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Synthesis, structure and magnetic properties of two mixed-valence icosanuclear nanocages

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Table S1 Selected bond lengths / Å and bond angles / º of **1**.

Co1–N4	1.848(6)	N2A–Co2–O1A	78.4(2)
Co1–N3	1.858(6)	O3–Co2–N5	165.8(2)
Co1–S1	2.180(2)	O2–Co2–N5	78.9(2)
Co1–S2	2.192(2)	N2A–Co2–N5	99.8(2)
Co2–O3	2.102(5)	O1A–Co2–N5	95.6(2)
Co2–O2	2.112(5)	O3–Co2–N8	78.7(2)
Co2–N2A	2.121(6)	O2–Co2–N8	93.5(2)
Co2–O1A	2.126(5)	N2A–Co2–N8	101.3(2)
Co2–N5	2.127(6)	O1A–Co2–N8	166.2(2)
Co2–N8	2.140(7)	N5–Co2–N8	98.1(3)
Co3–N10	1.843(7)	N10–Co3–N9	82.4(3)
Co3–N9	1.849(7)	N10–Co3–S3	166.8(2)
Co3–S3	2.183(2)	N9–Co3–S3	85.4(2)
Co3–S4	2.184(3)	N10–Co3–S4	85.0(2)
Co4–O4	2.116(5)	N9–Co3–S4	167.1(2)
Co4–O4B	2.116(5)	S3–Co3–S4	107.02(10)
Co4–O4C	2.116(5)	O4–Co4–O4B	88.1(2)
Co4–N11C	2.122(7)	O4–Co4–O4C	88.1(2)
Co4–N11B	2.122(7)	O4B–Co4–O4C	88.1(2)
Co4–N11	2.122(7)	O4–Co4–N11C	167.2(2)
N4–Co1–N3	82.1(3)	O4B–Co4–N11C	94.1(2)
N4–Co1–S1	166.7(2)	O4C–Co4–N11C	79.4(2)
N3–Co1–S1	85.3(2)	O4–Co4–N11B	94.1(2)
N4–Co1–S2	85.2(2)	O4B–Co4–N11B	79.4(2)
N3–Co1–S2	167.2(2)	O4C–Co4–N11B	167.2(2)
S1–Co1–S2	107.25(9)	N11C–Co4–N11B	98.7(2)
O3–Co2–O2	87.5(2)	O4–Co4–N11	79.4(2)
O3–Co2–N2A	94.4(2)	O4B–Co4–N11	167.2(2)
O2–Co2–N2A	165.2(2)	O4C–Co4–N11	94.1(2)
O3–Co2–O1A	87.6(2)	N11C–Co4–N11	98.7(2)
O2–Co2–O1A	87.0(2)	N11B–Co4–N11	98.7(2)

Symmetry codes: A) $z + 1/2, x, -y + 1/2$; B) $-y + 1, z + 1/2, -x + 1/2$; C) $-z + 1/2, -x + 1, y - 1/2$; D) $y, -z + 1/2, x - 1/2$.

Table S2 Selected bond lengths / Å and bond angles / º of **2**.

Ni1–N4	1.831(5)	N2A–Ni2–N8	101.30(19)
Ni1–N3	1.841(5)	O3–Ni2–O2	87.63(15)
Ni1–S1	2.1593(17)	N5–Ni2–O2	80.63(16)
Ni1–S2	2.1714(17)	N2A–Ni2–O2	166.36(17)
Ni2–O3	2.071(4)	N8–Ni2–O2	92.10(17)
Ni2–N5	2.072(5)	O3–Ni2–O1A	87.22(15)
Ni2–N2A	2.079(5)	N5–Ni2–O1A	92.91(18)
Ni2–N8	2.087(5)	N2A–Ni2–O1A	80.03(16)
Ni2–O2	2.092(4)	N8–Ni2–O1A	167.77(17)
Ni2–O1A	2.096(4)	O2–Ni2–O1A	86.33(15)
Ni3–N10	1.835(5)	N10–Ni3–N9	83.0(2)
Ni3–N9	1.837(5)	N10–Ni3–S3	168.35(17)
Ni3–S3	2.1664(19)	N9–Ni3–S3	86.02(15)
Ni3–S4	2.170(2)	N10–Ni3–S4	85.74(17)
Ni4–N11	2.070(5)	N9–Ni3–S4	168.57(16)
Ni4–N11B	2.070(5)	S3–Ni3–S4	105.14(8)
Ni4–N11C	2.070(5)	N11–Ni4–N11B	98.99(18)
Ni4–O4B	2.085(4)	N11–Ni4–N11C	98.99(18)
Ni4–O4C	2.085(4)	N11B–Ni4–N11C	98.99(18)
Ni4–O4	2.085(4)	N11–Ni4–O4B	168.73(18)
N4–Ni1–N3	82.4(2)	N11B–Ni4–O4B	80.66(17)
N4–Ni1–S1	168.35(15)	N11C–Ni4–O4B	92.17(18)
N3–Ni1–S1	86.12(15)	N11–Ni4–O4C	92.17(18)
N4–Ni1–S2	86.01(15)	N11B–Ni4–O4C	168.73(18)
N3–Ni1–S2	168.39(15)	N11C–Ni4–O4C	80.66(17)
S1–Ni1–S2	105.48(7)	O4B–Ni4–O4C	88.08(17)
O3–Ni2–N5	168.22(17)	N11–Ni4–O4	80.66(17)
O3–Ni2–N2A	91.99(17)	N11B–Ni4–O4	92.17(18)
N5–Ni2–N2A	99.63(18)	N11C–Ni4–O4	168.73(18)
O3–Ni2–N8	80.59(17)	O4B–Ni4–O4	88.08(17)
N5–Ni2–N8	98.81(19)	O4C–Ni4–O4	88.08(17)

