Mechanochemical synthesis of alkaline earth Mg – Ba saccharinates. Connectivity in the crystal structures of $Mg(sac)_2 \cdot 7H_2O$, $Ca(sac)_2 \cdot 7H_2O$ and $Ba(sac)_2 \cdot 4.5H_2O$ (sac = saccharinate)

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Supplementary data:

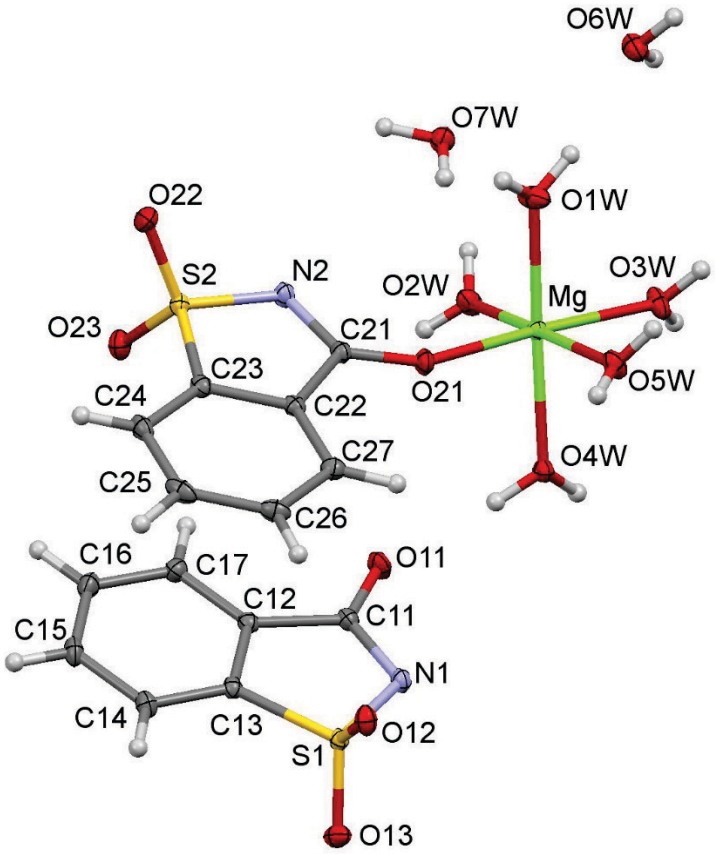

Figure S1. Drawing of the ions and molecules of $Mg(sac)_2 \cdot 7H_2O$ in the asymmetric unit with the atom numbering scheme.

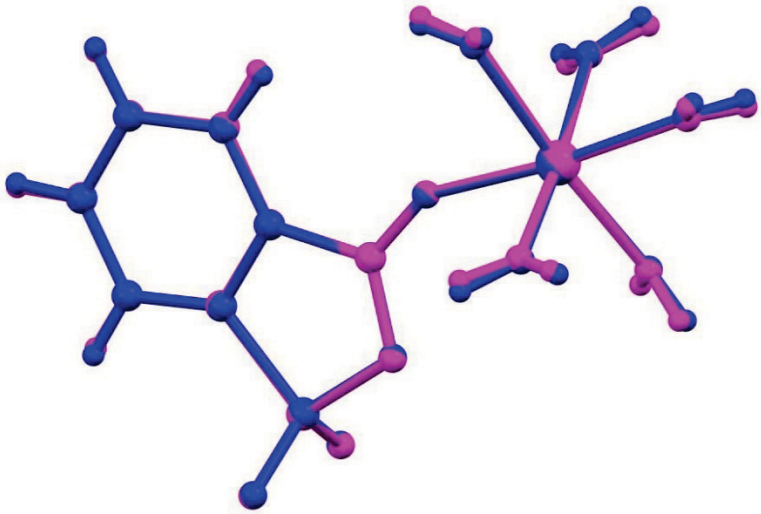

Figure S2. Overlay of the $Mg(sac)_2(H_2O)_5$ cation at 170 K (present structure; violet color) and at room temperature (MGSAC10, blue color).

