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# 1D chain structures of $M(dca)_2(phen)(H_2O) \cdot MeOH$ , $M = Mn, Fe, Co, Ni, Zn, Cd$ , $dca = dicyanamide$ , $N(CN)_2^-$ , $phen = 4,7$ -phenanthroline

Daniel S. Tonzing, Stuart R. Batten\*, Keith S. Murray

*School of Chemistry, Monash University, Clayton, Vic. 3800, Australia*

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## Abstract

The isomorphous structures of  $M(dca)_2(phen)(H_2O) \cdot MeOH$ ,  $M = Mn, Fe, Co, Ni, Zn$  and  $Cd$ ,  $dca = dicyanamide$ ,  $N(CN)_2^-$ ,  $phen = 4,7$ -phenanthroline contain 1D coordination polymer chains in which each metal atom is connected to two others by two pairs of  $\mu_{1,5}$  bridging  $dca$  anions, which coordinate in the equatorial positions. The axial positions of the metal are occupied by monodentate water and  $phen$  ligands. The chains are further linked into an overall 3D network by hydrogen bonding interactions between the water ligands, the uncoordinated nitrogen atoms of the  $phen$  ligands, and the intercalated methanol molecules.

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**Keywords:** Coordination polymer; Dicyanamide; 4,7-Phenanthroline; Crystal structure

## 1. Introduction

The dicyanamide ligand ( $dca$ ,  $N(CN)_2^-$ ) has, in recent years, been used to construct a large range of coordination polymers with interesting structural and magnetic properties [1]. Chief amongst these have been the 3D rutile-like structures of  $\alpha$ - $M(dca)_2$ , which were found to show long-range magnetic ordering [2]. Following this discovery, numerous new coordination polymers have been made which contain coligands (both bridging and terminal) in an effort to modify the  $M$ - $dca$  network topology and draw correlations between structure and magnetic properties. By and large, however, it has been found that long-range ordering requires the presence of the  $\mu_{1,3,5}$   $dca$  bridging mode (Scheme 1) within the structure (as is found in  $\alpha$ - $M(dca)_2$ ) [1]. Unfortunately, the  $\mu_{1,5}$   $dca$  bridging mode (Scheme 1), which is a poor mediator of magnetic exchange, is the most common one observed. Nonetheless, even when magnetic ordering is not present, the  $dca$  ligand has proven to be a remarkably proficient and versatile ligand for producing coordination polymers, many with structurally fascinating structures.

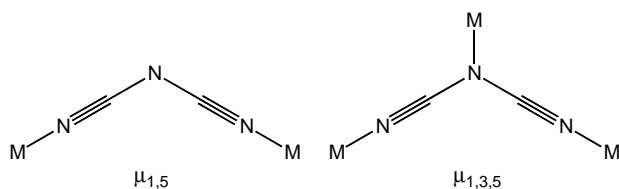
Of particular relevance to the work described here are the structures of  $M(dca)_2(H_2O) \cdot phz$ ,  $M = Co, Ni$ ,  $phz = phenazine$  [3]. They contain 2D layers in which metal ions are bridged by  $\mu_{1,3,5}$  and  $\mu_{1,5}$   $dca$  ligands; from a topological viewpoint the sheets are identical to 2D segments of the rutile-like  $\alpha$ - $M(dca)_2$  compounds. As a result, the  $Ni$  complex displays long-range order ( $T_c = 5.7$  K). The phenazine molecules lie between the sheets and hydrogen bond in a bridging fashion to water ligands attached to the sheets.

The steric bulk of the phenazine molecule is undoubtedly important in this structure; it is too large to coordinate directly to the metal, but does form hydrogen bonding interactions, which are important in the overall structure. By contrast, the sterically smaller pyrazine and 4,4'-bipyridine ligands form a series of different structures in which the pyridyl ligands coordinate (mostly in a bridging fashion) and the  $\mu_{1,3,5}$  bridging mode is not observed [4].

