Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Solid state transformation of the crystalline monohydrate $(CH_3NH_3)PbI_3(H_2O))$ to the $(CH_3NH_3)PbI_3$ perovskite

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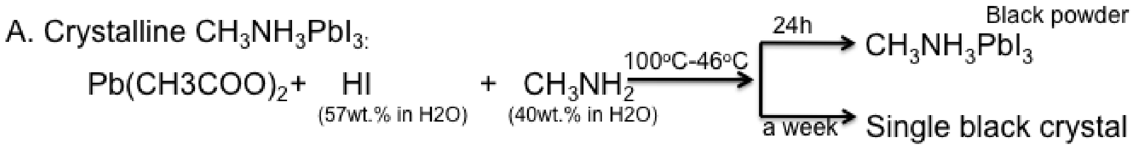
Preparation of CH_3NH_3I

Methylamine iodide was synthesized according to a previous literature procedure.[1] Aqueous hydroiodic acid (57 wt. %) was slowly added to a cooled (0°C) stirring methylamine solution (33 wt. % in ethanol). The solution was dried by rotary evaporator and the resulting white solid dried overnight at 60°C. Further purification was accomplished via recrystallization from cooling of a saturated hot ethanol solution.

Preparation of $CH_3NH_3PbI_3$ (1)[2,3]



In a 100ml flat bottom flask, lead acetate (2.5g, 7.69mmol) was added to a concentrated (57 wt.%) aqueous HI solution (10mL) and the mixture was heated to 100°C in a water bath. An additional 2ml of HI solution with CH_3NH_2 (40wt. % in H_2O, 1.7 mL, 19.6 mmol) was added dropwise to the hot solution and the color of the solution changed from colorless to yellow. A black precipitate formed upon cooling from 100°C to 46°C. After 24h of gradual cooling, a black powder was observed in the flask which was filtered and dried at 100°C for 10h. Larger crystals were obtained by repeating this procedure and increasing the duration of the cooling period.

Preparation of $CH_3NH_3PbI_3 \bullet H_2O$ (2)

The filtrate from the synthesis of **1** was collected in a flask and cooled at room temperature in the dark. After 4 days, clear needle crystals were observed in the flask. When the clear crystals were washed with ether/pentane (1:1), the color changed to black during drying under N_2 gas. Crystals of **2** turn black in air or under nitrogen very quickly but are stable in the filtrate solution over the observed period of 3 months. Placing crystals of **2** in paratone oil or Apiezon N grease slows the conversion significantly. A crystal structure of **2** has previously been obtained[4] and we have repeated this data collection. To study this material it was necessary to quickly place a crystal in Apiezon N grease and immediately mount a crystal on the XRD instrument at 100K.

SEM

All SEM images were obtained on (FEI Quanta 450FEG SEM) equipped with the latest Energy Dispersive Spectrometer (Oxford Aztec Energy Advanced EDS System).

