Supporting Information

A Tale of Hydrogen Abstraction, Initially Detected *via* X-ray Diffraction

Alice K. Hui,[a] Chun-Hsing Chen,[a] Adam M. Terwilliger,[b] Richard L. Lord*[b] and Kenneth G. Caulton*[a]

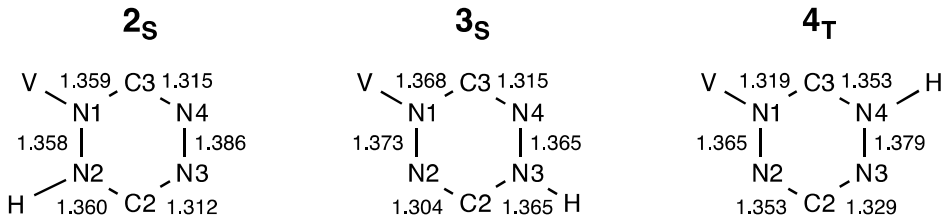

Figure SI-1. Comparison of bond lengths (Å) within hydrogenated tetrazine ring for $\mathbf{2}_S$, $\mathbf{3}_S$, and $\mathbf{4}_T$.

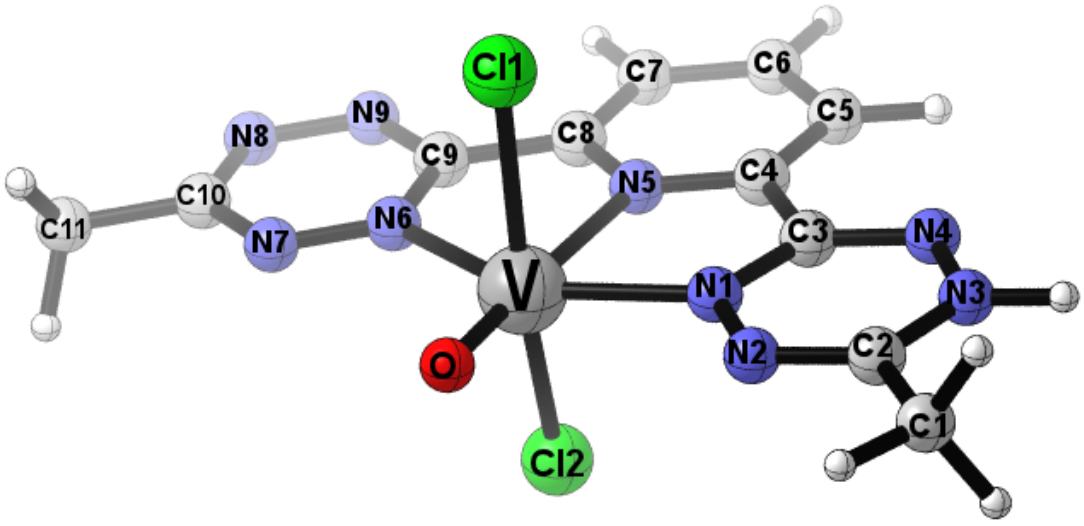

Figure SI-2. Optimized structure of singlet [(Hbtzp)VCl_2O] labelling the bond lengths that can be viewed in Table SI-1.

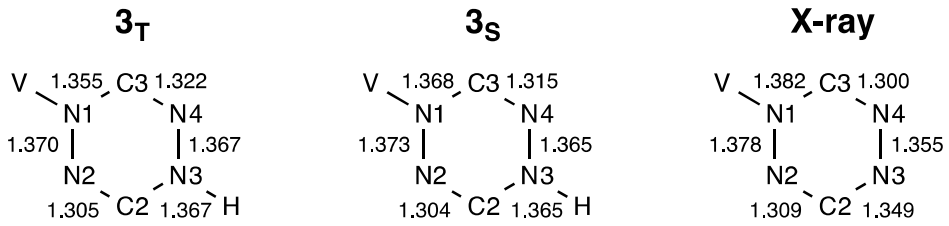

Figure SI-3. Comparison of bond lengths (Å) within hydrogenated tetrazine ring for $\mathbf{3_S}$, $\mathbf{3_T}$, and experiment.

