Supplementary Materials

for

Structures, optical and magnetic properties of two isomeric 2-bromomethyl pyridine Cu(II) complexes [Cu(C$_6$H$_9$N$_{Br}$)$_2$(NO$_3$)$_2$] with very different binding motives

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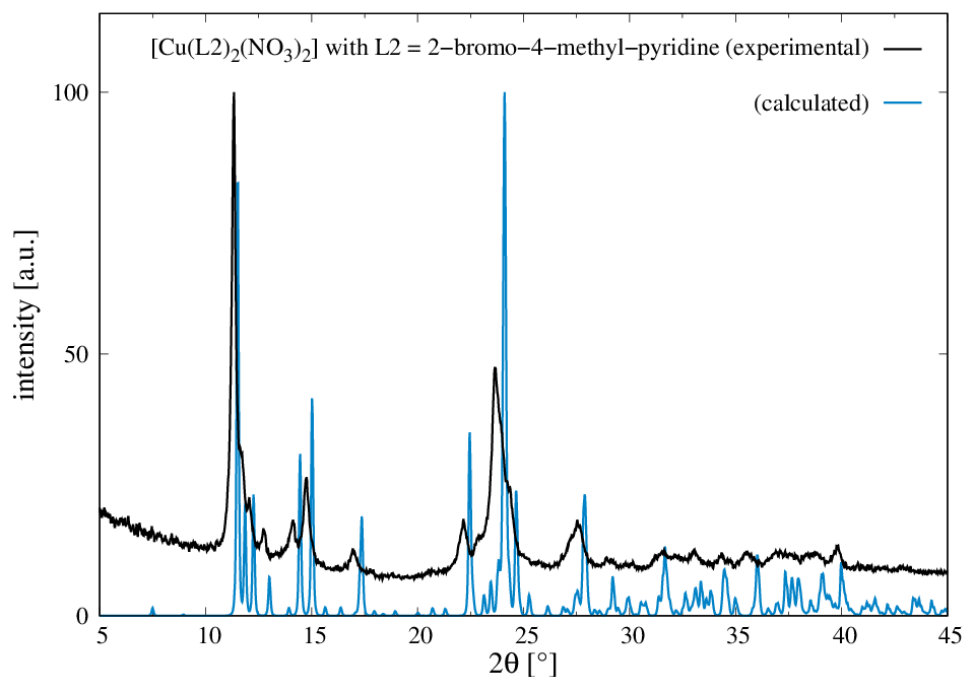
Figure S3. X-ray powder diffractogram of $[Cu(L^2)_2(NO_3)_2]$ (L^2 = 2-bromo-4-methylpyridine) measured with Cu-K$_\alpha$ radiation in reflection geometry (black) compared with a pattern simulated (blue) from the corresponding single crystal structure. Note: the positions of the Bragg reflections of the experimental and the simulated patterns differ due to different temperatures of the respective measurements (single-crystal data: 150(2) K; powder diffraction: 293(2) K).
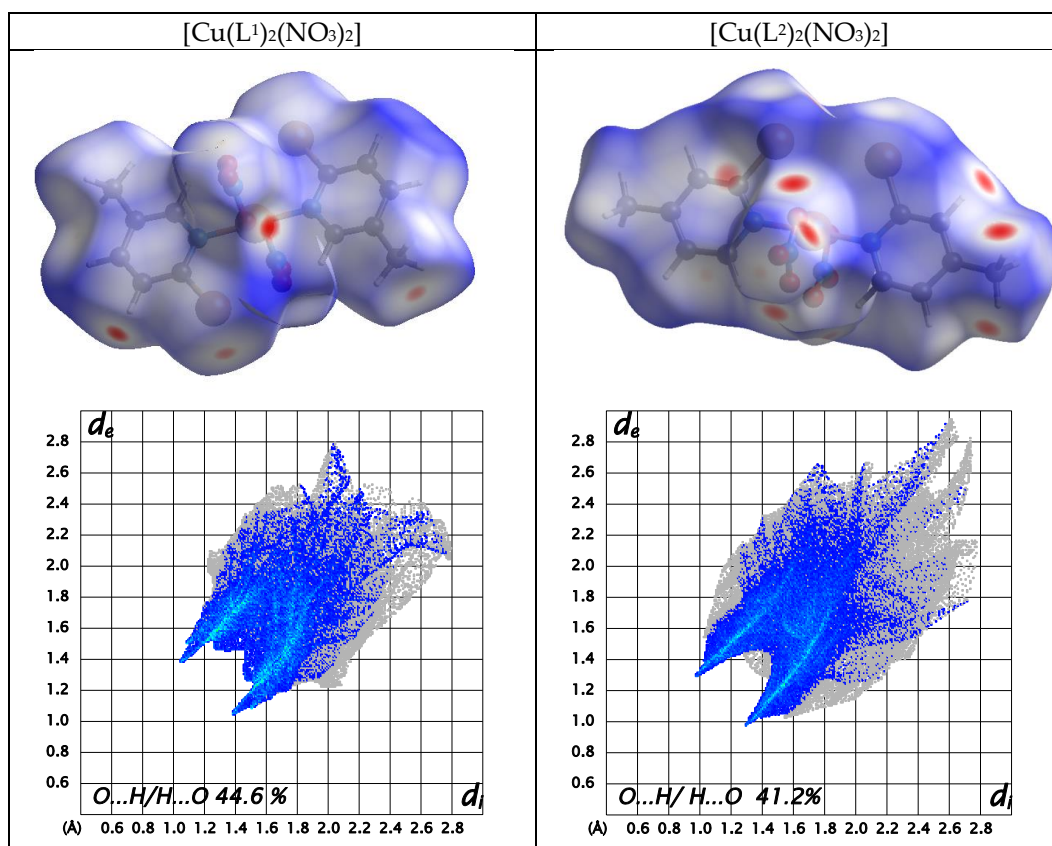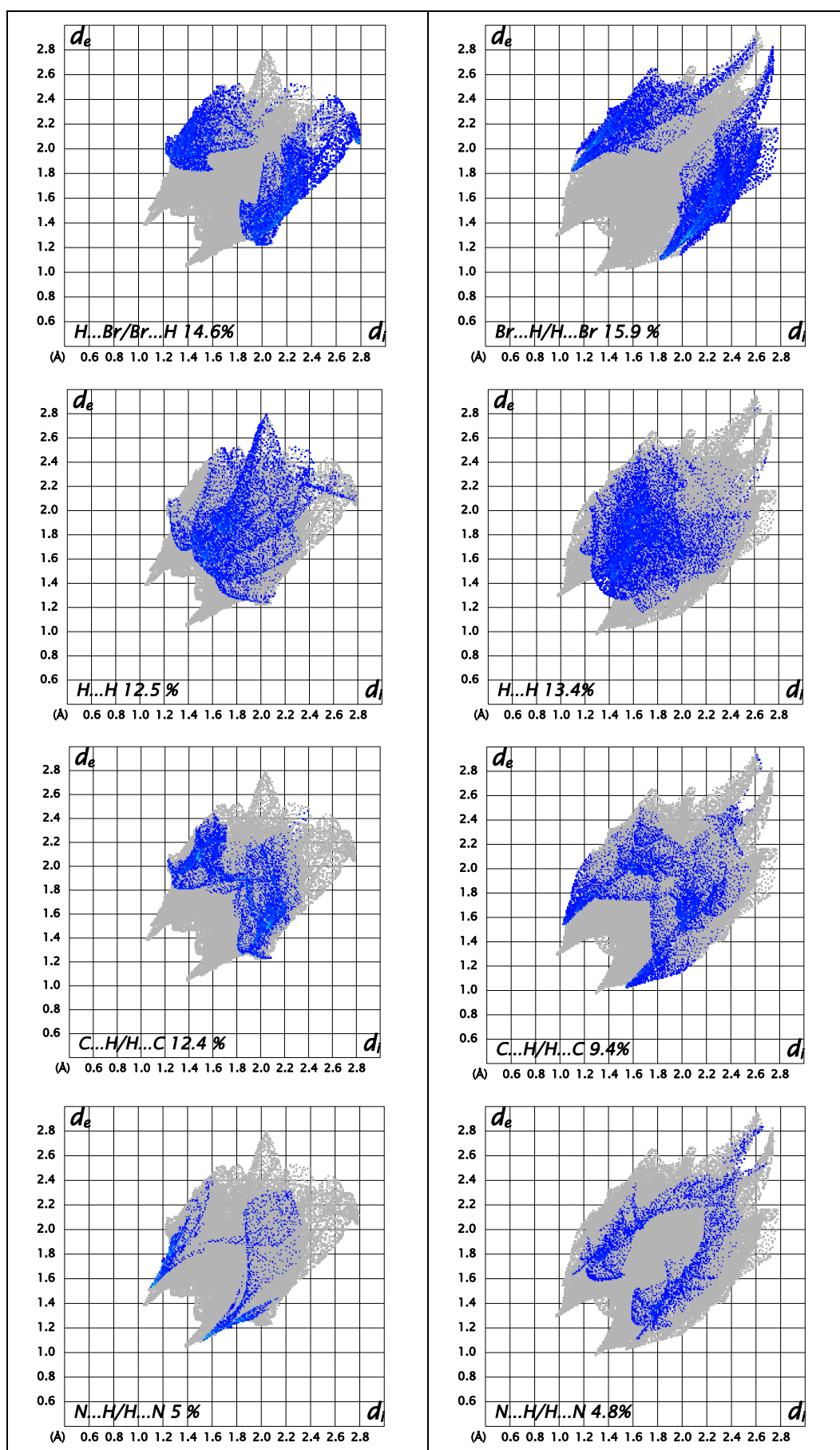
