Electronic Supplementary Information (ESI) for CrystEngComm

Ca^{2+} metal ion adducts with cytosine, cytidine and cytidine 5'-monophosphate. A comprehensive study of calcium reactivity towards building units of nucleic acids.

Nadia Marino, Donatella Armentano,* Claudia Zanchini, and Giovanni De Munno

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 12/C, 87036 Arcavacata di Rende (CS), Italy

Contents

Pages S2	**Tables S1-S3 (Selected bond lengths and angles for compounds 1-3)**
Pages S3	**Table S4 (Selected bond lengths and angles for compound 4)**
Pages S4	**Table S5 (Selected bond lengths and angles for compound 5)**
Pages S5	**Table S6 (Selected bond lengths and angles for compound 6)**
Pages S6	**Tables S7-S9 (Hydrogen bonds for compounds 1-3)**
Pages S7	**Tables S10-S11 (Hydrogen bonds for compounds 5-6)**

Table S1. Selected bond lengths [Å] and angles [°] for **1**.[a]

Ca(1)-O(2)	Ca(1)-O(2W)
Ca(1)-O(1W)	
O(2)-Ca(1)-O(2a)	O(2)-Ca(1)-O(2W)
O(2)-Ca(1)-O(1W)#1	O(1Wa)-Ca(1)-O(2W)
O(2)-Ca(1)-O(1W)	O(1W)-Ca(1)-O(2W)
O(2a)-Ca(1)-O(1W)	O(2)-Ca(1)-O(2Wa)
O(1Wa)-Ca(1)-O(1W)	O(2W)-Ca(1)-O(2Wa)

[a] Symmetry codes: (a) -x,-y,-z.

Table S2 Selected bond lengths [Å] and angles [°] for **2**.[a]

Ca(1)-O(2)#1	Ca(1)-O(5P)	2.521(3)
Ca(1)-O(1W)	Ca(1)-O(2)	2.540(3)
Ca(1)-O(2W)	Ca(1)-N(3)	2.555(3)
Ca(1)-O(1P)	Ca(1)-O(6P)	2.722(4)

O(2)#1-Ca(1)-O(1W)	O(2)#1-Ca(1)-N(3)
O(2)#1-Ca(1)-O(2W)	O(1W)-Ca(1)-N(3)
O(1W)-Ca(1)-O(2W)	O(2W)-Ca(1)-N(3)
O(2)#1-Ca(1)-O(1P)	O(1P)-Ca(1)-N(3)
O(1W)-Ca(1)-O(1P)	O(5P)-Ca(1)-N(3)
O(2W)-Ca(1)-O(1P)	O(2)-Ca(1)-N(3)
O(2)#1-Ca(1)-O(5P)	O(2)#1-Ca(1)-O(6P)
O(1W)-Ca(1)-O(5P)	O(1W)-Ca(1)-O(6P)
O(2W)-Ca(1)-O(5P)	O(2W)-Ca(1)-O(6P)
O(1P)-Ca(1)-O(5P)	O(1P)-Ca(1)-O(6P)
O(2)#1-Ca(1)-O(2)	O(5P)-Ca(1)-O(6P)
O(1W)-Ca(1)-O(2)	O(2)-Ca(1)-O(6P)
O(2W)-Ca(1)-O(2)	N(3)-Ca(1)-O(6P)
O(1P)-Ca(1)-O(2)	Ca(1)#1-O(2)-Ca(1)
O(5P)-Ca(1)-O(2)	

[a] Symmetry codes: #1 -x,-y,-z

Table S3 Selected bond lengths [Å] and angles [°] for **3**.[a]

Ca(1)-O(2)	Ca(1)-O(21)
Ca(1)-O(1W)	Ca(1)-N(31)
Ca(1)-O(2W)	Ca(1)-Cl(1)

O(2)-Ca(1)-O(1W)	O(2W)-Ca(1)-O(21)
O(2)-Ca(1)-O(2W)	O(21)#1-Ca(1)-O(21)
O(1W)-Ca(1)-O(2W)	O(2)-Ca(1)-N(31)
O(2)-Ca(1)-O(21)#1	O(1W)-Ca(1)-N(31)
O(1W)-Ca(1)-O(21)#1	O(2W)-Ca(1)-N(31)
O(2W)-Ca(1)-O(21)#1	O(21)#1-Ca(1)-N(31)
O(2)-Ca(1)-O(21)	O(21)-Ca(1)-N(31)
O(1W)-Ca(1)-O(21)	

[a] Symmetry codes: #1 #1 -x,-y,-z+1

Table S4 Selected bond lengths [Å] and angles [°] for **4**.

