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Dinitrosyl Vanadium Complexes

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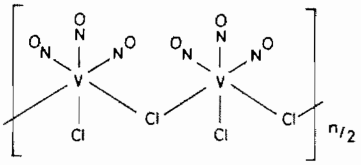
Solutions of $[V(NO)_3Cl_2]_n$ *(1) in nitromethane, tetrahydrofuran and acetonitrile have been characterized by both their nitrosyl stretching frequencies and their* ^{51}V *NMR absorptions. Only the acetonitrile solutions contain dinitrosyl vanadium species. Careful treatment of* 1 *in acetonitrile with sodium amalgam or zinc powder leads to solvated* cis*-dinitrosyl vanadium intermediates from which new complexes of the composition* $[V(NO)_2L_2Cl]$ *(L = acetonitrile (2) and methyl isonicotinate (3), respectively) and* $[V(NO)_2(^tBu{-}N{\equiv}C)_4]PF_6$ *(4) have been obtained.*

Introduction

Nearly all dinitrosyl vanadium complexes known so far are derived from the η^5-cyclopentadienyl half-sandwich compound $V(Cp)(CO)(NO)_2$ [1–4]. Displacement of the CO ligand by Lewis bases (L) leads to complexes of the type $V(Cp)(L)(NO)_2$ [4, 5], whereas photo-induced decarbonylation in inert solvents (hexane) gives polynuclear aggregates $[V(Cp)(NO)_2]_n$ [3]. A binuclear complex $[V(Cp)(NO)_2]_2$ was reported [6] to be formed by nitrosylation of vanadocene, VCp_2. The only other dinitrosyl vanadium complexes are cations $[V(NO)_2(L{-}L)_2]^+$ which were obtained in a redox reaction between $K_3[V(CN)_5NO]\cdot 2H_2O$ and excess 1,10-phenanthroline or 2,2′-bipyridyl (L–L) [7].

We have observed that the brown polynuclear dichloro-trinitrosylvanadium, $[V(NO)_3Cl_2]_n$ (*1*), first prepared and investigated by Beck and coworkers [8, 9], dissolves in acetonitrile to give solutions which contain – among other species – dinitrosyl vanadium intermediates. We now report upon our attempts to characterize these species by their nitrosyl stretching frequencies and ^{51}V NMR absorptions, and to obtain new dinitrosyl vanadium complexes.



(1) $[V(NO)_3Cl_2]_n$

(Proposed structure based on octahedral coordination of the vanadium atoms)

Experimental

All reactions were carried out under an argon atmosphere in dry solvents saturated with argon.

The parent complex, $[V(NO)_3Cl_2]_n$ (*1*), was prepared according to the literature [8, 9] by treating a *ca.* 0.2 *M* solution of VCl_4 in carbon tetrachloride with dry NO gas.

Bis(acetonitrile)dinitrosylchlorovanadium (2)

A suspension of 15 mmol freshly prepared 1% sodium amalgam in 25 ml acetonitrile was solidified by cooling to –46 °C, and 0.32 g (1.5 mmol) *1* was then added. The mixture was slowly brought to room temperature and the excess amalgam was then removed by filtration. The red-brown solution should not contain the mononitrosyl vanadium complex $[V(NO)(CH_3CN)_4Cl]Cl$ [9] (ν(NO) 1662 cm^{-1}). Heating overnight to 65 °C led to the precipitation of a brick-red powder which was washed with acetonitrile and diethylether and dried *in vacuo.* Yield 0.13 g (0.57 mmol, 37%), dec. above 103 °C. *Anal.* Found: C, 21.37; H, 2.74; N, 24.32; Cl, 15.61%; Calcd. for $C_4H_6ClN_4O_2V$ (288.54) C, 21.03; H, 2.64; N, 24.52; Cl, 15.62%.

Bis(methyl isonicotinate)dinitrosylchlorovanadium (3)

To a frozen suspension of 1.63 g (25 mmol) zinc powder in 15 ml acetonitrile was added 0.53 g (2.5

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TABLE I. IR and NMR Data of the Nitrosyl Vanadium Complexes.

