

*Supplementary Materials*

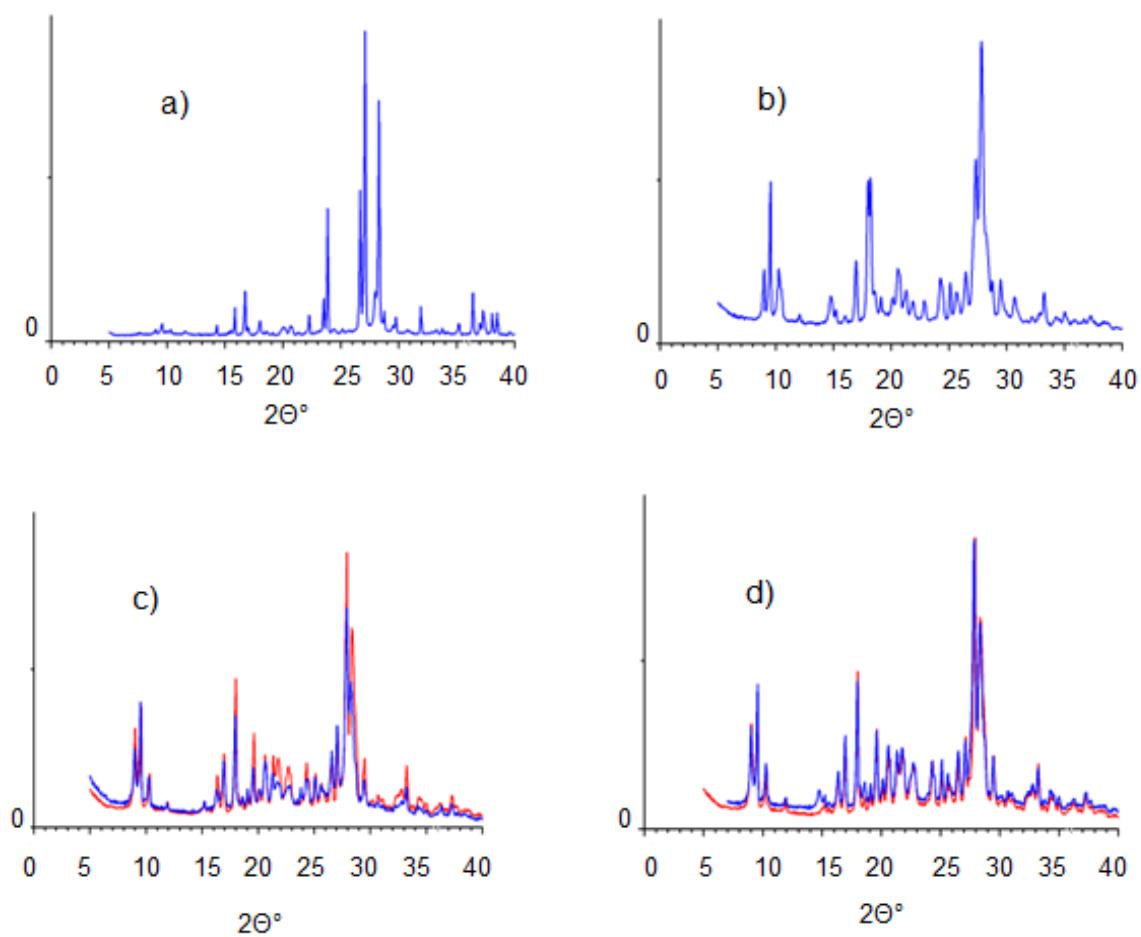
# **A Promising 1,3,5-Triazine-Based Anion Exchanger for Perrhenate Binding: Crystal Structures of Its Chloride, Nitrate and Perrhenate Salts**

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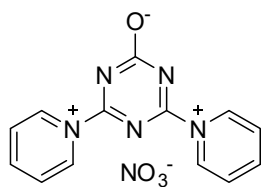
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**Supplementary Materials**

