Two Series of Luminescent Flexible Polycarboxylate Lanthanide Coordination Complexes with Double Layer and Rectangle Metallomacrocycle Structures

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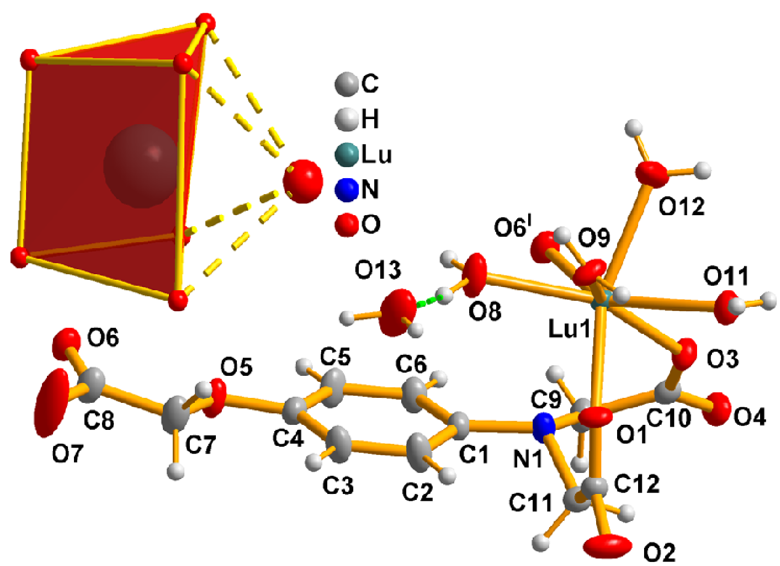

Figure S1. (a) Stick- ellipsoid representation of the asymmetric unit of complex **8** with thermal ellipsoids at 50% probability. The insert shows the coordination geometry of Lu(III) center. Symmetry codes: (I) –x, 1–y, –z.

