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Interchain relay of antiferromagnetic ordering in 1D Co(II) coordination polymers *via* π–π interactions†

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Two new Phen-Co(II) complexes bridged by a hydroxyl isophthalate ligand, $\{[Co(dimphen)(HIA)]\cdot H_2O\}_n$ (**1**) and $\{[Co(phen)(HIA)]\cdot H_2O\}_n$ (**2**) (dimphen = 2,9-dimethyl-1,10-phenanthroline, phen = 1,10-phenanthroline, HIA = 5-hydroxyisophthalic acid), have been synthesized by carefully tuning the basicity of the reaction medium. In addition to single-crystal X-ray crystallography, the complexes were also characterized by IR spectroscopy, thermogravimetric and elemental analyses. Structurally, both complexes are 1D zigzag polymers with different metal nuclearities. Variable-temperature magnetic susceptibility measurements revealed ferromagnetic coupling within the chain while antiferromagnetic ordering is propagated in parallel running interchain *via* π–π interactions at low temperature.

Introduction

Recent years have witnessed an intense research activity in the rational design and synthesis of coordination polymers (CPs) due to their novel architectures as well as potential applications as functional materials.[1] The study of molecule-based magnetic materials has aroused substantial interest among researchers, gradually becoming one of the most active fields in inorganic and materials chemistry. The assembly of coordination polymers with metal ions capable of showing magnetic anisotropy is particularly attractive. Various Co(II) magnetic units containing monomers, dimers, chains, ladders, layers and 3D polymers have been synthesized and characterized due to their appealing magnetic phenomena such as ferromagnetism,[2] antiferromagnetism,[3] spin canting,[4] metamagnetism,[5] single-chain magnetism,[6] *etc.*

Synthesis of 1D coordination polymers with a linear or zigzag geometry is of current interest as (i) they can exhibit slow relaxation dynamics (SCM) and may generate Haldane gap-type systems, (ii) they exhibit interesting optical properties, such as strong emission, and (iii) they constitute the simplest assemblies to generate mutually interacting spins to study various thermodynamic processes by application of statistical mechanics.[7]

Selection of appropriate multi-dentate bridging ligands,[8] such as cyano, carboxylato, hydroxyl, azido, *etc.*, is required for effectively mediating the magnetic information between the spin carriers. Therefore, in the present study we have chosen hydroxyisophthalic acid as the bridging ligand as (i) it can exhibit short bridging *via* the carboxylate group, and (ii) it can provide rigidity to the system with interesting electronic and magnetic interactions between the metal ions in the network through possible conjugative mechanism. On the other hand, the terminal ligands (phen units) play a crucial role in the process of self-assembly with non-covalent bonds, such as hydrogen bonds, π···π, –CH···π packing interactions, *etc.*,[9] leading to abundant varieties of multi-dimensional coordination polymers. Recently, some examples have been reported where non-covalent bonds play a major role in the transmission of magnetic ordering.[10]

As a part of our ongoing research efforts on coordination polymers, here we report two new 1D zigzag polymers, $\{[Co(dimphen)(HIA)]\cdot H_2O\}_n$ (**1**) and $\{[Co(phen)(HIA)]\cdot H_2O\}_n$ (**2**), bridged by carboxylato ligands (Scheme 1), which exhibit interchain ferromagnetic coupling and intrachain antiferromagnetic ordering at low temperature.

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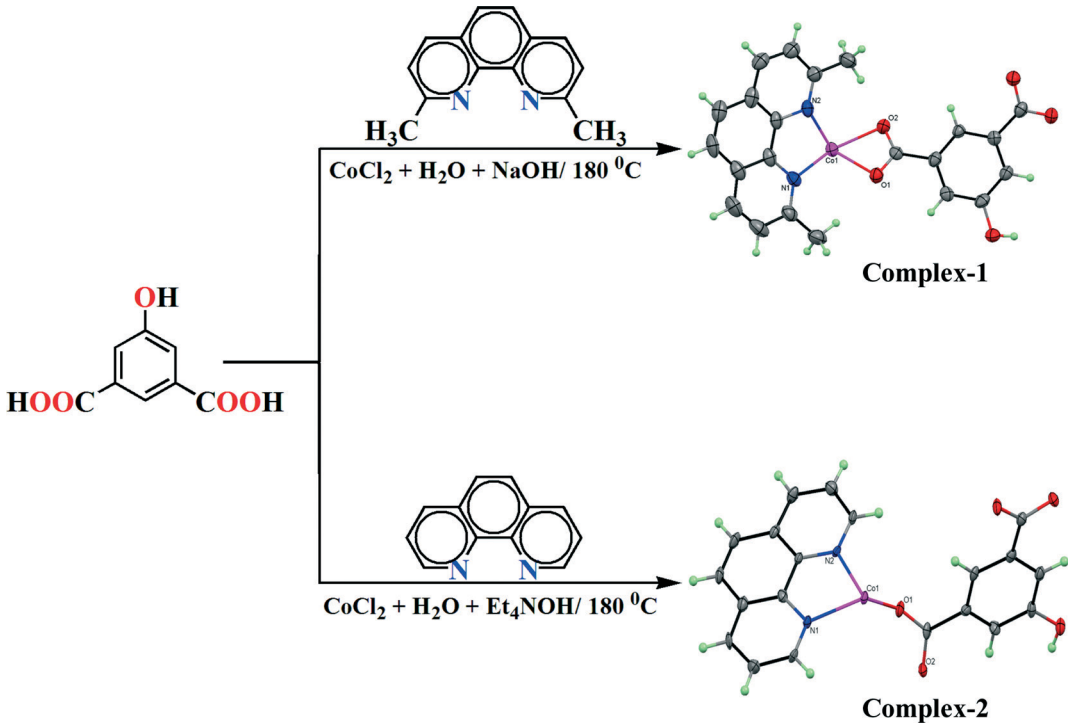
† Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format, table for selected bond angles and bond distances for complexes 1–2 and complete data for IR, TGA analysis and PXRD. Crystallographic data in CIF format have been deposited with the Cambridge Structural Database. CCDC 992590–992591. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce01010h



