

## Research Article

# Syntheses, Crystal Structures, Magnetic Behaviours, and Thermal Properties of Three Hydrogen-Bonding Networks Containing Dicyanamide and 4-Hydroxypyridine

Lingling Zheng

Guangzhou Vocational College of Technology & Business, Guangzhou 511442, China

Correspondence should be addressed to Lingling Zheng; zszhengll@yahoo.com.cn

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Three new dicyanamide-bridged polymeric complexes of  $\{[\text{Mn}(\text{dca})_2(\text{L})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Cd}(\text{dca})_2(\text{L})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**2**), and  $\{[\text{Co}(\text{dca})_2(\text{L})_2]2(\text{L})\}_n$  (**3**) (dca = dicyanamide, L = pyridinium-4-olate) have been synthesized and structurally characterized. In the three compounds, the protons of hydroxyl groups of 4-hydroxypyridine transfer to pyridyl nitrogen atoms. Compounds **1** and **2** are isomorphous forming one-dimensional  $[\text{M}(\text{dca})_2(\text{L})_2]_n$  chains where metals are connected by double dca anions. These one-dimensional chains are extended into two-dimensional layers through weak C–H···N hydrogen bonds. Further, these layers are assembled into a three-dimensional supramolecular network through N–H···O, O–H···O hydrogen bonds. Complex **3** is a coordination layer of (4, 4) topology with octahedral metal centers linked by four single  $\mu_{1,5}$ -bridges. These layers are interlocked by N–H···O, O–H···O hydrogen bonds from coordinated water molecules and free L molecules, which leads to a three-dimensional supramolecular architecture. The variable temperature magnetic susceptibilities measurement of compounds **1** and **3** shows the existence of weak antiferromagnetic interactions between the metal centers. The thermogravimetric analyses of the compounds **1–3** are also discussed.

## 1. Introduction

The coordination polymers [1] based on dicyanamide  $[\text{dca}, \text{N}(\text{CN})_2^-]$  have drawn great interest in the last two decades, due to their attractive structures and magnetic properties: three-dimensional rutile-like structure of  $[\text{M}(\text{dca})_2]$  shows long-range magnetic ordering [2–4] and low-dimensional system (one-dimension or two-dimension) when auxiliary ligand is introduced to form  $[\text{M}(\text{dca})_2(\text{L})_x]$  [5–11]. Other ways have been developed to obtain three-dimensional system, using auxiliary bridging ligand, such as nicotinic acid [12], pyrazine-dioxide [13], and pyrimidine [14] through coordination interaction. In addition to coordination interaction, some weak interactions, such as intra- and/or intermolecular hydrogen-bonding interactions, and  $\pi$ - $\pi$  stacking supramolecular interactions also greatly affect the ultimate structures, especially in the field of extending low-dimensional entities to higher-dimensional supramolecular frameworks [15, 16]. Compared with the bridging ligands,

the terminal ligands seem to only occupy one position of the coordination sphere; in fact, they have important impacts on the ultimate networks. For example, when terminal ligands are 4-picoline [17] and cyanopyridine [18], although only one-dimensional chains are obtained, the intermolecular  $\pi$ - $\pi$  stacking interactions extend these one-dimensional coordination chains into two-dimensional or three-dimensional networks, which indicates that intermolecular interactions play an important role in constructing supramolecular architectures. To date, the research focus on crystal engineering of dca through intramolecular interactions remains limited [19], especially using hydrogen-bonding interaction to construct higher-dimensional architectures. In our earlier research, we chose 4-(4H-imidazol-4-yl) benzenamine and isonicotinamide as the coligands, and five supramolecular architectures were obtained [20–22], in which the metal centers coordinates to the imidazole nitrogens or pyridyl nitrogen atoms, and the  $-\text{NH}_2$ ,  $-\text{CONH}_2$  groups act as hydrogen bond donor to form strong intermolecular hydrogen bonds. We

also found the *in situ* nucleophilic addition reactions between dca and some small molecules [23–25]. To further explore the work of metal dca and discuss the influence of hydrogen bonding interactions on the ultimate architecture, we now focus on the context with other terminal ligands, in which 4-hydroxypyridine is employed as the auxiliary ligand, and three coordination polymers  $\{[\text{Mn}(\text{dca})_2(\text{L})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Cd}(\text{dca})_2(\text{L})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**2**), and  $\{[\text{Co}(\text{dca})_2(\text{L})_2]2(\text{L})\}_n$  (**3**) (L = pyridinium-4-olate) via dca connectors are prepared and structurally determined by X-ray single crystal diffraction. To our knowledge, with dca and the 4-hydroxypyridine, no coordination compounds have been reported before.

## 2. Experimental

**2.1. Materials and Methods.** 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  $\text{cm}^{-1}$  with a Nicolet 5DX spectrometer. Variable-temperature magnetic susceptibility measurements were made using a SQUID magnetometer MPMS XL-7 (Quantum Design) at 0.5 T for **1** and **3**. The diamagnetic correction for each sample was determined from Pascal's constants [26]. Thermogravimetric analyses were carried out on a Netzsch TG-209 analyzer in atmosphere at a heating rate of 10 °C  $\text{min}^{-1}$ .

