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Coordination networks generated from transition metal chlorides and a flexible double betaine

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Abstract

The new flexible double betaine 1,4-bis(2-picolyloxyl)benzene-*N*,*N*′-diacetate (L) has been synthesized and used to generate five complexes with divalent metal chlorides: $[M(H_2O)_6]Cl_2\cdot L\cdot 2H_2O$ (M = Mn (**1**), Co (**2**)), $[Cu(\mu\text{-}L)Cl_2]_\infty$ (**3**), $\{[Zn(\mu\text{-}L)Cl_2]\cdot 2H_2O\}_\infty$ (**4**), and $\{[Cd_2(\mu\text{-}Cl)_2(\mu\text{-}L)Cl_2(H_2O)_2]\cdot 2H_2O\}_\infty$ (**5**). Isomorphous compounds **1** and **2** have a hydrogen-bonded three-dimensional network in which adjacent L ligands overlap through π–π stacking of the pyridine and benzene rings. Compounds **3**, **4**, and **5** display three different types of one-dimensional polymeric structures. Bridged by L acting in the *anti* mode, compound **3** exhibits an infinite zigzag chain in which consecutive, approximately planar L ligands are arranged in a crossed manner when viewed along the chain direction, the distance between adjacent copper(II) ions being about 13 Å. In contrast, compound **4** features a spring-like infinite helical chain with zinc ions lying on the axis and bridged by L acting in the *syn* fashion, and the Zn(II)···Zn(II) separation is approximately 9 Å. In compound **5**, the building unit is a centrosymmetric Cd_2Cl_2 moiety, and adjacent dimeric units are linked by the centrosymmetric L ligand acting in the *anti* mode to give an infinite zigzag chain running along the *c* axis; such chains are further connected through hydrogen bonds to form a three-dimensional network.

Keywords: Carboxylate; Coordination network; Double betaine; Transition metal

1. Introduction

Supramolecular assembly of metal-organic open frameworks with desired functions and fascinating structures has received significant attention in recent years [1]. A variety of infinitely extended frameworks are formed either by strong metal–ligand bonding or by weaker interactions such as hydrogen bonding and π–π interaction [2]. Rigid linear bridging ligands such as 4,4′-bipyridine [3] and 4,4′-bipyridine-*N*,*N*′-dioxide [4] have been used in self-assembly reactions to generate a variety of topological architectures.

Betaines, of which the prototype is $Me_3N^+\text{-}CH_2CO_2^-$, are of interest in biological research, especially in regard to their important role in amino acid synthesis as a methyl transfer agent [5]. A double betaine comprises two betaine moieties in the same molecule and accordingly possesses pairs of anionic carboxylate groups and quaternary ammonio groups [6]. Owing to their zwitterionic properties of permanent bipolarity and overall charge neutrality, double betaine compounds can be expected to be advantageous in the study of coordination polymers in several respects: (1) synthetic access to water-soluble polymeric metal dicarboxylates; (2) extended structural varieties of metal dicarboxylates, such as complexes with metal centers bearing additional anionic ligands, and those with variable metal to dicarboxylate molar ratios; (3) easy modification of dicarboxylate ligands [7]. In the present work, a new flexible double betaine, namely 1,4-bis(2-picolyloxyl)benzene-*N*,*N*′-diacetate (L), was synthesized and used to generate a series of transition metal complexes that exhibit different polymeric structures: $[M(H_2O)_6]Cl_2\cdot L\cdot 2H_2O$ (M = Mn (**1**), Co (**2**)), $[Cu(\mu\text{-}L)Cl_2]_\infty$ (**3**), $\{[Zn(\mu\text{-}L)Cl_2]\cdot 2H_2O\}_\infty$ (**4**), $\{[Cd_2(\mu\text{-}Cl)_2(\mu\text{-}L)Cl_2(H_2O)_2]\cdot 2H_2O\}_\infty$ (**5**). Ligand L can bridge a pair of metal cations in either the *anti* or *syn* mode, leading to different types of one-dimensional chains **3** and **4**. The

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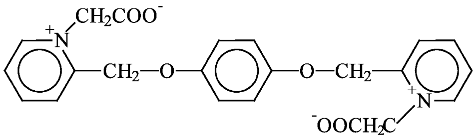
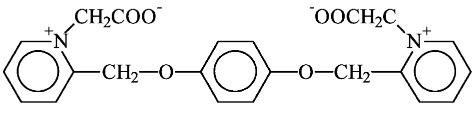
spacer distance between the pair of carboxylate ligating sites in these two cases is about 13 and 9 Å, respectively. Compounds **1**, **2** and **5** exhibit hydrogen-bonded three-dimensional networks.



