Construction of diverse supramolecular assemblies of dimetal subunits differing in coordinated water molecules via strong hydrogen bonding interactions: Synthesis, crystal structures and spectroscopic properties

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Abstract. Three new supramolecular assemblies (constructed through strong hydrogen bonding) of $[\text{Co}_2(\text{bpta})_2(\text{adc})(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Cu}_2(\text{bpta})_2(\text{fum})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**2**) and $[\text{Cu}_2(\text{bpta})_2(\text{tdc})(\text{H}_2\text{O})(\text{ClO}_4)](\text{ClO}_4) \cdot 3\text{H}_2\text{O}$ (**3**), which are synthesised by one pot self-assembly of the metal salt, bpta ligand and the corresponding dicarboxylate under the same reaction conditions, are reported (where adc = acetylene dicarboxylate, fum = fumarate, tdc = 2,5-thiophenedicarboxylate and bpta = N,N'-bis(2-pyridylmethyl)-tert-butylamine). These compounds have varying degrees of coordinated water molecules per dimetal subunits (four for **1**, two for **2** and one for **3**, respectively). Furthermore, the orientation of the coordinated water molecules in **1** and **2**, with respect to the mono (carboxylato)-bridged dimetal subunit, is different (cis and trans, respectively). On the other hand, there is a coordinated perchlorate ion in **3** making the two metal centers inequivalent. Unlike **1** and **3**, there are no lattice water molecules in **2**. This difference in the dimetal subunit in **1–3** and the presence or absence of the lattice water molecules are the keys to forming the diverse supramolecular assemblies. In **1** and **3**, the involvement of lattice water molecules in the construction of such assemblies is distinctly different. In case of **2**, the formation of supramolecular assembly depends on the coordinated water molecule (trans to each other) and thus a ladder shaped supramolecular assembly is the result. The strength of hydrogen bonding observed in the networks of **1–3** is indicated in the $\text{O} \cdots \text{O}$ distances (2.596 Å to 3.160 Å) and the $\text{O}-\text{H} \cdots \text{O}$ angles 124° to 176°. All are characterised by elemental analysis, FTIR spectroscopy and single crystal X-ray diffraction studies.

Keywords. Supramolecular; hydrogen bonding; flexible ligand; dicarboxylates.

1. Introduction

The field of supramolecular chemistry has seen an exponential growth in the last few decades due to interdisciplinary interests in crystal engineering of supramolecular assemblies that are targeted for a variety of potential applications, such as catalysis, separation, sensors, gas storage, luminescent materials, ion exchange, magnetism, etc.^{1–3} Synthons in a coordination supramolecular assembly are held together through various interactions, such as metal-donor atom coordinate bonds, strong and/or weak hydrogen bonds, $\pi - \pi$ stacking of aromatic moieties, $\text{C}-\text{H} \cdots \text{O}$ interactions, etc.⁴ Among these various interactions, hydrogen bonding is the most important one to study for its importance in the biological systems, in understanding the structure of water, etc. The use of metal centres or metal

atom clusters as building blocks adds to the advantage due to different binding abilities of the metal centre. The selection of ancillary ligands and the multitopic organic linkers is crucial in making such assemblies with varied dimensionality. The role of ancillary ligands that surround and protect the metal cores leaving open sites for the linkers is of great importance in making such supramolecular assemblies. The strategy of a step-wise association of discrete synthons, such as mono- or di-nuclear metal complexes, to construct supramolecular assemblies of higher dimensions shows the hierarchical importance of the two bondings (coordination bonds and hydrogen bonds) that are orthogonal in nature.^{5–10} For our interests to explore and identify the factors governing the formation of supramolecular assemblies through various interactions, a systematic study has been carried out using a flexible tridentate ancillary ligand and multitopic dicarboxylate linkers with Co(II) and Cu(II) as the metal centre.

