Coordination Polymers of Dicyanamide and Methylpyrazine: Syntheses, Structures, and Magnetic Properties

5 AUTHORS, INCLUDING:

Alexander R. Harris
University of Wollongong
37 PUBLICATIONS **563** CITATIONS

SEE PROFILE

Stuart R. Batten
Monash University (Australia)
311 PUBLICATIONS **14,498** CITATIONS

SEE PROFILE

Boujemaa Moubaraki
Monash University (Australia)
343 PUBLICATIONS **9,456** CITATIONS

SEE PROFILE

Keith S Murray
Monash University (Australia)
553 PUBLICATIONS **14,902** CITATIONS

SEE PROFILE

Delivered at the International Conference on Materials for Advanced Technologies 2003, Singapore, December 7−12, 2003

Coordination Polymers of Dicyanamide and Methylpyrazine: Syntheses, Structures, and Magnetic Properties

Anna M. Kutasi, Alexander R. Harris, Stuart R. Batten,* Boujemaa Moubaraki, and Keith S. Murray*

School of Chemistry, P.O. Box 23, Monash University 3800, Australia

ABSTRACT: The crystal structures of $M(dca)_2(Mepyz)_2 \cdot H_2O$, M = Co (**1**), Ni (**2**), dca = dicyanamide, $N(CN)_2^-$, and Mepyz = methylpyrazine; $[Mn(dca)_2(Mepyz)_2][Mn(dca)_2(Mepyz)]_2 \cdot 2MeCN$ (**3**); and $Mn_2(dca)_3(NO_3)(Mepyz)_2$ (**4**) are reported. Compounds **1** and **2** are isomorphous and consist of two-dimensional (2D) (4,4) sheets, with bridging $\mu_{1,5}$-dca ligands and trans-disposed monodentate Mepyz ligands. Compounds **3** and **4** were obtained as an intimate mixture from the same reaction mixture. Compound **3** contains both one-dimensional (1D) chains, in which Mn atoms are bridged by double $\mu_{1,5}$-dca bridges and the Mepyz ligands are trans and monodentate, and 2D (4,4) sheets, in which similar 1D chains are connected by bridging Mepyz ligands. The structure of **4** contains two interpenetrating 4,6-connected three-dimensional networks, with bridging $\mu_{1,5}$-dca anions, bridging Mepyz ligands, and chelating NO_3^- anions. Only very weak coupling and no long-range magnetic ordering intrinsic to these materials were observed for **1** or **2**, although traces of the ferromagnets α-Co(dca)$_2$ and α-Ni(dca)$_2$ were observable in very small applied fields, with ordering temperatures at 9 and 21 K, respectively.

Introduction

Dicyanamide [dca, $N(CN)_2^-$, Scheme 1] is currently a ligand of great interest, due mainly to the observation of long-range magnetic ordering in the binary α-M(dca)$_2$ compounds.[1−3] Of particular interest is the generation of new metal−dca architectures through the introduction of coligands into the structures.[4] More generally, however, dca is also a very interesting ligand in the wider context of coordination polymers, due to its anionic charge [meaning that other anions are not required to be incorporated into the structure to balance the charge on the metal in $M(dca)_2L_x$ species] and the variety of bridging modes displayed.[4] In fact, the metal−dca subnet has proved to be a particularly malleable system toward structural modification.[5]

In particular, we and others have studied the use of bridging pyrazine (pyz, Scheme 1) coligands.[6−10] Two polymorphs are formed. α-M(dca)$_2$(pyz), where M = Mn, Fe, Co, Ni, Cu, or Zn, contains two interpenetrating α-Po-like three-dimensional (3D) nets, in which the metal atoms are connected by bridging $\mu_{1,5}$-dca ligands (i.e., they coordinate via the nitrile nitrogen atoms only) into (4,4) sheets; these sheets are then connected by bridging pyz ligands. β-M(dca)$_2$(pyz), where M = Co, Ni, Cu, or Zn, consists of two-dimensional (2D) (4,4) sheets in which the metal atoms are bridged into chains by $M(\mu_{1,5}$-dca)$_2M$ double bridges; these chains are then connected by bridging pyz ligands. Both series of

Scheme 1
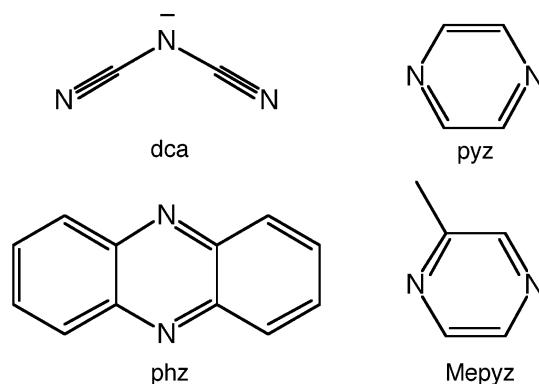
compounds generally show weak antiferromagnetic coupling, with no long-range ordering, except α-Mn-(dca)$_2$(pyz), which shows long-range antiferromagnetic ordering below $T_N = 2.5$ K.

