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Robust Heteromeric Hydrogen-bonded Self-assemblies Based on $[M(H_2biim)_2(H_2O)_{n-2}]^2$ ($M=Cd^{2+}, Co^{2+}, Zn^{2+}; n=1, 2$) Building Blocks and Carboxylates

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Robust Heteromeric Hydrogen-bonded Self-assemblies Based on $[M(H_2biim)_2(H_2O)_n]^{2+}$ ($M = Cd^{2+}, Co^{2+}, Zn^{2+}; n = 1, 2$) Building Blocks and Carboxylates

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Four new complexes $[Zn(H_2biim)_2(H_2O)_2](Hbdc)_2 \cdot (H_2biim) \cdot 2H_2O$ (1), $[Zn(H_2biim)_2(H_2O)](bdc) \cdot CH_3OH$ (2), $[Co(H_2biim)_2(H_2O)_2](Hbtc) \cdot 4H_2O$ (3) and $[Cd(H_2biim)_2(H_2O)(bdc)] \cdot H_2O$ (4) (where $H_2biim = 2,2'$ -biimidazole, $bdc = 1,3$ -benzenedicarboxylate and $btc = 1,3,5$ -benzenetricarboxylate) have been synthesized and characterized by single-crystal X-ray diffraction. The $[M(H_2biim)_2(H_2O)_n]^{2+}$ building blocks are assembled with carboxylates via charge-assisted $N-H \cdots O$ and $O-H \cdots N$ hydrogen bonds ($N \cdots O = 2.607 \sim 2.926 \text{ \AA}$, $\angle N-H \cdots O = 151 \sim 176^\circ$) into 1-D ribbons (1–3) and 3-D network (4). The ribbons are further arranged into 3-D networks via hydrogen bonds between carboxylate and water molecules as well as the free H_2biim molecule (1) or methanol molecule (2). In complex 2, the CH_3OH molecules are clathrated in the cavities. The results show that three robust heteromeric hydrogen-bonded synthons, namely $R_2^2(9)$, $R_1^1(7)$ and $C(4)[R_2^2(9)]$, can be exploited to assemble the $[M(H_2biim)_2(H_2O)_n]^{2+}$ ($M = Cd, Co$ and Zn , $n = 1, 2$) building blocks with dicarboxylates and tricarboxylate into multi-dimensional networks.

Keywords: 2,2'-Biimidazole; 1,3-Benzenedicarboxylate; 1,3,5-Benzenetricarboxylate; Hydrogen bond; Crystal engineering

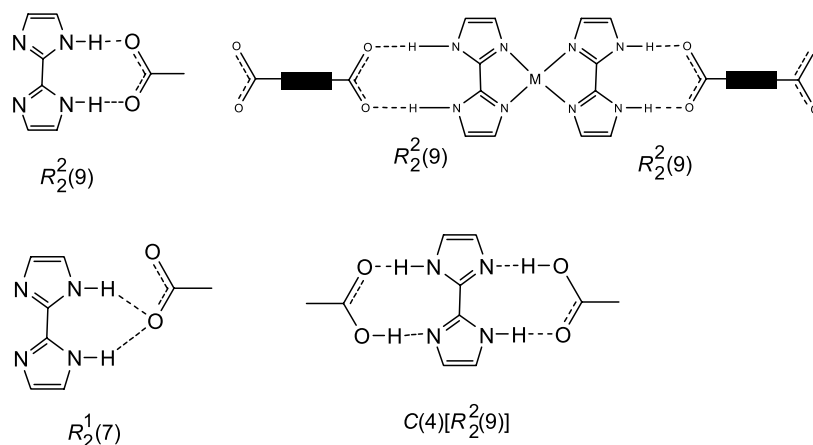
INTRODUCTION

The assembly of coordination polymers has been a great growth in supramolecular chemistry due to their structural diversities and potential applications as new materials [1–6]. The control of dimensionality is still a major challenge in the design and synthesis of organic–inorganic frameworks since the resultant structure can be frequently modulated by various factors such as medium, temperature, metal–ligand ratio, template and counter-ion.

Hydrogen bond is a powerful assembling force in constructing supramolecule and provides useful information to understand a complicated process in biological systems [7–9]. Hydrogen bond is regarded as less robust than the coordination bond in the construction of hybrid inorganic–organic materials. However, this disadvantage can be overcome via forming multiple hydrogen bonds. The neutral 2,2'-biimidazole (H_2biim) is an excellent candidate for construction of hybrid materials via supramolecular interactions [10–23]. It not only coordinates to metal ion but also provides two $N-H$ hydrogen-bond donating sites for multi-dimensional network assembly. Furthermore, it can form robust heteromeric hydrogen-bonded synthons such as $R_2^2(9)$, $R_1^1(7)$ and $C(4)[R_2^2(9)]$ (Scheme 1) with carboxylates in the solid state [24–31]. This type of interaction should be particularly strong, since the $N-H \cdots O$ unit is nearly linear ($\sim 165^\circ$) and the $N \cdots O$ separation (2.68 \AA) is close to the lower limit of the accepted range [32]. In addition, the carboxylate group and the H_2biim ligand form a nearly coplanar arrangement. However, the architecture of multi-dimensional networks based on H_2biim and dicarboxylates or tricarboxylate into hybrid materials are very rare [29–31].

Our previous work on the synthesis and structural characterization of $[M(H_2biim)_2(H_2O)_2](X)_2$ ($M = Zn^{2+}$ and Co^{2+} , $X =$ acetate or isonicotinate) has shown that two H_2biim ligands are on the same equatorial plane and *trans* to each other. The $[M(H_2biim)_2(H_2O)_2]^{2+}$ core is further connected to the other two carboxylate anions via strong $N-H \cdots O$ hydrogen bonds [33,34]. It suggests that multi-dimensional structure can be obtained when

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SCHEME 1 The robust heteromeric hydrogen-bonded synthons constructed by H₂biim and carboxylates.

dicarboxylate or tricarboxylate anions are employed [29–31,35]. By using this strategy, we report here on the syntheses and structural characterization of four new complexes [Zn(H₂biim)₂(H₂O)₂](Hbdc)₂·(H₂biim)·2H₂O (1), [Zn(H₂biim)₂(H₂O)](bdc)·CH₃OH (2), [Co(H₂biim)₂(H₂O)₂](Hbtc)·4H₂O (3) and [Cd(H₂biim)₂(H₂O)](bdc)·H₂O (4) (where bdc = 1,3-benzenedicarboxylate and btc = 1,3,5-benzenetricarboxylate), in which three robust hydrogen-bonded synthons $R_2^2(9)$, $R_2^1(7)$ and $C(4) \times [R_2^2(9)]$ (Scheme 1) have been exploited to construct 3-D networks through the assembly of the [M(H₂biim)₂(H₂O)_{*n*}]²⁺ (*n* = 1,2) building blocks and polycarboxylates.

