Supporting Information

Calcium and heterometallic manganese-calcium complexes supported by tripodal pyridine-carboxylate ligands: structural, EPR and theoretical investigations

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Table S1. Crystallographic data for complexes [Ca(Htpaa)(OH_2)]·4.5H_2O (**Ca$_1$**·4.5H_2O and [Ca(tpada)(OH_2)$_2$]$_2$·5.2H_2O (**Ca$_2$**·5.2H_2O).

	Ca$_1$·4.5H_2O	**Ca$_2$**·5.2H_2O
Empirical formula	$C_{21}H_{27}CaN_4O_{11.5}$	$C_{40}H_{50.4}Ca_2N_8O_{17.2}$
Formula weight	559.55	998.65
Colour, shape	Colourless, triclinic prism	Colourless, block
Crystal size, mm	0.45x0.32x0.17	0.48x0.17x0.11
Crystal system	Triclinic	Monoclinic
Space group	*P -1*	***P 2$_1$/n***
a, Å	9.4387(6)	10.1802(5)
b, Å	9.6164(7)	23.6482(6)
c, Å	15.1005(7)	10.2620(4)
α, deg.	98.239(5)	90.00
β, deg.	102.715(5)	113.840(5)
γ, deg.	109.697(6)	90.00
V, Å^3	1222.96(14)	2259.69(15)
Z	2	2
T, K	150(2)	150(2)
ρ (calc), Mg/m^3	1.520	1.468
μ, mm^{-1}	0.327	0.335
θ range, deg.	3.72 to 28.28	3.37 to 28.28
No.of rflcn/obsv	11522/6070	11187/5512
GooF	1.095	1.015
*R*1	0.0694	0.0466
*wR*2	0.1720	0.0817

Table S2**.** Selected bond lengths (Å) and angles (deg) for complex [Ca(Htpaa)(OH_2)]·4.5H_2O (**Ca$_1$**·4.5H_2O).

Ca(1)-O(31)	2.401(2)	Ca(1)-N(11)	2.503(3)
Ca(1)-O(11)	2.404(2)	Ca(1)-N(2)	2.547(3)
Ca(1)-O(1)	2.454(2)	Ca(1)-N(21)	2.581(2)
Ca(1)-O(21)	2.461(2)	Ca(1)-N(1)	2.741(2)
C(7)-O(1)	1.244(4)	C(17)-O(12)	1.233(4)
C(7)-O(2)	1.263(4)	C(27)-O(21)	1.214(4)
C(17)-O(11)	1.266(4)	C(27)-O(22)	1.304(4)
O(11)-Ca(1)-O(31)	88.83(9)	N(2)-Ca(1)-N(11)	115.04(8)
O(1)-Ca(1)-O(31)	77.24(8)	N(21)-Ca(1)-O(31)	155.84(9)
O(1)-Ca(1)-O(11)	106.57(8)	N(21)-Ca(1)-O(11)	99.62(8)
O(21)-Ca(1)-O(31)	140.16(8)	N(21)-Ca(1)-O(1)	120.91(8)
O(21)-Ca(1)-O(11)	78.66(8)	N(21)-Ca(1)-O(21)	63.99(8)
O(21)-Ca(1)-O(1)	70.62(7)	N(21)-Ca(1)-N(11)	91.70(8)
N(11)-Ca(1)-O(31)	71.18(8)	N(21)-Ca(1)-N(2)	94.92(8)
N(11)-Ca(1)-O(11)	65.43(8)	N(1)-Ca(1)-O(31)	94.09(8)
N(11)-Ca(1)-O(1)	147.36(8)	N(1)-Ca(1)-O(11)	123.77(8)
N(11)-Ca(1)-O(21)	132.590(8)	N(1)-Ca(1)-O(1)	128.84(8)
N(2)-Ca(1)-O(31)	78.05(9)	N(1)-Ca(1)-O(21)	124.34(7)
N(2)-Ca(1)-O(11)	165.44(8)	N(1)-Ca(1)-N(11)	62.77(8)
N(2)-Ca(1)-O(1)	64.66(7)	N(1)-Ca(1)-N(2)	64.22(8)
N(2)-Ca(1)-O(21)	107.47(8)	N(1)-Ca(1)-N(21)	62.38(8)

Table S3**.** Hydrogen bonds lengths (Å) and angles (deg) for **Ca$_1$**·4.5H_2O.

