Inorganica Chimica Acta, 20 (1976) 7–9

Preparation and Reactions of (2-Chloroethoxy)- and (2,2,2-Trifluoroethoxy)-trichlorotitanium(IV)

RAM CHAND PAUL, PRATIBHA SHARMA, P. K. GUPTA and S. L. CHADHA
Department of Chemistry, Panjab University, Chandigarh-160014, India

Received January 2, 1976

The title compounds have been prepared. Infrared spectra of these compounds indicate that titanium is four-coordinate in them. These compounds form complexes of the type $Ti(OR)Cl_3\cdot L$ *or 2L (where* $R = C_2H_4Cl$ *or* $C_2H_2F_3$ *and L is monodentate ligand) with various oxygen and nitrogen ligands. The complexes have been characterized by their analyses and infrared spectra.*

Introduction

Although the complexes of titanium(IV) halides have been extensively prepared and studied, complexes of corresponding alkoxides have not been well reported. The complexes of the alkoxides $TiCl_3(OC_2H_5)$, $TiCl_2(OC_2H_5)_2$ and $TiCl(OC_2H_5)_3$ with pyridine and trimethylamine have been reported by Anagnostopoulos[1] and those of $TiCl(OC_2H_5)_3$ with piperidine and hydrazine by Buerger,[2] but no information about the nature of these complexes from even their infrared spectra has been advanced. Recently Paul *et al.*[3] have reported the preparation of the complexes of dialkoxydichlorotitanium(IV), $Ti(OR)_2Cl_2$ with oxygen and nitrogen donor ligands but that work was more in the direction to assess the infrared spectral changes which the ligand molecule experiences on complex formation, rather than overall structure. Very recently Clark and McAlees[4] have reported some complexes of methoxytitanium (IV) trichloride with bidentate ligands and these complexes have been synthesised by the oxidation of corresponding methyltitanium(IV) trichloride compounds.

We report now the syntheses and characterisation of (2-chloroethoxy)- and (2,2,2-trifluoroethoxy)-trichlorotianium(IV) and the preparation and characterization of their complexes with a variety of oxygen and nitrogen donors.

Experimental

Preparation of (2-chloroethoxy)trichlorotitanium(IV)

Titanium(IV) chloride (11.0 ml, 0.1 mol) was added dropwise with constant stirring to a mixture of 2-chloroethanol (7.0 ml, 0.1 mol) and benzene (5.0 ml). The mixture was then refluxed on a water bath till hydrogen chloride gas ceased to come out. It was then chilled in ice bath when an orange-yellow solid separated out, which was filtered under anhydrous conditions, washed repeatedly with petroleum ether and dried under vacuum to give a dirty white hygroscopic solid (90% yield), which was recrystallised from benzene (m.pt. 71–72 °C). *Anal.* Found, Ti = 20.45%, Cl = 60.21%. Required for $TiCl_3(OC_2H_4Cl)$, Ti = 20.47%, Cl = 60.71%. Analysis of this solid confirms the formula $TiCl_3(OC_2H_4Cl)$.

Preparation of (2,2,2-trifluoroethoxy)trichlorotitanium(IV)

This compound was synthesised by a procedure as described above except for that 2,2,2-trifluoroethanol was used instead of 2-chloroethanol. A white hygroscopic solid was obtained (80% yield, m. pt. 51–52 °C). *Anal.* Found, Ti = 18.87%, Cl = 42.11%. Required for $TiCl_3(OC_2H_2F_3)$, Ti = 18.90, Cl = 42.02%. Analysis of this compound confirms the formula $TiCl_3(OC_2H_2F_3)$.

Preparation of the Complexes

The complexes of (2-chloroethoxy)trichlorotitanium(IV), $TiCl_3(OC_2H_4Cl)$ and (2,2,2-trifluoroethoxy)trichlorotitanium(IV), $TiCl_3(OC_2H_2F_3)$ were prepared by mixing their benzene solution with the benzene/chloroform/acetone solution of the ligand, when the solid precipitated out, in an exothermic reaction, either immediately on mixing or after standing overnight or by the addition of dry ether. The yield varied depending upon the ligand and it was within 60–80%.

The titanium[5] and chlorine[6] contents of the complexes were estimated as described earlier. Conductance of the complexes was measured in their 10^{-3} *M* solutions in acetonitrile or nitrobenzene by using a Toshniwal (India) Conductometer. Thermogravimetric analyses for a few of the complexes were done on a Stanton Thermorecording Balance. Infrared spectra of the complexes were recorded as nujol mulls on Perkin Elmer 337 and 621 spectrophotometers.

