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Synthesis, characterization and magnetism of metal–organic compounds: role of the positions of the coordinating groups of a meso-flexible ligand in placing anisotropy to exhibit spin-canting behaviour†‡

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In continuation of our recent investigation on flexible ligands, three new metal–organic coordination framework containing compounds, formulated as $\{Co_2(L1)_2(px3ampy)_2\}_n \cdot npx3ampy$ (**1**), $\{Co(L2)-(px3ampy)_{0.5}\}_n$ (**2**) and $\{Co_2(L3)(px3ampy)_2(H_2O)\}_n \cdot 3nH_2O$ (**3**) have been synthesized using three structurally different meso-flexible polycarboxylate ligands, **H₂L1** (4,4'-methylenebis-(oxy)dibenzoic acid), **H₂L2** (3,3'-methylenebis-(oxy)dibenzoic acid) and **H₄L3** (5,5'-methylene-bis(oxy)diisophthalic acid) bearing the flexible spacer in the middle of the skeleton, along with a long flexible pyridyl ligand px3ampy (1,4-bis-(3-pyridylaminomethyl)benzene). Compounds **1–3** have been characterized by single crystal X-ray diffraction analysis, IR spectroscopy and thermogravimetric (TG) studies including elemental analysis. The crystal structure determinations reveal that compound **1** has a 1D ladder-like structure and compounds **2** and **3** are characterized by 3D frameworks. Compound **2** possesses a tiling of a snz net and compound **3** has a 3D interpenetrated motif with a (4,4) connecting 2-nodal net. The variable temperature magnetic susceptibility measurements demonstrate the dominating antiferromagnetic nature of all three title compounds; interestingly, however, compounds **2** and **3** exhibit ferromagnetic interactions due to the uncompensated magnetic moment of the system at low temperatures. Compound **2** illustrates the occurrence of spin canted antiferromagnetic ordering at $T_c \approx 25$ K with a coercive field (H_c) of 900 Oe at 10 K due to the inclusion of magnetic anisotropy caused by the twisting of the concerned ligand skeleton. Compound **3** shows comparatively weak ferromagnetic ordering with $T_c \approx 9.5$ K, for which weak magnetic anisotropy is present because of two different coordination environments (octahedral and tetrahedral) between two cobalt centers. A structure–function relationship has been described based on the position of the coordinating groups with respect to the flexible center of the ligand skeleton as well as the coordination angle between the ligand and the metal ion.

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Introduction

Over the past two decades, much progress has been made in the development of organic–inorganic hybrid materials, namely, metal–organic materials (MOMs), metal–organic polyhedra (MOPs) and metal–organic frameworks (MOFs) or coordination polymers (CPs). MOMs have drawn considerable

interest because of their potential for exploiting the properties of both organic and inorganic components within a single material, in addition to their modular nature.¹ MOMs have been given lot of importance because of their potential applications in clean energy, most significantly as storage media for gases² with additional application in thin film devices,³ catalysis,⁴ nonlinear optics,⁵ luminescent substances,⁶ magnetic materials⁷ *etc.* The current research in the fields of MOFs and CPs has triggered the design of a target structure with specific properties and functions, which represents an eternal aspiration of modern inorganic chemists and materials scientists. Thus, an investigation of the correlation between the subtle conformation of a flexible ligand and the topology of the coordination network formed is a challenging task for synthetic inorganic chemists, and it is necessary to check some properties of the resulting coordination polymers.

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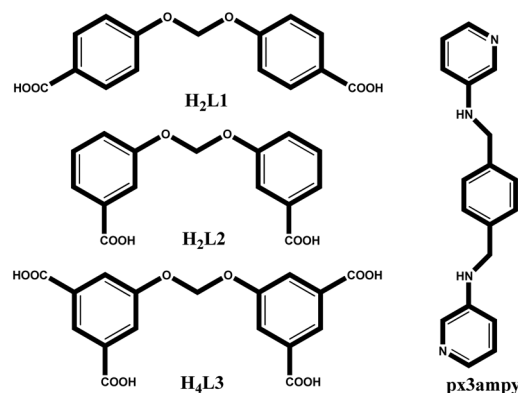
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‡We would like to dedicate this article to Professor Animesh Chakravorty on the occasion of his 80th birthday.

On the other hand, the rational design of molecular magnetic materials is of immense importance, not only to study relevant physical phenomena⁸ but also to study the correlation between molecular structure and observed magnetic properties, such as spin canting, *meta*-magnetism and spin-flop transitions.^{9–11} Molecule based magnets are continuously pursued for their potential applications in magnetic storage, magnetic shielding, switches, AC inductors and sensors.¹² The basic need of a molecular magnetic material is to incorporate paramagnetic centers (spin carriers) with suitable bridging ligands giving rise to magnetic exchange coupling. Organic molecular magnets, for example, TCNE and dinitroxide, contain strong electron acceptors.¹³ In contrast, metal–organic hybrid multi-layer magnets consist of metal coordination layers and organic spacers,¹⁴ in which the short bridges play an important role in mediating the strong intra-layer exchange interactions in metal coordination layers and organic spacers to tune interlayer separations, thereby influencing the magnetic ordering phenomena.¹⁵ Metal–organic molecular magnetic systems that contain magnetic sub-lattices separated by long distances (so that all possible pathways for spin exchange interactions are completely absent), are very rare; only a few such systems are known, but they exhibit considerably weaker magnetic ordering.¹⁶

We have been constantly involved in working on the basic principles underlying the self-assembly process of coordination architectures involving flexible linkers.¹⁷ If an organic linker is accompanied by flexibility in any part of its skeleton, the probability of obtaining a designed architecture with desired functionality is minimal, which is not the case for a rigid linker. When these flexible linkers are used to build coordination networks, several factors have to be addressed, such as non-covalent interactions (responsible for breathing behaviour of the concerned material), metal ion coordination spheres (for tuning dimensionality), the geometry of the secondary linker (for mediating conformational modulation), *etc.* A comprehensive study including all these primary factors is essential in analyzing the versatility of the networks in the concerned materials formed from flexible ligands. In our continuing efforts, we now intend to reduce the complexity in designing such systems that have potential functional applications. In this article, we have chosen three different meso-flexible carboxylic acids, namely, 4,4'-methylenabis(oxy)dibenzoic acid (**H₂L1**), 3,3'-methylenabis(oxy)dibenzoic acid (**H₂L2**), and 5,5'-methylene-bis(oxy)diisophthalic acid (**H₄L3**), that are unique in terms of the existence of flexibility in the middle of the skeleton (Scheme 1) rather than adjacent to coordinating groups, as observed in the case of conventional flexible linkers. The coordination networks based on these oxy acids (**H₂L1**, **H₂L2**, **H₄L3**) are less intensively studied in the literature. Su and Fu and their co-workers reported the interpenetrated coordination networks of **H₂L1** with Cd²⁺ and **H₂L2** with Zn²⁺.¹⁸ Karmakar and Goldberg reported a series of coordination-network containing compounds using ligand **H₄L3** with lanthanides and transition metals, without using secondary ligands.¹⁹ Zaworotko and co-workers described the selec-



Scheme 1 The ligands used in this study.

tive gas adsorption properties of coordination-framework containing compounds, formed from **H₄L3** ligand Cu(II).²⁰

A secondary N-donor linker px3ampy (1,4-bis(3-pyridyl-aminomethyl)benzene) has been used in the present study as it can modulate its coordination and adjust the length of the skeleton according to the coordination requirements imposed by the carboxylic acids (Scheme 1). We reported the same px3ampy linker earlier in the context of its significant role on steric hindrance at the cobalt coordination sphere.^{17b} We have reported the synthesis, structure, topology and magnetic properties of divalent cobalt coordination polymers {Co₂(**L1**)₂(px3ampy)₂}_n·npx3ampy (**1**), {Co(**L2**) (px3ampy)_{0.5}}_n (**2**) and {Co₂(**L3**) (px3ampy)₂(H₂O)}_n·3nH₂O (**3**). Compounds **2** and **3**, that have three-dimensional coordination networks, are molecule-based magnets. Compound **2** consists of anti-ferromagnetically coupled {Co₂} paddlewheels and compound **3** consists of two geometrically different Co(II) centers, separated by a long linker. Both **2** and **3** exhibit an exceptionally canted ferromagnetic ordering at low temperatures. The title compounds presented here have demonstrated that the position of the carboxylate groups of meso-flexible ligands (used in the present work) can provoke dramatic differences in divalent cobalt coordination polymer topology, even by employing the same dipyridyl co-ligand in all three compounds.

Materials and methods

All the chemicals were received as reagent grade and used without any further purification. The ligands **H₂L1**, **H₂L2** and **H₄L3**, as shown in Scheme 1 were prepared according to the literature procedures.^{18,19} Elemental analyses were determined by using a FLASH EA series 1112 CHNS analyzer.