EXPERIMENTAL

Materials and General Methods

The reagents and solvents employed were commercially available and used as received without further purification. The C, H and N microanalyses were carried out with a Vario EL elemental analyser. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ on a Bruker-EQUINOX 55 FT-IR spectrometer. ¹H NMR spectra were recorded on a Varian 300 MHz spectrometer at 25°C. The ligand H₂biim was synthesized in accordance with the published procedure [36].

Synthesis of [Zn(H₂biim)₂(H₂O)₂](Hbdc)₂·(H₂biim)·2H₂O (1)

To a methanolic solution (10 ml) containing H₂biim (0.469 g, 3.5 mmol), Zn(NO₃)₂·6H₂O (1 mmol) dissolved in methanol (10 ml) was added. The mixture was refluxed until the ligand had dissolved. An aqueous solution (10 ml) of sodium 1,3-benzenedicarboxylate (0.210 g, 1.0 mmol) was added into the solution. The resulting mixture was adjusted to

pH ≈ 5.0 with dilute nitric acid, and then stirred at 60°C for 2 h. The insoluble residues were removed by filtration, and the filtrate was evaporated slowly at room temperature for about one week to yield colorless crystalline product (45% yield). C₃₄H₃₆N₁₂O₁₂Zn 1 (870.14); C, 46.89 (calc. 46.99); H, 4.14 (4.17); N, 19.31 (19.18)%. IR (KBr, cm⁻¹): 3434–2529 m, 1604 s, 1536 vs, 1477 m, 1433 s, 1362 vs, 1271 m, 1126 m, 998 m, 894 m, 743 s, 712 s, 689 m.

Synthesis of [Zn(H₂biim)₂(H₂O)](bdc)·CH₃OH (2)

ZnCl₂·6H₂O (1 mmol) was dissolved in methanol (10 ml) and then added into a methanolic solution (10 ml) of H₂biim (0.268 g, 2 mmol). The mixture was refluxed until the ligand had dissolved. An aqueous solution (10 ml) of sodium 1,3-benzenedicarboxylate (0.210 g, 1.0 mmol) was added into the resulting solution which was then adjusted to pH ≈ 5.4 with dilute hydrochloric acid, and stirred at 60°C for 2 h. The insoluble materials were removed by filtration, and the filtrate was allowed to stand at room temperature. Colorless product was obtained in 50% yield by slow evaporation at room temperature for about one week. C₂₁H₂₂N₈O₆Zn 2 (547.86); C, 45.60 (calc. 46.04); H, 4.02 (4.05); N, 20.44 (20.45)%. IR (KBr, cm⁻¹): 3443 m, 3262 br, 2957 m, 2886 m, 27151 m, 2656 w, 1580 vs, 1512 m, 1361 vs, 1333 m, 1262 m, 1170 w, 1150 m, 1105 m, 1071 s, 953 m, 898 w, 845 m, 810 m, 746 s, 690 w, 659 m, 667 m, 585 m, 527 m.

Synthesis of [Co(H₂biim)₂(H₂O)₂](Hbtc)·4H₂O (3)

CoCl₂·6H₂O (1 mmol) was dissolved in methanol (10 ml) and added into a methanolic solution (10 ml) of H₂biim (0.268 g, 2 mmol). The mixture was refluxed until the ligand had dissolved. An aqueous solution (10 ml) of sodium 1,3,5-benzenetricarboxylate (0.210 g, 1.0 mmol) was added to the resulting solution. The resulting mixture was adjusted to pH ≈ 5.4 with dilute hydrochloric acid, and then stirred

TABLE I Crystal data and structure refinement for complexes 1–4

Complex	1	2	3	4
Molecular formula	C ₃₄ H ₃₆ N ₁₂ O ₁₂ Zn	C ₂₁ H ₂₂ N ₈ O ₆ Zn	C ₂₁ H ₂₈ N ₈ O ₁₂ Co	C ₂₀ H ₂₀ N ₈ O ₆ Cd
Formula weight	870.12	547.85	643.43	580.84
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	15.013(1)	13.274(1)	12.083(1)	13.403(1)
<i>b</i> /Å	8.985(1)	15.471(1)	13.180(1)	9.772(1)
<i>c</i> /Å	14.155(1)	21.836(1)	17.998(1)	34.461(2)
β /°	103.702(2)		102.358(2)	94.208(1)
<i>V</i> /Å ³	1855.1(3)	4484.3(4)	2799.7(4)	4501.5(4)
<i>Z</i>	2	8	4	8
ρ_{calc} (g cm ⁻³)	1.558	1.623	1.714	1.623
μ (cm ⁻¹)	0.744	1.154	1.026	1.154
Reflections collected	9431	36735	14421	18937
Data/parameters	3272/269	5398/327	4927/387	5255/324
<i>R</i> ₁ (<i>I</i> > 2 σ)*	0.0532	0.0357	0.0465	0.0318
<i>wR</i> ₂	0.1289	0.1157	0.1292	0.0936

$$^* R_1 = \sum \|F_o\| - |F_c| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

