

# Synthesis and Structure of a Hybrid Metal Phthalate Compound and Its Magnetic Property

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**Abstract.** The hybrid transition metal – alkali metal compound,  $[\text{Ni}(\text{H}_2\text{O})_6 \cdot (\mu\text{-H}_2\text{O})_2 \cdot \text{K}_2(\text{phth})_4(\text{H}_2\text{O})]$ , (phth = phthalate) (**1**), was synthesized from nickel(II) nitrate, KOH and potassium hydrogen phthalate, and was isolated by crystallization. Single-crystal X-ray analysis revealed that **1** belongs to the monoclinic system, space

group  $P2_1/c$  with  $a = 10.455(2) \text{ \AA}$ ,  $b = 6.8670(14) \text{ \AA}$ ,  $c = 29.704(6) \text{ \AA}$ ,  $\gamma = 98.14(3)^\circ$ ,  $R_1 = 0.0585$ ,  $wR_2 = 0.1503$ . In the title compound,  $[\text{K}_2(\text{phth})_4]^{2+}$  units are bonded to water-bridged Ni chains forming 2D lamellar-like compounds.

## Introduction

The rational design and synthesis of metal-organic framework compounds have received much attention in coordination chemistry because of their interesting molecular topologies and their tremendous potential applications in catalysis, molecular selection, non-linear optics, ion exchange and microelectronics [1–4]. During the past decade, many high-dimensional (especially two- and three-dimensional) coordination compounds have been designed and synthesized through symmetrical organic aromatic polycarboxylate ligands owing to their high symmetry and structural predictability [5–9]. In contrast, asymmetrical carboxylates remain largely unexplored for coordination compound synthesis. However, the strong curiosity for unknown structures increasingly evokes researchers' great interest for asymmetrical ligands. In general, asymmetric geometry may lead to more intriguing network topologies than can be achieved with symmetric ligands.

The o-phthalate anion is an excellent ligand, which has been efficiently used for creating an extensive range of supramolecular coordination compounds [10–16]. This fact is due to its coordination versatility, which ranges from monodentate up to heptadentate modes [10–16]. Here we report on the synthesis, characterization, and crystal structure of a hybrid metal phthalate compound which is synthesized by divalent transition metal Ni salt and phthalate acid in the presence of alkali metal (K) hydrate.

## Experimental Section

### Synthesis of $[\text{Ni}(\text{H}_2\text{O})_6 \cdot (\mu\text{-H}_2\text{O})_2 \cdot \text{K}_2(\text{phth})_4(\text{H}_2\text{O})]$ (**1**)

All the reagents were of AR grade and used without further purification. Potassium hydrogen phthalate (0.2040 g, 1 mmol) was dissolved in 10 mL EtOH/H<sub>2</sub>O (V:V = 1:1) solution, and then the resultant solution was added in 10 mL double-distilled water containing  $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.237 g, 1 mmol). The mixed solution was acidified with  $1 \text{ mol} \cdot \text{L}^{-1}$  KOH to pH = 8. The resulting solution was heated at 425 K for 96 h. After cooling to room temperature, green crystals were obtained in a yield up to 42.23 %.

### Structure Determination of **1**

**X-ray Crystallography.** Suitable single crystals of **1** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a siemens SMART CCD diffractometer with graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 291 K. An empirical absorption correction was applied using the SADABS program [17]. The structures were solved by direct methods and refined by full-matrix least-squares methods on  $F^2$  by using the SHELX-97 program package [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of phthalate acid were generated geometrically. Most hydrogen atoms of water molecules were constrained to ride on their parent atoms. The crystallography details for the structure determination of **1** are presented in Table 1. Selected bond distances and bond angles are listed in Table 2.

