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Synthesis, crystal structure and magnetic behavior of three polynuclear complexes: [Co(pyo)$_2$(dca)$_2$]$_n$, [Co$_3$(ac)$_4$(bpe)$_3$(dca)$_2$]$_n$ and [{Co(male)(H$_2$O)$_2$}(H$_2$O)]$_n$ [pyo, pyridine-*N*-oxide; dca, dicyanamide; ac, acetate; bpe, 1,2-bis-(4-pyridyl)ethane and male, maleate]

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Three polymeric cobalt(II) complexes of formulae [Co(pyo)$_2$(dca)$_2$]$_n$ (**1**), [Co$_3$(ac)$_4$(bpe)$_3$ (dca)$_2$]$_n$ (**2**) and [{Co(male)(H$_2$O)$_2$(H$_2$O)]$_n$ (**3**) [pyo, pyridine-*N*-oxide; dca, dicyanamide; ac, acetate; bpe, 1,2-bis-(4-pyridyl)ethane and male, maleate] have been synthesized and characterized structurally as well as magnetically. The structure determination of complex **1** shows that each octahedral Co(II) in the 1D coordination chain is attached with four μ-1,5-dicyanamide and two pendant pyridine-*N*-oxide ligands, which form mutual relationships with other 1D chains through non-covalent π-π interactions, giving rise to a 2D infinite sheet-like structure. The molecular structure reveals that complex **2** adopts an infinite three-leg ladder-like structure in which three parallel 1D Co(bpe) chains are connected by *syn-syn* and oxo bridging acetate ligands. The dicyanamide ligands are pendant to the terminal Co(II) centers. Complex **3** is an infinite 3D network in which carboxylate groups of the maleate ligand are linked to Co(II) centers in *syn-anti* fashion. The structure of complex **3** has already been reported. The variable temperature (300–2 K) magnetic measurements have been performed for all three complexes. In the case of **2**, the full structure can be rationalized as quasi-isolated trimers; the exchange Hamiltonian that describes magnetic interactions between the effective $S' = 1/2$ spins, at low temperature is $H = -2\sum_{i=x,y,z} J_{1i}(S_{1i}S_{2i} + S_{2i}S_{3i})$. Fixing $g_{\perp} = 6.01$ and $g_{||} = 2.25$, according to the EPR measurements at 4 K, $2J = -3.3$ cm^{-1} is the best-fit parameter. For **1** and **3**, complete fits are not possible for calculating the corresponding *J* parameters for the one- and three-dimensional structures, respectively. Only an approximate *J* value has been calculated for **1**.

Introduction

Molecular self-assembly has emerged as an attractive approach in materials science for the fabrication and design of new functional compounds with potentially useful properties for relevant scientific and technological applications.[1] This process involves the spontaneous aggregation of small molecular building blocks organized by covalent or non-covalent interactions, which recognize each other to form the extended architectures. One strategy to build a well-spanned framework is to utilize certain features of the potentially bridging ligands, such as azide,[2,3] dicyanamide,[4] carboxylate,[5] enolate[6] and different neutral organic spacers[7] having versatile binding modes, conformational flexibility, and the ability to form hydrogen bonds and π-π interactions.[8] Hence this can be utilized as useful connectors to metal centers to form higher dimensional molecular arrangements having exclusive structures and molecular properties.

The polynuclear architecture comprising paramagnetic metal centers connected through various bridging ligands shows unique magnetic properties. The magnetic properties of such systems depend on the nature of the paramagnetic metal center *i.e.*, the spin state, the dimensionality of the system and obviously, on the type of bridging ligand, as it is the pathway that transmits electronic effects between the paramagnetic metal centers.

The dicyanamide has been shown to be a versatile ligand and may coordinate to metal ions as a terminal ligand through a nitrile nitrogen[4,9a] or amide nitrogen,[4,9b] as a μ_2-1,3-bridge through the amide nitrogen and one nitrile nitrogen,[4,9c,d] as an end-to-end μ_2-1,5 bridge through the two nitrile nitrogen atoms with weak antiferromagnetic coupling,[4,9e] as a μ_3-1,3,5 bridge through all of the nitrogen atoms showing weak or strong ferromagnetic coupling[4,9f,10–12] and even *via* the unusual μ-1,1,3,5 mode[4,9g] to construct extended architectures. On the other hand, ligands of the carboxylate family (acetate, malonate, fumarate, maleate, terephthalate, succinate, adipate *etc.*) are among the most widely used O-donor bridging ligands for designing polynuclear complexes having interesting magnetic properties.[13–19] The versatility of carboxylates as ligands is illustrated by the variety of coordination modes they display while acting as bridges. The most common are the so-called

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syn-syn, *syn-anti*, *anti-anti* and oxo bridging modes; the nature and extent of magnetic coupling are highly dependent upon the conformations of these bridging modes.[13a,14a,16a] Neutral organic spacer ligands, such as 4,4′-bipyridine, 1,2-bis-(4-pyridyl) ethane (bpe),[7] *etc*., which generate structural versatility in the solid state due to their conformational flexibility and in combination with the metal, along with different dicarboxylates, produce interesting structures with novel magnetic properties.[13a,15a,16a]

Among the first row transition metal ions containing an unpaired electron, the magnetochemistry of Co(II) is interesting due to the presence of significant spin-orbit coupling in the ground state.[20] Thus, the interpretation of these magnetic results is challenging. To date, the synthesis of high spin polynuclear Co(II) complexes and their characterization by X-ray single crystal structure analysis and magnetic study at low temperature have been reported by several groups.[21]

In this work we attempt to sort out the effect of changes in the bridging ligand, as well as the coordination environment of octahedral Co(II), on the magnetic behavior. Keeping this in mind, in this paper we report the syntheses, structural characterizations and magnetic properties of three multi-dimensional architectures of cobalt(II): $[Co(pyo)_2(dca)_2]_n$ (**1**) $[Co_3(ac)_4(bpe)_3(dca)_2]_n$ (**2**) and $[\{Co(male)(H_2O)_2\}(H_2O)]_n$ (**3**) [pyo, pyridine-*N*-oxide; bpe, 1,2-bis-(4-pyridyl)ethane and male, maleate]. Complex **1** is a 1D coordination polymer where dca acts as bridging ligand and the oxygen of pyo is attached to Co(II) in a monodentate fashion. Complex **2** adopts a 1D three-leg ladder-like structure where the acetate ions and bpe ligands link octahedral Co(II) centers. Complex **3** generates a 3D network with bridging maleate and coordinated water, whose structure was previously reported in the literature.[15b] The low temperature magnetic measurements show all the complexes are weakly anti-ferromagnetically coupled, but the origins of the magnetic coupling are different.

Experimental

Materials and methods

Sodium dicyanamide (dca) and 1,2-bis(4-pyridyl)ethane (bpe) were purchased from Aldrich Chemical Co., Inc.; the other chemicals used were of AR grade.

Elemental analyses (C, H, N) were carried out using a Perkin –Elmer 240C elemental analyzer. The IR spectra were recorded (4000–400 cm^{-1}) on a Nicolet 520 FTIR spectrometer as KBr pellets. Magnetic measurements were carried out on polycrystalline samples (30–40 mg) in the Servei de Magnetoquímica, Universitat de Barcelona, with a Quantum Design MPMS SQUID susceptometer operating at a magnetic field of 0.1 T within the temperature range 2–300 K. The diamagnetic corrections were evaluated from Pascal's constants. EPR spectra were recorded on powder samples at X-band frequency with a Bruker 300E automatic spectrometer at 4 K.

