Inorg. Chem. **1986**, *25*, 2308–2314

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Vanadium(III)–Schiff Base Complexes: A Synthetic and Structural Study

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Received November 4, 1985

Vanadium(III)–tetradentate Schiff base complexes have been prepared by three different methods using conventional starting materials. Reductive deoxygenation of [VO(salophen)] (I) [salophen = *N,N'*-*o*-phenylenebis(salicylaldiminato) dianion] by a THF solution of $TiCl_3(THF)_3$ resulted in the formation of [V(salophen)(THF)(Cl)] (II) as crystalline solid in high yield. X-ray diffraction analysis of the structure of II showed a pseudooctahedral coordination for vanadium(III), which has two unpaired electrons ($\mu_{eff} = 2.74\ \mu_B$ at 296 K). The chlorine and THF ligands are trans to each other in the axial positions, while the equatorial plane is defined by the salophen ligand. Compounds II and $[V(salen)(Cl)]_2$ (III) [salen = *N,N'*-ethylenebis(salicylaldiminato) dianion] have been prepared equally well by reacting $VCl_3(THF)_3$ with the sodium salt of the corresponding Schiff bases, $salenNa_2$ and $salophenNa_2$. This procedure was successfully used in the synthesis of [V(sal-NMePr)(Cl)] (IV) [sal-NMePr = methyliminobis(3-(salicylideneamino)propanato) dianion]. The conformation of the pentadentate ligand is different from those previously reported for other metals. The V–Cl bond can undergo easy ionization by $NaBPh_4$ to form $\{[V(sal\text{-}NMePr)(THF)](BP_4)\}$ (V). Finally, deoxygenation of [VO(salen)] and I by $SOCl_2$ led to the dichloro derivatives $[V(salen)(Cl)_2]$ and $[V(salophen)(Cl)_2]$, which were then reduced by zinc dust in THF. After the addition of a small amount of pyridine, the reaction gave as crystalline solids $\{[V(salen)(py)_2][ZnCl_3py]\}$ (IX) and $\{[V(salophen)(py)_2][ZnCl_3py]\}$ (X). X-ray analysis of IX demonstrated a hexacoordinate vanadium(III) ion, where the two pyridine ligands are trans to each other and the salen ligand is in the equatorial plane. Crystallographic details for II·THF: space group $P2_1/c$ (monoclinic); $a = 16.179$ (4) Å; $b = 12.038$ (3) Å; $c = 14.506$ (4) Å; $\beta = 111.56$ (3)°; $V = 2628$ (1) $Å^3$; $Z = 4$; $D_{calcd} = 1.378$ g cm^{-3}. The final R factor was 0.061 for 1874 observed reflections. Crystallographic details for IV: space group $P2_1/c$ (monoclinic); $a = 7.940$ (3) Å; $b = 22.153$ (7) Å; $c = 11.652$ (3) Å; $\beta = 98.03$ (3)°; $V = 2029$ (1) $Å^3$; $Z = 4$; $D_{calcd} = 1.433$ g cm^{-3}. The final R factor was 0.035 for 2114 observed reflections. Crystallographic details for IX: space group $P\bar{1}$ (triclinic); $a = 15.155$ (3) Å; $b = 12.960$ (3) Å; $c = 9.065$ (2) Å; $\alpha = 93.28$°; $\beta = 105.46$ (2)°; $\gamma = 106.89$ (2)°; $V = 1624.4$ (7) $Å^3$; $Z = 2$; $D_{calcd} = 1.485$ g cm^{-3}. The final R factor was 0.057 for 1727 observed reflections.

Introduction

Reactive complexes of vanadium(IV), vanadium(III), and vanadium(II) that can be used as model compounds for studying chemical reactivity at the metal have, in the past, been limited to cyclopentadienyl derivatives.[1] Many different ligands have been used to form complexes with the oxovanadium(IV) ion, but the ion's stability and lack of reactivity make these complexes virtually useless for studies of chemical reactivity at the metal site.[2] Some of the most compelling reasons for our interest in the largely unexplored coordination chemistry of vanadium must, therefore, be mentioned:[3]

(i) Low oxidation states of vanadium promote activation of oxygen, nitrogen, and organic functionalities.[1,4,5]

(ii) Understanding of the role of vanadium in naturally occurring systems is very limited.[6]

(iii) There is a need to develop ligands other than the cyclopentadienyls that will stabilize organometallic functionalities, including metal–carbon bonds.[7]

(iv) Aggregation of vanadium ions in low oxidation states occurs via formation of metal–metal bonds.[8] In many cases, polydentate Schiff bases and other macrocyclic ligands produce the appropriate environment for the stabilization of various oxidation states at the metal[9] and provide active sites capable of binding small molecules.[10,11] These ligands also aid in the stabilization of metal–carbon bonds[12] and in the synthesis of polyfunctional compounds.[13] Synthetic approaches that can be applied for such complexes include the following:

(i) Halogen is displaced from VX_3 or VX_4 by the appropriate Schiff base ligands. Although this is the most obvious method, it is not always the most successful because it can lead to the formation of adducts without the loss of HX.[14]

(ii) The oxovanadium(IV) unit is deoxygenated with $SOCl_2$ or other reagents to form the corresponding dihalo derivatives,[15] which may then be reduced.

(iii) The oxovanadium(IV) unit is reductively deoxygenated to obtain the corresponding halogenovanadium(III) derivative.

The objective of this work was to synthesize vanadium(III)–Schiff base complexes that can be used as starting materials in the investigation of the chemistry of low oxidation states of vanadium and in the introduction of organometallic functionalities at vanadium.[7] Therefore, vanadium(III) and vanadium(IV) complexes LVX and LVX_2 (where L is a polydentate Schiff base ligand) have been synthesized that contain replaceable reactive ligands, i.e. X, on the metal.