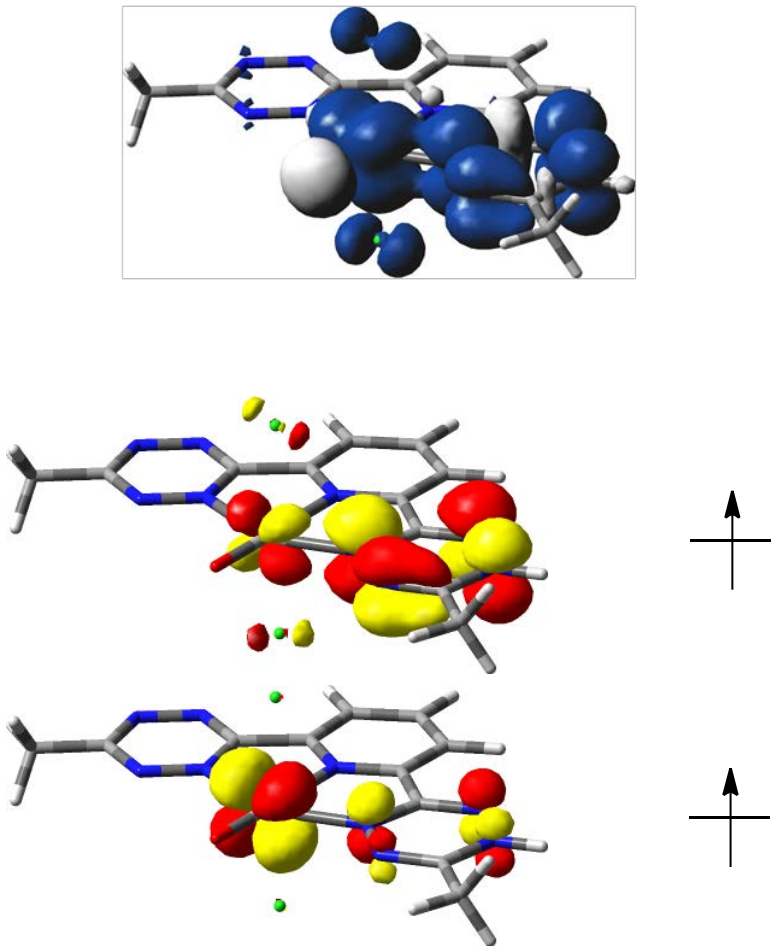

Figure SI-4. Isosurface plots for the spin density (top, 0.002 au) and the corresponding orbitals (bottom, 0.05 au) of $\mathbf{3_T}$.

Table SI-1. Bond lengths (Å) for Optimized Structures (**3_T** and **3_S**) and Experimental Results.

	3_T	**3_S**	**X-ray**
C1–C2	1.495	1.496	1.4840(15)
C2–N2	1.305	1.304	1.3097(12)
C2–N3	1.367	1.365	1.3499(13)
C3–C4	1.480	1.479	1.4696(13)
C3–N4	1.322	1.315	1.3008(12)
C4-N5	1.330	1.328	1.3269(12)
C4–C5	1.398	1.398	1.3955(12)
C5–C6	1.397	1.397	1.3889(15)
C6–C7	1.397	1.398	1.3926(15)
C7–C8	1.397	1.396	1.3885(13)
C8–C9	1.473	1.474	1.4706(13)
C9–N9	1.332	1.331	1.3391(13)
C10–C11	1.495	1.495	1.4853(16)
N1–C3	1.355	1.368	1.3816(11)
N1–N2	1.370	1.373	1.3786(11)
N3–N4	1.367	1.365	1.3542(13)
N5–C8	1.331	1.331	1.3366(12)
N6–C9	1.361	1.361	1.3459(12)
N6–N7	1.308	1.305	1.3178(12)
N7–C10	1.349	1.350	1.3426(13)
N8–C10	1.345	1.344	1.3487(15)
N8–N9	1.322	1.324	1.3180(15)
V1–Cl1	2.375	2.384	2.3821(3)
V1–Cl2	2.375	2.384	2.3673(3)
V1–N1	2.156	2.070	1.9740(8)
V1–N5	2.276	2.259	2.1864(8)
V1–N6	2.159	2.185	2.193(8)
V1–O1	1.579	1.578	1.5994(7)
N3-H	1.011	1.010	0.91(2)