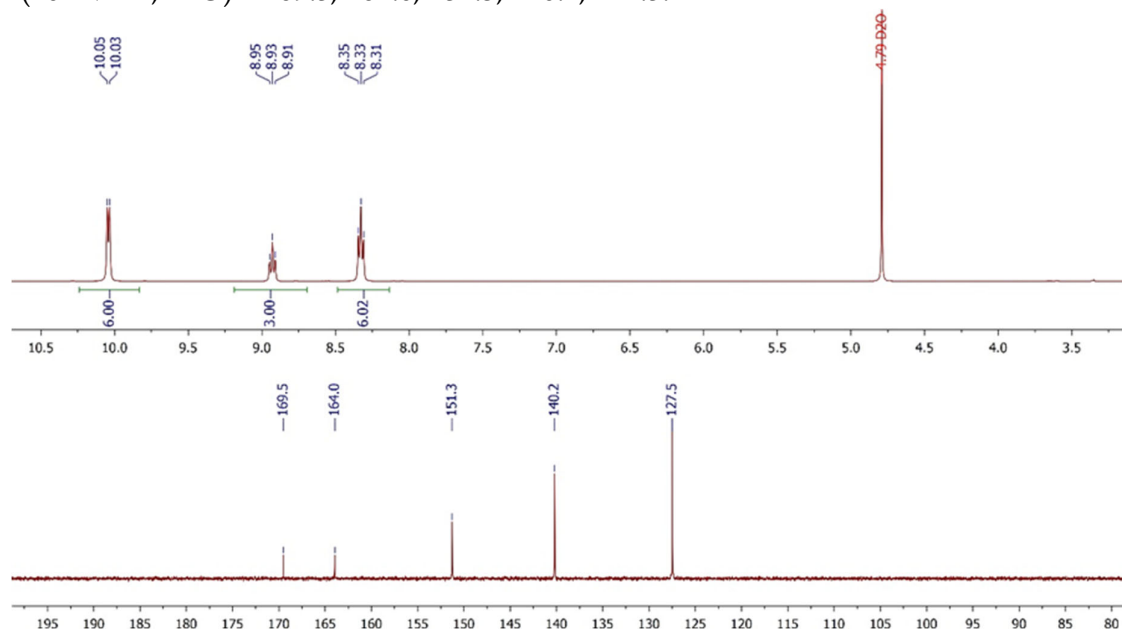


**Figure S1.** X-ray powder patterns for the precipitates that formed in reaction of pyridine and cyanuric chloride after (a) 5 minutes of reaction; b) 10 minutes of reaction; c) 20 minutes of reaction; d) 30 minutes of reaction

