Inorganica Chimica Acta, *74* (1983) 215–220

A Simple Route to Alkoxy-Chloro Ti(III) and V(III) Compounds

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Received February 23, 1983

$M(OR)_nCl_{3-n}$ compounds ($M = Ti$, V; $R = Me$, Et, Bu^n; $n = 1, 2$) were prepared by reaction of anhydrous metal trichlorides and trialkyl orthoformates. The reaction mechanism probably involves a six-member cyclic intermediate. The alkoxy-chloro compounds have been characterized by elemental analyses, X-ray powder diffraction, infrared spectroscopy and magnetic susceptibilities.

They show a polymeric nature, probably due to the presence of alkoxide bridges although chlorine bridges and partial direct metal–metal interaction cannot be ruled out.

Introduction

Transition metal alkoxides have been studied extensively and they are widely used in a number of organic reactions. Their chemistry and properties have been reviewed by Bradley [1, 2] and Mehrotra [3]. Tetra-alkyl and tetra-aryl titanates are probably the most well-known, and many simple synthetic routes are available [4]. Tetra-alkoxides of V(IV) have also been reported [5–7]. A similar situation is found for alkoxy and aryloxy-chlorides of formula $(RO)_{4-n}MCl_n$ (M = Ti, thin V; n = 1, 2, 3). Both these classes of compounds find a wide range of applications, *e.g.* as polymerization catalysts [9] and extremely efficient trans-esterification agents [10]. On the contrary, little is known about the low-valent alkoxides and halo-alkoxides of Ti(III) and V(III) [11–13].

As part of our work in the development of new Ziegler-Natta polymerization systems, we recently reported that alkoxy V(III) halides behave as efficient catalysts for ethylene polymerization in the presence of oxoalane compounds [14]. As no simple and reliable preparation of Ti(III) and V(III) alkoxy-halides has been described, it was thought worthwhile to look for some new synthetic routes. Accordingly, we wish now to report a simple general route to these compounds through the reaction of the metal trichlorides with boiling trialkyl orthoformates.

Experimental

All operations were carried out under dry, oxygen free, nitrogen using the standard Schlenk tube technique. For the infrared spectra a Perkin-Elmer 580 B spectrophotometer equipped with an Infrared Data Station 3500 was used, samples being nujol mulls between KBr or CsI plates. GC analyses were conducted on a Hewlett-Packard Model 5830 A chromatograph equipped with a flame ionization detector. Mass spectra were obtained on a Varian CH5 instrument. X-Ray powder diffraction data were recorded with a Philips PW 1060/70 diffractometer using a nickel filtered Cu K_α radiation ($\lambda = 1.54178$ Å). The samples were protected from moisture by intimate mixing with anhydrous paraffin oil under dry nitrogen. During pattern collection the specimens were enclosed in a steel cell equipped with Mylar windows, and a dry nitrogen atmosphere was maintained in the cell during the experiments. Line intensities were estimated visually. Magnetic susceptibilities of Ti(III) compounds at room temperature were determined by the Gouy method. The compounds were sealed from the air. Elemental analyses were performed by the Analytical Department of the Donegani Institute.

Analyses

Titanium was determined by the colorimetric method described by Kolthoff [15]. Vanadium was titrated with ferrous sulphate [16] and iron determined by complexometric titration as described by Schwarzenbach [17].

Alkoxy groups were determined by transforming them into the nitrito derivatives according to the method described by Skrabal [18].

Materials

n-Heptane was treated with concentrated H_2SO_4, washed with water, and distilled from $LiAlH_4$. It was stored over pre-baked type 3A Linde molecular sieves. Trialkyl orthoformates (Fluka) were purified by reduced-pressure distillation just prior to use. $TiCl_3$ and VCl_3 (Alfa) were used as received. $FeCl_3$ was sublimed under vacuum. $Ti(OMe)_3$ and $V(OEt)_3$ were prepared as described by Winter [11].

