

Novel one-dimensional lanthanide acrylic acid complexes: an alternative chain constructed by hydrogen bonding

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Abstract

Novel one-dimensional (1D) chains of three lanthanide complexes $\text{La}(\text{L}^1)_3(\text{CH}_3\text{OH}) \cdot \text{CH}_3\text{OH}$ ($\text{L}^1 = (\text{E})\text{-3-(2-hydroxyl-phenyl)-acrylic acid}$) **1**, $\text{La}(\text{L}^2)_3(\text{H}_2\text{O})_2 \cdot 2.75\text{H}_2\text{O}$ ($\text{L}^2 = (\text{E})\text{-3-(3-hydroxyl-phenyl)-acrylic acid}$) **2**, and $\text{La}(\text{L}^3)_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O}) \cdot \text{CH}_3\text{OH}$ ($\text{L}^3 = (\text{E})\text{-3-(4-hydroxyl-phenyl)-acrylic acid}$) **3** are reported. The crystal structure data are as follows for **1**: $\text{C}_{29}\text{H}_{29}\text{LaO}_{11}$, monoclinic, $P2_1/n$, $a = 15.4289(12) \text{ \AA}$, $b = 7.9585(6) \text{ \AA}$, $c = 23.041(2) \text{ \AA}$, $\beta = 99.657(2)^\circ$, $Z = 4$, $R_1 = 0.0637$, $wR_2 = 0.0919$; for **2**: $\text{C}_{27}\text{H}_{30.50}\text{LaO}_{13.75}$, triclinic, $P-1$, $a = 8.4719(17) \text{ \AA}$, $b = 13.719(3) \text{ \AA}$, $c = 14.570(3) \text{ \AA}$, $\alpha = 62.19(3)^\circ$, $\beta = 99.657(2)^\circ$, $\gamma = 78.22(3)^\circ$, $Z = 2$, $R_1 = 0.0384$, $wR_2 = 0.0820$; and for **3**: $\text{C}_{30}\text{H}_{35}\text{LaO}_{13}$, monoclinic, $P2(1)/c$, $a = 9.5667(6) \text{ \AA}$, $b = 24.3911(15) \text{ \AA}$, $c = 14.0448(9) \text{ \AA}$, $\beta = 109.245(2)^\circ$, $Z = 4$, $R_1 = 0.0374$, $wR_2 = 0.0630$. All the three structure data were collected using graphite monochromated molybdenum $K\alpha$ radiation and refined using full-matrix least-squares techniques on F^2 . These structures show that four kinds of the carboxylato bridge modes are included in these chains to link the La(III) ions. It is the first time that it has been found that the intra-chain hydrogen bonding can construct an alternative chain even, when the coordination bridge mode is the same along the chain (complex **2**). There are 2D and 3D hydrogen bonding in the crystal lattices of complexes **1–3**.

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Keywords: Lanthanide complex; One-dimensional chain; Carboxylato bridge mode; Hydrogen bonding; Acrylic acid; Alternative chain; Crystal structure

1. Introduction

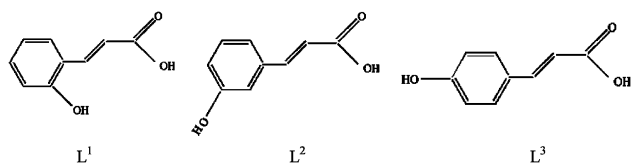
The carboxylate-type ligand is a ubiquitous ligand in coordination chemistry. The lanthanide carboxylate complexes have exhibited unusual structures and properties [1–6]. It makes them have wide potential applications in biochemistry (MRI) [7–13] and materials science (molecular magnet, high-temperature superconductors and liquid crystal) [14–20]. We are interested in a series of acrylic acids with different substitutes (Scheme 1). The common feature in the structures of L^1 to L^3 is the carboxylato group conjugated with benzene ring through $\text{C}=\text{C}$ double bond, which will make the electronic density delocalized in the ligand. Probably, it

may make them coordinate with metal ions more flexibly. Meanwhile, the subtle change in the positions of hydrogen bonding functional groups in these ligands could be important in the crystal lattices. Therefore, the three ligands should be interesting in regard to their coordination chemistry and supramolecular chemistry. To our knowledge, there has been no crystal structure with regard to these ligands reported previously. Some transition metal [21] and lanthanide complexes of these ligands are being studied.

