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Preparation and ^{51}V NMR Characteristics of Oxovanadium(V) Compounds. Relation between Metal Shielding and Ligand Electronegativity

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The light-sensitive vanadyl compounds $VOCl_2(O\text{-}t\text{-}Bu)$, $VOCl_{3-n}(NEt_2)_n$ and $VOF_{3-n}(O\text{-}i\text{-}Pr)_n$ ($n = 1, 2$), $VO(S\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2$, and $VOCl_3{\cdot}xNHEt_2$ have been prepared and investigated. Mixtures of $VOCl_{3-n}(O\text{-}i\text{-}Pr)_n$ and $LiNEt_2$ are shown to generate multicomponent systems containing, inter alia, $VO(NEt_2)(O\text{-}i\text{-}Pr)_2$, $VO(NEt_2)_2(O\text{-}i\text{-}Pr)$, and $Li[VO(NEt_2)(O\text{-}i\text{-}Pr)_3]$. Solutions of $VOCl_3$, VOF_3, or $VOCl_3/VOF_3$ in THF likely contain associated species composed of $\{VOX_3(X')^-\}$ subunits with one of the substituents (X′) labilized and interchangeable. $^1J(^{51}V-^{14}N)$ coupling constants have been observed for $VO(NEt_2)Z_2$ (1/1/1 triplets: Z = Cl, 55 Hz; Z = O-*i*-Pr, 110 Hz) and $[VO(NEt_2)(O\text{-}i\text{-}Pr)_3]^-$ (116 Hz) and $^1J(^{51}V-^{19}F)$ has been found for VOF_3/Me_2SO (binominal quintet; 85 Hz). Linear progressions exist between $\delta(^{51}V)$ and substituent (Z) parameters such as the electronegativity χ, Pearson's hardness parameter, and Taft's electronic and steric constants for both the $[VOF_{4-n}Cl_n]^-$ and VOZ_3 series. The shielding/χ correlations are rationalized on the basis of recently reported PE spectra and SCF–Xα calculations on $VOCl_3$ and VOF_3.

Introduction

A very common feature in metal NMR spectra of transition-metal complexes containing the metal in the d^0 configuration is an increase of shielding with increasing electronegativity χ of the ligand functions attached to the coordination center.[1] This trend, the "inverse" χ dependence of metal shielding, has been observed, among others, in the systems VOX_3 (X = Br, Cl, F),[2] $M^I_3[VE^{VI}_4]$ (M^I = Cu, Tl; E^{VI} = O, S, Se, Te),[3] TiX_4 (X = Cl, Br, I),[4a] Cp_2TiX_2 (Cp = η^5-C_5H_5; X = F, Cl, Br, I),[4a,b] $[NbE^{VI}X_4]^-$ and $[NbX_6]^-$ (X = F, Cl, Br; E^{VI} = O, S, Se),[5-7] and $[MoE^{VI}_4]^{2-}$ (E^{VI} = O, S, Se).[8,9] The same trend has also been noted as one goes across the periods (increasing metal shielding in the series $VO(NEt_2)_3 < VO(OR)_3 < VOF_3$;[2,5] $Ti(NEt_2)_4 < Ti(OPr)_4$[4a]). In contrast, an opposite ("normal") χ dependence, i.e. a decrease of metal shielding with increasing electronegativity of the ligating atoms, is apparent in d^n complexes with the metal center in low oxidation states[1] such as in $[CpV(CO)_3X]^-$ (X = F, Cl, Br, I),[10] $[CpV(CO)_3E^{IV}Ph_3]^-$ (E^{IV} = Si, Ge, Sn, Pb),[11] and $CpV(NO)_2L$[12] or $[V(CO)_5L]^-$[13] (L = OR_2, SR_2, NR_3). Instead of χ, parameters such as the polarizability, the bond ionicity, and Pearson basicity may be correlated in an analogous manner with δ(M).[11] While the normal χ dependence can be traced back to the increase of the covalency of the metal–ligand bond and the nephelauxetic effect of the ligand as its χ decreases (or its polarizability increases),[1] an appropriate explanation for the inverse dependence in d^0 compounds has not yet been carried out, although attempts have been undertaken for qualitative explanations based on the involvement of spin–orbit coupling[14] or metal d populations stemming from ligand (p_π) $\rightarrow$ M (d) interaction.[1]

In the present contribution, trends of ^{51}V shielding in series of vanadyl compounds are dicussed in the context of the bonding situation derived from PE spectra and the interpretation of PE spectra on the basis of MO calculations. A variety of diamagnetic compounds of the general formula VOZ_3 have been prepared and characterized by ^{51}V NMR for this purpose, many of them for the first time. Some earlier ^{51}V NMR reports on derivatives of orthovanadic acid and related systems have appeared, among them $[VOF_{4-n}Cl_n(NCCH_3)]^-$,[15] $VO(OR)_3$ and $VOCl_{3-n}(OR)_n$,[2,16,17] $[VOCl_n(OR)_mL_x]^q$ ($n + m = 3$, $q = 0$; $n + m = 4$, q = 1−; L = $NHEt_2$, ROH, CH_3CN; x = 1, 2),[18] and $[VOCl_{4-n}(NEt_2)_nNHEt_2]^-$ (n = 0, 2, 3),[19] and data for these complexes, if reliable, will be included in the discussion. Further, the question of the existence of $[VOF_4]^-$[15,20,21] and/or $[VO_2F_4]^{3-}$[22] will be dealt with.

Experimental Section

General and NMR Measurements. Since the compounds are sensitive to moisture and light, reactions were carried out in absolute solvents and under nitrogen, with use of brown Duran glassware throughout. $VO(O\text{-}i\text{-}Pr)_3$, $VOCl(O\text{-}i\text{-}Pr)_2$, $VOCl_2(O\text{-}i\text{-}Pr)$, $VO(O\text{-}t\text{-}Bu)_3$, $VOCl(O\text{-}t\text{-}Bu)_2$, and $VO(NEt_2)_3$ were prepared as described in the literature;[23-27] VOF_3 and $VOCl_3$ were purchased (Fluka). NaOR and NaS-*i*-Pr were prepared from alkali-free Na and the appropriate absolute alcohol and dried under high vacuum. $NHEt_2$ was dried over KOH and distilled under N_2; its in situ conversion to $LiNEt_2$ was carried out with Li-*t*-Bu (1.6 M in hexane; Merck).

