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Synthesis and crystal structure of new [Pyridine-4-boronic acid methyl ester and Nickel(II) dithiooxalate] compound

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Abstract

In this study, a new compound $[HNC_5H_4B(OH)(OCH_3)\text{-}4]_2[Ni(S_2C_2O_2)_2]$, [Pyridine-4-boronic acid methyl ester and Nickel(II) dithiooxalate] was synthesized and its crystal structure was determined by the single-crystal X-ray diffraction method. The compound crystallized in the monoclinic crystal system in the $P2_1/n$ space group. The Ni^{II} ion is four-coordinated and has a slightly distorted square-plane geometry. There is NH···O, OH···O and CH···O hydrogen bond interactions in the crystal structure. These interactions form a 3-dimension network stacked along the c axis in the ab plane.

Keywords: *Crystal structure, 4-pyridine boronic acid, hydrogen bond interactions.*

Yeni [Piridin-4-boronik asit metil ester ve Nikel(II) ditiooksalat] bileşiğinin sentezi ve kristal yapısı

Öz

Bu çalışmada yeni bir bileşik $[HNC_5H_4B(OH)(OCH_3)\text{-}4]_2[Ni(S_2C_2O_2)_2]$, [Piridin-4-boronik asit metil ester ve Nikel(II) ditiooksalat] sentezlendi ve onun kristal yapısı tek kristal X-ışını difraktometresi metodu ile belirlendi. Bileşik $P2_1/n$ uzay grubunda monoklinik kristal sisteminde kristallendi. Ni^{II} iyonu dört koordinasyonlu ve hafifçe bozulmuş kare düzlem geometriye sahiptir. Kristal yapıda, NH···O, OH···O ve CH···O

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hidrojen bağ etkileşimleri vardır. Bu etkileşimler ab düzleminde c ekseni boyunca paketlenir ve 3 boyutlu bir ağ oluşturur.

Anahtar kelimeler: *Kristal yapı, 4-pridin boronik asit, hidrojen bağ etkileşimleri.*

1. Introduction

Boronic acids are an important group of compounds used in molecular chemistry [1,2], organic catalysis [3,4] and medicinal chemistry [5–7]. The reversible covalent bond formation ability of their enables the synthesis of compounds suitable for use in fields such as live-cell imaging, anticancer, antibacterial, antiviral applications and drug delivery [5–8]. Therefore, there are boronic acid compounds in the structure of drugs used in medical fields such as oncology, virology, neurology and hematology [9–11]. It is used in many areas such as antiseptic solution in eyes and ears [12,13], insecticide in agriculture [14], lubricant on ceramic and metal surfaces [15], acne treatment and skin lotions [16] and liquid crystal display panel in industry [17]. The need for alternative new materials in all these areas is increasing day by day. Therefore, it has become important for researcher to design, synthesize and study the molecular structures of new molecules.

Since boronic acids show cross-linking reactions, their hydrogen-bonded derivatives are important in supramolecular chemistry. Systematic investigation of their hydrogen-bonded network allows the construction of supramolecular assemblies. For this purpose, researchers have tried to develop a strong and flexible strategy that will enable both component and structural diversity of molecules [1,4,18–22].

The compounds consisting of pyridinium and bipyridinium cation and metal anionic salts have been investigated in literature [23,24]. In these studies, it was reported that the stereochemistry of the hydrogen bond donor group in the cations caused the compound to have different behavior. Therefore, in this study, new $[HNC_5H_4B(OH)(OCH_3)\text{-}4]_2[Ni(S_2C_2O_2)_2]$ compound was synthesized with 4-Pyridine boronic acid and $K_2[Ni(dto)_2]$ salt, its crystal structure, intramolecular and intermolecular hydrogen bonding interactions were studied.

