

Article

Synthesis, Crystal Structure and Catalytic Activity of a 1D Chained Ca(II) Coordination Polymer with 3,5-Bis(4-pyridylmethoxy)benzoate Ligand

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Abstract: A new 1D chained Ca(II) coordination polymer—namely, $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$ (HL = 3,5-bis(4-pyridylmethoxy)benzoic acid)—was synthesized through the reaction of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, 3,5-bis(4-pyridylmethoxy)benzoic acid and NaOH in $\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH}$ ($v:v = 1:2$) solution. Its structure was determined by elemental analysis, infrared spectrum, and single-crystal XRD. Structural analyses show that each Ca(II) ion is eight-coordinated by six oxygen atoms of four 3,5-bis(4-pyridylmethoxy)benzoate ligands and two oxygen atoms of two coordinated H_2O molecules to form a square-antiprismatic CaO_8 polyhedron. The Ca(II) complex displays a 1D chained structure constructed by the bridging effect of the bidentate carboxyl group of 3,5-bis(4-pyridylmethoxy)benzoate ligand. The catalytic activity of the Ca-complex was tested for the preparation of propargylamine in the A^3 coupling reaction.

Keywords: 3,5-bis(4-pyridylmethoxy)benzoate; 1D chained structure; Ca(II) coordination polymer; synthesis; structural characterization

1. Introduction

Coordination polymers (CPs) materials have attracted great interest during the past two decades [1–6] because they show intriguing structures and excellent properties in many aspects, such as gas adsorption [7], fluorescence [8], magnetic [9], catalysis [10,11], biological activity [12], and so on. In previous studies, *N*-heterocyclic and polycarboxylate ligands have often been used to build coordination polymer materials as multidentate ligands [13–16]. Recently, our group synthesized and structurally characterized some new coordination polymer materials constructed from Ca(II), Cd(II), Zn(II), and Mg(II) with multidentate ligands containing $-\text{COO}^-$ or $-\text{SO}_3^-$ groups [17–20]. To continue our study on coordination polymer materials, in this paper, a new 1D chained Ca(II) coordination polymer— $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$ —has been synthesized through the reaction of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, 3,5-bis(4-pyridylmethoxy)benzoic acid, and NaOH in $\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH}$ ($v:v = 1:2$) solution. Its structure has been determined by EA, infrared spectrum, and single-crystal XRD. The catalytic activity of the Ca-complex was tested for the preparation of propargylamine in the A^3 coupling reaction.

2. Results and Discussion

2.1. Structural Description of $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$

The X-ray single-crystal structural analysis revealed that $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$ crystallizes in monoclinic C_2/c space group, and that the Ca(II) ion is surrounded by six O atoms from four 3,5-bis(4-pyridylmethoxy)benzoate ligands and two O atoms from two coordinated H_2O molecules (Figure 1). The Figure 1 displays that the eight-coordination Ca(II) ion forms a distorted square-antiprismatic CaO_8 polyhedron. The 3,5-bis(4-pyridylmethoxy)benzoate ligand only uses its O atoms for coordinating, and its pyridyl nitrogens do not coordinate to Ca(II) ion, which is different from the Zn(II), Ni(II), and Cd(II) complex with 3,5-bis(4-pyridylmethoxy)benzoate ligand [21–25]. The pyridyl rings have dihedral angles of 24.0° (C9–C10–C11–N1–C12–C13) and 19.2° (C15–C16–C17–N2–C18–C19) with phenyl ring (C2–C3–C4–C5–C6–C7) in an L ligand. $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$ forms a 2D layered structure by $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen bonds (Figure 2). Meanwhile, a looped structure and 3D supramolecular network structure have formed by $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen bonds (Figures 3 and 4). The selected bond lengths and bond angles for $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$ are listed in Table 1.

