New compounds with bridging dicyanamide and bis-chelating 2,2′-bipyrimidine ligands: syntheses, structural characterisation and magnetic properties of the two-dimensional materials $[Fe_2(dca)_4(bpym)] \cdot H_2O$ and $[Fe_2(dca)_4(bpym)(H_2O)_2]$

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The new polymeric, two-dimensional compounds $[Fe_2(dca)_4(bpym)] \cdot H_2O$ (**1**) and $[Fe_2(dca)_4(bpym)(H_2O)_2]$ (**2**) (dca^- = dicyanamide anion and bpym = 2,2′-bipyrimidine) have been synthesised and characterised by infrared spectroscopy and X-ray crystallography. Both compounds consist of two-dimensional networks of octahedrally co-ordinated iron(II) cations, bridged by bis-bidentate 2,2′-bipyrimidine and bridging dicyanamide anions. The metals are in a distorted octahedral environment due to the small bite angle of the bpym ligands [75.3(1)° in **1** and 73.7(1)° in **2**]. The main difference between the two structures is the co-ordination mode of the dca ligands. In compound **1**, the iron(II) cation is linked by four dca bridging ligands and by one bis-chelating bpym. In compound **2**, each iron cation is linked by two *trans*-bridging dicyanamide ligands, one bis-chelating bpym and two unidentate ligands in a *cis* arrangement (one terminal dicyanamide and one water molecule). The main consequence of the different dca co-ordination modes is that each metal cation is connected to four neighbouring metals in **1** but to only three in **2**. Magnetic measurements reveal a broad maximum in the χ_m *vs.* T plots at *ca.* 11 K for both compounds, which is characteristic of antiferromagnetic exchange interactions between the high-spin iron(II) centres ($J = -1.6\ \mathrm{cm}^{-1}$, $g = 2.20$ for **1** and $J = -1.8\ \mathrm{cm}^{-1}$, $g = 2.15$ for **2**).

Polynitrile transition metal compounds display rich structural and topological features and exhibit physical properties ranging from conductivity to magnetism.[1–5] The dicyanamide anion [dicyanamide = $N(CN)_2^-$ = dca^-] and related cyano-carbanion ligands such as the tricyanomethanide anion {tricyanomethanide = $[C(CN)_3]^-$ = tcm^-} and 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide anion {$[C_{10}N_6]^{2-}$ = $(C[C(CN)_2]_3)^{2-}$ = $tcpd^{2-}$} are interesting ligands due to their ability to adopt various co-ordination modes.[6–13] Among the prevalent binding modes are the μ_3-co-ordination mode of the dca^- and tcm^- ligands observed in the three-dimensional rutile-like structures of formulae $M(dca)_2$ and $M(tcm)_2$ [M = Cu(II), Ni(II), Co(II), Mn(II) and Cr(II)][6–10] and the μ_4-co-ordination mode of $tcpd^{2-}$ found in the three-dimensional structure of $[M(tcpd)(H_2O)_2]$ [M = Cu(II), Mn(II), Co(II), Fe(II), Ni(II)].[11–13] In addition to these "binary" compounds, mixed-ligand dca^- and tcm^- compounds with neutral bridging co-ligands such as pyrazine or hexamethylenetetramine have also been reported.[14,15]

We recently synthesised compounds that contain first row transition metal cations bridged by dicyanamide and 2,2′-bipyrimidine ligands (2,2′-bipyrimidine = bpym = $C_8N_4H_6$). During the preparation of this manuscript, the two-dimensional $[Co_2(dca)_4(bpym)] \cdot H_2O$ and the one-dimensional $[M(dca)_2(bpym)(H_2O)]$ [M = Mn(II), Fe(II), Co(II)] compounds were reported as the first class of compounds containing both types of bridging ligands.[16] Herein, we report the syntheses, structural characterisation and magnetic properties of two new compounds, with two-dimensional layered structures $[Fe_2(dca)_4(bpym)] \cdot H_2O$ (**1**) and $[Fe_2(dca)_4(bpym)(H_2O)_2]$ (**2**).

