318. *Amine Compounds of the Transition Metals. Part I. The Reaction of Vanadium Tetrachloride with Some Aliphatic Amines.*

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The reaction of vanadium tetrachloride with mono-, di-, and tri-methylamine has been studied over a wide range of experimental conditions; simple 1 : 1 adducts form at low amine concentrations, but with increasing amine : VCl_4 ratios more extensive reaction occurs. Compounds isolated and identified include $VCl_2(NHMe)_2,NH_2Me$, $VCl_2(NMe_2)_2$, and $VCl_3(NMe_3)_2$; their precise nature has been established by measuring their magnetic moments, and their molecular weights in nitrobenzene solution. Probable reaction mechanisms and the structure of the isolated products are discussed.

Ionic halides of metals of Groups IA, IIA, and IIIA form simple addition compounds—ammoniates—with ammonia, in which the ammonia molecules are bound to the metal by relatively weak forces [1] of the order of 8—20 kcal./mole. With the transition-metal ions, however, *e.g.*, Cr^{3+} and Co^{3+}, much stronger bonds may be formed between the metal ion and the ammonia molecules, because the metal ions can form donor–acceptor bonds by accepting electrons (from the nitrogen atoms) into their inner *d* orbitals. Some of the metal ions do however form weaker bonds because they make use of their outer *d* orbitals for the bond formation (*e.g.*, Cr^{2+}, Ni^{2+}).[2] Whereas the ammonia molecules are bonded unchanged in both the ammoniates and the co-ordination compounds, we find a different type of behaviour with the more covalent halides of a number of metals in the main groups around the centre of the Periodic Table (Be, B, Si, Ge, Sn, Pb, As, Sb, and Bi), and with most transition-metal halides in which the metal is in its highest valency state, since the initial co-ordination of the ammonia molecules is followed by the elimination of the

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[1] Biltz, *Z. anorg. Chem.*, 1923, **130**, 93.

[2] Cartmell and Fowles, " Valency and Molecular Structure," Butterworths, London, 1956, p. 184.

hydrogen halide and the formation of either ammonobasic halides or amides; the partial replacement of halogen atoms by NH_2 groups gives the ammonobasic halides, and complete replacement the amides.

The reaction of a number of transition-metal chlorides with ammonia has been examined recently by Fowles and Pollard,[3] who showed that as the metal–chlorine bond becomes more ionic, *e.g.*, in $SiCl_4$, $TiCl_4$, $ZrCl_4$, and $ThCl_4$, so the replacement of Cl atoms by NH_2 groups is less complete; such compounds as $Si(NH_2)_4$, $TiCl(NH_2)_3$, $ZrCl_3(NH_2)$, and $ThCl_4,6NH_3$ were reported. With the ammonobasic halides, structural investigations such as molecular-weight determinations are not possible, since the compounds are usually insoluble in all solvents with which they do not react and are probably polymeric. Now amines should yield substances which are more amenable to structural investigation than the ammonobasic chlorides, since there are fewer hydrogen atoms directly bound to the nitrogen atom, so that elimination of hydrogen chloride is less likely, and polymerisation (by subsequent elimination between neighbouring molecules) is reduced.

By analogy with their reaction with ammonia, we would expect the more ionic halides of Groups IA, IIA, and IIIA to form simple addition compounds with amines, and this has been confirmed by the preparation of amine complexes of lithium halides,[4] calcium chloride,[5] and the rare-earth chlorides.[6]

Little reliable work has been published concerning the reaction of amines with the transition-metal halides. Dermer and Fernelius [7] reported the formation of addition compounds of titanic chloride and aromatic amines, and they obtained $Ti(NPh_2)_4$ by the reaction of the chloride with $NaNPh_2$; the compound $Ti(NPh_2)_4$ is rather unexpected on steric grounds, since there seems to be insufficient room around the titanium atom to accommodate the four NPh_2 groups. More recently, Troost [8] reported the formation of a number of addition compounds of this chloride with various aliphatic amines, although he merely analyses the product and gives an overall formula to the adduct without emphasing the possibility that replacement may have occurred. Antler and Laubengayer [9] made a much fuller study of the gaseous phase reactions of titanic chloride with ammonia and mono-, di-, and tri-methylamine, and found that in addition to replacement of chlorine atoms by amino-residues there is also some reduction to Ti(III); this reduction is only significant however in the $TiCl_4$–NMe_3 reaction where $TiCl_3,2NMe_3$ was isolated.