^{51}V NMR spectra were obtained on a Bruker WH 90 PFT spectrometer at 23.66 MHz (2.11 T) and a pulse width of 5 μs in rotating 7 mm diameter vials, fitted into 10-mm vials containing acetone-d_6 as external lock. The measurements were carried out at slightly elevated room temperature (300 ± 2 K) against $VOCl_3$ (neat) as external standard. The absolute error is ±1 ppm.

Reactions. $VOCl_2(O\text{-}t\text{-}Bu)$. While $VO(O\text{-}t\text{-}Bu)_3$ and $VOCl(O\text{-}t\text{-}Bu)_2$ have been obtained previously by transesterification from $VO(OEt)_3$/HO-*t*-Bu[27] or treatment of $VO(O\text{-}t\text{-}Bu)_3$ with acetyl chloride,[26] the dichloride, to our knowledge, has not yet been described. We have obtained this compound as an azeotrope with CCl_4, following the procedures given by Funk et al.,[24] but tediously avoiding exposure to light.

I. To a solution containing 5.6 g (32.3 mmol) of $VOCl_3$ in 50 mL of CCl_4 was added dropwise, during 30 min, 2.4 g (32.3 mmol) of *t*-BuOH dissolved in 50 mL of CCl_4. HCl developed, which was driven off by a N_2 stream to be absorbed in NaOH. The reaction was completed by refluxing the solution until the liberation of HCl had ceased (ca. 1 h).

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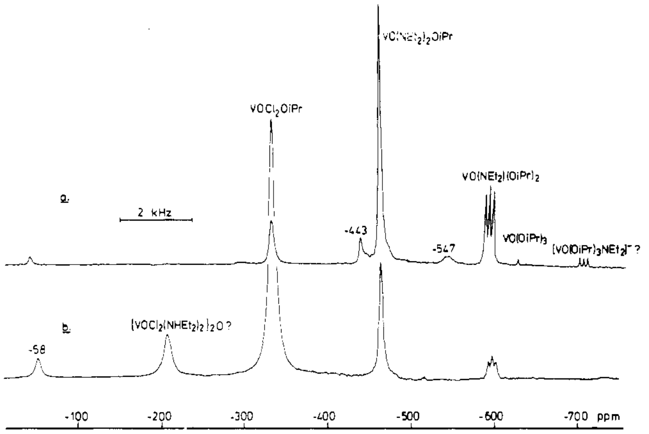

Figure 1. $^{51}V\{^1H\}$ NMR spectra of the reaction mixtures obtained from $VOCl_2$(O-*i*-Pr)/$LiNEt_2$ = 1/2 before (a, pentane solution) and after distillation at 10^{-2} torr and 96 °C (b, neat). See text for details and assignments. The weak signals at −58, −443, and −547 ppm have not been assigned.

A total of 22.6 mmol of HCl had evolved. Distillation at 295 K and 1 torr gave ca. 20 mL of a yellow liquid of spectroscopically pure $VOCl_2$(O-*t*-Bu). The compound decomposes when distilled under normal pressure and on exposure to daylight.

II. A 569-mg (1.99-mmol) amount of $VO(O\text{-}t\text{-}Bu)_3$ in 8 mL of *n*-pentane was treated dropwise with a solution of 172 mg (0.99 mmol) of $VOCl_3$ dissolved in 5 mL of pentane to yield a pentane solution of $VOCl_2$(O-*t*-Bu). The compound decomposes as the pentane is removed.

VOF_2(O-*i*-Pr). I. To 50 mL of a $CHCl_3$ solution containing 1.12 g (9 mmol) of VOF_3 was added 0.54 g (9 mmol) of *i*-PrOH in 50 mL of $CHCl_3$. The mixture was refluxed until development of gas had ceased (ca. 30 min). Distillation at 0.5 torr and 323 K yielded 1.1 g (74.5%) of a viscous, dark yellow, light-sensitive oil, which gave a satisfactory elemental analysis.

II. Following the preparative procedures for the corresponding alkoxy chlorides,[24,28] the compound was also obtained by stirring a mixture of 1.96 g (15.8 mmol) of VOF_3 and 1.29 g of NaO-*i*-Pr in 100 mL of THF for 40 min.

$VOF(O\text{-}i\text{-}Pr)_2$. A 2.1-g (17-mmol) amount of VOF_3 was dissolved in 50 mL of THF. To this solution was added within 20 min a suspension of 2.8 g of NaO-*i*-Pr (34 mmol) in 30 mL of THF. After 1 h of stirring, the reaction mixture was filtered and the residue washed with 15 mL of THF. From the joined filtrates, the THF was removed at 295 K and 0.2 torr to yield an oily, yellow-brown product, which after dissolution in $CHCl_3$ and filtration was directly measured.

Reaction between $VOCl_{3-n}(O\text{-}i\text{-}Pr)_n$ (n = 0–2) and $LiNEt_2$: Preparation of $VOZ_{3-n}(NEt_2)_n$ (Z = Cl, O-*i*-Pr; n = 1, 2). I. A 25.4-mL portion of a 1.6 M hexane solution of LiBu (40.6 mmol) was cooled to 223 K and treated, within 20 min, with 20 mL of a pentane solution containing an equimolar amount of $NHEt_2$. The solution was slowly brought to room temperature and stirred for 30 min. The $LiNEt_2$ suspension thus obtained was cooled back to 223 K, and 25 mL of a pentane solution of 9.0 g (40.6 mmol) of $VOCl(O\text{-}i\text{-}Pr)_2$ was added dropwise during 15 min. After the mixture was warmed to room temperature and stirred for 15 min, the solvent was removed in vacuo (0.3 torr, 295 K) to yield a viscous, brown residue that upon distillation at 343 K (0.01 torr), afforded an oil consisting of $VO(NEt_2)_2$O-*i*-Pr and $VO(O\text{-}i\text{-}Pr)_3$ as the main products. The reaction between $VOCl_2$(O-*i*-Pr) and $LiNEt_2$ was carried out accordingly; distillation (369 K, 0.01 torr) gave a dark red oil (cf. Figure 1 for the composition of the product mixtures before and after distillation).

