Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Singlet-triplet energy gaps and the degree of diradical character in binuclear copper molecular magnets characterized by spin-flip density functional theory. Supplemental Information.

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1. STRUCTURES

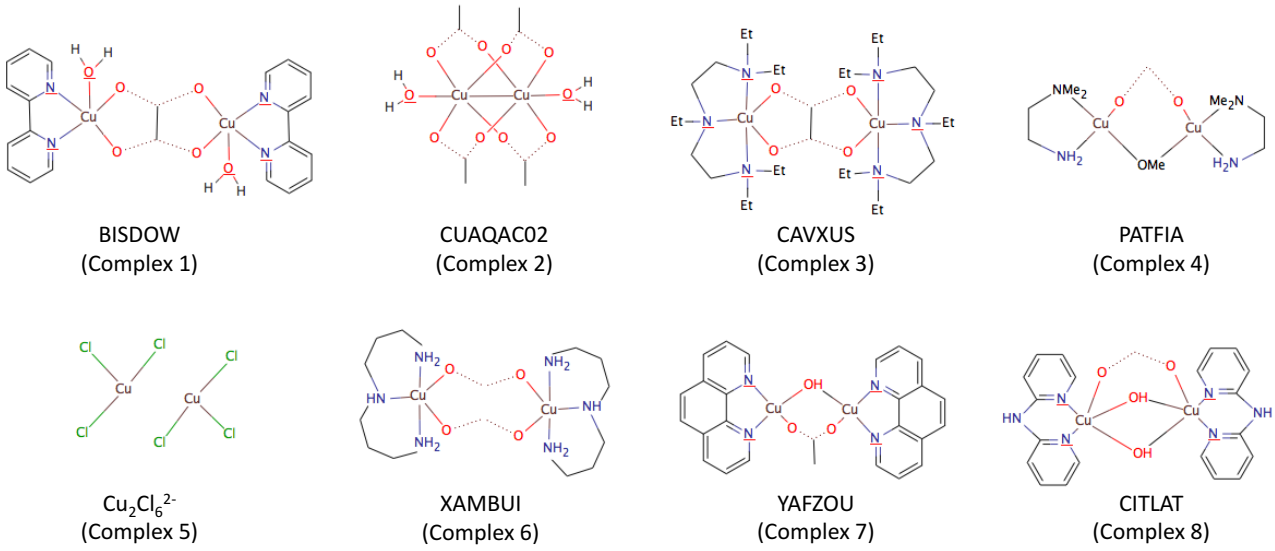

FIG. S1: Lewis structures of the eight binuclear copper complexes included in this study. Structures are denoted with their Cambridge Structural Database names [1, 2]. Complexes 1, 3, 4, 6, and 7 have a charge of 2+; Complex 2 is neutral; Complex 5 has charge of 2-; and Complex 8 has charge of 1+.

2. ECP DETAILS

TABLE S1: ECPs with matching basis sets and core electron approximations for Cu, Cl, C, O, N and H.

Atom	**LANL2DZ**		**SRSC**		**CRENBL**		**ECP10MDF**	
	Core	Valence	Core	Valence	Core	Valence	Core	Valence
Cu	[Ne]	(3s, 3p, 2d)	[Ne]	(6s, 5p, 3d)	[Ne]	(7s, 6p, 6d)	[Ne]	cc-pVDZ-PP, cc-pVTZ-PP
Cl	[Ne]	(2s, 2p)	None	6-311G*	[Ne]	(4s, 4p)	None	cc-pVDZ, cc-pVTZ
O, N, C	None	6-31G	None	6-311G*	[He]	(4s, 4p)	None	cc-pVDZ, cc-pVTZ
H	None	6-31G	None	6-311G*	None	6-311G*	None	cc-pVDZ, cc-pVTZ

3. ENERGY DIFFERENCE BETWEEN THE $M_s = 0$ AND $M_s = 1$ TRIPELT COMPONENTS IN CUAQAC02

TABLE S2: Energy difference (eV) between the $M_s = 0$ and $M_s = 1$ components of the lowest triplet state of **CUAQAC02** at the SF-TDDFT/cc-pVTZ and EOM-SF-CCSD/cc-pVDZ levels of theory.

Method	ΔE
NC-PBE50	0.340
COL-B5050LYP	0.176
NC-LDA	0.023
NC-B97	0.126
EOM-SF-CCSD	0.231

4. ERROR ANALYSIS

TABLE S3: Mean error (Δ_{ME}), mean absolute error (Δ_{MAE}), and standard deviation of the error (Δ_{STD}) in the calculated values of the exchange coupling constants of AF complexes 1-5 at different levels of theory[a]. Errors are reported relative to experiment in cm^{-1}.

BASIS	**PBE0**			**PBE50**			**B5050LYP**		
	Δ_{ME}	Δ_{MAE}	Δ_{STD}	Δ_{ME}	Δ_{MAE}	Δ_{STD}	Δ_{ME}	Δ_{MAE}	Δ_{STD}
cc-pVDZ	-45	52	62	+98	98	90	+102	102	96
cc-pVTZ	-31	61	75	+104	104	94	+101	104	97
ECP10MDF/ cc-pVDZ	-24	49	60	+87	92	104	+111	111	98
ECP10MDF/ cc-pVTZ	-14	46	58	+105	105	101	+110	110	107
LANL2DZ	-92	128	170	+63	63	70	+59	59	71
SRSC	-38	63	85	+81	83	94	+85	85	88
CRENBL	-52	68	84	+72	74	99	+72	75	96

[a] Calculations performed with non-collinear TDDFT kernel using experimental structures.

TABLE S4: Mean error (Δ_{ME}), mean absolute error (Δ_{MAE}), and standard deviation of the error (Δ_{STD}) in the calculated values of the singlet-triplet gap of F complexes 6-8 at different levels of theory. Errors are reported relative to experiment in cm^{-1}.

BASIS	**PBE0**			**PBE50**			**B5050LYP**		
	Δ_{ME}	Δ_{MAE}	Δ_{STD}	Δ_{ME}	Δ_{MAE}	Δ_{STD}	Δ_{ME}	Δ_{MAE}	Δ_{STD}
cc-pVDZ	+70	70	62	-10	10	8	-11	11	14
cc-pVTZ	+66	67	60	-6	9	14	-12	12	14
ECP10MDF/ cc-pVDZ	+57	59	54	-9	9	12	-17	17	18
ECP10MDF/ cc-pVTZ	+21	40	62	-11	11	14	-20	20	19
LANL2DZ	+97	98	86	+10	11	18	-6	6	7
SRSC	+58	59	52	-16	16	15	-21	21	19
CRENBL	+66	68	60	-12	12	9	-18	18	14

[a] Calculations performed with non-collinear TDDFT kernel using experimental structures.