Anti-mode



Syn-mode

2. Experimental

2.1. Materials

2-Picolyl chloride hydrochloride, NaOH, 1,4-dihydroxybenzene, ethyl chloroacetate, silver carbonate, and the metal chloride reagents were obtained commercially and used without further purification.

2.2. Synthesis of 1,4-bis(2-picolyloxyl)benzene-N,N′-diacetate (**L**)

1,4-Dihydroxybenzene [8] (18 mml, 2 g) and 2-picolyl chloride hydrochloride (40 mmol, 6.6 g) were mixed together in 20 ml water. With stirring and cooled by ice water under a N_2 atmosphere, 3 ml NaOH aqueous solution (92.5 mmol, 3.7 g) was added. After the addition was complete, the resulting solution was refluxed for 4 h. After cooling off, the brown precipitate was filtered and re-crystallized in MeOH. Light yellow 1,4-bis(2-picolyloxyl)benzene (2.2 g) was obtained in 42% yield. *Anal*. Calc. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.82; H, 5.50; N, 9.52%.

1,4-Bis(2-picolyloxyl)benzene (10 mmol, 2.92 g) was dissolved in 30 ml MeOH to give a yellow solution, to which 3 ml ethyl chloroacetate [9] (27 mmol, Aldrich) was added. The resulting solution was refluxed for 3 days. After the MeOH was removed by rotary evaporation under reduced pressure, 25 cm^3 of 3.7% (w/v) HCl were added to the yellow residue. The mixture was refluxed for 24 h to give a yellow solution. Removal of solvent afforded a light yellow powdery product. The product was then dissolved in 40 cm^3 water, and silver carbonate was added, with stirring, to remove the chloride ions. The precipitate was filtered off, and the filtrate was then dehydrated to yield L as a white solid, which was then re-crystallized in water and EtOH (2.2 g, yield 54%). *Anal*. Calc. for ligand $C_{22}H_{20}N_2O_6 \cdot 5H_2O$: C, 53.01; H, 6.07; N, 5.62. Found: C, 52.88; H, 5.69; N, 5.61%. IR (KBr, cm^{-1}): 3472s, 3074w, 1635s, 1512s, 1444s, 1372s, 1239s, 1211m, 1072m, 818m, 775w, 718w. ^1H NMR (300 Hz, D_2O): δ 8.79 (2H, d, py-3), 8.52 (2H, t, py-4), 8.18 (2H, d, py-6), 8.02 (2H, t, py-5), 7.01 (4H, s, C_6H_6), 5.42 (4H, s, $-CH_2-O$), 5.20 (4H, s, $-CH_2COO^-$).

2.3. Synthesis of $[Mn(H_2O)_6]Cl_2 \cdot L \cdot 2H_2O$ (**1**)

Aqueous solutions of L (6 ml; 0.2 mmol, 0.08 g) and $MnCl_2 \cdot 4H_2O$ (4 ml; 1 mmol, 0.197 g) were mixed together and heated for 10 min with stirring, and then filtered. Upon slow evaporation of the filtrate at room temperature, colorless crystals of **1** were obtained after several days. *Anal*. Calc. for $MnCl_2 \cdot L$ (thoroughly dried sample): C, 49.46; H, 3.77; N, 5.24. Found: C, 49.50; H, 4.25; N, 5.31%. IR (KBr, cm^{-1}): 3446s, 3066w, 1740s, 1629s, 1521m, 1454m, 1394m, 1209s, 1071m, 829m, 776w, 708w.

2.4. Synthesis of $[Co(H_2O)_6]Cl_2 \cdot L \cdot 2H_2O$ (**2**)

This compound was prepared as pink block-like crystals using L (0.2 mmol, 0.08 g) and $CoCl_2 \cdot 6H_2O$ (1 mmol, 0.237 g) in a way similar to that of **1**. *Anal*. Calc. for $[Co(H_2O)_6]Cl_2 \cdot L \cdot 2H_2O$: C, 38.72; H, 5.32; N, 4.11. Found: C, 38.54; H, 5.11; N, 4.14%. IR (KBr, cm^{-1}): 3447s, 3079w, 1640s, 1628s, 1508s, 1450m, 1384s, 1227m, 1075m, 823w, 770w, 722w.

