Impact of N-donor auxiliary ligands on two new Co(II)-based MOFs with N-heterocyclic ligands and magnetism study

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PXRD, IR and Thermogravimetric Analysis

Powder X-ray diffraction was used to determine the phase purity of the bulk sample in addition to the structural properties of complexes. Experiments revealed that the PXRD patterns of complexes **1** and **2** matches the patterns simulated by single-crystal structure data, implying that the obtained complexes have superior phase purity.

The broad absorption concentrated at 3448 cm^{-1} in the IR spectra (Fig. S5), which can be attributed to the O-H stretching vibration of the water molecule in **2**.The absence of the protonated carboxylic groups predicted absorption band near 1700 cm^{-1} suggests that the H_2L acid has been completely deprotonated. And it also exhibits the characteristic antisymmetric (1607 cm^{-1}) and symmetric (1505 and 1382 cm^{-1}) carboxylate group stretching bands in **1** and antisymmetric (1599 cm^{-1}) and symmetric (1535 and 1390 cm^{-1}) carboxylate group stretching bands in **2**.

The thermogravimetric (TG) analysis of **1**-**2** was carried out to examine their thermal stability. The TG data is shown in Figure S6. For **1**, the weight barely changed before 500 °C due to the lack of lattice and coordinated water molecules, and then the backbone decomposition occurred. For **2**, the TG curve shows a first weight loss from 150 to 200 °C, which corresponds to the loss of coordinated water molecules, and upon further heating, the structure is stable up to 400 °C, and then has a sharp weight loss between 400 and 500 °C owing to the collapse of the structure.

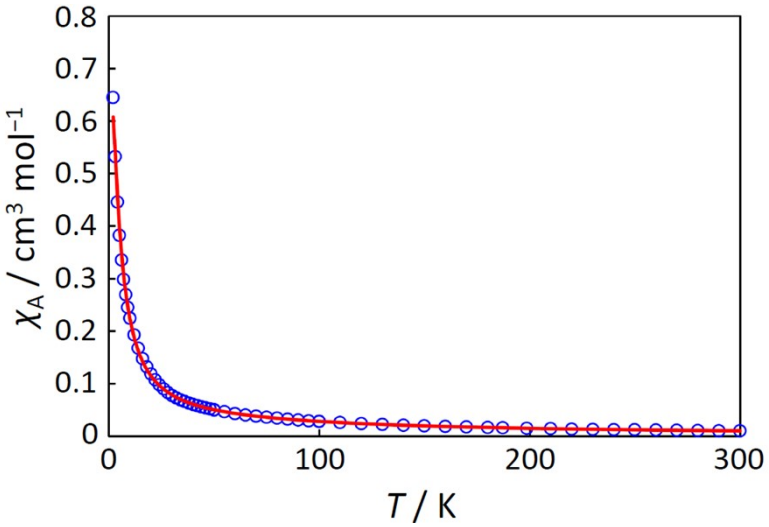

Figure S1. Temperature dependence of χ_A for **1** (○). Theoretical curve (—) is drawn with the parameters (λ, κ, Δ, J, zJ') = (–133 cm^{-1}, 0.93, 470 cm^{-1}, 4.39 cm^{-1}, –1.81 cm^{-1}).

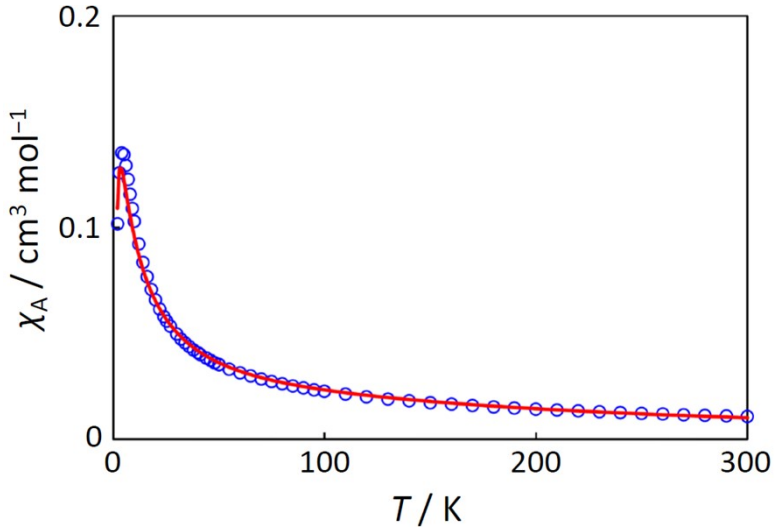

Figure S2. Temperature dependence of χ_A for **2** (○). Theoretical curve (—) is drawn with the parameters (λ, κ, Δ, J, zJ') = (–173 cm^{-1}, 0.90, –47 cm^{-1}, –1.42 cm^{-1}, –18.0 cm^{-1}).

