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Expanding the 2,2′-bipyrimidine bridged 1D homonuclear coordination polymers family: [M(II)bpymCl2] (M=Fe, Co) magnetic and structural characterization

Pablo Alborés* and Eva Rentschler*

We report the synthesis, structural characterization, and magnetic properties of two new members M=Fe(II), Co(II) of the [M(bpym)Cl2]n 1D coordination polymers family.
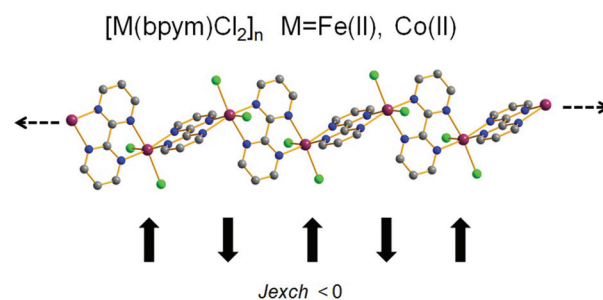
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Expanding the 2,2′-bipyrimidine bridged 1D homonuclear coordination polymers family: [M^II bpymCl_2] (M=Fe, Co) magnetic and structural characterization†

Pablo Alborés*[a,b] and Eva Rentschler*[a]

One pot reaction of hydrated chloride salts of Fe(II) and Co(II) with stoichiometric amounts of 2,2′-bipyrimidine (bpym) in a methanol–acetonitrile mixture afforded the corresponding 1D homonuclear coordination polymers, $[\mu\text{-(bpym)}MCl_2]_n$. Crystal structures of both complexes are isomorphous in the highly symmetric orthorhombic space group *Fddd*. The 1D coordination polymers are composed of almost orthogonal alternating bipyrimidine bridges linking the $\{MCl_2\}$ units. The magnetic behaviour of the Fe(II) compound can be well understood as a uniform $S = 2$ chain with an antiferromagnetic exchange interaction between metal ion sites. In the case of the Co(II) ion, also an antiferromagnetic interaction is operative along the uniform chain, while at low temperatures a long range-ordering is observed due to spin canting originating from the anisotropic behaviour of the Co(II) lowest energy Kramers doublets.

Introduction

Low-dimensional magnetic coordination polymers have attracted much attention since the discovery of anisotropic systems with fascinating physical properties, such as single-molecule magnets and single-chain magnets.[1] In order to design 0D or 1D molecule-based magnetic materials, with well defined and tuneable properties, it is important to choose appropriate bridging ligands able to transmit effectively the exchange interactions between the paramagnetic centers. Among possible bridging units, small organic molecules with coordinating donor atoms are especially interesting because of their enormous synthetic versatility. Focusing on 1D coordination polymers, a common strategy for their preparation so far has been to systematically block several coordination sites of metal ions with terminal ligands and to link them through

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†Electronic supplementary information (ESI) available: Single-crystal X-ray crystallographic information files (CIF) for **1** and **2**, Tables S1 and S2: main bond distances and angles of **1** and **2**; Fig. S1 and S2: molecular representation of the short contact interactions in the short packing of **1**; Fig. S3: χ_m *vs. T* plot in the range 2–80 K at 0.1 T of compound **1**. CCDC 928716 and 928717. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50691f

small ligands coordinating to the remaining vacancies. On the other hand, the spontaneous self-assembly of such polymer compounds upon mixing the starting metal ion source and appropriate ligands becomes a widespread but not a strictly rational alternative.[2]

The tetradentate 2,2′-bipyrimidine (bpym) ligand has been extensively employed due to its remarkable ability to mediate exchange interaction between transition metal ions[3–6] and it should easily allow growing of homometallic 1D chains.

1D polymers of Co(II) ions are particularly interesting due to the high spin ground state anisotropy of this ion which may lead to spin-canting or single chain magnetic properties depending, among other factors, on the type of exchange interaction operative between the constituent Co(II) ions.

With this background, we decided to explore the reaction between simple Fe(II) and Co(II) chloride salts and 2,2′-bipyrimidine in organic media. To the best of our knowledge, up to this report, the only known neutral homometallic 3d metal chloride polymerized through this ligand was the Mn(II) derivative.[5] In this work we are reporting the structural and magnetic characterization of two new derivatives of this neutral $[M^{II}bpymCl_2]_n$ family, the Fe(II) and Co(II) 1D coordination polymers.

