Supplementary Material (ESI) for Chemical Communications

Molecular Assembly of two [Co(II)$_4$] Linear Arrays.

David Aguilà,[a] Leoní A. Barrios,[a] Olivier Roubeau,[b] Simon J. Teat[c] and Guillem Aromí*[a]

SUPPORTING INFORMATION

X-Ray crystallography. Data for compound **2** were collected on a red block on a Bruker APEX II CCD diffractometer using Advanced Light Source beamline 11.3.1 at Lawrence Berkeley National Laboratory, which holds a silicon 111 monochromator (T=100 K, λ=0.7749 Å). The structure was solved by direct methods and refined on F^2 using the SHELXTL suite.[1] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in difference Fourier maps, placed geometrically on their carrier atom when possible and refined with a riding model. Hydrogen atoms on the coordinated water molecules as well as those on the lattice water molecules were refined freely with their thermal parameter 1.5 times that of their carrier oxygen and a soft 1,3 H···H distance restraint.

Data for compound **3** were collected on a red plate using a single-axis HUBER diffractometer on station BM16 of the European Synchrotron Radiation Facility, Grenoble, France (T=150 K and λ=0.7515 Å). Cell refinement, data reduction and absorption corrections were done with HKL-2000 suite.[2] The structure was solved by direct methods and refined on F^2 using the SHELXTL suite.[1] All non-hydrogen atoms were refined anisotropically. A lattice toluene molecule was disordered over two positions, while water molecules were partially occupied at 0.4 and 0.6, resulting in a total of four water molecules per asymmetric unit. All these as well as one of the free nitrate ions were refined with displacement parameters restraints. Hydrogen atoms were placed geometrically on their carrier atom when possible and refined with a riding model. Hydrogen atoms on the coordinated water molecule and hydroxyl moieties were found in difference Fourier maps and refined with their thermal parameter 1.5 times that of their carrier oxygen, as well as with soft distance restraints. Hydrogen atoms on the partial lattice water molecules could not be found nor fixed and are omitted in the structural model. Poor completeness (92.5%) is rather due to geometrical limitations of the single-axis goniometer on BM16 than to poor diffraction. Two datasets were acquired for two kappa positions manually fixed and differing by ca. 20º, close to the maximum permitted by the goniometer head.

1 a) G. M. Sheldrick, SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA: 2001; b) G. M. Sheldrick, *Acta Cryst.* 2008, A64, 112-122

2 Z. Otwinowski, W.Minor, *Methods in Enzymology* 1997, *276:* Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R. M. Sweet, Eds., Academic press (New York).

Table S1. Crystal data for compounds **2** and **3**.

Compound	**2**	**3**
formula	$C_{48}H_{66}Co_4N_{10}O_{34}$	$C_{138}H_{122}Co_8N_{26}O_{46}$
Fw, g/mol	1562.83	3352.06
crystal system	triclinic	triclinic
space group	*P*–1	*P*–1
a, Å	10.5822(7)	12.775(3)
b, Å	12.3023(8)	16.956(3)
c, Å	13.8898(10)	18.838(4)
α, deg	64.4450(10)	65.59(3)
β, deg	89.4460(10)	70.26(3)
γ, deg	72.1670(10)	87.57(3)
V, Å^3	1537.11(18)	3474.9(17)
Z	1	1
ρ_{calc}, g/cm^3	1.688	1.602
μ, mm^{-1}	1.467	1.190
T, K	100	150
transmission range	0.94 – 0.95	0.81 – 0.97
unique reflections	9091	13157
parameters/restrains	460 / 44	1066 / 330
w*R*2 [$I > 2\sigma(I)$]	0.0937	0.2113
*R*1 [$I > 2\sigma(I)$]	0.0342	0.0792
S [$I > 2\sigma(I)$]	1.019	1.040
w*R*2 (all data)	0.0977	0.2403
*R*1 (all data)	0.0394	0.1049
S (all data)	1.020	1.048

Table S2. Selected interatomic distances (Å) and angles (º) for $[Co_4(L)_2(H_2O)_6(MeOH)_2](NO_3)_4 \cdot 4MeOH \cdot 2H_2O$ (**2**)

