Electronic Supplementary Information

Binding of various anions in laterally non-symmetric aza-oxa cryptands through H-bonds: characterization of water clusters of different nuclearity

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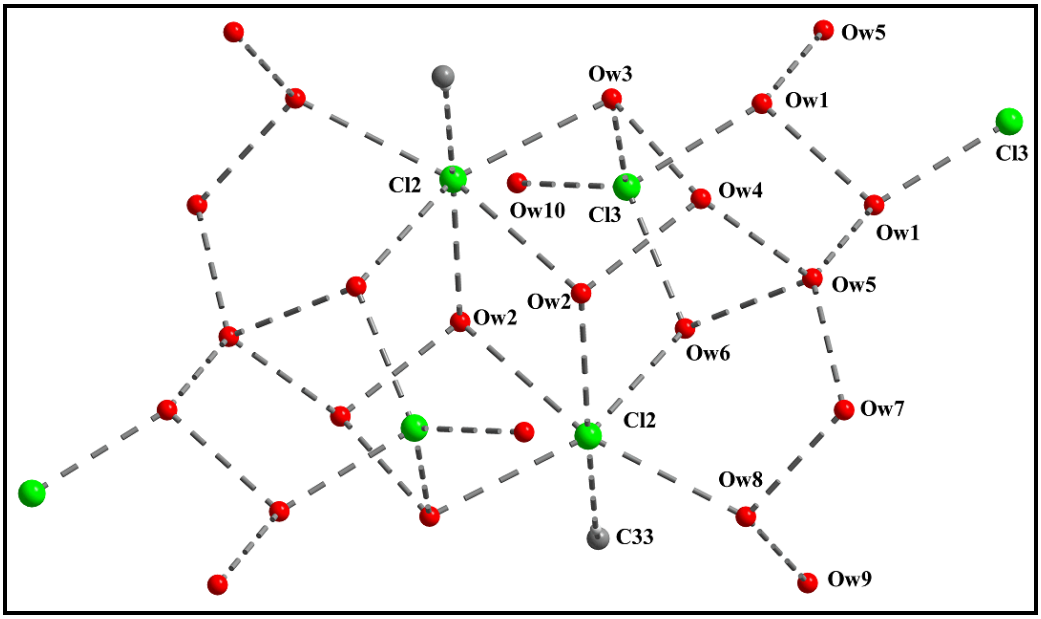

Figure S1: Formation of an infinite water-chloride chain through an intricate array of H-bonding interactions with a repeating unit of 20 water molecules and 4 chloride ions running along the crystallographic *a* axis.

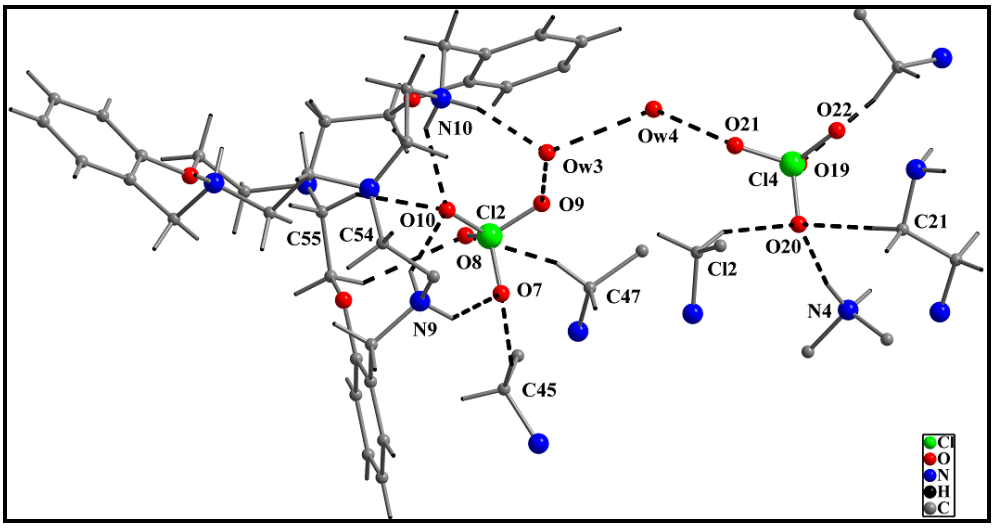

Figure S2: Depiction of the water dimer (Ow3…Ow4) connecting two perchlorate anions ($Cl(4)O_4^-$ and $Cl(2)O_4^-$) to from a discrete water-perchlorate adduct with its immediate H-bonding coordination environment.

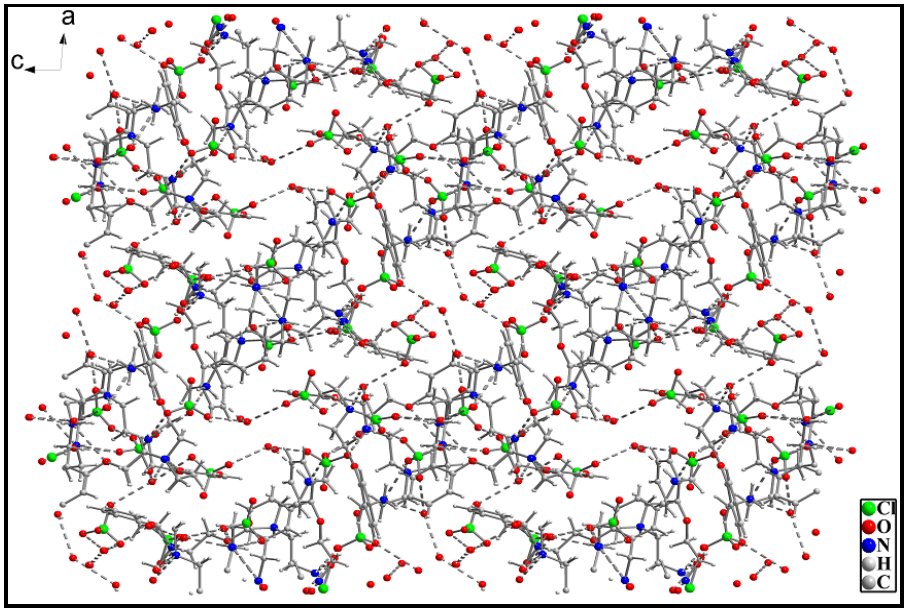

Figure S3: Representation of a 3-D packing diagram of complex **2** exhibiting various H-bonding interactions among the perchlorate anions, the lattice water molecules and the protonated receptor moieties.

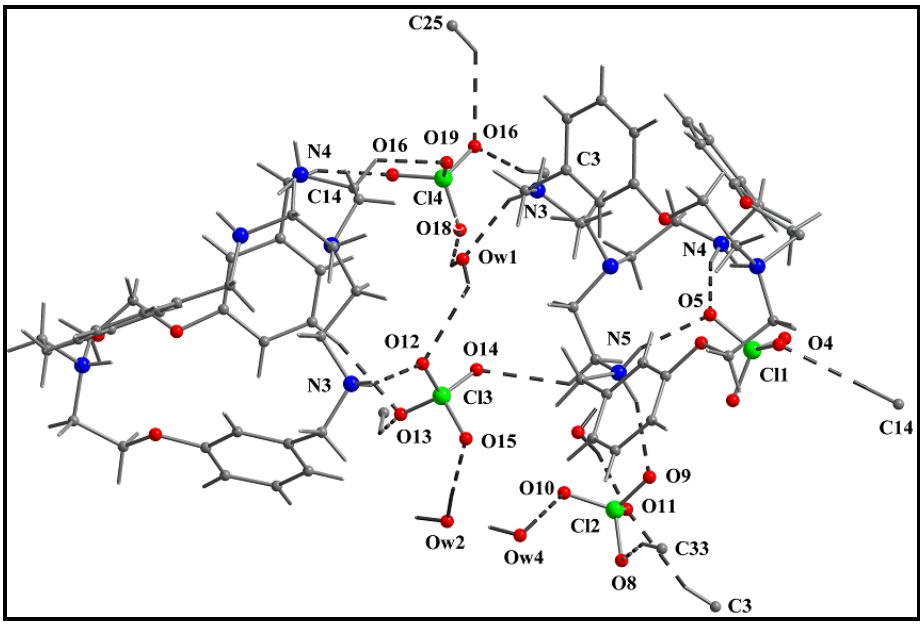

Figure S4: The coordination environment of all of the four perchlorate ions present in complex **3**.

