THE COMPLEXES OF VANADIUM (IV) OXYDICHLORIDE

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Abstract. Vanadium (V) oxytrichloride was reduced by sulphur into vanadium (IV) oxydichloride. The complexes of $VOCl_2$ with pyridine picolines and 8-hydroxyquinoline were prepared having the general formulae $VOCl_2 L_2$, $VOCl_2 L_3$, and $VOCl_2 L_4$ (here L = ligand). The IR spectra of the complexes were determined in Nujol and hexachlorobutadiene (HCB) mull and assignments of vanadium-oxygen ν (V−O), vanadium−nitrogen ν (V−N) and vanadium - chlorine ν (V−Cl) stretching vibrations were made. The electronic spectra of the complexes were determined in 1,2−dimethoxyethane (DME) and toluene. The λ_{max} in the electronic spectra of the complexes was shifted to longer wave-lengths by more polar solvents. Two interrelated factors were considered to account for the observed red shift in λ_{max} (1) a decrease in the energy required for the electronic excitation resulting from increased solvation of the excited state due to the polarizability and (2) dipole orientation of the solvent. The possible structural formations of the complexes were proposed.

Using the Ziegler − Natta catalyst system the polymerization of various monomers has been believed to occur by the successive insertion of monomer molecules between the carbon atom and the metal atom of the catalyst. Although catalytic activity has been shown by a great variety of mixtures containing organic carbon - metal compounds, exceptionally high activity has been restricted to bi − or multi − metallic combinations containing compounds of a transition metal and of aluminium. The mechanism of polymerization by Ziegler − Natta catalyst system is not yet completely understood due to two major reasons, namely the heterogeneity of the original catalyst systems and the instability of the compounds postulated as intermediates (initiators). The catalyst system introduced by Breslow et al[1] has been proved to be of great importance due to its solubility which enhanced its catalytic investigation by spectroscopic techniques.

The transition metal vanadium has been of great significance to many. Researchers for its new homogeneous polymerisation catalysts.[2] It has also been reported in the literature[3-5] that vanadium has some advantages over other transition metals in some copolymerisation and stereospecific polymerisation processes.

These facts illustrated the specific importance of vanadium in certain polymerisation processes and it thus appeared that a study of the vanadium chemistry would be of interest. In carrying out this study it was hoped that light could be thrown on the nature of the catalytically active systems containing vanadium.

The reduction of vanadium (V) oxytrichloride has been reported by many carboxylic acids with concomitant solvolysis to produce vanadyl (IV) craboxylates.[6,7] Baker et al[8] reported the reduction of $VOCl_3$ by a conventional method[9] using an excess of mono − di − or trimethylamine and range of thioethers. Funk et al[10] observed the formation of unstable adducts $VOCl_3 [N (C_2H_5)_3]_2$ and $VOCl_3 (C_5H_5N)_2$, but indicated that in pyridine the latter complex was soon reduced to $VOCl_2 (C_5H_5N)_3$. In their proceeding paper they reported the preparation of $VOCl_2 (C_5H_5N)_2$ and $VOCl_2 (C_5H_5N)_3$ by the reaction of $VOCl_2 (CH_3OH)_3$ and pyridine.

In this work it is found that under anhydrous conditions $VOCl_3$ can be reduced to $VOCl_2$ by refluxing it with sulphur. The $VOCl_2$ thus obtained is reacted with tetrahydrofuran to prepare $VOCl_2 (C_4H_8O)_2$ complex which is further reacted with pyridine, picolines and 8-hydroxyquinoline to form a number of complexes of, general formulas $VOCl_2 L_2$, $VOCl_2 L_3$ and $VOCl_2 L_4$ containing vanadium (IV). The formulas of the complexes are established by the elemental analysis and the probable structural formations are predicted on the evidences obtained from their IR and electronic spectra.

Materials

Vanadium Oxytrichloride . Vanadium oxytrichloride supplied by L − Light and Co. Ltd. was purified by fractional distillation under high vacuum condition $(10^{-5}$ torr).

Sulphur. The commercially available sulphur flowers (Fluorochem Ltd.) were dried at 60^0 for 48 hr prior to use.