Results and discussion

Synthesis and crystal structure

One pot reaction of simple hydrated chloride salts of Fe(II) and Co(II) with stoichiometric amounts of the potentially bridging

ligand 2,2′-bipyrimidine (bpym) in a 1 : 1 methanol–acetonitrile mixture afforded in high yield and high purity the corresponding 1D homonuclear coordination polymers, [μ-(bpym)-FeCl$_2$]$_n$ (**1**) and [μ-(bpym)CoCl$_2$]$_n$ (**2**), respectively. Both chain compounds are built from the direct stringing of the MCl$_2$ motif with the bpym ligand. It is important to note that the solvent mixture becomes the key factor to obtain crystalline compounds. Employing pure methanol or pure acetonitrile immediately affords insoluble amorphous solids. The only previously reported member of this family, [μ-(bpym)MnCl$_2$]$_n$, was prepared in a similar approach but employing water as a reaction solvent.[5]

Both compounds, **1** and **2**, are crystallizing isomorphous in the highly symmetric orthorhombic space group *Fddd*. The molecular structures will therefore be discussed jointly. The crystal structure shows isolated 1D chains running parallel to the $\overline{ab}$ plane (closest inter-chain M⋯M distances: 7.327(2) Å Fe⋯Fe in **1** and 7.374(1) Å Co⋯Co in **2**), and alternating their growing axis orientation with an angle of exactly 90° among them. The solvent molecules fill the space between chains. The acetonitrile is arranged in a complete inter-chain channel (Fig. 1). The methanol molecules are hydrogen-bond interacting with chloride ligands of neighbouring chains while the acetonitrile molecules exhibit N⋯H–C interactions[7] with bipyrimidine rings (see ESI†).

The 1D coordination polymers themselves are composed of almost orthogonal (contiguous bipyrimidine planes comprise a dihedral angle of *ca.* 86°) neighbouring alternating bipyrimidine bridges linking the {MCl$_2$} units. This affords a ladder-type arrangement with M–M–M angles of *ca.* 118° in **1** and *ca.* 122° in **2** and intra-chain M–M distances of 5.938(1) Å in **1** and 5.797(1) Å in **2** (Fig. 2 and Table 2). The presence of a crystallographically imposed inversion center in the middle of {M–bpym–M} motifs leaves the coordinated chloride ligands alternating in 180° at both sides along the chain. Additionally, due to a two-fold rotation axis a unique M–Cl bond distance is found with the following values: 2.3771(13) Å in **1**, and 2.357(2) Å in **2**. In spite of the equivalency of the chloride ligands, asymmetry in the two M–N distances is observed: Fe(1)–N(1) = 2.215(4) Å and Fe(1)–N(2) = 2.249(4) Å; and Co(1)–N(1) = 2.161(5) Å, Co(1)–N(2) = 2.194(6) Å. All M–N and M–Cl bond distance values are in agreement with the reported ones in closely related compounds. For example (μ-bpym)-[(bpym)-Fe^{II}Cl$_2$]$_2$[8] exhibits Fe–Cl distances of 2.402 Å and 2.390 Å
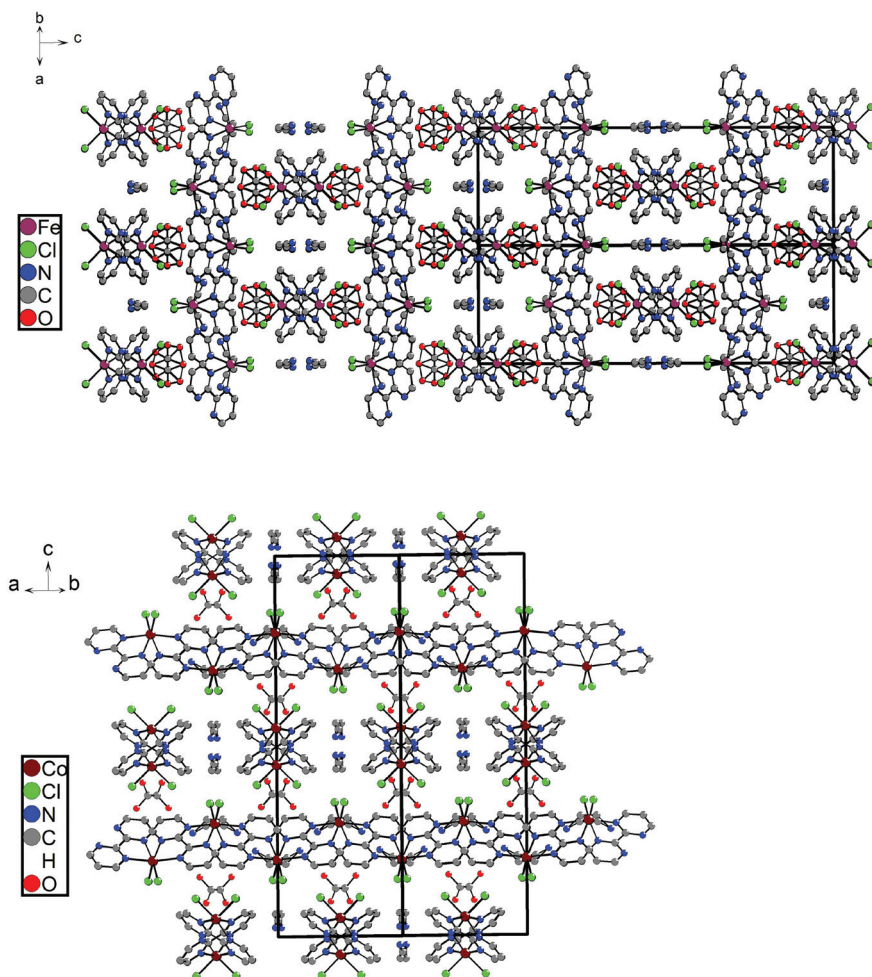