Results and Discussion

The compounds $TiCl_3(OC_2H_4Cl)$ and $TiCl_3(OC_2H_2F_3)$ are soluble in most of the common organic solvents. The cryoscopic data of the former in

TABLE I. Colour, Melting Points, Analyses and Conductances of (2-chloroethoxy)trichlorotitanium(IV) and (2,2,2-trifluoroethoxy)trichlorotitanium(IV) and Their Complexes.[a]

Complex	Colour	M. Pt. (°C)	Ti (%)		Cl (%)		Molar Conductance in Acetonitrile, cm^2 ohm^{-1} mol^{-1}	
			Found	Calc.	Found	Calc.	Molar Conc. × 10^3	
$TiCl_3(OC_2H_4Cl)$	Dirty white	71–72	20.45	20.47	60.21	60.71	0.97	8.9
$TiCl_3(OC_2H_4Cl)\cdot DMF$	Pale yellow	69–71	15.36	15.60	46.09	46.26	5.12	17.40
$TiCl_3(OC_2H_4Cl)\cdot DMA$	Light yellow	60–62	14.80	14.86	43.96	44.11	1.093	3.465
$TiCl_3(OC_2H_4Cl)\cdot 2DMU$	Light yellow	74–76	11.50	11.68	34.67	34.64	–	–
$TiCl_3(OC_2H_4Cl)\cdot TMU$	Yellow	113–115	13.68	13.68	40.59	40.86	3.132	7.494
$TiCl_3(OC_2H_4Cl)\cdot 2(Py\text{-}O)$	V. light yellow	72–74	11.07	11.30	32.74	33.49	–	–
$TiCl_3(OC_2H_4Cl)\cdot 2(2Pic\text{-}O)$	Light brown	55–57	10.06	10.13	31.26	31.38	0.99	26.27
$TiCl_3(OC_2H_4Cl)\cdot 2(3Pic\text{-}O)$	Light yellow	70–71	9.95	10.13	30.51	31.38	0.76	34.01
$TiCl_3(OC_2H_4Cl)\cdot 2(4Pic\text{-}O)$	Light brown	70–71	10.41	10.13	31.19	31.38	–	–
$TiCl_3(OC_2H_4Cl)\cdot TPPO$	Yellow	>290	9.96	9.35	27.90	27.70	–	–
$TiCl_3(OC_2H_4Cl)\cdot HMPA$	Yellow	232(d)	11.90	11.60	33.85	34.38	1.143	5.364
$TiCl_3(OC_2H_4Cl)\cdot 2Py$	White	90–92	11.72	12.22	36.09	36.22	–	–
$TiCl_3(OC_2H_2F_3)$	White	51–52	18.87	18.90	42.11	42.02	5.52	12.60
$TiCl_3(OC_2H_2F_3)\cdot DMF$	Yellow	56–57	14.84	14.36	32.53	32.61	4.14	28.07
$TiCl_3(OC_2H_2F_3)\cdot DMA$	Yellow	65–67	13.96	14.07	30.98	31.28	3.57	33.21
$TiCl_3(OC_2H_2F_3)\cdot 2DMU$	Yellow	86–89	11.54	11.14	24.73	24.77	–	–
$TiCl_3(OC_2H_2F_3)\cdot TMU$	Yellow	108–110	12.89	12.96	28.45	28.83	–	–
$TiCl_3(OC_2H_2F_3)\cdot 2(Py\text{-}O)$	Yellow	86–87	10.74	10.79	24.12	24.00	–	–
$TiCl_3(OC_2H_2F_3)\cdot (2Pic\text{-}O)$	Yellow	88–89	13.18	13.21	29.71	29.37	–	–
$TiCl_3(OC_2H_2F_3)\cdot (3Pic\text{-}O)$	Yellow	79–80	13.11	13.21	30.01	29.37	–	–
$TiCl_3(OC_2H_2F_3)\cdot (4Pic\text{-}O)$	Yellow	98–100	13.30	13.21	30.07	29.37	–	–
$TiCl_3(OC_2H_2F_3)\cdot TPPO$	Yellow	>300	9.02	9.01	20.31	20.04	–	–
$TiCl_3(OC_2H_2F_3)\cdot HMPA$	Yellow	224–227	11.32	11.07	24.69	24.60	–	–
$TiCl_3(OC_2H_2F_3)\cdot Py$	Dirty yellow	160(d)	14.15	14.39	32.12	32.03	–	–

