

Modulating topologies and magnetic properties of coordination polymers using 2,2'-bipyridine and 5-aminodiacetic isophthalic acid as ligands†

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We describe a synthetic methodology to prepare 1D coordination polymers using 5-aminodiacetic isophthalic acid (H₄adip) as chelating agent and 2,2'-bipyridine (bpy) as an auxiliary ligand. The function of the latter is to block two coordination sites on the metal(II) centres thus avoiding the formation of 3D networks and directing the assembly into low dimensional networks. The compounds [Co^{II}₂(adip)(bpy)(H₂O)₄]·3H₂O (**1**), [Ni^{II}₂(adip)(bpy)(H₂O)₄]·3H₂O (**2**) and [Cu^{II}(H₂adip)(bpy)] (**3**) were synthesised under hydrothermal reaction conditions with the motivation to investigate spin interactions in these 1D chain structures. We report the structures of the compounds and investigate and model their magnetic properties. The supramolecular structures of **1–3** are characterised by inter- and intra-chain π–π interactions and hydrogen bonding.

Introduction

Coordination networks, metal organic frameworks and other hybrid organic-inorganic materials are attracting an ever increasing scientific interest due to their structural characteristics and their associated intrinsic physicochemical properties which promote applications in the areas of heterogeneous catalysis, gas storage and separation science.¹ Depending on the electronic configurations of the selected metal ions, their bridging modes and ligand donor atoms involved, materials with remarkable magnetic attributes such as magnet-type behaviour, slow relaxation of the magnetization, giant coercivity and hysteresis effects, magnetic bistability or spin crossover can be generated.²

The development of synthetic approaches to coordination networks is of significant interest in order to create advanced materials whose physicochemical attributes can be influenced by both their organic and inorganic components thus offering some advantages to pure organic and inorganic compounds. In recent years, effective concepts to identify topologies and rationalize the synthesis of default structures have been developed.³ However as soon as flexible ligands are employed in the synthesis of hybrid organic-inorganic materials, the prediction of connectivity, topology, packing motifs and their associated physicochemical properties becomes challenging.

We have previously used flexible iminodiacetic acid substituted aromatic ligands to create fascinating types of counter-ion mediated coordination networks and we used the resulting

compounds to template the formation of nanomaterials.⁴ Iminodiacetic acid- or glycine-based ligands are excellent chelating agents and our interest in magnetic properties of molecular materials prompted us to exploit such iminodiacetic acid ligands for the preparation of spin chains or low-dimensional structures that display magnetic interactions.⁵ For this purpose we reacted M^{II} salts (M = Co, Ni, Cu) with 5-aminodiacetic isophthalic acid (H₄adip) under hydrothermal reaction conditions. To gain some degree of control of the assembly process and to limit propagation into three dimensions, we decided to apply 2,2'-bipyridine (bpy) as an additional co-ligand to block two coordination sites of the M^{II} centres (Fig. 1). The successful use of 2,2'-bipyridine or other amines as auxiliary ligands to encourage the formation of low dimensional structures and molecular capsules has been demonstrated by other researchers.⁶ Stimulated by the structure–property relationship of bipyridine complexes, we have previously used related ligands to prepare coordination networks.⁷

Our synthetic efforts resulted in two unprecedented, isostructural compounds [Co^{II}₂(adip)(bpy)(H₂O)₄]·3H₂O (**1**), [Ni^{II}₂(adip)(bpy)(H₂O)₄]·3H₂O (**2**) in which dinuclear secondary building units are further networked to give 1D coordination polymers. Gentle modification of the coordination environment

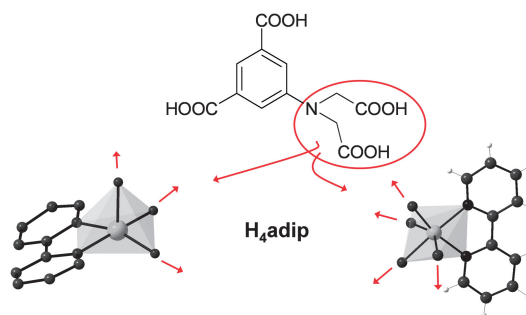


Fig. 1 5-Aminodiacetic isophthalic acid (H₄adip) and the role of 2,2'-bipyridine to block two sites of a square pyramidal or octahedral coordination environment.

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and the use of Cu^{II} ions under the related reaction conditions changes the nature of the 1D chain structure and the associated magnetic properties observed in $[\text{Cu}(\text{H}_2\text{adip})(\text{bpy})]$ (**3**). The packing motifs and supramolecular structures of the compounds **1–3** are further characterised by inter- and intra-chain π - π interactions and hydrogen bonding.

Results and discussion

The structures of $[\text{Co}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**1**) and $[\text{Ni}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**2**)

The isostructural coordination compounds $[\text{Co}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**1**) and $[\text{Ni}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**2**) form reproducibly in moderate yields under hydrothermal conditions in a temperature range between 160–180 °C.