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0020-1693/83/$3.00

Preparation of $M(OR)_nCl_{3-n}$. General Procedure

About 80 mmol of the metal trichlorides were added to 200 ml of the trialkyl orthoformate in a nitrogen-filled flask equipped with a magnetic stirrer and reflux condenser with a nitrogen inlet. The suspension was refluxed for 8 hours. After cooling, the solid was separated by filtration, washed with n-heptane and dried under vacuum (10^{-6} mmHg). Yields were practically quantitative.

A shorter reaction time was required for the reaction between VCl_3 and trimethyl orthoformate. Heating was stopped as soon as the suspension turned green.

Caution: reaction of $TiCl_3$ with trialkyl orthoformates is highly exothermic. The metal trichloride must be added slowly, the reaction vessel being cooled at 0 °C.

Preparation of $Ti(OEt)Cl_2\cdot 0.5H\overset{\overset{O}{\|}}{C}OEt$

$TiCl_3$ (50 mmol) was slowly added to an equimolecular solution of triethyl orthoformate in 200 ml of n-heptane. The suspension was refluxed a further 8 hours. During this time its colour gradually turned from violet to light brown. After cooling, the solid was filtered off, washed with n-heptane, and dried under vacuum (10^{-6} mmHg).

Analytical data of the alkoxy Ti(III) and V(III) chloro compounds are reported in Table I. All are practically insoluble in aprotic, even strong solvating solvents, and decompose at about 300 °C leaving black carbonaceous residues. Compared to the metal trichlorides they are relatively stable to air oxidation.

Results

Reaction between MCl_3 and Trialkyl Orthoformates

When violet anhydrous VCl_3 is allowed to react with a large excess of boiling trialkyl orthoformate a smooth reaction takes place. The colour of the suspension fades slowly, turning gradually to pale green. As shown in Table I, analytical data of compounds obtained by reaction with trimethyl or triethyl orthoformate are in agreement with alkoxy-chloro compounds of formula $V(OR)Cl_2$. The reaction with tributyl orthoformate leads to the dialkoxy-chloro compound, probably owing to more severe reaction conditions due to the higher boiling point of the orthoester. When trimethyl orthoformate is employed, prolonged contact time gives rise to a further reaction and the suspension turns back to violet.

The interaction between $TiCl_3$ and trialkyl orthoformates is far more violent and caution must be taken in adding the metal trihalide to the orthoester. Owing to its higher reactivity, $TiCl_3$ leads only to the dialkoxy Ti(III) chloro compounds. Dichloro-alkoxy derivatives can be prepared only when the reaction is carried out with an equimolecular amount of the orthoester in n-heptane, as a dispersing medium. In this case, however, only the adduct between the corresponding alkyl formate and $Ti(OR)Cl_2$ can be isolated.

In the course of the reaction of metal trichlorides with the orthoesters, volatile organic compounds were formed. The interaction between VCl_3 and tri-

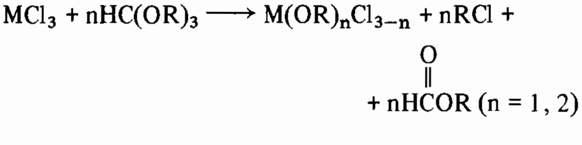
TABLE I. Analytical Data of $M(OR)_nCl_{3-n}$ Compounds[a].

Compound	Colour	Dec. Pt. °C	Metal %	Alkoxide %	Cl %
$V(OMe)Cl_2$	Pale green	290	32.13 (33.33)	19.78 (20.28)	46.35 (46.39)
$V(OEt)Cl_2$	Green	300	30.20 (30.53)	25.05 (26.97)	41.64 (42.50)
$V(OBu^n)_2Cl$	Green	270	21.46 (21.92)	63.20 (62.82)	14.87 (15.26)
$Ti(OMe)_2Cl$	Light brown	240	31.98 (32.95)	42.60 (42.65)	23.82 (24.39)
$Ti(OEt)_2Cl$	Yellow-brown	270	26.10 (27.63)	51.11 (51.92)	21.35 (20.45)
$Ti(OBu^n)_2Cl$	Brown	280	19.29 (20.88)	62.43 (63.66)	16.03 (15.46)
$Ti(OEt)Cl_2\cdot 0.5H\overset{\overset{O}{\|}}{C}OEt$	Light brown	n.d.	24.10 (23.85)	31.96 (33.61)[b]	35.96 (35.31)
$Fe(OEt)_2Cl$	Yellow-green	300	31.33 (30.80)	50.01 (49.64)	19.05 (19.55)

[a] Calculated percentages are given in parentheses. [b] Including ester etoxy group.

ethyl orthoformate was carefully followed and all the low-boiling organic compounds collected. A gas-mass analysis revealed as the main products ethyl chloride and ethyl formate, together with variable amounts of diethyl ether, ethanol and traces of methylene chloride.

