

Synthesis and structure of two polymeric barium–oxydiacetates: $[\text{Ba}(\text{oda}) \cdot \text{H}_2\text{O}]_n$ and $[\text{Ba}(\text{Hoda})_2]_n$ (H_2oda : oxydiacetic acid)

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Abstract

The reaction of barium carbonate or hydroxide with oxydiacetic acid leads to the self-assembly of two barium oxydiacetate polymers in good yield: $[\text{Ba}(\text{oda}) \cdot \text{H}_2\text{O}]_n$ (**1**) and $[\text{Ba}(\text{Hoda})_2]_n$ (**2**). The products have been characterized by elemental analysis, IR, TGA and single crystal X-ray diffraction studies. The central barium atom in each mononuclear fragment is nine-coordinate in **1** and 10-coordinate in **2**. These fragments are bridged by carboxylato groups in *anti-anti* conformation and through H-bonding interactions forming complex 3D networks.

Keywords: Barium complexes; Carboxylates; Crystal Structures; Hydrogen bonds

1. Introduction

The characterization of alkaline earth carboxylates is an area of continuous interest because of their relevance in a wide range of applications in materials science including their use as processible oxide precursors by soft chemistry routes [1–6]. The use of dicarboxylate ligands as small building blocks to generate metal–organic frameworks of different dimensionalities may lead to interesting network architectures [7]. The synthesis and characterization of metal oxydiacetates ($\text{oda} = ^-\text{O}_2\text{CCH}_2\text{OCH}_2\text{CO}_2^-$) has been extensively documented in recent publications [8]. In mononuclear compounds the most frequent coordination mode of the ligand is planar *O,O',O''*-tridentate. In polynuclear compounds, however, coordination may involve up to five O atoms of the ligand, thus giving rise to more complex coordination motifs. Studies of alkaline earth

oxydiacetates have been reported for mononuclear $[\text{Ca}(\text{oda})(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}$ [9] and for polymeric $[\text{Sr}(\text{oda})(\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$ [10]. The former shows a planar tridentate conformation, whereas the latter contains non-planar tridentate, chelating and monodentate coordination modes of the ligand. The formation of anhydrous $\text{Ca}(\text{Hoda})_2$ was also proposed from the vibrational study of this material, but its structure could not be unambiguously elucidated [9]. However, tridentate chelation of the Hoda anion has been more recently confirmed for some lanthanide cations [11]. We now wish to report our results on the synthesis and characterization of the first barium oxydiacetates $[\text{Ba}(\text{oda}) \cdot \text{H}_2\text{O}]_n$ (**1**) and $[\text{Ba}(\text{Hoda})_2]_n$ (**2**), isolated from the barium–oxydiacetic system in water.

2. Experimental

All starting materials were of AR grade and used without further purification. Elemental analyses (C,H) were performed on a Carlo Erba EA 1108 instrument.

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Infrared spectra were recorded on a Nicolet FT-IR 510 P spectrophotometer using the KBr pellet technique. Thermal analysis was performed on a Shimadzu DTG 50 thermal analyzer, under an air flow of 40 L/min at a heating rate of 5 °C min⁻¹.

2.1. Preparation of [Ba(oda)(H₂O)] (1)

Barium carbonate (1.0 g, 5 mmol) was added to a solution of oxydiacetic acid (1.0 g, 7.5 mmol) in water (250 ml). The reaction mixture was heated under reflux for 8 h under continuous stirring and filtered while hot. The clear solution was stored at room temperature, and compound **1** was collected by filtration as orthorhombic colorless X-ray quality crystals, washed with iced water, and dried in air. Yield: (1.15 g, 80%). *Anal.* Calc. for C₄H₆BaO₆: C, 16.70; H, 2.10. Found: C, 16.70; H, 2.00%. Main FT IR bands (KBr, cm⁻¹): 3500–3000 vbr, 1677 w, 1620 m, 1573 vs, 1469 m, 1427 s, 1349 m, 1339 m, 1253 m, 1113 vs, 1061 m, 995 m, 930 s, 723 s, 675 w. Compound **1** was also obtained when freshly precipitated barium hydroxide was used in the preparation.

