Inorganica Chimica Acta, *149* (1988) 285–288

Bonding in $VCl_x(CH_3CN)_{6-x}^{3-x}$

J. O'BRIEN

Chemistry Department, Southwest Missouri State University, Springfield, Mo., U.S.A.

(Received March 3, 1988)

Abstract

Solutions of vanadium(III) chloride in acetonitrile contain the solvate $VCl_3(CH_3CN)_3$. NMR spectra indicate that bound solvent molecules exchange positions with bulk solvent molecules in two distinct processes. One proposal claims that these two processes are due to separate exchange rates for the facial and meridional isomers of $VCl_3(CH_3CN)_3$. Another suggestion that has been made is that the two different types of acetonitrile molecules in meridional $VCl_3(CH_3CN)_3$ undergo chemical exchange at different rates, and that no facial $VCl_3(CH_3CN)_3$ is involved.

Extended Hückel calculations have been done in order to examine the bonding in facial and meridional $VCl_3(CH_3CN)_3$. The results suggest that acetonitrile molecules *trans* to Cl atoms have one rate of exchange, while those *trans* to another acetonitrile have a different rate, regardless of which isomer is present. Calculations have been done on other vanadium, chlorine, acetonitrile species in order to clarify the effect of changing the *trans* or the *cis* neighbor.

Introduction

Solutions of VCl_3 in CH_3CN have been shown to contain $VCl_3(CH_3CN)_3$. The evidence for this is that the absorption spectra of the solutions match the diffuse reflectance spectra of solid $VCl_3(CH_3CN)_3$ [1]; and the molar conductivity of the solutions is low [2]. The infrared spectrum of $VCl_3(CH_3CN)_3(s)$ has been used to infer that in the solid state the conformation is facial [3].

Temperature studies of NMR linewidth data have established that two distinct exchange processes occur in solutions of VCl_3 in CH_3CN [4–6]. This result parallels that found in the related $TiCl_3$–CH_3CN system [7, 8]. It has been suggested that only meridional $VCl_3(CH_3CN)_3$ is present, and that acetonitriles *trans* to Cl atoms exchange more rapidly ($k = 8.2 \times 10^5$ s^{-1}) than do acetonitriles *trans* to other acetonitrile molecules ($k = 7.9 \times 10^2$ s^{-1}) [4]. It has been noted that the magnitude and sign of the $\Delta S^{\neq}$ values for the exchange process in deuterated nitromethane (+26 and −28 J K^{-1} mol^{-1}) are surprisingly different for the two reactions [4, 5] This has led others to assume that the two exchange processes are due to acetonitrile in the facial and meridional isomers, both isomers being present simultaneously in solution [6]. The fact that the solid is the facial isomer supports the claim that it is present in solution. One of the main goals of the present work was to examine the V–N bonding in the facial and meridional isomers of $VCl_3(CH_3CN)_3$ to see if molecular orbital calculations could distinguish significant differences in the bonding and determine the reason for those differences. Extended Hückel calculations have been done on all ten species possible in the set $VCl_x(CH_3CN)_{6-x}^{3-x}$. In addition, bonding in the seven coordinate kinetic transition state has been studied.

Experimental

All calculations employed the extended Hückel method [9, 10]. The weighted H_{ij} formula was used [11]. Parameters for vanadium were obtained by charge integration on facial $VCl_3(CH_3CN)_3$, and standard parameters were used for C, H, N, and Cl. All values are given in Table I.