TABLE II Selected bond lengths [Å] and angles [°] for complexes 1–4

1			
Zn–N(1)	2.154(3)	Zn–N(2)	2.138(3)
Zn–O(1w)	2.161(3)	O(2)–C(16)	1.237(5)
O(3)–C(16)	1.250(5)	O(4)–C(17)	1.290(5)
O(5)–C(17)	1.228(5)	O(1w)–Zn–N(1)	90.7(1)
O(1w)–Zn–N(2)	83.1(1)	N(2)–Zn–N(1)	79.7(1)
O(2)–C(16)–O(3)	123.9(1)	O(4)–C(17)–O(5)	122.6(1)
2			
Zn–O(1W)	2.023(2)	Zn–N(1)	2.061(2)
Zn–N(3)	2.148(2)	Zn–N(5)	2.082(2)
Zn–N(7)	2.193(2)	O(2)–C(19)	1.245(2)
O(3)–C(19)	1.258(2)	O(4)–C(20)	1.246(2)
O(5)–C(20)	1.258(2)	O(1W)–Zn–N(1)	101.1(1)
O(1W)–Zn–N(3)	97.6(1)	O(1W)–Zn–N(5)	104.5(1)
O(1W)–Zn–N(7)	100.9(1)	N(1)–Zn–N(3)	79.4(1)
N(1)–Zn–N(5)	154.1(1)	N(1)–Zn–N(7)	92.0(1)
N(3)–Zn–N(5)	100.5(1)	N(3)–Zn–N(7)	160.8(1)
N(5)–Zn–N(7)	79.7(1)	O(4)–C(20)–O(5)	124.8(2)
O(2)–C(19)–O(3)	123.9(2)		
3			
Co–O(1W)	2.175(2)	Co–O(2W)	2.119(2)
Co–N(1)	2.140(3)	Co–N(3)	2.121(3)
Co–N(5)	2.151(3)	Co–N(7)	2.116(3)
O(3)–C(20)	1.232(3)	O(4)–C(20)	1.270(3)
O(5)–C(19)	1.240(4)	O(6)–C(19)	1.267(4)
O(7)–C(21)	1.211(4)	O(8)–C(21)	1.315(4)
N(1)–Co–N(3)	79.7(1)	N(1)–Co–N(5)	177.2(1)
N(1)–Co–N(7)	102.4(1)	N(5)–Co–N(7)	79.4(1)
N(5)–Co–N(3)	98.4(1)	N(3)–Co–N(7)	176.6(1)
O(1w)–Co–O(2w)	176.1(1)	O(1w)–Co–N(1)	86.6(1)
O(1w)–Co–N(3)	90.6(1)	O(1w)–Co–N(5)	91.3(1)
O(1w)–Co–N(7)	87.4(1)	O(2w)–Co–O(1w)	90.5(1)
O(2w)–Co–N(3)	92.1(1)	O(2w)–Co–N(5)	91.6(1)
O(2w)–Co–N(7)	90.5(1)	O(7)–C(21)–O(8)	122.4(3)
O(5)–C(19)–O(6)	124.2(3)	O(3)–C(20)–O(4)	124.3(3)
4			
Cd–O(1W)	2.376(2)	Cd–O(2)	2.485(2)
Cd–N(1)	2.278(2)	Cd–N(3)	2.304(2)
Cd–N(5)	2.360(2)	Cd–N(7)	2.291(2)
O(2)–C(19)	1.269(3)	O(3)–C(19)	1.242(3)
O(4)–C(20)	1.255(3)	O(5)–C(20)	1.243(3)
O(1W)–Cd–O(2)	176.94(6)	O(1W)–Cd–N(1)	88.37(7)
O(1W)–Cd–N(3)	88.76(7)	O(1W)–Cd–N(5)	92.21(7)
O(1W)–Cd–N(7)	91.48(7)	O(2)–Cd–N(1)	90.88(7)
O(2)–Cd–N(3)	88.18(6)	O(2)–Cd–N(5)	90.81(6)
O(2)–Cd–N(7)	89.77(6)	N(1)–Cd–N(3)	75.85(7)
N(1)–Cd–N(5)	95.61(7)	N(1)–Cd–N(7)	170.02(7)
N(3)–Cd–N(5)	171.39(7)	N(3)–Cd–N(7)	114.13(7)
N(5)–Cd–N(7)	74.42(7)	O(2)–C(19)–O(3)	123.14(7)
O(4)–C(20)–O(5)	124.66(7)		

TABLE III Hydrogen bonding parameters in 1–4

D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°	Symmetry operation for A
1					
O(1w)-H(1wa)...O(3)	0.82	1.86	2.657	164	$-x, -y, 1-z$
O(1w)-H(1wb)...O(6w)	0.92	1.88	2.791	170	$-x, -1/2+y, 1/2-z$
O(6w)-H(6wa)...O(2)	0.85	1.88	2.734	177	$x, 3/2-y, -1/2+z$
O(6w)-H(6wb)...O(5)	0.85	1.90	2.751	154	$x, 1/2-y, -1/2+z$
N(3)-H(3a)...O(2)	0.86	2.10	2.926	161	$x, 1/2-y, -1/2+z$
N(3)-H(4a)...O(3)	0.86	1.87	2.719	169	$x, 1/2-y, -1/2+z$
O(4w)-H(4wb)...N(6)	0.82	1.83	2.619	163	$1-x, -1/2+y, 1/2-z$
N(5)-H(5b)...O(5)	0.86	1.93	2.779	172	$x, 1/2-y, -1/2+z$
2					
O(1w)-H(1wa)...O(3)	0.82	1.85	2.667	180	$-1/2+x, 1/2-y, 1-z$
O(1w)-H(1wb)...O(5)	0.81	1.95	2.749	171	$-1/2+xy, 3/2+z$
N(2)-H(2b)...O(4)	0.86	1.76	2.607	168	$2-x, -1/2+y, 3/2-z$
N(4)-H(4a)...O(5)	0.86	1.93	2.776	169	$2-x, -1/2+y, 3/2-z$
N(6)-H(6b)...O(2)	0.86	1.94	2.729	152	$2-x, 1-y, 1-z$
N(8)-H(8b)...O(2)	0.86	1.96	2.746	151	$2-x, 1-y, 1-z$
O(6)-H(6)...O(3)	0.93	2.04	2.810	139	x,y,z
C(6)-H(6a)...O(6)	0.93	2.43	3.307	157	x,y,z
C(7)-H(7a)...O(6)	0.93	2.58	3.464	158	x,y,z
3					
O(1w)-H(1wa)...O(6)	0.82	1.91	2.719	170	$1-x, 1/2+y, 1/2-z$
O(1w)-H(1wb)...O(11w)	0.72	2.21	2.871	153	$x, 3/2-y, 1/2+z$
N(2)-H(2a)...O(4)	0.86	1.91	2.763	173	$x, 1+y, z$
O(2w)-H(2wa)...O(9w)	0.82	1.92	2.717	163	$-x, 1/2+y, 1/2-z$
O(2w)-H(2wb)...O(4)	0.84	1.91	2.738	173	$-x, 1/2+y, 1/2-z$
N(4)-H(4a)...O(3)	0.86	1.85	2.703	173	$x, 1+y, z$
O(9w)-H(9wa)...O(7)	0.95	2.02	2.964	170	x,y,z
O(9w)-H(9wb)...O(5)	0.67	2.20	2.857	169	$1-x, 1/2+y, 1/2-z$
N(6)-H(4a)...O(6)	0.86	1.98	2.835	172	$-1+x, 1/2-y, 1/2+z$
N(8)-H(8a)...O(5)	0.86	1.86	2.715	171	$-1+x, 1/2-y, 1/2+z$
O(8)-H(8cb)...O(12)	0.82	1.79	2.603	171	$1-x, 1/2+y, 1/2-z$
O(10w)-H(10a)...O(3)	1.03	1.89	2.870	158	$1-x, 1/2+y, 1/2-z$
O(10w)-H(10b)...O(6)	0.89	1.88	2.758	167	$x, 1/2-y, 1/2+z$
O(12w)-H(12b)...O(10w)	0.85	1.88	2.734	178	x,y,z
O(12w)-H(12c)...O(4)	1.00	1.84	2.777	156	x,y,z
O(11)-H(11a)...O(12w)	0.93	2.44	3.361	174	$-x, 1-y, 1-z$
4					
O(1w)-H(1a)...O(3)	0.89	1.88	2.754	166	$-1/2+x, -1/2+y, z$
O(6w)-H(6wa)...O(4)	0.85	2.44	2.822	108	$1-x,y, 1/2-z$
N(2)-H(2b)...O(4)	0.86	1.79	2.630	166	$3/2-x, -1/2+y, 1/2-z$
N(4)-H(4a)...O(5)	0.86	1.91	2.764	172	$3/2-x, -1/2+y, 1/2-z$
O(1w)-H(1b)...O(6w)	0.91	1.85	2.753	171	x,y,z
N(6)-H(6b)...O(3)	0.86	1.87	2.726	176	$1-x, 1-y, -z$
N(8)-H(8b)...O(2)	0.86	1.89	2.704	158	$1-x, 1-y, -z$

