Electronic Supplementary Material for CrystEngComm

π-Stacking of quinoid rings in crystals of alkali diaqua hydrogen chloranilates

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Supplement data

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S1 ORTEP drawings of hydrogen chloranilate and chloranilate anions

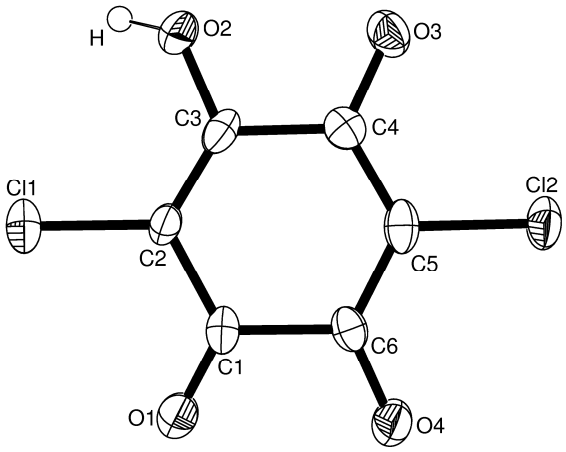

Figure S1.1 ORTEP-3 drawing of hydrogen chloranilate ion in [LiHCAEtOH]. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atom has been depicted as a sphere of an arbitrary radius.

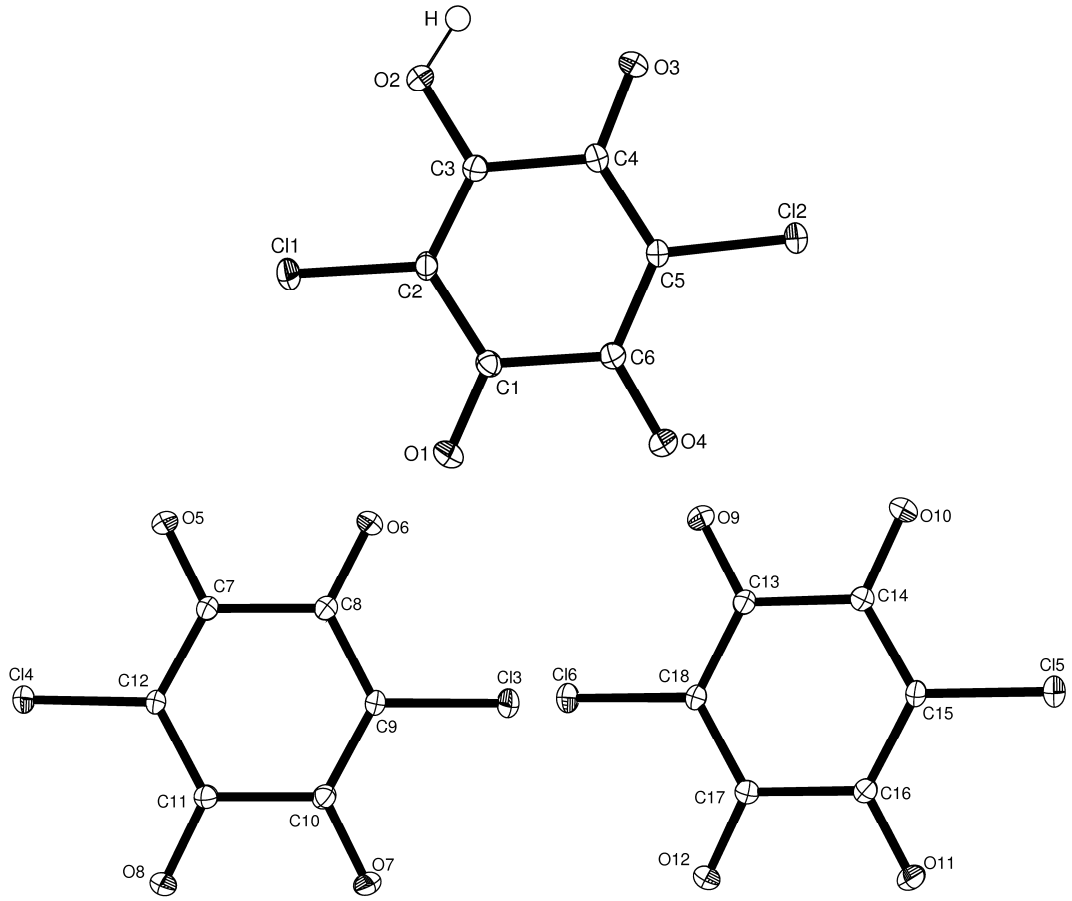

Figure S1.2 ORTEP-3 drawing of hydrogen chloranilate and chloranilate ions in $[Na_5HCA(CA)_2(H_2O)_{10}]$. Atomic displacement ellipsoids are drawn at the 50%

probability level and hydrogen atom has been depicted as a sphere of an arbitrary radius.

