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Structural diversification of coordination assemblies of M^{II}-dca – Hydroxylpyridine (dca = Dicyanamide)

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ABSTRACT

Three coordination polymers $[Mn(dca)_2(2\text{-pyEtOH})]_n$ (**1**), $[Co(dca)(MeOH)_2(3\text{-PyO})(3\text{-PyOH})]_n$ (**2**), $[Zn(dca)(3\text{-pyO})]_n$ (**3**) (2-pyEtOH = 2-ethanolpyridine; 3-pyOH = 3-hydroxypyridine) have been synthesized and their crystal structures determined. In the resulting crystalline materials, dca generally display the $\mu_{1,5}$ bridging fashion. 2-pyEtOH is used as bidentate terminal ligand in **1**; 3-pyOH is coordinated to Co^{II} in monodentate style in **2**; while 3-pyOH is used as a bridging ligand in **3**, affording diverse two-, one and three dimensional coordination networks. **3** shows rare eight coordinated bcu-type topology. Meanwhile, different hydrogen bonding interactions are observed in **1** and **2**. For **1** and **2**, weak antiferromagnetic interactions are observed.

1. Introduction

Currently, the realm of crystal engineering has achieved great success in the assembly of supramolecular systems of metal–organic solids and coordination polymers through hydrogen bonds and/or coordinate bonds, not only for the resultant crystalline materials having diverse structures, but also for their potential properties in gas storage, catalysis, ion exchange, optical, electric and molecular magnetism [1–2]. Judicious choice [3] of organic blockers is crucial, both for its metal coordination properties, and also for the provision of strong hydrogen bonds. In this paper, two hydroxylpyridine, namely, 2-ethanolpyridine (2-pyEtOH) and 3-hydroxypyridine (3-pyOH) were used as organic components.

Dicyanamide (dca) is now under active consideration in crystal engineering for its exciting coordination versatility, and thus provides a suitable "building block" in assembling novel metal–organic framework [4–5]. In recent years, we are engaged in the preparation dicyanamide polymer-based supramolecular units through variations of ligand backbones. 4-(1H-imidazol-1-yl)aniline [6], nicotinamide [7], isonicotinamide [8] were employed as coligands for the $M(dca)_2$ system, and a series of supramolecular architectures were constructed via coordination and hydrogen bonding. Both the amino and amide groups form strong hydrogen bonds with neighboring coordination units. To continue our work and probe the difference in construction of supramolecular networks, we combined hydroxylpyridine and dca together, and three hydrogen-bonding networks were obtained.

Herein, we reported the syntheses and crystal structures of three supramolecular networks, $[Mn(dca)_2(2\text{-pyEtOH})]_n$ (**1**), $[Co(dca)(MeOH)_2(3\text{-PyO})(3\text{-PyOH})]_n$ (**2**) and $[Zn(dca)(3\text{-pyO})]_n$ (**3**). The magnetic properties of **1** and **2** are also described.

2. Experimental

2.1. Materials and physical measurements

All 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 a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} with a Nicolet 5DX spectrometer. Variable-temperature magnetic susceptibility measurements were made using a SQUID magnetometer MPMS XL-7 (Quantum Design) at 0.1 T and 0.5 T for complex **1** and **2** respectively. The diamagnetic correction for each sample was determined from Pascal's constants.

2.2. Synthesis of complexes 1–3

2.2.1. Synthesis of $[Mn(dca)_2(2\text{-pyEtOH})]_n$ (1)

2-pyEtOH (0.123 g, 1.0 mmol) and Na(dca) (0.089 g, 1.0 mmol) were dissolved in a solvent mixture of CH_3OH/H_2O (25 mL, volume ratio 2:1). To the above solution was added a solution of $MnCl_24H_2O$

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(0.1 g, 0.5 mmol) in methanol (10 mL) under stirring. The resultant solution was filtered and left to stand at room temperature. Colorless block crystals of **1** were collected within 5 days (yield 51%, based on Mn(II)). *Anal.* Calc. for $C_{11}H_9MnN_7O$: C, 42.59; H, 2.92; N, 31.61. Found: C, 41.84; H, 3.07; N, 31.23%. IR data (KBr, cm^{-1}): 3597 (w), 3541 (w), 3286 (m), 3081 (w), 2954 (vw), 2901 (vw), 2310 (m), 2273 (m), 2242 (m), 2177 (s), 1606 (s), 1571 (m), 1488 (s), 1440 (s), 1419 (w), 1369 (s), 1308 (vs), 1249 (vw), 1155 (w), 1107 (m), 1075 (m), 1029 (s), 940 (m), 890 (vw), 866 (w), 759 (m), 658(w), 640(vw), 579(w), 515(m), 451 (vw), 416 (vw).