Fig. 2 visualizes the chain structure in **1**. $\text{Co}(1)$ and its symmetry equivalent form a dinuclear secondary building unit

(SBU), in which each metal centre is surrounded by the iminodiacetic acid functionalities of one fully deprotonated adip⁴⁻ ligand and the nitrogen donor atoms of a bipyridine ligand (Fig. 2a). The metal ions are doubly bridged through the carboxylate functions, O(3) and O(3'), of the iminodiacetic acid moieties. The structure results from the symmetry operation of an inversion, with the point of inversion situated in the centre of the dinuclear unit. The coordination environment of $\text{Co}(1)$ is best described as distorted octahedral in which N(1) and the carboxylate O-donors O(1) and O(3) of the iminodiacetic acid functionality occupy *facial* positions. The remaining sites are occupied by O(3') and the nitrogen atoms of a bipyridine ligand. Bipyridine N donors together with the oxygen atoms of the iminodiacetic acid functionality are situated in the equatorial positions whilst the amino group of the adip⁴⁻ ligand and an O-donor from an adjacent adip⁴⁻ ligand occupy the axial positions. These dinuclear SBUs of the structure are linked *via* deprotonated carboxylates of the isophthalic acid moiety of the

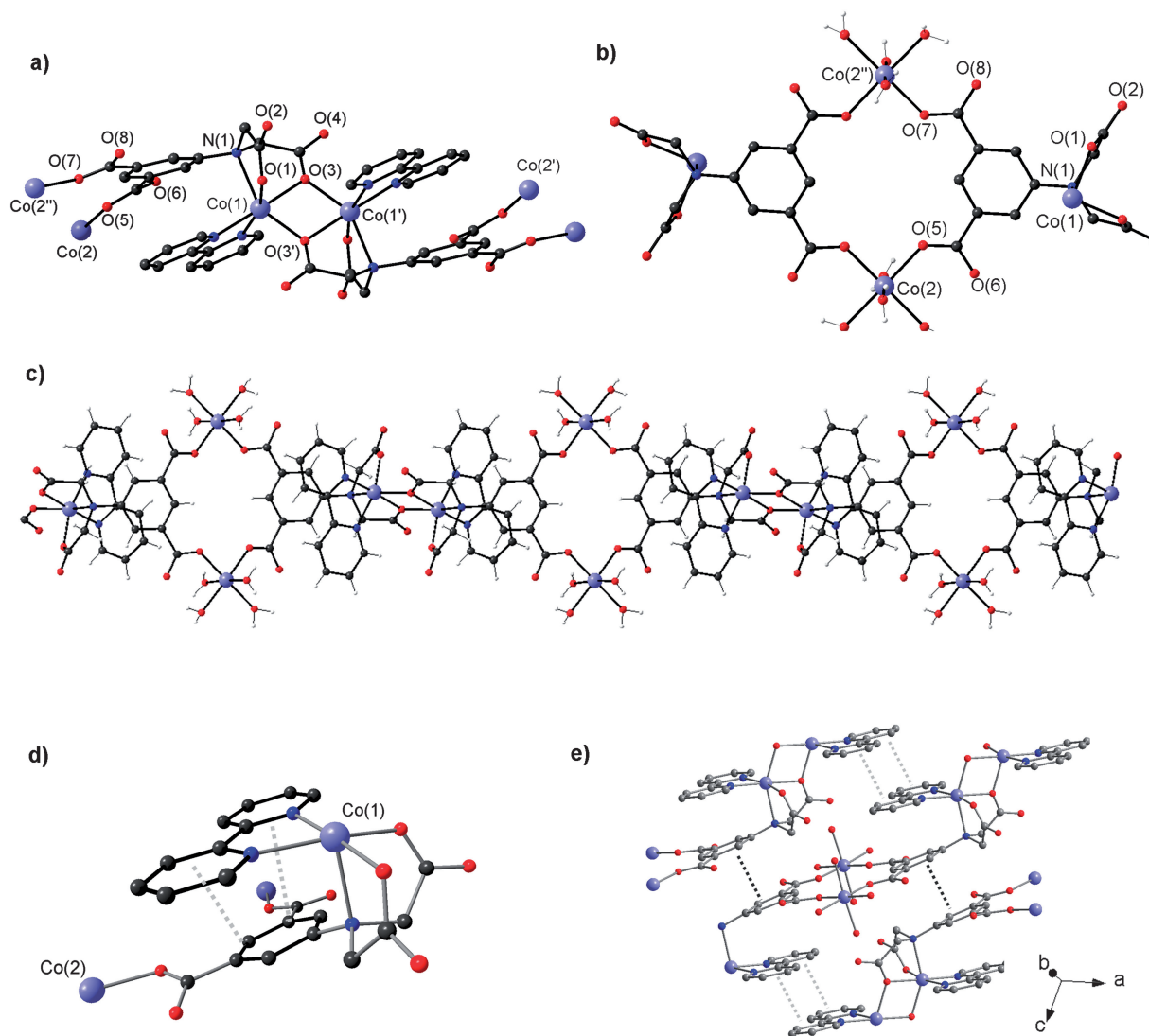
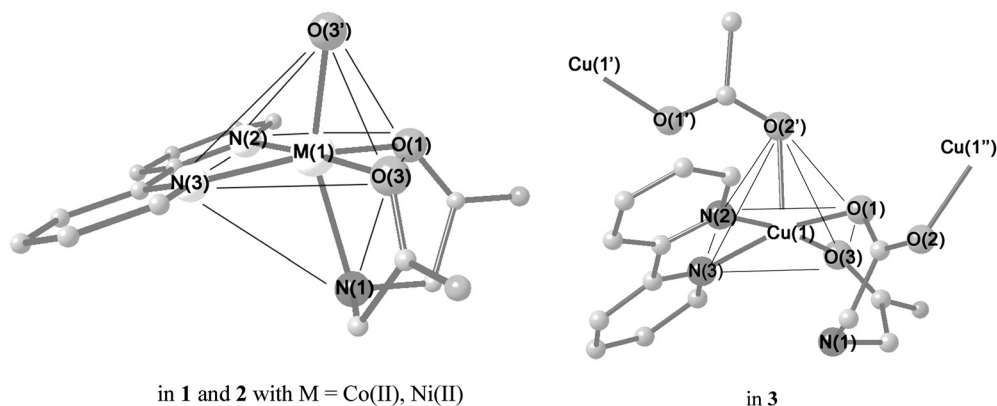


