Electronic Supplementary Material for CrystEngComm

Electronic Supplementary Information

Diversity of binding of sulfate and nitrate anions with laterally asymmetric aza cryptands

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Table S1: H-bonding interactions of the sulfate-water-bisulfate adduct in complex **1**∗

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
OW2–H1W2···O8^{i}	1.945(19)	2.735(12)	132.5(11)
OW2···O18		2.675(12)	
O19–H19···O11^{ii}	1.83	2.623(5)	161
O6–H6···O9	1.78	2.599(6)	176
N1–H1···O4^{iii}	1.88	2.769(5)	166
N3–H3A···O13^{iv}	1.98	2.845(6)	160
N3–H3B···O12	2.05	2.864(5)	150
OW1–H2W1···O15^{iv}	1.922(10)	2.673(7)	164.7(12)
N5–H5A···O12	2.06	2.860(5)	148

Symmetry codes: (i) x,1/2-y,1/2+z; (ii)1-x,-1/2+y,3/2-z; (iii) x,-1+y,z; (iv) -x,-y,1-z.
∗Please refer to Figure S1 for atom designation.

Table S2: H-bonding interactions associated with $N(7)O_3^-$ and $N(8)O_3^-$ in complex **2**

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
OW1–H1W1···O7	2.11(3)	2.904(5)	168(10)
OW1–H2W1···O10	1.97(5)	2.826(4)	171 (4)
OW2–H1W2···OW1^{i}	1.938(12)	2.725(4)	151.9(13)
OW2–H2W2···O7	2.45(15)	3.014(5)	123 (12)
N4–H4B···O10	1.87	2.766(3)	172
N3–H3C···OW2^{i}	1.91	2.756(4)	157

Symmetry code: (i) -1-x,-y,-z.

Table S3: H-bonding interactions associated with external nitrates and water molecules in complex **3**∗

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
N3–H3C···OW1^{i}	1.84	2.727(8)	169
N5–H5B···O29^{ii}	2.15	2.950(9)	148
N5–H5B···O30^{ii}	2.20	3.028(7)	152
N10–H10D···OW3^{iii}	1.46	2.320(17)	159

N4–H4B···O21	2.00	2.896(6)	172
N8–H8A···O21^{iii}	2.04	2.902(6)	159
N9–H9A···O13	1.87	2.740(6)	164
N10–H10D···OW3^{iii}	1.46	2.320(17)	159
OW2 ···O24		2.742(12)	
OW2 ···O27		2.853(19)	
OW2 ···O26		2.815(12)	
OW2 ···OW1		2.696(12)	
OW1 ···OW3		2.768(18)	
OW3 ···OW4		2.714(22)	
OW4 ···O28		2.948(16)	
OW4 ···O17		2.696(12)	
OW3 ···O25		2.789(19)	

Symmetry codes: (i) -1+x,y,z; (ii) 1-x,-y,-z; (iii) x,1/2-y,1/2+z.
∗Please refer to Figure S2 for atom designation.

Table S4: H-bonding Interactions in Complex **5**

H-bonding interactions associated with $N(7)O^{3-}$ in complex **5**

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
N3–H3D···O9^{i}	1.97	2.845(6)	163
N5–H5A···O8	1.95	2.820(6)	164

H-bonding interactions associated with $N(8)O_3^-$, $HS(1)O_4^-$ and Ow1 in complex **5**∗

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
OW1···OW1'		2.783(11)	
OW1···O14		2.766(14)	
O13–H13···O12	2.08	2.753(10)	139
N4–H4B···O16^{ii}	2.02	2.822(9)	148

OW1 is related to OW1' with the symmetry opreation 3-x, -y, -1-z. Other Symmetry codes: (i) -1+x,y,z; (ii) 2-x,-y,-z.
∗Please refer to Figure S6 for atom designation.