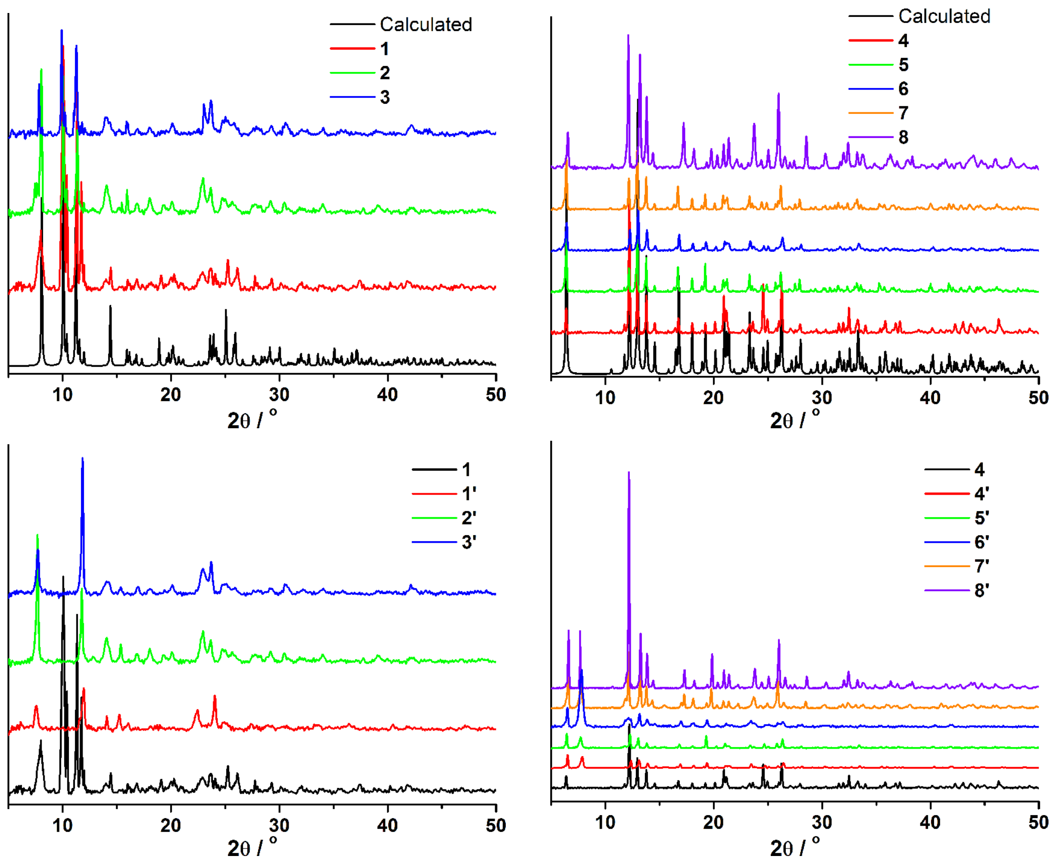

Figure S2. Calculated and experimented PXRD patterns of complexes **1**−**8**, and the experimented PXRD patterns complexes **1**’−**8**’ (complexes **1**’−**8**’ are the dehydrated product of complexes **1**−**8**).

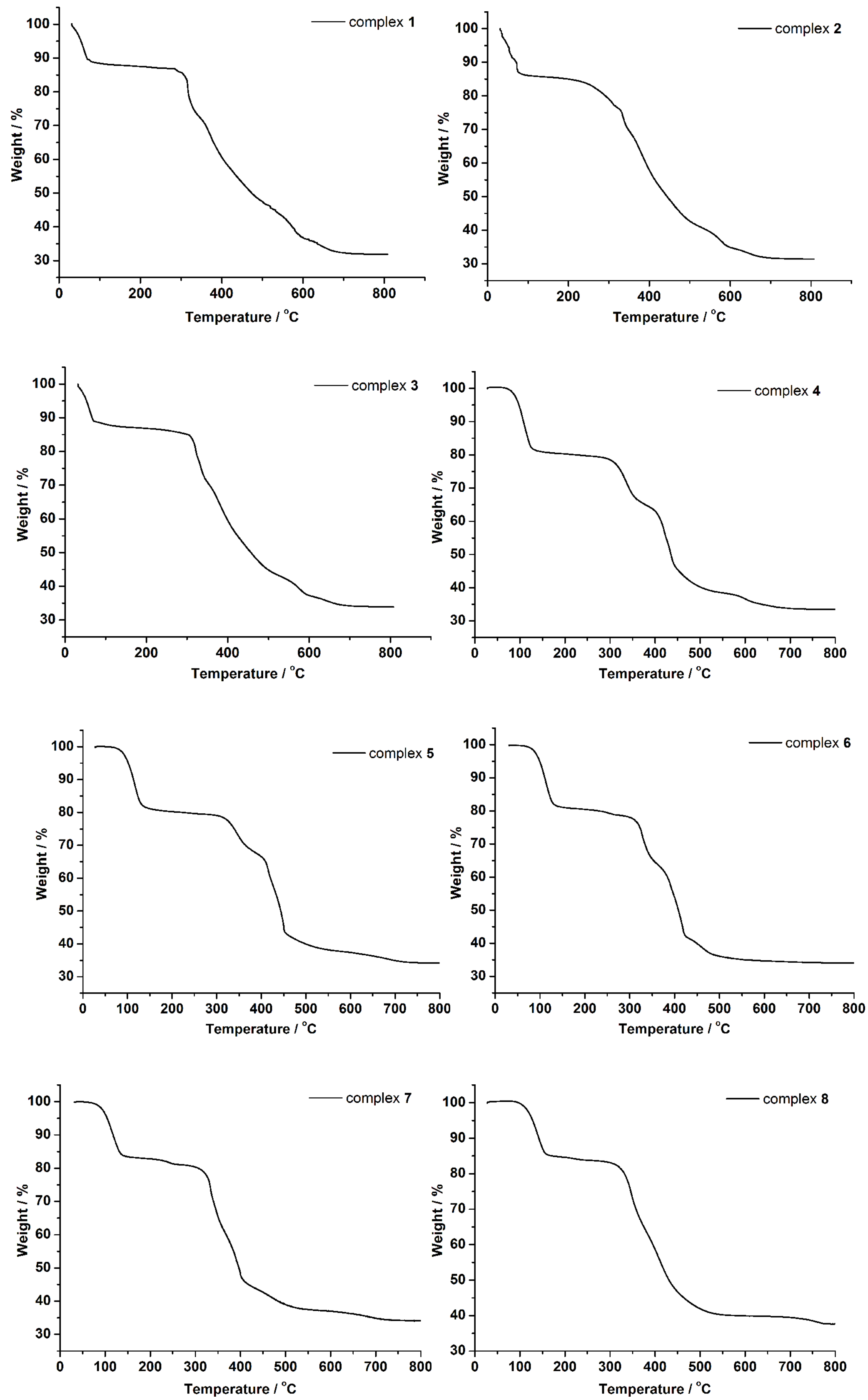

Figure S3. TGA curves of complexes **1**−**8**.

