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Vanadium(III)–Carbon and Titanium(III)–Carbon Functionalities Supported by a Tetradentate Schiff Base Ligand

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Alkylation of the titanium(III)– and vanadium(III)–Schiff base complexes [(THF)M(acacen)(Cl)] [M = Ti (**1**), V (**2**); acacen = *N,N'*-ethylenebis(acetylacetone iminato) dianion] by using Grignard reagents led to the corresponding organometallic derivatives [M(acacen)R] [M = Ti, R = CH₂Ph (**3**), Ph (**4**), Mes (**5**); M = V, R = Me (**6**), CH₂Ph (**7**), Ph (**8**), Mes (**9**)]. The alkylation occurred exclusively at the metal, and the simultaneous loss of the axial solvent was observed. The organometallic derivatives **3–9** occur either in the monomeric form, complexes **4**, **5**, **8**, and **9**, or in the dimeric form, complexes **3**, **6**, and **7**, as suggested by the X-ray analysis and the magnetic moment. Dimerization is achieved by a sharing of an oxygen of the Schiff base between two [M(acacen)] moieties. Complexes **3–9** are quite soluble in organic solvents and relatively thermally stable compared to the corresponding cyclopentadienyl derivatives. The solid-state structure determination revealed a significant intramolecular hydrogen bonding between the alkyl or aryl groups and the oxygens from the Schiff base ligand. M–C bond lengths (Å) [Ti–C = 2.216 (20), **5**; V–C = 2.156 (9), **7**; V–C = 2.064 (5), **8**] are in agreement with the presence of a σ bond. Crystallographic details for X-ray structures of **5**, **7**, and **8** are as follows. Complex **5**: space group $P2_1/n, a$ = 11.295 (2) Å, b = 12.561 (2) Å, c = 15.377 (2) Å, β = 104.72 (1)°, V = 2110.0 (6) Å³, Z = 4, D_{calcd} = 1.226 g cm⁻³. The final R factor was 0.105 for 1146 independent reflections. Complex **7**: space group $P2_1/c$, a = 11.856 (3) Å, b = 18.016 (5) Å, c = 8.775 (3) Å, β = 95.54 (2)°, V = 1865.6 (9) Å³, Z = 2, D_{calcd} = 1.297 g cm⁻³. The final R factor was 0.053 for 1248 independent reflections. Complex **8**: space group $P2_1/c$, a = 7.886 (2) Å, b = 15.180 (4) Å, c = 15.150 (4) Å, β = 104.45 (1)°, V = 1756.2 (8) Å³, Z = 4, D_{calcd} = 1.325 g $P2_1/c$, The final R factor was 0.068 for 2700 independent reflections.

Introduction

Although the vanadium–carbon and titanium–carbon bond functionalities are among the most reactive and attractive for their use in metal-induced stoichiometric[1,2a,b] and catalytic[1b,2a] transformations, their appearance is observed in cyclopentadienyl derivatives almost exclusively. Cyclopentadienyls, which are electronically flexible ligands, do not allow a significant steric control on the incoming substrate.

The geometry of their metal complexes is almost uniquely tetrahedral. Some of the most recent organometallic chemistry had turned the attention to the use of oxygen donor ligands for early transition metals.[3] Knowing how much ancillary ligands can affect through steric and electronic effects the chemistry of reactive functionalities, we turned our attention to a completely different chemical environment for V–C and Ti–C functionalities by using a tetradentate Schiff base ligand derived from acylacetone. Such an environment has a very well-known precedent in the organometallic chemistry of cobalt[4] and very few other metals.

We report here details on the synthesis and structural characterization of [M(acacen)R] [M = Ti, V; acacen = *N,N'*-ethylenebis(acetylacetone iminato) dianion] complexes, containing a Ti(III)–C and a V(III)–C functionality. This is a rather unusual class of organic derivatives of early transition metals. A single example of such a class, [PhCH₂V(acacen)]₂, has been communicated.[5]

Experimental Section

All reactions were carried out under inert atmosphere. Solvents were dried and purified by standard techniques. Infrared spectra were recorded on a Perkin-Elmer 883 spectrometer. Magnetic measurements were performed by using a Faraday balance. The syntheses of [(THF)V(acacen)(Cl)][6] and [(THF)Ti(acacen)(Cl)][7] were performed by published procedures.

Synthesis of [Ti(acacen)(PhCH₂)] (3). A THF solution of PhCH₂MgCl (3.21 mmol) was added to a THF solution (200 mL) of **1** (1.21 g, 3.20 mmol), cooled at –25 °C. The solution color changed suddenly from blue to turquoise. The solution was kept cooled on stirring for 1 h; then dioxane (3 mL) was added. The solid (magnesium salts) was removed by filtration of the cooled solution. The solution was partially evaporated; then cold toluene (200 mL) was added. Some undissolved solid was removed by filtration, and the resulting solution was concentrated to 20 mL; then *n*-hexane (30 mL) was added. The resulting

turquoise solution, cooled at –20 °C, gave a microcrystalline deep blue solid (71.6%). Anal. Calcd for C₁₉H₂₅N₂O₂Ti: C, 63.16; H, 6.93; N, 7.76. Found: C, 62.70; H, 6.47; N, 7.65. μ_{eff} = 1.81 μ_B at 290 K.

Synthesis of [Ti(acacen)(Ph)] (4). A THF solution of PhMgBr (9.85 mmol) was added to a THF solution (250 mL) of **1** (3.85 g, 9.84 mmol), cooled at –25 °C. Then the solution was warmed to 20 °C and stirred for 1 h. Addition of dioxane (6.0 mL) and cooling to –20 °C caused the precipitation of magnesium halides, which were removed by filtration. The resulting solution was evaporated to dryness and the solid dissolved in toluene (100 mL). By addition of *n*-hexane (30 mL) and cooling to –20 °C, the solution gave on standing for 4 h a microcrystalline blue solid (84.6%). Anal. Calcd for C₁₈H₂₃N₂O₂Ti: C, 62.24; H, 6.63; N, 8.07. Found: C, 61.80; H, 6.45; N, 7.88. μ_{eff} = 1.35 μ_B at 290 K.

