Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Structural diversity of five new bitriazole-based complexes: luminescence, sorption, and magnetic properties

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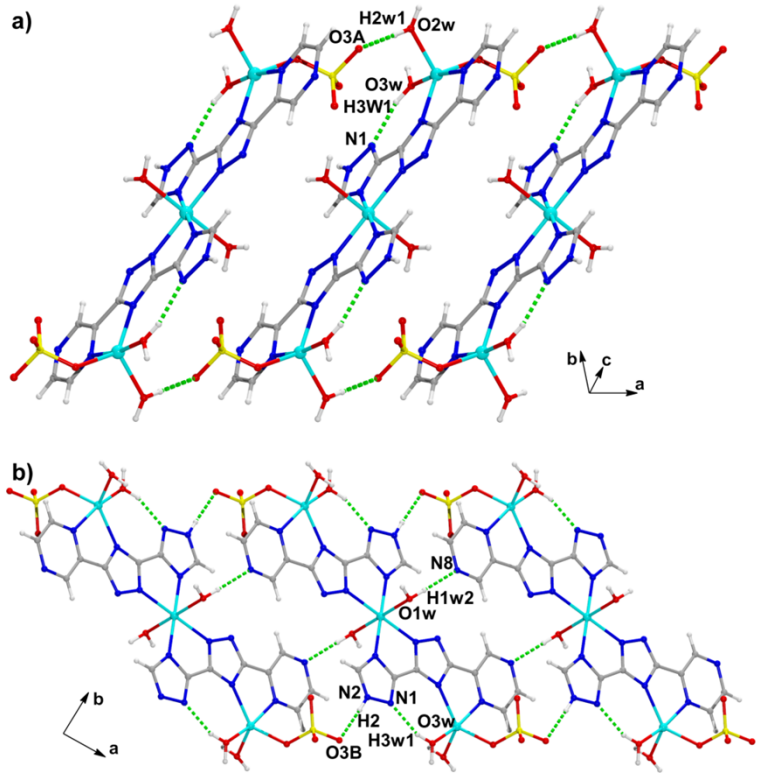

Fig. S1 The intra- and inter-molecular intra- and inter-molecular O-H···O, O-H···N and N-H···O hydrogen-bonging interactions in **3**.

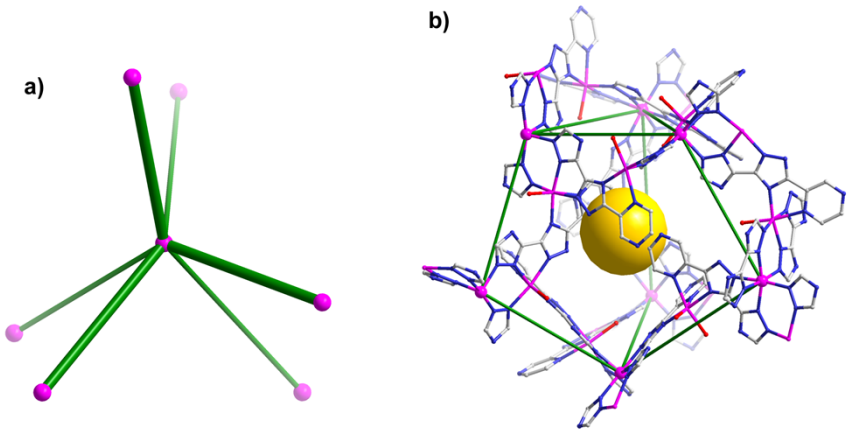

Fig. S2 a) The 6-connected triangular prism node, and b) a cage formed by seven trinuclear nodes with one triangular face and three pentagonal faces in **5**.

