

Preparation & Characterisation of Tris(2-chloroethoxy)vanadium(III) & Its Adducts

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Received 30 November 1984; revised and accepted 25 February 1985

Tris(2-chloroethoxy)vanadium(III), $V(OC_2H_4Cl)_3$, has been prepared and characterized on the basis of analytical data, magnetic moment, molar conductance, IR and electronic spectral studies. Addition compounds of $V(OC_2H_4Cl)_3$ with ligands containing C=O, S=O, N-O, P=O, As=O donor groups and with tertiary amines have been isolated. Its complexes with dimethylformamide, pyridine, α -, β -, γ -picolines, α -, β -, γ -picoline N-oxides and triphenylphosphine oxide are of 1:2 stoichiometry whereas those with tetramethylurea, dimethyl sulphoxide, hexamethylphosphoramide, triphenylarsine oxide and α,α' -bipyridyl have 1:1 stoichiometry. The title compound and its complexes have been assigned octahedral structures.

Despite the fact that metal alkoxides have been extensively prepared and studied, relatively few chloroalkoxides have been reported. The chloroethoxides of iron(III) and titanium(IV) have earlier been reported¹⁻³ and these were shown to form complexes with lewis bases unlike the corresponding metal methoxides/ethoxides which do not react with the ligands. The preparation of tris(2-chloroethoxy)vanadium(III) has not been reported yet. In the present note, we report the synthesis and characterization of tris(2-chloroethoxy)vanadium(III) and its adducts with some oxygen and nitrogen donors.

All the reagents were purified by standard methods before use and all the operations were conducted under an atmosphere of oxygen-free dry nitrogen (using a vacuum line).

Tris(2-chloroethoxy)vanadium(III), $V(OC_2H_4Cl)_3$

To a known amount of lithium metal in benzene was added 2-chloroethanol slightly in excess than required for 1:1 molar ratio and the contents were stirred for ~4 hr when whole of lithium metal dissolved. A benzene suspension of anhydrous vanadium(III) chloride was added to this [molar ratio of vanadium(III) chloride to lithium metal, 1:3] and the reactants were stirred for ~2 hr. Dry ether was added to separate lithium chloride from alkoxide and it was filtered under anhydrous conditions. The filtrate contained ether solution of tris(2-chloroethoxy)vanadium(III). Excess of ether was

removed under vacuum and the residue obtained was washed with petroleum ether (40-60°) to remove any trace of 2-chloroethanol. The viscous mass of tris(2-chloroethoxy)vanadium(III) so obtained was dried *in vacuo*.

The adducts were prepared by dissolving tris(2-chloroethoxy)vanadium(III) in respective ligands followed by precipitating out of the adducts by addition of solvent ether and dichloromethane. The adducts with solid ligands (α -Pic N-O, α,α' -Bipy, TPPO and $\varphi_3As=O$) were prepared by adding the alkoxide to solutions of respective ligands in chloroform.

Vanadium was estimated gravimetrically and volumetrically while chlorine was estimated gravimetrically as reported by Vogel⁴. Magnetic measurements were done by the Gouy method. Conductance measurements were done directly on a Toshniwal conductivity bridge type L01/02A, S. No. 418, using a conductivity cell of cell constant 0.521 cm⁻¹. Infrared spectra were recorded as such for the liquid alkoxide and in nujol for the adducts on a Perkin-Elmer 621 infrared spectrophotometer in the region 4000-200 cm⁻¹. Electronic spectrum of the alkoxide was recorded in acetonitrile solution in the range 200-800 nm on a Specord UV Vis spectrophotometer. The diffuse reflectance spectra of adducts were recorded on Unicam SP 700 and Hitachi Model 330 spectrophotometers in the range 5-50 kK.

Tris(2-chloroethoxy)vanadium(III) is a hygroscopic green viscous liquid and is soluble in most of the organic solvents except benzene, petroleum ether and pentane. Its magnetic moment is 1.707 B.M. which is sufficiently below the spin-only value of 2.83 B.M. for a d^2 ion. Many vanadium(III) compounds having μ_{eff} values lower than the spin-only value have been reported⁵. The subnormal magnetic moment of tris(2-chloroethoxy)vanadium(III) indicates the existence of exchange interaction between adjacent vanadium atoms or antiferromagnetic coupling interaction between two or more vanadium atoms through the bridged -OR groups in a polymeric structure of the alkoxide.

