Supplementary Materials: Activation of the Cyano Group at Imidazole via Copper Stimulated Alcoholysis

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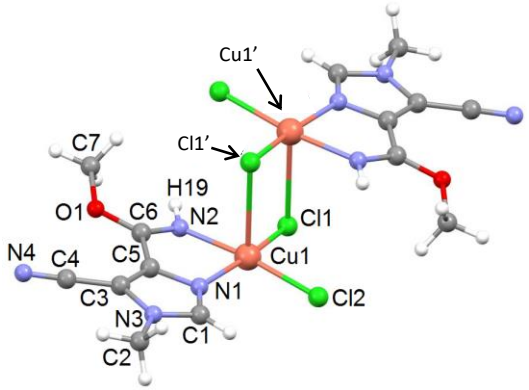
Table S1. Comparison of the experimental and optimized geometry parameters around the metal center for ***[CuCl$_2$(5-cyano-4-C(OEt)N-1-methylimidazole)(EtOH)]*** (**1**)

	Complex **1** (experimental)	Complex **1a** (doublet state)	**Error (%)**	**Structure**
Bond distance (Å)				
Cu1-N1	2.024	2.078	2.6	
Cu1-N2	2.038	2.066	1.5	
Cu1-O2	2.275	2.425	6.6	
Cu1-Cl1	2.265	2.217	2.1	
Cu1-Cl2	2.252	2.262	0.4	
Average deviation			**2.7**	
Angle (º)				**1**
O2-Cu1-Cl1	100.4	102.1	1.7	
O2-Cu1-Cl2	97.1	83.4	14.1	
O2-Cu1-N1	91.0	88.4	2.9	
O2-Cu1-N2	92.2	97.4	5.6	
Cl1-Cu1-N2	89.8	90.4	0.7	
Cl1-Cu1-N1	165.2	164.6	0.4	
Cl1-Cu1-Cl2	96.4	101.8	5.6	
Cl2-Cu1-N1	91.5	90.4	1.2	
Cl2-Cu1-N2	167.7	167.3	0.2	
N1-Cu1-N2	80.3	77.0	4.1	
Average deviation			**3.6**	**1a**

Table S2. Comparison of the experimental and optimized geometry parameters around the metal center for ***[Cu$_2$(μ-Cl)$_2$Cl$_2$(5-cyano-4-C(OMe)N-1-methylimidazole)$_2$]*** (**2**)

	Complex **2** (experimental)	Complex **2b** (triplet state)	**Error (%)**	**Structure**
Bond distance (Å)				
Cu1-N1	2.016	2.053	1.8	
Cu1-N2	2.009	2.047	1.9	
Cu1-Cl1'	2.781	2.789	0.3	
Cu1-Cl1	2.250	2.258	0.4	
Cu1-Cl2	2.250	2.256	0.2	
Cu1-Cu1'	3.395	3.224	5.1	
Average deviation			**1.6**	
Angle (º)				
Cl1'-Cu1-Cl1	95.8	101.4	5.8	
Cl1'-Cu1-Cl2	100.7	98.3	2.4	
Cl1'-Cu1- N1	89.8	88.7	1.2	
Cl1'-Cu1-N2	82.5	80.8	2.1	
Cl1-Cu1-N2	89.9	90.0	0.1	
Cl1-Cu1-N1	167.9	163.3	2.8	
Cl1-Cu1-Cl2	95.8	99.0	3.4	
Cl2-Cu1-N1	93.7	92.6	1.1	
Cl2-Cu1-N2	173.1	170.9	1.3	
N1-Cu1-N2	80.2	78.3	2.4	
Average deviation			**2.3**	



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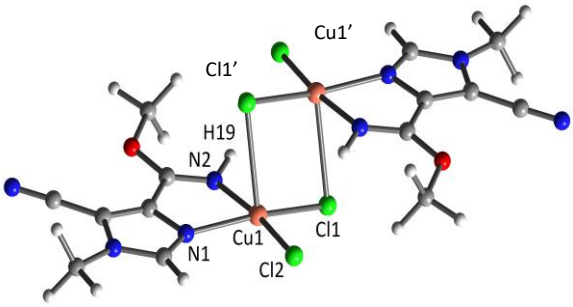


2b

Table S3. Comparison of the experimental and theoretical geometry parameters around the metal center for ***[Cu$_2$(μ-Br)$_2$Br$_2$(5-cyano-4-C(OMe)N-1-methylimidazole)$_2$]*** (**3**)

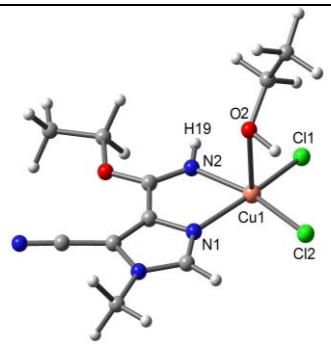
	Complex **3** (experimental)	Complex **3b** (triplet state)	**Error (%)**	**Structure**
Bond distance (Å)				
Cu1-N1	2.016	2.067	2.5	
Cu1-N2	2.010	2.048	1.9	
Cu1-Br1’	2.944	2.903	1.4	
Cu1-Br1	2.380	2.408	1.2	
Cu1-Br2	2.388	2.403	0.6	
Cu1-Cu1’	3.526	3.305	6.3	
Average deviation			**2.3**	
Angle (º)				
Br1’-Cu1-Br1	97.8	103.7	6.0	**3**
Br1’-Cu1-Br2	99.7	98.7	1.0	
Br1’-Cu1- N1	88.2	91.0	3.2	
Br1’-Cu1-N2	83.0	81.6	1.7	
Br1-Cu1-N2	90.3	90.2	0.1	
Br1-Cu1-N1	168.3	159.8	5.0	
Br1-Cu1-Br2	95.2	98.4	3.4	
Br2-Cu1-N1	93.8	92.9	0.9	
Br2-Cu1-N2	173.4	171.0	1.4	**3b**
N1-Cu1-N2	80.3	78.1	2.7	
Average deviation			**2.6**	

Table S4. Comparison of the experimental and theoretical geometry parameters around the metal center for ***[Cu$_2$(μ-Br)$_2$Br$_2$(5-cyano-4-C(OEt)N-1-methylimidazole)$_2$]*** (**4**)

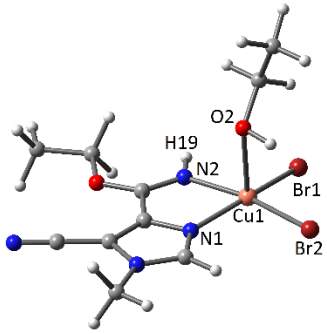
	Complex **4** (experimental)	Complex **4b** (triplet state)	**Error (%)**	**Structure**
Bond distance (Å)				
Cu1-N1	1.989	2.063	3.7	
Cu1-N2	2.032	2.046	0.7	
Cu1-Br1’	3.139	2.956	5.8	
Cu1-Br2	2.387	2.403	0.7	
Cu1-Br1	2.395	2.414	0.8	
Cu1-Cu1’	3.860	3.660	5.2	
Average deviation			**2.8**	
Angle (º)				**4**
Br1’-Cu1-Br2	105.6	105.1	0.4	
Br1’-Cu1-Br1	92.6	94.7	2.2	
Br1’-Cu1-N1	78.8	81.9	4.0	
Br1’-Cu1-N2	88.7	90.6	2.1	
Br2-Cu1-N2	93.3	90.4	3.1	
Br2-Cu1-N1	172.3	166.7	3.3	
Br2-Cu1-Br1	95.8	99.2	3.6	
Br1-Cu1-N1	90.3	91.3	1.2	
Br1-Cu1-N2	170.0	167.3	1.6	**4b**
N1-Cu1-N2	80.3	78.0	2.8	
Average deviation			**2.4**	

Table S5. Important optimized geometry parameters for complexes **1a, 1a**′ and **1a**′′

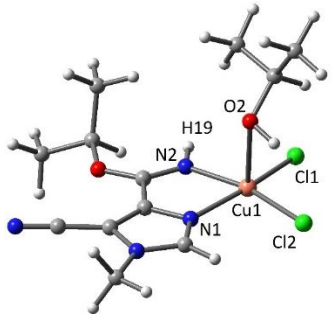
Complex	**1a**	**1a′**	**1a′′**	**Structure**
Bond distance (Å)				
Cu1-N1	2.078	2.091	2.076	
Cu1-N2	2.066	2.065	2.064	
Cu1-O2	2.425	2.408	2.445	
Cu1-X1	2.217	2.367	2.218	
Cu1-X2	2.262	2.408	2.264	
Angle (º)				
O2-Cu1-X1	102.1	104.5	101.1	
O2-Cu1-X2	83.4	85.2	82.9	
O2-Cu1-N1	88.4	87.8	87.6	
O2-Cu1-N2	97.4	95.0	99.8	
X1-Cu1-N2	90.4	90.5	90.3	
X1-Cu1-N1	164.6	163.3	165.7	
X1-Cu1-X2	101.8	100.8	102.0	
X2-Cu1-N1	90.4	91.3	90.1	
X2-Cu1-N2	167.3	168.3	166.7	
N1-Cu1-N2	77.0	77.1	77.0	
Cu1-N1-C5-C3	-176.0	-175.7	-175.8	
τ**	0.045	0.083	0.017	



1a



1a′



1a′′

**Geometry index τ = (β – α) / 60º, where 0 ≤ τ ≤ 1, α and β are two largest angles (β > α); τ = 0 for an ideal square-pyramid, τ = 1 for an ideal trigonal-bipyramid[37].

