Experimental Section

Synthesis

All reagents were used without any further purification: copper nitrate pentahydrate (≥98%) was purchased from Alfa Aesar, L-aspartic acid (≥98%, Fluka) and sodium hydrogen carbonate (Fisher Scientific). The synthesis was carried out using Parr Teflon-lined stainless steel autoclaves under autogenous pressure.

Blue needle-like crystals of CuAsp were synthesized by stirring Cu(NO3)·5H2O (0.209g, 0.751mmol), L-aspartic acid (0.1g, 0.751mmol) and NaHCO3 (0.063g, 0.751mmol¬) in a water/methanol mixture (2/2ml respectively), giving a molar composition for the reaction of 1:1 Cu:asp. The resulting mixture was sealed in a 23mL autoclave and heated at 100 ºC for 18hrs. Upon cooling at a rate of 0.2 ºC min-1 to room temperature, the product was filtered and washed with water and methanol.

High-Pressure Crystallography

General Procedures

High-pressure experiments were carried out with a Merrill-Bassett diamond anvil cell equipped with 600μm culet diamonds and a tungsten gasket. The sample and a chip of ruby (as a pressure calibrant) were loaded into the DAC with a 4:1 mixture of methanol and ethanol as a hydrostatic medium. The ruby fluorescence method was utilised to measure the pressure [1].

Data Collection, Reduction and Refinement

A sphere of data was collected on a crystal of [Cu(L-Asp)(H_2O)$_2$] at ambient temperature and pressure in order to provide data for comparison with the high pressure studies, which were also performed at ambient temperature (see below). Diffraction data were collected on a single crystal of [Cu(L-Asp)(H_2O)$_2$] solvate on a Bruker SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). These data were integrated using the program SAINT [2], while the absorption correction was carried out with the program SADABS [3]. Refinement was carried out against $|F|^2$ using all data [4] and the structure solved using Sir92[5]. The final conventional *R*-factor was 0.0329 for 2470 data. Listings of crystal and refinement data are given in Table S1.

High pressure diffraction data were collected with synchrotron radiation on a Bruker APEX II diffractometer at the CCLRC Daresbury Laboratory on Station 9.8 (λ = 0.4762 Å), see below. Data were collected in ω-scans in 8 settings of 2θ and ϕ with a frame and step size of one second and 0.3°, respectively. This data collection strategy was based on that described by [6]. The data were integrated using the program SAINT using 'dynamic masks' to avoid integration of regions of

the detector shaded by the body of the pressure cell [6]. Absorption corrections for the DAC and sample were carried out with the programs SHADE [7] and SADABS, respectively. Data were collected from 0.3 GPa up to a final pressure of 7.9 GPa, above which the sample became polycrystalline. On increasing pressure from 6.8 GPa to 7.9 GPa, the sample underwent a single-crystal to single-crystal phase transition.

Refinements of [Cu(L-Asp)(H_2O)$_2$]-I (the ambient pressure phase) to 6.8 GPa were carried out starting from our room temperature re-determination of the structure. Refinements were carried out against $|F|^2$ using all data (CRYSTALS). Because of the low completeness of the high-pressure data-sets, all 1,2 and 1,3 distances on the aspartate ligand were restrained to the values observed in the ambient pressure structure, however all torsion angles and metal to ligand distances were refined freely. Thermal similarity restraints were also applied to the aspartate ligand. All hydrogen atoms attached to carbon and nitrogen were placed geometrically and not refined. H-atoms attached to the water ligands were placed in idealised H-bonding positions, and then refined with restraints (O-H distance restraint = 0.84, 0.01) until the refinement converged. Once converged H-atoms were refined with a riding model. Only the Copper atom was refined anisotropically, while all other non-hydrogen atoms were refined with isotropic thermal parameters.

[Cu(L-Asp)(H_2O)$_2$]-II at 7.9 GPa (the high-pressure phase), was refined from the ambient pressure phase coordinates. On undergoing the transition, a large decrease was observed in the β-angle. The high-pressure phase was therefore refined with an unconventional β-angle that was less than 90 degrees. Listings of crystal and refinement data are given in Table S1.

