

Supporting Information

Dinitrogen binding at vanadium in a tris(alkoxide) ligand environment

Stanislav Groysman, Dino Villagrán, Danna E. Freedman, and Daniel G. Nocera*

*Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Ave.,
Cambridge, MA 02139-4307*

nocera@mit.edu

<i>Index</i>	<i>Page</i>
General methods	S2
X-ray crystallographic details	S2
Computational methods	S3
Synthesis and characterization of compounds	S4-S5
IR Spectra	S6-S13
Cyclic voltammogram of 1	S14
NMR spectra of 5	S15
X-ray structure of 5	S16
MO plot for the BS wave function model of 3	S17
Cartesian coordinates for the DFT optimized geometry for the models of 3	S18-S23

General methods

All reactions involving air-sensitive materials were executed in a nitrogen-filled glovebox, or using Schlenk techniques. Solvents were purified using SG Water Glass Contour Solvent System and stored over 4-Å molecular sieves. Compounds were routinely characterized by IR, NMR, and elemental analyses. IR spectra of powdered samples were recorded on a PerkinElmer Spectrum 400 FT-IR/FT-FIR Spectrometer outfitted with a Pike Technologies GladiATR attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. Samples were protected by Paratone-N oil; Paratone-N oil was collected as a background. NMR spectrum of **2** and **5** were recorded at the MIT Department of Chemistry Instrumentation Facility on a Varian Mercury 300 NMR Spectrometer in C₆D₆ at room temperature. Magnetic moment for **2** was determined in C₆D₆ at room temperature on a Varian Mercury 300 NMR Spectrometer using Evans method. Pascal constants were used to estimate diamagnetic correction. Elemental analyses were performed by Midwest Microlab LLC. Methyl Lithium (1.6 M in ether), 2,2,4,4-tetramethyl-3-pentanone, VCl₃THF₃, *t*butylisocyanide, and tetrabutylammonium azide were purchased from Aldrich. *t*Bu₂MeCOLi (Liditox hereafter) were prepared according to literature procedures.¹

X-ray crystallographic details

Structures of **3** and **5** were confirmed by X-ray analysis. The crystals were mounted on a Bruker three circle goniometer platform equipped with an APEX detector. A graphic monochromator was employed for wavelength selection of the Mo K α radiation ($\lambda = 0.71073$ Å). The data were processed and refined using the program SAINT supplied by Siemens Industrial Automation. Structures were solved by direct methods in SHELXS and refined by standard difference Fourier techniques in the SHELXTL program suite (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically; all other atoms were refined anisotropically. In the structure of **3**, one of the ditox ligands, and several *t*Bu groups are disordered over two positions; the disorder was modeled adequately. Crystals of **5** diffracted poorly, leading to the overall low quality of the high-angle data. In addition, one of the two tetrabutylammonium counterions is disordered over two positions. According to PLATON, the space group of **5** is *P*2₁2₁2; however, out attempts to refine the structure in this space group were not successful. The structure was solved and refined in the *P*2₁ space group.

1. E. Napolitano, E. Giovani, N. Ceccarelli, P. J. Pelosi, *Agric. Food Chem.* 1996, **44**, 2806.

Computational details

Density functional theory (DFT) calculations were performed with the hybrid functional Becke-3 parameter exchange functional² and the Lee–Yang–Parr nonlocal correlation functional (B3LYP)³ as implemented in the Gaussian 03, Revision B.05, software package.⁴ An effective core potential (ECP) representing the 1s2s2p core was used for vanadium (LANL2DZ).⁵ The double- ζ quality correlation-consistent polarized cc-pvdz basis set by Dunning and coworkers⁶ was used on all oxygen and nitrogen atoms, while double- ζ quality basis sets (D95) were used on carbon, and hydrogen.⁷ The calculations were performed on simplified model of V(ditox)₃, where ^tBu groups are replaced by methyl groups. All geometries were confirmed as local minima structures by calculating the Hessian matrices and checking that no negative eigenvalues were present.

We also used two other different functionals, the hybrid MPW91PW91 modified by Truhlar⁸, which strongly favors higher spin states due to its large exchange energy contribution, and the pure DFT functional BP86 (which favors lower spin states). Using MPW91PW91 the quintet state is further stabilized compared to the singlet state by 38 kcal/mol, and 24 kcal/mol when compared to the triplet state. Conversely, BP86 shows the opposite trend where the single state is more stable than the quintet state by 38 kcal/mol, and more stable than the triplet by 26 kcal/mol.

2. (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098. (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372. (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

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

4. Gaussian 03, Revision B.05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

5. (a) W. R. Wadt, P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284. (b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

6. T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007.

7. (a) T. H. Dunning, P. J. Hay, P. J. In *Modern Theoretical Chemistry. 3. Methods of Electronic Structure Theory*; H. F. Schaefer III, Ed.; Plenum Press, New York, 1977, p 1. (b) D. E. Woon, T. H. Dunning, *J. Chem. Phys.*, 1993, **98**, 1358.

8. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

Syntheses and characterization of compounds

Alternative synthesis of 3. LiDitox (320 mg, 1.949 mmol, 3 equiv) were dissolved in ether (2 mL) and added in one portion to the stirred pink suspension of VCl_3THF_3 (241 mg, 0.650 mmol) in THF/ether (1/2 mL). The mixture turned blue, and white precipitate formed. The reaction was stirred for 1 h, after which it was filtered and evaporated. The resulting blue solid was extracted with toluene (2 mL), and dried under vacuum. Extraction/drying sequence had been repeated for 3 more times, until the color of the solution was black. Black solid was dissolved in pentane (1 mL), and left at $-40\text{ }^\circ\text{C}$ for 1 day. $(\text{ditox})_3\text{V}(\mu\text{-N}_2)\text{V}(\text{ditox})_3$ (**3**) was obtained as dark brown crystals in 49% yield (173 mg, 0.322 mmol).

Reaction of 2 with CO. CO was admitted to the headspace of the flask (atmospheric pressure, RT) containing hexane solution of **2**. Dark green color developed within several minutes. After 15 min, the volatiles were removed under vacuum, forming a dark brown-green residue, that was analyzed by IR that displayed disappearance of the 775 cm^{-1} resonance, and was nearly identical to the IR spectrum of $\text{Cr}(\text{ditox})_3$ (**2**, see preparation below, and Figure S2). The residue was dissolved in hexane and left at $-40\text{ }^\circ\text{C}$ to crystallize. Dark brown-black crystals were obtained; IR spectrum (SI) was identical to the spectrum of **3**.

Synthesis of 2 from 3. **3** (42 mg, 0.039 mmol) was dissolved in pentane (2 mL) and concentrated, forming dark brown-green solid (38 mg, 0.073 mmol, 94% yield). **2** has been characterized by spectroscopic methods and magnetism (Evans method); its apparent instability has precluded attainment of analytical data (see below) or a crystal structure. $\mu_{\text{eff}} = 2.1\text{ }\mu\text{B}$ (C_6D_6). IR (cm^{-1}): 1478 (m), 1388 (m), 1367 (m), 1101 (s), 1079 (vs), 999 (vs), 943 (s), 922 (vs), 717 (s), 599 (m), 544 (w), 535 (w). $^1\text{H NMR}$ (C_6D_6) δ 4.4 (br s). Repeated elemental analyses consistently yield low C (62 % instead of 69%) and H. However, 0% N is observed in all samples.

