

Study on novel structure of tris-(4,4'-dimethyl-2,2'-dipyridyl) Nickel salicylic acid boric acid, $\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_2)_3 \bullet (\text{C}_7\text{H}_5\text{O}_3)_2 \bullet (\text{H}_3\text{BO}_3)$

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Abstract. A novel complex $\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_2)_3 \bullet (\text{C}_7\text{H}_5\text{O}_3)_2 \bullet (\text{H}_3\text{BO}_3)$ has been synthesized from a hydrothermal reaction and the crystal structure has been determined by means of single-crystal X-ray diffraction. Triclinic, P-1. $a = 12.5380(13) \text{ \AA}$, $b = 13.0100(15) \text{ \AA}$, $c = 15.1490(18) \text{ \AA}$, $\alpha = 102.760(3)^\circ$, $\beta = 94.480(2)^\circ$, $\gamma = 94.540(2)^\circ$. $V = 2390.9(5) \text{ \AA}^3$. $Z = 2$. $R_1 = 0.0661$, $wR_2 = 0.2128$, $T = 293(2) \text{ K}$. The Ni atom is coordinated by six N atoms from three 4,4'-dimethyl-2,2'-dipyridyl molecular. The molecular structure stabilized by the O-H...O hydrogen-bonding interactions.

1 Introduction

Metal-organic compounds become research hotspots and have the advantages in building porous materials [1, 2]. Many coordination polymers were investigated using rigid rod-like N-donor bridging ligands (bipyridine class) [3,4]. Metal-organic coordination polymers had excellent properties of magnetism, photoluminescence, conductivity, catalysis and adsorption [5,6]. It is very important for multifunctional ligands selecting in development of metal-organic coordination polymers [7,8]. Han Xiao et al [9] synthesized two transition metal compounds (Co, Ni cation) using 3,3'-(p-phenylene-3,5-diyl) dibenzoic acid ligand and discussed the magnetic properties, catalytic activity and the UV-Vis absorption spectra. Lv Muxuan et al [10] synthesized three Cu cation compounds using 1-(3-ethylpyrazin-2-yl)ethylidene-4-methylthiosemicarbazide ligand and analyzed the interactions of the compounds with DNA. Li Yu et al [11] developed cobalt coordination polymer $\{[\text{Co}(\mu_3\text{-4}((\text{carboxymethyl})\text{thio})\text{benzoic acid})(4,4'\text{-bipyridine})] \cdot \text{H}_2\text{O}\}_n$ and manganese polymer $\{[\text{Mn}(\mu\text{-4}((\text{carboxymethyl})\text{thio})\text{benzoic acid})(4,4'\text{-bipyridine})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ by hydrothermal synthesis method, while the photocatalytic properties and structure of them were investigated. In this paper, the tris-(4,4'-dimethyl-2,2'-dipyridyl) Nickel salicylic acid boric acid is reported.

2 Experimental

All commercially obtained reagent-grade chemicals were used without further purification. A mixture of NiCl_2 (0.1

mmol, 0.014g), 4,4'-dimethyl-2,2'-dipyridyl (0.01 mmol, 0.002g), salicylic acid (0.1 mmol, 0.014g) and boric acid (0.2 mmol, 0.012g) were added into 10 mL water with 10%(v/v) ethanol and heated for 8h at 404K. The solution was obtained by filtration after cooling the reaction to room temperature. Red block single crystals were obtained (a few weeks). The dimensions (0.34 x 0.33 x 0.30 mm) was selected for X-ray determination.

3 Results and discussions

The title crystal structure (Fig.1) is built up of tris-(4,4'-dimethyl-2,2'-dipyridyl) Ni cation, salicylic acid anion and boric acid molecular. The crystal data and structure refinement is shown in Table 1. The Ni atom is coordinated by six N atoms from three 4,4'-dimethyl-2,2'-dipyridyl molecular. The distance d (Ni-N) are in the range of 2.066-2.101 Å. The angles of N-Ni-N are in the range of 78.26-172.66°. Selected bond lengths and bond angles are shown in Table 2.