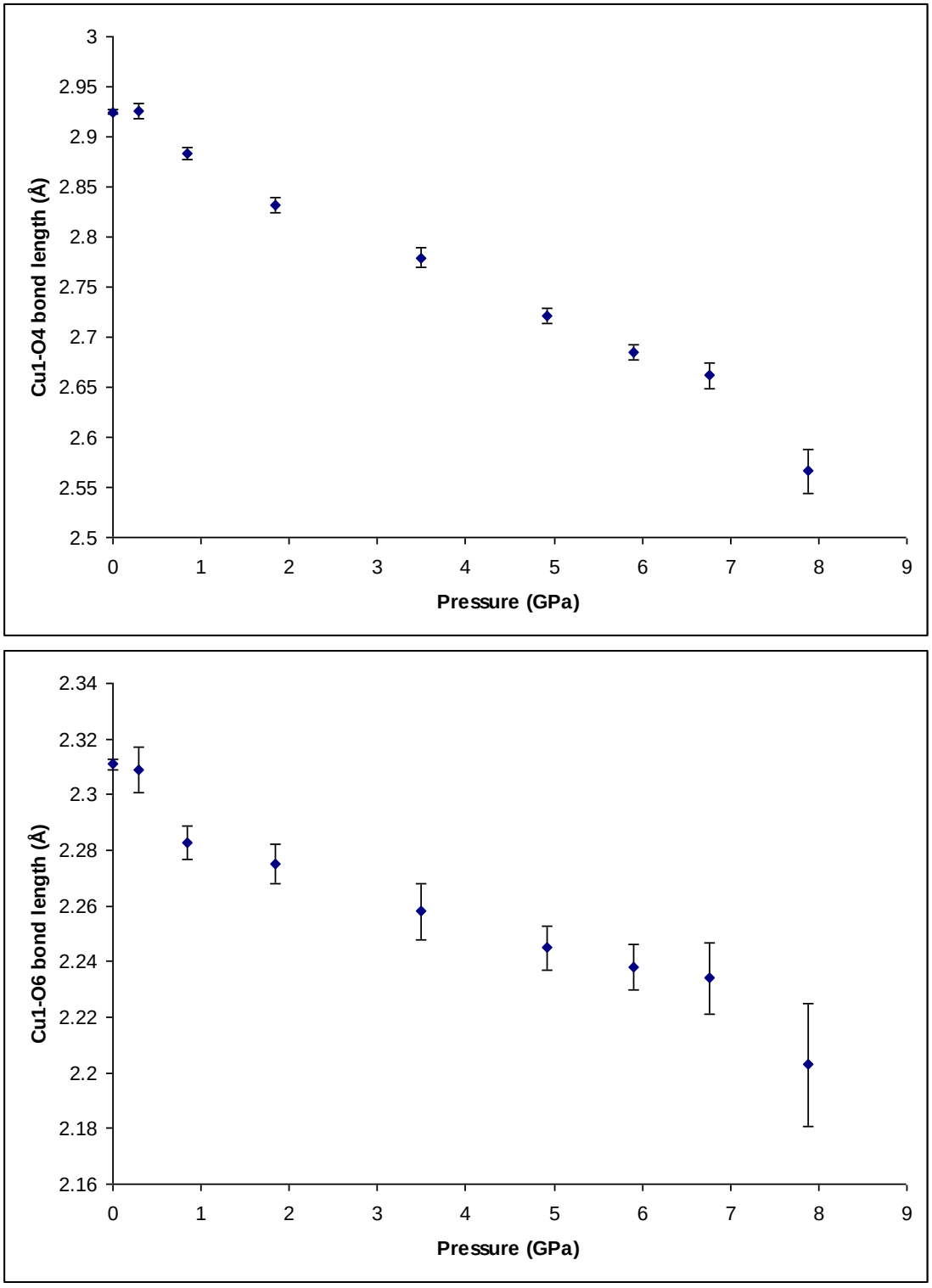
Table 1. Experimental details

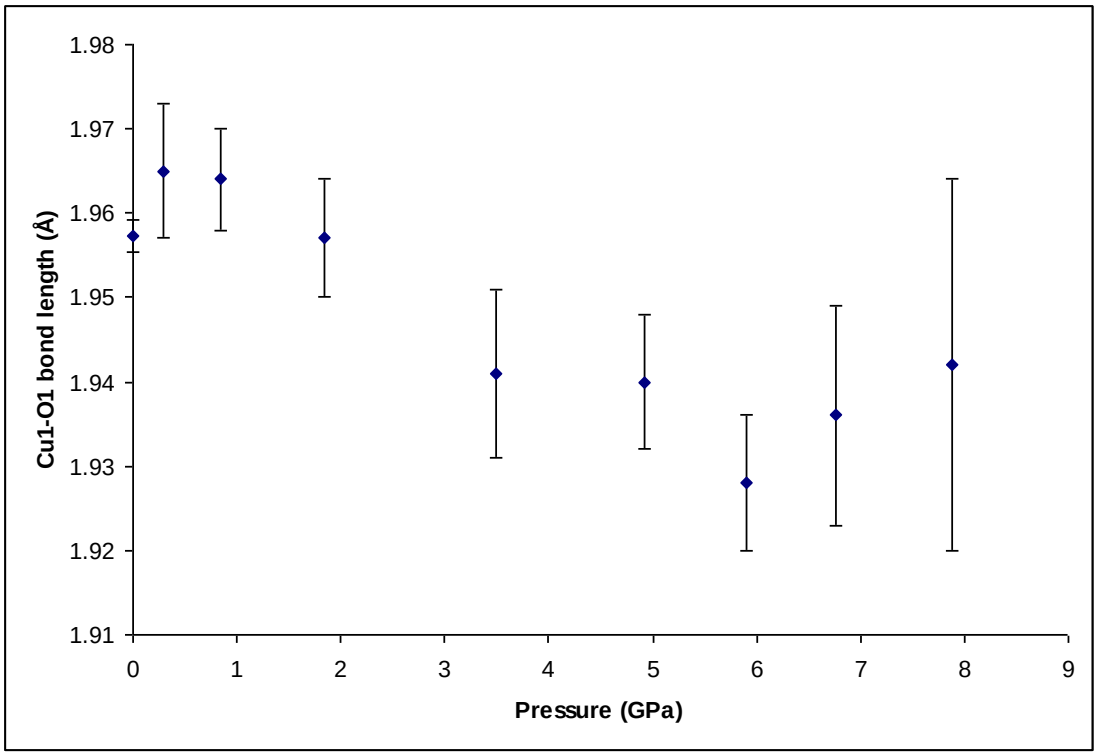
For all structures: monoclinic, *C*2, *Z* = 4. Experiments were carried out at 293 K. H-atom parameters were constrained.