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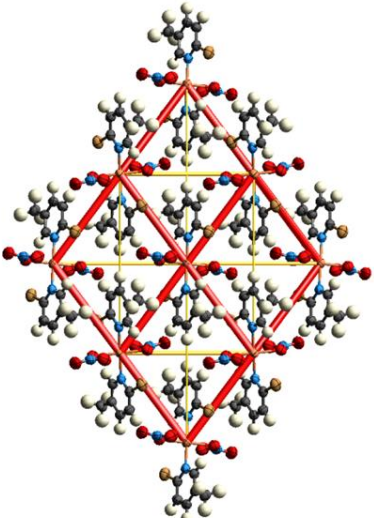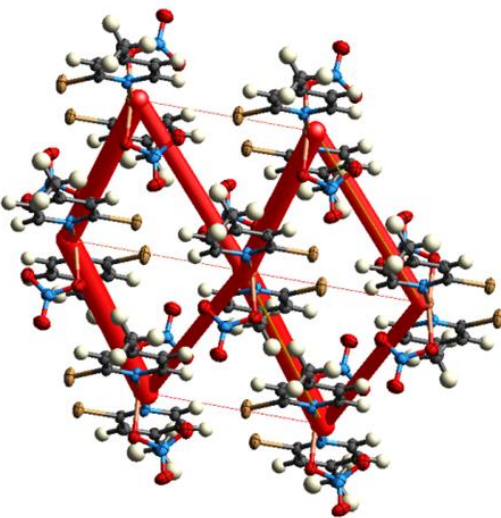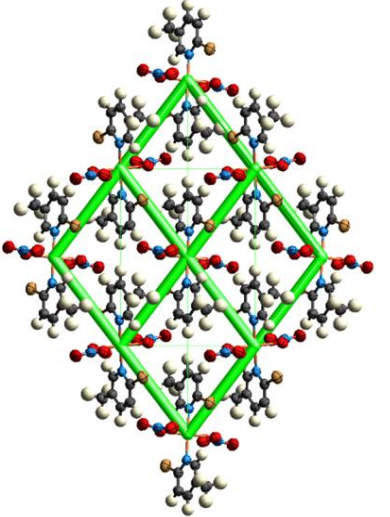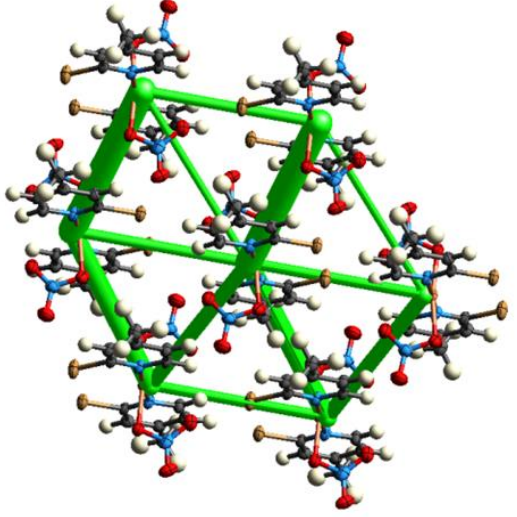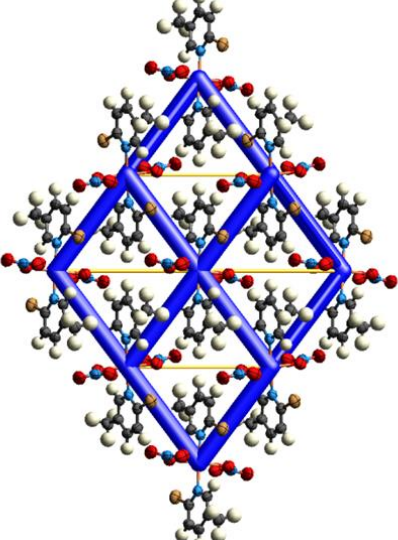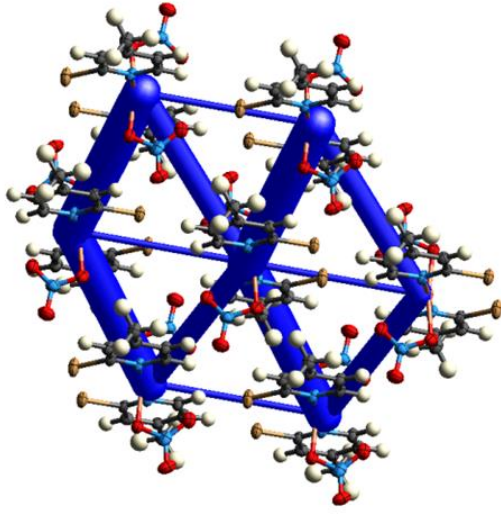
	$[Cu(L^1)_2(NO_3)_2]$ along a-axis	$[Cu(L^2)_2(NO_3)_2]$ along b-axis
Coulomb energy		
Dispersion energy		
Total energy		