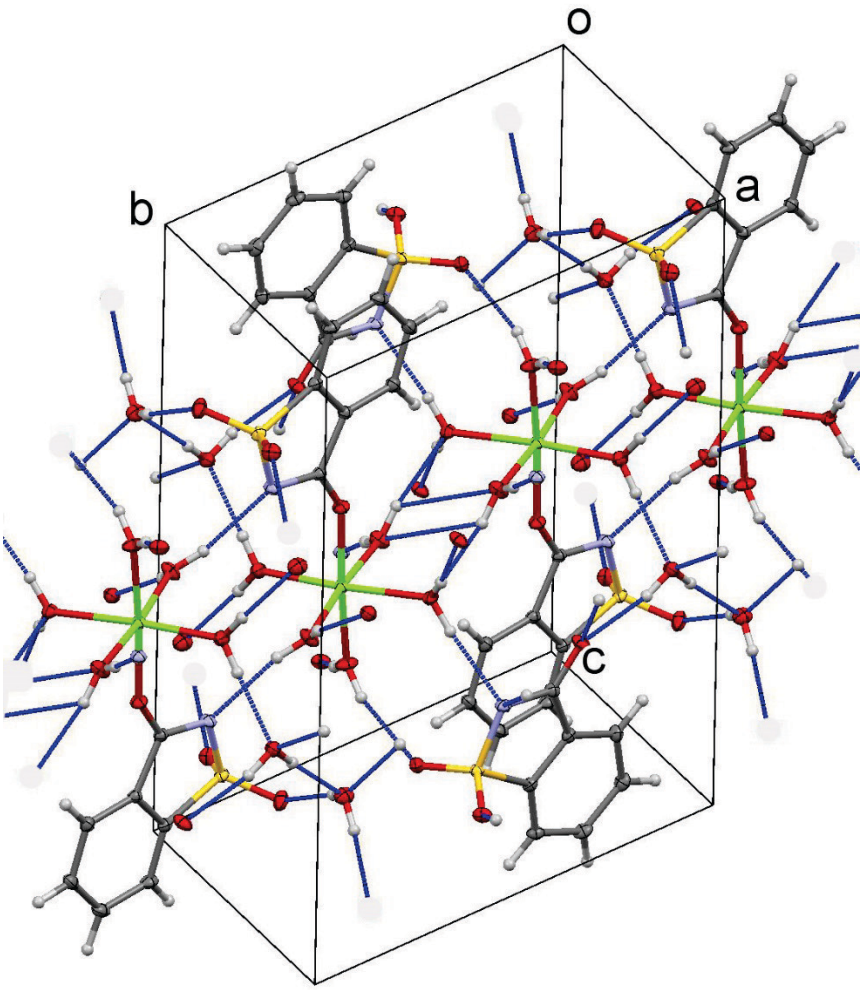

Figure S3. Packing of $Mg(sac)_2 \cdot 7H_2O$ in the unit cell. Hydrogen bonds are shown with blue dotted lines.

Figure S4. Crystal of $Ca(sac)_2 \cdot 7H_2O$ in the loop used for data collection. Dimensions of the crystal are 0.189 mm × 0.004 mm × 0.004 mm. It is elongated along [100].

Table S1. Bond lengths in $Mg(sac)_2 \cdot 7H_2O$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O12	1.4444(8)	N1	C11	1.3571(13)
S1	O13	1.4425(8)	N2	C21	1.3456(14)
S1	N1	1.6249(9)	C21	C22	1.4984(14)
S1	C13	1.7601(10)	C11	C12	1.4933(15)
S2	O23	1.4457(8)	C22	C27	1.3868(15)
S2	O22	1.4423(8)	C22	C23	1.3824(15)
S2	N2	1.6196(9)	C14	C13	1.3801(15)
S2	C23	1.7624(11)	C14	C15	1.3972(16)
Mg	O21	2.0135(8)	C12	C13	1.3839(14)
Mg	O4W	2.1082(8)	C12	C17	1.3879(15)
Mg	O2W	2.0490(9)	C27	C26	1.3967(16)
Mg	O5W	2.1092(8)	C17	C16	1.3918(17)
Mg	O3W	2.0511(9)	C23	C24	1.3819(15)
Mg	O1W	2.0311(9)	C26	C25	1.3896(19)
O21	C21	1.2414(13)	C24	C25	1.3972(17)
O11	C11	1.2402(13)	C15	C16	1.3916(17)

Table S2. Bond angles in $Mg(sac)_2 \cdot 7H_2O$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O12	S1	N1	110.98(5)	C11	N1	S1	110.72(7)
O12	S1	C13	110.53(5)	C21	N2	S2	110.53(7)
O13	S1	O12	114.62(5)	O21	C21	N2	125.50(10)
O13	S1	N1	111.55(5)	O21	C21	C22	120.47(9)
O13	S1	C13	110.61(5)	N2	C21	C22	114.03(9)
N1	S1	C13	97.23(5)	O11	C11	N1	123.02(10)
O23	S2	N2	111.41(5)	O11	C11	C12	123.22(9)
O23	S2	C23	109.47(5)	N1	C11	C12	113.76(9)
O22	S2	O23	114.13(5)	C27	C22	C21	128.15(10)
O22	S2	N2	111.73(5)	C23	C22	C21	111.27(9)
O22	S2	C23	111.19(5)	C23	C22	C27	120.58(10)
N2	S2	C23	97.72(5)	C13	C14	C15	116.72(10)
O21	Mg	O4W	86.75(3)	C13	C12	C11	111.22(9)
O21	Mg	O2W	96.80(4)	C13	C12	C17	120.10(10)
O21	Mg	O5W	86.81(3)	C17	C12	C11	128.68(10)
O21	Mg	O3W	174.76(4)	C14	C13	S1	129.84(8)
O21	Mg	O1W	91.80(4)	C14	C13	C12	123.10(10)
O4W	Mg	O5W	86.50(3)	C12	C13	S1	107.07(8)
O2W	Mg	O4W	90.30(4)	C22	C27	C26	117.39(11)
O2W	Mg	O5W	175.03(4)	C12	C17	C16	117.80(10)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2W	Mg	O3W	88.22(4)	C22	C23	S2	106.42(7)
O3W	Mg	O4W	91.74(4)	C24	C23	S2	130.61(9)
O3W	Mg	O5W	88.09(4)	C24	C23	C22	122.96(10)
O1W	Mg	O4W	175.23(4)	C25	C26	C27	121.41(11)
O1W	Mg	O2W	94.39(4)	C23	C24	C25	116.51(11)
O1W	Mg	O5W	88.88(4)	C16	C15	C14	120.84(11)
O1W	Mg	O3W	89.30(4)	C15	C16	C17	121.44(10)
C21	O21	Mg	149.30(7)	C26	C25	C24	121.14(10)

