## High-nuclearity heterometallic clusters with both anion and cation sandwiched by planar cluster units: synthesis, structure and properties

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## **Electronic Supplementary Information**

Cu1–O1	1.906(6)	O1–Cu1–N1	93.0(3)	O8-Cu4-N12	91.7(3)
Cu1–N1	1.940(7)	O1–Cu1–O2	172.9(3)	O7-Cu4-N13	95.0(4)
Cu1–O2	1.963(6)	N1–Cu1–O2	81.1(3)	N8-Cu4-N13	92.1(3)
Cu1–N5	2.012(8)	O1–Cu1–N5	92.2(3)	O8-Cu4-N13	93.0(3)
Cu1–N6	2.301(10)	N1–Cu1–N5	162.3(4)	N12-Cu4-N13	95.6(3)
Cu2–O6A	1.888(7)	O2–Cu1–N5	92.4(3)	O12B-Cu5-O9	178.6(3)
Cu2–O3	1.900(6)	O1–Cu1–N6	92.9(3)	O12B-Cu5-N11B	91.6(3)
Cu2–N4A	2.014(7)	N1–Cu1–N6	96.8(3)	O9–Cu5–N11B	87.6(3)
Cu2–N2	2.021(7)	O2–Cu1–N6	91.7(3)	O12B-Cu5-N9	99.8(3)
Cu2–N7	2.496(11)	N5–Cu1–N6	99.8(3)	O9–Cu5–N9	81.0(3)
Cu3–O3	1.875(6)	O6A-Cu2-O3	157.7(4)	N11B-Cu5-N9	167.7(3)
Cu3–O4A	1.917(6)	O6A-Cu2-N4A	93.0(3)	O9–Cu6–O10B	168.7(3)
Cu3–N3A	1.941(7)	O3–Cu2–N4A	88.5(3)	O9-Cu6-N10B	90.8(3)
Cu3–O4	1.959(6)	O6A-Cu2-N2	99.2(3)	O10B-Cu6-N10B	84.9(3)
Cu3–Cl1	2.825(4)	O3–Cu2–N2	79.9(3)	O9–Cu6–O10	85.5(2)
Cu4–O7	1.891(7)	N4A-Cu2-N2	167.8(3)	O10B-Cu6-O10	94.6(3)
Cu4–N8	1.941(8)	O6A-Cu2-N7	91.9(4)	N10B-Cu6-O10	157.7(3)
Cu4–O8	1.951(6)	O3-Cu2-N7	110.4(3)	O9–Cu6–Cl1	106.5(2)
Cu4–N12	2.002(9)	N4A-Cu2-N7	90.9(3)	O10B-Cu6-Cl1	84.8(2)
Cu4–N13	2.361(10)	N2-Cu2-N7	89.6(3)	N10B-Cu6-Cl1	118.0(3)
Cu5–O12B	1.882(6)	O3–Cu3–O4A	173.0(3)	O10-Cu6-Cl1	84.0(2)
Cu5–O9	1.903(6)	O3–Cu3–N3A	89.7(3)	O9–Cu6–Na1	124.8(2)
Cu5–N11B	1.997(7)	O4A-Cu3-N3A	85.7(3)	O10B-Cu6-Na1	49.86(19)
Cu5–N9	2.005(7)	O3–Cu3–O4	84.5(3)	N10B-Cu6-Na1	117.8(3)
Cu6–O9	1.888(6)	O4A-Cu3-O4	98.5(3)	O10-Cu6-Na1	49.91(19)
Cu6010B	1.928(6)	N3A-Cu3-O4	163.4(3)	Cl1-Cu6-Na1	99.98(11)
Cu6–N10B	1.937(7)	O3-Cu3-Cl1	101.2(2)	Cu6A–Cl1–Cu6B	73.64(11)
Cu6010	1.968(6)	O4A-Cu3-Cl1	85.4(2)	Cu6A–Cl1–Cu6	73.65(11)
Cu6–Cl1	2.748(4)	N3A-Cu3-Cl1	111.7(2)	Cu6B-Cl1-Cu6	73.64(11)
Cu6–Na1	3.218(6)	O4-Cu3-Cl1	84.7(2)	Cu6A-Cl1-Cu3	96.21(4)
Cl1–Cu6A	2.748(4)	O7-Cu4-N8	93.7(3)	Cu6B-Cl1-Cu3	126.71(3)
Cl1–Cu6B	2.748(4)	O7–Cu4–O8	170.6(3)	Cu6–Cl1–Cu3	154.59(3)
Na1–O13	2.347(10)	N8-Cu4-O8	81.1(3)	Cu6 – O9– Cu5	118.0(3)
Na1–O10	2.464(8)	O7-Cu4-N12	92.5(3)	Cu6A-O10-Cu6	115.5(3)
	~ /	N8-Cu4-N12	169.7(4)	Cu3–O3–Cu2	120.6(3)
				Cu3B-O4-Cu3	115.3(3)

Table S1 Selected Bond Lengths (Å) and Angles (deg) for 1<sup>a</sup>.