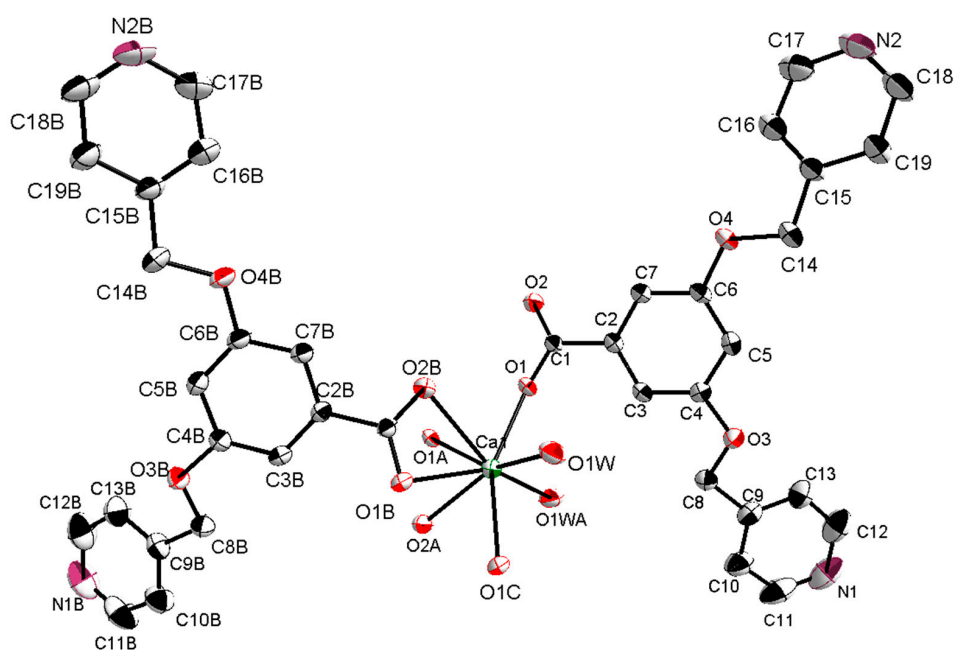


Figure 1. The coordination environment of Ca(II) ion.

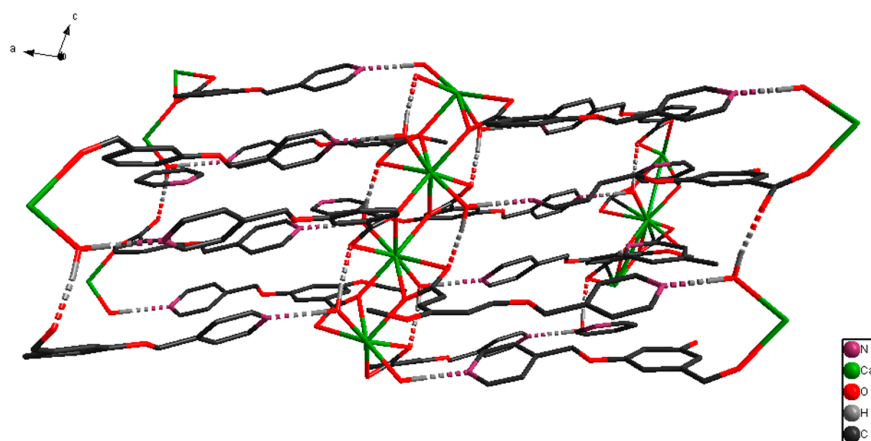
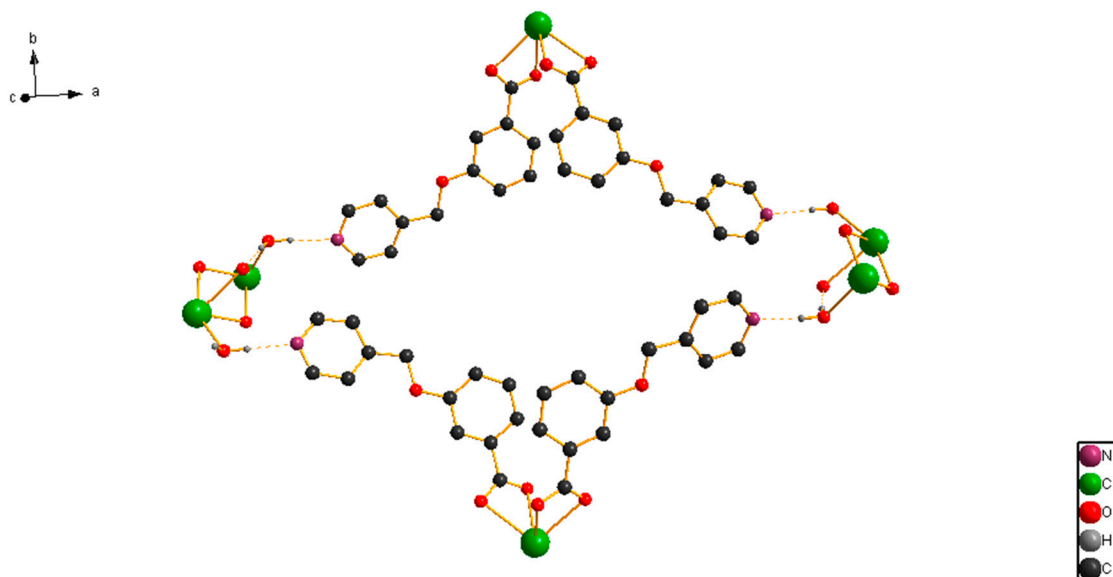


Figure 2. 2D layered structure of $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$.