**2.2. Preparation of Compounds.**  $\{[\text{Mn}(\text{dca})_2(\text{L})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**1**): a solution (10 mL) of L (0.095 g, 0.5 mmol) in methanol (10 mL) was added dropwise to an aqueous solution (5 mL) of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.100 g, 0.5 mmol), under stirring to form a mixture. A solution (5 mL) of sodium dicyanamide (0.089 g, 1.0 mmol) in water (5 mL) was added to the mixture slowly. After 30 min, the clear solution was filtered and the filtrate was evaporated under room temperature. After a few days, yellow single crystals suitable for X-ray analysis were obtained. Yield: ca. 54%. Anal. Calcd. for  $\text{C}_{14}\text{H}_{14}\text{MnN}_8\text{O}_4$ : C, 40.69; H, 3.41; N, 27.12%. Found: C, 39.68; H, 3.55; N, 26.49%. IR ( $\text{cm}^{-1}$ ): 3580 w, 3237 m, 3092 m, 2963 m, 2876 w, 2662 w, 2487 w, 2279 m, 2235 s, 2174 s, 1635 s, 1518 s, 1383 m, 1358 m, 1316 vw, 1252 vw, 1193 vs, 1083 w, 998 s, 1084 w, 851 m, 820 w, 669 w, 546 s, 524 w, 504 vw.

$\{[\text{Cd}(\text{dca})_2(\text{L})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**2**): yellow crystals of **2** were obtained in a method analogous to that for **1** using  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . Yield: ca. 66%. Anal. Calcd. for  $\text{C}_{14}\text{H}_{14}\text{CdN}_8\text{O}_4$ : C, 35.72; H, 3.00; N, 23.80%. Found: C, 35.16; H, 3.08; N, 23.71%. IR ( $\text{cm}^{-1}$ ): 3587 w, 3469 w, 3360 w, 3219 w, 3091 m, 2961 m, 2879 w, 2664 vw, 2280 w, 2233 m, 2180 s, 1636 s, 1516 vs, 1364 m, 1198 m, 1087 w, 999 m, 827 m, 543 m.

$\{[\text{Co}(\text{dca})_2(\text{H}_2\text{O})_2] \cdot (\text{L})_2\}_n$  (**3**): a solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.145 g, 0.5 mmol) in methanol (10 mL) was added dropwise to a mixture of L (0.095 g, 1.0 mmol) dissolved in methanol (5 mL) together with sodium dicyanamide (0.089 g, 1.0 mmol) in water (5 mL). The deep red single crystals suitable for X-ray analysis were obtained

by evaporating the solvent in a few days. Yield: 65%. Anal. Calcd. for  $\text{C}_{14}\text{H}_{14}\text{N}_8\text{CoO}_4$ : C, 40.30; H, 3.38; N, 26.86%. Found: C, 39.46; H, 3.47; N, 26.08%. IR ( $\text{cm}^{-1}$ ): 3587 w, 3237 m, 3124 m, 3089 m, 2976 m, 2888 w, 2665 w, 2490 vw, 2280 w, 2246 s, 2187 s, 1935 vw, 1635 vs, 1599 m, 1515 vs, 1375 m, 1354 m, 1298 vw, 1189 vs, 1082 vw, 1036 w, 1002 s, 853 s, 728 w, 671 vw, 548 s, 526 w, 505 m.

**2.3. X-Ray Crystallography.** Crystallographic data for all the complexes were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The frames were integrated with the Bruker SAINT<sup>+</sup> software package, and the data were corrected for absorption using the program SADABS [27]. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [28, 29]. All nonhydrogen atoms were fined with anisotropic thermal parameters on  $F^2$ . The organic hydrogen atoms were generated geometrically (C–H 0.96  $\text{\AA}$ ); the aqueous hydrogen atoms were located from different maps and refined with isotropic temperature factors. All crystallographic data and structural refinement details for the complexes are summarized in Table 1, selected bond distances and bond angles are listed in Table 2, and the hydrogen bonds are given in Table 3.

## 3. Result and Discussion

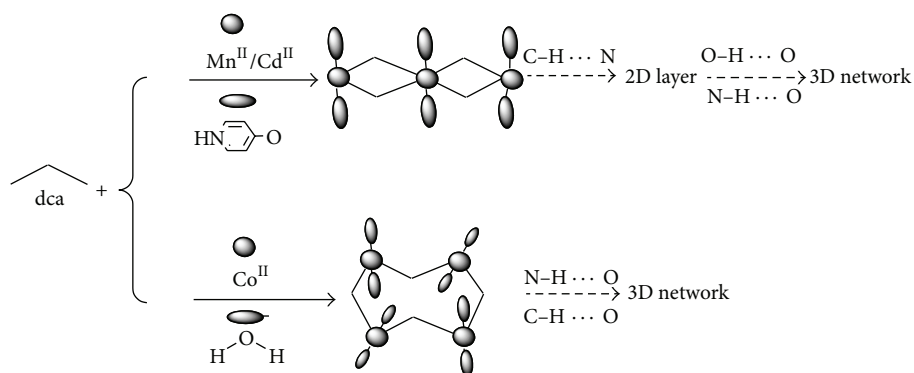
**3.1. Syntheses and Characterization.** Solution assemblies of dca and L with various metal salts led to complexes **1–3** at room temperature which were shown in Scheme 1. Complexes **1** and **2** have similar chains at ligand/dca/M ratios of 1 : 2 : 1, while **3** is synthesized at a 2 : 2 : 1 coordinative layer. In the specific self-assembled processes, the products are independent of the ligand-to-metal ratios (the results were confirmed by X-ray diffraction). In the three compounds, the protons of hydroxyl groups transfer to pyridyl nitrogen atoms to form pyridinium-4-olate, and similar cases have been reported before [30, 31], which leads to rich hydrogen bonds. In compounds **1** and **2**, the metal centers coordinate to oxygen atoms, while in **3**, the L molecules behave as free molecules. However, L molecules act as both hydrogen bond donor and hydrogen bond acceptor in the three compounds.

