Research paper

Random bimetallic $Ni_x^{II}Mn_{1-x}^{II}$ chains with mixed azido and carboxylato triple bridges: A gradual ferromagnetic-to-antiferromagnetic evolution

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ABSTRACT

A series of isomorphous random bimetallic Ni^{II}-Mn^{II} compounds with *N*-methylpyridinium-4-carboxylate (4-mpc) and azide, have been synthesized and characterized. They are of formula $[Ni_x^{II}Mn_{1-x}^{II}(N_3)_2(4\text{-mpc})]$ (**1**–**6**), ($x = 1$ (**1**), 0.86 (**2**), 0.83 (**3**), 0.71 (**4**), 0.56 (**5**), 0.47 (**6**)). Compounds **1**–**6** consist of one-dimensional uniform chains with $[(\mu\text{-EO-}N_3)_2(\mu\text{-COO})]$ triple bridges (EO = end-on). Magnetic measurements reveal that compounds **1**–**6** behave as antiferromagnets with a gradual ferromagnetic-to-antiferromagnetic evolution by the incorporating of isotropic Mn^{II} ions into Ni^{II} chain. The Ni^{II}-rich compounds **1**–**3** exhibit field-induced metamagnetism. And the T_N of the heterometallic compounds exhibit a composition-dependence of the content of Ni^{II}.

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1. Introduction

Molecular magnets constructed by the assembly of appropriate metal ions and organic groups, has been of considerable interest and seen great progress in recent years for their theoretical value and potential applications [1–3]. Among the large number of molecular magnets, the so-called long-range ordering magnets (LROs), which can be different coordination polymers that exhibit complex long-range ordering, are receiving increasing current attention [2–6]. However, rational design of LROs and tuning of their properties are still great challenges. Among others, to construct 1D ferromagnetic (FM) chains based on the strong ferromagnetic couplings between neighboring paramagnetic centers is an effective strategy. And in this case it is relatively convenient to control or to tune the interchain/interlayer interactions to get materials with specific bulk magnetic properties. To achieve 1D FM chains, elaborate selection of the bridges which can influence the nearest-neighbour magnetic coupling is very important. Up to now, several bridging ligands have been explored, such as carboxylate, azide, oxolate, tetrazolate, and so on [2–4]. And also, the mixed bridges of above-mentioned ligands have been found

to have advantages in constructing 1D FM chains in some system [7–31]. For example, the mixed azide-carboxylate triple bridges ($[(\mu\text{-EO-}N_3)_2(\mu\text{-COO})]$ or $[(\mu\text{-EO-}N_3)(\mu\text{-COO})_2]$) (EO = end-on) have been found usually mediate antiferromagnetic (AF) coupling in Mn^{II} materials while mediate FM coupling in Co^{II} and Ni^{II} materials [20–27]. Meanwhile, it has been found recently that the introduction of the second metal ions with random substitution can lead to great influence to the bulk magnetic properties of the materials. Few examples have been reported, including Mn^{II}-Fe^{II} systems which show the gradual AF-to-FM evolution, Co^{II}-Ni^{II} systems with $[(\mu\text{-EO-}N_3)(\mu\text{-COO})_2]$ bridges or with $[(\mu\text{-EO-}N_3)(\mu\text{-}N,N\text{-tetrazo-}late)]$ bridges which exhibit the enhancement of T_B [29,32,33]. Such composition-dependent magnetic behaviors in these random bimetallic compounds may have great potential in controllable synthesis of molecular magnetic materials. However, more examples with various kinds of metal ions should be provided to further investigation of such heterometallic compounds for the lack of theory. Thus, it may be interesting to investigate a series of isomorphous heterometallic compounds with mixed azide-carboxylate bridges.

We have reported previously a series of Co^{II} and Mn^{II} compounds with mixed azido and carboxylato bridges of *N*-methylpyridinium-4-carboxylate (4-mpc) ligand which exhibit interesting diversity in structure and magnetism [26]. For Co^{II}, a uniform 1D chain with $[(\mu\text{-EO-}N_3)_2(\mu\text{-COO})]$ triple bridges was obtained (Scheme 1, (a)). For Mn^{II}, the compound ($[Mn(N_3)_2(4\text{-mpc})]$) we obtained exhibits as a different