TABLE S5: Mean error (Δ_{ME}), mean absolute error (Δ_{MAE}), and standard deviation of the error (Δ_{STD}) in the calculated values of the singlet-triplet gap of all complexes at different levels of theory. Errors are reported relative to experiment in cm^{-1}.

BASIS	**PBE0**			**PBE50**			**B5050LYP**		
	Δ_{ME}	Δ_{MAE}	Δ_{STD}	Δ_{ME}	Δ_{MAE}	Δ_{STD}	Δ_{ME}	Δ_{MAE}	Δ_{STD}
cc-pVDZ	-2	58	83	+57	65	88	+59	68	94
cc-pVTZ	+6	63	82	+63	68	91	+61	70	95
ECP10MDF/ cc-pVDZ	+7	53	68	+51	61	93	+63	76	100
ECP10MDF/ cc-pVTZ	-1	44	58	+62	70	97	+61	76	105
LANL2DZ	-21	117	168	+43	44	60	+35	39	64
SRSC	-2	61	86	+45	58	88	+45	61	87
CRENBL	-7	68	94	+41	51	86	+38	54	87

[a] Calculations performed with non-collinear TDDFT kernel using experimental structures.

5. OPTIMIZED STRUCTURES

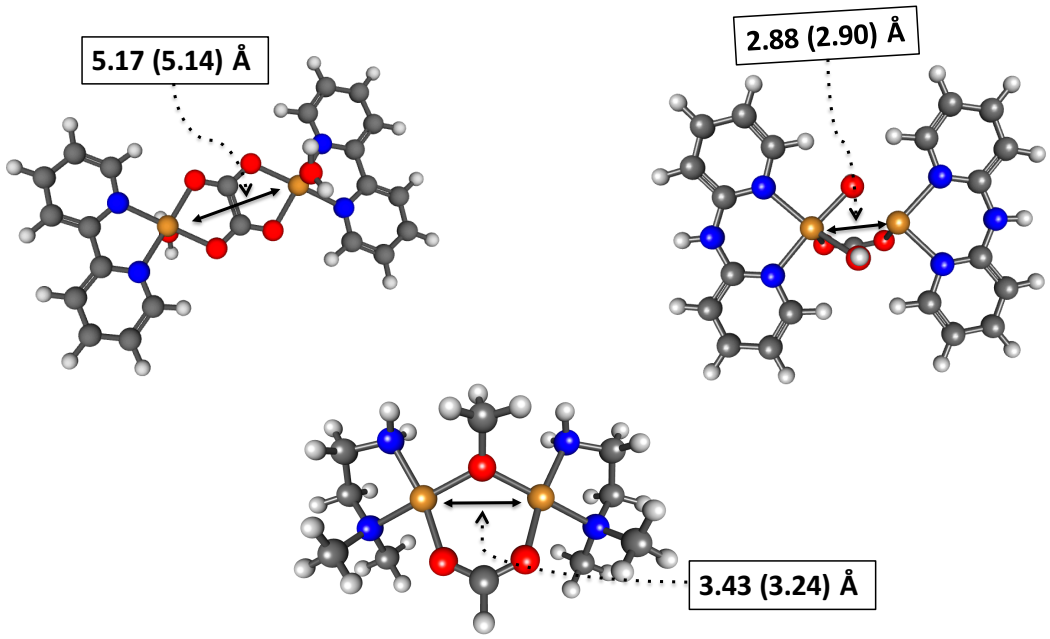

FIG. S2: Optimized triplet geometries of BISDOW (top left), PATFIA (middle), and CITLAT (top right). Interatomic Cu-Cu distances in parentheses correspond to experimental geometries. All three complexes were optimized at the ωB97X-D/cc-pVTZ level of theory.

6. EOM-SF-CCSD CALCULATIONS AT OPTIMIZED STRUCTURES

TABLE S6: EOM-SF-CCSD/cc-pVDZ singlet-triplet gaps and experimental exchange coupling constants for three binuclear copper diradicals at optimized geometries. Cholesky decomposition with a threshold of 1e-3 was used for two-electron integral calculations. The frozen core approximation was applied. Geometries were optimized at the ωB97X-D/cc-pVTZ level of theory.

Complex	ΔE_{ST} (cm^{-1})	$\langle S^2 \rangle^a$	Exp. J (cm^{-1})
BISDOW	-215	2.017	-382
PATFIA	-77	2.008	-11
CITLAT	123	2.011	113

[a] $\langle S^2 \rangle$ of the reference high-spin triplet.

7. SINGLET-TRIPLET GAPS WITH THE COLLINEAR TDDFT KERNEL

TABLE S7: Singlet-triplet gaps (cm^{-1}) for Complexes 1-8 calculated using SF-TDDFT with the LRC-ωPBEh method and the collinear TDDFT kernel. Experimentally determined molecular geometries were used.

BASIS	**COMPLEX**							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
cc-pVDZ	-733	-519	-44	-280	-188	-1	90	60
ECP10MDF/ cc-pVDZ	-725	-498	-44	-274	-173	-1	109	66
LANL2DZ	-846	-866	-38	-217	-265	-2	129	75
EXP. J	**-382**	**-286**	**-19**	**-11**	**(0, -40)**	**-2**	**111**	**113**

TABLE S8: Singlet-triplet gaps (cm^{-1}) for Complexes 1-8 calculated using SF-TDDFT with the PBE0 method and the collinear TDDFT kernel. Experimentally determined molecular geometries were used.

BASIS	**COMPLEX**							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
cc-pVDZ	-882	-582	-56	-290	-229	0	104	79
cc-pVTZ	-853	-600	-53	-282	-219	-2	105	74
ECP10MDF/ cc-pVDZ	-866	-558	-55	-280	-211	1	123	83
ECP10MDF/ cc-pVTZ	-809	-564	-50	-273	-195	-1	56	73
LANL2DZ	-1048	-269	-48	-248	-315	-2	146	108
SRSC	-826	-198	-42	-217	-285	-2	117	67
CRENBL	-823	-201	-68	-218	-365	-2	111	67
EXP. J	**-382**	**-286**	**-19**	**-11**	**(0, -40)**	**-2**	**111**	**113**

TABLE S9: Singlet-triplet gaps (cm^{-1}) for Complexes 1-8 calculated using SF-TDDFT with selected Minnesota functionals and the collinear TDDFT kernel; cc-pVDZ basis set. Experimentally determined molecular geometries were used.

