Reaction of Vanadyl Ions with Alkyl Dinitriles

Monther Y. Al-Janabi and Naseef J. Ali [1]

Ibin-Hayan Laboratory, Department of Chemistry, College of Science, University of Baghdad,
Baghdad — Iraq

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New complexes were prepared from the reaction of vanadyl ion with malononitrile and succinonitrile. Both complexes were found to exhibit a decrease in $C{\equiv}N$ streatching frequency.

The reaction of vanadyl ion with malononitrile ion gives a complex in which the $C{\equiv}N$ stretching frequency is increased. The increase or decrease is related to the type of bonding and to the difference in π-back bonding.

Introduction

Complexes of group (IV) halides with dinitriles $N{\equiv}C-(CH_2)_n-C{\equiv}N$ have been studied [2] extensively while chelates with such dinitriles are neither of these metal ions [3, 4] nor of copper (I) perchlorate [5]. Jain and Rivest [5, 6] prepared complexes of aminonitriles $R_2N-(CH_2)_n-C{\equiv}N$ with titanium, tin and zirconium tetrahalides and have shown from molecular weight and conductivity data that these complexes were monomeric, non-ionic compounds. Moreover, for diethylaminoacetonitrile ($n=1$) a decrease in $C{\equiv}N$ stretching frequency by 40 – 100 cm^{-1} was observed, indicating that chelation to the triple bond had taken place. For $n=2$, chelation occured through the lone pair electrons of the cyano group and through the triple bond. For $n=3$, normal chelation took place [8].

The first example of a cyano group being involved in π-bonding to a transition metal was a compound prepared from dialkylcyanamide ($R_2N-C{\equiv}N$) and nickel tetracarbonyl [9]. It has also been shown that succinonitrile may coordinate to manganese through its $C{\equiv}N$ triple bonds. Similarly, the compounds

$$M(CO)_3(NC-(CH_2)_3-CN)X,$$

(X = Cl, Br, I), (M = Mn, Re) were prepared and an octahedral structure was proposed for them [10, 11].

It is well known that succinonitrile [12, 13] exists as a mixture of trans and gauche conformations in the vapour and liquid phase, but crystallizes in the gauche form. Kubota and coworkers [4] demonstrated that polymeric structures arose when tin or titanium tetrachloride coordinate with dinitriles where the latter act as a bridging ligand. Succinonitrile assumes trans conformation in these compounds as well as in compounds with silver [14] and copper [15].

A series of complexes with the general formula $\{Cu[NC-(CH_2)_n-CN]_2\}NO_3$ has been studied by X-ray crystallographic and i.r. techniques, in which the ligands exist in gauche ($n=2$) [16] and gauche-gauche ($n=3$) conformations [17]. Another series of alkyl dinitrile complexes [8] of the type $\{M[NC-(CH_2)_n-CN]Cl_2\}_2$; n = 2, 3, 4, M = Co(II), Ni(II) or Zn(II) has been prepared and only blue shift $\nu_{C\equiv N}$ bands in the i.r. spectra of the complexes were observed. Also dinuclear species containing two N-bonded bridging dinitriles were prepared. It is suggested [18] for δ- and π-bonded dinitriles of Mn(I) and Re(I) carbonyl halides that the monomeric π-complexes are kinetically favoured, whereas the δ-bonded complexes are thermodynamically favoured. Zinc, but not Hg(II) [19] catalyzed a reaction between malononitrile and ethanol yielding a pyridine derivative. It was the aim of the present work to see if in changing the hybridization of an atom in the ligand and forming an anion the coordination properties of the alkyldinitrile are changed and to clarify the behaviour of those ligands with vanadyl ions.

Experimental

Preparation of VO^{++} Complexes

1. Preparation of sulfatodiaquamalononitrile oxovanadium (IV)

Twenty mmoles of vanadyl sulfate were dissolved in hot dimethylformamide (DMF) and added to a solution of 20 mmoles of malononitrile dissolved in DMF. The mixture was refluxed for about half an hour during which its color changed from blue to

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Reprint requests to M. Y. Al-Janaby, Department of Chemistry, College of Science, University of Baghdad, *Baghdad/Irak.*

green and a greenish precipitate appeared. After cooling, the precipitate was separated by filtration and washed with alcohol, ether and dried over calcium chloride under vacuum.

Analysis for $VOSO_4(NC-CH_2-CN)\cdot 2\,H_2O)$

Calcd.: $C\% = 13.57$; $H\% = 2.29$; $N\% = 10.69$

found: $C\% = 13.74$; $H\% = 2.76$; $N\% = 10.87$.