The crystal packing is stabilized by O-H...O hydrogen bonding interaction.

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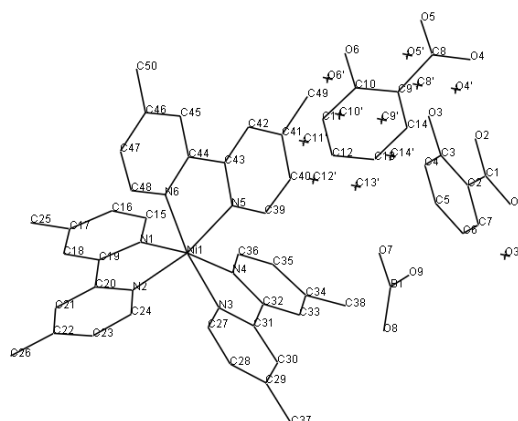


Fig.1 The molecular structure of $C_{50}H_{49}BN_6NiO_9$

Table 1. Crystal data and refinement for the title complex

Empirical formula	$C_{50}H_{49}BN_6NiO_9$
weight	947.47
T	293(2) K
λ	0.71073 Å
System, group	Triclinic, P-1
Cell	$a = 12.5380(13)$ Å $\alpha = 102.760(3)^\circ$
	$b = 13.0100(15)$ Å $\beta = 94.480(2)^\circ$
	$c = 15.1490(18)$ Å $\gamma = 94.540(2)^\circ$
Volume	2390.9(5) Å ³
Z; density	2, 1.316 Mg/m ³
Absorpting number	0.468 mm ⁻¹
F	992
Size	0.34 x 0.33 x 0.30 mm
Collecting range	3.03 to 25.02°
Limiting indices	$-13 \leq h \leq 13, -15 \leq k \leq 15, -18 \leq l \leq 18$
Reflection collected	17997/8106 [R(int)=0.0469]
Completeness to theta(25.02)	96.1 %
Absorptiing correction	Semi-empirical from equivalents
Transmissing	0.8724 and 0.8571
Refining	Full-matrix least-squares on F ²
Parameter	8106 / 0 / 711
GoF	1.080
Final R indices [I>2sigma(I)]	R1=0.0661, wR2=0.1920
R(all data)	R1 = 0.0805, wR2 = 0.2128
Largest peak difference ; hole	1.756 and -0.503 e. Å ⁻³

Table 2. Select bond lengths [Å] and angles [°] for the title complex

Ni(1)-N(2)	2.066(3)
Ni(1)-N(5)	2.073(3)
Ni(1)-N(3)	2.079(3)
Ni(1)-N(4)	2.093(3)
Ni(1)-N(6)	2.095(3)
Ni(1)-N(1)	2.101(3)
N(1)-C(19)	1.357(5)
N(2)-C(24)	1.334(5)
N(3)-C(31)	1.356(5)
N(4)-C(36)	1.342(5)
N(5)-C(43)	1.355(5)
N(6)-C(48)	1.348(5)
O(2)-C(1)	1.265(6)
C(19)-C(20)	1.486(5)
C(29)-C(37)	1.502(5)
C(34)-C(38)	1.510(6)

