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Bis(3-cyano-pentane-2,4-dionato) Co(II) as a linear building block for coordination polymers: combinations with two polypyridines

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Two types of bis(β -diketonato) Co(II) complexes, [Co(CNacac)₂] (CNacac=3-cyano-pentane-2,4-dionato), and [Co(dbm)₂] (dbm=dibenzoylmethanato or 1,3-diphenyl-propane-1,3-dionato) were examined as linear building blocks for the construction of coordination polymers in combination with two oligopyridines, 1,4-bis(4,2':6',4"-terpyridin-4'-yl)benzene (L1) and 1,3-bis(3,2':6',3"-terpyridin-4'-yl)benzene) (L2). From combinations of [Co(CNacac)₂] with L1 and L2, 2-D coordination polymers, [Co(CNacac)₂]₂(L1)·(CHCl₃)·(CH₃OH) (CoCN-1) and [Co(CNacac)₂](L2)_{1/} ₂·(tetrachloroethane)_{3/2} (CoCN-2), are obtained. Both CoCN-1 and CoCN-2 have 2D (4,4) net structures, in which L1 and L2 are tetradentate. In contrast, combination of [Co(dbm)₂] with L2 affords a 1-D coordination polymer, [Co(dbm)₂](L2)·4(CH₃OH) (Codbm-1), in which L2 is bidentate. L2 as a tetradentate ligand was inhibited by bulky phenyl rings in [Co(dbm)₂]. These results indicate that [Co(CNacac)₂] with a relatively simplified structure is useful as a linear building block in combinations with bulky oligopyridines.

Keywords: Coordination polymer; Linear building block; Polypyridines; β-Diketonato; Cobalt(II)

1. Introduction

Coordination polymers or metal-organic frameworks (MOFs) are typically formed from self assembly of metal ions, which serve as nodes and ligands that act as bridges [1]. This simple method has been applied to various combinations of metal ions and organic ligands. However, structural control of the resulting polymeric structure is difficult [2]. One of the reasons is that metal ions can have several coordination geometries depending on preparation conditions. For example, Ag(I) has often been used as a node with linear geometry [3], while it also can have other coordination geometries, trigonal, tetrahedral, trigonal pyramidal, and octahedral [3(b), 4]. Attempts to use a "bare" metal ion as a linear node often result in failure.

Bis(β -diketonato) metal complexes, which have a planar structure and can accept additional ligands at axial sites are known to function as linear building blocks [5, 6].

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Moreover, bis(β -diketonato) metal complexes have several useful characteristics. One is that employment of various metal ions is possible. The bis(β -diketonato) complexes with Mn(II) [6(a)], Co(II) [6(b)], Ni(II) [6(c,d)], Cu(II) [6(e,f)], and Zn(II) [6(g)] work as linear building blocks and add different magnetic properties in the resulting coordination polymers. The Lewis acidity of the metal center and stereochemistry of the whole building block can be tuned by changing β -diketonato ligands. For example, acetylacetonate (acac⁻), dibenzoylmethanate (dbm⁻), and 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac⁻) have been used as ligands [6]. Metal center of [M(dbm)₂] has high Lewis acidity compared to that of [M(acac)₂] [7]. Therefore, [M(dbm)₂] has been used as a superior building block in combinations with various ligands [6]. In contrast, the disadvantage of [M(dbm)₂] is bulkiness due to four phenyl rings, which could disturb linkage with specific ligands. It is necessary to satisfy both simple planar structure and moderate Lewis acidity in bis(β -diketonato) complexes for practical use as a linear building block.

We have focused on 3-cyano-pentane-2,4-dione (CNacacH) [8]. The electron-withdrawing cyano introduced in the 3-position of pentane-2,4-dione was expected to enhance Lewis acidity in the resulting bis(chelate) metal complexes, without hindering linkage with organic ligands. We have examined bis(3-cyano-pentane-2,4-dionato) Co(II) complex, [Co(CNacac)₂] [9], as a linear building block in combinations with bi- and tri-dentate ligands [8].