Scheme 1 Synthetic scheme for **1** and **2**.

Experimental section

Materials and methods

Reagent grade 5-hydroxyisophthalic acid, 2,9-dimethyl-1,10-phenanthroline, 1,10-phenanthroline and $CoCl_2 \cdot 6H_2O$ were procured from Aldrich and used as received. Tetraethylammonium hydroxide, sodium hydroxide and all solvents were acquired from S. D. Fine Chemicals, India. All solvents were purified prior to use.

Physical measurements

Infrared spectra were obtained (KBr disk, 400–4000 cm^{-1}) using a Perkin-Elmer Model 1320 spectrometer. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo Star System (heating rate of 5 °C min^{-1}). Microanalyses for the compounds were performed using a CE440 elemental analyzer (Exeter Analytical Inc.). Powder X-ray diffraction measurements (CuK_α radiation, scan rate 3° min^{-1}, 293 K) were performed on a Bruker D8 Advance Series 2 powder X-ray diffractometer operating at 40 kV and 40 mA.

Magnetic measurements

All magnetic measurements were carried out on polycrystalline samples using a Physical Property Measurement System (PPMS) from Quantum Design, Inc., San Diego, CA, USA, equipped with a 9 Tesla superconducting magnet and a vibrating sample magnetometer. The magnetic signal from the sample holder was negligible to affect our data accuracy.[11] DC magnetization *versus* T curves were taken at 100 Oe field in field cooled (FC) and zero field cooled (ZFC) modes with a heating/cooling rate of 2 K min^{-1}. Magnetization *versus* field loop curves were taken in field sweep from −50 kOe to +50 kOe at a rate of 75 Oe s^{-1}. AC magnetic measurements were performed using an AC susceptibility and DC magnetization option (ACMS) from Quantum Design, Inc., San Diego, CA, USA, with a sensitivity close to 10^{-8} emu.

Single-crystal X-ray studies

Single-crystal X-ray data for **1** and **2** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å). The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*.[12] Data integration and reduction were carried out with SAINT.[13] Empirical absorption correction was applied to the collected reflections with SADABS[14] and the space group was determined using XPREP.[15] The structure was solved by direct methods using SHELXTL-97[16] and refined on F^2 by full-matrix least-squares using the SHELXL-97 program[17] package. All non-hydrogen atoms were refined anisotropically. The H atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. The crystal and refinement data are shown in Table 1 while selective bond distances and angles are given in Table S1.†

Synthesis of $\{[Co(dimphen)(HIA)]\cdot H_2O\}_n$ (1). A mixture containing 5-hydroxyisophthalic acid (20 mg, 0.11 mmol), 2,9-dimethyl-1,10-phenanthroline (10 mg, 0.05 mmol) and $CoCl_2 \cdot 6H_2O$ (55 mg, 0.23 mmol) in 3 mL of H_2O and 0.1 mL