2.5. Synthesis of $[Cu(\mu\text{-}L)Cl_2]$ (**3**)

This compound was prepared as green block-like crystals using L (0.2 mmol, 0.08 g) and $CuCl_2 \cdot 2H_2O$ (1 mmol, 0.171 g) in a way similar to that of **1**. *Anal*. Calc. for $[Cu(\mu\text{-}L)Cl_2]$: C, 48.68; H, 3.71; N, 5.16. Found: C, 48.26; H, 3.81; N, 5.00%. IR (KBr, cm^{-1}): 3455w, 3086w, 1642s, 1508m, 1454m, 1373s, 1244m, 1236m, 1078m, 825w, 769w, 712w.

2.6. Synthesis of $[Zn(\mu\text{-}L)Cl_2] \cdot 2H_2O$ (**4**)

This compound was prepared as colorless block-like crystals using L (0.2 mmol, 0.08 g) and $ZnCl_2$ (1 mmol, 0.140 g) in a way similar to that of **1**. *Anal*. Calc. for $[Zn(\mu\text{-}L)Cl_2] \cdot 2H_2O$: C, 45.50; H, 4.17; N, 4.82. Found: C, 45.32; H, 3.98; N, 4.59%. IR (KBr, cm^{-1}): 3432w, 3079w, 1701s, 1630m, 1507s, 1444m, 1381m, 1222s, 1068m, 833w, 777w, 722w.

2.7. Synthesis of [$Cd_2(\mu\text{-}Cl)_2(\mu\text{-}L)Cl_2(H_2O)_2]\cdot 2H_2O$ (5)

This compound was prepared as colorless block-like crystals using L (0.2 mmol, 0.08 g) and $CdCl_2\cdot 2H_2O$ (1 mmol, 0.220 g) in a way similar to that of **1**. *Anal*. Calc. for [$Cd_2(\mu\text{-}Cl)_2(\mu\text{-}L)Cl_2(H_2O)_2]\cdot 2H_2O$: C, 31.19; H, 3.33; N, 3.31. Found: C, 30.85; H, 3.06; N, 3.09%. IR (KBr, cm^{-1}): 3473m, 3079w, 1606s, 1509m, 1451w, 1395s, 1234m, 1071w, 829w, 769w, 729w.

2.8. X-ray crystallography

Suitable single crystals of **1**–**5** were selected for the diffraction analysis. For **1** and **3**–**5**, data collection were performed on a Bruker SMART 1000 CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K [10]. For **2**, data collection was performed on a Siemens P4 four-circle diffractometer in the variable ω-scan mode [11] using Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXTL program package [12] (Table 1).

3. Results and discussion

Molar ratio 1:5 was chosen to carry out the reactions between L and $MCl_2\cdot nH_2O$ (M = Mn, Co, Cu, Zn and

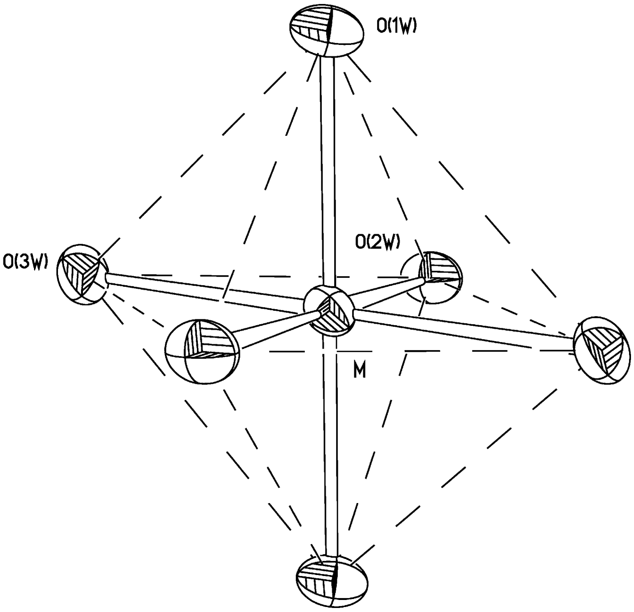


Fig. 1. Coordination environment of M^{2+} ions (M = Mn (**1**), Co (**2**)).