Compound	Infrared Spectra [cm^{-1}]^a		NMR Spectra [ppm]		
	ν(NO)	other bands	$^1H^b$	$^{13}C^b$	$^{51}V^c$
$[V(NO)_3Cl_2]_n$ (*1*)	1924s, 1765vs				
1 in nitromethane	1917, 1774				-605^d
1 in tetrahydrofuran	1663				-518^e
1 in acetonitrile	1738, 1610				−272
(*cf.* Figs. 1 and 2)	1718, 1584				−223
	1662				−517
1 + $NaHg_x$ in acetonitrile	1738, 1610				−272
	1718, 1584				−223
1 + Zn in acetonitrile	1738, 1610				−272
$[V(NO)_2(CH_3CN)_2Cl]_x$ (*2*)	1722, 1590	2294, CN	1.99	2.0, CH_3	−223
				118.7, CN	
$[V(NO)_2(NC_5H_4-COOCH_3)_2Cl]_y$ (*3*)	1712, 1569	1765, ester	3.94	52.1, OCH_3	−209
			7.88	123.0(*m*)	
				137.9(*p*) ring	
			8.75	151.4(*o*)	
$[V(NO)_2(^tBuNC)_4]PF_6$ (*4*)	1729, 1619	2206, 2189, NC	1.53, 1.55	30.1, 30.3, $\underline{C}H_3$	−1040
				59.5, $\underline{C}(CH_3)_3$	

^{a}Solid state spectra in nujol, unless otherwise stated (Perkin Elmer 297). ^{b}Solutions in CD_3CN, rel. TMS, at 30 °C (JEOL FX-90Q). ^{c}Solutions in CD_3CN, rel. ext. $VOCl_3$, at 30 °C (JEOL FX-90Q). ^{d}CD_3NO_2. ^{e}$[D_8]THF$.

mmol) $[V(NO)_3Cl_2]_n$ (*1*). The mixture was then slowly brought to room temperature while being stirred. After filtration 1.03 g (7.5 mmol) methyl isonicotinate was added. The solution was stirred for 1 h at room temperature, filtered and brought to dryness. The residue was taken up in 10 ml CH_2Cl_2, and the solution thus formed was stirred for 15–30 min at room temperature. An orange-yellow powder precipitated which was filtered off, washed with CH_2Cl_2 and pentane and dried *in vacuo*. Yield 0.60 g (57%), dec. above 131 °C. *Anal.* Found: C, 39.05; H, 3.49; N, 13.26; Cl, 9.50%; Calcd. for $C_{14}H_{14}ClN_4O_6V$ (420.66) C, 39.97; H, 3.35; N, 13.32; Cl, 8.43%.

Tetrakis(tert-butyl isocyanide)dinitrosylvanadium hexafluorophosphate (4)

Tert-butyl isocyanide was added dropwise to the red-brown acetonitrile solution obtained from the reaction of 0.53 g (2.5 mmol) *1* and excess zinc powder, until the bands of the free tert-butyl isocyanide appeared in the IR spectrum and remained present after prolonged stirring. Excess NH_4PF_6 was then added and the mixture stirred for 1 h. The solvent and free tert-butyl isocyanide were subsequently removed *in vacuo*. The dry residue was taken up in 10 ml CH_2Cl_2. After filtration over silica gel the solution was concentrated, then diluted with hexane/diethylether and kept overnight at −30 °C. The yellow-orange powder thus obtained was filtered off, washed with pentane and recrystallized from a small amount of methanol at −78 °C. Yield 0.82 g (1.40 mmol, 56%), m.p. 154 °C. *Anal.* Found: C, 40.71; H, 6.19; N, 14.28%; Calcd. for $C_{20}H_{36}F_6N_6O_2PV$ (588.40) C, 40.85; H, 6.16; N, 14.29%.

Results and Discussion

In agreement with the results of Beck and coworkers [8, 9], we have found that the polynuclear trinitrosylvanadium complex $[V(NO)_3Cl_2]_n$ (*1*) reacts with solvents such as tetrahydrofuran or acetonitrile losing NO. However, no loss of NO ligands is observed when *1* is dissolved in nitromethane.