II. $VOCl_2(NEt_2)$ was prepared from 25 mL of a pentane solution containing 4.34 g (25 mmol) of $VOCl_3$ and 2 g (25 mmol) of $LiNEt_2$ suspended in 20 mL of pentane. The solution, which essentially contained the expected monoamide, was investigated spectroscopically without distillation to avoid decomposition. $VOCl(NEt_2)_2$ was obtained by treating the above mixture with an additional 2-g portion of $LiNEt_2$.

$VO(NEt_2)(O\text{-}t\text{-}Bu)_2$. This compound was prepared from $VOCl(O\text{-}t\text{-}Bu)_2$ and $LiNEt_2$/hexane as described for $VO(NEt_2)(O\text{-}i\text{-}Pr)_2$. $VO(NEt_2)(O\text{-}t\text{-}Bu)_2$ is the main product in the reaction mixture (by ^{51}V NMR).

$VO(S\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2$. A 0.9-g (4.4-mmol) amount of $VOCl(O\text{-}i\text{-}Pr)_2$ in 7 mL of $CHCl_3$ was treated with a suspension of 0.27 g (3.5 mmol) of NaS-*i*-Pr in 7 mL of $CHCl_3$. The solution, which contains starting material and the expected product, is stable for several hours. When the solution is exposed to light, $VO(O\text{-}i\text{-}Pr)_3$ and $VO(S\text{-}i\text{-}Pr)_3$ (insoluble, green-black powder) are formed.

Table I. ^{51}V NMR Data of VOZ_3 Compounds

compd	solvent	$\delta(^{51}V)^a$	$\sum\chi z^b$
VOF_3 (**14**)	$CHCl_3$	−632	12.57
	THF[c]	−757 to −760	
	Me_2SO[c]	−722 and −781[d]	
VOF_2(O-*i*-Pr) (**13**)	$CHCl_3$	−620	12.02
	THF	−634	
$VOF(O\text{-}i\text{-}Pr)_2$ (**12**)	$CHCl_3$	−567	11.47
$VOCl_3$ (**2**)	CH_2Cl_2	0	8.52
	$CHCl_3$	−1	
	CCl_4	−3	
	n-pentane	−6	
	THF[c]	−33	
$VOCl_3 \cdot xNHEt_2$	CCl_4	−17	
$VOCl_3$ + VOF_3	THF[c,e]	−280 and −535	
$VOCl_2$(O-*i*-Pr) (**8**)	$CHCl_3$	−307	9.32
$VOCl(O\text{-}i\text{-}Pr)_2$ (**9**)	$CHCl_3$	−503	10.12
$VO(O\text{-}i\text{-}Pr)_3$ (**10**)	$C_6H_{11}CH_3$[f]	−623	10.92
	C_6D_6[g]	−641	
$VOCl_2$(O-*t*-Bu)	$CHCl_3$	−328	
$VOCl(O\text{-}t\text{-}Bu)_2$	$CHCl_3$	−537	
	C_6D_6[g]	−539	
$VO(O\text{-}t\text{-}Bu)_3$	$CHCl_3$	−669	
	C_6D_6[g]	−677	
$VOCl_2(NEt_2)$ (**3**)	*n*-pentane	−23[h]	8.74
$VOCl(NEt_2)_2$ (**4**)	*n*-pentane	−141	8.96
$VO(NEt_2)(O\text{-}i\text{-}Pr)_2$ (**7**)	*n*-pentane	−590[i]	10.34
$VO(NEt_2)(O\text{-}t\text{-}Bu)_2$	*n*-pentane	−488	
$VO(NEt_2)_2$(O-*i*-Pr) (**6**)	*n*-pentane	−467	9.76
$VO(NEt_2)_3$ (**5**)	neat	−389	9.18
$VO(S\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2$ (**11**)	$CHCl_3$	−623	9.76

[a] Relative to $VOCl_3$ (neat) at 300 (2) K. [b] Sum of the electronegativities (Zhang[43]) of the substituents Z employed in Figure 4. [c] The species actually present is more complex than VOZ_3; cf. Table II. [d] Binominal quintet: $^1J(^{51}V-^{19}F)$ = 85 Hz. [e] Cf. Figure 2. [f] From ref 16. [g] From ref 17. [h] Triplet (0.7/1/0.7): $^1J(^{51}V-^{14}N)$ = 55 Hz. [i] Approximate 1/1/1 triplet: $^1J(^{51}V-^{14}N)$ = 105 Hz.

Results and Discussion

Preparation and ^{51}V NMR Spectra of VOZ_3. ^{51}V chemical shifts of the compounds described in this work are collated in Table I. For the esters (Z = OR), mixed ester halides, and ester amides, we have chosen those with the bulky substituents *i*-Pr and *t*-Bu, since it is known that the triesters with R groups of minor steric requirement (such as Et or *n*-Pr) associate to dimers and/or oligomers[23,29–31] and thus give rise to ^{51}V NMR signals not directly comparable to those of other VOZ_3 compounds, since they are representing weighted equilibrium positions. As an example, a 0.2 M solution of $VO(O\text{-}n\text{-}Pr)_3$ in cyclohexane (degree of association α = 20%[24]) exhibits a $\delta(^{51}V)$ value of −575 (5), while an appropriate sample of $VO(O\text{-}i\text{-}Pr)_3$ (α = 5%) resonates at −625 (5) ppm. On the other hand, $VO(t\text{-}Bu)_3$ and $VOCl_{3-n}(O\text{-}i\text{-}Pr)_n$ (n = 1–3) have been shown to exist as equilibrium mixtures of rotamers,[32] the exchange of which may impose a strain resulting in (minor) influences upon ^{51}V shielding.