Table 1
Crystallographic data of complexes **1**–**5**

Complex	1	2	3	4	5
Empirical formula	$C_{22}H_{36}Cl_2MnN_2O_{14}$	$C_{22}H_{36}Cl_2CoN_2O_{14}$	$C_{22}H_{20}Cl_2CuN_2O_6$	$C_{22}H_{24}Cl_2ZnN_2O_8$	$C_{22}H_{28}Cl_4Cd_2N_2O_{10}$
Formula weight	678.37	682.36	542.84	580.70	847.06
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	6.6744(9)	6.6288(9)	19.739(4)	9.003(2)	13.682(7)
b (Å)	8.903(1)	8.867(1)	8.569(2)	11.805(2)	8.873(5)
c (Å)	13.307(2)	13.211(2)	13.020(2)	22.969(4)	13.826(7)
α (°)	72.319(3)	72.37(1)	90	90	90
β (°)	88.832(3)	88.90(1)	95.770(4)	92.904(4)	117.20(1)
γ (°)	75.640(3)	75.40(1)	90	90	90
V (Å^3)	728.6(2)	714.8(2)	2191.0(7)	2437.9(7)	1493.0(1)
Z	1	1	4	4	2
D_{calc} (g cm^{-3})	1.546	1.585	1.646	1.582	1.884
μ(Mo Kα) (mm^{-1})	0.706	0.858	1.284	1.277	1.836
$F(000)$	353	355	1108	1192	836
Crystal size	0.36 × 0.24 × 0.19	0.80 × 0.48 × 0.2	0.50 × 0.48 × 0.10	0.68 × 0.18 × 0.14	0.42 × 0.18 × 0.14
Reflections collected	4947	3543	7137	16 179	9790
Reflections observed [$I > 2\sigma(I)$]	2684	2369	2271	2690	2861
Independent reflections	3424 [$R_{int} = 0.0403$]	2778 [$R_{int} = 0.0147$]	2664 [$R_{int} = 0.0253$]	5888 [$R_{int} = 0.0542$]	3610 [$R_{int} = 0.0442$]
Parameters	187	187	150	307	197
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0671$	$R_1 = 0.0365$	$R_1 = 0.0369$	$R_1 = 0.0682$	$R_1 = 0.0538$
R indices (all data) [b]	$wR_2 = 0.1836$	$wR_2 = 0.0971$	$wR_2 = 0.1055$	$wR_2 = 0.2525$	$wR_2 = 0.1842$
Goodness-of-fit	1.000	1.047	1.090	0.949	1.084

[a] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$.

[b] $wR_2 = [\Sigma\,[w(F_o^2 - F_c^2)^2]/\Sigma\,[w(F_o^2)^2]]^{1/2}$.

Cd; $n = 2$, 4, 6). The use of excess metal salts is to prevent the deposit of the hydrated ligand.

Compound **1** consists of an assembly of the $[Mn(H_2O)_6]^{2+}$ cation (Fig. 1), two independent Cl^- anions, an uncoordinated L molecule, and two lattice water molecules. The Mn^{2+} ion is located in an elongated octahedral environment at an inversion center [Mn1–O1W = 2.173(2), Mn1–O2W = 2.163(2), Mn1–O3W = 2.230(2) Å]. Existing in the *anti* configuration, the ligand L has an inversion center in the center of its benzene ring. The two pyridyl rings of the ligand are parallel, each making a twist of angle of 4.8° with the benzene ring.

Aqua ligands O1W and O3W of the $[Mn(H_2O)_6]^{2+}$ cation form hydrogen bonds with the carboxylate groups of L [O1W···O2a = 2.838(3) Å, O1W–H1WB···O2a ~ 166°; O3W···O2 = 2.783(3) Å, O3W–H3WA···O2 ~ 170°; O3W···O1b = 2.773(3) Å, O3W–H3WB···O1b ~ 166°; a: $x-1, y, z$; b: $-x, -y+1, -z$]. Thus, each L molecule is connected to six $[Mn(H_2O)_6]^{2+}$ centers in *anti* position through hydrogen bonds to generate a three-dimensional network with channels running along the *a* direction (Fig. 2). The chloride ions and lattice water molecules (type O4W) are accommodated in these channels and stabilized by hydrogen bonding to the aqua ligands of surrounding $[Mn(H_2O)_6]^{2+}$ [O1W···Cl1c = 3.116(2) Å, O1W–H1WA···Cl1c ~ 160°; O2W···Cl1 = 3.076(2) Å, O2W–H2WA···Cl1 ~ 170°; O2W···O4Wd = 2.756(3) Å, O2W–H2WB···O4Wd ~ 169°; c: $-x-1, -y, -z$; d: $x, y-1, z$] [O4W···Cl1e = 3.100(2) Å, O4W–H4WA···Cl1e ~ 173°; O4W···O1 = 2.784(4) Å, O4W–H4WB···O1 ~ 162°; e: $x+1, y+1, z$]. The framework is additionally stabilized by π–π stack interactions [13,14] and the distance between the centroids of the pyridine ring and the benzene ring belonging to an adjacent L ligand is 3.53 Å (Fig. 3).

