Research Article

Synthesis, Crystal Structures, and Magnetic Properties of Ternary M(II)-Dicyanamide-hydroxypyridine Complexes

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Three two-dimensional (2D) and 3D supramolecular coordination architectures based on ternary M(II)-dicyanamide-2-hydroxypyridine systems, $[\text{Co}(\text{hmpH})_2(\text{dca})_2]$ (**1**), $[\text{Cu}(\text{hmpH})_2(\text{dca})_2]$ (**2**), and $[\text{Mn}(\text{hepH})_2(\text{dca})_2]$ (**3**) (dca = dicyanamide, hmpH = 2-(hydroxymethyl)pyridine, hepH = 2-(hydroxyethyl)pyridine), have been synthesized. **1** is a mononuclear Co(II) complex. The mononuclear units are interlinked into a 2D (4,4) hydrogen-bonded layer via O–H $\cdots$ N hydrogen bonds between the hydroxyl groups and the noncoordinating nitrile ends. These 2D layers are further extended into a 3D supramolecular architecture via the interlayer pyridyl-pyridyl stacking interaction. **2** has a 1D coordination chain structure formed by the double $\mu_{1,5}$ -dca bridged dinuclear $[\text{Cu}_2(\mu_{1,5}\text{-dca})_2(\text{hmpH})_2]$ unit and the $\mu_{1,3}$ -dca bridges via weak Cu–N coordination, and these 1D coordination chains are further extended into 2D hydrogen-bonded layers via strong O–H $\cdots$ N hydrogen-bonding interaction between the hydroxyl groups and the noncoordinating nitrile ends. **3** is a 2D (4,4) coordination network made of 1D $[\text{Mn}(\text{hepH})(\mu_{1,5}\text{-dca})]$ helical chain units and interchain double ($\mu_{1,5}$ -dca) bridges. Pairs of $[\text{Mn}(\text{hepH})(\mu_{1,5}\text{-dca})]$ helical chains are interlinked by the double ($\mu_{1,5}$ -dca) bridges into a racemic coordination layer structure, which is further extended into a 3D hydrogen-bonded network. Magnetic studies reveal that weak antiferromagnetic exchange occurs in **3**.

1. Introduction

Since the pioneering reports of Robson and coworkers in 1990 [1, 2], this realm of crystal engineering is growing interest, and great efforts have been devoted to the assembly of supramolecular systems of organic molecular solids and coordination polymers through hydrogen bonds and/or coordination bonds, with the resultant crystalline materials having a wide range of potential applications, such as electronic, magnetic, optical, absorbent, and catalytic materials [3–29]. In recent years, much attention has been devoted to dicyanamide-anion- (dca-) bridged coordination polymers [30–42] for the large variety of magnetic properties, especially the $\alpha\text{-M}(\text{dca})_2$ series of compounds, which have isomorphous rutile-like structure, display ferromagnetism (Co, Ni) [43–46], spin-canted antiferromagnetism (Cr, Mn, Fe) [47, 48], and paramagnetism (Cu) [45, 46]. Of further importance, from a structural perspective, when auxiliary L ligands are introduced to the ternary $\text{M}^{\text{II}}\text{-dca-L}$ systems, different coordination architectures, such as mononuclear

and dinuclear compounds [49], 1D chains [50–58], 2D (4,4) or (6,3) [59–63] sheets, and 3D network topologies [64–67], could be constructed (Scheme 1). Interestingly, interesting in situ nucleophilic addition reactions were observed between dca and the auxiliary ligands [68–73]. On the other hand, weak interactions such as hydrogen bonding and π - π interactions play an important role for construction of high-dimensional supramolecular systems [74–76]. From the viewpoint of rational network design, if the coligand can combine multifunctions such as coordination, hydrogen-bond donor or acceptor, and aromaticity, many interesting supramolecular architectures will be constructed.

In this work, two 2-hydroxypyridines, 2-(hydroxymethyl)pyridine (hmpH), and 2-(hydroxyethyl)pyridine (hepH) were chosen as the auxiliary ligands to the M(II)-dca-L systems to realize this rational crystal engineering for the following reasons: (1) hmpH and hepH can act as chelating ligand; (2) the hydroxyl groups of hmpH and hepH may act as the hydrogen bond donors, which generate strong hydrogen bond with the amide nitrogen atom of the dca

SCHEME 1: Schematic showing the coordination modes of dca.

ligand. We report herein three ternary supramolecular architectures $[\text{Co}(\text{dca})_2(\text{hmpH})_2]$ (**1**), $[\text{Cu}(\text{dca})_2(\text{hmpH})_2]$ (**2**), and $[\text{Mn}(\text{dca})_2(\text{hepH})]_n$ (**3**) obtained by this strategy.

