# Supporting Information for

# Luminescent humidity sensors based on porous $Ln^{3+}$-MOFs

**Yang Yu, Jian-Ping Ma and Yu-Bin Dong***

College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Molecular and Nano Probes, Engineering Research Center of Pesticide and Medicine Intermediate Clean Production, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan 250014, People's Republic of China.

Corresponding author. Email: yubindong@sdnu.edu.cn

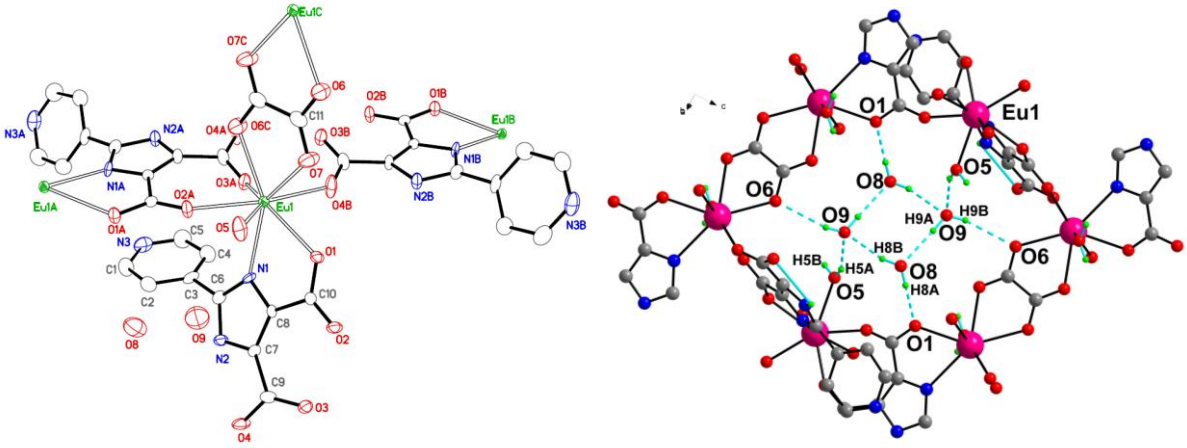


**Fig. S1** Left: The ORTEP figure of **2**. Right: water tetramer guest is fixed in the channel through H-binding interactions.

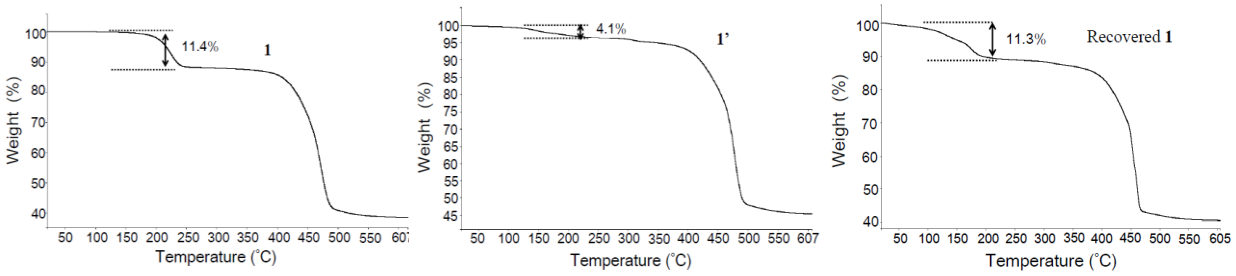


**Fig. S2** The TGA traces of **1** (left), **1'** (middle) and recovered **1**. For **1**: the calculated and observed weight losses are 11.1 and 11.4 %, respectively. For **1'**: the calculated and observed weight losses are 4.1 and 4.0 %, respectively. For recovered **1**: the observed weight loss is 11.3% (**1'** was exposed to air with RH at about 67 %). Elemental analysis (%) calcd for $C_{11}H_7TbN_3O_7$ (**1'**): C 29.20, H 1.55, N 9.29; Found: C 28.86, H 1.69, N 8.91.

