Electronic Supplementary Information (ESI)

Effect of N ancillary ligands on the structure, nuclearity and magnetic behavior of Cu(II)-pyrazolecarboxylate complexes

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Table of Contents

Figure S1 The infrared spectra of complexes **1**–**4**.·····S3

Figure S2 The 3D supramolecular structure of complex **1** viewing along the *a*-axis. Hydrogen bonds are indicated by dash lines, only hydrogen atoms involved in the hydrogen bonds are shown.·····S3

Figure S3. The 2D layer of the complex **2**. Only hydrogen atoms involved in the hydrogen bonds are shown. Hydrogen bonds are indicated by dashed lines.·····S4

Figure S4. The 3D network of **2**. Only hydrogen atoms involved in the hydrogen bonds are shown. Hydrogen bonds are indicated by dashed lines, the dicopper units are shown in the same color.··S4

Figure S5. The 3D network of **3** view along the *a*-axis. Only hydrogen atoms involved in the hydrogen bonds are shown. Hydrogen bonds are indicated by dashed lines, the 2D layers are shown in the same color.·····S4

Figure S6 The boat conformational 9-membered ring in **4**.·····S5

Figure S7 The C–H···π interactions and intramolecular π···π interactions in **4**. Only hydrogen atoms involved in C–H···π interactions are shown, π···π interactions and C–H···π interactions are indicated by dashed lines.·····S5

Figure S8 The PXRD spectra of **1**–**4**.·····S5

Figure S9 The TG-traces for complexes **1**–**4**.·····S6

Table S1. Selected bond lengths (Å) and angles (°) in **1**.·····S6

Table S2. Bond lengths (Å) and angles (°) of hydrogen bonds in **1**.·····S7

Table S3. Selected bond lengths (Å) and angles (°) in **2**·····S7

Table S4. Bond lengths (Å) and angles (°) of hydrogen bonds in **2.**·····S7

Table S5. Selected bond lengths (Å) and angles (°) in **3**.·····S8

Table S6. Bond lengths (Å) and angles (°) of hydrogen bonds in **3**.·····S8

Table S7. Selected bond lengths (Å) and angles (°) in **4**.·····S9

Table S8. Bond lengths (Å) and angles (°) of hydrogen bonds and C–H···π interactions in **4**.···S10