Reaction of 2 with KC_8 . Toluene or hexane solutions of **2** were reacted with 2, or 6 equiv of KC_8 . The reactions were allowed to stir for 2 h, or 2 d. No color change was observed. Work-up followed by recrystallization has led to formations of crystalline **3** (verified by XRD).

Preparation of 4. Solution of $\text{CN}t\text{Bu}$ (60 mg, 0.72 mmol, 4 equiv) in ether (2 mL) was added to the stirred blue solution of **1** (110 mg, 0.18 mmol) in ether (2 mL). The color of reaction mixture remained blue. After 30 min, volatiles were removed under vacuum, yielding blue crystalline solid (95 mg, 0.18 mmol, 87%). Anal. Calcd (Found) for $\text{C}_{40}\text{H}_{78}\text{NO}_3\text{V}$: C, 69.38 (68.90); H, 11.98 (11.90); N, 2.31 (2.18). $^1\text{H NMR}$ (C_6D_6 , 300 MHz) δ 5.80 (br s, ditoxMe, 3), 2.63 (br s, ditox t Bu, 18). IR (cm^{-1}): 2170 (sh), 2148 (m), 1474 (w), 1390 (sh), 1385 (w), 1363 (m), 1207

(m), 1100 (s), 1085 (s), 1003 (s), 938 (s), 922 (s), 860 (w), 797 (w), 705 (s), 683 (m), 594 (m), 546 (w), 530 (w), 520 (w).

Preparation of 5. A suspension of tetrabutylammonium azide (37 mg, 0.13 mmol) in ether (2 mL) was added to a stirring blue solution of **1** (77 mg, 0.13 mmol) in ether (2 mL). The reaction mixture turned brown, accompanied by vigorous gas evolution. After 10 min, the reaction mixture was filtered, volatiles were removed in vacuo, the resulting brown solid was washed with pentane (2 mL), and extracted with ether (1 mL), and stored at $-40\text{ }^{\circ}\text{C}$ overnight, leading to the formation of colorless crystals **5** in 86% yield (87 mg, 0.11 mmol). Anal. Calcd (Found) for $\text{C}_{40}\text{H}_{78}\text{NO}_3\text{V}$: C, 70.90 (70.52); H, 12.81 (12.67); N, 3.60 (3.83). IR data (cm^{-1}): 1486 (w), 1472 (sh), 1383 (w), 1357 (w), 1122 (w), 1102 (w), 1073 (s), 1051 (m), 1011 (s), 991 (vs), 978 (sh), 873 (w), 844 (m), 819 (m), 735 (w), 653 (s), 688 (m), 582 (m), 525 (w). ^1H NMR (C_6D_6 , 300 MHz) δ 2.24 (br s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 8H), 1.61 (s, *t*Bu, 54H), 1.07 (br s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 8H), ca. 0.8 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 20H).

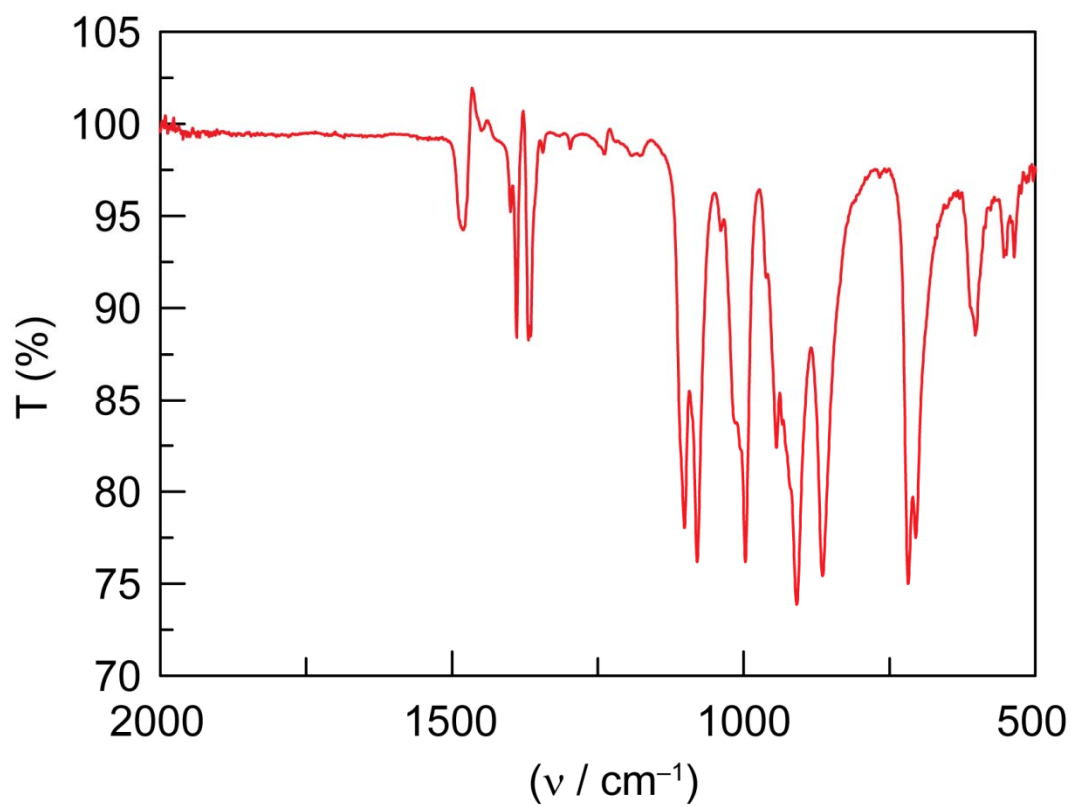


Figure S1. IR spectrum of $V(\text{ditox})_3\text{THF}$ (**1**)