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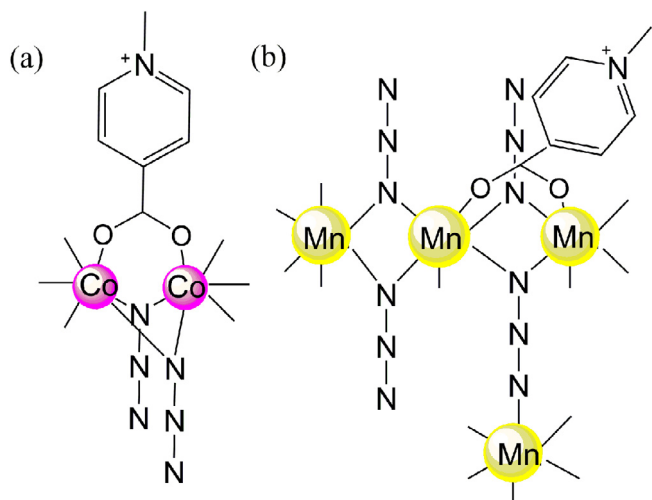
Scheme 1. (a) The $(\mu\text{-EO-N}_3)_2(\mu\text{-COO})$ triple bridging mode of the homometallic Co^{II} compound (b) the three bridging modes in the homometallic Mn^{II} compound.

two-dimensional (2D) layer with alternating triple $[(\mu\text{-EO-N}_3)_2 (\mu\text{-COO})]$, double $[(\mu\text{-EO-N}_3)(\mu\text{-COO})]$ and single (EE-N$_3$) bridges (EE = end-to-end) (Scheme 1, (b)). Magnetic measurements revealed that the $[(\mu\text{-EO-N}_3)_2(\mu\text{-COO})]$ triple bridges transmit strong ferromagnetic interactions in the 1D Co^{II} chain while the bulk material behaves as an antiferromagnet with field-induced metamagnetism due to the interchain AF interactions through π-π stacking. And the Mn^{II} compound exhibits spin-canted weak ferromagnetism. Encouraged by the ferromagnetic couplings between the neighboring metal ions in the 1D Co^{II} chain, we construct a similar 1D Ni^{II} chain by identical method because the isomorphous Co^{II} and Ni^{II} compounds often exhibit similar magnetic behavior. And also, by the isomorphous substitution of the Ni^{II} ions by Mn^{II} on the basis of the 1D Ni^{II} FM chain, we construct a series of bimetallic Ni^{II}-Mn^{II} compounds with random metal sites and variable metal ratios, and investigate the magnetic properties of them, to provide more examples for the further research of such random heterometallic compounds.

Here we present a systematic study on the coordination chemistry of these Ni$_x^{II}$Mn$_{1-x}^{II}$ (0 < x ≤ 1) chains with $[(\mu\text{-EO-N}_3)_2(\mu\text{-COO})]$ triple bridges, including the synthesis, structures, and magnetic properties of these six compounds.

2. Experimental

2.1. Materials and physical measurements

All the starting chemicals were used as received. The isonicotinic acid was purchased from Alfa-Aesar. Elemental analyses (C, H, N) were performed on an Elementar Vario EL analyzer. The IR spectrum was recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan Microscope. Magnetic measurements were carried out on a Quantum Design SQUID MPMS-5 magnetometer. The experimental susceptibility data were corrected for diamagnetism (Pascal's parameters) and background by an experimental measurement on a sample holder. Powder X-ray diffraction (PXRD) data were collected on a RigakuD/Max2550VB diffractometer equipped with Cu Kα at a scan speed of 1°min^{-1}.

2.2. Synthesis of compounds 1–6

All reagents purchased were of reagent grade and used without further purification. The hydroiodides of 4-mpc were prepared according to literature methods [34,35].

Synthesis of 1–6. Compounds **1–6** were synthesized by slow diffusion between the methanol solution containing sodium azide (0.013 g, 0.20 mmol), [H(4-mpc)]I (0.026 g, 0.10 mmol) and the methanol solution of the acetate salts of the two corresponding metal ions (manganese(II) acetate and nickel(II) acetate) at various ratio at room temperature for a few days. The metal ratios in the products were determined by the ICP atomic emission spectrometry. Nevertheless, the ratios of the two metal ions in products which were determined by ICP atomic emission spectrometry are not corresponding exactly to the ratios in reactants. These Ni$_x^{II}$Mn$_{1-x}^{II}$ compounds with x = 1 (**1**), 0.86 (**2**), 0.83 (**3**), 0.71(**4**), 0.56 (**5**), 0.47 (**6**) were obtained from the reactions with $x_{synthesis}$ = 1 (**1**), 0.91 (**2**), 0.83 (**3**), 0.50 (**4**), 0.17 (**5**), 0.09 (**6**). It is worth noting that when the second spin Mn(II) is introduced to the 1D chains, only a limited amount of the Ni(II) ions can be replaced (the maximum ratio of the Mn(II) is 0.53). Meanwhile, the yields of the heterometallic compounds **2–6** are very low. It may be due to the difference in radius between Ni(II) and Mn(II). In fact, the crystallization of heterometallic compounds is usually difficult in the cases we encounted. The CHN elemental analytic data of these compounds are very similar due to the similarity of Ni and Mn in atomic weight (see text below). The comparison of IR spectrum of these compounds is also presented in supplementary information (Fig. S1). Compounds **1–6** show two strong absorption bands characteristic of the v_{as}(COO) (1618–1624 cm^{-1}) and v_s(COO) (1341–1347 cm^{-1}) vibrations and a strong absorption band characteristic of the v_{as}(N$_3$) (2069–2076 cm^{-1}) vibration (see text below).

