INORGANIC REACTIONS IN LIQUID AMMONIA

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1. Introduction

Liquid ammonia, which is the best known non-aqueous ionising solvent, is quite a good solvent for many inorganic compounds, particularly halides and ammonium salts, even though it has an appreciably lower dielectric constant than water. It has a modest degree of auto-ionisation:

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

so that solutions of ammonium salts act as acids, and those of amides as bases; normal acid–base reactions can be carried out. Since N–H bonds of ammonia are less easily broken than O–H bonds of water compounds are less likely to be ammonolysed than hydrolysed, and for this reason liquid ammonia may sometimes be used as a medium for the preparation of compounds which can be obtained only in low yields from aqueous solutions. Germane, GeH_4, for instance, which may be prepared by the action of acids on Mg_2Ge, is obtained only in 20% yields when aqueous acids are used, but an 80% yield is made possible by the use of solutions of ammonium bromide in liquid ammonia. A unique property of liquid ammonia is that of dissolving alkali metals without further reaction. In contrast to the violent reaction between alkali metals and water, the liquid ammonia solutions are quite stable, although decomposition to the amide and hydrogen take place in the presence of suitable catalysts such as platinum black. As two recent reviews[1,2] have appeared on the nature of the metal–ammonia solutions, we need only very briefly summarise the situation. The metals are considered to dissolve in ammonia, giving metal cations and electrons

$$M \rightarrow M^+ + e$$

the electrons are associated with the solvent, and in concentrated solutions at least the cation also appears to play some part in determining the environment of the electron. The solutions thus contain a very ready source of electrons, and they accordingly constitute very powerful homogeneous reducing agents. In 1950, Watt[3] thoroughly reviewed the use of these solutions in the reduction of both inorganic and organic compounds, and Birch[4] has also summarised many organic reductions.

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[1] Jolly, "Progress in Inorganic Chemistry," 1959, **1**, 235.

[2] Symons, *Quart. Rev.*, 1959, **13**, 99.

[3] Watt, *Chem. Rev.*, 1950, **46**, 289.

[4] Birch, *Quart. Rev.*, 1950, **4**, 69.

Apart from a brief account by Watt[5] in 1957, and a survey of non-aqueous solvents by Gutmann,[6] there has been no recent general review of the various lines of liquid-ammonia research that have been developed since the war. In this present Review we shall first discuss the reactions of ammonia with metal halides, with especial emphasis on ammonolysis. Fernelius and Bowman[7] reviewed early work (prior to 1940) on the ammonolysis of both organic and inorganic compounds (including halides); in our account we shall restrict ourselves to those halides which either best illustrate the general principles or have been the most fully studied. The remainder of the Review is concerned with the synthetic procedures, in both the inorganic and the organometallic field, that have been evolved in the past decade or so.

2. Reactions of liquid ammonia with metal halides

We can conveniently consider these reactions as falling into two categories, one in which simple addition compounds are formed, and the other in which one or more metal–halogen bonds are ammonolysed, *i.e.*:

$$\text{(i)}\quad MX_n + xNH_3 \rightarrow MX_n{,}xNH_3$$

$$\text{(ii)}\quad MX_n + mNH_3 \rightarrow MX_{n-m/2}(NH_2)_{m/2} + \frac{m}{2}NH_4X$$

The ammonobasic metal halide formed by ammonolysis (reaction ii) may, of course, take up ammonia and form an addition compound.

It is not possible to classify the halides rigidly under these two headings because the products of the reaction depend on experimental conditions, and even those halides that are very easily ammonolysed do form addition compounds initially, and these intermediates can on occasion be isolated under suitable conditions. In general, though, it is true to say that ammonolysis occurs only with the more covalent halides.

(a) Ionic Halides of Non-transition Elements.—Thus, the ionic halides of non-transition metals (*e.g.*, alkali and alkaline-earth elements) form simple "ammoniates", in which the ammonia is but weakly held and can be removed *in vacuo* at relatively low temperatures, leaving the unchanged halide. A great deal of early work in this field has been done by Biltz, who, in a summary,[8] points out that (i) for a given metal halide the heat of formation of the ammoniate increases as the number of bonded ammonia molecules decreases, and (ii) for a given Periodic Group of metals the heat of formation of similar ammoniates decreases with increasing atomic weight. The ammonia molecules are undoubtedly associated with the cation, although the anion plays an indirect part in determining such details as lattice spacings.

[5] Watt, *J. Chem. Educ.*, 1957, **34**, 538.
[6] Gutmann, *Quart. Rev.*, 1956, **10**, 451.
[7] Fernelius and Bowman, *Chem. Rev.*, 1940, **26**, 3.
[8] Biltz, *Z. anorg. Chem.*, 1923, **130**, 93.

The bonding in these addition compounds is best regarded as ion–dipole in character, resulting from interaction between the cation and the lone-pair of electrons of the nitrogen atom, and, since the degree to which the electron charge cloud is distorted depends on both the size and the charge of the cation, small, highly-charged cations form the strongest bonds, *e.g.*, $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$.

(b) **Halides of Transition Metals in their Lower Valency States.**—These halides are usually considered to be highly polymeric with fairly polar metal–halogen bonding. The chlorides of bivalent manganese, iron, cobalt, and nickel, for instance, which come into this category, form addition compounds with ammonia, and these adducts do not differ markedly from those formed by the alkaline-earth halides, since the ammonia is still lost quite easily *in vacuo*. However, these transition elements of the first row have vacant 4*d*-orbitals energetically available, and the bonding is to be considered more donor–acceptor than ion–dipole in character.

The ammoniates formed by these halides of the transition metals in their lower-valency states are often true ammines, and the bonding of the ammonia groups to the metal ion is best understood in terms of ligand-field or the molecular-orbital theory.[9] However, some halides (*e.g.*, VCl_3, VBr_3, $MoBr_3$) have been incorrectly described[10] as forming hexa-ammines, $[M(NH_3)_6]X_3$, whereas they do in fact undergo ammonolysis. Thus both the chloride and the bromide of tervalent vanadium are ammonolysed in liquid ammonia,[11] and the so-called ammine is really a mixture:

$$[V(NH_3)_6]X_3 \equiv VX_2(NH_2),4NH_3 + NH_4X$$

Similarly, molybdenum(III) bromide is ammonolysed rapidly at room temperature with the formation of $MoBr(NH_2)_2,NH_3$. Titanium(III) chloride, on the other hand, is not appreciably ammonolysed even at room temperature, but much of the ammonia associated with the chloride can be removed by heat *in vacuo*, showing that the ammonia is only weakly bonded.

The dichlorides of both titanium and vanadium form adducts when treated with liquid ammonia at room temperature, but at —33·5° there is virtually no reaction.

(c) **Covalent Halides of Non-transition Metals.**—The more covalent halides invariably undergo at least partial ammonolysis when treated with liquid ammonia, and the extent to which the halogen atoms are replaced by amido-groups decreases as the metal–halogen bonds become more polar. For a given element in a particular valency state, the chloride, bromide, and

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[9] Orgel, "An Introduction to Transition Metal Chemistry: Ligand-field Theory," Methuen, London, 1960.

[10] Sidgwick, "The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950.

[11] Fowles, Lanigan, and Nicholls, *Chem. and Ind.*, 1961, 1167.

iodide usually react similarly with liquid ammonia, but the fluoride is always ammonolysed less readily and often only forms an ammoniate. We can illustrate these points by reference to the halides of the Group III and IV elements.

Boron(III) fluoride acts as a typical Lewis acid towards ammonia and forms an adduct, BF_3,NH_3, which does not undergo ammonolysis, even at 50°.[12] Although no analogous adducts have been isolated from the reactions of ammonia with the other three halides, it is probable that they are formed initially and subsequently undergo ammonolysis:

$$BX_3 + NH_3 \rightarrow BX_3{\leftarrow}NH_3 \xrightarrow{NH_3} BX_2(NH_2) + NH_4X$$

Further co-ordination and elimination of hydrogen halide then leads to the formation of the amide, which readily decomposes to the imide:

$$2B(NH_2)_3 \rightarrow B_2(NH)_3 + 3NH_3$$

The reluctance of boron(III) fluoride to undergo ammonolysis is a reflection of the high B–F bond strength. In the presence of amide ions or alkali metals, ammonolysis takes place, *e.g.*:

$$BF_3,NH_3 + K \xrightarrow{NH_3} BF_2(NH_2) + \tfrac{1}{2}H_2 + KF$$

This is to be expected since the amide ion is a much stronger nucleophilic reagent than ammonia, while the alkali metals provide a source of electrons and help the formation of fluoride ions.

