Electronic Supplementary Material (ESI) for Dalton Transactions.

High Selectivity towards Small Copper Ions by a Preorganized Phenanthroline-Derived Tetradentate Ligand and New Insight into the Complexation Mechanism

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Supplementary information

Contents

EXPERIMENTAL SECTION

General. Chemical reagents such as $Cu(NO_3)_2 \cdot 3H_2O$, $Ln(NO_3)_3 \cdot 6H_2O$ (Ln =La, Eu, and Yb), $UO_2(NO_3)_2 \cdot 6H_2O$, $Th(NO_3)_4 \cdot 5H_2O$, and other nitrate salts were of analytical grade. Stock solution of ^{241}Am in 1.0 M HNO_3 was provided by China Institute of Atomic Energy (CIAE). Methanol, dichloromethane, and other inorganic/organic reagents were of analytical grade and used without further purification. *N*,*N*'-diethyl-*N*,*N*'-ditolyl-2,9-dicarboxamide-1,10-phenanthroline(Et-Tol –DAPhen, ligand **1**) was synthesized according to our previous reported method[1].

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance III 500 MHz spectrometer with tetramethyl-silane as an internal solvent resonances reference. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet Nexus 670 Model instrument using the KBr self supported pellet technique. Electrospray ionization mass spectrometry (ESI-MS) data was obtained on a Bruker Amazon SL instrument in the form of positive model.

Solvent Extraction Experiments. The aqueous phases were prepared with stock solution of Cu^{2+}, Pb^{2+}, $^{241}Am^{3+}$, UO_2^{2+}, Th^{4+}, La^{3+}, Eu^{3+}, Yb^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Sr^{2+} in different HNO_3 concentration (0.1-4.0 mol/L). The organic phases were prepared by dissolving ligand **1** (0.01 mol/L) in cyclohexanone. Each aqueous phase (1 mL) was vigorously shaken with each organic phase (1 mL) for 60 min at 25 ^oC. This contact time was enough to reach extraction equilibrium. After phase separation by centrifugation, the activity of α-ray emitters ^{241}Am was measured by a low background α scintillation detector (FJ414, Beijing Nuclear Instrument Factory). The concentrations of other metal ions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, ULTIMA 2, Horiba). The distribution ratio (*D*) was calculated by the ratio between the concentration (radioactivity counts) in the organic phase and aqueous phase. The separation factor (*SF*) was calculated by the ratio of distribution ratios between two metal ions.

Fluorescence Measurements. The fluorescence spectra were carried out on a F-4600 fluorescence spectrophotometer (Hitachi, Japan) in a 1.0 cm quartz cell. The temperature was controlled at 25^{o}C by a circulated thermostat bath. The emission spectra were recorded in the range of 300–475 nm at an excitation wavelength of 280 nm. The width of excitation slit and emission slit were both set to 5 nm. Fluorometric titrations of 2×10^{-5} M Et-Tol-DAPhen were performed with addition of 1.0×10^{-3} M $Cu(NO_3)_2$ (0 to 3 equiv.) in CH_3CN solution at 25 ^{o}C. 0.01 M Et_4NNO_3 was used to control the ionic strength.

X-ray Crystallographic Measurements. X-ray crystallographic data of copper complex with Et-Tol-DAPhen was collected with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å) at 293 K on a Bruker SMART APEX II CCD X-ray diffractometer. Data treatments were carried out with the SAINT program[2]. The structure was solved using direct methods and refined on F_2 by full-matrix least-squares with the SHELXTL-97 program[3]. The non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculation. Because the second nitrate group can not be properly refined (bond angles within this nitrate group are highly off) even with several restraints (we tried both isor and dfix commends), we therefore "SQUEEZE" all the disordered units. Additionally, it is worthwhile to note that the actual formula of the title compound is $C_{64}H_{60}CuN_{10}O_{10}$, although the cif file shows a missing nitrate model with a formula of $C_{64}H_{60}CuN_9O_7$. X-ray crystallographic data of copper complex with Et-Tol-DAPhen are summarized in Table S1.