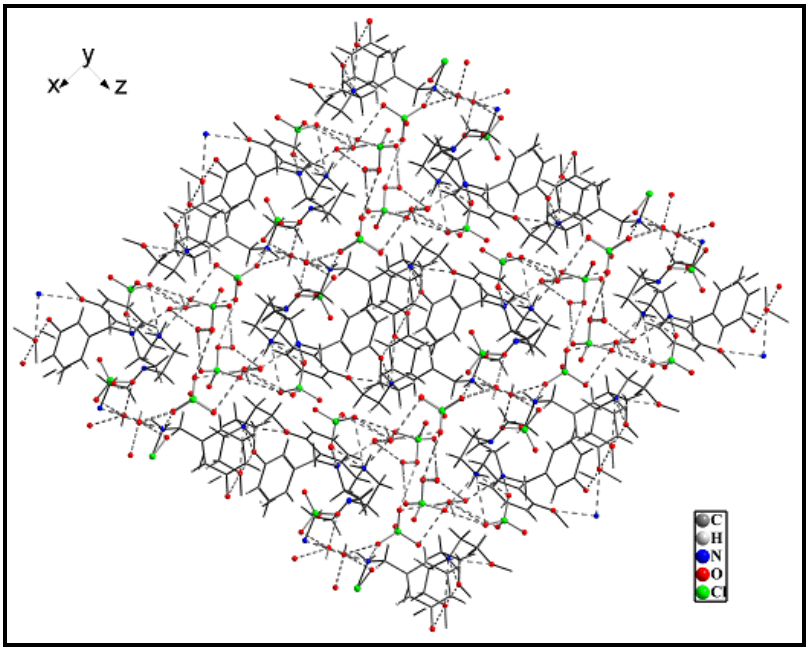

Figure S5: A packing diagram of complex **3** depicting three-dimensional H-bonded supramolecular array involving the protonated cryptand moieties, the perchlorate anions, and trimeric water clusters, along with several of their molecular interactions.

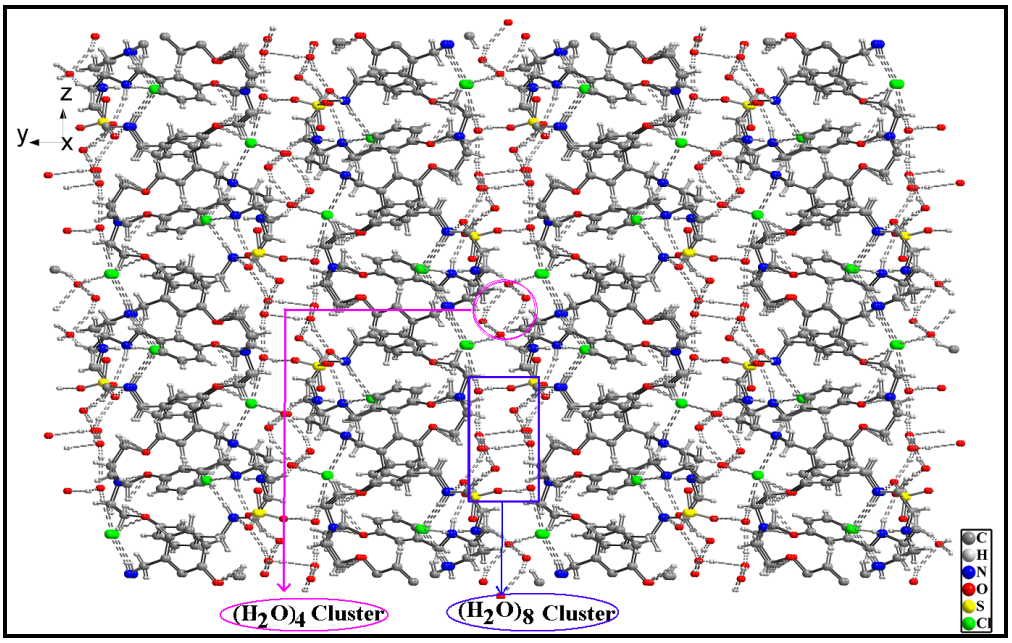

Figure S6: A representation of the 3-D H-bonded supramolecular network of complex **4** involving the protonated cryptand moiety, chloride and sulfate anions, the tetrameric and octameric water clusters.

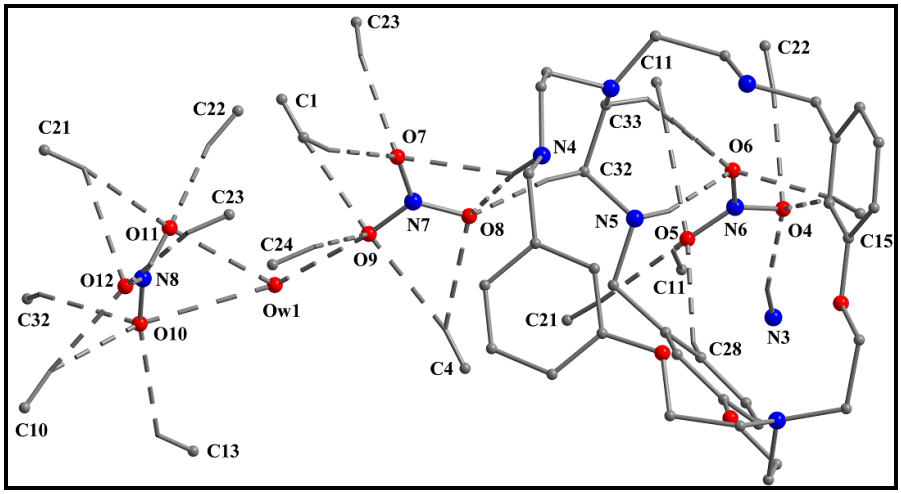

Figure S7: A diamond diagram depicting the H-bonding coordination environment of all the two external nitrates of complex **5**.

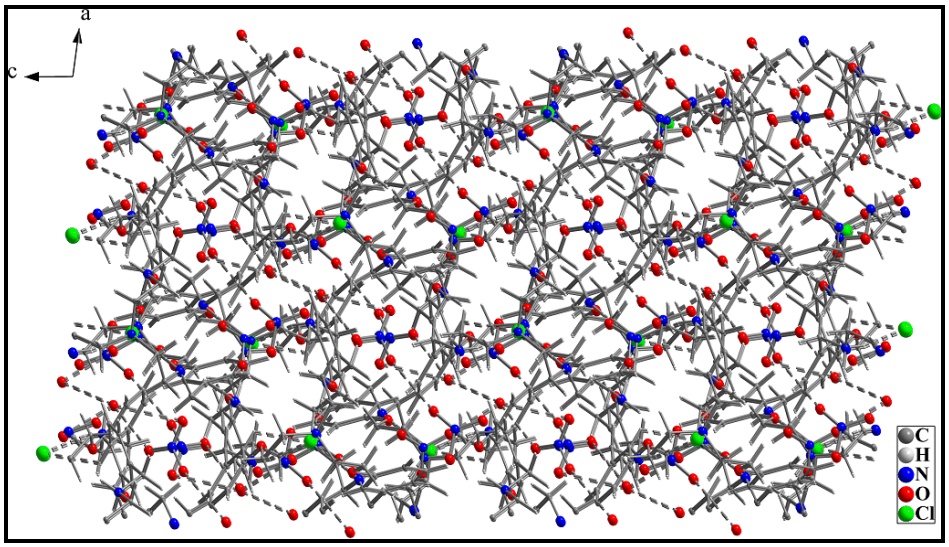

Figure S8: The packing diagram of complex **5** viewed down the C_3 axis.

