510. *Amine Compounds of the Transition Metals. Part VI.*[1] *The Reaction of Titanium*(IV) *Chloride with Some Aliphatic Amines.*

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The reactions of titanium(IV) chloride with several primary and secondary aliphatic amines have been examined. The titanium–chlorine bonds are solvolysed in every case, but whereas two chlorine atoms are replaced in reactions with the primary amines only one is replaced with secondary amines. The following compounds have been isolated: $TiCl_2(NHR)_2$ where R = Me, Et, and Pr^n, and $TiCl_3(NR_2)$ where R = Me and Et.

Much evidence is available[2,3] to show that the solvolytic reactions of covalent metal halides proceed by the initial co-ordination of a molecule of solvent (ammonia or amine), followed by the base-catalysed elimination of hydrogen halide. Thus in the reactions of ammonia with titanium(IV) chloride, bromide, and iodide, simple adducts can be isolated by passing diluted ammonia vapour through a solution of the halide, although with excess of ammonia (gaseous or liquid) ammonolysis takes place and up to three halogen atoms can be replaced by amide residues. As this replacement progresses, so the remaining titanium–halogen bonds become increasingly resistant to ammonolysis because of an increase in their ionic character, and even on reaction with liquid ammonia at room temperature only three of the titanium–chlorine bonds in titanium(IV) chloride can be ammonolysed.

We have now examined in some detail the reaction of titanium(IV) chloride with three primary aliphatic amines (methyl-, ethyl-, and n-propyl-amine) and two secondary aliphatic amines (dimethyl- and diethyl-amine). The primary amines are poorer ionising solvents than ammonia, but stronger than the secondary amines, so that we might expect decreasing solvolysis along the series NH_3, NH_2R, NHR_2; it is also possible that with a series of primary or secondary amines the extent of solvolysis might decrease as the alkyl group becomes larger. We have in fact found that solvolysis is greater with primary than with secondary amines, but that it is not dependent on the size of the alkyl group over the limited range that we have studied.

All three primary aliphatic amines force the solvolysis of two of the four titanium–chlorine bonds, and orange aminobasic titanium(IV) chlorides, $TiCl_2(NHR)_2$, are formed; these can be separated from the amine hydrochloride, which is formed at the same time, because they are insoluble in the parent amine. It is noteworthy that the methylamine compound has four mols. of methylamine fairly strongly associated with it, whereas the ethylamine and the n-propylamine compound do not hold any significant amounts of amine. The titanium atom is normally considered to have a covalency maximum of six,[4] but this would have to be increased to eight if the four mols. of methylamine were co-ordinated to the titanium atom. Such a high co-ordination is possible electronically, and may be reasonable sterically with the fairly small methylamine molecule, but it must be emphasised that in solid compounds the co-ordination number does not follow from the stoicheiometry alone, and that some amine might be held in the solid lattice. Although two mols. of methylamine are lost *in vacuo* at 40°, the other two remain firmly attached up to 60—70°, and it is probable that in $TiCl_2(NHMe)_2,2NH_2Me$ the methylamine is co-ordinated directly to the titanium atom, giving it an octahedral configuration (d^2sp^3). It is probable that although ethylamine is a stronger base than methylamine,[5] its greater steric requirements prevent co-ordination to the aminobasic titanium(IV) chloride to any great extent.

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[1] Part V, Drake and Fowles, *J.*, 1960, 1498.
[2] Fowles and Pollard, *J.*, 1953, 2588; Fowles and Nicholls, *J.*, 1959, 990.
[3] Fowles and Pleass, *J.*, 1957, 1674.
[4] Sidgwick, "Chemical Elements and Their Compounds," Oxford, 1950.
[5] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

Under more forcing conditions methylamine effected almost complete replacement of the third chlorine atom, but with ethylamine there was only about 60% replacement, which is consistent with the poorer ionising properties of the higher amine. The final methylamine product contained only two nitrogen atoms for each titanium atom, so it appears that, although the third titanium–chlorine bond is solvolysed, the product $TiCl(NHMe)_3$ loses methylamine at 40° *in vacuo* and forms the compound $TiCl(\colon NMe)(NHMe)$.

The only previous work on the titanium(IV) chloride–methylamine system was done by Antler and Laubengayer,[6] who mixed the reactants in the vapour phase and obtained an orange-red product with an overall composition reasonably close to $TiCl_4,4NH_2Me$. Although these workers were unable to effect any separation, it is highly likely that their product was also a mixture of aminolytic products.