This report is concerned with the synthesis and structural characterization of salen, salophen, and sal-NMepr [salen = *N,N'*-ethylenebis(salicylaldiminato) dianion; salophen = *N,N'*-*o*-phenylenebis(salicylaldiminato) dianion; sal-NMepr = methyliminobis(3-(salicylideneamino)propanato) dianion] derivatives

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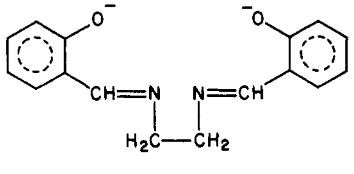
of vanadium(III). Two earlier papers[16,17] reported the synthesis of some derivatives of vanadium(III) with polydentate Schiff base ligands. The structure of these compounds has not been defined, and the presence of pyridine in some of these may cause problems for reactivity studies.[16]

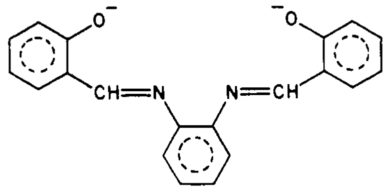
Experimental Section

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 283 spectrophotometer. Magnetic susceptibility data were determined by the Faraday method. $TiCl_3(THF)_3$,[18] $VCl_3(THF)_3$,[18] [V(salen)$(Cl)_2$],[15a] and [V(salophen)-$(Cl)_2$][15a] were prepared by published procedures. [VO(salen)] and [VO(salophen)] were synthesized by the procedure reported in detail for [VO(salophen)].

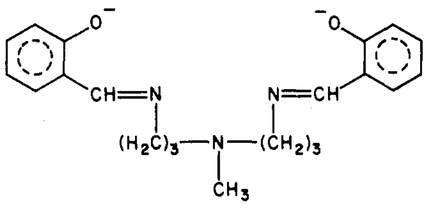
Abbreviations: salen = *N,N'*-ethylenebis(salicylaldiminato) dianion



salophen = *N,N'*-*o*-phenylenebis(salicylaldiminato) dianion



sal-NMePr = methyliminobis(3-(salicylideneamino)propanato dianion



Synthesis of [VO(salophen)]. An EtOH (500 mL; 95%) solution of salophenH_2 (20.50 g, 64.87 mmol) reacted with an aqueous (500 mL) solution of $VOSO_4\cdot 5H_2O$ (16.5 g, 65.23 mmol), and then a solution (250 mL) of $CH_3COONa\cdot 3H_2O$ (23.0 g, 169.1 mmol) was added. A green crystalline solid formed immediately. The mixture was refluxed for 1 h and then cooled overnight. The solid [VO(salophen)] was washed with H_2O, EtOH, and Et_2O and dried in vacuo (20.0 g, 80.9%). Anal. Calcd for $C_{20}H_{14}N_2O_3V$: C, 63.01; H, 3.70; N, 7.35. Found: C, 62.89; H, 3.75; N, 7.50.

Synthesis of [V(salophen)(Cl)(THF)] by Method A. A THF (200 mL) suspension of [VO(salophen)] (8.3 g, 21.8 mmol) was added to a THF solution (300 mL) of $TiCl_3(THF)_3$ (8.10 g, 21.8 mmol). The solid dissolved, and the color changed from blue to deep maroon. Upon being allowed to stand, the solution produced crystals of complex II (10.5 g, 88.9%). Absence of titanium in the solid was proven by atomic absorption.

Synthesis of [V(salophen)(Cl)(THF)] by Method B. Sodium hydride (0.21 g, 8.7 mmol) was slowly added to a THF (100 mL) solution of salophenH_2 (1.41 g, 4.5 mmol). The suspension was stirred until the NaH was completely dissolved. $VCl_3(THF)_3$ (1.62 g, 4.35 mmol) was then added while the resulting yellow solution was stirred. The color changed from red to deep maroon, and then a black solid started to crystallize. The solid contained NaCl, which might be removed by a THF extraction of complex IV (1.92 g, 80%). Anal. Calcd for [V-(salophen)(Cl)(THF)]·THF: $C_{28}H_{30}N_2O_4VCl$: C, 61.72; H, 5.55; N, 5.14. Found: C, 61.10; H, 5.20; N, 4.94. ν(C–N) (Nujol): centered at 1530 cm^{-1}. $\mu_{eff} = 2.74\ \mu_B$ at 296 K.

Synthesis of $[V(salen)(Cl)]_2$ by Method B. Sodium hydride (0.43 g, 17.7 mmol) was slowly added to a THF (100 mL) suspension of salenH_2 (2.38 g, 8.86 mmol): The suspension was stirred until the NaH was completely dissolved. $VCl_3(THF)_3$ (3.31 g, 8.86 mmol) was then added while the resulting yellow solution was stirred. A brown solid formed immediately, and the suspension was refluxed for 3 h. The filtered solid was extracted with THF from NaCl, and a microcrystalline compound was obtained (2.3 g, 74.1%). Anal. Calcd for [V(salen)(Cl)], $C_{16}H_{14}N_2O_2ClV$: C, 54.48; H, 4.00; N, 7.94; Cl, 10.05. Found: C, 54.34; H, 4.16; N, 8.12; Cl, 9.75. ν(C–N) (Nujol): centered at 1625 cm^{-1}. $\mu_{eff} = 2.73\ \mu_B$ at 294 K.

Synthesis of [V(sal-NMePr)(Cl)]. Sodium hydride (1.60 g, 66.6 mmol) was added to a THF (300 mL) solution of [sal-NMePrH_2] (11.8 g, 33.5 mmol). The suspension was stirred until the solid dissolved, and then the solution was refluxed for 1 h. To the yellow solution was added $VCl_3(THF)_3$ (12.52 g, 33.5 mmol). A red-orange solid suddenly formed. The suspension was stirred for 30 min. and then refluxed overnight. The solid was extracted for 3 days with the mother liquor. The solution, cooled to 0 °C, gave a red crystalline solid (10.0 g, 64.0%). ν(C–N) (Nujol) = 1610 cm^{-1}. ν(V–Cl) (Nujol): 380 cm^{-1}. Anal. Calcd for [V(sal-NMePr)(Cl)], $C_{21}H_{25}N_3O_2VCl$: C, 57.60; H, 5.75; N, 9.60; Cl, 8.10. Found: C, 54.15; H, 5.65; N, 9.32; Cl, 7.98. $\mu_{eff} = 2.65\ \mu_B$ at 297 K.

Synthesis of [V(sal-NMepr)(THF)](BPh_4). Sodium tetraphenylborate, $NaBPh_4$ (1.25 g, 3.7 mmol), was added to a THF (70 mL) suspension of [V(sal-NMePr)(Cl)] (1.60 g, 3.7 mmol). The suspension was stirred for 10 min, and its color changed from red to yellow-orange. The solid contained NaCl, which was removed by a THF extraction using the mother liquor. The resulting THF solution, cooled down to room temperature, gave an orange crystalline solid (2.30 g, 75.0%). Anal. Calcd for [V(sal-NMepr)(THF)](BPh_4), $C_{49}H_{53}N_3O_3BV$: C, 74.15; H, 6.73; N, 5.29. Found: C, 73.93; H, 7.04; N, 5.10. ν(C–N) (Nujol): 1610 cm^{-1}. $\mu_{eff} = 2.79\ \mu_B$ at 298 K.

