

Supporting Information for Manuscript Titled:

*Anisotropic Covalency Contributions to
Superexchange Pathways in Type One Copper Active
Sites*

Ryan G. Hadt,[†] Serge I. Gorelsky,^{†,‡} and Edward I. Solomon^{†,*}

[†]Department of Chemistry, Stanford University, Stanford, California 94305,
U.S.A.

[‡]Centre for Catalysis Research and Innovation, Department of Chemistry,
University of Ottawa, Ottawa, Ontario K1N 6N6, Canada

Supporting Information Figures

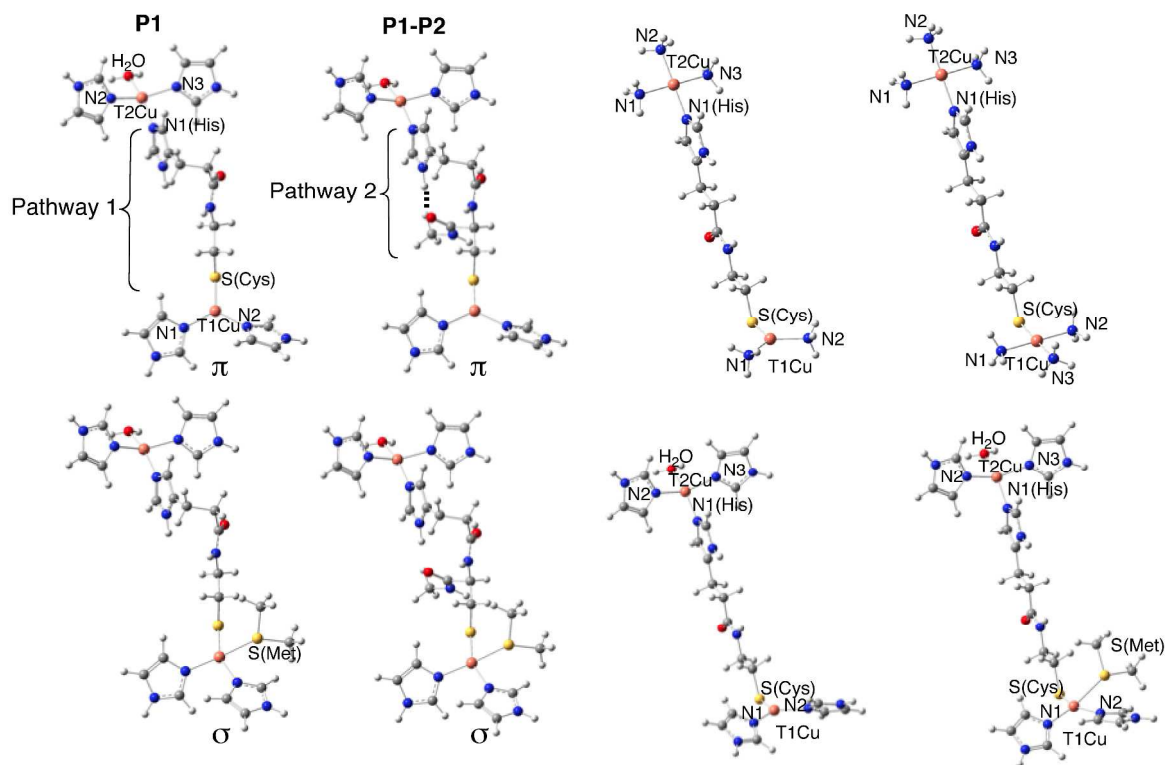


Figure S1. Structures and labeling for the linear and protein bridge models with both active site ligands and NH_3 ligands. Both pathway 1 and 2 are indicated.

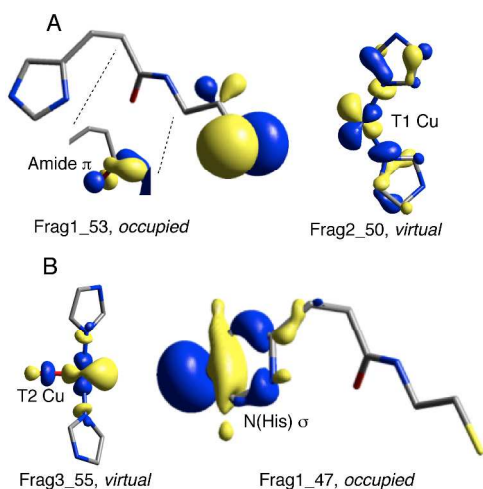


Figure S2. Representative fragment orbitals of the bridge for the 2Cu(II) and 2Cu(I) models. (A) T1 Cu and (B) T2 Cu.

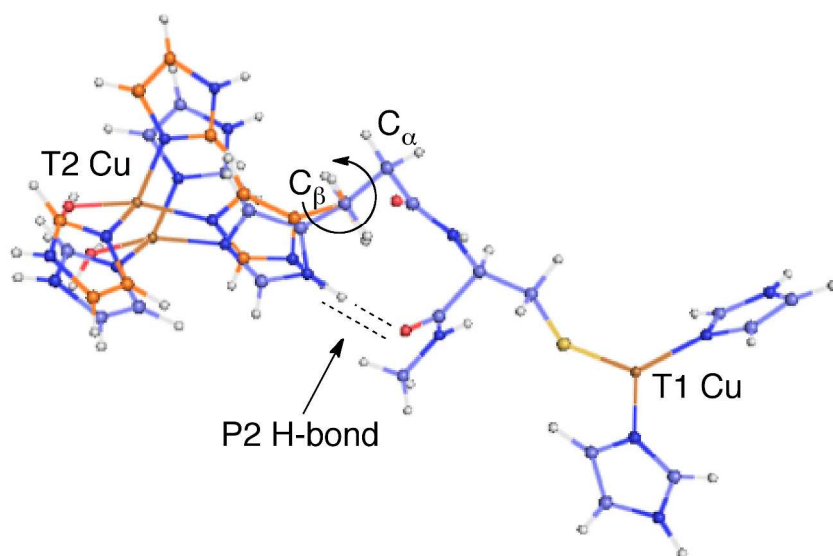


Figure S3. Variation in P2 H-bond distance: rotation about the His C_{α} - C_{β} bond.

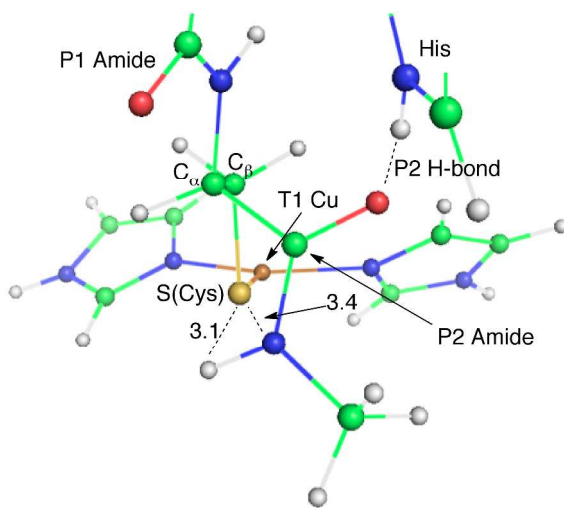


Figure S4. Location of P2 amide relative to the Cu-S(Cys) bond of the T1 site.

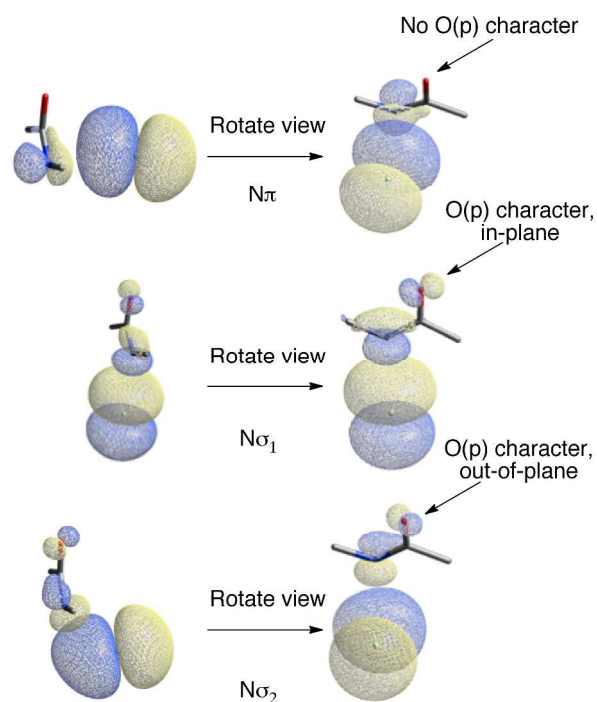


Figure S5. Interaction of anionic 2p-orbital (from fluoride) with the P2 amide: orientation dependence on O-character and directionality.

Further analysis can shed light on the molecular orbital basis for this difference in O(p)-character activation for between blue and green sites. It can be seen from the less expanded versions of the β -LUMO plots in the main text (Figure 8, middle) that the S(Cys)(3p) orbitals of the blue and green sites interact differently with the N-H unit of the P2 amide. The degree and nature of this interaction can be gauged by first noting the structural proximity of the P2 amide relative to the Cu(II)-S(Cys) bond (see Supporting Information Figure S4). It is located directly behind the Cu-S(Cys) bond, looking along the S(Cys)-Cu axis. In the blue, π -case, the S(3p) orbital interacting with the Cu(dx^2-y^2) orbital is out-of-plane with respect to the C_β -S bond. This necessitates an interaction with an out-of-plane orbital (with respect to the N-C-O plane) of the P2 amide (Figure 8, middle). In the green, σ -case, the S(3p) orbital interacting with the Cu(dx^2-y^2) orbital is roughly in-plane with respect to the C_β -S bond. This directs the S(3p) orbital at the H atom of the N-H bond. These differences in coupling to the P2 amide between green and

blue are also observed in the P2 amide coefficients of the T1 Cu β -LUMO (Supporting Information Table S6). Specifically, note: 1) the much larger N and C coefficients for blue vs. green, and 2) the larger H character for green relative to blue. It is thus the difference between the S(3p(π/σ))/P2(amide) interaction that leads to O(p)-character activation for the green site and no O(p)-character for the blue site. This hypothesis can be tested using a simple model, which can gauge the interactions between anionic 2p orbitals (of a fluoride in this case) and an isolated amide. From this simple model, the general orbital interactions outlined here for blue vs. green T1 sites are reproduced.