## Results and Discussion

### Crystal Structures

It is worth noting the coordination mode of phthalate ligand, which exhibits a great variety of bonding geometries such as monodentate [19], 1,3-chelating [20] and 1,6-chelating [21–24]. Neutral compound **1** possesses the simplest unit of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{K}_2(\text{phth})_4(\text{H}_2\text{O}) \cdot (\mu\text{-H}_2\text{O})_2]^{2-}$ , as

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**Table 1.** Crystal data and structure refinement parameters for **1**

Formula	C <sub>32</sub> H <sub>40</sub> K <sub>2</sub> NiO <sub>26</sub>
Molecular mass	977.55
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	10.455(2)
<i>b</i> /Å	6.8670(14)
<i>c</i> /Å	29.704(6)
$\beta$ /°	98.14(3)
<i>V</i> /Å <sup>3</sup>	2111.0(7)
<i>Z</i>	2
<i>T</i> /K	291(2)
<i>D</i> <sub>calc</sub> /g·cm <sup>−3</sup>	1.538
<i>F</i> (000)	1012
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.062
Final <i>R</i> indices	<i>R</i> 1 = 0.0585
[ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	<i>wR</i> <sub>2</sub> = 0.1503
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0658
	<i>wR</i> <sub>2</sub> = 0.1558

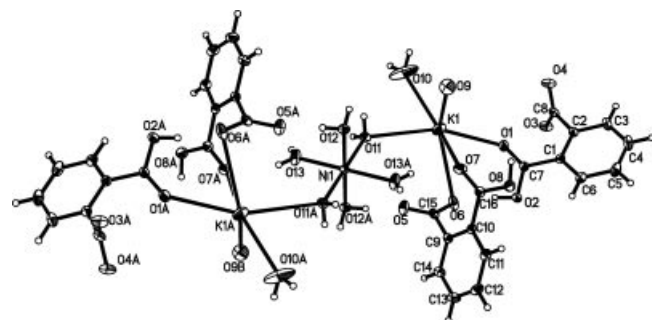
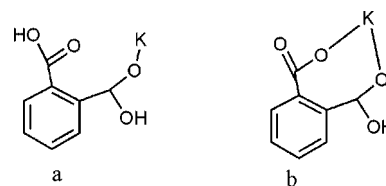
$$R_1 = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|; wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{0.5}$$

**Table 2.** Selected bond lengths /Å and angles /° for **1**

Ni(1)–O(13)#1	2.049(3)	O(13)#1–Ni(1)–O(13)	91.86(11)
Ni(1)–O(13)	2.049(3)	O(13)#1–Ni(1)–O(11)#1	90.3(2)
Ni(1)–O(11)#1	2.076(2)	O(13)–Ni(1)–O(11)#1	88.14(11)
Ni(1)–O(12)	2.082(2)	O(13)#1–Ni(1)–O(11)	88.14(11)
K(1)–O(10)	2.694(5)	O(13)–Ni(1)–O(11)	91.86(11)
K(1)–O(7)	2.745(3)	O(11)#1–Ni(1)–O(11)	180.00(13)
K(1)–O(1)	2.876(3)	O(13)–Ni(1)–O(12)	91.07(12)
K(1)–O(12)#2	2.933(3)	O(11)#1–Ni(1)–O(12)	87.99(10)
K(1)–O(9)	2.955(6)	O(10)–K(1)–O(1)	133.61(18)
K(1)–O(9)#3	3.053(6)	O(10)–K(1)–O(12)#2	73.13(17)

Symmetry transformations used to generate equivalent atoms:  
 #1  $-x+2, -y-4, -z-1$  #2  $x, y+1, z$  #3  $-x+1, -y-3, -z-1$

shown in Figure 1. In the structure of [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> cation, the nickel ion is coordinated by six water, exhibiting trivially elongated octahedron. The Ni–O distances range from 2.050(3) to 2.081(3) Å. In the structure the potassium atoms exhibit eight-coordinate environments consisting of three carboxyl O atoms from two phthalate acids, as well as three bridging and one terminal water molecule. One Phth<sup>2−</sup> ligand acts as monodentate (scheme 1(a)), whereas the other behaves both as 1,6-chelating being coordinated to nickel atoms as is shown by the structure representation scheme 1(b).

