# "Structural and magnetic characterization of a 1D chain of $[Co(II)_2(\mu\text{-aqua})(\mu\text{-carboxylate})_2]$ strung cores"†

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A novel 1D chain built up from stringing of $[Co_2(\mu\text{-}OH_2)(\mu\text{-}O_2CC(CH_3)_3)_2]$ units with the bridging 2,2′-bipyrimidine ligand has been synthesized and structurally characterized. The chains are well isolated from each other by the bulky *tert*-butyl groups of the carboxlyates and show an alternating zigzag configuration for the Co(II) metallic centres. DC magnetic measurements show anti-ferromagnetic coupling, $J$ *ca.* $-3$ cm$^{-1}$ between adjacent Co(II) ions along the chain. Noticeably, good data fitting was obtained by means of simple models that neglect any kind of first order orbital contribution to the spin ground state, which is normally observed in Co(II) complexes. These results were further confirmed by broken-symmetry DFT calculations performed on a tetranuclear model emulating the 1D chain structure. Field dependence magnetization measurements show an incipient field-induced energy level crossing at high magnetic field and low temperature (1.8 K).

## Introduction

The rational design of synthetic strategies to prepare systems with desired properties continues to be a challenge for inorganic chemists. In this context, many efforts are devoted to the development of synthetic routes for assembling well characterized pre-formed transition metal clusters which may show suitable properties for their application as molecular- based magnetic materials.[1,2] One of the key features is the selection of the bridging (stringing) moiety. Small organic molecules with coordinating donor atoms are one of the candidates because of their enormous synthetic versatility. Among them, the bidentate 2,2′-bipyrimidine (bpym) ligand has been extensively employed due to its remarkable ability to mediate electronic effects between the paramagnetic centres they bridge.[3–8]

On the other hand, μ-carboxylate metallic clusters are, undoubtedly, the most widespread building blocks used in the field of molecule-based magnetic systems.[9] Those containing Co(II) ions are particularly interesting because of the potential source of anisotropy this ion may provide. The possibility to observe spin-canting phenomena in high dimensional arrangements of these moieties and even SCM (single chain magnet) behaviour is one of the main reasons for Co(II) clusters current popularity.[2,3,10] With this background, we decided to explore the reaction between the dinuclear starting precursor $[Co_2(\mu\text{-}OH_2)(\mu\text{-}O_2CC(CH_3)_3)_2\text{-}(O_2CC(CH_3)_3)_2(HO_2CC(CH_3)_3)_4]$, possessing the $[Co_2(\mu\text{-}OH_2)(\mu\text{-}O_2CR)_2]$ fundamental core, with the 2,2′-bipyrimidine ligand. In spite of being known for several decades[11,12] only a few examples can be found where dinuclear Co cores appear as the building units in high dimensional materials.[13] Our first attempts afforded the chain $[[Co_2(\mu\text{-}OH_2)(\mu\text{-}O_2CC(CH_3)_3)_2](\mu\text{-bpym})]_n$ whose preparation, crystal structure determination, and magnetic study together with DFT calculations are presented here.

## Results and discussion

### Synthesis and crystal structure

Reaction of the dinuclear $Co_2(\mu\text{-}OH_2)(\mu\text{-Piv})_2(\text{Piv})_2(\text{HPiv})_4$, Piv=$O_2CC(CH_3)_3$, a common starting material in the synthesis of cobalt containing high nuclearity clusters,[14] with the potentially bridging ligand 2,2′-bipyrimidine afforded in reasonably yield and high purity a 1D chain complex. The chain is built up from the direct stringing of the $Co_2$ dinuclear moieties with the bipyrimidine ligand. Most probably the more labile neutral carboxylic acids weakly bound to the cobalt atoms are easily replaced by the much stronger bidentate ligand. In fact, a similar reaction was observed with pyridine, not a bidentate ligand but closely related to 2,2′-bipyrimidine.[14]

The crystal structure show well isolated 1D chains (closest inter-chain $Co\cdots Co$ distance ~9.5 Å), lying parallel to the *ab* plane (normal to the monoclinic axis) and alternating their main growing axis direction making an angle of about *ca.* 45° among them. The chains are also tilted with an angle of 21° with respect to the *a*-axis. They are composed of alternating bipyrimidine (~83°) bridges linking the dimeric units $[Co_2(\mu\text{-}OH_2)(\mu\text{-Piv})_2(\text{Piv})_2]$. The angle between the Co–Co axes and the bridging bipyrimidine planar ligand is *ca.* 150°, this affords a final zigzag arrangement of all the Co with this same value for the Co–Co–Co angle (see ESI†). Due to the presence of almost orthogonal bipyrimidine bridges, two different sets of Co–N distances are observed:

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† Electronic supplementary information (ESI) available: Additional figures showing: chains packing view along *c* axis direction; perspective of the zigzag arrangement of Co(II) sites along the chain; *ORTEP* representation showing the H-bond interaction of the non-bridging carboxylate with the bridging aqua ligand; additional $\chi_m T$ *vs* $T$ and $\chi_m$ *vs* $T$ plots with the corresponding fitting with models b) and d); $\chi_m$ *vs* $T$ plots in the 2-30 K range at 10 kOe, 50 kOe and 70 kOe; $Co_4$ tetranuclear model employed in the DFT calculations and spin density surfaces of the three possible spin topologies calculated. CCDC reference number 709651. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b820594a

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Co(2)–N(3) = 2.184(6) Å, Co(2)–N(2) = 2.231(9) Å and Co(1)–N(1) = 2.159(7) Å, Co(1)–N(4) = 2.229(7) Å. While the short distance is comparable to the observed one in other Co bridged systems,[5,8] the long one is unusually large with only one reported example of a dinuclear Co complex where the Co–N distance is even larger, 2.280 Å.[8] These values establish an alternating short and long Co–Co distances pattern of 3.515 Å and 5.587/5.843 Å along the zigzag chain of metals. The shorter Co–N bond is located *trans* to the μ-aqua O atom. The $Co_2$ moiety is clearly retained in the 1D structure with distances in the range of closely related dimeric complexes sharing the $[Co_2(\mu\text{-}OH_2)(\mu\text{-}O_2CR)_2]$ core.[14–16] The Co–μ-aquaO distances are Co(2)–O(4) = 2.168(6) Å and Co(1)–O(4) = 2.157(6) Å and the Co–(μ-aquaO)–Co angle is Co(2)–O(4)–Co(1) = 108.7(3)°. The Co–μ-carboxylateO distances are Co(2)–O(3) = 2.061(8) Å, Co(2)–O(2) = 2.042(7) Å, Co(1)–O(5)= 2.047(7) Å and Co(1)–O(11) = 2.072(5) Å with the short distances opposing the non-bridging carboxylates. Finally the non-bridging carboxylates are fully involved in hydrogen bonding with the μ-aqua O atom (see ESI†). These Co–O distances are Co(2)–O(10) = 2.078(7) Å and Co(1)–O(8) = 2.093(8) Å, slightly different from the Co–O distances involving the bridging carboxylates. The final local Co environment, corresponds to a strongly distorted octahedron with two long Co–N bonds and a long Co–O bond all arranged in facial mode, and three remaining Co–O short bonds. Probably the closer micro-symmetry of the Co sites belongs to $C_{2v}$ point symmetry group. Fig. 1 shows the structure of the repetitive unit of the 1D chain.

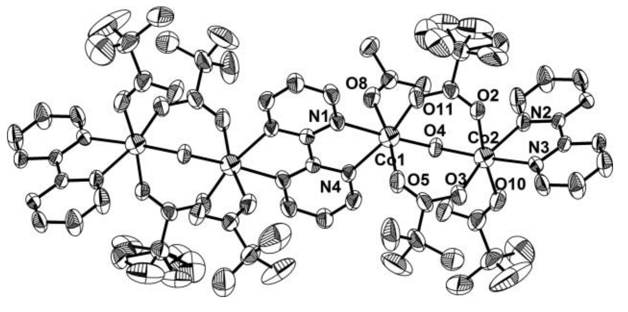


**Fig. 1** *ORTEP* diagram (50% ellipsoid probability) of the repetitive unit of the chain with main atoms labelling. Hydrogen atoms were omitted for clarity.