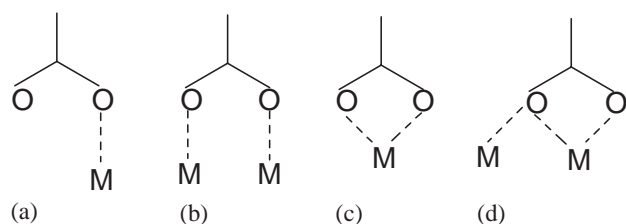
Here, the three crystal structures of lanthanide complexes with the three ligands $\text{La}(\text{L}^1)_3(\text{CH}_3\text{OH}) \cdot \text{CH}_3\text{OH}$ ($\text{L}^1 = (\text{E})\text{-3-(2-hydroxyl-phenyl)-acrylic acid}$) **1**, $\text{La}(\text{L}^2)_3(\text{H}_2\text{O})_2 \cdot 2.75\text{H}_2\text{O}$ ($\text{L}^2 = (\text{E})\text{-3-(3-hydroxyl-phenyl)-acrylic acid}$) **2**, and $\text{La}(\text{L}^3)_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O}) \cdot \text{CH}_3\text{OH}$ ($\text{L}^3 = (\text{E})\text{-3-(4-hydroxyl-phenyl)-acrylic acid}$) **3** are reported.

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Scheme 1.



Scheme 2.

The main structural feature of the three complexes is the one-dimensional (1D) chain. Four kinds of coordination and bridge modes of the carboxylato group are contained in the chain of complexes **1–3** (Scheme 2). Modes a and b are common monodentate coordination and bis-monodentate bridge mode, respectively. Mode c is bidentate chelate coordination mode that is uncommon for lanthanide carboxylato polymer; although it has been known for some mononuclear lanthanide carboxylato complex [22,23]. Mode d is bidentate chelate bridge mode of carboxylato group that has not been reported in transition metal carboxylato complex previously and is a rare example of main group elements (Sr, Ba, In) [24] and lanthanide (La, Er) carboxylato complexes [22,23]. Bridge modes b and d will be represented by the sign of η^2 -O bridge and η^3 -O bridge, respectively, in the text.

The four bridge modes have been included in the complexes **1–3** to link the La(III) ions. Complexes **2** and **3** are alternative chain structures with different La–La distances along the 1D chain. The alternative chain is not common in lanthanide 1D polymers [25–28].

2. Experimental

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was purchased from Aldrich and (E)-3-(2- (or 3-, or 4-) hydroxyl-phenyl)-acrylic acid was purchased from Fluka. All chemicals are used without further purification. The 1D coordination polymers were confirmed by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction analysis. Elemental analyses (C, H, N) were carried out at the Beijing

Institute of Technology. FT-IR spectrum is recorded in the Nicolet-360 FT-IR spectrometer. $[\text{La}(\text{L}^1)_3(\text{CH}_3\text{OH}) \cdot \text{CH}_3\text{OH}]$ (**1**): The solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (50.00 mg, 0.12 mmol) in 10 mL CH_3OH was added to the solution of (E)-3-(2-hydroxyl-phenyl)-acrylic acid (59.33 mg, 0.36 mmol) and NaOH (14.40 mg, 0.36 mmol) in 10 mL CH_3OH . After stirring for 2 h, the reaction solution was filtered. There are some NaNO_3 crystals appearing after a few days by evaporating and separating them. The resulting solution is diffused using diethyl ether. The colorless plate single crystals suitable for X-ray are obtained after 2 weeks. The yield: 59.2 mg, 73.93%. Calculated for $\text{C}_{29}\text{H}_{29}\text{LaO}_{11}$: C, 50.30; H, 4.22; N, 0.00. Found: C, 50.11; H, 4.26; N, 0.00. Selected IR (KBr, cm^{-1}): 3390.8 (m, $\nu_{\text{HO-H}}$), 3027.7 (m, $\nu_{\text{C-H}}$), 2962.0 (w, $\nu_{\text{as}}(\text{CH}_2)$), 1641.4, 1562.7 (vs, $\nu_{\text{as}}(\text{COO}^-)$), 1470.6, 1424.3 (s, $\nu_{\text{s}}(\text{COO}^-)$), 735.0, 695.6 (w, $\delta_{\text{C-H}}(\text{in plane})$). $[\text{La}(\text{L}^2)_3(\text{H}_2\text{O})_2 \cdot 2.65\text{H}_2\text{O}]$ (**2**): The solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (50.00 mg, 0.12 mmol) in 10 mL CH_3OH was added to the solution of (E)-3-(2-hydroxyl-phenyl)-acrylic acid (59.33 mg, 0.36 mmol) and NaOH (14.40 mg, 0.36 mmol) in 10 mL mixed solvent ($\text{H}_2\text{O}:\text{CH}_3\text{OH} = 8:2$). After mixing the two solutions slowly, there are cloudy precipitates produced. After a few days, these white precipitates changed to the colorless lath single crystals which are suitable for the X-ray analysis. The yield: 56.5 mg, 68.58%. Calculated for $\text{C}_{27}\text{H}_{30.50}\text{LaO}_{13.75}$: C, 45.14; H, 4.35; N, 0.00. Found: C, 45.01; H, 4.39; N, 0.00. Selected IR (KBr, cm^{-1}): 3400.8 (m, $\nu_{\text{HO-H}}$), 3031.7 (m, $\nu_{\text{C-H}}$), 2958.6 (w, $\nu_{\text{as}}(\text{CH}_2)$), 1640.5, 1560.3 (vs, $\nu_{\text{as}}(\text{COO}^-)$), 1467.8, 1423.6 (s, $\nu_{\text{s}}(\text{COO}^-)$), 735.7, 695.6 (w, $\delta_{\text{C-H}}(\text{in plane})$). $[\text{La}(\text{L}^3)_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O}) \cdot \text{CH}_3\text{OH}]$ (**3**): The process is similar with the complex **1**. The colorless needle single crystals are obtained by evaporation. The yield: 52.6 mg, 61.39%. Calculated for $\text{C}_{30}\text{H}_{35}\text{LaO}_{13}$: C, 48.53; H, 4.75; N, 0.00. Found: C, 48.57; H, 4.79; N, 0.00. Selected IR (KBr, cm^{-1}): 3396.5 (m, $\nu_{\text{HO-H}}$), 3029.8 (m, $\nu_{\text{C-H}}$), 2960.3 (w, $\nu_{\text{as}}(\text{CH}_2)$), 1638.8, 1563.5 (vs, $\nu_{\text{as}}(\text{COO}^-)$), 1469.2, 1422.7 (s, $\nu_{\text{s}}(\text{COO}^-)$), 735.6, 695.6 (w, $\delta_{\text{C-H}}(\text{in plane})$).

