

(2-Chloroethoxy)oxovanadium(V) derivatives: Synthesis and characterization

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(2-Chloroethoxy)oxovanadium(V) derivatives (**1-3**), $\text{VOCl}_n(\text{OCH}_2\text{CH}_2\text{Cl})_{3-n}$ (where $n=0-2$) have been prepared and characterized on the basis of elemental analyses, and IR, ^1H NMR and mass spectral data. Compounds **1-3** react with pyridine and dimethylformamide to give stable 1:1 adducts.

Metal alkoxides have been extensively studied¹. The corresponding chlorinated alkoxides are relatively less known and of these 2-chloroethoxy derivatives of oxovanadium(V) have not been reported. It has been estimated² that the conversion of two terminal M-OR bands into four M-OR bridging bonds, $2 \text{ M-OR} \rightarrow \text{M}_2(\mu\text{-OR})_2$, is enthalpically favoured. Consequently, the intermolecular alkoxy coordination is preferred and this precludes coordination from other bases to metal alkoxides. However, in chlorinated alkoxides, the poor basicity of oxygen may reduce the strength and extent of intermolecular alkoxy coordination and it is likely that another base may coordinate. Here, we describe the synthesis and characterization of new 2-chloroethoxyoxovanadium(V) derivatives and their stable adducts with pyridine and dimethylformamide.

Experimental

All reactions were done on vacuum line or under O_2 -free dry nitrogen. VOCl_3 was refluxed over mercury and doubly distilled to give pale yellow liquid.

Tris(2-chloroethoxy)oxovanadium(V)

Lithium metal (0.42g; 60.5 mmole) was added to 2-chloroethanol (~5 ml) and the reaction mixture stirred until whole of lithium dissolved. To this was added a solution of VOCl_3 (3.5 g; 20.1 mmole) in carbon tetrachloride (~5 ml) dropwise at room temperature. The reaction mixture was stirred for 2-3 hr and refluxed for another 3 hr. Diethyl ether was added to separate lithium chloride, which was filtered off under anhydrous con-

ditions and the filtrate was concentrated *in vacuo*, washed repeatedly with CCl_4 to remove 2-chloroethanol and again concentrated to yield brown solid.

The corresponding monochloro and dichloro derivatives, i.e. $\text{VOCl}(\text{OCH}_2\text{CH}_2\text{Cl})_2$ and $\text{VOCl}_2(\text{OCH}_2\text{CH}_2\text{Cl})$ were prepared in a similar manner except for the change in the amounts of Li and VOCl_3 (for monochloro derivative: Li, 0.258g, 36.8 mmole; VOCl_3 , 3.2g, 18.4 mmole; and for dichloro derivative Li, 0.145g, 20.7 mmole; VOCl_3 , 3.5g, 20.7 mmole).

The adducts were prepared by dissolving the oxovanadium(V) derivative in pyridine or dimethylformamide and precipitating out the solids by adding excess of diethyl ether.

Vanadium and chlorine were estimated gravimetrically. IR, ^1H NMR and mass spectra were recorded on Perkin-Elmer 1430, Varian EM 390 instrument at 90 MHz and VG Micromass 75 respectively.

Results and discussion

The reactions of VOCl_3 with $\text{LiOCH}_2\text{CH}_2\text{Cl}$ in 1:1, 1:2 and 1:3 molar proportions give brown hygroscopic solids, namely tris(2-chloroethoxy)oxovanadium(V), $\text{VO}(\text{OCH}_2\text{CH}_2\text{Cl})_3$ (**1**), chlorobis(2-chloroethoxy)oxovanadium(V), $\text{VOCl}(\text{OCH}_2\text{CH}_2\text{Cl})_2$ (**2**) and dichloro(2-chloroethoxy)oxovanadium(V), $\text{VOCl}_2(\text{OCH}_2\text{CH}_2\text{Cl})$ (**3**) respectively. Their analytical data (Table 1) are in accord with these formulations. These compounds are not soluble in benzene, hexane, CCl_4 etc. but are soluble to some extent in donor solvents. Their limited solubility in nitrobenzene, however, precludes cryoscopic measurements. Their IR spectra exhibit the $\nu(\text{V}=\text{O})$ mode³ at 1000-990 and the $\nu(\text{C}-\text{O})$, arising from $-\text{OCH}_2\text{CH}_2\text{Cl}$ group⁴ at 1085-1080 cm^{-1} (this is the region where terminal $\nu(\text{C}-\text{O})$ absorbs)⁵. Absence of any vibration due to bridging C-O group suggests that these compounds may be monomeric.

