Tai Xi-Shi*, Meng Qing-Guo, Liu Li-Li

Synthesis, Crystal Structure and Spectroscopic Analysis of a New Sodium Coordination Polymer

DOI 10.1515/chem-2016-0031
received September 31, 2016; accepted November 17, 2016.

Abstract: A new sodium coordination polymer, [Na₂(L)(H₂O)]₄ₙ (1), was synthesized by reflux reaction of p-aminobenzene sulfonic acid, p-hydroxy benzaldehyde and NaOH in ethanol/water solution and characterized by elemental analysis, UV-vis, IR and X-ray single crystal diffraction analysis. The crystal of 1 belongs to monoclinic, space group P2₁/c with a = 17.765(4) Å, b = 10.181(2) Å, c = 8.0450(16) Å, β = 91.67(3)°, V = 1454.5(5) Å³, Z = 4, Dc = 1.531 mg·m⁻³, μ = 0.28 mm⁻¹, F(000) = 696, and final R₁ = 0.0327, ωR₂ = 0.0854. The molecules of 1 are extended to a 2D layer structure along ab plane. The 2D layers form a 3D framework structure by the interaction of π-π stacking and hydrogen-bond interaction.

Keywords: p-Aminobenzene sulfonic acid, p-hydroxy benzaldehyde, synthesis, crystal structure, spectroscopic analysis

1 Introduction

In recent years, design and synthesis of novel coordination polymers have received much more attention than ever before [1-7]. The coordination polymers have potential applications in many aspects, such as gas storage, fluorescent, catalysis, separation, biological activity and so on [8-11]. Many coordination polymers with various structures and properties have been synthesized and reported [12-15]. Metal ions and ligands play an important role in the construction of coordination polymers. As an important kind of ligand, aromatic sulfonic acid derivatives have been extensively used in the synthesis of coordination polymer materials due to their various coordination modes and thermal stability [16-18].

In this paper, a new sodium coordination polymer, [Na₂(L)(H₂O)]₄ₙ (1), has been synthesized with p-aminobenzene sulfonic acid, p-hydroxy benzaldehyde and NaOH as raw material. Furthermore, the sodium coordination polymer has also been characterized by elemental analysis, IR spectrum, UV-vis spectrum, and single crystal X-ray crystallography.

2 Experimental Section

2.1 Materials and Instrumentation

p-Aminobenzene sulfonic acid, 4-benzoylbenzoic acid, NaOH and solvents were purchased commercially and used without further purification. The IR spectrum was recorded in the range 4000–400 cm⁻¹ on an infrared spectrophotometer (Beijing Purkinje General Instrument, Beijing, MA, China). UV-vis spectrum was obtained from UV-visible spectrophotometer (Beijing Purkinje General Instrument, Beijing, MA, China). Single crystal data of the sodium coordination polymer were collected by a Bruker smart CCD diffractometer (Bruker, Billerica, MA, USA).

2.2 Synthesis of [Na₂(L)(H₂O)]₄ₙ (1)

A mixture of p-aminobenzene sulfonic acid (173 mg, 1.0 mmol), 4-benzoylbenzoic acid (150 mg, 1.0 mmol), and NaOH (40 mg, 1.0 mmol) were dissolved in 15 mL mixed solvents of H₂O:CH₃CH₂OH (v:v = 1:2). The mixture was stirred for 6 h at 60 °C, and then colorless crystals were collected and dried in the air.

2.3 Crystal Structure Determination

A colorless single crystal of sodium coordination polymer 1 with dimensions of 0.21 mm × 0.18 mm × 0.17 mm was selected and mounted on a glass fiber for data collection. The X-ray diffraction data were measured at 293(2) K.
on a Bruker Smart CCD diffractometer with a graphite-monochromatized MoKα (λ = 0.71073 Å) radiation. The structure was solved by direct methods with SHELXL-97 [19] and refined on $F^2$ by full-matrix least-squares procedures with SHELXTL-97 [20]. The crystal data of 1 are given in Table 1.

### 3 Results and Discussion

#### 3.1 Elemental Analysis

Anal. Calcd. (%) for C$_{13}$H$_8$NaO$_6$S: C, 46.53; H, 4.18; N, 4.18. Found (%): C, 46.72; H, 4.46; N, 4.28. The result of elemental analysis shows that the symmetric unit of Na(I) coordination polymer conforms to 1:1 metal-to-ligand stoichiometry.