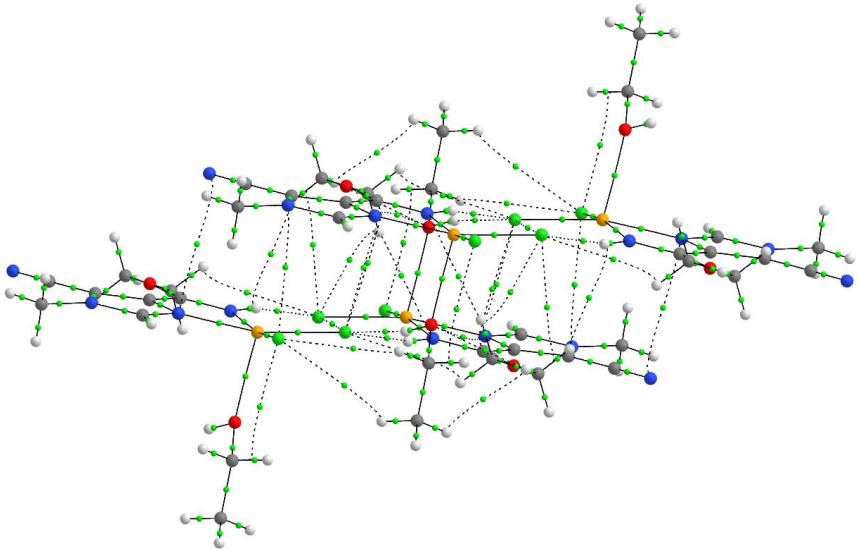


Figure S1. Bond paths and bond critical points according to QTAIM analysis for extended model **(1)**$_4$. The model contains four neighboring monomeric molecules cut from the crystal structure of **1**. The geometry of the model was fixed to the experimental structure.

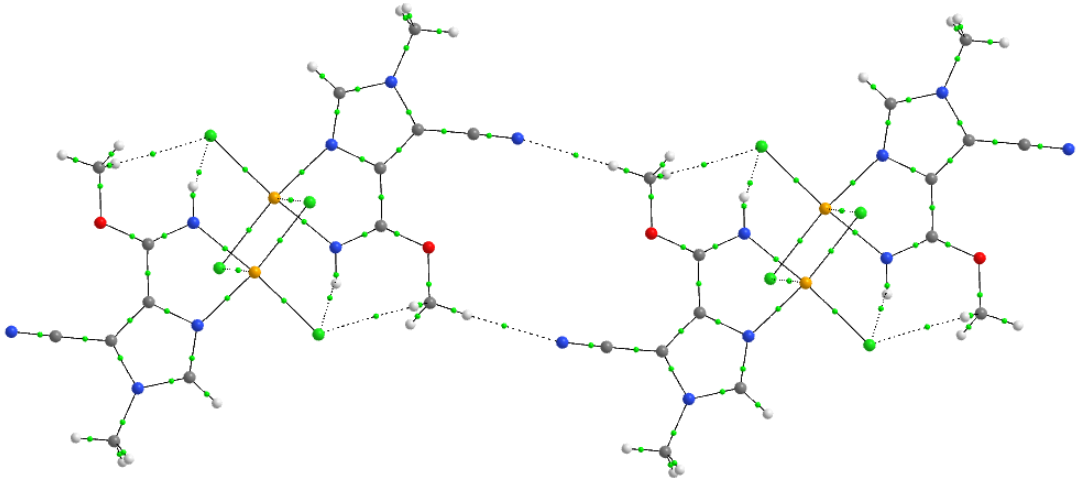


Figure S2. Bond paths and bond critical points according to QTAIM analysis for extended model **(2)**$_2$. The model contains two neighboring dimeric molecules cut from the crystal structure of **2**. The geometry of the model was fixed to the experimental structure.

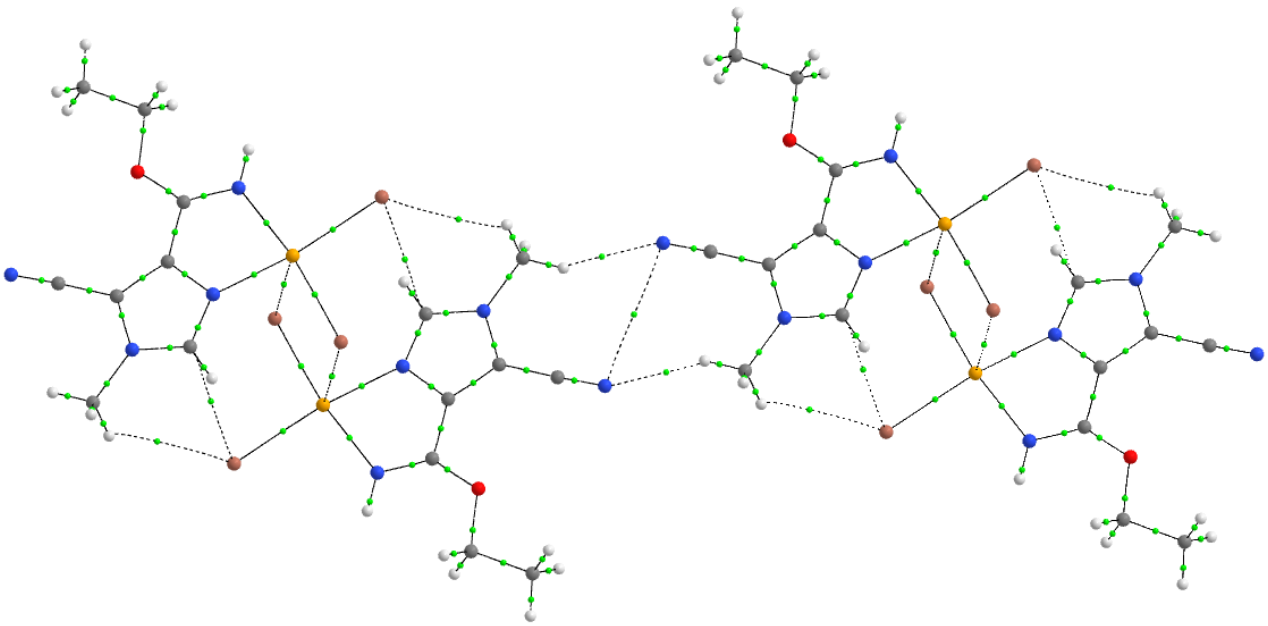


Figure S3. Bond paths and bond critical points according to QTAIM analysis for extended model **(4)**$_2$. The model contains two neighboring dimeric molecules cut from the crystal structure of **4**. The geometry of the model was fixed to the experimental structure.

Table S6. Properties of the electron density in the selected BCPs for compounds **1**,**2** and **4** representing weak intermolecular interactions. Model of compound **1** contains four neighboring molecules, **2**-**4** contain two neighboring dimers to maintain similar size of the models.