Experimental

Materials and measurements

The reagents 2,2′-bipyrimidine (Lancaster), ferrous sulfate heptahydrate (Acros Organics) and sodium dicyanamide (Aldrich) were used as received.

Infrared spectra were recorded in the range 4000–200 cm^{-1} from KBr pellets on a FT-IR Nexus Nicolet spectrometer. Magnetic studies were carried out on powder samples at 0.1 T after zero field cooling, in the temperature range 2–300 K with a Quantum Design MPMS-XL SQUID magnetometer housed in the Chemistry Department at Texas A&M University. The susceptibilities were corrected for the sample holder and the diamagnetic contributions of all the atoms.

Syntheses of compounds 1 and 2. All reactions were performed under aerobic conditions. 2,2′-Bipyrimidine (50 mg, 0.316 mmol) was slowly added to a hot aqueous solution of ferrous sulfate heptahydrate (175.8 mg, 0.632 mmol). The resulting solution was briefly stirred, after which time sodium dicyanamide (112.6 mg, 1.265 mmol) was slowly added with continuous stirring. The final red solution was slowly evaporated to yield orange crystals of $[Fe_2(dca)_4(bpym)] \cdot H_2O$ (**1**) which were removed by filtration and air dried. Further evaporation of the filtrate produced a mixture of orange crystals of **1** and black crystals of $[Fe_2(dca)_4(bpym)(H_2O)_2]$ (**2**).

Table 1 Crystal data and structure refinement for $[Fe_2(dca)_4(bpym)]\cdot H_2O$ (**1**) and $[Fe_2(dca)_4(bpym)(H_2O)_2]$ (**2**)

	1	**2**
Empirical formula[a]	$C_{16}H_8N_{16}OFe_2$	$C_{16}H_{10}N_{16}O_2Fe_2$
Formula weight[a]	552.04	570.06
Space group	*Pnma* (no. 62)	$P2_1/n$ (no. 14)
a/Å	16.203(3)	8.384(2)
b/Å	13.122(3)	9.223(2)
c/Å	10.438(2)	13.983(3)
β/°		90.95(3)
U/Å^3	2219(1)	1081.1(7)
Z[a]	4	2
μ/cm^{-1}	13.52	13.93
Measured reflections	16442	9113
Independent reflections (R_{int})	4897(0.047)	3128(0.033)
R[b], R_w[c]	0.035, 0.041	0.025, 0.031

[a] The asymmetric unit contains half of the chemical formula. [b] $R = \Sigma|F_o - F_c|/F_o$. [c] $R_w = [\Sigma w(|F_o|-|F_c|)^2/w(F_o)^2]^{1/2}$

The black crystals were manually separated from the orange ones. IR data: ν/cm^{-1} for **1**: 3452br, 3076w, 2310s, 2250s, 2239w, 2184s, 1627w, 1575s, 1416s, 1365s, 1350s, 1027w, 937w, 755m, 675m, 523m, 503m; for **2**: 3447br, 3237w, 3162w, 3084w, 2361m, 2312s, 2296s, 2250s, 2232s, 2189s, 2168s, 1616m, 1574s, 1559w, 1407s, 1373s, 1361s, 1024w, 928w, 754m, 668m, 503m.

X-Ray crystallography

Data were collected at $T = 110$ K on a Bruker CCD diffractometer equipped with an Oxford Cryosystems Cryostream cooling device using graphite monochromated Mo-Kα radiation. On the basis of systematic absences and intensity statistics, the space group was found to be *Pnma* for **1** and $P2_1/n$ for **2**. Both structures were solved by direct methods and successive Fourier difference syntheses, and were refined on F^2 by weighted anisotropic full-matrix least-squares methods.[17] All hydrogen atoms were located by difference Fourier maps and refined isotropically, except for the 2,2′-bipyrimidine hydrogen atoms of compound **2**, whose positions were calculated and refined as isotropic fixed contributors. Scattering factors and corrections for anomalous dispersion were taken from the literature.[18] The thermal ellipsoid drawings were made with the ORTEP program.[19] All calculations were performed on an Alphastation 255 4/233 computer. Pertinent crystal data and selected bond distances and angles are listed in Table 1 and Table 2 respectively. Complete crystallographic details are included in the supporting information.