In general, ligands containing 'hard' oxygen or nitrogen atoms convert *1* into mononitrosyl complexes [9] with two chloro ligands per metal atom. Thus, *1* reacts with the solvent tetrahydrofuran (THF) under NO evolution to give an orange product of the composition $V(NO)(THF)_2Cl_2$ [9]. Solutions of *1* in THF show only one single strong NO stretching absorption (1663 cm^{-1}) and only one ^{51}V NMR signal (−518 ppm), (Table I).

In acetonitrile, *1* also dissolves with partial loss of NO. However, both the IR and the ^{51}V NMR spectra of the brown solution indicate the presence of three distinct nitrosyl vanadium complexes (Figs. 1 and 2). The two pairs of ν(NO) absorptions at 1738/1610 and 1718/1584 cm^{-1} are tentatively ascribed to two

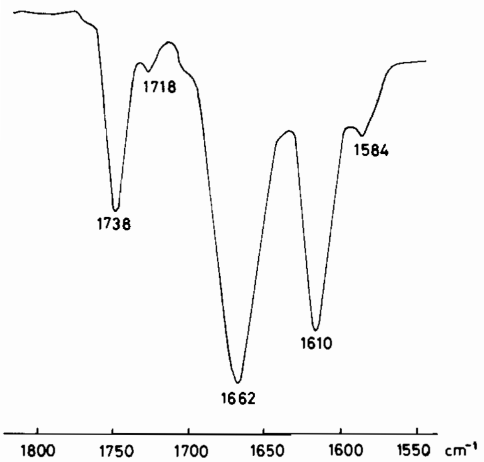

Fig. 1. IR spectrum of an acetonitrile solution of $[V(NO)_3Cl_2]_n$ (*1*) at room temperature (nitrosyl stretching region).

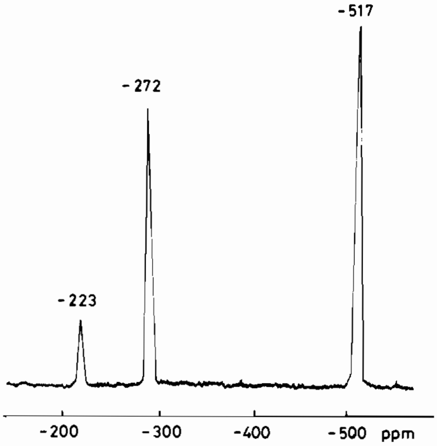

Fig. 2. ^{51}V NMR spectrum of an acetonitrile solution of $[V(NO)_3Cl_2]_n$ (*1*) at room temperature (rel. ext. $VOCl_3$).

cis-dinitrosyl vanadium compounds which might possibly be isomers. The additional intense absorption at 1662 cm^{-1} is due to the orange-yellow mononitrosyl species isolated and described as $[V(NO)(CH_3CN)_4Cl]Cl$ by Beck and coworkers [9]. The formation of the mononitrosyl complex is reduced when *1* is dissolved in acetonitrile at temperatures near to the melting point of this solvent (–46 °C). From the intensity ratios of the absorptions in the IR and ^{51}V NMR spectra, the bands can be unambiguously assigned to the three nitrosyl vanadium species (Table I).

The IR nitrosyl stretching pattern is simplified when $[V(NO)_3Cl_2]_n$ (*1*) is dissolved in acetonitrile in the presence of dehalogenating agents such as sodium amalgam or zinc powder.

In the presence of 1% sodium amalgam the mononitrosyl compound is not formed and the dinitrosyl species with ν(NO) absorptions at 1718/1584 cm^{-1} becomes the major dinitrosyl vanadium complex. Heating of this acetonitrile solution overnight to 65 °C results in precipitation of a brick-red product of the composition $[V(NO)_2(CH_3CN)_2Cl]_x$ (*2*). Although formulation of a binuclear complex containing chloro bridges (x = 2) would be plausible, the dimeric nature of the brick-red complex has not yet been established*.

The IR spectrum of the solution obtained from the addition of zinc powder to a frozen solution of *1* in acetonitrile, followed by slowly warming to room temperature, shows only one pair of ν(NO) bands at 1738/1610 cm^{-1}. The ^{51}V NMR spectrum of this same solution consists of a single resonance at –272 ppm. According to our previous work [5] with dinitrosyl vanadium complexes, the complementary IR and ^{51}V NMR data indicate that a single *cis*-dinitrosyl vanadium species is formed when *1* is allowed to react slowly with zinc powder. Addition of *p*-carbomethoxy pyridine (methyl isonicotinate) to the homogeneous solution leads to a yellow complex of the composition $[V(NO)_2(NC_5H_4COOCH_3)_2Cl]_y$ (*3*). Its molecular weight (y = 2 ?) has not yet been established*.