Infrared spectra of solid samples were recorded as KBr pellets on a JASCO-5300 FT-IR spectrophotometer. Thermo-gravimetric analyses were carried out on a STA 409 PC analyzer and corresponding masses were analyzed by using a QMS 403 C mass analyzer under a flow of N₂ gas at a heating rate of 5 °C min^{−1}, in the temperature range of 30–1000 °C. Powder X-ray diffraction patterns were recorded on a Bruker D8-Advance diffractometer using graphite monochromated CuK_{α1}

(1.5406 Å) and $K_{\alpha 2}$ (1.54439 Å) radiation. Temperature dependent magnetic studies were performed on a Quantum Design VSM-SQUID. All the compounds were synthesized hydrothermally in 23 mL Teflon-lined stainless vessels (Thermocon, India).

Synthesis of $\{\text{Co}_2(\text{L1})_2(\text{px3ampy})_2\}_n \cdot n \text{px3ampy}$ (1)

A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (59.5 mg, 0.25 mmol), $\text{H}_2\text{L1}$ (72.0 mg, 0.25 mmol) and px3ampy (72.5 mg, 0.25 mmol) was dissolved in 10.0 mL of distilled water and stirred for 30 min. The pH of the reaction mixture was adjusted to 6.52 by adding 0.5 M NaOH solution, and the resulting reaction mixture was placed in a 23 mL Teflon-lined stainless steel autoclave, which was sealed and heated at 160 °C for 3 days. The autoclave was allowed to cool to room temperature over 48 h to obtain red block crystals of compound 1. Yield 48% (based on Co). Anal. Calcd for $\text{C}_{42}\text{H}_{37}\text{CoN}_6\text{O}_6$ ($M_r = 780.71$): C, 64.61%; H, 4.77%; N, 10.76%. Found: C, 63.59%; H, 4.12%; N, 10.88%. IR (KBr pellet, cm^{-1}): 3309, 3086, 2812, 1594, 1550, 1506, 1397, 1293, 1210, 1172, 997, 854, 783, 706, 619.

Synthesis of $\{\text{Co}(\text{L2})(\text{px3ampy})_{0.5}\}_n$ (2)

The same synthesis procedure was followed to prepare compound 2 as that for compound 1 except that ligand $\text{H}_2\text{L2}$ was used in place of $\text{H}_2\text{L1}$ and the pH of the reaction was adjusted to 6.15. The reaction mixture was transferred to a stainless steel autoclave, sealed and heated to 130 °C for 4 days to obtain deep red crystals in 65% yield (based on Co). Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{CoN}_2\text{O}_6$ ($M_r = 490.34$): C, 58.76%; H, 3.90%; N, 5.71%. Found: C, 58.65%; H, 3.73%; N, 5.65%. IR (KBr pellet, cm^{-1}): 3391, 3063, 2997, 2887, 2843, 1632, 1583, 1484, 1402, 1315, 1227, 1024, 893, 767, 673.

Synthesis of $\{\text{Co}_2(\text{L3})(\text{px3ampy})_2(\text{H}_2\text{O})\}_n \cdot 3n\text{H}_2\text{O}$ (3)

Compound 3 was prepared by following the same procedure as described above, except that ligand $\text{H}_2\text{L2}$ was replaced by $\text{H}_4\text{L3}$ (47.0 mg, 0.12 mmol). The reaction mixture was heated at 130 °C for 3 days at an initial pH of 5.45. The resulting blue crystals were isolated by filtration in 56% yield (based on Co). Anal. Calcd for $\text{C}_{53}\text{H}_{38}\text{Co}_2\text{N}_8\text{O}_{14}$ ($M_r = 1128.77$): C, 56.37%; H, 3.39%; N, 9.93%. Found: C, 56.42%; H, 3.31%; N, 9.73%. IR (KBr pellet, cm^{-1}): 3309, 3057, 2849, 1578, 1545, 1452, 1375, 1238, 1112, 1024, 904, 783, 734, 701.

Single crystal X-ray structure determination of the compounds 1–3

Single-crystals suitable for structural determination of all the compounds 1–3 were mounted on a three circle Bruker SMARTAPEX CCD area detector system under a $\text{Mo-K}\alpha$ ($\lambda = 0.71073$ Å) graphite monochromated X-ray beam with a crystal-to-detector distance of 60 mm, and a collimator of 0.5 mm width. The scans were recorded with a ω scan width of 0.3°. Data reduction was performed using SAINTPLUS;^{21a} empirical absorption corrections using equivalent reflections were performed with the program SADABS.^{21b} Structure solutions were done using SHELXS-97^{21c} and full-matrix least-squares refine-

Table 1 Crystal data and structural refinement parameters for compounds 1–3

	1	2	3
Empirical formula	$\text{C}_{42}\text{H}_{37}\text{CoN}_6\text{O}_6$	$\text{C}_{24}\text{H}_{19}\text{CoN}_2\text{O}_6$	$\text{C}_{53}\text{H}_{38}\text{Co}_2\text{N}_8\text{O}_{14}$
Formula weight	780.71	490.34	1128.77
T (K)/ λ (Å)	298(2)/0.71073	298(2)/0.71073	298(2)/0.71073
Crystal system	Triclinic	Hexagonal	Triclinic
Space group	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
a (Å)	10.411(2)	24.5589(17)	10.0917(19)
b (Å)	14.051(3)	24.5589(17)	15.319(3)
c (Å)	15.034(3)	19.3712(13)	17.538(3)
α (°)	115.27(3)	90	70.053(3)
β (°)	92.53(3)	90	79.573(3)
γ (°)	110.65(3)	120	86.827(3)
Volume (Å ³)	1811.1(6)	10118.2(12)	2506.5(8)
Z , ρ_{calcd} (g cm ⁻³)	2, 1.432	18, 1.448	2, 1.496
μ (mm ⁻¹), $F(000)$	0.533/812	0.806/4535	0.739/1156
Goodness-of-fit on F^2	1.046	1.037	1.194
R_1/wR_2 [$I > 2\sigma(I)$]	0.0505/0.1295	0.0367/0.0975	0.0922/0.2145
R_1/wR_2 (all data)	0.0682/0.1425	0.0463/0.1034	0.1001/0.2187
Largest diff. peak/hole (e Å ⁻³)	1.826/−0.338	0.391/−0.198	1.661/−0.579

ment was carried out using SHELXL-97^{21d} for all three compounds. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the C atoms were introduced at calculated positions and were included in the refinement riding on their respective parent atoms. Attempts to locate all the hydrogen atoms for the solvent water molecules in the crystal structure of compound 3 through Fourier electron density map failed. However, no attempts were made to fix these atoms on their parent atoms. Crystal data and structure refinement parameters for compounds 1–3 are summarized in Table 1, and selected bond lengths and bond angles are presented in section 3 of the ESI.† Topological analyses of the compounds were performed by using the TOPOS software.^{21e} CCDC-1016482, CCDC-1016483 and CCDC-1016484 contain the supplementary crystallographic data for compounds 1, 2 and 3, respectively.

Results and discussion

Synthesis

Among the different synthetic methods (ionothermal, solvothermal/hydrothermal, mechanochemical, microwave-assisted) for the preparation of the coordination polymer-/metal-organic framework-containing compounds, the solvothermal/hydrothermal technique is the most conventional method which has received immense attention from the community of synthetic chemists. Hence, we have employed the hydrothermal technique to obtain all three coordination polymers (compounds 1–3) described in this article. For all three compounds we used the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ salt as the source of the Co^{2+} metal ion. The compositions of the reaction mixtures for compounds 1 and 2 were taken from an aqueous medium with a metal : acid : N-donor linker ratio of 1 : 1 : 1, whereas, for compound 3, this ratio was 2 : 1 : 2 to justify the requirement

of more Co^{2+} metal ions by the $\text{L}3^{4-}$ ligand (with four carboxylate groups) in comparison to $\text{L}1^{2-}$ and $\text{L}2^{2-}$ ligands (each with two carboxylate groups). After carrying out a series of experiments, we could optimize the condition of heating the reaction mixture at 130 °C to obtain the single crystals of compounds 2 and 3; compound 1 was obtained in better yield and quality at a higher temperature of 160 °C. In order to deprotonate the $-\text{COOH}$ groups of the ligands $\text{H}_2\text{L}1$ and $\text{H}_2\text{L}2$ in the synthesis of compounds 1 and 2 respectively, we have used 0.5 M NaOH solution to increase the initial pH (5.45) of the respective reaction mixtures (for compounds 1 and 2, the pH range is 6.10–6.50), whereas for compound 3, the required pH is the initial pH (5.45). All three compounds are air stable and insoluble in water.

