

NICKEL(II) COMPLEX DERIVED FROM 2-HYDROXY-3-METHOXYBENZALDEHYDE SEMICARBAZONE AND 2,2'-BIPYRIDINE

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Abstract. Reaction of 2-hydroxy-3-methoxybenzaldehyde semicarbazone with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in the presence of 2,2'-bipyridine, afforded a dinuclear complex (1). Crystal structure of **1** revealed the dinuclear complex, in which one nickel center is surrounded octahedrally by two monoanionic O,N,O-donor semicarbazone. The second nickel center also adopts an octahedral geometry created by two 2,2'-bipyridine ligands and the bridging phenolate oxygen of the monodeprotonated semicarbazones.

Keywords: semicarbazone, binuclear nickel(II) complex, crystal structure.

Introduction

Chemistry and pharmacological applications of semicarbazones have been extensively investigated due to their wide range of biological activities, such as antitumoral, antibacterial, antiviral and antimalarial effects [1,2]. By coordination to a metal ion, the biological properties of semicarbazones are often modified: lipophilicity, increasing of activity, decreasing of side effects, reduction of drug-resistance. Tridentate ONO Schiff base, obtained by condensation of salicylaldehyde with semicarbazide has been used for the synthesis of a large variety of synthesis of mononuclear complexes and multinuclear clusters of transition metals, such as Cu(II) [3-7], Cr(III) [8], Co(III) [9], as well as dioxovanadium(V) [10] complexes. A dinuclear zinc(II) complex with salicylaldehyde semicarbazone was prepared and structurally characterized, where the deprotonated phenol group of the ligand forms a bridge between the two zinc centers [11]. Additional coordinating groups attached to salicylaldehyde would increase both the denticity of the resulted Schiff bases, and as result the ability to generate polynuclear complexes. 2-Hydroxy-3-methoxybenzaldehyde was largely employed as carbonyl precursor for the synthesis of multimetallic assemblies due to ability of methoxy group to display a variety of bonding geometries, such as chelating, monodentate/bidentate bridging, and chelating bridging [12-14]. The Schiff base ligand, 2-hydroxy-3-methoxybenzaldehyde semicarbazone (H_2L , Figure 1) has been used to synthesize monomeric vanadium(V) and dimeric palladium complexes [15-16]. The structure of H_2L has been reported in [17].

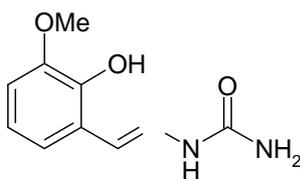


Figure 1. Structural formula of 2-hydroxy-3-methoxybenzaldehyde semicarbazone, H_2L

This variable mode of binding of 2-hydroxy-3-methoxybenzaldehyde semicarbazone has encouraged us to explore its coordination ability. We have chosen nickel as metal center due to its ability to take up different coordination environments (such as octahedral, square-planar and tetrahedral), which makes its coordination chemistry very interesting. To satisfy the remaining coordination sites on the metal center we selected 2,2'-bipyridine as additional ligand. Herein we report the synthesis and X-Ray structure characterization of a dinuclear nickel(II) complex $[\text{Ni}_2(\text{HL})_2(\text{bpy})_2](\text{NO}_3)_2$ (**1**), where H_2L - 2-hydroxy-3-methoxybenzaldehyde semicarbazone.

Results and discussion

The structure determination shows that compound **1** is a dinickel complex (Figure 2), which resides on two fold axis and thus having C_2 molecular symmetry. One Ni(II) ion is surrounded by two tridentate ONO monodeprotonated ligands HL, while the coordination sphere of the other involves two 2,2'-bipyridine ligands and two phenoxy oxygen

atoms of the HL^- . These two deprotonated oxygen atoms of two HL^- bridge the metal ions. The $\text{Ni}\cdots\text{Ni}$ distance and Ni-O-Ni angle are $3.163(1)$ Å and $99.71(9)^\circ$, respectively. These parameters corresponds to the 3.199 Å and $101.6(1)$ values observed in the similar dinickel complex $[\text{Ni}_2(\text{HL}')_2(2,2'\text{-bpy})_2](\text{ClO}_4)_2$ (**2**), $\text{H}_2\text{L}' = 2\text{-}[(1\text{E})\text{-N-(2-aminopropyl)ethanimidoyl}]\text{phenol}$ [18]. But in contrary to complex **2**, where the central $\text{Ni-O}_2\text{-Ni}$ core is symmetric, with identical Ni-O bond lengths $2.063(2)$ Å, in **1** Ni(1)-O(1) and Ni(2)-O(1) distances differ and are $2.032(2)$ and $2.105(2)$ Å, respectively. Both Ni atoms are hexacoordinated and have distorted octahedral surrounding but differ by the set of donor atoms: O_4N_2 for Ni(1) and O_2N_4 for Ni(2) (Table 1). Comparison of conformation of neutral H_2L molecule [17] with coordinated HL^- one reveals the transformation from *trans-trans* to *cis-cis* in mutual arrangement of ONO donor atoms.

