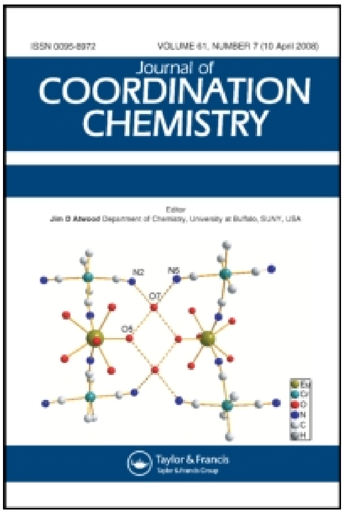

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Synthesis, crystal structure and magnetic properties of a 1D coordination polymer[Ni(phth)(phen)(H_2O)]$_n$ · $n$$H_2O$

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A new one-dimensional coordination polymer [Ni(phth)(phen)(H_2O)]$_n \cdot n$$H_2O$ was synthesized. The structure was determined by X-ray crystallography revealing that each nickel atom is five-coordinate bridged via phthalate ion to form a zigzag chain. The chains are further linked together via hydrogen-bonding interactions to construct a three dimensional supramolecular network. The magnetic properties of the complex show that there are weak antiferromagnetic interactions between Ni(II) centers.

Keywords: Synthesis; Coordination polymer; Crystal structure; Magnetic properties

1. Introduction

Self-assemblies based on building blocks and metal centers have attracted considerable interest in coordination chemistry and crystal engineering for the construction of a variety of discrete supramolecules and infinite polymers with wide applications. The main driving forces in such processes include coordination strength, hydrogen bonding, aromatic stacking and other weak interactions [1–5]. The heteroaromatic N-donor ligand 1,10-phenanthroline(phen) has proven to also be a good participator in creating metal organic frameworks because of its strong chelating ability, and the possibility for aromatic stacking interactions [6]. Phthalate(phth) has been used as a bridging ligand for coordination polymers [7–11]. Here we report the synthesis and crystal structure of a new phthalato-bridged nickel coordination polymer, [Ni(phth)(phen)(H_2O)]$_n \cdot n$$H_2O$, forming a 3D-supramolecule by hydrogen-bonding interactions.

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2. Experimental

2.1. *Materials and physical measurements*

All chemicals were of analytical reagent grade and were used directly without further purification. Elemental analysis (C, H, N) was performed with a Perkin–Elmer 2400 Elemental Analyzer. An IR spectrum was recorded from a KBr pellet in the range of 4000–400 cm^{-1} on a Perkin–Elmer 1710 spectrophotometer. A T4-1 thermal analysis balance was used to carry out the TG and DTA analyses in air with a heating rate of $10^{\circ}\mathrm{C\,min}^{-1}$.

2.2. *Synthesis of $[Ni(phth)(phen)(H_2O)]_n \cdot nH_2O$*

A mixture of phthalic acid (1 mmol), phen (1 mmol), $Ni(NO_3)_2 \cdot H_2O$ (1 mmol), H_2O and alcohol (v : v = 1 : 1, 20 mL) was stirred for 2 h at pH = 7.0. The resulting solution was allowed to stand at room temperature without further disturbance for 3 weeks to give green crystals. Anal. Calcd (%) for $C_{20}H_{16}N_2NiO_6$: C, 54.41; H, 3.70; N, 6.31. Found (%): C, 54.71; H, 3.67; N, 6.38%. IR (KBr): 3271(s), 2357(m), 1934, 1826(m), 1815(m), 1596(s), 1586(m), 1520(m), 1376(s), 1145(s), 848(s) and 417(m) cm^{-1}.

2.3. *X-ray crystallography*

A green single crystal with dimensions of $0.56 \times 0.54 \times 0.40\,\mathrm{nm}^3$ was mounted on a computer-controlled Siemens P4 diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were collected at $296(\pm 2)$ K with an ω–2θ scan technique (1.75–25.99°). A total of 2324 independent reflections were collected, giving 1869 observed reflections with $I_0 > 4\sigma(I)$. The corrections for Lp factors were applied. The structure was solved by direct methods with the SHELXTL-97 program and expanded by Fourier techniques. The non-hydrogen atoms were determined with theoretical calculation. A full-matrix least square refinement gave the final $R_1 = 0.0296$ and $wR_2 = 0.729$ $(W = 1/[\sigma2(F_o^2) + (0.0404P)^2])$ where $P = (F_o^2 + 2F_c^2)/3$. The largest peak and hole on the final difference–Fourier map were 2.92 and $-4.35 \times 10^{-4}\,\mathrm{nm}^{-3}$, respectively. Crystal data and structure refinement parameters are listed in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure*

The molecular structure of the title complex is shown in figure 1. The Ni atom is five-coordinate with two nitrogen atoms from one phenanthroline ligand and three oxygen atoms from two carboxylato-oxygen atoms and one water molecule. One distorted square pyramid is formed, in which the basal plane can be defined by two oxygen (O1, O1#1) atoms and two nitrogen atoms (N, N#1), and the corresponding axial site is occupied by one oxygen atom (O3) with Ni–O distance of 0.2407(3) nm.