Fig. 1 Crystalpacking molecular representation of coordination polymers **1** (top) and **2** (bottom). Hydrogen atoms are omitted for the sake of clarity.
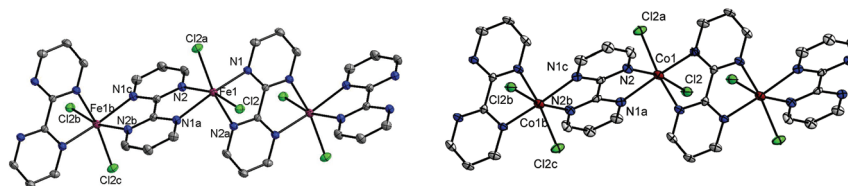
Fig. 2 Ellipsoid representation (at 30% probability level) of three repetitive units of coordination polymers **1** (left) and **2** (right). Hydrogen atoms are omitted for the sake of clarity. Symmetry codes: a: $0.25 - x$, $0.25 - y$, z; b: $0.5 - x$, $-y$, $0.5 - z$; c: $0.25 + x$, $-0.25 + y$, $0.5 - z$.

and Fe–N$_{bridging\ bpym}$ distances of 2.224 Å and 2.271 Å while the chain compound $[Fe^{II}(bpym)(SCN)_2]_n$[9] shows Fe–N bond distances ranging between 2.217 Å and 2.266 Å. For the cobalt compound **2**, the Co–Cl bond distances 2.376 Å and 2.399 Å compare well with those found for *cis*-Co^{II}(bpym)$_2$Cl$_2$[10] while Co–N bond distances range between 2.139 Å and 2.167 Å. The cationic chain $[Co^{II}(bpym)(H_2O)_2]^{2+}_n$[11] exhibits Co–N bond distances between 2.166 Å and 2.177 Å.

It should be noted that the reported bipyrimidine bridged 1D coordination polymer, $[\mu\text{-}(bpym)MnCl_2]_n$, was crystallized from water affording a monoclinic cell.[5] Hence, there is no isomorphism with the structures of $[\mu\text{-}(bpym)FeCl_2]_n$ (**1**) and $[\mu\text{-}(bpym)CoCl_2]_n$ (**2**).

To our knowledge, there are only eight structurally characterized 1D regular homonuclear coordination polymers $[\mu\text{-}(bpym)ML_2]_n$ systems for 3d transition metals,[4,5,12] with only one Fe example[9] and one Co example.[11] With these new examples reported herein, the $[\mu\text{-}(bpym)MCl_2]_n$ family becomes the biggest of them summing up just three members.

