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The Solution Structures of the $VOCl_3$ Complexes of Neutral Nitrogen and Oxygen Donors: a Vanadium-51 NMR Spectroscopic Study

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Abstract

$VOCl_3$ reacts with N-donors (secondary and tertiary aliphatic and aromatic, mono- to tridentate amines; nitrils) O-donors (ketones; esters; ethers; nitrobenzene) and ambidentate N,O-donors [dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), azoxibenzene and uracil], L, to form dark red to red–brown or yellow [DMF, NMP, *N*-methylimidazole (Me-im)], light-sensitive and often oxidatively labile systems which show up to three ^{51}V NMR resonances in the range of +39 (acetone) to −473 ppm (Me-im) relative to neat $VOCl_3$. Based on an analysis of the ^{51}V NMR spectra it is suggested that three classes (**I**, **II**, **III**) of complexes in mutual exchange can be present: oligomeric, solvated or charge-transfer complexes $\{VOCl_3 \cdot nL\}_x$ ($n = 1$, 2) (**I**), and the monomeric, neutral or ionic complexes $[VOCl_{3-m}L_n]Cl_m$ [$n = 1$, $m = 0$ or 1 (**II**); $n = 2$, $m = 0–2$ (**III**)].

Introduction

While anionic ligands such as halides (X^-), alkoxo (OR^-) and amido (NR_2^-) groups readily form vanadyl complexes of the general composition $VOX_{3-n-m}(OR)_n(NR_2)_m$ and $[VOX_{4-m-n}(OR)_m(NR_2)_n]^-$ [1–5], the coordination behaviour of neutral N-donors (amines and nitriles), O-donors (ethers, ketones and esters) and ambidentate ligands (carbonic acid amides) is much more complex. In the past, these compounds which, in many cases, have the constitution $VOX_3 \cdot nL$ ($n = 1$ or 2), have usually been described as metal-to-ligand charge-transfer complexes [6, 7], and only more recent structural analyses have revealed that, at least for nitril complexes and in the crystalline state, defined coordination compounds exist [8, 9]. On the other hand, the solution structure of these complexes is not yet well understood. In a recent study on VOF_3 and $VOCl_3$ in tetrahydrofurane (THF), we have shown that association phenomena accompanied by partial ligand labilization and adduct formation of the solvent is likely to occur [1]. The present investigation is a more comprehensive view of the various phenomena (complexation, dissociation, adduct formation and Cl substitution) observed with vanadyl chloride in the presence of sundry solvents exhibiting donor properties and hence acting as ligands.

The investigations are carried out on the basis of ^{51}V NMR spectra. The ^{51}V nucleus (natural abundance 99.76%) is highly receptive (the receptivity relative to $^1H = 1$ is 0.38 at constant field B_0 and 5.52 at constant frequency ν_0) and exhibits a favourable intrinsic sensitivity: the overall range of chemical shift values spans 3500 ppm [10]. Another favourable property is its small electric nuclear quadrupole moment (-0.05×10^{-28} m^2; nuclear spin $I = 7/2$), which allows for the observation of sufficiently sharp resonance signals at a reasonable signal-to-noise ratio even in compounds with C_1 symmetry.

Experimental

All operations were carried out under N_2 atmosphere (to avoid hydrolysis) and in brown glassware (to avoid decomposition by light). Only absolute and oxygen-free solvents were employed. Purification was carried out according to standard procedures. In several cases, it became necessary to put together the reactants at dry-ice temperature directly in the NMR tubes, and to thaw carefully while the NMR experiment was carried out under thermostatic conditions to ensure observation of signals before oxidation of the ligated solvent lead to substantial amounts of paramagnetic (blue to green) VO^{2+} species and thus to paramagnetic broadening of the signal(s) beyond detectability. Experimental details for the preparation of the samples are compiled in Table I. With secondary amines (imidazol, pyrrol, *N*-methylaniline), no HCl evolution occurred, *i.e.* these ligands behave in the same manner as tertiary amines.

