825. *Amine Compounds of the Transition Elements. Part IV.* The Reaction of Tantalum*(V) *Chloride with Some Aliphatic Amines.*

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The reaction of tantalum(V) chloride with a number of primary, secondary, and tertiary aliphatic amines has been studied. With methylamine and ethylamine, basic aminotantalum(V) chlorides $TaCl_3(NHR)_2,3NH_2R$ are thought to be formed. Reaction with n-propylamine and n-butylamine gives compounds $TaCl_3(NHR)_2,NH_2R$, and with dimethylamine, diethylamine, and di-n-propylamine gives analogues $TaCl_3(NR_2)_2,NHR_2$; these compounds have been extracted from the reaction mixture with benzene. Trimethylamine and triethylamine form simple adducts, $TaCl_5,2NMe_3$ and $TaCl_5,NEt_3$, respectively.

The probable reaction mechanisms and the structures of the products are discussed.

Recent investigations have shown that covalent transition metal halides undergo solvolysis when they react with liquid ammonia,[1] or with primary and secondary aliphatic amines.[2] With any specific halide, the degree of solvolysis decreases along the series NH_3,

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* Part III, Fowles and McGregor, *J.*, 1958, 136.

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

[2] Fowles and Pleass, *J.*, 1957, 2078.

NH_2R, NHR_2, and the products become increasingly soluble in organic solvents. Simple addition compounds are normally formed between the halide and tertiary amines, although prolonged interaction often results in reduction of the metal to a lower valency state.[3] While the reactions of vanadium(IV) chloride [3,4] and niobium(V) chloride [2,5] with ammonia, methylamine, dimethylamine, and trimethylamine have been examined, only the ammonolysis of tantalum(V) chloride has been studied in any detail. Lindner and Feit [6] made a brief study of the reactions of tantalum(V) chloride with several aldehydes and with one or two aromatic amines, although unfortunately they often used tantalum(V) chloride in ethanolic or acetone solution so that an enormous amount of solvolysis had occurred before reaction with the amines; these workers did not study reactions with aliphatic amines. We have accordingly extended our investigations to a fairly detailed study of the reaction of tantalum(V) chloride with primary (NH_2Me, NH_2Et, NH_2Pr^n, NH_2Bu^n), secondary ($NHMe_2$, $NHEt_2$, $NHPr_2{}^n$), and tertiary (NMe_3, NEt_3) amines. Analogous reactions of tantalum(V) bromide have been examined briefly.

EXPERIMENTAL

Materials.—Tantalum(V) chloride was prepared by passing dry gaseous chlorine over powdered tantalum metal (99·9% pure) at 300°, and purified by sublimation (Found: Cl, 48·8; Ta, 50·9. Calc. for $TaCl_5$: Cl, 49·5; Ta, 50·5%). Tantalum(V) bromide was made by the analogous reaction of bromine vapour with tantalum in an atmosphere of nitrogen (Found: Br, 68·5; Ta, 31·7. Calc. for $TaBr_5$: Br, 68·85; Ta, 31·15%). Methylamine, dimethylamine, and trimethylamine were purified as previously described.[3] Higher amines, of the best available purity, were dried by distilling them several times *in vacuo* from freshly crushed barium oxide.

Analysis.—The products were normally dissolved in anhydrous ethanol and aliquot parts taken for analysis, since aqueous solutions usually deposited part of the tantalum as insoluble hydrated tantalum(V) oxide. Many products adhered firmly to the sides of the vessel, and in such cases they were dissolved *in situ*, so that only ratios are quoted. Tantalum was determined by precipitation as hydrated oxide with tannin, followed by ignition to the oxide.[7] Nitrogen and chlorine were determined as described previously.[8] Bromine was determined by potentiometric titration with silver nitrate solution.

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

Molecular Weights.—These were measured at 20° by a modified form of the isoteniscope method.[9]

General.—Reactions were studied under completely anhydrous conditions in the usual type of all-glass closed vacuum system.[3,10] In preliminary experiments, amine was condensed on to a known weight of the halide and after reaction for several hours at room temperature the excess of amine was removed *in vacuo* at various temperatures. Experiments were also made in which the reactants were sealed in ampoules, sometimes in the presence of a solvent such as benzene, and the products were obtained by pumping off the excess of amine; where the products might be mixtures of the amine hydrochloride and a basic aminotantalum(V) chloride, separations were attempted by treatment with various solvents.

