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Spin canting and long-range magnetic ordering in a 2-D cobalt–organic framework incorporated with a new bent connector: 1,4-bis(5-(4-pyridyl)-1H-1,2,4-triazol-3-yl)benzene

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ABSTRACT

A 2-D cobalt–organic framework formulated as $[Co(bdc)(bptb)]_n$ (**1**), built from a mixed 1,2-benzenedicarboxylate anion (bdc), 1,4-bis(5-(4-pyridyl)-1H-1,2,4-triazol-3-yl)benzene (bptb), and cobalt salt, has been hydrothermally synthesized and characterized. Complex **1** has a $[Co(bdc)]_n$ chain structure in which the chains are isolated by the bptb ligands in a 2-D wave-like architecture. The magnetic behavior of complex **1** was studied, and it indicated the coexistence of spin-canted weak ferromagnetism with $T_N = 10$ K and long-range magnetic ordering.

Introduction. To better understand some fundamental magnetic phenomena such as: ferromagnetic, ferrimagnetic, antiferromagnetic, and so on, magnetic coordination polymers provide good examples in molecular magnetism [1]. The ferrimagnetic correlations can be attributed to spin canting, *i.e.*, perfect antiparallel alignment of the spins on the neighboring metal ions is not achieved, so that residual spins are generated [2]. It is well known that spin canting can arise from two contributions: (1) the presence of an antisymmetric exchange and (2) the existence of single-ion magnetic anisotropy. Beyond that, the mutually tilted orientation of the metal centers caused by bent spacers, could give further contribution to the canting effect [3].

In the recent years, various coordination polymers with interesting magnetic properties had been synthesized based on the rigid angular ligands [3,4]. Our group had reported a series of Co^{II}/Ni^{II} coordination polymers, based on three angular N-heterocyclic-like ligands: 1H-3,5-bis(4-pyridyl)-1,2,4-triazole (4,4′-bpt), 1H-3-(3-pyridyl)-5-(4-pyridyl)-1,2,4 -triazole (3,4′-bpt), 1H-3,5-bis(3-pyridyl)-1,2,4-triazole (3,3′-bpt) (Chart 1). Most of them have fascinating structures and interesting magnetic properties [5].

As an extension of this work, we introduce herein a new bridging ligand: 1,4-bis(5-(4-pyridyl)-1H-1,2,4-triazol-3-yl)benzene (bptb), which has a bent backbone: the angle subtended at the center of the benzene ring and two pyridyl N-donors is 174° (Scheme 1). Based on bptb, we have synthesized a new complex $[Co(bdc)(bptb)]_n$ (**1**), which possesses a 2-D wave-like architecture and shows the coexistence of spin canting and magnetic long-range ordering (LRO).

Experimental section: Materials and physical measurements. With the exception of the ligands of bptb which were prepared according to the literature procedure [6], all reagents and solvents for synthesis and analysis were commercially available and used as received. IR spectra were taken on a Perkin-Elmer Spectrum One FT-IR Spectrometer in the 4000–400 cm^{-1} region with KBr pellets. X-ray powder diffraction (XRPD) intensities were measured on a Rigaku D/max-IIIA diffractometer (Mo-Ka $\lambda = 0.71073$ Å). Elemental analyses for C, H, and N were carried out on a Perkin-Elmer model 2400 II elemental analyzer. Temperature- and field-dependent magnetic measurements were carried out on a SQUID-MPMS-XL-7 magnetometer. Diamagnetic corrections were made with Pascal's constants.

Preparation of **1**. A mixture containing $Co(NO_3)_2 \cdot 6H_2O$ (145 mg, 0.5 mmol), bptb (183 mg, 0.5 mmol), $H_2(bdc)$ (83 mg, 0.5 mmol), NaOH (40 mg, 1 mmol), water (10 mL) and ethanol (5 mL) was sealed in a Teflon-lined stainless steel vessel (25 mL), which was heated at 140 °C for 3 days and then cooled to room temperature at a rate of 5 °C/h. Red block crystals of **1** were obtained and picked out, washed with distilled water and dried in air. Yield: 47% (based on Co(II)). Elemental analysis for $C_{28}H_{18}CoN_8O_4$ (%) Calcd: C, 57.05; H, 3.06; N, 19.02. Found: C, 57.17; H, 3.15; N, 19.14. IR (KBr, cm^{-1}): 3215w, 1605 m, 1584 s, 1558 m, 1393 s, 852 m, 754 m, 718 s, 691 m.

