

### 333. *The Reaction between Ammonia and Transition-metal Halides. Part IV.<sup>1</sup> The Reaction of Ammonia with Vanadium(IV) Chloride.*

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The reaction between liquid ammonia and vanadium(IV) chloride has been shown to give ammonium chloride and the ammonobasic vanadium(IV) chloride,  $\text{VCl}(\text{NH}_2)_3$ . The solubility of the latter in liquid ammonia containing dissolved ammonium salts ( $\text{NH}_4\text{X}$ ) is attributed to the formation of a soluble ionic species  $[\text{NH}_4][\text{VClX}(\text{NH}_2)_3]$ . Tensimetric studies of the  $\text{VCl}_4\text{-NH}_3$  system at  $-36^\circ$  and  $-45^\circ$  support these postulates.

THE more covalent halides of the transition elements react with liquid ammonia to form ammonobasic halides and the ammonium halide; whenever the ammonobasic halide is insoluble in liquid ammonia it may be obtained pure by washing out the soluble ammonium halide. Recently, it has been shown that whereas titanium(IV) chloride<sup>2</sup> forms  $\text{TiCl}(\text{NH}_2)_3$ , and zirconium(IV) chloride<sup>1</sup> gives  $\text{ZrCl}_3(\text{NH}_2)$ , thorium(IV) chloride<sup>1</sup> forms only simple ammoniates with liquid ammonia. However, little reliable quantitative information is available concerning the corresponding reaction of vanadium(IV) chloride with liquid ammonia, since earlier workers did not appreciate the importance of studying it under rigorously anhydrous conditions. This can readily be seen from the analyses of the products obtained by Mertes and Fleck<sup>3</sup> and VanValkenburgh and Schoffmann,<sup>4</sup> where the total analysis (for vanadium, chlorine, and ammonia) is always considerably less than 100%; Mertes and Fleck in fact accounted for their discrepancy by assigning to their product an overall formula incorporating several molecules of water. Ephraim and Ammann<sup>5</sup> merely noted that a chocolate-brown solid was formed in the reaction but they quoted no analysis.

None of these workers seriously attempted to account for their results, and the idea that the chloride might be ammonolysed seems to have been neglected. In view of this, we have studied the vanadium(IV) chloride-liquid ammonia reaction both by removing soluble compounds by filtration and washing, and by tensimetric studies at  $-36^\circ$  and  $-45^\circ$ .

#### EXPERIMENTAL

*Materials.*—Vanadium(IV) chloride was prepared from the elements<sup>6</sup> and distilled into ampoules.<sup>7</sup> Liquid ammonia (from Imperial Chemical Industries Limited) was dried with sodium before distillation *in vacuo* into the apparatus. Other reagents were of "AnalaR" grade; they were kept under a vacuum for several hours immediately before use in order to remove traces of moisture.

*Analyses.*—Nitrogen and chlorine were determined as described previously.<sup>2</sup> Vanadium was determined by oxidation to the quinquivalent state with potassium permanganate, followed by reduction to vanadium(IV) with mercury<sup>8</sup> and titration with standard permanganate.

*Magnetic-moment Measurements.*—These were made on a Gouy-type balance at room temperature (cf. Table 1); the magnet gave a maximum field strength of 8000 gauss with a pole-piece gap of 3 cm.

*Reactions and Tensimetric Studies.*—Reactions were studied in the usual type of all-glass closed vacuum system.<sup>1,2</sup> Stopcocks were greased with Silicone lubricant wherever they were likely to be exposed at all to vanadium(IV) chloride.

(i) An ampoule of vanadium(IV) chloride was broken *in vacuo*, and the contents were condensed into the reaction vessel; ammonia was condensed on the chloride and allowed to

<sup>1</sup> The paper by Fowles and Pollard, *J.*, 1953, 4128, is regarded as Part III.

<sup>2</sup> *Idem*, *J.*, 1953, 2588.

<sup>3</sup> Mertes and Fleck, *Ind. Eng. Chem.*, 1915, **7**, 1037.

<sup>4</sup> van Valkenburgh and Schoffmann, *Univ. Colorado Studies, Ser. D1*, No. 1, 1940, p. 23.