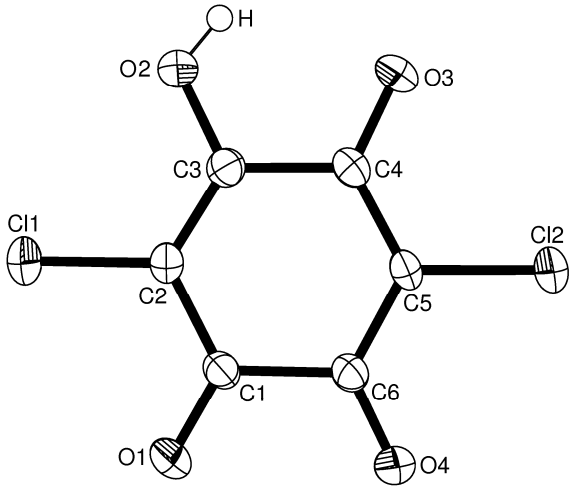

Figure S1.3 ORTEP-3 drawing of hydrogen chloranilate ion in [KHCA$(H_2O)_2$]. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atom has been depicted as a sphere of an arbitrary radius.

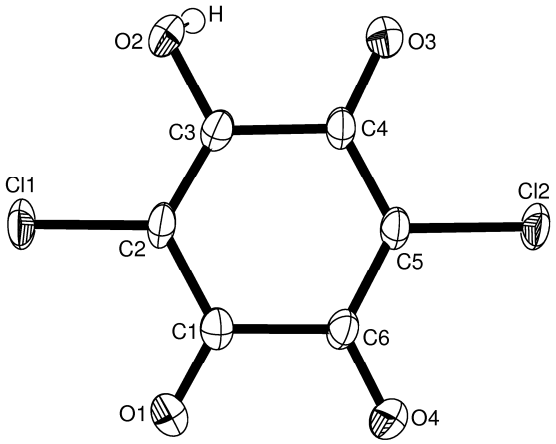

Figure S1.4 ORTEP-3 drawing of hydrogen chloranilate ion in [RbHCA$(H_2O)_2$]. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atom has been depicted as a sphere of an arbitrary radius.

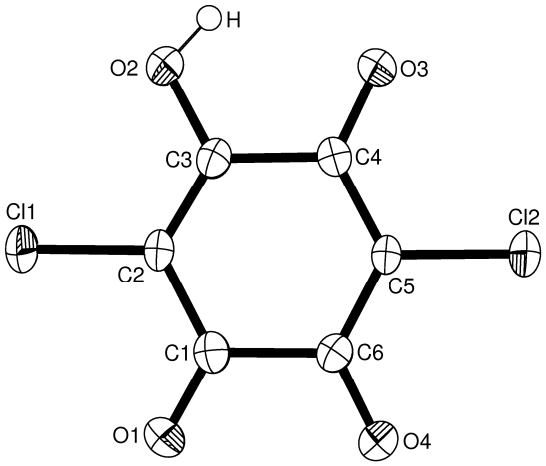

Figure S1.5 ORTEP-3 drawing of hydrogen chloranilate ion in [$CsHCA(H_2O)_2$]. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atom has been depicted as a sphere of an arbitrary radius.

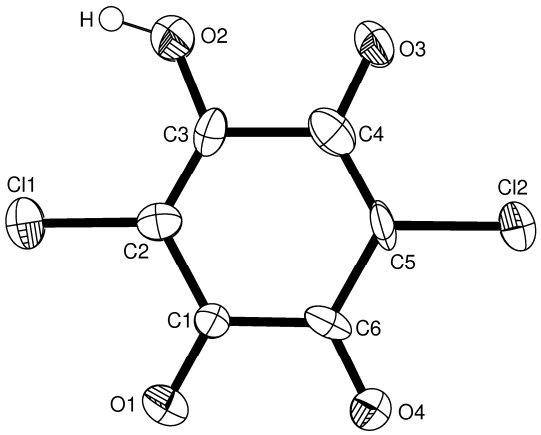

Figure S1.6 ORTEP-3 drawing of hydrogen chloranilate ion in $NH_4HCA{\cdot}2H_2O$. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atom has been depicted as a sphere of an arbitrary radius.