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In this paper, using the tridentate ligand, bpta = N,N'-bis(2-pyridylmethyl)-tert-butylamine, we report the formation of diverse supramolecular assemblies from the dinuclear metal complexes: $[\text{Co}_2(\text{bpta})_2(\text{adc})(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Cu}_2(\text{bpta})_2(\text{fum})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**2**) and $[\text{Cu}_2(\text{bpta})_2(\text{tdc})(\text{H}_2\text{O})(\text{ClO}_4)](\text{ClO}_4) \cdot 3\text{H}_2\text{O}$ (**3**), where adc = acetylene dicarboxylate, fum = fumarate and tdc = 2,5-thiophenedicarboxylate. The dimetal subunits in these complexes are connected through extensive hydrogen bonding network of coordinated water molecules, lattice water molecules (in case of **1** and **3**) and uncoordinated oxygen atoms of the carboxylate groups. Scheme 1 shows the structure of the ligand and dicarboxylate linkers used in this study.

2. Experimental

2.1 Materials and methods

All chemicals and solvents used for synthesis were obtained from commercial sources and were used as received, without further purification. All reactions were carried out under aerobic conditions. The bpta ligand was prepared by modifying the literature procedure.¹¹

2.2 Physical measurements

The ^1H NMR spectrum of the ligand was obtained in CDCl_3 solution at 25°C on a Bruker ARX-400 spectrometer; chemical shifts were reported relative to the residual solvent signals. The elemental analysis (C, H, N) was carried out using a Mettler CHNS analyzer. IR spectra were measured in the $4000\text{--}400\text{ cm}^{-1}$ range on

a Perkin-Elmer Spectrum I spectrometer with samples prepared as KBr pellets.

Caution! In this study metal perchlorates were used without any problem but special care should be taken while handling such dangerous salts.

2.3 General synthesis method

In a round bottom flask (RBF) y mmol of $\text{M}(\text{ClO}_4)_2$ and y mmol of the tridentate ligand were dissolved in 1.5 to 3 mL of methanol while stirring. To this was added a clear solution of the disodium salt of a dicarboxylate (Na_2dc) which was prepared using $y/2$ mmol of the dicarboxylic acid and y mmol of sodium hydroxide in 1 mL methanol and 1 mL to a minimum amount of water. The reaction mixture was stirred for another 3 to 4 hours at room temperature. Either a clear solution (in case of **1** and **3**) or a solid precipitate (in case of **2**) was obtained which was processed further to get the desired product.

2.3a $[\text{Co}_2(\text{bpta})_2(\text{adc})(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**1**): It was prepared using the sodium salt of acetylene dicarboxylic acid {14 mg (0.125 mmol) of acetylene dicarboxylic acid and 10 mg (0.25 mmol) of sodium hydroxide}, 48 mg (0.125 mmol) of $\text{Co}(\text{ClO}_4)_2$ in 3 mL methanol and 32 mg (0.125 mmol) of bpta. No precipitate was obtained; the pink filtrate was evaporated to dryness. After re-dissolving the solid residue in 2 mL of dry methanol completely, 10 mg of KCl was added and stirred for 10 h. A white solid that appeared was removed via filtration and the filtrate was evaporated to dryness to isolate a pink solid. Yield: 39 mg (54%). Anal. Calcd (%) for $\text{C}_{36}\text{H}_{54}\text{N}_6\text{Co}_2\text{Cl}_2\text{O}_{18}$ (MW 1047.6): C, 41.27; H, 5.15; N, 8.02. Found: C, 41.62; H, 5.25; N, 8.09. Selected FTIR peaks (KBr, cm^{-1}): 3404, 1567, 1435, 1345, 1096, 764, 621.

Scheme 1. Structures of the bpta ligand and the dicarboxylates.

Table 1. Crystal structure data and refinement parameters for **1**, **2** and **3**.