In this article, we examine the combination of $[Co(CNacac)_2]$ with potentially tetradentate oligopyridines to further examine feasibility as a linear building block (scheme 1). As oligopyridine ligands, 1,4-bis(4,2':6',4"-terpyridin-4'-yl)benzene (L1) and 1,3-bis(3,2':6',3"-terpyridin-4'-yl)benzene (L2) were used. L1 with 4-pyridyl moieties is expected to have a single conformation, while L2 can have various conformations due to rotation of four terminal 3-pyridyl moieties. Our interest was whether $[Co(CNacac)_2]$ and oligopyridines work as a linear building block and tetradentate ligands, respectively. As comparison, we also investigated the combination of $[Co(dbm)_2]$ with the oligopyridines. The difference of the two building blocks, $[Co(CNacac)_2]$ and $[Co(dbm)_2]$, clearly appear in the structures of resulting polymeric compounds.

2. Experimental

All reagents and solvents were purchased from commercial sources and used without purification. ¹H NMR spectra were recorded on a JEOL α -500 spectrometer. NMR spectra of **L1** and **L2** were measured in CDCl₃ with a drop of CH₃OH. 3-Cyano-pentane-2,4-dione (CNacacH), [Co(CNacac)₂], and [Co(dbm)₂(H₂O)₂] were synthesized according to the reported procedure [10, 11].

2.1. Syntheses of ligands

1,4-Bis(4,2':6',4"-terpyridin-4'-yl)benzene, **L1. L1** was synthesized by modifying the reported procedure [12]. 4-Acetyl-pyridine (3.63 g, mol) was added to an ethanol (120 mL) solution of isophthaladehyde (1.00 g, 7.46 mmol). This solution was stirred until complete dissolution. KOH pellets (2.3 g, 30.0 mmol) and aqueous NH_3 (28%, 45 ml) were successively added. The color of the solution turned yellow and gradually black. The reaction mixture was stirred for 4 h. During the stirring, a precipitate formed. The precipitate was filtered off and washed with water. Pinkish white solid was obtained (1.29 g, 32% yield).



Scheme 1. Schematic representation of the syntheses of CoCN-1, CoCN-2 and Codbm-1.

¹H NMR (500 MHz, CDCl₃, δ): 8.76–8.74 (m, 8H), 8.23–8.22 (m, 12H), 8.13 (s, 1H), 7.96 (dd, J=7.5, 1.8 Hz, 2H), 7.83 (t, J=7.5 Hz, 1H). Anal. Calc. for C₃₆H₂₅N₆O_{0.5} (L1·(H₂O)_{0.5}): C, 78.67; H, 4.58; N, 15.29%. Found: C, 78.38; H, 4.66; N, 14.64%.

1,3-Bis(3,2':6',3"-terpyridin-4'-yl)benzene, L2. L2 was synthesized according to the similar procedure to **L1** by using terephthalaldehyde and 3-acetyl-pyridine instead of isophthalaldehyde and 4-acetyl-pyridine, respectively. Recrystallization from methanol and chloroform mixture gave a yellowish white solid (3.45 g, 26% yield).

¹H NMR (500 MHz, CDCl₃, δ): 9.37 (d, J=2.0, 4H), 8.68 (dd, J=5.0, 1.5 Hz, 4H), 8.63–8.61 (m, 4H), 8.10 (s, 4H), 8.01 (s, 4H), 7.59–7.56 (m, 4H). Anal. Calc. for C₃₆H₂₆N₆O (**L1**·(H₂O)): C, 77.40; H, 4.69; N, 15.04%. Found: C, 77.96; H, 4.73; N, 14.72%.

2.2. Syntheses of coordination polymers

 $[Co(CNacac)_2]_2(L1) \cdot (CHCl_3) \cdot (CH_3OH)$ (CoCN-1). Methanol solution of $[Co(CNacac)_2]$ (15 mM, 6 ml) was added to a methanol–chloroform mixed solution (methanol/chloroform = 1/2, v/v) of L1 (10 mM, 4.5 ml). After the mixture was left for a few days, pink crystals were obtained (60 mg, 53% yield). Anal Calcd. for $C_{62}H_{53}O_9N_{10}Cl_3Co_2$: C, 57.00; H, 4.09; N, 10.72%. Found: C, 56.05; H, 4.25; N, 10.25%.

 $[Co(CNacac)_2](L2)_{1/2}$ (tetrachloroethane)_{3/2} (CoCN-2). Methanol solution of $[Co(CNacac)_2]$ (15 mM, 5 ml) was added to a methanol-tetrachloroethane mixed solution (methanol/tetrachloroethane = 1/1, v/v) of L2 (5 mM, 10 ml). After leaving the mixture for a week, pink crystals were obtained. Anal. Calcd. for $C_{66}H_{54}O_8N_{10}CL2_2Co_2$: C, 47.80; H, 3.28; N, 8.45%. Found: C, 48.07; H, 3.48; N, 8.15%.