It is interesting that when the ammonolytic mixture $[BF_2(NH_2) + KF]$ is passed down a cation-exchange column,[13] the potassium ions are removed, and the adduct (BF_3,NH_3) is re-formed. This is consistent with the initial formation of a complex boron anion, which breaks down on removal of excess of ammonia:

$$\text{(i)}\quad BF_2(NH_2) + KF \xrightarrow{NH_3} K[BF_3(NH_2)]$$

$$\text{(ii)}\quad K[BF_3(NH_2)] + NH_4(\text{Resin}) \xrightarrow{NH_3} NH_4[BF_3(NH_2)] + K(\text{Resin})$$

$$\text{(iii)}\quad NH_4[BF_3(NH_2)] \xrightarrow[\text{excess of } NH_3]{\text{Removal of}} BF_3,NH_3 + NH_3$$

Thus, when the excess of ammonia is removed, the solid complex is unstable and transference of a proton from the ammonium ion to the amino-group is followed by the loss of a molecule of ammonia. We shall see that the formation of similar complex ions helps to account for the behaviour of a number of other halides that are only partially ammonolysed.

As we go from the boron halides to those of aluminium, there is a marked change, since none of the aluminium halides is appreciably

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[12] Jenkins, *J. Amer. Chem. Soc.*, 1956, **78**, 5500.

[13] McDowell and Keenan, *J. Amer. Chem. Soc.*, 1956, **78**, 2065.

ammonolysed in liquid ammonia. The ammoniates are ammonolysed, however, on treatment with solutions of the alkali metals in liquid ammonia.[14]

The halides of the Group IV elements, carbon to tin, all undergo ammonolysis on direct treatment with ammonia (cf. Table 1).

TABLE 1. *Ammonolysis of Group* IV *halides.*

Halide	Reaction temp.	Ammonolysed product	Ref.
CCl_4	140°	$HN:C(NH_2)_2$	15
CBr_4	100—250	$HN:C(NH_2)_2$	16
CI_4	−33·5	$CI_4,2NH_3$	17
	25−150	$HN:C(NH_2)_2$	16
$SiCl_4$	−50	$Si(NH_2)_4$	18
Si_2Cl_6	−50	$[Si(:NH)(NH_2)]_2$	19
$GeCl_4$	−33·5	$Ge(:NH)_2$	20
GeI_4	−33·5	$Ge(:NH)_2$	21
$SnCl_4$	−33·5	$SnCl(NH_2)_3$	22
$SnBr_4$	−33·5	$SnBr(NH_2)_3$	23
SnI_4	−33·5	$SnI(NH_2)_3$	23
$PbCl_4$	20	No ammonolysis	7

Carbon tetrahalides are not ammonolysed unless the reactions are carried out above room temperature. This is understandable, since carbon has no vacant orbitals of low enough energy to accept electrons from an ammonia molecule, and no intermediate adduct can be formed. Hence the mechanism proposed for the ammonolysis of the boron halides is not applicable, and the breaking of a C–X bond occurs only at higher temperatures. It should be mentioned that carbon tetraiodide forms a diammoniate when treated with liquid ammonia, but the ammonia is held only by weak van der Waals interactions and will not modify the C–X bonds sufficiently to facilitate ammonolysis.

In contrast to the inertness of the carbon tetrahalides, the halides (other than fluorides) of quadrivalent silicon and germanium are readily and completely ammonolysed to the amides, $M(NH_2)_4$, at low temperatures; these readily break down to the imides, $M(:NH)_2$. Tin(IV) chloride,

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[14] Watt and Braun, *J. Amer. Chem. Soc.*, 1956, **78**, 5494; Taylor, Griswold, and Kleinberg, *ibid.*, 1955, **77**, 294.

[15] Stähler, *Ber.*, 1914, **47**, 909.

[16] Watt and Hahn, *J. Amer. Chem. Soc.*, 1955, **77**, 312.

[17] Watt, McBride and Sowards, *J. Amer. Chem. Soc.*, 1956, **78**, 1562.

[18] Vigoroux and Hugot, *Compt. rend.*, 1903, **136**, 1670.

[19] Schwarz and Sexauer, *Ber.*, 1926, **56**, 333; Billy, *Compt. rend.*, 1960, **250**, 4163.

[20] Schwarz, *Angew. Chem.*, 1935, **48**, 221.

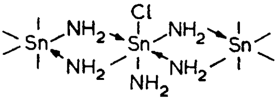
[21] Johnson and Sidwell, *J. Amer. Chem. Soc.*, 1933, **55**, 1884.

[22] Bannister and Fowles, *J.*, 1958, 751.

[23] Bannister and Fowles, *J.*, 1958, 4374.

bromide, and iodide are not completely ammonolysed, however, and even after prolonged washing with liquid ammonia the last tin–halogen bond remains intact.

The ammonobasic tin(IV) halides are almost insoluble in liquid ammonia, so that they can be obtained free from ammonium halide by extracting the latter with liquid ammonia. Schwarz and Jeanmaire,[24] who did earlier work with tin(IV) chloride, found that even on prolonged washing with ammonia the insoluble product still had a Sn:Cl ratio of 1:1·5, although this could be lowered to 1:1 if the product were heated to 100° between the washings. More recent work has, however, shown that $SnCl(NH_2)_3$ can be obtained without this heating. The insoluble ammonobasic tin(IV) halides are almost certainly polymers resulting from the elimination of hydrogen halide between neighbouring molecules, or from condensation through chlorine or nitrogen bridges, or both, *e.g.*:



The composition $SnCl(NH_2)_3$ is probably only an average one, the degree of ammonolysis being above average at the extremities of the polymer. The presence of some tin compounds in the ammonia-soluble portion of the products (solubility increasing in the order $Cl < Br < I$) suggests that the ammonium halide formed in the ammonolysis produces soluble, complex, anionic species, such as $[SnCl_3(NH_2)_3]^{2-}$. Solubility is not complete, however, because of the polymeric nature of the bulk of the product and the relatively low concentrations of ammonium halide.

The tin(IV) halide–ammonia systems have also been examined in some detail by a tensimetric procedure, in which a known excess of ammonia is condensed on to the halide ($SnX_4:NH_3 \sim 1:30$) and the resulting mixture is allowed to come to equilibrium over a period of days. Under these experimental conditions a small amount of liquid ammonia is present in the reaction bulb; small quantities of ammonia are then removed progressively and the vapour pressure of ammonia measured for each composition. The annexed Figure shows tensimetric plots for the ammonium chloride–ammonia and the tin(IV) chloride–ammonia system. From Fig. (a) it is clear that ammonium chloride forms a triammoniate with a characteristic dissociation pressure of 91 mm. at −36°, and the similar univariant portion in Fig. (b) shows that ammonium chloride is present in the product formed by the reaction of tin(IV) chloride with ammonia. The length of this univariant step is a direct measure of the amount of ammonium chloride that is present.

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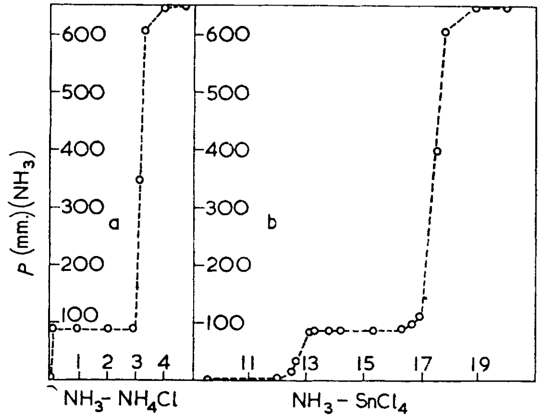
[24] Schwarz and Jeanmaire, *Ber.*, 1932, **65**, 1443.



