

Complexes of Alkoxy- & Dialkoxy-titanium(IV) Chlorides with Some Bidentate Ligands

R. C. PAUL, P. K. GUPTA, (Miss) KANWALJEET BINDRA & S. L. CHADHA

Department of Chemistry, Panjab University, Chandigarh 160014

Received 24 December 1975; accepted 17 February 1976

1:1 complexes of phthalimide and succinimide and 1:2 complexes of α,α' -dipyridyl and its dioxide and 1,10-phenanthroline with alkoxytitanium(IV) trichloride (where $R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_2\text{H}_4\text{Cl}$ and $\text{C}_2\text{H}_2\text{F}_3$) along with 1:1 complexes of phthalimide and succinimide with dimethoxytitanium(IV) dichloride have been prepared. These complexes have been characterized on the basis of analytical and infrared spectral data. It is presumed that Ti(IV) in these complexes acquires six-coordination by chloride bridging.

THE complexes of bidentate nitrogen ligands with titanium(IV) halides have been extensively prepared and studied. However, not much work has been reported on the complexes of bidentate oxygen ligands with titanium(IV) halides. There are only two references pertaining to the complexes with imides^{1,2}. Complexes with α,α' -dipyridyl-N,N'-dioxide do not seem to have been prepared. Only a few complexes of bidentate oxygen or nitrogen ligands with titanium halo- and halide alkoxides have been reported, e.g. complex of hydrazine with trialkoxy titanium(IV) monochloride³ and of ethylenediamine with dialkoxytitanium(IV) dichlorides⁴. The complexes of some of these ligands with alkoxyantimony(V) tetrachlorides⁵ and alkoxytin(IV) trichlorides^{6,7} have been reported only recently from our laboratory. The present study reports the preparation and characterization of new complexes of phthalimide, succinimide, α,α' -dipyridyl and its dioxide and of 1,10-phenanthroline with alkoxy- and dialkoxytitanium(IV) chlorides.

Materials and Methods

Anhydrous 1,10-phenanthroline was obtained by keeping monohydrate over conc. sulphuric acid in a desiccator for twenty days. The alkoxides, $\text{Ti}(\text{OR})\text{Cl}_3$ (where $R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_2\text{H}_4\text{Cl}$ and $\text{C}_2\text{H}_2\text{F}_3$) were prepared by refluxing an equimolar mixtures of the alcohol and titanium(IV) chloride in benzene till the evolution of hydrogen chloride gas ceased. The solid obtained on cooling was washed, recrystallized from dry benzene and dried in vacuum. The purity of these compounds was confirmed by analysis, m.p. and IR spectra. $\text{Ti}(\text{OCH}_3)_3\text{Cl}_3$: m.p. $95^\circ(\text{d})$ [reported⁸ m.p. $96^\circ(\text{d})$]; $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}_3$: m.p. $79-80^\circ$ (reported⁸ m.p. $80-81^\circ$); $\text{Ti}(\text{OC}_2\text{H}_4\text{Cl})_3\text{Cl}_3$: m.p. $71-72^\circ$ (reported⁹ m.p. $71-72^\circ$); $\text{Ti}(\text{OC}_2\text{H}_2\text{F}_3)_3\text{Cl}_3$: m.p. $51-52^\circ$ (reported⁹ m.p. $51-52^\circ$). For the preparation of the dialkoxides, $\text{Ti}(\text{OR})_2\text{Cl}_2$ (ref. 10), the proportion of the alcohol and titanium(IV) chloride was 2:1.

α,α' -Dipyridyl-N,N'-dioxide was prepared by the method of Quagliano¹¹ and its purity was checked by its melting point.

The complexes of alkoxytitanium(IV) trichloride and dialkoxytitanium(IV) dichloride with phthalimide and succinimide were prepared by stirring for about 6 hr solutions of the alkoxide in benzene/alcohol and a suspension of phthalimide or succinimide in chloroform or methylene chloride or their solutions in alcohol. The complexes with α,α' -dipyridyl and 1,10-phenanthroline were prepared by mixing the solutions of the two ligands in benzene/chloroform, whereas the complexes of α,α' -dipyridyl-N,N'-dioxide were prepared by refluxing solutions of alkoxide in benzene/chloroform and a suspension of the ligand in chloroform. Solid products which separated out, were filtered under dry conditions, repeatedly washed with alcohol, benzene and ether and dried under vacuum.

Titanium was estimated gravimetrically as titanium dioxide¹² and chlorine as silver chloride¹³. Infrared spectra of the complexes were examined on Perkin-Elmer 337 and 621 spectrophotometers.