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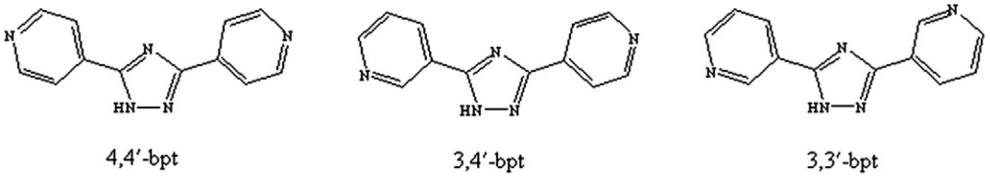
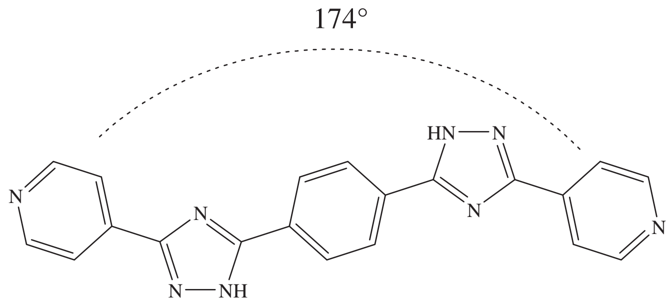


Chart 1. The three positional isomeric bent ligands used before.



Scheme 1. The possible coordination configuration of bptb.

X-ray structure determination. X-ray single-crystal diffraction data for bptb and **1** were collected with a Bruker SMART CCD instrument respectively by using graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 293(2) K and there was no evidence of crystal decay during data collection. A semiempirical absorption correction was applied using SADABS, and the program SAINT was used for integration of the diffraction profiles. The structure was solved by direct methods with the program SHELXS-97 and refined by full-matrix least-squares methods on all F^2 data with SHELXL-97 [7]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon and nitrogen were placed geometrically and allowed to ride during the subsequent refinements with isotropic displacement parameters. The starting positions for hydrogen atoms of water molecules were found in difference syntheses and then fixed in the given positions. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Crystallographic data and structural refinement details of bptb and **1** are summarized in Table S1. Selected bond lengths and bond angles of **1** are given in Table S2.

Results and discussion: Description of the crystal structures of **bptb·2H$_2$O**. X-ray single-crystal structural analysis reveals that **bptb·2H$_2$O** crystallizes in the monoclinic space group $P2_1/c$ with an asymmetric unit consisting of half a bptb and one water molecule (Fig. 1a). The adjacent bptb molecules are linked together by water molecules through O–H···N hydrogen bonds (Table S3), forming a three-dimensional supramolecular network (Fig. 1b).

Description of the crystal structures of **1**. Single-crystal X-ray structural analysis shows that the structure of **1** is a wave-like layer complex (Fig. 2). The asymmetric unit of **1** consists of one Co(II) cation, two bptb molecules, and two bdc anions. Each Co(II) ion lies in a distorted octahedral coordination environment, which is equatorially coordinated by four carboxylic O atoms from two bdc anions [Co1–O falls into the range from 2.069 (4) Å to 2.186 (4) Å], and axially occupied by two N atoms from two bptb ligands [Co1–N1 = 2.177 (4) Å; Co1–N8C = 2.168 (5) Å symmetry codes: C $x-1, y+1, z-1$].

Adjacent Co(II) centers are linked by the carboxylic groups of bdc anion *via* bis(μ-oxo) and bis(μ-O,O′-carboxylato) bridges alternately to form infinite [Co(bdc)]$_n$ chains running along the crystallographic *a* axis (Fig. 3). The distance of the adjacent Co(II) centers linked by the carboxylic groups of bdc anion *via* bis(μ-oxo) bridges is 3.328(8) Å. And the distance of the adjacent Co(II) centers linked by the carboxylic groups of bdc anion *via* bis(μ-O,O′-carboxylato) bridges league is 4.42(1) Å.

The neighboring [Co(bdc)]$_n$ chains are also bridged by bent bptb ligand to generate a wave-like layer structure (Fig. 4) with the Co···Co distance of 21.76(5) Å. In addition, the N3 of bptb as the H-donor link the uncoordinated carboxylate O (O2) of a neighboring layer through hydrogen bonding interactions to furnish a 3-D architecture (Fig. S1 in the Supporting information).

The XRPD result of **1**: In order to confirm the phase purity of the sample, X-ray powder diffraction (XRPD) experiments have been carried out for complexes **1**, before the magnetic measurements. The XRPD experimental and computer-simulated patterns of **1** are shown in Fig. S2. Although the experimental patterns have a few unindexed diffraction lines and some are slightly broadened in comparison with those simulated from the single crystal models, it still can be considered favorably that the samples of **1** are phase pure.