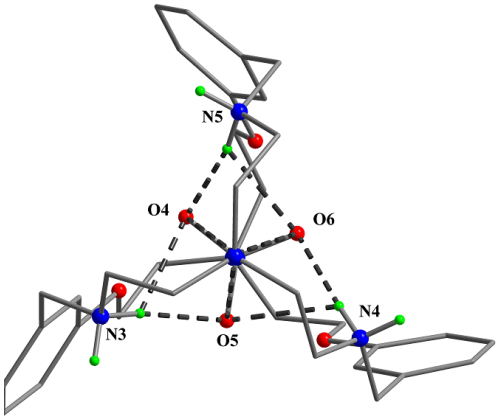

Figure S9: Representation of the encapsulated nitrate within the cavity of $\mathbf{L_m}$ present in complex **6**.

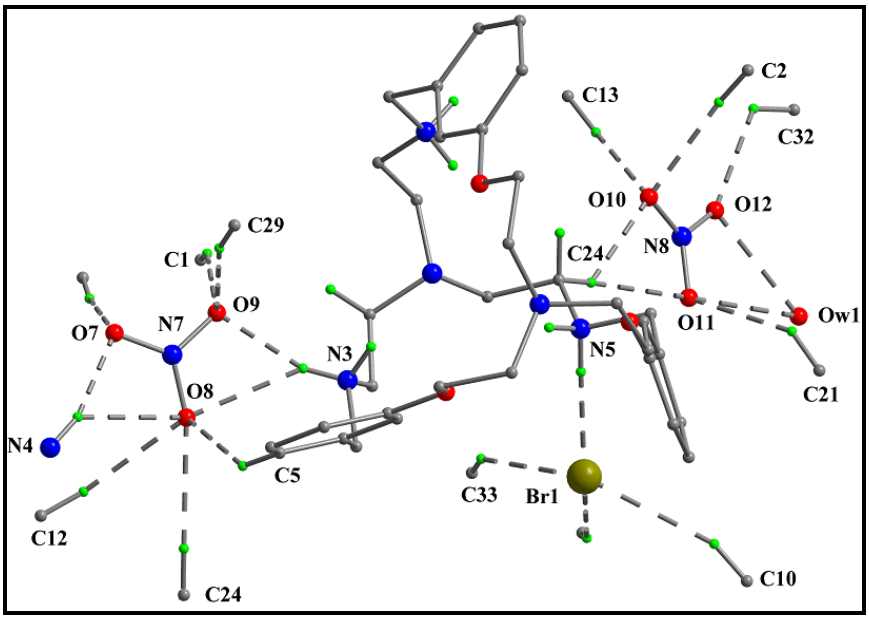

Figure S10: Depiction of various H-bonding interaction around the nitrate ions, the bromide ion and the lattice water molecule present in complex **6**.

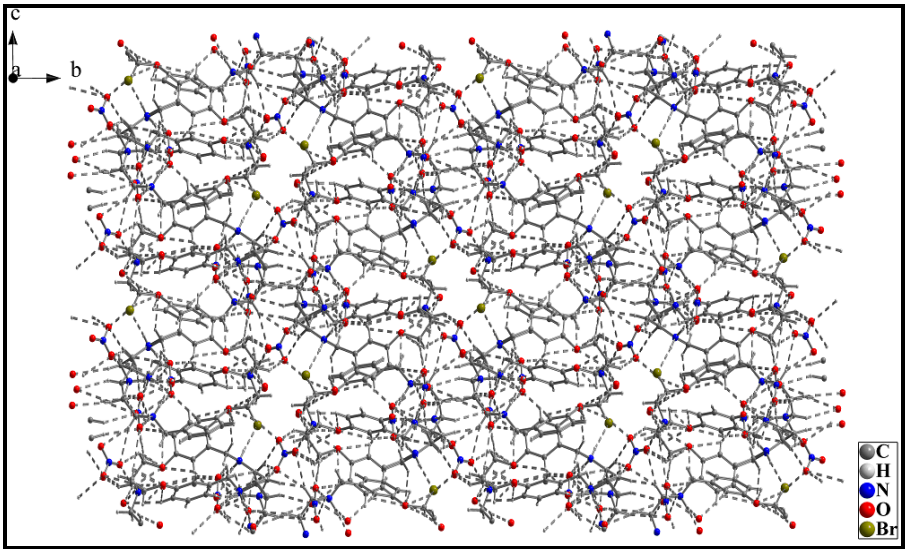

Figure S11: A 3-D H-bonded supramolecular network of complex **6** showing several N/C/O-H…anion interactions.

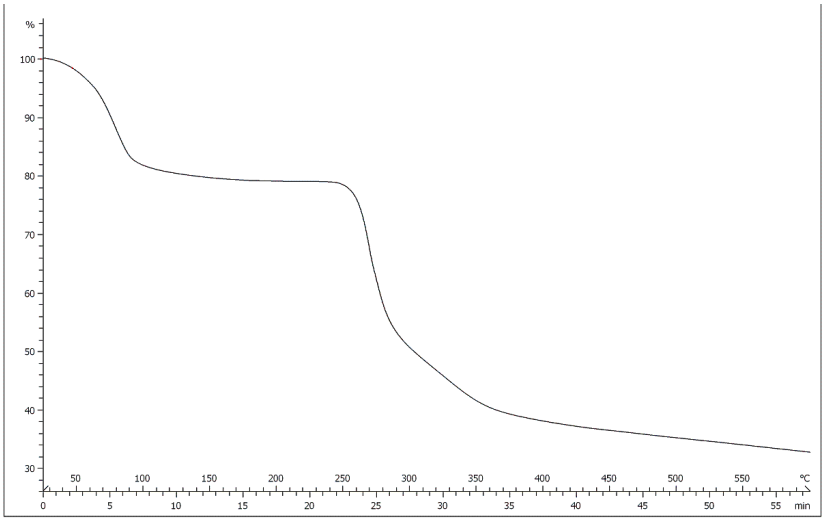

Figure S12: TGA of complex **1**.

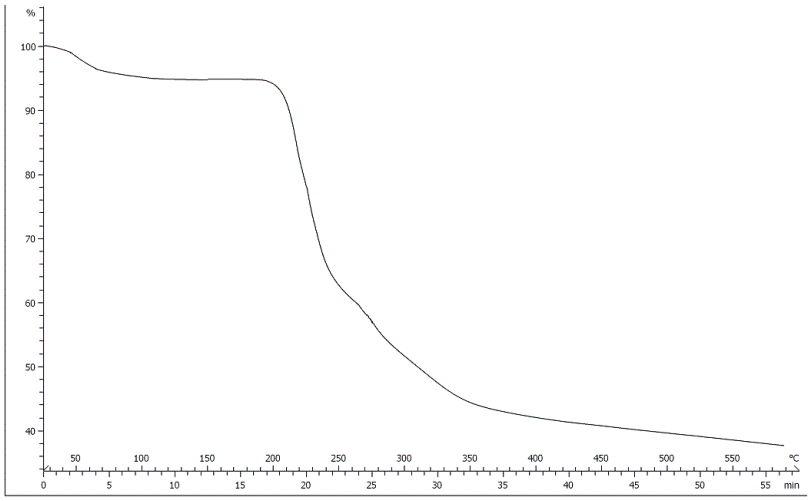

Figure S13: TGA of complex **2**.