BASIS	**COMPLEX**							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
GAM	-4882	-3110	-1320	-2687	-1725	-231	-334	-130
M06-L	-1217	-3149	-1283	-2546	-1651	-189	179	-44
M15-L	-4606	-3307	-1281	-2832	-1919	-253	-322	761
M06	-806	-581	DRS[a]	-214	-203	0	96	81
MN15	-290	-201	-19	-31	DRS[a]	0	130	102
EXP. J	**-382**	**-286**	**-19**	**-11**	**(0, -40)**	**-2**	**111**	**113**

[a] SCF calculation converged to a wrong reference state.

8. SINGLET-TRIPLET GAPS WITH THE NON-COLLINEAR TDDFT KERNEL

TABLE S10: Singlet-triplet gaps (cm^{-1}) for Complexes 1-8 calculated using SF-TDDFT with selected PBE functionals and the non-collinear TDDFT kernel; cc-pVDZ basis set. Experimentally determined molecular geometries were used.

BASIS	**COMPLEX**							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
PBEh	-725	-468	DRS[a]	-105	-56	2	196	231
LRC-ωPBEh	-444	-319	-24	-35	39	0	198	231
PBE0	-523	-354	-27	-35	-23	2	201	232
PBE50	-173	-121	-9	0	55	0	93	120
EXP. J	**-382**	**-286**	**-19**	**-11**	**(0, -40)**	**-2**	**111**	**113**

[a] SCF calculation converged to a wrong reference state.

9. WAVEFUNCTION ANALYSIS: B97 FRONTIER NATURAL ORBITALS OF THE CUAQAC02 COMPLEX

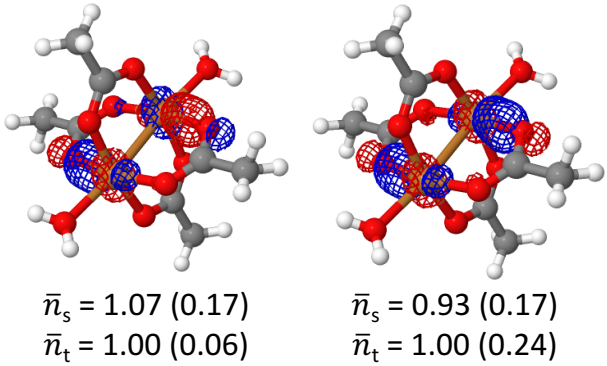

FIG. S3: SF-TDDFT/cc-pVTZ frontier orbitals of **CUAQAC02** with the B97 functional (non-collinear TDDFT kernel).

[1] Allen, F. H. The CSD system: The Cambridge structural database: A quarter of a million crystal structures and rising *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *B58*, 380–8.

[2] Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. ConQuest: New software for searching the Cambridge structural database and visualizing crystal structures *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *B58*, 389.

Cartesian geometries

Experimental geometry of BISDOW (Complex 1), taken from O. Castillo; I. Muga; A. Luque; J. M. Gutierrez-Zorrilla; J. Sertucha; P. Vitoria; P. Roman, Polyhedron 18, 1235 (1999).

Cu	-2.35254640	0.57677107	0.86384176
O	-1.07833077	-0.90965212	1.01996557
O	-0.96187584	1.42020443	-0.27484590
C	-0.03492785	-0.66732598	0.37029459
O	-1.46679874	1.88201362	2.60682569
N	-3.73778003	1.95253258	0.60794323
C	-3.57908589	3.14559856	0.03840417
C	-4.61404624	4.04749925	-0.08057997
C	-5.85665045	3.66888992	0.35738664
C	-6.03598320	2.44856997	0.95095211
C	-4.95514302	1.60222814	1.06881648
C	-5.00093520	0.29479636	1.73917028
N	-3.83897000	-0.37705060	1.76213853
C	-3.77611505	-1.55137619	2.39582430
C	-4.86428748	-2.09810499	3.03720592
C	-6.04580551	-1.41965076	3.01871321
C	-6.14361504	-0.21036119	2.34917081
H	6.96035423	-0.28296881	-2.38042154
H	6.82249448	1.67143857	-3.36395826
H	4.73282136	2.97028678	-3.48570631
H	2.94548681	1.87621280	-2.31503499
H	-2.70370579	3.40223394	-0.20212432
H	-4.49867539	4.86708750	-0.43102206
H	-6.51174152	4.27324389	0.36162699
H	-6.85732915	2.20590734	1.29095458
H	-2.94548681	-1.87621280	2.31503499
H	-4.73282136	-2.97028678	3.48570631
H	-6.82249448	-1.67143857	3.36395826
H	-6.96035423	0.28296881	2.38042154
H	-0.81875344	1.60541487	2.91912108
H	-1.95320317	1.58829473	3.04098458
O	0.96187584	-1.42020443	0.27484590
Cu	2.35254640	-0.57677107	-0.86384176
O	1.07833077	0.90965212	-1.01996557
C	0.03492785	0.66732598	-0.37029459
O	1.46679874	-1.88201362	-2.60682569
H	0.81875344	-1.60541487	-2.91912108
H	1.95320317	-1.58829473	-3.04098458
N	3.73778003	-1.95253258	-0.60794323
C	3.57908589	-3.14559856	-0.03840417
C	4.61404624	-4.04749925	0.08057997

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C       5.85665045      -3.66888992      -0.35738664
C       6.03598320      -2.44856997      -0.95095211
C       4.95514302      -1.60222814      -1.06881648
C       5.00093520      -0.29479636      -1.73917028
N       3.83897000       0.37705060      -1.76213853
H       6.85732915      -2.20590734      -1.29095458
H       6.51174152      -4.27324389      -0.36162699
H       4.49867539      -4.86708750       0.43102206
H       2.70370579      -3.40223394       0.20212432
C       3.77611505       1.55137619      -2.39582430
C       4.86428748       2.09810499      -3.03720592
C       6.04580551       1.41965076      -3.01871321
C       6.14361504       0.21036119      -2.34917081

Optimized $\omega$B97X-D/cc-pVTZ Kohn-Sham triplet
geometry of BISDOW (Complex 1).