at 60°C for 2 h. The insoluble components were removed by filtration, and the filtrate was allowed to evaporate at room temperature for about one week. Orange product was collected in 55% yield. $C_{21}H_{28}N_8O_{12}Co$ **3** (643.44); C, 39.17 (calc. 39.20); H, 4.35 (4.39); N, 17.41 (17.42)%. IR (KBr, cm^{-1}): 3533–2551 vs, 1686 s, 1612 vs, 1561 vs, 1439 vs, 1366 vs, 1263 m, 1184 m, 1123 s, 992 m, 928 m, 761 s, 719 s, 689 s.

Synthesis of $[Cd(H_2biim)_2(H_2O)(bdc)] \cdot H_2O$ (**4**)

$CdCl_2 \cdot 6H_2O$ (0.5 mmol), H_2biim (0.134 g, 1 mmol) and anhydrous ethanol (3 ml) were added into an aqueous solution (5 ml) of sodium 1,3-benzenedicarboxylate (0.105 g, 0.5 mmol). The resulting mixture was adjusted to $pH \approx 5.1$ with dilute hydrochloric acid and then stirred for 15 minutes in air. The mixture was transferred and sealed in a 16 ml Teflon reactor, which was heated at 120°C for four days and

then cooled to room temperature at a rate of $5^\circ C \cdot h^{-1}$. Colorless cubic crystals were obtained in 40% yield and they were washed with de-ionized water. $C_{20}H_{20}N_8O_6Cd$ **4** (580.85); C, 41.89 (calc. 41.36); H, 3.32 (3.47); N, 19.77 (19.29)%. IR (KBr, cm^{-1}): 3350–2551 m, 1599 s, 1551 s, 1519 s, 1434 s, 1371 vs, 1120 s, 988 s, 748 s, 710 m, 688 m.

Crystallography

Diffraction intensities for the complexes **1** to **4** were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied by using SADABS [37]. The structures were solved by direct methods and refined with full-matrix least-squares technique on F^2 using SHELXS-97 and SHELXL-97 programs, respectively [38,39]. All non-hydrogen atoms were refined anisotropically.

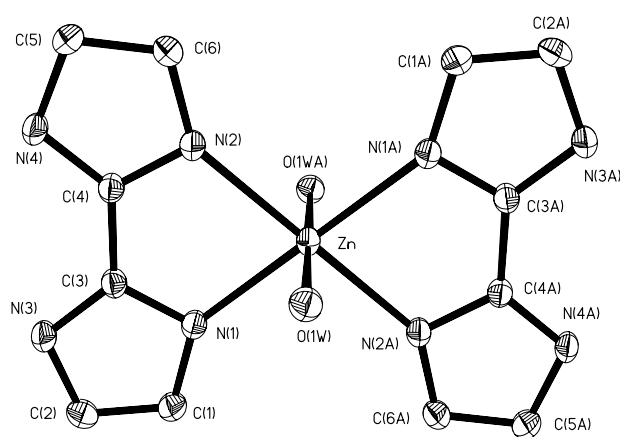


FIGURE 1 The coordination environment of zinc ion in 1.

cally. The hydrogen atoms on the organic ligands were generated geometrically (C–H 0.96 Å) and the hydrogen atoms on the water molecules were located from difference maps and refined isotropically. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal data including details of data collection and refinement for the complexes are summarized in Table I. Selected bond distances and bond angles are listed in Table II. Selected hydrogen-bonding parameters are given in Table III. Crystallographic data (excluding structure factors) for (1)–(4) in CIF format have been deposited in the Cambridge Crystallographic Data Center with CCDC nos. 235688–235691. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK. Fax: +44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Syntheses and Characterization

All reactions were carried out above $pH = 4.6$ [40] to ensure that the H_2biim ligand was in neutral form to coordinate with metal ions to form the building blocks $[M(H_2biim)_2(H_2O)_n]^{2+}$, which could be further assembled with carboxylates via charge-assisted hydrogen bonds into multi-dimensional network. Indeed, complexes 1 and 2 were obtained when the dicarboxylate bdc was introduced. The dicarboxylate connected the two coordinated H_2biim ligands into a zigzag chain via hydrogen bonds. Interestingly, when the metal to H_2biim molar ratio was increased to 1: 3.5 at $pH = 5.0$, complex 1 was formed, in which one of the H_2biim molecules was un-coordinated and one of the carboxyl groups was protonated, but they were

connected together by two pairs of hydrogen bonds. Furthermore, complex 3 was obtained when bdc was replaced by bdc, but one of the carboxyl groups was protonated. From the above observations, we notice that the carboxylate group tends to form pairs of robust double hydrogen bonds with the N–H donor of H_2biim via a charge-assisted heteromeric synthon of type $R_2^2(9)$ rather than binding to metal ion. Therefore, a solvothermal reaction was carried out to see whether the carboxylate was really coordinated to metal ion or not in this reaction system. Complex 4 was obtained when a mixture of $CdCl_2$, H_2biim and bdc were heated at $120^\circ C$ for four days. Unlike complexes 1 and 2, the bdc ligand is coordinated to Cd^{II} in 4.

The IR spectra of complexes 1–4 show one broad and strong band centered at $3500 \sim 2550\text{ cm}^{-1}$, which can be assigned to the $\nu(O-H)$ and $\nu(N-H)$ stretching vibrations of the water molecules, protonated carboxyl and H_2biim ligands, taking into account for their strong hydrogen-bonding interactions. The characteristic bands for both $COOH$ and COO^- were observed in complexes 1–4. The asymmetrical stretching for COO^- in these compounds was observed in the range of $1536 \sim 1612\text{ cm}^{-1}$. The bands at 1604 and 1686 cm^{-1} in 1 and 3, respectively, can be assigned to the asymmetric stretching of $COOH$. In complex 1, the shift of 86 cm^{-1} compared to the corresponding $COOH$ stretching in free acids (the $COOH$ group in free 1,3-benzenedicarboxylic acid appears at 1690 cm^{-1}) is presumably due to the formation of robust N–H...O hydrogen bonds. The C–O distances (listed in Table II) are also matched with the observed signals in the IR spectra.