[a] DMF = dimethylformamide, DMA = dimethylacetamide, DMU = dimethylurea, TMU = tetramethylurea, Py-O = Pyridine-N-oxide, 2-, 3-, 4-Pic-O = 2-, 3-, 4-picoline-N-oxide, TPPO = triphenylphosphine oxide, HMPA = hexamethylphosphoramide and Py = pyridine.

benzene (10^{-2} *M* solution) indicate that it is likely to be associated in this solvent at high concentrations (molecular wt.: found 304, 327, 341, 346; required for monomer, 233.9). The insufficient solubility of the latter in cold benzene precludes its cryoscopic study. The molar conductance values of these compounds in acetonitrile (Table I) suggest them to be predominantly covalent in nature. Infrared spectra of these compounds when compared with those of the corresponding alcohols show in $TiCl_3(OC_2H_4Cl)$ new bands at 1090 and 1015sh cm^{-1} assigned to the ν(C–O–Ti) stretch, at 610–600 cm^{-1} assigned to the ν(O–Ti) and at 485, 475 cm^{-1} for ν(Ti–Cl), while in $TiCl_3(OC_2H_2F_3)$ these bands are present at 1150, 630 and 490 cm^{-1} respectively. The position of ν(Ti–Cl) bands in these compounds compares well with that of pure titanium(IV) chloride.[7]

The reactions of $TiCl_3(OC_2H_4Cl)$ and $TiCl_3(OC_2H_2F_3)$ with some oxygen and nitrogen donors yield solid adducts and the stoichiometry of these adducts has been confirmed from their analyses (Table I). The very low solubility of these complexes in benzene or nitrobenzene precludes cryoscopic measurements. The thermogravimetric data for the complexes $TiCl_3(OC_2H_2F_3)\cdot(2Pic\text{-}O)$, $TiCl_3(OC_2H_2F_3)\cdot(3Pic\text{-}O)$, $TiCl_3(OC_2H_2F_3)$. (4Pic-O) and $TiCl_3(OC_2H_2F_3)\cdot TPPO$ suggest the following mode of decomposition:

$$TiCl_3(OC_2H_2F_3)\cdot L \rightarrow TiOCl_2 \rightarrow TiO_2$$

Infrared spectra of the complexes (Table II) is indicative of coordination of the ligands[8–15] through their oxygen atom to titanium. In the 600–200 cm^{-1} spectral region the ν(Ti–Cl) stretch is found to be present as one or more bands around 410–310 cm^{-1} and this is the region where six-coordinate titanium[16] absorbs. It is surprising that irrespective of the composition of the complexes, ν(Ti–Cl) is present at

TABLE II. Infrared Spectra (cm^{-1}) of (2-chloroethoxy)trichlorotitanium(IV) and (2,2,2-trifluoroethoxy)trichlorotitanium(IV) and Characteristic Vibrations of Their Complexes.

$TiCl_3(OC_2H_4Cl)$ (A)	1290s, 1235w, 1190s, 1090s (C–O)*, 1065sh, 1035s, 1015sh, 945s, 890m, 760m, 660s, 615m sh, 600s (O–Ti), *485vs, 475vs, 370s* (Ti–Cl).	$TiCl_3(OC_2H_2F_3)$ (B)	1270–90 Bs, 1170s, 1155–50vs (C–O)*, 1130s, 1050m, 950s, 835s, 665sh, 630vs (O–Ti), 570sh, 530m, 490vs (Ti–Cl)
A·DMF	1600vs (C=O), 115vs (O–O)*, 680, 425s, 390vs, 315s	B·DMF	1620vs (C=O)
A·DMA	1600vs (C=O), 1100vs (C–O)*.	B·DMA	1575vs (C=O), 1170vs (C–O)*, 600s
A·2DMU	1600vs (C=O), 1110vs (C–O)*, 410–420vs	B·2DMU	1575vs (C=O), 1150vs (C–O)*, 650, 425m, 370sh, 328s, 313s, 265m
A·TMU	1600vs (C=O), 1110vs (C–O)*, 410vs, 398m, 380m, 365vs, 280m	B·TMU	1570vs (C=O), 1145vs (C–O)*, 415s, 391vs, 355vs, 275m
A·2(Py-O)	1210vs (N–O), 1100vs (C–O)*, 830 (bN–O), 760 (C–H), 405m, 395vs, 360s, 270m	B·2(Py-O)	1210vs (N–O), 1150s (C–O)*, 820 (bN–O), 485, 468w, 450w, 345s
A·2(2Pic-O)	1210vs (N–O), 1110vs (C–O)*, 840 (bN–O), 765 (C–H)	B·(2Pic-O)	1205vs (N–O), 1155s (C–O)*, 850 (bN–O), 410m, 395vs
A·2(3Pic-O)	1240vs, 1135vs (N–O), 1090 (C–O)*, 810 (bN–O), 780vs (C–H), 400 m, 390vs, 380s	B·(3Pic-O)	1210vs (N–O), 1150s (C–O)*, 830 (bN–O), 390vs
A·2(4Pic-O)	1215vs (N–O), 1090s (C–O)*, 830s (bN–O), 760 (C–H)	B·(4Pic-O)	1210vs (N–O), 1150–40vs (C–O)*, 820 (bN–O), 415vs, 400m
A·TPPO	1110vs (C–O)*, 1060vs (P=O), 440s, 340s, 330vs	B·TPPO	1125vs (C–O)*, 1055vs (P=O), 445s, 350s, 340vs, 280m
A·HMPA	1150, 1110vs (C–O)*, 985 (P=O), 530s, 390vs, 355–340vs	B·HMPA	1150s (C–O)*, 1105vs, 990vs (P=O), 530m, 390m, 380s, 359m
A·2Py	*1630m, 1600vs* (C=C and C=N), 1085vs (C–O)*	B·Py	*1640m, 1600vs* (C=C and C=N), 1155–40vs (C–O)*, 430m, 410s, 385s

