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Doping effect of nonmagnetic impurity on the spin-Peierls-like transition in the quasi-one-dimensional (quasi-1D) spin system of 1-(4'-nitrobenzyl)pyridinium bis(maleonitriledithiolato)nickelate

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ABSTRACT

A nonmagnetic compound, $[NO_2BZPy][Cu(mnt)_2]$ (mnt²⁻ = maleonitriledithiolate; NO_2BZPy^* = 1-(4'nitrobenzyl)pyridinium), is isostructural with $[NO_2BZPy][Ni(mnt)_2]$, which is a quasi-1D spin system and exhibits a spin-Peierls-like transition with J = 192 K in the gapless state and spin energy gap = 738 K in the dimerization state, respectively. Further, five nonmagnetic impurity doped compounds $[NO_2BZ-Py][Cu_xNi_{1-x}(mnt)_2]$ (x = 0.04–0.74) were prepared, and their crystal structures as well as magnetic properties were investigated. The nonmagnetic doping causes the suppression of the spin transition with an average rate of 139(13) K/percentage of dopant concentration, and the transition collapse is estimated at around x > 0.5.

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1. Introduction

Impurity doping of a low-dimensional magnetic system often results in non-intuitive ground states and transition behavior differing from that of the parent material [1–7]. Lots of investigations for doping magnetic impurity with different spins have been done theoretically and experimentally for the low-dimensional inorganic magnetic systems since the first inorganic spin-Peierls compound CuGeO₃ was discovered [1–8]. In contrast, the examples of an impurity doping on the low-dimensional molecular magnetic system are very rare [9-12] even if the molecular spin-Peierls transition compounds have been known much earlier than the inorganic one [13-15]. One of crucial reasons to cause the abovementioned situation is that the molecular structure is usually so complicated that it is not easy to find a suitable dopant that match with the parent material in both molecular structure and valence. In our previous study, we observed a peculiar spin-Peierls-like transition in 1-(4'-nitrobenzyl)pyridinium bis(maleonitriledithiolato)nickelate (Scheme 1 and abbreviated as [NO₂BzPy][Ni(mnt)₂]) [12]. This compound possesses columnar stacks along *c*-axis with cations and anions segregated, and the regular anionic stack can be considered as a uniform magnetic chain with S = 1/2 since the [Ni(mnt)₂]⁻ monoanion bears a half spin. The magnetic exchange

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nature is antiferromagnetic (AFM) above transition temperature, while below that a spin gap is opened with the spin chain dimerization [16]. Instead of [Ni(mnt)₂]⁻ monoanion with nonmagnetic $[Au(mnt)_2]^-$ monoanion, the compound of $[NO_2BzPy][Au(mnt)_2]$, which is isostructural with [NO₂BzPy][Ni(mnt)₂], was obtained, and the effect of nonmagnetic [NO₂BzPy][Au(mnt)₂] doping in the lattice of [NO₂BzPy][Ni(mnt)₂] on the spin-Peierls-type transition was further investigated [17]. The doped systems $[NO_2BzPy][Au_xNi_{1-x}(mnt)_2]$ exhibit that: (1) within an anionic stack, $[Au(mnt)_2]^-$ substituting $[Ni(mnt)_2]^-$ does not change the crystal structure of [Ni(mnt)₂]⁻ compound, moreover, the $[Ni(mnt)_2]^-$ and $[Au(mnt)_2]^-$ anions could not be distinguished from the single-crystal structure temperatures above 10 K; (2) even though an anionic stack exhibits a disordered structural feature, the magnetic behavior does not show a random spin system characteristic in the heavier doped system ($x \ge 0.49$), additionally, the fits for temperature dependence of magnetic susceptibility indicated the presence of stronger AFM coupling interaction between the $[Ni(mnt)_2]^-$ anions which are separated by the nonmagnetic $[Au(mnt)_2]^-$ species; (3) the transition is suppressed by nonmagnetic doping and collapsed at around x > 0.27, and in a heavier doped system with x = 0.49, the spin gap vanishes and a gapless phase is achieved again, and this magnetic behavior resembles to the phenomena observed in inorganic spin-Peierls transition systems such as CuGO₃ [1–3] and TlCuCl₃ [4], however, the transition collapses when *x* value is much higher than those found in the inorganic spin-Peierls transition systems and (4) single-crystal EPR measurements and theoretical analysis for the



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(Abbr. as $[NO_2BzPy][M(mnt)_2]$ and M = Ni or Cu)

Scheme 1.

sample of $[NO_2BzPy][Au_{0.57}Ni_{0.43}(mnt)_2]$ disclosed the existence of intermolecular charge transfer between the adjacent $[Ni(mnt)_2]^-$ and $[Au(mnt)_2]^-$ species in an anionic stack [18].

