5. *The Reaction of Molybdenum*(V) *Chloride with Some Aliphatic Amines.*

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The reaction of molybdenum(V) chloride with a number of primary (NH_2R; R = Me, Et, Pr^n, and Bu^n), secondary (NHR_2; R = Me, Et, and Pr^n), and tertiary amines (NR_3; R = Me and Et) has been studied. Whereas the tertiary amines only formed simple adducts, the secondary and primary amines normally caused aminolysis of the molybdenum–chlorine bonds. In most cases the aminobasic molybdenum(V) chlorides have been isolated from the reaction products by extraction with benzene: *e.g.*, $MoCl_2(NHPr^n)_3$, $MoCl_3(NHBu^n)_2,NH_2Bu^n$, $MoCl_3(NMe_2)_2,NHMe_2$, $MoCl_3(NEt_2)_2$, and $MoCl_3(NPr^n{}_2)_2$.

It is known that covalent transition-metal halides are solvolysed when they react with liquid ammonia [1] or with primary or secondary amines.[2] Further, the degree of solvolysis usually decreases along the series NH_3, NH_2R, NHR_2, and the products become increasingly soluble in organic solvents; while the latter property is largely a function of the number of alkyl groups, it may also be a reflection of the formation of less polymeric products. On the other hand, simple addition compounds are usually formed between the halide and tertiary aliphatic amines,[3] although in some instances [4] the metal is reduced to a lower valency state on prolonged reaction.

Comparatively little is known of the reaction of covalent molybdenum halides with ammonia and amines. Thus cursory studies suggest that ammonolysis occurs when molybdenum(V) chloride reacts with gaseous [5] or liquid ammonia,[6] but the extent of ammonolysis is unknown. Malowan's observations [7] on the reaction of molybdenum(V) chloride with aniline and *o*-toluidine, on the other hand, are of little value because the studies were made in ethanolic solution, so that extensive solvolysis must have occurred before the amines were added. From the reaction of molybdenum(V) chloride with pyridine, Wardlaw and Webb [8] obtained several compounds of formula $MoCl_4,x$Py (with $x = 3$, 4, and 5), in which the molybdenum atom was in a lower valency state; but the precise nature of these compounds is unknown.

In view of the sparsity of information on molybdenum–nitrogen compounds, we are making a systematic study of a number of molybdenum(V) chloride–amine systems, and in this paper we report the results of work with several primary, secondary, and tertiary aliphatic amines.

Experimental

Materials.—Molybdenum(V) chloride was prepared by the action of dry chlorine on molybdenum powder (99·9%, Messrs. Johnson, Matthey & Co. Ltd.) at 350°, and purified by sublimation (Found: Mo, 35·1; Cl, 64·6. Calc. for $MoCl_5$: Mo, 35·1, 64·9%). The amines were purified as described previously.[2] All solvents were dried over phosphoric oxide before use.

Analysis.—Analyses were carried out wherever possible; when the products were inseparable mixtures, they were usually hydrolysed *in situ* to eliminate the risk of taking a non-representative sample, so that only a Mo : Cl : N ratio is reported. Molybdenum was determined

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[1] Fowles and Osborne, *J.*, 1959, 2275.
[2] Drake and Fowles, *J.*, 1960, 1498.
[3] Carnell and Fowles, *J.*, 1959, 4113.
[4] Fowles and Pleass, *J.*, 1957, 1674.
[5] Uhrlaub, *Pogg. Annalen*, 1857, **101**, 605.
[6] Bergström, *J. Amer. Chem. Soc.*, 1925, **47**, 2317.
[7] Malowan, *Arch. Pharm.*, 1930, **268**, 537.
[8] Wardlaw and Webb, *J.*, 1930, 2100.

by oxidation to the sexivalent state, followed by reduction with mercury [9] to the quinquevalent state and final titration with cerium(IV) sulphate, ferroin being used as indicator. Chlorine was determined by potentiometric titration with silver nitrate solution, by means of a Cambridge Electro-Titration apparatus. The amine was determined by the Kjeldahl procedure.

Magnetic-susceptibility Measurements.—These were made at room temperature by Gouy's method, at a field strength of 8000 gauss. We estimate the accuracy of our measurements on solids to be of the order ±0·3 B.M.

Molecular-weight measurements were made cryoscopically on benzene solutions, a modified form of the apparatus described previously [4] being used. Conductivity measurements were made in triply-distilled nitrobenzene that had been dried over phosphoric oxide.