Single-crystal X-ray diffraction analysis for complexes **1–3**: Single-crystal X-ray diffraction data were collected on a Bruker SMART1000 CCD area detector with graphite monochromated molybdenum $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at a temperature of $150 \pm 2 \text{ K}$. Unit-cell parameters were determined from automatic centering of 25 reflections and refined by the least-squares method. Crystallographic data are given in Table 1. Selected bond distances and angles are given in Tables 2–4. The diffraction data were corrected for Lorentz and polarization effects, and absorption (empirically from ψ scan data). No crystals showed significant decay. No extinction correction was necessary for all complexes. All structures were solved by direct methods [29] and refined using full-matrix least-squares techniques on F^2 [30]. All non-hydrogen

Table 1
Crystal data and structure refinement for 1–3

| | 1 | 2 | 3 |
|--|---|---|---|
| Formula | C ₂₉ H ₂₉ LaO ₁₁ | C ₂₇ H _{30.50} LaO _{13.75} | C ₃₀ H ₃₅ LaO ₁₃ |
| <i>M</i> | 692.43 | 713.92 | 742.49 |
| Temperature (K) | 150 (2) | 150 (2) | 150 (2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> -1 | <i>P</i> 2(1)/ <i>c</i> |
| <i>a</i> (Å) | 15.4289 (12) | 8.4719 (17) | 9.5667 (6) |
| <i>b</i> (Å) | 7.9585 (6) | 13.719 (3) | 24.3911 (15) |
| <i>c</i> (Å) | 23.041 (2) | 14.570 (3) | 14.0448 (9) |
| α (deg.) | 90 | 62.19 (3) | 90 |
| β (deg.) | 99.657 (2) | 75.91 (3) | 109.245 (2) |
| γ (deg.) | 90 | 78.22 (3) | 90 |
| Volume (Å ³) | 2789.1 (4) | 1444.6 (5) | 3094.1 (6) |
| <i>Z</i> | 4 | 2 | 4 |
| ρ (calculated) (g cm ⁻³) | 1.649 | 1.641 | 1.594 |
| μ mm ⁻¹ | 1.593 | 1.547 | 1.447 |
| <i>F</i> (000) | 1392 | 718 | 1504 |
| Crystal size (mm) | 0.22 × 0.12 × 0.05 | 0.64 × 0.06 × 0.03 | 0.41 × 0.08 × 0.03 |
| θ ° | 2.68–26.69 | 2.5–28.0 | 2.8–28.9 |
| Limiting indices | –20 ≤ <i>h</i> ≤ 16 –10 ≤ <i>k</i> ≤ 10 –28 ≤ <i>l</i> ≤ 30 | –11 ≤ <i>h</i> ≤ 11 –17 ≤ <i>k</i> ≤ 18 –19 ≤ <i>l</i> ≤ 19 | –12 ≤ <i>h</i> ≤ 11 –31 ≤ <i>k</i> ≤ 32 –18 ≤ <i>l</i> ≤ 18 |
| Reflection collected/unique | 7064/6611 [<i>R</i> (int) = 0.057] | 8426/6625 [<i>R</i> (int) = 0.024] | 7500/7373 [<i>R</i> (int) = 0.032] |
| Data/restraints/parameters | 6611/1/377 | 6625/14/400 | 7373/0/389 |
| Goodness-of-fit on <i>F</i> ² | 0.925 | 1.028 | 1.024 |
| Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>)) | <i>R</i> ₁ = 0.0352, <i>wR</i> ₂ = 0.0732 | <i>R</i> ₁ = 0.0292, <i>wR</i> ₂ = 0.0728 | <i>R</i> ₁ = 0.0261, <i>wR</i> ₂ = 0.0598 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0637, <i>wR</i> ₂ = 0.0919 | <i>R</i> ₁ = 0.0384, <i>wR</i> ₂ = 0.0820 | <i>R</i> ₁ = 0.0374, <i>wR</i> ₂ = 0.0630 |
| Largest diff. peak and hole (e Å ⁻³) | 1.23 and –0.72 | 1.05 and –0.67 | 0.97 and –0.63 |

Note: $R_1^a = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2^b = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]^2 \}^{1/2}$.