Accordingly, the overall stoichiometry can be deduced as follows:



$$MCl_3 + nHC(OR)_3 \longrightarrow M(OR)_nCl_{3-n} + nRCl + nH\overset{\overset{O}{\|}}{C}OR \ (n = 1, 2)$$

X-Ray Powder Diffraction

The X-ray powder diffraction patterns of many of the synthesized chloro-alkoxy compounds were recorded. 'd' spacings and relative line intensities are reported in Table II. As can be seen powder diffraction patterns were found to be different from those of a mixture of $M(OR)_3$ and MCl_3, thus suggesting the formation of a new class of compounds.

Infrared Studies

In Table III are listed the infrared absorption maxima and relative intensities of a few representative compounds. The spectra of metal alkoxides are very complicated and it is difficult to make assignments with certainty, particularly as many such compounds are associated in varying degrees [19]. Despite this, some common features can be found throughout all the spectra reported. The region between 1470 and 1200–1150 cm^{-1} contains a few peaks which may be due to the usual deformation modes of CH_3 and CH_2 groups. Characteristic strong absorptions of alkoxy groups appear around 1000 cm^{-1}, as mentioned by other authors [19–21]. These bands are due to modes variously described as ν(C–O) and ν(C–O–M). The presence of a larger number of C–O stretching bands than expected on theoretical grounds may be due to a polymeric nature of these compounds. ν(M–O) modes are expected to fall between 600 and about 500 cm^{-1} while bending modes must be located at lower wavenumbers. Although complete assignments have been made for tetra-alkoxides of Ti(IV) [21–22], there must be substantial interaction between ν(M–O) and δ(M–O) however, and, in the case of higher alkyl groups, with δ(O–C–C) as well. Hence, assignments for bands falling in this region should be used with extreme care even if the structure and degree of association are well known. No spectral data concerning ν(M–Cl) modes are available for alkoxy Ti(III) and V(III) chlorides. The spectra of $TiCl_3$ and VCl_3 contain strong bands at 289 and 295 cm^{-1} respectively, probably associated with bridging ν(M–Cl) vibrations [23]. Accordingly, metal–halogen stretchings of $M(OR)_nCl_{3-n}$ compounds are expected to fall around 300–250 cm^{-1} if chlorine bridges are involved, at higher frequencies if not.

Figure 1 shows the infrared spectra of three V(III) alkoxy-chlorides. The spectrum of $V(OEt)_3$ is also reported.

Partial hydrolysis experiments were found to be one of the most suitable methods for C–O stretching modes assignments [19]. Disappearance of one or more bands in the 1000–1100 cm^{-1} region should suggest the presence of bridging alkoxide groups which are removed by hydrolysis, while bands associated with terminal alkoxide groups are not hydrolysed until later.

TABLE II. X-ray Powder Diffraction Data of $M(OR)_nCl_{3-n}$ Compounds. 'd' Spacing Values (Å).