Table 1. Crystal data for the complex $[Ni(phth)(phen)(H_2O)]_n \cdot nH_2O$.

Deposition number	CCDC 608287
Empirical formula	$C_{20}H_{16}N_2NiO_6$
Formula weight	439.06
Crystal size (mm^3)	0.56 × 0.54 × 0.40
Crystal system	Orthorhombic
Space group	*Pbcm*
a (nm)	1.1638(2)
b (nm)	1.1161(3)
c (nm)	1.4051(6)
Z	4
V (nm^3)	1.8250(89)
Density (calculated) ($Mg\,m^{-3}$)	1.5982
Absorption coefficient (mm^{-1})	1.106
$F(000)$	904
θ_{max}, θ_{min} (°)	1.75, 25.99
H	$0 \rightarrow 14$
K	$0 \rightarrow 13$
L	$-17 \rightarrow 1$
No. of reflections collected	2324
No. of independent reflections	1869 [$R(\text{int}) = 0.0192$]
No. of variables	147
Max. and min. transmission	1.0000 and 0.7785
GOF	1.038
R	0.0296
wR_2	0.0729
Extinction coefficient	0.0016(2)

Table 2. Selected bond lengths (nm) and bond angles (°) of the complex.

Ni–N	0.2008(18)	C(2)–C(2)#2	0.1395(4)
Ni–N	0.2008(18)	C(3)–C(4)	0.1378(3)
Ni–O(1)	0.1931(15)	C(4)–C(4)#2	0.1385(5)
Ni–O(1)#1	0.1931(15)	C(5)–C(6)	0.1392(3)
Ni–O(3)	0.2407(3)	C(6)–C(7)	0.1370(3)
O(1)–C(1)	0.1277(2)	C(7)–C(8)	0.1407(4)
O(2)–C(1)	0.1233(2)	C(8)–C(9)	0.1390(3)
N–C(5)	0.1335(3)	C(8)–C(10)	0.1439(3)
N–C(9)	0.1355(3)	C(9)–C(9)#1	0.1436(4)
C(1)–C(2)	0.1505(3)	C(10)–C(10)#1	0.1341(5)
C(2)–C(3)	0.1387(3)		
N#1–Ni–N	81.96(10)	O(1)–Ni–O(1)#1	86.64(10)
O(1)–Ni–O(3)	91.52(6)	O(1)–Ni–N#1	176.86(7)
O(1)#1–Ni–O(3)	91.52(6)	O(1)#1–Ni–N#1	95.67(7)
N#1–Ni–O(3)	90.55(6)	O(1)–Ni–N	95.67(7)
N–Ni–O(3)	90.55(6)	O(1)#1–Ni–N	176.86(7)
C(1)–O(1)–Ni	123.35(13)	C(5)–N–Ni	129.20(17)
Ni–O(3)–H(3O)	106.8(16)	C(9)–N–Ni	112.38(14)

Symmetry transformation used to generate equivalent atoms: 1, $-X+1/2$, Y, $Z-1/2$; #2 $-X+1/2$, Y, $Z+1/2$.

The phenanthroline acts as terminal ligand with a typically average Ni–N distance of 0.20083(18) nm. Two phthlate ligands are symmetric on both sides of the phen plane. Carboxylate groups exhibit the expected C–O bond distances and O–C–O intracarboxylate bond angles: 0.1277(2) nm (O1–C1), 0.1233(2) nm (O2–C1), 125.97(19) (O1–C1–O2). The phth ligand adopts an μ_2-bridging coordination mode with a typically

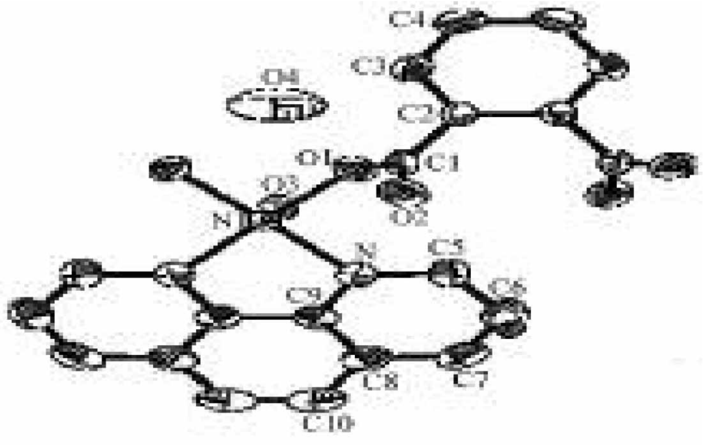

Figure 1. The molecular structure of the title complex.