2.2. Preparation of Ba(Hoda)₂ (2)

Barium carbonate (1.0 g, 5 mmol) was added to a solution of oxydiacetic acid (2.0 g, 15.0 mmol) in water (100 ml). The reaction mixture was heated under reflux for 5 h, filtered off and left standing in a stoppered flask for 5 days, whereupon tetragonal colorless crystals of compound **2** were filtered off and dried in air. Yield: 1.40 g (70%). *Anal.* Calc. for C₈H₁₀BaO₁₀: C, 23.80; H, 2.50.

Found: C, 23.70; H, 2.40%. Main FT IR bands (KBr, cm⁻¹): 3600–3000 vbr, 1744 vs, 1646 m, 1435 s, 1418 s, 1266 s, 1125 vs, 1062 vs, 1030 m, 964 w, 908 w, 732 m, 705 w, 681 m. Compound **1** was similarly obtained when freshly prepared barium hydroxide was used in the preparation.

2.3. X-ray crystallography

Diffraction data were collected at room temperature on a Bruker SMART 6000 CCD (**1**) and a Siemens R 3m (**2**) diffractometers. Both structures were primarily solved by direct methods using SHELXS 97 and completed through difference Fourier and refined by least squares procedures on F_o² with SHELXL 97 [12]. Hydrogens attached to carbon atoms were positioned theoretically and allowed to ride; those bound to oxygen were located in the last difference Fourier and refined with isotropic displacement factors. Crystal data, data collection and refinement parameters are given in Table 1.

3. Results and discussion

3.1. Preparation

The isolation of [Ba(oda)(H₂O)]_n (**1**) and [Ba(Hoda)₂]_n (**2**) was accomplished by the carbonate or the hydroxide route, and involved the addition of milky suspensions of the barium reactant to clear solutions of H₂oda in water (pH not adjusted). Polymer **1** crystallizes from fairly dilute 1:1.5 solutions, whereas polymer **2**

Table 1
Crystal data and structure refinement for [Ba(oda)·H₂O]_n (**1**) and [Ba(Hoda)₂]_n (**2**)

	1	2
Empirical formula	C ₄ H ₆ BaO ₆	C ₈ H ₁₀ BaO ₁₀
Formula weight	287.43	403.50
Temperature (K)	293(2)	293(2)
Wavelength (Mo Kα) (Å)	0.71073	0.71073
Crystal system	orthorhombic	tetragonal
Space group	<i>Pna</i> 2(1) (#33)	<i>P</i> -42(1) <i>c</i> (# 114)
Crystal dimensions (mm)	0.22 × 0.14 × 0.12	0.38 × 0.18 × 0.14
<i>a</i> (Å)	7.2537(7)	8.0650(11)
<i>b</i> (Å)	9.8052(10)	8.0650(11)
<i>c</i> (Å)	10.0811(10)	18.000(4)
<i>V</i> (Å ³)	717.01(12)	1170.8(3)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	2.663	2.289
<i>μ</i> (mm ⁻¹)	5.520	3.442
<i>F</i> (000)	536	776
Unique reflections, <i>R</i> _{int} , parameters	1434, 0.0833, 111	1056, 0.0892, 88
Maximum, minimum absorption correction	0.50, 0.37	0.58, 0.38
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>F</i> ² > 2σ(<i>F</i> ²)]	<i>R</i> ₁ = 0.0244, <i>wR</i> ₂ = 0.0685	<i>R</i> ₁ = 0.0268, <i>wR</i> ₂ = 0.0664
Final Δρ (e Å ⁻³)	0.911, -1.020	0.904, -1.340

^a *R*₁ = ∑||*F*_o| - |*F*_c|| / ∑|*F*_o|.

