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# 3D Self-penetrating coordination network constructed by dicyanamide and 1,2-bis(4-pyridyl)ethane-*N,N'*-dioxide (bpeado)<sup>†</sup>

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The complexes of formulae  $M(dca)_2(bpeado)$  ( $M = Mn$  (1),  $Fe$  (2),  $Co$  (3),  $Ni$  (4),  $Cu$  (5);  $dca$  = dicyanamide;  $bpeado$  = 1,2-bis(4-pyridyl)ethane-*N,N'*-dioxide) have been synthesized and characterized by X-ray single crystal diffraction. Compounds 1–5 contain 3D self-penetrating networks, in which bidentate  $dca$  ligands bridge the octahedral metal ions to form square-grid like  $M(dca)_2$  sheets and these sheets are further connected by criss-crossing  $bpeado$  to give a 3D self-penetrating network. Variable temperature magnetic susceptibility studies have shown that these compounds generally display very weak antiferromagnetic coupling because of the long  $bpeado$  and  $\mu_{1,5}$ - $dca$  pathways. Consequently, no magnetic ordering was found.

## Introduction

Dicyanamide ( $dca$ ) is a widely used ligand for the construction of high dimensional coordination polymers, due to its versatile bridging modes<sup>1–6</sup> and the diverse magnetic properties including ferromagnetism, weak ferromagnetism and paramagnetism found in its binary complexes with first row transition metals.<sup>2</sup> The addition of ancillary ligands to the binary series has built a lot of interesting extended architectures which provide more evidence for understanding the fundamental science of magnetic coupling and magneto-structure correlation. Unlike the single, rutile-like topology of the binary series ( $\alpha$  polymorph), the extended systems give us some new interesting structures, such as diamond-like networks,<sup>3</sup>  $\alpha$ -Po type networks<sup>4</sup> and  $CdSO_4$ -like networks.<sup>5</sup>

Bipyridine dioxide and its derivatives have been shown to have extremely versatile coordination modes. They may act as a terminal monodentate ligand through an oxygen atom,<sup>7</sup>  $\mu$ -O,O' (end-end bidentate, which may have *cis*- or *trans*-modes),<sup>8</sup>  $\mu$ -O,O (end-on bidentate),<sup>9</sup>  $\mu_3$ -O,O,O' tridentate mode<sup>9</sup> and the  $\mu_4$ -O,O,O',O' tetradentate mode.<sup>10</sup> In addition, bipyridine dioxide and its derivatives have a strong capacity for forming hydrogen bonds, which plays an important role in the assembly of supramolecular compounds. The coordinative versatility and the capability of forming hydrogen bond, together with the coordination nature of central metal ions, have allowed the possibility for the construction of different architectures.<sup>11</sup> In our previous work we have successfully introduced pyrazine-dioxide and its derivatives into the binary system of  $M(dca)_2$  and obtained interesting results, which were not found in the compounds containing pyrazine and its derivatives and  $dca$ .<sup>12</sup> Enlightened by this success, we synthesized 1,2-bis(4-pyridyl)ethane-*N,N'*-dioxide ( $bpeado$ ), and its series of complexes with  $dca$  and the first row transition

metal ions,  $M(dca)_2(bpeado)$  ( $M = Mn$  (1),  $Fe$  (2),  $Co$  (3),  $Ni$  (4),  $Cu$  (5)), determined their crystal structures and studied their magnetic behavior.

## Experimental

Elemental analyses of carbon, hydrogen and nitrogen were carried out with an Elementar Vario EL. Variable-temperature magnetic susceptibility and field dependence magnetization for 1, 3 and 4 were performed on a MagLab System 2000 magnetometer (Oxford Instruments).<sup>13</sup> Magnetic property measurements for 2 and 5 were made by using Quantum Design MPMSXL-5 SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).<sup>14</sup>

## Synthesis

1,2-bis(4-pyridyl)ethane-*N,N'*-dioxide ( $bpeado$ ) was prepared from 1,2-bis(4-pyridyl)ethane by the literature method.<sup>15</sup> Sodium dicyanamide ( $Na(dca)$ ) and other chemicals were purchased and used without further purification.

