Supplementary Information

Polymer-Bound Oxidovanadium(IV) and Dioxidovanadium(V) Complexes as Catalysts for the Oxidative Desulfurization of Model Fuel Diesel

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Description of Molecular Structures Determined by Single-Crystal X-Ray Diffraction

Description of the Molecular Structure of [$V^{IV}O$(sal-dmen)(acac)] 3. In the study of heterochelates of coordination type [VO(L)(L´)] based on tridentate L ($ONO^{i, ii}$ or $ONN^{iii, iv}$) and bidentate L´ (ON^{ii} or $OO^{i, ii}$) donating ligands, the tridentate ligand L occupies three positions in the equatorial plane and the fourth position is occupied for an O or N atom of the other bidentate ligand L´.

The crystal data and details on data collection and refinement are summarized in Table S1.

Table S1. Crystal Data and Structure Refinement Parameters for Compounds **3** and **4**.

	4	**3**
Formula	$C_{11}H_{15}N_2O_3V$	$C_{16}H_{22}N_2O_4V$
Mw	274.19	357.30
Space group	$P2_1/n$	P1
Crystal system	Monoclinic	Triclinic
a/Å	6.341(4)	10.327(5)
b/Å	12.202(6)	12.750(5)
c/ Å	15.727(9)	25.364(5)
α/deg		89.968(5)
β/deg	98.03(3)	89.946(5)
γ/deg		89.981(5)
V/Å^3	1204.9(11)	3340(2)
Z	4	8
T/K	153(2)	153(2)
λ, Å (Mo Kα)	0.71073	0.71073
D_{calc}/g cm^{-3}	1.511	1.421
μ/mm^{-1}	0.821	0.615
R_{int}	0.0586	0.0498
R_1[a]	0.0489	0.0476
wR_2 (all data)[b]	0.1359	0.1346

[a] $R_1 = \sum \| \|F_0\| - \|F_c\| \| / \sum |F_0|$. [b] $wR_2 = \{\sum[w(\| |F_0|^2 - |F_c|^2)^2] / \sum[w(F_0^4)]\}^{1/2}$

In complex **3**, the structure consists of eight independent vanadium monomers per asymmetric unit. The calculated Flack parameter indicated the presence of racemic twinning. The VO_4N_2 coordination sphere is a distorted octahedron in which the vanadium atoms of the eight independent vanadium monomers are displaced by the values indicated below for each:

For V1: 0.2761 Å from the equatorial plane of atoms N1 N2 O2 O2A, mean deviation 0.0537(15) Å;
For V2: 0.2951 Å from the equatorial plane of atoms N3 N4 O4 O3A, mean deviation 0.0523(15) Å;
For V3: 0.2968 Å from the equatorial plane of atoms N5 N6 O6 O5A, mean deviation 0.0538(15) Å;
For V4: 0.2776 Å from the equatorial plane of atoms N7 N8 O8 O7A, mean deviation 0.0546(15) Å;
For V5: 0.2947 Å from the equatorial plane of atoms N9 N10 O10 O10A, mean deviation 0.0545(15) Å;
For V6: 0.2758 Å from the equatorial plane of atoms N11 N12 O12 O12A, mean deviation 0.0495(15) Å;
For V7: 0.2952 Å from the equatorial plane of atoms N13 N14 O14 O14A, mean deviation 0.0543(15) Å;
For V8: 0.2757 Å from the equatorial plane of atoms N15 N16 O16 O15A, mean deviation 0.0538(15) Å.

The V=O bond distances found in the eight monomers of the asymmetric unit are:
V1-O1, 1.604(3) Å, V2-O3, 1.613(3) Å, V3-O5, 1.609(3) Å, V4-O7, 1.604(3) Å, V5-O9, 1.611(3) Å, V6-O11, 1.604(3) Å, V7-O13, 1.612(3) Å and V8-O15, 1.607(3) Å. These are slightly longer than the range normally found for other neutral VO^{3+} complexes of 1.55-1.60 Å.[v]

The V-O_{phe} bond distances found in the eight monomers of the asymmetric unit are:
V1-O2, 1.956(3) Å, V2-O4, 1.955 Å, V3-O6, 1.960(3) Å, 1.957(3) Å, V4-O8, 1.957(3) Å, V5-O10, 1.956(3) Å, V6-O12, 1.958(3) Å, V7-O14, 1.960(3) Å and V8-O16, 1.955(3) Å). These are longer than other similar compounds such as [VO(salhyb)(Q)], [VO(salhyp)(Q)] and [VO(salhyh)(Q)],[vi] which are in the range of 1.85-1.87 Å, but similar to those of compounds with a nitrogen atom *trans* in respect to oxygen atoms of the phenolate.[vii,viii,ix]

The vanadium-N_{imine} bond distances found in the eight monomers of the asymmetric unit are:
V1-N1, V2-N3, V3-N5, V4-N7, V5-N9, V6-N11, V7-N13 and V8-N15, see Table S1. These are in the range reported for the other similar compounds *e.g.* [VO(cat)(gsal)],[i] [VO(tBu_2-

cat)(vsal)],[i] [VO(hshed)(shi)][ii] [VO(cat)(salimh)],[iii] [VO(sal)(salimh)],[iv] [VO(acac)(salimh)],[v] [VO(acac)(hshed)],[vi] [VO(acac)(sal-aebmz)],[vii] [VO(bha)(sal-aebmz)][viii] and [VO(acac)(salimRH)].[ix]

Most of the V=O compounds induce a strong *trans* effect. The weakest bond of the ligands L´ should be *trans* to the vanadyl oxygen atom. The longer bond of the acac⁻ ligand is in fact *trans* to the oxido-O atom, in the order of 2.2 Å (see Table S2). Although the carbon-carbon and carbon-oxygen distances of the acac⁻ ligand does not allow to differentiate clearly the ketonic oxygen from the enolic oxygen one, the similarity of the our structure with [VO(acac)(salimh)],[iv] suggest that the neutral carbonyl oxygen atom is in the axial position.

Table S2. Selected bond lengths and angles for compound **3**. Angles are included only for the first three polyhedrons in compound **3**.

3	Å	**3**	Å	**3**	(º)
V(1)-O(1)	1.604(3)	V(5)-O(9)	1.611(3)	O(1)-V(1)-O(2)	100.67(13)
V(1)-O(2)	1.956(3)	V(5)-O(10)	1.956(3)	O(1)-V(1)-O(2A)	99.57(13)
V(1)-O(2A)	1.991(3)	V(5)-O(10A)	2.001(3)	O(2)-V(1)-O(2A)	92.06(12)
V(1)-N(1)	2.063(3)	V(5)-N(9)	2.057(3)	O(1)-V(1)-N(1)	98.87(14)
V(1)-O(1A)	2.187(3)	V(5)-O(9A)	2.198(3)	O(2)-V(1)-N(1)	89.08(12)
V(1)-N(2)	2.223(3)	V(5)-N(10)	2.222(3)	O(2A)-V(1)-N(1)	160.98(12)
N(1)-C(7)	1.278(5)	N(9)-C(51)	1.279(5)	O(1)-V(1)-O(1A)	173.77(12)
N(1)-C(8)	1.471(5)	N(9)-C(52)	1.468(5)	O(2)-V(1)-O(1A)	84.75(11)
C(1)-O(2)	1.306(5)	O(10)-C(45)	1.299(5)	O(2A)-V(1)-O(1A)	83.18(11)
V(2)-O(3)	1.613(3)	V(6)-O(11)	1.604(3)	N(1)-V(1)-O(1A)	78.01(12)
V(2)-O(4)	1.955(3)	V(6)-O(12)	1.958(3)	O(1)-V(1)-N(2)	91.58(13)
V(2)-O(3A)	1.999(3)	V(6)-O(12A)	1.985(3)	O(2)-V(1)-N(2)	165.75(12)
V(2)-N(3)	2.057(3)	V(6)-N(11)	2.063(3)	O(2A)-V(1)-N(2)	93.04(12)
V(2)-O(4A)	2.200(3)	V(6)-O(11A)	2.181(3)	N(1)-V(1)-N(2)	81.82(12)
V(2)-N(4)	2.217(3)	V(6)-N(12)	2.218(3)	O(1A)-V(1)-N(2)	82.66(11)
N(3)-C(18)	1.284(5)	N(11)-C(62)	1.279(5)	O(3)-V(2)-O(4)	100.53(13)
N(3)-C(19)	1.466(4)	N(11)-C(63)	1.464(5)	O(3)-V(2)-O(3A)	100.75(13)
O(4)-C(12)	1.307(5)	O(12)-C(56)	1.313(4)	O(4)-V(2)-O(3A)	91.71(11)
V(3)-O(5)	1.609(3)	V(7)-O(13)	1.612(3)	O(3)-V(2)-N(3)	98.72(13)
V(3)-O(6)	1.960(3)	V(7)-O(14)	1.960(3)	O(4)-V(2)-N(3)	89.32(12)
V(3)-O(5A)	2.000(3)	V(7)-O(14A)	1.994(3)	O(3A)-V(2)-N(3)	159.97(12)
V(3)-N(5)	2.059(3)	V(7)-N(13)	2.061(3)	O(3)-V(2)-O(4A)	173.55(12)
V(3)-O(6A)	2.200(3)	V(7)-O(13A)	2.197(3)	O(4)-V(2)-O(4A)	84.38(11)
V(3)-N(6)	2.222(3)	V(7)-N(14)	2.224(3)	O(3A)-V(2)-O(4A)	83.16(11)
N(5)-C(29)	1.278(5)	N(13)-C(73)	1.281(5)	N(3)-V(2)-O(4A)	77.03(11)
N(5)-C(30)	1.465(5)	N(13)-C(74)	1.469(4)	O(3)-V(2)-N(4)	92.78(13)
O(6)-C(23)	1.298(5)	O(14)-C(67)	1.300(5)	O(4)-V(2)-N(4)	164.79(12)
V(4)-O(7)	1.604(3)	V(8)-O(15)	1.607(3)	O(3A)-V(2)-N(4)	93.00(12)
V(4)-O(8)	1.957(3)	V(8)-O(16)	1.955(3)	N(3)-V(2)-N(4)	81.37(12)