When the more sterically bulky ligand phenazine (phz, Scheme 1) is used in place of pyz, completely different structures are obtained.[11] Of particular interest are the compounds $M(dca)_2(H_2O) \cdot phz$, where M = Fe, Co, or Ni.[4,11,12] The structures consist of sheets of metal ions bridged by both bidentate $\mu_{1,5}$-dca and tridentate $\mu_{1,3,5}$-dca anions. The topology of the sheets is identical to a 2D substructure that can be identified in the rutile-like α-M(dca)$_2$. These sheets alternate with layers of intercalated phz molecules, which do not coordinate to the metals but hydrogen bond to water ligands attached to the metals in the sheets. The Fe and Ni structures show long-range magnetic ordering, with

---

* To whom correspondence should be addressed. (S.R.B.) E-mail: stuart.batten@sci.monash.edu.au. (K.S.M.) E-mail: keith.s.murray@sci.monash.edu.au.

Table 1. Crystallographic Data

	1	**2**	**3**	**4**
formula	$C_{14}H_{14}N_{10}CoO$	$C_{14}H_{14}N_{10}NiO$	$C_{36}H_{30}N_{28}Mn_3$	$C_{16}H_{12}Mn_2N_{14}O_3$
fw	397.28	397.06	1019.70	558.28
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Pnna*	*Pnna*	*Pbam*	*Pbcn*
a (Å)	13.7982(3)	13.6754(6)	14.7318(9)	29.4481(9)
b (Å)	13.0362(2)	13.0449(4)	20.7684(13)	12.3608(4)
c (Å)	9.2955(2)	9.2508(4)	7.5127(3)	12.3821(3)
V (Å^3)	1672.04(6)	1650.29(11)	2298.6(2)	4507.1(2)
Z	4	4	2	8
D_c (g cm^{-3})	1.578	1.598	1.473	1.645
μ (mm^{-1})	1.055	1.204	0.874	1.172
data collected	11 397	12 189	17 239	19 948
unique data (R_{int})	2556 (0.0478)	2500 (0.0286)	2927 (0.1385)	6711 (0.0345)
obs. data [$I > 2\sigma(I)$]	2167	2113	1950	5259
$R1$, $wR2$ (obs. data)	0.0342, 0.0937	0.0411, 0.1070	0.0848, 0.1442	0.0598, 0.1253
$R1$, $wR2$ (all data)	0.0413, 0.0976	0.0531, 0.1127	0.1423, 0.1626	0.0815, 0.1310

T_c = 4.5 and 5.7 K, respectively. No long-range order is observed for Co, but unusual field-dependent effects were noted below 10 K.[4]

Given the difference in structures and magnetic properties obtained between the pyz and the related but more sterically hindered phz, it was of interest to look at other sterically hindered pyz derivatives as coligands. In particular, this paper describes four new compounds obtained with dca and methylpyrazine (Mepyz) ligands.

As further support of this study, two other structures with sterically hindered pyz ligands have also been reported to display long-range magnetic ordering. Mn-(dca)$_2$(H$_2$O)$_2$·2(2,5-Me$_2$pyz), where 2,5-Me$_2$pyz = 2,5-dimethylpyrazine, contains (4,4) sheets in which metal atoms are bridged by $\mu_{1,5}$-dca ligands and water ligands occupy the axial positions of the metals.[13] As for the above phz structures, the 2,5-Me$_2$pyz molecules lie between the layers and hydrogen bond to the water ligands, creating a 3D net. A spin-canted phase transition is observed in the magnetism at 1.78 K. The structure of Cu$_2$(dca)$_4$(2,5-Me$_2$pyz) contains two interpenetrating five-connected 3D nets, in which the five-coordinate Cu atoms are bridged by 2,5-Me$_2$pyz and $\mu_{1,5}$-dca ligands.[14] Long-range antiferromagnetic ordering (T_N = 5.0 K) is reported. In contrast, no long-range magnetic ordering has been observed for Mn(dca)$_2$-(H$_2$O)(NH$_2$pyz), where NH$_2$pyz = aminopyrazine, which contains one-dimensional (1D) ladders whose sides are composed of single $\mu_{1,5}$-dca bridges between metals and whose rungs are defined by double $\mu_{1,5}$-dca bridges.[13] The octahedral coordination geometries of the metals are completed by terminal NH$_2$pyz and water ligands. The structure of Mn(dca)$_2$(H$_2$O)$_2$·2Me$_4$pyz, where Me$_4$-pyz = tetramethylpyrazine, also displays a 1D motif and no long-range ordering.[15] This structure contains linear chains composed of metal atoms bridged in each direction by double $\mu_{1,5}$-dca bridges. The axial positions of the metal atoms are occupied by water ligands that hydrogen bond to uncoordinated Me$_4$pyz molecules to create H$_2$O···Me$_4$pyz···H$_2$O···Me$_4$pyz··· chains, which are parallel to and flank either side of each M(dca)$_2$ chain.