### $Mn(dca)_2(bpeado)$ (1)

0.25 mmol (49.5 mg)  $MnCl_2 \cdot 6H_2O$  and 0.25 mmol (54 mg)  $bpeado$  were dissolved in 5 mL water. 5 mL aqueous solution of  $dca$  (0.5 mmol, 44.5 mg) was added with continuous stirring. A yellow precipitate formed immediately. The solution was heated to give a clear yellow solution. The resulting solution was filtrated and allowed to slowly evaporate at room temperature. After a few days, yellow single crystals suitable for X-ray diffraction appeared. The crystals were collected, washed with water, and dried in air (yield 80%). Elemental anal. Calcd for  $C_{16}H_{12}MnN_8O_2$ : C, 47.66; H, 3.00; N, 27.79%. Found: C, 47.74; H, 3.04; N, 28.12%. IR ( $cm^{-1}$ , KBr disc): 2297 m, 2240 m, 2179 s.

### $Fe(dca)_2(bpeado)$ (2)

A method similar to that for compound 1 with  $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$  instead of  $MnCl_2 \cdot 6H_2O$  was used to prepare compound 2. Yellow single crystals suitable for X-ray structure

<sup>†</sup> Electronic supplementary information (ESI) available: Temperature dependence of  $\chi_M T$  and  $1/\chi_M$  for 2 (Fig. S1), 3 (Fig. S3), 4 (Fig. S5), 5 (Fig. S7) and the field dependence of magnetization measured at 1.8 K for 2 (Fig. S2), 3 (Fig. S4), 4 (Fig. S6), 5 (Fig. S8), the powder XRD patterns of 1, 2, 3, 4, 5 and the calculated one (Fig. S9). See <http://www.rsc.org/suppdata/ce/b4/b413812k/>

**Table 1** Crystal data and structure refinement for 1–5

	1	2	3	4	5
Formula	C <sub>16</sub> H <sub>12</sub> MnN <sub>8</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>12</sub> FeN <sub>8</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>12</sub> CoN <sub>8</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>12</sub> NiN <sub>8</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>12</sub> CuN <sub>8</sub> O <sub>2</sub>
<i>M</i> <sub>w</sub>	403.28	404.19	407.27	407.05	411.88
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	7.2169(2)	7.1346(2)	7.1375(2)	7.1642(2)	7.1005(2)
<i>b</i> /Å	12.1710(3)	12.1026(3)	12.0599(2)	12.0070(3)	12.0685(3)
<i>c</i> /Å	10.4779(3)	10.4061(2)	10.3669(2)	10.3284(2)	10.3404(2)
β/°	104.655(2)	104.662(1)	104.975(2)	105.587(1)	102.908(2)
<i>V</i> /Å <sup>3</sup>	890.40(4)	869.28(4)	862.05(3)	855.78(4)	863.70(4)
<i>Z</i>	2	2	2	2	2
<i>D</i> <sub>calcd</sub> /Mg m <sup>−3</sup>	1.504	1.544	1.569	1.580	1.584
μ/mm <sup>−1</sup>	0.771	0.898	1.026	1.165	1.295
<i>F</i> (000)	410	412	414	416	418
Data collected	14915	15520	14551	16092	17093
Unique data	2044	1987	1980	1960	1978
Observed data	1437	1567	1554	1422	1469
( <i>I</i> > 2σ( <i>I</i> ))					
<i>R</i> <sub>int</sub>	0.0609	0.0861	0.0486	0.0653	0.0494
GoF	0.932	0.988	1.021	0.978	1.039
<i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0311	0.0302	0.0282	0.0285	0.0365
<i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0714	0.0712	0.0644	0.1008	0.1008
<i>R</i> <sub>1</sub> <sup>a</sup> [all data]	0.0532	0.0447	0.0425	0.0534	0.0523
<i>wR</i> <sub>2</sub> <sup>b</sup> [all data]	0.0764	0.0787	0.0745	0.0696	0.1064