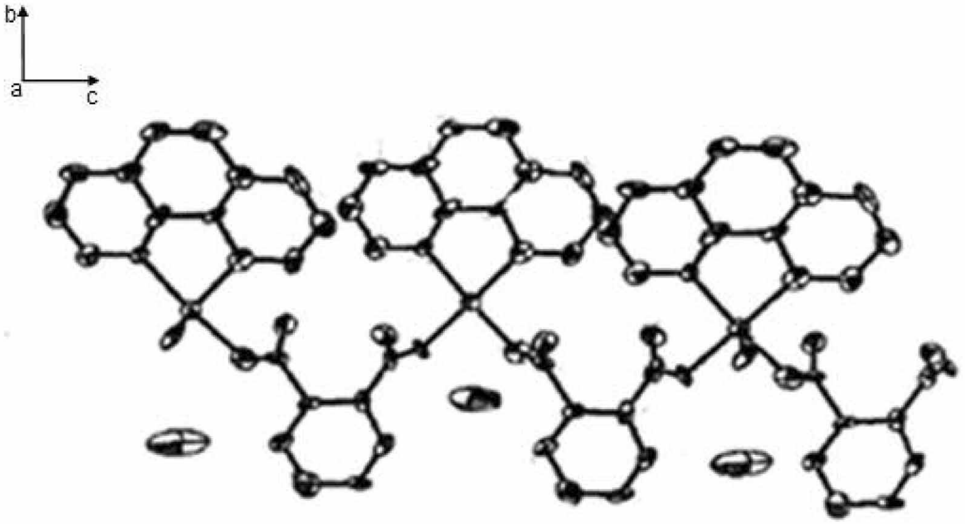

Figure 2. The zigzag chain-like structure of the title complex.

average Ni–O distance of 0.19306(15) nm. As shown in figure 2, each phth ligand bridges two metal centers and each metal center connects two phth ligands to form one zigzag, chain-like structure [12–13].

There exist hydrogen bonds in the crystal packing. The uncoordinationed water molecule acts as the hydrogen donor and the coordinationed water molecule acts as the acceptor with O4–H4A $\cdots$ O3 distance of 0.2966(6) nm, O4–H4A distance of 0.0823(10) nm, H4A $\cdots$ O3 distance of 0.292(8) and O4–H4A $\cdots$ O3 angle of 85(5)°. The coordinationed water molecule connects with the uncoordinationed carboxylato-oxygen atom of phth with O3–H30 $\cdots$ O2 distance of 0.2778(2) nm, O3–H30 distance of 0.0830(9) nm, H30 $\cdots$ O2 distance of 0.1953(10) nm and

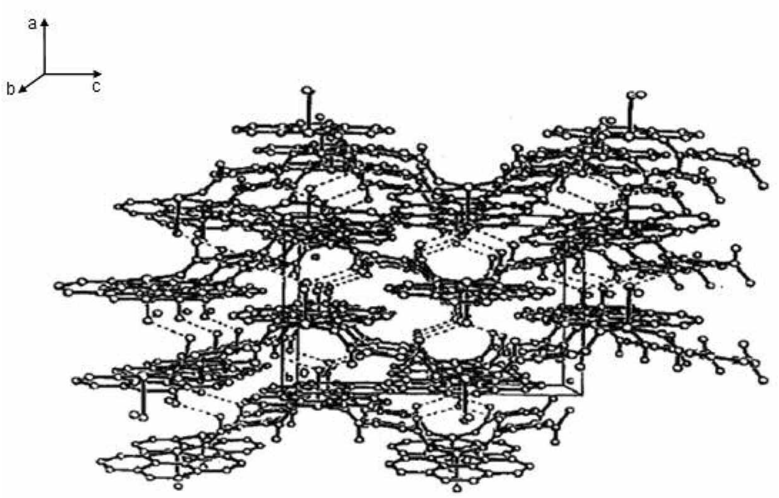

Figure 3. The three-dimensional packing structure of [Ni(phth)(phen)(H$_2$O)]$_n \cdot n$H$_2$O.

