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(*N*,*N*′-Ethylenebis(acetylacetone iminato))vanadium(III) Derivatives: Syntheses and Substitution Reactions at the V-Cl Bond

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Two syntheses are reported for the vanadium(III) complex [(THF)V(acacen)(Cl)] (**1**) [acacen = *N*,*N*′-ethylenebis(acetylacetone iminato) dianion], which is a useful precursor for a large number of complexes, including organometallic derivatives, which are obtained by replacing the chloride ligand. The first synthesis from $VCl_3(THF)_3$ is straightforward. The second synthesis is more complex and involves the reductive deoxygenation of [VO(acacen)] by $TiCl_3(THF)_3$. Performing this reaction at low temperature results in the isolation of a bimetallic vanadium(IV)–titanium(IV) μ-oxo complex, $[(Cl)(acacen)V–O–Ti(Cl)_3(THF)_2]$ (**3**), which sheds light on the pathway of reductive deoxygenation of oxo complexes by $TiCl_3(THF)_3$. The chloride ligand is easily replaced in **1** by monoanionic ligands; the complexes formed in each replacement contain a vanadium(III) center with a different redox potential. Reaction of **1** with PhONa, PhSNa, and NH_4SCN gives as crystalline solids [(THF)V(acacen)(OPh)] (**6**), $[V(acacen)(PhS)]_2$ (**7**), and [(THF)V(acacen)(NCS)] (**8**). The structures of four derivatives have been determined. [(THF)V(acacen)(Cl)] (**1**): space group $P2_1/n$ (monoclinic); $a = 15.573$ (2), $b = 15.030$ (3), $c = 7.961$ (1) Å; $\beta = 94.72$ (1)°; $V = 1857.1$ (5) Å^3; $Z = 4$; $D_{calcd} = 1.362$ g cm^{-3}. The final *R* factor was 0.046 for 1711 observed reflections. $[(Cl)(acacen)V–O–Ti(Cl)_3(THF)_2]$ (**3**): space group $P2_1/n$ (monoclinic); $a = 19.980$ (2), $b = 12.531$ (2), $c = 12.908$ (2) Å; $\beta = 93.20$ (1)°; $V = 3226.7$ (8) Å^3; $Z = 4$; $D_{calcd} = 1.431$ g cm^{-3}. The final *R* factor was 0.052 for 2477 observed reflections. [(THF)V(acacen)(OPh)] (**6**): space group $P2_1/n$ (monoclinic); $a = 13.287$ (2), $b = 18.788$ (3), $c = 9.325$ (1) Å; $\beta = 103.02$ (2)°; $V = 2268.0$ (6) Å^3; $Z = 4$; $D_{calcd} = 1.284$ g cm^{-3}. The final *R* factor was 0.039 for 1922 observed reflections. [(THF)V(acacen)(NCS)] (**8**): space group $P2_1/n$ (monoclinic); $a = 12.728$ (5), $b = 12.495$ (5), $c = 12.617$ (5) Å; $\beta = 91.27$ (1)°; $V = 2006.1$ (14) Å^3; $Z = 4$; $D_{calcd} = 1.336$ g cm^{-3}. The final *R* factor was 0.052 for 1554 observed reflections. The [V(acacen)] moiety has similar structural features in both **1** and **3**, except for the V–O distances, which decrease considerably from 1.954 (4) [V–O(1)] and 1.943 (5) Å [V–O(2)] in the former to 1.864 (5) and 1.875 (5) Å in the latter. A rather long V–O distance [1.973 (6) Å] and a rather short Ti–O [1.691 (6) Å] bond distance were found in the μ-oxo skeleton [V–O–Ti] of **3**. By contrast, complex **6** contains a rather short V–O distance, 1.881 (3) Å. The thiocyanate is N-bonded in **8** with a linear structure [V–N–C, 175.7 (7)°; S–C–N, 179.6 (8)°; V–N, 2.071 (7) Å; C–N, 1.08 (1) Å; C–S, 1.67 (1) Å] [ν(C=N) (Nujol), 2070 cm^{-1}].

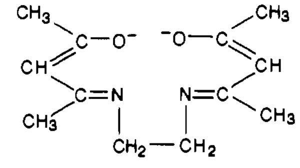
Introduction

The special metal-ligand electronic synergism between an tetradentate Schiff base ligand and a metal ion, along with some imposed rigid coordination geometry, accounts for the stabilization of different oxidation states for the metal[1] and for stabilization of an organometallic functionality such as the M–C σ bond.[2] These effects, which are relatively well-known in cobalt and to a lesser extent in iron chemistry,[3] suggest a design for analogous compounds in the rather less well-known coordination chemistry of vanadium.[4] Interesting compounds would be those in which the metal in a low oxidation state has lightly coordinated ligands or contains a reactive functionality, such as metal–halogen or metal–alkyl units. In this paper we report the synthesis of the vanadium(III) derivatives [(L)V(acacen)(X)] [X = Cl, OPh, SPh, NCS$^-$; L = solvent molecule, i.e. THF, py], complexes **1**, **6–8**. The nature of X influences significantly the redox potential[5] of the metal, which can be a one-electron donor to a variety of substrates. It is known that oxidation to vanadium(IV) is rather easy.[6] Two different synthesis are reported for the parent compound [(THF)V(acacen)(Cl)] (**1**). In addition, it should be mentioned that [(THF)V(acacen)(Cl)] has recently been used for the synthesis of stable organometallic derivatives of vanadium(III).[7]

Experimental Section

All the reactions were carried out under an atmosphere of purified nitrogen, in solvents that were purified by standard methods. Infrared spectra were recorded with a Perkin-Elmer Model 983 spectrophotometer. Magnetic susceptibility was determined by the Faraday method. $TiCl_3(THF)_3$,[8] $VCl_3(THF)_3$,[8] and $[VO(acac)_2]$[9] were prepared by published procedures.

Abbreviation. acacen = *N*,*N*′-ethylenebis(acetylacetone iminato) dianion:



acacen

Synthesis of [VO(acacen)] (2). A suspension of $[VO(acac)_2]$ (41.4 g, 156.2 mmol) in tetraline (300 mL) was heated up to 180 °C for 15 min in the presence of an excess of $acacenH_2$ (53.0 g, 236.6 mmol). The acacH formed was distilled out and the excess of $acacenH_2$ removed by filtration in air. When the blue solution was allowed to stand at room temperature, [VO(acacen)] crystallized as a deep blue solid, which was washed with *n*-hexane and THF in air (yield ca. 72%). Anal. Calcd for [VO(acacen)], $C_{12}H_{18}N_2O_3V$: C, 50.36; H, 6.34; N, 9.80. Found: C, 49.76; H, 6.32; N, 9.60. IR: ν(V=O) (Nujol), 980 cm^{-1}; ν(C=N) (Nujol), 1515 cm^{-1}.

