

Crystal Structure of Monoprotonated Ni(II) Nitrilotriacetate Tetrahydrate

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Abstract—A Ni(II) complex of the composition $\text{Ni}(\text{HNta}) \cdot 4\text{H}_2\text{O}$ (**I**) was synthesized. Its structure was found to consist of neutral mononuclear $[\text{Ni}(\text{HNta})(\text{H}_2\text{O})_3]$ complexes and crystallization water molecules. The Ni atom has octahedral surrounding and is coordinated to tridentate-chelate HNta^{2-} ligand through the N atom and O atoms of two deprotonated acetate groups and through the O atoms of three water molecules. The structure of **I** was compared with those of the $\text{Zn}(\text{HNta}) \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{HNta}) \cdot 4\text{H}_2\text{O}$ complexes isostructural to **I**. Thermogravimetric method showed that the decomposition of compound **I** occurs through several successive stages of dehydration, deaquation, decarboxylation, and the formation of inorganic residue.

The anions of nitrilotriacetic acid (H_3Nta) are known to form stable complexes with several metal ions where the metal : Nta ratio is commonly 1 : 1 [1]. In most cases, the nitrilotriacetic anions act as tetradentate ligands by coordinating the metal atom through the nitrogen atom and three oxygen atoms of carboxyl groups. However, in the case of protonation of one carboxyl group, the HNta^{2-} anion can behave as tridentate ligand: the protonated carboxyl group remains free [2, 3].

The Ni(II) nitrilotriacetate complexes containing the nucleic acid bases have been recently synthesized in [4]. The Nta^{3-} anion in these complexes performs the function of tetradentate ligand. It was of interest to synthesize and study the Ni(II) complex with the monoprotonated HNta^{2-} anion and to compare its structure with the analogous 3d metal complexes. This paper reports the experimental data on the synthesis and thermal behavior of $\text{Ni}(\text{HNta}) \cdot 4\text{H}_2\text{O}$ (**I**).

EXPERIMENTAL

Synthesis. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91 g, 0.01 mol) was dissolved in water and an excess of Na_2CO_3 solution was added. The precipitate obtained was filtered off, washed on a filter with distilled water, and then transferred to a conical flask containing 1.91 g (0.01 mol) of nitrilotriacetic acid in 50 ml of water. The suspension was heated on boiling water bath until the precipitate dissolved. The solution was filtered and concentrated to a half of its volume. After the solution was allowed to stay for several days, the green crystals precipitated that were isolated by filtering the solution. The crystals formed were washed with alcohol, ether, and dried in air to a constant mass. The obtained compound is solu-

ble in water, but insoluble in alcohols, acetone, acetonitrile, or ether; it can be recrystallized from aqueous solution with its composition remaining unchanged.

For $\text{C}_6\text{H}_{15}\text{NNiO}_{10}$ (**I**)

anal. calcd. (%): Ni, 18.35; N, 4.38; H_2O , 22.5.

Found (%): Ni, 17.6; N, 4.29; H_2O , (thermogr) 23.5.

The nickel content was determined by complexometric titration with Trilon B in an alkaline medium using murexide as indicator [5]. The nitrogen content was determined by the Dumas method [6].

The compound **I** derivatogram was recorded at the rate of 5 and 2.5 K/min on the Paulik-Paulik-Erdey derivatograph in the temperature interval 20–500°C in air.

X-ray diffraction analysis. The experimental data set for compound **I** was collected on a KUMA4 CCD diffractometer (MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$, at 140 K with the crystal positioned at a distance of 60 mm from the CCD chamber) from a single crystal with a light green color and linear dimensions $0.35 \times 0.05 \times 0.05 \text{ mm}$. The reflections from 532 frames were measured in four series ($\varphi = 0^\circ, 90^\circ, 180^\circ, \text{ and } 270^\circ$) with the ω angle between the frames equal to 0.80° and the recording time 37 s for each frame. The experimental data were processed with the Kuma Diffraction program (Wroclaw, Poland). The intensity data were corrected for the Lorentz and polarization effects. Absorption correction was not applied.