Cu      2.5833491351    -0.0009904119     0.1291850887
O       1.1170753802     1.3282000412     0.0327516014
C       0.0001048572     0.7718040969     0.0067932958
O      -1.1164196952     1.3291297510    -0.0094867315
C      -0.0001048570    -0.7718040965    -0.0067932958
O       1.1164196952    -1.3291297510     0.0094867315
O      -1.1170753800    -1.3282000408    -0.0327516014
Cu     -2.5833491348     0.0009904123    -0.1291850888
N      -4.0682174830     1.2998301754     0.0702348396
C      -3.9369618909     2.6242574996     0.1044843851
H      -2.9259219211     3.0047210936     0.0681946756
 C      -5.2869911318     0.7377507924     0.1316192026
C      -5.0320586571     3.4619974192     0.1983743645
H      -4.8953106009     4.5320752067     0.2295681032
C      -6.4251174566     1.5180750115     0.2168712828
H      -7.4049524306     1.0689921489     0.2557787966
C      -6.2941061480     2.8976613004     0.2476047560
H      -7.1722495965     3.5236083586     0.3199871198
C      -5.2854287130    -0.7431853280     0.1312140901
N      -4.0661698135    -1.3025307697     0.0559523575
C      -3.9317743705    -2.6269546064     0.0843456738
 H      -2.9201774419    -3.0041171469     0.0345072850
C      -5.0246994071    -3.4661520878     0.1905159932
H      -4.8862571322    -4.5363149421     0.2138596566
C      -6.4211580088    -1.5251490333     0.2329657269
H      -7.4014618567    -1.0789117305     0.2883650366
C      -6.2868171354    -2.9044466256     0.2604672494
H      -7.1626398125    -3.5319713878     0.3467616510
N       4.0682174832    -1.2998301750    -0.0702348396
C       3.9369618911    -2.6242574991    -0.1044843852
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H	2.9259219213	-3.0047210932	-0.0681946756
C	5.2869911320	-0.7377507920	-0.1316192027
C	5.0320586573	-3.4619974188	-0.1983743645
H	4.8953106011	-4.5320752062	-0.2295681033
C	6.4251174568	-1.5180750110	-0.2168712828
H	7.4049524308	-1.0689921485	-0.2557787967
C	6.2941061482	-2.8976613000	-0.2476047560
H	7.1722495967	-3.5236083582	-0.3199871199
C	5.2854287132	0.7431853284	-0.1312140902
N	4.0661698137	1.3025307701	-0.0559523576
C	3.9317743707	2.6269546069	-0.0843456738
H	2.9201774421	3.0041171473	-0.0345072851
C	5.0246994073	3.4661520882	-0.1905159933
H	4.8862571324	4.5363149425	-0.2138596566
C	6.4211580090	1.5251490337	-0.2329657270
H	7.4014618569	1.0789117309	-0.2883650366
C	6.2868171356	2.9044466260	-0.2604672495
H	7.1626398127	3.5319713882	-0.3467616510
O	-2.5412578917	0.0194927722	-2.4748985207
H	-2.5544074104	0.7915396360	-3.0420283833
H	-2.5437428892	-0.7442447095	-3.0533586924
O	2.5412578919	-0.0194927718	2.4748985207
H	2.5544074106	-0.7915396356	3.0420283832
H	2.5437428894	0.7442447099	3.0533586924

Experimental geometry of CUAQAC02 (Complex 2), taken from
P. de Meester; S. R. Fletcher; A. C. Skapski, J. Am. Chem. Soc.
Dalton Trans. 23, 2575 (1973).

Cu	5.64300000	0.71900000	0.55500000
C	5.31800000	0.18300000	-2.22700000
C	4.66600000	0.32500000	-3.56500000
C	7.78300000	2.12100000	-0.62600000
C	8.47800000	3.39400000	-1.03200000
H	5.31600000	0.37700000	-4.40700000
H	3.90600000	0.75400000	-3.60500000
H	4.45700000	-0.59100000	-3.96300000
H	8.72300000	3.29700000	-2.00000000
H	7.79600000	4.11900000	-0.80200000
H	9.34900000	3.46000000	-0.59300000
H	3.90800000	1.43900000	2.40700000
H	3.50700000	2.33800000	1.33300000
O	4.80000000	0.75400000	-1.24200000
O	6.79300000	0.51600000	2.17200000
O	6.68500000	2.26700000	0.00400000
O	4.86400000	-1.02900000	0.93000000
O	4.11000000	1.77500000	1.64200000

Cu	7.52500000	-0.71900000	-0.55500000
O	6.37500000	-0.51600000	-2.17200000
C	7.85000000	-0.18300000	2.22700000
O	8.30400000	1.02900000	-0.93000000
C	5.38500000	-2.12100000	0.62600000
O	8.36800000	-0.75400000	1.24200000
O	6.48300000	-2.26700000	-0.00400000
O	9.05800000	-1.77500000	-1.64200000
C	8.50200000	-0.32500000	3.56500000
C	4.69000000	-3.39400000	1.03200000
H	9.26000000	-1.43900000	-2.40700000
H	9.66100000	-2.33800000	-1.33300000
H	7.85200000	-0.37700000	4.40700000
H	9.26200000	-0.75400000	3.60500000
H	8.71100000	0.59100000	3.96300000
H	4.44500000	-3.29700000	2.00000000
H	5.37200000	-4.11900000	0.80200000
H	3.81900000	-3.46000000	0.59300000

Experimental geometry of CAVXUS (Complex 3), taken from
J. Sletten, Acta. Chem. Scand., Ser. A 37, 569 (1983).

Cu	0.55900000	1.49200000	7.08000000
O	-0.56900000	0.46400000	8.32700000
O	-0.99600000	0.72200000	5.68000000
N	2.07100000	0.01800000	7.02400000
N	1.67800000	2.52100000	5.75300000
N	-0.24300000	3.34400000	7.67900000
C	-1.61200000	-0.08200000	7.84800000
C	2.93900000	0.12500000	8.25800000
C	2.28100000	-0.35700000	9.53500000
C	1.54000000	-1.36600000	6.84400000
C	2.61000000	-2.46300000	6.74900000
C	2.89500000	0.40600000	5.83800000
C	3.03700000	1.90800000	5.77300000
C	1.05500000	2.43000000	4.39300000
C	1.69700000	3.27900000	3.31900000
C	1.69700000	3.93400000	6.25600000
C	0.27900000	4.30600000	6.64200000
C	0.23900000	3.79200000	9.02600000
C	-0.27800000	3.01100000	10.20000000
C	-1.75200000	3.29700000	7.61100000
C	-2.44900000	4.64300000	7.82400000
H	3.20100000	1.09200000	8.37800000
H	3.77400000	-0.33400000	8.06600000
H	2.93000000	-0.15600000	10.26400000
H	2.22600000	-1.20400000	9.51200000