Table S3. Hydrogen bond parameters in $Mg(sac)_2 \cdot 7H_2O$

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1W	H1WA	O6W[1]	0.828(19)	1.914(19)	2.7300(13)	168.6(17)
O1W	H1WB	O7W[2]	0.833(19)	1.88(2)	2.7071(12)	175.4(17)
O2W	H2WA	O7W[3]	0.79(2)	2.070(19)	2.8245(13)	160.4(17)
O2W	H2WB	N2[1]	0.844(19)	2.117(19)	2.9350(13)	163.3(17)
O3W	H3WA	O12[1]	0.847(19)	1.94(2)	2.7701(12)	167.7(17)
O3W	H3WB	O13	0.842(19)	1.986(19)	2.8022(12)	163.1(16)
O4W	H4WA	O11[3]	0.827(19)	1.93(2)	2.7513(12)	173.6(17)
O4W	H4WB	N1	0.865(19)	2.03(2)	2.8912(12)	174.3(16)
O5W	H5WA	N1[1]	0.814(15)	2.106(15)	2.9123(13)	174.4(17)
O5W	H5WB	O4W[2]	0.83(2)	2.24(2)	2.9889(12)	151.3(19)
O6W	H6WA	O23[4]	0.81(2)	1.97(2)	2.7657(13)	167.5(19)
O6W	H6WB	O22[2]	0.82(2)	2.03(2)	2.8172(13)	161.7(17)
O7W	H7WA	O6W[1]	0.857(19)	1.90(2)	2.7509(13)	170.8(16)
O7W	H7WB	O11[3]	0.824(19)	1.943(19)	2.7457(12)	164.5(17)
C15	H15	O23[5]	0.922(17)	2.494(16)	3.2034(14)	134.0(13)

[1]1+x, y, z; [2]1-x,1-y,1-z; [3]-x,1-y,1-z; [4]-x,-y,1-z; [5]-x,-y,1-z; [6]x,1+y,-1+z; [5]1+x,y,z;

Table S4. Analysis of short ring-ring interactions in $Mg(sac)_2 \cdot 7H_2O$

6-Membered Ring (1) C12 --> C13 --> C14 --> C15 --> C16 --> C17
6-Membered Ring (2) C22 --> C23 --> C24 --> C25 --> C26 --> C27

- Cg(I) = Plane number I (= ring number in () above)
- Cg-Cg = Distance between ring Centroids (Å)
- Alpha = Dihedral Angle between Planes I and J (°)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Å)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Å)

Cg(I)···Cg(J)	Cg···Cg	Alpha	CgI_Perp	CgJ_Perp

Cg(1)···Cg(2)	[-x,1-y,1-z]	3.6104(6)	3.91(5)	-3.5656(5)	-3.5354(4)
Cg(1)···Cg(2)	[1-x,1-y,1-z]	3.5898(6)	3.91(5)	3.3269(5)	3.4111(4)

Table S5. Bond lengths in $Ca(sac)_2 \cdot 7H_2O$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ca1	O1W	2.445(15)	O23	C21	1.31(3)
Ca1	O2W	2.390(19)	N2	C21	1.31(3)
Ca1	O3W	2.565(17)	C21	C22	1.43(3)
Ca1	O4W	2.35(2)	C22	C23	1.41(3)
Ca1	O5W	2.424(19)	C22	C27	1.43(4)
Ca1	O6W	2.395(16)	C23	C24	1.27(3)
Ca1	O11	2.586(16)	C24	C25	1.42(3)
Ca1	O12[1]	2.567(18)	C25	C26	1.50(3)
S1	O11	1.474(14)	C26	C27	1.35(3)
S1	O12	1.48(2)	S3	O31	1.364(18)
S1	N1	1.553(18)	S3	O32	1.409(19)
S1	C13	1.76(3)	S3	N3	1.56(2)
O12	Ca1[2]	2.567(17)	S3	C33	1.80(2)
O13	C11	1.25(2)	O33	C31	1.29(3)
N1	C11	1.31(3)	N3	C31	1.34(3)
C11	C12	1.52(3)	C31	C32	1.43(3)
C12	C13	1.41(3)	C32	C33	1.51(3)
C12	C17	1.42(3)	C32	C37	1.44(3)
C13	C14	1.35(3)	C33	C34	1.27(3)
C14	C15	1.43(4)	C34	C35	1.43(4)
C15	C16	1.41(4)	C35	C36	1.32(3)
C16	C17	1.41(3)	C36	C37	1.43(3)
Ca2	O7W	2.36(2)	S4	O41	1.45(2)
Ca2	O8W	2.33(3)	S4	O42	1.458(18)
Ca2	O9W	2.507(18)	S4	N4	1.54(2)
Ca2	O10W	2.384(16)	S4	C43	1.78(2)
Ca2	O11W	2.37(2)	O43	C41	1.22(3)
Ca2	O12W	2.481(18)	N4	C41	1.39(3)
Ca2	O21	2.460(17)	C41	C42	1.41(3)
Ca2	O22[2]	2.67(2)	C42	C43	1.42(3)
S2	O21	1.450(16)	C42	C47	1.49(3)
S2	O22	1.41(3)	C43	C44	1.34(3)
S2	N2	1.57(2)	C44	C45	1.37(3)
S2	C23	1.80(2)	C45	C46	1.41(3)
O22	Ca2[1]	2.67(2)	C46	C47	1.41(3)