Ca(1)-O(3')	Ca(2)-O(7W)
Ca(1)-O(3W)	Ca(2)-O(8W)
Ca(1)-O(2')	Ca(2)-O(5W)
Ca(1)-O(3'1)	Ca(2)-O(3'2)
Ca(1)-O(4W)	Ca(2)-O(2'3)
Ca(1)-O(1W)	Ca(2)-O(6W)
Ca(1)-O(2W)	Ca(2)-O(3'3)
Ca(1)-O(2'1)	Ca(2)-O(2'2)
O(3')-Ca(1)-O(3W)	O(7W)-Ca(2)-O(5W)
O(3')-Ca(1)-O(2')	O(8W)-Ca(2)-O(5W)
O(3W)-Ca(1)-O(2')	O(7W)-Ca(2)-O(3'2)
O(3')-Ca(1)-O(3'1)	O(8W)-Ca(2)-O(3'2)
O(3W)-Ca(1)-O(3'1)	O(5W)-Ca(2)-O(3'2)
O(2')-Ca(1)-O(3'1)	O(7W)-Ca(2)-O(2'3)
O(3')-Ca(1)-O(4W)	O(8W)-Ca(2)-O(2'3)
O(3W)-Ca(1)-O(4W)	O(5W)-Ca(2)-O(2'3)
O(2')-Ca(1)-O(4W)	O(3'2)-Ca(2)-O(2'3)
O(3'1)-Ca(1)-O(4W)	O(7W)-Ca(2)-O(6W)
O(3')-Ca(1)-O(1W)	O(8W)-Ca(2)-O(6W)
O(3W)-Ca(1)-O(1W)	O(5W)-Ca(2)-O(6W)
O(2')-Ca(1)-O(1W)	O(3'2)-Ca(2)-O(6W)
O(3'1)-Ca(1)-O(1W)	O(2'3)-Ca(2)-O(6W)
O(4W)-Ca(1)-O(1W)	O(7W)-Ca(2)-O(3'3)
O(3')-Ca(1)-O(2W)	O(8W)-Ca(2)-O(3'3)
O(3W)-Ca(1)-O(2W)	O(5W)-Ca(2)-O(3'3)
O(2')-Ca(1)-O(2W)	O(3'2)-Ca(2)-O(3'3)
O(3'1)-Ca(1)-O(2W)	O(2'3)-Ca(2)-O(3'3)
O(4W)-Ca(1)-O(2W)	O(6W)-Ca(2)-O(3'3)
O(1W)-Ca(1)-O(2W)	O(7W)-Ca(2)-O(2'2)
O(3')-Ca(1)-O(2'1)	O(8W)-Ca(2)-O(2'2)
O(3W)-Ca(1)-O(2'1)	O(5W)-Ca(2)-O(2'2)
O(2')-Ca(1)-O(2'1)	O(3'2)-Ca(2)-O(2'2)
O(3'1)-Ca(1)-O(2'1)	O(2'3)-Ca(2)-O(2'2)
O(4W)-Ca(1)-O(2'1)	O(6W)-Ca(2)-O(2'2)
O(1W)-Ca(1)-O(2'1)	O(3'3)-Ca(2)-O(2'2)
O(2W)-Ca(1)-O(2'1)	O(7W)-Ca(2)-O(8W)

Table S5 Selected bond lengths [Å] and angles [°] for **5**.