## Magnetic properties

The magnetic behaviour of the reported complex was studied in the temperature range 2–300 K under an applied field of 1 T (Fig. 2). The $\chi_m T$ value (per $Co_2$ moiety) at 300 K is with 5.87 $cm^3$ K $mol^{-1}$ well above the expected value for two isolated high spin Co(II) ions ($g$= 2.00), 3.75 $cm^3$ K $mol^{-1}$, but in good agreement for a $g$ value of 2.50 ($\chi_m T$= 5.86 $cm^3$ K $mol^{-1}$ for two isolated HS Co(II)) usual for this particular ion because of the well known strong first order orbital contribution to the spin ground state.[17] The almost temperature independent value for $\chi_m T$ down to 100 K is followed by a continuous drop upon cooling down to 2K, indicative of weak anti-ferromagnetic interaction between neighbouring Co(II). This is further confirmed by the maximum observed at 14 K in the $\chi_m$ *vs* $T$ plot. Due to the chain nature of this complex it is not possible to employ a full spin Hamiltonian for simulation of the magnetic behaviour. Furthermore, the strong anisotropic Co(II) ions may preclude a spin only modelling approach. All models so far reported in literature to tackle the latter problem suffer a considerable risk of over-parameterization even in the simpler cases.[17,18] Here, a further complication arises from the existence of two different magnetic exchange interactions as depicted in Scheme 1a. However, the almost negligible decrease of $\chi_m T$ up

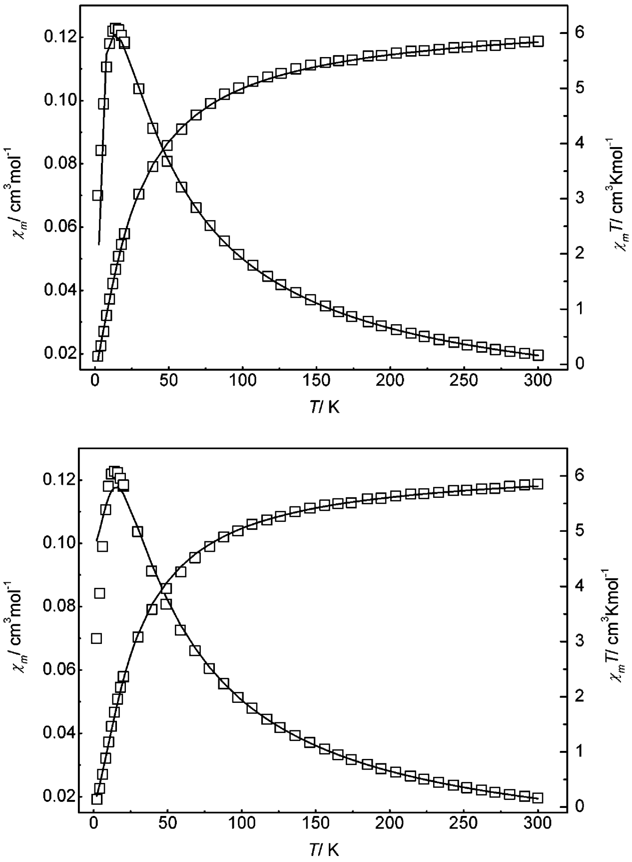
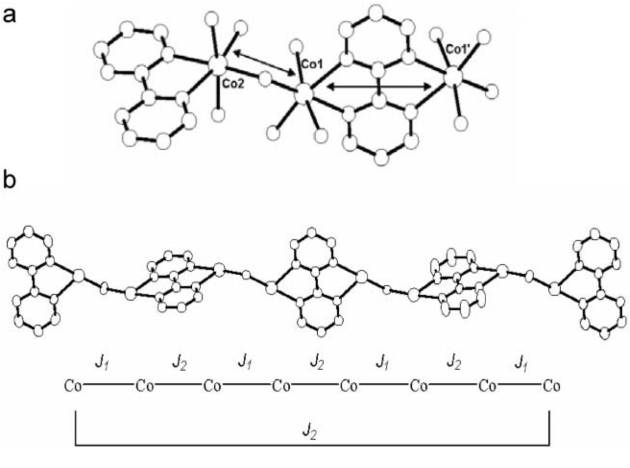


**Fig. 2** $\chi_m T$ *vs* $T$ and $\chi_m$ *vs* $T$ plots in the 2–300 K range. Empty squares: experimental data. Full line: best fitting curves with model (a) (top) and model (c) (bottom). For models (b) and (d) see ESI.†



**Scheme 1** (a) Representative picture of the two possible different magnetic exchange interactions between Co(II) ions in the reported 1D complex. (b) $Co_8$ ring model representation with the corresponding magnetic exchange interactions involved.