CCDC reference numbers 159694 and 159695. See http://www.rsc.org/suppdata/nj/b1/b102188p/ for crystallographic data in CIF or other electronic format.

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

1		**2**	
Fe–N1	2.134(3)	Fe–N1	2.116(2)
Fe–N2	2.147(3)	Fe–N2	2.116(2)
Fe–N4	2.120(4)	Fe–N4	2.092(2)
Fe–N6	2.108(4)	Fe–N7	2.226(2)
Fe–N8	2.211(3)	Fe–N8	2.236(2)
Fe–N9	2.222(3)	Fe–O	2.112(2)
N1–Fe–N2	167.6(1)	N1–Fe–N2	173.90(8)
N4–Fe–N9	170.8(1)	N4–Fe–N8	165.07(8)
N6–Fe–N8	171.5(1)	N7–Fe–O	163.72(7)
N1–Fe–N4	95.7(1)	N1–Fe–N4	89.51(8)
N1–Fe–N6	90.8(1)	N1–Fe–O	86.45(7)
N2–Fe–N4	96.7(1)	N2–Fe–N4	89.83(8)
N2–Fe–N6	88.4(1)	N2–Fe–O	87.85(8)
N4–Fe–N6	92.7(1)	N4–Fe–O	104.64(8)

Results and discussion

Syntheses

The two compounds $[Fe_2(dca)_4(bpym)]\cdot H_2O$ (**1**) and $[Fe_2(dca)_4(bpym)(H_2O)_2]$ (**2**) were obtained by successive addition of the two ligands (first bpym followed by the dca salt) into a hot aqueous solution of the metal salt. This stepwise procedure allows one to obtain products in which both the bpym and dca ligands act as bridging ligands. In the course of preparing this manuscript, similar compounds were reported by Miller and co-workers; these are $[M(dca)_2(bpym)(H_2O)]$ [M = Fe(II), Co(II), Mn(II)], synthesised by addition of concentrated aqueous solutions of the metal salts $[Fe(BF_4)_2\cdot 6H_2O$, $CoSO_4\cdot 7H_2O$ and $MnCl_2\cdot 4H_2O]$ into an aqueous solution containing the bpym and dca ligands.[16] This method produces one-dimensional chain compounds in which only one of the two dca ligands is bridging and the bpym ligand is terminal, whereas the present compounds **1** and **2** are two-dimensional. In the same paper, Miller *et al.*, also described the two-dimensional compound $[Co_2(dca)_4(bpym)]\cdot H_2O$, which is isomorphous to **1**. This phase was obtained as a 95 : 5 admixture of $[Co_2(dca)_4(bpym)]\cdot H_2O$ with the one-dimensional phase $[Co(dca)_2(bpym)(H_2O)]$. We have found that this mixture can be avoided by addition of the ligands in two steps.[20]

IR spectroscopy

The 2,2′-bipyrimidine (bpym) ligand can act as a terminal chelating or bis-chelating ligand toward transition metal ions. Fortunately, IR spectroscopy can be used as a diagnostic tool for identifying the co-ordination mode. The terminal chelating mode of bpym is typically characterised by two intense, sharp peaks of nearly equal intensities at approximately 1580 and 1560 cm^{-1} (ring stretching modes of bpym). The presence of the bis-chelating mode, however, is indicated either by an asymmetric doublet or a single strong broad feature in the same range.[21,22] The single broad band at 1575 cm^{-1} for **1** and the asymmetric doublet at 1574 and 1559 cm^{-1} in the spectrum of **2** points to the bis-chelate co-ordination mode for both compounds. For the dicyanamide ligand, several absorption bands assigned to ν_{CN} are observed in the 2370–2150 cm^{-1} region. A broad feature centred near 3450 cm^{-1} (ν_s and ν_{as}, OH) and a weak/medium absorption near 1620 cm^{-1} (**1**: 1627w; **2**: 1616m) are indicative of the presence of water molecules; the results do not allow any differentation to be made between free and co-ordinated H_2O in compounds **1** and **2**.

