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Research Article

Synthesis, Crystal Structure, and Catalytic Activity of a Calcuim(II) Complex with 4-Formylbenzene-1,3-disulfonate-isonicotinic Acid Hydrazone

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Abstract

A new calcium(II) complex was synthesized by one-pot synthesis method from disodium 4-formylbenzene-1,3-disulfonate, isonicotinic acid hydrazide and $Ca(ClO_4)_2 \cdot 2H_2O$. The structure of calcium(II) complex was determined by elemental analysis, IR and single crystal X-ray diffraction. The results show that the Ca(II) complex molecules form 3D network structure by the interactions of π-π stacking and hydrogen bonds. The Ca(II) complex catalyst could efficiently catalyse oxidation of benzylic alcohol with good conversion of benzyl alcohol (78 %) and excellent selectivity of benzaldehyde (98 %).

Keywords: Ca(II) Complex Catalyst; Synthesis; Structural Characterization; Catalytic Activity

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1. Introduction

The design and synthesis of metal-organic complex catalytic materials have been one of the most interesting researches in the materials chemistry [1-3]. Because they show outstanding catalytic activities for many organic reactions such as CO_2 cycloaddition [4,5], CO_2 coupling [6], degradation of organic dyes [7], A^3 coupling reaction [8, 9], iso-selective ring opening [10-12], cross-aldol condensation [13], knoevenagel condensation [14-19], tandem reaction [20], and so on. Benzaldehyde is an important intermediate of organic synthesis and fine chemical products, widely used in medicine, dyes, spices, resins, and other industries. However, the benzaldehyde was prepared by oxidation of benzyl alcohol with toxic metal oxides, peroxides, halides, and so on [21-23]. So, the development of environmentally friendly catalysts is very attractive. We have been devoted to the study on synthesis, structure and catalytic property of metal complexes [24-27]. In this paper, a new calcium (II) complex was synthesized by one-pot synthesis method from disodium 4-formylbenzene-1,3-disulfonate, isonicotinic acid hydrazide and $Ca(ClO_4)_2 \cdot 2H_2O$. The Ca(II) complex catalyst could efficiently catalyze oxidation of benzylic alcohol with good conversion of benzyl alcohol and excellent selectivity of benzaldehyde.

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2. Materials and Method

2.1 Materials and Equipments

Disodium 4-formylbenzene-1,3-disulfonate, isonicotinic acid hydrazide and $Ca(ClO_4)_2 \cdot 2H_2O$ were supplied by Aldrich. Elemental analysis was carried out on a Elemental Vario EL-III elemental analyzer. IR (4000-400 cm^{-1}) was obtained with a Nicolet Nexus 670 FTIR spectrophotometer. The crystal structure of calcium(II) complex was analyzed using a Bruker Amart CCD diffractometer.

2.2 Synthesis of Ca(II) Complex

Disodium 4-formylbenzene-1,3-disulfonate (0.1551 g, 0.5 mmol), isonicotinic acid hydrazide (0.6852 g, 0.5 mmol) and $Ca(ClO_4)_2 \cdot 2H_2O$ (0.110 g, 0.5 mmol) were dissolved in 15 mL ethanol/water (v:v = 2:1) solution. The above mixture was heated to 65 °C for 6 h with stirring. After cooled, the solution was filtered and the colorless block crystals were obtained by slowly evaporating the filtrate at room temperature. Yield: 61 %. IR υ/cm^{-1}: 3445 cm^{-1} (O-H stretch), 1656 cm^{-1} (C=N), 1227 cm^{-1} (SO_3^-), and 1165 cm^{-1} (SO_3^-). Anal. Calc. for $C_{26}H_{42}Ca_2N_6O_{26}S_4$: C, 29.35 %; H, 3.95 %; N, 7.90 %. Found: C, 29.08 %; H, 4.26 %; N, 7.75 %. The reaction equation for the formation of Ca(II) complex is shown in Figure 1.

2.3 Crystal Structure Determination

Single crystal data of Ca(II) complex was obtained from Bruker Smart Apex-II CCD area detector diffractometer by using MoKα radiation and φ~ω scan mode at 293 (2) K. The structure was solved by direct methods with SHELXS-97 [28] and refined by full-matrix least-squares techniques on F^2 with SHELXL [29]. The crystallographic data and refinement details for Ca(II) complex are listed in Table 1.