Synthesis of [Ti(acacen)(Mes)] (5). A THF solution of MesMgBr (35.90 mmol) was added to a cooled (–30 °C) solution of **1** (13.60 g, 35.90 mmol). The solution, stirred for 2 h and warmed to room temperature, became blue-turquoise. Addition of dioxane (7.0 mL) and cooling to –20 °C caused the precipitation of magnesium halides, which were removed by filtration. The resulting solution, evaporated to dryness, gave a solid soluble in toluene (100 mL). The addition of *n*-hexane (50 mL) allowed the crystallization of a blue solid (85.3%). Anal. Calcd for C₂₁H₂₉N₂O₂Ti: C, 64.73; H, 7.45; N, 7.19. Found: C, 64.19; H, 7.40; N, 7.06. μ_{eff} = 1.78 μ_B at 292 K.

(1) (a) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer: Berlin, 1986; *Top. Curr. Chem.* **1982,** *106*, 1. (b) Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983,** *22*, 31. Seebach, D.; Weidmann, B.; Widler, L. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Wiley: New York, 1983; Vol. 3. Connelly, N. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 3; Chapter 24.

(2) Bottrill, M.; Gavens, P. D.; Kelland, J. M.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 3: (a) Chapter 22.2; (b) Chapter 22.3 and 22.4; (c) Chapter 22.5.

(3) (a) Chamberlain, L. R.; Durfee, L. D.; Fau, P. E.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987,** *109*, 390, 6068 and references therein. Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987,** *109*, 4720. (b) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987,** *109*, 424 and references therein. Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989,** *28*, 66.

(4) Pratt, J. M.; Craig, P. J. *Adv. Organomet. Chem.* **1973,** *11*, 404.

(5) Gambarotta, S.; Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1985,** 829.

(6) Mazzanti, M.; Rosset, J. M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989,** 953.

(7) Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986,** *25*, 4158.

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Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes 7, 8, and 5

	7	8	5
cryst habit and color	thin brown plate	brown prism	e
formula	$C_{38}H_{50}N_4O_4V_2$	$C_{18}H_{23}N_2O_2V$	$C_{21}H_{29}N_2O_2Ti$
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
cell params at 295 K^a			
a, Å	11.856 (3)	7.886 (2)	11.295 (2)
b, Å	18.016 (5)	15.180 (4)	12.561 (2)
c, Å	8.775 (3)	15.150 (4)	15.377 (2)
α, deg	90	90	90
β, deg	95.54 (2)	104.45 (1)	104.72 (1)
γ, deg	90	90	90
V, Å^3	1865.6 (9)	1756.2 (8)	2110.0 (6)
Z	2	4	4
D_{calcd}, g cm^{-3}	1.297	1.325	1.226
mol wt	728.7	350.3	389.4
cryst dimens, mm	0.18 × 0.21 × 0.56	0.45 × 0.48 × 0.55	0.24 × 0.27 × 0.56
linear abs coeff, cm^{-1}	5.26	48.46	4.15
diffractometer	Philips PW 1100	Siemens AED	Philips PW 1100
diffraction geometry	equatorial	equatorial	equatorial
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan speed	0.100°/s	3–12°/min	0.050°/s
scan width, deg	1.20	b	1.20
radiation	c	d	c
2θ range, deg	6–46	6–140	6–47
reflcns measd	$\pm h,k,l$	$\pm h,k,l$	$\pm h,k,l$
no. of total data measd	3535	3937	3208
no. of unique total data	2596	3418	3208
criterion for obsn	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
no. of obsd data measd	1693	3110	1146
no. of unique obsd data	1248	2700	1146
agreement between equiv obsd reflcns	0.031	0.035	
no. of variables	217	208	235
overdetermination ratio	5.8	13.05	4.9
max Δ/σ on last cycle	0.3	0.1	0.1
$R = \sum|\Delta F|/\sum|F_o|$	0.053	0.068	0.105
$R_w = \sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|$	0.048	0.068	0.105
$GOF = [\sum w|\Delta F|^2/(NO - NV)]^{1/2}$	3.0		

^{a} Unit cell parameters were obtained by least-squares analysis of the setting angles of 25–30 carefully centered reflections chosen from diverse regions of reciprocal space. $^b(\theta - 0.5) - [\theta + (0.5 + \Delta h)]$; $\Delta\theta = [(\lambda\alpha_2 - \lambda\alpha_1)/\lambda]\tan\theta$. ^{c}Graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å). ^{d}Nickel-filtered Cu Kα ($\lambda = 1.5418$ Å). ^{e}Small brown fragment not well diffracting.

Synthesis of [V(acacen)(Me)] (6). A Et$_2$O solution of MeMgI (5.66 mmol) was added to a THF solution (50 mL) of 2 (2.16 g, 5.48 mmol) at room temperature. The solution turned from brown to red. Then dioxane (2 mL) was added to the solution. The magnesium salts precipitated have been removed by filtration. The solution was evaporated to dryness and the residue collected with toluene (70 mL). The undissolved solid (some magnesium salts left) was filtered out and the resulting solution cooled overnight at 5 °C gave a red microcrystalline solid (79.5%). Anal. Calcd for C$_{13}$H$_{21}$N$_2$O$_2$V: C, 54.17; H, 7.29; N, 9.72. Found: C, 54.51; H, 7.11; N, 9.42. μ_{eff} = 2.16 μ_B at 290 K.

