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Synthesis, Crystal Structure, and Cytotoxic Activity of a Novel Eight-Coordinated Dinuclear Ca(II)-Schiff Base Complex

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Abstract: A novel eight-coordinated dinuclear Ca(II) complex, $[Ca_2(L)_2(H_2O)_{10}]\cdot H_2O$ (L = 4-formylbenzene-1,3-disulfonate-3-pyridinecarboxylic hydrazone) (**1**), was synthesized by the reaction of 3-pyridinecarboxylic hydrazide, disodium 4-formylbenzene-1,3-disulfonate, and $Ca(ClO_4)_2\cdot 4H_2O$ in ethanol-water solution (v:v = 3:1) at 50 °C. Complex **1** was characterized by elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR, and X-ray single crystal diffraction analysis. Dinuclear Ca(II) complex **1** belongs to triclinic, space group *P*-1 with a = 7.186(3) Å, b = 11.978(5) Å, c = 12.263(5) Å, α = 90.318(5)°, β = 91.922(5)°, γ = 96.797(5)°, V = 1047.5(8) Å^3, Z = 1, D_c = 1.685 mg·m^{-3}, μ = 0.572 mm^{-1}, $F(000)$ = 552, and final R_1 = 0.0308, ωR_2 = 0.0770. Dinuclear Ca(II) molecules form a 1D chained structure by π–π stacking interaction. The 1D chains form a 3D framework structure by the π–π stacking interaction and hydrogen bonds. The in vitro cytotoxic activity activity of **1** against *HL*-60 and *MLTC*-1 was also investigated.

Keywords: 3-Pyridinecarboxylic hydrazide; disodium 4-formylbenzene-1,3-disulfonate; dinuclear Ca(II) complex; synthesis; crystal structure; in vitro cytotoxic activity

1. Introduction

The biological activities of metal complexes have been a hot research topic since cisplatin was used as an antitumor drug. Many metal complexes with transition metals as center ions show excellent antibacterial and antitumor activities, such as Cu(II) [1–3], Zn(II) [4–6], Mn(II) [7–9], Ni(II) [10–12], Ag(I) [13–15], and so on. Meanwhile, hydrazone compounds also exhibit good biological activities and are a kind of good ligand [16–18]. Hence, the design and synthesis of novel hydrazone compounds and their transition metal complexes have received more attention. However, compared with transition metal complexes, the studies on the antibacterial and antitumor activities of Ca(II) complexes are rare. The investigations of the synthesis and properties of Ca(II) complexes have always been one of our goals [19–25]. In this work, we synthesized a novel eight-coordinated dinuclear Ca(II) complex, $[Ca_2(L)_2(H_2O)_{10}]\cdot H_2O$ (1), by the reaction of 3-pyridinecarboxylic hydrazide, disodium 4-formylbenzene-1,3-disulfonate, and $Ca(ClO_4)_2\cdot 4H_2O$. Complex **1** was characterized by elemental analysis, IR spectrum, ^{1}H-NMR, ^{13}C-NMR, and single crystal X-ray crystallography. The in vitro cytotoxic activity of 1 against HL-60 and MLTC-1 was also investigated.

2. Results and Discussion

*2.1. Properties of **1***

The data of elemental analysis for C, H, and N are C, 29.35; H, 3.95; N, 7.90% (Calcd.); C, 29.17; H, 4.28; N, 7.75% (Found). Thus, the dinuclear Ca(II) complex conforms to the formula $C_{26}H_{42}Ca_2N_6O_{26}S_4$.

The dinuclear Ca(II) complex are soluble in DMF, DMSO, H_2O, and CH_3OH, insoluble in THF, $CHCl_3$, and benzene.

*2.2. IR Spectrum of **1***

The IR spectrum of the dinuclear Ca(II) complex is shown in Figure 1. The strong peak at 3473 cm^{-1} corresponds to the ν(OH) vibration of H_2O molecules in **1**. The peaks at 1683 cm^{-1} and 1561 cm^{-1} can be assigned to ν(C=O) and ν(C=N), showing that the C=O and C=N groups do not coordinate to Ca(II) ion [26]. The peaks at 1253 cm^{-1} and 1,192 cm^{-1} demonstrate the existence of coordination bonds between SO_3^- groups and Ca(II) [27].