$VOCl_{3-n}(NMePh)_n$ ($n = 1$ and 2): 1.16 g (15 mmol) of *N*-methylaniline dissolved in 50 ml of n-pentane were cooled to 223 K and treated with

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TABLE I. Experimental Details

$VOCl_3$ (mmol)	Solvent (ml)	Ligand[a] (mmol)	Solvent (ml)	Temperature (K)	Colour	Precipitation[b]	Soluble in	Decomposes[c]
	neat	ex. NBu_3, NEt_3	neat	253	red–brown			±inst.
0.5	2 CCl_4	5 $PhNMe_2$	10 CCl_4	243	red–brown	+		rapidly
0.5	5 CCl_4	6 pyridine	5 CCl_4	198	red–brown			rapidly
2.5	10 pentane	5 isochin	20 pentane	253	violet	+	$PhNO_2$, $CHCl_3$	
0.5	1 $CHCl_3$	1 chinox	5 $CHCl_3$	260	red			±inst.
5	12 pentane	10 chin	40 pentane	263	red–violet	+	$PhNO_2$	slowly[f]
5	10 CCl_4	5 bipy	20 CCl_4	250	red–brown	+	$PhNO_2$[d]	
5	10 $CHCl_3$	10 ophen	50 $CHCl_3$	273	black	+	CH_2Cl_2	
	neat	ex. terpy	5 $CHCl_3$	273	red–brown	+	$PhNO_2$	slowly
	CCl_4	ex. Me-im	CCl_4	260	dark red	oil	CH_2Cl_2, $CHCl_3$[e]	rapidly
	$CHCl_3$	ex. TM-im	$CHCl_3$	260	red–brown			rapidly
1	neat	9.3 PhNHMe	neat	198	dark red			rapidly
	neat	ex. pyrrol	neat	198	red–brown			±inst.
0.5	neat	2.9 imidazol	5 $CHCl_3$	273	red–brown	oil	CH_2Cl_2, toluene	rapidly
	neat	ex. MeCN, PhCN	neat/$CHCl_3$	295	red–brown			
5	pentane	10 ketone:	pentane	273				
		camphor			black–red	+	cyclohexane	
		Ph_2CO			black–red	+	CH_2Cl_2, $CHCl_3$	
		fluorenone			black–red	+	slightly CH_2Cl_2	slowly
	neat	ex. acetone	neat	240	red–brown			
	neat	ex. Et_2O	neat	273	dark red			±inst.
	neat	ex. diglyme	neat	243	red	+	CCl_4	rapidly
	neat	ex. MeC(O)OEt	neat	273	dark red			rapidly
2.5	10 heptane	2.5 azoxibenzene	10 heptane	263	red	+	$CHCl_3$	rapidly
	neat	ex. NMP	neat	295	light yellow			
	neat	ex. DMF	neat	295	light yellow			
	neat	uracil	CH_2Cl_2	295	light brown			slowly
	neat	ex. $PhNO_2$	neat	295	red–brown			

[a] ex. = large excess, *i.e.* molar ratio $VOCl_3/L > 1/20$. Abbreviations: chin = chinoline, chinox = chinoxaline, bipy = 2,2′-dipyridyl, ophen = ortho-phenanthroline, terpy = terpyridyl, Me-im = *N*-methylimidazole, TM-im = 1,2,4,5-tetramethylimidazole, NMP = *N*-methylpyrrolidone, DMF = *N,N*-dimethylformamide, diglyme = diethyleneglycol-dimethylether, $PhNO_2$ = nitrobenzene. [b] A precipitation is indicated by a + sign. [c] Decomposition is indicated by ±inst. (±instantaneously, *i.e.* within a few minutes), rapidly (within *ca.* half an hour) or slowly (within several hours). These indications are for room temperature and with the exclusion of light. [d] Addition of NMP or DMF to the red–brown solutions in CH_2Cl_2 or $PhNO_2$ leads to yellow solutions by (partial) exchange of the bipy and ophen ligands. [e] Freshly prepared, red–brown solutions show two signals in the ^{51}V NMR (−0.3 and −53 ppm). On standing for *ca.* 10 min, the solution becomes colourless to light violet, and a new signal at −473 ppm arises. Exposure to daylight gives a light brown solution and an additional rather broad signal at −658 ppm. [f] One of the decomposition products is $[VOCl_4]^-$ (δ = +49 ppm [11]).