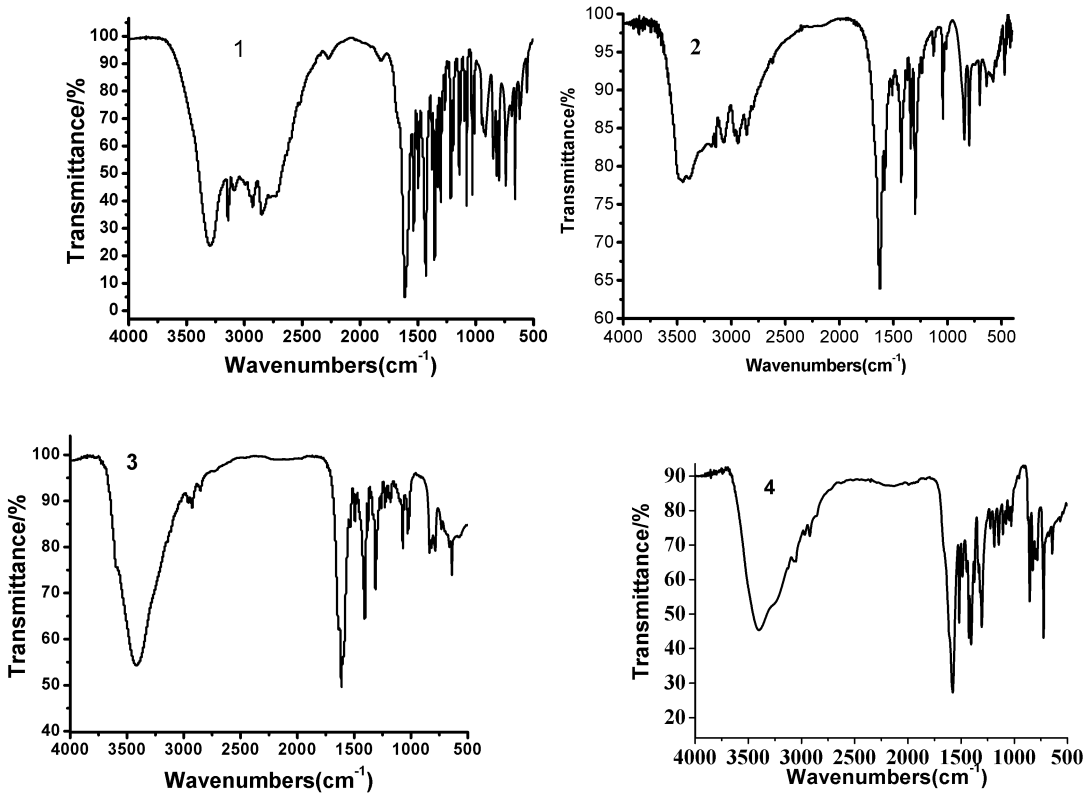

Figure S1 The infrared spectra of complexes **1**–**4**.

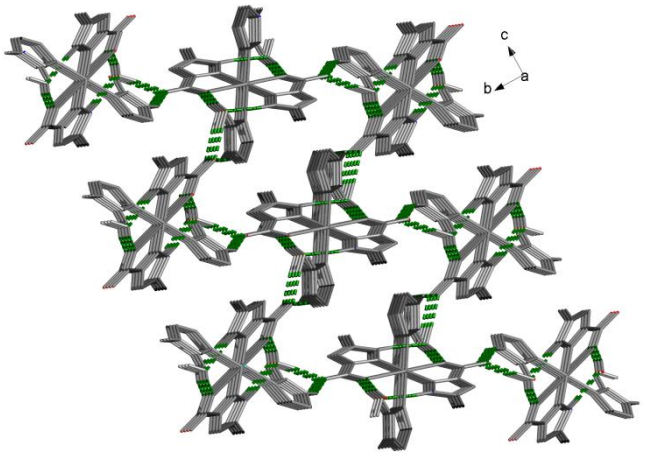

Figure S2 The 3D supramolecular structure of complex **1** viewing along the *a*-axis. Hydrogen bonds are indicated by dash lines, only hydrogen atoms involved in the hydrogen bonds are shown.

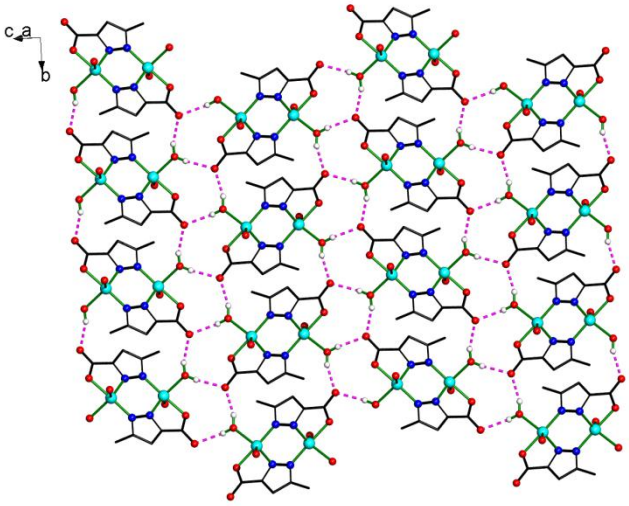

Figure S3. The 2D layer of the complex **2**. Only hydrogen atoms involved in the hydrogen bonds are shown. Hydrogen bonds are indicated by dashed lines.

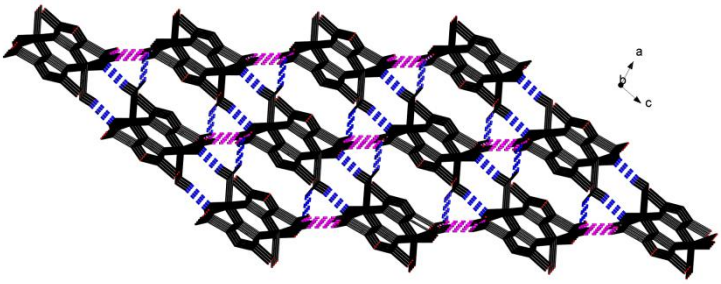

Figure S4. The 3D network of **2.** Only hydrogen atoms involved in the hydrogen bonds are shown. Hydrogen bonds are indicated by dashed lines, the dicopper units are shown in the same color.