Tensimetric plots (—36°) *for the systems formed by ammonia with* (a) *ammonium chloride and* (b) *tin*(IV) *chloride.*

TABLE 2. *Tensimetric studies on tin*(IV) *halide.*

Halide	Temp.	No. of mol. of NH$_4$X forming ammoniates
SnCl$_4$	−63°	2·6
	−45 and −36	1·0
(NH$_4$)$_2$SnCl$_6$	−36	2·8
K$_2$SnCl$_6$	−36	1·2
SnBr$_4$	−45 and −36	3·0
(NH$_4$)$_2$SnBr$_6$	−36	5·0
SnI$_4$	−36	2·0

At —63°, the tin(IV) chloride–ammonia system shows the presence of almost three mol. of ammonium chloride, in agreement with the reaction:

$$SnCl_4 + 6NH_3 \rightarrow SnCl(NH_2)_3 + 3NH_4Cl$$

but at somewhat higher temperatures only one mol. of ammonium chloride can be detected. Now, the degree of ammonolysis at the higher temperatures must be at least as great as that at —63°, so that the "missing" two mol. of ammonium chloride must for some reason be incapable of forming the characteristic ammoniates. The explanation is that at higher temperatures the ammonium chloride is more soluble in the excess of ammonia, and the more concentrated solution reacts with the ammonobasic tin(IV) chloride to give an anionic complex:

$$SnCl(NH_2)_3 + 2NH_4Cl \rightarrow (NH_4)_2[SnCl_3(NH_2)_3]$$

Three mol. of ammonium bromide are detected in the tin(IV) bromide–ammonia system at —45° and —36°, however, indicating that although complex formation may occur (giving the soluble product in washing experiments), the complex breaks down when it is precipitated as a solid upon removal of the excess of liquid ammonia. This agrees with the decrease in stability of complex hexahalogenostannate ions, $[SnX_6]^{2-}$, in the order $I > Br > Cl$.

Only two mol. of ammonium iodide are, however, found in the tin(IV) iodide–ammonia system, and this must be because ammonolysis of tin(IV) iodide is less complete than that of the bromide and chloride. (We have seen that complex formation is ruled out, since complexes formed by the bromide are unstable under tensimetric conditions.) The third stage of the ammonolysis of the iodide:

$$SnI_2(NH_2)_2 + 2NH_3 \rightarrow SnI(NH_2)_3 + NH_4I$$

is completed when ammonium iodide is removed by washing, but the high concentration of ammonium iodide (saturated solutions) suppresses the ammonolysis in the tensimetric experiments.

Lead(IV) chloride is reported to be resistant to ammonolysis, although no detailed study appears to have been made. While the lack of ammonolysis is not too surprising, it is in marked contrast to the behaviour of diammonium hexachloroplumbate(IV), $(NH_4)_2PbCl_6$, which is extensively ammonolysed. The explosive nature of the product precludes more rigorous examination, but the ratio Pb:Cl:N appears to be in the region of 1:1:1. The original workers obtained figures of 5:6:4 and proposed a cyclic constitution to account for the instability of the product, but it seems more likely to be a polymeric mixture which owes its explosive properties to the presence of unstable Pb–N bonds.

(d) Halides of Transition Metals in Their Higher Valency States.—We limit our review of the ammonolysis of these halides to the elements of the titanium, vanadium, and chromium sub-groups, as much more work has been done recently in this field. By and large, the investigations fall into two categories, those in which the extent of ammonolysis has been studied by tensimetric methods, and those in which the halides have been allowed to react with liquid ammonia at various temperatures and the products then washed with ammonia to remove the ammonium halide; the latter technique is not always possible, since in one or two cases [*e.g.*, niobium(V) chloride], the products are completely soluble in ammonia.

Table 3 summarises the results obtained by the two methods for many halides and for a number of complex anionic halides of the elements.

In their ammonolytic behaviour, the titanium(IV) halides resemble the halides of quadrivalent tin rather than those of germanium, in that only three titanium–halogen bonds can be ammonolysed even at room temperature. Contrary to the view sometimes expressed, the amide $Ti(NH_2)_4$ is not prepared by ammonolysis of the titanium(IV) halides, although it is formed when potassium amide is added. The ammonobasic titanium(IV) chloride,

TABLE 3. *Ammonolysis of halides and complex halides of the Group* IVA, VA, *and* VIA *transition elements in their higher valency states.*

Halide	Solubility (% of metal) with excess of ammonia	Insoluble product (Reaction at −33·5°, then washed with ammonia)	Mol. ratio NH_4X/M detected tensimetrically	Ref.
$TiCl_4$	5	$TiCl(NH_2)_3$	2·7	25
$(NH_4)_2TiCl_6$	90	$TiCl(NH_2)_3+TiCl_2(NH_2)_2$	4·0	26
K_2TiCl_6	70	$TiCl(NH_2)_3+TiCl_2(NH_2)_2+KCl$	2·0	26
$TiBr_4$	70	$TiBr(NH_2)_3+TiBr_2(NH_2)_2$	2·7	27
$(NH_4)_2TiBr_6$	100	—	4·0	26
TiI_4	100	—	2·5	27
$ZrCl_4$	10	$ZrCl_3(NH_2)$	1·0	28
$(NH_4)_2ZrCl_6$	70	$ZrCl_3(NH_2)$	3·0	29
Rb_2ZrCl_6	20	$ZrCl_3(NH_2)+RbCl$	1·0	29
Cs_2ZrCl_6	5	$ZrCl_3(NH_2)+CsCl$	1·0	29
$ZrBr_4$	—	$ZrBr_3(NH_2)+ZrBr_2(NH_2)_2$*	—	30
$ThCl_4$	—	—	0†	28
$ThBr_4$	—	—	0†	31
ThI_4	—	$ThI_4,7NH_3$	—	32
VF_5	0	VF_4,NH_3+NH_4F	—	33
VCl_4	50	$VCl(NH_2)_3+VCl_2(NH_2)_2$	2·0	34
NbF_5	0	$NbF_5,2NH_3$	—	33
$NbCl_5$	100	—	2·0	35
$TaCl_5$	100	—	2·0	36
$MoCl_5$	60	$MoCl_3(NH_2)_2$	2·0	37
	15	$MoCl(:NH)(NH_2)_2$*	—	—
WF_6	0	$WF_6,4NH_3$	—	38
WCl_6	90	$WCl_2(NH_2)_4+WCl_3(NH_2)_3$	<2·7	39

* Reaction at 25°. †Ammoniates formed.

[25] Fowles and Pollard, *J.*, 1953, 2588.

[26] Fowles and Nicholls, *J.*, 1961, 95.

[27] Fowles and Nicholls, *J.*, 1959, 990.

[28] Fowles and Pollard, *J.*, 1953, 4128; Drake and Fowles, *J. Less-Common Metals*, 1960, **2**, 401.

[29] Drake and Fowles, *J. Less-Common Metals*, 1961, **3**, 149.

[30] Bowerman and Fernelius, *J. Amer. Chem. Soc.*, 1939, **61**, 121.

[31] Young, *J. Amer. Chem. Soc.*, 1935, **57**, 997.

[32] Watt, Sowards, and Malhotra, *J. Amer. Chem. Soc.*, 1957, **79**, 4908.

[33] Cavell and Clark, *J. Inorg. Nuclear Chem.*, 1961, **17**, 257.

[34] Fowles and Nicholls, *J.*, 1958, 1687.

[35] Fowles and Pollard, *J.*, 1952, 4938.

[36] Moureu and Hamblett, *J. Amer. Chem. Soc.*, 1937, **59**, 33.

[37] Edwards and Fowles, *J. Less-Common Metals*, 1961, **3**, 181.

[38] Clark and Emeléus, *J.*, 1957, 4778.

[39] Fowles and Osborne, *J.*, 1959, 2275.

$TiCl(NH_2)_3$, is isolated from the reaction mixture by washing with ammonia, although the bromide is still somewhat contaminated with $TiBr_2(NH_2)_2$. With all three halides the tensimetric studies detect rather less than three mol. of ammonium halide, indicating that the third stage of the ammonolysis is somewhat suppressed by ammonium halide, the effect being greatest with the iodide. The marked increase in solubility of the ammonolysis products along the series $TiCl_4 < TiBr_4 < TiI_4$ may indicate a decreasing degree of polymerisation, while the modest solubility of the ammonobasic titanium(IV) chloride in a concentrated solution of ammonium chloride shows that the polymers can be broken down to some extent.