It is well known that the structural feature of a nonmagnetic dopant strongly influence the magnetic transition behavior in a spin-Peierls system, this very important theme forms the background of the present work. The nonmagnetic compound [NO₂BzPy][Cu(mnt)₂] is isostructural with the nonmagnetic compound [NO₂BzPy][Au(mnt)₂] as well as the spin-Peierls-like transition compound [NO₂BzPy][Ni(mnt)₂], compared with [NO₂BzPy][Au(mnt)₂], the molecular geometric parameters in [Cu(mnt)₂]⁻ species are much closer to those in [Ni(mnt)₂]⁻ anion than [Au(mnt)₂]⁻ species (the averaged M–S distances: $d_{Au-S} = 2.3085$, $d_{Cu-S} = 2.1886$ and $d_{Ni-S} = 2.1466$ Å; and the averaged

Table 1

Elemental analyses (C, H and N), molar ratio of $[Cu(mnt)_2]^-$ to $[Ni(mnt)_2]^-$ in the starting materials and the occupation factor of Cu(Ni) in the final crystal structural refinement for $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0.04–0.74).

	Calculated			Found			Cu:Ni ^a	Cu:Ni ^b
	С	Н	Ν	С	Н	Ν		
x = 0.04	43.3	2.00	15.2	43.1	2.05	15.0	0.05:0.95	0.04:0.96
<i>x</i> = 0.12	43.3	2.00	15.1	43.0	2.03	14.9	0.10:0.90	0.12:0.88
<i>x</i> = 0.32	43.2	1.99	15.1	43.4	2.06	14.8	0.33:0.67	0.32:0.68
x = 0.50	43.1	1.99	15.1	43.1	2.02	15.2	0.49:0.51	0.50:0.50
x = 0.74	43.1	1.99	15.1	42.8	2.00	15.3	0.75:0.25	0.74:0.26

^a The molar ratio in the starting materials.

^b The results from ICP measurements.

Table 2

 $Crystallographic \ data \ for \ [NO_2BzPy][Cu_xNi_{1-x}(mnt)_2] \ with \ molecular \ formula \ of \ C_{20}H_{11}Cu_xNi_{1-x}N_6O_2S_4 \ at \ 293 \ K.$

 \angle S-M-S bite angles: \angle S-Au-S = 90.50°, \angle S-Cu-S = 92.37° and \angle S-Ni-S = 92.44° in above-mentioned three compounds). In this contribution, we further investigate the crystal structures and magnetic properties of a series of compounds with a formula [NO₂BzPy][Cu_xNi_{1-x}(mnt)₂] (*x* = 0-1 and it represents the molar fraction of Cu in a doped system).

2. Experimental

2.1. Preparation of compounds

[NO₂BzPy][Ni(mnt)₂] and [NO₂BzPy]₂[Cu(mnt)₂] were prepared according to the published procedures [16,19].

 $[NO_2BZPy][Cu(mnt)_2]$: The compound $[NO_2BZPy]_2[Cu(mnt)_2]$ was oxidized by 0.75 equivalent of I₂ to afford $[NO_2BZPy][Cu(mnt)_2]$ (yield: ~72%). Single crystals suitable for X-ray structural analysis were obtained by diffusing diethyl ether into an acetonitrile solution of $[NO_2BZPy][Cu(mnt)_2]$. Elemental *Anal*. Calc. for $C_{20}H_{11}N_6O_2S_4Cu$: C, 43.0; H, 1.98; N, 15.0%. Found: C, 42.8; H, 2.04; N, 14.9%.

 $[NO_2BZPy][Cu_xNi_{1-x}(mnt)_2]$: Each doped compound was prepared according to the procedure employed in the literature [17], and the product is needle- or block-shaped crystals which are suitable for X-ray structural analysis. The molar ratio of $[NO_2BZPy][Ni(mnt)_2]$ to $[NO_2BZPy][Cu(mnt)_2]$ in the starting materials and the results of elemental analyses for C, H and N for $[NO_2BZPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0.04-0.74) are presented in Table 1.

2.2. Physical measurements

Elemental analyses were performed with a Perkin–Elmer 240 analytical instrument. IR spectra were recorded on Bruker Vector 22 spectrophotometer (KBr disc). The molar ratio of Ni-to-Cu for each alloy compound was determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Atomscan Advantage, USA). Magnetic susceptibility measurement over the range of 2– 350 K for each polycrystalline sample was carried out using a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer under 1.0 T.