General. All manipulations were carried out under an atmosphere of ultra high purity nitrogen using standard Schlenk techniques or in a glovebox. Solvents, including acetonitrile, were purchased from commercial sources, purified using Innovative Technology SPS-400 PureSolv solvent system and degassed by the freeze-pump-thaw method twice prior to use. Glassware was oven-dried at 150 ^{o}C overnight and flame dried prior to use. NMR spectra were recorded in various deuterated solvents at 25 ^{o}C on a Varian Inova-400 spectrometer (^{1}H: 400.11 MHz). Proton chemical shifts are reported in ppm versus solvent protic impurity, but referenced finally

to $SiMe_4$. Mass spectrometry analyses were performed in an Agilent 6130 MSD (Agilent Technologies, Santa Clara, CA) quadrupole mass spectrometer equipped with a Multimode (ESI and APCI) source. All starting materials have been obtained from commercial sources and used as received without further purification.

Synthesis of (Hbtzp)$VOCl_2$. btzp (10 mg, 37.42 μmol) was dissolved in neat acetonitrile (5 mL) and added to a solution of $VCl_3(THF)_3$ (13.82 mg, 37.42 μmol) in neat acetonitrile (5 ml). The solution immediately changed from bright pink to dark brown. Solid product was isolated by vacuum removal solvent. Dark brown needles were grown from slow diffusion of diethyl ether into a concentrated solution in acetonitrile. **MS:** The ESI mass spectrum of the crystalline product dissolved in MeCN showed no negative ions, but showed positive ions for $(M - Cl)^+$ and $(M - HCl + K)^+$ where M = (Hbtzp)$VOCl_2$. Reduction of cone voltage to ~25 V was necessary to get acceptable ion production. Both species thus support the presence of a hydrogen on the pincer ligand. The second of these ions shows that loss of the pincer hydrogen is a favorable process, together with Cl. The capture of K^+, to create a cation, is typical for the many nitrogen lone pairs in btzp, under these ESI injector conditions (i.e. rich in alkali metal cations); for example, ESI of btzp itself in MeCN yields the ions $Na(btzp)_n^+$ with n = both 1 *and* 2; also observed is $(M+H)^+$ the protonated ligand.

MSC#13504 X-ray diffraction single crystal structure determination of (Hbtzp)$VOCl_2$

The sample was investigated with synchrotron radiation at the ChemMatCARS beamline, Advanced Photon Source, Argonne National Laboratory, Chicago, utilizing the SCrAPS program (http://www.iumsc.indiana.edu/projects/SCrAPS/index.html). A violet crystal (approximate dimensions 0.012 x 0.011 x0.007 mm^3) was placed onto the tip of a glass capillary and mounted on a Bruker D8 Platform diffractometer and measured at 100(2) K.

Data collection

The data collection was carried out using synchrotron radiation (λ = 0.41328 Å, energy of 30 keV silicon 111 and 311 monochromators, two mirrors to exclude higher harmonics) with a frame time of 0.15 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of 2 hemispheres. Two major sections of frames were collected with 0.30º steps in ϕ and a detector position of -15° in 2θ. Data to a resolution of 0.55 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9905 strong reflections from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2]

Structure solution and refinement

The space group P2(1)/n was determined based on intensity statistics and systematic absences. The structure was solved using SHELXS-97[3] and refined with SHELXL-97.[3] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Wavelength dependence of anomalous dispersion (energy = 30 keV) was implemented as described by Brennan and Cowan (Brennan, S., Cowan, P. L. (1992) Rev. Sci Instrum. 63 (1), 850 – 853). Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. One acetonitrile (N12,C16,C17) is disordered over two sites (ratio 79.5/20.5) and was refined with equal anisotropic displacement parameters for each of the following atom pairs: N12/N12d, C16/C16d and C17/C17D. Additionally, rigid bond and same 1-2 and 1-3 distance restraints were applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with individual relative isotropic displacement parameters. However, H3N was located in a difference map and refined freely with its own isotropic displacement parameter. The final full matrix least squares refinement converged to R1 = 00.0410 and wR2 = 0.1135 (F^2,all data). The remaining electron density is located along the bonds.

