

250. The Reaction of Tungsten(VI) Chloride with Some Aliphatic Amines.

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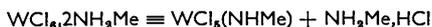
Tungsten(VI) chloride reacts with several primary (NH_2R where $\text{R} = \text{Me}$, Et , Pr^n , or Bu^n), secondary (NHMe_2 , NHEt_2), and tertiary (NMe_3 and NEt_3) amines under a variety of conditions. Aminolysis occurs with primary amines, and aminobasic tungsten(VI) chlorides, $\text{WCl}_2(\text{NHR})_4$, have been isolated from the reactions with propylamine and butylamine; analogous compounds are believed to be present in the products formed by methylamine and ethylamine. With secondary amines, initial co-ordination of amine is followed by reduction, giving the quadrivalent tungsten complex salts, $(\text{NH}_2\text{R}_2)_2[\text{WCl}_6]$; aminolysis then produces the compounds $\text{WCl}_3(\text{NR}_2)_2 \cdot 2\text{NHR}_2$. Tertiary amines also appear to give adducts, $\text{WCl}_6 \cdot \text{NR}_3$, initially, but subsequent reaction again leads to the production of quadrivalent tungsten complexes, $(\text{NHR}_3)_2[\text{WCl}_6]$.

HALIDES of transition metals in their higher valency states usually undergo solvolysis with primary and secondary amines, but form addition compounds with tertiary amines. When the metal is fairly easily reduced, *e.g.*, titanium,¹ tertiary amines often lower the oxidation state. Such reactions, which have been studied for a number of transition-metal halides,² have now been extended to tungsten(VI) chloride.

Reactions of tungsten(VI) chloride with primary aliphatic amines are reasonably straightforward, since in every case tungsten remains in the hexivalent state. With both propyl- and butyl-amine, prolonged reaction leads to the aminolysis of four tungsten-chlorine bonds:



These diamagnetic compounds are monomeric in benzene solution and evidently contain octahedrally bonded tungsten. Reaction with butylamine is complete only after several months, and products obtained for relatively short reaction periods (2—9 weeks) appear to be mixtures of compounds $\text{WCl}_2(\text{NHBu}^n)_4$ and $\text{WCl}_3(\text{NHBu}^n)_3$. While aminolytic mixtures are unquestionably formed with ethylamine and methylamine, no separation can be effected. In view of the overall compositions of the mixtures, $\text{WCl}_6 \cdot 8\text{NH}_2\text{Et}$ and $\text{WCl}_6 \cdot 9\text{NH}_2\text{Me}$, and by comparison with the propylamine and ammonia reactions, it is probable that the tungsten components are again $\text{WCl}_2(\text{NHR})_4$, although in the case of methylamine it is necessary to assume that a mole of amine is associated with the compound. In an effort to isolate products showing an intermediate degree of aminolysis, methylamine vapour was passed through a solution of tungsten(VI) chloride. Two diamagnetic products of overall composition $\text{WCl}_6 \cdot n\text{NH}_2\text{Me}$ ($n = 2$ and 4) were successively formed, and by analogy with the corresponding reaction with ammonia it is likely that these are mixtures corresponding to the first two aminolytic stages:



No separations could, however, be effected.

Prasad and Krishnaiah³ found that tungsten(VI) chloride with primary aromatic amines gave products of overall composition $\text{WCl}_6 \cdot 6\text{Amine}$, to which they assign ionic structures $[\text{W}(\text{Amine})_6]\text{Cl}_6$. These products are more likely to be aminobasic mixtures than to contain such tungsten cations, since hexivalent tungsten has little basic character.

¹ Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

² See Edwards and Fowles, *J.*, 1961, **24**, for earlier references.

³ Prasad and Krishnaiah, *J. Indian Chem. Soc.*, 1960, **37**, 588.

Solvolytic reactions with phenols and naphthols⁴ give compounds $WCl_2(OR)_4$, although complete replacement is possible under suitable conditions to give $W(OR)_6$. This is consistent with the general observation that phenols and alcohols bring about a more extensive solvolysis of halides than do amines.