#### 3.2 Description of 1

The result of X-ray diffraction reveals that the sodium coordination polymer 1 crystallizes in monoclinic $P2_1/c$ space group. The coordination environment of sodium ion of 1 is shown in Figure 1. The connection mode of sodium ion is shown in Figure 2. Figure 3 is the 2D layer of sodium coordination polymer 1 along $bc$ plane. Figure 4 is the 3D network structure of the sodium coordination polymer 1. From Figure 1, the asymmetrical unit contains one sodium ion, two new ligands and four coordinated H$_2$O molecules. In 1, sodium ion is six-coordination and resides in a octahedral environment defined by three oxygen atoms (O$_2$, O$_4$) from two new ligands, and other four oxygen atoms (O$_{1W}$, O$_{1WA}$, O$_{2W}$, O$_{2WA}$) from four coordinated H$_2$O molecules, and two coordinated H$_2$O (O$_{1W}$, O$_{1WA}$) were shared with another sodium ion (Na1b), the remaining oxygen atoms (O$_{2W}$, O$_{2WA}$) were shared with other two sodium ions (Na1c, Na1d), respectively. Four oxygen atoms (O$_2W$, O$_2WA$, O$_{1W}$, O$_2$) are at the equatorial plane of this octahedral, and the rest two oxygen atoms (O$_{1W}$, O$_{4}$) are at the axle of the octahedral, the angle O$_4$-Na1-01W is 164.313(54)°. The sodium ions in 1 are linked with the neighboring sodium ions through the bridging effect of oxygen atoms, and forming four-member rings and six-member rings (Figure 2). The sodium coordination polymer 1 is extended to a 2D layer structure along the $ab$ plane (Figure 3). The 2D layers form 3D framework structure by the interaction of π-π stacking and hydrogen-bond interaction. The oxygen atom of phenolic hydroxyl does not coordinate to Na(I), but phenolic hydroxyl group plays an important role in the stability of the structure by hydrogen bonds (Figure 5). The main bond lengths (Å) and angles (°) for 1 are given in Table 2.

#### 3.3 IR Spectrum

Figure 6 shows the IR spectrum of the sodium coordination polymer. From Fig.6, it can be seen that the asymmetrical stretching vibration of C=H in methylene and O-H stretching of inner hydroxyl groups are at 2902 cm$^{-1}$ and 3442 cm$^{-1}$, respectively, indicating that the coordination polymer contains water molecules. The asymmetrical stretching of C=C in benzene is at 1493 cm$^{-1}$, the symmetrical stretching

| Table 1: Crystal data for 1. |
|-----------------------------|
| Empirical Formula | C$_{13}$H$_8$NaO$_6$S |
| Formula weight | 335.3 |
| Temperature/K | 293(2) |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$/Å | 17.765(4) |
| $b$/Å | 10.181(2) |
| $c$/Å | 8.0450(16) |
| $β$/° | 91.67(3) |
| Volume/Å$^3$ | 1454.5(5) |
| Z | 4 |
| $ρ_{me}$ mg/mm$^3$ | 1.531 |
| $μ$/mm$^{-1}$ | 0.28 |
| $S$ | 1.02 |
| $F$(000) | 696 |
| Index ranges | $-21≤h≤21$ |
| | $-12≤k≤12$ |
| | $-9≤l≤9$ |
| Reflections collected | 10736 |
| Reflections with $h>2σ(h)$ | 2561 |
| Independent reflections | 2257 | R(int) = 0.034 |
| Data/restraints/parameters | 2561/5/199 |
| Goodness-of-fit on $R^2$ | 1.022 |
| Final $R$ indexes [≤2σ($I$)] | $R_1 = 0.0327$, w$R_2 = 0.0854$ |
| Final $R$ indexes [all data] | $R_1 = 0.0367$, w$R_2 = 0.0893$ |
| Largest diff. peak/hole/e Å$^{-3}$ | 0.36/−0.23 |
vibration of C-N and symmetrical deformation vibration of N-H in secondary amine are at 1230 cm\(^{-1}\) and 1567 cm\(^{-1}\), respectively. The symmetrical stretching vibration and asymmetrical stretching vibration of sulfonate are at 1041 cm\(^{-1}\) and 1156 cm\(^{-1}\)[21, 22]. The stretching vibration of C-O in phenol is at 1243 cm\(^{-1}\).
Table 2: Selected bond lengths (Å) and angles (°) for 1.