Figure S5. Energy frameworks constructed for Coulomb energy, dispersion energy and total energy for the both compounds $[Cu(L^1)_2(NO_3)_2]$ (L^1 = 2-bromo-5-methylpyridine) in $P2_1/c$ and $[Cu(L^2)_2(NO_3)_2]$ (L^2 = 2-bromo-4-methylpyridine) in $P\bar{1}$.
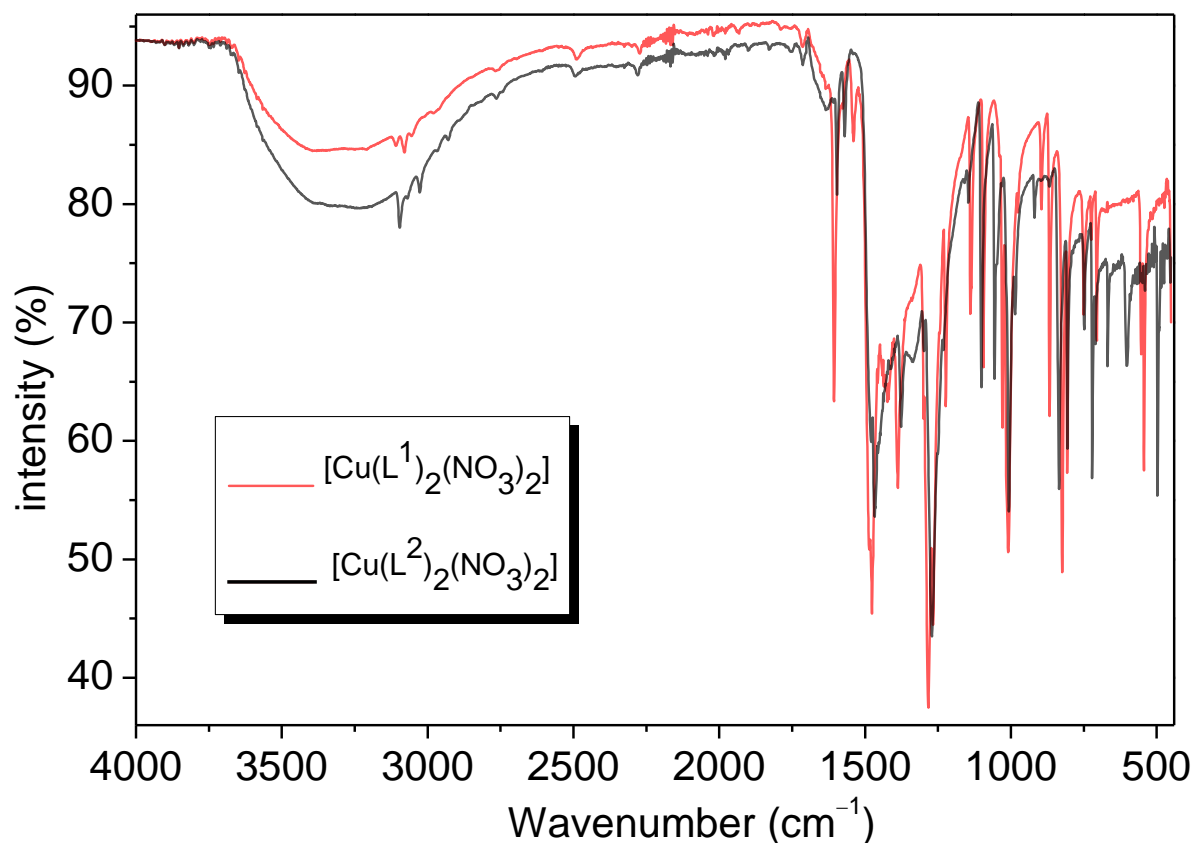