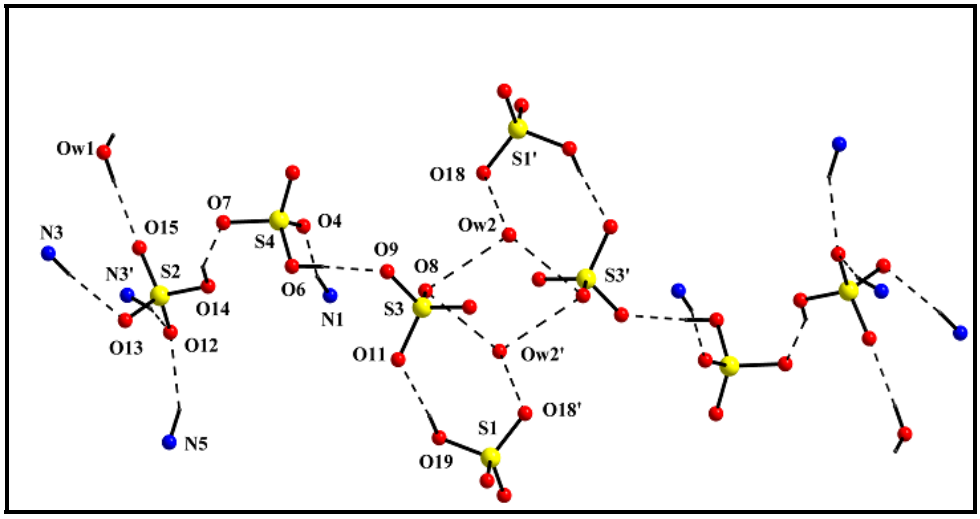

Fig. S1: A view of a discrete H-bonded sulfate-water-bisulfate adduct formed outside the molecular capsule in 1. Symmetry codes: (i) 1-x, -y, 2-z; (ii) 1-x, 1-y, 1-z; (iii) 1-x, -y, 2-z; (iv) -x, -y, 1-z.

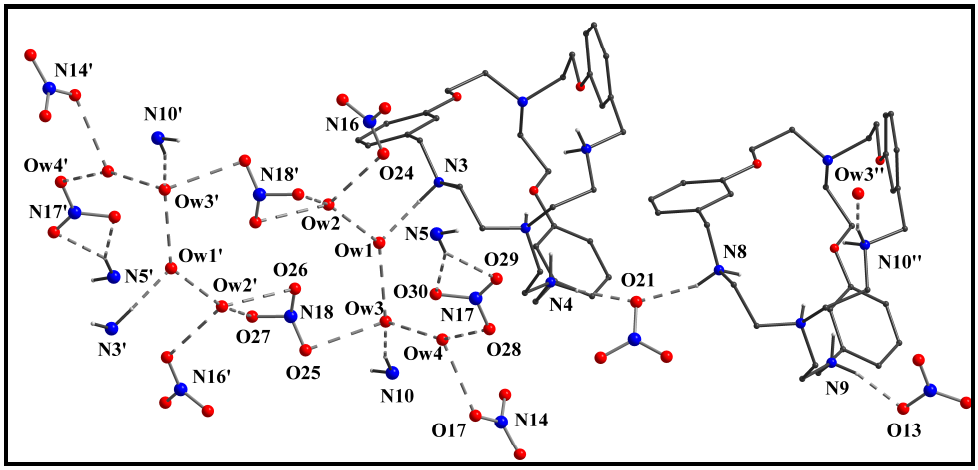

Fig. S2: A diagram depicting the H-bonding interactions among the six external nitrate ions and four external water molecules along with its contacts to the cryptand moieties in **3** (encapsulated nitrates and H atoms that do not take part in H-bonding are omitted for clarity). Symmetry codes: (i) -1+x, y, z; (ii) 1+x, y, z; (iii) 1-x, -y, -z; (iv) x, 0.5-y, 0.5+z; (v) x, 0.5-y, -0.5+z; (vi) 2-x, -y, -z; (vii) -x, -y, -z; (viii) -1+x, 0.5-y, -0.5+z; (ix) 1-x, 1-y, 1-z.