[Ni(N$_3$)$_2$(4-mpc)] (1): Yield, 33.4%. Anal. calcd. for C$_7$H$_7$NiN$_7$O$_2$: C: 30.02, H: 2.52, N: 35.03. Found: C: 29.83, H: 2.94, N: 35.42%. Main IR bands (cm^{-1}, KBr): 3378w, 3328w, 3118w, 3045w, 2076s, 1622s, 1574m, 1402s, 1348s, 1294m, 1217w, 1181w, 879m, 860m, 782m, 691w, 664w, 630m.

[Ni$_{0.86}$Mn$_{0.14}$(N$_3$)$_2$(4-mpc)] (2): Yield, 9.7%. Anal. calcd. for C$_7$H$_7$Ni$_{0.86}$Mn$_{0.14}$N$_7$O$_2$: C: 30.10, H: 2.53, N: 35.10%. Found: C: 29.54, H: 2.70, N: 34.77%. Main IR bands (KBr, cm^{-1}): 3375w, 3323w, 3116w, 3047w, 2071s, 1623s, 1572s, 1401s, 1347s, 1289m, 1217w, 1181w, 878m, 860m, 781m, 690w, 663w, 629w.

[Ni$_{0.83}$Mn$_{0.17}$(N$_3$)$_2$(4-mpc)] (3): Yield, 14.1%. Anal. calcd. for C$_7$H$_7$ Ni$_{0.71}$Mn$_{0.29}$N$_7$O$_2$: C: 30.16, H: 2.53, N: 35.17. Found: C: 30.10, H: 2.78, N: 35.07%. Main IR bands (KBr, cm^{-1}): 3371w, 3323w, 3118w, 3046w, 2074s, 1623s, 1572s, 1401s, 1345s, 1289m, 1215w, 1182w, 879m, 860m, 781m, 690w, 661w, 627w.

[Ni$_{0.71}$Mn$_{0.29}$(N$_3$)$_2$(4-mpc)] (4): Yield, 14.1%. Anal. calcd. for C$_7$H$_7$Ni$_{0.56}$Mn$_{0.44}$N$_7$O$_2$: C: 30.22, H: 2.54, N: 35.24. Found: C: 30.33, H: 2.66, N: 35.34%. Main IR bands (KBr, cm^{-1}): 3371w, 3319w, 3114w, 3045w, 2072s, 1618s, 1572s, 1400s, 1341s, 1288m, 1217w, 1180w, 878m, 860m, 781m, 690w, 662w, 627w.

[Ni$_{0.56}$Mn$_{0.44}$(N$_3$)$_2$(4-mpc)] (5): Yield, 5.1%. Anal. calcd. for C$_7$H$_7$Ni$_{0.83}$Mn$_{0.17}$N$_7$O$_2$: C: 30.11, H: 2.53, N: 35.11. Found: C: 29.89, H: 2.61, N: 34.84%. Main IR bands (KBr, cm^{-1}): 3373w, 3323w, 3116w, 3047w, 2069s, 1623s, 1572s, 1400s, 1344s, 1288m, 1217w, 1180w, 878m, 862m, 781m, 691w, 663w, 629w.

[Ni$_{0.47}$Mn$_{0.53}$(N$_3$)$_2$(4-mpc)] (6): Yield, 7.1%. Anal. calcd. for C$_7$H$_7$Ni$_{0.47}$Mn$_{0.53}$N$_7$O$_2$: C: 30.26, H: 2.54, N: 35.28. Found: C: 30.25, H: 2.62, N: 35.07%. Main IR bands (KBr, cm^{-1}): 3373w, 3323w, 3116w, 3046w, 2072s, 1624s, 1572s, 1400s, 1341s, 1290m, 1217w, 1180w, 880m, 860m, 781m, 691w, 661w, 627w.

Caution! Although not encountered in our experiments, metal complexes of azide are potentially explosive. Only a small amount of the materials should be prepared and handled with care.

2.3. Crystal data Collection and refinement

Diffraction intensity data of the single crystal of **6** were collected at 293 K on a Bruker Apex II CCD area detector equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).