Methylene-bis[(aminomethyl)phosphinic acids]: synthesis, acid-base and coordination properties

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Content:

Table S1. Overall protonation constants (logβ) of the title ligands.

Constant	$H_2\mathbf{L}^1$	$H_2\mathbf{L}^2$	$H_2\mathbf{L}^3$
$\log b_1$	10.00(1)	9.84(1)	9.49(3)
$\log b_2$	18.89(1)	18.39(1)	18.29(2)
$\log b_3$	20.24(2)	–	20.38(2)

Table S2. Overall stability constants ($\log\beta_{hlm}$) of complexes with the title ligands.

Metal ion	*h l m*	$H_2\mathbf{L}^1$	$H_2\mathbf{L}^2$	$H_2\mathbf{L}^3$
	0 1 1	10.76(2)	11.13(1)	9.87(1)
Cu^{2+}	–1 1 1	2.35(3)	3.06(2)	1.05(2)
	–2 1 1	–8.91(4)	–9.23(3)	–9.48(4)
	0 1 1	6.78(2)	6.51(1)	6.29(1)
Zn^{2+}	–1 1 1	–1.26(2)	–2.26(2)	–2.29(1)
	–2 1 1	–11.98(7)	–13.28(4)	–
	0 1 1	7.87(2)	7.13(1)	7.51(1)
Ni^{2+}	–1 1 1	–1.17(4)	–1.44(2)	–0.90(2)
	–2 1 1	–13.94(8)	–13.94(4)	–
	0 1 1	[a]	7.28(6)	5.79(1)
Co^{2+}	–1 1 1	–0.73(4)	–0.56(4)	[a]
	–2 1 1	–8.91(5)	–8.57(5)	[a]
	–3 1 1	–20.60(7)	–18.60(6)	[a]

[a] not determined due to the formation of precipitate

Figure S1. Distribution diagrams of $H_2\mathbf{L^2}$ (A) and $H_2\mathbf{L^3}$ (B) in absence of metal ions (c_L = 4 mM, I = 0.1 M KNO_3, 25°C).

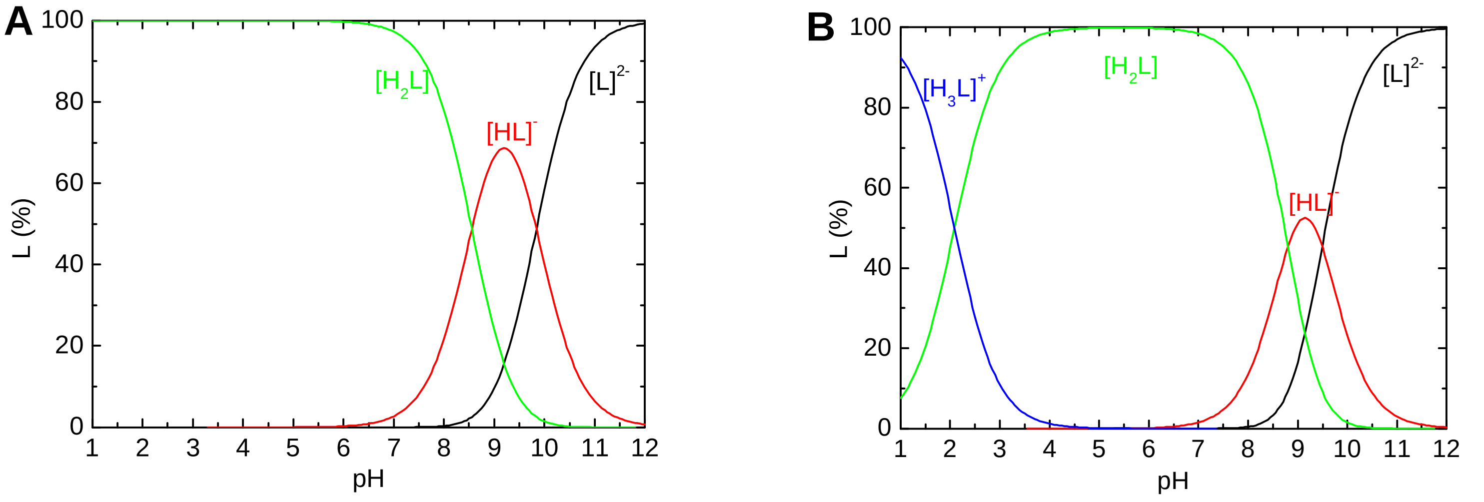

Figure S2. Distribution diagrams of $H_2\mathbf{L}^2$ in the presence of Cu^{2+} (A), Zn^{2+} (B), Ni^{2+} (C) and Co^{2+}(D) ions ($c_L = c_M$ = 4 mM, I = 0.1 M KNO_3, 25°C).