Thus, it was of interest to examine the incorporation of other large pyridyl-donor molecules into metal-dicyanamide coordination polymers, with a view to obtaining further coordination polymers containing the magnetically important  $\mu_{1,3,5}$  dicyanamide bridging mode. The ligand 4,7-phenanthroline was chosen for this purpose. It has been used previously, in a limited way, in the construction of low-dimensional coordination polymers, and has been found to display a variety of coordination modes: monodentate, bidentate bridging, and uncoordinated but bridging via hydrogen bonding [5]. The later

\* Corresponding author. Tel.: +61 3 9905 4606; fax: +61 3 9905 4597.

E-mail address: [stuart.batten@sci.monash.edu.au](mailto:stuart.batten@sci.monash.edu.au) (S.R. Batten).



Scheme 1. The two most common bridging modes of the dca ligands.

mode is that shown in the phenazine structures. We report here the results of this investigation.

## 2. Experimental

### 2.1. Materials and general methods

All reagents were purchased from Sigma–Aldrich Pty. Ltd, except Na(dca), which was kindly donated by Degussa AG, Trostberg, Germany. All chemicals were used as supplied. Elemental analyses (CHN) were carried out by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. IR spectra were recorded on a Perkin–Elmer 1600 Series Fourier Transform Spectrophotometer. Samples were prepared as KBr discs.

### 2.2. Synthesis of $Mn(dca)_2(phen)(H_2O) \cdot MeOH$ (1)

Sodium dicyanamide (100 mg, 1.12 mmol) was added to a solution of 4,7-phenanthroline (101 mg, 0.56 mmol) in MeOH (5 ml).  $Mn(NO_3)_2 \cdot 4H_2O$  (141 mg, 0.56 mmol) was dissolved in deionised water (5 ml). Crystals were grown by slow diffusion of the layered solutions of dicyanamide and 4,7-phenanthroline in MeOH over  $Mn(NO_3)_2 \cdot 4H_2O$  in water. Colourless crystals were filtered off after 3 weeks and dried by suction. Yield 115 mg, 49%. Anal. Calcd for  $C_{17}H_{14}N_8O_2Mn$ : C, 48.93; H, 3.38; N, 26.85%. Found: C, 49.11; H, 3.64; N, 26.98%. IR (KBr)/ $cm^{-1}$ : 3566w, 3383br, 3079m, 2780m, 2301s, 2234s, 2180s, 1641w, 1582w, 1524w, 1501m, 1447w, 1407w, 1386m, 1347s, 1305m, 1260w, 1106w, 1067w, 1013m, 938w, 842s, 797m, 721m, 675m, 632w, 566w, 529m, 506m, 496m, 446w.

### 2.3. Synthesis of $Fe(dca)_2(phen)(H_2O) \cdot MeOH$ (2)

A steam-bath warmed solution of sodium dicyanamide (100 mg, 1.12 mmol) and 4,7-phenanthroline (101 mg, 0.56 mmol) in MeOH (10 ml) was added to a solution of  $Fe(ClO_4)_2 \cdot xH_2O$  (143 mg, 0.56 mmol) in deionised water (10 ml). The orange crystals were filtered off and dried by suction. Yield 83 mg, 33%. Anal. Calcd for  $C_{17}H_{14}N_8O_2Fe$ : C, 48.83; H, 3.37; N, 26.79%. Found: C, 49.01; H, 3.68; N, 26.50%. IR (KBr)/ $cm^{-1}$ : 3676w, 3375m, 2296s, 2250m, 2237s, 2179s, 2153s, 1654w, 1582w, 1525w, 1501m, 1446w, 1407w, 1388w, 1340s, 1307m, 1106w, 1069w, 1008m, 941w, 843s, 800m, 782w, 724m, 677w, 634w, 567w, 536m, 496m, 448m, 438w, 430w, 420w.