Ca(1)-O(3W)	2.386(2)	Ca(2)-O(6W)	2.416(2)
Ca(1)-O(1W)		Ca(2)-O(2'3)	
Ca(1)-O(2'1)		Ca(2)-O(7W)	
Ca(1)-O(2W)		Ca(2)-O(5W)	
Ca(1)-O(2')		Ca(2)-O(2'2)	
Ca(1)-O(4W)		Ca(2)-O(8W)	
Ca(1)-O(3')		Ca(2)-O(3'2)	
Ca(1)-O(3'1)		Ca(2)-O(3'3)	
O(3W)-Ca(1)-O(1W)		O(6W)-Ca(2)-O(2'3)	
O(3W)-Ca(1)-O(2'1)		O(6W)-Ca(2)-O(7W)	
O(1W)-Ca(1)-O(2'1)		O(2'3)-Ca(2)-O(7W)	
O(3W)-Ca(1)-O(2W)		O(6W)-Ca(2)-O(5W)	
O(1W)-Ca(1)-O(2W)		O(2'3)-Ca(2)-O(5W)	
O(2'1)-Ca(1)-O(2W)		O(7W)-Ca(2)-O(5W)	
O(3W)-Ca(1)-O(2')		O(6W)-Ca(2)-O(2'2)	
O(1W)-Ca(1)-O(2')		O(2'3)-Ca(2)-O(2'2)	
O(2'1)-Ca(1)-O(2')		O(7W)-Ca(2)-O(2'2)	
O(2W)-Ca(1)-O(2')		O(5W)-Ca(2)-O(2'2)	
O(3W)-Ca(1)-O(4W)		O(6W)-Ca(2)-O(8W)	
O(1W)-Ca(1)-O(4W)		O(2'3)-Ca(2)-O(8W)	
O(2'1)-Ca(1)-O(4W)		O(7W)-Ca(2)-O(8W)	
O(2W)-Ca(1)-O(4W)		O(5W)-Ca(2)-O(8W)	
O(2')-Ca(1)-O(4W)		O(2'2)-Ca(2)-O(8W)	
O(3W)-Ca(1)-O(3')		O(6W)-Ca(2)-O(3'2)	
O(1W)-Ca(1)-O(3')		O(2'3)-Ca(2)-O(3'2)	
O(2'1)-Ca(1)-O(3')		O(7W)-Ca(2)-O(3'2)	
O(2W)-Ca(1)-O(3')		O(5W)-Ca(2)-O(3'2)	
O(2')-Ca(1)-O(3')		O(2'2)-Ca(2)-O(3'2)	
O(4W)-Ca(1)-O(3')		O(8W)-Ca(2)-O(3'2)	
O(3W)-Ca(1)-O(3'1)		O(6W)-Ca(2)-O(3'3)	
O(1W)-Ca(1)-O(3'1)		O(2'3)-Ca(2)-O(3'3)	
O(2'1)-Ca(1)-O(3'1)		O(7W)-Ca(2)-O(3'3)	
O(2W)-Ca(1)-O(3'1)		O(5W)-Ca(2)-O(3'3)	
O(2')-Ca(1)-O(3'1)		O(2'2)-Ca(2)-O(3'3)	
O(4W)-Ca(1)-O(3'1)		O(8W)-Ca(2)-O(3'3)	
O(3')-Ca(1)-O(3'1)		O(3'2)-Ca(2)-O(3'3)	

Table S6 Selected bond lengths [Å] and angles [°] for **6**.

Ca(1)-O(21)	Ca(2)-O(3'1)
Ca(1)-O(5W)	Ca(2)-O(11W)
Ca(1)-O(1W)	Ca(2)-O(9W)
Ca(1)-O(3')	Ca(2)-O(7W)
Ca(1)-O(3W)	Ca(2)-O(8W)
Ca(1)-O(4W)	Ca(2)-O(10W)
Ca(1)-O(2W)	Ca(2)-O(2'1)
Ca(1)-O(2')	Ca(2)-O(6W)
O(21)-Ca(1)-O(5W)	O(3'1)-Ca(2)-O(11W)
O(21)-Ca(1)-O(1W)	O(3'1)-Ca(2)-O(9W)
O(5W)-Ca(1)-O(1W)	O(11W)-Ca(2)-O(9W)
O(21)-Ca(1)-O(3')	O(3'1)-Ca(2)-O(7W)
O(5W)-Ca(1)-O(3')	O(11W)-Ca(2)-O(7W)
O(1W)-Ca(1)-O(3')	O(9W)-Ca(2)-O(7W)
O(21)-Ca(1)-O(3W)	O(3'1)-Ca(2)-O(8W)
O(5W)-Ca(1)-O(3W)	O(11W)-Ca(2)-O(8W)
O(1W)-Ca(1)-O(3W)	O(9W)-Ca(2)-O(8W)
O(3')-Ca(1)-O(3W)	O(7W)-Ca(2)-O(8W)
O(21)-Ca(1)-O(4W)	O(3'1)-Ca(2)-O(10W)
O(5W)-Ca(1)-O(4W)	O(11W)-Ca(2)-O(10W)
O(1W)-Ca(1)-O(4W)	O(9W)-Ca(2)-O(10W)
O(3')-Ca(1)-O(4W)	O(7W)-Ca(2)-O(10W)
O(3W)-Ca(1)-O(4W)	O(8W)-Ca(2)-O(10W)
O(21)-Ca(1)-O(2W)	O(3'1)-Ca(2)-O(2'1)
O(5W)-Ca(1)-O(2W)	O(11W)-Ca(2)-O(2'1)
O(1W)-Ca(1)-O(2W)	O(9W)-Ca(2)-O(2'1)
O(3')-Ca(1)-O(2W)	O(7W)-Ca(2)-O(2'1)
O(3W)-Ca(1)-O(2W)	O(8W)-Ca(2)-O(2'1)
O(4W)-Ca(1)-O(2W)	O(10W)-Ca(2)-O(2'1)
O(21)-Ca(1)-O(2')	O(3'1)-Ca(2)-O(6W)
O(5W)-Ca(1)-O(2')	O(11W)-Ca(2)-O(6W)
O(1W)-Ca(1)-O(2')	O(9W)-Ca(2)-O(6W)
O(3')-Ca(1)-O(2')	O(7W)-Ca(2)-O(6W)
O(3W)-Ca(1)-O(2')	O(8W)-Ca(2)-O(6W)
O(4W)-Ca(1)-O(2')	O(10W)-Ca(2)-O(6W)
O(2W)-Ca(1)-O(2')	O(2'1)-Ca(2)-O(6W)

