FULL PAPER

Dalton
www.rsc.org/dalton

One- and two-dimensional metal–dicyanamido complexes with a flexible bridging co-ligand: structural and magnetic properties†

En-Qing Gao,[a,b] Shi-Qiang Bai,[a,b] Zhe-Ming Wang[a] and Chun-Hua Yan*[a]

[a] *State Key Lab of Rare Earth Materials Chemistry and Applications & PKU-HKU Joint Lab on Rare Earth Materials and Bioinorganic Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. E-mail: chyan@chem.pku.edu.cn*

[b] *Department of Chemistry, Qufu Normal University, Qufu 273165, Shandong, China*

Received 2nd January 2003, Accepted 13th March 2003

First published as an Advance Article on the web 26th March 2003

Five coordination-polymers of formula $[M(dca)_2(bpp)]_\infty$ [bpp is the flexible 1,3-bis(4′-pyridyl)propane ligand, dca = dicyanamido anion, M = Mn (**1**), Co (**2**), Zn (**3**), and Cd (**4a** and **4b**)] have been synthesized and structurally characterized. Compounds **1**, **2**, **3** and **4a** are isomorphous and consist of uniform chains in which adjacent metal ions are triply linked by two 1,5-dca and one bpp bridges and each metal ion is octahedrally coordinated with a *trans* geometry. The $M(dca)_2$ chain motif adopts a sinusoidal topology with the $M(dca)_2M$ rings in a boat conformation, to adapt to the arc-shaped bpp ligand, which here acts as an intrachain bridge and takes an unusual *GG* conformation. Compound **4b** is thermodynamically more stable than **4a**. The structure of **4b** consists of extended 2D coordination layers in which neighboring metal ions are linked by a bpp or two 1,5-dca bridges and the metal ion is in a *cis*-octahedral environment. The $M(dca)_2$ chain motif adopts a zigzag topology with the $M(dca)_2M$ rings in the usual flat conformation, and the bpp ligand takes a *TT* conformation and acts as an “arch bridge” between adjacent chains to yield a corrugated (4,4) layer. Each layer is interpenetrated with two adjacent layers, generating an interesting 3D polycatenane. The temperature dependence of the magnetic susceptibility has been investigated for the Mn(II) and Co(II) species. **1** behaves as a 1D Heisenberg Mn(II) chain with a rather weak intrachain antiferromagnetic interaction, and **2** exhibits the complicated behavior characteristic of polynuclear Co(II) species with an octahedral coordination geometry.

Introduction

The metal complexes of the dicyanamido [dca, $N(CN)_2^-$] ligand have attracted continuous attention in the last four years, in connection with their interesting extended architectures and magnetic properties.[1–20] Dicyanamido ion has been shown to be a versatile ligand and may coordinate to metal ions as a terminal ligand through a nitrile nitrogen, a μ_2-1,3 bridge though the amido nitrogen and one nitrile nitrogen, an end-to-end μ_2-1,5 bridge through the two nitrile nitrogen atoms, a μ_3-1,3,5 bridge through all of the nitrogen atoms, and even the unusual μ_4-1,1,3,5 bridge with one of the two nitrile nitrogen atoms bonding two metal ions.[21] The coordinative versatility, together with the coordination requirements of specific metal ions, has allowed for the construction of different architectures with diverse magnetic properties. The binary $M(dca)_2$ systems exhibit a 3D rutile-like structure with octahedral metal ions linked through μ_3-dca bridges or a 2D sheet structure with tetrahedral metal ions linked through μ_2-1,5-dca, and they provide a rich diversity of magnetic properties including ferromagnetism, canted antiferromagnetism and paramagnetism.[2]

The incorporation of a third component into metal dicyanamides can lead to dramatic modification in the polymeric networks and magnetic properties. Recently, several compounds containing polymeric $[M(dca)_3]^-$ anions have been reported. The anionic polymeric topologies, 2D square or hexagonal sheets or 3D networks, are 1,5-dca bridged and cation templated.[3] More notably, a large number of coordination polymers have been obtained through the incorporation of auxiliary ligands or solvent molecules into the metal coordination spheres. In these ternary systems, the dca bridge generally adopts the μ_2-1,5 mode with only a few exceptions of μ_3-1,3,5[4] and μ_2-1,3.[4a,5] As far as magnetic properties are concerned, μ_2-1,5-dca is not a good linker since it generally propagates very weak magnetic interaction, if any, especially for Mn(II) species. However, it is an attractive linker from the point of view of crystal engineering since it is capable of forming a rich variety of bridging network topologies (See Electronic Supplementary Information†). Monodentate co-ligands (including coordinated solvent molecules) often led to 1D linear chains with double dca bridges[6–10] and 2D square grid-like sheet with single dca bridges,[7,11] with rare examples of ladder structures.[3d,11] The incorporation of bi- or tridentate chelating ligands has produced zigzag chains with double[8,13] or single[5b,10,14] bridges, 2D (6,3) sheets with mixed single–double bridges and a herring-bone-like topology.[10,13a] Some M–dca coordination polymers containing bridging co-ligands have also been reported recently[15–17] and their network topologies can be conveniently described based on the M–dca bridging motifs. For instance, various 2D (4,4) sheet structures[12a,15] and 3D networks[12,15] have been constructed by pillaring chains or sheets of $M(dca)_2$ with ditopic ligands such as pyrazine (pz), 4,4′-bipyridine (bpy), 2,2′-bipyramidine (bpym) or 2,5-dimethylpyrazine.

