Synthesis, Crystal Structure of a New Na (I) Complex with 4-Benzoylbenzoic Acid-*p*-Aminobenzene Sulfonic Acid

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Abstract. A novel sodium complex, [NaL·$(H_2O)_2$]n, was synthesized by reflux reaction of *p*-amino benzene sulfonic acid, 4-benzoylbenzoic acid and NaOH in ethanol /water solution and structurally characterized by elemental analysis, IR spectrum and X-ray single crystal diffraction analysis. The crystal of the complex belongs to monoclinic, space group $P2_1/c$ with a = 19.403(4) Å, b =8.0083(16) Å, c = 10.532(2) Å, β = 103.22(3) º, V = 1593.15(60) Å^3, Z = 4, Dc = 1.621 mg·m^{-3}, μ = 1.590 mm^{-1}, F (000) = 1576, and final R_1 = 0.1204, ωR_2 = 0.2951. The complex molecules form a 1D chain structure by the new ligand. The 1D chains generate a 2D layer structur through the intermolecular hydrogen bonds and the connection of sodium ions. And the 2D layers form 3D supramolecular architecture structure by the hydrogen-bond interaction.

1. Introduction

The design and synthesis of coordination polymer materials are an attractive area of researches due to their tremendous potential applications in nonlinear optics, catalysis, gas absorption, luminescence, magnetism and so on [1-3]. In recent years, many reports on sodium ion coordination polymer derivatives have been reported such as the sodium complex with 18-crown-6-sodium ligand [4], *p*-amino benzene sulfonic acid ligand [5], 5-aminonaphthalene sulfonic acid ligand, 1, 10-phenanthroline monohydrate ligand [6], 2-formylbenzenesulfonic acid ligand and thiosemicarbazide ligand [7] and so on.

In my paper, I incorporate *p*-amino benzene sulfonic acid and 4-benzoylbenzoic acid to produce a new ligand. A sodium coordination polymer of this ligand has been obtained and characterized by elemental analysis, IR, uv-vis and X-ray single crystal diffraction analysis.

2. Experimental Section

2.1. Materials and Instrumentation

P-Aminobenzene sulfonic acid, 4-benzoylbenzoic acid, NaOH and solvents were analytical grade. The IR spectrum was recorded in the range 4000–400 cm^{-1} on an Infrared Spectrophotometer. Elemental analysis for carbon, hydrogen and nitrogen was performed on the Elementar Vario EL III elemental analyzer. Single crystal data of [NaL· $(H_2O)_2$] n were collected by a Bruker Smart CCD diffract meter.

2.2. Synthesis of [NaL (H_2O)$_2$] n (1)

A mixture of *p*-amino benzene 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 H_2O: CH_3CH_2OH (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. Data Collection, Structural Determination, and Refinement

A colorless single crystal of sodium complex with dimensions of 0.21 mm × 0.20 mm × 0.19 mm was selected for data collection. The X-ray diffraction data were measured at 293(2) K on a Bruker Smart CCD diffract meter with a graphite-monochromatized MoKα (λ = 0.71073 Å) radiation. The structure was solved by direct methods with SHELXL-97 [8] and refined on F2 by full-matrix least-squares procedures with SHELXTL-97 [8]. The non-hydrogen atoms were located refined anisotropic ally, and hydrogen atoms were added according to heoretical models. Summary of crystal result for sodium complex are shown in Table 1.

Table 1. Summary of crystal result for Na (I) complex.

Empirical Formula	$C_{14}H_{14}NNaO_7S$
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/C$
a/Å	19.403(4)
b/Å	8.0083(16)
c/Å	10.532(2)
β/°	103.22(3)
Volume/Å^3	1593.1(6)
Z	4
ρ_{calc} mg/mm^3	1.515
μ/mm^{-1}	0.27
S	1.08
F (000)	752
Index ranges	−23≤ h ≤ 23 −9 ≤ k ≤ 9 12≤ l ≤ 12
Reflections collected	11589
Reflections with *I*> 2σ(*I*)	2182
Independent reflections	2761 [R(int) = 0.075]
Data/restraints/parameters	2761/0/411
Goodness-of-fit on F^2	1.079
Final *R* indexes [≥2σ (*I*)]	R_1 = 0.1204, wR_2=0.2871
Final *R* indexes [all data]	R_1= 0.1425, wR_2= 0.2951
Largest diff. peak/hole/e Å^{-3}	0.74/−0.61

3. Results and Discussion

3.1. Elemental Analysis

The data of elemental analysis for C14H14NNaO7S are as following: Anal. Calcd: C, 46.24%; H, 3.85%; N, 3.85%. Found: C, 45.96%; H, 4.15%; N, 4.06%. The result shows that the symmetric unit of Na (I) coordination polymer is [NaL· (H_2O)$_2$] n.