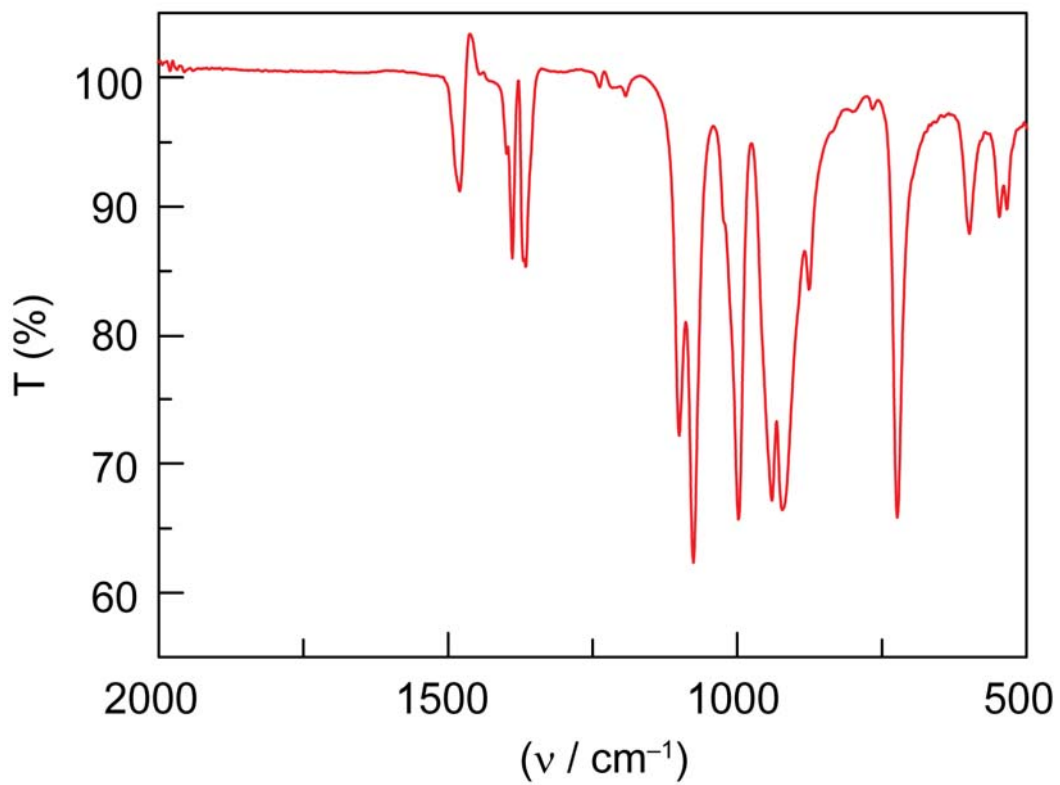


Figure S2. IR spectrum of Cr(ditox)₃

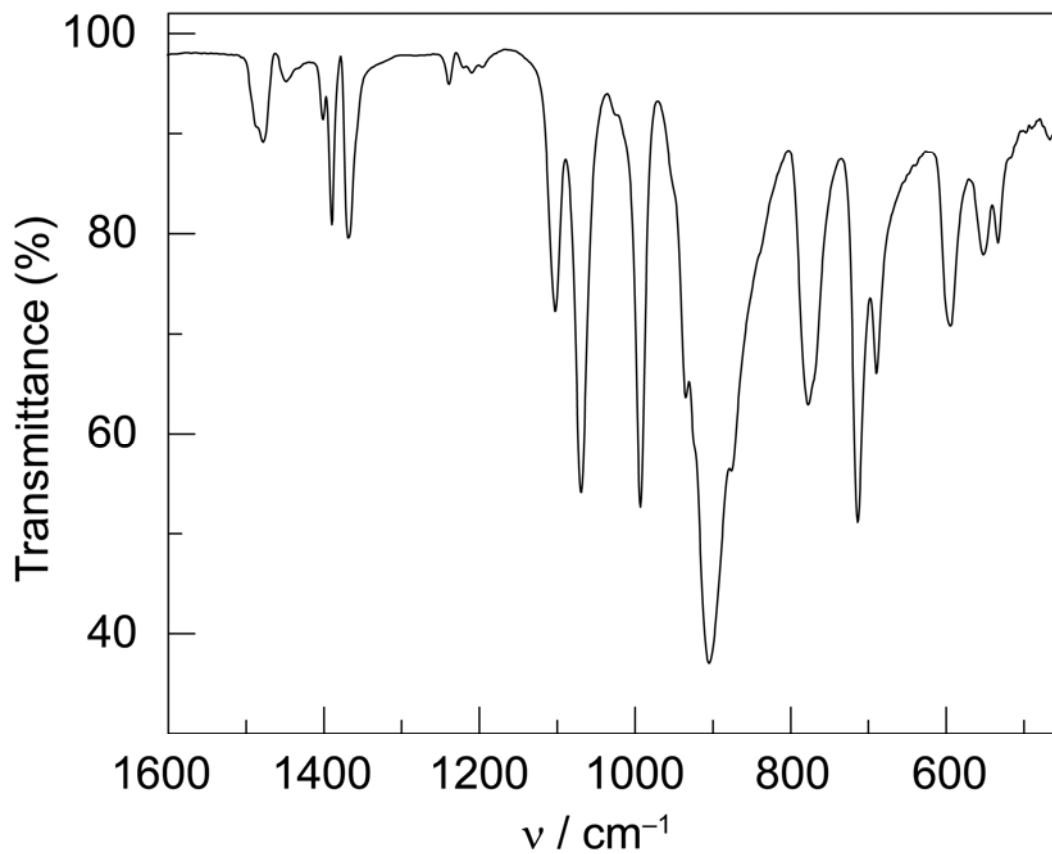


Figure S3. IR spectrum of $\text{V}(\text{ditox})_3(\mu_2\text{-N}_2)\text{V}(\text{ditox})_3$ (**3**).

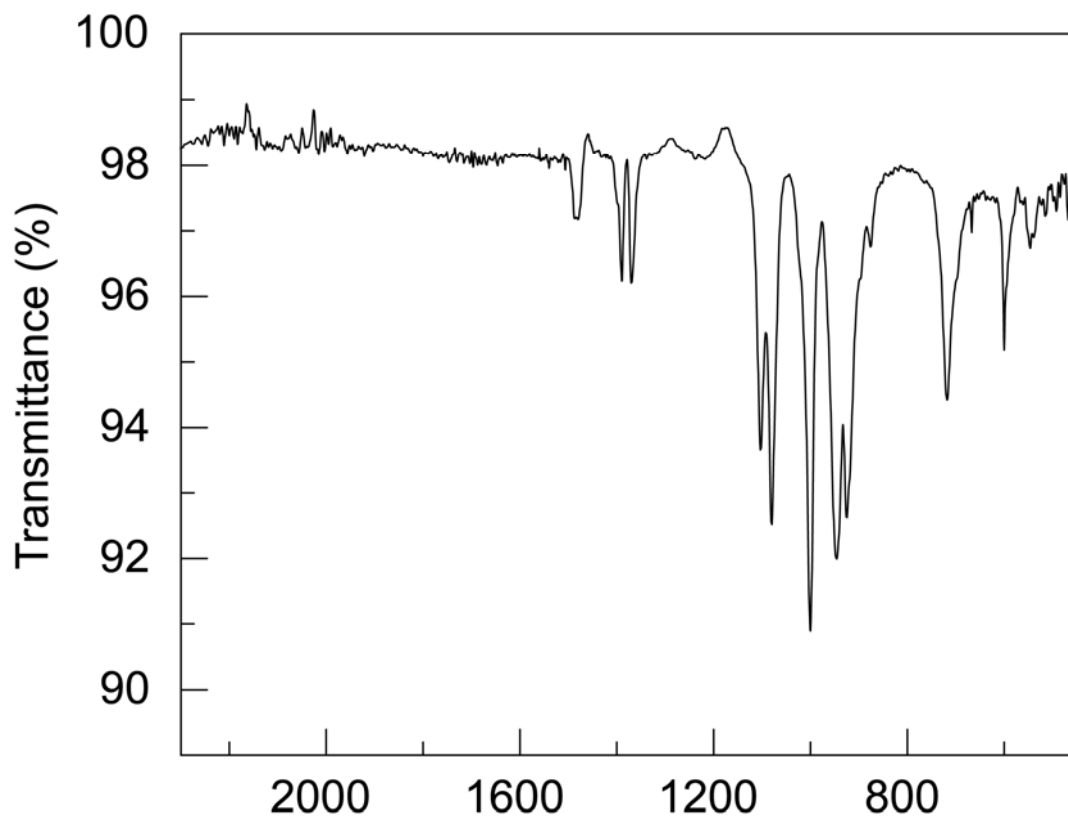


Figure S4. IR spectrum of **2**.