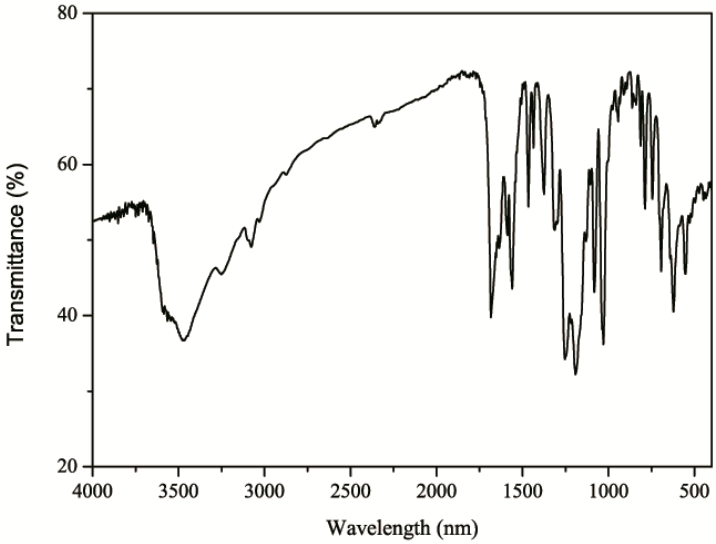

Figure 1. The IR spectrum of **1**.

*2.3. ^{1}HNMR and ^{13}CNMR Spectra of **1***

The ^{1}HNMR and ^{13}CNMR data of dinuclear Ca(II) complex are as follows: ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.10 (s, 1 H, CONH), 9.37 (s, 1 H, N=CH), 8.71 (d, J = 4.8 Hz, 1 H, H-C11A of pyridine), 8.03–8.15 (m, 3 H, H-C10A, H-C12A, H-C13A of pyridine), 7.96 (d, J = 8.0 Hz, H-C6A of Ph), 7.65–7.68 (m, 2 H,H-C3A, H-C2A of Ph). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.07 (C8A), 150.14 (C1A), 149.38 (C10A), 148.99 (C11A), 148.57 (C5A), 146.90 (C7A), 138.35 (C2A), 131.67 (C4A), 127.36 (C9A), 126.29 (C13A), 126.04 (C6A), 124.97 (C12A), 123.00 (C3A).

*2.4. Description of **1***

The result of X-ray single-crystal diffraction reveals that the novel eight-coordinated dinuclear Ca(II) complex **1** crystallizes in a triclinic *P*-1 space group. The coordination environment of Ca(II) of **1** is shown in Figure 2. From Figure 2, the asymmetric unit of **1** contains two Ca(II) ions, two 4-formylbenzene-1,3-disulfonate-3-pyridinecarboxylic hydrazone ligands, ten coordinated H_2O molecules, and one uncoordinated H_2O molecule. Each Ca(II) ion in **1** is eight-coordinated to three oxygen atoms (O2A, O5, O6 or O2, O5A, O6A) from two 4-formylbenzene-1,3-disulfonate-3-pyridinecarboxylic hydrazone ligands and five coordinated H_2O

molecules (O8, O9, O10, O11, O12 or O8A, O9A, O10A, O11A, O12A). The coordination geometry of Ca(II) can be described as a distorted trigonal dodecahedron. In **1**, the two sulfonate groups of each 4-formylbenzene-1,3-disulfonate-3-pyridinecarboxylic hydrazone ligand adopt different coordination modes, one is monodentate and the other is bidentate. The molecules of **1** form a 1D chained structure by the π–π stacking interaction, as shown in Figure 3, and the distance of two planes is 3.428 Å. The 1D chains form a 3D framework structure by the π–π stacking interaction and hydrogen bonds, as shown in Figure 4. The π–π stacking interaction and hydrogen bonds play an important role in stabilizing the 3D framework structure. The main bond lengths (Å) and angles (°) for **1** are given in Table 1. The lengths (Å) and angles (°) of hydrogen bonds for **1** are listed in Table 2.

The Ca–O distances range from 2.3882 (18) to 2.688 (2) Å (Table 1), which are comparable to those in reported Ca(II) complexes [19–25].