[1]-1+x,+y,+z; [2]1+x,+y,+z

Table S6. Bond angles in $Ca(sac)_2 \cdot 7H_2O$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1W	Ca1	O3W	139.4(6)	O11W	Ca2	O12W	80.5(8)
O1W	Ca1	O11	65.0(6)	O11W	Ca2	O21	74.6(8)
O1W	Ca1	O12[1]	72.0(6)	O11W	Ca2	O22[2]	131.6(8)
O2W	Ca1	O1W	99.0(7)	O12W	Ca2	O9W	144.3(7)
O2W	Ca1	O3W	75.7(7)	O12W	Ca2	O22[2]	70.3(6)
O2W	Ca1	O5W	81.8(7)	O21	Ca2	O9W	138.7(6)
O2W	Ca1	O6W	134.5(6)	O21	Ca2	O12W	69.0(6)
O2W	Ca1	O11	81.3(7)	O21	Ca2	O22[2]	125.0(8)
O2W	Ca1	O12[1]	74.4(6)	O21	S2	N2	112.5(11)
O3W	Ca1	O11	74.4(5)	O21	S2	C23	107.5(12)
O3W	Ca1	O12[1]	139.8(6)	O22	S2	O21	116.3(16)
O4W	Ca1	O1W	89.1(7)	O22	S2	N2	111.4(12)
O4W	Ca1	O2W	149.7(7)	O22	S2	C23	108.6(12)
O4W	Ca1	O3W	79.2(7)	N2	S2	C23	99.0(11)
O4W	Ca1	O5W	105.8(8)	S2	O21	Ca2	158.3(12)
O4W	Ca1	O6W	75.4(6)	S2	O22	Ca2[1]	145.4(14)
O4W	Ca1	O11	75.8(7)	C21	N2	S2	112.2(17)
O4W	Ca1	O12[1]	135.6(6)	O23	C21	N2	124(2)
O5W	Ca1	O1W	149.1(7)	O23	C21	C22	122(2)
O5W	Ca1	O3W	71.0(6)	N2	C21	C22	113(2)
O5W	Ca1	O11	144.3(6)	C23	C22	C21	116(2)
O5W	Ca1	O12[1]	78.6(7)	C23	C22	C27	117(2)
O6W	Ca1	O1W	81.8(6)	C27	C22	C21	127(2)
O6W	Ca1	O3W	130.7(6)	C22	C23	S2	99.8(16)
O6W	Ca1	O5W	76.3(6)	C24	C23	S2	132.8(18)
O6W	Ca1	O11	135.8(6)	C24	C23	C22	127(2)
O6W	Ca1	O12[1]	62.6(6)	C23	C24	C25	119(2)
O12[1]	Ca1	O11	125.8(6)	C24	C25	C26	116(2)
O11	S1	O12	115.1(12)	C27	C26	C25	122(2)
O11	S1	N1	113.6(11)	C26	C27	C22	118(2)
O11	S1	C13	104.8(11)	O31	S3	O32	124.3(15)
O12	S1	N1	111.3(10)	O31	S3	N3	107.7(10)
O12	S1	C13	112.2(11)	O31	S3	C33	107.2(11)
N1	S1	C13	98.5(11)	O32	S3	N3	109.3(11)
S1	O11	Ca1	141.7(11)	O32	S3	C33	105.1(10)
S1	O12	Ca1[2]	144.0(10)	N3	S3	C33	100.6(10)
C11	N1	S1	114.9(15)	C31	N3	S3	113.5(17)
O13	C11	N1	130(2)	O33	C31	N3	125(2)
O13	C11	C12	119(2)	O33	C31	C32	123(2)
N1	C11	C12	110.5(18)	N3	C31	C32	111(2)
C13	C12	C11	112(2)	C31	C32	C33	116(2)
C13	C12	C17	117(2)	C31	C32	C37	130(2)
C17	C12	C11	131(2)	C37	C32	C33	114.1(17)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	C13	S1	103.6(17)	C32	C33	S3	97.8(13)
C14	C13	S1	131(2)	C34	C33	S3	135(2)
C14	C13	C12	126(2)	C34	C33	C32	127(2)
C13	C14	C15	118(2)	C33	C34	C35	112(2)
C16	C15	C14	119(2)	C36	C35	C34	128(2)
C17	C16	C15	121(2)	C35	C36	C37	118(2)
C16	C17	C12	119(2)	C36	C37	C32	119(2)
O7W	Ca2	O9W	73.6(8)	O41	S4	O42	122.3(14)
O7W	Ca2	O10W	138.3(6)	O41	S4	N4	111.7(11)
O7W	Ca2	O11W	147.0(6)	O41	S4	C43	105.0(11)
O7W	Ca2	O12W	101.7(7)	O42	S4	N4	108.5(11)
O7W	Ca2	O21	75.6(7)	O42	S4	C43	109.5(10)
O7W	Ca2	O22[2]	78.2(8)	N4	S4	C43	96.7(12)
O8W	Ca2	O7W	85.4(10)	C41	N4	S4	117.5(18)
O8W	Ca2	O9W	69.2(9)	O43	C41	N4	123(2)
O8W	Ca2	O10W	107.2(10)	O43	C41	C42	131(2)
O8W	Ca2	O11W	76.5(9)	N4	C41	C42	106(2)
O8W	Ca2	O12W	146.5(8)	C41	C42	C43	120(2)
O8W	Ca2	O21	81.5(9)	C41	C42	C47	123(2)
O8W	Ca2	O22[2]	142.8(8)	C43	C42	C47	117.5(18)
O9W	Ca2	O22[2]	74.1(7)	C42	C43	S4	100.7(15)
O10W	Ca2	O9W	74.3(6)	C44	C43	S4	133(2)
O10W	Ca2	O12W	89.3(5)	C44	C43	C42	125(2)
O10W	Ca2	O21	144.4(7)	C43	C44	C45	117(2)
O10W	Ca2	O22[2]	67.9(7)	C44	C45	C46	121(2)
O11W	Ca2	O9W	123.0(9)	C47	C46	C45	124(2)
O11W	Ca2	O10W	74.2(6)	C46	C47	C42	114(2)