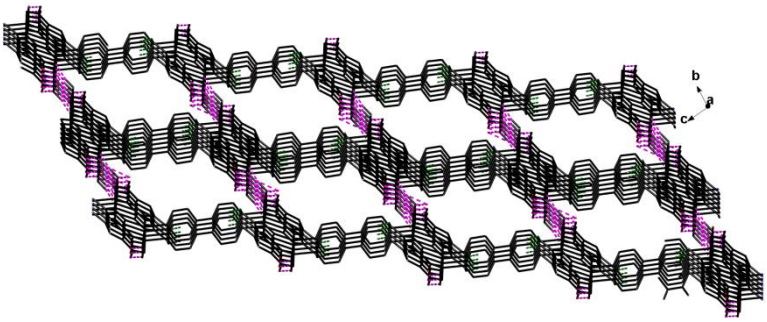

Figure S5. The 3D network of **3** view along the *a*-axis. Only hydrogen atoms involved in the hydrogen bonds are shown. Hydrogen bonds are indicated by dashed lines, the 2D layers are shown in the same color.

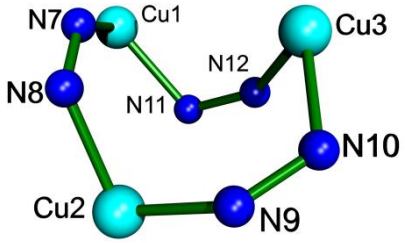

Figure S6 The boat conformational 9-membered ring in **4**.

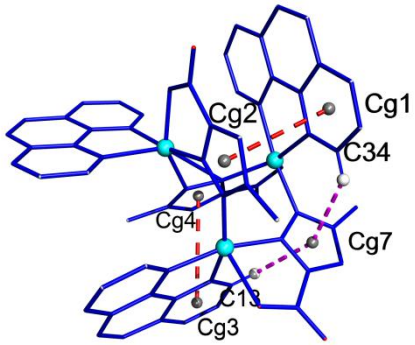

Figure S7 The C–H···π interactions and intramolecular π···π interactions in **4**. Only hydrogen atoms involved in C–H···π interactions are shown, π···π interactions and C–H···π interactions are indicated by dashed lines.