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

determination appear after a few days (yield 70%). Elemental anal. Calcd for C<sub>16</sub>H<sub>12</sub>FeN<sub>8</sub>O<sub>2</sub>: C, 47.55; H, 2.99; N, 27.72%. Found: C, 47.48; H, 3.03; N, 27.83%. IR (cm<sup>−1</sup>, KBr disc): 2285 m, 2239 m, 2172 s.

#### Co(dca)<sub>2</sub> (bpeado) (3)

A method similar to that for compound **1** with CoCl<sub>2</sub>·6H<sub>2</sub>O instead of MnCl<sub>2</sub>·6H<sub>2</sub>O was used to prepare compound **3**. Red single crystals suitable for X-ray structure determination appear after a few days (yield 90%). Elemental anal. Calcd for C<sub>16</sub>H<sub>12</sub>CoN<sub>8</sub>O<sub>2</sub>: C, 47.19; H, 2.97; N, 27.51%. Found: C, 46.98; H, 3.02; N, 27.70%. IR (cm<sup>−1</sup>, KBr disc): 2292 m, 2246 m, 2181 s.

#### Ni(dca)<sub>2</sub> (bpeado) (4)

A method similar to that for compound **1** with NiCl<sub>2</sub>·6H<sub>2</sub>O instead of MnCl<sub>2</sub>·6H<sub>2</sub>O was used to prepare compound **4**. Light green single crystals suitable for X-ray structure determination appear after a few days (yield 85%). Elemental anal. Calcd for C<sub>16</sub>H<sub>12</sub>NiN<sub>8</sub>O<sub>2</sub>: C, 47.22; H, 2.97; N, 27.53%. Found: C, 46.49; H, 3.16; N, 27.60%. IR (cm<sup>−1</sup>, KBr disc): 2299 m, 2255 m, 2190 s.

#### Cu(dca)<sub>2</sub> (bpeado) (5)

A method similar to that for compound **1** with CuCl<sub>2</sub>·2H<sub>2</sub>O instead of MnCl<sub>2</sub>·6H<sub>2</sub>O was used to prepare compound **5**. Green single crystals suitable for X-ray structure determination appear after a few days (yield 80%). Elemental anal. Calcd for

C<sub>16</sub>H<sub>12</sub>CuN<sub>8</sub>O<sub>2</sub>: C, 46.66; H, 2.94; N, 27.21%. Found: C, 46.84; H, 3.16; N, 27.41%. IR (cm<sup>−1</sup>, KBr disc): 2298 m, 2244 m, 2177 s.

#### Crystallography

Single crystal structure analysis for all compounds was performed on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å) at 293 K. All the data were collected, processed, and corrected for Lorentz and polarization effects using Nonius software. The structures were solved by direct methods and refined by a full-matrix least-squares technique based on *F*<sup>2</sup> using the SHELXL 97 program. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed by calculation positions and refined isotropically. The details of crystal data and selected bond lengths and angles for compounds **1–5** are listed in Tables 1 and 2, respectively. CCDC reference numbers 249217–249221. See <http://www.rsc.org/suppdata/ce/b4/b413812k/> for crystallographic data in CIF or other electronic format.

Powder X-ray diffraction data for all samples were collected at room temperature on bulk samples with Rigaku Dmax-2000 with Cu Kα radiation (1.54059 Å).

