399. *Amine Compounds of the Transition Metals. Part II.*[1] *The Reaction of Niobium Pentachloride with Some Aliphatic Amines.*

By G. W. A. Fowles and C. M. Pleass.

The reaction of niobium pentachloride with dimethylamine at −78° and room temperature, and with mono- and tri-methylamine at room temperature, has been investigated and shown to give $NbCl_3(NMe_2)_2,NHMe_2$, $NbCl_2(NHMe)_3$, and $NbCl_5,2NMe_3$ respectively. In nitrobenzene solution, $NbCl_3(NMe_2)_2,NHMe_2$ has been shown to dissociate into $NbCl_3(NMe_2)_2$ and $NHMe_2$; and $NbCl_2(NHMe)_3$ is found to be largely dimeric. The mechanism of the reactions is discussed.

An investigation of the reaction of transition-metal halides with ammonia has been extended recently [1] to some of the corresponding halide–amine reactions, where the products should be more amenable to structural investigation (*e.g.*, molecular-weight measurements). Fewer hydrogen atoms are directly attached to the nitrogen atom in the amines than in ammonia, and the substances formed should be less polymeric.

For the reaction of niobium pentachloride with ammonia Fowles and Pollard [2] have made a tensimetric study over the temperature range −36° to −63°, and concluded that the overall reaction is given by:

$$NbCl_5 + 4NH_3 \longrightarrow NbCl_3(NH_2)_2 + 2NH_4Cl$$

both the amidochloride and the ammonium chloride taking up loosely held ammonia in addition. There has, however, been no previously reported examination of the reaction of niobium halides with amines, where we would expect some of the halogen atoms to be replaced by amine residues, and in this paper we describe the results of an investigation of the reaction of the pentachloride with mono-, di-, and tri-methylamine.

Experimental

Preparation of Materials.—Niobium pentachloride was prepared by the reaction of dry chlorine on powdered niobium metal (previously treated *in situ* with hydrogen to reduce any oxide) at 400°, and purified by sublimation.[3] It was stored under nitrogen in about 1 g. quantities in sealed tubes, part of the sealed tube consisting of an extended B14 joint. The purity of the chloride was confirmed by analysis (Found: Nb, 34·55; Cl, 66·0. Calc. for $NbCl_5$: Nb, 34·5; Cl, 65·5%).

For the amines see Part I.[1]

Analysis.—The chlorine content was determined by titration with mercuric nitrate solution, with diphenylcarbazone as indicator.[4] Amine was determined by distillation from sodium hydroxide solution into excess of standard hydrochloric acid and back-titration with standard sodium hydroxide to B.D.H. 4·5 indicator. Niobium was determined gravimetrically by precipitation of the tannin complex and subsequent ignition to the pentoxide.[5]

Reaction of Niobium Pentachloride with Dimethylamine.—(*a*) A tube of the chloride was scratched with a glass knife near the tip beyond the greased B14 joint and "hot spotted," and the contents were quickly tipped into the reaction vessel against a countercurrent of dry nitrogen (cf. Part I for details of the apparatus). The apparatus was evacuated by a diffusion pump, and 20—30 c.c. of anhydrous dimethylamine were condensed into the reaction vessel, and the resultant solution was filtered into a second vessel. The extraction with dimethylamine was repeated four times, and the off-white solid remaining in the second vessel after the removal of amine at the pump was extracted with chlorobenzene through a sinter-stick into a third vessel. After the removal of the chlorobenzene from the red-brown solution, a brown

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[1] Part I, Fowles and Pleass, *J.*, 1957, 1674.
[2] Fowles and Pollard, *J.*, 1952, 4938.
[3] Alexander and Fairbrother, *J.*, 1949, S223.
[4] Hill, *Chem. and Ind.*, 1954, 852.
[5] Hillebrand, "Applied Inorganic Analysis," Wiley, New York, 2nd Edn., 1953, 603.

solid *product* remained [Found: Nb, 28·35; Cl, 31·7; N, 12·9%; Nb : Cl : N, 1 : 2·93 : 2·95. $NbCl_3(NMe_2)_2,NHMe_2$ requires Nb, 28·0; Cl, 31·0; N, 12·6%].