Co1–O3#	2.0179(11)	N1–Co1–O6	82.04(6)
Co1–O4#	2.0278(11)	O5–Co1–O6	170.87(5)
Co1–N1	2.0840(14)	O1–Co1–O6	94.23(5)
Co1–O5	2.0899(13)	O8–Co2–O7	178.29(5)
Co1–O1	2.1130(11)	O8–Co2–O2	88.09(5)
Co1–O6	2.1519(13)	O7–Co2–O2	91.99(4)
Co2–O8	2.0765(12)	O8–Co2–N2#	92.86(5)
Co2–O7	2.1051(12)	O7–Co2–N2#	88.13(5)
Co2–O2	2.1572(11)	O2–Co2–N2#	142.01(4)
Co2–N2#	2.1831(12)	O8–Co2–O1	92.54(5)
Co2–O1	2.1890(11)	O7–Co2–O1	85.80(5)
Co2–O3#	2.2250(11)	O2–Co2–O1	79.85(4)
Co2–O2#	2.2778(10)	N2#–Co2–O1	137.94(4)
Co2···Co2#	3.4754(4)	O8–Co2–O3#	85.49(5)
Co1···Co2#	3.6164(4)	O7–Co2–O3#	93.52(4)
Co2···Co2#	6.8721(6)	O2–Co2–O3#	147.29(4)
Co1···Co1#	10.2728(8)	N2#–Co2–O3#	70.44(4)
O3#–Co1–O4#	89.41(5)	O1–Co2–O3#	68.46(4)
O3#–Co1–N1	149.66(5)	O8–Co2–O2#	92.74(4)
O4#–Co1–N1	120.07(5)	O7–Co2–O2#	88.90(4)
O3#–Co1–O5	93.80(5)	O2–Co2–O2#	70.77(4)
O4#–Co1–O5	84.67(5)	N2#–Co2–O2#	71.24(4)
N1–Co1–O5	95.85(5)	O1–Co2–O2#	149.93(4)
O3#–Co1–O1	73.86(4)	O3#–Co2–O2#	141.50(4)
O4#–Co1–O1	163.10(5)	Co1−O3−Co2	109.90(6)
N1–Co1–O1	76.83(5)	Co1−O1#−Co2	107.76(5)
O5–Co1–O1	93.92(5)	Co2−O2−Co2#	109.23(5)
O3–Co1–O6	92.41(5)		
O4–Co1–O6	88.71(5)		

Symmetry operation #: -x, -y, -z

Table S3. Selected interatomic distances (Å) and angles (º) for $[Co_8(L)_4(bpy)_4(OH)_4(H_2O)_2(NO_3)_2](NO_3)_4 \cdot 2C_7H_8 \cdot 6H_2O$ (**3**)

