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# Synthesis, structure and properties of Nickel(II) and Cobalt(II) compounds with 1,5-dinitronaphthalene-3,7-dicarboxylate

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#### ABSTRACT

Two metal–organic compounds,  $[Co_2(NNDC)_2(H_2O)_6]\cdot 2H_2O$  (1) and  $[Ni(NNDC)(H_2O)_4]_n$  (2) (where  $H_2NNDC = 1,5$ -dinitronaphthalene-3,7-dicarboxylic acid) have been synthesized under hydrothermal reaction conditions, which are characterized by single crystal X-ray determination, IR and Thermogravimetric Analysis (TGA). Compound 1 consists of binuclear Co(II) molecules with di(µ-aqua)di(µ-carboxylato) bridges. In the compound, each dicarboxylate ligand bridges metal ions using only one carboxylate group, with the other carboxylate group involved in extensive hydrogen bonding with coordinated and uncoordinated water molecules. The 1,5-dinitronaphthalene groups serve as pillars between the hydrogen-bonded layers in which the dinuclear moieties are connected through the O-H···O···H–O hydrogen bonds mediated by uncoordinated carboxylate groups and lattice water molecules. In 2, the ligands serve as long bridges to link the metal ions into infinite chains. The uncoordinated oxygen atoms of carboxylate are hydrogen bonded to coordinated water molecules from the same and different chains to link the metal spheres into (4,4) layers, which are formally pillared by the 1,5-dinitronaphthalene spacers to generate a 3D architecture with the  $\alpha$ -Po topology. Based on a model taking into account both magnetic coupling and single-ion magnetic effects, detailed magnetic analysis on the Co(II) compound revealed a ferromagnetic intradimer interaction through the mixed aqua and carboxylate bridges.

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# 1. Introduction

The construction of metal-organic architectures sustained by coordination bonds and weak noncovalent forces such as hydrogen bonds is of current interest, not only because of their useful properties relevant to applications such as gas adsorption, catalysis, luminescence and magnetism, but also because of their fascinating supramolecular topologies [1-7]. In this context, the carboxylate ligands are among most extensively studied ligands. Taking advantages of the versatile coordination ability of the carboxylate group and the rigidity and stability of aromatic groups, aromatic dicarboxylates such as benzenedicarboxylates, biphenyldicarboxylates, and 2,6-naphthalenedicarboxylate (NDC), have been widely employed as bridging ligands to connect metal ions into metal-organic frameworks with extended coordination networks [2,8-10]. Meanwhile, the carboxylate group can form strong hydrogen bonds, which serve as additional forces to reinforce the coordination networks or as the main organizing forces to assemble low-dimensional or discrete coordination motifs into extended supramolecular structures [5,11,12].

One of the most intriguing characteristics of metal–organic structures is that the organic ligand can potentially be functionalized by different organic groups, such as amine, sulfonate, and carboxaldehyde [13–16]. We are interested in aromatic dicarboxylate ligands bearing nitro groups. The nitro group would not be involved in coordination, but it could impart high polarity to the expected metal–organic networks and hence may influence the properties. Here we report the synthesis and crystal structures of the first two coordination compounds derived from 1,5-dinitronaphthalene-3,7-dicarboxylic acid  $(H_2NNDC)$ , namely  $[Co_2-(NNDC)_2(H_2O)_6]\cdot 2H_2O$  (1) and  $[Ni(NNDC)(H_2O)_4]_n$  (2). The magnetic properties of **1** are also included.

# 2. Experimental

# 2.1. Materials and physical measurements

All the solvents and reagents for synthesis are commercially available and used as received. H<sub>2</sub>NNDC was synthesized according to the literature method [17]. Infrared spectra were recorded on a NEXUS 670 FT-IR spectrometer using the KBr pellets. Elemental analysis was carried out on an Elementar Vario El III elemental analyzer. Thermogravimetric Analysis (TGA) was performed using a Mettler TGALSDTA851e/5FL1100 instrument. The bulk phase





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purity of the samples has been confirmed by powder X-ray diffraction measurements, which were performed on a Bruker D8-Advance diffractometer equipped with Cu K $\alpha$  radiation. Temperature- and field-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-5 magnetometer. Diamagnetic corrections were made with Pascal's constants.