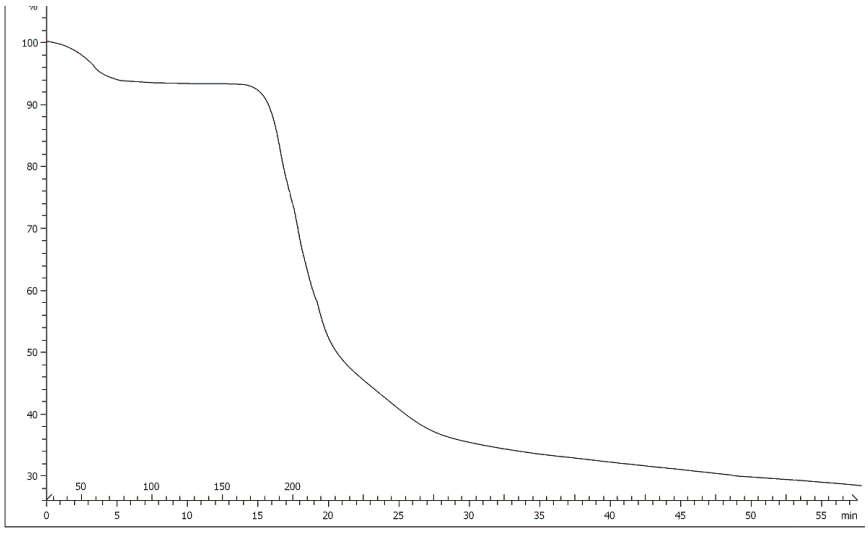

Figure S14: TGA of complex **3**.

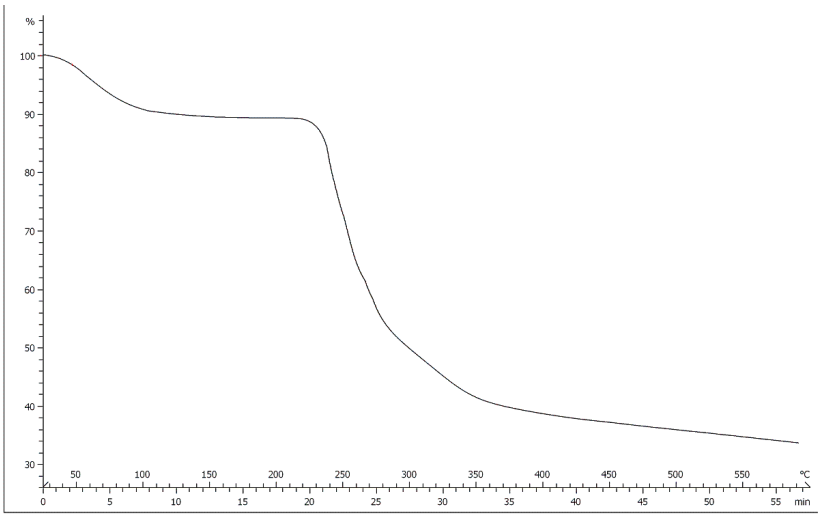

Figure S15: TGA of complex **4**.

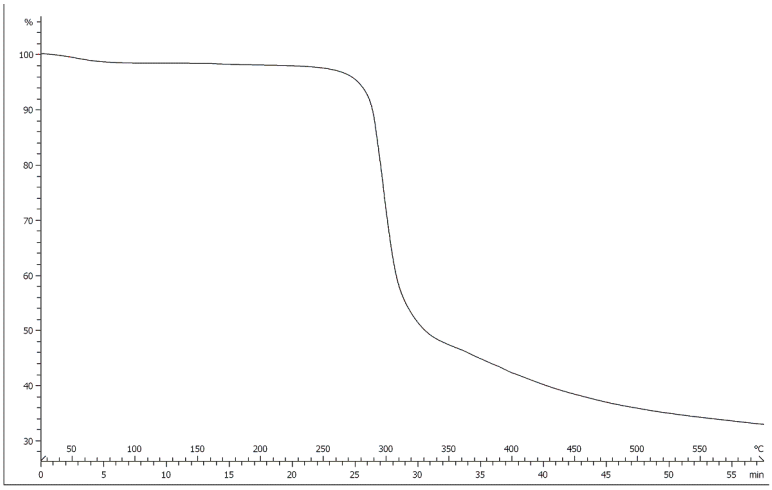

Figure S16: TGA of complex **5**.

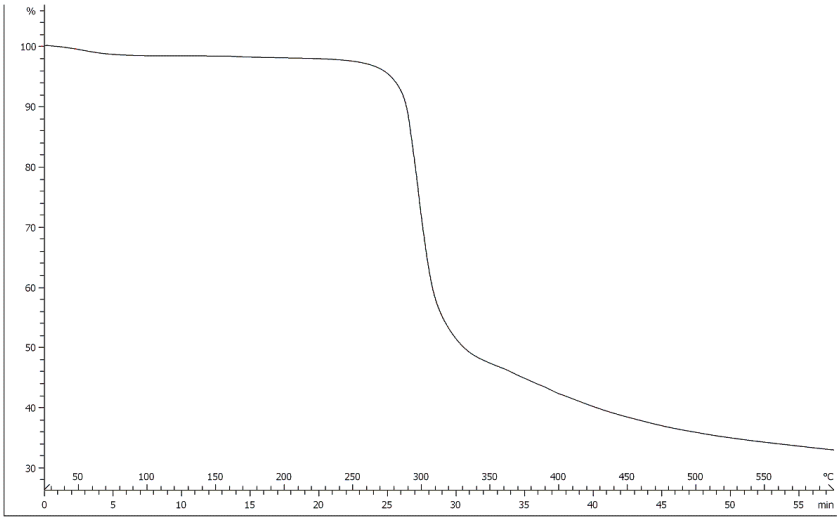

Figure S17: TGA of complex **6**.

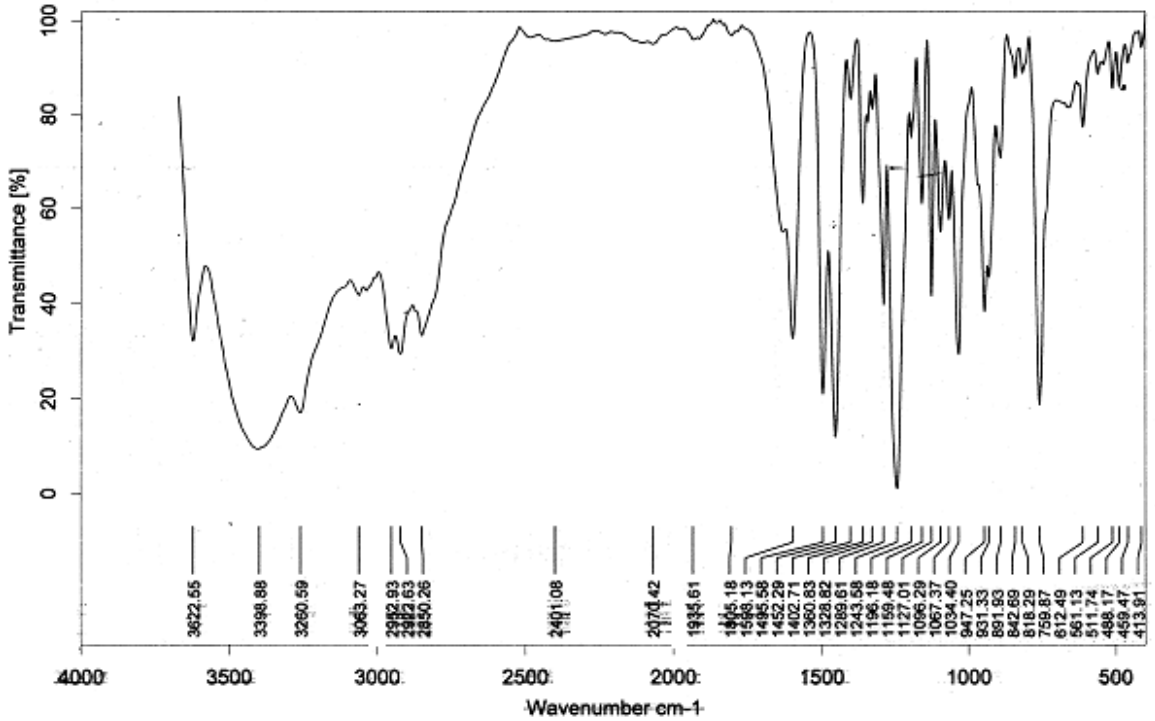

Figure S18: IR spectra of complex **1**.