2.3. X-ray structural analyses

Crystallographic data were collected using a Rigaku Raxis-Rapid diffractometer with Mo K α (λ = 0.71073 Å) radiation from a graphite monochromator. Structures were solved by direct method using the SHELXL-97 software package [20]. The non-hydrogen atoms were refined anisotropically using the full-matrix least-squares method on F^2 . It is similar to the [NO₂BzPy]-[Au_xNi

	x = 0.04	<i>x</i> = 0.12	<i>x</i> = 0.32	<i>x</i> = 0.50	x = 0.74	<i>x</i> = 1
CCDC no.	705213	705214	705215	705216	705217	705212
Molecular mass	554.49	554.88	555.84	556.71	557.87	559.13
Space group	P2(1)/c	P2(1)/c	P2(1)/c	P2(1)/c	P2(1)/c	P2(1)/c
a (Å)	12.192(2)	12.194(2)	12.198(2)	12.152(2)	12.180(2)	12.217(2)
b (Å)	26.543(5)	26.546(5)	26.516(5)	26.448(5)	26.479(5)	26.559(5)
c (Å)	7.2383(14)	7.2556(15)	7.2511(15)	7.2930(15)	7.3027(15)	7.3433(15)
β (°)	102.82(3)	102.94(3)	102.97(3)	103.15(3)	103.19(3)	103.42(3)
V (Å ³), Z	2284.0(8), 4	2289.0(8), 4	2285.4(8), 4	2282.6(8), 4	2293.1(8), 4	2317.6(8), 4
μ (mm ⁻¹)	1.251	1.257	1.280	1.301	1.320	1.334
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$ ho$ (g cm $^{-3}$)	1.613	1.610	1.615	1.620	1.616	1.602
R ₁	0.0331	0.0288	0.0572	0.1138	0.0439	0.0419
wR ₂	0.0817	0.0647	0.1100	0.3746	0.1271	0.0699

 $R_1 = \sum (||F_0| - |F_c||) / \sum |F_0|, \ wR_2 = \sum w (|F_0|^2 - |F_c|^2)^2 / \sum w (|F_0|^2)^2]^{1/2}.$

 $_{1-x}(mnt)_2$] compounds that the $[Cu(mnt)_2]^-$ anions distribute randomly in the $[Ni(mnt)_2]^-$ stack for all doped crystals of $[NO_2BzPy][-Cu_xNi_{1-x}(mnt)_2]$ at 293 K, and the occupancy factors of Cu and Ni atoms for each doped sample were defined by ICP measurement. All hydrogen atoms were placed at calculated positions (C-H = 0.930 Å for benzene or pyridine rings and 0.970 Å for methylene) and refined riding on the parent atoms with $U(H) = 1.2 \times U_{eq}$ (bonded C atom). Details of the lattice parameters, data collections, and refinements for $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0.04-1) at 293 K are summarized in Table 2.

3. Results and discussion

3.1. Description of crystal structures

Crystal structure of $[NO_2BZPy][Cu(mnt)_2]$ at 293 K: This compound crystallizes in monoclinic space group P2(1)/c, and it is isostructural with the compounds $[NO_2BZPy][Ni(mnt)_2]$ and $[NO_2BZPy][Au(mnt)_2]$. The asymmetric unit in a cell is comprised of a coupled of $[Cu(mnt)_2]^-$ and NO_2BZPy^+ . The $[Cu(mnt)_2]^-$ anion possesses roughly a planar geometry (Fig. 1a), and the Cu–S lengths range from 2.1844(8) to 2.1982(8) Å, these values are close to the Ni–S lengths [2.1409(7)-2.1565(6) Å] in $[NO_2BZPy]-[Ni(mnt)_2]$, and shorter than the Au–S lengths [2.303(2)-2.3153(19) Å] in $[NO_2BZPy][Au(mnt)_2]$. The S–Cu–S bite angles of 92.08(3)° and 92.66(3)° are also close to the S–Ni–S values



Fig. 1. (a) ORTEP view with displacement ellipsoids at 50% possibility level and (b) packing diagram of [NO₂BzPy][Cu(mnt)₂] projected along *c*-axis.



Fig. 2. (a) Distances of M...M (d_1 and d_2) and interplane between neighboring anions (h_1 and h_2) and (b) central-to-central distance between adjacent benzene rings (c_1 and c_2).

