crystals

MDPI

Communication

Synthesis, Crystal Structure and Catalytic Activity of a Novel Ba(II) Complex with Pyridine-2-Carboxaldehyde-2-Phenylacetic Acid Hydrazone Ligand

Li-Hua Wang [1], Xi-Shi Tai [2,*], Li-Li Liu [2,*] and Peng-Fei Li [3]

1 College of Information and Engineering, Weifang University, Weifang 261061, China; wanglihua929@wfu.edu.cn
2 College of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, China
3 College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266061, China; lipfei2013@163.com
* Correspondence: taixs@wfu.edu.cn (X.-S.T.); liulili122@126.com (L.-L.L.); Tel.: +86-536-8785363 (X.-S.T.)

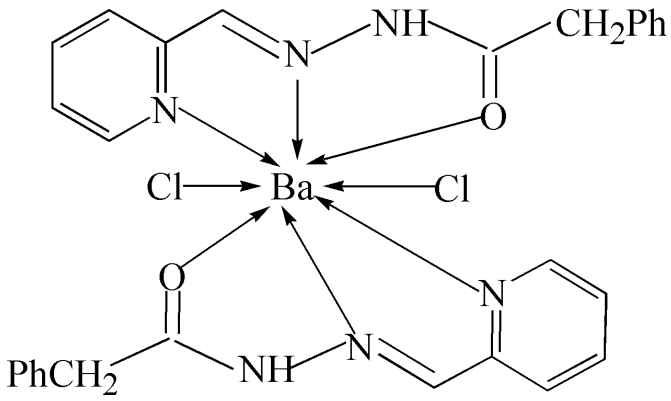
Academic Editor: Shujun Zhang
Received: 13 September 2017; Accepted: 5 October 2017; Published: 9 October 2017

Abstract: A novel Ba(II) complex, $[BaL_2Cl_2]$ (**1**) (L = pyridine-2-carboxaldehyde-2-phenylacetic acid hydrazone), has been synthesized using $BaCl_2$, pyridine-2-carboxaldehyde and 2-phenylacetohydrazide as raw materials. The structure of **1** has been determined by elemental analysis and X-ray single-crystal diffraction technique. X-ray structural analysis showed that the Ba(II) complex (**1**) crystallizes in monoclinic, space group $P2_1/c$ with cell parameters: a = 12.464(3) Å, b = 13.531(3) Å, c = 8.8035(18) Å, β = 95.06(3)°. In **1**, the Ba(II) atom is eight-coordinated in a distorted doubly-capped octahedral geometry through four N atoms and two O atoms from two different pyridine-2-carboxaldehyde-2-phenylacetic acid hydrazone ligands and two Cl^-. The complex (**1**) forms a 3D network structure by the interaction of intermolecular N-H···Cl hydrogen bonds and π···π stacking of neighboring pyridine rings and benzene rings. The optimum conditions for the benzyl alcohol oxidation reaction using the Ba(II) complex as catalyst was investigated.

Keywords: Ba(II) complex; pyridine-2-carboxaldehyde-2-phenylacetic acid hydrazone; synthesis; crystal structure; catalytic activity

1. Introduction

The studies on structures and properties of metal complex materials have achieved much attention in the past decades [1–5], because they show attractive applications in many ways such as magnetic properties [6–8], fluorescence [9–12], catalytic activities [13–15], pharmacological activities [16–18], and so on. However, to best of our knowledge, the structure and property of alkaline earth metal complexes have not been studied extensively comparing to transition metal complex. In recent years, our group have synthesized and structurally characterized some alkaline earth metal complexes [19–27]. In order to further investigate the structure and property of alkaline earth metal complexes, a novel Ba (II) complex with pyridine-2-carboxaldehyde-2-phenylacetic acid hydrazone (L), $[BaL_2Cl_2]$ (**1**) has been synthesized and characterized. The catalytic activity of Ba(II) complex has also been investigated. The chemical diagram of the Ba(II) complex is shown in Scheme 1.