V(4)-O(7A)	1.989(3)	V(8)-O(15A)	1.990(3)	O(4A)-V(2)-N(4)	81.83(11)
V(4)-N(7)	2.063(3)	V(8)-N(15)	2.062(3)	O(5)-V(3)-O(6)	100.48(14)
V(4)-O(8A)	2.183(3)	V(8)-O(16A)	2.186(3)	O(5)-V(3)-O(5A)	100.83(13)
V(4)-N(8)	2.220(3)	V(8)-N(16)	2.222(3)	O(6)-V(3)-O(5A)	91.97(12)
N(7)-C(40)	1.276(5)	N(15)-C(84)	1.279(5)	O(5)-V(3)-N(5)	98.82(13)
N(7)-C(41)	1.464(5)	N(15)-C(85)	1.463(5)	O(6)-V(3)-N(5)	89.04(12)
O(8)-C(34)	1.310(5)	O(16)-C(78)	1.313(5)	O(5A)-V(3)-N(5)	159.79(12)
				O(5)-V(3)-O(6A)	173.50(12)
				O(6)-V(3)-O(6A)	84.41(11)
				O(5A)-V(3)-O(6A)	83.17(10)
				N(5)-V(3)-O(6A)	76.84(11)
				O(5)-V(3)-N(6)	92.82(13)
				O(6)-V(3)-N(6)	164.77(12)
				O(5A)-V(3)-N(6)	92.80(12)
				N(5)-V(3)-N(6)	81.55(12)
				O(6A)-V(3)-N(6)	81.82(11)

Description of the Molecular Structure of [VO_2(sal-dmen)] 4. In the unit cell we meet a single discrete monomeric molecule. The dioxidovanadium(V) ion is five-coordinate with a distorted square pyramidal environment. The metal ion is 0.4782 Å above from the mean plane of the basal atoms (O1, O3, N1, N2) in the direction of the axial oxido ligand, O2. The τ value for this geometry is 0.22 indicating a significant distortion towards the trigonal bipyramidal form. The distances and angles are very similar to the structure published in the literature. [x] (see Table S3)

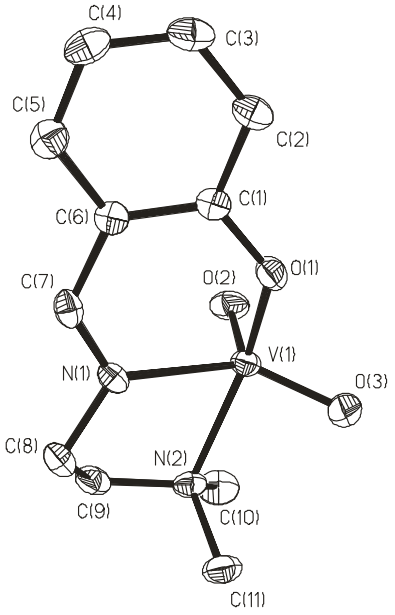

Figure S1. ORTEP diagrams of [VO_2(sal-dmen)] **4**. All non-hydrogen atoms are represented by their 30% probability ellipsoids.

Table S3. Selected geometric parameters (Å, º). Comparison between the data published in (x) M.-J. Xie, Y.-Ping, L.-D Zheng, J.-Z. Hui, C. Peng *Acta Cryst., Sect.* E, 2004, **60**, m1382-m1383] and our results for [VO_2(sal-dmen)] **4**

(Å)	**4**	Ref. x	(º)	**4**	AC
V1-O2	1.603(2)	1.6097(19)	O2-V1-O3	109.71(13)	109.54(11)
V1-O3	1.621(2)	1.622(2)	O2-V1-O1	105.09(11)	105.57(9)
V1-O1	1.911(2)	1.9190(18)	O3-V1-O1	98.26(11)	98.07(9)
V1-N1	2.148(3)	2.138(2)	O2-V1-N1	107.14(11)	107.57(9)
V1-N2	2.185(2)	2.188(2)	O3-V1-N1	141.09(11)	140.78(10)
			O1-V1-N1	83.69(9)	83.72(7)
			O2-V1-N1	95.67(11)	94.70(9)
			O3-V1-N2	88.67(11)	88.87(9)
			O1-V1-N2	154.25(9)	154.78(8)
			N1-V1-N2	75.63(10)	75.84(8)

References (x-ray part)

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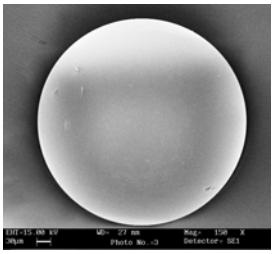
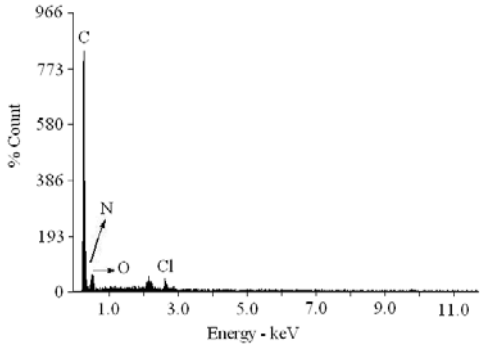
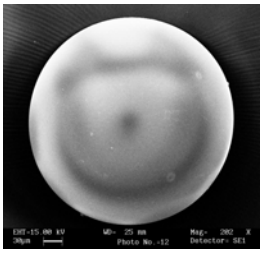
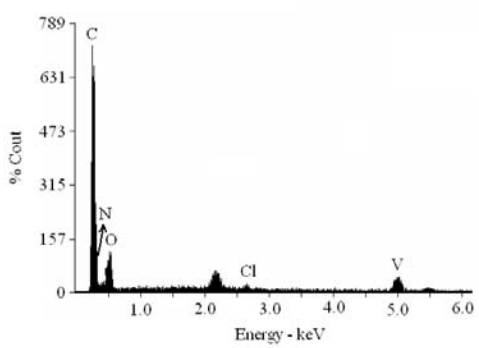
Field emission-scanning electron microscope (FE-SEM) and energy dispersive X-ray analysis (EDX) studies.



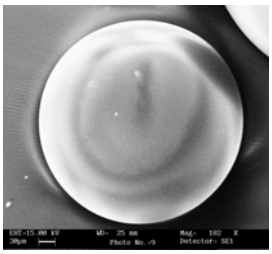


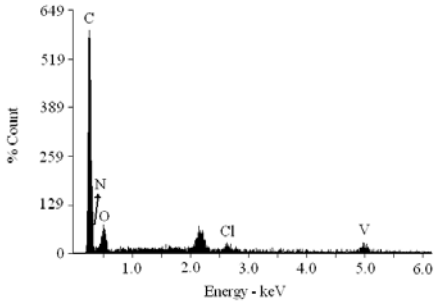
(a) PS-[Hfsal-dmen], **I**





(b) PS-[$V^{IV}O$(fsal-dmen**)**(MeO)**], 1**





(c) PS-[$V^{V}O_2$(fsal-dmen)], **2**

Figure S2. FE-SEM & Energy dispersive X-ray analysis (EDAX) profile of (a) PS-Hfsal-dmen **I** (b) PS-[$V^{IV}O$(fsal-dmen**)**(MeO)**] 1** and (c) PS-[$V^{V}O_2$(fsal-dmen)] **2**.

Additional ^{51}V NMR experiments

To the second portion of the MeOH solution (*ca*. 4 mM) of complex **4**, 1.0 + 1.0 equivalents of an HCl solution (11.6 M) were added - see Figure S3 (b) and (c)]. The new peak at –488 ppm is detected, the one at –543 ppm increased intensity and the resonance at –515 ppm decreased intensity. This is in agreement with the assignments given in Scheme 4 involving the protonations of the ligand and of the oxido group. Upon further additions of the 30% aqueous solution of H_2O_2 a new resonance is detected at –559 ppm. As mentioned in the text it is assigned to **CIII**, corresponding to the protonation of the amine nitrogen of N,N-dimethylethylenediamine and generation of [$V^VO(O_2)$(sal-dmenH^+)].[59,60] As evaluated by DFT, both **CIIIa**- and **CIIIb**-type isomers may exist, but according to DFT data **CIIIb** is slightly more stable (by 1.4 kcal/mol). However, only one species is detected by ^{51}V NMR assignable to the peroxo-protonated species **CIII**, and the calculated ^{51}V NMR chemical shifts for **CIIIa** (–549 ppm, in MeOH) gives both a better absolute and relative (compared with the δ values for **CI** and **CII**) agreement with the experimental one than for **CIIIb** ($\delta_{calculated}$ = –575 ppm; in MeOH). Therefore, we assign the –559 ppm resonance to **CIIIa**.

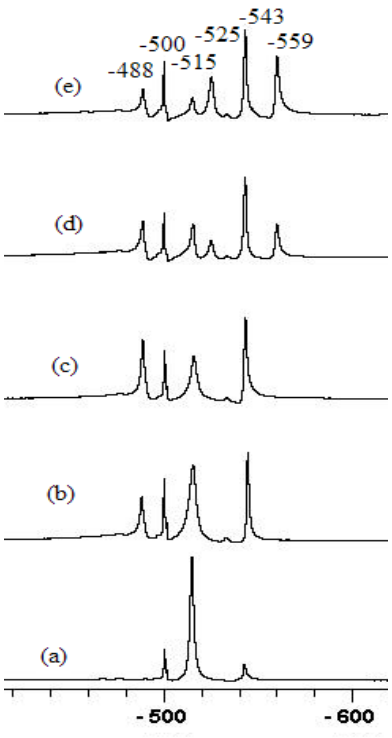


Figure S3. (V-NMR-S1). (a) ^{51}V NMR spectrum of a 4 mM solution of [$V^{V}O_2$(sal-dmen)] **4** in MeOH; (b) addition of 1.0 equiv. HCl (11.6 M) to the solution of (a); (c) after addition of 2.0 equiv HCl (total) to the solution of (a) the pH being ~ 4; (d) after addition of 2.0 equiv (30%) H_2O_2 (total) to the solution of (c); (e) after addition of 3.0 equiv (30%) H_2O_2 (total) to the solution of (c) the pH being ~3.5-4.0.