 $[92.32(3)^{\circ}$ and $92.56(3)^{\circ}]$ in $[NO_2BzPy][Ni(mnt)_2]$. The molecular conformation of $[NO_2BzPy]^+$ cation in $[Cu(mnt)_2]^-$ compound resembles to that in $[Ni(mnt)_2]^-$ compound. For example, the dihedral angles of pyridine ring and benzene ring with the reference plane $C_{Ar}-CH_2-N_{Py}$ are 88.3° and 64.8° in $[Cu(mnt)_2]^-$ compound versus 86.9° and 65.2° in $[Ni(mnt)_2]^-$ compound, respectively. The pyridine and benzene rings makes a dihedral angle of 90.2° in $[NO_2BzPy][Cu(mnt)_2]$ and 95.0° in $[NO_2BzPy][Ni(mnt)_2]$.

Both anions and cations form, respectively, the segregated stacks that run parallel to *c*-axis (Fig. 1b). Within anionic stacks, the face-to-face anions slid along *b*-axis and eclipse each other. The interplane distances between the adjacent $[Cu(mnt)_2]^-$ anions, which is defined by four coordinated S atoms, are $h_1 = 3.507$ and $h_2 = 3.493$ Å (Fig. 2a), while the adjacent Cu…Cu distances are exactly identical with $d_1 = d_2 = 3.895$ Å. The cationic stack is also regular with a uniform central-to-central distance of 4.280 Å between neighboring benzene rings (cf. Fig. 2b).

Crystal structures of $[NO_2BZPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0.04-0.74) at 293 K: As shown in Table 2, each compound with formula $[NO_2BZPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0.04-0.74) is isostructural to the parent compounds with very similar lattice parameters. The M–S lengths and S–M–S bite angles along with their estimated standard deviations are presented in Table 3. With the doping concentration x increases, the distances of M···M, M···S, S···S and interplanar distances between the nearest neighbors (h_1 , h_2 refer to Fig. 2a) within an anionic stack change gradually and monotonically (cf. Fig. 3), and this characteristic of structural variation is distinct from the $[NO_2BZPy][Au_xNi_{1-x}(mnt)_2]$ systems.

3.2. Magnetic susceptibilities

The magnetic behavior of each $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0-1) was determined on its polycrystalline sample from 2 to 350 K. These compounds are isostructural with each other. Therefore, it is reasonable to suppose that the diamagnetism for each compound of $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ is equal roughly to the magnetic susceptibility of $[NO_2BzPy][Cu(mnt)_2]$. The corrected

Table 3

The coordinated bond lengths (Å) and angles (°) in an anionic moiety for $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0–1).



	x = 0	<i>x</i> = 0.04	<i>x</i> = 0.12	<i>x</i> = 0.32	<i>x</i> = 0.50	x = 0.74	<i>x</i> = 1
M-S ₁	2.1409(7)	2.1418(9)	2.1452(7)	2.1426(12)	2.158(4)	2.1647(9)	2.1844(8)
$M-S_2$	2.1442(6)	2.1443(9)	2.1488(6)	2.1451(12)	2.160(4)	2.1649(8)	2.1844(9)
$M-S_3$	2.1446(7)	2.1450(9)	2.1511(7)	2.1481(12)	2.162(4)	2.1668(9)	2.1872(9)
$M-S_4$	2.1565(6)	2.1555(8)	2.1611(6)	2.1562(12)	2.180(4)	2.1757(8)	2.1982(8)
$S_1 - M - S_2$	92.32(3)	92.22(4)	92.16(3)	92.26(5)	92.15(15)	92.16(4)	92.08(3)
$S_3 - M - S_4$	92.56(3)	92.48(4)	92.43(3)	92.51(5)	92.56(15)	92.62(3)	92.66(3)



Fig. 3. Variations of interatomic and interplane distances between neighboring anions in a stack (h_1 and h_2 ; see Fig. 2) as x for [NO₂BzPy][Cu_xNi_{1-x}(mnt)₂] (x = 0-0.74) at 293 K and [NO₂BzPy][Ni(mnt)₂] at 273 K [16].

molar paramagnetic susceptibilities of $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0-0.74) as well as the nonmagnetic compound of $[NO_2BzPy][-Cu(mnt)_2]$ are given in Fig. 4 as $\chi_m = f(T)$, from which it can be found that the nonmagnetic compound of $[NO_2BzPy][Cu(mnt)_2]$ clearly shows diamagnetism behavior (with negative magnetic susceptibilities).