Structure description

The structure found includes three acetonitriles in the solvent accessible region.

1 SAINT, Bruker Analytical X-Ray Systems,Madison, WI, current version.

2 An empirical correction for absorption anisotropy,R. Blessing, Acta Cryst. A51, 33 - 38 (1995).

3 SHELXTL-Plus, Bruker Analytical X-Ray Systems,Madison, WI, current version.

Table SI-2. Hydrogen bonds for 13504 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N3-H3N...Cl1#1	0.91(2)	2.24(2)	3.1306(9)	166(2)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+1/2,z-1/2

Computational Supporting Information

Electronic structure calculations were carried out using DFT[1] as implemented in Gaussian09.[2] Geometry optimizations were performed at the B3LYP/LANL2DZ/6-31G(d,p)[3-7] level of theory with no symmetry constraints. All optimized structures were confirmed to have stable wavefunctions,[8-9] and to be local minima by analyzing the harmonic frequencies.[10-11] Cartesian coordinates and frequencies for all optimized species may be found in Tables A and B, respectively. Thermodynamics may be found in Table C.

1. Parr, R.G.; Yang, W. *Density-functional theory of atoms and molecules*; Oxford University Press: New York, 1989.

2. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A.

Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

3. Vosko, S.H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

4. Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785.

5. Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648.

6. Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. *J. Phys. Chem.* **1994**, *98*, 11623.

7. a) Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82***,** 270. b) Wadt, W.R.; Hay, P.J. *J. Chem. Phys.* **1985**, *82*, 284. c) Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 299.

8. Schlegel, H.B.; McDouall, J.J. In *Computational Advances in Organic Chemistry*; Oegretir, C.; Csizmadia, I.G., Eds.; Kluwer Academic: Amsterdam, The Netherlands, 1991.

9. Bauernschmitt, R.; Ahlrichs, R. *J. Chem. Phys.* **1996**, *104*, 9047.

10. Schlegel, H.B. *J. Comput. Chem.* **1982**, *3*, 214.

11. Schlegel, H.B. *WIREs Comput. Mol. Sci.* **2011**, *1*, 790.

Table A. Cartesian coordinates (Å) for all optimized structures.

2S - $[V(btzp\text{-}H_{N2})OCl_2]^0$ *S*=0

C	-1.188026	1.778383	-0.000001
C	-1.272009	3.171971	0.000017
C	-0.076263	3.897067	0.000009
C	1.152195	3.233593	-0.000013
C	1.134788	1.836923	-0.000032
N	-0.008963	1.154137	-0.000027
H	-0.104511	4.981832	0.000023
H	-2.240282	3.658132	0.000036
H	2.098299	3.761723	-0.000016
C	2.314494	0.946747	-0.000047
C	-2.332260	0.849562	0.000014
N	-3.576995	1.321841	0.000022
N	-4.576456	0.455053	0.000062
N	-3.014835	-1.343422	0.000039
N	-2.037975	-0.478560	0.000003
N	3.052308	-1.206311	-0.000066
N	1.981355	-0.371125	-0.000065
N	4.596712	0.550940	-0.000023
N	3.533429	1.439205	-0.000038
C	-4.273370	-0.854658	0.000120
C	4.326953	-0.732476	-0.000013
C	5.437706	-1.734348	0.000130
C	-5.392629	-1.845180	0.000202
H	-6.349914	-1.323966	-0.000975
H	6.387168	-1.200109	-0.000653
H	-5.322162	-2.491093	-0.880414
H	-5.323523	-2.489323	0.882240
H	5.382754	-2.374790	0.887024
H	5.381936	-2.376053	-0.885793
V	0.063430	-1.088259	-0.000056
O	0.589889	-2.593449	-0.000053
Cl	-0.220611	-0.768177	2.328329
Cl	-0.220686	-0.768166	-2.328408
H	2.784747	-2.188802	-0.000065