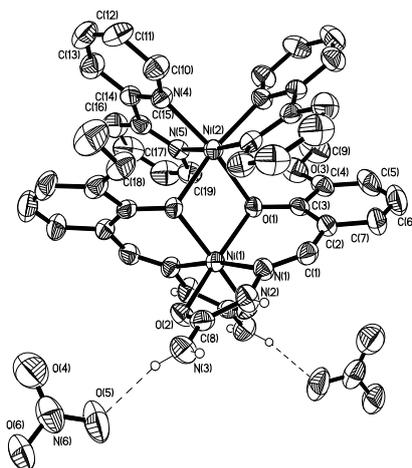


Figure 2. The molecular structure of $[(\text{Ni}_2(\text{HL})_2(\text{bpy})_2)](\text{NO}_3)_2$.

Table 1.

Bond lengths (Å) and angles (deg) in coordination polyhedra of nickel atoms.

Atom-atom	d, Å	Atom-atom-atom	ω , °
Ni(1)-O(1)	2.032(2)	O(1)-Ni(1)-N(1)	87.14(10)
Ni(1)-N(1)	2.015(3)	O(1)-Ni(1)-O(2)	162.94(9)
Ni(1)-O(2)	2.090(2)	O(1)-Ni(1)-O(1)*	82.0(1)
Ni(2)-O(1)	2.105(2)	O(1)-Ni(1)-N(1)*	100.69(10)
Ni(2)-N(4)	2.080(3)	O(1)-Ni(1)-O(2)*	92.87(9)
Ni(2)-N(5)	2.068(3)	N(1)-Ni(1)-O(2)	77.79(10)
Ni(1)-Ni(2)	3.163(1)	N(1)-Ni(1)-N(1)*	169.7(2)
		N(1)-Ni(1)-O(2)*	95.26(10)
		O(2)-Ni(1)-O(2)*	96.4(1)
		O(1)-Ni(2)-O(1)*	78.57(11)
		O(1)-Ni(2)-N(4)	168.32(9)
		O(1)-Ni(2)-N(4)*	95.53(9)
		O(1)-Ni(2)-N(5)	91.69(10)
		O(1)-Ni(2)-N(5)*	92.94(9)
		N(4)-Ni(2)-N(4)*	92.0(2)
		N(4)-Ni(2)-N(5)	78.5(1)
		N(4)-Ni(2)-N(5)*	97.3(1)
		N(5)-Ni(2)-N(5)*	174.0(2)

Symmetry transformations used to generate equivalent atoms: * $-x, y, -z+3/2$

The crystal packing of compound **1** is shown in Figure 3. The dinickel complex cations in the crystal are connected with NO_3^- anions by $\text{N-H}\cdots\text{O}$ hydrogen bonds (Table 2), in undulated layers parallel to (*ac*) crystallographic plane.

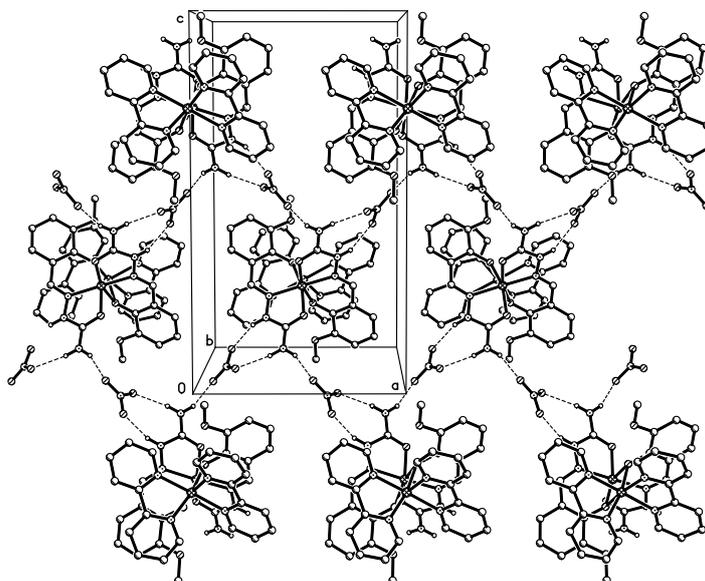


Figure 3. The crystal structure of $[(\text{Ni}_2(\text{HL})_2(\text{bpy})_2)](\text{NO}_3)_2$: undulated layers parallel to (*ac*) crystallographic plane.

Table 2.

Hydrogen bond distances for **1** (Å and deg.).