Scheme 1. Chemical diagram of the Ba(II) complex.

2. Results and Discussion

2.1. Structural Description of Ba(II) Complex

The Ba(II) complex crystallizes in monoclinic system with space group $P2_1/c$. There are one Ba(II) ion, two pyridine-2-carboxaldehyde-2-phenylacetic acid hydrazone ligands, two Cl^- in the complex molecule. Figure 1 shows the coordination environment of Ba(II) ion in the complex. As shown in Figure 1, the Ba(II) ion is eight-coordinated with four N atoms and two O atoms from two different pyridine-2-carboxaldehyde-2-phenylacetic acid hydrazone ligands and two Cl^-, forming a distorted doubly-capped octahedral geometry. The dihedral angle between the pyridine ring (N1-C1-C2-C3-C4-C5) and benzene ring (C9-C10-C11-C12-C13-C14) is 76.2°, showing that the hydrazone molecule is non-planar. In the crystal packing, the complex molecules form 1D chained structure by the intermolecular hydrogen bonds (N-H···Cl) present between the pyridine-2-carboxaldehyde-2-phenylacetic acid hydrazone ligand and coordinated Cl^- (Figure 2), or by the π···π stacking interactions of pyridine rings (Figure 3). Meanwhile, hydrogen bonds and π···π stacking interactions of pyridine rings and benzene rings assemble the 1D chains into a 3D network structure (Figure 4). The important bond lengths and bond angles are shown in Table 1.

Table 1. Selected bond lengths (Å) and bond angles (°) for Ba(II) complex.

Bond	*d*	Bond	*d*
Ba1-Cl1	3.0214(11)	Ba1-O1	2.8330(19)
Ba1-N1	2.957(2)	Ba1-N2	2.8984(19)
C6-N2	1.268(3)	N3-C7	1.344(3)
C7-O1	1.221(3)	C1-N1	1.338(3)
C5-N1	1.343(3)	N2-N3	1.378(3)
Angle	ω	Angle	ω
O1-Ba1-Cl1	91.50(4)	O1-Ba1-Cl1A	88.50(4)
Cl1A-Ba1-Cl1	180.0	O1-Ba1-O1A	180.0
N1-Ba1-Cl1A	91.59(4)	Cl1-Ba1-N1	88.41(4)
O1A-Ba1-N1	71.15(5)	O1-Ba1-N1	108.85(5)
N1-Ba1-N1A	180.0	N2-Ba1-Cl1A	78.78(4)
N2-Ba1-Cl1	101.22(4)	N2-Ba1-O1	55.32(5)
N2-Ba1-O1A	124.68(5)	N2-Ba1-N1	55.12(5)
N2-Ba1-N1A	124.88(5)	N2-Ba1-N2A	180.0

Symmetry code: $-x, 1-y, 1-z$.

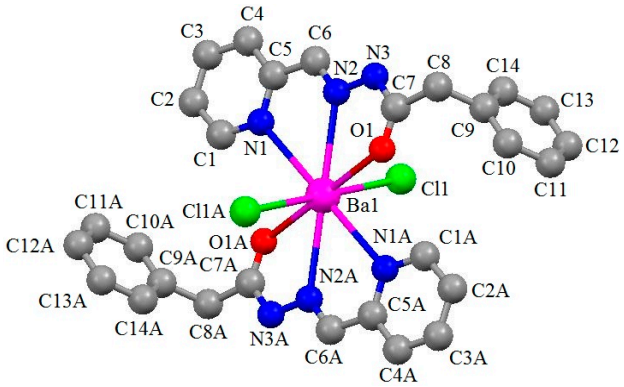


Figure 1. Coordination environment of Ba(II) ion in the complex.