Co1–O8	2.023(4)	N7#–Co2–O1	92.41(16)
Co1–O7	2.032(4)	O10–Co2–O1	87.91(15)
Co1–N1	2.089(5)	N5–Co2–O1	137.35(15)
Co1–O1	2.099(4)	O2–Co2–O1	79.04(14)
Co1–N9#	2.130(4)	N7#–Co2–O7	88.69(15)
Co1–O9	2.154(4)	O10–Co2–O7	95.33(14)
Co2–N7#	2.114(4)	N5–Co2–O7	70.40(15)
Co2–O10	2.117(4)	O2–Co2–O7	147.38(14)
Co2–N5	2.160(4)	O1–Co2–O7	68.58(14)
Co2–O2	2.177(4)	N7#–Co2–O6	88.62(15)
Co2–O1	2.185(4)	O10–Co2–O6	89.02(15)
Co2–O7	2.219(4)	N5–Co2–O6	71.73(15)
Co2–O6	2.258(4)	O2–Co2–O6	71.15(14)
Co3–N8	2.128(4)	O1–Co2–O6	150.15(13)
Co3–N2	2.183(4)	O7–Co2–O6	141.26(14)
Co3–O6	2.186(4)	N8–Co3–N2	93.77(16)
Co3–O5	2.187(4)	N8–Co3–O6	91.20(15)
Co3–O3	2.225(4)	N2–Co3–O6	142.05(15)
Co3–O2	2.259(4)	N8–Co3–O5	89.55(15)
Co3–O11	2.340(4)	N2–Co3–O5	138.52(16)
Co4–O4	2.012(4)	O6–Co3–O5	79.04(14)
Co4–O3	2.019(4)	N8–Co3–O3	88.29(15)
Co4–N4	2.084(5)	N2–Co3–O3	70.27(15)
Co4–O5	2.102(4)	O6–Co3–O3	147.56(14)
Co4–N10	2.132(4)	O5–Co3–O3	68.52(14)
Co1···Co2	3.4707(14)	N8–Co3–O2	91.08(15)
Co3···Co4	3.4666(14)	N2–Co3–O2	71.32(15)
Co2···Co3	3.6139(13)	O6–Co3–O2	70.98(13)
Co1···Co3	6.847(2)	O5–Co3–O2	150.03(14)
Co2···Co4	6.8475(19)	O3–Co3–O2	141.46(14)
Co1···Co4	10.236(3)	N8–Co3–O11	174.33(15)
Co1···Co4#	11.358(3)	N2–Co3–O11	91.71(14)
Co4–O12	2.201(4)	O6–Co3–O11	83.58(13)
O8–Co1–O7	88.97(16)	O5–Co3–O11	87.29(13)
O8–Co1–N1	119.83(17)	O3–Co3–O11	94.92(14)
O7–Co1–N1	150.25(16)	O2–Co3–O11	89.32(13)
O8–Co1–O1	162.71(16)	O4–Co4–O3	88.68(17)
O7–Co1–O1	73.80(15)	O4–Co4–N4	119.32(19)
N1–Co1–O1	77.11(16)	O3–Co4–N4	150.58(17)
O8–Co1–N9#	90.04(16)	O4–Co4–O5	162.74(17)
O7–Co1–N9#	92.24(16)	O3–Co4–O5	74.10(15)
N1–Co1–N9#	94.84(17)	N4–Co4–O5	77.51(17)
O1–Co1–N9#	91.98(15)	O4–Co4–N10	90.40(17)
O8–Co1–O9	85.07(16)	O3–Co4–N10	93.48(17)
O7–Co1–O9	89.59(16)	N4–Co4–N10	95.02(18)
N1–Co1–O9	85.96(17)	O5–Co4–N10	91.87(16)
O1–Co1–O9	93.27(15)	O4–Co4–O12	88.40(16)

N9#–Co1–O9	174.74(16)	O3–Co4–O12	85.57(16)
N7#–Co2–O10	175.80(16)	N4–Co4–O12	86.38(18)
N7#–Co2–N5	97.87(16)	O5–Co4–O12	89.01(15)
O10–Co2–N5	84.68(15)	Co1−O1−Co2	108.17(18)
N7#–Co2–O2	88.75(15)	Co1−O7−Co2	109.41(18)
O10–Co2–O2	87.20(14)	Co2−O2−Co3	109.09(16)
N5–Co2–O2	142.08(15)	Co2−O6−Co3	108.77(16)
N7#–Co2–O1	92.41(16)	Co3−O3−Co4	109.43(18)
O10–Co2–O1	87.91(15)	Co3−O5−Co4	107.82(18)
N5–Co2–O1	137.35(15)		