	1	2	3
Chemical formula	C ₃₆ H ₅₄ Cl ₂ Co ₂ N ₆ O ₁₈	C ₃₆ H ₄₈ Cl ₂ Cu ₂ N ₆ O ₁₄	C ₃₈ H ₅₂ Cl ₂ Cu ₂ N ₆ O ₁₆ S
Formula Weight	1047.65	986.78	1078.90
Temperature (K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	15.2144(15)	19.9346(10)	12.3812(4)
<i>b</i> (Å)	23.344(2)	18.8069(10)	26.8191(9)
<i>c</i> (Å)	26.753(3)	13.6719(8)	14.3028(5)
α (°)	90	90	90
β (°)	99.364(5)	122.227(3)	96.322(2)
γ (°)	90	90	90
<i>Z</i>	8	4	4
Volume (Å ³)	9375.1(16)	4336.0(4)	4720.4(3)
Density (g/cm ³)	1.484	1.512	1.518
μ (mm ⁻¹)	0.898	1.175	1.132
Theta range	1.16° to 25.14°	1.86° to 25.10°	1.52° to 25.10°
<i>F</i> (000)	4352	2040	2232
Reflections Collected	87093	12866	32255
Independent reflections	16568	3863	8388
Reflections with <i>I</i> > 2 σ (<i>I</i>)	7608	2476	4788
<i>R</i> _{int}	0.1225	0.0555	0.0825
Number of parameters	1133	278	589
GOF on <i>F</i> ²	1.049	0.967	0.983
Final <i>R</i> ₁ / <i>wR</i> ₂ ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0841/0.2216	0.0536/0.1527	0.0541/0.1395
<i>R</i> ₁ / <i>wR</i> ₂ ^b (all data)	0.1896/0.2819	0.0908/0.1839	0.1012/0.1589
Largest diff. peak and hole (eÅ ⁻³)	1.401 and -1.029	0.561 and -0.533	0.864 and -0.575

^a*R*₁ = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^b*wR*₂ = $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

2.3b [Cu₂(*bpta*)₂(*fum*)(H₂O)](ClO₄)₂ (**2**): It was prepared using the sodium salt of fumaric acid {14.5 mg (0.125 mmol) of fumaric acid and 10 mg (0.25 mmol) of sodium hydroxide}, 46.5 mg (0.125 mmol) of Cu(ClO₄)₂ in 3 mL methanol and 32 mg (0.125 mmol) of *bpta*. A blue precipitate was collected via filtration, washed with methanol and air-dried. Yield: 41 mg (69%). Anal. Calcd (%) for C₃₆H₄₈N₆Cu₂Cl₂O₁₄ (MW 986.8): C, 44.98; H, 4.86; N, 8.57. Found: C, 45.34; H, 4.63; N, 8.38. Selected FTIR peaks (KBr, cm⁻¹): 3438, 1606, 1563, 1481, 1441, 1380, 1077, 762, 698, 619.

2.3c [Cu₂(*bpta*)₂(*tdc*)(H₂O)](ClO₄)](ClO₄)·3H₂O (**3**): It was prepared using the sodium salt of thiophene dicarboxylic acid {21.5 mg (0.125 mmol) of thiophene dicarboxylic acid and 10 mg (0.25 mmol) of sodium hydroxide}, 46.5 mg (0.125 mmol) of Cu(ClO₄)₂ in 3 mL methanol and 32 mg (0.125 mmol) of *bpta*. No precipitate was obtained and the dark blue filtrate was evaporated to dryness. After re-dissolving the solid residue in 2 mL of dry methanol completely, 10 mg of KCl was added and stirred for 3 h. A white solid that appeared was filtered off and the filtrate was evaporated to dryness to isolate a dark blue solid. Yield: 64

Scheme 2. Synthesis of **1–3**. **Figure 1.** Structure of the dimetal subunit in **1**.

mg (98%). Anal. Calcd (%) for $C_{38}H_{50}N_6Cu_2Cl_2SO_{15}$ (MW 1060.9): C, 43.02; H, 4.71; N, 7.92. Found: C, 43.36; H, 4.58; N, 7.93. Despite our best efforts, in the

CHN analysis two water molecules could be included while three water molecules were found in its X-ray crystal structure. Selected FTIR peaks (KBr, cm^{-1}):

Table 2. Selected bond distances and bond angles for **1**, **2** and **3**.