Synthesis of [(THF)V(acacen)(Cl)] (1). Method A. A THF solution (500 mL) of $acacenH_2$ (18.0 g, 80.4 mmol) was slowly reacted with solid NaH (3.80 g, 158.3 mmol) with vigorous stirring. An abundant H_2

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Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **1**, **3**, **6**, and **8**

	1	3	6	8
	$C_{16}H_{26}ClN_2O_3V$	$C_{24}H_{42}Cl_4N_2O_6TiV$	$C_{22}H_{31}N_2O_4V$	$C_{17}H_{26}N_3O_3SV$
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
cell params[a]				
a, Å	15.573 (2)	19.980 (2)	13.287 (2)	12.728 (5)
b, Å	15.030 (3)	12.531 (2)	18.788 (3)	12.495 (5)
c, Å	7.961 (1)	12.908 (2)	9.325 (1)	12.617 (5)
α, deg	90	90	90	90
β, deg	94.72 (1)	93.20 (1)	103.02 (2)	91.27 (1)
γ, deg	90	90	90	90
V, Å^3	1857.1 (5)	3226.7 (8)	2268.0 (6)	2006.1 (14)
Z	4	4	4	4
D_{calcd}, g cm^{-3}	1.362	1.431	1.284	1.336
M_r	380.8	695.3	438.4	403.4
cryst dimens, mm	0.37 × 0.40 × 0.64	0.26 × 0.47 × 0.72	0.32 × 0.48 × 0.56	0.11 × 0.39 × 0.66
linear abs coeff, cm^{-1}	6.75	8.96	4.49	5.96
diffractometer	*b*	*b*	*b*	*b*
scan type	ω	ω	ω	$\omega/2\theta$
scan speed, deg/s	0.100	0.100	0.100	0.100
scan width, deg	1.80	1.80	1.40	1.20
radiation	*c*	*c*	*c*	*c*
2θ range, deg	6–50	6–48	6–48	6–48
reflcns measd	$\pm h,\pm k,l$	$\pm h,\pm k,l$	$\pm h,k,l$	$\pm h,\pm k,l$
no. of measd total data	3820	6320	3789	4113
no. of unique total data	2734	5047	3558	3200
criterion for observn	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
no. of measd obsd data	2396	3102	2047	1997
no. of unique obsd data	1711	2477	1922	1554
agreement between equiv obsd reflcns	0.026	0.038	0.028	0.032
no. of variables	208	298	262	263
overdetermination ratio	8.2	8.3	7.3	5.9
max shift/error on last cycle	0.1	0.1	0.02	0.3
R	0.046	0.052	0.039	0.052

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 carefully centered reflections chosen from diverse regions of reciprocal space. [b] Philips PW 1100. [c] Graphite-monochromated Mo Kα (λ = 0.7107 Å).

evolution was observed. The final suspension was stirred for 3 h and then refluxed for 30 min. [Na_2(acacen)] is a white solid largely insoluble in THF. The suspension was reacted with $VCl_3(THF)_3$ (30.0 g, 80.9 mmol) at room temperature for 30 min and refluxed for 1 h. The suspension changed from white to red during this time. The solid was collected on a pressure-equalized Schlenk filter, and the mother liquor was collected in a round-bottom flask below. Then the Schlenk filter was fitted with a condenser, and the mother liquor in the round-bottom flask was heated to boiling. After 3 days at reflux, NaCl was left on the frit. The system was then cooled to room temperature, and the round-bottom flask was removed. The resulting solution cooled to 0 °C gave as a red crystalline solid [(THF)V(acacen)(Cl)] (**1**) (yield ca. 82%). Anal. Calcd for $C_{16}H_{26}ClN_2O_3V$: C, 50.47; H, 6.88; N, 7.35. Found: C, 51.00; H, 6.64; N, 7.23. IR: ν(C=N) (Nujol), 1510 cm^{-1}. μ_{eff} = 2.80 μ_B at 298 K.

Method B. To a THF solution (100 mL) of $TiCl_3(THF)_3$ (3.80 g, 10.2 mmol), [VO(acacen)] (2.97 g, 10.2 mmol) was added under stirring as solid. All the solid dissolved in a few minutes producing a red-brown solution. The solution was refluxed for 1 h and then kept standing at room temperature overnight. Complex **1** crystallized and was filtered out. By addition of Et_2O (50 mL), the yield of **1** was increased up to ca. 65%. The complex was found to be the same as that obtained by method A. Anal. Calcd for $C_{16}H_{26}ClN_2O_3V$: C, 50.47; H, 6.88; N, 7.35. Found: C, 50.7; H, 6.42; N, 7.45.

Synthesis of [(Cl)(acacen)V–O–Ti(Cl)$_3$(THF)$_2$]·THF (3). $TiCl_3(THF)_3$ (3.50 g, 9.44 mmol) was reacted with a suspension of [VO(acacen)] (2.75 g, 9.61 mmol) in 50 mL of THF. The reaction mixture was stirred for a few minutes, producing a red-brown solution. The undissolved solid was filtered out. The resulting solution was immediately cooled to −30 °C and then to −70 °C. In a few hours **3** precipitated as a red crystalline solid (yield ca. 23%). Anal. Calcd for $C_{24}H_{42}Cl_4N_2O_6TiV$: C, 41.42; H, 6.09; N, 4.03. Found: C, 41.67; H, 6.05; N, 4.12. IR: ν(C=N) (Nujol), 1510 cm^{-1}; ν(M-O), 835 cm^{-1}. μ_{eff} = 1.85 μ_B at 295 K.

Synthesis of [(py)V(acacen)(Cl)] (5). Pyridine (py) (0.25 mL, 3.13 mmol) was added to a THF solution (50 mL) of **1** (1.03 g, 2.7 mmol). A golden crystalline solid formed in a few minutes (yield ca. 70%). Anal. Calcd for $C_{17}H_{23}ClN_3O_2V$: C, 52.65; H, 5.98; N, 10.84. Found: C, 52.26; H, 6.09; N, 10.40. IR: ν(C=N) (Nujol), 1490 cm^{-1}. μ_{eff} = 3.15 μ_B at 294 K.