H	1.44200000	0.24500000	9.69600000
H	1.01600000	-1.29300000	5.92600000
H	0.91900000	-1.42700000	7.54200000
H	3.25300000	-2.22900000	5.95400000
H	3.05200000	-2.63000000	7.55600000
H	2.08100000	-3.29900000	6.52100000
H	3.72100000	-0.02200000	5.91100000
H	2.48300000	0.04500000	5.03300000
H	3.47700000	2.07300000	5.08900000
H	3.57800000	2.29600000	6.60600000
H	1.07500000	1.56000000	4.08300000
H	0.16300000	2.60800000	4.40900000
H	2.55500000	3.18700000	3.24600000
H	1.29100000	3.12100000	2.42400000
H	1.65600000	4.19100000	3.57200000
H	2.04700000	4.50300000	5.55700000
H	2.32900000	3.96800000	7.10200000
H	-0.27300000	4.25700000	5.81200000
H	0.27600000	5.14900000	7.14500000
H	0.14800000	4.85900000	9.32800000
H	1.07700000	3.58900000	8.98800000
H	-0.33100000	1.82800000	10.13600000
H	0.05400000	3.38800000	10.93000000
H	-1.30600000	3.07600000	10.33400000
H	-1.99200000	2.65300000	8.35000000
H	-1.94100000	3.03100000	6.70500000
H	-2.10700000	5.17100000	6.94600000
H	-3.14700000	4.52500000	7.68300000
H	-2.29000000	4.92600000	8.74700000
C	-1.83900000	0.08200000	6.32800000
O	-2.45500000	-0.72200000	8.49600000
O	-2.88100000	-0.46400000	5.84900000
Cu	-4.01000000	-1.49200000	7.09600000
N	-5.52200000	-0.01800000	7.15200000
N	-5.12800000	-2.52100000	8.42300000
N	-3.20700000	-3.34400000	6.49700000
C	-6.38900000	-0.12500000	5.91900000
C	-4.99000000	1.36600000	7.33200000
C	-6.34500000	-0.40600000	8.33800000
C	-6.48700000	-1.90800000	8.40400000
C	-4.50500000	-2.43000000	9.78300000
C	-5.14700000	-3.93400000	7.92000000
C	-3.73000000	-4.30600000	7.53500000
C	-3.69000000	-3.79200000	5.15000000
C	-1.69900000	-3.29700000	6.56500000
C	-5.73200000	0.35700000	4.64100000
H	-6.65100000	-1.09200000	5.79800000

H	-7.22400000	0.33400000	6.11000000
C	-6.06000000	2.46300000	7.42700000
H	-4.46700000	1.29300000	8.25000000
H	-4.36900000	1.42700000	6.63400000
H	-7.17100000	0.02200000	8.26500000
H	-5.93400000	-0.04500000	9.14400000
H	-6.92800000	-2.07300000	9.08700000
H	-7.02900000	-2.29600000	7.57000000
C	-5.14700000	-3.27900000	10.85700000
H	-4.52600000	-1.56000000	10.09300000
H	-3.61400000	-2.60800000	9.76700000
H	-5.49700000	-4.50300000	8.61900000
H	-5.77900000	-3.96800000	7.07400000
H	-3.17800000	-4.25700000	8.36400000
H	-3.72700000	-5.14900000	7.03100000
C	-3.17300000	-3.01100000	3.97600000
H	-3.59900000	-4.85900000	4.84800000
H	-4.52800000	-3.58900000	5.18800000
C	-1.00200000	-4.64300000	6.35200000
H	-1.45800000	-2.65300000	5.82600000
H	-1.50900000	-3.03100000	7.47100000
H	-6.38000000	0.15600000	3.91300000
H	-5.67700000	1.20400000	4.66400000
H	-4.89300000	-0.24500000	4.48000000
H	-6.70400000	2.22900000	8.22200000
H	-6.50200000	2.63000000	6.62000000
H	-5.53100000	3.29900000	7.65500000
H	-6.00600000	-3.18700000	10.93000000
H	-4.74200000	-3.12100000	11.75200000
H	-5.10700000	-4.19100000	10.60400000
H	-3.12000000	-1.82800000	4.04000000
H	-3.50400000	-3.38800000	3.24600000
H	-2.14400000	-3.07600000	3.84200000
H	-1.34300000	-5.17100000	7.23000000
H	-0.30400000	-4.52500000	6.49300000
H	-1.16000000	-4.92600000	5.42900000

Simplified experimental structure of PATFIA (Complex 4) without
the ferrocene group, taken from M. Julve; M. Verdaguer; A. Gleizes;
M. Pohiloche-Levisalles; O. Kahn, Inorg. Chem. 23, 3808 (1984).

Cu	0.000000	0.000000	0.000000
Cu	0.925000	1.720000	-2.581000
H	-1.006000	-0.187000	-3.472000
H	2.069000	0.732000	2.139000
O	-0.181000	0.318000	-1.874000
O	2.524000	0.972000	-1.839000

```
O         1.892000   -0.349000   -0.158000
H         1.253000    0.938000    3.462000
C         1.203000    0.934000    2.503000
H         0.915000    1.792000    2.191000
H         0.122000   -2.063000    2.097000
N         0.218000   -0.118000    2.058000
N        -1.942000    0.181000    0.393000
H        -2.227000    0.999000    0.145000
H        -2.405000   -0.431000   -0.076000
N         2.064000    3.355000   -3.079000
N        -0.499000    2.585000   -3.664000
H        -0.800000    2.003000   -4.281000
H        -1.190000    2.803000   -3.128000
H         3.773315   -0.253545   -0.829399
H         1.627000    4.936000   -4.249000
C         1.138000    4.370000   -3.637000
H        -1.504000   -0.959000   -2.201000
H         2.790000    3.400000   -1.215000
C         3.051000    2.978000   -4.104000
H        -0.712000    4.452000   -4.377000
H         0.812000    4.925000   -2.911000
C         2.731000    0.106000   -0.917000
H        -1.948000    0.525000   -2.439000
C        -0.001000    3.794000   -4.333000
C        -1.230000   -0.106000   -2.540000
H         2.292000    4.800000   -1.712000
H         3.655000    4.224000   -2.228000
C         2.761000    4.003000   -1.962000
H         3.308000    2.060000   -3.979000
H         2.663000    3.083000   -4.977000
H         3.825000    3.539000   -4.028000
H         0.259000    3.573000   -5.242000
C        -1.030000    0.395000    2.631000
H        -1.136000    0.061000    3.533000
H        -0.989000    1.366000    2.672000
C        -2.185000   -0.009000    1.814000
H        -2.960000    0.509000    2.080000
H        -2.380000   -0.944000    1.984000
C         0.639000   -1.379000    2.522000
H         0.514000   -1.423000    3.474000
H         1.568000   -1.499000    2.316000

Optimized $\omega$B97X-D/cc-pVTZ Kohn-Sham triplet geometry
of the simplified PATFIA (Complex 4) structure.

Cu      1.7087227025    -0.1792834903     0.1608894488
O       1.1510877085     1.5186111353     0.8977506371
```