Distances from vanadium to the coordinated Cl and N atoms were held constant at 2.59 and 1.60 Å,

TABLE I. Extended Hückel Parameters

Orbital	H_{ij} (eV)	Exponents	
		ζ_1	ζ_2
H_{1s}	−13.6	1.3	
C_{2s}	−21.4	1.625	
C_{2p}	−11.4	1.625	
N_{2s}	−26.0	1.950	
N_{2p}	−13.4	1.950	
Cl_{3s}	−30.0	2.033	
Cl_{3p}	−15.0	2.033	
V_{4s}	−8.81	1.30	
V_{4p}	−5.52	0.875	
V_{3d}	−11.00	4.70(.4755)	1.70(.7052)

0020-1693/88/$3.50

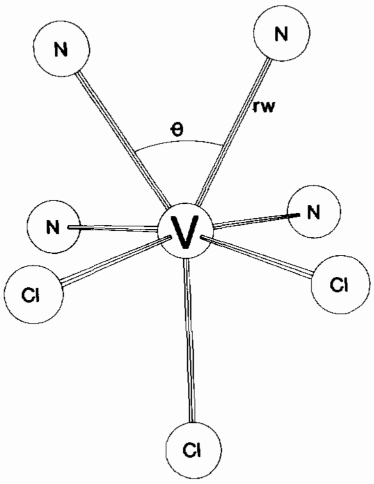

Fig. 1. Octahedral wedge conformation resulting from attack of a fourth acetonitrile on the 2N,1Cl face of facial $VCl_3(CH_3CN)_3$.

respectively. These values represent those distances which result in the minimum calculated energies for the two $VCl_3(CH_3CN)_3$ isomers. They agree reasonably well with the sums of the covalent radii [11, 12] which are 2.45 Å for V–Cl and 1.51 Å for V–N.

The geometry of the seven coordinate kinetic transition state was calculated assuming that approach of the fourth acetonitrile on one of the faces of the octahedron would lead to the 'octahedral wedge' [13] conformation. The wedge angle, θ, and distance, r_w, shown in Fig. 1, were then varied until an energy minimum was found. The five non-exchanging sites were kept at their six coordinate positions. This approach overestimates the distance r_w compared to values calculated by *ab initio* methods [14], but it leads to the same final conclusion [14].

Results and Discussion

$VCl_3(CH_3CN)_3$

Overlap population values indicate that the magnitude of the interaction of a N atom in acetonitrile with the central vanadium atom depends principally upon which atoms are *trans* and, secondarily, upon which atoms are *cis*. Thus, the sum of all overlap population values between two atoms, *i.e.* the reduced overlap population (*ROPM*) values shown in Table II, indicate that N atoms in facial $VCl_3(CH_3CN)_3$ have essentially the same strength interaction with the vanadium as does the N in meridional $VCl_3(CH_3CN)_3$ which is *trans* to a Cl. These N atoms all have a Cl *trans*, and 2N and 2Cl *cis*. On the other hand, the mutually *trans* Ns in the meridional isomer have a smaller *ROPM* value, 0.494 compared with 0.566 and 0.563. This suggests that these N atoms will behave differently and must be responsible for the second exchange process observed in both ^{14}N [4] and ^{1}H [6] NMR.

TABLE II. Reduced Overlap Population Matrix Values of $VCl_3(CH_3CN)_3$

Species	*trans* Atom	*ROPM*
mer-$VCl_3(CH_3CN)_3$	N	0.494
mer-$VCl_3(CH_3CN)_3$	Cl	0.566
fac-$VCl_3(CH_3CN)_3$	Cl	0.563

Of course, kinetic processes depend on the transition state as well as the ground state. Accordingly, calculations were done to find the geometry of the transition state and the resulting overlaps.

Energy calculations on the seven coordinate $VCl_3(CH_3CN)_4$ gave energy minima at an average distance of $r_w = 3.21$ Å at an angle of 55°. Consequently, all four possible exchange processes were examined with this configuration. The four processes are: (i) exchange *trans* to a N in the meridional isomer; (ii) exchange *trans* to a Cl in the meridional isomer; (iii) exchange in the facial isomer with attack on the 3N face; (iv) exchange in the facial isomer with attack on a 2N, 1Cl face. Table III gives *ROPM* values for these four processes at the transition state. These values lend support to the six coordinate results. Clearly the process involving a *trans* N is different. Not only is the reduction in bonding to the exchanging N smaller than in the other three cases, but the process is helped along by an increase in overlap of the N atoms not exchanging.