Tetrahydrofuran . The commercial tetrahydrofuran (BDH Laboratory Reagent) was refluxed over potassium hydroxide and then fractionally distilled in a anhydrous atmosphere at ordinary pressure. The middle fraction, about 70% of the starting material, was collected at 65 - 66^0. Sodium wire was then added rapidly to this fraction and refluxed for two more days, and then fractionally distilled. Sodium wire was extruded in the middle fraction collected in a conical flask. This tetrahydrofuran was then stored in a dry box for few weeks prior to use.

1 , 2-*Dimethoxyethane.* Dimethoxyethane (BDH Laboratory Reagent) was purified and dried in a similar fashion as described for tetrahydrofuran.

Hexane. Hexane (Fisons Laboratory Reagent) was treated with conc sulphuric acid, then with 0.1 N solution of potassium permanganate in 10% sodium hydroxide solution.[6] The hexane was then washed with water and dried over $MgSO_4$. It was then fractionally distilled and the middle fraction was collected and refluxed for one day over sodium wire. This hexane was stored in a dry box prior to use.

Pyridine. (BDH Laboratory Reagent) was stored over freshly fused potassium hydroxide for two weeks and then fractionally distilled in an anhydrous atmosphere. The middle fraction was collected and the fractional distillation was repeated twice.

Picolines. (BDH Laboratory Reagent) were purified using the same procedure as described for pyridine.

Toluene. Toluene (BDH Laboratory Reagent) was purified by successive shaking with H_2SO_4 NaOH and mercury. It was then dried over P_2O_5 and then fractionally distilled. The middle fraction collected at 110-111^0 was finally refluxed with sodium wire and stored in a dry box prior to use.

Experimental and Results

Since vanadium oxydichloride complexes with tetrahydrofuran, pyridine and picolines are very susceptible to atmospheric vapours, it was necessary to conduct all the experiments under condition of stringent purity and in an inert atmosphere. This was accomplished by drying the solvent over sodium, purifying and drying the reagents very carefully with the aid of a dry box and a high vacuum apparatus which was capable of producing a pressure of 10^{-5} torr. $VOCl_2$ $(C_4H_8O)_2$: Vanadium oxydichloride 2-tetrahydrofuranate was prepared in two steps namely (1) the reduction of $VOCl_3$ to $VOCl_2$ by sulphur and (2) the reaction of $VOCl_2$ with tetrahydrofuran. Throughout the experiment precau-

tions were taken to avoid unnecessary contact with atmospheric moisture. A mixture of vanadium oxytrichloride (17.35g, 0.1 mole) and sulphur flowers (3.2 g, 0.1 g atom) was refluxed for 3 hr in a three necked R.B. flask carrying a condenser and an inlet for dry nitrogen gas and subsequently was cooled. The unreacted $VOCl_3$ was then distilled off under reduced pressure joining the flask to a high vacuum line through quick-fit joints. The residual material thus obtained was a mixture of green layer of $VOCl_2$ and a black lower layer of oxidized sulphur. The $VOCl_2$ was then freed from black material in a dry box and stored in an air tight flask. For the preparation of $VOCl_2$ complex with tetrahydrofuran, a mixture of 5 g $VOCl_2$ and 250 ml of pure tetrahydro-furan was refluxed in a three-necked R.B. flask under the atmosphere of pure nitrogen as described for the first step for 3 hr. The mixture was then cooled and filtered. The excess tetrahydrofuran (about 200ml) was then distilled off from the blue coloured filtrate. The residual filtrate was then cooled and about 50 ml of pure hexane was added in it and stored in a dry box. The green precipitate of $VOCl_2$ $(C_4H_8O)_2$ appeared after a few hours. The complex was then recovered by filtration and dried under high vacuum conditions. The $VOCl_2$ $(C_4H_8O)_2$ complex thus prepared was stored in an air tight flask in a dry box.

$VOCl_2$ $(C_5H_5N)_2$: Vanadium oxydichloride complex with pyridine was prepared by the reaction of $VOCl_2$ $(C_4H_8O)_2$ with pyridine in tetrahydrofuran. A mixture of $VOCl_2$ $(C_4H_8O)_2$ (8.38 g, 30 m moles) and pyridine (4.7 g, 60 m moles) in 150 ml of pure tetrahydrofuran was stirred in a three-necked R.B. Flask for 1 hr and then stored in a dry box. The precipitate of $VOCl_2$ $(C_5H_5N)_2$ which appeared after sometime were recovered by filtration. The $VOCl_2$ $(C_5H_5N)_2$ thus prepared was dried under high vacuum conditions and then stored in an air tight flask in a dry box.