Table 2
Selected bond lengths and bond angles for 1

| | | | |
|--------------|-------------|---------------|-------------|
| La–O1A#1 | 2.449 (3) | La–O2 | 2.559 (3) |
| La–O2#1 | 2.539 (3) | La–O3#1 | 2.511 (3) |
| La–O3 | 2.685 (3) | La–O4 | 2.475 (3) |
| La–O5 | 2.590 (3) | La–O6 | 2.599 (3) |
| La–O7 | 2.600 (3) | La–La#2 | 4.2357 (3) |
| O2–C3 | 1.291 (5) | C1–O3 | 1.286 (5) |
| O5–C1 | 1.255 (5) | O4–C12 | 1.264 (5) |
| C12–O1A | 1.258 (5) | O6–C2 | 1.391 (6) |
| C3–O7 | 1.259 (5) | | |
| La–O3–La#2 | 109.20 (10) | La–O2–La#2 | 112.40 (10) |
| C3–O2–La#2 | 136.8 (3) | C3–O2–La | 96.2 (2) |
| C1–O3–La#2 | 157.8 (3) | C1–O3–La | 93.0 (3) |
| C12–O1A–La#2 | 143.2 (3) | C12–O4–La | 138.1 (3) |
| O1A#1–La–O4 | 140.68 (10) | O1A#1–La–O3#1 | 79.93 (10) |
| O3#1–La–O2#1 | 69.78 (9) | O1A#1–La–O2 | 127.92 (9) |
| O4–La–O2 | 78.04 (9) | O2#1–La–O2 | 146.69 (3) |
| O1A#1–La–O5 | 100.66 (9) | O2–La–O5 | 115.41 (9) |
| O4–La–O7 | 119.93 (10) | O2–La–O7 | 50.25 (9) |
| O5–La–O3 | 49.10(9) | O3#1–La–C1 | 156.72(11) |

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, y - 1/2, -z + 3/2$ and #2 $-x + 1/2, y + 1/2, -z + 3/2$.

atoms were refined anisotropically. Hydrogen atoms are located geometrically and refined by mixed methods.

Table 3
Selected bond lengths and bond angles for 2

| | | | |
|-----------------|-------------|---------------|------------|
| La–O3#1 | 2.487 (2) | La–O2 | 2.526 (2) |
| La–O7#2 | 2.535 (2) | La–O1 | 2.586 (3) |
| La–O3 | 2.664 (2) | La–O4 | 2.634 (2) |
| La–O5 | 2.549 (2) | La–O6 | 2.559 (2) |
| La–O7 | 2.860 (2) | La–O8 | 2.621 (2) |
| La–La#1 | 4.368 | La–La#2 | 4.595 |
| O(1)–C(20) | 1.259 (4) | O(3)–C(20) | 1.273 (4) |
| O(7)–C(10) | 1.262 (3) | O(5)–C(10) | 1.272 (3) |
| La–O3–La#1 | 115.90 (8) | La–O7–La#2 | 116.70 (6) |
| C(10)–O(7)–La#2 | 153.77 (18) | C(10)–O(7)–La | 88.54 (16) |
| C(20)–O(3)–La#1 | 150.1 (2) | C(20)–O(3)–La | 93.57 (18) |
| O2–La–O7#2 | 73.70 (8) | O3#1–La–O5 | 150.57 (7) |
| O3–La–O7 | 159.79 (6) | O7#2–La–O5 | 110.77 (6) |
| O3#1–La–O6 | 126.24 (7) | O5–La–O7 | 47.55 (6) |
| O6–La–O7 | 68.01 (6) | O8–La–O7 | 112.64 (6) |
| O3#1–La–O1 | 113.22 (7) | O1–La–O7 | 110.70 (7) |

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z$ and #2 $-x + 1, -y + 1, -z$.

3. Results and discussion

3.1. One-dimensional chain structures of complexes 1–3

The crystal data of complexes 1–3 are listed in Table 1. The coordination environments of La(III)