2T - $[V(btzp\text{-}H_{N2})OCl_2]^0$ *S*=1

C	-1.190997	1.770065	-0.000045
C	-1.272860	3.164420	-0.000089
C	-0.076151	3.886592	-0.000135
C	1.150681	3.219261	-0.000138
C	1.131099	1.822870	-0.000096
N	-0.014356	1.141902	-0.000051
H	-0.101544	4.971432	-0.000170
H	-2.240130	3.652533	-0.000087
H	2.098395	3.744494	-0.000173
C	2.318663	0.938986	-0.000092
C	-2.340728	0.847346	0.000006
N	-3.582716	1.330402	-0.000002
N	-4.589665	0.474186	0.000080
N	-3.047066	-1.339750	0.000167
N	-2.060590	-0.483828	0.000068
N	3.069027	-1.205503	-0.000036
N	2.003126	-0.366919	-0.000046
N	4.602741	0.560732	-0.000105
N	3.539824	1.451526	-0.000126
C	-4.299978	-0.839448	0.000296
C	4.344203	-0.723529	-0.000055
C	5.460833	-1.718822	-0.000005
C	-5.429825	-1.817910	0.000064
H	-6.381303	-1.286161	-0.001075
H	6.407439	-1.179533	-0.000176
H	-5.366606	-2.464346	-0.880704
H	-5.368052	-2.462927	0.881987
H	5.409354	-2.360284	0.886488
H	5.409188	-2.360577	-0.886275
V	0.019740	-1.114885	0.000026
O	0.520455	-2.627278	0.000100
Cl	-0.161794	-0.754135	2.325567
Cl	-0.161909	-0.754344	-2.325516
H	2.806636	-2.188143	0.000021

3S - $[V(btzp\text{-}H_{N3})OCl_2]^0$ *S*=0

C	1.184174	1.782528	-0.000005
C	1.250133	3.177280	-0.000025
C	0.042954	3.882490	-0.000063
C	-1.175108	3.199377	-0.000086
C	-1.136540	1.801833	-0.000079
N	0.016807	1.142650	-0.000040
H	0.052975	4.967619	-0.000077
H	2.210569	3.678789	-0.000023
H	-2.124346	3.721707	-0.000100
C	-2.299592	0.888751	-0.000030

C	2.333825	0.860892	-0.000013
N	3.574500	1.342247	0.000010
N	4.580612	0.482364	0.000047
N	3.028703	-1.326033	0.000148
N	2.043865	-0.469223	0.000097
N	-3.039725	-1.346595	-0.000072
N	-2.002899	-0.447686	-0.000022
N	-4.498878	0.472634	0.000050
N	-3.507085	1.408577	0.000006
C	4.283821	-0.828240	0.000116
C	-4.253386	-0.873820	-0.000040
C	-5.421962	-1.807018	-0.000072
C	5.407768	-1.813804	0.000070
H	6.363023	-1.288772	0.000217
H	-6.045251	-1.650653	-0.887435
H	5.339924	-2.459501	0.881025
H	5.340077	-2.459236	-0.881095
H	-5.048533	-2.830622	-0.000544
H	-6.044779	-1.651318	0.887739
V	-0.043744	-1.115658	0.000018
O	-0.167105	-2.688767	-0.000092
Cl	0.149297	-0.710047	-2.340944
Cl	0.148851	-0.709919	2.340959
H	-5.437050	0.847540	0.000162

