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Deoxygenation of Oxovanadium(IV) Complexes: A Novel Synthetic Route to Dichlorovanadium(IV) Chelate Complexes

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Oxovanadium(IV) chelate complexes of the type VO(chel)$_2$ [where chel = acac, oxine, sal-*N*-R, $^1/_2$salen] react under mild conditions with SOCl$_2$ in benzene to produce the much more reactive V(chel)$_2$Cl$_2$ hexacoordinate vanadium(IV) complexes. The same deoxygenation reaction could be accomplished in dioxane by PCl$_5$, which is even more reactive than SOCl$_2$. The coordination geometry was established by an X-ray analysis carried out on V(sal-*N*-Bu)$_2$Cl$_2$. The monomeric vanadium complex has C_i symmetry, so the two chlorines are mutually trans, as are the two oxygen and the two nitrogen atoms. The V–N and V–O bond distances resemble those found in oxovanadium(IV) complexes containing similar ligands and suggest a metal–ligand π-bonding interaction. Crystallographic details for V(sal-*N*-Bu)$_2$Cl$_2$·C$_6$H$_6$: space group $P2_1/c$ (monoclinic); a = 12.415 (4), b = 14.073 (5), c = 8.351 (3) Å; β = 103.86 (9)°; V = 1416 Å^3; Z = 2. The final R factor is 4.8% for 1186 observed reflections.

Introduction

Vanadium(IV) coordination chemistry is restricted to that of the VO^{2+} unit, which remains intact during many reactions.[1] Moreover, the reactivity of oxovanadium(IV) complexes is rather poor, whereas a higher reactivity is expected for vanadium in a lower oxidation state and for the case where the V=O unit is not present. Although easy to synthesize, oxovanadium(IV) complexes do not represent the appropriate source for complexes containing vanadium in an oxidation state different from +4, since they are hardly oxidized or reduced by means of chemical reagents. In spite of these synthetic difficulties, at present much interest is focused on vanadium chelate redox chemistry, for which model compounds are not so far available.[2]

Cobalt and iron chelate chemistry suggests that the presence of suitable polydentate unsaturated ligands around the metal would stabilize a wide range of interrelated oxidation states.[3] Actually, it was reported that [V(salen)]$^+$ is an oxygen carrier complex;[4] the 8-quinolinato ligand is known to stabilize the +4 as well as the +5 oxidation state for vanadium;[5,6] and the reversible fixation of O$_2$, CO, and NO was found to occur on bis(3,5-di-*tert*-butylcatecholato)vanadium(IV).[7]

This report concerns a facile conversion of VO(chel)$_2$ into V(chel)$_2$Cl$_2$ complexes where [chel = acac, oxine, sal-*N*-R, $^1/_2$salen] showing that the classic statment concerning the low reactivity of the VO^{2+} must be revised.[1] These easily available materials would be appropriate compounds for alkylation, reduction, and substitution reactions. Besides this, they represent d^1 hexacoordinate coordination models for ESR studies. A brief account of a part of this work was previously reported.[8]

Experimental Section

All the syntheses were carried out in an atmosphere of dry oxygen-free nitrogen and in carefully dried solvents. The synthesis of all oxovanadium(IV) Schiff base complexes was performed by the reported procedures.[9] The synthesis of bis(pentane-2,4-dionato)oxovanadium(IV), VO(acac)$_2$, was carried out as reported in the literature,[10] while a new synthetic procedure was employed for the synthesis of bis(8-quinolinato)oxovanadium(IV), VO(Ox)$_2$.[6] IR spectra were recorded on a Perkin-Elmer 337 spectrophotometer and magnetic susceptibility measurements were made with a Gouy balance. Two typical syntheses using SOCl$_2$ are described in detail, the preparation of the other complexes being carried out under very similar conditions. The analytical, magnetic, and IR data obtained for all of the compounds reported here are summarized in Table I.

Bis[*N*-*n*-butyl(salicylideniminato)]dichlorovanadium(IV), V(sal-*N*-Bu)$_2$Cl$_2$. Bis[*N*-*n*-butyl(salicylideniminato)]oxovanadium(IV) (2.10 g, 5.08 mmol) was dissolved in dry benzene (50 mL). By addition of SOCl$_2$ (0.5 mL, 6.95 mmol) the color of the solution immediately turned from red-maroon to blue; then green-blue crystals of bis[*N*-*n*-butyl(salicylideniminato)]dichlorovanadium(IV) started to precipitate. The green-blue solid was filtered off and dried in vacuo (2.5 g, 95% yield). It was shown to contain a benzene of crystallization (Table I). The complex, when recrystallized from dry acetone, was recovered as V(sal-*N*-Bu)$_2$Cl$_2$, without solvent.