Description of crystal structures

$\{\text{Co}_2(\text{L}1)_2(\text{px}3\text{ampy})_2\}_n \cdot n\text{px}3\text{ampy}$ (1). Compound 1 is a 1D extended coordination polymer that crystallizes in a triclinic space group $P\bar{1}$. The relevant asymmetric unit consists of one crystallographically independent $\text{Co}(\text{II})$ ion in a distorted tetrahedral geometry, one coordinated $\text{L}1^{2-}$ ligand, one coordinated $\text{px}3\text{ampy}$ and one uncoordinated $\text{px}3\text{ampy}$ ligand. The coordination geometry around the $\text{Co}(\text{II})$ metal ion is found to be distorted tetrahedral (instead of usual octahedral geometry) with a calculated distortion parameter τ_4 value of 0.80. The tetrahedral $\{\text{CoN}_2\text{O}_2\}$ geometry around the $\text{Co}(\text{II})$ ion is comprised of two oxygen atoms from two different $\text{L}1^{2-}$ ligand units, and two nitrogen atoms from two different $\text{px}3\text{ampy}$ ligands (Fig. 1a). The bond distances of $\text{Co}-\text{O}$ and $\text{Co}-\text{N}$ are in the range 1.998–2.108 Å and the bond angles around the $\text{Co}(\text{II})$ centre are in the range 91.58°–137.30°. Each $\text{L}1^{2-}$ ligand connects to two cobalt atoms on either side in a monodentate ($\mu_1-\eta^1:\eta^0$) coordination mode and connects the adjacent $\{\text{CoN}_2\text{O}_2\}$ tetrahedra in a V-shaped conformation, characterized by the $\text{C}_{\text{phenyl}}-\text{O}\cdots\text{O}-\text{C}_{\text{phenyl}}$ torsion angle of ($\tau' = 125.99^\circ$) in the central part of the ligand and the dihedral angle (δ') between two phenyl rings is 66.80°. The ligand $\text{L}1^{2-}$ separates two $\text{Co}(\text{II})$ centres with a distance of 15.31 Å to form a 1D metal–acid chain along the crystallographic c -axis (Fig. 1b). In this compound, the N-donor pyridyl ligand $\text{px}3\text{ampy}$ occurs in two different ways: one involves the coordination and the other is a lattice component without coordinating to the metal center. The coordinating $\text{px}3\text{ampy}$ ligand connects two $\text{Co}(\text{II})$ centres in the 1D metal–acid chains through the N atoms of the pyridyl rings, creating a separation of 14.69 Å resulting in the formation of a molecular loop $[\text{Co}_2(\text{px}3\text{ampy})_2]$ as shown in Fig. 1c. In order to furnish the molecular loop, the $\text{px}3\text{ampy}$ ligand adopts a *trans-cis-trans* conformation, where the $-\text{CH}_2-\text{NH}-$ groups are *trans* to each other with an anticlinal torsion angle ($\tau_{\text{tor}1}$) of 119.26°. Interestingly, the pyridine rings at the $-\text{NH}-$ groups are *cis* to each other with a torsion angle ($\tau_{\text{tor}2}$) of 76.03° and the nitrogen atoms in the pyridine rings are coordinated to metal ions in a typical *trans* fashion. The uncoordinated $\text{px}3\text{ampy}$ molecule is characterized by an expected stable *trans-trans* conformation having both $\tau_{\text{tor}1}$ and $\tau_{\text{tor}2}$ values of 180°. Each $[\text{Co}_2(\text{px}3\text{ampy})_2]$ molecular loop connects to other such molecular loops

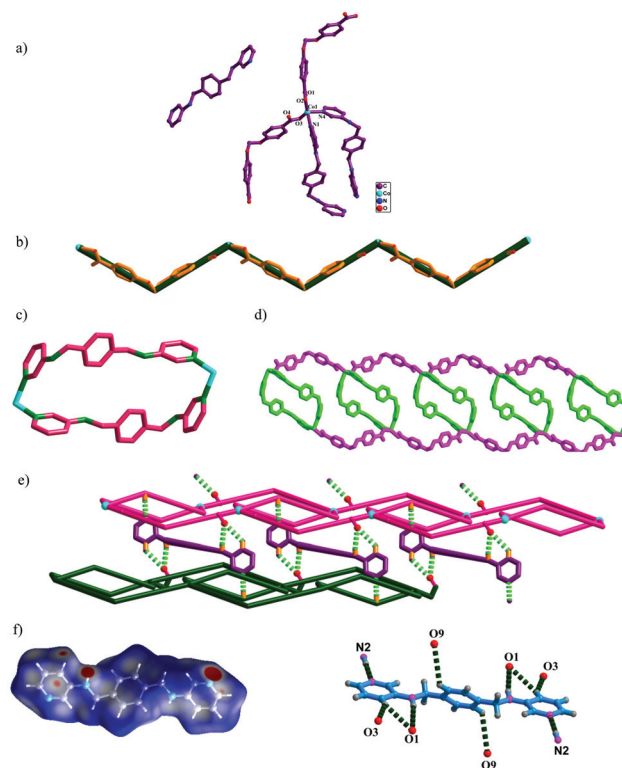


Fig. 1 (a) Molecular diagram of compound 1; hydrogen atoms are omitted for clarity. (b) 1D metal–acid chain with the V-shaped geometry of the $\text{L}1^{2-}$ ligand. (c) Molecular loop, created by the $\text{px}3\text{ampy}$ linker by connecting to the $\text{Co}(\text{II})$ metal ion. (d) 1D Ladder-like chain, formed by the connectivity of the molecular loops and the metal–acid chain. (e) 2D Supramolecular network, furnished by the interconnecting 1D chains through lattice $\text{px}3\text{ampy}$. (f) Non-covalent interactions, exhibited by the uncoordinated $\text{px}3\text{ampy}$ ligand and its Hirshfeld surface diagram.

through the metal–acid chain to generate an 1D ladder-like chain, in which each $\text{Co}(\text{II})$ metal ion behaves as a four connector and connects to other three $\text{Co}(\text{II})$ metal ions through a pair of $\text{L}1^{2-}$ and a pair of $\text{px}3\text{ampy}$ linkers (Fig. 1d).

Additionally, these 1D chains are connected by the lattice uncoordinated $\text{px}3\text{ampy}$ ligands by hydrogen bonding interactions to form a 2D supramolecular architecture. The $\text{px}3\text{ampy}$ molecule consists of potential H-donors from the C and N atoms and connects the adjacent ladders through $\text{C}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding interactions. Notably, a strong short $\text{N}-\text{H}\cdots\text{O}$ H-bond has been observed between the $-\text{NH}-$ group of the free $\text{px}3\text{ampy}$ molecule and the uncoordinated oxygen atom (O1) of the carboxylate group of the $\text{L}1^{2-}$ ligand ($\text{N}10-\text{H}10\text{N}\cdots\text{O}1 = 3.226$ Å). Further, the uncoordinated oxygen atom (O1) participates in the formation of a long-bonded $\text{C}-\text{H}\cdots\text{O}$ interaction with the CH group of the pyridyl ring of the lattice $\text{px}3\text{ampy}$ molecule ($\text{C}32-\text{H}32\cdots\text{O}1 = 3.620$ Å). Along with these interactions, the N atoms in the pyridine rings of uncoordinated $\text{px}3\text{ampy}$ molecules are involved in strong hydrogen bonding interactions with the NH groups of the coordinated $\text{px}3\text{ampy}$ linkers ($\text{N}2-\text{H}2\text{N}\cdots\text{N}12 = 3.002$ Å). The same hydrogen bonding situation has been observed on the other symmetry

side of the px3ampy molecule. Overall, one lattice px3ampy molecule takes part in two N–H...O, two N–H...N and two long C–H...O hydrogen bonding interactions to join two 1D ladders. Thus, the 1D chains are interconnected by the supra-molecular interactions leading to the formation of 2D supra-molecular networks (Fig. 1e). The hydrogen bonding situation has been explained by visualization of intermolecular interactions by mapping the Hirshfeld surface (by using Crystal explorer).²² The red spots on the Hirshfeld surface in Fig. 1f represent the closest hydrogen bonding whereas the blue spots indicate the areas without close contacts. The H...O interactions of C and N atoms contribute 6.8% of total supra-molecular interactions with a strong N10–H10N...O1 interaction with a di + de value of 2.25 Å (di + de value represents the shortest possible interaction between the atoms in the molecular surface and the outer surface). The N–H...N interaction of the NH group of the coordinated px3ampy with un-coordinated px3ampy contributes 8.8% of total hydrogen bonding interactions with a di + de value of 2.1 Å.

