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Electron density topology in Ca^{II}-Cu^{II} alanine hydroximate metallacrowns: crystal invariom *vs* DFT calculation

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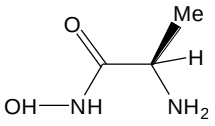
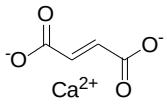
Content

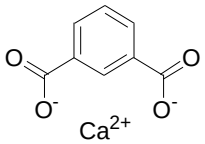
A chart with chemical structures of used compounds



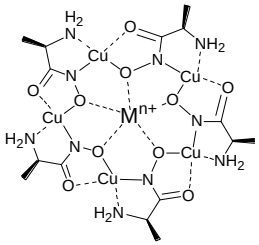
Alaninehydroxamic acid



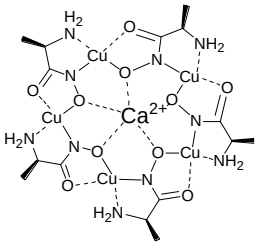
Calcium fumarate



Calcium isophthalate



Alaninehydroximate



Ca[15-$MC_{Cu(II)Alaha}$-5]
15-MC-5 metallacrown

Materials, Methods and Synthesis

All chemicals were reagent-grade and were used as received from Sigma Aldrich without further purification. The C, H, N elemental analyses were performed by the Microanalytical laboratory of IOMC on Euro EA 3000 Elemental Analyser. Electronic absorption spectra were recorded with the Perkin Elmer Lambda 25 UV/Vis spectrophotometer at room temperature, at 200–1100 nm. IR spectra were obtained on a Perkin Elmer 577 spectrometer and recorded from 4000 to 450 cm^{-1} as a Nujol mull on KBr plates

$Ca(C_8H_4O_4)(H_2O)[15\text{-}MC_{Cu(II)Alaha}\text{-}5](H_2O)_{16}$ ***(1)***. $Cu(OAc)_2{\cdot}H_2O$ (0.199 g, 1 mmol) was added to a stirred solution of L-alaninehydroxamic acid (0.09 g, 1 mmol) and Ca isophthalate (0.04 g, 0.2 mmol) in 30 ml of water. After stirring overnight and filtering the solution was left to evaporate slowly. Blue-violet needle crystals formed. Yield: 0.24 g (43%). Anal. Calcd. For $C_{23}H_{68}CaCu_5N_{10}O_{31}$ (1338.65): C 20.64, H 5.12, N 10.46. Found: C 20.59, H 5.16, N 10.53. IR (ν, cm^{-1}): 3233br, 1612 s, 1580 s, 1437 m, 1408 s, 1312 s, 1335 w, 1173 m, 1147 s, 1128 w, 1070 s, 1032 s, 935 w, 808 m, 605 w, 582 w, 565 w, 479 m. λmax (H_2O)/nm 565.

$Ca(C_4H_2O_4)(H_2O)[15\text{-}MC_{Cu(II)Alaha}\text{-}5](H_2O)_{15}$ ***(2)***. $Cu(OAc)_2{\cdot}H_2O$ (0.199 g, 1 mmol) was added to a stirred solution of L-alaninehydroxamic acid (0.09 g, 1 mmol) and Ca fumarate (0.03 g, 0.2 mmol) in 30 ml of water. After stirring overnight and filtering the solution was left to evaporate slowly. Blue-violet needle crystals formed. Yield: 0.14 g (63%). Anal. Calcd. For $C_{19}H_{64}CaCu_5N_{10}O_{30}$ (1270.57): C 17.96, H 5.08, N 11.02. Found: C 17.77, H 5.24, N 11.08. IR (ν, cm^{-1}): 3233br, 1612 s, 1580 s, 1437 m, 1408 s, 1312 s, 1335 w, 1173 m, 1147 s, 1128 w, 1070 s, 1032 s, 935 w, 808 m, 605 w, 582 w, 565 w, 479 m. λmax (H_2O)/nm 565.

1. Calculation of the asymmetric unit cell aspherical scattering factor (crystal invariom) in 1 and 2.

The single point calculation of periodical 3D structure of complexes **1** and **2** was performed within the PBE0 exchange-correlation functional[S1,S2] using CRYSTAL17.[S3] Atomic cores were described using all electron DZP basis set.[S4-S6] The information from X-ray crystallography was used as geometry the atomic coordinates. The convergence of the PBE0 functional was optimized using the «FMIXING 30» and «LEVSHIFT 6 1» options. The shrinking factor of the reciprocal space was set to four, corresponding to 30 k points in the irreducible Brillouin zone at which the Hamiltonian matrix was diagonalized.

The VESTA (ver. 3.5.7) program[S7] was applied to generate 61589 (for complex **1**) and 61242 (for **2**) unique Miller indices up to s = 1.15 $Å^{-1}$ reciprocal resolution. The option XFAC of the CRYSTAL17 program was used to generate a set of theoretical structure factors from the electron density function, obtained by single-point calculation of the non-optimized experimental geometry. Based on the calculated structural amplitudes, using the MoPro program,[S8] the populations of the spherically symmetric valence shell (P_{val}) and the multipole parameters (P_{lm}) describing its deformation were obtained together with the corresponding expansion – contraction coefficients (k, k') for each atoms of complexes **1** and **2**. The obtained values of P_{val}, P_{lm}, k, and k' were used (but they were not refined themselves) to refine the coordinates and thermal parameters of atoms by experimental reflections ($\sin\theta/\lambda$ = 0.7 $Å^{-1}$) in real symmetry of complexes. The expansion – contraction coefficients (k, k') for hydrogen atoms were equal 1.2.

2. Density functional theory studies.

Full structure optimizations of complexes **1** and **2** were carried out at the same level of PBE0/DZP with the Gaussian 09 program package.[S9] Complexes **1** and **2** including five Cu(II) ions were treated as a high-spin sextet systems with a neutral charge, no water molecules being involved in the optimizations. Topological analysis of the electron density and computation of the atomic charges were realized with the Bader's theory as it implemented in the AIMAll program.[S10] Wavefunctions obtained for the DFT optimized structures of complexes **1** and **2** were employed for corresponding AIMAll calculations.

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Table S1. The main crystallographic data and structure refinement details for complexes **1** and **2.**

Compound	**1**	**2**
Empirical formula	$C_{23}H_{68}CaCu_5N_{10}O_{31}$	$C_{19}H_{64}CaCu_5N_{10}O_{30}$
Formula weight	1338.65	1270.58
Temperature [K]	100(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions		
a[Å]	15.5141(15)	15.5261(3)
b[Å]	16.7298(16)	16.5887(3)
c[Å]	19.3080(19)	18.0577(4)
Volume [Å^3]	5011.3(8)	4650.90(16)
Z	4	4
Calculated density [Mg/m^3]	1.774	1.815
Absorption coefficient [mm^{-1}]	2.291	2.461
Crystal size [mm^3]	0.27 × 0.10 × 0.08	0.46 × 0.10 × 0.09
F(000)	2756	2612
θ [°]	2.435–29.130	2.884–29.131
Reflections collected / unique	45084/13428	82344/12493
R_{int}	0.0989	0.0784
R_1, wR_2 [$I > 2\sigma(I)$]	0.0645 0.1277	0.0353 0.0787
R_1, wR_2 (all data)	0.1197 0.1448	0.045 0.0840
S	1.032	1.047
Absolute structure parameter	0.031(6)	-0.017(5)
Largest diff. peak and hole [e/Å^3]	1.972/–1.016	0.715/–0.626

Table S2. Selected distances (Å) and angles (deg) in **1** and **2**.