Almost no work has been carried out on the amine compounds of the Group VA elements. Some early investigations of Mertes and Fleck [10] indicated that vanadium tetrachloride reacts with most amines, but the results have little value since they were not carried out under rigorously anhydrous conditions; indeed, a number of analytical figures are accounted for by assuming water molecules to be present in the complexes. A similar criticism must be made of the cursory study of the VCl_4–NH_3 reaction due to van Valkenburg and Schoffman.[11]

Because of this unsatisfactory situation, we are carrying out a systematic investigation of the reaction of amines with the transition-metal halides, and in this paper we report an investigation of the reaction of vanadium tetrachloride with mono-, di-, and tri-methylamine. Any simple 1 : 1 addition compounds would constitute complexes of the unusual co-ordination number five.

EXPERIMENTAL

Materials.—Vanadium tetrachloride was prepared by the action of chlorine on vanadium-metal powder (99% pure) at 400° in an all-glass apparatus; traces of oxide in the metal were

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[3] Fowles and Pollard, *J.*, 1953, 4128.

[4] Simon and Glauner, *Z. anorg. Chem.*, 1929, **178**, 177.

[5] Maillard, *Compt. rend.*, 1936, **203**, 187.

[6] Popov and Wendtlandt, *J. Amer. Chem. Soc.*, 1955, **77**, 857.

[7] Dermer and Fernelius, *Z. anorg. Chem.*, 1953, **221**, 83.

[8] Troost, *Canad. J. Chem.*, 1952, **30**, 835, 842.

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

[10] Mertes and Fleck, *Ind. Eng. Chem.*, 1915, **7**, 1037.

[11] van Valkenburg and Schoffman, Univ. Colorado Studies, Ser. D1, No. 1, 1940, p. 23.

removed by reduction with hydrogen before chlorination. The vanadium tetrachloride was collected in an ice-cooled container and sealed off *in situ*; it was degassed by pumping out dissolved chlorine through the stopcock (greased with Silicone grease) attached to the container, and finally distilled into ampoules which were sealed off. The purity of the tetrachloride was confirmed by analysis (Found: V, 26·8; Cl, 73·9. Calc. for VCl_4: V, 26·4; Cl, 73·6%).

Vanadium trichloride was made by the thermal decomposition of vanadium tetrachloride in an atmosphere of carbon dioxide.[12]

Trimethylamine (from Messrs. British Drug Houses) was dried and freed from traces of primary and secondary amines by distillation *in vacuo* from phosphoric oxide.[13]

Dimethylamine (from Messrs. British Drug Houses) was dried by repeated distillation *in vacuo* from freshly crushed barium oxide, followed by a final treatment with freshly distilled titanium tetrachloride. Titanium tetrachloride was used for the final drying, since both it and the products it forms with dimethylamine are very sensitive to traces of moisture.

Monomethylamine was obtained in an anhydrous state from a 30 w/w aqueous solution (from Messrs. British Drug Houses) by distillation *in vacuo* on to freshly crushed barium oxide; only the first 20—25% was collected, and this was treated in a similar manner a further 3—4 times, and finally allowed to react with titanium tetrachloride or a thin film of potassium metal.

Chlorobenzene and "iso-octane" (2:2:4-trimethylpentane) were each fractionated in an efficient Fenske column, only the middle fractions being taken, and finally distilled from phosphoric oxide.

Nitrobenzene (from Messrs. May and Baker) was fractionally crystallised four times and distilled (still surface) *in vacuo* from phosphoric oxide directly into the molecular-weight apparatus.

Analyses.—Wherever possible, the products were completely analysed, but on occasion the product firmly adhered to the vessel walls and could not be removed; it was then hydrolysed *in situ*, so that the subsequent analysis gave only the V : Cl : N ratio.

Nitrogen was determined by distilling the amine from an alkaline solution into an excess of standard sulphuric acid and back-titration with standard sodium hydroxide solution (B.D.H. 4·5 indicator). Any amine present was always removed in this way before the estimation of vanadium, since it interfered with the vanadium(IV)–potassium permanganate titration.