Theoretical Methods. All the theoretical calculations were carried out by using the density functional theory (DFT) method with the Gaussian 09 package[4]. The species were optimized at the B3LYP, BP86 and M06-2x level of theory, respectively. For geometry optimizations, the LANL2DZ ECP basis set was applied for copper atom while the 6-311G(d,p) basis set was utilized for the other light atoms H, C, N and O. Harmonic vibrational frequencies were calculated to verify the minimum character of the optimized structures. The Wiberg bond indices (WBIs)[5] were calculated by natural bond orbital (NBO) analyses at the the same method as geometry optimization. The frequencies of all the chemical species were calculated at the same level of theory on the basis of the optimized geometries. Other detailed methods were the same as our previous studies[6].

To explore the stability of the 1:2 copper complex, the binding energy of the Cu^{2+} and Et-Tol-DAPhen ligands was also calculated. The binding energy is defined as

$$\Delta G = G([CuL_2]^{2+}) - G(Cu^{2+}) - 2G(L) \qquad (1)$$

Were G is the Gibbs free energy.

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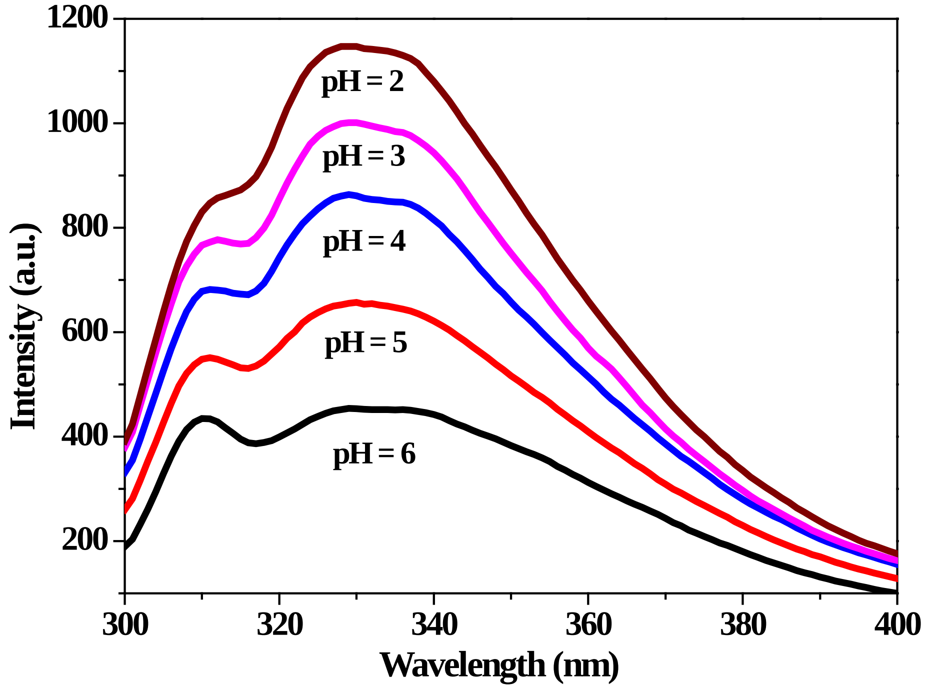

Fig. S1 Fluorescence spectra of Et-Tol-DAPhen at various pH values in CH_3OH/H_2O (vol/vol 50%/50%) solution. $C_L = 2\times10^{-5}$ M, T = 25 ^{o}C, I = 0.1 M Et_4NNO_3.