For the parent compound of $[NO_2BzPy][Ni(mnt)_2]$ (x = 0), as reported in our previous work [16], a magnetic transition occurs around 181 K, and the phenomenology of the magnetic transition closely resembles that of a spin-Peierls transition. The spin gap with the value of 738 K in dimerized state was estimated from the fits of the magnetic susceptibility data in low temperature phase, and the magnetic exchange interaction with $J/k_B =$ 192(3) K [17] in high temperature phase was evaluated from the analysis for magnetic susceptibility data utilizing a regular antiferromagnetic Heisenberg model for a $S = \frac{1}{2}$ linear chain system [21].

As displayed in Fig. 4a and b, the nonmagnetic doping causes (1) the molar magnetic susceptibility decreasing with *x* value increase when x < 0.5; (2) an onset of a strong paramagnetic background in the low temperature region and (3) a damping of the spin transition. These behaviors are similar to the doped systems of $[NO_2BzPy][Au_xNi_{1-x}(mnt)_2]$ [17]. It is understandable that the nonmagnetic doping induces the strong paramagnetic background in the low temperature region for the doped sample since the antiferromagnetic spin chains of $[Ni(mnt)_2]^-$ are broken at the position of



Fig. 4. Plots of $\chi_m(T)$ versus *T* for $[NO_2B2Py][Cu_xNi_{1-x}(mnt)_2]$ (*x* = 0–1) in the temperature range of (a) 70–350 K and (b) 2–80 K.

nonmagnetic dopants $[Cu(mnt)_2]^-$, moreover, the spin number in a chain should be randomly even and odd in equal probability. Therefore, the spin at the end of any odd numbered spin chain becomes uncoupled, giving a contribution to the paramagnetic susceptibility, and this contribution is dominant especially for heavily doped systems. In the doped system at x = 0.5, the broad maximum of magnetic susceptibility appears in the χ_m -T plot which is a typical characteristic of a lowered dimensionality of spin system due to the existence of short-range ordering. It is



Fig. 5. (a) Plots of $d(\chi_m T)/dT$ versus *T* for $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0-0.5) and (b) the *x* dependences of T_C .

noteworthy that the transition is still observed with the χ_m value clear dropping in the χ_m -T plot even if the change is small. In the heavily doped system of x = 0.74, the shape of $\gamma_m(T) - T$ plot is totally different from other doped systems, in which the typical characteristic of a lowered dimensionality of spin system (with a broad maximum of magnetic susceptibility) and the magnetic transition disappear, and the temperature dependences of magnetic susceptibility exhibits a simple Curie-Weiss behavior. Fig. 5a depicts the derivative curves of $\chi_m T$ versus T for $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0-0.5) and Fig. 5b plots the corresponding x dependences of T_c , which is defined as the peak temperature in the $d(\chi_m T)/dT - T$ plot. The values of $T_C(x)$ reduce linearly up to $x \le 0.5$, and it is expressed as $T_C = 182(3) - 139(13)x$ (K). Compared with the $[NO_2BzPy][Au_xNi_{1-x}(mnt)_2]$ system, where $T_{C} = 180(2) - 221(12)x$ (K), the [NO₂BzPy][Cu_xNi_{1-x}(mnt)₂] system exhibits higher x value of the transition collapsing and smaller x dependence of T_C shift.

4. Conclusion

Summarily, we synthesized and characterized structurally five nonmagnetic doped compounds with a formula [NO₂BzPy]

 $[Cu_xNi_{1-x}(mnt)_2](x = 0.04-0.74)$, and investigated the nonmagnetic impurities effects on the spin-Peierls-like transition in a quasi-1D spin system of $[NO_2BzPy][Ni(mnt)_2]$. The nonmagnetic impurities suppress the spin-Peierls-like transition, and the transition temperature T_C reduces at an average rate of 139(13) K/percentage of nonmagnetic dopant. The transition collapse is estimated around x > 0.5. Compared with the $[NO_2BzPy][Au_xNi_{1-x}(mnt)_2]$ system, the $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ system shows higher x values of the transition collapsing and smaller x dependence of T_C shift, and these differences may be originate from the molecular structure distinction between $[Cu(mnt)_2]^-$ and $[Au(mnt)_2]^-$ anions, for example, the average Au–S length is around 0.15 Å longer than the average Ni–S length whereas the average Cu–S length is similar to the Ni–S distance.

Supplementary data

CCDC 705212–705217 contain the supplementary crystallographic data for each compound of $[NO_2BzPy][Cu_xNi_{1-x}(mnt)_2]$ (x = 0.04-1). These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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