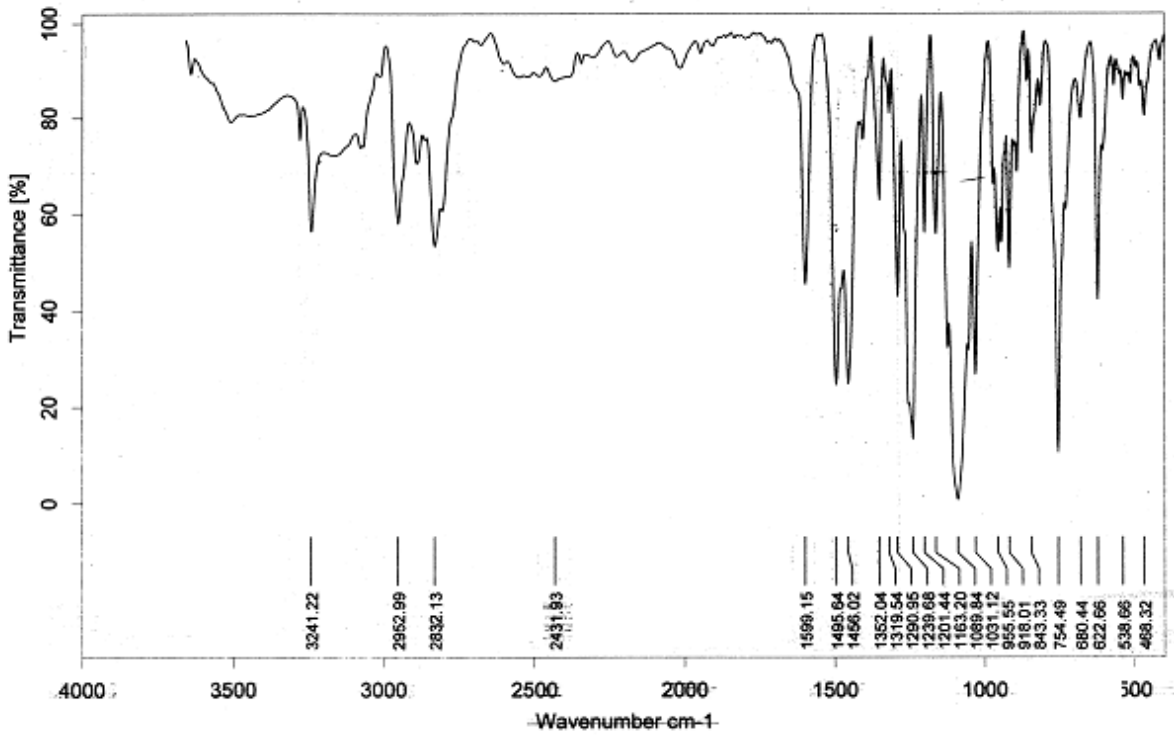

Figure S19: IR spectra of complex **2**.

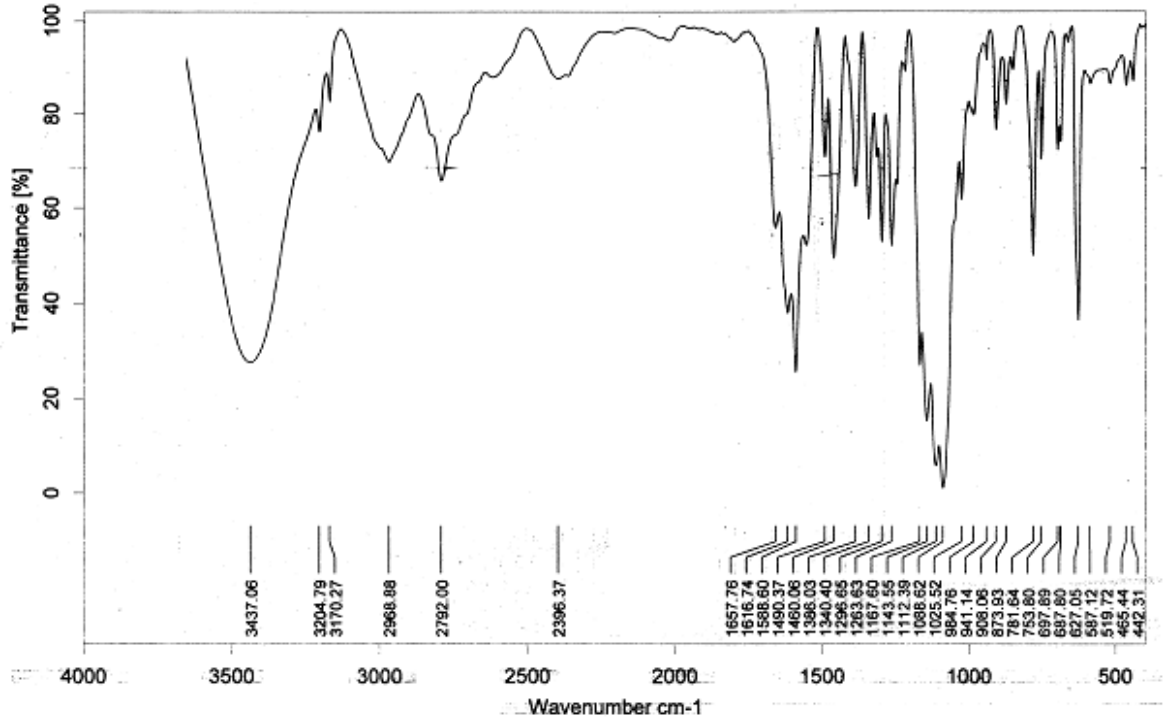

Figure S20: IR spectra of complex **3**.

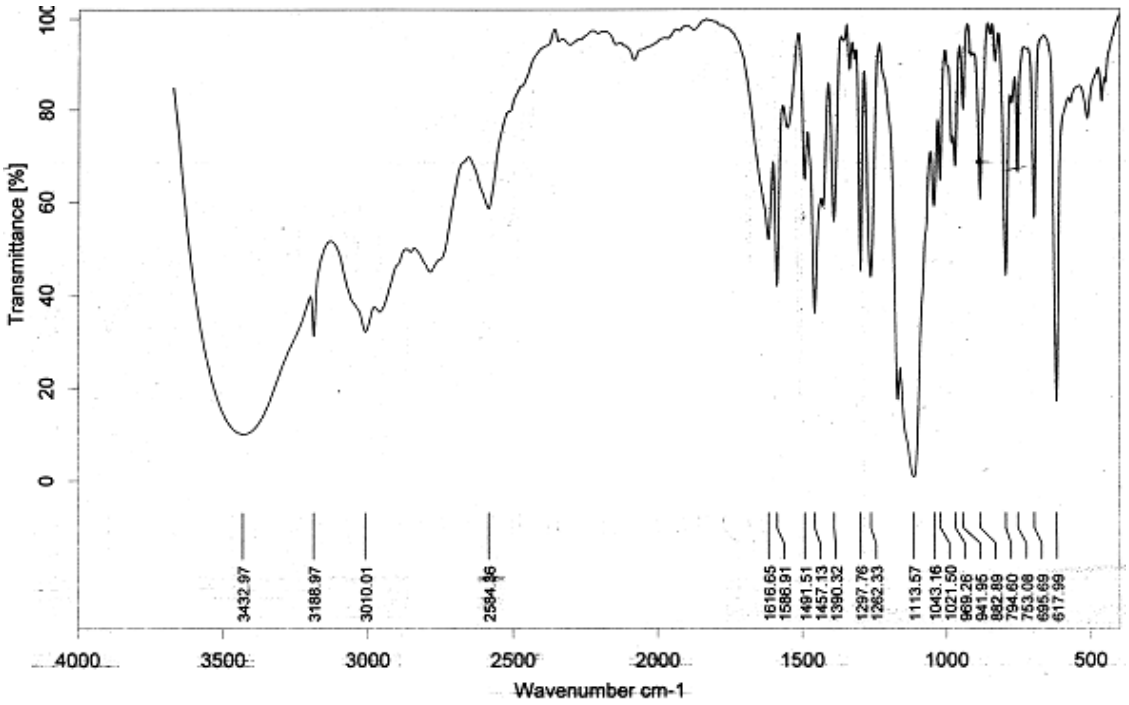

Figure S21: IR spectra of complex **4**.

