

SYNTHESIS AND CRYSTAL STRUCTURE OF A Ni(II) COMPLEX WITH 1,5-NAPHTHALENEDISULFONATE

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Abstract: A new Ni(II) complex, $[\text{Ni}(\text{H}_2\text{O})_6] \cdot (\text{L})$ (L=1,5-naphthalenedisulfonate) has been obtained by the reaction of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with sodium 1,5-naphthalenedisulfonate in the $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (V:V=1:1) solution. The complex was characterized by elemental analysis, IR and X-ray single crystal diffraction analysis. The results showed that the local geometry around central Ni(II) ion can be described as distorted octahedral environment which connected by six coordinated water molecules. The complex molecules formed one dimensional chained structure by hydrogen bonds and π - π stacking.

Keywords: *1,5-naphthalenedisulfonate, Ni(II) complex, synthesis, structure characterization*

INTRODUCTION

During the past few decades, the modular approach to metal-organic framework structures (MOFs) has been an active area of research in coordination chemistry [1-4]. The construction of MOFs based on transition metals and rare earth metals with multifunctional bridging ligands has proven to be a promising field due to their intriguing topologies and potential functions in adsorption, catalysis, fluorescence, magnetic materials and biological activity [5-8].

Bridging ligands containing N- or/and O-donors have been used widely for the syntheses through the direct interaction between the donors and metal ions to construct various coordination polymers. In the previous work of our group, the ligands containing carboxylic acids group had been paid much attention [9-11]. To the best of our knowledge, the coordination polymers constructed by Ni(II) ion with the ligands containing carboxylic acids group had been widely studied. However, the Ni(II) coordination polymers with ligands containing SO_3^- group is very rare [12-14]. We are interested in the coordination chemistry of the ligands containing SO_3^- group. Herein we report on the crystal structure of $[\text{Ni}(\text{H}_2\text{O})_6] \cdot (\text{L})$ ($\text{L}=1,5\text{-naphthalenedisulfonate}$).

EXPERIMENTAL

Materials and methods

The 1,5-naphthalenedisulfonic acid disodium salt and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ were purchased from Aldrich. All other reagents used were analytical grade and used without further purification. Elemental analysis (C, H, N) was carried out using a Elementar Vario III EL elemental analyzer. Infrared spectra were recorded as KBr discs using a Nicolet AVATAR 360 FTIR spectrophotometer in the range $4,000 \text{ cm}^{-1} \sim 400 \text{ cm}^{-1}$. X-ray single crystal diffraction data of the Ni(II) complex was collected on a Bruker smart CCD diffractometer.

Synthesis of the Ni (II) complex

A mixture of 1,5-naphthalenedisulfonic acid disodium salt (1.0 mmol, 0.3325 g) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol, 0.2488 g) and 10 mL $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ ($v:v=1:1$) was stirred at room temperature for 0.5 h. Then the mixture was transferred to a Teflon-lined stainless steel vessel, heated to $120 \text{ }^\circ\text{C}$ for 24 h, and then cooled to room temperature. The resulting solution was filtered. The colourless crystals were obtained after the filtrate was kept in air for 15 days. Yield: 56%. Elementary analysis: calcd for $\text{C}_{10}\text{H}_{18}\text{NiO}_{12}\text{S}_2$: C, 26.49; H, 3.97 %; found: C, 26.78; H, 4.29 %. IR ν_{max} (cm^{-1}): $\nu(\text{SO}_3^-)$: $1,335 \text{ cm}^{-1}$, $1,200 \text{ cm}^{-1}$, $\nu(\text{H}_2\text{O})$: 3328 cm^{-1} .

X-ray Crystallography

The single crystal was placed on a Bruker Smart Apex CCD diffractometer equipped with a Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The diffraction data of the single crystal were collected by using a $\varphi\sim\omega$ scan mode in the range $3.08\text{-}27.48^\circ$ at $293(2) \text{ K}$.

A total of 7744 reflections were collected, of which 1921 were independent ($R_{\text{int}} = 0.0191$) and 1798 were observed with $I > 2\sigma(I)$. The data were corrected for Lp factors. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 . The structure was solved by direct methods [15] using SHELXL-97 and expanded using Fourier techniques.