<sup>5</sup> Ephraim and Ammann, *Helv. Chim. Acta*, 1933, **16**, 1273.

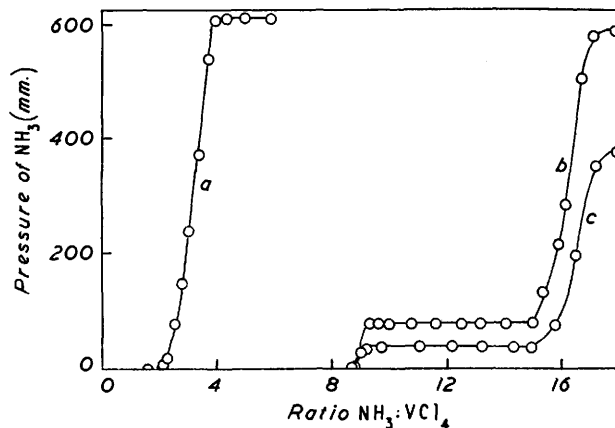
<sup>6</sup> Fowles and Pleass, *J.*, 1957, 1674.

<sup>7</sup> *Idem*, *J. Chem. Educ.*, 1956, **33**, 640.

<sup>8</sup> McCay and Anderson, *J. Amer. Chem. Soc.*, 1922, **44**, 1018.

liquefy. The subsequent reaction gave a brown solution and a greenish-brown solid. The solution was filtered off through a filter-pad (no. 3 sinter), and the ammonia then condensed back on the solid product, which was shaken; the solution was then filtered again. The second filtrate was paler than the original solution, and subsequent filtrates were paler still, until after 4–5 washings they were colourless. The product was normally “pumped” between washings to break up the lumps and make subsequent extractions more efficient.

The insoluble greenish-brown product was ground to a fine powder by agitation with a glass-encased ball-bearing, and then quickly tipped, in a nitrogen atmosphere, through an adaptor into a magnetic susceptibility tube. After its magnetic susceptibility had been measured, the substance was analysed (see Table 1). As the number of washings increased, the V : Cl : N ratio became close to the 1 : 1 : 3 expected for a composition  $VCl(NH_2)_3$ . Prolonged pumping around 40–60° gradually removed ammonia.



The magnetic moment is higher than might be expected for quadrivalent vanadium (1.73 B.M.), suggesting that a small amount of reduction has taken place. Because the ammonio-basic vanadium(IV) chloride is insoluble in all solvents with which it does not react (*e.g.*, hexane, carbon tetrachloride, chlorobenzene) its spectra and molecular weight could not be studied.

TABLE 1. Insoluble product of the reaction between liquid ammonia and vanadium(IV) chloride, washed with liquid ammonia.

Run no.	Analyses (%)			Mol. ratio	No of	$\mu$	Comments
	V	Cl	N	V : Cl : N	washings	(B.M.)	
1	30.7	32.9	30.8	1 : 1.54 : 3.65	6	—	Pumped at 40° for 6 hr. after washing.
2	33.3	32.3	30.1	1 : 1.39 : 3.39	8	—	Pumped at 50–60° between and after washings (15 hr. in all).
3	32.6	32.2	30.2	1 : 1.42 : 3.37	12	1.91	Pumped at 50–60° between and after washings (17 hr. in all).
4	30.4	32.6	28.6	1 : 1.54 : 3.42	15	2.03	Pumped 40–60° between and after washings (13 hr. in all).
5	33.8	31.8	28.9	1 : 1.31 : 3.12	21	1.93	Pumped 40–60° between and after washings (22 hr. in all).

Ammonia was allowed to evaporate from the final filtrate, and the residue which remained (accumulated from all the washings) appeared to be a mixture of a white and a greenish-brown substance. Loosely held ammonia was removed by warming the mixture to 40° and “pumping” for several hours, and the whole of the remaining solid was hydrolysed *in situ* and analysed. The results (Table 2) show that the soluble vanadium compound is most probably  $VCl(NH_2)_3$ , since the N : Cl ratio then corresponds closely to that for ammonium chloride.