The ^1H NMR spectrum of pyridine solution of **1, 2** and **3** display strong signals at δ 3.4, 3.5 and 3.6 respectively assignable to $-\text{CH}_2$ protons of $-\text{OCH}_2\text{CH}_2\text{Cl}$ group⁶.

The mass spectra of **1, 2** and **3** do not exhibit any peak corresponding to the dimeric species or the parent ion and this is indicative of the instability of these molecules under electron impact. The presence of peak at m/z at 135 in **1** may be

Table 1 — Analytical data of (2-chloroethoxy)oxovanadium (V) compounds

Compound	m.p. (°C)	Found (Calc), %			
		V	Cl	C	H
VO(OCH ₂ CH ₂ Cl) ₃	> 260	15.95 (16.69)	34.1 (34.8)	22.3 (23.5)	3.8 (3.9)
VOCl(OCH ₂ CH ₂ Cl) ₂	95	19.4 (19.5)	40.5 (40.7)	17.4 (18.3)	3.2 (3.0)
VOCl ₂ (OCH ₂ CH ₂ Cl)	90	22.9 (23.4)	48.6 (48.9)	— —	— —
VO(OCH ₂ CH ₂ Cl) ₃ .Py	> 260	12.9 (13.2)	27.4 (27.7)	34.1 (34.3)	4.2 (4.1)
VOCl ₂ (OCH ₂ CH ₂ Cl) ₂ .Py	> 260	14.6 (14.97)	31.0 (31.3)	— —	— —
VOCl(OCH ₂ CH ₂ Cl).Py	> 260	16.1 (17.27)	34.6 (35.9)	28.1 (28.3)	3.0 (3.03)
VO(OCH ₂ CH ₂ Cl) ₃ .DMF	> 260	12.8 (13.26)	27.5 (28.2)	28.1 (28.6)	5.0 (5.4)
VOCl(OCH ₂ CH ₂ Cl) ₂ .DMF	> 260	14.5 (15.3)	31.2 (32.0)	24.2 (25.2)	4.3 (4.5)
VOCl ₂ (OCH ₂ CH ₂ Cl).DMF	> 260	17.1 (17.58)	36.2 (36.5)	20.3 (20.7)	3.5 (3.8)

assigned to [VOCl₂]⁺. This suggests that one OCH₂CH₂Cl moiety and two oxirane moieties get detached from the parent ion. In the mass spectrum of **2**, strong peaks at m/z 119 and 118 may be assigned to [VO(OH)Cl]⁺ and [VO₂Cl]⁺ species respectively. The appearance of these peaks indicates that (–OCH₂CH₂Cl, –CHCH₂Cl) and (–OCH₂CH₂Cl, –CH₂CH₂Cl) are detached from the molecular ions respectively. The peaks at m/z 167, 132, 119 and 118 in the mass spectrum of **3** may be assigned to [VO(OCH₂)Cl₂]⁺, [VO(OCH₂)Cl]⁺ and [VO₂Cl]⁺ species, respectively.

These compounds react exothermally with pyridine and dimethylformamide to give brown hygroscopic solid adducts having 1:1 stoichiometry (Table 1). Coordination of pyridine in these compounds is ascertained⁷ from the IR spectra of the adducts of **1,2** and **3**. Coordination of dimethylformamide⁸ is evident from the lowering of its ν(C=O) from 1680 cm⁻¹ to 1650–40 cm⁻¹ and an increase in δ(N–C=O) from 662 cm⁻¹ to 680–75 cm⁻¹ in the adducts. The νV=O modes of **1-3** shift to lower wavenumber in the spectra of

adducts. This is expected of coordination of the ligand *trans* to the V=O bond. There is no shift in the νC–O arising from the –OCH₂CH₂Cl group both in the spectra of the adducts as well as the parent **1-3** confirming the absence of any bridging –OCH₂CH₂Cl group in the adducts.

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