3$_T$ - [V(btzp-H$_{N3}$)OCl$_2$]^0 *S*=1

C	-1.185104	1.781037	0.000012
C	-1.245479	3.176887	-0.000103
C	-0.035970	3.875945	-0.000310
C	1.178192	3.184967	-0.000380
C	1.133870	1.788043	-0.000234
N	-0.022801	1.132607	-0.000058
H	-0.039895	4.961107	-0.000414
H	-2.203852	3.682305	-0.000024
H	2.130523	3.701572	-0.000527
C	2.303322	0.880381	-0.000229
C	-2.342214	0.869342	0.000212
N	-3.578955	1.364782	0.000488
N	-4.594616	0.518707	0.000482
N	-3.066424	-1.309263	0.000313
N	-2.068595	-0.464188	0.000324
N	3.053289	-1.344924	-0.000008
N	2.020405	-0.444602	-0.000080
N	4.505012	0.478561	-0.000415
N	3.511638	1.417440	-0.000351
C	-4.313832	-0.796795	0.000088
C	4.267390	-0.867536	-0.000172
C	5.439655	-1.795879	-0.000153
C	-5.450538	-1.767766	-0.001201
H	-6.398808	-1.230348	0.011228
H	6.061982	-1.637714	-0.887841
H	-5.398244	-2.404517	-0.889771
H	-5.384343	-2.423771	0.872089
H	6.062281	-1.637363	0.887271
H	5.070358	-2.821002	0.000131
V	-0.019330	-1.143513	0.000327
O	-0.039065	-2.722086	0.000381
Cl	-0.040824	-0.716906	2.336853
Cl	-0.041180	-0.717420	-2.336411
H	5.442778	0.855195	-0.000270

4$_S$ - [V(btzp-H$_{N4}$)OCl$_2$]^0 *S*=0

C	-1.179580	1.776243	-0.000037
C	-1.244809	3.173025	-0.000008
C	-0.038218	3.873869	0.000029
C	1.179247	3.185809	0.000041
C	1.142764	1.787690	0.000012
N	-0.016785	1.133890	-0.000031
H	-0.042433	4.958780	0.000053
H	-2.204199	3.676287	-0.000015
H	2.112202	3.740020	0.000076
C	2.286416	0.853994	0.000028
C	-2.334739	0.859886	-0.000053
N	-3.570442	1.353044	-0.000077
N	-4.584732	0.503758	-0.000082
N	-3.049297	-1.319585	-0.000118
N	-2.055417	-0.471865	-0.000086
N	3.059271	-1.345000	0.000020
N	2.029701	-0.441673	-0.000001
N	4.655578	0.449349	0.000149
N	3.563931	1.289182	0.000062
C	-4.299755	-0.810314	-0.000191
C	4.307020	-0.837579	0.000170
C	5.422891	-1.837735	0.000111
C	-5.432148	-1.785402	0.000371
H	-6.382860	-1.252316	-0.000448

H	6.388588	-1.331707	-0.000699	Cl	-0.073776	-0.700021	2.330494
H	-5.368955	-2.432568	-0.879862	Cl	-0.073913	-0.699768	-2.330628
H	-5.369639	-2.430820	0.881958	H	3.807274	2.272741	-0.000094
H	5.340918	-2.480590	0.881424				
H	5.339919	-2.481677	-0.880303				
V	0.009050	-1.142171	-0.000069				
O	0.038486	-2.718519	-0.000049				
Cl	-0.094299	-0.697452	2.333577				
Cl	-0.094168	-0.697430	-2.333691				
H	3.797167	2.271067	0.000051				

4$_T$ - [V(btzp-H$_{N4}$)OCl$_2$]^0 *S*=1

C	-1.178755	1.776599	0.000044
C	-1.244191	3.173691	0.000080
C	-0.037386	3.873738	0.000071
C	1.179870	3.185215	0.000028
C	1.143778	1.786862	-0.000009
N	-0.016735	1.133158	-0.000002
H	-0.041007	4.958682	0.000099
H	-2.203445	3.677102	0.000114
H	2.113144	3.738784	0.000027
C	2.288324	0.856255	-0.000056
C	-2.334730	0.861355	0.000051
N	-3.570156	1.356689	0.000084
N	-4.585852	0.509933	0.000097
N	-3.054799	-1.316817	0.000019
N	-2.058612	-0.471062	0.000004
N	3.054200	-1.343782	-0.000125
N	2.033641	-0.437967	-0.000089
N	4.656963	0.444761	-0.000005
N	3.569344	1.292486	-0.000058
C	-4.303657	-0.805162	0.000079
C	4.308506	-0.837613	-0.000016
C	5.418901	-1.843517	0.000196
C	-5.438475	-1.777497	0.000227
H	-6.387808	-1.241951	-0.001055
H	6.387466	-1.343021	-0.001081
H	-5.376621	-2.424930	-0.879892
H	-5.378053	-2.422921	0.881943
H	5.333355	-2.485555	0.881840
H	5.331909	-2.487560	-0.879821
V	-0.002250	-1.145236	-0.000076
O	-0.004103	-2.721985	-0.000212

Table B. Frequencies (cm^{-1}) of all optimized structures.