TABLE III. Reduced Overlap Population Matrix Values of Transition States

Species	Attack face	*trans* Atom	Exchanging N	Not exchanging N	Δ*ROPM*	
					Exch. N	Not exch. N
fac-$VCl_3(CH_3CN)_4$	3N	Cl	0.089	0.651	−0.474	+0.088
fac-$VCl_3(CH_3CN)_4$	2N, 1Cl	Cl	0.089	0.651	−0.474	+0.089
mer-$VCl_3(CH_3CN)_4$		Cl	0.087	0.613	−0.479	+0.047
mer-$VCl_3(CH_3CN)_4$		N	0.088	0.660	−0.406	+0.167

TABLE IV. Effect of *cis* and *trans* Positions on *ROPM*

Species	*trans* Atom	*cis* Atoms	σ	π	Total
$V(CH_3CN)_6^{+3}$	N	4N	0.261	0.182	0.443
$VCl(CH_3CN)_5^{+2}$	Cl	4N	0.330	0.198	0.528
$VCl(CH_3CN)_5^{+2}$	N	3N, 1Cl	0.263	0.196	0.459
cis-$VCl_2(CH_3CN)_4^+$	Cl	3N, 1Cl	0.328	0.217	0.545
cis-$VCl_2(CH_3CN)_4^+$	N	2N, 2Cl	0.263	0.212	0.475
trans-$VCl_2(CH_3CN)_4^+$	N	2N, 2Cl	0.261	0.215	0.476
mer-$VCl_3(CH_3CN)_3$	Cl	2N, 2Cl	0.324	0.242	0.566
mer-$VCl_3(CH_3CN)_3$	N	1N, 3Cl	0.262	0.232	0.494
fac-$VCl_3(CH_3CN)_3$	Cl	2N, 2Cl	0.326	0.236	0.563
cis-$VCl_4(CH_3CN)_2^-$	Cl	1N, 3Cl	0.323	0.262	0.585
trans-$VCl_4(CH_3CN)_2^-$	N	4Cl	0.263	0.251	0.515
$VCl_5(CH_3CN)^{-2}$	Cl	4Cl	0.322	0.287	0.609

Other Species

Calculations were done on the eight other possible species in this set. Table IV contains the overlap populations. The σ and π contributions are listed separately. The following facts emerge from perusal of this data.

(1) Changing a *trans* atom has a much larger effect on an atom's bonding than does changing a *cis* atom. The *ROPM* value increases by an average of 0.092 (19%) whenever a *trans* N is replaced by a Cl and the number of *cis* nitrogens and chlorines is unchanged. When the *trans* atom is the same and a *cis* atom is changed from N to Cl, the *ROPM* value increases by an average of 0.021. Thus, changes in the *trans* position cause more than four times as much change in *ROPM* than do *cis* changes.

(2) The σ contribution to the *ROPM* is insensitive to the *cis* position. The values in Table IV show the effect of the *cis* position when a N is *trans* to another N. Despite five different combinations of *cis* neighbors, the σ *ROPM* values all fall in the range 0.261 to 0.263. When a Cl is the *trans* atom, the effect of the *cis* position is not much larger, with all six values between 0.322 and 0.330. These changes of 1 and 2 percent can be contrasted with the 24% increase in the σ contribution to *ROPM* when a *trans* N is replaced by a Cl. The majority of the σ overlap is between the s and σ-p orbital of N with either the $d_{x^2-y^2}$ or d_{z^2} of the V. These results are in agreement with our expectation that competition for σ bonding occurs mainly with atoms that are *trans*. The values also indicate that N is a better σ bonder than Cl since the *ROPM* value increases whenever a Cl replaces a N. The relative positions of Cl and CN groups in the σ bonding series [15] are in agreement with this conclusion.

(3) The π contribution to *ROPM* depends on both the *cis* and *trans* positions. The average change upon replacement of a N with a Cl at a *trans* site is 15%. Changing the *cis* position causes an average change of 9%. This dependence on both the *cis* and *trans* positions is due to the fact that most of the π bonding is with the t_{2g} d orbitals which interact with both *cis* and *trans* positions. In agreement with the π bonding series [15] we see that whenever a Cl replaces CH_3CN in a *cis* position, the π interaction with a N increases.