Model	Type	ρ (eÅ^{-3})	|V|/G	E_{INT} (kJmol^{-1})
(1)$_4$	Cl…Cl	0.026	0.74	-2.1
	N…N	0.028	0.79	-1.9
	Cl…π	0.048	0.74	-4.7
	Cl…H(O)	0.134	0.89	-18.9
	Cl…H(N)	0.065	0.74	-6.4
(2)$_2$	CN…H(MeO)	0.057	0.73	-5.8
	Cl…H(MeO)	0.058	0.75	-5.4
	CN…H(MeN)	0.020	0.74	-2.0
(4)$_2$	CN…H(MeN)	0.075	0.73	-8.1
	CN…NC	0.023	0.78	-2.3
	Br…H(MeN)	0.047	0.76	-4.0
	Br…H(EtO)	0.007	0.63	-0.6

Table S7. IR data for complex ***[CuCl$_2$(5-cyano-4-C(OEt)N-1-methylimidazole)(EtOH)]*** (**1**)

IR band, cm^{-1}*	**Assignment****
3368 (w)	υ(O2-H)
3283 (w)	υ(N2-H19)
3123 (w)	υ(C1-H)
2236 (w)	υ(C4≡N4)
1644 (s)	υ(C6=N2), υ(C3=C5)
1587 (vs)	υ(C3=C5), υ(C6=N2)
1516 (m)	β(C1-H), υ_{as}(N1-C1-N3), , δ_s(CH$_3$) in imidazole ring
1304 (s)	υ_{as}(C7-O1-C6), β(N2-H19), β(C1-H), υ(C5-N1), ω(CH$_2$) in ethoxy group
1173 (m)	β(C1-H)
1111 (w)	ρ(CH$_3$) and ρ(CH$_2$) in ethoxy group, υ_{as}(C7-O1-C6), β(N2-H19)
1079 (w)	β(N2-H19), υ_{as}(C7-O1-C6), ρ(CH$_3$) in ethoxy group
1049 (w)	ρ(CH$_3$) and ρ(CH$_2$) in ethanol molecule, υ(C9-O2), β(O2-H)
1007 (w)	β(C1-H), β(N2-H19), υ(C7-O1) in ethoxy, υ(C7-C8), ω(CH$_3$) and ω(CH$_2$) in ethoxy
883 (w)	ω(CH$_3$) and ω(CH$_2$) in ethanol molecule, υ(C10-C9), υ(O2-C9)
873 (w)	γ(C1-H)
839 (w)	β(N2-H19), υ_s(C7-O1-C6), υ(C2-N3), β(ring), ρ(CH$_3$) and ρ(CH$_2$) in ethanol molecule
818 (m)	γ(N2-H19), ρ(CH$_3$) and ρ(CH$_2$) in ethanol molecule

* s, strong; m, medium; w, weak; v, very

**υ, stretching; subscript "s", symmetric; subscript "as", asymmetric; β, bending in-plane; γ, bending out-of-plane; ω, wagging; ρ, rocking

Table S8. IR data for complex ***[Cu$_2$(μ-Cl)$_2$Cl$_2$(5-cyano-4-C(OMe)N-1-methylimidazole)$_2$]*** (**2**)

IR band, cm^{-1}*	**Assignment****
3353 (m)	υ(N2-H19)
3100 (m)	υ(C1-H)
2242 (w)	υ(C4≡N4)
1653 (vs)	υ(C6=N2), υ(C3=C5)
1593 (s)	υ(C3=C5), υ(C6=N2)
1514 (m)	β(C1-H), υ_{as}(N3-C1-N1), δ_s(CH$_3$) in imidazole ring
1298 (s)	β(N2-H19), β(C1-H), υ(C5=N1), υ_{as}(C7-O1-C6)
1181 (w)	β(C1-H)
1145(w)	β(N2-H19), ρ(CH$_3$) in methoxy group
1041 (w)	β(C1-H), β(N2-H19), ρ(CH$_3$) in imidazole
941 (w)	υ_s(C7-O1-C6)
812 (m)	γ (N2-H19),
777 (m)	γ(ring), γ(N2-H19)
754 (w)	β (N2-H19), ρ(CH$_3$) in methoxy group

* s, strong; m, medium; w, weak; v, very

**υ, stretching; subscript “s”, symmetric; subscript “as”, asymmetric; β, bending in-plane; γ, bending out-of-plane; ρ, rocking

Table S9. IR data for complex ***[Cu$_2$(μ-Br)$_2$Br$_2$(5-cyano-4-C(OMe)N-1-methylimidazole)$_2$]*** (**3**)

IR band, cm^{-1}*	**Assignment****
3347 (m)	υ(N2-H19)
3097 (m)	υ(C1-H)
2242 (w)	υ(C4≡N4)
1651 (vs)	υ(C6=N2), υ(C5=C3)
1591 (s)	υ(C5=C3), υ(C6=N2)
1514 (m)	β(C1-H), υ_{as}(N3-C1-N1), δ_s(CH$_3$) in imidazole ring
1296 (s)	β(N2-H19), β(C1-H), υ(C5-N1), υ_{as}(C7-O1-C6)
1180 (w)	β(C1-H)
1144(w)	ρ(CH$_3$) in methoxy group
1039 (w)	β(C1-H), β(N2-H19), ρ(CH$_3$) in imidazole ring
937 (w)	υ_s(C7-O1-C6)
810 (m)	γ(N2-H19)
773 (m)	γ(ring), γ(N2-H19)
752 (w)	β (N2-H19), ρ(CH$_3$) in methoxy group

* s, strong; m, medium; w, weak; v, very

**υ, stretching; subscript "s", symmetric; subscript "as", asymmetric; β, bending in-plane; γ, bending out-of-plane; ρ, rocking

Table S10. IR data for complex ***[Cu$_2$(μ-Br)$_2$Br$_2$(5-cyano-4-C(OEt)N-1-methylimidazole)$_2$]*** (**4**)

IR band, cm^{-1}*	**Assignment****
3289 (w)	υ(N2-H19)
3153 (w)	υ(C1-H)
2245 (w)	υ(C4≡N4)
1639 (s)	υ(C6=N2), υ(C5=C3)
1586 (vs)	υ(C5=C3), υ(C6=N2)
1515 (m)	β(C1-H), υ_{as}(N3-C1-N1), δ_s(CH_3) in imidazole ring
1302 (s)	β(C1-H), β(N2-H19), υ(C5-N1), υ_{as}(C7-O-C6), ω(CH_2) in ethoxy group
1227 (w)	β(C1-H), β(N2-H19), β(ring), ρ(CH_3) in imidazole ring
1171 (m)	β(C1-H)
1151 (vw)	β(N2-H19)
1106 (w)	β(N2-H19), ρ(CH_3) in ethoxy group, υ(C7-C8)
1043 (w)	β(C1-H), β(N2-H19), υ_{as}(C7-O1-C6)
1005 (w)	β(C1-H), υ(C7-C8)
869 (w)	γ(C1-H)
821 (m)	υ_s(C-O), β(ring), β(N8-H)
802 (w)	γ(N2-H19), ρ(CH_3) and ρ(CH_2) in ethoxy group

* s, strong; m, medium; w, weak; v, very

**υ, stretching; subscript “s”, symmetric; subscript “as”, asymmetric; β, bending in-plane; γ, bending out-of-plane; ω, wagging; ρ, rocking

Table S11. Comparison main IR bands of free ligand with main experimental IR bands for complexes **1** – **4**

	υ(O2-H)	**υ(N2-H19)**	**υ(C1-H)**	**υ(C4≡N4)**	**υ(C6=N2)**, υ(C5=C3)	**υ(C5=C3)**, υ(C6=N2)	**υ(C7-O-C6)**, β(N2H19), β(C1H), υ(C5-N1)
Free ligand	-	-	3126	2240(vs)	-	-	1316(m)*
1	3368 (w)/*3694*	3283 (w)/*3622*	3123 (w)/*3289*	2236(w)/*2371*	1644(s)/*1714*	1587(vs)/*1642*	1304(s)/*1349*
2	-	3353 (m)/*3561*	3100 (m)/*3293*	2242(w)/*2370*	1653(vs)/*1724*	1593(s)/*1647*	1298(s)/*1355*
3	-	3347 (m)/*3555*	3097 (m)/*3289*	2242(w)/*2370*	1651(vs)/*1722*	1591(s)/*1645*	1296(s)/*1353*
4	-	3289 (w)/*3625*	3153 (w)/*3306*	2245(w)/*2368*	1639(s)/*1706*	1586(vs)/*1642*	1302(s)/*1351*