Trost [7] examined the reaction of titanium(IV) chloride with ethylamine, but he did his experiments with diethyl ether solutions, and isolated a product with composition $TiCl_{3\cdot64}(NH_2Et)_{4\cdot07}$. He also obtained a " tetra-aminate " from the titanium(IV) chloride–triethylamine reaction,[8] and considered this product to be a simple adduct, because the obvious alternatives are so much less attractive; $[Ti(NEt_3)_4]Cl_4$ necessitates a tetrapositive titanium ion, and the solvolytic mixture, $TiCl_2(NEt_2)_2 + 2NEt_4Cl$, requires the breaking of strong nitrogen–carbon bonds and the insolubility of both components of the mixture. The objections to the formulation of the ethylamine product as an aminolytic mixture such as $TiCl_3(NHEt),2NH_2Et + NH_2Et,HCl$ do not apply, however, and Trost's thermal decomposition studies support this suggestion. Thus, at 140° *in vacuo,* the product lost 0·7 mol. of ethylamine and 1·3 mol. of ethylamine hydrochloride; this is in agreement with the sublimation of the ethylamine hydrochloride from the mixture, and the simultaneous liberation of ethylamine and hydrogen chloride, the latter arising from an internal degradation. Decompositions similar to this have been observed with the ammonobasic tungsten(IV) chlorides.[9]

From the analogous reaction of titanium(IV) bromide with n-butylamine in ether, Prasad and Tripathi [10] claim to have obtained a " tetra-aminate," and consider it to contain a tetrapositive titanium ion to which are co-ordinated four molecules of n-butylamine. It is much more likely that this substance is an aminolytic mixture such as $TiBr_3(NHBu^n),2NH_2Bu^n + NH_2Bu^n,HBr$, because n-butylamine hydrobromide is insoluble in diethyl ether, and by analogy with other aminobasic titanium(IV) halides we should also expect $TiBr_3(NHBu^n),2NH_2Bu^n$ to be insoluble.

As we might expect from their poorer ionising properties, the secondary amines produce less solvolysis, and with both dimethyl- and diethyl-amine only one chlorine atom is replaced by an amine residue. Thus the heterogeneous brown product formed in the titanium(IV) chloride–dimethylamine reaction, which has the overall composition $TiCl_4,4NHMe_2$, has been shown to be the mixture $TiCl_3(NMe_2),2NHMe_2 + NHMe_2,HCl$, by extracting the aminobasic titanium(IV) chloride with benzene. It was found, however, that the benzene-soluble product had the composition $Ti : Cl : N = 1\cdot0 : 3\cdot0 : 2\cdot3$, showing that on prolonged evacuation both before and after the benzene-extraction the product slowly lost its co-ordinated amine. The two mols. of co-ordinated amine were completely lost on heating *in vacuo.* Diethylamine is held less readily to $TiCl_3(NEt_2)$, which is presumably a reflection of the larger steric volume associated with the ethyl groups both in the ligand and in the diethylamino-groups.

Prasad and Tripathi have obtained " tetra-aminates " from the reaction of titanium(IV) with both dimethylamine and diethylamine in diethyl ether, and they again assign an ionic structure to the products. These compounds are likely to be aminolytic mixtures. A

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[6] Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

[7] Trost, *Canad. J. Chem.*, 1952, **30**, 842.

[8] Trost, *Canad. J. Chem.*, 1952, **30**, 835.

[9] Fowles and Osborne, *J.*, 1959, 2275.

[10] Prasad and Tripathi, *J. Indian Chem. Soc.*, 1957, **34**, 749.

similar explanation is probable for the heterogeneous material (overall analysis gave Ti : Cl : N = 1·00 : 3·90 : 2·75) obtained by Antler and Laubengayer from the gas-phase reaction of titanium(IV) chloride with dimethylamine.

More recently, it has been reported [11] that when titanium(IV) chloride is refluxed with the lithium salt, $Li{\cdot}NMe_2$, in light petroleum, complete replacement of the chlorine atoms can be achieved; this shows that, although only one chlorine atom is replaced in liquid dimethylamine, yet complete replacement takes place when the more strongly nucleophilic negative ion is used.

When titanium(IV) chloride and liquid dimethylamine have reacted for some months, the product contains an appreciable amount of tervalent titanium. It is known [12] that titanium(III) chloride dissolves in dimethylamine to give a green solution from which the compound $TiCl_3,3NHMe_2$ can be obtained, and it seems from our analysis that the same compound may be slowly formed in the titanium(IV) chloride–dimethylamine reaction.