D-H…A	d(D-H)	d(H…A)	d(D…A)	< (DHA)
O(34)-H(1O4)…O(1)	0.82(5)	2.10(5)	2.923(3)	173(5)
O(34)-H(2O4)…O(21)	0.87(5)	2.54(5)	3.204(4)	133(4)
O(34)-H(2O4)…O(1)	0.87(5)	2.38(5)	3.193(4)	155(4)
O(33)-H(2O3)…O(11)	0.82(6)	1.99(6)	2.803(4)	173(5)
O(33)-H(1O3)…O(34)	0.85(6)	2.27(6)	3.095(5)	162(5)
O(32)-H(2O2)…O(33)	0.90(5)	1.97(5)	2.866(4)	172(5)
O(31)-H(2O1)…O(32)	0.86(5)	1.88(5)	2.706(4)	161(4)
O(31)-H(1O1)…O(2)	0.82(5)	1.97(5)	2.777(3)	166(4)
O(22)-H(22O)…O(2)	0.97(4)	1.61(4)	2.535(3)	158(3)

Table S4**.** Selected bond lengths (Å) and angles (deg) for complex $[Ca(tpada)(OH_2)_2]_2 \cdot 5.2H_2O$ (**Ca₂**·$5.2H_2O$).

Ca(1)-O(12)	2.4196(16)	Ca(1)-O(1)#	2.4954(13)
Ca(1)-O(3)	2.4253(14)	Ca(1)-N(2)	2.5355(16)
Ca(1)-O(11)	2.4273(15)	Ca(1)-N(3)	2.5543(16)
Ca(1)-O(1)	2.4664(13)	Ca(1)-N(1)	2.7616(16)
C(7)-O(1)	1.261(2)	C(14)-O(3)	1.261(2)
C(7)-O(2)	1.246 (2)	C(14)-O(4)	1.251 (2)
O(3)-Ca(1)-O(12)	109.13(5)	N(2)-Ca(1)-O(1)#	137.21(5)
O(11)-Ca(1)-O(12)	83.11(6)	N(3)-Ca(1)-O(12)	76.91(5)
O(11)-Ca(1)-O(3)	150.67(5)	N(3)-Ca(1)-O(3)	64.08(5)
O(1)-Ca(1)-O(12)	148.91(5)	N(3)-Ca(1)-O(11)	145.10(5)
O(1)-Ca(1)-O(3)	77.32(4)	N(3)-Ca(1)-O(1)	130.07(5)
O(1)-Ca(1)-O(11)	79.13(5)	N(3)-Ca(1)-O(1)#	124.40(5)
O(1)#-Ca(1)-O(12)	79.15(5)	N(3)-Ca(1)-N(2)	90.01(5)
O(1)#-Ca(1)-O(3)	78.08(4)	N(1)-Ca(1)-O(12)	75.45(5)
O(1)#-Ca(1)-O(11)	78.32(5)	N(1)-Ca(1)-O(3)	122.81(5)
O(1)#-Ca(1)-O(1)	72.42(5)	N(1)-Ca(1)-O(11)	85.64(5)
N(2)-Ca(1)-O(12)	138.59(6)	N(1)-Ca(1)-O(1)	127.77(5)
N(2)-Ca(1)-O(3)	99.44(5)	N(1)-Ca(1)-O(1)#	151.34(5)
N(2)-Ca(1)-O(11)	86.34(5)	N(1)-Ca(1)-N(2)	63.87(5)
N(2)-Ca(1)-O(1)	65.52(5)	N(1)-Ca(1)-N(3)	61.89(5)

= -x+1, -y+1, -z+2

Table S5**.** Hydrogen bonds lengths (Å) and angles (deg) for **Ca₂**·$5.2H_2O$.

D-H…A	d(D-H)	d(H…A)	d(D…A)	< (DHA)
O(11)-H(1O1)...O(3) #1	0.84(3)	1.94(3)	2.775(2)	172(3)
O(11)-H(2O1)...O(15B)	0.87(3)	1.96(3)	2.812(5)	165(3)
O(11)-H(2O1)...O(15)	0.87(3)	2.00(3)	2.853(5)	166(3)
O(12)-H(1O2)...O(13)	0.84(3)	2.05(3)	2.885(2)	176(3)
O(12)-H(2O2)...O(2) #1	0.90(3)	1.73(3)	2.625(2)	170(3)
O(12)-H(2O2)...O(1) #1	0.90(3)	2.65(3)	3.132(2)	114(2)
O(13)-H(1O3)...N(4)	0.89(3)	1.96(3)	2.845(2)	178(3)
O(13)-H(2O3)...O(4) #2	0.85(3)	1.97(3)	2.819(2)	172(3)
O(15)-H(2O5)...O(2) #1	0.82(7)	2.45(7)	3.219(17)	156(6)
O(15B)-H(3O5)...O(15B) #3	0.71(6)	1.61(5)	2.25(3)	149(7)
O(14)-H(1O4)...O(2) #4	0.848(19)	1.94(2)	2.774(3)	169(4)
O(14)-H(2O4)...O(13)	0.844(19)	2.21(2)	3.030(3)	165(4)