Synthesis of [V(acacen)(CH$_2$Ph)]$_2$ (7). A THF solution of PhCH$_2$MgCl (3.94 mmol) was added slowly to a THF solution (70 mL) of 2 (2.15 g, 5.65 mmol). The solution color changed from brown to red. The addition of dioxane (2 mL) caused the precipitation of magnesium salts, which were removed by filtration. The solution was evaporated to dryness and the residue collected with toluene (30 mL). By addition of n-hexane (30 mL), 7 crystallized as a red solid (63%). Anal. Calcd for C$_{38}$H$_{50}$N$_4$O$_4$V$_2$: C, 62.63; H, 6.92; N, 7.69. Found: C, 61.95; H, 6.47; N, 7.75. MW by cryoscopy in benzene: calcd 364.0, found 349.0. μ_{eff} = 2.40 μ_B at 293 K.

Synthesis of [V(acacen)(Ph)] (8). A THF solution of PhMgBr (5.77 mmol) was added dropwise at room temperature to a THF solution (50 mL) of 1 (2.19 g, 5.76 mmol). The solution color changed from brown to red. The addition of dioxane (3 mL) caused the precipitation of magnesium salts, which were removed by filtration, and the resulting solution gave, upon addition of n-hexane (30 mL), a crystalline red solid (40%). Anal. Calcd for C$_{18}$H$_{23}$N$_2$O$_2$V: C, 61.71; H, 6.62; N, 8.00. Found: C, 59.80; H, 6.60; N, 7.80. μ_{eff} = 2.70 μ_B at 290 K.

Synthesis of [V(acacen)(Mes)] (9). A THF solution (35 mL) of 2 (18.90 g, 49.7 mmol) cooled at −25 °C was reacted with MesMgBr in THF (42.0 mL, 49.7 mmol). After solution was warmed to 20 °C and stirred for 2 h, the color became red. The magnesium salts, precipitated by addition of dioxane (7.0 mL) and cooling to −20 °C, were then removed by filtration. The solvent was completely evaporated and the residue dissolved in toluene (250 mL). The toluene was evaporated to

80 mL and n-hexane added (30 mL). A microcrystalline red solid formed (87.4%). Anal. Calcd for C$_{21}$H$_{29}$N$_2$O$_2$V: C, 64.29; H, 7.40; N, 7.14. Found: C, 64.62; H, 7.12; N, 7.28. μ_{eff} = 2.75 μ_B at 290 K.

X-ray Crystallography. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[8] Crystal data and details associated with data collection are given in Table I. Data were collected at room temperature (295 K) on a single-crystal diffractometer. For intensities and background the profile measurement technique[9] was used for 8 while the three-point technique was used for 5 and 7. The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[10] and the absolute scale was established by the Wilson method.[11] The crystal quality was tested by ψ scans, showing that crystal absorption effects could be neglected for complex 7. Data of complexes 5 and 8 were corrected for absorption by using a semiempirical method[12] for complex 5 and the program ABSORB[13] for complex 8. The function minimized during the least-squares refinement was $\sum w|\Delta F|^2$. A weighting scheme based on counting statistics[10] was applied for complex 7. Unit weights were used for complexes 5 and 8, since these gave a satisfactory analysis

(8) Lawton, S. L.; Jacobson, R. A. *TRACER, a cell reduction program.* Ames Laboratory, Iowa State University of Science and Technology: Ames, IA, 1965.

(9) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Cryst. Chem.* **1974**, *A30*, 580.

(10) Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using: Sheldrick, G. *SHELX-76. System of Crystallographic Computer Programs;* University of Cambridge: Cambridge, England, 1976.

(11) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151.

(12) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Cryst. Chem.* **1968**, *A24*, 351.

(13) Ugozzoli, F. *ABSORB, a program for F$_0$ absorption correction following Walker and Stuart* (Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158); University of Parma: Parma, Italy, 1985.

Table II. Fractional Atomic Coordinates (×10⁴) for Complex 7

atom	x/a	y/b	z/c
V	1185 (1)	240 (1)	1079 (2)
O1	835 (4)	−245 (4)	2982 (6)
O2	−284 (4)	703 (3)	329 (6)
N1	2688 (5)	−327 (4)	1176 (7)
N2	1763 (5)	655 (4)	−909 (7)
C1	897 (8)	−980 (6)	5206 (11)
C2	1428 (7)	−727 (5)	3825 (10)
C3	2480 (7)	−978 (5)	3509 (11)
C4	3105 (7)	−766 (6)	2275 (12)
C5	4300 (8)	−1062 (7)	2309 (12)
C6	3423 (6)	−90 (5)	−7 (10)
C7	2678 (7)	187 (6)	−1398 (10)
C8	1917 (9)	1503 (6)	−3061 (12)
C9	1383 (7)	1237 (5)	−1643 (10)
C10	463 (8)	1653 (5)	−1146 (11)
C11	−319 (7)	1390 (5)	−252 (11)
C12	−1292 (8)	1858 (5)	219 (11)
C21	3053 (8)	1381 (6)	2341 (12)
C22	3870 (10)	1032 (7)	3329 (13)
C23	5014 (12)	1148 (10)	3269 (18)
C24	5363 (11)	1665 (11)	2165 (25)
C25	4589 (12)	2008 (7)	1212 (18)
C26	3438 (8)	1867 (5)	1222 (13)
C27	1847 (7)	1191 (5)	2361 (10)

Table III. Fractional Atomic Coordinates (×10⁴) for Complex 8

atom	x/a	y/b	z/c
V	226 (1)	1165 (1)	2679 (1)
O1	1834 (4)	2116 (2)	2831 (2)
O2	−97 (4)	1087 (2)	1361 (2)
N1	119 (6)	1387 (3)	4003 (3)
N2	−2323 (6)	952 (3)	2533 (3)
C1	3896 (9)	3241 (4)	3366 (5)
C2	2671 (7)	2546 (3)	3558 (3)
C3	2440 (8)	2414 (4)	4409 (4)
C4	1150 (8)	1855 (3)	4636 (4)
C5	1067 (10)	1858 (4)	5624 (4)
C6	−1324 (8)	868 (4)	4185 (4)
C7	−2903 (8)	971 (4)	3389 (4)
C8	−5437 (7)	745 (5)	1749 (4)
C9	−3538 (7)	843 (3)	1746 (4)
C10	−3150 (7)	844 (4)	894 (3)
C11	−1522 (7)	977 (3)	735 (3)
C12	−1314 (9)	1019 (5)	−233 (3)
C21	1476 (6)	−26 (3)	3029 (3)
C22	976 (7)	−772 (3)	2488 (3)
C23	1891 (8)	−1562 (4)	2673 (4)
C24	3287 (9)	−1635 (4)	3415 (4)
C25	3813 (8)	−915 (4)	3967 (4)
C26	2930 (7)	−117 (4)	3776 (3)

of variance.[10] Anomalous scattering corrections were included in all structure factor calculations.[14b] Scattering factors for neutral atoms were taken from ref 14a for non-hydrogen atoms and from ref 15 for H. Among the low-angle reflections, no correction for secondary extinction was deemed necessary.

Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method, starting from a three-dimensional Patterson map. The structures were refined first isotropically, and then anisotropically for non-H atoms, by a full-matrix least-squares method. For 7 and 8 all the hydrogen atoms were located from difference Fourier maps while for 5 they were put in geometrically calculated positions. In all cases the hydrogen atoms were introduced into the subsequent refinements as fixed-atom contributions with isotropic U values fixed at 0.10 Å². For 5 the low percentage of observed reflections, due to the poor quality of the crystals available, prevented a better accuracy from being obtained (see Table I). The final difference maps showed no unusual feature, with no significant peak above the general background.

Final atomic coordinates are listed in Tables II–IV for non-H atoms and in Tables SI–SIII (supplementary material) for hydrogens. Thermal

(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol IV, (a) p 149.
(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table IV. Fractional Atomic Coordinates (×10⁴) for Complex 5

atom	x/a	y/b	z/c
Ti	2535 (3)	836 (3)	1096 (2)
O1	2358 (12)	597 (10)	2295 (9)
O2	1126 (11)	1710 (10)	595 (9)
N1	3504 (15)	−610 (12)	1307 (12)
N2	2133 (14)	152 (13)	−220 (11)
C1	2102 (24)	−40 (20)	3688 (14)
C2	2547 (21)	−157 (21)	2875 (17)
C3	3158 (22)	−1114 (18)	2724 (15)
C4	3661 (20)	−1270 (17)	1970 (19)
C5	4412 (25)	−2303 (19)	2046 (21)
C6	3987 (22)	−824 (22)	553 (15)
C7	3004 (21)	−720 (20)	−294 (14)
C8	972 (26)	−275 (22)	−1780 (16)
C9	1193 (19)	323 (17)	−911 (13)
C10	324 (17)	1133 (19)	−875 (14)
C11	287 (19)	1804 (21)	−149 (14)
C12	−657 (19)	2632 (21)	−230 (18)
C13	4104 (18)	1911 (14)	1137 (12)
C14	4109 (15)	2558 (15)	423 (13)
C15	5117 (20)	3255 (15)	506 (14)
C16	6124 (19)	3317 (16)	1225 (14)
C17	6121 (18)	2620 (17)	1909 (13)
C18	5167 (19)	1953 (16)	1908 (12)
C19	3123 (20)	2662 (17)	−417 (14)
C20	7199 (19)	4050 (20)	1266 (16)
C21	5184 (19)	1234 (18)	2693 (15)

Table V. Selected Bond Distances (Å) and Angles (deg) for Complexes 7 (M = V, X = C27), 8 (M = V, X = C21), and 5 (M = Ti, X = C13)

bond length	7	8	5
M–O1	1.960 (5)	1.897 (3)	1.928 (15)
M–O2	1.989 (4)	1.952 (3)	1.926 (12)
M–N1	2.047 (5)	2.056 (3)	2.103 (16)
M–N2	2.075 (7)	1.993 (5)	2.138 (17)
M–X	2.156 (9)	2.064 (5)	2.216 (20)
M–O2ᵃ	2.296 (5)		
O1–C2	1.304 (9)	1.308 (5)	1.281 (29)
O2–C11	1.334 (9)	1.288 (5)	1.292 (22)
N1–C4	1.305 (11)	1.302 (6)	1.291 (31)
N1–C6	1.476 (9)	1.465 (7)	1.427 (33)
N2–C7	1.485 (10)	1.479 (8)	1.496 (30)
N2–C9	1.284 (10)	1.341 (6)	1.315 (23)
C1–C2	1.486 (11)	1.507 (9)	1.469 (38)
C2–C3	1.382 (11)	1.361 (7)	1.434 (36)
C3–C4	1.422 (13)	1.431 (9)	1.428 (40)
C4–C5	1.516 (11)	1.515 (8)	1.538 (33)
C6–C7	1.520 (10)	1.510 (7)	1.487 (28)
C8–C9	1.526 (12)	1.506 (8)	1.498 (32)
C9–C10	1.433 (11)	1.399 (7)	1.425 (41)
C10–C11	1.360 (12)	1.380 (8)	1.408 (33)
C11–C12	1.521 (11)	1.516 (7)	1.472 (34)

bond angle	7	8	5
N2–M–X	91.0 (3)	106.9 (2)	104.3 (7)
N1–M–X	95.9 (3)	91.5 (2)	98.1 (7)
N1–M–N2	81.7 (2)	81.3 (2)	77.1 (7)
O2–M–X	95.9 (3)	98.1 (2)	103.8 (6)
O2–M–N2	85.4 (2)	90.3 (2)	84.0 (6)
O2–M–N1	162.6 (2)	168.8 (1)	154.0 (6)
O1–M–X	90.3 (3)	111.9 (2)	110.1 (6)
O1–M–N2	171.8 (2)	139.6 (1)	142.5 (6)
O1–M–N1	90.1 (2)	86.9 (1)	83.9 (6)
O1–M–O2	102.5 (2)	94.8 (1)	101.3 (6)
X–M–O2ᵃ	173.4 (2)		
M–O1–C2	129.5 (5)	131.6 (3)	137.9 (1.5)
M–O2–C11	120.4 (4)	129.0 (3)	138.8 (1.4)
M–O2–Mᵃ	102.4 (2)		
M–N1–C4	126.3 (5)	129.6 (4)	129.7 (1.6)
M–N1–C6	113.9 (4)	108.6 (3)	109.2 (1.3)
C4–N1–C6	118.9 (6)	121.7 (4)	121.1 (1.9)
M–N2–C7	110.4 (5)	115.1 (4)	112.4 (1.2)
M–N2–C9	126.4 (5)	126.6 (4)	129.3 (1.4)
C7–N2–C9	123.2 (7)	118.3 (5)	118.0 (1.7)

ᵃSymmetry transformation: −x, −y, −z.