Light-sensitive $VOCl_2$(O-*t*-Bu) was obtained in analogy to, e.g., $VOCl_2(OEt)$[24] from $VOCl_3$ and *t*-BuOH as a CCl_4 solution. As for other compounds of the general formula $VOCl_{3-n}(OR)_n$, there is a drastic increase of ^{51}V shielding in the sequence $VOCl_2$(O-*t*-Bu), $VOCl(O\text{-}t\text{-}Bu)_2$, $VO(O\text{-}t\text{-}Bu)_3$ (cf. Table I). The corresponding reaction between VOF_3 and *i*-PrOH in $CHCl_3$ needs heating of the reactants. HF is liberated, and a green-black substance precipitates that has the same properties as the product obtained from the thermolysis of $VO(OEt)_3$ formerly described

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by Lachowicz and Thiele.[29] The filtrates contain practically pure $VOF_2(O\text{-}i\text{-}Pr)$ and $VOF(O\text{-}i\text{-}Pr)_2$, respectively. Without thermic strain, the compounds can be prepared by the procedure described for the corresponding chlorides,[28] i.e. from VOF_3 and NaO-*i*-Pr. The dark yellow, oily compounds are light-sensitive. Solutions exposed to diffuse daylight or UV turn to a light blue (V(IV)), and simultaneously, a black powder precipitates. The ^{51}V NMR resonances of $VOF_2(O\text{-}i\text{-}Pr)$ and $VOF(O\text{-}i\text{-}Pr)_2$ are unresolved signals; half-widths are 200 and 850 Hz, respectively. $^1J(^{51}V\text{–}^{19}F)$ coupling constants reported for fluorovanadium compounds range from 88 to 140 Hz[14,16,20-22] and hence should give rise to a resolved spectrum in the case of $VOF_2(O\text{-}i\text{-}Pr)$ except if there is fast intermolecular or dissociative intramolecular rearrangement of the ligands or if quadrupole relaxation decoupling due to slow molecular reorientation is effective (see also below).

The reaction between $VOCl_2(O\text{-}i\text{-}Pr)$ and NaS-*i*-Pr in $CHCl_3$ rapidly proceeds with the formation of degradation products ($VO(S\text{-}i\text{-}Pr)_3$ and $VO(O\text{-}i\text{-}Pr)_3$) of the intermediate $VO(S\text{-}i\text{-}Pr)_2O\text{-}i\text{-}Pr$. $VO(S\text{-}i\text{-}Pr)_3$ precipitates as an insoluble black powder, which has also been observed in the redistribution reactions between $VO(NR_2)(O\text{-}i\text{-}Pr)_2$ and HSEt.[33] In the case of the reaction between $VOCl(O\text{-}i\text{-}Pr)_2$ and NaS-*i*-Pr, the intermediate $VO(S\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2$ is formed, which is sufficiently long-lived (if light is again excluded) to be detectable by ^{51}V NMR. The signal position (−623 ppm) is close to that of $VO(O\text{-}i\text{-}Pr)_3$ (−626 ppm). The resonance for the latter emerges ca. 45 min after the reactants have been brought together and slowly gains intensity until, after ca. 4 h, the integral intensities of the two signals for $VO(S\text{-}i\text{-}Pr)(O\text{-}i\text{-}Pr)_2$ and $VO(O\text{-}i\text{-}Pr)_3$ are about the same. The formation of $VO(S\text{-}i\text{-}Pr)_3$ is accelerated by light.

The preparation of mixed ester amides of the general formula $VO(NR_2)_{3-n}(OR')_n$ ($n = 1, 2$) from $VOCl_{3-n}(O\text{-}i\text{-}Pr)_n$ and MNR_2 has been reported by Wannagat et al.[25] (R = $SiMe_3$, $Si(i\text{-}Pr)_3$; R′ = *i*-Pr; M = Na), Preuss et al.[34] (R = *t*-Bu, *i*-Pr, $SiMe_3$; R′ = *t*-Bu, *i*-Pr), and Choukroun and Gervais[33] (R = Et; M = Li), who also obtained $Li[VO(NEt_2)(O\text{-}i\text{-}Pr)_3]$. We have not been able to confirm the results reported by the last group. Rather, mixtures of several compounds are obtained, probably as a result of dismutation and redistribution reactions accompanying the formation of the compounds from the starting products and the separation by distillation. Reproduction of the experimental route described for the reaction between $VOCl_2(O\text{-}i\text{-}Pr)$ and $LiNEt_2$ in the 1/2 molar ratio led—as evidenced by the ^{51}V NMR spectrum (Figure 1a)—to a mixture of 59% $VO(NEt_2)_2(O\text{-}i\text{-}Pr)$, 25% $VO(NEt_2)(O\text{-}i\text{-}Pr)_2$ (triplet, J = 110 Hz), and 11% $VOCl_2(O\text{-}i\text{-}Pr)$. There are a few additional signals belonging to smaller amounts of other species, among them a triplet at −709 ppm (J = 116 Hz), which we tentatively assign to $Li[VO(NEt_2)(O\text{-}i\text{-}Pr)_3]$. Since the nucleus ^{14}N has a nuclear spin of 1, a 1/1/1 pattern as observed formerly for $V(N\text{-}t\text{-}Bu)(OSiMe_3)_3$ (J = 95 Hz)[35] is expected. The somewhat increased intensity of the central peak of the $VO(NEt_2)(O\text{-}i\text{-}Pr)_2$ triplet is a consequence of beginning relaxation decoupling between the two quadrupolar nuclei ^{14}N and ^{51}V (nuclear spin $^7/_2$). In the case of $VO(NEt_2)_2(O\text{-}i\text{-}Pr)$, relaxation decoupling is fully effective and only a singlet is observed (compare also $VOF_2(O\text{-}i\text{-}Pr)$; vide supra). The phenomenon of relaxation decoupling has recently been discussed for the temperature-dependent $^1J(^{95}Mo\text{–}^{14}N)$ coupling pattern of $CpMo(CO)_2NO$.[36] Working up of the reaction mixture by vacuum distillation under the conditions noted in ref 33 leads to ligand redistributions in the coordination sphere of the vanadyl ion. The distillate (Figure 1b) contains ca. 70% $VOCl_2(O\text{-}i\text{-}Pr)$, 16% $VO(NEt_2)_2(O\text{-}i\text{-}Pr)$, and 0.6% $VO(NEt_2)(O\text{-}i\text{-}Pr)_2$. The peaks at −58 and −210 ppm (Figure 1b) remain unassigned; the latter may correspond to $\{VOCl_2NHEt_2\cdot NHEt_2\}_2(\mu\text{-}O)$, for which Buslaev et al. report $\delta(^{51}V) = -206$.[19]