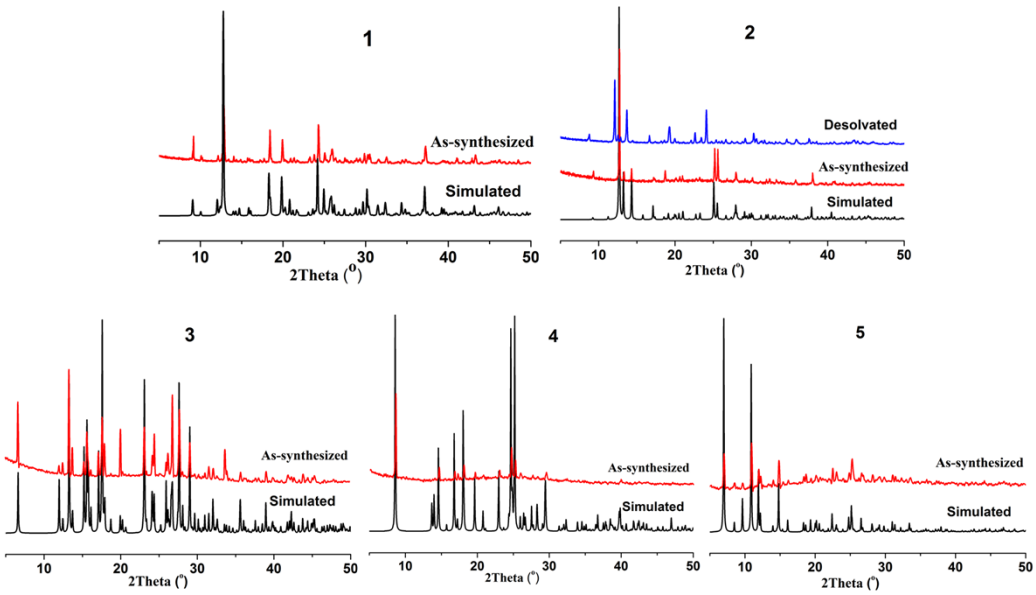

Fig. S3 PXRD patterns of **1-5** simulated from the X-ray single-crystal structures and as-synthesized samples.

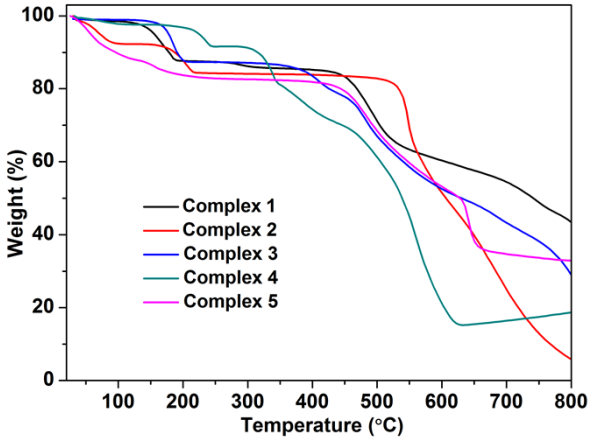

Fig. S4 TGA plots of the synthesized samples of **1-5**

Calculation of sorption heat of 2 for CO_2 uptake using Virial 2 model.

$$\ln P = \ln N + 1/T\sum_{i=0}^{m} aiN^i + \sum_{i=0}^{n} biN^i \qquad Q_{st} = -R\sum_{i=0}^{m} aiN^i$$

The above virial equation was used to fit the combined CO_2 isotherm data for **2** at 273 and 293 K, where P is the pressure, N is the adsorbed amount, T is the temperature, a_i and b_i are virial coefficients, and m and n are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.

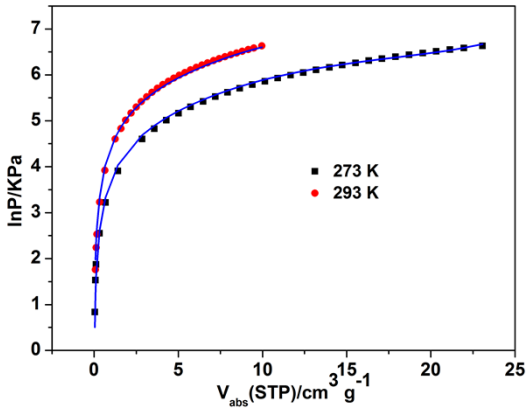

Fig. S5 CO_2 adsorption isotherms of **2** with fitting by Virial 2 model. Fitting results: a0 = -2869.12557, a1 = -19.77529, a2 = 2.85308, a3 = -0.1767, a4 = 0.00367, b0 = 14.278. Chi^2 = 0.00889, R^2 = 0.99605.