The reactions of the secondary aliphatic amines are somewhat complicated by the reduction of tungsten to lower valency states. Thus, while a simple adduct ($WCl_6, NHMe_2$) seems to be formed initially in flow runs, an excess of either dimethylamine or diethylamine at room temperature (in ampoules) produces lower-valent tungsten compounds. Analysis of the benzene-soluble aminobasic tungsten chlorides cannot differentiate between $WCl_3(NR_2)_2, NHR_2$ and $WCl_3(NR_2), 2NHR_2$, which would contain quinquevalent and quadrivalent tungsten, respectively. However, the magnetic moments of the products (1.86 B.M. for $R = Me$, and 1.92 B.M. for $R = Et$) favour the quadrivalent compound, in view of Kotani's observation⁵ that spin-orbit coupling should result in magnetic moments for octahedral d_{e^2} complexes of quadrivalent tungsten appreciably less than that predicted by the spin-only formula. Further, the solutions formed by the compounds in concentrated hydrochloric acid contain quadrivalent tungsten, since their absorption spectra show peaks at 515–520 $m\mu$.⁶ Bradley and his co-workers⁷ also observe the formation of quadrivalent tungsten compounds in the reaction of tungsten(VI) chloride with diethylamine.

We have also carried out the reactions at low temperatures to isolate products of intermediate stages and obtained high yields of quadrivalent tungsten compounds; these we formulate as salts $[NH_2R_2]_2[WCl_6]$ because of their infrared spectra, which are almost identical with those of the analogous amine hydrochlorides and hexachloroplumbate(IV) salts. The complexes are insoluble in solvents such as nitrobenzene, so that conductivity studies could not be made.

Tungsten(VI) chloride does not react significantly with liquid trimethylamine, although a very slow reaction takes place in the presence of light petroleum. The lack of reaction is evidently a result of the chloride crystals' not being wetted by the amine and the insolubility of products in light petroleum, since when the chloride is dissolved in carbon tetrachloride and amine vapour passed in reaction readily takes place with the initial formation of green compounds of overall composition WCl_6, NR_3 ($R = Me$ or Et). Because of their lack of solubility in all the usual organic solvents, these compounds could not be characterised, but they still contain sexivalent tungsten and, in view of the characterisation² of similar molybdenum compounds ($MoCl_5, NR_3$) as simple adducts, it is probable that the tungsten compounds are also addition compounds.

With an excess of either amine, tungsten is reduced to the quadrivalent state, so that the products cannot be simple adducts $WCl_6, 2NR_3$, as suggested by Prasad and Krishnaiah.⁸ We consider the products to be ionic compounds, $[NHR_3]_2[WCl_6]$, since their infrared spectra show strong absorptions in the N-H stretching region (3100 cm^{-1}) (which must be absent in simple adducts) and are almost identical with those of the analogous complex lead salts and trialkylammonium hydrochlorides.

Both the dimethylammonium and the trimethylammonium salt slowly take up an additional mole of amine if the flow runs are prolonged. The products could not be further characterised but, since the infrared spectrum of the trimethylamine product shows that the trimethylammonium ion is still present, we consider both products as adducts $(NH_2Me)_2[WCl_6], NHMe_2$ and $(NHMe_3)_2[WCl_6], NMe_3$.

The mechanism by which the simple adducts of tungsten(VI) chloride undergo reduction is unknown; we tentatively suggest that co-ordination of a molecule of secondary or

⁴ Funk and Baumann, *Z. anorg. Chem.*, 1937, **231**, 264.

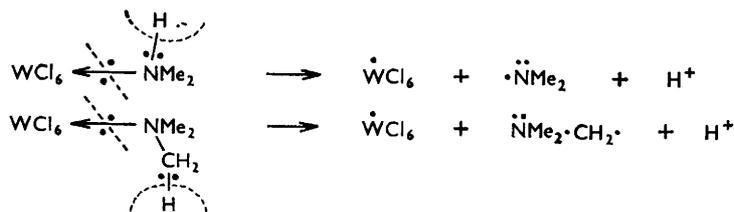
⁵ Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

⁶ Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 83.

⁷ Bradley, personal communication.

⁸ Prasad and Krishnaiah, *J. Indian Chem. Soc.*, 1961, **38**, 182.

tertiary amine (only one shown) to tungsten(vi) chloride is followed by the transfer of an electron from nitrogen to tungsten and the elimination of a proton by the splitting of an N-H (for secondary amines) or C-H (for tertiary amines) bond.



It seems that it is a C-H rather than a C-N bond that is broken with the tertiary amines since trialkylammonium salts are formed rather than tetra-alkylammonium salts. The radicals formed could dimerise or react further with solvent or excess of amine. A second electron transfer would complete the reduction to the quadrivalent state.

Further investigations are under way on these reductions and related ones in which quadrivalent titanium and vanadium and quinquevalent molybdenum undergo reduction with a variety of ligands.