Crystal Structures

Complex 1 consists of one $[Zn(H_2biim)_2(H_2O)_2]^{2+}$ cation, two $Hbdc$ anions, one H_2biim molecule and two lattice water molecules. As shown in Fig. 1, the Zn^{II} ion locates at an inversion centre and it is coordinated to four nitrogen atoms from two H_2biim ligands [$Zn-N(1) = 2.154(3)$ and $Zn-N(2) = 2.138(3)\text{ Å}$] which are *trans* to each other and arranged on the same equatorial plane. Two remaining water molecules [$Zn-O(1W) = 2.161(3)\text{ Å}$] occupy the apical coordination site to furnish an octahedral geometry. The $Zn-N$ distances are comparable to the previously reported values [33,34], but the $Zn-O(1W)$ distance is slightly shorter than that of $[Zn(H_2biim)_2(H_2O)_2]^{2+}$ (*ina*) $_2 \cdot 4H_2O$ [$Zn-O = 2.218(2)\text{ Å}$]. The increase in the $Zn-O(1W)$ distance can be attributed to the formation of hydrogen bonds. The distance of $C(17)-O(4) = 1.290(5)\text{ Å}$ is longer than those of $C(17)-O(5) = 1.228(5)$, $C(16)-O(2) = 1.237(5)$ and $C(16)-O(3) = 1.250(5)\text{ Å}$, indicating that the O(4) atom of carboxyl group is protonated and the

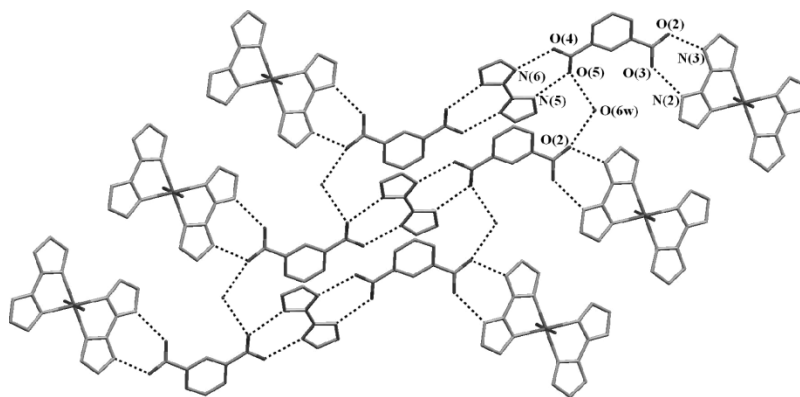


FIGURE 2 2-D hydrogen-bonded motif on the *bc* plane in **1**. All hydrogen atoms were omitted for clarity.

Hbdc ligand contains a carboxylate group. Each $[\text{Zn}(\text{H}_2\text{biim})_2(\text{H}_2\text{O})_2]^{2+}$ building unit attaches to two Hbdc anions via a charge-assisted DD = AA hydrogen bonds $[\text{N}(3)\cdots\text{O}(2) = 2.926$ and $\text{N}(4)\cdots\text{O}(3) = 2.719 \text{ \AA}]$ to give a neutral molecular complex $[\text{Zn}(\text{H}_2\text{biim})_2(\text{H}_2\text{O})_2](\text{Hbdc})_2$. The two protonated carboxyl groups are further connected to the free H_2biim molecules via robust heteromeric DA = DA hydrogen bonds $[\text{O}(4)\cdots\text{N}(6) = 2.619$ and $\text{N}(5)\cdots\text{O}(5) = 2.779 \text{ \AA}]$ by $C(4)[R_2^2(9)]$ synthon (Scheme 1) to form an infinite ribbon along the *c*-axis, as shown in Fig. 2. The $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond $[\text{O}(4)-\text{H}\cdots\text{N}(6) = 2.619 \text{ \AA}]$ is significantly shorter than those of the $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds $[\text{N}(5)-\text{H}\cdots\text{O}(5) = 2.779 \text{ \AA}$, $\text{N}(3)-\text{H}\cdots\text{O}(2) = 2.926 \text{ \AA}$ and $\text{N}(4)-\text{H}\cdots\text{O}(3) = 2.719 \text{ \AA}]$. These chains are further interlinked together via hydrogen bonds $[\text{O}(6w)\cdots\text{O}(2) = 2.734$, $\text{O}(5)\cdots\text{O}(6w) = 2.751$, $\text{O}(1w)\cdots\text{O}(3) = 2.657$, $\text{O}(6w)\cdots\text{O}(1) = 2.791 \text{ \AA}]$ to assemble into a 2-D layer lying parallel to the *bc*-plane and the coordinated water molecules lie above and below the hydrogen-bonded layer respectively. Adjacent layers are interlinked by the coordinating water molecules $\text{O}(1w)$, the lattice water molecule $\text{O}(6w)$ and the oxygen atom $\text{O}(3)$ on the carboxylate group to form a 3-D framework (Fig. 3).

Complex **2** is built of a $[\text{Zn}(\text{H}_2\text{biim})_2(\text{H}_2\text{O})]^{2+}$ cation, a bdc anion and one CH_3OH molecule. Each Zn^{II} ion is coordinated by four nitrogen atoms from two H_2biim [$\text{Zn}-\text{N}(1) = 2.061(2)$, $\text{Zn}-\text{N}(3) = 2.148(2)$, $\text{Zn}-\text{N}(5) = 2.082(2)$, $\text{Zn}-\text{N}(7) = 2.193(2) \text{ \AA}]$ and a water molecule [$\text{Zn}-\text{O}(1w) = 2.023(2) \text{ \AA}]$ resulting in a distorted square pyramid and the Zn^{II} ion deviates from the least-square plane [defined by $\text{N}(1)$, $\text{N}(3)$, $\text{N}(5)$ and $\text{N}(7)$] by 0.4 \AA , as shown in Fig. 4. The above $\text{Zn}-\text{N}$ and $\text{Zn}-\text{O}$ bond distances are comparable to those found in the five-coordinated complex $[\text{Zn}(\text{H}_2\text{biim})_2(\text{HCO}_2)](\text{ClO}_4)$, in which the $\text{Zn}-\text{N}$ and $\text{Zn}-\text{O}$ distances are $2.043 \sim 2.231$ and 2.006 \AA , respectively [41].