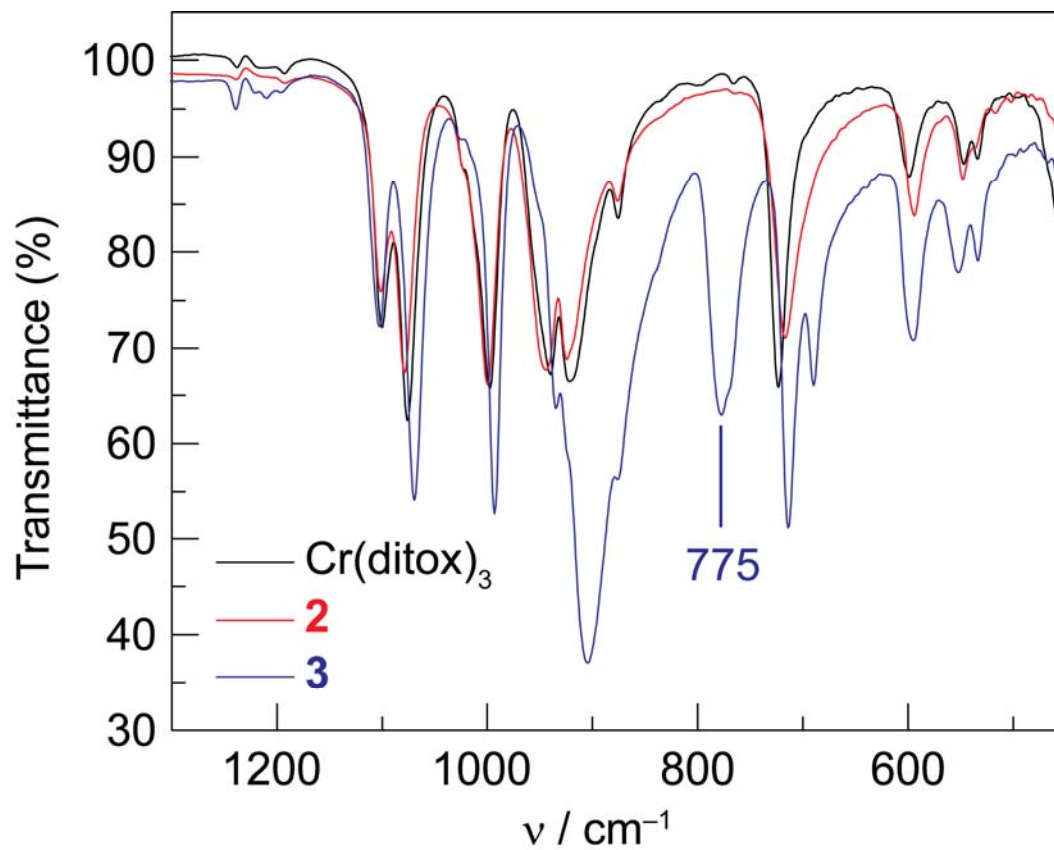


Figure S5. Overlay of the IR spectra of $\text{Cr}(\text{ditox})_3$, **3**, and **2** ($\text{V}(\text{ditox})_3$)

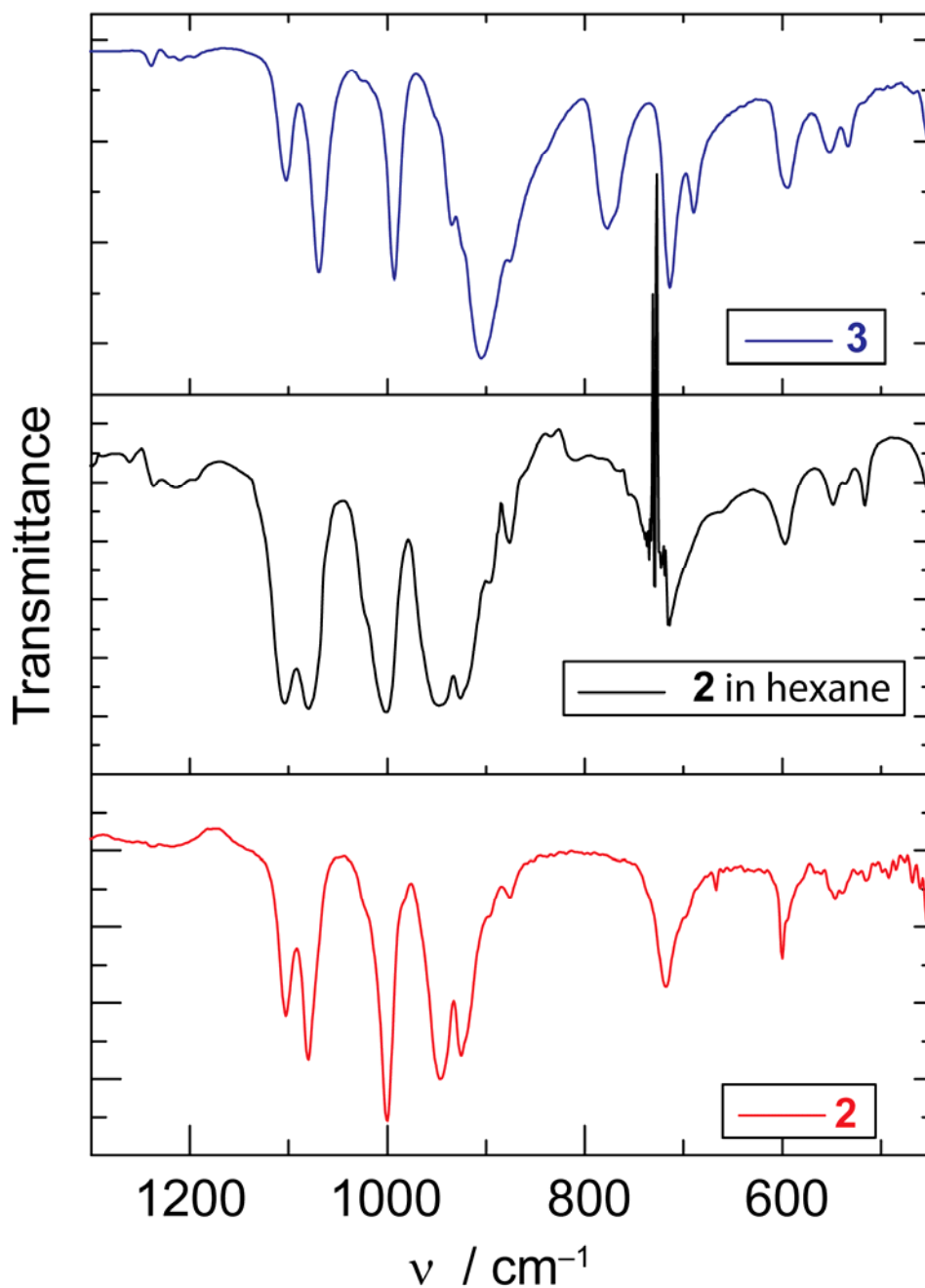


Figure S6. IR spectrum of the complex **2** dissolved in hexane (middle), compared with the IR spectra of **2** in solid state (bottom), and crystalline **3** (top).