2.2.2. Synthesis of $[Co(dca)(MeOH)_2(3\text{-PyO})(3\text{-PyOH})]_n$ (**2**)

3-PyOH (0.095 g, 1.0 mmol) and sodium dicyanamide (0.089 g, 1.0 mmol) were dissolved in a CH_3OH/H_2O mixture (25 mL, volume ratio 2:1). To the above solution was added a methanol solution (10 ml) of $Co(NO_3)_2{\cdot}6H_2O$ (0.145 g, 0.5 mmol) under stirring. The resultant clear solution was filtered and left to stand at room temperature. Light block red crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvents within 1 week in 45% yield (based on Co(II)). *Anal.* Calc. for $C_{14}H_{17}CoN_5O_4$: C, 44.45; H, 4.53; N, 18.52. Found: C, 44.30; H, 4.62; N, 18.46%. IR data (KBr, cm^{-1}): 3584 (m), 3299 (s), 3100 (vw), 3064 (vw), 2764 (vw), 2563 (vw), 2288 (m), 2257 (m), 2190 (s), 1892 (vw), 1836 (vw), 1614 (w), 1582 (s), 1486 (s), 1336 (vs), 1280 (s), 1225 (m), 1182 (m), 1107 (m), 1055 (w), 1025 (w), 928 (s), 849 (w), 794 (s), 697 (vs), 664 (w), 642 (m), 548 (w), 517 (vs), 422 (w).

2.2.3. Synthesis of $[Zn(dca)(3\text{-pyO})]_n$ (**3**)

The same synthetic method as that for **2** was used, except that $Co(NO_3)_2{\cdot}6H_2O$ was replaced by $Zn(NO_3)_2{\cdot}4H_2O$ (0.130 g, 0.5 mmol). Colorless block crystals were afforded upon evaporation of the solvents after *ca.* one week in a yield of 52% (based on Zn(II)). *Anal.* Calc. for $C_7H_5ZnN_4O$: C, 37.28; H, 1.79; N, 24.84. Found: C, 37.28; H, 1.85; N, 25.30%. IR data (KBr, cm^{-1}): 3622 (m), 3425 (w), 3119 (vw), 3063 (m), 3027 (w), 2589 (vw), 2430 (w), 2330 (s), 2261 (m), 2174 (s), 1592 (vw), 1569 (s), 1482 (s), 1419 (s), 1372 (s), 1290 (m), 1184 (m), 1102 (s), 1050 (m), 1026 (m), 952(w), 914 (w), 874 (s), 804 (s), 699 (s), 673 (m), 654 (w), 589 (m), 573 (m), 523 (s), 440 (m).

2.3. X-ray Crystallography

Data collections for complexes **1**–**3** were performed on a Bruker Apex CCD diffractometer with Mo *K*α radiation ($\lambda = 0.071073$ nm) at 293(2) K. The raw data frames were integrated with SAINT$^+$ [9], and corrections were applied for Lorentz and polarization effects. Absorption corrections were applied using the multi-scan program SADABS [10]. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least squares on F^2 using the SHELXTL program [11]. Hydrogen atoms on organic ligands were generated by the riding mode (C–H = 0. 93 Å). Crystal data as well as details of data collection and refinements for three complexes are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2.

3. Results and discussion

3.1. Preparation and IR spectra

Complexes **1**–**3** were prepared using direct solution assemblies of different metal ions with hydroxylpyridine and Na(dca) in moderate yields. The three complexes have the metal/ligand composition of 1:2:2 (M^{II}:L:dca), but the final products are indeed independent of the molar ratio of reactants, which was confirmed by IR spectra and elemental analysis. All complexes are air stable and soluble in warm methanol, ethanol, dimethylformamide and dimethylsulphoxide. The IR spectra of complexes **1**–**3** are quite similar, and their profiles being determined to a large extent by the dca ligand. Characteristic stretching vibration bands of dca [12] are observed in the range of 2310–2100 cm^{-1}, which corresponding to the $\nu_s + \nu_{as}$ (C≡N) (2286 cm^{-1}), ν_{as} (C≡N) (2232 cm^{-1}) and ν_s (C≡N) (2179 cm^{-1}). The three complexes show two series of bands: strong absorptions in the region 2170–2190 cm^{-1} [**1**: 2177 cm^{-1}, **2**: 2190 cm^{-1} and **3**: 2174 cm^{-1}] and two weak medium absorptions in the range of 2240–2320 cm^{-1} [**1**: 2237 and 2242 cm^{-1}, **2**: 2288 and 2257 cm^{-1}, **3**: 2310 and 2261 cm^{-1}] that shifted towards higher values due to the coordination of dca [13].

