Supplementary Material (ESI) for Dalton Transactions

Supporting Information for the Full Paper entitled

"Experimental electron density study of a Cu-ciprofloxacin complex - the role of metal ions in the activity of quinolones."

by

Jacob Overgaard, Iztok Turel, and David E. Hibbs

Content of the ESI:

❖ Table S1: Highest peaks in residual density from XDFFT

	comments	x	y	z	peak height
Peak(1)	0.10 Å from S	-0.0255	0.6938	0.7626	0.41
Peak(2)		0.1052	0.1994	0.6640	0.41
Peak(3)		0.9731	0.3840	0.2608	0.38
Peak(4)		0.9449	0.2094	0.6680	0.37
Peak(5)		0.0365	0.2905	0.3702	0.35
Peak(6)	0.48 Å from O(12)	-0.0896	0.6075	1.1080	0.34
Peak(7)		0.0162	0.0775	0.7557	0.33
Peak(8)	0.57 Å from Cu	0.1577	0.5982	0.5206	0.32
Peak(9)	0.45 Å from O(7)	0.0148	0.7606	0.7430	0.31
Peak(10)	1.09 Å from Cu	0.2036	0.6126	0.4216	0.29
Hole(1)	0.43 Å from O(12)	-0.1421	0.6319	1.0757	-0.37
Hole(2)	0.80 Å from Cu	0.1477	0.5795	0.4999	-0.32
Hole(3)	0.38 Å from O(7)	0.0368	0.7723	0.7240	-0.31
Hole(4)	0.77 Å from Cu	0.2402	0.5981	0.4879	-0.29
Hole(5)	0.30 Å from S	-0.0271	0.6937	0.7918	-0.26
Hole(6)	0.69 Å from S	-0.0642	0.6630	0.7435	-0.25
Hole(7)	0.34 Å from O(5)	-0.1332	0.7200	0.7586	-0.24
Hole(8)	0.41 Å from H(8A)	0.0960	0.6677	0.3901	-0.23
Hole(9)		0.5849	0.4021	0.5771	-0.22
Hole(10)		0.7985	0.1605	0.1625	-0.22

❖ Table S2: Bond distances (in Å)

Bond	Distance
Cu-O(1)	1.9128(3)
Cu-O(3)	1.9393(3)
Cu-O(8)	1.9794(3)
Cu-O(9)	1.9988(3)
Cu-O(10)	2.1692(3)
S-O(4)	1.4853(3)
S-O(5)	1.4717(3)
S-O(6)	1.4739(4)
S-O(7)	1.4826(4)
F-C(7)	1.3528(5)
O(1)-C(31)	1.2799(4)
O(2)-C(31)	1.2459(4)
O(3)-C(4)	1.2745(4)
N(1)-C(2)	1.3386(3)
N(1)-C(10)	1.3912(4)
N(1)-C(11)	1.4520(4)
N(81)-C(8)	1.3882(3)
N(81)-C(82)	1.4716(4)
N(81)-C(86)	1.4675(4)
N(84)-C(83)	1.4879(4)
N(84)-C(85)	1.4937(4)
C(2)-C(3)	1.3822(4)
C(3)-C(4)	1.4270(4)
C(3)-C(31)	1.5011(3)
C(4)-C(5)	1.4515(3)
C(5)-C(6)	1.4119(4)
C(5)-C(10)	1.4065(3)
C(6)-C(7)	1.3698(3)
C(7)-C(8)	1.4263(4)
C(8)-C(9)	1.3967(4)
C(9)-C(10)	1.4046(3)
C(11)-C(12)	1.5031(5)
C(11)-C(13)	1.4978(5)
C(12)-C(13)	1.5083(5)
C(82)-C(83)	1.5163(4)
C(85)-C(86)	1.5181(4)

❖ Table S3: Full Topological analysis

Table S2 Topological analysis of all covalent bonds not involving Cu. Units of distance are Å, angles in degrees, ρ in eÅ^{-3} and $\nabla^2\rho$ as well as individual λ_i in eÅ^{-5}.