Table 4
Selected bond lengths and angles for **3**

| | | | |
|--------------|-------------|------------|-------------|
| La–O1#1 | 2.4213 (17) | La–O3#2 | 2.5019 (15) |
| La–O3 | 2.7622 (16) | La–O5 | 2.6051 (18) |
| La–O6 | 2.6150 (17) | La–O4 | 2.6273 (19) |
| La–O7 | 2.5395 (16) | La–O8 | 2.5745 (16) |
| La–O9 | 2.4780 (15) | La–La#2 | 5.174 |
| La–La#1 | 4.429 | C1–O3 | 1.286 (5) |
| O2–C3 | 1.291 (5) | O5–C1 | 1.255 (5) |
| O6–C2 | 1.391 (6) | C3–O7 | 1.259 (5) |
| O(8)–C(30) | 1.275 (3) | O(2)–C(30) | 1.263 (3) |
| La#1–O3–La | 114.50 (6) | La#2–O3–La | 109.17 (10) |
| C1–O3–La#2 | 157.8 (3) | C1–O3–La | 93.0 (3) |
| C12–O1A–La#2 | 143.2 (3) | O7–La–O3 | 48.90 (5) |
| C10–O1–La#1 | 166.91 (16) | C10–O9–La | 125.17 (14) |
| O8–La–O3 | 66.29 (5) | O5–La–O3 | 69.34 (5) |
| O6–La–O3 | 109.69 (5) | O4–La–O3 | 125.47 (5) |
| O9–La–O3 | 137.87 (5) | O1#1–La–O3 | 122.41 (5) |
| O3#2–La–O4 | 80.73 (5) | O7–La–O6 | 72.07 (5) |
| O1#1–La–O3#2 | 152.71 (5) | O3#2–La–O7 | 114.16 (5) |

Note: Symmetry transformations used to generate equivalent atoms:
#1 $-x+1, -y, -z$ and #2 $-x+2, -y, -z$.

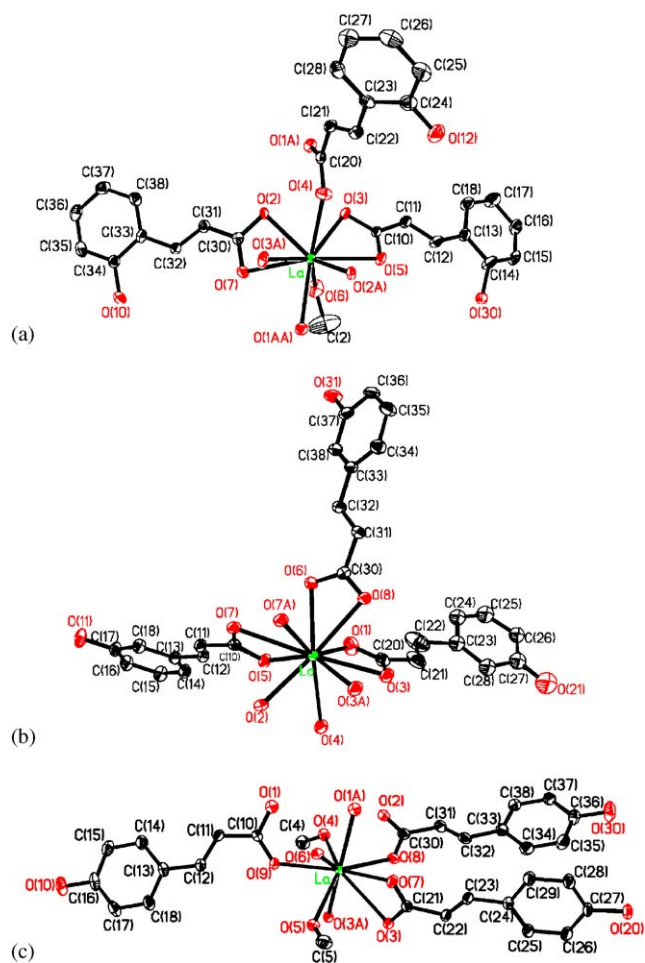


Fig. 1. ORTEP drawing of coordination environment of La(III) ions in complexes **1** (a), **2** (b) and **3** (c) (50% thermal ellipsoids).

ions in these 1D coordination polymers are shown in Fig. 1. From the stoichiometry of these polymers, the La(III) ions are coordinated with three ligands and form a neutral species.

In **1**, each La(III) is coordinated with nine oxygen atoms in which eight oxygen atoms come from the L¹ ligands and the left one from the coordinated methanol molecule. The coordination geometry of La(III) is a distorted tricapped trigonal prism. Two of the L¹ ligands coordinate with La(III) in bidentate mode (mode c) and one is in the monodentate mode (mode a) (Fig. 1a). So, there are two η^3 -O bridges and one η^2 -O bridge to link La(III) ions (Fig. 2a). The η^2 -O bridge links La(III) ions in *syn-syn* configuration (C12–O4–La 138.1(3)°; C12–O4–LaA 143.2(3)°). The distance between the La(III) ions is 4.236 Å (Table 2). It is the shortest distance between La(III) ions in 1D chain structures which has been found in CSD. A similar distance has been found in Nd–Nd chain (4.243(3) Å).

