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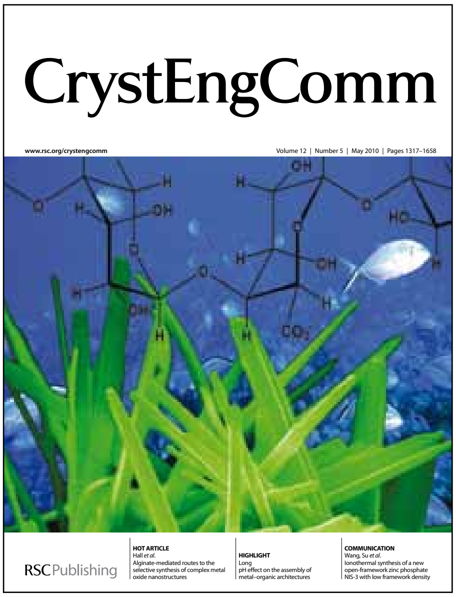

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An unusual cobalt(II)-based single-walled metal–organic nanotube

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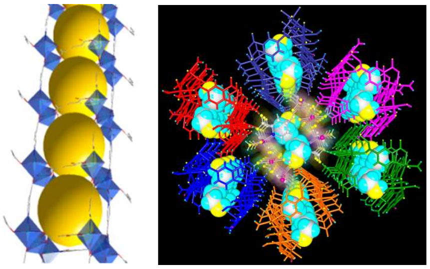

Self-adaption to the formation of an unusual cobalt(II)-based single-walled metal–organic nanotube is reported. In addition, a pseudo-merohedral twinning problem encountered in the X-ray diffraction analysis was solved, which significantly improves the crystallographic results.

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PAPER

An unusual cobalt(II)-based single-walled metal–organic nanotube

Tien-Wen Tseng,*[a] Tzuoo-Tsair Luo,[b] Chong-Cheng Su,[a,b] Hui-Huan Hsu,[a,b] Chen-I Yang*[c] and Kuang-Lieh Lu*[b]

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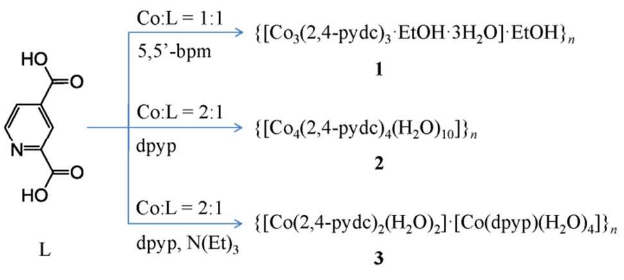
Three rare Co(II)–organic frameworks were synthesized by tuning the relative reactant ratios of Co^{II}:2,4-H_2pydc (2,4-H_2pydc = 2,4-pyridinedicarboxylic acid) and introducing different structure-directing amines under hydrothermal conditions. Compound $\{[Co_3(2,4\text{-pydc})_3(EtOH)(H_2O)_3]\cdot EtOH\}_n$ (**1**), which was prepared using a 1:1 ratio of Co^{II}:2,4-H_2pydc, consisted of a tricobalt(II) cluster that was employed to form a two-side-open box and these boxes were further self-assembled into a rare single-walled metal–organic nanotube (MONT). When the ratio was adjusted to 2:1 and accompanied with 4,4'-dipyridylpiperazine (dpyp), the formation of zigzag chains of $\{[Co_4(2,4\text{-pydc})_4(H_2O)_{10}]\}_n$ (**2**) with a tetracobalt(II) cluster unit occurred, finally these chains were linked into a 2D sheet with a 4^4-**sql** topology. However, compound $\{[Co(2,4\text{-pydc})_2(H_2O)_2]\cdot[Co(dpyp)(H_2O)_4]\}_n$ (**3**) was synthesized under similar reaction conditions as for **2** except that triethylamine was added. **3** contained the polymeric chains of $\{[Co(dpyp)\cdot(H_2O)_4]^{2+}\}_n$ and the monocobalt complex $[Co(2,4\text{-pydc})_2(H_2O)_2]^-$, which were cooperatively connected via hydrogen bondings to form a 2D layer with a 4^4-**sql** topology. A pseudo-merohedral twinning law was applied to the twin case during the X-ray structural analysis of **2** that facilitated the R_1 value dropped drastically.

Introduction

Seeking intriguing structures, unique topologies, exploring self-adaptation processes, and solving subtle X-ray crystallographic problems have attracted great deal of attention in crystal engineering, from the standpoint of potential applications of these new innovative materials.[1] Conceptually, even in a simple or well-known synthesis system, if metal centers[2] and molecular building blocks are judiciously selected,[3–6] it is possible to prepare many more functional materials. Thanks to effective design and synthesis strategies, in particular, the development of metal–organic nanotubes (MONTs) is of particular interest, because these materials are amenable to structural engineering and they have distinguishing properties.[6–7] On the other hand, a number of complex manipulations have been performed in using distinct chemical templates, such as a molecule or an ionic species, to act as effective and direct stimuli for the formation of the final structures.[8] Organic amines with easily selected functional structures can be designed to be critical stimuli to trigger specific self-adaptation processes, such as the self-assembly of a unique MONT that is currently intriguing and rare.[9]

As part of our ongoing efforts in the exploration of functional crystalline materials,[2f,6f,6g,10] herein, we report on the preparation of three Co(II)–organic frameworks: $\{[Co_3(2,4\text{-pydc})_3(EtOH)\cdot(H_2O)_3]\cdot EtOH\}_n$ (**1**, 2,4-$pydc^{2-}$ = 2,4-pyridinedicarboxylate), $\{[Co_4(2,4\text{-pydc})_4(H_2O)_{10}]\}_n$ (**2**), and $\{[Co(2,4\text{-pydc})_2(H_2O)_2]\cdot[Co(dpyp)\cdot(H_2O)_4]\}_n$ (**3**, dpyp = 4,4'-dipyridylpiperazine) that were formed in distinct self-adaptation processes by adjusting the molar ratios of Co^{II}:2,4-H_2pydc and the selected amines (Scheme 1). Compound **1** consisted of a tricobalt(II) cluster that was further assembled into a rare single-walled metal–organic nanotube. Compared to other MOFs containing pyridinedicarboxylate derivatives,[11–16] surprisingly, the systematic use of the 2,4-H_2pydc ligand to form metal–organic frameworks has not yet been fully explored.[16] In addition, a pseudo-merohedral twinning problem encountered in the X-ray diffraction analysis of **2** was solved, which significantly improves the crystallographic analysis results.

Scheme 1. Systematic synthesis strategies for compounds **1–3**



Experimental Section

Materials and general methods

All reagents were purchased commercially and used as received without further purification. The thermogravimetric analysis (TGA) was performed under nitrogen with a Perkin-Elmer Pyris 6 analyzer. The IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets on a Perkin-Elmer Paragon 1000 spectrometer. Elemental analyses were determined by a Perkin-Elmer 2400 elemental analyzer. The powder X-ray diffraction patterns (PXRD) were carried out on a MPD Philips Analytical diffractometer at 40 kV, 30 mA for Cu K_α ($\lambda = 1.5406$ Å). The solid-state photoluminescence was recorded on a Hitachi F4500 spectrometer. Using powder samples, magnetic susceptibility data were collected in the temperature range of 1.8–300 K with a MPMS XL-7 SQUID magnetometer.