### 2.4. Synthesis of $Co(dca)_2(phen)(H_2O) \cdot MeOH$ (3)

Sodium dicyanamide (100 mg, 1.12 mmol) was added to a solution of 4,7-phenanthroline (101 mg, 0.56 mmol) in MeOH (5 ml).  $Co(NO_3)_2 \cdot 6H_2O$  (163 mg, 0.56 mmol) was dissolved in deionised water (5 ml). Crystals were grown by slow diffusion of the layered solutions of dicyanamide and 4,7-phenanthroline in MeOH over  $Co(NO_3)_2 \cdot 6H_2O$  in water. The deep pink crystals were filtered off and dried by suction. Yield 182 mg, 77%. Anal. Calcd for  $C_{17}H_{14}N_8O_2Co$ : C, 48.47; H, 3.35; N, 26.60%. Found: C, 48.45; H, 3.62; N, 26.14%. IR (KBr)/ $cm^{-1}$ : 3855w, 3802w, 3738w, 3676w, 3638w, 3424s, 2360w, 2301s, 2242s, 2186s, 2158s, 1686w, 1654w, 1582w, 1560w, 1522w, 1501m, 1404w, 1384m, 1341s, 1308m, 1107w, 1069w, 1009m, 942w, 843s, 800m, 723w, 673w, 568w, 527m, 506m, 496m, 458w, 420w, 407w.

### 2.5. Synthesis of $Ni(dca)_2(phen)(H_2O) \cdot MeOH$ (4)

Sodium dicyanamide (100 mg, 1.12 mmol) was added to a solution of 4,7-phenanthroline (101 mg, 0.56 mmol) in MeOH (5 ml). This solution was then added to a solution of  $Ni(NO_3)_2 \cdot 6H_2O$  (163 mg, 0.56 mmol) dissolved in deionised water (5 ml). A pale green powder was filtered off and dried by suction. Crystal growing attempts were unsuccessful. Yield 193 mg, 81%. Anal. Calcd for  $C_{17}H_{14}N_8O_2Ni$ : C, 48.50; H, 3.35; N, 26.61%. Found: C, 47.93; H, 3.44; N, 25.86%. IR (KBr)/ $cm^{-1}$ : 3380br, 2302s, 2264m, 2248s, 2194s, 2164s, 1654w, 1583w, 1526w, 1502m, 1447w, 1407w, 1388w, 1340s, 1308m, 1260w, 1149w, 1108w, 1071w, 1010m, 977w, 945w, 843s, 801m, 781w, 724m, 680w, 634w, 568w, 534m, 506m, 497m, 451w, 441w, 416w.

### 2.6. Synthesis of $Zn(dca)_2(phen)(H_2O) \cdot MeOH$ (5)

Sodium dicyanamide (100 mg, 1.12 mmol) was added to a solution of 4,7-phenanthroline (101 mg, 0.56 mmol) in MeOH (5 ml).  $Zn(NO_3)_2 \cdot 6H_2O$  (167 mg, 0.56 mmol) was dissolved in deionised water (5 ml). Crystals were grown by slow diffusion of the layered solutions of dicyanamide and 4,7-phenanthroline in MeOH over  $Zn(NO_3)_2 \cdot 6H_2O$  in water. The yellow rod crystals were filtered off and dried by suction. Yield 161 mg, 67%. Anal. Calcd for  $C_{17}H_{14}N_8O_2Zn$ : C, 47.74; H, 3.30; N, 26.20%. Found: C, 49.01; H, 3.68; N, 26.47%. IR (KBr)/ $cm^{-1}$ : 3854w, 3802w, 3735w, 3680w, 3630w, 3350m, 2305s, 2257m, 2243s, 2189s, 2155s, 1686w, 1652w, 1582w, 1560w, 1526w, 1502m, 1447w, 1408w, 1388w, 1348s, 1307m, 1108w, 1070w, 1010m, 941m, 843s, 801m, 723w, 675w, 632w, 567w, 527m, 496m, 448w, 429w, 418w.