#### Result and discussion

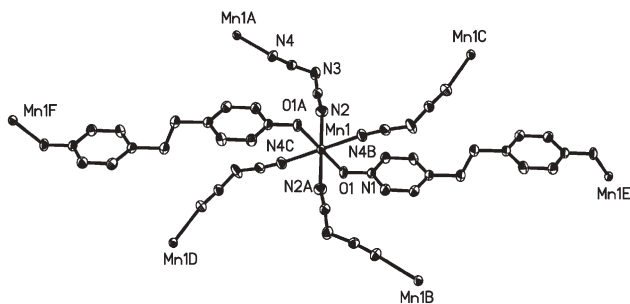
##### Description of the structures

X-ray single crystal structure determination reveals that compounds **1–5** are isomorphous and contain 3D self-penetrating networks.

**Table 2** Selected bond lengths (Å) and angles (°) for 1–5

	1	2	3	4	5
M1–O1	2.1847(11)	2.1054(11)	2.0816(11)	2.0883(12)	1.9810(16)
M1–N2	2.2363(15)	2.1865(13)	2.1340(13)	2.0911(16)	2.5622(28)
M1–N4b	2.2011(14)	2.1453(13)	2.1191(13)	2.0621(15)	1.9579(19)
O1–M1–N4b	91.41(5)	92.42(5)	92.36(5)	92.97(5)	94.30(7)
O1–M1–N4c	88.59(5)	87.58(5)	87.64(5)	87.03(5)	85.70(7)
O1–M1–N2a	90.75(5)	90.73(5)	90.88(5)	90.85(5)	91.50(8)
O1–M1–N2	89.25(5)	89.27(5)	89.12(5)	89.15(5)	88.50(8)
N4b–M1–N2	89.70(6)	89.83(5)	90.13(5)	90.24(6)	87.92(9)
N4c–M1–N2	90.30(6)	90.17(5)	89.87(5)	89.76(6)	92.08(9)
N1–O1–M1	118.63(9)	118.54(9)	118.59(9)	118.06(10)	118.12(12)

<sup>a</sup> Symmetry code: a  $-x, -y, -z$ ; b  $-x + 1/2, y - 1/2, -z + 1/2$ ; c  $x - 1/2, -y + 1/2, z - 1/2$ .

