

Research Article

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Synthesis, Structure and Thermogravimetric Analysis of Two Ni (II) Complexes Based on Pyridine-2,4,6-tricarboxylic Acid

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Abstract. Two new Ni(II) complexes based on pyridine-2,4,6-tricarboxylic acid, [Ni(Hpyta)(H₂O)₂(NM-3Py)].4H₂O (1) and [Ni₃(pyta)₂(H₂O)₈].4H₂O (2) (H₃pyta = pyridine-2,4,6-tricarboxylic acid; NM-3py = N-methyl-3-pyridinamine) were synthesized by hydrothermal methods. The complexes were characterized by elemental analysis, IR spectrum and single-crystal X-ray diffraction. Complex 1 crystallizes in the triclinic system and belongs to P-1 space group, with crystallographic data a = 7.13408(8) Å, b = 11.0133(16) Å, c = 13.6180 (18) Å, α = 66.585(13)°, β = 76.670(11)°, γ = 88.186(10)°, V = 977.3(3) Å³; complex 2 crystallizes in the monoclinic crystal system and belongs to P2₁/c space group, with crystallographic data a=0.71356(16) Å, b=1.8574(4) Å, c=1.0761 (2) Å, α=90°, β=103.225(3)°, γ=90°, V=1388.3(5) Å³. TGA curves show that these complexes first removes water molecules and then the ligand, the remained residue being NiO.

Supporting information: X-Ray (Cif file), IR**Keywords:** Nickel (II), synthesis; structure ; thermogravimetric; pyridine-2,4,6-tricarboxylic acid.

1. INTRODUCTION

Synthesis and structural analysis of coordination polymers based on organic carboxylic acids and transition metal ions are of particular interest in coordination chemistry and materials science and their potential application and multifarious novel structures are attractive to researchers[1-4]. The design and synthesis of metal-organic coordination polymers is of great interest due to their novel structural topologies examined and potential applications in host-guest chemistry, catalysis, and electrical conductivity[5-7]. In the rational design and synthesis of metal-organic coordination compounds several factors, such as the coordination nature of metal ions, the functionality, flexibility and symmetry of organic ligands, and the template effect of structure-directing agents, are taken into consideration[8-10]. 3- and 4-pyridinecarboxylate have recently been found to act as excellent building blocks with charge and multi-connecting ability in the construction of functional coordination polymers with porosity, photo-luminescent or magnetic properties[11-12]. Compared to the previously investigated pyridinecarboxylate

ligands, pyridine-2,4,6-tricarboxylic acid (H₃pyta) has the advantages of multiple bridging moieties, which leads to a variety of connection modes with transition metal centers and provides abundant structural motifs. It can act not only as N-donors but also as O(carboxylate)-donors to chelate or bridge metal ions to coordination polymers[13]. It has been reported that pyridine-2,4,6-tricarboxylic acid and suitable metal ions have been used to construct coordination polymers with magnetic and fluorescence properties[14-19]. In this paper, we report the synthesis and characterization of two new Ni(II) complexes based on pyridine-2,4,6-tricarboxylic acid: [Ni(Hpyta)(H₂O)₂(NM-3Py)].4H₂O (1) and [Ni₃(pyta)₂(H₂O)₈].4H₂O (2).

2. EXPERIMENTAL

All solvents and chemicals were commercial reagents and used without further purification. Pyridine-2,4,6-tricarboxylic acid was synthesized according to references[4]. C, H and N elemental analysis were performed in a Perkin-Elmer 240 elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet 5DX FT-IR spectrometer. The crystal structure was determined by an Agilent SuperNOVA diffractometer. The thermal stability of complexes was tested in the range from 45 to 1000°C under a nitrogen atmosphere at a heating rate of 5° C.min⁻¹ using a Pyris Daimond TG-DTG Analyzer.

2.1 Synthesis of [Ni(Hpyta)(H₂O)₂(NM-3Py)].4H₂O (1)

A mixture of NiCl₂·6H₂O (0.0476 g, 2 mmol), H₃pyta (0.0211 g, 1 mmol), NaOH (0.0120 g, 0.3 mmol), N-Methyl-3-pyridinamine (0.0108 g, 1 mmol) and 10ml water was stirred at room temperature for 30 min and then sealed in a 23 ml Teflon-lined stainless steel autoclave. The mixture was heated in an oven at 90 °C for one day, and cooled to room temperature at a rate of 4 °C.h⁻¹. Green crystals of compound 1 were obtained. Yield: 30%.(based on H₃pyta). Anal. Calcd for C₁₄H₂₄NiN₃O₁₂: C, 34.67; H, 4.99; N, 8.66. Found: C, 34.67; H, 4.81; N, 8.71. IR(cm⁻¹): 3751m, 3423s, 2348w, 1670s, 1615s, 1430w, 1377s, 1365w, 1287w,1113w, 921w, 744m, 521m, 513w.