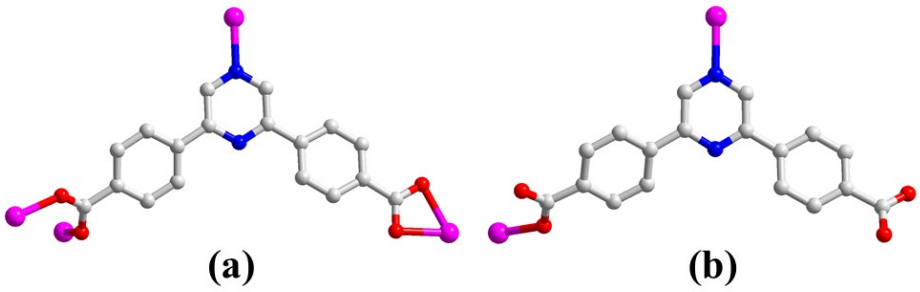

Figure S3. The coordination modes of **L** in **1**-**2**.

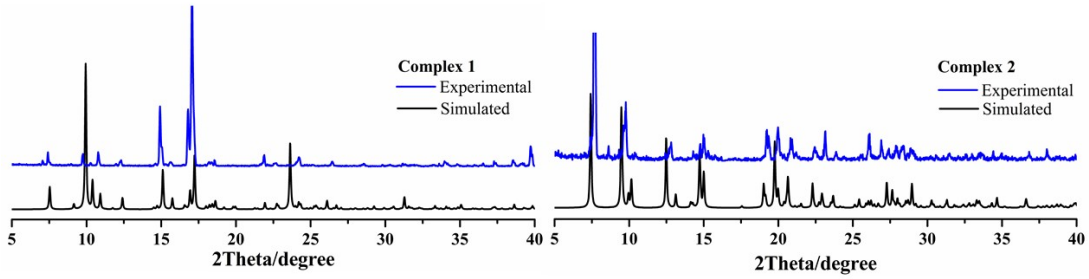

Figure S4. Simulated and observed PXRD patterns of complexes **1-2**.

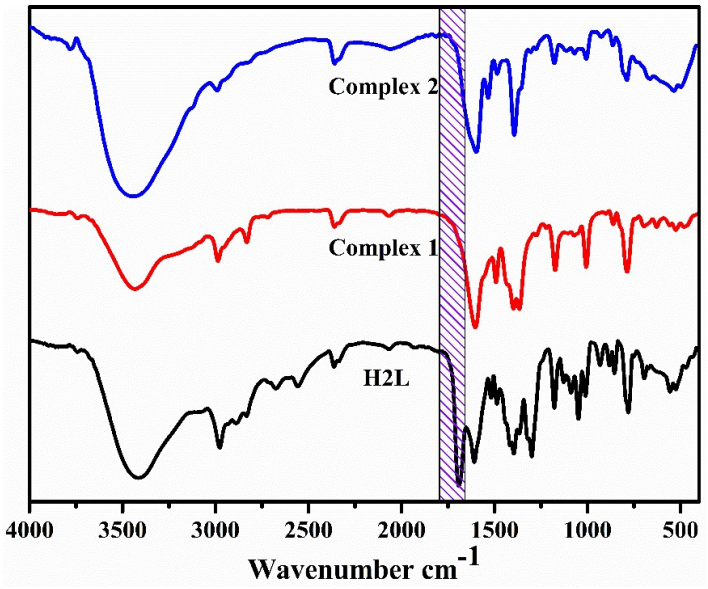

Figure S5. Infrared spectra of complexes **1-2**.

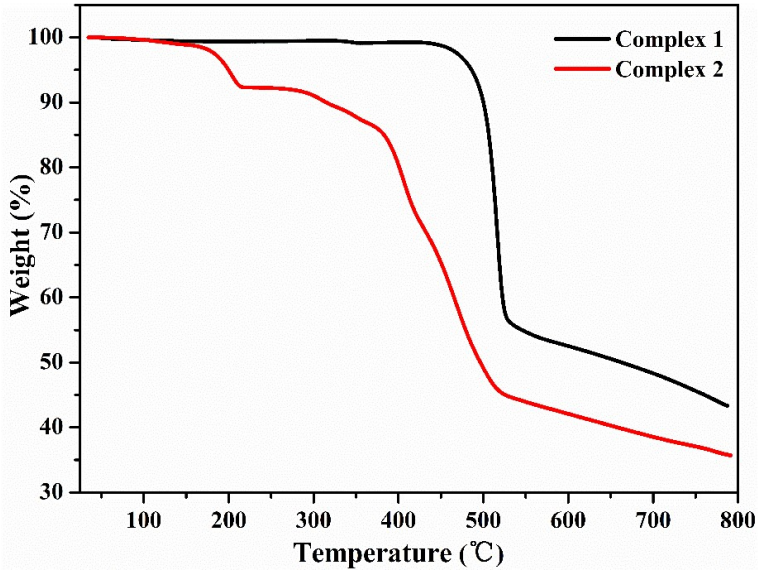

Figure S6. The TG curves of complexes **1-2**.