While the co-bridges that have been used are essentially rigid, we are interested in incorporating flexible ditopic ligands into metal dicyanamides, expecting that the flexibility of the co-bridges, combined with the coordinative diversity of the dca ion, may lead to novel polymeric topologies. We have chosen 1,3-bis(4′-pyridyl)propane (bpp), which can assume four different conformations (*TT*, *TG*, *GG* and *GG*′) and has been widely used in crystal engineering of supramolecular coordination architectures.[18] The preliminary results of our investigation of the Cd–dca–bpp system have been briefly communicated.[19] Two reports on the M–dca–bpa systems (M = Cu and Mn), which also contain a flexible co-bridge, 1,2-bis(4′-pyridyl)ethane (bpa), have appeared very recently.[20] Herein, we report in detail the synthesis and crystal structures of five coordination polymers, $[M(dca)_2(bpp)]_\infty$, where M = Mn (**1**), Co (**2**), Zn (**3**), and Cd (**4a** and **4b**), together with the magnetic properties of the Mn(II) and Co(II) species.

---

† Electronic supplementary information (ESI) available: a scheme of the different bridging network topologies of dca complexes. See http://www.rsc.org/suppdata/dt/b2/b212886a/

DOI: 10.1039/b212886a

Table 1 Summary of crystallographic data for the complexes

	1	**2**	**3**	**4a**	**4b**
Formula	$C_{17}H_{14}N_8Mn$	$C_{17}H_{14}N_8Co$	$C_{17}H_{14}N_8Zn$	$C_{17}H_{14}N_8Cd$	$C_{17}H_{14}N_8Cd$
Formula weight	385.30	389.29	395.73	442.76	442.76
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*Fddd*
a/Å	16.0806(5)	15.9615(4)	16.0448(3)	16.3548(5)	13.2140(2)
b/Å	10.4123(4)	10.2737(3)	10.3215(2)	10.4935(4)	21.7332(4)
c/Å	12.7979(5)	12.7113(5)	12.8434(3)	13.0115(4)	28.7125(5)
β/°	122.0554(12)	122.4209(12)	122.3988(9)	122.0231(19)	
V/Å^3	1816.12(11)	1759.55(10)	1795.87(6)	1893.23(11)	8245.7(2)
Z	4	4	4,	4	16
μ(Mo Kα)/mm^{-1}	0.745	0.994	1.386	1.171	1.075
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
Unique reflections	2081	2022	2024	2132	2346
R_{int}	0.0804	0.0755	0.0355	0.0760	0.0559
R_1 [$I > 2\sigma(I)$]	0.0462	0.0436	0.0364	0.0341	0.0438
wR_2 (all data)	0.1194	0.1125	0.1057	0.0801	0.1493

Experimental

Synthesis

$[Mn(dca)_2(bpp)]_\infty$ (1). An aqueous solution (10 mL) containing sodium dicyanamide [Na(dca), 0.40 mmol, 36 mg] and manganese(II) acetate tetrahydrate (0.20 mmol, 49 mg) was added to the ethanol solution (25 mL) of 1,3-bis(4′-pyridyl)-propane (0.20 mmol, 40 mg), The clear mixture solution was stirred for a few minutes and then allowed to evaporate at room temperature. Well-shaped colorless crystals of **1** appeared in three weeks. The crystalline product was filtered, washed with ethanol and dried in air for analytical, spectroscopic and magnetic measurements. Yield, 63%. The use of methanol instead of ethanol in the synthesis also led to crystalline products, which gave the same analytical and spectroscopic results but the quality was not good enough for crystallographic measurements. Anal. Calcd. for $C_{17}H_{14}MnN_8$: C, 53.00; H, 3.66; N, 29.08%; found for **1**: C, 53.42; H, 3.88; N, 28.76%.

$[Co(dca)_2(bpp)]_\infty$ (2). Using cobalt(II) nitrate or acetate instead of manganese(II) acetate in the above procedure yielded overnight a red polycrystalline precipitate. The raw product was dissolved in an access of methanol and the solution was left to evaporate at room temperature. Good crystals suitable for single-crystal X-ray diffraction analyses were obtained in a week. The polycrystalline product and the final product gave essentially the same analytical and spectroscopic results. Yield, 55%. Anal. Calcd. for $C_{17}H_{14}CoN_8$: C, 52.45; H, 3.62; N, 28.78%; found for **2**: C, 52.28; H, 3.84; N, 28.36%.

$[Zn(dca)_2(bpp)]_\infty$ (3). The complex was prepared as colorless crystals in the same way as **1**, using zinc(II) sulfate or nitrate instead of manganese(II) acetate and methanol instead of ethanol. Yield, 64%. Anal. Calcd. for $C_{17}H_{14}N_8Zn$: C, 51.60; H, 3.57; N, 28.32%; found for **3**: C, 52.02; H, 3.78; N, 28.30%.

$[Cd(dca)_2(bpp)]_\infty$ (4a and 4b). A methanol solution (25 mL) of bpp (0.2 mmol, 40 mg) was added to the aqueous solution (10 mL) containing Na(dca) (0.4 mmol, 36 mg) and cadmium(II) nitrate tetrahydrate (0.2 mmol, 62 mg). The mixture was stirred for a few minutes and then filtered to remove the white precipitate. The evaporation of the filtrate at room temperature yielded overnight two kinds of colorless crystals with different shapes. If the crystals were allowed to remain in the solution for two months, the colomn-shaped crystals (**4a**) disappeared and the amount of the block-shaped ones (**4b**) increased. In another experiment, the crystal mixture of **4a** and **4b** was filtered off and re-dissolved in methanol, and the solution was left to stand. Only crystals of **4b** were obtained. Anal. Calcd. for $C_{17}H_{14}CdN_8$: C, 46.12; H, 3.19; N, 25.31%; found for **4a**: C, 45.93; H, 3.39; N, 25.46%; found for **4b**: C, 46.43; H, 3.28; N, 25.30%.