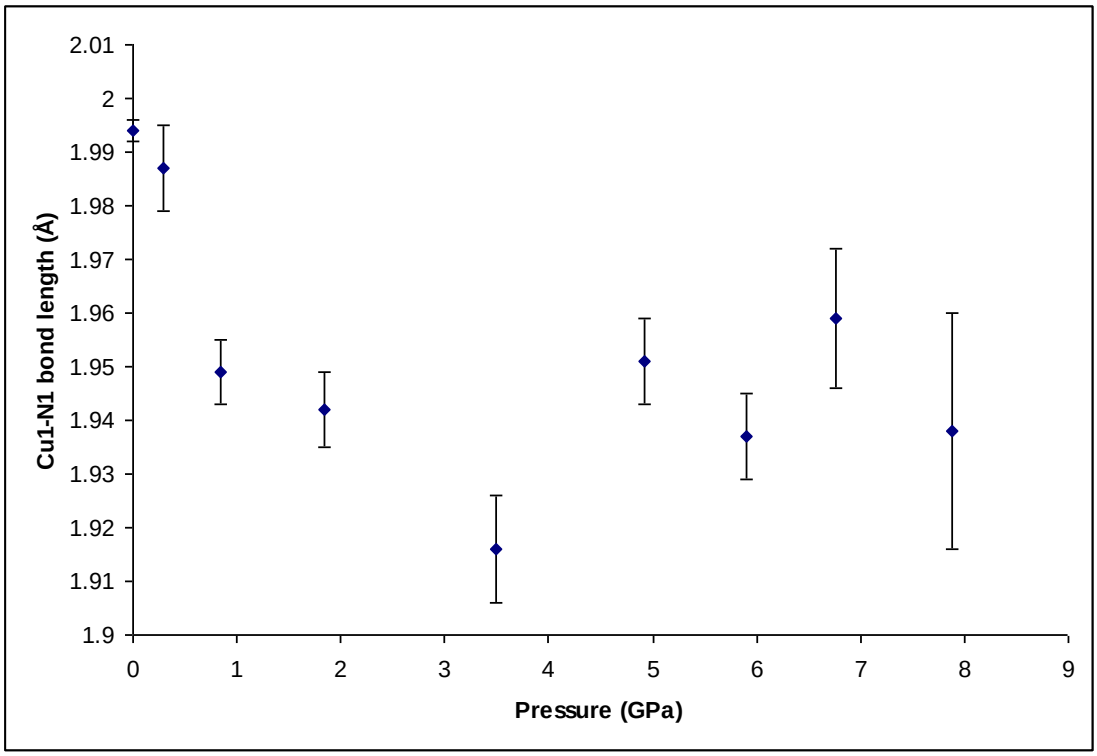
	ambient	0.3 GPa	0.9 GPa	1.8 GPa	3.5 GPa
Crystal data					
Chemical formula	$C_8H_{18}Cu_2N_2O_{12}$	$C_4H_9CuNO_6$	$C_4H_9CuNO_6$	$C_4H_9CuNO_6$	$C_4H_9CuNO_6$
M_r	230.67	230.66	230.66	230.66	230.66
a, *b*, *c* (Å)	9.5172 (1), 10.0418 (1), 7.5621 (1)	9.4817 (3), 10.0118 (3), 7.5433 (7)	9.3964 (3), 9.9334 (4), 7.5076 (9)	9.2843 (3), 9.8358 (4), 7.4532 (7)	9.1425 (9), 9.7138 (11), 7.361 (2)
β (°)	93.984 (1)	93.856 (4)	93.536 (6)	93.071 (5)	92.265 (16)
V (Å^3)	720.96 (1)	714.46 (7)	699.41 (9)	679.64 (7)	653.2 (2)
Radiation type	Mo *K*α	Synchrotron, λ = 0.47620 Å	Synchrotron, λ = 0.47620 Å	Synchrotron, λ = 0.47620 Å	Synchrotron, λ = 0.47620 Å
μ (mm^{-1})	3.02	3.05	3.12	3.21	3.34
Crystal size (mm)	0.2 × 0.2 × 0.1	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
Data collection					
Diffractometer	Unknown diffractometer	Bruker Apex2 diffractometer	Bruker Apex2 diffractometer	Bruker Apex2 diffractometer	Bruker Apex2 diffractometer
Absorption correction	–	Multi-scan *SADABS* (Siemens, 1996)	Multi-scan *SADABS* (Siemens, 1996)	Multi-scan *SADABS* (Siemens, 1996)	Multi-scan *SADABS* (Siemens, 1996)
T_{min}, T_{max}	–	0.53, 0.74	0.52, 0.73	0.55, 0.73	0.62, 0.72
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	5337, 1732, 1607	2706, 855, 639	2725, 838, 486	2659, 810, 626	2568, 786, 595
R_{int}	0.026	0.044	0.039	0.037	0.041
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.022, 0.051, 0.98	0.032, 0.087, 0.92	0.027, 0.057, 0.84	0.031, 0.068, 0.96	0.038, 0.092, 0.93
No. of reflections	1732	846	834	807	786
No. of parameters	110	55	55	55	55
No. of restraints	1	39	37	37	37
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.42, -0.40	0.91, -0.94	0.48, -0.41	0.50, -0.51	0.68, -1.20
Absolute structure	Flack (1983), 732 Friedel-pairs	Flack (1983), 390 Friedel-pairs	Flack (1983), 382 Friedel-pairs	Flack (1983), 369 Friedel-pairs	Flack (1983), 350 Friedel-pairs
Flack parameter	0.066 (14)	0.27 (3)	0.23 (2)	0.27 (3)	0.31 (4)

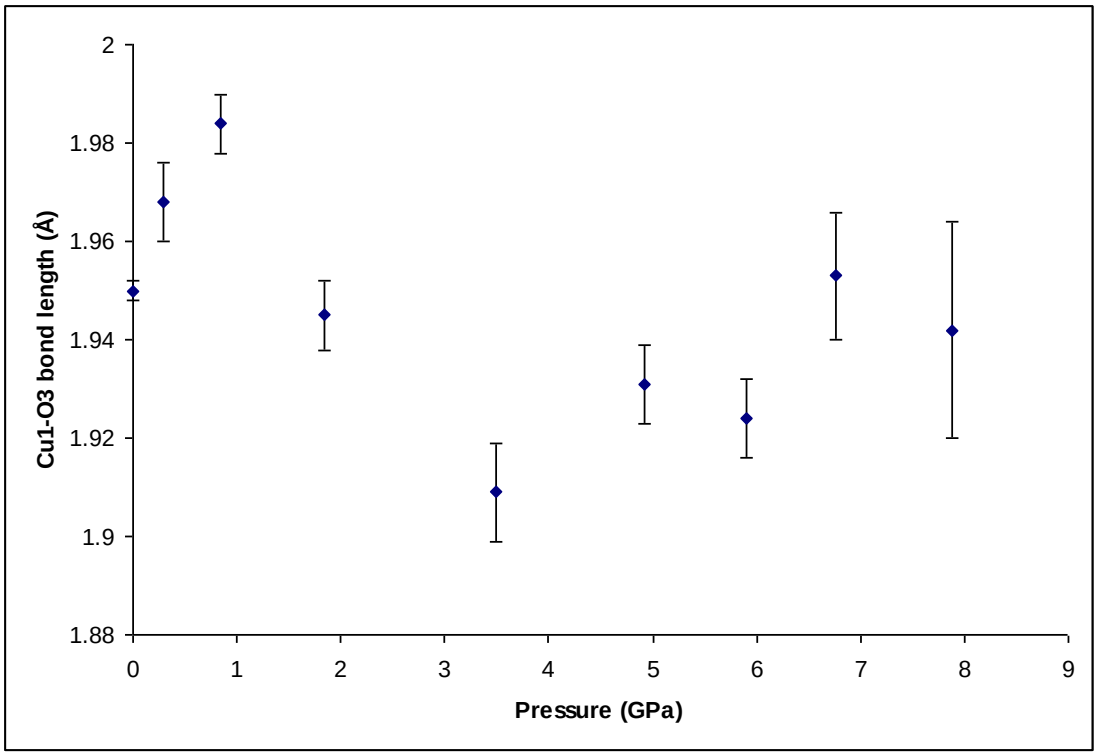
	4.9 GPa	5.9 GPa	6.8 GPa	7.9 GPa
Crystal data				
Chemical formula	$C_4H_9CuNO_6$	$C_4H_9CuNO_6$	$C_4H_9CuNO_6$	$C_4H_9CuNO_6$
M_r	230.66	230.66	230.66	230.66
a, b, c (Å)	9.0447 (5), 9.6337 (7), 7.3016 (14)	8.9747 (5), 9.5739 (6), 7.2465 (11)	8.9403 (6), 9.5601 (8), 7.2112 (14)	8.9493 (9), 9.6210 (13), 7.059 (2)
β (°)	91.765 (10)	91.332 (8)	90.949 (12)	89.829 (18)
V (Å^3)	635.92 (14)	622.47 (11)	616.26 (14)	607.8 (2)
Radiation type	Synchrotron, λ = 0.47620 Å	Synchrotron, λ = 0.47620 Å	Synchrotron, λ = 0.47620 Å	Synchrotron, λ = 0.47620 Å
μ (mm^{-1})	3.43	3.50	3.54	3.58
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
Data collection				
Diffractometer	Bruker Apex2 diffractometer	Bruker Apex2 diffractometer	Bruker Apex2 diffractometer	Bruker Apex2 diffractometer
Absorption correction	Multi-scan *SADABS* (Siemens, 1996)	Multi-scan *SADABS* (Siemens, 1996)	Multi-scan *SADABS* (Siemens, 1996)	Multi-scan *SADABS* (Siemens, 1996)
T_{min}, T_{max}	0.62, 0.71	0.61, 0.70	0.56, 0.70	0.49, 0.70
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	2538, 728, 566	2505, 723, 582	2337, 674, 512	1994, 647, 230
R_{int}	0.042	0.043	0.060	0.091
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.062, 0.87	0.031, 0.064, 0.96	0.040, 0.096, 0.87	0.048, 0.247, 1.01
No. of reflections	728	714	669	647
No. of parameters	55	55	55	55
No. of restraints	37	37	37	37
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.32, -0.31	0.51, -0.50	0.76, -0.81	1.08, -1.16
Absolute structure	Flack (1983), 322 Friedel-pairs	Flack (1983), 322 Friedel-pairs	Flack (1983), 309 Friedel-pairs	Flack (1983), 300 Friedel-pairs
Flack parameter	0.29 (3)	0.26 (3)	0.27 (5)	0.04 (12)

