Supporting Information for

Tetradentate N_2S_2 Vanadyl(IV) Coordination Complexes: Synthesis, Characterization And Reactivity Studies

*Roxanne M. Jenkins, Tiffany A. Pinder, Michelle L. Hatley, Joseph H. Reibenspies, and Marcetta Y. Darensbourg**

Department of Chemistry
Texas A&M University
College Station, TX 77845

Email: marcetta@mail.chem.tamu.edu
Tel.: 979 845 2981

Table S1-S2. Summary of crystal data and full listing of metric parameters for complex **1** and molecular structure with atom numbering scheme.

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Table S1. Crystal data and structure refinement for [(bme-daco)(V=O)].

Empirical formula	C10 H20 N2 O S2 V	
Formula weight	299.34	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 7.590(3) Å	α = 90°.
	b = 20.689(9) Å	β = 109.55(4)°.
	c = 8.565(3) Å	γ = 90°.
Volume	1267.4(9) $Å^3$	
Z	4	
Density (calculated)	1.569 Mg/m^3	
Absorption coefficient	1.093 mm^{-1}	
F(000)	628	
Crystal size	2.00 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.97 to 25.00°.	
Index ranges	-9<=h<=8, -24<=k<=24, -10<=l<=9	
Reflections collected	11094	
Independent reflections	2159 [R(int) = 0.0584]	
Completeness to theta = 25.00°	96.9 %	
Max. and min. transmission	0.8110 and 0.2185	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2159 / 0 / 145	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1066	
R indices (all data)	R1 = 0.0637, wR2 = 0.1113	
Largest diff. peak and hole	0.432 and -0.604 e.$Å^{-3}$	

Table S2. Full listing of metric parameters for complex 1 and molecular structure with atom numbering scheme.

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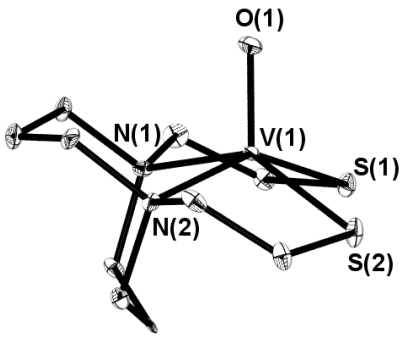
Bond lengths [Å] and angles [°] for [(bme-daco)(V≡O)].

V(1)-O(1)	1.599(3)
V(1)-N(2)	2.154(3)
V(1)-N(1)	2.159(3)
V(1)-S(1)	2.3482(14)
V(1)-S(2)	2.3617(18)
S(1)-C(1)	1.825(4)
S(2)-C(3)	1.837(4)
N(2)-C(7)	1.499(5)
N(2)-C(4)	1.506(5)
N(2)-C(10)	1.511(5)
N(1)-C(2)	1.493(5)
N(1)-C(5)	1.504(5)
N(1)-C(8)	1.519(5)
C(1)-C(2)	1.519(6)
C(8)-C(9)	1.528(5)
C(3)-C(4)	1.510(6)
C(5)-C(6)	1.507(6)
C(6)-C(7)	1.525(6)
C(9)-C(10)	1.513(5)
O(1)-V(1)-N(2)	102.94(14)
O(1)-V(1)-N(1)	101.26(14)
N(2)-V(1)-N(1)	84.11(13)
O(1)-V(1)-S(1)	112.27(11)
N(2)-V(1)-S(1)	144.33(9)
N(1)-V(1)-S(1)	83.65(10)
O(1)-V(1)-S(2)	110.26(11)
N(2)-V(1)-S(2)	84.23(10)
N(1)-V(1)-S(2)	148.11(9)
S(1)-V(1)-S(2)	88.80(5)
C(1)-S(1)-V(1)	100.53(14)
C(3)-S(2)-V(1)	100.55(13)
C(7)-N(2)-C(4)	106.3(3)
C(7)-N(2)-C(10)	110.7(3)



C(4)-N(2)-C(10)	110.8(3)
C(7)-N(2)-V(1)	110.7(2)
C(4)-N(2)-V(1)	108.7(2)
C(10)-N(2)-V(1)	109.6(2)
C(2)-N(1)-C(5)	106.7(3)
C(2)-N(1)-C(8)	110.7(3)
C(5)-N(1)-C(8)	109.9(3)
C(2)-N(1)-V(1)	107.7(2)
C(5)-N(1)-V(1)	110.9(2)
C(8)-N(1)-V(1)	110.8(2)
C(2)-C(1)-S(1)	111.4(3)
N(1)-C(8)-C(9)	111.5(3)
C(4)-C(3)-S(2)	111.4(3)
N(2)-C(4)-C(3)	113.9(3)
N(1)-C(5)-C(6)	114.5(3)
C(5)-C(6)-C(7)	116.6(3)
N(2)-C(7)-C(6)	114.9(3)
C(10)-C(9)-C(8)	117.0(3)
N(2)-C(10)-C(9)	113.3(3)
N(1)-C(2)-C(1)	112.3(3)

Table S3. Crystal data and structure refinement for [(bme-dach)(V=O)].