Physical measurements

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyser. IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan Microscope. Variable-temperature magnetic susceptibilities were measured on an Oxford MagLab 2000 magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.[22]

Crystallography

Intensity data were collected on a NONIUS KappaCCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were made empirically.[23] The structures were solved by direct methods and refined on F^2 using the full-matrix least-squares method.[24] The hydrogen atoms were located geometrically and refined isotropically. Crystal data and structure refinements are summarized in Table 1.

CCDC reference numbers 185726, 185727 and 200571–200573.

See http://www.rsc.org/suppdata/dt/b2/b212886a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and IR spectra

As have been described in our preliminary communication,[19] the reaction of Na(dca) with $Cd(NO_3)_2$ and bpp yields two topologic isomers of formula $[Cd(dca)_2(bpp)]_\infty$, **4a** and **4b**. The former is a kinetic phase and upon standing in the mother solution or being recrystallized from methanol, it transformed into the latter, which is believed to be thermodynamically more stable. Based on structural characterization, the thermodynamic preference of **4b** to **4a** has been discussed.[19] It is rather surprising that the replacement of the Cd(II) salt with Mn(II), Zn(II) or Co(II) salt in the reaction led to only a single product, which is isostructural with **4a** (*vide infra*). All our efforts to get the phases corresponding to the thermodynamic Cd(II) phase, **4b**, came out in vain. We could tentatively attribute the difference to the influence of the sizes of the metal ions. The replacement of Cd(II) in **4b** with smaller metal ions would reduce the space in the structure, discouraging the interpenetration that should have helped to stabilize the structure.

The IR spectra of the four complexes are quite similar and exhibit three strong absorptions in the 2290–2180 cm^{-1} region characteristic of the dca ligand.[25] The bands at about 2170 cm^{-1}

Table 2 Selected bond distances (Å) and angles (°) for complexes **1**,**2**, **3** and **4a**[a]

	1	2	3	4a
M(1)–N(1)	2.261(2)	2.143(2)	2.145(2)	2.317(3)
M(1)–N(2)	2.216(3)	2.119(3)	2.162(2)	2.325(3)
M(1)–N(3C)	2.220(2)	2.130(3)	2.171(2)	2.331(3)
N(2)–C(8)	1.142(3)	1.147(3)	1.137(3)	1.129(4)
N(3)–C(9)	1.147(3)	1.146(3)	1.134(3)	1.123(4)
N(4)–C(8)	1.290(4)	1.295(4)	1.291(3)	1.284(4)
N(4)–C(9)	1.301(4)	1.301(4)	1.298(3)	1.300(5)
N(1)–M(1)–N(1A)	180.0	180.0	180.0	180.0
N(2)–M(1)–N(2A)	180.00(19)	180.00(19)	180.00(18)	180.0(2)
N(3B)–M(1)–N(3C)	180.00(17)	180.00(14)	180.00(17)	180.00(14)
N(1)–M(1)–N(2)	89.95(9)	89.55(10)	89.89(9)	90.50(12)
N(1)–M(1)–N(2A)	90.05(9)	90.45(10)	90.11(9)	89.50(12)
N(1)–M(1)–N(3C)	89.81(9)	89.85(10)	89.92(9)	89.78(12)
N(1)–M(1)–N(3B)	90.19(9)	90.15(10)	90.08(9)	90.22(12)
N(2)–M(1)–N(3C)	90.21(10)	90.84(10)	90.39(10)	89.27(12)
N(2)–M(1)–N(3B)	89.79(10)	89.16(10)	89.61(10)	90.73(12)
C(8)–N(2)–M(1)	155.6(2)	156.5(2)	155.1(2)	152.9(3)
C(9)–N(3)–M(1B)	149.6(2)	152.8(2)	150.5(2)	146.5(3)
C(8)–N(4)–C(9)	120.0(3)	118.9(3)	120.0(3)	121.7(4)
N(2)–C(8)–N(4)	174.2(3)	174.6(3)	173.4(3)	172.5(4)
N(3)–C(9)–N(4)	174.2(3)	174.8(3)	174.0(3)	172.5(4)

[a] Symmetry codes: A $-x + 1/2, -y + 1/2, -z$; B $-x + 1, y, -z + 1/2$; C $x - 1/2, -y + 1/2, z - 1/2$.

(very strong) and 2230 cm^{-1} (medium) are due to the ν_s(C≡N) and ν_{as}(C≡N) vibrations, respectively, and the medium band at a higher frequency (around 2297 cm^{-1}) is attributable to the ν_s(≡N) + ν_s(C≡N) combination mode. The somewhat lower frequencies of these bands in compound **4b** may be due to the difference in coordination geometry (*trans vs. cis*). The characteristic absorptions of the pyridyl rings in the bpp ligand are observed as four medium or weak bands in the 1420–1620 cm^{-1} region. The medium absorption at about 1350 cm^{-1} may be attributed to ν_{as}(C–N) of the dca ligand.[25]

Description of the structures

[M(dca)$_2$(bpp)]$_\infty$ (M = Mn(II), 1, Co(II), 2, Zn(II), 3, and Cd(II), 4a). The three complexes are isomorphous and exhibit some differences in structural parameters. The structure of the Cd(II) species has been briefly communicated previously.[19] Here we describe and compare the structures in detail. Selected bond lengths and angles are collected in Table 2, and a perspective view of the structure of **1** is depicted in Fig. 1.

The structures consist of uniform chains in which adjacent metal ions are triply linked by two dca and one bpp bridges. Each metal ion, which resides at an inversion center, is coordinated by two pyridyl nitrogens from bpp ligands and four nitrile nitrogens from dca, with the two pyridyl groups in *trans* positions. The octahedral geometry is only slightly distorted with all the coordination bond angles deviating from the ideal angles by less than 0.8°. The average M–N distance increases from 2.13 Å for **2** and 2.16 Å for **3** to 2.22 Å for **1** and to 2.32 Å for **4a**, consistent with the sizes of the M(II) ions.