#1 : -x+1, -y+1, -z+2 ; #2 : x, y, z-1 ; #3 : -x+1, -y+1, -z+1 ; #4 : -x+1/2, y-1/2, -z+3/2

Table S6**.** Crystallographic data for complexes [{Mn(tpaa)}$_2${Ca(OH$_2$)$_5$(μ-OH$_2$)}$_2$][Mn(tpaa)]$_2$·25H$_2$O (**Mn$_2$Ca$_2$·2Mn**·25H$_2$O) and [Mn(tpada)ClCa(OH$_2$)$_{2.67}$(MeOH)$_{2.33}$]Cl·1.67CH$_3$OH·0.84H$_2$O (**MnCa**·1.67MeOH·0.84H$_2$O).

	Mn$_2$Ca$_2$·2Mn·25H$_2$O	**MnCa**·1.67MeOH·0.84H$_2$O
Empirical formula	$C_{42}H_{67}CaMn_2N_8O_{30.50}$	$C_{24}H_{39}CaCl_2MnN_4O_{11.5}$
Formula weight	1321.99	733.51
Colour, shape	Colourless, block	Light yellow, plate
Crystal size, mm	0.59x0.38x0.23	0.32x0.15x0.05
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 2_1
a, Å	13.6565(4)	8.7202(2)
b, Å	15.3462(5)	14.6163(3)
c, Å	15.7441(5)	13.0992(3)
α, deg.	70.109(3)	90.00
β, deg.	70.736(3)	93.324(2)
γ, deg.	72.793(3)	90.00
V, Å^3	2865.69(18)	1666.79(6)
Z	2	2
T, K	150(2)	150(2)
ρ (calc), Mg/m^3	1.532	1.462
μ, mm^{-1}	0.628	0.770
θ range, deg.	3.43 to 28.28	3.41 to 30.51
No.of rflcn/obsv	22657/14155	18389/10046
GooF	1.030	1.037
R1	0.0607	0.0511
wR2	0.1449	0.0775

Table S7**.** Selected bond lengths (Å) and angles (deg) for the cationic unit $[\{Mn(tpaa)\}_2\{Ca(OH_2)_5(\mu\text{-}OH_2)\}_2]^{2+}$ (**Mn_2Ca_2**) of **Mn_2Ca_2·2Mn**·25H_2O.