A 4 mM solution of [V^{IV}O(sal-dmen)(acac)] **3** MeOH after 12 hr of contact with air [Figure S4 (a)] showed resonances at –515 and –544 ppm corresponding to the dioxido-complexes C**I** and **CII** (see Scheme 4). Upon stepwise additions of an aqueous solution of H_2O_2 [Figure S4 (b-e)], the peaks at –559 ppm (1^{st}), –576 ppm (2^{nd}) (and –488 ppm) were detected, these results being compatible with the assignments given in Scheme 4. Additions of HCl solution (11.6 M) gave spectra [Figure S4 (f-i)] with patterns similar to those of Figures 3 and S1, again in agreement with the assignments discussed here and in the main text. The presence of the acac ligand did not change neither the type of spectra obtained nor

the chemical shifts recorded, indicating that the $acac^-$ ligand is not bound to the V(V)-complexes present in solution.

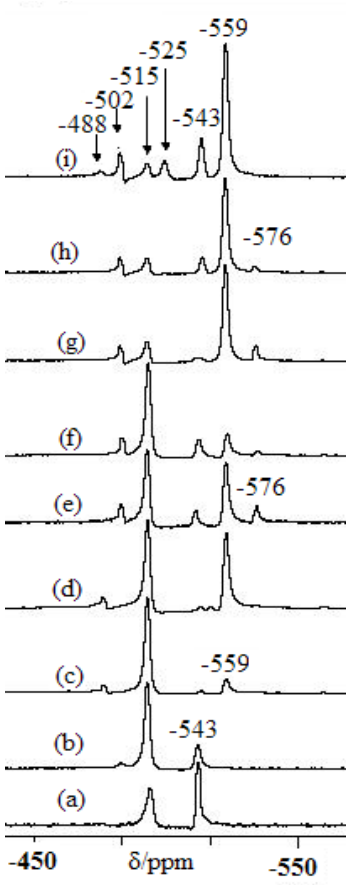


Figure S4 (V-NMR-S2). (a) ^{51}V NMR spectrum of a 4 mM solution of [$V^{IV}O$(acac)(sal-dmen)] **3** in MeOH after 12 h of contact with air. (b) addition of 1.0 equiv. H_2O_2 (30%) to the solution of (a); (c) after addition of a total of 2.0 equiv of a H_2O_2 solution (30%) to the solution of (a); (d) after addition of a total of 3.0 equiv H_2O_2 to the solution of (a); (e) after addition of a total of 4.0 equiv H_2O_2 to the solution of (a); the pH is *ca*. 4.0; (f) after addition of 0.5 equiv of a HCl solution (11.6 M) to the solution of (e); (g) after addition of a total of 0.8 equiv HCl to the solution of (e); (h) after addition of a total of 1.0 equiv HCl to the solution of (e); (i) after addition of a total of 1.5 equiv HCl; the pH is *ca*. 3.5.

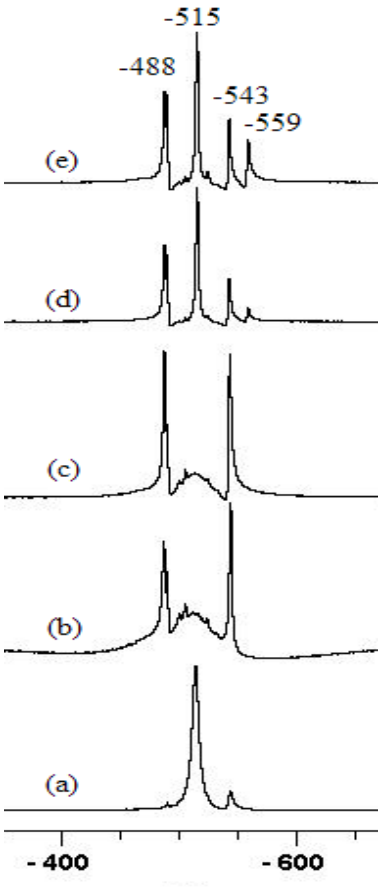


Figure S5 (V-NMR-S3). (a) ^{51}V NMR spectrum of a 4 mM solution of [V^{IV}O(acac)(sal-dmen)] **3** in MeOH after 24 hr; (b) addition of 1.0 equiv. HCl (11.6 M) to the solution of (a); (c) after addition of 2.0 equiv HCl (total) to the solution of (a) the pH being ~3.5-4.0; (d) after addition of 1.5 equiv (30%) H_2O_2 to the solution of (c); (e) after addition of a total of 3.0 equiv (30%) H_2O_2 to the solution of (c) the pH being ~3.5-4.0; The spectra are compatible with the assignments made in the text and with the presence of a small amount of V^{IV}O-complexes in solution.

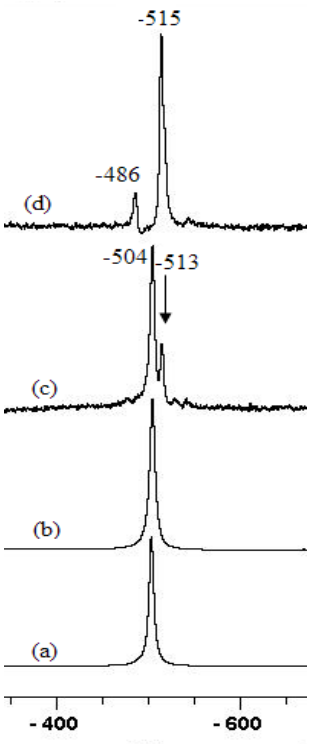


Figure S6 (V-NMR-S4). (a) ^{51}V NMR spectrum of a 4 mM solution of PS-[$V^{V}O_2$(fsal-dmen)] **4** in DMSO; (b) solution of (a) after 24 h leaving tube open; (c) 4 mM solution of PS-[$V^{V}O$(fsal-dmen)] **4** in DMSO after 24 h leaving tube open; (d) addition of 50% MeOH to the solution of (c).

Optimization of catalytic reactions

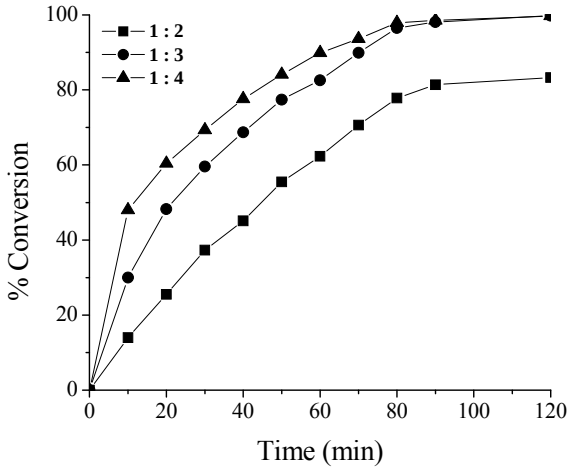


Figure S7. Effect of the H_2O_2 : sulfur ratio as a function of time on the desulfurization of thiophene. Reaction conditions: Catalyst PS-[V^VO_2(fsal-dmen)] **2** (0.0715 mmol) and thiophene (S: 500 ppm) in n-heptane at 60 °C.

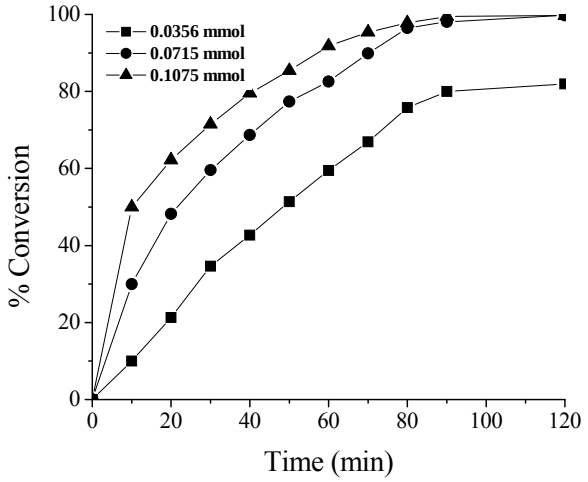


Figure S8. Effect of the amount of catalyst PS-[$V^{V}O_2$(fsal-dmen)] **2** on the desulfurization of thiophene as function of time. Reaction conditions: Thiophene (S: 500 ppm), H_2O_2 (1.02 g, 9.0 mmol) in n-heptane at 60 °C.

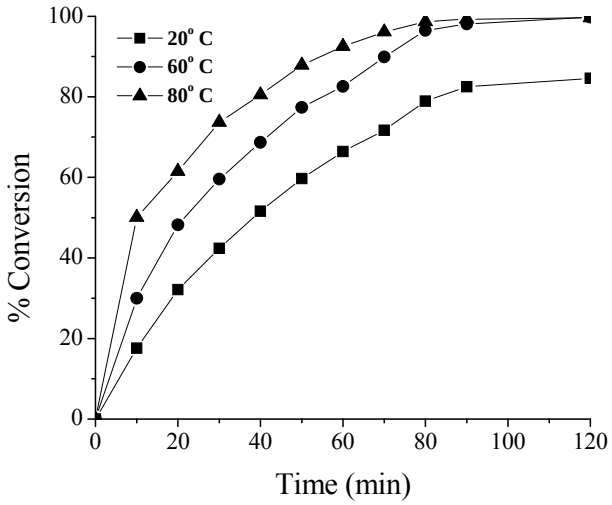


Figure S9. Effect of temperature on the desulfurization of thiophene. Reaction conditions: Thiophene (S: 500 ppm), H_2O_2 (1.02 g, 9.0 mmol) and catalyst PS-[V^VO_2(fsal-dmen)] **2** (0.0715 mmol).

