 20°C$. The yield of **I** was 0.036 g (48% based on the initial amount of zinc).

For $C_{12}H_{18}O_{11}CaZn$

Anal. calcd., %	C, 32.48	H, 4.09
Found, %	C, 32.75	H, 4.23

IR (ATR; ν, cm^{-1}): 3530 m, 3450 m, 3414 m, 3383 m, 3226 w, 2999 w, 2967 w, 2945 w, 2872 w, 2324 w, 2280 w, 2162 w, 2030 w, 1672 w, 1634 m, 1591 s, 1463 m, 1402 m, 1342 s, 1264 m, 1236 m, 1160 m, 1123 m, 1077 w, 1067 w, 1012 m, 955 w, 928 w, 909 m, 858 m, 799 w, 764 m, 709 m, 656 m, 642 m, 592 s, 551 s, 520 s, 494 s, 447 s, 427 m, 419 m.

Synthesis of $[BaZn(Cbdc)_2(H_2O)_2]_n$ (II) was carried out by a procedure similar to that used for **I**. Reactant amounts: $Ba(OH)_2 \cdot H_2O$ (0.132 g, 0.70 mmol), H_2Cbdc (0.101 g, 0.70 mmol), $ZnSO_4 \cdot 7H_2O$ (0.100 g, 0.35 mmol). The yield of **II** was 0.042 g (23% based on the initial amount of zinc).

For $C_{12}H_{16}O_{10}ZnBa$

Anal. calcd., %	C, 27.56	H, 3.08
Found, %	C, 27.68	H, 3.28

IR (ATR; ν, cm^{-1}): 3478 w, 3883 w, 2989 w, 2941 w, 2899 w, 2869 w, 2324 w, 2284 w, 2163 w, 2036 w, 1979 w, 1649 m, 1574 s, 1468 w, 1394 m, 1319 s, 1254 m, 1224 m, 1156 m, 1126 m, 1079 m, 950 w, 923 w, 899 m, 860 w, 795 m, 776 w, 757 m, 690 m, 638 m, 575 s, 516 s, 469 s, 430 s, 414 m.

X-ray diffraction. Single crystals of **I** and **II** were taken from the reaction mixture. The experimental set of reflections was obtained on a Bruker APEX II diffractometer equipped with a CCD array detector (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). The absorption corrections were applied empirically by the SADABS program [26]. The structures were solved using the SHELXT program [27]. All non-hydrogen atoms were located in difference electron density maps and refined in the anisotropic approximation on F^2_{hkl} using the SHELXL-14 [28] and OLEX2 [29] programs. The hydrogen atoms were found geometrically and refined in the isotropic approximation in the rigid body model, with $U_{iso}(H) = 1.5U_{equiv}(X_i)$ for water molecules or $1.2U_{equiv}(X_i)$ for other atoms, where $U_{equiv}(X)$ is the equivalent thermal parameter of the atom bearing the hydrogen atom. Crystallographic characteristics and X-ray experiment details are given in Table 1, and selected geometric parameters of the coordination bonds are in Table 2.

The atom coordinates, thermal parameters, and the list of all reflections for these structures were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2055176 (**I**), 2055177 (**II**)) and can be obtained upon request to deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/structures.

RESULTS AND DISCUSSION

The reaction of zinc sulfate with cyclobutane-1,1-dicarboxylic acid and calcium hydroxide in 1 : 2 : 2 ratio gives the polymer $[CaZn(Cbdc)_2(H_2O)_3]_n$ (**I**). The complex crystallizes in the orthorhombic system, space group $Pca2_1$. The independent part of the cell contains one zinc and one calcium cation, two anions, and three water molecules. In compound **I**, the zinc occurs in a distorted tetrahedral environment (ZnO_4 chromophore) formed by oxygen atoms of four different cyclobutane-1,1-dicarboxylate dianions (Fig. 1a). The dianions connect zinc atoms into a 2D polymer network with the square lattice (**sql**) topology.

