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Syntheses, crystal structures and magnetic properties of coordination polymers $Ni(NO_2)_2$ and $Ni(4,4'\text{-bipy})(NO_2)_2$

Vien Vo [a], Youngmee Kim [a], Nguyen Van Minh [b], Chang Seop Hong [c], Sung-Jin Kim [a,*]

[a] Department of Chemistry and Nono Science, Ewha Womans University, 11-1 Daehyun-dong, Seodaemun-gu, Seoul 120-750, Republic of Korea
[b] Center for Nano Science and Technology, Hanoi National University of Education, Hanoi, Vietnam
[c] Department of Chemistry, Korea University, Seoul 136-713, Republic of Korea

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ABSTRACT

Two new coordination polymer frameworks $Ni(NO_2)_2$ (**1**) and $Ni(4,4'\text{-bipy})(NO_2)_2$ (**2**) (4,4′-bipy = 4,4′-bipyridine) were synthesized by solvothermal reaction in formamide, and were characterized by elemental analysis, IR spectroscopy, single crystal X-ray diffraction, and magnetic measurement. In compound **1**, each Ni^{2+} ion is linked with four neighboring Ni^{2+} ions through $\mu_{1,3}$-nitrito bridges forming 2D layered structure. In compound **2**, each Ni^{2+} ion is bridged with six neighboring Ni^{2+} ions through four $\mu_{1,3}$-nitrito groups and two 4,4′-bipy ligands forming 3D structure. Magnetic measurements show weak ferromagnetism within framework of the two compounds with T_N = 19 K (**1**) and 21 K (**2**).

1. Introduction

The field of inorganic coordination polymeric complexes has developed rapidly in recent years, owing to their interesting molecular topologies and crystal packing motifs [1–4] along with potential applications as functional materials [5–7]. Many of them were constructed from paramagnetic metal ions bridged through cyanide or organic compounds, and this resulted in the formation of a large number of one-, two-, and three-dimensional polymers that exhibit various magnetic behaviors [8,9]. In designing such polymers, properties of linking ligands such as various coordination modes, variable lengths, and relative orientation of donor atoms play a fundamental role in determining the structure of target polymers. The nitrito group (NO_2^-) has been shown as short ligands which can coordinate metal ions in various ways [10]. However, to the best of our knowledge, rare works on 2D or 3D polymeric complexes containing nitrite bridges have been documented. The frameworks of $[M(pyrazine)_2NO_2]ClO_4$ were reported as the first examples containing $\mu_{1,3}$-nitrito bridges and showing antiferromagnetism [11]. On the other hand, 4,4′-bipyridine (4,4′-bipy) is a neutral linear bifunctional ligand widely used as an excellent spacer in the construction of coordination polymer architectures. It has been shown that the use of 4,4′-bipy as linear building units along with suitably chosen metal ions can lead to the spontaneous formation of infinite 1D chains [12,13], 1D ladders [14–16], 2D grids [17–20], 2D bilayer [14–16], 2D sheet pillared by 4,4′-bipy to form a 3D network [21,22], and 3D network with microporous channels [21–26].

So far, numerous studies are focused on the selection of the donor or acceptor building blocks or on the influences of the robust covalent bonds or weak intermolecular interactions [27] while the reaction solvent plays an important role in the design of molecular structures. Formamide is a very interesting solvent which has been used for various processes in biochemistry, materials sciences [28] because its dielectric constant is higher than that of water and it can act as a reducing agent under suitable conditions. Solvothermal reduction route is widely used to prepare novel metal materials because of its advantages such as high temperature and high pressure [29]. Until now, this route has been reported to the synthesis of molecular magnetic materials [30,31]. Here, we present the use of solvothermal reaction in formamide to synthesize two new frameworks of $Ni(NO_2)_2$ and $Ni(4,4'\text{-bipy})(NO_2)_2$ containing $\mu_{1,3}$-nitrito bridges. They are the first examples of synthesis of polymeric complexes using solvent as a reducing agent in solvothermal condition. Both materials are weak ferromagnets.

2. Experimental

2.1. Materials

$Ni(NO_3)_2 \cdot 6H_2O$, formamide, and 4,4′ bipyridine were obtained from Aldrich and used as received.