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to almost 100 K, is a first evidence that there is an important quenching of the orbital momentum contribution, as oppositely a more pronounced continuous dropping of $\chi_m T$ should be observed.[17]

Hence, we employed a battery of spin-only models to fit the magnetic data in the whole temperature range neglecting any kind of orbital contribution:

(a) Heisenberg–Dirac–van Vleck (HDvV) Hamiltonian[19] describing the isotropic exchange coupling ($J$) between two Co(II) ions ($S = 3/2$) with a mean-field correction ($zJ'$) that accounts for a weak interaction between the preceding coupled Co(II) pair,

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2) \tag{1}$$

The susceptibility for all possible field orientations was obtained with eqn 2 after getting the energies by full matrix diagonalization of the Hamiltonian in eqn 1:

$$\chi_m = \frac{1}{H} \frac{N \sum_i \left(-\partial E_i/\partial H\right) \exp\left(-E_i/kT\right)}{\sum_i \exp(-E_i/kT)} \tag{2}$$

The mean field correction was applied as follows:

$$\chi_m = \frac{\chi_m}{1 - \frac{2zJ'}{Ng^2\beta^2}\chi_m} \tag{3}$$

This "HDvV + mean field correction" approach relies in the different strength expected, in principle, for the two possible Co–Co exchange interactions mediated by aqua ligand and bipyrimidine ligand with Co–Co distances of *ca.* 3.5 and 5.6 Å respectively.

(b) An eight member Co ring as a model for the infinite 1D chain (Scheme 1b), with the corresponding HDvV Hamiltonian:

$$\hat{H} = -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4 + \hat{S}_5 \cdot \hat{S}_6 + \hat{S}_7 \cdot \hat{S}_8) - 2J_2(\hat{S}_2 \cdot \hat{S}_3 + \hat{S}_4 \cdot \hat{S}_5 + \hat{S}_6 \cdot \hat{S}_7 + \hat{S}_8 \cdot \hat{S}_1) \tag{4}$$

The simulated susceptibility was obtained employing the CLUMAG routine,[20] based in the ITO (Irreducible Tensor Operators) formalism. Simulation with more than eight metallic sites was out of our computing possibilities because of computing memory depletion due to the huge dimension of the basis sets matrix. Fitting with $J_1 = J_2$ restraint was also performed to test for over-parameterization.

(c) Fisher model[21] for an infinite chain of identical $S = 3/2$ spins with an isotropically $J$ coupling constant:

$$\chi_m = \frac{N\beta g^2}{3kT} S(S+1) \frac{(1+u)}{(1-u)} \tag{5}$$

$$u = \coth\left(\frac{2JS(S+1)}{kT}\right) - \left(\frac{2JS(S+1)}{kT}\right)^{-1} \tag{6}$$

**Table 1** $\chi_m T$ *vs* $T$ (2–300 K) data fitting results

| | |
|---|---|
| (a) HDvV + mean field (eqn 1 + eqn 3) | $g = 2.60 \pm 0.01$<br>$J = -3.1 \pm 0.1$ cm$^{-1}$<br>$J'$ $(z = 2) = -1 \pm 0.2$ cm$^{-1}$<br>$R = 2.97 \times 10^{-5}$[a] |
| (b) HDvV $Co_8$ ring[b] (eqn 4) | $g = 2.56 \pm 0.01$<br>$J_1 = -3.1 \pm 0.1$ cm$^{-1}$<br>$J_2 = -2.2 \pm 0.1$ cm$^{-1}$<br>$R = 2.20 \times 10^{-4}$ |
| | *(uniform chain)*<br>$g = 2.56 \pm 0.01$<br>$J_1 = J_2 = -2.65 \pm 0.1$ cm$^{-1}$<br>$R = 2.16 \times 10^{-4}$ |
| (c) Fisher (eqn 5 + eqn 6) | $g = 2.58 \pm 0.01$<br>$J = -3.0 \pm 0.1$ cm$^{-1}$<br>$R = 2.58 \times 10^{-4}$ |
| (d) Rueff (eqn 7) | $A = 1.9 \pm 0.2$ cm$^3$Kmol$^{-1}$<br>$g = 2.60 \pm 0.01$<br>$J = -2.9 \pm 0.4$ cm$^{-1}$<br>$U = 23 \pm 2$ cm$^{-1}$<br>$R = 1.72 \times 10^{-4}$ |

[a] Agreement factor, $R = 1/(N - n_p)[\sum(\chi_{calc}T - \chi_{obs}T)^2/\sum(\chi_{obs}T)^2]^{1/2}$, $N$: number of data points, $n_p$: number of fit parameters, [b] A $Co_6$ ring model already afforded exactly the same results.