Symmetry code: A) $z + 1/2, x, -y + 1/2$; B) $-y + 1, z + 1/2, -x + 1/2$; C) $-z + 1/2, -x + 1, y-1/2$; D) $y, -z + 1/2, x - 1/2$.

Table S3 Bond valence sum (BVS) calculation results of **1** and **2**.

	1	**2**
M1	3.354	3.011
M2	2.334	2.165
M3	3.400	3.000
M4	2.354	2.199

Table S4 Hydrogen bonds in **1**.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N1-H1A...N8D	0.86	2.67	3.342(9)	136.2
N1-H1B...S1F	0.86	2.91	3.742(7)	165.1
N6-H6B...N1A	0.87	2.70	3.473(10)	148.4
N6-H6B...N2A	0.87	2.51	3.329(9)	156.6
N7-H7A...N15	0.88	2.53	3.238(11)	138.6
N7-H7A...N6	0.88	2.69	3.553(12)	168.7
N7-H7B...S3G	0.88	2.68	3.416(7)	141.8
N12-H12)...N11B	0.87	2.47	3.183(10)	139.7
N12-H12B...S1H	0.86	3.02	3.428(8)	110.9
O91-H91...O4C	0.92	2.58	3.494(10)	180.0
O10-H101...S1E	0.88	2.95	3.828(18)	179.4
O10-H102...O12	0.94	2.59	3.53(3)	180.0
C11-H11A...S4I	0.98	2.65	3.34(4)	127.7
C11-H11B...O81	0.98	2.46	2.97(4)	112.3

A) $z + 1/2, x, -y + 1/2$; B) $–z + 1/2, -x + 1, y - 1/2$; C) $-y + 1, z + 1/2, -x + 1/2$; D) $y, -z + 1/2, x - 1/2$; E) $-x + 1, -y + 1, -z$; F) $z + 1, x, y - 1$; G) $-z + 1/2, x + 1/2, y - 1$; H) $z + 1/2, -x + 3/2, -y + 1$; I) $-x + 1, y - 1/2, -z + 1/2$

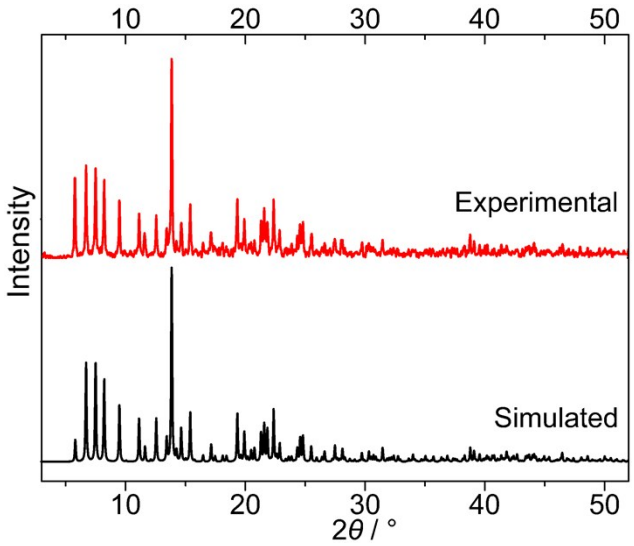


Fig. S1 PXRD patterns of **1**.

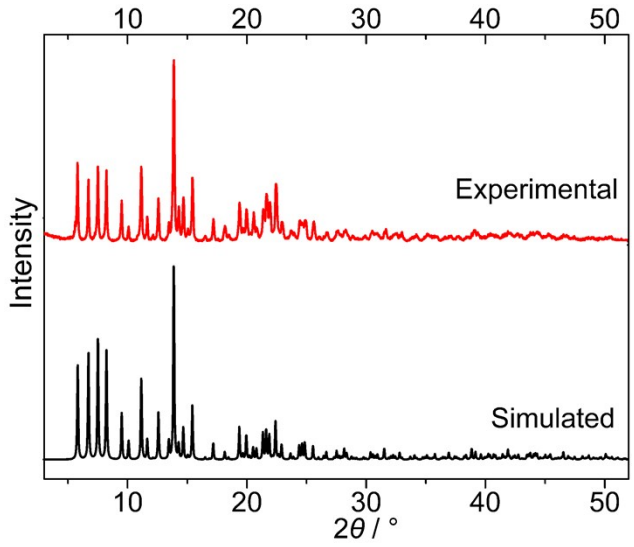


Fig. S2 PXRD patterns of **2**.

