301. *Amine Compounds of the Transition Elements. Part V.*[1] *The Reaction of Zirconium*(IV) *Chloride with Some Aliphatic Amines.*

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Zirconium(IV) chloride forms simple adducts with a number of secondary and tertiary aliphatic amines, but aminolysis takes place with primary amines. The following aminobasic zirconium(IV) chlorides have been isolated: $ZrCl_2(NHMe)_2,NH_2Me$, and $ZrCl_3(NHR),NH_2R$ (R = Et, Pr^n, and Bu^n). The mechanism of the reactions and the probable structures of the products are discussed.

Reactions of halides of the transition elements in their higher valency states with ammonia and with aliphatic amines have been studied in some detail in recent years.[1,2] Ammonia, and primary and secondary amines, normally solvolyse the halides, to an extent increasing in the order $NHR_2 < NH_2R < NH_3$; with a particular amine (or with ammonia), the amount of solvolysis decreases as the halides become more ionic, *e.g.*, solvolysis is in the order $TiCl_4 > ZrCl_4 > ThCl_4$. Tertiary amines tend to form simple adducts with the halides, although in one or two instances they reduce the metal to a lower valency state. Considerable progress has been made with investigations of the solvolytic reactions of the Group VA halides,[2-5] but less has been reported on the analogous reactions of the Group IVA halides. Thus although the ammonolysis of the chlorides of titanium(IV),[6] zirconium(IV),[7] and thorium(IV) [7] has been studied in some detail, very little is known of the corresponding reactions of these halides with aliphatic amines. With zirconium(IV) chloride, for instance, nothing has been reported * since the work of Matthews in 1898,[9] who observed that compounds of overall composition $ZrCl_4,4NH_2R$ (R = Me, Et, and Pr^n) were formed when amine vapour was passed through solutions of the halide in diethyl ether. We have now examined the reactions of zirconium(IV) chloride with a number of anhydrous primary, secondary, and tertiary aliphatic amines. We have been particularly interested in finding out whether the products are simple adducts or mixtures of aminolytic products.

Experimental

Materials.—Zirconium(IV) chloride was prepared by passing chlorine over pure zirconium metal strip at 400°, and was purified by sublimation. Methylamine was obtained from a 30 w/w aqueous solution by the action of potassium hydroxide pellets; it was dried over freshly crushed barium oxide and finally distilled several times from potassium metal. Other primary and secondary amines, of the purest anhydrous grades commercially available, were repeatedly

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* A detailed discussion of many of our results and others concerned with the aminolysis of halides of titanium, tantalum, molybdenum, and tungsten was given at a seminar held at Birkbeck College on October 9th, 1958. Since then some work has been done on the reactions of titanium(IV), zirconium(IV), and tantalum(V) chloride with lithium dimethylamide and a preliminary report has been published.[8]

[1] Part IV, Carnell and Fowles, *J.*, 1959, 4113.
[2] Fowles and Osborne, *J.*, 1959, 2275.
[3] Fowles and Pleass, *J.*, 1957, 1674.
[4] Fowles and Pollard, *J.*, 1952, 4938.
[5] Fowles and Pleass, *J.*, 1957, 2078; Fowles and Nicholls, *J.*, 1958, 1687.
[6] Fowles and Pollard, *J.*, 1953, 2588.
[7] Fowles and Pollard, *J.*, 1953, 4128.
[8] Bradley and Thomas, *Proc. Chem. Soc.*, 1959, 225.
[9] Matthews, *J. Amer. Chem. Soc.*, 1898, **20**, 815.

distilled *in vacuo* from barium oxide. After reaction with the zirconium(IV) chloride, the amine was usually distilled from the product on to the next sample of halide, thus restricting any hydrolysis (arising from residual traces of moisture) to the first reaction mixture. Tertiary amines were dried *in vacuo* over phosphoric oxide.

Analysis.—Weighed samples of the products were taken for analysis wherever possible, but in a few instances the products adhered very firmly to the sides of the reaction vessel, and they were then hydrolysed *in situ*, so that only analytical ratios were obtained. All products were dissolved in dilute sulphuric acid and aliquot parts taken for analysis. Zirconium was estimated gravimetrically as the oxide, after precipitation as the hydroxide. Chloride was estimated by potentiometric titration with silver nitrate solution. Nitrogen was determined by the Kjeldahl procedure (B.D.H. 4·5 indicator).