Table 1. Selected bond lengths d (Å) and bond angles ($^\circ$) for $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$.

| Bond | d | Angle | ($^\circ$) |
|----------|------------|--------------|--------------|
| Ca1–O1W | 2.3811(12) | O1W–Ca1–O1WA | 105.58(6) |
| Ca1–O1WA | 2.3811(12) | O1W–Ca1–O1WA | 76.31(4) |
| Ca1–O1A | 2.3815(11) | O1A–Ca1–O1WA | 87.98(4) |
| Ca1–O1 | 2.3815(11) | O1W–Ca1–O1 | 87.98(4) |
| Ca1–O1B | 2.4935(12) | O1–Ca1–O1WA | 76.31(4) |
| Ca1–O1C | 2.4935(12) | O1–Ca1–O1A | 154.00(5) |
| Ca1–O2B | 2.6350(11) | O1W–Ca1–O1B | 152.63(4) |
| Ca1–O2C | 2.6350(11) | O1B–Ca1–O1WA | 88.93(4) |
| O1–C1 | 1.2592(17) | O1B–Ca1–O1A | 128.26(4) |
| O2–C1 | 1.2512(17) | O1–Ca1–O1B | 72.79(4) |
| O3–C4 | 1.3741(18) | O1W–Ca1–O1C | 88.93 (4) |
| O3–C8 | 1.4302(19) | O1C–Ca1–O1WA | 152.63(4) |
| N1–C12 | 1.324(3) | O1C–Ca1–O1A | 72.79(4) |
| N1–C11 | 1.328(3) | O1–Ca1–O1C | 128.26(4) |
| N2–C17 | 1.323(3) | O1B–Ca1–O1C | 88.08(5) |
| N2–C18 | 1.324(3) | O1W–Ca1–O2B | 152.45(4) |
| | | O2B–Ca1–O1WA | 82.41(4) |
| | | O2B–Ca1–O1A | 77.71(4) |
| | | O1–Ca1–O2B | 119.57(4) |
| | | O2B–Ca1–O1B | 50.71(4) |
| | | O2B–Ca1–O1C | 74.71(4) |
| | | O2C–Ca1–O1W | 82.41(4) |
| | | O1WA–Ca1–O2C | 152.45(4) |
| | | O2C–Ca1–O1A | 119.57(4) |
| | | O1–Ca1–O2C | 77.71(4) |
| | | O2C–Ca1–O1B | 74.71(4) |
| | | O1C–Ca1–O2C | 50.71(4) |
| | | O2B–Ca1–O2C | 102.80(5) |

Symmetry codes: A, $-x, y, -z + 1/2$; B, $-x, -y, -z$; C, $x, -y, z + 1/2$.**Figure 3.** The looped structure by hydrogen bonds in $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$.

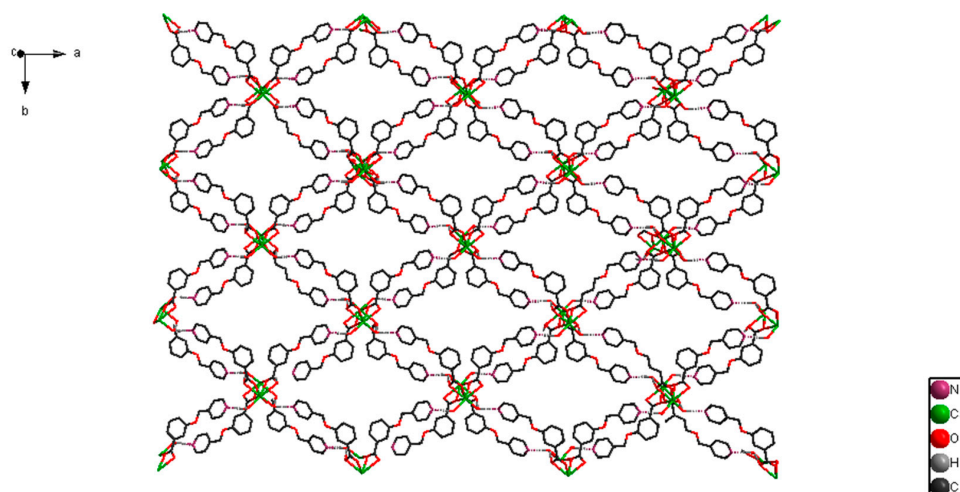


Figure 4. 3D supramolecular network structure of $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$.