S2 Coordination geometries of alkali cations

Table S2.1 Geometric parameters of lithium coordination sphere (Å). Coordination polyhedron is a tetragonal pyramid.

Li1 – O1	(HCA)	2.09(1)
Li1 – O2^{i}	(HCA)	2.10(1)
Li1 – O3^{i}	(HCA)	2.00(1)
Li1 – O4	(HCA)	2.05(1)
Li1 – O5	(ethanol)	2.002(8)

Symmetry code: *i*) 1–*x*, 1–*y*, ½+*z*.

Table S2.2 Geometric parameters of sodium coordination spheres (Å). Coordination polyhedra are distorted octahedra.

	Na1	
Na1 – O1	(HCA)	2.533(1)
Na1 – O20	(water)	2.370(1)
Na1 – O21	(water)	2.374(1)
Na1 – O22	(water)	2.323(1)
Na1 – O4	(HCA)	2.425(1)
Na1 – O6	(CA)	2.379(1)
	Na2	
Na2 – O1	(HCA)	2.361(1)
Na2 – O23	(water)	2.507(1)
Na2 – O24	(water)	2.371(1)
Na2 – O5	(CA)	2.375(1)
Na2 – O6	(CA)	2.380(1)
Na2 – O8^{i}	(CA)	2.603(1)
	Na3	
Na3 – Cl3^{ii}	(CA)	3.0000(7)
Na3 – O23	(water)	2.372(1)
Na3 – O24	(water)	2.399(1)
Na3 – O25	(water)	2.406(1)
Na3 – O26	(water)	2.331(1)
Na3 – O7^{ii}	(CA)	2.343(1)
	Na4	
Na4 – Cl6	(CA)	3.1400(7)
Na4 – O25	(water)	2.383(1)
Na4 – O26	(water)	2.392(1)
Na4 – O27	(water)	2.338(1)
Na4 – O28	(water)	2.390(1)
Na4 – O9	(CA)	2.330(1)
	Na5	
Na5 – O11^{ii}	(CA)	2.408(1)
Na5 – O12^{ii}	(CA)	2.398(1)
Na5 – O12^{iii}		2.316(1)
Na5 – O27	(water)	2.404(1)
Na5 – O28	(water)	2.379(1)
Na5 – O29	(water)	2.484(1)

Symmetry codes: *i*) 2–*x*, 2–*y*, -*z*; *ii*) –1+*x*, *y*, *z*; *iii*) 1–*x*, 3–*y*, –*z*.

Table S2.3 Geometric parameters of potassium coordination sphere (Å). Coordination polyhedron is tricapped trigonal prism (6+3).

K1 – Cl1^{i}	(HCA)	3.583(1)
K1 – Cl2^{ii}	(HCA)	3.335(1)
K1 – Cl2^{iii}		3.511(1)
K1 – O1	(HCA)	2.912(2)
K1 – O1^{i}		2.842(2)
K1 – O3^{ii}	(HCA)	2.919(2)
K1 – O4	(HCA)	2.693(2)
K1 – O5	(water)	2.830(2)
K1 – O6	(water)	2.830(3)

Symmetry code: *i*) –*x*, 2–*y*, –*z*; *ii*) –*x*, ½+*y*, ½–*z*; *iii*) *x*, 3/2–*y*, –½+*z*.

Table S2.4 Geometric parameters of rubiduim coordination sphere (Å). Coordination polyhedron is a mono-capped pentagonal bipyramid (7+1).

Rb1 – Cl1^{i}	(HCA)	3.508(3)
Rb1 – O1	(HCA)	3.131(3)
Rb1 – O1^{i}		2.990(3)
Rb1 – O2^{ii}	(HCA)	3.134(3)
Rb1 – O3^{iii}	(HCA)	3.438(4)
Rb1 – O4	(HCA)	2.859(3)
Rb1 – O5	(water)	2.986(5)
Rb1 – O6	(water)	2.934(4)

Symmetry code: *i*) 1–*x*, –*y*, 1–*z*; *ii*) –½+*x*, ½–*y*, –½+*z*; *iii*) 2–*x*, –*y*, 1–*z*.