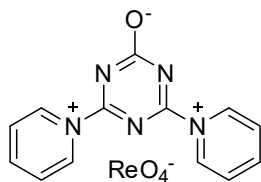
## NMR, IR and HRMS spectra



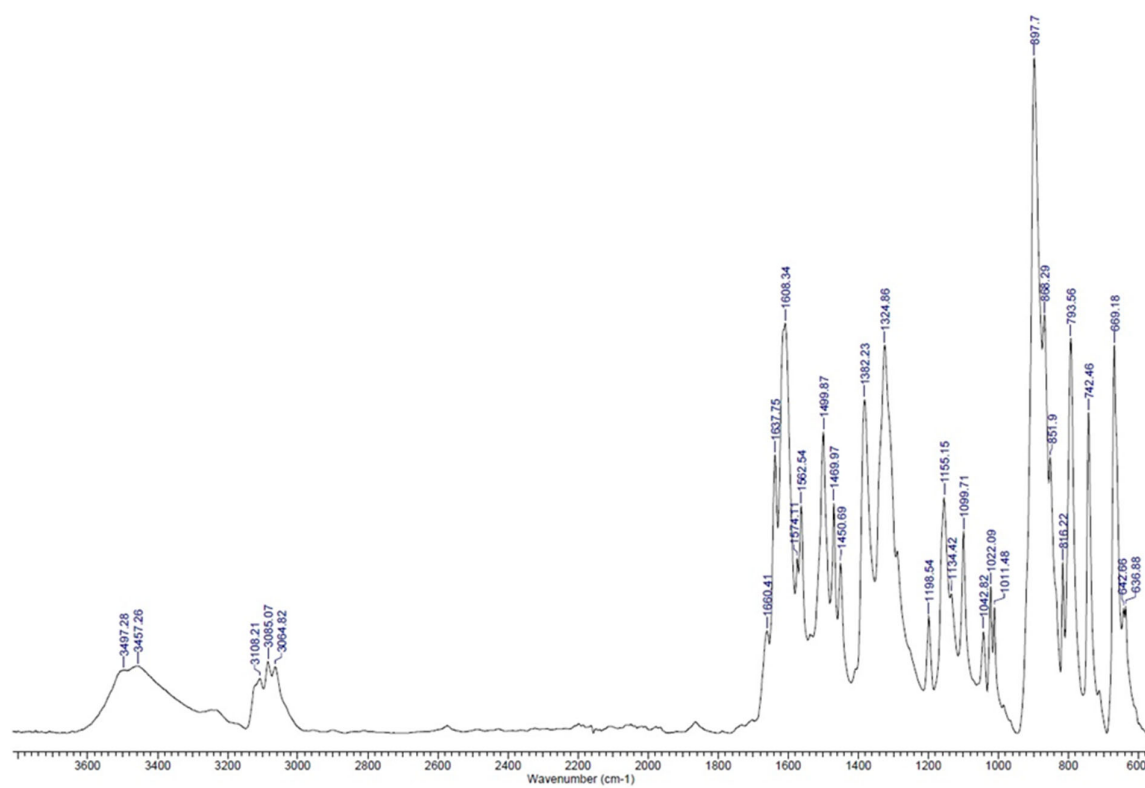
**4,6-di(pyridin-1-ium-1-yl)-1,3,5-triazin-2-olate nitrate 4b.**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  10.04 (d,  $J$  = 6.3 Hz, 6H), 8.93 (t,  $J$  = 7.7 Hz, 3H), 8.33 (t,  $J$  = 7.1 Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  169.5, 164.0, 151.3, 140.2, 127.5.



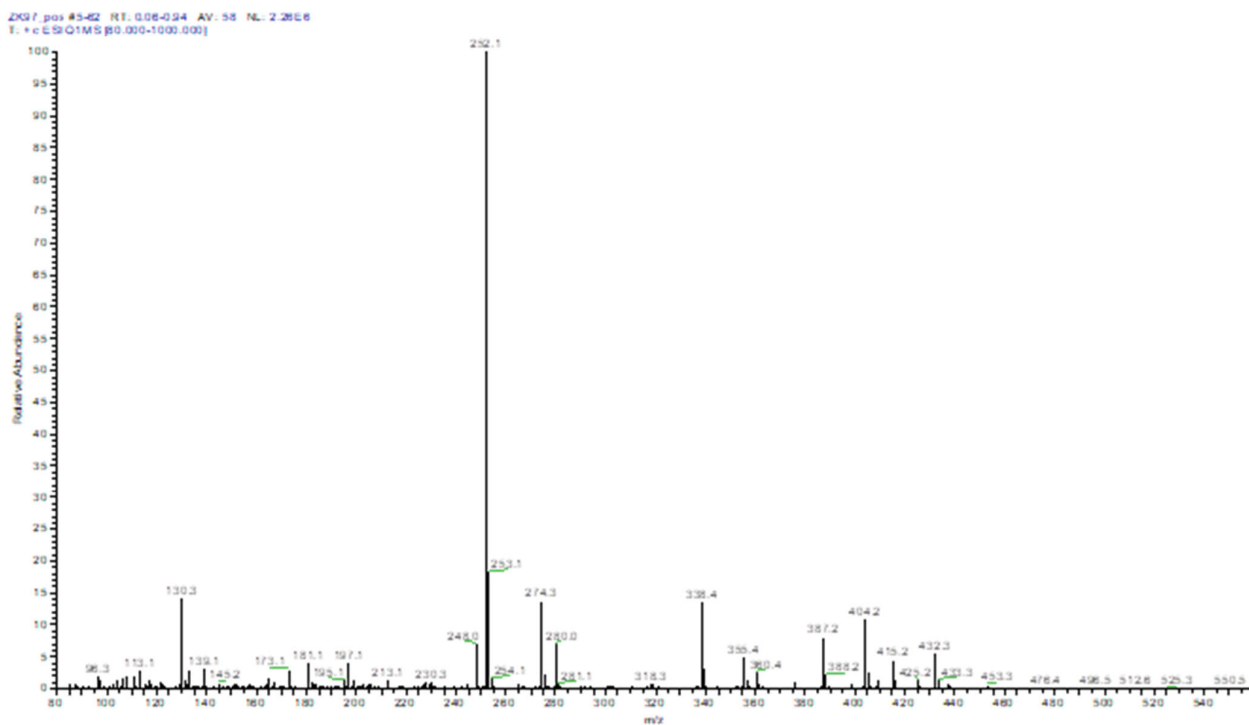
**Figure S2.** NMR  $^1\text{H}$  and  $^{13}\text{C}$  spectra ( $\text{D}_2\text{O}$ ,  $25^\circ\text{C}$ ) of compound **4b**.