Mn(2)-O(31)	2.257(2)	Ca(1)-O(61)	2.472(3)
Mn(2)-O(33)	2.226(2)	Ca(1)-O(62)	2.470(3)
Mn(2)-O(35)	2.230(2)	Ca(1)-O(63)	2.476(3)
Mn(2)-N(32)	2.297(3)	Ca(1)-O(64)	2.427(2)
Mn(2)-N(33)	2.307(3)	Ca(1)-O(65)	2.487(3)
Mn(2)-N(34)	2.323(3)	Ca(1)-O(66)	2.482(2)
Ca(1)-O(32)	2.428(3)	Ca(1)-O(66)#	2.530(2)
C(37)-O(31)	1.270(4)	C(44)-O(34)	1.246(4)
C(37)-O(32)	1.239(4)	C(51)-O(35)	1.248(5)
C(44)-O(33)	1.264(4)	C(51)-O(36)	1.253(4)
O(35)-Mn(2)-O(33)	81.83(10)	O(63)-Ca(1)-O(64)	143.72(9)
O(31)-Mn(2)-O(33)	81.28(9)	O(63)-Ca(1)-O(32)	79.24(10)
O(31)-Mn(2)-O(35)	78.60(9)	O(63)-Ca(1)-O(62)	109.05(10)
N(32)-Mn(2)-O(33)	106.49(10)	O(63)-Ca(1)-O(61)	71.14(9)
N(32)-Mn(2)-O(35)	146.47(10)	O(65)-Ca(1)-O(64)	140.72(9)
N(32)-Mn(2)-O(31)	70.96(9)	O(65)-Ca(1)-O(32)	142.94(9)
N(33)-Mn(2)-O(33)	70.79(10)	O(65)-Ca(1)-O(62)	73.27(9)
N(33)-Mn(2)-O(35)	106.38(10)	O(65)-Ca(1)-O(61)	117.90(10)
N(33)-Mn(2)-O(31)	150.31(9)	O(65)-Ca(1)-O(63)	73.83(9)
N(33)-Mn(2)-N(32)	107.02(10)	O(66)-Ca(1)-O(64)	74.59(8)
N(34)-Mn(2)-O(33)	150.28(10)	O(66)-Ca(1)-O(32)	118.90(9)
N(34)-Mn(2)-O(35)	71.33(10)	O(66)-Ca(1)-O(62)	78.32(9)
N(34)-Mn(2)-O(31)	104.95(9)	O(66)-Ca(1)-O(61)	144.05(9)
N(34)-Mn(2)-N(32)	102.96(10)	O(66)-Ca(1)-O(63)	140.77(9)
N(34)-Mn(2)-N(33)	104.31(10)	O(66)-Ca(1)-O(65)	72.32(9)
		O(66)#-Ca(1)-O(64)	114.75(9)
O(32)-Ca(1)-O(64)	73.03(9)	O(66)#-Ca(1)-O(32)	75.92(8)
O(62)-Ca(1)-O(64)	79.87(9)	O(66)#-Ca(1)-O(62)	141.87(9)
O(62)-Ca(1)-O(32)	141.25(9)	O(66)#-Ca(1)-O(61)	141.93(9)
O(61)-Ca(1)-O(64)	79.39(9)	O(66)#-Ca(1)-O(63)	79.56(9)
O(61)-Ca(1)-O(32)	75.18(9)	O(66)#-Ca(1)-O(65)	74.55(9)
O(61)-Ca(1)-O(62)	72.98(6)	O(66)#-Ca(1)-O(66)	72.83(9)

: -x,-y,-z+1

Table S8**.** Selected bond lengths (Å) and angles (deg) for the anionic unit [Mn(tpaa)]$^-$ (**Mn**) of **Mn_2Ca_2·2Mn**·25H_2O.

Mn(1)-O(1)	2.233(2)	Mn(1)-N(2)	2.251(3)
Mn(1)-O(3)	2.260(2)	Mn(1)-N(3)	2.262(3)
Mn(1)-O(5)	2.251(2)	Mn(1)-N(4)	2.287(3)
C(7)-O(1)	1.264(4)	C(14)-O(4)	1.255(4)
C(7)-O(2)	1.246(4)	C(21)-O(5)	1.250(4)
C(14)-O(3)	1.254(4)	C(21)-O(6)	1.249(4)
O(5)-Mn(1)-O(1)	83.15(9)	N(3)-Mn(1)-N(2)	107.00(10)
N(2)-Mn(1)-O(1)	72.32(9)	N(3)-Mn(1)-O(3)	71.54(9)
N(2)-Mn(1)-O(5)	101.27(9)	N(4)-Mn(1)-O(1)	153.22(10)
O(3)-Mn(1)-O(1)	82.41(8)	N(4)-Mn(1)-O(5)	70.98(9)
O(3)-Mn(1)-O(5)	81.86(9)	N(4)-Mn(1)-N(2)	105.45(10)
O(3)-Mn(1)-N(2)	153.85(9)	N(4)-Mn(1)-O(3)	100.13(9)
N(3)-Mn(1)-O(1)	102.57(9)	N(4)-Mn(1)-N(3)	103.49(10)
N(3)-Mn(1)-O(5)	151.58(10)		

Table S9**.** Hydrogen bonds lengths (Å) and angles (deg) for complex [{Mn(tpaa)}$_2${Ca(OH$_2$)$_5$(μ-OH$_2$)}$_2$][Mn(tpaa)]$_2$·25H$_2$O (**Mn$_2$Ca$_2$·2Mn**·25H$_2$O).