(d) Rueff phenomenological model for describing an infinite Co(II) chain based in two exponential terms, one describing the isotropic exchange interaction ($J$) and the second one describing all possible anisotropic contributions ($U$)[22]:

$$\chi_m = \frac{A \exp\left(\frac{-U}{kT}\right) + B \exp\left(\frac{-2J}{kT}\right)}{T} \tag{7}$$

Where $A + B$ must equal the Curie constant expected for an $S = 3/2$ and hence fixed by the $g$ factor value.

The latter approach is the only one we employed, where the possible orbital momentum contribution is considered in a very simple way. However it should be stressed that it may suffer from over-parameterization due to the increased number of fitting parameters.

In all cases the whole range of temperature data (2–300 K), was used for fitting procedures. Results are shown in Table 1, Fig. 2 and ESI.† All models afforded a good fitting of the data with the exception of the Fisher model that poorly describes the low $T$ region, clearly noticed in the $\chi_m$ *vs* $T$ plot. This model is expected to work better in a classical limit and for high spin values, with $S = 5/2$ being the lower limit showing satisfactory results. In spite of this, the agreement between all models is remarkably good with an almost unique $g$ value close to the one expected from the high temperature $\chi_m T$ value, and $J$ exchange coupling constants ranging between −1 and −3 cm$^{-1}$. These obtained values for the isotropic $J$ constant are in agreement with other values previously found in different μ-bipyrimidine and μ-aqua–μ-carboxylate Co systems.[3,4,7,8,11,15] The results obtained with model (b) show that it seems not to be possible to distinguish between a unique $J$ model or a $2J$ model, even if the latter is demanded by the structure of the chain complex itself. Nevertheless, results with both models (a) and (b) contemplating the $2J$ case show consistency, affording only a small difference between both $J$ values. The phenomenological model (d), probably over-parameterizing the fitting,[23] that includes a term accounting for the orbital contribution to the spin ground state of the HS Co(II) centres, also agrees with the $g$ and $J$ obtained values. However, this latter result should be considered with care, as there are no clear evidences of an important anisotropy influencing the magnetic behaviour of this 1D Co(II) chain. Only the exceedingly big $g$ value (2.56), in comparison to the free electron value appears as the unique feature of some remaining orbital contribution. The low symmetry of the Co(II) site, close to $C_{2v}$, could be most probably the main reason of the important quenching of orbital momentum in the Co(II) sites. Interestingly, evaluation of the $J$ coupling constant (under assumption of a unique $J$ model) through a recently proposed correlation between $J$ and $T_{\max}$ (of $\chi_m$ *vs* $T$ plot) for anti-ferromagnetically coupled HS Co(II) ions (eqn 8),[4]

$$2J = 0.02517 + 0.39564T_{max} – 0.00079T_{max}^2 \tag{8}$$

afforded $J = -2.7$ cm$^{-1}$ in strict accordance with values obtained through $\chi_m T$ data fitting.

In order to gain a deeper insight on the magnetic properties of this compound, we performed magnetization measurements at low temperature under different applied magnetic fields, ranging up to 7 T (see ESI†). At 10 K the almost linear increasing of $M$ upon increasing the field is compatible with a non-magnetic ground state ($S = 0$) arising from the anti-ferromagnetic coupled $S = 3/2$ Co(II) ions. On lowering temperature the shape of the $M$ vs $H$ plot becomes noticeably sigmoidal. At 1.8 K this feature is clearly recognized and confirmed by the sudden rising of the magnetization derivative when approaching the maximum magnetic field value. Regrettably, higher magnetic fields are out of our current capabilities, thus it is not possible to observe a saturation regime. This behaviour of the magnetization is compatible with a field-induced energy level crossing of the non-magnetic ground state with excited spin states.[24] This is further confirmed by the field dependence measurements of $\chi_m$ in the range 2–30 K (Fig. 3). It can be observed that the maximum at 14 K in a 10 kOe field shifts to 11 K at 50 kOe and almost disappears at the limit of 70 kOe field, in agreement with the magnetization data. The best fitting parameters of the $\chi_m T$ *vs* $T$ plot in the whole temperature range by means of model (b) allows obtaining the energy levels plot for the lowest spin multiplets (Fig. 4). Even if this model corresponds to a $Co_8$ ring, it gives a first insight into the origin of the field induced level crossing. A first crossing of the $S = 0$ ground state occurs around 25 kOe, while a definitive crossing is observed around 50 kOe. After this final level crossing, magnetization should slowly reach saturation upon further increasing of the magnetic field, as the new magnetic ground state starts becoming well isolated from the excited sates.