Syntheses

$[Co(pyo)_2(dca)_2]_n$ (1). An aqueous solution (5 mL) of pyridine-*N*-oxide (0.190 g, 2 mmol) was added to an aqueous solution (10 mL) of cobalt nitrate hexahydrate (0.291 g, 1 mmol) with constant stirring. After a few minutes (~10 min) an aqueous solution (5 mL) of sodium dicyanamide (0.178 g, 2 mmol) was added slowly to the reaction mixture and stirred for 30 min. A deep pink compound was separated out, filtered and the filtrate was kept in a $CaCl_2$ desiccator. After a few days shiny pink crystals suitable for X-ray structure determination were obtained. Yield 80%. Anal. calcd for $C_{14}H_{10}CoN_8O_2$ (**1**): C, 44.07; H, 2.65; N, 29.38%. Found: C, 44.1; H, 2.6; N, 29.3%.

$[Co_3(ac)_4(bpe)_3(dca)_2]_n$ (2). Cobalt acetate tetrahydrate (0.249 g, 1 mmol) dissolved in 10 mL of water was allowed to react with 5 mL of an aqueous solution of sodium dicyanamide (0.178 g, 2 mmol) and stirred for 20 min. A methanolic solution (5 mL) of 1,2-bis(4-pyridyl)ethane (0.184 g, 1 mmol), was poured slowly into the resulting solution and the entire mixture was stirred for 2 h. A pale pink compound was precipitated out, filtered and the pink filtrate was allowed to evaporate slowly in an open atmosphere. After a few days needle-like light pink single crystals suitable for X-ray structural study were obtained. Yield 80%. Anal. calcd for $C_{48}H_{48}Co_3N_{12}O_8$ (**2**): C, 52.47; H, 4.38; N, 15.31%. Found: C, 52. 5; H, 4.3; N, 15.3%.

$[\{Co(male)(H_2O)_2\}(H_2O)]_n$ (3). Cobalt nitrate hexahydrate (0.291 g, 1 mmol) dissolved in 10 mL of water was allowed to react with 5 mL of an aqueous solution of disodium maleate (0.160 g, 1 mmol). The entire reaction mixture was stirred for 5 h. The resulting red solution was filtered and the filtrate was kept in a $CaCl_2$ desiccator. After a few days shiny red block crystals suitable for X-ray diffraction were obtained. Yield 80%. Anal. calcd. for $C_4H_8CoO_7$ (**3**): C, 21.12; H, 3.53%. Found: C, 21.1; H, 3.5%.

Crystallographic data collection and refinement†

The X-ray single crystal data collection of complex **1** was carried out on a Nonius DIP-1030H system with Mo-Kα ($\lambda = 0.71073$ Å) radiation. A total of 30 frames were collected, each with an exposure time of 15 min and a rotation angle of 6° about φ, the detector being at 80 mm from the crystal. Cell refinement, indexing and scaling of the data sets were carried out using programs Mosflm[22] and Scala.[22] A total 2213 data (unique reflections, 1199; $R_{int} = 0.0375$) reflections were measured and 1171 data observed [$I > 2\sigma(I)$] for complex **1**. A suitable single crystal of the complex **2** was mounted on a Bruker SMART CCD diffractometer equipped with a graphite monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was also employed using the SAINT[23] program. A total 32487 reflections (unique reflections, 12137, $R_{int} = 0.101$) were collected and 4195 were observed applying the condition $I > 2\sigma(I)$. Both the structures were solved by Patterson syntheses and followed by successive Fourier and difference Fourier syntheses. Full-matrix least-squares refinements on F^2 were carried out for both cases using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. During refinement, the floppy dca groups were found to be disordered over two positions, C46/N9 : C46A/N9A and C48/N12 : C48A/N12A, with occupancy ratio 0.6 : 0.4. The refinement converged to residual indices $R_1 = 0.0350$; $wR_2 = 0.0904$ for complex **1**, and $R_1 = 0.0576$; $wR_2 = 0.0828$ for complex **2** with $I > 2\sigma(I)$. The final difference Fourier map showed the maximum and minimum peak heights at (0.76 and −0.22 e $Å^{-3}$) and (0.36 and −0.23 e $Å^{-3}$) for complexes **1** and **2**, respectively. Complex neutral atom scattering factors[24] were used throughout. All calculations were carried out using SHELXS 97,[25] SHELXL 97,[26] PLATON 99,[27] ORTEP[28] programs and the WinGX System, Ver 1.64.[29] Selected crystallographic data and refinement parameters of both complexes are summarized in Table 1. Selected bond lengths and angles are displayed in Tables 2 and 3 for complexes **1** and **2**, respectively.

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† CCDC reference numbers 220281 and 220282. See http://www.rsc.org/suppdata/nj/b4/b401928h/ for crystallographic data in .cif or other electronic format.

Table 1 Crystallographic data and details of structure refinement for complexes **1** and **2**

	1	**2**
Formula	$C_{14}H_{10}CoN_8O_2$	$C_{48}H_{48}Co_3N_{12}O_8$
Formula weight	381.23	1097.78
Crystal system	Monoclinic	Monoclinic
Space group	$C\,2/m$	$P2_1/c$
a/Å	17.329(4)	13.6306(12)
b/Å	7.318(3)	22.1417(19)
c/Å	6.679(2)	17.3317(15)
β/°	109.10(2)	106.304(2)
U/Å^3	800.4(4)	5020.4(8)
Z	2	4
D_{calcd}/g cm^{-3}	1.582	1.452
μ(Mo-K$_\alpha$)/mm^{-1}	1.099	1.044
$F(000)$	386	2260
$\theta_{\max}$/°	30.49	28.3
Reflections collected	2213	32487
Unique reflections	1199	12137
R_{int}	0.0375	0.101
Obs reflections $[I > 2\sigma(I)]$	1171	4195
$R_1{}^a$ $[I > 2\sigma(I)]$	0.0357	0. 0576
$wR_2{}^a$ $[I > 2\sigma(I)]$	0.0965	0.0828

^{a} $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Results and discussion

IR spectroscopy

Complexes **1** and **2** display strong absorptions at 2290, 2242 and 2161 cm^{-1}, respectively, which correspond to the ν(CN) of the dicyanamide ligand. The higher stretching frequency in complex **1** corroborates that the dicyanamide ligand is bridged between two metal centers, while in **2** the lower frequency is due to the terminally bound pendant dicyanamide ligand.[30] In complex **1** another strong absorption is observed at 1215 cm^{-1}, which may be assigned as the ν(NO) of coordinated pyridine-*N*-oxide. On complexation this NO stretching band shifts by 60 cm^{-1} to a lower frequency from its original position (1265 cm^{-1}).[30] In complex **2** the strong absorptions at 1551 and 1401 cm^{-1} are assigned as ν_{as}(OCO) and ν_s(OCO), respectively, for the bridging acetate. The ν_{as}(OCO) and ν_s(OCO) bands of free acetate ion are at 1560 and 1416 cm^{-1}, respectively. This shifting to lower frequency corroborates the coordination of the acetate to the Co(II) center. The IR spectrum of complex **3** shows absorption bands in the range of 3552–3200 cm^{-1}, corresponding to symmetric and asymmetric OH stretching vibrations, which clearly indicate the presence of crystal water. The bands at 1541 and 1384 cm^{-1} are assigned to the ν_{as}(OCO) and ν_s(OCO) stretching vibrations, respectively, of the bridging maleate ligand.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Co–O1	2.075(2)	N2–C6	1.149(2)
Co–N2	2.121(2)	N3–C6	1.307(2)
N1–O1	1.319(3)		
O1–Co–O1*	180.00	N2–Co–N2**	180.00
O1–Co–N2	86.32(7)	N1–O1–Co	132.42(17)
O1–Co–N2*	93.68(7)	C6–N2–Co	153.22(15)
O1–Co–N2**	93.68(7)	C6–N3–C6#	117.7(2)
O1–Co–N2***	86.32(7)	C5–N1–C1	120.9(2)
N2–Co–N2*	89.31(9)	O1–N1–C1	122.7(2)
N2*–Co–N2**	90.69(9)	O1–N1–C5	116.4(2)