* Corresponding author. Tel.: +82 2 3277 2350; fax: +82 2 3277 3419.
E-mail address: sjkim@ewha.ac.kr (S.-J. Kim).

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2.2. Synthesis

In a typical synthesis, a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.67 mmol) in 10 ml formamide for **1**, or $Ni(NO_3)_2 \cdot 6H_2O$ (0.67 mmol) and 4,4′-bipyridine (1.34 mmol) in 10 ml formamide for **2** was transferred into a Teflonlined autoclave and then heated under autogenous pressure at 70 °C for 72 h, followed by cooling to room temperature naturally. Green large single crystals in regular cubic shape were collected and washed with ethanol several times, yield 75% for **1** and **2** upon Ni. *Anal.* Calc. for **1**: N, 23.08. Found: N, 23.05%. *Anal.* Calc. for **2**: C, 39.13; H, 2.63; N, 18.26. Found: C, 39.03; H, 2.93; N, 18.32%.

2.3. Characterization

Elemental analyses for C, H, and N were performed on an EA 1110 elemental analyzer. The IR spectra were obtained on a FT/IR-6100 (JASCO) spectrometer. The variable temperature magnetic susceptibilities were measured using a PPMS 6000 (Quantum Design Inc., USA) instrument.

2.4. X-ray crystallography

Data for compounds were collected on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo Kα (λ = 0.71073 Å) incident beam. The crystals were mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structures were solved and refined using SHEXTL V6.12 [32]. Hydrogen atoms were located in the calculated positions. The crystallographic data for **1** and **2** is listed in Table 1.

3. Results and discussion

3.1. Synthesis

Recently, hydro(solvo)thermal synthesis has gained impressive progress. This technique provides a powerful tool for the construction of materials containing unique structures and special properties. In this work, using solvothermal reaction between $Ni(NO_3)_2 \cdot 6H_2O$ and formamide for **1**, $Ni(NO_3)_2 \cdot 6H_2O$ and 4,4′-bipyridine in formamide for **2** at 70 °C for 72 h yields green cubic crystals. This synthetic procedure gave a good yield of about 75% based on nickel in the both cases. Anion NO_2^- in the compounds may come from reduction of NO_3^- by formamide [33]. Indeed, at high temperature and pressure of the solvothermal condition, the reaction is suggested to be as follows:

$$NO_3^- + NH_2{-}CHO \rightarrow NO_2^- + NH_2{-}COOH.$$

To evidence the reaction mechanism above, the analysis of nitrite anion was carried out by a standard method, spectrophotometric determination. A liquid part of the reaction products was isolated and analyzed by using sulfanilamide and *N*-(1-naphthyl)ethylenediamine as indicators with using light at 543 nm. The analysis results showed that almost NO_3^- was reduced to NO_2^-. The oxidation of *N*,*N*-dimethylformamide to form carbamic acid by oxidant such as Ag^+ was also reported in the previous literature [33]. Compounds **1** and **2** can be obtained in a wide temperature range from 70 to 150 °C.

Table 1
Crystallographic data for compounds **1** and **2**.

Empirical formula	N_4NiO_8 (**1**)	$C_{10}H_8N_4NiO_4$ (**2**)
Formula weight	242.75	306.91
T (K)	293(2)	293(2)
Crystal system	monoclinic	tetragonal
Space group	$C2/c$	$P4_32_12$
a (Å)	12.7799(16)	7.9101(7)
b (Å)	8.3600(10)	7.9101(7)
c (Å)	8.2511(10)	17.457(2)
α (°)	90.00	90.00
β (°)	93.167(2)	90.00
γ (°)	90.00	90.00
V (Å^3)	880.20(19)	1092.27(19)
Z	4	4
Absorption coefficient (mm^{-1})	2.231	1.794
Number of data collected	2252	5961
Number of unique data	811	1307
R_{int}	0.1821	0.1151
Goodness-of-fit	1.025	1.054
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0569, wR_2 = 0.1416	R_1 = 0.0643, wR_2 = 0.1828
Final R indices (all data)	R_1 = 0.0691, wR_2 = 0.1544	R_1 = 0.0867, wR_2 = 0.2306