{Co(L2) (px3ampy)}_{0.5}_n (2). Single-crystal X-ray structure determination of compound 2 reveals a three-dimensional (3D) framework that crystallizes in the hexagonal space group *R* $\bar{3}$. In the crystal structure, each asymmetric unit contains one Co atom, one L2^{2−} ligand and half of the px3ampy ligand. Compound 2 adopts the formation of {Co₂(COO)₄} paddle wheels as the secondary building units (SBUs) in which the Co–Co distance is 2.763 Å and the distances of Co(II) atom and oxygen of the carboxylate groups of the L2^{2−} ligand range from 2.003 Å to 2.075 Å, while the distance of Co(II) and the N atom of the px3ampy ligand is 2.049 Å. Each carboxylate group of the L2^{2−} ligand bridges two Co(II) ions in a bidentate (μ_2 - η^1 : η^1) fashion and coordinates at the basal plane of the {Co₂(COO)₄} paddle wheel; the apical positions of the dimeric paddle wheel unit are occupied by the N atoms of the px3ampy ligand (Fig. 2a). The dihedral angle between the two carboxylate groups on the benzene rings in the bent L2^{2−} is 67.23°, and the separation created between the two paddle-wheels along length of the L2^{2−} unit is 9.589 Å (viewed through the centre of the adjacent metal atoms in the paddle-wheel). Each {Co₂(COO)₄} paddle wheel unit acts as a four connector node (Fig. 2b) and is connected to four other paddle wheel units through four different L2^{2−} ligands, resulting in the formation of a 3D framework. Usually the 4-connected paddle wheels generate a 2D sheet of a layered topology and in some cases two such layers interpenetrate to form helical double layers.²³ Interestingly, however, in the relevant crystal structure, the 4-connected paddle wheels create a 3D framework through the linker L2^{2−}. In an SBU approach, the formation of the 3D framework can be explained by the connectivity of paddle-wheels through the surrounding linker L2^{2−}, in which the adjacent paddle wheels connected by the L2^{2−} ligand along any axis are perpendicular to each other. In the crystal structure, this peculiar arrangement of paddle-wheels results in a situation in which if one paddle wheel is connected to the adjacent four paddle wheel units in the crystallographic *ab* plane, then the next paddle wheel connects to its adjacent four

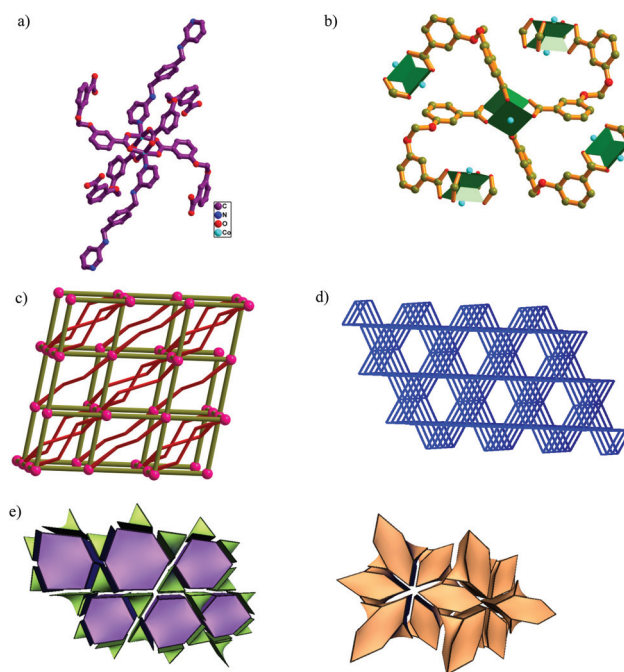


Fig. 2 (a) Molecular diagram of the compound 2. (b) Four connector node of the {Co₂(COO)₄} paddle wheel by L2^{2−} ligand. (c) The 3D framework, assuming the pink atom as the paddlewheel and the green bond as the L2^{2−} ligand connectivity, where the red bonds present the px3ampy ligand. (d) 3D Topological diagram of the compound. (e) Natural tiling and the dualized tiling of a natural tile.

paddle wheels in the crystallographic *ac* (perpendicular to *ab*) plane. The overall connectivity of these paddle-wheels along both the planes results in the formation of a 3D framework (Fig. 2c) in contrast to an usual 2D layered structure, generally formed by 4-connected paddle wheels. In this 3D framework (in the present work, in the crystal structure of compound 2), the paddle wheels are further inter-connected by the long flexible px3ampy ligand, creating a separation of 19.37 Å between the two paddle wheels. The ligand px3ampy implements its most favourable and longest (in length) *trans-trans-trans* conformation to create a one-dimensional (1D) chain by connecting the paddle-wheel units. The connectivity of the paddle wheels with the px3ampy ligand generates two types of 1D chains, one which passes through the paddle wheels having connectivity in the crystallographic *ac* plane (through the L2^{2−} ligand) and the other, through the paddle wheels having connectivity in the crystallographic *ab* plane. The overall connectivity represents the paddle wheels as the six-connector nodes and L2^{2−}, px3ampy ligands as two-connector nodes. The overall structure has a 2,2,6-connected 3-nodal net with the Schläfli symbol {8¹⁰·12⁵}{8}₃. By considering the linkers as linear connectors and ignoring their flexibilities, the structural topology can be simplified to a 6-connected uninodal net with the Schläfli symbol {4¹⁰·6⁵} (Fig. 2d). The network structure exhibits a tiling of the snz net with 3 nodes and 9 edges which have been represented as 6[4³] (shown in green) and [4⁶·6²] (shown in purple) in Fig. 2e.

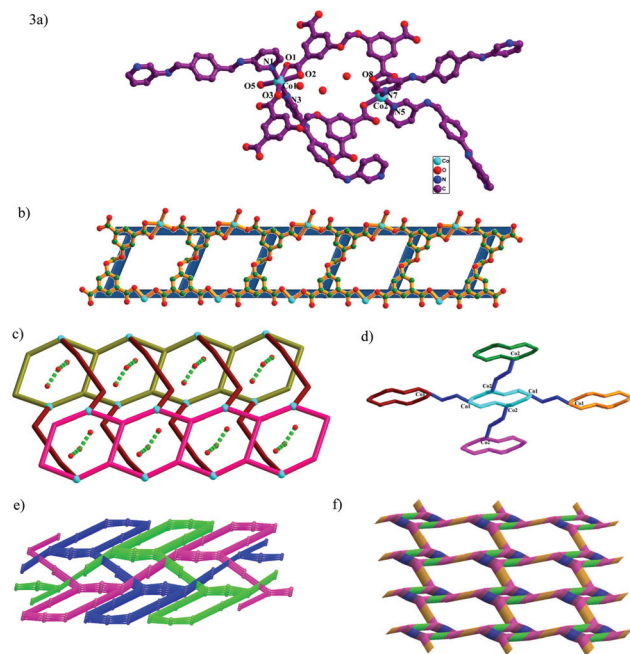


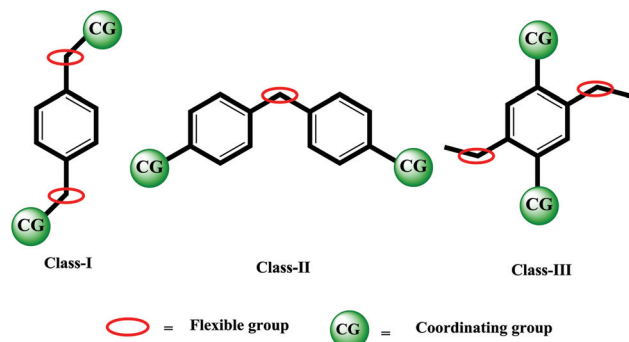
Fig. 3 (a) Molecular diagram representing the coordination environment around the Co(II) metal ions. (b) 1D Ladder structure, formed by the connectivity of the $L3^{4-}$ ligand and the Co(II) metal ion. (c) Interconnectivity of the ladder by the px3ampy to form a 1D channel. (d) 4-Connectivity of the 1D channel with other channels. (e) Topological representation of the 3D interpenetrating framework, formed due to interpenetration of three 3D frameworks. (f) Topological representation of a single 3D framework.