Preparation, and IR and UV-Vis absorption spectra of [$VO(O_2)$(sal-dmen)]

[$V^VO(O_2)$(sal-dmen)] (5). Complex **3** (0.27 g, 1 mmol) was dissolved in methanol (20 mL). The solution was cooled to *ca*. 10 ^oC and H_2O_2 (1 mL dissolved in 3 mL of methanol) was added drop-wise with stirring. Stirring was continued along with cooling of the reaction mixture and a yellow solid separated out within *ca*. 1 h. This was filtered, washed with cold methanol and kept at *ca*. -10 ^oC. This complex is unstable (it looses oxygen at room temperature) and it could not be properly characterized. Only IR and electronic spectra could be recorded with the semi dried sample.

The freshly prepared complex **5** gave an IR spectrum, Figure S9, including peaks: 1621 ν(C=N), (V=O, s) 957, (O-O, s) 886, (V-O_2, s, as) 610 cm^{-1}. These peaks are close to those reported for several [$V^VO(O_2)$L] complexes,[48] being in agreement with its formulation as a peroxo complex

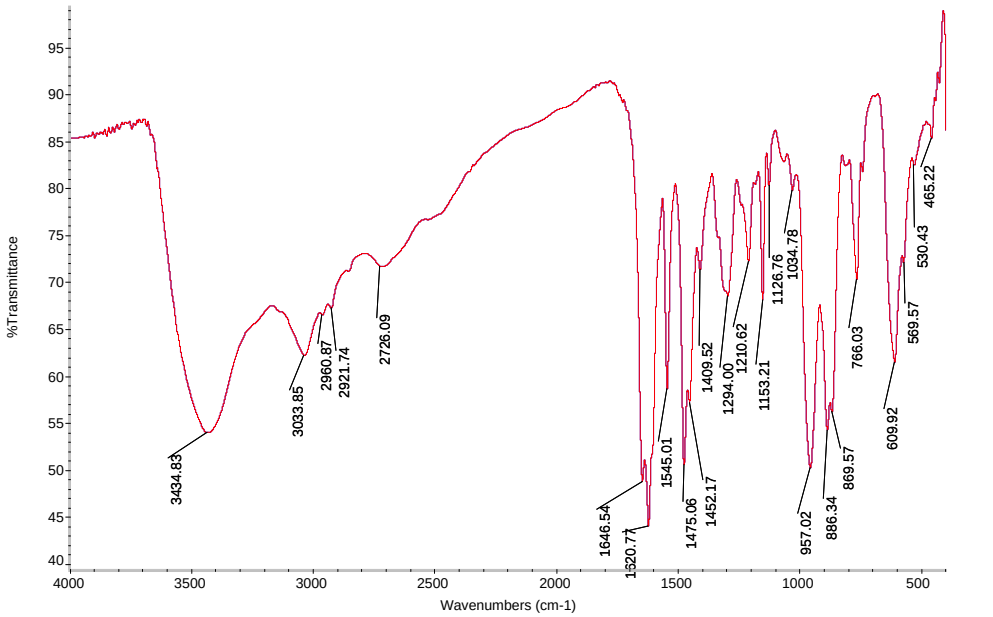


Figure S10. IR spectrum of freshly prepared [$VO(O_2)$(sal-dmen)] **5**.

The electronic spectrum of this complex exhibits a broad charge transfer band at *ca*. 390 nm. The broadness of this band suggests interference of this band with bands due to the C=N group. During titration of either [$V^{IV}O$(sal-dmen)(acac)] **3** or [$V^{V}O_2$(sal-dmen)] **4** with H_2O_2 (see Fig. 7) similar bands were observed and are indications of the presence of a peroxo-to-vanadium charge transfer transition with maxima at *ca*. 390 nm[48].

GC-MS of the liquid part of [PS-[VO(fsal-dmen)(MeO)] (1) suspended in DMSO

25 mg of complex **1** was mixed/ suspended in 2 mL of DMSO and one drop of water in a test tube and the mixture was stirred for *ca*. 15 h. GC-MS analysis of the liquid phase (see below) showed one very weak signal with mass of 32. Its mass fragmentation matches with the library for methanol. It shows that MeO^- is present in the complex which may be replaced by DMSO present in much higher concentration in this experiment followed by the reaction of MeO^- with water to give MeOH. This observation is compatible with the conclusion drawn while recording EPR in DMSO after 12 h of mixture. The complex is slowly oxidized, MeO^- detaches from the coordination sphere

and a dioxo species is formed. Therefore the polymer-anchored complex **1** may be formulated as [PS-[V^{IV}O(fsal-dmen)(MeO)].

Details of the GC-MS experiment:

Instrument: Perkin Elmer Clarus 500.
GC: Injection Temp. 280 ^{o}C, Detector 250 ^{o}C.
GC program: Initial 50 ^{o}C, 1 min hold; Ramp 14 ^{o}C/min. Final temp 225 ^{o}C.
GC column: Elite-5 (cross bond 5 % diphenyl-95 % dimethyl polysiloxane): 30 m x 0.25 mm (id).
Mass Range selected: 10 - 400 mass. Solvent delay 0 min.
Mode used: EI+
Retention time for methanol in complex was 1.717 min. For pure methanol, it is 1.744 min.

DFT computational details

Calculations of entropies in solution

The entropies in solutions (S_s) were calculated according to the procedure described by Wertz[80] and Cooper and Ziegler[81] using equations (1) – (4)

$$\Delta S_1 = R \ln V^{s}_{m,liq}/V_{m,gas} \quad (1)$$

$$\Delta S_2 = R \ln V^{o}_{m}/V^{s}_{m,liq} \quad (2)$$

$$\alpha = \frac{S^{o,s}_{liq} - (S^{o,s}_{gas} + R \ln V^{s}_{m,liq}/V_{m,gas})}{(S^{o,s}_{gas} + R \ln V^{s}_{m,liq}/V_{m,gas})} \quad (3)$$

$$S_s = S_g + \Delta S_{sol} = S_g + [\Delta S_1 + \alpha(S_g + \Delta S_1) + \Delta S_2] \quad (4)$$

where S_g – gas-phase entropy of solute, ΔS_{sol} – solvation entropy, $S^{o,s}_{liq}$, $S^{o,s}_{gas}$, and $V^{s}_{m,liq}$ – standard entropies and molar volume of the solvent in liquid or gas phases (127.19 J/mol•K, 239.90 J/mol•K and 40.46 mL/mol, respectively, for methanol and 328.57 J/mol•K, 427.98 J/mol•K and 146.51 mL/mol, respectively, for heptane), $V_{m,gas}$ – molar volume of the ideal gas at 25 °C (24450 mL/mol), $V°_m$ – molar volume of the solution corresponding to the standard conditions (1000 mL/mol). The resulting expressions (5)

and (6) correspond to methanol and heptane, respectively.

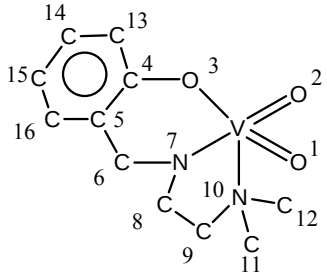
$$S_s = S_g + [(-12.72 \text{ cal/mol·K}) - 0.32(S_g - 12.72 \text{ cal/mol·K}) + 6.37 \text{ cal/mol·K}] \quad (5)$$

$$S_s = S_g + [(-10.16 \text{ cal/mol·K}) - 0.15(S_g - 10.16 \text{ cal/mol·K}) + 3.81 \text{ cal/mol·K}] \quad (6)$$

Comparison of B3LYP, B3P86 and B3PW91 functionals

The comparison of the structural parameters of **CI** found from X-ray analysis (this work) and calculated using B3LYP, B3P86, and P3PW91 functionals (Table 1TS) indicates that the second functional better reproduces the structure of this species. The maximum deviations between the experimental and calculated bond lengths are 0.07 Å (B3LYP, the VN10 bond), 0.03 Å (B3P86, the C14C15 bond), and 0.04 Å (B3PW91, the VN10 bond). Furthermore, the ^{51}V chemical shifts calculated at the B3P86 level (Table 2TS) usually agree slightly better with the experimental value (Scheme 4) than the chemical shifts obtained using the B3LYP functional (Table 3TS). Thus, only values calculated at the B3P86 level are discussed in the text, although tables with the B3LYP values are also included to Supporting Information.

Table 1TS. Experimental and calculated bond lengths (Å) of **CI** and differences between experimental and calculated values.