*ν(C–O) arising from C–O–Ti group.

nearly the same position. In the $TiCl_3(OR)\cdot 2L$ complexes, apparently the coordination number of titanium is six, but in the corresponding 1:1 complexes titanium may have coordination number five as evident from the formulae of these complexes, or six which can be acquired by dimerization either by the formation of alkoxy bridging analogous to dimeric structure with bridging alkoxy group[17,18] for the complexes having composition $SnCl_3(OR)\cdot L$ (where L = monodentate ligand) or the chlorine bridging.[19,20] The former possibility can be ruled out in the light of absence of any vibration which may be assigned to $\mathrm{Ti}\overset{\mathrm{O}}{\diagup\ \searrow}\mathrm{Ti}$ mode in these complexes. The presence of bands around 260–280 cm^{-1} in the spectra of some of the complexes lends support to the second possibility.

References

1 A. Anagnostopoulos, *Chim. Chron., 32(1),* 1 (1967).
2 H. Buerger, *Monatsch., 94,* 574 (1963).
3 R. C. Paul, P. Singh, H. S. Makhni and S. L. Chadha, *J. Less Common Metals, 17,* 437 (1969).
4 R. J. H. Clark and A. J. McAlees, *J. Chem. Soc. Dalton,* 640 (1972).
5 D. C. Bradley, D. C. Hancock and W. Wardlaw, *J. Chem. Soc.,* 2773 (1952).
6 A. I. Vogel, "A Text Book of Inorganic Quantitative Analysis", Longmans, Green, London, p. 461 (1961).
7 M. F. A. Dove, J. A. Creighton and L. A. Woodward, *Spectrochim. Acta, 18,* 267 (1962).
8 R. C. Paul and S. L. Chadha, *J. Inorg. Nucl. Chem., 31,* 1679, 2753 (1969).
9 R. C. Paul, H. S. Makhni, P. Singh and S. L. Chadha, *J. Inorg. Nucl. Chem., 32,* 108 (1970).
10 S. C. Jain and R. Rivest, *J. Inorg. Nucl. Chem., 31,* 399 (1969).
11 G. Vicentini and C. Airoldi, *J. Inorg. Nucl. Chem., 33,* 1733 (1971).
12 A. R. Katritzky and J. N. Gardner, *J. Chem. Soc.,* 2192, 2195 (1958).
13 N. M. Karayannis, A. N. Spaca, L. L. Pytlewski and M. M. Labes, *J. Less Common Metals, 22,* 117 (1970).
14 J. T. Donoghue and R. S. Drago, *Inorg. Chem., 2,* 1158 (1963).
15 J. P. Clark, V. M. Langford and C. J. Wilkins, *J. Chem. Soc. A,* 792 (1967).
16 R. J. H. Clark and W. Errington, *J. Chem. Soc. A,* 258 (1967).
17 R. C. Paul, V. Nagpal and S. L. Chadha, *Inorg. Chim. Acta, 6,* 335 (1972).
18 G. Sterr and R. Mattes, *Z. Anorg. Chem., 322,* 319 (1963).
19 C. I. Branden and I. Lindqvist, *Acta Chem. Scand., 14,* 726 (1966).
20 R. J. H. Clark and M. A. Coles, *J. Chem. Soc. Dalton,* 1463 (1974).