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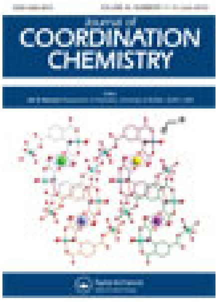

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Five new metal(II) complexes with 3-D network structures based on carboxylate and bis(imidazole) ligands: syntheses and structures

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Five new metal(II) complexes with 3-D network structures based on carboxylate and bis(imidazole) ligands: syntheses and structures

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The imidazolyl ligands, bis(*N*-imidazolyl)methane (L1) and 1,4-bis(*N*-imidazolyl)butane (L2) reacted with Zn(II), Cu(II), and Ni(II) salts of carboxylic acids resulting in the formation of five metal–organic coordination architectures, $[Zn(L1)(CO_3)] \cdot H_2O$ (**1**), $[Cu(L2)(cnic)_2] \cdot H_2O$ (**2**) (cnic = 2-chloronicotinate), $[Cu_2(L2)_2(adip)_2] \cdot 6H_2O$ (**3**) (adip = adipate), $[Ni(mal)(L1)(H_2O)]$ (**4**) (mal = malonate), and $[Ni_3(ctc^{3-})_2(L1)_6] \cdot 35H_2O$ (**5**) (ctc^- = citrate). All complexes have been characterized by elemental analysis, infrared, TG, and X-ray diffraction analyses. The different coordination modes of the carboxylates due to their chain length and rigidity lead to a range of different coordination structures. All these complexes display 3-D framework structures with a number of non-conventional weak interactions. The carboxylates can adopt bridging μ_2, chelating μ_2, chelating-bridging μ_3, and chelating μ_3 coordination modes. The metals are coordinated in N_2O_2, N_2O_3, N_2O_4, N_3O_3, and N_6 fashions depending on the metal and ancillary ligands. The frameworks of the five compounds are thermally stable.

Keywords: Carboxylic acid; Zn(II); Cu(II); Ni(II); Mixed ligands; Coordination polymers

1. Introduction

Coordination polymers attract attention for structural variety, intriguing physical properties, and promising applications in optics [1], electrical conductivity [2], magnetism [3], host–guest chemistry [4], molecular separation [5], gas adsorption [6], sensors [7], catalysis [8], etc. The framework structure of coordination polymers is primarily dependent upon the coordination preferences of the metal and the functionality of the ligands. Aside from coordination bonding, hydrogen-bonding, π–π stacking interactions, the solvent, counterions, the ratio of metal salt to ligand, and templates also influence the formation of the ultimate architectures.

Carboxylates play an important role in coordination chemistry, adopting binding modes as diverse as terminal monodentate, chelating to one metal, bridging bidentate in a *syn–syn*, *syn–anti*, and *anti–anti* configuration to two metals, and bridging tridentate to two metals [9]. Rigid rod-like spacer molecules, 4,4′-bipyridine (bipy) and pyrazine

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(pz) have been useful building blocks for construction of metal–organic coordination frameworks [10]. Flexible dicarboxylates ($R(COO)_2^{2-}$) and rigid planar bidentate diimines (bipy or pyz) as building blocks to construct metal assemblage are of growing interest in molecular materials [11]. Recently, success has been achieved by combination of flexible aliphatic dicarboxylates and bipy as chelating bridging ligands, resulting in compounds having 2-D layer-like structures or 3-D frameworks and unique physicochemical properties [12–17].

In contrast to rigid spacers, flexible/semi-flexible ligands bearing imidazolyl groups, which can adopt various conformations, may form coordination polymers with new topologies [18]. However, ligands containing imidazolyl groups and carboxylate ligands have not been well studied to date [19–24]. Therefore, development of synthetic routes to polymeric coordination compounds with mixed bridging ligands remains to be explored. Bis(*N*-imidazolyl)methane (L1) and 1,4-bis(*N*-imidazolyl)butane (L2) can be used as semi-flexible/flexible divergent ligands to construct coordination polymers. The remarkable coordination abilities of carboxylic acids and semi-flexible bidentate diimines have prompted us to synthesize new coordination polymeric compounds containing both ligands.

As an extension of our study of mixed-ligand coordination compounds based on bis(imidazole) and carboxylate [25], herein we report the preparation and structure of five metal–organic coordination polymers by reacting transition metal salts, carboxylates, and bis(imidazole) ligands L1/L2 in water. Their structures are fully characterized by elemental analysis, infrared (IR), TG, and X-ray diffraction analyses.

2. Experimental

2.1. *Materials and methods*

L1 and L2 were prepared according to the reported procedure [26]. All other reagents and solvents for syntheses were purchased from commercial sources and used as received. Elemental analyses were determined with a Carlo Erba 1110 instrument. IR spectra were measured as KBr discs using a Bruker Vector 22 spectrophotometer. Thermogravimetric analyses were studied by a Delta Series TA-SDT Q600 in N_2 from room temperature to 800°C (heating rate = $10^\circ C\,min^{-1}$) using Al crucibles.

2.2. *Preparation of the compounds*

2.2.1. Preparation of $[Zn(L1)(CO_3)]\cdot H_2O$ (1). To an aqueous solution (8 mL) of Na_2CO_3 (10.6 mg, 0.1 mmol) and 2,2′-bipyridine-3,3′-dicarboxylic acid (24.4 mg, 0.1 mmol), $ZnSO_4\cdot 7H_2O$ (28.8 mg, 0.1 mmol) was added, the solution was stirred for 10 min at 60°C and then L1 (15 mg, 0.1 mmol) was added to the mixture. After stirring for 30 min, a large amount of precipitate formed; to the reaction mixture concentrated ammonia was added until the precipitate dissolved completely. The solution was filtered into a test tube, allowed to stand at ambient temperature, and colorless block crystals separated from the mother liquor by slow evaporation at ambient temperature after 3 weeks. Yield: 21 mg, 72.02%. Anal. Calcd for $C_8H_{10}N_4O_4Zn$ (291.57): C, 32.92;

H, 3.43; N, 19.21. Found: C, 32.86; H, 3.36; N, 19.12. IR (KBr, cm^{-1}): 3459w, 3213s, 3115w, 2242w, 1662m, 1572m, 1504m, 1395m, 1354m, 1282m, 1234s, 1087s, 1032w, 936m, 842m, 766m, 714m, 658m, 611w.

2.2.2. Preparation of $[Cu(L2)(cnic)_2]\cdot H_2O$, 2 (cnic = 2-chloronicotinate). A mixture of $CuCl_2\cdot 2H_2O$ (17.1 mg, 0.1 mmol), NaOH (8 mg, 0.2 mmol), and 2-chloronicotinic acid (31.4 mg, 0.2 mmol) in 10 mL water was stirred for 10 min at 60°C, then 1,4-bis(*N*-imidazolyl)butane L2 (19 mg, 0.1 mmol) was added to the mixture. After stirring for 30 min, a blue precipitate was collected and dissolved in a minimum amount of ammonia. Blue single crystals of **2** were obtained by slow evaporation of the ammonia solution at ambient temperature. Yield: 32 mg, 54.71%. Anal. Calcd for $C_{22}H_{22}Cl_2CuN_6O_5$ (584.90): C, 45.13; H, 3.76; N, 14.36. Found: C, 45.08; H, 3.68; N, 14.29. IR spectrum (cm^{-1}): 3746w, 3435m, 3240w, 2938m, 1658s, 1580m, 1540m, 1452m, 1408m, 1368s, 1300s, 1276w, 1228w, 1140m, 1096m, 1020m, 934m, 895m, 852m, 816m, 774m, 730m, 662m, 620m.