# 2.2. Synthesis of $[Co_2(NNDC)_2(H_2O)_6] \cdot 2H_2O(1)$

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.012 g, 0.04 mmol) was added to an aqueous solution of H<sub>2</sub>NNDC (0.006 g, 0.02 mmol), the pH value of which had been adjusted to approximately 7 with 0.1 mol L<sup>-1</sup> NaOH solution. The mixture was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 130 °C for 48 h, and then slowly cooled to room temperature. The red rod-like products were collected after washing with distilled water and ethanol, and dried in air at ambient temperature. Yield: 50% based on Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. IR (KBr, cm<sup>-1</sup>): 3550 (br), 3360 (br), 3250 (w), 1625 (s), 1596 (s), 1407 (s), 1359 (s), 924 (w), 842 (w), 781 (s), 714 (s). Elemental analysis calcd for C<sub>24</sub>H<sub>24</sub>Co<sub>2</sub>N<sub>4</sub>O<sub>24</sub> (%): C 33.12, H 2.78, N 6.44. Found (%): C 33.25, H 3.14, N 6.71.

#### 2.3. Synthesis of $[Ni(NNDC)(H_2O)_4]_n$ (2)

The compound was prepared as pale green sheet-like crystals by the procedure described above for **1** except that cobalt nitrate hexahydrate was replaced by nickel nitrate hexahydrate, and the pH value of the solution was 8. Yield: 48% based on Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. Elemental analysis calcd for  $C_{12}H_{12}NiN_2O_{12}$  (%) (1): C 33.14, H 2.78, N 6.44. Found (%): C 33.22, H 2.92, N 6.58. IR (KBr, cm<sup>-1</sup>): 3540 (s), 3438 (w), 1618 (s), 1403 (s), 1360 (s), 924 (w), 893 (w), 846 (w), 784 (s), 722 (s).

#### 2.4. Crystal data collection and refinement

Diffraction intensity data were collected at 293 K on a Bruker APEX II diffractometer equipped with a CCD area detector and graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Empirical absorption corrections were applied using the SADABS program [18]. The structures were solved by the direct method and refined by the full-matrix least-squares method on  $F^2$ , with all non-hydrogen atoms refined with anisotropic thermal parameters [19,20]. The hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model. Pertinent crystallographic data and structure refinement parameters are summarized in Table 1.

# 3. Results and discussion

#### 3.1. Description of the structure of compound 1

According to X-ray crystallographic analyses, the structure of compound **1** consists of binuclear Co(II) molecules with mixed carboxylate and water bridges. The molecular structure of **1** is shown in Fig. 1, with selected bond distances and angles listed in Table 2. The unique Co1 ion assumes the octahedral geometry completed by two carboxylate oxygen atoms (O1, O2A) from two NNDC ligands at *trans* positions and four water molecules through O9 O10, and O11 O11A. Each NNDC ligates two metal ions through two carboxylate oxygen atoms. Two equivalent Co(II) ions are quadruply bridged by two carboxylate groups in the syn–syn mode and two water molecules (O9, O10/ O9A, O10A, respectively) to give a centrosymmetric binuclear di( $\mu$ -aqua)di( $\mu$ -carboxylato) moiety. The Co–O<sub>bridging</sub> distances (2.179(3) Å and 2.245(3) Å) are longer than other distances (2.026(3) Å –2.096(4) Å) around the

#### Table 1

Crystal data and structure refinements for compounds 1 and 2.

Compound	1	2
Formula	C <sub>24</sub> H <sub>24</sub> Co <sub>2</sub> N <sub>4</sub> O <sub>24</sub>	C12H12NiN2O12
Mr	870.33	434.95
Temperature, K	273	296
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	ΡĪ
a, Å	7.2588(16)	6.0335(2)
b, Å	8.984(2)	6.0515(2)
<i>c</i> , Å	12.369(3)	11.3412(4)
α, °	103.834(3)	103.6910(10)
β, °	101.434(3)	91.3570(10)
γ, °	91.374(3)	102.5920(10)
<i>U</i> , Å <sup>3</sup>	765.5(3)	391.40(2)
Ζ	1	1
$D_{\rm c}$ , g cm <sup>-3</sup>	1.888	1.845
$\mu$ , mm $^{-1}$	1.198	1.314
Reflns collected	4460	5246
Unique reflns/ R <sub>int</sub>	3076/0.0347	1716/0.0156
$R_1 \left[ I > 2\sigma(I) \right]$	0.0538	0.0219
wR <sub>2</sub> (All data)	0.1284	0.0742
GOF	0.988	0.712



**Fig. 1.** ORTEP drawing of compound **1** with atomic numbering scheme (thermal ellipsoids at 50% probability). The hydrogen atoms attached to C atoms are omitted for clarity. Symmetry codes: A, -x, -y, -z.