Synthesis of [(THF)V(acacen)(OPh)] (6). Sodium phenoxide, PhONa·*n*THF (4.9 mmol), was added to a solution of **1** (1.74 g, 4.56 mmol) in THF (50 mL) with stirring. The reaction mixture, whose color changed from red-brown to red-orange, was stirred for 10 min at 50 °C. NaCl formed and was removed by filtration. The resulting solution, on standing overnight, crystallized **6** as a red solid. The yield of **6** was increased by cooling the mother liquor to −30 °C, bringing the yield to ca. 65%. Anal. Calcd for $C_{22}H_{31}N_2O_4V$: C, 60.69; H, 7.17; N, 6.43. Found: C, 56.26; H, 6.34; N, 6.65. IR: ν(C=N) (Nujol), 1505 cm^{-1}. μ_{eff} = 2.93 μ_B at 294 K.

Synthesis of [V(acacen)(SPh)]$_n$ (7). Sodium thiophenoxide, PhSNa·*n*THF (5.1 mmol), was added to a solution of **1** (2.0 g, 5.25 mmol) in THF (50 mL). The reaction mixture was stirred for 10 min at 60 °C. The suspension changed from red-brown to red, and NaCl formed. The NaCl was filtered out. The red solution was evaporated to 10 mL, and then Et_2O (40 mL) was added. A microcrystalline solid formed (yield ca. 75%), which was recrystallized from THF/Et_2O. Anal. Calcd for $C_{36}H_{46}N_4O_4S_2V_2$: C, 56.49; H, 6.06; N, 7.32. Found: C, 56.45; H, 6.42; N, 7.20. IR: ν(C=N) (Nujol), 1505 cm^{-1}; μ_{eff} = 2.72 μ_B at 293 K.

Synthesis of [(THF)V(acacen)(NCS)] (8). Dried NH_4SCN (0.22 g, 2.77 mmol) was added to a THF solution (50 mL) of **1** (1.12 g, 2.94 mmol). A sudden formation of an orange solid was observed. The reaction mixture was stirred at 50 °C for 30 min and then filtered while being boiled to remove NaCl. The filtered solution gave, on cooling at 0 °C, complex **8** as red crystals (yield ca. 85%). Anal. Calcd for $C_{17}H_{26}N_3O_3SV$: C, 50.57; H, 6.49; N, 10.41. Found: C, 50.56; H, 6.49; N, 10.18. IR: ν(C=N) (Nujol), 1505 cm^{-1}; ν(C≡N), 2070 (s) cm^{-1}. μ_{eff} = 2.97 μ_B at 294 K.

X-ray Crystallography

The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Data were collected at room temperature on a single-crystal four-circled diffractometer. Crystal data and details of the parameters associated with data collection are given in Table I. The reduced cells quoted were obtained with use of TRACER.[10] For intensities and background the "three-point" technique was used. The structure

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Table II. Fractional Atomic Coordinates ($\times 10^4$) for Complex **1**

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
V	2612 (1)	−165 (1)	4582 (1)	C(7)	4151 (3)	−253 (5)	7083 (7)
Cl	3394 (1)	157 (1)	2252 (2)	C(8)	4175 (4)	1519 (5)	8256 (8)
O(1)	1766 (2)	−916 (3)	3309 (5)	C(9)	3504 (4)	1204 (4)	6902 (7)
O(2)	1979 (3)	950 (3)	4464 (6)	C(10)	2861 (4)	1833 (4)	6350 (8)
N(1)	3342 (2)	−1276 (3)	5179 (5)	C(11)	2146 (4)	1692 (4)	5232 (8)
N(2)	3512 (3)	390 (3)	6334 (5)	C(12)	1492 (5)	2407 (4)	4842 (9)
C(1)	900 (4)	−2156 (4)	2399 (9)	O(3)	1814 (2)	−472 (4)	6622 (5)
C(2)	1721 (3)	−1773 (4)	3275 (7)	C(13)	2002 (4)	−380 (5)	8373 (8)
C(3)	2343 (4)	−2342 (4)	3915 (7)	C(14)	1186 (7)	−449 (8)	9099 (11)
C(4)	3153 (3)	−2095 (4)	4743 (7)	C(15)	540 (5)	−431 (9)	7842 (12)
C(5)	3786 (4)	−2846 (4)	5062 (9)	C(16)	885 (4)	−446 (8)	6305 (9)
C(6)	4209 (3)	−1037 (4)	5931 (8)				

Table III. Fractional Atomic Coordinates ($\times 10^4$) for Complex **3**

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
V(1)	−1377 (1)	2791 (1)	3070 (1)	C(9)	−1405 (4)	5230 (6)	2853 (6)
Ti(1)	403 (1)	2633 (1)	2594 (1)	C(10)	−1776 (4)	5114 (6)	1874 (6)
Cl(1)	−2473 (1)	2912 (2)	3636 (2)	C(11)	−1885 (4)	4193 (6)	1357 (6)
Cl(2)	363 (1)	780 (2)	2368 (2)	C(12)	−2230 (5)	4135 (7)	305 (7)
Cl(3)	738 (1)	2483 (2)	4334 (2)	O(4)	1500 (3)	2461 (5)	2226 (4)
Cl(4)	628 (1)	4492 (2)	2572 (2)	C(13)	1955 (5)	1672 (10)	2668 (9)
O(1)	−1368 (3)	1304 (4)	3103 (4)	C(14)	2617 (6)	1879 (12)	2297 (11)
O(2)	−1662 (3)	3269 (4)	1741 (4)	C(15)	2542 (6)	2791 (14)	1553 (9)
O(3)	−431 (3)	2785 (4)	2705 (4)	C(16)	1891 (6)	3254 (11)	1714 (11)
N(1)	−1015 (3)	2686 (5)	4647 (4)	O(5)	317 (3)	2728 (5)	935 (4)
N(2)	−1215 (3)	4428 (5)	3430 (5)	C(17)	−118 (6)	3454 (8)	367 (7)
C(1)	−1202 (5)	−546 (6)	3285 (8)	C(18)	−38 (9)	3256 (11)	−728 (9)
C(2)	−1159 (4)	544 (6)	3742 (7)	C(19)	395 (8)	2336 (11)	−818 (8)
C(3)	−915 (4)	767 (6)	4717 (7)	C(20)	559 (7)	1969 (9)	190 (8)
C(4)	−860 (4)	1820 (6)	5160 (6)	O(1S)	7957 (7)	816 (10)	−1064 (7)
C(5)	−607 (4)	1861 (7)	6291 (7)	C(1S)	7474 (6)	722 (13)	−303 (11)
C(6)	−956 (5)	3733 (6)	5154 (7)	C(2S)	7839 (6)	783 (9)	708 (9)
C(7)	−777 (4)	4568 (6)	4378 (6)	C(3S)	8582 (7)	659 (12)	490 (10)
C(8)	−1203 (5)	6357 (6)	3157 (7)	C(4S)	8614 (7)	970 (13)	−602 (13)