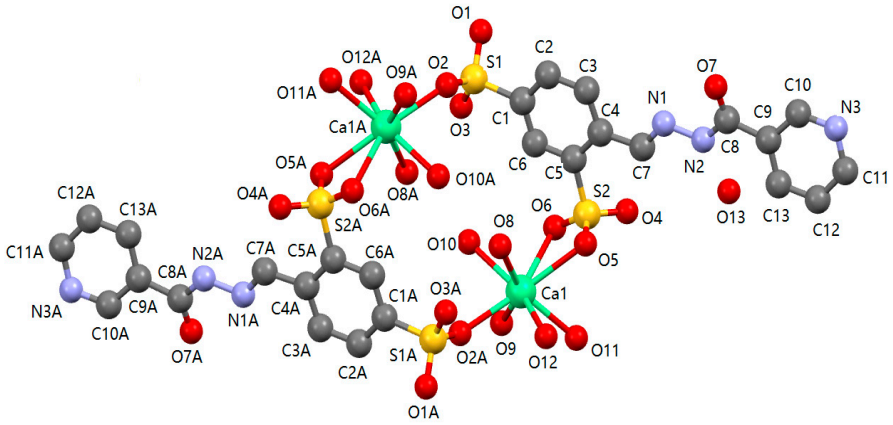

Figure 2. The coordination environment of **1**.

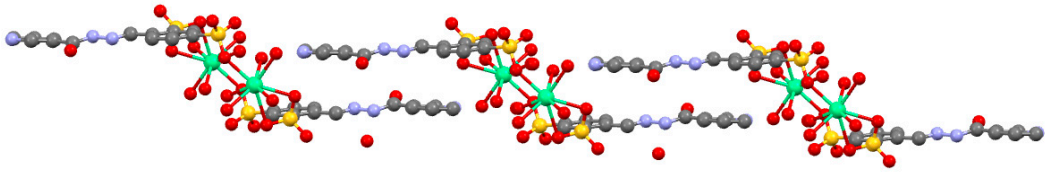

Figure 3. 1D chained structure of **1**.

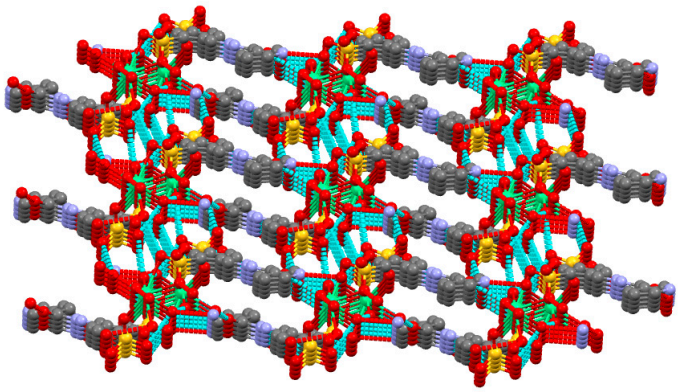

Figure 4. 3D network structure of **1**.

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

Bond	Distance	Bond	Distance
Ca1-O11	2.3882 (18)	Ca1-O6	2.688 (2)
Ca1-O10	2.4110 (17)	S2-O4	1.4396 (14)
Ca1-O2^{i}	2.4221 (15)	S2-O6	1.4504 (15)
Ca1-O8	2.4333 (18)	S2-O5	1.4556 (17)
Ca1-O9	2.4448 (19)	S1-O1	1.4454 (16)
Ca1-O12	2.4799 (19)	S1-O2	1.4501 (16)
Ca1-O5	2.5823 (16)	S1-O3	1.4546 (17)
C7-N1	1.266 (3)	N1-N2	1.381 (2)
Angle	°	Angle	°
O11-Ca1-O10	139.72 (7)	O11-Ca1-O2^{i}	114.65 (7)
O10-Ca1-O2^{i}	79.62 (6)	O11-Ca1-O8	140.87 (6)
O10-Ca1-O8	76.19 (7)	O8-Ca1-O2^{i}	80.77 (6)
O11-Ca1-O9	72.33 (6)	O10-Ca1-O9	73.73 (6)
O9-Ca1-O2^{i}	80.05 (6)	O8-Ca1-O9	146.67 (5)
O11-Ca1-O12	72.44 (6)	O12-Ca1-O10	147.10 (6)
O12-Ca1-O2^{i}	78.36 (6)	O8-Ca1-O12	76.39 (6)
O12-Ca1-O9	125.36 (6)	O11-Ca1-O5	75.96 (6)
O10-Ca1-O5	108.77 (6)	O5-Ca1-O2^{i}	153.19 (6)
O8-Ca1-O5	76.89 (6)	O9-Ca1-O5	126.56 (6)
O5-Ca1-O12	82.12 (6)	O11-Ca1-O6	84.33 (6)
O10-Ca1-O6	69.68 (5)	O6-Ca1-O2^{i}	147.52 (95)
O8-Ca1-O6	101.30 (6)	O9-Ca1-O6	81.40 (6)
O12-Ca1-O6	133.92 (6)	O5-Ca1-O9	53.40 (5)

Symmetry codes: (i) = –x + 1, −y + 2, −z.