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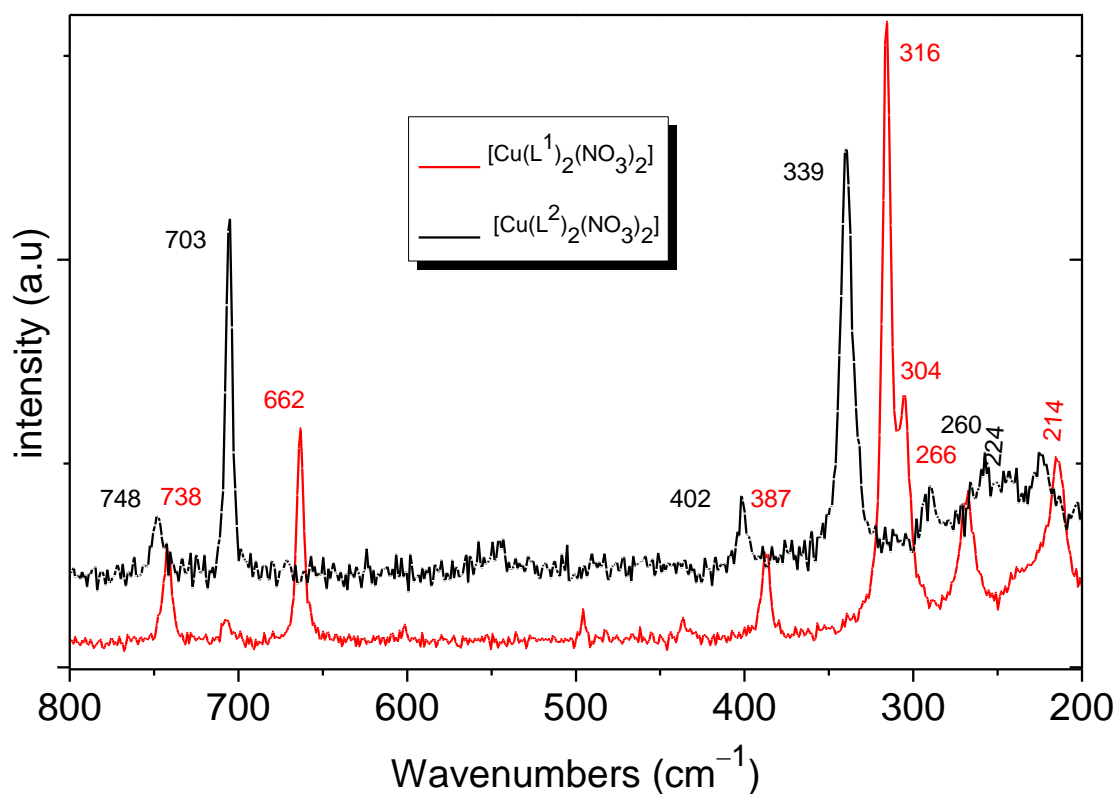
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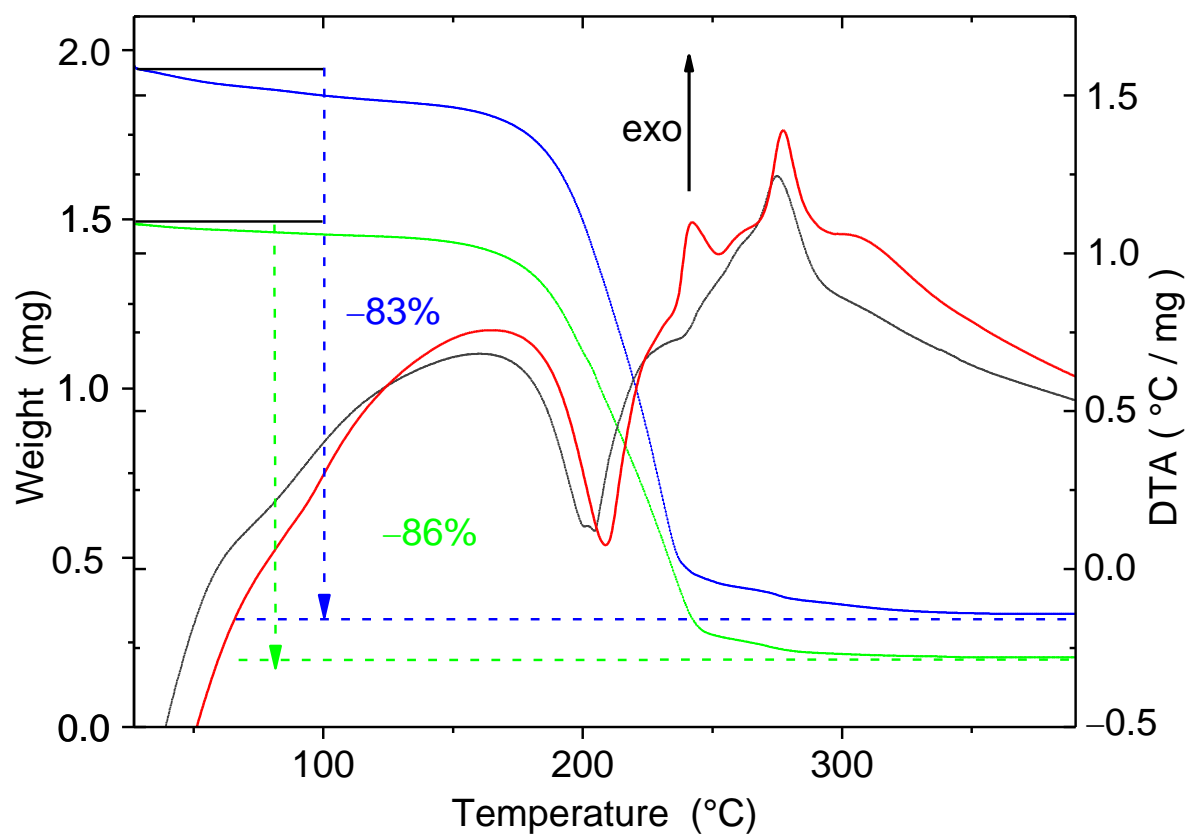
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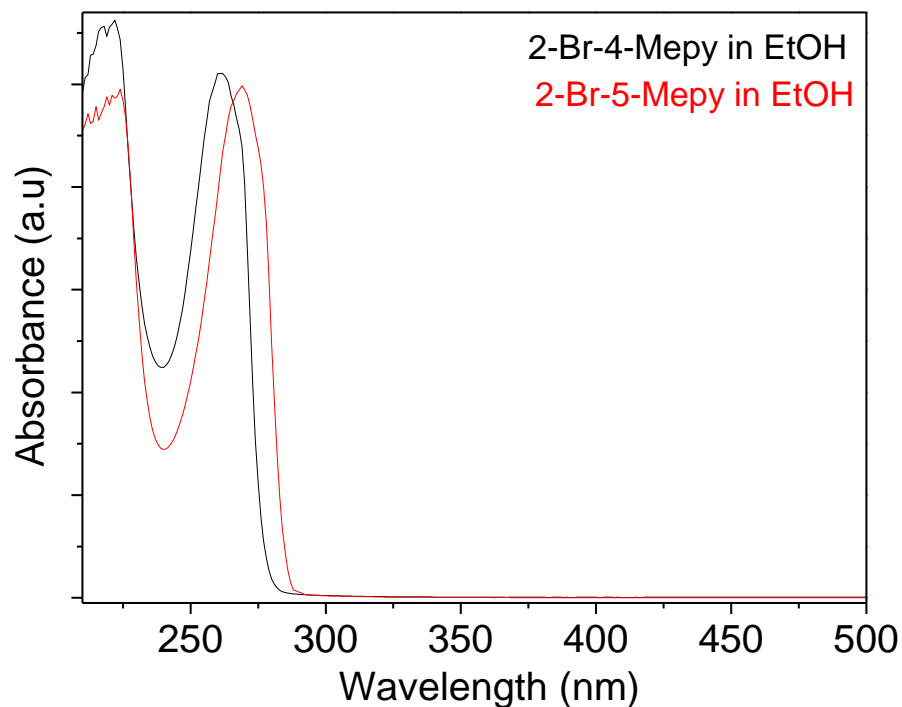