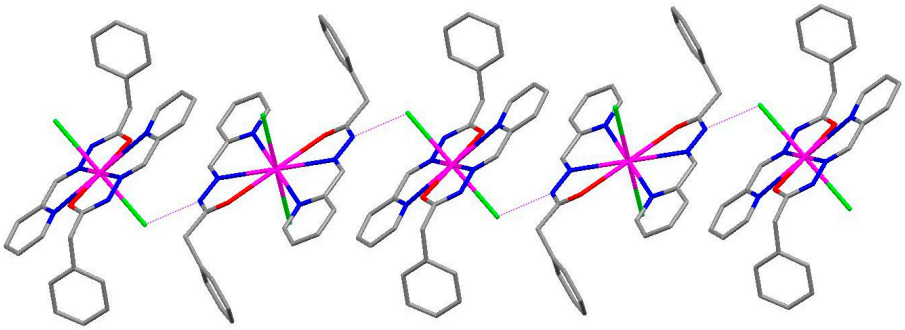


Figure 2. 1D chained structure by the hydrogen bonds.

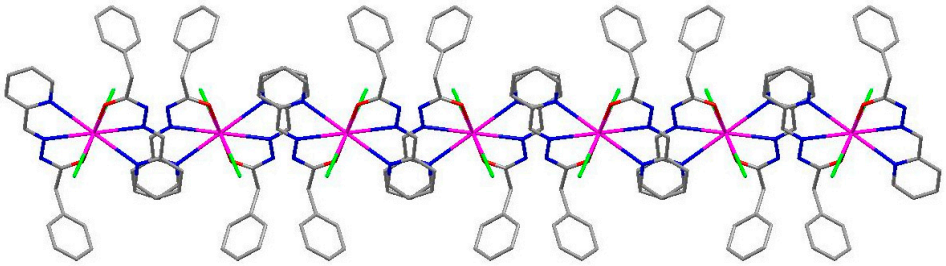


Figure 3. 1D chained structure by π-π stacking.

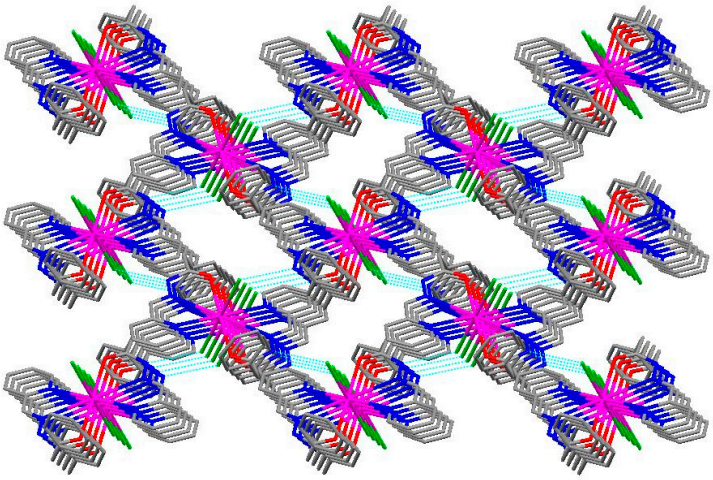


Figure 4. 3D supramolecular network structure of Ba(II) complex.