<sup>a</sup> Symmetry codes: A) -x + y, -x + 1, z; B) -y + 1, x - y + 1, z.

Table S2 Selected Bond Lengths (Å) and Angles (deg) for 2<sup>a</sup>.

Tuble 52 Selected Bond Lengths (11) and Tingles (deg) for 2.							
Cu1–O1	1.901(5)	O1–Cu1–N1	92.9(2)	O8-Cu4-N13	92.7(2)		
Cu1–N1	1.940(6)	O1–Cu1–O2	172.7(2)	N12-Cu4-N13	95.5(2)		
Cu1–O2	1.977(5)	N1–Cu1–O2	80.9(2)	O12B-Cu5-O9	178.1(2)		
Cu1–N5	2.016(6)	O1–Cu1–N5	92.4(2)	O12B-Cu5-N11B	91.1(2)		
Cu1–N6	2.310(7)	N1–Cu1–N5	162.1(3)	O9-Cu5-N11B	87.8(2)		
Cu2–O6A	1.891(5)	O2-Cu1-N5	92.4(2)	O12B-Cu5-N9	99.9(2)		
Cu2–O3	1.893(4)	O1–Cu1–N6	93.4(2)	O9–Cu5–N9	81.00(19)		
Cu2–N4A	2.010(5)	N1-Cu1-N6	96.5(2)	N11B-Cu5-N9	167.9(2)		
Cu2–N2	2.022(5)	O2-Cu1-N6	91.3(2)	O9-Cu6-O10B	169.6(2)		
Cu2–N7	2.493(8)	N5-Cu1-N6	100.2(2)	O9-Cu6-N10B	90.9(2)		
Cu3–O3	1.878(5)	O6A-Cu2-O3	158.5(3)	O10B-Cu6-N10B	85.3(2)		
Cu3–O4A	1.927(5)	O6A-Cu2-N4A	93.4(2)	O9-Cu6-O10	85.54(18)		
Cu3–N3A	1.950(5)	O3–Cu2–N4A	88.0(2)	O10B-Cu6-O10	94.6(3)		
Cu3–O4	1.971(5)	O6A-Cu2-N2	98.8(2)	N10B-Cu6-O10	159.1(2)		
Cu3–Br1	2.8754(16)	O3–Cu2–N2	80.0(2)	O9-Cu6-Br1	105.44(16)		
Cu4–O7	1.899(5)	N4A-Cu2-N2	167.6(2)	O10B-Cu6-Br1	84.90(15)		
Cu4–N8	1.951(6)	O6A-Cu2-N7	90.8(3)	N10B-Cu6-Br1	116.45(18)		
Cu4–O8	1.955(5)	O3-Cu2-N7	110.6(3)	O10-Cu6-Br1	84.25(15)		
Cu4–N12	2.024(6)	N4A-Cu2-N7	91.6(2)	O9-Cu6-Na1	124.94(16)		
Cu4–N13	2.356(7)	N2-Cu2-N7	89.8(2)	O10B-Cu6-Na1	50.12(15)		
Cu5–O12B	1.887(4)	O3–Cu3–O4A	172.6(2)	N10B-Cu6-Na1	118.52(19)		
Cu5–O9	1.903(4)	O3–Cu3–N3A	89.1(2)	O10-Cu6-Na1	50.17(14)		
Cu5–N11B	1.990(5)	O4A-Cu3-N3A	85.9(2)	Br1-Cu6-Na1	101.05(7)		
Cu5–N9	2.021(5)	O3–Cu3–O4	84.8(2)	Cu6A-Br1-Cu6	71.96(5)		
Cu6–O9	1.892(4)	O4A-Cu3-O4	98.6(3)	Cu6–Br1–Cu6B	71.96(5)		
Cu6–O10B	1.925(4)	N3A-Cu3-O4	164.0(2)	Cu6A-Br1-Cu3	98.01(3)		
Cu6–N10B	1.935(5)	O3–Cu3–Br1	100.53(17)	Cu6–Br1–Cu3	155.08(2)		
Cu6–O10	1.962(4)	O4A-Cu3-Br1	86.30(16)	Cu6B–Br1–Cu3	127.71(2)		
Cu6–Br1	2.8131(15)	N3A–Cu3–Br1	110.16(19)	Cu6–Br1–Cu3B	98.01(3)		
Cu6–Na1	3.228(5)	O4–Cu3–Br1	85.52(16)	Cu3–Br1–Cu3B	69.61(4)		
Na1–O13	2.343(9)	O7–Cu4–N8	93.5(2)	Cu6–Br1–Cu3A	127.71(2)		
Na1-O10	2.482(7)	O7–Cu4–O8	170.7(3)	Cu6B-Br1-Cu3A	98.01(3)		
		N8-Cu4-O8	81.3(2)	Cu3–Br1–Cu3A	69.60(4)		
		O7-Cu4-N12	91.9(2)	Cu3B-Br1-Cu3A	69.60(4)		
		N8-Cu4-N12	170.7(3)	Cu6–O9–Cu5	117.8(2)		
		O8-Cu4-N12	92.3(2)	Cu6A-O10-Cu6	116.5(2)		
		O7-Cu4-N13	95.1(3)	Cu3–O3–Cu2	121.5(2)		
		N8-Cu4-N13	91.6(2)	Cu3B-O4-Cu3	114.7(3)		