Magnetic properties

DC magnetic susceptibility of the 1D coordination polymers **1** and **2** was recorded in the temperature range 2–300 K under an applied field of 0.1 T (Fig. 3). In the case of compound **1**, the $\chi_m T$ value at 300 K of 3.07 cm^3 K mol^{-1} is in close agreement with the expected value of 3.00 cm^3 K mol^{-1} for isolated high spin Fe(II) ions (g = 2.00). The almost temperature independent value for $\chi_m T$ with lowering the temperature down to 100 K is followed by a continuous decline upon further cooling down to 2 K, indicative of weak anti-ferromagnetic interaction between neighbouring Fe(II) ions, further confirmed by the maximum observed at *ca.* 20 K in the χ_m *vs.* T plot. At 10 K a plateau of 0.058 cm^3 mol^{-1} is reached before χ_m drops again to reach a second plateau at 2 K. For compound **2**, the $\chi_m T$ value at 300 K of 2.59 cm^3 K mol^{-1} is well above the expected value of 1.875 cm^3 K mol^{-1} for an isolated high spin Co(II) ion (g = 2.00). If first order orbital contributions to the spin ground state are considered a g value of 2.35 ($\chi_m T$ = 2.59 cm^3 K mol^{-1} for an isolated HS Co(II)) is not unusual for this particular ion, although in this case exhibiting a high degree of quenching.[15] With decreasing temperatures below 100 K the $\chi_m T$ values for **2** decrease considerably, indicating a weak anti-ferromagnetic interaction between neighbouring Co(II) ions. In the χ_m *vs.* T plot a maximum is observed at 18 K. However, upon further
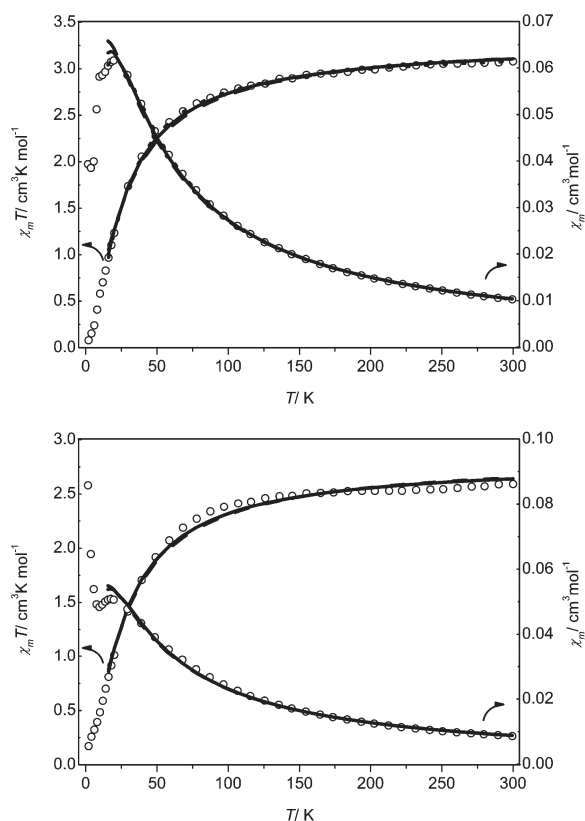

Fig. 3 $\chi_m T$ *vs.* T and χ_m *vs.* T plots in the range 2–300 K at 0.1 T of compounds **1** (top) and **2** (bottom). Open circles: experimental data. Full line: best fittings with the Fisher model; dashed line: best fittings with the ring model; dotted line (only for **1**): best fitting including a ZFS term. See text for fitting details.

cooling, a sharp increase in $\chi_m T$ is observed close to 10 K suggesting collective long-range effects. The low temperature $1/\chi_m$ *vs.* T plot profile (Fig. 4) excludes a simple explanation based on some paramagnetic impurity and supports the long-range interaction hypothesis.