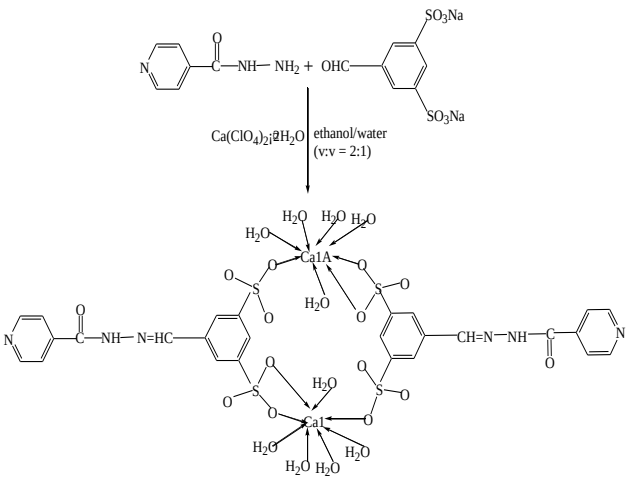

Figure 1. The reaction equation for the formation of Ca(II) complex

2.4 Catalytic Test of Benzyl Alcohol Oxidation

In a typical experiment, benzyl alcohol (0.2 mmol, 0.0216 g), solvent (1.50 g), and catalyst (0.060 g) were added into a 10 mL stainless steel autoclave. After the reactor was sealed, the pure O_2 was pumped to replace the atmosphere for six times. Then under pressure of 1 MPa, the mixture was kept at 120-140 °C for 6 h with vigorous stirring. After the reaction, the mixture was centrifuged to remove the catalyst. The conversion of benzyl alcohol and the selectivity of benzaldehyde were determined by gas chromatography equipped with a SE-54 capillary column (GC-1100, 0.25 mm × 0.25 mm × 30 m).

Table 1. Crystallographic data and refinement details for Ca(II) complex

Empirical formula	$C_{26}H_{42}Ca_2N_6O_{26}S_4$
Formula weight	1063.05
Temperature/K	293(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	7.1961(14)
b/Å	11.972(2)
c/Å	12.275(3)
α/°	89.76(3)
β/°	88.09(3)
γ/°	83.21(3)
Volume/Å^3	1049.5(4)
Z	1
ρ_{calc}mg/mm^3	1.682
μ/mm^{-1}	0.571
S	1.048
F(000)	552
Index ranges	$-8 \le h \le 9$, $-15 \le k \le 15$, $-15 \le l \le 15$
Reflections collected	10314
Independent reflections	4771 [R(int) = 0.0228]
Data/restraints/parameters	4771/0/297
Goodness-of-fit on F^2	1.085
Final R indexes [$I \ge 2\sigma$ (I)]	R_1 = 0.0413, wR_2 = 0.1258
Final R indexes [all data]	R_1 = 0.0452, wR_2 = 0.1187
Largest diff. peak and hole	0.837 and -0.659 e·Å^{-3}

3. Results and Discussion

3.1 IR Spectra of Ca(II) Complex

The IR spectrum (Figure 2) of Ca(II) complex shows the bands at 3445 cm^{-1} (O–H stretch), 1656 cm^{-1} (C=N), 1227 cm^{-1} (SO_3^-), and 1165 cm^{-1} (SO_3^-), respectively. The results of IR show that the Ca(II) complex contains H_2O molecules and only the O atoms of SO_3^- groups take part in coordination with Ca(II) ion by comparison with ref. [30]. The results are also confirmed by crystal structure analysis.

3.2 Structural Description of Ca(II) Complex

The Ca(II) complex crystallizes in the triclinic space group *P*-1. The detailed analysis of the crystal structure indicates that the Ca(II) complex is made up of two Ca(II) ions, two 4-formylbenzene-1,3-disulfonate-isonicotinic acid hydrazone ligands, ten coordinated water molecules and two lattice water molecules (Figure 3). Each Ca(II) ion is coordinated with three O atoms of SO_3^- groups from two dif-ferent 4-formylbenzene-1,3-disulfonate-isonicotinic acid hydrazone ligands and five O atoms from five coordinated water molecules to form a distorted trigonal dodecahedron geometry. The dihedral angle between two rings (ring 1: C1-C2-C3-C4-C5-C6, ring 2: C9-C10-C11-N1-C12-C13) is 8.2°, indicating that the ligand is almost coplanar. The complex molecules form 1D chained structure by π-π interactions (Figure 4), and further to form a three-dimensional network structure (Figure 5). The important bond lengths and angles are given in Table 2.