Table IV. Fractional Atomic Coordinates ($\times 10^4$) for Complex **6**

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
V	5080 (1)	2482 (0)	296 (1)	C(11)	5913 (4)	1085 (3)	1371 (6)
O(1)	4549 (2)	3094 (2)	1699 (3)	C(12)	6282 (5)	615 (3)	2731 (7)
O(2)	5429 (3)	1650 (2)	1629 (4)	O(3)	3495 (2)	2058 (2)	−249 (4)
N(1)	4616 (3)	3226 (2)	−1323 (4)	C(13)	2559 (3)	2486 (3)	−611 (6)
N(2)	5298 (3)	1882 (2)	−1427 (4)	C(14)	1735 (4)	2008 (4)	−320 (7)
C(1)	4017 (4)	4087 (3)	2863 (6)	C(15)	2068 (5)	1273 (4)	−672 (7)
C(2)	4269 (4)	3752 (3)	1521 (6)	C(16)	3216 (4)	1326 (3)	−589 (7)
C(3)	4161 (4)	4130 (3)	219 (6)	O(4)	6439 (2)	2834 (2)	824 (3)
C(4)	4318 (4)	3877 (3)	−1144 (5)	C(21)	7053 (3)	3146 (3)	52 (5)
C(5)	4119 (5)	4397 (3)	−2418 (6)	C(22)	7642 (4)	2738 (3)	−699 (5)
C(6)	4815 (5)	2994 (3)	−2738 (6)	C(23)	8331 (4)	3068 (4)	−1415 (6)
C(7)	4852 (4)	2203 (3)	−2855 (6)	C(24)	8433 (4)	3800 (4)	−1397 (6)
C(8)	5898 (5)	876 (3)	−2715 (7)	C(25)	7830 (5)	4201 (3)	−662 (7)
C(9)	5745 (4)	1246 (3)	−1334 (6)	C(26)	7142 (4)	3884 (3)	48 (6)
C(10)	6099 (4)	890 (3)	32 (7)				

amplitudes were obtained after the Lorentz and polarization reduction,[11] and the absolute scale was established by the Wilson method.[12] The crystal quality was tested by ψ scans, showing that crystal absorption effects could be neglected for complexes **1**, **6**, and **8**, but, not for complex **3**, so the data for this last compound were corrected for absorption by a semiempirical method[13] with maximum and minimum absorption corrections of 1.10–1.00. The function minimized during the least-squares refinement was $\sum w|F|^2$. Unit weights were used since these gave acceptable agreement analyses; in addition, attempts to apply a weighting scheme made the results worse in all cases. Anomalous scattering corrections were included in all structure factor calculations. Scattering factors for neutral atoms were taken from ref 14 for V, Ti, Cl, S, O, N, and C and from ref 15 for H. Among the low-angle reflections, no corrections for secondary extinction were deemed necessary.

All the structures were solved by the heavy-atom method, starting from a three-dimensional Patterson map. They were refined first isotropically, then anisotropically for non-H atoms, by full-matrix least-squares techniques. Solutions and refinements were based on the observed reflections. Refinements were continued until no parameter shifted by more than 0.3 times its standard deviation. All the hydrogen atoms were located in difference maps except those associated with the THF molecule in complex **8**. This molecule was found to be disordered over two positions, sharing the oxygen atoms. Disorder was solved in terms of "partial" carbon atoms, which were refined anisotropically; at the end of the refinement the site occupation factors were 0.51 for C(13), C(14), C(15), and C(16), and 0.49 for the corresponding primed atoms. The H atoms associated with these atoms were ignored. For each structure the hydrogen atoms were introduced in the refinement as fixed contributors with isotropic U's fixed at 0.08 Å^2 for **1**, 0.10 Å^2 for **3** and **6**, and 0.12 Å^2 for **8**. The final difference maps showed no unusual

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(11) Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using the SHELX-76 system of crystallographic computer programs: Sheldrick, G. University of Cambridge, 1976.

(12) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151–152.

(13) *International Tables* For *X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) p 99; (b) p 149.

(14) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Chem.* **1968**, *A24*, 351–359.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Table V. Fractional Atomic Coordinates ($\times 10^4$) for Complex **8**[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	atom	*x*/*a*	*y*/*b*	*z*/*c*
V	1636 (1)	1869 (1)	1357 (1)	C8	2478 (8)	4723 (7)	−555 (8)
S	5271 (2)	1401 (2)	2405 (3)	C9	2328 (6)	3572 (6)	−188 (6)
C	4015 (8)	1606 (6)	2059 (6)	C10	2650 (7)	2740 (7)	−876 (6)
N	3200 (5)	1738 (5)	1828 (5)	C11	2406 (6)	1690 (7)	−790 (6)
O(1)	1272 (4)	603 (4)	2158 (4)	C12	2703 (8)	891 (8)	−1647 (7)
O(2)	1887 (4)	1277 (4)	−24 (4)	O3	16 (4)	1958 (5)	817 (4)
N(1)	1222 (4)	2789 (4)	2630 (5)	C13	−926 (13)	1632 (23)	1337 (15)
N(2)	1917 (4)	3371 (4)	734 (5)	C14	−1866 (22)	1917 (46)	633 (24)
C(1)	365 (7)	−601 (6)	3259 (8)	C15	−1411 (23)	2321 (41)	−300 (32)
C(2)	700 (6)	530 (6)	2996 (6)	C16	−281 (16)	2267 (27)	−283 (16)
C(3)	443 (7)	1373 (7)	3611 (7)	C13′	−448 (16)	1011 (15)	364 (24)
C(4)	746 (6)	2461 (7)	3480 (6)	C14′	−1401 (22)	1466 (30)	−234 (33)
C(5)	485 (7)	3221 (8)	4365 (6)	C15′	−1700 (30)	2477 (33)	232 (60)
C(6)	1605 (7)	3908 (6)	2554 (7)	C16′	−553 (15)	2899 (14)	625 (24)
C(7)	1552 (8)	4251 (6)	1420 (8)				

[a] The site occupation factors for disordered carbon atoms are 0.51 for C(13), C(14), C(15), and C(16) and 0.49 for the corresponding primed atoms.

feature, with no peaks above the general background.