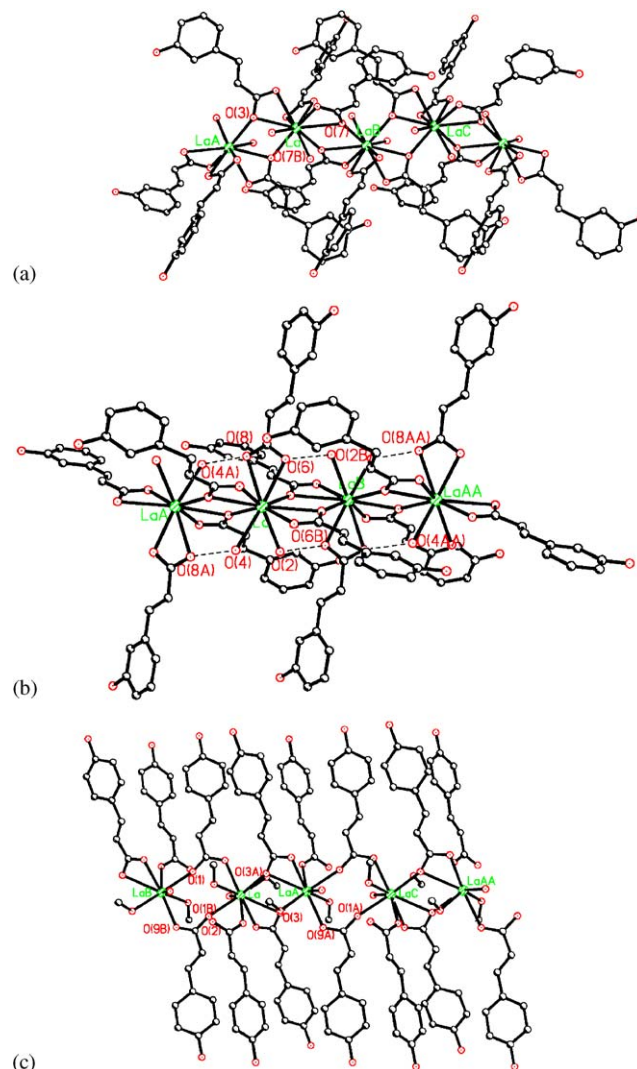


Fig. 2. 1D chain structures of complexes **1** (a), **2** (b) and **3** (c).

All ligands in **2** coordinate with La(III) in the bidentate mode (mode c) (Fig. 1b). One of the benzene rings of ligand is in disorder. The coordination number of La(III) ions is 10 in which eight oxygen atoms come from the ligands and the other two from the coordinated water molecules. Only two of the L^2 ligands are bridge ligands to link La(III) forming 1D chain in η^3 -O type. However, it is not a uniform chain as complex **1** although the bridge mode is the same in complex **2**. The distance between La(III) ions is different with La–LaA (4.368 Å) and La–LaB (4.595 Å) arranged alternatively along the chain (Fig. 2b). It should be pointed that the coordination water molecules form strong hydrogen bonding with the carboxylato oxygen atoms of ligand in adjacent La(III) ion along the chain. The hydrogen bonding formed by two coordinated water molecules with the ligand is not the same. They are O2...O6B, 2.680 Å, O2–H2A...O6, 175.87° and O4...O8A 2.729 Å, O4–H4A...O8 173.44° and arrange alternatively along the chain. The intra-chain hydrogen bonding is the significant factor in constructing the alternative chain even when the coordination bridge mode is the same along the chain. To the best of our knowledge, it is the first example of hydrogen bonding in constructing the alternative chain.

In complex **3**, each La(III) ion is coordinated with nine oxygen atoms in which six of them come from ligands, two of them from coordinated methanol molecules and the left one from coordinated water molecules. Two of the L^3 ligands are coordinated with La(III) ion in monodentate mode and one of them is in bidentate mode (Fig. 1c). Comparing with **1** and **2**, the bridge mode between La(III) ions is not the same along the chain. La and LaA are linked by two η^3 -O bridges and the distance of La–LaA is 4.428 Å. La and LaB are linked by two η^2 -O bridges with La–LaB: 5.175 Å (Fig. 2c). Obviously, η^3 -O bridge can create a shorter distance between La(III) ions than η^2 -O bridge. The η^2 -O bridge coordinates with La(III) in *syn-anti* configuration (C10–O1–La#1, 166.91(16)°; C10–O9–La, 125.17(14)°). One of the ligands in **3** coordinates with the La(III) ions in monodentate mode (mode a). Then, the uncoordinated carboxylato oxygen atom (O(2)) forms strong hydrogen bonding with the hydroxyl group of the ligand in adjacent chains (O(20A)...O(2) 2.649 Å, O(20A)–H(20B)...O(2) 160.6°). This hydrogen bonding constructs the 2D layer structure in the crystal lattice. The bond lengths of C30–O2 and C30–O8 are 1.263(3) Å and 1.275(3) Å, respectively. It indicates delocalization of the carboxylate negative charge in