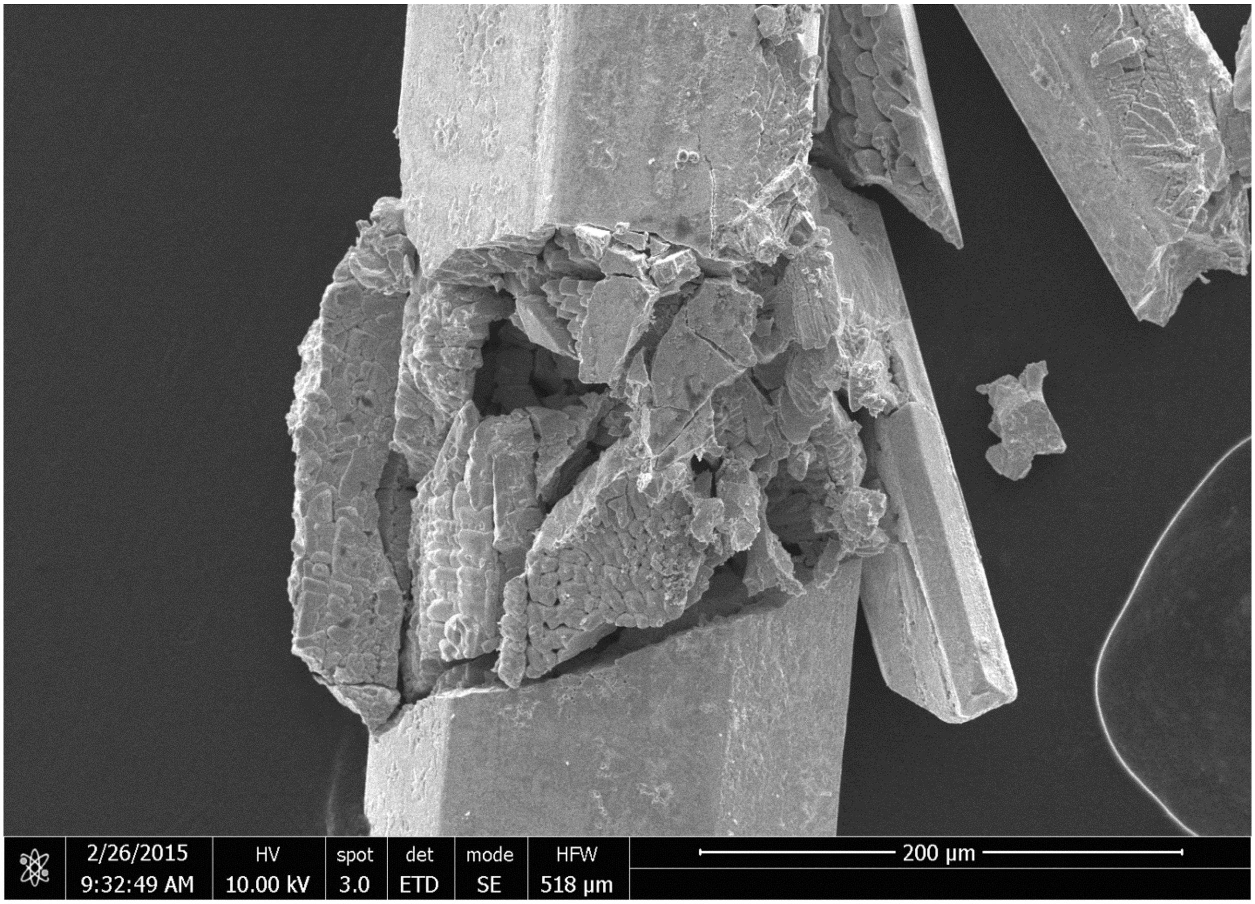


Figure S1: SEM image from crystal of **2** that has converted to **1** in air.