Distances [Å] and angles [°]	**1**	**2**
Ca(1)-O(oxime)	2.413(6) – 2.491(6)	2.426(3) – 2.546(3)
Ca(1)-O(acid)	2.308(7)	2.349(3)
Ca(1)-O(H_2O)	2.371(7)	2.363(3)
Cu-O(oxime)	1.901(7) – 1.930(6)	1.907(3) – 1.945(3)
Cu-O(carbonyl)	1.920(6) – 1.946(6)	1.928(3) – 1.960(3)
Cu-O(H_2O)	2.539(10) – 2.598(8)	2.375(4) – 2.715(4)
Cu-N(imine)	1.893(8) – 1.910(8)	1.890(4) – 1.923(4)
Cu-N(amine)	1.993(8) – 2.011(7)	1.999(4) – 2.007(4)
O(12)-C(16)	1.269(11)	1.270(6)
O(13)-C(16)	1.241(11)	1.257(6)
O(14)-C(23)/C(19)	1.251(11)	1.246(6)
O(15)-C(23)/C(19)	1.250(11)	1.285(6)
O(oxime)-Cu-O(carbonyl)	84.3(3) – 85.7(3)	84.63(13) – 85.71(14)
O(oxime)-Cu-N(imine)	90.2(3) – 93.6(3)	91.54(15) – 92.73(15)
O(oxime)-Cu-N(amine)	168.5(3) – 174.1(3)	169.01(16) – 175.12(16)
O(carbonyl)-Cu-N(imine)	168.3(3) – 176.7(3)	167.79(16) – 177.10(16)
O(carbonyl)-Cu-N(amine)	99.3(3) – 101.9(3)	97.46(15) – 99.92(16)
N(imine)-Cu-N(amine)	82.3(3) – 82.8(3)	82.68(17) – 83.44(17)
O(oxime)-Ca(1)-O(oxime)	69.4(2) – 73.4(2); 141.9(2) – 146.0(2)	71.28(11) – 72.25(11); 140.10(11) – 143.75(11)
O(oxime)-Ca(1)-O(acid)	84.9(2) – 99.9(2)	88.91(12) – 109.98(12)
O(oxime)-Ca(1)-O(H_2O)	83.7(2) – 90.4(2)	78.22(11) – 89.34(12)
O(acid)-Ca(1)-O(H_2O)	169.4(3)	166.35(13)

Table S3. Geometrical characteristics corresponding to C-H···O, N-H···O, O-H···O, N-H···N and O-H···N interactions in crystals of complexes **1** and **2**.

1				
D-H…A	D-H [Å]	H…A [Å]	D…A [Å]	∠(DHA) [°]
N(2)-H(2A)…O(13S)	0.91	2.39	3.044(14)	128.6
N(2)-H(2B)…O(5S)_$1*	0.91	2.16	3.068(11)	172.9
N(4)-H(4A)…O(9)_$2	0.91	2.15	3.010(10)	157.1
N(4)-H(4B)…O(8S)_$2	0.91	2.32	3.061(11)	138.4
N(6)-H(6A)…O(15)_$3	0.91	2.08	2.971(10)	165.9
N(8)-H(8A)…O(3)_$4	0.91	2.22	3.056(11)	152.5
N(8)-H(8A)…N(3)_$4	0.91	2.56	3.194(12)	127.1
N(8)-H(8A)…O(11)_$4	0.91	2.54	3.099(10)	119.9
N(8)-H(8B)…O(2S)_$4	0.91	2.34	3.164(11)	150.6
N(10)-H(10A)…O(12S)	0.91	2.52	3.104(12)	122.3
N(10)-H(10B)…O(6S)_$5	0.91	2.25	3.071(12)	149.0
C(2)-H(2C)…O(13S)	1.00	2.59	3.107(14)	111.9
C(8)-H(8C)…O(3S)_$3	1.00	2.44	3.343(13)	150.2
C(9)-H(9A)…O(2S)_$6	0.98	2.63	3.436(14)	140.0
C(14)-H(14A)…O(15)_$7	1.00	2.51	3.231(11)	129.0
O(11)-H(11C)…O(8S)	0.96(1)	2.07(5)	2.864(11)	139(6)
O(16)-H(16A)…O(13S)_$1	0.96(1)	2.32(8)	2.932(15)	121(6)
O(16)-H(16B)…O(12S)_$1	0.96(1)	2.11(8)	2.862(14)	134(9)
O(17)-H(17A)…O(14)_$3	0.96(1)	1.77(2)	2.722(9)	172(7)
O(17)-H(17B)…O(4)_$4	0.96(1)	1.97(2)	2.909(8)	167(6)
O(18)-H(18B)…O(13)	0.96(1)	2.11(2)	2.710(10)	119(2)
O(18)-H(18C)…O(10S)	0.96(1)	2.19(3)	2.933(12)	133(3)
O(1S)-H(1S1)…O(17)	0.96(1)	1.84(3)	2.705(9)	149(5)
O(1S)-H(1S2)…O(2S)	0.96(1)	1.88(4)	2.739(11)	148(6)
O(2S)-H(2S2)…O(18)_$2	0.96(1)	1.99(3)	2.763(10)	136(4)
O(3S)-H(3S1)…O(15)	0.96(1)	1.74(3)	2.669(10)	163(8)
O(3S)-H(3S2)…O(8S)_$1	0.96(1)	1.92(7)	2.629(11)	128(7)
O(4S)-H(4S1)…O(6)_$4	0.96(1)	1.91(3)	2.779(10)	149(4)
O(4S)-H(4S2)…O(6S)	0.96(1)	2.22(4)	2.804(12)	118(3)
O(5S)-H(5S1)…O(14)_$8	0.96(1)	1.84(2)	2.778(10)	164(5)
O(5S)-H(5S2)…O(7S)_$9	0.96(1)	1.86(2)	2.783(12)	161(2)
O(6S)-H(6S1)…O(5S)	0.96(1)	1.95(4)	2.842(12)	154(8)
O(6S)-H(6S2)…O(2)_$8	0.96(1)	1.88(2)	2.808(10)	161(6)
O(8S)-H(8S1)…O(4S)	0.96(1)	1.86(3)	2.754(11)	155(6)
O(8S)-H(8S2)…O(9S)	0.96(1)	1.76(2)	2.683(12)	161(6)
O(9S)-H(9S1)…O(1)	0.96(1)	2.12(6)	2.945(12)	144(9)
O(9S)-H(9S1)…N(1)	0.96(1)	2.12(5)	2.991(13)	150(8)
O(9S)-H(9S2)…O(13S)	0.96(1)	1.87(2)	2.803(13)	162(6)
O(10S)-H(102)…O(8)_$10	0.96(1)	1.98(2)	2.895(10)	159(4)
O(11S)-H(111)…O(10S)	0.96(1)	2.21(2)	2.839(12)	122(2)
O(12S)-H(121)…O(4S)	0.96(1)	2.31(3)	2.807(12)	112(2)
O(12S)-H(122)…O(9S)	0.96(1)	2.08(4)	2.868(13)	139(5)
O(13S)-H(131)…O(12)_$11	0.96(1)	2.35(5)	2.911(12)	117(4)