1

Bond distances (Å)							
Co1-O1	2.106(5)	Co2-O5	2.119(5)	Co3-O9	2.106(5)	Co4-O13	2.093(5)
Co1-O3	2.115(6)	Co2-O8	2.095(5)	Co3-O11	2.126(5)	Co4-O15	2.073(6)
Co1-O4	2.144(7)	Co2-O7	2.120(5)	Co3-O12	2.123(5)	Co4-O16	2.178(5)
Co1-N1	2.253(6)	Co2-N4	2.235(6)	Co3-N7	2.242(6)	Co4-N10	2.271(6)
Co1-N2	2.121(7)	Co2-N5	2.095(6)	Co3-N8	2.140(7)	Co4-N11	2.103(7)
Co1-N3	2.102(6)	Co2-N6	2.116(6)	Co3-N9	2.118(6)	Co4-N12	2.134(7)
Bond angles (°)							
N3-Co1-O1	173.3(3)	N5-Co2-N6	97.3(2)	O9-Co3-N9	174.6(2)	O15-Co4-O13	88.1(2)
O1-Co1-O3	89.3(2)	N5-Co2-O5	91.0(2)	N9-Co3-O12	87.7(2)	O13-Co4-N11	172.2(2)
O1-Co1-N2	88.1(2)	N6-Co2-O5	171.7(2)	N9-Co3-O11	92.1(2)	O13-Co4-N12	83.0(2)
N3-Co1-O4	87.6(3)	O8-Co2-O7	91.6(2)	O11-Co3-N8	90.4(2)	O15-Co4-O16	87.1(3)
O3-Co1-O4	87.6(3)	O5-Co2-O7	85.8(2)	N9-Co3-N7	78.4(2)	N11-Co4-O16	93.3(3)
N3-Co1-N1	77.6(2)	O8-Co2-N4	163.0(2)	O11-Co3-N7	162.9(2)	O15-Co4-N10	107.9(2)
O3-Co1-N1	166.4(3)	O5-Co2-N4	104.9(2)	O9-Co3-N8	84.1(2)	N11-Co4-N10	77.6(3)
O4-Co1-N1	97.8(3)	N5-Co2-O8	91.7(2)	O12-Co3-N8	172.5(2)	O16-Co4-N10	162.0(2)
N3-Co1-O3	90.2(3)	O8-Co2-N6	89.6(2)	O9-Co3-N7	98.6(2)	O15-Co4-N11	88.5(3)
N3-Co1-N2	98.6(3)	O8-Co2-O5	89.7(2)	O12-Co3-N7	106.3(2)	O15-Co4-N12	170.7(2)
O3-Co1-N2	97.3(3)	N5-Co2-O7	175.4(2)	N8-Co3-N7	77.4(2)	N11-Co4-N12	100.6(3)
O1-Co1-O4	85.7(2)	N6-Co2-O7	86.0(2)	O9-Co3-O12	88.8(2)	O13-Co4-O16	93.6(2)
N2-Co1-O4	172.1(2)	N5-Co2-N4	79.5(2)	O9-Co3-O11	91.9(2)	N12-Co4-O16	90.9(3)
O1-Co1-N1	103.5(2)	N6-Co2-N4	77.2(2)	O12-Co3-O11	87.3(2)	O13-Co4-N10	96.8(2)
N2-Co1-N1	78.8(2)	O7-Co2-N4	98.1(2)	N9-Co3-N8	99.5(2)	N12-Co4-N10	75.8(2)

2

Bond distances (Å)			
Cu1-N1	1.967(4)	Cu1-O1	2.485(4)
Cu1-N2	1.955(4)	Cu1-O2	1.945(3)
Cu1-N3	2.065(4)		
Bond angles (°)			
O2-Cu1-N2	94.35(15)	O2-Cu1-N1	97.12(16)
N2-Cu1-N1	165.78(17)	O2-Cu1-N3	170.12(14)
N2-Cu1-N3	84.99(15)	N1-Cu1-N3	85.14(16)
O2-Cu1-O1	103.37(15)	N2-Cu1-O1	83.39(15)
N1-Cu1-O1	85.79(15)	N3-Cu1-O1	86.37(14)

