

Article

Synthesis and Crystal Structure of a 1D Chained Coordination Polymer Constructed from Ca^{2+} and 2-[(E)-(2-Furoylhydrazono)methyl]benzenesulfonate

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Abstract: A new Ca(II) coordination polymer, $[\{\text{CaL}_2 \cdot (\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}\}]_n$ (**1**) (L = 2-[(E)-(2-furoylhydrazono)methyl]benzenesulfonate), has been obtained by one-pot method, and characterized by elemental analysis, IR spectrum, and X-ray single-crystal diffraction. The results showed that the Ca(II) coordination crystallizes in the orthorhombic space group with $P2_12_12$, $a = 16.355(3)$ Å, $b = 17.478(4)$ Å, $c = 5.4549(11)$ Å, $\alpha = \beta = \gamma = 90.00^\circ$, $V = 1559.3(5)$ Å³, $Z = 2$, $Mr = 698.69$, $D_c = 1.488$ g/cm³, $T = 293(2)$ K, $F(000) = 724$, $\mu(\text{MoK}\alpha) = 0.408$ mm^{−1}, $R = 0.0703$ and $wR = 0.1848$. The Ca(II) ion is coordinated with four O atoms from two L ligands and two O atoms from two coordinated H₂O molecules, and generates a distorted octahedral geometry. The 1D chained structure of Ca(II) coordination polymer is constructed from the bridging of SO₃[−] groups. The 3D network structure is formed by the hydrogen bonds and π - π interaction between 1D chains.

Keywords: 2-[(E)-(2-furoylhydrazono)methyl]benzenesulfonate; Ca(II) coordination polymer; synthesis; crystal structure

1. Introduction

Coordination polymer materials have been demonstrated to have excellent properties and potential applications, such as catalysis, magnetism, optical materials, gas adsorption, antibacterial agents,

antitumor drugs, and so on [1–8]. In recent years, In order to study the novel structures and applications, many transition metal and rare earth metal coordination polymer materials have been prepared [9–16]. However, the novel structures and applications of main metal coordination polymer materials have not been paid much attention relative to that of transition metal and rare earth metal coordination polymer materials [17]. All the time, we have always been committed to the study of alkaline earth metal coordination polymer materials [18–21]. In this paper, a new Ca(II) coordination polymer, $[\{CaL_2 \cdot (H_2O)_2 \cdot 2H_2O\}]_n$ (**1**) ($L = 2\text{-}[(E)\text{-(2-furoylhydrazono)methyl}]benzenesulfonate$, Figure 1), has been obtained and characterized by elemental analysis, IR, and X-ray single crystal diffraction analysis.

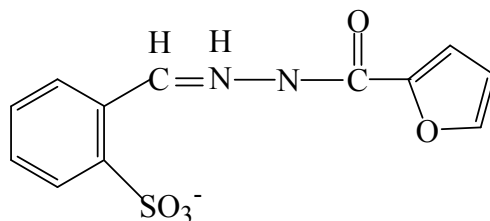


Figure 1. The structure of ligand.

2. Results and Discussion

2.1. Elemental Analysis and IR Spectra

The result of elemental analysis shows that the asymmetric unit of Ca(II) coordination polymer is $[CaL_2 \cdot (H_2O)_2] \cdot 2H_2O$, indicating that the Ca(II) coordination polymer conforms to 1:2 metal-to-ligand stoichiometry. The IR spectrum of Ca(II) coordination polymer displays characteristic bands at 3228 cm^{-1} , 1651 cm^{-1} , 1230 cm^{-1} , and 1202 cm^{-1} , which can be assigned to ν (OH), ν (C=N) and ν (SO_3^-) vibrations, respectively. The band at 3228 cm^{-1} shows that the Ca(II) coordination polymer contains water molecules. The band at 1651 cm^{-1} (ν (C=N)) shows that the C=N group do not coordinate to Ca(II) ion [22]. The bands at 1230 cm^{-1} and 1202 cm^{-1} show that the O atoms of SO_3^- group take part in coordination with Ca(II) ion [23].