EXPERIMENTAL

Materials.—Titanium(IV) chloride was purified by refluxing with finely divided copper to remove traces of iron(III) chloride and vanadium(IV) chloride, and then distilled *in vacuo* (Found: Ti, 25·2; Cl, 74·7. Calc. for $TiCl_4$: Ti, 25·25; Cl, 74·75%). The pure anhydrous amines were obtained from the commercially available materials as described previously.[3, 13]

Analysis.—The products were dissolved in ~2N-sulphuric acid, and aliquot parts taken for analysis; products obtained by extraction with benzene adhered firmly to the walls of the reaction vessel in a thin film, and were dissolved *in situ* so that only ratios are quoted in their analysis. Titanium, nitrogen, and chlorine were estimated as previously described.

Magnetic-susceptibility Measurements.—These were made at room temperature on a Gouy-type balance at a field strength of 8000 gauss.

Reactions.—These were studied under completely anhydrous conditions in the usual type of all-glass closed vacuum system.[3] The usual two procedures (weighed bulb and ampoule) were adopted. All products appeared to be mixtures of aminolytic products, and they were extracted either with the pure amine or with various organic solvents, so that the aminobasic titanium(IV) chlorides could be separated from the appropriate amine hydrochloride.

Reaction between Titanium(IV) *Chloride and Methylamine.*—Dense white fumes were produced in the reaction, and a red solid and a pale-green solution were formed. This red solid gradually became orange, and after 24 hr. it had formed crystals of up to 3 mm. in length. On removal of excess of methylamine the solid remaining had the overall composition $TiCl_4,8NH_2Me$ (Found: $TiCl_4 : NH_2Me$ = 1·00 : 8·01). The orange crystals were filtered off *in vacuo*, and washed with pure anhydrous methylamine. This substance, which was diamagnetic, was analysed after it had been heated *in vacuo*, with the results shown in Table 1. The soluble portion contained very little titanium, a typical analysis of the residue remaining after removal of excess of amine giving Ti : Cl : N = 1·0 : 31·8 : 34·0.

TABLE 1. *Insoluble product of the* $TiCl_4$–NH_2Me *reaction.*

Run No.	Analysis (%)			Ratios Ti : Cl : N	No. of washes	Temp.	Evacn. (hr.)	Colour
	Ti	Cl	N					
1	16·3	23·0	27·1	1·00 : 1·91 : 5·70	5	20°	1·5	Orange
2	17·1	23·8	27·1	1·00 : 1·90 : 5·30	4	20	4	Orange
3	19·4	27·8	23·1	1·00 : 1·93 : 4·07	8	40	12	Red
4	19·8	34·3	20·9	1·00 : 2·30 : 3·60	5	60	10	Red
5	27·0	36·1	17·3	1·00 : 1·81 : 2·19	10	75	10	Maroon
6	26·6	38·3	15·8	1·00 : 1·95 : 2·03	10	95	10	Maroon
7	28·6	38·8	12·7	1·00 : 1·83 : 1·52	6	150	3	Maroon
8	39·6	36·5	8·3	1·00 : 1·25 : 0·72	6	200	6	Dark brown
9	44·8	—	—	— — —	6	400	10	Black *

* This crystalline product was insoluble in concentrated sulphuric, nitric, and hydrochloric acid, and in sodium hydroxide solution. The titanium content was determined as TiO_2 by heating the sample in air for 6 hr. at 800°.

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[11] Bradley and Thomas, *Proc. Chem. Soc.*, 1959, 225.

[12] Cowdell and Fowles, unpublished work.

[13] Carnell and Fowles, *J.*, 1959, 4113.

Further experiments were made in an attempt to effect a greater replacement of the chlorine atoms. The compound $TiCl_2(NHMe)_2,2NH_2Me$ was repeatedly washed with fresh methylamine with evacuation between washes, and after some 7 treatments, with evacuation for a total of 18 hr. at 40°, the product had the composition Ti : Cl : N = 1·00 : 1·12 : 2·10. In other experiments, the compound was sealed in an ampoule with methylamine, and after continuous shaking for 6 hr. the ampoule was opened and the insoluble residue filtered off and washed with methylamine; the final product had the composition Ti : Cl : N = 1·00 : 1·01 : 2·19.

Reaction between Titanium(IV) *Chloride and Ethylamine.*—This reaction closely resembled the preceding one, except that the overall composition of the mixture was now about $TiCl_4,5NH_2Et$; the exact amount of amine varied with the time of pumping. Analysis of the insoluble diamagnetic orange product gave the results shown in Table 2.