The IR spectra of **1–3** are shown in experimental section, and the absorption peaks in 1400–1600  $\text{cm}^{-1}$  can be ascribed to the vibrations of pyridyl groups of L [32]. The characteristic peaks of dca are quite similar, and they all show strong absorptions in 2300–2100  $\text{cm}^{-1}$  region, corresponding to the  $\nu_s + \nu_{as}(\text{C} \equiv \text{N})$ ,  $\nu_{as}(\text{C} \equiv \text{N})$ , and  $\nu_s(\text{C} \equiv \text{N})$  modes of the dca ligand, which shift to higher frequencies compared with those of free dca in its sodium salts (2286  $\text{cm}^{-1}$ , 2232  $\text{cm}^{-1}$ , and 2129  $\text{cm}^{-1}$ ) and reveal the coordination of the ligand [33]. Bands of the  $\nu_{as}(\text{C}–\text{N})$  (1400–1300  $\text{cm}^{-1}$ ) and  $\nu_s(\text{C}–\text{N})$  (950–900  $\text{cm}^{-1}$ ) vibration were also displayed in the spectra of **1–3**.

**3.2. The Crystal Structures of Compounds 1–3.** Single-crystal X-ray analysis shows that **1** and **2** are isostructural one-dimensional linear complexes, so only **1** is described here. The

TABLE 1: Crystal data and structure refinements for compounds 1-3.

	1	2	3
Empirical formula	C <sub>7</sub> H <sub>7</sub> Mn <sub>0.5</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>7</sub> Cd <sub>0.5</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>7</sub> Co <sub>0.5</sub> N <sub>4</sub> O <sub>2</sub>
Formula weight	206.64	235.37	208.63
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
a (Å)	8.2850 (12)	8.3385 (7)	7.8788 (16)
b (Å)	14.661 (2)	14.7789 (12)	12.896 (3)
c (Å)	7.4097 (11)	7.4739 (6)	9.1106 (18)
β (°)	101.555 (2)	103.2170 (10)	96.11 (3)
V (Å <sup>3</sup> )	881.8 (2)	896.64 (13)	920.5 (3)
Z	4	4	4
Dc/g·cm <sup>-3</sup>	1.556	1.744	1.506
Absorption coefficient (mm <sup>-1</sup> )	0.788	1.257	0.971
F(000)	422	468	426
Crystal size (mm)	0.25 × 0.23 × 0.18	0.25 × 0.22 × 0.17	0.28 × 0.24 × 0.19
θ range (°)	2.5–25.99	2.51–27.00	2.60–26.00
Limiting indices	-10 ≤ h ≤ 4 -14 ≤ k ≤ 18 -9 ≤ l ≤ 8	-10 ≤ h ≤ 9 -18 ≤ k ≤ 16 -5 ≤ l ≤ 9	-9 ≤ h ≤ 9 -15 ≤ k ≤ 10 -10 ≤ l ≤ 11
Reflections collected	3329	5184	4900
Independent reflections	1646	1929	1804
Max. and min. transmissions	0.8273 and 0.8711	0.7440 and 0.8147	0.7728 and 0.8371
Data/restraints/parameters	1646/0/136	1929/0/137	1804/9/136
Goodness-of-fit on F <sup>2</sup>	1.071	1.039	1.261
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0413, wR <sub>2</sub> = 0.1180	R <sub>1</sub> = 0.0200, wR <sub>2</sub> = 0.0506	R <sub>1</sub> = 0.0789, wR <sub>2</sub> = 0.2185
R indices (all data)	R <sub>1</sub> = 0.0443, wR <sub>2</sub> = 0.1217	R <sub>1</sub> = 0.0234, wR <sub>2</sub> = 0.0529	R <sub>1</sub> = 0.0844, wR <sub>2</sub> = 0.2205
Largest diff. peak and hole (eÅ <sup>-3</sup> )	0.685 and -0.237	0.234 and -0.349	-0.422 and 1.142



SCHEME 1: The progress of syntheses.

metal coordination sphere with the atom-labeling scheme of **1** is given in Figure 1(a). Each unit consists of the neutral [Mn<sub>0.5</sub>(dca)(L)] and one water molecule. The octahedral manganese atom lies on a symmetric centre and is coordinated to four  $\mu_{1,5}$ -dca anions via nitrile nitrogen atoms and two *trans*-L ligands via the oxygen atoms. The Mn-N(nitrile) bond distances of 2.212(2) and 2.221(2) Å are slightly longer than that involving the L, of 2.210(2) Å, but all the values are comparable to those found in the pyridine derivatives [34].

The dca anions connect the metal centers through end-to-end  $\mu_{1,5}$  bridging mode, producing linear one-dimensional chains via double dca bridges (Mn...Mn distance within chain is 7.409(2) Å), which is smaller than similar one-dimensional double chains Mn(dca)<sub>2</sub>(im)<sub>2</sub> (im = imidazole), where the doubly bridged Mn...Mn distance is 7.529 Å [35].

The packing view of **1** shows interdigitation of adjacent chains through weak C7-H7a...N2 hydrogen-bonding interaction (C7...N2 = 3.387(2) Å, C7-H7a...N2 = 148(3)°)

TABLE 2: The selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for complexes 1–3.