**4,6-di(pyridin-1-ium-1-yl)-1,3,5-triazin-2-olate perrhenate 4c.** Brown solid, m.p.  $200\text{--}203^\circ\text{C}$  (with decomp.). IR ( $\nu$ ,  $\text{cm}^{-1}$ ) 898 ( $\text{ReO}_4^-$ ).



**Figure S3.** Solid-state IR spectrum of compound **4c**.



**Figure S4.** Mass spectrum with predominant content of 4,6-dipyridinio-2-oxido-1,3,5-triazine ions.

**Table S1.** Crystal data for **4a**, **4b** and **4c**.

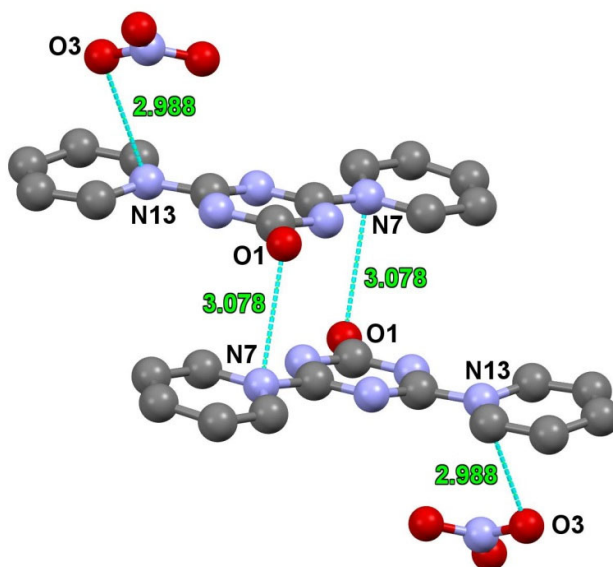
	<b>4a</b>	<b>4b</b>	<b>4c</b>
empirical formula	C <sub>13</sub> H <sub>10</sub> N <sub>5</sub> O <sup>+</sup> ·Cl <sup>-</sup> ·H <sub>2</sub> O	C <sub>13</sub> H <sub>10</sub> N <sub>5</sub> O <sup>+</sup> ·NO <sub>3</sub> <sup>-</sup>	C <sub>26</sub> H <sub>26</sub> N <sub>10</sub> O <sub>13</sub> Re <sub>2</sub>
Mr	305.73	314.27	1058.97
Temperature, K			295(2)
crystal system	Monoclinic	Triclinic	Monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
wavelength, Å	1.54059	1.54059	1.54186
unit cell dimensions			
<i>a</i> , Å	10.1956(11)	10.1065(11)	14.5239(3)
<i>b</i> , Å	14.9491(14)	10.2800(12)	20.3202(6)
<i>c</i> , Å	9.3480(9)	6.6028(7)	22.6058(6)
$\alpha$ , °	90	93.740(13)	90
$\beta$ , °	108.377(19)	102.313(19)	102.615(2)
$\gamma$ , °	90	86.345(11)	90
volume, Å <sup>3</sup>	1352.1(2)	667.91(13)	6510.6(3)
Z	4	2	8
D <sub>x</sub> (Mg m <sup>-3</sup> )	1.502	1.563	2.161
$\mu$ , mm <sup>-1</sup>	2.630	1.027	15.045
F(000)			4048
Crystal size			23 x 17 x 14 mm <sup>3</sup>
2 $\theta_{\min}$ - 2 $\theta_{\max}$ , $\Delta 2\theta$ (°)	7.00 – 75.00, 0.01	7.00 – 75.00, 0.01	
no. params/restraints	97/122	101/136	
Data/restraints /parameters			5742 / 11 / 478
R <sub>p</sub> , R <sub>wp</sub> , R <sub>exp</sub>	0.0195, 0.0249, 0.0140*	0.0209, 0.0271, 0.0151	
Theta range for data collection			4.352 to 66.899°
Index ranges			-12 ≤ h ≤ 17, -24 ≤ k ≤ 22, -26 ≤ l ≤ 26
Reflections collected			32189
Independent reflections			5742 [R(int) = 0.0901]
Completeness to theta =			66.899° 99.2 %
Refinement method			Full-matrix least-squares on F <sup>2</sup>
Final R indices			R1 = 0.0475, wR2 =
[I > 2σ(I)]			0.1014
R indices (all data)			R1 = 0.1030, wR2 =
			0.1163
Largest diff. peak and hole			3.025 and -1.065 e. Å <sup>-3</sup>
GOF	1.778	1.791	0.818
diffractometer	Huber G670 Guinier	Huber G670 Guinier	STOE diffractometer Pilatus 100K detector
CCDC code	2214608	2214607	2224951