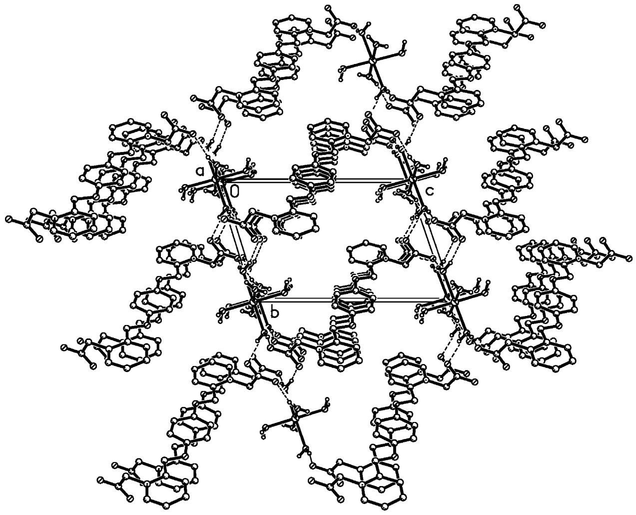


Fig. 2. Three-dimensional network formed by hydrogen bonding between ligands and hydrated $[M(H_2O)_6]^{2+}$ (M = Mn (**1**), Co (**2**)) cations in compounds **1** and **2**. Hydrogen atoms of the ligands, Cl^- ions and lattice water molecules have been omitted for clarity.

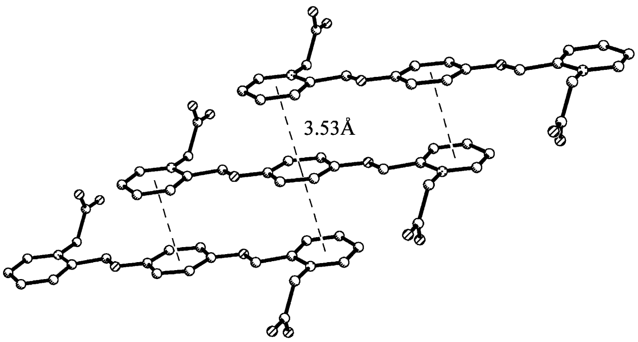


Fig. 3. The π–π interaction pattern in **1** and **2**.

Compound **2** is isomorphous to **1** with Co^{2+} replacing Mn^{2+}. And each pyridyl ring of ligand L makes the same twist angel 4.8° with the central benzene ring as in **1**.

Compound **3** exhibits an infinite zigzag chain architecture in the solid state. The Cu(II) center lies on a crystallographic twofold axis; it is in a severely distorted tetrahedral environment, being coordinated by two chloride ions and two oxygen atoms belonging to different L ligands, with bond lengths Cu1–Cl1, 2.247(1), Cu1–O1, 1.953(1) Å. The double betaine ligand L is located at an inversion center, with each pyridine ring making a twist angle of 10.1° with the central benzene ring, which is larger than those in **1** and **2**. Ligand L functions in the *anti* mode to link the Cu(II) ions into an infinite zigzag chain, with a separation of about 13 Å between adjacent metal centers (Fig. 4). The consecutive, approximately planar backbones of the L ligands are arranged in a crossed manner when viewed down the chain direction (Fig. 5). No distinct π–π stacking of the benzene and pyridine rings results from the present geometrical configuration.

Compound **4** shows a helical chain structure that self-assembles to form a spring-like columnar polymer. Each Zn(II) center is located in a severely distorted tetrahedral environment, being coordinated by two chloride ions and two monodentate L ligands [Zn1–Cl1, 2.2714(9), Zn1–Cl2, 2.3379(8), Zn1–O1, 1.990(2), Zn1–O5a, 1.986(2) Å; a: $x-1, y, z$]. Each L ligand acts in the *syn* mode to span two Zn(II) centers that are 9.0 Å apart, generating an infinite helical chain along the [100] direction (Fig. 6). A perspective view down the chain direction showing some water molecules of partial site occupancy included in the channel region of the spring-like chain is illustrated in Fig. 7. Since L acts in