$VOCl_2$ $(\alpha\ C_6H_7N)_2$, $VOCl_2$ $(\beta - C_6H_7N)_2$ and $VOCl_2$ $(\alpha - C_6H_7N)_2$ were prepared by the reaction of $VOCl_2$ $(C_4H_8O)_2$ and the respective picoline in tetrahydrofuran using the same molar ratios of the reactants and the procedure as described for the preparation of $VOCl_2$ $(C_5H_5N)_2$.

$VOCl_2$ $(C_5H_5N)_3$: Tri (pyridine) oxovanadium (IV) dichloride was prepared by the reaction of $VOCl_2$ $(C_4H_8O)_2$ and pyridine adopting the three slightly different procedures. (1) The first experiment was carried out using the one to three molar ratio of $VOCl_2$ $(C_4H_8O)_2$ and pyridine in tetrahydrofuran. The reaction mixture was stored in a dry box for a few days during which time the precipitates of $VOCl_2$ $(C_5H_5N)_3$ appeared at the bottom of the flask. It was then filtered and the soil material, $VOCl_2$ $(C_5H_5N)_3$ was dried under

high vacuum conditions and stored in an air tight flask in a dry box. (2) In the second experiment an excess of pyridine was used as compared to $VOCl_2 (C_4H_8O)_2$ and rest of the procedure was similar as described for the first experiment. (3) In the third experiment pyridine was used as a ligand as well as solvent. The reaction was observed by the gradual change of colour from green to dark blue which went to completion within a few minutes. The resultant complex was soluble in pyridine. Therefore, it was allowed to stand for a few days during which time the precipitate of $VOCl_2 (C_5H_5N)_3$ appeared, which were filtered and dried under high vacuum conditions.

$VOCl_2 (\beta - C_6H_7N)_3$ and $VOCl_2 (\gamma - C_6H_7N)_3$ were prepared by the reaction of $VOCl_2 (C_4H_8O)_2$ and respective picoline using the same procedures as described for $VOCl_2 (C_5H_5N)_3$.

$VOCl_2 (C_9H_7NO)_3$ was also prepared by the reaction of $VOCl_2 (C_4H_8O)_2$ and 8 - hydroxyquinoline in tetrahydrofuran using the similar method as described for $VOCl_2 (C_5H_5N)_3$.

$VOCl_2 (C_5H_5N)_3$ was prepared by the reaction of commercially available $VOCl_2$ (K. & K. Laboratories) and pyridine in pyridine solution. The mixture of $VOCl_2$ (5 g) and 100 ml pyridine was stirred for 1 hr and then the reaction mixture was allowed to stand for a few hours. The precipitate of $VOCl_2 (C_5H_5N)_4$ appeared in the reaction mixture were recovered by filtration and subsequently were dried under high vacuum conditions. The resultant blueish powder was stored in an air tight flask in a dry box.

The elemental analyses were carried out* on all the complexes the results are summarized in Table 1.

The IR spectrum of all the complexes were determined in Nujol and HCB. The IR absorption frequencies (Cm^{-1}) and bond assignments of the complexes are given in Table 2.

The electronic spectra of the complexes were determined in two solvents of different polarity, 1,2-dimethoxyethane and toluene. The spectral values are given in Table. 3.

Discussion

The preparation of vanadium (IV) oxydichloride complexes with organic bases are carried by the reaction of $VOCl_2 (C_4H_8O)_2$ and respective organic bases because it is not convenient to isolate pure $VOCl_2$ after reducing $VOCl_3$ with sulphur without losing most of it, and also it is not possible to purify $VOCl_2$ by

recrystallization due to its insolubility in nonpolar solvents and formation of complexes with polar solvents. Therefore, $VOCl_2 (C_4H_8O)_2$ is considered an appropriate starting material to prepare the $VOCl_2$ complexes with organic bases, such as pyridine, picolines and 8-hydroxyquinoline. Another advantage of this complex is that tetrahydrofuran can be easily replaced by the stronger field ligands.

The preparation of $VOCl_2 (C_5H_5N)_4$ by the reaction of $VOCl_2$ and pyridine and not by the reaction of $VOCl_2 (C_4H_8O)_2$ and pyridine could not be explained without an adequate experimental data.