Reduction of [V(salophen)$(Cl)_2$] with Zinc. A THF suspension (50 mL) of [V(salophen)$(Cl)_2$] (2.37 g, 5.43 mmol) was reacted with zinc dust (2.0 g) and stirred (24 h) until all solid dissolved, giving a violet solution. The excess of zinc was filtered out, and the resulting solution was cooled at –30 °C. A violet crystalline solid formed. Anal. Calcd for $[V(salophen)(THF)_2]_2[ZnCl_4]$ (XI), $C_{56}H_{60}N_4O_8Cl_4V_2Zn$: C, 54.85; H, 4.93; N, 4.56; Cl, 11.56. Found: C, 54.28; H, 4.17; N, 5.55; Cl, 11.70. $\mu_{eff} = 2.62\ \mu_B$ at 296 K.

Synthesis of $[V(salophen)(py)_2][ZnCl_3py]$. A THF (50 mL) suspension of [V(salophen)$(Cl)_2$] (2.19 g, 5.0 mmol) was reduced with zinc dust (2.0 g, 30.5 mmol). The maroon suspension was stirred overnight, and the color of the solution changed from maroon to violet. The excess zinc was removed by filtration, and pyridine (5.0 mL) was added to the solution. The solution became deep green, and a black crystalline solid formed (1.90 g, 48.7%). Anal. Calcd for $[V(salophen)(py)_2](ZnCl_3py)$, $C_{35}H_{29}N_5O_2Cl_3VZn$: C, 54.28; H, 3.77; N, 9.04. Found: C, 54.22; H, 3.82; N, 7.69. ν(C–N) (Nujol): centered at 1525 cm^{-1}. $\mu_{eff} = 2.30\ \mu_B$ at 295 K.

Synthesis of $[V(salen)(py)_2][ZnCl_3py]$. A THF (50 mL) suspension of [V(salen)$(Cl)_2$] (1.10 g, 2.80 mmol) was reacted with zinc dust (1.10 g, 16.8 mmol). The color of the suspension changed from blue to green-yellow in a few minutes. The suspension was stirred continuously for 4 h until all the solid dissolved when the excess zinc was removed by filtration. The isolation of a solid from the solution was very difficult unless pyridine (4.0 mL) was added. The resulting solution gave a red crystalline solid after being allowed to stand for 24 h (1.08 g, 45%). Anal. Calcd for $[V(salen)(py)_2][ZnCl_3py]$, $C_{31}H_{29}N_5O_2Cl_3VZn$: C, 51.27; H, 4.03; N, 9.64. Found: C, 51.25; H, 3.99; N, 9.21. ν(C–N) (Nujol): centered at 1610 cm^{-1}. $\mu_{eff} = 2.18\ \mu_B$ at 295 K.

X-ray Crystallography.[19] Crystals of complexes II, IV, and IX were sealed in thin-walled glass capillaries. The reduced cells were obtained by using TRACER.[20] Crystal data and a summary of the data collection are given in Table I.

The intensity data were collected at room temperature (22 °C) with the three-point technique. The absorption effects of the crystal were studied with ψ scans and were considered not negligible for the three complexes; the data were corrected for absorption following a semiempirical method,[21] with maximum and minimum correction factors at 1.080–1.002, 1.087–1.000, and 1.120–1.003 for II, IV, and IX, respec-

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	$C_{28}H_{30}ClN_2O_4V$	$C_{31}H_{29}Cl_3N_5O_2VZn$	$C_{21}H_{25}ClN_3O_2V$
mol wt	544.9	726.3	437.8
cell dimens at 295 K[a]			
a, Å	16.179 (4)	15.155 (3)	7.940 (3)
b, Å	12.038 (3)	12.960 (3)	22.153 (7)
c, Å	14.506 (4)	9.065 (2)	11.652 (3)
α, deg	90	93.28	90
β, deg	111.56 (3)	105.46 (2)	98.03 (3)
γ, deg	90	106.89 (2)	90
V, Å^3	2628 (1)	1624.4 (7)	2029 (1)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.378	1.485	1.433
radiation	Mo Kα[b]	Mo Kα[b]	Mo Kα[b]
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
max cryst dimens, mm	0.10 × 0.52 × 0.54	0.06 × 0.24 × 0.56	0.15 × 0.25 × 0.52
μ, cm^{-1}	5.0	13.2	6.3
diffractometer	Philips PW 1100	Philips PW 1100	Philips PW 1100
diffraction geom	equatorial	equatorial	equatorial
scan type	ω	$\omega/2\theta$	$\omega/2\theta$
scan speed, deg s	0.100	0.100	0.100
scan width, deg	1.40	1.50	1.10
2θ range, deg	5–50	5–46	6–48
reflcns measd	$\pm h,\pm k,l$	$\pm h,\pm k,l$	$\pm h,\pm k,l$
no. of measd total data	6296	4459	4504
agreement between equiv reflcns	0.032		0.028
no. of unique total data	4615	4459	3264
no. of unique obsd data (NO)	1874	1727	2114
criterion for observns	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
no. of params varied (NV)	325	388	253
R	0.061	0.057	0.035
NO/NV	5.8	4.5	8.3

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 25 carefully centered reflections chosen from diverse regions of reciprocal space. [b] Graphite monochromated (λ = 0.7107 Å).

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

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
V	2232 (1)	979 (1)	1820 (1)	C13	686 (5)	−131 (7)	2141 (6)
Cl	1257 (1)	2215 (2)	645 (2)	C14	909 (5)	−796 (7)	702 (6)
O1	3065 (4)	2161 (5)	2316 (5)	C15	1352 (5)	−928 (8)	10 (6)
O2	2601 (4)	200 (5)	903 (5)	C16	946 (6)	−1647 (9)	−807 (7)
N1	1784 (4)	1228 (6)	2980 (5)	C17	1341 (7)	−1847 (9)	−1485 (8)
N2	1171 (4)	−160 (6)	1483 (5)	C18	2127 (7)	−1320 (9)	−1379 (8)
C1	3447 (6)	2521 (7)	3250 (7)	C19	2552 (6)	−622 (8)	−589 (7)
C2	4266 (6)	3074 (8)	3531 (8)	C20	2162 (5)	−417 (7)	126 (6)
C3	4649 (6)	3499 (8)	4476 (8)	O3	3202 (4)	−47 (6)	2903 (5)
C4	4253 (7)	3393 (9)	5166 (8)	C21	4106 (7)	−100 (11)	2949 (10)
C5	3466 (6)	2839 (9)	4905 (7)	C22	4543 (8)	−963 (14)	3589 (13)
C6	3041 (6)	2373 (7)	3957 (7)	C23	3891 (8)	−1478 (11)	3930 (10)
C7	2230 (6)	1802 (7)	3772 (6)	C24	3024 (7)	−986 (10)	3358 (10)
C8	1002 (6)	622 (7)	2918 (6)	O4	6472 (13)	1516 (16)	3139 (15)
C9	569 (6)	696 (9)	3586 (7)	C25	7196 (24)	1736 (22)	3886 (18)
C10	−142 (7)	18 (10)	3496 (8)	C26	7714 (15)	775 (42)	4148 (19)
C11	−444 (6)	−727 (9)	2732 (8)	C27	7141 (29)	−39 (17)	3701 (27)
C12	−44 (6)	−803 (8)	2035 (7)	C28	6474 (19)	466 (24)	3004 (20)