2. Materials and methods

2.1. Materials and measurements

The chemicals and solvents used in the experiment were purchased commercially from Sigma-Aldrich and were used without any purification. Elemental analysis of the compound was carried out with LECO-CHNS-932 brand device. Diffraction data were obtained with the Bruker Apex II X-Ray Single Crystal Diffractometer device (MoK_α). Absorption, Lorentz and polarization corrections were applied to the data in the SAINT [25] program. The structure of the compound was solved in the OLEX2 program [26], with the SHELXTL [27] interface. The shapes of the compound were created with the MERCURY [28] program and used to determine intermolecular interactions.

2.2. Syntheses of $[HNC_5H_4B(OH)(OCH_3)\text{-}4]_2[Ni(S_2C_2O_2)_2]$ (1)

It was synthesized from the $K_2[Ni(dto)_2]$ salt according to the previous study [29]. 4-Pyridine boronic acid is regenerated from concentrated hydrochloric acid to form the

hydrochloride salt. 4-Pyridinylboronic acid, (1 mmol) was dissolved in %37 hydrochloric acid solution and water. The solution was maintained at the boiling point with stirring for 1 h. The solvent was evaporated, and the white crystals were obtained upon filtration. Single crystals were obtained by slow diffusion of stoichiometric amounts of 4-pyridine boronic acid hydrochloride and $K_2[Ni(dto)_2]$ salt, as we are called 'mini Htube'. In this method, 4-Pyridine boronic acid hydrochloride (84.5 mg, 0.53 mmol) in 5 ml of distilled water and $K_2[Ni(dto)_2]$ (0.10 g, 0.265 mmol) in 10 ml of distilled water were filled into two small glass tubes separately. Then the small glass tubes were placed inside a larger capped glass bottle. The bottle was filled with distilled water and closed and left to stand for slow diffusion. The resulting red crystals were collected by vacuum filtration, washed with ethanol (5 ml), diethyl ether (5 ml) and dried in a vacuum pump. The structure of the cation and anion in the compound is shown in Figure 1. Yield: 79.9 %. Anal. Calcd (%) for $C_{16}H_{18}B_2N_2NiO_8S_4$: C, 33.43; H, 3.16; N, 4.87. Found: C, 33.41; H, 3.19; N, 4.84.

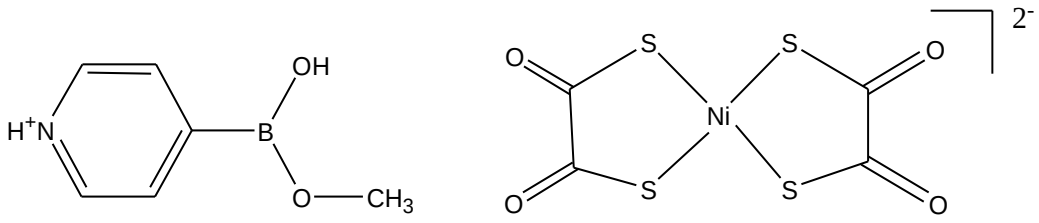

Figure 1. Molecular structure of cation and anion in 1

3. Results and discussion

The compound $[HNC_5H_4B(OH)(OCH_3)\text{-}4]_2[Ni(S_2C_2O_2)_2]$ consists of $[Ni(S_2C_2O_2)_2]$ anion and 4-pyridineboronic acid methyl ester cation. It crystallizes in the monoclinic crystal system, the $P2_1/n$ space group (Table 1). The asymmetric unit of **1** includes a $\{[HNC_5H_4B(OH)(OCH_3)\text{-}4]_2\}^{2+}$ cation and half of $[Ni(S_2C_2O_2)_2]^{2-}$ anion. The Ni^{II} ion in the anion of the compound is at the inversion center and has four-coordination with four S atoms. The *cis* S-Ni-S bond angles of the compound are 87.48(3)° and 95.52(3)°, and with these angles, the Ni^{II} ion has a slightly distorted square plane geometry.

The sum of the angles around the boron (B1) atom on the pyridine ring is 360˚ (Table 2). The mean B-C and B-O bond lengths of **1** are 1.595 (4) Å and 1.350 (4) Å, respectively. These values are similar to the parameters of similar systems previously found in the literature [23,30].