3

Bond distances (Å)			
Cu1-N1	1.950(4)	Cu2-N4	1.980(4)
Cu1-N2	2.053(4)	Cu2-N5	2.062(4)
Cu1-N3	1.964(4)	Cu2-N6	1.970(4)
Cu1-O1	1.940(3)	Cu2-O3	1.942(3)
		Cu2-O5	2.361(4)
Bond angles (°)			
O1-Cu1-N1	98.27(17)	O3-Cu2-N4	96.47(16)
N1-Cu1-N3	163.54(18)	O3-Cu2-N5	169.19(16)
N1-Cu1-N2	85.03(17)	N4-Cu2-N5	84.23(16)
O1-Cu1-N3	94.09(16)	N6-Cu2-O5	90.01(16)
O1-Cu1-N2	169.15(16)	N5-Cu2-O5	97.99(15)
N3-Cu1-N2	84.83(16)	O3-Cu2-N6	96.36(17)
O3-Cu2-O5	92.82(16)	N6-Cu2-N4	166.60(18)
N4-Cu2-O5	85.50(15)	N6-Cu2-N5	83.90(17)

3435, 1610, 1586, 1377, 1352, 1121, 1108, 1091, 777, 624.

2.4 Single crystal X-ray data collection and refinement

From a batch of crystals of each compound that was transferred from mother liquor to mineral oil for manipulation and selection, a single crystal was placed inside a nylon loop on a goniometer head. Initial crystal evaluation and data collection were performed on a Kappa APEX II diffractometer equipped with a CCD detector (with the crystal-to-detector distance fixed at 60 mm) and sealed-tube monochromated MoK α radiation and interfaced to a PC that controlled the crystal centering, unit cell determination, refinement of the cell parameters and data collection through the program APEX2.¹² By using the program SAINT¹² for the integration of the data, reflection profiles were fitted, and values of F^2 and $\sigma(F^2)$ for each reflection were obtained. Data were also corrected for Lorentz and polarization effects. The subroutine XPREP¹² was used for the processing of data that included determination of space group, application of an absorption correction (SADABS),¹² merging of data, and generation of files necessary for solution and refinement. The crystal structures were solved and refined using SHELX 97.¹³ In each case, the space group was chosen based on systematic absences and confirmed by the successful refinement of the structure. Positions of most of the non-hydrogen atoms were obtained from a direct method solution. Several full-matrix least-squares/difference Fourier cycles were performed, locating the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. In order to obtain reasonable thermal parameters compared to other atoms, the lowest residual factors and optimum goodness of fit with convergence of refinement, occupancy factors of the oxygen atoms in the disordered perchlorate anions were adjusted accordingly. All hydrogen atoms of **1–3** except those for lattice water molecules O37 and O15 in **1** and **3**, respectively, were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. In the final difference Fourier map of **1**, the largest residual peak of 1.401 e/Å³ located close to one of the perchlorate ions has been found to be insignificant while in those of **2** and **3** there was no significant peaks >1 e/Å³. Crystallographic parameters and basic information pertaining to data collection and structure refinement for all compounds are summarized in table 1. All figures were drawn using MERCURY V 3.0¹⁴ and hydrogen bonding parameters were generated

using PLATON.¹⁵ The final positional and thermal parameters of the non-hydrogen atoms for all structures are listed in the CIF files.