tively. The structures were solved by the heavy-atom method and refined by blocked full-matrix least squares first isotropically and then anisotropically for all non-H atoms. Atomic scattering factors were taken from ref 22a for Zn, V, Cl, O, and N and from ref 23 for H. Anomalous dispersion terms were included for all atoms.[22b] Because of the limited quality of the available crystals for complexes II and IV, just a low percentage of reflections could be considered observed (Table I). Probably the crystal's poor scattering is an inherent property because of the presence of uncoordinating moieties affected by high thermal motion. These moieties are THF molecules of crystallization in complex II and [$ZnCl_3py$] counterions in complex IX. Since the peripheral part of the complexes is rather extensive and so free to librate, this could be an additional reason for the loss of reflections up to a certain value of θ. The isotropic refinement stopped at R = 0.095 and 0.099 for II and IX, respectively. So the anisotropic refinement was attempted, and this gave satisfactory agreement R indices and thermal parameters despite poor parameter to data ratios. Most of the hydrogen atoms were located from difference Fourier syntheses; the remainder were put in calculated positions. They were included in calculation prior to the final refinement as fixed contributors (U = 0.08 Å^2 for I, U = 0.05 Å^2 for IV and IX). Unit weights were used in the refinements since these gave acceptable agreement in analyses. No corrections for extinction were deemed necessary. The final difference Fourier syntheses showed no unusual feature except for the presence in complex IX of two peaks (0.6 e Å^{-3}) in the middle point of the Zn–Cl and V–N(py) bonds.

The final positional parameters for complexes II, IV, and IX are given in Tables II, III, and IV, respectively. The anisotropic thermal parameters, atomic coordinates for the hydrogen atoms, and nonessential bond lengths and angles are available as supplementary material.

Results and Discussion

The main goal of this work was to find convenient syntheses of vanadium(III)–polydentate Schiff base complexes containing the dianions of salen (*N,N'*-ethylenebis(salicylaldiminate)), salophen (*N,N'*-*o*-phenylenebis(salicylaldiminato)), or sal-NMePr (methyliminobis(3-(salicylideneamino)propanato as ligands. Therefore, we devised three synthetic methods.

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

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

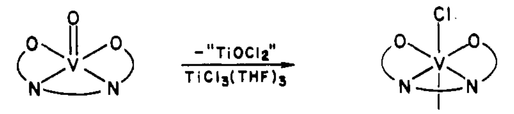
Table III. Fractional Atomic Coordinates (×10^4) for Complex IV

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
V	3907 (1)	826 (1)	2193 (1)	C8	3670 (6)	1331 (2)	4684 (3)
Cl	5677 (1)	107 (1)	3319 (1)	C9	1834 (6)	1105 (2)	4548 (4)
O1	5853 (3)	1169 (1)	1601 (2)	C10	1595 (6)	463 (2)	4101 (3)
O2	2453 (3)	1411 (1)	1321 (2)	C11	1 (5)	648 (2)	2205 (4)
N1	4259 (4)	1448 (2)	3556 (3)	C12	1555 (5)	−291 (2)	2657 (4)
N2	3352 (4)	256 (1)	757 (3)	C13	1550 (5)	−527 (2)	1433 (4)
N3	1606 (4)	381 (1)	2822 (3)	C14	3190 (5)	−402 (2)	918 (3)
C1	6287 (5)	1747 (2)	1643 (3)	C15	3029 (4)	453 (2)	−285 (3)
C2	7306 (5)	1972 (2)	835 (4)	C16	2688 (4)	1073 (2)	−616 (3)
C3	7758 (5)	2570 (2)	825 (4)	C17	2485 (5)	1219 (2)	−1810 (3)
C4	7262 (6)	2974 (2)	1634 (4)	C18	1892 (6)	1774 (2)	−2200 (3)
C5	6328 (6)	2763 (2)	2458 (4)	C19	1469 (6)	2201 (2)	−1406 (4)
C6	5812 (5)	2152 (2)	2484 (3)	C20	1673 (5)	2075 (2)	−246 (4)
C7	4966 (5)	1966 (2)	3442 (3)	C21	2312 (4)	1511 (2)	193 (3)