Table VI. Comparison of Structural Parameters within the M(acacen) Unit

parameter	7		8		5	
dist of O1, O2, N1, N2, M from	-0.070 (6)	0.059 (5)	0.179 (3)	-0.210 (4)	0.083 (14)	-0.079 (14)
the N_2O_2 core, Å	0.109 (7)	-0.118 (5)	-0.287 (4)	0.283 (4)	-0.137 (17)	0.136 (17)
	-0.119 (2)		-0.421 (1)		-0.499 (4)	
folding[a] along the N1···O1 line, deg	1.2 (2)		10.5 (2)		7.0 (6)	
folding along the N2···O2 line, deg	32.5 (3)		1.4 (2)		3.5 (7)	
angle between M-N1-O1 and M-N2-O2 planes, deg	11.7 (2)		40.4 (1)		40.0 (6)	
angle between the OC_3N planes, deg	25.3 (3)		33.2 (1)		50.3 (8)	
N1-C6-C7-N2 torsion angle, deg	42.9 (8)		40.5 (6)		35.4 (2.6)	
dist of C6 and C7 from the M-N1-N2 plane, Å	0.173 (9)	-0.399 (9)	0.652 (6)	0.128 (6)	0.805 (27)	0.402 (25)

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

parameters are given in Tables SIV-SVI (supplementary material); selected bond distances and angles, in Table V.

Results and Discussion

The choice of the ancillary ligand acacen for titanium(III) and vanadium(III) was mainly suggested by the usually very good solubility of the [M(acacen)] derivatives in organic solvents, and because of its steric flexibility, compared to other tetradentate Schiff base complexes like salen, salophen, etc.

The synthesis and the characterization of the starting materials [(THF)M(acacen)Cl] have been recently published both for vanadium[6] and titanium.[7] The reaction of the corresponding chloride with a Grignard derivative was carried out in THF at room temperature:
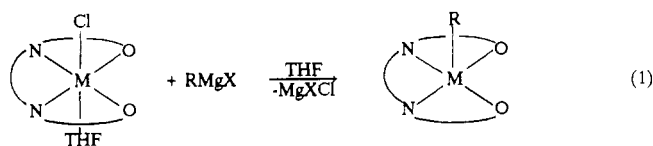

[M(acacen)]

1, M = Ti
2, M = V

[M(acacen)R]

3: M = Ti, R = CH₂Ph
4: M = Ti, R = Ph
5: M = Ti, R = Mes
6: M = V, R = Me
7: M = V, R = CH₂Ph
**8**: M = V, R = Ph
9: M = V, R = Mes
Mes = 2,4,6-Me₃C₆H₂

Reaction 1 is almost quantitative; the only serious problem is how to make free complexes **3-9** from the inorganic salts. The separation of the magnesium halide from the reaction mixture is difficult because of the likely complexation of MgX_2 by the O···O' bite of the Schiff base ligand. Decomplexation and precipitation of MgX_2 is achieved by using dioxane, but sometimes separation has to be carried out in more than one step. Schiff base complexes functioning as bidentate ligands are known, and the resulting bimetallic complexes have been structurally characterized.[16] The relatively fast separation of MgX_2 is rather crucial because it causes a significant decomposition of the organometallic derivatives. The solid-state structural determinations gave us some insight into the role of MgX_2. It is probably in competition with the alkyl or aryl groups for the oxygens from

the Schiff bases, as exemplified in reaction 2 for the phenyl derivative (see the structure of **8**, Figure 3).
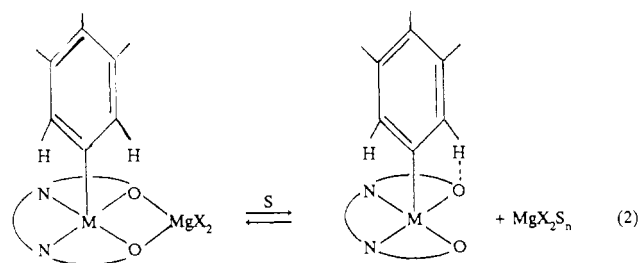
S = THF, dioxane, etc.

As a matter of fact, the unusual stability of the M-C functionality may come from the well-identified hydrogen bonding observed in the structures of **5**, **7**, and **8** (vide infra). Complexes **3-9** are formulated either as monomers (structure A) or dimers (structure B), at least in the solid state.

A   B
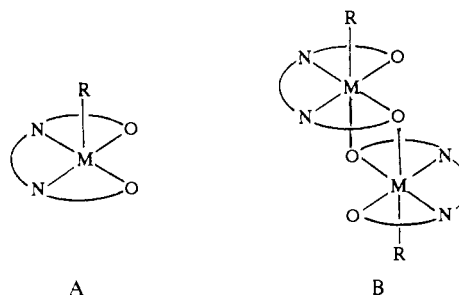
The X-ray structure determination showed the monomeric form for **5** and **8** and the dimeric one for **7**. Complex **7** has a significantly reduced magnetic moment for a d^2 system (2.40 μ_B at 293 K). This is probably due to some antiferromagnetic coupling between two d^2 systems. Therefore reduced magnetic moments for d^1 and d^2 systems have been used as a criterion for the existence of a dimeric form in the solid state for complexes **6** (2.16 μ_B at 290 K) and **4** (1.35 μ_B at 290 K). MW determination in solution was possible only for **7**, having the appropriate solubility in benzene. It is monomeric in solution (see Experimental Section), thus suggesting that dimerization is a solid-state consequence.