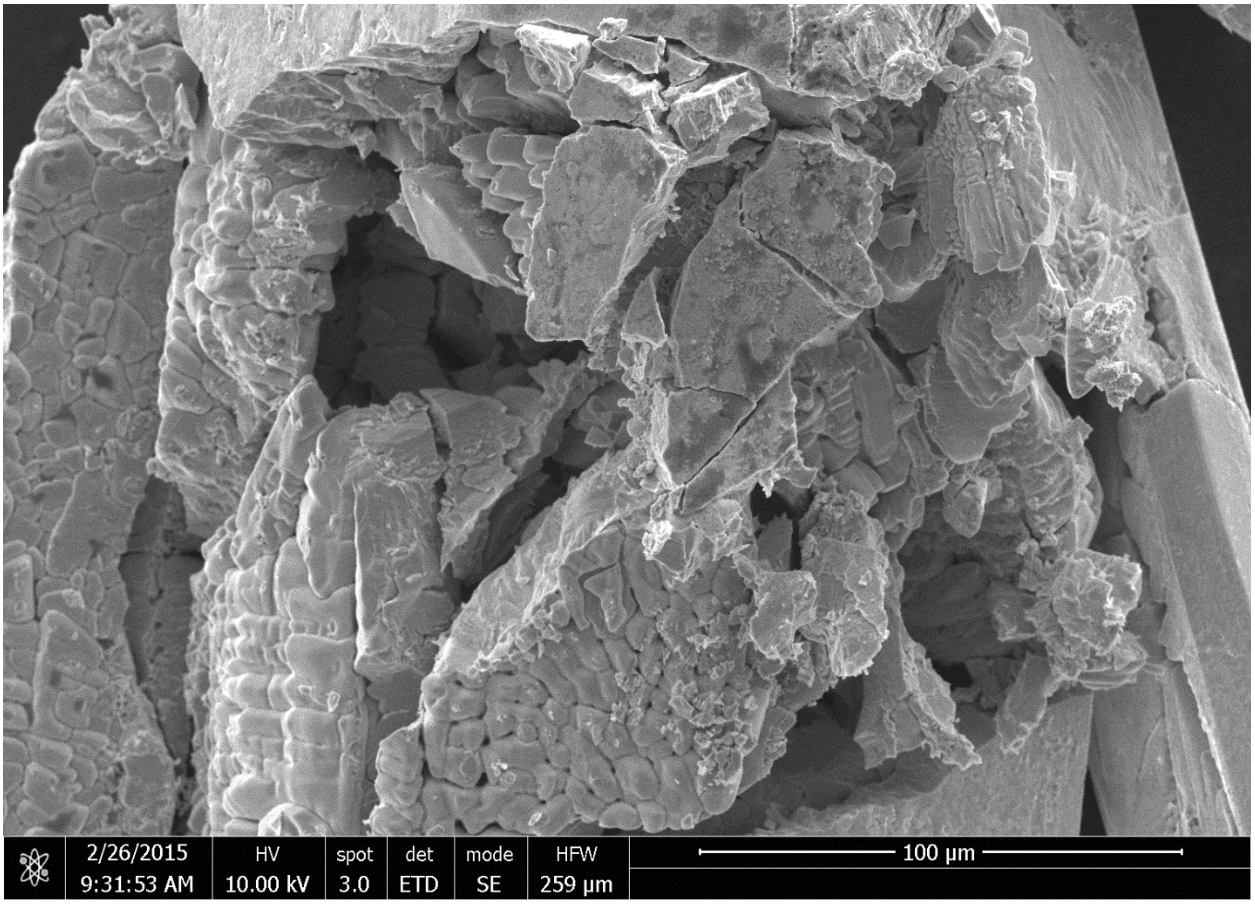


Figure S2: SEM image from crystal of **2** that has converted to **1** in air.

TEM

The size distributions of particles were analyzed by a JEOL JEM-1400 transmission electron microscope operating at an accelerating voltage of 120 kV .

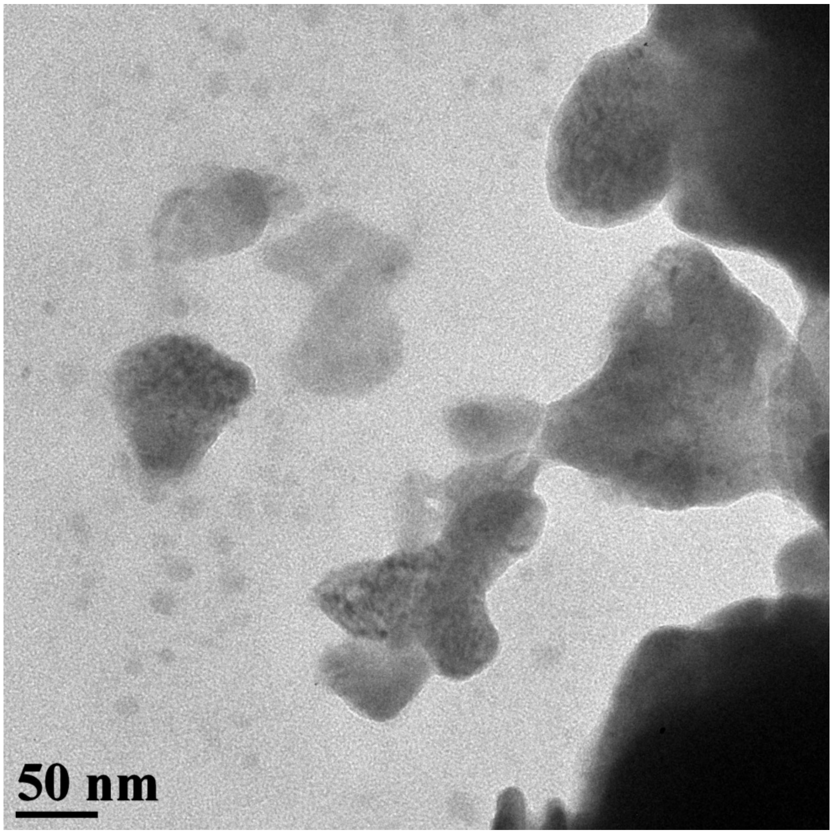


Figure S3: TEM image from crystal of **2** that has converted to **1** and crushed to examine nanoscale structure.