2.2 Synthesis of [Ni₃(pyta)₂(H₂O)₈].4H₂O (2)

A mixture of NiCl₂·6H₂O (0.0724g, 3mmol) and H₃pyta (0.0211g, 1mmol) was dissolved in 7ml of distilled water and 3ml of ethanol. The pH was adjusted to 7 with 1M NaOH, and

then the solution was sealed in a 23 ml Teflon-lined stainless steel autoclave and heated in an oven at 100 °C for two days, and cooled to room temperature at a rate of 10 °C.h⁻¹. Green crystals of compound 2 were obtained. Yield: 86%.(based on H₃pyta). Anal. Calcd for C₁₆H₂₈Ni₃N₂O₂₄: C, 23.77; H, 3.49; N, 3.46. Found: C, 23.81; H, 3.41; N, 3.52. IR(cm⁻¹): 3853m, 3747m, 3429s, 2348w, 1607s, 1430w, 1383s, 1289w,1113w, 926w, 748m, 524m.

2.3 Crystallographic Data Collection and Refinement.

Single-crystal X-ray diffraction data were collected on a Agilent supernova diffractometer equipped with graphite-monochromated Mo K α radiation with radiation wavelength 0.71073 Å at 293(2) K, by using the x-scan technique. The structures of 1 and 2, were solved by direct methods using SHELXS-2013, and refined by full-matrix least-squares on F² using the Olex2 program[20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically and refined isotropically with the riding mode. Crystallographic crystal data and structure processing parameters for complexes 1 and 2 are summarized in Table 1 (S1). Selected bond lengths and bond angles for complexes 1 and 2 are listed in table 2(SI), Hydrogen bonds for complexes 1 and 2 are listed in table 3(SI). CCDC: 971011 for compound 1, and 1000880, for compound 2.

3. RESULTS AND DISCUSSION

3.1 Synthesis

It is well know that in hydrothermal methods of synthesis there is a variety of parameters such as temperature, time, pH, and

molar ratio of reactants to be considered and small changes in one or more of those parameters can have a profound influence on the final reaction outcome[21].

2D coordination polymers based on trinuclear [Ni₃(pyta)₂] units has been synthesized by reaction of Ni(CH₃COO)₂·4H₂O, H₃pyta, NM-3py and NaOH in 1:2:2:2, molar ratio in suitable hydrothermal systems at 185 °C [18].

Considering the various connection modes of H₃pyta ligand, the complex 2, based on trinuclear [Ni₃(pyta)₂] units, was obtained by reaction of NiCl₂·6H₂O, H₃pyta, and NaOH in the molar ratio of 3:1:3 in the hydrothermal system at 100 °C., i.e. NM-3py was not added. When the auxiliary ligand, NM-3Py, was added complex 1 was obtained (i.e. by reaction of NiCl₂·6H₂O, H₃pyta, NM-3Py, and NaOH in the molar ratio of 2:1:1:0.3 in the hydrothermal system at 90 °C).

3.2 Structure description of Complex 1

X-ray single-crystal diffraction analysis reveals that complex 1 crystallizes in triclinic system, *P*-1 space group. The coordination environment of Ni(II) in complex 1 is shown in Fig. 1a. The asymmetric unit consists of one Ni(II) ion, one deprotonated Hpyta²⁻ ligand, one NM-3Py ligand, two coordinated water molecules, and four free water molecules.

The Ni(II) ion in **1** is coordinated by two nitrogen atoms of deprotonated Hpyta²⁻ ligand and NM-3Py ligand (N(1), N(2)) and four oxygen atoms (O(1) and O(3) from deprotonated Hpyta²⁻ ligand, while O(5) and O(6) are from two coordinated water molecules). The center Ni(II) ion in **1** is six-coordinated. The Ni–O distances fall in the range of 2.074(2) to 2.2953 (17) Å. The Ni–N distance fall in the range of 1.972(2) to 2.043(2) Å. The bond angles of O(1)–Ni(1)–N(1) and O(5)–Ni(1)–O(6) are 77.79(7)° and 177.06(8)°, respectively. All bond angles and