1			
<i>Bonds</i>			
Mn(1)-N(1)	2.221(2)	Mn(1)-O(1)	2.2099(16)
Mn(1)-N(3 <i>b</i> )	2.212(2)		
<i>Angles</i>			
O(1)-Mn(1)-N(1 <i>a</i> )	93.72(8)	O(1)-Mn(1)-N(3 <i>b</i> )	89.78(8)
N(3 <i>b</i> )-Mn(1)-N(1 <i>a</i> )	88.00(8)	O(1)-Mn(1)-N(1)	86.28(8)
N(3 <i>c</i> )-Mn(1)-N(1 <i>a</i> )	92.00(8)	O(1)-Mn(1)-N(3 <i>c</i> )	90.22(8)
2			
<i>Bonds</i>			
Cd(1)-N(2 <i>a</i> )	2.3066(16)	Cd(1)-N(4 <i>c</i> )	2.3166(17)
Cd(1)-O(1)	2.3279(12)		
<i>Angles</i>			
N(2 <i>a</i> )-Cd(1)-N(4)	88.38(6)	N(2 <i>a</i> )-Cd(1)-O(1)	90.47(6)
N(2 <i>b</i> )-Cd(1)-N(4)	91.62(6)	N(2 <i>b</i> )-Cd(1)-O(1)	89.53(6)
N(4 <i>c</i> )-Cd(1)-O(1)	95.34(6)	N(4)-Cd(1)-O(1)	84.66(6)
3			
<i>Bonds</i>			
Co(1)-O(1 <i>W</i> )	2.057(5)	Co(1)-N(1)	2.124(6)
Co(1)-N(3 <i>b</i> )	2.124(7)		
<i>Angles</i>			
O(1 <i>W</i> )-Co(1)-N(1 <i>a</i> )	89.8(3)	O(1 <i>W</i> )-Co(1)-N(3 <i>b</i> )	88.3(3)
O(1 <i>W</i> )-Co(1)-N(1)	90.2(3)	N(1)-Co(1)-N(3 <i>b</i> )	94.1(3)
O(1 <i>W</i> )-Co(1)-N(3 <i>c</i> )	91.7(3)	N(1)-Co(1)-N(3 <i>c</i> )	85.9(3)

Symmetry codes: (a)  $-x + 2, -y + 2, -z$ ; (b)  $x, -y + 5/2, z - 1/2$ ; (c)  $-x + 2, y - 1/2, -z + 1/2$  for 1; (a)  $-x + 2, -y + 2, -z$ ; (b)  $-x + 2, y + 1/2, -z + 1/2$ ; (c)  $x, -y + 3/2, z - 1/2$  for 2; (a)  $-x + 1, -y + 1, -z$ ; (b)  $x, y, z - 1$ ; (c)  $-x + 1, -y + 1, -z + 1$  for 3.

TABLE 3: Hydrogen bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for complexes 1–3.

D-H...A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{D-H}\cdots\text{A}$
1				
N4-H4N...O1W	0.83(4)	2.03(4)	2.810(3)	156(3)
O1W-H1WA...O1 <i>a</i>	0.80(4)	2.13(4)	2.872(3)	155(4)
O1W-H1WB...O1 <i>b</i>	0.79(5)	2.49(5)	3.158(3)	144(5)
2				
N1-H1C...O1W	0.76(3)	2.05(3)	2.789(2)	166(3)
O1W-H1WA...O1 <i>a</i>	0.77(4)	2.35(4)	3.100(2)	168(4)
O1W-H2WA...O1 <i>b</i>	0.81(3)	2.04(3)	2.849(2)	170(3)
3				
N7-H3...O2 <i>a</i>	0.95(13)	1.90(13)	2.788(9)	154(11)
O1-H1...O2 <i>b</i>	0.849(10)	1.894(19)	2.728(7)	167(6)
O1-H2...O2 <i>c</i>	0.849(10)	1.86(2)	2.698(8)	167(6)

Symmetry codes: (a)  $x - 1, y, z$ ; (b)  $x - 1, -y + 1/2, z - 1/2$  for 1; (a)  $x - 1, -y + 5/2, z - 1/2$ ; (b)  $x - 1, y, z$  for 2; (a)  $-x + 1, y + 1/2, -z + 1/2$ ; (b)  $x + 1, y + 1, z$ ; (c)  $x + 1, y + 1, z$  for 3.

between amine nitrogen atom of dca and hydrogen atom of carbon atom from adjoining chains, generating a two-dimensional supramolecular layer along *a*-axis (Figure 1(b)). It is different from similar pyridine analogues that the one-dimensional chains are cross-linked through  $\pi$ - $\pi$  stacking interactions [17], and the hydrogen bonding interactions might make the distance of pyridyl rings slightly larger.

The existence of water molecules makes the hydrogen-bonding interactions more complicated. These water molecules locate in the place of interchain, which is illustrated in Figure 1(c). The water molecule behaves as both hydrogen bond donor and acceptor. As an acceptor, the oxygen atom forms a strong N-H...O (N4...O1W = 2.810(3)  $\text{\AA}$ , N4-H4N...O = 156(3) $^\circ$ ) hydrogen bond with