***** There is no υ(C-O)

** experimental value/*computational value (non-scaled)*

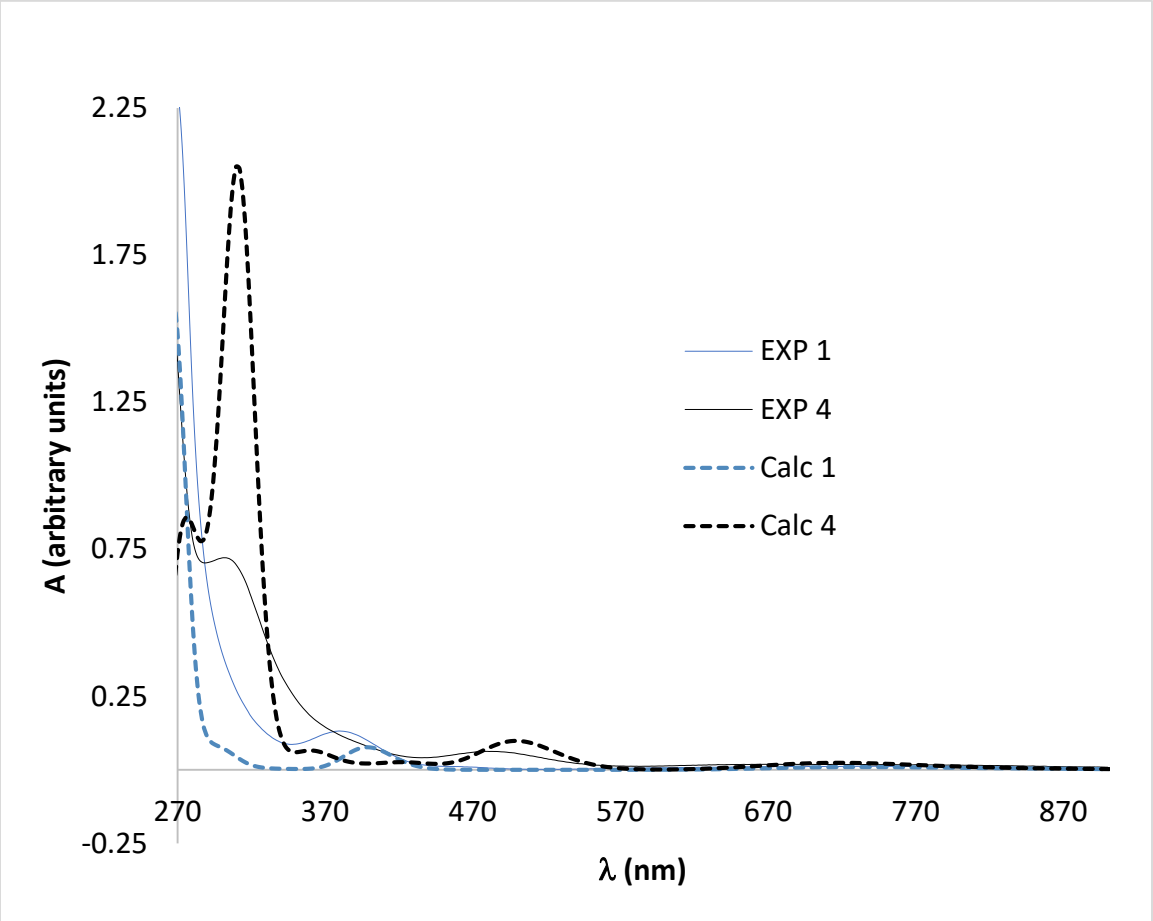


Figure S4. Comparison of the experimental and computational UV-Vis spectra for compounds **1** and **4**. The simulated spectra are shown as dashed lines.

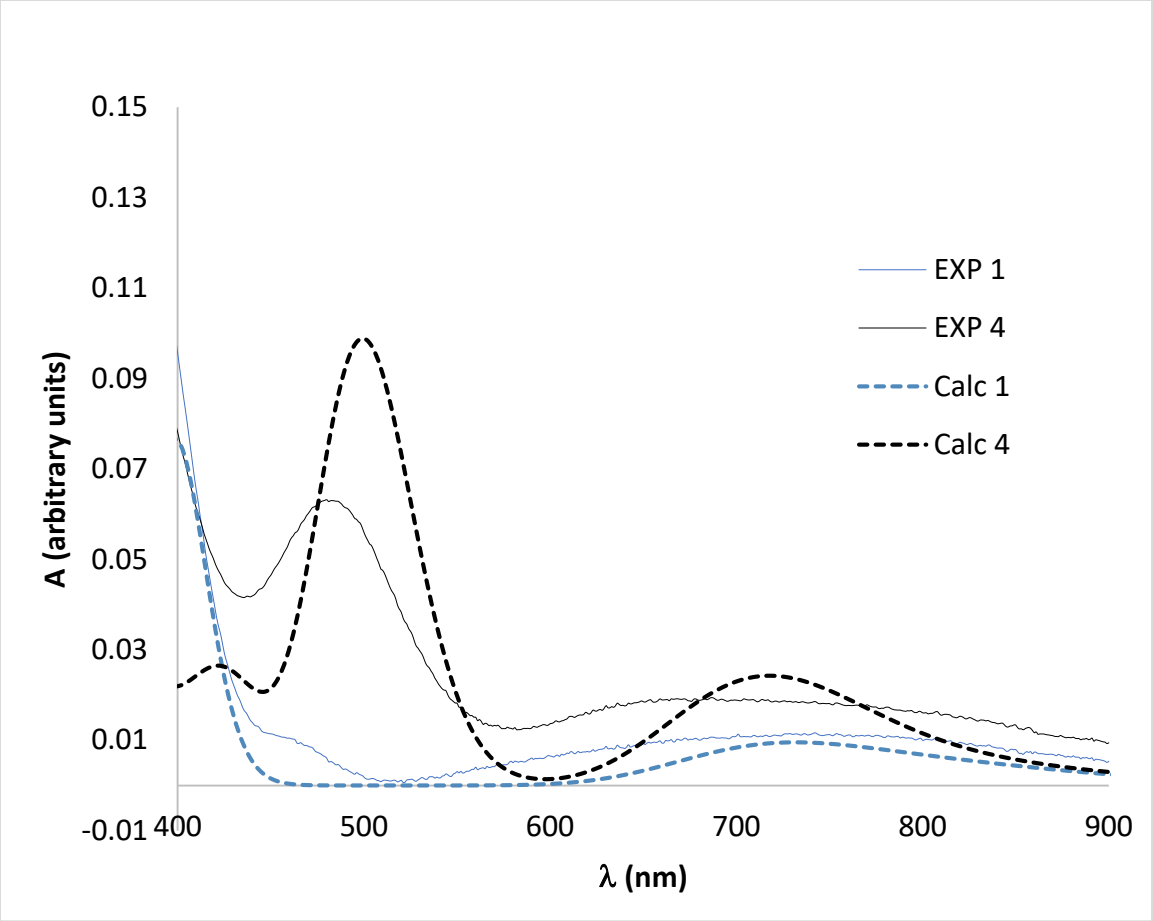


Figure S5. The lowest energy excitation peaks in experimental and computational UV-Vis spectra for compounds **1** and **4**. The simulated spectra are shown as dashed lines.