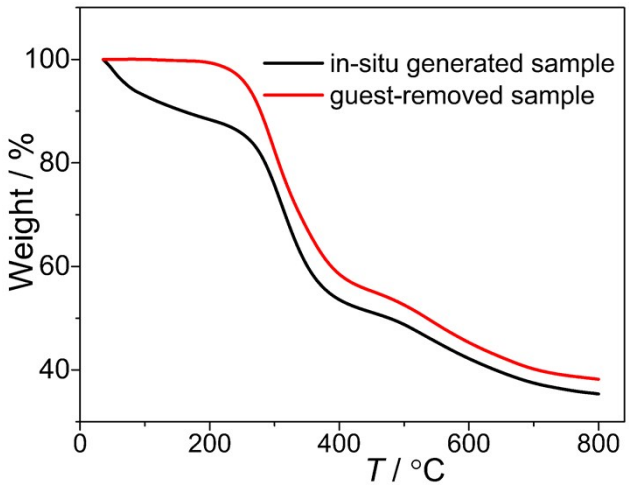


Fig. S3 TG curves of **1**.

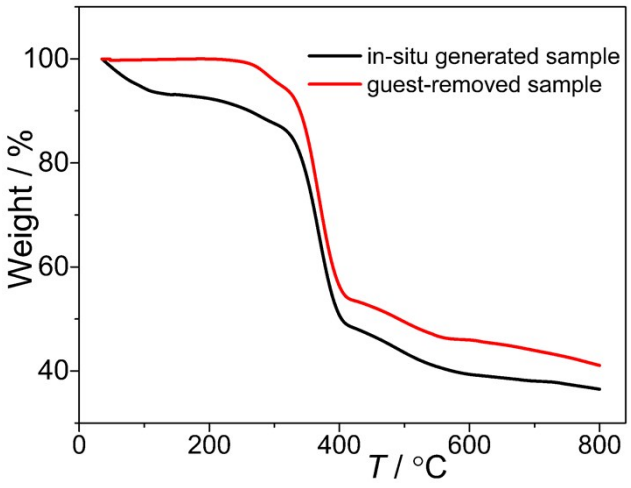


Fig. S4 TG curves of **2**.

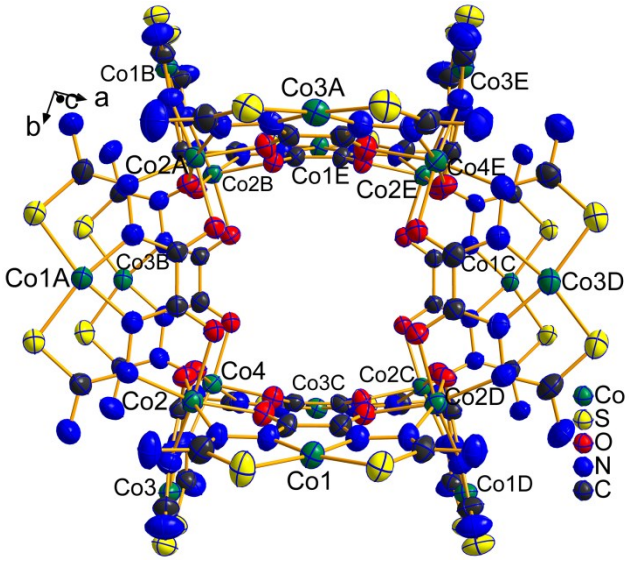


Fig. S5 Molecular structure of **1** with selected atoms labelled. Displacement ellipsoids are drawn at the 30% probability level. Guest molecules and hydrogen atoms are omitted for clarity. Symmetry codes: A) $z + 1/2, x, -y + 1/2$; B) $-y + 1, z + 1/2, -x + 1/2$; C) $-z + 1/2, -x + 1, y - 1/2$; D) $y, -z + 1/2, x - 1/2$; E) $1 - x, 1 - y, -z$.