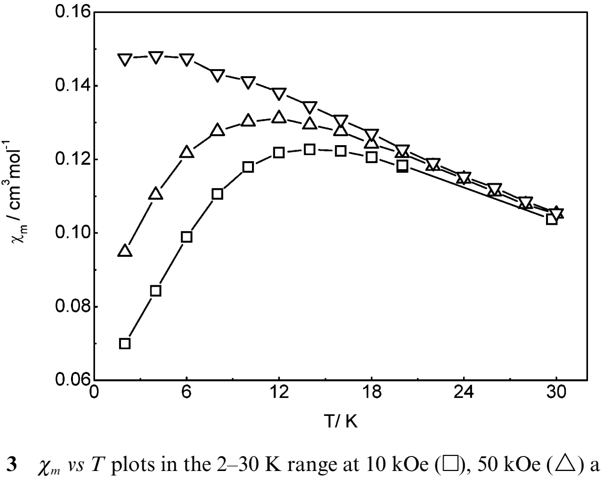

**Fig. 3** $\chi_m$ *vs* $T$ plots in the 2–30 K range at 10 kOe (□), 50 kOe (△) and 70 kOe (▽). Lines are only eye guideline.

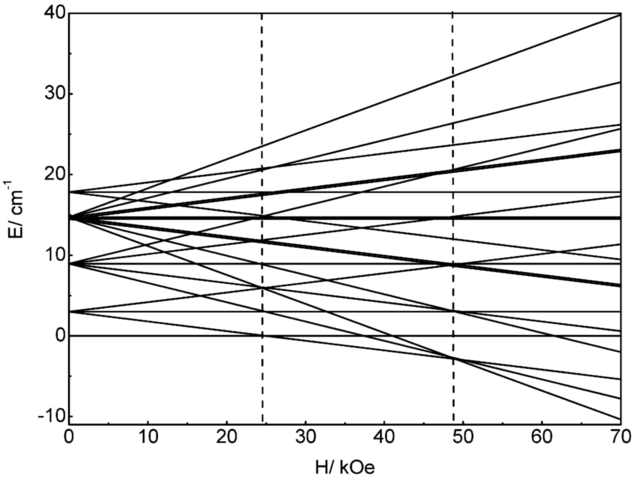

**Fig. 4** Energy levels diagram of the six lowest spin multiplets obtained with the best fitting parameters with model (b) (see text). Vertical dashed lines delimited the crossing levels range.

The field range of the level crossings agrees quite well with the experimentally observed.

## DFT calculations

As complementary information we performed DFT calculations to obtain $J$ exchange coupling constants between Co centres in the 1D chain. We employed the X-ray geometry of the smallest repetitive moiety along the chain that allows including the two different $J$ constants, $J_1$ and $J_2$ (see ESI†). This tetranuclear model fragment retains all the features of the 1D chain, also the neutral charge, but obviously cannot exactly reproduce the electronic distribution of the terminal bipyrimidine ligands. Nevertheless, the calculated values are in excellent agreement with the experimental results. The Ruiz approach (see Experimental) affords $J_1 = -2.4$ cm$^{-1}$ and $J_2 = -1.7$ cm$^{-1}$ while the Ising approach (see Experimental) affords $J_1 = -3.2$ cm$^{-1}$ and $J_2 = -2.2$ cm$^{-1}$. The good agreement of these DFT results confirms that this 1D chain system shows little orbital contribution to the magnetic behaviour, as the broken-symmetry approach completely relies on the isotropic spin-only HDvV Hamiltonian (eqn 1).

Inspection of the magnetic orbitals gives some insight on the origin of the anti-ferromagnetic exchange coupling between the Co centres (Fig. 5). The broken symmetry state BS1, where the spin has been flipped over Co1, allows analysing only the exchange pathways governed by $J_1$. Of the three possible pathways, two are mainly occurring through the overlap of Co d orbitals with the bridging aqua ligand orbitals and the third one through the bridging carboxylate orbitals. The overlaps are rather small because they are of $\delta$–$\pi$ nature. When looking at BS2 magnetic orbitals, the Co–Co bipyrimidine mediated exchange pathways, ruled by $J_2$, can be additionally analysed. Clearly it is mediated by $\sigma$–$\sigma$ overlap between Co d orbitals and the bridging ligand orbitals. By comparison of the overlaps ($S$) obtained for BS1 (only $J_1$ mediated interaction) and BS2 (both $J_1$ and $J_2$ interactions), it can be inferred that overlaps related to the $J_2$ coupling constants are rather small in comparison with $S$ values for $J_1$. Hence, the weakness of the $\pi$–$\delta$ interaction relative to the $\sigma$–$\sigma$ one is