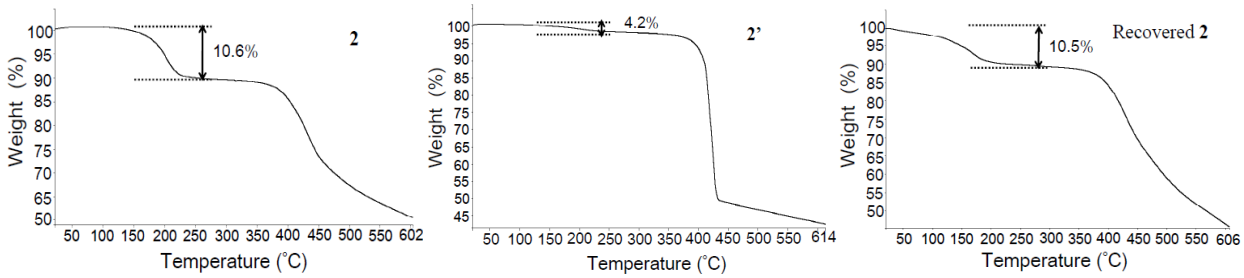


**Fig. S3** The TGA traces of **2** (left), **2'** (middle) and recovered **2**. For **2**: the calculated and observed weight losses are 11.2 and 10.6 %, respectively. For **2'**: the calculated and observed weight losses are 4.2 and 4.0 %, respectively. For recovered **2**: the observed weight loss is 10.5% (**2'** was exposed to air with RH at about 67 %). Elemental analysis (%) calcd for $C_{11}H_7EuN_3O_7$ (**2'**): C 29.66, H 1.57, N 9.44; Found: C 29.39, H 1.85, N 9.22.