$\{Co_2(L3)(px3ampy)_2(H_2O)\}_n \cdot 3nH_2O$ (**3**). The asymmetric unit of compound **3** consists of two crystallographically independent Co(II) ions (Co1 and Co2), one $L3^{4-}$, two px3ampy ligands, one coordinated water molecule and three lattice water molecules. It crystallizes in the triclinic space group $P\bar{1}$. As shown in the molecular structural diagram (Fig. 3a), Co1 is coordinated by the three oxygen atoms of the carboxylate groups from two different $L3^{4-}$ ligands and two nitrogen atoms from the two different px3ampy ligands and one aqua ligand, thus exhibiting a distorted $[CoO_4N_2]$ octahedral coordination geometry. On the other hand, the Co2 centre in $[CoO_2N_2]$ has a tetrahedral geometry, defined by two oxygen atoms from two $L3^{4-}$ ligands and two nitrogen atoms from two different px3ampy ligands. The Co–O bond lengths are in the range of 1.991–2.103 Å and the Co–N bond distances are in the range of 2.048–2.166 Å. All the four carboxylate groups of the $L3^{4-}$ ligand adopt two different coordination modes; two of them are coordinated to the Co(II) metal ion in a monodentate ($\mu_1-\eta^1: \eta^0$) coordination fashion, and the remaining two carboxylate groups adopt a chelating bidentate ($\mu_2-\eta^1: \eta^1$) coordination mode towards Co(II) ions. In other words, in the $L3^{4-}$ ligand, two carboxylate groups of the one benzene ring are connected to two different Co1 (O_h geometry) metal ions in a chelating bidentate mode and the carboxylate groups on other benzene ring adopt a monodentate coordination mode to connect two Co2 (t_d geometry) metal ions. The combined

connectivity of the four carboxylate groups on the $L3^{4-}$ ligand with Co1 and Co2 metal ions generates a 1D ladder running parallel to the crystallographic b axis, whereby the $[Co_2L3_2]$ metallocycle acts as a basic repeating unit of the ladder (Fig. 3b). Interestingly, one edge of the ladder consists of Co(II) metal ions in their octahedral geometry (Co1), whereas at the opposite edge, all Co(II) centres are in a tetrahedral geometry (Co2). The tetracarboxylate $L3^{4-}$ is characterized by the torsion angle (τ'), measured in the flexible part of the ligand ($C_{phenyl}-O-O-C_{phenyl}$), of 140.0° and the dihedral angle (δ') of 33.91° between two phenyl rings; both these parameters indicate that the linker adopts a flattened geometry rather than a bent or twisted geometry. Adjacent ladders are then interconnected by a set of px3ampy linkers at each basic repeating unit *i.e.* the $[Co_2L3_2]$ metallocycle to form 1D channels. A channel is formed from two ladders that are laterally interlinked from both sides by px3ampy linkers to take a cylindrical form as shown in Fig. 3c. During the formation of these channels, each px3ampy linker connects two ladders in its *cis-cis-trans* conformation. These channels behave as 4-connector nodes and thus each channel connects to four other such surrounding channels through px3ampy linkers to form a robust 3D framework (Fig. 3d). In the 3D network, the tetrahedral Co1 coordination spheres of the channels are connected only to other such tetrahedral coordination spheres of other channels along the crystallographic c -axis, creating a distance of 16.82 Å between the channels. In a similar way, the octahedral Co2 coordination spheres of a channel are connected to only such octahedral coordination spheres of other channels along the crystallographic a -axis with a distance of 16.79 Å between the concerned channels. In both the cases, the linker px3ampy adopts its most favourable *trans-trans-trans* configuration. The relevant crystal structure contains three lattice water molecules that form a classic supramolecular water trimer, formed by hydrogen bonding interactions between O10...O11 (3.074 Å) and O11...O12 (3.071 Å). These water trimers remain in the void space of the crystal structure near the metallocycle of the ladder (Fig. 3c). The overall crystal structure exhibits a 3D framework with three interpenetrating nets as shown in Fig. 3e. The network was simplified by Topos and can be presented as a (4,4) connecting 2-nodal net with the Schläfli symbol $\{4 \cdot 6^4 \cdot 8\}2\{4^2 \cdot 6^4\}$ (Fig. 3f).

Influence of position of coordinating groups of the ligand on coordination chemistry of title compounds

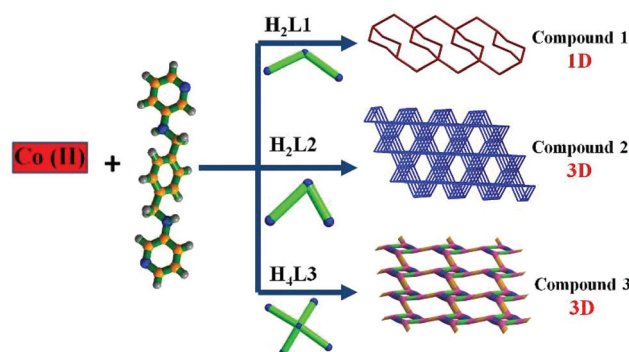
The ligands employed in this study are versatile in terms of occurrence of flexibility in the central position of the skeleton rather than at the terminus of the linker (see Scheme 1 for the ligands used in this work). As shown in Scheme 2, three different classes of flexible linkers are given based on the position of the flexibility in the linker. The linkers presented in this study (Scheme 1) belong to class-II flexible linkers where the flexible groups are separated from the coordinating groups through rigid spacers. Class-II flexible linkers with spacers, separated by the mono atom flexible groups ($-O-$, $-CH_2-$, $-S-$), which are also termed bent ligands, are well reported in the



Scheme 2 Scheme representing the different classes of flexible ligands based on their position in the skeleton.

literature.^{21a} But in the ligands employed in this work, the rigid spacers are separated by a three-atom-flexible group ($-\text{O}-\text{CH}_2-\text{O}-$).

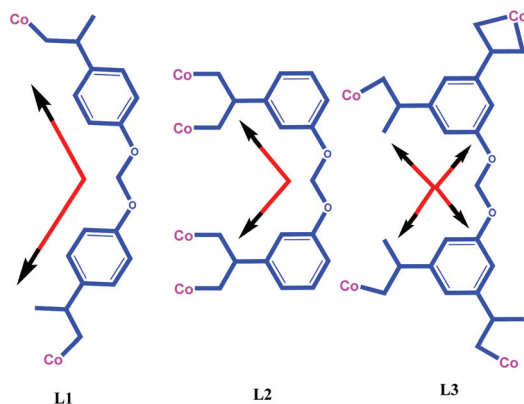
In these linkers, the positions of the coordinating groups are explained with respect to the flexible group rather than with respect to each other. In the case of compound 1, the linker $\text{H}_2\text{L1}$ is employed, in which the carboxylate groups are in the *para* positions with respect to the flexible group. The connectivity of the L1^{2-} ligand with the Co(II) ion results in the formation of 1D chains, which are further connected by a pair of px3ampy linkers to form a 1D ladder-like arrangement. When the $\text{H}_2\text{L2}$ ligand is used (compound 2), where the carboxylate groups are in *meta* positions with respect to the flexible group, it results in the formation of a 3D framework. The torsion angles (τ'), at the flexible groups ($\text{C}_{\text{phenyl}}-\text{O}-\text{O}-\text{C}_{\text{phenyl}}$) in both the ligands are almost similar, *i.e.* 125.99° in 1 and 121.78° in 2, which clearly indicates that the degrees of flexibility in both the ligands are nearly the same. The coordination angle, created by the connectivity of the L1^{2-} with the two Co(II) centres in compound 1, is 116.92° (viewed through $\text{Co}-\text{C}_{\text{sp}^2}-\text{Co}$) which is considerably larger than the coordination angle of 75.94° , created by the connectivity of deprotonated ligand L2^{2-} with two Co(II) centres in compound 2. Thus by a simple change in the position of the carboxylate group from *para* ($\text{H}_2\text{L1}$) to *meta* ($\text{H}_2\text{L2}$), keeping other compositional constituents the same, the metal–acid architecture has been changed from a 1D framework (compound 1) to a 3D framework (compound 2). In the case of compound 2, due to the bending nature in the central part of L2^{2-} ($\text{C}_{\text{phenyl}}-\text{O}-\text{O}-\text{C}_{\text{phenyl}} = 121.78^\circ$) and the lower coordination angle between two Co(II) centers (75.94°), the linker adopts a twisted geometry that seems to be responsible for the adjacent paddlewheels to be orthogonal to each other. This arrangement of the paddle wheels (*i.e.*, consecutive paddle wheels are orthogonal to each other, thereby every second paddle wheel has the same configuration) in the crystals of compound 2 plays an important role in exhibiting interesting and unusual magnetic properties (*vide infra*). By considering the positions of the carboxylate groups in $\text{H}_2\text{L1}$ and $\text{H}_2\text{L2}$ linkers and the resulting dimensionality in the crystal structures of compounds 1 and 2, a tetrapodal carboxylate ligand $\text{H}_4\text{L3}$ has been used with the same



Scheme 3 Scheme representing the coordinating geometry of ligands employed and the corresponding dimensionality in the resulting compounds.