Results and Discussion

While solid adducts of phthalimide and succinimide were obtained with $\text{Ti}(\text{OR})\text{Cl}_3$ ($R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_2\text{H}_4\text{Cl}$) and $(\text{OCH}_3)_2\text{TiCl}_2$, no adducts were obtained when these ligands were treated with $\text{Ti}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$, $\text{Ti}(\text{OC}_2\text{H}_4\text{Cl})_2\text{Cl}_2$ and $\text{Ti}(\text{OC}_2\text{H}_2\text{F}_3)_2\text{Cl}_2$ (Table 1). Phthalimide and succinimide adducts are of 1:1 stoichiometry whereas those of α,α' -dipyridyl and its dioxide and 1,10-phenanthroline are of 2:1 stoichiometry (alkoxide:ligand). These complexes are slightly hygroscopic and some of them tend to polymerize on keeping for long time even in sealed tubes. The complexes are insoluble in most of the common organic solvents, which precludes conductance and cryoscopic measurements.

In its IR spectrum succinimide shows two bands at 1770 and 1695 cm^{-1} due to $\nu\text{C}=\text{O}$. In the spectra of the complexes with $\text{Ti}(\text{OR})\text{Cl}_3$ only band at 1695 cm^{-1} shifts to lower frequency (1650 cm^{-1}). In the adduct with $\text{Ti}(\text{OCH}_3)_2\text{Cl}_2$ the band at 1770 cm^{-1} also shifts to lower frequency region (1680 cm^{-1}). Both the $\nu\text{C}=\text{O}$ of phthalimide at 1770 and 1740 cm^{-1} are shifted to lower frequency region and appear at 1640 and 1550 in its various adducts.

TABLE 1 — COLOUR, MELTING POINTS AND ANALYSES OF THE COMPLEXES OF ALKOXYTITANIUM(IV) TRICHLORIDE AND DIALKOXYTITANIUM(IV) DICHLORIDE

Complex*	Colour	m.p. (°C)	Ti (%)		Cl (%)	
			Found	Calc.	Found	Calc.
TiCl ₃ (OCH ₃).D ₁	Light yellow	160 (d)	14.0	14.4	31.2	32.0
TiCl ₃ (OC ₂ H ₅).D ₁	White	140-42	14.0	13.8	31.2	30.7
TiCl ₃ (OC ₂ H ₄ Cl).D ₁	do	165-68	12.2	12.6	36.4	37.3
TiCl ₃ (OCH ₃) ₂ .D ₁	do	>290	—	—	20.9	21.6
TiCl ₃ (OCH ₃) ₂ .D ₂	do	130-32	17.3	16.8	36.9	37.4
TiCl ₃ (OC ₂ H ₅).D ₂	do	70-73	15.7	16.0	35.7	35.6
TiCl ₃ (OC ₂ H ₄ Cl).D ₂	do	83-85	14.2	14.4	42.2	42.7
TiCl ₃ (OCH ₃) ₂ .D ₂	do	115-18	16.5	17.2	24.8	25.3
2TiCl ₃ (OCH ₃).D ₃	do	>300	18.2	17.1	37.6	38.1
2TiCl ₃ (OC ₂ H ₅).D ₃	do	>300	16.2	16.3	36.9	37.2
2TiCl ₃ (OC ₂ H ₄ Cl).D ₃	Light yellow	240 (d)	14.2	14.6	41.1	43.3
2TiCl ₃ (OCH ₃) ₂ .D ₃	White	>290	17.6	17.4	24.9	25.8
2TiCl ₃ (OCH ₃).D ₄	do	>290	17.9	18.1	40.0	40.4
2TiCl ₃ (OC ₂ H ₅).D ₄	Yellow	>290	18.2	17.3	37.9	38.3
2TiCl ₃ (OC ₂ H ₄ Cl).D ₄	Light yellow	235-237	15.1	15.4	43.9	45.4
2TiCl ₃ (OC ₂ H ₂ F ₃).D ₄	Dirty white	185-187	14.4	14.6	32.1	32.0
2TiCl ₃ (OCH ₃).D ₅	White	>290	17.0	17.4	38.0	38.6
2TiCl ₃ (OC ₂ H ₅).D ₅	Yellow	>290	16.1	16.5	35.9	36.8
2TiCl ₃ (OC ₂ H ₄ Cl).D ₅	do	240 (d)	14.3	14.4	40.6	42.6
2TiCl ₃ (OC ₂ H ₂ F ₃).D ₅	Light yellow	169-170 (d)	14.2	14.1	30.8	30.7

*D₁ = phthalimide; D₂ = succinimide; D₃ = α, α' -dipyridyl-N,N'-dioxide; D₄ = α, α' -dipyridyl; D₅ = 1,10-phenanthroline.

This indicates that in these adducts phthalimide is possibly functioning as of a bidentate ligand, coordinating through both carbonyl oxygen atoms with the central metal ion.

In α, α' -dipyridyl-N,N'-dioxide the two bands at 1264 and 1252 cm⁻¹ assigned to the ν N-O shift to lower frequencies and appear \sim 1255 and \sim 1220 cm⁻¹ in its various adducts. This is in keeping with its coordination through both of its oxygen atoms^{11,14} with Ti(IV). Infrared spectra of the complexes of α, α' -dipyridyl and 1,10-phenanthroline show usual features of their being coordinated to titanium¹⁵⁻¹⁷. For instance the ν C...C and ν C...N of the pure ligands appearing \sim 1580 and 1560 cm⁻¹ respectively are shifted to higher frequency region (\sim 1605 and 1580 cm⁻¹ respectively) in their adducts.