D-H…A	d(D-H)	d(H…A)	d(D…A)	< (DHA)
O(61)-H(61A)...O(82) #2	0.88	2.06	2.937(6)	175
O(62)-H(62A)...O(82) #2	0.87	2.12	2.941(6)	156.8
O(62)-H(62B)...O(76)	0.87	2.25	3.094(5)	165.1
O(63)-H(63A)...O(79) #2	0.88	2.01	2.829(4)	154.2
O(64)-H(64A)…O(76)	0.89	1.99	2.860(5)	165.5
O(64)-H(64B)...O(1)	0.89	2.06	2.889(3)	156.2
O(65)-H(65A)...O(4) #3	0.87	2.38	3.107(4)	141.7
O(65)-H(65B)...O(33) #3	0.87	2.28	2.775(4)	115.9
O(66)-H(66A)...O(31) #3	0.90(5)	1.84(5)	2.728(3)	166(4)
O(66)-H(66B)…O(79) #1	0.76(5)	2.01(5)	2.772(4)	178(5)
O(72)-H(72A)...O(6) #4	0.87	1.93	2.773(5)	164.7
O(72)-H(72B)…O(73) #5	0.87	2.03	2.805(6)	148.1
O(73)-H(73A)…O(75) #5	0.87	2.19	2.803(6)	127.4
O(73)-H(73B)…O(74)	0.87	1.89	2.746(7)	167.4
O(74)-H(74A)…O(75)	0.87	2.14	2.863(7)	139.9
O(74)-H(74B)…O(80)	0.87	1.84	2.692(6)	165.9
O(75)-H(75A)...O(34) #6	0.87	2.3	2.831(5)	119.5
O(76)-H(76A)…O(78)	0.87	2.21	3.020(6)	155.2
O(76)-H(76B)...O(36) #3	0.87	1.95	2.708(5)	144
O(77)-H(77A)...O(2)	0.87	2.34	2.888(5)	120.7
O(77)-H(77A)…O(83) #7	0.87	2.19	2.728(11)	119.6
O(77)-H(77B)…O(84) #2	0.87	2.05	2.586(17)	119.0
O(78)-H(78A)...O(3)	0.87	1.93	2.776(4)	164
O(79)-H(79A)…O(71)	0.87	1.93	2.785(4)	168.0
O(79)-H(79B)...O(4) #6	0.87	1.85	2.713(4)	169.4
O(80)-H(80A)...O(4) #6	0.87	2.14	2.933(5)	151.6
O(80)-H(80B)…O(81)	0.87	1.91	2.762(6)	168.0
O(81)-H(81A)…O(71)	0.87	1.99	2.820(5)	157.9
O(81)-H(81B)...O(6) #8	0.87	1.97	2.776(5)	154.5
O(82)-H(82A)…O(72)	0.87	2.28	3.058(7)	149.3
O(83)-H(83C)...O(5) #4	0.87	1.98	2.820(10)	160.9
O(83)-H(83D)…O(77) #4	0.87	1.87	2.728(11)	167.6
O(83B)-H(83A)…O(72)	0.87	2.13	2.973(12)	163.1
O(83B)-H(83A)…O(84)	0.87	2.10	2.57(2)	113.2
O(84)-H(84A)…O(72)	0.87	2.02	2.520(19)	115.9
O(84)-H(84A)…O(83B)	0.87	2.12	2.57(2)	111.4

#1 : -1+x, +y, +z ; #2 : 1-x, -y, 1-z ; #3 : -x, -y, 1-z ; #4 : +x, +y, 1+z ; #5 1-x, 1-y, 1-z ; #6 : 1+x, +y, +z ; #7 : +x, +y, -1+z ; #8 : 1-x, 1-y, -z.

Table S10**.** Selected bond lengths (Å) and angles (deg) for complex $[Mn(tpada)ClCa(OH_2)_{2.67}(MeOH)_{2.33}]Cl{\cdot}1.67MeOH\cdot0.84H_2O$ (**MnCa**$\cdot1.67MeOH\cdot0.84H_2O$).