Bond	$\rho_b(r)$	$\nabla^2\rho(r)$	d_{1-2}	d_{1-bcp}	λ_1	λ_2	λ_3	ε
S-O(4)	2.29(3)	-6.8(1)	1.486	0.603	-14.25	-12.70	20.17	0.12
S-O(5)	2.12(3)	-3.7(1)	1.474	0.608	-13.36	-11.89	21.58	0.12
S-O(6)	2.28(3)	-4.3(1)	1.474	0.598	-14.92	-12.97	23.54	0.15
S-O(7)	1.92(4)	-0.7(1)	1.483	0.622	-10.80	-10.38	20.48	0.04
F-C(7)	1.92(2)	-12.85(8)	1.353	0.825	-15.40	-14.36	16.92	0.07
O(1)-C(31)	2.53(2)	-28.1(1)	1.281	0.801	-22.71	-20.70	15.35	0.10
O(2)-C(31)	2.85(2)	-30.9(1)	1.246	0.799	-27.44	-24.15	20.72	0.14
O(3)-C(4)	2.52(2)	-25.9(1)	1.275	0.809	-22.45	-20.05	16.58	0.12
N(1)-C(2)	2.39(2)	-23.71(8)	1.339	0.805	-19.66	-16.63	12.58	0.18
N(1)-C(10)	2.14(2)	-16.69(6)	1.391	0.815	-16.89	-14.49	14.68	0.17
N(1)-C(11)	1.76(2)	-10.19(5)	1.452	0.842	-12.70	-11.70	14.21	0.09
N(81)-C(8)	2.21(2)	-15.50(5)	1.389	0.767	-17.90	-15.18	17.58	0.18
N(81)-C(82)	1.84(2)	-9.50(4)	1.472	0.828	-13.18	-12.54	16.22	0.05
N(81)-C(86)	1.74(2)	-8.92(4)	1.468	0.829	-12.36	-11.77	15.22	0.05
N(84)-C(83)	1.64(2)	-7.93(5)	1.488	0.850	-11.42	-10.92	14.42	0.05
N(84)-C(85)	1.71(2)	-8.59(5)	1.494	0.858	-11.88	-11.63	14.93	0.02
C(2)-C(3)	2.21(2)	-18.45(4)	1.383	0.723	-17.25	-13.91	12.71	0.24
C(3)-C(4)	2.06(1)	-16.48(3)	1.427	0.706	-16.24	-13.33	13.09	0.22
C(3)-C(31)	1.79(1)	-12.24(3)	1.501	0.752	-13.54	-11.75	13.06	0.15
C(4)-C(5)	1.98(1)	-14.81(3)	1.452	0.741	-15.46	-12.65	13.29	0.22
C(5)-C(6)	2.11(2)	-16.72(4)	1.412	0.707	-16.41	-13.63	13.32	0.20
C(5)-C(10)	2.12(1)	-16.59(4)	1.407	0.695	-16.26	-13.54	13.20	0.20
C(6)-C(7)	2.31(2)	-20.99(4)	1.370	0.660	-19.00	-14.52	12.52	0.31
C(7)-C(8)	2.05(1)	-16.66(3)	1.427	0.726	-16.56	-12.97	12.87	0.28
C(8)-C(9)	2.25(2)	-18.78(4)	1.397	0.699	-17.91	-14.33	13.47	0.25
C(9)-C(10)	2.16(1)	-17.17(4)	1.405	0.683	-16.84	-13.75	13.42	0.22
C(11)-C(12)	1.63(2)	-5.07(3)	1.504	0.764	-12.14	-5.96	13.03	1.04
C(11)-C(13)	1.61(2)	-4.70(3)	1.498	0.769	-12.05	-5.62	12.97	1.14
C(12)-C(13)	1.68(2)	-6.27(3)	1.508	0.752	-12.52	-6.88	13.14	0.82
C(82)-C(83)	1.67(1)	-9.68(3)	1.517	0.756	-11.32	-11.07	12.70	0.02
C(85)-C(86)	1.69(1)	-10.59(3)	1.518	0.759	-11.92	-11.25	12.58	0.06