2. Experimental

2.1. Materials and General Methods. The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker TENSOR27 spectrometer. Variable-temperature magnetic susceptibility measurements were made using a SQUID magnetometer MPMS XL-7 (Quantum Design) at 0.1 T for **3**. The diamagnetic correction for each sample was determined from Pascal's constants.

2.2. Synthesis

2.2.1. Synthesis of $[\text{Co}(\text{hmpH})_2(\text{dca})_2]$ (1**).** Amethanol solution (10 mL) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (145 mg, 0.5 mmol) was added dropwise to a $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution (20 mL) containing sodium dicyanamide (89 mg, 1.0 mmol) and hmpH (109 mg, 1.0 mmol). A red solution formed on addition of metal salt to the ligands. The mixture solution was filtered and solvent evaporated at room temperature. Well-shaped red block crystals of **1** were obtained within 1 week in 62% yield. Anal. calcd. for $\text{C}_{16}\text{H}_{14}\text{CoN}_8\text{O}_2$: C, 46.95; H, 3.45; N, 27.38%. Found: C, 46.53; H, 3.52; N, 27.21%. IR: 3081m, 2215vs, 1602m, 1561m, 1483s, 1432m, 1385w, 1347w, 1298vs, 1250s, 1142vs, 1081m, 988w, 861m, 754m, 675m, 646w, 612w, 450vw.

2.2.2. Synthesis of $[\text{Cu}(\text{hmpH})_2(\text{dca})_2]$ (2**).** Amethanol solution (10 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (121 mg, 0.5 mmol) was added dropwise to a $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution (20 mL) containing sodium dicyanamide (89 mg, 1.0 mmol) and hmpH (109 mg, 1.0 mmol). A blue solution formed on addition of metal salt to the ligands. The mixture was filtered and solvent evaporated at room temperature. Well-shaped blue block crystals of **2** were obtained within 1 week in 83% yield. Anal. calcd. for $\text{C}_{10}\text{H}_7\text{CuN}_7\text{O}$: C, 39.41; H, 2.32; N, 32.17%. Found: C, 39.32; H, 2.41; N, 32.03%. IR: 3706w, 3429m, 3074w, 2855m, 2378s, 2214vs, 1613s, 1571m, 1485m, 1440s, 1366m, 1292m, 1223vw, 1159vw, 1092vs, 931vw, 821vw, 762s, 722m, 673s, 623s, 533m, 483w, 438m.

2.2.3. Synthesis of $[\text{Mn}(\text{hepH})_2(\text{dca})_2]_n$ (3**).** hepH (123 mg, 1.0 mmol), dissolved in a minimum amount of methanol, was added to an aqueous solution containing $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99 mg, 0.5 mmol) and sodium dicyanamide (89 mg, 1.0 mmol). Block colorless crystals of **3** were grown after 5 days. Yield: ca 74%. Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{MnN}_7\text{O}$: C, 42.59; H, 2.92; N, 31.61%. Found: C, 41.84; H, 3.07; N, 31.23%. IR: 3597w, 3541w, 3286m, 3081w, 2954vw, 2901vw, 2310m, 2273m, 2242m, 2177s, 1606s, 1571m, 1488s, 1440s, 1419w, 1369s, 1308vs, 1249vw, 1155w, 1107m, 1075m, 1029s, 940m, 890vw, 866w, 759m, 658w, 640vw, 579w, 515m, 451vw, 416vw.

2.3. X-Ray Crystallographic Study. Single-crystal data of **1–3** were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). All empirical absorption corrections were applied using the SADABS program [77]. The structure was solved using direct method, which yielded the positions of all nonhydrogen atoms. These were refined first isotropically and then anisotropically. All calculations were performed using the SHELXTL programs [78]. The crystallographic data for **1–3** are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

CCDC 711609–711611 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

3. Results and Discussion

3.1. Synthesis and Characterization. Air-stable complexes **1–3** were obtained from the reactions of metal(II) salts, $\text{Na}(\text{dca})$, and 2-hydroxypyridine-type ligands (Scheme 2), in which the hydroxypyridines act as chelating ligands. Moreover, the products are independent of the ligand-to-metal ratios.

In contrary, under base condition, 2-hydroxypyridine-type ligands, such as hmpH, hepH, and 2,6-pyridinedimethanol, have been found to act as bridging ligands to generate some fascinating polynuclear metal-clusters [79–82] and the extended 1D or 2D metal cluster-based coordination polymers with dca as bridges in recent years [83–85].