\* For 4a, which contains 10% of 4b, R-factors were obtained in two-phase refinement.

**Table S2.** Hydrogen-bonding geometry (Å, °) in **4b** crystalline phase.

D-H...A	D-H	H...A	D...A	D-H...A
C12-H12...O3	0.95	2.24	3.076(10)	147
C8-H8...O4 <sup>i</sup>	0.95	2.44	3.145(10)	131
C9-H9...O2 <sup>i</sup>	0.95	2.20	3.101(10)	158
C10-H10...O1 <sup>ii</sup>	0.95	2.48	3.351(10)	152
C16-H16...O1 <sup>iii</sup>	0.95	2.21	3.083(10)	152
C17-H17...O2 <sup>iv</sup>	0.95	2.33	3.163(10)	146

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $x-1, y, z$ ; (iii)  $x, 1+y, z$ ; (iv)  $1+x, y, z$ .

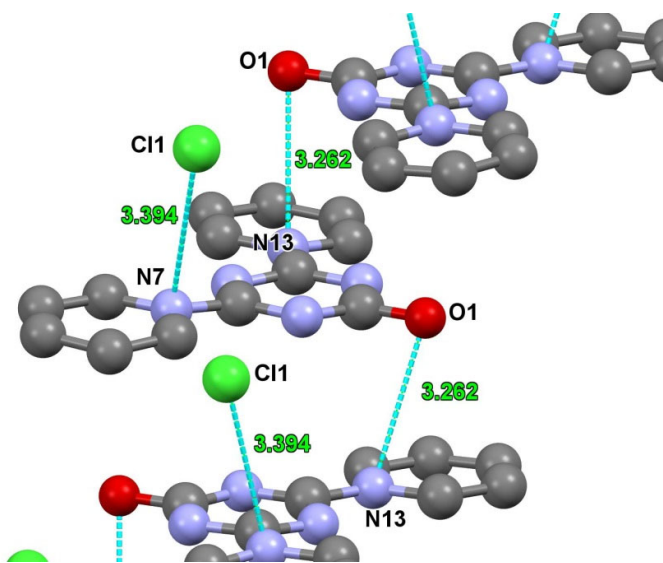


**Figure S5.** Short intermolecular N...O contacts (dotted cyan lines) in the crystal structure **4b**.

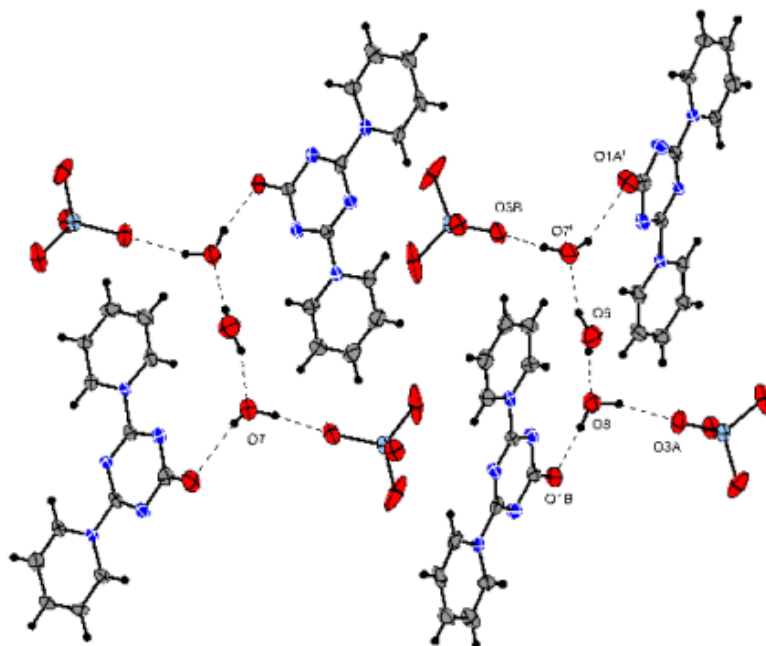
**Table S3.** Hydrogen-bonding geometry (Å, °) in **4a** crystalline phase.

D-H...A	D-H	H...A	D...A	D-H...A
O2-H2A...Cl1 <sup>i</sup>	0.85	2.18	3.036(6)	173
O2-H2B...Cl1 <sup>ii</sup>	0.85	2.47	3.315(6)	171
C9-H9...Cl <sup>iii</sup>	0.95	2.79	3.476(9)	129
C16-H16...Cl1 <sup>iv</sup>	0.95	2.80	3.554(10)	136
C17-H17...Cl1	0.95	2.69	3.560(9)	152
C14-H14...O1 <sup>v</sup>	0.95	2.17	3.071(11)	158
C12-H12...O1 <sup>v</sup>	0.95	2.23	3.150(11)	162
C10-H10...O2	0.95	2.34	3.114(12)	139

Symmetry codes: (i) 1-x, 1-y, 1-z; (ii) 1-x, y-1/2, 1/2-z; (iii) x-1, 3/2-y, z-3/2; (iv) 2-x, 1-y, 2-z; (v) 1-x, y-1/2, 1/2-z.