Fable 2					
Bond lengths	Ål and	angles [	l for	compound 1	

Co(1)-O(2)A Co(1)-O(1) Co(1)-O(10)	2.026(3) 2.032(3) 2.047(4)	Co(1)-O(9) Co(1)-O(11)A Co(1)-O(11)	2.096(4) 2.179(3) 2.245(3)
$\begin{array}{l} C(1) - C(1) \\ O(2) A - Co(1) - O(1) \\ O(1) - Co(1) - O(10) \\ O(1) - Co(1) - O(9) \\ O(2) A - Co(1) - O(11) A \\ O(2) A - Co(1) - O(11) A \\ O(2) A - Co(1) - O(11) \\ O(10) - Co(1) - O(11) \\ O(11) A - Co(1) - O(11) \\ O(11) - O(1) - Co(1) \\ C(1) - O(1) \\ C(1) - O(1) \\ C(1) - O(1) \\ C(1) - Co(1) \\ C(1) \\ C(1) - Co(1) \\ C(1) \\$	2.047(4) 158.16(11) 95.15(13) 96.43(13) 83.55(11) 89.12(14) 81.57(11) 174.81(13) 94.22(10) 127.2(3)	$\begin{array}{c} O(1)-O(11)\\ O(2)A-Co(1)-O(10)\\ O(2)A-Co(1)-O(9)\\ O(10)-Co(1)-O(9)\\ O(1)-Co(1)-O(11)A\\ O(9)-Co(1)-O(11)A\\ O(1)-Co(1)-O(11)\\ O(9)-Co(1)-O(11)\\ O(9)-Co(1)-O(11)\\ C(1)-O(2)-Co(1)A\\ Co(1)-O(9)-H(9W2)\\ Co(1)-O(9)-H(9W2)\\ O(1)-O(1)-O(1)\\ O(1)-O(1)-O(1)\\ O(1)-O(1)-O(1)\\ O(1)-O(1)-O(1)\\ O(1)-O(1)-O(1)\\ O(1)-O(1)-O(1)\\ O(1)-O(1)-O(1)\\ O(1)-O(1)\\ O(1)-O($	2.243(3) 102.78(13) 95.84(13) 90.34(14) 84.37(12) 179.07(13) 81.26(11) 86.37(12) 127.9(3) 112(4)
Co(1)-O(9)-H(9W1) Co(1)-O(9)-H(9W1) Co(1)-O(10)-H(0W1) Co(1)A-O(11)-H(1W) Co(1)A-O(1)A-O(11)-H(1W) Co(1)A-O(1	$104(4) \\ 104(4) \\ 105(4) \\ 121(3) \\ 116(2)$	Co(1)-O(9)-H(9W2) Co(1)-O(10)-H(0W2) Co(1)A-O(11)-Co(1) Co(1)-O(11)-H(1W) Co(1)-O(11)-H(1W)	112(4) 117(4) 85.78(10) 113(3) 112(2)
$CO(1)A - O(11) - \Pi(1002)$	110(5)	$CO(1) = O(11) = \Pi(1002)$	112(5)

Symmetry code: A, -x, -y, -z.

metal ion. The two bridging water molecules generate a strictly planar  $[Co_2(\mu_2-O)_2]$  pseudo-rhombic ring, with Co–O–Co = 85.78(10)°. The two bridging carboxylate groups are disposed trans to each other across the  $[Co_2(\mu_2-O)_2]$  plane, and form an planar eight-membered ring perpendicular to the  $[Co_2(\mu_2-O)_2]$  plane. With the carboxylate groups being essentially coplanar with the naphthalene ring, the whole dinuclear molecule except for the water ligands and the nitro oxygen atoms are quasi-planar. It is

Table 3	
Hydrogen bond lengths (Å) and	angles (°) for compound <b>1</b> .