Table 1 Crystal data and structure refinement for **1** and **2**

Parameters	1	2
Formula	$C_{22}H_{18}N_2O_6Co$	$C_{20}H_{14}N_2O_6Co$
F_w (g mol^{-1})	465.3134	437.2634
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2/n$
a (Å)	10.271(5)	8.515(5)
b (Å)	18.615(3)	12.058(5)
c (Å)	10.814(5)	17.046(5)
α (deg)	90.000	90.000
β (deg)	105.695(5)	101.675(5)
γ (deg)	90.000	90.000
U (Å^3)	1990.5(14)	1714.0(13)
Z	4	4
ρ_{calc} (g cm^{-3})	1.546	1.687
μ (mm^{-1})	0.906	1.046
F(000)	948	884
Temp (K)	100(2)	100(2)
Measured reflns	10 718	7499
Unique reflns	3706	2450
GOOF[a]	1.072	1.163
Final R^b indices [$I > 2\sigma(I)$]	R_1 = 0.0603	R_1 = 0.0465
	wR_2 = 0.1542	wR_2 = 0.1229
R^b indices (all data)	R_1 = 0.0886	R_1 = 0.0641
	wR_2 = 0.1825	wR_2 = 0.1608

[a] GOF is defined as $\{\sum[w(F_o^2 - F_c^2)]/(n-p)\}^{1/2}$ where n is the number of data and p is the number of parameters. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

of 1 M NaOH solution was sealed in a Teflon-lined autoclave, heated under autogenous pressure to 180 °C for 3 days and then allowed to cool to room temperature at a rate of 1 °C min^{-1}. Block-shaped red crystals of **1** were collected in ~53% yield. The crystals were repeatedly washed with water, followed by acetone and air-dried. Anal. calcd. for $C_{22}H_{18}CoN_2O_6$: C, 56.78; H, 3.89; N, 6.02%. Found: C, 56.53; H, 3.67; N, 6.13%. IR (cm^{-1}): 3066(s, br), 1621(m), 1594(m), 1549(s), 1393(s), 1297(m), 1277(m), 1220(s), 1000(m), 858(s), 779(s), 729(s).

Synthesis of $\{[Co(phen)(HIA)]\cdot H_2O\}_n$ (2). A mixture containing 5-hydroxyisophthalic acid (20 mg, 0.11 mmol), 1,10-phenanthroline (10 mg, 0.06 mmol) and $CoCl_2\cdot 6H_2O$ (55 mg, 0.23 mmol) in 3 mL of H_2O and 0.1 mL of tetraethylammonium hydroxide solution was sealed in a Teflon-lined autoclave, heated under autogenous pressure to 180 °C for 3 days and then allowed to cool to room temperature at a rate of 1 °C min^{-1}. Block-shaped red crystals of **2** were collected in ~46% yield. The crystals were repeatedly washed with water followed by acetone and air-dried. Anal. calcd. for $C_{20}H_{14}CoN_2O_6$: C, 54.93; H, 3.22; N, 6.41%. Found: C, 54.49; H, 3.16; N, 6.59%. IR (cm^{-1}): 3050(s, br), 1572(m), 1538(s), 1442(m), 1421(s), 1353(s), 1270(m), 1220(m), 1106(m), 846(s), 782(s), 724(s).

Results and discussion

As part of our investigations on the structural diversity and magnetic properties of Co(II)-containing coordination polymers, we have synthesized complexes **1** and **2** by a hydrothermal technique that affords moderate yields. Both complexes are stable in air and insoluble in common organic solvents such as acetonitrile, chloroform, ethanol, methanol, acetone and water. The IR spectra of the complexes show a broad peak centering at ~3050 cm^{-1} indicating the presence of lattice water molecules.[18] Before magnetic susceptibility measurements, the phase purity of the materials was confirmed by comparing the experimental and simulated powder X-ray diffraction patterns. The as-synthesized and simulated PXRD patterns of **1** and **2** match closely with each other. Thermogravimetric analyses exhibit a gradual weight loss of ~3.8% (expected = 3.9%) and ~4.10% (expected = 4.12%) for complexes **1** and **2**, respectively, that correspond to the removal of lattice water molecules. Decomposition is observed beyond 300 °C for **1** and beyond 400 °C for **2**, indicating good thermal stabilities. The elemental analysis results are also in excellent agreement with the calculated values (Fig. S1–S6, ESI†).

Structural description of $\{[Co(dimphen)(HIA)]\cdot H_2O\}_n$ (1)

Complex **1** crystallizes in the monoclinic space group $P2_1/n$ with the asymmetric unit consisting of one Co(II) ion, one dimphen ligand and one HIA^{2-} ligand besides one lattice water molecule. The metal ion exhibits a distorted octahedral CoN_2O_4 configuration (Fig. 1a) with ligation from N atoms of the dimphen ligand (Co–N = 2.099(4)–2.133(4) Å) and carboxylate groups from two HIA^{2-} ligands (Co–O = 2.050(3)–2.230(3) Å) in chelating mode. All Co–O and Co–N bond distances are quite similar compared to those of the reported octahedral Co(II) complexes.[19]

Each HIA^{2-} ligand bridges two Co(II) metal centers in a bis-monodentate fashion to form a 1D zigzag chain (Fig. 2(a)). Within the chain, the distance between successive Co(II) ions is 9.526 Å, and the closest Co···Co separation between the neighboring strands is 6.462 Å, which suggests that the chains are well isolated from each other due to steric crowding caused by the phen moiety. The dihedral angle between the molecular planes of the two phen moieties of two different Co(II) ions is 71.9°. Moreover, the chains interdigitate to form layers parallel to the [101] plane. Finally, the layers stack along the c axis, resulting in a 3D supramolecular structure (Fig. 4a). Fig. 2(b) displays a packing diagram of the polymers, where interchain interactions are mainly π···π forces between phen rings of the adjacent layers.