2.2. Description of $[\{CaL_2 \cdot (H_2O)_2 \cdot 2H_2O\}]_n$

X-ray analysis reveals that the section of the coordination polymer **1** is made of one Ca(II) cation, two L ligands, two coordinated water molecules and two lattice water molecule. The section of the coordination polymer **1** is shown in Figure 2. The Ca(II) ion is coordinated with four O atoms from two 2-[(E)-(2-furoylhydrazono)methyl]benzenesulfonate ligands and two O atoms from two coordinated water molecules. Among the six coordinated atoms, O2, O2A, O1C, and O1D locate at the equatorial plane, and O1W and O1WA occupy the axial positions. The bond angles around Ca(II) in the equatorial plane are O2–Ca1–O2A ($99.3(2)^\circ$), O2–Ca1–O1C ($87.04(15)^\circ$), O1C–Ca1–O1D ($90.4(2)^\circ$), O1D–Ca1–O2A ($87.04(15)^\circ$), and the sum of the above bond angles is 363.78° , indicating O2, O2A, O1C, O1D, and Ca(II) are coplanar. The bond angle of O1W–Ca1–O1WA is $177.1(3)^\circ$, displays a distorted octahedral geometry. The C=N group of L do not take part in coordination with Ca(II) cation. The Ca–O lengths are in the range of $2.306(4)\text{ \AA}$ – $2.325(4)\text{ \AA}$. In Ca(II) coordination polymer, the coordination mode of SO_3^- groups are bidentate, which is in accordance with that reported previously [19].

The dihedral angle of plane 1 (O5–C9–C10–C11–C12) and plane 2 (C1–C2–C3–C4–C5–C6) is 4.9° , indicating two planes are also coplanar. The molecules form a one-dimensional chain by the bridging of SO_3^- groups (Figure 3). The distances of adjacent benzene rings is 3.431 \AA and that of adjacent furan ring is 3.095 \AA . The Ca(II) coordination polymer forms 3D network structure by hydrogen bonds (Table 1) and π – π interaction of 1D chains (Figure 4).

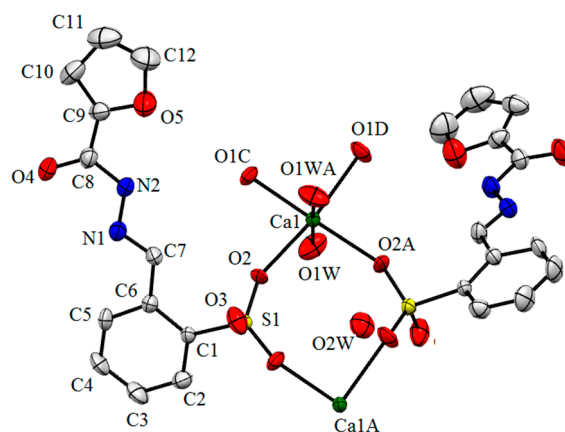


Figure 2. The section of the coordination polymer **1**. Symmetry code: A: $-x + 1, -y, z$; C: $-x + 1, -y, z + 1$; D: $x, y, z + 1$.

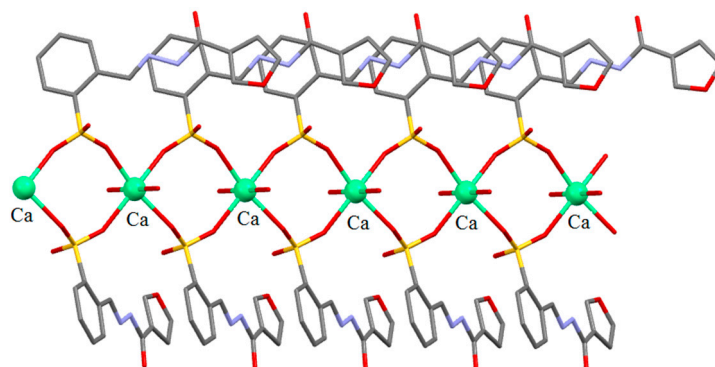


Figure 3. 1D chained structure of **1**.