Single crystal X-ray studies of compounds 1 and 2

Structure of $[Fe_2(dca)_4(bpym)]\cdot H_2O$ (1). As in the isomorphic structure of the recently reported compound $[Co_2(dca)_4(bpym)]\cdot H_2O$,[16] the iron(II) cations in **1** are linked by four dca ligands and by one bis-chelating bpym. Owing to the presence of the bpym ligand, each iron cation resides in a distorted octahedral environment with approximate C_{2v} symmetry (Fig. 1). This distortion is mainly due to the small bite angle of the bpym ligand [75.3(1)°]. The Fe–N(dca) bond lengths lie in the range 2.108–2.147 Å and are close to those reported for iron dicyanamide compounds,[7,8,16] while the two Fe–N(bpym) (2.222 and 2.211 Å) are substantially longer and are in the range of those reported for di- and polynuclear Fe(II)–bpym–Fe(II) complexes.[23,24] The two-dimensional structure consists of alternating double-μ-dca [Fe(NC–N–CN)$_2$Fe] and bis-chelating bpym chains of iron(II) ions along the b axis that are axially connected by dca ligands

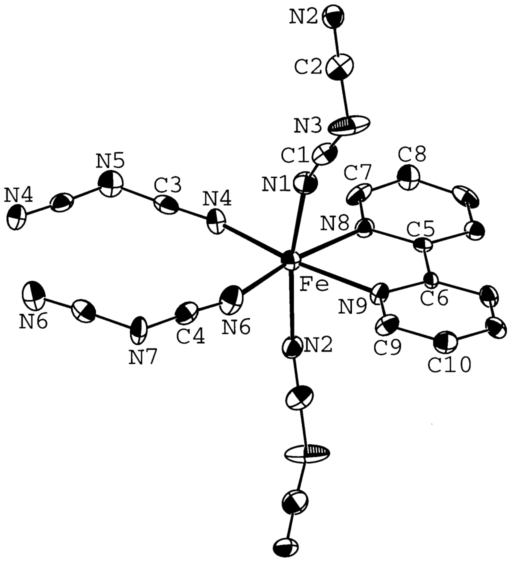

Fig. 1 ORTEP diagram showing the atom labeling scheme for **1**. Selected bond lengths (Å) and angles (°): N1–C1 1.152(6); N2–C2 1.144(6); N3–C1 1.314(6); N3–C2 1.308(6); N4–C3 1.156(6); N5–C3 1.314(5); N6–C4 1.149(6); N7–C4 1.322(5); C1–N3–C2 121.2(4); C3–N5–C3 118.9(5); C4–N7–C4 115.2(5).