Experimental Section

General Synthetic Details. Sodium dca [Na(dca)] was supplied by Fluka Chemicals or Degussa AG and Mepyz by Aldrich. Both were used as supplied.

Synthesis of Co(dca)$_2$(Mepyz)$_2$·H$_2$O (1). An ethanol solution (5 mL) of Co(NO$_3$)$_2$·4H$_2$O (326 mg, 1.12 mmol) was added to an ethanol solution (10 mL) containing Mepyz (105 mg, 1.12 mmol) and Na(dca) (200 mg, 2.25 mmol). A light purple solution formed on addition of metal to the ligands. Two days later, pink crystals of **1** formed. Yield, 158 mg (36%). Anal. calcd for C$_{14}$H$_{14}$CoN$_{10}$O: C, 42.33; H, 3.55; N, 35.26. Found: C, 42.76; H, 3.74; N, 35.30. IR (KBr, cm^{-1}): 3444 (m, br), 2344 (m), 2311 (s), 2244 (m), 2178 (s), 1617 (m), 1383 (s), 1294 (w), 1167 (m), 1078 (m), 1028 (m), 911 (w), 833 (m), 739 (w), 644 (m), 511 (m). Powder XRD: The diffractogram matched that calculated from the crystal structure.

Synthesis of Ni(dca)$_2$(Mepyz)$_2$·H$_2$O (2). An ethanol solution (5 mL) of Ni(NO$_3$)$_2$·6H$_2$O (320 mg, 1.12 mmol) was added to an ethanol solution (10 mL) containing Mepyz (105 mg, 1.12 mmol) and Na(dca) (200 mg, 2.25 mmol). A pale green solution formed on addition of the metal to the ligands. Four days later, blue crystals of **2** formed. Yield, 137 mg (31%). Anal. calcd for C$_{14}$H$_{14}$NiN$_{10}$O: C, 42.35; H, 3.55; N, 35.28. Found: C, 42.05; H, 3.63; N, 35.36. IR (KBr, cm^{-1}): 3449 (m, br), 3088 (w), 2363 (m), 2316 (s), 2252 (m), 2191 (s), 1611 (w), 1384 (s), 1295 (w), 1161 (m), 1078 (m), 1026 (m), 968(w), 916 (w), 838 (m), 741 (w), 647 (m), 506 (m), 421 (m). Powder XRD: The diffractogram matched that calculated from the crystal structure.

Synthesis of [Mn(dca)$_2$(Mepyz)$_2$][Mn(dca)$_2$(Mepyz)]$_2$·2MeCN (3) and Mn$_2$(dca)$_3$(NO$_3$)(Mepyz)$_2$ (4). A solution of Na(dca) (400 mg, 4.49 mmol) in water/acetonitrile (1:1; 2 mL) was added to a solution of Mepyz (200 mg, 2.125 mmol) in acetonitrile (3 mL). The resulting solution was mixed with a solution of Mn(NO$_3$)$_2$·4H$_2$O (520 mg, 2.07 mmol) in acetonitrile (5 mL). The next day, an intimate mixture of colorless needles of **3** and colorless octahedra of **4** appeared.

Crystal Structure Determinations. Single-crystal data and details of the structure determinations are presented in Table 1. Data were collected at 123 K on a Nonius KappaCCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å), using ϕ and ω rotations with 1° frames. The images were processed with the HKL suite of programs.[16] Solutions were obtained using SHELXS-97[17] followed by successive difference Fourier methods, and structures were refined against F^2 using SHELXL-97.[17] Face-indexed absorption corrections were applied to all structures except **4**. All hydrogen atoms except those belonging to the water molecules in **1** and **2** were placed at calculated positions and not refined. In **1**, the water hydrogens were found in the difference maps and refined; in **2**, they were neither found nor assigned. In **3**, one of the Mepyz ligands lies across a mirror plane, and thus, the disordered methyl group was refined with half occupancy; the correspondingly disordered aromatic hydrogen was not assigned. All nonhydrogen atoms were refined anisotropically.

Powder X-ray Diffraction. Patterns were measured on a Scintag Automated Powder Diffractometer using a Cu Kα monochromatic radiation source (λ = 1.54059 Å), a solid state Ge detector, a 2 mm divergence slit, and a 3 mm receiving slit.

Magnetic Measurements. Magnetic measurements were carried out as described previously[18] using a Quantum Design MPMS 5 Squid magnetometer for DC magnetization measurements. To check for crystallite orientation effects in **1**, the variable field DC magnetization data were determined for neat-powdered and Vaseline-dispersed samples and both showed the same results.