<sup>a</sup> Symmetry codes: A) -y + 1, x - y, z; B) -x + y + 1, -x + 1, z.

Cu1-O1	1.903(6)	O1-Cu1-N1	93.1(3)	O7-Cu4-O8	169.7(3)
Cu1-N1	1.946(7)	O1-Cu1-O2	172.3(3)	N8-Cu4-O8	80.5(2)
Cu1-O2	1.961(5)	N1-Cu1-O2	80.8(2)	O7-Cu4-N12	91.4(3)
Cu1-N5	2.012(7)	O1-Cu1-N5	91.8(3)	N8-Cu4-N12	170.5(3)
Cu1-N6	2.316(8)	N1-Cu1-N5	163.6(3)	O8-Cu4-N12	92.7(3)
Cu2-O6A	1.875(6)	O2-Cu1-N5	92.8(3)	O7-Cu4-N13	95.8(3)
Cu2-O3	1.902(5)	O1-Cu1-N6	93.3(3)	N8-Cu4-N13	92.4(3)
Cu2-N4A	1.992(6)	N1-Cu1-N6	96.4(3)	O8-Cu4-N13	93.2(3)
Cu2-N2	2.019(6)	O2-Cu1-N6	92.1(3)	N12-Cu4-N13	94.5(3)
Cu2-N7	2.647(14)	N5-Cu1-N6	99.0(3)	O(12)B-Cu5-O9	178.6(3)
Cu3-O3	1.867(5)	O6A-Cu2-O3	159.5(4)	O(12)B-Cu5-N11B	91.2(2)
Cu3-O4A	1.919(5)	O6A-Cu2-N4A	94.2(3)	O9-Cu5-N11B	88.0(2)
Cu3-N3A	1.955(6)	O3-Cu2-N4A	88.7(2)	O(12)B-Cu5-N9	99.8(3)
Cu3-O4	1.961(5)	O6A-Cu2-N2	98.2(3)	O9-Cu5-N9	80.9(2)
Cu3-Cl1	2.828(3)	O3-Cu2-N2	80.5(2)	N11B-Cu5-N9	167.9(2)
Cu4-O7	1.884(6)	N4A-Cu2-N2	167.3(3)	O9-Cu6-O10B	169.9(2)
Cu4-N8	1.929(7)	O6A-Cu2-N7	90.8(4)	O9-Cu6-N10B	90.8(2)
Cu4-O8	1.955(5)	O3-Cu2-N7	109.5(3)	O10B-Cu6-N10B	85.2(2)
Cu4-N12	2.026(8)	N4A-Cu2-N7	87.6(3)	O9-Cu6-O10	85.38(19)
Cu4-N13	2.387(9)	N2-Cu2-N7	89.9(3)	O10B-Cu6-O10	95.2(3)
Cu5-O(12)B	1.881(5)	O3-Cu3-O4A	173.3(2)	N10B-Cu6-O10	159.6(3)
Cu5-O9	1.902(5)	O3-Cu3-N3A	90.1(2)	O9-Cu6-Cl1	105.71(17)
Cu5-N11B	1.996(6)	O4A-Cu3-N3A	85.6(2)	O10B-Cu6-Cl1	84.31(17)
Cu5-N9	2.025(6)	O3-Cu3-O4	84.3(2)	N10B-Cu6-Cl1	116.7(2)
Cu6-O9	1.890(5)	O4A-Cu3-O4	98.3(3)	O10-Cu6-Cl1	83.56(16)
Cu6-O10B	1.924(5)	N3A-Cu3-O4	162.1(3)	Cu6-Cl1-Cu3	154.28(3)
Cu6-N10B	1.930(6)	O3-Cu3-Cl1	100.59(19)	Cu3-O3-Cu2	120.2(3)
Cu6-O10	1.967(5)	O4A-Cu3-Cl1	85.83(17)	Cu3B-O4-Cu3	114.8(3)
Cu6-Cl1	2.793(3)	N3A-Cu3-Cl1	112.7(2)	Cu6-O9-Cu5	117.9(3)
K(1)-O(13)	2.605(15)	O4-Cu3-Cl1	85.08(18)	Cu6A-O10-Cu6	116.9(3)
K(1)-O10	2.769(7)	O7-Cu4-N8	94.3(3)		