The IR spectra (Nujol and H C B mull) of the complexes are recorded on a Perkin-Elmer 621 spectrophotometer. All the complexes show strong absorption band for the vanadium-oxygen multiple bonds in the region varying from 922 to 1010 cm^{-1} depending on the number and the nature of other ligands in a complex (see Table 2). The shift to lower frequencies of the V = O stretching is observed in the complexes of general formula $VOCl_2 L_2$ and $VOCl_2 L_3$ could be realted to the ligands in the following decreasing order: Pyridine $< \beta$ -picoline $< \gamma$ -picoline $< \alpha$-picoline and pyridine $= \gamma$ -picoline $<$ 8-hydroxyquinoline $< \beta$ -picoline, respectively. In accordance with these results it could be suggested tentatively that steric effects may play an important role when the ligand becomes bulky, but the shift to higher frequencies of the V = O stretching is mainly due to the transfer of increasing amounts of charge on to the vanadium by ligands of increasing donor strength. This latter effect also justify the arguments put forward in favour of $VOCl_2 (C_5H_5N)_4$ formation and the failure to prepare $VOCl_2 (\beta -, \gamma - C_6H_7N)_4$ complexes. The V = O stretching frequencies found for the $VOCl_2$ complexes with pyridine, picolines and 8-hydroxyquinoline do agree with its frequencies reported in the literature for various oxovanadium (IV) complexes.[8,12,16] There are no absorption bands, which could be assigned to V-O-V bridging modes.

The vanadium to nitrogen (V - N) stretching frequencies are of particular importance because they provide the valuable information about the coordinate bonds. It is assumed that the V - N stretching vibration should appear in the lower frequency region because of the relatively heavy mass of the metal vanadium and the low bond order of the coordinate bond. The band assignments of the V - N stretching vibration of the $VOCl_2$ complexes with pyridine, picolines and 8-hydroxyquinoline are given in Table 2. The band frequencies vary from 413 cm^{-1} to 550 cm^{-1}. A significant shift to longer frequencies of the V - N stretching is observed in the case of $VOCl_2$ complexes with γ -picoline and a slight shift to lower frequencies is observed by increasing the number of ligands attached to the

TABLE 1. FORMULAS, YIELDS AND ANALYTICAL DATA FOR THE COMPLEXES

Compound*		Yield %	C%		H%		N%		Cl%	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$VOCl_2$	$(C_5H_5N)_2$	90	40.5	40.8	3.4	3.1	9.5	9.2	24.0	24.2
$VOCl_2$	$(C_5H_5N)_3$	95	48.0	48.3	4.0	4.5	11.2	11.6	18.9	18.1
$VOCl_2$	$(C_5H_5N)_4$	95	52.8	52.7	4.4	4.5	12.3	12.3	15.6	15.6
$VOCl_2$	$(\alpha\text{-}C_6H_7N)_2$	93	44.4	44.1	4.3	4.4	8.6	8.5	21.9	22.1
$VOCl_2$	$(\beta\text{-}C_6H_7N)_2$	94	44.4	44.3	4.3	4.4	8.6	8.6	21.9	21.9
$VOCl_2$	$(\gamma\text{-}C_6H_7N)_2$	92	44.4	44.7	4.3	4.5	8.6	8.3	21.9	21.6
$VOCl_2$	$(\beta\text{-}C_6H_7N)_3$	95	51.8	51.2	5.0	5.2	10.0	9.2	17.0	16.8
$VOCl_2$	$(\gamma\text{-}C_6H_7N)_3$	94	51.8	51.5	5.0	5.1	10.0	9.5	17.0	16.9
$VOCl_2$	$(C_9H_7NO)_3$	95	56.5	57.0	3.7	4.1	7.3	7.3	12.4	13.5

* Here C_5H_5N is Pyridine, α ---, β ---, and γ --- C_6H_7N are Picolines and C_9H_7NO is 8 - Hydroxyquinoline.

TABLE 2. INFRARED ABSORPTION FREQUENCIES (Cm⁻¹) AND BAND ASSIGNMENTS OF THE COMPLEXES.