Co-px3ampy composition matrix to obtain compound 3 (see Scheme 3). In the ligand $\text{H}_4\text{L3}$, four carboxylate groups are present in its skeleton with two carboxylate groups on each phenyl ring, and each carboxylate group is located on the *meta* position to the flexible group. The connectivity of L3^{4-} with the Co(II) metal ions results in the formation of 1D ladder-like arrangements that are further connected by the px3ampy linkers to give a 3D framework. In other words, in the case of compound 3, the 3D framework is formed by linking metal–acid ladders with px3ampy linkers, whereas in the case of compound 2, the 3D framework is formed solely from metal–acid coordination (cobalt metal ion + L2^{2-} ligand). In the case of compound 3, on viewing from the C atom of the L3^{4-} ligand, which is located exactly on the centre of the ligand, it is observed that the four carboxylate groups are arranged in a square planar mode; as a result the metal–acid coordination geometry is planar and its repetition in one dimension forms 1D metal–acid ladders rather than a 3D metal–acid framework as expected from *meta*-positioned (with respect to flexible group) carboxylate groups of the linker, as is observed in the crystal structure of compound 2. Due to the coordination of four carboxylate groups of the L3^{4-} ligand with four Co(II) ions (that are positioned at four vertices of a square), the degree of flexibility of L3^{4-} is restricted *i.e.*, the dihedral angle (δ') between two phenyl rings is 28.94° (compound 3) compared to 66.80° in compound 1 and 68.75° in 2. The skeletons and coordination modes of the carboxylate groups of ligands L1^{2-} , L2^{2-} and L3^{4-} with cobalt centers in compounds 1, 2 and 3, respectively, are shown in Scheme 4. The linkers $\text{H}_2\text{L1}$ and $\text{H}_2\text{L2}$ are already known in the literature and they have been shown to form 2D interpenetrated nets with the secondary linkers,¹⁸ which are not observed in the case of compounds 1 and 2 (present work). The linker $\text{H}_4\text{L3}$ is known to form a pcu topology with metal centres²⁰ and by the introduction of a secondary linker (in the present study), a (4,4) connected interpenetrated network is observed in the case of compound 3.

In most of the cases, the secondary linker px3ampy favors *trans-trans-trans* configuration unless it is forced to change its configuration due to the coordination requirement at the metal coordination sphere. In the case of compound 1, the



Scheme 4 The coordination modes and skeleton of the ligands $L1^{2-}$, $L2^{2-}$ and $L3^{4-}$.

coordinated px3ampy linker has *trans-cis-trans* configuration to meet the coordination requirements and the free uncoordinated px3ampy molecule remains in the normal *trans-trans-trans* form. In case of compound 2, px3ampy exists in a *trans-trans-trans* arrangement, which is the usual conformation to connect the paddlewheels. However, in the crystal structure of compound 3, the px3ampy linkers coordinate in two different modes: one in a peculiar *cis-cis-trans* form to connect the 1D ladders to form 1D channels and the other in the usual *trans-trans-trans* form which connects these 1D channels to the 3D network.

Magnetic properties

Compound 1. Compound 1 in the solid state consists of a 1D ladder-like arrangement, in which two Co(II) ions are separated by large distances and no plausible exchange interactions are possible through long bridges. The plots of both χ_M vs. T and $\chi_M T$ vs. T for compound 1 are shown in Fig. 4. The room temperature $\chi_M T_{300}$ value of compound 1 is $2.07 \text{ cm}^3 \text{ K mol}^{-1}$ which is slightly higher than the expected value for an isolated Co^{II} ion ($\chi_M T = 1.875 \text{ cm}^3 \text{ K mol}^{-1}$ for a $S = 3/2$ ion). As the

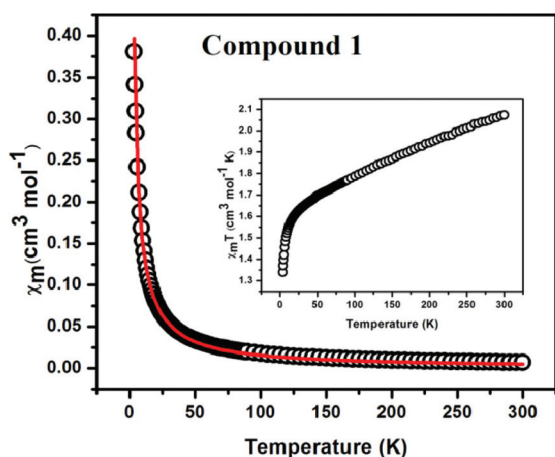


Fig. 4 Magnetic susceptibility of compound 1, plotted as $\chi_M T$ vs. T (inset) and χ_M vs. T in the temperature range of 2–300 K.

temperature decreases, the $\chi_M T$ also decreases smoothly to $1.33 \text{ cm}^3 \text{ K mol}^{-1}$ at 3.5 K. $1/\chi_M$ vs. T plot follows the Curie–Weiss law (see ESI, Fig. S1†) at high temperature with a negative Weiss constant $\theta = -18.20$ (1) K. In this compound, the higher value of $\chi_M T$ than the expected spin-only value indicates the orbital contribution of the Co(II) ion. The observed spin–orbit coupling in compound 1 can be calculated by the expression for $S = 3/2$ systems with dominant zero field splitting effects, D (eqn (1)–(4)).^{24a}

$$\chi_{\parallel} = (Ng^2\beta^2/k_B T)[A/B] \quad (1)$$

where $A = [1 + 9 \exp(-2D/k_B T)]$ and $B = [4(1 + \exp(-2D/k_B T))]$

$$\chi_{\perp} = (Ng^2\beta^2/k_B T)[C/D] \quad (2)$$

where $C = [4 + (3k_B T/D)(1 - \exp(-2D/k_B T))]$ and $D = [4(1 + \exp(-2D/k_B T))]$

$$\chi'_M = [(\chi_{\parallel} + \chi_{\perp})/3] \quad (3)$$

$$\chi_M = \chi'_M / \{1 - \chi'_M (2zJ'/Ng^2\beta^2)\} \quad (4)$$

The parameters N , β and k_B have their normal meanings. The best fit is obtained from 2 to 300 K with $g = 2.37$ (2), $D = -19.33$ (1) cm^{-1} and $zJ' = 0.79$ (6), with an agreement factor of 2.08×10^{-5} . The value of D calculated from the above expressions is in the range expected for a tetrahedral metal center (*i.e.* $D = -36$ to $+13 \text{ cm}^{-1}$).^{24b}

Compound 2. Temperature dependent magnetic studies for polycrystalline compound 2 were performed at 500 Oe. As shown in Fig. 5a, the room temperature $\chi_M T$ value of $6.85 \text{ cm}^3 \text{ K mol}^{-1}$ per dimer is much higher than the calculated spin-only value for two isolated Co(II) atoms ($3.875 \text{ cm}^3 \text{ K mol}^{-1}$, $S = 3/2$), indicating the important orbital contribution arising from the high-spin octahedral Co(II). Upon cooling, the $\chi_M T$ value continuously decreases until 45 K, suggesting an intra-dimer antiferromagnetic interaction between two Co(II) ions. The exchange parameter (J) of -47.23 cm^{-1} , obtained from the χ_M plot (fitted assuming the carboxylate bridges of the two Co(II) ions form an isolated spin dimer, see ESI† section-2), suggests an antiferromagnetic exchange interaction between two Co(II) ions in the intra-dimer. Interestingly, just below 45 K, the $\chi_M T$ value abruptly increases upon further cooling and reaches the maximum value of $1.77 \text{ cm}^3 \text{ K mol}^{-1}$ at 25 K and then decreases sharply to a minimum value of $0.020 \text{ cm}^3 \text{ K mol}^{-1}$ at 3.5 K. This rapid increase in the $\chi_M T$ value followed by the sharp decrease indicates a magnetic phase transition. The magnetic studies show that the maximum around the 25 K in the “ $\chi_M T$ vs. T ” plot has a field dependent nature (Fig. S2, ESI†); on decreasing the field, the $(\chi_M T)_{\text{max}}$ rises to significantly higher values, which is characteristic of the spin canted nature of the compound. The zero field-cooled (ZFC) and field-cooled (FC) susceptibility measurements at 50 Oe have been plotted in Fig. 5b, showing a sharp bifurcation at 25 K; above this temperature, the FC curve rises quickly and reaches the maximum value at 2.5 K. These characteristic features confirm the occurrence of the antiferromagnetic