D–HA	d(D-H)	<i>d</i> (HA)	<i>d</i> (DA)	(DHA)
0(9)-H(9W2)0(4)#1 0(9)-H(9W1)0(3)#2 0(10)-H(0W2)0(12)#3 0(10)-H(0W1)0(12)#4 0(11)-H(1W1)0(3)#1 0(11)-H(1W2)0(4)#2	0.839(19) 0.846(19) 0.849(19) 0.832(19) 0.837(18) 0.854(18)	2.12(3) 2.05(2) 1.92(2) 2.23(3) 1.863(19) 1.82(2)	2.879(4) 2.882(5) 2.759(5) 3.035(7) 2.699(4) 2.666(4)	151(4) 168(6) 169(6) 164(6) 178(4) 171(4)
O(11)-H(1W2)O(4)#2 O(12)-H(2W1)O(3) O(12)-H(2W2)O(9)#5	0.834(18) 0.83(2) 0.852(17)	2.12(6) 2.147(17)	2.666(4) 2.742(5) 2.969(5)	171(4) 131(7) 162(6)

-*z* + 1; #4, *x*, *y*, *z* - 1; #5, *x*, *y*, *z* + 1.

noteworthy that the di( $\mu$ -aqua)di( $\mu$ -carboxylato)dicobalt(II) moiety is very rare in the literature [21]. The Co $\cdots$ Co distance (3.011(1) Å) in **1** is comparable to those (3.05–3.07 Å) for the few previous compounds with this bridging system [21], and significantly shorter than those (3.45–3.70 Å) for some Co(II) compounds with mono( $\mu$ -aqua)di( $\mu$ -carboxylato) bridges [22–24].

It is noted that the NNDC ligand uses only one carboxylate group for coordination, although the other carboxylate group is also deprotonated. The latter group, together with the coordinated water molecules (either bridging or terminal), provides a rich store of hydrogen bonding sites for intermolecular interactions. Actually, all the water hydrogen atoms and all the uncoordinated carboxylate oxygen atoms are involved in hydrogen bonding. The relevant hydrogen-bonding parameters are listed in Table 3. As shown in Fig. 2a, each uncoordinated carboxylate oxygen atom (O3 or O4) accepts two hydrogen atoms from a bridging (O11) and a terminal (O9) water molecule from different binuclear units, and in turn, the O11 and O9 water molecules each form two hydrogen bonds with two carboxylate groups from different ligands. Thus, each uncoordinated carboxylate group is linked to two binuclear units, forming two cyclic hydrogen bonding motifs (graph set  $R_2^2(8)$  [25], each motif consisting of a Co(II) ion, two coordinated water molecules and a carboxylate group). The adjacent binuclear  $[Co_2(\mu_2-O)_2(\mu_2-COO)_2]$  moieties are linked by two uncoordinated carboxylate groups via a total of eight O–H···O hydrogen bonds to give a hydrogen-bonded tape along the a direction. The eight hydrogen bonds arrange the eight oxygen atoms (four from uncoordinated carboxylates and four from coordinated waters) into a distorted cube (or tetragonal prism), for which each of the two basal faces is defined by a quadruple hydrogen-bonded  $R_4^2(8)$  cyclic motif consisting of two uncoordinated oxygen atoms from different carboxylates and two water molecules from different binuclear units.

In addition, the coordinated O10 water molecule donates its hydrogen atoms to two equivalent lattice water molecules (O12). and consequently, two O10 waters from different binuclear units and two O12 waters form another  $R_4^2(8)$  cyclic motif (marked in Fig. 2b), which serves as the linker between the neighboring binuclear units along the *b* direction. Finally, the hydrogen atoms of the lattice water molecule form hydrogen bonds with the uncoordinated carboxylate O3 atom and the coordinated O9 water molecule. With all the above O-H. O hydrogen bonds involving carboxylate groups and water molecules, the  $[Co_2(\mu_2-O)_2(\mu_2-O$ COO)<sub>2</sub> moieties are organized into an elegant 2D supramolecular network along the *ab* plane. The whole 3D structure of **1** may be regarded as a pillared multilayer architecture, where the naphthalene groups serve as pillars between the hydrogen-bonded layers (Fig. 2c). The 3D structure is simultaneously reinforced by  $\pi$ - $\pi$ interactions between the naphthalene rings stacked along a direc-



Fig. 2. (a) A hydrogen-bonded tape along the a direction. (b) The 2D hydrogen bonding layer structure of compound 1. (c) The 3D hydrogen bonding network.