Reaction of Tantalum(V) *Chloride with Tertiary Aliphatic Amines.*—When sealed in ampoules, tantalum(V) chloride and trimethylamine reacted to give a flesh-coloured solid and a colourless solution. Evaporation of the excess of amine left a solid of composition Ta : Cl : N = 1·00 : 4·81 : 1·94. This product, which was diamagnetic, was insoluble in both trimethylamine

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[3] Fowles and Pleass, *J.*, 1957, 1674.

[4] Fowles and Nicholls, *J.*, 1959, 990.

[5] Fowles and Pollard, *J.*, 1952, 4938.

[6] Lindner and Feit, *Z. anorg. Chem.*, 1923, **132**, 10.

[7] Hillebrand, Lundell, Bright, and Hoffman, " Applied Inorganic Analysis," Wiley, 2nd edn., New York, 1953.

[8] Bannister and Fowles, *J.*, 1958, 751.

[9] Weissberger, " Physical Methods of Organic Chemistry," Vol. I, Part 1, Interscience, New York, 1949, p. 173.

[10] Fowles and Pollard, *J.*, 1953, 2588.

and benzene. In the analogous reaction with triethylamine, tantalum(v) chloride formed a brown solid (Found: Ta : Cl : N = 1·00 : 4·93 : 0·99).

Reaction of Tantalum(v) *Chloride with Secondary Aliphatic Amines.*—Tantalum(v) chloride dissolved in dimethylamine to give an orange solution and a small quantity of white crystals. After excess of amine had been pumped away at 40°, an orange powder remained (Found: Ta : Cl : N = 1·00 : 4·96 : 4·98 and 1·00 : 4·93 : 4·82). When this solid was treated with benzene, an orange solution was formed, leaving a white residue; evaporation of benzene from the solution left an orange solid *adduct* (Found: Ta : Cl : N = 1·00 : 3·06 : 2·88 and 1·00 : 2·84 : 2·92) [Found: *M* 448 in benzene solution. $TaCl_3(NMe_2)_2,NHMe_2$ requires *M*, 420].

Tantalum(v) chloride reacted with diethylamine in a similar manner, although the orange product remaining after removal of excess of amine at the pump was now a thick oil, and it was probably a concentrated solution of the reaction products in excess of amine,[11] since diethylamine was slowly lost on prolonged pumping and the product had a Ta : N ratio of 1·0 : 5·5—6·6, depending on the time for which pumping was carried out. A solid product could be obtained if the initial reaction was carried out in benzene solution with only a slight excess of amine (6 $NHEt_2$: 1 $TaCl_5$). The product dissolved in benzene to an orange solution, leaving an insoluble white residue; the orange solid obtained by evaporation of benzene from the solution was analysed (typical analysis, Ta : Cl : N = 1·00 : 3·43 : 3·20). No matter how the experimental conditions were varied the Cl : Ta ratio remained greater than 3 : 1, and it seems that the extracted product is $TaCl_3(NEt_2)_2,NHEt_2$ contaminated by small amounts of diethylamine hydrochloride; thus although the hydrochloride is insoluble in pure benzene it probably dissolves slightly under the experimental conditions where a little free diethylamine is present.[3] When the initial product was washed with ethylene glycol dimethyl ether a white residue of diethylamine hydrochloride remained (Found: Cl, 32·5; N, 12·9. Calc. for $C_4H_{11}N,HCl$: Cl, 32·3; N, 12·8%).

Di-n-propylamine also reacted with tantalum(v) chloride to give an orange solution and white crystals; the white solid, which was isolated by the direct filtration of the contents of the ampoule, was shown by analysis to be di-n-propylamine hydrochloride (Found: Cl, 25·7. Calc. for $C_6H_{15}N,HCl$: Cl, 25·8).

Reaction of Tantalum(v) *Chloride with Primary Aliphatic Amines.*—Tantalum(v) chloride reacted with methylamine to give a colourless solution together with a small amount of undissolved white solid. After removal of excess of amine at the pump (12 hr. at 40°), a white solid remained with a composition Ta : Cl : N = 1·00 : 4·97 : 7·06 (duplicate 1·00 : 5·04 : 6·89). Since seven moles of methylamine were associated with each mole of tantalum(v) chloride, it seemed likely that the substance was a mixture of solvolysis products; however, no part of the product dissolved in such solvents as benzene and chlorobenzene. The product was therefore heated *in vacuo*, so that information about its composition might be obtained by a study of its thermal decomposition. Any gases liberated by the product were trapped and analysed, and the residue was weighed at all stages. In 16 hours' heating to 100° three mols. of methylamine were lost, leaving a red solid (Found: $TaCl_5,3{\cdot}98NH_2Me$); a further mol. of amine was lost when this substance was heated to 150° for 10 hr., and the residue was green (Found: $TaCl_5,3{\cdot}02NH_2Me$). More extensive breakdown occurred above 200°, a white sublimate and a dark green residue being formed. Magnetic-susceptibility measurements showed the product remaining at 150° to be diamagnetic.