Infrared spectra were used for detecting any change in the Schiff base ligand. Alkylation of the imino groups has been observed in titanium(IV)- and zirconium(IV)-Schiff base or related macrocyclic complexes.[16] This fact is, however, associated with the high electrophilicity of imino groups induced by the high oxidation state of the metal. Complexes **3-9** show an unusual thermal stability compared with that of similar cyclopentadienyl derivatives[1b,2a,b] and with the corresponding organic derivatives of titanium(IV)-Schiff base complexes.[17] Among different factors that may be responsible for such overstabilization, the solid-state structure determination revealed as a general phenomenon the intramolecular hydrogen bonding between the alkyl or aryl residue

(16) Sinn, E.; Harris, C. M. *Coord. Chem. Rev.* **1969**, *4*, 391. Gruber, S. J.; Harris, C. M.; Sinn, E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1805. O'Connor, C. J.; Freyberg, D. P.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 1077. Leslie, K. A.; Drago, R. S.; Stucky, G. D.; Kitko, D. J.; Breese, J. A. *Inorg. Chem.* **1979**, *18*, 1885. Hobday, M. D.; Smith, T. D. *Coord. Chem. Rev.* **1972**, 311. Bresciani-Pahor, N.; Calligaris, M.; Delise, P.; Nardin, G.; Randaccio, L.; Zotti, E.; Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 2310 and references cited therein. Armstrong, L. G.; Lip, H. C.; Lindoy, L. F.; McPartin, M.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1771. Milburn, H.; Truter, M. R.; Vickery, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 841. Pasquali, M.; Marchetti, F.; Floriani, C.; Cesari, M. *Inorg. Chem.* **1980**, *19*, 1198. Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1978**, *17*, 3002. Fenton, D. E.; Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Chem. Commun.* **1979**, 39.

(17) Floriani, C.; Solari, E.; Corazza, F.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 64.
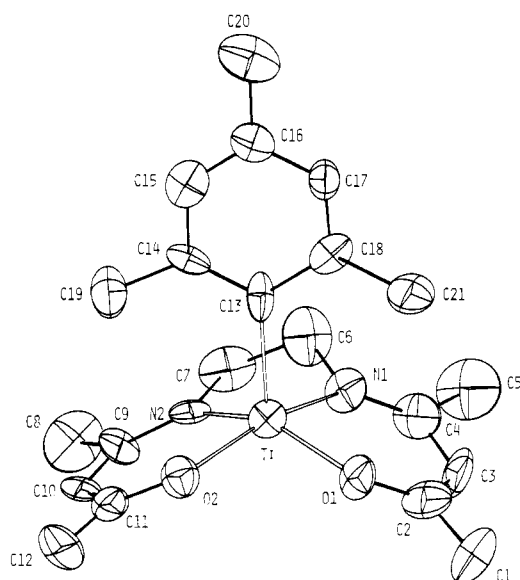
Figure 1. ORTEP drawing for complex **5** (50% probability ellipsoids).

and the two oxygen atoms from the Schiff base ligand. The X-ray analysis ensured an unquestionable structure assignment to these rather unusual organometallic derivatives, which are similar to some cobalt(III)–Schiff base organometallic derivatives.[4]

Structure for Complexes 5, 7, and 8. Selected bond distances and angles for complexes **5, 7,** and **8,** are listed in Table V. Structural parameters concerning the conformation of the [M-(acacen)] unit are compared in Table VI.[18]

Complex **5** is monomeric, as shown in Figure 1. Titanium is strongly out of the N_2O_2 core toward the apical aromatic carbon, the two six-membered chelation rings being folded on the opposite side to give an umbrella conformation already present, albeit to a lesser extent, in the six-coordinate [(THF)Ti(acacen)(Cl)] (**1**).[6] This implies significant changes in the bond angles around titanium, the titanium–oxygen and titanium–nitrogen bond distances remaining practically unchanged with respect to complex **1**. The titanium–carbon bond distance appears to be rather long [2.22 (2) Å].[19] Titanium is only 0.039 (4) Å from the plane through the aromatic ligand. It is nearly perpendicular to the mean plane through the N_2O_2 core [dihedral angle 87.8 (3)°], giving rise to symmetrical interactions with the N_2O_2 core, as can be seen from the following interatomic contacts: O1···C21 = 3.20 (2) Å; N1···C21 = 3.38 (3) Å; O2···C19 = 3.27 (3) Å; N2···C19 = 3.28 (3) Å. The basicity of the oxygen atoms along with the geometry of the C–H···O contacts suggests they could be regarded as intramolecular hydrogen bonds: C21–H213 = 1.07 Å; H213···O1 = 2.27 Å; C21–H213···O1 = 144°; C19–H193 = 1.09 Å; H193···O2 = 2.24 Å; C19–H193···O2 = 158°. Formation of intramolecular hydrogen bonds seems to play a fundamental role in stabilizing the metal–carbon bond in such compounds (vide infra).