(ii) *Effect of added salts on the solubility of  $VCl(NH_2)_3$  in liquid ammonia.* Samples of various soluble salts were added to the ammonio-basic vanadium(IV) chloride, and liquid ammonia was condensed on the mixture. The solid dissolved completely in liquid ammonia to a deep-brown solution when ammonium chloride, ammonium bromide, ammonium nitrate, or potassium iodide was added, but dissolved only to a very small extent in the presence of sodium nitrate.

(iii) *Tensimetric study of the  $VCl(NH_2)_3-NH_3$  system.* To confirm the absence of ammonium chloride from the ammonobasic vanadium(IV) chloride, the  $VCl(NH_2)_3-NH_3$  system was examined tensimetrically at  $-36^\circ$ ; the result is shown in plot *a*. The two molecules of ammonia which attached themselves fairly strongly to the ammonobasic chloride were lost on prolonged "pumping" at room temperature. When  $VCl(NH_2)_3$  was heated *in vacuo* to  $\sim 300^\circ$

TABLE 2. *Analysis of the soluble portion.*

N : Cl ratio \* on the assumption that soluble vanadium is present as:

Run	$V(NH_2)_4$	$VCl(NH_2)_3$	$VCl_2(NH_2)_2$
1	1.00 : 1.17	1.00 : 0.99	1.00 : 0.81
2	1.00 : 1.23	1.00 : 1.00	1.00 : 0.81
3	1.00 : 1.13	1.00 : 0.98	1.00 : 0.86

\* We assume that the soluble portion is a mixture of ammonium chloride and an ammonobasic vanadium(IV) chloride, so that, from the determined vanadium content, the associated nitrogen and chlorine required for each of the more likely compounds may be calculated. The N : Cl ratio for the remaining nitrogen and chlorine should then be 1 : 1, corresponding to ammonium chloride.

for several hours it decomposed to give a black residue; this residue, which was hydrolysed only slowly by sodium hydroxide solution, gave an analysis corresponding to a V : Cl : N ratio of 1.00 : 1.13 : 0.82.

(iv) *Tensimetric studies of the  $VCl_4-NH_3$  system.* A known excess of ammonia was condensed on a known weight of vanadium(IV) chloride, the mixture surrounded by a constant temperature bath, and the final equilibrium pressure of ammonia measured. Small portions of ammonia were successively removed and measured, and the new pressures measured after equilibrium had again been reached—this often required several days. The results of the investigations at  $-36^\circ$  and  $-45^\circ$  are illustrated in plots *b* and *c* respectively.

(v) *Thermal decomposition (0—400°) of the product of the  $VCl_4-NH_3$  reaction.* After all ammonia had been removed at the reaction temperature (in the tensimetric runs) the mixed product was heated *in vacuo*, in stages, to  $400^\circ$ . Ammonia was lost steadily up to  $200^\circ$ ; then a white sublimate, tinged with pink, began to be formed. The residue at this point was khaki-coloured with a violet tinge. Analysis gave: V, 26.9; Cl, 56.9; N, 16.3%; corresponding to V : Cl : N = 1 : 3.03 : 2.20 (duplicate V, 24.7; Cl, 58.1; N, 14.5%; V : Cl : N = 1 : 3.38 : 2.13). When further heated, to  $400^\circ$ , the substance became blue-black; its analysis gave a V : Cl : N ratio of 2.00 : 1.01 : 1.02. It was pyrophoric, and soluble in nitric acid with the evolution of nitrous fumes, only partly soluble in boiling sodium hydroxide solution, and almost insoluble in dilute sulphuric acid.

#### DISCUSSION

Vanadium(IV) chloride is undoubtedly ammonolysed by liquid ammonia, since not only is the product heterogeneous, but repeated extraction with liquid ammonia leaves an insoluble greenish-brown solid with an analysis close to that expected for  $VCl(NH_2)_3$ . When the initial product is extracted with liquid ammonia, about half of the vanadium dissolves to a greenish-brown solution; although no more dissolves after the first two or three washings, addition of ammonium chloride makes the insoluble residue dissolve. It seems therefore that  $VCl(NH_2)_3$ , or any other ammonobasic vanadium chloride formed, reacts with ammonium chloride produced in the initial reaction to form a soluble substance, and that once the ammonium chloride has been washed away the vanadium compound is insoluble.