Synthesis of $\{[Co_3(2,4\text{-pydc})_3(EtOH)(H_2O)_3]\cdot EtOH\}_n$ (1)

The ligand 2,4-H_2pydc (33.5 mg, 0.20 mmol), 5,5'-bipyrimidine (12.2 mg, 0.10 mmol), and cobalt(II) chloride hexahydrate (48.0 mg, 0.20 mmol) were dissolved in 10.0 mL ethanol solution (water:ethanol = 1:1). The mixture was placed in a 23.0 mL Teflon-lined Parr acid digestion autoclave and heated at 140 °C for 72 h. After slowly cooling down to room temperature, the red crystals of **1** were isolated by filtration, washed with water and ethanol, and dried in air. Yield: 24.2% (13.2 mg, 0.016 mmol) based on Co^{II}. Elemental anal. Calcd for $C_{25}H_{27}N_3O_{17}Co_3$: C, 35.77; H, 2.74; N, 5.44%. Found: C, 35.56; H, 3.04; N, 4.92%. IR data (KBr, cm^{-1}): 3387(s), 3241(s), 2968(w), 1667(s), 1611(s), 1555(m), 1481(w), 1388(s), 1333(m), 1247(w), 1193(w), 1085(w), 1049(w), 1022(w), 882(w), 829(w), 782(w), 731(m), 704(w), 686(w).

Synthesis of $\{[Co_4(2,4\text{-pydc})_4(H_2O)_{10}]\}_n$ (2)

The ligand 2,4-H_2pydc (16.9 mg, 0.101 mmol), 4,4'-dipyridylpiperazine (24.1 mg, 0.101 mmol), and cobalt(II) nitrate hexahydrate (58.3 mg, 0.20 mmol) were dissolved in 10.0 mL of ethanol solution (water:ethanol = 1:1). The mixture was placed in a 23.0 mL Teflon-lined Parr acid digestion autoclave and heated at 120 °C for 72 h. After slowly cooling down to room temperature at a rate 1.88 °C/h. The orange crystals of **2** were isolated by filtration, washed with water and ethanol, and dried in air. Yield: 72.1% (19.6 mg, 0.018 mmol) based on the L ligand. Elemental anal. Calcd for $C_{28}H_{32}N_4O_{26}Co_4$: C, 31.25; H, 3.00; N, 5.21%. Found: C, 31.21; H, 2.98; N 5.27%. IR data (KBr, cm^{-1}): 3449(s), 3068(w), 2970(w), 1637(s), 1605(s), 1552(m), 1475(m), 1450(m), 1396(s), 1257(w), 1097(w), 1019(w), 783(m), 732(s), 700(m).

Synthesis of $\{[Co(2,4\text{-pydc})_2(H_2O)_2]\cdot[Co(dpyp)(H_2O)_4]\}_n$ (3)

The ligand 2,4-H_2pydc (16.9 mg, 0.101 mmol), 3.0 mL ethanol, 0.1 mL triethylamine, dpyp (4,4'-dipyridylpiperazine, 24.0 mg, 0.10 mmol), cobalt(II) nitrate hexahydrate (58.3 mg, 0.20 mmol) were dissolved in 7.0 mL ethanol solution (water:ethanol = 1:1). The mixture was placed in a 23.0 mL Teflon-lined Parr autoclave and heated at 120 °C for 72 h. The orange crystals of **3** were isolated by filtration, washed with water and ethanol, and dried in air. Yield: 57.2% (22.8 mg, 0.029 mmol) based on the L ligand. Elemental anal. Calcd for $C_{28}H_{34}N_6O_{14}Co_2$: C, 42.22; H, 4.30; N, 10.55%. Found: C, 42.59; H, 4.39; N 10.55%. IR data (KBr, cm^{-1}): 3339(s), 1608(s), 1552(m), 1519(m), 1434(w), 1401(m), 1377(m), 1364(s), 1236(s), 1086(w), 1071(w), 1006(s), 821(m), 775(m), 731(m).

Table 1. Summary of crystal data and structure refinement for **1–3**

compound	**1**	**2**	**3**
empirical formula	$C_{25}H_{27}N_3O_{17}Co_3$	$C_{28}H_{32}N_4O_{26}Co_4$	$C_{28}H_{34}N_6O_{14}Co_2$
M_w	818.29	1076.3	796.47
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$	$C2/c$
a (Å)	9.1893(3)	19.0317(8)	16.4253(4)
b (Å)	26.0295(8)	7.4124(4)	15.1866(4)
c (Å)	12.8033(4)	26.326(1)	12.6499(3)
α (deg)	90	90	90
β (deg)	93.311(1)	90.092(2)	101.602(1)
γ (deg)	90	90	90
V (Å^3)	3057.35(17)	3713.8(3)	3090.98(13)
Z	4	4	4
T (K)	200(2)	200(2)	200(2)
λ (Å)	0.71073	0.71073	0.71073
D_{calc} ($g\cdot cm^{-3}$)	1.778	1.925	1.712
μ (mm^{-1})	1.694	1.864	1.156
F_{000}	1660	2176	1640
no. reflections collected	20715	25321	12330
no. of unique reflections [R(int)]	5391(0.0251)	6351(0.0485)	3151(0.0209)
GOF	1.105	1.037	0.997
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0271	0.0272	0.0361
$wR_2{}^b$ ($I > 2\sigma(I)$)	0.06661	0.0671	0.0908
$R_1{}^a$ (all data)	0.0334	0.0283	0.0399
$wR_2{}^b$ (all data)	0.0790	0.0680	0.0935

$^aR_1(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $^bwR_2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Crystal structure determination

Single-crystal X-ray diffraction data were collected using a Nonius Kappa CCD diffractometer, equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). All of the structures were solved using direct methods. All hydrogen atoms of the ligands were placed in the calculated positions with isotropic thermal parameters and were included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELX-97 program package.[17] In particular, the included ethanol molecules within compound **1** were disordered and compound **2** represents a noteworthy example of pseudo-merohedral twinning in a monoclinic (β = 90.092°) structure. Crystal data and structure refinement data for **1–3** are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Results and discussion

Synthesis of compounds 1–3

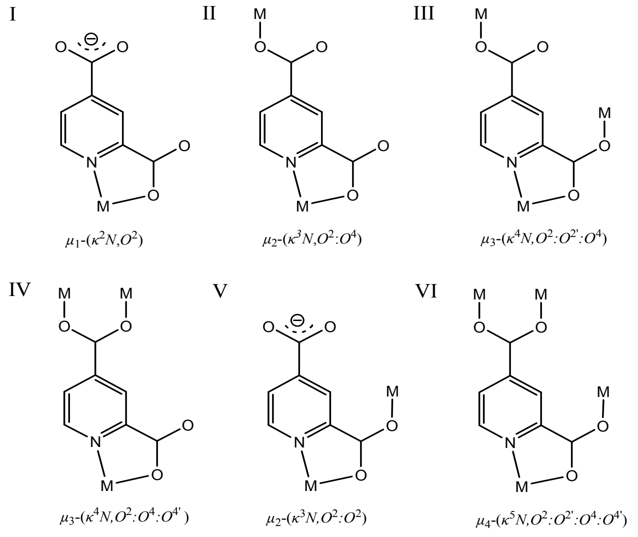
The ligand 2,4-pyridinedicarboxylic acid (2,4-H_2pydc) possesses versatile multidentate nature (Chart 1), the 2,4-H_2pydc ligand appears to be an ideal building unit for elucidating the correlations between molecular topology and structure-directing amines. As illustrated in Scheme 1, in this work, the molar