Experiments with anion-exchange resins prove that in the iodide solution, at any rate, all the titanium is present in anionic form, so that similar complex anions are probably present in the solutions formed by the other halides. These complexes are stable only in solution, and break down to the ammonolytic mixture on removal of the excess of ammonia. Hexachloro- and hexabromo-titanates with liquid ammonia give products that are much more soluble than those formed by the tetrahalides. It is tempting to consider these complexes as though they react as a mixture of the tetrahalide and ammonium halide. *e.g.*:

$$(NH_4)_2TiCl_6 \rightarrow 2NH_4Cl + TiCl_4 \xrightarrow{NH_3} \text{Ammonolytic mixture}$$

and then to explain the increased solubility and decreased ammonolysis as resulting from the presence of the extra ammonium halide; but if the potassium salt behaved like this, the liberated potassium chloride would have no marked effect on the ammonolysis of the titanium(IV) chloride since it has only a slight solubility in ammonia.

A more convincing explanation requires the direct ammonolysis of the anion, followed by the precipitation of potassium chloride when the potassium salt reacts, *i.e.*:

$$\begin{aligned} K_2TiCl_6 &\rightarrow K_2[TiCl_4(NH_2)_2] + 2NH_4Cl \\ &\rightarrow (NH_4)_2[TiCl_4(NH_2)_2] + 2KCl \\ &\qquad \Big\downarrow \text{Removal of excess } NH_3 \\ &\quad TiCl_2(NH_2)_2 + 2NH_4Cl \end{aligned}$$

Thus virtually all the titanium is found in solution. The chloro-complexes are the least soluble in ammonia, so that small amounts remain undissolved in the first washing; on removal of ammonia these complexes break down, and the usual ammonobasic titanium(IV) chloride is formed on further treatment with ammonia.

Zirconium(IV) halides are less extensively ammonolysed, and zirconium(IV) chloride, for instance, forms $ZrCl_3(NH_2)$ when treated with liquid ammonia at —33·5°; the product is again insoluble in ammonia in the absence of ammonium chloride and probably is polymeric in nature.

It has been observed that when the compound is heated to 100° *in vacuo* and treated again with ammonia, further ammonolysis takes place, such that the Zr:Cl ratio may be lowered to 1·0:2·5; this indicates that the heating tends to break down the polymer so that part of it may be further ammonolysed. The diammonium hexachlorozirconate(IV) behaves as might be expected, three mol. of ammonium chloride being detected tensimetrically. The products formed from the rubidium and cæsium salts are not very soluble, presumably because the original complexes themselves are almost insoluble. The ammonolysis of zirconium(IV) bromide was studied at 25° by Bowerman and Fernelius who obtained an insoluble product which they formulated as $3Zr(NH)_2,7NH_4Br,5NH_3$; it seems more likely that this product is either a mixture of $ZrBr_3(NH_2),xNH_3$ and $ZrBr_2(NH_2)_2,yNH_3$, or a polymer with an average composition corresponding to $Zr:Br = 1{\cdot}0:2{\cdot}3$. At room temperature one might expect the second Zr–Br bond to be partly ammonolysed.

None of the thorium(IV) halides shows any evidence of ammonolysis in liquid ammonia, although all form well-defined ammoniates.

3. Reactions of ammono-bases

In view of its relatively high solubility in ammonia, potassium amide is the most extensively used ammono-base. Sodium amide is practically insoluble but can be used as a suspension, or when only a low concentration of amide ions is required. These amides are readily prepared *in situ* by catalytic decomposition of their alkali-metal solutions, and their reactions in ammonia show striking resemblances to the reactions of alkali-metal hydroxides in aqueous systems. Thus simple neutralisation reactions occur:

$$KNH_2 + NH_4Cl \rightarrow KCl + 2NH_3$$

and potassium permanganate (which forms a violet solution in ammonia) gives a green precipitate of the manganate, K_2MnO_4, when treated with potassium amide; this precipitate redissolves to a violet solution upon treatment with ammonium salts.[40] Ammonolytic reactions proceed much further in basic solutions than in ammonia alone, since by removal of ammonium ions, ammonolytic equilibria, *e.g.*:

$$MX_2(NH_2)_2 + 2NH_3 \rightleftharpoons MX(NH_2)_3 + NH_4X$$

are disturbed and many compounds which show practically no ammonolysis in ammonia alone are ammonolysed in basic solutions.

Thus while carbon(IV) iodide is not ammonolysed in liquid ammonia at low temperatures, the addition of potassium amide leads to the formation of iodoform and iodoamine:[41]

$$CI_4,2NH_3 + NH_3 \rightarrow HCI_3 + INH_2 + 2NH_3$$

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[40] Inone, Takamoto and Kurokawa, *Nippon Kaguku Zasshi*, 1957, **78**, 274.
[41] Watt, McBride, and Sowards, *J. Amer. Chem. Soc.*, 1956, **78**, 1562.

The reaction is complicated by the secondary reactions:

$$INH_2 + KNH_2 \rightarrow N_2H_4 + KI$$
$$2CI_4 + N_2H_4 + 2NH_3 \rightarrow N_2 + 2NH_4I + 2HCI_3.$$

The decomposition products of chloramine in liquid ammonia depend upon the basicity of the medium.[42] In acidic solutions the formation of hydrazine by the ammonolysis

$$NH_2Cl + 2NH_3 \rightarrow NH_2{\cdot}NH_2 + NH_4Cl$$

is suppressed, whereas in solutions of potassium amide, potassium chloride is precipitated and hydrazine produced.

Again, nitrogen tri-iodide merely forms an ammoniate in liquid ammonia, but ammonolysis occurs when potassium amide is added:[43]

$$NI_3 + 3KNH_2 \rightarrow 3KNHI + NH_3 \quad \text{(Fast)}$$
$$3KNHI \rightarrow 3KI + N_2 + NH_3 \quad \text{(Slow)}$$

Franklin has given an account[44] of the reactions of potassium amide with the salts of many non-transition metals, which lead to the formation of amides, imides, or nitrides, *e.g.*:

$$AgNO_3 \rightarrow AgNH_2$$
$$PbI_2 \rightarrow PbNH$$
$$HgI_2 \rightarrow Hg_3N_2$$

Of late, interest has centred around the polymeric transition-metal amides, which have been prepared from ammonobasic compounds by further solvolysis, or by metathetical reactions of the more ionic salts with potassium amide.

(a) Reactions of Ammonobasic Compounds with Alkali-metal Amides.[45]—The extent to which metal halides are ammonolysed may be greatly increased by the addition of potassium amide, and in some instances complete ammonolysis can thus be effected. The resulting amides are inclined to lose ammonia and form the corresponding imides [cf. $B(NH_2)_3$]. The halides that are completely ammonolysed are those of the transition metals in their higher valency (*i.e.*, more acidic) states, so that the amides formed are invariably amphoteric and react with either potassium or potassium amide to give potassium salts; consequently it is very difficult to isolate these amides in an uncombined state. Table 4 summarises the products obtained by the reaction of the halides of a number of transition metals. It can be seen that potassium salts are formed with the halides of quadrivalent titanium and zirconium, and of quinquevalent tantalum, molybdenum, and tungsten.

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[42] Jander, *Z. anorg. Chem.*, 1955, **280**, 264.
[43] Jander and Schmid, *Z. anorg. Chem.*, 1957, **292**, 178.
[44] Franklin, "The Nitrogen Systems of Compounds," Reinhold Publ. Inc., New York, 1935.
[45] Levine and Fernelius, *Chem. Rev.*, 1954, **54**, 452.

Since cerium(III) iodide and thorium(IV) bromide are considerably less acidic, they are incompletely ammonolysed. The product formed by cerium(III) iodide was originally considered to be $CeI_3,Ce(NH_2)_3,10NH_3$, but it is more likely to be an ammonobasic cerium(III) iodide polymer [cf. $SnCl(NH_2)_3$] in which the Ce:I ratio averages 2:3. For simplicity, this is represented in Table 4 as a mixture; in the same way, most of the other products listed in this Table are likely to contain polymeric anions.