2.2. UV-Vis Spectra

The UV-Vis spectra of 3,5-bis(4-pyridylmethoxy)benzoic acid ligand and its Ca(II) coordination polymer are shown in Figure 5. The 3,5-bis(4-pyridylmethoxy)benzoic acid ligand displays one absorption peak at 302 nm ($\epsilon = 1.59 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), and the Ca(II) coordination polymer shows an absorption peak at 299 nm ($\epsilon = 1.99 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), respectively, which may be due to the π - π^* transition of 3,5-bis(4-pyridylmethoxy)benzoate.

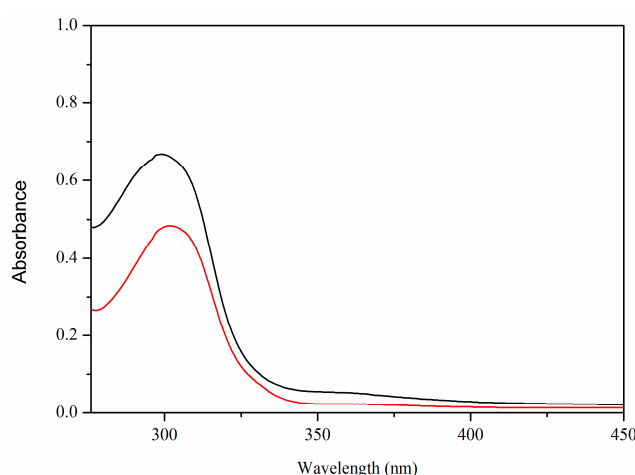


Figure 5. The UV-Vis spectra of 3,5-bis(4-pyridylmethoxy)benzoic acid (HL) and $[\text{CaL}_2(\text{H}_2\text{O})_2]_n \cdot \text{HL}$ ligand (red) and Ca(II) complex (black).

2.3. Catalytic Studies of Three Component Coupling Reaction

The catalytic activity of Ca-complex was tested for the preparation of propargylamine in the A^3 coupling reaction according to the literature method [26]. The benzaldehyde conversion of 38.3% was obtained over Ca-complex for the coupling reaction of benzaldehyde, phenylacetylene, and piperidine with 1,4-dioxane as solvent at 120 °C for 12 h. Recovery and reusability of catalysts was an important theme in catalysis. This allows the catalysts to be used in many catalytic cycles, and thereby more commercial for industrial catalysis. The reusability of the Ca-complex was investigated in the A^3 coupling reaction of benzaldehyde, phenylacetylene, and piperidine in 1,4-dioxane at 120 °C. The recovered catalyst worked well up to four catalytic runs. In four successive cycles, the conversion of benzaldehyde was 38.3%, 35.4%, 32.5%, and 29.8% at 120 °C for 12 h, respectively.

3. Experimental Section

3.1. Materials and Instrumentation

3,5-Bis(4-pyridylmethoxy)benzoic acid, $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, and solvent used in this work were purchased from Jinan Henghua Chemical Reagent Company and used without purification. Element analyses (C, H, and N) were determined on an Elementar Vario III EL elemental analyzer (Hanau, Germany). IR spectra (KBr discs, range 4000 cm^{-1} – 400 cm^{-1}) were recorded on a Nicolet AVATAR 360 Fourier transform infrared (FTIR) spectrophotometer (Nicolet Instrument Inc., Madison, WI, USA). UV-Vis spectra (190–700 nm) were recorded in $\text{CH}_3\text{CH}_2\text{OH}$ on a TU-1901 spectrophotometer (Persee Instrument Inc., Beijing, China). Single crystal X-ray diffraction was carried out by a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA).

