



Supramolecular assemblies of copper(II)–pyridine-2,3-dicarboxylate complexes with *N*-donor ligands and clustered water molecules



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ABSTRACT

Four new dinuclear and polynuclear Cu(II)–pyridine-2,3-dicarboxylate complexes with *N*-donor ligands, $[\text{Cu}_2(\mu\text{-pydc})_2(\text{dmim})_4] \cdot 6\text{H}_2\text{O}$ (**1**), $\{[(4\text{-mimH})_2[\text{Cu}(\mu\text{-pydc})_2] \cdot 2\text{H}_2\text{O})_n]\}$ (**2**), $\{[\text{Cu}(\mu\text{-pydc})(\text{eten})] \cdot 2\text{H}_2\text{O}\}_n$ (**3**) and $\{[\text{Cu}(\text{pen})_2\text{Cu}(\mu_3\text{-pydc})_2] \cdot \text{H}_2\text{O}\}_n$ (**4**) (pydcH₂ = pyridine-2,3-dicarboxylic acid, dmim = 1,2-dimethylimidazole, 4-mim = 4-methylimidazole, eten = *N,N*-diethylethylenediamine and pen = 1,3-diaminopropane) have been prepared by utilizing metalloligand approach in a two-stage synthesis and characterized by elemental analysis, FT-IR spectroscopy, thermal analysis and X-ray diffraction techniques. In **1**, the dinuclear units are connected each other by cyclic discrete water tetramers to form a 2D hydrogen bonded supramolecular compound, which are extended into a three-dimensional network by C–H···π interactions. In **2**, the adjacent 1D chains are connected by the water cluster to form a 2D layer structure. The 2D layers of **4** are further extended into 3D supramolecular network by only weak C–H···π interaction.

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1. Introduction

Supramolecular assemblies fabricated from metal ions and bridging ligands have been of great interest owing not only to their structural diversity but also their many properties [1–9]. The design of coordination polymers with structural motif is of current interest in the field of coordination chemistry. In this context, two synthetic approaches which are the secondary building unit [10,11] and the metalloligand emerge [12–19]. During the past decade, the controlled self-assembly of metal complexes containing metalloligands have attracted a great deal of attention because of the resulting supramolecular entities as functional materials.

Non-covalent interactions are responsible for crystal packing and chemical properties, which play an important role in fundamental biological processes [20–22]. Researches have shown that water clusters play the key role in synthesis of supramolecular complexes because of the fact that they exhibit strong hydrogen bonding interactions [23–32]. Furthermore, synthesis and characterization of small water clusters are important to understanding of hydrogen bonding interactions between water molecules in bulk water or ice [32]. In the past decades, small water clusters involving two-, four-, five- and six-membered rings have been characterized both theoretical and experimental study [23–25,27]. Among

the clusters, the cyclic water tetramers are rare due to unfavorable H···H repulsion across the smaller ring. In addition to typical coordination bonds, weak intra- or intermolecular interactions such as hydrogen bonding, C–H···π, π···π stacking interactions often play crucial roles in supramolecular complexes and many biological systems.

Metalloligands can be prepared by means of chelating ligands. 2,3-, 2,4- and 2,5-Pyridinedicarboxylic acids are able to chelating and they are suitable for metalloligand approach [33,34]. This ligand are used to assemble supramolecular networks organized by coordination bonds, hydrogen bonds, π···π and C=O···π stacking interaction [33,35–38]. Among these heterodicarboxylic acid ligands, pyridine-2,3-dicarboxylic acid (pydcH₂) is one of such interesting ligand and deprotonated pyridine-2,3-dicarboxylates (pydcH[−] and pydc^{2−}) are useful tool for constructing supramolecular structures and act as a versatility ligand and coordinate to metal ions as bidentate, tridentate, bridging ligand [34,39–46]. Pydc was less studied than 2,4- and 2,5-pydcH₂ for metalloligand approach because neighboring carboxylate groups are considered as steric hindrance but this problem can be solved with the rotation of carboxylate groups. Furthermore, structural properties of pydc complexes containing protonated cation have been rarely reported to date [42,43].

This work offers four new coordination compounds synthesized in two steps. Complex **1**, **2** and **4** were prepared by ligand exchange, proton transfer and cation exchange reaction of

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Table 1
Crystal data and structure refinement parameters for complexes **1–4**.

	1	2	3	4
Empirical formula	C ₃₄ H ₅₀ Cu ₂ N ₁₀ O ₁₄	C ₂₂ H ₂₄ CuN ₆ O ₁₀	C ₁₃ H ₂₃ CuN ₃ O ₆	C ₁₀ H ₁₅ CuN ₃ O ₅
Formula weight	949.92	596.01	380.88	320.79
T (K)	293 (2)	293 (2)	293 (2)	293 (2)
Wavelength (Å) Mo Kα	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.901 (1)	6.866 (1)	7.3452 (2)	6.5531 (4)
<i>b</i> (Å)	9.989 (1)	8.172 (1)	13.6255 (4)	8.1689 (5)
<i>c</i> (Å)	11.085 (1)	11.354 (2)	16.7375 (5)	12.1297 (7)
α (°)	93.69 (1)	95.23 (1)	90	100.011 (5)
β (°)	102.31 (1)	91.73 (1)	90.770 (2)	103.989 (4)
γ (°)	98.79 (1)	102.11 (1)	90	101.064 (5)
<i>V</i> (Å ³)	1053.2 (2)	619.5 (1)	1674.97 (8)	601.59 (6)
<i>Z</i>	1	1	4	2
Absorption coefficient (mm ⁻¹)	1.09	0.95	1.34	1.84
<i>D</i> _{calc} (Mg m ⁻³)	1.498M	1.598	1.510	1.771
θ (°)	1.89–28.12	2.56–27.48	1.9–26.5	1.8–26.5
Measured reflections	14309	8338	17099	9334
Independent reflections	4366	2563	3466	2492
Absorption correction		integration Stoe XRED		
Refinement method	full-matrix least-squares on <i>F</i> ²			
<i>R</i> _{int}	0.046	0.052	0.043	0.082
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.038	0.031	0.047	0.038
w <i>R</i> (<i>F</i> ²)	0.093	0.081	0.138	0.092
Goodness of fit (GOF) on <i>F</i> ²	1.10	1.05	1.06	1.11
$\Delta\rho_{\max}$ (e Å ⁻³)	0.45	0.28	1.20	0.68
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.30	-0.22	-0.79	-1.23

Table 2
Selected bond distances (Å) and angles (°) for **1**.

Bond lengths (Å)			
Cu1–N1	2.010 (2)	Cu1–N4	1.994 (2)
Cu1–O1	1.967 (2)	Cu1–O3 ⁱ	2.174 (2)
Cu1–N2	1.997 (2)		
Cu1...H12C	2.977 (2)	Cu1...H17A	2.907(2)
Angles (°)			
O1–Cu1–N4	160.40 (8)	N2–Cu1–N1	169.78 (8)
O1–Cu1–N2	92.02 (8)	O1–Cu1–O3 ⁱ	106.85 (8)
N4–Cu1–N2	90.25 (9)	N4–Cu1–O3 ⁱ	92.48 (8)
O1–Cu1–N1	81.10 (7)	N2–Cu1–O3 ⁱ	92.75 (8)
N4–Cu1–N1	93.75 (8)	N1–Cu1–O3 ⁱ	96.47 (8)
C12–H12C...Cu1	111	C12–H12C...Cu1	107
D–H...A			
D–H...A	<i>d</i> (H...A) (Å)	<i>d</i> (D...A) (Å)	\angle (DHA) (°)
O5–H5A...O7 ⁱⁱ	2.01 (2)	2.791 (5)	159 (5)
O5–H5B...O4	2.05 (3)	2.848 (4)	160 (5)
O5–H5B...O3	2.62 (3)	3.332 (3)	145 (5)
O6–H6A...O2	1.99 (3)	2.814 (4)	164 (5)
O6–H6B...O7 ⁱⁱⁱ	2.53 (4)	2.897 (5)	108 (3)
O7–H7B...O6 ^{iv}	2.41 (5)	2.897 (5)	120 (4)
O7–H7A...O5 ⁱ	2.04 (2)	2.804 (5)	157 (5)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x-1, y, z+1$; (iii) $x, y, z+1$; (iv) $x, y, z-1$; (v) $-x+1, -y, -z+1$.

[Cu(pydcH)₂] [34]. Complex **1** is rare example of tetranuclear water cluster. Metalloligand approach did not work in **3** because of strong chelating and steric effect of branched eten ligand.

2. Experimental

2.1. Prepare of complexes

2.1.1. [Cu₂(μ-pydc)₂(dmim)₄]-6H₂O (**1**) and {[Cu(μ-pydc)(eten)]-2H₂O}_n (**3**)

An aqueous solution (10 mL) of dmim or eten (0.24 g, 2.53 mmol or 0.29 g 2.53 mmol) was added dropwise to a stirred

Table 3
Selected bond distances (Å) and angles (°) for **2**.