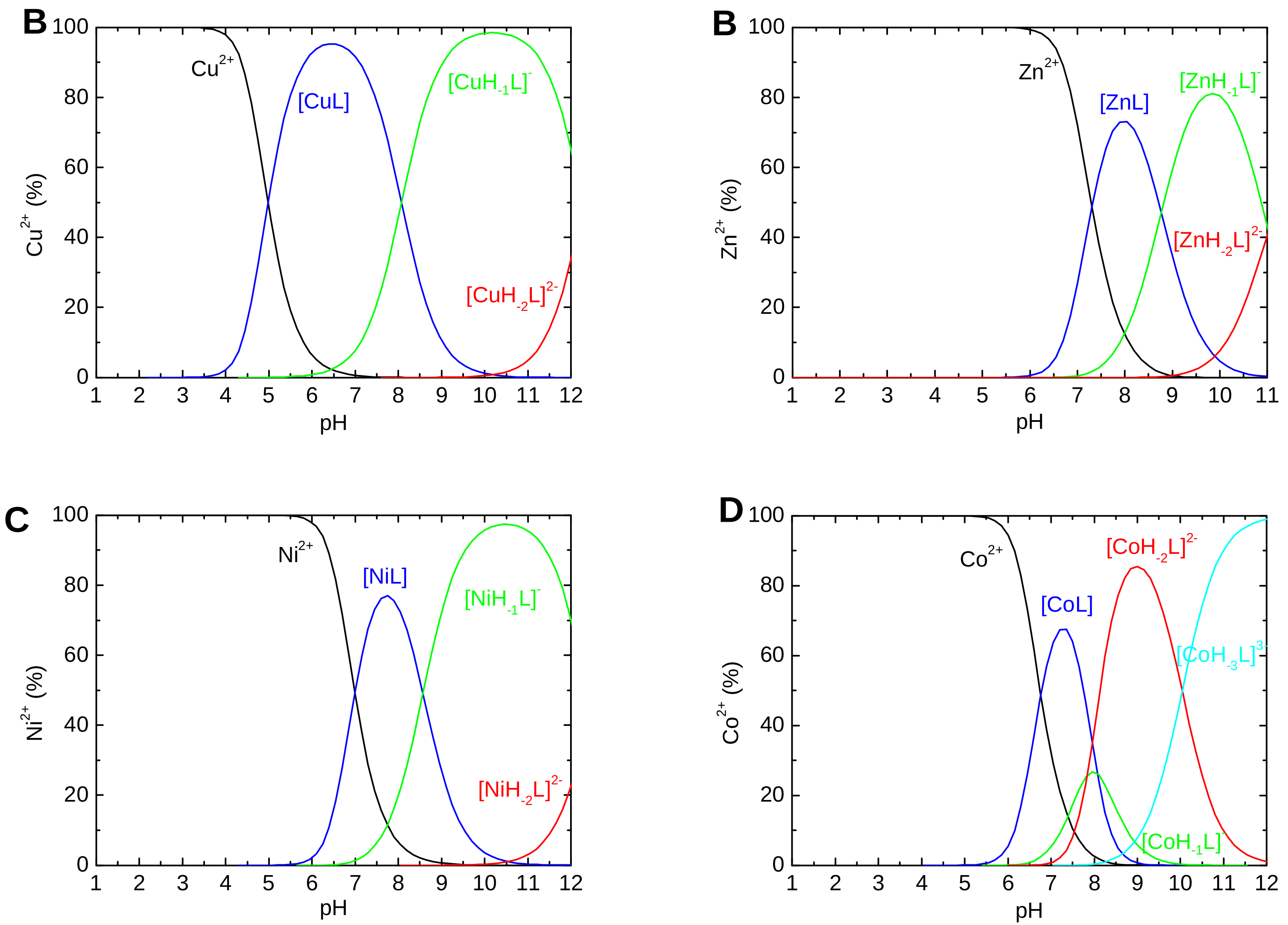

Figure S3. Distribution diagrams of $H_2\mathbf{L^3}$ in the presence of Cu^{2+} (A), Zn^{2+} (B), Ni^{2+} (C) and Co^{2+}(D) ions ($c_L = c_M$ = 4 mM, I = 0.1 M KNO_3, 25°C).

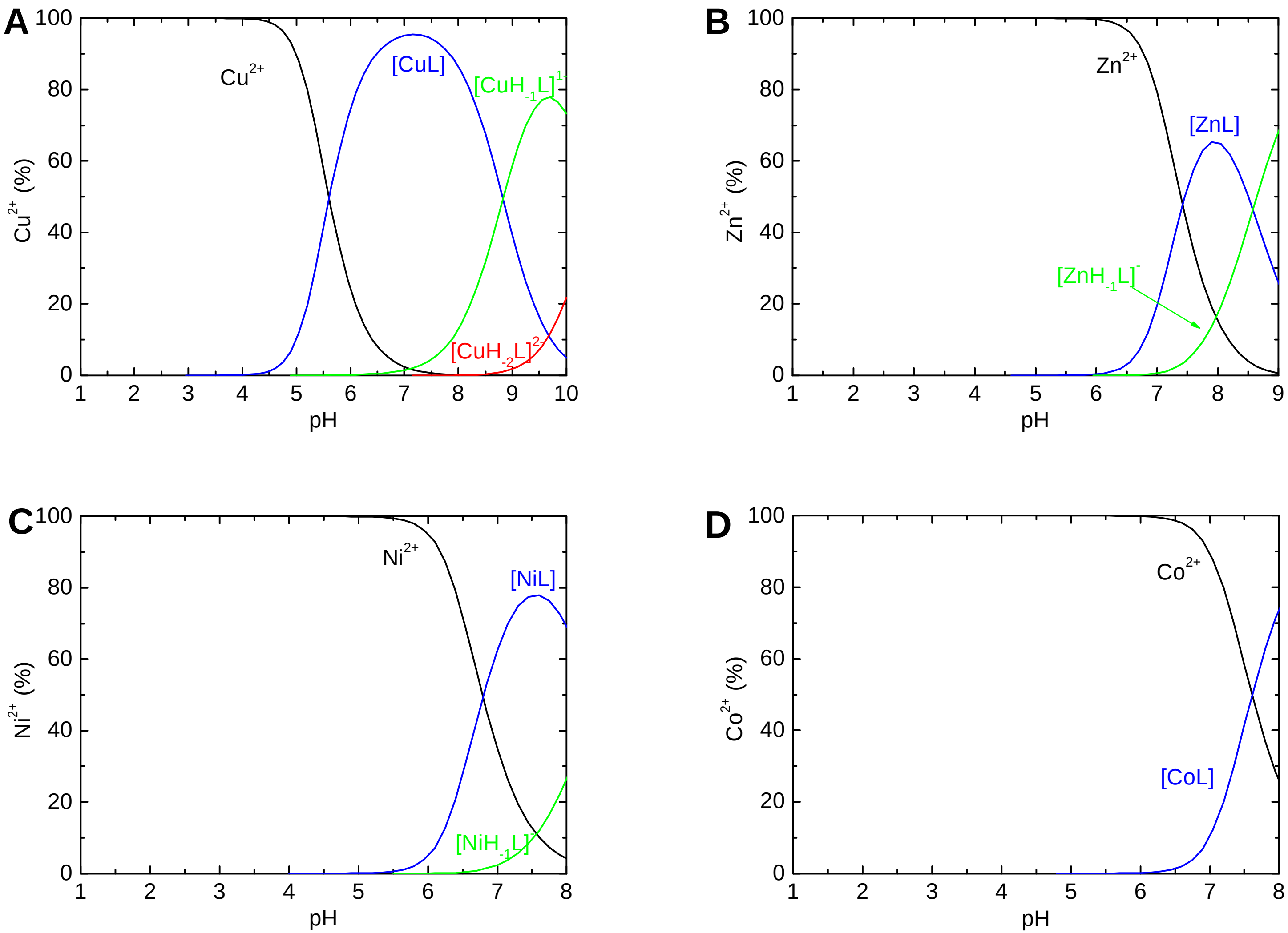

Figure S4. High resolution MS spectra of [Cu**L**[1]] (A) and [Cu**L**[2]] (B) complexes (M:L = 1:1, pH 10).