3.2. Structural Description of [NaL (H_2O)$_2$] n

The result of X-ray diffraction reveals that the complex **1** crystallizes in the monoclinic space group $P2_1/c$. As shown in Figure 1, each molecule consists of one sodium ion, one new ligand, and two coordination water. As far as Na ion is concerned, it exhibits a octahedron coordination geometry, being coordinated by each of the three oxygen atoms of the new ligands with the Na–O distances are 2.394(5) Å, 2.396 (5) Å and 2.472 (5) Å, respectively, and three oxygen atoms from the coordinated H_2O molecules with the Na-O distances are 2.458 (5) Å, 2.526 (6) Å and 2.526 (6) Å. The Na-O mena bond distance of the new ligands (Na-O3 2.394 (5) Å, Na-O4 2.396 (5) Å, Na-O5 2.472(5) Å) is shorter than the Na-O distance of coordination water (Na-O1w 2.458 (5) Å, Na-O2w 2.526 (6) Å, Na-O2w 2.526 (6) Å), suggesting a slightly disorder octahedron coordination. With the crystal structure of the complex, hydrogen-bonding interactions play an important role in forming unique framework without π-π stacking. The carbon atom interacts with coordinated oxygen atom of the ligand to form a weak intra molecular hydrogen bond C3-H3A…O1, which enhances the stability of the complex. In an axis, neighboring two asymmetric units are bridged by the new ligand to form a 1D chain structure (Figure 2a). And the 1D china are combined through the intermolecular hydrogen bonds and the connected of sodium ions to generate a 2D layer (Figure 2b) in *ab* plane. And the 2D layer forms to a 3D supramolecular architecture structure by the hydrogen-bond interaction. In addition, the sodium ion Na1a linked with the neighboring sodium ion Na1b through the oxygen atoms (O2w) of coordination water molecules, Na1a, Na1b linked with Na1c by two sulfonic acid group of the new ligands, and an element ring is formed. All sodium ions in the complex are connected by this method, and the complex is extended to a 2D net structure in *bc* plane. The main bond lengths (Å) and angles (º) for **1** are given in Table 2.

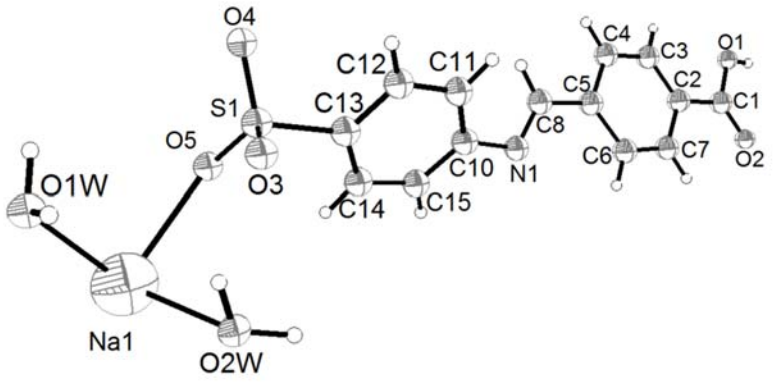

Figure 1. Asymmetric unit of the Na (I) complex with labeling scheme at 30% ellipsoidal probability.