When an anionic 2p orbital interacts with the out-of-plane N orbital of the amide (as in the blue site), this does not result in O(p)-character (Supporting Information Figure S5, top, $N\pi$). However, when the anionic 2p orbital is allowed to interact with the N-H in-plane orbital (as is the green site), O(p)-character is activated (Supporting Information Figure S5, middle, $N\sigma_1$). Interestingly, the O(p)-character in this case is directed in-plane with respect to the amide, which would be perpendicular to the N-H group of the T2 His, an orientation that would not be productive in mediating superexchange. However, twisting the anionic 2p orbital out-of-plane (with respect to the amide) has the effect of twisting the N-H in-plane orbital so that it becomes partially out-of-plane (Supporting Information Figure S5, bottom, $N\sigma_2$). This type of interaction ($N\sigma_2$) is in fact present for the green site and can be seen in Figure 8 of the main text. Thus, the twist in the N-H orbital rotates the O(p) character towards a more favorable orientation relative to the N-H of the T2 His, which results in the high orbital overlap necessary for superexchange.

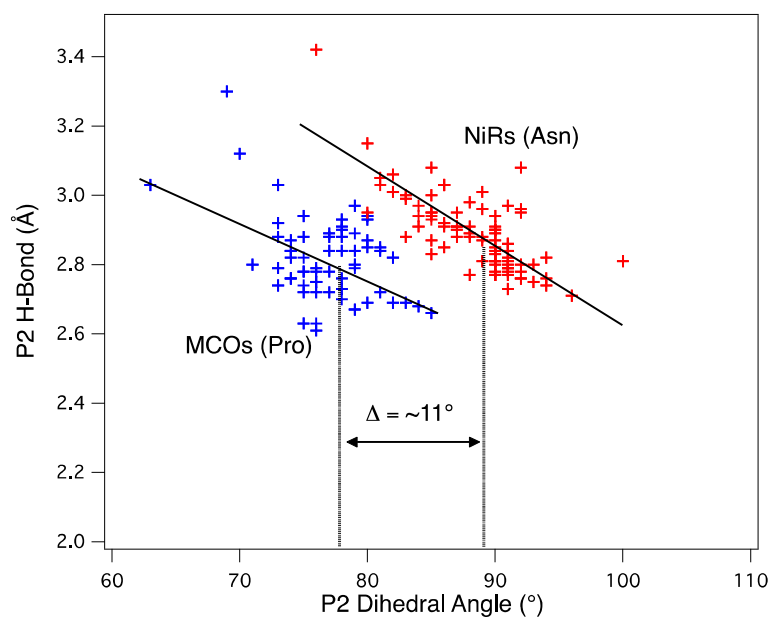


Figure S6. Plot of P2 H-bond(A) distance (between P2 O and N(His)) versus the P2 dihedral angle for NiRs (red crosses) and MCOs (blue crosses). The average values are indicated by the dotted lines, and a rough linear fit has been added for clarity.

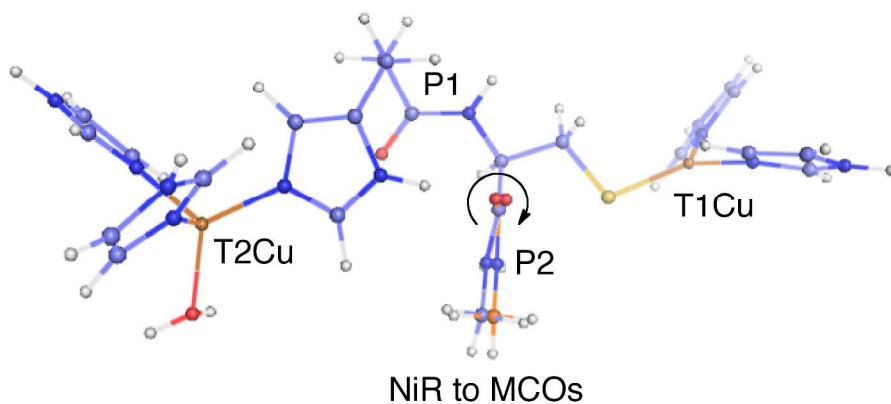


Figure S7. Structural overlays of T1/T2 of NiR and 'MCOs': Rotation of P2 in the T2(NiR) containing P-P1-P2-B and P-P1-P2-G models.

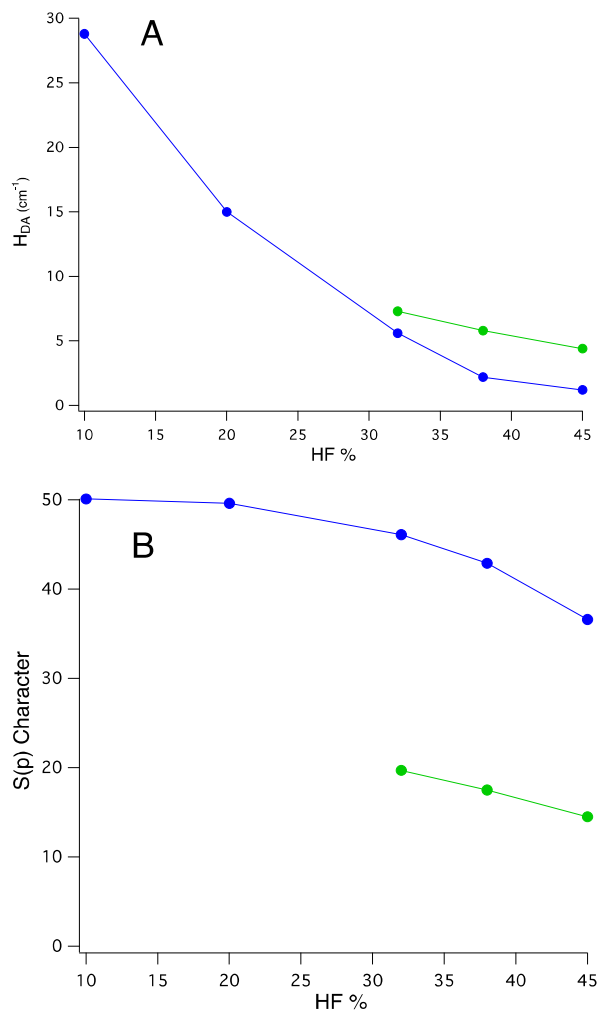


Figure S8. H_{DA} (A) and S(p)-character dependence on HF exchange for the **P-P1-P2-B** (blue) and **P-P1-P2-G** (green) models from Section 3.2.1.

The dependence of H_{DA} on the amount of HF is given in Supporting Information Figure S8A, while the dependence of S(p)-character on HF % is given in Supporting Information Figure S8B. Both H_{DA} and S(p)-character decrease as the amount of HF exchange increase, and the calculated H_{DA} for the blue site is more sensitive than the green site (for the green site, decreasing the amount of HF below 32% leads to interaction of valence orbitals without charge tuning). This reflects the greater sensitivity of the S(p)-character for the blue relative to the green site (Supporting Information Figure S8B). Thus, it is important to first calibrate the calculation of H_{DA} to the amount of HF exchange that reproduces the experimental blue T1 covalency obtained from S K-edge XAS data.¹

Supporting Information Tables

Table S1. Select bond distances and angles for blue and green T1 Cu sites and the T2 Cu sites discussed in the main text.

Active Site Model	Blue	Green
T1		
Cu-N1/2(His)	1.99	1.99
Cu-S(Cys)	2.13	2.17
Cu-S(Met)	--	2.48
S(Cys)-Cu-N1(His)	120	105
S(Cys)-Cu-N2(His)	120	153
C _β -Cu-S(Cys)	109	109
S(Cys)-Cu-S(Met)	--	88
C _β -Cu-S(Cys)-N1(His)	90	107
C _β -Cu-S(Cys)-N1(His)	-90	-90
C _β -S(Cys)-Cu-S(Met)	--	-54
T2^a	T2(σ)^a	T2(NiR)^a
Cu-N1(His)	1.99	1.98
Cu-N2(His)	1.99	2.02
Cu-N3(His)	1.99	2.00
Cu-OH ₂	1.99	2.14
N1-Cu-N2	90	119
N1-Cu-N3	90	103
N1-Cu-OH ₂	160	108
N2-Cu-N3	150	100
N2-Cu-OH ₂	95	119
N3-Cu-OH ₂	95	106
Ammine Model		
T1^b		
Cu-NH ₃ ^c	1.99	
Cu-S(Cys)	2.13	
T2(σ)		
Cu-N1(His)	1.97	
Cu-N1	1.97	
Cu-N2	1.97	
Cu-N3	1.97	

^a T2 Cu sites are the same for blue and green models.

^b Parameters are the same for blue and green models.

^c 2NH₃s with 120° S(Cys)-Cu-NH₃ angles for the blue site; 2NH₃s and 1NH₃ with 90° and 180° S(Cys)-Cu-NH₃ angles, respectively, for the green site.

Table S2. Population analyses and calculated H_{DA} for the T1 Cu sites in the 2Cu(II) T1/T2 Cu models with a linear bridge (**L-P1**).

