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Dichloro(2,2,2-trichloroethoxy)vanadium(III)dietherate: Synthesis and Coordination Chemistry

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Abstract

The compound, dichloro(2,2,2-trichloroethoxy)-vanadium(III) dietherate, has been synthesized; its infrared spectrum, magnetic susceptibility and reflectance data are consistent with an alkoxy-bridged structure having an approximately octahedral geometry for vanadium(III). Its mass spectrum indicates a dimeric structure. It reacts with oxygen and nitrogen donor ligands (L) to yield complexes, $VCl_2(OCH_2CCl_3)\cdot 2L$, for which the IR spectra, magnetic susceptibility and reflectance spectra suggest a structure similar to the parent compound and the ligands are probably *cis*. The ^1H NMR spectra of some of the compounds confirm the presence of a bridging $-OCH_2CCl_3$ group.

Introduction

As a consequence of intermolecular alkoxy bridge-aided [1] polymerization [2], the metal alkoxides show coordinative saturation and ususally do not react with ligands [3] to yield complexes. In fact, normal alkoxides of vanadium(III) such as $V(OMe)_3$ or $V(OEt)_3$ do not form complexes with ligands even under forcing conditions. Incorporation of Cl atoms in the –R group or in place of the –OR group in $M(OR)_n$ decreases the extent and strength of polymerization [4] and the metal trichloroethoxides which have not been synthesized very often are, therefore, expected to form adducts with ligands. Here, we report the synthesis and characterization of an hitherto unknown dichloro(2,2,2-trichloroethoxy)vanadium(III)dietherate and its reactions with some oxygen and nitrogen donor ligands.

Experimental

All reactions were carried out in an atmosphere of oxygen free dry nitrogen.

Preparation of $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$

Lithium 2,2,2-trichloroethoxide was prepared by the reaction of lithium metal and 2,2,2-trichloroethanol in dry benzene. Anhydrous vanadium(III) chloride was added to lithium 2,2,2-trichloroethoxide in a 1:1 molar ratio in dry diethylether. The contents were refluxed on a water bath for 24 h until the reaction was completed. Dry ether was added to separate lithium chloride and the reaction mixture was filtered under anhydrous conditions. The filtrate was dried in vacuum to yield a green coloured solid which on analysis was found to be $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$.

Complexes were obtained by dissolving the alkoxide with different ligands in an exothermic reaction and stirring the contents for 3–4 h. Green coloured adducts were separated by addition of dichloromethane/diethylether/petroleum ether (Table I).

Vanadium and chlorine were estimated gravimetrically [5]. C, H and N analyses were done on an Elemental analyzer M00.1106 from the Regional Sophisticated Instrumentation Centre, Panjab University, Chandigarh. Molar conductance was determined on a Toshniwal conductivity bridge using a cell of cell constant 0.521. Infrared spectra were recorded in nujol on a Perkin-Elmer 621 spectrophotometer. Diffuse reflectance spectra were carried on a Hitachi specord 300 in 1400–200 nm. ^1H NMR spectra of a few compounds were run on a Varian EM 390 spectrophotometer at 90 MHz on the scale using TMS as a reference. The mass spectrum of the compound was done on a V.G. Micromass 7075 instrument.

Results and Discussion

Dichloro(2,2,2-trichloroethoxy)vanadium(III)dietherate, $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$, is a greenish hygroscopic solid, insoluble in common non-polar solvents such as nitrobenzene, benzene etc. which precludes cryoscopic studies. However, it is soluble in acetonitrile and its molar conductance increases with an increase in its molar concentration (Table II)

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TABLE I. Analytical Data and Physical Properties of Dichloro(2,2,2-trichloroethoxy)vanadium(III)dietherate and its Complexes with some Oxygen and Nitrogen Donor Ligands

Compound	Colour and state	Melting point (°C)	μ_{eff} (BM)	Analysis, found(calc.) (%)				
				V	Cl	C	H	N
$VCl_2(OCH_2CCl_3)\cdot 2Et_2O$	dark green solid	180[d]	1.82	12.0 (12.1)	42.3 (42.4)	28.5 (28.5)	4.9 (5.23)	
$VCl_2(OCH_2CCl_3)\cdot 2TMU$	green solid	160[d]		10.3 (10.1)	34.9 (35.3)	27.0 (28.6)	4.5 (5.1)	10.5 (11.1)
$VCl_2(OCH_2CCl_3)\cdot 2\alpha$-pic-N-O	green solid	184[d]	2.0	10.6 (10.4)	36.2 (36.3)	33.1 (34.3)	3.0 (3.27)	4.9 (5.73)
$VCl_2(OCH_2CCl_3)\cdot 2\gamma$-pic-N-O	green solid	118[d]		10.8 (10.4)	36.1 (36.3)	33.0 (34.0)	3.1 (3.27)	4.5 (5.73)
$VCl_2(OCH_2CCl_3)\cdot 2THF$	green viscous liquid		2.15	12.5 (12.3)	42.6 (42.8)			
$VCl_2(OCH_2CCl_3)\cdot 2Py$	green solid	120[d]	1.95	12.1 (11.9)	41.0 (41.4)	33.0 (33.6)	2.6 (2.8)	5.5 (6.53)
$VCl_2(OCH_2CCl_3)\cdot 2\alpha$-pic	green solid	150[d]		11.0 (11.1)	38.7 (38.8)	36.0 (36.8)	3.0 (3.5)	5.7 (6.13)
$VCl_2(OCH_2CCl_3)\cdot 2\beta$-pic	green solid	155[d]		11.1 (11.1)	38.5 (38.8)	35.6 (36.8)	2.9 (3.5)	5.9 (6.1)