Figure S1. Cu-O bond lengths as a function of pressure.









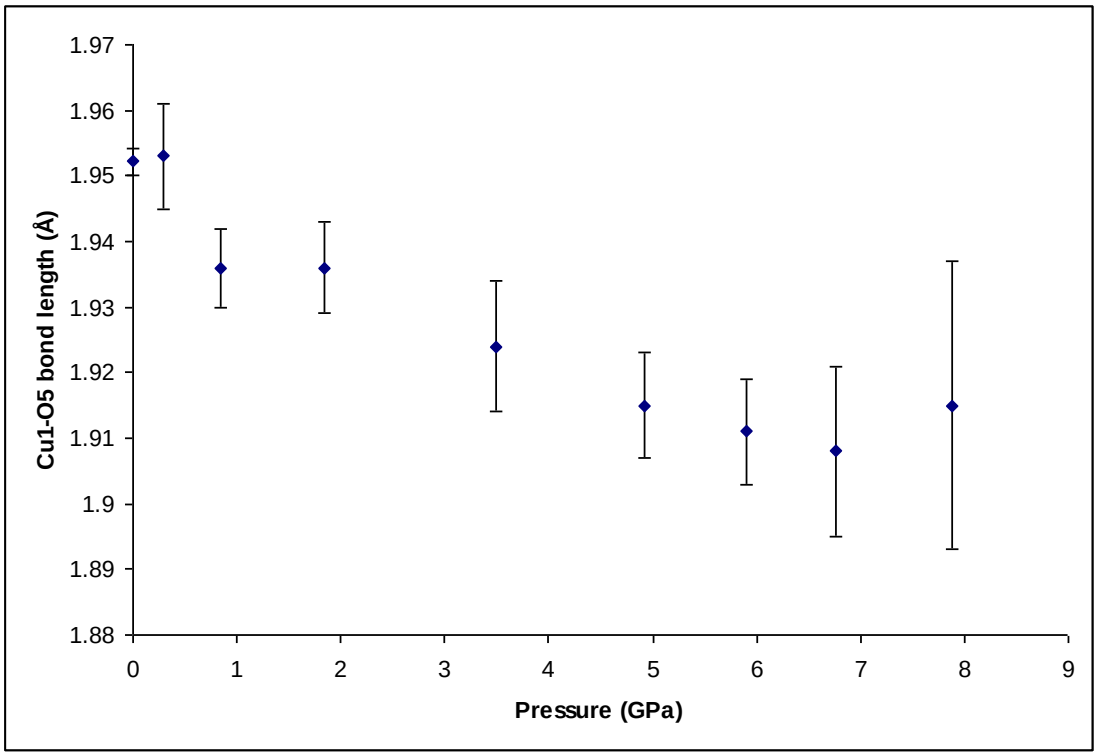
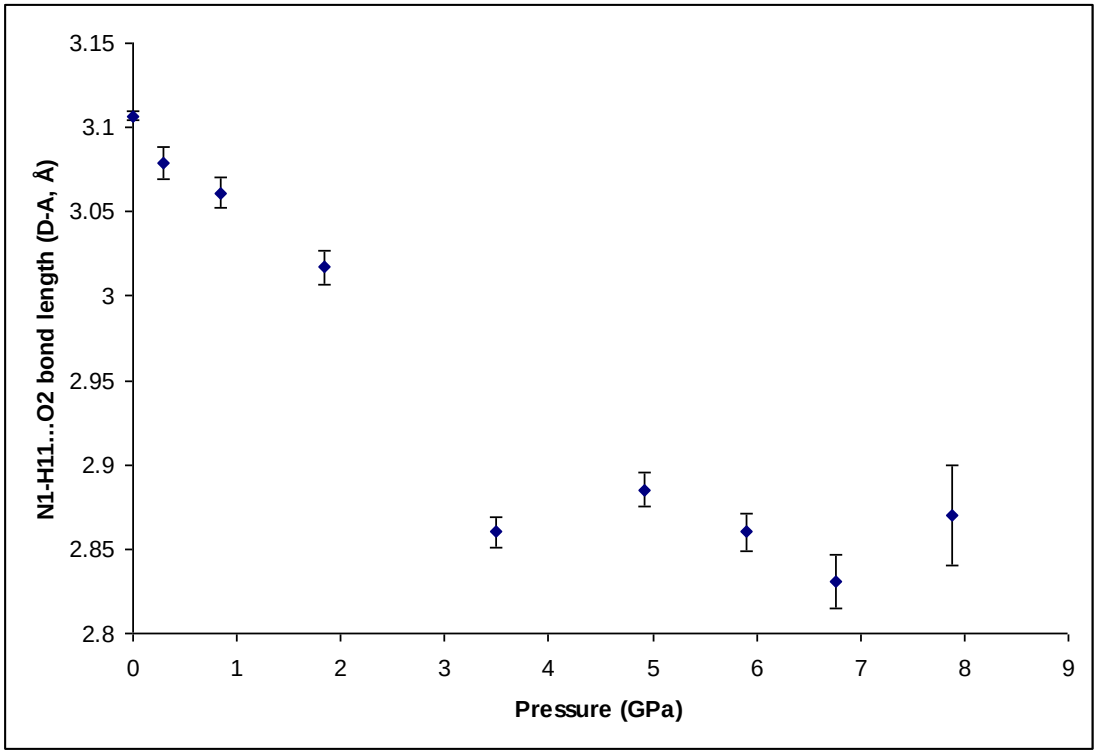