TABLE 4. *Reaction of transitional-metal halides with potassium amide–liquid ammonia solutions.*

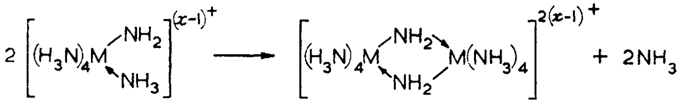
Halide	Product of reaction with potassium amide	Ref.
CeI_3	$CeI(NH_2)_2+CeI_2(NH_2)$	46
$TiBr_4$	$Ti(:NH)(:NK)$	47
$ZrBr_4$	$Zr(:NK)_2$	30
$ThBr_4$	$ThBr_2(NH_2)_2$	48
$TaBr_5$	$Ta(NH_2)_3(NHK)_2+Ta(NH_2)_4(NHK)$	45
$MoCl_5$	$Mo(NH_2)(:NK)_2$	49
WBr_5	$W(NH_2)(:NK)_2$	49

(b) Reactions of Ammono-bases with Transition-metal Salts.—Where the metal halides are not ammonolysed the metal amides are more conveniently prepared by metathetical reactions of the more soluble nitrates or thiocyanates with potassium amide. Schmitz-Dumont and his associates have in this way succeeded in preparing a large number of transition-metal amides.

The mechanism involved in the formation of these amides from metal salts is comparable to that encountered in the formation of metal hydroxides in water. Equilibria of the type:

$$[M(NH_3)_6]^{x+} + NH_3 \rightleftharpoons [M(NH_3)_5(NH_2)]^{(x-1)+} + NH_4^+$$

may exist, and in the presence of amide ions the ammonium-ion concentration is reduced and ammonolysis is favoured. A process analogous to olation can then occur:



so that ultimately polymeric metal amide ammoniates are produced; usually these lose their ammonia quite readily *in vacuo*. Thus hexamminechromium(III) nitrate reacts[50] with potassium amide to give the bright red amide:

$$[Cr(NH_3)_6](NO_3)_3 + 3KNH_2 \rightarrow 3KNO_3 + 6NH_3 + Cr(NH_2)_3$$

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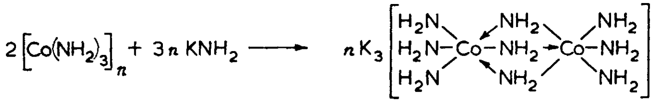
[46] Bergstrom, *J. Amer. Chem. Soc.*, 1937, **59**, 1374.
[47] Franklin and Hine, *J. Amer. Chem. Soc.*, 1912, **34**, 1497.
[48] Watt and Malhotra, *J. Inorg. Nuclear Chem.*, 1959, **11**, 255.
[49] Bergstrom, *J. Amer. Chem. Soc.*, 1925, **47**, 2317.
[50] Schmitz-Dumont, Pilzecker, and Pepenbrink, *Z. anorg. Chem.*, 1941, **248**, 175.

With an excess of potassium amide some of the bridging bonds are broken and a potassium salt of a polymeric anion is obtained:

$$\{\mathrm{Cr(NH_2)_3}\}_n + \mathrm{KNH_2} \rightarrow \{\mathrm{K[Cr(NH_2)_4]}\}_n$$

The salt produced from the corresponding cobalt(III) amide[51] appears to be less polymeric and accordingly soluble in liquid ammonia:



When the solution is evaporated, however, de-ammoniation results in polymerisation, and thermal decomposition of the product gives a nitrido-salt:

$$\{\mathrm{K_3[Co_2(NH)_3(NH_2)_3]}\}_n \rightarrow \mathrm{K_{3n}[(Co_2N_3)_n]} + 3n\mathrm{NH_3}$$

Bergstrom[52] used the anhydrous thiocyanates as starting materials for the preparation of the amides of bivalent manganese and cobalt, and more recently complex thiocyanates have been used of metals that do not form simple thiocyanates. Thus the amides of tervalent titanium[53] and vanadium[54] can be prepared:

$$\mathrm{K_3M(SCN)_6} + 3\mathrm{KNH_2} \rightarrow \mathrm{M(NH_2)_3} + 6\mathrm{KSCN}$$

both amides react with an excess of potassium amide to give the imide salt, $\mathrm{K[M(:NH)_2]}$. The same vanadium compounds are formed by reaction between a solution of potassium in ammonia and vanadium(III) bromide.[55]

Because of their solubility in ammonia, complex nitrates may also be useful starting materials for the preparation of amides. Thus the unstable amide, $\mathrm{Th(NH_2)_4}$, of quadrivalent thorium may be prepared[56] by treating the anhydrous complex nitrate, $\mathrm{K_2Th(NO_3)_6}$, with four equivalents of potassium amide. The amide decomposes spontaneously:

$$\mathrm{Th(NH_2)_4} \rightarrow \mathrm{Th(:NH)(NH_2)_2} + \mathrm{NH_3}$$

and forms a variety of complex imidoamide salts with an excess of potassium amide, the composition depending on the amount of potassium amide used; *e.g.*, with a 6-fold excess, $\mathrm{K[Th(:NH)(NH_2)_3]}$ is believed to be formed.

The reaction of potassium amide with halides of the Group VIII metals has been studied extensively by Watt and his associates.[57] Cationic nickel(II)

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[51] Schmitz-Dumont and Kron, *Z. anorg. Chem.*, 1955, **280**, 180.
[52] Bergstrom, *J. Amer. Chem. Soc.*, 1924, **46**, 1552, 2631.
[53] Schmitz-Dumont, Simons, and Broja, *Z. anorg. Chem.*, 1949, **258**, 308.
[54] Schmitz-Dumont and Broja, *Z. anorg. Chem.*, 1948, **255**, 299.
[55] Nicholls, *J. Inorg. Nuclear Chem.*, in the press.
[56] Schmitz-Dumont and Raabe, *Z. anorg. Chem.*, 1954, **277**, 297.
[57] Watt and Dawes, *J. Amer. Chem. Soc.*, 1959, **81**, 8; Watt, Walling, and Mayfield, *ibid.*, 1953, **75**, 6175; Watt and Davies, *ibid.*, 1948, **70**, 3753; Watt, Choppin, and Hall, *J. Electrochem. Soc.*, 1954, **101**, 235.

salts react at $-33°$ to give nickel(II) amide diammoniate, and this amide yields elemental nickel when thermally decomposed *in vacuo* at 585°. Tetrammineplatinum(II) bromide yields platinum(II) amide diammoniate:

$$[Pt(NH_3)_4]Br_2 + 2KNH_2 \rightarrow Pt(NH_2)_2,2NH_3 + 2KBr + 2NH_3$$

This amide also gives the metal when thermally decomposed:

$$3Pt(NH_2)_2,2NH_3 \rightarrow 3Pt + 10NH_3 + N_2$$

With bis(ethylenediamine)platinum(II) iodide, potassium amide causes replacement of the iodine atoms according to the equations:

$$[Pt\,en_2]I_2 + KNH_2 \rightarrow [Pt(en\text{-}H)\,en]I + KI + NH_3$$
$$[Pt\,en_2]\,I_2 + 2KNH_2 \rightarrow Pt(en\text{-}H)_2 + 2KI + 2NH_3$$

[where (en-H) represents the abstraction of a proton from a nitrogen atom bonded to the central platinum atom]. With an excess of potassium amide the potassium salt K[Pt(en-H)(en-2H)] is formed; the addition of ammonium halides to these compounds regenerates the original complex:

$$Pt(en\text{-}H)_2 + 2NH_4X \rightarrow [Pt\,en_2]X_2 + 2NH_3$$

The titration of iridium(III) bromide with potassium amide provides evidence for the stepwise replacement of bromine atoms by amide groups, followed by conversion of the resultant yellow iridium(III) amide into a red-brown solution of potassium hexa-amidoiridate(III). The reactions (co-ordinated ammonia omitted) are:

$$IrBr_3 + KNH_2 \rightarrow IrBr_2NH_2 + KBr$$
$$IrBr_2NH_2 + KNH_2 \rightarrow IrBr(NH_2)_2 + KBr$$
$$IrBr(NH_2)_2 + KNH_2 \rightarrow Ir(NH_2)_3 + KBr$$
$$Ir(NH_2)_3 + 3KNH_2 \rightarrow K_3[Ir(NH_2)_6]$$

Bromopentamminerhodium(III) bromide reacts similarly with potassium amide but only as far as the formation of rhodium(III) amide.