Vanadium was determined in dilute sulphuric solution by reduction with sulphur dioxide, removal of excess of sulphur dioxide with nitrogen, and titration with standard potassium permanganate solution at 70°.[14]

Chlorine was determined by the Volhard method, with an occasional gravimetric silver chloride check.

Reactions.—Reactions were studied under rigorously anhydrous conditions in vacuum systems.

(a) *Vanadium chloride and dimethylamine.* This reaction is described first in the greatest detail since it was investigated the most fully; the products are potentially the simplest, since there is only one replaceable hydrogen atom in the amine.

(1) Preparation by passing dimethylamine vapour (in a stream of nitrogen) into a solution of the chloride in "iso-octane." The solution of chloride in "iso-octane" was prepared in reaction vessel *D* (Figure) by breaking an ampoule of chloride *in vacuo* and condensing it into *D via* tap 5, then condensing it in dried "iso-octane" from reservoir E. The contents of vessel *D* were allowed to warm to room temperature and then agitated with a stream of oxygen-free nitrogen (dried by passage through vertical 70 cm. columns of magnesium perchlorate and phosphoric oxide). As soon as the pressure in the reaction vessel became equal to the head of of mercury in bubbler *A*, tap 4 was opened and the nitrogen allowed to pass to the fume chamber through a drying tube of silica gel. By closing tap 1 and opening taps 2 and 3, the nitrogen stream was passed through the trap *B* of liquid dimethylamine held at −78° until dimethylamine could be freely detected in the gases issuing from the fume chamber outlet; the reaction was then assumed to be complete. The solvent was then drawn through the sinter-pad into vessel *C*; fresh solvent was distilled into *D*, the suspension agitated with nitrogen, and the solvent again drawn off into *C*; this procedure was repeated until no trace of colour remained in the solvent, so that all traces of unchanged tetrachloride were removed. The buff-coloured *product* remaining in *D* was evacuated for 3—4 hours and then shaken into a weighed vessel

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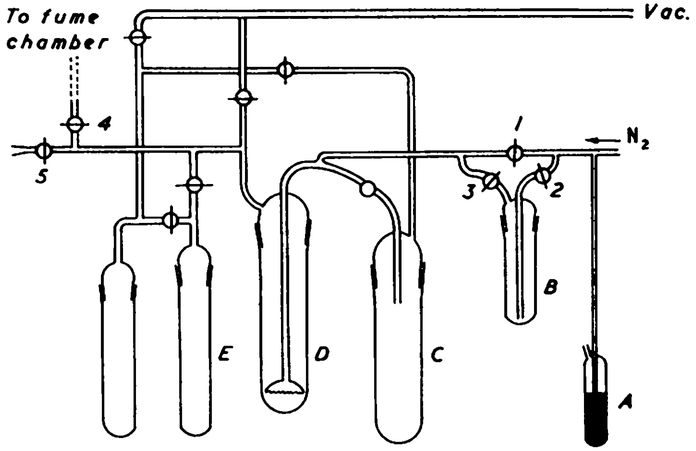
[12] *Inorg. Synth.*, **4**, 128.

[13] Brown, Taylor, and Gerstein, *J. Amer. Chem. Soc.*, 1944, **66**, 431.

[14] Hillebrand, Lunden, Bright, and Hoffman, "Applied Inorganic Analysis," 2nd Edn., Wiley, New York, 1953, p. 458.

for analysis [Found: (i) V, 20·9; Cl, 57·1; N, 7·0%; V : Cl : N ratio, 1 : 3·92 : 1·19. (ii) V, 21·4; Cl, 57·3; N, 6·9%; ratio 1 : 3·96 : 1·15. $VCl_4,NHMe_2$ requires V, 21·4; Cl. 59·5; N, 5·9%].

When this product was heated *in vacuo* to 150° for 1—2 hr.—conditions under which dimethylammonium chloride readily sublimes—a very small amount of this chloride (coloured slightly by a trace of vanadium-containing material) sublimed away, leaving the bulk of the product almost unchanged (Found: V, 21·0; Cl, 57·4; N, 7·2%).