**Fig. 3.** ORTEP drawing of compound **2** with atomic numbering scheme (thermal ellipsoids at 50% probability). The hydrogen atoms attached to C atoms are omitted for clarity. Symmetry codes: A, -x + 1, -y + 1, -z + 1; B, -x + 2, -y, -z; C, x - 1, y + 1, z + 1.

tion (Fig. 2c), with each ring overlapping with two neighboring rings. The interplane distances are 3.45 and 3.42 Å for the two independent interactions, respectively, with the center-to-center distances being 3.62 and 3.64 Å, respectively.

#### 3.2. Description of the structure of compound 2

The structure of compound 2 consists of one-dimensional coordination chains. The chain structure is shown in Fig. 3, with selected bond distances and angles listed in Table 4. The unique Ni1 ion resides at a crystallographic inversion center, and assumes the trans-octahedral geometry completed by two carboxylate oxygen atoms (01, 01B) from two NNDC ligands at axial positions and four water molecules (05, 05B, 06, 06B) at equatorial positions. The equatorial Ni–O<sub>water</sub> distances (2.0548(10) and 2.0615(10) Å) are a little longer than Ni-O<sub>carboxylate</sub> (2.0426(10) Å). The NNDC ligand is centrosymmetric and links two metal ions through two monodentate carboxylate groups, with Ni...Ni = 13.72 Å. Consequently, a linear neutral chain in which [Ni(H<sub>2</sub>O)<sub>4</sub>] cations are linked by NNDC anions is formed along the  $(-1 \ 1 \ 1)$  direction. With the carboxylate groups being essentially coplanar with the naphthalene ring, the whole chain except for the water ligands and the nitro oxygen atoms is guasi-planar. The uncoordinated carboxylate oxygen atoms and the coordinated water molecules provide a rich store of interaction sites for intra- and intermolecular hydrogen bonding. As in 1, all the water hydrogen atoms and all the uncoordinated carboxylate oxygen atoms are involved in hydrogen bonding. The relevant hydrogen-bonding parameters are listed in Table 5. As shown in Fig. 3, each uncoordinated carboxylate oxygen atom (O2) forms an intrachain hydrogen bond with a coordinated water molecule (O6), resulting in two cyclic hydrogen bonding motifs [graph set S(6)] around Ni(II). The O2 atom is also involved in two independent hydrogen bonds with the O5 water molecules from different chains. With these interchain hydrogen bonds, two independent hydrogen bonding motifs, each consisting of two

Table 4				
Selected bond	lengths (Å)	and ang	les (°) for	compound 2

Ni(1)-O(1)B Ni(1)-O(6) Ni(1)-O(1)	2.0426(10) 2.0615(10) 2.0426(10)	Ni(1)-O(5)B Ni(1)-O(6)B Ni(1)-O(5)	2.0548(10) 2.0615(10) 2.0548(10)
O(1)B-Ni(1)-O(1)	180.00(6)	O(1)B-Ni(1)-O(5)	89.62(4)
O(1)-Ni(1)-O(5)	90.38(4)	O(1)B-Ni(1)-O(5)B	90.38(4)
O(1)-Ni(1)-O(5)B	89.62(4)	O(5)-Ni(1)-O(5)B	180.00(4)
O(1)B-Ni(1)-O(6)	87.11(4)	O(1)-Ni(1)-O(6)	92.89(4)
O(5)-Ni(1)-O(6)	87.86(4)	O(5)B-Ni(1)-O(6)	92.14(4)
O(1)B-Ni(1)-O(6)B	92.89(4)	O(1)-Ni(1)-O(6)B	87.11(4)
O(5)-Ni(1)-O(6)B	92.14(4)	O(5)B-Ni(1)-O(6)B	87.86(4)
O(6)-Ni(1)-O(6)B	180.00(6)	C(1)-O(1)-Ni(1)	127.20(9)
Ni(1)-O(5)-H(5W2)	118.0(18)	Ni(1)-O(5)-H(5W1)	109.4(14)
Ni(1)-O(6)-H(6W2)	118.5(17)	Ni(1)-O(6)-H(6W1)	104.4(15)

Symmetry codes: B, -x + 2, -y, -z.

Table 5
Hydrogen bond lengths (Å) and angles (°) for compound <b>2</b> .