The chain nature of complexes **1** and **2** does not allow employing a full spin Hamiltonian for the simulation of the magnetic behaviour. Furthermore, in the case of compound **2**, the strong anisotropic Co(II) ions preclude a spin-only modelling approach. At the same time, the almost negligible decrease of $\chi_m T$ upon cooling down to 100 K evidences a significant quenching of the orbital momentum contribution, further confirmed by the only moderately deviating high temperature $\chi_m T$ value from the expected spin-only value.[15]
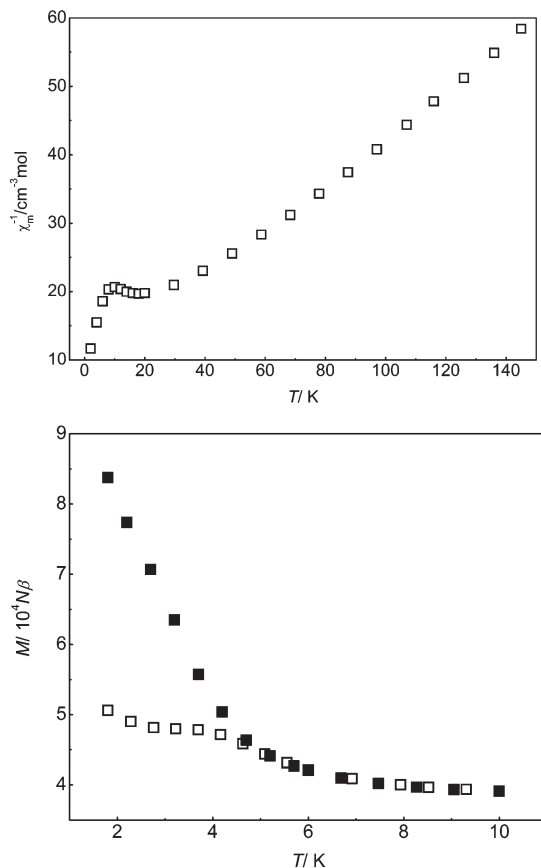
Fig. 4 χ_m^{-1} *vs.* T plot zoomed in the range 2–140 K at 0.1 T (top) and FC-ZFC magnetization plot at 50 Oe in the range 1.8–10 K (bottom) of compound **2**.

We therefore applied essentially two spin-only models to fit the magnetic data in nearly the whole temperature range neglecting any kind of orbital contributions:

(a) Fisher model[16] for an infinite chain of identical $S = 2$ (**1**) and $S = 3/2$ (**2**) spins with an isotropic coupling constant J:

$$\chi_m = \frac{N\beta g^2}{3kT} S(S+1) \frac{(1+u)}{(1-u)} \tag{1}$$

$$u = \coth\left(\frac{2JS(S+1)}{kT}\right) - \left(\frac{2JS(S+1)}{kT}\right)^{-1} \tag{2}$$

(b) Rings from 4 to 8 metal units as models for the infinite 1D chain, with the corresponding HDvV Hamiltonian:

$$\hat{H} = -2J\left(\sum_{i=1,\dots,n} (\hat{S}_i \cdot \hat{S}_{i+1}) + \hat{S}_1 \cdot \hat{S}_n\right) \tag{3}$$

The simulated susceptibilities were obtained employing the MAGPACK package.[17] Simulation with more than eight metallic sites was outside our computing possibilities because of computing memory depletion due to the huge dimension of the basis sets matrix.

For compound **1** an axial ZFS contribution arising from local Fe(II) ions D parameter, usually non-negligible for this

ion configuration, was included adding the following term to the Hamiltonian of eqn (3):

$$\hat{H} = \frac{2}{3}D\sum_i S_{zi}^2 \tag{4}$$

For the fitting of the susceptibility data of compound **1** (Fig. 3), only values down to 15 K were used due to the badly characterized low temperature behaviour. Best fitting parameters with all the different approaches are listed in Table 1. The ring approach affords better fittings than the Fisher model, although no great modifications are observed in the final parameters g and J. However, it is well known that the semi-classical basis of the Fisher model makes it more successful for large S values. Using a 4- or a 6-membered ring model provides almost negligible differences in the fittings, showing that even a small ring model is suitable for describing the magnetic behaviour of polymeric 1D Fe(II) compound **1**. As also considered in previous reports, the Fe(II) ion high-spin d^6 configuration demands testing the existence of sizeable zero-field splitting contributions.[8,9,13,14] In fact, the low temperature region of the susceptibility data (Fig. 3) cannot be precisely modelled with only Hamiltonian of eqn (3). Including an axial ZFS contribution by means of eqn (4) improves the

Table 1 $\chi_m T$ *vs.* T data fitting results[a]