2				
N(2)-H(2A)...O(9S)	0.91	2.13	3.011(6)	164.2
N(2)-H(2B)...O(14)	0.91	2.10	2.967(5)	159.3
N(4)-H(4A)...O(6S)_$1**	0.91	2.09	2.950(5)	156.4
N(4)-H(4B)...O(7S)_$2	0.91	2.16	3.045(6)	165.5
N(6)-H(6A)...O(1)_$1	0.91	2.19	2.982(5)	145.3
N(6)-H(6A)...O(11)_$1	0.91	2.64	3.157(5)	117.1
N(6)-H(6B)...O(14)_$3	0.91	2.04	2.949(5)	177.5
N(8)-H(8A)...O(8S)_$4	0.91	2.10	3.008(6)	177.9
N(8)-H(8B)...O(5S)_$4	0.91	2.18	3.015(6)	153.0
N(10)-H(10A)...O(5)_$5	0.91	2.36	3.110(6)	140.1
N(10)-H(10A)...O(11)_$5	0.91	2.38	3.062(5)	131.7
C(8)-H(8C)...O(9)_$1	1.00	2.60	3.444(6)	142.0
C(8)-H(8C)...O(11)_$1	1.00	2.49	3.126(6)	121.3
C(9)-H(9C)...O(4)_$3	0.98	2.60	3.537(6)	160.3
C(12)-H(12A)...O(3S)_$6	0.98	2.57	3.501(7)	157.8
C(12)-H(12A)...O(12S)_$6	0.98	2.64	3.423(9)	136.6
O(11)-H(11B)...O(4S)	0.96(1)	1.90(2)	2.765(5)	150(4)
O(11)-H(11C)...O(1S)	0.96(1)	1.82(2)	2.728(5)	158(5)
O(16)-H(16A)...O(9S)	0.96(1)	2.04(4)	2.790(6)	134(5)
O(16)-H(16B)...O(15)_$7	0.96(1)	1.84(2)	2.783(5)	166(5)
O(17)-H(17A)...O(12)	0.96(1)	1.93(2)	2.877(5)	170(4)
O(17)-H(17B)...O(2S)_$3	0.96(1)	1.98(3)	2.831(5)	147(5)
O(18)-H(18A)...O(8S)_$4	0.96(1)	2.00(2)	2.883(6)	153(4)
O(18)-H(18B)...O(6)_$5	0.96(1)	1.93(2)	2.878(5)	172(5)
O(1S)-H(1SA)...O(11S)_$1	0.96(1)	1.88(2)	2.798(6)	158(4)
O(1S)-H(1SB)...O(18)	0.96(1)	1.83(2)	2.780(5)	169(4)
O(2S)-H(2SA)...O(4)	0.96(1)	1.86(3)	2.740(5)	151(5)
O(2S)-H(2SB)...O(10S)_$8	0.96(1)	1.87(2)	2.805(5)	165(5)
O(3S)-H(3SA)...O(12S)	0.96(1)	1.98(4)	2.777(7)	139(5)
O(3S)-H(3SB)...O(4S)	0.96(1)	1.92(2)	2.880(6)	174(6)
O(4S)-H(4SA)...O(15)_$7	0.96(1)	1.98(2)	2.896(5)	160(5)
O(4S)-H(4SB)...O(3)	0.96(1)	1.84(2)	2.762(5)	160(5)
O(4S)-H(4SB)...N(3)	0.96(1)	2.42(3)	3.286(5)	150(4)
O(5S)-H(5SA)...O(6S)_$9	0.96(1)	1.84(2)	2.781(5)	167(6)
O(5S)-H(5SB)...O(15)	0.96(1)	1.85(2)	2.772(5)	161(5)
O(6S)-H(6SA)...O(3S)_$5	0.96(1)	1.95(3)	2.807(6)	147(5)
O(6S)-H(6SB)...O(8)	0.96(1)	1.80(2)	2.742(5)	166(4)
O(7S)-H(7SA)...O(13)	0.96(1)	1.99(2)	2.869(6)	151(4)
O(7S)-H(7SB)...O(10S)	0.96(1)	2.42(4)	2.898(6)	111(3)
O(8S)-H(8SA)...O(13)	0.96(1)	1.83(3)	2.729(6)	153(6)
O(8S)-H(8SB)...O(11S)	0.96(1)	1.99(3)	2.890(7)	156(6)
O(9S)-H(9SB)...O(10S)_$8	0.96(1)	1.91(2)	2.856(6)	167(4)
O(10S)-H(10C)...O(7S)	0.96(1)	2.17(3)	2.898(6)	132(4)
O(10S)-H(10D)...O(5S)_$4	0.96(1)	1.91(3)	2.750(6)	145(5)
O(11S)-H(11E)...O(9S)_$10	0.96(1)	1.84(3)	2.718(7)	151(6)
O(12S)-H(12D)...O(15)_$7	0.96(1)	2.09(3)	2.899(7)	141(4)
O(12S)-H(12E)...O(11S)_$7	0.96(1)	2.01(4)	2.912(9)	155(7)

* – Symmetry operations used to generate equivalent atoms in the complex **1**: ($1) -x+3/2, -y+1, z+1/2; ($2) -x+2, y-1/2, -z+3/2; ($3) x+1, y, z; ($4) -x+2, y+1/2, -z+3/2; ($5) x-1/2, -y+3/2, -z+1; ($6) -x+5/2, -y+1, z+1/2; ($7) -x+1, y+1/2, -z+3/2; ($8) x+1/2, -y+3/2, -z+1; ($9) x, y, z-1; ($10) x-1/2, -y+3/2, -z+2; ($11) -x+3/2, -y+1, z-1/2.

