Volkson Press

Contents List available at VOLKSON PRESS

New Materials and Intelligent Manufacturing (NMIM)

DOI: http://doi.org/10.26480/icnmim.01.2018.323.325

Journal Homepage: https://topicsonchemeng.org.my/



ISBN: 978-1-948012-12-6

A NEW NICKEL COORDINATION POLYMER CONSTRUCTED FROM 4-[(8-HYDROXY 5-QUINOLINYL) AZO]-BENZENESULFONIC ACID: SYNTHESIS, STRUCTURE AND PROPERTY

Ya-Nan Luo*, Zhi-Chen Liu, Hui-Ying Jiang, Li-Ying Yu, Xiao-Yang Yu*

Jilin Institute of Chemical Technology, Jilin City, Jilin, 132022, P. R. China *Corresponding Author Email: 107850005@qq.com

This is an open access article distributed uder the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

ARTICLE DETAILS

ABSTRACT

Article History:

Received 26 June 2018 Accepted 2 July 2018 Available online 1 August 2018 One new supramolecular compound based on H_2L ($H_2L = 4$ -[(8-hydroxy-5-quinolinyl) azo]-benzenesulfonic acid), {[NiL(en)]• DMF}n (1) (en = ethylenediamine, DMF = N,N-dimethylformamide), has been synthesized by solvothermal technique. Compound 1 exhibits a one-dimensional (1-D) zig-zag chain structure. In addition, it exhibits blue fluorescence at room temperature in the solid state.

KEYWORDS

Crystal structure, Coordination polymer, Solvothermal technique, Supramolecular structure.

1. INTRODUCTION

Over the past decade, supramolecular chemistry of coordination compounds has attracted great interest because of their intriguing architectures and potential applications in molecular recognition, sensors, catalysis and photoelectricity [1-5]. In the construction of these supramolecular materials, judicious selection of multifunctional organic ligands is an effective approach [6-9]. As one of the azo organic ligands, 4-[(8-hydroxy-5-quinolinyl)azo]-benzenesulfonic acid may be an ideal ligand because of its structural features: (i) It shows potential coordination activities because it presents diverse coordination points [10-14]. (ii) It could act as hydrogen bond acceptors or donors to assist in assembling various supramolecular structures, for they can be partly or fully deprotonated to generate various species with different proton numbers. (iii) Benzene rings joints quinoline rings through -N=N- bond, so the two rings not only can rotate around the -N=N- bond, but also lead to π - π stacking interactions to meet different coordination requirements in the assembly process of the compound. (iv) Quinoline ring has stronger chelating ability in combining with metal ions because of the ortho position between hydroxyl and N atom. Based on the above, H2L may be an excellent candidate for constructing the coordination polymers with diverse structures and outstanding fluorescent performance.

Taking inspiration from the afore mentioned points, we solvothermally synthesized one new supramolecular compound, $\{[NiL(en)]\cdot DMF\}_n$ (1), which crystal structure has not been reported. Compound 1 consists of 1-D zig-zag chain structure. The fluorescent property has also been investigated. The results show that compound 1 may have potential application in photoactive material field.

2. EXPERIMENTAL

2.1 Materials

All the starting materials were reagent grade and used as purchased without further purification. Distilled water was used throughout. The ligand H_2L , 4-[(8-hydroxy-5-quinolinyl)azo]-benzenesulfonic acid, was prepared according to the literature method [15].

2.2 Physical measurements

Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 Elemental Analyzer. IR (KBr pellets) spectra were recorded in the 4000–400 cm $^{-1}$ range using a Nicolet Impact 410 FT-IR spectrometer. The thermal behavior was studied by thermogravimetric analyses (TGA) on a Perkin-Elmer TGA 7 thermogravimetric analyzer under N_2 with a heating rate of 10 °C min $^{-1}$. PXRD were collected on a Siemens D5005 diffractometer by using Cu-K α (λ = 1.5418 Å) with a graphite monochromator. The fluorescence measurement was performed on LS55 luminescence spectrometer.