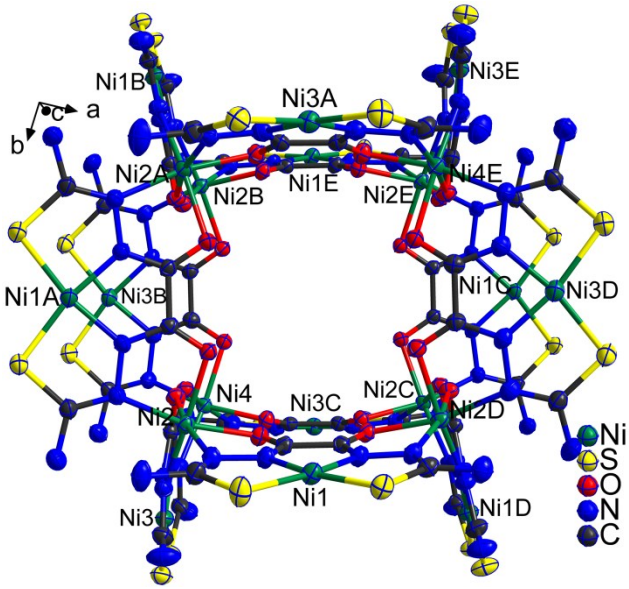
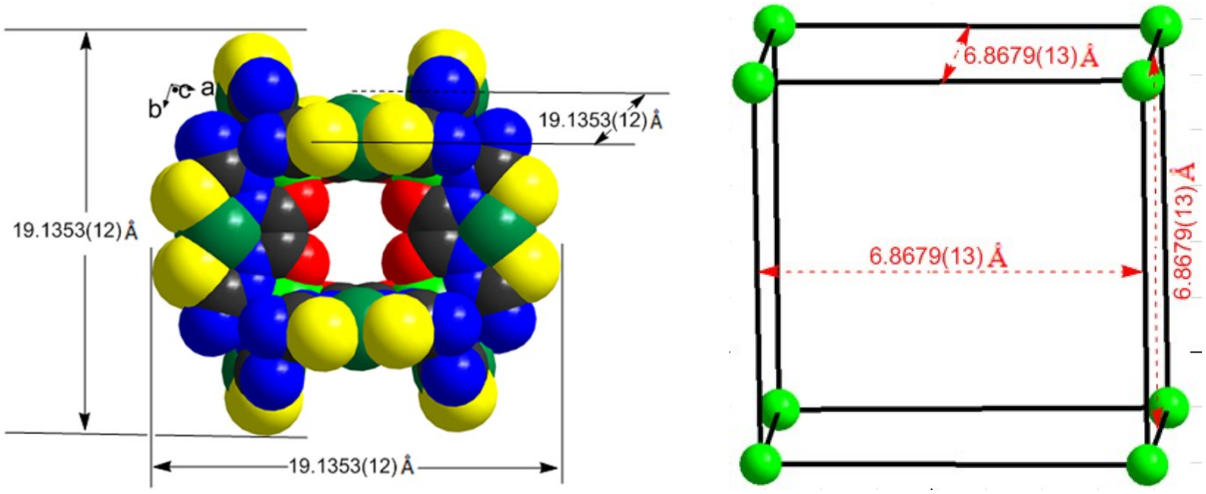
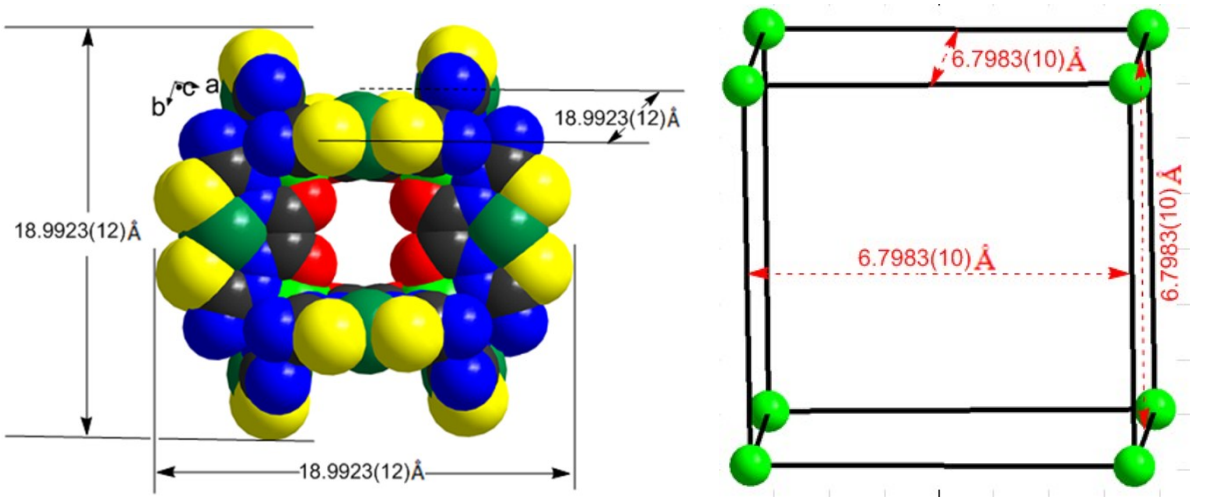


Fig. S6 Molecular structure of **2** with selected atoms labelled. Displacement ellipsoids are drawn at the 30% probability level. Guest molecules and hydrogen atoms are omitted for clarity. Symmetry codes: A) $z + 1/2, x, -y + 1/2$; B) $-y + 1, z + 1/2, -x + 1/2$; C) $-z + 1/2, -x + 1, y - 1/2$; D) $y, -z + 1/2, x - 1/2$; E) $1 - x, 1 - y, -z$.



(a) (b)

Fig. S7 (a) Peripheral sizes of **1**: 19.1353(12) × 19.1353(12) × 19.1353(12) Å; (b) Cage dimensions of **1**: 6.8679(13) × 6.8679(13) × 6.8679(13) Å.