[*N*,*N'*-Ethylenebis(salicylideniminato)]dichlorovanadium(IV), V(salen)Cl$_2$. Method A. To a benzene (100 mL) suspension of [*N*,*N'*-ethylenebis(salicylideniminato)]oxovanadium(IV), VOsalen (2.1 g, 6.30 mmol), was added SOCl$_2$ (0.53 mL, 7.22 mmol). No reaction was observed at room temperature. The suspension was refluxed for 30 min, when a new crystalline deep blue solid appeared. This was filtered off and washed with dry benzene (2.1 g, 86% yield). The same procedure was employed for V(sal-*o*-ph)Cl$_2$.

Method B. A toluene (40 mL) solution of VCl$_4$ (5 ml, 47.12 mmol) was added to THF (200 mL) containing salenH$_2$ (13 g, 48.5 mmol). A green crystalline solid rapidly formed, which was converted into the final crystalline blue solid, refluxing the suspension for 20 h and partially distilling off THF in order to eliminate HCl. The solid was filtered off and washed with THF (15.4 g, 84% yield).

Method C. A 1,4-dioxane (50 mL) suspension of VO(salen) (1.1 g, 3.30 mmol) when reacted with PCl$_5$ (1.03 g, 4.95 mmol) immediately gave the final V(salen)Cl$_2$ (1.15 g, 90% yield). The final V(salen)Cl$_2$ may contain variable amounts of dioxane.

Crystal Structure Determination of V(salen-*N*-Bu)$_2$Cl$_2$. Data Collection. Some crystals of V(salen-*N*-Bu)$_2$Cl$_2$ were sealed in Lindemann capillaries under nitrogn atmosphere. Unit cell dimensions and symmetry were estimated from rotation, Weissenberg, and precession photographs by using Cu Kα radiation, λ 1.54178 Å. The space group was $P2_1/c$ from systematic absences. A single crystal of roughly prismatic shape (dimensions 0.12 × 0.20 × 0.35 mm) mounted on a Philips PW 1100 four-circle diffractometer, employing graphite-monochromatized Mo Kα radiation (λ 0.71069 Å), was used for intensity data collection. The unit cell dimensions were accurately determined by a least-squares procedure using the values of the setting angles of 25 strong reflections. The θ–2θ scan technique to a limit of 2θ = 50° was adopted. Each reflection was measured with a scan width of 1.2° and a scan speed of 0.05° s^{-1} and two background measurements for 10 s of each side of the reflection. Three reflections were monitored after every 180 min, and no detectable decay in intensities was observed. Among the 3776 available reflections, 1299 were discarded, as they had $I_{top} - 2I_{top}^{1/2} < I_{back}$, with I_{top} and I_{back} indicating peak intensity and background intensity, respectively. A total of 1477 independent reflections were collected, 1186 having intensity $I > 3\sigma(I)$. Structure amplitudes were corrected for Lorentz and polarization effects; absorption corrections seemed to be unnecessary. Crystal data are displayed in Table II.

Solution and Refinement of the Structure. The structure was solved by using standard Fourier and least-squares refinement procedures.[11] The function $\sum w(|F_o| - |F_c|)^2$ was minimized where $|F_o|$ and $|F_c|$ are observed and calculated structure factor amplitudes, respectively. The atomic scattering factors were taken from ref 12. The Patterson function located the Cl atom relative to the vanadium atom which was placed at 0.5, 0.5, 0.5. Two successive Fourier maps revealed the position of all the nonhydrogen atoms. Two least-squares refinement cycles gave $R_1 = \sum[|F_o| - |F_c|]/F_o$ = 0.099 and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ = 0.110, where $w = 1/\sigma^2$.