Mn(1)-N(2)	2.226(2)	Ca(1)-O(23)	2.337(3)
Mn(1)-N(3)	2.245(2)	Ca(1)-O(26)	2.355(2)
Mn(1)-O(1)	2.2646(19)	Ca(1)-O(22)	2.364(2)
Mn(1)-N(4)	2.269(2)	Ca(1)-O(25)	2.381(2)
Mn(1)-O(3)	2.280(2)	Ca(1)-O(21)	2.410(2)
Mn(1)-N(1)	2.466(2)	Ca(1)-O(1)	2.465(2)
Mn(1)-Cl(1)	2.5256(8)	Ca(1)-O(3)	2.4810(19)
C(7)-O(1)	1.279(3)	C(14)-O(3)	1.268(3)
C(7)-O(2)	1.239(3)	C(14)-O(4)	1.247(3)
N(3)-Mn(1)-N(2)	140.35(9)	O(26)-Ca(1)-O(23)	134.86(10)
O(1)-Mn(1)-N(2)	72.42(8)	O(22)-Ca(1)-O(23)	81.90(10)
O(1)-Mn(1)-N(3)	146.84(8)	O(22)-Ca(1)-O(26)	82.84(9)
N(4)-Mn(1)-N(2)	90.86(9)	O(25)-Ca(1)-O(23)	74.56(11)
N(4)-Mn(1)-N(3)	82.56(8)	O(25)-Ca(1)-O(26)	73.42(9)
N(4)-Mn(1)-O(1)	94.36(7)	O(25)-Ca(1)-O(22)	113.83(9)
O(3)-Mn(1)-N(2)	147.83(8)	O(21)-Ca(1)-O(23)	105.47(9)
O(3)-Mn(1)-N(3)	71.50(8)	O(21)-Ca(1)-O(26)	99.60(8)
O(3)-Mn(1)-O(1)	75.48(7)	O(21)-Ca(1)-O(22)	165.58(8)
O(3)-Mn(1)-N(4)	89.54(8)	O(21)-Ca(1)-O(25)	80.34(9)
N(1)-Mn(1)-N(2)	69.92(8)	O(1)-Ca(1)-O(23)	141.57(9)
N(1)-Mn(1)-N(3)	70.68(8)	O(1)-Ca(1)-O(26)	78.37(8)
N(1)-Mn(1)-O(1)	140.21(7)	O(1)-Ca(1)-O(22)	85.08(7)
N(1)-Mn(1)-N(4)	74.03(8)	O(1)-Ca(1)-O(25)	143.16(8)
N(1)-Mn(1)-O(3)	140.28(8)	O(1)-Ca(1)-O(21)	81.54(7)
Cl(1)-Mn(1)-N(2)	88.11(6)	O(3)-Ca(1)-O(23)	76.72(9)
Cl(1)-Mn(1)-N(3)	91.25(6)	O(3)-Ca(1)-O(26)	146.81(8)
Cl(1)-Mn(1)-O(1)	95.78(5)	O(3)-Ca(1)-O(22)	94.53(8)
Cl(1)-Mn(1)-N(4)	168.98(6)	O(3)-Ca(1)-O(25)	135.63(8)
Cl(1)-Mn(1)-O(3)	97.17(5)	O(3)-Ca(1)-O(21)	75.59(7)
Cl(1)-Mn(1)-N(1)	95.34(6)	O(3)-Ca(1)-O(1)	68.44(6)

Table S11. Hydrogen bonds lengths (Å) and angles (deg) for complex **MnCa**·1.67MeOH·0.84H_2O.

D-H…A	d(D-H)	d(H…A)	d(D…A)	< (DHA)
O(21)-H(1O)...Cl(1)	0.80(4)	2.31(4)	3.100(2)	169(4)
O(22)-H(2O)…Cl(2) #1	0.83(4)	2.28(4)	3.057(2)	156(3)
O(23)-H(1O3)...O(4)	0.82(6)	1.84(6)	2.657(4)	169(6)
O(23)-H(2O3)...O(24)	0.67(7)	2.10(8)	2.691(5)	149(8)
O(24)-H(4O)…O(32) #1	0.84	1.89	2.707(6)	163.0
O(24)-H(4O)…O(33) #1	0.84	2.59	3.34(2)	149.2
O(25)-H(1O5)…O(31) #2	0.90(4)	1.80(4)	2.698(4)	176(4)
O(25)-H(2O5)…Cl(2) #3	0.80(3)	2.32(3)	3.124(3)	175(3)
O(26)-H(1O6)…Cl(2) #3	0.90(5)	2.29(5)	3.154(3)	162(4)
O(26)-H(2O6)...O(2)	0.82(3)	1.90(3)	2.668(3)	154(3)
O(31)-H(31O)...O(4) #4	0.89(5)	1.87(5)	2.734(4)	164(4)