2_S - $[V(btzp\text{-}H_{N2})OCl_2]^0$ S=0

32.18	46.79	56.82
62.78	68.51	82.66
83.67	98.56	107.10
128.14	135.21	148.58
176.05	187.79	209.31
214.09	227.48	240.26
259.16	296.63	302.04
305.38	328.61	332.74
342.14	344.96	372.82
384.79	412.37	474.97
475.06	514.65	548.93
584.67	617.22	620.41
632.74	652.36	670.63
689.50	699.91	741.96
769.90	822.42	825.97
859.62	878.83	891.87
962.20	987.92	989.05
1024.42	1042.09	1053.31
1056.42	1062.52	1062.89
1065.19	1093.36	1109.88
1122.00	1132.93	1169.90
1188.46	1270.69	1301.12
1323.61	1339.55	1344.48
1376.28	1411.30	1417.76
1434.60	1444.05	1448.34
1471.84	1485.02	1490.17
1494.01	1508.27	1521.70
1529.34	1557.69	1581.41
1636.99	1650.65	3057.28
3066.52	3119.09	3129.47
3178.52	3183.28	3214.52
3241.28	3243.77	3531.56

2_T - $[V(btzp\text{-}H_{N2})OCl_2]^0$ S=1

30.69	43.52	55.11
62.34	68.14	81.58
85.48	94.30	109.59
125.96	131.05	133.53
174.81	185.04	203.71
215.51	218.13	240.84
261.88	288.17	294.52
308.50	326.88	335.63
336.82	344.53	368.37
382.03	411.94	471.94
473.35	511.40	548.38
575.26	584.82	619.84
633.43	657.48	662.70
690.21	699.53	737.35
769.18	821.92	826.11
859.97	880.63	894.97
962.89	982.27	988.98
1024.56	1041.32	1053.55
1059.82	1062.23	1062.52
1066.63	1096.74	1109.19
1128.21	1144.63	1168.71
1187.31	1272.08	1293.13
1319.93	1332.74	1347.13
1374.15	1409.96	1416.58
1436.02	1442.89	1458.99
1468.92	1485.12	1490.11
1491.41	1501.07	1519.84
1525.60	1554.96	1588.39
1636.18	1650.16	3056.13
3066.68	3117.46	3129.68
3178.57	3182.96	3214.39
3241.35	3243.94	3551.35

3_S - $[V(btzp\text{-}H_{N3})OCl_2]^0$ S=0

32.23	47.32	54.32
58.63	60.30	75.37
79.24	89.06	97.57
127.71	128.31	152.52
180.30	189.49	194.60
202.63	214.96	232.23
249.67	284.18	289.94
295.06	312.68	317.54
341.98	349.85	374.94
381.56	412.45	463.68
474.36	478.05	514.18
545.55	583.09	615.98
632.07	653.43	657.05
687.86	699.22	745.67

767.78 820.14 825.08
857.32 876.42 890.70
956.42 988.76 989.84
1019.39 1042.62 1050.92
1062.33 1062.64 1062.67
1086.29 1096.82 1099.42
1125.53 1159.74 1174.27
1179.48 1195.68 1282.65
1309.74 1327.90 1351.43
1378.59 1411.67 1419.91
1438.83 1443.20 1460.34
1477.19 1484.96 1490.36
1494.02 1518.85 1523.00
1548.73 1563.08 1627.51
1643.64 1647.88 3053.61
3066.60 3114.77 3129.62
3177.80 3182.95 3212.69
3239.47 3242.29 3636.93