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Table I. Analytical,[a] Magnetic, and IR Data

compd	% C	% H	% N	% Cl	μ_{eff}(293 K), μ_B	ν(C=N),[f,g] cm^{-1}
V(acac)$_2$Cl$_2$ (I)	37.17 (37.50)	4.35 (4.38)		22.40 (22.19)		
V(Ox)$_2$Cl$_2$ (II)	52.03 (52.70)	3.20 (2.93)	6.35 (6.83)	17.50 (17.30)	1.72	
V(sal-*N*-Bu)$_2$Cl$_2$[b] (III)	55.35 (55.71)	6.07 (5.90)	5.93 (5.90)	14.68 (14.96)	1.77	1630
V(sal-*N*-Bu)$_2$Cl$_2$·C$_6$H$_6$ (III)	60.70 (60.88)	6.10 (6.17)	5.12 (5.07)	12.72 (12.85)		
V(sal-*N*-CH$_2$Ph)$_2$Cl$_2$[c] (III)	62.10 (62.00)	4.50 (4.42)	5.10 (5.17)	12.86 (13.08)	1.73	1620
V(sal-*N*-Ph)$_2$Cl$_2$ (III)	61.00 (60.72)	4.22 (3.89)	5.25 (5.44)	14.20 (13.80)	1.72	1610
V(sal-*N*-C$_6$H$_4$Cl-4)$_2$Cl$_2$ (III)	54.10 (53.53)	3.70 (3.08)	4.72 (4.80)	24.20 (24.33)	1.79	1645
V(sal-*N*-C$_6$H$_4$NO$_2$-4)$_2$Cl$_2$[c] (III)	51.80 (51.68)	3.20 (2.98)	9.10 (9.27)	11.60 (11.74)	1.75	1640
V(salen)Cl$_2$[d] (IV)	49.40 (49.51)	3.60 (3.61)	7.36 (7.22)	18.20 (18.28)		
V(salen)Cl$_2$[e] (IV)	49.70 (49.51)	3.70 (3.61)		18.50 (18.28)	1.69	1605
V(sal-*o*-ph)Cl$_2$[c] (IV)	55.30 (55.06)	3.52 (3.21)	6.71 (6.42)	16.00 (16.26)	1.74	1595

[a] Calculated figures in parentheses. [b] Recrystallized from acetone. [c] The crystals contain C$_6$H$_6$ which is eliminated by heating. [d] From VO(salen). [e] From VCl$_4$. [f] Nujol mulls. [g] Multiple bands of the C=N imino group centered at the reported value.

Table II. Crystal Data for VCl$_2$(sal-*N*-Bu)$_2$·C$_6$H$_6$

C$_{22}$H$_{28}$N$_2$O$_2$Cl$_2$V·C$_6$H$_6$	β = 103.86 (9)°
mol wt 552.4	V = 1416 (1) Å^3
monoclinic *P*2$_1$/*c*	μ(Mo Kα) = 5.85 cm^{-1}
a = 12.415 (4) Å	*Z* = 2
b = 14.073 (5) Å	D_{calcd} = 1.295 g cm^{-3}
c = 8.351 (3) Å	

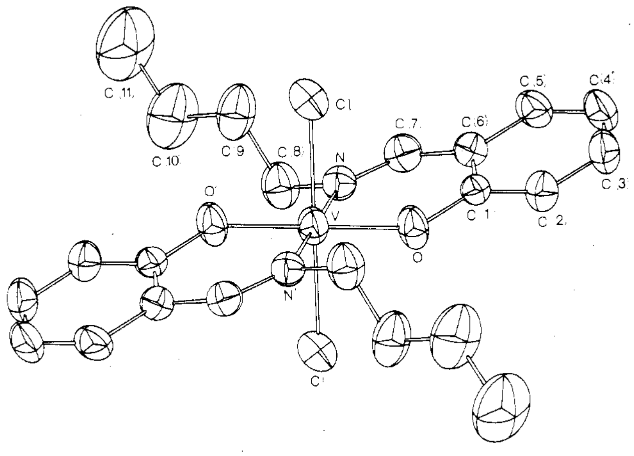


Figure 1. An ORTEP view of the complex V(sal-*N*-Bu)$_2$Cl$_2$ showing the atomic numbering scheme.