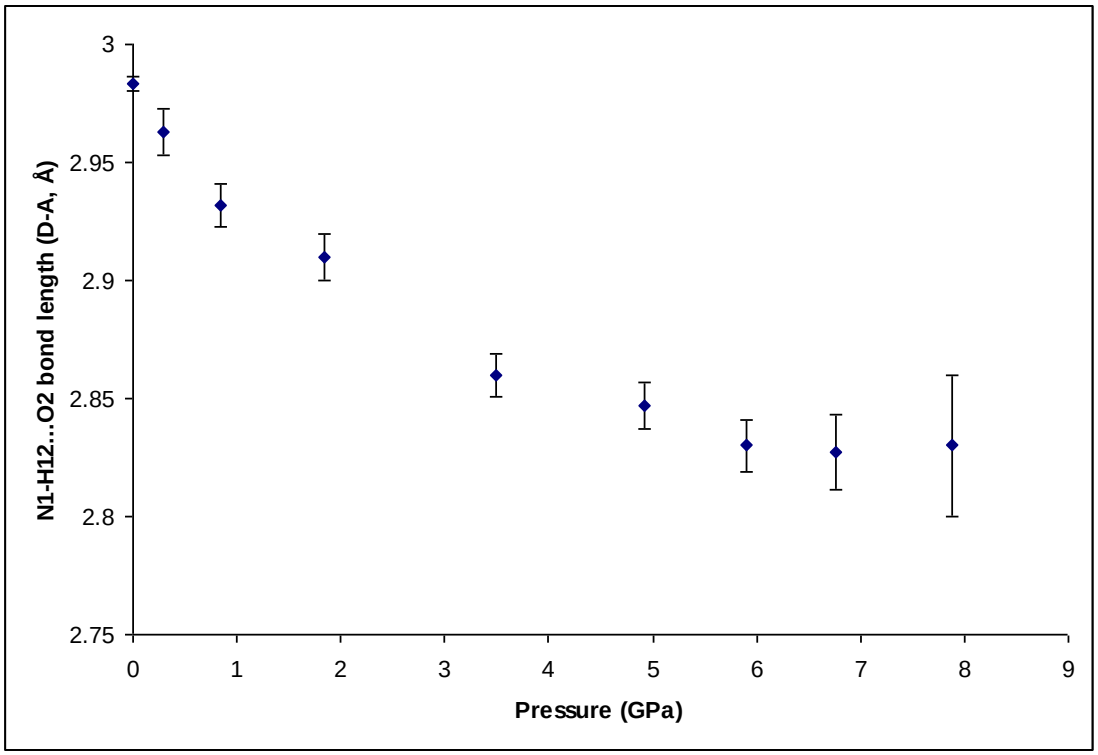
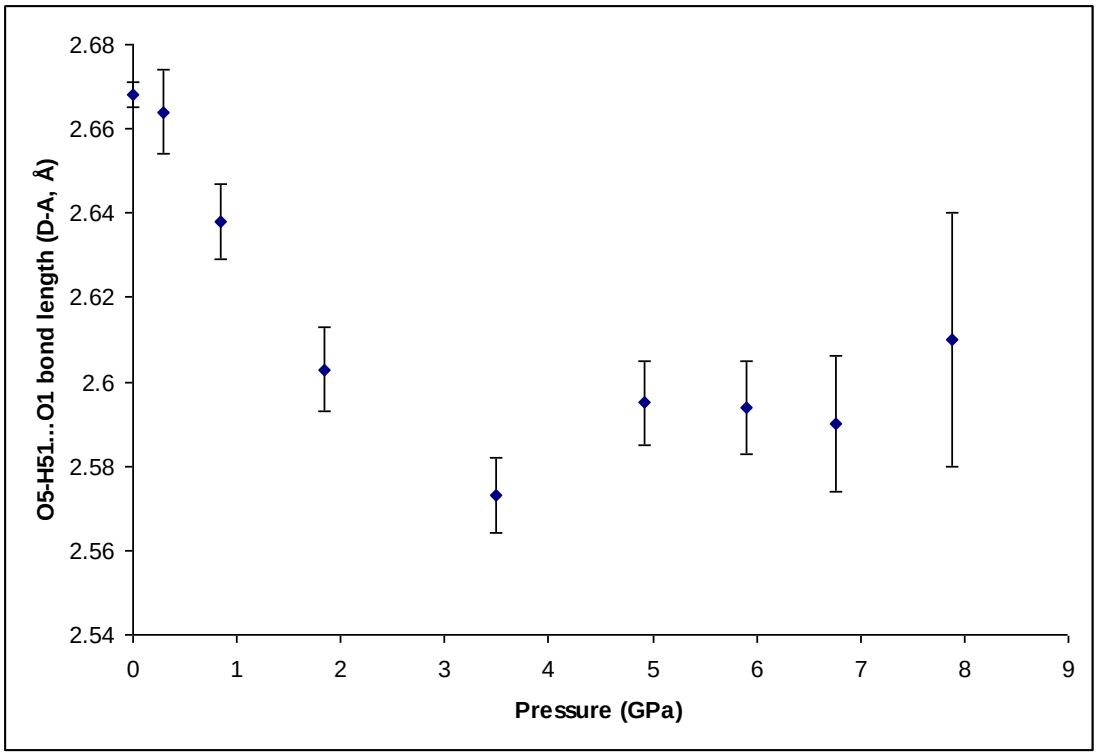
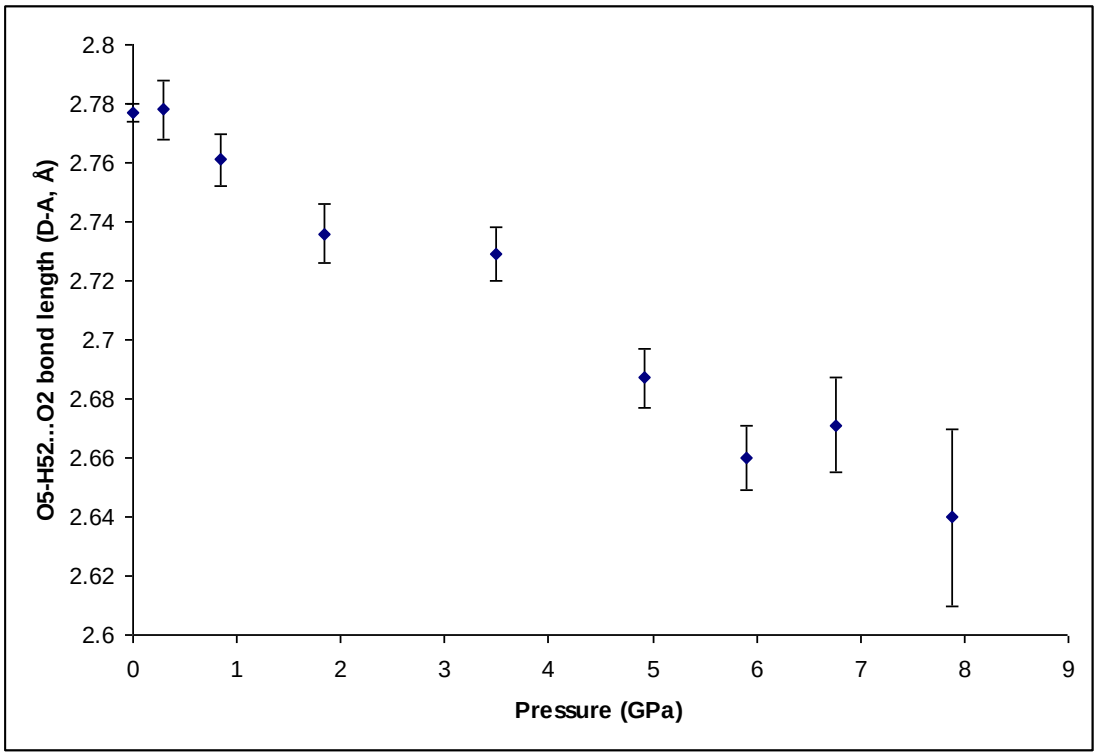


