-SUPPORTING INFORMATION-

Hydrogen-Bonded Supramolecular Architectures Based on $[Zr(C_2O_4)_4]^{4-}$ Anion and Protonated Polyamine Cations

Monia Hamdouni,*[†]Siwar Walha,[†]Carine Duhayon,[‡§] Ahlem Kabadou,[†] Jean-Pascal Sutter,*[‡§]

[†]Laboratoire des Sciences des Matériaux et de l'Environnement ; Faculté des Sciences de Sfax, Université de Sfax, Sfax, BP 1171, 3000, Tunisie.

[‡]CNRS, LCC (Laboratoire de Chimie de Coordination), 205, route de Narbonne, F-31077 Toulouse, France.

[§]Université de Toulouse, UPS, INPT, LCC, F-31077 Toulouse, France.

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Figure S1. ORTEP view of the asymmetric unit of [{$(H_2$-L1$)_2[Zr(C_2O_4)_4]$}·$2H_2O$] (**1**) with ellipsoids cut at the 30% probability level.

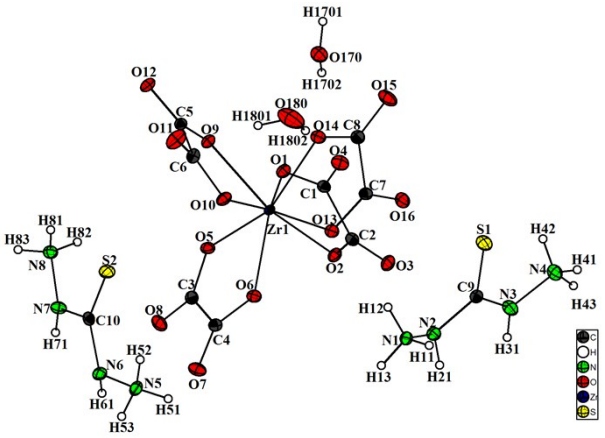

Figure S2. Connection of (a) the first $(H_2$-L1$)^{2+}$ di-cations and (b) the second one with different $[Zr(C_2O_4)_4]^{4-}$ metallotectons via H-bonds (Symmetry transformations: ***i***, *x, y-1, z* **; *ii***, *1-x, 1-y , 1-z* **; *iii***, *1-x, 1-y, -z* **; *iv***, *2-x, 1-y, -z* **; *v***, *x, y, z-1* **; *vi***, *x-1, y, z* **; *vii***, *1-x, 2-y, 1-z* **; *viii***, *1-x, 2-y, -z* **; *ix***, *x-1, y+1, z*).

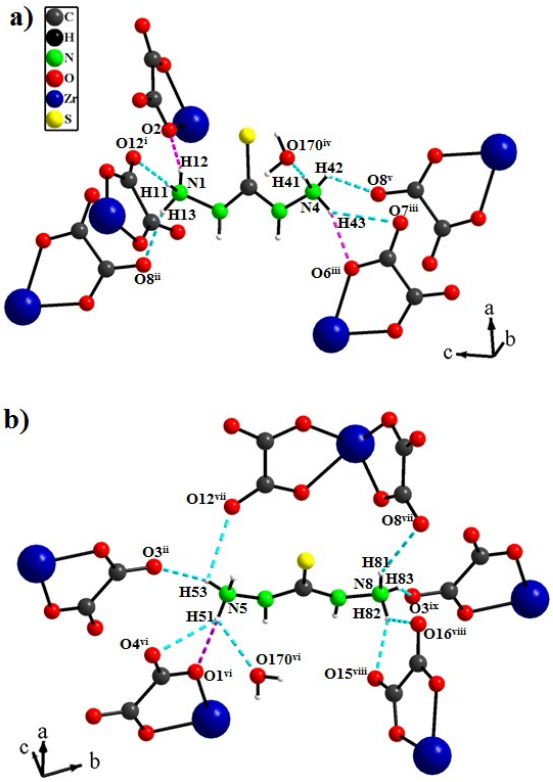

Figure S3. Two layers (in green and purple) interconnected via H-bonds (drown in red).