2.2. Catalytic Performance of Ba(II) Complex

The aerobic oxidation of benzyl alcohol was catalyzed by Ba(II) complex at 130 °C with 1 MPa oxygen as the sole oxidant. The results of the catalytic activity of the Ba(II) complex are given in Table 2. We set out to examine the catalytic activity of Ba(II) complex catalyst in the aerobic oxidation of benzyl alcohol in different solvent (such as dimethylformamide, acetonitrile, 1,4-dioxane, and tetrahydrofuran) and different reaction times. The conversion of benzyl alcohol and selectivity of benzaldehyde at 130 °C for 6 h in dimethylformamide and acetonitrile are 9%, 11% and 28%, 21%, respectively (Table 2, entries 1 and 2). The conversion of benzyl alcohol and selectivity of benzaldehyde in 1,4-dioxane are 48% and 89% at 130 °C for 6 h, respectively (Table 2, entry 3). The conversion of benzyl alcohol reached 57% for Ba-complex at 130 °C for 7 h (Table 2, entry 4). However, the selectivity of benzaldehyde in 1,4-dioxane at 130 °C for 7 h over Ba(II) complex catalyst was decreased to 17%. It was found that the benzyl alcohol conversions in tetrahydrofuran at 130 °C are 15%, 67%, and 75% within 3 h, 4 h, and 6 h, respectively. Meanwhile, the selectivities of benzaldehyde in tetrahydrofuran at 130 °C are 80%, 53%, and 35% within 3 h, 4 h, and 6 h, respectively (Table 2, entries 5–7). Clearly, when increasing the reaction time, it gave an increase in benzyl alcohol conversion and a decrease in benzaldehyde selectivity. The optimum conditions for the benzyl alcohol oxidation reaction over the Ba(II) complex was 130 °C, 6 h, and using 1,4-dioxane as solvent. In four successive cycles, the conversion of benzyl alcohol was 45%, 40%, 37%, and 32% at 130 °C for 6 h, respectively. In addition, the selectivity of benzaldehyde in 1,4-dioxane is only 4.5% at 130 °C for 6 h, so the Ba(II) complex catalyst shows good catalytic activity.

Table 2. Catalytic performance of the Ba(II) complex in the oxidation of benzyl alcohol.

Entry	Solvent	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)
1	dimethylformamide	130	6	9	28
2	acetonitrile	130	6	11	21
3	1,4-dioxane	130	6	48	89
4	1,4-dioxane	130	7	57	17
5	tetrahydrofuran	130	3	15	80
6	tetrahydrofuran	130	4	67	53
7	tetrahydrofuran	130	6	75	35

3. Experimental Section

3.1. Materials and Instrumentation

Pyridine-2-carboxaldehyde (A. R.), 2-phenylacetic acid hydrazone (A. R.) and $BaCl_2$ (A. R.) were purchased from Shanghai Chemical Reagent Company. Elemental analysis (C, H and N) was performed on an Elementar Vario III EL elemental analyzer (Hanau, Germany). Crystal data of Ba(II) complex was collected on a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA).

3.2. Synthesis of Ba(II) Complex

Pyridine-2-carboxaldehyde (1.0 mmol, 0.1071 g) and 2-phenylacetic acid hydrazone (1.0 mmol, 0.1502 g) were dissolved in 15 mL 95% ethanol solution with stirring. Then 5.0 mL water solution containing $BaCl_2$ (0.5 mmol, 0.1041 g) was added to the above mixture. The reaction mixture was heated at 60 °C for 7 h with stirring and cooled to room temperature. The mixture was filtered, and the block crystals were obtained from filtrate after 40 days. Yield ca. 52%. Anal. Calcd. for $C_{28}H_{26}N_6O_2Cl_2Ba$: C, 48.92; H, 3.79; N, 12.23. Found: C, 48.73; H, 4.07; N, 12.38.

3.3. Crystal Data Collection and Handling

A suitable crystal of Ba(II) complex was selected on a Brucker Smart Apex CCD diffractometer (Bruker, Karlsruhe, Germany) with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at

293(2) K. The structure was solved by direct method using the SHELXL-2014/7 program [28], and refined on F^2 by full-matrix least squares with the OLEX2. refine [29] refinement package using Gauss-Newton minimisation. The data collection and handling for Ba(II) complex are given in Table 3.

Table 3. Data collection and handling for Ba(II) complex.