^b *wR*₂ = [∑[*w*(*F*_o² - *F*_c²)²] / ∑[*w*(*F*_o²)]^{1/2}.

crystallizes from more concentrated 1:3 aqueous solutions. The compounds are obtained in high yield as well shaped crystals and stored in air for extended periods of time. Characterization was carried out by microanalysis, IR, TGA and single crystal XRD.

The IR spectrum of **1** shows the characteristic absorptions corresponding to the presence of carboxylate anions (1573 and 1427 cm^{-1}) and water molecules (1620 and $3550\text{--}3000\text{ cm}^{-1}$), whereas that of **2** shows the presence of carbonyl (1744 cm^{-1}) and hydroxyl groups ($3600\text{--}3400\text{ cm}^{-1}$) of COOH. The Δ values [$\nu_{\text{asym}}(\text{CO}_2^-) - \nu_{\text{sym}}(\text{CO}_2^-)$] in the range $200\text{--}150\text{ cm}^{-1}$ for **1** and **2** suggest that the coordinated carboxylate groups are likely to be of the bridging type [13]. The presence of strong and well defined bands at 1113 cm^{-1} in **1** and at 1124 and 1061 cm^{-1} in **2** suggests that the oda ligands adopt non-planar conformations [8]. Thermal decomposition of the complexes was investigated by TGA in the range $50\text{--}1000\text{ }^\circ\text{C}$. The thermogram of **1** shows that the first mass loss in the range $178\text{--}244\text{ }^\circ\text{C}$ corresponds to one coordinated water molecule per formula unit (calc. 6.3%, found 5.8%). This high temperature range suggests that the water molecule is strongly bonded. The TGA curve of **2** shows that decomposition occurs in three steps beyond $252\text{ }^\circ\text{C}$. The final residual mass for **1** and **2** (65% and 47%, respectively) suggests the formation of BaCO_3 , as confirmed by XRD [14]. No attempt was made to identify intermediate products.

3.2. Crystal structures

In compound **1** the barium cation is surrounded by an O_9 donor set in an approximate monocapped square antiprism environment, Fig. 1(a). The four coordination sites of the basal plane are occupied by three oxygen atoms from a single tridentate oda (O1, O3 and O5) and by one coordinated water molecule (O1W). The adjacent plane contains two pairs of the remaining carboxylate oxygens O2 and O4 from four different oda units, related to the ligand at the basal plane by the symmetry operations #1 to #4 (see Fig. 1 caption for symmetry codes). Finally, the capping site is occupied by a second coordinated water oxygen O1W#5 through a rather long bond of $3.311(4)\text{ \AA}$. As a result each oda ligand in the extended structure connects five different barium centers, and each of these is, in turn, surrounded by ten Ba atoms, Fig. 1(b). The two nearest neighbors Ba#5 and Ba#6 are linked to the central Ba by three short bridges of the Ba–O–Ba type, at a distance of 4.374 \AA . The next four pairs of neighbors are found at considerably larger distances and each pair is connected at least through one *anti-anti* type carboxylate bridge, (see Fig. 1(b) and Table 2). The Ba–O bond distances are in the range $2.747(6)\text{--}3.311(4)\text{ \AA}$, close to the corresponding values in barium acetate ($2.64\text{--}3.09\text{ \AA}$), which contains eight- and nine-coordinate metal centers [15]. This