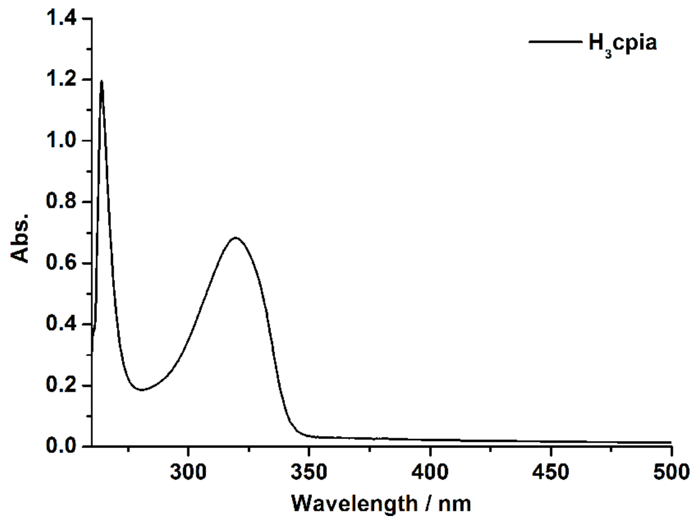

Figure S4. UV-Vis spectrum of H_3cpia in MeOH.

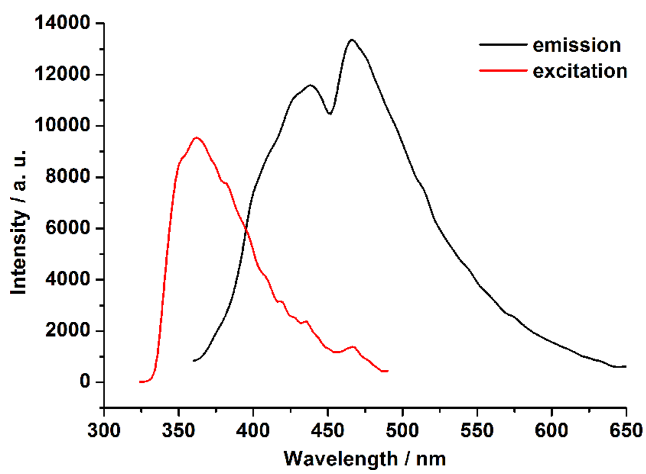

Figure S5. Solid-state excitation and emission spectra of H_3cpia.