D–HA	d(D-H)	<i>d</i> (HA)	<i>d</i> (DA)	(DHA)
O(6)-H(6W1)O(2)	0.852(15)	1.888(16)	2.6825(15)	155(2)
O(5)-H(5W2)O(2)#1	0.801(15)	2.005(19)	2.7507(14)	155(2)
O(5)-H(5W1)O(2)#3	0.829(14)	1.923(16)	2.7363(15)	166.9(19)
O(6)-H(6W2)O(4)#2	0.821(15)	2.131(17)	2.9341(15)	166(2)

Symmetry codes: #1, *x*, *y* – 1, *z*; #2, *x*, *y*, *z* – 1; #3, –*x* + 1, –*y*, –*z*.

complementary and equivalent O-H···O interactions, are formed between the adjacent metal spheres along the a and b directions, respectively. Consequently, the metal spheres are interlinked into a 2D network along the *ab* plane. The network features a quadruple hydrogen-bonded  $R_4^2(8)$  cyclic motif consisting of two carboxylate oxygen atoms and two water molecules from four metal spheres (Fig. 4a). Similar to that of 1, the whole 3D structure of 2 (Fig. 4b) may be regarded as a pillared multilayer architecture, where the naphthalene groups serve as pillars between the hydrogen-bonded layers. Topologically, the metal coordination spheres can be reduced into nodes, and then the hydrogen-bonded layer can be regarded as a  $4^4$  net and the 3D architecture as  $\alpha$ -Po net (Fig. 4c). Finally, the O6 water molecule uses the remaining hydrogen atom to form a hydrogen bond with a nitro oxygen atom (O4), providing additional stabilization energy for the 3D structure (Fig. 4b). No  $\pi$ - $\pi$  interactions are observed in **2**.

#### 3.3. Infrared spectra and thermogravimetric analysis

The FT-IR spectra of compounds **1** and **2** exhibit broad adsorption bands in the range of 3550–3250 cm<sup>-1</sup> due to v(OH) vibrations of water molecules. The bands in the ranges of 1625–1596 cm<sup>-1</sup> and 1407–1403 cm<sup>-1</sup> may be attributed to the  $v_{as}(COO)$  and  $v_{s}(COO)$  absorptions of the NNDC ligand. The  $v_{as}(NO_2)$  and  $v_{s}(NO_2)$  vibrations appear at about 1520 and 1360 cm<sup>-1</sup> [26].

Thermogravimetric analysis (TGA) was carried out in nitrogen atmosphere from room temperature to 800 °C with heating and cooling rates of 5.0 °C/min. The removal of water molecules in compound **1** is characterized by a rapid weight loss between 70 and 112 °C (15.7%, calcd: 16.6% for eight water molecules per formula). Upon heating up to 235 °C, a small weight loss (0.3%), which may correspond to the release of residue water, was observed. The compound shows rapid decomposition above 360 °C, and the residue mass is consistent with CoO (17.5%, calcd: 17.2%). Compound **2** loses the coordinated water molecules from 85 to 140 °C (calcd: 16.6%, obsd: 17.5%), and evident decomposition begins above 380 °C, the residue mass corresponding to NiO (17.1%, calcd: 17.2%).

#### 3.4. Magnetic properties of 1

The magnetic susceptibility of compound **1** was measured in the 2–300 K temperature range and is shown as  $\chi T$  and  $\chi^{-1}$  versus T



Fig. 4. (a) The 2D hydrogen bonding layer structure of compound 2. (b) The hydrogen-bonded three-dimensional structure of 2. (c) The  $\alpha$ -Po net derived from the 4<sup>4</sup> net.

plots in Fig. 5. The  $\gamma T$  value per dimer at 300 K is 6.03 emu mol<sup>-1</sup> K, much larger than the spin-only value  $(3.75 \text{ cm}^3 \text{ K mol}^{-1})$  for S = 3/2, but typical of octahedral Co(II) systems with a significant contribution from unquenched orbital momentum. The  $\chi^{-1}$  versus T plot above 60 K follows the Curie–Weiss law with C = 7.99 emu mol<sup>-1</sup> K and  $\theta$  = 5.86 K. The positive  $\theta$  value suggests that a ferromagnetic interaction between adjacent metal ions is mediated through the quadruple bridge. Upon cooling, the  $\chi T$  value increases smoothly to an approximate plateau in the range from 50 to 20 K, then increases rapidly below 20 K to a maximum of 7.69 emu mol<sup>-1</sup> K at 6 K, and finally drops rapidly to 6.45 emu mol<sup>-1</sup> K at 2 K. Such a complex temperature-dependent behavior of  $\gamma T$  is the consequence of the interplay and competition of several concurrent effects, including first-order spin-orbital coupling, ligand-filed distortion of Co(II) sites, and intra- and intermolecular magnetic interactions between Co(II) ions. The overall increase of  $\chi T$  from 300 K down to 6 K suggests that ferromagnetic interactions dominate in 1. The dominating ferromagnetic interactions are also reflected in the  $\gamma T$ value (6.45 emu mol<sup>-1</sup> K) of **1** at 2 K, which is significantly larger than expected for two isolated Co(II) centers. The typical  $\gamma T$  value for an isolated Co(II) ion with  $S_{eff} = 1/2$  at 2 K is 1.6–2.0 emu mol<sup>-1</sup> K [27-30].