Empirical formula	C9 H18 N2 O S2 V	
Formula weight	285.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 7.2514(18) Å	α = 90°.
	b = 9.816(2) Å	β = 90°.
	c = 16.378(5) Å	γ = 90°.
Volume	1165.8(5) $Å^3$	
Z	4	
Density (calculated)	1.626 Mg/m^3	
Absorption coefficient	1.184 mm^{-1}	
F(000)	596	
Crystal size	0.10 x 0.10 x 0.02 mm^3	
Theta range for data collection	2.49 to 25.00°.	
Index ranges	-8<=h<=8, -6<=k<=11, -19<=l<=13	
Reflections collected	2642	
Independent reflections	1917 [R(int) = 0.0354]	
Completeness to theta = 25.00°	96.5 %	
Max. and min. transmission	0.9767 and 0.8908	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1917 / 0 / 137	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0582	
R indices (all data)	R1 = 0.0476, wR2 = 0.0619	
Absolute structure parameter	0.00(6)	
Largest diff. peak and hole	0.365 and -0.307 $e.Å^{-3}$	

Table S4. Full listing of metric parameters for complex **2** and molecular structure with atom numbering scheme.

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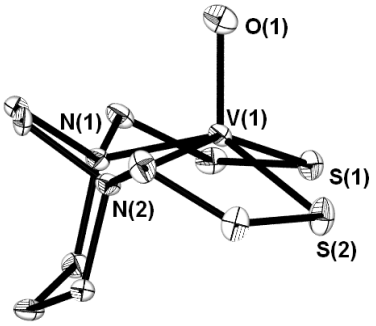
Bond lengths [Å] and angles [°] for [(bme-dach)(V≡O)].

V(1)-O(1)	1.605(3)
V(1)-N(2)	2.111(3)
V(1)-N(1)	2.122(3)
V(1)-S(1)	2.3407(12)
V(1)-S(2)	2.3455(12)
S(1)-C(1)	1.841(4)
S(2)-C(3)	1.840(4)
N(1)-C(8)	1.489(4)
N(1)-C(5)	1.489(5)
N(1)-C(2)	1.491(4)
N(2)-C(9)	1.487(4)
N(2)-C(4)	1.490(5)
N(2)-C(7)	1.499(5)
C(1)-C(2)	1.523(5)
C(3)-C(4)	1.513(5)
C(5)-C(6)	1.512(5)
C(6)-C(7)	1.511(5)
C(8)-C(9)	1.553(5)
O(1)-V(1)-N(2)	102.17(13)
O(1)-V(1)-N(1)	105.02(13)
N(2)-V(1)-N(1)	74.35(11)
O(1)-V(1)-S(1)	108.46(10)
N(2)-V(1)-S(1)	146.39(9)
N(1)-V(1)-S(1)	84.50(8)
O(1)-V(1)-S(2)	110.66(10)
N(2)-V(1)-S(2)	83.34(9)
N(1)-V(1)-S(2)	141.09(9)
S(1)-V(1)-S(2)	98.20(5)
C(1)-S(1)-V(1)	99.17(12)
C(3)-S(2)-V(1)	98.23(13)
C(8)-N(1)-C(5)	111.0(3)
C(8)-N(1)-C(2)	111.3(3)



C(5)-N(1)-C(2)	109.8(3)
C(8)-N(1)-V(1)	104.8(2)
C(5)-N(1)-V(1)	112.3(2)
C(2)-N(1)-V(1)	107.6(2)
C(9)-N(2)-C(4)	110.9(3)
C(9)-N(2)-C(7)	110.7(3)
C(4)-N(2)-C(7)	109.4(3)
C(9)-N(2)-V(1)	104.8(2)
C(4)-N(2)-V(1)	106.6(2)
C(7)-N(2)-V(1)	114.3(2)
C(2)-C(1)-S(1)	111.2(2)
N(1)-C(2)-C(1)	110.8(3)
C(4)-C(3)-S(2)	112.4(2)
N(2)-C(4)-C(3)	110.1(3)
N(1)-C(5)-C(6)	113.2(3)
C(7)-C(6)-C(5)	114.8(3)
N(2)-C(7)-C(6)	112.4(3)
N(1)-C(8)-C(9)	109.9(3)
N(2)-C(9)-C(8)	109.5(3)

Table S5. Crystal data and structure refinement for $[Et_4N]_2[(V{=}O)(ema)]$.

Empirical formula	C22 H50 N4 O4 S2 V	
Formula weight	549.72	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.894(5) Å	α = 72.63(5)°.
	b = 12.219(7) Å	β = 79.92(4)°.
	c = 13.832(7) Å	γ = 80.36(5)°.
Volume	1401.9(13) $Å^3$	
Z	2	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	0.536 mm^{-1}	
F(000)	594	
Crystal size	0.10 x 0.10 x 0.01 mm^3	
Theta range for data collection	2.00 to 25.00°.	
Index ranges	-10<=h<=10, -14<=k<=14, -16<=l<=16	
Reflections collected	19908	
Independent reflections	4891 [R(int) = 0.0457]	
Completeness to theta = 25.00°	98.9 %	
Max. and min. transmission	0.9947 and 0.9484	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4891 / 0 / 298	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0397, wR2 = 0.0899	
R indices (all data)	R1 = 0.0561, wR2 = 0.0983	
Largest diff. peak and hole	0.432 and -0.309 $e.Å^{-3}$	

Table S6. Full listing of metric parameters for complex **3** and molecular structure with atom numbering scheme.