| Bond      | Distance  | Bond      | Distance  |
|-----------|-----------|-----------|-----------|
| N1—C7     | 1.268 (3) | O1W—Na1   | 2.3850 (15) |
| N1—C8     | 1.418 (2) | O1W—Na1   | 2.5705 (16) |
| S1—O2     | 1.4496 (13)| O2—Na1    | 2.3981 (15) |
| S1—O4     | 1.4505 (13)| O4—Na1    | 2.4196 (14) |
| S1—O3     | 1.4611 (13)| Na1—O1W   | 2.3850 (15) |
| S1—C11    | 1.7704 (17)| Na1—O4    | 2.4196 (14) |
| O1—C1     | 1.368 (2) | Na1—O2W   | 2.4700 (15) |

| Bond      | Angle      | Bond      | Angle      |
|-----------|------------|-----------|------------|
| Na1—O1W—Na1 | 98.40 (5) | O1W—Na1—O2 | 85.81 (5) |
| Na1—O1W—H1WB | 122.4   | O1W—Na1—O4     | 109.13 (6) |
| Na1—O1W—H1WB | 102.1   | O2—Na1—O4     | 108.14 (5) |
| Na1—O1W—H1WA | 108.1   | O1W—Na1—O2W   | 164.82 (6) |
| Na1—O1W—H1WA | 118.3  | O2—Na1—O2W    | 164.82 (6) |
| Na1—O2W—Na1  | 123.00 (6)| O4—Na1—O2W   | 85.69 (5)  |
| Na1—O2W—H2WB | 109.6   | O1W—Na1—O2W   | 76.74 (5)  |
| Na1—O2W—H2WB | 104.6  | O2—Na1—O2W    | 159.74 (5) |
| Na1—O2W—H2WA | 104.6   | O4—Na1—O2W    | 87.51 (5)  |
| Na1—O2W—H2WA | 107.1  | O2W—Na1—O2W   | 108.08 (5) |
| O2W—Na1—O1W  | 84.59 (5)| O1W—Na1—O1W   | 81.60 (5)  |
| O2W—Na1—O1W  | 83.84 (5)| O2—Na1—O1W    | 83.51 (5)  |
| S1—O4—Na1  | 144.73 (8)| O4—Na1—O1W    | 164.31 (5) |

Symmetry codes: (i) −x, −y+1, −z+1; (ii) x, −y+3/2, z+1/2; (iii) x, −y+3/2, z−1/2.

3.4 UV-vis Spectrum

Figure 7 is the UV-vis spectrum of the sodium coordination polymer. The absorption spectrum shows that the maximum absorption peak of the sodium coordination polymer was located at 312 nm, which can be assigned to intraligand π-π* transitions [23].

4 Conclusions

In this paper, a new sodium coordination polymer was synthesized by p-aminobenzene sulfonic acid and p-hydroxy benzaldehyde. And it was characterized by elemental analysis, IR, UV-vis and X-ray single-crystal diffraction. The results showed that the sodium...
coordination polymer is extended to a 2D layer structure along ab plane. The 2D layers form 3D framework structure by the interaction of π-π stacking and hydrogen-bond interaction.

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

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 1482473. 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).