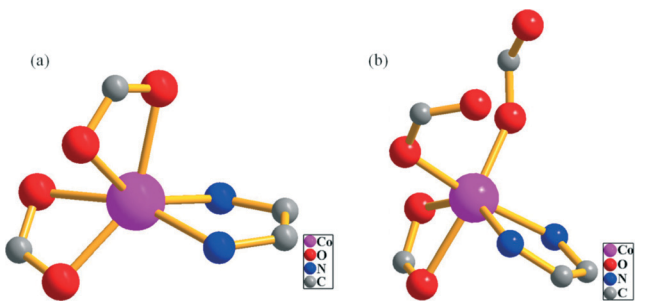


Fig. 1 Metal coordination modes in (a) complex **1** and (b) complex **2**.

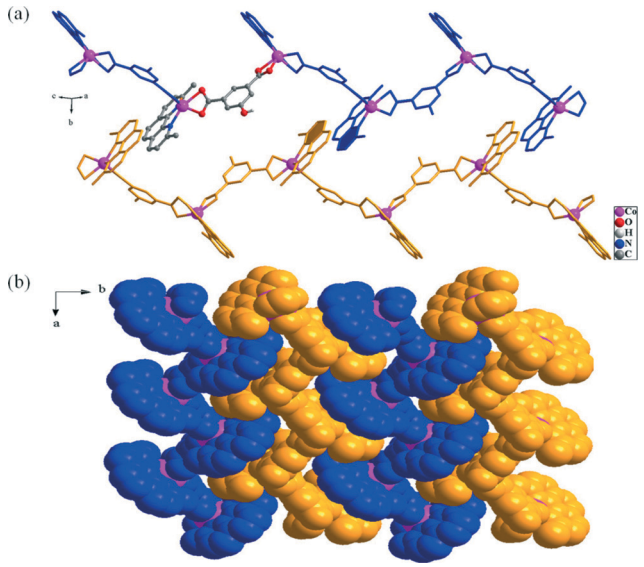


Fig. 2 Representation of (a) the 1D zigzag chain and (b) the packing mode of **1**.

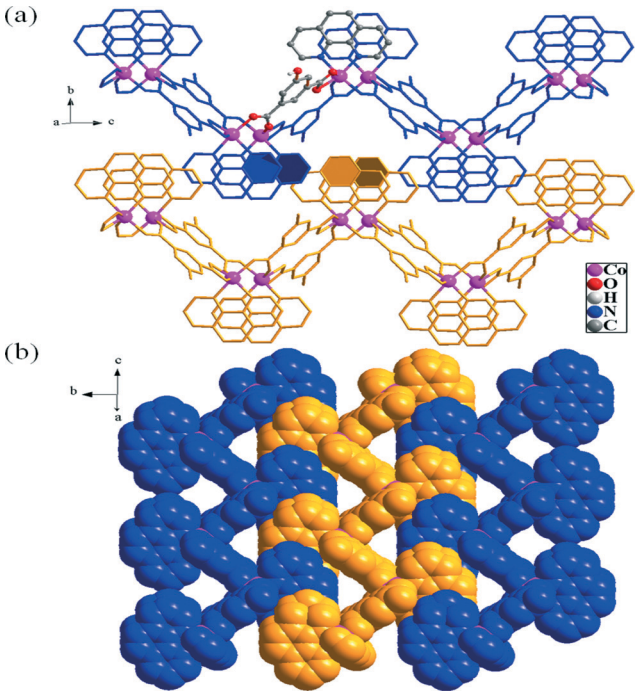


Fig. 3 View of (a) the 1D zigzag chain and (b) the packing mode of **2**.