Results and Discussion

Syntheses and Crystal Structures. Reaction of metal nitrate with Mepyz and Na(dca) in ethanol gave pink crystals (Co) or blue crystals (Ni) of $M(dca)_2$-(Mepyz).H_2O, M = Co (**1**), Ni (**2**). The structures were determined by X-ray crystallography and found to be isomorphous. The asymmetric unit consists of one octahedral metal atom, which lies on a 2-fold axis, one bridging bidentate $\mu_{1,5}$-dca anion, coordinating via the nitrile nitrogens [M−N = 2.1210(12), 2.1008(12) Å (**1**); 2.0831(15), 2.0646(15) Å (**2**)], one monodentate Mepyz ligand [M−N = 2.1553(12) Å (**1**), 2.0998(16) Å (**2**)], and one water molecule. The dca anions bridge the metal atoms into (4,4) sheets (Figure 1), with the coordination sphere completed by trans monodentate Mepyz ligands, which coordinate via the less sterically hindered nitrogen. The water molecules lie within the square windows of the sheets and hydrogen bond to the uncoordinated nitrogens of Mepyz ligands belonging to sheets above and below the sheet in which they are contained [for **1**: O1−H1 = 0.90(3) Å, H1···N5 = 2.40(3) Å, O1···N5 = 3.228(2) Å, O1−H1···N5 = 152(3)°; for **2**: O1···N5 = 3.263(2) Å]. This generates two interpenetrating networks; however, there are further weak interactions between the waters and the methyl groups of the Mepyz ligands of the sheet in which they lie [for **1** (**2**): H7C···O1 = 2.614 Å (2.582 Å), C7···O1 = 3.456(2) Å (3.254(3) Å), C7−H7C···O1 = 144.1° (144.4°)]. There are also intersheet interactions between the pyz hydrogens para to the methyl groups and the amide dca nitrogens [for **1** (**2**): H3A···N3 = 2.491 Å (2.488 Å), C3···N3 = 3.262(2) Å (3.254(3) Å), C3−H3A···N3 = 138.4° (137.7°)]. The sheets are significantly corrugated, with the M{N-(dca)}$_4$ plane inclined to the mean plane of the sheet. The sheets interdigitate, as shown in Figure 1, creating π stacks of Mepyz ligands from alternating sheets. There are two crystallographically distinct $\pi-\pi$ interactions that alternate along the stacks (closest nonhydrogen contacts are 3.416 and 3.522 Å for **1** and 3.387 and 3.481 Å for **2**).

Reaction of manganese nitrate with Mepyz and Na-(dca) in acetonitrile/water gave two sorts of colorless crystals—rods of **3** and small octahedra of **4**. However, because the syntheses were difficult to reproduce consistently and the crystal mixtures obtained were difficult to separate, only the crystal structures are reported here.