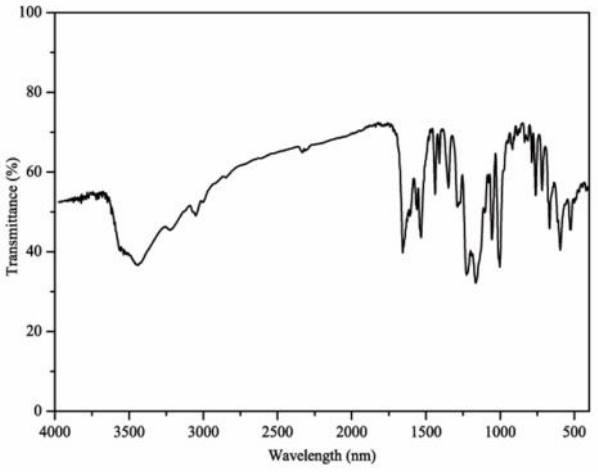

Figure 2. The IR spectrum of Ca(II) complex

3.3 Catalytic Testing Studies

The catalytic performance of the Ca(II) complex was assessed in the oxidation of benzyl alcohol. The equation of conversion of benzyl alcohol oxidation is shown in Figure 6. The results of the catalytic activity of the Ca(II) complex are given in Table 3. First, we investigated the effect of the solvent system on the efficiency and found that 1,4-dioxane is the best solvent for the benzyl alcohol oxidation reaction. As shown in Table 3, the conversion of benzyl alcohol and selectivity of benzaldehyde in 1,4-dioxane are 78 % and 98 % at 130 °C for 6 h, respectively (Table 3, entry 1). Meanwhile, the corresponding conversion and selectivity in tetrahydrofuran were 57 % and 61 % at 130 °C for 6 h, respectively (Table 3, entry 2). However, the benzyl alcohol conversion and the benzaldehyde selectivity were 12 %, 10 %, 9 % and 25 %, 14 %, 14 % when dimethylformamide, acetonitrile, and ethyl acetate was used as solvent at 130 °C within 6 h, respectively (Table 3, entry 3-5). In addition, the reaction temperature was investigated for the impact on the benzyl alcohol conversion and benzalde-