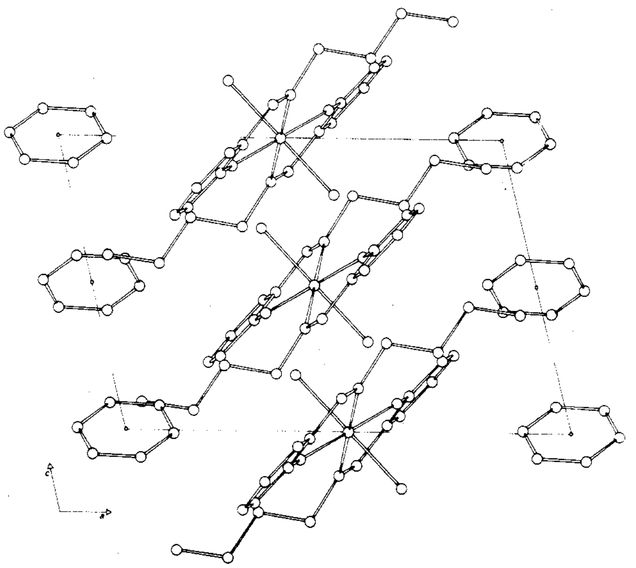


Figure 2. Molecular packing for V(sal-*N*-Bu)$_2$Cl$_2$ as viewed along *b*.

Two full-matrix cycles on all nonhydrogen atoms using individual anisotropic thermal parameters for V, Cl, N, and O atoms and isotropic for carbon atoms gave R_1 = 0.072 and R_2 = 0.080. The hydrogen atom positions were calculated and they were added as fixed contributions to the structure, with values of isotropic thermal factors like those of the bonded carbon atoms. Three other full-matrix cycles were performed attributing anisotropic thermal factors to C atoms. A final cycle gave R_1 = 0.047 and R_2 = 0.048 with 1186 observed reflections and 160 variables. All shifts were less than half of one standard deviation and a subsequent difference Fourier map did not reveal peaks larger than 0.2 e/Å^3.

Final atomic positional and anisotropic thermal parameters with their estimated standard deviations are given in Table III. The

Table III. Final Atomic Positional and Anisotropic Temperature Parameters (× 10^4)[a]

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	0.5000 (0)	0.5000 (0)	0.5000 (0)	48 (1)	29 (1)	159 (3)	5 (1)	5 (1)	1 (1)
Cl	0.5902 (1)	0.5656 (1)	0.3080 (2)	78 (1)	44 (1)	201 (3)	6 (1)	31 (1)	18 (1)
O	0.3757 (2)	0.5644 (2)	0.4024 (4)	53 (3)	30 (2)	175 (7)	1 (2)	−9 (3)	−6 (4)
N	0.5446 (3)	0.6204 (2)	0.6489 (5)	54 (3)	37 (3)	139 (9)	−1 (2)	16 (5)	1 (4)
C(1)	0.3458 (3)	0.6561 (3)	0.3778 (6)	49 (4)	30 (3)	140 (11)	5 (3)	36 (5)	11 (5)
C(2)	0.2516 (4)	0.6795 (3)	0.2567 (6)	48 (4)	56 (4)	158 (12)	7 (3)	14 (6)	22 (6)
C(3)	0.2215 (4)	0.7744 (4)	0.2329 (7)	63 (5)	63 (4)	179 (13)	24 (4)	21 (6)	35 (6)
C(4)	0.2849 (5)	0.8448 (3)	0.3266 (8)	93 (6)	38 (4)	219 (15)	21 (4)	44 (8)	27 (6)
C(5)	0.3776 (4)	0.8218 (3)	0.4472 (6)	80 (5)	31 (3)	187 (13)	3 (3)	50 (7)	5 (5)
C(6)	0.4099 (3)	0.7263 (3)	0.4760 (6)	51 (4)	38 (3)	137 (11)	5 (3)	30 (6)	7 (5)
C(7)	0.5007 (4)	0.7036 (3)	0.6139 (6)	61 (4)	39 (3)	132 (11)	−2 (3)	26 (6)	−9 (5)
C(8)	0.6330 (4)	0.6128 (3)	0.8051 (6)	65 (5)	52 (4)	155 (12)	3 (3)	−11 (6)	−9 (5)
C(9)	0.7451 (4)	0.6372 (4)	0.7753 (7)	69 (5)	78 (5)	229 (15)	3 (4)	−9 (8)	−23 (7)
C(10)	0.8375 (5)	0.6231 (5)	0.9301 (9)	81 (6)	126 (7)	305 (19)	−5 (5)	−38 (9)	−33 (9)
C(11)	0.9498 (6)	0.6453 (6)	0.9040 (11)	95 (7)	145 (8)	487 (27)	−13 (6)	−44 (11)	−37 (12)
C(12)	0.9126 (5)	0.5546 (5)	0.4158 (8)	74 (6)	84 (5)	261 (16)	−8 (5)	32 (8)	−18 (8)
C(13)	0.8930 (4)	0.4799 (5)	0.5085 (9)	78 (6)	73 (5)	248 (16)	−22 (4)	52 (8)	−43 (7)
C(14)	0.9799 (6)	0.4252 (4)	0.5927 (8)	101 (7)	73 (5)	256 (16)	−15 (5)	60 (9)	3 (7)

[a] The temperature factors are of the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$. Estimated standard deviations are in parentheses.