**Figure 1.** View of **1** with 30 % probability ellipsoid.**Scheme 1.**

The phthalate ligand shows a high degree of self-organization upon compound formation. Dihedral angles between the carboxylate groups and aromatic rings range from 23.932(3) to 88.4722(3)°. Delocalization of electron density over the carboxylate groups is observed, which is typical for the part deprotonated RCOO<sup>−</sup> fragments. The C–O distances range from 1.216(5) to 1.320(4) Å. In **1** the redistribution of electron density occurs over chelating and monodentate carboxylate groups. The C(sp<sup>2</sup>)–COO distances ranging from 1.492(5) to 1.517(5) Å can be considered as single bonds. The mean C–C distances in the aromatic rings are 1.3961 Å. An interesting aspect of this crystal structure is the hydrogen-bonding pattern.

The partly deprotonation of both carboxylate groups in *o*-phthalic acid makes impossible the formation of hydrogen bonds. Van der Waals and weak C–H⋯O contacts are the only interactions between the chains.

In the crystal structure, the molecules are linked via three intermolecular O–H⋯O hydrogen bonds, forming a three-dimensional network (details are given in Table 3 and Fig. 2). The compound **1** form a three-dimensional network through intermolecular hydrogen bonds with the counter anions and water molecules. Details of the compound hydrogen-bonding scheme can be created from the deposited cif-files.

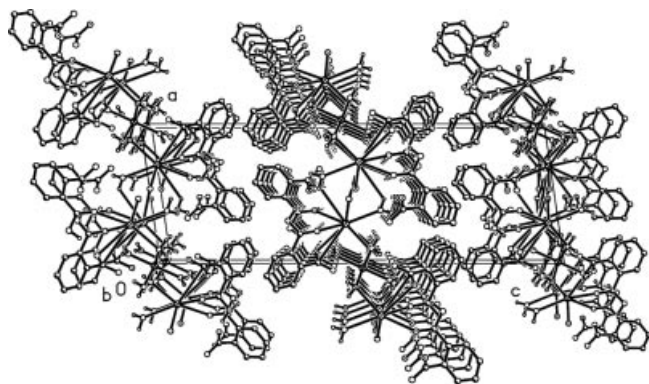
**Table 3.** Hydrogen-bonding parameter and close contacts /Å, ° for **1**

D–H⋯A	<i>d</i> (D–H)	<i>d</i> (H⋯A)	<i>d</i> (D⋯A)	<(DHA)
O(8)–H(8E)⋯O(3)#4	0.95(4)	1.60(4)	2.546(4)	176(6)
O(10)–H(10F)⋯O(1)#3	0.89(7)	2.26(8)	3.145(8)	172(9)
O(11)–H(11E)⋯O(4)#3	0.85(3)	1.94(4)	2.769(4)	165(4)
O(12)–H(12E)⋯O(4)#3	0.85(4)	1.92(5)	2.732(4)	159(6)
O(13)–H(13E)⋯O(7)#1	0.85(4)	2.14(5)	2.947(5)	162(6)
O(12)–H(12F)⋯O(5)#1	0.85(4)	1.86(4)	2.689(4)	167(4)
O(11)–H(11F)⋯O(5)#5	0.85(5)	1.86(4)	2.696(4)	168(5)
O(13)–H(13F)⋯O(6)#5	0.79(5)	1.93(5)	2.714(4)	175(5)
O(10)–H(10E)⋯O(3)#6	0.89(3)	2.10(5)	2.809(6)	136(6)
O(2)–H(2E)⋯O(6)	0.89(4)	1.69(4)	2.576(4)	174(5)

Symmetry transformations used to generate equivalent atoms:  
 #1  $-x+2, -y, -z+1$ ; #2  $x, y+1, z$ ; #3  $-x+1, -y+1, -z+1$ ; #4  $x, y-1, z$ ; #5  $-x+2, -y+1, -z+1$ ; #6  $-x+1, -y+2, -z+1$

### IR Spectra

In compound **1**, a strong and broad band has been observed at 3339 cm<sup>−1</sup> was assigned to ν(OH) absorption with the hydrogen bonds or water molecules. The bands of 1585 and 1366 cm<sup>−1</sup> are showed in IR spectra are related to