Ligands	Ammines	Ammines	Ammines	Ammines
T1 Cu	Blue	Blue	Green	Green
Pop Method	MULL	CSPA	MULL	CSPA
Active Site				
T1				
Cu(d)	31.67	31.38	51.77	36.83
S(Cys)(p σ)	0.00	0.00	21.33	13.43
S(Cys)(p π)	57.26	47.25	0.00	0.00
2His ^a	5.97	8.48	21.81	34.51
Met ^a	-	--	--	--
T2(σ)				
Cu(d)	65.37	52.13	65.36	52.10
N1(His)(σ)	7.08	9.91	7.13	9.90
2N(His)/H ₂ O	25.76	35.32	25.72	35.37
H_{DA} (cm⁻¹)	0.0		28.1	
Ligands	Residues	Residues	Residues	Residues
T1 Cu	Blue	Blue	Green	Green
Pop Method	MULL	CSPA	MULL	CSPA
Active Site				
T1				
Cu(d)	41.63	36.33	52.50	33.41
S(Cys)(p σ)	0.05	0.04	15.90	8.50
S(Cys)(p π)	46.28	35.44	2.39	1.23
2His ^a	7.36	15.84	11.29	13.65
Met ^a	--	--	10.83	17.89
T2(σ)				
Cu(d)	71.80	56.01	71.79	56.02
N1(His)(σ)	6.19	7.68	6.21	7.69
2N(His)/H ₂ O	17.67	25.11	17.65	25.15
H_{DA} (cm⁻¹)	0.7		22.7	

^a Total character.

Table S3. Population analyses and calculated H_{DA} for the T1 Cu sites in the 2Cu(II) T1/T2 Cu models with different protein bridges (**P-P1** and **P-P1-P2**) and different T2 Cu sites (T2(σ) vs. T2(NiR)).

T1 Cu	Blue	Blue	Blue	Blue
Pathway	P-P1	P-P1	P-P1-P2	P-P1-P2
Method	MULL	CSPA	MULL	CSPA
Active Site				
T1				
Cu(d)	42.84	36.80	45.06	31.17
S(Cys)(p)	45.46	34.68	42.28	26.31
2His ^a	7.01	14.42	7.45	11.36
Met ^a	--	--	--	--
T2(σ)				
Cu(d)	70.96	54.90	70.53	54.67
N1(His)(σ)	6.70	9.47	7.16	9.54
2N(His)/H ₂ O ^a	17.80	25.13	17.63	25.70
H_{DA} (cm⁻¹)	8.7		6.9	
T1 Cu	Green	Green	Green	Green
Pathway	P-P1	P-P1	P-P1-P2	P-P1-P2
Method	MULL	CSPA	MULL	CSPA
Active Site				
T1				
Cu(d)	52.25	33.34	53.68	35.87
S(Cys)(p)	18.96	10.44	17.27	10.33
2His ^a	10.51	13.82	10.89	14.60
Met ^a	11.98	17.52	12.21	18.19
T2(σ)				
Cu(d)	70.92	54.90	70.56	54.67
N1(His)(σ)	6.75	9.48	7.24	9.57
2N(His)/H ₂ O ^a	17.78	25.21	17.62	25.80
H_{DA} (cm⁻¹)	1.2		16.4	
T1Cu	Blue	Blue	Green	Green
Pathway	P-P1-P2	P-P1-P2	P-P1-P2	P-P1-P2
Method	MULL	CSPA	MULL	CSPA
T1				
Cu(d)	44.64	31.06	53.51	35.74
S(Cys)(p)	42.90	26.78	17.46	10.41
2His ^a	7.38	11.35	10.84	14.57
Met ^a	--	--	12.20	18.20
T2(NiR)				
Cu(d)	76.84	58.74	76.85	58.65
N(His)(σ)	1.88	1.83	1.94	1.87
2N(His)/H ₂ O ^a	14.22	25.26	14.14	25.33
H_{DA} (cm⁻¹)	2.2		5.8	

^a Total character.

Table S4. Fragment analyses for the 2Cu(II) and 2Cu(I) models in **P-P1-B**.

	Blue (ox)	Blue (ox)	Blue (ox)
	P1	P1 ^a	P1 ^a
	MULL	MULL	MULL
T1		LUMO	LUMO+1
Frag1_53	49.54	25.95	26.32
Frag2_50	37.93	17.69	17.94
Frag2_48	8.98	4.21	4.27
T2(σ)			
Frag3_55	72.68	36.80	36.39
Frag3_56	10.05	5.06	4.99
Frag1_47	8.04	3.95	3.87
	Blue (red)	Blue (red)	Blue (red)
	P1	P1 ^a	P1 ^a
	MULL	MULL	MULL
T1		HOMO-1	HOMO
Frag1_53	75.91	40.60	39.25
Frag2_48	14.89	6.04	5.83
Frag2_49	6.03	2.44	2.35
T2(σ)			
Frag3_55	74.47	37.43	38.73
Frag1_47	10.49	4.70	4.85
Frag3_50	3.00	2.46	2.55

^a At resonance

Table S5. Population analyses and calculated H_{DA} for the 2Cu(II) and 2Cu(I) models in **P-P1-B**.

	Blue (ox)	Blue (ox)	Blue (ox)	Blue (ox)
	P1^a	P1^a	P1^a	P1^a
Method	MULL	MULL	CSPA	CSPA
T1	LUMO	LUMO+1	LUMO	LUMO+1
Cu(d)	20.15	20.44	16.31	16.66
S(Cys)(p)	23.84	24.21	16.95	17.34
2His	3.30	3.35	6.47	6.54
T2(σ)				
Cu(d)	35.80	35.31	29.46	29.26
N(His)(sp)	3.26	3.23	5.02	5.02
2N(His)/H ₂ O	9.01	9.88	13.33	13.28
H_{DA} (cm⁻¹)	8.7			
	Blue (red)	Blue (red)	Blue (red)	Blue (red)
	P1^a	P1^a	P1	P1
Method	MULL	MULL	CSPA	CSPA
T1	HOMO-1	HOMO	HOMO-1	HOMO
Cu(d)	8.27	7.98	7.66	7.50
S(Cys)(p)	37.57	36.34	26.49	25.96
2His	1.76	1.70	5.46	5.32
T2(σ)				
Cu(d)	33.49	34.64	29.40	30.81
N(His)(sp)	3.89	4.03	5.56	5.70
2N(His)/H ₂ O	10.06	10.41	13.55	14.23
H_{DA} (cm⁻¹)	9.2			

^a At resonance.

To perform the fragment analyses, models were divided into three fragments: 1) the bridge (including both the S(Cys) and N(His) ligands); 2) the T1 site (including the T1 Cu and 2N(His)); and 3) the T2 Cu site (including the T2 Cu, 2N(His), and H₂O). Out of resonance, three fragment orbitals contribute to the T1 β -LUMO: Frag1_53 (50 %), Frag2_50 (38 %), and Frag2_48 (9 %) (Supporting Information Table S4); and three major fragment orbitals contribute to the T2 β -LUMO: Frag3_55 (73 %), Frag3_56 (10 %), and Frag1_47 (8 %). For the T1 Cu, the major fragment orbitals, Frag1_53 and Frag2_50 are shown in Supporting Information Figure S2A. Importantly, Frag1_53 is an occupied bridge orbital while Frag2_50 is the virtual Cu(3dx²-y²) orbital. Expansion of Frag1_53 (dotted lines in Supporting Information Figure S2A) further indicates that the P1 amide π contribution is present in this occupied bridge level. The major fragment molecular orbitals for the T2 site (Frag3_55 and Frag1_47) are given in Supporting Information Figure S2B. Frag3_55 is the virtual Cu(3dx²-y²) orbital while Frag1_47 is the occupied N(His) σ orbital. Thus, both of the T1 and T2 β -LUMOs contain

contributions from the occupied bridge valence orbitals (T1 Cu: Frag1_53 and T2 Cu: Frag1_47).

Table S6. Coefficients for select P1 and P2 atoms in the β -LUMOs of the 2Cu(II) models. (T2sigma)

	Blue	Blue	Blue	Blue
	P1(P1&P2)	P1(P1&P2)	P2(P1&2)	P2(P1&2)
	MULL	CSPA	MULL	CSPA
O(s)/O(p)	0.00/0.05	0.00/0.04	0.01/-0.01	0.08/0.01
C(s)/C(p)	0.00/0.02	0.01/0.08	1.13/0.22	11.58/2.27
N(s)/N(p)	0.01/0.03	0.15/0.12	-0.17/0.10	0.76/0.26
H(total)	0.00	0.00	0.01	0.06
	Green	Green	Green	Green
	P1(P1&2)	P1(P1&P2)	P2(P1&2)	P2(P1&P2)
	MULL	CSPA	MULL	CSPA
O(s)/O(p)	0.00/0.01	0.00/0.01	0.00/0.04	0.01/0.03
C(s)/C(p)	-0.01/0.04	0.07/0.10	-0.03/-0.08	0.04/0.16
N(s)/N(p)	0.04/0.07	0.42/0.26	0.01/0.02	0.05/0.15
H(total)	0.05	0.07	0.32	0.16

Table S7. Coefficients for the P1 and P2 atoms in the β -LUMOs of the 2Cu(II) models. (T2(NiR))

	Blue	Blue	Blue	Blue
	P1(P1&P2)	P1(P1&P2)	P2(P1&2)	P2(P1&2)
	MULL	CSPA	MULL	CSPA
O(s)/O(p)	0.00/0.05	0.00/0.04	0.01/-0.01	0.07/0.01
C(s)/C(p)	0.00/0.02	0.01/0.08	1.12/0.21	11.36/2.21
N(s)/N(p)	0.01/0.04	0.16/0.12	-0.17/0.11	0.73/0.26
H(total)	0.00	0.00	0.01	0.06
	Green	Green	Green	Green
	P1(P1&2)	P1(P1&P2)	P2(P1&2)	P2(P1&P2)
	MULL	CSPA	MULL	CSPA
O(s)/O(p)	0.00/0.01	0.00/0.01	0.00/0.04	0.01/0.03
C(s)/C(p)	-0.01/0.04	0.07/0.10	-0.03/-0.08	0.04/0.16
N(s)/N(p)	0.04/0.07	0.41/0.26	0.01/0.02	0.05/0.15
H(total)	0.05	0.07	0.32	0.15

Table S8. Dihedral Angles and N-O distances from several MCO and NiR X-ray crystal structures.