 $[Co(dbm)_2](L2)\cdot 4(CH_3OH)$ (Codbm-1). $[Co(dbm)_2(H_2O)_2]$ was dissolved in a 1:1 mixed solution of methanol and chloroform (8 mM, 1 ml). To this solution, a chloroform–methanol mixed solution of L2 (8 mM, 1 ml) was added. After the mixture was left for a week, the pink crystals of $[Co(dbm)_2](L2)\cdot 4(CH_3OH)$ were obtained (6 mg, 66% yield).

2.3. Single crystal X-ray diffraction and structure determination

The crystal structures of the three coordination polymers (CoCN-1, CoCN-2 and Codbm-1) were determined by single crystal X-ray diffraction and their crystallographic and experimental data are summarized in table 1. Each crystal was coated with epoxy resin to prevent spontaneous liberation of the neutral guest. For the collection of diffraction data, a Rigaku R-AXIS RAPID imaging plate diffractometer was used. All measurements were carried out at 153 K. The structures were solved by direct methods using SHELXS-97 [13]. The refinement and all further calculations were carried out using SHELXL-97 [13]. The nonH atoms were refined anisotropically using weighted full-matrix least-squares on F². Hydrogens were generated geometrically.

CoCN-1	CoCN-2	Codbm-1
C ₆₂ H ₅₃ Cl ₃ Co ₂ N ₁₀ O ₉	C ₃₃ H ₂₇ Cl ₆ Co N ₅ O ₄	C ₃₅ H ₃₁ Co _{0.5} N ₃ O ₄
1306.35	829.23	587.10
Monoclinic	Triclinic	Triclinic
$P 2_{I}/c$	P-1	P-1
15.1718(3)	10.870(5)	11.5807(4)
14.8239(3)	12.677(5)	11.7297(4)
42.5645(7)	14.946(5)	12.7257(5)
90	105.810(5)	67.6410(10)
139.329(1)	107.144(5)	68.6070(10)
90	93.760(5)	73.6640(10)
6238.8(2)	1869.6(13)	1468.00(9)
4	2	2
1.391	1.473	1.328
153(2)	153(2)	153(2)
$0.52 \times 0.33 \times 0.25$	$0.40 \times 0.29 \times 0.18$	$0.50 \times 0.20 \times 0.19$
0.724	0.931	0.356
2688.0	842.0	615.0
102768/21240	30329/8284	18439/6696
7216	5572	6052
778	450	389
0.860	1.322	1.114
0.0767	0.1018	0.0609
0.2500	0.3432	0.1650
	$\begin{array}{c} \textbf{CoCN-1} \\ \hline C_{62}H_{53}Cl_3Co_2N_{10}O_9 \\ 1306.35 \\ \hline \text{Monoclinic} \\ P 2_{j}/c \\ 15.1718(3) \\ 14.8239(3) \\ 42.5645(7) \\ 90 \\ 139.329(1) \\ 90 \\ 6238.8(2) \\ 4 \\ 1.391 \\ 153(2) \\ 0.52 \times 0.33 \times 0.25 \\ 0.724 \\ 2688.0 \\ 102768/21240 \\ 7216 \\ 778 \\ 0.860 \\ 0.0767 \\ 0.2500 \\ \end{array}$	$\begin{array}{c c} \textbf{CoCN-1} & \textbf{CoCN-2} \\ \hline C_{62}H_{53}Cl_3Co_2N_{10}O_9 & C_{33}H_{27}Cl_6Co N_5O_4 \\ 1306.35 & 829.23 \\ \hline Monoclinic & Triclinic \\ P 2_{1/C} & P-1 \\ 15.1718(3) & 10.870(5) \\ 14.8239(3) & 12.677(5) \\ 42.5645(7) & 14.946(5) \\ 90 & 105.810(5) \\ 139.329(1) & 107.144(5) \\ 90 & 93.760(5) \\ 6238.8(2) & 1869.6(13) \\ 4 & 2 \\ 1.391 & 1.473 \\ 153(2) & 153(2) \\ 0.52 \times 0.33 \times 0.25 & 0.40 \times 0.29 \times 0.18 \\ 0.724 & 0.931 \\ 2688.0 & 842.0 \\ 102768/21240 & 30329/8284 \\ 7216 & 5572 \\ 778 & 450 \\ 0.860 & 1.322 \\ 0.0767 & 0.1018 \\ 0.2500 & 0.3432 \\ \end{array}$

Table 1. Crystallographic and experimental data for CoCN-1, CoCN-2, and Codbm-1.