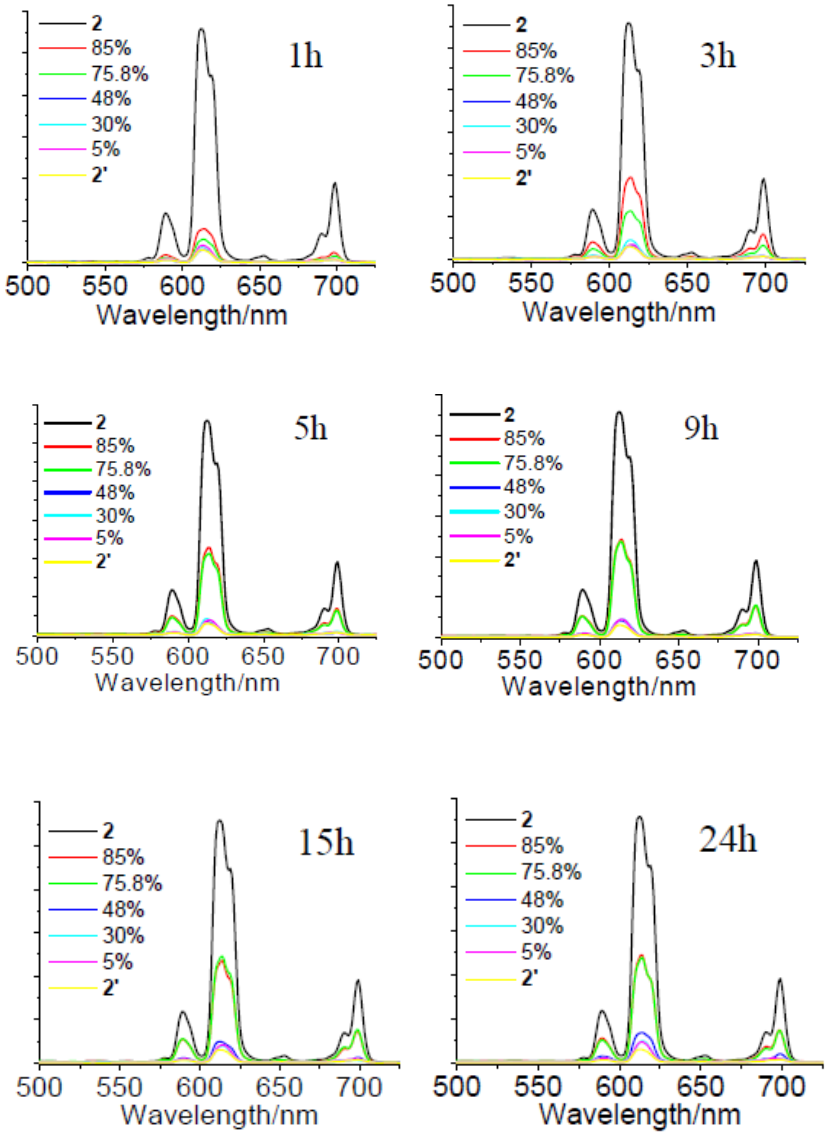


**Fig. S4** Solid-state emission spectra of **2'** in different atmospheres with different relative humidity recorded at 1, 3, 5, 9, 15, 24 h. The emission bands arise from the $^5D_0 \rightarrow {}^7F_J$ ($J$ = 1, 2, 3, 4) transitions of $En^{3+}$. The corresponding emission bands are 589, 612, 653 and 699 nm.

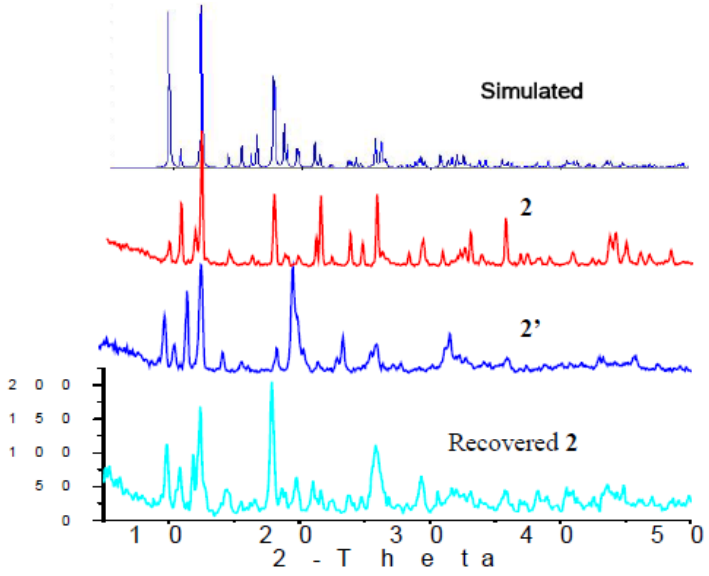


**Fig. S5** The XRPD patterns of **2**, **2'** and recovered **2.**

## Experimental Section

**Materials and Methods.** All the reagents (Acros) were used as obtained without further purification. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000 $cm^{-1}$ range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 2400 analyzer. $^{1}H$ NMR data were collected using an AM-300 spectrometer. Chemical shifts are reported in $\delta$ relative to TMS. All fluorescence measurements were carried out on a Cary Eclipse Spectrofluorimeter (Varian, Australia) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960 simultaneous DTA-TGA under flowing nitrogen at a heating rate of 10°C/min. XRD pattern were obtained on a D8 ADVANCE X-ray powder diffractometer (XRD) with CuKa radiation ($\lambda$ =1.5405 Å). Humidity-controlled solutions of 96% $H_2SO_4$, 54% $H_2SO_4$, 44% $H_2SO_4$, saturated NaCl, saturated KCl were put in closed glass chambers of 1L, which respectively provide different constant RH: about 5%, 30%, 48%, 75.8%, and 85% after 24 h. The solid-state emissions in different RH atmospheres were recorded after

humidity sensors **1'** and **2'** were placed in the chamber with different RH at 1, 3, 5, 9, 15, 24 h, respectively.

**Synthesis of L.** 2-(4-pyridyl benzimidazole) (2.0 g，10.26 mol) was added to $H_2SO_4$ (98 %, 23.1 g), the mixture was heated to 100°C, and then $H_2O_2$ (30 %, 16.0 g) was slowly added to the system. After the solution was heated at 140-150°C for 1h, the system was cooled down to 40°C, water (200 mL) was added, and **L** was obtained as yellow crystalline solids. Yield, 56.7%. IR(KBr pellet cm-1): 3438(s), 1740(s), 1555(s), 1351(s), 1284(s), 1241(s), 1204(s), 1054(s), 964(m),839(s), 777(s), 739(s), 700(s), 546(s). $^1$H NMR (300MHz, DMSO, 25◦C, TMS, ppm) δ: 9.35(s, 1H, -$C_5H_4N$), 8.76(d, 1H, -$C_5H_4N$), 8.64(d, 1H, -$C_5H_4N$), 7.72(t, 1H, -$C_5H_4N$). Elemental analysis (%) calcd for $C_{10}H_7N_3O_4$: C 51.50, H 3.00, N 18.03; Found: C 51.58, H 3.08, N 17.95.