Bond lengths (Å)			
Cu1–N1	1.956 (1)	Cu1–O4 ⁱ	2.512(1)
Cu1–O1	1.972 (1)		
Angles (°)			
O1–Cu1–N1	82.86 (6)	O4 ⁱ –Cu1–O1	96.18 (6)
O1 ⁱ –Cu1–N1	97.14 (6)	O4 ⁱ –Cu1–N1	83.61 (6)
D–H...A			
D–H...A	<i>d</i> (H...A) (Å)	<i>d</i> (D...A) (Å)	\angle (DHA) (°)
N2–H2A...O4 ⁱⁱ	1.87	2.726 (3)	176
N3–H3A...O1W ⁱⁱⁱ	1.89	2.742 (2)	173
O1W–H1W...O3	1.95 (2)	2.731 (2)	161 (3)
O1W–H2W...O3 ^{iv}	1.971 (18)	2.784 (2)	172 (3)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $-x, -y, -z$; (iv) $-x, 1-y, z$.

Table 4
Selected bond distances (Å) and angles (°) for **3**.

Bond lengths (Å)			
N1–Cu1	2.001 (3)	O1–Cu1	1.966 (2)
N2–Cu1	1.977 (3)	N3–Cu1	2.364 (3)
O4–Cu1 ⁱ	1.981 (2)		
Angles (°)			
O1–Cu1–N2	87.12 (11)	O4 ⁱⁱ –Cu1–N1	96.52 (10)
O1–Cu1–O4 ⁱⁱ	170.50 (12)	O1–Cu1–N3	97.40 (13)
N2–Cu1–O4 ⁱⁱ	92.41 (11)	N2–Cu1–N3	83.30 (13)
O1–Cu1–N1	82.19 (10)	O4 ⁱⁱ –Cu1–N3	91.96 (12)
N2–Cu1–N1	165.51 (12)	N1–Cu1–N3	107.69 (12)
D–H...A			
D–H...A	<i>d</i> (H...A) (Å)	<i>d</i> (D...A) (Å)	\angle (DHA) (°)
N2–H2A...O2 ⁱⁱ	1.95	2.845 (4)	175
N2–H2B...O2 ⁱⁱⁱ	2.32	3.082 (4)	143
O1W–H1W...O3	2.10 (3)	2.915 (5)	170 (11)
O1W–H2W...O2 W	2.05 (4)	2.845 (6)	157 (9)
O2W–H3W...O3 ⁱⁱ	2.09 (3)	2.892 (4)	169 (6)
O2W–H4W...O2 ⁱⁱⁱ	2.23 (3)	3.019 (4)	162 (6)
O2W–H4W...O1 ⁱⁱⁱ	2.51 (4)	3.203 (4)	143 (5)

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$.

Table 5
Selected bond distances (Å) and angles (°) for **4**.

Bond lengths (Å)			
O1–Cu1	1.951 (2)	Cu1–N1 ⁱⁱ	1.968 (2)
Cu2–O3	2.536 (2)	Cu2–N2 ⁱⁱⁱ	2.059 (2)
Cu1–O4 ⁱ	2.644 (2)	Cu2–N3 ⁱⁱⁱ	2.009 (2)
Angles (°)			
O1–Cu1–N1	83.33 (7)	N3–Cu2–N2	88.54 (8)
O1–Cu1–N1 ⁱⁱ	96.67 (7)	N3 ⁱⁱⁱ –Cu2–N2	91.46 (8)
D–H···A		<i>d</i> (H···A) (Å)	\angle (DHA) (°)
N2–H2A···O1W ⁱⁱⁱ	2.44	3.043 (3)	125
N2–H2B···O4 ⁱⁱⁱ	2.25	3.085 (3)	154
N3–H3A···O2 ⁱⁱⁱ	2.07	2.957 (3)	167
N3–H3B···O1W	2.05	2.909 (3)	159
O1W–H1W···O3 ^{iv}	1.95 (1)	2.768 (2)	169 (4)
O1W–H2W···O4	2.25 (2)	3.029 (3)	160 (4)

Symmetry codes: (i) $-1+x, y, z$; (ii) $-x, -y+1, -z+2$; (iii) $-x+1, -y+1, -z+1$; (iv) $x+1, y, z$.

water solution (0.61 g, 1.26 mmol) containing [Cu(pydcH)₂] [34]. The solution was heated to 50 °C in a temperature-controlled bath and was stirred for 5 h. The resulting solution was filtered and left to stand under ambient condition. The dark blue crystals were formed. Yield: 26% (based on Cu) for **1**. (948.21 g/mol) (C₃₄H₅₀Cu₂N₁₀O₁₄) *Anal. Calc.* for C, 43.14; H, 5.67; N, 14.23. Found: C, 42.99; H, 5.31; N, 14.75%. IR (cm⁻¹, KBr): ν (H₂O), 3386 w; ν (CH), 3161 w, 3143 w, 3092 m, 3079 m; ν_{as} (COO), 1639 vs 1600 vs 1585 vs; ν (C=N), 1514 m; ν_s (COO), 1396 vs 1357 vs; $\Delta\nu$, 243, 235. Yield: 77% (based on Cu) for **3**. (728.48 g/mol C₃₁H₇₁CuN₉O₆) *Anal. Calc.* for C, 51.04; H, 9.81; N, 17.28. Found: C, 51.14; H, 9.77; N, 17.21%; IR (cm⁻¹, KBr): ν (H₂O), 3314 w; ν (CH), 3260 m, 3177 m, 3098 m; 3074 m ν_{as} (COO), 1671 vs 1606 vs 1584 vs; ν (C=N), 1437 m; ν_s (COO), 1378 vs; $\Delta\nu$, 228.

2.1.2. $\{(4\text{-mimH})_2[\text{Cu}_2(\mu\text{-pydc})_2]\cdot 2\text{H}_2\text{O}\}_n$ (**2**) and $\{[\text{Cu}(\text{pen})_2\text{Cu}(\mu_3\text{-pydc})_2]\cdot \text{H}_2\text{O}\}_n$ (**4**)

An aqueous solution (10 mL) of 4-mim or pen (0.21 g, 2.53 mmol or 0.19 g 2.53 mmol) was added dropwise to a stirred solution (water 10 mL) containing [Cu(pydcH)₂] [34] (0.61 g, 1.26 mmol). The mixture was refluxed at 60 °C for two days in a temperature-controlled bath. Then the solution was cooled to room temperature. The blue crystals of **2** and **4** were obtained. Yield: 33% (based on Cu) for **2**. (658.02 g/mol) (C₂₂H₂₄Cu₂N₆O₁₀) *Anal. Calc.* for C, 40.06; H, 3.67; N, 12.74. Found: C, 40.11; H, 3.74; N, 12.46%. IR (cm⁻¹, KBr): ν (H₂O), 3357 w; ν (NH), 3138 ν (CH), 3072 w, 3018 w, 2746 m; 2634 m, ν_{as} (COO), 1643vs, 1583 vs; ν (C=N), 1465 m; ν_s (COO), 1398 vs 1338 vs; $\Delta\nu$, 245, 245. Yield: 41% (based on Cu) for **4**. (658.07 g/mol) (C₂₀H₃₂Cu₂N₆O₁₁) *Anal. Calc.* for C, 36.42; H, 4.89; N, 12.74. Found: C, 35.98; H, 4.23; N, 13.01%. IR (cm⁻¹, KBr): ν (H₂O), 3142 w; ν (CH), 3075 w, 3013 w, 2978 m, 2939 m, 2893 m, ν_{as} (COO), 1660 vs 1573 vs; ν (C=N), 1434 m; ν_s (COO), 1381 vs 1340 vs; $\Delta\nu$, 279, 233.

2.2. Materials and measurements

All chemicals used were analytical reagent and commercially purchased. IR spectra were obtained with a Bruker Tensor FT-IR spectrometer using KBr pellets in the 4000–400 cm⁻¹ range. Elemental analysis for C, H and N were performed using a Carlo Erba 1106 microanalyser. Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in the static air atmosphere at a heating rate of 10 °C min⁻¹ in the temperature range 30–700 °C using platinum crucibles.