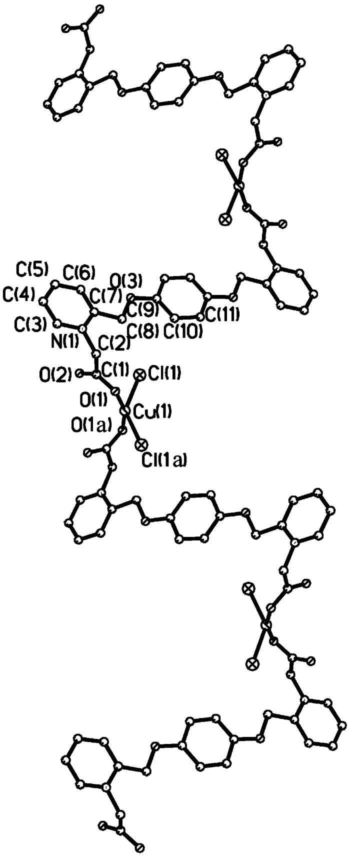


Fig. 4. Zigzag chain running along the [100] direction in compound **3**. Hydrogen atoms of the ligands have been omitted for clarity.

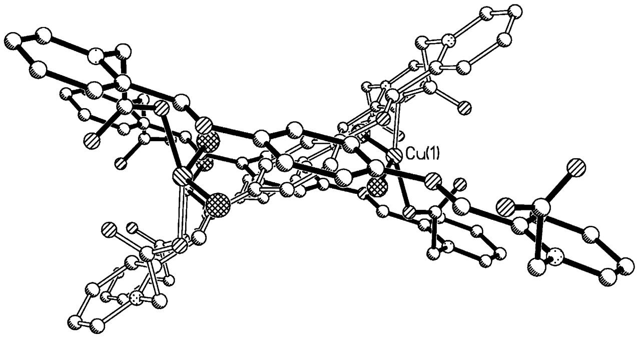


Fig. 5. Crossed arrangement of two consecutive, approximately planar L ligands viewed along the chain direction in **3**.

the *syn* coordination mode, the pair of pyridine rings are not parallel to each other but make with a dihedral angle of 33.2°. It is noteworthy that the distinct bridge modes of L (*anti* in **3** and *syn* in **4**) lead to the formation of different kinds of one-dimensional polymeric structures.

Compound **5** is also a polymeric chain with a centrosymmetric Cd_2Cl_4 dimeric building unit with Cd–Cl1 = 2.572(1) Å. Each Cd(II) ion is in a distorted octahedral environment involving two bridging chlorides, one aqua ligand, one terminal chloride and a chelating carboxylate group of L. The bond distances between the Cd(II) ion and the two craboxylate oxygen atoms are significantly different [Cd–O1, 2.491(2); Cd–O2, 2.350(2) Å], which correlate with the difference between the two C–O bond lengths [C1–O1, 1.230(3); C2–O2, 1.243(4) Å]. As a consequence of the chelating

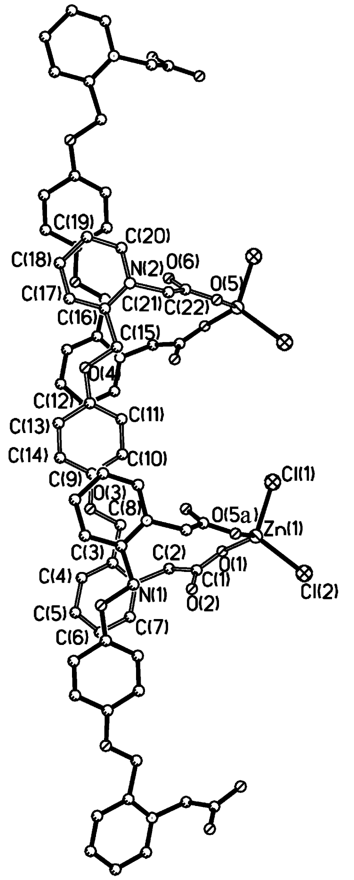


Fig. 6. Helical chain running along the [100] direction in compound **4**. Hydrogen atoms and water molecules have been omitted for clarity.