**Synthesis of 1.** **L** (14.0 mg, 0.06 mmol), oxalic acid (5.4 mg, 0.06 mmol), $Tb(NO_3)_3$ (62.1 mg, 0.18mmol) and water (2 mL) were sealed in a 10-mL glass tube. The mixture was heated at 180°C for 3 days under autogenous pressure. After the mixture was allowed to cool to room temperature, yellow crystals were isolated from the tube in 39.3 % yield. IR (KBr pellet $cm^{-1}$ ): 3442.38(m), 3152.03(m), 1647.85(s), 1603.40(s), 1538.24(m), 1485.44(s), 1439.66(m), 1400.06(s), 1363.78(s), 1264.91(w), 1144.69(w), 1121.85(w), 1006.59(w), 984.32(w), 921.14(w), 865.65(w), 793.57(m), 738.00(w), 667.17(w), 540.19(w). Elemental analysis (%) calcd for $C_{11}H_{11}TbN_3O_9$: C 27.05, H 2.25, N 8.61; Found: C 26.92, H 2.31, N 8.47.

**Synthesis of 2.** **L** (14.0 mg, 0.06 mmol), oxalic acid (5.4 mg, 0.06 mmol), $Eu(NO_3)_3$ (60.8 mg, 0.18mmol) and water (2 mL) were sealed in a 10-mL glass tube. The mixture was heated at 180°C for 3 days under autogenous pressure. After the mixture was allowed to cool to room temperature, yellow crystals were isolated from the tube in 41.9 % yield. IR(KBr pellet $cm^{-1}$):

3449.27(s), 3156.33(s), 1646.09(s), 1600.07(s), 1537.16(m), 1484.79(m), 1439.24(s), 1400.33(s), 1362.78(s), 1310.46(w), 1264.79(w), 1144.70(w), 1121.08(w), 1007.44(w), 984.67(w), 917.40(w), 864.27(w), 792.44(m), 738.79(w), 666.94(w), 538.30(w). Elemental analysis (%) calcd for $C_{11}H_{11}EuN_3O_9$: C 27.44, H 2.29, N 8.73; Found: C 27.18, H 2.38, N 8.52.

**Single-crystal analysis.** For **1**-**2**, X-ray intensity data were measured on a Bruker SMART APEX CCD-based diffractometer (Mo K$\alpha$ radiation, $\lambda$ = 0.71073 Å). The raw frame data were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[1] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[1] None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against $F^2$ by the full-matrix least squares technique. Crystal data, data collection parameters, and refinement statistics are listed in Table S1. Relevant interatomic bond distances, bond angles and H-bonds for **1** are given in Tables S2-3. Relevant interatomic bond distances, bond angles and H-bonds for **2** are given in Tables S4-5.

**Table S1.** Crystal data of **1-2**

| No. | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{11}H_{11}N_3O_9Tb$ | $C_{11}H_{11}EuN_3O_9$ |
| Formula weight | 488.15 | 481.19 |
| Crystal system | Monoclinic | Monoclinic |
| *a* (Å) | 8.3136(19) | 8.2862(17) |
| *b* (Å) | 14.719(4) | 14.865(3) |
| *c* (Å) | 11.526(3) | 11.559(2) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 90.807(5) | 90.870(3) |
| $\gamma$ (°) | 90 | 90 |
| Volume ($Å^3$) | 1410.4(6) | 1423.7(5) |
| space group | *P2(1)/c* | *P2(1)/c* |
| *Z* value | 4 | 4 |
| Density($g\ cm^{-1}$) | 2.299 | 2.245 |
| $\mu$(Mo-Kα)($mm^{-1}$) | 5.072 | 4.463 |
| temp(K) | 298(2) | 298(2) |
| Data / restraints / parameters | 2611 / 0 / 205 | 2638 / 0 / 217 |
| Final R indices [I>2sigma(I)]: R; Rw | 0.0608; 0.1072 | 0.0402; 0.0782 |