The crystallographic parameters, the summary of data collection, and refinement parameters for structure **I** are given in Table 1. Structure **I** was solved by the

Table 1. Crystallographic parameters and details of data collection and refinement of structure **I**

Parameter	Value
<i>M</i>	319.90
Crystal system	Rhombic
Space group	<i>Pbca</i>
<i>a</i> , Å	12.268(2)
<i>b</i> , Å	6.5730(10)
<i>c</i> , Å	27.798(6)
<i>V</i> , Å ³	2241.6(7)
<i>Z</i>	8
ρ(calcd.), g/cm ³	1.896
μ, mm ⁻¹	1.782
<i>F</i> (000)	1328
Range of θ, deg	3.37–25.01
Range of indices	$-13 \leq h \leq 10, -7 \leq k \leq 7,$ $-17 \leq l \leq 33$
Number of measured/independent reflections, <i>I</i> > 2σ(<i>I</i>)	5321/1657 [<i>R</i> _{int} = 0.0669]
Number of refined parameters	222
Final <i>R</i> -factor [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0443, <i>wR</i> ₂ = 0.096
<i>R</i> -factor (for all reflections)	<i>R</i> ₁ = 0.0589, <i>wR</i> ₂ = 0.1058
GOOF on <i>F</i> ²	1.031
Δρ(max), Δρ(min), e Å ⁻³	0.497, -0.507

heavy-atom method with the SHELX97 program package [7] and refined by the least-squares method in anisotropic full-matrix approximation (isotropic approximation for the hydrogen atoms). Positions of all H atoms were located from the Fourier difference synthesis.

The coordinates of atoms and their thermal parameters in structure **I** are listed in Table 2; the selected bond lengths and angles are presented in Table 3; the geometric characteristics of hydrogen bonds are given in Table 4.

Table 2. Coordinates of atoms (×10⁴) and their equivalent thermal parameters *U*_{eq} (×10³) in structure **I**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
Ni	4843(1)	2214(1)	6666(1)	15(1)
O(1)	3480(3)	3729(5)	6464(1)	21(1)
O(2)	2457(3)	4422(5)	5832(1)	23(1)
O(3)	5678(3)	4791(5)	6813(1)	22(1)
O(4)	6765(3)	7109(5)	6486(1)	24(1)
O(5)	5733(3)	2497(5)	4914(1)	37(1)
O(6)	7114(3)	440(6)	098(1)	30(1)
N(1)	5272(3)	2931(5)	5937(1)	14(1)
C(1)	4217(4)	3065(7)	5686(1)	16(1)
C(2)	3320(4)	3807(7)	6016(1)	16(1)
C(3)	5820(6)	4950(8)	5957(2)	29(1)
C(4)	6119(4)	5653(6)	6459(1)	16(1)
C(5)	5997(5)	1363(8)	5732(2)	25(1)
C(6)	6265(4)	1536(7)	5201(1)	21(1)
O(1w)	4124(4)	2065(5)	7337(1)	26(1)
O(2w)	6261(4)	753(6)	6884(1)	21(1)
O(3w)	4199(3)	-593(5)	6490(1)	24(1)
O(4w)	3136(3)	6772(6)	7158(1)	30(1)

RESULTS AND DISCUSSION

Thermogravimetric study showed that the decomposition of complex **I** proceeded through three endothermic stages and one exothermic stage. The first endothermic effect is observed on a derivatogram in the temperature interval 80–170°C; in terms of the mass loss, it corresponds to elimination of three water molecules (found 17.5%, calcd. 16.9%). In the range of 180–

220°C, one more water molecule is lost (found 6.0%, calcd. 5.6%). At 230–330°C, a broad endothermic effect is observed that corresponds to decarboxylation of one carboxyl group and liberation of the carbon oxide molecule (found 13.0%, calcd. 13.8%). The pronounced exothermic effect and a noticeable mass loss are observed in the temperature interval 340–450°C, confirms a full decomposition of the complex and elimination of its organic part (found 46%, calcd. 45.5%). The final product of the complex pyrolysis is likely to be Ni(II) oxide.

The structural units of crystal **I** are mononuclear complexes [Ni(HNta)(H₂O)₃] and crystallization water molecules (Fig. 1). Previously, isostructural compounds were reported, namely, Co(HNta) · 4H₂O (**II**) [2] and Zn(HNta) · 4H₂O (**III**) [3].