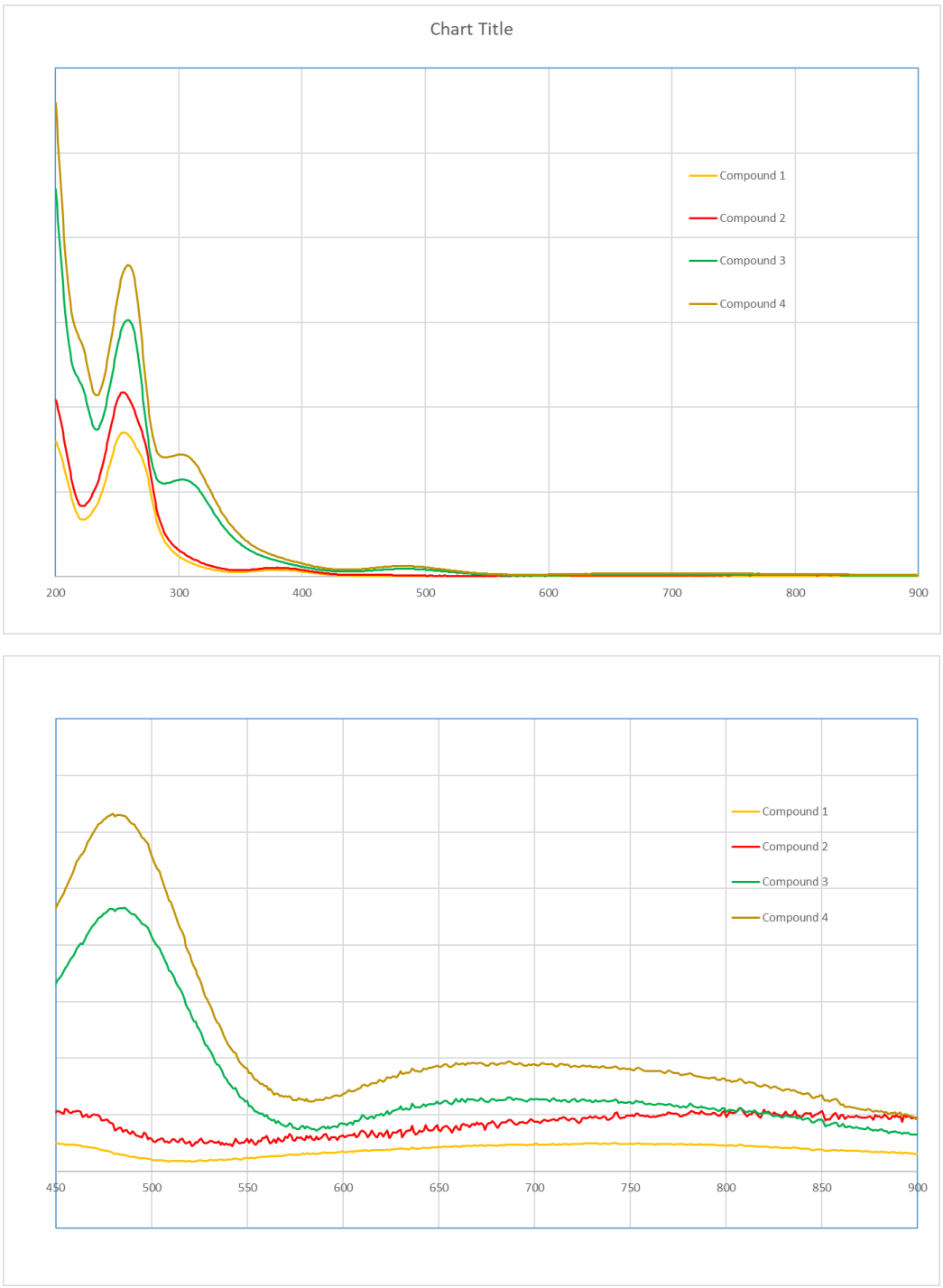


Fig S6. Experimental UV-Vis spectra for **1** – **4** in acetonitrile

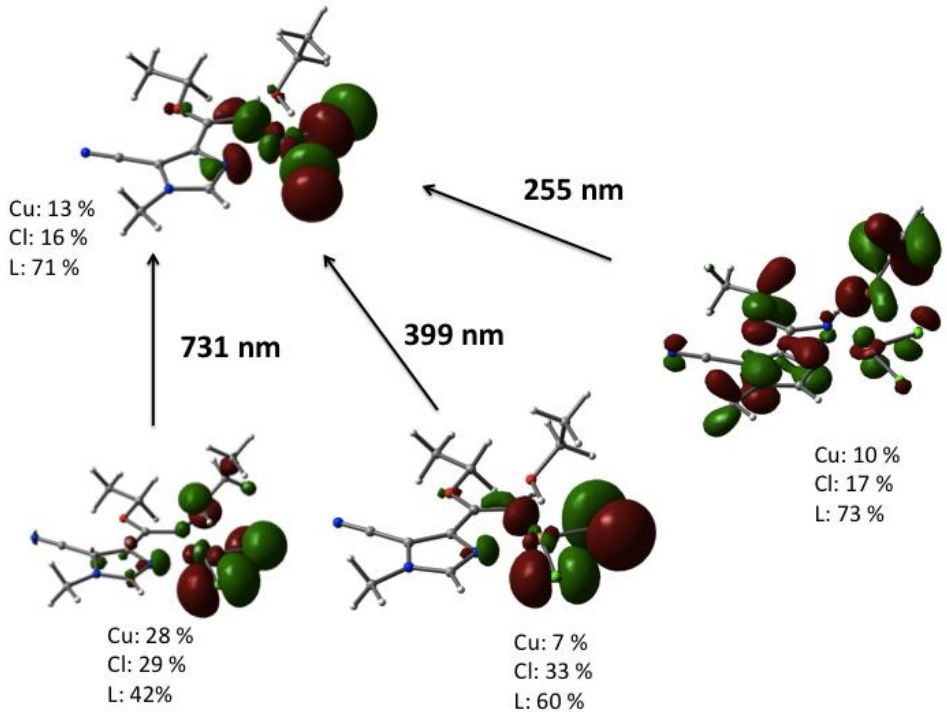


Figure S7. The appearance of the molecular orbitals involved in the main excitations in the copper(II) compound **1**.

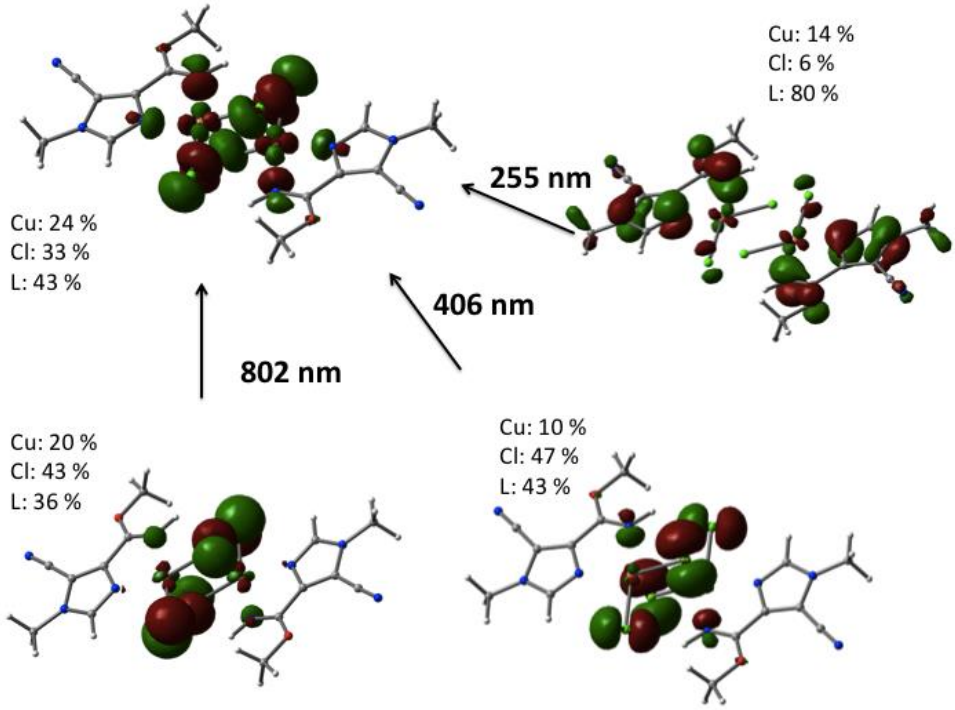


Figure S8. The appearance of the molecular orbitals involved in the main excitations in the copper(II) compound **2**.

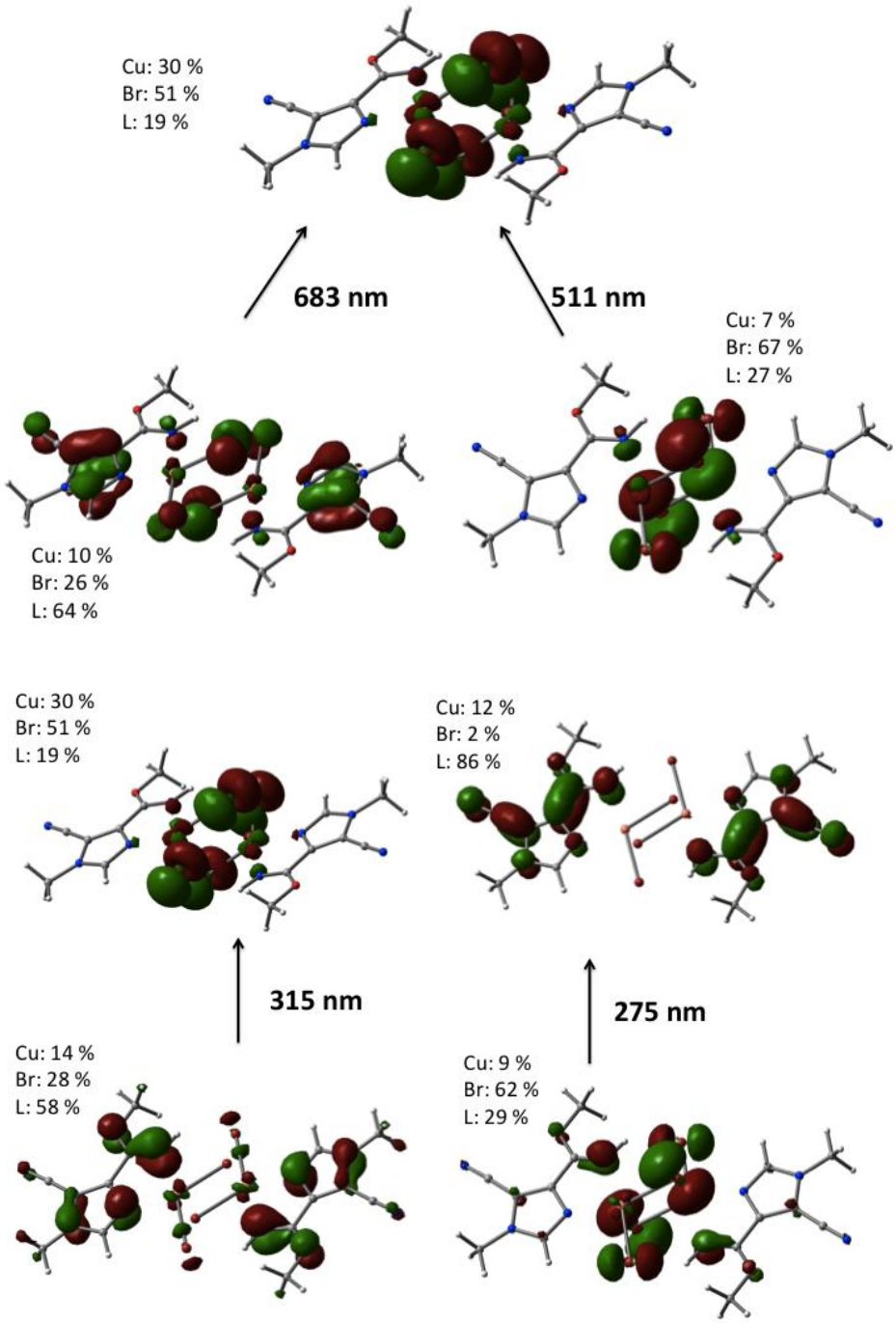


Figure S9. The appearance of the molecular orbitals involved in the main excitations in the copper(II) compound **3.**