### 2.7. Synthesis of $Cd(dca)_2(phen)(H_2O) \cdot MeOH$ (6)

A steam-bath warmed solution of sodium dicyanamide (100 mg, 1.12 mmol) and 4,7-phenanthroline (101 mg, 0.56 mmol) in MeOH (10 ml) was added to a solution of  $Cd(NO_3)_2 \cdot 4H_2O$  (173 mg, 0.56 mmol) in deionised water (10 ml). The pale yellow, needle-like crystals were filtered

Table 1  
Crystallographic data for M(dca)<sub>2</sub>(phen)(H<sub>2</sub>O)·MeOH

Compound	Mn	Fe	Co	Ni <sup>a</sup>	Zn	Cd
Formula	C <sub>17</sub> H <sub>14</sub> N <sub>8</sub> O <sub>2</sub> Mn	C <sub>17</sub> H <sub>14</sub> N <sub>8</sub> O <sub>2</sub> Fe	C <sub>17</sub> H <sub>14</sub> N <sub>8</sub> O <sub>2</sub> Co	C <sub>17</sub> H <sub>14</sub> N <sub>8</sub> O <sub>2</sub> Ni	C <sub>17</sub> H <sub>14</sub> N <sub>8</sub> O <sub>2</sub> Zn	C <sub>17</sub> H <sub>14</sub> N <sub>8</sub> O <sub>2</sub> Cd
<i>FW</i>	417.30	418.21	421.29	421.04	427.73	474.76
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>		<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	7.4702(1)	7.3943(1)	7.3244(1)	7.270(4)	7.3546(1)	7.5852(1)
<i>b</i> (Å)	18.6763(3)	18.4655(2)	18.4489(3)	18.350(9)	18.5094(2)	18.7913(2)
<i>c</i> (Å)	13.0026(3)	13.0301(2)	13.0270(2)	13.116(8)	13.0060(2)	13.0245(2)
$\beta$ (°)	92.640(1)	92.876(1)	92.882(1)	93.55(6)	92.963(1)	92.461(1)
<i>U</i> (Å <sup>3</sup> )	1812.14(6)	1776.88(4)	1758.07(5)	1746(1)	1768.13(4)	1854.74(4)
<i>Z</i>	4	4	4	4	4	4
<i>D</i> <sub>c</sub> , (g cm <sup>−3</sup> )	1.530	1.563	1.592	1.602	1.607	1.700
<i>F</i> (000)	852	856	860		872	944
$\mu$ (Mo K $\alpha$ ) (mm <sup>−1</sup> )	0.761	0.882	1.009		1.422	1.209
Data collected	26947	20019	27937		23621	21609
Unique data ( <i>R</i> <sub>int</sub> )	5476 (0.0627)	5003 (0.0697)	5330 (0.0882)		5259 (0.0458)	4416 (0.0441)
Observed data [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4025	3888	3510		4321	3780
Parameters, restraints	266, 3	266, 3	266, 3		266, 3	266, 3
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> <sup>b</sup>						
(Obs. data)	0.0398, 0.0859	0.0345, 0.0887	0.0536, 0.1097		0.0372, 0.0869	0.0251, 0.0557
(All data)	0.0698, 0.0977	0.0543, 0.0988	0.1053, 0.1289		0.0568, 0.1338	0.0353, 0.0593
<i>S</i> (GOF)	1.046	1.066	1.066		1.194	1.047
$\Delta\rho_{\min}$ , $\Delta\rho_{\max}$ , (e Å <sup>−3</sup> )	−0.389, 0.515	−0.648, 0.403	−0.897, 0.905		−1.265, 0.804	−0.914, 0.602

<sup>a</sup> From powder diffraction.

<sup>b</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ,  $wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ ,  $w = [\sigma^2(F_o)^2 + (0.1(\max(0, F_o^2) + 2F_c^2)/3)^2]^{-1}$ .