Table S2.5 Geometric parameters of caesium coordination sphere (Å). Coordination polyhedron is a mono-capped pentagonal bipyramid (7+1).

Cs1 – Cl1^{i}	(HCA)	3.6498(8)
Cs1 – O1	(HCA)	3.247(2)
Cs1 – O1^{i}		3.155(2)
Cs1 – O2^{ii}	(HCA)	3.214(2)
Cs1 – O3^{iii}	(HCA)	3.447(2)
Cs1 – O4	(HCA)	3.023(2)
Cs1 – O5	(water)	3.231(3)
Cs1 – O6	(water)	3.140(3)

Symmetry code: *i*) 2–*x*, 2–*y*, –*z*; *ii*) ½+*x*, ½-*y*, ½+*z*; *iii*) 1–*x*, 1–*y*, –*z*.

S3 ORTEP drawings of alkali cation coordination spheres

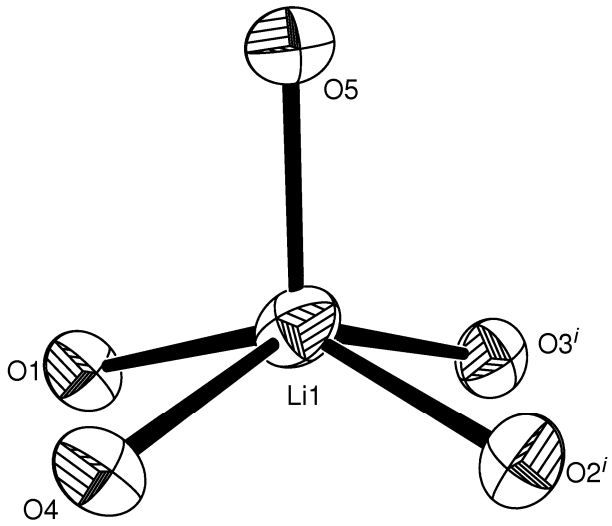

Figure S3.1 ORTEP-3 drawing of coordination sphere of Li^{+} in [LiHCAEtOH]. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms have been depicted as a sphere of arbitrary radii.Symmetry code: *i*) 1–*x*, 1–*y*, ½+*z*.