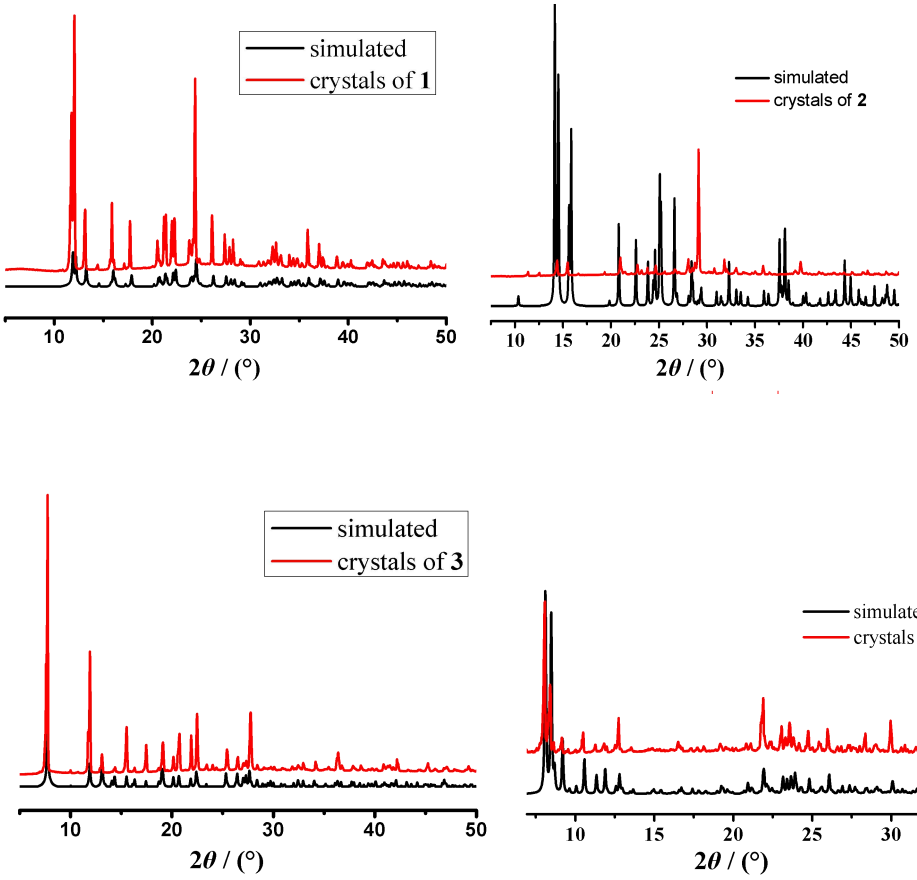

Figure S8 The PXRD spectra of **1**–**4**.

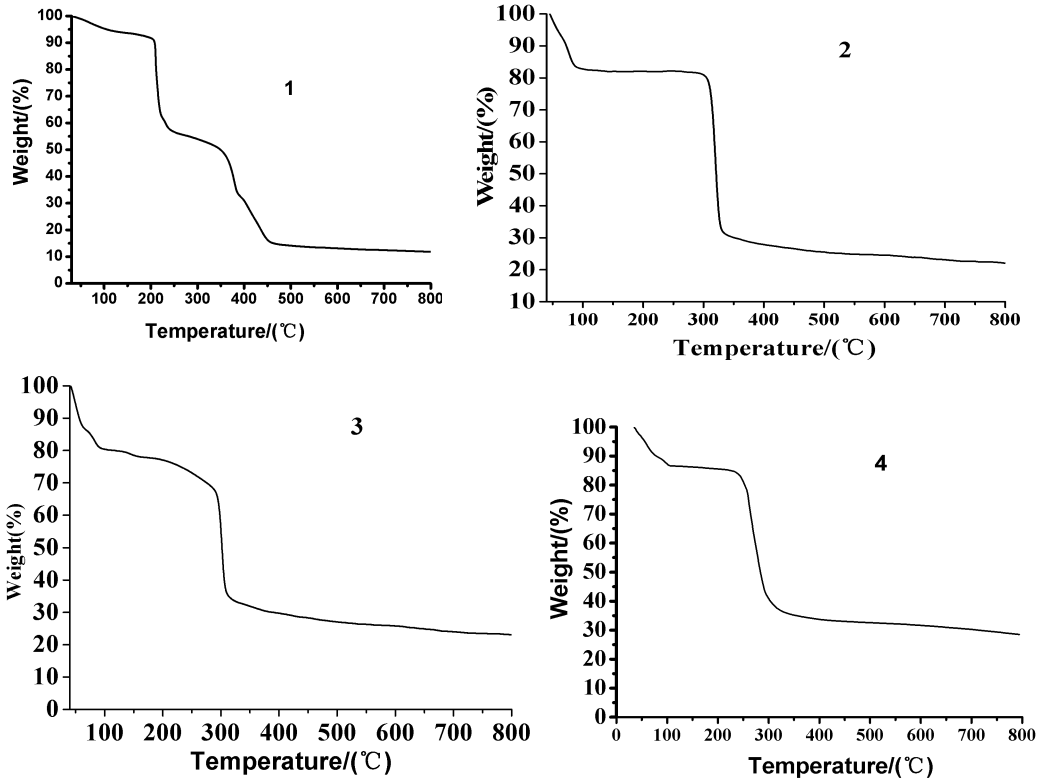

Figure S9 The TG-traces for complexes **1**–**4**.

Table S1. Selected bond lengths (Å) and angles (°) in **1**.

Cu1–N3	2.0111(15)	Cu1–N1	2.0266(13)
Cu1–O1	2.3840(14)		
N3–Cu1–N1	90.35(6)	N3—Cu1—N1A	89.66(6)
N3A–Cu1–N1	89.66(6)	N3A—Cu1—N1A	92.01 (6)
N3–Cu1–O1	92.01 (6)	N3—Cu1—O1A	87.99 (6)
N1–Cu1–O1	74.16(5)	N1—Cu1—O1A	105.84 (5)
O1–Cu1–N3A	87.99 (6)	O1A—Cu1—N3A	92.01(6)
O1–Cu1–N1A	105.84(5)	O1A—Cu1—N1A	74.16 (5)

Symmetry codes: A: *–x*, *–y*, *–z*.