	1	**2**
(a) Fisher (eqn (1) + eqn (2))	$g = 2.11 \pm 0.02$ $J = -1.8 \pm 0.1$ cm^{-1} $(R = 3.84 \times 10^{-4})$	$g = 2.46 \pm 0.03$ $J = -2.9 \pm 0.3$ cm^{-1} $(R = 8.01 \times 10^{-4})$
	$n = 4$ $g = 2.10 \pm 0.01$ $J = -1.63 \pm 0.04$ cm^{-1} $(R = 2.94 \times 10^{-4})$	**$n = 6$** $g = 2.45 \pm 0.03$ $J = -2.6 \pm 0.3$ cm^{-1} $(R = 6.65 \times 10^{-4})$
(b) HDvV ring (eqn (3) + eqn (4))	$g = 2.08$ (fixed) $J = -1.35$ cm^{-1} (fixed) $D = 10.8 \pm 0.7$ cm^{-1} $(R = 7.56 \times 10^{-4})$	**$n = 8$** $g = 2.45 \pm 0.03$ $J = -2.6 \pm 0.3$ cm^{-1} $(R = 6.83 \times 10^{-4})$
	$n = 6$ $g = 2.10 \pm 0.01$ $J = -1.67 \pm 0.05$ cm^{-1} $(R = 3.67 \times 10^{-4})$	

[a] Agreement factor, $R = 1/(N - n_p)[\Sigma(\chi_{calc}T - \chi_{obs}T)^2/\Sigma(\chi_{obs}T)^2]^{1/2}$, N: the number of data points, n_p: the number of fit parameters.

Table 2 M⋯M distances and exchange coupling constants in the [M(bpym)Cl$_2$]$_n$ family

	M⋯M distance/Å	J/cm^{-1}
Mn[a]	6.164(1)	−0.6
Fe[b]	5.938(1)	−1.3
Co[b]	5.797(1)	−2.6

[a] Ref. 5. [b] This work.

low temperature fitting. However, in order to obtain a well defined value for the D parameter it is necessary to add some restraints in the fitting as there is a strong correlation between J and D parameters. After a set of simulations at different fixed D values in the range 0–20 cm^{-1}, suggested by previous reported values in related systems, we found that g and J values can be reasonably fixed. The g value remains constant at $g = 2.09$ while the J value ranging between −1.2 cm^{-1} and −1.5 cm^{-1} can be fixed at a mean value of −1.35 cm^{-1}. Under these restraints the obtained value for the D parameter is 10.8 ± 0.7 cm^{-1}. Interestingly, the inclusion of the ZFS term, in addition to the improvement of the low temperature data, also reproduces the striking plateau at 10 K in the χ_m vs. T profile although shifted in the temperature scale with respect to the experimental data (see ESI†). The obtained value for the exchange coupling constant is in good agreement with previous reported Fe(II) bpym bridged examples.[8,9,13,14]

For compound **2** fitting of the magnetic data (Fig. 3) was employed down to 15 K. The sharp increase in χ_m below this temperature is probably related to cooperative effects. This limitation precludes a precise determination of the exchange coupling constant and completely avoids any attempt at including anisotropic components to the simulation models, as for example in Rueff approximation.[18] Best fitting parameters with all the different approaches are listed in Table 1. As also observed for compound **1**, the Fisher model recovers the right values for the relevant g and J parameters but the overall fitting quality is poorer than the ring approach model. Increasing the ring size above six cobalt sites does not improve the experimental data fitting. The high g value of 2.45 for a Co(II) ion is owing to the not considered orbital contribution under a spin-only modelling. In spite of this, the obtained value for the exchange coupling constant is in good agreement with other reported Co(II) bpym bridged examples.[6,11,19]