Table S7. Hydrogen bonds for **1** [Å and °]. [a]

D-H...A	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1W1)...O(21)#2	1.870(14)	2.807(5)	170(4)
O(1W)-H(1W2)...N(31)#3	1.879(19)	2.789(5)	159(4)
O(2W)-H(2W1)...O(21)#3	1.92(3)	2.775(5)	149(5)
O(2W)-H(2W2)...O(3W)	1.80(4)	2.646(7)	147(6)
N(1)-H(1)...O(2W)#1	2.38	3.170(6)	152.1
N(4)-H(4A)...O(21)	2.15	3.008(7)	172.1
N(4)-H(4B)...O(4P1)#4	2.19	3.02(2)	163.0
N(11)-H(11)...N(3)	1.96	2.823(6)	177.1
N(41)-H(41A)...O(3P1)#5	2.28	2.934(16)	133.3
N(41)-H(41B)...O(2P1)	2.09	2.942(17)	169.2
N(41)-H(41B)...O(2P)	2.32	3.136(12)	157.8

[a] Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z #2 x,y+1,z #3 -x+1,-y-1,-z #4 x,y,z-1 #5 -x+1,-y-2,-z+1

Table S8 Hydrogen bonds in **2**[a] [Å and °]. [a]

D-H···A	d(H···A)	d(D···A)	<(DHA)
O(1W)-H(1W1)...O(7P)#2	2.06(3)	2.895(5)	145(5)
O(1W)-H(1W2)...O(6P)#3	2.50(3)	3.383(5)	155(5)
O(2W)-H(2W1)...O(8P)#1	2.18(4)	3.033(5)	148(5)
O(2W)-H(2W2)...O(5P)#2	2.16(2)	3.108(5)	171(6)
N(1)-H(1)...O(2P)#4	2.16	2.969(5)	157.2
N(4)-H(4A)...O(1P)	2.23	3.000(5)	149.1
N(4)-H(4B)...O(4P)#5	2.39	3.118(6)	142.3

[a] Symmetry codes: #1 -x,-y,-z #2 x-1,y,z #3 -x,-y,-z+1 #4 x,y,z-1 #5 -x+1,-y+1,-z

Table S9 Hydrogen bonds in **3**[a] [Å and °]. [a]

D-H···A	d(H···A)	d(D···A)	<(DHA)
O(1W)-H(1W1)...Cl(2)#2	2.214(19)	3.155(4)	170(6)
O(1W)-H(1W2)...Cl(2)	2.145(14)	3.098(4)	178(7)
O(2W)-H(2W1)...Cl(2)#1	2.24(2)	3.165(4)	165(5)
O(2W)-H(2W2)...Cl(1)#3	2.258(18)	3.193(4)	168(5)
N(1)-H(1)...Cl(1)	2.63	3.427(4)	153.9
N(4)-H(4A)...Cl(1)#4	2.77	3.601(5)	162.2
N(11)-H(11)...O(2)#1	2.09	2.855(5)	148.2
N(11)-H(11)...N(3)#1	2.40	3.179(5)	151.4
N(41)-H(41A)...Cl(1)	2.66	3.472(5)	158.5
N(41)-H(41B)...Cl(2)#5	2.51	3.346(4)	164.8

[a] Symmetry codes: #1 -x,-y,-z+1 #2 -x,-y,-z #3 -x,-y+1,-z+1 #4 x-1,y,z #5 x+1,y,z.