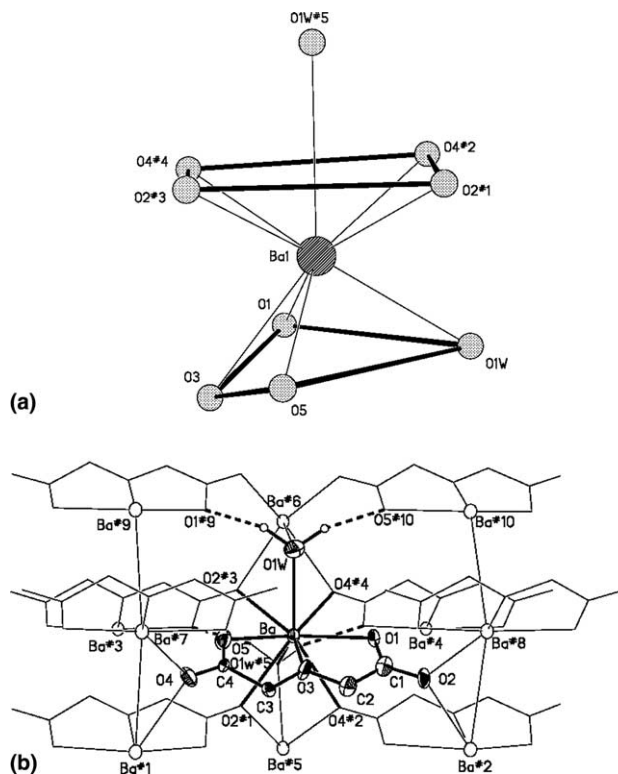


Fig. 1. (a) Schematic view of the barium coordination polyhedron in **1**. (b) Schematic diagram of **1**. Full shaded ellipsoids of the asymmetric unit at the 50% probability level. Open ellipsoids show the symmetry-generated atoms, which complete the coordination polyhedron and lead to the polymeric structure. The aqua H-bonds are drawn in broken lines. Non-interacting H atoms not shown, for clarity. Symmetry codes: #1: $-x + 1/2, y + 1/2$; #2: $-x + 1/2, y + 1/2, z + 1/2$; #3: $-x + 1, -y + 2, z - 1/2, z - 1/2$; #4: $-x + 1, -y + 2, z + 1/2$; #5: $x + 1/2, -y + 5/2, z$.

type of multiple bridges connecting the BaO9 polyhedra leads to an efficiently packed 3D structure of density 2.66 g cm^{-3} . Fig. 2 shows a packing view along the c -axis. The hydrogen atoms of the water molecule make two very strong H-bonds of which the carboxylate oxygens O1 and O5 are acceptors, Table 3.

The oda ligand in **1** is bonded in a non-planar conformation mode characterized by torsion angles O1–C1–C2–O3 and O5–C4–C3–O3 of $-4.4(1)^\circ$ and $6.9(1)^\circ$, respectively. These are quite similar to the corresponding values calculated for $[\text{Sr}(\text{oda})(\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$: $-7.2(1)^\circ$ and $15.0(1)^\circ$, respectively. However, in $[\text{Ca}(\text{oda})(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}$ a tridentate planar conformation mode is found, as in most mononuclear compounds [8].

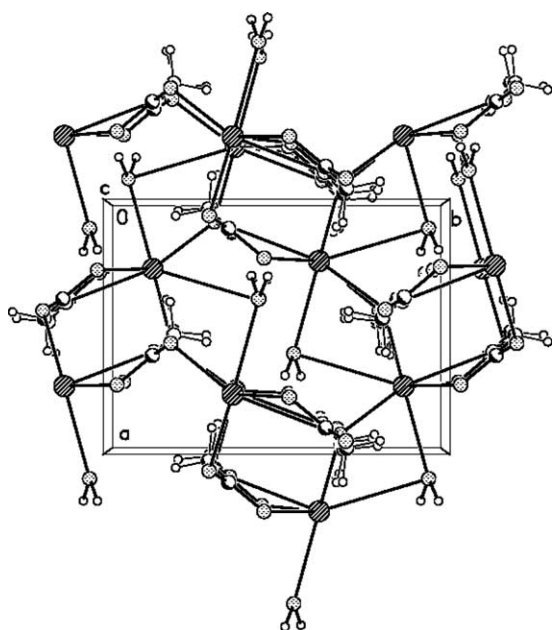
The barium cation in **2** is 10-coordinate via the duplication of five independent bonds through the symmetry operation $[-x, -y, z]$, Fig. 3(a). The Hoda ligand coordinates in the tridentate fashion involving the ether atom O3 and the two carboxylate oxygen atoms O1 and O5. The remaining two bonds are provided by O1 and O4 from two symmetry related odas through symmetry operations #11 and #12, respectively. As a result each