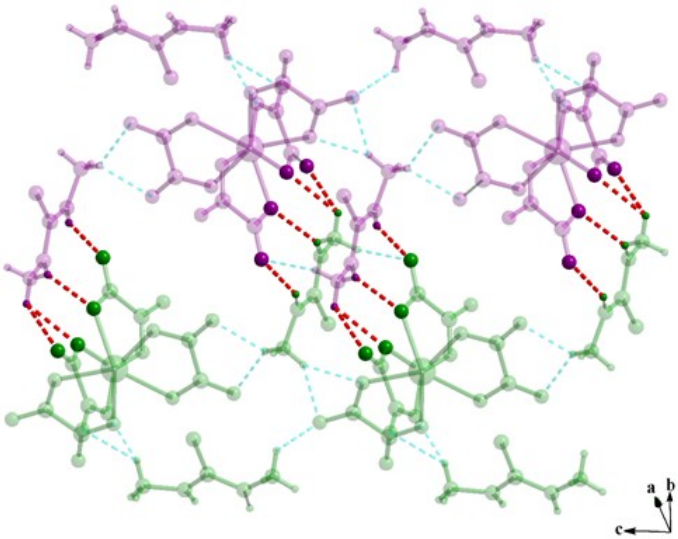

Figure S4. ORTEP view of the asymmetric unit of $\{(H_2\text{-}L2)_2[Zr(C_2O_4)_4]\}\cdot 4H_2O$ (**2**) with ellipsoids cut at the 30% probability level.

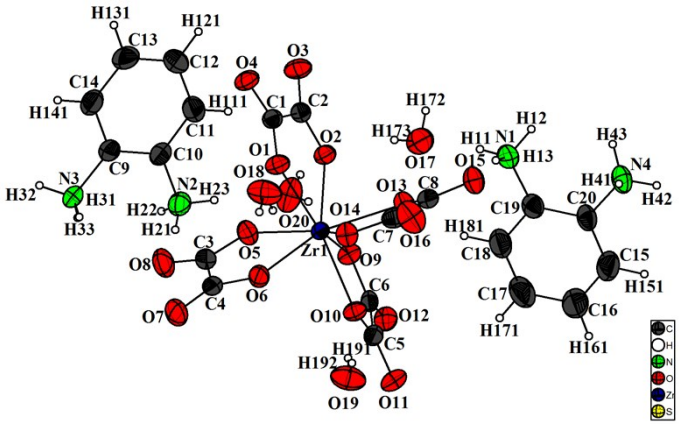

Figure S5. Connection of (a) the first $(H_2\text{-}L2)^{2+}$ di-cation and (b) the second one with $[Zr(C_2O_4)_4]^{4-}$ metallotectons via H-bonds (Symmetry transformations : ***xi***, *1-x, 1-y, 2-z* ***; xii***, *-x, 1-y, 1-z* ***; xiii***, *-x, 1-y, 2-z* ***; xiv***, *-x, y+1/2, 3/2-z* ***; xv***, *1-x, y-1/2, 3/2-z*).

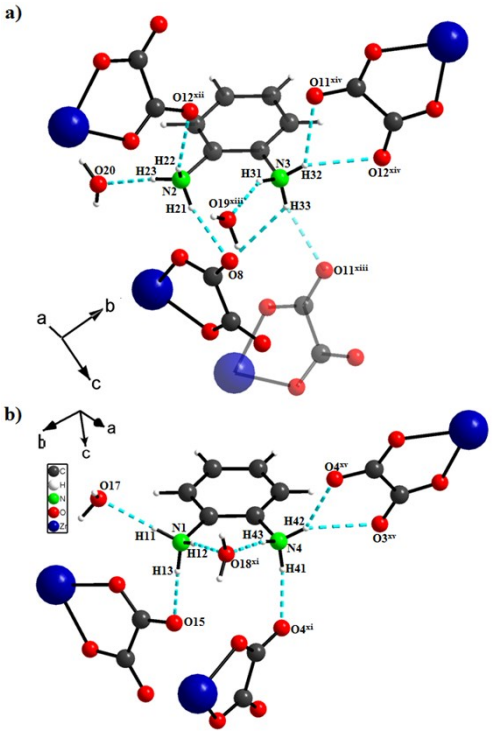

Figure S6. ORTEP view of the asymmetric unit of $\{(H_2\text{-}L3)_2[Zr(C_2O_4)_4]\}\cdot 4H_2O$ (**3**) with ellipsoids cut at the 30% probability level.