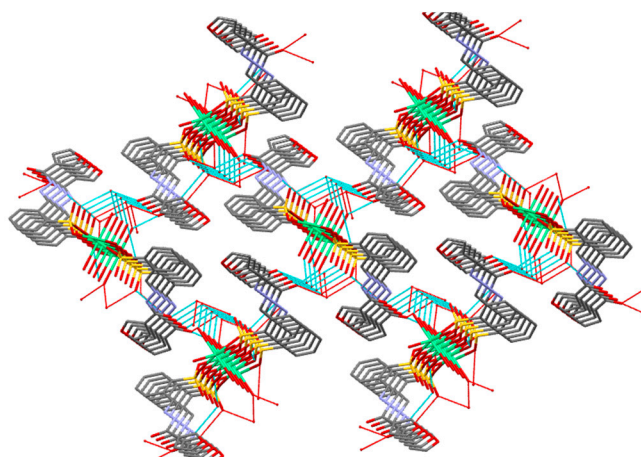


Figure 4. 3D network structure by the interaction of 1D chain.

Table 1. Hydrogen bonds data of **1**.

D-H...A	D-H/Å	H...A/Å	D...A/Å	∠D-H-A/(°)	Symmetry Code
N2-H2B...O3	0.86	2.37	3.000(7)	131	$x, y, 1 + z$
O1W-H99...O4	0.95	1.83	2.765(7)	169	$-x + 1/2, y + 1/2, -z + 1$
O1W-H98...O2W	0.93	1.86	2.760(7)	161	$-x + 1/2, y + 1/2, -z$
O2W-H97...O4	0.96	2.03	2.861(7)	143	—
O2W-H96...O3	0.96	1.88	2.828(6)	170	$x - 1/2, -y - 1/2, -z$

3. Experimental Section

3.1. Materials and Instrumentation

2-Formylbenzenesulfonic acid sodium, $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, 2-furoic acid hydrazide and solvents were analytical grade and used without further purification. Elemental analysis for carbon, hydrogen, and nitrogen was performed on the Elementar Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). The Infrared spectrum ($4000\text{--}400\text{ cm}^{-1}$) was recorded on a Nicolet AVATAR 360 FT-IR spectrophotometer (Nicolet Instrument Inc., Madison, WI, USA) using the KBr pellet. The crystal data collection was performed on a Bruker Smart CCD Area Detector (Bruker, Billerica, MA, USA).

3.2. Preparation of $[\{\text{CaL}_2 \cdot (\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}\}]_n$

A mixture of 1.0 mmol (0.2080 g) of 2-formylbenzenesulfonic acid sodium, 1.0 mmol (0.1260 g) of 2-furoic acid hydrazide and 0.5 mmol (0.1555 g) of $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ were added to the 10 mL of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ ($v:v = 1:2$) solution. The above mixture was stirred at $60\text{ }^\circ\text{C}$ for 4 h and then naturally cooled to room temperature. The precipitate was collected by filtration. The single crystal of the title complex suitable for X-ray determination was obtained by slow evaporation from the filtrate after 15 days at room temperature. Yield 72%. Anal. Calcd. (%) for $\text{C}_{24}\text{H}_{26}\text{CaN}_4\text{O}_{14}\text{S}_2$: C, 41.22; H, 3.72; N, 8.01. Found (%): C, 41.52; H, 3.46; N, 8.28.