Fig. 2 (a) Dinuclear carboxylate-bridged SBU (H atoms on the organic ligands are omitted for clarity). (b) Macrocyclic motif in **1** (H atoms on the organic ligands are omitted for clarity). (c) One-dimensional structure in **1** and coordination environment of the Co^{II} centres. (d) and (e) Intra and inter-chain π - π interactions in **1**, respectively (H atoms on the organic ligands are omitted for clarity). Colour code: Co light blue, O red, C dark grey, N blue, H white. Symmetry operators: ' = $-1 - x, -1 - y, 1 - z$; '' = $-x, -1 - y, -z$.

Table 1 Selected bond length and angles in **1–3**

Atoms	Distance (Å)/Angle (°) in 1	Distance (Å)/Angle (°) in 2	Distance (Å)/Angle (°) in 3
M(1)–O(1)	2.0163(15)	2.0089(14)	1.9955(13)
M(1)–O(3)	2.1107(14)	2.0762(14)	1.9489(12)
M(1)–O(3')	2.0787(14)	2.0578(14)	—
M(1)–O(2')	—	—	2.1775(12)
M(1)–M(1')	3.291(1)	3.256(3)	—
M(1)–N(1)	2.3177(17)	2.2516(17)	2.6087(11)
M(1)–N(2)	2.1068(17)	2.0455(17)	2.0148(15)
M(1)–N(3)	2.1090(17)	2.0708(17)	2.0049(12)
M(2)–O(5)	2.0197(15)	2.0326(15)	—
M(2)–O(7'')	2.0645(15)	2.0282(15)	—
M(2)–H ₂ O	2.0706(15)–2.1357(16)	2.0454(18)–2.0882(16)	—
N(1)–M(1)–O(3') (N(2) in 3)	149.60(6)	151.23(6)	—
O(1)–M(1)–O(3)	92.12(6)	90.20(6)	—
M(1)–O(3)–M(1')	103.56(6)	103.93(6)	—
Ring _{Bpy} –Ring _{Tereph} –intrachain	3.991(3)	3.935(6)	3.509(1)
Ring _{Bpy} –Ring _{Bpy}	3.862(2)	3.901(4)	—
Ring _{Tereph} –Ring _{Tereph}	3.711(2)	3.735(5)	3.740(2)
O(7)–O(4)	—	—	2.502(1)
O(5)–O(8)	—	—	2.617(1)

adip⁴⁻ ligand to Co(2) and symmetry related Co ions to give a 1-D coordination polymer. As visualized in Fig. 2b, two partially hydrated Co ions, with distorted octahedral coordination environment, mediate between two dinuclear SBUs through *cis* coordinated carboxylates resulting in a 16-membered macrocyclic structural motif. The supramolecular structure of **1** is further characterised by π – π interactions. Within the 1-D polymer, intramolecular π – π stacking takes place between the phenyl ring of the adip⁴⁻ ligand and the bipyridine rings. Weak intermolecular π – π stacking involving both adip⁴⁻–adip⁴⁻ and the bpy–bpy interactions further link the 1D strands into 2D sheets (Fig. 2d and e). Symmetry inverted arrangements of the ligand moieties in these π – π pairs maximise the electron density contribution from both ring systems and avoid an eclipsed conformation of nitrogen hetero atoms.

