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New 2D coordination polymers containing both bi- and tri-dentate dicyanamide bridges and intercalated phenazine

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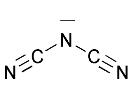
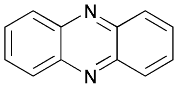
The isomorphous structures of $M(dca)_2(H_2O)\cdot phz$ [M = Co, Ni; dca = dicyanamide, $N(CN)_2^-$; phz = phenazine] contain phz molecules intercalating between 2D $M(dca)_2(H_2O)$ sheets containing bi- and tri-dentate dca ligands; the Ni complex displays long-range order (T_c = 5.7 K).

Coordination polymers of the dicyanamide [dca, $N(CN)_2^-$] ligand are of great current interest as potential molecule-based magnetic materials. The ligand has a range of coordination modes, however the two most common are bidentate (with both nitrile nitrogens coordinating) and tridentate (with all three nitrogens coordinating). The series of compounds with the general formulae α-$M(dca)_2$ (M = Cr, Mn, Fe, Co, Ni) and M(dca)(tcm) [M = Co, Ni; tcm = tricyanomethanide, $C(CN)_3^-$] show long-range magnetic ordering.[1,2] Significantly, tridentate dca is present in all of these structures, allowing access to M–NCN–M magnetic exchange pathways. In contrast, apart from a few exceptions,[3–5] when only bidentate dca is present long-range ordering is generally not observed.

We have been modifying metal–dca networks by introducing monodentate and bridging coligands. In particular, we and others have recently reported a number of compounds containing pyrazine and 4,4′-bipyridine coligands.[6] Although a number of network topologies were found, none of the compounds contained tridentate dca, and we therefore looked towards more sterically hindered bridging ligands. We report here preliminary results of our investigations with the use of phenazine (phz) as a potential coligand, and the structures and magnetism of two new coordination polymers containing both bi- and tri-dentate dca ligands.



dca



phz

Reaction of metal nitrate, sodium dicyanamide and phenazine in ethanol results in formation of $M(dca)_2(H_2O)\cdot phz$ [M = Co (**1**), Ni (**2**)].† The two crystal structures are isomorphous,[7] and consist of 2D layers of $M(dca)_2(H_2O)$ alternating with intercalated phz molecules which hydrogen bond to the water ligands.

The structure of one of these 2D coordination nets is shown in Fig. 1. There are two sorts of octahedral metal atoms and two types of dca ligands (one bidentate, one tridentate). The M(1) ions, which lie on two-fold axes, coordinate to four equatorial bidentate dca ligands *via* the nitrile nitrogens [M(1)–N = 2.080(2) and 2.086(2) Å (**1**), 2.040(3) and 2.032(3) Å (**2**)] and two axial tridentate dca ligands *via* the amide nitrogens [M(1)–N = 2.213(2) Å (**1**), 2.198(3) Å (**2**)]. The M(2) ions, which lie on inversion centres, coordinate to nitrile nitrogens of four axial tridentate dca ligands [M(2)–N = 2.121(2) and 2.163(2) Å (**1**), 2.072(3) and 2.125(3) Å (**2**)] and to two axial water ligands [M(2)–O = 2.049(2) Å (**1**), 2.038 Å (**2**)].

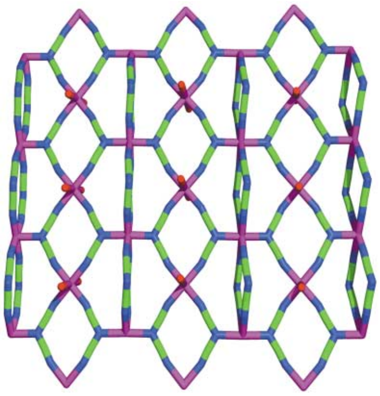


Fig. 1 A 2D coordination polymer sheet in the structure of $Ni(dca)_2(H_2O)\cdot phz$ (**2**). Hydrogens and phz molecules are omitted for clarity.

The resulting 2D sheets, which lie parallel to the *bc* plane, can be thought of as being composed of two alternating chains which are roughly perpendicular to each other but propagate in the same direction (the *b* axis). These chains—$M(1)(dca)_2$ chains and $M(2)(dca)_2(H_2O)_2$ chains—are of a type commonly seen in dca chemistry, and are connected by coordination of the amide dca nitrogens of the M(2) chains to the axial positions of the M(1) cations.