Table IV. Interatomic Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations in Parentheses

(a) Coordination Polyhedron			
V–Cl	2.354 (2)	Cl–V–O	89.5 (1)
V–O	1.807 (3)	Cl–V–N	89.2 (1)
V–N	2.096 (4)	O–V–N	86.5 (1)
		O–V–N[a]	93.5 (1)
(b) sal-*N*-Bu			
O–C(1)	1.345 (6)	V–O–C(1)	136.4 (3)
C(1)–C(2)	1.390 (6)	O–C(1)–C(2)	119.5 (4)
C(1)–C(6)	1.404 (7)	O–C(1)–C(6)	119.3 (4)
C(2)–C(3)	1.389 (8)	C(2)–C(1)–C(6)	121.2 (4)
C(3)–C(4)	1.384 (8)	C(1)–C(2)–C(3)	118.9 (5)
C(4)–C(5)	1.375 (8)	C(2)–C(3)–C(4)	120.7 (5)
C(5)–C(6)	1.405 (7)	C(3)–C(4)–C(5)	120.6 (5)
C(6)–C(7)	1.441 (6)	C(4)–C(5)–C(6)	120.3 (5)
C(7)–N	1.295 (6)	C(5)–C(6)–C(1)	118.3 (4)
C(8)–N	1.493 (6)	C(5)–C(6)–C(7)	119.0 (4)
C(8)–C(9)	1.511 (9)	C(1)–C(6)–C(7)	122.4 (4)
C(9)–C(10)	1.522 (9)	C(6)–C(7)–N	126.0 (4)
C(10)–C(11)	1.494 (11)	C(7)–N–V	124.0 (3)
		C(7)–N–C(8)	116.3 (4)
		C(8)–N–V	119.6 (3)
		C(9)–C(8)–N	110.7 (5)
		C(8)–C(9)–C(10)	111.5 (6)
		C(9)–C(10)–C(11)	112.9 (7)

[a] $1-x, 1-y, 1-z$.

molecular structure of $V(sal\text{-}N\text{-}Bu)_2Cl_2$ is shown in Figure 1. Figure 2 shows the packing of the molecules in the unit cell viewed along the *b*-axis direction. Table IV reports a listing of bond distances and angles in $V(sal\text{-}N\text{-}Bu)_2Cl_2$.

Results and Discussion

A benzene solution or suspension of an oxovanadium(IV) chelate complex, $VO(chel)_2$ [where chel = acetylacetonato anion, acac; 8-quinolinato anion, oxine, Ox; N-substituted salicylideniminato anion, sal-*N*-R; *N,N′*-ethylenebis(salicylideniminato) anion, salen; *N,N′*-*o*-phenylenebis(salicylideniminato) anion, sal-*o*-ph], reacts with $SOCl_2$ producing the corresponding dichloro complexes, $V(chel)_2Cl_2$, I–IV (eq 1).

$$VO(chel)_2 + SOCl_2 \rightarrow \underset{\text{I-IV}}{V(chel)_2Cl_2} + SO_2 \tag{1}$$

I, chel = acac

II, chel = Ox

III, chel = sal-*N*-R
  [R = *n*-Bu, Ph, $PhCH_2$, $C_6H_4Cl\text{-}4$, $C_6H_4NO_2\text{-}4$]