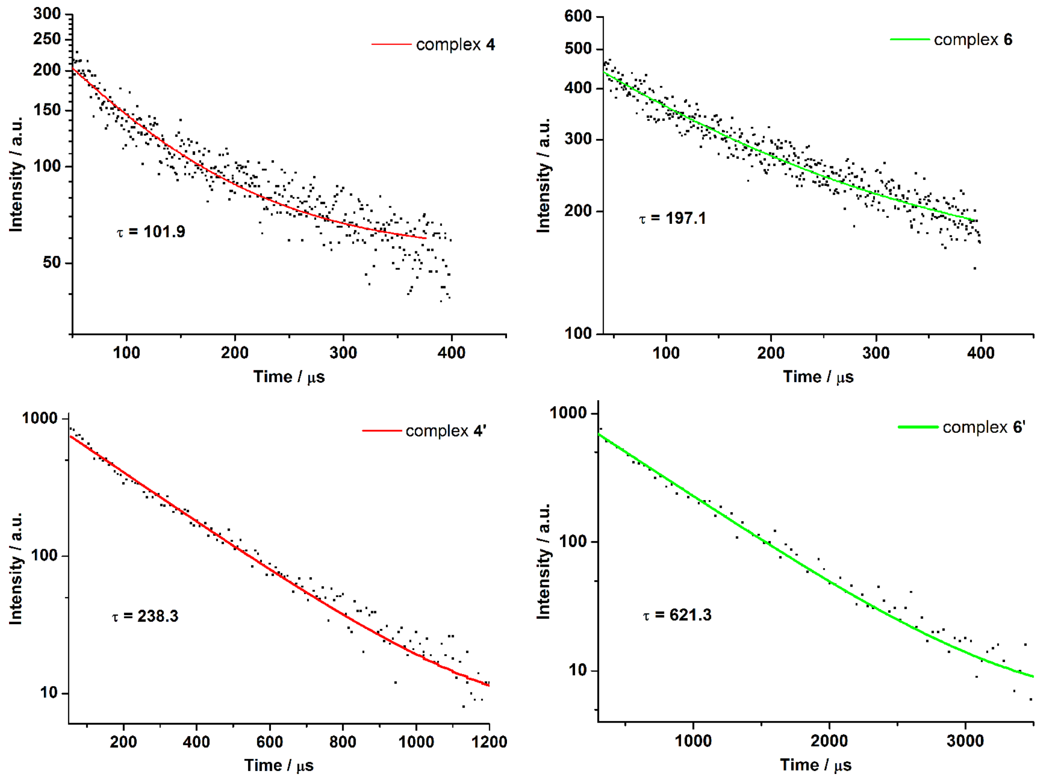

Figure S6. Luminescent decay curves for complex **4** and **6**.

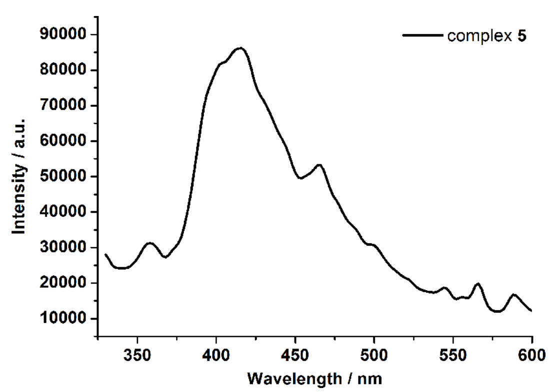

Figure S7. Phosphorescence spectra of complex **5** at 77K.

Table S1. Selected Bond Lengths (Å) for Complexes **1−8**.

	1-Ce	**2-Nd**	**3-Sm**
Ln(1)−O(1)	2.627(2)	2.603(2)	2.576(2)
Ln(1)−O(1)#1	2.431(3)	2.398(2)	2.365(2)
Ln(1)−O(2)	2.626(3)	2.592(2)	2.560(2)
Ln(1)−O(3)#1	2.461(2)	2.438(3)	2.414(2)
Ln(1)−O(4)#6	2.467(2)	2.436(2)	2.401(2)
Ln(1)−O(6)#3	2.522(3)	2.479(3)	2.448(2)
Ln(1)−O(7)#7	2.493(2)	2.456(3)	2.425(3)
Ln(1)−O(8)	2.586(3)	2.556(3)	2.526(3)
Ln(1)−O(9)	2.599(3)	2.567(3)	2.544(3)

Symmetry codes: #1 -x+1,-y+1,-z+2 #2 x-1,y,z #3 -x+1,-y+2,-z+1 #4 x,y+1,z-1 #5 -x+1,-y,-z #6 x+1,y,z #7 x,y-1,z+1

	4-Eu	**5-Gd**	**6-Tb**	**7-Er**	**8-Lu**
Ln(1)−O(1)	2.383(2)	2.377(2)	2.362(2)	2.328(2)	2.244(3)
Ln(1)−O(3)	2.410(2)	2.404(2)	2.384(2)	2.346(2)	2.277(3)
Ln(1)−O(8)	2.384(2)	2.375(2)	2.354(2)	2.313(2)	2.252(3)
Ln(1)−O(9)	2.477(2)	2.472(2)	2.456(2)	2.427(2)	2.328(3)
Ln(1)−O(10)	2.435(2)	2.415(2)	2.404(2)	2.364(2)	
Ln(1)−O(11)	2.433(2)	2.418(2)	2.404(2)	2.360(2)	2.349(2)
Ln(1)−O(12)	2.511(2)	2.498(2)	2.483(2)	2.453(2)	2.286(3)
Ln(1)−O(6)#1	2.314(2)	2.304(2)	2.291(2)	2.257(2)	2.209(3)

Symmetry codes: #1 -x,-y+1,-z

Table S2. Selected Hydrogen Bond Interactions in Complexes **1–8**.