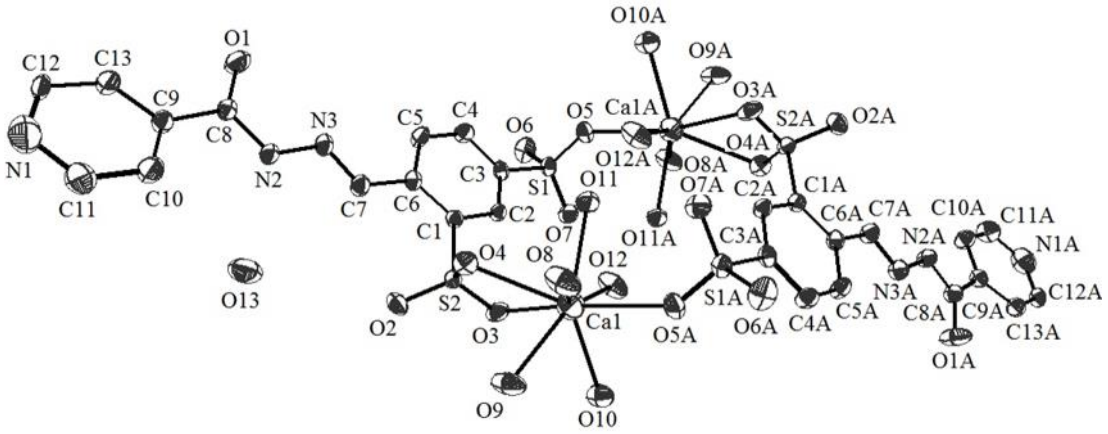

Figure 3. The molecular structure of Ca(II) complex

hyde selectivity of the oxidation reactions. Upon increase the reaction temperature from 120 °C to 130 °C in 1,4-dioxane, the conversion of benzyl alcohol dramatically enhanced (Table 3, entries 1 and 6). Notably, 98 % selectivity toward benzaldehyde was maintained during the temperature increasing from 120 °C to 130 °C (Table 3, entries 1 and 6). The conversion of benzyl alcohol and the selectivity of benzaldehyde were 80 % and 67 % at 140 °C for 6 h (Table 3, entry 7). The good conversion of benzyl alcohol (78 %) and excellent selectivity of benzaldehyde (98 %) was achieved when the reaction was carried out at 130 °C in 1,4-dioxane. Therefore, it appears that 130 °C is the optimum temperature for the benzyl alcohol oxidation reaction over the complex. Based on the above results, the optimum conditions of the benzyl alcohol oxidation reaction over the Ca(II) complex catalyst are 130 °C, 1,4-dioxane as solvent and 6 h (reaction time).

As the structure of Ca(II) complex (Figure 4 and Figure 5) shows, coordinatively unsaturated calcium is completely exposed to the pore of the Ca(II) complex. The coordinatively unsaturated calcium could be easily contact with the reactant (benzyl alcohol and O_2) which is benefit to the catalytic reaction. In addition, it can also promote rapidly removal of the product (benzaldehyde), and prevent further reaction of the benzaldehyde. A possible mechanism for the selective benzyl alcohol oxidation over the