The Ni atom has octahedral coordination; it coordinates tridentate-chelate HNta²⁻ ligand through the N(1) atom and atoms O(1) and O(3) of two deprotonated acetate groups. The vertices of one face of an octahedron are occupied by the atoms of HNta²⁻, while an opposite face is formed by the oxygen atoms of water molecules O(1w), O(2w), and O(3w). The analogous M–L bonds in structure **I** are nonequivalent; they are shorter than in **II** and **III**. The Ni–N(1) distance is equal to 2.146(3) Å (2.215(3) Å for Zn in **III** and 2.205(1) Å for Co in **II**). The M–O bonds (Nta³⁻) are 2.021(3) Å and 2.025(3) Å in **I**, 2.056(1) and 2.055(1) Å in **III**, 2.076(2) Å and 2.078(3) Å in **II**. The average distance M–O(H₂O) in compound **I** is 2.098 Å, whereas in **II**, it is 2.105 Å. Two Ni–O(H₂O) bonds in complex **I** are almost equal (2.065(3) and 2.067(3) Å for O(1w) and O(3w), respectively); the Ni–O(2w) bond is somewhat longer (2.077(4) Å). This can be explained by the fact that in the hydrogen bonding system of a crystal, water molecule w₂ is involved in two donor (with water molecules w₂ and w₃) and one acceptor hydrogen bonds (Table 4).

The HNta²⁻ ligand coordinates a metal and forms two glycinate metal cycles. The NiN(1)C(1)C(2)O(1) (**A**) cycle is more corrugated as compared to cycle **B**: an average deviation of atoms from its mean plane (Δ) is 0.149 Å, while in the NiN(1)C(3)C(4)O(3) cycle (**B**), it is 0.049 Å. The conformation of cycle **A** is a Ni-envelope (for atoms N(1), C(1), C(2), O(1), $\Delta = 0.061$ Å, $\Delta(\text{Ni}) = 0.727$ Å), that of the **B** cycle is a flattened C(3)-envelope (for atoms NiN(1)C(4)O(3), $\Delta = 0.016$ Å, $\Delta(\text{C}(3)) = 0.173$ Å).

Two five-membered metal cycles bring about the distortion of the angular parameters of the Ni polyhedron: the endocyclic angles O(1)NiN(1) (80.4(1)°) and O(3)NiN(1) (83.2(1)°) are the smallest in the NiNO₅ octahedron. The effect of intermolecular interactions on the angular parameters of the Ni coordination polyhedron is confirmed by the high scattering in exocyclic angles O(H₂O)NiO(Nta) and O(H₂O)NiN (from 84.5° to 99.9°).

Table 3. Selected bond lengths and angles in structure **I**

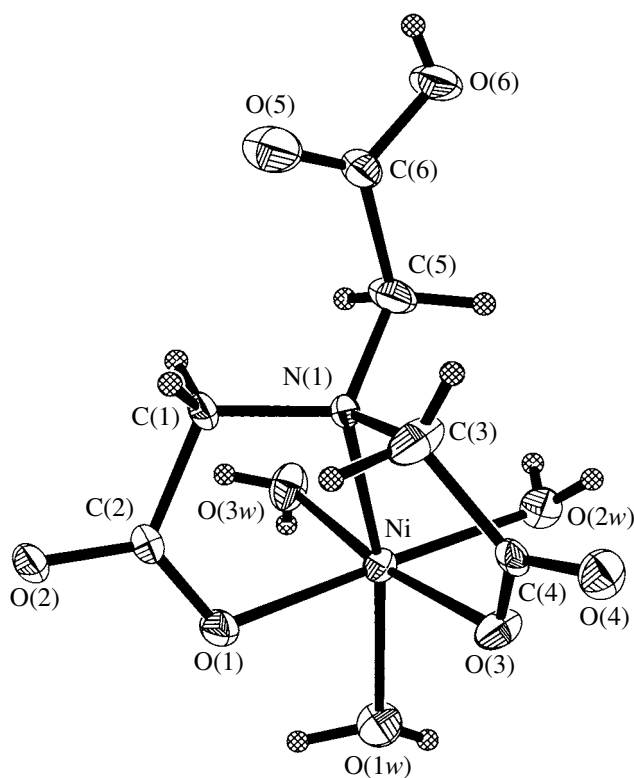
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Ni–O(3)	2.021(3)	O(4)–C(4)	1.245(6)
Ni–O(1)	2.025(3)	O(5)–C(6)	1.209(6)
Ni–O(1w)	2.065(3)	O(6)–C(6)	1.298(6)
Ni–O(3w)	2.067(3)	N(1)–C(1)	1.473(6)
Ni–O(2w)	2.077(4)	N(1)–C(5)	1.476(6)
Ni–N(1)	2.146(3)	N(1)–C(3)	1.489(6)
O(1)–C(2)	1.262(5)	C(1)–C(2)	1.513(6)
O(2)–C(2)	1.244(5)	C(3)–C(4)	1.515(6)
O(3)–C(4)	1.258(5)	C(5)–C(6)	1.518(6)
Angl	ω , deg	Angl	ω , deg
O(3)NiO(1)	93.6(1)	C(1)N(1)C(5)	112.9(4)
O(3)NiO(1w)	94.3(1)	C(1)N(1)C(3)	111.1(4)
O(1)NiO(1w)	85.5(1)	C(5)N(1)C(3)	111.4(5)
O(3)NiO(3w)	171.9(1)	C(1)N(1)Ni	104.2(3)
O(1)NiO(3w)	93.3(1)	C(5)N(1)Ni	111.1(3)
O(1w)NiO(3w)	90.5(1)	C(3)N(1)Ni	105.8(2)
O(3)NiO(2w)	84.5(1)	N(1)C(1)C(2)	111.8(3)
O(1)NiO(2w)	178.0(1)	O(2)C(2)O(1)	123.5(4)
O(1w)NiO(2w)	94.2(2)	O(2)C(2)C(1)	118.3(3)
O(3w)NiO(2w)	88.6(2)	O(1)C(2)C(1)	118.2(4)
O(3)NiN(1)	83.2(1)	N(1)C(3)C(4)	114.5(4)
O(1)NiN(1)	80.4(1)	O(4)C(4)O(3)	124.9(4)
O(1w)NiN(1)	165.4(1)	O(4)C(4)C(3)	116.4(4)
O(3w)NiN(1)	93.7(1)	O(3)C(4)C(3)	118.6(4)
O(2w)NiN(1)	99.8(1)	N(1)C(5)C(6)	117.0(4)
C(2)O(1)Ni	115.0(3)	O(5)C(6)O(6)	125.3(4)
C(4)O(3)Ni	116.0(3)	O(5)C(6)C(5)	124.3(5)
O(6)C(6)C(5)	110.3(4)		