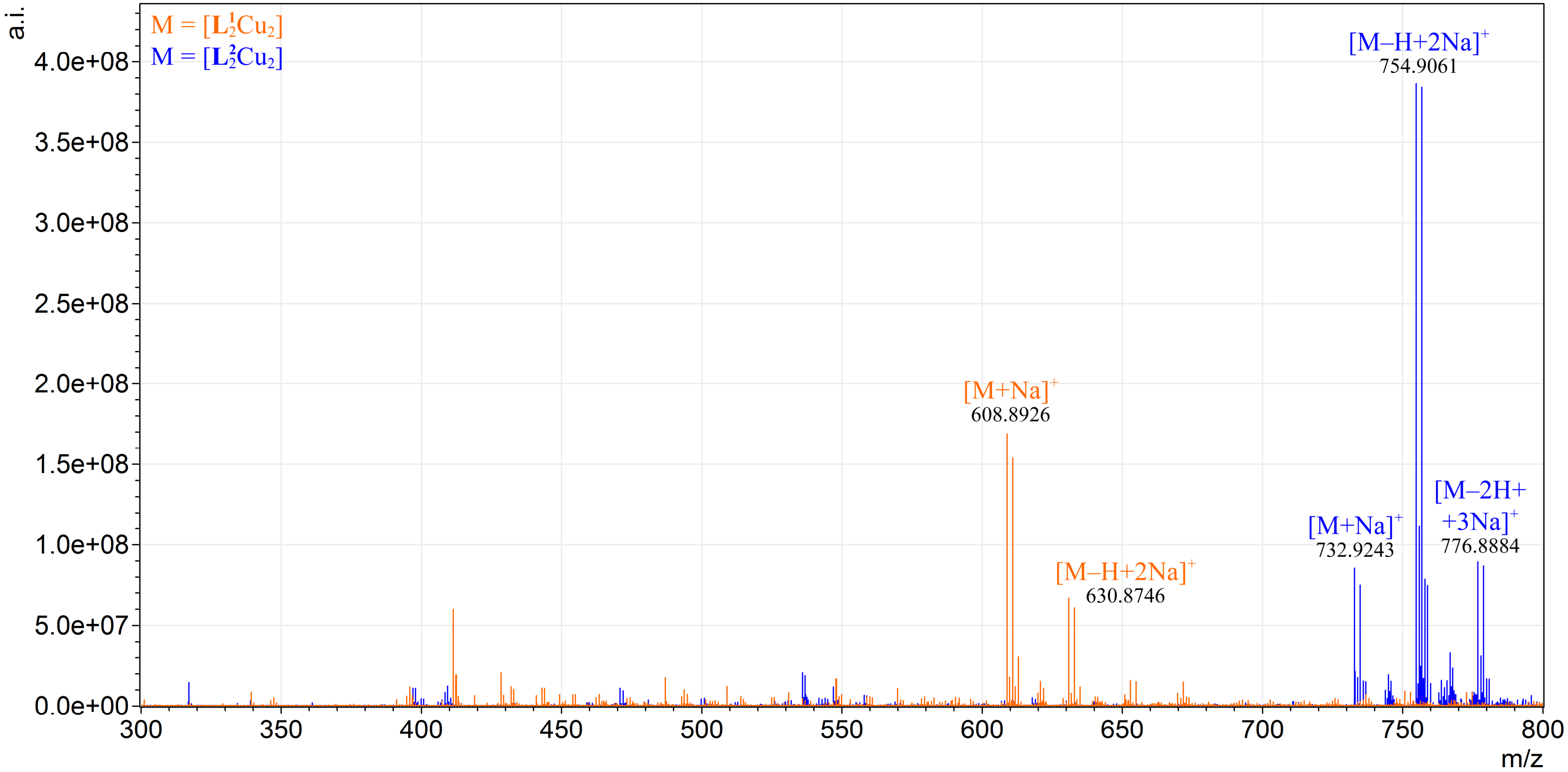

Table S3. Geometry of the bis(phosphinate) moiety.