[Ni^{II}₂(adip)(bpy)(H₂O)₄]·3H₂O (**2**) is isostructural to **1**. Differences in the coordination geometry arise from the slightly decreased ionic radius of the Ni^{II} ion and slightly different occupancies of lattice water molecules. Table 1 highlights these geometrical differences in **1** and **2** and gives an overview of the important bond distances and angles. The structures of **1** and **2** underline the chelating ability of the iminodiacetate moiety of the adip⁴⁻ ligand and demonstrate that the carboxylates attached to the aromatic ring system promote the linkage of the subunits into

1D structures. In the absence of auxiliary ligands which block some of the coordination sites of Co(II), Cu(II) and Zn(II) ions, complicated and almost unpredictable 1D tubular, 2D layered or 3D structures result in which the carboxylate groups act as mono- and bi-dentate, bridging and non-bridging functionalities.^{5a}

The magnetic properties of [Co^{II}₂(adip)(bpy)(H₂O)₄]·3H₂O (**1**) and [Ni^{II}₂(adip)(bpy)(H₂O)₄]·3H₂O (**2**)

The temperature dependences of the magnetic susceptibility (normalized per two formula units) of **1** and **2** were measured at 1000 Oe. The room temperature χT values of 12.7 and 5.0 cm³ K mol⁻¹ for **1** and **2** respectively, are in good agreement with the presence of four Co^{II} ions ($S = 3/2$ spins with a Curie constant around 3.2 cm³ K mol⁻¹)⁶ and four Ni^{II} ions ($S = 1$ $C = 1.25$ cm³ K mol⁻¹ expected for $g = 2.2$). On lowering the temperature, the χT product continuously decreases. The values reach a minimum of 4.3 cm³ K mol⁻¹ at 1.8 K for **1**, whilst the χT product of **2** reaches an initial plateau of 2.5 cm³ K mol⁻¹ at *ca.* 5 K before dropping to 1.4 cm³ K mol⁻¹ at 1.8 K.

For **1**, the decrease of the χT product is a result of antiferromagnetic interactions within the dinuclear SBUs and the spin–orbit coupling which is characteristic for Co^{II} systems. This latter effect results in the splitting of the energy levels arising from the

$^4T_{1g}$ ground term that stabilises a doublet ground state at low temperatures.^{8a} The temperature dependent susceptibility values for such Co^{II} complexes are usually not theoretically reproducible as no simple analytical expression can be applied to model both, the magnetic exchange interactions and the complex intrinsic magnetic properties of the Co^{II} sites. The field dependence of the magnetization of **1**, measured at 1.8 K (Inset Fig. 3a), reveals initial saturation effects at *ca.* $5.3 \mu_{\text{B}}$. Above 3 T, the magnetization increases again to reach a value of $7.3 \mu_{\text{B}}$ and resulting in an “S shape” feature of the magnetization curve. This phenomenon most likely originates from field induced population of low lying excited states in the system and thus highlights the presence of weak antiferromagnetic interactions. The observed behaviour is further related to a significant magnetic anisotropy of the Co^{II} metal ions.

In contrast to **1**, the observed magnetic properties of **2** can be fully modelled. The decrease of the χT product on lowering the temperature is clearly the result of intra-dimer exchange interactions between the $\mu\text{-COO}^-$, doubly bridged Ni^{II} centres. Below 4 K, weaker effects, like the magnetic anisotropy of the Ni^{II} ions or weak antiferromagnetic interactions, become apparent and explain the decrease of the χT product (Fig. 3b).

In agreement with the structural motif of a 1D chain *i.e.* the presence of two isolated Ni^{II} centres and two coupled $S = 1$ Ni^{II} ions, the Heisenberg spin Hamiltonian of the dinuclear motif can be written as follows: $H = -2JS_{\text{Ni}(1)}S_{\text{Ni}(2)}$; where J is the exchange interactions within the dinuclear $\text{Ni}(\text{II})$ SBU; S_i the

spin operators for each centres. The application of the van Vleck equation to the Kambe's vector coupling scheme allows a determination of the low field analytical expression of the magnetic susceptibility.^{8–11} As seen in Fig. 3b, this model which includes the isolated $\text{Ni}(2)$ sites as a paramagnetic Curie component, allowed us to reproduce the experimental χT vs T data from 300 to 4 K very well. The best fit was achieved with the following parameters: $J/k_{\text{B}} = -15.1(2)$ K and $g_{\text{av}} = 2.23(5)$. The sign of the magnetic interaction implies that the dinuclear Ni unit possesses an $S_{\text{T}} = 0$ spin ground state. Hence the magnetic behaviour of **2** below 4 K is characterised by two isolated Ni centres and a diamagnetic dinuclear SBU. The field dependence of the magnetization at 1.8 K can be very well fitted by the sum of two $S = 1$ Brillouin functions and reveals a saturation value of $4.3 \mu_{\text{B}}$ at 7 T. This behaviour confirms the presence of two isolated $S = 1$ $\text{Ni}(1)$ sites. In agreement with the M vs. H data at 1.8 K that does not show any sign of slow relaxation *i.e.* hysteresis effect, the ac susceptibility in zero dc field shows a complete absence of out-of-phase component above 1.8 K.