Calcium atoms are located in a six-membered chelate ring formed by the cyclobutane-1,1-dicarboxylate (2.390(4)–2.403(4) Å) (Fig. 1b). The coordination environment of calcium is completed to seven by oxygen atoms (the polyhedron is a one-cap trigonal prism; the chromophore is CaO_7 (calculations by the Shape 2.1 program, see Table 2 [30])) via the interaction with the oxygen atoms of two other dianions (2.280(5)–2.305(5) Å) and three oxygen atoms of the monodentate water molecules (Fig. 2).

In compound **I**, one of the two independent acid anions (O1/O2/C1–C6/O3/O4) has a μ_4-type of coordination, while the second dianion forms a chelate ring with the calcium atom, $\{Ca(Cpdc)(H_2O)_3\}$, and has κ^2,μ_3-type of coordination.

Table 1. Crystallographic data and X-ray experiment and structure refinement parameters for **I** and **II**

Parameter	Value	
	I	**II**
M	443.73	522.96
T, K	150	120
System	Orthorhombic	
Space group	$Pca2_1$	$C222_1$
Z	4	16
a, Å	12.497(2)	17.5620(17)
b, Å	6.9353(13)	18.8077(17)
c, Å	19.238(4)	19.8175(19)
V, Å^3	1667.3(6)	6545.7(11)
ρ(calcd.), g cm^{-3}	1.768	2.123
μ, cm^{-1}	1.837	3.907
F(000)	888	4064
$2\theta_{\max}$, deg	30.738	30.623
Number of measured reflections	21450	36476
Number of unique reflections	5099	9969
Number of reflections with $I > 2\sigma(I)$	4371	9410
Number of refined parameters	230	439
R_1, wR_2 ($I > 2\sigma(I)$)	0.0525, 0.1286	0.0374, 0.0837
R_1, wR_2 (for all data)	0.0636, 0.1360	0.0403, 0.0852
GOOF	1.037	1.050
Residual electron density (min/max), e Å^{-3}	−0.852/2.657	−1.364/3.407
Flack	0.47(2)	0.030(7)

Table 2. Selected geometric characteristics of compounds **I** and **II**

Parameter	**I**	**II**
	M = Ca	M = Ba
Bond	d, Å	
Zn–O(Cbdc^{2-})	1.985(4)–1.997(4)	1.958(4)–1.985(4)
M–O(Cbdc^{2-})	2.280(5)–2.403(4)	2.670(5)–3.047(4)
M–O(H_2O-κO)	2.334(5)–2.418(5)	2.735(5)–2.707(5)
Angle	ω, deg	
O–Zn–O	Zn(1): 95.76(17)–120.94(18)	Zn(1): 91.99(18)–126.1(3) Zn(2): 104.32(19)–118.93(18) Zn(3): 93.3(2)–131.66(18)
O–M–O (chelate)	71.66(14)	67.24(12)–72.03(13)
Symmetry of the environment of M	$S_Q(P)$	
M(1)	CaO_7: C_{2v}, monocapped trigonal prism (0.369)	BaO_8: D_{4d}, square antiprism (1.125)
M(2)		BaO_9: C_{4v}, monocapped cube (3.896)
M(3)		BaO_8: D_{4d}, square antiprism (2.973)