9.4 ml of 1.6 M butyl-lithium solution in n-hexane (containing 15 mmol BuLi), warmed to room temperature and, after stirring for 1 h, cooled back to 223 K. To this suspension, a solution of 0.475 ml (5 mmol) of $VOCl_3$ in 50 ml of pentane were added slowly and with stirring. The brownish, powdery precipitate was separated by filtration (still maintaining *ca.* 230 K), dissolved in nitrobenzene and investigated by ^{51}V NMR. Two signals were observed, corresponding to a mixture of the mono- and dichlorovanadylamide.

^{51}V NMR spectra were obtained on a Bruker WH 90 PFT spectrometer (signals with line widths at half height < 500 Hz) or on a Bruker SWL 3-100 wide-line spectrometer. All chemical shifts have been measured and are quoted relative to neat $VOCl_3$. Measuring parameters:

– Bruker WH 90: 23.66 MHz (2.11 T); sweep width 25 kHz (acquisition time 0.16 ms), pulse width 5–8 μs; resolution 6 Hz (0.25 ppm)/point. Temperature, if not indicated otherwise, 300(1) K. Rotating 7.5 mm vials fitted into 10 mm vials with acetone-d_6 as external lock.

– Bruker SWL 3-100: 16.0 MHz, magnetic field for the standard ($VOCl_3$) = 1.4297 T; sweep width 2 mT; modulation amplitude 0.1 mT; time constant 0.5 s. Temperature 303(2) K. 14 mm diameter tubes (non-rotating).

TABLE II. Compilation of ^{51}V Chemical Shifts and Assignments

Ligand[a]	Medium	$\delta(^{51}V)$[b] (ppm)	Assignment[c]
NEt_3, NBu_3	neat	−3.4[d]	I
$PhNMe_2$	$PhNO_2$	−17	I/II
pyrrol	neat	−80	II
chin	$PhNO_2$	−350	III
pyridine	CCl_4	−28, −59, −412[e]	I/II, II, III
isochin	$CHCl_3$	−2	I
chinox	$CHCl_3$	−28	I/II
imidazole	$CHCl_3$	−6	I
Me-im	$CHCl_3$	−0.3[f], −53[f], −472[g]	I, II[g]
TM-im	$CHCl_3$	−10, −80	I, II
bipy	$PhNO_2$	−120	II/III
ophen	$PhNO_2$	−135, −315	II/III, III
	$PhNO_2$/DMF	−380[h], −470[g]	
terpy	$PhNO_2$	−378	III
MeCN*	CCl_4	−114, −391	II/III, III
	$CHCl_3$	−20[i]	I/II
	neat	+14, −125, −368[j]	I, II/III, III
PhCN	$CHCl_3$	−10[i]	I
Ph_2CO	CH_2Cl_2/pentane	+4	I
fluorenone	CH_2Cl_2/pentane	+9[k]	I
camphor	cyclohexane	+5	I
acetone	neat	+39[l], −388	[l], III
MeC(O)OEt	neat	−326	III
THF[m]	pentane	−15, −32, −316	I/II, III
Et_2O	neat	−26, −293, −323	I/II, III
diglyme	CCl_4	−19	I/II
$PhNO_2$	neat	0, −79	I, II
azoxibenzene	$CHCl_3$	−0.5	I
DMF	neat	−366	III
NMP	neat	−364	III
uracil	CH_2Cl_2	+7, −245[n], −322[n]	I, II/III, III