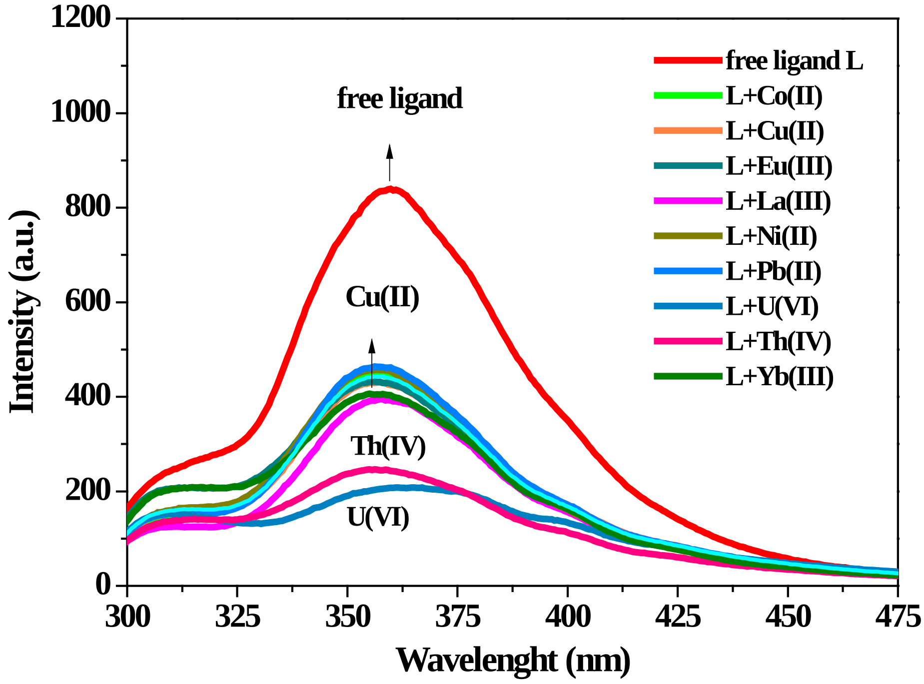

Fig. S2 Fluorescence spectra of Et-Tol-DAPhen before and after adding metal ion in CH_3CN solution. $C_L = 2\times10^{-5}$ M, $C_M = 2\times10^{-5}$ M, T = 25 ^oC, I = 0.01 M Et_4NNO_3.

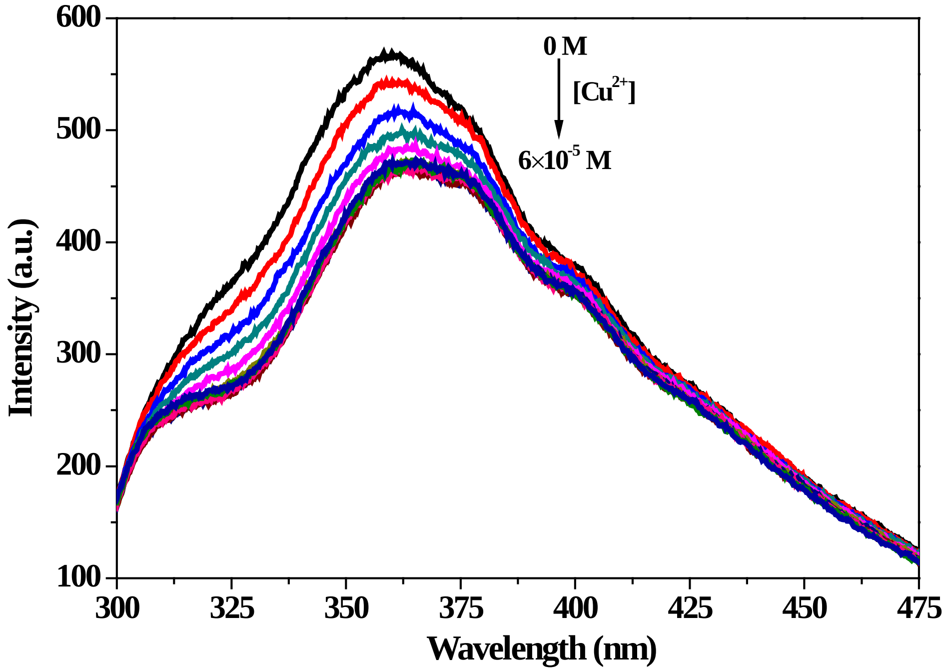

Fig. S3 Fluorescence spectra of Et-Tol-DAPhen before and after adding 0-6×10^{-5} M Cu^{2+} in CH_3CN solution. C_L = 2×10^{-5} M, C_M = 1.0×10^{-3} M, T = 25 °C, I = 0.01 M Et_4NNO_3.