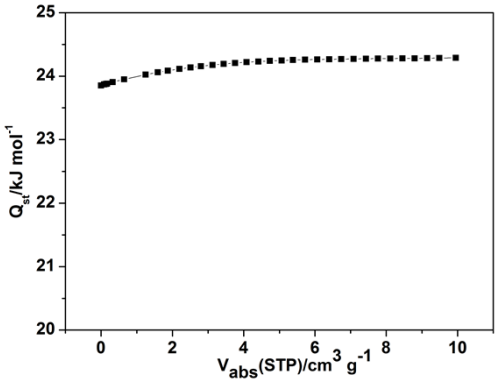

Fig. S6 Heat of CO_2 adsorption for **2** estimated by the virial equation.

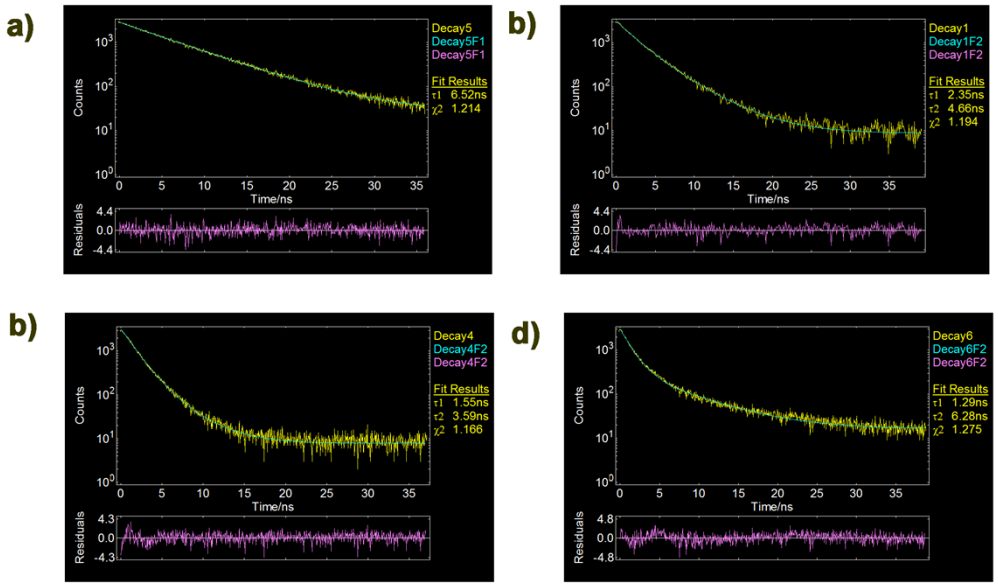

Fig. S7 The luminescence decays of **1** a), **2** b), **3** c), H_2pzbtz d) monitored at corresponding excitation/emission maxima.

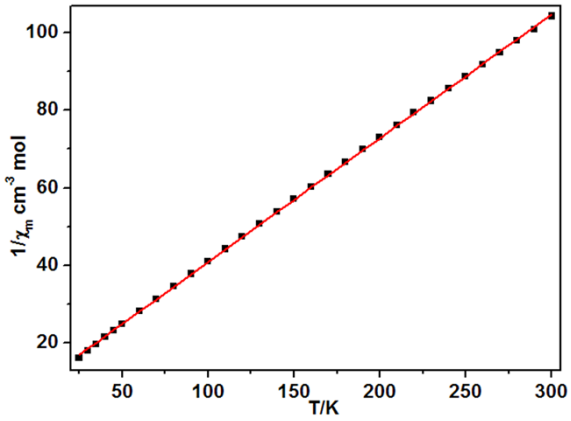

Fig. S8 The temperature dependence of the reciprocal susceptibilities (χ_M^{-1}), red line corresponds to the best fit according to Curie-Weiss law.

Table S1. Selected bond lengths (Å) and bond angles (°) of complexes **1**-**5**.