[a] For abbreviations see Table I, footnote a. [b] Relative to $VOCl_3$ (neat) at room temperature if not indicated otherwise. [c] **I**; $\{VOCl_3 \cdot nL\}_x$ ($n = 1$ or 2; oligomeric solvated or CT complex); **II**: $VOCl_3(L) \cdot L$ or $[VOCl_2L]Cl$ (one V–L bond with substantial HOMO and LUMO participation of vanadium orbitals); **III**: $VOCl_3(L)_2$, $[VOCl_2L_2]Cl$ or $[VOClL_2]Cl_2$ (two V–L bonds with substantial vanadium character). The notations **I/II** and **II/III** indicate signals representing weighted equilibrium positions between **I** and **II** or **II** and **III**, respectively. [d] For NBu_3, additional very weak signals at −317 and −436 ppm are observed at 253 K. [e] At 303 K; see Table III for details. [f] Only in freshly prepared solutions. [g] Cannot be assigned unambiguously. [h] $VOCl_3$-(DMF). [i] Irrespective of the molar ratios $VOCl_3$/RCN. [j] At 233 K. Only one signal (−105 ppm) is observed at 303 K (*cf.* Table III). [k] No additional signal arises at lower temperatures (down to 253 K). [l] The signal at +39 ppm may be attributed to an anionic species such as $[VOCl_4 \cdot OCMe_2]^-$; *bona fide* $[Et_4N][VOCl_4]^-$ in THF has a resonance signal at +46 ppm [11]. [m] See also Table III. [n] These two weak signals may correspond to different coordination modes (N or O or N, O).
*See note added in proof, p. 20.

Results

^{51}V chemical shift values are summarized in Table II. For three selected systems – $VOCl_3$/NCMe, $VOCl_3$/pyridine and $VOCl_3$/THF – shift variations with temperature and molar ratios are listed in Table III. Figure 1 contains typical spectra obtained on a PFT spectrometer at constant B_0 (Fig. 1a) and on a wide-line instrument at constant ν_0 (Fig. 1b).

Inspection of Table II shows that the shift ranges in which the one to three signals are observed can be allocated to three distinct classes, referred to in the succeeding discussion as class **I** (typically +10 to −10 ppm), class **II** (−25 to −90 ppm) and class **III** typically between −360 and −390, with extensions to −316 (THF) and −472 ppm (*N*-methylimidazole). The dependence of the signal positions upon temperature, molar ratio, the steric and electronic nature of the ligand, the number of signals observed and their relative intensities, exhibited in Tables II and III, indicate that equilibria with the participation of at least three different species have to be considered. In many cases, there is only one single resonance at room temperature, standing for fast equilibration of the complete system or the presence of only one of the three species.

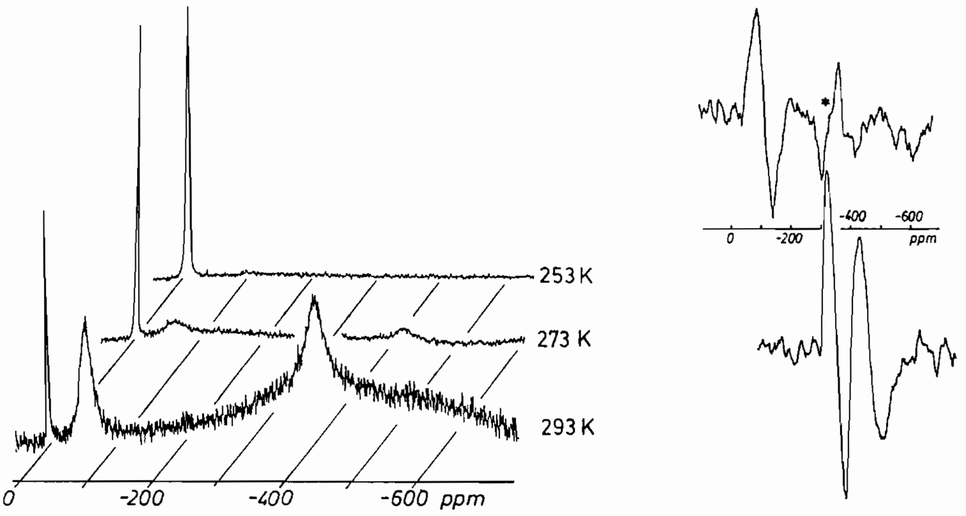

Fig. 1. Representative ^{51}V NMR spectra: (a) $VOCl_3$/pyridine 1/10, obtained at three selected temperatures on a Bruker WH 90 instrument (number of transients: 2100, 2700, 8400; from top to bottom). The broadening of the signal at –403 ppm partially arises from paramagnetic impurities due to VO^{2+} (possibly $VOCl_2py_3$ [6]). (b) Broad-line spectra (first derivatives) of a solution of $VOCl_3$/*ortho*-phenanthroline in nitrobenzene (above) and in nitrobenzene/DMF (bottom). For signal assignments see Table II. The signal denoted with an asterisk is over-modulated. Scan number: 11 (top) and 24.