$TiCl_3$ [a]	VCl_3 [a]	$Ti(OMe)_3$	$V(OEt)_3$	$V(OMe)Cl_2$	$V(OEt)Cl_2$	$V(OBu^n)_2Cl$	$Ti(OMe)_2Cl$	$Ti(OEt)_2Cl$ [b]
5.85(80)	5.75(100)	8.50(vs)	8.51(vs)	8.35(ms)	9.50(vs)	10.17(vs)	14.50(m)	11.1(vs)
2.93(30)	2.89(18)	5.21(vw)	5.31(w)	7.44(m)	6.76(m)	8.51(w)	10.30(m)	4.67(mb)
2.72(100)	2.67(55)	4.87(w)	5.10(w)	6.60(m)	4.72(m)	7.56(mb)	9.20(mw)	3.63(w)
2.12(65)	2.09(25)	3.785(mw)	4.77(mw)	5.14(w)	4.13(vw)	6.86(mw)	8.35(sm)	3.09(wb)
1.772(79)	1.93(2)	3.625(w)	4.58(w)	4.77(w)	3.53(m)	5.12(m)	7.63(m)	
1.701(30)	1.74(20)	3.23(mw)	4.40(w)	2.975(w)	3.28(vw)	4.80(m)	7.30(m)	
1.650(35)	1.67(6)	2.960(w)	4.15(w)	2.615(w)	3.15(w)	4.44(m)	6.97(w)	
1.519(20)	1.63(10)	2.564(vw)	3.80(m)	2.455(vw)	2.876(w)	4.23(mw)	6.51(m)	
1.487(25)	1.485(2)		3.68(mw)	2.281(mw)	2.814(vw)	4.11(w)	6.11(w)	
1.467(25)	1.462(4)		3.41(w)		2.309(w)	3.74(m)	4.40(w)	
1.363(25)	1.454(4)		3.186(w)		2.132(vw)	3.44(w)	2.903(w)	
	1.340(6)		3.078(w)			3.13(w)	2.858(w)	
			2.978(vw)			2.722(w)		
						2.386(w)		
						2.321(w)		
						2.137(w)		

[a] Relative intensities in parentheses. [b] Partially amorphous.

TABLE III. Infrared Spectral Data of $M(OR)_nCl_{3-n}$ Compounds[a].

$V(OMe)Cl_2$[b]	$V(OEt)Cl_2$	$V(OBu^n)_2Cl$	$Ti(OMe)_2Cl$	$Ti(OEt)_2Cl$	$\mathrm{Ti(OEt)Cl_2\cdot 0.5H\overset{O}{\overset{\|}{C}}OEt}$[b]	$Fe(OEt)_2Cl$[b]
1397(m)	1279(w)	1290(w)	1112(mw)	1355(w)	1646(s)	1361(m)
1125(m)	1150(m)	1260(w)	1055(s)	1145(mw)	1310(m)	1155(m)
1055(s)	1080(s)	1225(w)	1036(s)	1098(vs)	1270(m)	1091(s)
1004(s)	1040(vs)	1155(w)	1004(msh)	1059(vs)	1159(w)	1033(vs)
972(s)	898(s)	1140(w)	687(w)	9035	1098(m)	880(s)
660(wb)	800(w)	1112(m)	595(mb)	545(s)	1058(s)	555(msh)
520(s)	665(w)	1055(s)	515(m)	445(ms)	990(w)	470(mb)
456(s)	550(s)	1039(vs)	4915(m)	255(w)	905(m)	
410(w)	430(s)	993(s)	460(s)		850(m)	
	390(s)	948(m)	410(w)		798(w)	
	325(m)	901(m)	335(w)		534(mb)	
	277(m)	845(w)			477(m)	
	253(w)	732(w)				
		593(s)				
		465(s)				
		397(s)				
		372(m)				
		306(m)				
		250(w)				

[a] Nujol mull between CsI plates, unless otherwise stated. [b] KBr plates.