1					
Zn(1)-O(1)	2.0606(18)	Zn(1)-N(2)#1	2.078(2)	Zn(1)-N(1)	2.122(2)
Zn(1)-O(1W)	2.1463(19)	Zn(1)-N(8)#2	2.223(2)	Zn(1)-N(4)	2.229(2)
Zn(2)-O(2)	2.0261(19)	Zn(2)-O(2W)	2.0713(19)	Zn(2)-N(3)#3	2.090(2)
Zn(2)-N(5)	2.129(2)	Zn(2)-N(7)	2.249(2)	N(2)#1-Zn(1)-N(1)	98.73(8)
O(1)-Zn(1)-N(2)#1	88.74(8)	O(1)-Zn(1)-N(1)	171.22(8)	N(1)-Zn(1)-O(1W)	91.76(8)
O(1)-Zn(1)-O(1W)	92.74(8)	N(2)#1-Zn(1)-O(1W)	90.87(8)	N(1)-Zn(1)-N(8)#2	87.88(8)
O(1)-Zn(1)-N(8)#2	86.76(8)	N(2)#1-Zn(1)-N(8)#2	95.91(8)	N(2)#1-Zn(1)-N(4)	174.62(8)
O(1W)-Zn(1)-N(8)#2	173.19(8)	O(1)-Zn(1)-N(4)	96.62(8)	N(8)#2-Zn(1)-N(4)	84.88(8)
N(1)-Zn(1)-N(4)	75.96(8)	O(1W)-Zn(1)-N(4)	88.43(8)	O(2W)-Zn(2)-N(3)#3	97.62(8)
O(2)-Zn(2)-O(2W)	87.97(8)	O(2)-Zn(2)-N(3)#3	117.68(9)	N(3)#3-Zn(2)-N(5)	99.46(8)
O(2)-Zn(2)-N(5)	88.84(8)	O(2W)-Zn(2)-N(5)	162.10(8)	N(3)#3-Zn(2)-N(7)	91.77(8)
O(2)-Zn(2)-N(7)	148.81(8)	O(2W)-Zn(2)-N(7)	98.65(8)	N(5)-Zn(2)-N(7)	75.54(8)
2					
Cd(1)-N(2)#1	2.254(4)	Cd(1)-N(6)#2	2.267(4)	Cd(1)-N(4)	2.342(4)
Cd(1)-N(3)	2.349(4)	Cd(1)-N(8)#3	2.449(5)	Cd(1)-N(7)#2	2.485(5)
N(2)-Cd(1)#5	2.254(4)	N(8)-Cd(1)#3	2.449(4)	N(6)-Cd(1)#4	2.267(4)
N(2)#1-Cd(1)-N(6)#2	111.58(15)	N(2)#1-Cd(1)-N(4)	93.12(16)	N(6)#2-Cd(1)-N(4)	155.25(16)
N(2)#1-Cd(1)-N(3)	100.57(18)	N(6)#2-Cd(1)-N(3)	104.66(16)	N(4)-Cd(1)-N(3)	70.85(15)
N(2)#1-Cd(1)-N(8)#3	88.53(18)	N(6)#2-Cd(1)-N(8)#3	86.01(16)	N(4)-Cd(1)-N(8)#3	93.32(15)
N(3)-Cd(1)-N(8)#3	161.97(17)	N(2)#1-Cd(1)-N(7)#2	169.95(17)	N(6)#2-Cd(1)-N(7)#2	73.52(15)
N(4)-Cd(1)-N(7)#2	81.83(15)	N(3-Cd(1)-N(7)#2	86.03(17)	N(8)#3-Cd(1)-N(7)#2	83.13(17)
3					
Zn(1)-N(4)#1	2.083(6)	Zn(1)-N(4)	2.083(6)	Zn(1)-N(3)#1	2.134(5)
Zn(1)-N(3)	2.134(5)	Zn(1)-O(1W)#1	2.245(5)	Zn(1)-O(1W)	2.245(5)
Zn(2)-O(1)	1.975(5)	Zn(2)-O(2W)	2.015(5)	Zn(2)-O(3W)	2.016(5)
Zn(2)-N(6)	2.077(6)	Zn(2)-N(7)	2.234(6)	N(4)#1-Zn(1)-N(4)	180.0(3)
N(4)#1-Zn(1)-N(3)#1	78.3(2)	N(4)-Zn(1)-N(3)#1	101.7(2)	N(4)#1-Zn(1)-N(3)	101.7(2)