Table 1
Crystallographic data and structure refinement for complexes **1**–**3**.

	1	**2**	**3**
Formula	$C_{11}H_9MnN_7O$	$C_{14}H_{17}CoN_5O_4$	$C_7H_4N_4OZn$
Mr. (g mol^{-1})	310.19	378.26	225.51
Crystal system	monoclinic	orthogonal	monoclinic
Space group	*P*2(1)/*c*	*C*222(1)	*P*2(1)/*n*
a (Å)	12.828(3)	8.6653(13)	8.8973(15)
b (Å)	8.0561(18)	12.949(2)	9.6026(15)
c (Å)	12.982(3)	14.927(2)	9.7319(17)
α (°)	90.00	90.00	90.00
β (°)	103.162(5)	90.00	98.633(3)
γ (°)	90.00	90.00	90.00
V ($Å^3$)	1306.4(5)	1674.8(4)	822.0(2)
Z	4	4	4
ρ_c (g cm^{-3})	1.577	1.500	1.822
F(000)	628	780	448
Reflections collected	7093	2904	2295
Independent reflections (R_{int})	2551, 0.0524	1563, 0.0252	1480, 0.0171
Data/restrains/parameters	2551/0/185	1563/6/111	1480/1/118
R_1, wR_2 [$I > 2\sigma(I)$]	0.0487, 0.1034	0.0493, 0.1297	0.0336, 0.0813
R_1, wR_2 (all data)	0.0955, 0.1222	0.0526, 0.1325	0.0396, 0.0850
Largest difference in peak (e $Å^{-3}$)	0.807, −0.415	1.016, −0.441	0.652, −0.309

Table 2
Selected bond length (Å) and bond angles (°).

1			
Mn(1)–N(3*a*)	2.175(4)	N(3*a*)–Mn(1)–O(1)	174.70(14)
Mn(1)–O(1)	2.188(3)	N(3*a*)–Mn(1)–N(1)	86.76(15)
Mn(1)–N(1)	2.224(4)	O(1)–Mn(1)–N(1)	88.30(14)
Mn(1)–N(6*b*)	2.227(4)	N(3*a*)–Mn(1)–N(6*b*)	96.58(14)
Mn(1)–N(4)	2.238(4)	O(1)–Mn(1)–N(6*b*)	82.12(13)
Mn(1)–N(7)	2.291(3)	N(1)–Mn(1)–N(6*b*)	96.92(14)
N(1)–Mn(1)–N(4)	174.39(14)	N(3*a*)–Mn(1)–N(4)	88.85(15)
N(3*a*)–Mn(1)–N(7)	99.24(13)	O(1)–Mn(1)–N(4)	96.20(13)
N(1)–Mn(1)–N(7)	91.22(13)	N(6*b*)–Mn(1)–N(4)	87.05(14)
N(6*b*)–Mn(1)–N(7)	162.58(13)	O(1)–Mn(1)–N(7)	82.76(12)
2			
Co(1)–N(1)	2.138(3)	N(2*a*)–Co(1)–N(2)	174.7(2)
Co(1)–N(2)	2.103(4)	N(1*a*)–Co(1)–N(1)	91.74(17)
Co(1)–O(2)	2.123(3)	N(2)–Co(1)–O(2*a*)	90.31(19)
N(2)–Co(1)–N(1*a*)	91.7(2)	N(2)–Co(1)–O(2)	85.8(2)
O(2)–Co(1)–N(1*a*)	91.05(13)	O(2*a*)–Co(1)–O(2)	86.2(2)
N(2)–Co(1)–N(1)	92.0(2)	O(2)–Co(1)–N(1)	176.51(19)
3			
O(1)–Zn(1*a*)	1.976(2)	O(1*c*)–Zn(1)–N(3)	131.90(13)
O(1)–Zn(1*b*)	2.161(3)	O(1*c*)–Zn(1)–N(4)	114.80(11)
Zn(1)–N(3)	2.006(3)	N(3)–Zn(1)–N(4)	111.81(13)
Zn(1)–N(4)	2.023(3)	O(1*c*)–Zn(1)–N(2*c*)	93.17(12)
Zn(1)–N(2*c*)	2.100(3)	N(3)–Zn(1)–N(2*c*)	91.24(14)
N(4)–Zn(1)–N(2*c*)	98.48(14)	O(1*c*)–Zn(1)–O(1*d*)	74.49(10)
N(3)–Zn(1)–O(1*d*)	90.36(12)	N(4)–Zn(1)–O(1*d*)	95.15(11)

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