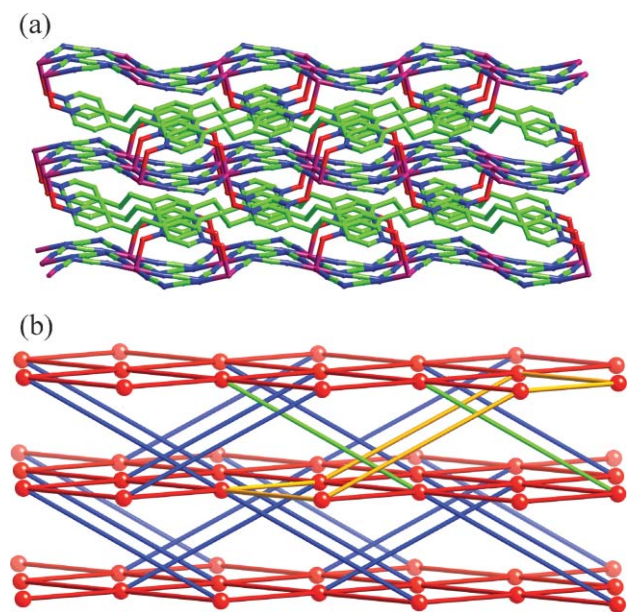


**Fig. 1** Coordination environment of Mn1 of compound **1**. Click here to access a 3-D image of compound **1**.

### Complex $[\text{Mn}(\text{dca})_2(\text{bpeado})]$ (**1**)

The structure of **1** consists of octahedral manganese ions, which are all related by symmetry and lie on inversion centres, bridged by bidentate dca anions, coordinating *via* the nitrile nitrogens ( $\text{Mn1-N2} = 2.2363(15)$  and  $\text{Mn1-N2a} = 2.2011(14)$  Å,  $a = -x + 1/2, y - 1/2, -z + 1/2$ ), and bidentate 1,2-bis(4-pyridyl-*N*-oxide)ethane (bpeado) ligands ( $\text{Mn1-O1} = 2.1847(11)$  Å) (Fig. 1). The dca ligands coordinate in the equatorial positions of the metal atoms, and bridge them into undulating (4,4) 2D sheets. These sheets are then linked into a 3D network *via* axially bound bpeado 'pillars' (Fig. 2a), which also lie across inversion centres. The Mn–Mn separation is 8.242(4) Å across the dca bridges and 14.15 Å across the bpeado bridges. The Mn...Mn separations bridged by  $\mu_{1,5}$ -dca are comparable with those found in other reported compounds containing dca.<sup>1–6</sup>

The network topology is shown schematically in Fig. 2b. It is different to other related structures, such as  $\text{M}(\text{dca})_2\text{L}$ , L = pyrazine ( $\alpha$  form), 4,4'-bipyridine, which also contain 2D (4,4) sheets of  $\text{M}(\text{dca})_2$  bridged by bidentate 'pillars'.<sup>4</sup> In these structures the pillars are all parallel and connect the sheets into  $\alpha$ -Po type networks (Schläfli symbol  $4^{12.63}$ ). In **1** the pillar ligands criss-cross to bridge at two different angles relative to the sheets (Fig. 2b), giving a new network topology, with the Schläfli symbol  $4^4.6^{10.8}$ . The large angular deviation of the bridge from perpendicular to the sheets is due mainly to the bend around



**Fig. 2** (a) 3D network constructed by both dca and bpeado of **1**. Mn atoms are purple, carbon atoms green, nitrogen atoms blue and oxygen atoms red. (b) The network topology of **1**. Only the Mn atoms and the connections between them are shown. A 6-membered shortest circuit is highlighted in yellow; the two rods passing through it are highlighted in green.

the coordinating oxygen ( $\text{N1-O1-Mn1} = 118.63(9)^\circ$ ). This also has an effect of bringing the (4,4) sheets closer together, making the net less spacious, and thus only one net is formed. In comparison, when the shorter linear 4,4'-bipyridine or even pyrazine ligands are used, two interpenetrating networks are formed. The structure is also different to the related structures of  $\text{M}(\text{dca})_2(\text{bpe})$ , M = Mn, Cu, bpe = 1,2-bis(4-pyridyl)ethane, which contain only 1D chains,<sup>6</sup> with the bpe ligands adopting a U-shape (in **1** the bpeado ligands have a Z geometry).

The schematic representation of the network also reveals that it is a self-penetrating network, *i.e.* some of the 'shortest circuits' of the network are penetrated by links in the same network.<sup>16</sup> As highlighted in Fig. 2, there are six-membered shortest circuits which are penetrated by two bpeado links. The network topology is thus closely related to, but different from, the structures of  $\text{Cd}(\text{CN})_2\text{L}$ , L = pyrazine, 1,4-bis(4-pyridyl)-butadiene (bpb).<sup>17</sup> These structures also have 2D (4,4) sheets bridged by criss-crossing pillars, however in the pyrazine structure the same equivalent six-membered ring is penetrated by only one link, and in the bpb structure the six-membered ring is penetrated by three links.

### Complex $[\text{M}(\text{dca})_2(\text{bpeado})]$ (M = Fe **2**, Co **3**, Ni **4**)

The crystal structures of **2–4** are very similar to that of **1**, and it is worthwhile noting that M...M separations bridged by  $\mu_{1,5}$ -dca are 8.187(2), 8.149(4) and 8.099(2) Å for **2**, **3** and **4**, respectively, and the M...M separations bridged by bpeado are 14.049, 14.014 and 13.982 Å for **2**, **3** and **4**, respectively. The gradual decrease of the M...M separations should arise from the gradual decrease of the radius of metal ions. The N1–O1–M1 angles are 118.54(9), 118.59(9) and 118.06(10)° for **2**, **3** and **4**, respectively.