C	0.0259987040	2.0401407554	1.0578341471
H	0.0146802968	3.0227985586	1.5416296736
O	-1.0863580177	1.5872962809	0.7045453660
Cu	-1.7153965803	-0.1621452984	0.1726197439
O	-0.0071181378	-1.0311286136	0.5412325888
C	0.0030057456	-2.2756009208	1.2155946223
H	0.9333350080	-2.4176420955	1.7706126488
H	-0.7895151328	-2.3283409390	1.9661011991
H	-0.1154330288	-3.1118706257	0.5180707573
N	-2.7336423434	-1.9056433478	-0.1370361317
H	-2.5876357917	-2.5933835980	0.5932900883
H	-2.3832137993	-2.3341014358	-0.9887331535
C	-4.1779826589	-1.6063992118	-0.2812385809
H	-4.5995491335	-1.5088882249	0.7167569764
H	-4.7040744188	-2.4177316843	-0.7819519177
C	-4.3021627019	-0.3226480645	-1.0701279691
H	-3.9509652816	-0.4827683024	-2.0904271954
H	-5.3399705359	0.0104030531	-1.1255563887
N	-3.4558063585	0.7337142466	-0.4641119051
C	-3.1877799322	1.7885317544	-1.4640335437
H	-2.5934196416	2.5748372585	-1.0094502121
H	-2.6523323100	1.3669152040	-2.3133245196
H	-4.1278307542	2.2120268177	-1.8243815287
C	-4.1337542238	1.3399052215	0.7052696848
H	-3.4822453447	2.0864572595	1.1483079253
H	-4.3596974913	0.5819780017	1.4521592151
H	-5.0663404102	1.8100631123	0.3869947656
N	2.6201735674	-1.8968553219	-0.4678369142
H	2.4357916814	-2.7001126866	0.1223649203
H	2.2456395244	-2.1388704123	-1.3807648385
C	4.0798535321	-1.6552639611	-0.5721153213
H	4.5006453777	-1.7281982560	0.4282594133
H	4.5713720983	-2.4004889581	-1.1950634155
C	4.2637661191	-0.2692572306	-1.1472915868
H	3.8892250618	-0.2476605094	-2.1715119771
H	5.3175409713	0.0140447135	-1.1748259443
N	3.4875316595	0.7156442408	-0.3589983072
C	3.2835211482	1.9414419703	-1.1598403187
H	2.7641842796	2.6793528630	-0.5581710474
H	2.6879045539	1.7117465834	-2.0420692295
H	4.2450530380	2.3463113052	-1.4814884068
C	4.1992063212	1.0681887976	0.8912164078
H	3.5810602997	1.7434307266	1.4745666489
H	4.3989122355	0.1783492095	1.4853492250
H	5.1497006857	1.5522941282	0.6575385510

Experimental structure of PATFIA including the ferrocene group,

taken from M. Julve; M. Verdaguer; A. Gleizes;
M. Pohiloche-Levisalles; O. Kahn, Inorg. Chem. 23, 3808 (1984).

Cu	-2.12986	-1.03325	0.57368
Cu	-1.20483	0.68621	-2.00729
Fe	3.39024	-0.45780	0.94495
O	-2.31122	-0.71618	-1.30040
O	0.39423	-0.06124	-1.26598
O	-0.23800	-1.38309	0.41582
N	-1.91186	-1.15181	2.63117
N	-4.07216	-0.85241	0.96659
H	-4.35689	-0.03505	0.71825
H	-4.53547	-1.46468	0.49696
N	-0.06583	2.32123	-2.50520
N	-2.62923	1.55103	-3.09038
H	-2.93019	0.96944	-3.70753
H	-3.32049	1.76884	-2.55437
C	2.04553	-1.38459	-0.24804
C	2.50561	-2.30974	0.76005
H	2.00021	-2.75959	1.39687
C	3.90669	-2.37635	0.55843
H	4.49809	-2.87785	1.07231
C	4.26863	-1.57172	-0.53326
H	5.12639	-1.46917	-0.87995
C	3.09046	-0.94148	-1.01764
H	3.03668	-0.34043	-1.72577
C	2.50756	1.08995	1.96977
H	1.61975	1.36091	1.92305
C	2.99897	0.17528	2.85000
H	2.50791	-0.29253	3.48683
C	4.43570	0.05777	2.61888
H	5.01867	-0.50211	3.07867
C	4.77700	0.91705	1.60095
H	5.63753	1.05402	1.27393
C	3.57011	1.57947	1.11903
H	3.49871	2.18501	0.41582
C	-3.15977	-0.63834	3.20407
H	-3.26612	-0.97292	4.10644
H	-3.11923	0.33247	3.24587
C	-4.31512	-1.04253	2.38776
H	-5.08996	-0.52456	2.65330
H	-4.50978	-1.97815	2.55741
C	-1.49146	-2.41228	3.09588
H	-1.61635	-2.45719	4.04743
H	-0.56175	-2.53279	2.88935
H	-2.00825	-3.09641	2.67051
C	-0.92720	-0.09942	3.07621

```
H         -0.87703       -0.09567        4.03513
H         -1.21538        0.75836        2.76395
H         -0.06112       -0.30151        2.71231
C          0.60126       -0.92726       -0.34394
C         -0.99239        3.33620       -3.06334
H         -1.31806        3.89159       -2.33800
H         -0.50343        3.90206       -3.67557
C         -2.13113        2.75985       -3.75917
H         -1.87172        2.53979       -4.66891
H         -2.84219        3.41853       -3.80343
C          0.92071        1.94399       -3.53050
H          1.69482        2.50536       -3.45428
H          0.53267        2.04953       -4.40337
H          1.17773        1.02633       -3.40510
C          0.63093        2.96943       -1.38891
H          1.52523        3.19024       -1.65446
H          0.66000        2.36614       -0.64145
H          0.16221        3.76584       -1.13812
C         -3.35978       -1.13983       -1.96672
H         -3.63441       -1.99237       -1.62741
H         -3.13654       -1.22067       -2.89860
```