Symmetry codes: (*) $-x, y, -z$; (**) $-x, -y, -z$; (***) $x, -y, z$; (#) $x, -y + 1, z$.

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Co1–O1	2.086(2)	Co1–O3	2.152(2)
Co1–O5	2.088(2)	Co1–O7	2.144(2)
Co1–N1	2.148(3)	Co1–N2	2.125(3)
Co2–O2	2.013(2)	Co2–O3	2.270(2)
Co2–O4	2.135(2)	Co2–N3	2.174(3)
Co2–N4	2.187(3)	Co2–N7	2.037(4)
Co3–O6	2.020(3)	Co3–O7	2.257(2)
Co3–O8	2.117(2)	Co3–N5	2.183(4)
Co3–N6	2.181(3)	Co3–N10	2.052(4)
O1–Co1–O3	88.99(10)	O4–Co2–N7	100.18(12)
O1–Co1–O5	178.57(10)	O4–Co2–C39	29.31(11)
O1–Co1–O7	90.06(10)	N3–Co2–N4	178.15(13)
O1–Co1–N1	89.57(12)	N3–Co2–N7	90.64(15)
O1–Co1–N2	90.22(12)	N3–Co2–C39	86.35(13)
O3–Co1–O5	89.64(10)	N4–Co2–N7	88.19(15)
O3–Co1–O7	179.05(9)	N4–Co2–C39	93.30(13)
O3–Co1–N1	91.22(11)	N7–Co2–C39	129.37(13)
O3–Co1–N2	89.76(10)	O6–Co3–O7	97.39(10)
O5–Co1–O7	91.32(10)	O6–Co3–O8	157.18(11)
O5–Co1–N1	90.08(12)	O6–Co3–N5	89.49(12)
O5–Co1–N2	90.16(12)	O6–Co3–N6	91.30(12)
O7–Co1–N1	88.83(11)	O6–Co3–N10	101.38(16)
O7–Co1–N2	90.18(11)	O6–Co3–C43	127.21(13)
N1–Co1–N2	178.99(12)	O7–Co3–O8	59.79(9)
O2–Co2–O3	95.97(10)	O7–Co3–N5	92.32(11)
O2–Co2–O4	155.08(10)	O7–Co3–N6	90.75(11)
O2–Co2–N3	90.92(12)	O7–Co3–N10	161.23(15)
O2–Co2–N4	90.76(12)	O7–Co3–C43	29.82(12)
O2–Co2–N7	104.74(12)	O8–Co3–N5	91.47(11)
O2–Co2–C39	125.81(12)	O8–Co3–N6	89.05(11)
O3–Co2–O4	59.12(9)	O8–Co3–N10	101.44(16)
O3–Co2–N3	87.20(11)	O8–Co3–C43	29.97(13)
O3–Co2–N4	93.40(11)	N5–Co3–N6	176.70(13)
O3–Co2–N7	159.21(11)	N5–Co3–N10	87.91(15)
O3–Co2–C39	29.86(11)	N5–Co3–C43	92.60(13)
O4–Co2–N3	88.61(11)	N6–Co3–N10	88.80(15)
O4–Co2–N4	90.19(11)	N6–Co3–C43	89.48(13)
N1–Co3–C43	131.41(17)	Co3–N6–C32	123.1(3)
Co1–O1–C37	145.1(3)	Co3–N6–C36	118.9(3)
Co2–O2–C37	135.4(3)	Co1–O3–Co2	124.78(11)
Co2–N7–C45	176.5(4)	Co1–O3–C39	148.0(2)
Co2–O3–C39	86.7(2)	Co2–O4–C39	93.5(2)
Co3–N10–C47	174.2(5)	Co1–O5–C41	143.7(3)
Co3–O6–C41	134.7(3)	Co1–O7–Co3	123.47(11)
Co1–O7–C43	149.2(3)	Co3–O7–C43	87.3(2)
Co3–O8–C43	93.5(3)	Co1–N1–C1	120.4(3)
Co1–N1–C5	121.3(3)	Co1–N2–C8	120.9(3)
Co1–N2–C12	120.4(3)	Co2–N3–C13	119.8(3)
Co2–N3–C17	121.7(3)	Co2–N4–C20	120.3(3)
Co2–N4–C24	121.0(3)	Co3–N5–C25	124.4(3)
Co3–N5–C29	117.7(3)	Co2–C39–O3	63.40(18)
Co2–C39–C40	172.3(3)		

Electronic spectra

Electronic spectra have been measured in the solid state by the diffuse reflectance method. Distorted octahedral Co(II) complexes usually show three d-d transitions, corresponding to $\nu_1(^4T_{1g} \rightarrow {}^4T_{2g})$, $\nu_2(^4T_{1g} \rightarrow {}^4A_{2g})$ and $\nu_3(^4T_{1g} \rightarrow {}^4T_{2g}(P))$.[31] The first one generally appears in the near-infrared zone; the second one is normally a weak shoulder, not easy to identify, and the third one is normally the best defined.[31] Complexes **1**, **2** and **3** have different chromophores: CoN_4O_2, CoN_2O_4 and CoO_6, respectively. The environment of the Co(II) in complex **1** is slightly axially distorted (4 N at 2.121 Å and 2 O at 2.075 Å). In complex **2** there are three non-equivalent Co(II) ions, which are more distorted in comparison to **1**: for the three different cobalt ions there are six different Co–L distances between 2.013–2.270 Å. Complex **3** is similar to complex **2** (six different Co–L distances between 2.067–2.137 Å). The three d-d transitions, together

Table 4 The d-d transition bands and the calculated crystal-field parameters for complexes **1–3**

Complex	v_1/cm^{-1} (nm)	v_2/cm^{-1} (nm)	v_3/cm^{-1} (nm)	Dq/cm^{-1}	B/cm^{-1}	A
1	8265 (1210)	15870 (630)	19300 (518)	938.2	810.1	1.32
2	8795 (1137)	~14300 (~700)	19610 (480, 510, 540)	994.1	793.3	1.42
3	8196 (1220) 6869 (1455)	~14300 (~700)	20000 (475, 525)	934.0	863.2	1.18

with the ligand-field parameters, Dq, B and A, calculated from the formula given by Dou,[32] employing v_1 and v_3 (v_2 is too weak and is only a shoulder), are summarized in Table 4. The A factor, in the frame of T and P isomorphism, is 1.5 in the limit of the weak field and 1 in the limit of the strong field. A factors for complexes **2** and **3** have some uncertainty because v_1 is split into two bands in complex **3** and the v_3 band is split into three bands in complex **2** and two bands in complex **3**. This is logical taking into consideration the low symmetry of the Co(II) chromophores. To calculate Dq, B and A we have taken the possible envelop (average) of these multiple bands.