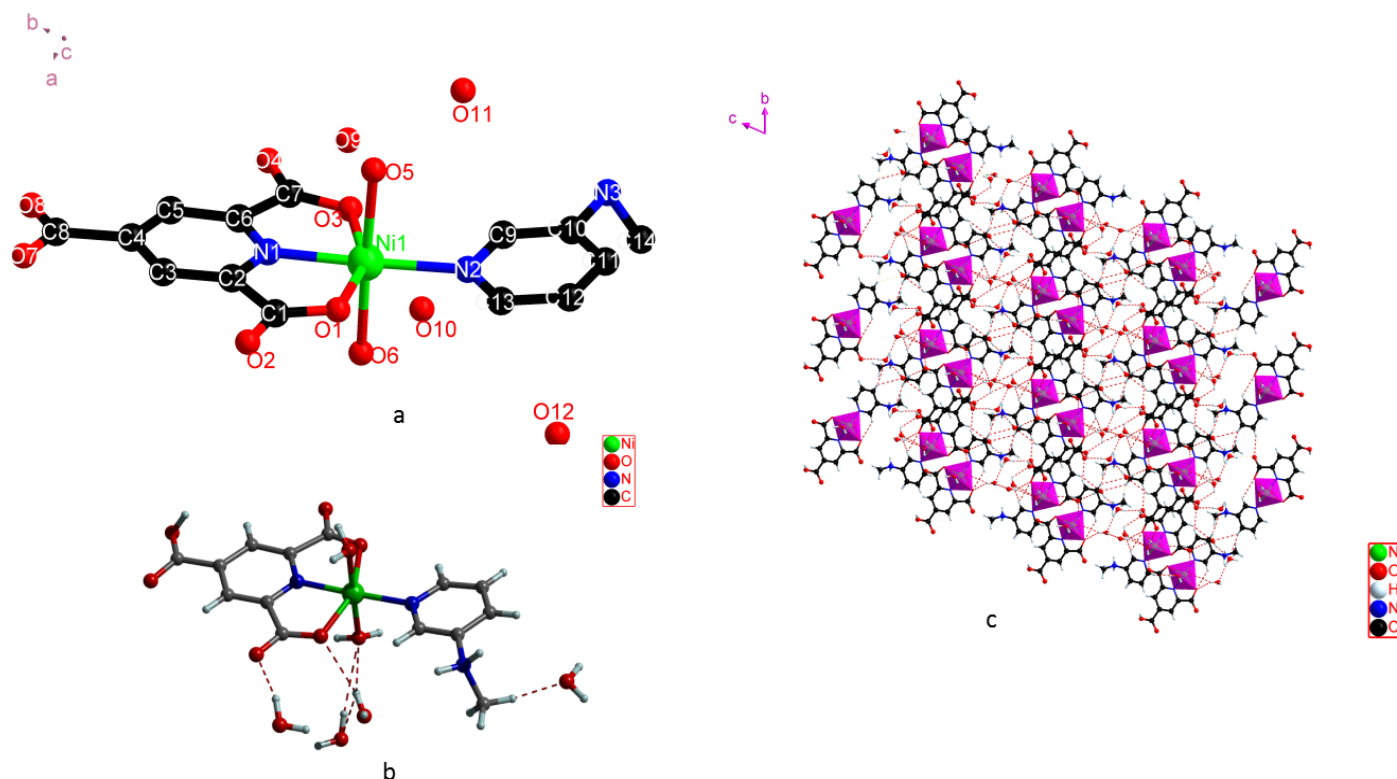


Figure 1: (a) molecular structure with thermal ellipsoids at 50% level (hydrogen atoms have been removed), (b) intramolecular hydrogen bonds, (c) 2D structure (a-axis), for complex **1**.