The structure of $[\text{Cu}(\text{H}_2\text{adip})(\text{bpy})]$ (**3**)

When the outlined hydrothermal preparation method is applied to copper salts, a 1D coordination polymer $[\text{Cu}(\text{H}_2\text{adip})(\text{bpy})]$ (**3**) forms, which displays structural similarities to **1** and **2**. As opposed to **1** and **2**, the 1D chain structure of **3** is comprised from mononuclear sub-units. The coordination polyhedron of the Cu^{II} ion is best described as a square pyramid. In this polyhedron the O-donors O(1) and O(3) of the carboxylate functionalities of the iminodiacetic acid group and the N-donors of the bipyridine ligand are situated in the square plane of the pyramid. The coordination environment of the Cu^{II} centre is completed by a symmetry generated carboxylate O-donor O(2') of an iminodiacetate functionality of another symmetry generated $\text{H}_2\text{adip}^{2-}$ ligand. The symmetry equivalents are generated by the operation of a 2_1 screw axis which runs in the direction of the crystallographic b -axis and which links the copper centres through coordination bonds into a 1D coordination polymer (Fig. 4).

The N-donor of the iminodiacetic acid moiety interacts fairly weakly with the Cu centre leading to a $\text{Cu-N}(1)$ distance of $2.608(11)$ Å, thus being considerably longer than expected for Cu^{II} coordination bonds. As for **1** and **2** the aromatic ring systems of the H_2adip ligand and the bipyridine moieties are involved in an intra-chain $\pi\text{-}\pi$ stacking interaction ($3.509(1)$ Å mean distance between aromatic ring systems). The packing motif of the 1D chain in the crystal structure is shown in Fig. 5. Parallel aligned strands interdigitate with alternating protrusion of the isophthalic acid moiety of the $\text{H}_2\text{adip}^{2-}$ ligand into the grooves of adjacent polymers and resulting in an average distance between two $\text{H}_2\text{adip}^{2-}$ ring planes of is $3.740(2)$ Å. The two non-coordinating isophthalic acid functionalities of the aromatic ring system of the H_2adip ligand remain protonated. Their H-atoms were located in the Fourier difference map and their coordinates were refined; these H-atoms are engaged in two different type of hydrogen bonds which network the strands parallel to the (011) plane as illustrated by Fig. 5c and d. A relatively strong interaction is observed between one of the isophthalic acid functionalities and a carboxylic group of an

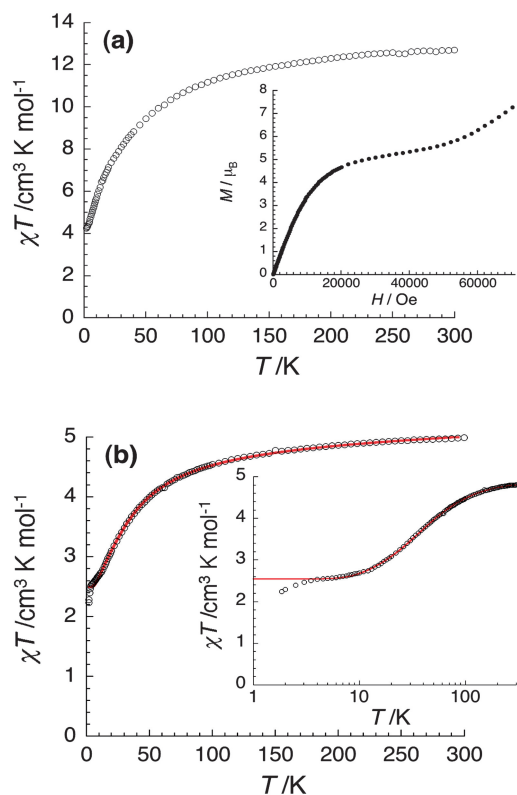


Fig. 3 Temperature dependence of the magnetic susceptibility (normalized per four metal ions) measured at 1000 Oe for **1** (a) and **2** (b). Inset of Fig. 3a, the field dependence of the magnetization at 1.8 K is shown. The red solid line on Fig. 3b is the best fit obtained for **2** (see text).

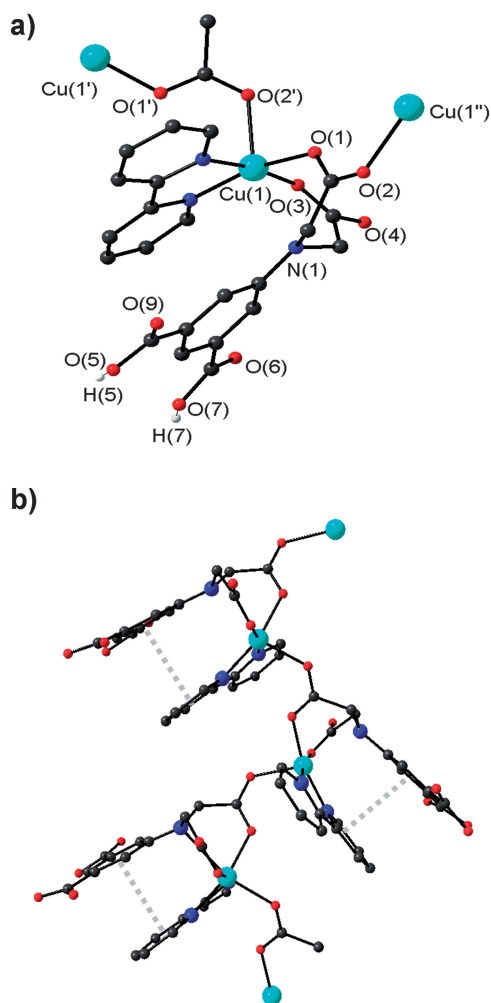


Fig. 4 (a) Coordination environment of the Cu^{II} ion in **3**. (b) 1D chain structure and intra chain π - π interactions in **3**. H atoms, bound to the carbon atoms, of the organic ligands are omitted for clarity. Colour code: Cu turquoise, O red, C dark grey, N blue, H white. Symmetry operators: ' = $-x, -0.5 + y, 0.5 - z$; " = $-x, 0.5 + y, 0.5 - z$.