The magnetic properties of **1**: Solid-state variable-temperature magnetic susceptibility measurements were performed on a powder sample of complex **1** in the 2–300 K range in a 1 kOe magnetic field (Fig. 5a). The Curie–Weiss fit of the inverse magnetic susceptibility above 70 K provides a Curie constant $C = 3.80$ cm^3 K·mol^{-1} and Weiss temperature $\theta = -34.05$ K. The $\chi_M T$ value per Co(II) at 300 K is about 3.44 emu·K·mol^{-1}, much larger than the spin-only value 1.88 emu·K·mol^{-1} for a magnetically Co(II) ion with ($S = 3/2$, $g = 2.0$), as expected for the presence of a strong orbital contribution in octahedral Co(II). From 300 to 35 K, the magnetic moments decrease with the decreasing temperature, which basically corresponds to a single-ion behavior, which accounts for the splitting of the ${}^4T_1$ term into six Kramers doublets as a consequence of the combined effect of spin-orbit coupling and distortion from ideal octahedral symmetry [1d,8]. However, the observed increase in $\chi_M T$ below this

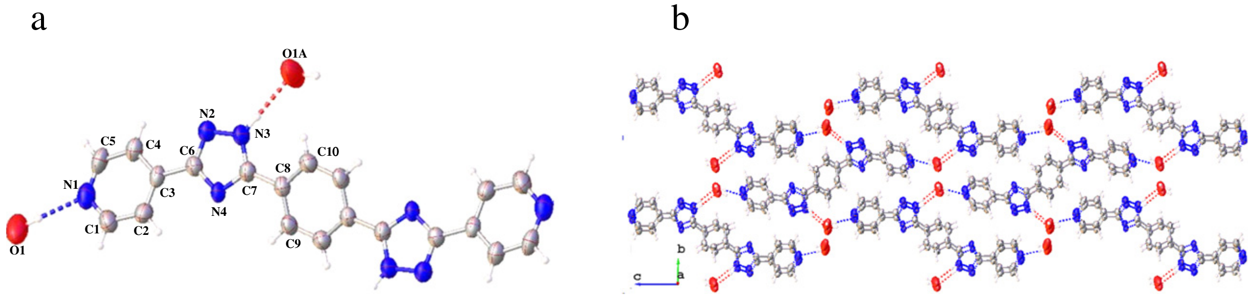


Fig. 1. The molecular structure (a) and the extended structure of the three-dimensional supramolecular network of **bptb·2H$_2$O** (b).

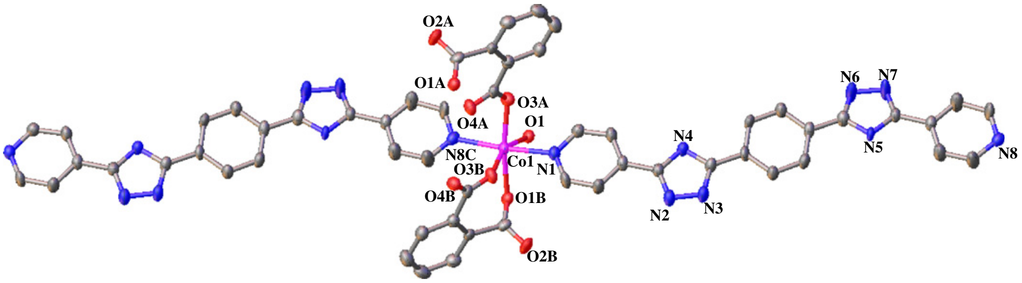


Fig. 2. The local coordination environments of the Co(II) atoms.

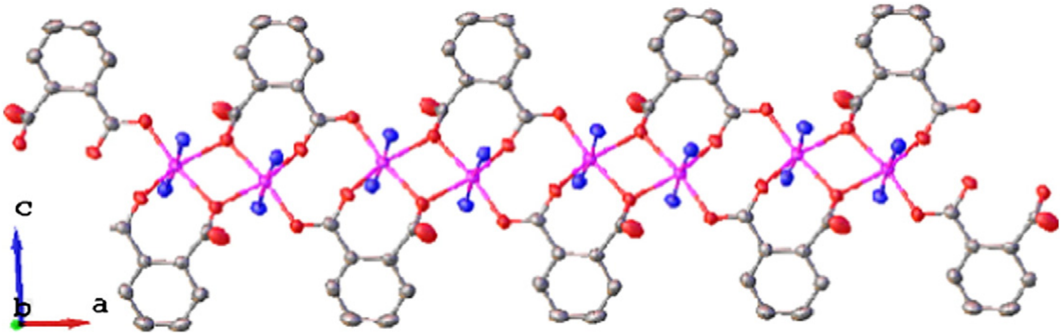


Fig. 3. The $[Co(bdc)]_n$ chain viewed down the *b* axis.

temperature is no longer coming from the single-ion behavior but rather from a canted antiferromagnetic Co(II)–Co(II) exchange interaction. The final down–up behavior in $\chi_M T$ below 10 K indicate a magnetic phase transition and some impurity [9].