The dca ligand adopts the μ_2-1,5-dca coordination mode. Two dca ions link two metal ions to form a 12-membered M(dca)$_2$M ring and neighboring rings share the metal ions to form a chain of M(dca)$_2$. Similar chains with double dca bridges have been found in a number of 1D complexes.[6–10] The chains are usually linear with the M(dca)$_2$M rings being flat or in a slight chair conformation. In the present complexes, however, the M(dca)$_2$M rings are bent into an unusual boat conformation, yielding a sinusoidal chain. As a consequence of the bend, the M ··· M distances spanned by the bridging ligands are significantly reduced, with the values of 7.14, 7.05, 7.10 and 7.26 Å for **1**, **2**, **3** and **4a**, respectively. By contrast, the distances in the linear chains are 7.22–7.58 Å for Mn(II), Co(II), and Zn(II) species[7–9,15b] and 7.67 Å for a Cd(II) species.[10]

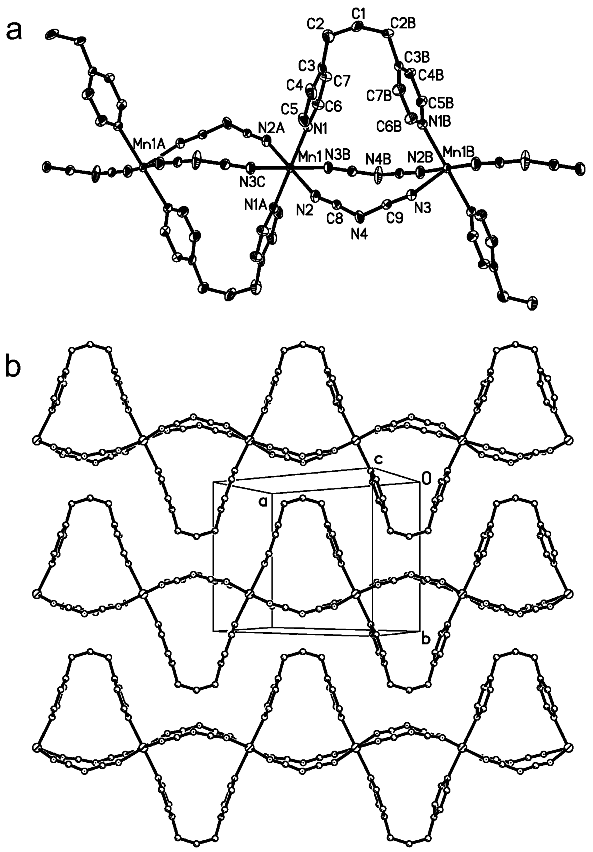

Fig. 1 ORTEP view of the chain structure with the atom labeling scheme (*a*) and view down the *c* axis showing the interchain interdigitation and the resulting quasi-2D sheet (*b*) in **1**. Hydrogen atoms are omitted for clarity.

Obviously, the distortion of the M(dca)$_2$ chain from linear to sinusoidal is induced by the coordination of the bpp ligand, whose arc-like shape is complementary with the boat conformation of the M(dca)$_2$M ring. The ligand acts as an additional intrachain bridge between neighboring metal ions, without dimensional increase. This behavior of bpp contrasts strikingly with those of 4,4′-bpy and analogous rigid bridges, which would act as interchain bridges to increase the dimensionality. Another interesting feature of the structure is the unusual

Table 3 Selected bond distances (Å) and angles (°) for complex **4b**[a]

Cd(1)–N(1)	2.333(3)	N(3)–C(8)	1.110(6)
Cd(1)–N(3A)	2.337(4)	N(4)–C(8)	1.283(7)
Cd(1)–N(2)	2.339(4)	N(4)–C(9)	1.295(8)
N(2)–C(9)	1.109(6)		
N(1B)–Cd(1)–N(1)	91.31(16)	N(3A)–Cd(1)–N(2)	88.79(16)
N(1)–Cd(1)–N(3A)	88.58(17)	N(3C)–Cd(1)–N(2)	89.33(16)
N(1)–Cd(1)–N(3C)	179.01(14)	N(2B)–Cd(1)–N(2)	177.3(2)
N(3A)–Cd(1)–N(3C)	91.5(3)	C(8)–N(4)–C(9)	120.8(6)
N(1)–Cd(1)–N(2B)	92.19(13)	N(3)–C(8)–N(4)	169.7(6)
N(1)–Cd(1)–N(2)	89.70(13)	N(2)–C(9)–N(4)	170.2(6)

[a] Symmetry codes: A, $-x + 1/2, -y + 1/2, -z$; B $-x + 3/4, -y + 3/4, z$; C $x + 1/4, y + 1/4, -z$; D $-x + 5/4, -y + 1/4, z$.

conformation of the bpp ligand. This flexible ligand usually assume *TT*, *TG* or *GG'* conformations with quite different N-to-N distances (within the 6.7–10.1 Å range).[18] Very recently, the only example of the *GG* conformation was recognized by Carlucci and his coworkers in a binuclear species, $[Cu_2(\mu\text{-bpp})_2(\mu\text{-NO}_3)_2(NO_3)_2]\cdot 2CH_2Cl_2$ (**5**).[18a] In **5**, the two pyridyl rings of the bpp ligand are in facing positions, with a small dihedral angle of 13° and a short N-to-N distance of 3.87 Å. The Cu ··· Cu distance spanned by the bpp and nitrate bridges is 3.90 Å. Complexes **1**, **2**, **3** and **4a** represent new examples exhibiting this unusual conformation. The two pyridyl groups of each bpp ligand are also in facing positions. However, to adapt to the longer M ··· M distances (7.05–7.26 Å) imposed by the double dca bridges, the dihedral angles between the two pyridyl rings are significantly larger (37.4, 38.5, 39.4 and 38.7° for **1**, **2**, **3** and **4a**, respectively), and so do the N-to-N distances (5.14, 5.22, 5.27 and 5.23 Å, respectively). The differences demonstrate the high flexibility of the *GG* conformation and its remarkable adaptability to co-bridges of different length.