** – Symmetry operations used to generate equivalent atoms in the complex **2**: ($1) -x+1, y+1/2, -z+1/2; ($2) x+1/2, -y+3/2, -z+1; ($3) x-1/2, -y+3/2, -z+1; ($4) -x+1/2, -y+1, z-1/2; ($5) -x+1, y-1/2, -z+1/2; ($6) x-1, y, z; ($7) -x+3/2, -y+1, z-1/2; ($8) x+1, y, z; ($9) -x+1/2, -y+1, z+1/2; ($10) x-1/2, -y+1/2, -z+1.

Table S4. Selected topological characteristics of the electron density of some intra- and intermolecular interactions in **1** and **2**.

Bond	Distance Å	$\rho(r_{cp})$ a.u.	$\nabla^2\rho(r_{cp})$ a.u.	$h_e(r_{cp})$ a.u.	E,[a] kcal/mol
1					
Ca(1)-O(11)	2.371(7)	0.034	0.169	0.004	10.9
Ca(1)-O(12)	2.308(7)	0.040	0.197	0.003	13.7
Cu(1)-O(13)	3.391(8)	0.005	0.015	0.0008	0.7
Cu(2)-C(22)	3.493(11)	0.005	0.013	0.0006	0.6
O(1S)-H(11B)	1.79(2)	0.027	0.168	0.007	8.8
O(8S)-H(11C)	2.07(5)	0.014	0.076	0.004	3.5
2					
Ca(1)-O(11)	2.363(3)	0.034	0.176	0.004	11.0
Ca(1)-O(12)	2.349(3)	0.036	0.175	0.004	11.5
Cu(1)-O(13)	3.029(4)	0.009	0.027	0.001	1.4
O(1S)-H(11C)	1.82(2)	0.029	0.161	0.006	9.0
O(4S)-H(11B)	1.90(2)	0.022	0.126	0.006	6.4

[a] The energy of intermolecular interactions was calculated according to the EML correlation [E =313.76 ν(r), kcal/ mol].

Table S5. Topological characteristics of the electron density of the Cu-O(H_2O) interactions in **1** and **2**.

Bond	Distance Å	$\rho(\mathbf{r}_{cp})$ a.u.	$\nabla^2\rho(\mathbf{r}_{cp})$ a.u.	$h_e(\mathbf{r}_{cp})$ a.u.	E,[a] kcal/mol
1					
Cu(1)-O(13)	3.391(8)	0.005	0.015	0.0008	0.7
Cu(1)-O(12S)	2.957(9)	0.010	0.034	0.001	1.8
Cu(3)-O(16)	2.539(10)	0.020	0.082	0.002	4.9
Cu(4)-O(11S)	3.156(9)	0.007	0.021	0.001	1.0
Cu(4)-O(17)	2.592(7)	0.020	0.078	0.002	4.7
Cu(5)-O(18)	2.598(8)	0.019	0.076	0.002	4.5
2					
Cu(2)-O(16)	2.552(4)	0.021	0.085	0.002	5.2
Cu(3)-O(17)	2.375(4)	0.031	0.137	0.002	9.2
Cu(5)-O(18)	2.715(4)	0.016	0.056	0.002	3.2
Cu(5)-O(7S)	2.982(5)	0.010	0.030	0.001	1.5

[a] The energy of intermolecular interactions was calculated according to the EML correlation [E =313.76 $\nu(\mathbf{r})$, kcal/ mol].

Table S6. The main topological characteristics of the electron density in **1** and **2**[a].

Bond	Distance Å	$v(\mathbf{r}_{cp})$ a.u.	$\rho(\mathbf{r}_{cp})$ a.u.	$\nabla^2\rho(\mathbf{r}_{cp})$ a.u.	$h_e(\mathbf{r}_{cp})$ a.u.
1					
Ca(1)-O(1)	2.474(7) [2.439]	-0.023 [-0.030]	0.024 [0.027]	0.134 [0.167]	0.005 [0.006]
Ca(1)-O(3)	2.491(6) [2.492]	-0.021 [-0.025]	0.024 [0.024]	0.122 [0.145]	0.005 [0.006]
Ca(1)-O(5)	2.413(6) [2.516]	-0.028 [-0.023]	0.027 [0.022]	0.160 [0.135]	0.006 [0.006]
Ca(1)-O(7)	2.444(7) [2.524]	-0.025 [-0.022]	0.026 [0.022]	0.146 [0.133]	0.005 [0.005]
Ca(1)-O(9)	2.447(6) [2.539]	-0.025 [-0.022]	0.027 [0.022]	0.139 [0.129]	0.005 [0.005]
Cu(1)-O(1)	1.912(6) [1.917]	-0.150 [-0.160]	0.092 [0.095]	0.497 [0.554]	-0.013 [-0.011]
Cu(1)-O(2)	1.944(7) [1.940]	-0.140 [-0.146]	0.088 [0.088]	0.480 [0.518]	-0.010 [-0.008]
Cu(1)-N(9)	1.902(8) [1.942]	-0.185 [-0.153]	0.110 [0.097]	0.479 [0.485]	-0.033 [-0.016]
Cu(1)-N(10)	2.005(8) [2.033]	-0.133 [-0.112]	0.090 [0.079]	0.366 [0.375]	-0.021 [-0.009]
O(1)-N(1)	1.383(9) [1.371]	-0.845 [-0.502]	0.312 [0.336]	**0.261**[b] **[-0.394]**	-0.390 [-0.300]
O(2)-C(1)	1.306(11) [1.284]	-0.915 [-0.980]	0.350 [0.340]	**-0.990 [-0.195]**	-0.581 [-0.514]
N(1)-C(1)	1.279(12) [1.311]	-1.060 [-0.908]	0.384 [0.352]	**-1.230 [-0.633]**	-0.684 [-0.533]
N(9)-C(13)	1.284(11) [1.300]	-1.034 [-0.956]	0.379 [0.359]	**-1.288 [-0.588]**	-0.678 [-0.551]
N(10)-C(14)	1.492(12) [1.471]	-1.141 [-0.404]	**0.409 [0.257]**	**-1.850 [-0.651]**	-0.802 [-0.283]
C(13)-C(14)	1.525(12) [1.520]	-0.545 [-0.283]	0.254 [0.256]	**-0.493 [-0.677]**	-0.334 [-0.226]
2					
Ca(1)-O(1)	2.459(3) [2.505][a]	-0.025 [-0.024]	0.027 [0.024]	0.133 [0.140]	0.004 [0.005]
Ca(1)-O(3)	2.546(3) [2.465]	-0.019 [-0.027]	0.022 [0.026]	0.111 [0.156]	0.004 [0.006]
Ca(1)-O(5)	2.426(3) [2.551]	-0.027 [-0.020]	0.028 [0.021]	0.152 [0.124]	0.005 [0.005]
Ca(1)-O(7)	2.462(3) [2.543]	-0.024 [-0.021]	0.025 [0.022]	0.143 [0.128]	0.006 [0.005]