	Distances P–C [Å]	Distances P–O [Å]	Distances C–O [Å]	Angles P–C–P (°)
H_2**L**^{1}·0.5H_2O	1.846(2) 1.854(2)	1.5049(11) 1.5121(11) 1.5024(11) 1.5106(11)	1.436(2)	114.39(8)
H_2**L**^{3}·H_2O	1.8123(9)	1.5055(9) 1.5100(9)	–	119.44(9)
$Li_2[Co_4(H_{-1}$**L**$^1)_3(OH)]$·17.5H_2O	1.849(3) 1.855(3) 1.846(3) 1.854(3) 1.847(3) 1.851(3)	1.503(2) 1.528(2) 1.509(2) 1.526(2) 1.509(2) 1.520(2) 1.513(2) 1.521(2) 1.502(2) 1.526(2) 1.493(2) 1.531(2)	1.442(4) 1.440(3) 1.449(3)	107.2(2) 107.2(1) 108.6(2)
$(CN_3H_6)_4[Cu_2(H_{-1}$**L**$^2)_2]CO_3$·10H_2O	1.859(2) 1.866(2) 1.868(2) 1.872(2)	1.496(2) 1.511(2) 1.508(2) 1.511(2) 1.495(2) 1.504(2) 1.503(2) 1.509(2)	1.430(3) 1.430(3)	109.57(11) 109.32(11)

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Table S4. Geometry of the coordination sphere of Cu^{2+} ions in $(H_2N{=}C(NH_2)_2)_4[Cu_2(H_{-1}\mathbf{L}^2)_2]CO_3{\cdot}10H_2O$.