N(4)-Zn(1)-N(3)	78.3(2)	N(3)#1-Zn(1)-N(3)	180.0(4)	N(4)#1-Zn(1)-O(1W)#1	89.8(2)
N(4)-Zn(1)-O(1W)#1	90.2(2)	N(3)#1-Zn(1)-O(1W)#1	91.3(2)	N(3)-Zn(1)-O(1W)#1	88.7(2)
N(4)#1-Zn(1)-O(1W)	90.2(2)	N(4)-Zn(1)-O(1W)	89.8(2)	N(3)#1-Zn(1)-O(1W)	88.7(2)
N(3)-Zn(1)-O(1W)	91.3(2)	O(1W)#1-Zn(1)-O(1W)	180.0(2)	O(1)-Zn(2)-O(2W)	102.7(2)
O(1)-Zn(2)-O(3W)	91.2(2)	O(2W)-Zn(2)-O(3W)	94.1(2)	O(1)-Zn(2)-N(6)	133.7(2)
O(2W)-Zn(2)-N(6)	122.6(2)	O(3W)-Zn(2)-N(6)	94.2(2)	O(1)-Zn(2)-N(7)	93.2(2)
O(2W)-Zn(2)-N(7)	92.4(2)	O(3W)-Zn(2)-N(7)	171.2(2)	N(6)-Zn(2)-N(7)	77.3(2)
4					
Co(1)-O(1W)#1	2.083(3)	Co(1)-O(1W)	2.083(3)	Co(1)-N(7)#1	2.108(3)
Co(1)-N(7)	2.108(3)	Co(1)-N(5)	2.155(3)	Co(1)-N(5)#1	2.155(3)
O(1W)#1-Co(1)-O(1W)	0.00(17))	O(1W)#1-Co(1)-N(7)#1	90.41(12)	O(1W)-Co(1)-N(7)#1	89.59(12)
O(1W)#1-Co(1)-N(7)	89.59(12)	O(1W)-Co(1)-N(7)	90.41(12)	N(7)#1-Co(1)-N(7)	180.000(1)
O(1W)#1-Co(1)-N(5)	90.76(12)	O(1W)-Co(1)-N(5)	89.24(12)	N(7)#1-Co(1)-N(5)	101.84(12)
N(7)-Co(1)-N(5)	78.16(12)	O(1W)#1-Co(1)-N(5)#1	89.24(12)	O(1W)-Co(1)-N(5)#1	90.76(12)
N(7)#1-Co(1)-N(5)#1	78.16(12)	N(7)-Co(1)-N(5)#1	101.84(12)	N(5)-Co(1)-N(5)#1	180.000(1)
5					
Co(2)- N(2)#1	2.078(3)	Co(2)- N(2)	2.078(3)	Co(2)- N(9)#1	2.127(3)
Co(2)-N(9)	2.127(3)	Co(2)-N(12)	2.145(3)	Co(2)-N(12)#1	2.145(3)
Co(1)-N(10)#2	2.072(3)	Co(1)-N(6)	2.093(3)	Co(1)-O(1W)	2.114(3)
Co(1)-N(1)#3	2.122(3)	Co(1)-N(4)#3	2.139(3)	Co(1)-N(7)	2.225(3)
Co(3)-O(2W)#4	2.087(3)	Co(3)-O(2W)	2.087(3)	Co(3)-N(14)	2.104(3)
Co(3)- N(14)#1	2.104(3)	Co(3)-N(15)	2.200(3)	Co(3)- N(15)#4	2.200(3)
N(4)-Co(1)#5	2.139(3)	N(1)-Co(1)#5	2.122(3)	N(10)-Co(1)#6	2.072(3)
N(2) #1-Co(2)-N(2)	90.84(16)	N(2) #1-Co(2)-N(9) #1	92.66(10)	N(2) -Co(2)-N(9) #1	96.83(10)
N(2) #1-Co(2)-N(9)	96.83(10)	N(2)-Co(2)-N(9)	92.66(10)	N(9) #1-Co(2)-N(9)	166.47(14)
N(2) -Co(2)-N(12)	88.83(11)	N(12)#1-Co(2)-N(2)	173.57(10)	N(9) #1-Co(2)-N(12) #1	76.77(10)
N(12)#1-Co(2)-N(9)	93.75(10)	N(12)-Co(2)-N(2)#1	173.57(10)	N(2)#1-Co(2)-N(12)#1	88.83(11)
N(12)-Co(2)-N(9)#1	93.75(10)	N(9)-Co(2)-N(12)	76.77(10)	N(12)-Co(2)-N(12)#1	92.19(16)
N(10)#2-Co(1)-N(6)	92.84(11)	N(10)#2-Co(1)-O(1W)	92.92(12)	N(6)-Co(1)-O(1W)	96.35(10)
N(10)#2-Co(1)-N(1)#3	96.57(10)	N(6)-Co(1)-N(1)#3	168.68(10)	O(1W)-Co(1)-N(1)#3	89.47(10)
N(10)#2-Co(1)-N(4)#3	171.57(12)	N(6)-Co(1)-N(4)#3	92.77(10)	O(1W)-Co(1)-N(4)#3	92.71(11)
N(10)#3-Co(1)-N(7)#3	77.21(10)	N(10)#2-Co(1)-N(7)	93.05(12)	N(6)-Co(1)-N(7)	77.18(10)
O(1W)-Co(1)-N(7)	171.40(11)	N(1)#3-Co(1)-N(7)	95.99(11)	N(4)#3-Co(1)-N(7)	82.07(11)
O(2W)#4-Co(3)-O(2W)	96.4(2)	O(2W)#4-Co(3)-N(14)	87.54(11)	O(2W)-Co(3)-N(14)	93.58(11)
O(2W)#4-Co(3)-N(14)#4	93.58(11)	O(2W)-Co(3)-N(14) #4	87.54(11)	N(14)#4-Co(3)-N(14)	178.33(16)
O(2W)#4-Co(3)-N(15)	92.08(14)	O(2W)-Co(3)-N(15)	166.65(14)	N(14)-Co(3)-N(15)	76.50(12)
N(15)-Co(3)-N(14)#4	102.20(11)	O(2W)#4-Co(3)-N(15) #4	166.66(14)	O(2W)-Co(3)-N(15) #4	166.66(13)
N(15)#4-Co(3)-N(14)	102.20(11)	N(14) #4-Co(3)-N(15) #4	76.50(12)	N(15)#4-Co(3)-N(15)	81.50(18)
N(3)-N(4)-Co(1)#5	138.1(2)	N(2)-N(1)-Co(1)#5	139.6(2)	N(9)-N(10)-Co(1)#6	121.25(19)