Methods.—Reactions between molybdenum(V) chloride and the various amines were studied in the usual type of closed, all-glass vacuum-apparatus.[4] Initial experiments were carried out in a detachable jointed tube with stopcock. Excess of amine was condensed on to a known amount of molybdenum(V) chloride, and after about an hour at room temperature (constant shaking) the excess of amine was taken off *in vacuo* and the vessel reweighed.

Molybdenum(V) chloride was also sealed in ampoules with excess of the various amines and allowed to react for some weeks. The ampoules were then opened, the excess of amine was distilled off, and the residue analysed. Where the analysis suggested that the products might be mixtures of aminolysis products, separations were attempted by extracting the products with various organic solvents.

The reactions between molybdenum(V) chloride and mono-, di-, and tri-methylamine were also studied by passing the amine vapour (in a stream of oxygen-free nitrogen) into a solution of the chloride in carbon tetrachloride. In each case two products appeared to be formed; that which was formed initially changed colour when excess of amine was passed. The initial product was isolated by stopping the flow run at the appropriate stage.

(*a*) *Reaction of molybdenum*(V) *chloride with methylamine.* A greenish-brown solid and a brown solution were formed in the initial experiments, and the solid remaining after the removal of methylamine at room temperature had the overall composition $MoCl_5,5NH_2Me$ (Found: $MoCl_5 : NH_2Me = 1{\cdot}00 : 5{\cdot}02$; $1{\cdot}00 : 5{\cdot}00$). The product was heated *in vacuo* and liberated gases were trapped and identified at all temperature stages (cf. table). Above 200° hydrogen chloride was liberated and methylamine hydrochloride sublimed away.

	Temp.	25°	50°	100°	150°	200°
Amine remaining (moles/mole $MoCl_5$)	Run 1	5·02	4·96	4·65	4·10	3·91
	Run 2	5·00	4·84	4·73	4·15 *	

* Confirmed by analysis.

The paramagnetic greenish solid obtained from the ampoule reactions was $MoCl_5,7NH_2Me$ (Found: $Mo : Cl : N = 1{\cdot}00 : 5{\cdot}10 : 6{\cdot}90$; $1{\cdot}00 : 5{\cdot}00 : 7{\cdot}15$; $\mu = 2{\cdot}09$ B.M.). Although the overall analysis suggested that this product was a mixture of aminolysis products, we have been unable to find any solvent that will extract either component—benzene, 2,2,4-trimethylpentane, chlorobenzene, and methyl cyanide have been tried.

In the flow-run experiments a dark green solid was formed at first, but this became olive-green with excess of methylamine [Found (for dark green *product*): $Mo : Cl : N = 1{\cdot}00 : 4{\cdot}80 : 1{\cdot}16$; $\mu = 1{\cdot}98$ B.M. Found (for olive-green *product*): Mo, 28·4; Cl, 52·0; N, 7·96%; $\mu = 1{\cdot}74$ B.M. $MoCl_5,2NH_2Me$ requires Mo, 28·6; Cl, 52·9; N, 8·34%].

(*b*) *Reaction of molybdenum*(V) *chloride with other primary amines.* These were all carried out by the ampoule procedure. Molybdenum(V) chloride reacted with excess of ethylamine, n-propylamine, and n-butylamine to form brown solutions, from which a brown solid was obtained on removal of excess of amine. Analysis of the *product* of the ethylamine reaction gave: Mo, 17·3; Cl, 31·6; N, 15·5 ($MoCl_5,6NH_2Et$ requires Mo, 17·6; Cl, 32·6; N, 15·5%). Although the usual solvents were tried, no component of the mixture could be extracted.

Excess of amine was only slowly removed from the products of the n-propylamine and n-butylamine reactions, so that, although the overall composition approached $MoCl_5,6NH_2R$ in each case, this only represented the possible upper limit; thus previous work [10, 11] has shown that in reactions of this kind viscous solutions are formed, and all the free amine may not be removed

[9] Furman and Murray, *J. Amer. Chem. Soc.*, 1936, **58**, 1689.

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

[11] Bannister and Fowles, *J.*, 1959, 310.

even on prolonged pumping. The products of both reactions partly dissolved in benzene, the butylamine product being much more soluble. The aminobasic molybdenum(v) chloride $MoCl_2(NHPr^n)_3$ was first extracted from the n-propylamine *product* {Found: Mo, 27·1; Cl, 20·0; N, 12·1%; *M* (in 1·6% solution), 706. $[MoCl_2(NHPr^n)_3]_2$ requires Mo, 28·1; Cl, 20·8; N, 12·3%; *M*, 682}; it had m. p. 74° (decomp.). Even after some three washes with 50 ml. of benzene the residue was still somewhat soluble in benzene, and smaller amounts of a different compound, probably $MoCl_3(NHPr^n)_2,NH_2Pr^n$, could be extracted (Found: Mo : Cl : N = 1·00 : 3·00 : 2·68).