Magnetic Susceptibility Measurements.—These were made on a Gouy-type balance at room temperature.

Reactions.—These were carried out in the usual type of all-glass vacuum system.[3] Two experimental procedures were adopted. First, preliminary studies were usually made by condensing a small excess of amine on to a known weight of zirconium(IV) chloride in a detachable jointed tube (complete with stopcock), and removing the excess of amine after a few hours' reaction; the amount of amine remaining in association with the halide was then determined by simple weighing. In a few instances the products were heated at various temperatures for several hours [4] and any liberated amine was estimated. More thorough investigations were then made in which the reactants (a large excess of amine) were sealed in ampoules and allowed to react for quite long periods, ranging from a few weeks to several months. The ampoules were then opened,[3] excess of amine was removed *in vacuo*, and the product remaining analysed to determine its overall composition. Wherever it seemed possible for the product to be an aminolytic mixture, it was extracted with various organic solvents in an attempt to isolate the pure components.

(a) *Reaction of zirconium*(IV) *chloride with tertiary aliphatic amines.* Zirconium(IV) chloride with trimethylamine gave a white solid of overall composition $ZrCl_4,2NMe_3$ (Found: $ZrCl_4,2{\cdot}01NMe_3$; $ZrCl_4,2{\cdot}00NMe_3$), which was stable *in vacuo* to 40°. Above this temperature trimethylamine was slowly lost, and at 100° one mol. of amine was evolved, leaving a brown substance, $ZrCl_4,NMe_3$ (Found: $ZrCl_4,1{\cdot}02NMe_3$); this was stable *in vacuo* up to 200°. Both the di- and the mono-amine complex were diamagnetic. The product of the prolonged reaction in ampoules was also the diamine complex (Found: Zr, 26·5; Cl, 40·6; N, 8·1. $ZrCl_4,2NMe_3$ requires Zr, 26·0; Cl, 40·3; N, 8·0%). The complex was insoluble in trimethylamine.

Even after reaction for several months in ampoules, the only product of the reaction of zirconium(IV) chloride with triethylamine was a brown powder of composition $ZrCl_4,NEt_3$, which was insoluble in benzene (Found: Zr, 27·8; Cl, 42·7; N, 4·2. $ZrCl_4,NEt_3$ requires Zr, 27·4; Cl, 42·3; N, 4·2%).

(b) *Reaction of zirconium*(IV) *chloride with secondary aliphatic amines.* The removal *in vacuo* (several days) of excess of dimethylamine from the product of its reaction with zirconium(IV) chloride left an off-white solid with the composition $ZrCl_4,2NHMe_2$ (Found: $ZrCl_4,1{\cdot}98NHMe_2$; $ZrCl_4,2{\cdot}03NHMe_2$). Even after some days *in vacuo* to 100° the *product* was unchanged (Found, in a different experiment from those quoted above: Zr, 27·7; Cl, 44·1; N, 8·7. $ZrCl_4,2NHMe_2$ requires Zr, 28·2; Cl, 43·9; N, 8·7%). Even when the reactants were allowed to remain together in ampoules for several weeks, the product was still the diamine complex (Found: Zr, 27·8; Cl, 43·1; N, 9·0%). This compound dissolved in dimethylamine but not in benzene.

In the analogous reaction between zirconium(IV) chloride and diethylamine, the weighed-bulb experiments again indicated the formation of a diamine complex (Found: $ZrCl_4,2{\cdot}03NHEt_2$), which lost ethylamine fairly readily when heated *in vacuo*. Thus after some 9 hr. at 100° between 0·5 and 1 mol. of ethylamine was lost (Found: $ZrCl_4,1{\cdot}40NHEt_2$; $ZrCl_4,1{\cdot}25NHEt_2$), and the reddish oily solid changed to a dark red oil. Reaction in ampoules gave yellow crystals and a pale green solution; removal of excess of amine left a brown powder of composition Zr : Cl : N = 1·00 : 3·99 : 2·01. The *product* was soluble in benzene, showing the absence of diethylamine hydrochloride [Found (for the solid left on evaporation of benzene from the solution): Zr, 24·9, 25·0; Cl, 37·8, 37·4; N, 7·3, 7·4. $ZrCl_4,2NHEt_2$ requires Zr, 24·1; Cl, 37·4; N, 7·4%].