Ca(1)-O(9)	2.426(3) [2.470]	-0.027 [-0.027]	0.027 [0.026]	0.155 [0.154]	0.006 [0.006]
Cu(1)-O(1)	1.917(3) [1.942]	-0.155 [-0.147]	0.095 [0.089]	0.505 [0.520]	-0.014 [-0.009]
Cu(1)-O(2)	1.938(3) [1.935]	-0.140 [-0.148]	0.088 [0.089]	0.475 [0.524]	-0.010 [-0.009]
Cu(1)-N(9)	1.893(4) [1.909]	-0.192 [-0.170]	0.113 [0.106]	0.475 [0.516]	-0.010 [-0.020]
Cu(1)-N(10)	2.004(4) [2.014]	-0.135 [-0.120]	0.090 [0.085]	0.372 [0.386]	-0.021 [-0.012]
O(1)-N(1)	1.389(5) 1.374	-0.807 [-0.496]	0.303 [0.335]	**0.259** **[-0.376]**	-0.371 [-0.295]
O(2)-C(1)	1.299(6) [1.281]	-0.893 [-0.994]	0.344 [0.343]	**-0.936** **[-0.186]**	-0.563 [-0.520]
N(1)-C(1)	1.290(6) [1.311]	-0.987 [-0.903]	0.366 [0.353]	**-1.082** **[-0.651]**	-0.628 [-0.533]
N(9)-C(13)	1.289(6) 1.308	-1.025 [-0.919]	0.376 [0.354]	**-1.199** **[-0.622]**	-0.663 [-0.537]
N(10)-C(14)	1.494(6) [1.473]	-0.516 [-0.399]	0.242 [0.257]	**-0.288** **[-0.648]**	-0.516 [-0.280]
C(13)-C(14)	1.512(6) [1.521]	-0.548 [-0.283]	0.255 [0.256]	**-0.487** **[-0.675]**	-0.335 [-0.226]

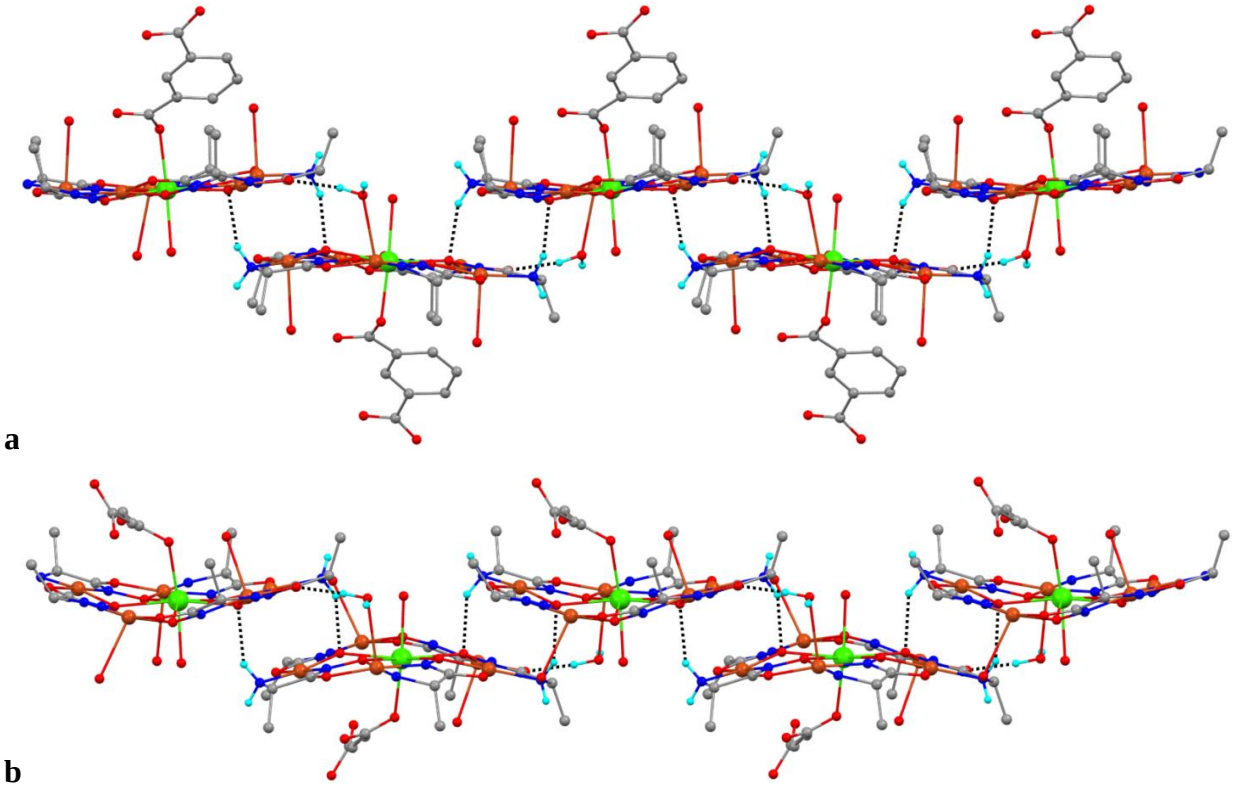
[a] Values of the experimental-theoretical electron density characteristics are given without brackets and theoretical values in square brackets.

[b] Differences in topological characteristics exceeding the transferability index are highlighted in bold.

Table S7. Populations of copper d–orbitals in complexes **1** and **2.**

d-orbitals	Experimental-theoretical	DFT	d-orbitals	Experimental-theoretical	DFT
1			2		
Cu(1)			Cu(1)		
d_{z^2}	2.16	1.96	d_{z^2}	2.13	1.97
d_{xz}	2.20	1.99	d_{xz}	2.20	1.96
d_{yz}	2.21	1.87	d_{yz}	2.19	1.98
$d_{x^2-y^2}$	1.87	1.57	$d_{x^2-y^2}$	1.84	1.99
d_{xy}	2.22	1.90	d_{xy}	2.22	1.41
Cu(2)			Cu(2)		
d_{z^2}	2.13	1.96	d_{z^2}	2.20	1.97
d_{xz}	2.20	1.99	d_{xz}	1.84	1.90
d_{yz}	2.19	1.99	d_{yz}	2.22	1.92
$d_{x^2-y^2}$	1.85	1.87	$d_{x^2-y^2}$	2.19	1.73
d_{xy}	2.21	1.49	d_{xy}	2.19	1.80
Cu(3)			Cu(3)		
d_{z^2}	2.20	1.97	d_{z^2}	2.21	1.96
d_{xz}	1.82	1.98	d_{xz}	1.83	1.99
d_{yz}	2.21	1.97	d_{yz}	2.22	1.91
$d_{x^2-y^2}$	2.19	1.97	$d_{x^2-y^2}$	2.19	1.47
d_{xy}	2.20	1.43	d_{xy}	2.20	1.98
Cu(4)			Cu(4)		
d_{z^2}	2.20	1.97	d_{z^2}	2.15	1.97
d_{xz}	1.83	1.99	d_{xz}	2.21	1.99
d_{yz}	2.20	1.97	d_{yz}	2.21	1.97
$d_{x^2-y^2}$	2.18	1.67	$d_{x^2-y^2}$	1.80	1.67
d_{xy}	2.19	1.72	d_{xy}	2.23	1.72
Cu(5)			Cu(5)		
d_{z^2}	2.16	1.97	d_{z^2}	2.17	1.97
d_{xz}	2.21	1.91	d_{xz}	2.21	1.91
d_{yz}	2.19	1.97	d_{yz}	2.20	1.97
$d_{x^2-y^2}$	1.77	1.48	$d_{x^2-y^2}$	1.84	1.48
d_{xy}	2.21	1.98	d_{xy}	2.21	1.98