2.2.3. Preparation of $[Cu_2(L2)_2(adip)_2]\cdot 6H_2O$, 3 (adip = adipate). A mixture of $CuCl_2\cdot 2H_2O$ (17.1 mg, 0.1 mmol), NaOH (8 mg, 0.2 mmol), and adipic acid (14.6 mg, 0.1 mmol) in 5 mL water was stirred for 10 min at 60°C, then 1,4-bis(*N*-imidazolyl)butane L2 (19 mg, 0.1 mmol) was added to the mixture. After stirring for 30 min, a blue precipitate was collected and dissolved in a minimum of ammonia. Blue single crystals of **3** were obtained by slow evaporation of the ammonia solution at ambient temperature. Yield: 35 mg, 77.44%. Anal. Calcd for $C_{32}H_{56}Cu_2N_8O_{14}$ (903.93): C, 42.48; H, 6.19; N, 12.39. Found: C, 42.42; H, 6.12; N, 12.31. IR spectrum (cm^{-1}): 3729 cm^{-1} (m), 3438w, 3393m, 3216w, 2939w, 1654s, 1570m, 1551m, 1433s, 1403m, 1355s, 1310m, 1239m, 1103m, 940w, 857m, 753m, 652m.

2.2.4. Preparation of $[Ni(mal)(L1)(H_2O)]$, 4 (mal = malonate). An aqueous solution (3 mL) of malonic acid (10.4 mg, 0.1 mmol) and NaOH (8 mg, 0.2 mmol) was treated by $NiCl_2\cdot 6H_2O$ (24 mg, 0.1 mmol). After the mixture was stirred for a few minutes, L1 (15 mg, 0.1 mmol) in 3 mL water was added to give a pale green solution. Slow evaporation of the resulting solution yielded green block crystals after a few days, which were collected and washed with water and ethanol. Yield: 23 mg, 70.36%. Elemental analysis performed on crystals exposed to the atmosphere: Anal. Calcd for $C_{10}H_{12}N_4NiO_5$ (326.95): C, 36.70; H, 3.67; N, 17.13. Found: C, 36.59; H, 3.63; N, 17.08. IR data (KBr pellet, cm^{-1}): 3346s, 3142w, 1656m, 1566m, 1454m, 1392w, 1349m, 1296w, 1227m, 1159m, 1103m, 1026m, 932m, 848m, 764m, 704m, 659m, 617w, 566m, 468m.

2.2.5. Preparation of $[Ni_3(ctc^{3-})_2(L1)_6]\cdot 35H_2O$, 5 ($ctc^{3-}$ = citrate trianion). An aqueous solution (5 mL) of citric acid (12.8 mg, 0.067 mmol) and NaOH (8 mg, 0.2 mmol) was treated by $NiCl_2\cdot 6H_2O$ (24 mg, 0.1 mmol). After the mixture was stirred for a few minutes, L1 (15 mg, 0.1 mmol) in 3 mL water was added to give a pale green solution. Slow evaporation of the solution yielded light green crystals after a few days, which were collected and washed with water and ethanol. Yield: 35 mg, 50.63% (based on $NiCl_2\cdot 6H_2O$). Anal. Calcd for $C_{54}H_{128}N_{24}Ni_3O_{49}$ (2073.93): C, 31.25; H, 6.17;

N, 16.20. Found: C, 31.22; H, 6.08; N, 16.14. IR data (KBr, cm^{-1}): 3684s, 3462s, 3122s, 1660s, 1598s, 1516m, 1358s, 1284s, 1236s, 1098s, 1036w, 954m, 852m, 784s, 726s, 654m, 608m, 548m.

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction data for **1**–**5** were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) by using an ω–2θ scan mode. Data collection and reduction were performed using *SMART* and *SAINT* software [27]. The structures were solved by direct methods and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the *SHELXTL* package [28]. Hydrogen positions for all of the structures were calculated and allowed to ride on their respective carbons with C–H distances of 0.93–0.97 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$. Hydrogen atoms bound to water were located in the Fourier difference map and their distances were fixed. Further details of the structural analysis are summarized in table 1. Selected bond lengths and angles for **1**–**5** are listed in table 2 and relevant hydrogen-bond parameters are provided in table 3. The *R*-value of **5** is very high, which is attributed to the fact that **5** contains a large amount of lattice water. For the presence of these water molecules, **5** is relatively unstable such that X-ray diffraction data collected at the final section are not useable leading the data to be incomplete.

3. Results and discussion

3.1. *Syntheses and general characterization*

Complexes **1**–**5** were prepared by conventional solution method. All complexes are insoluble in water and common organic solvents. Crystals of **1**–**3** were obtained by slow evaporation of their ammonia solutions, but crystals of **4** and **5** suitable for X-ray diffraction analysis were obtained by standing their solutions at room temperature. Elemental analysis data for the five compounds are in agreement with their formulae.

The IR spectra of **1**–**5** are consistent with their chemical formulae determined by elemental analysis and further confirmed by X-ray diffraction analysis. The very strong and broad features at approximately 3700–3100 cm^{-1} in the spectra of all compounds arise from O–H stretching frequencies of water. Aromatic and imidazolyl ring stretching and bending are attributed to medium intensity bands at 1500–1630 cm^{-1} and 600–750 cm^{-1}, respectively.

3.2. *Structural description*

3.2.1. Crystal structure of $[Zn(L1)(CO_3)]\cdot H_2O$ (1). Compound **1**, $[Zn(L1)(CO_3)]\cdot H_2O$, was obtained by reacting Zn^{2+}, 2,2′-bipyridine-3,3′-dicarboxylic acid, and bis(*N*-imidazolyl)methane (L1) in basic aqueous solution. However, 2,2′-bipyridine-3,3′-dicarboxylic acid moiety did not appear in **1**. Colorless single crystals of **1** suitable for X-ray diffraction analysis were obtained by evaporating its concentrated