(a) (b)

Fig. S8 (a) Peripheral sizes of **2**: 18.9923(12) × 18.9923(12) × 18.9923(12) Å; (b) Cage dimensions of **2**: 6.7983(10) × 6.7983(10) × 6.7983(10) Å.

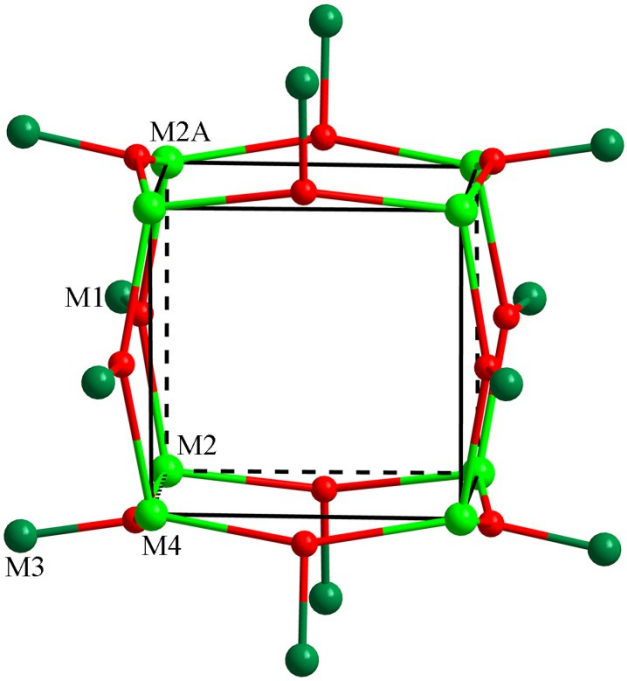


Fig. S9 A topological view of the cubic cage showing the three-connecting linker and three-connecting node. Co2···Co4: 6.8448(13) Å, Co2···Co2A: 6.8910(13) Å, Co2···Co3: 4.7051(14) Å, Co1···Co2: 4.6973(13) Å, Co1···Co2A: 4.7139(13) Å; Ni2···Ni4: 6.7726(10) Å, Ni2···Ni2A: 6.8240(10) Å, Ni2···Ni3: 4.6245(11) Å, Ni1···Ni2: 4.6206(10) Å, Ni1···Ni2A: 4.6413(10) Å. Symmetry codes: A) y, 0.5-z, -0.5+x.

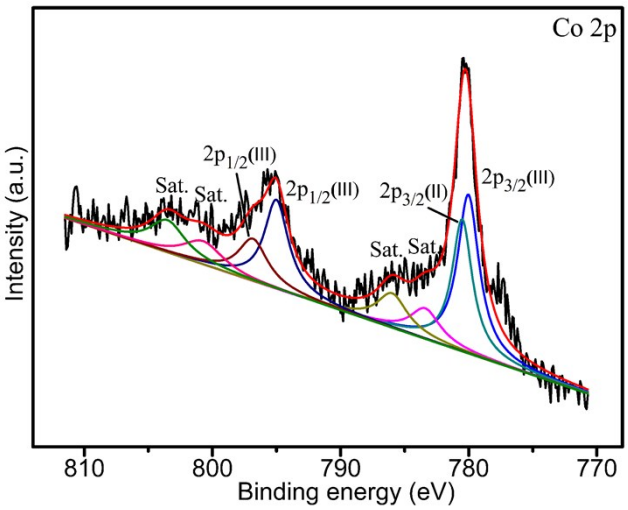


Fig. S10 XPS spectra of Co 2p for **1**. It shows XPS signals at 797.4 and 780.6 eV, and 795.1 and 780.1 eV for Co(II) and Co(III) ions, respectively, with a peak area ratio of 1:1.54.