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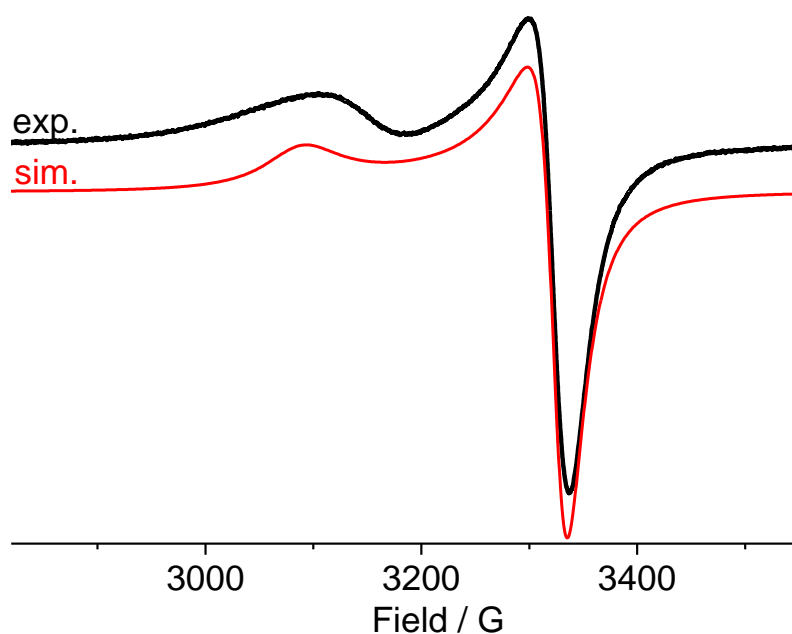
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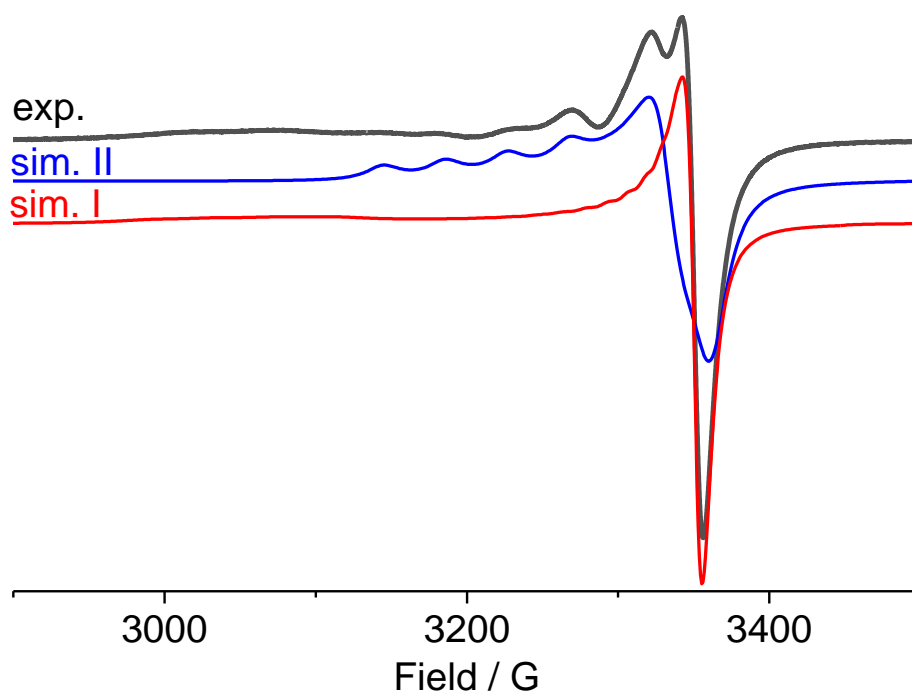
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Supplementary Tables