The IR spectra of **1–3** are quite similar. They all show strong absorptions in the range of 2310–2100 cm^{-1} , which correspond to the $\nu_s + \nu_{as}$ ($\text{C} \equiv \text{N}$), ν_{as} ($\text{C} \equiv \text{N}$), and ν_s ($\text{C} \equiv \text{N}$) modes of the dca ligand [86].

SCHEME 2: Schematic showing the synthesis of complexes 1–3.

TABLE 1: Crystal and structure refinement for compounds 1–3.

Compound	1	2	3
Formula	$C_{16}H_{14}CoN_8O_2$	$C_{10}H_7CuN_7O$	$C_{11}H_9MnN_7O$
Formula mass	409.28	304.77	310.19
Cryst. syst.	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P-1$	$P2_1/c$
a (Å)	18.5091 (19)	7.4025 (10)	12.828 (3)
b (Å)	7.8876 (8)	7.5004 (9)	8.0561 (18)
c (Å)	14.0965 (15)	11.4982 (15)	12.982 (3)
α (°)	90.00	78.557 (2)	90.00
β (°)	118.124 (2)	89.574 (2)	103.162 (5)
γ (°)	90.00	72.701 (2)	90.00
V (Å ³)	1815.0 (3)	596.50 (13)	1306.4 (5)
Z	4	2	4
T (K)	293 (2)	293 (2)	293 (2)
F (000)	836	306	628
D_c (g cm ⁻³)	1.498	1.697	1.577
μ (mm ⁻¹)	0.975	1.834	1.017
Final R indexes [$I > 2\sigma(I)$]	0.0319, 0.0832	0.0391, 0.0926	0.0488, 0.1032
Final R indexes [all data]	0.0345, 0.0847	0.0449, 0.0963	0.0955, 0.1219

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

3.2. Structure Description. Compound **1** crystallizes in monoclinic space group $C2/c$ with the asymmetric unit consisting of half formula unit. The CoI ion lies on a special position and adopts a greatly distorted octahedral environment (Figure 1(a)) ligated by two N atoms (Co–N = 2.114(2) Å) and two O atoms (Co–O = 2.165(7) Å) from two chelate hmpH ligands and two nitrile N (Co–N = 2.077(2) Å) atoms from two trans-dca ligands. The dca ligand is in μ_1 coordination mode and acts as a terminal ligand. The dca anions adopt nonlinear bonding configurations about the Co ions with Cl–N1–CoI = 162.08(3)°.

These mononuclear units are further cross-linked by strong $N \cdots H-O$ [87] hydrogen-bonding interaction between

hydroxyl groups and uncoordinated nitrile ends of the dca ligands ($O1 \cdots N3b = 2.728(2)$ Å; $O1-H1O \cdots N3b = 169.0^\circ$) to form a 2D sheet with (4,4) topology, as shown in Figure 1(b).

Analysis of the crystal packing of **1** shows that these sheets again interdigitate to form 3D supramolecular architecture (Figure 1(c)), with the average interplanar distance between pyridine rings being ca. 3.55 Å.

Compound **2** crystallizes in triclinic $P-1$ space group with the asymmetric unit containing half formula unit. The copper atoms are coordinated to one chelating hmpH ligand, coordinating via the pyridyl nitrogen atom donor (Cu–N = 1.988(2) Å) and hydroxyl oxygen atom (Cu–O = 1.986(2) Å), two bridging $\mu_{1,5}$ -dca anions (Cu–N = 1.968(3) and 2.323(3) Å), and one “terminal” dca anion (Cu–N = 1.965(3) Å). The coordination geometry of Cu^{II} center (CuN_4O) can be described as a square pyramid. The N3 atom occupied the apical position. Similar to **1**, the dca anions adopt nonlinear bonding configurations about Cu ion with $C2-N3-Cu = 151.5(2)^\circ$, $C2-N1-Cu = 161.7(2)^\circ$, and $C3-N4-Cu = 165.4(2)^\circ$. The bridging dca anions extend the Cu^{II} centers to generate a dinuclear with double dca bridges (Figure 2(a)). The $Cu \cdots Cu$ separation is 7.311(2) Å. These dinuclear units are further linked by weak Cu–N interactions (2.866(3) Å) between the copper atoms and “uncoordinated” amide nitrogen atoms of the terminal dca anions to form double dca bridges ($Cu \cdots Cu = 5.827(6)$ Å). The $Cu \cdots Cu$ separations through 1,3- μ_2 -dca are significantly shorter than those through 1,5- μ_2 -dca. These weak interactions generated 1D chains as shown in Figure 2(b). These 1D chains are linked by alternative $\mu_{1,5}$ - and $\mu_{1,3}$ -dca bridges, which are less common for the dca ligand [88–95]. The weak copper (II) coordination leads to a pseudo-Jahn-Teller elongated octahedral geometry.