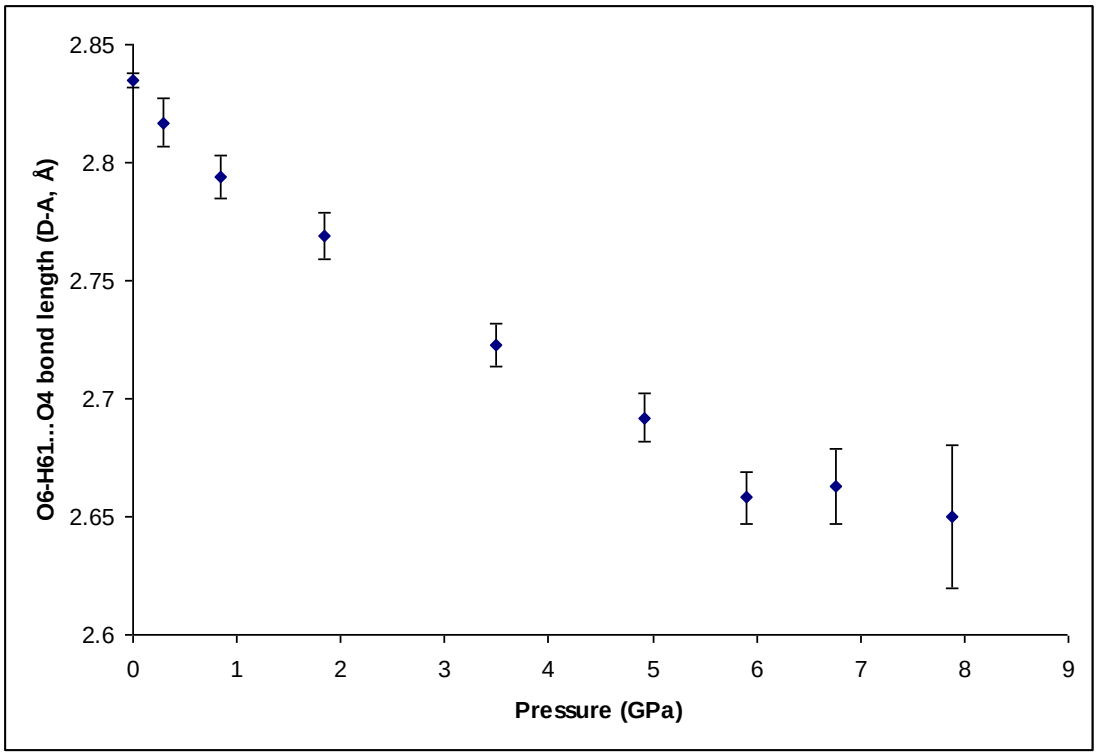
Figure S2. N-H…O and O-H…O H-bonding interactions as a function of pressure (D-A distances are quoted).