iminodiacetic acid residue of a neighbouring chain resulting in an O(7)⋯O(4') bond distance of 2.502(1) Å. The second type of H-bond involves two isophthalic acid functionalities of adjacent polymers leading to a O(5)⋯O(8') bond length of 2.617(1) Å.

The magnetic properties of [Cu(H₂adip)(bpy)] (**3**)

The magnetic susceptibility of **3** was studied from 300 to 1.8 K at 1000 Oe. The χT vs T plot (Fig. 6) is constant between 300 and 20 K at 0.41 cm³ K mol⁻¹ and then increases slowly at lower temperature to reach 0.44 cm³ K mol⁻¹ at 1.8 K. This feature is indicative of a paramagnetic behaviour with weak ferromagnetic interactions. Fitting the data to the Curie-Weiss law leads to $C = 0.42(1)$ cm³ K mol⁻¹ and $\theta = +0.11(1)$ K. The Curie constant obtained is in good agreement with the expected value of one independent Cu^{II} $S = 1/2$ centre with a g factor of 2.12. The 1D structure in **3** can be viewed as a regular chain with single *syn-anti axial-equatorial* carboxylate bridges between Cu(II) metal ions (Fig. 4). Based on this structural analysis, a chain model of

ferromagnetically coupled $S = 1/2$ Heisenberg spins¹² ($H = -2J \sum_i S_i S_{i+1}$) was used to fit the magnetic susceptibility and to obtain the magnetic interaction, J , between the Cu^{II} ions. The interaction parameter obtained, $J/k_B = +0.04(1)$ K (with $g = 2.11(2)$), is in good agreement with other 1D chain structures or molecular complexes with similar single *syn-anti axial-equatorial* carboxylate bridging mode.¹³ For example, the ferromagnetic nature of this type of interaction has been well discussed for malonate-based copper(II) compounds.^{13c}

Conclusions

In summary, we report the synthesis, structure and magnetic properties of three unprecedented coordination polymers. Our synthetic approach takes advantage of 2,2'-bipyridine as an auxiliary ligand that blocks two sites of a distorted octahedral coordination environment in the Ni^{II} and Co^{II} compounds **1** and **2** or of a square pyramidal environment in the Cu^{II} compound **3**. The use of the 5-amino isophthalic acid ligand, that maintains a strong chelating ability through its flexible iminodiacetic acid moiety and bridging ability through its isophthalic acid functions, results in novel chain structures.

The supramolecular structures of the coordination compounds are characterised by intra- and inter-chain π - π interactions and hydrogen bonds. The observed magnetic properties of **1** and **2** result from antiferromagnetic interactions within the dinuclear carboxylate-bridged SBUs and paramagnetic Curie behaviour of the partially hydrated transition metal ions that link the dinuclear units into 1D coordination polymers. In the case of compound **2** we successfully reproduced quantitatively the temperature dependence of the susceptibility. The magnetic properties of **3** were successfully modelled using a 1D chain model that considers weak ferromagnetic interactions between the Cu^{II} centres.

Experimental

Single crystal analyses were performed at 150 K with a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A full sphere of data was obtained using the ω scan method. Data was collected, processed, and corrected for Lorentz and polarization effects using SMART and SAINT-NT software. The structures were solved using direct methods and refined with the SHELXTL program package. The crystallographic data for **1-3** are given in Table 2.

The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL housed at the Centre de Recherche Paul Pascal. This magnetometer operates between 1.8 and 300 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on a polycrystalline samples of 9.44, 9.52 and 4.74 mg for **1**, **2** and **3** compounds. The magnetic data were corrected for the sample holder and the diamagnetic contributions. Before any measurement, the samples have been checked for the presence of ferromagnetic impurities by measuring the magnetization as a function of the field at 100 K. For pure paramagnetic or diamagnetic systems, a perfect straight line is expected and is