(c) **Reactions of Ammono-acids with Transition-metal Amides.**—We have seen that ammonobasic metal halides are almost invariably soluble in liquid ammonia solutions of ammonium halides, and this solubility has been attributed to the formation of soluble complex anionic species of the metal, *e.g.*:

$$TiI(NH_2)_3 + 2NH_4I \rightarrow (NH_4)_2[TiI_3(NH_2)_3]$$

With the amides (or potassium derivatives) of those metals whose halides are ammonolysed in ammonia, we should expect dissolution to occur upon treatment with ammonium halide solutions (provided that the amides are not resistant to attack through polymerisation), *e.g.*:

$$Mo(NH_2)(:NK)_2 \underset{KNH_2}{\overset{NH_4Cl}{\rightleftharpoons}} Mo(NH_2)_5 \underset{NH_2^-}{\overset{NH_4Cl}{\rightleftharpoons}} [Mo(NH_2)_5Cl]^- \underset{NH_2^-}{\overset{NH_4Cl}{\rightleftharpoons}} [Mo(NH_2)_4Cl_2]^-$$

Where the metal halide or salt is not ammonolysed in ammonia it is often possible to regenerate this compound by treatment of the amide with the corresponding ammonium salt, *e.g.*:

$$\mathrm{Ni(NH_2)_2,2NH_3 + 2NH_4I \rightarrow NiI_2,6NH_3}$$

Even with the polymeric diamidothorium(IV) imide $\{\mathrm{HN{:}Th(NH_2)_2}\}_n$, all the existing bridging bonds are broken upon treatment with ammonium iodide in ammonia, and colourless crystals of thorium(IV) iodide octa-ammoniate $\mathrm{ThI_4,8NH_3}$ are obtained.

Low-temperature treatment of the polymeric chromium(III) and cobalt(III) amides with ammonium salts results in dissolution of the amides. Schmitz-Dumont suggests[50] that the residues remaining after removal of ammonia from these solutions contain high polymers such as $\{\mathrm{[Cr(NH_3)_3(NH_2)Br]Br}\}_n$ and $\{\mathrm{[Co(NH_3)_3(NH_2)_2]NO_3}\}_n$.

4. Reactions of alkali-metal solutions

(a) Reduction and Effect on Ammonolysis.—Solutions of the alkali and alkaline-earth metals in liquid ammonia have attracted widespread interest, not only in the physical nature of the solutions themselves,[1,2] but also in the use of the solutions as reducing agents. Early work utilising alkali-metal solutions as reducing agents for inorganic substances is reviewed elsewhere.[3] Attention in recent years has been largely devoted to the production of unusual valency states of metals, and to the synthetic uses of the solutions, particularly in the field of organic and organometallic chemistry.

With many metal salts reduction by an alkali metal in ammonia yields the elemental metal. Such reductions are usually complicated, however, since the metal formed is in a finely divided and highly reactive state. Thus many metals, *e.g.*, zinc, cadmium, mercury, tin, and lead, form poly-ide salts with an excess of alkali metal, and others catalyse the decomposition of the alkali-metal solution, *i.e.*:

$$\mathrm{K + NH_3 \rightarrow KNH_2 + \tfrac{1}{2}H_2}$$

so that the final products of the reduction may contain the metal amide; *e.g.*, with nickel salts[58] there are the reactions:

$$\mathrm{NiBr_2 + 2K \rightarrow Ni + 2KBr}$$
$$\mathrm{2K + 2NH_3 \rightarrow 2KNH_2 + H_2}$$
$$\mathrm{2KNH_2 + NiBr_2 + 2NH_3 \rightarrow Ni(NH_2)_2,2NH_3 + 2KBr}$$

The catalytic breakdown of the alkali-metal solutions to the amides may, however, occur without permanent reduction of the transition metal, and

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[58] Burgess and Eastes, *J. Amer. Chem. Soc.*, 1941, **63**, 2674; Watt and Davies, *ibid.*, 1948, **70**, 3753.

many halides give the same products with alkali-metal solutions as they do with solutions of alkali-metal amides, *e.g.*:

$$ZrBr_4 \xrightarrow{NH_3} ZrBr_3(NH_2) \xrightarrow{K\text{–}NH_3} Zr(:NK)_2$$
$$VBr_3 \xrightarrow{NH_3} VBr_2(NH_2) \xrightarrow{K\text{–}NH_3} V(:NH)(NHK)$$

and hydrogen gas is liberated. We have already seen that neither boron(III) fluoride nor the aluminium(III) halides are ammonolysed unless an alkali metal is present, and it is interesting that, while only one B–F bond is ammonolysed on addition of potassium, both sodium and lithium effect greater ammonolysis, namely,

$$\begin{aligned} BF_3 &\xrightarrow{K\text{–}NH_3} BF_2(NH_2) \\ &\xrightarrow{Na\text{–}NH_3} (NH_2)_2B{\cdot}NH{\cdot}BF(NH_2) \\ &\xrightarrow{Li\text{–}NH_3} (NH_2)_2B{\cdot}NH{\cdot}B(:NH) \end{aligned}$$

Sometimes a difference in reactivity of the various alkali-metal solutions may be attributed to the difference in the solubilities of the alkali-metal amides ($LiNH_2$ and $NaNH_2$ almost insoluble; KNH_2 soluble). Thus tetramethyl-lead reacts with alkali metals in ammonia to give $[Pb(CH_3)_3]^-$ ions and methyl radicals (which yield methane and ethane):[59]

$$Pb(CH_3)_4 + e^- \rightarrow [Pb(CH_3)_3]^- + CH_3{\cdot}$$

In the presence of potassium, solvolysis of the $[Pb(CH_3)_3]^-$ ions occurs, giving lead imide as the final product:

$$[Pb(CH_3)_3]^- + NH_3 \rightarrow [Pb(CH_3)_2NH_2]^- + CH_4$$
$$[Pb(CH_3)_2NH_2]^- + NH_3 \rightarrow [Pb(CH_3)(NH_2)_2]^- + CH_4$$
$$[Pb(CH_3)(NH_2)_2]^- + NH_3 \rightarrow [Pb(NH_2)_3]^- + CH_4$$
$$[Pb(NH_2)_3]^- \rightarrow PbNH + NH_3 + [NH_2]^-$$

With lithium and sodium, however, the insolubility of the amides (at −78°) retards the ammonolysis through the reaction

$$[Pb(CH_3)_2NH_2]^- + Na^+ \rightarrow Pb(CH_3)_2 + NaNH_2$$

so that only two methyl groups are removed and the product is dimethyl-lead.

With the tetra-alkylammonium salts, R_4NX, the N–C bond is ruptured by potassium solutions,[60] to give a trialkylamine and a hydrocarbon; *e.g.*, for $(CH_3)_4NCl$:

$$[N(CH_3)_4]^+ + e \rightarrow N(CH_3)_3 + CH_3{\cdot}$$
$$CH_3{\cdot} + e \rightarrow [CH_3]^-$$
$$[CH_3]^- + NH_3 \rightarrow CH_4 + [NH_2]^-$$

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[59] Holliday and Pass, *J.*, 1958, 3485.
[60] Hazlehurst, Holliday, and Pass, *J.*, 1956, 4653.