To quantitatively interpret the behavior, we employed the empirical approach proposed recently by Lloret et al. [31]. In the framework of this approach, each Co(II) ion in the ground Kramer's doublet arising from spin–orbital coupling is considered to have an effective spin  $S_{\text{eff}} = 1/2$ , which is related to the real spin (S = 3/2) by a factor of 5/3 (Eq. (1)), and the magnetic exchange is assumed to



**Fig. 5.** Plot of temperature dependence of  $\chi_m T$  and  $1/\chi_m$  for compound **1**.

occur between the ground doublets of the relevant Co(II) ions, the effective spin Hamiltonian for a dinuclear Co(II) system being described by Eq. (2).

$$\hat{S} = (5/3)\hat{S}_{\text{eff}} \tag{1}$$

$$\hat{H} = -(25/9)\hat{S}_{\text{eff}}^{\text{A}} \cdot \hat{S}_{\text{eff}}^{\text{B}} - G(T,J)\beta H\left(\hat{S}_{\text{eff}}^{\text{A}} + \hat{S}_{\text{eff}}^{\text{B}}\right)$$
(2)

$$\chi_{\rm dim} = \frac{2N\beta^2 [G(T,J)]^2}{kT} \frac{1}{3 + \exp[(25/9)J/(kT)]}$$
(3)

The expression of the magnetic susceptibility (Eq. (3)) is derived in the form similar to the Lines model for systems with ideal octahedral Co(II) environments [32]. In Eqs. (2) and (3), the fictitious Landé factor G(T, J) is a temperature and exchange dependent function accounting for the magnetic contributions from the excited states through spin–orbital coupling, ligand-field distortion, and exchange coupling. An empirical expression of G(T, J) has been derived, and the variable parameters include  $\lambda$  (spin–orbital coupling parameter),  $\alpha$  (orbital reduction factor) and  $\Delta$  (ligand-field distortion factor. An axial distortion is assumed), besides the magnetic exchange parameter (*J*). The fit of the experimental data using Eq. (3) failed to simulate the increase of  $\chi T$  below 20 K. Therefore, the molecular field approximation accounting for the possible intermolecular interaction was applied (Eq. (4)).

$$\chi = \frac{\chi_{\rm dim}}{1 - z J' (N \beta^2)^{-1} [G(T, J)]^{-2} \chi_{\rm dim}}$$
(4)

According to the structural data, the dimer is associated with four neighbors through O<sub>Coordinated</sub>-H···O···H-O<sub>Coordinated</sub> hydrogen bonding bridges, the central O atom arising from either uncoordinated carboxylate or lattice water (see Fig. 2c). It follows that z = 4, assuming that the intermolecular magnetic interactions through the similar pathways have the same value (l'). The leastsquares fit using Eqs. (3) and (4) can satisfactorily simulates the experimental  $\chi T(T)$  plot above 10 K, including the approximate plateau region from 50 to 20 K and the rapidly increasing region below 20 K. The best-fit parameter set is  $J = 15.4 \text{ cm}^{-1}$ ,  $J' = 0.74 \text{ cm}^{-1}$ ,  $\lambda = -120 \text{ cm}^{-1}$ ,  $\alpha = 1.42 \text{ and } \Delta = 881 \text{ cm}^{-1}$ . The values of the single-ion parameters  $\lambda$ ,  $\alpha$  and  $\Delta$  fall within the most common ranges expected for six-coordinated Co(II) complexes. The large  $\varDelta$  value suggests significant magnetic anisotropy arising from ligand-field distortion. Notably, the J value suggests an intramolecular ferromagnetic interaction through the quadruple  $di(\mu$ aqua) $di(\mu$ -carboxylato) bridge. It is noted that no information on the magnetic exchange through such quadruple bridges is available in the literature, but antiferromagnetic interactions have been reported for the triple ( $\mu$ -aqua)di( $\mu$ -carboxylato) bridges [23,24].