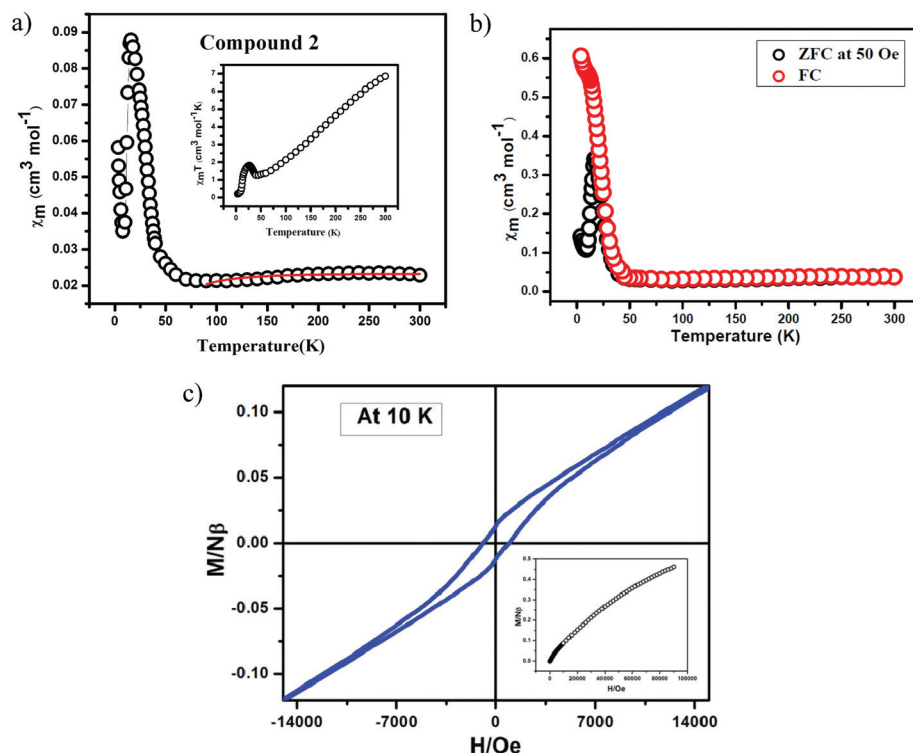


Fig. 5 (a) Plots of $\chi_M T$ vs. T (inset) and χ_M vs. T for the compound 2 in the temperature range of 2–300 K. (b) ZFC and FC curves of the compound 2 at 50 Oe. (c) Hysteresis loop of the compound 2 and the virgin magnetization curve (inset) at 10 K.

ordering phenomenon due to spin canting configuration of local spin vectors among adjacent cobalt dimers (paddlewheels).

The occurrences of such antiferromagnetic ordering have been additionally characterized by the field-dependent isothermal magnetization $M(H)$ at 10 K (Fig. 5c). It is notable that the typical hysteresis loop for the canted antiferromagnetic behaviour is observed, with remnant magnetization (M_r) of $0.0125N\beta$ at 10 K, which is coupled with a high coercive field (H_c) of 900 Oe. We performed isothermal magnetization experiments at higher temperatures, namely, at 20 K and 30 K (see Fig. S4, ESI† for details). The fate of the hysteresis loop upon heating shows a lowering of the area of the hysteresis loop on increasing the temperature, and at 30 K, no hysteresis was observed. The difference between the χ_M values ($\Delta\chi_M^{(FC-ZFC)}$), obtained from ZFC and FC curves at 2.5 K is invariably field dependent, because it goes down by increasing the field (see Fig. S3 in ESI†).

In the present work, the $\{Co_2\}$ paddlewheels (cobalt dimers) are separated by a rather large distance, which distinctly rules out short range magnetic exchange interactions. In order to understand why the present system exhibits an unusual antiferromagnetic ordering of a large coercive field (despite the fact that the paddle wheels are not connected by any shorter non-centrosymmetric ligand), we have investigated the observed solid state structure–function relationship. We found that the adjacent paddlewheels in the 3D framework are tilted to each other in an almost orthogonal arrangement (Fig. 6a),

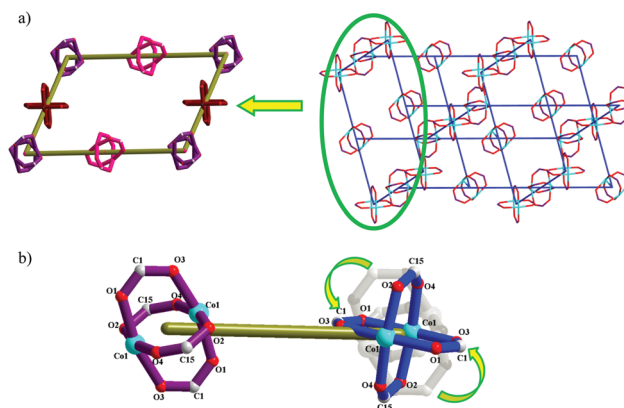


Fig. 6 (a) Packing of the $\{Co_2\}$ paddlewheels in the crystal of compound 2 showing the orthogonal arrangement of the successive paddlewheels in the 3D net (cyan colour bonds represent $L2^{2-}$ ligands) to generate local anisotropy. (b) Projection displaying the tilting of the adjacent paddlewheels.

which plays a vital role for this material (compound 2) in exhibiting spin-canting behaviour. In the 3D network, the tilted assembly of anti-ferromagnetic paddlewheels lacks an inversion center and is therefore attributed to a magnetic anisotropy resulting in an antiferromagnetic ordering (Fig. 6b). The lower coordination angle of 75.94° between two $Co(II)$ dimers (compound 2) causes the $L2^{2-}$ ligand skeleton to adopt a twisted geometry, which makes the successive paddle wheels

orthogonal to each other (*vide supra*) to bring about magnetic anisotropy. The lower coordination angle between two cobalt dimers (in compound **2**) arises because of the *meta*-position (with respect to the flexible center) of the carboxylate groups on the phenyl ring of the ligand skeleton. When the coordinated carboxylate groups of the ligand skeleton are in the *para*-position with respect to the flexible center (of ligand **L1**²⁻, compound **1**), the coordination angle is much larger and thereby twisting of the ligand skeleton does not occur. Thus the position of the coordinated carboxylate groups on the skeleton of the ligand is very important. A related antiferromagnetic ordering phenomenon has recently been reported by Bharadwaj and co-workers in a Co(II) paddle-wheel-based compound ($T_c = 10.5$ K), in which the {Co₂} paddle-wheels are orthogonally arranged, leading to an uncompensated magnetic moment.²⁵

Compound 3. The temperature dependent magnetic susceptibility measurement of compound **3** was performed under an applied field of 1000 Oe over the temperature range 2–300 K. Fig. 7a shows the temperature dependence of χ_M and $\chi_M T$ values for compound **3**. The room temperature $\chi_M T$ value is $6.14 \text{ cm}^3 \text{ K mol}^{-1}$, which is much higher than the spin only value of two isolated Co(II) ions ($\chi_M T = 3.75 \text{ cm}^3 \text{ K mol}^{-1}$ for a $S = 3/2$ ion), and is attributed to the fact of the orbital contribution arising from the high spin Co(II) ion. Upon cooling, the $\chi_M T$ value first decreases smoothly up to 19.5 K to reach a minimum value of $3.52 \text{ cm}^3 \text{ K mol}^{-1}$ and then beyond this point, an increase of the $\chi_M T$ value has been observed on

decreasing the temperature to reach a maximum of $3.92 \text{ cm}^3 \text{ K mol}^{-1}$ at 9.5 K. Furthermore, the $\chi_M T$ value started decreasing to a minimum value of $3.09 \text{ cm}^3 \text{ K mol}^{-1}$ at 3.5 K. The $1/\chi_M$ vs. T plot (Fig. S5†) above 80 K follows the Curie–Weiss law with a negative Weiss constant $\theta = -48.55$ K. The weak onset magnetic ordering at 9.5 K was characterized through ZFC–FC measurements. A sharp bifurcation was observed at 9.5 K in the ZFC–FC measurement at 50 Oe (Fig. 7b). The difference between the χ_M values ($\Delta\chi_M^{(\text{FC-ZFC})}$), obtained from ZFC and FC curves at 3.0 K, is $\sim 0.63 \text{ cm}^3 \text{ mol}^{-1}$, and this $\Delta\chi_M^{(\text{FC-ZFC})}$ is invariably field dependent, because it decreases to $\sim 0.50 \text{ cm}^3 \text{ mol}^{-1}$ at 100 Oe (Fig. S6†). The occurrence of such weak ferromagnetic ordering has been additionally characterized by the field-dependent isothermal magnetization $M(H)$ at 3.0 K (Fig. 7c). It is notable that the typical hysteresis loop for the canted ferromagnetic behaviour is observed at 3.0 K with a negligible coercive field (H_c) of 25 Oe.