Descriptions of structures

Complex 1. The X-ray structural determination of complex **1** displays a 1D polymeric pattern built up of colinear octahedral cobalt ions, each located on a $2/m$ site connected by pairs of bridging dca ligands. The latter anions coordinate through the nitrile nitrogens and span the metals at 7.318(3) Å (Fig. 1), corresponding to the length of the crystallographic b axis. The metal-metal separation through the dca anions is in good agreement with the distance of 7.370 Å found in the anionic dicyanamidometallate ladder-like 1D polymer $[(Ph_4As)_2\{Co_2(dca)_6(H_2O)\} \cdot H_2O \cdot CH_3OH]_n$.[33]

The slightly distorted octahedral coordination sphere of the metal is completed by two neutral pyridine oxide ligands. A selection of bond lengths and angles is reported in Table 2. The Co–N distances, of 2.121(2) Å, are longer by about 0.05 Å with respect to the Co–O(1) of 2.075(2) Å. The terminal C≡N and amide C–N dca distances indicate triple and single bond character [1.149(2) and 1.307(2) Å, respectively], as typically observed for this bonding mode (Table 2). For symmetry reasons, the nitrogen atom N2 and its symmetry related counter parts lie in the equatorial plane along with the Co atom. The pyo oxygen atom O1 and its symmetry related counter part occupy the *trans*-axial position (Fig. 1). It is interesting to note that the Co–O–N bond angle, of 132.42(17)° [to which corresponds a very short N–O bond of 1.319(3) Å], is significantly larger than the values reported in several hexakis(pyridine oxide)cobalt(II) salts,[34] which average 119°. On the other hand, the Co–O and the N–O bond lengths in the mentioned structures appear comparable (means of 2.08, 1.33 Å, respectively) to those here reported. The present Co–O–N angle is closer to the values of *ca.* 124.3° for a bridging pyo ligand detected in the polymeric compound $[CoCl_2(pyo)(H_2O)]_n$.[35]

This feature, together with the slight larger value observed for O(1)–N(1)–C(1) with respect to the O(1)–N(1)–C(5) bond angle [122.7(2) *vs.* 116.4(2)°], might be invoked to favor a stacking arrangement of the pyridine rings. In fact, the crystal packing evidences pyo rings of nearby polymers interlocking at alternating distances of *ca.* 3.5 and 3.8 Å. Thus, the chains are held together by face-to-face π-π interactions arising among the heterocyclic rings, giving rise to 2D layers, as shown in Fig. 2. The shorter Co–Co separation between two interacting chains is 9.757 Å, while that between two described sheets is 6.679 Å.

Complex 2. The coordination environment of the Co(II) ions, with atom labelling scheme, is shown in Fig. 3. The structure determination of complex **2** discloses an infinite three-leg ladder-like topology elongated in the direction of the crystallographic a axis. This type of interesting topology has also been observed in complex $[Zn_3(ac)_4(4,4'\text{-bipyridine})_3\{N(CN)_2\}_2]$ where acetate (ac) acts as a bridging ligand to the octahedral metal center.[36] As shown in Fig. 4 the Co(II) ions are located at the cross points of the rungs and rails. Each of the three Co(II) ions (Co1, Co2, Co3) is coordinated to two bpe ligands, which act as the rails of the ladder, to give three linear chains. The Co…bpe…Co distances in the three chains are equal (13.63 Å). These three chains are linked by ac rungs, which adopt

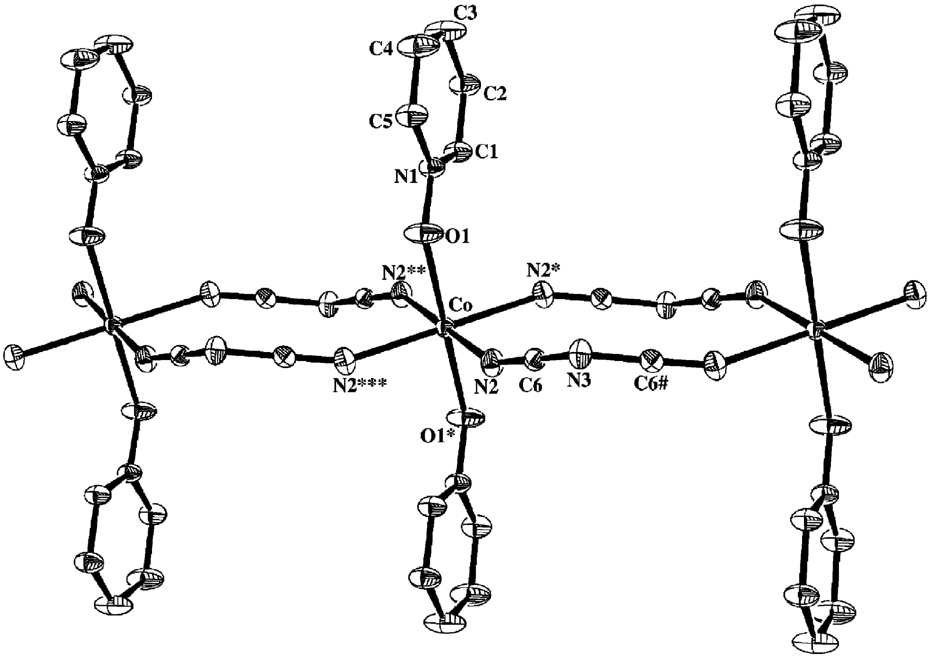

Fig. 1 Molecular structure of complex **1** with atom labelling scheme.