Experimental structure of Cu$_2$Cl$_6^{2-}$ (Complex 5), taken from O. Castell; J. Miralles; R. Caballol, Chem. Phys. 179, 377 (1994).

```
Cu      -0.44198447       1.04236051      -0.03573258
Cl       1.34164711      -0.39956189       0.13607601
Cu       2.94244268       1.24888730       0.03573258
Cl       1.15881110       2.69080969      -0.13607601
Cl      -1.89798505      -0.68257133       0.07504862
Cl      -2.09088015       2.57782327      -0.21207639
Cl       4.59133836      -0.28657547       0.21207639
Cl       4.39844326       2.97381913      -0.07504862
```

Experimental structure of XAMBUI (Complex 6), taken from C. L?opez; R. Costa; F. Illas; C. de Graaf; M. M. Turnbull; C. P. Landee; E. Espinosa; I. Mata; E. Molins, Dalton Trans. 13, 2322 (2005).

```
Cu        0.883000    1.658000    1.047000
N         1.772000    0.049000    1.855000
H         1.819000    0.193000    2.743000
H         1.215000   -0.648000    1.735000
N         2.654000    2.688000    0.968000
H         2.830000    2.938000    1.825000
N        -0.270000    3.270000    0.633000
H        -0.868000    2.991000    0.020000
H        -0.739000    3.433000    1.384000
```

C	3.100000	-0.388000	1.425000
H	3.051000	-0.711000	0.510000
H	3.394000	-1.122000	1.985000
C	4.100000	0.725000	1.502000
H	4.981000	0.370000	1.305000
H	4.116000	1.070000	2.409000
C	3.805000	1.862000	0.548000
H	4.590000	2.429000	0.479000
H	3.625000	1.497000	-0.332000
C	2.633000	3.936000	0.191000
H	2.484000	3.722000	-0.745000
H	3.500000	4.365000	0.260000
C	1.571000	4.904000	0.647000
H	1.566000	4.926000	1.617000
H	1.805000	5.792000	0.334000
C	0.190000	4.573000	0.165000
H	-0.425000	5.255000	0.475000
H	0.181000	4.583000	-0.805000
H	-1.566000	-4.926000	-1.617000
O	-0.859000	1.012000	1.755000
O	0.999000	1.144000	-1.161000
C	-1.353000	-0.156000	1.847000
H	-2.162251	-0.270057	2.598516
H	-0.181000	-4.583000	0.805000
O	0.859000	-1.012000	-1.755000
C	1.353000	0.156000	-1.847000
H	-4.590000	-2.429000	-0.479000
N	0.270000	-3.270000	-0.633000
N	-2.654000	-2.688000	-0.968000
H	0.868000	-2.991000	-0.020000
H	0.739000	-3.433000	-1.384000
H	-3.500000	-4.365000	-0.260000
C	-0.190000	-4.573000	-0.165000
H	-2.484000	-3.722000	0.745000
H	-1.805000	-5.792000	-0.334000
H	-2.830000	-2.938000	-1.825000
C	-2.633000	-3.936000	-0.191000
H	0.425000	-5.255000	-0.475000
C	-1.571000	-4.904000	-0.647000
H	2.162251	0.270057	-2.598516
H	-3.625000	-1.497000	0.332000
O	-0.999000	-1.144000	1.161000
Cu	-0.883000	-1.658000	-1.047000
N	-1.772000	-0.049000	-1.855000
H	-1.819000	-0.193000	-2.743000
H	-1.215000	0.648000	-1.735000
C	-3.100000	0.388000	-1.425000

H	-3.051000	0.711000	-0.510000
H	-3.394000	1.122000	-1.985000
C	-4.100000	-0.725000	-1.502000
H	-4.981000	-0.370000	-1.305000
H	-4.116000	-1.070000	-2.409000
C	-3.805000	-1.862000	-0.548000

Experimental structure of YAFZOU (Complex 7), taken from T. Tokii; N. Hamamura; M. Nakashima; Y. Muto, Bull. Chem. Soc. Jpn. 65, 1214 (1992).

Cu	0.70500000	3.58600000	12.98500000
Cu	0.60200000	0.61700000	13.51000000
O	-0.44600000	2.21900000	13.69500000
O	0.72000000	2.87600000	11.18800000
O	0.71700000	0.67000000	11.57900000
H	1.68900000	1.75100000	9.02600000
N	0.52400000	4.76500000	14.61500000
N	1.75000000	5.17700000	12.31800000
N	1.58600000	-1.16000000	13.47400000
N	0.19300000	0.00400000	15.39800000
C	0.75300000	1.67700000	10.81600000
C	0.85900000	1.41900000	9.34600000
C	-0.10900000	4.53800000	15.74600000
C	-0.18700000	5.47300000	16.77500000
C	0.38200000	6.70900000	16.60400000
C	1.05600000	6.99300000	15.41300000
C	1.67400000	8.25800000	15.11200000
C	2.28000000	8.48300000	13.92800000
C	2.35600000	7.44800000	12.92500000
C	2.96500000	7.60300000	11.68000000
C	2.95000000	6.55000000	10.78900000
C	2.34200000	5.35700000	11.13100000
C	1.75600000	6.21200000	13.20600000
C	1.10400000	5.98900000	14.44500000
C	2.26300000	-1.71100000	12.47800000
C	2.77400000	-3.00800000	12.56600000
C	2.57300000	-3.75300000	13.69100000
C	1.85200000	-3.20100000	14.76600000
C	1.56200000	-3.87400000	16.01400000
C	0.88600000	-3.26900000	16.99000000
C	0.42400000	-1.91500000	16.86900000
C	-0.28400000	-1.21700000	17.84100000
C	-0.78300000	0.01900000	17.62200000
C	-0.52400000	0.60500000	16.32300000
C	0.66400000	-1.24900000	15.64800000
C	1.39600000	-1.88000000	14.60600000

H	-0.83600000	5.26700000	17.64300000
H	0.51300000	7.20300000	17.42200000
H	1.56200000	8.88900000	15.79700000
H	2.81200000	9.26400000	13.76100000
H	3.34200000	8.43700000	11.39400000
H	3.59300000	6.49000000	10.00200000
H	2.13400000	4.51800000	10.43000000
H	2.33900000	-1.18900000	11.62100000
H	3.24600000	-3.36000000	11.79400000
H	3.15100000	-4.73900000	13.72400000
H	1.77400000	-4.96900000	15.96600000
H	0.63500000	-3.82600000	17.75800000
H	-0.67000000	-1.32700000	18.75500000
H	-1.26600000	0.71600000	18.26800000
H	-0.93100000	1.72200000	16.15400000
H	-0.53400000	3.66800000	15.91300000
H	0.80900000	0.48400000	9.18400000
H	-1.47700000	2.22800000	13.23300000
H	0.14700000	1.85700000	8.89600000

Experimental structure of CITLAT (Complex 8), taken from S. Youngme; J. Phatchimkun; N. Wannarit; N. Chaichit; S. Meejoo; G. A. Van Albada; J. Reedijk, Polyhedron 18, 1235 (1999).