#1: -x+1, y+1/2, -z ; #2: x-1, y+1, z ; #3: x, y+1, z ; #4: -x+1, y-1/2, -z

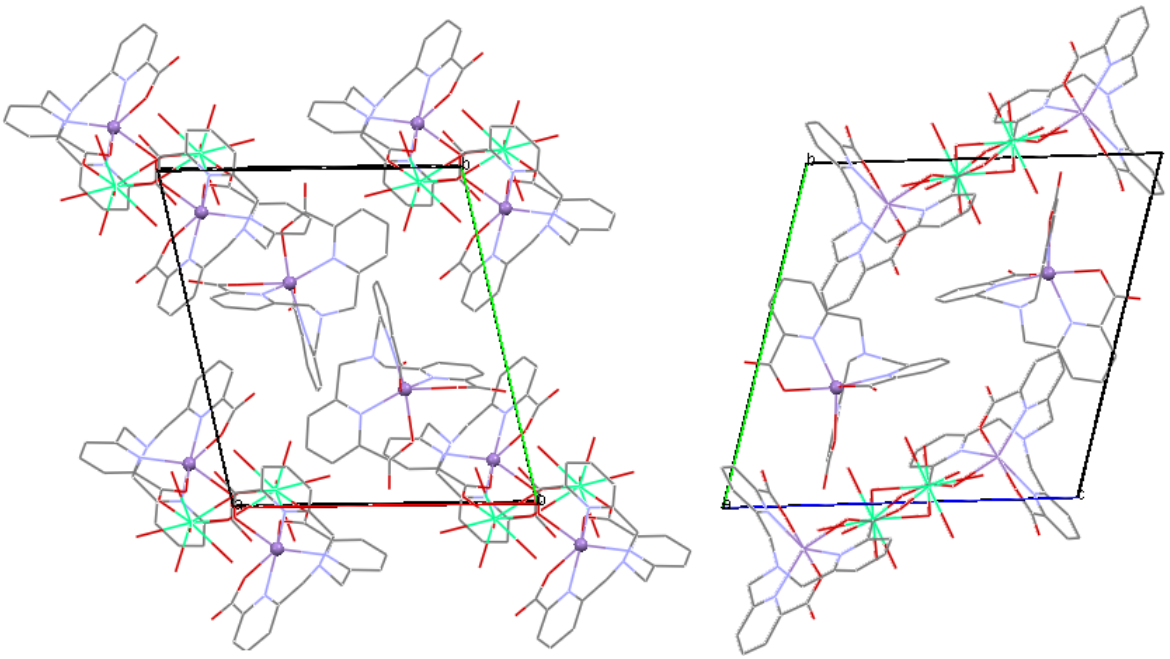

Figure S1. Views of the unit cell of **Mn_2Ca_2·2Mn**·25H_2O in projection on the *ab* (left) and *bc* (right) planes. Hydrogen atoms and co-crystallized water molecules have been omitted for clarity.

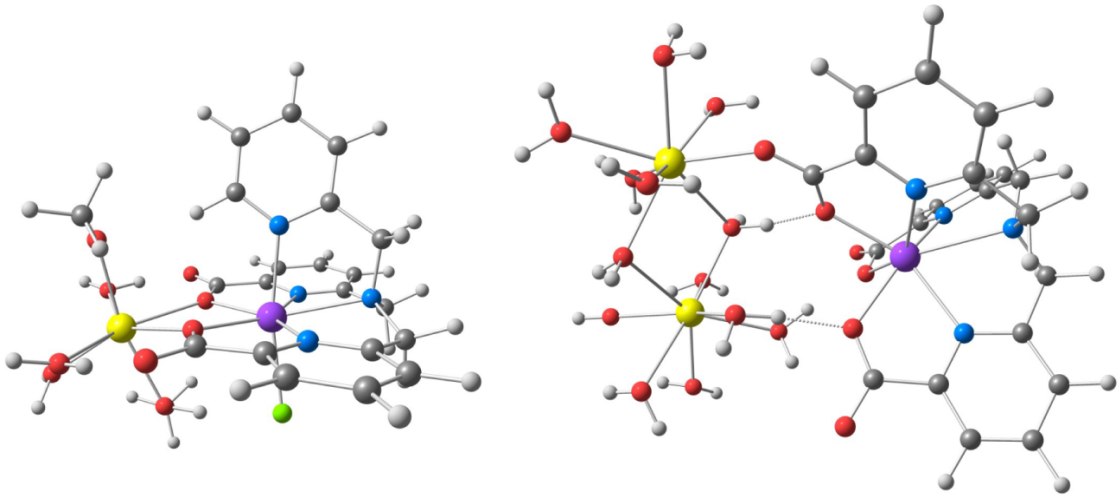

Figure S2**.** Structural models of the **MnCa** complex (left) and of the **$MnCa_2$** unit of **Mn_2Ca_2·2Mn** (right), used in DFT calculations for the analysis of the bonding and the topology of the electron density following the theory of atoms-in-molecules. Mn: purple; Ca: yellow; Cl: green; C: grey; N: blue; O: red; H; white.