To further clarify the magnetic behaviour of compound **2** at low temperatures, the temperature dependencies of the zero-field-cooled (ZFC) and the field cooled (FC) magnetization were measured at a low field of 50 Oe (Fig. 4). The obvious divergence of the ZFC and FC data below 4 K indicates long-range magnetic order, which is consistent with the maxima in χ' and the nonzero χ'' signal around 3 K in the ac susceptibility at 1500 Hz (Fig. 5). The isothermal magnetization with the field up to 70 kOe at 1.8 K is depicted in Fig. 5. The initial increase of magnetization shows a slight positive curvature and is not linear with the field up to 10 kOe. It becomes then almost linear up to $0.609N\beta$ at 70 kOe, far from the theoretical saturation magnetization of the Co(II) ion, suggesting that there is an overall antiferromagnetic coupling between Co(II) ions in agreement with the susceptibility data. These results suggest that a spin canting effect along the 1D antiferromagnetically coupled Co(II) ions may be operative. Inter-chain interactions between the residual moments might propagate through short-contacts involving the solvent molecules affording a weak long-range ordering. A few examples of this type of behaviour have been previously reported for other Co(II) 1D chains.[20] It is well known that two mechanisms lead to
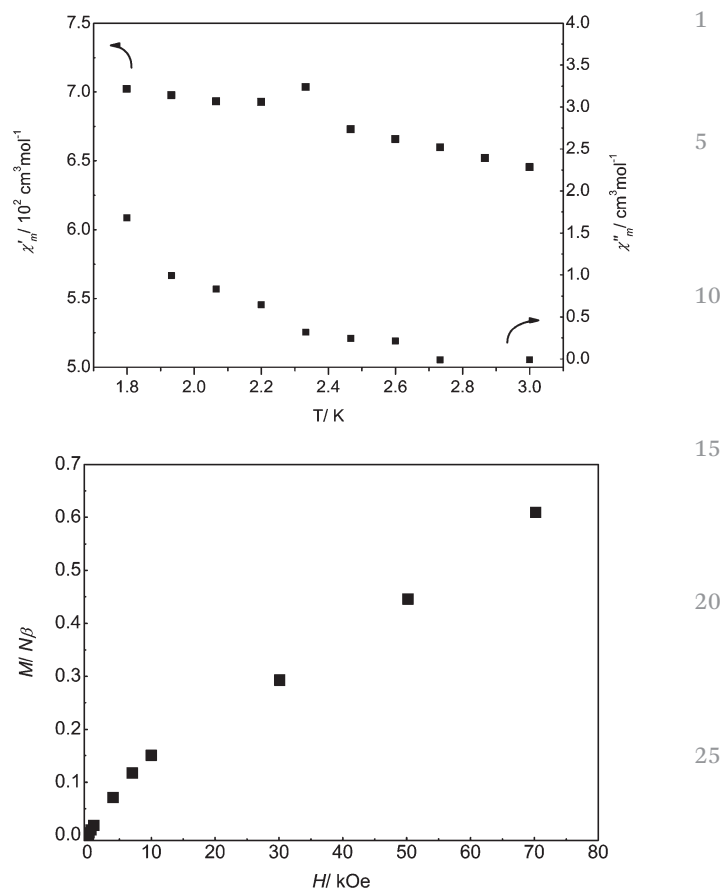

Fig. 5 AC susceptibility measurements at 0 DC field with a 3 Oe driving field and 1500 Hz frequency in the range 1.8–3 K (top); DC magnetization plot at 1.8 K up to a 70 kOe external field (bottom). Both graphics correspond to compound **2** data.

spin canting: (i) magnetic anisotropy and (ii) antisymmetric exchange.[21] However, while the occurrence of antisymmetric interactions is not compatible with the crystal structure of **2** showing an inversion centre between the bridged Co(II) sites, the observation of the spin canting can still be attributed to the single-ion anisotropy of the Co(II) ions.

Conclusions

We have successfully prepared and structurally characterized two new members of the [M(bpym)Cl$_2$]$_n$ family of neutral 1D coordination polymers. The Fe(II) and Co(II) containing derivatives add to the only one reported Mn(II) compound. Both new compounds crystallize isostructurally in well isolated alternating polymeric chains. The magnetic behaviour of the Fe(II) compound can be well understood as a uniform $S = 2$ chain with antiferromagnetic exchange interaction between the metal ion sites. A ZFS contribution expected for this ion affects the low temperature data where an anomalous feature is observed. In the case of the Co(II) ion, also antiferromagnetic interactions are operative along the uniform chain. The low

temperature behaviour suggests a long range-ordering originating from spin-canting due to the anisotropy of the Co(II) lowest energy Kramers doublets. These two new examples constitute a further contribution towards the design of homonuclear polymeric 1D systems with potential interesting magnetic properties, starting from simple building units in simple one pot reactions.