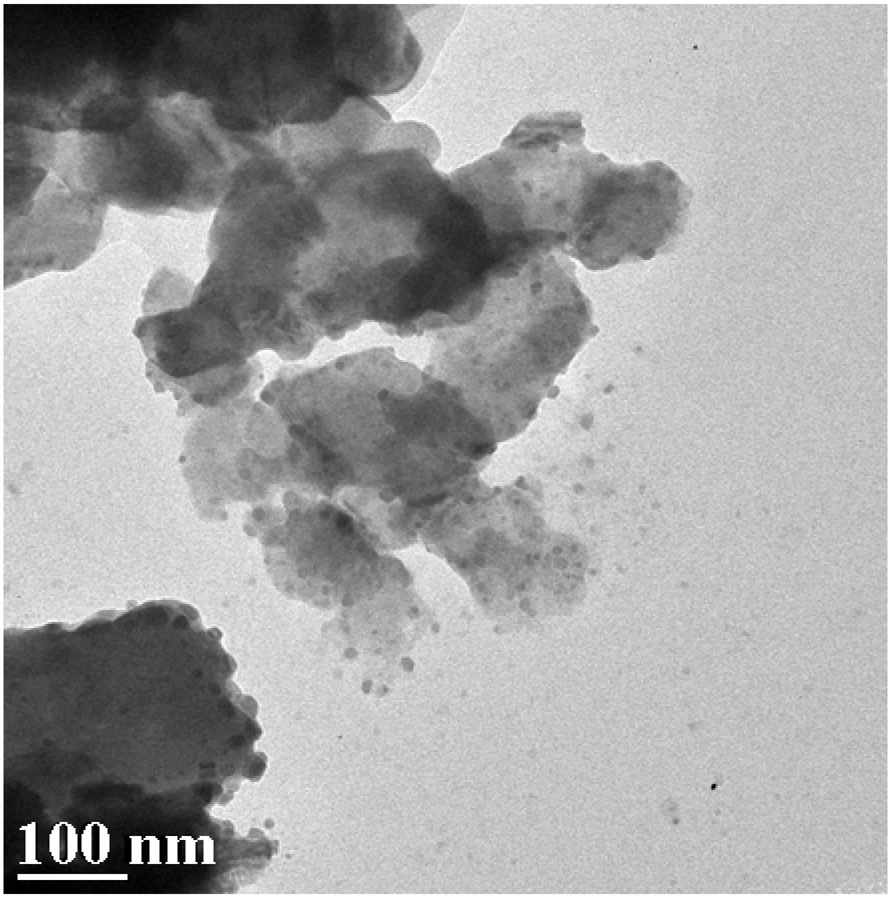


Figure S4: TEM image from crystal of **2** that has converted to **1** and crushed to examine nanoscale structure.

DFT calculations for estimation of protonated amine ionic radius

The effective ionic radius of the hydrogen bonded methylammonium hydrate ($[CH_3NH_3 \bullet H_2O]^+$) was estimated using structural coordinates predicted by energy minimized DFT calculations (B3LYP, 3-21G). Treating this polyatomic cation as a rigid sphere using a procedure recently proposed by Cheetham[5] ($r_{\mathrm{Aeff}} = r_{\mathrm{mass}} + r_{\mathrm{ion}}$ where r_{mass} is the distance between the center of mass of the molecule and farthest non-hydrogen atom and where r_{ion} is the ionic radius of the farthest non-hydrogen atom) gives an effective ionic radius of 346nm ($r_{\mathrm{mass}} = 2.06$Å and $r_{\mathrm{ion}}(O^{2-}) = 1.4$ Å).[6]

X-Ray Powder Method Description

Powder XRD patterns were obtained on a Bruker Kappa Apex II Duo X-Ray diffractometer with Cu Kα radiation. (λ = 1.5418 Å).