The analytical composition of *2* and *3* indicates that a well-defined elimination of both a chloro and a nitrosyl ligand from $[V(NO)_3Cl_2]_n$ (*1*) takes place in the presence of reducing metals. The dinitrosyl intermediates in the acetonitrile solution of *1* might therefore be tentatively formulated as either '$[V(NO)_2(CH_3CN)_3Cl]$' or '$[V(NO)_2(CH_3CN)_2(\mu\text{-}Cl)]_2$'.

The *cis*-dinitrosyl vanadium unit is stabilized as the cation $[V(NO)_2(^tBu{-}N{\equiv}C)_4]^+$ when excess tert-butyl isocyanide is added to the acetonitrile solution. The cation which can be conveniently isolated as the salt $[V(NO)_2(^tBu{-}N{\equiv}C)_4]PF_6$ (*4*) is isoelectronic with the dication of the salt $[Cr(NO)_2(^tBu{-}N{\equiv}C)_4](PF_6)_2$ (*5*) recently synthesized in our laboratory [10].

In the ^1H and ^{13}C NMR spectra of both *4* and *5*, two signals of equal intensity are observed for the methyl groups of the tert-butyl isocyanide ligands, indicating two types of isocyanides (*cis*/*cis* and *cis*/*trans* with respect to the nitrosyl ligands).

The characteristic IR and NMR absorptions of the nitrosyl vanadium complexes *1*–*4* are collected in Table I. In addition to the nitrosyl stretching

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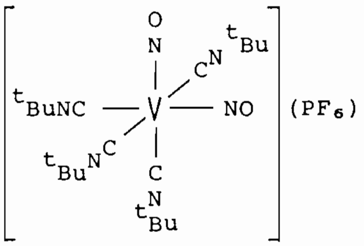
*Attempts to use vapour pressure osmometry (in nitromethane solution) gave erratic results due to decomposition of the complex. Conventional mass spectra could not be obtained, and loss of NO prevented the use of FD mass spectroscopy.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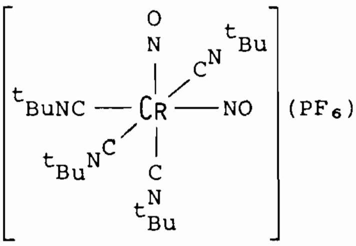
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	4	5	
IR spectra (in CH_2Cl_2, [cm^{-1}]):			
ν(NO)	1939, 1833	1915, 1820	
ν(–N≡C)	2199, 2183	2233	
NMR spectra (in CD_3CN, [ppm]):			
^1H	δ 1.53, 1.55	δ 1.58, 1.63	(CH_3)
^{13}C	δ 30.08, 30.31	δ 29.36, 29.47	($C(\underline{C}H_3)_3$)
	δ 59.5	δ 61.8	($\underline{C}(CH_3)_3$)

bands in the IR spectra, the ^{51}V NMR signals are of particular diagnostic value [11]. The neutral dinitrosyl derivatives *2* and *3* possess a ^{51}V chemical shift betwen δ –200 and –300 ppm (relative to $VOCl_3$), whereas mononitrosyl complexes are characterized by a single nitrosyl stretching absorption around 1650 cm^{-1} [9] and a ^{51}V NMR signal near δ –500 ppm.

Conductivity measurements in nitromethane confirm that $[V(NO)_2(^tBu{-}N{\equiv}C)_4]PF_6$ (*4*) is a 1:1 electrolyte; the extrapolated equivalent conductivity Λ_o is close to that of $[Cr(L)(^tBu{-}N{\equiv}C)_5]PF_6$ (L = NO or NS) [12]. On the other hand, compounds *2* and *3* show only very small conductivity in nitromethane, comparable to that of $[V(NO)_3Cl_2]_n$ (*1*) and $[Fe(NO)_2Cl]_2$.

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