C(41)-C(49)	1.500(5)
C(46)-C(50)	1.507(6)
O(7)-B(1)	1.334(7)
B(1)-O(9)	1.371(7)
B(1)-O(8)	1.376(6)
N(2)-Ni(1)-N(5)	168.38(12)
N(2)-Ni(1)-N(3)	94.28(12)
N(5)-Ni(1)-N(3)	95.05(12)
N(2)-Ni(1)-N(4)	96.89(12)
N(5)-Ni(1)-N(4)	91.78(11)
N(3)-Ni(1)-N(4)	78.26(12)
N(2)-Ni(1)-N(6)	92.76(12)
N(5)-Ni(1)-N(6)	78.63(12)
N(3)-Ni(1)-N(6)	171.27(11)
N(4)-Ni(1)-N(6)	95.78(12)
N(2)-Ni(1)-N(1)	78.94(12)
N(5)-Ni(1)-N(1)	93.21(12)
N(3)-Ni(1)-N(1)	95.93(12)
N(4)-Ni(1)-N(1)	172.66(11)
N(6)-Ni(1)-N(1)	90.47(12)
C(15)-N(1)-C(19)	117.7(3)
C(15)-N(1)-Ni(1)	127.9(2)
C(19)-N(1)-Ni(1)	114.3(2)
C(24)-N(2)-C(20)	118.4(3)
C(24)-N(2)-Ni(1)	126.1(3)
C(20)-N(2)-Ni(1)	115.4(2)
C(27)-N(3)-C(31)	117.6(3)
C(27)-N(3)-Ni(1)	127.0(3)
C(31)-N(3)-Ni(1)	115.4(2)
C(36)-N(4)-C(32)	117.1(3)
C(36)-N(4)-Ni(1)	127.3(3)
C(32)-N(4)-Ni(1)	115.0(2)
C(39)-N(5)-C(43)	118.1(3)
C(39)-N(5)-Ni(1)	126.2(2)
C(43)-N(5)-Ni(1)	115.5(2)
C(44)-N(6)-C(48)	117.2(3)
C(44)-N(6)-Ni(1)	115.2(2)
C(48)-N(6)-Ni(1)	127.7(3)
O(1)-C(1)-O(2)	124.1(6)
O(1)-C(1)-C(2)	118.8(5)
O(2)-C(1)-C(2)	117.2(5)
C(7)-C(2)-C(1)	120.8(5)
O(3)-C(3)-C(2)	122.2(7)
O(3)-C(3)-C(4)	117.4(6)
C(2)-C(7)-C(6)	121.3(5)
C(14)-C(13)-C(12)	121(3)
N(1)-C(15)-C(16)	123.1(3)
C(17)-C(16)-C(15)	119.8(4)
C(16)-C(17)-C(18)	117.2(3)
C(16)-C(17)-C(25)	123.3(4)
C(18)-C(17)-C(25)	119.6(4)
N(1)-C(19)-C(18)	121.6(3)
N(1)-C(19)-C(20)	115.0(3)
C(18)-C(19)-C(20)	123.4(3)
N(2)-C(20)-C(21)	121.7(3)
N(2)-C(20)-C(19)	116.1(3)
C(23)-C(22)-C(21)	117.1(3)
C(23)-C(22)-C(26)	123.1(4)
C(21)-C(22)-C(26)	119.8(4)
N(2)-C(24)-C(23)	122.6(4)
C(27)-C(28)-C(29)	119.4(4)

C(30)-C(29)-C(28)	117.7(4)
C(31)-C(30)-C(29)	120.3(4)
N(3)-C(31)-C(30)	121.7(4)
N(3)-C(31)-C(32)	115.3(3)
N(4)-C(32)-C(33)	121.7(4)
N(4)-C(32)-C(31)	114.8(3)
C(34)-C(33)-C(32)	121.2(4)
C(33)-C(34)-C(35)	116.5(4)
C(33)-C(34)-C(38)	122.7(4)
N(4)-C(36)-C(35)	123.9(4)
N(4)-C(36)-H(36)	118.1
N(5)-C(39)-C(40)	123.0(4)
C(40)-C(41)-C(49)	121.6(4)
C(43)-C(42)-C(41)	119.6(3)
N(5)-C(43)-C(42)	122.0(3)
N(5)-C(43)-C(44)	115.1(3)
C(42)-C(43)-C(44)	122.8(3)
N(6)-C(44)-C(45)	122.5(3)
N(6)-C(44)-C(43)	115.2(3)
C(45)-C(44)-C(43)	122.4(3)
C(44)-C(45)-C(46)	119.8(4)
C(47)-C(46)-C(45)	117.0(4)
C(47)-C(46)-C(50)	122.1(4)
C(45)-C(46)-C(50)	120.9(4)
C(48)-C(47)-C(46)	120.2(4)
N(6)-C(48)-C(47)	123.2(4)
O(7)-B(1)-O(9)	116.5(4)
O(7)-B(1)-O(8)	123.2(5)
O(9)-B(1)-O(8)	120.3(5)