Table 1. Summary of X-ray crystallographic data for **1–5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_8H_{10}N_4O_4Zn$	$C_{22}H_{22}Cl_2CuN_6O_5$	$C_{32}H_{56}Cu_2N_8O_{14}$	$C_{10}H_{12}N_4NiO_5$	$C_{54}H_{128}N_{24}Ni_3O_{49}$
Formula weight	291.57	584.90	903.93	326.95	2073.93
Temperature (K)	298(2)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*Pbca*	*C*2/*c*	*P*2(1)	*P*2(1)/*c*	*P*-1
Unit cell dimensions (Å, °)					
a	9.1272(9)	16.7035(17)	9.3138(12)	8.3345(7)	12.8501(13)
b	15.1014(12)	13.5879(13)	17.237(2)	21.8289(19)	13.4601(14)
c	15.9165(16)	12.0050(11)	13.4443(19)	8.3383(9)	15.3799(16)
α	90	90	90	90	115.750(2)
β	90	111.0090(10)	108.0770(10)	116.9630(10)	92.6600(10)
γ	90	90	90	90	101.8000(10)
Volume (Å^3), Z	2193.8(4), 8	2543.6(4), 4	2051.9(5), 2	1352.1(2), 4	2317.6(4), 1
Calculated density (Mg m^{-3})	1.766	1.527	1.463	1.606	1.486
Absorption coefficient (mm^{-1})	2.249	1.114	1.109	1.459	0.711
$F(000)$	1184	1196	948	672	1096
Crystal size (mm^3)	0.29 × 0.20 × 0.11	0.44 × 0.41 × 0.38	0.35 × 0.11 × 0.08	0.40 × 0.32 × 0.31	0.37 × 0.36 × 0.31
θ range for data collection (°)	2.56–25.01	2.36–25.01	2.30–25.02	2.74–25.00	1.64–25.02
Limiting indices	$-10 \le h \le 10$; $-17 \le k \le 16$; $-15 \le l \le 18$	$-19 \le h \le 15$; $-15 \le k \le 16$; $-14 \le l \le 14$	$-11 \le h \le 1$; $-20 \le k \le 20$; $-15 \le l \le 9$	$-9 \le h \le 9$; $-25 \le k \le 22$; $-8 \le l \le 9$	$-8 \le h \le 15$; $-16 \le k \le 14$; $-17 \le l \le 16$
Reflections collected	9265	6226	10,528	6743	9404
Independent reflection	1928 [R(int) = (0.0510)]	2244 [R(int) = (0.0278)]	7057 [R(int) = (0.0648)]	2381 [R(int) = (0.0297)]	7382 [R(int) = (0.1344)]
Goodness-of-fit on F^2	0.942	1.091	0.888	1.023	0.964
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0286$, $wR_2 = 0.0630$	$R_1 = 0.0455$, $wR_2 = 0.1090$	$R_1 = 0.0616$, $wR_2 = 0.1296$	$R_1 = 0.0289$, $wR_2 = 0.0691$	$R_1 = 0.1647$, $wR_2 = 0.3860$
R indices (all data)	$R_1 = 0.0468$, $wR_2 = 0.0683$	$R_1 = 0.0692$, $wR_2 = 0.1298$	$R_1 = 0.1072$, $wR_2 = 0.1477$	$R_1 = 0.0353$, $wR_2 = 0.0707$	$R_1 = 0.3667$, $wR_2 = 0.4716$
Largest difference peak and hole (e Å^{-3})	0.520 and −0.326	1.112 and −1.062	0.709 and −0.495	0.318 and −0.264	1.219 and −1.080

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

1			
Zn(1)–O(2)#1	1.949(2)	Zn(1)–O(1)	1.977(2)
Zn(1)–N(4)	2.004(2)	Zn(1)–N(2)	2.016(2)
O(1)–C(8)	1.309(3)	O(2)–C(8)	1.300(3)
O(3)–C(8)	1.250(3)	O(2)#1–Zn(1)–O(1)	99.63(8)
O(2)#1–Zn(1)–N(4)	108.30(9)	O(1)–Zn(1)–N(4)	109.36(9)
O(2)#1–Zn(1)–N(2)	114.18(9)	O(1)–Zn(1)–N(2)	108.62(9)
N(4)–Zn(1)–N(2)	115.52(10)	O(3)–C(8)–O(2)	121.6(3)
O(3)–C(8)–O(1)	121.1(3)	O(2)–C(8)–O(1)	117.2(2)
2			
Cu(1)–O(1)	1.964(3)	Cu(1)–N(2)	1.974(3)
O(1)–C(6)	1.255(5)	O(2)–(6)	1.217(5)
O(1)#1–Cu(1)–O(1)	180.000(1)	O(1)#1–Cu(1)–N(2)	91.12(12)
O(1)–Cu(1)–N(2)	88.88(12)	C(1)–N(1)–C(3)	107.1(3)
C(1)–N(1)–C(4)	125.6(3)	C(3)–N(1)–C(4)	127.3(3)
C(1)–N(2)–C(2)	106.0(3)	N(2)–C(1)–N(1)	111.3(3)
O(2)–C(6)–O(1)	126.9(4)		
3			
Cu(2)–O(3)	1.932(6)	Cu(2)–N(6)	1.974(7)
Cu(2)–N(8)	1.976(7)	Cu(2)–O(7)	1.989(5)
Cu(2)–O(8)	2.622(7)	O(4)–C(26)	1.256(11)
Cu(1)–O(1)	1.926(6)	Cu(1)–N(4)	1.958(6)
Cu(1)–N(2)	1.976(7)	Cu(1)–O(5)	1.985(6)
Cu(1)–O(6)	2.626(7)	O(1)–C(21)	1.269(11)
O(2)–C(21)	1.234(13)	O(3)–C(26)	1.263(10)
O(5)–C(27)	1.245(13)	O(6)–C(27)	1.228(12)
O(7)–C(32)	1.285(12)	O(8)–C(32)	1.227(12)
O(3)–Cu(2)–N(6)	91.3(3)	O(3)–Cu(2)–N(8)	93.1(3)
N(6)–Cu(2)–N(8)	157.1(3)	O(3)–Cu(2)–O(7)	161.0(3)
N(6)–Cu(2)–O(7)	93.2(2)	N(8)–Cu(2)–O(7)	89.8(3)
O(3)–Cu(2)–O(8)	106.2(2)	N(6)–Cu(2)–O(8)	98.0(3)
N(8)–Cu(2)–O(8)	102.3(3)	O(7)–Cu(2)–O(8)	54.9(3)
O(1)–Cu(1)–N(4)	93.5(3)	O(1)–Cu(1)–N(2)	92.9(3)
N(4)–Cu(1)–N(2)	156.4(3)	O(1)–Cu(1)–O(5)	158.8(3)
N(4)–Cu(1)–O(5)	91.3(3)	N(2)–Cu(1)–O(5)	90.9(3)
O(1)–Cu(1)–O(6)	104.7(3)	N(4)–Cu(1)–O(6)	97.8(3)
N(2)–Cu(1)–O(6)	102.4(3)	O(5)–Cu(1)–O(6)	54.1(3)
C(1)–N(1)–C(3)	107.6(8)	C(1)–N(1)–C(7)	126.9(9)
C(3)–N(1)–C(7)	125.4(8)	C(1)–N(2)–C(2)	105.6(8)
O(2)–C(21)–O(1)	125.9(10)	O(4)–C(26)–O(3)	122.0(9)
O(6)–C(27)–O(5)	123.0(11)	O(8)–C(32)–O(7)	122.1(10)
4			
Ni(1)–O(4)	2.0634(15)	Ni(1)–N(2)	2.0648(19)
Ni(1)–N(4)	2.0717(19)	Ni(1)–O(5)	2.0798(16)
Ni(1)–O(1)	2.0979(15)	Ni(1)–O(2)#1	2.1020(16)
O(1)–C(8)	1.255(3)	O(2)–C(8)	1.267(3)
O(3)–C(10)	1.256(3)	O(4)–C(10)#1	1.266(3)
O(4)–Ni(1)–N(2)	91.97(10)	O(4)–Ni(1)–N(4)	88.89(7)
N(2)–Ni(1)–N(4)	90.04(8)	O(4)–Ni(1)–O(5)	176.06(6)
N(2)–Ni(1)–O(5)	91.75(7)	N(4)–Ni(1)–O(5)	92.40(7)
O(4)–Ni(1)–O(1)	87.89(6)	N(2)–Ni(1)–O(1)	178.71(7)
N(4)–Ni(1)–O(1)	91.24(7)	O(5)–Ni(1)–O(1)	88.36(6)
O(4)–Ni(1)–O(2)#1	87.00(6)	N(2)–Ni(1)–O(2)#1	87.08(7)
N(4)–Ni(1)–O(2)#1	174.89(7)	O(5)–Ni(1)–O(2)#1	91.91(6)
O(1)–Ni(1)–O(2)#1	91.64(6)		
5			
Ni(1)–N(6)	1.939(18)	Ni(1)–O(7)	1.968(14)

(*continued*)

Table 2. Continued.