Bond	exp.	B3LYP	$\delta_{exp-theor}$	B3P86	$\delta_{exp-theor}$	B3PW91	$\delta_{exp-theor}$
V=O1	1.621	1.607	0.014	1.6	0.021	1.601	0.02
V=O2	1.604	1.602	0.002	1.594	0.01	1.595	0.009
V-O3	1.911	1.894	0.017	1.885	0.026	1.89	0.021

O3C4	1.331	1.311	0.02	1.304	0.027	1.305	0.026
C4C5	1.410	1.427	0.017	1.423	0.013	1.425	0.015
C5C6	1.439	1.431	0.008	1.426	0.013	1.428	0.011
C6N7	1.280	1.299	0.019	1.297	0.017	1.297	0.017
N7V	2.147	2.193	0.046	2.173	0.026	2.181	0.034
N7C8	1.460	1.463	0.003	1.455	0.005	1.457	0.003
C8C9	1.495	1.524	0.029	1.516	0.021	1.519	0.024
C9N10	1.473	1.48	0.007	1.471	0.002	1.473	0.000
N10V	2.185	2.254	0.069	2.212	0.027	2.224	0.039
N10C11	1.489	1.483	0.006	1.473	0.016	1.476	0.013
N10C12	1.479	1.484	0.005	1.474	0.005	1.477	0.002
C4C13	1.395	1.414	0.019	1.419	0.024	1.413	0.018
C13C14	1.380	1.384	0.004	1.381	0.001	1.382	0.002
C14C15	1.373	1.41	0.037	1.406	0.033	1.408	0.035
C15C16	1.363	1.38	0.017	1.377	0.014	1.379	0.016
C5C16	1.412	1.416	0.004	1.411	0.001	1.413	0.001

Table 2TS. ^{51}V NMR chemical shifts (ppm) for gas-phase and methanol solution calculated at the B3P86 level. Values including the empirical correction of –42 ppm are in parentheses.

Structure	gas phase	methanol
CI	–453	–500

CII	–415	–438
CII•MeOH	–514	–527
CII•2MeOH	–471, –399[a]	–481, –426[a]
CIIIa	–473 (–515)	–507 (–549)
CIIIb	–456 (–498)	–485 (–527)
CIIIb•MeOH	–437 (–479)	–458 (–500)
CIV	–442 (–484)	–504 (–546)
CVI	–410	–419
CVII	–498	–504
CVIII	–503 (–545)	–507 (–549)
CIX	–283 (–325)	–298 (–340)
$[V(=O)(OO)(ox)(bpy)]^-$	–515	–571, –573[b]

[a] Two isomers were found for the complex **CII•2MeOH**. [b] For water solution.

Table 3TS. ^{51}V NMR chemical shifts (ppm) for gas-phase and methanol solution calculated at the B3LYP level. Values including the empirical correction of –34 ppm are in parentheses.

Structure	gas phase	methanol
CI	–480	–532
CII	–454	–480
CII•MeOH	–547	–563
CII•2MeOH	–501, –453[a]	–513, –480[a]
CIIIa	–504 (–539)	–540 (–575)
CIIIb	–487 (–522)	–519 (–554)
CIIIb•MeOH	–469 (–504)	–491 (–526)
CIV	–443 (–478)	–510 (–545)
CVI	–425	–433

CVII	–525	–533
CVIII	–512 (–546)	–515 (–550)
CIX	–273 (–307)	–288 (–323)
$[V(=O)(OO)(ox)(bpy)]^-$	–517	–579, –581[b]

[a] Two isomers were found for the complex **CII•2MeOH**. [b] For water solution.

Table 4TS. Total energies, enthalpies, Gibbs free energies (in Hartree) and entropies (in cal/mol•K) of the equilibrium structures for gas-phase and MeOH solution calculated at the B3P86 level.

	E_g	E_s	H_g	H_s	S_g	S_s	G_g	G_s
H_2O_2	-151.851341	-151.941903	-151.820524	-151.911086	55.72	35.61	-151.846996	-151.928005
H_2O	-76.587853	-76.647502	-76.562673	-76.622322	45.12	28.40	-76.584110	-76.635817
H_3O^+	-76.869273	-77.081201	-76.830849	-77.042777	48.38	30.62	-76.853834	-77.057325
MeOH	-116.037605	-116.098862	-115.981619	-116.042876	56.71	36.28	-116.008562	-116.060115
CI	-837.662404	-837.910128	-837.386666	-837.634390	125.47	83.04	-837.446282	-837.673845
CII	-838.037206	-838.338779	-837.747484	-838.049057	129.43	85.73	-837.808981	-838.089791
CII•MeOH	-954.118781	-954.459676	-953.770531	-954.111426	149.72	99.53	-953.841667	-954.158716
CII•2MeOH$_1$	-1070.169636	-1070.550196	-1069.763227	-1070.143787	168.79	112.50	-1069.843425	-1070.197238
CII•2MeOH$_2$	-1070.154724	-1070.534421	-1069.749214	-1070.128911	169.29	112.84	-1069.829646	-1070.182524
CIIIa	-913.320988	-913.649222	-913.026729	-913.354963	133.53	88.52	-913.090171	-913.397022
CIIIb	-913.327296	-913.651812	-913.032698	-913.357214	133.28	88.35	-913.096022	-913.399192
CIIIb•MeOH	-1029.383920	-1029.748695	-1029.030897	-1029.395672	151.42	100.69	-1029.102842	-1029.443511

CIV	-912.932529	-913.206646	-912.652221	-912.926338	132.84	88.05	-912.715337	-912.968174
CVI	-838.041025	-838.343059	-837.753480	-838.055514	128.27	84.94	-837.814423	-838.095874
CVII	-954.370657	-954.875605	-954.010785	-954.515733	155.16	103.23	-954.084505	-954.564781
CVIII	-913.316787	-913.642624	-913.023128	-913.348965	130.76	86.64	-913.085256	-913.390129
CIX	-913.308885	-913.631977	-913.017121	-913.340213	129.70	85.92	-913.078748	-913.381035
$[V(=O)(OO)(ox)(bpy)]^-$	-1173.031070	-1173.475766	-1172.812823	-1173.257519	141.76	94.12	-1172.880176	-1173.302237

Table 5TS. Total energies, enthalpies, Gibbs free energies (in Hartree) and entropies (in cal/mol•K) of the equilibrium structures for gas-phase and MeOH solution calculated at the B3LYP level.

	E_g	E_s	H_g	H_s	S_g	S_s	G_g	G_s
H_2O_2	–151.533215	–151.627761	–151.502760	–151.597306	55.85	35.70	–151.529295	–151.614268
H_2O	–76.408953	–76.471632	–76.383999	–76.446678	45.14	28.42	–76.405444	–76.460181
H_3O^+	–76.689084	–76.902735	–76.650930	–76.864581	48.39	30.63	–76.673921	–76.879134
MeOH	–115.714405	–115.778702	–115.658699	–115.722996	56.74	36.30	–115.685656	–115.740243
CI	–835.237867	–835.494855	–834.963050	–835.220038	125.76	83.24	–835.022805	–835.259587
CII	–835.615594	–835.925632	–835.326713	–835.636751	129.94	86.08	–835.388449	–835.677650
CII•MeOH	–951.372247	–951.721590	–951.025049	–951.374392	150.35	99.96	–951.096487	–951.421885
CII•2MeOH$_1$	–1067.098571	–1067.490545	–1066.693464	–1067.085438	170.99	113.99	–1066.774707	–1067.139600
CII•2MeOH$_2$	–1067.085122	–1067.475562	–1066.680409	–1067.070849	173.91	115.98	–1066.763041	–1067.125954
CIIIa	–910.758241	–911.095614	–910.464979	–910.802352	134.28	89.03	–910.528779	–910.844653
CIIIb	–910.764044	–911.097432	–910.470438	–910.803826	134.03	88.86	–910.534122	–910.846047
CIIIb•MeOH	–1026.496278	–1026.871662	–1026.144486	–1026.519870	153.57	102.15	–1026.217450	–1026.568404
CIV	–910.365971	–910.649685	–910.086878	–910.370592	132.47	87.80	–910.149817	–910.412309

CVI	–835.616354	–835.926422	–835.329880	–835.639948	129.25	85.61	–835.391292	–835.680624
CVII	–951.626034	–952.138936	–951.267454	–951.780356	155.33	103.34	–951.341258	–951.829456
CVIII	–910.750652	–911.085059	–910.458241	–910.792648	131.72	87.29	–910.520826	–910.834122
CIX	–910.742398	–911.073571	–910.451792	–910.782965	130.30	86.32	–910.513701	–910.823981

Table 6TS. Total energies, enthalpies, Gibbs free energies (in Hartree) and entropies (in cal/mol•K) of the equilibrium structures for gas-phase and *n*-heptane solution calculated at the B3P86 level.

	Eg	Es	Hg	Hs	Sg	Ss	Gg	Gs
H_2O_2	-151.851341	-151.927418	-151.820524	-151.896601	55.72	42.54	-151.846996	-151.916811
H_2O	-76.587853	-76.639303	-76.562673	-76.614123	45.12	33.53	-76.584110	-76.630052
H_3O^+	-76.869273	-76.978187	-76.830849	-76.939763	48.38	36.30	-76.853834	-76.957009
CI	-837.662404	-837.889595	-837.386666	-837.613857	125.47	101.82	-837.446282	-837.662237
CIIIa	-913.320988	-913.596859	-913.026729	-913.302600	133.53	108.67	-913.090171	-913.354235
CIIIb	-913.327296	-913.602219	-913.032698	-913.307621	133.28	108.46	-913.096022	-913.359155
CVIII	-913.316787	-913.593901	-913.023128	-913.300242	130.76	106.32	-913.085256	-913.350758
CIX	-913.308885	-913.585702	-913.017121	-913.293938	129.70	105.42	-913.078748	-913.344026

Table 7TS. Total energies, enthalpies, Gibbs free energies (in Hartree) and entropies (in cal/mol•K) of the equilibrium structures for gas-phase and heptane solution calculated at the B3LYP level.

	Eg	Es	Hg	Hs	Sg	Ss	Gg	Gs
H_2O_2	–151.533215	–151.613117	–151.502760	–151.582662	55.85	42.65	–151.529295	–151.602926
H_2O	–76.408953	–76.463366	–76.383999	–76.438412	45.14	33.54	–76.405444	–76.454348
H_3O^+	–76.689084	–76.799354	–76.650930	–76.761200	48.39	36.31	–76.673921	–76.778452
CI	–835.237867	–835.474177	–834.963050	–835.199360	125.76	102.07	–835.022805	–835.247857
CIIIa	–910.758241	–911.042318	–910.464979	–910.749056	134.28	109.31	–910.528779	–910.800993
CIIIb	–910.764044	–911.047066	–910.470438	–910.753460	134.03	109.10	–910.534122	–910.805297
CVIII	–910.750652	–911.036045	–910.458241	–910.743634	131.72	107.14	–910.520826	–910.794540
CIX	–910.742398	–911.027315	–910.451792	–910.736709	130.30	105.93	–910.513701	–910.787040

Table 8TS. Cartesian atomic coordinates (Å) of the equilibrium structures calculated at the B3P86 level. First column – symbol of the element or its nuclear charge, second, third and fourth columns – x, y and z coordinates, respectively.