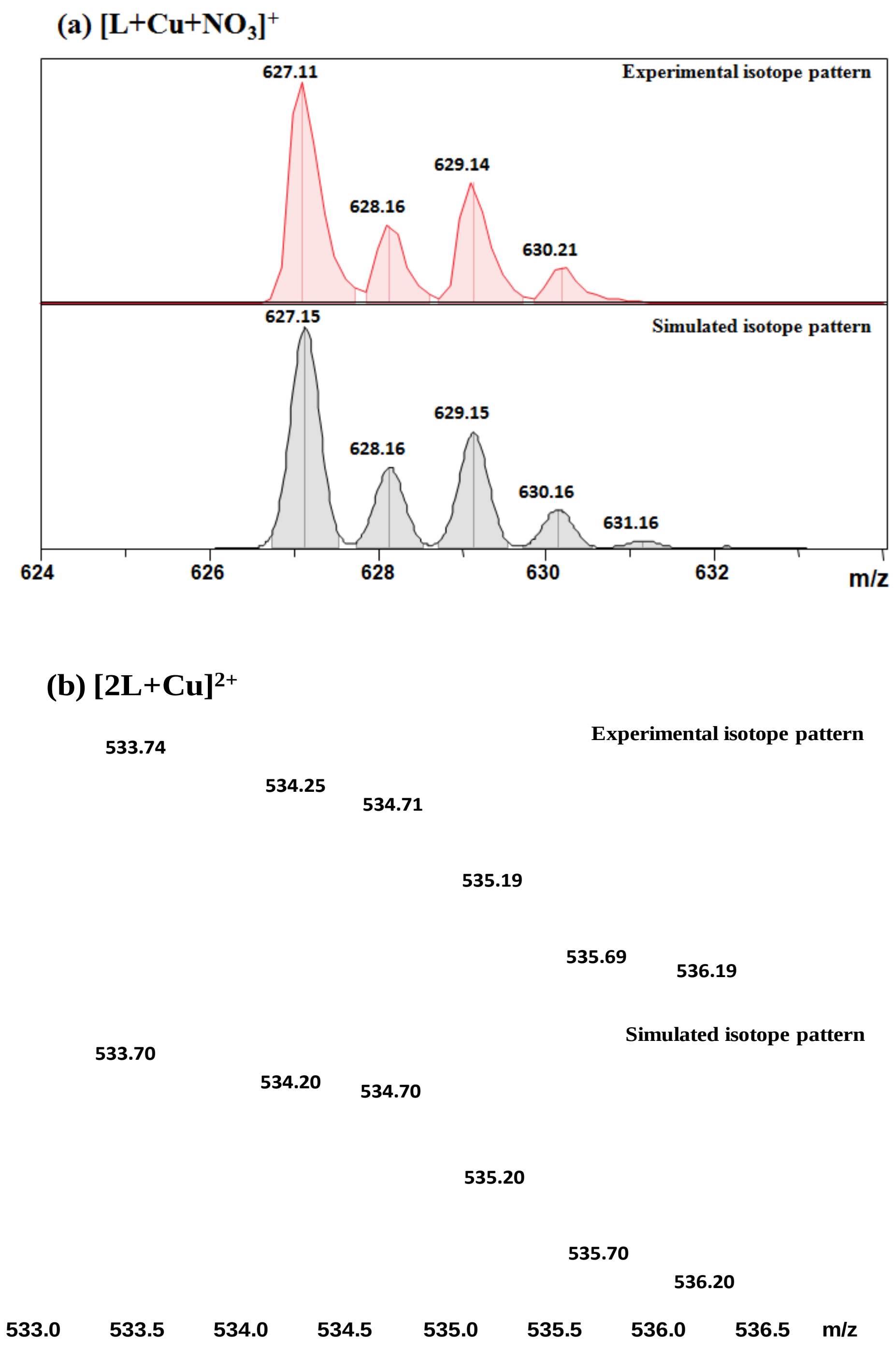

Fig. S4 Experimental and simulated isotope patterns of (a) $[CuL(NO_3)]^+$ and (b) $[CuL_2]^{2+}$ complexes detected by ESI-MS in positive mode.