2. Triaquooxovanadium (IV)-μ-dimalononitrilo triaquooxovanadium(IV) sulfate

Twenty mmoles of malononitrile were dissolved in a small amount of ethanol, then 20 mmoles of sodium metal were added gradually. A solution of 20 mmoles of vanadyl sulfate in ethanol was added to the previous solution at low temperature (0 – 5 °C). A greenish precipitate appeared which was filtered, washed with ethanol and dried in vacuo over calcium chloride.

Analysis for

$(H_2O)_3VO(NC-CH-CN)_2VO(H_2O)_3\,SO_4$

Calcd.: $C\% = 15.31$; $H\% = 2.78$; $N\% = 11.91$

found: $C\% = 15.04$; $H\% = 2.80$; $N\% = 9.67$.

3. Sulfatodiaquosuccinonitrileoxovanadium (IV)

A hot solution of 20 mmoles of vanadyl sulfate in DMF was added to a solution of 20 mmoles of succinonitrile in DMF. The mixture was then refluxed for 5 hours under nitrogen atmosphere during which the colour changed from blue to greenish. The solution was evaporated nearly to dryness, and then alcohol was added causing a brown precipitation, which was filtered and washed with alcohol, ether and dried in vacuo over calcium chloride.

Analysis for $VOSO_4(NC-CH_2CH_2CN)\,(H_2O)_2$

Calcd.: $C\% = 16.21$; $H\% = 2.70$; $N\% = 10.3$

found: $C\% = 16.85$; $H\% = 1.92$; $N\% = 10.58$.

Analyses: The carbon, hydrogen and nitrogen analyses were performed by Alfred-Bernhardt Microanalytisches Laboratorium, West Germany.

Infrared Spectra: The infrared spectra were obtained on a Perkin-Elmer Model 137E Spectrophotometer and a Perkin-Elmer Model 257 grating infrared spectrophotometer.

Conductance Measurements: The electric conductances at 25 °C of 10^{-3} M solutions of the complexes in DMF were obtained on a Mullard Type E 7566/3 conductivity bridge, using a cell with platinized electrodes.

Nuclear Magnetic Resonance Spectra: NMR data were recorded on a Varian A-60A Nuclear Magnetic Resonance Spectrometer. D_2O and dimethylsulfoxide were used as solvents. The resonance signal of tetramethylsilane was used as reference.

Results and Discussion

The decrease in the C≡N stretching frequency of malononitrile and succinonitrile upon complexing with vanadyl ion is the evidence for a coordination through the π-bond of alkyldinitrile to the metal ion. Their bondings are analogous to those reported for $[Pt(P(C_6H_5)_3)_2(NC-CH_2CH_2-CN)]$[20] and $[M(CO)_3(NC-CH_2CH_2-CN)X]$[10, 11].

Table 1. Characteristic bands of vanadyl complexes.

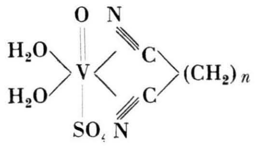
Complexes	ν_{V-O}	$\nu_{C\equiv N}$	$\Delta\nu_{C\equiv N}$
$VOSO_4\cdot 5\,H_2O$	1020, 1003, 987 [21]		
$VO(dipy)SO_4$	(979) [22]		
$VO(ophen)SO_4$	(978) [22]	2210 (s, sp)	−65
$VO(mal)SO_4\cdot 2\,H_2O$	978	2275 [a] (s, sp)	
$VO(suc)-SO_4\cdot 2\,H_2O$	955	2200 s, sp (2258) [a] v·s, sp	−58
$(VO)_2(malo)_2SO_4\cdot 6\,H_2O$	965	2210 s, sp (2080) [a] s, sp	+120

(dipy) = dipyridyl; (ophen) = orthophenanthroline; (mal) = malononitrile; (suc) = succinonitrile; (malo) = malononitrilo; (s) = strong; sp = sharp; (a) = $\nu_{C\equiv N}$ of the free ligand.