Table S1. Structure solution and refinement data for the two isomeric forms of [Cu(L)$_2$(NO$_3$)$_2$]

	L^1 = 2-bromo-5-methylpyridine	L^2 = 2-bromo-4-methylpyridine
Formula weight (g mol^{-1})	531.62	531.62
Crystalsystem	monoclinic	triclinic
Temperature (K)	293(2)	150(2)
Space group	$P2_1/c$	$P\bar{1}$
cell a (Å)	6.7738(7)	7.4916(5)
b (Å)	13.1890(9)	10.0404(7)
c (Å)	10.0999(10)	12.0723(8)
α (°)	90	86.176(6)
β (°)	103.298(8)	77.769(5)
γ (°)	90	79.793(5)
V (Å^3)	878.13(14)	873.00(10)
Z	2	2
Abs. coefficient (mm^{-1})	5.830	5.865
Density calcd. (g·cm^{-3})	2.011	2.022
$F(000)$	518	518
θ range (°)	2.584 to 29.354	1.727 to 29.142
Index range	$-9 \le h \le 9$	$-8 \le h \le 10$
	$-18 \le k \le 18$	$-13 \le k \le 13$
	$-13 \le l \le 13$	$-16 \le l \le 16$
completeness to θ = 25.35°	100%	98.8%
Reflections collected (R_{int})	16219 (0.102)	10362 (0.065)
Independent refl. (R_{sigma})	2401 (0.046)	4614 (0.065)
Goodness-of-fit on F^2	1.01	1.02
Weighting scheme ($P = (F_o^2+2F_c^2)/3$)	w = [$\sigma^2(F_o^2)$ + (0.1161P)^2]$^{-1}$	w = [$\sigma^2(F_o^2)$+(0.0532P)^2+0.6888P]$^{-1}$
Extinct. coefficient	0.026(4)	-
Final R indices [I>2sigma(I)]	0.063	0.041
R indices (all data)	0.100	0.069
Largest diff. peak / hole (eÅ^{-3})	-0.78 / 0.69	-1.02 / 0.65
CCDC	2207776	2207769