The magnetic phase transition is also consistent with the presence of the bifurcation point between the field-cooled (FC)/zero-field-cooled (ZFC) magnetization curves below 10 K (Fig. 5b) [10]. At very low temperatures, the FC/ZFC curves undergo a slight increase which could be attributed to the presence of a paramagnetic contribution arising from defects in the crystal structure [11]. In addition, the FC magnetizations of **1** are quite field-dependent, in which the rise of the $\chi_M T$ values at low temperature becomes less obvious at higher fields (Fig. 5b, inset). This is an important feature of spin canting behavior [12].

The zero-field ac magnetic susceptibility measurement (Fig. 6a) only exhibits the characteristic of an antiferromagnet. The in-phase part χ_M' reaches a maximum at $T_N = 10.0$ K, while no obvious out-of-phase χ_M'' reflection was observed. This kind of phenomenon clearly revealed the occurrence of a magnetic long-range ordering and agreed with the previous magnetic studies, although detailed information of the magnetic entropy could not be derived yet from the current specific heat data, with the lattice contribution unknown [13]. Therefore, we consider that complex **1** should be a hidden weak ferromagnet due to spin canting. Furthermore, the absence of a frequency dependence of ac susceptibility rules out the presence of glassiness or the magnetic domain wall motion in **1**. The FO transition is further demonstrated by the field-dependent isothermal magnetization M(H) performed at 2 K (Fig. 6b, inset). The sharp increase of magnetization is observed below 5 kOe. When the external field is further increased, the magnetization increases smoothly and reaches 2.61 $N\beta$ at 50 kOe. The appearance of a maximum around 1.004 kOe in the d*M*/d*H* curve measured at 2 K confirms that *M vs. H* curve increase rapidly at low fields corroborates the spontaneous magnetization behavior and a long-range FO phase transition of **1** [14]. The magnetizations measured at 2 K show hysteresis loops with a small coercive field (*Hc*) of *ca.* 50 Oe, and a remnant magnetization (*Mr*) of 0.057 $N\beta$ indicating a soft-magnetic behavior of **1**. The spontaneous

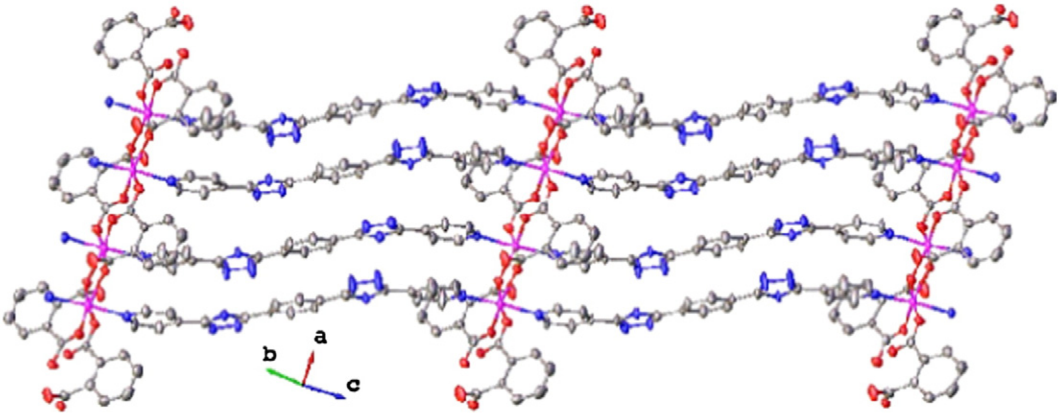


Fig. 4. The wave-like layer structure of **1**.