When the amine concentration in the initial reaction was increased by raising the bath temperature to −35°, and lowering that of the vanadium tetrachloride–" iso-octane " solution to −23°, the nature of the *product* changed noticeably, and the buff product was heterogeneous and mixed with a red substance (Found: V, 15·2; Cl, 42·6; N, 12·5%; V : Cl : N, 1 : 4·05 : 2·99. $VCl_3\cdot NMe_2,NHMe_2 + NH_2Me_2Cl$ requires V, 15·5; Cl, 43·2; N, 12·8%).

Note. The apparatus shown in the Figure includes the additional taps, etc., that are necessary for the washing and recycling of solvents in subsequent reactions.

The product prepared with the higher concentration of amine vapour was agitated with liquid dimethylamine at −78° for 1 hr. by means of a stream of nitrogen; the initial product then largely dissolved to give a deep red solution. The amine was distilled from the product, the solid remaining being pumped at room temperature for 2 hr. The heterogeneous product, which contained a considerably greater proportion of red constituent than it did before, was hydrolysed *in situ* and gave an analysis corresponding to a V : Cl : N ratio of 1 : 3·94 : 3·78, *i.e.*, $VCl_2(NMe_2)_2 + 2NH_2Me_2Cl$. When this product was washed with chlorobenzene, the extract gave a solid (on removal of chlorobenzene) which was hydrolysed *in situ* and gave an analysis corresponding to V : Cl : N = 1 : 2·25 : 2·52.

(2) Ampoules made from 150 c.c. Pyrex flasks and extended B19 joints were flamed *in vacuo*, and vanadium tetrachloride and excess of dimethylamine were condensed into them. Dry nitrogen was admitted, to 0·75 atm., to the bulb which was then sealed off at a constriction just beyond the extended ground joint. The contents of the ampoule were allowed to warm to room temperature, shaken mechanically for several hours, and set aside for at least 2 days. The ampoules were then cooled to rather below the b. p. of dimethylamine, scratched with a glass file near the tip, and " hot-spotted "; the tip was removed and the ground joint quickly inserted into a B19 sidearm on the reaction vessel *D* (full of dry nitrogen so that any hydrolysis is negligible), and the contents of the ampoule were tipped into *D*. After the amine had distilled away, the solid was extracted with chlorobenzene; analysis of the product gave: V, 21·8, 21·2; Cl, 33·2, 33·2; N, 14·1, 14·9%; V : Cl : N, 1 : 2·19 : 2·31, 1 : 2·25 : 2·51. Although dimethylammonium chloride is insoluble in chlorobenzene, it seemed likely from the non-stoicheiometric analytical figures that loosely bound amine of the product would modify the solubility,[15] so that traces of the chloride might dissolve in addition to the vanadium compound, and thereby give a product whose overall composition did not correspond to integral

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[15] Anderson, *J. Amer. Chem. Soc.*, 1952, **74**, 1421.

V : Cl ratios. In subsequent runs, the loosely held amine was removed by evacuation at 40° for 2 hr. and the product was then extracted as before with chlorobenzene. An analysis of the product gave V : Cl : N = 1 : 2·03 : 1·70, and the molecular weight in nitrobenzene was 260 (a monomer has *M* 197). The departure from integral V : Cl ratios in earlier runs can thus be definitely accounted for by the dissolution of small amounts of dimethylammonium chloride in the chlorobenzene which contained small amounts of free amine, previously loosely associated with the vanadium aminochloride.

Repeating these preparations but extracting each sample several times with chlorobenzene gave products whose V : N ratios approached more closely to 1 : 2 and whose molecular weights were nearer the monomeric value [Found: V : Cl : N, 1 : 2·03 : 1·88; *M*, 227 (required *M*, 206)].

It seems that a small amount of dimer is formed and is almost completely dissolved in the first chlorobenzene washing, and that continued extraction of the same sample then removes monomer, so that the overall composition and molecular weight of the dissolved material get closer to that required by the monomer. Measurements of the magnetic susceptibility of the nitrobenzene solutions gave $\mu = 1{\cdot}62$ B.M., corresponding to one unpaired electron.

A large number of solvents were examined in an attempt to find one which would dissolve either the amine hydrochloride or the vanadium aminochloride but not both. The only ones found were chlorobenzene and nitrobenzene, which dissolved only the aminochloride; chlorobenzene was preferred since it was more readily distilled.