Table IV. Fractional Atomic Coordinates (×10^4) for Complex IX

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Zn	864 (1)	3308 (1)	3379 (2)	C11	3800 (11)	2115 (11)	−4223 (16)
V	3144 (2)	950 (2)	−1317 (3)	C12	4124 (13)	2846 (14)	−5215 (18)
Cl1	144 (3)	2524 (3)	5099 (5)	C13	5069 (14)	3383 (14)	−5023 (19)
Cl2	1051 (3)	2087 (4)	1746 (6)	C14	5778 (13)	3186 (14)	−3793 (24)
Cl3	2186 (3)	4709 (4)	4500 (5)	C15	5511 (10)	2506 (12)	−2749 (16)
O1	3490 (6)	845 (7)	848 (9)	C16	4524 (10)	1985 (12)	−2927 (17)
O2	4287 (6)	1332 (7)	−1895 (10)	C17	2304 (10)	−1586 (11)	−2531 (15)
N1	1718 (7)	426 (9)	−1289 (13)	C18	2318 (11)	−2590 (12)	−2972 (17)
N2	2401 (8)	1051 (9)	−3614 (12)	C19	3199 (13)	−2788 (13)	−2729 (18)
N3	3073 (8)	−738 (8)	−1858 (12)	C20	4015 (11)	−1916 (15)	−2052 (20)
N4	3292 (8)	2658 (9)	−707 (14)	C21	3920 (11)	−921 (13)	−1654 (18)
N5	−158 (9)	3964 (12)	2010 (16)	C22	3798 (16)	3177 (15)	679 (19)
C1	3025 (11)	135 (11)	1670 (16)	C23	3982 (15)	4269 (17)	1151 (21)
C2	3554 (10)	−157 (13)	2991 (17)	C24	3729 (14)	4915 (14)	87 (26)
C3	3041 (15)	−851 (14)	3808 (17)	C25	3149 (16)	4403 (16)	−1358 (21)
C4	2051 (13)	−1249 (14)	3373 (19)	C26	2954 (15)	3307 (13)	−1706 (18)
C5	1523 (10)	−966 (12)	2040 (18)	C27	−722 (12)	3403 (14)	629 (19)
C6	2013 (11)	−293 (12)	1147 (17)	C28	−1356 (14)	3844 (23)	−326 (23)
C7	1392 (10)	−62 (11)	−234 (17)	C29	−1389 (18)	4807 (25)	92 (29)
C8	1013 (10)	645 (12)	−2640 (17)	C30	−838 (17)	5373 (16)	1510 (28)
C9	1340 (10)	479 (11)	−4058 (15)	C31	−202 (13)	4941 (14)	2508 (21)
C10	2832 (12)	1579 (13)	−4562 (17)				

The first method uses $TiCl_3(THF)_3$ to promote a reductive deoxygenation of the corresponding oxovanadium(IV) complexes, as in reaction 1. A THF suspension of I was reacted with a THF solution of $TiCl_3(THF)_3$ and gave, upon mixing, a solution or suspension from which complex II crystallized in high yield. Since no contamination of the solid by any titanium compound was observed, this compound is presumed to be soluble under the reaction conditions. This is consistent with the little information available on the so-called oxotitanium(IV) dichloride,[24] which we have been unable to separate and identify in the solution left after the isolation of complex II.



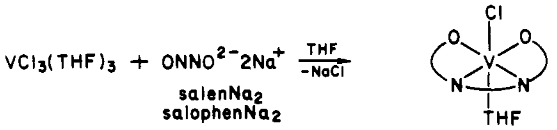
[VO(salophen)] (I)

[V(salophen)(Cl)(THF)] (II)

(1)

It should be mentioned that the occurrence of reaction 1 is dependent on the nature of the ligand around the VO^{2+} ion. When ligands other than salophen were used, compounds were isolated that are probable intermediates in the formation of the final vanadium(III) complex and different results were obtained. Reaction 1 does not seem, at present, to be a general route to vanadium(III) complexes, like II and [V(acacen)(Cl)(THF)],[7] so we pursued other synthetic approaches. The mechanism of the reductive deoxygenation of various oxo complexes by $TiCl_3{\cdot}(THF)_3$ will be discussed in a forthcoming paper.

The second synthetic method we used is reported in reaction 2. A THF solution of $VCl_3(THF)_3$ was reacted with the sodium salt of the salen or salophen ligand. Due to the low solubilities of complexes II and III, reaction 2 forms crystalline vanadium complexes that precipitate from the solution along with NaCl. NaCl was separated from the vanadium complex by a long extraction of the mixture by THF. Reaction 2 is a convenient synthesis when the final complex is soluble in THF, when the corresponding vanadyl complex is not available, or when the lithium salts of the Schiff base are employed, since LiCl is somewhat soluble in THF.[25] A significant difference between reactions 1 and 2 arises when we deal with bidentate ligands, since then we expect that 2 will lead, mainly, to the tris derivative, while reaction 1 will produce the bis monochloro derivative.



[V(salophen)(Cl)(THF)] (II)
[V(salen)(Cl)]$_2$ (III)

(2)

Complexes II and III are paramagnetic, having two unpaired electrons, as expected for a d^2 configuration in a pseudooctahedral geometry. The structure proposed for II and III is based on an X-ray analysis carried out on complex II.

The structure of complex II consists of discrete [V(salophen)(Cl)(THF)] molecules (Figure 1). Coordination of salophen to vanadium is not strictly planar; the four coordinating atoms

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[24] Beattie, I. R.; Fawcett, V. *J. Chem. Soc. A* **1967**, 1583–1586. Dehnicke, K. *Z. Anorg. Allg. Chem.* **1961**, *308*, 266–275.

[25] Mazzanti, M.; Floriani, C., observations made on the synthesis of analogues Schiff base complexes, unpublished results.

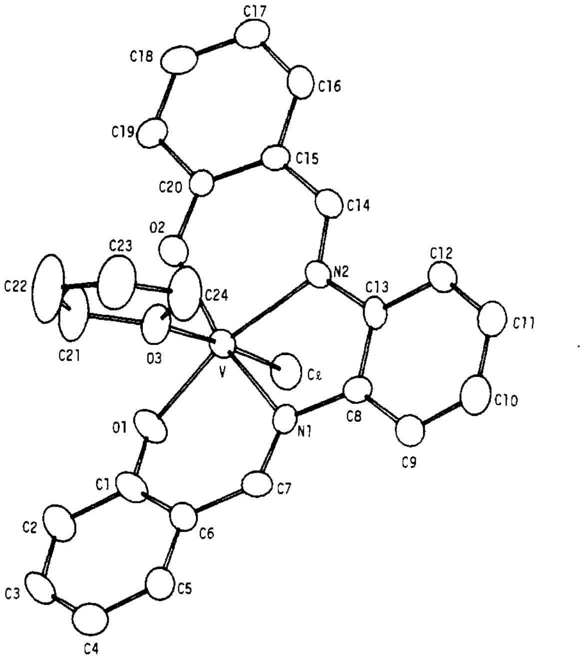


Figure 1. ORTEP drawing of [V(salophen)(Cl)(THF)] (II) (30% probability ellipsoids).