[1] -1+x,y,z; [2]1+x,y,z

Table S7. Analysis of short ring-ring interactions in $Ca(sac)_2 \cdot 7H_2O$

6-Membered Ring (1) C(12) --> C(13) --> C(14) --> C(15) --> C(16) --> C(17)
6-Membered Ring (2) C(22) --> C(23) --> C(24) --> C(25) --> C(26) --> C(27)
6-Membered Ring (3) C(32) --> C(33) --> C(34) --> C(35) --> C(36) --> C(37)
6-Membered Ring (4) C(42) --> C(43) --> C(44) --> C(45) --> C(46) --> C(47)

- Cg(I) = Plane number I (= ring number in () above)
- Cg-Cg = Distance between ring Centroids (Å)
- Alpha = Dihedral Angle between Planes I and J (°)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Å)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Å)

Cg(I)···Cg(J)	Cg···Cg	Alpha	CgI_Perp	CgJ_Perp

Cg(1)···Cg(3]	3.672(13)	10	3.355(10)	-3.549(9)
Cg(1)···Cg(3) [1+x,y,z]	3.853(13)	10	-3.567(10)	3.306(9)
Cg(2)···Cg(4) [-1+x,y,z]	3.717(13)	4	3.436(10)	-3.396(9)
Cg(2)···Cg(4)	3.715(13)	4	-3.377(10)	3.474(9)
Cg(3)···Cg(2) [-1+x,y,z]	3.853(13)	10	3.306(9)	-3.568(10)
Cg(3)···Cg(2)	3.672(13)	10	-3.549(9)	3.355(10)

Table S8. Interatomic distances between possible donors and acceptors of hydrogen bonds in $Ca(sac)_2 \cdot 7H_2O$

D	**A**	**d(D···A)/Å**
O1W	O(11)	2.71(2)
O1W	O(31) [-1+x,-1+y,z]	2.90(2)
O1W	O(12) [-1+x,-1+y,z]	2.94(2)
O1W	O(32) [x,-1+y,z]	2.97(3)
O2W	O(33)	2.68(2)
O2W	O(9W) [-1+x,-1+y,z]	2.95(3)
O2W	O(12) [-1+x,-1+y,z]	3.00(3)
O2W	O(3W)	3.04(3)
O2W	N(1) [-1+x,-1+y,z]	3.04(3)
O3W	O(13W)	2.81(2)
O3W	O(5W)	2.90(3)
O3W	N(2)	3.02(3)
O4w	N(3) [x,-1+y,z]	2.90(3)
O4w	O(6W)	2.91(3)
O4w	O(11)	3.04(3)
O5W	O(13W) [-1+x,y,z]	2.78(3)
O5W	O(23)	2.82(2)
O5W	O(6W)	2.98(3)
O6W	O(12) [-1+x,-1+y,z]	2.58(2)
O6W	O(13) [-1+x,-1+y,z]	2.83(2)
O6W	N(3) [-1+x,-1+y,z]	3.01(3)
O7W	O(43)	2.70(2)
O7W	O(9W)	2.92(3)
O7W	O(21)	2.95(3)
O8W	O(9W)	2.76(4)
O8W	O(13)	2.80(3)
O8W	O(14W)	2.82(4)
O8W	O(11W)	2.91(4)
O9W	O(14W) [1+x,y,z]	2.68(3)
O9W	O(2W) [-1+x,y,z]	2.95(3)
O9W	O(10W)	2.95(3)
O10W	O(22)d [1+x,1+y,z]	2.84(3)
O10W	O(23) [1+x,1+y,z]	2.85(2)
O10W	O(11W)	2.87(3)
O10W	N(4) [1+x,1+y,z]	2.91(3)
O11W	O(12)	2.50(2)
D	**A**	**d(D···A)/Å**