3$_T$ - [V(btzp-H$_{N3}$)OCl$_2$]^0 *S*=1
31.69 44.63 55.17
57.97 60.61 78.77
79.12 90.33 93.77
121.82 128.84 152.33
176.17 184.41 191.79
204.56 210.00 232.07
256.55 284.33 288.05
300.23 318.02 319.96
340.34 342.94 373.39
374.56 413.23 463.27
471.95 484.21 513.14
546.58 581.05 617.08
631.50 654.62 656.79
688.62 698.85 742.71
766.78 820.40 825.40
858.08 878.87 896.22
957.05 988.72 990.38
1019.50 1041.49 1054.95
1062.44 1062.60 1063.50
1089.02 1097.26 1098.51
1131.61 1164.49 1171.51
1186.97 1204.71 1281.93
1310.04 1328.73 1346.94
1376.24 1411.00 1418.23
1435.06 1443.49 1459.20
1475.35 1484.99 1490.39
1492.94 1516.27 1521.00
1531.00 1556.81 1619.34
1642.48 1647.70 3053.83
3066.87 3115.06 3130.00
3177.82 3182.67 3212.69
3239.83 3242.41 3633.65

4$_S$ - [V(btzp-H$_{N4}$)OCl$_2$]^0 *S*=0
29.98 46.19 54.24
56.22 60.85 73.00
78.34 86.48 89.48
123.34 128.26 138.89
162.27 177.15 192.30
210.13 214.51 228.44
254.63 281.77 284.61
292.28 316.66 319.22
338.17 339.82 376.27
380.63 409.16 448.65
461.85 474.79 514.77
539.38 584.04 620.78
634.60 651.84 657.01
688.26 698.22 728.66
754.14 815.30 817.59
846.12 876.62 890.05
931.46 983.77 990.28
1012.88 1037.50 1049.78
1060.29 1062.22 1062.96
1068.92 1097.28 1107.16
1110.93 1150.78 1174.00
1195.04 1226.18 1269.01
1313.93 1333.50 1366.45
1381.72 1407.68 1410.96
1435.07 1443.41 1452.72
1469.47 1482.87 1484.17
1495.44 1509.66 1514.66
1519.16 1556.11 1558.15
1640.88 1648.02 3066.89
3069.18 3129.95 3134.63
3175.24 3178.81 3204.43
3221.07 3244.10 3652.25

4_T - $[V(btzp\text{-}H_{N4})OCl_2]^0$ S=1

29.94	45.32	54.72
56.04	62.55	76.97
80.42	89.47	90.76
122.59	128.80	138.72
161.12	176.76	192.11
210.07	215.63	229.07
256.25	282.01	284.49
295.11	316.15	320.32
336.28	339.53	373.77
380.27	398.65	417.27
463.25	474.80	513.93
541.01	580.80	620.45
634.93	653.79	656.61
688.51	698.30	726.00
753.76	814.63	817.62
846.01	876.46	889.59
929.25	979.21	990.35
1012.08	1036.10	1049.66
1060.25	1062.23	1063.70
1075.05	1096.73	1106.98
1108.96	1148.07	1173.56
1193.75	1212.04	1267.97
1313.83	1332.46	1365.68
1380.54	1409.59	1412.03
1436.57	1444.88	1455.09
1472.15	1482.57	1484.23
1497.41	1509.66	1518.18
1528.83	1553.39	1556.88
1640.26	1646.72	3066.96
3068.71	3130.05	3133.92
3175.34	3178.78	3204.73
3220.85	3244.36	3658.88

Table C. Energies (hartrees) for all species.

filename	E (SCF)	H	G
2$_S$ - [V(btzp-H$_{N2}$)OCl$_2$]^0 *S*=0	-1984.956578	-1984.705087	-1984.781286
2$_T$ - [V(btzp-H$_{N2}$)OCl$_2$]^0 *S*=1	-1984.951887	-1984.700511	-1984.778228
3$_S$ - [V(btzp-H$_{N3}$)OCl$_2$]^0 *S*=0	-1984.952900	-1984.701545	-1984.778834
3$_T$ - [V(btzp-H$_{N3}$)OCl$_2$]^0 *S*=1	-1984.949503	-1984.698202	-1984.776668
4$_S$ - [V(btzp-H$_{N4}$)OCl$_2$]^0 *S*=0	-1984.939776	-1984.688985	-1984.766927
4$_T$ - [V(btzp-H$_{N4}$)OCl$_2$]^0 *S*=1	-1984.939157	-1984.688430	-1984.767349