Species	PDB ID	Res (Å)	Dih. Angle (°)	N-O Dist. (Å)
NiRs				
<i>A. c.</i> ^a	1NIA	2.50	87/86	2.91/3.03

	1NIB	2.70	89/89	2.96/3.01
	1NIC	1.90	82	3.01
	1NID	2.20	83	3.00
	1NIE	1.90	85	2.95
	1NIF	1.70	85	3.00
	2NRD	2.10	86	2.91
	2BW4	0.90	88	2.77
	2BW5	1.12	90	2.77
	2BWD	1.15	89	2.81
	2BWI	1.10	91	2.84
	1KCB	1.65	86	2.85
	2Y1A	1.95	90	2.83
<i>A. f.</i> ^a	1AQ8	2.00	92/90	3.08/2.94
	1AS7	2.00	76/85	3.42/3.08
	1AS6	1.80	81/88	3.05/2.98
	1AS8	1.85	86/87	3.03/2.90
	1SJM	1.40	90/92	2.81/2.80
	1SNR	1.31	92/93	2.78/2.80
	2FJS	1.85	90/89	2.77/2.88
	3H4F	2.10	88/80	2.89/2.95
	2E86	1.50	91/91	2.79/2.81
	2PPC	1.58	91/90	2.80/2.87
	2PP7	1.65	91/90	2.77/2.84
	2PP8	1.80	91/89	2.82/2.87
	2PP9	1.80	87/87	2.88/2.95
	2PPA	1.69	85/88	2.83/2.88
<i>R. s.</i> ^b	2A3T	1.85	86	2.92
	1ZV2	1.74	90	2.85
	1MZY	1.46	85	2.87
	1MZZ	2.00	83/91	2.88/2.73
	2DWS	1.85	91	2.79
	2DWT	1.90	83	2.99
	2DY2	2.26	80	3.15
<i>A. x</i> ^c	1OE1	1.04	90	2.81
	2XWZ	2.34	96/92	2.71/2.76
	2JFC	2.40	91/92	2.86/2.76
	1GS8	1.90	94	2.74
	1GS6	2.20	84	2.91
	1BQ5	2.05	93	2.75
	2VM3	1.80	91	2.86
	2VM4	1.90	91	2.97
	2VN3	2.35	82	3.06
	2VW4	1.90	90/88	2.90/2.91
	2VW6	1.90	90/89	2.90/2.86
	2VW7	1.90	87/90	2.91/2.91
	1NDT	2.10	94	2.76
	2BPO	1.90	100/92	2.81/2.95
	2BP8	1.90	94/90	2.82/2.89
	1HAU	1.90	92	2.96
	1HAW	1.90	90	2.81
	2XXO	1.46	91/	2.78/
	2XXG	1.60	90/90	2.78/2.80
<i>N. g.</i> (AniA)	1KBW	2.02	85/85/84 85/84/81	2.93/2.95/2.97 2.94/2.94/3.03

<i>H.d.</i>	2DV6	2.20	88/92/89 87/90/86	2.85/2.62/2.86 2.80/2.71/2.82
MCOs				
	1GYC	1.90	75	2.78
	2H5U	1.90	75	2.72
	2HRH	2.60	71	2.80
	2Q9O	1.30	77/80	2.78/2.69
	3FU7	1.67	79/78	2.84/2.76
	2XU9	1.50	79	2.80
	2YAR	1.80	81	2.72
	4JHU	1.89	74	2.76
	3FPX	1.80	74	2.82
	2YAE	1.80	79	2.67
	3SQR	1.67	76	2.75
	3DIV	1.76	76	2.61
	3T6V	2.00	73/77/82	2.74/2.72/2.82
	3PPS	2.50	75/76/76 78	2.78/2.75/2.79 2.73
	2QT6	1.50	73/76	2.79/2.72
	4A2E	1.80	74	2.84
	4A2H	2.30	70	3.12
	2HZH	2.60	74	2.76
	3DKH	2.40	75	2.63
	2FQD	2.40	80	2.87
	2FQE	1.92	78	2.91
	2FQF	2.00	77	2.89
	2FQG	2.30	74	2.87
	2IH8	2.00	75/75	2.94/2.88
	2IH9	2.00	73/73	2.92/3.03
	3ZDW	2.40	76	2.78
	4AKQ	2.10	78	2.90
	4AKO	1.70	80	2.83
	4AKP	2.00	80	2.94
	4A66	1.95	78	2.84
	4A67	2.10	81	2.84
	4A68	2.00	78	2.88
	2X87	2.00	79	2.97
	1GSK	1.70	78	2.93
	1W6L	2.00	77	2.84
	1W6W	2.22	74	2.84
	1W8E	2.20	77	2.88
	2BHF	2.50	80	2.85
	1AOZ	1.90	73/63	2.88/3.03
	3ZX1	1.95	81	2.85
	1V1O	1.70	69	3.30
	2XLL	2.31	84/83/85 83	2.68/2.69/2.66 2.69
	3KW8	2.29	79	2.67
	4M3H	2.20	82	2.80
	3T9W	1.50	78	2.85
	3TAS	2.30	82	2.82
	3CG8	2.68	72/77/78	2.82/2.68/2.78
	2ZWN	1.70	94/94/93	2.79/2.84/2.79

	3G5W	1.90	91/89/85 91/89/90	2.80/2.88/2.86 2.76/2.88/2.91
	3ENZ	2.60	78	2.79
	1ZPU	2.80	76/75/79 79/78/79	2.63/2.74/2.67 2.79/2.70/2.89
	3OD3	1.10	75	2.82

^a Green T1 Cu sites

^b Blue and green T1 Cu sites

^c Blue T1 Cu sites

Table S9. Population analyses and calculated H_{DA} for the 2Cu(II) T1/T2 Cu models with a protein bridge: affect of dihedral rotation.

	Blue	Blue	Blue	Blue
	P-P1-P2	P-P1-P2	P-P1-P2^a	P-P1-P2^a
Pop Method	MULL	CSPA	MULL	CSPA
T1				
Cu(d)	45.06	31.17	43.99	28.84
S(Cys)(p)	42.28	26.31	43.65	25.53
2His	7.45	11.36	7.28	10.45
T2(NiR)				
Cu(d)	76.84	58.74	76.86	58.78
N(His)(sp)	1.88	1.83	1.78	1.78
2N(His)/H ₂ O	14.22	25.26	14.35	25.10
H_{DA} (cm⁻¹)	2.2		5.5	
	Green	Green	Green	Green
	P-P1-P2	P-P1-P2	P-P1-P2^a	P-P1-P2^a
Pop Method	MULL	CSPA	MULL	CSPA
T1				
Cu(d)	53.51	35.74	53.30	35.05
S(Cys)(p)	17.46	10.41	17.86	10.37
2His	10.84	14.57	10.81	14.42
Met	12.20	18.20	11.99	17.81
T2(NiR)				
Cu(d)	76.85	58.65	76.87	58.66
N(His)(sp)	1.94	1.87	1.83	1.81
2N(His)/H ₂ O	14.14	25.33	14.26	25.14
H_{DA} (cm⁻¹)	5.8		0.4	

^a Rotate P2 to 75°

Table S10. Coefficients for P1 and P2 atoms in the β -LUMOs of the 2Cu(II) and 2Cu(I) models. (T2(NiR)-75.3°)

	Blue	Blue	Blue	Blue
	P1(P1&P2)	P1(P1&P2)	P2(P1&P2)	P2(P1&P2)
Pop Method	MULL	CSPA	MULL	CSPA
O(s)/O(p)	0.00/0.05	0.00/0.04	0.01/0.01	0.01/0.05
C(s)/C(p)	0.00/0.02	0.00/0.08	1.33/0.13	14.49/2.47
N(s)/N(p)	0.02/0.01	0.12/0.11	0.01/0.02	0.12/0.11
H(total)	0.00	0.01	0.01	0.02
	Green	Green	Green	Green
	P1(P1&2)	P1(P1&P2)	P2(P1&2)	P2(P1&P2)
Pop Method	MULL	CSPA	MULL	CSPA
O(s)/O(p)	0.00/0.01	0.00/0.01	0.00/0.01	0.01/0.00
C(s)/C(p)	-0.01/0.04	0.06/0.10	0.04/-0.02	0.06/0.08
N(s)/N(p)	0.04/0.07	0.48/0.30	-0.01/0.03	0.04/0.08
H(total)	0.05	0.08	0.18	0.09

Table S11. Hartree-Fock dependence of H_{DA} for **L-P1-G** for both 2Cu(II) and 2Cu(I) models.

%HF	H_{DA}^a (cm^{-1})	-2J (cm^{-1})	$H_{DA}(\text{MV})$ (cm^{-1})
32	24.7	0.137	42.4
38	22.7	0.066	29.5
50	18.7	0.027	18.7

^a H_{DA} obtained using charge tuning as outline in the Methods section.^b H_{DA} obtained using eqns. 3 and 4 and $U = 6.5 \text{ eV}$ ($52\,426 \text{ cm}^{-1}$).

Full Reference 34:

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Supporting Information References

(1) Shadle, S. E.; Penner-Hahn, J. E.; Schugar, H. J.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1993**, *115*, 767.