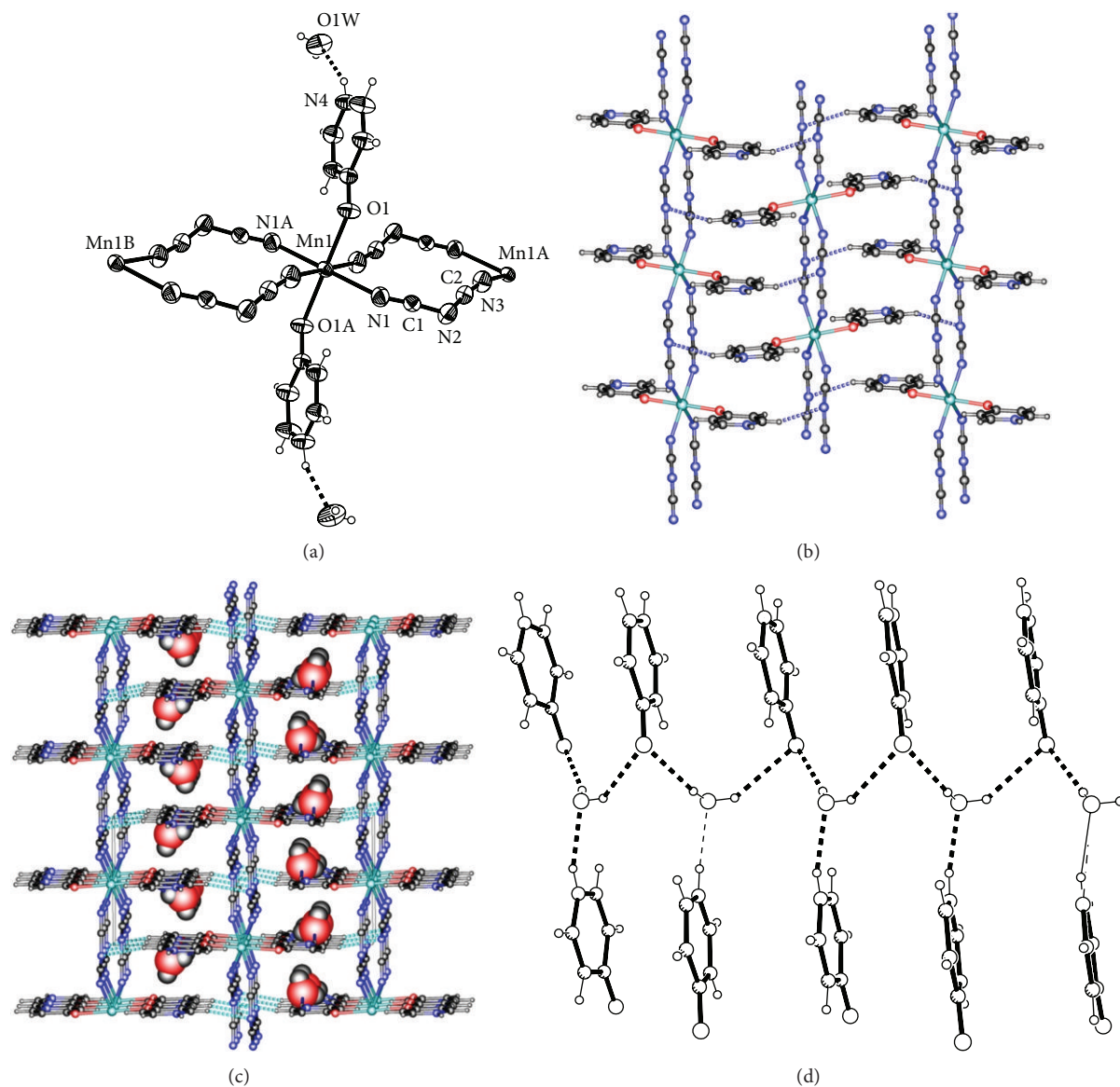


FIGURE 1: Views of (a) the coordination environment of Mn<sup>II</sup> atoms, (b) the 2D network formed by the interchain C–H...N hydrogen-bonding interactions, (c) the water molecules in the architecture, and (d) the hydrogen-bonding interactions between water molecules and L in **1**.

protonated pyridyl nitrogen atom of L. Meanwhile, one of the hydrogen atom of water molecule and oxygen atoms from L forms an O–H...O (O1W...O1 = 2.872(3) Å, O1W–H1WA...O1 = 155(4)°) hydrogen bond, and the remaining hydrogen atom links another oxygen atom from neighbouring chains through O1W–H1WB...O1 (O1W...O1 = 3.158(3) Å, O1W–H1WB...O1 = 144(5)°) hydrogen bond. The hydrogen bonding interactions are shown in Figure 1(d). These hydrogen bonding interactions extend the two-dimensional layers into a three-dimensional supramolecular architecture.

X-ray crystallographic analysis reveals that complex **3** is made up of [Co(dca)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] units and free L molecule, which is depicted in Figure 2(a). The coordination sphere

is slightly distorted from *O<sub>h</sub>* symmetry. Nitrogen atoms of four different dca ligands are positioned in the equatorial plane with Co–N1 and Co–N3 in distances of 2.124(6) and 2.124(7) Å, respectively. The octahedron is constructed by axial coordination of *trans*-H<sub>2</sub>O molecules which have Co–O1W distance of 2.057(5) Å. The  $\mu_{1,5}$ -dca anions connect different cobalt centres to a two-dimensional layer (Figure 2(b)). The Co...Co distance within the same layer is 7.894(1) Å, which is shorter than similar two-dimensional layer [36, 37]. It should be noted that only small number of compounds containing two-dimensional networks without bridging coligands have been reported [5–8].

Different to **1** and **2**, the L ligands are used as free molecules and located in interlayer, which interact with the