The molybdenum *component*, m. p. 128° (decomp.), of the n-butylamine reaction was very soluble in benzene [Found: Mo, 22·6; Cl, 24·9; N, 10·4. $MoCl_3(NHBu^n)_2,NH_2Bu^n$ requires Mo, 22·9; Cl, 25·4; N, 10·0%]. A white residue of n-butylamine hydrochloride remained (Found: N, 11·7; Cl, 32·3. Calc. for $C_4H_{12}NCl$: N, 12·7; Cl, 32·3%).

(c) *Reaction of molybdenum*(v) *chloride with dimethylamine.* The brown solid obtained from the initial reaction had an overall composition close to $MoCl_5,3NHMe_2$ (Found: $MoCl_5$: $NHMe_2$ = 1·00 : 3·04). 1—2 Moles of dimethylamine hydrochloride sublimed away at 200°, leaving a brown residue of composition Mo : Cl : N = 1·00 : 3·20—3·60 : 1·30—1·60.

The product of several months' reaction in ampoules had the overall composition $MoCl_5,5NHMe_2$ (Found: Mo : Cl : N = 1·00 : 5·00 : 5·08). Part of this compound was sparingly soluble in benzene [Found: Mo : Cl : N = 1·00 : 3·10 : 3·06; *M* (in 0·11% solution), 274. $MoCl_3(NMe_2)_2,NHMe_2$ requires *M*, 336] and had m. p. 162° (decomp.).

In flow experiments, the light brown solid formed at first became very dark brown with excess of amine [Found (for the light brown *product*): Mo, 29·8; Cl, 55·0; N, 3·9. $MoCl_5,NHMe_2$ requires Mo, 30·1; Cl, 55·7; N, 4·4%. Found (for the dark brown *product*): Mo, 26·4; Cl, 49·2; N, 7·6. $MoCl_5,2NHMe_2$ requires Mo, 26·4; Cl, 48·8; N, 7·7%].

(d) *Reaction of molybdenum*(v) *chloride with other secondary amines.* Reactions with diethylamine and di-n-propylamine were carried out in ampoules, and gave products with overall compositions $MoCl_5,4NHR_2$ [Found (for the $NHEt_2$ *product*): Mo : Cl : N = 1·00 : 5·00 : 3·99. Found (for the $NHPr^n{}_2$ *product*): Mo, 13·6; Cl, 26·8; N, 8·3. $MoCl_5,4NHPr^n{}_2$ requires Mo, 14·1; Cl, 26·2; N, 8·3%]. The aminobasic molybdenum(v) chlorides $MoCl_3(NR_2)_2$ were extracted from the products with benzene {Found (for the $NHEt_2$ *product*): Mo, 26·9; Cl, 30·0; N, 8·15%; *M* (in 0·75% solution), 681. $[MoCl_3(NEt_2)_2]_2$ requires Mo, 27·7; Cl, 30·7; N, 8·1%; *M*, 693. Found (for the $NHPr^n{}_2$ *product*): Mo, 23·5; Cl, 26·3; N, 7·0%; *M* (in 0·87% solution), 775. $[MoCl_3(NPr^n{}_2)_2]_2$ requires Mo, 23·8; Cl, 26·4; N, 7·0%; *M*, 805}; m. p.s (decomp.) were 147° and 206° respectively.

(e) *Reaction of molybdenum*(v) *chloride with tertiary amines.* The slow reaction with trimethylamine (several days) gave a black solid [Found: Mo, 29·4; Cl, 54·5; N, 4·25%; *M* (in 0·13% solution), 294. $MoCl_5,NMe_3$ requires Mo, 28·9; Cl, 53·4; N, 4·2%; *M*, 332], with μ = 1·80 B.M. This *compound*, m. p. 69° (decomp.), gave a non-conducting solution in nitrobenzene. When ampoules were left for 6 months or more, a brick-red solid was formed, having μ = 1·85 B.M.; m. p. 156° (decomp.) (Found: Mo, 25·2; Cl, 45·4; N, 7·2. $MoCl_5,2NMe_3$ requires Mo, 24·5; Cl, 45·3; N, 7·2%). The *compound* is insoluble in nitrobenzene. In flow runs, a black solid (Mo : Cl : N = 1·00 : 4·75 : 0·85) was formed at first, but this became brick-red with excess of amine (Found: Mo : Cl : N = 1·00 : 4·80 : 1·80); it had μ = 1·95 B.M.