The *J'* value suggests that weak ferromagnetic intermolecular interactions are operative through the  $O-H \cdots O \cdots H-O$  hydrogen bonding pathways. Magnetic interactions through hydrogen bonds have been reported for many systems, but the nature and magnitude differs with the diverse hydrogen bonding patterns [33–35]. The magnetic analyses failed to reproduce the rapid decrease of  $\chi T$  below 6 K. Qualitatively, this very-low-temperature behavior may be due to the presence of weak antiferromagnetic intermolecular interactions, which can operate between the hydrogen-bonded layers separated by the long organic ligands and should be dipolar in nature, and/or the occurrence of zero-field splitting, which can be anticipated for a ferromagnetic ground state with S > 1/2.

The ferromagnetic interactions in **1** are also supported by the isothermal magnetization behavior measured at 2 K. The experimental curve is compared with two theoretical ones predicted according to the Brillouin function, one for two isolated Co(II) ions in the ground Kramer's doublet with  $S_{eff} = 1/2$ , and the other for the  $S_{\text{eff}}$  = 1 system arising from two ferromagnetically coupled Co(II) ions. Using the I,  $\lambda$ ,  $\alpha$  and  $\Delta$  values obtained by modeling the  $\chi T(T)$  data (see above), the G(T, I) factor in Eqs. (2) and (3) is calculated to be 4.4 at 2 K. Notably, this value is in good agreement with the typical  $g_{eff}$  factor (4.3) expected for Co(II). Therefore,  $g_{eff}$  = 4.4 was used in calculating the Brillouin function. As can be seen from Fig. 6, the experimental magnetization increases significantly more rapidly than that predicted for isolated Co(II) ions, evidently supporting the overall ferromagnetic interactions between Co(II) ions in 1. Furthermore, the increase of the experimental magnetization is more rapid than that predicted for the  $S_{eff}$  = 1 state, indicating that ferromagnetic interactions not only occur within the dinuclear molecule but also dominate among the molecules. This supports the intermolecular ferromagnetic interactions through hydrogen bonds. Finally, it is noted that the magnetization does not reach saturation at 50 kOe but tends to increase slowly upon further increasing the field. This is different from the behaviors expected for isotropic systems (see the theoretical curves in Fig. 6), and is typical of Co(II) systems with large magnetic anisotropy. Further magnetic measurements revealed no indications of long-range ordering (no hysteresis and no out-of-phase ac susceptibility signals).

#### 4. Conclusions

We have described two metal–organic architectures derived from 1,5-dinitronaphthalene-3,7-dicarboxylate and Co(II) or Ni(II). Both compounds exhibit intriguing hydrogen-bonded layers pillared by organic spacers. The Co(II) compound contains dinuclear



Fig. 6. The isothermal magnetization for 1 at 2 K.

molecules with  $di(\mu$ -aqua) $di(\mu$ -carboxylato) guadruple bridges. In the compound, each dicarboxylate ligand bridges metal ions using only one carboxylate group, with the other carboxylate group involved in extensive hydrogen bonding with coordinated and uncoordinated water molecules. The 1,5-dinitronaphthalene groups serve as pillars between the hydrogen-bonded layers in which the dinuclear moieties are connected through the O-H···O···H–O hydrogen bonds mediated by uncoordinated carboxvlate groups and lattice water molecules. In the Ni(II) compound, the ligands serve as long bridges to link the metal ions into infinite chains. The uncoordinated oxygen atom of carboxylate is hydrogen bonded to coordinated water molecules from the same and different chains to generate a 3D architecture with the  $\alpha$ -Po topology. Based on a model taking into account both magnetic coupling and single-ion magnetic effects, detailed magnetic analysis on the Co(II) compound revealed a ferromagnetic intradimer interaction through the mixed agua and carboxylate bridges.

#### 5. Supplementary material

Crystallographic data as .cif files for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. CCDC Nos. are 722341 for **1** and 722342 for **2**. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.05.054.

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