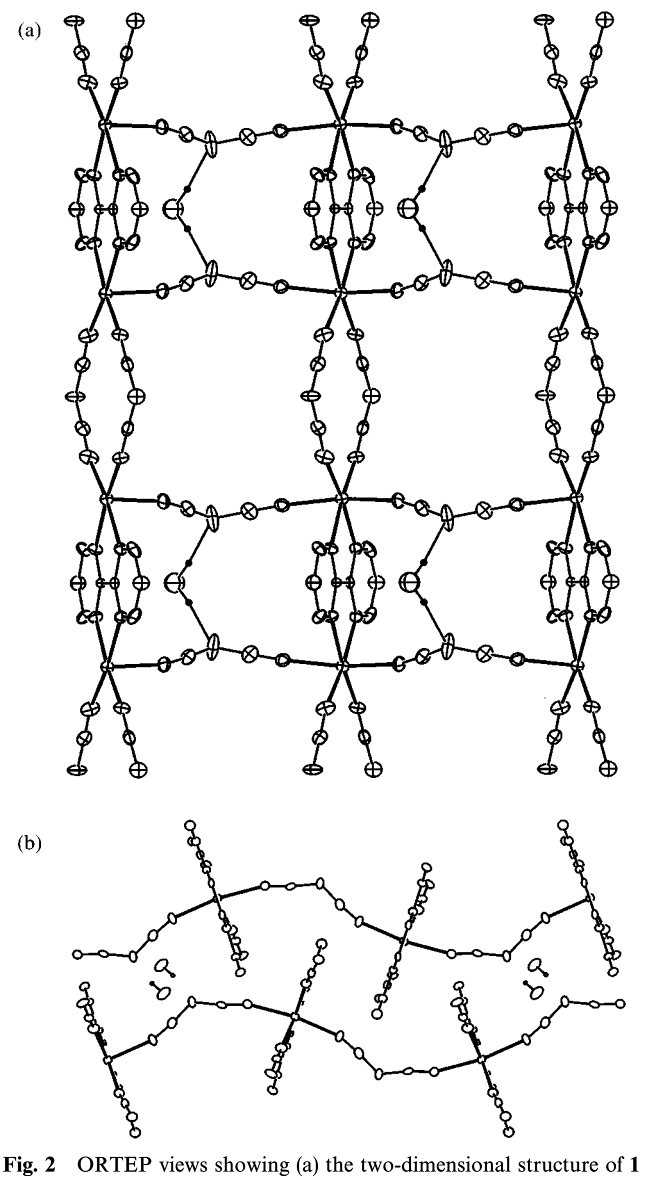

Fig. 2 ORTEP views showing (a) the two-dimensional structure of **1** and (b) the inter-layer packing in **1**.

along the *a* direction [Fig. 2(a)]. The 2-D layers form non-eclipsed stacks parallel to the [001] direction separated by 5.219 Å as shown in Fig. 2(b). Each iron(II) cation is connected to four neighbouring metals in the *ab* plane with three different Fe···Fe separations: 5.899 Å through the bis-chelating bpym, 7.223 and 8.322 Å through the double-μ-dca and the μ-dca [Fe(NC–N–CN)Fe] bridges, respectively. As shown in Fig. 2(a), the water molecules are located in special positions between the layers and form hydrogen bonds with the amido nitrogen atoms of two dca ligands in the same layer [H01···N3 2.13(3), H01–O 0.96(3), N3–O 3.079(5) Å and N3···H01–O 171°].

Structure of [$Fe_2(dca)_4(bpym)(H_2O)_2$] (2). The asymmetric unit in **2** consists of one iron(II) cation, one bpym molecule in a special position (1/2, 1/2, 0), two dca anions, and a water molecule (Fig. 3). Each metal cation is linked by two *trans*-bridging dicyanamide ligands, one bis-chelating bpym, and two unidentate ligands in a *cis* arrangement (one terminal dicyanamide and one water molecule). The selected bond lengths listed in Table 2 reveal the highly distorted octahedral environment of the metal cation. As in compound **1**, a significant distortion also arises from the small bite angle of the bpym ligand [73.7(1)°]. The extended structure is best described as dca-bridged, zigzag chains connected by bridging bpym ligands [Fig. 4(a)]. The shortest Fe···Fe separation through the bpym bridges (5.960 Å) is close to that observed in compound **1** and the corresponding distances in iron(II) bpym derivatives.[23,24] The metal–metal separation through the dca bridge is longer (8.097 Å) than the bpym bridge separation, but slightly shorter than the analogous distances in **1** (8.322 Å) and the 1-D compound [$Fe(dca)_2(bpym)(H_2O)$] (8.630 Å).[16] An examination of the *inter*-layer distances reveals the presence of hydrogen bonds between the co-ordinated water molecule and the nitrile group of the unidentate dca ligand. These hydrogen bonds occur between two adjacent sheets as shown in Fig. 4(b) [H05···N5 1.90(3), H05–O 0.89(3), N5···O 2.787(3) Å and N5···H5–O 174.5°), giving rise to a 3-D structure overall.