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex II

V–O1	1.909 (6)	V–O2	1.894 (8)
V–N1	2.084 (8)	V–N2	2.109 (7)
V–O3	2.155 (6)	V–Cl	2.373 (3)
O1–C1	1.34 (1)	O2–C20	1.32 (1)
N1–C7	1.31 (1)	N2–C14	1.30 (1)
N1–C8	1.43 (1)	N2–C13	1.44 (1)
C1–C6	1.42 (2)	C15–C20	1.40 (1)
C6–C7	1.42 (1)	C14–C15	1.44 (1)
C8–C13	1.39 (1)		
O1–V–N1	89.7 (3)	O2–V–N2	87.4 (3)
O1–V–O2	105.8 (3)	N1–V–N2	77.6 (3)
O3–V–Cl	175.4 (2)		
V–O1–C1	128.5 (6)	V–O2–C20	132.0 (6)
V–N1–C8	115.9 (5)	V–N2–C13	115.2 (5)
V–N1–C7	122.8 (7)	V–N2–C14	124.1 (6)
V–O3–C21	120.9 (7)	V–O3–C24	126.1 (7)

are tetrahedrally displaced from the mean coordination plane [O1, 0.126 (7) Å; O2, –0.128 (7) Å; N1, –0.168 (7) Å; N2, 0.171 (7) Å; V, 0.108 (2) Å]. A chlorine atom and oxygen atom from a THF molecule complete the coordination polyhedron to form a distorted octahedron elongated along the O(THF)–V–Cl direction. Bond distances and angles within the V(salophen) (Table V) unit are similar to those found in $[(VO(salen))_2Na]^+$[26] except for a great enlargement of the O1–V–O2 angle [105.8 (3)° vs. 85.8 (1)°] and a small but significant lengthening of the V–N distances [2.098 (10) Å vs. 2.044 (5) Å, mean values]. It shows a distorted "umbrella" conformation: the dihedral angle between the mean planes through the two salicylideneamine residues is 16.2 (2)°, and the angles that these planes form with the coordination plane are 24.3 (2) and 12.8 (2)°.[27] The *N*,*N'*-*o*-phenylene moiety is nearly parallel to the coordination plane, the dihedral angle they form being 6.8 (1)°.

The V–O(THF) distance [2.155 (6) Å] is significantly longer than the V–O distances involving salophen [V–O1, 1.909 (6) Å; V–O(2), 1.894 (8) Å], but the V–Cl bond length [2.373 (3) Å] agrees with other V–Cl bond distances.[15a] The directions of the V–O and V–Cl bonds are nearly perpendicular to the coordination plane [dihedral angles 85.3 (2) and 88.8 (1)°, respectively]. The coordinating THF molecule shows an envelope conformation [C_s(C24) = 0.011 (7)].[28] The THF-free molecule, as revealed by the X-ray analysis, has a skew conformation [C_2(O4) = 0.004 (14)],[28] and both THF molecules appear to be affected by high thermal motion.

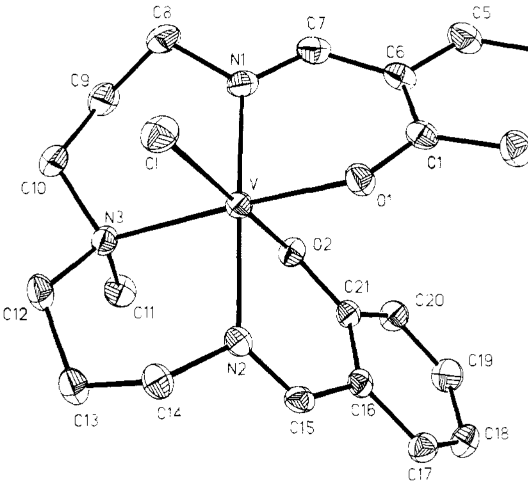
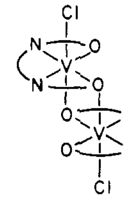


Figure 2. ORTEP drawing of [V(sal-NMePr)(Cl)] (IV).

Table VI. Selected Bond Distances (Å) and Angles (deg) for Complex IV

V–O1	1.934 (3)	V–O2	1.928 (3)
V–N1	2.092 (4)	V–N2	2.093 (4)
V–N3	2.285 (4)	V–Cl	2.391 (2)
O1–C1	1.325 (5)	O2–C21	1.322 (4)
N1–C7	1.292 (6)	N2–C15	1.282 (5)
N1–C8	1.478 (5)	N2–C14	1.478 (5)
N3–C10	1.503 (5)	N3–C12	1.501 (5)
N3–C11	1.495 (5)		
C1–C6	1.418 (6)	C16–C21	1.413 (6)
C6–C7	1.441 (6)	C15–C16	1.442 (6)
N1–V–O2	87.9 (2)	N2–V–Cl	94.5 (1)
O2–V–N2	86.6 (1)	N1–V–Cl	90.9 (1)
O1–V–O2	89.9 (1)	N3–V–O1	177.0 (1)
N1–V–N2	174.3 (2)	O2–V–C1	178.5 (1)
V–O1–C1	125.7 (3)	V–O2–C21	126.7 (2)
V–N1–C7	121.4 (3)	V–N2–C15	122.9 (3)
V–N1–C8	122.3 (3)	V–N2–C14	120.4 (3)
C7–N1–C8	116.3 (4)	C14–N2–C15	116.5 (3)
V–N3–C10	112.4 (2)	V–N3–C12	113.3 (3)
V–N3–C11	110.0 (2)	C10–N3–C11	107.9 (3)
C10–N3–C12	104.1 (3)	C11–N3–C12	109.0 (3)

It is important that for all the vanadium(III) Schiff base complexes we studied, the metal achieves hexacoordination exclusively. This enables us to suggest that complex III, which does not contain any molecule of solvent, has the dimeric structure shown. Further support for this structure for III is given by the



$[V(salen)(Cl)]_2$ (III)

very similar structure found for the vanadium(III)–Schiff base derivative $[V(acacen)(CH_2Ph)]_2$ [acacen = *N*,*N'*-ethylenebis(acetylacetone iminato)].[7]

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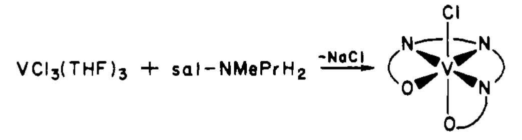
(26) Pasquali, M.; Marchetti, F.; Floriani, C.; Cesari, M. *Inorg. Chem.* **1980**, *19*, 1198–1202.

(27) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385–403. Hobday, M. D.; Smith, T. D. *Ibid.* **1972–1973**, *9*, 311–337.

(28) Nardelli, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 1141–1142.