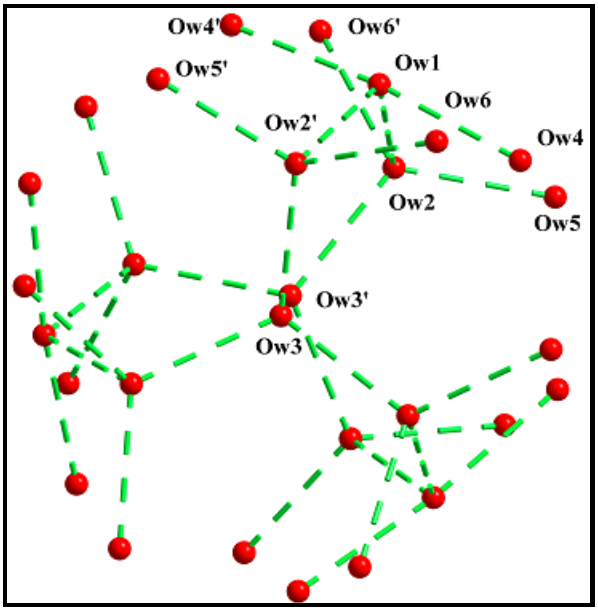

Fig. S3: A clear view of the 3-fold symmetric discrete $(H_2O)_{29}$ cluster. Symmetry codes: (i) -0.25+x, 0.25+y, 0.75-z; (ii) 2.25-x, 1.25-y, 1.25-z.

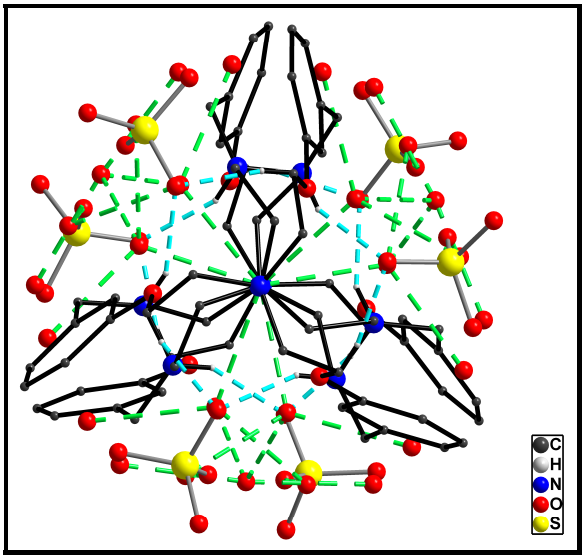

Fig. S4: A representation of the $(H_2O)_{29}$ cluster along with sulfate ions and cryptand moieties viewed down C3 axis that joins the two bridgehead N atoms of the cryptand (non-covalent interactions among the water cluster are shown in green, whereas interactions of sulfates with cryptand moieties are shown in cyan).

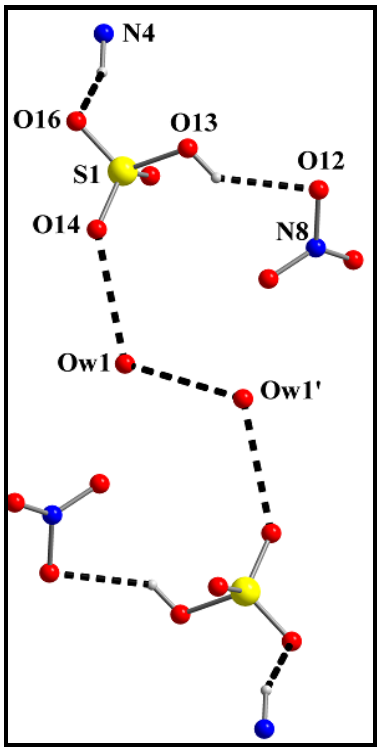

Fig. S5: A representation of the 'S' shaped nitrate-bisulfate-water adduct along with its immediate H-bonding interactions in complex **5**. Symmetry code: 3-x, -y, -1-z.