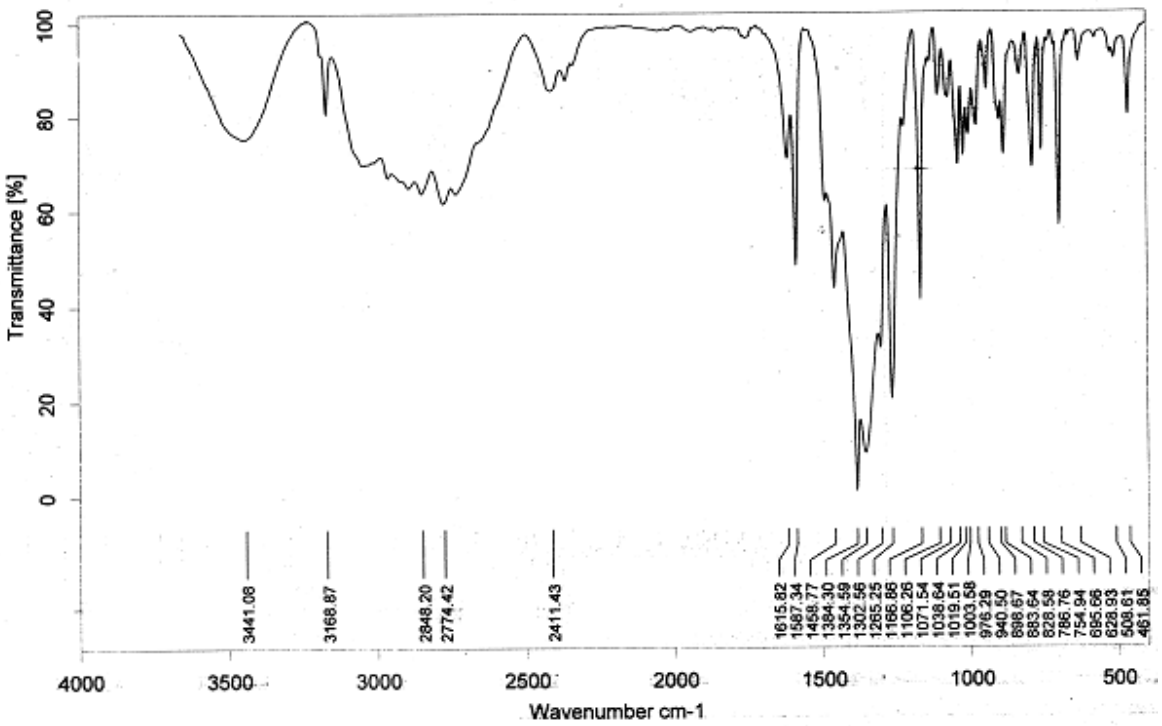

Figure S22: IR spectra of complex **5**.

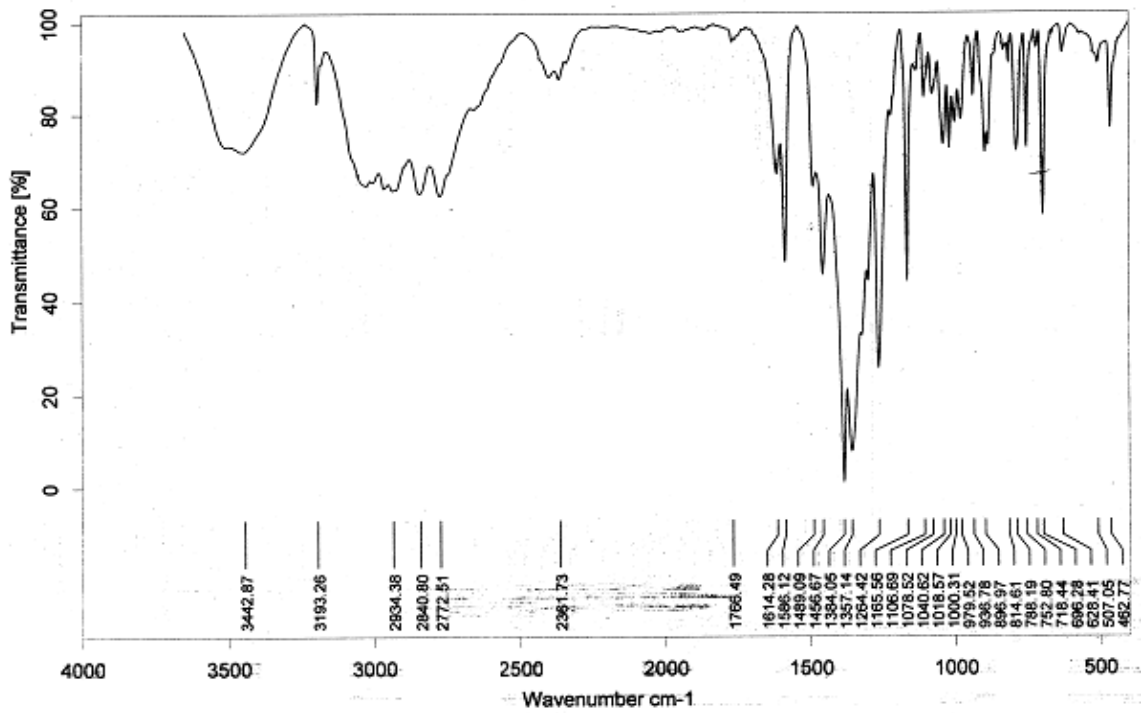

Figure S23: IR spectra of complex **6**.

Table S1: H-bonding distances and angles in complex **1**

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
N3–H3A···Cl1	2.07	2.964(9)	170
N4–H4A···Cl1	2.01	2.893(10)	165
N5–H5B··· Cl1	1.88	2.767(9)	167
N4–H4B···Ow9	1.88	2.741(11)	161
N5–H5A···Ow10	1.82	2.665(10)	154
N3–H3B···Ow3[a]	2.17	2.900(10)	138
C33–H33A···Cl2	2.91	3.814(7)	156

Ow1–Ow1[a]	2.767(5)	Ow8–Ow9	2.764(5)	Ow3–Cl3	2.837(5)
Ow1–Ow5	2.688(5)	Ow5–Ow6	2.800(5)	Ow6–Cl3	2.770(5)
Ow5–Ow4	2.730(5)	Ow4–Ow2	2.730(5)	Ow6–Cl2	3.145(5)
Ow5–Ow7	2.714(5)	Ow3–Cl2	3.167(5)	Ow2–Cl2	3.032(5)
Ow7–Ow8	2.722(5)	Ow1–Cl3	2.808(5)	Ow8–Cl2	3.072(5)
Ow4–Ow3	2.719(5)	Ow2–Cl2	3.268(5)	Ow10–Cl3	2.806(5)