Symmetry operation #: -x,-y,-z

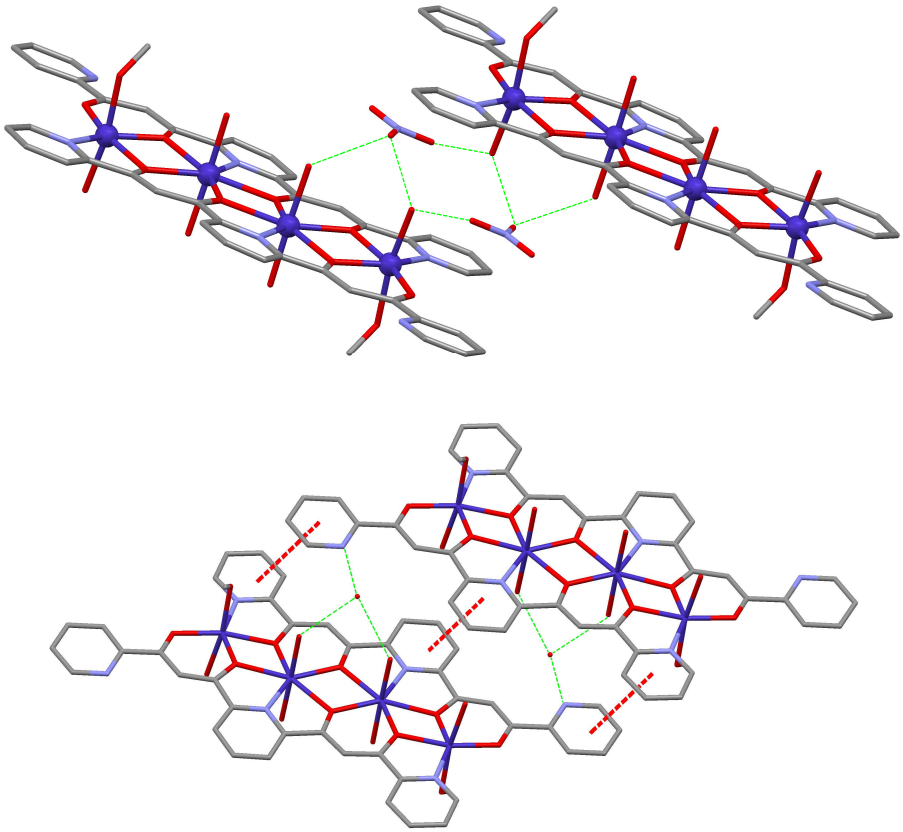

Figure S1. Representation of the most relevant hydrogen bonding interactions (green) and π···π stacking interactions (red) contributing to the crystal packing within the lattice of $[Co_4L_2(H_2O)_6(MeOH)_2](NO_3)_4$ (**2**).

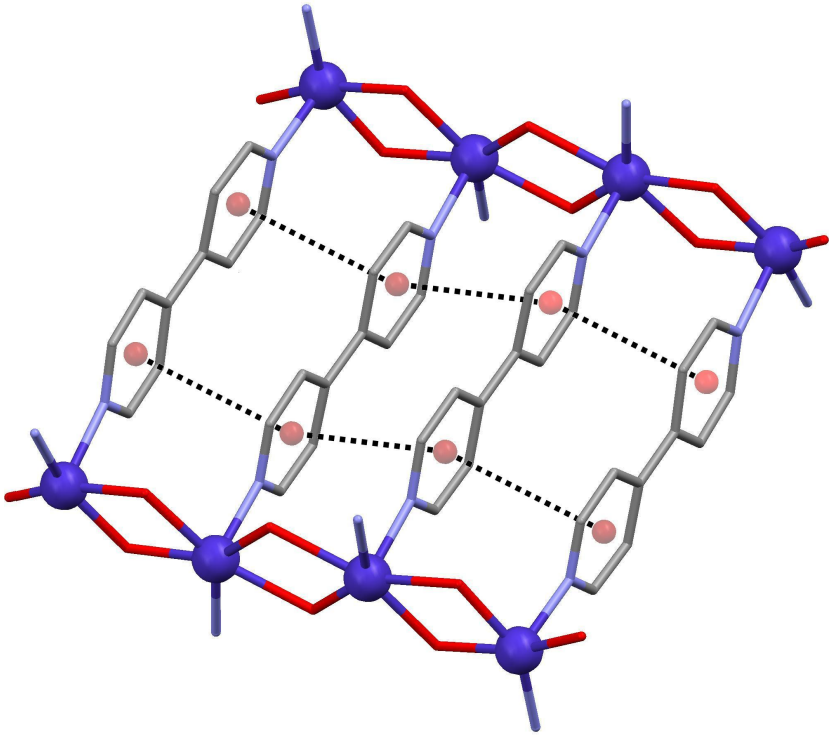

Figure S2. Representation of the core of the complex cation of $[Co_8L_4(OH)_2(H_2O)_4(NO_3)_2(bpy)_4](NO_3)_4$ (**3**), emphasizing the set of intramolecular π···π stacking interactions.