TABLE III. Temperature and Concentration Dependencies of $\delta(^{51})$ Values for Selected $VOCl_3$/L Systems[a]

T (K)	δ_I	δ_{II}	δ_{III}
L = py[b,c]			
253	–0.2		
263	–5.5vs	–66vw	–414vw
273	–5.2s	–65w	–409w
283	–4.8s	–61m	–405m
293	–4.7m	–63s	–403s
303		–62s	–405s
L = NCMe[b]			
233	+14m	–125vs	–368m
243	+15m	–126vs	–369m
253	+27m	–123vs	–371m
263	+33w	–123vs	–399w
283		–120s	–391vw
293		–114vs[d]	–387vw
303		–105[d]	
313		–97[d]	
323		–89[d]	
L = THF[e]			
Molar ratio			
1/0.4	–3.6vs	–14vw	
1/0.7	–3.4s	–13m	
1/1.3	–2.3s	–17s	
1/∞		–32s	–324s

[a] δ_I, δ_{II} and δ_{III} correspond to species mainly represented by class **I**, **II** and **III** complexes, respectively. [b] Molar ratio $VOCl_3$/L = 1/10. [c] The compound begins to decompose at $T > 285$ K. [d] The signal indicates a weighted equilibrium position under conditions where exchange is fast. [e] At 298 K.

Discussion

It has been known for some time that vanadyl compounds $VOCl_{3-n}(OR)_n$ tend to associate to oligomers in the neat (solid or liquid) state and also in inert solvents. Cryscopic measurements [12], mass spectroscopic studies of the thermal decomposition of the compounds [12, 13], ^{1}H [14] and ^{51}V NMR evidence [15, 16] have been employed to support this view. More recently, ^{51}V NMR studies of mixtures of $VOCl_3$ and VOF_3 in polar solvents such as THF have revealed that these vanadyl halides also tend to associate, *viz.* $\{\cdots V(O)Cl_2{-}Cl\cdots V(O)F_2{-}F\cdots\}_n$ [1] (compare **2b** in Fig. 2). In this oligomeric structure, one of the V–X bonds per VOX_4 unit is labile. An alternative association scheme (**1b** in Fig. 2) has been proposed for vanadyl alkoxides [12–14]. Based on these structures in the liquid state and on X-ray results for $VO(OMe)_3$ [17], $[\{VOF_2(OH_2)\}_2(\mu\text{-}F)_2]^{2-}$ [18, 19] and $[\{VOCl_2(OH_2)\}_2(\mu\text{-}Cl)_2]^{2-}$ [20], which all show asymmetrical V–(μ-Z)–V bridges (**1a** and **2a** in Fig. 2; the asymmetrically bridging ligands Z are indicated by an asterisk), we interpret our NMR results in the following manner:

The molecular parameters contributing to variations in ^{51}V shielding are the mean HOMO-LUMO separation, $\overline{\Delta E}$ (which is closely connected to the electronegativities of the substituents on the metal centre [1]), the expansion of the vanadium-d electrons, r, and the vanadium-d LCAO coefficients, C, of the HOMOs and LUMOs taking part in electronic transitions. These three quantities are related to the overall shielding σ by

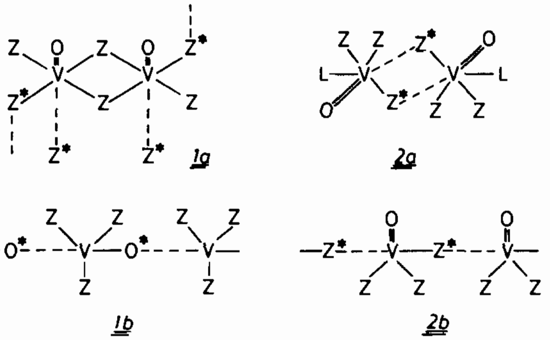

Fig. 2. Possible oligomeric structures of the compounds VOZ_3, based on the X-ray structural analyses of $VO(OMe)_3$ (**1a**) [17] and $[\{VOX_2(OH_2)\}_2(\mu\text{-}X)_2]^{2-}$ (**2a**) (X = F [18, 19], Cl [20]) and spectroscopic evidence (**1b** Z = OR [12–14, 16]); **2b**, Z = Cl and F [1]). Dashed lines represent comparatively weak V–Z interactions.

$$\sigma = A - b\cdot\overline{\Delta E^{-1}}\langle r^{-3}\rangle\overline{C^2}$$

where A and b are constants (A is the diamagnetic shielding, the second term the paramagnetic deshielding contribution)*.