References

[1] Norbert S., Shyam B., Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites, Chem. Rev., 2012, 112, 933-969.
[2] Pramanik S., Zheng C., Zhang X., Emge T.J., Li J., New microporous metal-organic framework demonstrating unique selectivity for detection of high explosives and aromatic compounds, J. Am. Chem. Soc., 2011, 133, 4153-4155.
[3] Tanabe K.K., Cohen S.M., Postsynthetic modification of metal-organic frameworks— a progress report, Chem. Soc. Rev., 2011, 40, 498-519.
[4] Yang P.P., Wang X.L., Li L.C., Liao D.Z., Synthesis, structure and magnetic properties of a novel family of heterometallic nonnuclear NaI,MnII,LnIII (Ln = Eu, Gd, Tb, Dy) complexes, Dalton Trans., 2011, 40, 4155-4161.
[5] Zheng S.T., Zhang J., Li X.X., Fang W.H., Yang G.Y., Cubic polyoxometalate-organic molecular cage, J. Am. Chem. Soc., 2010, 132, 15102-15103.
[6] Wang X.Y., Zhang Y.N., Li D., Synthesis, structure and characterization of a new iron coordination polymer: [FeL (trans-1,4-chdc)]n, Chinese J. Struct. Chem., 2012, 31, 1589-1593.
[7] Tai X.S., Zhao W.H., Synthesis, crystal structure and antitumor activity of Ca(II) coordination polymer based on 1,5-naphthalenedisulfonate, J. Inorg. Organomet. Polym., 2013, 23, 1354-1357.
[8] Aboshyan-Sorgho L., Besnard C., Pattison P., Kittilstved K.R., Aebischer A., et al., Near-infra-red-visible light up conversion in a molecular trinuclear d-f-d complex, Angew. Chem. Int. Edit., 2011, 50, 4108-4112.
[9] Zhao X.Q., Cui P., Zhao B., Shi W., Cheng P., Investigation on structures, luminescent and magnetic properties of Ln(III)-M (M = Fe(H5)(O), Co(II)) coordination polymers, Dalton Trans., 2011, 40, 805-819.
[10] Tai X.S., Zhao W.H., 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.
[11] Freitas M.C.R., António J.M.S., Ziolli R.L., Yoshida M.I., Rey N.A., et al., Synthesis and structural characterization of a zinc(II) complex of the mycobactericidal drug isoniazid-toxicity against Artemia salina, Polyhedron, 2011, 30, 1922–1926.
[12] Xu Y.H., Jin S.B., Xu H., Nagai A., Jiang D.L., Conjugated microporous polymers: design, synthesis and application, Chem. Soc. Rev., 2013, 42, 8012-8031.
[13] Wang J., Zhao X.Q., Recent advances of lanthanide-transition heterometallic coordination polymers, Chinese J. Struct. Chem., 2014, 33, 7-18.
[14] Adrian A., Garikoitz B., Oscar C., Antonio L., Sonia P.Y., et al., Aerogels of 1D coordination polymers: from a non-porous metal-organic crystal structure to a highly porous material, Polymers, 2016, 8, 12.
[15] Tai X.S., You H.Y., A new 1D chained coordination polymer: synthesis, crystal structure, antitumor activity and luminescent property, Crystals, 2015, 5, 608-616.
[16] Fang X.Q., Chen P.G., Zhu Z.B., Deng Z.P., Gao S.H., Synthesis, crystal structure and properties of 1D manganese(II) coordination polymer, Chinese J. Inorg. Chem., 2011, 27, 1733-1737.
[17] Qian B.H., Ma W.X., Lu L.D., Yang X.J., Wang X., Synthesis, characterization, crystal structure and quantum chemistry calculation of an arenedisulfonate bridged Zn(II) coordination polymer, Acta Physico-Chimica Sinica, 2010, 26, 610-616.
[18] Tai X.S., Wang X., Synthesis, characterization and antitumor activity of a Ca(II) coordination polymer based on 3-amino-2-pyrazinecarboxylic acid, Sci. Study & Res. Chem. & Chem. Eng., Biotech., Food Indus., 2015, 16, 253-259.
[19] Sheldrick G.M., SHELXL-97, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1997.
[20] Sheldrick G.M., SHELXTL-97, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.
[21] Yang X., Chen P., An electrochemical investigation of p-sulfophenylazo calixarene in a buffer solution, J. Electrochem., 2016, 22, 37-42.
[22] Xu Y.T., Preparation, stability and in vitro antioxidant activity of pigment from chirocephalus diaphanous eggshell, Food Sci., 2016, 37, 94-101.
[23] Liu S.G., Chen Z.L., Su W.Y., Pan R.K., Shi X.B., Synthesis, crystal structure and luminescent properties of iridium(III) complex based on 2,6-bis(1-phenylbenzimidazol-2-yl)pyridine, Chinese J. Inorg. Chem., 2013, 29, 403-408.