The structure of **3** contains two types of coordination polymers—1D chains and 2D sheets. The 1D chains (Figure 2a), of formula $Mn(dca)_2(Mepyz)_2$, consist of Mn atoms, which lie on sites of $2/m$ symmetry, bridged by double $\mu_{1,5}$-dca bridges, which coordinate via the nitrile nitrogens only [Mn−N = 2.194(4) Å]. The axial positions of the octahedral Mn atoms are occupied by monodentate Mepyz ligands [Mn−N = 2.303(7) Å], which coordinate via the less sterically hindered nitrogen atoms, and are disordered across a mirror plane. The chains
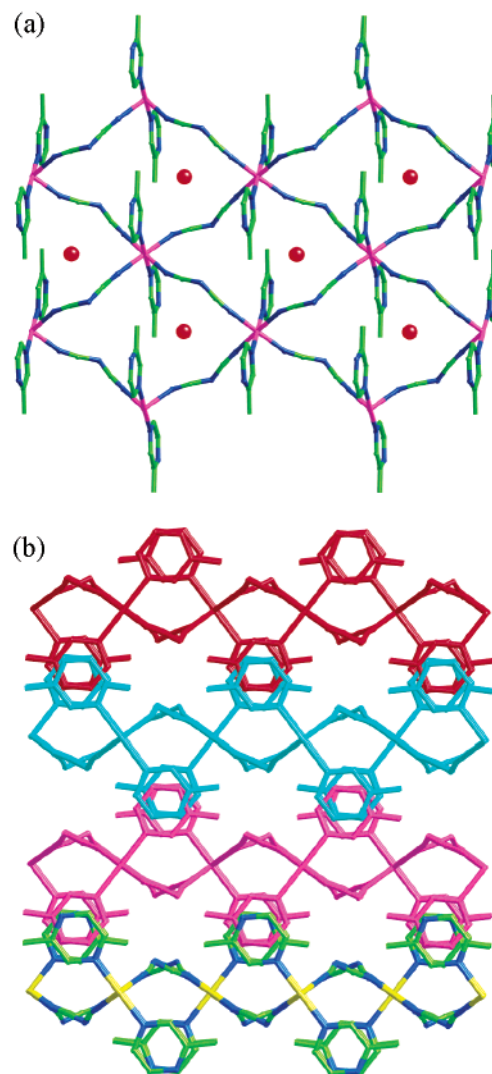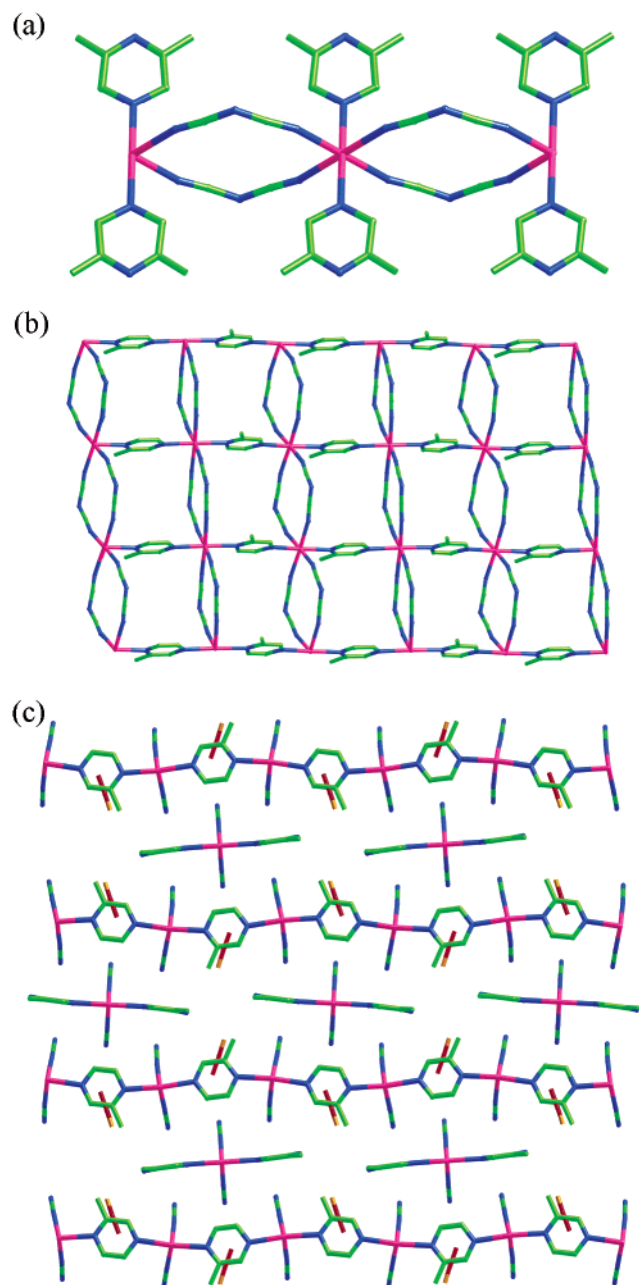

Figure 1. (a) Two-dimensional sheet structure of **2**. Ni atoms are represented in purple, carbons are represented in green, and nitrogens are represented in blue; hydrogens are omitted for clarity. Also shown are the intercalated water molecules (red). The structure of **1** is isomorphous. (b) Interdigitation of the undulating sheets in **2**.

are similar to those seen for other $M(dca)_2L_2$ structures,[4] including the L = pyridine derivatives. The sheets (Figure 2b), of formula $Mn(dca)_2(Mepyz)$, also contain chains of Mn atoms, which lie on mirror planes, bridged by double $\mu_{1,5}$-dca bridges coordinating via the nitrile nitrogens [Mn−N = 2.226(4), 2.202(4) Å]. In this case, however, the Mepyz ligands, which again occupy the axial positions of the Mn cations, bridge the chains into 2D (4,4) sheets [Mn−N = 2.323(5), 2.301(5) Å]. This sheet topology is also seen in the structures of β-$M(dca)_2$-(pyz).[6-8] The steric bulk of the methyl groups in **3**, however, induces a slight undulation in the sheets not present in the pyz analogues, as the $Mn(dca)_2$ chains within the sheets tilt away from the methyl group (Figure 2c). This tilting is possible because the Mepyz ligands bridge such that each Mn is coordinated to one ligand with the methyl group ortho to the metal and to another with a meta methyl group.