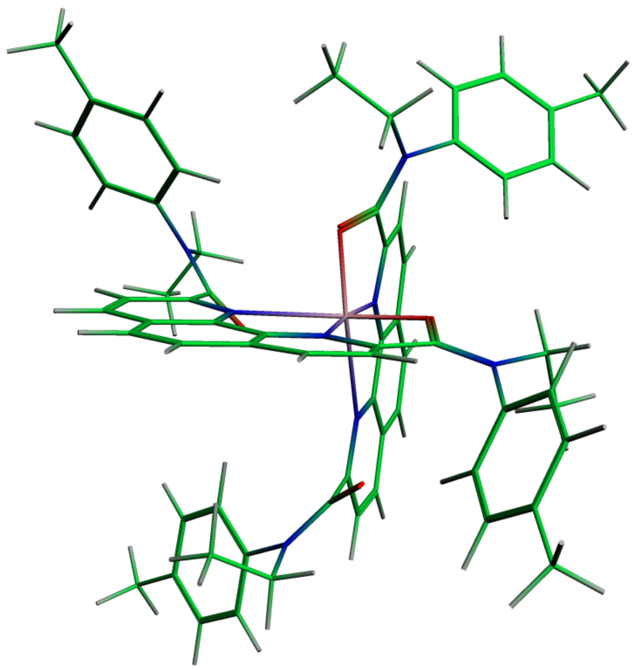

Fig. S5 Optimized of [Cu**L**$_2$]$^{2+}$ at the BP86 level of theory. The structures optimized at the M06-2x and B3LYP level of theory are similar. Only some bond lengths are different, some of which are listed in **Table S2**.