In the crystals, all chains are aligned in parallel along the crystallographic [101] direction. In the *b* direction, complementary interchain interdigitation occurs with the convex $(CH_2)_3$ groups of one chain extending into the concave regions of the neighbouring chains, resulting in an overall 2D sheet parallel to the $(10\bar{1})$ plane (Fig. 1b).

$[Cd(dca)_2(bpp)]_\infty$ (4b). The structure of **4b** consists of neutral 2D coordination layers in which neighboring metal ions are linked by two dca or a bpp bridge. A perspective view with the atom-numbering scheme is depicted in Fig. 2. Selected bond lengths and angles are listed in Table 3.

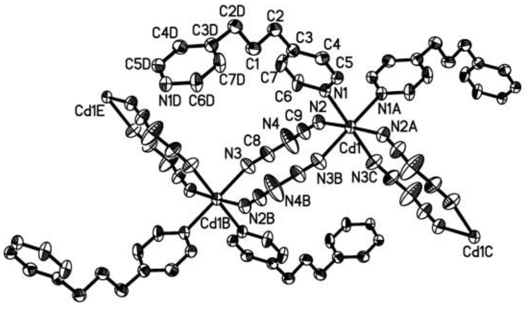

Fig. 2 ORTEP view with the atom labeling scheme, showing the metal environment and the zigzag $Cd(dca)_2$ chains in **4b**.

Again, the metal atom, which now resides on a two-fold axis, is octahedrally coordinated to four dca and two bpp bridging ligands with slightly longer Cd–N distances (2.33–2.34 Å). Now, however, the two pyridyl groups are in *cis* positions. This *cis* coordination geometry generates a zigzag chain of $M(dca)_2$, in which the $M(dca)_2M$ rings adopt the usual flat conformation. The zigzag $M(dca)_2$ motif have been found in only three complexes in which the *cis* geometry is dictated by a bidentate ligand (2,2′-bipyridine or 2,2′-bipyrimidine).[8,13] In **4b**, the arc-shaped bpp ligand adopts a *TT* conformation with a much longer N-to-N distance (9.41 Å) and a much larger pyridyl-to-pyridyl dihedral angle (79.7°) than those in **4a**. It acts as an "arch bridge" between adjacent zigzag chains that are aligned shoulder to shoulder, yielding an corrugated 2D layer along the (001) plane (Fig. 3). The layer may be described as a (4,4) network composed of quadrilateral loops, each of which consists of four Cd atoms (as 4-connecting nodes), two bpp ligands (as two opposite laterals) and four dca ions (each two as a lateral). The Cd-to-Cd distances spanned by the dca double bridges and the bpp ligand are 7.65 and 12.72 Å, respectively.

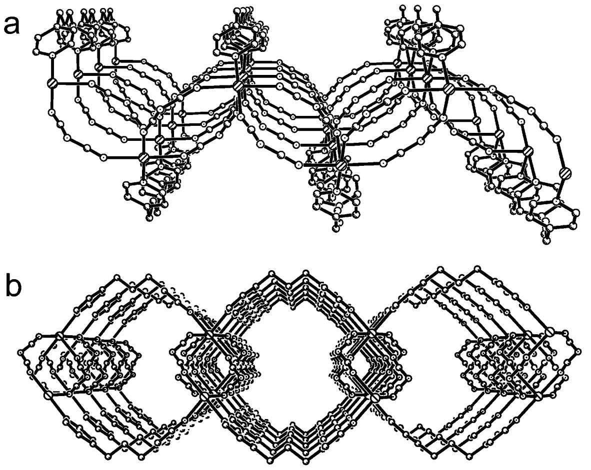

Fig. 3 Side views of a layer in **4b**, showing the undulation (*a*) and the "channels" (*b*, down the Cd–dca chains).

A unique feature of the layer is that the arc-shaped bpp ligands protrude from both sides of the layer, increasing the "empty" space within the layer. This is evidenced by the existence of the 1D infinite channels that run parallel to the $M(dca)_2$ chains (Fig. 3b). To fill the empty space, each arc (*i.e.* the bpp ligand) protruding from a layer is catenated with the adjacent arc from another layer generated by a 2-fold axis that threads through the arcs and parallels the layers but not the $M(dca)_2$ chains. Thus, each quadrilateral loop of the (4,4) layer is interlocked with two identical loops from the adjacent layers, defining the 3-fold interpenetration shown in Fig. 4a. As a consequence, each layer is entangled with two adjacent layers (one above, one below), generating a 3D polycatenane (Fig. 4). Interpenetrating nets have been paid considerable attention recently in the fields of crystal engineering and supramolecular chemistry and particularly attractive is the interpenetration accompanied by dimensional increase.[26,27] The structure of **4b** represents a novel type of 2D⟶3D parallel interpenetration, as stated elsewhere.[19] Due to the interpenetration, the shortest Cd-to-Cd distance between adjacent layers (7.22 Å) is much shorter than the intralayer distances.

Magnetic properties

The magnetic susceptibilities of the Mn(II) (**1**) and Co(II) (**2**) complexes were measured in the 2–300 K temperature range and are shown as χ_M and $\chi_M T$ *versus* T plots in Fig. 5.

The experimental $\chi_M T$ value of **1** at room temperature is 4.35 emu mol^{-1} K per Mn(II), close to the spin-only value (4.38 emu K mol^{-1}) expected for an uncoupled high-spin Mn(II) ion. As the temperature is lowered, the $\chi_M T$ product decreases slowly to 3.8 emu K mol^{-1} at about 25 K, and then decreases rapidly to 1.3 emu K mol^{-1} at 2 K. The overall behaviour corresponds to weak antiferromagnetically coupled systems.