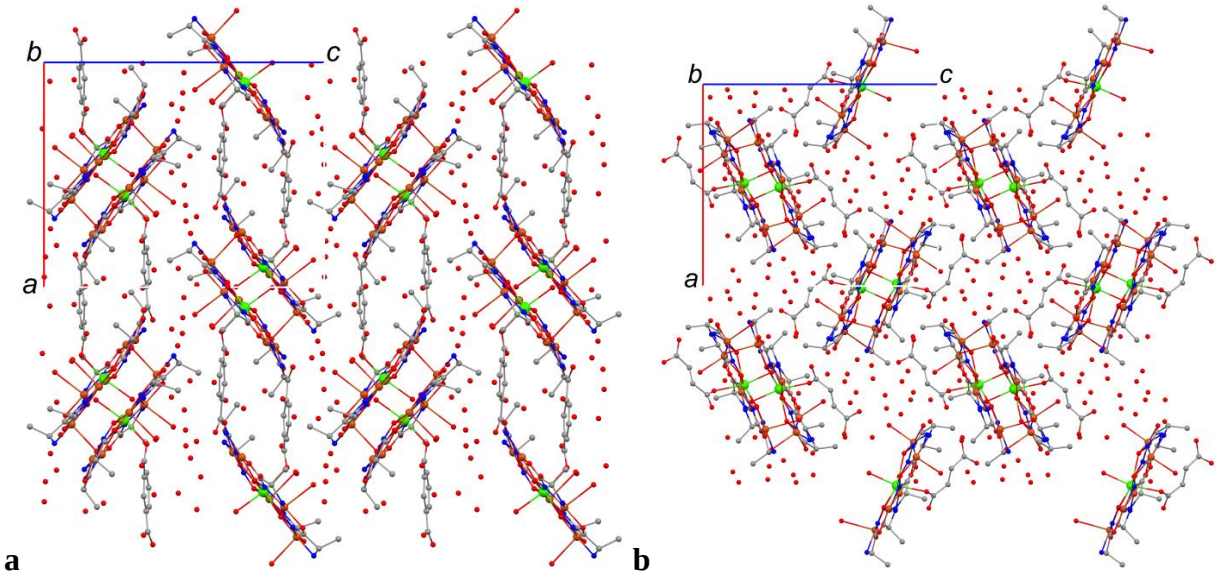
Figure S1. Fragments of molecular chains in crystals of complexes **1** (a) and **2** (b). Uncoordinated water molecules and some hydrogen atoms are not shown for clarity.



a

b

Figure S2. Crystal packing of complexes **1 (a)** and **2 (b).** View along the crystallographic *b*-axis. Hydrogen atoms are not shown for clarity.



a **b**

Figure S3. Section of the deformation electron density (contour ±0.05 e/Å^3) in the Ca(1)O(1)O(3) (**a**) plane in **1**. Sections of the deformation electron density (contour ±0.05 e/Å^3) in the Ca(1)O(1)O(3) (**b**) and Ca(1)O(7)O(9) (**c**) planes in **2**. Due to the fact that 15-MC-5 in **2** is less flat than in **1**, two cross-sections are shown (**b**, **c**).

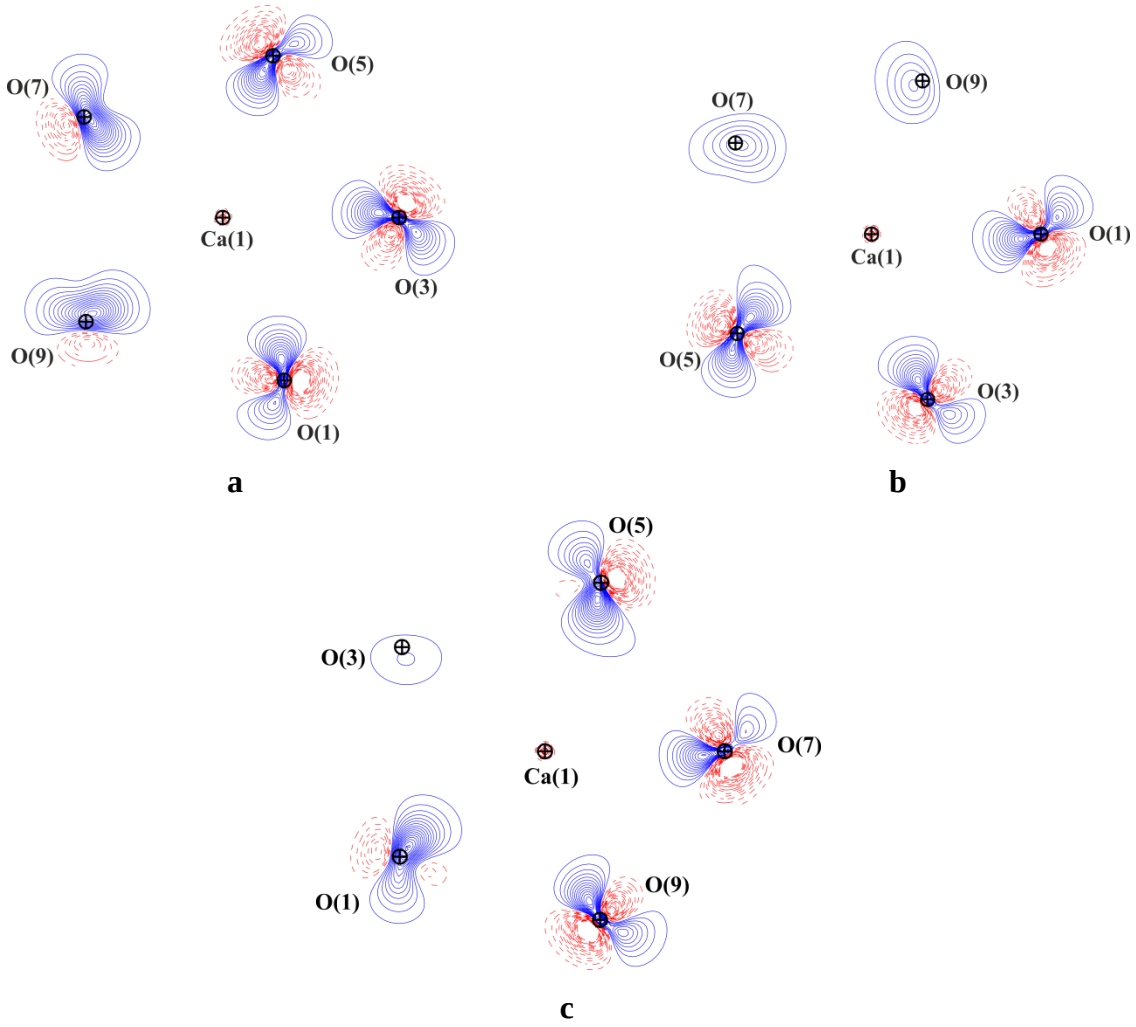


Figure S4. Experimental-theoretical molecular graph of **1** and **2**. Three water molecules are presented. The remaining water molecules and hydrogen atoms are omitted for clarity. Critical points (3,-1) are highlighted in blue.