In summary, compounds **1** and **2** differ essentially in the co-ordination mode of the dca ligands. In compound **1**, the four dca ligands act as bridging ligands and the water molecule is not co-ordinated. In **2**, only two of the four dca ligands adopt the bridging co-ordination mode, the other two being unidentate ligands. The octahedral environment of each

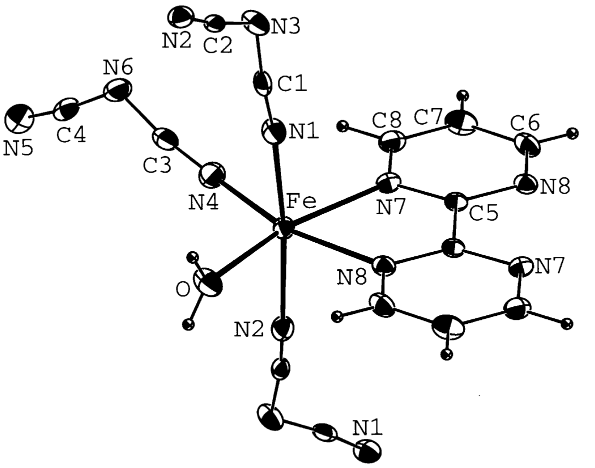

Fig. 3 ORTEP diagram showing the atom labeling scheme in **2**. Selected bond lengths (Å) and angles (°): N1–C1 1.148(3); N2–C2 1.158(3); N3–C1 1.316(3); N3–C2 1.305(3); N4–C3 1.158(3); N5–C4 1.151(3); N6–C3 1.302(3); N6–C4 1.327(3); C1–N3–C2 122.3(2); C3–N6–C4 121.9(2).

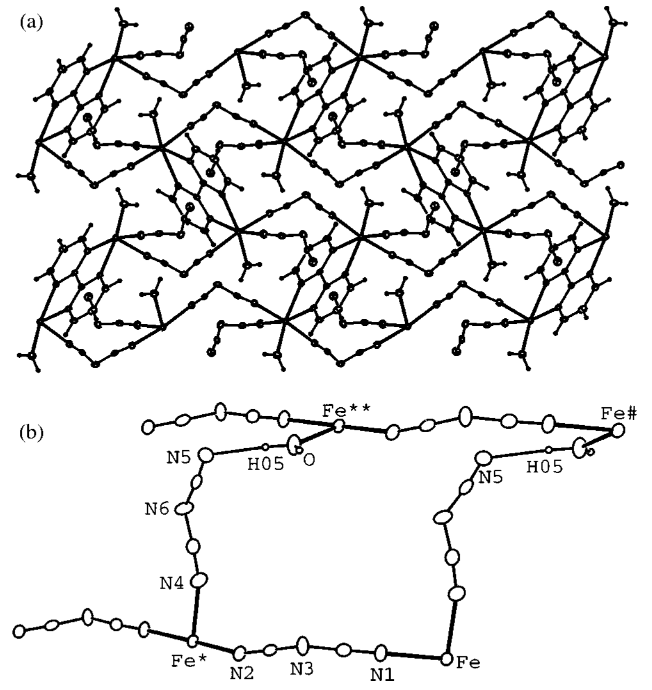

Fig. 4 ORTEP views showing (a) the two-dimensional structure of **2** and (b) hydrogen bonding between two adjacent sheets in **2**: Fe *x*, *y*, *z*; Fe# $1 + x, y, z$; Fe* $-1/2 + x, 1/2 - y, -1/2 + z$; Fe** $1/2 + x, 1/2 - y, -1/2 + z$.