Table S2. Selected metrical data of the isomeric forms of [Cu(L)$_2$(NO$_3$)$_2$].

| distances (Å)	L^1 = 2-bromo-5-methylpyridine	L^2 = 2-bromo-4-methylpyridine
Cu–O1	2.030(5)	1.967(2)
Cu–O1^i (L^1)	2.030(5)	
Cu–O6 (L^2)		2.4462(2)
Cu–O2	2.515(7)	2.445(3)
Cu–O2^i (L^1)	2.515(7)	
Cu–O4 (L^2)		1.967(3)
Cu–N1	1.990(5)	2.007(3)
Cu–N1^i(L^1)	1.990(5)	
Cu–N2(L^2)		2.013(3)
Cu$\cdots$N3	2.673(6)	2.609(4)
Cu$\cdots$Br1	3.328(9)	3.2614(2)
Cu$\cdots$Br1^i(L^1)	3.328(9)	
Cu$\cdots$Br2(L^2)		3.2621(7)

Br··Br		3.6929(8)
angles (°)		
N1–Cu–N1i(L1)	180.00	
N1–Cu–N2(L2)		177.3(1)
N1–Cu–O2(L1)	89.7(2)	
N1–Cu–O1(L2)		90.4(1)
N1–Cu–O2i(L1)	88.0(2)	
N1–Cu–O4(L2)		89.6(1)
O2–Cu–O2i(L1)	180.00	
O4–Cu–O1(L2)		170.2(1)
Cu–O1–N3(L1)	105.7(4)	
Cu–O1–N3(L2)		102.7(2)
Cu–O1–N3i(L1)	152.7(4)	
Cu–O4–N4(L2)		109.7(3)
CCDC	2207776	2207769

Symmetry code: (i) −x+2, −y, −z+2.

Table S3. Hydrogen bond details of the isomeric forms of [Cu(L)$_2$(NO$_3$)$_2$][a].

L1 = 2-bromo-5-methylpyridine in P2₁/c					L2 = 2-bromo-4-methylpyridine in P1̄				
D–H··A	d_{D-H}[b]	$d_{H··A}$	$d_{D··A}$	angle D–H··A	D–H··A	d_{D-H}[b]	$d_{H··A}$	$d_{D··A}$	angle D–H··A
C4–H4··O2	0.930	2.576	3.482	164	C4–H4··O3	0.930	2.586	3.513	174
C6–H6A··O3	0.960	2.580	3.477	155	C7–H7··O6	0.930	2.556	3.074	115
C6–H6C··Br1	0.960	2.930	3.740	143	C10–H10··O5	0.930	2.493	3.371	157
					C12–H12A··O6	0.960	2.480	3.298	143
					C12–H12C··O4	0.960	2.390	3.236	147

[a] Distances d (Å) and angles (°). [b] Distances fixed through AFIX instructions.

Table S4. Interaction energies (kJ/mol) of the molecular pairs calculated from energy framework calculation of [Cu(L1)$_2$(NO$_3$)$_2$] (top) and [Cu(L2)$_2$(NO$_3$)$_2$] (bottom).[a]

[Cu(L1)$_2$(NO$_3$)$_2$]:

	N	Symmetry operation	R	Electron Density	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
	1	x, y, z	6.77	HF/3-21G	−19.5	−12.6	−48.4	27.0	−49.7
	4	−x, y+1/2, −z+1/2	8.31	HF/3-21G	−29.3	−11.4	−47.1	22.9	−61.2
	2	−x, y+1/2, −z+1/2	9.96	HF/3-21G	−17.1	−5.1	−8.6	3.3	−25.8
	1	x, y, z	13.19	HF/3-21G	5.2	−1.3	−4.0	0.1	0.1
	2	−x, y+1/2, −z+1/2	11.43	HF/3-21G	0.5	−0.5	−8.4	5.6	−2.9
	0	x, y, z	10.79	HF/3-21G	14.5	−1.3	−1.8	0.0	12.4
	1	x, y, z	14.83	HF/3-21G	5.9	−0.8	−2.3	0.0	3.5

[Cu(L2)$_2$(NO$_3$)$_2$]:

	N	Symmetry operation	R	Electron Density	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
	1	x, y, z	10.04	HF/3-21G	−18.3	−7.8	−47.4	25.0	−46.2
	0	−x,−y,−z	9.50	HF/3-21G	−30.4	−11.5	−35.1	26.3	−48.8
	1	x, y, z	7.49	HF/3-21G	0.3	−5.0	−25.4	13.9	−14.7
	0	−x,−y,−z	7.58	HF/3-21G	−43.2	−17.8	−62.4	37.6	−81.3
	0	−x,−y,−z	9.87	HF/3-21G	−35.6	−10.2	−17.9	10.5	−50.5
	1	−x,−y,−z	8.68	HF/3-21G	−5.2	−9.6	−17.6	6.7	−22.0
	1	x, y, z	11.41	HF/3-21G	−1.3	−1.5	−8.7	2.1	−8.4
	1	−x,−y,−z	7.88	HF/3-21G	−48.3	−17.8	−45.4	32.9	−75.0
	1	−x,−y,−z	16.37	HF/3-21G	3.8	−0.6	−2.2	0.2	1.6

			R						
	0	−x,−y,−z	15.87	HF/3-21G	5.3	−0.9	−5.4	2.5	2.0
	1	−x,−y,−z	15.96	HF/3-21G	4.3	−0.4	−1.4	0.0	2.8

Energy model	K_{ele}	K_{pol}	K_{dis}	K_{rep}
CE–HF··HF/3-21G electron densities	1.019	0.651	0.901	0.811

[a] R is the distance between molecular centroids (mean atomic position) in Å.