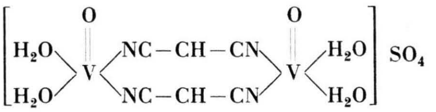
The vanadyl complex of succinonitrile is much less susceptible to dissociation in DMF than its malononitrile counterpart. Their molar conductivities were found to be 14.9 and 40 $ohm^{-1}\,cm^{-2}\,mole^{-1}$, respectively. The complex of malononitrile is found to be more stable than either one of the previous complexes, its molar conductivity being 77.5 $ohm^{-1}\,cm^{-2}\,mole^{-1}$, which is in the normal range for the proposed structure. The nuclear magnetic resonance spectra of the complex of malononitrile, dissolved in D_2O, shows a single peak at 280 cps (5.34 ppm) while the peak for the succinonitrile complex, dissolved in dimethylsulfoxide, appeared at 148 cps (7.58 ppm). This result proves that the four protons of succinonitrile in the complex are in the same environment and that they are more shielded than in the malononitrile complex.

Lowering the stretching and raising the bending frequencies from those of free water molecules, i. e. 3445, 3219, 1627 cm^{-1} [23] to 3305, 3200 and 1650 cm^{-1} in the complexes, and the appearance of rocking modes of vibration of the water molecules as weak bands around 800 cm^{-1} in each of the three complexes, prove the coordination of water molecules. The strong bands at 978, 955 and 965 cm^{-1} indicate a monomeric V – O unit and rule out the possibility of V – O – V – O polymer chaining[21, 24].

The proposed structure of these complexes was derived from their i.r. spectra. In $VO(mal)SO_4 \cdot 2\,H_2O$ and $VO(suc)SO_4 \cdot 2\,H_2O$, ν_3 of the sulfate ion does not split and appears at 1065 cm^{-1} and 1040 cm^{-1} respectively, while for $(VO)_2(malo)_2SO_4 \cdot 6\,H_2O$ it does split and appears at (1090) and (1050). This result can be explained by assuming lowering of the symmetry T_d in the first two complexes to C_{3v} in the third complex upon the coordination of the sulfate ion. From the previous discussion we propose the following structure for the three complexes:



n = I, 2



The anionic form of malononitrile

$$(NC - CH - CN)$$

was obtained as a result of the acidic nature of the proton in malononitrile by the following reaction:

$$2\,Na + 2\,NC - CH_2 - CN \rightarrow 2\,Na^{(+)} + 2\,(NC - CH - CN)^- + H_2\,.$$

The removal of a proton by such a reaction was expected to have a two-fold effect on the coordination properties of the ligand. The increases in the C – C – C bond angle, resulting from the change in the hybridization of the central carbon atom from $sp^3 \rightarrow sp^2$ would be expected to increase the ability of the ligand to act as a bridging ligand, since the steric interaction of the metal coordination polyhedra of the ends of the bridge would be decreased by larger angle. Likewise, the enhanced nucleophilicity of the nitrogen atoms resulting from the charge delocalization would be expected to increase the tendency of the ligand to form normal σ-bonds through the lone pair electrons of the nitrogen. Therefore, if the malononitrilo acted as a bridge, the C≡N stretching frequency would increase, as was found (see Table 1).

The donation of electrons from the ligands to the metal ion would affect the donation ability of oxygen to vacant d-orbitals in VO^{++}, resulting in changing the frequency of the V – O band. It was concluded[24] that the frequency change is directly related to a decrease in $P_\pi \rightarrow d_\pi$ donation from oxygen to metal and an increased electrostatic repulsion of the vanadium and oxygen species. Their effect was written as:

$$\Delta\bar{\nu} = -\sigma(L \rightarrow M) - \pi_{\parallel}(L \rightarrow M) - \pi_{\perp}(L \rightarrow M)\,.$$

This behaviour is reflected in the lowering of the stretching frequency of V – O (cf. Table 1). In comparing the ability to cause this shift we find that the coordination ability is stronger for the malononitrilo ion than for orthophenanthroline and dipyridyl. This is an expected result of the resonance in the orthophenanthroline molecule which decreases the electron donation ability of the nitrogen lone pair, while in malononitrilo there is a delocalization of charge and an enhancement of the nucleophilicity of the nitrogen atoms. According to the extent of change in the V – O stretching frequency upon chelation we found that succinonitrile is more able to coordinate than malononitrile. This interesting result is due to the fact that succinonitrile is more flexible (spatially) than malononitrile.

Thus both π – d donation and d – π back donation of electron is much weaker than π – p electron transfer[25]. The net result is then a transfer of electrons from π-bonds of the C≡N group to the p-atomic orbital of the ion, a decrease of the CN bond order and a red shift of its frequency. Terminal coordination of CN to metal causes an increase in its vibration frequency due to the decrease of electron repulsion.

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