These parameters indicate that a very weak onset antiferromagnetic ordering has been observed at 9.5 K, which is probably due to the presence of two Co(II) centers in different coordination environments. The relevant crystal structure reveals that the connectivity of the linker **L3**⁴⁻ with Co(II) centers results in the formation of two different coordination environments, namely octahedral and tetrahedral geometries (Fig. 8) around cobalt ions (*vide supra*) in the Co(II)–**L3**⁴⁻ chains, whereby all the octahedral Co(II) centers form one type of chain and the tetrahedral Co(II) centers form another type of chain. This probably results in a weak magnetic anisotropy

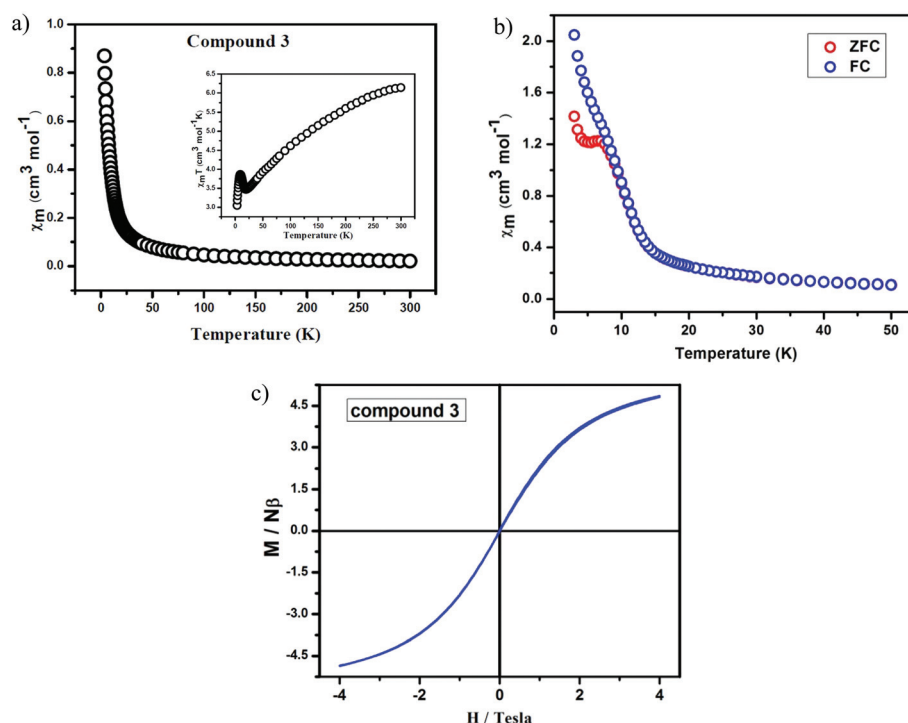


Fig. 7 (a) Plots of $\chi_M T$ vs. T (inset) and χ_M vs. T for the compound **3** in the temperature range of 2–300 K. (b) ZFC and FC curves of the compound **3** at 50 Oe. (c) Field dependence magnetization curve of compound **3** at 3 K.

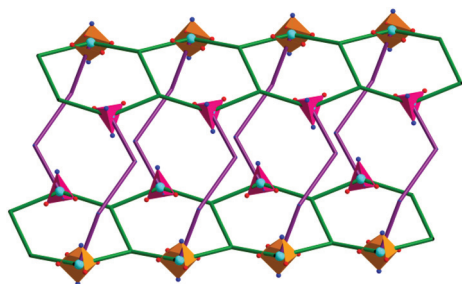


Fig. 8 The presence of two different geometries (tetrahedral and octahedral) of Co(II) centers in compound 3.

developed between two different types of chains at lower temperatures where the molecule is supposed to be in a less-entropy state. Magnetic ordering in three-dimensional metal-organic frameworks, based on carboxylate bridged layers separated by long distances, was reported by Gao and co-workers.^{26a} Long-range ferromagnetic ordering through H-bonding interactions or interactions between the metal centers *via* $\pi\cdots\pi$ stacking was reported by Jana *et al.*^{26b}

XRPD studies and thermogravimetric analysis (TGA)

The phase purity of all the compounds has been ensured by recording the X-ray powder diffraction data. Similar diffraction patterns for the simulated data (calculated from the single crystal data) and the observed data confirm the bulk homogeneity of the crystalline solids (see ESI† section-1 for the PXRD patterns of the compounds 1–3). All major peaks of the experimental PXRD patterns of compounds 1–3 matches well that of stimulated PXRD patterns, confirming the bulk phase purity of the synthesised compounds.

Thermogravimetric plots (TGA) for the crystalline samples of compounds 1–3 were recorded under flowing N_2 gas in the temperature range of 30–1000 °C (Fig. 9). The TGA curves of all

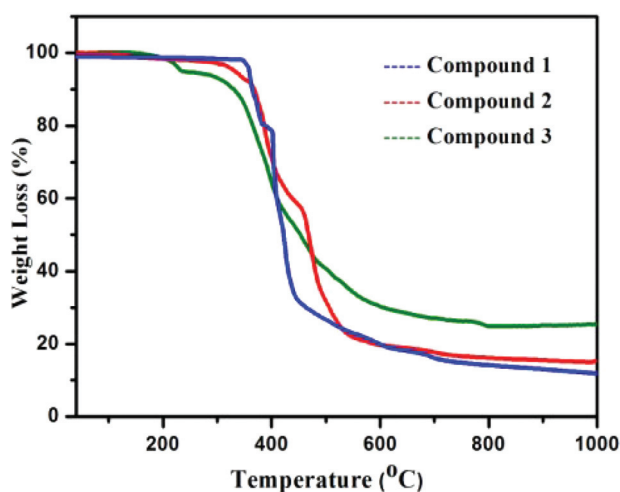


Fig. 9 Thermogravimetric curves of the compounds 1–3.

three compounds demonstrate excellent thermal stability, as no strictly clean weight loss step occurred below 300 °C. Compound 1 undergoes a significant continuous weight loss at 350 °C, reflecting the fact that the lattice px3ampy ligand in the framework is stable up to 350 °C and does not undergo decomposition at low temperatures. This indicates the high stability of the framework involving strong H-bonding interactions with lattice px3ampy. The compound 2 exhibits stability up to 310 °C followed by decomposition with a weight loss up to 1000 °C attributed to the consecutive losses of the $L2^{2-}$ ligand and the px3ampy molecule. The remaining mass (15.30%) at 1000 °C is in accordance with the CoO (calcd 12.71%). The TGA curve of compound 3 consists of two consecutive steps of weight loss. First a very small weight loss (4.95%) has been observed in the temperature range 200–240 °C, which seems to be due to the loss of the lattice water molecules (calcd 4.78%) and then the compound begins to collapse after 320 °C through a sharp weight loss up to 800 °C due to the decomposition of the organic part of the framework. Then, a gradual linear weight loss was observed up to 1000 °C for the remaining mass of the metal oxide.

Conclusion

Among the many influential factors, ligand flexibility and the position of its coordinating groups are important factors in altering the dimensionality and hence, some fundamental properties of the resulting metal-organic framework containing compounds. Based on the concept of employing flexibility in the central position of the skeleton of carboxylate ligands instead of putting flexibility directly to the coordinating groups, three inorganic-organic hybrid compounds are reported in this article. Three different meso-flexible oxo-acid ligands H_2L1 , H_2L2 , H_4L3 , varying the position of the coordination carboxylate groups, have been used along with a long flexible pyridyl ligand px3ampy to synthesise the compounds 1–3. We have demonstrated that the position of the coordinated carboxylate groups on the skeleton of a meso-flexible ligand is very important in the sense that the change in position of the coordinating group from *para* to *meta* on a phenyl ring (with respect to the flexible center of the ligand skeleton) tunes the coordination angle from 116.92° (compound 1, 1D coordination polymer) to 75.94° (compound 2, 3D framework). This compels the $L2^{2-}$ ligand skeleton in compound 2 to adopt a twisted geometry, making the successive paddle wheels orthogonal to each other to induce magnetic anisotropy.

Weak ferromagnetism due to spin canting, also termed “canted antiferromagnetism”, is a fundamental magnetic phenomenon for hybrid inorganic-organic materials. In this study, we successfully obtained two 3D hybrid framework containing compounds exhibiting antiferromagnetic ordering at low temperatures. In the case of compound 2, in spite of the fact that the paddle wheels are separated by long linkers, the tilted arrangement of the $\{Co_2(COO)_4\}$ paddle wheel units in the 3D framework gives rise to local anisotropy and hence a

canting phenomenon has been observed near 25 K. This tilting or an orthogonal arrangement of the successive $\{\text{Co}_2(\text{COO})_4\}$ paddle wheels arises from the twisted ligand skeleton, which in turn arises from the low coordination angle in compound 2.

Compound 3 has been found to experience a very weak magnetic ordering near 9.5 K, probably due to the presence of two geometrically different Co(II) metal centers. Thus we have offered a structure–function relationship through the position of the coordinating groups with respect to the flexible center of the ligand skeleton as well as the coordination angle between the ligand and the metal ion.

Definition of symbols

- τ' Torsion angle $\text{C}_{\text{phenyl}}-\text{O}\cdots\text{O}-\text{C}_{\text{phenyl}}$ in the central part of the acid ligand
- δ' Dihedral angle between the two phenyl rings of the acid ligand
- τ_{tor1} The orientation of the $-\text{CH}_2-\text{NH}-$ bond of one side of the xylylene ring with respect to the $-\text{CH}_2-\text{NH}-$ bond of the other side of the ring along the $-(\text{CH}_2-\text{Ph}-\text{CH}_2)-$ of px3ampy linker
- τ_{tor2} The skewing of two pyridine rings on $-\text{NH}-$ groups through $-(\text{NH}-\text{CH}_2-\text{Ph}-\text{CH}_2-\text{NH})-$ of the px3ampy linker

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