(b) *Vanadium tetrachloride and methylamine.* A vapour-flow preparation was agitated with liquid methylamine at −78°, and then extracted eight times with 100 c.c. of liquid amine; the product of this extraction was then further extracted with chlorobenzene. The chlorobenzene solution was deep red and on evaporation gave a small quantity of a brown-red solid (Found: V : Cl : N, 1 : 2·26 : 2·63). This appears to be $VCl_2(NHMe)_2$ together with a little methylammonium chloride dissolved by the chlorobenzene containing traces of amine.

Next, the reactants, in sealed ampoules, were allowed to react at room temperature; the ampoules were opened [see (a) for details] and the contents extracted with liquid methylamine (6 × 100 c.c.) to remove any methylamine hydrochloride. The solid remaining behind was yellow-green [Found: V, 17·2, 17·6; Cl, 23·3, 23·7; N, 27·7, 27·2. $VCl_2(NHMe)_2,4NH_2Me$ requires V, 17·0; Cl, 23·6; N, 28·0%]. The molecular weight could not be determined since insufficient material dissolved in nitrobenzene; the magnetic susceptibility of the *solid* at room temperature was 1·61 B.M., corresponding to one unpaired electron.

(c) *Vanadium tetrachloride and trimethylamine.* (1) Preliminary experiments were made by condensing the chloride (*ca.* 1 g.) and excess of amine into a tube equipped with a stopcock and ground joint; the tube was detached from the vacuum-line and the contents were allowed to react at 0° (the tube being occasionally shaken), and then the excess of amine was distilled off *in vacuo*. The composition of the reddish-mauve product corresponded to the addition of 1·5—2·0 moles of amine per mole of chloride. When the product was heated by *ca.* 20° intervals to 200°,[16] trimethylamine was steadily lost, together with a small amount of reddish material which sublimed on to the cooler parts of the vessel walls, until the residue had the overall composition VCl_4,NMe_3.

(2) A vapour-flow preparation with the amine at −78° and the chloride–" iso-octane " solution at room temperature gave a buff-coloured product (Found: V, 19·4; Cl, 51·1; N, 6·8%; V : Cl : N, 1 : 3·80 : 1·29). During the preparation, a small amount of almost colourless fine powder was formed above the solution and carried into the outlet tube to the fume chamber. It seems that while the product is largely the adduct VCl_4,NMe_3, a small amount of side reaction occurs giving a replaced body together with the amine hydrochloride (which is found in the outlet tube).

(3) Ampoules of the reactants were prepared and opened in the usual way and after the removal of amine by distillation *in vacuo* the solid remaining was extracted with chlorobenzene; this permanganate-red solution gave a brownish-red solid when the chlorobenzene was evaporated. When this product was heated at 80—100° *in vacuo*, a red crystalline solid sublimed (Found: V, 19·3; Cl, 37·4; N, 10·2%; V : Cl : N, 1 : 2·79 : 1·88). The residue had a similar composition (V, 20·0; Cl, 39·4; N, 10·4%; V : Cl : N, 1 : 2·84 : 1·86). The sublimed crystals were readily hydrolysed in moist air.

With more careful sublimation, carried out by placing the extracted solid in the bottom of a Pyrex vessel containing two constrictions, evacuating the apparatus at the diffusion pump,

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

sealing it at the upper constriction, and then placing the lower end in a bath at 80—100°, crystals formed in the upper part of the vessel (Found : V, 18·5; Cl, 39·6; N, 10·6. $VCl_3,2NMe_3$ requires V, 18·5; Cl, 38·6; N, 10·4%). Sublimation with direct pumping, or sublimation above 100°, always gave poorly formed crystals (Found : V : Cl : N, 1 : 2·7—2·8 : 1·7—1·8). Later experiments showed that better yields of the initial crude *product* could be obtained if the ampoules of the reactants contained some chlorobenzene; presumably the solvent action of the chlorobenzene prevented the formation of gross surface products and allowed the reaction to take place more readily.

The molecular weight of the sublimate in nitrobenzene was found to be 280 and 254 in successive runs (monomeric $VCl_3,2NMe_3$ requires *M*, 275); after the nitrobenzene solution had been warmed to 40° and evacuated for 1 hr., the molecular weight increased to 356 (in the first instance) while the V : N ratio dropped to 1 : 1·65, showing dimerisation with loss of amine.