Each $[\text{Zn}(\text{H}_2\text{biim})_2(\text{H}_2\text{O})]^{2+}$ building unit in complex **2** links with two bdc anions via charge-assisted

heteromeric DD = AA hydrogen bonds $[\text{N}(2)\cdots\text{O}(4) = 2.607$, $\text{N}(4)\cdots\text{O}(5) = 2.776$, $\text{N}(6)\cdots\text{O}(2) = 2.729$ and $\text{N}(8)\cdots\text{O}(2) = 2.746 \text{ \AA}]$ to form a zigzag chain along the *c*-axis, as shown in Fig. 5. Two types of robust synthons, namely $R_2^2(9)$ and $R_2^1(7)$ (Scheme 1) were found in complex **2**, whereas $R_2^2(9)$ and $C(4)[R_2^2(9)]$ were found in complex **1**. It is the coordinated water molecule that connects the oxygen atoms $\text{O}(3)$ and $\text{O}(5)$ of two carboxylates from two adjacent chains respectively via $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds $[\text{O}(1w)\cdots\text{O}(3) = 2.667(2)$ and $\text{O}(1w)\cdots\text{O}(5) = 2.749(2) \text{ \AA}]$ to form a 2-D layer parallel to the *bc*-plane (see Fig. 5). Interestingly, the CH_3OH molecules are clathrated in the cavities. The oxygen atom of methanol points to the larger coordinate-angle site of $\text{N}(3)-\text{Zn}-\text{N}(5)$ (100.5° , the other coordinated angles on the equatorial plane are 79.4 , 79.7 and

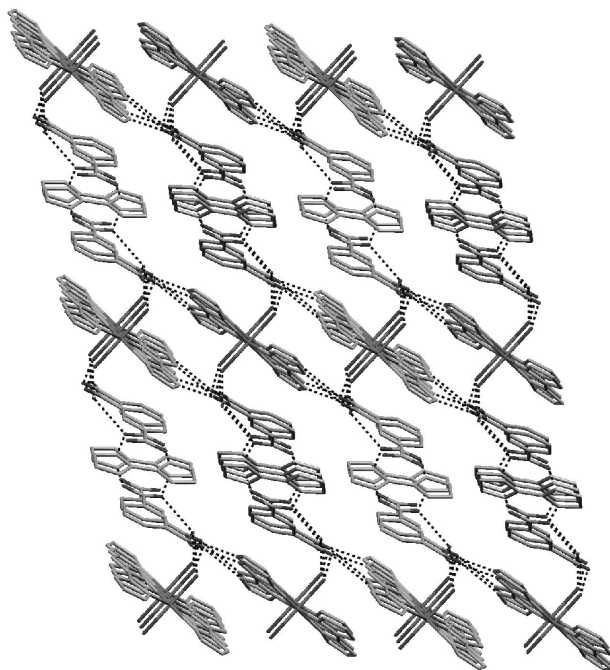


FIGURE 3 3-D network formed by hydrogen bonds in **1**. All hydrogen atoms were omitted for clarity.

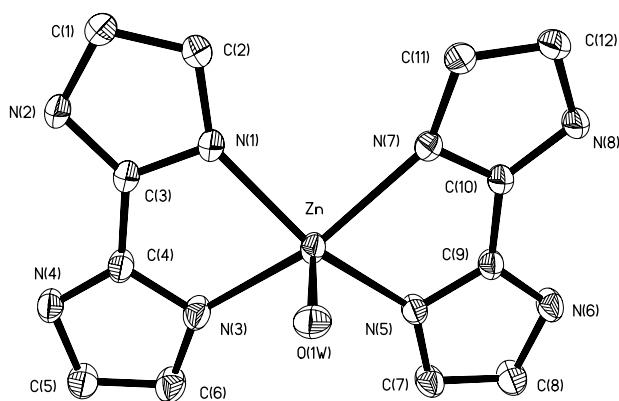


FIGURE 4 The coordination environment of zinc ion in 2.

92.0°) and the solvent molecule is further stabilized by C—H...O hydrogen bonds [C(6)...O(6) = 3.307 and C(7)...O(6) = 3.464 Å]. All of the aqua ligands are arranged in the same direction (either above or below the layer) within a layer. These layers are further assembled into double layers in a head-to-head fashion (Fig. 6) via O—H...O hydrogen bonds [O(1w)...O(3) = 2.667 Å and O(1w)...O(5) = 2.749 Å] and strong π – π interactions (3.423 Å) between the H₂biim ligands. The O—H bonds of methanol molecules are pointing away from both sides of the double layers, and further interlink adjacent double layers carboxylate oxygen O(3) via O—H...O hydrogen bonds [O(6)...O(3) = 2.797 Å] in a tail-to-tail fashion to form a complicated 3-D network (Fig. 6).

Complex 3 consists of a [Co(H₂biim)₂(H₂O)₂]²⁺ cation, a Hbtc anion and four lattice water molecules. The coordination environment of Co^{II} ion is very similar to that of complex 1. The oxygen atom O(8) is protonated which can be confirmed by the IR spectra (see above) and the measured C—O bond distances. The bond length of C(21)—O(8) [1.317(4) Å] is significantly longer than those of C(21)—O(7) [1.211(4) Å], C(20)—O(3) [1.232(3) Å], C(20)—O(4)

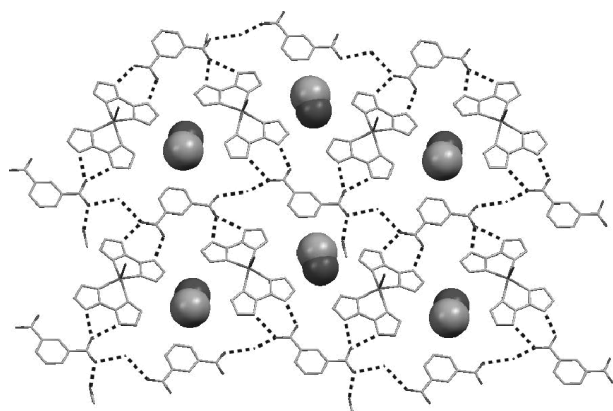


FIGURE 5 View of the layer on the *bc* plane in 2. All hydrogen atoms were omitted for clarity and ethanol molecules (oxygen, black; carbon, grey) were drawn in space filling.

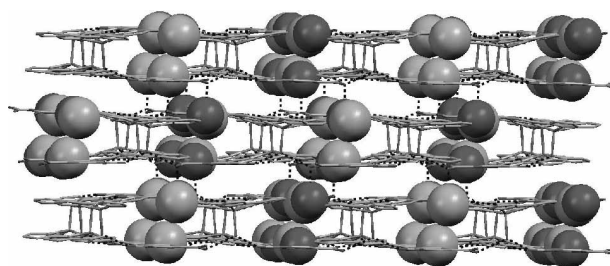


FIGURE 6 The assembly of layers into 3-D network in head-to-head and tail-to-tail arrangement in 2. All hydrogen atoms were omitted for clarity and methanol molecules were shown in space filling.

[1.270(3) Å], C(19)—O(5) [1.240(4) Å] and C(19)—O(6) [1.267(4) Å].