Powder patterns from $CH_3NH_3PbI_3{\bullet}H_2O$ that had converted to $CH_3NH_3PbI_3$ in air displayed key peaks that closely match the room temperature tetragonal (*I4/mcm*) phase of $CH_3NH_3PbI_3$ (lattice parameters $a = b = 8.849$ $c = 12.642$).[3,7]

Crystal Structure Report for $CH_3NH_3PbI_3$•H_2O

A specimen of CH_8I_3NOPb, approximate dimensions 0.150 mm x 0.150 mm x 0.700 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a monoclinic unit cell yielded a total of 6477 reflections to a maximum θ angle of 27.88° (0.76 Å resolution), of which 1430 were independent (average redundancy 4.529, completeness =100.0%, R_{int} = 3.28%, R_{sig} = 2.64%) and 1405 (98.25%) were

greater than 2σ(F^2). The final cell constantsof a = 10.469(2) Å, b = 4.6557(9) Å, c = 11.214(2) Å, β = 101.251(3)°, volume = 536.07(19) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0210 and 0.1214.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/m 1, with Z = 2 for the formula unit, CH_8I_3NOPb. The final anisotropic full-matrix least-squares refinement on F^2 with 52 variables converged at R1 = 2.07%, for the observed data and wR2 = 5.72% for all data. The goodness-of-fit was 1.101. The largest peak in the final difference electron density synthesis was2.245 e$^-$/Å^3 and the largest hole was -2.162 e$^-$/Å^3 with an RMS deviation of 0.217 e$^-$/Å^3. On the basis of the final model, the calculated density was 3.953 g/cm^3 and F(000), 540 e$^-$.

Table 1. Sample and crystal data for 2214b.

Identification code	2214b	
Chemical formula	CH_8I_3NOPb	
Formula weight	637.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.150 x 0.150 x 0.700 mm	
Crystal system	monoclinic	
Space group	P 1 21/m 1	
Unit cell dimensions	a = 10.469(2) Å	α = 90°
	b = 4.6557(9) Å	β = 101.251(3)°
	c = 11.214(2) Å	γ = 90°
Volume	536.07(19) Å^3	
Z	2	
Density (calculated)	3.953 g/cm^3	
Absorption coefficient	24.311 mm^{-1}	
F(000)	540	

Table 2. Data collection and structure refinement for 2214b.

Theta range for data collection	1.85 to 27.88°
Index ranges	-13<=h<=13, -6<=k<=3, -14<=l<=14

Reflections collected	6477
Independent reflections	1430 [R(int) = 0.0328]
Max. and min. transmission	0.1214 and 0.0210
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1430 / 3 / 52
Goodness-of-fit on F^2	1.101
Δ/σ_{max}	0.001
Final R indices	1405 data; I>2σ(I) R1 = 0.0207, wR2 = 0.0568
	all data R1 = 0.0211, wR2 = 0.0572
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0312P)^2+0.7995P]$ where $P=(F_o^2+2F_c^2)/3$
Extinction coefficient	0.0048(3)
Largest diff. peak and hole	2.245 and -2.162 eÅ^{-3}
R.M.S. deviation from mean	0.217 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 2214b.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Pb1	0.09771(2)	0.25	0.68007(18)	0.01879(10)
I1	0.80472(4)	0.25	0.48594(3)	0.02126(12)
I2	0.98520(4)	0.75	0.82746(3)	0.02203(12)
I3	0.36006(4)	0.25	0.85801(3)	0.02290(12)
O1	0.2608(4)	0.75	0.0873(4)	0.0289(10)
N1	0.3918(6)	0.25	0.1947(5)	0.0305(12)
C1	0.4128(9)	0.25	0.3293(7)	0.048(2)

Table 4. Bond lengths (Å) for 2214b.