3. Results and Discussion

3.1 Synthesis

Supramolecular assemblies of **1–3** were prepared from the one pot self-assembly reaction of the metal salt, bpta and the respective sodium salt of the acid (scheme 2). In case of **1** and **3**, the desired product was obtained from the filtrate utilizing the process to remove free NaClO₄ with slight excess of KCl in dry methanol. On the other hand, a blue solid of **2** was obtained directly under the same reaction conditions. It should be noted here that the combination of Cu(II) and adc linker did not allow the isolation of a product similar to **1**; in fact, there are only a few adc complexes reported in the literature where any ancillary ligand is used.^{16,17}

3.2 Spectroscopic data

The IR spectra of **1**, **2** and **3** were recorded in the solid state as KBr pellets. The peaks at 3404 cm⁻¹ (**1**), 3438 cm⁻¹ (**2**) and 3434 cm⁻¹ (**3**) correspond to the O-H stretching frequencies of water molecules. The asymmetric and symmetric stretching frequencies for the carboxylate group appears at 1567 and 1345 cm⁻¹ (**1**), 1563 and 1380 cm⁻¹ (**2**) and 1586 and 1377 cm⁻¹ (**3**), respectively. A difference of 183 to 222 cm⁻¹ between the two stretching frequencies corresponds to the monodentate binding mode of the carboxylate. The peaks at 1096 and 621 cm⁻¹ (**1**) and 1077 and 619 cm⁻¹ (**2**) are due to the anionic perchlorate. In case of **3**, the peaks at 1121, 1108, 1091 and 623 cm⁻¹ can be attributed to the anionic and coordinated perchlorates present in it.

Figure 2. A perspective view of the 3D supramolecular assembly in **1** (hanging contacts are deleted for clarity).

Other peaks with a shift by few wave numbers are due to the bpta ligand which is common in all.

3.3 Description of the structures

Single crystals of all three compounds were grown by slow evaporation of the solution in a mixture of methanol and water.

3.3a $[Co_2(bpta)_2(adc)(H_2O)_4](ClO_4)_2 \cdot 2H_2O$ (**1**): It is a dinuclear cobalt(II) complex that crystallizes in the monoclinic $P2_1/c$ space group. There are two independent molecules in the asymmetric unit. Each hexacoordinated Co(II) center is surrounded by three nitrogens of the bpta ligand, two coordinated water molecules and one oxygen of the adc (figure 1). The carboxylate binds to the Co(II) centers in a bis(monodentate) syn-syn fashion which is different from those found in the