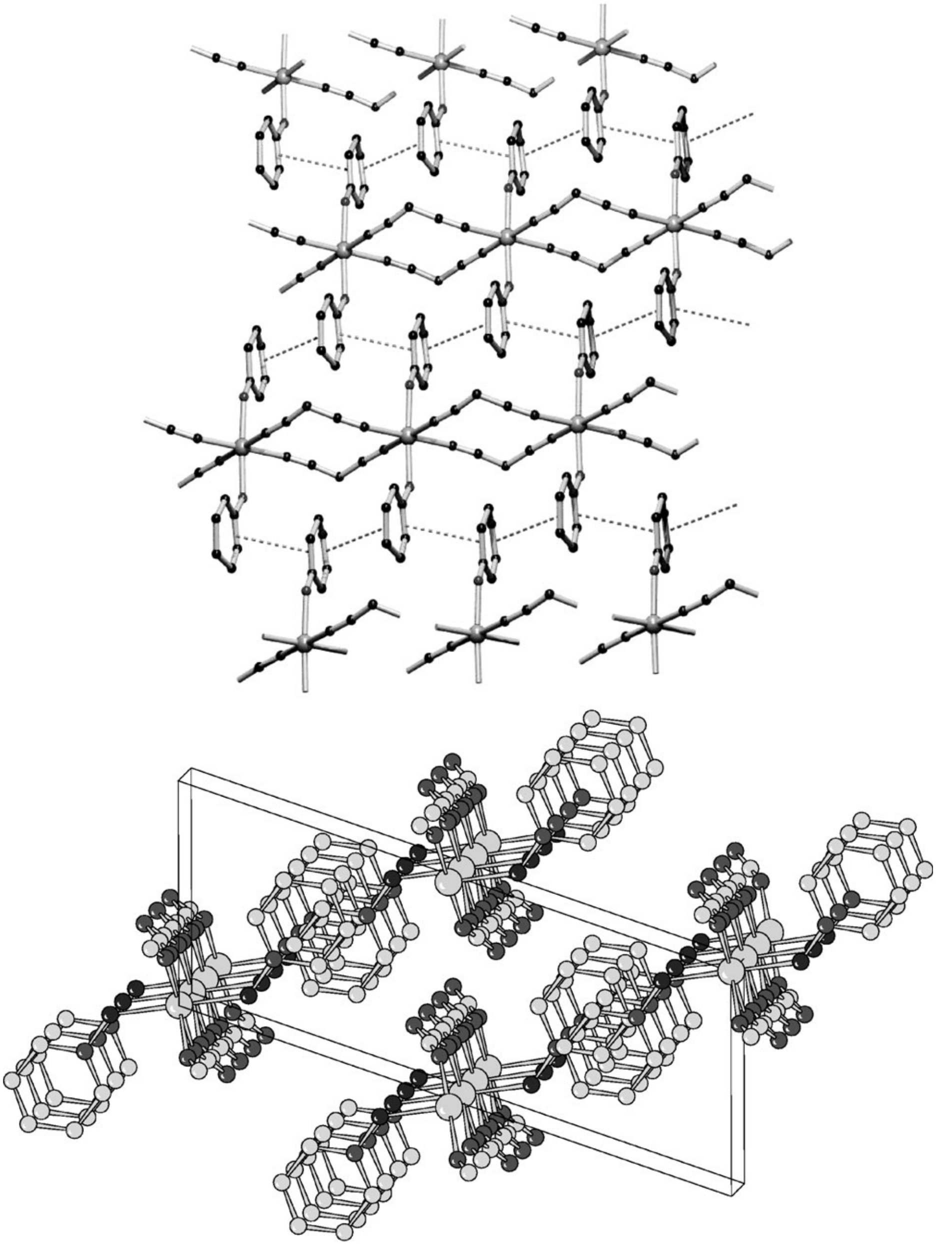

Fig. 2 Crystal packing of complex **1**: (top) three adjacent π interacting polymeric chains; (bottom) view down the crystallographic *b* axis showing the stacking of pyridine rings with the formation of 2D layers.

positions perpendicular to the bpe–Co–bpe axis to give distorted octahedral geometries at the Co(II) centers. The Co…(ac)$_2$…Co distances are 3.92 Å for Co1…Co2 and 3.88 Å for Co1…Co3. It is worth mentioning that there is a strong discrepancy between the coordination environment of Co1 (central) and Co2 or Co3. The Co1 ion coordination is almost perfectly octahedral as the three *trans* angles, O3–Co1–O7 [179.05(9)°], O1–Co1–O5 [178.57(10)°] and N1–Co1–N2 [178.99(12)°], are very close to 180°. The *cisoid* angles are in the range 88.83(11)–91.32(10)°. The six Co1–L (where L is any bonded atom to Co1) distances are between 2.086(2) and 2.152(2) Å. Thus the spin-orbit contribution in this Co1 ion must be very important. On the contrary, Co2 and Co3 are very distorted, mainly in the plane of the molecule, due to the small bite angles of 59.12(9)°, 59.79(9)° by the chelated O4–C39–O3 and O7–C43–O8. The other angles between *trans* ligands in the main plane are O2–Co2–O4 [155.08(10)°] and N7–Co2–O3 [159.21(11)°] for Co2 and O7–Co3–N10 [161.23(15)°] and O8–Co3–O6 [157.18(11)°] for Co3. On the contrary, the *trans* vertical angles N3–Co2–N4, 178.15(13)°, and N5–Co3–N6, 176.70(13)°, are close to 180°. Co1 links Co2 and Co3 with a typical *syn-syn* carboxylate bridging conformation through O2–C37–O1 and O5–C41–O6 and with an oxygen bridge (O3 and O7). The Co–L distances are in the range 2.013(2)–2.270(2) Å for Co2 and 2.020(3)–2.257(2) Å for Co3 (where L is any bonded atom to Co2 or Co3). Thus, in these two Co(II) ions the spin-orbit contribution will be partially quenched due to the distortion from octahedral geometry. Adjacent parallel chains are engaged in π-π interactions: the distance between the barycenters of the N1–C1→C5 and N5–C25→C29 rings is 3.86 Å and that of N2–C8→C12 ring and N4–C20→C24 ring is 3.75 Å, which further stabilize the formation of the three-leg ladder.

Complex 3. We have determined the crystal structure of complex **3** and found that all the parameters are same as those reported by Pajtášová *et al.*[15b] In addition to the crystal structure description given in the above paper, some other interesting features are given below. The complex is a 3D polymeric network structure, in which each Co(II) ion is linked to other four Co(II) analogs by one carboxylate bridging ligand

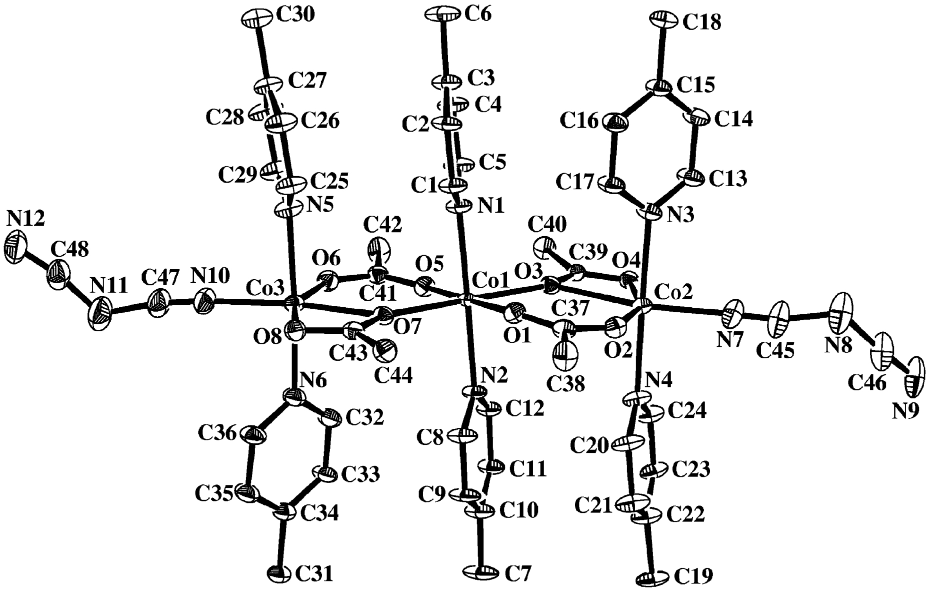

Fig. 3 The coordination environment of the Co(II) ions in complex **2**, with atom labelling scheme.