The structure of complex **7** consists of centrosymmetric dimers, V(acacen)(CH$_2$Ph)]$_2$ (Figure 2), where each vanadium exhibits an octahedral coordination involving the N_2O_2 set of donor atoms from the acacen ligand in the equatorial plane and the benzyl group in an axial position. The sixth coordination site is achieved by sharing an oxygen atom from an adjacent centrosymmetric monomer, giving rise to the dimer. The V–O2$_{ax}$ distance [2.296 (5) Å] is much longer than the V–O2$_{eq}$ one. In addition, V–O2$_{eq}$ [1.989 (4) Å] is a little, even though significantly, longer than
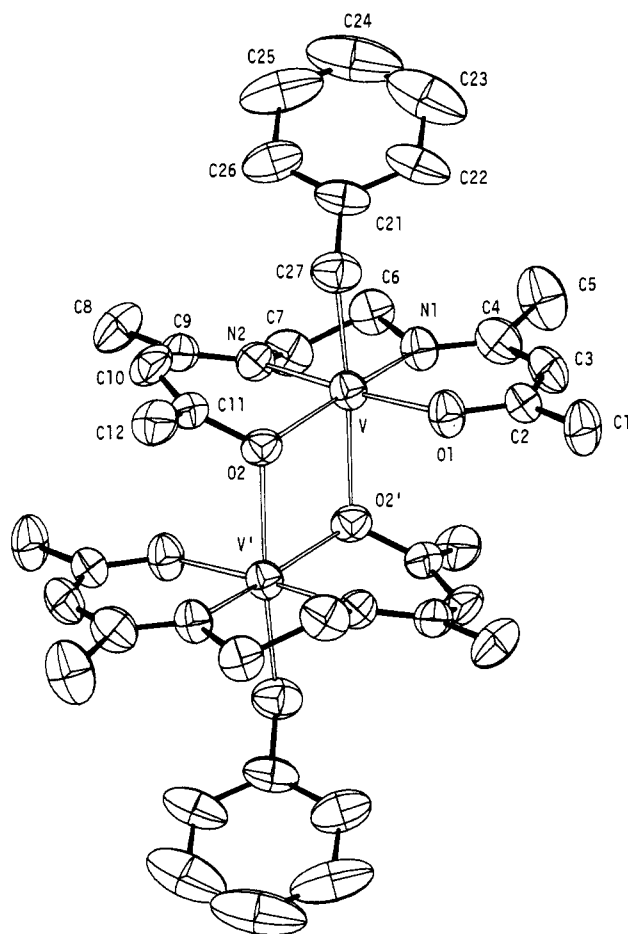

Figure 2. ORTEP drawing for complex **7** (50% probability ellipsoids).

V–O1 [1.960 (5) Å], as a probable consequence of the bridging role of the O2 atom. Bond distances and angles in the [V(acacen)] moiety are close to those observed in [(THF)V(acacen)(Cl)].[7] The most dramatic difference concerns the conformation of the N2···O2 chelation ring, which is strongly distorted from planarity, as indicated by the folding angle of 32.5 (3)° along the N2···O2 line (Table VI). This could be a consequence of intramolecular steric interactions due to dimerization. The V–C bond distance [2.156 (9) Å] is comparable to those observed in [(cp)$_2$V-(EtO$_2$CCHCHCO$_2$Et)][20] [2.186 (12) and 2.213 (12) Å] for an sp^3 carbon, while it is significantly longer than those found in [(cp)$_2$V(MeO$_2$CC=CCO$_2$Me)][20] [2.084 (3) and 2.097 (3) Å], in [VMes$_3$(THF)]^{21a} [2.099 (6) and 2.116 (7) Å], in [VMes$_4$]^{21b} [2.071–2.095 Å], and in [(TMTAA)V(Mes)]^{21c} (TMTAA = 7,16-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato anion) [2.085 (8) Å], all having an sp^2 carbon. The orientation of the benzyl group is mainly determined by almost symmetric interactions of the methylene hydrogen atoms with the oxygen atoms of the N_2O_2 core: C27···O1 = 2.924 (11) Å, H271···O1 = 2.60 Å, C27–H271···O1 = 100°; C27···O2 = 3.077 (10) Å, H272···O2 = 2.73 Å, C27–H272···O2 = 97°. Considering the high basicity of these oxygen atoms, the above interactions could be regarded as intramolecular hydrogen bonds that could be responsible for the stabilization of the compound.

The structure of complex **8** consists of discrete monomeric units [V(acacen)(Ph)], where vanadium exhibits a square-pyramidal coordination (Figure 3). The metal is strongly displaced out of the N_2O_2 plane toward the aromatic carbon, resulting in a con-

(18) Corazza, F.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Dalton Trans.* **1987,** 709.

(19) (a) Atwood, J. L.; Baker, G. K.; Holton, J.; Hunter, W. E.; Lappert, M. F.; Pearce, R. *J. Am. Chem. Soc.* **1977,** *99,* 6645. (b) Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1972,** *46,* 313. (c) Sekutowski, O. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976,** *98,* 1376. (d) Mattia, J.; Humphrey, M. B.; Rogers, R. D.; Atwood, J. L.; Rausch, M. D. *J. Am. Chem. Soc.* **1978,** *17,* 3257. (e) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976,** *98,* 2454.

(20) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1979,** *18,* 2282 and references therein.

(21) (a) Seidel, W.; Kreisel, G. *Z. Anorg. Allg. Chem.* **1977,** *435,* 146. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1984,** 886. (b) Seidel, W.; Kreisel, G. *Z. Chem.* **1976,** *16,* 115. (c) Ciurli, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1986,** 1401.
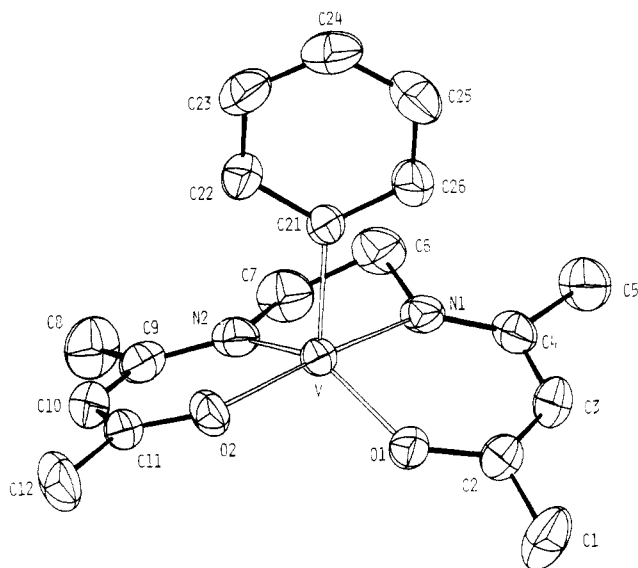
Figure 3. ORTEP drawing for complex **8** (50% probability ellipsoids).