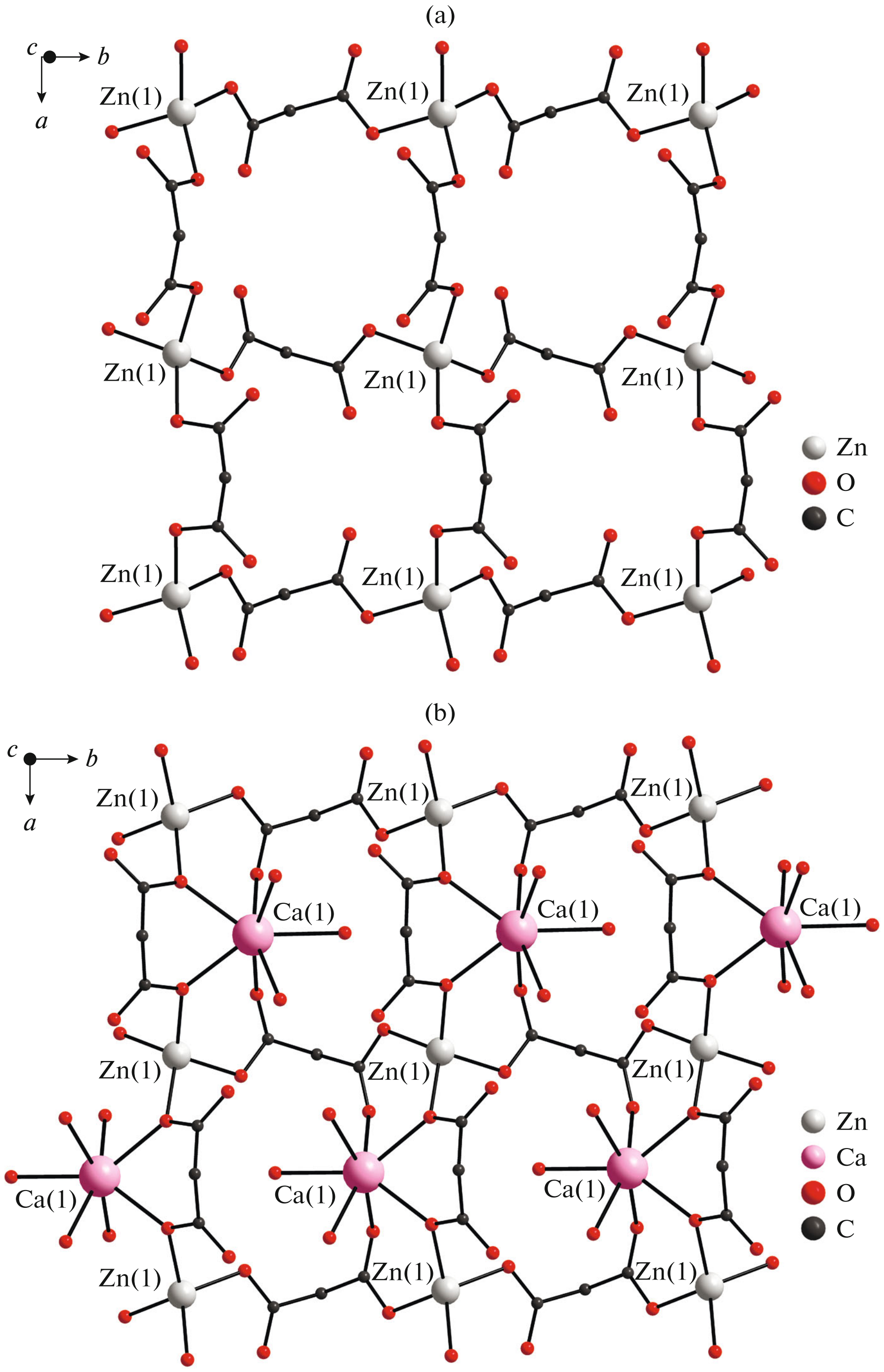

Fig. 1. (a) Network of zinc atoms in compound **I**; (b) fragment of the layer of compound **I** (hydrogen atoms and hydrocarbon substituents of the dianions are omitted).