Empirical Formula	$C_{28}H_{26}N_6O_2Cl_2Ba$
Formula weight	686.78
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.464(3)
b/Å	13.531(3)
c/Å	8.8035(18)
β/°	95.06(3)
Volume/Å^3	1478.9(6)
Z	2
ρ_{calc}mg/mm^3	1.542
μ/mm^{-1}	1.559
S	1.098
F(000)	684
Index ranges	$-16 \leq h \leq 15$, $-17 \leq k \leq 17$, $-11 \leq l \leq 11$
Reflections collected	13,738
Independent reflections	3353 [R(int) = 0.0755]
Data/restraints/parameters	3353/0/178
Goodness-of-fit on F^2	1.098
Final R indexes [I $\geq 2\sigma$ (I)]	R_1 = 0.0455, wR_2 = 0.1079
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1109

3.4. Catalytic Test of Benzyl Alcohol Oxidation

Aerobic oxidation of benzyl alcohol catalyzed by Ba(II) complex was performed in a 10 mL stainless steel autoclave under 1 MPa. In a typical reaction, benzyl alcohol (0.2 mmol, 21.6 mg), solvent (1.5 g), and catalyst (0.060 g) were added into stainless steel autoclave, and then pure O_2 (99.999%) was purged into the stainless steel autoclave. The mixture was kept at 130 °C for 3–7 h at stirring speed of 700 rpm. The mixture was centrifuged to remove the catalyst when the reaction is over. 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). The conversion of benzyl alcohol and the selectivity of products were determined by gas chromatography-massspectrometer equipped with a SE-54 column (GC-1100, 0.25 mm × 0.25 mm × 30 m). The products were identified by comparison with known authentic standards, and anexternal standard method was used for the qualitative analysis.

4. Conclusions

In summary, a novel eight-coordinated Ba(II) complex with pyridine-2-carboxaldehyde-2-phenylacetic acid hydrazone ligand has been synthesized and structural characterized. The optimum conditions for the benzyl alcohol oxidation reaction over the Ba(II) complex catalyst was 130 °C, 6 h, and using 1,4-dioxane as solvent.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4352/7/10/305/s1, Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1568754. 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).

Acknowledgments: This project was supported by the National Natural Science Foundation of China (No. 21171132), the Natural Science Foundation of Shandong (ZR2014BL003), the project of Shandong Province Higher Educational Science and Technology Program (J14LC01) and Science Foundation of Weifang.

Author Contributions: Xi-Shi Tai designed the method and wrote the manuscript; Li-Li Liu tested the catalytic activity of Ba(II) complex and wrote the manuscript; Li-Hua Wang and Peng-Fei Li synthesized the Ba(II) complex and analyzed the crystal data of the Ba(II) complex. Both authors have read and approved the final manuscript.