It is to be noted that complex **1** crystallizes in three different crystalline modifications, all of them belonging to the monoclinic system but having different symmetries. Crystal data for the other two forms containing the same geometry of the complex are as follows: space group $P2_1$, $a = 9.164$ (3) Å, $b = 12.226$ (4) Å, $c = 8.430$ (3) Å, $\beta = 91.59$ (4)°, $V = 944.1$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.340$ g cm^{-3}; space group $P2_1/c$, $a = 8.835$ (4) Å, $b = 16.234$ (9) Å, $c = 26.493$ (10) Å, $\beta = 94.95$ (4)°, $V = 3786$ (3) Å^3, $Z = 8$, $D_{\text{calcd}} = 1.336$ g cm^{-3}.

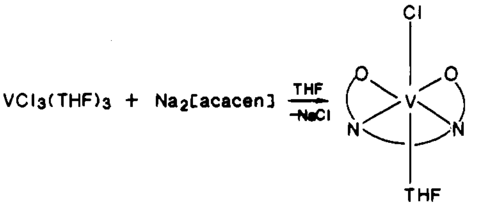
The structural parameters of these two forms will be published elsewhere.[16] Here we report the best refined structure.

Final atomic coordinates are listed in Tables II–V and SI–SIV, and thermal parameters are given in Tables SV–SVII.[17]

Results and Discussion

The two syntheses of complex **1** follow synthetic methods we recently devised for other Schiff base complexes.[18]

In the first, a THF suspension of Na_2[acacen] was reacted with $VCl_3(THF)_3$:



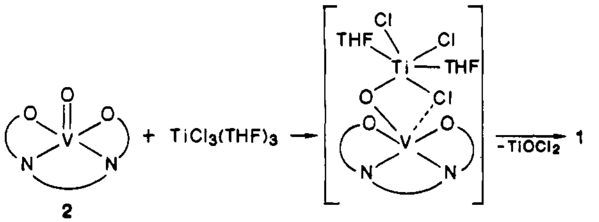
1 (1)

Following the procedure reported in the Experimental Section, **1** was isolated as a red crystalline solid in high yield (82%). Related syntheses, using the sodium salt of the Schiff base ligand, have been applied to a few other vanadium(III) complexes.[19] The second synthetic method we used, while very interesting in its implications for other vanadium–Schiff base derivatives, is a less attractive pathway to **1** because of the difficult synthesis of complex **2**[20] (see Experimental Section). Reductive deoxygenation of [VO(acacen)] (**2**) by $TiCl_3(THF)_3$ afforded **1**, when the reaction was carried out in refluxing THF:

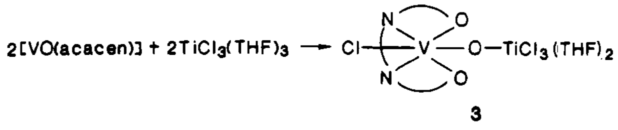
$$\underset{\mathbf{2}}{[\mathrm{VO(acacen)}]} + \mathrm{TiCl_3(THF)_3} \xrightarrow[-\mathrm{TiOCl_2}]{} \mathbf{1} \qquad (2)$$

Very good yields of **1** (65%) were observed for reaction 2. Reactions 1 and 2 were found to produce the same complex **1**, which is paramagnetic with two electrons, being a d^2 configuration in an octahedral field. Complex **1** is rather soluble in organic solvents, as expected for M–acacen derivatives, and very air-sensitive. Its structure in the solid state was determined by an X-ray analysis, which will be discussed along with that of related compounds.

The synthetic method reported in reaction 2 deserves some comment. On the basis of the stoichiometry of the reaction, complex **1** and $TiOCl_2$ form in a 1:1 molar ratio; since the crystalline product does not contain $TiOCl_2$, it remains in solution. The properties of this oligomeric oxochlorotitanium derivative are not very well-known, but for a few derivatives. Its solubility seems good in organic solvents.[21] Carrying out reaction 2 at low temperature, we expected to identify some intermediates of the reductive deoxygenation, like that involving the preliminary interaction between $TiCl_3(THF)_3$ and the vanadyl oxygen, i.e. an adduct like A. In some similar cases, the oxygen of a vanadyl unit interacted with a metal cation in the early stage, preceding an electron-transfer process.[22] When reaction 2 was started and maintained at room temperature for a few minutes and then cooled to −30 °C and later to −70 °C, complex **3** was isolated (yield ca. 23%). The stoichiometry of **3** in reaction 4 implies the concomitant formation of **4**, which has never been identified. Complex **3**, which contains vanadium(IV) and titanium(IV) is not a direct intermediate to **1**, unless it is allowed to react with **4** at high temperature. On the basis of the isolation of **3** in significant yields,



2 **A** (3)



3

(acacen)V—O—$TiCl_2(THF)_n$ (4)

4

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(16) Chiesi-Villa, A.; Guastini, C., submitted for publication in *Acta Crystallogr.*

(17) See paragraph at the end of the paper regarding supplementary material.

(18) Gambarotta, S.; Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.*, in press.

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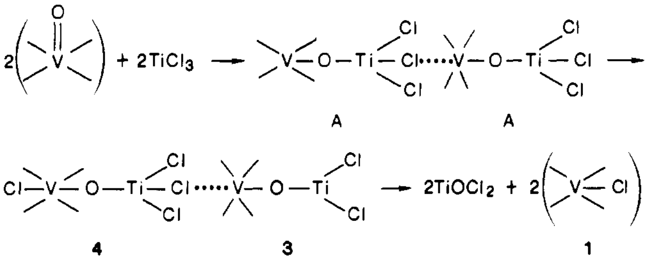
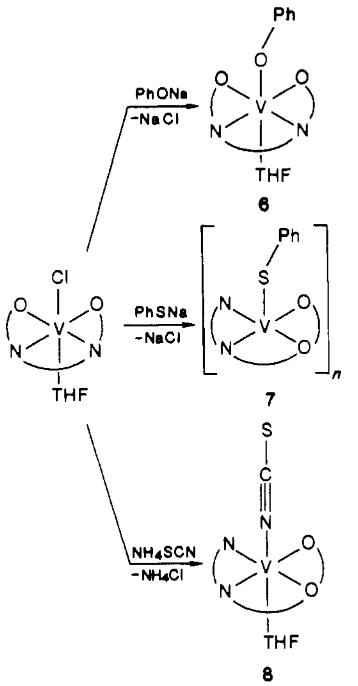
we can suggest that a plausible pathway of the reductive deoxygenation of **2** is that reported in eq 5, where acacen ligand around vanadium and the THF around titanium have been omitted for clarity. The intramolecular reductive deoxygenation depicted in reaction 3 seems much less likely, because of the isolation of **3** in a significant yield at low temperature. Complex **3**, which is a paramagnetic species with one unpaired electron, has some interesting structural features, which will be discussed later.