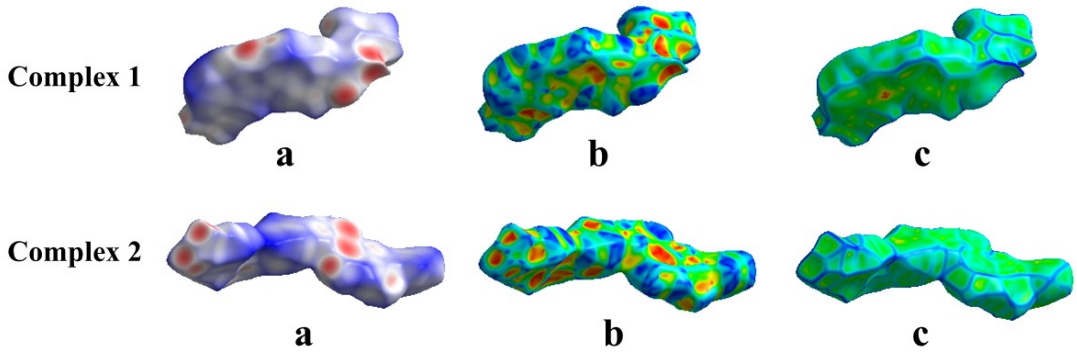

Figure S7. Hirshfeld surfaces of complexes **1-2** mapped with d $_{norm}$, shape-Index and curvedness.

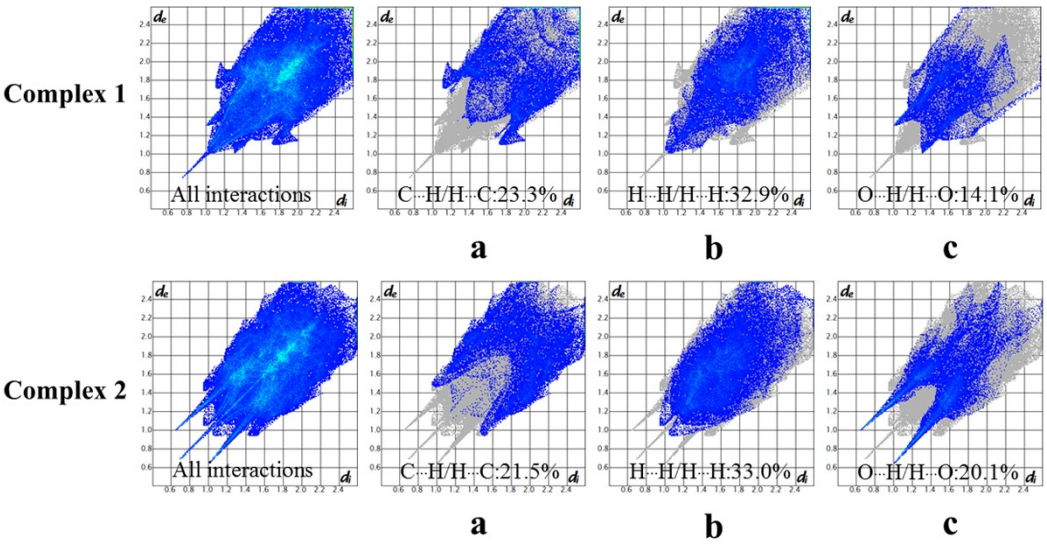

Figure S8. Two-dimensional fingerprint plots overall plot, and those delineated into H···H, C···H/H···C, O···H/H···O contacts.