Table 3. Hydrogen bonding parameters for **1**, **2** and **3**.^a

D—H...A	r (D-H), Å	r (H...A), Å	r (D...A), Å	<D—H... (°)	Symmetry
1					
O3 —H3A...O2	0.89	1.93	2.646(10)	137	
O4 —H4A...O32	0.87	2.36	3.160(19)	153	$x, 1/2-y, -1/2+z$
O4 —H4B...O21	0.87	2.21	3.068(14)	168	$1-x, 1-y, -z$
O7 —H7A...O30	0.85	2.28	3.086(17)	158	$2-x, -1/2+y, 1/2-z$
O7 —H7B...O35	0.85	2.21	2.775(8)	124	$1-x, -1/2+y, 1/2-z$
O8 —H8A...O2	0.86	1.87	2.702(9)	163	$2-x, -y, -z$
O8 —H8B...O6	0.86	1.8	2.596(8)	153	
O11 —H11A...O14	0.87	1.89	2.732(7)	164	$1-x, 1-y, -z$
O11 —H11B...O38	0.87	1.81	2.673(8)	174	
O12 —H12A...O28	0.85	2.28	2.932(15)	133	$1-x, -1/2+y, 1/2-z$
O15 —H15B...O36	0.86	1.94	2.727(10)	153	$x, 1/2-y, -1/2+z$
O16 —H16A...O35	0.85	2.18	2.869(8)	138	$x, 1/2-y, -1/2+z$
O35 —H35D...O6	0.85	1.82	2.668(8)	176	
O35 —H35E...O11	0.85	2.26	3.092(7)	165	$1-x, 1/2+y, 1/2-z$
O36 —H36E...O25	0.85	2.55	3.367(18)	162	
O38 —H38C...O10	0.85	1.9	2.681(9)	153	$1-x, 1-y, -z$
O38 —H38D...O2	0.85	2.36	3.150(10)	156	
C1 —H1A...O18	0.97	2.6	3.558(13)	172	
C1 —H1B...O21	0.97	2.29	3.105(11)	142	$1-x, 1-y, -z$
C5 —H5...O19	0.93	2.6	3.368(12)	141	$1-x, 1-y, -z$
C16 —H16E...O1	0.96	2.51	3.355(10)	147	
C17 —H17A...O1	0.96	2.51	3.359(9)	147	
C27 —H27A...O17	0.97	2.49	3.284(13)	139	$2-x, -1/2+y, 1/2-z$
C28 —H28A...O30	0.97	2.56	3.276(18)	130	$2-x, -1/2+y, 1/2-z$
C33 —H33...O8	0.93	2.56	3.098(9)	117	
C36 —H36A...O5	0.96	2.47	3.346(11)	151	
C44 —H44A...O23	0.97	2.55	3.338(11)	139	
C49 —H49...O33	0.93	2.39	3.29(2)	163	
C53 —H53A...O15	0.96	2.5	3.387(11)	153	
C64 —H64A...O23	0.97	2.52	3.357(11)	145	$1-x, -1/2+y, 1/2-z$
C64 —H64B...O24A	0.97	2.55	3.21(2)	125	$1-x, -1/2+y, 1/2-z$
C68 —H68...O33	0.93	2.41	3.27(3)	153	$2-x, -1/2+y, 1/2-z$
C72 —H72A...O12	0.96	2.55	3.413(10)	150	
2					
O1 —H1A...O3	0.85	1.97	2.750(5)	149	$x, -y, -1/2+z$
O1 —H1B...O6	0.86	2.35	3.112(15)	146	
O1 —H1B...O7	0.86	2.28	3.114(10)	163	
C13—H13...O6	0.93	2.33	3.227(15)	162	$1/2-x, 1/2-y, 1-z$
3					
O5—H5A...O14	0.87	1.91	2.747	162	$1/2+x, 1/2-y, -1/2+z$
O14—H14D...O15	0.85	2.32	2.954(10)	131	
O16—H16A...O4	0.85	2.31	3.055(13)	147	$-1+x, y, z$
C24—H24...O6	0.93	2.51	3.362(9)	152	

^aValues in parenthesis are estimated standard deviations in the last significant digits.

Mn(II)-adc complex of the same ligand.¹⁶ The Co-O_{water} distances vary from 2.073 Å to 2.178 Å whereas Co-O_{adc} distances vary from 2.093 Å to 2.119 Å. All other selected bond distances and angles are listed in table 2.

Two discrete dinuclear units are hydrogen bonded with each other via coordinated and lattice water molecules to form a supramolecular assembly as shown in figure 2. All the hydrogen bonding parameters are listed in table 3. The coordinated water molecule O4 of one discrete dinuclear unit is hydrogen bonded to the O32 (perchlorate oxygen atom), O8 is hydrogen bonded to O2 (uncoordinated oxygen atom of adc of the next same subunit), O8 is intramolecularly hydrogen bonded to O6 (uncoordinated oxygen atom of adc of same subunit), O7 is hydrogen bonded to O35 (lattice water molecule) which is further hydrogen bonded to O16 (coordinated water molecule on second subunit) connecting the two subunits. Similar hydrogen bonding pattern is found for the second dinuclear unit. Thus, these two subunits are connected with each other via a network of hydrogen bonding which can be clearly seen in figure 3. In another view shown in figure 4 the two layers formed by hydrogen bonding of two subunits are arranged in a spiral manner and it forms a channel in which perchlorate anions are sitting; in other words, a perchlorate channel is formed between the two hydrogen bonded units.

3.3b $[Cu_2(bpta)_2(fum)(H_2O)_2](ClO_4)_2$ (**2**): It is a discrete dinuclear Cu(II) complex that crystallizes in the *C2/c* space group. Due to the presence of a 2-fold axis, the five coordinated Cu(II) centers are crystallographically equivalent. The fumarate binds in a bis(monodentate) syn-anti mode. The Cu-O_{water}

Figure 3. Hydrogen bonded network in **1** along the 'a' axis.