❖ Table S4: Final parameter list - xd.res file

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LIMITS nat  2000 ntx  31 lmx  4 nzz  30 nto  0 nsc  20 ntb  20 nov   5000
USAGE    63   4 4   7   0   1   0   1   7   2   936   1  15  0
 0.018649  0.020852  0.018649  0.020852  0.013943  0.027724  1.480004 0.455E+05
-2.000000  0.000000  0.000000  0.000000  0.000000  0.333300
Cu       1 2    4   1   6 4  1  1 4  1    0  0.196062  0.598536  0.523326 1.0000
 0.006786  0.010091  0.008228  0.000299 -0.000862  0.000124
      0.000000      0.000000      0.000000      0.000000      0.000000
      0.000000      0.000000      0.000000      0.000000      0.000000
      0.244139      0.044478      0.157697      0.000000      0.000000
      0.000000      0.000000      0.000000      0.000000      0.046341
      0.000000      0.080860      0.000000      0.000000      0.000000
 9.6883  0.0000 -0.0510 -0.0242  0.0205  0.1879  0.2417 -0.0643  0.1495 -0.1301
 0.0033 -0.0129 -0.0098  0.0324 -0.0104 -0.0133 -0.0125  0.0163 -0.0065  0.0618
-0.0308 -0.1236 -0.0830  0.0444 -0.3066 -0.0040
S        1 2   11   2  12 2  2  2 4  1    0 -0.026663  0.687604  0.764267 1.0000
 0.007694  0.010830  0.008937  0.001064 -0.000470  0.000083
 5.7289  0.0000 -0.0237  0.0755 -0.1344 -0.0274  0.0203  0.1722 -0.0937  0.0167
-0.0128 -0.3797 -0.4696  0.0309 -0.0133  0.4641 -0.0678  0.0684  0.0752  0.0325
-0.0734  0.1500  0.0208 -0.0016  0.0600  0.1536
F        3 2   24   3  23 2  3  3 4  1    0  0.521721  0.392609  0.897001 1.0000
 0.012455  0.019276  0.016661 -0.002691 -0.002137  0.009633
 7.4133  0.0000 -0.0384 -0.0055 -0.0118 -0.0707  0.0510  0.0249  0.0104  0.0338
 0.0215  0.0135 -0.0005  0.0346 -0.0017 -0.0071  0.0121  0.0000  0.0000  0.0000
O(1)     1 2   31   4   1 2  4  4 4  1    0  0.248513  0.652039  0.376667 1.0000
 0.007762  0.018076  0.009564 -0.000215 -0.000774  0.002376
 6.5990  0.0000 -0.0601  0.0358 -0.0148 -0.0407 -0.0107  0.0232 -0.0762 -0.0149
 0.0058 -0.0096 -0.0043 -0.0018 -0.0285  0.0797 -0.0110  0.0000  0.0000  0.0000
O(2)     1 2   31   5   4 2  4  4 4  1    0  0.352356  0.737621  0.291023 1.0000
 0.011212  0.020405  0.015321 -0.001335 -0.002095  0.008734
 6.6001  0.0000  0.0041  0.0075 -0.0051 -0.0561 -0.0385  0.0135 -0.0225 -0.0168
 0.0171 -0.0022 -0.0193 -0.0122  0.0035  0.0475 -0.0119  0.0000  0.0000  0.0000
O(3)     1 2   21   6   1 2  4  4 4  1    0  0.308690  0.546117  0.588038 1.0000
 0.006429  0.013872  0.014526 -0.000283 -0.000825  0.003910
 6.6660  0.0000 -0.0588 -0.0167  0.0180 -0.0169 -0.0093 -0.0742 -0.0476 -0.0029
 0.0022 -0.0152  0.0036  0.0060  0.0137  0.0666  0.0034  0.0000  0.0000  0.0000
O(8)     3 2    1   7  36 2  4  4 4  1    0  0.076173  0.623605  0.440337 1.0000
 0.008733  0.018655  0.012846  0.001310 -0.000954  0.003271
 6.5454  0.0000 -0.0019  0.0150  0.0191 -0.0089 -0.0335 -0.0016  0.0229  0.0030
 0.0782  0.0298  0.0192  0.0458 -0.0411  0.0178 -0.0516  0.0000  0.0000  0.0000
O(9)     3 2    1   8  38 2  4  4 4  1    0  0.133624  0.524279  0.652827 1.0000
 0.010158  0.013173  0.013425 -0.000370  0.000256  0.001850
 6.6074  0.0000 -0.0119  0.0005  0.0280  0.0183  0.0485  0.0335  0.0328  0.0225
 0.0893 -0.0133  0.0005  0.0096  0.0482  0.0111 -0.0789  0.0000  0.0000  0.0000
O(10)    3 2    1   9  41 2  4  4 4  1    0  0.204929  0.720137  0.638763 1.0000
 0.013886  0.013418  0.013210 -0.000952 -0.001584 -0.003296
 6.6910  0.0000 -0.0625 -0.0376  0.0069 -0.0080  0.0349 -0.0101  0.0453 -0.0392
 0.0732  0.0158  0.0053  0.0516 -0.0486  0.0124 -0.0263  0.0000  0.0000  0.0000
O(4)     3 2    2  10  37 2  4  4 4  1    0 -0.026638  0.624620  0.653058 1.0000
 0.013045  0.015294  0.013618  0.000057  0.000524 -0.004231
 6.3411  0.0000 -0.0103 -0.0155 -0.0808 -0.0744  0.0111 -0.0466  0.0029 -0.0322
-0.0142  0.0126  0.0149 -0.0007 -0.0144  0.0027 -0.0063  0.0000  0.0000  0.0000
O(5)     3 2    2  11  12 2  4  4 4  1    0 -0.114875  0.732233  0.767429 1.0000