In the analogous reaction between tantalum(v) chloride and ethylamine, the initial product was a pale greenish-yellow solution, which left an orange solid *adduct* on removal of excess amine (Found: Ta, 27·4; Cl, 26·5; N, 14·3. $TaCl_5,7NH_2Et$ requires Ta, 26·8; Cl, 26·3; N, 14·5%). The orange-coloured, glass-like product obtained on removal of excess of n-propylamine from the product of its reaction with tantalum(v) chloride had an analysis corresponding to a ratio Ta : Cl : N = 1·00 : 4·83 : 5·27 (and 1·00 : 4·78 : 4·83). On treatment with benzene, an orange solution was formed and a white residue of propylamine hydrochloride remained (Found: Cl, 36·7; N, 14·5. Calc. for C_3H_9N,HCl: Cl, 37·1; N, 14·7%). The orange solid remaining after evaporation of the benzene from the solution gave Ta : Cl : N = 1·00 : 2·94 : 3·00.

Tantalum(v) chloride and n-butylamine also reacted to give an orange solution and a white residue. After evaporation of excess of n-butylamine, the product was extracted with benzene to give an orange solution (Found: Ta : Cl : N = 1·00 : 2·99 : 3·12) and a white residue (Found: N, 12·7; Cl, 32·4. Calc. for $C_4H_{11}N,HCl$: N, 12·8; Cl, 32·4).

[11] Fowles and McGregor, *J.*, 1958, 136.

Reaction of Tantalum(V) *Bromide with Aliphatic Amines.*—Tantalum(V) bromide was treated with methylamine and with dimethylamine in ampoules. The general appearance and preliminary analyses of the products showed them to be very similar to those formed by tantalum(V) chloride. These reactions were not studied further.

DISCUSSION

Tantalum(V) chloride reacts with trimethylamine and triethylamine to give products of overall composition $TaCl_5,2NMe_3$ and $TaCl_5,NEt_3$ respectively. These products are somewhat analogous to the 1 : 1 adducts formed between diethyl ether and the chlorides and bromides of both niobium(V) and tantalum(V), which appear to be monomeric in ether solution at room temperature.[12] Although we have no evidence that the amine compounds are monomeric, it at least seems reasonable to consider them as simple adducts. The only alternatives are either that tantalum has been reduced to a lower valency state, or that solvolysis has occurred, so that $TaCl_5,2NMe_3$ for instance might be a mixture such as $TaCl_4NMe_2 + NMe_4Cl$. Reduction is extremely unlikely in view of the reluctance of tantalum to assume a valency state lower than five, and indeed the colours of the solid products and the solutions they form on hydrolysis, together with the diamagnetism of the trimethylamine product, indicate that no reduction has taken place. While solvolysis cannot be completely ruled out in the trimethylamine reaction, it is unlikely, because it requires the breaking of a strong nitrogen–carbon bond in the amine molecule. With triethylamine, the product is almost certainly a simple adduct, because either reduction or solvolysis would involve reaction with at least two molecules of the amine, and the observed composition of the product then implies that the reaction only goes just halfway despite the prolonged reaction time.

We therefore consider both products to be simple addition compounds in which tantalum(V) chloride acts as a Lewis acid and uses its vacant 5*d*-orbitals to accept electrons from the nitrogen atoms of the amine ligands. Since triethylamine is a stronger base than trimethylamine[13] it is at first rather surprising that it is co-ordinated to tantalum(V) chloride to a small extent. It must be remembered, however, that steric considerations are more important that inductive effects when the reference acid is bulky,[14] so that the increased size of the triethylamine molecule accounts for its lower order of co-ordination. The compound said[6] to be formed between tantalum(V) chloride and pyridine, $TaCl_5,2py$, is presumably of a similar nature to $TaCl_5,2NMe_3$.