Table II. ^{51}V NMR Data of $[VOZ_4]^-$ and Related Complexes

compd	solvent	$\delta(^{51}V)$	ref
$[Et_4N][VOCl_4]$ (a)	THF	+46	39
$[As_4P][VOCl_4]$ (a)	CH_2Cl_2; THF	+50	39
$[VOCl_4(NCMe)]^{-a}$ (b)	CH_3CN	−38	15
$[VOCl_4(NCMe)]^-$ (b)	CH_3CN	+30	19
$[pyH][VOCl_4]^b$	CH_2Cl_2	−319	40
$\{VOCl_3(Cl)^-\}^c$ (c)	THF	−32	*d*
$[VOCl_3F(NCMe)]^-$ (d)	CH_3CN/HF	−205	15
$\{VOCl_3(F)^-\}^c$ (e)	THF	−280	*d*
trans-$[VOCl_2F_2(NCMe)]^-$ (f)	CH_3CN/HF	−380	15
cis-$[VOCl_2F_2(NCMe)]^-$ (g)	CH_3CN/HF	−456	15
$\{VOF_3(Cl)^-\}^c$ (h)	THF	−535	*d*
$[VOClF_3(NCMe)]^-$ (j)	CH_3CN/HF	−608	15
$\{VOF_3(F)^-\}^c$ (k)	THF	−756	*d*
$[VOF_4(NCMe)]^-$ (m)	CH_3CN/HF	−778	15
$[VOF_4(Me_2SO)]^-$	Me_2SO	-782^e	*d*
$[VOCl_3NR_2]^{-f}$	$CHCl_3$	−481	40
$[VOCl_2(NEt_2)_2L]^{-g}$	CCl_4/L	−133	19
$[VOCl(NEt_2)_3L]^{-g}$	$CCl_4/L/CH_3CN$	−272	19
$[VO(O\text{-}i\text{-}Pr)_3NEt_2]^{-h}$	*n*-pentane	−698, −709	*d*
$[VOCl_2(O\text{-}i\text{-}Pr)_2L]^{-i}$	CH_3CN	−361	18
$[VOCl(O\text{-}i\text{-}Pr)_3L]^{-i}$	CH_3CN; CCl_4/L	−494	18
$[VO(O\text{-}i\text{-}Pr)_4L]^{-i}$	CH_3CN; CCl_4/L	−623	18

[a] In exchange with $VOCl_3\cdot 2CH_3CN + Cl^-$. [b] No simple $[VOCl_4]^-$ present. [c] Cf. text for discussion, and Figure 2. [d] This work. [e] See footnote *d* in Table I. [f] $NR_2 = {}^1/_2$ *meso*-tetraphenylporphine; the compound has been ascribed the constitution of an internal salt, $[(TPPH_2)^{2+}(VOCl_3^-)_2]$. [g] L = $NHEt_2$. [h] Tentative assignment: 1/1/1 triplet; $^1J(^{51}V\text{–}^{14}N)$ = 116 Hz. [i] L is *i*-PrOH, NCMe, and/or $NHEt_2$.

Similarly, the reaction between $VOCl(O\text{-}i\text{-}Pr)_2$ and $LiNEt_2$ does not lead to a well-defined compound but to a product spectrum with $VO(NEt_2)_2(O\text{-}i\text{-}Pr)$ and $VO(O\text{-}i\text{-}Pr)_3$ as the main constituents. A triplet centered at −698 ppm (J = 114 Hz) again is likely an anionic compound ($[VO(NEt_2)(O\text{-}i\text{-}Pr)_3]^-$). The reaction between $VOCl(O\text{-}t\text{-}Bu)_2$ and $LiNEt_2$ is less complex; the main product (about 90%) is $VO(NEt_2)(O\text{-}t\text{-}Bu)_2$ (singlet at −488 ppm).

A partially decoupled triplet (J = 55 Hz) at −23 ppm is observed as $VOCl_3$ is reacted with $LiNEt_2$ in pentane in the molar ratio 1/1, while a singlet at −141 ppm arises if the molar ratio is 1/2. If the reaction is carried out with exposure to daylight and the resulting solution worked up by distillation (0.01 torr, 410 K), a green oil can be collected, the ^{51}V NMR spectrum of which exhibits two relatively broad resonances at −212 (30%) and −291 ppm (65%). These signals correspond to the $\delta(^{51}V)$ values reported for $\{VOCl_2(NHEt_2)\cdot NHEt_2\}_2(\mu\text{-}O)$ and $\{VOCl(NEt_2)(NHEt_2)\cdot NHEt_2\}_2(\mu\text{-}O)$, which the Russian workers have observed in the $VOCl_3/NHEt_2/CCl_4$ system.[19] We have treated $VOCl_3$ with $NHEt_2$ in CCl_4 with the strict exclusion of moisture and in the dark. Only one product of the reaction, the dark red adduct $VOCl_3\cdot xNHEt_2$ ($\delta = -16.8$; $\delta(VOCl_3)$ in the reaction mixture is −3.4) is formed under these conditions, and this is in accord with what has been described by Funk et al.[24]

^{51}V NMR Characteristics of $[VOZ_4]^-$. The number of authentic anionic complexes of the composition $[VOZ_4]^-$ (or $[VOZ_4(L)]^-$) is scarce. Only $[VOCl_4]^-$ and $[VOBr_4]^-$ appear to have been fully characterized, including their X-ray structures,[37,38] but anionic species such as $[VOF_4]^-$[20,21] and $[VOF_{4-n}Cl_n(NCMe)]^-$,[15] $[VOCl_{4-n}(O\text{-}i\text{-}Pr)_nL]^-$,[18] and $[VOCl_{4-n}(NEt_2)_nL]^-$[19] have been claimed to exist in polar solvents containing VOF_3, $VOCl_{3-n}(O\text{-}i\text{-}Pr)_n$, or $VOCl_3$. ^{51}V NMR data for a selected number of complexes, for which the anionic constitutions have been suggested, are collected in Table II.