Table 2. Selected bond lengths [Å] and angles [°] for **1–3**^{a}

1			
Co(1)-O(1)	2.074(2)	Co(2)-O(14)	2.112(2)
Co(1)-O(13)	2.066(2)	Co(3)-N(3)#1	2.119(2)
Co(1)-N(1)	2.119(2)	Co(3)-O(15)	2.074(2)
Co(1)-O(30)	2.081(2)	O(13)-Co(1)-N(1)	97.65(8)
O(1)-Co(1)-O(5)	89.52(7)	O(6)-Co(2)-O(9)	84.30(7)
O(6)-Co(2)-O(14)	171.55(8)	O(12)#1-Co(2)-O(9)	90.51(7)
O(15)-Co(3)-N(3)#1	87.09(9)	O(10)-Co(3)-O(15)	92.72(8)
O(10)-Co(3)-N(3)#1	175.92(8)		
2			
Co(1)-O(1)	2.091(2)	Co(2)-O(20)	2.035(3)
Co(1)-O(19)	2.131(2)	Co(2)-O(21)	2.041(3)
Co(1)-O(17)	2.083(2)	Co(2)-O(6)#1	2.125(2)
Co(1)-O(18)	2.097(2)	Co(2)-N(2)	2.146(2)
Co(2)-O(7)	2.147(2)	Co(4)-O(26)	2.022(2)
Co(3)-O(9)	2.027(2)	Co(4)-O(25)	2.038(2)
Co(3)-O(22)	2.099(2)	Co(4)-O(11)	2.146(2)
Co(3)-O(24)	2.140(2)	Co(4)-O(15)	2.163(2)
O(5)#1-Co(1)-O(17)	88.99(9)	O(7)-Co(3)-O(1)	101.78(8)
O(5)#1-Co(1)-N(1)	178.4(1)	O(9)-Co(3)-N(3)	176.9(1)
O(17)-Co(1)-N(1)	89.94(9)	O(22)-Co(3)-O(24)	88.37(9)
O(20)-Co(2)-N(2)	92.98(11)	O(26)-Co(4)-N(4)	88.7(1)
O(21)-Co(2)-O(1)	87.94(9)	O(25)-Co(4)-O(15)	95.74(9)
3			
Co(1)-O(1)	2.091(2)	N(1)#1-Co(1)-O(1)	101.20(7)
Co(1)-O(5)	2.082(2)	N(1)#1-Co(1)-N(1)	179.43(11)
Co(1)-O(6)	2.075(3)	O(5)-Co(1)-O(1)	89.93(5)
Co(1)-N(1)	2.083(2)	O(8)#2-Co(2)-O(7)	89.18(7)
Co(2)-O(7)	2.151(2)	O(8)-Co(2)-N(2A)	91.19(10)
Co(2)-O(8)	2.078(2)	O(8)#2-Co(2)-O(7)#2	90.82(7)
Co(2)-N(2B)	2.191(2)	O(8)#2-Co(2)-N(2A)	88.81(10)
O(5)-Co(1)-N(1)	89.72(5)	O(7)#2-Co(2)-N(2A)	88.84(9)
O(6)-Co(1)-O(1)	90.07(5)	O(7)-Co(2)-N(2A)	91.16(9)
N(1)-Co(1)-O(1)	78.80(7)	O(7)#2-Co(2)-N(2B)	88.57(9)

^{a}Symmetry transformations used to generate equivalent atoms: for **1**: #1 x-1, y, z; for **2**: #1 x, -y+1/2, z+1/2; for **3**: #1 -x+1, y, - z+3/2; #2 -x+3/2, -y+1/2, -z+1.

Chart 1. The available coordination modes for the 2,4-pydc^{2-} ligand



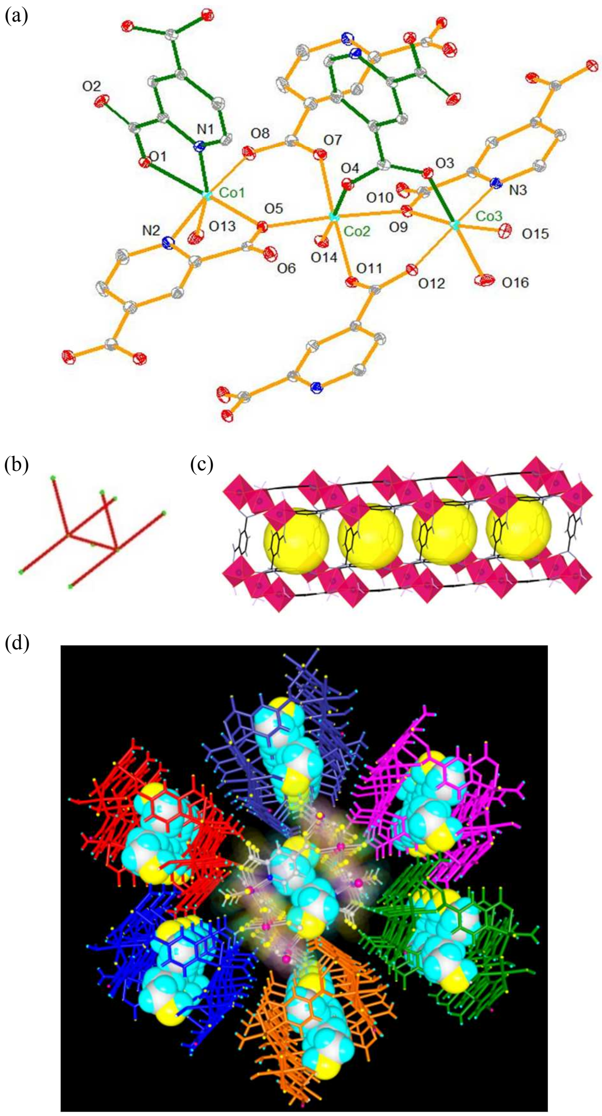


Figure 1. (a) ORTEP drawing of **1**. (b) The slider-like building unit. (c) The extended nanotube. (d) Packing arrays of the nanotubes along the *a* axis (the trapped ethanol molecules were highlighted).

ratios of Co^{II}:2,4-H$_2$pydc and different amines were fine tunned to study the corresponding structural self-adaptation. When the molar ratio of Co(II):2,4-H$_2$pydc was 1:1, in the presence of 5,5'-bipyrimidine amine (5,5'-bpm), compound **1** was exclusively formed. However, if the ratio was changed to 2:1 and 4,4'-dipyridylpiperazine (dpyp) was used, compound **2** was formed, which is comprised of a tetracobalt unit. Compound **3** was only obtained under reaction conditions similar to that for **2**, except that an additional amine N(Et)$_3$ was added, which acted as an organic base.