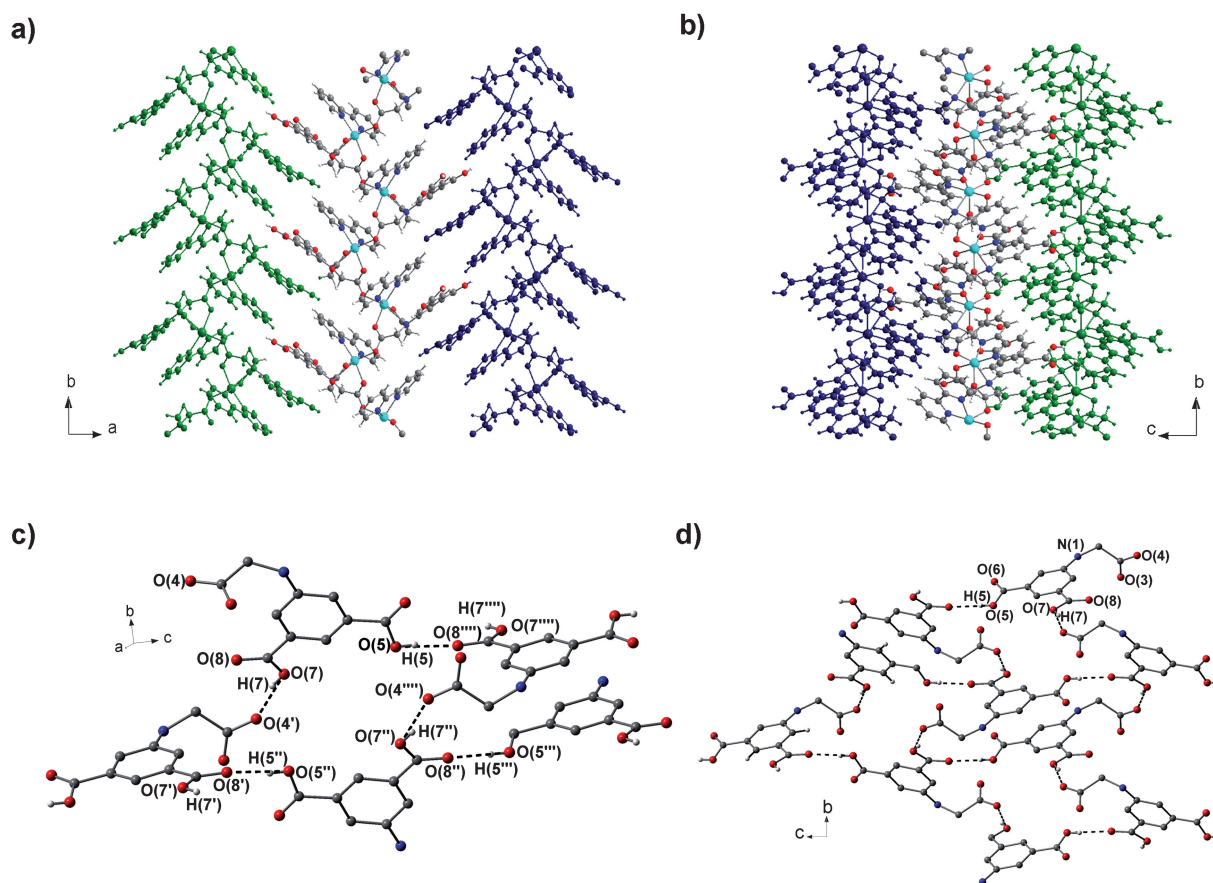


Fig. 5 a) and b) Arrangement of the chain structure in **3**. (a) View in the direction of the crystallographic *c* axis. (b) View in the direction of the crystallographic *a* axis. (c) Hydrogen bond motif in **3**. (d) H-bonded network parallel to the *bc* plane (H bonds indicated by black intersected lines). Symmetry operators: $' = 1 - x, -0.5 + y, 0.5 - z$, $'' = 1 - x, -y, 1 - z$, $''' = 1 - x, -0.5 + y, 1.5 - z$, $'''' = x, 0.5 - y, 0.5 + z$.

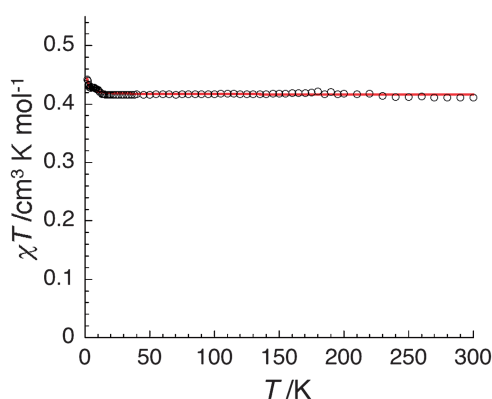


Fig. 6 Temperature dependence of the magnetic susceptibility (normalized per one Cu^{II}) measured at 1000 Oe for **3**. The red solid line is the best fit obtained for **3** with the $S = \frac{1}{2}$ chain model described in the text.

observed for these compounds indicating the absence of any ferromagnetic impurities.