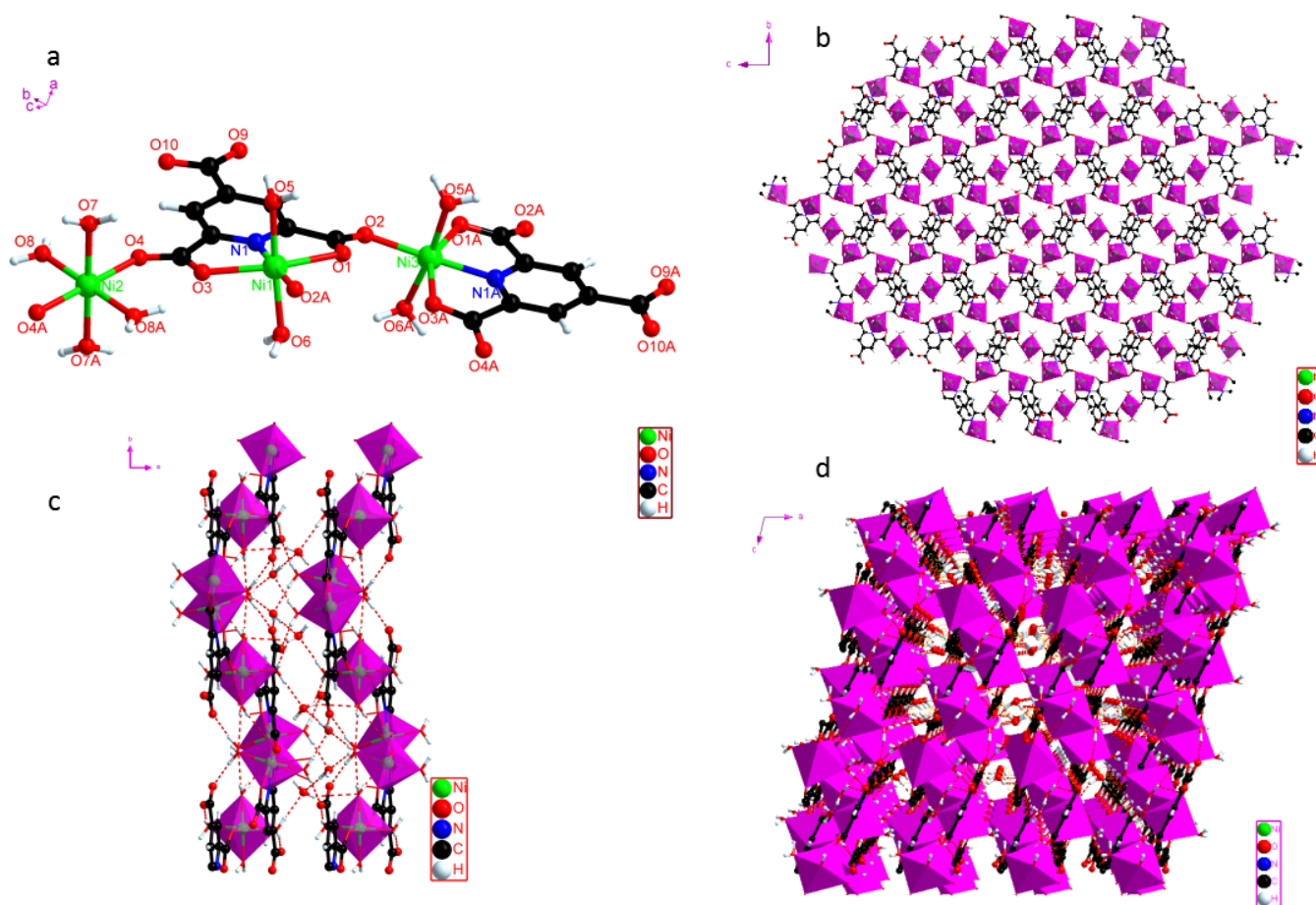


Figure 2: (a) molecular structure with thermal ellipsoid at 50% level (hydrogen atoms have been removed), (b) the two-dimensional network structure along a axis, (c) Hydrogen bonds forming a 2D structure, (d) 3D structure (b-axis) formed by hydrogen bonds, for complex 2.

bond distances fall in normal ranges[13,18].

There are four free water molecules and two coordinated water molecules in the complex 1 (Fig.1a) and due to its presence, complex 1 has not only intramolecular but also intermolecular hydrogen bonds (Fig.1b). Meanwhile a two-dimensional structure along an axis was formed by hydrogen bonds between coordinated water molecules (Fig. 1c).

X-ray single-crystal diffraction analysis reveals that complex 2 crystallizes in monoclinic crystal system, $P2_1/c$ space group. The coordination environment of Ni(II) in 2 is shown in Fig. 2a. The asymmetric unit consists of three Ni(II) ions, two deprotonated pyta^{3-} ligand, eight coordinated water molecules, and four free water molecules.