Complex **1**				
D−H···A	D−H/ Å	H···A/ Å	D···A/ Å	∠D − H···A/deg
O(12)−H(121)···O(13')#8	0.85	2.04	2.838(12)	155.6
O(12)−H(122)···O(10)#3	0.85	1.87	2.582(8)	140.2
O(11)−H(112)···O(4)#8	0.85	2.10	2.839(4)	144.6
O(11)−H(111)···O(6)#9	0.85	2.38	3.099(4)	142.5
O(11)−H(111)···O(5)#9	0.85	2.21	2.948(5)	144.9
O(10)−H(102)···O(11)#1(	0.85	1.87	2.707(6)	167.9
O(10)−H(101)···O(2)#11	0.85	2.06	2.781(7)	142.6
O(9)−H(92)···O(12)#1	0.85	2.03	2.847(6)	159.9
O(9)−H(91)···O(10)#11	0.85	2.63	3.379(6)	147.4
O(9)−H(91)···O(12)#12	0.85	2.43	3.123(10)	151.9
O(8)−H(82)···O(13)#13	0.85	2.42	3.19(5)	139.8
O(8)−H(82)···O(13')#10	0.85	2.27	2.852(10)	126.3
O(8)−H(82)···O(13)#10	0.85	2.16	2.99(5)	166.2
O(8)−H(81)···O(3)#6	0.85	2.25	2.991(4)	145.1

Symmetry Code: #1 -x+1,-y+1,-z+2 #2 x-1,y,z #3 -x+1,-y+2,-z+1
#4 x,y+1,z-1 #5 -x+1,-y,-z #6 x+1,y,z #7 x,y-1,z+1 #8 -x,-y+1,-z+1
#9 x,y-1,z #10 -x+1,-y+1,-z+1 #11 -x+2,-y+1,-z+1 #12 x+1,y-1,z
#13 x,y+1,z+1

Complex **2**				
D−H···A	D−H/ Å	H···A/ Å	D···A/ Å	∠D − H···A/deg
O(12)−H(121)···O(13')#8	0.84	2.01	2.795(12)	153.4
O(12)−H(122)···O(10)#3	0.85	1.89	2.609(8)	141.4
O(11)−H(112)···O(4)#8	0.85	2.11	2.841(4)	144.4
O(11)−H(111)···O(6)#9	0.85	2.39	3.105(4)	141.9
O(11)−H(111)···O(5)#9	0.85	2.20	2.938(5)	145.8
O(10)−H(102)···O(11)#1(	0.85	1.88	2.721(5)	168.9
O(10)−H(101)···O(2)#11	0.85	2.06	2.792(5)	143.1
O(9)−H(92)···O(12)#1	0.85	2.08	2.883(7)	158.5
O(9)−H(91)···O(10)#11	0.85	2.58	3.332(6)	148.3