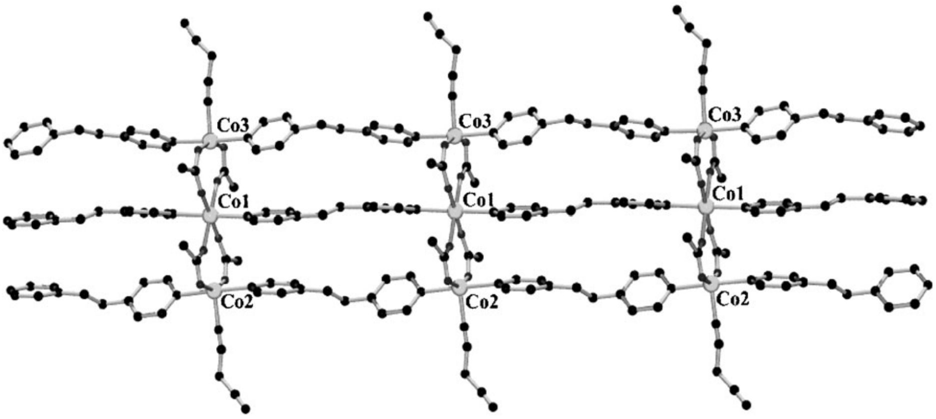

Fig. 4 Infinite three-leg ladder-like topology elongated in the direction of the crystallographic *a* axis in complex **2** [Co(II) ions are located at the cross points of the rungs and rails]

through the oxygen atoms O1, O2, O3 and O4 in *syn-anti* conformation [Fig. 5(Top)]. The torsion angles, Co–O4–O3–Co and Co–O1–O2–Co are 113.1° and 100°, respectively, reflecting a very distorted coordination. Complex **3** possesses small channels along [101] filled with solvent water molecules [Fig. 5(Bottom)] with a dimension of *ca.* 5.0 × 5.5 Å^2 (atom to atom).

Magnetic properties

Considering the spin-orbit coupling due to the $^4T_{1g}$ ground state for octahedral Co(II) complexes,[20] exact calculations for deriving the J parameter from experimental data over the full temperature range is not possible except for dinuclear complexes.[37,38] Other small polynuclear systems can also be fitted through sophisticated computer programs, based on full diagonalization methods in the low temperature region (where the effective spin S' is 1/2).[39] One-dimensional systems of Co(II) are frequently associated with anisotropic Ising systems, and they can be fitted in the low temperature zone assuming again an effective spin $S' = 1/2$.[40] More recently, Rueff *et al.*[40c,41] have proposed a phenomenological approach for some low-dimensional Co(II) systems that gives an estimate of the strength of the antiferromagnetic exchange interactions. They have postulated the phenomenological equation: $\chi_M T = A\exp(-E_1/kT) + B\exp(-E_2/kT)$ in which $A + B$ equals the Curie constant [$\approx$2.8–3.4 cm^3 mol^{-1} K for octahedral cobalt(II) ions] and E_1, E_2 represent the "activation energies" corresponding to the spin-orbit coupling and the antiferromagnetic exchange interaction. E_1/k, the effect of spin-orbit coupling and site distortion, is of the order of +100 K.[40c,41,42] This equation adequately describes the spin-orbit coupling, which results in a splitting between discrete levels, and the exponential low-temperature divergence of the susceptibility. Very good results have been reported in one- and two-dimensional cobalt(II) complexes.[40c,41]

An important experimental feature in almost all octahedral cobalt(II) complexes is that the $\chi_M T$ (or μ_{eff}) values at room temperature are greater than those expected for one isolated spin-only ion ($\chi_M T = 1.87$ cm^3 mol^{-1} K for a $S = 3/2$ ion), indicating that an important orbital contribution is involved.[20] Typical values of $\chi_M T$ (or μ_{eff}) are 2.75–3.4 cm^3 mol^{-1} K (4.7–5.2 μ_β).[20,43] Lower values at room temperature. indicate deviations from ideal octahedral geometry.[43]

Complex 1. The $\chi_M T$ *vs.* T plot for **1** (χ_M is the molar magnetic susceptibility for one Co^{II} ion) is shown in Fig. 6(A). $\chi_M T$ value at 300 K is 2.7 cm^3 mol^{-1} K. The $\chi_M T$ value of **1** continuously decreases to 1.4 cm^3 mol^{-1} K at 2 K. At lower temperatures (from 15 to 2 K) there are significant differences in the $\chi_M T$ values when applying small magnetic fields. This feature indicates the presence of a small amount of ferromagnetic or canted antiferromagnetic-ordered impurities, likely α- or β-[Co(dca)$_2$], which have T_c at 9–10 K, respectively.[4] The presence of this small amount of impurities was

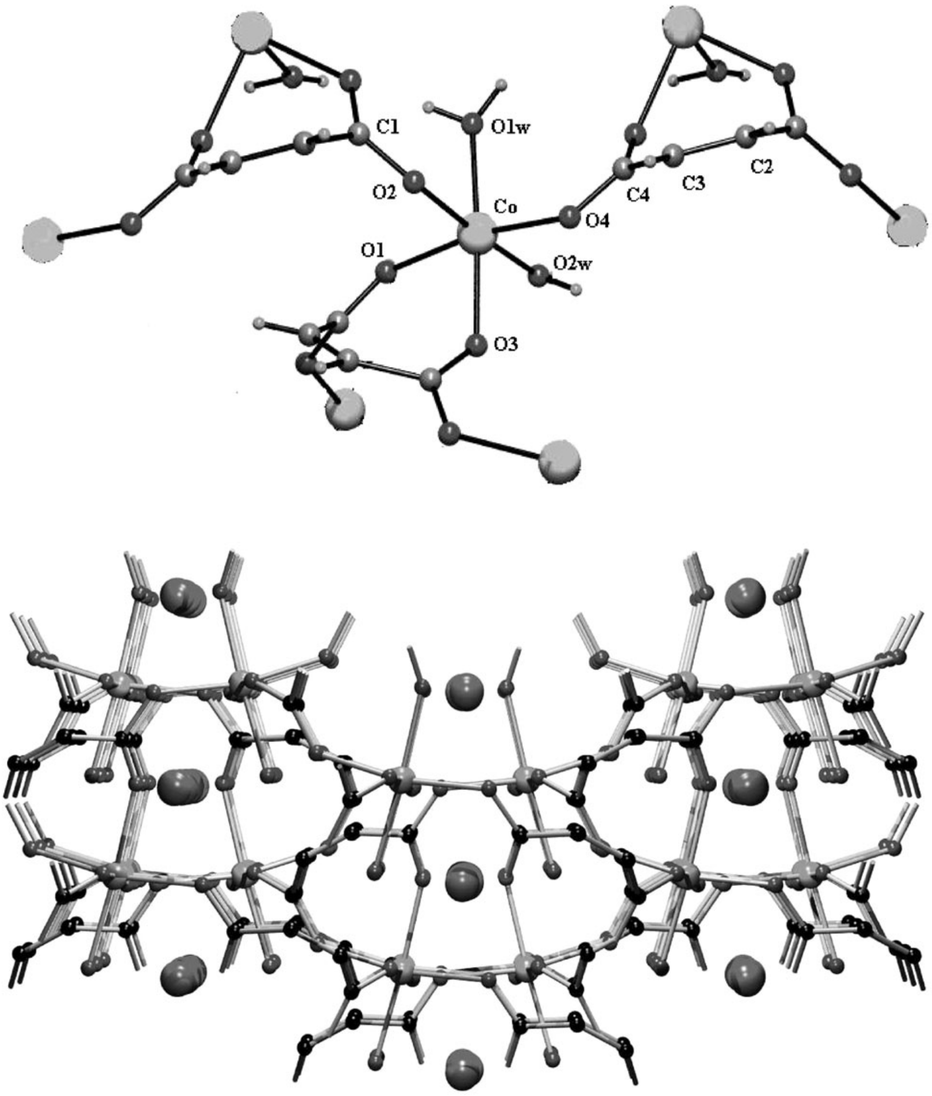

Fig. 5 (Top) Schematic representation of the environment of each Co(II) ion in complex **3**, linked to four crystallographically equivalent Co(II) ions through *syn-anti* carboxylate bridges. (Bottom) A view of channels along [101] filled with solvent water molecules in complex **3**.

found in three different samples, obtained in different syntheses. This feature (the presence of these magnetic ordered impurities) is, unfortunately, very frequent in most of the Co-dca-L derivatives.[44] All calculations given below refer to the sample with the smallest amount of impurities, as indicated by the deviation of $\chi_M T$ at low temperature and low field.