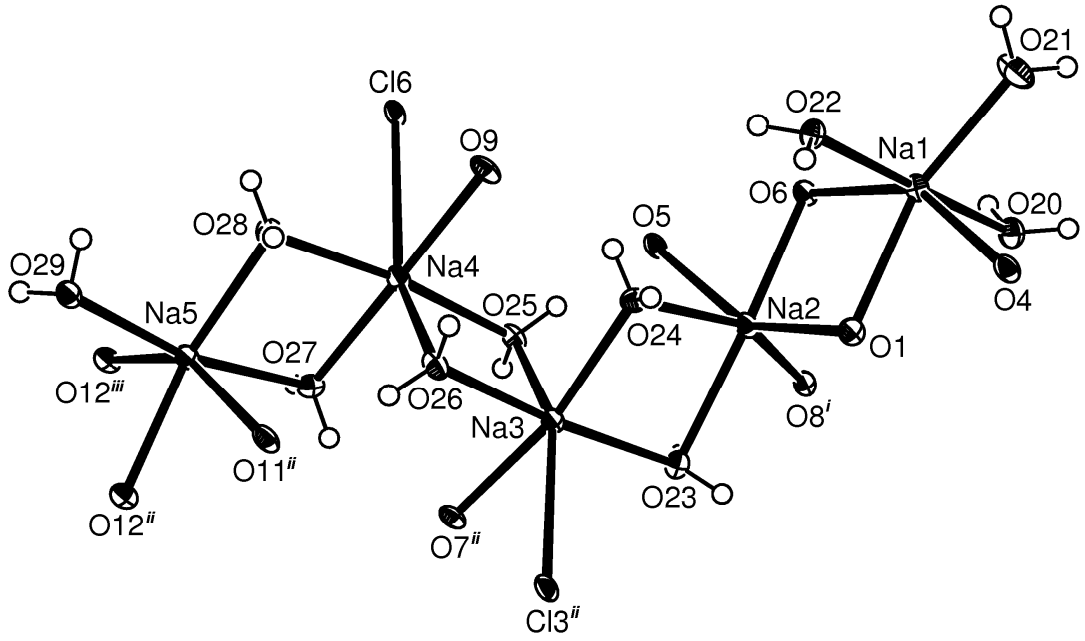

Figure S3.2 ORTEP-3 drawings of coordinations spheres of Na^{+} in $[Na_5HCA(CA)_2(H_2O)_{10}]$. The common edges in pentameric octahedral ribbon are: O1 from HCA^{-} and O6 from CA^{2-} between Na1/Na2, whereas in the polyhedra Na2/Na3, Na3/Na4, and Na4/Na5 water molecules function as double bridges. Atomic displacement ellipsoids are drawn at 50% probability and hydrogen atoms have been depicted as a sphere of arbitrary radii. Symmetry code: *i*) 2–*x*, 2–*y*, –*z*; *ii*) –1+*x*, *y*, *z*; *iii*) 1–*x*, 3–*y*, –*z*.

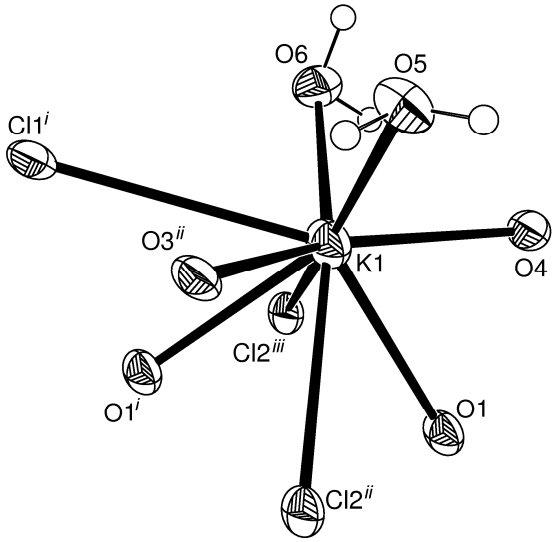

Figure S3.3 ORTEP-3 drawing of coordination sphere of K^+ in [KHCA$(H_2O)_2$]. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms have been depicted as a sphere of arbitrary radii. Symmetry code: *i*) *–x*, 2*–y*, *–z*; *ii*) *–x*, ½+*y*, ½*–z*; *iii*) *x*, 3/2-*y*, *–*½+*z*.

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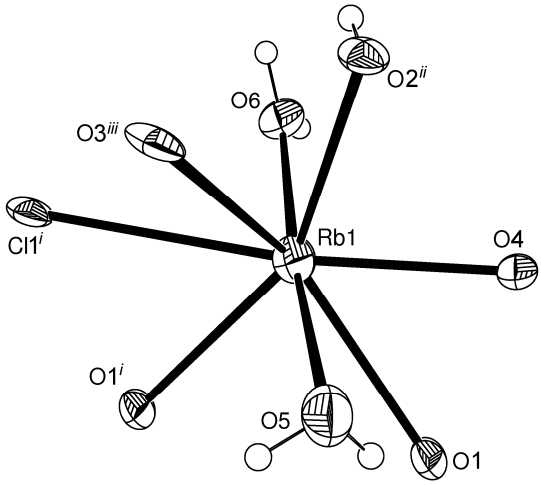

Figure S3.4 ORTEP-3 drawing of coordination sphere of Rb^+ in [RbHCA$(H_2O)_2$]. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms have been depicted as a sphere of arbitrary radii.Symmetry code: *i*) 1*–x*, *–y*, 1*–z*;
ii) *–*½+*x*, ½*–y*, *–*½+*z*; *iii*) 2*–x*, *–y*, 1*–z*.

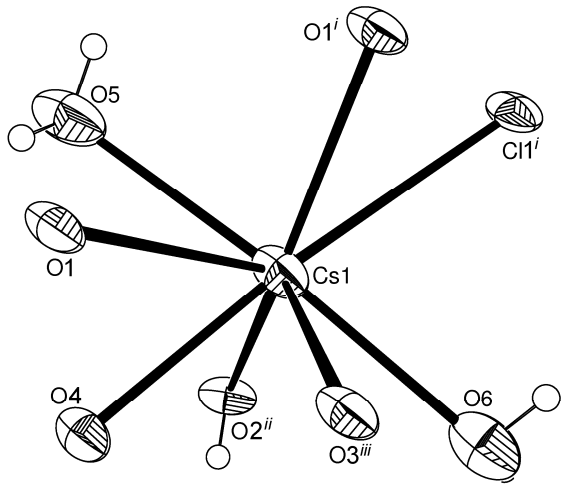

Figure S3.5 ORTEP-3 drawing of coordination sphere of Cs^{+} in $[CsHCA(H_2O)_2]$. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms have been depicted as a sphere of arbitrary radii. Symmetry code: *i*) 2–*x*, 2–*y*, –*z*; *ii*) ½+*x*, ½–*y*, ½+*z*; *iii*) 1–*x*, 1–*y*, –*z*.