Ni(1)–O(1)	2.001(16)	Ni(1)–O(5)	2.006(16)
Ni(1)–N(10)	2.008(18)	Ni(1)–N(2)	2.022(19)
Ni(2)–N(4)	2.027(19)	Ni(2)–N(8)	2.082(18)
Ni(2)–N(12)	2.086(18)	N(6)–Ni(1)–O(7)	171.6(7)
N(6)–Ni(1)–O(1)	89.3(7)	O(7)–Ni(1)–O(1)	84.5(6)
N(6)–Ni(1)–O(5)	95.3(7)	O(7)–Ni(1)–O(5)	79.0(6)
O(1)–Ni(1)–O(5)	87.9(6)	N(6)–Ni(1)–N(10)	94.3(7)
O(7)–Ni(1)–N(10)	91.5(6)	O(1)–Ni(1)–N(10)	174.1(7)
O(5)–Ni(1)–N(10)	87.0(7)	N(6)–Ni(1)–N(2)	90.4(7)
O(7)–Ni(1)–N(2)	95.3(7)	O(1)–Ni(1)–N(2)	92.3(6)
O(5)–Ni(1)–(2)	174.3(7)	N(10)–Ni(1)–N(2)	92.4(7)
N(4)–Ni(2)–N(8)	89.2(8)	N(4)–Ni(2)–N(12)	88.9(8)
N(8)–Ni(2)–N(12)	88.6(7)		

Symmetry code for **1**: #1: $x-1/2$, y,$-z+3/2$. Symmetry code for **2**: #1: $-x+1$, $-y+1$, $-z+1$. Symmetry transformations used to generate equivalent atoms for **4**: #1: x, $-y+1/2$, $z-1/2$.

ammonia solution. Compound **1** belongs to the orthorhombic, *pbca* space group. X-ray diffraction analysis showed that the asymmetric unit of **1** consists of one Zn, one carbonate, one bis(*N*-imidazolyl)methane molecule, and one lattice water molecule.

As shown in figure 1, each zinc is coordinated by two nitrogen atoms from two independent bis(*N*-imidazolyl)methane molecules as bridging ligands and two oxygen atoms from two carbonates, completing its tetrahedral geometry in an N_2O_2 donor set. The coordination environment of the Zn is similar to benzimidazole-based Zn^{II} polymers [29]. The Zn–O bond distances, being 1.949(2) and 1.977(2) Å, are much shorter than those of the Zn–O(carbonate) bond distances (2.129(2) and 2.091(2) Å) reported by Hanauer [30]. The Zn–N distances of 2.004(2) and 2.016(2) Å are normal and consistent with distances of known Zn-imidazole complexes (2.005(4) and 2.008(3) Å) [31, 32].

The carbonate is a bis-unidentate ligand, connecting with two Zn's; L1 also is a bis-unidentate ligand. Two carbonates, two L1, and two zincs form a 24-membered ring. The Zn–Zn distance bridged by carbonate is 4.721 Å, while the Zn–Zn distance connected by L1 is 9.441 Å. L1 displays *trans* conformation. The zinc cations connect by carbonate to form a 1-D chain running along the *a*-axis. These chains were linked by L1 through Zn–N bonds and CH–O interaction between 5-CH of the imidazole moiety and one coordinated oxygen atom of carbonate with C–O distance of 3.467 Å to form a 2-D grid extending along the *ab*-plane (figure 2). In the grid, L1 protrude from the plane defined by the chain formed by carbonate and Zn. The 2-D grids further stack along the *c*-axis *via* the O–H···O hydrogen bonds between the lattice water molecules and carbonates with O–O distance of 2.764(3) Å and 2.786(3) Å, respectively, to form a 3-D layer network structure.

3.2.2. Crystal structure of $[Cu(L2)(cnic)_2]\cdot H_2O$, (2) (cnic = 2-chloronicotinate).

Compound **2**, $[Cu(L2)\cdot(cnic)_2]\cdot H_2O$, was obtained by reacting Cu^{2+}, 2-chloronicotinic acid, and 1,4-bis(*N*-imidazolyl)butane (L2) in basic aqueous solution and was isolated as blue crystals. Compound **2** belongs to the monoclinic *C*2/*c* space group. X-ray diffraction analysis shows that **2** is a 1-D chain, and the asymmetric unit consists of one Cu, one 2-chloronicotinate, half of L2, and one water molecule.