2.3. Crystallographic analyses

X-ray diffraction data for compounds **1–4** were collected at 293 (2) K on a Stoe IPDS diffractometer. Data collection: Stoe X-AREA

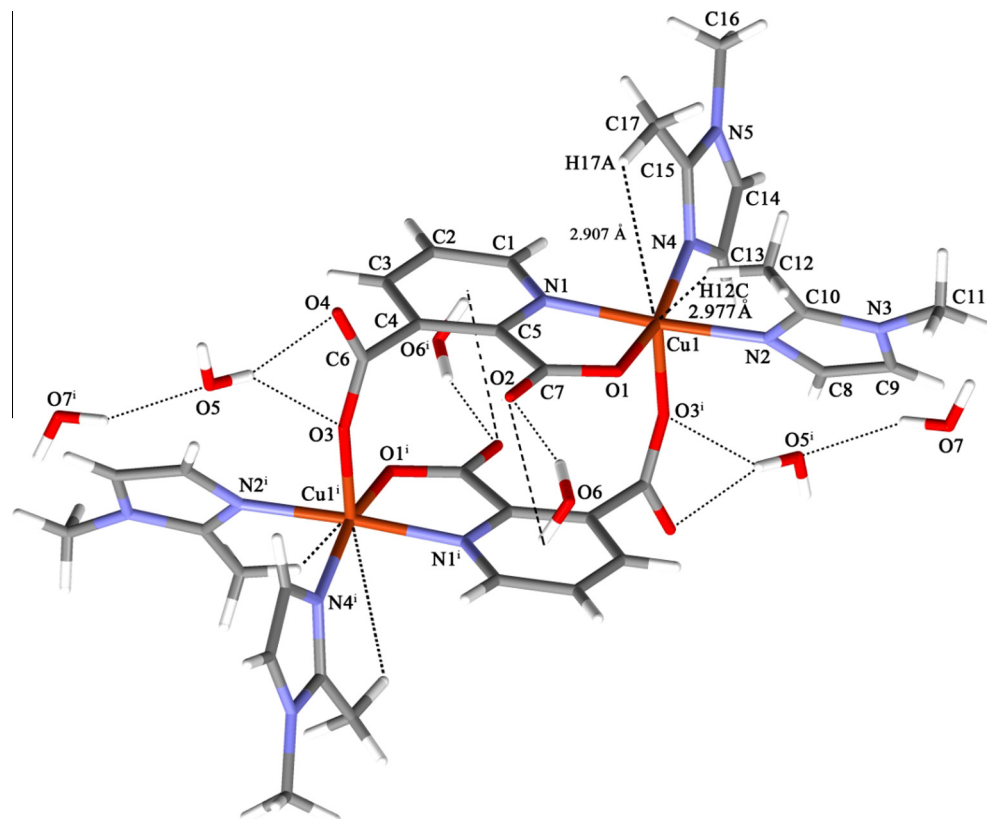


Fig. 1. The molecular structure of **1** with atom-labelling scheme ((i) $1-x, -y, 1-z$).

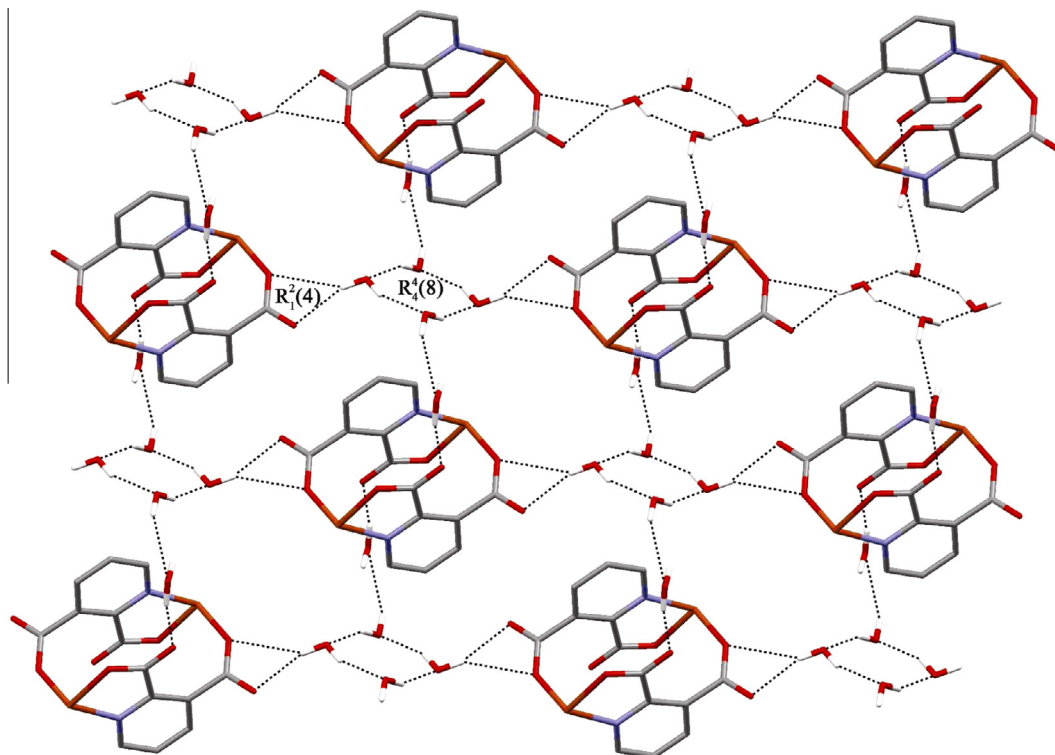


Fig. 2. A view of the 2D network of **1**, showing the $R_2^2(4)$, $R_4^4(8)$ and $R_2^2(4)$ ring patterns.

[47]. Cell refinement: Stoe X-AREA [47]. Data reduction: Stoe X-RED [47]. The structures were solved by direct methods using the program SHELXS97 [48] with anisotropic thermal parameters for all non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods SHELXL-97 [48]. Water H atoms were located in a difference map and refined subject to a DFIX restraint of O–H = 0.83(2) Å. Other H atoms were located from different maps and then treated as riding atoms with C–H distances of 0.93–0.97 Å and N–H distances of 0.86–0.90 Å. Molecular drawings were obtained using Mercury [49]. The crystal data and the refinement details of complexes are given in Table 1.

3. Results and discussion

3.1. Synthesis

In the synthesis of complexes, we used Cu(II) containing metalloligand $[\text{Cu}(\text{pydcH})_2]_n$ [34] as a ligand source because Cu(II) is a good building block for the formation of metalloligands because it easily exhibits Jahn–Teller distortion. As a result of Jahn–Teller effect of copper(II) ions, metalloligands get coordination flexibility and Lewis base properties [50]. Synthesis of complexes was performed in two stages. Firstly, water-soluble $[\text{Cu}(\text{pydcH})_2]$ [34] as a metalloligand source was synthesized according to the literature. In the second step, complexes were obtained by adding auxiliary ligands into the water solution of $[\text{Cu}(\text{pydcH})_2]$ [34]. The reaction of $[\text{Cu}(\text{pydcH})_2]$ [34] with 1,2-dimethylimidazole in an aqueous solution was induced a ligand exchange to form a new neutral metalloligand, $[\text{Cu}_2(\mu\text{-pydc})_2(\text{dmim})_4]$. Take into consideration that polynuclear metalloligand split up neutral metalloligand dimer by four 1,2-dimethylimidazole ligands. Using corresponding dinuclear metalloligand but prepared by 2,4-pyridinedicarboxylate a porous coordination polymer was synthesized and characterized [51]. When 4-methylimidazole was added to metalloligand solution in a 1:2 ratio, an intermolecular proton transfer reaction oc-

curred, forming hydrogen bond network of $\{[(4\text{-mimH})_2\text{Cu}(\mu\text{-pydc})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**2**). The protons located on metalloligand emigrated to 4-methylimidazole without changing 1D double-chain structure. Metalloligand could not work in **3**. Bidentate eten ligand may not suitable for metalloligand method, presumably, steric hindrance of its ethyl groups prevent formation of metalloligand. In complex **4**, 1D double chain metalloligand chains connect to each other via bis(propanediamine)Cu(II) units aqueous medium induced a cation exchange to form a 2D layered coordination polymer. A couple of proton of monoanionic pydcH leave to chain and donor atom of anionic metalloligand, $[\text{Cu}(\mu\text{-pydc})_2]^{2-}$ bridge to cationic unit of $[\text{Cu}(\text{pen})_2]^{2+}$ as Lewis base.

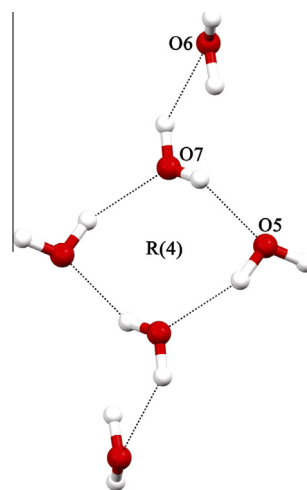


Fig. 3. View of R_4 (or $R_4^4(8)$) water cluster motif.