EXPERIMENTAL

The preparation and purification of tungsten(vi) chloride and the various amines, the analytical procedures, and the methods used to determine magnetic susceptibilities and molecular weights were similar to those previously described.⁹ The usual techniques were used to study the reactions and to separate the products. Valency-change titrations were made by treating the product with a known excess of cerium(iv) sulphate solution, and back-titration with iron(II) sulphate solution. Infrared spectra were measured for Nujol mulls on a Unicam SP100 spectrophotometer.

Reaction of Tungsten(vi) Chloride with Methylamine.—This gave a reddish-brown solution, from which a brown diamagnetic solid of overall composition $\text{WCl}_6 \cdot 8 \cdot 8\text{NH}_2\text{Me}$ was obtained by removal of excess of methylamine *in vacuo* at room temperature; about 0.5 mol. of methylamine was removed *in vacuo* at 70°. None of the product dissolved in benzene or chlorobenzene. When methylamine vapour was passed in a nitrogen stream through a solution of tungsten hexachloride in carbon tetrachloride, a green precipitate was formed, but changed to reddish-brown with an excess of amine. Both products were isolated, washed with carbon tetrachloride to remove unchanged tungsten hexachloride, and kept *in vacuo* for several hours (the reddish-brown product became pink); the substance was diamagnetic and contained sexivalent tungsten (Found, for the green product: W, 40.2; Cl, 45.9; N, 6.2. $\text{WCl}_6 \cdot 2\text{NH}_2\text{Me}$ requires W, 40.1; Cl, 46.4; N, 6.1. Found, for the pink product: W, 35.5; Cl, 40.8; N, 10.3%; no valency change. $\text{WCl}_6 \cdot 4\text{NH}_2\text{Me}$ requires W, 35.3; Cl, 40.8; N, 10.7%). The pink product had χ_M^1 120×10^{-6} c.g.s. unit. Neither product dissolved in the usual organic solvents.

Reaction of Tungsten(vi) Chloride with Other Primary Aliphatic Amines.—Removal of the excess of amine from the red-brown solutions gave brown solids of overall composition close to $\text{WCl}_6 \cdot 8\text{NH}_2\text{R}$ (Found: $7.9\text{NH}_2\text{Et}$. $7.7\text{NH}_2\text{Pr}^n$. $7.9\text{NH}_2\text{Bu}^n$). None of the ethylamine product dissolved in the usual organic solvents, but part of the products formed by the two higher amines dissolved in benzene; these soluble portions were shown to be amino-basic tungsten(vi) chlorides. [Found, for the propylamine product: W, 37.5; Cl, 14.2; N, 11.4%; M , 493 (in 0.6% solution). $\text{WCl}_6(\text{NHPr}^n)_4$ requires W, 37.8; Cl, 14.6; N, 11.5%; M , 487. Found, for the butylamine product: W, 33.0; Cl, 12.7; N, 10.2%; M , 566 (in 1.3% solution). $\text{WCl}_6(\text{NHBu}^n)_4$ requires W, 33.8; Cl, 13.1; N, 10.3%; M , 543]. The propylamine and the butylamine product had m. p. 90° and 133–136°, respectively. The latter was diamagnetic. The white benzene-insoluble residue from the butylamine reaction was butylamine hydrochloride (Found: Cl, 32.4. Calc. for $\text{C}_4\text{H}_9\text{NCl}$: Cl, 32.3%). Analysis of the

⁹ Fowles and Osborne, *J.*, 1959, 2275; Fowles and Pleass, *J.*, 1957, 1674.

benzene-soluble component of the butylamine product formed after a relatively short reaction time indicated the presence of $WCl_3(NHBU^a)_3$ as well as $WCl_3(NHBU^a)_4$ [Found: (2 weeks' reaction) W : Cl : N = 1.00 : 2.56 : 3.41; (9 weeks' reaction) 1.00 : 2.15 : 3.74].

Reaction of Tungsten(VI) Chloride with Secondary Aliphatic Amines.—A green product was precipitated initially in flow runs with dimethylamine (Found: W, 41.4; Cl, 48.0; N, 3.3. $WCl_6, NHMe_2$ requires W, 41.6; Cl, 48.2; N, 3.2%). An excess of amine appeared to bring about further reaction, but the product was tarry and could not be isolated. Removal of the excess of diethyl- or dimethyl-amine from the products of several months' reaction (ampoules) left brown tars which partly dissolved in benzene and chlorobenzene [Found, for $NHMe_2$ product: W, 43.3; Cl, 24.2; N, 9.7%; M, 396 (in 0.9% solution). Calc. for $WCl_3(NMe_2)_2, 2NHMe_2$: W, 43.4; Cl, 25.1; N, 9.9%; M, 424]. The dimethylamine product had μ 1.86 B.M. and did not dissolve in water or dilute sulphuric acid but in warm concentrated hydrochloric acid gave a red solution with an absorption peak at 520 μ . The diethylamine product [Found: W, 35.7; Cl, 20.8; N, 8.4%; M, 550 (in 1.2% solution). Calc. for $WCl_3(NEt_2)_2, 2NHEt_2$: W, 36.1; Cl, 21.0; N, 8.25%; M, 509] had μ 1.92 B.M. in benzene and with concentrated hydrochloric acid gave a solution showing an absorption peak at 515 μ .