O11W	N(1)	2.53(2)
O12W	O(21)	2.80(3)
O12W	O(41) [x,1+y,z]	2.89(3)
O12W	O(42) [1+x,1+y,z]	2.89(3)
O12W	O(22) [3-x,2-y,1-z]	2.97(3)
O13W	O(14W) [x,-1+y,z]	2.68(2)
O13W	O(43)	2.78(2)
O14W	O(33)	2.83(2)
C45-H45	O(41) [3-x,1-y,1-z]	3.17(3)

Table S9. Bond lengths in $Ba(sac)_2 \cdot 4.5H_2O$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ba1	$Ba1^1$	4.4749(10)	O23	$Ba1^3$	2.917(7)
Ba1	O11	2.629(6)	O31	C31	1.237(11)
Ba1	O22	2.853(7)	O41	C41	1.246(11)
Ba1	$O23^2$	2.917(7)	N1	C11	1.348(13)
Ba1	N1	3.048(7)	N2	C21	1.362(11)
Ba1	O1W	2.842(6)	N3	C31	1.354(11)
Ba1	O2W	2.807(6)	N4	C41	1.340(11)
Ba1	O3W	2.788(7)	C11	$O11^1$	1.219(11)
Ba1	$O4W^2$	2.843(6)	C11	C12	1.489(12)
Ba1	O8W	2.795(6)	C12	C13	1.360(12)
Ba2	O12	2.740(7)	C12	C17	1.403(14)
Ba2	O13	2.711(7)	C13	C14	1.402(12)
Ba2	$O21^1$	2.705(7)	C14	C15	1.368(15)
Ba2	O31	3.015(7)	C15	C16	1.400(16)
Ba2	O1W	2.918(7)	C16	C17	1.360(15)
Ba2	O4W	2.894(6)	C21	C22	1.493(13)
Ba2	O5W	2.859(7)	C22	C23	1.367(13)
Ba2	O6W	2.821(7)	C22	C27	1.393(13)
Ba2	O7W	2.692(7)	C23	C24	1.384(14)
S2	O22	1.443(7)	C24	C25	1.396(14)
S2	O23	1.451(7)	C25	C26	1.408(18)
S2	N2	1.616(7)	C26	C27	1.398(18)
S2	C23	1.774(9)	C31	C32	1.501(12)
S1	O12	1.446(7)	C32	C33	1.393(12)
S1	$O13^2$	1.430(8)	C32	C37	1.401(12)
S1	N1	1.611(7)	C33	C34	1.384(14)
S1	C13	1.763(9)	C34	C35	1.397(15)
S3	O32	1.451(7)	C35	C36	1.367(17)
S3	O33	1.428(7)	C36	C37	1.393(15)
S3	N3	1.621(8)	C41	C42	1.485(12)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S3	C33	1.771(10)	C42	C43	1.386(13)
S4	O42	1.446(7)	C42	C47	1.396(12)
S4	O43	1.449(7)	C43	C44	1.396(12)
S4	N4	1.635(8)	C44	C45	1.404(14)
S4	C43	1.760(9)	C45	C46	1.377(15)
O11	C11[1]	1.219(11)	C46	C47	1.388(13)
O13	S1[3]	1.430(8)	O2W	Ba1[1]	2.807(6)
O21	Ba2[1]	2.705(6)	O4W	Ba1[3]	2.843(6)
O21	C21	1.211(11)	O8W	Ba1[1]	2.795(6)