Structural description of {[Co(phen)(HIA)]·H_2O}$_n$ (2)

Compound **2** crystallizes in the monoclinic space group $P2/n$ with the asymmetric unit consisting of one Co(II) ion, one phen ligand and one HIA^{2-} ligand besides a lattice water molecule. Each Co(II) center is octahedrally coordinated to two nitrogen atoms (Co–N = 2.113(3)–2.120(3) Å) of a phen ligand and four oxygen atoms (Co–O = 2.042(3)–2.249(3) Å) of three independent HIA^{2-} ligands in bridging and chelating modes, respectively (Fig. 1(b)). The Co–O and Co–N distances are within the normal statistical errors of published octahedral Co(II) complexes.[19] In contrast to the structural motif of **1**, four HIA^{2-} ligands (two in chelating and two in bridging mode) and two phen moieties in chelating mode link two Co(II) centers to form a binuclear cluster with a Co(II)···Co(II) distance of 3.96(4) Å.

Interestingly, in each dimeric unit phen rings are aligned perfectly parallel to each other and thus stabilized by π···π interactions with a face-to-face distance of 3.58 Å and a nearest C···C distance of 3.91 Å. These dimeric Co_2 units propagate parallel to the [−101] plane into a 1D zigzag network interconnected *via* the HIA^{2-} ligands (Fig. 3a). Within the chain, the distance between Co(II) ions in a successive binuclear cluster is 10.06(5) Å, and the closest Co···Co separation between the neighboring strands is 6.461 Å. The relative disposition of the dimeric building units in the 1D chain is depicted in Fig. 3(b). It is worth noting that the neighboring chains are linked to each other *via* π···π interactions between phen rings of the adjacent layers, leading to a 3D supramolecular framework (Fig. 4b).

Magnetic studies of {[Co(dimphen)(HIA)]·H_2O}$_n$ (1)

At 300 K, the $\chi_M T$ value of **1** is 3.89 emu K mol^{-1} per Co(II) ion, which is much higher than the expected spin-only value for high-spin Co(II) (S = 3/2, $\chi_M T$ = 1.87 cm^3 mol^{-1} K^{-1} with g = 2) ions (Fig. 5). It can be attributed to the spin–orbital coupling of the Co(II) ions. The $\chi_M T$ values of complex **1** increase slowly with decreasing temperature with a minimum around 22 K, followed by an increase until 9 K and then a decrease.

For complex **1**, below 20 K, the ZFC and FC magnetization curves show a gradual increase, which changes its slope further at 11 K (Fig. 6). The bifurcation of ZFC and FC magnetization is observed below 10 K. ZFC magnetization shows a steeper increase below the bifurcation temperature (10 K) and a hump at 9 K which can be due to the long-range antiferromagnetic ordering of Co(II) ions induced by π···π interaction of two parallel chains.

The shortest distance between two Co(II) ions in parallel chains is 6.462 Å. Below 5 K, ZFC and FC magnetization curves show a Curie tail which could be due to very small ionic impurities or weak ferromagnetic exchange among Co(II) ions within the chains.

It is worth mentioning that the distance between two Co(II) ions within the chain is 9.526 Å. The derivative of the ZFC magnetization curve shows a peak at 11 K, which could be the temperature dependence of paramagnetic-to-antiferromagnetic transition. The $\chi^{-1}T$ plot above 150 K follows the Curie–Weiss law with C = 0.27 emu K mol^{-1} and θ = −20 K. The negative θ value suggests a weak antiferromagnetic exchange between the two Co(II) ions, which may be due to the short 'Co–Co' distance between two chains.

At 25 K, the magnetization *versus* field (M–H) loop (Fig. 7) shows complete linear behavior indicating a paramagnetic state. At 2, 5, 8 and 10 K the M–H loops show non-linear behavior. A well-defined hysteresis is observed at 2 and 5 K,

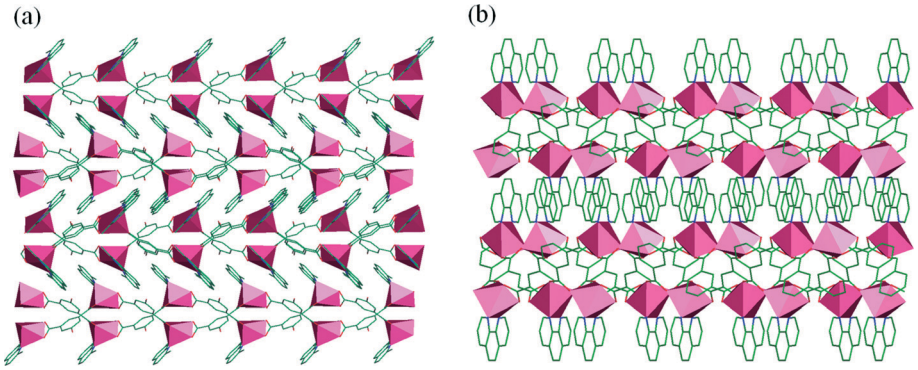


Fig. 4 Polyhedral representations of the 3D view of (a) complex **1** and (b) complex **2**.