2.3 Preparation of $\{[NiL(en)]\cdot DMF\}_n$ (1)

A mixture of H_2L (10 mg, 0.030 mmol), NiCl₂ (30 mg, 0.23 mmol), H_2O (2 mL), DMF (10 mL) and en (0.03 mL) was dissolved at room temperature. The suspension was put into a Teflon-lined autoclave and kept under autogenous pressure at 130 °C for 72 h. After slow cooling to room temperature, red block crystals were filtered and washed with DMF and dried in air, in about 40 % yield (based on Ni). Anal. calcd. for $C_{20}H_{25}NiN_6O_5S$ (520.22): C 46.15; H 4.80; N 16.15 %; found: C 46.75; H 4.50; N 15.98 %. IR data (KBr pellet, cm⁻¹, Figure 1,), \tilde{v}/cm^{-1} : 3267 (m), 3178 (w), 2933(w), 2876(w), 1658 (s), 1596 (m), 1569(s), 1500(s), 1461 (s), 1403 (s), 1383(s), 1313 (s), 1246 (s), 1177 (s), 775 (m), 696 (s), 647(s), 558 (m), 460 (m).

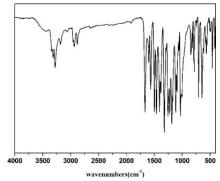


Figure 1: IR curve of compound 1

2.4 Structure determination

Compound 1 was stable under ambient conditions and single crystals were glued on thin glass fibers. Diffraction intensities were collected on Bruker Apex II CCD area-detector diffractometer (Mo Ka, 0.71073 Å). An empirical absorption correction was applied by using the SADABS program. The structure was solved by the direct methods (SHELXS-97) and refined by full matrix least squares [16]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located geometrically by the program OLEX 2 [17]. The final formula was derived from crystallographic data combined with elemental and thermogravimetric analyses data. CCDC-1843548 contains the supplementary crystallographic data for this paper.

3. RESULTS AND DISCUSSION

3.1 Description of the crystal structure of 1

Single-crystal X-ray diffraction analysis reveals that compound ${\bf 1}$ crystallizes in the monoclinic system, space group $P2_1/c$, which exhibits an infinite 1-D zig-zag chain structure. Data collection and structure refinement details are summarized in Table 1.

Table 1: Crystal data collections and structure refinements for compound 1

Compound 1			
Formula	$C_{20}H_{25}N_6NiO_5S$	Space group	P2 ₁ /c
Fw	520.21	Temperature (K)	296(2)
Crystal system	Monoclinic	$V(Å)^3$	2290.09(14)
a (Å)	14.6550(5)	α (º)	90.00
b (Å)	13.3943(5)	β ($^{\circ}$)	101.2370(10)
c (Å)	11.8947(4)	γ (º)	90.00
Z	4	ρ_{calc} (g/m ³)	1.509
F(000)	1080	μ (mm ⁻¹)	0.984
θ range (°)	1.42-25.10	Reflections collected	11429
Independent reflections (R_{int})	4083(0.0138)	GOF	1.712
Final Ra,b	$R_1 = 0.0948$	R indices (all	$R_1 = 0.0986$
indices	$wR_2 = 0.3301$	data)	$wR_2 = 0.3444$
$[I>2\sigma(I)]$			

^{*} $R_1 = \sum ||F_0| - |F_c|| / \sum |F|$. b $wR_2 = |\sum w(|F_0|^2 - |F_c|^2)^2 / \sum |w(F)^2|^{1/2}$

There are one Nickel (II) ions, one L^{2-} ligand, one en molecule and one uncoordinated DMF molecule in the asymmetric unit (Figure 2(a)). Ni1 is five coordinated by two oxygen atoms and three nitrogen atoms. Among them, there are one nitrogen atom N1 and one oxygen atom O1 from the quinolinol group of one L^{2-} ligand, one one oxygen atom O2 $^{\rm I}$ (symmetry code: i, -1+x, y,z) from sulfonate group of another L^{2-} ligand, and two nitrogen atoms (N6 and N7) from one en molecule to form a distorted rectangular pyramid geometry. N1 is the apex of the rectangular pyramid geometry, and O1, O2 $^{\rm I}$, N6 and N7 form a plane (Figure 2(b)). The distances of Ni-O/N [2.311(7) – 2.370(6) Å] are comparable with those found in other related Nickel (II) complexes [18]. Selected bond lengths are listed in Table 2.