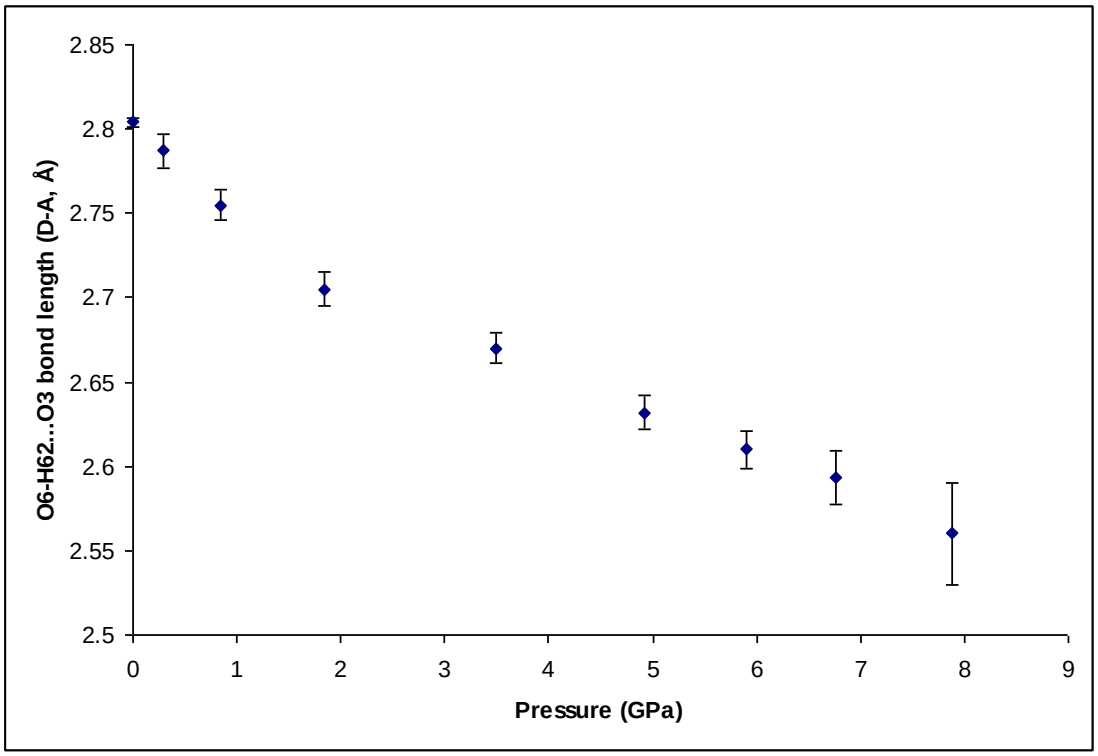












S2. Intramolecular angles in CuAsp as a function of pressure.

	Pressure (GPa)								
Bond/Valence Angles	**0**	**0.3**	**0.9**	**1.8**	**3.5**	**4.9**	**5.9**	**6.8**	**7.9**
O(1) - Cu(1) - O(5)	172.71(7)	172.6(3)	173.0(2)	173.6(2)	173.9(3)	173.8(3)	173.4(3)	174.0(5)	175.1(9)
O(1) - Cu(1) - O(3)b	90.80(10)	91.3(3)	90.7(3)	90.2(3)	90.2(3)	89.9(3)	89.5(3)	90.2(4)	89.6(7)
O(5) - Cu(1) - N(1)	89.70(8)	89.9(3)	89.9(2)	90.2(3)	91.1(4)	89.8(3)	89.3(3)	90.0(6)	90.1(11)
O(6) - Cu(1) - N(1)	96.81(8)	97.1(3)	98.0(3)	98.4(3)	99.7(4)	100.2(3)	101.2(3)	101.4(5)	107.8(11)
N(1) - Cu(1) - O(3)b	168.17(11)	167.7(2)	166.96(19)	167.0(2)	166.4(3)	166.5(2)	166.2(2)	166.3(3)	165.1(7)
Cu(1) - O(1) - C(1)	115.72(17)	115.8(5)	114.4(4)	114.1(5)	114.7(6)	114.6(4)	114.5(5)	114.6(7)	113.4(12)
Cu(1) - N(1) - C(2)	110.50(15)	110.9(4)	110.6(4)	111.2(4)	111.9(5)	109.3(4)	109.2(4)	108.7(6)	107.9(10)
O(1) - Cu(1) - O(6)	91.90(7)	91.96(17)	92.73(14)	92.41(15)	92.9(2)	93.29(17)	94.04(19)	94.1(3)	95.4(6)
O(1) - Cu(1) - O(4)b	88.00(7)	88.1(2)	86.7(2)	86.1(2)	85.3(3)	84.7(2)	83.8(2)	83.8(4)	81.9(6)
O(5) - Cu(1) - O(3)b	95.99(10)	95.6(3)	95.1(3)	94.9(3)	94.1(4)	95.2(3)	95.8(3)	94.9(6)	94.7(12)
O(6) - Cu(1) - O(3)b	93.53(8)	93.8(3)	94.0(3)	93.5(3)	92.7(4)	92.4(3)	91.7(3)	91.5(4)	86.6(10)
N(1) - Cu(1) - O(4)b	119.69(8)	119.3(2)	117.40(18)	116.2(2)	114.3(3)	113.1(2)	112.2(2)	111.9(3)	108.1(7)
C(4) - O(3) - Cu(1)a	115.36(17)	114.9(4)	113.3(4)	112.0(4)	110.5(5)	108.6(4)	107.7(4)	105.7(6)	101.8(12)
O(1) - Cu(1) - N(1)	83.15(8)	82.9(3)	83.7(2)	84.0(3)	83.7(3)	84.4(2)	84.7(3)	84.3(4)	85.2(7)
O(5) - Cu(1) - O(6)	90.33(8)	90.39(19)	90.71(15)	91.20(16)	91.2(2)	89.97(18)	89.7(2)	89.1(4)	87.2(7)
O(5) - Cu(1) - O(4)b	94.36(6)	94.2(3)	94.0(2)	94.0(3)	93.8(4)	95.5(3)	96.1(3)	96.4(6)	98.5(11)
O(6) - Cu(1) - O(4)b	143.16(7)	143.3(3)	144.2(3)	144.9(3)	145.5(4)	146.2(3)	146.1(3)	146.2(4)	143.6(9)
O(3)b - Cu(1) - O(4)b	49.65(7)	49.47(17)	50.30(13)	51.58(16)	52.9(2)	53.94(17)	54.62(19)	54.9(3)	57.2(5)
C(4) - O(4) - Cu(1)a	70.01(14)	69.7(5)	71.2(4)	70.8(4)	70.8(6)	72.6(4)	73.0(5)	73.6(7)	74.6(12)

Symmetry operator: a =[1554.01] = x,y,-1+z, b =[1556.01] = x,y,1+z

Table S3. Torsion angles in CuAsp as a function of pressure.