[1]1-x, y,1/2-z; [2] x,1+y, z; [3] x,-1+y, z

Table S10. Bond angles in $Ba(sac)_2 \cdot 4.5H_2O$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O11	Ba1	Ba1[1]	57.20(17)	O12	S1	N1	111.9(4)
O11	Ba1	O22	70.3(2)	O12	S1	C13	110.8(4)
O11	Ba1	O23[2]	69.7(2)	O13[2]	S1	O12	113.4(4)
O11	Ba1	N1	130.3(2)	O13[2]	S1	N1	111.5(4)
O11	Ba1	O1W	138.4(2)	O13[2]	S1	C13	111.0(5)
O11	Ba1	O2W	63.74(18)	N1	S1	C13	97.2(4)
O11	Ba1	O3W	97.0(2)	O32	S3	N3	112.5(4)
O11	Ba1	O4W[2]	135.1(2)	O32	S3	C33	109.8(5)
O11	Ba1	O8W	64.98(19)	O33	S3	O32	114.5(4)
O22	Ba1	Ba1[1]	101.28(13)	O33	S3	N3	111.1(4)
O22	Ba1	O23[2]	110.31(19)	O33	S3	C33	110.4(4)
O22	Ba1	N1	121.7(2)	N3	S3	C33	97.3(4)
O23[2]	Ba1	Ba1[1]	101.66(13)	O42	S4	O43	114.5(4)
O23[2]	Ba1	N1	127.9(2)	O42	S4	N4	110.7(4)
N1	Ba1	Ba1[1]	73.16(15)	O42	S4	C43	110.7(4)
O1W	Ba1	Ba1[1]	129.06(14)	O43	S4	N4	111.3(4)
O1W	Ba1	O22	68.24(19)	O43	S4	C43	111.6(4)
O1W	Ba1	O23[2]	129.08(19)	N4	S4	C43	96.8(4)
O1W	Ba1	N1	72.2(2)	C11[1]	O11	Ba1	168.6(7)
O1W	Ba1	O4W[2]	78.85(19)	S1	O12	Ba2	146.5(4)
O2W	Ba1	Ba1[1]	37.14(16)	S1[3]	O13	Ba2	154.0(4)
O2W	Ba1	O22	69.52(18)	C21	O21	Ba2[1]	177.3(8)
O2W	Ba1	O23[2]	130.23(17)	S2	O22	Ba1	146.4(4)
O2W	Ba1	N1	75.82(16)	S2	O23	Ba1[3]	142.0(4)
O2W	Ba1	O1W	98.1(2)	C31	O31	Ba2	131.3(6)
O2W	Ba1	O4W[2]	151.07(14)	S1	N1	Ba1	134.0(4)
O3W	Ba1	Ba1[1]	154.15(18)	C11	N1	Ba1	114.3(5)
O3W	Ba1	O22	68.3(2)	C11	N1	S1	111.1(6)
O3W	Ba1	O23[2]	63.1(2)	C21	N2	S2	112.4(6)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3W	Ba1	N1	132.7(2)	C31	N3	S3	111.6(6)
O3W	Ba1	O1W	70.6(2)	C41	N4	S4	110.5(6)
O3W	Ba1	O2W	137.5(2)	O11[1]	C11	N1	125.2(9)
O3W	Ba1	O4W[2]	69.1(2)	O11[1]	C11	C12	121.9(9)
O3W	Ba1	O8W	134.5(2)	N1	C11	C12	112.8(7)
O4W[2]	Ba1	Ba1[1]	126.13(13)	C13	C12	C11	112.5(8)
O4W[2]	Ba1	O22	132.54(19)	C13	C12	C17	120.5(8)
O4W[2]	Ba1	O23[2]	66.04(19)	C17	C12	C11	126.9(8)
O4W[2]	Ba1	N1	75.9(2)	C12	C13	S1	106.3(6)
O8W	Ba1	Ba1[1]	36.83(16)	C12	C13	C14	122.9(9)
O8W	Ba1	O22	131.20(17)	C14	C13	S1	130.8(8)
O8W	Ba1	O23[2]	71.37(18)	C15	C14	C13	116.1(10)
O8W	Ba1	N1	77.40(16)	C14	C15	C16	121.3(10)
O8W	Ba1	O1W	149.59(15)	C17	C16	C15	122.1(11)
O8W	Ba1	O2W	74.0(2)	C16	C17	C12	117.0(10)
O8W	Ba1	O4W[2]	94.0(2)	O21	C21	N2	124.3(9)
O12	Ba2	O31	120.5(2)	O21	C21	C22	123.8(9)
O12	Ba2	O1W	75.7(2)	N2	C21	C22	111.9(8)
O12	Ba2	O4W	142.30(19)	C23	C22	C21	112.6(8)
O12	Ba2	O5W	134.3(2)	C23	C22	C27	121.2(10)
O12	Ba2	O6W	63.7(2)	C27	C22	C21	126.2(9)
O13	Ba2	O12	122.8(2)	C22	C23	S2	106.9(7)
O13	Ba2	O31	115.4(2)	C22	C23	C24	123.3(9)
O13	Ba2	O1W	144.5(2)	C24	C23	S2	129.8(8)
O13	Ba2	O4W	73.1(2)	C23	C24	C25	117.1(10)
O13	Ba2	O5W	63.3(2)	C24	C25	C26	119.6(11)
O13	Ba2	O6W	69.1(2)	C27	C26	C25	122.5(10)
O21[1]	Ba2	O12	70.0(2)	C22	C27	C26	116.3(10)
O21[1]	Ba2	O13	73.2(2)	O31	C31	N3	123.8(8)
O21[1]	Ba2	O31	143.1(2)	O31	C31	C32	123.2(8)
O21[1]	Ba2	O1W	88.3(2)	N3	C31	C32	112.9(7)
O21[1]	Ba2	O4W	85.4(2)	C33	C32	C31	111.9(8)
O21[1]	Ba2	O5W	136.5(2)	C33	C32	C37	118.9(9)
O21[1]	Ba2	O6W	81.9(2)	C37	C32	C31	129.3(8)
O1W	Ba2	O31	63.76(19)	C32	C33	S3	106.2(7)
O4W	Ba2	O31	65.33(18)	C34	C33	S3	130.2(8)
O4W	Ba2	O1W	75.47(19)	C34	C33	C32	123.6(9)
O5W	Ba2	O31	64.58(19)	C33	C34	C35	115.8(10)
O5W	Ba2	O1W	128.3(2)	C36	C35	C34	122.2(11)
O5W	Ba2	O4W	83.13(19)	C35	C36	C37	121.5(10)
O6W	Ba2	O31	134.98(18)	C36	C37	C32	118.0(10)
O6W	Ba2	O1W	139.2(2)	O41	C41	N4	123.0(8)
O6W	Ba2	O4W	142.1(2)	O41	C41	C42	122.2(8)
O6W	Ba2	O5W	81.9(2)	N4	C41	C42	114.8(8)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O7W	Ba2	O12	67.9(2)	C43	C42	C41	110.8(8)
O7W	Ba2	O13	127.6(3)	C43	C42	C47	120.4(8)
O7W	Ba2	O21[1]	137.5(2)	C47	C42	C41	128.8(9)
O7W	Ba2	O31	68.0(2)	C42	C43	S4	107.2(6)
O7W	Ba2	O1W	86.5(2)	C42	C43	C44	122.3(8)
O7W	Ba2	O4W	133.3(2)	C44	C43	S4	130.5(7)
O7W	Ba2	O5W	75.0(2)	C43	C44	C45	115.9(9)
O7W	Ba2	O6W	75.1(2)	C46	C45	C44	122.6(9)
O22	S2	O23	114.4(4)	C45	C46	C47	120.6(9)
O22	S2	N2	111.0(4)	C46	C47	C42	118.3(9)
O22	S2	C23	111.5(4)	Ba1	O1W	Ba2	136.7(3)
O23	S2	N2	110.6(4)	Ba1[1]	O2W	Ba1	105.7(3)
O23	S2	C23	111.7(4)	Ba1[3]	O4W	Ba2	138.2(2)
N2	S2	C23	96.2(4)	Ba1[1]	O8W	Ba1	106.3(3)