CI

V	1.719250	0.440076	-0.772574
O	1.153965	2.094353	-0.068102
N	-0.308347	-0.166501	-0.278665
C	0.023006	2.742950	-0.048460
N	1.759587	-1.769876	-0.861813
O	1.775311	0.593427	-2.358143
C	0.025764	4.148303	0.078949
H	0.986754	4.649296	0.129429
O	3.185996	0.328498	-0.143645
C	-1.162078	4.850690	0.126441
H	-1.133811	5.933685	0.214707
C	-2.404890	4.195323	0.063623
H	-3.328123	4.763952	0.103005
C	-2.429576	2.822636	-0.045715
H	-3.378383	2.291345	-0.088736
C	-1.233045	2.076376	-0.106381
C	-1.306839	0.654686	-0.180491
H	-2.318219	0.230849	-0.145381
C	-0.608504	-1.589484	-0.330403
H	-0.552611	-2.013749	0.680385
H	-1.623003	-1.777836	-0.704794
C	0.416983	-2.236916	-1.240491
H	0.354199	-3.334624	-1.197624
H	0.243866	-1.914950	-2.271671
C	2.746058	-2.165946	-1.883322
H	3.718188	-1.760085	-1.600553
H	2.801700	-3.262084	-1.954259
H	2.458861	-1.734996	-2.842635
C	2.177349	-2.315109	0.441686
H	1.508665	-1.974163	1.234996
H	2.178169	-3.414471	0.416294
H	3.176032	-1.939375	0.663802

CII

V	3.022907	-0.521226	-0.795834
O	1.964967	-1.990524	-0.768142
N	1.562782	0.651606	-1.451695
C	0.676598	-2.032158	-0.434204
N	3.769334	2.776128	-0.484077
O	3.402019	0.312845	0.543199
C	0.124496	-3.207027	0.079609
H	0.776059	-4.058393	0.243012
C	-1.231378	-3.264514	0.362422
H	-1.647272	-4.182048	0.767807
C	-2.075672	-2.168831	0.123821
H	-3.135338	-2.238726	0.342767
C	-1.546814	-1.009180	-0.398612
H	-2.190086	-0.155786	-0.596785
C	-0.163028	-0.902845	-0.674656
C	0.318266	0.318609	-1.232761
H	-0.446487	1.048583	-1.512899
C	1.878865	1.948372	-2.046158
H	2.587053	1.786914	-2.863323
H	0.971300	2.377945	-2.488195
C	2.392996	2.989558	-1.047287
H	2.405810	3.967485	-1.539322
H	1.714596	3.044834	-0.191675
C	4.042353	3.775155	0.587099
H	5.022034	3.565319	1.017294

H	4.030635	4.779014	0.157412
H	3.279378	3.685734	1.361451
C	4.840029	2.789276	-1.521578
H	4.716654	1.930543	-2.181188
H	4.791264	3.730366	-2.073720
H	5.803773	2.703052	-1.018714
O	4.141250	-0.359067	-1.906398
H	3.772259	1.821769	-0.023399

CII•MeOH

23	-0.356495	0.962663	-0.309391
8	1.496899	0.925076	-0.231493
7	-0.236732	-1.097578	-0.563292
6	2.444793	0.023475	-0.051844
7	-3.281890	-0.733712	0.501445
8	-1.247596	0.852681	1.046155
6	3.764571	0.427790	0.189941
1	3.984510	1.489143	0.231804
6	4.757260	-0.521873	0.364867
1	5.774574	-0.193215	0.556583
6	4.478032	-1.895939	0.290899
1	5.271137	-2.623167	0.425107
6	3.187818	-2.305880	0.035646
1	2.951649	-3.364761	-0.038055
6	2.150826	-1.361381	-0.130664
6	0.838473	-1.819775	-0.438037
1	0.742668	-2.897433	-0.605170
6	-1.457103	-1.786258	-0.978191
1	-1.866507	-1.254765	-1.841861
1	-1.210235	-2.801632	-1.312645
6	-2.503395	-1.958748	0.123053
1	-3.236043	-2.708183	-0.194140
1	-2.021093	-2.315495	1.037086
6	-4.086634	-0.991697	1.724847
1	-4.611422	-0.076155	2.000118
1	-4.808043	-1.787116	1.524674
1	-3.418461	-1.284671	2.535727
6	-4.131994	-0.216852	-0.605321
1	-3.493423	0.113048	-1.424100
1	-4.820638	-1.001755	-0.926951
1	-4.696985	0.638740	-0.233137
8	-1.319174	1.084481	-1.577310
1	-2.562148	0.013745	0.746520
8	-0.034908	3.022032	-0.317355
1	-0.800355	3.494959	-0.677812
6	0.537938	3.731834	0.797009
1	0.783388	4.748433	0.484151
1	1.448870	3.194895	1.055262
1	-0.152748	3.735124	1.644318

CII•2MeOH$_1$

23	1.132577	-0.105077	2.422873
8	-0.752038	-0.445467	2.595014
7	0.863967	-0.365331	0.389007
6	-1.773659	-0.409467	1.772159
7	3.857572	1.018499	0.690985
8	1.237548	1.476299	2.318259
6	-3.088208	-0.417042	2.271822
1	-3.232149	-0.429349	3.347398
6	-4.165913	-0.405329	1.405028
1	-5.172666	-0.404677	1.813213
6	-3.985816	-0.399692	0.011521
1	-4.843527	-0.395481	-0.651948
6	-2.706284	-0.404793	-0.495948
1	-2.543090	-0.406745	-1.571209
6	-1.583257	-0.401759	0.362917
6	-0.285094	-0.419641	-0.219023

1	-0.265916	-0.487390	-1.311501
6	2.059901	-0.367416	-0.448609
1	2.698181	-1.199450	-0.133250
1	1.777041	-0.547420	-1.492583
6	2.825237	0.962225	-0.396835
1	3.346033	1.143772	-1.341873
1	2.123329	1.779677	-0.221264
6	4.111433	2.412780	1.135312
1	4.873686	2.399159	1.915917
1	4.464170	3.005769	0.287892
1	3.181257	2.817628	1.534116
6	5.114048	0.334154	0.297357
1	4.889238	-0.684340	-0.020833
1	5.588289	0.885524	-0.517912
1	5.781325	0.297812	1.159561
8	2.694237	-0.626395	2.340179
1	3.447000	0.455008	1.510653
8	1.086677	-0.177607	4.531616
1	2.001483	-0.152175	4.851791
6	0.282104	0.776236	5.256969
1	0.300725	0.522155	6.318762
1	-0.725476	0.671389	4.860673
1	0.646296	1.791978	5.084191
8	0.812366	-2.457442	2.757789
6	1.696119	-3.363669	3.409464
1	-0.078922	-2.524820	3.130951
1	2.689798	-3.159299	3.011228
1	1.420565	-4.400539	3.191151
1	1.703973	-3.207189	4.494319

CII•2MeOH$_2$

23	1.324869	0.464728	0.610550
8	-0.527525	0.366413	0.262620
7	1.154300	0.344006	-1.922191
6	-1.489298	0.634405	-0.609404
7	4.009672	1.704706	-1.896296
8	0.845119	2.491672	0.820224
6	-2.793164	0.843487	-0.132781
1	-2.962497	0.786634	0.938182
6	-3.833398	1.097179	-1.013859
1	-4.834444	1.257090	-0.624014
6	-3.610415	1.136213	-2.394971
1	-4.430553	1.327324	-3.078648
6	-2.333454	0.915578	-2.877214
1	-2.146194	0.929216	-3.948656
6	-1.255061	0.677393	-2.005738
6	0.045240	0.430396	-2.573450
1	0.048652	0.296452	-3.665733
6	2.324323	0.031624	-2.732240
1	2.920050	-0.721236	-2.204892
1	2.032742	-0.410754	-3.695710
6	3.171673	1.262758	-3.051570
1	3.841394	1.064000	-3.894603
1	2.516529	2.093399	-3.326367
6	4.245881	3.165908	-1.899531
1	4.860732	3.427733	-1.036796
1	4.760844	3.457647	-2.818670
1	3.286161	3.680741	-1.832734
6	5.285200	0.953085	-1.818181
1	5.073301	-0.116495	-1.829431
1	5.921819	1.216669	-2.666655
1	5.783868	1.204016	-0.881141
8	2.877379	0.876787	0.229168
1	3.458020	1.431313	-0.980155
8	1.349078	0.177853	2.159482
8	1.433093	-1.585235	0.174694
6	2.126646	-2.446773	1.106486

1	0.499636	-1.852548	0.120652
1	3.164819	-2.119332	1.105011
1	2.054945	-3.477447	0.752878
1	1.708503	-2.335186	2.108912
1	-0.106249	2.479619	1.021702
6	1.542994	3.242131	1.838222
1	1.190384	4.275589	1.820779
1	2.598574	3.193303	1.578766
1	1.387741	2.782489	2.817063