Description of the crystal structures

Crystal structure of 1

Compound **1** crystallized in the monoclinic space group $P2_1/c$ and consisted of a tricobalt(II) cluster unit with three types of coordination environments for the Co^{2+} ions (Fig. 1). Co1 is coordinated to an oxygen atom (O8) from the 2,4-pydc^{2-} ligand, two pairs of chelated atoms (N2, O5; N1, O1) from another two 2,4-pydc^{2-} ligands, and a coordinated water molecule. The Co2 atom is surrounded by three 2,4-pydc^{2-} ligands (O4, O7, and O11) in a μ_2- *syn*-η^2-bidentated manner, and two chelated 2,4-pydc^{2-} ligands (O5 and O9), and one coordinated water molecule (O14). The Co3 is coordinated by a pair of chelated atoms atoms (N3 and O9) from a 2,4-pydc^{2-} ligand, two oxygen atoms (O3 and O12), an ethanol (O16), and a water molecule (O15). Each cobalt center is coordinated by a water molecule, and the Co–O bond lengths fall in the range of 2.072(2)–2.110(2) Å. The positions of the carbon atoms for the coordinated ethanol molecules are drastically disordered. Each 2,4-pydc^{2-} ligand is bridged to four cobalt(II) (mode VI). It is interesting that this trinuclear cluster $[Co_3(2,4\text{-pydc})_3(EtOH)(H_2O)_3]$ is assembled into a slider form adopting a six-connected nod (Fig. 1b). Empolying these slider unit to form a two-side-open box that acts as a secondary building unit (SBU). The dimension of the box is estimated to be 7.2 × 9.1 × 9.2 Å^3 (Fig. S8 in the ESI†). These box are futher extented into a single-walled nanotubular MOF (Fig. 1c). It is interesting that there are two open windows located on two sides, which are vertical to each box of column (Fig. 1d). Furthermore, the cross-section sizes (considering the van der Waals radii of atoms) of two open windows on two sides of **1** were estimated in 6.0 × 7.1 Å^2.

Finally, these single-walled metal–organic nanotubes (MONTs) are regularly held together in an analogous way to a packet of straws, leading to 3D framework with unique nanotubular arrays (Fig. 1e). Each stacked column is separated by 9.9 Å, estimating by a distance of Co⋯Co between adjacent columns. Interestingly, each cavity of the nanotubes trapped one ethanol molecule inside. To the best of our knowledge, this single-walled MONT of **1**, which is constructed from a specific two-side-open box unit, is reported for the first time.

Crystal structure of 2

Compound **2** crystallized in the monoclinic space group $P2_1/c$, and possessed a zigzag chain involving $[Co_4(2,4\text{-pydc})_4(H_2O)_{10}]$ as the building unit (Fig. 2a). There are four kinds of coordination environments for the Co^{II} ions. The Co1 atom is coordinated by a chelated pydc^{2-} ligand (atoms N1 and O1), another 2,4-pydc^{2-} ligand (O15), and is completed by three coordinated water molecules (O17, O18, O25). The Co2 center is surrounded by three pydc^{2-} ligands and is completed by two coordinated water molecules (O19, O20). The separation of Co1⋯Co2 is 3.743(6) Å, and that of Co3⋯Co4 is 3.726(6) Å, respectively. It should be noted that the 2,4-pydc^{2-} ligand of **2** displays two kinds of coordination modes. First, it exhibits a μ_3-($\kappa^4N,O^2{:}O^4{:}O^{4'}$) fashion (mode IV) that is bridged to three Co^{II} ions, whereas the second is the μ_2-($\kappa^3N,O^2{:}O^2$) mode (mode V). The uncoordinated carboxylates from the 2,4-pydc^{2-} ligands are located bilateral with respect to the chain (Fig. 2). These zigzag chains are hydrogen-bonded together (Fig. S4, Table S2 in the ESI†), resulting in the formation a 2D layer with a 4^4-**sql** topology (Fig. 2c). Finally, these adjacent layers are further hydrogen-bonded in an ABAB manner, extending to a 3D structure (Fig. S5 in the ESI†).

It should be noted that compound **2** represents a noteworthy example of pseudo-merohedral twinning of a monoclinic structure. Pseudo-merohedral twinning can occur if the cell constant from a specimen imitates a higher crystal system, but this was not systematically observed in all the synthesized crystals. A monoclinic with a β near 90º could imitate an orthorhombic structure. Before the twinning problem was overcome, the value of R$_1$ was very high (0.2367). However, when it was treated by a suitable twin law (TWIN –1 0 0 0 –1 0 0 0 1),[18] the resulting value of R$_1$ suddenly dropped to 0.0273 (the twin weight of each component is 47.6% and 52.4%).

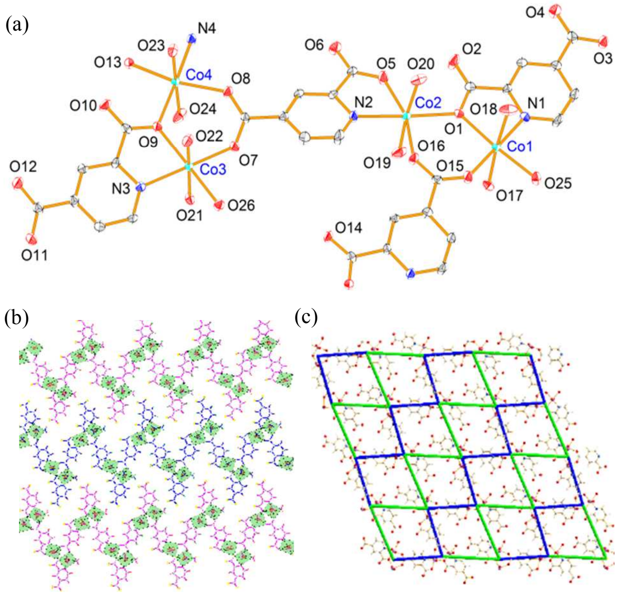


Fig. 2 Structures of **2**: (a) ORTEP drawing (50% probability ellipsoids); (b) zigzag chains of $\{[Co_4(2,4\text{-pydc})_4(H_2O)_{10}]\}_n$ are stacked into a layer; (c) a simplified representation for a 2D layer with a 4^4-**sql** topology.

Crystal structure of 3

Compound **3** crystallized in the monoclinic space group $C2/c$, and consisted of the cationic $[Co(dpyp)(H_2O)_4]^{2+}$ and the anionic complex $[Co(2,4\text{-pydc})_2(H_2O)_2]^{2-}$ (Fig. 3a). Two 2,4-pydc^{2-} ligands are chelated to the Co1 center in a trans form and display a coordination mode of μ_1-(κ^2N,O^2) (mode I). The discrete complex $[Co(2,4\text{-pydc})_2(H_2O)_2]^{2-}$ possesses two uncoordinated carboxylate moieties and the C–O (C7–O3 and C7–O4) bond distances are found as 1.244(3) Å and 1.257(3) Å, respectively. This result was also verified by IR spectra, showing strong peak at 1608 cm^{-1} (Fig. S24 in the ESI†). Two coordinated water molecules (O5, O6) of the Co1 atom are located vertically out of the skeleton. The Co2 center is coordinated to two bridging 4,4'-dipyridylpiperazine (dpyp) ligands in a trans fashion, and is completed by four water molecules. It is interesting to note that the Co^{2+} ion and the dpyp ligand are assembled into a cationic coordination polymeric chain with a formula of $\{[Co(dpyp)(H_2O)_4]^{2+}\}_n$. The bond length of Co–N is, on average, 2.082(2) Å, and the Co–O bond lengths fall in a range of 2.091(2) to 2.075(3) Å. The neighbouring coordination polymers are stacked with an angle of 93.3° (Fig. S9 in the ESI†). Each rectangular void of the 2D layer, contains two $[Co(2,4\text{-pydc})_2(H_2O)_2]^{2-}$ as the guests. The