The chains and sheets pack such that layers of chains alternate with the sheets, as shown in Figure 2c. The most significant contacts between the chains and the
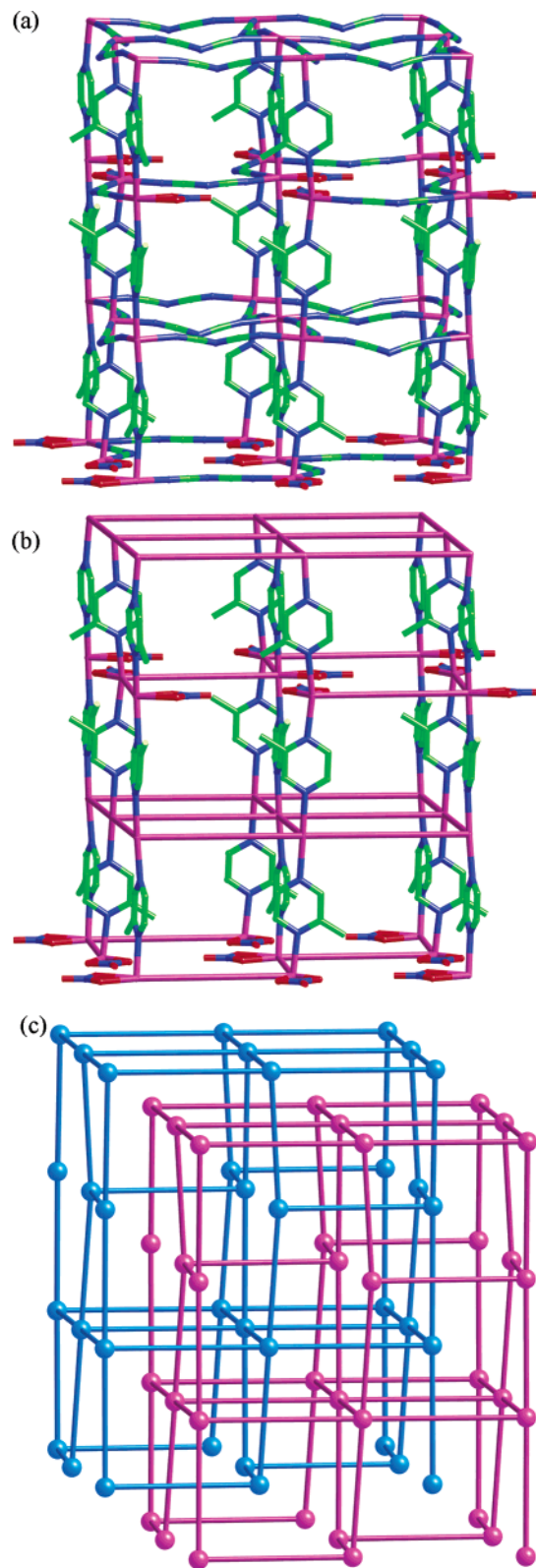
(a)

(b)

(c)

Figure 2. (a) View of a 1D chain contained in **3**. Mn atoms are represented in purple, carbons are represented in green, and nitrogens are represented in blue; hydrogens are omitted for clarity. (b) A view of a 2D (4,4) sheet also contained in **3**. (c) The packing of the chains and sheets in the structure of **3**. The intercalated MeCN molecules are also shown in red (carbon atoms) and orange (nitrogen atoms).

sheets are weak C−H···N contacts between a methyl hydrogen of the chain and a sheet dca amide nitrogen [H10C···N4 = 2.67 Å, C10···N4 = 3.55(1) Å, C10−H10C···N4 = 149°] and between the sheet Mepyz hydrogens ortho to the methyl groups and the uncoordinated nitrogens of the chain Mepyz ligands [H3A···N8 = 2.66 Å, C3···N8 = 3.55(1) Å, C3−H3A···N8 = 156°]. The structure also contains uncoordinated acetonitrile molecules within the lattice. These lie within the square windows of the (4,4) sheets (Figure 2c).

The structure of **4** consists of two interpenetrating 4,6-connected 3D nets (Figure 3). The nets can be described in terms of 1D chains of Mn atoms bridged by Mepyz

(a)

(b)

(c)

Figure 3. (a) Structure of a single 4,6-connected net in **4**. Mn atoms are represented in purple, carbons are represented in green, nitrogens are represented in blue, and oxygens are represented in red; hydrogens are omitted for clarity. (b) The same net shown in panel a, except with the dca ligands represented by schematic Mn···Mn connections (for clarity). (c) Schematic representation of the two interpenetrating nets in **4**. For clarity, only the Mn atoms and the connections between them (via bridging dca and Mepyz ligands) are shown. The orientation is similar to panels a and b, with the Mn(Mepyz) chains vertical.
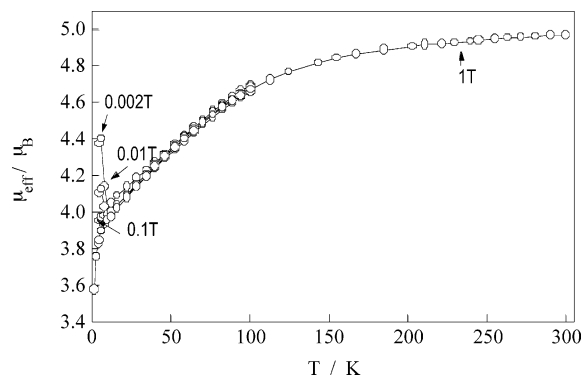
Figure 4. Plots of effective magnetic moment, per Co, vs temperature for **1** in the applied field values shown. The solid lines are not calculated values. The rapid increase occurring at 9 K, in low fields, is due to traces of α-Co(dca)$_2$; see text [N.B. $\mu^2 = 7.991(\sigma T)$; 1 T = 10 000 Oe].