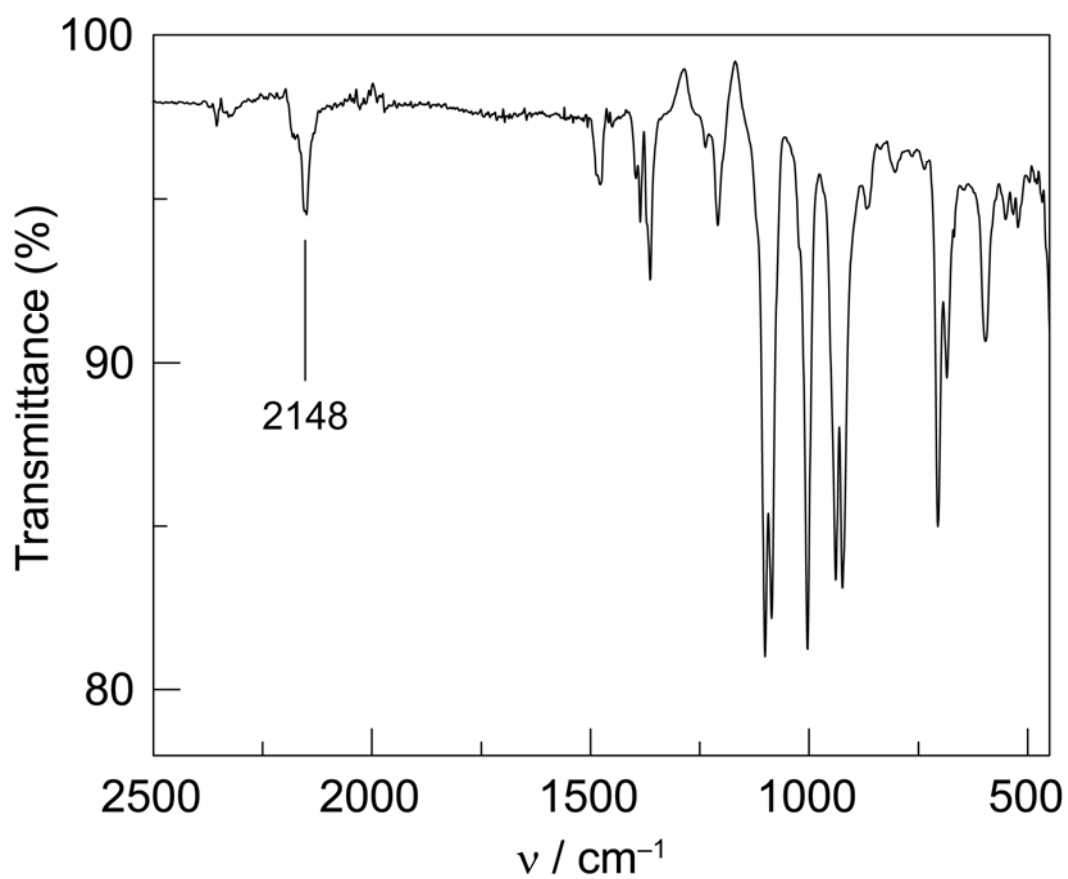


Figure S7. IR spectrum of V(ditox)₃CN*t*Bu (**4**) The resonance at 2148 cm⁻¹ signifies CN stretch.

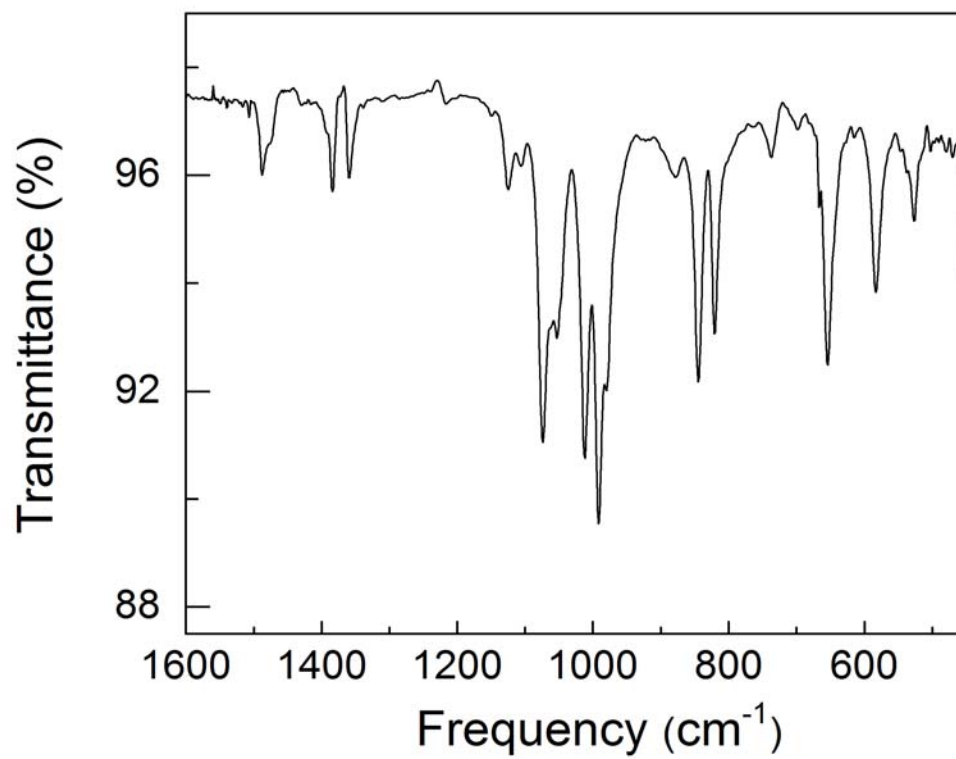


Figure S8. IR of [V(ditox)₃N](NBu₄) (**5**).