H	-1.219148	8.422300	12.395086
H	-4.824884	8.422300	11.143813
H	-0.668144	2.122420	12.384391
H	-1.580903	7.327401	7.935422
H	-1.937515	2.543535	8.266956
H	0.287625	5.171292	15.090135
H	-1.504874	3.116251	10.459356
H	-2.108325	6.013522	5.924830
H	-2.440758	3.453143	6.192196
H	-0.054372	6.822063	13.272046
H	0.337745	2.897271	14.576792
Cu	-1.064279	6.971306	10.628332
O	-0.751436	8.422300	11.899924
N	-1.262633	3.707496	10.449731
N	-0.697154	5.464388	11.938425
N	-1.431483	5.679999	9.140707
C	-1.668384	6.210604	7.914032
O	-0.607388	8.422300	9.408073
O	-3.372154	7.309714	10.860405
C	-1.512714	4.342538	9.249793
C	-1.849356	3.518837	8.174982
C	-0.833693	4.155563	11.676406
C	0.026621	4.891672	14.154354

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C      -0.269691    5.808018   13.174725
C      -2.079241    4.084816    6.946168
C      -1.998220    5.469442    6.813554
C      -0.528307    3.176892   12.621812
C      -0.097081    3.542419   13.870946
C      -3.908969    8.422300   10.971630
H       0.148940    8.422300    9.208084
H      -0.668144   14.722180   12.384391
H      -1.580903    9.517199    7.935422
H      -1.937515   14.301065    8.266956
H       0.287625   11.673308   15.090135
H      -1.504874   13.728349   10.459356
H      -2.108325   10.831078    5.924830
H      -2.440758   13.391457    6.192196
H      -0.054372   10.022537   13.272046
H       0.337745   13.947329   14.576792
Cu     -1.064279    9.873294   10.628332
N      -1.262633   13.137104   10.449731
N      -0.697154   11.380212   11.938425
N      -1.431483   11.164601    9.140707
C      -1.668384   10.633996    7.914032
O      -3.372154    9.534886   10.860405
C      -1.512714   12.502062    9.249793
C      -1.849356   13.325763    8.174982
C      -0.833693   12.689037   11.676406
C       0.026621   11.952928   14.154354
C      -0.269691   11.036582   13.174725
C      -2.079241   12.759784    6.946168
C      -1.998220   11.375158    6.813554
C      -0.528307   13.667708   12.621812
C      -0.097081   13.302181   13.870946
```

Optimized ωB97X-D/cc-pVTZ Kohn-Sham triplet geometry
of CITLAT (Complex 8).

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Cu     -0.0730822308     0.0887543490     1.4463209949
O       0.1963213404     1.3935693921     0.0000000000
H       1.1388404125     1.5796172815     0.0000000000
Cu     -0.0730822308     0.0887543490    -1.4463209949
O      -1.0697306915    -0.8929854865     0.0000000000
H      -2.0145095732    -0.7424336971     0.0000000000
N      -0.3194045620    -1.3725424431    -2.8182377381
C      -0.2077106385    -1.2411017902    -4.1361913994
C      -0.3775229840    -2.6148509399    -2.3016680362
H      -0.4613016849    -2.6430449547    -1.2266080247
C      -0.3297549917    -3.7513730297    -3.0649424262
H      -0.3730432446    -4.7237351293    -2.6011612967
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N	-0.1316561306	0.0012665462	-4.7303882939
H	-0.0771810535	-0.0414506000	-5.7322233869
C	-0.1398518047	1.2896986011	-4.2407970530
N	-0.1425212461	1.5356338365	-2.9327641994
C	-0.1626320700	2.8218674030	-2.5291504919
H	-0.1779485926	2.9491277063	-1.4572148956
C	-0.1617656483	3.8846864627	-3.3938698797
H	-0.1660002714	4.8925871558	-3.0100534873
C	-0.1451313324	3.6225478278	-4.7604324222
H	-0.1442531405	4.4276563301	-5.4818225863
C	-0.1404703499	2.3216420590	-5.1898911247
H	-0.1386936301	2.0811777972	-6.2436861728
C	-0.2196685908	-3.6115492312	-4.4450954622
H	-0.1721535683	-4.4781434081	-5.0893558134
C	-0.1614646143	-2.3535873868	-4.9858415415
H	-0.0771908322	-2.2161966441	-6.0547551149
N	-0.3194045620	-1.3725424431	2.8182377381
C	-0.2077106385	-1.2411017902	4.1361913994
C	-0.3775229840	-2.6148509399	2.3016680362
H	-0.4613016849	-2.6430449547	1.2266080247
C	-0.3297549917	-3.7513730297	3.0649424262
H	-0.3730432446	-4.7237351293	2.6011612967
N	-0.1316561306	0.0012665462	4.7303882939
H	-0.0771810535	-0.0414506000	5.7322233869
C	-0.1398518047	1.2896986011	4.2407970530
N	-0.1425212461	1.5356338365	2.9327641994
C	-0.1626320700	2.8218674030	2.5291504919
H	-0.1779485926	2.9491277063	1.4572148956
C	-0.1617656483	3.8846864627	3.3938698797
H	-0.1660002714	4.8925871558	3.0100534873
C	-0.1451313324	3.6225478278	4.7604324222
H	-0.1442531405	4.4276563301	5.4818225863
C	-0.1404703499	2.3216420590	5.1898911247
H	-0.1386936301	2.0811777972	6.2436861728
C	-0.2196685908	-3.6115492312	4.4450954622
H	-0.1721535683	-4.4781434081	5.0893558134
C	-0.1614646143	-2.3535873868	4.9858415415
H	-0.0771908322	-2.2161966441	6.0547551149
O	1.9122864545	-0.6622436998	-1.1242579786
C	2.4185555355	-0.8815298070	0.0000000000
H	3.4311512747	-1.3172547860	0.0000000000
O	1.9122864545	-0.6622436998	1.1242579786