Cartesian Coordinates of several models discussed in the text:

L-P1-B

C	-1.30067612	-2.32080961	0.00000000
N	-0.57938920	-1.06505330	0.00000000
C	-1.18958294	0.11220770	0.00000000
O	-2.41200783	0.25157333	0.00000000
C	-0.27234275	1.31232937	0.00000000
C	-1.10891470	2.60235501	0.00000000
C	-0.29067101	3.86427177	0.00000000
N	1.08852485	3.90038367	0.00000000
C	-0.69267267	5.15936545	0.00000000
C	1.47652879	5.18927072	0.00000000
N	0.43675405	5.98634790	0.00000000
C	-0.29105824	-3.46900489	0.00000000
H	0.33850343	-3.33022970	-0.88043555
H	0.33850343	-3.33022970	0.88043555
H	0.42561107	-1.11203283	0.00000000
H	2.50307001	5.50066866	0.00000000
H	1.69471850	3.07414452	0.00000000
H	-1.68826888	5.55994231	0.00000000
H	0.34594706	1.28855398	0.87225103
H	-1.73104846	2.60414073	0.89674672
H	-1.73104846	2.60414073	-0.89674672
H	-1.91558858	-2.38255077	-0.87317825
H	0.34594706	1.28855398	-0.87225103
H	-1.91558858	-2.38255077	0.87317825
S	-1.03822104	-5.11503693	0.00000000
Cu	0.50902202	-6.57891497	0.00000000
H	2.37555834	-9.18540944	3.91052022
N	2.01577677	-8.40562030	3.36072650
C	1.82683581	-7.12790927	3.82205159
C	1.65798078	-8.46275512	2.09295340
C	1.31614894	-6.40432095	2.79565945
H	2.04484125	-6.76557986	4.81573014
N	1.22617237	-7.26868834	1.72337113
H	1.70760005	-9.33817019	1.46182713
H	1.03623285	-5.36196248	2.81359792
N	1.22617237	-7.26868834	-1.72337113
C	0.48637696	-7.46613346	-2.87086543
C	2.48061361	-7.60692462	-1.94353326
C	1.34779520	-7.96694359	-3.79040706

H	-0.56549006	-7.26336361	-3.00890229
N	2.58247266	-8.04564561	-3.18686453
H	3.28882918	-7.53645381	-1.23069424
H	1.11110060	-8.25015738	-4.80589641
H	3.43660946	-8.38867159	-3.62699803
Cu	0.39199573	7.97584449	0.00000000
N	0.90051623	8.17250849	1.91385218
O	-0.33045825	9.83005270	-0.00849414
N	0.90051623	8.17250850	-1.91385219
C	1.65706295	9.13794464	2.44294261
C	0.53770812	7.33256857	2.95888231
H	-0.79466619	10.07025283	0.7967479
H	-0.77136474	10.06677884	-0.82773903
C	0.55159409	7.36471612	-2.91888522
C	1.68717110	9.17636590	-2.46399870
N	1.78219571	8.94334988	3.77958171
H	2.11873607	9.95784007	1.90276296
C	1.07867636	7.80510937	4.12786881
H	-0.07660933	6.45357133	2.79953395
N	1.08247865	7.82096796	-4.08083413
H	-0.05603113	6.46940240	-2.83907552
C	1.80472971	8.96973602	-3.81527771
H	2.11356257	9.96671892	-1.85658914
H	1.02881898	7.44209976	5.14814927
H	0.97299854	7.38408750	-4.99295214
H	2.32502269	9.52127667	-4.59008871
H	2.30623965	9.53601451	4.41906940

L-P1-G

C	-1.30067612	-2.32080961	0.00000000
N	-0.57938920	-1.06505330	0.00000000
C	-1.18958294	0.11220770	0.00000000
O	-2.41200783	0.25157333	0.00000000
C	-0.27234275	1.31232937	0.00000000
C	-1.10891470	2.60235501	0.00000000
C	-0.29067101	3.86427177	0.00000000
N	1.08852485	3.90038367	0.00000000
C	-0.69267267	5.15936545	0.00000000
C	1.47652879	5.18927072	0.00000000
N	0.43675405	5.98634790	0.00000000
C	-0.29105824	-3.46900489	0.00000000
H	0.33850343	-3.33022970	-0.88043555
H	0.33850343	-3.33022970	0.88043555
H	0.42561107	-1.11203283	0.00000000
H	2.50307001	5.50066866	0.00000000
H	1.69471850	3.07414452	0.00000000

H	-1.68826888	5.55994231	0.00000000
H	0.34594706	1.28855398	0.87225103
H	-1.73104846	2.60414073	0.89674672
H	-1.73104846	2.60414073	-0.89674672
H	-1.91558858	-2.38255077	-0.87317825
H	0.34594706	1.28855398	-0.87225103
H	-1.91558858	-2.38255077	0.87317825
S	-1.03822104	-5.11503693	0.00000000
Cu	0.53807823	-6.60640564	0.00000000
H	0.53938120	-9.40319856	4.21282415
N	0.52555145	-8.58591665	3.60319637
C	0.44014791	-7.28280037	4.02231353
C	0.58727947	-8.61129547	2.28635296
C	0.42783278	-6.50609609	2.91125963
H	0.39276905	-6.93941901	5.04507964
N	0.52597294	-7.36861812	1.83820173
H	0.67221237	-9.49817581	1.67531805
H	0.35573060	-5.42972849	2.87357584
S	1.47643077	-5.48868099	-2.00513992
C	1.92695470	-3.74342900	-1.93674645
C	1.20510972	-5.43071560	-3.77048348
H	1.97177380	-3.41963328	-0.89676732
H	1.17894924	-3.15401304	-2.46761616
H	2.90112192	-3.60000508	-2.40432830
H	0.99942145	-6.43505516	-4.13878141
H	2.09445235	-5.03785955	-4.26282465
H	0.35484588	-4.78345232	-3.98645483
N	1.82312129	-7.82811629	-0.90343091
C	2.81594440	-8.54739084	-0.27099800
C	1.85623996	-8.07416801	-2.19759461
C	3.47111104	-9.22098061	-1.24846538
H	3.02859878	-8.56939844	0.78772188
N	2.85415781	-8.90774887	-2.43848244
H	1.18223102	-7.66605724	-2.93615777
H	4.31724383	-9.88029861	-1.11880395
H	3.12448057	-9.26008489	-3.35702418
Cu	0.39199573	7.97584449	0.00000000
N	0.90051623	8.17250849	1.91385218
O	-0.33045825	9.83005270	-0.00849414
N	0.90051623	8.17250850	-1.91385219
C	1.65706295	9.13794464	2.44294261
C	0.53770812	7.33256857	2.95888231
H	-0.79466619	10.07025283	0.79674799
H	-0.77136474	10.06677884	-0.82773903
C	0.55159409	7.36471612	-2.91888522
C	1.68717110	9.17636590	-2.46399870

N	1.78219571	8.94334988	3.77958171
H	2.11873607	9.95784007	1.90276296
C	1.07867636	7.80510937	4.12786881
H	-0.07660933	6.45357133	2.79953395
N	1.08247865	7.82096796	-4.08083413
H	-0.05603113	6.46940240	-2.83907552
C	1.80472971	8.96973602	-3.81527771
H	2.11356257	9.96671892	-1.85658914
H	1.02881898	7.44209976	5.14814927
H	0.97299854	7.38408750	-4.99295214
H	2.32502269	9.52127667	-4.59008871
H	2.30623965	9.53601451	4.41906940

P-P1-B

N	-2.06995483	0.52684021	-0.16208373
N	-4.25196841	0.40206572	-0.04409605
N	1.03687468	-1.23451310	-1.13598871
C	-0.95016145	-1.69036241	-2.39698626
C	-0.17118080	-1.78038966	-1.10597648
C	-1.57201863	-0.28930475	-2.52904717
C	-2.49199016	0.08083357	-1.39706926
C	-3.84399753	0.01397338	-1.32207731
C	-3.15294351	0.69998096	0.61790077
C	1.90387024	-1.18755453	0.02301630
C	3.30291669	-0.76371400	-0.42498954
O	-0.65224412	-2.32830139	-0.11495841
S	4.46193506	-0.47577706	0.93200816
H	3.66984358	-1.54831154	-1.08750697
H	3.19324621	0.14691794	-1.02061347
H	1.35192990	-0.75357798	-1.96200542
H	-3.10691540	1.05701666	1.62788687
H	-1.09293927	0.70075161	0.09491708
H	-4.54802549	-0.31998479	-2.05806955
H	-0.29217271	-1.86646199	-3.22297400
H	-2.14600813	-0.25828370	-3.45605296
H	-0.78094196	0.46061129	-2.62707085
H	1.94998290	-2.15568947	0.47632454
H	-1.72623592	-2.42628388	-2.39696301
H	1.52258366	-0.47876717	0.72809858
Cu	6.34595473	0.10247330	0.12392625
N	6.74747180	2.02682490	-0.18551671
C	7.93084865	2.62852390	-0.03738116
C	5.85166082	3.00510803	-0.59746521
N	7.81852062	3.94525984	-0.34351558
H	8.85276507	2.15674614	0.28613162
C	6.50885408	4.20487304	-0.70297266

H	4.80695461	2.78257867	-0.78316276
H	8.57198982	4.62766473	-0.30586670
H	6.17053231	5.19342986	-0.99198434
N	7.71067912	-1.28042604	-0.30644196
C	7.93071679	-2.41791866	0.35843437
C	8.61936878	-1.25029762	-1.35648583
N	8.93801306	-3.10817442	-0.23235376
H	7.40188896	-2.75421139	1.24410530
C	9.38770951	-2.38651086	-1.32267923
H	8.66089475	-0.42095915	-2.05354197
H	9.30521326	-4.00341308	0.08152751
H	10.19340623	-2.73559171	-1.95846954
Cu	-6.11889520	0.48776737	0.63952636
N	-6.42825926	2.14778860	-0.41343299
C	-7.56586520	2.51299725	-1.01079548
C	-5.50323211	3.15165692	-0.66992847
N	-7.39695304	3.70829179	-1.62955962
H	-8.49338104	1.95015081	-1.01990041
C	-6.09682643	4.13188171	-1.42443229
H	-4.48464853	3.09857695	-0.30239073
H	-8.10761834	4.20422079	-2.16230622
H	-5.72011584	5.06644983	-1.82431417
N	-6.15878411	-1.49691003	0.77939956
C	-5.13885591	-2.29386379	1.10951735
C	-7.25254918	-2.32244882	0.55272704
N	-5.54626783	-3.58774193	1.10458808
H	-4.12762751	-1.97646768	1.34155503
C	-6.88366971	-3.62824379	0.75594693
H	-8.21747735	-1.92566458	0.25795619
H	-4.96110904	-4.39293453	1.31450180
H	-7.43760931	-4.55731936	0.68381184
O	-7.64246984	0.78281135	1.88522671
H	-7.78229581	1.70377251	2.11734573
H	-7.66566218	0.16241093	2.61745989