Molybdenum(v) chloride and triethylamine reacted to form a dark brown product, m. p. 178° (decomp.) [Found: Mo, 25·5; Cl, 48·0; N, 3·7%; *M* (in 0·18% solution), 407. $MoCl_5,NEt_3$ requires Mo, 25·6; Cl, 47·3; N, 3·7%; *M*, 374].

(f) The molecular weight of molybdenum(v) chloride in benzene was found to be 289 in 0·15% solution (Calc. for $MoCl_5$: *M*, 273).

DISCUSSION

Recent *X*-ray work [12] has shown solid molybdenum(v) chloride to be dimeric with chlorine–chlorine bridges giving the molybdenum atom an octahedral configuration, but in benzene solution it is monomeric and presumably has the same trigonal–bipyramidal structure as the vapour. It is also likely to be monomeric in carbon tetrachloride, so that reactions of the chloride with amines will occur more readily in the flow runs than in the ampoule reactions where the amine has to break down the solid lattice.

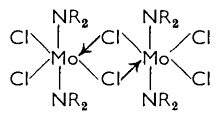
[12] Zalkin and Sands, *Acta Cryst.*, 1959, **12**, 723.

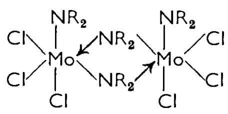
Thus trimethylamine reacts very rapidly with a solution of the chloride, giving first $MoCl_5,NMe_3$ and subsequently $MoCl_5,2NMe_3$; the same compounds are formed in the ampoule reactions, albeit more slowly: triethylamine gives only $MoCl_5,NEt_3$. In neither of the 1 : 1 compounds has molybdenum been reduced to a lower valency state, and in view of the monomeric nature of these compounds in benzene, and of the non-conducting solutions they form in nitrobenzene, it is apparent that they are simple adducts containing a co-ordinate $Mo \leftarrow N$ bond and six-covalent molybdenum. $MoCl_5,2NMe_3$, which is analogous to $MoCl_5,2OEt_2$,[8] may also be a simple adduct, and as such it would be readily formed in the flow runs; the slowness of the reaction in ampoules could be caused by the insolubility of the 1 : 1 adduct in liquid trimethylamine. The alternative formulations are less attractive. Thus ionisation, giving $[MoCl_4(NMe_3)_2]^+Cl^-$, would be unlikely to occur in the flow runs, and aminolysis is also improbable, since it requires the breaking of a strong nitrogen–carbon bond; *e.g.*, $MoCl_5,2NMe_3 = MoCl_4(NMe_2) + NMe_4Cl$. In view of the magnetic-susceptibility measurements it also seems that reduction has not occurred to any appreciable extent. It is unfortunate that the insolubility of this compound precludes further investigations.

Simple adducts again appear to be formed initially in the reactions of molybdenum(V) chloride with secondary and primary amines, since $MoCl_5,NHMe_2$ and $MoCl_5,NH_2Me$ have been isolated in flow runs. The secondary and primary amine reactions differ from the tertiary ones, however, in that solvolysis may subsequently occur very readily indeed. Because the amine concentration in the solution remains low in the flow runs, the replacement appears to stop at the first stage; the compounds ($MoCl_5$,2Amine) isolated when an excess of amine is passed in are presumably the mixtures $MoCl_4(NMe_2) + NHMe_2,HCl$ and $MoCl_4(NHMe) + NH_2Me,HCl$. With an excess of liquid amine, further replacement takes place.