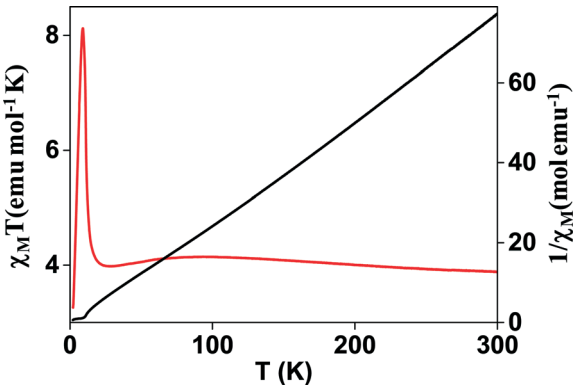


Fig. 5 Experimental magnetic data plotted as $\chi_M T$ and $1/\chi_M$ *versus* T for **1**.

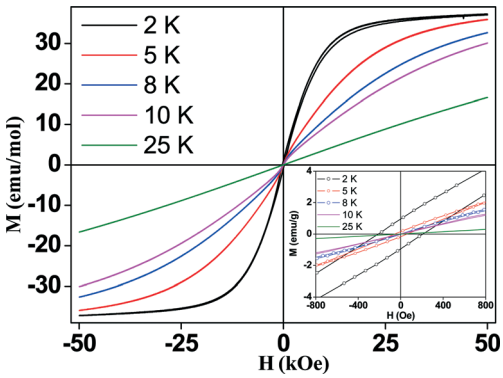


Fig. 7 Magnetic hysteresis loops of **1**. The inset shows the expanded plots of hysteresis loops at the indicated temperature values.

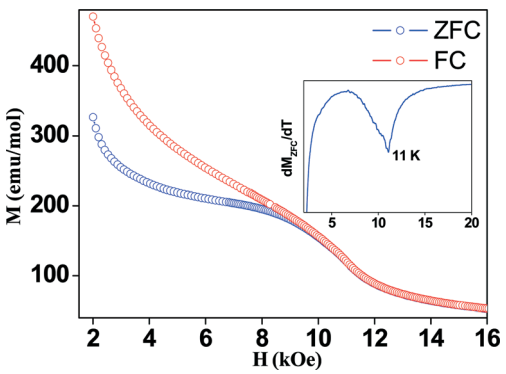


Fig. 6 Temperature dependence of the magnetization in zero field cooling (ZFC) and field cooling (FC) modes with an applied field of 200 Oe for complex **1**. The inset shows the derivative of ZFC magnetization showing a sharp paramagnetic-to-antiferromagnetic transition at 11 K.

indicating ferromagnetic ordering. The value of the coercive field (H_c) at 5 K is 63 Oe which increases to 212 Oe at 2 K. The opening of the hysteresis curve below 5 K suggests the onset of ferromagnetic interaction. From the Arrott plot, we noticed that at temperatures of 2 and 5 K, the isotherm passes through negative H/M, whereas at 8 and 10 K, the isotherm passes through positive H/M. It follows, therefore, that in between 8 and 5 K, it shows an antiferromagnetic-to-ferromagnetic transition. All isotherms show non-linear behavior which indicates the absence of mean field-like behavior.

The real part of ac magnetization for **1** shows an increasing trend below 20 K and peaks at ~9.5 K (Fig. 8). At low temperature (below the peak), the real part of ac magnetization again shows an increasing trend (similar to the static magnetization curves discussed earlier). The imaginary part of ac magnetization shows a broad peak centered at 7 K. The peak at 9.5 K in the real part of ac magnetization could be due to the interchain antiferromagnetic ordering of Co(II) ions. The increasing trend below the antiferromagnetic peak could be due to weak ferromagnetic coupling between Co(II) ions within the chain. The broad peak in the imaginary part of ac magnetization could be due to the overlapping of peaks of interchain antiferromagnetic ordering and intrachain weak ferromagnetic coupling between the metal ions.

Magnetic studies of {[Co(phen)(HIA)]·H_2O}$_n$ (2)

At 300 K, the $\chi_M T$ value of **2** is 3.87 cm^3 mol^{-1} K per Co(II) ion, which is much higher than the expected spin-only value for high-spin Co(II) (S = 3/2, $\chi_M T$ = 1.87 cm^3 mol^{-1} K with g = 2) ions (Fig. 9a). It can be attributed to the spin–orbital coupling of Co(II) ions. The $\chi_M T$ values of complex **2** increase upon cooling, reach a maximum of 5.18 cm^3 mol^{-1} K at 10 K,