[d] Decomposed.

TABLE II. Molar Conductance of Dichloro(2,2,2-trichloroethoxy)vanadium(III)dietherate and its Adducts with some Oxygen and Nitrogen Donor Ligands

Compound	Molar concentration $\times 10^{-3}$	Molar conductance[a]
$VCl_2(OCH_2CCl_3)\cdot 2Et_2O$	2.7	54.4
$VCl_2(OCH_2CCl_3)\cdot 2Et_2O$	3.9	78.5
$VCl_2(OCH_2CCl_3)\cdot 2Et_2O$	5.4	88.0
$VCl_2(OCH_2CCl_2)\cdot 2\alpha$-pic-N-O	1.5	15.5
$VCl_2(OCH_2CCl_3)\cdot 2\gamma$-pic-N-O	1.7	20.1
$VCl_2(OCH_2CCl_3)\cdot 2\alpha$-pic	1.2	16.0

[a] In acetonitrile.

which is in contrast to Ostwald's dilution law and may be explained on the basis of ion-pair formation in acetonitrile as:

$$2VCl_2(OCH_2CCl_3)\cdot 2Et_2O \xrightarrow[-2Et_2O]{4CH_3CN} [V(OCH_2CCl_3)_2(CH_3CN)_4]^+[VCl_4]^-$$

The IR spectrum of $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$ shows only one band at 1010 cm^{-1} in the region where C–O absorbs (Table III) which may be assigned to the bridging $-OCH_2CCl_3$ group [6–8] and the band at 450 cm^{-1} may be attributed to $\nu(\mathrm{V}\overset{\mathrm{O}}{\frown}\mathrm{V})$ of the bridging –OR group. In addition the bands at 425 and 395 cm^{-1} (Table III) may be assigned to ν(V–Cl) and the position of these bands compares well with those in the six coordinated vanadium(III) complexes [9].

The magnetic moment of $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$ (1.82 BM) (Table I) is sufficiently below the required spin-only value for an octahedral spin-free d^2 ion (2.83 BM), suggesting the existence of antiferromagnetic interactions between vanadium(III) atoms [10].

The spectra of octahedral d^2 complexes of vanadium(III) usually give three spin allowed electronic transitions assigned as $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ and $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$. These transitions are expressed by the bands present at 14000–17000, 22000–25000 and 30000–40000 cm^{-1} [11]. The band corresponding to a third spin-allowed transition should be very weak because it is attributed to simultaneous excitation of two d electrons $t_{2g}{}^2 \rightarrow e_g{}^2$. The diffuse reflectance spectrum of $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$ shows bands at 15.6 kK and 25.5 kK (1 kK = 1000 cm^{-1}) assigned to $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transitions suggesting the presence of vanadium(III) in an octahedral environment (Table IV). The spectrum of $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$ also shows an intense charge transfer band above 30000 cm^{-1}. This band may be due to transfer of an electron from the π orbital of the oxygen atom to vanadium(III). This band is quite broad and intense obscuring the detection of the weak intensity band $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$. The interelectronic repulsion parameter (B) and ligand field parameter (10

TABLE III. Infrared Spectral Frequencies (cm^{-1}) of Dichloro(2,2,2-trichlorethoxy)vanadium(III)dietherate and its Adducts with some Oxygen and Nitrogen Donor Ligands

Compound	ν(C=O)^a, ν(N–O)^b, ν(C–O–C)^c, ν(C=O), ν(C=N)^d	ν(C–O) bridging	ν(V–O–V)	ν(V–Cl)
$VCl_2(OCH_2CCl_3)\cdot 2Et_2O$		1010	450	425, 395
$VCl_2(OCH_2CCl_3)\cdot 2TMU$	1600 (1650)^a	1000	450	415, 395
$VCl_2(OCH_2CCl_3)\cdot 2\alpha$-pic-*N*-O	1205, 1200 (1245)^b	1040	460	415, 395
$VCl_2(OCH_2CCl_3)\cdot 2\gamma$-pic-*N*-O	1210, 1200 (1255)^b	1035	460	
$VCl_2(OCH_2CCl_3)\cdot 2THF$	1045 (1070)^c	1010	470	
$VCl_2(OCH_2CCl_3)\cdot 2Py$	1600, 1565 (1583, 1572, 1482, 1439)^d	1040	450	410
$VCl_2(OCH_2CCl_3)\cdot 2\alpha$-pic	1600, 1580–1560 (1574, 1550, 1481)^d	1015	470	415, 405
$VCl_2(OCH_2CCl_3)\cdot 2\beta$-pic	1610, 1595 (1580, 1485, 1420)^d	1030		

^{a}The values given in parenthesis represent the wave number due to pure ligands.