Distances (Å)		Angles (°)		Angles (°)	
		Unit 1			
Cu1 – N1A	2.001(2)	N1A – Cu1 – O41A	90.02(7)	N1B – Cu2 – O41B	89.05(7)
Cu1 – O41A	1.988(2)	N1A – Cu1 – O41B	164.70(7)	N1B – Cu2 – O41A	163.77(7)
Cu1 – O41B	1.928(2)	N1A – Cu1 – N7B	93.02(8)	N1B – Cu2 – N7A	92.23(8)
Cu1 – N7B	1.998(2)	N1A – Cu1 – O31A	85.38(7)	N1B – Cu2 – O31B	85.83(7)
Cu1 – O31A	2.639(2)	N1A – Cu1 – O51B	104.57(6)	N1B – Cu2 – O51A	101.96(7)
Cu1 – O51B	3.090(2)	O41A – Cu1 – O41B	78.37(6)	O41B – Cu2 – O41A	78.49(6)
		O41A – Cu1 – N7B	174.52(7)	O41B – Cu2 – N7A	175.49(8)
Cu2 – N1B	1.987(2)	O41A – Cu1 – O31A	73.92(6)	O41B – Cu2 – O31B	72.57(6)
Cu2 – O41B	1.984(2)	O41A – Cu1 – O51B	114.64(5)	O41B – Cu2 – O51A	114.39(6)
Cu2 – O41A	1.927(2)	O41B – Cu1 – N7B	99.38(7)	O41A – Cu2 – N7A	101.00(7)
Cu2 – N7A	2.004(2)	O41B – Cu1 – O31A	100.68(6)	O41A – Cu2 – O31B	100.07(6)
Cu2 – O31B	2.717(2)	O41B – Cu1 – O51B	72.08(6)	O41A – Cu2 – O51A	74.41(6)
Cu2 – O51A	2.908(2)	N7B – Cu1 – O31A	101.78(7)	N7A – Cu2 – O31B	103.20(7)
		N7B – Cu1 – O51B	68.95(6)	N7A – Cu2 – O51A	69.56(6)
		O31A – Cu1 – O51B	166.41(5)	O31B – Cu2 – O51A	169.35(5)
		Unit 2			
Cu3 – N1C	2.031(2)	N1C – Cu3 – O41C	94.04(7)	N1D – Cu4 – O41D	95.30(8)
Cu3 – O41C	1.959(1)	N1C – Cu3 – O41D	167.67(7)	N1D – Cu4 – O41C	168.18(9)
Cu3 – O41D	1.976(2)	N1C – Cu3 – N7D	96.32(8)	N1D – Cu4 – N7C	98.75(9)
Cu3 – N7D	2.026(2)	N1C – Cu3 – O31C	79.69(7)	N1D – Cu4 – O31D	79.20(7)
Cu3 – O31C	2.534(2)	N1C – Cu3 – O51D	93.17(7)	N1D – Cu4 – O51C	91.49(7)
Cu3 – O51D	2.503(2)	O41C – Cu3 – O41D	78.72(6)	O41D – Cu4 – O41C	78.58(6)
		O41C – Cu3 – N7D	167.96(7)	O41D – Cu4 – N7C	163.04(7)
Cu4 – N1D	2.024(2)	O41C – Cu3 – O31C	79.60(6)	O41D – Cu4 – O31D	81.02(6)
Cu4 – O41D	1.962(1)	O41C – Cu3 – O51D	101.60(6)	O41D – Cu4 – O51C	104.19(6)
Cu4 – O41C	1.979(2)	O41D – Cu3 – N7D	92.08(7)	O41C – Cu4 – N7C	89.13(7)
Cu4 – N7C	2.025(2)	O41D – Cu3 – O31C	108.41(6)	O41C – Cu4 – O31D	109.44(6)
Cu4 – O31D	2.529(2)	O41D – Cu3 – O51D	78.72(6)	O41C – Cu4 – O51C	80.38(6)
Cu4 – O51C	2.434(2)	N7D – Cu3 – O31C	96.23(7)	N7C – Cu4 – O31D	92.29(7)
		N7D – Cu3 – O51D	83.96(7)	N7C – Cu4 – O51C	84.96(7)
		O31C – Cu3 – O51D	172.84(5)	O31D – Cu4 – O51C	169.81(5)

Table S5. Geometry of the coordination sphere of Co^{2+} ions in $Li_2[Co_4(H_{-1}\mathbf{L^1})_3(OH)]\cdot 17.5H_2O$.