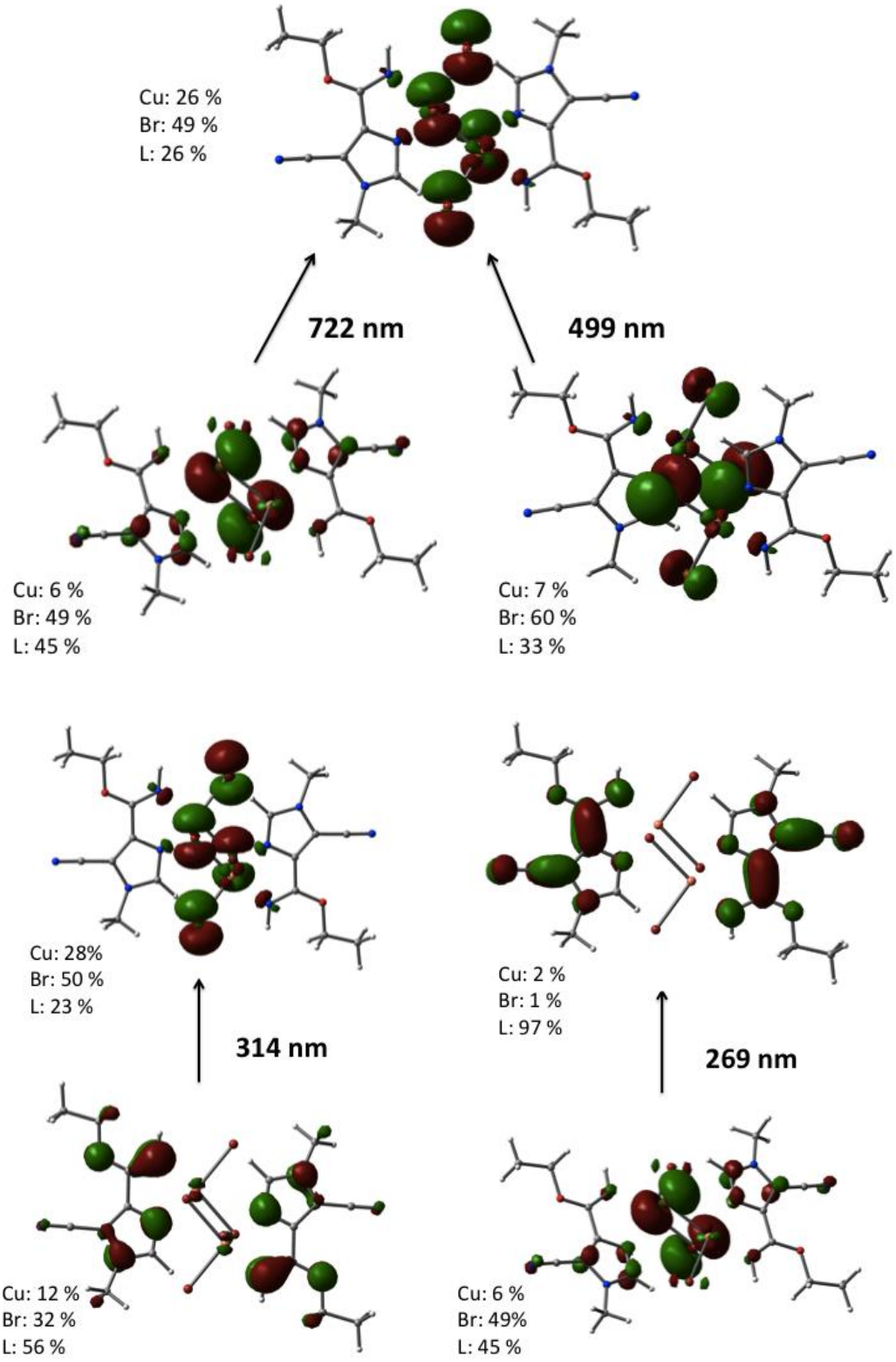


Figure S10. The appearance of the molecular orbitals involved in the main excitations in the copper(II) compound 4

Table S12. CheckCIF reports for **1 - 4**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.
No syntax errors found. CIF dictionary Interpreting this report

Datablock: 1

Bond precision: C-C = 0.0040 A Wavelength=0.71073
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alpha=108.336(3) beta=95.921(3) gamma=98.615(3)
Temperature: 150 K
Calculated Reported
Volume 732.01(10) 732.01(10)
Space group P -1 P -1
Hall group -P 1 -P 1
Moiety formula C10 H16 Cl2 Cu N4 O2 C10 H16 Cl2 Cu N4 O2
Sum formula C10 H16 Cl2 Cu N4 O2 C10 H16 Cl2 Cu N4 O2
Mr 358.72 358.71
Dx,g cm-3 1.628 1.627
Z 2 2
Mu (mm-1) 1.859 1.859
F000 366.0 366.0
F000’ 367.32
h,k,lmax 7,14,18 7,14,18
Nref 3890 3882
Tmin,Tmax 0.813,0.955 0.707,0.955
Tmin’ 0.689
Correction method= # Reported T Limits: Tmin=0.707 Tmax=0.955
AbsCorr = NUMERICAL
Data completeness= 0.998 Theta(max)= 29.000
R(reflections)= 0.0363(3092) wR2(reflections)= 0.0878(3882)
S = 1.023 Npar= 172

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 3.54 Report
PLAT971_ALERT_2_C Check Calcd Resid. Dens. 0.86A From Cu1 1.63 eA-3
PLAT975_ALERT_2_C Check Calcd Resid. Dens. 1.01A From N4 0.52 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H5C -0.34 eA-3

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 2 Report
PLAT154_ALERT_1_G The s.u.’s on the Cell Angles are Equal ..(Note) 0.003 Degree
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C2 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 2 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1 (II) . 2.13 Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 8 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 2 Info
0 **ALERT level A** = Most likely a serious problem - resolve or explain

```
0 ALERT level B = A potentially serious problem, consider carefully
4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
8 ALERT level G = General information/check it is not something unexpected
2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check
```

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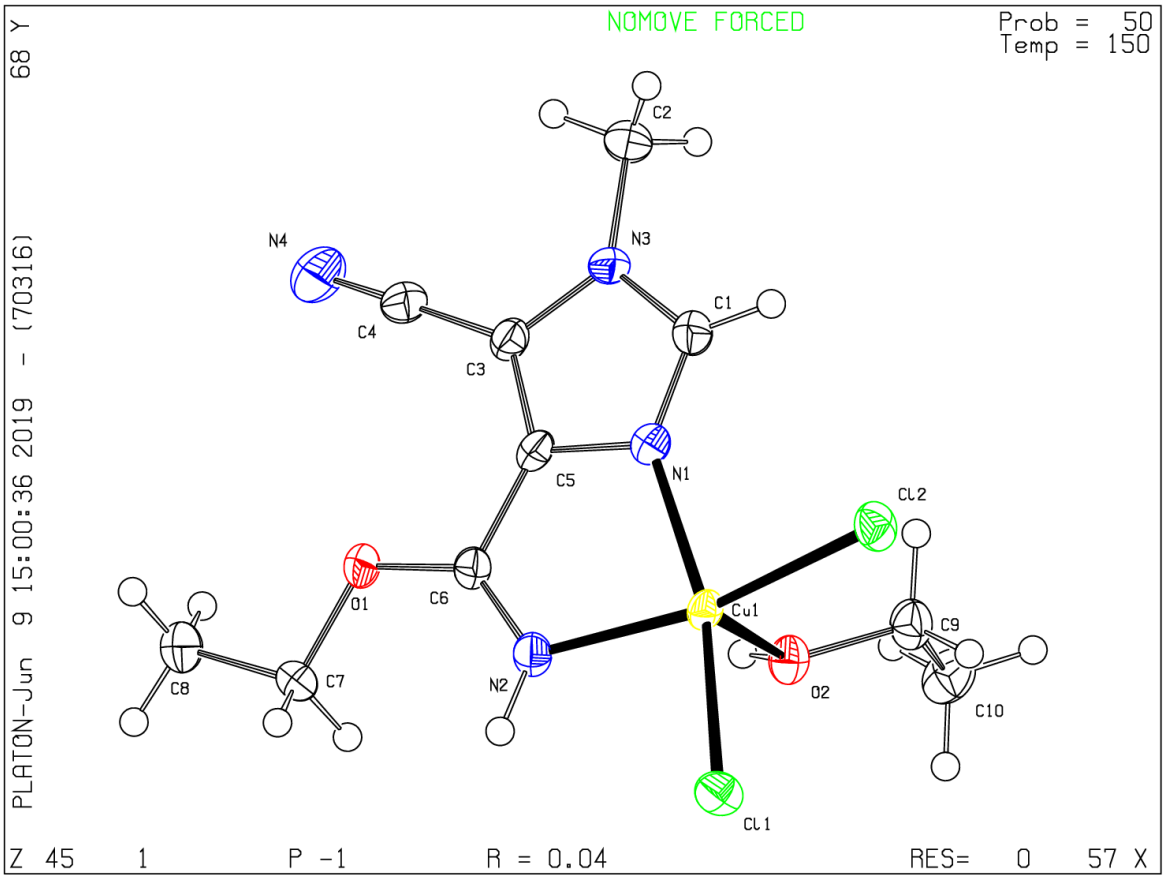
PLATON version of 03/05/2019; check.def file version of 29/04/2019