There are three separate Ni(II) ions and two coordination modes in complex 2. The first Ni(II) ion coordination mode (Ni1 and Ni1A, Fig. 2a) is by one nitrogen atom, three oxygen atoms from deprotonated pyta^{3-} ligand and two coordinated water molecules. The other Ni(II) ion coordination mode (Ni2, Fig 2a) is by six oxygen atoms (two oxygen atoms from different deprotonated pyta^{3-} ligand and four oxygen atoms from coordinated water molecules). These two different Ni(II) ions in complex 2 both are six-coordinated. The Ni–O distances fall in the 2.0228 (15) to 2.1317 (18), Å range. The Ni–N distance is 1.9972 (17) Å. The bond angles of N(1)—Ni(1)—O(1) and O(4)B—Ni(2)—O(4) are 74.65 (6)° and 180.0°, respectively. These bond angles and bond distances fall in observed normal ranges for analogous compounds[13,18].

In complex 2, the five coordination sites on the pyta^{3-} ligand are involved in the coordination. So, the pyridine-2,4,6-tricarboxylic acid ligand adopts a $\mu_5\text{-}\eta_1:\eta_2:\eta_2$ bridging style to participate in coordination. Two O atoms from carboxyl of ligand are coordinated with two Ni(II) ions, so carboxyl adopts a $\mu_2\text{-}\eta_1:\eta_1$ bridging style to participate in the coordination. As the ligand adopts a $\mu_5\text{-}\eta_1:\eta_2:\eta_2$ bridging style and carboxyl takes a $\mu_2\text{-}\eta_1:\eta_1$ bridging style, the complex 2 exhibits a very special two-dimensional network structure along an axis (See Fig. 2b).

Owing to the introduction of water molecules, complex 2 has a large number of hydrogen bonds. Complex 2 has not only intramolecular but also intermolecular hydrogen bonds. The O atom in carbonyl group on the ligand formed $\text{O-H}\cdots\text{O}$ intramolecular hydrogen bonds with coordinated water molecules and between coordinated water molecules. These four free water molecules in 2 formed $\text{O-H}\cdots\text{O}$ intermolecular hydrogen bonds with coordinated water molecules (Fig.2c). These hydrogen bonds finally generating a three-dimensional network structure along b axis (Fig. 2d).

3.4 XRD spectra

In order to check the purity of complexes 1 and 2, powder X-ray diffraction of the as-synthesized sample was measured at room temperature. The peak positions of experimental patterns are in good agreement with the simulated ones, which clearly

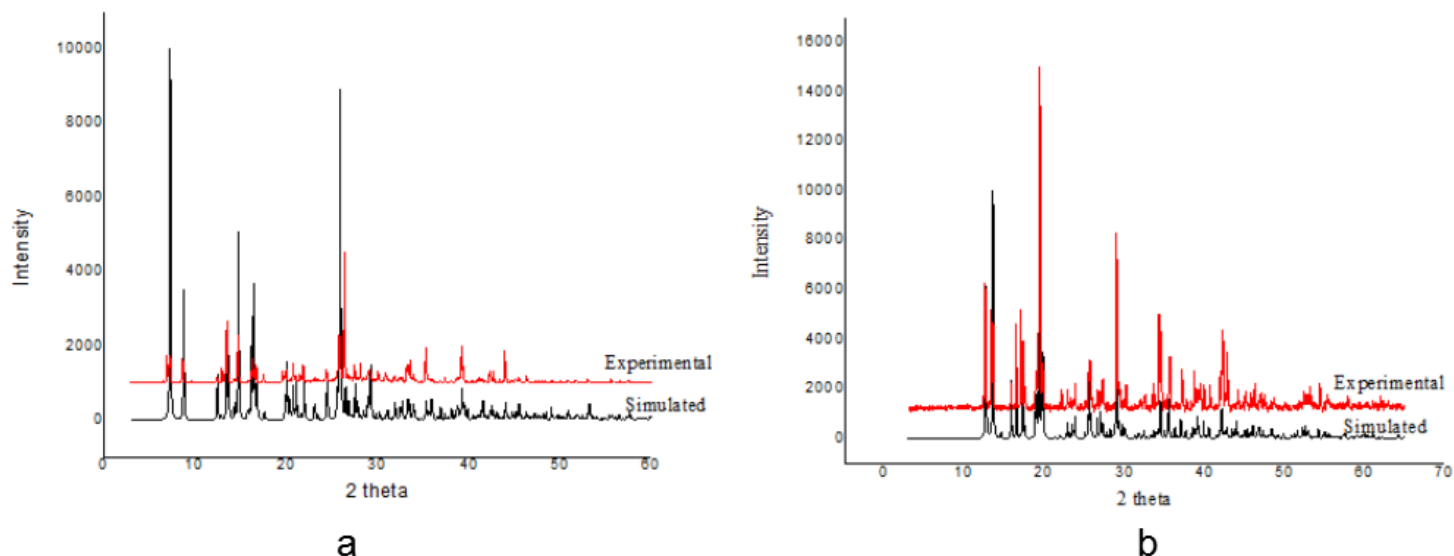


Figure 3 Powder diffraction for a, complex 1; b, complex 2. In red, experimental; in black, simulated.