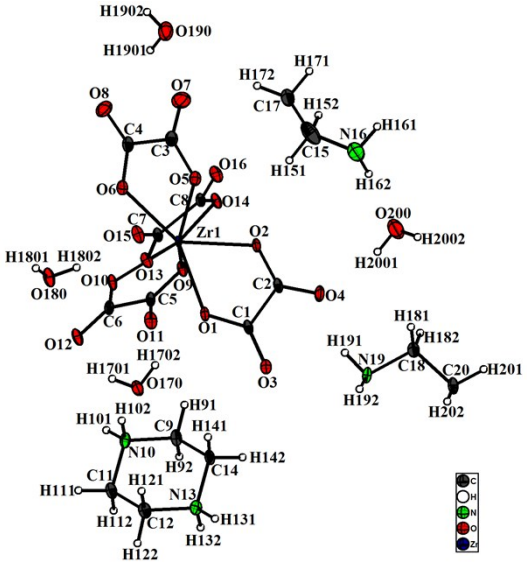

Figure S7. Connection of the three different $(H_2\text{-}L3)^{2+}$ di-cations with $[Zr(C_2O_4)_4]^{4-}$ metallotectons via H-bonds. (a) the first T1 bridging organic molecule **;** (b) the second T1 bridging organic molecule **;** (c) T2 organic molecule (Symmetry transformations: ***iii****, 1-x, 1-y, -z* **;** ***vi****, x-1, y, z* **;** ***viii****, 1-x, 2-y, -z* **;** ***xix****,2-x, 2-y, 1-z* **;** ***xx****, x, y+1, z* **;** ***xxx****, -x, 2-y, -z*).

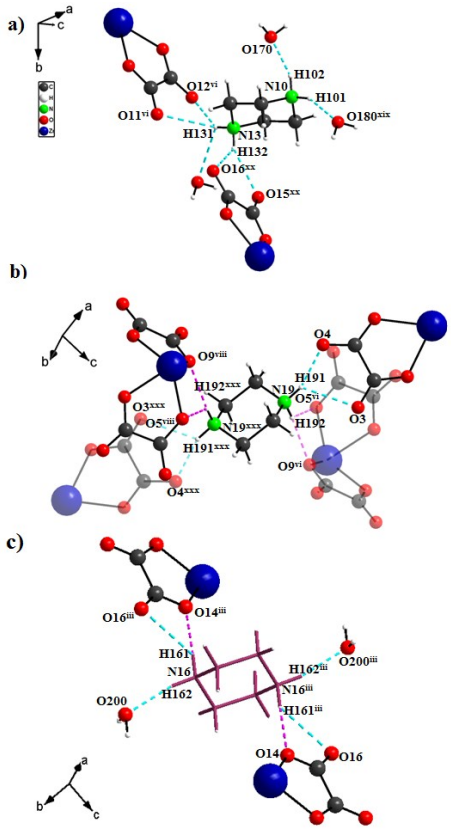

Figure S8. Differences in organizations of (a) polymorphic structure[17] **;** (b) compound **3**.

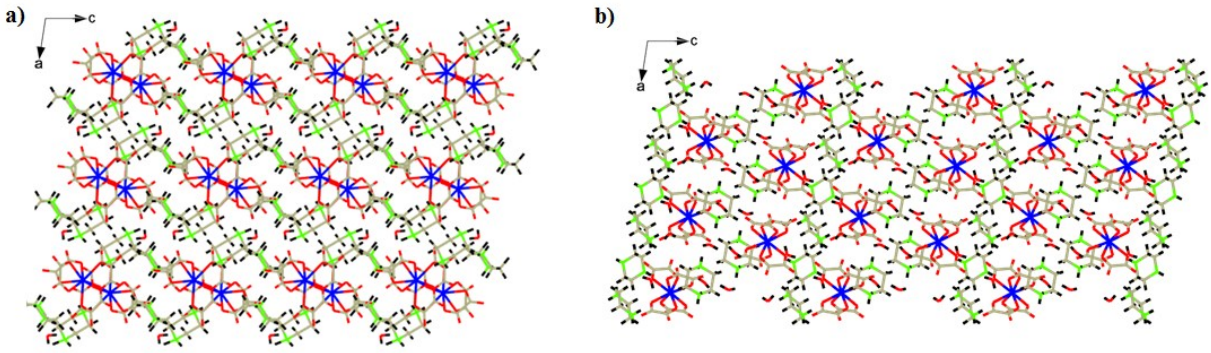

Figure S9. ORTEP view of the asymmetric unit of $\{(H\text{-}L4)_4[Zr(C_2O_4)_4]\}\cdot 2H_2O$ **(4)** with ellipsoids cut at the 30% probability level.