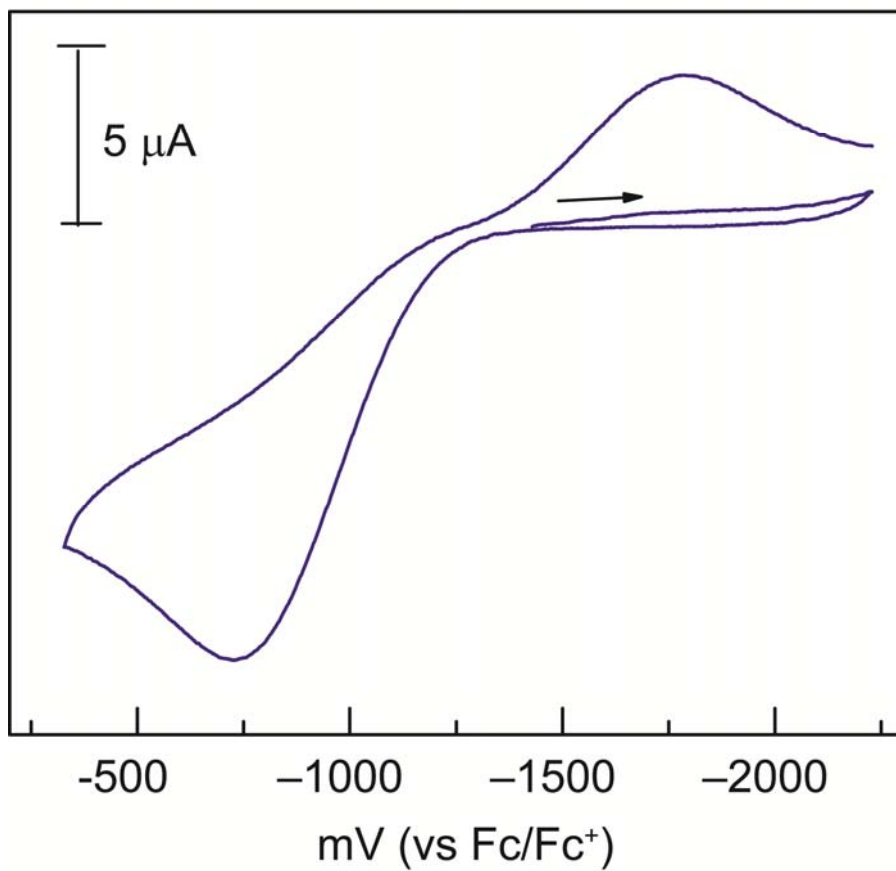


Figure S9. CV of **1** in THF (0.1 M NBu₄PF₆, scan rate = 50 mV/sec).

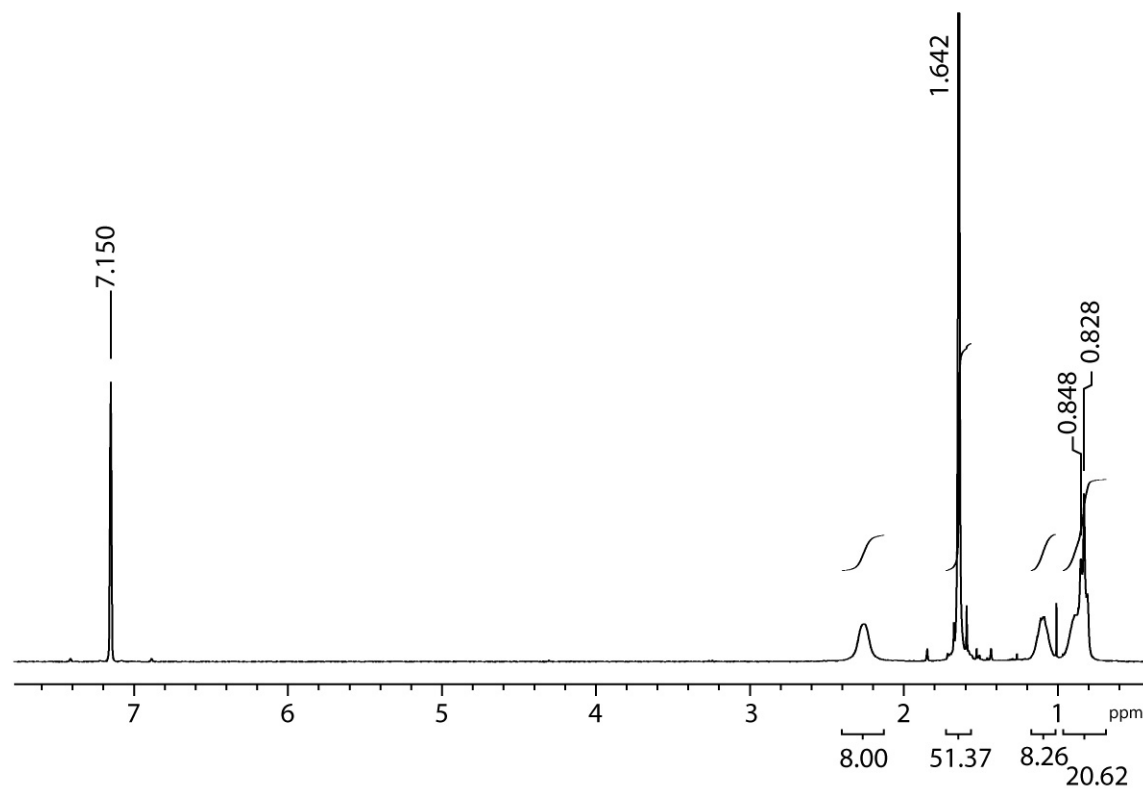


Figure S10. ¹H NMR spectrum of **5**.

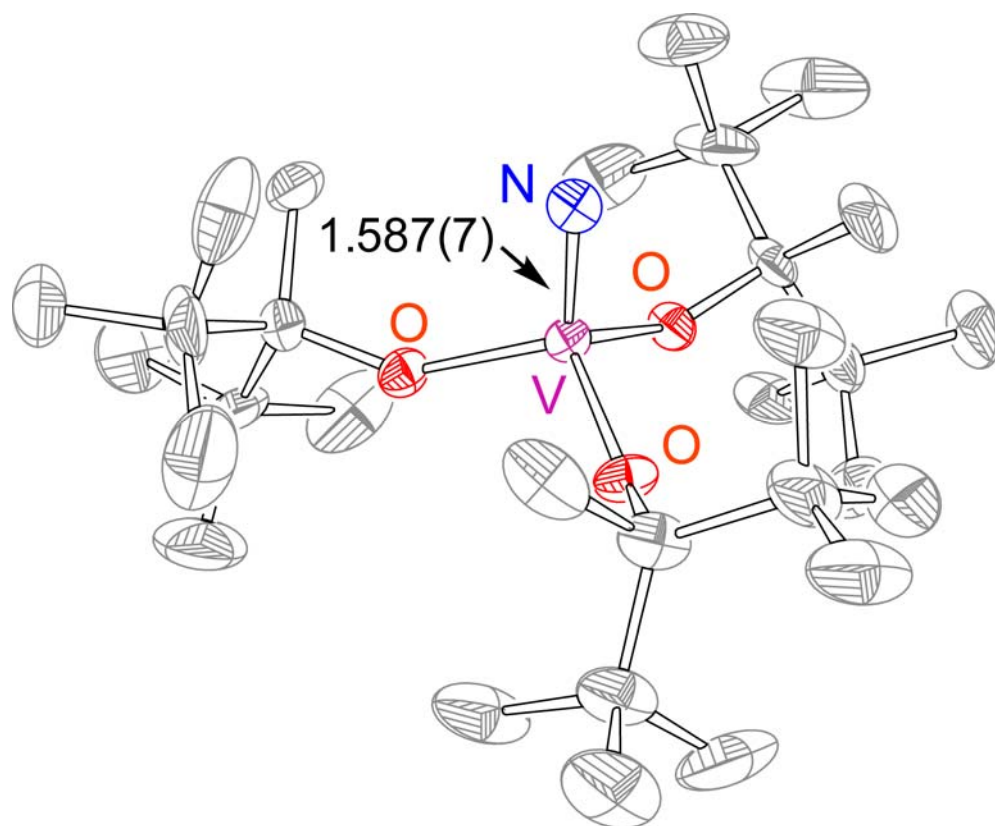


Figure S11. X-ray structure of **5**, ellipsoids at 50% probability. Only one of the two independent anions of **5** in the asymmetric unit is shown. Second molecule of **5** presents V–N bond of 1.609(7) Å. Cations (tetrabutyl ammonium) and hydrogens are omitted for clarity.