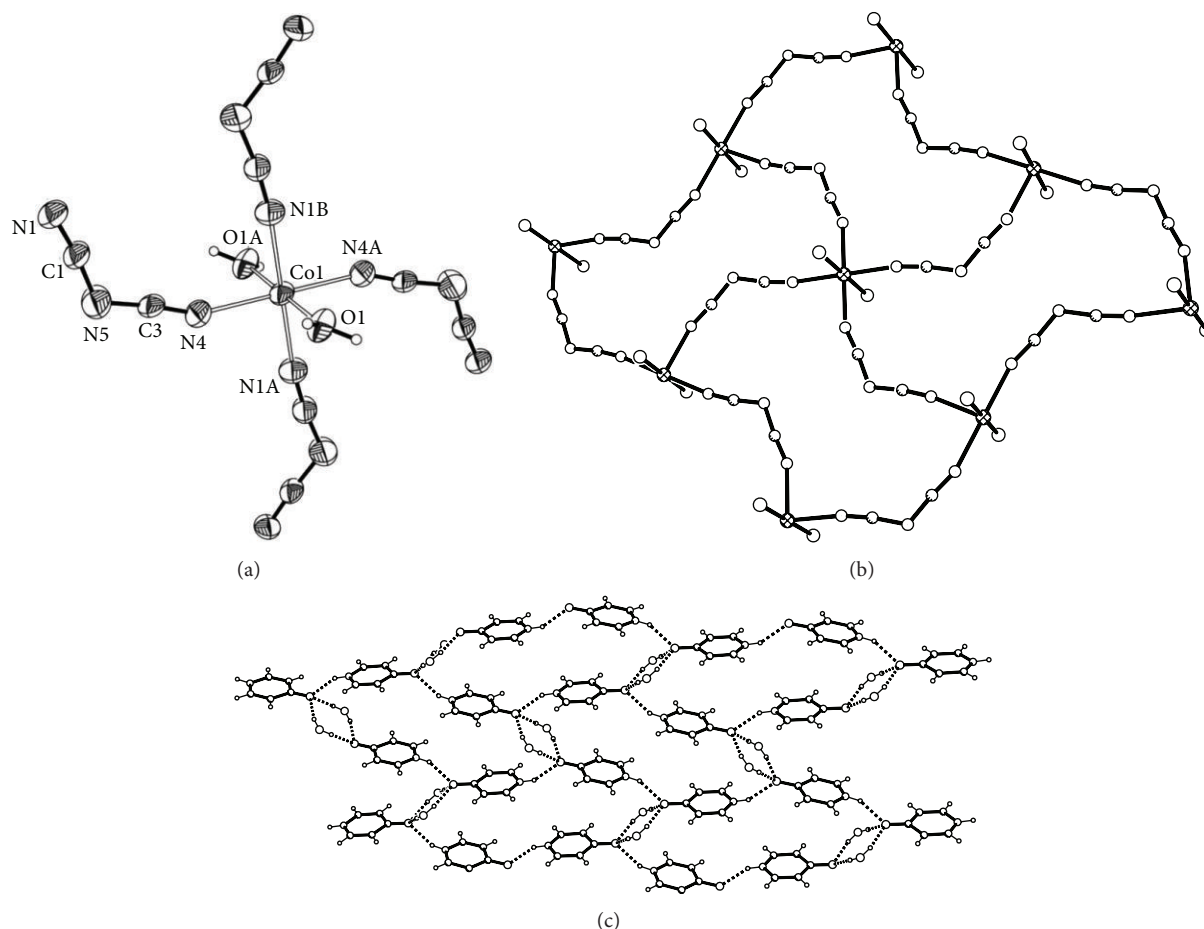


FIGURE 2: Views of (a) the coordination environment of Co<sup>II</sup> atoms, (b) the 2D (4, 4) layer, and (c) the hydrogen-bonding interactions between water molecules and free pyridinium-4-olate molecules in **3**.

layer through strong hydrogen bonding interactions. The L molecule acts as both hydrogen bond donor and acceptor. The oxygen atom is linked to two hydrogen atoms of two water molecules through O–H $\cdots$ O (O1 $\cdots$ O2 = 2.728(7), 2.698(8) Å, O1–H1 $\cdots$ O2 = 167(6) $^\circ$ , and O1–H2 $\cdots$ O2 = 167(6) $^\circ$ ) hydrogen bonds, forming a  $R_4^2(8)$  synthon. Moreover, the oxygen atom interacts with another L molecule through N–H $\cdots$ O (N7 $\cdots$ O2 = 2.788(9) Å, N7–H3 $\cdots$ O2 = 154(11) $^\circ$ ) hydrogen bonds. The L molecule also interacts with another L molecule through protonated N atom via N–H $\cdots$ O hydrogen bond. The free L molecules are linked together through N–H $\cdots$ O hydrogen bonds and interact with two-dimensional layer through O–H $\cdots$ O hydrogen bonds, which is displayed in Figure 2(c). The two-dimensional layers are extended into a three-dimensional supramolecular framework through these hydrogen bonding interactions.

Thus the H-bonding acts here as a tool for controlling the whole coordinative architecture. The dca anion coordinates to metal centers in a  $\mu_{1,5}$  mode through two nitrile nitrogen atoms, the cases of amide nitrogen atom bind to metal centre are very few in dca chemistry [8, 38]. However, the amide nitrogen atom forms strong hydrogen bonds with other hydrogen donors. The hydrogen bonding interactions

make the coordination polymer to higher dimensionality, which reveals the coordinative interaction of coordination and supramolecular interaction.

**3.3. Magnetic Properties of Compounds 1 and 3.** Solid state *dc* magnetic susceptibility studies were carried out on samples **1** and **3** in a field of 0.5 T. Plots of  $\chi_M$  versus  $T$  and  $\chi_M T$  versus  $T$  plots are shown in Figure 3. For **1**, taking into consideration the one-dimensional structure, magnetic data are taken for a Mn(II) ion. The  $\chi_M T$  value at room temperature is 3.86 cm<sup>3</sup> mol<sup>-1</sup> K, which is lower than a spin only value of 4.38 cm<sup>3</sup> mol<sup>-1</sup> K, expected for an uncoupled high-spin  $S = 5/2$  ions ( $g = 2.0$ ). This value is almost constant up to 100 K, decreasing sharply to 2 K, owing to an increase of antiferromagnetic correlations. When the temperature is reduced, the  $\chi_M$  value increases as expected. This is due to the fact that there are more and more spins that are correlated in the lattice, showing that a peak maximum at ca. 3.5 K for 1D ordering occurs. This feature is indicative of weak antiferromagnetic coupling among Mn(II) ions. In order to estimate the intrachain exchange interaction between isotropic Mn<sup>II</sup> centers,  $\chi_M$  was also fit to the Heisenberg