To date it is impossible to fit the high-temperature region of a one-dimensional Co(II) complex such as **1**, owing to the existence of λ (spin-orbit coupling), A (measure of the strength of the crystal field, which is 1.32 in complex **1**, Table 4) distortion with respect to the regular octahedral geometry and J. Theoretically it could be possible to use the Ising formula for an $S' = 1/2$ one-dimensional system,[40] but the presence of the small amount of α- or β-[Co(dca)$_2$] impurities (*vide supra*) makes this procedure unsuitable. Thus, the only method that we can try to calculate an estimated J value is by using the two-exponential Rueff expression, mentioned above, which is suitable for any temperature greater than the possible T_c.[40c,41] The fit values obtained with this procedure are: $A + B = 3.01$ cm^3 mol^{-1} K, which perfectly agree with those given in the literature for the Curie constant ($C \approx 2.8$–3.4 cm^3 mol^{-1} K);[40c,41] $E_1/\mathrm{k} = 67.19$ K is of the same magnitude than those reported by Rueff *et al.* for several one- and two-dimensional cobalt(II) complexes.[41] As for the value found for the antiferromagnetic exchange interaction, it is very weak ($E_2/\mathrm{k} = 0.77$ K), corresponding to $J = -1.54$ K (-1.07 cm^{-1}), according to the Ising chain approximation, $\chi_M T \propto \exp(J/2kT)$. The small J value is compatible with the $\mu_{1,5}$-dca bridging ligands, which always give almost negligible coupling parameters.[20b] Our attempts to fit complex **1**, assuming isolated Co(II) ions with octahedral geometry,[20,45] did not give good results. Thus, we can conclude that complex **1** actually behaves as a one-dimensional system, which is weakly magnetically coupled by the dca ligands and, perhaps , by intramolecular π-π interactions (see structural part). The EPR spectrum at 4 K is shown in the inset of Fig. 6(B) with its best simulation. The calculated g values, $g_\perp = 5.0$ and $g_{||} = 2.7$, indicate a significant amount of the spin-orbit coupling, as expected. The reduced magnetization curve, $M/N\beta$, at 2 K tends to $2.1N\beta$ at 5 T. Simulating the Brillouin law for the average g value deduced from the EPR spectrum, the theoretical curve lies slightly above the experimental one, in agreement with the small antiferromagnetic J value [Fig. 6(B)].

Complex 2. The magnetic properties of complex **2** in the form of $\chi_M T$ *vs.* T plot (χ_M is the molar magnetic susceptibility for three Co^{II} ions) are shown in Fig. 7(A). The value of $\chi_M T$ at 300 K is 9.6 cm^3 mol^{-1} K and continuously decreases from room temperature to 2.50 cm^3 mol^{-1} K at 2.06 K.

As shown in the crystallographic part (Fig. 3), complex **2** is comprised of trinuclear Co(II) entities in which all Co2 and Co3 ions are linked to the central Co1 ion by two carboxylate ligands in two different ways: with a typical *syn-syn*

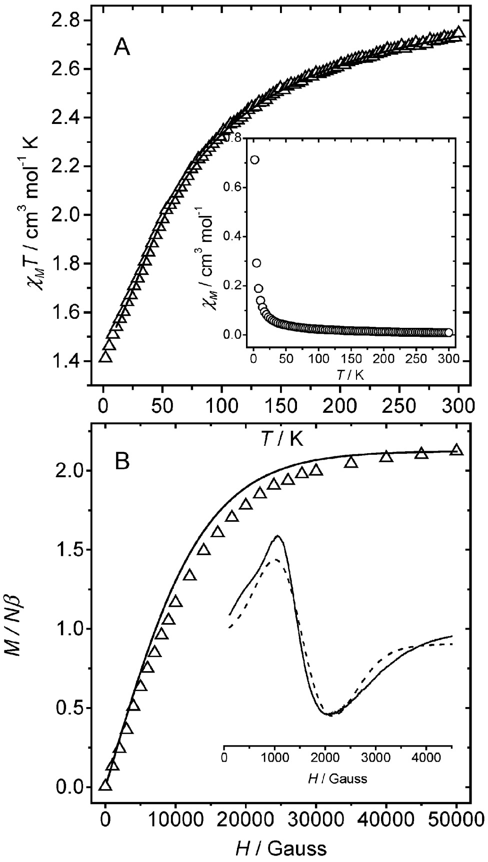

Fig. 6 (A) χ_M (inset) and $\chi_M T$ plots from room temperature to 2 K for complex **1**. Solid line in the $\chi_M T$ plot represents the best-fit curve (see text). (B) Plot of the reduced magnetization ($M/N\beta$) with the Brillouin law simulation for an average *g* value drawn from EPR data. Inset: solid X-band EPR spectrum at 4 K. The dotted line represents the best simulation made with the parameters given in the text.

carboxylate conformation (O2–C37–O1 and O5–C41–O6) and with an oxygen bridge (O3, O7). Thus, we can assume that only one *J* parameter is necessary for studying the coupling between Co3–Co1 and Co1–Co2, considering that the two theoretical *J* parameters (J_{12} and J_{13}) are equal due to the very small geometrical differences in distances and angles in each moiety (Co1–Co2 and Co1–Co3). Each trinuclear entity is linked to two other trinuclear entities by the long bpe to give a 1D system. These ligands cannot transmit any magnetic coupling. Thus, from the magnetic point of view, the 1D structure can be reduced to trinuclear Co3 entities, almost isolated among themselves. Antiferromagnetic interactions are observed in carboxylato-bridged complexes when the carboxylate adopts the *syn-syn* conformation. A few Co(II) complexes with this interaction have been rigorously studied from the magnetic point of view and they are always antiferromagnetically coupled.[46] The μ-oxo (or μ-hydroxo) bridging ligand usually exhibits antiferromagnetic coupling.[47,48]

As indicated above, the full magnetic data (300–2 K) is impossible to fit, owing to the spin-orbit coupling of Co(II) ion. But at low temperature we can assume that only the effective $S' = 1/2$ is populated.[20] Thus, the magnetic data of **2**, from 40–2 K [Fig. 7(A) inset] were fitted to a trimer model that considers anisotropic exchange interactions between the magnetic Co(II) ions.[39] Here, the exchange Hamiltonian that describes the exchange interactions between the effective $S = 1/2$ spins is written as:

$$H = -2\sum_{i=x,y,z} J_{1i}(S_{1i}S_{2i} + S_{2i}S_{3i})$$

In this Hamiltonian the coupling (J_{23}) between the two terminal Co(II) ions is assumed to be nil. If we assume that *g* values