 0.011612  0.017045  0.015493  0.005672 -0.000839  0.000173
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6.4310 0.0000 -0.0173 0.0671 -0.0776 -0.1113 -0.0061 -0.0220 -0.0387 0.0036
0.0040 0.0296 -0.0656 -0.0084 -0.0072 0.0330 0.0154 0.0000 0.0000 0.0000
O(6) 3 2 2 12 63 2 4 4 4 1 0 -0.008521 0.636670 0.884624 1.0000
0.016377 0.025938 0.012414 0.008495 0.000821 0.006525
6.3892 0.0000 -0.0179 -0.0028 -0.0925 -0.0687 0.0310 -0.0365 -0.0028 -0.0483
-0.0073 0.0115 -0.0133 0.0015 -0.0229 -0.0284 0.0165 0.0000 0.0000 0.0000
O(7) 3 2 2 13 40 2 4 4 4 1 0 0.044837 0.755811 0.749306 1.0000
0.016503 0.019389 0.021080 -0.007227 0.005273 -0.006237
6.4613 0.0000 -0.0799 0.0091 0.0225 -0.0900 0.0273 -0.0404 0.0496 -0.0154
-0.0475 0.0367 -0.0129 0.0262 -0.0867 -0.0401 0.0401 0.0000 0.0000 0.0000
O(11) 1 2 61 14 60 2 4 4 4 1 0 0.153181 0.362165 0.554924 1.0000
0.012991 0.015089 0.016676 -0.001809 -0.000326 -0.000326
6.5898 0.0000 -0.0258 -0.0183 0.0099 -0.0145 -0.0290 -0.0159 0.0224 -0.0343
0.0113 -0.0213 -0.0159 0.0115 0.0211 0.0720 -0.0176 0.0000 0.0000 0.0000
O(12) 1 2 62 15 63 2 4 4 4 1 0 -0.117084 0.620358 1.089271 1.0000
0.029451 0.017624 0.020486 -0.009260 0.009592 -0.007294
6.6335 0.0000 -0.0055 0.0741 -0.2727 0.0246 0.0000 -0.0078 0.0004 -0.0317
-0.1166 0.0026 0.0810 0.0190 -0.0175 0.0993 -0.0247 0.0000 0.0000 0.0000
N(1) 1 2 19 16 27 2 5 5 4 1 0 0.557168 0.656482 0.530772 1.0000
0.007140 0.011368 0.010662 -0.000859 -0.001176 0.002804
5.3854 0.0000 0.0048 0.0165 -0.0117 -0.0542 -0.0256 0.0181 0.0310 -0.0334
-0.0197 0.0054 0.0003 0.0105 0.0032 0.2471 0.0103 0.0000 0.0000 0.0000
N(81) 1 2 25 17 35 2 5 5 4 1 0 0.693081 0.469797 0.870884 1.0000
0.007747 0.014016 0.008555 0.000656 -0.001121 0.001788
5.3222 0.0000 -0.0192 -0.0248 0.0316 0.0306 0.0058 -0.0160 -0.0048 0.0399
0.0538 -0.0090 -0.0683 0.0349 -0.0775 0.1820 -0.0173 0.0000 0.0000 0.0000
N(84) 1 2 50 18 51 2 5 5 4 1 0 0.849773 0.442463 1.037301 1.0000
0.011338 0.012216 0.013238 0.001362 -0.004312 0.001009
5.4174 0.0000 0.0319 0.0592 -0.0271 -0.0208 0.0213 0.0408 0.0132 0.0126
0.0085 -0.1348 -0.1920 -0.0140 0.0206 0.1845 -0.0616 0.0000 0.0000 0.0000
C(2) 1 2 20 19 16 2 6 6 4 1 0 0.485296 0.681008 0.456614 1.0000
0.007939 0.012279 0.011086 -0.000486 -0.001249 0.002853
3.9745 0.0000 0.0791 -0.0366 -0.0075 -0.2258 -0.0130 0.0310 0.0335 0.0482
0.0059 0.0071 0.0216 -0.0108 0.0086 0.2794 0.0181 0.0000 0.0000 0.0000
C(3) 1 2 19 20 21 2 6 6 4 1 0 0.399367 0.647616 0.469116 1.0000
0.007377 0.011571 0.009930 0.000167 -0.001236 0.001708
4.0136 0.0000 0.0207 0.0316 0.0137 -0.1357 0.0044 -0.0336 -0.0277 0.0092
-0.0081 0.0245 0.0096 -0.0314 0.0073 0.2487 0.0172 0.0000 0.0000 0.0000
C(4) 1 2 6 21 20 2 6 6 4 1 0 0.384441 0.581658 0.565830 1.0000
0.006627 0.010699 0.009941 0.000340 -0.000818 0.001109
3.8160 0.0000 -0.0493 -0.0010 -0.0074 -0.2491 -0.0094 0.0391 -0.0288 0.0044
-0.0155 -0.0082 0.0061 -0.0026 0.0210 0.3152 0.0503 0.0000 0.0000 0.0000
C(5) 1 2 27 22 23 2 6 6 4 1 0 0.463193 0.553382 0.643234 1.0000
0.006666 0.010841 0.009267 0.000065 -0.000603 0.001420
4.0505 0.0000 0.0203 0.0006 -0.0065 -0.1591 -0.0026 -0.0396 -0.0179 -0.0286
0.0209 -0.0030 -0.0122 -0.0030 -0.0153 0.2616 -0.0154 0.0000 0.0000 0.0000
C(6) 1 2 43 23 24 2 6 6 4 1 0 0.456590 0.486296 0.738725 1.0000
0.007508 0.012589 0.010680 -0.000389 -0.000182 0.002558
3.9878 0.0000 -0.0190 0.0010 0.0133 -0.1798 0.0047 0.0465 -0.0221 0.0130
0.0189 -0.0121 0.0035 0.0142 -0.0022 0.2575 -0.0047 0.0000 0.0000 0.0000
C(7) 1 2 3 24 23 2 6 6 4 1 0 0.531232 0.460427 0.811706 1.0000
0.008072 0.012897 0.010703 -0.000386 -0.000599 0.003382
3.9078 0.0000 -0.1552 0.0405 0.0191 -0.1359 -0.0385 0.0010 -0.1172 -0.0279
0.0068 -0.0710 0.0223 0.0034 0.0087 0.3131 -0.0113 0.0000 0.0000 0.0000
C(8) 1 2 17 25 26 2 6 6 4 1 0 0.618046 0.499183 0.798216 1.0000
0.007499 0.011381 0.008770 0.000261 -0.000958 0.001233