O(9)−H(91)···O(12)#12	0.85	2.49	3.181(9)	139.5
O(8)−H(82)···O(13)#13	0.85	2.45	3.23(3)	152.3
O(8)−H(82)···O(13’)#10	0.85	2.25	2.845(10)	127.1
O(8)−H(82)···O(13)#10	0.85	2.17	2.99(3)	164.6
O(8)−H(81)···O(3)#6	0.85	2.25	2.986(4)	145.9
Symmetry Code: #1 -x+1,-y+1,-z+2 #2 x-1,y,z #3 -x+1,-y+2,-z+1 #4 x,y+1,z-1 #5 -x+1,-y,-z #6 x+1,y,z #7 x,y-1,z+1 #8 -x,-y+1,-z+1 #9 x,y-1,z #10 -x+1,-y+1,-z+1 #11 -x+2,-y+1,-z+1 #12 x+1,y-1,z #13 x,y+1,z+1				
Complex **3**				
O(12)−H(121)···O(13’)#8	0.84	2.01	2.772(11)	151.4
O(12)−H(122)···O(10)#3	0.84	1.92	2.637(7)	142.2
O(11)−H(112)···O(4)#8	0.85	2.12	2.847(4)	144.2
O(11)−H(111)···O(6)#9	0.85	2.39	3.097(4)	141.4
O(11)−H(111)···O(5)#9	0.85	2.18	2.925(4)	146.3
O(10)−H(102)···O(11)#10	0.85	1.89	2.731(5)	169.1
O(10)−H(101)···O(2)#11	0.85	2.06	2.786(4)	143.9
O(9)−H(92)···O(12)#1	0.85	2.06	2.865(6)	157.8
O(9)−H(91)···O(10)#11	0.85	2.56	3.314(5)	148.8
O(9)−H(91)···O(12)#12	0.85	2.52	3.207(8)	138.8
O(8)−H(82)···O(13)#13	0.85	2.49	3.27(3)	152.6
O(8)−H(82)···O(13’)#10	0.85	2.21	2.822(9)	128.8
O(8)−H(82)···O(13)#10	0.85	2.14	2.96(3)	162.9
O(8)−H(81)···O(3)#6	0.85	2.23	2.968(4)	146.0
Symmetry Code: #1 -x+1,-y+1,-z+2 #2 x-1,y,z #3 -x+1,-y+2,-z+1 #4 x,y+1,z-1 #5 -x+1,-y,-z #6 x+1,y,z #7 x,y-1,z+1 #8 -x,-y+1,-z+1 #9 x,y-1,z #10 -x+1,-y+1,-z+1 #11 -x+2,-y+1,-z+1 #12 x+1,y-1,z #13 x,y+1,z+1				
Complex **4**				
O(8)−H(81)···O(5)#1	0.85	2.01	2.850(3)	167.3
O(8)−H(82)···O(13)	0.86	1.87	2.718(3)	170.4
O(9)−H(91)···O(2)#2	0.86	1.93	2.733(3)	154.9
O(9)−H(92)···O(3)#3	0.86	1.94	2.782(3)	169.8

O(10)−H(101)···O(2)#2	0.85	2.08	2.880(3)	156.3
O(10)−H(102)···O(4)#4	0.86	1.97	2.758(3)	152.6
O(11)−H(111)···O(1)#5	0.85	1.97	2.820(3)	172.6
O(11)−H(111)···O(9)#5	0.85	2.66	3.111(3)	114.4
O(11)−H(112)···O(4)#3	0.85	2.05	2.889(3)	167.4
O(12)−H(121)···O(13)#6	0.85	2.04	2.866(3)	161.9
O(12)−H(122)···O(2)#5	0.85	1.89	2.737(3)	171.3
O(13)−H(131)···O(4)#7	0.86	2.12	2.939(3)	161.5
O(13)−H(132)···O(7)#8	0.86	1.81	2.660(3)	176.9
Symmetry Code: #1 -x,-y+1,-z #2 x,-y+1,z-1/2 #3 -x+1/2,y+1/2,-z+1/2 #4 x,-y,z-1/2 #5 -x+1/2,y-1/2,-z+1/2 #6 x,y-1,z #7 x,y+1,z #8 -x,-y+2,-z				
Complex **5**				
O(8)−H(81)···O(5)#1	0.85	2.00	2.843(3)	167.1
O(8)−H(82)···O(13)	0.86	1.87	2.715(3)	170.0
O(9)−H(91)···O(2)#2	0.86	1.95	2.745(3)	154.6
O(9)−H(92)···O(3)#3	0.85	1.93	2.771(3)	168.9
O(10)−H(101)···O(2)#2	0.85	2.086	2.888(4)	157.5
O(10)−H(102)···O(4)#4	0.86	1.97	2.761(3)	152.5
O(11)−H(111)···O(1)#5	0.86	1.98	2.827(3)	172.4
O(11)−H(111)···O(9)#5	0.85	2.65	3.107(3)	114.8
O(11)−H(112)···O(4)#3	0.85	2.04	2.878(3)	167.6
O(12)−H(121)···O(13)#6	0.85	2.05	2.875(3)	163.0
O(12)−H(122)···O(2)#5	0.85	1.89	2.732(3)	171.5
O(13)−H(131)···O(4)#7	0.86	2.11	2.933(3)	160.8
O(13)−H(132)···O(7)#8	0.86	1.81	2.663(3)	176.9
Symmetry Code: #1 -x,-y+1,-z #2 x,-y+1,z-1/2 #3 -x+1/2,y+1/2,-z+1/2 #4 x,-y,z-1/2 #5 -x+1/2,y-1/2,-z+1/2 #6 x,y-1,z #7 x,y+1,z #8 -x,-y+2,-z				
Complex **6**				
O(8)−H(81)···O(5)#1	0.85	2.01	2.847(2)	167.1
O(8)−H(82)···O(13)	0.85	1.87	2.713(2)	170.0

