The first slow magnetic relaxation in a ferromagnetic Cu(II) chain compound, Cu(dipic)(OH)2 (dipicH2 = pyridine-2,6-dicarboxylic acid), induced by a phonon bottleneck effect under a magnetic field of 0.6 T, with a relaxation time of 2.2 s at 2.8 K, was observed.

The realisation of slow magnetic relaxation is central to achieving technological break-throughs in the fields of high-density information storage, quantum computing, spintronics, etc. This has spurred intense research activity in the field of molecular magnetism involving physicists, chemists, theoreticians, and materials scientists for the past few decades. Such slow magnetic relaxation has been envisaged to be achievable in multinuclear 3d metal clusters (single-molecule magnets, SMMs) or 1-D chains (single-chain magnets, SCMs) having a high spin and large uni-axial anisotropy. In the seminal report involving the pioneering work by Gatteschi et al., Mn12OAc exhibiting slow magnetic relaxation showed catalysed great activity leading to the isolation of several SMMs based on transition metal clusters. Later, the focus shifted to lanthanide-based mono- and poly-nuclear complexes, of which DyIII-based complexes are the most explored, under the label single ion magnets (SIMs). The first report of Caneschi et al. on a CoII polymer chain with slow magnetic relaxation offered experimental evidence for Glauber’s prediction that 1-D chain systems exhibiting slow magnetic relaxation could be potential candidates towards reaching technologically relevant blocking temperatures. Interestingly, the definition of SMMs (a large spin S and a negative zero-field axial splitting D) has hindered the exploration of the magnetic relaxation behaviour of CuII complexes, for both monomeric and polymeric ones. The first study of a CuII monomer exhibiting slow magnetic relaxation, [Cu(pydca)2(dmpy)]·0.5H2O, was reported only recently in 2017 by Boča et al. Subsequently, Chen et al. reported slow magnetic relaxation in a Cu(n)-cyclen complex, followed by another report by Bora et al. on CuLL′H2O, (L = 2,6-dimethanolpyridine and L′ = 3,5-dinitrocarboxylato(1-)). More recently, one-dimensional antiferromagnetic [Cu(chxn)]I (chxn = 1R,2R-diaminocyclohexane) has been reported. In this chain, magnetic relaxation proceeds via the Raman process under the field. Here, we report the first example of a 1-D ferromagnetic CuII chain compound with a pyridine-2,6-dicarboxylato ligand (abbreviated as [DCu]) that exhibits slow magnetic relaxation. Pyridine-2,6-dicarboxylic acid (dipicH2) is a versatile ligand that exhibits diverse bridging modes in connecting metal centres. In particular, with CuII, dipicH2 leads to different products based on a delicate balance of the reaction conditions. The title compound was obtained as blue blocks at RT, upon layering of methanolic dipicH2 over aqueous Cu(CH3COO)2·H2O solution (synthetic details and Fig. S1†). The crystal structure of the title compound has been reported previously, where the crystals were obtained by the reaction between Cu(NO3)2·3H2O and dipicH2 in the presence of DABCO.

The title complex crystallises in the monoclinic P21/c space group; the asymmetric unit contains one CuII in a distorted square pyramidal geometry (Fig. 1, left). The square plane is defined by the pyridyl N, two carboxylate oxygens (O1 and O3) and one coordinated water oxygen (O5). The axial position is occupied by another coordinated water oxygen (O6). The CuII ion is located exactly at the centre of the plane without any deviation from the mean plane defined by N1, O1, O3, and O5. The O3 oxygen connects neighbouring monomeric units into a polymeric chain through Cu–O bonds (2.4 Å). As a result, Cu(n) displays a distorted octahedral geometry in the polymer chain (Fig. 1, left, green shaded polyhedra). Within the chain, the Cu(n) centres are separated by 3.855 Å. The equatorial
Fig. 1 (left) ORTEP diagram of the complex [DCu] showing atoms as 30% probability ellipsoids. (right) Packing diagram showing the polymeric propagation of the Cu chain with important hydrogen bonding and π⋯π interactions among the pyridine rings.†

[(O5I⋯H5A⋯O1: 1.810 Å) and axial water (O6I⋯H6A⋯O2: 1.915 Å) hydrogens are involved in strong hydrogen bonding interactions with the carboxylato oxygens, stabilising the polymeric chain. Additionally, the neighbouring chains of the unit cell are stabilised by aromatic π⋯π stacking interactions (3.794 Å and 3.803 Å, alternately) (Fig. 1, right). Important crystal data are presented in ESI Table S1† and important bond lengths, hydrogen bonds, and bond angles are presented in ESI Table S2.†