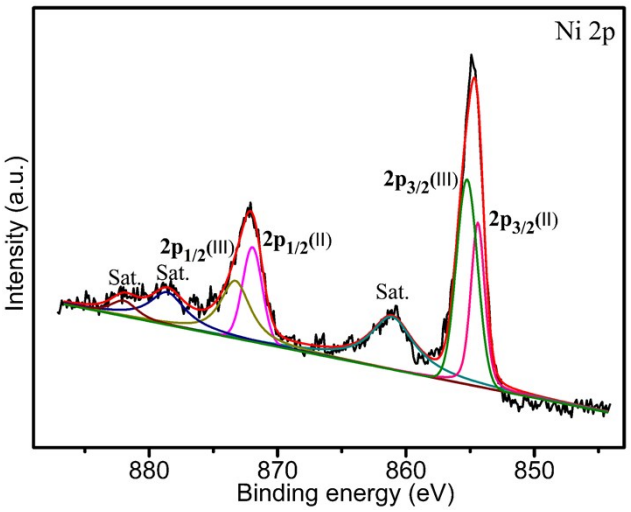
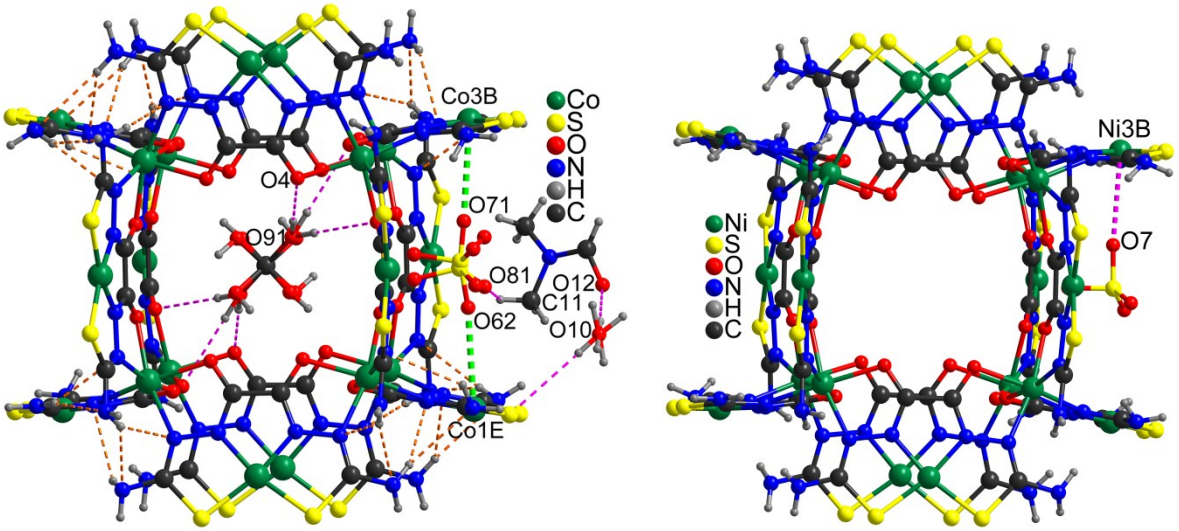


Fig. S11 XPS spectra of Ni 2p for **2**. It shows XPS signals at 854.3 and 871.9 eV, and 855.2 and 873.1 eV for Ni(II) and Ni(III) ions, respectively, with a peak area ratio of 1:1.49.



(a) (b)

Fig. S12 Hydrogen bonds for **1** (a) and Weak interaction between sulphate and cage in **2**. Symmetry codes: B) −z + 1/2, −x + 1, y − 1/2; E) −x + 1, −y + 1, −z.

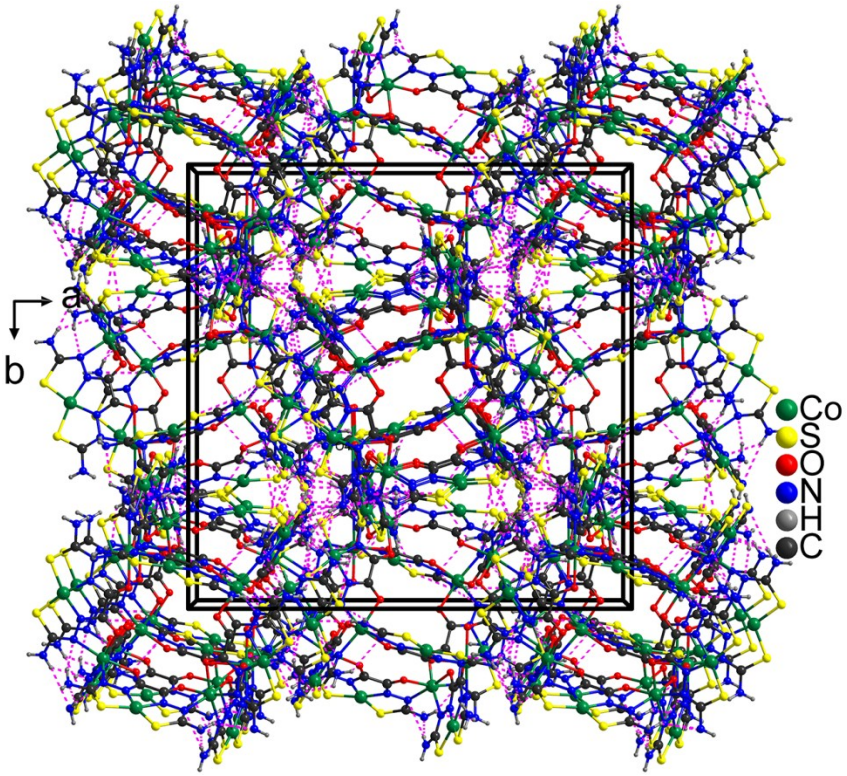


Fig. S13 3D H-bonded framework of **1** without sulphate anions and guest molecules.