ligands [Mn−N = 2.272(3)−2.336(3) Å] running parallel to the z-axis. These chains are cross-linked by dca anions, bridging in a bidentate $\mu_{1,5}$ fashion, in two different types of layers, which alternate. In one type of layer, each Mn atom is coordinated to four dca ligands [Mn−N = 2.190(3)−2.222(3) Å], to give a (4,4) sheet. Therefore, the Mn atoms in these layers are 6-connecting. In the second type of layer, each Mn atom is coordinated to a chelating nitrate anion [Mn−O = 2.262-(2) and 2.290(3) Å] and to two cis dca anions [Mn−N = 2.143(3) and 2.140(3) Å], to generate layers of zigzag 1D chains. The Mn atoms in this layer are thus 4-connecting. The overall network is therefore a 4,6-connected net; the Schafli symbol is $(4^4 \cdot 6^2)(4^8 \cdot 6^6 \cdot 8)$.

One explanation for the cross-linking of the Mn-(Mepyz) chains by two different sorts of layers may be found in the positioning of the methyl groups of the Mepyz ligands. The methyl groups are ortho to the manganese atoms in the layers composed of the 1D zigzag chains (Figure 3); the methyl groups (both above and below the layer) project into the space where, in the other type of layer, the extra bridging dca anions would have been. For the (4,4) sheet type layers, the methyl groups are meta to the Mn cations. Thus, the methyl groups of the Mepyz ligands have an important structure-directing effect. For comparison, in the structure of α-Mn(dca)$_2$(pyz),[7−10] Mn(pyz) 1D chains similar to the Mn(Mepyz) chains described above are cross-linked only by (4,4) sheets of dca anions, and the structure contains two interpenetrating α-Po 3D nets, in which all Mn nodes are 6-connecting.

Magnetic Measurements. A plot of effective magnetic moment, μ_{eff}, per metal ion for **1** is given in Figure 4. The μ_{eff} value for the Co(II) compound of 4.95 μ_B, at 300 K in a field of 1 T, decreases in a manner typical of an orbitally degenerate $^4T_{1g}$ (d^7 octahedral) system undergoing spin−orbit coupling.[19] The more rapid decrease toward 3.58 μ_B at 2 K provides evidence for very weak antiferromagnetic coupling also occurring, as anticipated for $\mu_{1,5}$-dca bridging. Similar behavior was noted in other Co(dca)$_2$L adducts[20−23] and in anionic Co(dca)$_3^-$ 2D and 3D networks.[18,24] The rapid increase in μ_{eff} occurring at ca. 9 K when applied fields of 100 or 20 Oe were used is most likely due to traces of the ferromagnetically ordered "parent" compound α-Co(dca)$_2$ being present in the crystalline sample, rather than to

any intrinsic ordering. α-Co(dca)$_2$ is known to order at T_c = 9.0 K.

The Ni(II) complex shows temperature-independent μ_{eff} values of 3.12 μ_B when measured between 300 and 21 K in a field of 1 T (Figure S1). There is a slight increase in μ_{eff} below this, which becomes a very sharp rise, up to 28 μ_B, in a field of 20 Oe. The shape of the μ_{eff} behavior in these low applied fields is typical of that displayed by the ordered ferromagnet α-Ni(dca)$_2$, which has a T_c = 21 K. As in the Co(II) complex, above, we believe that traces of α-Ni(dca)$_2$ are responsible for the observed plots, at low temperatures, rather than **2**. If this new 2D species was fully responsible for the ordered behavior, the μ_{eff} vs temperature plot between 21 and 300 K would not remain horizontal as shown. In our experience with M(dca)$_2$−Lewis base adducts[6,7] and with anionic M(dca)$_3^-$ networks,[18] it is the Ni(II) derivative that commonly shows magnetic phase transitions at ca. 21 K. In some cases, it is likely, from AC susceptibility and DC magnetization hysteresis comparisons,[18] that traces of a material different to α-Ni(dca)$_2$ are responsible for the rapid jump in μ_{eff} but that the bulk product is not ordering, while in other cases traces of α-Ni(dca)$_2$ are responsible. The latter is the case here.