Table S3 Selected Bond Lengths (Å) and Angles (deg) for 3<sup>a</sup>.

<sup>a</sup> Symmetry codes: A) -y + 1, x - y, z; B) -x + y + 1, -x + 1, z.

Cu1-O1	1.90(3)	O1-Cu1-N1	92.2(4)	O8-Cu4-N13	93.9(7)
Cu1-N1	1.95(3)	O1-Cu1-O2	173.0(4)	N8-Cu4-N13	91.8(4)
Cu1-O2	1.97(3)	N1-Cu1-O2	81.4(4)	N12-Cu4-N13	94.9(4)
Cu1-N5	2.00(3)	O1-Cu1-N5	92.6(4)	O(12)B-Cu5-O9	179.1(4)
Cu1-N6	2.337(11)	N1-Cu1-N5	162.9(5)	O(12)B-Cu5-N11B	91.8(4)
Cu2-O6A	1.89(3)	O2-Cu1-N5	92.7(4)	O9-Cu5-N11B	87.5(4)
Cu2-O3	1.90(3)	O1-Cu1-N6	93.2(5)	O(12)B-Cu5-N9	99.7(4)
Cu2-N4A	2.01(3)	N1-Cu1-N6	95.9(4)	O9-Cu5-N9	81.0(4)
Cu2-N2	2.03(3)	O2-Cu1-N6	90.4(5)	N11B-Cu5-N9	167.5(4)
Cu2-N7	2.508(15)	N5-Cu1-N6	100.3(4)	O9-Cu6-O10B	171.1(4)
Cu3-O3	1.88(3)	O6A-Cu2-O3	158.6(6)	O9-Cu6-O10	85.4(4)
Cu3-O4A	1.92(3)	O6A-Cu2-N4A	94.3(4)	O10B-Cu6-O10	95.2(5)
Cu3-N3A	1.95(3)	O3-Cu2-N4A	87.7(4)	O9-Cu6-N10B	91.3(4)
Cu3-O4	1.99(3)	O6A-Cu2-N2	99.0(4)	O10B-Cu6-N10B	85.3(4)
Cu3-Br1	2.85(2)	O3-Cu2-N2	79.5(4)	O10-Cu6-N10B	161.1(5)
Cu4-O7	1.92(3)	N4A-Cu2-N2	166.7(4)	O9-Cu6-Br1	105.1(6)
Cu4-O8	1.95(3)	O6A-Cu2-N7	88.8(8)	O10B-Cu6-Br1	83.8(6)
Cu4-N8	1.95(3)	O3-Cu2-N7	112.5(5)	O10-Cu6-Br1	83.4(6)
Cu4-N12	2.03(3)	N4A-Cu2-N7	91.2(4)	N10B-Cu6-Br1	115.4(5)
Cu4-N13	2.337(11)	N2-Cu2-N7	90.2(4)	Cu6A-Br1-Cu6B	71.8(7)
Cu5-O(12)B	1.88(3)	O3-Cu3-O4A	171.8(4)	Cu6A-Br1-Cu6	71.8(7)
Cu5-O9	1.92(3)	O3-Cu3-N3A	89.6(4)	Cu6B-Br1-Cu6	71.8(7)
Cu5-N11B	2.02(3)	O4A-Cu3-N3A	85.1(4)	Cu6A-Br1-Cu3A	154.8(2)
Cu5-N9	2.03(3)	O3-Cu3-O4	84.4(4)	Cu6B-Br1-Cu3A	97.8(9)
Cu6-O9	1.88(3)	O4A-Cu3-O4	99.0(6)	Cu6-Br1-Cu3A	127.9(5)
Cu6-O10B	1.92(3)	N3A-Cu3-O4	163.1(4)	Cu6A-Br1-Cu3B	127.9(5)
Cu6-O10	1.95(3)	O3-Cu3-Br1	100.5(6)	Cu6B-Br1-Cu3B	154.8(2)
Cu6-N10B	1.95(3)	O4A-Cu3-Br1	87.2(6)	Cu6-Br1-Cu3B	97.8(9)
Cu6-Br1	2.84(2)	N3A-Cu3-Br1	110.8(5)	Cu3A-Br1-Cu3B	69.9(7)
		O4-Cu3-Br1	85.8(6)	Cu6A-Br1-Cu3	97.8(9)
		O7-Cu4-O8	169.5(4)	Cu6B-Br1-Cu3	127.9(5)
		O7-Cu4-N8	93.5(4)	Cu6-Br1-Cu3	154.8(2)
		O8-Cu4-N8	81.3(4)	Cu3A-Br1-Cu3	69.9(7)
		O7-Cu4-N12	91.8(4)	Cu3B-Br1-Cu3	69.9(7)
		O8-Cu4-N12	92.2(4)	Cu3-O3-Cu2	121.3(5)
		N8-Cu4-N12	171.0(4)	Cu3B-O4-Cu3	113.2(6)
		O7-Cu4-N13	95.4(6)	Cu6-O9-Cu5	117.3(5)
				Cu6A-O10-Cu6	118.3(6)