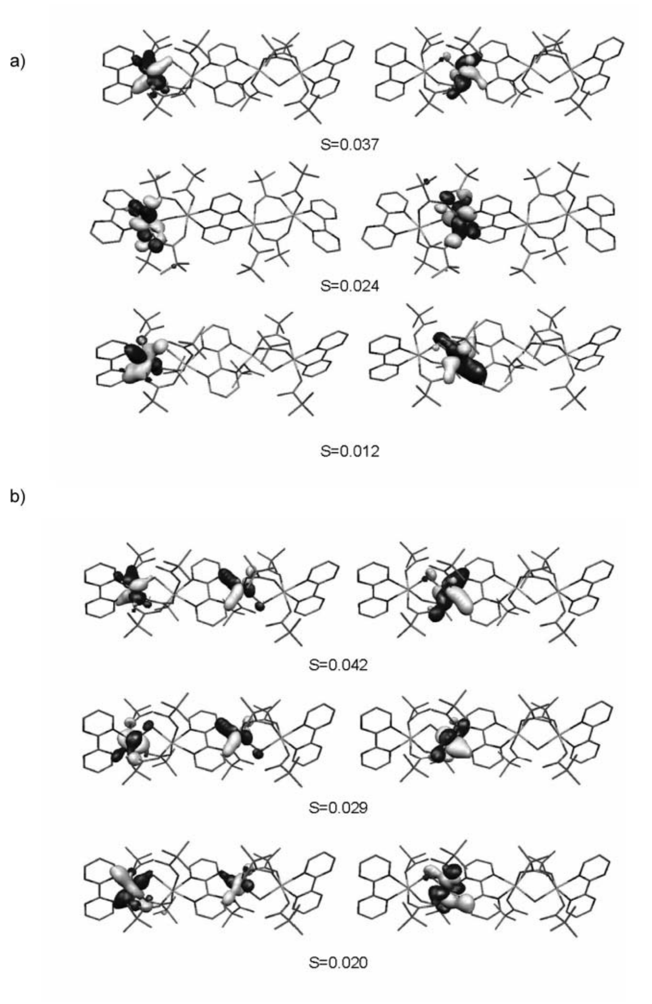

**Fig. 5** $\alpha$ and $\beta$ interacting magnetic orbitals pairs arising from a COT over the broken symmetry MO's from BS1 state (a) and BS2 state (b). Overlap integrals values (*S*) are shown.

compensated by larger *S* values giving the overall comparable values for $J_1$ and $J_2$.

## Conclusions

We have successfully strung pre-formed $[Co_2(\mu\text{-}OH_2)(\mu\text{-}O_2CR)_2]$ moieties by means of the bidentate ligand 2,2′-bipyrimidine. In spite of the usual lability of the Co(II) ion, the starting dinuclear entity is preserved in the final alternating 1D chain product. Magnetic studies revealed the existence of anti-ferromagnetic exchange coupling between the Co(II) centres (*J ca.* $-3\ cm^{-1}$) with no real possibility of recognizing a differential coupling strength between the two different bridging unities. Uncommonly for this type of system, we have found evidences of a high degree of first order orbital momentum quenching of the Co(II) ion spin ground state. This is further supported by theoretical DFT computations. Consequently, no related phenomena as SCM behaviour or spin-canting were observed. Additionally, an incipient field induced spin level crossing is observed at high magnetic field that we cannot currently further explore due to our setup limitation (7 T maximum applied DC external magnetic field). In order to get further understanding of the magnetic behaviour of this type of Co(II) 1D system, reactions involving different stringing moieties are in progress.

## Experimental

### Material and physical measurements

$[Co_2(\mu\text{-}OH_2)(\mu\text{-}Piv)_2(Piv)_2(HPiv)_4]$[14] and 2, 2′-bipyrimidine[25] were prepared following previously reported procedures. All other chemicals were reagent grade and used as received without further purification. Elemental analysis 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. All experimental magnetic data were corrected for the diamagnetism of the sample holders and of the constituent atoms (Pascal's tables).