Adjacent coordination chains are extended into 2D hydrogen-bonded layers by the $O1-H1 \cdots N6b$ hydrogen-bonding interaction between the hydroxyl groups and the uncoordinated nitrile ends of the dca ligands ($O1 \cdots N6b = 2.661(4)$ Å; $O1-H1O \cdots N6b = 172.5^\circ$), as shown in Figure 2(c).

Compound **3** crystallizes in monoclinic space group $P2_1/c$ with the asymmetric unit consisting of half formula unit. The manganese ion is coordinated to one chelating hepH ligand, coordinating via the pyridyl nitrogen atom donor

TABLE 2: Selected bond distances (Å) and angles (deg) for **1**–**3**.

1			
Co(1)–N(1)	2.0767 (18)	Co(1)–O(1)	2.1653 (15)
Co(1)–N(4)	2.1136 (16)	O(1)–H(1O)···N(3b)	2.728 (2)
N(1)–Co(1)–N(1a)	95.73 (10)	N(4)–Co(1)–O(1)	75.41 (6)
N(1)–Co(1)–N(4)	95.51 (7)	N(1)–Co(1)–O(1a)	86.87 (7)
N(1)–Co(1)–N(4a)	96.88 (7)	N(4)–Co(1)–O(1a)	91.63 (6)
N(4)–Co(1)–N(4a)	161.49 (10)	O(1)–Co(1)–O(1a)	91.94 (8)
N(1)–Co(1)–O(1)	170.81 (6)	O(1)–H(1O)···N(3b)	169.0
2			
Cu(1)–N(4)	1.965 (3)	Cu(1)–N(7)	1.988 (2)
Cu(1)–N(1)	1.968 (3)	Cu(1)–N(3a)	2.323 (3)
Cu(1)–O(1)	1.985 (2)	O(1)···N(6b)	2.661 (4)
N(4)–Cu(1)–N(1)	94.42 (13)	O(1)–Cu(1)–N(7)	80.68 (10)
N(4)–Cu(1)–O(1)	89.38 (11)	N(4)–Cu(1)–N(3a)	99.62 (12)
N(1)–Cu(1)–O(1)	176.08 (10)	N(1)–Cu(1)–N(3a)	90.43 (12)
N(4)–Cu(1)–N(7)	161.11 (11)	O(1)–Cu(1)–N(3a)	89.90 (11)
N(1)–Cu(1)–N(7)	95.41 (11)	N(7)–Cu(1)–N(3a)	96.41 (11)
O(1)–H(1O)···N(6b)	172.5		
3			
Mn(1)–N(3a)	2.175 (4)	Mn(1)–N(6b)	2.227 (4)
Mn(1)–O(1)	2.187 (3)	Mn(1)–N(4)	2.238 (4)
Mn(1)–N(1)	2.224 (4)	Mn(1)–N(7)	2.290 (3)
O(1)···N(5d)	2.859 (4)		
N(3a)–Mn(1)–O(1)	174.77 (14)	N(1)–Mn(1)–N(4)	174.38 (14)
N(3a)–Mn(1)–N(1)	86.76 (15)	N(6b)–Mn(1)–N(4)	87.05 (14)
O(1)–Mn(1)–N(1)	88.34 (13)	N(3a)–Mn(1)–N(7)	99.25 (13)
N(3a)–Mn(1)–N(6b)	96.57 (14)	O(1)–Mn(1)–N(7)	82.67 (11)
O(1)–Mn(1)–N(6b)	82.21 (12)	N(1)–Mn(1)–N(7)	91.21 (13)
N(1)–Mn(1)–N(6b)	96.92 (14)	N(6b)–Mn(1)–N(7)	162.59 (13)
N(3a)–Mn(1)–N(4)	88.84 (15)	N(4)–Mn(1)–N(7)	86.05 (13)
O(1)–Mn(1)–N(4)	96.15 (13)	O(1)–H(1O)···N(5d)	165.2

Symmetry codes: (a) $-x, y, -z + 3/2$; (b) $x - 1/2, y - 1/2, z$ for **1**; (a) $-x + 1, -y + 2, -z + 2$; (b) $-x + 1, -y + 3, -z + 1$ for **2**. (a) $-x, y + 1/2, -z + 1/2$; (b) $-x + 1, -y - 1, -z + 1$; (d) $x, -y - 3/2, z - 1/2$ for **3**.