Each [Co(H₂biim)₂(H₂O)₂]²⁺ building block is connected to two Hbtc anions via N—H...O charge-assisted DD = AA hydrogen bonds [N(2)...O(4) = 2.763, N(4)...O(3) = 2.704, N(6)...O(6) = 2.836 and N(8)...O(5) = 2.715 Å] to form a ribbon extending along the *c*-axis. These chains are further linked together via O—H...O hydrogen bonds between the carboxyl oxygen atoms O(8) and O(3) as well as the lattice water molecules O(12w) and O(10w) [O(8)...O(12w) = 2.603, O(12w)...O(10w) = 2.734 and O(10w)...O(3) = 2.870 Å] into 2-D layer, as shown in Fig. 7. These layers are further connected together by multiple hydrogen bonds between the carboxylate oxygens and the lattice molecules [O(1w)...O(6) = 2.719, O(2w)...O(4) = 2.738, O(2w)...O(9w) = 2.717, O(10w)...O(6) = 2.758, O(9w)...O(5) = 2.857 and O(12w)...O(4) = 2.777 Å] as well as strong π – π interactions between H₂biim and the phenyl ring (3.35 Å), and between H₂biim and H₂biim (3.27 Å) to form a 3-D network.

Complex 4 was synthesized under hydrothermal condition and it consists of a neutral [Cd(H₂biim)₂(bdc)(H₂O)] molecule and a lattice water molecule. Each Cd^{II} ion is coordinated to four nitrogen atoms of two H₂biim [Cd—N(1) = 2.278(2), Cd—N(3) = 2.304(2), Cd—N(5) = 2.360(2), Cd—N(7) = 2.291(2) Å], two oxygen atoms from carboxylate [Cd—O(2) = 2.485(2) Å] and water molecule [Cd—O(1w) = 2.376(2) Å] to form a distorted octahedron, as shown in Fig. 8. The bond distance of O(2)—C(19) [1.269(3) Å] is slightly longer than those of O(3)—C(19) [1.241(3) Å], O(4)—C(20) [1.257(3) Å] and O(5)—C(20) [1.242(3) Å]. These may be attributed to the formation of heteromeric hydrogen-bonded synthon R₂²(9) between the carboxylate groups and the un-coordinated nitrogen atoms of H₂biim (Scheme 1). The hydrogen bond can also affect the electron delocalization in the carboxylate group, which can be reflected by the measured bond distances. The dihedral angle between the phenyl ring of bdc and H₂biim plane is about 6.8°,

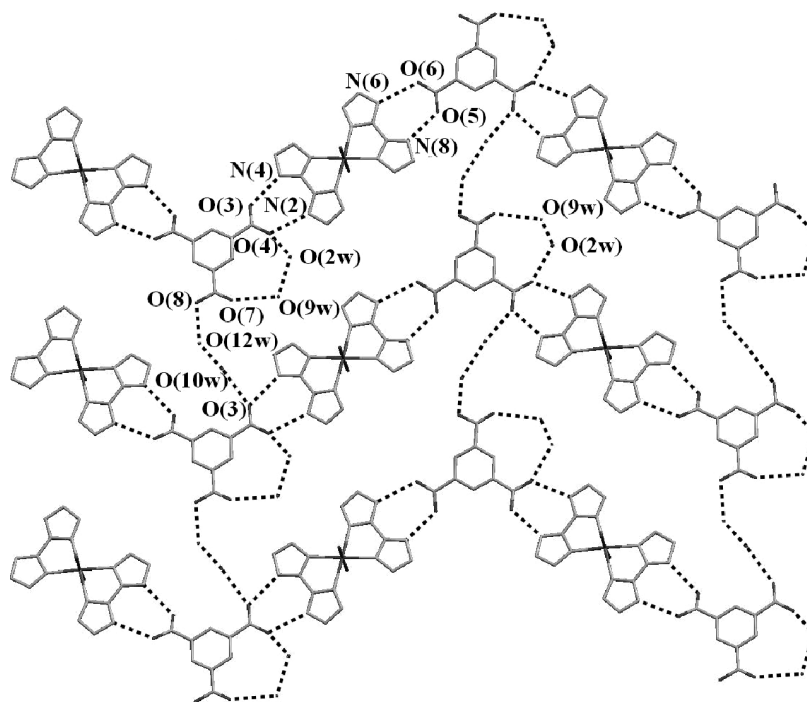


FIGURE 7 2-D hydrogen-bonded motif in 3. All hydrogen atoms were omitted for clarity.

and a strong π - π interaction with a face-to-face distance of 3.36 Å is observed between these two planes.

A pair of $[\text{Cd}(\text{H}_2\text{biim})_2(\text{OH}_2)(\text{bdc})]$ building blocks form a dimer in a head-to-tail fashion by N-H...O charge-assisted DD = AA hydrogen bonds $[\text{N}(6)\cdots\text{O}(3) = 2.726$ and $\text{N}(8)\cdots\text{O}(2) = 2.704$ Å] and π - π interactions between the H_2biim ligands (3.673 Å). These dimeric units are further connected together to form a double-strand via hydrogen bonds between the coordinated water molecule O(1w) and carboxylate oxygen O(3) [$\text{O}(1\text{w})\cdots\text{O}(3) = 2.754$ Å] as shown in Fig. 9. The double strands are further assembled into a 3-D network via hydrogen bonds between the free carboxylate and H_2biim [$\text{N}(2)\cdots\text{O}(4) = 2.630$, $\text{N}(4)\cdots\text{O}(5) = 2.764$ Å].

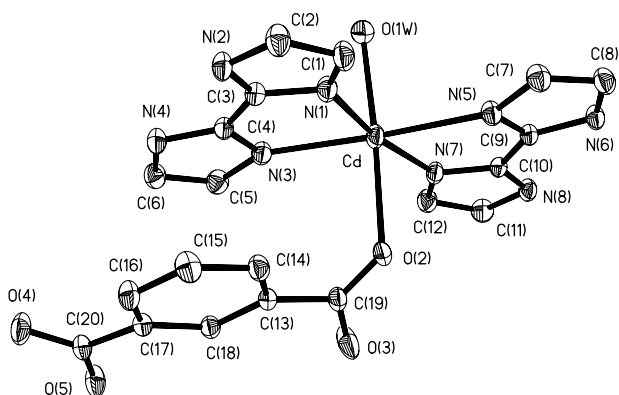


FIGURE 8 The coordination environment of Cd^{II} ion in 4.