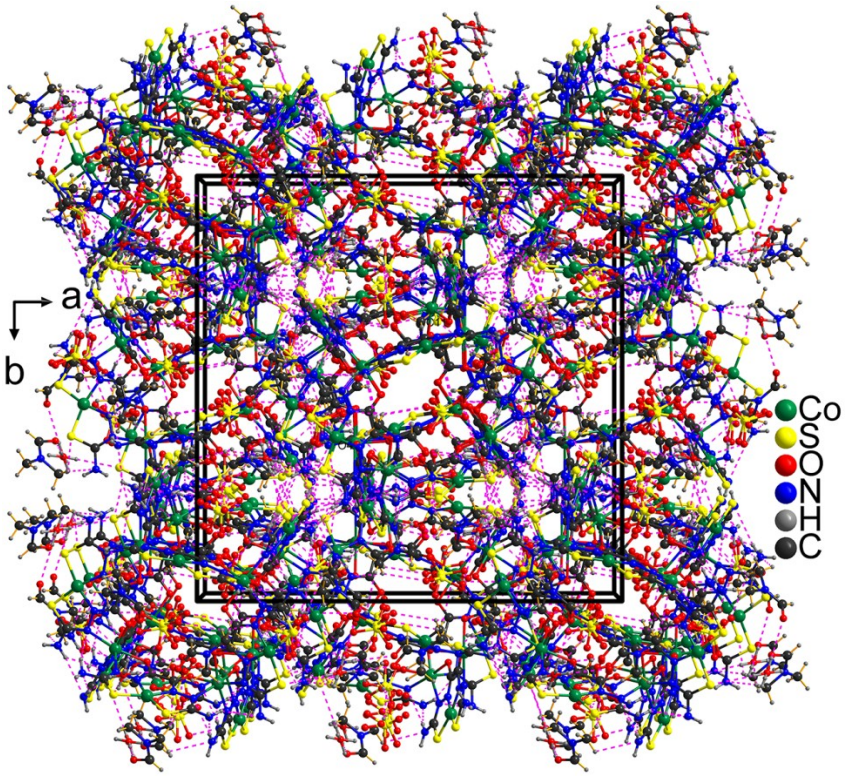


Fig. S14 3D H-bonded framework of **1** with sulphate anions and guest molecules.

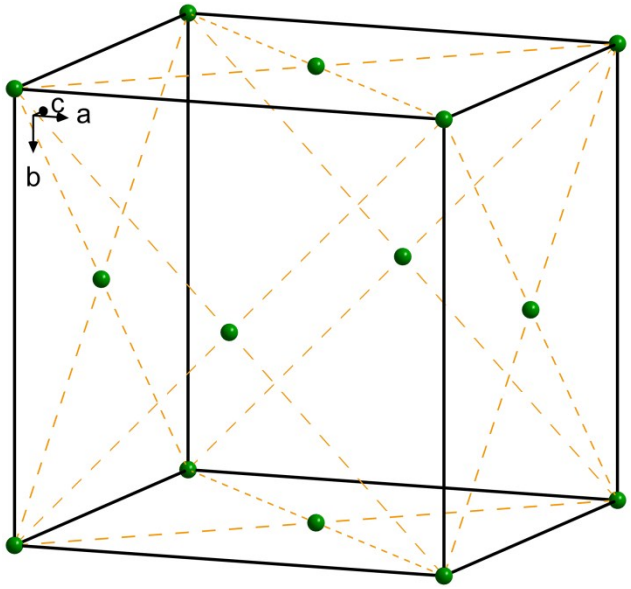


Fig. S15 A show of the face-centered cubic stacking for the cages in **1**.

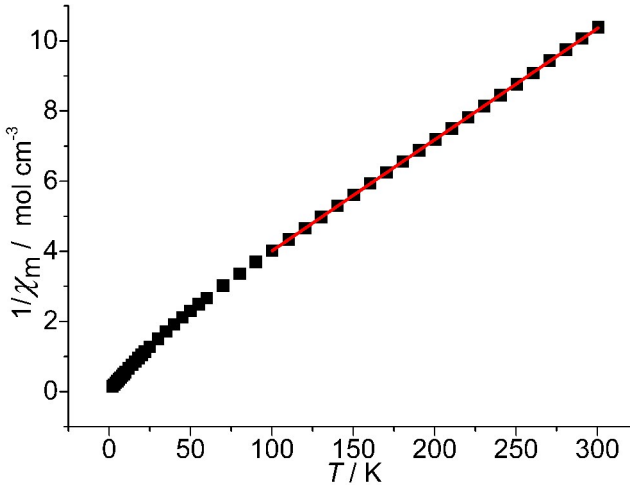


Fig. S16 The plot of $1/\chi_M$ versus T for **1**.

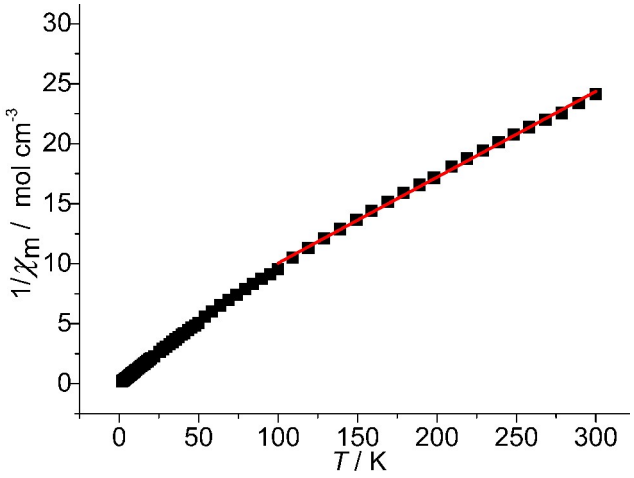


Fig. S17 The plot of $1/\chi_M$ versus T for **2**.