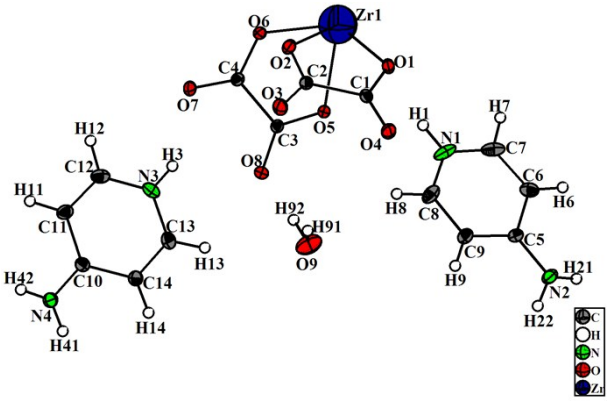

Figure S10. Connection of (a) the first $(H\text{-}L4)^{+}$ cations and (b) the second one with $[Zr(C_2O_4)_4]^{4-}$ metallotectons via H-bonds (Symmetry transformations: ***xxiii****, 3/2-x, y, 1/2-z* ***; xxiv****, 1-x,-y, 1-z* ***; xxvi****, 3/2-x, y, 3/2-z* ***; xxvii****, x-1/2, 1-y, z+1/2*).

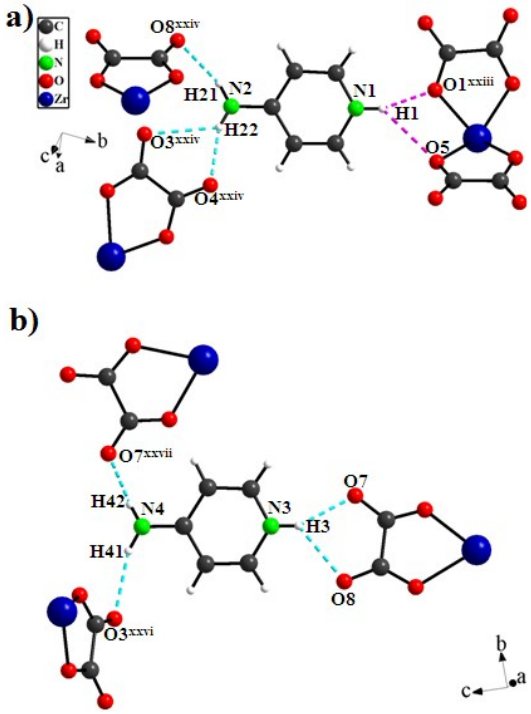

Figure S11. TGA/DTA curves for compounds **1** (a), **2** (b) and **3** (c) recorded under N_2 flow.