D-H...A	D-H	H...A	D...A	< DHA	Symmetry transformations for A
N(2)–H(1)···O(6)	0.86	2.04	2.816(4)	150	$x+1/2, -y+5/2, -z+1$
N(3)–H(1)···O(5)	0.86	2.10	2.919(4)	158	x, y, z
N(3)–H(2)···O(4)	0.86	2.11	2.966(4)	171	$x+1/2, -y+5/2, -z+1$

In concordance with the mentioned tridentate coordination mode the bands of interest which change frequency on coordination are the following: the absence of the characteristic $\nu(\text{OH})$ band in the IR spectrum of the complex, which in the ligand spectrum appears at apr. 3466 cm^{-1} , as well as the shift to lower energies (*ca.* 30 cm^{-1}) of the bands $\nu(\text{C}=\text{O})$ which in the spectrum of H_2L appears at 1670 cm^{-1} ; a sharp but weak band at 1582 cm^{-1} , assigned as $\nu(\text{C}=\text{N})$, shifts to 1568 cm^{-1} in nickel complex.

Experimental part

All reagents and solvents were obtained from commercial sources and used without further purification. Elemental analysis was performed on Vario El III elemental analyzer. The IR spectra were obtained in Vaseline on a FT IR Spectrum-100 Perkin Elmer spectrometer.

Synthesis of 2-hydroxy-3-methoxybenzaldehyde semicarbazone (HL). The ligand was prepared by a slight modification of the procedure reported previously [19]. Briefly, to a solution of semicarbazide hydrochloride (1.12 g, 10 mmol) and sodium acetate (1.36 g, 10 mmol) dissolved in a mixture of distilled water (5 mL) and ethanol (15 mL), 2-hydroxy-3-methoxybenzaldehyde (1.12 g, 10 mmol) in ethanol (15 mL) was added. The mixture was stirred at reflux for 1 h, and the resultant precipitate was filtered off, washed with ethanol, diethyl ether and dried in air. Yield: 1.65g (80%). Anal. found for $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_3$ (%):C, 51.83; H, 5.41; N, 20.16. Calculated, %: C, 51.67; H, 5.30; N, 20.10.

Synthesis of $[(\text{Ni}_2(\text{HL})_2(\text{bpy})_2)](\text{NO}_3)_2$ (I). To a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.14 g, 0.5 mmol) in methanol (20 mL) solid 2-hydroxy-3-methoxybenzaldehyde semicarbazone (0.10 g, 0.5 mmol) was added, followed by 2,2'-bipyridine (0.08 g, 0.5 mmol). The suspension was stirred until the ligand dissolved, after which the resulting greenish solution was filtered and allowed to stand overnight. The small, light green rectangular crystals which appeared were filtered off and air-dried. Yield: 0.04g (33%). Anal. found for $\text{C}_{19}\text{H}_{18}\text{NiN}_6\text{O}_6$, %: C 47,18; H 3,78; N 17.43. Calculated: C 47,04; H 3,74; N 17.33.

X-ray Crystallography. Diffraction measurement for **1** was carried out at room temperature on a CCD Xcalibur E diffractometer equipped with a graphite monochromator utilizing MoK α ($\lambda = 0.71073\text{\AA}$) radiation and ω scans. Final unit cell dimensions were obtained and refined on an entire data set. The crystal structure was solved by direct methods. All calculations to solve the structures and to refine the models were carried out with the programs SHELX97 [20]. The C- and N- bound H atoms were placed in calculated positions and were treated using a riding model approximation with Uiso(H)=1.2Ueq(C). Crystal data and details on the structure refinement are given in Table 3. Selected geometric parameters for **1** are given in Table 1. CCDC 975158 contains the supplementary crystallographic data for **1**.

Table 3.

Crystal data and structure refinement for compound (**1**).

Empirical formula	$C_{19}H_{18}N_6NiO_6$
Formula weight	485.10
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
Unit cell dimensions	
<i>a</i> , \AA	11.7026(4)
<i>b</i> , \AA	17.2571(6)
<i>c</i> , \AA	20.5159(8)
<i>V</i> , \AA^3	4143.2(3)
<i>Z</i>	8
ρ (calc), mg/m^3	1.555
μ , mm^{-1}	0.987
<i>F</i> (000)	2000
Crystal size, mm^3	0.12x0.10x0.06
θ range for data collection, deg	2.89 - 25.50
Index ranges	$-14 \leq h \leq 11, -13 \leq k \leq 20, -24 \leq l \leq 24$
Reflections collected	17003
Independent reflections	3858 (R(int) = 0.0709)
Completeness to $\theta = 25.05^\circ$, %	99.8
Data / parameters	3858 / 290
<i>GOOF</i>	0.999
Final <i>R</i> indices ($I > 2\sigma(I)$)	$R1 = 0.0488, wR2 = 0.0758$
<i>R</i> indices (all data)	$R1 = 0.1055, wR2 = 0.0873$
Largest diff. peak and hole, $e\text{-\AA}^{-3}$	0.430 / -0.351

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