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

References

1. More, M.S.; Pawal, S.B.; Lolage, S.R.; Chavan, S.S. Syntheses, structural characterization, luminescence and optical strudies of Ni(II) and Zn(II) complexes containing salophen ligand. *J. Mol. Struct.* **2017**, *1128*, 419–427. [CrossRef]
2. Hazari, D.; Jana, S.K.; Puschmann, H.; Zangrando, E.; Dalai, S. Three new Coordination polymers of zinc(II) and cadmium(II) with dicarboxylate and bipyridine ligands: Synthesis, structure and luminescence study. *J. Inorg. Organomet. Polym.* **2015**, *25*, 1151–1159. [CrossRef]
3. Li, T.R.; Shao, Y.L.; Zhang, S.T.; Qin, J.C.; Fan, L.; Liu, L.; Wang, B.D.; Yang, Z.Y.; Wang, Y.H. Two dinuclear Zn(II) complexes for the fluorescent detection of 2,4,6-trinitrophenol. *J. Lumin.* **2017**, *181*, 345–351. [CrossRef]
4. Wang, F.Y.; Xi, Q.Y.; Huang, K.B.; Tang, X.M.; Chen, Z.F.; Liu, Y.C.; Liang, H. Crystal structure, cytotoxicity and action mechanism of Zn(II)/Mn(II) complexes with isoquinoline ligands. *J. Inorg. Biochem.* **2017**, *169*, 23–31. [CrossRef] [PubMed]
5. Nanjundan, N.; Narayanasamy, R.; Butcher, R.J.; Jasinski, J.P.; Velmurugan, K.; Nandhakumar, R.; Balakumaran, M.D.; Kalaichelvan, P.T.; Gnanasoundari, V.G. Synthesis, crystal structure, biomolecular interactions and anticancer properties of Ni(II), Cu(II) and Zn(II) complexes bearing S-allyldithiocarbazate. *Inorg. Chim. Acta* **2017**, *455*, 283–297. [CrossRef]
6. Yang, Q.; Zhang, X.F.; Zhao, J.P.; Hu, B.W.; Bu, X.H. Cobalt(II)-azido coordination polymers with dicarboxylate and di(1H-imidazol-1-yl)methane ligands exhibiting ferromagnetic behaviors. *Cryst. Growth Des.* **2011**, *11*, 2839–2845. [CrossRef]
7. Zeng, Y.F.; Zhao, J.P.; Hu, B.W.; Hu, X.; Liu, F.C.; Ribas, J.; Ribas-Arino, J.; Bu, X.H. Structures with tunable strong ferromagnetic coupling: From unordered (1D) to ordered (discrete). *Chem. Eur. J.* **2007**, *13*, 9924–9930. [CrossRef] [PubMed]
8. Ferko, P.J.; Withers, J.R.; Nguyen, H.; Allison, C.; Ema, J.; Ema, T.; Rath, N.P.; Zhang, Y.Z.; Holmes, S.M. Synthesis and characterization of first row transition metal p-toluenesulfonate complexes and chains. *Polyhedron* **2017**, *123*, 344–352. [CrossRef]
9. Tyagi, P.; Tyagi, M.; Agrawal, S.; Chandra, S.; Ojha, H.; Pathak, M. Synthesis, characterization of 1,2,4-triazole Schiff base derived 3d-metal complexes: Induces cytotoxicity in HepG2, MCF-7 cell line, BSA binding fluorescence and DFT study. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2016**, *171*, 246–257. [CrossRef] [PubMed]
10. Zhang, Y.C. Synthesis, crystal structure, and fluorescent property of a Zn(II) complex with *N*-nicotinoylglycine ligand. *Crystals* **2017**, *7*, 151. [CrossRef]
11. Wang, X.L.; Sha, X.T.; Liu, G.C.; Tian, A.X.; Lin, H.Y. Structural influencing factors on ZnII/CdII coordination polymers based on a "V"-like bis-pyridyl-bis-amide derivative: Construction, fluorescent sensing and photocatalysis properties. *Inorg. Chim. Acta* **2016**, *440*, 94–101. [CrossRef]
12. Tai, X.S.; Wang, X.; Li, P.F. Synthesis, crystal structure and luminescent property of a Cd(II) coordination polymer with a *N*-nicotinoylglycine ligand. *Crystals* **2017**, *7*, 33. [CrossRef]
13. Luo, M.; Li, X.Y.; Chen, W.; Zhang, J.H. The catalytic activity of Zn(II) and Mn(II) organometallic complexes. *Res. Chem. Intermed.* **2013**, *39*, 2715–2721.
14. Wang, X.L.; Wu, X.M.; Liu, G.C.; Li, Q.M.; Lin, H.Y.; Wang, X. Four thiophene-pyridyl-amide-based ZnII/CdII coordination polymers: Assembly, structures, photocatalytic properties and fluorescent recognition for Fe^{3+}. *J. Solid State Chem.* **2017**, *249*, 51–57. [CrossRef]