[1]1-x, y,1/2-z; [2]x,1+y, z; [3]x,-1+y, z

Table S11. Hydrogen bond parameters in $Ba(sac)_2 \cdot 4.5H_2O$

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1W	H1WA	O9W[1]	0.99	1.78	2.763(10)	171
O1W	H1WB	N3	0.99	1.94	2.861(11)	154
O2W	H2WA	N2	0.99	1.87	2.807(10)	156
O2W	H2WB	N2[2]	0.99	1.87	2.807(10)	156
O3W	H3WA	O33[1]	0.96	2.32	2.975(11)	124
O3W	H3WB	O32	0.95	1.92	2.837(10)	161
O4W	H4WA	N3	0.99	2.10	2.882(10)	135
O4W	H4WB	O9W	0.99	1.81	2.723(10)	153
O5W	H5WA	O11W	0.97	1.90	2.785(9)	149
O5W	H5WB	N4[3]	0.97	1.97	2.910(11)	162
O6W	H6WA	O42[3]	0.79	2.13	2.901(10)	166
O6W	H6WB	O43[4]	0.94	2.18	3.059(10)	155
O7W	H7WA	O10W[1]	0.99	1.79	2.778(9)	170
O7W	H7WB	N4[4]	0.87	2.09	2.925(13)	161
O8W	H8WA	N2[5]	0.99	1.86	2.793(10)	156
O8W	H8WB	N2[1]	0.99	1.86	2.793(10)	156
O9W	H9WA	O41	0.87	1.98	2.811(10)	160
O9W	H9WB	O5W	0.87	1.97	2.788(10)	156
O10W	H10A	O41[6]	0.87	2.00	2.702(9)	136
O10W	H10B	O41	0.87	1.86	2.702(9)	162
O11W	H11B	O31	0.87	2.16	3.023(9)	174

[1] x,1+y,z; [2]1-x,y,1/2-z; [3]-x,y,1/2-z; [4]-x,1+y,1/2-z; [5]1-x,1+y,1/2-z; [6]-x,y,1/2-z

Table S11. Analysis of short ring-ring interactions in $Ba(sac)_2 \cdot 4.5H_2O$

6-Membered Ring (1) C12 --> C13 --> C14 --> C15 --> C16 --> C17
6-Membered Ring (2) C22 --> C23 --> C24 --> C25 --> C26 --> C27
6-Membered Ring (3) C32 --> C33 --> C34 --> C35 --> C36 --> C37
6-Membered Ring (4) C42 --> C43 --> C44 --> C45 --> C46 --> C47

- Cg(I) = Plane number I (= ring number in () above)
- Alpha = Dihedral Angle between Planes I and J (°)
- Cg-Cg = Distance between ring Centroids (Å)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Å)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Å)

Cg(I)···Cg(J)	**Cg···Cg**	**Alpha**	**CgI_Perp**	**CgJ_Perp**
Cg1···Cg2 [1-x,1+y,1/2-z]	3.882(6)	3.3(5)	-3.540(5)	3.455(5)
Cg3···Cg4	3.821(6)	3.0(5)	3.624(4)	-3.692(4)
Cg3···Cg4 [x,-1+y,z]	3.737(6)	3.6(5)	-3.534(4)	3.453(4)