### Complex $[\text{Cu}(\text{dca})_2(\text{bpeado})]$ (**5**)

Although compounds **1**, **2**, **3**, **4** and **5** are isomorphous, the crystal structure of **5** is somewhat different from that of **1**, **2**, **3** and **4** due to the Jahn–Teller effect of Cu(II) ions. The M–N2 distance of **5** is 2.5622(28) Å, which is longer than the corresponding distances of 2.2363(15), 2.1865(13), 2.1340(13) and 2.0911(16) Å found in **1**, **2**, **3** and **4**, respectively. Cu...Cu separations bridged by  $\mu_{1,5}$ -dca and bpeado are 8.219(4) and 14.002 Å, respectively. The N1–O1–Cu1 angle is 118.12(12)°.

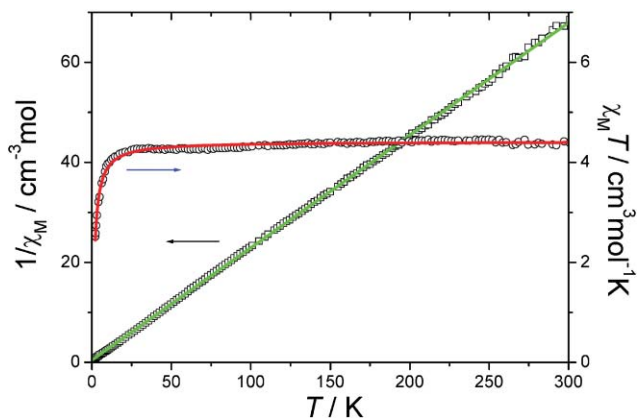
Due to the fact that complexes containing dca are rife with polymorphism, we measured the powder X-ray diffraction for **1**, **2**, **3**, **4** and **5**. The X-ray patterns of all the samples and the calculated one based on single crystal diffraction data reveal that all the samples are homogenous, excluding any polymorphs (Fig. S9).†

## Magnetic properties

### $\text{Mn}(\text{dca})_2(\text{bpeado})$

The variable-temperature magnetic susceptibility  $\chi_M$  for a collection of crystals of **1** in the temperature range of 2–300 K was measured in a field of 10 kOe, and the results are shown in Fig. 3. The value of  $\chi_M T$  at room temperature,  $4.419 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  is in good agreement with the spin-only value ( $4.375 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ) expected for an uncoupled Mn(II) system. The  $\chi_M T$  value remains nearly constant to about 30 K, then decreases rapidly to  $2.52 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K. The magnetic susceptibilities of **1** can be fit by the Curie–Weiss law  $\chi = C/(T - \theta)$ , with  $\theta = -1.90(2) \text{ K}$ ,  $C = 4.44 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for **1**. The small negative  $\theta$  value suggests a very weak antiferromagnetic interaction through the dca bridge. The field dependence of magnetization of **1** measured at 1.8 K shows a typical behaviour of paramagnetic material. With increasing magnetic field, the magnetization increases slowly and reaches





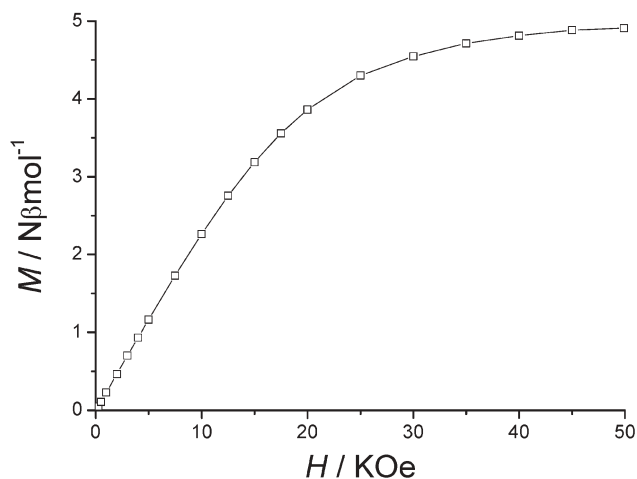
**Fig. 3** Temperature dependence of  $\chi_M T$  and  $1/\chi_M$  for **1**. The red line shows the best-fit curve. The green one shows the Curie–Weiss fit result.

the value of  $4.91 N\beta$  at 50 kOe, which is very close to the expected value of  $5 N\beta$  for  $S = 5/2$  spins (Fig. 4).