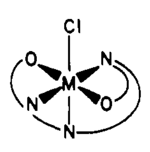
Vanadium(III) achieves hexacoordination either by the intervention of a solvent molecule or by sharing an oxygen of the Schiff base ligand, unless the Schiff base provides five donor atoms to the metal, as for complex IV (reaction 3). The synthesis of



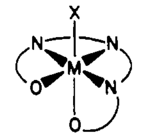
(3)

IV

IV was carried out as reported for reaction 2. Analytical data for IV are given in the Experimental Section, while the structure is reported in Figure 2 and the related bond distances and angles in Table VI. The two chelate rings V, N1, C8, C9, C10, N3 and V, N3, C12, C13, C14, N2 have a chair conformation, the first one being less puckered than the second one, as shown by the torsional angle within them (Table SIX) and the displacement of vanadium from the planes N1, C8, C10, N3 and N3, C12, C14, N2), which is 0.569 (2) and −1.083 (1) Å, respectively (Table SVIII). Different conformations of the pentadentate ligand have been found in bromo(iminobis(3-(salicylideneamino)-propanato))(1-methylimidazole)cobalt(III) (A)[29] and (μ-peroxo)bis[iminobis(3-(salicylideneamino)propanato)cobalt(III)] (B).[29] Very recently a reported appeared, dealing with vanadium(III) pentadentate-related ligands. Conformation A was suggested for those complexes,[17] while the X-ray analysis showed that our ligand has the conformation reported in B.

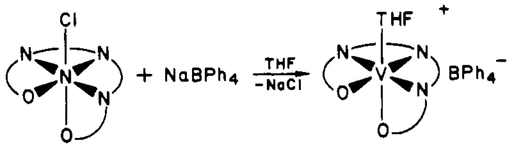


A



B

Compound IV has a coordination site that can be made free via the ionization of the V–Cl bond. Such a reaction was performed by adding $NaBPh_4$ to a THF suspension of complex IV.



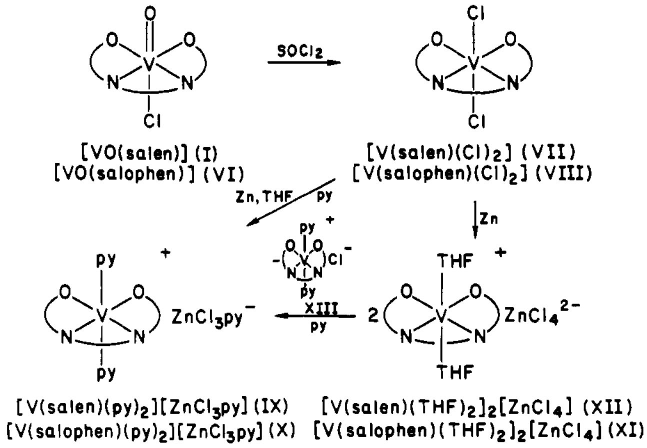
(4)

IV V

Complex V has been isolated as crystalline orange solid. The suggested structure is based on that of its precursor, IV, in which Cl^- has been replaced by a THF molecule. The easy ionization of the V–Cl bond was observed in related chloro(pentadentate ligand)vanadium(III) complexes recently reported.[17] Complex V may be an interesting model compound, having a labile ligand, which can be replaced by a small molecule. With respect to this, a very similar cationic complex, i.e. $[V(salen)(py)(L)]^+$, was suggested to bind dioxygen.[4]

We took advantage of the deoxygenation reaction with $SOCl_2$ to produce complexes VII and VIII from the corresponding vanadyl compound (Scheme I).[15] Reduction of VII and VIII with zinc dust in THF gave vanadium(III) complexes selectively. We were able to isolate the crystalline compounds, IX and X, by adding a small amount of pyridine to the THF solution. Isolation of a crystalline compound from THF was successful only for the salophen ligand, complex XI. The corresponding salen derivative, XII, was impossible to recover from solution, because of its high solubility. The analysis and spectroscopic properties of compound XI are consistent with the proposed formula, and its structure is strictly related to that of IX, which was determined by X-ray analysis. The pyridine replaces THF and promotes the transformation of $ZnCl_4^{2-}$ into $[ZnCl_3py]^-$, which makes complexes IX and X significantly less soluble. We must admit at the same time that complex XIII, which never contaminated our solid, remained in solution.

Scheme I



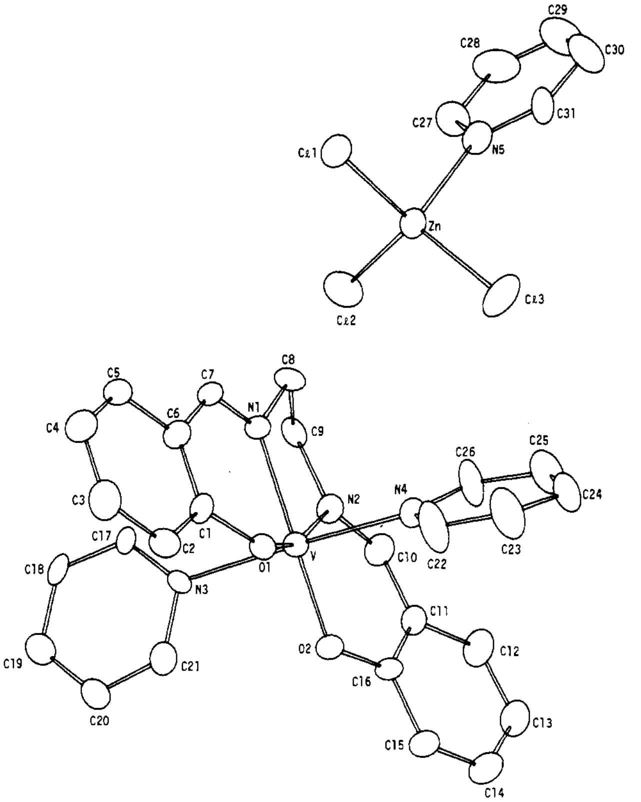


Figure 3. ORTEP projection of the cation and anion in $[V(salen)(py)_2][ZnCl_3py]$ (IX).

The structure we proposed for complexes IX and X is based on a single-crystal X-ray study carried out on complex IX. The paramagnetism found for complexes VIII and IX is very close to the spin only values expected for a d^2 configuration (see Experimental Section).

The literature reports an alternative synthesis of complexes related to II, IX, and X, carried out by reacting VCl_3 with the corresponding Schiff base in presence of pyridine (py).[16] The problems associated with this synthesis are the contamination of the product by some $C_5H_5N{\cdot}HCl$ and the production of the two solvated compounds, [V(chel)(Cl)(py)] and $[V(chel)(Cl)(py)_2]$ (chel = salen, salophen), which contain pyridine, a molecule difficult to deal with in reduction or alkylation reactions. These compounds are conducting in solution, and this seems to suggest ionic forms such as $[V(chel)(py)_2]^+$, which have been not conclusively excluded or confirmed even in the solid state. The syntheses of compounds II and IX and their structural identifi-

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(29) Kistenmacher, T. J.; Marzilli, L. G.; Marzilli, P. A. *Inorg. Chem.* **1974**, *13*, 2089–2093.