(5)

Complex **1**, which has a labile ligand (THF) in the coordination sphere can serve as interesting model compound for acceptor molecules, like molecular oxygen.[6] Exchange of THF by pyridine in complex **1** showed the lability of the axial ligand, and [(py)-V(acacen)(Cl)] (**5**) was isolated. Substitution of chloride by other monoanionic ligands results in a change in the redox potential of the metal. To this purpose, the Cl^- ligand was exchanged with O, N, and sulfur donor ligands, as reported in eq 6. THF solutions of **1** have been reacted with PhONa, PhSNa, and NH_4SCN to form complexes **6**–**8** respectively, which have been isolated in crystalline form. All these compounds are fairly soluble in organic solvents and are very air-sensitive. They have a paramagnetism very close to the spin-only value expected for two unpaired electrons. While the structures of **6** and **8** have been determined by an X-ray analysis, we do not have any information on the molecular complexity of **7**, which can be either monomeric or dimeric, as was observed for a formally five-coordinate vanadium(III) in $[V(acacen)(CH_2Ph)]_2$.[7]



(6)

Structures of Complexes 1, 3, 6, and 8. Selected bond distances and angles for complexes **1**, **3**, **6**, and **8** are listed in Tables VI and VII. Structural parameters concerning the conformations of the [V(acacen)] units are compared in Table VIII.

Table VI. Selected Bond Distances (Å) and Angles (deg) for Complexes **1** (X = Cl), **3** (X = Cl(1)), **6** (X = O(4)), and **8** (X = N)

	1	**3**	**6**	**8**
V–O(1)	1.954 (4)	1.864 (5)	1.987 (3)	1.939 (5)
V–O(2)	1.943 (5)	1.875 (5)	1.986 (4)	1.926 (5)
V–N(1)	2.054 (4)	2.126 (5)	2.048 (4)	2.053 (6)
V–N(2)	2.070 (4)	2.124 (6)	2.036 (4)	2.069 (5)
V–O(3)	2.174 (4)	1.973 (6)	2.201 (3)	2.160 (5)
V–X	2.352 (2)	2.352 (3)	1.881 (3)	2.071 (7)
O(1)–C(2)	1.290 (8)	1.31 (1)	1.291 (7)	1.30 (1)
O(2)–C(11)	1.288 (8)	1.33 (1)	1.292 (7)	1.29 (1)
N(1)–C(4)	1.306 (7)	1.30 (1)	1.308 (7)	1.31 (1)
N(1)–C(6)	1.476 (6)	1.47 (1)	1.469 (7)	1.48 (1)
N(2)–C(7)	1.477 (8)	1.48 (1)	1.460 (6)	1.48 (1)
N(2)–C(9)	1.305 (7)	1.30 (1)	1.329 (7)	1.31 (1)
C(1)–C(2)	1.518 (8)	1.49 (1)	1.504 (8)	1.52 (1)
C(2)–C(3)	1.359 (8)	1.35 (1)	1.386 (8)	1.35 (1)
C(3)–C(4)	1.424 (8)	1.44 (1)	1.416 (8)	1.42 (1)
C(4)–C(5)	1.506 (8)	1.52 (1)	1.515 (8)	1.51 (1)
C(6)–C(7)	1.501 (9)	1.51 (1)	1.492 (8)	1.49 (1)
C(8)–C(9)	1.514 (8)	1.52 (1)	1.517 (9)	1.52 (1)
C(9)–C(10)	1.420 (9)	1.44 (1)	1.422 (8)	1.42 (1)
C(10)–C(11)	1.383 (9)	1.35 (1)	1.376 (9)	1.35 (1)
C(11)–C(12)	1.500 (9)	1.49 (1)	1.532 (8)	1.53 (1)
N–C				1.08 (1)
C–S				1.67 (1)
O(1)–(V)–O(2)	98.9 (2)	110.0 (2)	96.4 (1)	101.8 (2)
O(1)–(V)–N(1)	89.3 (2)	85.1 (2)	89.9 (1)	88.9 (2)
N(1)–(V)–N(2)	80.8 (2)	79.1 (3)	82.5 (2)	80.7 (2)
N(2)–(V)–O(2)	89.9 (2)	85.8 (2)	90.2 (2)	88.4 (2)
N(1)–(V)–O(2)	169.0 (2)	164.9 (2)	171.0 (2)	166.7 (2)
N(2)–(V)–O(1)	166.6 (2)	163.6 (3)	167.1 (2)	169.6 (2)
V–O(1)–C(2)	128.4 (3)	137.9 (5)	127.2 (3)	128.7 (5)
V–O(2)–C(11)	130.0 (4)	134.4 (5)	125.9 (3)	128.5 (5)
V–N(1)–C(4)	126.6 (3)	126.7 (5)	126.4 (3)	126.7 (5)
V–N(1)–C(6)	111.5 (3)	112.7 (4)	112.0 (3)	112.7 (5)
C(4)–N(1)–C(6)	121.1 (4)	120.5 (6)	120.9 (4)	120.4 (7)
V–N(2)–C(7)	113.9 (4)	111.9 (5)	113.0 (3)	113.1 (5)
V–N(2)–C(9)	125.9 (4)	126.0 (5)	126.0 (3)	125.9 (5)
C(7)–N(2)–C(9)	119.9 (5)	121.8 (6)	121.0 (4)	120.9 (6)
V–O(3)–C(13)	129.3 (3)		125.2 (3)	129.9 (8)
V–O(3)–C(16)	119.2 (4)		125.6 (3)	122.1 (9)
V–N–C				175.7 (7)
S–C–N				179.6 (8)
Ti–O(3)–V		169.1 (3)		
V–O(4)–C(21)			132.7 (3)	

Table VII. Selected Bond Distances (Å) and Angles (deg) in the Titanium Coordination Sphere of **3**

Ti–C(12)	2.341 (3)	Ti–O(3)	1.691 (6)
Ti–C(13)	2.315 (3)	Ti–O(4)	2.279 (6)
Ti–C(14)	2.373 (3)	Ti–O(5)	2.142 (5)
O(3)–Ti–O(5)	93.1 (3)	O(5)–Ti–C(13)	167.7 (2)
O(3)–Ti–C(13)	99.2 (2)	Ti–O(4)–C(13)	125.2 (6)
O(4)–Ti–O(5)	79.7 (2)	Ti–O(4)–C(16)	125.5 (6)
O(4)–Ti–C(13)	88.0 (2)	Ti–O(5)–C(17)	124.0 (5)
O(3)–Ti–O(4)	172.8 (2)	Ti–O(5)–C(20)	127.9 (6)