Compound		$\nu(V=O)$	$\nu(V-N)$	$\nu(V-N)$ or $\nu(V-Cl)$	$\nu(V-Cl)$
$VOCl_2$	$(C_5H_5N)_2$	922 (s)	442 (s)	432 (sh)	374 (s)
				285 (m)	336 (s)
$VOCl_2$	$(C_5H_5N)_3$	950 (s)	435 (s)	302 (s)	370 (s)
				270 (m)	330 (s)
$VOCL_2$	$(C_5H_5N)_4$	950 (s)	434 (s)	270 (m)	330,300
					(doublet (s)
$VOCl_2$	$(\alpha\text{-}C_6H_7N)_2$	1010 (s)	444 (s)	297 (sh)	386 (s)
					312 (s)
$VOCl_2$	$(\beta\text{-}C_6H_7N)_2$	980 (s)	416 (s)	410 (sh)	375 (s)
				307 (s)	342 (s)
				273 (m)	
$VOCl_2$	$(\gamma\text{-}C_6H_7N)_2$	982 (s)	490,550	307 (s)	375 (s)
					345 (s)
$VOCl_2$	$(\beta\text{-}C_6H_7N)_3$	978 (s)	414 (s)	300 (s)	376 (s)
				270 (m)	334 (s)
$VOCl_2$	$(\gamma\text{-}C_6H_7N)_3$	950 (s)	493,546?	310 (s)	360 (s)
				225 (m)	334 (s)
				248-262	
				(mw. d)	
$VOCl_2$	$(C_9H_7NO)_3$	970 (s)	413 (s)	362 (m)	385 (s)
				342 (m)	
				322 (m)	

s=Strong, m=Medium, sh=Shoulder and mw. d = medium wide doublet.

vanadium atom.

It is known for the complexes of having a general formula ML_2X_2.[17] (M=Transition metal, L=nitrogen containing Ligand and X = Cl) that M - X stretching modes fall at lower frequencies than the M-L stretching modes. The terminal M - X stretching bands usually appear in the region of 400 to 200 cm^{-1}. The V-Cl stretching frequencies observed for the $VOCl_2$ complexes with pyridine, picolines and 8-hydroxyquinoline are given in Table 2. All the V-Cl stretching bands in the IR except some significant difference in the case of $VOCl_2$ $(C_5H_5N)_4$ and $VOCl_2$ $(C_9H_7NO)_3$ complexes.

In order to establish the solvent effects on the electronic spectra of $VOCl_2$ complexes with pyridine, picolines and 8-hydroxyquinoline, the spectra are determined in solvents of different polarity namely 1,2 - dimethoxyethane (DME) and toluene (see Table 3). The absorption of light by a molecule results in its electronic excitation from some ground state energy to a more energetic excited state. In solution, the extent of the solvation of the molecule in each of these two electronic states influences their relative position in energy. It is apparent from the results that in all the complexes of vanadium (IV) oxydichloride with pyridine, picolines and 8-hydroxyquinoline, the more polar medium (DME) reduces the energy difference between the ground and excited states, thus causing a red shift in absorption maximum, λ_{max}. This pronounced red shift in absorption maximum of such species with more polar solvents, might be explained by considering that the systems under discussion consist of a polar solute in both polar and non-polar solvent medium. It is generally believed that conjugated bonds in electronic spectra are frequently shifted toward the visible region by a more polar solvent. This is because the absorbing molecule which is imbedded in a dielectric medium, polarizes the medium and thus decreases the work required for electronic excitation.[18,19] The lowering in energy is dependent on the polarizability of the solvent. There may also be a solvent effect due to orientation of the solvent dipoles by the solute. It has been reported by Bayliss and his coworker[20] that the spectrum of a polar solute in a polar solvent may cause a strong red shift if the solute experiences an increase in dipole moment on excitation. The increase in solute dipole moment in the excited state results in a gain in solvation energy for this state, relative to the ground state,

TABLE 3. COLOUR AND ELECTRONIC ABSORPTION SPECTRAL VALUES FOR THE COMPLEXES.