The amide ion produced yields an olefin if R contains a β-carbon atom, *e.g.*:

$$[N(C_2H_5)_4]^+ + [NH_2]^- \rightarrow N(C_2H_5)_3 + C_2H_4 + NH_3$$
$$[(CH_3{\cdot}CH_2{\cdot}CH_2)_3N{\cdot}CH_3]^+ + [NH_2]^- \rightarrow (CH_3{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}CH_3 + C_3H_6 + NH_3$$

Evolution of hydrogen during an alkali-metal reduction was used by earlier workers to infer the presence of an ammonium ion. Thus the "diammoniate" of diborane was formulated[61] as an ammonium salt (NH_4) $[H_3B(NH_2)BH_3]$ on account of its reaction with a sodium solution:

$$(NH_4)[H_3B(NH_2)BH_3] + Na \xrightarrow{NH_3} Na[H_3B(NH_2)BH_3] + \tfrac{1}{2}H_2 + NH_3$$

More recent work by Parry and his co-workers[62] has shown the compound to be a borohydride, $[NH_3(BH_2)NH_3]BH_4$, whose reaction with sodium may be written:

$$[NH_3(BH_2)NH_3]BH_4 + Na \xrightarrow{NH_3} NaBH_4 + BH_2NH_2 + \tfrac{1}{2}H_2 + NH_3$$

Trimethylboron gives hydrogen when treated with a solution of sodium or potassium, and the salt $M[B(CH_3)_3NH_2]$, is formed:[63]

$$(CH_3)_3B,NH_3 + M \xrightarrow{NH_3} M[B(CH_3)_3NH_2] + \tfrac{1}{2}H_2$$

the trimethylboron can be regenerated by treatment with a solution of ammonium bromide.

Tetramethyldiborane is split symmetrically into $BH(CH_3)_2,NH_3$ and the salt $Na_2BH(CH_3)_2$ when treated with an excess of sodium in ammonia at −78°,[64] and an analogous calcium salt $CaBH(CH_3)_2,NH_3$ can be prepared. The $[BH(CH_3)_2]^-$ ion in the sodium salt shows the high base strength expected of a boron atom with a lone pair of electrons, in that it forms a stable compound, $Na_2[BH(CH_3)_2],B(CH_3)_3$, with trimethylboron; this compound appears to contain B–B links.

Conductimetric studies of the reactions of alkali-metal solutions with a number of covalent hydrides[65] have shown that disubstitution by alkali metals can occur in SnH_4, AsH_3, SbH_3, and GeH_4, but not in PH_3. Thus disodiostannane, SnH_2Na_2, may be isolated after reaction of stannane with a ten-fold excess of sodium; in the presence of excess of the hydride, however, conversion into the monosubstituted derivative occurs:

$$SnH_2Na_2 + SnH_4 \rightarrow 2SnH_3Na$$

The analogous germanium compound, $NaGeH_3$, reacts with phenyl bromide to give germanium(II) hydride:

$$NaGeH_3 + C_6H_5Br \rightarrow C_6H_6 + GeH_2 + NaBr$$

[61] Schlesinger and Burg, *J. Amer. Chem. Soc.*, 1938, **60**, 290.

[62] Schultz and Parry, *J. Amer. Chem. Soc.*, 1958, **80**, 4.

[63] Smith and Kraus, *J. Amer. Chem. Soc.*, 1951, **73**, 2751; Holliday and Thompson, *J.*, 1960, 2695.

[64] Burg and Campbell, *J. Amer. Chem. Soc.*, 1952, **74**, 3744; 1957, **79**, 4023.

[65] Emeléus and Kettle, *J.*, 1958, 2445; Emeléus and Mackay, *J.*, 1961, 2676.

this hydride may be recrystallised from liquid ammonia, and it reacts with one atom of sodium to form a soluble red salt which gives germane, GeH_4, on treatment with ammonium bromide. Alkylgermanes with sodium give the monosubstituted salts,[66] *e.g.*, $NaEtGeH_2$.

(b) The Production of Unusual Valency States.—Whereas simple nickel(II) salts are reduced to the metal with alkali metal–ammonia solutions, the complex nickel(II) cyanides[67] yield products in which the metal appears to exhibit a valency of less than two. Thus, when an excess of potassium tetracyanonickelate(II) is treated with sodium or potassium in ammonia, a bright red precipitate is formed of composition $K_2[Ni(CN)_3]$:

$$[Ni(CN)_4]^{2-} + e \rightarrow [Ni(CN)_3]^{2-} + CN^-$$

If an excess of alkali metal is used in the reduction a bulky yellow precipitate of the tetracyanonickelate(0) separates:

$$[Ni(CN)_4]^{2-} + 2e \rightarrow [Ni(CN)_4]^{4-}$$

The potassium salt can be isolated as a copper-coloured solid, extremely unstable in air and blackening on exposure. It dissolves in water, evolving hydrogen and giving a red solution with the characteristic properties of the tricyanonickelate(I) anion. The tetracyanonickelate(0) ion, $[Ni(CN_4]^{4-}$, is, of course, isoelectronic with the carbonyl, $Ni(CO)_4$. The corresponding zero-valent palladium ion,[68] $[Pd(CN)_4]^{4-}$, may be made by the reduction of $[Pd(CN)_4]^{2-}$ salts. In liquid ammonia, both of the zero-valent salts reduce azobenzene to hydrazobenzene and silver and mercury(II) salts to the metals.

The analogous cobalt salt may be prepared[69] by reduction of potassium hexacyanocobaltate(III):

$$K_3[Co(CN)_6] + 3K^+ + 3e \rightarrow K_4[Co(CN)_4] + 2KCN$$

although potentiometric titrations suggest[70] the intermediate formation of a cobalt(I) complex, $K_3[Co(CN)_4]$. The reduction of the hexacyanochromate(III) ion[71] yields a product containing chromium(I), while the hexacyanomanganate(III) ion appears to give a product containing both the uni- and the zero-valent state of manganese:

$$2K_3[Mn(CN)_6] + 5K^+ + 5e \rightarrow K_5[Mn(CN)_6],K_6[Mn(CN)_6],2NH_3$$

This formulation of the product is consistent with the amount of potassium used in the reduction, its reducing action towards silver nitrate, and chemical analysis.

[66] Glarum and Kraus, *J. Amer. Chem. Soc.*, 1950, **72**, 5398.
[67] Eastes and Burgess, *J. Amer. Chem. Soc.*, 1942, **64**, 1187.
[68] Burbage and Fernelius, *J. Amer. Chem. Soc.*, 1943, **65**, 1484.
[69] Hieber and Bartenstein, *Naturwiss.*, 1952, **39**, 300; *Z. anorg. Chem.*, 1954, **276**, 12.
[70] Watt, Hall, Choppin, and Gentile, *J. Amer. Chem. Soc.*, 1954, **76**, 373; Watt and Thompson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 311.
[71] Davidson and Kleinberg, *J. Phys. Chem.*, 1953, **57**, 571.

Some unusual ammine complexes of platinum and iridium have been prepared by Watt and his co-workers.[57] When tetrammineplatinum(II) bromide is reduced with potassium in ammonia at the boiling point, exactly two gram-atoms of potassium are consumed per mole of the bromide and a yellowish-white solid is precipitated. Thermal decomposition of this solid yields only platinum and ammonia and the solid appears to be tetrammineplatinum(0):

$$[Pt(NH_3)_4]Br_2 + 2K^+ + 2e \rightarrow Pt(NH_3)_4 + 2KBr$$

Diamagnetic pentammineiridium(0) is similarly obtained[72] when bromopentammineiridium(III) bromide is reduced with potassium in boiling ammonia:

$$[Ir(NH_3)_5\,Br]Br_2 + 3K^+ + 3e \rightarrow Ir(NH_3)_5 + 3KBr$$

The stability of these zero-valent complex ammines is unusual in that the ligands are incapable of forming π-bonds with the metal.

A co-ordination compound with a bidentate nitrogen ligand that may contain platinum(0) has been obtained[73] as an unstable pink precipitate [identifiable as bisethylenediamineplatinum(0) only by its thermal decomposition products] when two equivalents of potassium react with bisethylenediamineplatinum(II) iodide. At room temperature it decomposes by two paths:

$$Pt + 2en \leftarrow Pt\ en_2 \rightarrow Pt(\ en\text{-}H)_2 + H_2$$

When only one equivalent of potassium is used in the reduction of the iodide, an unstable compound [Pt en_2]I is formed, which disproportionates at room temperature:

$$2\ Pt\ en_2I \rightarrow Pt\ en_2 + [Pt\ en_2]I_2$$

5. Recent synthetical reactions

So far we have discussed reactions involving ammonia, reactions of alkali-metal amides, and reductions with alkali-metal solutions. There remains the large field of reactions in which ammonia acts merely as a solvent medium. The advantages of liquid ammonia as a solvent medium for synthetic procedures are by now well known. The solubility relationships shown by ammonia, especially those which show different trends from those found in water, are often most valuable. The smaller tendency of ammonia than of water to solvolysis, and the greater stability of products at the lower temperatures employed, often permit the study and isolation of compounds which cannot be prepared, or which can be obtained only with difficulty, from other solvents. Many examples of metathetical reactions are already reviewed[74] and we shall mention only those syntheses

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[72] Watt and Mayfield, *J. Amer. Chem. Soc.*, 1953, **75**, 6178.