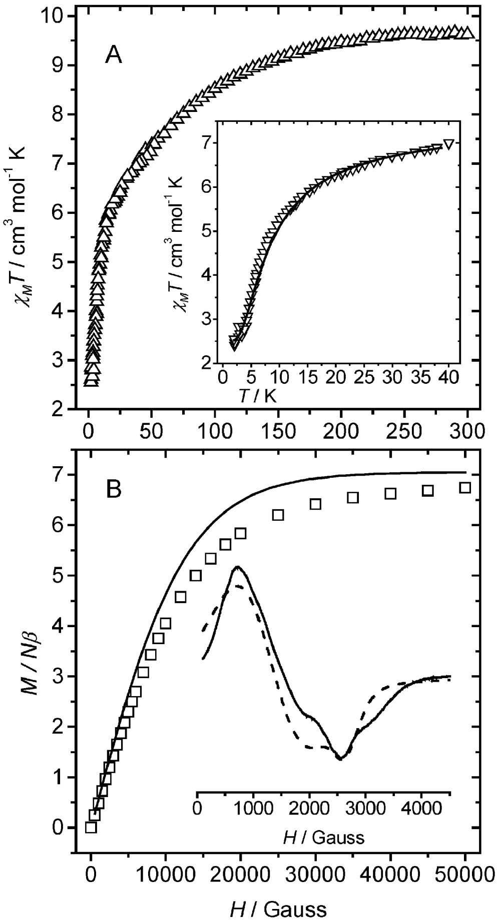

Fig. 7 (A) $\chi_M T$ *vs.* *T* plots for complex **2**: full temperature range and low temperature range (inset). Solid line represents the best fit according to the method indicated in the text. (B) Plot of the reduced magnetization ($M/N\beta$) with the Brillouin law simulation for an average *g* value drawn from EPR data. Inset: EPR spectrum of complex **2** at 4 K. The dotted line represents the best simulation made with the parameters given in the text.

are the same for the three cobalt(II) ions, these can be obtained (at least as an average) from the EPR spectrum at 2 K, being $g_\perp = 6.01$ and $g_{||} = 2.25$ [Fig. 7(B), inset]. With this hypothesis and using the MAGPACK program,[39] the exchange parameter $2J = -3.3$ cm^{-1} is obtained. The *J* and *g* values have the same order of magnitude as those reported for other different distorted octahedral Co$_x$ complexes.[42,49] The reduced magnetization ($M/N\beta$) for **2** at 2 K [Fig. 7(B(] tends to 6.7$N\beta$, as expected for three cobalt(II) ions. Simulating the reduced magnetization curve at 2 K for an effective $S_{\text{eff}} = 1/2$ and $g = 4.7$ (average from EPR spectrum), the calculated curve lies above the experimental one, indicating small antiferromagnetic coupling, as calculated by the susceptibility measurements [Fig. 7(B)].

Complex 3. χ_M and $\chi_M T$ *vs.* *T* plots for **3** (χ_M is the molar magnetic susceptibility for one Co^{II} ion) are shown in Fig. 8(A). The $\chi_M T$ value at 300 K is 3.03 cm^3 mol^{-1} K and continuously decreases to 1.45 cm^3 mol^{-1} K at 2.0 K. These values and the shape of the curve are typical for almost isolated Co(II) ions.[42] No fit is possible for a 3D net, for which the formula given above for an anisotropic 1D system is not suitable. The reduced magnetization $M/N\beta$ curve at 2 K, which tends to 2.1 $N\beta$ at 5 T, is given in Fig. 8(B), together with the EPR spectrum at 4 K (inset) with its best simulation. The calculated *g* values, $g_\perp = 5.25$ and $g_{||} = 2.21$, indicate a significant presence of the spin-orbit coupling. g_{average} is thus 4.23, in very good agreement with the standard *g* values for Co(II) in

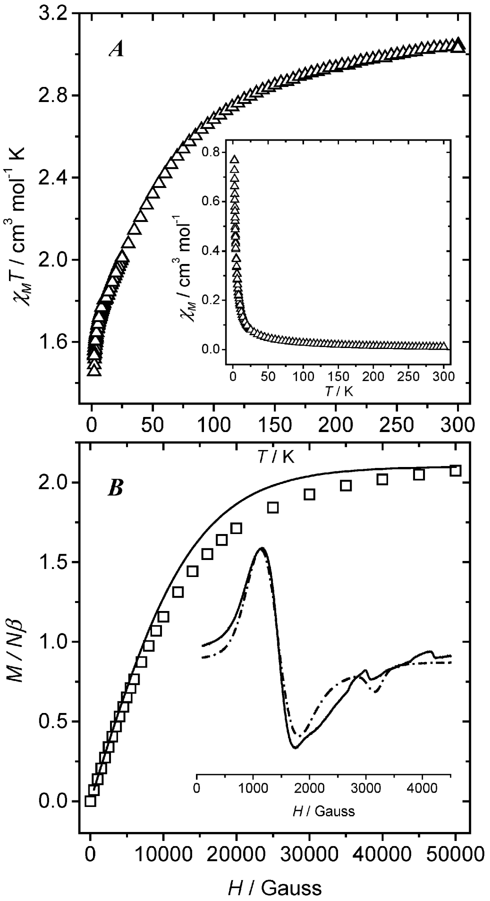

Fig. 8 (A) $\chi_M T$ and χ_M (inset) *vs.* *T* plots for complex **3**. (B) Plot of the reduced magnetization ($M/N\beta$) with the Brillouin law simulation for an average *g* value drawn from EPR data. Inset: EPR spectrum of complex **3** at 4 K. The dotted line represents the best simulation made with the parameters given in the text.

octahedral symmetry ($g_{iso} = 4.33$).[42] Simulating the reduced magnetization curve at 2 K for an effective $S_{eff} = 1/2$ and $g = 4.23$, the calculated curve lies slightly above the experimental one, indicating very small antiferromagnetic coupling, undoubtedly due to the carboxylate bridge in the *syn-anti* conformation [Fig. 8(B)].

Conclusion

We have synthesized and shown the structural dependence of three complexes of novel high-spin Co(II) polymers with different bridging environments. The obtained compounds have a 1D coordination chain interlocked by π-π interactions to generate a 2D sheet in **1**, a novel and very uncommon 1D chain in **2**, and a 3D network structure in **3**. Complex **2** has a three-leg ladder topology of coupled cobalt(II) ions. Such a structure is very uncommon. We have studied the variation in magnetic behavior of these high-spin Co(II) complexes with the change of bridging environment as well as structural features. Complex **2** is analyzed as a trinuclear entity with two types of bridges, *syn-syn* carboxylate and μ-oxo. The *J* value for the trinuclear entity has been calculated employing full diagonalization methods through specific computational programs, using the susceptibility data at low temperature, in which $S' = 1/2$ is a good spin number for Co(II) ions. Very likely, the μ-oxo bridge is the main source of the non-negligible antiferromagnetic coupling in **2**. It is impossible to calculate the exact *J* parameter in complexes **1** and **3** owing to their topology, but the magnetic parameters clearly indicate non-negligible antiferromagnetic couplings.

Acknowledgements

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