Table 2  
Selected bond lengths (Å) for  $M(dca)_2(phen)(H_2O) \cdot MeOH$

	Mn	Fe	Co	Zn	Cd
M–N11	2.2129(15)	2.1456(15)	2.102(2)	2.128(3)	2.3116(18)
M–N15 <sup>(i)</sup>	2.2015(15)	2.1424(15)	2.106(2)	2.115(2)	2.2970(19)
M–N21	2.2067(15)	2.1480(14)	2.112(2)	2.123(2)	2.3027(19)
M–N25 <sup>(i)</sup>	2.2257(16)	2.1634(15)	2.126(2)	2.146(3)	2.318(2)
M–N101	2.3187(15)	2.2405(14)	2.210(2)	2.200(2)	2.3600(18)
M–O1	2.2081(14)	2.1418(13)	2.127(2)	2.157(2)	2.3276(16)

Symmetry operation: (i)  $x+1, y, z$ .

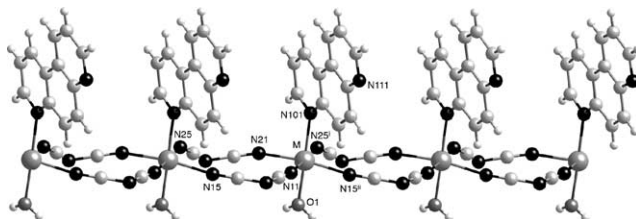


Fig. 1. The 1D chain structure of  $M(dca)_2(phen)(H_2O) \cdot MeOH$ .

off and dried by suction. Yield 230 mg, 86%. Anal. Calcd for  $C_{17}H_{14}N_8O_2Cd$ : C, 43.01; H, 2.97; N, 23.60%. Found: C, 43.19; H, 3.01; N, 23.84%. IR (KBr)/ $cm^{-1}$ : 3422.3m, 2301s, 2247m, 2234s, 2179s, 2149s, 1637w, 1582w, 1524w, 1501m, 1447w, 1408m, 1388w, 1348s, 1306m, 1106w, 1068w, 1016s, 1008s, 936m, 841s, 800m, 724m, 675m, 566m, 524m, 504m, 494m, 447m, 419w, 404w.

## 2.8. Crystal structure determinations

Crystal data and details of the structure determinations are presented in Table 1. X-ray crystallographic measurements were performed at 123(2) K using a Nonius Kappa CCD diffractometer, fitted with a Mo  $K\alpha$  radiation source and graphite monochromator ( $\lambda=0.71073$ ). DENZO-SMN [6] was used for data integration and SCALEPACK [6] corrected data

for Lorentz-polarisation effects. Face-indexed absorption corrections were also applied to the data. Direct methods (SHELXS 97 [7]) and successive Fourier difference methods with refinement of full matrix least squares on  $F_{obs}^2$  (SHELXL 97 [7]) afforded structural solutions. All non-hydrogen atoms in the structures were made anisotropic. All carbon-bound hydrogen atoms were assigned to calculated positions but not refined, while all oxygen-bound hydrogen atoms were located in the difference maps and refined with the restraint of being no closer than 0.84(2) Å from the oxygen atom.

Powder X-ray diffraction data were collected at room temperature on a bulk sample of the Ni complex with a Scintag automated powder diffractometer using Cu  $K\alpha$  radiation ( $\lambda=1.54059$  Å). The programs CrystalDiffract [8] and UnitCell [9] were used to refine the unit cell, as shown in Table 1, using the known cells of the other complexes as a starting point.