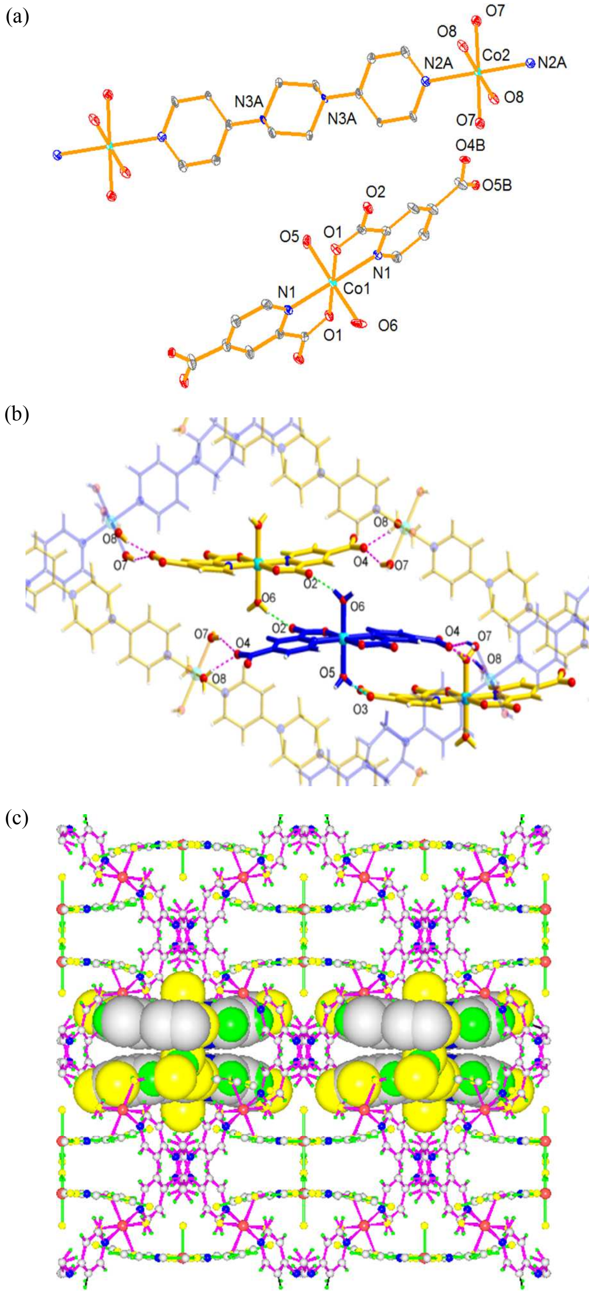


Fig. 3 (a) ORTEP drawing (50% probability ellipsoids) of **3**. (b) Showing a grid-type 2D network is linked by hydrogen bonding. (c) A 3D packing view in a space-filling model along the *c* axis.

hydrogen bonds are linked between two terminal carboxylates (O4) of the guest complex and the coordinated water (O7, O8) of host (Fig. 3b, O8–H8⋯O4 is 2.642(3) Å). In addition, two entrapped species are also hydrogen-bonded to each other via the carboxylate group (O2) and the coordinated water (O6, Table S3 in the ESI†). Finally, these layers are regularly stacked into a 3D framework (Fig. 3c).

It is interesting that these variable MOFs were synthesized using the optimized control of the reaction temperature, solvent, pH, and reactant stoichiometry.[19–21] In this work, it is found that the accompanying organic 5,5'-bipyrimidine (5,5'-bpm) did not coordinate to the Co^{II} center. It is noteworthy that, while in the absence of 5,5'-bpm, a similar reaction produced different compounds, namely, {[Co_3(2,4-pydc)$_2$(μ_3-OH)$_2$]·5H_2O}$_n$ and {[Co_3(2,4-pydc)$_2$(μ_3-OH)$_2$(H_2O)]·7H_2O}$_n$, as reported in the literature.[16c] Hence, it would appear that the 5,5'-bpm functions as a base to deprotonate the 2,4-H_2pydc ligand and may play a crucial role in the assembly of **1** via hydrogen bonding interactions.

The results showed that the organic 4,4'-dipyridylpiperazine (dpyp) did not coordinate to the Co^{II} center of **2**. Here, it appears that that the dpyp ligand acted as a base to deprotonate 2,4-H_2pydc species and then served as a template for the formation of **2**, which consisted of the tetranuclear unit. However, when a similiar reaction was utilized in preparing **3**, the triethylamine is likely a stronger base than the 4,4'-dipyridylpiperazine (dpyp) amine and effectively deprotonates the 2,4-H_2pydc species, leading to the dpyp ligand to participate in the assembly of the 1D polymer of [Co(dpyp)(H_2O)$_4$]$_n$. In addition, during the formation of **3**, the included [Co(2,4-pydc)$_2$(H_2O)$_2$]$^{2-}$ acts as a template to direct the structure. Hence, the effect of pH value of the media appears to have a crucial influence on the crystallization of different crystal architectures under the same hydrothermal synthesis conditions.

Upon the self-adaption process, the unique tricobalt(II) cluster was formed and further extended by the 2,4-pydc^{2-} ligand, leading to the formation of an individual metal–organic nanotube of **1**. In addition, **2** comprised of a tetracobalt(II) unit, which was finally hydrogen-bonded into a layered structure. On the other hand, compound **3** contained two types of monocobalt(II) units with a discrete anion of [Co(2,4-pydc)$_2$(H_2O)$_2$]$^{2-}$ and a cationic 1D chain of [Co(dpyp)(H_2O)$_4$]$^{2+}{}_n$.

Compound **1** adopted the mode VI, μ_4-(κ^4N,O^2:$O^{2'}$:O^4:$O^{4'}$), whereas the modes μ_3-(κ^4N,O^2:O^4:$O^{4'}$) (mode IV) and μ_2-(κ^3N,O^2:O^2) (mode V) were used in compound **2**. However, mode I, μ_1-(κ^2N,O^2) was preferred by compound **3**. Hence, the coordination modes of the 2,4-pydc^{2-} ligand and the resulting structures are cooperatively influenced by the molar ratios of Co^{2+}: 2,4-H_2pydc and the accompanying amines.