Table 2. The lengths (Å) and angles (°) of hydrogen bonds for **1**.

Hydrogen Bonds	*d*(D-H)	*d*(H ... A)	*d*(D ... A)	DHA	Symmetry Code
O(8)-H(8WB) ... O(3)	0.853	2.05	2.812(2)	149	$1-x, 2-y, -z$
O(8)-H(8WA) ... N(3)	0.849	1.94	2.771(3)	166	$1-x, 3-y, 1-z$
N(2)-H(2B) ... O(13)	0.86	1.97	2.766(3)	153	x, y, z
O(9)-H(9WB) ... O(7)	0.856	1.99	2.815(2)	159	$x, -1+y, z$
O(9)-H(9WA) ... O(1)	0.85	2.03	2.869(2)	170	$2-x, 2-y, -z$
O(11)-H(1WB) ... O(5)	0.85	2.01	2.817(2)	160	$1-x, 2-y, 1-z$
O(11)-H(1WA) ... O(7)	0.85	1.90	2.717(3)	163	$x, -1+y, z$
O(12)-H(2WA) ... O(6)	0.86	2.06	2.910(3)	169	$-1+x, y, z$
O(12)-H(2WB) ... O(4)	0.85	2.06	2.887(2)	163	$1-x, 2-y, 1-z$
O(10)-H(10C) ... O(8)	0.85	2.14	2.900(2)	149	$1-x, 2-y, -z$
O(10)-H(10D) ... O(3)	0.86	1.95	2.801(3)	170	$2-x, 2-y, -z$
O(13)-H(13B) ... O(1)	0.96	2.45	3.187(3)	133	$x, y, 1+z$
O(13)-H(13B) ... O(2)	0.96	2.41	3.079(3)	126	$x, y, 1+z$
O(13)-H(13C) ... O(12)	0.96	2.16	3.039(3)	152	$1-x, 2-y, 1-z$

2.5. In Vitro Cytotoxic Activity

The data of in vitro cytotoxic activity of dinuclear Ca(II) complex **1** against *HL*-60 and *MLTC*-1 are given in Table 3. The concentration of DMSO was controlled under 1% to assure not to affect the results. The results show that the dinuclear Ca(II) complex **1** has an obvious cytotoxic effect against *HL*-60 cells and *MLTC*-1 cells. The dinuclear Ca(II) complex **1** has a stronger cytotoxicity against *MLTC*-1 cells with lower IC50 (19.51 μg/mL).

Table 3. In vitro cytotoxic activities of **1**.

Compound	IC50 (μg/mL)	
	HL-60	*MLTC*-1
Ca(II) complex	27.68 ± 0.9	19.51 ± 1.2

3. Experimental Section

3.1. Materials and Instrumentation

3-Pyridinecarboxylic hydrazide, disodium 4-formylbenzene-1,3-disulfonate, $Ca(ClO_4)_2{\cdot}4H_2O$, and solvents were obtained from commercial sources and used without further purification. Elemental analysis was carried out on an Elementar Vario EL III analyzer (Elementar, Hanau, Germany). The IR spectrum was recorded in the 4000–400 cm^{-1} range on an infrared spectrophotometer (Beijing Purkinje General Instrument, Beijing, China). ^1H NMR and ^{13}CNMR spectra were recorded on a Bruker Avance-400 spectrometer with DMSO-d_6 as the solvent. Crystal data of the dinuclear Ca(II) complex **1** were collected by a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA).