CIIIa

V	0.534674	1.811555	2.685752
O	-0.920260	1.204384	3.550082
N	-0.125752	0.818207	1.022451
C	-2.182220	1.235427	3.120714
N	2.302950	-1.301263	1.146835
O	0.312066	3.273894	2.193372
C	-3.233495	1.394550	4.023675
H	-3.006121	1.527003	5.075694
O	2.179699	1.027787	2.311541
C	-4.538320	1.402234	3.553446
H	-5.351727	1.547830	4.257918
C	-4.827476	1.224551	2.191352
H	-5.855938	1.232136	1.847788
C	-3.795642	1.033183	1.298019
H	-4.004393	0.882203	0.242113
C	-2.452686	1.043152	1.738361
C	-1.412537	0.755602	0.806446
H	-1.741506	0.425536	-0.183799
C	0.766168	0.351720	-0.038471
H	0.251495	0.414523	-1.004704
H	1.628470	1.022699	-0.089308
C	1.200844	-1.106251	0.141457
H	0.348587	-1.706576	0.469598
H	1.560021	-1.514170	-0.807794
C	3.647721	-1.049592	0.553368
H	4.390834	-1.071750	1.350967
H	3.862310	-1.823908	-0.185945
H	3.657812	-0.063880	0.088708
C	2.238681	-2.640347	1.792163
H	1.290904	-2.735358	2.324022
H	2.318514	-3.414812	1.026492
H	3.065422	-2.731241	2.497897
O	2.069447	1.653337	3.583091
H	2.184267	-0.553076	1.886048

CIIIb

V	2.930861	0.192450	0.288853
O	1.397526	-0.392394	-0.395985
N	2.455942	2.094037	-0.319137
C	0.253015	0.143794	-0.817120
N	4.280453	2.813276	2.208425
O	2.859031	0.531860	1.851772
C	-0.849761	-0.669789	-1.072062
H	-0.764560	-1.738142	-0.907174
O	4.500089	0.550192	-0.536437
C	-2.025474	-0.094360	-1.532997
H	-2.882752	-0.731442	-1.728397
C	-2.125034	1.286638	-1.755790
H	-3.052349	1.714595	-2.120127
C	-1.033039	2.093347	-1.513048
H	-1.092978	3.164636	-1.686786
C	0.175191	1.542399	-1.032320
C	1.288392	2.405841	-0.807070
H	1.132615	3.450534	-1.091917
C	3.453847	3.156131	-0.206843
H	4.401256	2.788086	-0.608198

H	3.157982	4.006765	-0.832604
C	3.616539	3.715039	1.207312
H	4.216790	4.629400	1.163675
H	2.636343	3.968146	1.620739
C	4.164018	3.382664	3.580469
H	4.608719	2.682210	4.287937
H	4.691763	4.337660	3.620362
H	3.109610	3.523537	3.821011
C	5.700745	2.503849	1.871366
H	5.736144	1.947423	0.934786
H	6.261238	3.438252	1.799698
H	6.113932	1.882418	2.666603
O	4.384567	-0.767545	-0.039292
H	3.753228	1.902853	2.199257

CIIIb•MeOH

V	2.758657	1.664907	2.077204
O	0.973506	1.507465	2.241669
N	2.633474	1.171432	0.089064
C	0.026918	0.898581	1.543951
N	4.733850	3.600087	-0.143092
O	2.967280	3.230972	1.827534
C	-1.244609	0.720246	2.095504
H	-1.431045	1.077256	3.102674
O	4.403792	0.854137	1.976786
C	-2.236125	0.098490	1.350355
H	-3.218992	-0.039739	1.791068
C	-1.994102	-0.349625	0.044397
H	-2.782078	-0.832249	-0.523017
C	-0.745276	-0.164282	-0.512208
H	-0.543819	-0.500201	-1.526288
C	0.288743	0.457771	0.219988
C	1.552051	0.651321	-0.415528
H	1.601576	0.321237	-1.457511
C	3.807483	1.283243	-0.770126
H	4.655928	0.809332	-0.268728
H	3.637152	0.724439	-1.698817
C	4.141695	2.712777	-1.198605
H	4.863527	2.680632	-2.021156
H	3.236873	3.212262	-1.554803
C	4.766040	5.013270	-0.609892
H	5.160216	5.637820	0.192327
H	5.407844	5.088436	-1.490328
H	3.751888	5.331814	-0.854312
C	6.078233	3.151525	0.319078
H	5.986031	2.175622	0.794999
H	6.758113	3.119836	-0.535050
H	6.442201	3.867103	1.057387
O	4.021773	1.250954	3.277925
H	4.085218	3.556883	0.688862
O	2.408808	-0.780207	2.317188
C	1.828289	-1.355457	3.490016
H	3.363217	-0.958270	2.319894
H	0.760901	-1.134854	3.455789
H	2.261502	-0.924466	4.398815
H	1.964122	-2.441360	3.493095

CIV

23	2.159192	-1.260673	0.737759
8	2.080711	0.685050	0.531164
7	0.051671	-1.066834	0.532885
6	1.267488	1.544911	0.019958
7	1.377456	-3.408083	0.976984
8	2.657940	-1.651304	-0.699359
6	1.719044	2.859456	-0.265258
1	2.759156	3.090055	-0.060396
8	3.198617	-2.021466	2.008731

6	0.856529	3.795241	-0.790042
1	1.227720	4.793450	-1.008478
6	-0.497706	3.492171	-1.051238
1	-1.157556	4.248087	-1.464027
6	-0.962666	2.230384	-0.772130
1	-2.003312	1.970754	-0.957217
6	-0.099566	1.242748	-0.240007
6	-0.606042	-0.038399	0.067831
1	-1.678710	-0.175477	-0.108802
6	-0.743834	-2.277033	0.731831
1	-1.014734	-2.374516	1.790504
1	-1.680916	-2.232413	0.163433
6	0.087358	-3.452618	0.277308
1	-0.428214	-4.408004	0.458996
1	0.286549	-3.362013	-0.794739
6	2.332064	-4.330930	0.336602
1	3.291999	-4.252694	0.847891
1	1.961196	-5.364557	0.397330
1	2.467929	-4.039741	-0.704701
6	1.216723	-3.803736	2.387918
1	0.580648	-3.095211	2.921489
1	0.772206	-4.807476	2.451412
1	2.191674	-3.802930	2.872526
8	3.537418	-0.681118	1.784093

CVI

23	2.095176	-0.818834	0.497816
8	1.485823	0.853752	0.671822
7	0.060704	-1.310818	0.341314
6	0.393188	1.590924	0.518121
7	2.113093	-3.002741	0.432007
8	3.029184	-0.738351	-0.984133
6	0.468903	2.982007	0.599974
1	1.430064	3.450226	0.781579
8	3.030062	-0.946919	1.738368
6	-0.691798	3.728631	0.448824
1	-0.633855	4.811147	0.510241
6	-1.934301	3.115077	0.228298
1	-2.827410	3.720373	0.119370
6	-2.012420	1.738775	0.156249
1	-2.968253	1.247759	-0.006486
6	-0.848707	0.954177	0.295503
6	-0.925435	-0.463282	0.224504
1	-1.921675	-0.877930	0.046617
6	-0.280887	-2.733826	0.210716
1	-0.556553	-3.133651	1.192634
1	-1.140547	-2.869532	-0.453581
6	0.936487	-3.435587	-0.346836
1	0.825846	-4.526777	-0.309828
1	1.098495	-3.142024	-1.388886
6	3.362511	-3.477451	-0.211606
1	4.219640	-3.085639	0.337892
1	3.388192	-4.573463	-0.194128
1	3.407204	-3.117207	-1.238401
6	2.062313	-3.552930	1.810547
1	1.230102	-3.127161	2.373029
1	1.954644	-4.643333	1.768981
1	2.984909	-3.291965	2.327294
1	2.790502	-0.109935	-1.685795

CVII

23	1.344133	2.101944	0.554024
8	0.010508	2.213297	-0.621481
7	1.050711	0.095555	0.503594
6	-1.202580	1.631790	-0.573664
7	4.015117	-0.344075	-0.876610
8	2.781896	2.075733	-0.085770

6	-2.309767	2.266799	-1.125199
1	-2.200385	3.249938	-1.569596
6	-3.542125	1.622342	-1.087202
1	-4.411799	2.124462	-1.500069
6	-3.681471	0.340147	-0.535271
1	-4.652832	-0.141729	-0.521216
6	-2.574739	-0.309636	-0.025543
1	-2.665654	-1.312296	0.383167
6	-1.314019	0.326092	-0.023703
6	-0.157074	-0.393686	0.389001
1	-0.295365	-1.458011	0.596816
6	2.144481	-0.831907	0.816743
1	2.790940	-0.375639	1.571981
1	1.725134	-1.733594	1.277494
6	2.939724	-1.292343	-0.409431
1	3.441135	-2.239348	-0.190214
1	2.264134	-1.454851	-1.252963
6	4.394078	-0.622292	-2.298363
1	5.185458	0.067615	-2.593340
1	4.752600	-1.650520	-2.372144
1	3.520631	-0.481143	-2.936150
6	5.221693	-0.371816	0.007353
1	4.929995	-0.167862	1.037345
1	5.686023	-1.356865	-0.064164
1	5.920433	0.394484	-0.329857
8	1.241990	2.105603	2.290265
1	3.628668	0.614291	-0.829122
8	1.339193	4.180066	0.696846
1	0.729052	4.549575	1.357159
6	1.476006	5.077522	-0.436665
1	0.576224	5.043509	-1.053958
1	2.340599	4.727939	-0.998691
1	1.659344	6.084639	-0.060823
1	1.952154	2.272692	2.934505