Table 3. Hydrogen bond distances (Å) and angles (°) in **1–5**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
1				
O(4)–H(4B)···O(3)#5	0.85	1.92	2.764(3)	176.3
O(4)–H(4A)···O(1)	0.85	1.94	2.786(3)	169.9
2				
O(3)–H(3)···O(2)#3	0.85	1.88	2.722(4)	168.0
3				
O(14)–H(14D)···O(2)#5	0.85	1.73	2.58(3)	175.4
O(14)–H(14C)···O(13)	0.85	1.89	2.73(3)	176.0
O(13)–H(13D)···O(12)#5	0.85	1.94	2.769(17)	164.7
O(13)–H(13C)···O(6)#6	0.85	2.25	3.059(17)	159.4
O(12)–H(12D)···O(11)#7	0.85	1.90	2.746(10)	178.9
O(12)–H(12C)···O(5)#8	0.85	1.97	2.816(12)	179.3
O(11)–H(11D)···O(9)#9	0.85	1.88	2.729(11)	178.2
O(11)–H(11C)···O(4)	0.85	1.83	2.682(9)	178.9
O(10)–H(10F)···O(7)#10	0.85	1.99	2.813(11)	162.3
O(10)–H(10E)···O(2)#9	0.85	1.93	2.754(10)	162.6
O(9)–H(9F)···O(10)#11	0.85	1.92	2.763(11)	172.6
O(9)–H(9E)···O(8)#10	0.85	1.94	2.783(10)	172.0
4				
O(5)–H(5E)···O(3)#4	0.85	1.89	2.731(2)	171.0
O(5)–H(5D)···O(1)	0.85	2.45	2.911(2)	114.5
O(5)–H(5D)···O(2)	0.85	1.94	2.787(2)	171.4
5				
O(26)–H(26D)···O(19)	0.85	1.78	2.63(8)	177.3
O(26)–H(26C)···O(14)	0.85	2.16	3.01(5)	173.4
O(25)–H(25F)···O(23)#2	0.85	2.88	3.39(4)	120.0
O(25)–H(25F)···O(26)#3	0.85	1.93	2.74(5)	160.1
O(25)–H(25E)···O(26)#4	0.85	1.85	2.67(4)	161.9
O(24)–H(24D)···O(12)#5	0.85	1.83	2.67(3)	169.4
O(24)–H(24C)···O(25)	0.85	2.04	2.89(4)	175.0
O(23)–H(23D)···O(20)#6	0.85	2.28	3.12(7)	171.7
O(23)–H(23C)···O(16)	0.85	1.69	2.54(4)	173.6
O(22)–H(22C)···O(13)#7	0.85	2.23	3.01(8)	151.9
O(20)–H(20D)···O(21)	0.85	2.23	3.07(7)	175.3
O(20)–H(20C)···O(13)	0.85	2.10	2.94(8)	167.7
O(19)–H(19D)···O(23)#8	0.85	1.94	2.78(9)	170.6
O(19)–H(19C)···O(22)	0.85	1.59	2.43(10)	173.5
O(18)–H(18D)···O(21)#6	0.85	1.81	2.65(3)	173.9
O(17)–H(17D)···O(24)	0.85	2.11	2.96(4)	176.5
O(17)–H(17C)···O(10)#6	0.85	1.82	2.67(4)	175.1
O(16)–H(16D)···O(9)	0.85	2.18	3.03(3)	175.0
O(15)–H(15D)···O(12)	0.85	2.79	3.21(3)	112.5
O(15)–H(15D)···O(24)#5	0.85	2.04	2.89(4)	175.8
O(15)–H(15C)···O(22)#9	0.85	1.66	2.50(7)	167.2
O(14)–H(14F)···O(16)#8	0.85	1.94	2.78(3)	169.9
O(14)–H(14E)···O(11)#8	0.85	1.77	2.60(3)	165.6
O(13)–H(13D)···O(17)#10	0.85	1.89	2.73(4)	174.2
O(12)–H(12D)···O(14)#8	0.85	1.95	2.79(3)	169.0
O(12)–H(12C)···O(15)	0.85	2.37	3.21(3)	170.2
O(11)–H(11D)···O(8)#8	0.85	1.77	2.61(2)	166.0
O(10)–H(10D)···O(18)#6	0.85	1.74	2.59(3)	177.9
O(9)–H(9D)···O(11)	0.85	2.18	3.00(3)	159.8
O(8)–H(8D)···O(15)#8	0.85	1.77	2.62(3)	177.4
O(7)–H(7)···O(3)	0.82	1.85	2.544(19)	141.4

Symmetry transformations used to generate equivalent atoms for **1**: #5: $-x+1, -y, -z+2$; for **2**: #3: $-x+1/2, -y+1/2, -z+1$; for **3**: #5: $x, y+1, z$; #6: $-x, y+1/2, -z+1$; #7: $-x+1, y-1/2, -z+1$; #8: $x+1, y, z$; #9: $-x+1, y+1/2, -z+1$; #10: $x, y, z+1$; #11: $-x+2, y-1/2, -z+2$; for **4**: #4: $x-1, -y+1/2, z-1/2$; for **5**: #2: $x+1, y, z$; #3: $-x+2, -y+1, -z+1$; #4: $x, y-1, z$; #5: $-x+1, -y, -z+1$; #6: $-x+1, -y+1, -z+2$; #7: $x, y, z-1$; #8: $-x+1, -y+1, -z+1$; #9: $x-1, y-1$, z; #10: $-x+2, -y+1, -z+2$.

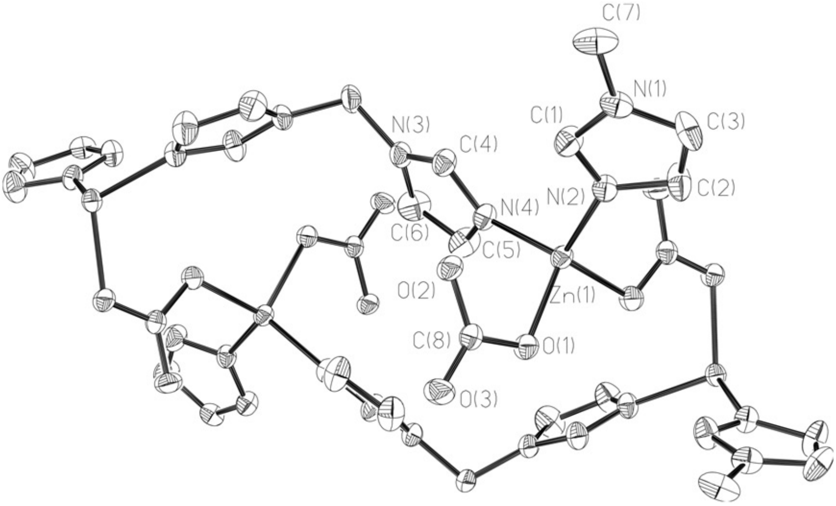

Figure 1. X-ray crystal structure of **1** with atom-numbering scheme. The thermal ellipsoids are drawn at 30% probability.

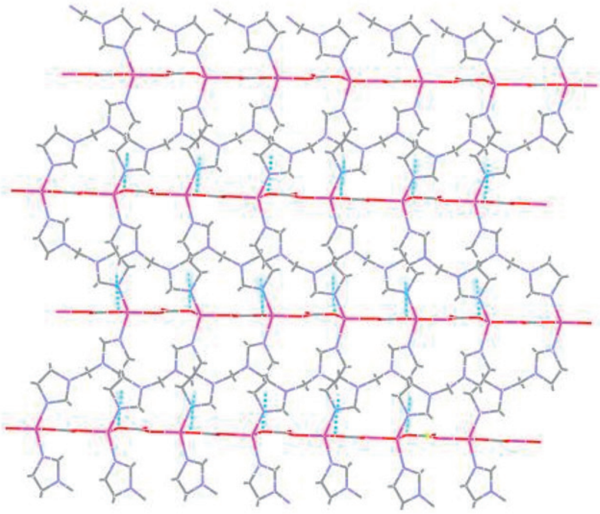

Figure 2. Infinite 2-D grid structure of **1**; the dashed line represents the CH–O interaction.

As shown in figure 3, Cu is tetrahedral, coordinated by two nitrogen atoms from two independent 1,4-bis(*N*-imidazolyl)butane bridging ligands, and two oxygen atoms from two monodentate 2-chloronicotinates with a N_2O_2 donor set. The Cu–N distances of 1.974(3) Å are normal and consistent with known Cu-imidazole complexes, which range from 1.876(13) Å to 2.049(8) Å [33]. The Cu-O(carboxylate) bond distance (1.964(3) Å) is similar to the documented Cu complex (1.971(2) Å) [34].