The fitting of **1** using Lines' model for a quadratic layer<sup>18</sup> seems reasonable because the interlayer interaction mediated by bpeado seems to be quite smaller than the intralayer interaction mediated by dca, and the layer constructed by the  $\mu_{1,5}$ -dca is an exact quadratic layer. The best fitting of the data using Lines' model did give satisfactory results:  $J = -0.105(7) \text{ cm}^{-1}$ ,  $zJ' = 0.061(2) \text{ cm}^{-1}$ ,  $g = 2.01(1)$  with  $R = 1.06 \times 10^{-4} \{R = \sum [(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calcd}}]^2 / \sum (\chi_M)_{\text{obs}}^2\}$ . The intralayer coupling  $J$  value compares well with those found in many complexes containing Mn(II) and dca.<sup>4b</sup>

#### M(dca)<sub>2</sub> (bpeado) (M = Fe **2**, Co **3**, Ni **4**, Cu **5**)

The magnetic behaviour of **2**, **3** and **4** is similar to that of **1** with weak antiferromagnetic interaction transported by dca or bpeado; however, the magnetic behaviour of **5** is a little bit different. With decreasing temperature the  $\chi_M T$  value is almost constant during the full temperature range, indicating very weak interaction between Cu(II) ions. The Curie–Weiss law fitting gives a very small  $\theta$  value of  $-0.05 \text{ K}$ . The antiferromagnetic coupling between the Cu(II) ions in **5** is much weaker than that found in **1**, **2**, **3** and **4**, this might be due to the Jahn–Teller effect of Cu(II) and/or the fact that even in the binary system of Cu(dca)<sub>2</sub> only very weak antiferromagnetic coupling was observed.<sup>2</sup> The  $\chi_M T$  value at room temperature, the magnetic moments at 5 kOe and Curie–Weiss constants are collected in Table 3.



**Fig. 4** Field dependence of magnetization measured at 1.8 K for **1**.

**Table 3** Magnetic data of **2**, **3**, **4** and **5**

	<b>2</b> (Fe)	<b>3</b> (Co)	<b>4</b> (Ni)	<b>5</b> (Cu)
$\chi_M T(300 \text{ K}) / \text{cm}^3 \text{ mol}^{-1} \text{ K}$	3.38	3.26	1.10	0.376
Magnetic moment at 50 kOe / $N\beta \text{ mol}^{-1}$	3.31	2.54	1.84	1.05
$\theta/\text{K}$	−0.66	−13.4	−2.82	−0.05
$C/\text{cm}^3 \text{ mol}^{-1} \text{ K}$	3.34	3.34	1.09	0.375

## Conclusions

Reaction of first-row transition metals with the ligands 1,2-bis(4-pyridyl)ethane-*N,N'*-dioxide (bpeado) and dca resulted in a series of five new compounds. These materials displayed different structures in comparison to the related bipyridine series, namely 3D self-penetrating networks, which is quite different from the  $\alpha$ -Po type networks of bipyridine series. The Cu(II) compound is a little bit different from Mn(II), Fe(II), Co(II) and Ni(II) compounds due to the Jahn–Teller effect of Cu(II) ions. No long-range magnetic ordering was found in all these compounds. This is not surprising, in terms of the length of the bpeado ligands and the  $\mu_{1,5}$ -bidentate bridging mode of dca.

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