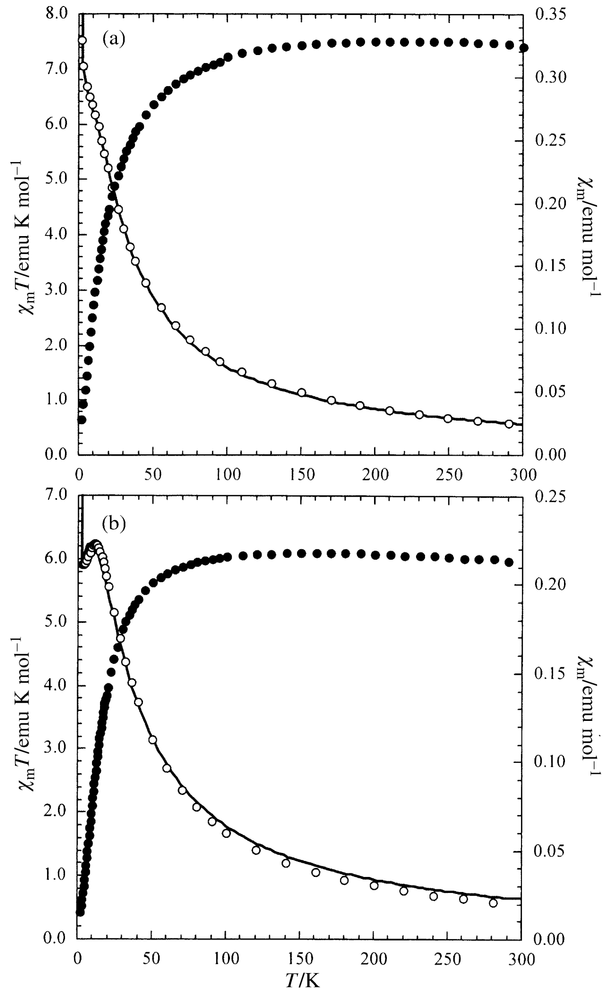

Fig. 5 Thermal variation of the magnetic susceptibility in the forms $\chi_m T$ *vs.* T(●) and χ_m *vs.* T (○) for **1** (a) and **2** (b). The solid lines through ○ show the best fits to the model (see text).

metal cation is completed by a co-ordinated water molecule. The main consequence of the different dca co-ordination modes is that each metal cation is connected to four neighbouring metals in compound **1** but to only three in compound **2** [Fig. 2(a) and 4(a)].

Magnetic properties

Magnetic data for **1** and **2** are depicted in Fig. 5. Both compounds exhibit similar behaviour, namely the $\chi_m T$ values remain essentially constant at high temperatures, with room temperature values of 7.4 and 6.0 emu K mol^{-1}, respectively. These values are in good agreement with the expected magnitude for two magnetically dilute, high-spin Fe(II) ions ($S = 2$) per formula unit. The small difference in the room temperature $\chi_m T$ values between the two compounds may be attributed to differences in g factors due to the different co-ordination environments. Below 100 K, the $\chi_m T$ values decrease rapidly with temperature and approach zero at very low temperatures. This behaviour is indicative of antiferromagnetic interactions between the local Fe(II) paramagnetic centres. In accord with this conclusion is the presence of a maximum in χ_m at 11 K for compound **2**. The presence of a Curie tail precludes the observation of a similar maximum for **1**. This paramagnetic contribution, also observed for **2**, could be due to the presence of paramagnetic impurities in the samples. But since the magnetic measurements were carried out on ground single crystals, a more plausible explanation is the presence of defects in the crystal structure in the form of vacancies that would create magnetically isolated Fe(II) centres.