**Figure S6.** Short intermolecular N...O and N...Cl contacts (dotted cyan lines) in the crystal structure **4a**.



**Figure S7.** Visualization of the hydrogen bonds in the crystal **4c** (code i = -x, y, 0.5-z).

**Table S4** Hydrogen bonds for R1 [ $\text{\AA}$  and angles  $^\circ$ ].

	D-H...A	d(D-H)d(H...A)	d(D...A)	<(DHA)
C(7A)-H(7A)...O(8)#1	0.93	2.53	3.402(17)	155.9
C(9A)-H(9A)...O(5B)#2	0.93	2.47	3.094(16)	124.4
C(10A)-H(10A)...O(5B)#2	0.93	2.58	3.142(14)	119.8
C(11A)-H(11A)...O(4B)#2	0.93	2.49	3.104(15)	123.4
C(12A)-H(12A)...O(4B)#2	0.93	2.57	3.145(17)	120.6
C(14A)-H(14A)...O(8)#3	0.93	2.63	3.536(16)	165.5
C(15A)-H(15A)...O(1B)#3	0.93	2.38	3.169(16)	142.2
C(6B)-H(6B)...O(1A)#3	0.93	2.29	3.069(16)	140.8
C(10B)-H(10B)...O(3A)#4	0.93	2.64	3.405(17)	139.5
C(11B)-H(11B)...O(3A)#4	0.93	2.48	3.286(16)	145.6
C(15B)-H(15B)...O(6)	0.93	2.28	3.111(18)	149.1
O(6)-H(61)...O(7)#1	0.86(2)	1.91(6)	2.733(17)	160(16)
O(6)-H(62)...O(8)	0.86(2)	1.97(5)	2.780(15)	156(12)
O(7)-H(71)...O(1A)	0.87(2)	2.30(14)	2.912(14)	128(15)
O(7)-H(72)...O(3B)	0.86(2)	2.01(5)	2.837(12)	160(12)
O(8)-H(81)...O(3A)	0.866(19)	2.00(3)	2.843(11)	163(9)
O(8)-H(82)...O(1B)	0.85(2)	1.97(3)	2.787(12)	160(9)

Symmetry transformations used to generate equivalent atoms:

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

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