4.0108 0.0000 -0.0214 0.0427 0.0318 -0.1808 0.0578 -0.0293 -0.0143 -0.0416
-0.0058 -0.0298 0.0276 0.0122 -0.0030 0.2889 0.0469 0.0000 0.0000 0.0000
C(9) 1 2 44 26 25 2 6 6 4 1 0 0.624031 0.564768 0.702528 1.0000
0.007414 0.011331 0.009936 -0.000250 -0.001367 0.001839
4.1192 0.0000 -0.0142 0.0325 -0.0178 -0.1732 0.0229 -0.0323 -0.0293 -0.0149
0.0078 -0.0076 -0.0103 -0.0065 -0.0086 0.2567 -0.0110 0.0000 0.0000 0.0000
C(10) 1 2 16 27 26 2 6 6 4 1 0 0.548441 0.591285 0.625646 1.0000
0.006880 0.010350 0.009174 -0.000238 -0.000966 0.001420
4.0015 0.0000 -0.1008 0.0016 -0.0104 -0.1857 0.0414 -0.0127 -0.0724 -0.0366
-0.0131 -0.0071 0.0041 0.0018 0.0141 0.2583 0.0025 0.0000 0.0000 0.0000
C(11) 1 2 45 28 16 2 6 6 4 1 0 0.645919 0.692867 0.509619 1.0000
0.008264 0.013993 0.014758 -0.001512 -0.000461 0.004251
4.0585 0.0000 0.1063 -0.0858 -0.0125 0.0637 -0.0115 -0.0042 0.0612 0.0761
-0.0191 -0.1220 -0.1841 -0.0098 0.0017 0.2349 -0.0269 0.0000 0.0000 0.0000
C(12) 1 2 28 29 30 2 6 6 4 1 0 0.682486 0.763231 0.601940 1.0000
0.015597 0.018289 0.020999 -0.005988 -0.005555 0.003188
3.9995 0.0000 -0.0135 -0.0092 -0.0224 0.0296 0.0180 0.0097 0.0196 0.0832
-0.0182 -0.2383 -0.1534 -0.0188 0.0040 -0.0156 -0.1280 0.0000 0.0000 0.0000
C(13) 1 2 29 30 28 2 6 6 4 1 0 0.655508 0.787910 0.464440 1.0000
0.014162 0.017502 0.023151 -0.004479 -0.003043 0.009404
3.9893 0.0000 -0.0173 -0.0173 -0.0114 0.0234 -0.0268 -0.0212 0.0805 0.0345
0.0388 -0.2400 -0.1200 0.0013 0.0196 0.0162 -0.0863 0.0000 0.0000 0.0000
C(31) 1 2 5 31 4 2 6 6 4 1 0 0.329074 0.681945 0.372914 1.0000
0.008145 0.013266 0.009556 0.000623 -0.000877 0.001863
3.7532 0.0000 0.0413 -0.0155 0.0086 -0.2700 -0.0443 -0.0090 0.0636 -0.0193
-0.0017 0.0268 0.0188 -0.0228 -0.0112 0.3191 0.0694 0.0000 0.0000 0.0000
C(82) 1 2 53 32 52 2 6 6 4 1 0 0.686720 0.463978 1.011926 1.0000
0.011016 0.016670 0.009208 0.001388 -0.000495 0.001322
3.9572 0.0000 0.0683 0.0394 0.0122 -0.0145 -0.0209 -0.0359 -0.0273 -0.0066
-0.0208 -0.1455 -0.2171 0.0118 -0.0053 0.1756 -0.0469 0.0000 0.0000 0.0000
C(83) 1 2 54 33 55 2 6 6 4 1 0 0.760989 0.405040 1.070763 1.0000
0.014080 0.013668 0.011997 -0.000510 -0.003048 0.003541
3.9229 0.0000 0.0746 0.0493 -0.0599 -0.0912 0.0546 0.0619 0.0411 -0.0196
0.0238 -0.1521 -0.2116 -0.0142 -0.0014 0.1972 -0.0583 0.0000 0.0000 0.0000
C(85) 1 2 57 34 56 2 6 6 4 1 0 0.856605 0.447492 0.894137 1.0000
0.009426 0.011392 0.014104 0.001992 -0.001476 -0.000297
3.8693 0.0000 0.0491 0.0854 0.0508 -0.0371 -0.0522 -0.0427 -0.0123 -0.0212
-0.0241 -0.1389 -0.2332 -0.0093 0.0186 0.1852 -0.0554 0.0000 0.0000 0.0000
C(86) 1 2 59 35 58 2 6 6 4 1 0 0.780846 0.504509 0.834740 1.0000
0.008357 0.011715 0.010734 0.000814 -0.001017 0.000984
3.9301 0.0000 0.0475 0.0480 0.0392 -0.0588 -0.0412 -0.0545 0.0607 -0.0094
-0.0055 -0.1669 -0.2294 0.0015 -0.0140 0.1551 -0.0820 0.0000 0.0000 0.0000
H(8A) 3 2 7 36 37 1 7 7 2 1 0 0.070577 0.670096 0.374829 1.0000
0.020737 0.000000 0.000000 0.000000 0.000000 0.000000
0.6832 0.0000 0.0000 0.0000 0.1461 0.0000 0.0000 0.0000 0.0000 0.0000
H(8B) 3 2 7 37 36 1 7 7 2 1 36 0.031678 0.637226 0.503121 1.0000
0.020517 0.000000 0.000000 0.000000 0.000000 0.000000
0.6832 0.0000 0.0000 0.0000 0.1461 0.0000 0.0000 0.0000 0.0000 0.0000
H(9A) 3 2 8 38 39 1 7 7 2 1 36 0.070420 0.539979 0.655610 1.0000
0.018118 0.000000 0.000000 0.000000 0.000000 0.000000
0.6832 0.0000 0.0000 0.0000 0.1461 0.0000 0.0000 0.0000 0.0000 0.0000
H(9B) 3 2 8 39 38 1 7 7 2 1 36 0.136275 0.462282 0.624186 1.0000
0.020366 0.000000 0.000000 0.000000 0.000000 0.000000
0.6832 0.0000 0.0000 0.0000 0.1461 0.0000 0.0000 0.0000 0.0000 0.0000
H(10A) 3 2 9 40 41 1 7 7 2 1 36 0.153475 0.732216 0.690405 1.0000
0.017562 0.000000 0.000000 0.000000 0.000000 0.000000

```
  0.6832  0.0000  0.0000  0.0000  0.1461  0.0000  0.0000  0.0000  0.0000  0.0000
H(10B)    3 2    9  41  40 1  7  7 2  1  36  0.256440  0.736814  0.694403 1.0000
  0.019100  0.000000  0.000000  0.000000  0.000000  0.000000
  0.6832  0.0000  0.0000  0.0000  0.1461  0.0000  0.0000  0.0000  0.0000  0.0000
H(2)      3 2   19  42  16 1  7  7 2  1   0  0.496381  0.730244  0.382000 1.0000
  0.027108  0.000000  0.000000  0.000000  0.000000  0.000000
  0.9021  0.0000  0.0000  0.0000  0.1810  0.0000  0.0000  0.0000  0.0000  0.0000
H(6)      3 2   23  43  24 1  7  7 2  1  42  0.392700  0.453382  0.752046 1.0000
  0.024866  0.000000  0.000000  0.000000  0.000000  0.000000
  0.9021  0.0000  0.0000  0.0000  0.1810  0.0000  0.0000  0.0000  0.0000  0.0000
H(9)      3 2   26  44  25 1  7  7 2  1  42  0.688213  0.596771  0.687977 1.0000
  0.024669  0.000000  0.000000  0.000000  0.000000  0.000000
  0.9021  0.0000  0.0000  0.0000  0.1810  0.0000  0.0000  0.0000  0.0000  0.0000
H(11)     3 2   28  45  16 1  7  7 2  1   0  0.693656  0.643362  0.474280 1.0000
  0.029287  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(12A)    3 2   29  46  47 1  7  7 2  1  45  0.754287  0.760621  0.630236 1.0000
  0.034567  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(12B)    3 2   29  47  46 1  7  7 2  1  45  0.636382  0.784151  0.675744 1.0000
  0.035895  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(13A)    3 2   30  48  49 1  7  7 2  1  45  0.594802  0.828903  0.448977 1.0000
  0.029447  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(13B)    3 2   30  49  48 1  7  7 2  1  45  0.709114  0.799179  0.397201 1.0000
  0.034461  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(84A)    3 2   18  50  51 1  7  7 2  1   0  0.901541  0.403362  1.077244 1.0000
  0.013715  0.000000  0.000000  0.000000  0.000000  0.000000
  0.5951  0.0000  0.0000  0.0000  0.1151  0.0000  0.0000  0.0000  0.0000  0.0000
H(84B)    3 2   18  51  50 1  7  7 2  1  50  0.858989  0.506363  1.075438 1.0000
  0.011281  0.000000  0.000000  0.000000  0.000000  0.000000
  0.5951  0.0000  0.0000  0.0000  0.1151  0.0000  0.0000  0.0000  0.0000  0.0000
H(82A)    3 2   32  52  53 1  7  7 2  1  45  0.621453  0.435950  1.035915 1.0000
  0.023644  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(82B)    3 2   32  53  52 1  7  7 2  1  45  0.692462  0.531649  1.053101 1.0000
  0.021974  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(83A)    3 2   33  54  55 1  7  7 2  1  45  0.757234  0.404446  1.176030 1.0000
  0.028288  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(83B)    3 2   33  55  54 1  7  7 2  1  45  0.756483  0.336799  1.031337 1.0000
  0.026514  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(85A)    3 2   34  56  57 1  7  7 2  1  45  0.852265  0.378557  0.857272 1.0000
  0.024331  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(85B)    3 2   34  57  56 1  7  7 2  1  45  0.921772  0.476826  0.872498 1.0000
  0.025925  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(86A)    3 2   35  58  59 1  7  7 2  1  45  0.789848  0.574530  0.865322 1.0000
  0.021247  0.000000  0.000000  0.000000  0.000000  0.000000
  0.8775  0.0000  0.0000  0.0000  0.1651  0.0000  0.0000  0.0000  0.0000  0.0000
H(86B)    3 2   35  59  58 1  7  7 2  1  45  0.784803  0.500835  0.729629 1.0000
```