The position of the resonance signal of VOF_3 shows a strong dependence upon the solvent ($CHCl_3$, −632 ppm; Me_2SO, −722 and −782 ppm; THF −760 ppm): These variations by far exceed those to be expected for the common solvent effect and led to the

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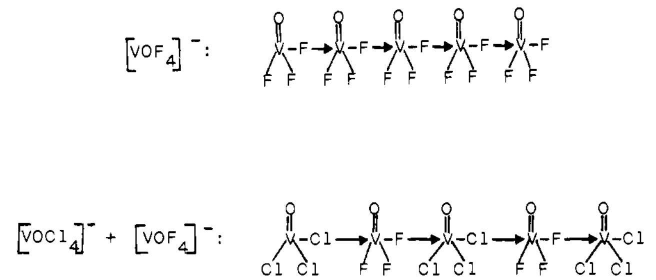

Figure 2. Possible association of VOX_3 and VOX_3/VOX'_3 (X, X′ = F, Cl) in polar solvents.

formulation of anionic species such as $[VOF_4]^-$ or $[VOF_4(L)]^{-}$[15] in organic solvents L with donor properties. The solution of VOF_3 in Me_2SO shows a (relatively broad; half-width 370 Hz) singlet at −722 ppm and a weaker, binominal quintet at −781 ppm ($^1J(^{51}V-^{19}F)$ = 85 Hz), for which we propose the constitution $[VOF_4(Me_2SO)]^-$. Dissolving $VOF(O\text{-}i\text{-}Pr)_2$ in Me_2SO yields two strong signals, which can be assigned to the dismutation products $[VOF_4(Me_2SO)]^-$ and $VO(O\text{-}i\text{-}Pr)_3$, the latter showing a downfield solvent shift with respect to neat $VO(O\text{-}i\text{-}Pr)_3$ or $VO(O\text{-}i\text{-}Pr)_3$ in nonpolar solvents of 30 ppm.

The anion $[VOF_4]^-$ has also been postulated as a constituent in the oxovanadium/HF system.[20,21] This has been argued recently by Gillespie and Rao,[22] who restrict the possible existence of $[VOF_4]^-$ to water-free media (V_2O_5/HF), while the species formed in the presence of water is ascribed the $[VO_2F_4]^{3-}$ anion, characterized by a quintet (117 Hz) at −770 to −775 ppm. However, these are the same signal parameters as for V_2O_5 in HF and VOF_3 in THF or Me_2SO. Also, keeping in mind the large separation between $[VOCl_4]^-$ (+50 ppm) and $[VO_2Cl_2]^-$ (−359 ppm),[39] one should presume a comparable effect in the fluoro complexes. Further, a recent X-ray structure of $Rb[VOF_4(H_2O)]$[41] clearly demonstrates that the $\{VOF_4^-\}$ structure unit can exist where water plays its part.

A less pronounced shift of the ^{51}V resonance is observed as $VOCl_3$ (δ = 0 to −3 in nonpolar solvents) is dissolved in THF (deep red-brown solution, δ = −32). The IR spectra show bands at 995 ($\nu(VO)$) and 430, 390, and 380 cm^{-1} ($\nu(VCl)$ and deformation modes), reminiscent of $[AsPh_4][VOCl_4]$[37] and clearly distinct from the $\nu(VO)$ (1042 cm^{-1}) and $\nu(VCl)$ (509 cm^{-1}) values for $VOCl_3$.[42] On the other hand, the signal position of $VOCl_3$/THF does not correspond with that of $[AsPh_4][VOCl_4]$ (+50 ppm[39]).

In order to further elucidate the nature of the species present if VOF_3 or $VOCl_3$ are dissolved in solvents such as THF, we have treated THF solutions of VOF_3 and $VOCl_3$ with $VOCl_3$ and VOF_3, respectively. Irrespective of the molar ratios of the two components, only two new species are formed, characterized by their ^{51}V NMR signals at −280 and −535 ppm. If the anions $[VOF_4]^-$ and $[VOCl_4]^-$ were present in the original solutions, all of the halide ligands should be subject to exchange and the complete series of $[VOF_{4-n}Cl_n]^-$ should be observed as in the $VOCl_3/CH_3CN$/HF systems investigated by Buslaev and co-workers.[15] Hence, solutions of VOX_3 in THF do not seem to contain the simple $[VX_4]^-$ (or $[VX_4(THF)]^-$) ion but rather units with three of the substituents bonded strongly to vanadium and a fourth labilized by some kind of intermolecular interaction as shown in Figure 2. We may symbolize these species by $\{VOCl_3(Cl)^-\}$ and $\{VOF_3(F)^-\}$ and the two new compounds by $\{VOCl_3(F)^-\}$ and $\{VOF_3(Cl)^-\}$, which is in accord with the findings in the IR and the ^{51}V NMR spectra and with the exchange behavior.

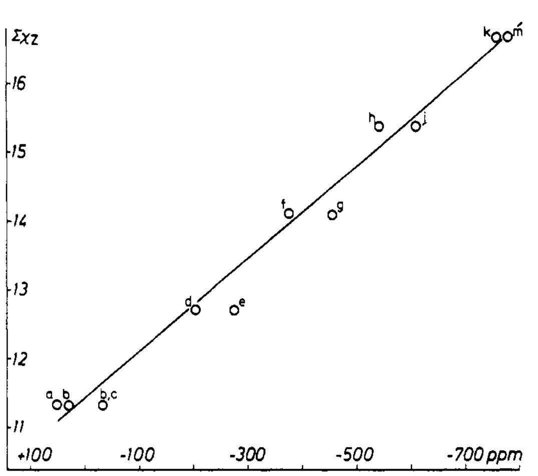

Figure 3. Graphical presentation of the dependence of ^{51}V shielding in $[VOX_{4-n}X'_n]^-$ (X, X′ = F, Cl) upon the sum of the electronegativities (Zhang[43]) $\sum\chi_Z$. For the letter designations see Table II. VF_5 (δ = −875 in $CDCl_3$) also fits this line (W. Priebsch and D. Rehder, unpublished).