^aGOF = { $\Sigma[w(F_0^2 - F_c^2)^2]/(n-p)]$ }^{1/2} $\sum[w(F_0^2 - F_c^2)^2]/(n-p)]^{1/2}(n: \text{ number of reflections; } p: \text{ total number of parameters refined}).$ ^bRl = $\Sigma(|F_0| - |F_c|)/\Sigma|F_0|$. ^c $wR^2 = {\Sigma[w(F_0^2 - (F_c^2)^2]/[w(F_0^2)^2]}^{1/2}$.

3.1. Preparation and crystal structure of CoCN-1

A planar complex $[Co(CNacac)_2]$ has weakly coordinated nitrile groups and empty axial sites. Therefore, $[Co(CNacac)_2]$ itself forms a 3-D polymeric structure by alternate linkage [9]. Polymeric $[Co(CNacac)_2]_{\infty}$ is insoluble to common organic solvents. However, it is soluble in methanol by destroying the polymeric structure with ultrasonic wave. To methanol solution of $[Co(CNacac)_2]_{\alpha}$, a chloroform–methanol mixed solution of L1 was added. Pink crystals of $[Co(CNacac)_2]_2(L1) \cdot (CHCl_3) \cdot (CH_3OH)$ (CoCN-1) were obtained after leaving the solution at ambient temperature for a few days.

Figure 1 shows the crystal structure of **CoCN-1**, where $[Co(CNacac)_2]$ and **L1** are linear building block and tetradentate ligand, respectively. Alternate linkage of $[Co(CNacac)_2]$ and **L1** forms a 2-D hexagonal structure. The 2-D net structure is classified into 2-D (4,4) net by regarding $[Co(CNacac)_2]_2(L1)_2$ as a pseudo-tetradentate ligand (figure 1(a) and (b)) [14]. Three equivalent 2-D (4,4) networks are woven through large hexagonal windows into a threefold interpenetrated structure. Such a triply interpenetrated structure was previously found in the 2-D coordination polymer formed with $[Co(CNacac)_2]$ and a tridentate polypyridyl ligand, 2',4',6'-tri(4-pyridyl)pyridine [8(a)]. π -interactions are observed between the triply interpenetrated nets (distances and angles are summarized in table 2). The triply interpenetrated 2-D sheets further stack along the *a* axis, incorporating methanol and chloroform molecules between the sheets. The cyano group in [Co(CNa $cac)_2]$ forms a hydrogen bond with methanol (table 3).



Figure 1. (a) 2-D (4,4) net in **CoCN-1** and (b) ORTEP representation of the pseudo-tetradentate ligand with ellipsoids drawn at 50% probability level (symmetry code; x, 1 - y, 1 - z). Triply interpenetrated 2-D (4,4) nets in **CoCN-1** (shown in black, violet and orange and guest molecules were omitted for clarity) are shown (c) normal and (d) edge-on to the nets (see http://dx.doi.org/10.1080/00958972.2013.800865 for color version).

In **CoCN-1**, $[Co(CNacac)_2]$ keeps its planar structure and works as a linear building block. Co^{II} is six-coordinate by four oxygens of two CNacac ligands (Co-O for 2.025–2.054 Å) and two nitrogens of **L1** at the axial positions (Co-N for 2.136–2.171 Å, table 4). These Co-O and Co-N lengths are comparable with reported values (Co-O for 2.036–2.058 Å and Co-N for 2.123–2.155 Å) observed in polymeric structures formed with [Co (CNacac)₂] and bi- and tri-dentate ligands [8].