**Table S2.** Selective bond lengths [Å] and angles [°] for **1.**

| | | | |
|---|---|---|---|
| Tb(1)-O(3)#2 | 2.280(8) | Tb(1)-O(2)#2 | 2.339(7) |
| Tb(1)-O(4)#3 | 2.370(8) | Tb(1)-O(1) | 2.375(7) |
| Tb(1)-O(5) | 2.378(8) | Tb(1)-O(6)#1 | 2.410(7) |
| Tb(1)-O(7) | 2.411(7) | Tb(1)-N(1) | 2.525(9) |
| O(3)#2-Tb(1)-O(2)#2 | 75.7(3) | O(3)#2-Tb(1)-O(4)#3 | 76.4(3) |
| O(2)#2-Tb(1)-O(4)#3 | 152.1(3) | O(3)#2-Tb(1)-O(1) | 128.8(3) |
| O(2)#2-Tb(1)-O(1) | 126.7(2) | O(4)#3-Tb(1)-O(1) | 71.5(3) |
| O(3)#2-Tb(1)-O(5) | 147.7(3) | O(2)#2-Tb(1)-O(5) | 72.0(3) |
| O(4)#3-Tb(1)-O(5) | 135.9(3) | O(1)-Tb(1)-O(5) | 74.1(3) |
| O(3)#2-Tb(1)-O(6)#1 | 78.3(3) | O(2)#2-Tb(1)-O(6)#1 | 76.5(3) |
| O(4)#3-Tb(1)-O(6)#1 | 99.6(3) | O(1)-Tb(1)-O(6)# | 1145.0(3) |
| O(5)-Tb(1)-O(6)#1 | 93.0(3) | O(3)#2-Tb(1)-O(7) | 128.7(3) |
| O(2)#2-Tb(1)-O(7) | 127.7(3) | O(4)#3-Tb(1)-O(7) | 73.1(3) |
| O(1)-Tb(1)-O(7) | 77.5(3) | O(5)-Tb(1)-O(7) | 73.2(3) |
| O(6)#1-Tb(1)-O(7) | 67.6(2) | O(3)#2-Tb(1)-N(1) | 84.2(3) |
| O(2)#2-Tb(1)-N(1) | 74.1(3) | O(4)#3-Tb(1)-N(1) | 101.3(3) |
| O(1)-Tb(1)-N(1) | 64.8(3) | O(5)-Tb(1)-N(1) | 88.1(3) |
| O(6)#1-Tb(1)-N(1) | 148.7(3) | O(7)-Tb(1)-N(1) | 141.4(3) |
| C(6)-N(1)-C(8) | 104.8(9) | C(6)-N(1)-Tb(1) | 138.0(8) |
| C(8)-N(1)-Tb(1) | 114.5(7) | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 x,-y+1/2,z-1/2 #3 -x,y-1/2,-z+1/2

#4 x,-y+1/2,z+1/2 #5 -x,y+1/2,-z+1/2

**Table S3.** Hydrogen bonds for **1** [Å and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(2)-H(2A)...O(8)#6 | 0.86 | 1.97 | 2.824(11) | 170.4 |
| O(9)-H(9B)...O(6)#7 | 0.85 | 2.34 | 3.159(12) | 162.9 |
| O(5)-H(5B)...N(3)#8 | 0.85 | 1.90 | 2.751(12) | 173.4 |
| O(8)-H(8B)...O(9)#9 | 0.85 | 2.04 | 2.876(12) | 167.5 |
| O(8)-H(8A)...O(1)#7 | 0.85 | 1.89 | 2.734(11) | 170.5 |
| O(5)-H(5A)...O(9) | 0.85 | 2.08 | 2.868(12) | 154.3 |
| O(9)-H(9A)...O(8) | 0.85 | 1.97 | 2.816(13) | 178.6 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 x,-y+1/2,z-1/2 #3 -x,y-1/2,-z+1/2