3.2. IR spectra

IR spectra of complexes show strong bands between 3386 and 3142 cm^{-1} due to the O–H stretching vibrations of H_2O molecules. The intense band at 3186 cm^{-1} is attributed to the $\nu(\text{NH})$ vibration of protonated 4-mimH cation in the IR spectrum of **2**. The weak peaks at 3079 and 2634 cm^{-1} are the characteristic of aliphatic

C–H stretching bands of the $\text{CH}_3/\text{CH}_2/\text{CH}$ groups. This confirms the existence of the dmim, 4-mimH, eten and pen ligands in **1–4**. The absence of strong absorption bands around 1720 cm^{-1} indicates the full deprotonation of carboxylate groups of the pydc ligands, as revealed by the single-crystal structure analysis. The very strong peaks range from 1671 – 1573 and 1398 – 1338 cm^{-1}

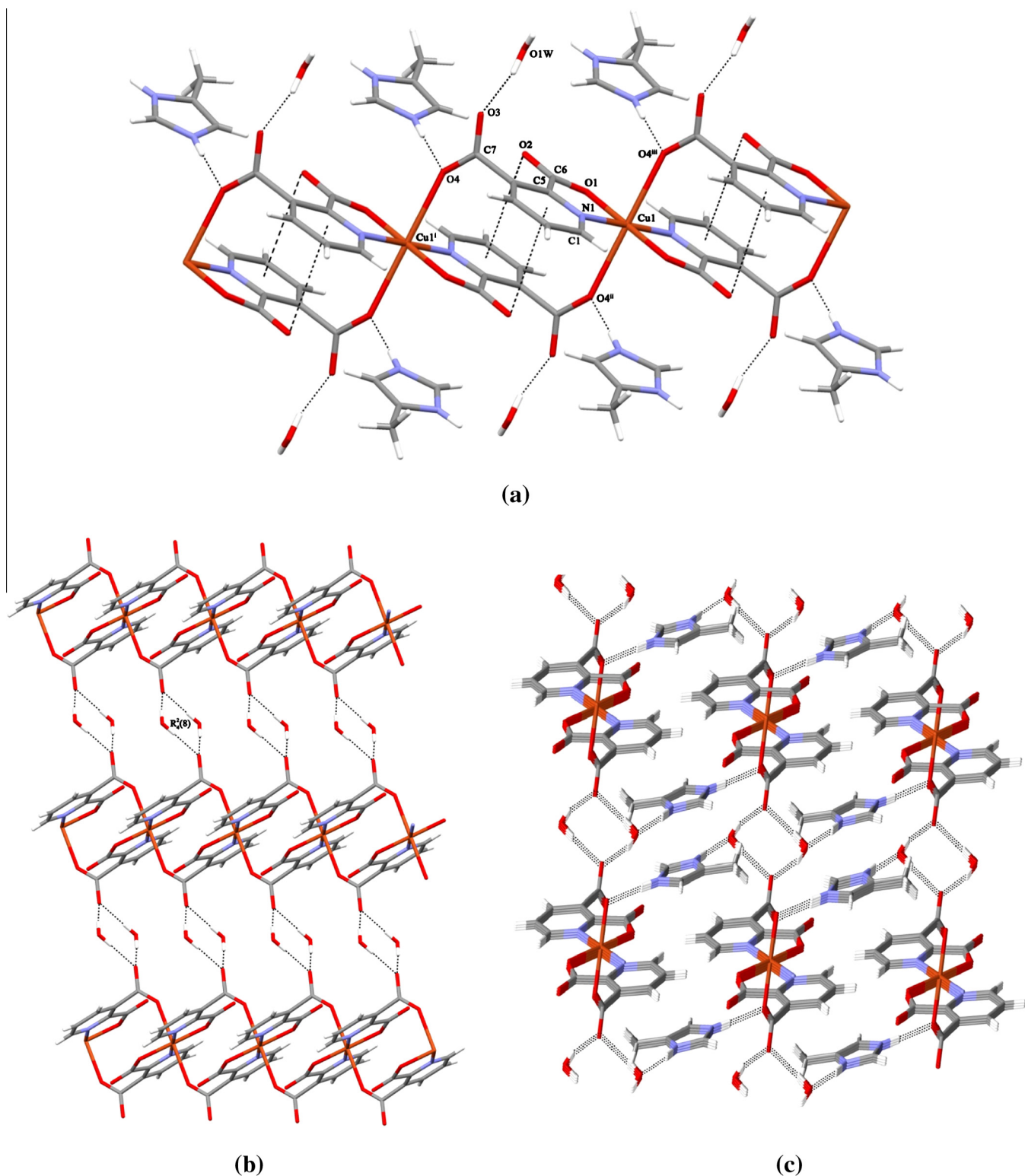


Fig. 4. (a) The one-dimensional chain structure of **2** ((i) $-1 + x, y, z$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 + x, y, z$). (b) A view of the hydrogen-bonding interactions in **2**, showing the $R_4^2(8)$ ring and (c) A view of the 3D supramolecular network of **2**.

Table 6
Comparison of the bond distances (Å) and angles (°) of the copper(II)-pyridine-2,3-dicarboxylate complexes.

Ref.	Complexes	Pydc mode	Cu1–N1 (Å)	Cu1–O1 (Å)	Cu1–O3 (Å)	O1–Cu1–N1 (°)
	1 (this work)	μ -(κ^3 N,O ² :O ³)	2.010 (2)	1.967 (2)	2.174 (2)	81.10 (7)
	2 (this work)	μ -(κ^3 N,O ² :O ³)	1.972 (1)	1.956 (1)	2.512(1)	82.86 (6)
	3 (this work)	μ -(κ^3 N,O ² :O ³)	2.001 (3)	1.966 (2)	1.981 (2)	82.19 (10)
	4 (this work)	μ -(κ^3 N,O ² :O ³ ,O ⁴)	1.968 (2)	1.951 (2)	2.536 (2)	83.33 (7)
[42]	{[Cu(pydcH) ₂]-2CH ₃ OH} _n	μ -(κ^3 N,O ² :O ³)	1.985	1.967	2.419	83.42
[39]	[Cu(pydcH) ₂](H ₂ O) ₂	κ^2 N,O ²	2.028	2.018	–	100.83
[46]	{[Cu ₂ (pydc) ₂ (2,2'-bpy)(H ₂ O) ₂]-4H ₂ O} _n	μ -(κ^3 N,O ² :O ³)	1.966	1.936	1.955	83.22
[45]	[Cu ₂ (pydc) ₂ (phen)(H ₂ O) ₂]-4H ₂ O	μ -(κ^3 N,O ² :O ³)	1.964	1.934	1.949	83.06
[46]	{[Cu ₂ (pydc) ₂ (phen)(H ₂ O) ₂]-4H ₂ O} _n	μ -(κ^3 N,O ² :O ³)	1.971	1.934	1.951	82.91
[46]	Cu(pydcH) ₂ ·2(4,4'-bpy)·6H ₂ O _n	μ -(κ^3 N,O ² :O ³)	1.982	1.968	2.504	82.40
[46]	{[Cu(pydcH) ₂]-4H ₂ O} _n	μ -(κ^3 N,O ² :O ³)	2.057	2.028	2.276	80.24
[55]	{[pnH ₂][Cu(pydc) ₂]-3H ₂ O} _n	μ -(κ^3 N,O ² :O ³)	1.970	1.960	2.549	83.38
[44]	{[Cu ₂ (pydc) ₂ (phen)(H ₂ O) ₂]-3H ₂ O} _n	μ -(κ^3 N,O ² :O ³)	1.982	1.945	1.959	83.69
[58]	[Cu(pydc) ₂][Na ₂ (H ₂ O) ₆ (μ -H ₂ O) ₂]	μ -(κ^3 N,O ² :O ³)	1.965	1.958	2.661	83.51
[43]	{[Cu(pydc)(H ₂ O) ₃]-H ₂ O} _n	μ -(κ^3 N,O ² :O ³)	2.187	2.071	2.119	78.54
[41]	[Cu(pydcH)(terpyridine)]BF ₄	κ^2 N,O ²	2.004	2.165	–	77.54
[54]	[Cu(pydc)(bpp)]·5H ₂ O _n	μ -(κ^3 N,O ² :O ³)	1.988	1.963	1.987	82.93
[40]	[Cu(pydcH) ₂]	μ -(κ^3 N,O ² :O ³)	1.926	1.970	2.659	83.72
[34]	[Cu(pydc) ₂][Mn(H ₂ O) ₆]-2H ₂ O	μ -(κ^3 N,O ² :O ³)	1.957	1.985	2.543	82.24

correspond to ν_{asym} and ν_{sym} of the chelating carboxylate group, respectively.

3.3. Thermal analyses

Complex **1** exhibits three stages of decomposition. The first stage from 52 to 101 °C corresponds to endothermic removal of six crystal water molecules (found 12.04%, calc. 11.39%, DTA_{max} = 82 and 94 °C). The complex **1** is stable up to 178 °C and plateau region is observed from 101 to 178 °C. The second stage from 178 to 207 °C is the successive endothermic and exothermic decomposition of dmim ligands (found. 40.16, calcd. 40.55 %, DTA_{max} = 188 and 199 °C). The last stage between 207 and 403 °C is related to the consecutive decomposition of pydc ligand with exothermic effects with two DTA_{max}. (found. 38.06, calcd. 34.83 %, DTA_{max} = 308 and 366 °C).

The first stage between 59 and 107 °C for **2** corresponds to the endothermic elimination of two crystal water molecules with an experimental mass loss of 6.00% (calcd. mass loss 6.04%, DTA_{max} = 86 °C). In the last stage between 152 and 475 °C is related

to the decomposition of pydc and 4-meim ligands with endothermic and exothermic effects (DTA_{max} = 236, 255, 305, 357, 426 °C, found. 81.65, calcd. 83.29%).