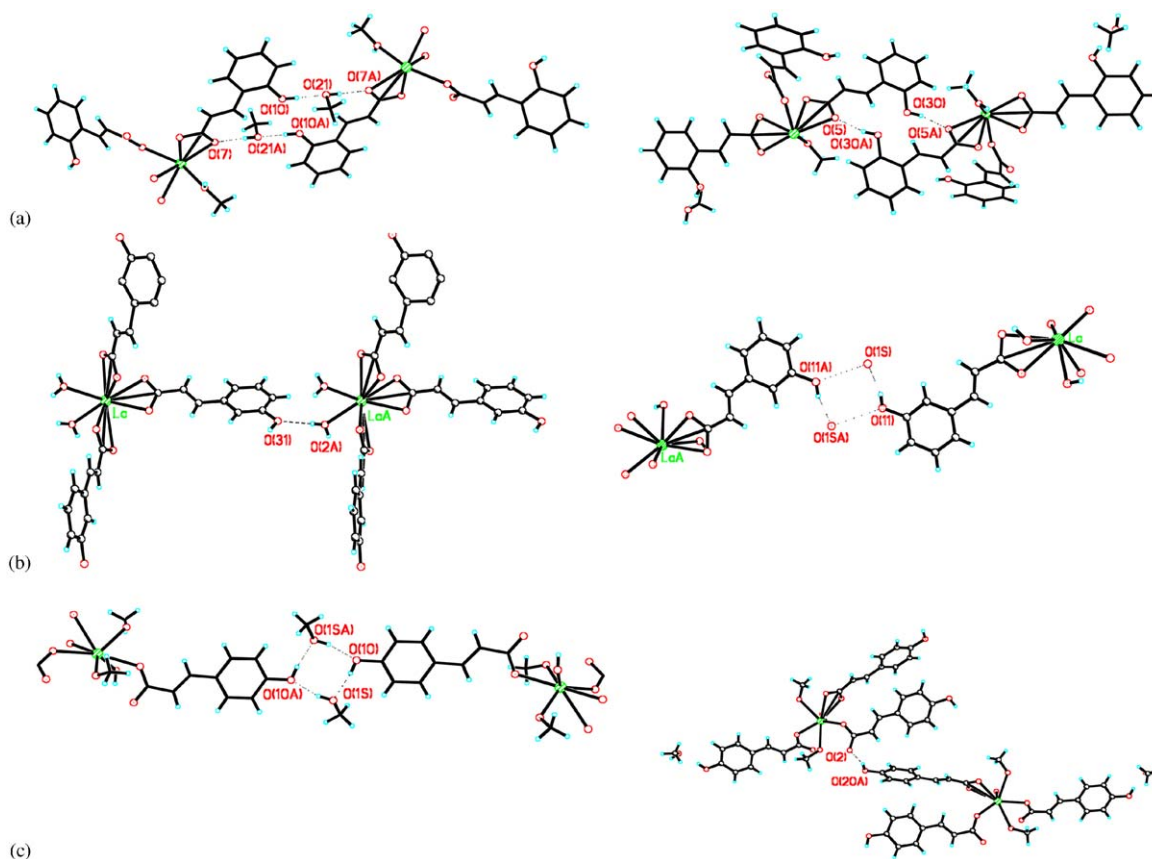


Fig. 3. 3D H-bonding details in **1** (a), **2** (b) and **3** (c).

spite of the coordinated or uncoordinated oxygen atoms in carboxylato ligand.

The bond lengths of La–O in the three complexes is over the wide range (2.421–2.861 Å) which falls in the normal scale [31–35]. The longest and the shortest distance of La(III)–O are 2.861 Å in complex **2** and 2.421 Å in complex **3**, respectively. The distances between La(III) ions in the three complexes range from 4.236 to 5.175 Å, which are mainly dependent on the bridge mode between La(III) ions. Particularly, the uncommon bridge mode of carboxylato ligand, η^3 -O, has been included in the three complexes. This phenomenon can be explained by the electronic character of these ligands. The flexibility in the coordination ability of the carboxylato oxygen atoms results from the small adjustment in the electronic density of the carboxylato oxygen atoms through the conjugation system. Although complexes **2** and **3** are alternative chain with different La–La distances along the chain alternatively, they are quite different. In complex **2**, the bridge mode between La(III) ions is the same. The intra-chain hydrogen bonding interaction is the cause for making the distance between the La(III) ions different. It indicates that the hydrogen bonding can play an important role in constructing the alternative chain. No example has been reported previously in this issue. Obviously, the different bridge modes link the La(III) ions with different distances in complexes **3** alternatively. Based on the different interactions, the difference in La–La distance of complex **3** (La–LaA, 4.428 Å; La–LaB, 5.175 Å) is larger than that in complex **2** (La–LaA, 4.368 Å; La–LaB, 4.595 Å). The alternating chain complexes are the potential candidates to offer interesting magnetic interactions in the intra-chain and inter-chain and arouse wide attention [36–41]. To extend this study, the other paramagnetic metal ions instead of La(III) will be investigated further.