3.2. Preparation and crystal structure of CoCN-2

To methanol solution of $[Co(CNacac)_2]$, a mixed solution of methanol and tetrachloroethane containing L2 was added. Pink crystals were obtained after leaving the solution at ambient temperature for a week. Single crystal X-ray diffraction found that it has a 2-D polymeric structure with the formula of $[Co(CNacac)_2](L2)_{1/2}$ (tetrachloroethane)_{3/2} (CoCN-2). In CoCN-2, L2 is tetradentate, alternately bridged by $[Co(CNacac)_2]$, making a 2-D (4,4) net (figure 2). The 2-D (4,4) nets obliquely stack along the *a* axis without interpenetration. Normal-to-weak interactions, long centroid–centroid distances (>3.9 Å), large slip angles (>30°), and vertical displacements (>2.0 Å) between the ring centroids, are observed between the pyridyl planes of stacked L2 [15]. These parameters for π -interactions in CoCN-2 are summarized in table 2. As a result of π -stacking, 1-D channels are formed along the *a* axis. In the channel, tetrachloroethane molecules are included as a guest. No specific interaction is observed between the host structure and guest molecule.

The asymmetric unit in the **CoCN-2** crystal contains two independent cobalts. Each Co^{II} is six-coordinate by four oxygens of two CNacac and two nitrogens of **L2**. Co-O lengths (Co-O for 2.045–2.059 Å, table 4) are comparable with those observed in **CoCN-1**. The bond length of 2.149(5) Å for Co(2)–N(4) is also comparable with those observed in **CoCN-1**, while the bond length of 2.232(5) Å for Co(1)–N(2) Å is slightly longer. The [Co(CNacac)₂] unit with Co(2) is linked with **L2** with its long molecular axis perpendicular to **L2**, while the [Co(CNacac)₂] unit with Co(1) stands sideways toward **L2**. As a result, methyl and cyano groups in the unit are positioned near the *p*-phenylene ring of **L2** (figure 2(b), (c)). To minimize steric repulsion, linkage between [Co(CNacac)₂] and **L2** (Co(1)–N(2) length) is slightly long.

Table 2. Distances/Å and angles/° for the π -contacts in **CoCN-1**, **CoCN-2**, and **Codbm-1**, where α =dihedral angle between planes *I* and *J*, β =angle Cg(I) \rightarrow Cg(J) vector and normal to plane I, γ =angle Cg(I) \rightarrow Cg(J) vector and normal to plane *J* and Cg-Cg=distance between ring centroids.

	Cg-Cg/Å	α/°	β/°	γ/°	Cg-Cg/Å
CoCN-1 ^a					
Ring N(6)-ring N(8)	3.668(3)	12.1(3)	17.23	21.86	3.405(2)
CoCN-2 ^b					
Ring N(2)-ring N(3)	4.109(4)	6.3(3)	27.98	26.24	3.628(2)
Ring N(3)-ring N(3)	4.364(4)	0	34.23	34.23	3.608(2)
Codbm-1 ^c					
Ring N(1)-ring N(2)	4.472 (2)	22.25(16)	47.74	30.56	3.008(1)
Ring N(3)-ring N(3)	3.747(2)	0	20.84	20.84	3.502(2)

^aCoCN-1, ring N(6): N(6), C(30)–C(34); ring N(8): N(8), C(46)–C(50)

^bCoCN-2, ring N(2): N(2), C(7)–C(11); ring N(3): N(3), C(12)–C(16).

^cCodbm-1, ring N(3): N(1), C(16)-C(20); ring N(2): N(2), C(21)-C(25); ring N(3): N(3), C(27)-C(30).

D–HA	<i>d</i> (D–H)/Å	$d(H \cdot \cdot \cdot A)/Å$	$d(\mathrm{H}\cdot\cdot\cdot\mathrm{A})/\mathrm{\AA}$	D–H· · · A/°
CoCN-1				
O(9)-H(52)···N(4)	0.84	2.21	2.973(14)	152
Codbm-1				
O(3)-H(24)···O(1)	0.84	2.08	2.881(4)	158
$O(4)-H(31)\cdots N(3)$	0.84	2.01	2.810(5)	159

Table 3. Hydrogen bond lengths/Å and angles/° for CoCN-1 and Codbm-1.

3.3. Preparation and crystal structure of Codbm-1

The use of $[Co(dbm)_2]$ as a building block was also examined for a comparison with $[Co(CNacac)_2]$. $[Co(dbm)_2(H_2O)_2]$ was dissolved in a mixed solution of methanol and chloroform. To this solution, chloroform-methanol mixed solutions of L1 and L2 were added, respectively. No crystalline compound has been obtained for L1. In contrast, for L2, pink crystals of $[Co(dbm)_2](L2) \cdot 4(CH_3OH)$ (Codbm-1) were obtained after leaving the solution at ambient temperature for a week. Figure 3 shows the crystal structure of Codbm-1, where $[Co(dbm)_2]$ and L2 are a linear building block and a bidentate ligand,



Figure 2. (a) The crystal structure of **CoCN-2** is shown along the *a* axis. The packing of tetrachloroethane molecules were drawn with space-filling model, while host framework was drawn by stick model. (b) ORTEP representation with ellipsoids drawn at 50% probability level and (c) space-filling representation of the repeating unit. (Symmetry code; II: 1 - x, 1 - y, -z).