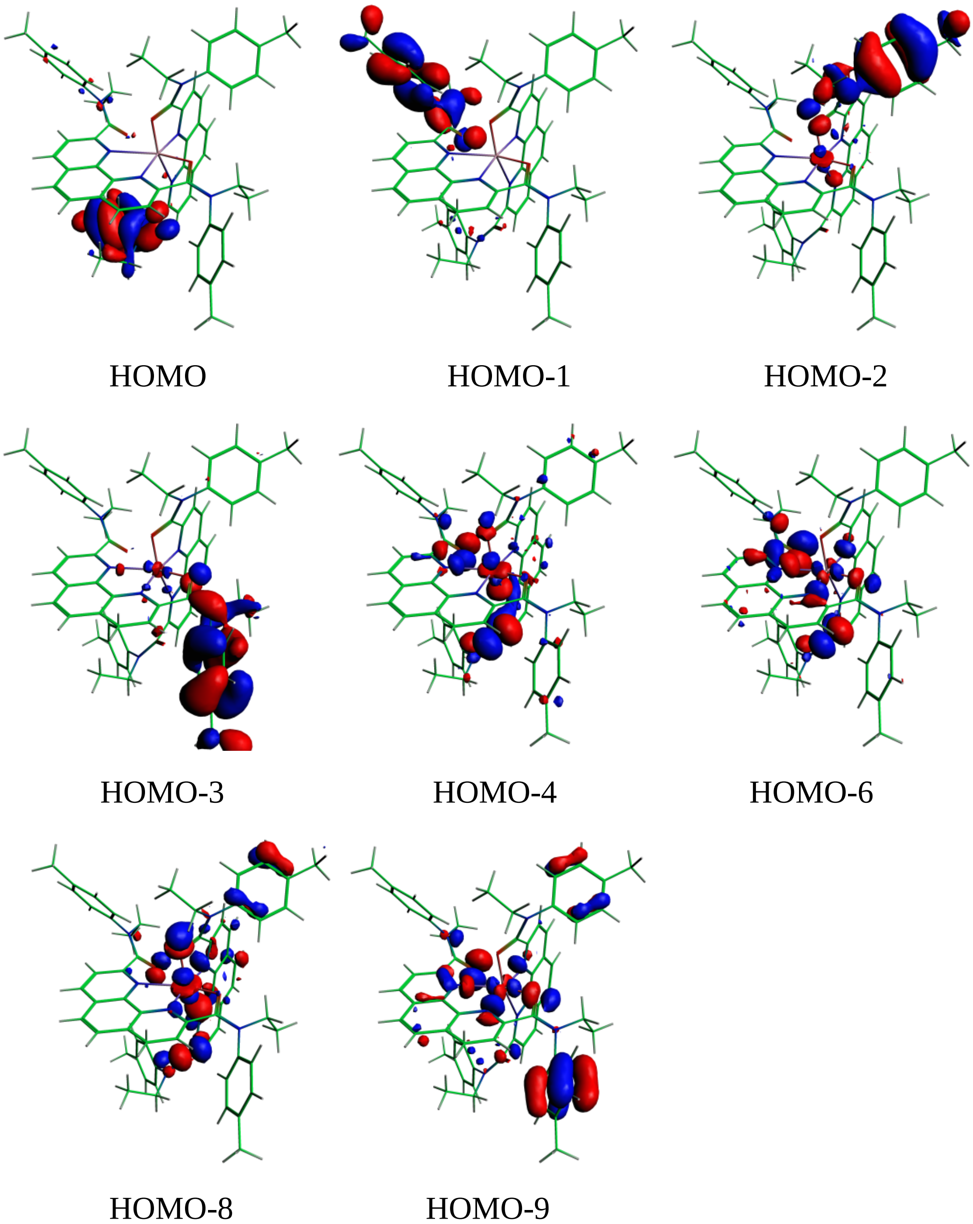

Fig. S6 Selected α-spin frontier molecular orbitals of the copper complex. The isosurface value of the molecular orbitals is set to be 0.03 au.

Table S1. Crystal data and structure refinements for copper complex with Et-Tol-DAPhen.

Compound	Copper Complex with Et-Tol-DAPhen
CCDC No.	986236
empirical formula	$C_{64}H_{60}CuN_9O_7$
M	1130.75
crystal system	monoclinic
space group	P2(1)/n
a (Å)	17.9529(5)
b (Å)	18.4150(4)
c (Å)	20.5742(6)
α (deg)	90.00
β (deg)	107.485(3)
γ (deg)	90.00
V (Å^3)	6487.6(3)
Z	4
ρ (g/cm^3)	1.197
No. of reflns collected	23523
R_1/wR_2 (I>2σ(I))[a]	0.0609/0.0.2107
R_1/wR_2 (all data)	0.0861/0.2331

[a] $R_1 = \sum(\Delta F / \sum(F_o))$ $wR_2 = \left(\sum\left[w\left(F_o^2 - F_c^2\right)\right]\right) / \sum\left[w\left(F_o^2\right)^2\right]^{1/2}$

Table S2. Selected calculated geometrical parameters concerning the copper atom and the corresponding WBIs at BP86, M06-2x and B3LYP level of theory, respectively.

	bond length				**WBIs**		
	Crys.	BP86	M06-2x	B3LYP	BP86	M062X	B3LYP
$\mathbf{Cu_1\text{-}N_6}$	1.962(3)	2.004	2.023	2.003	0.264	0.225	0.254
$\mathbf{Cu_1\text{-}N_5}$	2.254(2)	2.330	2.241	2.341	0.196	0.190	0.186
$\mathbf{Cu_1\text{-}O_2}$	2.335(2)	2.396	2.148	2.255	0.157	0.192	0.180
$\mathbf{Cu_1\text{-}N_2}$	2.264(3)	2.300	2.293	2.346	0.204	0.175	0.186
$\mathbf{Cu_1\text{-}N_1}$	1.936(3)	1.983	2.025	1.991	0.272	0.225	0.259
$\mathbf{Cu_1\text{-}O_4}$	2.092(3)	2.180	2.149	2.154	0.224	0.195	0.214

Table S3. Cartesian coordinates of optimized structures of copper complex at the BP86 level of theory.