	Pressure (GPa)								
Torsion/Dihedral Angles	**0**	**0.3**	**0.9**	**1.8**	**3.5**	**4.9**	**5.9**	**6.8**	**7.9**
O(6) Cu(1) O(1) C(1)	-81.1(2)	-81.9(4)	-81.0(4)	-82.5(4)	-83.6(6)	-85.3(4)	-86.3(5)	-86.6(7)	-93.1(14)
O(4)b Cu(1) O(1) C(1)	135.74(19)	134.8(4)	134.9(3)	132.6(3)	130.9(5)	128.5(4)	127.6(4)	127.3(6)	123.4(11)
O(6) Cu(1) N(1) C(2)	72.84(16)	72.6(4)	71.8(3)	71.0(4)	70.0(5)	70.8(4)	71.0(4)	70.9(6)	69.1(12)
O(5) Cu(1) O(3)b C(4)b	96.5(2)	97.9(4)	97.9(3)	98.3(3)	98.7(4)	100.0(3)	100.4(4)	102.3(6)	104.4(11)
O(5) Cu(1) O(4)b C(4)b	-100.03(18)	-100.7(4)	-100.2(3)	-100.2(3)	-99.5(5)	-99.5(3)	-100.0(4)	-99.5(6)	-97.8(12)
O(2) C(1) O(1) Cu(1)	170.5(2)	170.1(4)	171.1(3)	171.4(3)	172.3(5)	172.3(4)	172.6(5)	173.5(7)	175.6(12)
O(1) C(1) C(2) C(3)	115.0(3)	113.2(5)	113.7(5)	110.9(5)	107.8(7)	104.8(6)	103.2(6)	102.5(9)	97.8(15)
C(1) C(2) N(1) Cu(1)	18.1(2)	18.9(5)	20.1(4)	21.3(4)	23.3(6)	24.2(5)	25.1(5)	25.4(7)	30.1(13)
C(1) C(2) C(3) C(4)	157.0(2)	156.1(4)	156.6(4)	156.3(4)	157.4(6)	156.9(4)	156.9(5)	158.0(7)	160.3(12)
O(4) C(4) O(3) Cu(1)a	-12.8(3)	-15.5(7)	-14.8(6)	-15.4(6)	-15.3(9)	-14.7(6)	-14.9(7)	-16.7(10)	-15.5(2)
C(3) C(4) O(4) Cu(1)a	-167.2(3)	-168.7(5)	-167.7(5)	-168.9(5)	-168.6(7)	-168.3(5)	-169.0(5)	-168.2(8)	-164.4(16)
N(1) Cu(1) O(1) C(1)	15.51(19)	15.1(4)	16.8(3)	15.7(3)	15.8(5)	14.6(4)	14.6(5)	14.5(7)	14.3(12)
O(1) Cu(1) N(1) C(2)	-18.27(15)	-18.5(4)	-20.1(3)	-20.6(4)	-21.9(5)	-21.5(4)	-22.1(4)	-22.1(6)	-25.0(11)
O(4)b Cu(1) N(1) C(2)	-102.01(15)	-102.3(4)	-103.1(3)	-103.2(4)	-103.9(5)	-103.3(4)	-103.2(4)	-103.1(6)	-104.8(11)
O(6) Cu(1) O(3)b C(4)b	-172.8(2)	-171.4(4)	-171.1(3)	-170.2(3)	-169.9(4)	-169.9(3)	-169.7(3)	-168.5(5)	-168.7(10)
O(6) Cu(1) O(4)b C(4)b	-3.6(2)	-4.4(4)	-3.3(3)	-2.4(4)	-1.7(5)	-1.2(4)	-1.4(4)	-1.5(7)	-0.8(14)
C(2) C(1) O(1) Cu(1)	-8.7(3)	-7.7(5)	-9.0(5)	-6.8(5)	-5.5(7)	-3.4(6)	-2.8(7)	-2.6(9)	0.6(16)
O(2) C(1) C(2) N(1)	174.1(2)	174.4(4)	172.4(3)	172.1(4)	170.5(6)	169.9(4)	169.3(5)	168.1(7)	163.9(13)
C(3) C(2) N(1) Cu(1)	-102.6(2)	-101.5(6)	-99.8(5)	-97.9(6)	-94.4(7)	-94.0(6)	-92.7(6)	-91.7(8)	-87.9(14)
C(2) C(3) C(4) O(3)	170.6(2)	169.9(5)	169.1(4)	168.7(4)	168.7(6)	168.7(4)	168.3(5)	166.6(7)	166.2(14)
C(3) C(4) O(3) Cu(1)a	162.8(2)	163.3(4)	162.9(3)	163.9(3)	163.7(5)	164.0(4)	164.7(4)	163.7(6)	161.0(12)
O(3)b Cu(1) O(1) C(1)	-174.7(2)	-175.8(4)	-175.0(3)	-176.0(3)	-176.4(5)	-177.7(4)	-177.9(4)	-178.2(6)	-179.7(12)
O(5) Cu(1) N(1) C(2)	163.14(15)	163.0(4)	162.5(3)	162.3(4)	161.5(5)	160.8(4)	160.6(5)	160.0(7)	156.2(13)
O(1) Cu(1) O(3)b C(4)b	-80.8(2)	-79.3(4)	-78.3(3)	-77.8(3)	-76.9(4)	-76.6(3)	-75.7(4)	-74.4(5)	-73.3(10)
O(1) Cu(1) O(4)b C(4)b	86.88(18)	86.3(3)	86.9(3)	86.3(3)	86.6(4)	86.8(3)	86.7(3)	86.6(5)	87.2(11)
N(1) Cu(1) O(4)b C(4)b	167.83(18)	167.1(3)	168.0(3)	167.6(3)	167.6(4)	168.4(3)	168.3(3)	167.9(5)	169.4(10)
O(1) C(1) C(2) N(1)	-6.7(3)	-7.8(6)	-7.5(5)	-9.7(5)	-11.6(7)	-14.2(6)	-15.1(6)	-15.7(9)	-20.9(16)
O(2) C(1) C(2) C(3)	-64.3(3)	-64.6(6)	-66.4(5)	-67.3(5)	-70.1(8)	-71.1(6)	-72.4(6)	-73.7(9)	-77.3(16)
N(1) C(2) C(3) C(4)	-82.2(3)	-83.7(6)	-83.5(6)	-85.2(6)	-86.2(8)	-84.6(6)	-85.4(7)	-84.1(10)	-81.8(18)
C(2) C(3) C(4) O(4)	-13.5(3)	-11.3(7)	-13.2(6)	-12.1(7)	-12.2(9)	-12.7(7)	-12.1(8)	-13.0(11)	-17(2)
O(3) C(4) O(4) Cu(1)a	8.2(2)	10.0(5)	9.8(4)	10.3(5)	10.4(6)	10.3(5)	10.6(5)	12.2(8)	11.9(16)

Symmetry operator: a =[1554.01] = x,y,-1+z, b =[1556.01] = x,y,1+z

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