(*b*) Ampoules of chloride and amine were made up (see Part I); as the contents of the ampoule warmed, the pale yellow colour first appearing faded, but at room temperature it reappeared and changed steadily to deep red. After 24 hr. at room temperature, only a trace of crystalline material remained as a residue. The contents of the ampoules were transferred to the reaction vessel, and after the amine had been thoroughly removed at the diffusion pump the residue was extracted with chlorobenzene; removal of the chlorobenzene *in vacuo* at 40° left a brown solid [Found: Nb, 27·2; Cl, 30·2; N, 13·1%; Nb : Cl : N, 1 : 2·91 : 3·13; *M* in nitrobenzene, 171. Calc. for $NbCl_3(NMe_2)_2,NHMe_2$: *M*, 332]. Another solution of the substance in nitrobenzene was warmed to 40°, stirred and evacuated for 1 hr. through a trap cooled in liquid oxygen; a considerable amount of dimethylamine condensed in the trap, and the nitrobenzene solution remained a clear red-brown, the molecular weight of the residual niobium compound being 304 [*M* for $NbCl_3(NMe_2)_2$, 288]. A further run under identical conditions gave *M* 281 after evacuation. The nitrobenzene solutions were examined on a Gouy-type magnetic balance, and the niobium compound was found to be diamagnetic, corresponding to quinquevalent niobium.

Reaction with Monomethylamine.—The reactants were enclosed in ampoules. The chloride dissolved completely in the amine at room temperature to a very pale yellow solution, which gave an almost white product on removal of the amine. Only a small part of this product was dissolved by chlorobenzene, but three extractions at 40° gave a substance whose analysis corresponded to a Nb : Cl : N ratio of 1 : 1·96 : 2·97. Molecular-weight determinations in nitrobenzene solution gave 411 and 443 in successive experiments [Calc. for $NbCl_2(NHMe)_3$: *M*, 254]. The compound was diamagnetic.

Reaction with Trimethylamine.—The ampoule procedure gave a very pale brown solution and a flocculent buff precipitate, but the amine solution contained a negligible amount of solid and extensive extraction of the buff precipitate with trimethylamine did not yield a significant quantity of material; the buff substance was insoluble in the more usual solvents. Direct analysis of this substance after removal of the amine at the pump gave a Nb : Cl ratio of 1 : 5·0 as might be expected, but the Nb : N ratio ranged from 1 : 1·7 to 1 : 2·2.

DISCUSSION

The reaction between niobium pentachloride and dimethylamine at either −78° or room temperature leads to an " amine-solvated " aminobasic chloride $NbCl_3(NMe_2)_2,NHMe_2$. The reaction can be visualised as proceeding through the initial addition of an amine molecule to the pentachloride, the lone pair electrons of the nitrogen atom being donated into a vacant 4*d*-orbital of the niobium atom:

Nb 

$$NbCl_5 + NHMe_2 \longrightarrow Me_2HN{\rightarrow}NbCl_5$$

Hydrogen chloride is then split out, by a base-catalysed elimination, leaving $Me_2N{\cdot}NbCl_4$, to which another amine molecule becomes co-ordinated, and so on, leading finally to $NbCl_3(NMe_2)_2,NHMe_2$. It seems likely that a third chlorine atom is not split out because dimethylamino-groups would then occupy three of the five trigonal bipyramidal positions (the same configuration as for niobium pentachloride [6] being assumed) and thereby give rise to considerable steric strain. The observed molecular weight of 171 in nitrobenzene solution is consistent with the dissociation $NbCl_3(NMe_2)_2,NHMe_2 \rightleftharpoons NbCl_3(NMe_2)_2 + NHMe_2$, which gives an average molecular weight of 166 for complete dissociation. This free amine in solution has been removed by warming to 40° and evacuation, and the amine has been trapped and identified. The higher molecular weight of the remaining substance (304, 281) compares well with the predicted value (288) for $NbCl_3(NMe_2)_2$ which would remain in solution. The diamagnetism of the compound shows that there has been no reduction of the niobium to a lower valency state.