P-P1-G

N	-2.06995483	0.52684021	-0.16208373
N	-4.25196841	0.40206572	-0.04409605
N	1.03687468	-1.23451310	-1.13598871
C	-0.95016145	-1.69036241	-2.39698626
C	-0.17118080	-1.78038966	-1.10597648
C	-1.57201863	-0.28930475	-2.52904717
C	-2.49199016	0.08083357	-1.39706926
C	-3.84399753	0.01397338	-1.32207731
C	-3.15294351	0.69998096	0.61790077
C	1.90387024	-1.18755453	0.02301630

C	3.30291669	-0.76371400	-0.42498954
O	-0.65224412	-2.32830139	-0.11495841
S	4.46193506	-0.47577706	0.93200816
H	3.66984358	-1.54831154	-1.08750697
H	3.19324621	0.14691794	-1.02061347
H	1.35192990	-0.75357798	-1.96200542
H	-3.10691540	1.05701666	1.62788687
H	-1.09293927	0.70075161	0.09491708
H	-4.54802549	-0.31998479	-2.05806955
H	-0.29217271	-1.86646199	-3.22297400
H	-2.14600813	-0.25828370	-3.45605296
H	-0.78094196	0.46061129	-2.62707085
H	1.94998290	-2.15568947	0.47632454
H	-1.72623592	-2.42628388	-2.39696301
Cu	6.38133539	0.11333246	0.10875100
Cu	-6.11889520	0.48776737	0.63952636
N	6.53314948	2.05908872	0.49744762
C	7.60492919	2.69515390	0.97815121
C	5.54525192	3.01947857	0.32158831
N	7.33439231	4.01803902	1.10820576
H	8.55481185	2.24093430	1.24001404
C	6.03441505	4.24553393	0.69572541
H	4.56028212	2.76508743	-0.05328981
H	7.97947381	4.72201006	1.45906802
H	5.58539477	5.23219126	0.70677388
N	8.20374118	-0.27184442	-0.59166026
C	8.82943980	-1.45199201	-0.58073036
C	9.07209875	0.63422819	-1.18681091
N	10.05499336	-1.32775737	-1.14880925
H	8.43889202	-2.37981838	-0.17603872
C	10.22840902	-0.01344696	-1.54168322
H	8.81059823	1.67874270	-1.31338455
H	10.73473545	-2.07656496	-1.25857079
H	11.13501614	0.33426824	-2.02375338
N	-6.42825926	2.14778860	-0.41343299
C	-7.56586520	2.51299725	-1.01079548
C	-5.50323211	3.15165692	-0.66992847
N	-7.39695304	3.70829179	-1.62955962
H	-8.49338104	1.95015081	-1.01990041
C	-6.09682643	4.13188171	-1.42443229
H	-4.48464853	3.09857695	-0.30239073
H	-8.10761834	4.20422079	-2.16230622
H	-5.72011584	5.06644983	-1.82431417
N	-6.15878411	-1.49691003	0.77939956
C	-5.13885591	-2.29386379	1.10951735
C	-7.25254918	-2.32244882	0.55272704

N	-5.54626783	-3.58774193	1.10458808
H	-4.12762751	-1.97646768	1.34155503
C	-6.88366971	-3.62824379	0.75594693
H	-8.21747735	-1.92566458	0.25795619
H	-4.96110904	-4.39293453	1.31450180
H	-7.43760931	-4.55731936	0.68381184
O	-7.64246984	0.78281135	1.88522671
H	-7.78229581	1.70377251	2.11734573
H	-7.66566218	0.16241093	2.61745989
S	6.32092705	-1.94337545	-1.27569958
C	6.89404884	-3.61124384	-0.89935339
C	4.92546220	-2.47569523	-2.25572533
H	7.60614104	-3.57392329	-0.07496671
H	7.25990313	-4.08452251	-1.81053256
H	6.07750821	-4.18684655	-0.46331617
H	4.25853890	-1.63090022	-2.42820684
H	4.30673105	-3.15483766	-1.66907409
H	5.28264818	-2.97631915	-3.15557375
H	1.52258366	-0.47876717	0.72809858

P-P1-P2-B (T2 σ)

N	-2.06995483	0.52684021	-0.16208373
N	-4.25196841	0.40206572	-0.04409605
N	1.03687468	-1.23451310	-1.13598871
N	1.39093612	-0.36041297	2.26697918
C	-0.95016145	-1.69036241	-2.39698626
C	-0.17118080	-1.78038966	-1.10597648
C	-1.57201863	-0.28930475	-2.52904717
C	-2.49199016	0.08083357	-1.39706926
C	-3.84399753	0.01397338	-1.32207731
C	-3.15294351	0.69998096	0.61790077
C	1.90387024	-1.18755453	0.02301630
C	3.30291669	-0.76371400	-0.42498954
C	1.27596805	-0.14745359	0.95896976
C	0.81502149	0.56068475	3.25393781
O	-0.65224412	-2.32830139	-0.1149584
O	0.64306834	0.80759208	0.49892658
S	4.46193506	-0.47577706	0.93200816
H	3.66984358	-1.54831154	-1.08750697
H	3.19324621	0.14691794	-1.02061347
H	1.35192990	-0.75357798	-1.96200542
H	-3.10691540	1.05701666	1.62788687
H	-1.09293927	0.70075161	0.09491708
H	-4.54802549	-0.31998479	-2.05806955
H	-0.29217271	-1.86646199	-3.22297400
H	-2.14600813	-0.25828370	-3.45605296

H	-0.78094196	0.46061129	-2.62707085
H	1.96262468	-1.13592437	2.57373359
H	-0.24385033	0.61940374	3.11166149
H	1.92976783	-2.16153778	0.50805542
H	-1.72623592	-2.42628388	-2.39696301
Cu	6.34595473	0.10247330	0.12392625
Cu	-6.11889520	0.48776737	0.63952636
N	6.74747180	2.02682490	-0.18551671
C	7.93084865	2.62852390	-0.03738116
C	5.85166082	3.00510803	-0.59746521
N	7.81852062	3.94525984	-0.34351558
H	8.85276507	2.15674614	0.28613162
C	6.50885408	4.20487304	-0.70297266
H	4.80695461	2.78257867	-0.78316276
H	8.57198982	4.62766473	-0.30586670
H	6.17053231	5.19342986	-0.99198434
N	7.71067912	-1.28042604	-0.30644196
C	7.93071679	-2.41791866	0.35843437
C	8.61936878	-1.25029762	-1.35648583
N	8.93801306	-3.10817442	-0.23235376
H	7.40188896	-2.75421139	1.24410530
C	9.38770951	-2.38651086	-1.32267923
H	8.66089475	-0.42095915	-2.05354197
H	9.30521326	-4.00341308	0.08152751
H	10.19340623	-2.73559171	-1.9584695
N	-6.42825926	2.14778860	-0.41343299
C	-7.56586520	2.51299725	-1.01079548
C	-5.50323211	3.15165692	-0.66992847
N	-7.39695304	3.70829179	-1.62955962
H	-8.49338104	1.95015081	-1.01990041
C	-6.09682643	4.13188171	-1.42443229
H	-4.48464853	3.09857695	-0.30239073
H	-8.10761834	4.20422079	-2.16230622
H	-5.72011584	5.06644983	-1.82431417
N	-6.15878411	-1.49691003	0.77939956
C	-5.13885591	-2.29386379	1.10951735
C	-7.25254918	-2.32244882	0.55272704
N	-5.54626783	-3.58774193	1.10458808
H	-4.12762751	-1.97646768	1.34155503
C	-6.88366971	-3.62824379	0.75594693
H	-8.21747735	-1.92566458	0.25795619
H	-4.96110904	-4.39293453	1.31450180
H	-7.43760931	-4.55731936	0.68381184
O	-7.64246984	0.78281135	1.88522671
H	-7.78229581	1.70377251	2.11734573
H	-7.66566218	0.16241093	2.61745989

H	1.02300780	0.20208902	4.24037118
H	1.24605107	1.53206438	3.12929787

P-P1-P2-G (T2 σ)

N	-2.06995483	0.52684021	-0.16208373
N	-4.25196841	0.40206572	-0.04409605
N	1.03687468	-1.23451310	-1.13598871
N	1.39093612	-0.36041297	2.26697918
C	-0.95016145	-1.69036241	-2.39698626
C	-0.17118080	-1.78038966	-1.10597648
C	-1.57201863	-0.28930475	-2.52904717
C	-2.49199016	0.08083357	-1.39706926
C	-3.84399753	0.01397338	-1.32207731
C	-3.15294351	0.69998096	0.61790077
C	1.90387024	-1.18755453	0.02301630
C	3.30291669	-0.76371400	-0.42498954
C	1.27596805	-0.14745359	0.95896976
C	0.81502149	0.56068475	3.25393781
O	-0.65224412	-2.32830139	-0.1149584
O	0.64306834	0.80759208	0.49892658
S	4.46193506	-0.47577706	0.93200816
H	3.66984358	-1.54831154	-1.08750697
H	3.19324621	0.14691794	-1.02061347
H	1.35192990	-0.75357798	-1.96200542
H	-3.10691540	1.05701666	1.62788687
H	-1.09293927	0.70075161	0.09491708
H	-4.54802549	-0.31998479	-2.05806955
H	-0.29217271	-1.86646199	-3.22297400
H	-2.14600813	-0.25828370	-3.45605296
H	-0.78094196	0.46061129	-2.62707085
H	1.96262468	-1.13592437	2.57373359
H	-0.24385033	0.61940375	3.11166149
H	1.92976783	-2.16153778	0.50805542
H	-1.72623592	-2.42628388	-2.39696301
Cu	6.38133539	0.11333246	0.10875100
Cu	-6.11889520	0.48776737	0.63952636
N	6.53314948	2.05908872	0.49744762
C	7.60492919	2.69515390	0.97815121
C	5.54525192	3.01947857	0.32158831
N	7.33439231	4.01803902	1.10820576
H	8.55481185	2.24093430	1.24001404
C	6.03441505	4.24553393	0.69572541
H	4.56028212	2.76508743	-0.05328981
H	7.97947381	4.72201006	1.45906802
H	5.58539477	5.23219126	0.70677388
N	8.20374118	-0.27184442	-0.59166026