When calcium sulfate is replaced with barium sulfate, the synthesis under conditions used to prepare **I** gives the polymer $[BaZn(Cbdc)_2(H_2O)_2]_n$ (**II**) (Fig. 3). In this compound, the independent part of the cell contains three structurally nonequivalent zinc atoms, three barium cations, four anions, and four water molecules coordinated by an alkaline earth metal cation. Two of the three independent zinc cations and two of the three barium cations are located on a twofold screw axis. Each zinc atom is in a distorted tetrahedral

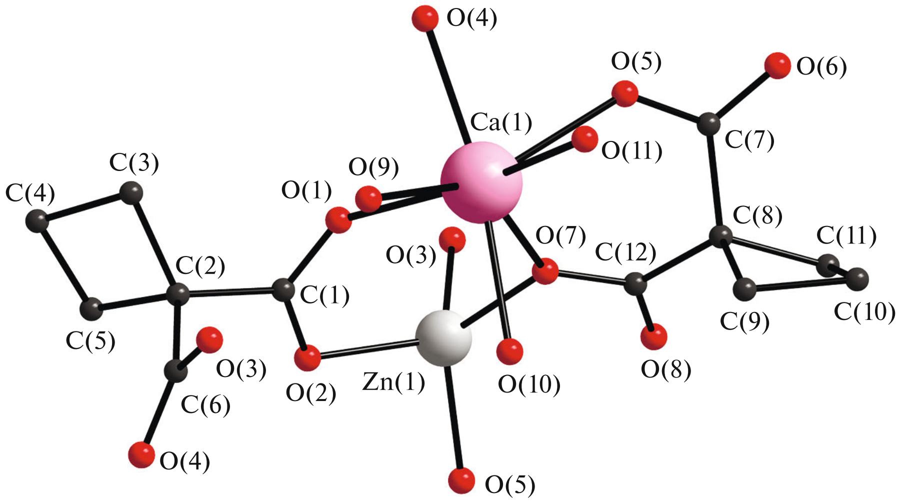

Fig. 2. Main fragment of compound **I** (hydrogen atoms are omitted).

environment (ZnO_4 chromophore) formed by four oxygen atoms of four different bridging dianions (Table 2, Fig. 3a). As in the case of compound **I**, the anions, together with zinc atoms, form a layered structure with the square lattice (**sql**) topology. The structures of coordination polymers differ due to the fact that barium tends to have higher coordination numbers than calcium.

Polymer **II** contains three structurally nonequivalent barium atoms. The Ba(1) and Ba(3) polyhedra are distorted square antiprisms (BaO_8 chromophore); that of Ba(2) is a distorted monocapped cube (BaO_9 chromophore) (calculated by the Shape 2.1 program, see Table 2 [31–33]). The cyclopropane-1,1-dicarboxylate anions forms the bis-chelate $\{Ba(Cpdc)_2(H_2O)_2\}^{2-}$ moiety with Ba(1) and Ba(3) and a tris-chelate moiety with Ba(2) (Fig. 3b). In this compound, all cyclopropane-1,1-dicarboxylate anions have κ^2,μ_4-coordination.

In the previously described zinc barium complex with dimethylmalonate anion [18], the barium atoms bind the $\{Zn(Me_2Mal)_2(H_2O)_2\}^{2-}$ moieties to form a framework. In compound **II**, like in the case of complex **I**, alkaline earth element atoms do not affect the packing dimensionality, but complete the layered structure of the compound. The parallel layers are perpendicular to the *c* axis of the unit cell and, hence, at least two faces of the single crystal are formed by hydrophobic alkyl groups. Figure 4 shows the assumed shape of crystals **I** and **II** calculated by the BFDH (Bravais, Friedel, Donnay, and Harker) Mercury 2020.2.0 method [34], as described previously [35]. It coincides with the really observed shape (plates for **I** and prisms for **II**). This means that complex **I** can be used to fabricate materials with the superhydrophobic surface [36].