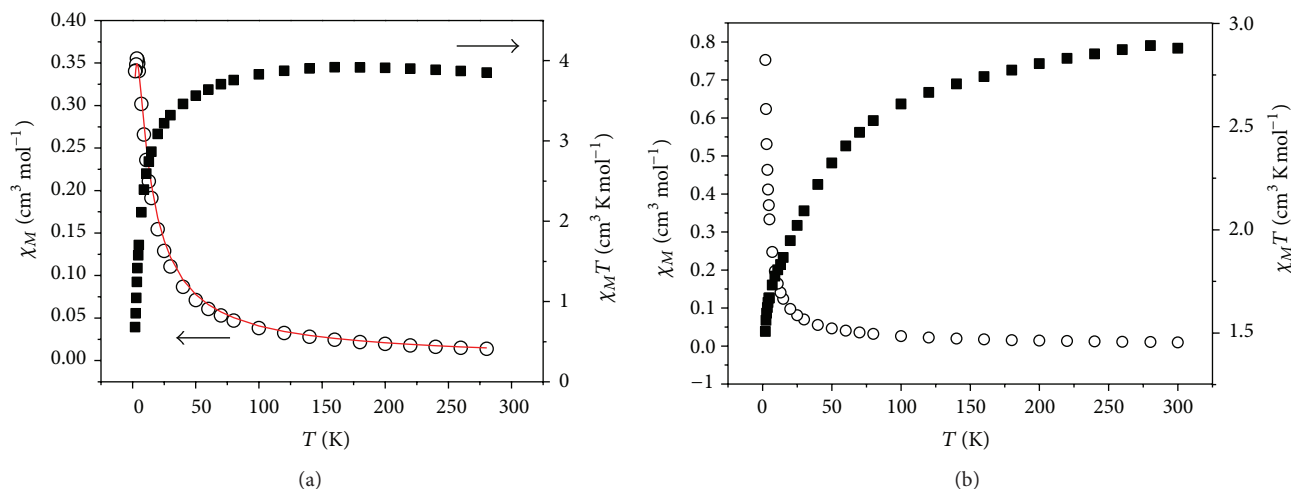


FIGURE 3: (a) Plots of the  $\chi_M T$  versus  $T$  and  $\chi_M$  versus  $T$ . Solid lines represent the best fit with the parameters given in the text in 1. (b) Plots of the  $\chi_M T$  versus  $T$  and  $\chi_M$  versus  $T$  in 3.

infinite chain model derived by the spin Hamiltonian [39],  $H = -2J\hat{S}_i\hat{S}_{i+1}$ ,

$$\chi_M = \frac{Ng^2\mu_B S(S+1)}{3k_B T} \cdot \frac{1+u(K)}{1-u(K)}, \quad (1)$$

$$K = \frac{2JS(S+1)}{k_B T}, \quad u(K) = \coth K - \frac{1}{K},$$

where  $N$  is Avogadro number,  $k_B$  is the Boltzmann constant, and  $J$  is intrachain coupling constant. The best-fit parameters of the experimental data to theoretical model are  $J = -0.29 \text{ cm}^{-1}$ ,  $g = 1.98$ , and  $R = 6.0 \times 10^{-6}$  ( $R = [\sum(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \sum \chi_{\text{obs}}^2]^{1/2}$ ).  $J$  and  $g$  values are typical for this type of Mn-dca complexes [40]. The value of  $J$  is very small, indicating that the dicyanamide has a poor ability in mediating antiferromagnetic interactions when  $\mu_{1,5}$  bridging mode (metal-metal separation of ca. 7.0 Å) is adopted.

For 3, the  $\chi_M T$  value is  $2.86 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , which is significantly larger than that expected for an isolated spin-only  $\text{Co}^{\text{II}}$  ( $\chi_M T = 1.87 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for a  $S = 3/2$  ion,  $g = 2.0$ ), indicating that obvious orbital contribution is involved, typical of the  $4T_{1g}$  ground term for  $\text{Co}(\text{II})$  in an octahedral field [41]. No maximum in the corresponding susceptibilities is down to 2 K. The  $\chi_M T$  value is in the range of typical range of a  $\text{Co}^{\text{II}}$  of 2.75–3.40  $\text{cm}^3 \text{ mol}^{-1} \text{ K}$  [42]. This temperature-dependent behavior is largely contributed to the combination of spin-orbit coupling and low symmetry ligand field effects that causes splitting of the  $4T_{1g}$  levels [43]. The lack of an appropriate magnetic model to describe the complicated situation has precluded quantitative magnetic analyses for polynuclear or polymeric  $\text{Co}(\text{II})$  complexes [44, 45].

**3.4. Thermogravimetric Analysis.** Thermogravimetric experiments for complexes 1–3 were performed to explore their

thermal stabilities (Figure 4). The samples of 1–3 were heated to 425°C under atmosphere. With regard to 1, the weight loss of 8.2% appeared between room temperature and 97.3°C corresponding to the loss of two crystallized water molecules (calcd. 8.7%). The framework kept stable until ca. 326°C for the appearance of a long platform. Then, the whole network started to decompose quickly. For 2, the TG profile is similar to compound 1. The two water molecules were released below ca. 152°C, as revealed by a total weight loss of 7.5% (calcd. 7.6%). Compared to 1, the water molecules were gotten off at higher temperature, which is ascribed to the more strong hydrogen bonding interactions in 2 (O1W...O1 2.849, 3.100 Å; N1...O1, 2.789 Å). Then, the skeleton kept stable until ca. 300°C. When further heated, it began to decompose. Complex 3 was thermally stable up to 100°C, and then it began to dehydrate. The weight loss of 8.1% appeared between 100°C and 160°C, corresponding to the loss of two coordinated water molecules (calcd. 8.6%) in one unit cell, and when further heated it started to decompose. The coordinate water molecules were released in higher temperature than crystallization water molecules.