Table S1. Crystal data and structure refinement for complexes **1-2.**

Complex	1	2
Empirical formula	$C_{46}H_{28}Co_2N_6O_8$	$C_{24}H_{21}CoN_4O_7$
Formula weight	910.60	536.38
Temperature (K)	298	193
Wavelength (Å)	1.54184	1.34139
Crystal system	Monoclinic	Triclinic

Space group	C2/c	*P*-1
Unit cell dimension		
a (Å)	17.1211(2)	9.4774(3)
b (Å)	16.1892(2)	10.1088(3)
c (Å)	15.1628(2)	13.6080(4)
α (°)	90	111.289(1)
β (°)	97.034(1)	107.704(1)
γ (°)	90	92.871(1)
V (Å^3)	4171.15(9)	1138.15(6)
D_x (Mg/m^3)	1.450	1.565
μ (mm^{-1})	6.753	4.443
Z	4	2
F (000)	1856	552
GOF	1.070	1.115
Crystal size (mm)	0.05 × 0.03 × 0.02	0.110 × 0.08 × 0.07
θ range (°)	3.771 to 67.046	3.232 to 53.890
Index ranges	$-20 \le h \le 15$,	$-11 \le h \le 10$,
	$-17 \le k \le 19$,	$-12 \le k \le 12$,
	$-17 \le l \le 18$	$-16 \le l \le 16$
Reflections collected	12530	17385
Independent reflections	3671 [R(int) = 0.0330]	4155 [R(int) = 0.0338]
Completeness to θmax (%)	θ=67.684 (97.5%)	θ=53.594 (99.8%)
Data/restraints/parameters	3671/1/280	4155/4/329
Final R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0354, 0.0876	0.0364, 0.1267
R_1, wR_2 indices (all data)	0.0441, 0.0966	0.0374, 0.1279
$\Delta\rho_{max, min}$ (e Å^{-3})	0.290, -0.408	0.772, -0.942

Table S2. Selected Bond Lengths (Å) and angles (°) for complexes **1-2**.

Complex 1					
Co1—O1#1	2.1150 (17)	Co1—O3	2.0317 (16)	Co1—N1#3	2.119 (2)
Co1—O2#2	2.1880 (17)	Co1—O4#2	2.1386 (17)	Co1—N3	2.183 (2)
O1#1—Co1—O2#2		91.10 (7)	O3—Co1—N3		85.48 (7)
O1#1—Co1—O4#2		95.12 (7)	O4#2—Co1—O2#2		60.82 (6)
O1#1—Co1—N1#3		83.62 (7)	O4#2—Co1—N3		90.68 (8)
O1#1—Co1—N3		172.34 (7)	N1#3—Co1—O2#2		90.65 (7)
O3—Co1—O1#1		98.96 (7)	N1#3—Co1—O4#2		151.45 (7)
O3—Co1—O2#2		154.58 (7)	N1#3—Co1—N3		88.90 (8)
O3—Co1—O4#2		94.88 (7)	N3—Co1—O2#2		87.37 (7)
O3—Co1—N1#3		113.54 (7)			

Symmetry codes for #1 -x+2, y, -z+3/2; #2 x+1, y, z; #3 x+1/2, y-1/2, z; #4 x-1, y, z; #5 x-1/2, y+1/2, z; #6 -x+2, y, -z+1/2.

Complex 2					
Co1—O2	2.0450 (15)	Co1—N3	2.0995 (18)	Co1—O6	2.1748 (15)
Co1—O5	2.0585 (16)	Co1—N1#2	2.1727 (19)	Co1—O6#3	2.1751 (15)
O2—Co1—O5		89.99 (6)	N3—Co1—O6		94.60 (7)
O2—Co1—N3		178.89 (6)	N1#2—Co1—O6		92.66 (6)
O5—Co1—N3		88.94 (7)	O2—Co1—O6#3		86.24 (6)
O2—Co1—N1#2		87.29 (6)	O5—Co1—O6#3		88.35 (6)
O5—Co1—N1#2		95.74 (7)	N3—Co1—O6#3		93.45 (7)
N3—Co1—N1#2		93.10 (7)	N1#2—Co1—O6#3		172.34 (6)
O2—Co1—O6		86.42 (6)	O6—Co1—O6#3		82.85 (6)
O5—Co1—O6		170.69 (6)			

Symmetry codes for #1 -x, -y, -z+2; #2 -x+1, -y+1, -z+1; #3 -x, -y, -z+1.

Table S3. Hydrogen bond parameters [Å, °] for complex **2**.

Compound 2				
D–H···A	D–H	H···A	D···A	D–H···A
O1S–H1S1···N2#2	0.98	2.39	3.1207(1)	131
O1S–H1S3···O1#4	0.98	2.19	2.9155(1)	129
O5–H5B···O3#1	0.98	1.66	2.6344(1)	169
O5–H5C···O3#2	0.96	1.78	2.6895(1)	157
O6–H6A···O4#3	0.97	1.70	2.6620(1)	167
O6–H6B···O1	0.97	1.61	2.5748(1)	169
O6–H6B···O2	0.97	2.42	2.8907(1)	109
C19–H19···O4#3	0.95	2.20	3.1473(1)	171

Symmetry code: #**1** 1-x, -y, -z; #**2** x, y, 1+z; #**3** -1+x, y, 1+z; #**4** 1+x, y, z.