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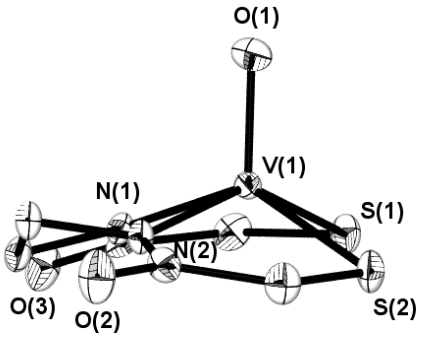
Bond lengths [Å] and angles [°] for $[Et_4N]_2[(ema)(V{\equiv}O)]$.

V(1)-O(1)	1.6229(19)
V(1)-N(1)	2.028(2)
V(1)-N(2)	2.028(2)
V(1)-S(2)	2.3632(15)
V(1)-S(3)	2.3688(17)
S(2)-C(1)	1.828(3)
S(3)-C(6)	1.830(3)
O(2)-C(2)	1.260(3)
O(3)-C(5)	1.256(3)
N(1)-C(2)	1.328(3)
N(1)-C(3)	1.457(3)
N(2)-C(5)	1.333(3)
N(2)-C(4)	1.465(3)
C(1)-C(2)	1.507(4)
C(3)-C(4)	1.531(4)
C(5)-C(6)	1.511(4)
N(3)-C(10)	1.511(3)
N(3)-C(8)	1.520(3)
N(3)-C(11)	1.525(3)
N(3)-C(13)	1.527(3)
C(7)-C(8)	1.509(4)
C(9)-C(10)	1.507(4)
C(11)-C(12)	1.513(4)
C(13)-C(14)	1.505(4)
N(4)-C(19)	1.517(3)
N(4)-C(15)	1.518(3)
N(4)-C(17)	1.521(3)
N(4)-C(21)	1.523(3)
C(15)-C(16)	1.503(4)
C(17)-C(18)	1.513(4)
C(19)-C(20)	1.506(4)
C(21)-C(22)	1.500(4)



O(1)-V(1)-N(1)	105.62(10)
O(1)-V(1)-N(2)	109.72(10)
N(1)-V(1)-N(2)	78.41(10)
O(1)-V(1)-S(2)	111.79(8)
N(1)-V(1)-S(2)	81.27(8)
N(2)-V(1)-S(2)	137.28(7)
O(1)-V(1)-S(3)	108.27(8)
N(1)-V(1)-S(3)	145.03(7)
N(2)-V(1)-S(3)	82.32(8)
S(2)-V(1)-S(3)	93.91(6)
C(1)-S(2)-V(1)	98.83(10)
C(6)-S(3)-V(1)	97.51(10)
C(2)-N(1)-C(3)	120.1(2)
C(2)-N(1)-V(1)	126.01(17)
C(3)-N(1)-V(1)	112.86(16)
C(5)-N(2)-C(4)	117.0(2)
C(5)-N(2)-V(1)	125.28(17)
C(4)-N(2)-V(1)	117.59(16)
C(2)-C(1)-S(2)	114.39(18)
O(2)-C(2)-N(1)	125.8(2)
O(2)-C(2)-C(1)	118.8(2)
N(1)-C(2)-C(1)	115.4(2)
N(1)-C(3)-C(4)	107.9(2)
N(2)-C(4)-C(3)	108.3(2)
O(3)-C(5)-N(2)	125.1(2)
O(3)-C(5)-C(6)	119.1(2)
N(2)-C(5)-C(6)	115.8(2)
C(5)-C(6)-S(3)	114.24(18)
C(10)-N(3)-C(8)	112.2(2)
C(10)-N(3)-C(11)	108.1(2)
C(8)-N(3)-C(11)	109.1(2)
C(10)-N(3)-C(13)	107.8(2)
C(8)-N(3)-C(13)	107.7(2)
C(11)-N(3)-C(13)	111.8(2)
C(7)-C(8)-N(3)	115.4(2)
C(9)-C(10)-N(3)	115.0(2)
C(12)-C(11)-N(3)	114.4(2)

C(14)-C(13)-N(3)	115.2(2)
C(19)-N(4)-C(15)	106.0(2)
C(19)-N(4)-C(17)	111.2(2)
C(15)-N(4)-C(17)	111.7(2)
C(19)-N(4)-C(21)	111.5(2)
C(15)-N(4)-C(21)	111.0(2)
C(17)-N(4)-C(21)	105.52(19)
C(16)-C(15)-N(4)	115.0(2)
C(18)-C(17)-N(4)	115.5(2)
C(20)-C(19)-N(4)	115.9(2)
C(22)-C(21)-N(4)	115.2(2)