0.020134 0.000000 0.000000 0.000000 0.000000 0.000000
0.8775 0.0000 0.0000 0.0000 0.1651 0.0000 0.0000 0.0000 0.0000 0.0000
H(11A) 3 2 14 60 61 1 7 7 2 1 36 0.135662 0.312053 0.608178 1.0000
0.019042 0.000000 0.000000 0.000000 0.000000 0.000000
0.6832 0.0000 0.0000 0.0000 0.1461 0.0000 0.0000 0.0000 0.0000 0.0000
H(11B) 3 2 14 61 60 1 7 7 2 1 36 0.116556 0.358845 0.475219 1.0000
0.018539 0.000000 0.000000 0.000000 0.000000 0.000000
0.6832 0.0000 0.0000 0.0000 0.1461 0.0000 0.0000 0.0000 0.0000 0.0000
H(12C) 3 2 15 62 63 1 7 7 2 1 36 -0.107543 0.663177 1.159146 1.0000
0.024376 0.000000 0.000000 0.000000 0.000000 0.000000
0.6832 0.0000 0.0000 0.0000 0.1461 0.0000 0.0000 0.0000 0.0000 0.0000
H(12D) 3 2 15 63 62 1 7 7 2 1 36 -0.074055 0.635950 1.025297 1.0000
0.018122 0.000000 0.000000 0.000000 0.000000 0.000000
0.6832 0.0000 0.0000 0.0000 0.1461 0.0000 0.0000 0.0000 0.0000 0.0000
1 0.954673 0.801808 0.801808 0.801808 0.801808 0.801808
2 1.036803 1.204677 1.204677 1.204677 1.204677 1.204677
3 0.983679 0.981619 0.981619 0.981619 0.981619 0.981619
4 0.969228 0.929537 0.929537 0.929537 0.929537 0.929537
5 0.990833 0.880140 0.880140 0.880140 0.880140 0.880140
6 1.028072 0.953933 0.953933 0.953933 0.953933 0.953933
7 1.182246 1.200000 1.200000 1.200000 1.200000 1.200000
0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00
0.0000E+00
0.211523E+00