## 4. Conclusions

The new three-dimensional supramolecular networks have been synthesized by using dca anions together with 4-hydroxypyridine as coligands. The results demonstrate that the dca anions link metal ions through  $\mu_{1,5}$ -bridge, which is most common in dca chemistry. However, the introduction of coligand plays an important role in the crystal packing of polymers. The hydrogen bonding interactions between coligand and polymer extend the polymers into higher dimensionality. Finally, magnetic studies of 1 and 3 display only very weak antiferromagnetic interactions between metal centers through  $\mu_{1,5}$ -dca anions and the long distance of metal centers.

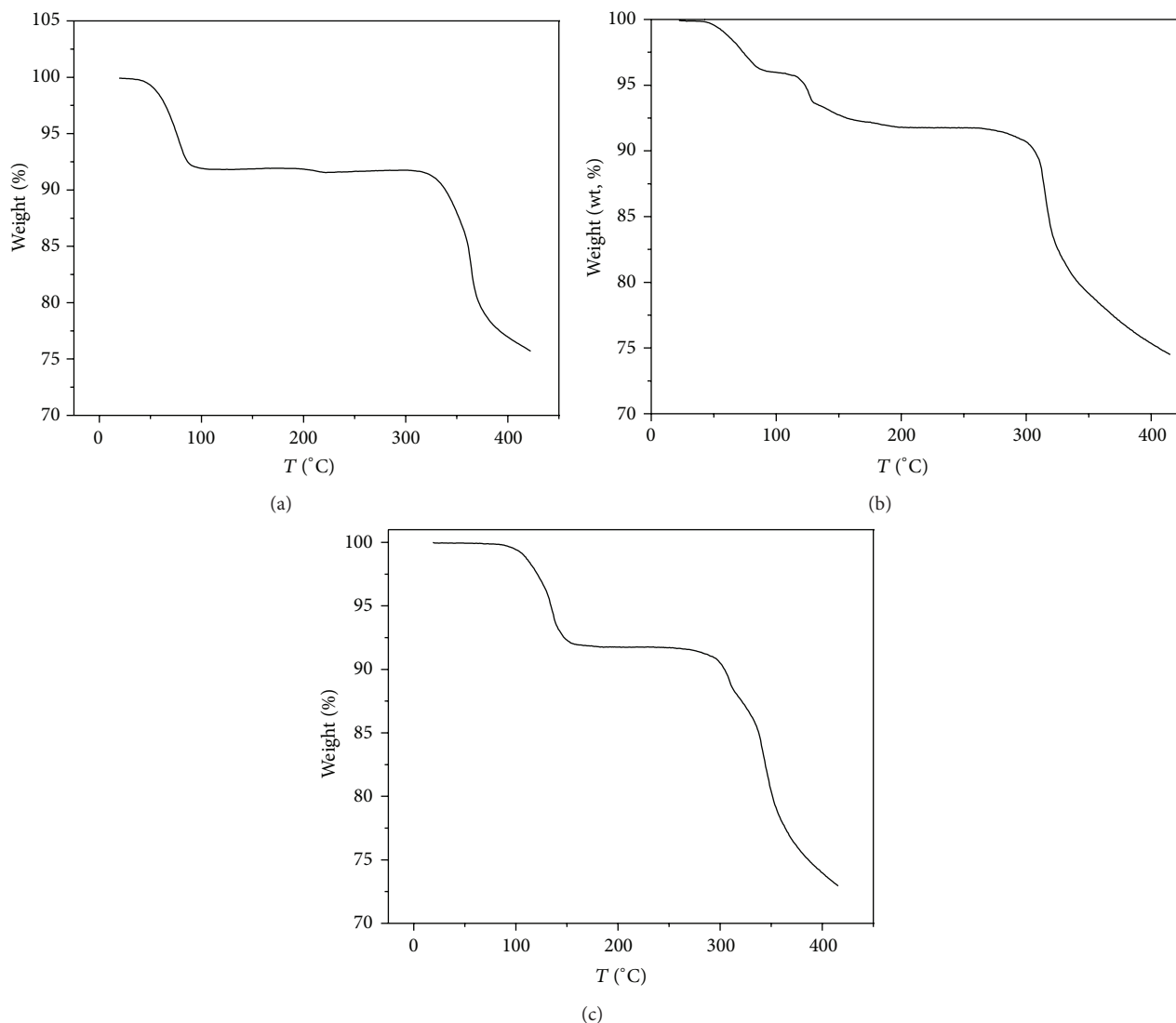


FIGURE 4: The thermogravimetric curves of **1** (a), **2** (b), and **3** (c).

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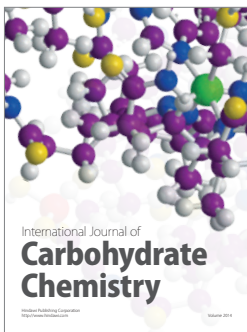
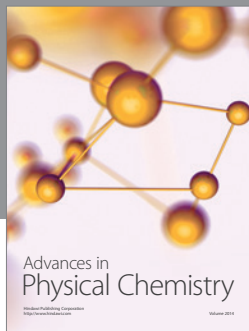
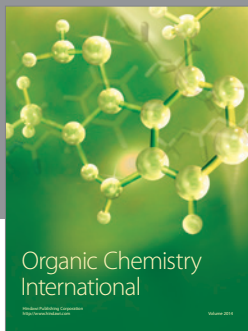
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