The first stage between 56 and 115 °C for **3** corresponds to the endothermic elimination of two crystal water molecules with an experimental mass loss of 8.52% (calcd. mass loss 9.45%, DTA_{max} = 121 °C). The complex **3** is stable up to 198 °C. The exothermic removal of eten and pydc ligands occurs in the second and third stage between 198 and 451 °C, with an experimental mass loss of 73.85% (DTA_{max} = 224, 357, 366, 413 °C calc. mass loss 69.82).

Complex **4** exhibits three stages of decomposition. The first stage from 101 to 123 °C endothermic removal of one crystal water molecules (found 3.71%, calc. 2.89%, DTA_{max} = 121 °C). The complex **4** is stable up to 219 °C. The second and third stages from 219 to 475 °C are the successive endothermic and exothermic decomposition of pen ligands (found. 66.9, calcd. 71.56%, DTA_{max} = 230, 409 and 464 °C).

The final solid products of thermal decomposition were identified by IR spectroscopy as CuO. (For **1**, found. 90.78, calcd. 91.62%;

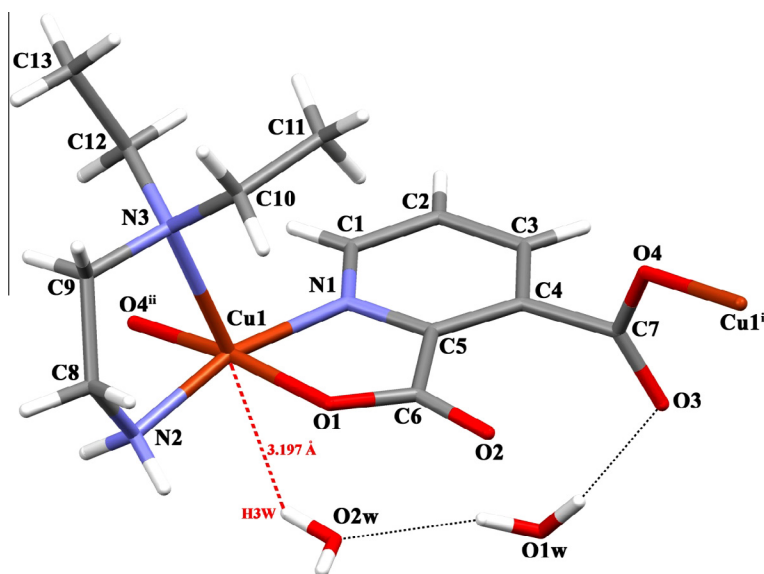


Fig. 5. The asymmetric units of **3** (i) $-1 + x, y, z$; (ii) $1 + x, y, z$.

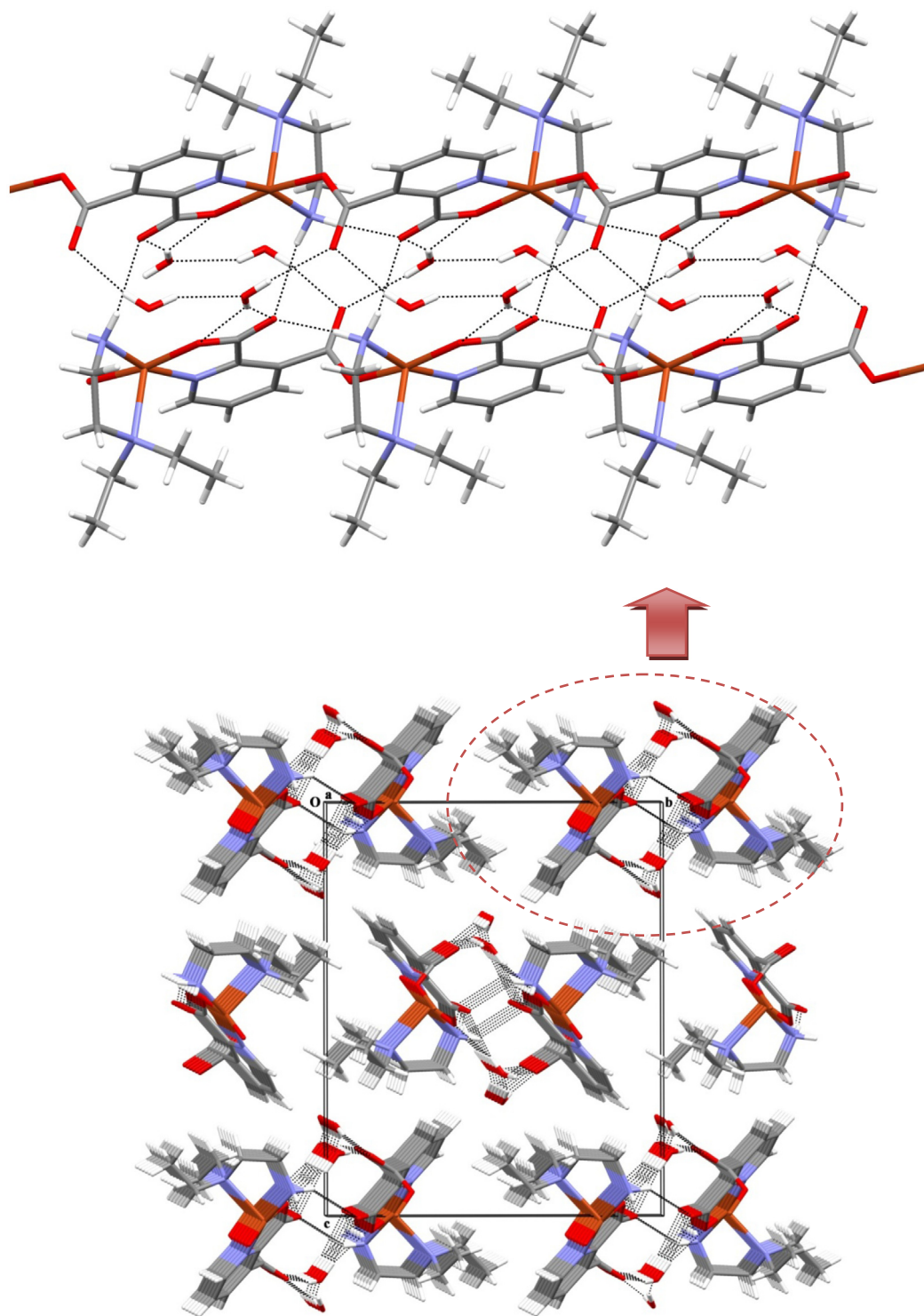


Fig. 6. Hydrogen-bonding interaction between the chains of **3**.

For **2**, found. 87.59, calcd. 86.63% ;For **3**, found. 79.89, calcd. 79.08%; For **4**, found. 71.70, calcd. 74.48%). After the dehydration process, thermal stability order of the anhydrous compounds are found as **4** (220 °C) > **3** (198 °C) > **1** (178 °C) > **2** (148 °C).

3.4. Crystal structures

Details of data collection and crystal structure determinations are given in Table 1. The selected bond distances and angles to-

gether with the hydrogen bonding geometry are given in Tables 2–5.

3.4.1. $[Cu_2(\mu\text{-pydc})_2(\text{dmim})_4]\cdot 6H_2O$ (**1**)

The molecular structure of **1** with the atom labeling is shown Fig. 1 and the selected bond lengths and angles are given in Table 2. The structure consists of a dinuclear metalloligand, $[Cu_2(\mu\text{-pydc})_2(\text{dmim})_4]$ and six crystal water molecules which assemble by hydrogen-bonding interactions directed by clustered water to

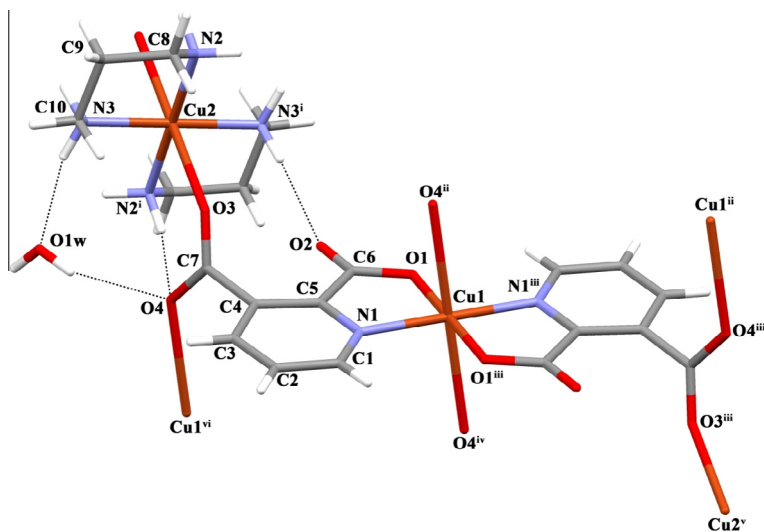


Fig. 7. Molecular structure of $[\text{Cu}(\text{pen})_2\text{Cu}(\mu_3\text{-pydc})_2]\cdot\text{H}_2\text{O}$ (**4**) with atom-labeling scheme (symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-1+x, y, z$; (iii) $-x, 1-y, 2-z$; (iv) $1-x, 1-y, 2-z$; (v) $-1+x, y, 1+z$; (vi) $1+x, y, z$).