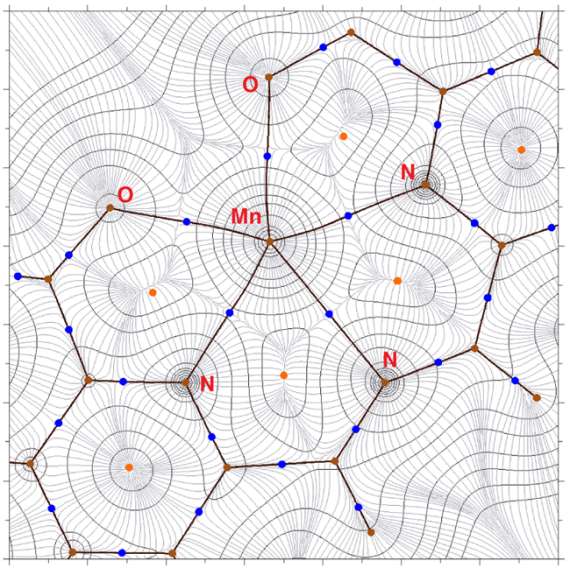

Figure S3**.** Electron density plot within the equatorial plane of the Mn ion in the **MnCa** complex. The topology of the electron density reflects the presence of five bonding interactions within the plane and supports the assignment of a genuine pentagonal bipyramidal coordination to the Mn ion.

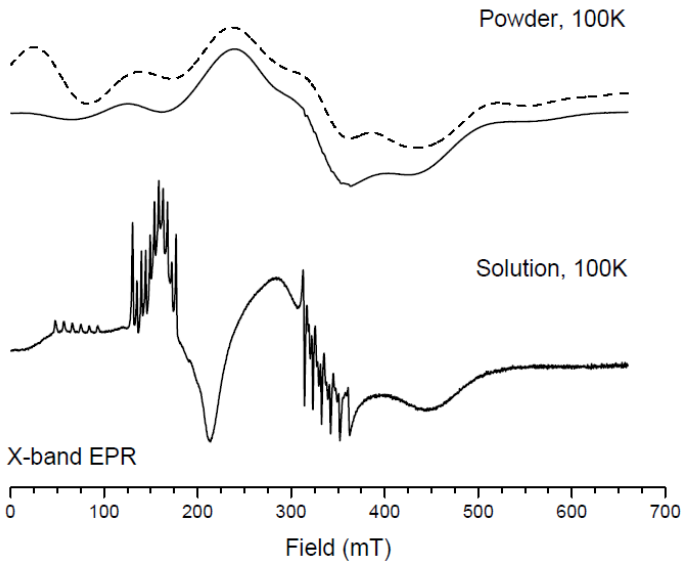

Figure S4**.** Experimental (solid line) and simulated (dashed line) X-band EPR spectra recorded at 100 K on powder and on a MeOH solution of **MnCa**.

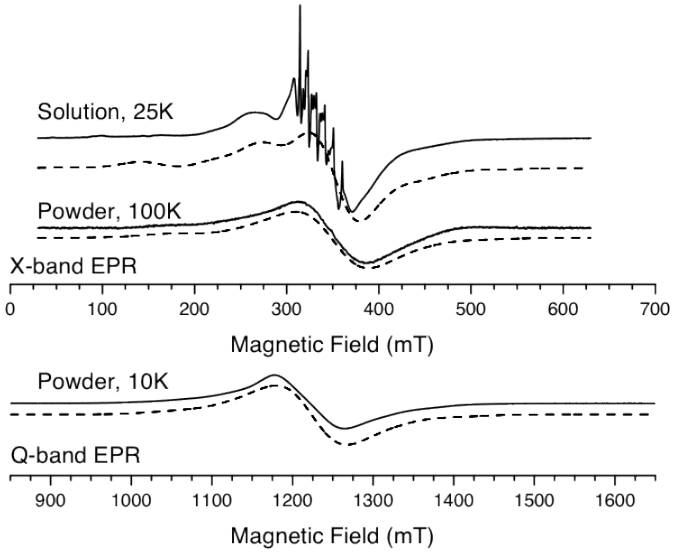

Figure S5. Experimental (solid line) and simulated (dashed line) X- and Q-band EPR spectra recorded on powder and on a MeOH solution of **Mn_2Ca_2·2Mn**. Parameters used for the simulation of the MeOH solution: D_{exp} = 0.046 cm^{-1} and E/D_{exp} = 0.120.