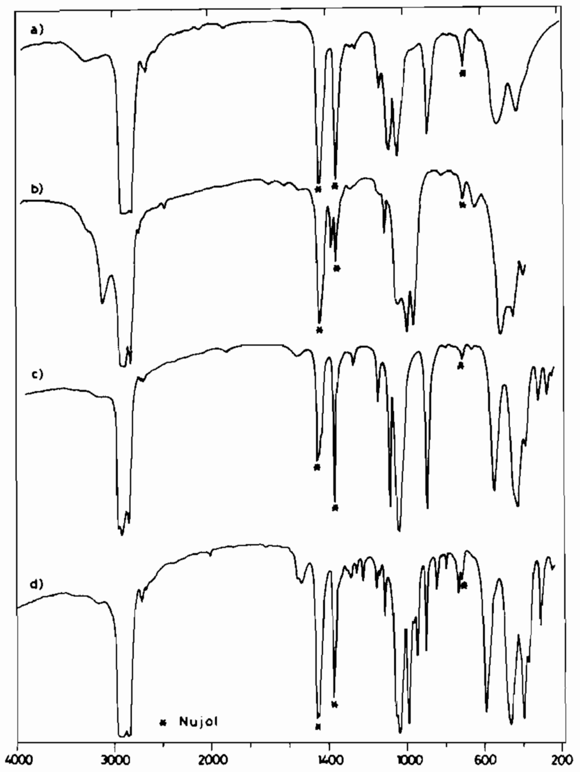


Fig. 1. Infrared spectra of: a) $V(OEt)_3$; b) $V(OMe)Cl_2$ (KBr plates); c) $V(OEt)Cl_2$; d) $V(OBu^n)_2Cl$.

Hydrolysis experiments carried out on some representative alkoxy Ti(III) and V(III) chloro compounds, led to a gradual disappearance of all the bands falling in the C–O stretching region, suggesting thus that most of the alkoxide groups are present as a bridging moiety.

Table IV lists some tentative IR assignments which have been deduced on the grounds of published data on Ti(IV) and V(IV) alkoxides and chloro-alkoxides. Uncertainty arises, especially for the less intense ν(M–Cl) modes owing to a complete lack of published data. However, the supposed M–Cl stretchings fall generally at lower frequencies than those of the corresponding metal trichlorides, in accordance with what is reported for $VO(OR)_nCl_{3-n}$ compounds [24]. In this case it was observed that the higher the degree of substitution of Cl ligands by alkoxy groups, the lower was the ν(M–Cl) frequency.

Magnetic Susceptibilities

Preliminary magnetic susceptibility determinations were performed on $Ti(OR)_2Cl$ (R = Me, Et) at 17 °C and 18 °C respectively. For $Ti(OMe)_2Cl$ a $\chi_g = 4.28 \times 10^{-6}$ c.g.s. was found. After correction for diamagnetism using the appropriate Pascal constants, this value leads to a $\mu_{eff} = 1.27$ B.M., quite close to $\mu_{eff} = 1.31$ B.M. (at 300 K) found for violet $TiCl_3$ [25].

Although magnetic behaviour studies over a wide temperature range are needed to make significant conclusions, the magnetic moment of $Ti(OMe)_2Cl$ is significantly lower than that of the spin-only value and might be suggestive of some magnetic exchange. If true, intermolecular spin–spin interaction, due either to direct or indirect through-bond magnetic exchange, should imply some clustering phenomena

TABLE IV. Tentative IR Assignment for some $M(OR)_nCl_{3-n}$ Compounds.[a]

Compound	ν(C–O)	$\nu + \delta$(M–O)	ν(M–Cl)
$V(OMe)Cl_2$	1055, 1004	520, 456	
$V(OEt)Cl_2$	(1080), 1040	550, 430	277
$V(OBu^n)_2Cl$	1055, 1039	593, 465	(250)
$Ti(OMe)_2Cl$	1055, 1036	595, 460	(335)
$Ti(OEt)_2Cl$	1098, 1059	545, 445	250
$Ti(OEt)_2Cl\cdot 0.5H\overset{\overset{O}{\|}}{C}OEt$	1058	534, 477	

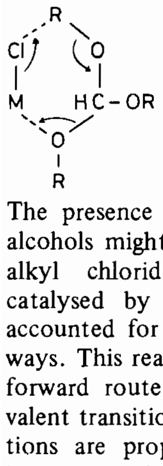
[a] Assignments in parentheses are doubtful.

as reported for some Ti(III) compounds [12]. For $Ti(OEt)_2Cl$ a $\chi_g = 9.94 \times 10^{-6}$ c.g.s. was found. This is an unusually high value for a Ti(III) compound. Further studies are in progress in order to understand the magnetic behaviour of such compounds.

Discussion

Although a great number of synthetic routes to transition metal alkoxides have been reported [2], the reaction between metal salts and trialkyl orthoformates seems to be a completely new one. Some analogies might be found however, with the reaction between VCl_3 and $(EtO)_3P{=}O$ which leads to $V[O_2P(OEt)_2]_3$ and ethyl chloride [26].