From our previous experience in the analogous reactions of dimethylamine with niobium(V) chloride and vanadium(IV) chloride, it was evident that the product, $TaCl_5,5NHMe_2$, formed with tantalum(V) chloride must be a mixture of aminolytic products, and we have been able to confirm this by extraction of the basic aminotantalum(V) chloride, $TaCl_3(NMe_2)_2,NHMe_2$, from the reaction mixture. $TaCl_5,5NHMe_2$ is thus the mixture, $TaCl_3(NMe_2)_2,NHMe_2 + 2NHMe_2,HCl$. This basic aminotantalum(V) chloride is monomeric in benzene solution, showing the tantalum atom to have an octahedral configuration (d^2sp^3). It is directly analogous to the previously reported niobium compound, $NbCl_3(NMe_2)_2,NHMe_2$, but differs in that the co-ordinated molecule of dimethylamine is apparently more strongly bonded to the tantalum compound; thus, unlike the niobium compound, the tantalum compound in solution does not lose its co-ordinated molecule of dimethylamine. While this seems unexpected, since tantalum(V) is rather more basic than niobium(V) and should attract electrons from the nitrogen ligands less readily, a probable explanation is that the investigations were made in different solvents (niobium in nitrobenzene, tantalum in benzene), and that the dissociation is a function of the polarity of the solvent rather than of the strength of the metal–nitrogen link.

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[12] Cowley, Fairbrother, and Scott, *J.*, 1958, 3133.
[13] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.
[14] Brown and Taylor, *J. Amer. Chem. Soc.*, 1947, **69**, 1332.

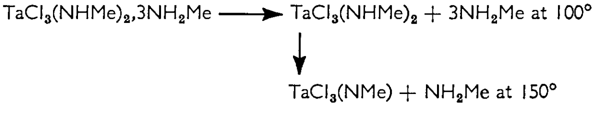
The initial reaction takes place between solid tantalum(v) chloride and liquid dimethylamine, and it is probable that an amine molecule is first co-ordinated to the halide, hydrogen chloride being then eliminated (with excess of amine it forms dimethylamine hydrochloride). Solid tantalum(v) chloride presumably has the same dimeric bridged structure as niobium(v) chloride,[15] so that the tantalum atom must assume a co-ordination number of seven in the intermediate co-ordination stage of the reaction with dimethylamine.

A similar aminolytic reaction occurs between tantalum(v) chloride and either diethylamine or di-n-propylamine, since the appropriate amine hydrochloride has been isolated from the products. With the higher secondary amines it is more difficult to free the basic aminotantalum(v) chloride from the amine hydrochloride, but fairly pure $TaCl_3(NEt_2)_2,NHEt_2$ has been obtained. It is interesting to note that, although diethylamine is a stronger base than dimethylamine,[13] the reaction with tantalum(v) chloride proceeds no further.

It is not surprising that aminolysis should occur with secondary amines but not with tertiary amines, since a nitrogen–hydrogen bond is more readily broken than a nitrogen–carbon bond. Moreover, the reaction of tantalum(v) chloride with secondary amines closely resemble those with alcohols. Thus when tantalum(v) chloride reacts with methyl alcohol or ethyl alcohol, three tantalum(v)–chlorine bonds are solvolysed, giving $TaCl_2(OR)_3$,[16] although complete solvolysis to the alkoxide, $Ta(OR)_5$, may be effected under suitable conditions.[17] Various phenol derivatives have also been prepared,[18,19] *e.g.*, $TaCl_3(OC_{14}H_9)_2$, $TaCl_2(OC_{10}H_7)_3$, $TaCl(OPh)_4$, $Ta(OC_{10}H_7)_5$, and $Ta(OPh)_5$. As we should expect, solvolysis is normally more extensive with alcohols than with amines, because the O–H bonds yield protons more readily than do N–H bonds. It was particularly noticeable that our basic aminotantalum(v) chlorides reacted vigorously with anhydrous ethanol.

The product of the tantalum(v) chloride–methylamine reaction, $TaCl_5,7NH_2Me$, is again unquestionably a mixture of aminolytic products, although in this instance we have been unable to separate them since neither component is soluble in any solvent which will not react irreversibly with the tantalum component. Alcohols, for instance, will react to produce compounds with tantalum–oxygen bonds. The overall formula allows only three simple compositions for the reaction mixture, corresponding to the replacement of one, two, or three chlorine atoms: (i) $TaCl_4(NHMe),5NH_2Me + NH_2Me,HCl$; (ii) $TaCl_3(NHMe)_2,3NH_2Me + 2NH_2Me,HCl$; (iii) $TaCl_2(NHMe)_3,NH_2Me + 3NH_2Me,HCl$. Since dimethylamine and ammonia[20] both force the replacement of two chlorine atoms, it seems probable that methylamine reacts in the same way, *i.e.*, according to reaction (ii). Some of the three mols. of methylamine may be held in the lattice,* rather than co-ordinated directly to the tantalum atom; in the latter instance the tantalum atom has a co-ordination number of eight.