The molecular weight of the less clearly defined crystalline product prepared by sublimation at 110—125° was found to be 343.

The magnetic moment, for solutions in chlorobenzene, gave 2·69 and 2·75 B.M., corresponding to two unpaired electrons. The precise nature of the sublimate was confirmed by treating vanadium trichloride with trimethylamine; the reaction was slow, probably because of the difficulty of wetting the chloride, but fair yields of $VCl_3,2NMe_3$ were obtained from the ampoules.

Single crystals were examined by paramagnetic-resonance methods, but no absorption was observed down to the temperature of liquid hydrogen, presumably owing to spin-spin coupling which is commonly found with vanadium compounds. During these studies, the crystals had to be exposed to the atmosphere for some minutes, and to prevent hydrolysis they were covered with a thin film of Silicone oil (previously allowed to stand over phosphoric oxide), and admitted to the crystals *in vacuo*.

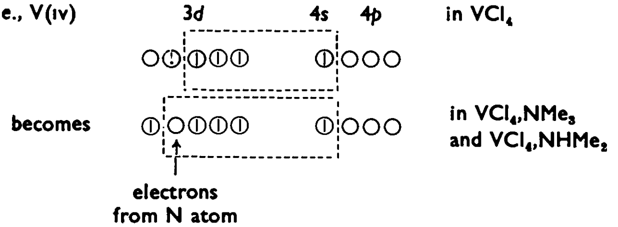
Magnetic Moments.—These were determined at room temperature on a Gouy type balance with a field strength of 8000 gauss.

Molecular Weights.—These were determined cryoscopically under rigorously anhydrous conditions. Temperature changes were recorded on a Beckmann thermometer inserted through a rubber bung (coated with Picein wax, to allow the vessel to be evacuated), and stirring was effected with a stainless-steel spiral agitated through the side of the vessel by an electric motor (connection was made by length of rod fixed with Picein into a pressure-tubing sleeve).

Spectral Measurements.—The absorption spectrum of $VCl_3,2NMe_3$ in chlorobenzene solution shows peaks at 510 and 770 mμ.

DISCUSSION

It seems that the reaction of vanadium tetrachloride with di- and tri-methylamine at low amine concentrations in " iso-octane " solutions gives mainly 1 : 1 adducts $VCl_4,NHMe_2$ and VCl_4,NMe_3, which appear to be thermally stable up to 150° in the absence of free amine. It may be supposed that this adduct is formed by the donation of the lone pair of electrons from the nitrogen atom into a vacant *d* orbital of vanadium, producing a substance of co-ordination number five.



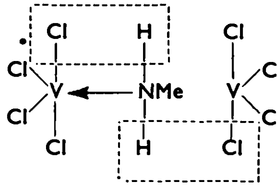
In the diagram, we have assumed that the vanadium atom uses d^3s rather than sp^3 orbitals for the tetrahedral bonds in vanadium tetrachloride, since the 3*d* orbitals are of lower energy that the 4*p*. This leads to the adducts' using d^4s rather than dsp^3 orbitals.

The formation of these 1 : 1 adducts is in agreement with Antler and Laubengayer's finding [9] that the analogous compound $TiCl_4,NMe_3$ is the main product of the corresponding gas-phase reaction.

When the dimethylamine concentration is increased, the adduct undergoes a base-catalysed elimination of hydrogen chloride, forming first VCl_3,NMe_2 and finally $VCl_2(NMe_2)_2$. The compound $VCl_2(NMe_2)_2$ is largely monomeric.

The fact that only two of the four chlorine atoms can be replaced by NMe_2 groups is best attributed to the steric difficulty of forming $VCl_2(NMe_2)_2,NHMe_2$ as the necessary intermediate. There is of course no electronic difficulty about forming this compound, because the vanadium atom has the necessary vacant *d* orbital for the formation of the donor–acceptor bond, but once there are two chlorine atoms and two dimethylamino-groups attached to the vanadium atom there will be no space around the vanadium atom to accommodate an extra dimethylamine molecule; the limit appears to be $VCl_3(NMe_2),NHMe_2$, where there is only one amino-group.