Thus, we obtained two zinc-based coordination polymers with the cyclobutane-1,1-dicarboxylate dianions and calcium $[CaZn(Cbdc)_2(H_2O)_3]_n$ (**I**) or barium $[BaZn(Cbdc)_2(H_2O)_2]_n$ (**II**) cations. In these compounds, anions in combination with zinc atoms form a layered structure. In the structures of polymers, dicarboxylate anions form six-membered chelate rings with alkaline earth elements, while anion binding to zinc atoms is only bridging. The composition and structure of the complexes differ due to different coordination numbers of *s*-metals (CaO_7, $BaO_8/_9$) and their binding to dicarboxylate anions, but this does not affect the structure dimensionality and topology, which is a square lattice (**sql**).

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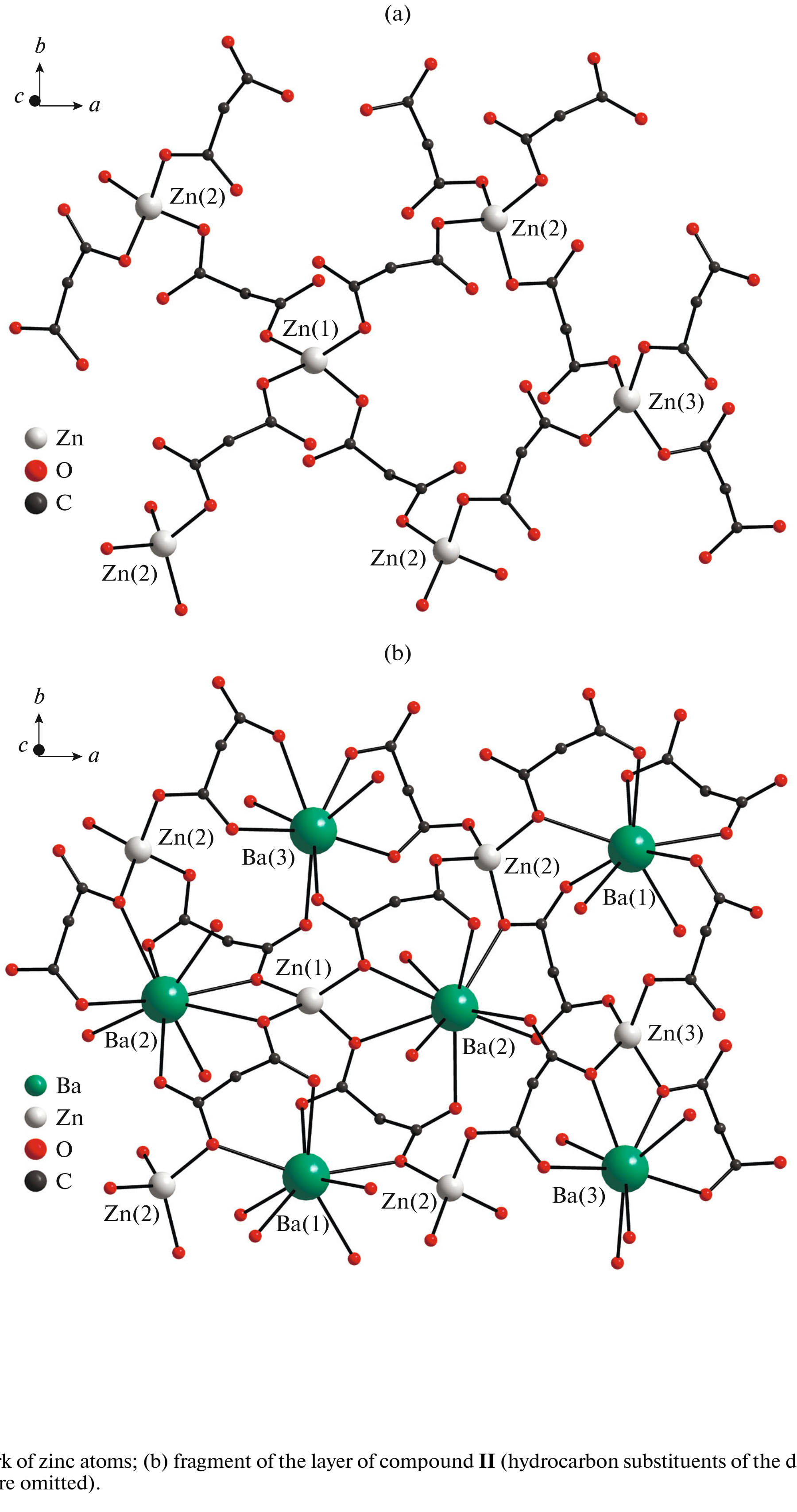