One $[Ni(S_2C_2O_2)_2]^{2-}$ anion and six $\{[HNC_5H_4B(OH)(OCH_3)\text{-}4]_2\}^{2+}$ cation in the hydrogen-bonded primary motif of the compound is linked to by NH···O and OH···O and CH···O hydrogen bond interactions (Figure 3). Ni···Ni distances in this hydrogen-bonded network are 11.169 Å. This hydrogen-bonded primary motif is linked to other motifs by CH···O and OH···O hydrogen bonds, forming a 1D chain structure. As seen in Figure 4, anion and cation molecules in the motifs form the 3D structure with the NH···O OH···O and CH···O hydrogen bond interactions by stacking along the c axis in the ab plane (Table 3).

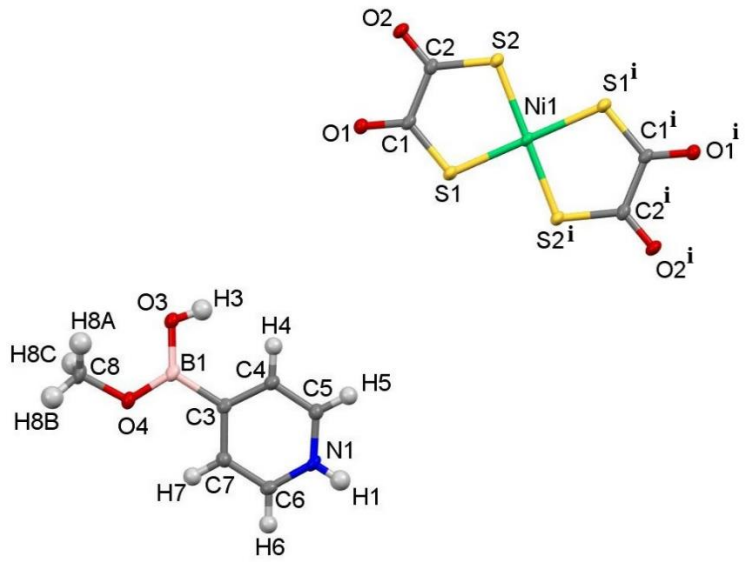

Figure 2. The molecular structure of 1 (symmetry code i: −x, −y, −z).

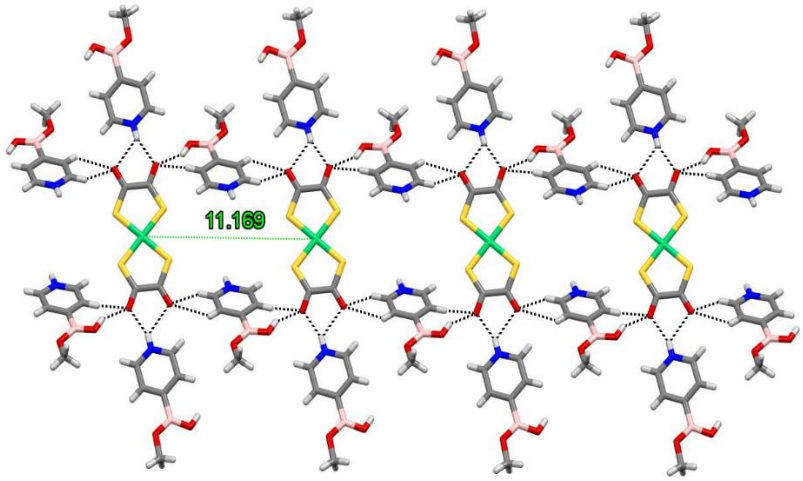

Figure 3. Hydrogen-bonded 1D chain structure of 1.