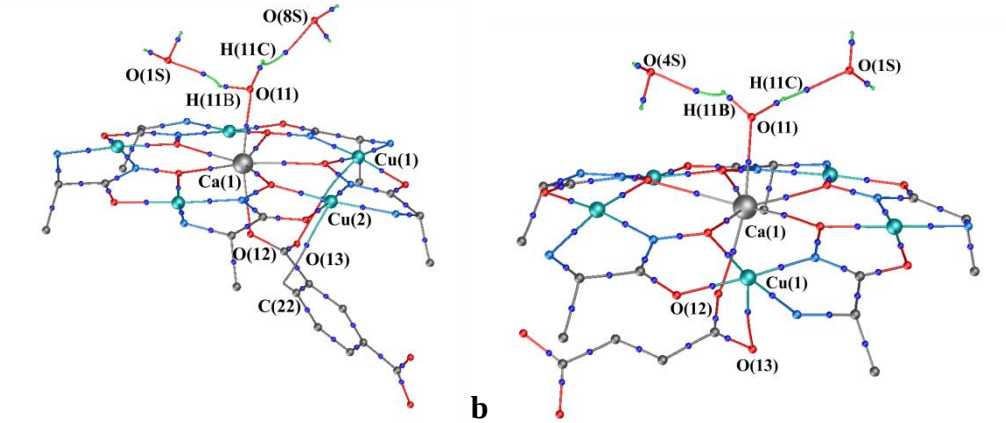


Figure S5. Experimental-theoretical molecular graph of **1** and **2**. The oxygen atoms of water molecules coordinated on metal atoms are presented. The remaining water molecules and hydrogen atoms are omitted for clarity. Critical points (3,-1) are highlighted in blue.

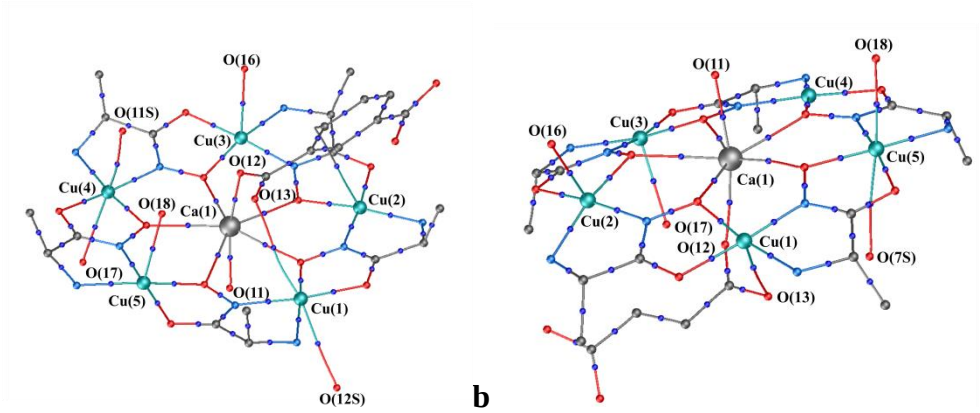


Figure S6. The theoretical molecular structures of complexes **1** (**a**, **c**) and **2** (**b**, **d**). The top view are shown in Figs. **a** and **b** and the side view are shown in Figs. **c** and **d**. The hydrogen atoms are omitted for clarity.