On reaction of vanadium tetrachloride with monomethylamine the product $VCl_2(NHMe)_2$ was only very slightly soluble in chlorobenzene and nitrobenzene and insoluble in all other solvents with which it did not react. In view of this very limited solubility, the reaction product is evidently considerably polymerised, which is not of course unexpected since the presence of two hydrogen atoms in the initially co-ordinated amine molecule allows elimination of hydrogen chloride from two neighbouring molecules, and leads to V–NMe–V bridges.



In the analogous reactions of titanic chloride with di- and mono-methylamine, Antler and Laubengayer [9] only studied the room-temperature gas-phase reaction, and they were unable to separate the mixture of products by either vacuum-sublimation or solvents, although the appearance and analysis of these materials agreed with the presence of a mixture of compounds analogous to those we have isolated in the vanadium tetrachloride–amine reactions. These authors showed by chemical tests that a small amount of reduced titanium was present in each product, but we do not find any evidence of vanadium's being reduced to the tervalent state by mono- or di-methylamine.

It seems then, that with both these amines the main product is an aminobasic chloride with two chlorine atoms replaced by amine residues. While only two atoms are replaced in these reactions, the reaction of vanadium tetrachloride with ammonia gives $VCl(NH_2)_3$,[17] showing that the presence of the three hydrogen atoms attached to the nitrogen permits a greater replacement. This can be attributed in part to the greater steric ease with which the ammonia molecule can be co-ordinated, and in part to the greater possibility of elimination of hydrogen chloride.

It is not perhaps surprising that reduction takes place in the reaction with trimethylamine since this is a stronger reducing agent than di- or mono-methylamine; a similar reduction in the analogous reaction of titanium tetrachloride and trimethylamine has been observed by Antler and Laubengayer.[9] It is not at all clear, however, just how this reduction takes place, and we have not yet identified any products other than $VCl_3,2NMe_3$ and trimethylammonium chloride; the latter is no doubt formed by the reaction of eliminated acid with excess of trimethylamine. The breaking of a C–H bond which is required if hydrogen chloride is eliminated is in agreement with Meyer and Taube's observations [18] on the splitting out of this acid in the reaction of vanadium tetrachloride with aromatic hydrocarbons. For the titanium reaction, Antler and Laubengayer [9] proposed two possible mechanisms, *viz.*, chlorination of trimethylamine (analogous to the chlorination of pyridine by molybdenum pentachloride proposed by Wardlaw and Webb [19] to account for the reduction of the chloride), and formation of radicals of the type $NMe_2{\cdot}CH_2{\cdot}$. We postpone our discussion until further results are available.

While the exact mechanism of the reduction is unknown, there can be no doubt but

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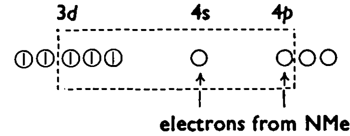
[17] Fowles, unpublished observations.

[18] Meyer and Taube, *Z. anorg. Chem.*, 1935, **222**, 167.

[19] Wardlaw and Webb, *J.*, 1930, 2100.

that the principal product of the reaction of vanadium tetrachloride with excess of trimethylamine at room temperature is $VCl_3,2NMe_3$. The tervalency of vanadium in this complex is confirmed by measurement of its magnetic moment in chlorobenzene solution, which corresponds to two unpaired electrons if we assume the spin-only formula. Molecular-weight measurements show that the substance is monomeric in nitrobenzene solution, so that $VCl_3,2NMe_3$ is a compound in which the vanadium atom has the rather unusual co-ordination number 5. While there is no evidence that this co-ordination remains in the solid state, the ease with which the compound sublimes suggests that it has a low molecular weight. Above 40° in nitrobenzene solution the compound dimerizes with the loss of trimethylamine.

If we accept that 3*d* orbitals will be used for bonding in preference to 4*p* orbitals because of their lower energy, then the most likely arrangement of bonds in $VCl_3,2NMe_3$ is trigonal-bipyramidal with the three chlorine atoms in the planar positions; the vanadium atom would use d^3sp hybrid orbitals, with its two unpaired electrons in the two remaining *d* orbitals.



In a discussion of orbitals used for the alternative arrangements for 5-co-ordination compounds, with particular reference to $VCl_3,2NMe_3$ and $TiCl_3,2NMe$, it has been pointed out [20] that this arrangement would seem more probable than the alternative tetragonal pyramidal one.

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[20] Fowles and Pleass, *Chem. amd Ind.*, 1955, 1743.