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 2

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 2

```
Bond precision: C-C = 0.0030 A Wavelength=0.71073
Cell: a=7.1887(4) b=7.4368(5) c=10.5356(7)
alpha=82.585(3) beta=89.776(3) gamma=84.799(3)
Temperature: 150 K
Calculated Reported
Volume 556.22(6) 556.22(6)
Space group P -1 P -1
Hall group -P 1 -P 1
Moiety formula C14 H16 Cl4 Cu2 N8 O2 C14 H16 Cl4 Cu2 N8 O2
Sum formula C14 H16 Cl4 Cu2 N8 O2 C14 H16 Cl4 Cu2 N8 O2
Mr 597.25 597.23
Dx,g cm-3 1.783 1.783
```

```
Z 1 1
Mu (mm-1) 2.421 2.421
F000 298.0 298.0
F000' 299.28
h,k,lmax 10,10,14 10,10,14
Nref 3228 3229
Tmin,Tmax 0.788,0.937 0.611,0.938
Tmin' 0.579
Correction method= # Reported T Limits: Tmin=0.611 Tmax=0.938
AbsCorr = NUMERICAL
Data completeness= 1.000 Theta(max)= 29.999
R(reflections)= 0.0295( 2624) wR2(reflections)= 0.0750( 3229)
S = 1.051 Npar= 136
The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
Alert level C
PLAT420_ALERT_2_C D-H Without Acceptor N2 --H1N2 . Please Check
PLAT977_ALERT_2_C Check Negative Difference Density on H6A -0.55 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H6B -0.48 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H6C -0.58 eA-3
Alert level G
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.003 Degree
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Cu1 --N1 . 5.4 s.u.
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C2 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 1 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1 (II) . 2.12 Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 2 Info
0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
8 ALERT level G = General information/check it is not something unexpected
2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check
```

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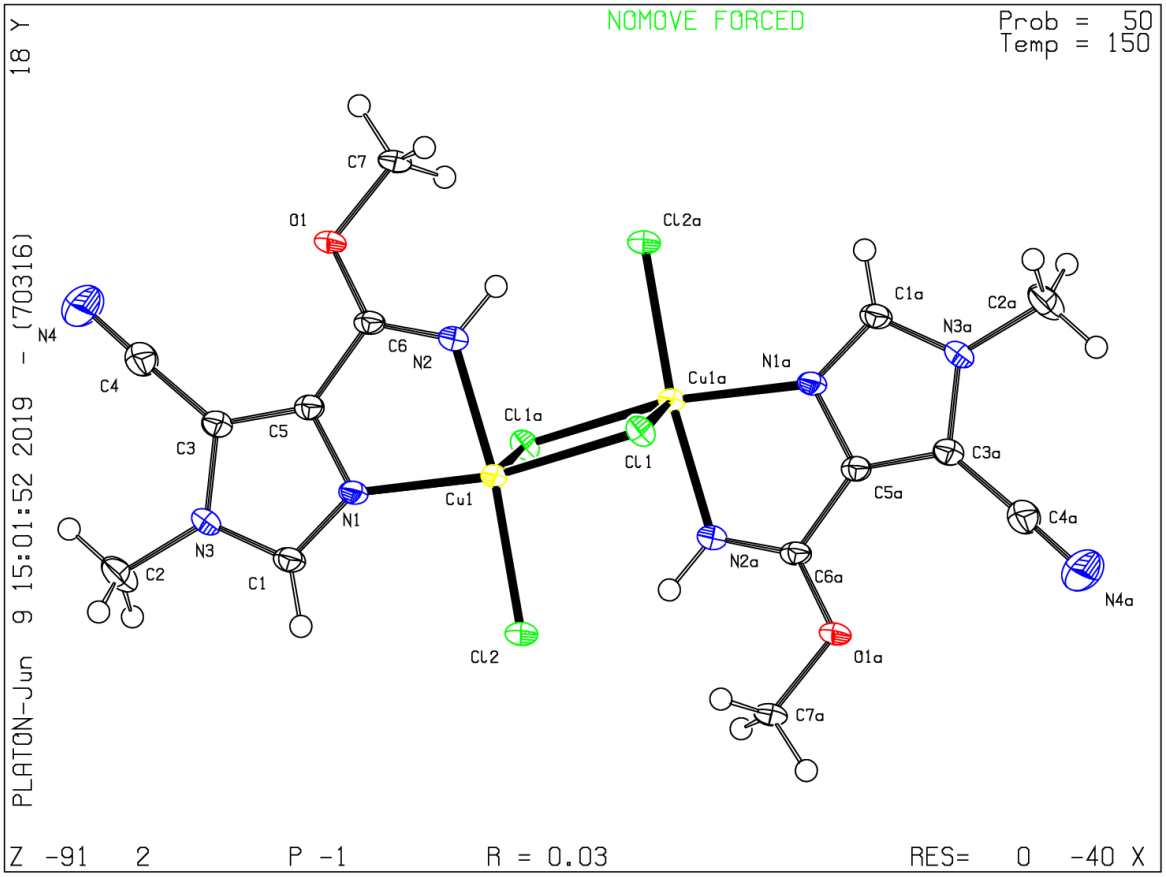
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.
PLATON version of 03/05/2019; check.def file version of 29/04/2019



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 3
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.
No syntax errors found. CIF dictionary Interpreting this report

Datablock: 3

```
Bond precision: C-C = 0.0087 A Wavelength=0.71073
Cell: a=7.3978(2) b=7.6151(2) c=10.7043(3)
alpha=81.023(2) beta=88.684(2) gamma=84.835(2)
Temperature: 150 K
Calculated Reported
```

Volume 593.20(3) 593.20(3)
Space group P -1 P -1
Hall group -P 1 -P 1
Moiety formula C14 H16 Br4 Cu2 N8 O2 C14 H16 Br4 Cu2 N8 O2
Sum formula C14 H16 Br4 Cu2 N8 O2 C14 H16 Br4 Cu2 N8 O2
Mr 775.05 775.07
Dx,g cm-3 2.170 2.170
Z 1 1
Mu (mm-1) 8.556 8.556
F000 370.0 370.0
F000' 369.69
h,k,lmax 10,10,14 10,10,14
Nref 3150 3143
Tmin,Tmax 0.003,0.513 0.065,0.555
Tmin' 0.002
Correction method= # Reported T Limits: Tmin=0.065 Tmax=0.555
AbsCorr = NUMERICAL
Data completeness= 0.998 Theta(max)= 28.998
R(reflections)= 0.0546(2595) wR2(reflections)= 0.1068(3143)
S = 1.079 Npar= 136

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C Non-Solvent Resd 1 N Ueq(max)/Ueq(min) Range 3.2 Ratio
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00867 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor N2 --H1N2 . Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 4.692 Check
PLAT977_ALERT_2_C Check Negative Difference Density on H1N2 -0.34 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H10D -0.31 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H10E -0.35 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H10F -0.31 eA-3
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density. 0 Info

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 2 Note
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT012_ALERT_1_G N.O.K. _shelx_res_checksum Found in CIF ..... Please Check
PLAT063_ALERT_4_G Crystal Size Likely too Large for Beam Size .... 0.70 mm
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 8.17 Why ?
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.002 Degree
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br1 --Cu1_a . 5.3 s.u.
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C2 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 1 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 1 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 7 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 4 Note