Table VII. Selected Bond Distances (Å) and Angles (deg) for Complex IX

V–O1	1.915 (9)	V–O2	1.88 (1)
V–N1	2.08 (1)	V–N2	2.12 (1)
V–N3	2.18 (1)	V–N4	2.18 (1)
O1–C1	1.37 (2)	O2–C16	1.35 (2)
N1–C7	1.30 (2)	N2–C10	1.32 (2
N1–C8	1.50 (2)	N2–C9	1.49 (2)
C1–C6	1.40 (2)	C11–C16	1.43 (2)
C6–C7	1.46 (2)	C11–C10	1.37 (2)
C8–C9	1.52 (2)		
O1–V–N1	86.7 (4)	O2–V–N2	87.6 (4)
O1–V–O2	107.6 (4)	N1–V–N2	78.5 (5)
N3–V–N4	177.1 (5)		
V–O1–C1	130.5 (8)	V–O2–C16	128.8 (9)
V–N1–C8	114.9 (9)	V–N2–C9	113.7 (8)
V–N1–C17	126.8 (10)	V–N2–C10	123.3 (10)
V–N3–C17	128.2 (10)	V–N4–C22	120.6 (11)
V–N3–C21	116.2 (9)	V–N4–C26	125.5 (10)
C17–N3–C21	115.1 (12)	C22–N4–C26	113.7 (14)
Zn–Cl1	2.258 (5)	Zn–Cl3	2.221 (4)
Zn–Cl2	2.234 (6)	Zn–N5	2.13 (1)
Cl1–Zn–Cl2	112.4 (2)	Cl2–Zn–Cl3	114.8 (2)
Cl1–Zn–Cl3	112.5 (2)	Cl2–Zn–N5	105.7 (4
Cl1–Zn–N5	104.0 (4)	Cl3–Zn–N5	106.4 (4)
Zn–N5–C27	118.4 (12)	C27–N5–C31	121.4 (15)
Zn–N5–C31	120.0 (12)		

cation reported here have solved some of the problems associated with the nature of the compounds from the alternative synthesis reported years ago.[16] The structure of complex IX consists of discrete $[V(salen)(py)_2]^+$ cations and $[ZnCl_3(py)]^-$ anions separated by van der Waals contacts (Figure 3). As observed in complex II, the four coordinating atoms of the Schiff base are tetrahedrally displaced from the mean coordination plane [O1, –0.048 (9) Å; O2, 0.048 (9) Å; N2, –0.092 (11) Å; N1, 0.092 (11) Å; V, –0.004 (3) Å]. Two nitrogen atoms from two pyridine molecules, mutually *trans*, complete the coordination polyhedron to form a slightly elongated distorted octahedron, the V–N(py) distances [mean value 2.18 (1) Å] being significantly longer than the V–N(salen) distances [mean value 2.10 (1) Å].

Bond distances and angles within the V(salen) unit (Table VII) are similar to those found in complex II, showing the same enlargement of the O1–V–O2 angle [107.6 (4)°] and lengthening of the V–N distances. The five-membered chelation ring (VN_2C_2) has a skew conformation; the two atoms of the ethylene bridge (C8 and C9) are displaced by 0.32 (1) Å on opposite sides of the VNN plane. The torsion angle around the C8–C9 bond is –46 (1)°. The two six-membered chelation rings ($VONC_3$) have the same twist conformation with a twofold axis running through the vanadium–oxygen bond, as indicated by the asymmetry parameters [C_2(O1–V) = 0.021 (4), C_2(O2–V) = 0.027 (5)].[28] The two halves of salen have the same geometry and are related by a pseudotwofold axis running through vanadium and the middle point of the C8–C9 bond. Bond distances and angles agree well with those found in other M(salen) complexes.[27] The configuration of the V(salen) moiety is stepped: the dihedral angle between the planes defined by the two salicylideneamine residues is 4.3 (3)° and those that these planes form with the coordination plane are 25.1 (2) and 23.6 (3)°.

The two pyridine rings are planar, and vanadium is 0.204 (3) and 0.243 (3) Å, respectively, out of the planes through N3–C17···C21 and N4–C22···C26. The dihedral angle that they form is 58.3 (7)°.

The three Cl atoms and the N5 atoms form a distorted tetrahedral arrangement around the zinc atom (Figure 3). The Zn–Cl distances [mean value 2.238 (5) Å] are in agree with those found in trichloro[*N*-(4′-pyridyl)-4-ethoxypyridinium]zinc(II) [2.243 (4) Å][30] and are at the short end of the range observed in the $[ZnCl_4]^{2-}$ ion, e.g. 2.223 (5)–2.290 (4) Å[31] and 2.229 (1)–2.298 (1) Å.[32] The Zn–N distance [2.13 (1) Å] is somewhat longer than that observed in the complex cited above [2.055 (8) Å]. The metal atom lies 0.144 (2) Å out of the planar pyridine ring. The Cl–Zn–N angles are smaller than tetrahedral, while the Cl–Zn–Cl angles are larger, probably as a consequence of the nonbonded Cl···Cl contacts.

Complexes derived from reactions in Scheme I, although they are new and interesting in vanadium chemistry, are not very useful as starting materials mainly because of their ionic form and the presence of $ZnCl_2$-derived species. Complexes II and III, on the other hand, have already been found to be very useful starting materials for the generation of organometallic derivatives of vanadium(III)[7] and in reduction reactions leading to polyfunctional complexes of vanadium.[33]

Acknowledgment. We thank the NSF (Grant CHE-8512660) and MPI (Rome).

Registry No. I, 32065-17-1; II·THF, 102340-21-6; III, 102261-16-5; IV, 102261-17-6; V, 102261-19-8; VII, 70629-75-3; VIII, 70681-03-7; IX, 102261-23-4; X, 102261-25-6; XI, 102261-21-2; $TiCl_3(THF)_3$, 18039-90-2; $VCl_3(THF)_3$, 19559-06-9; Zn, 7440-66-6.

Supplementary Material Available: Listings of hydrogen coordinates (Tables SI–III), thermal parameters (Tables SIV–SVI), nonessential bond distances and angles (Table SVII), and least-squares planes (Table SVIII) for complexes II, IV, and IX and selected torsion angles for complex IV (Table SIX) (12 pages). Ordering information is given on any current masthead page.

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