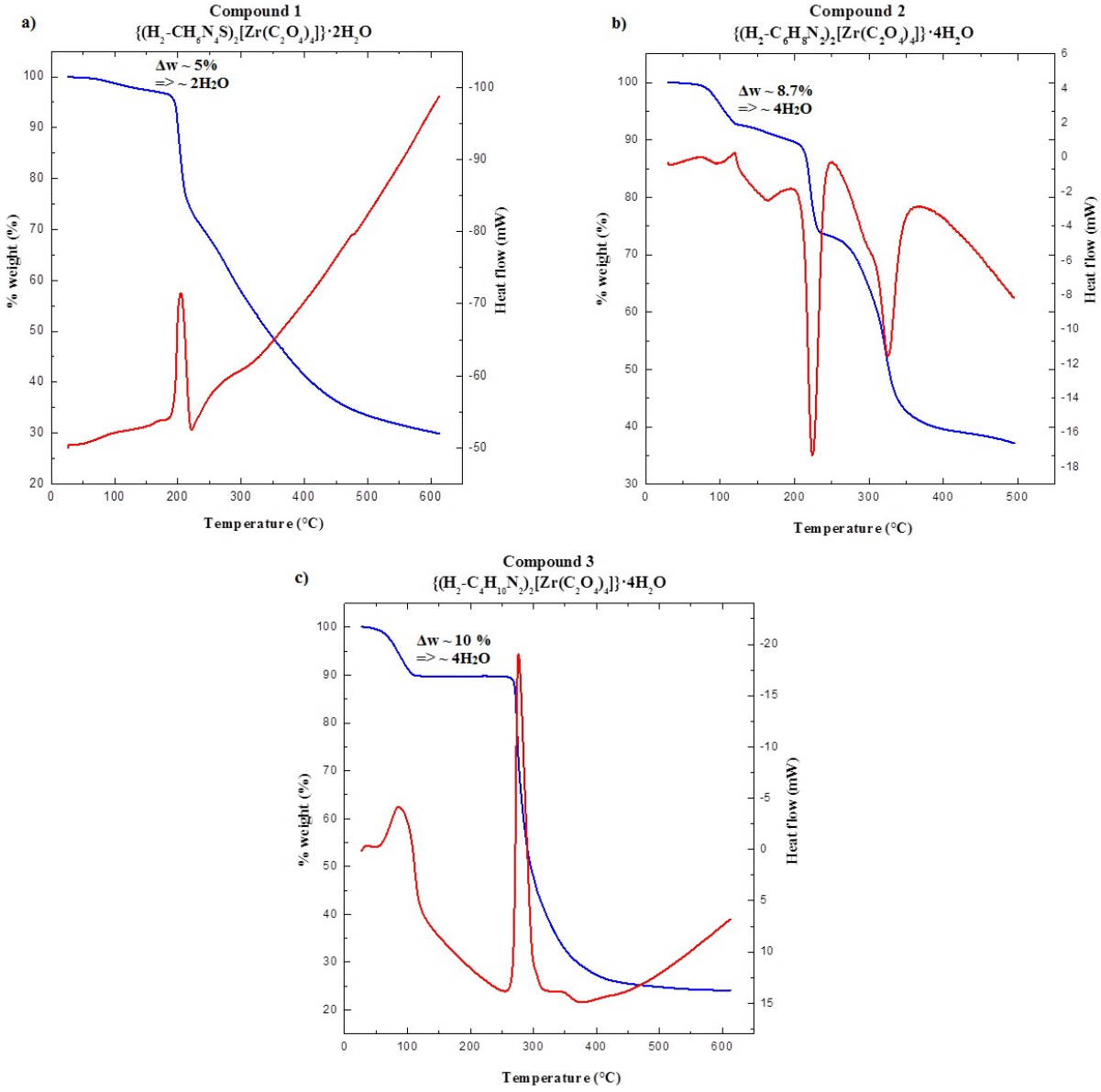

Table S1. Formula deduced from XRD, elemental analysis, and evacuated materials stability upon thermal treatment for materials **1-3**.

	Single Crystal-XRD	**Elemental Analysis**	**TGA**
1	$\{(H_2\text{-}CH_6N_4S)_2[Zr(C_2O_4)_4]\}\cdot 2H_2O$ 2 O_w-atoms, occupancy rate =1	Anal. (%) calcd.: C, 17.25; H, 2.87; N, 16.10 ; Found: C, 17.55; H, 2.77; N, 15.99.	Slightly decreasing plateau from 55°C to 200°C[(a)] ; $\Delta w \approx 5.0\%$, corresponding to $2H_2O$[(b)].
2	$\{(H_2\text{-}C_6H_8N_2)_2[Zr(C_2O_4)_4]\}\cdot 4H_2O$ 4 O_w-atoms, occupancy rate =1	Anal. (%) calcd.: C, 32.64; H, 3.8; N, 7.61 ; Found: C, 32.59; H, 3.5; N, 7.55.	Plateau between 110°C and 210°C[(a)] ; $\Delta w \approx 8.7\%$, corresponding to 4 H_2O[(b)].
3	$\{(H_2\text{-}C_4H_{10}N_2)_2[Zr(C_2O_4)_4]\}\cdot 4H_2O$ 4 O_w-atoms, occupancy rate =1	Anal. (%) calcd.: C, 29.11; H, 4.85; N, 8.49 ; Found: C, 28.98; H, 4.52; N, 4.32.	Plateau between 110°C and 210°C[(a)] ; $\Delta w \approx 10\%$, corresponding to 4 H_2O[(b)].

(a) Thermal stability window for the guest free architecture. Material decomposition occurs above the temperature plateau upper-limit.

(b) H_2O molecules number was calculated considering the weight (w) at the temperature plateau upper-limit.