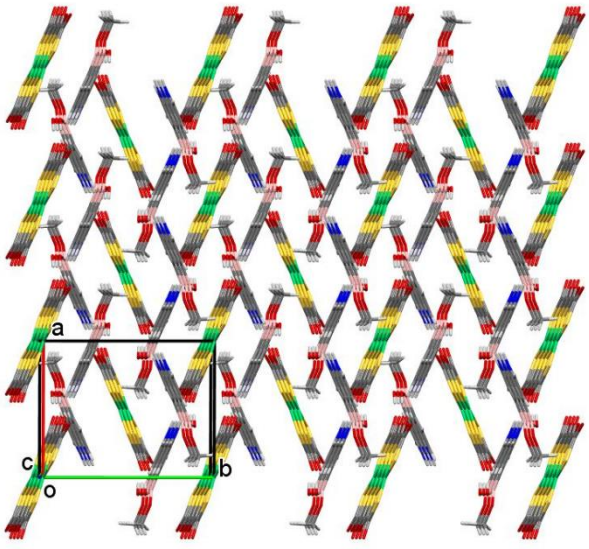

Figure 4. Packing of layers in 1.

Table 1. Crystallographic information for 1.

	1
CCDC	2149587
Chemical Formula	$C_{16}H_{18}B_2N_2NiO_8S_4$
Crystal System	Monoclinic
Space Group	$P2_1/_n$
Molecular Weight ($gmol^{-1}$)	574.89
Unit cell parameter	a = 9.1363 (18) Å
	b = 11.346 (2) Å
	c= 11.169 (2) Å
	$\alpha = \gamma = 90°$
	$\beta = 98.03\ (3)°$
V ($Å^3$)	1146.4 (4)
T (K)	100
Z	2
d (g/cm^{-3})	1.665
S	1.073
μ (mm^{-1})	1.257
Measured reflections	12511
Independent reflections (R_{int})	2625 [R_{int} = 0.059]
Final R_1 [I > 2σ(I)]	0.040
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.90, −0.44
wR_2	0.1003

Table 2. Selected bond lengths [Å] and angles [°] for 1.

Bond Distances		**Bond Angles**	
Ni1–S1	2.179 (9)	S1–Ni1–$S1^i$	180
Ni1–$S1^i$	2.179 (9)	S1–Ni1–$S2^i$	87.48 (3)
Ni1–S2	2.184 (8)	S1–Ni1–S2	92.52 (3)
Ni1–$S2^i$	2.184 (8)	S1i–Ni1–S2	87.48 (3)
O3–B1	1.352 (4)	S1i–Ni1–$S2^i$	92.52 (3)
O4–B1	1.350 (4)	S2–Ni1–$S2^i$	180
C3–B1	1.595 (4)	C1–S1–Ni1	105.98 (9)
Ni Ni	11.170	C2–S2–Ni1	105.65 (9)
		O3–B1–C3	123.27
		O3–B1–O4	121.20
		O4–B1–C3	115.53

Symmetry code: (i) −x, −y, −z.

Table 3. Hydrogen-bond parameters (Å, °) of 1.

D–H···A*	**D–H**	**H···A**	**D···A**	**D–H···A**	**Symmetry**
N1–H1···O1	0.83	2.01	2.794	158	x,y,1+z
N1–H1···O2	0.83	2.37	2.937	127	x,y,1+z
O3–H3···O1	0.84	1.99	2.760	151	1/2+x,1/2-y,1/2+z
C4–H4···O1	0.95	2.46	3.342	155	1/2+x,1/2-y,1/2+z
C5 –H5···O2	0.95	2.41	2.978	118	x,y,1+z
C6–H6···O2	095	2.57	3.226	126	1/2+x,1/2-y,3/2+z

4. Conclusion

The compound $[HNC_5H_4B(OH)(OCH_3)\text{-}4]_2[Ni(S_2C_2O_2)_2]$ was synthesized using the 'Mini Htube' method and was characterized by single crystal X-ray diffraction technique. The compound consists of $[Ni(S_2C_2O_2)_2]$ anion and 4-pyridineboronic acid methyl ester cation. Ni^{II} ion in the compound has a slightly distorted square plane geometry. There is NH···O and OH···O and CH···O hydrogen bond interactions between the anion and cation molecules in the compound. The molecules in the compound with these hydrogen bond interactions are stacked and a three-dimensional structure is formed.

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