Distances (Å)		Angles (°)		Angles (°)	
Co1 – O1	2.090(2)	O41A – Co1 – O1	82.56(8)	O1 – Co3 – O41C	83.95(8)
Co1 – O41A	2.101(2)	N1A – Co1 – O1	96.99(10)	O31B – Co3 – O41C	167.91(8)
Co1 – N1A	2.109(3)	O31C – Co1 – O1	92.40(9)	N1C – Co3 – O41C	100.73(9)
Co1 – O31C	2.121(2)	O51C – Co1 – O1	164.57(8)	O51B – Co3 – O41C	92.60(8)
Co1 – O51C	2.141(2)	O41C – Co1 – O1	81.79(8)	O41B – Co3 – O41C	83.62(7)
Co1 – O41C	2.145(2)	N1A – Co1 – O41A	100.01(9)	O31B – Co3 – O1	91.60(8)
		O31C – Co1 – O41A	168.56(8)	N1C – Co3 – O1	94.79(10)
Co2 – O1	2.063(2)	O51C – Co1 – O41A	94.25(8)	O51B – Co3 – O1	164.54(8)
Co2 – O41B	2.091(2)	O41C – Co1 – O41A	83.88(8)	O41B – Co3 – O1	81.90(8)
Co2 – O51A	2.120(2)	O31C – Co1 – N1A	90.77(9)	N1C – Co3 – O31B	90.82(9)
Co2 – N1B	2.124(3)	O51C – Co1 – N1A	98.44(10)	O51B – Co3 – O31B	88.71(8)
Co2 – O31A	2.131(2)	O41C – Co1 – N1A	175.77(9)	O41B – Co3 – O31B	84.63(8)
Co2 – O41A	2.162(2)	O51C – Co1 – O31C	87.88(9)	O51B – Co3 – N1C	100.65(10)
		O41C – Co1 – O31C	85.24(8)	O41B – Co3 – N1C	174.28(9)
Co3 – O41C	2.071(2)	O41C – Co1 – O41C	82.85(8)	O41B – Co3 – O51B	82.75(8)
Co3 – O1	2.075(2)				
Co3 – O31B	2.084(2)	O41B – Co2 – O1	84.70(8)	O41B – Co4 – N7B	94.95(9)
Co3 N1C	2.111(3)	O51A – Co2 – O1	165.12(8)	N7C – Co4 – N7B	89.35(10)
Co3 – O51B	2.138(2)	N1B – Co2 – O1	97.05(9)	N7A – Co4 – N7B	90.99(10)
Co3 – O41B	2.192(2)	O31A – Co2 – O1	89.41(8)	O41A – Co4 – N7B	174.15(9)
		O41A – Co2 – O1	81.75(8)	O41C – Co4 – N7B	92.96(9)
Co4 – N7B	2.128(3)	O51A – Co2 – O41B	96.48(8)	N7C – Co4 – O41B	174.28(9)
Co4 – O41B	2.1470(2)	N1B – Co2 – O41B	98.64(9)	N7A – Co4 – O41B	91.91(9)
Co4 – N7C	2.148(3)	O31A – Co2 – O41B	167.09(8)	O41A – Co4 – O41B	83.05(8)
Co4 – N7A	2.154(3)	O41A – Co2 – O41B	84.22(8)	O41C – Co4 – O41B	81.68(7)
Co4 – O41A	2.155(2)	N1B – Co2 – O51A	97.43(9)	N7A – Co4 – N7C	91.78(10)
Co4 – O41C	2.201(2)	O31A – Co2 – O51A	86.31(8)	O41A – Co4 – N7C	92.30(9)
		O41A – Co2 – O51A	83.61(8)	O41C – Co4 – N7C	94.36(9)
		O31A – Co2 – N1B	93.47(9)	O41A – Co4 – N7A	94.57(8)
		O41A – Co2 – N1B	176.80(9)	O41C – Co4 – N7A	172.73(8)
		O41A – Co2 – O31A	83.56(8)	O41C – Co4 – O41A	81.32(7)

Table S6. Geometry of the Co_4O_4 cage in $Li_2[Co_4(H_{-1}\mathbf{L^1})_3(OH)]\cdot 17.5H_2O$.

Distances (Å)				Angles (°)						Angles (°)					
Co1	–	Co2	3.1629(5)	O1	–	Co1	–	O41A	82.56(8)	Co1	–	O1	–	Co2	99.22(9)
Co1	–	Co3	3.1261(6)	O1	–	Co1	–	O41C	81.79(8)	Co1	–	O41A	–	Co2	95.78(8)
Co1	–	Co4	3.2207(5)	O41A	–	Co1	–	O41C	83.88(8)	Co1	–	O1	–	Co3	97.27(8)
Co2	–	Co3	3.1335(6)	O1	–	Co2	–	O41A	81.75(8)	Co1	–	O41C	–	Co3	95.69(8)
Co2	–	Co4	3.1761(5)	O1	–	Co2	–	O41B	84.70(8)	Co1	–	O41A	–	Co4	98.33(8)
Co3	–	Co4	3.2272(6)	O41A	–	Co2	–	O41B	84.22(8)	Co1	–	O41C	–	Co4	95.64(8)
				O1	–	Co3	–	O41B	81.90(8)	Co2	–	O1	–	Co3	98.46(9)
				O1	–	Co3	–	O41C	83.95(8)	Co2	–	O41B	–	Co3	94.01(8)
				O41B	–	Co3	–	O41C	83.62(7)	Co2	–	O41A	–	Co4	94.74(8)
				O41A	–	Co4	–	O41B	83.05(8)	Co2	–	O41B	–	Co4	97.08(8)
				O41B	–	Co4	–	O41C	81.68(7)	Co3	–	O41B	–	Co4	96.09(8)
				O41C	–	Co4	–	O41A	81.32(7)	Co3	–	O41C	–	Co4	98.08(8)