Ow1···Ow1[a]···Ow5	105.80	Ow1···Ow5···Ow7	135.46
Ow1···Ow5···Ow4	115.48	Ow1···Ow5···Ow6	90.12
Ow7···Ow5···Ow6	100.89	Ow7···Ow5···Ow4	108.62
Ow5···Ow4···Ow3	118.02	Ow5···Ow4···Ow2	111.01
Ow3···Ow4···Ow2	94.47	Ow5···Ow7···Ow8	104.40
Ow7···Ow8···Ow9	110.82		

Symmetry codes: (a) 2-x,1-y,1-z

Table S2: H-bonding interactions in complex **2**

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
N8–H8A···O14	2.08	2.921(9)	155
N5–H5A···O14	2.15	2.966(9)	150
Ol3···Ow2		2.931(7)	
N4–H4B···O20	1.98	2.853(10)	164
O21···Ow4		2.989(7)	
N8–H8B···O24	1.99	2.870(9)	165
N9–H9B···O10	2.07	2.836(9)	142
N9–H9A···O7	2.34	2.968(9)	126
N9–H9A···O25[a]	2.12	2.916(9)	146
N10–H10A···O10	2.14	2.907(10)	143
N10–H10B···Ow3	1.90	2.767(13)	161
N5–H5B ···Ow1[b]	1.84	2.732(11)	170
N4–H4A ···Ow7[c]	1.93	2.825(11)	175
N3–H3A···O15[d]	2.30	3.010(10)	136
N3–H3B···O16[d]	2.18	2.888(10)	135
N3–H3B···O38[b]	2.25	2.956(9)	135
C21–H21A···O20	2.53	3.502(10)	179
C11–H11A···O20	2.66	3.323(9)	126
C12–H12B···O20	2.46	3.366(8)	155
C33–H33B···O20	2.69	3.397(9)	130
C35–H35B···O19	2.47	3.276(9)	140
C50–H50···O21	2.70	3.501(10)	145
C6–H6···O11	2.64	3.279(9)	127
C35–H35A···O12	2.71	3.479(9)	137
C44–H44B···O12	2.68	3.542(9)	148
N8–H8A···O12	2.38	3.126(10)	141
C44–H44B···O13	2.71	3.626(10)	157
C45–H45A···O7[e]	2.57	3.515(9)	164
C57–H57B···O7	2.66	3.598(9)	163
C43–H43a···O8	2.70	3.436(9)	133
C47–H47A···O8[e]	2.44	3.323(10)	152
C54–H54B···O8	2.63	3.249(9)	122
Ow3···O9		2.880(6)	
N10–H10A···O10	2.140	2.907(6)	143
C55–H55B···O10	2.56	3.402(10)	146
C11–H11B···O15[d]	2.40	3.214(11)	141
C65–H65B···O16	2.64	3.595(10)	170
C32–H32A···O16[f]	2.52	3.423(11)	156
C63–H63A···O17	2.58	3.399(11)	147
C21–H21B···O17	2.61	3.483(9)	150

C3–H3C···O18[f]	2.39	3.107(10)	131
C60–H60A···O23	2.51	3.427(9)	171
C20–H20B···O24	2.35	3.313(10)	170
C60–H60···O24	2.63	3.287(9)	128
N8–H8B···O25	2.69	3.274(6)	123
C46–H46B···O26	2.67	3.427(10)	136
C47–H47A···O26[g]	2.58	3.278(11)	129
C49–H49···O26	2.71	3.118(9)	134
Ow2···O27		2.884(6)	
C8–H8···O27[f]	2.58	3.312(10)	136
C66–H66A···O28[h]	2.60	3.434(9)	144
C44–H44A···O28	2.56	3.446(9)	152
C8–H8···O29	2.61	3.513(9)	163
Ow6···O30		2.891(6)	
Ow8···O31		2.979(6)	
C12–H12A···O31[f]	2.29	3.226(10)	162
Ow8···O32		2.868(6)	
C51–H51A···O32	2.51	3.252(9)	137
C52–H52···O34	2.68	3.481(9)	145
Ow6···O34		2.813(6)	
Ow8···O35		3.013(6)	
C66–H66B···O35[h]	2.54	3.323(14)	138
C2–H2A···O36[b]	2.43	3.339(12)	156
Ow7···O37		2.659(6)	
C5–H5···O37[b]	2.50	3.373(11)	156
Ow7···O38		2.941(6)	
Ow1···Ow2		2.702(6)	
Ol3···Ow2		2.931(7)	
O27···Ow2		2.884(5)	
C17–H17···Ow2	2.71	3.513(10)	146
Ow5···Ow8		2.806(6)	
Ow8···O35		3.013(6)	
Ow8···O31		2.979(6)	
Ow8···O32		2.868(6)	
C38–H38···Ow8	2.57	3.50(3)	172
Ow3···Ow4		2.788(6)	
Ow3···O9		2.800(6)	
Ow4···O21		2.989(6)	

Ow2 ···O13	2.931(6)	Ow2 ···O27	2.884(6)	Ow6 ···O30	2.891(6)
Ow6 ···O34	2.813(6)	Ow5 ···O31	2.979(6)	Ow5 ···O32	2.868(6)
Ow5 ···O35	3.013(6)	Ow7 ···O37	2.659(6)	Ow8 ···Ow5	2.806(6)
Ow1 ···Ow2	2.702(6)	Ow3···Ow4	2.788(6)	Ow3···O9	2.880(6)
Ow4···O21	2.989(6)				

Symmetry Codes: (a) 3-x,-1/2+y,2-z; (b) 3-x,-1/2+y,1-z; (c) 1+x,-1+y,z; (d) 3-x,1/2+y,1-z; (e) 3-x,1/2+y,2-z ; (f) 1+x,y,z; (g) 3-x,-1/2+y,2-z; (h) x,-1+y,z

Table S3: H-bonding distances and angles in complex **3**

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
N4–H4A···Ow3[a]	1.89	2.783(4)	169
N3–H3A···Ow1[a]	2.02	2.794(5)	143
Ow3–H1w3···Ow2	2.00(3)	2.792(5)	161(5)
Ow3–H2w3···Ow4	2.00(4)	2.825(5)	175(4)
C14–H14B···O4[b]	2.59	3.532(5)	163
N5–H5A···O5	2.04	2.882(4)	155
N4–H4B···O5	2.07	2.930(4)	161
C33–H33B···O8[c]	2.35	3.254(5)	154
Ow4–H1w4···O9[a]	2.20(3)	3.029(5)	174(5)
N5–H5B···O10	2.06	2.909(4)	158
Ow4–H2w4···O11	2.06(4)	2.863(5)	162(5)
C3–H3D···O11[d]	2.58	3.504(5)	159
N3–H3B···O12[a]	1.95	2.798(5)	157
Ow1–H1w1···O12[e]	2.40(3)	2.963(6)	126(4)
C17–H17···O13[a]	2.50	3.388(6)	161
C21–H21A···O13[f]	2.47	3.180(5)	130
C24–H24A···O14	2.51	3.160(5)	124
Ow2–H2w2···O15	2.07(4)	2.916(5)	175(4)
C14–H14A···O16[g]	2.52	3.437(5)	158
C3–H3C···O17	2.26	3.203(6)	165
C25–H25A···O17	2.53	3.280(6)	134
Ow1–H2w1···O18	2.34(5)	2.969(5)	136(4)
C13–H13A···O19	2.36	3.293(6)	125
N3–H3A···O19	2.58	3.312(5)	139

Symmetry Codes: (a) -x,1/2+y,3/2-z; (b) 1-x,1-y,2-z; (c) 1-x,-y,2-z; (d) -1+x,y,z; (e) -x,-1/2+y,3/2-z; (f) x,1/2-y,1/2+z ; (g) x,1+y,z.