TABLE IV. Electronic Spectral Frequencies, *B* (Repulsion Parameter) and 10 *Dq* (Ligand Field Splitting Parameter) of some of the Adducts of Dichloro(2,2,2-trichloroethoxy)vanadium(III)

Compound	*A* (kK)	*B* (kK)	*B*	10 *Dq*
$VCl_2(OCH_2CCl_3)\cdot 2Et_2O$	15.6	25.5	0.755	17.02
$VCl_2(OCH_2CCl_3)\cdot 2TMU$	15.4	25.8	0.791	16.865
$VCl_2(OCH_2CCl_3)\cdot 2\alpha$-pic-*N*-O	16.0	24.5	0.654	17.31
$VCl_2(OCH_2CCl_3)\cdot 2\gamma$-pic-*N*-O	16.2	24.0	0.603	17.245
$VCl_2(OCH_2CCl_3)\cdot 2\alpha$-pic	15.7	25.2	0.726	17.1

$A = {}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F); B = {}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$.

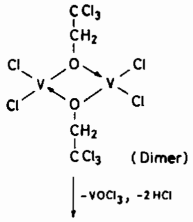
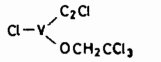
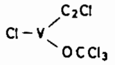
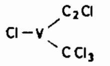
Dq) values have been calculated and were found to be in accord with those of six coordinated vanadium(III) compounds [12, 13].

The ^1H NMR spectrum of $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$ in pyridine shows a peak at $\delta = 4.50$ ppm, assigned to the presence of a bridging trichloroethoxy group [14], in addition to peaks due to pyridine. The mass spectrum of $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$ has been recorded and the *m*/*e* peak positions for the main peaks and their possible assignments are given in Table V. The *m*/*e* peaks at the position of the dimer/monomer have not been observed; instead a strong peak appears at 294 which can be attributed to the fragmentation of the dimeric compound. The spectrum also shows a strong peak at *m*/*e* = 148 which may be due to $-OCH_2CCl_3$.

$VCl_2(OCH_2CCl_3)\cdot 2Et_2O$ reacts with various oxygen and nitrogen donor ligands to form adducts formulated as $VCl_2(OCH_2CCl_3)\cdot 2L$ (Table I) [L = tetramethylurea (TMU), α- and γ-picoline-*N*-oxide (α- and γ-pic-*N*-O), tetrahydrofuran (THF), pyridine (Py), α- and β-picoline (α- and β-pic). Some of the adducts are soluble in acetonitrile and their molar conductance shows them to be non-ionic in nature (Table II).

The infrared spectra of the adducts show the presence of a bridged alkoxy group at 1010–1040 cm^{-1} and the bands due to the ligands, the position of which indicates their coordination [15–17]. The IR spectra of amine-oxide adducts show the ν(N–O) absorptions at 1205 and 1200 cm^{-1} for $VCl_2(OCH_2$-

TABLE V. Mass Spectral Data of $VCl_2(OCH_2CCl_3)\cdot 2Et_2O$

Peak position (*m*/*e*)	Possible assignment
	
294 Vv, s	
280s	
264m	
148v, s	$-OCH_2CCl_3$
144s	$CCl_3 + C_2H_2$
132s	$CCl_3 + CH_2$
125	$CCl_2 + O + C_2H_2$
118v, s	CCl_3

$CCl_3)\cdot 2\alpha$-pic-*N*-O and at 1210 and 1200 cm^{-1} for $VCl_2(OCH_2CCl_3)\cdot 2\gamma$-pic-*N*-O compared to 1245 and 1255 cm^{-1} respectively for the free ligands. The splitting of the N–O vibrations suggests that the two ligands occupy *cis* positions in these complexes [18]. The magnetic susceptibility shows a decrease in antiferromagnetic interactions on complexation of the parent alkoxide. The reflectance spectra confirm the existence of an octahedral stereochemistry for these complexes. The ^1H NMR spectrum of $VCl_2(OCH_2CCl_3)\cdot 2Py$ in acetonitrile shows slightly broad peaks at $\delta = 4.55$ ppm (*a*) assigned to the presence of $-OCH_2CCl_3$ [14] and at $\delta = 7.7$ and 8.8 ppm (*b*) for coordinated pyridine, in addition to a strong peak at 2.0 ppm for acetonitrile. The integration ratio of $a:b = 2:10$ or 1:5 supports the existence of a 1:2 stoichiometry for this complex.

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