Thermogravimetric and powder X-ray diffraction analyses

A thermogravimetric analysis (TGA) of **1** revealed a weight loss of 17.15% (calculated at 16.86%) in the range of 80–200 °C, which can be attributed to the loss of coordinated water and ethanol, and included ethanol molecules (Fig. S13 in the ESI†). After the loss of the water molecules, no further weight loss occurred, up to 400 °C. The material began to decompose with a continuous weight loss at temperatures over 400 °C, which can be attributed to the loss of the coordinating ligands. The TGA profiles of complexes **2** and **3** (Figs. S14 and S15 in the ESI†) indicated that the water molecules were removed at temperatures below 200 °C. Furthermore, no further significant weight loss occurred at temperatures up to 350 °C, indicating their highly thermal stability. The powder X-ray diffraction (PXRD) patterns were used to check the purity of **1**–**3** (Figs. S16–S18 in the ESI†). The results showed that all peaks in the measured patterns at the room temperature matched closely with the simulated patterns.

Luminescence properties

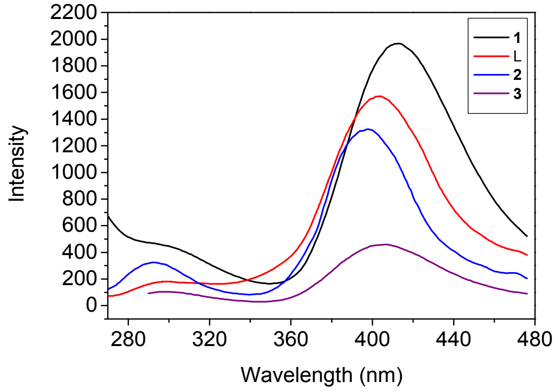


Fig. 4 Comparing the emission spectra of complexes **1**–**3** and the 2,4-H_2pydc (L) ligand in the solid state at room temperature, which were excited at 249 nm.

The luminescent properties of complexes **1**–**3** and organic 2,4-H_2pydc ligand were measured in the solid state at ambient temperature. The maximum emission peaks of **1** appeared at about 415 nm upon photo excitation at 249 nm (Fig. 4). An intense emission of the 2,4-H_2pydc ligand appeared at 403 nm. When the emission of **1** is compared with that of the 2,4-H_2pydc ligand, it shows slightly red-shift. This can be tentatively attributed to the charge transfers arising from the ligand moiety (n to π^* or π to π^*). However, for the 2,4-pydc^{2-} ligand of compounds **2** and **3**, the emission peaks occurred at 398 and 413 nm, respectively.

Magnetic studies of compounds 1 and 2

Variable temperature dependence of magnetic susceptibility of compounds **1** and **2** were measured on powdered samples in the temperature range of 1.8–300 K at a 1.0 kG magnetic field. The magnetic susceptibility of compounds **1** and **2** were very similar at temperatures above 50 K and obeyed the Curie–Weiss law very well (Fig. 5, Fig. S20 in the ESI†). The plot of $\chi_M T$ versus T for **1** is shown in Figure 5. The $\chi_M T$ value of **1** remained constant with decreasing temperature with a value of 10.8 emu K mol^{-1} from 300 to 70 K, but below it the $\chi_M T$ value decreased rapidly to 1.42 emu K mol^{-1} at 1.8 K. The spin-only value at 300 K was 10.8 emu K mol^{-1}, which is consistent with three magnetically isolated high-spin Co(II) atoms with S = 3/2 exhibiting strong spin–orbit coupling.[22] The monotonic decrease in $\chi_M T$ with temperature is characteristic of compound with overall antiferromagnetic interactions and/or spin–orbital coupling within **1**. The magnetic susceptibility data were further examined in a plot of 1/χ_M vs. T (Fig. S19 in the ESI†). The result was well fitted to the Curie–Weiss law, with a Curie constant of 12.3 cm^3 mol^{-1} K and a Weiss constant θ of −48.65.5 K.

The magnetic susceptibility data of **2** were examined in a plot of 1/χ_M vs. T (Fig. S21 in the ESI†). Compound **2** contains two pairs of [Co_2(2,4-pydc)$_2$(H_2O)$_5$] units, but both Co_2 units show simillar bonding paramaters. Thus, the Curie constant and Weiss constant θ of **2**, which only applied one Co_2 unit (Co1 and Co2) for calculation, were 5.89 cm^3 mol^{-1} K and −9.8 K, respectively. The negative θ values for **1** and **2** are also indicative of antiferromagnetic coupling via the 2,4-pydc^{2-} bridging ligands within the Co^{II} centers and/or the spin–orbital contributions.

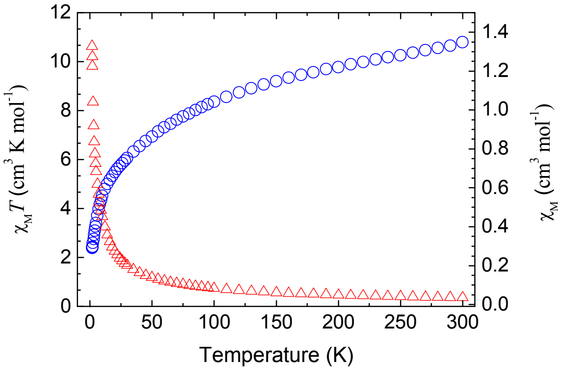


Fig. 5 Plots of $\chi_M T$ vs. T (○) and $\chi_M T$ vs. T (Δ) for a powder sample of complex **1**.

Additionally, taking into account the relationship between the crystal structures of compounds **1** and **2** with their antiferromagnetic interactions, there are two sets of magnetic exchange pathways within the Co_3 and Co_2 units: **1** consists of a *syn-syn* μ_2-carboxylate bridge and **2** is comprised of μ_2-O bridges, in which the Co−O−Co angles were 121.2° and 114.2° for **1**; 123.4° and 123.2° for **2**, respectively. All of them were in the reported range of 100.5−122.9°, where they exhibited the antiferromagnetic interactions.[23] Indeed, the presence of weak antiferromagnetic interactions in **1** and **2** is also possibly dominated through 2,4-pydc^{2-} ligands in the low temperature region.

Conclusions

In conclusion, three Co(II)-2,4-pydc frameworks with mono-, tri-, tetra-cobalt(II) units, respectively, were successfully synthesized via distinct self-adaptation processes that were triggered by adjusting the molar ratios of Co^{II}:2,4-H_2pydc and/or the accompanying amines. An intriguing metal–organic nanotube (MONT) constructed in the form of a two-side-open box unit is currently unprecedented. A suitable pseudo-merohedral twinning law was applied to the twin case that facilitated a drastic decrease in the R_1 value. We believe that the fancier stimulus that is introduced into such similar synthesis systems, the more innovative framework structures may be created.

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References

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[†] Electronic supplementary information (ESI) available: hydrogen bonding, additional figures for the crystal structures and TGA, PXRD, CCDC 961773−961775. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

1 (*a*) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939; (*b*) M. J. Zaworotko, *Nature*, 2008, **451**, 410; (*c*) K. Sanderson, *Nature*, 2007, **448**, 746; (*d*) S. Kitagawa, *Nature*, 2006, **441**, 584; (*e*) J. F. Eubank, H. Mouttaki, A. J. Cairns, Y. Belmabkhout, L. Wojtas, R. Luebke, M. Alkordi and M. Eddaoudi, *J. Am. Chem. Soc*., 2011, **133**, 14204.