Confirmation is provided by a study of the thermal decomposition of the product *in vacuo*, which is in excellent accord with the scheme:



Moreover, the compound evidently undergoes a fairly fundamental change upon losing the last molecule of amine, since it changes from red to green. The colour change might, alternatively, arise from the reduction of tantalum to a lower valency state, although the

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* We are grateful to a referee for pointing this out.

[15] Zalkin and Sands, *Acta Cryst.*, 1958, **11**, 615.

[16] Funk and Niederländer, *Ber.*, 1929, **62***B*, 1688.

[17] Bradley, Wardlaw, and Whitley, *J.*, 1955, 726.

[18] Funk and Niederländer, *Ber.*, 1928, **61***B*, 249.

[19] Funk and Baumann, *Z. anorg. Chem.*, 1937, **231**, 264.

[20] Moureu and Hamblett, *J. Amer. Chem. Soc.*, 1937, **59**, 33.

diamagnetism of the green product indicates that no such valency change has occurred. The magnetic properties are not complete proof, however, because the paramagnetism normally associated with the unpaired electrons might not exhibit itself at room temperature in such a magnetically concentrated material.[21] It is not possible to write down a simple scheme for the thermal decomposition if we assume that three tantalum–chlorine bonds are aminolysed in the initial reaction; it becomes necessary to propose a solid–solid back reaction between the basic aminotantalum(v) chloride and methylamine hydrochloride, which is much less likely:

$$TaCl_2(NHMe)_3,NH_2Me + 3NH_2Me,HCl \longrightarrow TaCl_3(NMe) + 2NH_2Me,HCl + 4NH_2Me$$

In the analogous reaction of niobium(v) chloride with methylamine,[2] small amounts of dimeric $NbCl_2(NHMe)_3$ were extracted from the reaction mixture, although this was not so with the tantalum product. The niobium(v) chloride–methylamine reaction was not examined further, and it was assumed that the product was entirely the mixture, $NbCl_2(NHMe)_3 + 3NH_2Me,HCl$, in which most of the basic aminoniobium(v) chloride was highly polymeric and insoluble in chlorobenzene. In view of the close similarity of niobium(v) chloride and tantalum(v) chloride, however, it seems probable that the insoluble bulk of the niobium(v) chloride reaction product contains $NbCl_3(NHMe)_2$. To clarify this point, and to obtain further structural information, work has been initiated on the reaction of niobium(v) chloride with a series of primary aliphatic amines.

Ethylamine evidently reacts with tantalum(v) chloride in a directly analogous manner to methylamine, since the initial product is again $TaCl_5,7NH_2Et$. The overall composition of the products of the reaction of tantalum(v) chloride with both n-propylamine and n-butylamine is $TaCl_5,5NH_2R$, and from these products we have been able to extract the basic aminotantalum(v) chlorides $TaCl_3(NHPr^n)_2,NH_2Pr$ and $TaCl_3(NHBu^n)_2,NH_2Bu$ respectively; the appropriate amine hydrochlorides have also been isolated. It seems that in both instances the basic aminotantalum(v) chloride co-ordinates only one mol. of amine. We attribute the solubility of the compounds in organic solvents to the increasing size of the alkyl group.

Thus we suggest that tantalum possibly assumes a co-ordination number of eight with the methylamine and ethylamine products, but that with primary amines containing larger alkyl groups or with secondary amines the increasing steric volume of the ligand lowers the co-ordination to six.

It is interesting to consider why only two of the five chlorine atoms in tantalum(v) chloride are normally replaced in reactions of the halide with ammonia or with primary and secondary aliphatic amines. It has been suggested[3] that solvolysis is limited by the inability of the partly replaced metal halide to form the intermediate compound necessary for subsequent reaction, but this is certainly not the case with the reactions of tantalum(v) chloride because all the replaced compounds co-ordinate at least one mol. of ammonia or amine. The explanation appears to be that as tantalum–chlorine bonds become replaced by tantalum–nitrogen bonds so the remaining tantalum–chlorine bonds become stronger—through an increase in their ionic character—and are less easily broken.

The tantalum(v) bromide–amine reactions were not studied in any detail because the preliminary experiments showed them to be essentially the same as the analogous reactions of tantalum(v) chloride.

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[21] Selwood, " Magnetochemistry," 2nd edn., Interscience, New York, 1956, p. 174.