In the chain there are intramolecular Cl–O contacts between the Cl and coordinated oxygen of the anion with Cl–O distance of 3.229 Å. The anions and the cations form a

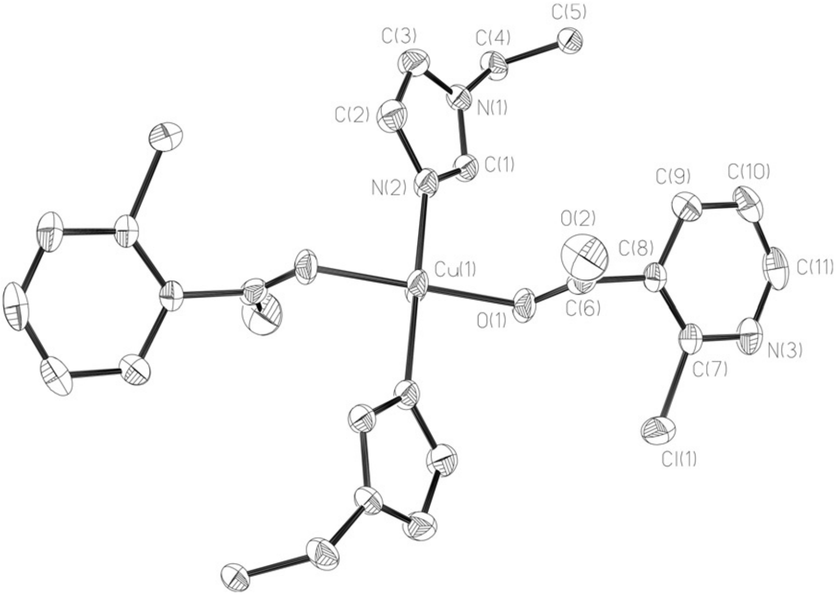

Figure 3. Structure of **2** showing the coordination environment of metal with the atomic-numbering scheme. The thermal ellipsoids are drawn at 30% probability.

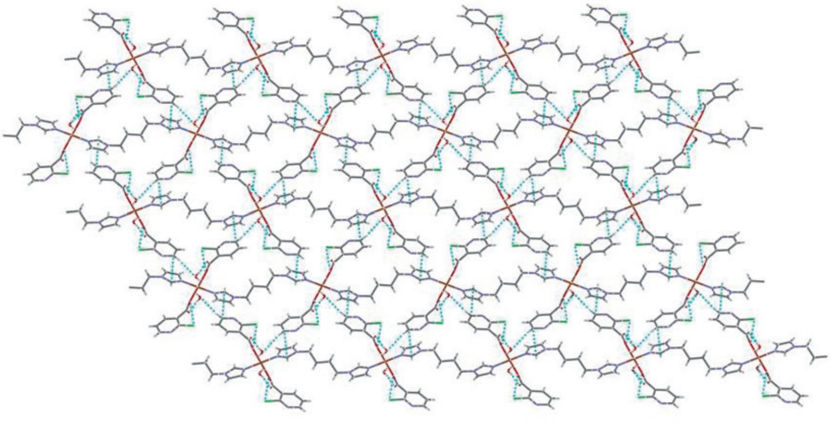

Figure 4. 2-D sheet structure of **2** extending along the *ab*-plane.

1-D chain running along the *b*-axis. In the chain there are bound water molecules at the uncoordinated oxygen of carboxylate through O–H···O hydrogen bond with O–O separation of 2.722(4) Å. Such chains are joined *via* π–π interactions between pyridine of 2-chloronicotinate and the imidazole ring of L2 with Cg–Cg distance of 3.331 Å, and CH–O interaction between water and the aromatic CH of pyridine with C–O distance of 3.404 Å to form a 2-D sheet extending along the *ab*-plane (figure 4). Such sheets were further stacked along the *c*-axis *via* intersheet O–H···O hydrogen bonds (between the carboxylate of the second sheet and the water bonded with carboxylate at the first sheet

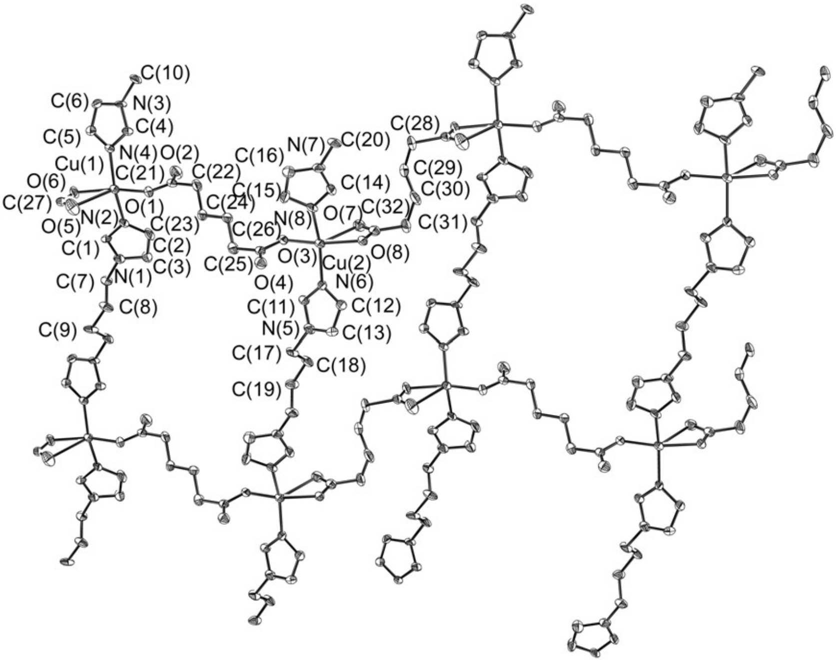

Figure 5. Structure of **3** showing the coordination environment of metal with the atomic-numbering scheme. The thermal ellipsoids are drawn at 30% probability.

with O–O separation of 2.722(4) Å), CH–N association (between the N–CH–N of L2 and the ring N of the anion with C–N distance of 3.537 Å), and CH–O interactions (between 4-CH of L2 and the carboxylate with C–O distance of 3.284 Å and between water and 6-CH of the anion with C–O distance of 3.404 Å) to form a 3-D network structure.

3.2.3. Crystal structure of [$Cu_2(L2)_2(adip)_2$]·$6H_2O$, (3) (adip = adipate). Similar to **2**, **3** was prepared by reacting $CuCl_2 \cdot 2H_2O$ with L2 in the presence of disodium adipate. Single crystals of **3** suitable for X-ray diffraction analysis were obtained by evaporating an ammonia solution of **3**. Compound **3** consists of two coppers, two L2, two adipates, and six water molecules. The coordination arrangement around Cu^{II} is distorted pseudo-square planar with a N_2O_3 binding set, figure 5. Each copper is coordinated by two imidazolyl nitrogen atoms from two individual L2 and three oxygen atoms from two carboxylates of two different adipates; one carboxylate coordinates to Cu in chelating fashion, while another coordinates monodentate.

The Cu–N distances range from 1.958(7) to 1.976(7) Å, within the range expected [35]. In the chelating carboxylate the Cu–O bond lengths are 1.989(5) Å for Cu(2)–O(7) and 2.622(7) Å for Cu(2)–O(8), in the range of weak Cu–O bonds [35]. The Cu–O bond distances for monodentate carboxylate are 1.932(6) Å for Cu(2)–O(3) and 1.926(6) Å for Cu(1)–O(1), while O4 and O2 are 2.912 and 3.077 Å away from Cu, indicating no bonding interactions.

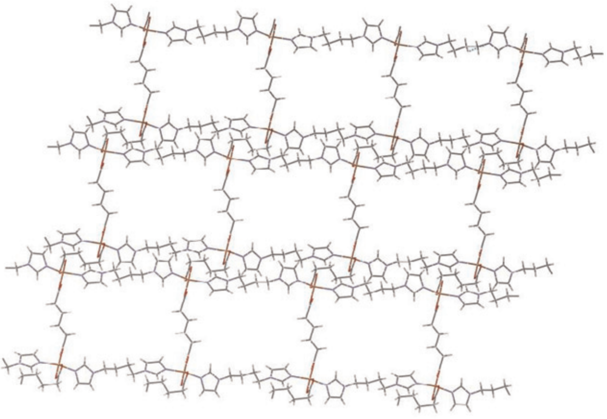

Figure 6. 2-D corrugated grid sheet of **3** extending along the *ac*-plane.