4 Conclusions

A novel complex $\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_2)_3 \bullet (\text{C}_7\text{H}_5\text{O}_3)_2 \bullet (\text{H}_3\text{BO}_3)$ has been synthesized from a hydrothermal reaction. The Ni atom is coordinated by six N atoms from three 4,4'-dimethyl-2,2'-dipyridyl molecular. The molecular structure stabilized by the O-H...O hydrogen-bonding interactions.

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References

- Lin Z., Tong M.L., (2011) The coordination chemistry of cyclohexanepolycarboxylate ligands. Structures, conformation and functions, *Coord. Chem. Rev.*, 255: 421-450.
- Qi Y.F., Wang X.L., Wang E.B., Qin C., Na H., (2005) Two new metal coordination polymers containing mixed ligands: hydrothermal synthesis and crystal structures of $[\text{Co}_2(1,2,4,5\text{-btc})(\text{phen})_2(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ and $[\text{Mn}_3(1,2,4\text{-btc})_2(\text{phen})_2(\text{H}_2\text{O})_2]_n$, *Journal of Coordination Chemistry*, 58: 1289-1297.
- Kaes C., Katz A., Hosseini M.W., (2000) Bipyridine: The Most Widely Used Ligand. A Review of Molecules Comprising at Least Two 2,2'-Bipyridine Units, *Chem. Rev.*, 100: 3553-3590.
- Cussen E.J., Claridge J.B., Rosseinsky M.J., Kepert C.J., (2002) Flexible sorption and transformation behavior in a microporous metal-organic framework, *J. Am. Chem. Soc.*, 124: 9574-9581.
- Zhang J.P., Zhang Y.B., Lin J.B., Chen X.M., (2012) Metal Azolate Frameworks: From Crystal Engineering to Functional Materials, *Chem. Rev.*, 112: 1001-1033.
- Leong W.L., Vittal J.J., (2011) One-dimensional coordination polymers: complexity and diversity in structures, properties, and applications, *Chem. Rev.*, 111: 688-764.
- Liu Z.Q., Cao S.H., Zhang Z., Wu J.F., Zhao Y., Sun W.Y., (2019) Metal-Organic Frameworks with 2,6-Di(1H-imidazol-1-yl)naphthalene and Dicarboxylate Ligands: Synthesis, Crystal Structure and Photoluminescence Sensing Property, *Chinese Journal of Inorganic Chemistry*, 35(11): 2145-2151.
- Chen X.M., Tong M.L., (2007) Solvothermal In-situ Metal/Ligand Reactions: A New Bridge between Coordination Chemistry and Organic Synthetic Chemistry, *Acc. Chem. Res.*, 40(2): 162-170.
- Han X., Shao Z.C., Zhao B., Ren N., Meng X.R., Ding J., Hou H.W., (2019) Synthesis, Crystal Structure, Magnetic Properties and Catalytic Activity of Co /Ni cation Complexes with 3,3'-(Pyridine-3,5-diyl) Dibenzoic Acid, *Chinese*

Journal of Inorganic Chemistry, 35(11): 2159-2167.

10. Lv M.X., Bian L.Y., Li M.R., Yang Y., Wu W.N., Wang Y., Chen Z., (2019) Three Cu Complexes with 1-(3-Ethylpyrazin-2-yl)ethylidene-4methylthiosemicarbazide: Crystal Structures and DNA-Binding Properties, Chinese Journal of Inorganic Chemistry, 35(8): 1463-1469.
11. Li Y., Jiang H.F., Chen X.L., Qiu W.D., (2021) Syntheses, Crystal Structures, and Photocatalytic Properties of Cobalt and Manganese Coordination Polymers Assembled from 4-((Carboxymethyl)thio)benzoic Acid, Chinese Journal of Inorganic Chemistry, 37(2): 361-367.