Table 3  
Hydrogen bond distances (Å) and angles (°) for  $M(dca)_2(phen)(H_2O) \cdot MeOH$

	Mn	Fe	Co	Zn	Cd
O1–H1 $\cdots$ O3 <sup>(i)</sup>					
D–H	0.83(2)	0.86(3)	0.83(2)	0.84(2)	0.83(2)
H $\cdots$ A	1.94(2)	1.90(3)	1.94(2)	1.95(2)	1.95(2)
D $\cdots$ A	2.765(2)	2.759(2)	2.771(3)	2.782(3)	2.775(2)
D–H $\cdots$ A	171(3)	179(3)	172(4)	176(5)	175(3)
O1–H2 $\cdots$ O3					
D–H	0.84(4)	0.82(2)	0.83(2)	0.84(2)	0.82(2)
H $\cdots$ A	1.96(2)	1.97(2)	2.02(3)	1.98(2)	1.98(2)
D $\cdots$ A	2.777(2)	2.770(2)	2.779(3)	2.791(3)	2.778(2)
D–H $\cdots$ A	165(3)	164(3)	153(5)	163(5)	164(3)
O3–H3 $\cdots$ N111 <sup>(ii)</sup>					
D–H	0.82(2)	0.82(2)	0.81(2)	0.84(2)	0.83(2)
H $\cdots$ A	1.92(2)	1.92(2)	1.92(2)	1.90(2)	1.92(2)
D $\cdots$ A	2.726(2)	2.718(2)	2.726(3)	2.731(3)	2.739(2)
D–H $\cdots$ A	167(3)	167(3)	171(4)	169(5)	171(3)

Symmetry operations: (i)  $1-x, 1-y, 1-z$ ; (ii)  $x, 1/2-y, z-1/2$ .

### 3. Results and discussion

Reaction of metal salt, Na(dca) and phen in methanol/water gave crystals of  $M(\text{dca})_2(\text{phen})(\text{H}_2\text{O}) \cdot \text{MeOH}$ ,  $M = \text{Mn, Fe, Co}$ ,