C	8.82943980	-1.45199201	-0.58073036
C	9.07209875	0.63422819	-1.18681091
N	10.05499336	-1.32775737	-1.1488095
H	8.43889202	-2.37981838	-0.17603872
C	10.22840902	-0.01344696	-1.54168322
H	8.81059823	1.67874270	-1.31338455
H	10.73473545	-2.07656496	-1.2585707
H	11.13501614	0.33426824	-2.02375338
N	-6.42825926	2.14778860	-0.41343299
C	-7.56586520	2.51299725	-1.01079548
C	-5.50323211	3.15165692	-0.66992847
N	-7.39695304	3.70829179	-1.62955962
H	-8.49338104	1.95015081	-1.01990041
C	-6.09682643	4.13188171	-1.42443229
H	-4.48464853	3.09857695	-0.30239073
H	-8.10761834	4.20422079	-2.16230622
H	-5.72011584	5.06644983	-1.82431417
N	-6.15878411	-1.49691003	0.77939956
C	-5.13885591	-2.29386379	1.10951735
C	-7.25254918	-2.32244882	0.55272704
N	-5.54626783	-3.58774193	1.10458808
H	-4.12762751	-1.97646768	1.34155503
C	-6.88366971	-3.62824379	0.75594693
H	-8.21747735	-1.92566458	0.25795619
H	-4.96110904	-4.39293453	1.31450180
H	-7.43760931	-4.55731936	0.68381184
O	-7.64246984	0.78281135	1.88522671
H	-7.78229581	1.70377251	2.11734573
H	-7.66566218	0.16241093	2.61745989
S	6.32092705	-1.94337545	-1.27569958
C	6.89404884	-3.61124384	-0.89935339
C	4.92546220	-2.47569523	-2.25572533
H	7.60614104	-3.57392329	-0.07496671
H	7.25990313	-4.08452251	-1.81053256
H	6.07750821	-4.18684655	-0.46331617
H	4.25853890	-1.63090022	-2.42820684
H	4.30673105	-3.15483766	-1.66907409
H	5.28264818	-2.97631915	-3.15557375
H	1.02300780	0.20208902	4.24037118
H	1.24605108	1.53206438	3.12929787

P-P1-P2-B (T2(NiR))

N	-2.06995483	0.52684021	-0.16208373
N	-4.25196841	0.40206572	-0.04409605
N	1.03687468	-1.23451310	-1.13598871
N	1.39093612	-0.36041297	2.26697918

C	-0.95016145	-1.69036241	-2.39698626
C	-0.17118080	-1.78038966	-1.10597648
C	-1.57201863	-0.28930475	-2.52904717
C	-2.49199016	0.08083357	-1.39706926
C	-3.84399753	0.01397338	-1.32207731
C	-3.15294351	0.69998096	0.61790077
C	1.90387024	-1.18755453	0.02301630
C	3.30291669	-0.76371400	-0.42498954
C	1.27596805	-0.14745359	0.95896976
C	0.81502149	0.56068475	3.25393781
O	-0.65224412	-2.32830139	-0.1149584
O	0.64306834	0.80759208	0.49892658
S	4.46193506	-0.47577706	0.93200816
H	3.66984358	-1.54831154	-1.08750697
H	3.19324621	0.14691794	-1.02061347
H	1.35192990	-0.75357798	-1.96200542
H	-3.10691540	1.05701666	1.62788687
H	-1.09293927	0.70075161	0.09491708
H	-4.54802549	-0.31998479	-2.05806955
H	-0.29217271	-1.86646199	-3.22297400
H	-2.14600813	-0.25828370	-3.45605296
H	-0.78094196	0.46061129	-2.62707085
H	1.96262468	-1.13592437	2.57373359
H	-0.24385033	0.61940375	3.11166149
H	1.92976783	-2.16153778	0.50805542
H	-1.72623592	-2.42628388	-2.39696301
Cu	6.34595474	0.10247330	0.12392625
Cu	-6.10576104	0.48716444	0.63471696
N	6.74750635	2.02681528	-0.18553176
C	7.93089363	2.62849453	-0.03739925
C	5.85171334	3.00511090	-0.59748963
N	7.81858938	3.94522997	-0.34354457
H	8.85280119	2.15670309	0.28611881
C	6.50892800	4.20486342	-0.70300582
H	4.80700348	2.78259852	-0.78318700
H	8.57207060	4.62762183	-0.30590007
H	6.17062418	5.19342388	-0.99202608
N	7.71070282	-1.28039840	-0.30645563
C	7.93076188	-2.41789247	0.35841113
C	8.61938999	-1.25024542	-1.35650095
N	8.93806927	-3.10812563	-0.23238444
H	7.40194165	-2.75420170	1.24408033
C	9.38775091	-2.38644533	-1.32270493
H	8.66089999	-0.42090061	-2.05355049
H	9.30528592	-4.00336032	0.08148894
H	10.19345263	-2.73550679	-1.9584995

N	-7.26720033	2.06377441	0.12688946
C	-6.99950009	2.98496714	-0.80268417
C	-8.49781103	2.39857387	0.67709252
N	-8.01327259	3.88420714	-0.86402058
H	-6.10860298	3.03110386	-1.42021019
C	-8.97449897	3.53001110	0.06464721
H	-8.94869945	1.81219540	1.46972982
H	-8.05326657	4.68906723	-1.48483488
H	-9.88591532	4.10019475	0.20409185
N	-7.01987863	-0.97273839	-0.38168491
C	-8.08150418	-0.84342329	-1.18205694
C	-6.67410213	-2.31793015	-0.39238560
N	-8.41624255	-2.05148528	-1.70038683
H	-8.61591001	0.07699248	-1.39279339
C	-7.53555242	-3.00001089	-1.21405473
H	-5.84192785	-2.69938479	0.18846918
H	-9.19175220	-2.22876743	-2.33439434
H	-7.59999058	-4.04713062	-1.48722491
O	-6.07997633	-0.15673654	2.67853096
H	-5.42851417	-0.83710099	2.86373696
H	-6.95436851	-0.30920324	3.04430713
H	1.02300780	0.20208902	4.24037118
H	1.24605108	1.53206438	3.12929787

P-P1-P2-G (T2(NiR))

N	-2.06995483	0.52684021	-0.16208373
N	-4.25196841	0.40206572	-0.04409605
N	1.03687468	-1.23451310	-1.13598871
N	1.39093612	-0.36041297	2.26697918
C	-0.95016145	-1.69036241	-2.39698626
C	-0.17118080	-1.78038966	-1.10597648
C	-1.57201863	-0.28930475	-2.52904717
C	-2.49199016	0.08083357	-1.39706926
C	-3.84399753	0.01397338	-1.32207731
C	-3.15294351	0.69998096	0.61790077
C	1.90387024	-1.18755453	0.02301630
C	3.30291669	-0.76371400	-0.42498954
C	1.27596805	-0.14745359	0.95896976
C	0.81502149	0.56068475	3.25393781
O	-0.65224412	-2.32830139	-0.11495841
O	0.64306834	0.80759208	0.49892658
S	4.46193506	-0.47577706	0.93200816
H	3.66984358	-1.54831154	-1.08750697
H	3.19324621	0.14691794	-1.02061347
H	1.35192990	-0.75357798	-1.96200542
H	-3.10691540	1.05701666	1.62788687

H	-1.09293927	0.70075161	0.09491708
H	-4.54802549	-0.31998479	-2.05806955
H	-0.29217271	-1.86646199	-3.22297400
H	-2.14600813	-0.25828370	-3.45605296
H	-0.78094196	0.46061129	-2.62707085
H	1.96262468	-1.13592437	2.57373359
H	-0.24385033	0.61940375	3.11166149
H	1.92976783	-2.16153778	0.50805542
H	-1.72623592	-2.42628388	-2.39696301
Cu	6.38133539	0.11333246	0.10875100
Cu	-6.10576104	0.48716444	0.63471696
N	6.53314948	2.05908872	0.49744762
C	7.60492919	2.69515390	0.97815121
C	5.54525192	3.01947857	0.32158831
N	7.33439231	4.01803902	1.10820576
H	8.55481185	2.24093430	1.24001404
C	6.03441505	4.24553393	0.69572541
H	4.56028212	2.76508743	-0.05328981
H	7.97947381	4.72201006	1.45906802
H	5.58539477	5.23219126	0.70677388
N	8.20374118	-0.27184442	-0.59166026
C	8.82943980	-1.45199201	-0.58073036
C	9.07209875	0.63422819	-1.18681091
N	10.05499336	-1.32775737	-1.1488092
H	8.43889202	-2.37981838	-0.17603872
C	10.22840902	-0.01344696	-1.54168322
H	8.81059823	1.67874270	-1.31338455
H	10.73473545	-2.07656496	-1.25857079
H	11.13501614	0.33426824	-2.02375338
N	-7.26720033	2.06377441	0.12688946
C	-6.99950009	2.98496714	-0.80268417
C	-8.49781103	2.39857387	0.67709252
N	-8.01327259	3.88420714	-0.86402058
H	-6.10860298	3.03110386	-1.42021019
C	-8.97449897	3.53001110	0.06464721
H	-8.94869945	1.81219540	1.46972982
H	-8.05326657	4.68906723	-1.48483488
H	-9.88591532	4.10019475	0.20409185
N	-7.01987863	-0.97273839	-0.38168491
C	-8.08150418	-0.84342329	-1.18205694
C	-6.67410213	-2.31793015	-0.39238560
N	-8.41624255	-2.05148528	-1.70038683
H	-8.61591001	0.07699248	-1.39279339
C	-7.53555242	-3.00001089	-1.21405473
H	-5.84192785	-2.69938479	0.18846918
H	-9.19175220	-2.22876743	-2.33439434