All of the non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically by full-matrix least squares refinement. The final refinement gave $R = 0.0617$, $wR = 0.1676$ ($w = 1/[\delta^2(Fo^2) + (0.1000P)^2 + 0.0000P]$, $P = (Fo^2 + 2Fc^2)/3$, $S = 1.213$ and $(\Delta/\sigma)_{\text{max}} = 0.000$). The largest peak in the final difference fourier map is $1.148 \text{ e} / \text{\AA}^3$ and the minimum peak is $-1.575 \text{ e} / \text{\AA}^3$.

Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package [16].

The most relevant crystal data for complex are quoted in Table 1, and the selected bond distances and angles are listed in Table 2.

Table 1. Crystallographic data for Ni (II) complex

Formula	$\text{C}_{10}\text{H}_{18}\text{NiO}_{12}\text{S}_2$
Formula weight	453.2
Crystal system	Monoclinic
Space group	P21/c
a [\AA]	13.218(3)
b [\AA]	6.6314(13)
c [\AA]	9.6007(19)
β [$^\circ$]	92.03(3)
Z	2
F [000]	444
Temperature [K]	293(2)
V [\AA^3]	841.0(3)
Calculated density [$\mu\text{g}\cdot\text{m}^{-3}$]	1.741
Crystal size [mm^3]	$0.32 \times 0.28 \times 0.22$
μ [mm^{-1}]	1.461
S	1.213
Limiting indices	$-17 \leq h \leq 16$, $-8 \leq k \leq 8$, $-12 \leq l \leq 12$
Reflections collected	7744
Unique reflections	1921
R_1 , wR_2 [all data]	0.0630, 0.1695
R_1 , wR_2 [$I > 2\sigma(I)$]	0.0617, 0.1676
Largest diff. peak and hole [$\text{e}\cdot\text{\AA}^{-3}$]	1.148, -1.575

Table 2. Selected bond lengths and angles for Ni(II) complex

Bond	Distance [Å]	Bond	Distance [Å]
S1-O4	1.454(2)	S1-O5	1.459(2)
S1-O6	1.461(2)	Ni1-O2	2.029(2)
Ni1-O2A	2.029(2)	Ni1-O1	2.0576(19)
Ni1-O1A	2.0577(19)	Ni1-O3	2.0831(17)
Ni1-O3A	2.0831(17)	C3-S1	1.779(2)
C1-C2	1.408(4)		
Angle	[°]	Angle	[°]
O4-S1-O5	111.52(13)	O4-S1-O6	112.97(12)
O6-S1-O5	111.53(13)	O4-S1-C3	106.87(11)
C3-S1-O5	106.04(12)	O6-S1-C3	107.46(13)
O2-Ni1-O2A	180.00(14)	O2-Ni1-O1	92.16(8)
O1-Ni1-O2A	87.84(8)	O2-Ni1-O1A	87.84(8)
O1A-Ni1-O2A	92.16(8)	O1-Ni1-O1A	180.00(10)
O2-Ni1-O3	92.66(8)	O3-Ni1-O2A	87.34(8)
O1-Ni1-O3	90.77(8)	O3-Ni1-O1A	89.23(8)
O2-Ni1-O3A	87.34(8)	O3A-Ni1-O2A	92.66(8)
O1-Ni1-O3A	89.23(8)	O1A-Ni1-O3A	90.77(8)
O3-Ni1-O3A	180.00(13)		

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

RESULTS AND DISCUSSION

IR spectra

The ν (SO_3^-) vibrations show at $1,336\text{ cm}^{-1}$ and $1,201\text{ cm}^{-1}$ in the free 1,5-naphthalenedisulfonic acid disodium salt ligand. For the Ni(II) complex, they do not shift, indicating that the oxygen atoms of SO_3^- do not take part in coordination with Ni(II) ions [17]. At lower frequency the complex exhibits band around 413 cm^{-1} which may be assigned to ν (Ni-O) vibration. In addition, the broad band at 3258 cm^{-1} shows that the complex contains water molecules, which are in accordance with the results of elemental analysis.