CONCLUSIONS

Four new complexes based on the $[\text{M}(\text{H}_2\text{biim})_2(\text{H}_2\text{O})_n]^{2+}$ building blocks and carboxylates have been synthesized and characterized by single-crystal X-ray diffraction. The results show that the

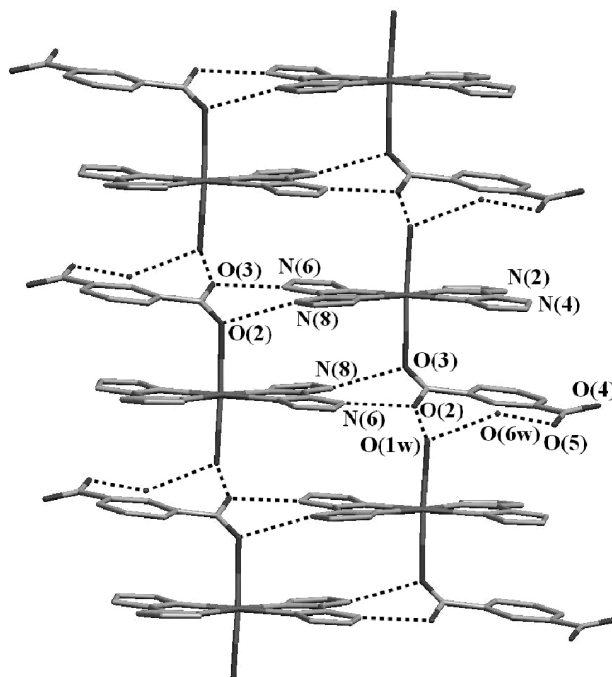


FIGURE 9 View of the dimeric structure extending into double-strand chain along *a*-axis via O-H...O hydrogen-bonds in 4. All hydrogen atoms were omitted for clarity.

charge-assisted heteromeric synthons such as $R_2^2(9)$, $R_2^1(7)$ and $C(4)[R_2^2(9)]$ constructed by the coordinated H_2biim or un-coordinated H_2biim and carboxylate via $N-H\cdots O$ and $O-H\cdots N$ hydrogen bonds are robust enough to act as a 'supramolecular glue' to assemble coordination complexes and carboxylates into multidimensional hybrid inorganic-organic materials.

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References

- [1] Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
- [2] Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483.
- [3] Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629.
- [4] Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, *236*, 91.
- [5] Barnett, S. A.; Chempness, N. R. *Coord. Chem. Rev.* **2003**, *246*, 145.
- [6] Ye, B.-H.; Tong, M.-L.; Chen, X.-M. *Coord. Chem. Rev.* **2005**, *249*, 545.
- [7] Jeffrey, D. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, Heidelberg, New York, 1991.
- [8] Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120.
- [9] Beatty, A. M. *Coord. Chem. Rev.* **2003**, *246*, 131.
- [10] Schwiebert, K. E.; Chin, D. N.; MacDonald, J. C.; Whitesides, G. M. *J. Am. Chem. Soc.* **1996**, *118*, 4018.
- [11] MacDonald, J. C.; Iversen, B. B. *Angew. Chem. Int. Ed.* **1999**, *38*, 1239.
- [12] MacDonald, J. C.; Dorrestein, P. C.; Pilley, M. M. *Cryst. Growth Des.* **2001**, *1*, 29.
- [13] Akutagawa, T.; Hasegawa, T.; Nakamura, T.; Inabe, T.; Saito, G. *Chem. Eur. J.* **2002**, *8*, 4402.
- [14] Akutagawa, T.; Hasegawa, T.; Nakamura, T.; Inabe, T.; Saito, G. *Cryst. Eng. Comm.* **2003**, *5*, 54.
- [15] Tadokoro, M.; Nakasuji, M. *Coord. Chem. Rev.* **2000**, *198*, 205.
- [16] Aakerøy, C. B.; Hitchcock, P. B. *J. Mater. Chem.* **1993**, *3*, 1129.
- [17] Aakerøy, C. B.; Nieuwenhuyzen, M. *J. Am. Chem. Soc.* **1994**, *116*, 10983.
- [18] Aakerøy, C. B.; Hughes, D. P. B.; Nieuwenhuyzen, M. *J. Am. Chem. Soc.* **1996**, *118*, 10134.
- [19] Czugler, M.; Angyan, J. G.; Naray-Szabo, G.; Weber, E. *J. Am. Chem. Soc.* **1986**, *108*, 1275.
- [20] Czugler, M.; Kalman, A.; Weber, E.; Ahrendt, J. *Supramol. Chem.* **1993**, *1*, 163.
- [21] Fuller, J.; Carlin, R. T.; Simpson, L. J.; Furtak, T. E. *Chem. Mater.* **1995**, *7*, 909.
- [22] Hong, S. S.; Romstedt, K. J.; Feller, D. R.; Hsu, F. -L.; George, C.; Cupps, T. L.; Lyon, R. A.; Miller, D. D. *Chirality* **1992**, *4*, 432.
- [23] Trivedi, D. R.; Ballabh, A.; Dastidar, P. *Cryst. Eng. Comm.* **2003**, *5*, 358.
- [24] Boinnard, A.; Cassoux, P.; Petrouleas, V.; Savariault, J.-M.; Tuchagues, J.-P. *Inorg. Chem.* **1990**, *29*, 4114.
- [25] Martinez-Lorente, M. A.; Daham, F.; Sanakis, Y.; Petrouleas, V.; Bousseksou, A.; Tuchagues, J.-P. *Inorg. Chem.* **1995**, *34*, 5346.
- [26] Fortin, S.; Beauchamp, A. L. *Inorg. Chem.* **2001**, *40*, 105.
- [27] Ramirez, K.; Reyes, J. A.; Briceno, A.; Atencio, R. *Cryst. Eng. Comm.* **2002**, *6*, 208.
- [28] Rau, S.; Böttcher, L.; Schebesta, S.; Stollenz, M.; Görls, H.; Walther, D. *Eur. J. Inorg. Chem.* **2002**, 2800.
- [29] Atencio, R.; Chacón, M.; González, T.; Briceno, A.; Agrifoglio, G.; Sierralta, A. *Dalton Trans.* **2004**, 505.
- [30] Larsson, K.; Öhrström, L. *Cryst. Eng. Comm.* **2004**, *6*, 354.
- [31] Öhrström, L.; Larsson, K. *Dalton Trans.* **2004**, 347.
- [32] Stout, G. H.; Jensen, L. H. *X-ray Structure Determination. A Practical Guide*; Macmillan: New York, 1968.
- [33] Ye, B. -H.; Xue, F.; Xue, G. -Q.; Ji, L. -N.; Mak, T. C. W. *Polyhedron* **1999**, *18*, 1785.
- [34] Ye, B. -H.; Ding, B. -B.; Weng, Y. -Q.; Chen, X. -M. *Inorg. Chem.* **2004**, *43*, 6866.
- [35] Ye, B. -H.; Ding, B. -B.; Weng, Y. -Q.; Chen, X. -M. *Cryst. Growth Des.* **2005**, *5*, 801.
- [36] Bernarducci, E. E.; Bharadwa, P. K.; Lalancette, R. A.; Krogh-Jes-Persen, K.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1983**, *22*, 3911.
- [37] Blessing, R. *Acta Crystallogr. Sect. A* **1995**, *51*, 33.
- [38] Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Göttingen University: Germany, 1997.
- [39] Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Göttingen University: Germany, 1997.
- [40] Akutagawa, T.; Saito, G. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1753.
- [41] Kirchner, C.; Krebs, B. *Inorg. Chem.* **1987**, *26*, 3569.