3.2. Synthesis of $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$

A mixture of 3,5-bis(4-pyridylmethoxy)benzoic acid (0.2 mmol) and NaOH (0.2 mmol) was dissolved in 15 mL $\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH}$ ($v:v = 1:2$). After 0.5 h, 0.1 mmol of solid $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ was added to the above solution. The reactant mixture was heated to 60°C and kept for 5 h. Then, the reactant mixture was cooled and filtered. The block crystals were obtained by evaporation after 15 days at room temperature. Yield 38%. Analytical calculate for $\text{C}_{38}\text{H}_{34}\text{CaN}_4\text{O}_{10}$: C, 61.06; H, 4.55; N, 7.50. Found: C, 61.32; H, 4.87; N, 7.11. Most IR bands ($\text{Ca}(\text{II})$ complex): 3398 cm^{-1} ($\nu_{\text{as}}(\text{H}_2\text{O})$), 1569 cm^{-1} ($\nu_{\text{as}}(\text{COOH})$), and 1415 cm^{-1} ($\nu_{\text{s}}(\text{COOH})$).

3.3. Crystal Structure Determination

The single crystal data of $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$ were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at $293(2)\text{ K}$. The structure was solved by direct method and refined by full-matrix least squares on F^2 using the SHELX-97 program (University of Göttingen, Göttingen, Germany) [27]. The crystallographic data and structural refinement are listed in Table 2.

Table 2. Crystallographic data and structure refinement for $[\text{CaL}_2(\text{H}_2\text{O})_2]_n$.

| Empirical Formula | $\text{C}_{38}\text{H}_{34}\text{CaN}_4\text{O}_{10}$ |
|---|--|
| Formula weight | 746.77 |
| Temperature/K | 293(2) |
| Crystal system | Monoclinic |
| Space group | $C2/c$ |
| $a/\text{\AA}$ | 25.791(5) |
| $b/\text{\AA}$ | 18.986(4) |
| $c/\text{\AA}$ | 7.4359(15) |
| $\alpha/^\circ$ | 90 |
| $\beta/^\circ$ | 102.17(3) |
| $\gamma/^\circ$ | 90 |
| Volume/ \AA^3 | 3559.4(12) |
| Z | 4 |
| $\rho_{\text{calc}}/\text{mg/mm}^3$ | 1.394 |
| μ/mm^{-1} | 0.24 |
| S | 1.06 |
| $F(000)$ | 1560 |
| Index ranges | $-30 \leq h \leq 30, -22 \leq k \leq 22, -8 \leq l \leq 8$ |
| Reflections collected | 13,423 |
| Independent reflections | 3121 [$R(\text{int}) = 0.032$] |
| Data/restraints/parameters | 3121/2/240 |
| Goodness-of-fit on F^2 | 1.06 |
| Final R indexes [$I \geq 2\sigma(I)$] | $R_1 = 0.0354, wR_2 = 0.0903$ |
| Final R indexes [all data] | $R_1 = 0.0403, wR_2 = 0.0948$ |
| Largest diff. peak/hole/ $\text{e} \cdot \text{\AA}^{-3}$ | 0.321/−0.213 |

3.4. General Procedure for the Three Component Coupling Reaction (A^3)

A mixture of catalyst (40 mg), aldehyde (0.13 mmol), amine (0.15 mmol), alkyne (0.17 mmol), and 1,4-dioxane (1.5 g) was stirred for 12 h at 120 °C. After completion of the reaction, the mixture was cooled to room temperature and the product was obtained by centrifugation. The catalyst was dried at 60 °C under vacuum for 3 h and stored in a desiccator for its use in subsequent catalytic runs. The conversion of aldehyde was determined by GC analysis (GC-1100, capillary column, SE-54).

4. Conclusions

In summary, we obtained a new $[CaL_2(H_2O)_2]_n$ coordination polymer by the reaction of $Ca(ClO_4)_2 \cdot 4H_2O$, 3,5-bis(4-pyridylmethoxy)benzoic acid and NaOH in H_2O/CH_3CH_2OH ($v:v = 1:2$) solution. Structural analyses show that the Ca(II) complex forms a 1D chained structure constructed by the bridging effect of bidentate carboxyl group of 3,5-bis(4-pyridylmethoxy)benzoate ligand. The catalytic activity of Ca-complex was tested for the preparation of propargylamine in the A^3 coupling reaction.

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Author Contributions: Xi-Shi Tai designed the method and wrote the manuscript; Li-Hua Wang synthesized the Cd(II) coordination polymer; Xin Wang analyzed the crystal data of Cd(II) coordination polymer.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1524859. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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