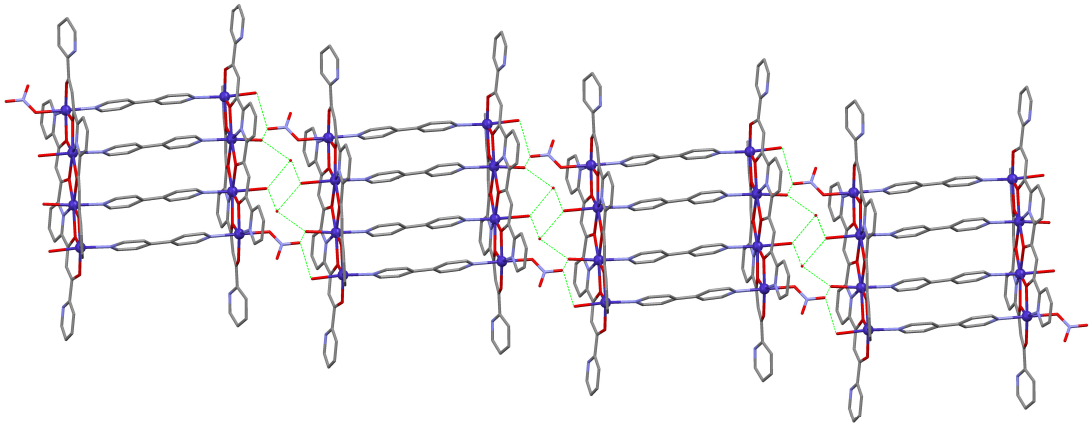

Figure S3. Representation of a chain of complex cations of $[Co_8L_4(OH)_2(H_2O)_4(NO_3)_2(bpy)_4](NO_3)_4$ (**3**), linked in the crystal lattice through a network of hydrogen bonding interactions (green) involving hydroxide, water and nitrate axial ligands.

Table S4. Geometrical parameters describing the hydrogen bonds contributing to the crystal packing in $[Co_4L_2(H_2O)_6(MeOH)_2](NO_3)_4$ (**2**) and depicted in Figure S1.

D–H···A	D–H bond distance (Å)	H···A distance (Å)	D···A distance (Å)	D–H–A angle (º)
O1S–H1S···O13#1	0.8400	1.9900	2.815(2)	169.00
O1S–H1S···O14#1	0.8400	2.6000	3.253(2)	136.00
O1W–H1W···N3#2	0.92(3)	1.89(3)	2.808(2)	175(2)
O2S–H2S···O14	0.8400	1.9600	2.787(2)	170.00
O1W–H2W···O1S	0.83(3)	1.87(3)	2.700(2)	172(2)
O5–H5A···O9#3	0.86(2)	2.60(3)	3.274(2)	137(2)
O5–H5A···O10#3	0.86(2)	1.95(2)	2.797(2)	168(2)
O5–H5B···O9	0.82(2)	1.93(2)	2.697(2)	155(3)
O6–H6···O13#4	0.8400	1.9700	2.791(2)	164.00
O7–H7B···O1W#5	0.77(2)	2.00(2)	2.7610(19)	173(2)
O7–H7C···O9	0.85(3)	2.04(3)	2.824(2)	154(2)
O8–H8A···O1W	0.74(2)	2.02(2)	2.7487(19)	171(3)
O8–H8B···O2S	1.08(2)	1.62(2)	2.681(2)	167(2)

Symmetry operations: #1= -1+x,y,z; #2 = -x,1-y,-z; # = 2-x,-y,-z; #4 = 2-x,-y,1-z; #5 = 1-x,1-y,-z

Table S5 Geometrical parameters describing the hydrogen bonds contributing to the crystal packing in $[Co_8L_4(OH)_2(H_2O)_4(NO_3)_2(bpy)_4](NO_3)_4$ (**3**) and depicted in Figure S3.

D–H···A	D–H bond distance (Å)	H···A distance (Å)	D···A distance (Å)	D–H–A angle (º)
O9−H9B .. O16#1	0.92(4)	2.11(4)	3.010(8)	168(6)
O9−H9B .. O17#1	0.92(4)	2.26(8)	2.807(10)	118(6)
O9−H9C .. O13#2	0.92(4)	2.02(3)	2.828(7)	146(3)
O10−H10B .. O13#2	0.91(5)	1.83(5)	2.723(7)	167(6)
O11−H11B .. O1W#2	0.90(4)	2.00(3)	2.740(10)	138(4)
O11−H11C .. O1W	0.91(4)	2.44(4)	2.991(9)	119(5)

Symmetry operations: #1 = x,y,1+z; #2 = 1-x,1-y,2-z