Pb1-I3	3.0637(6)	Pb1-I2#2	3.2089(5)
Pb1-I2	3.2090(5)	Pb1-I1#3	3.2665(5)
Pb1-I1#4	3.2665(5)	Pb1-I1	3.3972(7)
I1-Pb1#3	3.2665(5)	I1-Pb1#4	3.2665(5)
I2-Pb1#1	3.2090(5)	N1-C1	1.482(9)

Symmetry transformations used to generate equivalent atoms:

#1 x, y-1, z

#2 x, y+1, z

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

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

Table 5. Bond angles (°) for 2214b.

I3-Pb1-I2#2	92.123(14)	I3-Pb1-I2	92.123(14)
I2#2-Pb1-I2	93.009(17)	I3-Pb1-I1#3	91.771(14)
I2#2-Pb1-I1#3	175.963(11)	I2-Pb1-I1#3	87.912(16)
I3-Pb1-I1#4	91.771(14)	I2#2-Pb1-I1#4	87.912(16)
I2-Pb1-I1#4	175.963(11)	I1#3-Pb1-I1#4	90.902(18)
I3-Pb1-I1	179.236(11)	I2#2-Pb1-I1	87.352(14)
I2-Pb1-I1	87.352(14)	I1#3-Pb1-I1	88.765(14)
I1#4-Pb1-I1	88.765(14)	Pb1#3-I1-Pb1#4	90.903(18)
Pb1#3-I1-Pb1	91.236(14)	Pb1#4-I1-Pb1	91.236(14)
Pb1-I2-Pb1#1	93.008(17)		

Symmetry transformations used to generate equivalent atoms:
#1 x, y-1, z
#2 x, y+1, z
#3 -x, -y, -z+1
#4 -x, -y+1, -z+1

Table 6. Torsion angles (°) for 2214b.

I3-Pb1-I1-Pb1#3	-134.535(9)	I2#2-Pb1-I1-Pb1#3	178.896(7)
I2-Pb1-I1-Pb1#3	-87.966(16)	I1#3-Pb1-I1-Pb1#3	0
I1#4-Pb1-I1-Pb1#3	90.929(18)	I3-Pb1-I1-Pb1#4	134.535(10)
I2#2-Pb1-I1-Pb1#4	87.966(16)	I2-Pb1-I1-Pb1#4	-178.896(7)
I1#3-Pb1-I1-Pb1#4	-90.929(18)	I1#4-Pb1-I1-Pb1#4	0
I3-Pb1-I2-Pb1#1	-87.761(15)	I2#2-Pb1-I2-Pb1#1	180.0
I1#3-Pb1-I2-Pb1#1	3.934(11)	I1#4-Pb1-I2-Pb1#1	76.91(11)
I1-Pb1-I2-Pb1#1	92.794(15)		

Symmetry transformations used to generate equivalent atoms:
#1 x, y-1, z
#2 x, y+1, z
#3 -x, -y, -z+1
#4 -x, -y+1, -z+1

Table 7. Anisotropic atomic displacement parameters (Å^2) for 2214b.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U_{11} + ... + 2\ h\ k\ a^* b^* U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	0.01893(14)	0.01848(15)	0.01851(14)	0	0.00256(9)	0
I1	0.0209(2)	0.0229(2)	0.0208(2)	0	0.00607(14)	0
I2	0.0227(2)	0.0211(2)	0.0244(2)	0	0.00969(15)	0

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I3	0.01754(19)	0.0254(2)	0.0246(2)	0	0.00107(14)	0
O1	0.026(2)	0.030(3)	0.030(2)	0	0.0054(18)	0
N1	0.030(3)	0.026(3)	0.038(3)	0	0.012(2)	0
C1	0.059(6)	0.052(6)	0.036(4)	0	0.015(4)	0

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 2214b.

	x/a	y/b	z/c	U(eq)
H1A	0.3567	0.0790	0.1657	0.046
H1B	0.4694	0.2759	0.1711	0.046
H1C	0.3366	0.3951	0.1647	0.046
H1D	0.4774	0.1035	0.3618	0.072
H1E	0.3304	0.2073	0.3548	0.072
H1F	0.4443	0.4392	0.3603	0.072
H7	0.284(5)	0.7500	0.014(3)	0.009(16)
H8	0.1730(19)	0.7500	0.069(6)	0.05(3)

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