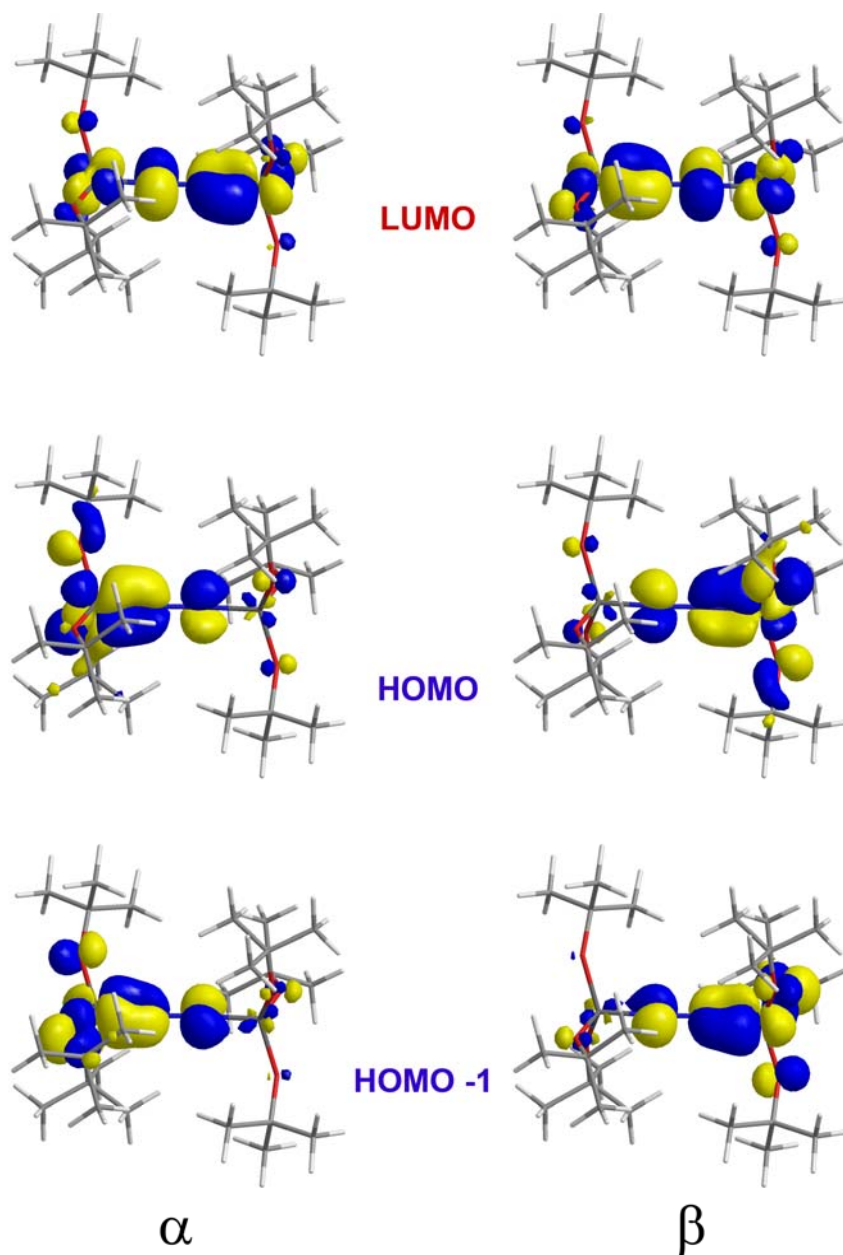


Figure S12. Molecular orbital plots at the 0.04 isodensity value of the broken-symmetry wave function. Note the localization of the electron density between the alpha and beta orbitals.

Table S1. Cartesian coordinates of the triplet model of **3'**
 (Total E = 1650.75425016 hartrees)

Atom Label	Atomic No.	Atom	Coordinates (Å)		
			x	y	z
1	6	C	2.777711	-3.170608	0.386281
2	6	C	-2.800024	-1.236097	2.688569
3	6	C	2.658090	1.958911	2.377650
4	6	C	-2.686833	-2.012332	-2.331179
5	6	C	2.746038	1.275534	-2.692515
6	6	C	-2.686481	3.186598	-0.431153
7	7	N	0.577580	-0.021056	0.018099
8	7	N	-0.596090	-0.006100	0.024593
9	8	O	2.961180	-1.782970	-0.000169
10	8	O	2.820576	0.757186	1.577808
11	8	O	-3.124257	-0.701297	1.376534
12	8	O	3.063348	0.770257	-1.367321
13	8	O	-2.817427	-0.784046	-1.568581
14	8	O	-2.939910	1.802385	-0.074661
15	23	V	2.431439	-0.093176	0.062170
16	23	V	-2.445530	0.100717	-0.068964
17	6	C	-4.028531	-2.764651	-2.194843
18	1	H	-4.849061	-2.140289	-2.567552
19	1	H	-4.012399	-3.702703	-2.765669
20	1	H	-4.225744	-2.996115	-1.141077
21	6	C	-2.427987	-1.599391	-3.796111
22	1	H	-2.351349	-2.482553	-4.444253
23	1	H	-3.246839	-0.967251	-4.159393
24	1	H	-1.493784	-1.029071	-3.870463
25	6	C	-3.927176	3.672945	-1.211015
26	1	H	-4.825080	3.571793	-0.590115
27	1	H	-3.817816	4.725630	-1.503866
28	1	H	-4.065613	3.068193	-2.115312
29	6	C	-2.515325	3.975468	0.884452
30	1	H	-2.368510	5.045081	0.683793
31	1	H	-3.406104	3.854760	1.512091
32	1	H	-1.647393	3.602987	1.442371
33	6	C	-1.416264	3.268002	-1.303183
34	1	H	-0.550801	2.877258	-0.755944
35	1	H	-1.545339	2.677228	-2.218708
36	1	H	-1.208107	4.308084	-1.586562
37	6	C	1.454392	0.615515	-3.221887
38	1	H	1.563052	-0.476631	-3.228096
39	1	H	0.594569	0.878407	-2.595610
40	1	H	1.246666	0.947974	-4.247415