2 (*a*) R. S. Forgan, R. A. Smaldone, J. J. Gassensmith, H. Furukawa, D. B. Cordes, Q. W. Li, C. E. Wilmer, Y. Y. Botros, R. Q. Snurr, A. M. Z. Slawin and J. F. Stoddart, *J. Am. Chem. Soc*., 2012, **134**, 406; (*b*) X. P. Zhou, M. Li, J. Liu and D. Li, *J. Am. Chem. Soc*., 2012, **134**, 67; (*c*) S. L. Cai, S. R. Zheng; Z. Z. Wen; J. Fan and W. G. Zhang, *Cryst. Growth Des.*, 2012, **12**, 2355; (*d*) D. Banerjee and J. B. Parise, *Cryst. Growth Des*., 2011, **11**, 4704; (*e*) E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc*., 2010, **132**, 14382; (*f*) T. T. Luo, H. L. Tsai, S. L. Yang, Y. H. Liu, R. D. Yadav, C. C. Su, C. H. Ueng, L. G. Lin and K. L. Lu, *Angew. Chem., Int. Ed*., 2005, **44**, 6063.

3 (*a*) O. K. Farha, C. E. Wilmer, I. Eryazici, B. G. Hauser, P. A. Parilla, K. O'Neill, A. A. Sarjeant, S. B. T. Nguyen, R. Q. Snurr and J. T. Hupp, *J. Am. Chem. Soc*., 2012, **134**, 9860; (*b*) M. C. Das, Q. S. Guo, Y. B. He, J. Kim, C. G. Zhao, K. L. Hong, S. C. Xiang, Z. J. Zhang, K. M. Thomas, R. Krishna and B. L. Chen, *J. Am. Chem. Soc*., 2012, **134**, 8703; (*c*) J. S. Hu, X. Q. Yao, M. D. Zhang, L. Qin, Y. Z. Li, Z. J. Guo, H. G. Zheng and Z. L. Xue, *Cryst. Growth Des*., 2012, **12**, 3426.

4 (*a*) J. R. Li, A. A. Yakovenko, W. G. Lu, D. J. Timmons, W. J. Zhuang, D. Q. Yuan and H. C. Zhou, *J. Am. Chem. Soc*., 2010, **132**, 17599; (*b*) K. Koh, A. G. Wong-Foy and A. Matzger, J. *J. Am. Chem. Soc*., 2010, **132**, 15005; (*c*) S. I. Swamy, J. Bacsa, J. T. A. Jones, K. C. Stylianou, A. Steiner, L. K. Ritchie, T. Hasell, J. A. Gould, A. Laybourn, Y. Z. Khimyak, D. J. Adams, M. J. Rosseinsky and A. I. Cooper, *J. Am. Chem. Soc*., 2010, **132**, 12773.

5 (*a*) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res*., 2005, **38**, 176; (*b*) H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc*., **2008**, *130*, 11650; (*c*) G. Férey, *Chem. Soc. Rev*., 2008, **37**, 191; (*d*) Z. P. Deng, H. L. Qi, L. H. Huo, S. W. Ng, H. Zhao and S. Gao, *Dalton Trans*., 2010, **39**, 10038. (*e*) K. Kim, S. Park, K. M. Park and S. S. Lee, *Cryst. Growth Des*., 2011, **11**, 4059; (*f*) J. Y. Zhang, X. H. Jing, Y. Ma, A. L. Cheng and E. Q. Gao, *Cryst. Growth Des*., 2011, **11**, 3681.

6 (*a*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.,* 2004, **43**, 2334; (*b*) B. Zhao, P. Cheng, X. Y. Chen, C. Cheng, W. Shi, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc*., 2004, **126**, 3012; (*c*) P. S. Lakshminarayanan, E. Suresh and P. Ghosh, *J. Am. Chem. Soc*., 2005, **127**, 13132; (*d*) L. J. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard and O. M. Yaghi, *Science*, 2005, **309**, 1350. (*e*) F. N. Dai, H. Y. He and D. F. Sun, *Inorg. Chem*., 2009, **48**, 4613; (*f*) T. T. Luo, H. C. Wu, Y. C. Jao, S. M. Huang, T. W. Tseng, Y. S. Wen, G. H. Lee, S. M. Peng and K. L. Lu, *Angew. Chem., Int. Ed*., 2009, **48**, 9461; (*g*) J. F. Yin, J. G. Chen, J. T. Lin, D. Bhattacharya, Y. C. Hsu, H. C. Lin, K. C. Ho and K. L. Lu, *Mater. Chem.*, 2012, **22**, 130.

7 (*a*) H. Reinsch, B. Marszałek, J. Wack, J. Senker, B. Gil and N. Stock, *Chem. Commun*., 2012, **48**, 9486; (*b*) T. Panda, T. Kundu and R. Banerjee, *Chem. Commun.*, 2012, **48**, 5464; (*c*) Z. Z. Lu, R. Zhang, Y. Z. Li, Z. J. Guo and H. G. Zheng, *J. Am. Chem. Soc*., 2011, **133**, 4172; (*d*) Y. G. Huang, B. Mu, P. M. Schoenecker, C. G. Carson, J. R. Karra, Y. Cai and K. S. Walton, *Angew. Chem., Int. Ed*., 2011, **50**, 436; (*f*) S. Banerjee, N. N. Adrash and P. Dastidar, *CrystEngComm*, 2013, **15**, 245.

8 (*a*) H. Y. Lin, C. Y. Chin, H. L. Huang, W. Y. Huang, M. J. Sie, L. H. Huang, Y. H. Lee, C. H. Lin, K. H. Li, X. Bu and S. L. Wang, Science, 2013, **339**, 811; (*b*) F. B. L. Cougnon and J. K. M. Sanders, *Acc. Chem. Res*., 2012, **45**, 2211; (*c*) J. Cepeda, G. Beobide, O. Castillo, A. Luque, S. Pérez-Yáñez and P. Román, *Cryst. Growth Des*., 2012, **12**, 1501; (*d*) Z. X. Chen, Y. M. Zhou, L. H. Weng and D. Y. Zhao, *Cryst. Growth Des*., 2008, **8**, 4045; (*e*) A. L. Lu, N. Li, Y. F. Ma, H. B. Song, D. P. Li, N. J. Guan, H. G. Wang and S. H. Xiang, *Cryst. Growth Des*., 2008, **8**, 2377.

9 (*a*) D. K. Unruh, K. Gojdas, A. Libo and T. Z. Forbes, *J. Am. Chem. Soc*., 2013, **135**, 7398; (*b*) D. Sun, Z. H. Yan, V. A. Blatov, L. Wang and D. F. Sun, *Cryst. Growth Des*., 2013, **13**, 1277; (*c*) G. Q. Kong, S. Ou, C. Zou and C. D. Wu, *J. Am. Chem. Soc*., 2012, **134**, 19851; (*d*) C. Fang, Q. K. Liu, J. P. Ma and Y. B. Dong, *Inorg. Chem*., 2012, **51**, 3923; (*e*) J. T. Yu, J. L.Sun, Z. T. Huang and Q. Y. Zheng, *CrystEngComm*, 2012, **14**, 112; (*f*) F, Bu and S. J. Xiao, *CrystEngComm*, 2010, **12**, 3385.

10 (*a*) T. W. Tseng, T. T. Luo, S. Y. Chen, C. C. Su, K. M. Chi and K. L. Lu, *Cryst. Growth Des*., 2013, **13**, 510; (*b*) T. W. Tseng, T. T. Luo, C. C. Tsai, J. Y. Wu, H. L. Tsai and K. L. Lu, *Eur. J. Inorg. Chem*., 2010, 3750.