To simulate the experimental magnetic behavior, we used the analytical expression derived by Fisher[28] for a 1D Heisenberg chain of classical spins ($S = 5/2, \boldsymbol{H} = -J\Sigma_i\Sigma_{i+1}$):

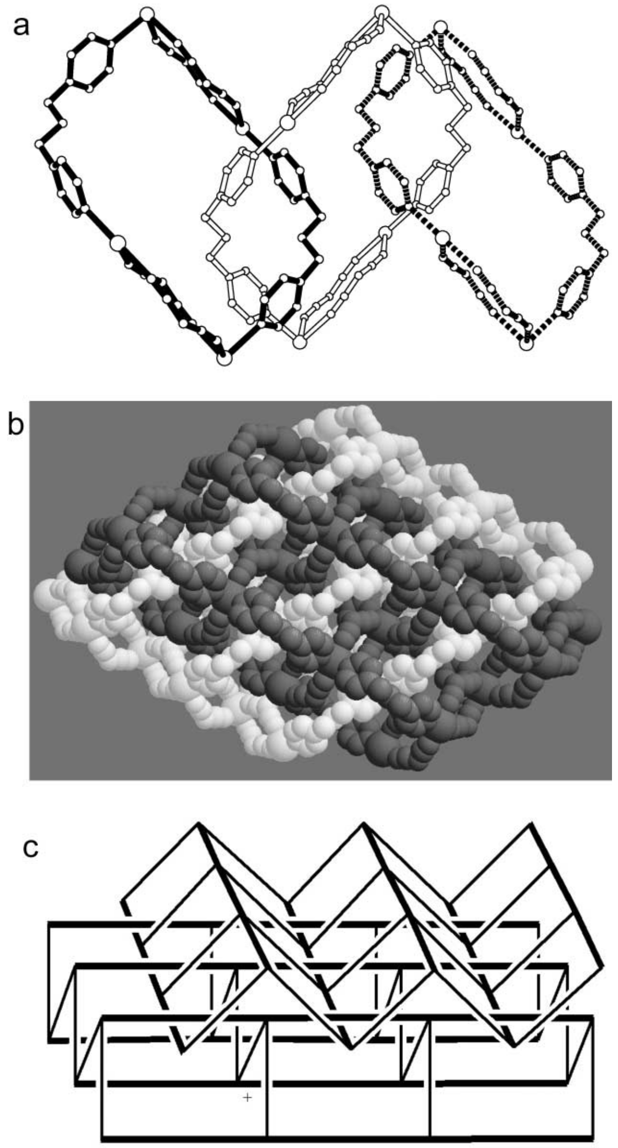

Fig. 4 Views showing the interpenetration in **4b**. *a*: the interlock between neighboring 4-noded loops. *b*: Space-filling view of the polycatenation between adjacent (4,4) layers. *c*: schematic representations of the interpenetration, where bold lines stand for the bpp linkages and thin lines for the double dca linkages.

$$\chi = [Ng^2\beta^2S(S + 1)/(3kT)][(1 + u)/(1 - u)] \qquad (1)$$

where N is Avogadro's number, β Bohr's magneton, k Boltzmann's constant, and u the well known Langevin function: $u = \coth[JS(S + 1)/kT] - kT/[JS(S + 1)]$. The best least-squares fit of the theoretical equation to experimental data leads to $g = 2.00$ and $J = -0.36$ cm^{-1}. The J value suggests a rather weak antiferromagnetic interaction between neighboring Mn(II) ions triply bridged by two dca and one bpp ligands. The interaction could be attributed to the dca pathways since the superexchange coupling *via* the bpp bridge should be much weaker, if any. The J value for **1** is comparable to those reported for other Mn(II) species with double 1,5-dca bridges (0.2–1.6 cm^{-1}).[7–9,13a,20a]

For **2**, the experimental $\chi_M T$ value per Co at room temperature is 3.11 emu mol^{-1} K, significantly larger than the spin-only value of high-spin cobalt(II) (1.88 emu mol^{-1} K, $S = 3/2$), but slightly smaller than the value expected for the free ion in the ^4F state with negligible spin–orbital coupling (3.38 emu mol^{-1} K). This indicates a significant contribution of the orbital angular momentum, typical of the $^4T_{1g}$ ground term for Co(II) in an octahedral field. Upon cooling, the $\chi_M T$ value decreases monotonously and reaches 1.59 emu mol^{-1} K at 2 K. This temperature-dependent behavior is largely due to a combination of spin–orbit coupling and low-symmetry ligand field effects that cause splitting of the $^4T_{1g}$ levels.[15b] However, intrachain and interchain antiferromagnetic interactions cannot be excluded, although their contributions, if any, should be minor due to the large Co ··· Co separation across the μ_2-1,5-dca bridge. The lack of an appropriate magnetic model to describe the complicated situation has precluded quantitative magnetic analyses for polynuclear or polymeric Co(II) complexes.[9,14a,29]