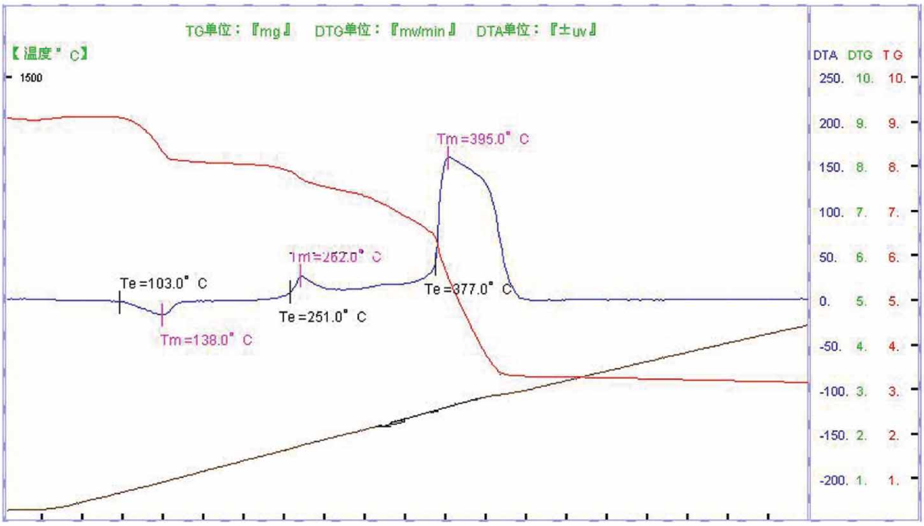

Figure 4. The DTA-TG curve for [Ni(phth)(phen)(H$_2$O)]$_n \cdot n$H$_2$O.

O3–H30 · · · O2 angle of 172.0(18)°. The zigzag chains are linked *via* hydrogen bonds to a three-dimensional supramolecular network shown in figure 3.

3.2. *Thermogravimetric analysis*

The TG curve of the title complex exhibits three steps of weight loss (figure 4). The first weight loss occurs in the range of 100–150°C, corresponding to the removal of the uncoordinationed water molecule, and the second weight loss occurs in the range of

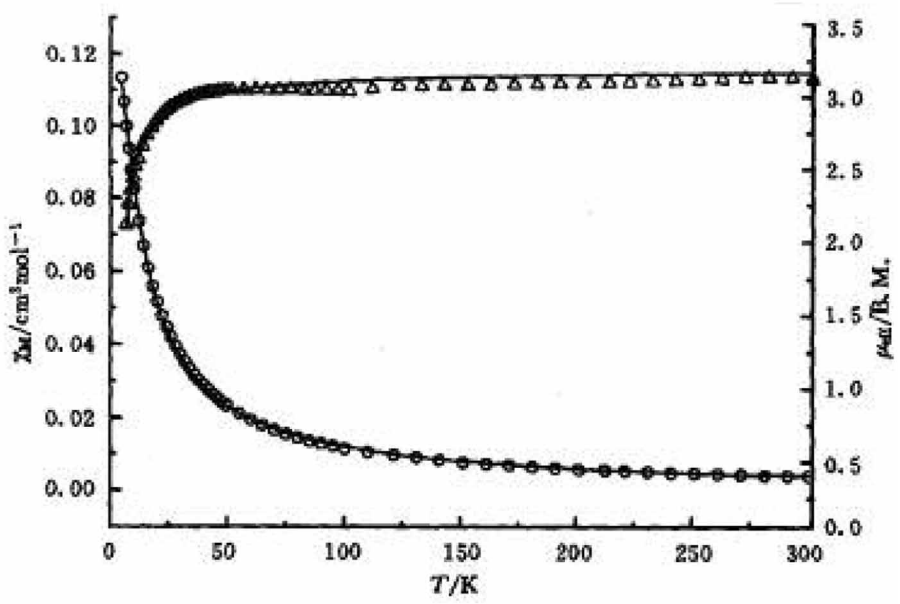

Figure 5. Temperature dependence of x_{M} *vs.* T and μ_{eff} *vs.* T for the title complex. The solid line represents the theoretical values for x_{M} and the dotted line represents μ_{eff}.

250–280°C, corresponding to the breaking of Ni–O bonds. The last weight loss occurs in the range of 370–450°C, corresponding to the release of phen. The total weight loss is 81.84%, basically in agreement with the calculated value (83.00%). On further heating, the complex does not lose any more weight at temperatures higher than 700°C.

3.3. *Magnetic susceptibility measurements*

The magnetic properties of the title complex in the range 5–300 K were studied and the results are given in figure 5 in the form of a plot of μ_{eff} *versus* T. The effective magnetic moments, μ_{eff} at 300 K is 3.15 μ_{B}, which is larger than the spin-only value of 2.83 μ_{B}. On lowering the temperature, μ_{eff} decreases slowly. Below 25 K, the value of μ_{eff} decreases more rapidly, reaching 2.26 μ_{B} at 5 K, which indicates weak antiferromagnetic interactions between Ni(II) centers.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 608287. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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