#4 x,-y+1/2,z+1/2 #5 -x,y+1/2,-z+1/2 #6 x-1,y,z

#7 -x+1,y+1/2,-z+1/2 #8 x+1,-y+1/2,z+1/2 #9 -x+1,-y+1,-z

**Table S4.** Selective bond lengths [Å] and angles [°] for **2.**

| | | | |
|---|---|---|---|
| Eu(1)-O(3)#2 | 2.297(4) | Eu(1)-O(2)#2 | 2.352(4) |
| Eu(1)-O(4)#3 | 2.390(5) | Eu(1)-O(1) | 2.397(4) |
| Eu(1)-O(5) | 2.406(5) | Eu(1)-O(7) | 2.424(5) |
| Eu(1)-O(6)#1 | 2.437(5) | Eu(1)-N(1) | 2.556(5) |
| O(3)#2-Eu(1)-O(2)#2 | 75.18(15) | O(3)#2-Eu(1)-O(4)#3 | 76.86(16) |
| O(2)#2-Eu(1)-O(4)#3 | 151.96(16) | O(3)#2-Eu(1)-O(1) | 128.79(16) |
| O(2)#2-Eu(1)-O(1) | 126.64(15) | O(4)#3-Eu(1)-O(1) | 71.39(16) |
| O(3)#2-Eu(1)-O(5) | 147.05(16) | O(2)#2-Eu(1)-O(5) | 71.87(15) |
| O(4)#3-Eu(1)-O(5) | 136.06(16) | O(1)-Eu(1)-O(5) | 73.62(16) |
| O(3)#2-Eu(1)-O(7) | 128.93(18) | O(2)#2-Eu(1)-O(7) | 126.54(18) |
| O(4)#3-Eu(1)-O(7) | 74.19(19) | O(1)-Eu(1)-O(7) | 78.84(15) |
| O(5)-Eu(1)-O(7) | 73.68(19) | O(3)#2-Eu(1)-O(6)#1 | 78.55(17) |
| O(2)#2-Eu(1)-O(6)#1 | 76.45(17) | O(4)#3-Eu(1)-O(6)#1 | 99.97(19) |
| O(1)-Eu(1)-O(6)#1 | 145.18(15) | O(5)-Eu(1)-O(6)#1 | 93.78(18) |
| O(7)-Eu(1)-O(6)#1 | 66.41(16) | O(3)#2-Eu(1)-N(1) | 84.59(17) |
| O(2)#2-Eu(1)-N(1) | 74.10(16) | O(4)#3-Eu(1)-N(1) | 101.33(19) |
| O(1)-Eu(1)-N(1) | 64.21(15) | O(5)-Eu(1)-N(1) | 86.32(17) |
| O(7)-Eu(1)-N(1) | 141.78(16) | O(6)#1-Eu(1)-N(1) | 148.95(16) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 x,-y+1/2,z-1/2 #3 -x,y-1/2,-z+1/2

#4 x,-y+1/2,z+1/2 #5 -x,y+1/2,-z+1/2

**Table S5.** Hydrogen bonds for **2** [Å and deg.].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(2)-H(2A)...O(8)#6 | 0.86 | 1.96 | 2.811(7) | 169.3 |
| O(9)-H(9B)...O(6)#7 | 0.85 | 2.35 | 3.174(8) | 163.7 |
| O(5)-H(5B)...N(3)#8 | 0.84 | 1.90 | 2.744(7) | 173.5 |
| O(8)-H(8B)...O(9)#9 | 0.85 | 2.06 | 2.892(7) | 165.5 |
| O(8)-H(8A)...O(1)#7 | 0.85 | 1.90 | 2.739(7) | 170.5 |
| O(5)-H(5A)...O(9) | 0.85 | 2.08 | 2.871(7) | 154.1 |
| O(9)-H(9A)...O(8) | 0.85 | 1.99 | 2.833(9) | 178.3 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 x,-y+1/2,z-1/2 #3 -x,y-1/2,-z+1/2

#4 x,-y+1/2,z+1/2 #5 -x,y+1/2,-z+1/2 #6 x-1,y,z

#7 -x+1,y+1/2,-z+1/2 #8 x+1,-y+1/2,z+1/2 #9 -x+1,-y+1,-z

**References**

(1) Sheldrick, G. M. SHELXTL Version 5.12; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.