H	-7.59999058	-4.04713062	-1.48722491
O	-6.07997633	-0.15673654	2.67853096
H	-5.42851417	-0.83710099	2.86373696
H	-6.95436851	-0.30920324	3.04430713
S	6.32092705	-1.94337545	-1.27569958
C	6.89404884	-3.61124384	-0.89935339
C	4.92546220	-2.47569523	-2.25572533
H	7.60614104	-3.57392329	-0.07496671
H	7.25990313	-4.08452251	-1.81053256
H	6.07750821	-4.18684655	-0.46331617
H	4.25853890	-1.63090022	-2.42820684
H	4.30673105	-3.15483766	-1.66907409
H	5.28264818	-2.97631915	-3.15557375
H	1.02300780	0.20208902	4.24037118
H	1.24605108	1.53206438	3.12929787

P-P1-P2-B (T2(NiR); dihedral rotated)

N	-2.06995483	0.52684021	-0.16208373
N	-4.25196841	0.40206572	-0.04409605
N	1.03687468	-1.23451310	-1.13598871
N	1.17430855	-0.47149711	2.24509539
C	-0.95016145	-1.69036241	-2.39698626
C	-0.17118080	-1.78038966	-1.10597648
C	-1.57201863	-0.28930475	-2.52904717
C	-2.49199016	0.08083357	-1.39706926
C	-3.84399753	0.01397338	-1.32207731
C	-3.15294351	0.69998096	0.61790077
C	1.90387024	-1.18755453	0.02301630
C	3.30291669	-0.76371400	-0.42498954
C	1.27596805	-0.14745359	0.95896976
C	0.57588394	0.44030803	3.22727937
O	-0.65224412	-2.32830139	-0.1149584
O	0.83487954	0.91429486	0.50903072
S	4.46193506	-0.47577706	0.93200816
H	3.66984358	-1.54831154	-1.08750697
H	3.19324621	0.14691794	-1.02061347
H	1.35192990	-0.75357798	-1.96200542
H	-3.10691540	1.05701666	1.62788687
H	-1.09293927	0.70075161	0.09491708
H	-4.54802549	-0.31998479	-2.05806955
H	-0.29217271	-1.86646199	-3.22297400
H	-2.14600813	-0.25828370	-3.45605296
H	-0.78094196	0.46061129	-2.62707085
H	1.59887980	-1.33620671	2.55227703
H	-0.43661127	0.64804573	2.95051506
H	1.92976783	-2.16153778	0.50805542

H	-1.72623592	-2.42628388	-2.39696301
Cu	6.34595474	0.10247330	0.12392625
Cu	-6.10576104	0.48716444	0.63471696
N	6.74750635	2.02681528	-0.18553176
C	7.93089363	2.62849453	-0.03739925
C	5.85171334	3.00511090	-0.59748963
N	7.81858938	3.94522997	-0.34354457
H	8.85280119	2.15670309	0.28611881
C	6.50892800	4.20486342	-0.70300582
H	4.80700348	2.78259852	-0.78318700
H	8.57207060	4.62762183	-0.30590007
H	6.17062418	5.19342388	-0.99202608
N	7.71070282	-1.28039840	-0.30645563
C	7.93076188	-2.41789247	0.35841113
C	8.61938999	-1.25024542	-1.35650095
N	8.93806927	-3.10812563	-0.23238444
H	7.40194165	-2.75420170	1.24408033
C	9.38775091	-2.38644533	-1.32270493
H	8.66089999	-0.42090061	-2.05355049
H	9.30528592	-4.00336032	0.08148894
H	10.19345263	-2.73550679	-1.9584995
N	-7.26720033	2.06377441	0.12688946
C	-6.99950009	2.98496714	-0.80268417
C	-8.49781103	2.39857387	0.67709252
N	-8.01327259	3.88420714	-0.86402058
H	-6.10860298	3.03110386	-1.42021019
C	-8.97449897	3.53001110	0.06464721
H	-8.94869945	1.81219540	1.46972982
H	-8.05326657	4.68906723	-1.48483488
H	-9.88591532	4.10019475	0.20409185
N	-7.01987863	-0.97273839	-0.38168491
C	-8.08150418	-0.84342329	-1.18205694
C	-6.67410213	-2.31793015	-0.39238560
N	-8.41624255	-2.05148528	-1.70038683
H	-8.61591001	0.07699248	-1.39279339
C	-7.53555242	-3.00001089	-1.21405473
H	-5.84192785	-2.69938479	0.18846918
H	-9.19175220	-2.22876743	-2.33439434
H	-7.59999058	-4.04713062	-1.48722491
O	-6.07997633	-0.15673654	2.67853096
H	-5.42851417	-0.83710099	2.86373696
H	-6.95436851	-0.30920324	3.04430713
H	0.59470434	-0.01570166	4.19506083
H	1.13329252	1.35330843	3.25229851
H	13.42208497	2.27430565	-2.9111231
H	-13.61099436	0.83169369	3.3829477

P-P1-P2-G (T2(NiR): dihedral rotated)

N	-2.06995483	0.52684021	-0.16208373
N	-4.25196841	0.40206572	-0.04409605
N	1.03687468	-1.23451310	-1.13598871
N	1.17430855	-0.47149711	2.24509539
C	-0.95016145	-1.69036241	-2.39698626
C	-0.17118080	-1.78038966	-1.10597648
C	-1.57201863	-0.28930475	-2.52904717
C	-2.49199016	0.08083357	-1.39706926
C	-3.84399753	0.01397338	-1.32207731
C	-3.15294351	0.69998096	0.61790077
C	1.90387024	-1.18755453	0.02301630
C	3.30291669	-0.76371400	-0.42498954
C	1.27596805	-0.14745359	0.95896976
C	0.57588394	0.44030803	3.22727937
O	-0.65224412	-2.32830139	-0.11495841
O	0.83487954	0.91429486	0.50903072
S	4.46193506	-0.47577706	0.93200816
H	3.66984358	-1.54831154	-1.08750697
H	3.19324621	0.14691794	-1.02061347
H	1.35192990	-0.75357798	-1.96200542
H	-3.10691540	1.05701666	1.62788687
H	-1.09293927	0.70075161	0.09491708
H	-4.54802549	-0.31998479	-2.05806955
H	-0.29217271	-1.86646199	-3.22297400
H	-2.14600813	-0.25828370	-3.45605296
H	-0.78094196	0.46061129	-2.62707085
H	1.59887980	-1.33620671	2.55227703
H	-0.43661127	0.64804573	2.95051506
H	1.92976783	-2.16153778	0.50805542
H	-1.72623592	-2.42628388	-2.39696301
Cu	6.38133539	0.11333246	0.10875100
Cu	-6.10576104	0.48716444	0.63471696
N	6.53314948	2.05908872	0.49744762
C	7.60492919	2.69515390	0.97815121
C	5.54525192	3.01947857	0.32158831
N	7.33439231	4.01803902	1.10820576
H	8.55481185	2.24093430	1.24001404
C	6.03441505	4.24553393	0.69572541
H	4.56028212	2.76508743	-0.05328981
H	7.97947381	4.72201006	1.45906802
H	5.58539477	5.23219126	0.70677388
N	8.20374118	-0.27184442	-0.59166026
C	8.82943980	-1.45199201	-0.58073036
C	9.07209875	0.63422819	-1.18681091

N	10.05499336	-1.32775737	-1.14880925
H	8.43889202	-2.37981838	-0.17603872
C	10.22840902	-0.01344696	-1.54168322
H	8.81059823	1.67874270	-1.31338455
H	10.73473545	-2.07656496	-1.25857079
H	11.13501614	0.33426824	-2.02375338
N	-7.26720033	2.06377441	0.12688946
C	-6.99950009	2.98496714	-0.80268417
C	-8.49781103	2.39857387	0.67709252
N	-8.01327259	3.88420714	-0.86402058
H	-6.10860298	3.03110386	-1.42021019
C	-8.97449897	3.53001110	0.06464721
H	-8.94869945	1.81219540	1.46972982
H	-8.05326657	4.68906723	-1.48483488
H	-9.88591532	4.10019475	0.20409185
N	-7.01987863	-0.97273839	-0.38168491
C	-8.08150418	-0.84342329	-1.18205694
C	-6.67410213	-2.31793015	-0.39238560
N	-8.41624255	-2.05148528	-1.70038683
H	-8.61591001	0.07699248	-1.39279339
C	-7.53555242	-3.00001089	-1.21405473
H	-5.84192785	-2.69938479	0.18846918
H	-9.19175220	-2.22876743	-2.33439434
H	-7.59999058	-4.04713062	-1.48722491
O	-6.07997633	-0.15673654	2.67853096
H	-5.42851417	-0.83710099	2.86373696
H	-6.95436851	-0.30920324	3.04430713
S	6.32092705	-1.94337545	-1.27569958
C	6.89404884	-3.61124384	-0.89935339
C	4.92546220	-2.47569523	-2.25572533
H	7.60614104	-3.57392329	-0.07496671
H	7.25990313	-4.08452251	-1.81053256
H	6.07750821	-4.18684655	-0.46331617
H	4.25853890	-1.63090022	-2.42820684
H	4.30673105	-3.15483766	-1.66907409
H	5.28264818	-2.97631915	-3.15557375
H	0.59470434	-0.01570166	4.19506083
H	1.13329252	1.35330843	3.25229851