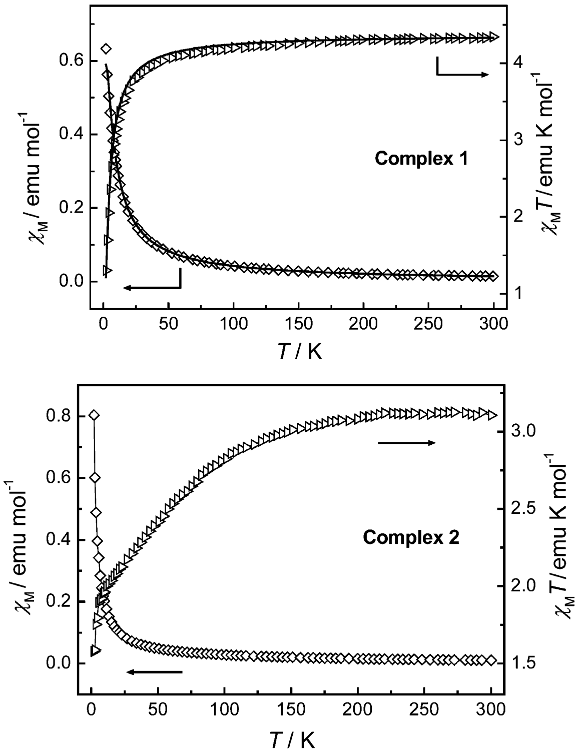

Fig. 5 χ_M *versus* T and $\chi_M T$ *versus* T plots for complexes **1** and **2**. The solid lines represent the best fit of the experimental data of **1** to eqn. (1), but are only guides for eyes in **2**.

Acknowledgements

We are thankful for the financial supports of NSFC (Nos. 20201009 and 90201014) and MOST (G19980613).

References

1 J. S. Miller and J. L. Manson, *Acc. Chem. Res.*, 2001, **34**, 563.

2 (*a*) S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.*, 1998, 439; (*b*) M. Kurmoo and C. J. Kepert, *New J. Chem.*, 1998, **22**, 1515; (*c*) M. Kurmoo and C. J. Kepert, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 693; (*d*) J. L. Manson, C. R. Kmety, Q.-Z. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein and J. S. Miller, *Chem. Mater.*, 1998, **10**, 2552; (*e*) P. Jensen, S. R. Batten, G. D. Fallon, B. Moubaraki, K. S. Murray and D. J. Price, *Chem. Commun.*, 1999, 177; (*f*) J. L. Manson, C. R. Kmety, A. J. Epstein and J. S. Miller, *Inorg. Chem.*, 1999, **38**, 2552; (*g*) C. R. Kmety, Q. Huang, J. W. Lynn, R. W. Erwin, J. L. Manson, S. McCall, J. E. Crow, K. L. Stevenson, J. S. Miller and A. J. Epstein, *Phys. Rev. B*, 2000, **62**, 5576.

3 (*a*) S. R. Batten, P. Jensen, B. Moubaraki and K. S. Murray, *Chem. Commun.*, 2000, 2331; (*b*) P. M. van der Werff, S. R. Batten, P. Jensen, B. Moubaraki and K. S. Murray, *Inorg. Chem.*, 2001, **40**, 1718; (*c*) J. W. Raebiger, J. L. Manson, R. D. Sommer, U. Geiser, A. L. Rheingold and J. S. Miller, *Inorg. Chem.*, 2001, **40**, 2578; (*d*) P. M. van der Werff, S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and E. H. K. Tan, *Polyhedron*, 2001, **20**, 1129.

4 (*a*) P. Jensen, D. J. Price, S. R. Batten, B. Moubaraki and K. S. Murray, *Chem. Eur. J.*, 2000, **6**, 3186; (*b*) P. Jensen, S. R. Batten,

B. Moubaraki and K. S. Murray, *Chem. Commun.*, 2000, 793; (*c*) S. R. Batten, A. R. Harris, P. Jensen, K. S. Murray and A. Ziebell, *J. Chem. Soc., Dalton Trans.*, 2000, 3829; (*d*) A. M. Kutasi, S. R. Batten, B. Moubaraki and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, 2002, 819.

5 (*a*) Z.-M. Wang, B.-W. Sun, J. Luo, S. Gao, C.-S. Liao, C.-H. Yan and Y. Li, *Inorg. Chim. Acta*, 2002, **332**, 127; (*b*) B. Vangdal, J. Carranza, F. Lloret, M. Julve and J. Sletten, *J. Chem. Soc., Dalton Trans.*, 2002, 566.

6 (*a*) I. Dasna, S. Golhen, L. Ouahab, O. Peña, J. Guillevic and M. Fettouhi, *J. Chem. Soc., Dalton Trans.*, 2000, 129; (*b*) G. A. van Albada, M. E. Quiroz-Castro, I. Mutikainen, U. Turpeinen and J. Reedijk, *Inorg. Chim. Acta*, 2000, **298**, 221.

7 (*a*) S. R. Batten, P. Jensen, C. J. Kepert, M. Kurmoo, B. Moubaraki, K. S. Murray and D. J. Price, *J. Chem. Soc., Dalton Trans.*, 1999, 2987; (*b*) I. Dasna, S. Golhen, L. Ouahab, M. Fettouhi, O. Pena, N. Daro and J. P. Sutter, *Inorg. Chim. Acta*, 2001, **326**, 37.

8 (*a*) A. Escuer, F. A. Mautner, N. Sanz and R. Vicente, *Inorg. Chem.*, 2000, **39**, 1668; (*b*) J. L. Manson, A. M. Arif, C. D. Incarvito, L. M. Liable-Sands, A. L. Rheingold and J. S. Miller, *J. Solid State Chem.*, 1999, **145**, 369.

9 B.-W. Sun, S. Gao, B.-Q. Ma and Z.-M. Wang, *Inorg. Chem. Commun.*, 2001, **4**, 72.

10 J. Luo, M. Hong, J. Weng, Y. Zhao and R. Cao, *Inorg. Chim. Acta*, 2002, **329**, 59.

11 (*a*) J. L. Manson, J. A. Schlueter, U. Geiser, M. B. Stone and D. H. Reich, *Polyhedron*, 2001, **20**, 1423; (*b*) I. Dasna, S. Golhen, L. Ouahab, O. Pena, N. Daro and J.-P. Sutter, *Chemistry*, 2001, **4**, 125.