Reaction with dimethylamine at -34° for 2 hr. gave a different product, which appeared to contain very little of the aminobasic tungsten chloride; washing with dimethylamine or ethanol removed any such material, together with dimethylamine hydrochloride, and left a pink product with μ 1.59 B.M. {Found: W, 37.7; Cl, 43.1; N, 5.8%; valency change, 1.90. $(C_2H_5N)_2[WCl_6]$ requires W, 37.6; Cl, 43.5; N, 5.7%}. Prolonged reaction at -34° or fairly short reaction (24 hr.) at room temperature gave increased amounts of the aminobasic tungsten chloride, and the ethanol-insoluble residue was then buff in colour and had μ 1.69 B.M. {W, 34.5; Cl, 39.6; N, 7.9. $(C_2H_5N)_2[WCl_6], NHMe_2$ requires W, 34.5; Cl, 40.0; N, 7.9%}.

In the analogous reaction with diethylamine, one buff-coloured product was isolated, that had μ 1.59 B.M. [Found: W, 34.1; Cl, 38.8; N, 5.3%; valency change, 1.98. $(C_4H_{12}N)_2WCl_6$ requires W, 33.8; Cl, 39.1; N, 5.1%].

Reaction of Tungsten(VI) Chloride with Trimethylamine and Triethylamine.—No reaction occurred between tungsten hexachloride and liquid trimethylamine, but in the presence of light petroleum (b. p. 60–80°) a slow reaction took place, over a period of months, giving a black solid admixed with a small amount of white solid. These solids were filtered off and the overall composition of the mixture (no separation could be effected) was determined (Found: W, 41.3; Cl, 47.6; N, 2.6%; W : Cl : N = 1.00 : 5.93 : 0.83); it had μ 0.7 B.M.

When flow runs were carried out, a green precipitate was formed initially, but this changed to khaki (yellow when "dry") with an excess of amine, and on very prolonged passage of amine a white product was formed. The three products were isolated and examined (cf. Table).

Flow runs yielded a green and a brown product (cf. Table).

Products of WCl_6-NR_3 flow runs.

Formula	Colour	Found (%)			Required (%)			χ_M^1 (10^6 c.g.s.)	Valency change
		W	Cl	N	W	Cl	N		
<i>Trimethylamine</i>									
WCl_6, NMe_3	Green	39.8	46.4	3.15	40.3	46.7	3.1	153	—
$(C_2H_5N)_2, WCl_6$	Yellow	35.5	40.4	5.6	35.6	41.2	5.4	1045 ^a	1.93
$(C_2H_5N)_2, WCl_6, NMe_3$...	White	32.2	36.5	7.25	31.9	36.9	7.3	852 ^b	1.87
<i>Triethylamine</i>									
WCl_6, NEt_3	Green	36.5	42.6	2.8	36.9	42.7	2.8	48	0.10
$(C_2H_5N)_2, WCl_6$	Brown	32.0	35.9	4.3	30.7	35.4	4.7	766 ^c	1.93

μ : (a) 1.55, (b) 1.44, (c) 1.34 B.M.

None of the trimethylamine or triethylamine products was soluble in benzene, chlorobenzene, or nitrobenzene.

Preparation of Bistrimethylammonium and Bistriethylammonium Hexachloroplumbate.—These salts were prepared by a method analogous to that described¹⁰ for the diammonium salt

¹⁰ Friedrich, *Ber.*, 1893, **26**, 1434.

[Found: Pb, 38.3; Cl, 39.3; N, 5.1. $(C_8H_{10}Cl_6N)_2Pb$ requires Pb, 38.4; Cl, 39.4; N, 5.2.
Found: Pb, 33.6; Cl, 33.8; N, 4.3. $(C_8H_{16}N)_2PbCl_6$ requires Pb, 33.4; Cl, 34.1; N, 4.5%].

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