11 2,3-pydc: (*a*) G. H.; Z. G. Li, H. Q. Jia, N. H. Hu and J. W. Xu, *CrystEngComm*, **2009**, *11*, 292; (*b*) M. Frisch and C. L. Cahill, *Cryst. Growth Des*., 2008, **8**, 2921; (*c*) P. Kanoo, R. Matsuda, R. Kitaura, S. Kitagawa and T. K. Maji, *Inorg. Chem*., 2012, **51**, 9141.

12 2,5-pydc: (*a*) P. Silva, L. Cunha-Silva, N. J. O. Silva, J. Rocha and F. A. A. Paz, *Cryst. Growth Des*., 2013, **13**, 2607; (*b*) A. C. Wibowo, M. D. Smith and H. C. zur Loye, *Cryst. Growth Des*., 2011, **11**, 4449; (*c*) Z. Wang, F. Y. Bai, Y. H. Xing, Y. Xie, M. F. Ge and S. Y. Niu, *Inorg. Chim. Acta*, 2010, **363**, 669; (*d*) P. M. Cantos, M. Frisch and C. L. Cahill, *Inorg. Chem. Commun*., 2010, **13**, 1036; (*e*) P. Mahata, K. V. Ramya and S. Natarajan, *Inorg. Chem*., 2009, **48**, 4942; (*f*) J. W. Ji, G. X. Han and Z. B. Han, *Russ. J. Coord. Chem*., 2009, **35**, 473.

13 2,6-pydc: (*a*) H. Aghabozorg, E. Motieiyan, A. R. Salimi, M. Mirzaei, F. Manteghi, A. Shokrollahi, S. Derki, M. Ghadermazi, S. Sheshmani and H. Eshtiagh-Hosseini, *Polyhedron*, 2010, **29**, 1453; (*b*) X. Feng, J. S. Zhao, L. Y. Wang and X. G. Shi, *Inorg. Chem. Commun*., 2009, **12**, 388.

14 3,4-pydc: (*a*) X. D. Zhu, S. Y. Gao, Y. F. Li, H. X. Yang, G. L. Li, B. Xu and R. Cao, *J. Solid State Chem*., 2009, **182**, 421; (*b*) X. J. Gu and D. F. Xue, *CrystEngComm*, 2007, **9**, 471; (*c*) J. F. Eubank, R. D. Walsh, P. Poddar, H. Srikanth, R. W. Larsen and M. Eddaoudi, *Cryst. Growth Des*., 2006, **6**, 1453.

15 3,5-pydc: (*a*) J. Y. Hu, J. P. Li, J. A. Zhao, H. W. Hou and Y. T. Fan, *Inorg. Chim. Acta*, 2009, **362**, 5023; (*b*) Y. J. Song, X. Chen and Z. B. Han, *Russ. J. Coord. Chem.*, 2009, **35**, 746; (*c*) H. Chun and J. Seo, *Inorg. Chem*., 2009, **48**, 9980; (*d*) Y. L. Lu, J. Y. Wu, M. C. Chan, S. M. Huang, C. S. Lin, T. W. Chiu, Y. H. Liu, Y. S. Wen, C. H. Ueng, T. M. Chin, C. H. Hung and K. L. Lu, *Inorg. Chem.*, 2006, **45**, 2430.

16 2,4-pydc: (*a*) Y. H. Liu, H. P. Fang, P. C. Jhang, C. C. Peng, P. H. Chien, H. C. Yang, Y. C. Huang and Y. L. Lo, *CrystEngComm*, 2010, **12**, 1779; (*b*) G. H. Wang, Z. G. Li, H. Q. Jia, N. H. Hu and J. W. Xu, *Acta Cryst.*, 2009, **E65**, m1568; (*c*) Y. G. Huang, D. Q. Yuan, L. Pan, F. L. Jiang, M. Y. Wu, X. D. Zhang, W. Wei, Q. Gao, J. Y. Lee, J. Li and M. C. Hong, *Inorg. Chem*., 2007, **46**,

9609; (*d)* Z. G. Li, G. H. Wang, H. Q. Jia, N. H. Hu and J. W. Xu, *CrystEngComm*, 2007, **9**, 882; (*e*) E. E. Sileo, A. S. de Araujo, G. Rigotti, O. E. Piro and E. E. Castellano, *J. Mol. Struct.*, 2003, **644**, 67.

17 (*a*) G. M. Sheldrick, *SHELXS-97*, *Programs for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *A Short History of SHELX*, *Acta Cryst*., 2008, **A64**, 112.

18 S. Parsons, *Introduction to twinning*, *Acta Cryst*., 2003, **D59**, 1995.

19 (*a*) S. Hu, Z. S. Meng and M. L. Tong, *Cryst. Growth Des*., 2010, **10**, 1742; (*b*) Z. Su, J. Fan, T. A. Okamura, M. S. Chen, S. S. Chen, W. Y. Sun and N. Ueyama, *Cryst. Growth Des*., 2010, **10**, 1911; (*c*) P. Kar, Y. Ida, T. Ishida and A. Ghosh, *CrystEngComm*, 2013, **15**, 400.

20 (*a*) X. L. Wang, C. Qin, Y. Q. Lan, K. Z. Shao, Z. M. Su and E. B. Wang, *Chem. Commun*., 2009, 410; (*b*) S. Hu, Z. S. Meng and M. L. Tong, *Cryst. Growth Des*., 2010, **10**, 1742; (*c*) J. Chen, Y. L. Feng, Z. G. Jiang and J. W. Cheng, *CrystEngComm*, 2011, **13**, 6071; (*d*) F. Y. Yi and Z. M. Sun, *Cryst. Growth Des*., 2012, **12**, 5693; (*e*) M. Mazaj, T. B. Člič, M. Rangus, V. Kaučič and N. Z. Logar, *Cryst. Growth Des*., 2013, **13**, 3825; (*f*) R. Medishetty, D. Jung, X. K. Song, D. W. Kim, S. S. Lee,M. S. Lah and J. J. Vittal, *Inorg. Chem*., 2013, **52**, 2951.

21 (*a*) J. Q. Liu, Y. Y.Wang, T. Wu and J. Wu, *CrystEngComm*, 2012, **14**, 2906; (*b*) X. G. Guo, W. B. Yang, X. Y. Wu, Q. K. Zhang, L. Lin, R. M. Yu and C. Z. Lu, *CrystEngComm*, 2013, **15**, 3654.

22 O. Kahn, *Molecular Magnetism*; VCH: Weinheim, Germany, New York, 1993.

23 (*a*) P. Lama, J. Mrozinsk and P. K. Bharadwa, *Cryst. Growth Des*., 2012, **12**, 3159; (*b*) O.Fabelo, J. Pasán, L. Cañadillas-Delgado, F. S. Delgado, F. Lloret, M. Julve, C. Ruiz-Pérez, *Inorg. Chem.*, 2008, **47**, 8053; (*c*) L. Cañadillas-Delgado, O. Fabelo, J. Pasán, F. S. Delgado, F. Lloret, M. Julve, C. Ruiz-Pérez, *Inorg. Chem.*, 2007, **46**, 7458.