### Preparation of $[[Co_2(\mu\text{-}OH_2)(\mu\text{-}O_2CC(CH_3)_3)_2(O_2CC(CH_3)_3)_2](\mu\text{-}bpym)]_n$

$Co_2(\mu\text{-}OH_2)(\mu\text{-}Piv)_2(Piv)_2(HPiv)_4$, 0.4 g (0.42 mmols) were dissolved in 10 ml of methanol to give a purple solution. 0.064 g (0.41 mmols) of solid 2, 2′-bipyrimidine (bpym) were added and the solution immediately turned orange. It was left slowly evaporating at room temperature. After 1 day prism shaped orange crystals of the product were obtained. One of them was used for X-ray determination, the rest of them were collected by filtration washed with cold methanol and vacuum dried. Yield: 0.078 g, 27% (based on $Co_2$ repetitive moieties). Anal.Calcd. for $C_{28}H_{44}Co_2N_4O_9$ C: 48.14, H: 6.35, N: 8.02 Found: C: 48.14, H: 6.46, N: 8.23.

### X-Ray structure determination

Crystals suitable for X-ray diffraction were obtained directly from the synthetic procedure, collected from the methanolic solution and mounted in a glass fiber. The crystal structure was determined with a Bruker Smart APEX II CCD area-detector diffractometer using graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 173 K. Data was corrected for absorption with *PLATON*[26] using a multi-scan semi-empirical method. The structure was solved by direct methods with *SHELXS-97*[27] and refined by full-matrix least-squares on $F^2$ with *SHELXL-97.*[28] Hydrogen atoms were added geometrically and refined as riding atoms with a uniform value of $U_{iso}$ with the exception of hydrogen atoms of the bridging water that were found in the difference map. In one of the *tert*-butyl groups of the pivalate ligands, methyls were disordered over two positions with 0.5 site occupancy. The solvent water molecule was found to be disordered over four positions, two of them related by the crystallographic symmetry operation ($-x + 1, y, -z - 1/2$), with 0.5 site occupancy factors.

### Crystal data

$C_{58}H_{96}Co_4N_8O_{21}$, $M = 1477.15$, monoclinic, $a = 33.93(12)$, $b = 13.31(5)$, $c = 20.23(8)$ Å, $\beta = 116.1$ (2) deg., $V = 8199(76)$ Å$^3$, $T = 173$K, space group $C_{2/c}$ (no. 15), $Z = 4$, 92006 reflections measured, 9322 unique ($R_{int} = 0.19$), 3920 observed. $R_1 = 0.054$, 0.155 (all data), $wR_2 = 0.105$, 0.125 (all data), GooF= 0.806.

### DFT quantum computations

Density functional theory (DFT) spin-unrestricted calculations were performed at the X-ray geometry using the *Gaussian03* package (revision *D.01*)[29] at the B3LYP level employing the *LanL2DZ* basis set. Tightly converged ($10^{-8}$ Eh in energy) single point calculations were performed in order to analyze the exchange coupling between the cobalt centres. The methodology applied here relies on the broken symmetry formalism, originally developed by Noodleman for SCF methods,[30] which involves a variational treatment within the restrictions of a single spin-unrestricted Slater determinant built upon using different orbitals for different spins. This approach has been later applied within the frame of DFT. The HS (high spin) and BS (broken symmetry) energies were then combined to estimate the exchange coupling parameter $J$ involved in the widely used Heisenberg–Dirac–van Vleck Hamiltonian (eqn 1). We have calculated the two possible spin topologies of broken symmetry nature (see ESI†) by flipping spin on the two different Co sites. The exchange coupling constants $J_i$ can be obtained after considering the individual pair-like components spin interactions involved in the description of the different broken symmetry states. We used two main reported methodologies: the Ising approach,[31] where the broken symmetry states are directly considered as eigenstates of the HDvV Hamiltonian (eqn 1) with the corresponding equation:

$$E_{BS} - E_{HS} = 2J_{12}(2S_1S_2) \tag{9}$$

and the method proposed by Ruiz and co-workers,[32] where the following equation is applied:

$$E_{BS} - E_{HS} = 2J_{12}(2S_1S_2 + S_2), \text{ with } S_2 < S_1 \tag{10}$$

In both cases a set of linear equations must be solved to obtain the $J$ parameters. Further details about these methodologies can be found in ref. 31–32. Additionally, we have also employed the BS-type spin unrestricted solutions after a corresponding orbital transformation (COT) as a means to visualize the interacting non-orthogonal magnetic orbitals.[33] These orbitals do not have a well-defined orbital energy, for this reason, orbital energies are not given explicitly but just their overlapping magnitudes as well as the spin-coupling exchange pathways.

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