Table S10. Hydrogen bonds for **5** [Å and °]. [a]

D-H...A	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1W1)...Cl(1)#3	2.39(3)	3.177(2)	140(4)
O(1W)-H(1W2)...O(9W)	1.902(16)	2.821(3)	164(4)
O(2W)-H(2W1)...Cl(1)#3	2.288(13)	3.229(2)	167(4)
O(2W)-H(2W2)...O(22)#1	1.94(2)	2.826(3)	152(3)
O(3W)-H(3W2)...O(23)#4	1.832(15)	2.757(3)	164(4)
O(4W)-H(4W1)...O(2)	1.867(19)	2.768(3)	155(3)
O(4W)-H(4W2)...Cl(2)	2.50(2)	3.384(2)	154(3)
O(3')-H(3A)...O(21)	1.854(11)	2.809(3)	178(4)
O(5')-H(5'A)...O(10W)	1.90	2.706(4)	168.6
N(4)-H(4A)...Cl(1)#5	2.59	3.393(3)	155.8
N(4)-H(4B)...Cl(3)#6	2.30	3.152(3)	169.4
O(2')-H(2A)...N(32)#1	1.829(14)	2.768(3)	167(4)
O(3'1)-H(31A)...O(12W)	1.835(18)	2.749(3)	159(4)
O(5'1)-H(5'1)...O(10W)#7	1.98	2.736(4)	152.4
N(41)-H(41B)...Cl(3)#8	2.41	3.233(3)	159.7
O(2'1)-H(21A)...N(33)#4	1.758(13)	2.709(3)	170(4)
O(5W)-H(5W1)...O(23)	1.92(3)	2.784(3)	149(4)
O(5W)-H(5W2)...O(15W)	2.162(15)	3.120(10)	175(5)
O(6W)-H(6W1)...Cl(2)#2	2.38(2)	3.242(2)	149(3)
O(6W)-H(6W2)...O(2)#2	1.817(16)	2.743(3)	163(4)
O(7W)-H(7W1)...Cl(1)#9	2.362(14)	3.306(2)	169(3)
O(7W)-H(7W2)...O(11W)#10	2.02(3)	2.843(4)	144(4)
O(8W)-H(8W1)...O(21)#9	2.03(3)	2.885(3)	148(4)
O(8W)-H(8W2)...O(11W)#10	2.07(2)	2.943(4)	152(4)
O(3'2)-H(32A)...O(13W)	1.842(15)	2.788(6)	168(4)
O(5'2)-H(5'2)...Cl(2)	2.50	3.306(4)	168.5
N(42)-H(42B)...Cl(4)#11	2.51	3.319(3)	158.0
O(2'2)-H(22A)...N(3)#2	1.800(16)	2.734(3)	163(4)
O(3'3)-H(33A)...O(22)	1.913(16)	2.837(3)	163(4)
O(5'3)-H(5'3)...O(12W)#2	1.97	2.781(4)	172.7
N(43)-H(43A)...O(9W)#9	2.09	2.933(4)	166.7
N(43)-H(43B)...O(5'2)#7	2.05	2.892(4)	164.8
O(2'3)-H(23A)...N(31)#9	1.845(17)	2.762(3)	162(4)
O(9W)-H(9W1)...O(6W)#12	2.08(2)	2.980(3)	157(4)
O(9W)-H(9W2)...Cl(4)	2.18(2)	3.088(3)	159(4)
O(10W)-H(101)...Cl(1)	2.268(19)	3.219(3)	168(7)
O(11W)-H(111)...O(14W)	2.24(3)	3.132(11)	153(5)
O(11W)-H(112)...Cl(4)	2.168(19)	3.126(4)	168(6)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 x-1,y,z #3 x+1,y+1,z+1 #4 x,y,z-1
#5 x+1,y,z+1 #6 x,y-1,z-1 #7 x,y+1,z+1 #8 x-1,y,z-1
#9 x,y,z+1 #10 x-1,y-1,z #11 x-1,y-1,z-1
#12 x+1,y+1,z

Table S11. Hydrogen bonds for **6** [Å and °]. [a]

D-H...A	d(H...A)	d(D...A)	<(DHA)
O(2')-H(2A)...O(1P)#1	1.75(2)	2.629(3)	152(3)
O(3')-H(3A)...O(3P)#2	1.73(2)	2.609(2)	151(4)
O(3'1)-H(31A)...O(5P)#3	1.77(3)	2.577(3)	140(4)
N(4)-H(4A)...O(6P)#4	2.10	2.943(3)	167.0
N(4)-H(4B)...O(15W)#5	2.05	2.892(4)	167.6
N(41)-H(41B)...O(12W)#6	2.08	2.917(3)	163.0
N(41)-H(41A)...O(1P)#7	2.07	2.899(3)	162.2

Symmetry transformations used to generate equivalent atoms:
#1 -x,y-1/2,-z+1 #2 -x,y+1/2,-z+1 #3 -x+1,y-1/2,-z
#4 x,y,z+1 #5 -x+1,y-1/2,-z+1 #6 -x+1,y+1/2,-z+1
#7 x+1,y,z