The structure of **3** consists of 2-D corrugated grid sheets extending along the *ac*-plane (figure 6). In the sheet there are two kinds of grids. One has a dimension of 13.776 × 10.937 Å and are enclosed by two L2, two adipates, and four Cu(II) with carboxylate coordinated unidentate to Cu. The other grid has two bisbidentate coordinated adipates, two L2, and four Cu's with a dimension of 13.776 × 9.835 Å. Coordination of imidazole ring nitrogen atoms causes significant change in conformation of (1-(4-(1*H*-imidazol-1-yl)butyl)-1*H*-imidazole) in **3** in comparison to the corresponding neutral molecule (1-(4-(1*H*-imidazol-1-yl)butyl)-1*H*-imidazole) [36]. The imidazole rings in **3** have gauche (*trans*) conformation with respect to C8–C9, and C18–C19 bond (angle C7–C8–C9–C10, 72.35°; C17–C18–C19–C20, 68.03°), which is different from the adduct formed between L2 and fumaric acid [37]. Two adjacent sheets interpenetrate through each other to form a 2-D double sheet structure. In the double sheet there are CH_2–O contacts between the butane spacer and carboxylate with C–O distances of 3.548–3.569 Å and O–π interactions between monodentate carboxylate and the imidazole of L2 with O–Cg distance of 3.163 Å. The double sheets were further joined along the *b*-axis *via* water molecules to form a 3-D layer network. In **3** the water molecules form a water hexamer *via* O–H···O hydrogen bonds. There also exist CH_2–O associations between adjacent double-sheets with C–O distance of 3.496 Å to consolidate the 3-D structure.

3.2.4. Crystal structure of [Ni(mal)(L1)(H_2O)], (4) (mal = malonate).

[Ni(mal)(L1)(H_2O)] (**4**) was obtained from a basic aqueous solution of $NiCl_2$, malonic acid, and bis(*N*-imidazolyl)methane in 1 : 1 : 1 ratio. X-ray diffraction analysis revealed **4** consists of one nickel, one malonate dianion, one L1, and one coordinated water molecule (figure 7). The malonate coordinates to one metal in chelating form with two of the four oxygen atoms and bridges the second metal with one of the remaining oxygen atoms. Ni is six coordinate in a compressed octahedral environment. Two imidazolyl nitrogen donors coordinate to metal with Ni–N distances of 2.0648(19) and 2.0717(19) Å; Ni–N is close to reported values [38]. Another four sites are occupied by oxygen atoms, one from water and the others from carboxylates of two different malonates with Ni–O distances ranging from 2.0634(15) Å to 2.1020(16) Å. The Ni–O_w

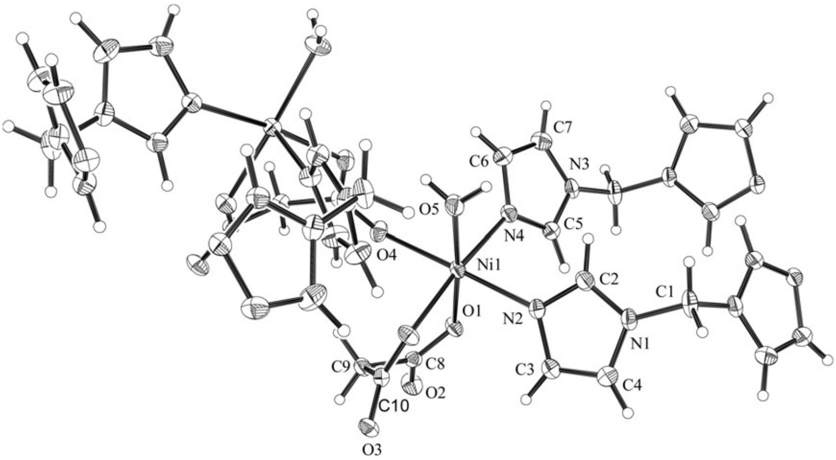

Figure 7. Structure of **4** showing the coordination environment with the atomic-numbering scheme. The thermal ellipsoids are drawn at 30% probability.

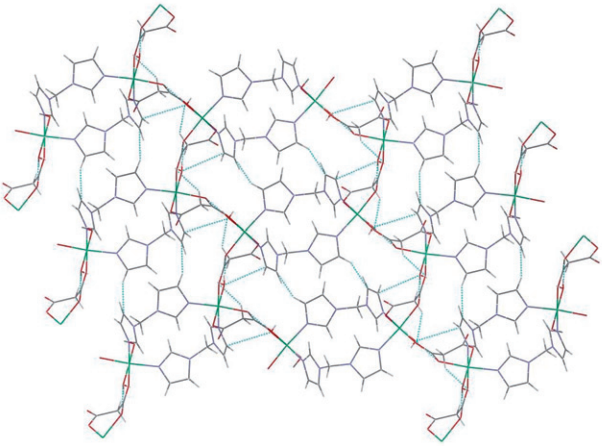

Figure 8. A segment of the 2-D sheet.

distance of 2.0798(16) Å is similar to the value in $\{[Ni(bbbm)_2(H_2O)_2](NO_3)_2 \cdot 2CH_3OH \cdot 6H_2O\}_n$ [bbbm = 1,1′-(1,4-butanediyl)bis-1H-benzimidazole] [39]. This coordination has only been observed in a few examples [34, 40].

Thus **4** may be viewed as an aggregate of the dimeric unit $[Ni_2(mal)_2(L1)_2]$ in which two Ni centers are doubly bridged by two bis(N-imidazolyl)methane ligands. The dimeric units are further held together *via* malonates in a μ_3 mode. This linkage leads to a 2-D sheet structure (figure 8).

In the sheet, there are O–H···O associations between water and carboxylate coordinated to the neighboring Ni with O–O separation of 2.787(2) Å, CH_2–O interaction between the methylene of one anion and oxygen of another anion

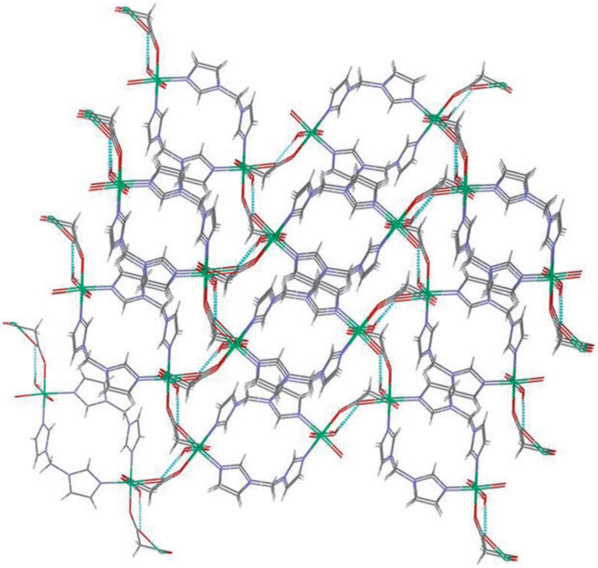

Figure 9. 3-D network structure showing the microchannels built by parallel chains.

coordinated to the same Ni with C–O distance of 3.124 Å. There are also CH–π interactions between 4-CH of one imidazole and the neighboring imidazole ring coordinated to different metals with C–Cg distance of 3.534 Å, and O–π interaction between water and imidazole ring with O–Cg distance of 3.199 Å. Here the O–Cg distance is smaller than the distances reported for O$\cdots\pi$ interaction [41]. The sheets were further stacked along the *a*-axis to form a 3-D network structure with channels as shown in figure 9, when viewed down the *a*-axis.