CVIII

V	1.175258	-0.603847	0.772034
O	-0.526245	-1.227097	0.978974
N	0.641143	-0.483811	-1.224550
C	-1.713554	-1.046766	0.406057
N	3.074765	-0.806629	-0.259541
O	1.351439	0.915206	1.051575
C	-2.888209	-1.311864	1.111089
H	-2.828199	-1.648789	2.140240
O	2.144600	-1.655763	1.910022
C	-4.111387	-1.129028	0.481166
H	-5.023840	-1.326002	1.035893
C	-4.193144	-0.696686	-0.851283
H	-5.161089	-0.560891	-1.320714
C	-3.034104	-0.452238	-1.557594
H	-3.076477	-0.126275	-2.593498
C	-1.777043	-0.618482	-0.938245
C	-0.580080	-0.427641	-1.678036
H	-0.702413	-0.229884	-2.746483
C	1.713130	-0.338306	-2.218651
H	1.829968	-1.282436	-2.763483
H	1.461107	0.436003	-2.950526
C	2.973557	0.029412	-1.478258
H	3.864403	-0.108374	-2.103695
H	2.934512	1.071903	-1.152577
C	4.188634	-0.284940	0.575415
H	4.301816	-0.902626	1.464439
H	5.115927	-0.304915	-0.009122
H	3.963291	0.738739	0.876529
C	3.341266	-2.225874	-0.596376
H	2.507913	-2.651625	-1.159262
H	4.257053	-2.303386	-1.194354

H	3.469058	-2.794499	0.325540
O	1.233011	-1.117026	2.857778
H	0.537844	-1.805891	2.931107

CIX

V	0.799991	-1.312311	0.820233
O	-0.757749	-0.392100	0.826116
N	0.783407	-0.895310	-1.191187
C	-1.788077	-0.271372	-0.005603
N	2.906517	-0.688477	0.439871
O	1.189749	-0.869222	2.469027
C	-3.060376	0.024600	0.487490
H	-3.204588	0.116748	1.558404
O	1.377282	-2.971498	0.515156
C	-4.110634	0.188519	-0.404118
H	-5.102095	0.407109	-0.019479
C	-3.915157	0.079237	-1.789106
H	-4.750918	0.212105	-2.467297
C	-2.654805	-0.194130	-2.283598
H	-2.488025	-0.272816	-3.354548
C	-1.573000	-0.383926	-1.402273
C	-0.264205	-0.628499	-1.911404
H	-0.138769	-0.579774	-2.996613
C	2.077617	-1.116256	-1.829482
H	2.287275	-2.192091	-1.818739
H	2.079875	-0.772010	-2.869420
C	3.078034	-0.342614	-1.001183
H	4.111018	-0.532793	-1.313831
H	2.880670	0.727133	-1.114754
C	3.252441	0.503301	1.254016
H	3.235059	0.240740	2.309945
H	4.252782	0.856303	0.974787
H	2.527452	1.300525	1.073274
C	3.820015	-1.795446	0.816263
H	3.664317	-2.654516	0.162229
H	4.859440	-1.457447	0.728384
H	3.621588	-2.093276	1.846540
O	-0.010626	-2.857754	0.724485
H	0.445274	-0.684209	3.068634

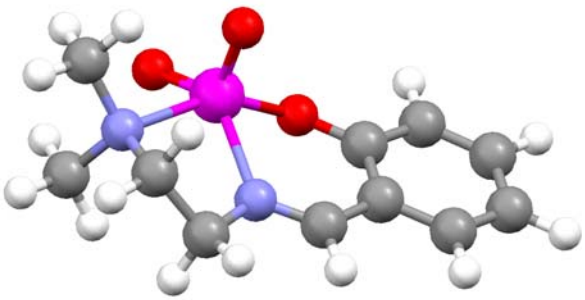
$[V(=O)(OO)(ox)(bpy)]^-$

23	-1.542975	2.008318	-0.283762
8	-1.417244	3.547107	-0.634652
8	-3.261869	1.594070	-0.858715
8	-3.165032	1.754338	0.536613
8	0.406879	1.582208	-0.472425
8	-0.986602	1.887084	1.598502
8	2.336691	1.315523	0.645002
8	0.756082	1.692956	3.000743
7	-1.249450	1.390025	-2.362197
7	-1.508362	-0.341823	-0.382470
6	1.135967	1.523245	0.606149
6	0.280979	1.724844	1.879728
6	-1.063001	2.328551	-3.287430
6	-0.832071	2.019223	-4.623717
6	-0.785212	0.680796	-4.993057
6	-0.976457	-0.293844	-4.022495
6	-1.214606	0.091051	-2.701490
6	-1.431751	-0.878790	-1.603570
6	-1.562558	-2.255091	-1.799570
6	-1.778429	-3.069318	-0.692618
6	-1.858872	-2.494896	0.570023
6	-1.717426	-1.112204	0.677927
1	-1.099199	3.345724	-2.909273
1	-0.686205	2.814560	-5.347218
1	-0.596488	0.394181	-6.024110
1	-0.927203	-1.343920	-4.287924

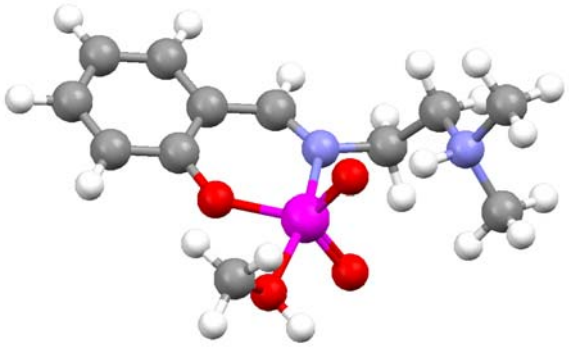
1	-1.511890	-2.688676	-2.792559
1	-1.885135	-4.143238	-0.820650
1	-2.027585	-3.097646	1.456571
1	-1.768907	-0.586206	1.627021

Calculated Structures of several V-sal-dmen complexes

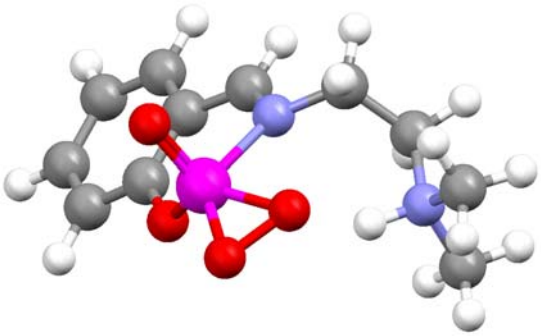
CI



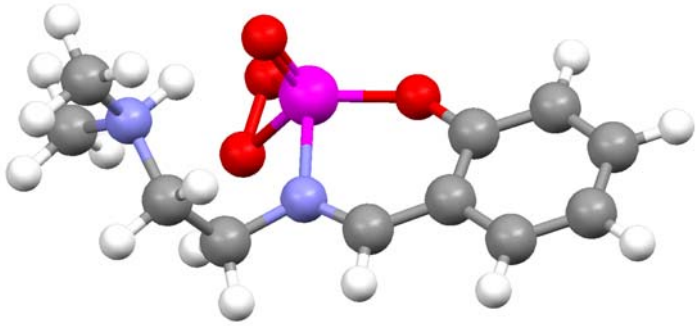
CII



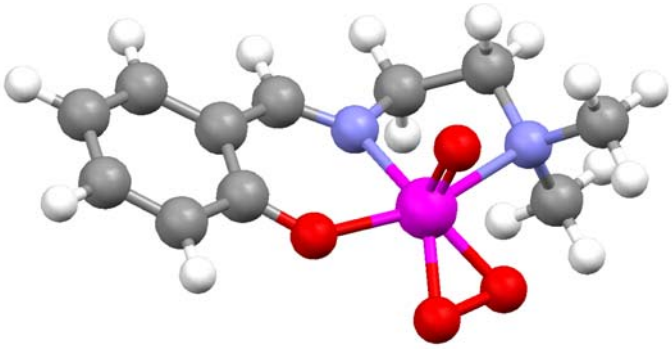
CIIIa



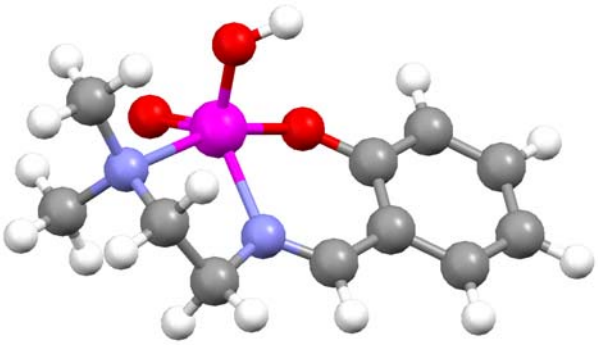
CIIIb



CIV



CVI



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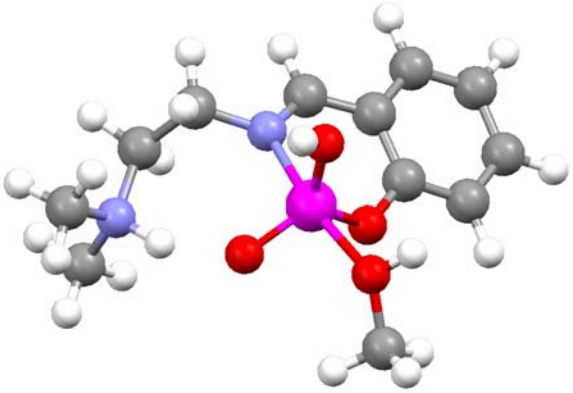
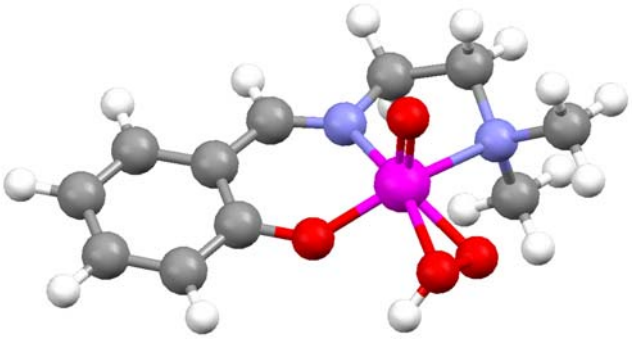


CVIII



CIX