IV, $(chel)_2$ = salen, sal-*o*-ph

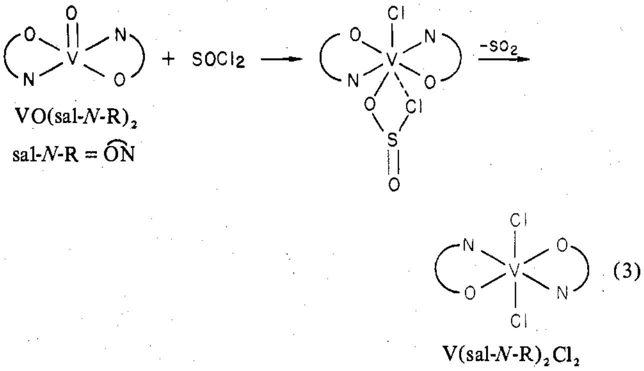
While complexes I–III are formed very easily in reaction 1 at room temperature and in a few minutes, rather more drastic conditions were required for IV. Moreover, the (phthalocyaninato)oxovanadium(IV) complex is not deoxygenated even when refluxed for several hours in benzene containing an excess of $SOCl_2$. Both PCl_5 and $COCl_2$ can be used in benzene solution to realize reaction 1. PCl_5 deoxygenates complexes IV much more easily than $SOCl_2$ does.

While the reaction of $SOCl_2$ with metal oxides producing anhydrous metal chlorides is a classic procedure in inorganic chemistry,[13] its extension to convert oxocation complexes into the corresponding dichloro complexes should represent a useful synthetic route in coordination chemistry, since the synthesis of oxocation complexes is normally easy to realize even in aqueous solutions. An alternative synthesis for $V(salen)Cl_2$ uses VCl_4,[14] which, however, is a material that is very difficult to handle. By reacting VCl_4 with $salenH_2$, we produce the same complex, IV [$(chel)_2$ = salen], but reaction 2 is carried out under more drastic conditions (see Experimental Section). Moreover, reaction 1 produces dichloro derivatives only, while it could be rather difficult to control a stepwise substitution of the Cl ligands, which is expected to occur on VCl_4 in reaction 2. Cl ligands can be, indeed, further and easily replaceable in $V(chel)_2Cl_2$.

$$VCl_4 + salenH_2 \rightarrow V(salen)Cl_2 + 2HCl \tag{2}$$

For formulation of a qualitative hypothesis concerning the mechanism of reaction 1 both the reaction conditions and their dependence on the nature of the chelating ligands, along with the mechanism usually proposed for the deoxygenation of organic substrates by means of $SOCl_2$,[15] must be taken into account.

As reaction 1 occurs in benzene, the presence of separated charged species may be unlikely:

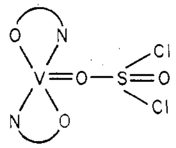


VO(sal-*N*-R)$_2$

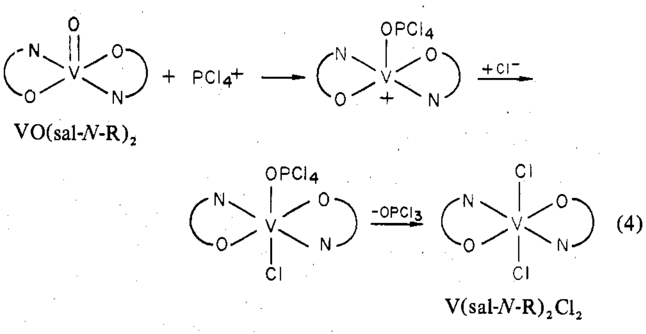
sal-*N*-R = ON

V(sal-*N*-R)$_2$Cl$_2$

Therefore a multicenter, concerted attack by $SOCl_2$ on the VO unit,[16] as schematically exemplified in reaction 3, is expected. This probably requires a first step in which an acid–base adduct is formed:



The weak-acid properties of $SOCl_2$ are known,[17] while the donor behavior of the vanadyl oxygen to alkali cations has been recently found.[18] For a mechanism as that exemplified in (3), we expect that flexible ligands around the metal promote reaction 1, which is slowed down in fact by the presence of a more rigid tetradentate ligand. As a further support to this fact, we did not observe the deoxygenation of the vanadyl unit in the presence of a closed-ring equatorial ligand such as phthalocyanine. PCl_5 seems to operate in deoxygenating carbonyl functional groups[19] with a mechanism which is different from that for $SOCl_2$ and which is exemplified for an oxovanadium chelate complex in reaction 4. However, in spite of the probable intervention of ionic species,[15] (phthalocyaninato)oxovanadium(IV) does not undergo a deoxygenation reaction with PCl_5. This suggests that the factor controlling the deoxygenation of oxocation complexes is probably not only steric. While complexes I–III present good solubilities in solvents such as acetone, from which they can be recrystallized, complexes IV, because of the presence of a tetradentate ligand, are usually much less soluble. In many cases, these complexes