Table 4. Geometric parameters of hydrogen bonds in structure **I**

D–H...A	Distance, Å			DHA angle, deg	Coordinates of atom A
	D–H	H...A	D...A		
O(6)–H(14)...O(2)	0.67(6)	1.95(6)	2.619(4)	172(7)	$x + 1/2, -y + 1/2, -z + 1$
O(1w)–H(1w1)...O(3)	0.82(6)	2.04(6)	2.807(4)	155(5)	$-x + 1, y - 1/2, -z + 3/2$
O(1w)–H(2w1)...O(4w)	0.94(7)	1.88(8)	2.823(6)	178(6)	$-x + 1/2, y - 1/2, z$
O(2w)–H(1w2)...O(4)	0.84(6)	1.92(6)	2.710(5)	157(5)	$x, y - 1, z$
O(2w)–H(2w2)...O(4)	0.77(9)	2.05(9)	2.809(6)	169(9)	$-x + 3/2, y - 1/2, z$
O(3w)–H(1w3)...O(4w)	0.79(6)	2.07(6)	2.855(5)	168(5)	$x, y - 1, z$
O(3w)–H(2w3)...O(2)	0.74(7)	1.99(7)	2.733(5)	176(7)	$-x + 1/2, y - 1/2, z$
O(4w)–H(1w4)...O(1)	0.99(7)	1.82(7)	2.810(5)	173(6)	x, y, z
O(4w)–H(2w4)...O(2w)	0.63(6)	2.23(6)	2.845(5)	167(8)	$-x + 1, y + 1/2, -z + 3/2$

The HNta²⁻ ligand has standard N–C and C–C distances (the average values being 1.479 and 1.515 Å, respectively). The C–O distances in the deprotonated acetate groups coordinated to a metal are almost equal

(1.253 and 1.252 Å on the average). The protonated carboxyl group is not involved in coordination with nickel. The difference in the distances C(6)–O(5) 1.209(6) Å and C(6)–O(6) 1.298(6) Å corresponds to standard difference in the length of a single and double bonds in the COOH groups. This agrees with the fact that in the most strong hydrogen bond O(6)–H(14)...O(2) (O...O 2.619(4) Å), the proton is bonded to the O(6) atom.