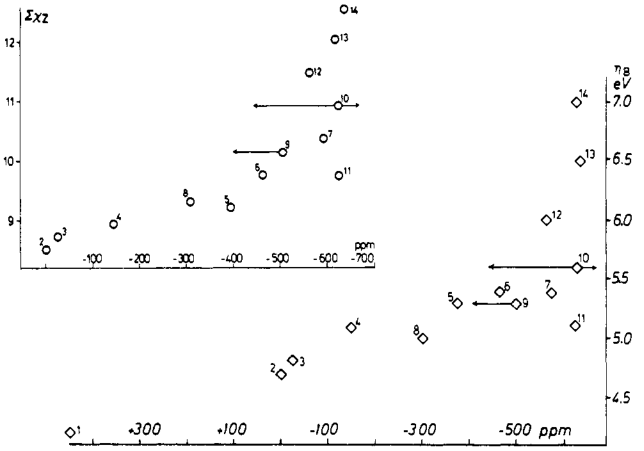

Figure 4. Plot of $\sum\chi_Z$ against $\delta(^{51}V)$ (insertion at the upper left) and $\delta(^{51}V)$ against Pearson's hardness parameter[44] $\eta_B = {}^1/_2(I_{B^+} - A_{B^+})$, where B is a base ($Z^-$ in our case) and I and A are the ionization potentials and electron affinities, respectively. χ is the Zhang electronegativity.[43] Data are for neutral VOZ_3 complexes; for numbering see Table I (1 = $VOBr_3$).[2,16] The arrows indicate the shift ranges spanned by $VO(OR)_3$ and $VOCl(OR)_2$ (cf. Figure 5).

Correlations. We have shown earlier[16] that, for a selected number of VO^{3+} compounds, there is a close relation between ^{51}V shielding and the electronegativity χ of the substituents Z in VOZ_3 and $[VOZ_4]^-$ in that shielding increases as χ increases, slight irregularities (e.g. in the series $VOCl_{3-n}(OR)_n$) being due to association phenomena. Figure 3 exemplifies the almost exact linear progression (correlation coefficient 0.99) between $\delta(^{51}V)$ and $\sum\chi_Z$ for the $[VOF_{4-n}Cl_n]^-$ series, i.e. for complexes containing monoatomic ligands only. For VOZ_3 (Figure 4, insertion), the general trend prevails, but apparently there are superimposed effects. The situation somewhat improves if Pearson's absolute hardness parameters η_B[44] are employed (Figure 4). We can attribute the effects to steric and electronic influences imposed by R which, considering the esters only, will affect the electronegativity of the OR group and induce steric strains either through association (small R) or through overlap perturbations (large R). To quantify these influences, we make use of the electronic and steric Taft constants E_s and σ^*.[45,46] In Figure 5, $\delta(^{51}V)$ values for the two series $VOCl(OR)_2$ and $VO(OR)_3$ are plotted against the empirically optimized functionality $2 \ln \sigma^* + \ln E_s$.

Further elucidation of the shielding/χ correlation comes from semiquantitative considerations based on PE spectra and MO calculations (EHMO, SCF-Xα) on $VOCl_3$ and VOF_3[47,48] (Figure

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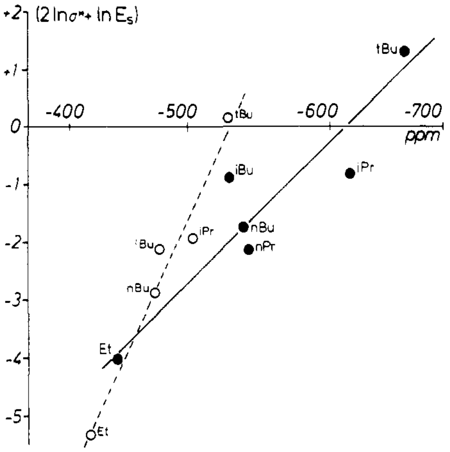

Figure 5. Plot of 2 ln σ^* + ln E_s vs. $\delta(^{51}V)$ for $VO(OR)_3$ (solid line and full symbols) and $VOCl(OR)_2$ (broken line and open symbols). σ^* and E_s are the steric and electronic Taft constants[45] for R. $\delta(^{51}V)$ values were taken from ref 2 and 16 and from this work (Table I).

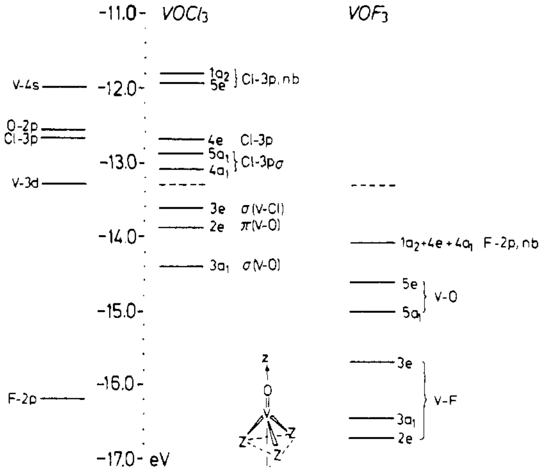

Figure 6. MO schemes for $VOCl_3$ and VOF_3 under local C_{3v} symmetry, adapted from PE measurements and MO calculations.[47,48]

6). The levels indicated for O^{2-}, Cl^-, and F^- in Figure 6 have been adapted from those employed in calculations on MnO_3Cl and MnO_3F.[49] Approximate V 3d and V 4s levels have been obtained from the VSIEs listed by Basch, Viste, and Gray,[50] assuming an effective charge on the vanadium of 0.35+; these values come close to the V 3d (−13.99 eV) and V 4s (−12.00) levels that have been used in the MO description of $[VO(H_2O)_6]^{2p}$.[51]

The overall shielding σ' of the vanadium nucleus can be expressed, if nonlocal contributions are neglected, by $\sigma' = \sigma^{dia} + \sigma^{para}$, where the paramagnetic term is

$$\sigma^{para} = -\text{const}\ \overline{\Delta E^{-1}}[\overline{C_{3d}^2}\langle r^{-3}\rangle_{3d} + \overline{C_{4p}^2}\langle r^{-3}\rangle_{4p}]$$

The diamagnetic term for $[VO_4]^{3-}$ amounts to +1703 ppm.[52] This is practically the same as the calculated (SCCC–MO) values for other vanadium complexes such as $[V(CO)_6]^-$ (+1730 ppm) and $CpV(CO)_4$ (+1712 ppm),[53] which unequivocally demonstrates that this term can be considered invariant in our series of VO^{3+} compounds. Hence, variations in shielding are dominated by paramagnetic deshielding contributions. σ^{para} is related to electronic transitions (ΔE), to the vanadium LCAO coefficients C_{3d} and C_{4p} of the levels taking part in transitions (which are those with the transformation properties of the angular momentum operator: A_2 + E under C_{3v} symmetry), and to the orbital expansion ($\langle r^{-3}\rangle$).