VO(sal-*N*-R)$_2$

V(sal-*N*-R)$_2$Cl$_2$

Table V. Equations of Least-Squares Mean Planes

plane	Angles (deg) between this plane and the plane 1	2	3
1: through V,O,N $7.9996x + 5.3042y - 6.6840z = 3.3099$			
2: through O,C(1),C(2),C(3),C(4), C(5),C(6),C(7),N $9.3999x + 1.1656y - 6.7684z = 1.4427$	18.2		
3: through O,V,Cl $1.9808x + 10.8876y + 4.6525z = 8.7605$	89.2	77.7	
4: through N,V,Cl $9.4419x - 6.3191y + 2.2814z = 2.7020$	89.5	76.4	86.5

crystallize out with the reaction solvent, which is lost by heating. They are quite sensitive to hydrolysis, which regenerates the starting oxovanadium complexes. This behavior suggests an easy substitution of the two chlorines with different nucleophiles. All the complexes I–IV have been characterized by analytical, magnetic, and IR data (Table I). All of them are in agreement with the formulation reported, including the magnetic moment which approximates the spin-only value expected for a d^1 system. The IR spectra show only a slight shift of the C=N stretching bands of the Schiff base ligands, depending on the nature, e.g., of the substituent R in complexes III (Table I). As pseudooctahedral coordination geometry is suggested for complexes III and IV, with the two chlorides occupying two positions trans to each other, as was verified by an X-ray analysis on $V(sal\text{-}N\text{-}Bu)_2Cl_2{\cdot}C_6H_6$.

Description of the Structure of $V(sal\text{-}N\text{-}Bu)_2Cl_2$.

The crystals consist of monomeric units $V(sal\text{-}N\text{-}Bu)_2Cl_2$ with a rigorous C_i symmetry and a benzene molecule, which is present as crystallization solvent and resides on an inversion center. The molecules are separated by the usual van der Waals interactions. Figure 1 shows a view of the molecule and defines the labeling scheme for the atoms. The packing arrangement is shown in Figure 2, and Table IV gives pertinent intermolecular distances and angles. The six donor atoms, two N, two O, and two Cl atoms around vanadium, define an octahedron elongated along the Cl–V–Cl direction. Since the vanadium atom resides on an inversion center, this requires the two chlorine atoms to be mutually trans, as are the two oxygens and the two nitrogen atoms. The substitution of the vanadyl oxygen by two Cl ligands induces a significant shortening of the V–O [1.807 (3) Å] bond length (Table IV) vs. a mean value observed in other oxovanadium(IV) chelate complexes, which always is higher than 1.90 Å.[9,19] The V–N bond distance [2.096 (4) Å] resembles those found in oxovanadium chelate complexes with π-delocalized unsaturated ligands.[9,19,20] These values suggest a significant metal–ligand π-bonding interaction, as it was found in many transition metal–Schiff base complexes. The V–Cl bond length agrees with other V–Cl bond distances in vanadium(IV) complexes.[21] Bond distances and angles within the salicylideniminato bidentate ligand are in general agreement with mean values reported from a study of several such complexes.[22] The plane equations are given in Table V. The angle between the planes O,O′,N,N′ and O,N,C(1)–C(8) is 18.2° and the two *N*-butylsalicylaldimine groups are therefore bent in a symmetric stepped configuration analogous to that adopted by salen in many complexes.[23] The V–Cl bond is perpendicular to the best plane defined by V,O,O′,N,N′ (Table V).

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Registry No. I, 42532-52-5; II, 70550-50-4; III (R = *n*-Bu), 70550-51-5; III·C_6H_6 (R = *n*-Bu), 70550-52-6; III (R = CH_2Ph), 70613-69-3; III (R = Ph), 70613-70-6; III (R = C_6H_4Cl-4), 70613-71-7; III (R = $C_6H_4NO_2$-4), 70562-36-6; IV ($(chel)_2$ = salen), 70629-75-3; IV ($(chel)_2$ = sal-*o*-ph), 70681-03-7; $VO(sal\text{-}N\text{-}Bu)_2$, 70613-72-8; VOsalen, 22785-40-6; VCl_4, 7632-51-1.

Supplementary Material Available: A listing of calculated and observed structure factors, Table SI giving positional and isotropic thermal parameters for hydrogen atoms, and Table SII giving the bond distances and angles within the benzene molecule (9 pages). Ordering information is given on any current masthead page.

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