	Compound		Colour	Solvent	λ_{max} (nm)	λ_{max}	λ_{max} (nm)	λ_{max}
I	$VOCl_2$	$(C_5H_5N)_2$	Light blue	DME	722	36.7	833	47.5
				Toluene	720	-----	833	-----
	(I+Al (iBu)$_3$)			DME	730	-----	814	-----
II	$VOCl_2$	$(C_5H_5N)_3$	Light blue	DME	725	47.7	833	60.7
				Toluene	719	-----	833	-----
	(II+Al (iBu)$_3$)			DME	730	-----	820	-----
III	$VOCl_2$	$(C_5H_5N)_3$	Light blue	DME	730	48.1	833	57.4
				Toluene	725	-----	833	-----
	(III+Al (iBu)$_3$			DME	747	-----	820	-----
IV	$VOCl_2$	$(\alpha\text{-}C_6H_7N)_2$	Light blue	DME	736	70.2	---	-----
				Toluene	736	-----	---	-----
V	$VOCl_2$	$(\beta\text{-}C_6H_7N)_2$	Green	DME	725	38.2	833	49.0
				Toluene	719	-----	833	-----
VI	$VOCl_2$	$(\gamma\text{-}C_6H_7N)_2$	Turquose	DME	725	39.1	833	51.0
				Toluene	712	-----	833	-----
VII	$VOCl_2$	$(\beta\text{-}C_6H_7N)_3$	Light blue	DME	728	43.6	833	55.0
				Toluene	714	-----	833	-----
VIII	$VOCl_2$	$(\gamma\text{-}C_6H_7N)_3$	Light blue	DME	725	38.2	833	50.0
				Toluene	709	-----	833	-----
IX	$VOCl_2$	$(C_9H_7NO)_3$	Green	DME	618	1324	---	-----

through increased interaction with the oriented solvent molecules. Another factor which might be responsible for the red shift caused in the spectra of $VOCl_2$ complexes is the promotion of ionization of these species in polar solvents.[21] However, this latter factor should not be considered very important in this work bacause it seems very unlikely that $VOCl_2$ complexes exists in ionic form.

The electronic spectra of $VOCl_2$ pyridine complexes are also determined with added Al $(iBu)_3$ in DME. It is noted that the complexes react rapidly with Al $(iBu)_3$ to form a green coloured product. These new products gave the spectra in which the λ_{max} are shifted towards the visible region from $5 - 17$ nm as compared to their parent complexes. The red shifts found in the λ_{max} for the reaction products of $VOCl_2$ $(C_5H_5N)_2$ —, $VOCl_2$ $(C_5H_5N)_3$ —, and $VOCl_2$ $(C_5H_5N)_4$ —— Al $(iBu)_3$ (Aluminium isobutyl) were 8,5 and 17 nm, respectively. These spectral shifts could be of significant importance as regards the activities of these catalyst systems. It is found in the polymerization of vinyl chloride by $VOCl_2$ $(C_5H_5N)_n$ — Al$(iBu)_3$, (n=2,3, or 4) catalyst systems that the catalyst system is most reactive when n=3 and least reactive when n=4.[22]

The spectroscopic investigations of the complex having the stoichiometry $VOCl_2 L_2$ support the idea that the coordination polyhedron about the vanadium atom is basically trigonal bipyramidal with the oxygen and chlorine atoms forming the equatorial plane as described for $VOCl_2$ [$N(CH_3)_3$]$_2$.[8,16]

VOCl$_2$ (C$_5$H$_5$N)$_2$ VOCl$_2$ (C$_5$H$_5$N)$_3$
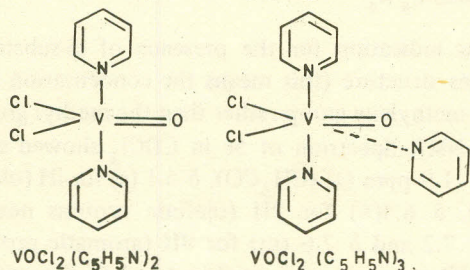
The structural data for the oxovanadium (IV) species have shown to be based on the polyhedron tetragonal pyramid with the short metal to oxygen bond lying in the direction of the four-fold ——axis.[23-25] It seems likely that the structures of the complexes having stoichiometry $VOCl_2 L_3$ is in the form of distorted tetragonal pyramid. Although the conductivity of $VOCl_2$ $(C_5H_5N)_4$ complex has not been studied yet it seems unlikely from its IR Spectrum that it exists in the ionic form, [$VOCl$ $(C_5H_5N)_4$]$^+$ Cl^-. Therefore, a polymeric structure with terminal V-O bonds and chlorine bridges, with some pyridine loosely held in the lattice is proposed for $VOCl_2$ $(C_5H_5N)_4$.

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