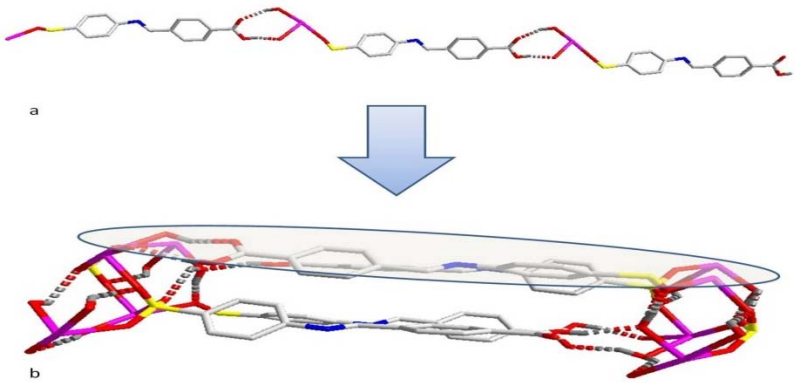

Figure 2. 1D chain (a) and 2D layer structure (b) of Na (I) complex

Table 2. Selected bond lengths (Å) and angles (º) for Na (I) complex

Bond	Distance	Band	Distance
Na1-O5^{iii}	2.472 (5)	Na1-O4^{ii}	2.396 (5)
Na1-O2W^{i}	2.526 (6)		
Angle	°	Angle	°
O4^{ii}-Na1-O5^{iii}	85.96 (16)	O2W-Na1-O3	99.00 (18)
O1W-Na1-O5^{iii}	83.96 (16)	O2W-Na1-O4^{ii}	110.47 (18)
O2W-Na1-O2W^{i}	81.39 (19)	O3-Na1-O4^{ii}	88.53 (17)
O3-Na1-O2W^{i}	170.82 (18)	O2W-Na1-O1W	82.79 (17)
O4^{ii}-Na1-O2W^{i}	99.96 (17)	O3-Na1-O1W	77.70 (15)
O1W-Na1-O2W^{i}	93.29 (17)	O4^{ii}-Na1-O1W	162.41 (18)
O3-Na1-Na1^{i}	140.45 (16)		

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

3.3. IR Spectrum

The IR spectrum of Na(I) complex shows that asymmetrical stretching vibration of C-H in methylene at 2851 cm^{-1}, O-H stretching of inner hydroxyl groups at 3439 cm^{-1}, inciting that the coordination polymer contains water molecules. The asymmetrical stretching of C=C in benzene at 1614 cm^{-1}, symmetrical stretching vibration of C-N and symmetrical deformation vibration of N-H in secondary amine at 1223 cm^{-1}, 1552 cm^{-1}, respectively. Symmetrical stretching vibration and asymmetrical stretching vibration of suffocate are at 1032 cm^{-1} and 1184 cm^{-1}. The above results demonstrate that the Na (I) complex has been obtained.

4. Conclusion

In this study, we have successfully synthesized and structurally characterized a sodium ion complex [NaL $(H_2O)_2$] n. The complex molecules form a 1D chain structure by the new ligand. The 1D chains generate a 2D layer structur through the intermolecular hydrogen bonds and the connection of sodium ions. And the 2D layers form 3D supramolecular architecture structure by the hydrogen-bond interaction.

Acknowledgments

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References

[1] J.R. Long, O.M. Yaghi, The pervasive chemistry of metal-organic frameworks, Chem. Soc. Rev. 38 (2009) 1213 - 1214.
[2] K. Liu, W. Shi, The coordination chemistry of Zn (II), Cd (II) and Hg (II) complexes with 1, 2, 4-triazole derivatives, Dalton Trans. 40 (2011)74 - 122.
[3] H.C. Zhou, S. Kitagawa, Metal-Organic Frameworks, Chem. Soc. Rev. 43 (2014) 5415 - 5418.
[4] T. Mihelj, V. Tomasic, N. Biliskov, 18-Crown-6-sodium cholate complex: thermochemistry, structure, and stability, Langmuir 30 (2014) 6274 - 6285.
[5] M.L. Huang, P. Ma, Synthesis and characterization of crystal structure of two-dimensional layer coordination polymer: [Na $(C_6H_6NSO_3)$ $(H_2O)_2$]$_n$, Chinese J. Spectro. Lab. 28 (2011) 2272 - 2275.
[6] Y.M. Chen, Q.F. Xie, Synthesis, crystal structure and characterization of a cyclic dinuclear sodium complex [Na (H_2O) (μ_2-Ans) (Phen)$_2$], J. Synth. Ctyst. 42 (2013) 2449 - 2454.
[7] Z.B. Zhao, X.S. Tai, Y.T. Chen, Synthesis and characterization of crystal structure of a new three-dimensional network coordination polymer, Chem. Reagents 32 (2010) 588 - 590.
[8] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. A64 (2008) 112 - 122.