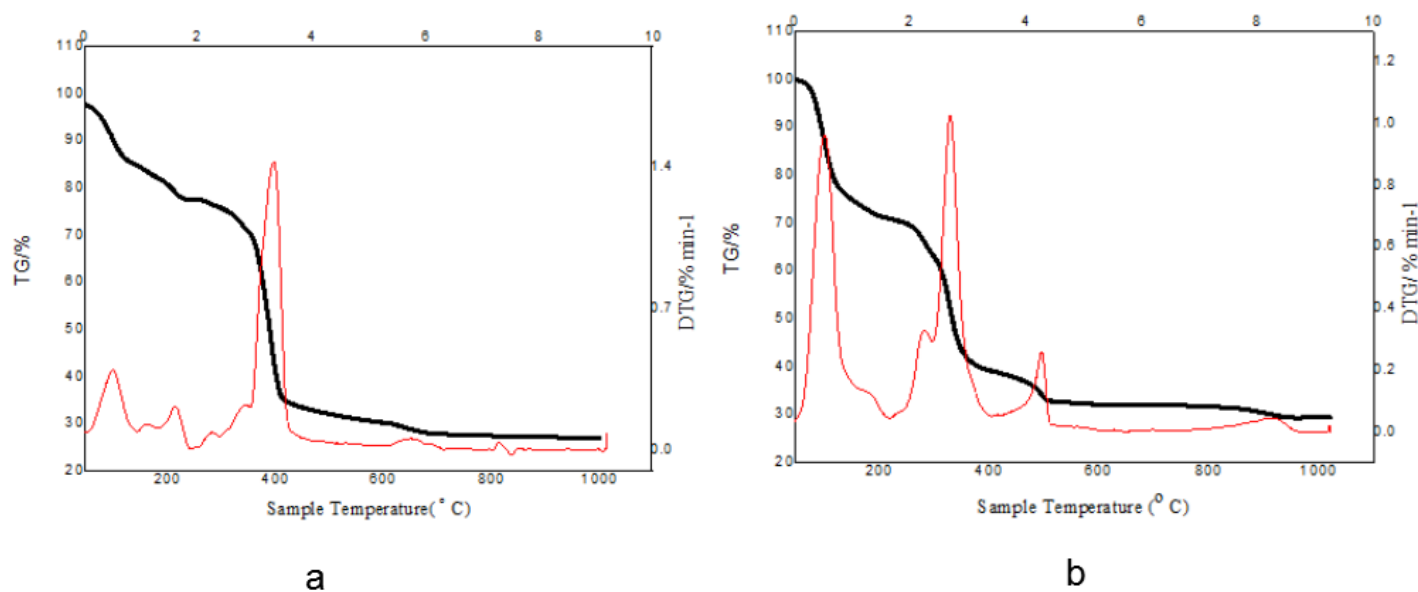


Figure 4 TG (black) and DTG (red) curves for complexes 1 and 2.

indicates good purity of the complexes 1 and 2. The powder diffraction of complexes 1 and 2 are shown in Fig.3a and Fig. 3b, respectively.

3.5 Thermal Gravimetric Analysis of Complexes 1 and 2.

TG and DTG curves for complexes 1 and 2 are shown in Fig. 4. The thermal gravimetric analysis curves show that the complexes first lose water molecules, then the ligand split, being the residue NiO.

Thermal gravimetric curve for complex 1 shows that it loses four free water molecules (observed 14.67%, calculated 14.86%) in the 45 °C to 131 °C range; then it loses two coordinated water molecules (observed 7.72%, calculated 7.42%) in the 131°C to 228°C range; further weight loss is responsible for all organic components as it is observed in the 228°C to 659°C range; the remaining amount, 26,57%, could be attributed to NiO and some impurities, Fig. 4a.

Thermal gravimetric curve for complex 2 shows that it loses twelve water molecules (observed 23.52 %, calculated 26,74 %)

in the 45 °C to 123 °C range; further weight loss is responsible for all organic components as it is observed in the 123 °C to 503 °C range; the remaining amount, 28,79%, could be attributed to NiO, and some impurities, Fig. 4b.

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