Conclusions

The introduction of the methyl group to the pyz ring induces a range of structures different to those obtained with the unmethylated pyz. The structures of **1** and **2** contain 2D (4,4) sheets, **3** contains both 1D chains and 2D (4,4) sheets, while **4** contains two interpenetrating 3D 4,6-connected nets. The structure-directing effect of the methyl group is apparent in the fact that only the Mn structures (**3** and **4**) contain bridging Mepyz ligands. The structure of **3** contains both bridging (sheets) and terminal (chains) Mepyz ligands, while in **4** the directing effect of the steric bulk of the methyl group is apparent when the structure is compared to the α-M(dca)$_2$(pyz) compounds. The (4,4) sheets in **3** are analogous to those seen in β-M(dca)$_2$(pyz); however, no 1D chains are seen in the latter. Unlike the structures obtained with the more bulky pyz derivatives, such as Me$_4$pyz[15] and phz,[4,11,12] in which both nitrogens are sterically hindered, there are no uncoordinated Mepyz ligands in the structures described here. The structures also differ from that of Mn(dca)$_2$(H$_2$O)(NH$_2$pyz), where NH$_2$pyz = aminopyrazine, which contains 1D ladders.[13] Compounds **1**−**4** all contain dca anions bridging in the $\mu_{1,5}$ bridging mode; therefore, as expected, only weak coupling and no long-range magnetic order were observed for compounds **1** and **2**, with rapid increases in μ_{eff} at low temperatures and low fields believed to be due to traces of the corresponding α-M(dca)$_2$ contaminant being present. These strongly magnetic species can be observed even in the most crystalline and apparently analytically pure M(dca)$_2$(L)$_n$ species. Gao et al. were able to distinguish similar contaminants as well as intrinsic order in adducts of the type Co(dca)$_2$·L, where L = pyrazinedioxide or 2-methylpyrazinedioxide.[25]

Supporting Information Available: Crystallographic information files (CIF) for the structures reported herein and

a plot of effective magnetic moment vs temperature for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Batten, S. R.; Jensen, P.; Moubaraki, B.; Murray, K. S.; Robson, R. *Chem. Commun.* **1998**, 439.

(2) Kurmoo, M.; Kepert, C. *New J. Chem.* **1998**, *22*, 1515.

(3) Manson, J. L.; Kmety, C. R.; Huang, Q.-Z.; Lynn, J. W.; Bedele, G.; Pagola, S.; Stephens, P.; Liable-Sands, L.; Rheingold, A. L.; Miller, J. S. *Chem. Mater.* **1998**, *10*, 2552.

(4) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103.

(5) Batten, S. R.; Murray, K. S. *Aust. J. Chem.* **2001**, *54*, 605.

(6) Jensen, P.; Batten, S. R.; Fallon, G.; Hockless, D. C. R.; Moubaraki, B.; Murray, K. S.; Robson, R. *J. Solid State Chem.* **1999**, *145*, 387.

(7) Jensen, P.; Batten, S. R.; Moubaraki, B.; Murray, K. S. *J. Solid State Chem.* **2001**, *159*, 352.

(8) Brown, C. M.; Manson, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 12600.

(9) Manson, J. L.; Huang, Q.-Z.; Lynn, J. W.; Koo, H.-J.; Whangbo, M.-H.; Bateman, R.; Otsuko, T.; Wada, N.; Argyriou; Miller, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 162.

(10) Manson, J. L.; Incarvito, C. D.; Rheingold, A. L.; Miller, J. S. *J. Chem. Soc., Dalton Trans.* **1998**, 3705.

(11) Kutasi, A. M.; Batten, S. R.; Moubaraki, B.; Murray, K. S. *J. Chem. Soc., Dalton Trans.* **2002**, 819.

(12) Kutasi, A. M.; Batten, S. R.; Moubaraki, B.; Murray, K. S. Unpublished results.

(13) Manson, J. L.; Schlueter, J. A.; Geiser, U.; Stone, M. B.; Reich, D. H. *Polyhedron* **2001**, *20*, 1423.

(14) Yeung, W.-F.; Gao, S.; Wong, T.-C.; Lau, T.-C. *New J. Chem.* **2002**, *26*, 523.

(15) Kutasi, A. M.; Batten, S. R.; Harris, A. R.; Moubaraki, B.; Murray, K. S. *Aust. J. Chem.* **2002**, *55*, 311.

(16) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Sweets, R. M., Eds.; Academic Press: New York, 1996.

(17) Sheldrick, G. M. *SHELX 97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(18) van der Werff, P. M.; Batten, S. R.; Jensen, P.; Moubaraki, B.; Murray, K. S.; Tan, E. H.-K. *Polyhedron* **2001**, *20*, 1129.

(19) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

(20) Shi, Y.-J.; Chen, X.-T.; Li, Y.-Z.; Xue, Z.; You, X.-Z. *New J. Chem.* **2002**, *26*, 1711.

(21) Jurgens, B.; Hoppe, H. A.; Schnick, W. *Solid State Sci.* **2002**, *4*, 821.

(22) Marshall, S. R.; Incarvito, C. D.; Manson, J. L.; Rheingold, A. L.; Miller, J. S. *Inorg. Chem.* **2000**, *39*, 1969.

(23) Sun, B.-W.; Gao, S.; Ma, B.-Q.; Wang, Z.-M. *New J. Chem.* **2000**, *24*, 953.

(24) van der Werff, P. M.; Batten, S. R.; Jensen, P.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Cryst. Growth Des.* **2004**, *4*, 503−508.

(25) Sun, H.-L.; Gao, S.; Ma, B.-Q.; Su, G. *Inorg. Chem.* **2003**, *42*, 5399.