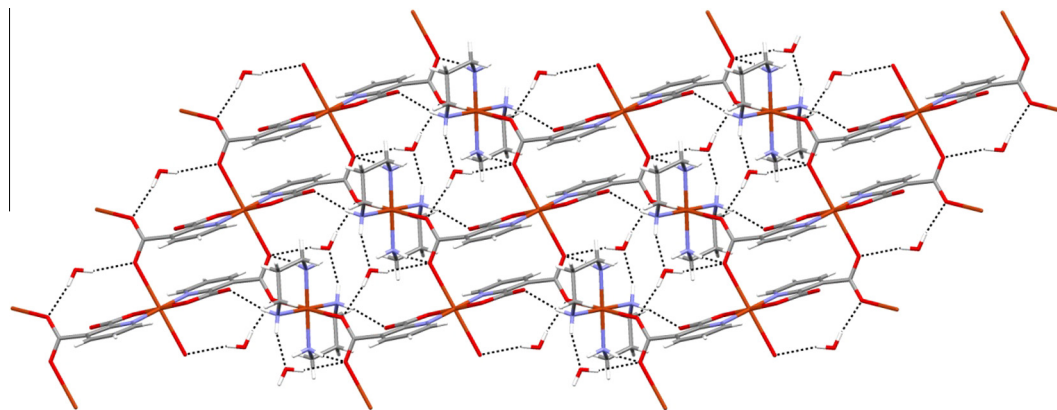


Fig. 8. Intermolecular hydrogen-bonding geometry of **4**.

form 2D metalloligand sheet (Fig. 2). Although there are many metal complexes of pydc forming mononuclear and polynuclear structures, only one dinuclear Co(II)-complex has been reported [52].

Each Cu(II) center in **1** shows a distorted CuN_3O_2 square pyramidal geometry. The distortion is calculated value of the Addison parameters (τ) [53], which is 0.16 (the τ values for square pyramidal and trigonal bipyramidal metal environments are 0 and 1, respectively). The basal plane of **1** consists of one nitrogen atom N1 and one oxygen atom O1 from the chelating pydc ligand and two nitrogen atoms N2 and N4 of two dmim ligands. The Cu1–N1 and Cu1–O1 bond distances of 2.010 (2) and 1.967 (2) Å are practically similar to those found in $\{[\text{Cu}(\text{pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}\}_n$ (2.187 and 2.071 Å) [43], $[\text{Cu}_2(\text{pydc})_2(\text{phen})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ (1.964 and 1.934 Å) [46], $\{[\text{Cu}(\text{pydc})(\text{bpp})005\text{D}\cdot 5\text{H}_2\text{O}_3]\}$ (1.988 and 1.963 Å) [54] but somewhat longer than those found in $\{[\text{Cu}_2(\text{pydc})_2(2,2'\text{-bpy})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}\}_n$ (1.966 and 1.936 Å). Cu1–O3 bond distance (2.174 (2) Å) is significantly shorter than elongated Jahn–Teller distortion observed corresponding distances found in $\{[\text{Cu}(\text{pydcH})_2]\cdot 2\text{CH}_3\text{OH}\}_n$ (2.419 Å) [42], $\text{Cu}(\text{pydcH})_2\cdot 2(4,4'\text{-bpy})\cdot 6\text{H}_2\text{O}\}_n$ (2.504 Å) [46], $\{(\text{pnH}_2)\text{-Cu}(\text{pydc})_2\cdot 3\text{H}_2\text{O}\}_n$ (2.549 Å) [55], $[\text{Cu}(\text{pydcH})_2]\}_n$ (2.659 Å) [40] and $[\text{Cu}(\text{pydc})_2][\text{Mn}(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$ (2.543 Å) [34], while it is in agreement with the corresponding values in $\{[\text{Cu}(\text{pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}\}_n$ (2.119 Å) [43], $\{[\text{Cu}(\text{pydc})(\text{bpp})]\cdot 5\text{H}_2\text{O}\}_n$ (1.987 Å) [54]. The apical position of the Cu(II) atom is occupied by a carboxylate oxygen from

the nearest-neighboring metalloligand moiety (2.173(2) Å for Cu1–O3i ($i = -x + 1, -y, -z + 1$)). Neighboring two metalloligands assemble via coordination bonds between the Cu(II) ions and the 3-carboxylate oxygen atoms, aided by C–O $\cdots\pi$ interactions between the 2-carboxylate group and pyridine ring (distance ~ 3.6 Å) in neighboring metalloligands, to form the metalloligand dimers.

A notable feature of hydrogen-bonding assemblies of **1** is the presence of hexameric $(\text{H}_2\text{O})_6$ water clusters (Fig. 3). These water molecules are stabilized the crystal structure by strong hydrogen bonding interactions. Within the water cluster, four water molecules (O5 \cdots O7 \cdots O5 $^i\cdots$ O7 i) act as both hydrogen-bonding donors and acceptors to form a cyclic water tetramer. Another two water molecules (O6 and O6 i) are connected two diagonal water corners of the cyclic water tetramer, giving rise to a hexamer (Fig. 3). Each hexamer cluster links by four dinuclear $[\text{Cu}_2(\mu\text{-pydc})_2(\text{dmim})_4]$ complex through O5, O6, O5 i and O6 i atoms. The O \cdots O distance within the dimer is 2.897 (5) Å [O6 \cdots O7], while the hydrogen bond lengths between the tetramer and the dangling dimers are slightly longer than the intratetramer length [2.791(5) Å, O5 \cdots O7], the liquid water (2.854 Å) and comparable to those in the ice phase (2.77–2.84 Å) [30]. Whereas these distances are very close to the corresponding value of 2.743 Å calculated in the discrete water tetramer [56,57]. To the best of our knowledge, such cyclic water clusters are not common. These water clusters filled the voids in

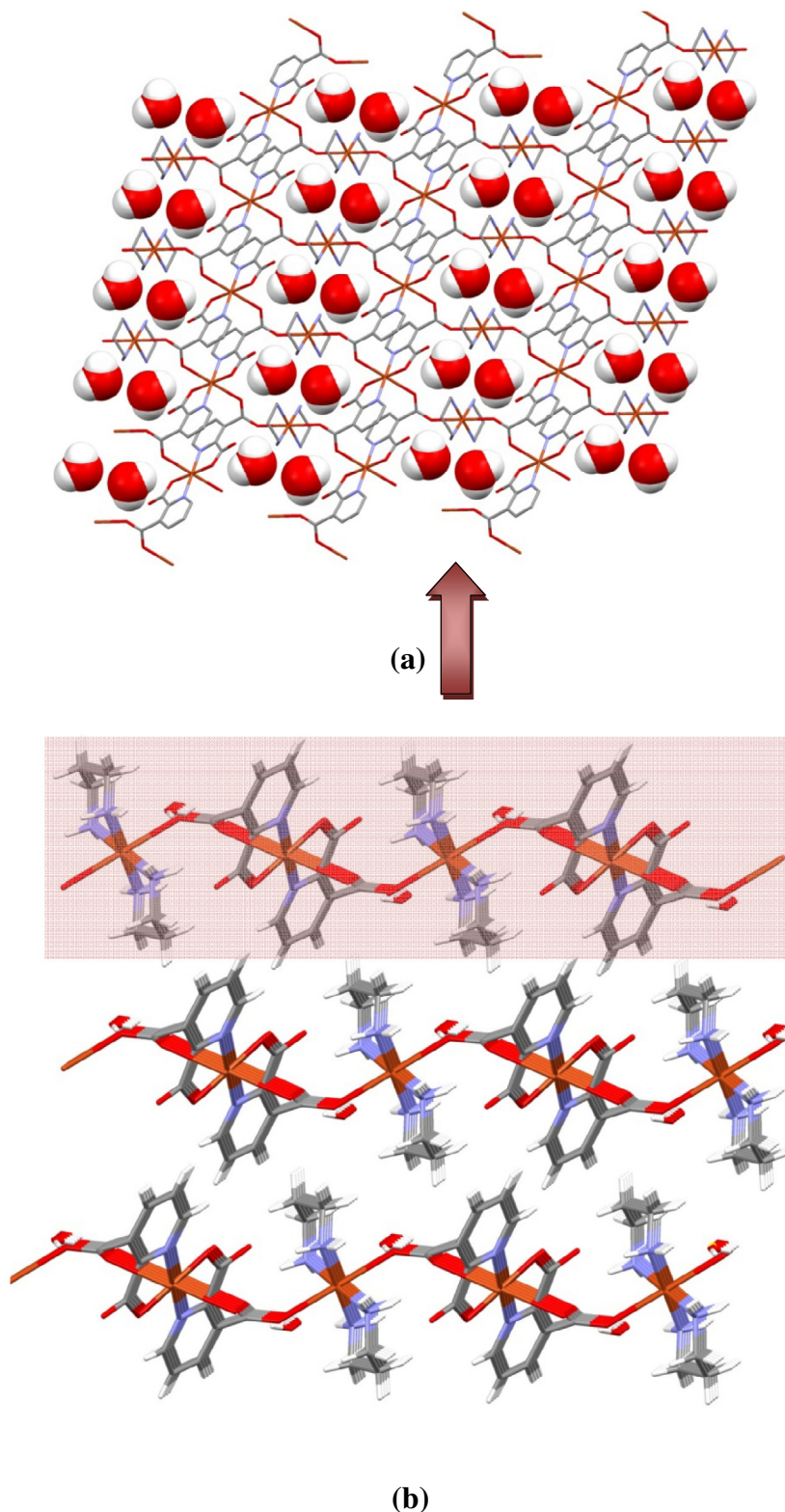


Fig. 9. (a) 2D layers filled with water molecules and (b) 3D supramolecular network in **4**.