Table S4: H-bonding parameters in complex **4**

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
N3–H3B···Cl1	2.22	3.121(3)	173
N4–H4B···Cl1	2.21	3.093(3)	166
N5–H5A···Cl1	2.28	3.166(3)	169
N1–H1···Cl1	2.51	3.412(3)	174
C9–H9···Cl1	2.82	3.353(3)	118
C20–H20···Cl1	2.91	3.404(3)	115
C31–H31···Cl1	2.82	3.372(3)	119
N4–H4A···O6	1.89	2.731(3)	155
N3–H3A···Cl2	2.27	3.126(3)	160
N5–H5B···O4[a]	1.91	2.772(3)	161
C22–H22A···O7	2.61	3.492(4)	152
C7–H7···O4[b]	2.41	3.267(4)	154
C23–H23B···O4	2.62	3.361(4)	133
C24–H24A···O5	2.71	3.328(4)	122
C2–H2B···O5[c]	2.46	3.390(4)	160
C12–H12B···O5[c]	2.51	3.470(4)	171
Ow4–H1w4···Ow3[d]	1.94(2)	2.775(4)	172(5)
Ow4–H2w4···Ow2	1.92(5)	2.771(4)	172(4)
Ow3–H2w3···Ow4[e]	2.05(2)	2.898(4)	168(3)
Ow3–H1w3···O6[e]	1.90(3)	2.730(4)	166(3)
Ow5–H2w5···Ow4[e]	2.05(4)	2.884(4)	171(4)
Ow5–H1w5···O4	2.07(4)	2.889(4)	166(4)
Ow2–H2w2···O7	1.92(3)	2.693(4)	154(4)
Ow2–H1w2···Cl2	2.35(3)	3.202(3)	173(3)
Ow6–H1w6···Ow1	1.95(3)	2.798(4)	176(3)
Ow6–H2w6···Ow1[a]	2.11(10)	2.884(4)	154(11)
Ow1–H2w1···Cl2	2.36(5)	3.188(3)	172(4)
Ow1–H1w1···O5	1.95(5)	2.756(4)	158(5)

Ow1···Ow6···Ow1′	101.54	Ow4···Ow3···Ow4′	94.89
Ow3···Ow4···Ow3′	85.11	Ow3···Ow4···Ow2	84.92
Ow3···Ow4···Ow5	76.65	Ow3···Ow4···Ow5	110.60
Ow3···Ow4···Ow2	112.04	Ow2···Ow4···Ow5	131.46

Ow1 is related to Ow1′with the symmetry operation1-x, -y, -z
Ow4 is related to Ow4′ with the symmetry operation -x, -y, -1-z
Ow3 is related to Ow3′ with the symmetry operation 2-x, -y, -1-z
Other symmetry codes: (a) 1-x,-y,-z; (b) 1/2-x,1/2+y,-1/2-z; (c) -x,-y,-z; (d) -1+x,y,z; (e) 1-x,-y,-1-z;

Table S5: H-bonding distances and angles in Complex **5**

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
N3–H3A···Cl1	2.22	3.101(5)	167
N4–H4B···Cl1	2.26	3.157(5)	175
N5–H5B···Cl1	2.26	3.156(4)	174
N2–H2···Cl1	2.50	3.404(5)	173
C8–H8···Cl1	2.86	3.348(8)	114
C19–H19···Cl1	2.98	3.326(6)	104
C30–H30···Cl1	2.88	3.433(6)	120
N3–H3B···O4	2.06	2.913(4)	157
C15–H15···O4	2.72	3.552(6)	150
C221–H22B···O4	2.67	3.624(6)	167
C21–H21A···O5	2.49	3.462(7)	175
C11–H11A···O5	2.55	3.453(5)	155
C28–H28···O5[a]	2.47	3.204(9)	136
C11–H11B···O5	2.72	2.5686)	147
N5–H5A···O6[a]	1.97	2.845(7)	164
C33–H33A···O6	2.63	3.406(6)	137
C15–H15···O6[b]	2.34	3.184(8)	151
C11–H11B···O6	2.61	3.498(6)	153
N4–H4A···O7	2.48	3.163(11)	133
C1–H1A···O7[b]	2.52	3.473(8)	168
C23–H23A···O7[c]	2.29	3.148(14)	146
N4–H4A···O8	1.83	2.715(6)	167
C4–H4···O8	2.67	3.350(6)	130
C32–H32A···O8	2.39	3.343(8)	169
C24–H24A···O9	2.58	3.272(9)	128
C4–H4···O9	2.70	3.554(6)	152
C1–H1B···O9[c]	2.51	3.480(12)	175
C32–H32B···O10	2.53	3.263(7)	132
C10–H10B···O10[d]	2.55	3.404(8)	148
C13–H13B···O10[c]	2.53	3.222(6)	129
C2–H2B···O11[e]	2.50	3.368(10)	149
C21–H21B···O11[f]	2.56	3.509(8)	166
C23–H23B···O12[g]	2.60	3.199(8)	120
C10–H10B···O12[d]	2.45	3.348(8)	153
C21–H21B···O12	2.65	3.344(7)	129
Ow1···O9		2.631(5)	
Ow1···O10		3.026(5)	
Ow1···O11		2.756(5)	
C12–H12B···Ow1[e]	2.02	2.922(16)	154
C2–H2A···Ow1[e]	2.15	2.947(15)	139

Symmetry codes: (a) 1+x,y,z; (b) 1/2+x,1/2-y,-1/2+z; (c) 1/2-x,-1/2+y,1/2-z; (d) 1-x,1-y,1-z; (e) -1/2+x,1/2-y,1/2+z; (f) -1+x,y,z; (g) 3/2-x,-1/2+y,1/2-z.

Table S6: Non-bonding distances and angles in complex **6**

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
N3–H3A···O4	2.28	2.916(7)	127
N3–H3A···O5	1.94	2.838(7)	172
N4–H4B···O5	2.40	2.999(7)	124
N4–H4B···O6	1.89	2.785(7)	175
N5–H5B···O6	2.38	3.035(7)	130
N5–H5B···O4	1.88	2.763(7)	169
N1–H1···O4	2.39	3.215(8)	151
N1–H1···O5	2.45	3.239(7)	145
N1–H1···O6	2.42	3.237(7)	150
N4–H4A···O7[a]	1.99	2.864(7)	164
C23–H23A···O7	2.63	3.586(7)	170
N3–H3B···O8	2.46	3.223(7)	142
N4–H4A···O8[a]	2.44	3.168(7)	138
C5–H5A···O8	2.54	3.260(9)	135
C24–H24B···O8[a]	2.56	3.502(8)	165
C12–H12B···O8[a]	2.56	3.454(9)	153
N3–H3B···O9	2.02	2.881(7)	160
C1–H1A···O9[b]	2.55	3.396(9)	146
C29–H29···O9[c]	2.36	3.256(9)	163
C2–H2A···O10[d]	2.35	3.278(10)	161
C24–H24A···O10	2.36	3.099(9)	132
C13–H13A···O10[e]	2.40	3.312(11)	156
C21–H21A···O11[f]	2.48	3.311(12)	144
C24–H24A···O11	2.54	3.498(10)	170
Ow1···O11		2.974(5)	
Ow1···O12		2.723(5)	
C32–H32A···O12	2.65	3.296(10)	124
N5–H5A···Br1	2.30	3.199(5)	174
C22–H22A···Br1[g]	2.86	3.724(5)	149
C33–H33A···Br1	2.96	3.769(7)	141
C10–H10B···Br1[f]	2.85	3.763(8)	157
C21–H21B···Ow1[h]	2.37	3.267(12)	153
C33–H33BB···Ow1[h]	2.41	3.345(13)	161

Symmetry codes: (a) 1+x,y,z; (b) 1-x,-y,1-z; (c) 1/2+x,1/2-y,1/2+z; (d) -1+x,y,z; (e) 2-x,-y,1-z; (f) -1/2+x,1/2-y,-1/2+z; (g) 3/2-x,1/2+y,3/2-z; (h) 5/2-x,1/2+y,3/2-z.