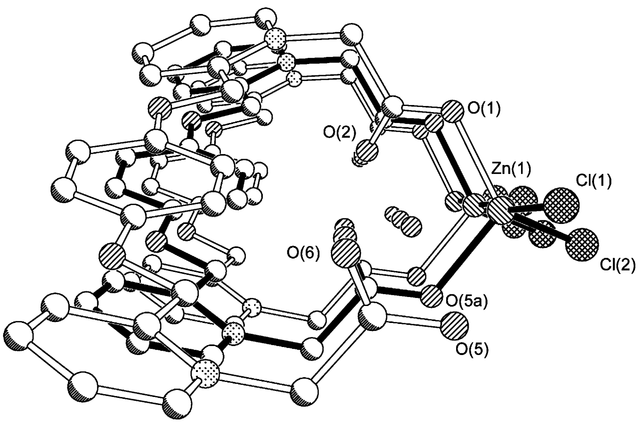


Fig. 7. Spring-like helical chain in compound **4** viewed in the *a* direction, showing water molecules of partial site occupancy included inside the channel.

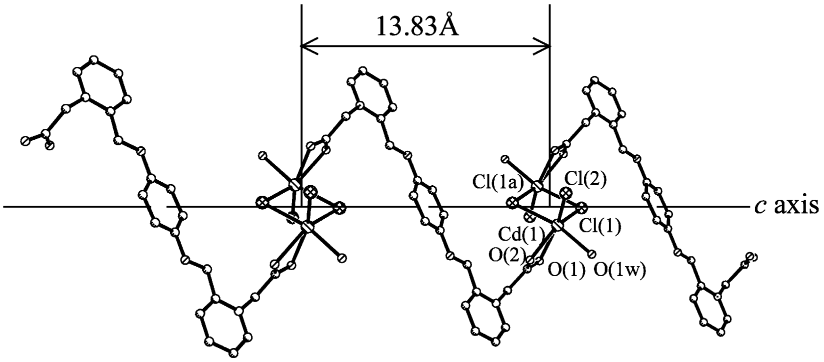


Fig. 8. Zigzag chain with binuclear moieties running along the [001] direction in compound **5**. Hydrogen atoms have been omitted for clarity.

coordination mode of L, the observed carboxylato O–C–O angle (124.3°) is smaller than those in **3** and **4** (126°, 128°). Nevertheless, this angle in **5** is still larger than those of unsymmetrical chelating carboxylate groups found in $[\{Cd(MeCO_2)_2(H_2O)_2\}_n]$ (mean 120.4°) [15] and $[Cd(C_6H_5OCH_2CO_2)_2(H_2O)_2]$ (121.1°) [16]. The Cd_2Cl_4 dimeric units are linked by the centrosymmetric, *anti* ligating L ligand to construct an infinite zigzag chain running along *c* (Fig. 8). The two pyridine rings of L are necessarily parallel to each other, but each makes a twist angle of 14.9° with the benzene ring. These adjacent zigzag chains are further connected through hydrogen bonds: [O2W···O2 = 2.757(3) Å, O2W–H2WB···O2 ~ 127°; O1W···O2Wa = 3.062(5) Å, O1W–H1WA···O2Wa ~ 160°; O1···C5a = 3.471(4) Å, C5a–H5a···O1 ~ 164°; a: $x+1/2$, $-y+1/2$, $z+1/2$] between the bridging ligands, lattice water molecules and the aqua ligands, which lead to the formation of a three-dimensional network (Fig. 9). No significant π–π stack interactions are found between the ligand molecules. (See Table 2 for selected bond angles and lengths for complexes **1**–**5**.)

The present study has shown that the flexible double betaine L is a useful ligand for the assembly of metal-organic coordination frameworks consolidated by hydrogen bonding and π–π interactions, and that the metal cations employed have an important influence on the formation of the resulting crystal structures of their complexes. In **1** and **2**, the affinity between the aqua ligand and Mn^{2+}(or Co^{2+}) is stronger than that between L and the metal ion. This leads to the formation of hydrated metal centers and uncoordinated L ligands in the crystal structure. Only one oxygen atom of the carboxylate group of L is coordinated to Cu(II), Zn(II) of the first transition series, while both oxygen atoms of the carboxylate group chelate the second-row transition metal ion Cd(II). This maybe attributed to the difference in size between the metal cations. Furthermore, L can display two principal types of bridging modes (*anti* and *syn*) that lead to different separations between consecutive metal centers, thereby generating various solid-state structures in the series of complexes reported here, particularly the different types of polymeric chains observed in **3** and **4**.