Structure Description

The crystal structure of the title complex is revealed in Figure 1. The molecular packing arrangement is shown in Figure 2. As shown in Figure 1, in the Ni(II) complex, Ni(II) atom is six-coordinated by six O atoms from six coordinated water molecules and adopts a slightly distorted NiO_6 octahedral geometry. In addition, the 1,5-naphthalenedisulfonate ligand do not take part in coordination with Ni(II) atoms. The bond lengths of Ni-O are Ni1-O2 = $2.029(2)\text{ \AA}$, Ni1-O2A = $2.029(2)\text{ \AA}$, Ni1-O1 = $2.0576(19)\text{ \AA}$, Ni1-O1A = $2.0577(19)\text{ \AA}$, Ni1-O3 = $2.0831(17)\text{ \AA}$ and Ni1-O3A = $2.0831(17)\text{ \AA}$, which are similar to the Ni-O bond lengths reported previously [18]. The angles subtended at the Ni(II) atom are O2-Ni1-O2A, $180.00(14)^\circ$, O2-Ni1-O1,

92.16(8)°, O1-Ni1-O2A, 87.84(8)°, O2-Ni1-O1A, 87.84(8)°, O2-Ni1-O3, 92.66(8)°, respectively.

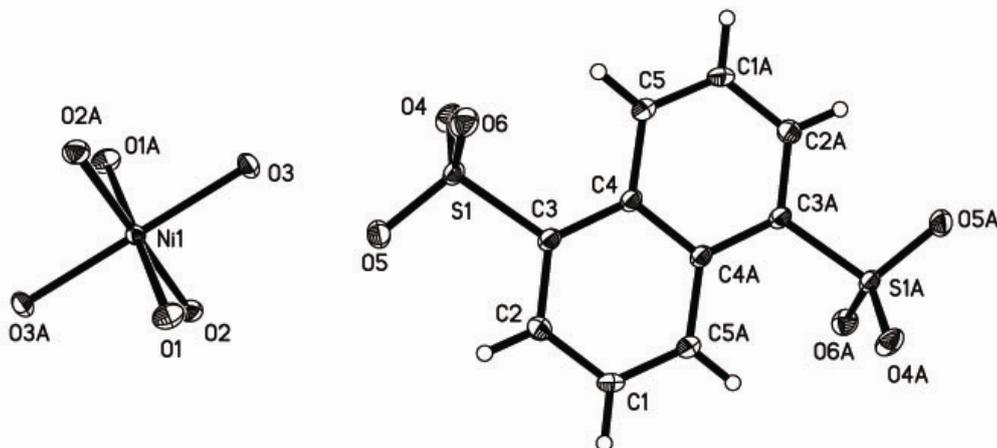


Figure 1. Molecular structure of the Ni(II) complex, where the thermal ellipsoids were drawn at 30% possibility

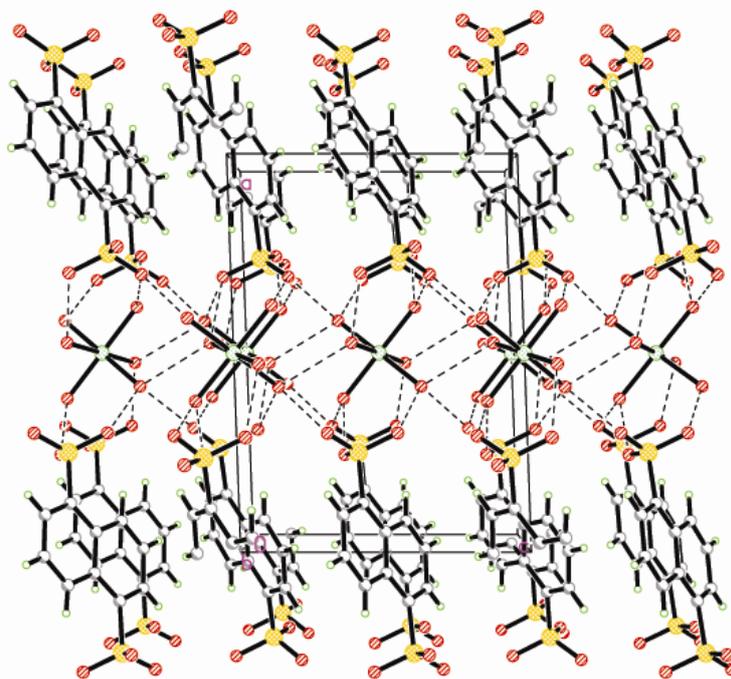


Figure 2. Molecular packing of the Ni (II) complex

The complex molecules form one dimensional chain structure along by hydrogen bonds and π - π stacking (Figure 3). The π - π interactions increase the stability of the crystal structure, and play an important role in the formation of 1D chained structure (Figure 4).