3.2. Structure description

Compound **1** crystallizes in monoclinic space group $C2/c$ with two-dimensional framework (Fig. 1). In this structure, there is only one crystallographical type of Ni^{2+} ion with a nearly octahedral environment surrounded by six oxygen atoms. Each Ni^{2+} ion is bridged with four neighboring Ni^{2+} ions through NO_2^- ligands. The Ni1–O1, O1–N1, N1–O2($0.5 - x$, $-0.5 + y$, $0.5 - z$) and O2–Ni1 lengths are 2.075(3), 1.273(6), 1.256(5), and 2.083(3) Å; and the Ni1–O1–N1, O1–N1–O2($0.5 - x$, $-0.5 + y$, $0.5 - z$) and N1($0.5 - x$, $0.5 + y$, $0.5 - z$)–O2–Ni1 angles are 123.6(3)°, 122.6(4)°, and 22.0(3)°, respectively. The distance between two neighboring Ni^{2+} ions is 5.873(1) Å. These bond lengths and angles may play an important role to the magnetic coupling between the Ni^{2+} ions. The relative Ni1–O1–N1–O2 and O1–N1–O2–Ni1 torsion angles are 177.7(1)° and 174.06(1)°. This means that Ni1, O1, N1, and O2 atoms are arranged nearly in a plane. Linking Ni^{2+} ions and bridging NO_2^- ligands forms a two-dimensional framework. In addition, each Ni^{2+} ion also coordinates with two NO_2 molecules with bond lengths Ni–O3 (2.080(3) Å), N2–O3 (1.251(7) Å), N2–O4 (1.192(11) Å). Compared with N2–O3 bond, shorter length of N2–O4 may be due to double bond of this terminal link. The double bond can be evidenced further by a comparison of the IR data for 4,4′-bipyridine, **1**, and **2** (Fig. S1). Compound **2** crystallizes in tetragonal space group $P4_32_12$. Asymmetric unit contains half metal atom, half 4,4′-bipy ligand, and a NO_2^- ligand. Symmetry operations ($x - 1$, $y - 1$, z), ($x - 1/2$, $-y+1/2$, $-z + 1/4$), ($-y + 1/2$, $x - 1/2$, $z - 1/4$), (y, x, $-z$), ($x + 1$, $y + 1$, z), and ($y + 1/2$, $-x + 1/2$, $z + 1/4$) generate three-dimensional structure (Fig. 2). There is only one type of Ni^{2+} ion in the structure, coordinated by six atoms. The coordination environment of Ni can be considered as a octahedron compressed along N1–Ni1–N2($x - 1$, $y - 1$, z) axis with Ni–N bond lengths for Ni1–N1 (2.051(8) Å) and Ni1–N2($x - 1$, $y - 1$, z) (2.063(7) Å) are shorter than those of four equatorial bonds Ni–O (2.124(5)–2.126(5) Å). Each Ni^{2+} ion is bridged with four neighboring Ni^{2+} ions via NO_2^- ligands. The Ni1–O1, O1–N3, N3–O2 and O2–Ni1($y + 1/2$, $-x + 1/2$, $Z + 1/4$) lengths are 2.126(5), 1.236(7), 1.275(8), and 2.124(5) Å; and the Ni1–O1–N3, O1–N3–O2 and N3–O2–Ni1($y + 1/2$, $-x + 1/2$, $Z + 1/4$) angles are 126.6(5)°, 127.8(8)°, and 120.0(5)°, respectively. The distance between two neighboring Ni^{2+} ions bridged by NO_2^- is 5.893(1) Å. The relative Ni1–O1–N3–O2 and O1–N3–O2–Ni1($y + 1/2$, $-x + 1/2$, $Z + 1/4$) torsion angles are −178.1(5)° and −156.6(6)°. This shows that the configuration of NO_2^- for **2** is different from that for **1**. Along direction N1–Ni1–N2, two neighboring Ni^{2+} ions are bridged by a ligand 4,4′-bipy molecule with a torsion angle of two pyridine rings to be 47.7(2)°. The distance between these two Ni^{2+} ions is 11.187(1) Å. Two 4,4′-bipyridine molecules of two neighboring Ni^{2+} ions bridged by NO_2^- have perpendicular N–N directions.