Reaction of $V(OC_2H_4Cl)_3$ with ligands such as hexamethylphosphoramide (HMPA), dimethylformamide(DMF), tetramethylurea(TMU), dimethyl sulphoxide (DMSO), pyridine(Py), α -, β -, γ -picolines(Pic), α -, β -, γ -picoline N-oxides(Pic-N-O), triphenylphosphine oxide(TPPO), triphenylarsine oxide ($\varphi_3As=O$) and α,α' -bipyridyl(α,α' -Bipy) yield solid addition compounds. The compositions of these

Table 1—Analyses, Colour, Melting Point and Electronic Spectral Data of Tris(2-chloroethoxy)vanadium(III) and Its Adducts

Compound	Colour	m.p. (°C)	Found (Calc.), %		$\lambda_{\max}^+$ (kK)
			V	Cl	
V(OC ₂ H ₄ Cl) ₃	Dark green liquid	—	17.40 (17.62)	36.81 (36.78)	16, 24
V(OC ₂ H ₄ Cl) ₃ .HMPA	Green solid	180	10.92 (10.88)	22.73 (22.98)	
V(OC ₂ H ₄ Cl) ₃ .2DMF	Grey solid	130	11.97 (11.71)	23.42 (24.45)	15, 25.3 39
V(OC ₂ H ₄ Cl) ₃ .TMU	Light green solid	*	12.72 (12.57)	26.31 (26.26)	
V(OC ₂ H ₄ Cl) ₃ .DMSO	Green solid	124	14.31 (13.88)	27.80 (28.90)	
V(OC ₂ H ₄ Cl) ₃ .2Py	Dark green solid	*	11.10 (11.39)	24.08 (23.79)	16, 23.52
V(OC ₂ H ₄ Cl) ₃ .2 α -pic	Green solid	—	10.85 (10.72)	22.11 (22.39)	
V(OC ₂ H ₄ Cl) ₃ .2 β -pic	Blackish green	135	10.93 (10.72)	21.93 (22.39)	15.38, 27.7
V(OC ₂ H ₄ Cl) ₃ .2 γ -pic	Grey solid	75	11.50 (10.72)	24.85 (22.39)	16, 27.2
V(OC ₂ H ₄ Cl) ₃ .2 α -pic-N-O	Green solid	180	10.02 (10.05)	19.87 (20.93)	
V(OC ₂ H ₄ Cl) ₃ .2 β -pic-N-O	Green solid	180	9.33 (10.05)	20.56 (20.93)	
V(OC ₂ H ₄ Cl) ₃ .2 γ -pic-N-O	Green solid	185	10.37 (10.05)	20.38 (20.93)	
V(OC ₂ H ₄ Cl) ₃ .2TPPO	Light green	*	5.89 (6.03)	13.83 (12.59)	16, 24 37
V(OC ₂ H ₄ Cl) ₃ . φ_3 As=O	Green solid	-do-	8.78 (8.34)	16.85 (17.42)	16.32, 25 37.5
V(OC ₂ H ₄ Cl) ₃ . α,α' -Bipy	Green solid	-do-	11.10 (11.44)	24.09 (23.89)	

*Did not melt upto 260°C.

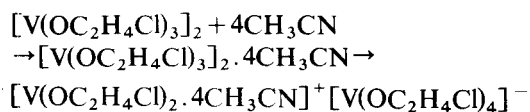
†Assignments are given in the text.

adducts have been ascertained from their analyses (Table 1).

The magnetic moments of the adducts V(OC₂H₄Cl)₃.2Py, V(OC₂H₄Cl)₃.2TPPO, V(OC₂H₄Cl)₃. α,α' -Bipy and V(OC₂H₄Cl)₃. φ_3 As=O at room temperature are 2.175, 1.850, 2.341 and 1.893 B.M. respectively. These values are lower than the spin-only value for a d^2 ion indicating the antiferromagnetic coupling between vanadium atoms through oxygen atom of bridging-OR groups in these complexes.

The reported values of molar conductance for univalent electrolytes in nitrobenzene, acetonitrile, dimethyl sulphoxide and dimethylformamide fall in the ranges 20-30, 120-160, 50-70 and 60-90 ohm⁻¹ mol⁻¹ cm² respectively⁶. But the molar conductances of the alkoxide and its complexes are much lower than

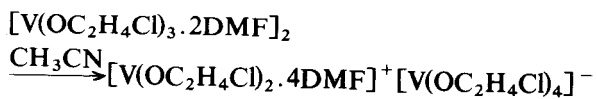
these values thereby showing that the present compounds are non-electrolytes in these solvents. However, the conductance of V(OC₂H₄Cl)₃ in acetonitrile increases with an increase in its concentration (14.67 ohm⁻¹ cm² mol⁻¹ at 1.89×10^{-3} M and 17.43 ohm⁻¹ cm² mol⁻¹ at 5.04×10^{-3} M concentration) in contrast to the Ostwald dilution law. This observation may be explained in terms of the complexation of the alkoxide with acetonitrile to a small extent in solution followed by the ionization of acetonitrile adduct as:



This view is further supported by the fact that the IR spectrum of acetonitrile adduct of V(OC₂H₄Cl)₃

exhibits two strong bands at 2295 and 2270 cm^{-1} which have been assigned to $\text{C}\equiv\text{N}$ stretching frequency of coordinated acetonitrile⁷.