12 (*a*) P. Jensen, S. R. Batten, B. Moubaraki and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, 2002, 3712; (*b*) S. Martin, M. G. Barandika, J. M. Ezpeleta, R. Cortes, J. I. R. de Larramendi, L. Lezama and T. Rojo, *J. Chem. Soc., Dalton Trans.*, 2002, 4275.

13 (*a*) S. Martin, M. G. Barandika, J. I. R. de Larramendi, R. Cortes, M. Font-Bardia, L. Lezama, Z. E. Serna, X. Solans and T. Rojo, *Inorg. Chem.*, 2001, **40**, 3687; (*b*) J.-H. Luo, M.-C. Hong ., R. Cao, Y.-C. Liang, Y.-J. Zhao, R.-H. Wang and J.-B. Weng, *Polyhedron*, 2002, **21**, 893.

14 (*a*) S. R. Marshall, C. D. Incarvito, J. L. Manson, A. L. Rheingold and J. S. Miller, *Inorg. Chem.*, 2000, **39**, 1969; (*b*) A. Claramunt, A. Escuer, F. A. Mautner, N. Sanz and R. Vicente, *J. Chem. Soc., Dalton Trans.*, 2000, 2627.

15 (*a*) P. Jensen, S. R. Batten, G. D. Fallon, D. C. R. Hockless, B. Moubaraki, K. S. Murray and R. Robson, *J. Solid State Chem.*, 1999, **145**, 387; (*b*) P. Jensen, S. R. Batten, B. Moubaraki, K. S. Murray and R. Robson, *J. Solid State Chem.*, 2001, **159**, 352; (*c*) I. Riggio, G. A. van Albada, D. D. Ellis, A. L. Spek and J. Reedijk, *Inorg. Chim. Acta*, 2001, **313**, 120; (*d*) B.-W. Sun, S. Gao, B.-Q. Ma and Z.-M. Wang, *New J. Chem.*, 2000, **24**, 953; (*e*) W.-F. Yeung, S. Gao, W.-T. Wong and T.-C. Lau, *New J. Chem.*, 2002, **26**, 523; (*f*) J. L. Manson, C. D. Incarvito, A. L. Rheingold and J. S. Miller, *J. Chem. Soc., Dalton Trans.*, 1998, 3705; (*g*) J. L. Manson, Q.-Z. Huang, J. W. Lynn, H.-J. Koo, M.-H. Whangbo, R. Bateman, T. Otsuka, N. Wada, D. N. Argyriou and J. S. Miller, *J. Am. Chem. Soc.*, 2001, **123**, 162; (*h*) J. L. Manson, C. D. Incarvito, A. M. Arif, A. L. Rheingold and J. S. Miller, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 605.

16 S. Martin, M. G. Barandika, R. Cortes, J. I. R. de Larramendi, M. K. Urtiaga, L. Lezama, M. I. Arriortua and T. Rojo, *Eur. J. Inorg. Chem.*, 2001, 2107.

17 S. Triki, F. Thetiot, J.-R. Galan-Mascaros, J. S. Pala and K. R. Dunbar, *New J. Chem.*, 2001, **25**, 954.

18 (*a*) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *CrystEngComm*, 2002, **4**, 121 and references therein; (*b*) F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 11982.

19 E.-Q. Gao, Z.-M. Wang, C.-S. Liao and C.-H. Yan, *New J. Chem.*, 2002, **26**, 1096.

20 (*a*) S. Dalai, P. S. Mukherjee, E. Zangrando and N. R. Chaudhuri, *New J. Chem.*, 2002, **26**, 1185; (*b*) J. Carranza, C. Brennan, J. Sletten, F. Lloret and M. Julve, *J. Chem. Soc., Dalton Trans.*, 2002, 3164.

21 Y. M. Chow and D. Britton, *Acta Crystallogr., Sect. B*, 1975, **B31**, 1934.

22 C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 203.

23 (*a*) R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **A51**, 33; (*b*) R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421.

24 (*a*) G. M. Sheldrick, SHELXTL Version 5.1, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1998; (*b*) G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, PC Version, University of Göttingen, Germany, 1997.

25 (*a*) H. Köhler, A. Kolbe and G. Lux, *Z. Anorg. Allg. Chem.*, 1977, **428**, 103; (*b*) A. J. Civadze and H. Köhler, *Z. Anorg. Allg. Chem.*, 1984, **510**, 31; (*c*) B. JuKrgens, W. Milius, P. Morys and W. Schnick, *Z. Anorg. Allg. Chem.*, 1998, **624**, 91.

26 (*a*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*b*) S. R. Batten, *CrystEngComm*, 2001, **3**, 76 and references therein; (*c*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629 and references therein.

27 For some recent examples, see: (*a*) N. R. Brooks, A. J. Blake, N. R. Champness, J. W. Cunningham, P. Hubberstey, S. J. Teat, C. Wilson and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 2001, 2530; (*b*) D. M. Ciurtin, Y.-B. Dong, M. D. Smith, T. Barclay and H.-C. zur Loye, *Inorg. Chem.*, 2001, **40**, 2825; (*c*) K. Biradha and M. Fujita, *Chem. Commun.*, 2001, 15; (*d*) J. Tao, X.-M. Zhang, M.-L. Tong and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2001, 770; (*e*) Z.-Y. Fu, X.-T. Wu, J.-C. Dai, L.-M. Wu, C.-P. Cui and S.-M. Hu, *Chem. Commun.*, 2001, 1856; (*f*) J. Y. Lu and A. M. Babb, *Inorg. Chem.*, 2001, **40**, 3261; (*g*) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *Chem. Commun.*, 2000, 1319.

28 M. E. Fisher, *Am. J. Phys.*, 1964, **32**, 343.

29 G. DeMunno, R. Ruiz, F. Lloret, J. Faus, R. Sessoli and M. Julve, *Inorg. Chem.*, 1995, **34**, 408.