Table 2

Selected atomic distances (Å) and angles (°) for [Ba(oda)·H₂O]_n (1) and [Ba(Hoda)₂]_n (2)

1			
Ba–O(1)	2.744(10)	Ba–O(1W)	2.777(3)
Ba–O(2)#1	2.750(7)	Ba–O(1W)#5	3.316(3)
Ba–O(2)#3	2.771(9)		
Ba–O(3)	2.771(2)	Ba...Ba[#5,#6]	4.374 (1)
Ba–O(4)#2	2.751(7)	Ba...Ba[#1,#2]	6.585(1)
Ba–O(4)#4	2.791(8)	Ba...Ba[#9,#10]	6.776(1)
Ba–O(5)	2.872(10)	Ba...Ba[#3,#4,#7,#8]	7.034(1)
O(1)–Ba(1)–O(4)#2	86.9(3)	O(4)#2–Ba(1)–O(1W)	72.69(19)
O(2)#1–Ba(1)–O(4)#2	67.82(7)	O(3)–Ba(1)–O(1W)	95.88(9)
O(1)–Ba(1)–O(3)	56.9(2)	O(2)#1–Ba(1)–O(5)	85.8(3)
O(3)–Ba(1)–O(2)#3	86.07(18)	O(3)–Ba(1)–O(5)	56.7(3)
O(1)–Ba(1)–O(4)#4	70.4(3)	O(2)#3–Ba(1)–O(5)	69.8(3)
O(4)#2–Ba(1)–O(4)#4	87.2(2)	O(1W)–Ba(1)–O(5)	82.4(2)
O(3)–Ba(1)–O(4)#4	85.35(18)	O(2)#1–Ba(1)–O(1W)#5	61.19(17)
O(2)#3–Ba(1)–O(4)#4	66.97(7)	O(4)#2–Ba(1)–O(1W)#5	60.98(17)
O(1)–Ba(1)–O(1W)	83.3(2)	O(2)#3–Ba(1)–O(1W)#5	62.31(16)
O(2)#1–Ba(1)–O(1W)	70.3(2)	O(4)#4–Ba(1)–O(1W)#5	64.20(16)
2			
Ba–O(1) [#0, #13]	3.180(3)	Ba–O(4) [#12,#14]	2.833(2)
Ba–O(3) [#0, #13]	3.023(3)		
Ba–O(5) [#0, #13]	2.760(3)	Ba...Ba#11	4.471(1)
Ba–O(1) [#11, #15]	2.779(3)	Ba...Ba[#12,#14,#16,#17]	7.283(1)
O(5)–Ba(1)–O(5)#13	75.03(11)	O(1)#15–Ba(1)–O(3)	86.97(8)
O(1)#11–Ba(1)–O(1)#15	89.81(11)	O(4)#12–Ba(1)–O(3)	88.74(7)
O(5)–Ba(1)–O(4)#12	75.63(8)	O(4)#14–Ba(1)–O(3)	92.31(7)
O(1)#15–Ba(1)–O(4)#12	67.38(7)	O(1)#11–Ba(1)–O(3)#13	86.97(8)
O(5)–Ba(1)–O(4)#14	69.32(8)	O(1)#11–Ba(1)–O(1)	56.13(5)
O(5)–Ba(1)–O(3)	54.21(7)	O(3)–Ba(1)–O(1)	50.58(6)
O(1)#11–Ba(1)–O(3)	91.08(8)	O(1)#13–Ba(1)–O(1)	76.20(10)