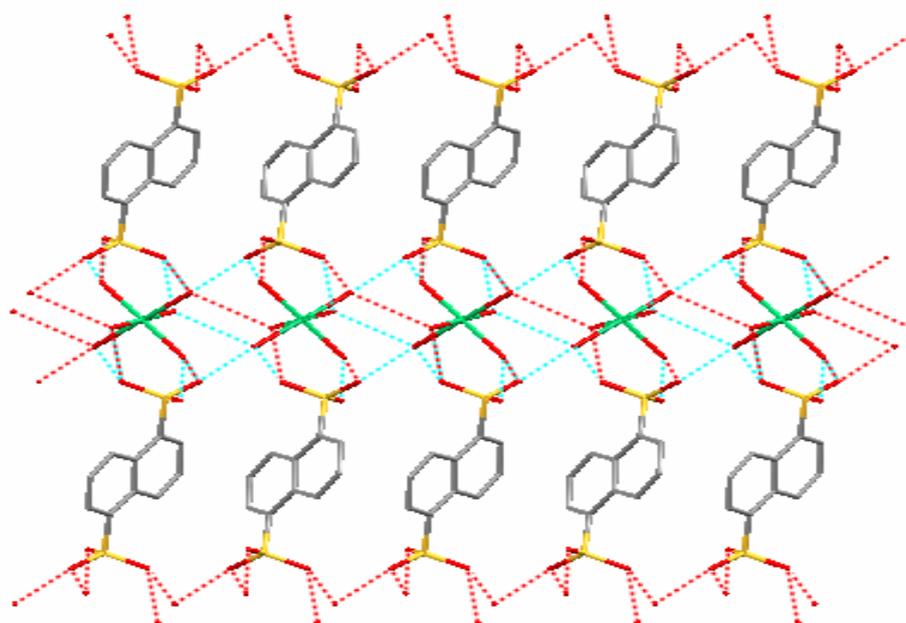


Figure 3. One dimensional chain structure of the Ni(II) complex by hydrogen bonds and π - π stacking

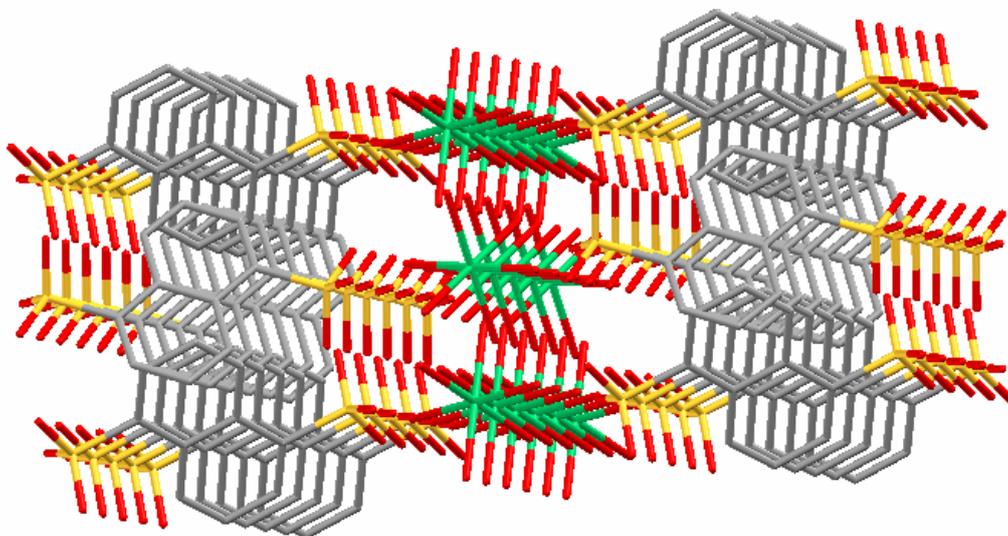


Figure 4. π - π stacking of Ni(II) complex

CONCLUSIONS

In summary, a novel Ni(II) complex, $[\text{Ni}(\text{H}_2\text{O})_6]\cdot(\text{L})$, has been synthesized and structurally characterized. The results show that the local geometry around central Ni(II) ion can be described as distorted octahedral environment which connected by six coordinated water molecules. The complex molecules are connected by hydrogen bonds and π - π stacking to form one dimensional chain structure.

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