Interestingly, the sheet topology can also be related to the rutile network that is displayed by the α-$M(dca)_2$ compounds. Sheets in the rutile network can be defined with the same connectivity as those described here, as shown in Fig. 2. Indeed, the rutile network can be generated by simply stacking and joining sheets together, with the amide nitrogens of the bidentate dca ligands coordinating to the M(2) cations of adjoining sheets (replacing the water ligands), and *vice versa*. A number of other dca coordination polymers can also be related to parts of the rutile network [such as 1D tubes and $M(dca)_2L_2$ chains] or the rutile network as a whole [*e.g.* the M(dca)(tcm) series].[1b,2,8]

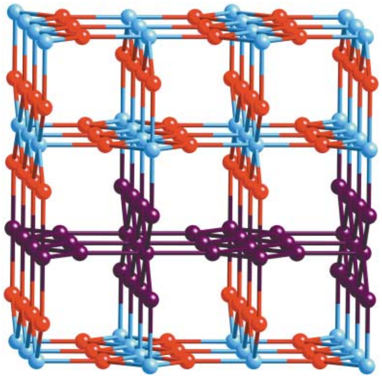


Fig. 2 The rutile (TiO_2) network; the section highlighted has the same topology as the coordination polymer sheets in **1** and **2**.

The sheets stack in the *a* direction, and alternate with layers of phz molecules (Fig. 3) which, perhaps not surprisingly (given their steric bulk), do not coordinate directly to the metal atoms.

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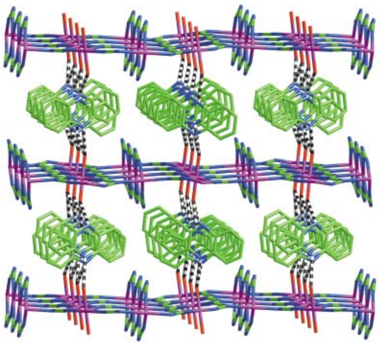

Fig. 3 The alternate stacking of 2D $M(dca)_2(H_2O)$ coordination polymer sheets and layers of intercalated phz molecules. The hydrogen bonding interactions between phz molecules and water ligands are highlighted by the striped bonds. For clarity, hydrogen atoms are omitted.

Instead, they hydrogen bond to the water ligands of the sheets. Each water ligand hydrogen bonds to two different phz molecules {H ··· N = 2.00(3) [O–H ··· N = 160(3)°] and 2.14(3) Å [162(3)°] for **1**, 2.10(5) [148(4)°] and 2.16(5) Å [165(4)°] for **2**}, and each phz (all of which are related by symmetry) hydrogen bonds to two water ligands, one each from sheets above and below the phz layer. As a result, zigzag hydrogen bonded chains of ··· H_2O ··· phz ··· H_2O ··· phz ··· propagate along the *b* direction and connect the sheets into a 3D network. The phz molecules in these chains are also within π stacking distance of each other, with the closest non-hydrogen contacts being 3.32 Å (**1**) and 3.30 Å (**2**) and the average distance between the plane of each phz to the atoms of adjoining phz molecules being 3.40 Å (**1**) and 3.36 Å (**2**) (adjoining phz molecules are close to but not exactly parallel).

The presence of tridentate dca ligands, and the topological relationship of the 2D sheets to the 3D rutile-like structures, meant that the magnetic properties were of great interest. Details are provided for complex **2**, which contains high-spin octahedral Ni(II) (d^8) centres. The powder X-ray diffraction patterns of the samples matched that calculated from the crystal structure. In a field of 1 T, the μ_{Ni} values remain essentially constant at 3.14 μ_B between 300–50 K, then increase gradually, reaching a maximum of 5.77 μ_B at 6 K (Fig. 4). The corresponding Curie–Weiss constants are $\theta = +4.7$ K, $C = 1.2$ (20–300 K). This behavior is indicative of weak ferromagnetic coupling. In low fields such as 100 or 20 Oe there is a dramatic increase in μ values at 21 K, due to traces of the ferromagnet α-$[Ni(dca)_2]$[1a,c,d] in the crystals, which persisted despite a number of synthetic approaches being explored. This was followed by a second sharp and large increase at 5 K due to a magnetic phase transition that is intrinsic to this 2D material. It is likely that a sharp maximum in μ_{eff} will occur in the 100 and 20 Oe data below 5 K (*vide infra*).