formation of the [V(acacen)] moiety markedly different from that observed in the six-coordinated complexes 7 and [(THF)V(aca-cen)(Cl)]^7 (2), as clearly indicated by the dihedral angle between the two O–V–N planes [40.4 (1)°] (Table VI). The V–O distances [V–O1 = 1.897 (3) Å; V–O2 = 1.952 (3) Å] are significantly different from each other, as well as the V–N distances [V–N1 = 2.056 (3) Å; V–N2 = 1.993 (5) Å]. This could be the result of an asymmetric interaction of the phenyl ligand with the

Schiff base. In fact the aromatic ring, which is perpendicular to the mean plane through the N$_2$O$_2$ core [dihedral angle 89.5 (1)°], does not bisect the N–V–O angles, being oriented to form the shortest intramolecular contacts between its ortho hydrogen atoms and the O2 and N1 atoms, respectively (H22···O2 = 2.86 Å; H26···N1 = 3.01 Å). The basicity of the oxygen atom along with the geometry of the C–H···O group suggests this could be interpreted as an intramolecular hydrogen bond: C22···O2 = 3.298 (6) Å, C22–H22 = 1.04 Å, C22–H22···O2 = 106°. The vanadium–carbon distance [V–C21 = 2.064 (5) Å] is in good agreement with that observed in [(TMTAA)V(Mes)]^{21c} [2.085 (8) Å], where vanadium exhibits a very similar geometry. Vanadium is 0.130 (1) Å out from the plane through the phenyl ring.

The data in Table VI indicate that no part of the [M(acacen)] moieties is strictly planar. The N$_2$O$_2$ cores exhibit relevant twisting. All the six-membered chelation rings are folded along the N···O lines, albeit to different extents. The five-membered chelation rings have different conformation. In the six-coordinate complex 7 it shows a gauche conformation, while in the five-coordinate complexes 5 and 8 they are folded with respect to the N···N line with the C6 and C7 carbons upward on the same side as a consequence of the downward folding of the six-membered chelation rings.

Contribution from the Instituto de Quimica, Universidad Católica de Valparaiso, Valparaiso, Chile, and The University of Texas at Austin, Austin, Texas 78712

Synthesis, Characterization, and Electrochemistry of *cis*-Dioxomolybdenum(VI) Complexes of Schiff Bases Derived from Carbohydrazide, Thiocarbohydrazide, and Salicylaldehyde. Crystal Structures of [MoO$_2$(*o*-OC$_6$H$_4$CH=NN=CSNHN=CHC$_6$H$_4$OH-*o*)Me$_2$SO] and [(MoO$_2$)$_2$(*o*-OC$_6$H$_4$CH=NN=CONN=CHC$_6$H$_4$O-*o*)(Me$_2$SO)$_2$]·0.5Me$_2$SO

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Bis(acetylacetonato)dioxomolybdenum(VI), [MoO$_2$(acac)$_2$], reacts with Schiff bases derived from thiocarbohydrazide and carbohydrazide (*o*-HOC$_6$H$_4$CH=NNH)$_2$CX, (X = S,O) and salicylaldehyde in methanol, to afford mono- and binuclear complexes respectively. These complexes have been characterized by elemental analysis and IR and ^{1}H NMR spectroscopy, and formulated as [MoO$_2$(*o*-OC$_6$H$_4$CH=NN=CSNHN=CHC$_6$H$_4$OH-*o*)L], and [(MoO$_2$)$_2$(*o*-OC$_6$H$_4$CH=NN=CONN=CHC$_6$H$_4$O-*o*)L$_2$] (L = MeOH, Me$_2$SO). All complexes exhibit an irreversible voltammetric peak that is attributed to an electron transfer centered at molybdenum (~−0.90 V vs SCE). Coulometric reduction at −0.95 V is either a two- or four-electron process depending on whether the complex is mono- or binuclear. The X-ray crystal structures of the title complexes are described. Crystals of the mononuclear complex (L = Me$_2$SO) are triclinic, space group group P$\bar{1}$, with *a* = 10.138 (2) Å, *b* = 13.489 (2) Å, *c* = 7.964 (1) Å, α = 106.80 (2)°, β = 100.00 (2)°, γ = 95.546 (2)°, and Z = 2. The structure was solved by using 2812 unique reflections, and refinement gave final R and R$_w$ values of 0.038 and 0.047, respectively. The binuclear complex (L = Me$_2$SO) crystallizes in the space group P2$_1$/c with *a* = 11.419 (4) Å, *b* = 8.390 (4) Å, *c* = 31.075 (9) Å, β = 92.09 (3)°, and Z = 4. The structure was solved using 2873 reflections, and refinement gave final R and R$_w$ values of 0.067 and 0.087, respectively.

Introduction

The presence of the *cis*-dioxomolybdenum(VI) cation, [MoO$_2$]$^{2+}$, in the oxidized forms of certain molybdoenzymes^2 has stimulated both the search for new structures in which this moiety

is coordinated to ligands containing nitrogen, oxygen, and/or sulfur donors and also the study of their chemical, spectroscopic, electrochemical, and structural properties.^{3} At present, a large number of *cis*-dioxomolybdenum(VI) complexes are known, some of which have been proposed as models for the active sites of oxo-transfer molybdoenzymes, viz. sulfite and aldehyde oxidase, xanthine oxidase/dehydrogenase, and nitrate reductase.$^{4-6}$

(1) (a) Universidad Católica de Valparaiso. (b) The University of Texas at Austin.
(2) Stiefel, E. I. In *Molybdenum and Molybdenum-Containing Enzymes*; Coughlan, M. P., Ed.; Pergamon Press: Oxford, England, 1979; p 43.

(3) Stiefel, E. I. *Prog. Inorg. Chem.* **1979**, *22*, 1.