Figure 4. A schematic view of the perchlorate channel between the hydrogen bonded network of two independent units in **1**.

distance is 2.485 Å whereas Cu-O_{fum} distance is 1.946 Å. In figure 5, the schematic drawing of the dimetal synthon in **2** shows trans orientation of the coordinated water molecules that are involved in the formation of a supramolecular assembly (*vide infra*). Similar types of complexes are reported with 1,10-phenanthroline but with no coordinated water molecule on the Cu(II) center.¹⁸ The selected bond distances and angles are listed in table 2.

Due to the trans orientation of the coordinated water molecules on the Cu(II) centers, O1 (coordinated

Figure 5. Structure of the dimetal subunit in **2**.

Figure 6. A ladder-shaped supramolecular assembly in **2** (perchlorates are not included for clarity).

Figure 7. A view of the dimetal subunit (along with the free perchlorate ion) in **3**.

water molecule) is hydrogen bonded to the uncoordinated oxygen O3 of the fumarate of next dinuclear unit forming a ladder shaped supramolecular assembly shown in figure 6 (O1... O3 distance: 2.750 Å and O1-H1A... O3 angle: 149°). The coordinated water molecule O1 is also hydrogen bonded to one of the perchlorate anions which is not shown in the figure for clarity. All hydrogen bonding parameters are listed in table 3.

3.3c $[\text{Cu}_2(\text{bpta})_2(\text{tdc})(\text{H}_2\text{O})(\text{ClO}_4)](\text{ClO}_4) \cdot 3\text{H}_2\text{O}$ (**3**): The Cu (II) centers in **3** are pentacoordinated and inequivalent. One Cu(II) center is surrounded by three nitrogens of the ligand, one coordinated water molecule and one oxygen of tdc while the other does not have coordinated water molecule and its fifth site is occupied by the perchlorate oxygen. The tdc binds in a bis(monodentate) syn-syn mode between the two Cu(II) centers as shown in figure 7, similar to the ones with 1,10-phenanthroline and imidazole ligands reported in the literature.^{19–21} The selected bond distances and angles are listed in table 2.

The dinuclear subunit forms a polymeric chain structure in one direction due to hydrogen bonding of the coordinated perchlorate oxygen (O10) with uncoordinated oxygen atom of tdc (O2) via a lattice water molecule (O15) (figure 8), which is further hydrogen bonded to another lattice water molecule O14. In the next layer, the dinuclear subunits are hydrogen bonded via the third lattice water molecule (O16) and the coordinated water molecule (O05) and uncoordinated

Figure 8. A perspective view of the 3D supramolecular assembly in **3** (hanging contacts are deleted for clarity).

carboxylate oxygen atom (O4). These alternate layers are repeated to form the 3D supramolecular assembly in **3**. The hydrogen bonding parameters for **3** are listed in table 3.

4. Conclusion

We have reported structural diversities in the supramolecular assemblies with varying degrees of coordinated water molecules per dimetal subunits of Co(II) or Cu(II) (four for **1**, two for **2** and one for **3**, respectively) comprised of a flexible tridentate ligand and different dicarboxylate linkers. It is clear that these carboxylates play an important role in determining the coordination architectures with respect to their size, conformation and properties. Unlike **1** and **3**, there is no lattice water molecule in **2**. However, the role played by lattice water molecules in **1** and **3** in the construction of such assemblies is distinctly different. The formation of a ladder shaped supramolecular assembly in **2** is the result of the trans orientation of the coordinated water molecules in the dimetal subunit. Based on the results presented here, further work continues in our laboratory to understand the effect of the change in the ancillary ligands and other metal centres.

Supplementary Information

Crystallographic data of the structures **1–3** in CIF format (CCDC 1000552–1000554, respectively). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)

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