15. Selvamurugan, S.; Ramachandran, R.; Prakash, G.; Nirmala, M.; Viswanathamurthi, P.; Fujiwara, S.; Endo, A. Ruthenium(II) complexes encompassing 2-oxo-1,2-dihydroquinoline-3-carbaldehyde thiosemicarbazone hybrid ligand: A new versatile potential catalyst for dehydrogenative amide synthesis. *Inorg. Chim. Acta* **2017**, *454*, 46–53. [CrossRef]
16. Sherif, Y.E.; Gouda, M.A.; El-Asmy, A.A. Synthesis, characterization, analgesic and anti-inflammation activity of new phthalazines and their Cu(II) and Zn(II) complexes. *Med. Chem. Res.* **2015**, *24*, 3853–3862. [CrossRef]
17. Tai, X.S.; Wang, X.; You, H.Y. Synthesis, crystal structure and antitumor activity of a new Zn(II) complex based on *N*-acetyl-L-phenylalanine and 1,10-phenanthroline. *Chin. J. Struct. Chem.* **2016**, *35*, 586–590.
18. Sayin, K.; Karakaş, D. Computational investigations of trans-platinum(II) oxime complexes used as anticancer drug. *Spectrochim. Acta Part A* **2018**, *188*, 537–546. [CrossRef] [PubMed]
19. Tai, X.S.; Wang, G.L.; Liu, Y.Y. Synthesis and crystal structure of a Mg(II) complex with 2,6-pyridinecarboxylic acid. *Sci. Study Res. Chem. Chem. Eng. Biotechnol. Food Ind.* **2015**, *16*, 87–91.
20. Tai, X.S.; Zhao, W.W. Synthesis, crystal structure and antitumor activity of Ca(II) coordination polymer based on 1,5-naphthalenedisulfonate. *J. Inorg. Organomet. Polym.* **2013**, *23*, 1354–1357. [CrossRef]
21. Tai, X.S.; Zhao, W.W.; Li, F.H. Synthesis, crystal structure and antitumor activity of Ca(II) coordination polymer constructed by *N*-benzenesulphonyl-L-phenylalanine. *Chin. J. Inorg. Chem.* **2013**, *29*, 2200–2204.
22. Tai, X.S.; Zhao, W.W.; Li, F.H. Synthesis, structural characterization and antitumor activity of a Ca(II)-schiff base complex. *Chin. J. Inorg. Chem.* **2013**, *29*, 1328–1332.
23. Tai, X.S.; Zhao, W.W. Synthesis, spectral characterization, and luminescence properties of a cup-like ligand and its magnesium(II) complex. *Res. Chem. Intermed.* **2014**, *40*, 2075–2082. [CrossRef]
24. Tai, X.S.; Yin, J. Synthesis, crystal structure and antibacterial activity of Mg(II) complex $[Mg(H_2O)_6]\cdot(4\text{-amino-3-methylbenzenesulfonate})_2$. *Crystals* **2015**, *5*, 294–301. [CrossRef]
25. Tai, X.S.; Wang, X. Synthesis and crystal structure of a 1D chained coordination polymer constructed from Ca^{2+} and 2-[(*E*)-(2-furoylhydrazono)methyl]benzenesulfonate. *Crystals* **2015**, *5*, 458–465. [CrossRef]
26. Tai, X.S.; Zhao, W.W. Synthesis, structural characterization, and antitumor activity of a Ca(II) coordination polymer based on 1,6-naphthalenedisulfonate and 4,4′-bipyridyl. *Materials* **2013**, *6*, 3547–3555. [CrossRef] [PubMed]
27. Tai, X.S.; Wang, X. Synthesis, structural characterization and antitumor activity of a Ca(II) coordination polymer based on 4-formyl-1,3-benzenedisulfonate-2-furoic acid hydrazide ligands. *Crystallogr. Rep.* **2017**, *62*, 242–245. [CrossRef]
28. Sheldrick, G.M. *SHELXT*-Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **2015**, *A71*, 3–8. [CrossRef] [PubMed]
29. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *OLEX2*: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. [CrossRef]