Reaction of zirconium(IV) chloride with di-n-propylamine closely resembled that with diethylamine, and the overall composition of the product again corresponded to a diamine complex (Found: Zr : Cl : N = 1·00 : 3·90 : 2·15). The complex was partly soluble in the dipropylamine since filtration of the ampoule contents gave two products, one soluble, one insoluble, of similar composition [Found: Zr : Cl : N = 1·00 : 3·90 : 2·10 (soluble), and 1·00 : 3·91 : 1·98 (insoluble)]. The *product* dissolved completely in benzene and in chlorobenzene, showing the absence of di-n-propylamine hydrochloride, and was recovered unchanged from either solvent (Found: Zr, 21·3; Cl, 32·6; N, 6·25. $ZrCl_4,2NHC_6H_{14}$ requires Zr, 21·0; Cl, 32·6; N, 6·4%).

(c) *Reaction of zirconium*(IV) *chloride with primary aliphatic amines.* When zirconium(IV) chloride was allowed to react with methylamine in a sealed ampoule, the product consisted of yellow crystals and a colourless solution. The overall composition of the product remaining after evaporation of excess of methylamine varied within the range $ZrCl_4,3·9$—$4·9NH_2Me$ and it was evident that the composition $ZrCl_4,4NH_2Me$ was only reached on prolonged evacuation. None of the product dissolved in benzene or chlorobenzene. The contents of the ampoule were filtered, and the yellow crystals washed with fresh methylamine; under a vacuum the crystals crumbled to a white powder [Found: Zr, 36·5; Cl, 28·7; N, 16·85. $ZrCl_2(NH{\cdot}CH_3)_2,NH_2{\cdot}CH_3$ requires Zr, 36·0; Cl, 28·0; N, 16·6%. Zr : Cl : N = 1·00 : 1·92, 1·90 : 2,91, 3·10]. The solid which was obtained by evaporation of the filtrate was almost pure methylamine hydrochloride.

In the analogous reaction with ethylamine, zirconium(IV) chloride dissolved completely to give a colourless solution; a white amorphous powder remained on evaporation of excess of amine (Found: Zr : Cl : N = 1·00 : 3·98, 3·90 : 2·83, 3·14, after evacuation for 7 hr. at room temperature; 1·00 : 3·91, 3·90 : 2·11, 1·98 after evacuation for 7 hr. at 70°). Part of the *product* dissolved in benzene [Found: Zr, 32·3; Cl, 38·0; N, 9·9. $ZrCl_3(NH{\cdot}C_2H_5),NH_2C_2H_5$ requires Zr, 31·8; Cl, 37·1; N, 9·8%]. Other similar products gave Zr : Cl : N = 1·00 : 3·01 : 2·11 and 1·00 : 2·99 : 2·05.

The zirconium(IV) chloride–propylamine reaction was very similar to the ethylamine reaction, except that the excess of propylamine was not quite so easily removed. After being warmed *in vacuo* to 40° for 12 hr. the white product had an overall composition close to $ZrCl_4,3NH_2Pr^n$ (Found: Zr : Cl : N = 1·00 : 3·90 : 3·10), but a mol. of propylamine was lost when the product was heated to 70° for a further 12 hr. (Found: Zr : Cl : N = 1·00 : 3·92, 3·95 : 2·05, 2·01). Part of the initial *product* dissolved in both benzene and chlorobenzene [Found: Zr, 28·2, 29·4; Cl, 34·6, 34,4, N, 8·8, 9·15. $ZrCl_3(NH{\cdot}C_3H_7),NH_2{\cdot}C_3H_7$ requires Zr, 29·0; Cl, 33·8; N, 8·9%]. Similar products from other runs gave Zr : Cl : N = 1·00 : 3·16 : 2·05 and 1·00 : 3·18 : 2·15. The insoluble residue, which contained no zirconium, appeared to be propylamine hydrochloride (Found: N : Cl = 1·00 : 0·93).