*3.2. Synthesis of $[Ca_2(L)_2(H_2O)_{10}]{\cdot}H_2O$ (**1**)*

A mixture of 3-pyridinecarboxylic hydrazide (0.1371 g, 1.0 mmol), disodium 4-formylbenzene -1,3-disulfonate (0.310 g, 1.0 mmol), and $Ca(ClO_4)_2{\cdot}4H_2O$ (0.119 g, 0.5 mmol) were dissolved in 15-mL mixed solvents of H_2O:CH_3CH_2OH (v:v = 1:3). The mixture was stirred for 5 h at 50 °C and was then cooled to obtain colorless crystals. The product was filtered and dried in the air. Anal. Calcd for $C_{26}H_{42}Ca_2N_6O_{26}S_4$ (M_r = 1063.06): C, 29.35; H, 3.95; N, 7.90%. Found: C, 29.17; H, 4.28; N, 7.75%. Main IR (cm^{-1}, KBr Pellet): ν(H_2O) 3473 cm^{-1} (s), ν(C=O): 1683 cm^{-1} (s), ν($SO_3{}^-$): 1253 (s), 1,192 cm^{-1} (s), ν(C=N): 1561 cm^{-1} (s), ν(Ca–O): 447 cm^{-1} (w).

3.3. Crystal Structure Determination

A single crystal of dinuclear Ca(II) complex **1** with dimensions of 0.22 mm × 0.21 mm × 0.20 mm was chosen for data collection. The X-ray diffraction data of dinuclear Ca(II) complex **1** were collected on a Bruker Smart CCD diffractometer with a graphite-monochromatized Mo*K*α (λ = 0.71073 Å) radiation using the ω–φ scan mode ($1.66° \leq \theta \leq 25.09°$). The structure was solved by direct methods with SHELXL-97 [28] and refined on F^2 by full-matrix least-squares procedures with SHELXTL-97 [29]. The crystal data of **1** are given in Table 4.

Table 4. Crystal data for complex 1.

Empirical Formula	**$C_{26}H_{42}Ca_2N_6O_{26}S_4$**
Formula weight	1063.06
Temperature/K	296(2)
Crystal system	Triclinic
Space group	*P*-1
a/Å	7.186(3)
b/Å	11.978(5)
c/Å	12.263(5)
α/°	90.318(5)
β/°	91.922(5)
γ/°	96.797(5)
Volume/Å^3	1047.5(8)
Z	1
ρ_{calc}mg/mm^3	1.685
μ/mm^{-1}	0.572
S	1.093
F(000)	552
Index ranges	$-8 \leq h \leq 8$, $-14 \leq k \leq 13$, $-14 \leq l \leq 13$
Reflections collected	5175
Independent reflections	3646 [R(int) = 0.0169]
Data/restraints/parameters	3646/10/329
Goodness-of-fit on F^2	1.094
Final *R* indexes [$I \geq 2\sigma$ (*I*)]	R_1 = 0.0308, wR_2 = 0.0770
Final *R* indexes [all data]	R_1 = 0.0355, wR_2 = 0.0792
Largest diff. peak/hole / e Å^{-3}	0.354/−0.358

3.4. In Vitro Cytotoxic Activity

The tested cells (*HL*-60 and *MLTC*-1) were provided by Taishan Medical University. The harvested *HL*-60 and *MLTC*-1 cells were incubated for 48 h at 37 °C in a humidified 5%CO_2-90%N_2-5%O_2 atmosphere. The drug (complex **1**) with different concentrations (5, 10, 20, 30, 40, and 60 μg ml^{-1}) was tested for its IC50 against *HL*-60 and *MLTC*-1 cells, following the procedure previously described [23].

4. Conclusions

In this paper, a novel eight-coordinated dinuclear Ca(II) complex, $[Ca_2(L)_2(H_2O)_{10}]\cdot H_2O$ (L = 4-formylbenzene-1,3-disulfonate-3-pyridinecarboxylic hydrazone) (**1**), was synthesized by the reaction of 3-pyridinecarboxylic hydrazide, disodium 4-formylbenzene-1,3-disulfonate, and $Ca(ClO_4)_2\cdot 4H_2O$ in ethanol–water solution (v:v = 3:1) at 50 °C. Dinuclear Ca(II) complex **1** was characterized by elemental analysis, IR, and X-ray single crystal diffraction analysis. The molecules of **1** form a 1D chained structure by π–π stacking. 1D chains form a 3D framework structure by the interaction of π–π stacking and hydrogen bonds. The dinuclear Ca(II) complex **1** has marked cytotoxic effect against *HL*-60 cells and *MLTC*-1 cells.

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Author Contributions: Meng Qing-Guo synthesized the complex **1**. Liu Li-Li analyzed the crystal data. Tai Xi-Shi designed the experiments and wrote the manuscript.

Conflicts of Interest: The authors declare that this article content has no conflict of interest.

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