Relevant for electronic transitions are occupied and unoccupied MO levels with substantial V 3d and V 4p character. V 4p participation in the V–O bond has been evidenced for $[VO_4]^{3-}$[54] and $[VO(H_2O)_6]^{2+}$.[51] In the VOZ_3 molecule, V 4p orbitals seemingly do not give a sizable contribution to the overlap with oxygen or Z, and the factor C_{4p}^2 $\langle r^{-3}\rangle_{4p}$ in the expression for σ^{para} is therefore attributed only minor importance. Also, $d_{x^2-y^2}$ and d_{xy} remain essentially nonbonding (and unoccupied). Transitions into these low-lying levels can proceed from bonding orbitals with V 3d participation. In $VOCl_3$, these are $3a_1$, which represents d_σ–p_σ(O) interaction, 2e, which represents d_π–p_π(O) and also some V–Cl π interaction, and 3e (σ(V–Cl)). Hence, in $VOCl_3$, the main contribution to ΔE is the transition from strong VO bonding orbitals to essentially empty and nonbonding V 3d, modulated by excitations from bonding σ(V–Cl) orbitals.

A decrease of χ_Z (Z = Br, for example), i.e. destabilization of the Z *n*p orbital relative to that of $VOCl_3$, will destabilize the 3e (and also the 2e level). thus giving rise to a decrease of ΔE and increase of the V 3d coefficients for these MOs. The two factors point into the same direction and lead to a deshielding of the ^{51}V nucleus relative to $VOCl_3$.

An inverse effect arises as χ_Z becomes greater than χ_{Cl}, and the extreme case is represented through VOF_3. Although the scheme for VOF_3 (Figure 6) is more qualitative, the essential features allow convincing conclusions as to the impact on ^{51}V shielding: The V–Z bonding levels now are stabilized. The molecular orbitals which represent the V–O bond ($5a_1$ and 5e) become predominant for transition into the nonbonding V 3d levels. The (relative to $VOCl_3$) substantially increased ΔE gap and reduced C_{3d} value give rise to diminished σ^{para} contributions and to an increase of the overall shielding σ'.[55]

The overall situation will not change as V 4p contributions to the σ levels representing the V–O bond are included. $\langle r^{-3}\rangle_{3d}$, which should induce increased shielding as χ_Z decreases, apparently is overpowered by the influences via ΔE and C_{3d} and may therefore be considered a less variable quantity which, in a first approximation and for VOZ_3 with identical Z substituents, may be treated as a constant factor in shielding of V(V) compounds.

Conclusion

We have shown that ^{51}V shielding in vanadyl complexes VOZ_3 is mainly determined by the extent of the energy separation ΔE between bonding MOs essentially of $\sigma(V_{3d}$–O) and $\pi(V_{3d}$–O) character and nonbonding, unoccupied V 3d levels. The decrease of the electronegativity of Z (Z = F, OR, NR_2, Cl, Br) leads to a decrease of ΔE and increasing participation of V–Z bonding levels to excitations. The V 3d LCAO coefficients of the levels, from which excitations occur, increase with decreasing χ_Z and contributes to the deshielding effect observed in the sequence F < OR < NR_2 < Cl < Br. These relations are reflected in correlations between $\delta(^{51}V)$ and χ_Z or Pearson's hardness parameter η_B (where B corresponds with Z^-). In the series $VO(OR)_3$ and $VOCl(OR)_2$, steric factors arising from R and quantified by Taft's steric substituent constant σ^* also come in, the reason being variations in the tendency of these compounds to associate to oligomers.

Registry No. **2**, 7727-18-6; **3**, 97295-40-4; **4**, 16530-84-0; **5**, 16530-83-9; **6**, 66723-84-0; **7**, 66723-83-9; **8**, 1636-01-7; **9**, 1636-00-6; **10**, 5588-84-1; **11**, 97295-41-5; **12**, 23323-41-3; **13**, 97295-42-6; **14**, 13709-31-4; $VOCl_2$(O-*t*-Bu), 25288-97-5; $VOCl(O\text{-}t\text{-}Bu)_2$, 1735-11-1; $VO(O\text{-}t\text{-}Bu)_3$, 1686-24-4; $VO(NEt_2)(O\text{-}t\text{-}Bu)_2$, 97295-43-7; $\{VOCl_3(Cl^-)\}$, 36695-42-8; $\{VOCl_3(F^-)\}$, 97226-30-7; $\{VOF_3(Cl^-)\}$, 97295-44-8; $\{VOF_3(F^-)\}$, 78280-02-1; $[VOF_4(Me_2SO)]^-$, 97295-45-9; $[VO(O\text{-}i\text{-}Pr)_3NEt_2]^-$, 97295-46-0.

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(55) A recent PE and SCC-Xα investigation of VOX_3 (X = F, Cl, Br) suggests the following assignment of MO levels relevant for transitions into empty V(3d) orbitals (in the order of increasing energy). $VOCl_3$ and $VOBr_3$: 3e (V–O), $4a_1$ and 2e (V–X), $3a_1$ (V–O). VOF_3: 5e (V–O), $5a_1$ (V–O) (Elbel, S.; Kudnig, J.; Rünger, G.; Grodzicki, M. *J. Electron Spectrosc.*, in press). These assignments in part differ from those given by Tse et al.;[48] they further support our conclusions, including the extrapolation to $VOBr_3$.