The parameter $\overline{C^2}$ excludes all transitions with zero or negligible V(3d) contributions to either the HOMO or the LUMO. Hence, class **I** with its complexes exhibiting shift values very close to $VOCl_3$ comprises compounds, where the interaction of $VOCl_3$ and the solvent leads to a solvated species or a charge-transfer complex $\{VOCl_3\cdot nL\}_x$. The deep red–brown colour of most of the systems is in favour of strong metal-to-ligand charge transfer [7]. In either case, the minimum unit present may be a dimer analogous to **2a** in Fig. 2 and formed by solvation and rearrangement of **1b** or **2b**, or by rupture of some of the weaker Z-bridges in a polymeric structure (**1a** in Fig. 2). We shall denote this minimal structural unit $\{VOCl_3\cdot 2L\}_2$. It has been shown, in fact, by the quintet resolution of the ^{51}V NMR signal of VOF_3 dissolved in DMSO [1] and CH_3CN (at 243 K) [21], that intact subunits with four halide ligands in close contact with the vanadyl group exist in solution apart from other species.

Class **II** complexes can be formed by breaking the remaining V–(μ-Z) bonds in **2a** (Fig. 2) and 'firm' (*vide infra*) coordination of the solvent molecule to produce either a neutral species or, by displacement of one Cl^- from the first coordination sphere, an ionic complex. The signals found in the −25 to −90 ppm region should therefore represent weighted positions of equilibria of the kind

$$\{VOCl_3\cdot 2L\}_x \rightleftharpoons x\{VOCl_3(L)\cdot L\} \rightleftharpoons x\{[VOCl_2L]Cl\cdot L\} \qquad (1)$$

With this formulation of the monomeric compounds in equilibrium (1), it is postulated that (i) there is significant participation of vanadium orbitals to the relevant HOMO(s) and LUMO(s) and (ii) that ligands with a more pronounced electronegativity than Cl are attached to the vanadyl group in addition to or in exchange of Cl. The latter point is a consequence of the increase of the HOMO-LUMO splitting with increasing electronegativity of the substituents Z, χ_Z, *i.e.* in the order Cl < N < O, which gives rise to an increase of the overall shielding of the ^{51}V nucleus in the same order via the decrease of the paramagnetic deshielding term. We have recently verified this so-called inverse dependence of metal shielding upon χ_Z in d^0 systems for various complexes $VO(Z)(Z')(Z'')$ (Z, Z′, Z″ = Cl^-, NR_2^-, OR^-, F^-) [1].

In class **III** species with typical δ values around 350 ppm, the interactions between V and L appear to be still stronger and point to the generation of at least one additional compound with an additional solvent molecule in covalent contact to the vanadyl group [(equilibrium (2)]:

$$VOCl_3(L)\cdot L \rightleftharpoons VOCl_3L_2 \rightleftharpoons [VOCl_2L_2]Cl \rightleftharpoons [VO(Cl)L_2]Cl_2 \qquad (2)$$

The equilibrium shifts to the right-hand side with increasing temperature and molar ratio solvent/$VOCl_3$ (see Table III). If the exchange rates are sufficiently low on the NMR time scale, all three signals for the type **I**, **II** and **III** complexes may be observed. Otherwise, one or two signals arise, representing specific equilibrium positions. In a few cases (terpyridine, ethyl acetate, DMF and NMP), the only species present at room temperature is a class **III** complex. A number of other solvents form CT compounds only (*cf.* Table II).