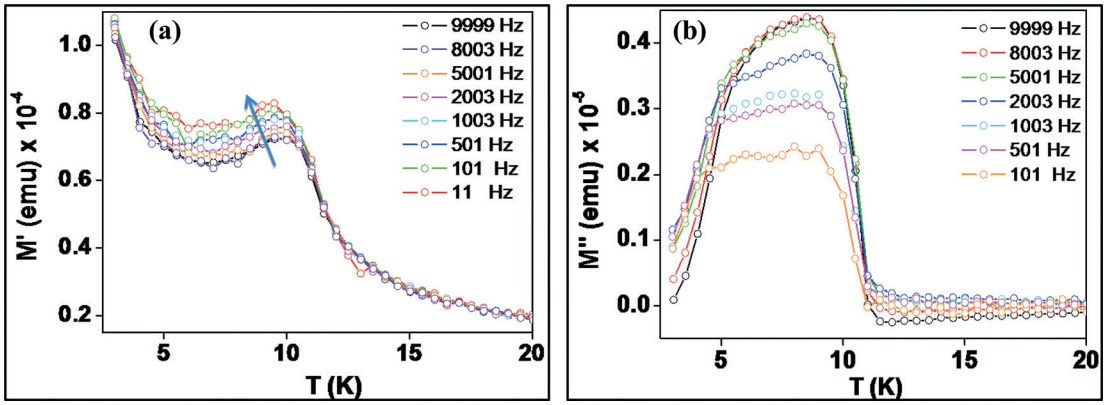


Fig. 8 Temperature dependence of the (a) real and (b) imaginary parts of ac susceptibility measured in various frequencies for **1**.

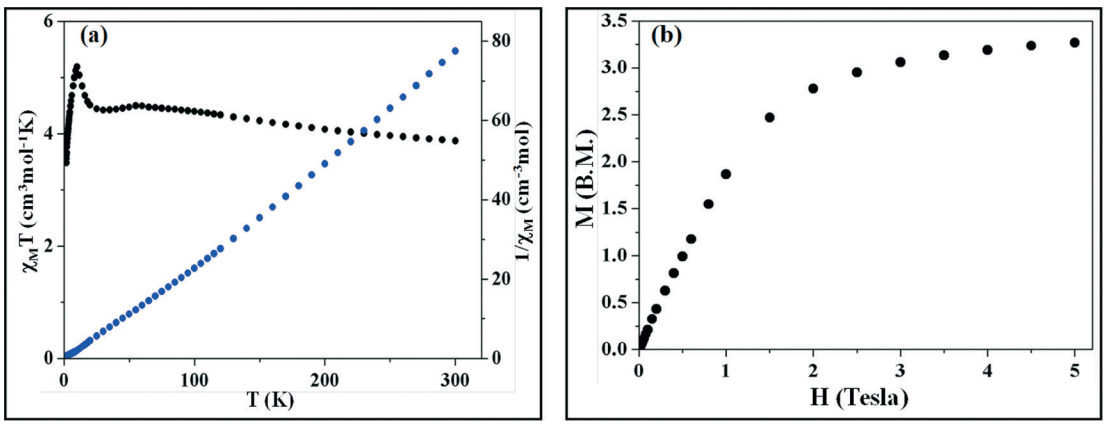


Fig. 9 Experimental magnetic data plotted as (a) $\chi_M T$ *versus* T and (b) $1/\chi_M$ *versus* T for **2**.

and then decrease. The final decrease of the $\chi_M T$ value may be attributed to the saturation effect caused by the zero field splitting of Co(II) metal ions and also the presence of inter-chain antiferromagnetic coupling interactions.

The magnetization (M) *versus* the magnetic field (H) plot for **2** at 2 K is shown in Fig. 9b. The value of magnetization is 3.27 B.M. at 5 Tesla. The increase in magnetic moment below 30 K suggests ferromagnetic interaction between Co(II) ions within the chain. Interestingly, the onset of ferromagnetic interactions at a Curie temperature of 10 K could be due to the uncompensated magnetic moments.

To achieve better understanding of the magnetic behavior of **2** at low temperatures, zero field cooled (ZFC) and field cooled (FC) magnetic susceptibility measurements were carried out at 25 and 100 Oe applied fields, respectively (Fig. 10a). Below 20 K, the ZFC and FC magnetization curves show a gradual increase, which changes its slope further at 13 K. The bifurcation of ZFC and FC magnetization is