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[6] Skinner and Sutton, *Trans. Faraday Soc.*, 1940, **36**, 668.

The reaction can then be summarised as :

$$NbCl_5 + 5NHMe_2 = NbCl_3(NMe_2)_2,NHMe_2 + 2NH_2Me_2Cl$$

followed by

$$NbCl_3(NMe_2)_2,NHMe_2 \rightleftharpoons NbCl_3(NMe_2)_2 + NHMe$$

in nitrobenzene.

In the analogous reactions of niobium pentachloride with alcohols and phenols, various workers have succeeded in replacing all five of the chlorine atoms with alkoxy- or phenoxy-residues;[7, 8] Funk and Niederlander[9] isolated $NbCl(OPh)_4$ and $NbCl_2(C_{10}H_7O)_3$ from the reaction with phenol and β-naphthol. We should, of course, expect greater replacement with alcohols than with amines, since protons are more readily lost from the initially co-ordinated alcohol molecule; by analogy, hydrolysis of halides is always more extensive than ammonolysis because of the larger ion-product of water.

With monomethylamine, the reaction again undoubtedly involves initial co-ordination of amine molecules to the chloride, followed by the elimination of hydrogen chloride, giving finally $NbCl_2(NHMe)_3$. Reduction of the niobium is again ruled out by the diamagnetism of the product. It seems reasonable to suppose that the replacement of chlorine atoms by methylamino-groups is able to proceed further than with that by the larger dimethylamino-group; there are, moreover, now two replaceable hydrogen atoms in the co-ordinated amine. The molecular weights of 411 and **443** suggest that the molecule is present largely as a dimer, $[NbCl_2(NHMe)_3]_2$ (Required : *M*, 508), although an equilibrium is more probable. Higher polymers may well be present in this original product, although it is unlikely that such compounds would be extracted by the chlorobenzene in the isolation process. The dimerisation is not unexpected, since it enables the niobium atom to achieve an octahedral configuration; a bridging by two methylamino-groups seems more probable than a Nb–Nb link. Bridging by two chlorine atoms, as in Al_2Cl_6 and many platinum and palladium complexes, is of course possible, but it is less likely. Bridging by methylamino-groups may readily arise if the amine initially co-ordinated to one niobium pentachloride molecule takes part with another of the latter in the elimination of hydrogen chloride.

On reaction of trimethylamine with niobium pentachloride the products are unfortunately not separable. It may well be that a simple co-ordination compound $NbCl_5,2NMe_3$ is formed, at least in part, although studies on the formation of alkyls from niobium pentachloride and hydrocarbons, where hydrogen chloride appears to be liberated (see Cotton[10] for a critical review), suggest that some replacement could take place. The overall ratio Nb : Cl : N of approximately 1 : 5 : 2 only tells us that the maximum possible overall replacement must be of one chlorine atom, to give $NbCl_4NMe_2$ plus some chlorinated amine or tetramethylammonium chloride (see Part I).

Reduction to a lower valency state (cf. vanadium; Part I) is rather unlikely since a two-electron change to the tervalent state would be necessary—the quadrivalent state is unstable.

Replacement of chlorine in niobium pentachloride certainly does not proceed further than one stage with trimethylamine, but with dimethylamine two and with monomethylamine three chlorine atoms can be replaced by amine residues in reactions at room temperature. This can be attributed in part to steric requirements and, in part, to the greater ease of removal of hydrogen chloride as more hydrogen atoms are present on the nitrogen.

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[7] Bradley, Chakravati, and Wardlaw, *J.*, 1956, 2381.
[8] Funk and Baumann, *Z. anorg. Chem.*, 1937, **231**, 264.
[9] Funk and Niederländer, *Ber.*, 1928, **61***B*, 249.
[10] Cotton, *Chem. Rev.*, 1955, **55**, 551.