Symmetry codes: #0: x, y, z ; #1: $-x + 1/2, y + 1/2$; #2: $-x + 1/2, y + 1/2, z + 1/2$; #3: $-x + 1, -y + 2, z - 1/2, z - 1/2$; #4: $-x + 1, -y + 2, z + 1/2$; #5: $x + 1/2, -y + 5/2, z$; #6: $x - 1/2, -y + 5/2, z$; #9: $-x, -y + 2, z - 1/2$; #10: $-x, -y + 2, z + 1/2$; #11: $y, -x, -z$; #12: $-x + 1/2, y - 1/2, -z + 1/2$; #13: $-x, -y, z$; #14: $x - 1/2, -y + 1/2, -z + 1/2$; #15: $-y, x, -z$; #16: $-x + 1/2, y + 1/2, -z + 1/2$; #17: $-x + 1/2, -y - 1/2, -z + 1/2$; #18: $-y + 1/2, -x + 1/2, z - 1/2$.

Fig. 2. Packing view of 1 along the *c*-axis.

oda ligand binds to five different barium centers and each Ba, in turn, is surrounded by only one nearest neighbor, Ba#11, linked by four short bridges of the Ba–O–Ba type at a distance of 4.471(1) Å, Fig. 3(b). The next nearest neighbors, Ba#12, Ba#14, Ba#16 and Ba#17, are connected through long *anti-anti* type carboxylate bridges at 7.283(1) Å. The Ba–O bond distances in 2 vary in the range 2.760(3)–3.180(3) Å, comparable with the literature values for 10-coordinate Ba–O_{carboxylate} bonds [16]. These bonds distribute in space in two interleaving, perpendicular planes (90.3°): those from the tridentate Hodas on one side (maximum deviation from planarity 0.15 Å for O5 and O5') and those due to O2 and O4 on the other (maximum deviation: 0.02 Å for O4 and O4'). The conformation of the oda skeleton in 2 is only slightly non-planar, with O1–C1–C2–O3 = 2.4(1)° and O5–C4–C3–O3 = 1.2(1)°. The protonated oxygen O2, even if not directly engaged in coordination, is firmly linked to the rest of the structure through a strong H-bond, Table 3. The resulting 3D network (Fig. 4) is more open than that observed for 1,

Table 3
Hydrogen bonding in $[\text{Ba}(\text{oda}) \cdot \text{H}_2\text{O}]_n$ (**1**) and $[\text{Ba}(\text{Hoda})_2]_n$ (**2**)

D–H...A	$d(\text{D–H})$ (Å)	$D(\text{H...A})$ (Å)	$d(\text{D...A})$ (Å)	$\angle(\text{DHA})$ (°)
1				
O(1W)–H(1WA)...O(2)#9	0.92(2)	2.24(2)	3.126(8)	163(4)
O(1W)–H(1WB)...O(5)#10	1.00(1)	2.02(2)	2.991(13)	162(4)
2				
O(2)–H(2)...O(4)#18	0.87(1)	1.62(1)	2.481(3)	177(2)

Symmetry codes: #0: x, y, z ; #1: $-x + 1/2, y + 1/2$; #2: $-x + 1/2, y + 1/2, z + 1/2$; #3: $-x + 1, -y + 2, z - 1/2, z - 1/2$; #4: $-x + 1, -y + 2, z + 1/2$; #5: $x + 1/2, -y + 5/2, z$; #6: $x - 1/2, -y + 5/2, z$; #9: $-x, -y + 2, z - 1/2$; #10: $-x, -y + 2, z + 1/2$; #11: $y, -x, -z$; #12: $-x + 1/2, y - 1/2, -z + 1/2$; #13: $-x, -y, z$; #14: $x - 1/2, -y + 1/2, -z + 1/2$; #15: $-y, x, -z$; #16: $-x + 1/2, y + 1/2, -z + 1/2$; #17: $-x + 1/2, -y - 1/2, -z + 1/2$; #18: $-y + 1/2, -x + 1/2, z - 1/2$.