(Mn–N = 2.291(3) Å) and hydroxyl oxygen atom (Mn–O = 2.188(3) Å) and four nitrile nitrogen atoms from four $\mu_{1,5}$ -dca anions (Mn–N = 2.175(4)–2.271(4) Å), featuring a distorted MnN_5O octahedron environment. The surrounding of manganese ion is shown in Figure 3(a). Each manganese ion is connected to another three manganese ions by means of two single (Mn···Mn = 8.192(1) Å) and one double dca bridges (Mn···Mn = 7.467(1) Å), in an end-to-end ($\mu_{1,5}$) coordination mode, leading to 2D (6,3) coordination layers (Figure 3(b)), which have been found in dca chemistry [30]. As expected, the dca anions do not coordinate linearly to the metal centers with C–N–Mn angles of 153.4(1)°–169.7(1)°. As a result, the topology of the coordination network is that of a herringbone-waved grid since the rings have a slight chair conformation. The bidentate hepH ligands are located on both sides of each layer.

The 2D coordination layers are cross-linked by strong O–H···N hydrogen-bonding interactions between hydroxyl group and amido nitrogen atoms of dca anions (O1···N5d = 2.859(4) Å; O1–H1O···N5d = 165.2°). These hydrogen-bonding interactions extend these 2D layers into a 3D supramolecular architecture, which is further consolidated by the nonclassical C–H···N hydrogen-bonding interaction, as shown in Figure 3(c).

3.3. Magnetic Properties. The magnetic properties of **3** are shown in Figure 4 as χ_M (inset) and $\chi_M T$ versus T plots (χ_M is the molar magnetic susceptibility for one Mn^{II} ion). Taking into consideration the two-dimensional structure, magnetic data are taken for one manganese ion. The value of $\chi_M T$ product at 300 K is 4.19 cm³ mol^{−1} K, which is the typical value for one isolated Mn(II) ion ($g = 2.0$). This

(a)

(b)

(c)

FIGURE 1: Coordination environments of the metal ions in **1** (a) and the hydrogen-bonded 2D layer (b). 3D molecular architecture with interbilayer π - π interaction (c).

value remains unchanged up to 50 K, and then decreases rapidly from $3.98 \text{ cm}^3 \text{ mol}^{-1}$ K at ca. 50 K to $1.63 \text{ cm}^3 \text{ mol}^{-1}$ K at 2.0 K. This feature is indicative of weak antiferromagnetic coupling interaction among the Mn(II) ions. Because of the long Mn $\cdots$ Mn separation of $8.192(1) \text{ \AA}$ by single μ -1,5-dca bridge in **3**, a simplified dinuclear Mn(II) model was used to analyze the magnetic exchange interaction via the two single and one double μ -1,5-dca bridges ($\hat{H} = -JS_{\text{Mn}(1)} \cdot S_{\text{Mn}(2)}$) [96], similar to the reported method in [97]. The best-fit parameters are obtained to be $g = 1.99$, $J = -0.011 \text{ cm}^{-1}$, and $R = 1 \times 10^{-5}$. J is the exchange interaction through double $\mu_{1,5}$ -dca

(a)

(b)

(c)

FIGURE 2: Coordination environments of the metal ions in **2** (a) and the 1D chain extended by Cu-N weak interaction (b). 2D layer built by N $\cdots$ H-O hydrogen bond (c).

bridges, g is the Landé factor, and R is the agreement factor for defined as $R = [\sum (\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \sum \chi_{\text{obs}}^2]^{1/2}$. This fitting result is in accordance with the very weak antiferromagnetic coupling existing in the reported Mn(II)- $\mu_{1,5}$ -dca-coligand systems [97]

FIGURE 3: Coordination environments of the metal ions in **3** (a) and 2D layer (b). Hydrogen-bonded 3D network (c) (the uncoordinated atoms are deleted for clarity).

FIGURE 4: Plot of the $\chi_M T$ versus T . Solid lines represent the best fit with the parameters given in the text for **3**.

4. Conclusion

In this study, we have demonstrated the construction of ternary $M(\text{II})$ -dca-2-hydroxypyridine supramolecular

architectures from low to high dimensionality via both metal coordination and hydrogen-bonding interactions. The dca ligand displays quite different coordination modes of monodentate in **1**, double-bridge in **2**, and single- and double-bridge fashion in **3**. We are extending this strategy to construct new supramolecular architectures by using other functional coligands.

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