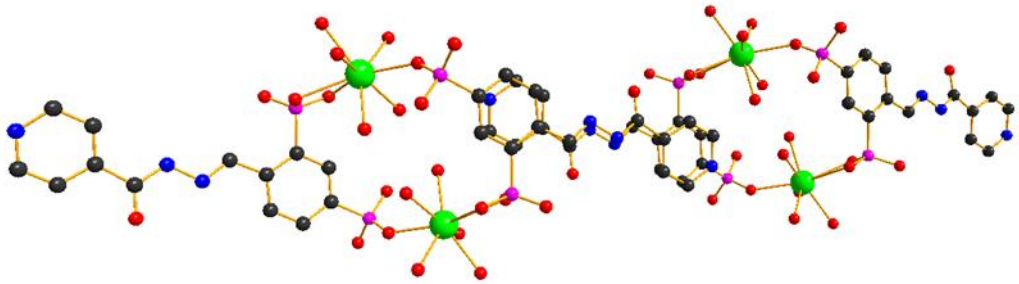

Figure 4. The 1D chained structure of Ca(II) complex

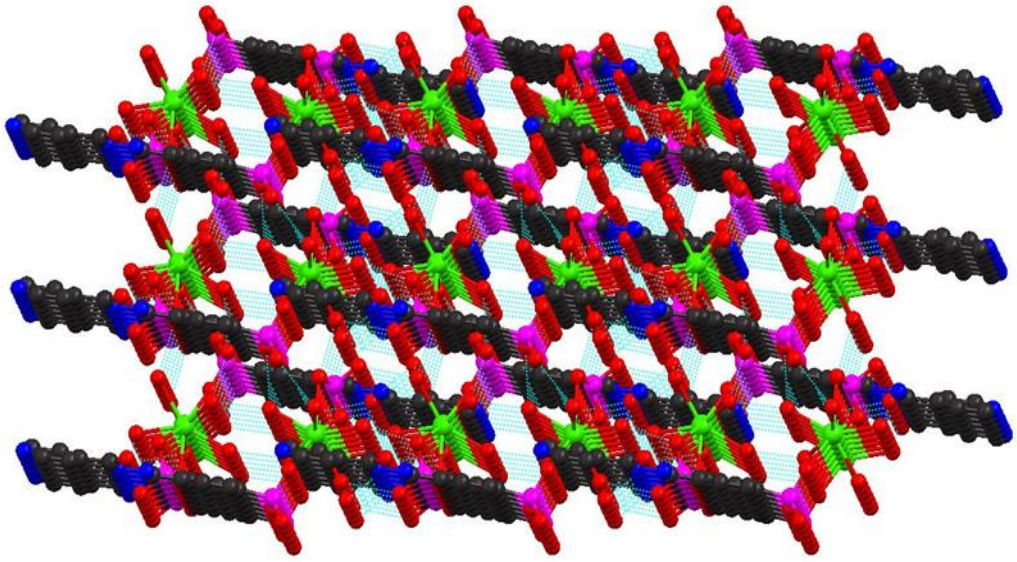

Figure 5. The 3D network structure of Ca(II) complex

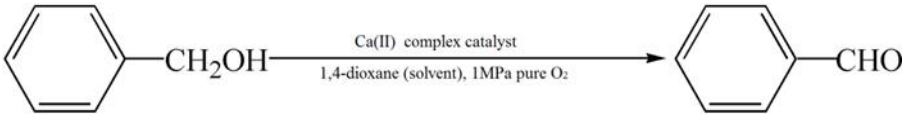

Figure 6. The conversion of benzyl alcohol oxidation

Table 2. The important bond lengths and angles of Ca(II) complex

Bond	Distance (Å)	Angle	(°)
O3-Ca1	2.691(2)	O4-Ca1-O3	53.47(6)
Ca1-O4	2.590(19)	O5-Ca1-O3	147.45(6)
Ca1-O5	2.4302(19)	O4-Ca1-O5	153.35(6)
Ca1-O8	2.486(2)	O5-Ca1-O8	78.46(7)
Ca1-O9	2.3910(19)	O5-Ca1-O10	79.85(7)
Ca1-O10	2.4481(19)	O5-Ca1-O11	80.70(6)
Ca1-O12	2.4157(19)	O8-Ca1-O3	133.92(7)
Ca1-O11	2.4309(19)	O8-Ca1-O4	82.06(7)
		O9-Ca1-O3	83.81(7)
		O4-Ca1-O9	75.23(7)
		O9-Ca1-O5	115.19(8)
		O9-Ca1-O8	72.48(7)
		O10-Ca1-O9	72.82(7)
		O9-Ca1-O12	139.61(7)
		O9-Ca1-O11	140.40(7)
		O10-Ca1-O3	81.34(6)
		O4-Ca1-O10	126.59(6)
		O10-Ca1-O8	125.41(7)
		O12-Ca1-O3	70.07(7)
		O12-Ca1-O4	109.42(7)
		O12-Ca1-O5	79.15(7)
		O8-Ca1-O12	147.11(7)
		O12-Ca1-O10	73.21(7)
		O12-Ca1-O11	76.71(7)
		O11-Ca1-O3	101.68(6)
		O11-Ca1-O4	77.09(6)
		O11-Ca1-O8	76.14(7)
		O11-Ca1-O10	146.65(6)

Table 3. Catalytic performance of the Ca(II) complex in the oxidation of benzyl alcohol

Entry	Solvent	Temperature (°C)	Conversion (%)	Selectivity (%)
1	1,4-dioxane	130	78	98
2	tetrahydrofuran	130	57	61
3	dimethylformamide	130	12	25
4	acetonitrile	130	10	14
5	ethyl acetate	130	9	14
6	1,4-dioxane	120	6	98
7	1,4-dioxane	140	80	67

Ca(II) coordination polymer catalyst was supposed. First the hydroxyl group in benzyl alcohol can coordinate with coordinatively unsaturated calcium sites to obtain the intermediate calcium-alcoholate species. And the proton in the hydroxyl group is abstracted to the support to form surface adsorbed H species and alkoxide intermediates. Then the alkoxide intermediates undergo a β-hybride elimination to give the target product benzaldehyde. At the same time, Ca-hydride species is created that is then oxidized by the O_2, which ultimately regenerated the original Ca(II) coordination polymer with releasing of H_2O and O_2.

4. Conclusions

We have synthesized a new calcium(II) complex by one-pot method. Its structure was determined by elemental analysis, IR and single crystal X-ray diffraction. The results of catalytic activity show that the calcium (II) complex exhibits good catalytic activity for oxidation of benzylic alcohol with the conversion of benzyl alcohol and selectivity of benzaldehyde in 1,4-dioxane are 78 % and 98 %, respectively.

Acknowledgements

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