Fig. 3. (a) Network of zinc atoms; (b) fragment of the layer of compound **II** (hydrocarbon substituents of the dianions in (b) and hydrogen atoms are omitted).

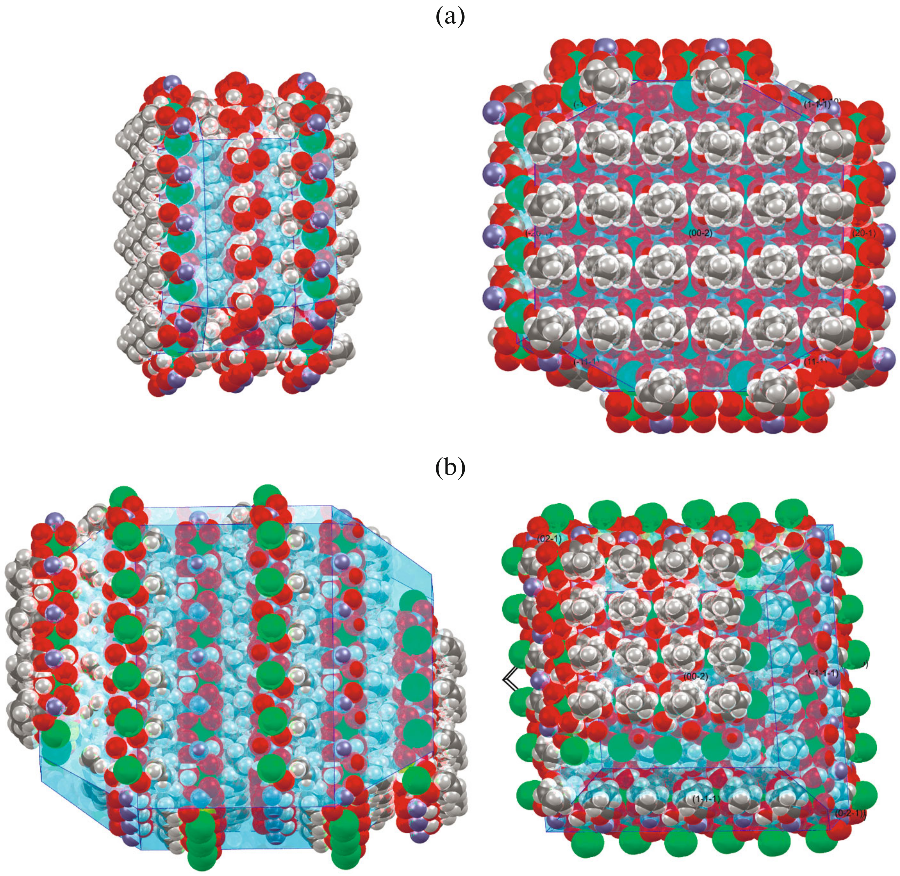

Fig. 4. Calculated shape of crystals of compounds (a) **I** and (b) **II**. The crystal surfaces are shown in light blue; the atoms represented by van der Waals spheres (carbon, hydrogen, oxygen, zinc, and alkaline earth metal, respectively are shown in gray, white, red, blue, and green). The picture on the left is the view parallel to the crystallographic *c* axis, that on the right is the view perpendicular to this axis.

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