The structures of complexes **1**, **6**, and **8** consist of discrete molecules of formula [(THF)V(acacen)(X)] [X = Cl, OPh, and NCS for **1**, **3**, and **8**, respectively] containing the same [(THF)V(acacen)] unit (Figure 1, 3, and 4). The coordination polyhedron can be described as a square bipyramid whose equatorial plane is formed by the two oxygen and two nitrogen atoms of the tetradentate ligand. An oxygen atom from a THF molecule occupies an apex of the bipyramid, the other apex being occupied by a chlorine atom (complex **1**), an oxygen atom O(4) from phenoxide (complex **6**), or a nitrogen atom from isocyanate complex (complex **8**). The vanadium atom is displaced out of the plane of the four coordinating atoms by 0.143 (1), 0.151 (1), and 0.082 (2) Å for **1**, **6**, and **8**, respectively, toward the X ligand. The N_2O_2 core is not exactly planar, showing small but significant tetrahedral distortions which fall in the ranges −0.029 (4) to 0.033 (5), −0.046 (4) to 0.050 (4), and −0.056 (5) to 0.056 (5) for **1**, **6**, and **8** respectively (Table SXI). The V–O(3) and V–X bonds are nearly perpendicular to that plane, the dihedral angles they form with it being 85.7 (1) and 88.8 (1)° for **1** (X = Cl), 88.9

Table VIII. Comparison of Structural Parameters within the V(acacen) Unit

	1	3	6	8
folding[a] along the N(1)···O(1) line, deg	5.5 (2)	4.4 (3)	10.2 (2)	11.6 (2)
folding along the N(2)···O(2) line, deg	1.2 (2)	12.7 (3)	12.8 (2)	15.1 (2)
angle between V–N(1)–O(1) and V–N(2)–O(2) planes, deg	168.5 (2)	175.7 (3)	167.8 (2)	172.2 (2)
N(1)–C(6)–C(7)–N(2) torsion angle, deg	−39.4 (6)	46.5 (8)	−34.5 (6)	−41.8 (9)
dist of C(6) and C(7) from the V–N(1)–N(2) plane, Å	−0.485 (6), 0.033 (5)	0.208 (10), −0.402 (8)	−0.190 (6), 0.257 (6)	−0.370 (9), 0.187 (9)

[a] The folding is defined as the dihedral angle between the VNO and OC_3N planes of a six-membered chelation ring.

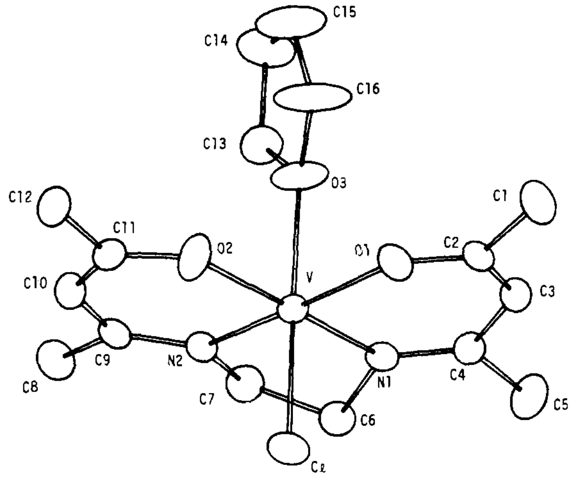


Figure 1. ORTEP drawing for complex **1** (30% probability ellipsoids).

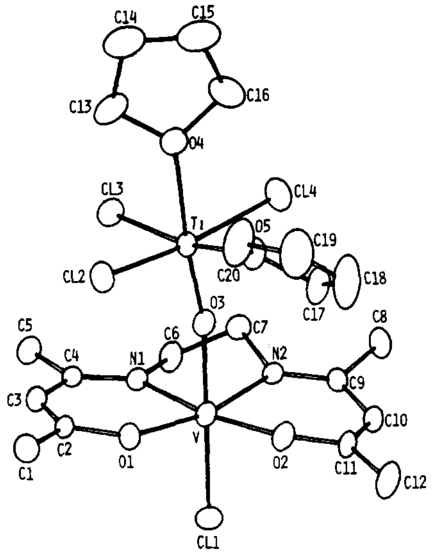


Figure 2. ORTEP drawing for complex **3** (30% probability ellipsoids).

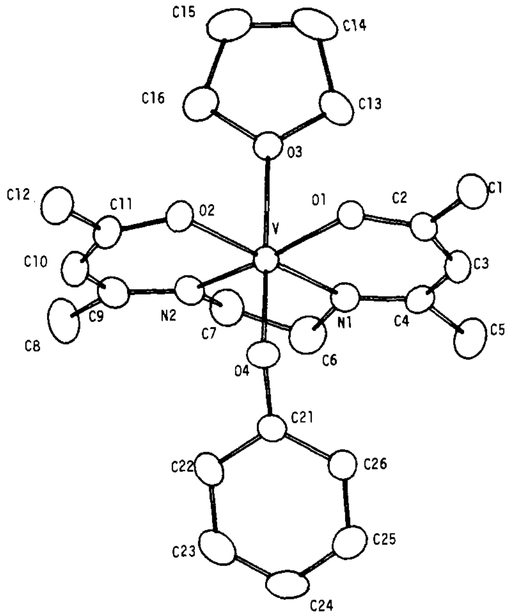


Figure 3. ORTEP drawing for complex **6** (30% probability ellipsoids).

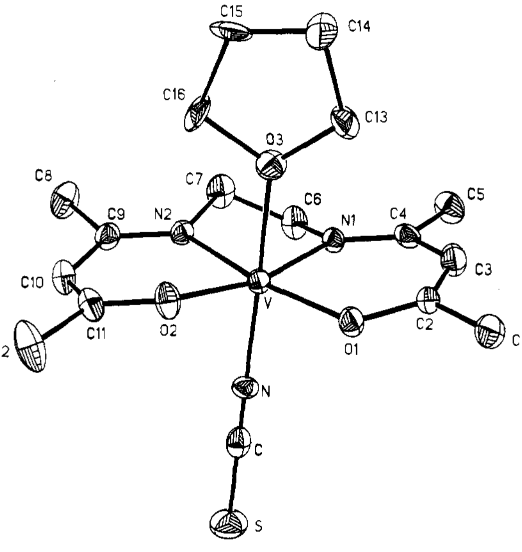


Figure 4. ORTEP drawing for complex **8** (30% probability ellipsoids).