Since it is well known that the 2,2′-bipyrimidine bridge constitutes a better pathway for magnetic exchange ($-J = 0.6$–10 cm^{-1})[25] than the μ-mode of dicyanamide ($-J \approx 0.05$–0.15 cm^{-1}),[26,27] the data were fit to a dimer model, $H = -2JS_a S_b$ with $S_a = S_b = 2$. This treatment assumes that the behaviour for these compounds is similar to that of isolated Fe(II) dimers with a bpym superexchange pathway. A similar approach was adopted by Miller *et al.*[16] for the recently reported Co(II) analogue of **1**, but in this case one cannot account for the zero-field splitting of high-spin Co(II) in an octahedral environment. Although the same could be expected in our case, since Fe(II) ions in an octahedral environment are also known to show strong anisotropy, it was sufficiently small that the data were successfully fittted to the model:

$$\chi = C\,\frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x}} + \frac{P}{T}$$

where $C = Ng^2\mu_B^2/(k_B T)$, N = Avogadro's number, g = Landé factor, μ_B = Bohr magneton, k_B = Boltzmann's constant, $x = J/(k_B T)$ and P = paramagnetic contribution. The best fit for χ_m was obtained with the following sets of parameters: $g = 2.20$, $J = -1.6$ cm^{-1} and $P = 0.37$ emu mol^{-1} for **1** and $g = 2.15$, $J = -1.8$ cm^{-1} and $P = 0.16$ emu mol^{-1}, for **2**. The calculated g value for **1** is larger than for **2**; in both cases J is small and negative, indicating the presence of weak antiferromagnetic exchange. These values are in good agreement with each other and with the values reported in the literature for a related Fe$_2$(II,II) bipyrimidine bridged dinuclear compound.[23,24] Our assumption that the magnetic exchange through the dicyanamide ligands is negligible compared to the interactions through the bpym ligands appears to be justified. The introduction of a fourth parameter (θ) to account for inter-dimer interactions did not improve the fits. Finally, the use of a more specific magnetic model that would include spin–orbit coupling would also be useful to understand the magnetic behaviour of these compounds.

Conclusion

This study involves the design of two-dimensional iron(II) compounds with both dicyanamide and 2,2′-bipyrimidine bridging ligands. The two new compounds $[\mathrm{Fe}_2(\mathrm{dca})_4(\mathrm{bpym})]\cdot\mathrm{H}_2\mathrm{O}$ (**1**) and $[\mathrm{Fe}_2(\mathrm{dca})_4(\mathrm{bpym})(\mathrm{H}_2\mathrm{O})_2]$ (**2**) differ in the co-ordination mode of the dca ligand and the hydrogen bonds involving the water molecules. The magnetic data of both compounds fit well to a dimer model ($S_a = 2$, $S_b = 2$) with an isotropic exchange interaction J that describes the superexchange pathway through the bpym ligand. In an effort to increase the dimensionality and the cooperativity between the metal cation sites in these types of materials, we are turning to the use of highly conjugated polynitriles (cyanocarbanions or azacyanocarbanions) such as the tcpd^{2-} anion[11] and the $[\mathrm{C}_{10}\mathrm{N}_8]^{\cdot-}$ radical anion[28] in conjunction with a bridging co-ligand such as pyrimidine or pyrazine. These studies are currently in progress.

Acknowledgements

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20. During the preparation of this manuscript, using the procedure described in the experimental section for Fe(II), we obtained four other phases as prismatic crystals [**3** with Co(II); **4** with Cu(II), **5** with Mn(II) and **6** with Zn(II)]. Their IR spectra are similar to that of compound **2**. Compounds **3**, **5** and **6** show asymmetric doublets in the range 1567–1579 cm^{-1} (1579s, 1572w for **3**; 1573s, 1567w for **5** and 1574s, 1569w cm^{-1} for **6**) characteristic of the bis-chelating mode of the bpym ligand, while the IR spectrum of **4** contains a strong, broad feature at 1591 cm^{-1} which is very similar to that observed for **1**.
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