Table 2: Bond lengths (Å) and angles (°) of compound 1

	0 ()	0 ()	•
Compound 1			
Bond	Dist.	Bond	Dist.
Ni1-O1	2.311(7)	Ni1-N1	2.350(6)
Ni1-O2 ⁱ	2.370(6)	Ni1-N7	2.361(6)
Ni1-N6	2.339(8)	N2-N3	1.288(9)
Angle	(°)	Angle	(°)
O1-Ni1-N1	70.9(2)	O1-Ni1-N7	102.6(2)
N6-Ni1-N7	75.6(2)	N6-Ni1-O2 ⁱ	78.2(2)
N1-Ni1-O2 ⁱ	94.2(2)		

Symmetry code: i, -1+x, y,z

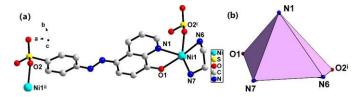


Figure 2: (a) The coordination environment of Ni1; (b) rectangular pyramid geometry in compound 1. (symmetry codes: i, -1+x, y,z; ii, 1+x, y,z. All hydrogen atoms are omitted for clarity).

In compound 1, L^{2-} ligand adopts μ_2 -tridentate mode (Figure 3) with the 8-hydroxyquinoline group displaying bidentate chelating mode and the sulfonate group adopting monodentate coordination mode (Scheme 1). Two neighboring L^{2-} ligands link Ni(II) cations into an infinite 1D zig-zag chain structure with a Ni···Ni distance of 14.655 Å.

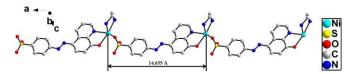
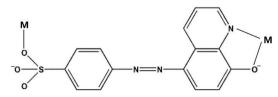


Figure 3: 1-D zig-zag chain structure in compound 1



Scheme 1: The coordination mode of L2- ligand

3.2 Powder X-Ray Diffractions

In order to confirm the structural homogeneity of the bulk power materials, Power X-ray diffraction (PXRD) experiment has been carried out. The PXRD experimental and computer-simulated patterns are in good agreement with each other (Figure 4), indicating phase purity of compound 1.

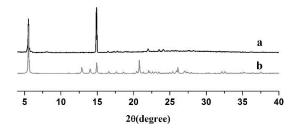


Figure 4: The experimental (a) and simulative (b) powder X-ray diffraction patterns for compound 1

3.3 Thermogravimetric Analysis

In order to gauge the thermal stability of compound 1, TGA was carried out from room temperature to 800 $^{\circ}$ C in flowing N₂ at 10 $^{\circ}$ C min⁻¹ (Figure 5). For compound 1, the weight loss of 13.52% from 248 to 352 $^{\circ}$ C corresponds to the departure of free DMF molecule (calculated value is 13.47%). The second weight loss was observed from 383 to 652 $^{\circ}$ C due to the removal of the ligand and en (expt. 56.64%, calcd. 56.76%). The residua may be NiSO₄ (expt. 30.12%, calcd. 29.79%).

3.4 Fluorescent Property

Taking into account of the excellent fluorescent properties of azo metal coordination polymers, the solid fluorescence at room temperature of compound ${\bf 1}$ was investigated. Compound ${\bf 1}$ exhibits one blue fluorescent emission with maximum at ca. 434 nm upon excitation at 375 nm, comparing with free ligand that the emission band of compound ${\bf 1}$ is slightly shifted. So we can know the fluorescent properties of compound ${\bf 1}$ may be mainly caused by the intraligand electronic transfer, which can be

attributed to the π - π * or n- π * intraligand electronic transitions including the -N=N- based π - π * transition (Figure 6) [19-21].

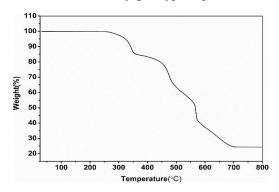


Figure 5: TGA curve of compound 1

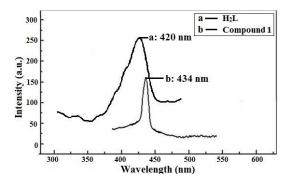


Figure 6: Solid-state fluorescent spectrum of the H_2L (a) and compound 1 (b) at room temperature

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (grant No.20831002, No.21531003), Project of Science and Technology Development of Jilin City (No.20166024).