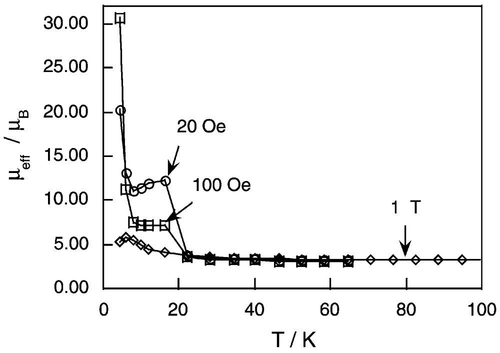

Fig. 4 Plot of μ_{eff} *versus* temperature for **2** in fields of 1 T (◇), 100 (□) and 20 Oe (○).

The long-range order was probed by measurement of the field-cooled (FCM; $H = 20$ Oe) and zero-field cooled magnetisation data (ZFCM), shown in Fig. 5. Bifurcation at 20 K is due to traces of the ferromagnet α-$[Ni(dca)_2]$. An abrupt increase in both the FCM and ZFCM occurs at 5.7 K, followed by a sharp maximum at 5 K, then a shoulder at 4.6 K. The FCM values then decrease, in a cusp, to approximately $M_{2K}/M_{max} = 0.56$, while the ZFCM values decrease towards zero. In conjunction with the positive θ value, we assign this rather unusual behavior to a ferromagnetic transition at 5.7 K followed by 3D antiferromagnetic order below 5 K. Cognizant of the possible contribution of traces of α-$[Ni(dca)_2]$, we measured the magnetisation hysteresis loops at 12, 8, 6, 4.5 and 2 K (Fig. 5). The 6–12 K data show no hysteresis, and display shapes unlike those observed[1a,c,d] for α-$[Ni(dca)_2]$, even when it is added in small quantities.[4] Thus α-$[Ni(dca)_2]$ is not contributing and the 4.5 and 2 K plots are intrinsic to **2** and typical of a soft ferromagnet with coercive field, at 2 K, of 65 Oe and remnant magnetisation of 3177 cm^3 mol^{-1} Oe. At 2 K, the low-field *M* values are spontaneous while high-field values are approaching saturation with *M*, at 5 T, of 1.85 $N\beta$. It is tempting to relate the 5.7 K transition to ferromagnetic order within the sheets of the network and the antiferromagnetic behavior below 5 K to 3D interactions between sheets *via* the H_2O ··· phz pathways. The μ_3-dca bridging mode within the sheets is important in allowing ferromagnetic exchange to occur.

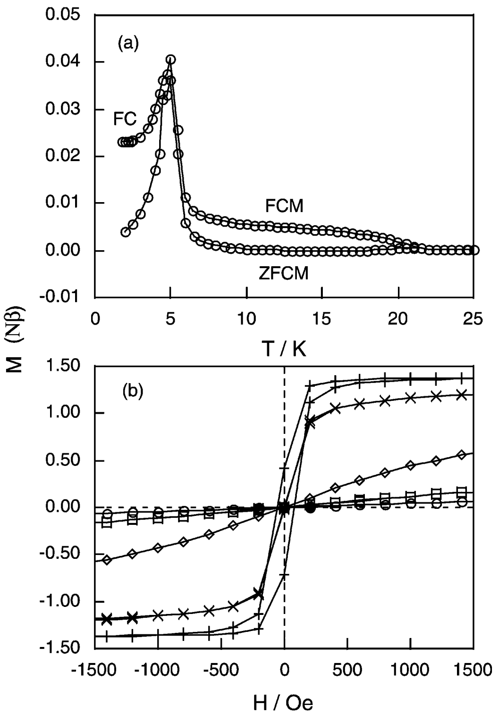

Fig. 5 Plots of (a) FCM (upper curve) and ZFCM for **2**; (b) hysteresis loop for **2** at 2 (+), 4.5 (×), 6 (◇), 8 (□) and 12 K (○).