Table S2. Bond lengths (Å) and angles (°) of hydrogen bonds in **1**.

D – H ⋯ A	D – H / Å	H ⋯A / Å	D ⋯ A / Å	D – H ⋯A / (°)
N(2)–H(2) ⋯O(3B)	0.86	1.89	2.742(2)	167
O(3)–H(3X) ⋯O(2)	0.93	1.79	2.702(2)	163
O(3)–H(3Y) ⋯O(1C)	0.83	1.90	2.706(2)	164
N(4)–H(4) ⋯O(2D)	0.98	1.83	2.738(3)	151
C(6)–H(6) ⋯O(3D)	0.93	2.55	3.295(2)	137

Symmetry codes: B: 1/2 – *x*, –1/2 – *y*, 1/2 – *z*; C: 1/2 + *x*, 1/2 – *y*, 1/2 + *z*; D: –1/2 + *x*, –1/2 + *y*, 1/2 – *z*.

Table S3. Selected bond lengths (Å) and angles (°) in **2**.

Cu1–N2A	1.928(3)	Cu1–O3	2.082(3)
Cu1–N1	1.991(3)	Cu1–O4	2.118(3)
Cu1–O1	1.976(2)		
N2A–Cu1–O1	177.33(10)	N1–Cu1–O3	122.96(12)
N2A–Cu1–N1	100.62(11)	N2A–Cu1–O4	95.04(11)
O1–Cu1–N1	82.00(10)	O1–Cu1–O4	83.26(10)
N2A–Cu1–O3	95.27(11)	N1–Cu1–O4	115.82(12)
O1–Cu1–O3	83.68(11)	O3–Cu1–O4	116.79(13)

Symmetry code: A: 1 – *x*, 2 – *y*, 1 – *z*.

Table S4. Bond lengths (Å) and angles (°) of hydrogen bonds in **2**.

D – H ⋯ A	D – H	H ⋯ A	D ⋯ A	D – H ⋯ A
O3–H3X⋯O2B	0.81	2.03	2.824(4)	168
O3–H3Y⋯O2C	0.85	1.97	2.797(4)	162
O4–H4X⋯O1D	0.90	1.95	2.814(4)	161
O4–H4Y⋯O2E	0.88	1.99	2.755(4)	144

Symmetry codes: B: 1/2 – *x*, 1/2 + *y*, 1/2 – *z*; C: *x*, 1 + *y*, *z*; D: 1 – *x*, *y*, 1/2 – *z*; E: 1/2 + *x*, 1/2 + *y*, *z*.

Table S5. Selected bond lengths (Å) and angles (°) in **3**.

Cu1–N2A	1.978(3)	Cu1–N1	1.994(3)
Cu1–O1	2.018(3)	Cu1–N3	2.052(3)
Cu1–O3	2.217(3)		
N2A–Cu1–N1	98.70(13)	N2A–Cu1–O1	177.69(13)
N1–Cu1–O1	81.46(13)	N2A–Cu1–N3	94.46(14)
N1–Cu1–N3	141.78(14)	O1–Cu1–N3	86.78(13)
N2A–Cu1–O3	93.30(14)	N1–Cu1–O3	109.52(15)
O1–Cu1–O3	84.48(13)	N3–Cu1–O3	105.31(15)

Symmetry codes: A: $–x + 2, –y, –z$.

Table S6. Bond lengths (Å) and angles (°) of hydrogen bonds in **3**.

D – H ⋯ A	D – H / Å	H ⋯A / Å	D ⋯ A / Å	D – H ⋯A / (°)
O3–H3X ⋯O2B	0.79	2.06	2.761(6)	148
O3–H3Y ⋯O1C	0.97	2.00	2.879(5)	149
O3–H3Y ⋯O2C	0.97	2.55	3.431(5)	151

Symmetry codes: B: $1 + x, y, z$; C $2 – x, 1 – y, –z$.

Table S7. Selected bond lengths (Å) and angles (°) in **4**.