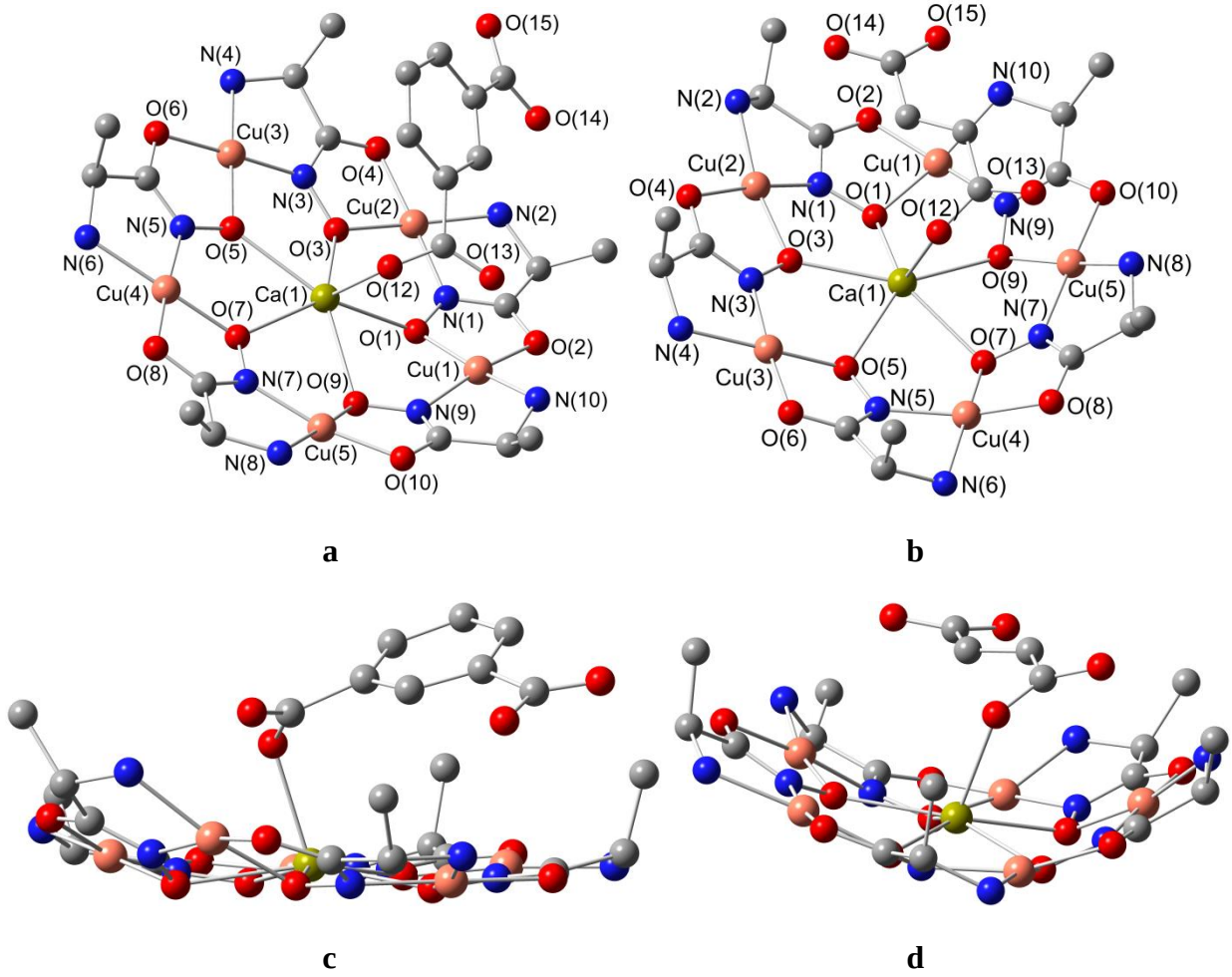
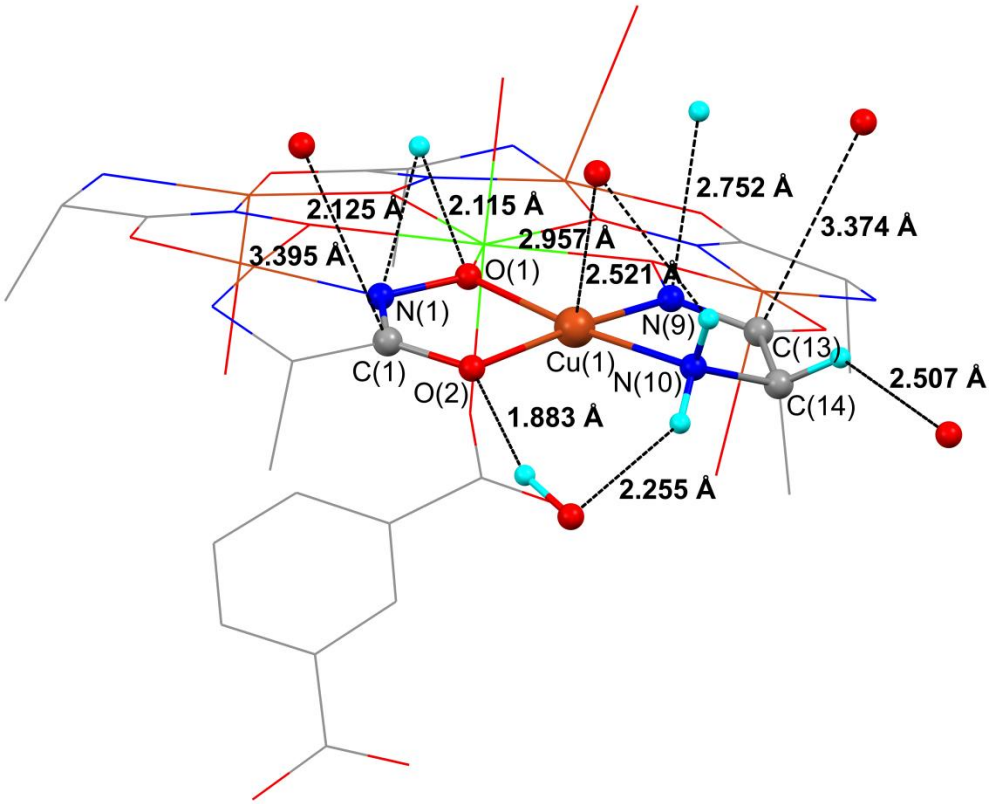
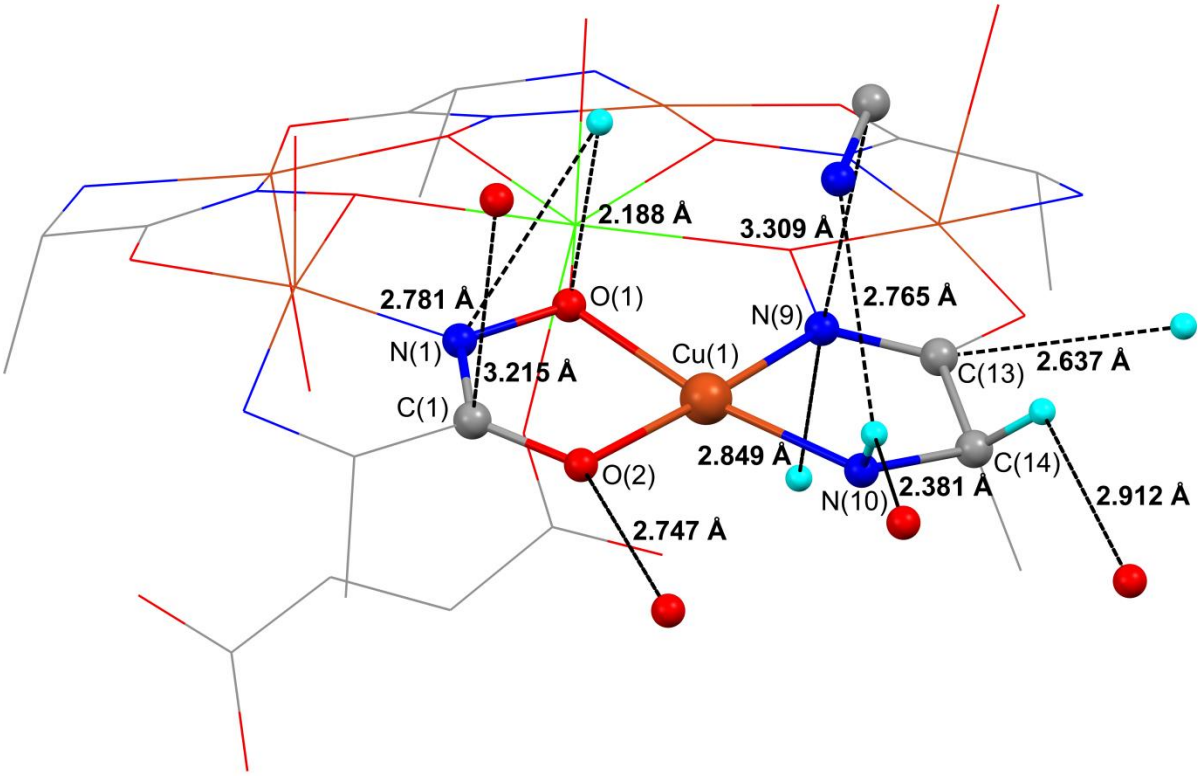


Figure S7. Intermolecular environment of the O(1)N(1)C(1)O(2)Cu(1)N(9)C(13)C(14)N(10) fragment in crystal **1** (**a**) and **2** (**b**).



a



b