S4 Geometric parameters of hydrogen bonds in $[Na_5HCA(CA)_2(H_2O)_{10}]$

Table S4.1 Geometric parameters of hydrogen bonds in $[Na_5HCA(CA)_2(H_2O)_{10}]$.

	d(*D*-H)/Å	d(H···*A*)/Å	d(*D*···*A*)/Å	*D*-H···*A*/º	Symm. operation on *A*
O2-H···O29	0.88(2)	2.27(2)	2.657(1)	106(2)	–*x*, 2–*y*, 1–*z*
O20-H20A···O4	0.90(2)	1.92(2)	2.817(1)	170(2)	2–*x*, 2–*y*, 1–*z*
O20-H20B···Cl1	0.92(2)	2.73(2)	3.311(1)	122(1)	2–*x*,2–*y*,1–*z*
O20-H20B···Cl4	0.92(2)	2.67(2)	3.360(1)	132(1)	2–*x*, 2–*y*, *z*
O21-H21A···O2	0.89(3)	2.32(2)	3.014(2)	147(2)	1+*x*, *y*, *z*
O21-H21B···O11	0.88(3)	2.22(3)	2.949(1)	139(2)	2–*x*, 2–*y*, 1–*z*
O22-H22A···O9	0.89(2)	1.93(2)	2.784(1)	158(2)	1–*x*, 2–*y*, 1–*z*
O22-H22B···O10	0.90(1)	1.97(1)	2.861(1)	168(2)	*x*, *y*, *z*
O23-H23A···O2	0.87(1)	2.18(1)	3.009(1)	159(2)	1–*x*, 1–*y*, 1–*z*
O23-H23B···O7	0.91(1)	1.84(1	2.738(1)	169(2)	2–*x*, 2–*y*, 1–*z*
O24-H24A···O10	0.88(1)	2.05(1)	2.981(1)	159(2)	1–*x*, 2–*y*, 1–*z*
O24-H24B···O9	0.88(2)	2.40(2)	3.165(1)	146(2)	*x*, *y*, *z*
O24-H24B···O10	0.88(2)	2.22(2)	2.959(1)	142(2)	*x*, *y*, *z*
O25-H25A···O5	0.90(2)	1.88(2)	2.735(1)	158(2)	*x*, *y*, *z*
O25-H25B···O23	0.88(2)	2.31(2)	3.091(1)	148(2)	1–*x*, 2–*y*, –*z*
O26-H26A···O22	0.92(2)	1.90(2)	2.791(1)	162(2)	1–*x*, 2–*y*, 1–*z*
O26-H26B···O11	0.89(2)	1.98(2)	2.829(1)	159(2)	–1+*x*, *y*, *z*
O27-H27A···O7	0.89(2)	2.40(2)	3.151(1)	142(2)	–1+*x*, *y*, *z*
O27-H27A···O8	0.89(2)	2.17(2)	2.950(1)	146(2)	–1+*x*, *y*, *z*
O27-H27B···O3	0.89(1)	1.97(1)	2.807(1)	155(2)	*x*, 1+*y*, 1+*z*
O28-H28A···O4	0.90(2)	2.51(2)	2.941(1)	110(2)	1–*x*, 2–*y*, 1–*z*
O28-H28A···O21	0.90(2)	2.17(2)	3.035(2)	163(2)	1–*x*, 2–*y*, 1–*z*
O28-H28B···Cl2	0.90(2)	2.54(2)	3.433(1)	171(2)	1–*x*, 2–*y*, 1–*z*
O28-H28B···O4	0.90(2)	2.54(2)	2.941(1)	107(1)	1–*x*, 2–*y*, 1–*z*
O29-H29A···O8	0.89(1)	1.90(2)	2.784(1)	175(1)	1–*x*, 3–*y*, –*z*
O29-H29B···O20	0.90(2)	1.94(2)	2.834(1)	179(2)	–1+*x*, 1+*y*, *z*