The molar conductances of the adducts $\text{V(OR)}_3 \cdot 2\text{DMF}$, $\text{V(OR)}_3 \cdot \text{TMU}$, $\text{V(OR)}_3 \cdot \text{DMSO}$, $\text{V(OR)}_3 \cdot \text{HMPA}$, $\text{V(OR)}_3 \cdot 2\text{TPPO}$ (where $\text{R} = \text{C}_2\text{H}_4\text{Cl}$) in acetonitrile are 135.49, 82.94, 40.61, 99.15 and 22.26 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ respectively. The molar conductance of $\text{V(OR)}_3 \cdot 2\text{DMF}$ complex in acetonitrile lies in the range expected for 1:1 electrolytes in this solvent. This behaviour could be explained by the following formulation:



This type of ion-pair formulation is similar to the one obtained for $\text{Fe(OC}_2\text{H}_4\text{Cl)}_3$ in nitrobenzene¹ which was shown to exist as $[\text{Fe(OC}_2\text{H}_4\text{Cl)}_2 \cdot \text{L}_4]^+ [\text{Fe(OC}_2\text{H}_4\text{Cl)}_4]^-$.

This view is corroborated by the conductance of the complexes of the type $\text{VCl}_3 \cdot 1.5\text{L}'$ which were shown⁸ to be present as $[\text{VCl}_2 \cdot \text{L}'_2]^+ [\text{VCl}_4\text{L}']^-$ where L' is a bidentate ligand.

The visible spectrum of V(III) ion in octahedral environment is characterized by two bands around 16 and 24 kK for oxygen donors due to the transition ${}^3T_{1g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ and ${}^3T_{1g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ respectively⁹. Absorption bands due to these transitions occur around 13.0 and 18.0 kK respectively for complexes with sulphur donors. The band due to the third spin-allowed transition ${}^3T_{1g}(\text{F}) \rightarrow {}^3A_{2g}$ usually occurs around 35-37 kK in UV region. The spectral data of $\text{V(OC}_2\text{H}_4\text{Cl)}_3$ in acetonitrile and the diffuse reflectance spectral data of the complexes with various ligands are given in Table I. The presence of ${}^3T_{1g} \rightarrow {}^3T_{2g}$, ${}^3T_{1g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ and ${}^3T_{1g}(\text{F}) \rightarrow {}^3A_{2g}(\text{F})$ transitions in all the cases clearly establishes that V(III) is present in octahedral environment.

The infrared spectrum of $\text{V(OC}_2\text{H}_4\text{Cl)}_3$ shows no band in the region 3385-3310 cm^{-1} indicating the absence of coordinated or free alcohol. The two absorption bands exhibited at 1070-60 cm^{-1} and 1020 cm^{-1} in the spectrum of $\text{V(OC}_2\text{H}_4\text{Cl)}_3$ are attributed to the terminal and bridging $\text{C}-\text{O}$ stretching modes respectively¹⁰. A band present at 550 cm^{-1} in the

spectrum of $\text{V(OC}_2\text{H}_4\text{Cl)}_3$ has been assigned to $\nu(\text{V}-\text{O})$ ¹¹. Another band at 465 cm^{-1} may be assigned to $\nu(\text{V}-\text{O} \rightarrow \text{V})$ (arising from the bridging unit of associated alkoxide).

The IR spectra of adducts with DMF, TMU, HMPA, Py, α -, β -, γ -Pic, Pic N-oxides, TPPO and $\phi_3\text{As}=\text{O}$ show that these ligands are coordinated to metal through oxygen^{12,13} or nitrogen atom as shown by lowering of $\nu(\text{C}=\text{O})$ of DMF, TMU, $\nu(\text{S}=\text{O})$ ^{14,15} of DMSO, $\nu(\text{N}-\text{O})$ of amine oxides¹⁶, $\nu(\text{P}=\text{O})$ of TPPO, HMPA¹⁷ and $\nu(\text{As}=\text{O})$ of TPAsO ¹⁸ and increase in $\nu(\text{C} \equiv \text{C})$ and $\nu(\text{C} \equiv \text{N})$ of amines^{19,20}. In the spectra of these complexes two absorption bands arising from $\nu(\text{C}-\text{O})$ and two bands arising from $\nu(\text{V}-\text{O})$ are observed.

As is clear from the UV/VIS spectra, the alkoxide and its complexes have octahedral stereochemistry. Such a geometry is evidently achieved by association of the alkoxide/its complexes through alkoxy bridging and this is borne out by the IR studies.

Thanks are due to the CSIR, New Delhi for financial support.

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