Table S4 Selected Bond Lengths (Å) and Angles (deg) for 4<sup>a</sup>.

<sup>a</sup> Symmetry codes: A) -x + y, -x + 1, z; B) -y + 1, x - y + 1, z.

	1	2	3	4		
Cu1-N1-N2-Cu2	174.4(5)	174.5(4)	175.4(5)	177.5(6)		
Cu3B-N3-N4-Cu2B	-3.7(9)	-3.0(7)	-2.4(7)	-4.0(11)		
Cu4-N8-N9-Cu5	-175.3(5)	-175.5(4)	-175.9(5)	-175.5(6)		
Cu6A-N10-N11-	-6.5(9)	-5.0(7)	-2.5(7)	-3.8(11)		
Cu5A						
[a] Summatry adds for 1: (A) $x + y + 1 = 2$ (D) $y + 1 = 2$ (y + 1)						

Table S5 Selected torsion angles (deg) for 1-4<sup>[a]</sup>.

[a] Symmetry codes for 1: A) -x + y, -x + 1, z; B) -y + 1, x - y + 1, z.
Symmetry codes for 2: A) -y + 1, x - y, z; B) -x + y + 1, -x + 1, z.
Symmetry codes for 3: A) -y + 1, x - y, z; B) -x + y + 1, -x + 1, z.
Symmetry codes for 4: A) -x + y, -x + 1, z; B) -y + 1, x - y + 1, z



Fig. S1 PXRD patterns of 1.



Fig. S2 PXRD patterns of 2.



Fig. S3 PXRD patterns of 3.



Fig. S4 PXRD patterns of 4.



Fig. S5 TG-DTG curves for 1-4 (a-d, respectively)







Fig. S6 Ortep plots of 1-4 (a-d, respectively) with 30% probabilities.



Scheme S1 Coordination modes of  $L^{6-}$  ligands in 1-4.



**Fig. S7** Topological views of the titled cluster with (left) and without (right) the sodium ion. The red, green and teal spheres represent 2R,3R-SBH<sup>6-</sup>, Cu(II) and Na<sup>+</sup>, respectively.



Fig. S8 The defective heterometallic vertex-sharing dicubane core in the titled cluster



Fig. S9 A side view (left) and a perspective view (right) of 1 in ball-and-stick and spacefilling style with the value of size.



Fig. S10 A packing diagram of 1 (green spheres represent the heterometallic nonadecanuclear clusters).



Fig. S11 Electric hysteresis loops of 1 measured at the indicated applied electric field and frequency.



Fig. S12 Electric hysteresis loops of 2 measured at the indicated applied electric field and frequency.



Fig. S13 Electric hysteresis loops of 3 measured at the indicated applied electric field and frequency.



Fig. S14 Electric hysteresis loops of 4 measured at the indicated applied electric field and frequency.



**Fig. S15** Dielectric constant measurements of **1** as a function of the temperature (a and b) and frequency (c and d).



**Fig. S16** Dielectric constant measurements of **2** as a function of the temperature (a and b) and frequency (c and d).



**Fig. S17** Dielectric constant measurements of **3** as a function of the temperature (a and b) and frequency (c and d).



Fig. S18 Dielectric constant measurements of 4 as a function of the temperature (a) and frequency (b).