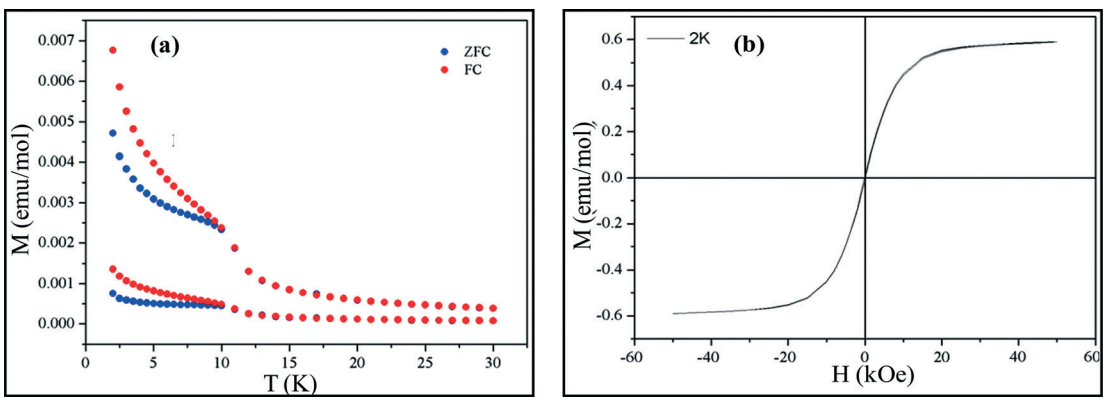


Fig. 10 (a) Temperature-dependent magnetization in the magnetic field of 25 Oe and 100 Oe and (b) magnetic hysteresis loops of complex **2**.

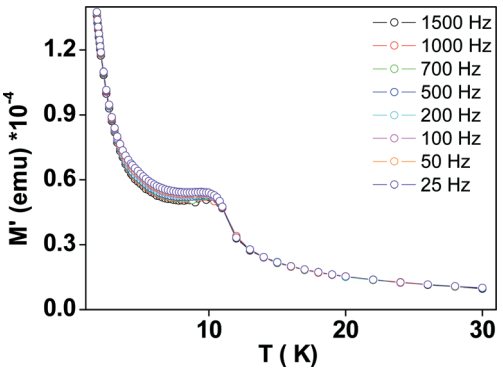


Fig. 11 Temperature dependence of the real part of ac magnetization measured in various frequencies for **2**.

observed below 9 K. ZFC magnetization shows a steeper increase below the bifurcation temperature (9 K) and a hump at 9 K which can be due to long-range antiferromagnetic ordering of Co(II) ions induced by π···π interactions between two parallel chains. The shortest distance between two Co(II) ions between parallel chains is 6.461 Å. Even at a low temperature of 2 K, a hysteresis loop could not be obtained (Fig. 10b).

Similar to complex **1**, the real part of ac magnetization for complex **2** shows an increasing trend below 20 K and a peak at ~10 K (Fig. 11). At low temperature (below the peak), the real part of ac magnetization shows an increasing trend (similar to the static magnetization curves discussed earlier). The peak at 10 K in the real part of ac magnetization could be due to the interchain antiferromagnetic ordering of Co(II) ions.

The increasing trend below the antiferromagnetic peak could be due to weak ferromagnetic coupling between Co(II) ions within the chain (10.06 Å).

In order to estimate the strength of ferromagnetic interactions between the magnetic centers within the chain, we have used the exact solutions of the uniform chain as expanded by Fisher,[20] Katsura[21] and Coronado *et al.*,[22] namely,

$$\chi = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$$

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4kT}\exp(2x)$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8kT}\left(\frac{\tanh x}{x} + \operatorname{sech}^2 x\right)$$

$$x = \frac{J}{4kT}$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are the parallel and the perpendicular susceptibilities, respectively.

The criterion used in the determination of the best fit is based on the minimalization of the sum of squares of the deviation:

$$R = \sqrt{\sum_{i=1}^{n}\frac{1}{\left(\chi_i^{\exp}\right)}\left(\chi_i^{\exp} - \chi_i^{\text{calc}}\right)^2} \Big/ \sqrt{\sum_{i=1}^{n}\frac{1}{\left(\chi_i^{\exp}\right)^2}}$$

In the studied temperature range, this model leads equally to a very good description of the relationship $\chi_M T = f(T)$ in the temperature region of 100–300 K for both complexes. The calculated exchange parameters are J = 75.8 cm^{-1}, factor g = 6.28 and error $R = 1.74 \times 10^{-4}$ and J = 71.3 cm^{-1}, factor g = 6.09 and error $R = 1.99 \times 10^{-4}$ for complexes **1** and **2**, respectively. The main ferromagnetic magnetic exchange pathway is the exchange between neighboring Co(II) metal ions *via* the bridged isophthalate ligand.

Conclusion

In the present contribution, we have prepared two new 1D coordination polymers based on Co(II) phen ligand and carboxylate as bridging anions. Both complexes are 1D zigzag supramolecular polymers with different metal nuclearities. Furthermore, the modulation of the coordination environment of the metal center results in a variation of the magnetic properties of the obtained materials. Variable-temperature magnetic measurements confirm that both complexes show ferromagnetic behavior within the chain which is propagated *via* bridged isophthalate ligand units. Interestingly, weak interchain antiferromagnetic coupling is observed through π–π interactions.

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