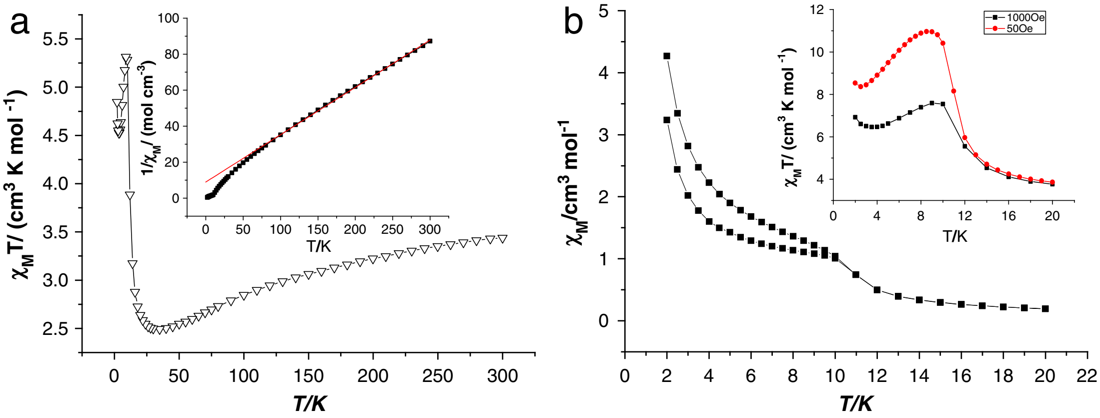


Fig. 5. (a) Plots of $\chi_M T$ vs. T for **1**. Inset: the temperature dependence of $1/\chi_M$, the best fit of the curve (red) to the Curie–Weiss law; (b) the FC and ZFC of **1**. Inset: the plots of χMT vs. T at various fields. (For interpretation of the references to color in this figure legend, the reader is referred to the web of this article.)

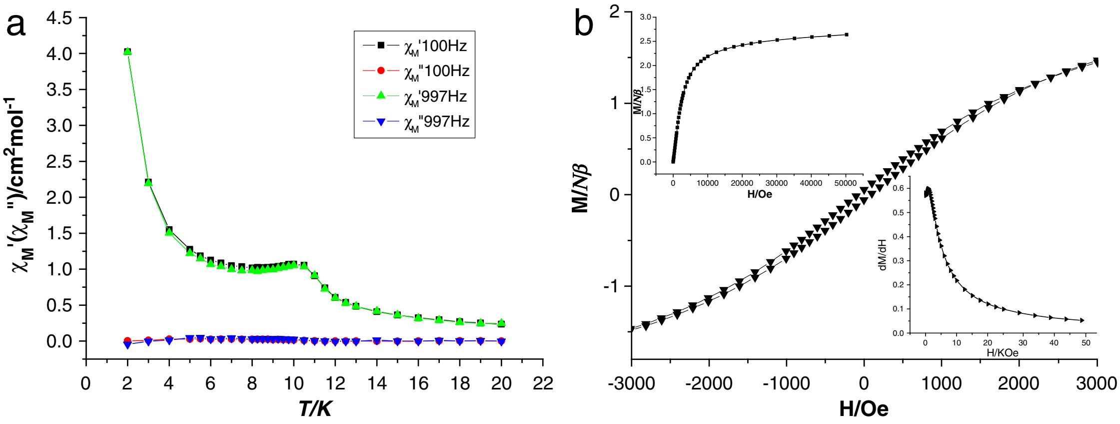


Fig. 6. (a) The temperature dependence of the in-phase (χ') and the out-of-phase (χ'') ac magnetic susceptibilities for **1**; (b) the hysteresis loop of **1** at 2 K. Inset: field dependence of magnetization (up) and the dM/dH derivative curve (down).

magnetization observed is due to spin canting, with an estimated canting angle of 1.24° ($\psi = \tan^{-1}$(Mr/Ms)) [15].

The ferromagnetic correlations can be attributed to spin canting. *i.e.*, perfect antiparallel alignment of the spins on the neighboring metal ions is not achieved so that residual spins are generated [16]. Usually, there are two mechanisms for the spin canting: the anti-symmetric exchange (Dzyaloshinsky–Moriya interaction) and the single-ion anisotropy [2]. The canting in compound **1** may be caused by the single-ion anisotropy of the Co(II) centers. Moreover, the mutually tilted orientation of the Co(II) centers caused by bptb ligands may give further contribution.

Conclusion. In summary, this paper describes the synthesis and crystal structure of a 2-D wave-like framework formulated as [Co(bdc)(bptb)]$_n$ (**1**) exhibiting weak ferromagnetic behaviors caused by spin canting. In line with previous studies, the present results further demonstrate that long bent bridging ligand (bptb) has the potential to generate novel coordination frameworks with promising structural features and magnetic properties.

Acknowledgements

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