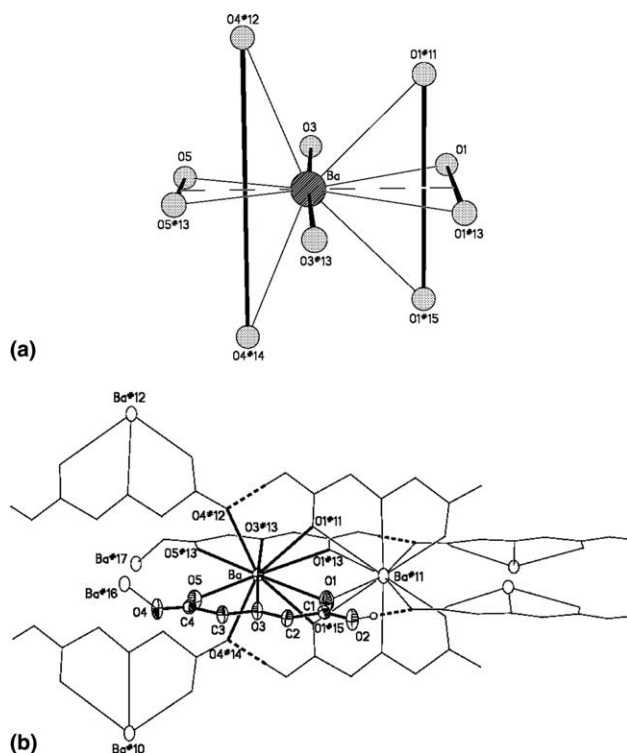


Fig. 3. (a) Schematic view of the barium coordination polyhedron in **2**. (b) Schematic diagram of **1**. Full shaded ellipsoids of the asymmetric unit at the 50% probability level. Open ellipsoids show the symmetry-generated atoms which complete the coordination polyhedron and lead to the polymeric structure. The Hoda H-bonds are drawn in broken lines. Non-interacting H atoms not shown, for clarity. Symmetry codes: #6: $y, -x, -z$; #7: $-x + 1/2, y - 1/2, -z + 1/2$; #8: $-x, -y, z$; #9: $x - 1/2, -y + 1/2, -z + 1/2$; #10: $-y, x, -z$.

as evidenced by the lower calculated density of 2.29 g cm^{-3} .

In conclusion, we have isolated and unambiguously characterized two polymeric compounds, which crystallize by self-assembly from the barium–oxydiacetic acid system in water at different concentrations and similar acidity level. The two ligands, oda and Hoda, serve as tridentate to each Ba^{2+} and at the same time form carboxylate bridges with neighboring Ba^{2+} cations giving rise to supramolecular 3D networks.

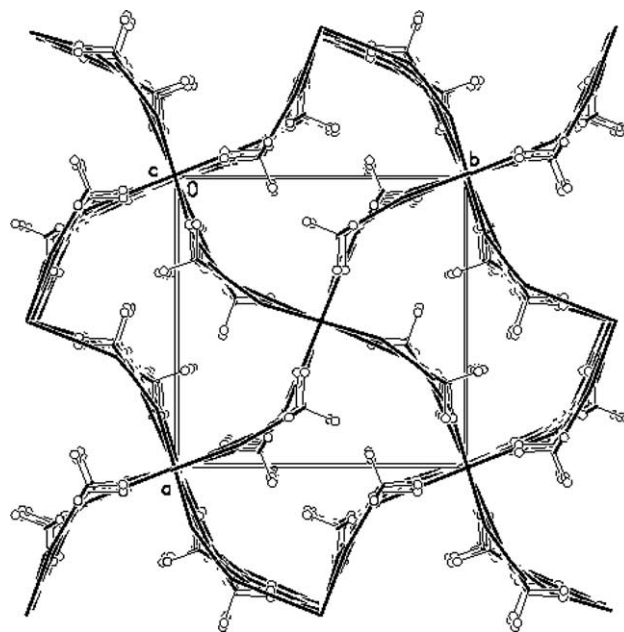


Fig. 4. Packing view of **2** along c -axis, showing structural channels filled by hydrogen atoms.

4. Supplementary material

Supporting material in the form of CIF files for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as deposition numbers CCDC 215007 for **1** and CCDC 215008 for **2**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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