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
9 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
13 **ALERT level G** = General information/check it is not something unexpected
3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
11 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

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strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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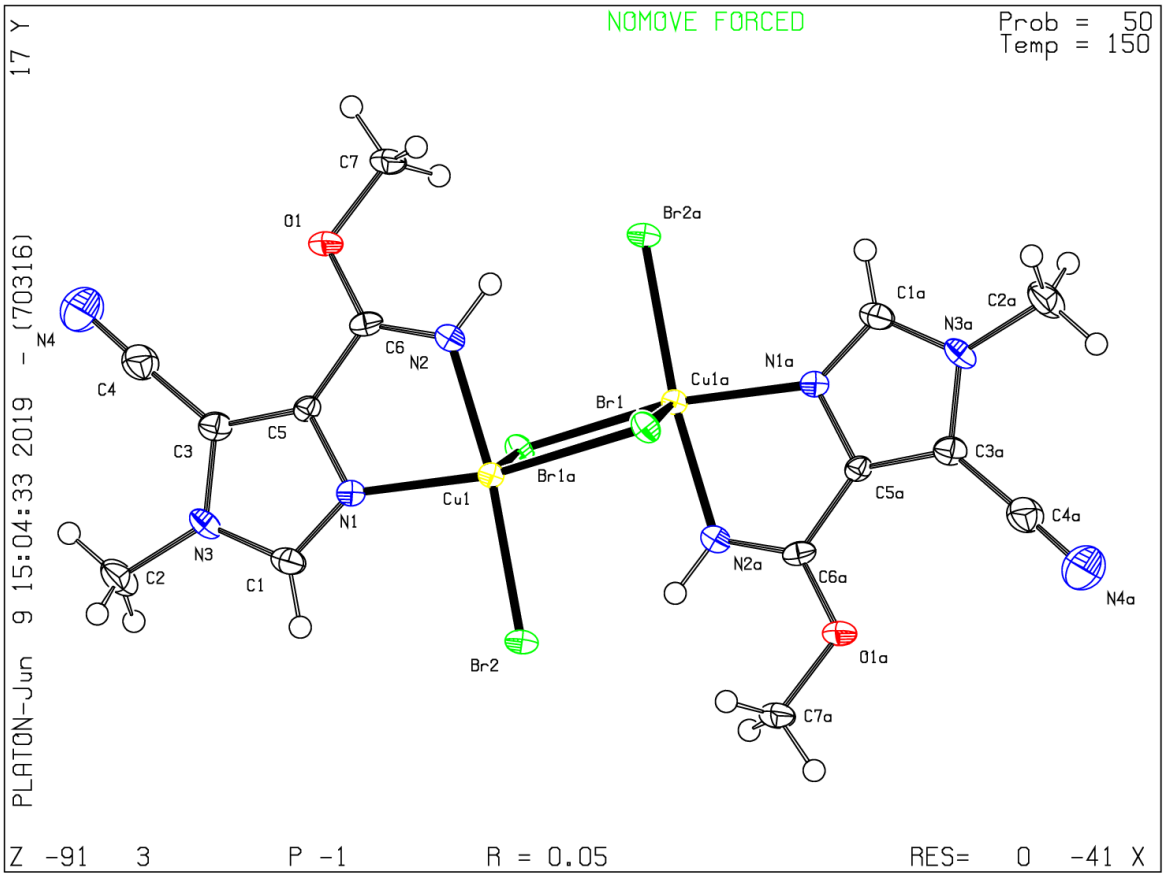
PLATON version of 03/05/2019; check.def file version of 29/04/2019



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 4
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.
No syntax errors found. CIF dictionary Interpreting this report

Datablock: 4

```
Bond precision: C-C = 0.0070 A Wavelength=0.71073
Cell: a=7.3737(9) b=8.4147(11) c=10.6554(14)
alpha=83.614(5) beta=76.079(5) gamma=75.706(5)
Temperature: 150 K
Calculated Reported
Volume 620.91(14) 620.91(14)
Space group P -1 P -1
Hall group -P 1 -P 1
Moiety formula C8 H10 Br2 Cu N4 O C8 H10 Br2 Cu N4 O
Sum formula C8 H10 Br2 Cu N4 O C8 H10 Br2 Cu N4 O
Mr 401.55 401.56
Dx,g cm-3 2.148 2.148
Z 2 2
Mu (mm-1) 8.178 8.178
F000 386.0 386.0
F000' 385.69
h,k,lmax 9,10,13 9,10,13
Nref 2727 2728
Tmin,Tmax 0.413,0.569 0.208,0.602
Tmin' 0.097
Correction method= # Reported T Limits: Tmin=0.208 Tmax=0.602
AbsCorr = NUMERICAL
Data completeness= 1.000 Theta(max)= 26.998
R(reflections)= 0.0349( 1899) wR2(reflections)= 0.0771( 2728)
S = 1.024 Npar= 145
```

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..............  0.007 Ang.
PLAT905_ALERT_3_C Negative K value in the Analysis of Variance ... -2.247 Report
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density. 0 Info
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............. 1 Report
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.005 Degree
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C2 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........  1 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
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5 **ALERT level G** = General information/check it is not something unexpected
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1 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low

```
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check
```

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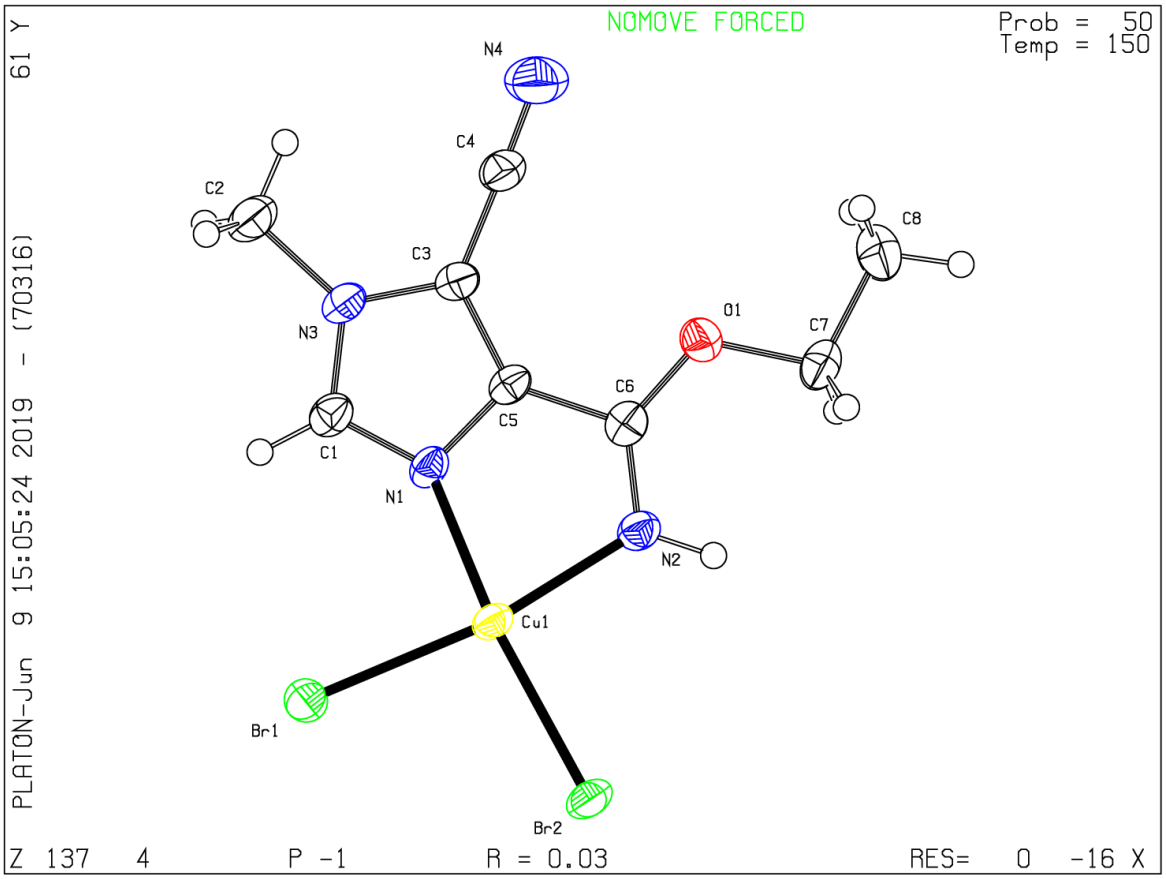
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Prob = 50
Temp = 150
61 Y
PLATON-Jun 9 15:05:24 2019 - (70316)
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C4
C2
C3
C8
O1
C7
N3
C6
C5
C1
N1
N2
Cu1
Br1
Br2
Z 137 4
P -1
R = 0.03
RES= 0 -16 X