REFERENCES

- [1] Lu, J., Liu, H.T., Zhang, X.X., Wang, D.Q., Niu, M.J. 2010. Important Roles of Weak Interactions: Syntheses and Supramolecular Structures of Four Coll/Nill-Thiocyanato Compounds. Z. Anorg. Allg. Chem, 636 (3-4), 641–647. doi: org/10.1002/zaac.200900286
- [2] Liu, C.B., Wen, H.L., Gong, Y.N., Liu, X.M., Tan, S.S. 2011. Supramolecular Architectures of Four New Transition Metal Complexes with 3-[4-(Carboxymethoxy) phenyl] propanoic Acid and N-[4-(Carboxymethoxy)phenyl] iminodiacetic Acid. Z. Anorg. Allg. Chem, 637 (1), 122–129. doi: org/10.1002/zaac.201000228
- [3] Huang, C.W., Mohamed, M.G., Zhu, C.Y., Kuo, SW. 2016. Functional Supramolecular Polypeptides Involving π - π Stacking and Strong Hydrogen-Bonding Interactions: A Conformation Study toward Carbon Nanotubes (CNTs) Dispersion. Macromolecules, 49 (15), 5374–5385. doi: 10.1021/acs.macromol.6b01060
- [4] Long, J.R., Bloch, E.D., Britt, D., Lee, C., Donna, C.J., Uribe-Romo, F.J., Furukawa, H., Yaghi, O.M. 2010. Metal Insertion in a Microporous Metal-Organic Framework Lined with 2,2'-Bipyridine. J. Am. Chem. Soc, 132 (41), 14382–14384. doi: 10.1021/ja106935d
- [5] Karthikeyan, A., Zellerb, M., Muthiaha, P.M. 2016. Supramolecular Hydrogen-Bonding Patterns in the Organic-Inorganic Hybrid Compound bis(4-Amino5-Chloro-2,6-Dimethylpyrimidinium) TetrathiocyanatoZinc (II)–4-Amino-5-Chloro-2,6-Dimethylpyrimidine–Water (1/2/2). Acta Cryst, C72, 337–340. doi: org/10.1107/S2053229616004186
- [6] Wu, L., Guo, X.L., Wang, Z.J., Chen, J.X. 2015. Syntheses, Crystal Structure, and Fluorescent Property of a New (4, 10)-Connected 3D Cd (II) Coordination Polymer. Chem. Lett, 44 (4), 451–453. doi: org/10.1246/cl.141146