3.2.5. Crystal structure of $[Ni_3(ctc^{3-})_2(L1)_6]\cdot 35H_2O$ (5). Complex **5** is a trinuclear compound, $[Ni_3(ctc^{3-})_2(L1)_6]\cdot 35H_2O$ (ctc^{-} = citrate), shown in figure 10. In the molecule the inversion center is located at Ni(2). There are two crystallographically unique Ni(II) cations in the asymmetric unit and the Ni's are in different coordination environments. Each Ni(II) adopts a distorted square-bis-pyramidal geometry. One Ni(II) is coordinated by six nitrogen atoms from six independent L1, while the other kind Ni(II) has three oxygen atoms of the citrate tri-anion and three nitrogen atoms of three different L1. Of the oxygen atoms coordinated to Ni, two come from two different carboxylates of the same citrate, the other comes from the alcohol of the same citrate. Thus the citrate tri-anions coordinate to Ni in chelating μ_3 mode. The Ni–N bond distances range from 1.939(18) Å to 2.086(18) Å, comparable to published data [39]. The Ni–O bond distances vary from 1.968(14) Å to 2.006(16) Å. Normally carboxylates coordinate more strongly to metals than alcohol, however, this case deviates from the normal rule. Here the Ni–$O_{carboxylate}$ bond distance is longer than the Ni–$O_{alcohol}$ bond distance. Complex **5** has a trinuclear moiety with Ni–Ni separation of 7.739 Å. Adjacent trinuclear moieties connect *via* lattice water molecules to form a 1-D chain running along the *c*-axis. Such chains were joined by free water molecules to generate a

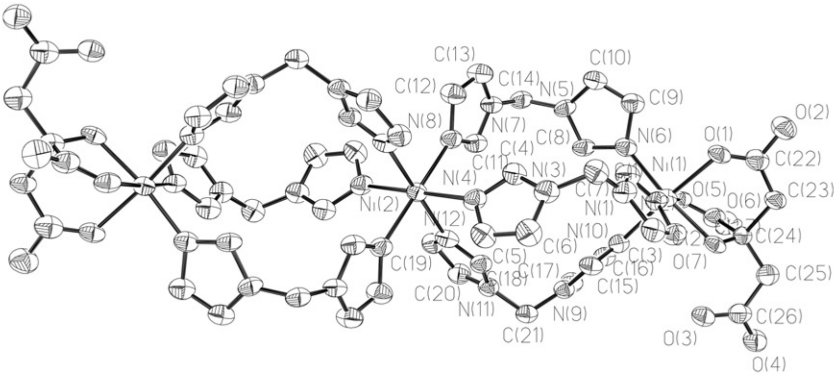

Figure 10. X-ray crystal structure of **5** with atom-numbering scheme. The thermal ellipsoids are drawn at 30% probability. For clarity some atoms were not labeled.

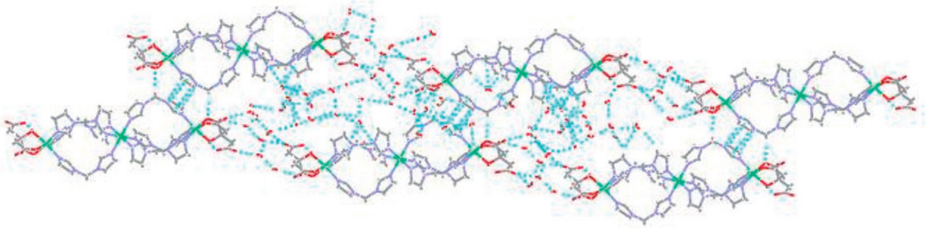

Figure 11. 2-D sheet structure connected *via* hydrogen bonds.

2-D sheet structure extending on the *ac*-plane (figure 11). Between adjacent chains in the 2-D sheet there are π–π interactions between two imidazole rings with Cg–Cg distance of 3.213 Å. The 2-D sheets were further stacked along the *b*-axis through intersheet CH–O, and CH–π interactions to form a 3-D layer network.

3.3. *Thermal properties*

For **1**, weight loss of 6.09% (Calcd 6.17%) approximately corresponds to loss of one water molecule from 59°C to 78°C and the second weight loss of 50.64% (Calcd 50.76%) corresponds to loss of one L1 at 292–340°C. The first weight loss of 2.98% (Calcd 3.07%) for **2** corresponds to the liberation of one water molecule between 78°C and 90°C; further decomposition occurred at 238–456°C with a weight loss of 85.76% (Calcd 85.83%) attributing to loss of two 2-chloronicotinates and one L2. Water molecules were removed between 85°C and 106°C (obsd. 11.86%, Calcd 11.95%) for **3**. The second weight loss is 41.92% (Calcd 42.04%) at 237–477°C, assigned to release of L2. Drastic weight losses corresponding to the removal of adipate were observed from 477°C to 556°C for **3** (Obsd. 31.93%, Calcd 32.08%). Complex **4** begins decomposition at 250°C although coordinated water was removed at 96.6–113.3°C (Obsd. 5.42%, Calcd 5.50%). The weight loss of 31.08% (Calcd 31.19%) corresponds to decomposition of one malonate at 244.8–286.1°C, whereas **4** releases L1 (Obsd. 45.18%, Calcd 45.26%) at 296.9–343.1°C. For **5**, the weight loss of 30.32% (Calcd 30.38%) corresponds approximately to loss of 35 free water molecules at 91.1–126.9°C; two citrates were removed between 198°C and 234°C (Obsd. 18.18%, Calcd 18.24%) and all six L1 decomposed from 287°C to 335°C.

4. Conclusion

Five coordination polymers with different topologies have been synthesized and structurally characterized. The different coordination modes of carboxylates due to their different chain length, rigidity, and diimidazolyl functionality lead to a range of structures. The coordination polymers exhibit 3-D layer networks and 3-D network structures with channels. The carboxylates are bridging μ_2, chelating μ_2, chelating–bridging μ_3, and chelating μ_3. The metals are coordinated in N_2O_2, N_2O_3, N_2O_4, N_3O_3, and N_6 fashions depending on the ancillary ligands. Bis(imidazole) ligands are bidentate bridging. The results illustrate that it is feasible to prepare various coordination polymers of different network structures by utilization of different carboxylates and bis(imidazole) as building blocks. The structural features observed within the five polymers indicate that various structural motifs can be achieved through selection of suitable ligands.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 791904 for **1**, 841397 for **2**, 841394 for **3**, 809861 for **4**, and 791902 for **5**. Copies of this information may be obtained free of charge *via* Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk

Acknowledgments

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