the supramolecular framework and contribute to the total lattice energy (Fig. S1). The 2D sheets are further linked by C-H...π interactions between C11–H11C, C16–H16C and imidazole rings [C11–H11C...Cg1 = 2.84 and C16–H16C...Cg2 = 2.80 Å, Cg1=N2–C8–C9–N3–C10 and Cg2=N4–C13–C14–N5–C15] to form a 3D supramolecular network (Fig. S2). There also found C–O...π interactions between the uncoordinated carboxylate oxygen (O2) and pyridine

rings [3.612 Å]. Similar C–O...π interactions that were reported as 3.163 and 3.239 Å were previously reported in two polynuclear copper(II) complexes of pydc [34,43].

3.4.2. $\{(4\text{-mimH})_2[\text{Cu}_2(\mu\text{-pydc})_2]\cdot 2\text{H}_2\text{O}\}_n$ (**2**)

Single crystal X-ray analysis showed that the crystal structure of **2** is one dimensional metalloligand double chain polymer along

the *a* axis. The Cu(II) compound is composed of an anionic complex, $[\text{Cu}(\text{pydc})_2]^{2-}$, two 4-methylimidazolium as a counter-ion, $(4\text{-mimH})^+$ and two crystal water molecules (Fig. 4(a)). The Cu(II) ion adopts a distorted octahedral geometry and is coordinated by two N and four O atoms from four pydc ligands. Two oxygen atoms of carboxylate group (O1 and O1ⁱ) and two nitrogen atoms (N1 and N1ⁱ) comprise the equatorial plane, while two oxygen atoms of carboxylate group from symmetry related pydc ligands occupy the axial position. This axial Cu–O4ⁱ bond distance is clearly elongated on account of the Jahn–Teller distortion and it is significantly longer than those reported complexes 1.955 [46] and 2.119 Å [43] (Table 3). The Cu1–O1 (1.956 (1) Å) and Cu1–N1 (1.972 (1) Å) bond distances are similar that reported for the related Cu(II) complexes [40,42,44,46,54,55] (Table 6), however shorter than those found $[\text{Cu}(\text{pydcH})_2(\text{H}_2\text{O})_2]$ (2.018 and 2.028 Å) [39] and $\{[\text{Cu}(\text{pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}\}_n$ (2.187 and 2.071 Å) [43]. One of the two carboxyl groups is coplanar with the pyridine ring [7.42°], but the other carboxyl group is twisted out of the pyridine ring by about 86.72° and this pyridine–3-carboxylate twist shows semi-rigid behavior of pydc and supports construction of the 1D double-chain. The Cu1...Cu1ⁱ distance in the 1D chain is 6.866 Å, while between chains distance Cu1...Cu1ⁱⁱ and Cu1...Cu1ⁱⁱⁱ are 8.172 and 13.45 Å, respectively [(i): –1 + *x*, *y*, *z*, (ii) 1 + *x*, 1 + *y*, *z*; (iii) *x*, *y*, 1 + *z*]. The crystal packing of complex is a composite of intra- and intermolecular hydrogen bonding and $\pi\cdots\pi$ interactions. The adjacent chains interact each other through water bridges by strong hydrogen bonds to form a 2D layer and generate $R_2^2(8)$ motif [O1W...O3 = 2.731 (2) and O1W...O3^{iv} = 2.784 (2) Å] (Fig. 4 (b)). The 2D layers are connected together by 4-mimH cations through N–H...O [N2...O1W = 2.726(3) and N3...O4ⁱⁱ = 2.742(2) Å] interactions resulting in the three-dimensional supramolecular network (Fig. 4(c)). Furthermore, there is also $\pi\cdots\pi$ interaction between 4-mimH cation (Cg1) and pyridine ring (Cg2) (Cg1 = N(2)–C(8)–N(3)–C(9)–C(10) and Cg2 = N(1)–C(1)–C(2)–C(3)–C(4)–C(5); Cg1...Cg2 = 4.065 Å) and 4-mimH cations (Cg1...Cg1 = 3.778 Å), resulting in a three-dimensional (3D) supramolecular network (Fig. S3).

3.4.3. $\{[\text{Cu}(\mu\text{-pydc})(\text{eten})]\cdot 2\text{H}_2\text{O}\}_n$ (3)

The asymmetric units of **3** consist of a polynuclear 1D chain with one Cu(II) ion, one pydc bridging ligand, one eten chelating ligand and two lattice water molecules (Fig. 5). The Cu(II) ion is five-coordinated by two nitrogen atoms from the eten ligand and two carboxyl oxygen and one pyridine nitrogen atoms from the pydc ligand. The two nitrogen and two carboxyl oxygen atoms comprise the equatorial plane, while nitrogen atom of eten occupies the apical position. The Cu–O1 and Cu–N1 bond distances being 1.951 (2) and 1.968 (2) Å, respectively. **3** has a τ value of 0.348 and it clearly indicates that the copper atom in **3** is slightly distorted square pyramidal geometry [53]. The pydc ligand bridges two Cu(II) ions giving rise to a 1D polynuclear chain oriented along a axis of the monoclinic unit cell (Fig. 6). The adjacent Cu1...Cu1ⁱ distance in the chain is 7.345 Å, while between chains distance Cu1...Cu1ⁱⁱ is 6.415 Å [(i) –1 + *x*, *y*, *z*, (ii) 1 – *x*, 1 – *y*, 1 – *z*].

In the chain, intramolecular hydrogen bonds are formed between the lattice water molecules (O1W and O2W) and uncoordinated carboxyl oxygen atom (O3), and between the NH₂ group of eten ligand (N2) and uncoordinated carboxyl oxygen atom (O2). Between chains, water molecules and NH₂ group form intermolecular hydrogen bonds, giving rise to a one dimensional hydrogen-bonding double chain motif (Fig. 6). The 1D double chains are further connected into a 3D structure through only van der Waals interactions (Fig. 6). All of these intermolecular interactions bring about a three-dimensional network (Fig. S4).

3.4.4. $\{[\text{Cu}(\text{pen})_2\text{Cu}(\mu_3\text{-pydc})_2]\cdot\text{H}_2\text{O}\}_n$ (4)

Single crystal X-ray diffraction analysis reveals a 2D layered coordination structure of **4**. The asymmetric unit is composed of two Cu(II) ions, two pydc ligands, two pen ligands, and one lattice water molecule (Fig. 7). Both Cu1 and Cu2 centers are six-coordinated by four pydc and two pen ligands. The Cu(1) atom is surrounded by an N₂O₄ unit [N1, N1ⁱⁱⁱ, O1 and O1ⁱⁱⁱ] from two pydc ligands in the equatorial plane and two oxygen atom (O4ⁱⁱ and O4^{iv}) from two symmetry related pydc ligands [Cu1–O1 = 1.951(2), Cu1–N1 = 1.968(2) Å and Cu1–O4 = 2.644 (2) Å]. The Cu2 ion exhibits a distorted octahedral geometry with an N₄O₂ coordination sphere from two bidentate pen and two pydc ligands. The equatorial plane is provided by four nitrogen atoms from two pen ligands [Cu2–N2 = 2.059(2) and Cu2–N3 = 2.009(2) Å]. The axial position of the octahedron is occupied by two carboxylate oxygen atoms from symmetry related pydc ligands [Cu2–O3 = 2.536(2) Å]. The axial bond distances are longer than those the equatorial Cu1–N/O or Cu2–N bond lengths due to the Jahn–Teller effect.

Intra-layer hydrogen bonds are observed between lattice water molecule (O1W) and oxygen atoms of carboxyl groups (O3 and O4) [O1W...O3 = 2.768 and O1W...O4 = 3.029 Å] (Fig. 8). Furthermore there are also weak hydrogen bonding interactions between nitrogen atoms of pen ligand [N2 and N3] and oxygen atoms of carboxylate groups (O2 and O4) and water molecules (O1W), with the N...O distances range from 2.909(3) to 3.085(3) Å. The 2D network is extended into a 3D supramolecular framework by only weak C–H... π interaction between C9–H9A and pyridine ring (Cg) [C9–H9A...Cgⁱ = 3.396 Å, (i) 1 + *x*, 1 + *y*, *z*] (Fig. 9).