(1) and 89.1 (1)° for **6** [X = O(4)], and 88.3 (1) and 89.1 (1)° for **8** (X = N). Bond distances and angles within the [(THF)-V(acacen)] units are practically the same for complexes **1** and **8** and are in good agreement with those observed, for example, in [VO(acacen)].[23] A small but significant lengthening of all the V–O distances is observed in complex **6** (Table VI). This could be a consequence of intraligand steric hindrance due to the short V–O(4) distance with respect to the V–X distances in complexes **1** and **8**.

The data in Tables VIII and SIX indicate that no part of the molecules is strictly planar. The five-membered chelation rings are twisted in complexes **6** and **8**, while complex **1** assumes almost an envelope conformation, C(7) being only 0.033 (5) Å out of the plane running through V–N(1)–N(2). All the six-membered chelation rings are folded along the O··N line, albeit to different extents, and the two N_2O_2 cores exhibit a slight twisting.

The THF molecules show an envelope conformation in complexes **1** and **6** with the C(13) carbon atom out of the plane passing through the other four atoms [0.141 (8) and 0.476 (6) Å for **1** and **6**, respectively] (Table SXI).

The disorder of the THF molecule in complex **8** prevents any sound discussion on the structural parameters. The most interesting structural features are related to the V–X functionalities in complex **6** and **8**. The V–O bond distance in **6** [1.881 (3) Å], which is significantly shorter than that observed in **3** [1.973 (6) Å], and the bond angle V–O(4)–C(21) [132.7 (3)°] suggest the existence of a V–O multiple bond. The thiocyanate group has a linear arrangement in complex **8** [V–N–C, 175.7 (7)°; N–C–S,

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(23) Bruins, D.; Weaver, D. L. *Inorg. Chem.* **1970**, *9*, 130–135.

179.6 (8)°] with a very short N–C bond distance [1.08 (1) Å] vs. a much longer C–S distance [1.67 (1) Å]. This seems to suggest a significant contribution of the canonic form $V—N^+\equiv C—S^-$ for the [V(NCS)] functionality. The C–N stretching vibration at 2070 cm^{-1} is in the region expected for a linear M–NCS structure.[24]

The structure of complex **3** consists of binuclear species [V(Cl)(acacen)O{$TiCl_3(THF)_2$}] and THF crystallization molecules in the molar ratio 1:1. In the complex an oxygen atom bridges a [V(Cl)(acacen)] unit and a $TiCl_3(THF)_2$ molecule (Figure 2). As can be seen from the data in Table VI the [V(Cl)(acacen)] moiety shows a significant shortening of the V–O distance and a significant lengthening of the V–N distance. An enlargement of the O(1)–V–O(2) angle is also observed. The V–Cl distance is not significantly different from that of complex **1**, so it is not affected by the different nature of the trans ligand and the oxidation state of +4 for vanadium. The V–O bond distance is significantly longer [1.937 (6) Å] than observed in a few μ-oxo vanadium complexes: [$(THF)_3Cl_2V–O–VCl_2(THF)_3$] [1.769 (5) Å];[22c] [(Q)(O)V–O–V(O)(Q)] (Q = 8-quinolinato anion) [1.779 (2) Å];[25a] and [(Cl)(2Me-Q)V–O–V(2Me-Q)(Cl)] [1.799 (3) Å].[25b] The angle at the bridging oxygen atom [169.1 (3)°] indicates an sp hybridization state for this atom in agreement with the multiple character of the Ti–O(3) bond [1.691 (6) Å], which is much shorter than other Ti–O bonds belonging to almost linear Ti–O–Ti fragments, in [$(cp)TiCl_2]_2O$[26a] [1.777 (1) Å], [$cp_2Ti(H_2O)]_2O^{2+}$ [1.829 (2)Å],[26b] $(acac)_2Ti(Cl)]_2O$[26c] [1.79 (2)–1.81 (2) Å], $[Ti(acacen)(Cl)]_2O$[26d] [1.813 (1) Å], and $[Ti(N_4C_{12}H_{25})]_2O$[26e] [$N_4C_{12}H_{24}$ = 1,5,9,13-tetraazacyclohexadecane]. The rather high M–O stretching frequency we found in the IR spectrum at 835 cm^{-1} has to be assigned to Ti═O. Vanadium lies approximately in the plane of the N_2O_2 core, its displacement from it being 0.042 (2) Å toward chlorine. As observed in complexes **1**, **6**, and **8** no isolated portion of the [V(acacen)] unit is strictly planar. The five-membered chelation ring shows a twist conformation and the two six-membered chelation rings are folded with respect to the N···O line (Table VIII). The two V–O–N parts are almost coplanar, the dihedral angle between them being 175.7 (3)°. They are slightly twisted as shown by the small tetrahedral distortions of the N_2O_2 core [−0.034 (6) to 0.034 (6) Å]. The directions of the V–Cl and V–O(3) bonds form with equatorial plane angles of 87.8 (2) and 86.6 (2)°, respectively. Bond distances and angles in the acacen ligand are close to those observed in the other three complexes.

Coordination around titanium is pseudooctahedral; the best equatorial plane contains O(3), O(4), O(5), Cl(3), and Ti (Table SXI). The Ti–Cl(2) and Ti–Cl(4) bonds are tilted by 6.3 (1) and 5.9 (1)° with respect to the normal to that plane. The two Ti–O(THF) distances are significantly different, the longer one being that trans to the Ti–O(3) multiple bond (Table VII). The three Ti-Cl distances are significantly different from each other probably as a consequence of intraligand steric hindrance. Intramolecular contacts (Å) less than 3.5 Å are as follows: Cl(2)··C(13), 3.37 (1); Cl(2)··C(20), 3.22 (1); Cl(3)–C(13), 3.49 (1); Cl(4)··C(16), 3.21 (1); Cl(4)··C(17), 3.40 (1).

Bond distances and angles involving the THF molecules (Table SIX) are as expected. All of them show an envelope conformation (Table SXI).

In all complexes the intermolecular distances are consistent with van der Waals interactions.

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Registry No. **1**, 99324-33-1; **2**, 19195-97-2; **3**, 103711-96-2; **5**, 103711-97-3; **6**, 103711-98-4; **7**, 103711-99-5; **8**, 103712-00-1; $VO(acac)_2$, 3153-26-2; $TiCl_3(THF)_3$, 18039-90-2; $VCl_3(THF)_3$, 19559-06-9.

Supplementary Material Available: Listings of unrefined hydrogen coordinates (Tables SI–SIV), thermal parameters (Tables SV–SVIII), nonessential bond distances and angles (Table SIX), torsion angles (Table SX), and least-squares planes (Table SXI) (15 pages); listings of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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