❖ Table S5: Scattering factor table

```
SCAT CORE SPHV DEFV 1S2S3S4S2P3P4P3D 4D4F5S5P6S6P5D7S6D5F DELF' DELF'  NSCTL
Cu2+ CHFW CHFW CHFW 2 2 2 0 6 6 0 -9 0 0 0 0 0 0 0 0 0 0 0 0.3200 1.2650 0.772
0 CHFW (3D3D)
1 CHFW (3P3D)
2 CHFW (3D3D)
3 CHFW (3P3D)
4 CHFW (3D3D)
S CHFW CHFW RDSD 2 2 -2 0 6 -4 0 0 0 0 0 0 0 0 0 0 0 0 0 0.1250 0.1230 0.285
6 3.8512 6 3.8512 6 3.8512 7 3.8512 7 3.85126 3.8512
F CHFW CHFW CSZD 2 -2 0 0 -5 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0.0170 0.0100 0.565
O CHFW CHFW CSZD 2 -2 0 0 -4 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0.0110 0.0060 0.580
N CHFW CHFW CSZD 2 -2 0 0 -3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0.0060 0.0030 0.936
C CHFW CHFW CSZD 2 -2 0 0 -2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0.0030 0.0020 0.665
H CHFW RHFT CSZD -1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0.0000 0.0000 -0.374
END SCAT
```