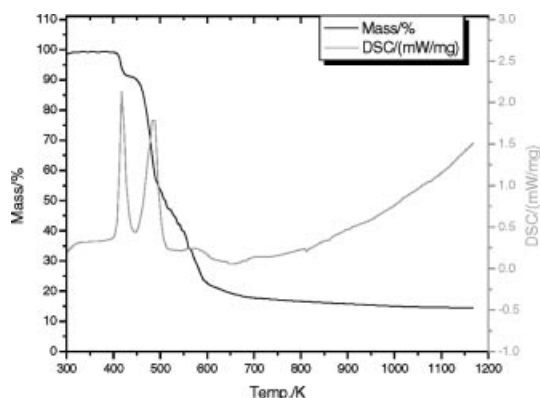


**Figure 2.** Packing of **1** showing a three-dimensional network.

$\nu_{\text{asym}}(\text{OCO}^-)$  and  $\nu_{\text{sym}}(\text{OCO}^-)$ , respectively. For the compound **1**, the  $\Delta(\nu_{\text{as}} - \nu_{\text{s}})$  values is larger than  $200 \text{ cm}^{-1}$ , which is a general indication of unidentate or unsymmetrical bridging coordination [25]. Chelating carboxyl vibration leading to a small  $\Delta(\nu_{\text{as}} - \nu_{\text{s}})$  value was not found.

### TG-DTG Properties

The TGA diagrams (Fig. 3) show the compound **1** exhibits obvious weight loss of seven water molecules between 390–430 K (11.2 % weight loss observed; 12.6 % calculated). In  $[\text{Ni}(\text{H}_2\text{O})_6 \cdot (\mu\text{-H}_2\text{O})_2 \cdot \text{K}_2(\text{phth})_4(\text{H}_2\text{O})]$ , the second mass loss stage with 39.92 % starts at 430 K and ends at 620 K while reaching its highest rate at 486.6 K, if four phthalates ligands are lost at this stage, the mass loss will be 74 %. It is inferred that four phthalates are lost at this stage. The residues are 16 % of the total mass, and at the same time certain types of compound formed in the residues. Thus, the two mass loss stages together with the exothermic process in DSC curves are assigned to the decomposition of the coordination compound and the formation of non-crystalline inorganic compounds.

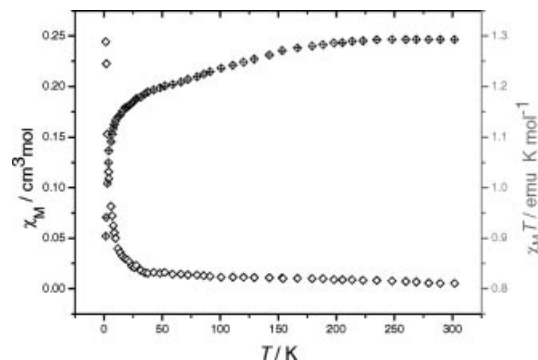


**Figure 3.** TG-DTG curves of polymer **1**

### Magnetic Properties of Compounds **1**

Magnetic susceptibility measurements of compound **1** were performed on crushed crystals of the compound. Ran-

dom crystals from the batches were selected from the samples and subjected to unit cell determinations. The magnetic susceptibilities of compound **1** were measured in the 2–300 K temperature range and are shown as  $\chi_m$  and  $\chi_m T$  versus  $T$  plots in Figure 4. The magnetic moment per  $\text{Ni}^{\text{II}}$  ( $3.16 \mu\text{B}$ ) is close to the expected spinonly value for  $S = 1$  ion ( $2.97 \mu\text{B}$  for  $g = 2.1$ ). Upon cooling from room temperature, the  $\chi_m T$  value increases continuously from  $1.235 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K to a maximum of  $1.296 \text{ cm}^3 \text{ K mol}^{-1}$  at 18 K, this behavior is characteristic of a ferromagnetic coupling between the  $\text{Ni}^{\text{II}}$  ions.



**Figure 4.**  $\chi_m$  and  $\chi_m T$  vs.  $T$  plots for **1**.

**Supplementary data:** Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC: 662312. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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