Table S2. Selected Hydrogen Bonds for compounds **1-4**.

atoms D-H···A	dist. D-H (Å)	dist. H-A (Å)	dist. D-A (Å)	angles D-H···A (°)
		Compound 1		
N1-H11···O12^{i}	0.894	2.079	2.961(3)	169.0
N1-H12···C2	0.895	2.591	3.387(3)	149.0
N1-H12···O2	0.895	1.921	2.793(3)	164.0
N1-H13···O8^{ii}	0.896	1.958	2.816(3)	160.0
N2-H21···O16^{iii}	0.865	1.964	2.825(3)	173.0
N3-H31···O13^{iii}	0.854	1.954	2.795(3)	168.0
N4-H41···O170^{iv}	0.890	1.843	2.714(3)	166.0
N4-H42···O8^{v}	0.888	2.395	3.039(3)	130.0
N4-H43···C4^{iii}	0.911	2.519	3.422(3)	171.0
N4-H43···O6^{iii}	0.911	1.972	2.839(3)	158.0
N4-H43···O7^{iii}	0.911	2.513	3.285(3)	143.0
N5-H51···C1^{vi}	0.890	2.556	3.294(3)	141.0
N5-H51···O1^{vi}	0.890	2.241	2.850(3)	125.0
N5-H51···O4^{vi}	0.890	2.314	3.052(3)	140.0
N5-H51···O170^{vi}	0.890	2.308	2.922(3)	126.0
N5-H53···O3^{ii}	0.889	1.946	2.809(3)	163.0
N6-H61···O9^{vi}	0.859	1.994	2.852(3)	179.0
N7-H71···O12^{vi}	0.857	1.983	2.837(3)	174.0
N8-H81···C3^{vii}	0.885	2.547	3.284(3)	141.0
N8-H81···O8^{vii}	0.885	2.165	2.938(3)	145.0
N8-H82···O15^{viii}	0.899	1.898	2.706(3)	148.0
N8-H82···O16^{viii}	0.899	2.303	2.893(3)	123.0
N8-H83···O3^{ix}	0.884	1.988	2.758(3)	145.0
O170-H1701···O180^{x}	0.847	1.969	2.737(3)	150.0
O170-H1702···O14	0.821	2.125	2.925(3)	165.0
O180-H1801···O11	0.821	2.233	2.978(3)	151.0
O180-H1802···O10^{viii}	0.806	2.346	3.083(3)	153.0
		Compound 2		
N1-H11··· O17	0.906	1.894	2.796(4)	174.0
N1-H12··· O18^{xi}	0.895	1.953	2.839(4)	170.0
N1-H13··· O15	0.930	1.788	2.709(4)	170.0
N1-H13··· C8	0.930	2.427	3.241(4)	146.0
N2-H21··· O8	0.867	1.975	2.792(4)	157.0
N2-H22··· O12^{xii}	0.875	2.126	2.895(4)	146.0
N2-H23··· O20	0.891	1.870	2.756(4)	172.0
N3-H31··· O19^{xiii}	0.904	1.943	2.768(4)	151.0
N3-H32··· O11^{xiv}	0.872	2.195	2.832(4)	130.0
N3-H32··· O12^{xiv}	0.872	2.236	3.021(4)	150.0
N3-H33··· O8	0.882	2.423	3.011(4)	124.0
N3-H33··· O11^{xiii}	0.882	2.251	2.980(4)	140.0
N4-H41··· O4^{xi}	0.889	1.814	2.696(4)	171.0
N4-H42··· O3^{xv}	0.910	2.422	3.177(4)	140.0
N4-H42··· O4^{xv}	0.910	1.969	2.747(4)	142.0
N4-H43··· O18^{xi}	0.921	1.871	2.778(4)	168.0
C12-H121··· O4^{xvi}	0.921	2.570	3.353(4)	143.0
C14-H141··· O7^{xvi}	0.921	2.522	3.291(4)	141.0
C15-H151··· O3^{xv}	0.935	2.517	3.337	147.0