Synthesis of 5-aminodiacetic isophthalic acid, H_4adip

The organic ligand was prepared according to a literature method which involves a condensation reaction between chloroacetic acid and 5-aminoisophthalic acid.^{5a}

Synthesis of $[\text{Co}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**1**)

The monosodium salt of H_4adip (0.091 g, 0.285 mmol), cobalt acetate tetrahydrate (0.075 g, 0.303 mmol), 2,2'-bipyridine (0.036 g, 0.214 mmol) and 10 ml of de-ionised water were placed inside a 25 ml-Teflon lined autoclave. The cloudy red reaction mixture was initially stirred. The autoclave was sealed and heated for 60 h at 160 °C. The autoclave was allowed to cool to room temperature for 2–3 h. The resulting reaction mixture contained crystalline small red plates of **1** suitable for single X-ray analysis. Yield: 61%; IR (KBr) ν_{max} cm^{-1} : 3248(br), 1607(vs), 1550(vs), 1477(w), 1446(m), 1404(m), 1380(vs), 1286(w), 1249(w), 1224(w), 1180(w), 1161(w), 1131(w), 1063(w), 1024(w), 984(w), 963(w), 984(w), 892(w), 783(m), 767(m), 736(m), 634(w). CHN analysis for **1**: Expected: C, 38.11%; H, 4.22%; N, 6.06%. Found: C, 37.89%; H, 4.20%; N, 7.19%.

Synthesis of $[\text{Ni}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**2**)

Synthesis as for **1** but at 180 °C using nickel(II) acetate tetrahydrate (0.075 g, 0.303 mmol) as starting materials. **2** crystallises as blue/green plates. Yield: 54%; IR (KBr) ν_{max} cm^{-1} : 3502(w), 3435(w), 3059(br), 2460(w), 1919(w), 1673(m), 1601(vs), 1488(m), 1449(m), 1404(m), 1355(m), 1339(w), 1294(m), 1263(m), 1250(m), 1190(w), 1130(w), 1099(w), 1081(w), 1037(w),

Table 2 Crystallographic data for the compounds 1–3

Compound	1	2	3
Empirical formula	C ₂₂ H ₂₉ Co ₂ N ₃ O ₁₅	C ₂₂ H ₂₉ N ₃ Ni ₂ O ₁₅	C ₂₂ H ₁₇ CuN ₃ O ₈
Temp. (K)	150	150	150
Crystal colour/shape	Pink plates	Green plates	Green–blue plates
Crystal size/Å ³	0.2 × 0.15 × 0.15	0.2 × 0.2 × 0.15	0.25 × 0.15 × 0.1
Molecular mass/g mol ⁻¹	693.34	692.90	514.93
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> /Å	10.1987(7)	10.0968(10)	14.0403(8)
<i>b</i> /Å	12.1765(8)	12.1101(12)	9.0493(5)
<i>c</i> /Å	12.6676(8)	12.5860(13)	17.2277(10)
α /°	103.8970(10)	103.193(2)	90
β /°	105.9730(10)	106.046(2)	106.9620(10)
γ /°	107.5480(10)	107.178(2)	90
<i>V</i> /Å ³	1349.43(15)	1330.1(2)	2093.6(2)
<i>Z</i>	2	2	4
Density/Mg m ⁻³	1.706	1.730	1.634
Absorp. coef./mm ⁻¹	1.310	1.497	1.101
<i>F</i> (000)	712	716	1052
$2\theta_{\max}$ /°	56.6	50.5	51
Reflections collected	18836	14632	22967
Independent reflections	6713 [<i>R</i> (int) = 0.0257]	4816 [<i>R</i> (int) = 0.0555]	3895 [<i>R</i> (int) = 0.0549]
Parameters	427	435	313
<i>S</i> on <i>F</i> ²	1.073	1.063	1.120
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0370, 0.1061	0.0285, 0.0775	0.0271, 0.0766
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0407, 0.1082	0.0312, 0.0787	0.0315, 0.0778

977(w), 961(w), 934(w), 910(w), 897(w), 850(w), 809(w), 796(m), 768(w), 744(w), 717(w). CHN analysis for **2**: Expected: C, 38.14%; H, 4.22%; N, 6.06%. Found: C, 37.84%; H, 3.86%; N, 5.88%.

Synthesis of [Cu(H₂adip)(bpy)] (**3**)

The monosodium salt of H₄adip (0.100 g, 0.365 mmol), copper nitrate trihydrate (0.081 g, 0.365 mmol), 2,2'-bipyridine (0.053 g, 0.365 mmol) and 8 ml of de-ionised water were placed inside a 25 ml Teflon-lined autoclave. The cloudy green/blue reaction mixture was initially stirred. The autoclave was sealed and heated for 17 h at 140 °C. The autoclave was allowed to cool to room temperature for 2–3 h. The resulting reaction mixture contained crystalline green rectangular plates suitable for single X-ray analysis. Yield: 49%; IR (KBr) ν_{\max} cm⁻¹: 3193(w), 2931(w), 2454(w), 1920(w), 1726(s), 1677(m), 1592(s), 1577(m), 1495(w), 1445(w), 1404(m), 1389(m), 1352(w), 1310(m), 1280(m), 1246(s), 1226(s), 1198(m), 1169(m), 1150(m), 1102(w), 1064(w), 1031(w), 996(w), 968(w), 908(w), 872(w), 811(w), 773(s), 757(s), 732(m), 666(m). CHN analysis for **3**: Expected: C, 51.31%; H, 3.33%; N, 8.16%. Found: C, 50.84%; H, 3.43%; N, 8.00%.

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