**Fig. 1.** The structure of [NiHNta(H₂O)₃] complex.

All oxygen atoms in the HNta²⁻ ligand (except for O(5)) and the O atoms of the water molecules participate in intermolecular hydrogen bonds (Table 4) that unite the [Ni(HNta)(H₂O)₃] complexes and solvate water molecules into three-dimensional network. A fragment of the crystal structure **I** is shown in Fig. 2. Every structural unit [Ni(HNta)(H₂O)₃] is linked to the neighboring six complexes through hydrogen bonds. The coordinated water molecules are involved in either two donor (w1 and w3) or two donor and one acceptor hydrogen bonds (w2), whereas crystallization water molecule w4 is involved in two donor and two acceptor hydrogen bonds.

The study of isostructural compounds of Ni, Co, Zn with monoprotonated nitrilotriacetic acid **I**, **II**, and **III**, respectively, revealed their close structures and showed that the protonation of one acetate chain results in the formation of mononuclear complexes [M(HNTA)(H₂O)₃].

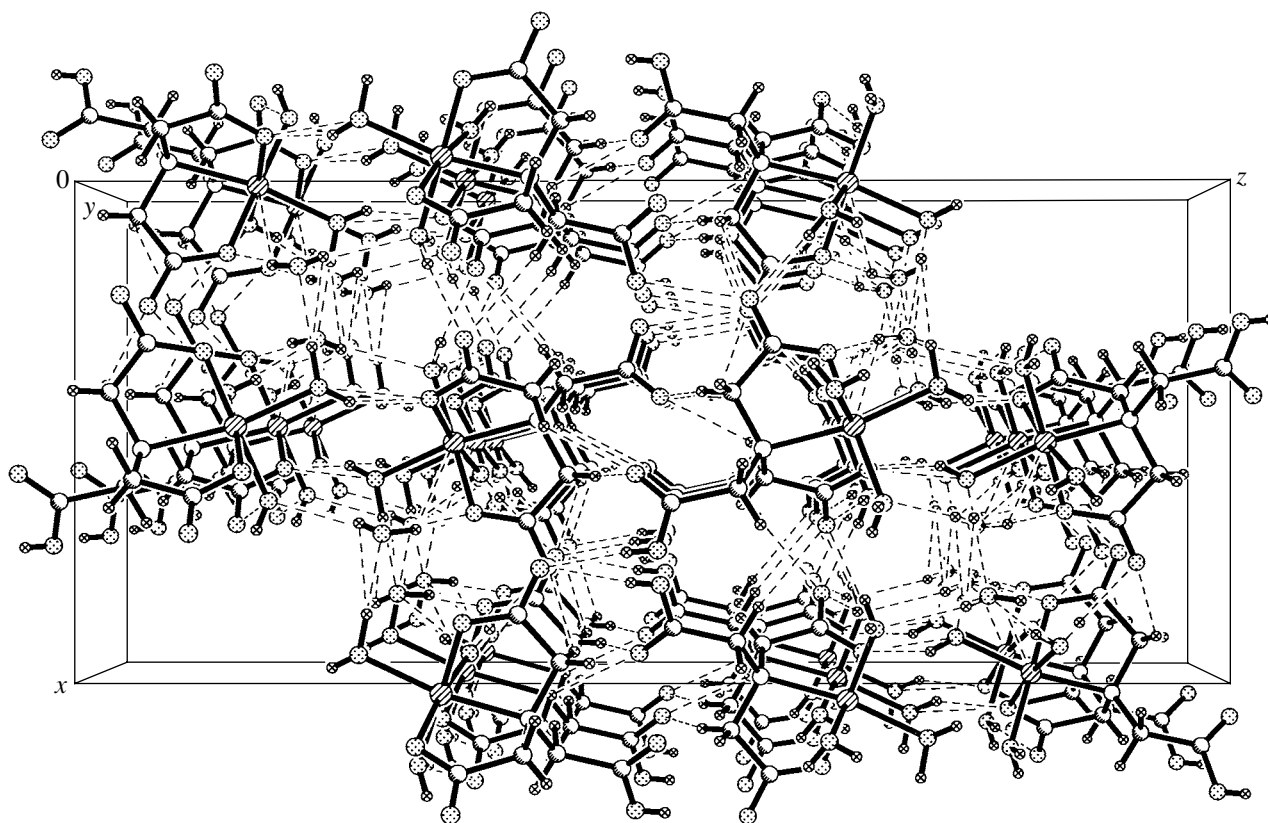


Fig. 2. A fragment of crystal structure of $[\text{NiHNTa}(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$.

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