TABLE 2. *Insoluble product of the* $TiCl_4$–NH_2Et *reaction.*

Run No.	Analysis (%) Ti	Cl	N	Ratios Ti : Cl : N	No. of washes	Temp.	Evacn. (hr.)	Colour
1	21·4	27·8	17·6	1·00 : 1·80 : 2·80	6	20°	12	Red
2	22·9	30·5	14·7	1·00 : 1·80 : 2·19	6	40	12	Red
3	24·0	32·7	13·4	1·00 : 1·84 : 1·91	6	60	5	Red

An attempt was made to replace the third chlorine atom, by shaking portions of the product from run no. 3 with fresh ethylamine at 40° for 10—15 hr. in an ampoule. The insoluble residue in the ampoule was isolated in the usual way and analysed [Found: Ti, 25·6; Cl, 26·5; N, 15·1% (Ti : Cl : N = 1·00 : 1·40 : 2·01), and Ti, 24·9; Cl, 26·2; N, 15·6% (Ti : Cl : N = 1·00 : 1·42 : 2·14)]. As the substance was slightly soluble in ethylamine, the experiment had to be stopped while there was still sufficient material for analysis, and so could not be extended.

Reaction between Titanium(IV) *Chloride and n-Propylamine.*—The compositions of the diamagnetic solids obtained by the filtration of the contents of the ampoules are given in Table 3.

TABLE 3. *Insoluble product of the* $TiCl_4$–NH_2Pr^n reaction.

Run No.	Analysis (%) Ti	Cl	N	Ratios Ti : Cl : N	No. of washes	Temp.	Evacn. (hr.)	Colour
1	10·8	14·9	17·6	1·00 : 1·87 : 5·60	5	20°	2·5	Yellow-orange
2	18·6	24·7	13·5	1·00 : 1·80 : 2·49	5	40	12	Orange-pink
3	19·0	27·0	13·2	1·00 : 1·92 : 2·38	4	60	5	Deep orange
4	21·1	27·9	12·4	1·00 : 1·78 : 2·01	4	100	5	Orange-brown

Reaction between Titanium(IV) *Chloride and Dimethylamine.*—The initial product was a clear red-brown liquid from which a heterogeneous brown solid was obtained on removal of excess of amine (Found: $TiCl_4$: $NHMe_2$ = 1·00 : 3·94). When this compound was heated *in vacuo*, dimethylamine was steadily lost until by 200° two mols. of amine had been lost (Found, for the residue: $TiCl_4$: $NHMe_2$ = 1·00 : 1·98). The small amount of white sublimate formed is considered as part of the residue, so far as the overall composition is concerned. Above 200° a general decomposition set in with the formation of a black residue and a substantial white sublimate.

Part of the product dissolved in benzene to a yellowish-green solution, from which a brown residue was obtained by evaporation. Analytical figures for this residue are given in Table 4.

TABLE 4. *Benzene-soluble product of the* $TiCl_4$–$NHMe_2$ *reaction.*

Run No.	Ratios Ti : Cl : N	Time for which the mixture was pumped at 20° before benzene-extraction (hr.)
1	1·00 : 3·15 : 2·39	4
2	1·00 : 2·94 : 2·35	7
3	1·00 : 3·01 : 2·24	12

After reaction for several months the solution (main reaction) became lime-green, although the removal of excess of amine left an orange solid with composition Ti, 15·2; Cl, 39·3; N, 14·3%, corresponding to Ti : Cl : N = 1·00 : 3·50 : 3·21. This solid was somewhat paramagnetic ($\chi_M = 54·6 \times 10^{-6}$) and dissolved in sulphuric acid to give a mauve solution.

TABLE 5. *Products of the* $TiCl_4$–$NHEt_2$ *reaction.*

	Ratios (Ti : Cl : N)		Conditions of pumping the reaction mixture	
Run No.	Mixture	Benzene-soluble product	Temp.	Time (hr.)
1	1·00 : 3·86 : 2·85	—	40°	2
2	1·00 : 3·90 : 2·69	—	20	5
3	1·00 : 3·92 : 2·43	—	20	12
4	—	1·00 : 3·05 : 1·87	20	13
5	—	1·00 : 3·02 : 1·82	20	15
6	—	1·00 : 2·96 : 1·64	20	19

Reaction between Titanium(IV) *Chloride and Diethylamine.*—After a vigorous initial reaction with the formation of white fumes, an orange solid and a red-brown solution were formed. After excess of diethylamine had been removed *in vacuo* a diamagnetic red-brown solid was obtained by extraction of the residue with benzene. The nitrogen content both of this benzene-soluble portion and of the whole reaction mixture depended on the length of time for which the products were kept *in vacuo* (cf. Table 5).

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