The ν (C—O) arising from the ν (Ti—O—C) (R) vibration is present around 1085-1100 cm⁻¹ in the spectra of these complexes.

The empirical formula suggests a penta-coordination for titanium in these complexes except for those of phthalimide where the IR spectra, suggest that titanium acquires six-coordination. The position of ν Ti—Cl stretching frequencies for the complexes [at 390, 360, 270 cm⁻¹ in 2TiCl₃(OC₂H₅)- α, α' -dipyridyl; at 540, 390, 320, 330 in 2TiCl₃(OC₂H₄Cl)- α, α' -dipyridyl; at 538, 451*, 390, 379, 360, 320 in 2TiCl₃(OC₂H₂F₃)- α, α' -dipyridyl; at 430*, 380, 365, 345 in 2TiCl₃(OC₂H₄Cl)-1,10-phenanthroline; and at 440*, 400 (sh), 385, 365 cm⁻¹ in 2TiCl₃(OC₂H₂F₃)-1,10-phenanthroline] are close to those reported for six-coordinated titanium. Thus, there is a likelihood that in these complexes, titanium acquires hexa-coordination either by alkoxy bridging or by chloride bridging. The former possibility exists in some pure alkoxides¹⁸⁻²⁰ and their adducts^{6,7,12} but seems unlikely in the present cases as no band could be assigned with certainty to Ti—O→Ti in these complexes. Analogous to the

complex, TiCl₄.POCl₃ (ref. 21) and others²², these complexes may have chloride bridge which is known to absorb around 260-280 cm⁻¹ and amongst the present complexes, the complex formulated as [Ti(OC₂H₅)Cl₃]₂.1,10-phenanthroline shows the presence of a medium intensity band at 270 cm⁻¹.

References

- PAUL, R. C. & CHADHA, S. L., *J. inorg. nucl. Chem.*, **31** (1969), 1679, 2753.
- JAIN, S. C. & RIVEST, R., *J. inorg. nucl. Chem.*, **31** (1969), 399.
- BUERGER, H., *Mh. Chem.*, **94** (1963), 574.
- PAUL, R. C., SINGH, P., MAKHINI, H. S. & CHADHA, S. L., *J. less common Metals*, **17** (1969), 437.
- PAUL, R. C., MADAN, H. & CHADHA, S. L., *J. inorg. nucl. Chem.*, **36** (1974), 737; **37** (1975), 447.
- PAUL, R. C., SINGH, P., MAKHINI, H. S. & CHADHA, S. L., *J. inorg. nucl. Chem.*, **32** (1970), 2142; *Z. anorg. Chem.*, **377** (1970), 108.
- PAUL, R. C., NAGPAL, V. & CHADHA, S. L., *Inorg. chim. Acta*, **6** (1972), 335.
- CLARK, R. J. H., *The chemistry of titanium and vanadium* (Elsevier, London), 1968, 301.
- PAUL, R. C., SHARMA, P., GUPTA, P. K. & CHADHA, S. L., *Inorg. chim. Acta* (in press).
- JENNINGS, J. S., WARDLAW, W. & WAY, W. J. R., *J. chem. Soc.*, (1936), 637.
- VINCIGUERRA, A., SIMPSON, P. G., KAKIUTI, Y. & QUAGLIANO, J. V., *Inorg. Chem.*, **2** (1963), 286.
- BRADLEY, D. C., HANCOCK, D. C. & WARDLAW, W., *J. chem. Soc.*, (1952), 2773.
- VOGEL, A. I., *A text book of inorganic quantitative analysis* (Longmans Green, London), 1961, 461.
- AHUJA, I. S. & SINGH, R., *Spectrochim. Acta*, **30A** (1974), 2055.
- DORETTI, L., SITRAM, S., ZANELLA, P. & FARAGLIA, G., *J. inorg. nucl. Chem. Lett.*, **9** (1973), 7.
- VULETIC, N. & DJORDJEVIC, C., *J. chem. Soc. Dalton*, (1973), 551.
- CLARK, R. J. H., *J. chem. Soc.*, (1963), 763.
- PREISS, H., *Z. anorg. Chem.*, **362** (1968), 24.
- STERR, G. & MATTES, R., *Z. anorg. Chem.*, **322** (1963), 319.
- HOPPE, H. & HAASE, W., *Acta Cryst.*, **B24** (1968), 281.
- BRANDEN, C. I. & LINDQVIST, I., *Acta chem. scand.*, **14** (1966), 726.
- CLARK, R. J. H. & COLES, M. A., *J. chem. Soc. Dalton*, (1974), 1463.