CoCN-1	CoCN-2	Codbm-1
Co(1)–O(2) 2.025(4)	Co(1)–O(1) 2.045(4)	Co(1)–O(1) 2.061(2)
Co(1)-O(1) 2.028(3)	Co(1)-O(2) 2.051(4)	Co(1)-O(2) 2.034(2)
Co(1)-O(3) 2.046(3)	Co(2)-O(3) 2.059(4)	Co(1)-N(1) 2.169(3)
Co(1) - O(4) 2.032(3)	Co(2) - O(4) 2.048(4)	
Co(1)-N(5) 2.171(3)	Co(1)-N(2) 2.232(5)	
Co(1)-N(10) 2.169(3)	Co(2)–N(4) 2.149(5)	
Co(2)-O(5) 2.030(3)		
Co(2)-O(6) 2.052(3)		
Co(2)-O(7) 2.054(3)		
Co(2)-O(8) 2.038(3)		
Co(2)-N(7) 2.136(3)		
Co(2)-N(9) 2.159(3)		

Table 4. Selected bond distances/Å in CoCN-1, CoCN-2, and Codbm-1.

respectively. Two pyridyl moieties at diagonal positions in L2 coordinate to axial sites of $[Co(dbm)_2]$. As a result, a 1-D zigzag chain structure is formed. In the asymmetric unit of this crystal, there are two methanols. One forms hydrogen bonds with non-coordinating pyridyl, while another one forms hydrogen bond with O of acac. The distance and angle of the hydrogen bonds are summarized in table 3. The 1-D chains further stack along the *a* axis through weak interactions between pyridyl planes of L2 (table 4).

In our previous study, we compared $[Co(acac)_2]$ and $[Co(CNacac)_2]$ as building blocks with different Lewis acidity [8(a)]. When they were linked with tridentate ligands, their difference was clearly observed in the bond length between cobalt and nitrogen at the axial site. $[Co(acac)_2]$, in which its metal center has lower Lewis acidity as compared to [Co $(CNacac)_2]$ with electron-withdrawing cyano, which has a longer Co-N distance. Co^{II} in **Codbm-1** is six-coordinate by four oxygens of two dbm and two nitrogens of L2 at axial positions. Co-O distances (2.034(2) and 2.061 Å) and Co-N distance (2.169 Å) were observed in **Codbm-1** are comparable with those observed in **CoCN-1** and **CoCN-2**. The result indicates that metal center in $[Co(dbm)_2]$ has Lewis acidity almost equivalent to that of $[Co(CNacac)_2]$. Steric hindrance between the four phenyl rings in $[Co(dbm)_2]$ and



Figure 3. (a) Crystal structure of **Codbm-1** viewed from the *a* axis and (b) ORTEP representation of the repeating unit in the 1-D chain with ellipsoids drawn at 50% probability level (symmetry code; III: 1 - x, 1 - y, 1 - z).

oligopyridine is probably the reason why L2 does not function as a tetradentate ligand in combination with $[Co(dbm)_2]$.

4. Conclusions

Three coordination polymers (CoCN-1, CoCN-2, and Codbm-1) were synthesized using $[Co(CNacac)_2]$ and $[Co(dbm)_2]$ as linear building blocks in combinations with oligopyridines (L1 and L2). Both CoCN-1 and CoCN-2 have 2-D (4,4) net structures formed by the alternate linkage of $[Co(CNacac)_2]$ and tetradentate oligopyridines. In contrast, L2 is bidentate in Codbm-1, in which a 1-D chain structure is formed. The four bulky phenyl rings in $[Co(dbm)_2]$ present L2 as a tetradentate ligand. These results indicate the usability of $[Co(CNacac)_2]$ as a linear building block with moderate Lewis acidity and less-hindered structure.

Supplementary material

Crystallographic data for the structural analyses have been deposited to the Cambridge Crystallographic Data Center, CCDC Nos. 912488–912490. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: b44–1223-336033; Email: deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk).

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