Interestingly, the Co(II) analogue, **1**, also shows a field dependence in μ_{Co}, below 20 K, leading to a rapid and small increase, under applied fields of 1000, 100 and 20 Oe, from the 20 K value of 4.20 μ_B (μ_{Co} is 4.84 μ_B at 300 K). The 10000 Oe data show that the increase in μ_{Co}, below 20 K, goes through a maximum at 4.3 K, in much the same way observed for $Co[C(CN)_3]_2$[9] and for $Co(dca)_2(pyrimidine)$,[5] both of which have 3D network structures. There is no bifurcation in the FCM and ZFCM plots of **1**, between 20 and 2 K, in line with a lack of long-range order and due to the presence of weak intranetwork ferromagnetic coupling. We are presently pursuing the isostructural $Fe(dca)_2(H_2O)\cdot phz$ (**3**) derivative, for which we have the structure and only a few pure crystals, the bulk sample being difficult to separate from traces of a solvated phase, $Fe(dca)_2(H_2O)_2\cdot 2phz\cdot 2EtOH$ (**4**), when prepared in ethanol. The latter compound shows long-range order at $T_c = 4.5$ K which is surprising in view of bridging in the network being of $\mu_{1,5}$-dca type only.[10] Clearly, further work is required in attempting to relate long-range magnetic order to dca bridging modes in these coordination polymers.

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Notes and references

† **1**: A hot ethanol solution (5 ml) of $Co(NO_3)_2\cdot6H_2O$ (207 mg, 0.71 mmol) was added to a hot ethanol solution (10 ml) of Na(dca) (100 mg, 1.12 mmol) and phenazine (100 mg, 0.55 mmol). A few days later a small quantity of red cubic crystals of **1** formed in a red solution (76 mg, 0.195 mmol, 35%). Found: C, 49.73; H, 2.94; N, 28.48. Calc. for $C_{16}H_{10}CoN_8O$: C, 49.37; H, 2.59; N, 28.79%. IR (cm^{-1}, KBr disc): 2363m, 2325m, 2255m, 2185s, 1656m, 1365s, 1292m, 1147w, 828w, 752s, 670m, 497w. Powder XRD: The diffractogram of the bulk product matches that calculated from the crystal structure.

2: A hot ethanol solution (5 ml) of $Ni(NO_3)_2\cdot6H_2O$ (320 mg, 1.10 mmol) was added to a hot ethanol solution (10 ml) of Na(dca) (200 mg, 2.25 mmol) and phenazine (200 mg, 1.11 mmol), resulting in a pale green solution. A few days later green cubic crystals of **2** formed (57 mg, 0.147 mmol, 13%). Found: C, 49.58; H, 2.75; N, 28.42. Calc. for $C_{16}H_{10}NiN_8O$: C, 49.40; H, 2.59; N, 28.80%. IR (cm^{-1}, KBr disc): 2326m, 2261m, 2190s, 1664m, 1516m, 1475w, 1434w, 1384m, 1293s, 1215w, 1147m, 1121w, 1073w, 996w, 957w, 907w, 828m, 750s, 673m, 595m, 533m, 501w. Powder XRD: The diffractogram of the bulk product matches that calculated from the crystal structure.

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7 X-Ray data for $C_{16}H_{10}CoN_8O$ **1**: M = 389.25, orthorhombic, space group *Pbcn* (no. 60), a = 22.3876(4), b = 7.4110(1), c = 19.5978(3) Å, U = 3251.56(9) $Å^3$, T = 123 K, Z = 8, D_c = 1.590 g cm^{-3}, $F(000)$ = 1576, μ(Mo-Kα) = 1.080 mm^{-1}, orange rod, 32505 reflections measured, 4006 unique (R_{int} = 0.0375), 245 parameters, R_1 = 0.0360 for 2870 reflections with $I > 2\sigma(I)$, wR_2 = 0.0896 (all data). For $C_{16}H_{10}NiN_8O$ **2**: M = 389.03, orthorhombic, space group *Pbcn* (no. 60), a = 22.4149(7), b = 7.3152(1), c = 19.5234(4) Å, U = 3201.2(1) $Å^3$, T = 123 K, Z = 8, D_c = 1.614 g cm^{-3}, $F(000)$ = 1584, μ(Mo-Kα) = 1.237 mm^{-1}, green block, 32930 reflections measured, 3894 unique (R_{int} = 0.0730), 245 parameters, R_1 = 0.0506 for 2066 reflections with $I > 2\sigma(I)$, wR_2 = 0.1519 (all data). CCDC reference numbers 175180 and 175181. See http://www.rsc.org/suppdata/dt/b1/b110920k/ for crystallographic data in CIF or other electronic format.

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