Atom	Coordinates (Angstroms)		
	X	Y	Z
Cu	0.02627600	0.41218600	0.04274400
N	-1.37088900	0.68976700	-1.36699200
O	-1.92472000	1.18548300	1.19812600
N	1.03737800	-0.49822800	-1.84921600
O	0.78190400	2.43091100	-0.28399100
N	1.28769000	0.66974100	1.55055700
N	-0.32180800	-1.48432200	1.29711100
O	3.39898300	-0.07604500	-0.28176400
O	-1.36670900	-2.43945300	-1.18486100
N	3.90439700	-2.27943800	-0.71685000
N	2.62865400	3.70779700	0.11747700
C	1.30245800	-0.24044200	2.55000900
C	0.15628600	-0.38927200	-2.88001300
N	-3.37206400	2.88507700	0.68723700
C	-2.50959000	1.35226200	-1.09025500
C	-1.12376200	0.22699700	-2.61750900
C	2.21582100	-1.08773000	-2.08271900
N	-3.26434100	-3.01324500	-0.02472300
C	0.46247200	-1.40332600	2.40839200
C	2.03226200	1.78804200	1.61636800
C	-2.08501400	0.35729500	-3.66389600
C	2.10144600	-0.06098600	3.71634300
C	1.81082600	2.67050800	0.41274300
C	-2.58908500	1.82201700	0.34759300
C	3.54229900	-3.54793600	-1.29493000
C	0.44142500	-0.83537800	-4.20291700
C	-1.14881500	-2.53013900	1.18049000
C	3.20786600	-1.11546400	-0.93165200
C	-3.88599800	3.84580400	-0.25811500
C	4.52361900	-4.33016400	-1.93249000
C	0.48260400	-2.39360400	3.43135200
C	-3.32097800	0.96369800	-3.33393800
C	2.84077300	1.14338300	3.80409900
C	3.96257000	3.87432200	0.64735500
C	2.80584500	2.06447400	2.76622900
C	-3.53032700	1.47080600	-2.06083300
C	2.59754400	-1.54025100	-3.37253000

C	-1.76650700	-0.12458400	-4.97705700
C	4.93069300	2.87901300	0.44343100
C	-5.26122300	4.13398700	-0.29930200
C	4.18489800	-5.56889600	-2.47962700
C	-0.54585000	-0.69153300	-5.23636100
C	-4.87340400	5.80236100	-2.04959300
C	-5.74080600	5.10135600	-1.18669100
C	-1.94765900	-2.63056400	-0.10841600
C	-1.17288700	-3.58329600	2.13330800
C	2.22600100	-4.03081600	-1.21088300
C	2.09331000	-1.07949800	4.72763200
C	-3.49979200	5.50061300	-1.98906200
C	-3.00314700	4.54320200	-1.09833800
C	-0.35434800	-3.52241800	3.24633200
C	4.29900100	5.06272900	1.31817500
C	1.71793800	-1.40549300	-4.43024200
C	-4.86014500	-4.08243500	1.51539800
C	1.32277100	-2.20595600	4.58266100
C	-3.47746300	3.22243800	2.13719800
C	4.99670200	-2.26619400	0.28929000
C	2.86597100	-6.06428200	-2.41583100
C	-4.02632000	-2.99462600	1.19213400
C	6.59117900	4.25550900	1.60704600
C	-5.61268500	-4.06250800	2.69083100
C	1.89825700	-5.26716100	-1.77960600
C	-5.55291000	-2.97294000	3.58460400
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C	-4.71793100	-1.89437000	3.24383200
C	5.60061700	5.24242200	1.79317800
C	-3.97549100	-1.88709300	2.05669900
C	2.24551600	4.60484900	-1.00985100
C	8.00347400	4.47850000	2.08984400
C	4.59268200	-2.93507200	1.60579900
C	2.51972800	-7.41574500	-2.99245300
C	-5.40146300	6.86677200	-2.98010300
C	-6.38080100	-2.96292900	4.84680700
C	2.85509400	4.16432600	-2.34353000
C	-4.57293900	2.44007300	2.86687000
C	-3.95820000	-3.31556000	-1.30754900
C	-3.59732600	-4.68431700	-1.89240400
H	-2.51262300	-0.02263500	-5.76878000
H	-0.30410900	-1.04780400	-6.24096900
H	2.71013500	-0.94045100	5.61873500
H	1.32402300	-2.97737600	5.35693500

H	-1.93085800	4.33929800	-1.04140100
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H	-5.95406200	3.59320200	0.34919800
H	3.54203900	5.83431500	1.48164200
H	5.85407400	6.16682800	2.31935100
H	6.98122400	2.29935300	0.76754100
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H	-4.65998100	-1.03177400	3.91372300
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H	3.75524200	-2.39829400	2.07758600
H	4.29474200	-3.98290200	1.44922200
H	5.44364700	-2.92589500	2.30427700
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H	2.56627300	4.87653100	-3.13168200
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