- [7] Luo, Y.N., Xu, X.Z., Sun, F.X., Yu, X.Y., Zhang, X., Zhang, T., Yu, L.Y. 2014. Synthesis, Structure and Properties of Two New Coordination Polymers Based on 4-[(8-Hydroxy-5-Quinolinyl) azo]-Benzenesulfonic Acid. Chem. Res. Chin. Univ, 30 (1), 27–31. doi: 10.1007/s40242-013-3236-y
- [8] Zhu, X.F., Zhang, H., Zhou, Y.H., Guan, L. 2010. Hydrothermal Synthesis, Crystal Structure, and Magnetic Properties of Two New Coordination Polymers [Ni(IHQS)(4,4'-bipy)0.5(H2O)2]n and [Cu(IHQS)(4,4'-bipy)0.5H2O]n, Z. Anorg. Allg. Chem, 636 (3-4), 457–461. doi: org/10.1002/zaac.200900347
- [9] Wu, T., Xu, H.Y., Kong, F.Z., Yu, Z.Y., Wang, R.H. 2012. Synthesis and Structure of a Mn(II)-Triazolyl Coordination Polymer Consisting of Dinuclear Units. Chin. J. Struct. Chem, 31, 1557–1562.
- [10] Wang, J. J., Gou, L., Hu, H.M., Han, Z.X., Li, D.S., Xue, G.L., Yang, M.L., Shi, Q.Z. 2007. Ligand and pH-Controlled ZnII Bilayer Coordination Polymers Based on Biphenyl-3,3',4,4'-Tetracarboxylate. Cryst. GrowthDes, 7 (8), 1514–1521. doi: 10.1021/cg0703240
- [11] Feng, X., Wang, L.Y., Wang, J.G., Xie, C.Z., Zhao, J.S., Sun, Q. 2010. A Unique Example of a 3D Framework based on the Binuclear Dysprosium (III) Azobenzene-3,5,4'-Tricarboxylate with 3,6-Connected Topology showing Ferromagnetic Properties. Cryst. Eng. Comm., 12, 3476–3482. doi: 10.1039/C0CE00119H
- [12] Gu, X.J., Lu, Z.H., Xu, Q. 2010. High-Connected Mesoporous Metal-Organic Framework. Chem. Commun, 46, 7400–7402. doi: 10.1039/C0CC02808H
- [13] Li, L., Yang, Y.L., Fan, R.Q., Wang, X., Zhang, Q.M., Zhang, L.Y., Yang, B., Cao, W. W., Zhang, W.Z., Wang, Y.Z., Ma, L.Q. 2014. Photocurrent enhanced Dye-Sensitized Solar Cells based on TiO2 loaded K6SiW11039Co(II)(H2O)·xH2O Photoanode Materials. Dalton Trans, 43, 1577–1582. doi: 10.1039/C3DT52201F
- [14] Zhang, L.L., Lu, C.Y., Chen, S.P., Yu, F.S., Li, X., Tan, J.T., Yang, X.W. 2011. Synthesis, Structure and Properties of Novel 3-D Porous Lanthanide-3, 4′, 5-Azobenzenetricarboxylate Frameworks. Inorg. Chem. Commun, 14 (1), 143–145. doi: org/10.1016/j.inoche.2010.10.007
- [15] Prabhakaran, A., Raj, J.N. 2018. Mapping and analysis of tectonic lineaments of Pachamalai hills, Tamil Nadu, India using geospatial technology. Geology, Ecology, and Landscapes, 2 (2), 81-103. doi: org/10.1080/24749508.2018.1452481
- [16] Sheldrick, G.M. 1998. SHELXTL V. 5.10. Structure determination software suite. Bruker AXS, Madison
- [17] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., Puschmann, H. 2009. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. Appl. Cryst, 42, 339–341. doi: org/10.1107/S0021889808042726
- [18] Amin, H., Arain, B.A., Abbasi, M.S., Jahangir, T.M., Amin, F. 2018. Comparative study of Zn-phytoextraction potential in guar (Cyamopsis tetragonoloba L.) and sesame (Sesamum indicum L.): tolerance and accumulation. Geology, Ecology, and Landscapes, 2 (1), 29-38.
- [19] Yu, X.Y., Cui, X.B., Zhang, X., Jin, L., Luo, Y.N., Yang, J.J., Zhang, H., Zhao, X. 2011. A novel 3D Cadmium Coordination Polymer Constructed from Hydrazine and Benzene-1,2,4,5-Tetracarboxylic Acid: Synthesis, Structure and Fluorescent Property. Inorg. Chem. Commun, 14 (6), 848–851. doi: 10.1016/j.inoche.2011.03.005
- [20] Lan, A.J., Padmanabhan, M., Li, K.H., Wu, H.H., Emge, T.J., Hong, M.C., Li, J. 2011. Two-Dimensional Coordination Polymers of Zn(II) and Cd(II) Derived from 3,3',5,5'-Azobenzenetetracarboxylic Acid Exhibiting Solvent Facilitated Structure Reversibility. Inorg. Chim. Acta, 366 (1), 68–75. doi: org/10.1016/j.ica.2010.10.009
- [21] Wei, K.J., Xie, Y.S., Ni, J., Zhang, M., Liu, Q.L. 2006. Syntheses, Crystal Structures, and Photoluminescent Properties of a Series of M(II) Coordination Polymers Containing M–X2–M Bridges: From 1-D Chains to 2-D Networks. Cryst. Growth Des, 6 (6), 1341–1350. doi: 10.1021/cg0505822