The zirconium(IV) chloride–n-butylamine reaction closely resembled the two previously described. The overall composition of the *product* was Zr, 20·3; Cl, 31·5; N, 9·1. ($ZrCl_4,3NH_2{\cdot}C_4H_9$ requires Zr, 20·2; Cl, 31·3; N, 9·3%). This product lost a mol. of amine in 12 hr. *in vacuo* to 70° (Found: Zr : Cl : N = 1·00 : 3·96 : 2·07). The benzene-soluble portion gave Zr : Cl : N = 1·00 : 3·14, 3·12 : 2·06, 1·90. The white insoluble residue contained no zirconium. Extractions with chlorobenzene were not successful, since most of the butylamine hydrochloride dissolved as well—probably because a trace of free butylamine was present—and analysis of the soluble portion gave ratios such as Zr : Cl : N = 1·00 : 3·65 : 3·40.

The reaction of zirconium(IV) chloride with s-butylamine gave a red-brown oil, after removal of excess of amine; after 3 hr. at 100° *in vacuo* the *product* had the composition Zr : Cl : N = 1·00 : 3·90 : 2·17.

DISCUSSION

The reactions we have studied have been between anhydrous liquid amines and solid zirconium(IV) chloride, and for their understanding we must briefly consider the structure of the solid halide. While zirconium(IV) chloride is monomeric in the vapour state, the solid is presumably polymerised in view of its moderate volatility and lack of solubility in covalent solvents. Blumenthal[10] has suggested an ionic structure $(ZrCl_{4-n})^{n+}(ZrCl_{4+n})^{n-}$,

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[10] Blumenthal, " The Chemical Behaviour of Zirconium," Van Nostrand, New York, 1958, p. 108.

by analogy with phosphorus(V) chloride. An alternative and perhaps preferable formulation is that of a polymer with Zr–Cl–Zr bridges, similar to niobium(V) chloride [11] (dimeric) or iron(III) chloride [12] (layer lattice); the zirconium–chlorine bonds would be appreciably polar and possibly have some double-bond character. With either an ionic or a polymeric structure, zirconium(IV) chloride would not be soluble in non-polar solvents, but should dissolve in donor solvents such as ethers and amines.

Thus trimethylamine, which is a typical Lewis base with an available lone pair of electrons, will force the breakdown of the halide lattice to give the adduct $ZrCl_4,2NMe_3$, in which the zirconium atom achieves a co-ordination number of six (d^2sp^3). The insolubility of the compound precluded studies of its molecular weight, so that there is no evidence that it is monomeric, and it is quite possible that the zirconium atom has increased its covalency to eight through polymerisation.

The stable 1 : 1 adduct which remains when the compound is heated *in vacuo* is similar to the product of the zirconium(IV) chloride–triethylamine reaction; it is unlikely that either compound will be monomeric. Although triethylamine is the stronger base [13] it co-ordinates to zirconium(IV) chloride to a smaller extent, owing to the larger volume occupied by the ethyl groups.

The only alternative to considering these compounds as adducts is to suppose that either solvolysis or reduction has taken place. Solvolysis, *e.g.*, the possibility that $ZrCl_4,2NMe_3$ could be a mixture $ZrCl_3{\cdot}NMe_2 + NMe_4Cl$, is unlikely since it involves the breaking of a strong nitrogen–carbon bond. It is incompatible with the results of the thermal decomposition of the trimethylamine product, since one mol. of amine is lost and there is no tetramethylammonium chloride; it is quite ruled out with triethylamine since only one mol. of amine is involved in the reaction. Reduction takes place in the corresponding reaction of titanium(IV) chloride with trimethylamine,[14] and $TiCl_3,2NMe_3$ was formed, but zirconium is much more reluctant to form lower-valent compounds than titanium, and in view of the diamagnetism and colour of the products it is unlikely that any significant amount of reduction has taken place.