$\delta(^{51}V)$ values for class **II** and **III** compounds with nitrogen donors are around those which have been noted for V(V) chlorides containing, in addition to one or two chloro ligands, amido and imido groups. Examples are $VCl_2(Nt\text{-}Bu)(NHt\text{-}Bu)(NH_2t\text{-}Bu)$ (−188 ppm [22]), $VCl_2(Nt\text{-}Bu)(Nt\text{-}Bu\text{-}SiMe_2\text{-}NHt\text{-}Bu)$ (−127 ppm [23]), $VOCl(NEt_2)_2$ (−141 [1]) and $VOCl_{2/1}(NMePh)_{1/2}$ (−111/−265 ppm; this work). These data are further support for the involvement of solvent molecules in direct coordination to the vanadium centre. The same conclusion holds for some neutral oxygen donors such as Et_2O, THF, and acetone (−250 to −388 ppm) if compared to the δ values of, e.g. $VOCl_2OEt$ (−300) and $VOCl(OEt)_2$ (−414 ppm) [10, 16], $VOCl_2(acac)$

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*For a more detailed treatment of the factors influencing ^{51}V shielding in VO^{3+} compounds see ref. 1. A more general treatment of metal shielding is given in ref. 10.

(–203) and $VOCl(acac)_2$ (–336 ppm) (acac = acetylacetonato) [24].

The compounds formed between $VOCl_3$ and bipy or ophen, which have been characterized formerly in the solid state as 1:1 adducts [6, 7], give rise, in nitrobenzene or dichloromethane solution, to one and two signals, respectively, assigned to class **II** and **III** complexes. On addition of DMF or NMP, the red–brown solutions turn to yellow, and new signals at a higher field show up (*cf.* Table II and Fig. 1b). Only one of these (–380 ppm) may coincide with the compound obtained by treating $VOCl_3$ with DMF only (–366 ppm), *i.e.* with complete removal of the bidentate nitrogen ligand by the possibly also bidentate N,O ligand DMF. The nature of the second component (–470 ppm), which is also observed in the system $VOCl_3$/*N*-methylimidazole (see footnote in Table I), is not clear.

Conclusion

As evidenced by the ^{51}V NMR spectra, $VOCl_3$ dissolved in polar nitrogen and oxygen donor solvents may exist in the form of at least three species (**I**, **II**, **III**) which are in mutual equilibrium $\mathbf{I} \rightleftharpoons \mathbf{II} \rightleftharpoons \mathbf{III}$ with each other. **I** is probably an oligomeric solvated or charge transfer species with a signal position very close to that of neat $VOCl_3$ or $VOCl_3$ in inert solvents. CT transitions do not significantly contribute to the vanadium shielding, since the V(3d) LCAO coefficient of the LUMO, localized almost completely on the ligating solvent, is close to zero. **II** and **III** represent compoounds with the ^{51}V nucleus substantially more shielded. These (possibly) monomeric species contain one (**II**) or two (**III**) solvent molecules firmly ligated to vanadium in the first coordination sphere, *i.e.* in a molecular arrangement where at least one of the ground state HOMOs and low lying excited state levels constitute sizable participation of vanadium orbitals. Suggested formulations are $VOCl_3L$ or $[VOCl_2L]Cl$ for **II**, and $VOCl_3L_2$, $[VOCl_2L_2]Cl$ or $[VO(Cl)L_2]Cl_2$ for **III**. The ionic formulation has also been proposed by Buslaev and co-workers for the products obtained from the reaction of $VOCl_3$ and *N,N*-dimethylacetamide [25]. Support for the ionic formulation also comes from the $^{35,37}Cl$ NMR spectra and from ^{19}F NMR results on the corresponding VOF_3 systems (W. Priebsch and D. Rehder, to be published).

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Note added in proof (August 13, 1986)

While this paper was in press, an independent study of the system $VOCl_3$/MeCN appeared (R. C. Hibbert, N. Logan, O. W. Howarth, *Dalton Trans.*, 369 (1986)), in which only one signal at –117 ppm is described. On addition of H_2O, this signal shifts to –365 ppm, assigned $[VO_2Cl_2]^-$ (the chemical shift for *bona fide* $[VO_2Cl_2]^-$ is –359 ppm [11]). Hibbert's species more likely is a class **III** complex with coordinated H_2O.