❖ Table S6: Local coordinate system

Atom 1	Atom 2	Axis	Atom 1	Atom 2	Axis
CU	O(1)	X	CU	O(3)	Y
S	O(5)	X	S	O(6)	Y
F	C(7)	Z	F	C(6)	Y
O(1)	C(31)	X	O(1)	CU	Y
O(2)	C(31)	X	O(2)	O(1)	Y
O(3)	C(4)	X	O(3)	CU	Y
O(8)	CU	Z	O(8)	H(8A)	Y
O(9)	CU	Z	O(9)	H(9A)	Y
O(10)	CU	Z	O(10)	H(10B)	Y
O(4)	S	Z	O(4)	H(8B)	Y
O(5)	S	Z	O(5)	O(6)	Y
O(6)	S	Z	O(6)	H(12D)	Y
O(7)	S	Z	O(7)	H(10A)	Y
O(11)	H(11B)	X	O(11)	H(11A)	Y
O(12)	H(12C)	X	O(12)	H(12D)	Y
N(1)	C(2)	X	N(1)	C(10)	Y
N(81)	C(8)	X	N(81)	C(86)	Y
N(84)	H(84A)	X	N(84)	H(84B)	Y
C(2)	C(3)	X	C(2)	N(1)	Y
C(3)	C(2)	X	C(3)	C(4)	Y
C(4)	O(3)	X	C(4)	C(3)	Y
C(5)	C(10)	X	C(5)	C(6)	Y
C(6)	H(6)	X	C(6)	C(7)	Y
C(7)	F	X	C(7)	C(6)	Y
C(8)	N(81)	X	C(8)	C(9)	Y
C(9)	H(9)	X	C(9)	C(8)	Y
C(10)	N(1)	X	C(10)	C(9)	Y
C(11)	H(11)	X	C(11)	N(1)	Y
C(12)	C(11)	X	C(12)	C(13)	Y
C(13)	C(12)	X	C(13)	C(11)	Y
C(31)	O(2)	X	C(31)	O(1)	Y
C(82)	H(82B)	X	C(82)	H(82A)	Y
C(83)	H(83A)	X	C(83)	H(83B)	Y
C(85)	H(85B)	X	C(85)	H(85A)	Y
C(86)	H(86B)	X	C(86)	H(86A)	Y
H(8A)	O(8)	Z	H(8A)	H(8B)	Y
H(8B)	O(8)	Z	H(8B)	H(8A)	Y
H(9A)	O(9)	Z	H(9A)	H(9B)	Y
H(9B)	O(9)	Z	H(9B)	H(9A)	Y
H(10A)	O(10)	Z	H(10A)	H(10B)	Y
H(10B)	O(10)	Z	H(10B)	H(10A)	Y
H(2)	C(2)	Z	H(2)	N(1)	Y
H(6)	C(6)	Z	H(6)	C(7)	Y
H(9)	C(9)	Z	H(9)	C(8)	Y
H(11)	C(11)	Z	H(11)	N(1)	Y
H(12A)	C(12)	Z	H(12A)	H(12B)	Y
H(12B)	C(12)	Z	H(12B)	H(12A)	Y
H(13A)	C(13)	Z	H(13A)	H(13B)	Y
H(13B)	C(13)	Z	H(13B)	H(13A)	Y
H(84A)	N(84)	Z	H(84A)	H(84B)	Y
H(84B)	N(84)	Z	H(84B)	H(84A)	Y
H(82A)	C(82)	Z	H(82A)	H(82B)	Y
H(82B)	C(82)	Z	H(82B)	H(82A)	Y
H(83A)	C(83)	Z	H(83A)	H(83B)	Y
H(83B)	C(83)	Z	H(83B)	H(83A)	Y
H(85A)	C(85)	Z	H(85A)	H(85B)	Y
H(85B)	C(85)	Z	H(85B)	H(85A)	Y
H(86A)	C(86)	Z	H(86A)	H(86B)	Y
H(86B)	C(86)	Z	H(86B)	H(86A)	Y
H(11A)	O(11)	Z	H(11A)	H(11B)	Y
H(11B)	O(11)	Z	H(11B)	H(11A)	Y
H(12C)	O(12)	Z	H(12C)	H(12D)	Y
H(12D)	O(12)	Z	H(12D)	H(12C)	Y

❖ Table S7: d-orbital populations

$d(x^2-y^2)$	$d(z^2)$	d(xy)	d(yz)	d(xz)	SUM
1.26(1)	2.16(2)	2.23(1)	1.91(1)	2.13(1)	9.69
13.0	22.3	23.0	19.7	22.0	100

Derived using the method from:
A. Holladay, P. Leung and P. Coppens, *Acta Crystallogr. Sect. A*, **1983**, *39*, 377-387.

❖ Figure S1: Laplacian distribution in selected planes