C17-H171⋯ O11^{xvii}	0.956	2.535	3.285(4)	135.0
O17-H172⋯ O16^{v}	0.832	2.073	2.854(4)	156.0
O17-H173⋯ O2	0.819	2.066	2.868(4)	166.0
O18-H182⋯ O3^{xviii}	0.827	1.799	2.596(4)	161.0
O18-H183⋯ O14	0.811	2.272	2.942(4)	140.0
O19-H191⋯ O17^{xviii}	0.844	2.133	2.961(4)	167.0
O19-H192⋯ O10	0.836	1.992	2.826(4)	175.0
O20-H201⋯ O6^{v}	0.804	2.442	3.238(4)	170.0
O20-H202⋯ O9	0.809	2.256	3.015(4)	156.0
		Compound 3		
N10-H101⋯ O180^{xix}	0.894	1.902	2.725(3)	153.0
N10-H102⋯ O170	0.892	1.876	2.726(3)	159.0
N13-H131⋯ O11^{vi}	0.887	2.558	3.124(3)	122.0
N13-H131⋯ O12^{vi}	0.887	2.067	2.822(3)	142.0
N13-H132⋯ O15^{xx}	0.879	2.163	2.941(3)	147.0
N13-H132⋯ O16^{xx}	0.879	2.189	2.852(3)	132.0
N16-H161⋯ C8^{iii}	0.926	2.477	3.258(3)	142.0
N16-H161⋯ O14^{iii}	0.926	1.869	2.788(3)	172.0
N16-H162⋯ O200	0.921	1.876	2.777(3)	165.0
N19-H191⋯ O4	0.891	1.866	2.718(3)	159.0
N19-H192⋯ O5^{vi}	0.884	2.409	3.038(3)	128.0
N19-H192⋯ O9^{vi}	0.884	2.063	2.899(3)	157.0
C11-H111⋯ O6^{xix}	0.970	2.297	3.207(3)	156.0
C14-H141⋯ O3	0.961	2.560	3.172(3)	122.0
C14-H141⋯ O170	0.961	2.549	3.245(3)	129.0
C15-H151⋯ O2	0.977	2.545	3.458(3)	155.0
C15-H152⋯ O190^{iv}	0.979	2.423	3.382(3)	166.0
C20-H202⋯ O2^{vi}	0.963	2.584	3.502(3)	159.0
O170-H1701⋯ O12^{xix}	0.819	1.931	2.729(3)	164.0
O170-H1702⋯ O1	0.806	2.009	2.809(3)	172.0
O180-H1801⋯ O8^{xix}	0.822	2.071	2.885(3)	170.0
		Compound 4		
N1-H1⋯ O1^{xxiii}	0.869	1.918	2.738(1)	157.0
N1-H1⋯ O5	0.869	2.574	3.235(1)	134.0
N2-H21⋯ O8^{xxiv}	0.863	2.184	2.989(1)	155.0
N2-H22⋯ O3^{xxv}	0.858	2.466	3.021(1)	123.0
N2-H22⋯ O4^{xxv}	0.858	2.062	2.884(1)	160.0
N3-H3⋯ O7	0.876	2.022	2.807(1)	149.0
N3-H3⋯ O8	0.876	2.291	2.927(1)	129.0
N4-H41⋯ O3^{xxvi}	0.874	2.176	3.017(1)	161.0
N4-H42⋯ O7^{xxvii}	0.862	2.118	2.969(1)	170.0

Symmetry transformations: ***i***, *x, y-1, z* ***; ii***,*- x+1,- y+1, -z+1* ***; iii***, *-x+1, -y+1, -z* ***; iv***, *-x+2, -y+1, -z* ***; v***, *x, y, z-1* ***; vi***, *x-1, y, z* ***; vii***, *-x+1, -y+2,- z+1* ***; viii***, *-x+1, -y+2, -z* ***; ix***, *x-1, y+1, z* ***; x***, *-x+2, -y+2, -z* ***; xi***, *-x+1, -y+1, -z+2 ;* ***xii*** ***;*** *-x, -y+1, -z+1 ;* ***xiii ;*** *-x, -y+1, -z+2* ***; xiv***, *-x, y+1/2,- z+3/2* ***; xv***, *-x+1, y-1/2, -z+3/2* ***; xvi***, *x, -y+3/2, z-1/2* ***; xvii***, *x, -y+1/2, z-1/2* ***; xviii***, *x, y, z+1* ***; xix***, *-x+2, -y+2, -z+1* ***; xx***, *x, y+1, z* ***; xxi***, *x+1, y+1, z* ***; xxii***, *-x+2, -y+1, -z+1* ***; xxiii***, *-x+3/2, y,-z+1/2* ***; xxiv***, *-x+1,- y, -z+1* ***; xxv***,*- x+2, -y,- z+1* ***; xxvi***,*-x+3/2, y,- z+3/2* ***; xxvii***, *x-1/2,-y+1,z+1/2* ***; xxviii***, *x-1/2,-y, z-1/2****;*** ***xxix***, *x+1/2,1-y, z-1/2.*