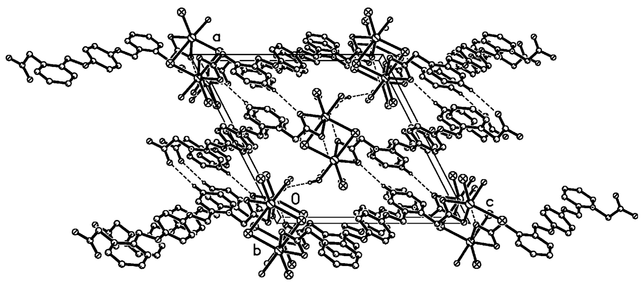


Fig. 9. Packing diagram of compound **5** showing the three-dimensional hydrogen-bonded network. Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Ctystallographic Data Centre, CCDC Nos. 193988–193992 for compounds **1**–**5**. Copies of this information may be obtained free of charge from the The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 2
Selected bond lengths (Å) and angles (°) for complexes **1**–**5**

Complex **1**			
Bond lengths			
Mn(1)–O(1w)	2.173(2)	Mn(1)–O(2w)	2.163(2)
Mn(1)–O(3w)	2.230(2)		
Bond angles			
O(1W)–Mn(1)–O(2W)	89.99(8)	O(1W)–Mn(1)–O(3W)	85.19(8)
O(2W)–Mn(1)–O(3W)	89.65(9)		
Complex **2**			
Bond lengths			
Co(1)–O(1w)	2.101(2)	Co(1)–O(2w)	2.063(2)
Co(1)–O(3w)	2.125(2)		
Bond angles			
O(1W)–Co(1)–O(2W)	89.73(7)	O(1W)–Co(1)–O(3W)	86.88(7)
O(2W)–Co(1)–O(3W)	88.84(7)		
Complex **3**			
Bond lengths			
Cu(1)–O(1)	1.953(2)	Cu(1)–Cl(1)	2.2470(7)
Bond angles			
O(1)–Cu(1)–Cl(1)	94.22(5)	O(1)–Cu(1)–Cl(1a)	92.13(5)
O(1a)–Cu(1)–O(1)	161.9(1)	Cl(1a)–Cu(1)–Cl(1)	138.86(5)
Complex **4**			
Bond lengths			
Zn(1)–O(1)	1.990(2)	Zn(1)–O(5a)	1.986(2)
Zn(1)–Cl(1)	2.2714(9)	Zn(1)–Cl(2)	2.3379(8)
Bond angles			
O(5a)–Zn(1)–O(1)	114.31(6)	O(5a)–Zn(1)–Cl(1)	109.81(5)
O(1)–Zn(1)–Cl(1)	104.27(6)	O(5a)–Zn(1)–Cl(2)	99.47(5)
O(1)–Zn(1)–Cl(2)	117.04(6)	Cl(1)–Zn(1)–Cl(2)	112.07(3)
Complex **5**			
Bond lengths			
Cd(1)–O(1)	2.491(2)	Cd(1)–O(2)	2.350(2)
Cd(1)–Cl(1)	2.572(1)	Cd(1)–Cl(2)	2.502(1)
Cd(1)–O(1w)	2.3643(3)	C(1)–O(1)	1.230(3)
C(1)–O(2)	1.243(4)	Cd(1)–Cl(1a)	2.746(1)
Bond angles			
O(2)–Cd(1)–O(1W)	85.32(8)	O(2)–Cd(1)–O(1)	53.62(7)
O(1W)–Cd(1)–O(1)	80.95(9)	O(2)–Cd(1)–Cl(2)	156.64(5)
O(1W)–Cd(1)–Cl(2)	94.19(8)	O(1)–Cd(1)–Cl(2)	103.18(6)
O(2)–Cd(1)–Cl(1)	96.13(6)	O(1W)–Cd(1)–Cl(1)	94.96(8)
O(1)–Cd(1)–Cl(1)	149.59(5)	Cl(2)–Cd(1)–Cl(1)	107.17(4)
O(1W)–Cd(1)–Cl(1a)	166.07(7)	O(2)–Cd(1)–Cl(1a)	81.23(5)
Cl(2)–Cd(1)–Cl(1a)	96.73(4)	O(1)–Cd(1)–Cl(1a)	88.14(5)
O(1)–C(1)–O(2)	124.3(2)	Cl(1)–Cd(1)–Cl(1a)	90.08(5)

Symmetry codes: (a) $-x+1$, y, $-z-1/2$ for **3**; (a) $x-1$, y, z for **4**; (a) $-x+1$, $-y$, $-z+1$ for **5**.

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