Other compounds formed by zirconium(IV) chloride with donor nitrogen and oxygen molecules, *viz.* $ZrCl_4,2py$,[9,15] $ZrCl_4,2RCN$ (R = Me, Et, and Pr),[9] and $ZrCl_4,2OEt_2$,[16] are presumably very similar to the diamine complex formed by trimethylamine.

Zirconium(IV) chloride reacts with all three secondary amines (dimethylamine, diethylamine, and dipropylamine), to give products of overall composition $ZrCl_4,2NHR_2$. These substances can also be considered as simple addition compounds in which the zirconium(IV) chloride forms two donor–acceptor bonds with the nitrogen atoms. This formulation is strongly supported by the absence of the appropriate amine hydrochloride, which would be present if aminolysis had occurred, $ZrCl_4,2NHR_2 = ZrCl_3(NR_2) + NHR_2,HCl$. The solubility of the diethylamine and dipropylamine products in benzene also rules out the possibility of an ionic formulation, *e.g.*, $[ZrCl_3(NHR_2)_2]Cl$. Zirconium(IV) chloride thus resembles tin(IV) chloride [17] in its reactions with secondary aliphatic amines, but differs from titanium(IV) chloride which undergoes aminolysis [18] under similar conditions to form compounds $TiCl_3(NR_2),2NHR_2$. The greater resistance of the zirconium–chlorine bond to aminolysis we attribute to its greater ionic character. Only under very strong forcing conditions (refluxing with the lithium salt in light petroleum [8] at 60°) can the bonds be broken.

In the analogous work with oxygen-containing molecules,[16] zirconium(IV) chloride

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[11] Zalkin and Sands, *Acta Cryst.*, 1958, **11**, 615.
[12] Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, 2nd edn., 1950, p. 287.
[13] Hare and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.
[14] Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.
[15] Emeléus and Rao, *J.*, 1958, 4245.
[16] Rosenheim and Hertzmann, *Ber.*, 1907, **40**, 810.
[17] Bannister and Fowles, *J.*, 1959, 310.
[18] Cowdell and Fowles, unpublished observations.

forms addition compounds with many esters and hydroxy-acids at low temperatures, but hydrogen chloride is eliminated when the temperature is allowed to rise. Thus between one and two chlorine atoms are replaced by ethoxy-groups when the chloride is refluxed with ethyl alcohol.[19]

The reaction of zirconium(IV) chloride with methylamine differs from that with other primary amines (NH_2R, R = Et, Pr^n, Bu^n, and Bu^s) in that the overall composition and the solubility of the products are different. This is summarised in the Table, which shows that two of the zirconium–chlorine bonds are aminolysed by methylamine, but only one with the remaining amines. These results indicate that as the amine becomes less ionising so aminolysis decreases in extent.

	Overall composition		Extracted products	
Amine	Initial	Final (50—100° *in vacuo*)	Insol. in parent amine	Sol. in benzene
NH_2Me	$ZrCl_4,5NH_2Me$	$ZrCl_4,4NH_2Me$	$ZrCl_2(NHMe)_2,NH_2Me$	None
NH_2Et	$ZrCl_4,3NH_2Et$	$ZrCl_4,2NH_2Et$	None	$ZrCl_3(NHEt),NH_2Et$
NH_2Pr^n	$ZrCl_4,3NH_2Pr^n$	$ZrCl_4,2NH_2Pr^n$	None	$ZrCl_3(NHPr^n),NH_2Pr^n$
NH_2Bu^n	$ZrCl_4,3NH_2Bu^n$	$ZrCl_4,2NH_2Bu^n$	None	$ZrCl_3(NHBu^n),NH_2Bu^n$
NH_2Bu^s	—	$ZrCl_4,2NH_2Bu^s$	—	—

Some comment must be made on the early work of Matthews, who obtained white tetra-amine complexes on passing gaseous methylamine, ethylamine, and propylamine through solutions of zirconium(IV) chloride in diethyl ether. Our reactions were carried out with excess of liquid amine with a reaction time of several weeks, and we should therefore expect to get much more aminolysis than Matthews did. It therefore seems probable that the tetra-amines obtained by the gas-flow method are simple adducts.

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[19] Bradley and Wardlaw, *J.*, 1950, 3450.