The ultimate products of the prolonged reaction of molybdenum(V) chloride with dimethylamine, diethylamine, and di-n-propylamine have the overall compositions $MoCl_5,5NHMe_2$, $MoCl_5,4NHEt_2$, and $MoCl_5,4NHPr^n_2$, respectively, but these products are aminolytic mixtures from which we have been able to extract with benzene the amino-basic molybdenum(V) chlorides $MoCl_3(NMe_2)_2,NHMe_2$, $MoCl_3(NEt_2)_2$, and $MoCl_3(NPr^n_2)_2$. The dimethylamine product is monomeric, showing that the molybdenum atom achieves a co-ordination number of six through the co-ordination of a mole of dimethylamine [cf. $NbCl_3(NMe_2)_2,NHMe_2$ [13]]. However, the diethylamine and di-n-propylamine products have no co-ordinated amine, even though these higher amines are stronger bases than dimethylamine,[14] but the molybdenum atoms nevertheless attain an octahedral configuration through dimerisation. We have no direct evidence on whether the bridging is through chlorine atoms or amino-groups, and although structure (*A*) gives the more symmetrical structure, structure (*B*) is perhaps more likely since, as a Referee pointed out, the chlorine bridging in molybdenum(V) chloride breaks down in benzene solution. For the analogous alkoxy-compounds $[MoCl_3(OR)_2]_2$ Bradley *et al.*[15] favour bridging through alkoxy-groups. Larson,[16] on the other hand, who prepared analogous but polymeric compounds $[MoCl_3(O{\cdot}CO{\cdot}R)_2]_n$ by the reaction of solutions of molybdenum(V) chloride in carbon tetrachloride with several monocarboxylic acids, suggests that the chlorine–chlorine bridging of the solid chloride remains intact throughout the reaction. Since molybdenum(V) chloride is monomeric in solution, it is clear that Larson's mechanism is incorrect.

(*A*)





(*B*)

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

[14] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

[15] Bradley, Multani, and Wardlaw, *J.*, 1958, 4647.

[16] Larson, *J. Amer. Chem. Soc.*, 1960, **82**, 1223.

When the reaction between molybdenum(v) chloride and dimethylamine is allowed to proceed for only a few hours, the product has the overall composition $MoCl_5,3NHMe_2$. This compound is probably the same as that formed in the flow runs with excess of amine, except that the molybdenum compound has taken up a mole of amine. The aminobasic molybdenum(v) chloride would be a good electron-acceptor, and the co-ordinated amine remains firmly attached on heating *in vacuo*, although decomposition sets in above 200°:

$$2MoCl_4(NMe_2),NHMe_2 \longrightarrow MoCl_4(NMe_2) + MoCl_3(NMe_2)_2 + \underbrace{NHMe_2 + HCl}_{\substack{\downarrow \\ NHMe_2,HCl}}$$

The dimethylamine and hydrogen chloride combine on the cooler parts of the reaction vessel, making a total sublimate of 1—2 moles of dimethylamine hydrochloride, and leaving a mixture of aminobasic molybdenum(v) chlorides.

The product of the molybdenum(v) chloride–methylamine reaction, $MoCl_5,7NH_2Me$, is again undoubtedly a mixture of aminolytic products, although we have been unable to effect a separation. The magnetic-susceptibility measurements show that molybdenum is still quinquevalent, and since the degree of solvolysis must be at least as great as that with dimethylamine, the overall formula must correspond to the replacement of either two or three chlorine atoms:

$$\text{(i)}\ MoCl_3(NHMe)_2,3NH_2Me + 2NH_2Me,HCl$$
$$\text{(ii)}\ MoCl_2(NHMe)_3,NH_2Me + 3NH_2Me,HCl$$

In the initial experiments $MoCl_5,5NH_2Me$ was formed. When heated *in vacuo* to 200° this compound liberated only one mole of amine, which is in agreement with the composition $MoCl_3(NHMe)_2,NH_2Me + 2NH_2Me,HCl$, but inconsistent with any other mixture. It therefore seems likely that two chlorine atoms are replaced easily in the initial experiments, and that the third is only slowly aminolysed, giving the mixture (ii).

Ethylamine evidently reacts with molybdenum(v) chloride in the same way as methylamine, except that the aminobasic molybdenum(v) chloride no longer adds on a mole of amine:

$$\textit{i.e.},\ MoCl_5,6NH_2Et = MoCl_2(NHEt)_3 + 3NH_2Et,HCl.$$

n-Propylamine forms a mixture of molybdenum compounds, and $MoCl_2(NHPr^n)_3$ and $MoCl_3(NHPr^n)_2,NH_2Pr^n$ have been extracted from the reaction product. The first compound is dimeric in benzene solution. In the butylamine–molybdenum(v) chloride reaction the product is a simple mixture $MoCl_3(NHBu^n)_2,NH_2Bu + 2NH_2Bu^n,HCl$, from which the aminobasic molybdenum(v) chloride can be completely extracted with benzene.

The reactions of molybdenum(v) chloride with the primary amines thus show an interesting sequence in which the aminolysis decreases from methylamine to n-butylamine. Thus three molybdenum–chlorine bonds are solvolysed in methylamine and ethylamine, but the replacement of the third chlorine atom is only partly complete with n-propylamine and does not take place at all in n-butylamine. This decreasing solvolysis is a reflection of the decreasing ionising power of the amine solvents.

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