TABLE V. Effect of Charge on *ROPM*

Species	*ROPM*	Charge on V
cis-$VCl_2(CH_3CN)_4^+$	0.475	1.31
trans-$VCl_2(CH_3CN)_4^+$	0.476	1.44
fac-$VCl_3(CH_3CN)_3$	0.563	1.19
mer-$VCl_3(CH_3CN)_3$	0.566	1.30
mer-$VCl_3(CH_3CN)_3$	0.494	1.30
trans-$VCl_4(CH_3CN)_2^-$	0.515	1.29

Table V shows that the charge on the vanadium atom has little effect on the *ROPM* value. The first two entries have the same *ROPM* despite a 10% difference in charge. The last three entries have the same calculated charge on the vanadium, yet the *ROPM* values vary by up to 15%. The overall charge on the complex is also seen to have little effect. The fact that the neutral facial isomer has an *ROPM* value larger than either $VCl_2(CH_3CN)_4^+$ or $VCl_4(CH_3CN)_2^-$ shows that there is no trend in *ROPM* values as charge changes.

Conclusions

The bonding of acetonitrile molecules to vanadium in $VCl_3(CH_3CN)_3$ depends most strongly on what atom occupies the *trans* position. Thus, the unique position in meridional $VCl_3(CH_3CN)_3$ differs in bonding from the other two positions more than do the Ns in facial $VCl_3(CH_3CN)_3$. This shows that the meridional isomer alone may account for the observed two exchange processes in these solutions. Given that the solid $VCl_3(CH_3CN)_3$ is probably facial, it is possible that both isomers are present simultaneously since the facial isomer alone cannot give rise to two solvent exchange processes.

The calculations confirm that CN groups are better σ and π bonders than is chlorine. The σ and π overlap populations for the two $VCl_3(CH_3CN)_3$ isomers indicate that the principal difference in their bonding to the central vanadium is in the σ interaction.

References

1 R. J. H. Clark, J. Lewis, D. J. Machin and R. S. Nyholm, *J. Chem. Soc.*, 379 (1963).

2 M. W. Duckworth, G. W. A. Fowles and R. A. Hoodless, *J. Chem. Soc.*, 5665 (1963).

3 R. J. H. Clark, *Spectrochim. Acta, 21,* 955 (1965).

4 P. Moore, *Pure Appl. Chem., 57,* 347 (1985).

5 Y. Ducommun and A. E. Merbach, in R. van Eldik (ed.), 'Inorganic High Pressure Chemistry', Elsevier, Amsterdam, 1986, p. 84.

6 J. F. O'Brien, *Inorg. Chem., 26,* 3264 (1987).

7 J. F. O'Brien, M. P. Eastman and M. Alei, Jr., *Inorg. Chem., 9,* 1000 (1970).

8 G. D. McDonald, M. Thompson and E. A. Larsen, *Inorg. Chem., 7,* 648 (1968).

9 R. Hoffman, *J. Chem. Phys., 39,* 1397 (1963).

10 J. Howell, A. Rossi, D. Wallace, K. Haraki and R. Hoffman, 'FORTICON8', *Quantum Chemistry Program Exchange,* 11, 344 (1977).

11 J. Huheey, 'Inorganic Chemistry', 3rd edn., Harper and Row, New York, 1983, pp. 74–75.

12 B. Douglas, D. H. McDaniel and J. J. Alexander, 'Concepts and Models of Inorganic Chemistry', 2nd edn., Wiley, New York, 1983, p. 556.

13 M. L. Tobe, 'Inorganic Reaction Mechanisms', Nelson, London, 1972.

14 T. A. Albright, J. F. O'Brien and S. J. Bjorling, in preparation.

15 C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', W. A. Benjamin, Reading, Mass., 1966, p. 27.