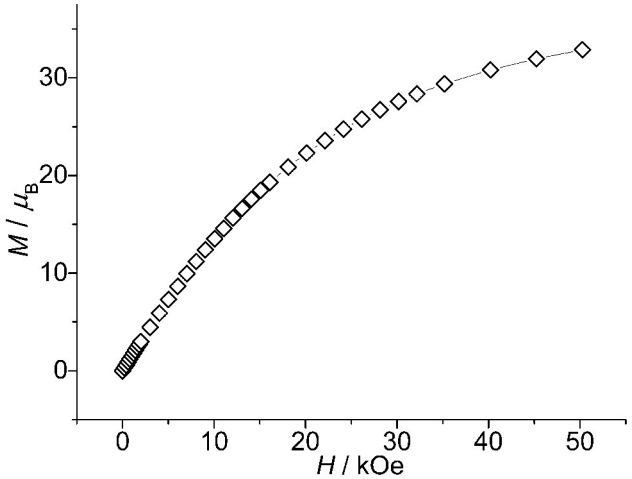


Fig. S18 The plot of M versus H for **1**.

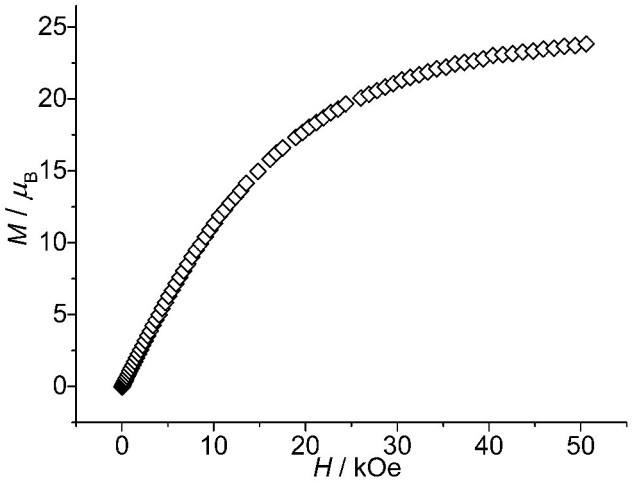


Fig. S19 The plot of *M* versus *H* for **2**.

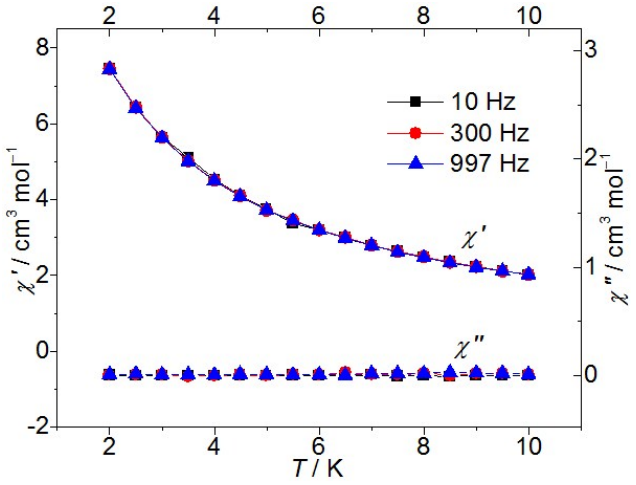


Fig. S20 The plot of ac susceptibilities ((χ' and χ'') versus *T* for **1**.

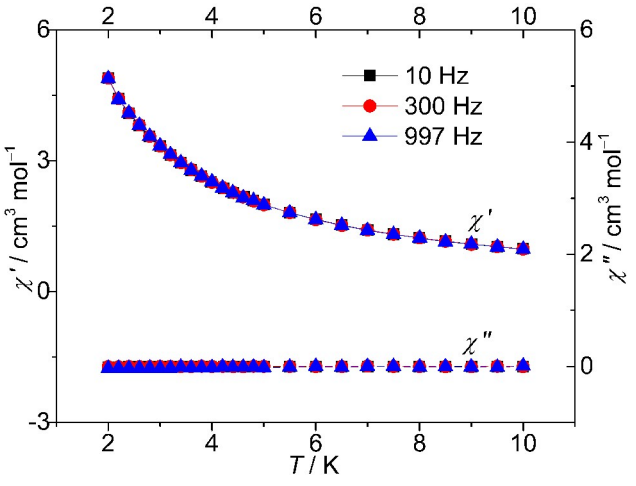


Fig. S21 The plot of ac susceptibilities ((χ' and χ'') versus *T* for **2**.