3.3. Crystal Structure Determination

A single crystal with dimensions of $0.21\text{ mm} \times 0.20\text{ mm} \times 0.19\text{ mm}$ was selected for structural analysis on a Bruker Smart Apex CCD diffractometer with $\text{MoK}\alpha$ radiation and $\varphi\text{-}\omega$ scan mode at 293 (2) K. The structure was solved by direct methods using SHELXS-97 [24] program and refined on F^2 by full-matrix least-squares methods. All the non-hydrogen atoms were refined anisotropically. The H atoms of water were determined according to difference Fourier method and refined with a riding model. All the remaining H atoms were located theoretically and refined with a riding model. A total of 11112 reflection data were collected in the range of $3.41^\circ\text{--}24.99^\circ$, and 2538 were observed with $I > 2\sigma(I)$. The SHELXL-97 and Bruker SHELXTL program package [24] were used to refine structure, and the Mercury program [25] was used to draw molecular graphics. The final refinement shows $R = 0.0703$, and $wR = 0.01848$ ($w = 1/[\delta^2(F_o^2) + (0.905P)^2 + 2.5943P]$, $P = (F_o^2 + 2F_c^2)/3$). Technical details of the data collection and refinement parameters for $[\{\text{CaL}_2 \cdot (\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}\}]_n$ are listed in Table 2. The selected bond lengths and bond angles are listed in Table 3.

Table 2. Crystal data for **1**.

Formula	$\text{C}_{24}\text{H}_{26}\text{CaN}_4\text{O}_{14}\text{S}_2$
Formula weight	698.69
Crystal system	orthorhombic
Space group	$P2_12_12$
a (Å)	16.355(3)
b (Å)	17.478(4)
c (Å)	5.4549(11)
$\alpha = \beta = \gamma$ (°)	90.00
Z	2
$F(000)$	724
V (Å ³)	1559.3(5)
Calculated density (μg·m ^{−3})	1.488
μ (mm ^{−1})	0.408
S	1.133
Limiting indices	$-19 \leq h \leq 19, -20 \leq k \leq 20, -6 \leq l \leq 6$
Unique reflections	2750
Parameters	216
Restraints	7
R_{int}	0.0810
Flack x parameter [26]	0.10(11)
R_1, wR_2 [all data]	0.0750, 0.1884
R_1, wR_2 [$I > 2\sigma(I)$]	0.0703, 0.1848
Largest diff. peak and hole (e·Å ^{−3})	0.706, −0.530

Table 3. Selected bond lengths (Å) and angles (°) for **1**.

Bond	Distance
Ca1–O2	2.306(4)
Ca1–O1W	2.312(4)
Ca1–O1C	2.325(4)
N1–C7	1.262(7)
S1–O1	1.449(3)
S1–O2	1.445(4)
S1–O3	1.442(4)
Angle	(°)
O2–Ca1–O2A	99.3(2)
O2–Ca1–O1W	93.3(2)
O2–Ca1–O1WA	84.83(19)
O1W–Ca1–O1WA	177.1(3)
O2A–Ca1–O1C	164.54(16)
O2–Ca1–O1C	87.04(15)
O1W–Ca1–O1C	101.39(19)
O2–Ca1–O1D	164.54(16)
O1W–Ca1–O1D	80.71(17)
O1C–Ca1–O1D	90.55(19)
O2–S1–O3	112.5(3)
O3–S1–O1	113.0(3)

Symmetry code: A: $-x + 1, -y, z$; C: $-x + 1, -y, z + 1$; D: $x, y, z + 1$.

4. Conclusions

In summary, a new Ca(II) coordination polymer, $[\{\text{CaL}_2 \cdot (\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}\}]_n$ (**1**) ($\text{L} = 2\text{-}[(\text{E})\text{-(2-furoylhydrazono)methyl]benzenesulfonate}$), has been obtained by one-pot method, and characterized by elemental analysis, IR spectrum and X-ray single-crystal diffraction. The results showed that the Ca(II) coordination polymer the Ca(II) ion is coordinated with four O atoms from two L ligands and two O atoms from two coordinated H_2O molecules, and generates a distorted octahedral geometry. The 1D chained structure of Ca(II) coordination polymer is formed by the bridging of SO_3^- groups. The 3D network structure is formed by the hydrogen bonds and π - π interaction between 1D chains.

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Author Contributions

Xi-Shi Tai designed the method and wrote the manuscript. Xin Wang analyzed the crystal data for the Ca(II) coordination polymer and wrote the manuscript.

Supplementary Materials

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.CCDC 1417619. 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).

Conflicts of Interest

The authors declare no conflict of interest.

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