An obvious explanation is that a soluble ionic species is formed by complexing of the type:  $VCl(NH_2)_3 + NH_4Cl \longrightarrow [NH_4][VCl_2(NH_2)_3]$ . Such behaviour is confirmed by the demonstration that the insoluble residue can be dissolved equally well by a liquid-ammonia solution of potassium iodide, so that it is a complex-forming action rather than just the effect of an acidic solution (ammonium salts in liquid ammonia). Analysis of the soluble portion of the products (Table 2) shows that the only ammonobasic vanadium(IV) chloride present in the mixture with ammonium chloride is  $VCl(NH_2)_3$ . The formula  $[NH_4][VCl_2(NH_2)_3]$  does not necessarily imply a 5-co-ordinate state for vanadium, and the dimer  $[NH_4]_2[V_2Cl_4(NH_2)_6]$  would, for instance, be equally satisfactory.

The insoluble residue apparently contains a little reduced vanadium, since the average magnetic moment is between 1.9 and 2.0 B.M. This is not entirely unexpected in such a basic solvent as ammonia, and it probably accounts for the apparent difficulty of removing the last traces of ammonium chloride from the insoluble residue, where the V : Cl ratio is still 1 : 1.3 even when the compound has been washed twenty times. Any product involving a lower valency for vanadium formed will probably have a V : Cl ratio greater than 1 : 1 since the V-Cl bond will not be ammonolysed so readily as in vanadium(IV) compounds. The presence of a little trivalent vanadium seems a better explanation for the high V : Cl ratio than the presence of some still undissolved ammonium chloride, since the tensimetric study of the  $VCl(NH_2)_3-NH_3$  system shows that there is no free ammonium chloride in the insoluble residue. Indeed, the ammonium chloride would make some of the insoluble residue soluble. A fairly stable 2-ammoniate  $VCl(NH_2)_3 \cdot 2NH_3$  is however formed, in which the vanadium atom presumably acquires an octahedral configuration. The insolubility of the ammonobasic vanadium(IV) chloride in liquid ammonia and other solvents with which it does not react suggests that it is highly polymeric. This polymeric nature is not incompatible with the ready complex-formation by potassium iodide and ammonium salts, in view of the similar reactions shown by the polymeric halides of mercury(II) and palladium(II).\*

The tensimetric study of the vanadium(IV) chloride-ammonia system at  $-36^\circ$  and  $-45^\circ$  shows that two free molecules of ammonium chloride are produced by the ammonolysis of each molecule of vanadium(IV) chloride. In the tensimetric approach, the ammonium chloride is detected because it forms a triammoniate with a characteristic dissociation pressure, so that if any ammonium chloride undergoes complex-formation with the ammonobasic vanadium(IV) chloride, it will no longer be detected. Thus the reaction gives an initial mixture of  $VCl(NH_2)_3$  and ammonium chloride, which then undergoes complex-formation:



Only the two non-complex-forming ammonium chloride molecules are then detected. While the tensimetric studies show that between eight and nine molecules of ammonia are associated with each molecule of vanadium(IV) chloride at  $-36^\circ$ , the equation shown above accounts for only six of these; the remaining two or three are weakly associated with the vanadium species.

Since washing experiments show that  $VCl(NH_2)_3$  is the only ammonobasic vanadium(IV) chloride formed in the reaction, the tensimetric results cannot be interpreted as the formation of a mixture of  $VCl_2(NH_2)_2$  with  $2NH_4Cl$  (which reacts further only when the ammonium chloride is removed on washing).

When the tensimetric mixture is thermally decomposed, it loses ammonia, and around  $200^\circ$  ammonium chloride sublimes. In view of the high V : Cl ratio (1 : 3) found for the involatile product, it seems that there must be some interaction between the ammonobasic vanadium(IV) chloride and ammonium chloride, similar to that proposed for the tin(IV) chloride-ammonia system.<sup>9</sup> The decomposition is unfortunately too complicated for detailed study.

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\* We are grateful to a Referee for pointing this out.

<sup>9</sup> Bannister and Fowles, *J.*, 1958, 751.