Cu1–N7	1.953(4)	Cu1–N1	2.030(4)
Cu1–N12	1.988(4)	Cu1–N2	2.208(4)
Cu1–O1	2.027(3)	Cu2–N9	1.959(4)
Cu2–N8	1.972(4)	Cu2–N4	2.013(4)
Cu2–N3	2.054(4)	Cu2–O3	2.286(3)
Cu3–N10	1.965(4)	Cu3–N5	2.011(4)
Cu3–N6	2.057(4)	Cu3–N11	2.073(4)
Cu3–O5	2.193(3)		
N7–Cu1–N12	96.09(17)	N9–Cu2–O3	78.04(15)
N7–Cu1–O1	81.85(16)	N8–Cu2–O3	112.97(15)
N12–Cu1–O1	148.76(17)	N4–Cu2–O3	90.11(15)
N7–Cu1–N1	171.59(18)	N9–Cu2–N8	94.94(17)
N12–Cu1–N1	91.33(17)	N3–Cu2–O3	89.75(15)
O1–Cu1–N1	89.75(17)	N10–Cu3–N5	170.93(18)
N7–Cu1–N2	101.77(18)	N10–Cu3–N6	91.48(17)
N12–Cu1–N2	117.97(18)	N5–Cu3–N6	79.76(18)
O(1)–Cu(1)–N(2)	92.78(17)	N10–Cu3–N11	95.34(16)
N(1)–Cu(1)–N(2)	78.07(18)	N5–Cu3–N11	93.24(17)
N9–Cu2–N4	166.73(17)	N6–Cu3–N11	145.42(17)
N8–Cu2–N4	95.20(17)	N10–Cu3–O5	92.11(16)
N9–Cu2–N3	92.84(17)	N5–Cu3–O5	92.64(17)
N8–Cu2–N3	157.05(16)	N6–Cu3–O5	136.39(16)
N4–Cu2–N3	81.01(17)	N11–Cu3–O5	77.28(15)

Table S8. Bond lengths (Å) and angles (°) of hydrogen bonds and C–H···π interactions in **4**.

D – H ··· A/Cg	D – H	H ··· A/Cg	D ··· A/Cg	D – H ··· A/Cg
O7–H0BA···O8F	0.85	2.08	2.855(6)	151
O7–H2BA···O2	0.85	1.98	2.752(5)	151
O8–H3BA···O7D	0.83	2.24	2.855(6)	131
O8–H4BA···O3	0.83	1.94	2.776(5)	175
O9–H5BA···O6G	0.85	1.91	2.734(6)	163
O9–H6BA···O4A	0.85	1.94	2.779(7)	168
O10–H8BA···O4F	0.85	1.95	2.796(6)	173
O10–H7BA···O7	0.85	2.07	2.908(7)	167
O11–H0CA···O7	0.85	2.05	2.858(8)	157
O11–H9BA···O6G	0.85	1.98	2.820(7)	172
O12–H4CA···O9E	0.85	1.88	2.704(9)	163
O12–H5CA···O10	0.85	1.97	2.779(9)	160
O13–H13CA···O14A	0.85	1.99	2.744(11)	148
O14–H14A···O8C	0.81	2.13	2.921(10)	171
O14–H14B···O11B	0.81	1.99	2.730(10)	152
C5–H5···O4H	0.93	2.59	3.402(7)	146
C17–Hk···O4I	0.93	2.42	3.325(6)	165
C22–Ho···O12	0.93	2.33	3.124(9)	143
C25–Hp···O13J	0.93	2.54	3.196(8)	128
C27–Hr···O1J	0.93	2.57	3.486(7)	167
C27–Hr···O2J	0.93	2.54	3.240(7)	133
C34–Hw···Cg7	0.93	2.71	3.461(4)	138
C13–Hh···Cg7	0.93	2.81	3.525(5)	134

Symmetry codes: A: 1 – x, –1/2 + *y*, 1/2 – *z*; B: 1 – *x*, 1/2 + *y*, 1/2 – *z*; C: –1 + *x*, *y*, *z*; D: 2 – *x*, 1/2 + *y*, 1/2 – *z*; E: 1 + *x*, *y*, *z*; F: 2 – *x*, –1/2 + *y*, 1/2 – *z*; G: *x*, 3/2 – *y*, 1/2 + *z*; H: *x*, 3/2 – *y*, –1/2 + *z*; I: 2 – *x*, 2 – *y*, –*z*; J: 1 – *x*, 1 – *y*, –*z*.