3.2. Hydrogen bonding in the crystal lattices of complexes **1–3**

Hydrogen bonding is an important interaction in the creation of a variety of molecular architectures for molecular self-assembly [42–44]. Many attempts have been made to control the molecular arrangements in crystals by simultaneous use of coordination bonds of metal ions and complementary intermolecular hydrogen bonding [45–47]. The hydroxylato group in the ligand is a resource to form hydrogen bonding with coordinated methanol or water molecules and solvent methanol or water molecules, which link the 1D chains of complexes **1–3** in 2D and 3D directions in crystal lattice. The type of hydrogen bonding in the crystal lattice of complexes **1–3** is O–H...O.

In **1** and **3**, the carboxylate and hydroxyl groups in ligands form hydrogen bonding with solvent methanol

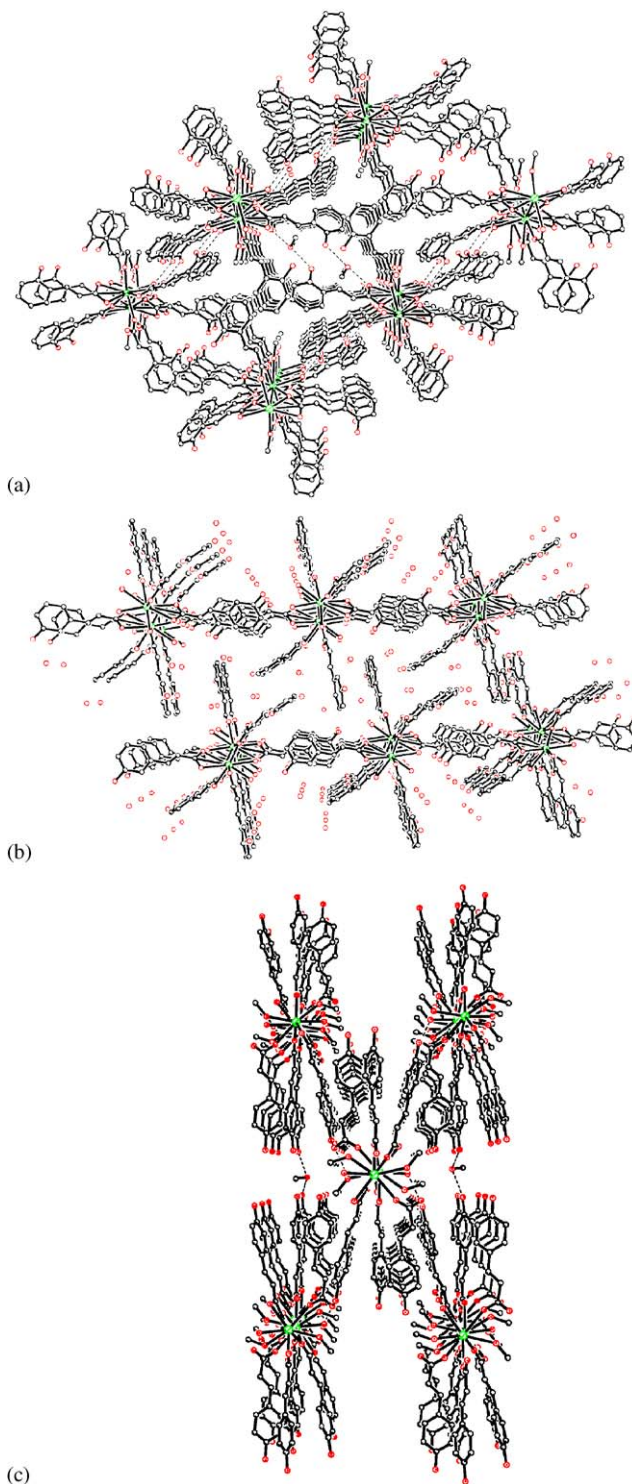


Fig. 4. 3D packing pictures of **1** (a), **2** (b) and **3** (c).

molecules (O–H...O) to link the chains to a layer. The details are O...O 2.619, 2.742 Å; and O–H...O 174.8°, 173.9° in **1** (Fig. 3a) and O...O 2.713, 2.647 Å; O–H...O, 158.8°, 172.2° in **3** (Fig. 3c). Further, these layers are linked by hydrogen bonding between the carboxylate oxygen atoms and hydroxyl groups to

complete the 3D structure. They are O...O 2.667 Å, O–H...O 165.6° in **1** and O...O 2.649 Å, O–H...O 160.6° in **3**. In **2**, the 2D layer structure is constructed by the hydrogen bonding of coordinated water molecule with hydroxyl group of L² ligand [O...O 2.827 Å, O...H–O 175.7°] (Fig. 3b). Consequently, these layers are linked to 3D hydrogen bonding network by solvent water molecules (O...O 2.853 Å, O...H–O 165.2°). So, there are 2D and 3D of strong hydrogen bonding interactions in the crystal lattices of complexes **1–3** (Fig. 4).

In summary, this study shows that acrylic acids are flexible ligands with many kinds of coordination modes. It is the first time that it has been found that hydrogen bonding plays an important role in constructing an alternative 1D chain.

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