The reaction mechanism probably involves a six-member cyclic intermediate as shown below.



The presence of small amounts of alkyl ethers and alcohols might be due to a further reaction between alkyl chlorides and the orthoesters, probably catalysed by the transition metal salt. It can be accounted for only by more complex reaction pathways. This reaction appears to be a general, straightforward route to alkoxy-chloro compounds of tervalent transition metals, provided that reaction conditions are properly chosen. Thus, as stated before, interaction between trimethyl orthoformate and VCl_3 leads quickly to the green mono-alkoxy derivative. Prolonged contact time gives rise to a disproportionation into the dialkoxy compound and VCl_3, as clearly indicated by the X-ray powder diffraction pattern and the strong band at 297 cm^{-1} in the infrared spectrum. $FeCl_3$ reacts with triethyl orthoformate affording $Fe(OEt)_2Cl$. Analytical and infrared data are reported in Table I and Table II respectively. On the contrary, $CrCl_3$ can be recovered unchanged even after several days.

The alkoxide group displays a great propensity to bridge two or more metal atoms, so that the formation of polynuclear molecular clusters dominates the structural chemistry of these compounds. Thus Ti(IV) alkoxides are polymeric to a degree depending upon the steric effect of the alkoxides. X-Ray diffraction studies of $[Ti(OEt)_4]_4$, $[Ti(OMe)(OEt)_3]_4$ and $[Ti(OMe)_4]_4$ show that in each case Ti atoms are octahedrally coordinated to six oxygen atoms [27, 28]. V(IV) alkoxides too have shown to be polymeric, the degree of association being 3 for the methoxide and decreasing with increase of the alkyl chain length [5]. Only a few papers on tervalent alkoxides of Ti(III) and V(III) have appeared. The methoxides $M(OMe)_3$ have been prepared by reaction of the anhydrous trichlorides and lithium methoxide [11, 13]. They are green, non-volatile solids which are undoubtedly polymeric. $Ti(OMe)_3$ was reported to be diamagnetic with strong metal–metal interaction. Lappert [29] prepared the triethoxy Ti(III) compounds by alcoholysis of tris(dimethylamido)titanium(III) in benzene. It was a diamagnetic, dark blue-green crystalline tetramer $Ti_4(OEt)_{12}$. The only report on alkoxy-chloro compound of Ti(III) is due to Winter [12]. $TiCl_2(OMe)\cdot 2CH_3OH$ and $TiCl(OMe)_2\cdot 2CH_3OH$ were prepared by proportionation reaction between $Ti(OMe)_3$ and $TiCl_3$ in methanol. However, on the grounds of its magnetic behaviour, it was suggested that $TiCl_2(OMe)\cdot 2CH_3OH$ is a complex with a trinuclear cation $[Ti_3(OMe)_3(CH_3OH)_6]^{6+}$. By the same method a number of green V(III) chloride methoxide complexes $V(OMe)_2Cl$, $V(OMe)_2Cl\cdot MeOH$, $V(OMe)_2Cl\cdot Me_2CO$ and $V(OMe)Cl_2\cdot 2MeOH$ were prepared by Kakos and Winter [30]. Also in this case the anomalously low magnetic moments were accounted for by spin interactions of neighbouring metal atoms in trimeric or tetrameric clusters.

The insolubility of $M(OR)_nCl_{3-n}$ compounds prepared by the method we have discovered clearly indicates a polymeric nature; however, examination is needed as to whether discrete polymeric species similar to those in Ti(IV) alkoxides are present or an infinite network is involved. Infrared studies are in accordance with the presence of akoxide bridges. The anomalously low frequencies of the supposed ν(M—Cl) modes might also be due to halogen bridges. Magnetic behaviour of Ti(III) compounds, even if not determined over a temperature range, is probably the result of some intramolecular spin—spin interaction, at least for the methoxide derivative. Hence, the polymeric nature of the alkoxy-chloro Ti(III) and V(III) compounds may be due to ligand bridges, as indicated by the interaction between transition metal atoms.

Acknowledgements

The authors are indebted to Dr. G. Fochi of Pisa University for magnetic susceptibility determinations.

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