O(9)−H(91)···O(2)#2	0.85	1.95	2.744(2)	154.6
O(9)−H(92)···O(3)#3	0.86	1.94	2.778(2)	168.9
O(10)−H(101)···O(2)#2	0.85	2.06	2.867(3)	157.5
O(10)−H(102)···O(4)#4	0.85	1.97	2.755(2)	152.5
O(11)−H(111)···O(1)#5	0.85	1.98	2.832(2)	172.4
O(11)−H(111)···O(9)#5	0.85	2.65	3.102(3)	114.8
O(11)−H(112)···O(4)#3	0.85	2.04	2.874(2)	167.6
O(12)−H(121)···O(13)#6	0.85	2.05	2.871(2)	163.0
O(12)−H(122)···O(2)#5	0.85	1.88	2.724(2)	171.5
O(13)−H(131)···O(4)#7	0.85	2.11	2.929(3)	160.8
O(13)−H(132)···O(7)#8	0.86	1.81	2.662(3)	176.9
Symmetry Code: #1 -x,-y+1,-z #2 x,-y+1,z-1/2 #3 -x+1/2,y+1/2,-z+1/2 #4 x,-y,z-1/2 #5 -x+1/2,y-1/2,-z+1/2 #6 x,y-1,z #7 x,y+1,z #8 -x,-y+2,-z				
Complex **7**				
O(8)−H(81)···O(5)#1	0.85	2.01	2.841(3)	166.8
O(8)−H(82)···O(13)	0.85	1.87	2.710(3)	169.5
O(9)−H(91)···O(2)#2	0.85	1.96	2.747(3)	154.4
O(9)−H(92)···O(3)#3	0.85	1.94	2.775(3)	167.8
O(10)−H(101)···O(2)#2	0.85	2.04	2.847(3)	158.8
O(10)−H(102)···O(4)#4	0.85	1.97	2.751(3)	152.6
O(11)−H(111)···O(1)#5	0.85	2.00	2.845(3)	172.2
O(11)−H(111)···O(9)#5	0.85	2.63	3.095(3)	115.4
O(11)−H(112)···O(4)#3	0.85	2.03	2.871(3)	167.7
O(12)−H(121)···O(13)#6	0.85	2.04	2.871(3)	164.3
O(12)−H(122)···O(2)#5	0.85	1.88	2.722(3)	171.8
O(13)−H(131)···O(4)#7	0.85	2.10	2.914(3)	160.1
O(13)−H(132)···O(7)#8	0.86	1.80	2.653(4)	176.9
Symmetry Code: #1 -x,-y+1,-z #2 x,-y+1,z-1/2 #3 -x+1/2,y+1/2,-z+1/2 #4 x,-y,z-1/2 #5 -x+1/2,y-1/2,-z+1/2 #6 x,y-1,z #7 x,y+1,z #8 -x,-y+2,-z				
Complex **8**				

O(8)−H(81)···O(5)#1	0.83	1.99	2.794(4)	166.0
O(8)−H(82)···O(13)	0.85	1.84	2.651(5)	158.8
O(9)−H(91)···O(2)#2	0.85	1.91	2.658(4)	145.8
O(9)−H(92)···O(3)#3	0.82	1.95	2.764(3)	168.6
O(11)−H(111)···O(1)#4	0.85	1.89	2.718(4)	165.9
O(11)−H(111)···O(9)#4	0.85	2.56	3.078(3)	120.4
O(11)−H(112)···O(4)#3	0.84	2.05	2.848(4)	158.1
O(12)−H(121)···O(13)#5	0.85	1.97	2.796(4)	162.1
O(12)−H(122)···O(2)#4	0.85	1.89	2.736(5)	169.1
O(13)−H(131)···O(4)#6	0.85	1.87	2.687(5)	160.3

Symmetry Code: #1 -x,-y+1,-z #2 x,-y+1,z-1/2 #3 -x+1/2,y+1/2,-z+1/2
#4 -x+1/2,y-1/2,-z+1/2 #5 x,y-1,z #6 x,y+1,z