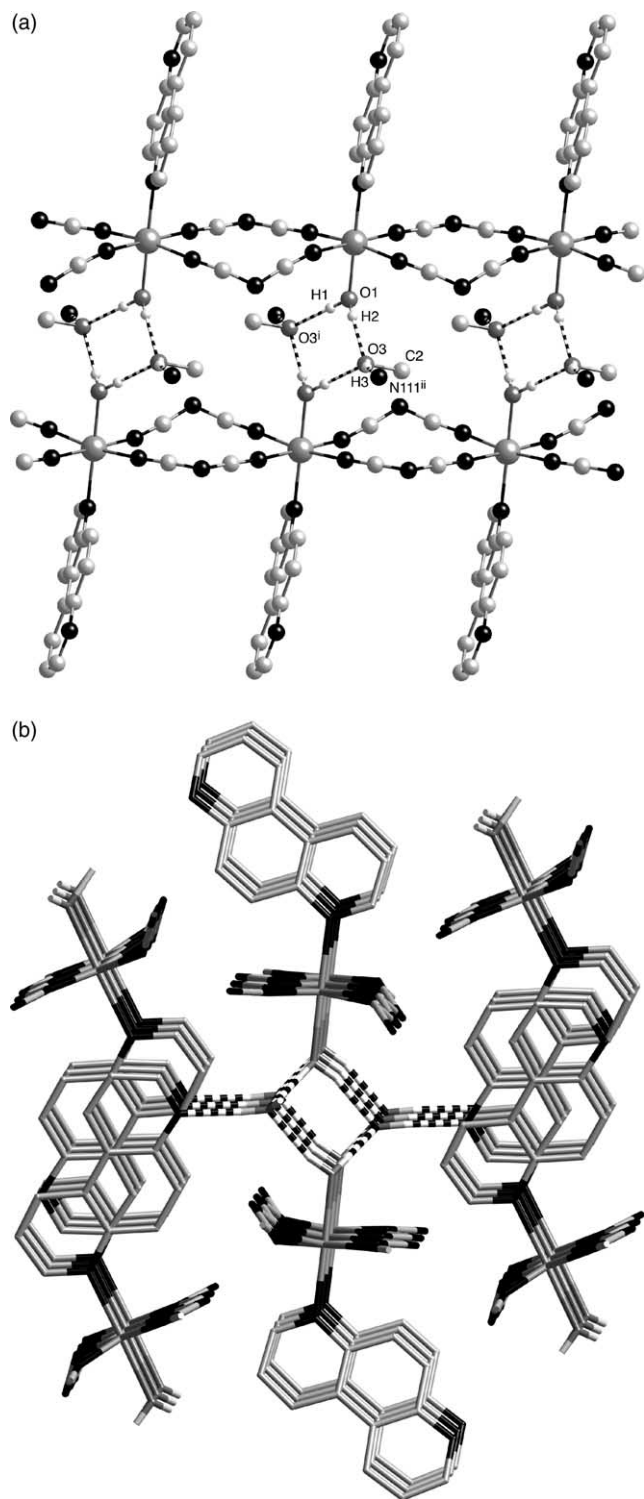


Fig. 2. (a) The  $(\text{H}_2\text{O})_2(\text{MeOH})_2$  hydrogen bonding motif, which connects pairs of chains; for clarity, only the nitrogen atoms (black spheres) of the phen ligands, which also hydrogen bond to the methanol molecules are shown. (b) The hydrogen bonding of additional chains via the uncoordinated nitrogens of the phen ligands, generating an overall 3D network.

Zn and Cd, and a microcrystalline powder for  $M = \text{Ni}$ . The crystal structures of all these compounds were determined by single crystal X-ray diffraction (Table 1), except Ni, which was shown to be isomorphous via powder diffraction. As all the structures are isomorphous they will be discussed in a generic sense.

The asymmetric unit contains one metal atom, two dca ligands, one phen ligand, one water ligand, and an intercalated methanol molecule. Selected bond lengths and angles are given in Table 2. The metal atom, which lies on a general position, coordinates to four equatorial  $\mu_{1,5}$  bridging dca ligands, one monodentate phen ligand and one water ligand. The bridging dca ligands connect the metal atoms into 1D chains (Fig. 1) of the sort, which are common in metal dicyanamide chemistry [1]. These  $\mu_{1,5}$  dca containing chains have been shown previously to contain only weak magnetic coupling between metal atoms, with no long-range order [1], and thus magnetic measurements were not pursued.

Although the phen molecule coordinates, and 1D coordination polymers are formed, the overall supramolecular structure is still of considerable interest. The chains are linked into a 3D network by hydrogen bonding interactions between the coordinated water ligands, the intercalated methanol molecules, and the uncoordinated nitrogens of the phen ligands (Table 3). Pairs of chains are linked by cyclic  $(\text{H}_2\text{O})_2(\text{MeOH})_2$  hydrogen bonding motifs defined by  $\text{O}-\text{H} \cdots \text{O}(\text{Me})$  interactions (Fig. 2(a)). These pairs of chains are then further linked by  $(\text{Me})\text{O}-\text{H} \cdots \text{N}$  hydrogen bonds between the uncoordinated phen nitrogen atoms and the methanol molecules, to give the overall 3D network (Fig. 2(b)). Adjoining chains also interdigitate, such that the phen ligands form  $\pi$  bonding stacks (Fig. 2(b)) in which each phen ligand lies between two phen ligands of an adjoining chain. The phen ligands each associate with one adjoining phen ligand more closely than the other (closest non-hydrogen contacts are 3.485 Å on one side, and 3.577 Å on the other). However, this interdigitation is common for similar 1D chain polymers of dca, even when the terminal ligands are molecules such as DMF, which do not have delocalised  $\pi$  systems [1].

### 4. Conclusions

Although the desired  $\mu_{1,3,5}$  dca containing structure was not achieved, the phen ligand did participate in an interesting hydrogen bonding motif, which linked the 1D chains into a 3D network. These results also further underline the malleability of the metal dicyanamide system to the influences of subtle changes in coligands [10], and the unpredictable nature of the structures observed.

### 5. Supplementary material

CCDC 294998–295002 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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