41	6	C	2.586253	2.808102	-2.590872
42	1	H	3.500434	3.255265	-2.182169
43	1	H	2.393215	3.248105	-3.578397
44	1	H	1.749597	3.062628	-1.928947
45	6	C	3.953054	0.908311	-3.583625
46	1	H	3.813688	1.277693	-4.608337
47	1	H	4.869713	1.347220	-3.172410
48	1	H	4.080646	-0.180499	-3.615296
49	6	C	4.052195	2.617429	2.466192
50	1	H	4.016754	3.529857	3.076138
51	1	H	4.769473	1.921067	2.916411
52	1	H	4.410767	2.878070	1.463163
53	6	C	1.641371	2.905292	1.705694
54	1	H	1.986246	3.179731	0.701680
55	1	H	0.663060	2.418202	1.617546
56	1	H	1.520631	3.823176	2.295823
57	6	C	2.167677	1.512180	3.771633
58	1	H	2.880353	0.804778	4.212073
59	1	H	2.067592	2.374120	4.444569
60	1	H	1.192943	1.015422	3.693335
61	6	C	1.525081	-3.296086	1.277767
62	1	H	1.634945	-2.679331	2.178550
63	1	H	0.634327	-2.962595	0.733488
64	1	H	1.373763	-4.338842	1.586081
65	6	C	2.622947	-3.988773	-0.913486
66	1	H	3.495948	-3.835826	-1.558828
67	1	H	2.532286	-5.060683	-0.692755
68	1	H	1.728354	-3.668949	-1.461860
69	6	C	-1.658172	-0.411454	3.321835
70	1	H	-0.738216	-0.505296	2.732946
71	1	H	-1.939072	0.648251	3.366543
72	1	H	-1.449303	-0.758902	4.342291
73	6	C	-2.394631	-2.716684	2.525093
74	1	H	-3.204422	-3.278074	2.043207
75	1	H	-1.495303	-2.800018	1.903446
76	1	H	-2.184817	-3.175446	3.500583
77	6	C	-4.093620	-1.110312	3.522343
78	1	H	-4.907424	-1.662266	3.037226
79	1	H	-3.950976	-1.510151	4.535250
80	1	H	-4.392579	-0.057890	3.596906
81	6	C	4.050744	-3.586846	1.154510
82	1	H	3.993250	-4.638009	1.466820
83	1	H	4.933731	-3.456854	0.517808
84	1	H	4.175560	-2.960536	2.046015
85	6	C	-1.519035	-2.858142	-1.781108
86	1	H	-0.576591	-2.301375	-1.843890

87	1	H	-1.699337	-3.122117	-0.732019
88	1	H	-1.412846	-3.785657	-2.358915

Table S2. Cartesian coordinates of the singlet model of **3'**
(Total E = -1650.77131440 hartrees)

Atom Label	Atomic No.	Atom	Coordinates (Å)		
			x	y	z
1	6	C	-2.611973	-1.655324	-2.593176
2	6	C	2.632616	1.409638	-2.722951
3	6	C	-2.600419	3.084864	-0.148632
4	6	C	2.605745	-3.082219	0.146356
5	6	C	-2.633078	-1.414070	2.720498
6	6	C	2.607053	1.655910	2.597394
7	7	N	-0.622244	0.002374	-0.001301
8	7	N	0.622276	-0.002478	0.001065
9	8	O	-2.921753	-0.804630	-1.454486
10	8	O	-2.917781	1.674169	0.006016
11	8	O	2.933698	0.832245	-1.422564
12	8	O	-2.934402	-0.830766	1.422872
13	8	O	2.921171	-1.670363	-0.000617
14	8	O	2.919100	0.811959	1.454344
15	23	V	-2.323179	0.009866	-0.005994
16	23	V	2.323253	-0.007189	0.007380
17	6	C	3.785906	-3.842483	-0.495719
18	1	H	4.722937	-3.579758	0.009104
19	1	H	3.637619	-4.927947	-0.422137
20	1	H	3.879248	-3.570688	-1.553981
21	6	C	2.505529	-3.390920	1.655666
22	1	H	2.343279	-4.464054	1.823419
23	1	H	3.431045	-3.092115	2.161775
24	1	H	1.671629	-2.838377	2.104242
25	6	C	3.759425	1.441597	3.601875
26	1	H	4.716011	1.715696	3.141924
27	1	H	3.612173	2.053477	4.501642
28	1	H	3.811398	0.387064	3.898056
29	6	C	2.565903	3.120348	2.109097
30	1	H	2.403684	3.806355	2.951241
31	1	H	3.512956	3.380164	1.621720
32	1	H	1.754597	3.260894	1.385116
33	6	C	1.255482	1.227217	3.202224
34	1	H	0.453674	1.331881	2.463516
35	1	H	1.297804	0.178980	3.522543
36	1	H	1.010556	1.847730	4.074594
37	6	C	-1.311578	-2.204123	2.639279
38	1	H	-1.391801	-3.006638	1.895633
39	1	H	-0.487601	-1.543559	2.349181
40	1	H	-1.072881	-2.654763	3.611829

41	6	C	-2.538207	-0.263477	3.745035
42	1	H	-3.460968	0.328382	3.730944
43	1	H	-2.387912	-0.656827	4.759197
44	1	H	-1.698676	0.397221	3.499335
45	6	C	-3.819418	-2.347379	3.044130
46	1	H	-3.682381	-2.829106	4.021307
47	1	H	-4.754753	-1.775725	3.061061
48	1	H	-3.908310	-3.126061	2.277110
49	6	C	-3.776385	3.850012	0.495430
50	1	H	-3.626296	4.934886	0.416955
51	1	H	-4.716068	3.587156	-0.004379
52	1	H	-3.865794	3.582579	1.555142
53	6	C	-1.273478	3.398840	0.570618
54	1	H	-1.352402	3.154327	1.636946
55	1	H	-0.453522	2.813581	0.139910
56	1	H	-1.028963	4.465184	0.475919
57	6	C	-2.506408	3.386614	-1.659713
58	1	H	-3.434334	3.086362	-2.160509
59	1	H	-2.343809	4.458802	-1.832979
60	1	H	-1.674936	2.831182	-2.109336
61	6	C	-1.261293	-1.230419	-3.202747
62	1	H	-1.303850	-0.183994	-3.528919
63	1	H	-0.458212	-1.331244	-2.464867
64	1	H	-1.018080	-1.855924	-4.072025
65	6	C	-2.570587	-3.117163	-2.097138
66	1	H	-3.516622	-3.373811	-1.606110
67	1	H	-2.410884	-3.807718	-2.936032
68	1	H	-1.757540	-3.254492	-1.374437
69	6	C	1.311335	2.200398	-2.645252
70	1	H	0.487092	1.541452	-2.352230
71	1	H	1.391939	3.006150	-1.905194
72	1	H	1.072815	2.646814	-3.619792
73	6	C	2.537834	0.254785	-3.742836
74	1	H	3.460462	-0.337222	-3.725861
75	1	H	1.698007	-0.404830	-3.495208
76	1	H	2.388160	0.644016	-4.758693
77	6	C	3.819170	2.341286	-3.050441
78	1	H	4.754328	1.769294	-3.065344
79	1	H	3.682046	2.819259	-4.029430
80	1	H	3.908342	3.122842	-2.286413
81	6	C	-3.765999	-1.446036	-3.596827
82	1	H	-3.620830	-2.063227	-4.493297
83	1	H	-4.721922	-1.716809	-3.133528
84	1	H	-3.817797	-0.393205	-3.899034
85	6	C	1.282538	-3.395250	-0.580132
86	1	H	0.460080	-2.812340	-0.150958

87	1	H	1.366038	-3.146704	-1.645199
88	1	H	1.038760	-4.462204	-0.490431