4. Conclusion

In conclusion, four new supramolecular assemblies were constructed by utilizing the metalloligand approach with some imidazole and chelating bidentate aliphatic diamine derivatives by two step synthesis with the aid of the $[\text{Cu}(\text{pydcH})_2]_n$, which could be relevant for chemical modification of coordination compounds. When 4-methylimidazole is added to, as a result of proton transfer reaction 4-methylimidazolium is occurred. But using 1,2-dimethylimidazole instead of 4-methylimidazole, ligand exchange reaction is occurred and gave rise to a new metalloligand. In **4**, 2D layered coordination polymer synthesized by connecting the metalloligand units with pen ligand, but in **3**, metalloligand could not work because of the steric hindrance groups of eten. The complex **1** display tetrameric water clusters.

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Appendix A. Supplementary material

CCDC 778997, 778998, 829458 and 829457 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2013.10.006>.

References

- [1] C. Janiak, Dalton Trans. (2003) 2781.
- [2] D. Maspoch, D. Ruiz-Molina, J. Veciana, J. Mater. Chem. 14 (2004) 2713.
- [3] S. Ma, H.C. Zhou, Chem. Commun. 46 (2010) 44.
- [4] L.J. Murray, M. Dinc, J.R. Long, Chem. Soc. Rev. 38 (2009) 1294.

- [5] R.J. Kuppler, D.J. Timmons, Q.R. Fang, J.R. Li, T.A. Makal, M.D. Young, D. Yuan, D. Zhao, W. Zhuang, H.C. Zhou, *Chem. Soc. Rev.* 253 (2009) 3042.
- [6] A.U. Czaja, N. Trukhan, U. Müller, *Chem. Soc. Rev.* 38 (2009) 1284.
- [7] S. Takaiishi, M. Hosoda, T. Kajiwara, H. Miyasaka, M. Yamashita, Y. Nakanishi, Y. Kitagawa, K. Yamaguchi, A. Kobayashi, H. Kitagawa, *Inorg. Chem.* 48 (2008) 9048.
- [8] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* 43 (2004) 2334.
- [9] O. Kahn, *Acc. Chem. Res.* 33 (2000) 647.
- [10] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, *Nature* 423 (2003) 705.
- [11] M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk, *Chem. Soc. Rev.* 38 (2009) 1330.
- [12] S.R. Halper, L. Do, J.R. Stork, S.M. Cohen, *J. Am. Chem. Soc.* 128 (2006) 15255.
- [13] S. Noro, S. Kitagawa, T. Wada, *Inorg. Chim. Acta* 358 (2005) 423.
- [14] S. Noro, H. Miyasaka, S. Kitagawa, T. Wada, T. Okubo, M. Yamashita, T. Mitani, *Inorg. Chem.* 44 (2005) 133.
- [15] V. Vreshch, A. Chernega, J. Howard, J. Sieler, K. Domasevitch, *Dalton Trans.* (2003) 1707.
- [16] Y.H. Liu, H.P. Fang, P.C. Jhang, C.C. Peng, P.H. Chien, H.C. Yang, Y.C. Huang, Y.L. Lo, *CrystEngComm* 12 (2010) 1779.
- [17] L. Carlucci, G. Ciani, S. Maggini, D.M. Proserpio, M. Visconti, *Chem.-Eur. J.* 16 (2010) 12267.
- [18] K. Youm, S. Huh, Y. Park, S. Park, M. Choi, M. Jun, *Chem. Commun.* (2004) 2384.
- [19] G.H. Wang, Z.G. Li, H.Q. Jia, N.H. Hu, J.W. Xu, *Acta Crystallogr., Sect. C* 65 (2009) m333.
- [20] K. Muller-Dethlefs, P. Hobza, *Chem. Rev.* 100 (2000) 143.
- [21] M. Nishio, *CrystEngComm* 6 (2004) 130.
- [22] C. Janiak, *J. Chem. Soc., Dalton* (2000) 3885.
- [23] A. Milet, R. Moszynski, P. Wormer, A. van der Avoird, *J. Phys. Chem. A* 103 (1999) 6811.
- [24] C. Gruenloh, J. Carney, C. Arrington, T. Zwier, S. Fredericks, K. Jordan, *Science* 276 (1997) 1678.
- [25] U. Buck, I. Ettischer, M. Melzer, V. Buch, J. Sadlej, *Phys. Rev. Lett.* 80 (1998) 2578.
- [26] S. Karthikeyan, K.S. Kim, *J. Phys. Chem. A* 113 (2009) 9237.
- [27] S. Manikumari, V. Shivaiah, S.K. Das, *Inorg. Chem.* 41 (2002) 6953.
- [28] A. Sediki, F. Lebsir, L. Martiny, M. Dauchez, A. Krallafa, *Food Chem.* 106 (2008) 1476.
- [29] Y. Jin, Y. Che, S. Batten, P. Chen, J. Zheng, *Eur. J. Inorg. Chem.* 13 (2007) 1925.
- [30] N.S. Oxtoby, A.J. Blake, N.R. Champness, C. Wilson, *Chem.-Eur. J.* 11 (2005) 4643.
- [31] M. Mascal, L. Infantes, J. Chisholm, *Angew. Chem., Int. Ed.* 45 (2005) 32.
- [32] R. Ludwig, *Angew. Chem., Int. Ed.* 40 (2001) 1808.
- [33] S.M. Humphrey, G.F. Weldon, P.T. Wood, *J. Nanosci. Nanotechnol.* 10 (2010) 34.
- [34] B.O. Patrick, C.L. Stevens, A. Storr, R.C. Thompson, *Polyhedron* 22 (2003) 3025.
- [35] Q. Gao, F.L. Jiang, M.Y. Wu, Y.G. Huang, D.Q. Yuan, W. Wei, M.C. Hong, *CrystEngComm* 11 (2009) 918.
- [36] J.Q. Liu, Y.N. Zhang, Y.Y. Wang, J.C. Jin, E.K. Lermontova, Q.Z. Shi, *Dalton Trans.* (2009) 5365.
- [37] D. Ang, G.B. Deacon, P.C. Junk, D.R. Turner, *Polyhedron* 26 (2007) 385.
- [38] Y.B. Xie, Q. Gao, C.Y. Zhang, J.H. Sun, *J. Solid State Chem.* 182 (2009) 1761.
- [39] J.F. Xiang, M. Li, S.M. Wu, L.J. Yuan, J.T. Sun, *Acta Crystallogr., Sect. E* 62 (2006) M1122.
- [40] T. Suga, N. Okabe, *Acta Crystallogr., Sect. C* 52 (1996) 1410.
- [41] S. Martinez-Vargas, R.A. Toscano, J. Valdes-Martinez, *Acta Crystallogr., Sect. E* 63 (2007) M1975.
- [42] D.R. Turner, S.R. Batten, *Acta Crystallogr., Sect. E* 63 (2007) M452.
- [43] L.J. Hao, C.H. Mu, B.B. Kong, *Acta Crystallogr., Sect. E* 64 (2008) M1229.
- [44] S. Shit, J. Chakraborty, S. Sen, G. Pilet, C. Desplanches, S. Mitra, *J. Mol. Struct.* 891 (2008) 19.
- [45] S.H. Yan, X.X. Li, X.J. Zheng, *J. Mol. Struct.* 929 (2009) 105.
- [46] H. Yin, S.X. Liu, *J. Mol. Struct.* 918 (2009) 165.
- [47] C. Stoe, *Stoe & Cie, Darmstadt, Germany, 2002.*
- [48] G.M. Sheldrick, *SHELXL-97 Program for the Solution on of Crystal Refinement*, University of Göttingen, Germany, 1997. p. 97.
- [49] C. Macrae, P. Edgington, P. McCabe, E. Pidcock, G. Shields, R. Taylor, M. Towler, J. Streek, *J. Appl. Crystallogr.* 39 (2006) 453.
- [50] S. Kitagawa, S. Noro, T. Nakamura, *Chem. Commun.* (2006) 701.
- [51] A. Das, G. Pilet, D. Luneau, M.S. El Fallah, J. Ribas, S. Mitra, *Inorg. Chim. Acta* 358 (2005) 4581.
- [52] A.W. Addison, T.N. Rao, J. Reedijk, J. Vanrijn, G.C. Verschoor, *J. Chem. Soc., Dalton* (1984) 1349.
- [53] T.K. Maji, G. Mostafa, R. Matsuda, S. Kitagawa, *J. Am. Chem. Soc.* 127 (2005) 17152.
- [54] H. Aghabozorg, R. Khadivi, M. Ghadermazi, H. Pasdar, S. Hooshmand, *Acta Crystallogr. Sect. E* 64 (2008) M267.
- [55] S.S. Xantheas, *J. Chem. Phys.* 100 (1994) 7523.
- [56] S.S. Xantheas, *J. Chem. Phys.* 102 (1995) 4505.
- [57] D. Braga, F. Grepioni, E. Tedesco, K. Biradha, G.R. Desiraju, *Organometallics* 16 (1997) 1846.
- [58] E.E. Sileo, D. Vega, R. Baggio, M.T. Garland, M.A. Blesa, *Aust. J. Chem.* 52 (1999) 205.