Fig. 2a shows the temperature-multiplied magnetic susceptibility ($\chi_mT$) of [DCu]. $\chi_mT$ exhibits an almost constant value around room temperature, but increases steeply below 50 K. The increase in $\chi_mT$ indicates ferromagnetic interactions between Cu(n) sites. The magnetisation-field loop strongly supports ferromagnetism, but has no hysteresis (Fig. 2b). The $\chi_mT$ plots were fitted using the program PHI with the spin Hamiltonians shown in eqn (1) and (2):†

\[
H_{\text{Zee}} = \mu_B \hat{S} \cdot g \cdot \hat{B}
\]

\[
H_{\text{Ex}} = -2J\hat{S}_1 \cdot \hat{S}_2
\]

where $\mu_B$, $g$, $J$, $S$ and $B$ refer to the Bohr magneton, $g$-factor, coupling constant, operators of spin and magnetic field, respectively. The heat capacities of the Cu chains show a peak at around 10–11 K (Fig. 2c and d), indicating a phase transition, which is due to the interactions between the chains. The mean field approximation parameter ($zJ$) was used for the inter-chain interactions. When the 1D Heisenberg ferromagnet model is applied, $J = +3.4$ cm$^{-1}$ is obtained (Fig. S2†). However, this model would not be sufficient, because interactions between chains cannot be negligible. The infinite chains were approximated using an 8-ring model together with the chain interactions, as shown in Fig. 2a, as infinite chains are not supported by the PHI. The fitted curve matches well with the experimental data, and the following parameters were obtained: $g_{\text{iso}} = 2.3$, $J = +1.6$ cm$^{-1}$, and $zJ = +0.002$ cm$^{-1}$. The positive signs of $J$ and $zJ$ are reasonable in ferromagnetism. The steep rise of the magnetisation-field curve also indicates ferromagnetism (Fig. S3†).

[DCu] shows slow magnetic relaxation under appropriate magnetic fields (ESI Fig. S4†). Fig. 3 and S5a† show the temperature dependence of the out-of-phase component of the alternating current (AC) susceptibility of [DCu]; those of the in-phase component and the Cole–Cole plots are shown in ESI Fig. S3a, S6 and S7.† A higher frequency region does not show any signals for slow relaxation (Fig. S8†). Curve fitting was applied using the expression for the Cole–Davidson model due to asymmetric distortion (eqn (3) and (4)):†

\[
\chi''(\omega) = (\chi_T - \chi_S)(\cos \theta)^\beta \sin(\beta \theta)
\]

\[
\theta = \tan^{-1}(\omega \tau)
\]

where $\omega (=2\pi\nu)$, $f_I$, $\chi_T$, $\chi_S$, $\tau$, and $\beta$ refer to the AC angular frequency, AC frequency, isothermal susceptibility, adiabatic sus-
such behaviour was reported for $[\text{Mn}_{2}\text{(saltmen)}_{2}\text{Ni}(L)_{2}(\text{py})_{2}]$ molecular chains with slow magnetic relaxation are very rare; magnetic relaxation, which have traditionally been overlooked.

Magnetic relaxation, which have traditionally been overlooked. Chains that have ferromagnetic interactions and exhibit slow magnetic relaxation has not been reported. In contrast, the magnetic relaxation in a mononuclear five-coordinate Cu(II) complex, $\text{Cu}(\text{II})\text{ClO}_{4}$ (Saltmen2), is reported to show ferromagnetism, although slow magnetic relaxation tends to be ferrimagnetic due to super-exchange interactions. However, this Cu(II) chain exhibits ferromagnetism because the Cu(II) moieties adopt an almost orthogonal orientation in the chain that removes the overlap of orbitals (Table S4 and Fig. S7). Ferromagnetic molecular chains with slow magnetic relaxation are very rare; such behaviour was reported for $[\text{Mn}_{2}\text{(saltmen)}_{2}\text{Ni}(L)_{2}(\text{py})_{2}]$ (ClO$_4$)$_2$ (saltmen$^{2-}$ = $N,N'-(1,1,2,2$-tetramethylethylene)bis(salicylideneiminate); L = 1-methylimidazole-2-aldoximate (miao$^{-}$)). The intermolecular interactions in the chain are ferromagnetic, but the intramolecular (Mn⋯Ni⋯Mn) ones are ferrimagnetic. On the other hand, oxalato-bridged Cu(II) chains were reported to show ferromagnetism, although slow magnetic relaxation has not been reported. In contrast, the Cu(II) centres of the chain in this study are all ferromagnetically coupled and show slow magnetic relaxation. This work thus presents a new insight into the potential of Cu(II) polymer chains that have ferromagnetic interactions and exhibit slow magnetic relaxation, which have traditionally been overlooked.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This work was supported by “IoE Research Grant for Faculty (Development Scheme No. 6031), BHU” and the JSPS KAKENHI Grant [JP19H05631] as well as the National Natural Science Foundation of China (NSFC, 22150710513). M. Y. thanks the 111 Project (B18030) from China. S. S. S. thanks Dr. J. Reibenspies, X-ray Diffraction Laboratory, Department of Chemistry, Texas A & M University, USA for the crystal data and Dr. S. Sabiah, Department of Chemistry, Pondicherry University, India for CHN analysis.

**Notes and references**

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