Symmetry codes for **1**: #1 -x+2, -y+2, -z+1; #2 -x+1, y+1/2, -z+1/2; #3 x, -y+3/2, z-1/2; #4 x, -y+3/2, z+1/2; #5 -x+1, y-1/2, -z+1/2. For **2**: #1 -x, y-1/2, -z+1/2; #2 x, -y+1/2, z-1/2; #3 -x+1, -y, -z+1; #4 x, -y+1/2, z+1/2; #5 -x, y+1/2, -z+1/2. For **3**: #1 -x, -y, -z. For **4**: #1 -x+3/2, -y+5/2,-z+1. For **5**: #1 y, x, -z; #2 x-1/2, -y+3/2, -z+1/4; #3 y-1/2, -x+3/2, z+1/4; #4 -y+2, -x+2, -z+1/2; #5 -y+3/2, x+1/2, z-1/4; #6 x+1/2, -y+3/2, -z+1/4.

Table S2. The hydrogen bond parameters in complexes **3** and **4**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	<D-H···A (^{o})
3				
O3W -H3W1···N1	0.85	1.93	2.753(9)	162
O3W-H3W2···O1#1	0.85	2.59	3.170(9)	126
O3W-H3W2···O3#1	0.85	1.92	2.726(8)	157
N2-H2···O3#2	0.86	1.88	2.726(7)	170
O1W-H1W1···O4#3	0.85	2.00	2.805(7)	157
O1W-H1W2···N8#2	0.85	2.00	2.852(10)	176
O2W-H2W2···O2#4	0.85	1.84	2.691(8)	180
O2W-H2W1···O3#3	0.85	1.90	2.745(11)	180
C6-H6···O2W#5	0.93	2.59	3.377(11)	143
4				
O1W-H1W1···N6#6	0.85	2.04	2.868(4)	164
N2-H2···N4#7	0.86	2.34	3.183(5)	164
O1W-H1W2···N3#8	0.85	2.28	3.100(5)	162
C1-H1···N8#9	0.93	2.33	3.117(6)	142

Symmetry codes: #1 x, -1/2-y, -1/2+z; #2 x, y, -1+z; #3 1+x, y, z; #4 1+x, -1/2-y, 1/2+z ; #5 x, -1/2-y, 1/2+z; #6 1/2+x, 1/2+y, z; #7 3/2-x, -1/2+y, 3/2-z; #8 3/2-x, 1/2-y, 1-z; #9 1-x, -y, 1-z.