Experimental

Material and physical measurements

2,2′-bipyrimidine was prepared following a previously reported procedure.[22] All other chemicals were of reagent grade and used as received without further purification. Elemental analyses for C, H and N were performed on a Foss Heraeus Vario EL elemental analyzer. Magnetic measurements were performed with a Quantum Design MPMS XL SQUID magnetometer. DC measurements were conducted from 2 to 300 K and from 0 kOe to 70 kOe. AC measurements were performed at the maximum available frequency of 1500 Hz with an AC driving field amplitude of 3 Oe and under no applied DC field. All experimental magnetic data were corrected for the diamagnetism of the sample holders and of the constituent atoms (Pascal's tables).

Preparation of $[Fe(\mu\text{-bpym})Cl_2]_n\cdot 1.5H_2O$ (1) and $[Co(\mu\text{-bpym})Cl_2]_n\cdot 1.5H_2O$ (2)

0.5 mmol of $FeCl_2\cdot 4H_2O$ (0.15 g) (1) or $CoCl_2\cdot 6H_2O$ (0.12 g) (2) were dissolved in 50 ml of methanol. To the resulting clear solution, a solution of 0.5 mmol (0.08 g) of 2,2′-bipyrimidine in 50 ml of acetonitrile was added under continuous vigorous stirring. Immediately a dark red solution was obtained. It was then left undisturbed at room temperature and after a few hours dark red block crystals suitable for X-ray single crystal characterization were obtained. One specimen was separated for this purpose and the remaining solid was filtered, washed with acetonitrile and methanol and air dried.

(1) Yield: 0.106 g, 68% (based on $Fe(bpym)Cl_2$ units). Anal. calcd for $C_8H_9Cl_2FeN_4O_{1.5}$ C: 30.80, H: 2.91, N: 17.96 Found: C: 30.24, H: 2.85, N: 17.84. (2) Yield: 0.126 g, 80% (based on $Co(bpym)Cl_2$ units). Anal. calcd for $C_8H_9Cl_2CoN_4O_{1.5}$ C: 30.50, H: 2.88, N: 17.79 Found: C: 30.17, H: 2.82, N: 17.89.

X-ray structure determination

Crystals of 1 and 2 suitable for X-ray diffraction were obtained directly from the synthetic procedure, collected from the methanol–acetonitrile solution and mounted in a glass fibre. The crystal structure was determined with a Bruker Smart APEX II CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 173 K. Data were corrected for absorption with $SADABS$[23] using a multi-scan semi-empirical method. The structure was solved by direct methods with $SHELXS\text{-}97$[23] and refined by full-matrix least-squares on F^2 with $SHELXL\text{-}97$.[24] Hydrogen atoms were added geometrically and refined as riding atoms with a

uniform value of U_{iso} with the exception of the hydrogen atoms of the solvent methanol and acetonitrile molecules that were not included in the model due to the extensive disordering of these moieties.

In both structures, the acetonitrile solvent molecule is disordered around a 2-fold rotation axis and was modelled as two split positions with identical occupation factors. In the case of the methanol solvent molecule, it is disordered around two perpendicular 2-fold rotation axes and was modelled as six and four split positions with identical occupation factors in compounds 1 and 2, respectively.

Crystal data

(1) $C_{10.50}H_6Cl_2FeN_5O_{0.50}$, M = 336.95, orthorhombic, a = 11.978(4), b = 16.464(5), c = 29.114(9) Å, V = 5741(5) Å³, T = 173 K, space group $Fddd$ (no. 70), Z = 16, 15 768 reflections measured, 1739 unique (R_{int} = 0.11), 1289 observed. R_1 = 0.058, 0.079 (all data), wR_2 = 0.145, 0.152 (all data), GooF = 1.074. (2) $C_{10.5}H_6Cl_6CoN_5O_{0.5}$, M = 340.03, orthorhombic, a = 11.7256(14), b = 16.5129(19), c = 29.182(3) Å, 5650(1) Å³, T = 173 K, space group $Fddd$ (no. 70), Z = 16, 9531 reflections measured, 1513 unique (R_{int} = 0.097), 1100 observed. R_1 = 0.079, 0.106 (all data), wR_2 = 0.174, 0.168 (all data), GooF = 1.236.

The main bond distances and angles for both compounds are listed in the ESI.† CCDC 928716–928717 contains the supplementary crystallographic data for this paper.

Acknowledgements

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