[73] Watt, McCarley, and Dawes, *J. Amer. Chem. Soc.*, 1957, **79**, 5163; 1959, **81**, 8.

[74] Audrieth and Kleinberg, "Non-aqueous Solvents," J. Wiley & Sons Inc., New York, 1953.

which have been used in the last decade. These are conveniently divided into two sections, (*a*) inorganic, and (*b*) organo-metallic syntheses.

(a) **Inorganic Syntheses.**—One interesting preparation is that of ammonium nitrite,[75] which is obtained when sodium nitrite and ammonium chloride are mixed in ammonia at −33·5°.

Phosphine reacts rapidly with alkali-metal solutions in ammonia to give the salts $MIPH_2$, which are valuable for the synthesis of a variety of phosphine derivatives. Treatment of a solution of the sodium salt ($NaPH_2$) with methyl chloride results in precipitation of sodium chloride and the formation of methylphosphine[76] which can be obtained in good yield from the filtrate:

$$CH_3Cl + NaPH_2 \rightarrow NaCl + CH_3{\cdot}PH_2$$

When trimethylene dichloride is used in place of methyl chloride, trimethylenediphosphine and polymeric alkylphosphines of formula $PH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}[PH{\cdot}CH(CH_3){\cdot}CH_2]_n{\cdot}PH_2$ are obtained.[77] Heavy-metal hydrogen phosphides have been prepared by metathesis of KPH_2 and an ammonia-soluble metal salt.[78] From hexamminecobalt(III) nitrate a dark brown pyrophoric phosphine, $Co(PH_2)_3$, is obtained:

$$[Co(NH_3)_6](NO_3)_3 + 3KPH_2 \rightarrow Co(PH_2)_3 + 3KNO_3 + 6NH_3$$

This compound decomposes spontaneously at 0°, to leave a black residue of $Co(PH)_3$, and from this a crystalline phosphide $CoP_{2{\cdot}37}$ is formed at 560°. With an excess of KPH_2 and the hexammine nitrate the insoluble amorphous salt $KCo_2(PH_2)_7$ is obtained. Nickel(II) thiocyanate gives $Ni(PH_2)_2$, which is unstable at 0° and reacts with an excess of KPH_2 to give a soluble complex which is probably $K_2[Ni(PH_2)_4]$.

Peroxides of magnesium, cadmium, and zinc have been isolated for the first time[79] by treatment of the metal nitrates with sodium or potassium superoxides (which are sparingly soluble and insoluble, respectively, in ammonia). The unstable superoxide intermediate dissociates to give the peroxide:

$$Zn(NO_3)_2 + 2KO_2 \rightarrow Zn(O_2)_2 + 2KNO_3$$
$$Zn(O_2)_2 \rightarrow ZnO_2 + O_2$$

Strontium nitrate gives strontium peroxide, but reaction of barium nitrate with four equivalents of potassium superoxide gives a compound whose analysis suggests the stoicheiometry:[80]

$$Ba(NO_3)_2 + 4KO_2 \rightarrow K_2Ba(O_2)_2O_2 + 2KNO_3 + O_2$$

This is the only case found of mixed superoxide–peroxide formation; it is

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[75] Larbouillat-Linemann, *Compt. rend.*, 1954, **238**, 902.
[76] Wagner and Burg, *J. Amer. Chem. Soc.*, 1953, **75**, 3869.
[77] Leffler, Groch, and Teach, Abs. Papers, Amer. Chem. Soc. meeting, Sept. 1959.
[78] Schmitz-Dumont, Nagel, and Schaal, *Angew. Chem.*, 1958, **70**, 105.
[79] Schechter and Kleinberg, *J. Amer. Chem. Soc.*, 1954, **76**, 3297.
[80] Seyb and Kleinberg, *J. Amer. Chem. Soc.*, 1951, **73**, 2308.

noteworthy that in this compound the cations have almost identical ionic radii: K^+, 1·33 Å; Ba^{2+}, 1·35 Å.

The reactions of solutions of alkali-metal borohydrides in ammonia have been used to afford,[81] by metathesis, borohydrides such as $[Cr(NH_3)_6][BH_4]_3$ and $[Mg(NH_3)_6][BH_4]_2$.

(b) Organo-metallic Syntheses.—(i) *Coupling reactions.* In early synthetic work on organometallic compounds, Kraus made extensive use of liquid ammonia and alkali metal–ammonia solutions. The reactions of organometallic compounds with alkali-metal solutions were reviewed in 1950,[82] so that coupling reactions of the type

$$R_3MNa + XR' \rightarrow R_3MR' + NaX$$

(R, R′ = alkyl or aryl, X = halogen) need not be considered here in detail; as general illustrations of this type of reaction two examples may be cited:[83,84]

$$2Ph_3GeNa + Br{\cdot}[CH_2]_3{\cdot}Br \rightarrow Ph_3Ge{\cdot}[CH_2]_3{\cdot}GePh_3 + 2NaBr$$

$$Et_3PbCl + 2Li + Ph{\cdot}CH_2Cl \rightarrow Et_3Pb{\cdot}CH_2Ph + 2LiCl$$

When the ammoniate of trimethyl-lead borohydride is distilled at −5°, a most interesting reaction occurs,[85] in which trimethylplumbane is obtained with elimination of ammonia–borine:

$$\begin{aligned} Me_3PbCl + KBH_4 &\xrightarrow[-33^\circ]{NH_3} [Me_3Pb]BH_4{,}xNH_3 \\ &\xrightarrow{-5^\circ} Me_3PbH + H_3B{,}NH_3 + (x-1)NH_3 \end{aligned}$$

This hydride reacts rapidly with ammonia at −78° to form ammonium trimethylplumbate, and addition of trimethyl-lead chloride then gives hexamethyldiplumbane:

$$Me_3PbH + NH_3 \rightarrow NH_4[PbMe_3]$$

$$NH_4[PbMe_3] + Me_3PbCl \rightarrow (Me_3Pb)_2 + NH_4Cl$$

(ii) "*Sandwich*" *compounds.* Cyclopentadienyl and indenyl compounds of a number of transition metals have been prepared[86] in liquid ammonia by reactions of the type:

$$[Co(NH_3)_4](SCN)_2 + 2C_5H_5Li \rightarrow [Co(NH_3)_4](C_5H_5)_2 + 2LiSCN$$

The ammoniates are readily decomposed thermally *in vacuo*, and the resulting cyclopentadienyl compounds may then be obtained by sublimation. The method has been used in particular for the preparation of the

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[81] Parry, Schultz, and Girardot, *J. Amer. Chem. Soc.*, 1958, **80**, 1.
[82] Watt, *Chem. Rev.*, 1950, **46**, 317.
[83] Smith and Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 1418.
[84] Gilman and Leeper, *J. Org. Chem.*, 1951, **16**, 466.
[85] Duffy and Holliday, *J.*, 1961, 1678.
[86] Fischer and Fritz, *Adv. Inorg. Chem. and Radiochem.*, 1959, **1**, 55.

cyclopentadienyls of chromium(III), manganese(II), iron(II), cobalt(II), and nickel(II), and the indenyl of cobalt(II).

(iii) *Acetylene derivatives.* Acetylene derivatives of the main-group elements have been known for some time. When acetylene is bubbled through a solution of sodium in ammonia the monosodium derivative, $\mathrm{NaC{:}CH}$, can be obtained, and this is a useful starting material for liquid-ammonia preparations of metal-acetylene compounds. With the Group IV metals, for example,[87] those triaryl- or trialkyl-metal halides ($\mathrm{R_3MX}$) which are not ammonolysed in ammonia (*i.e.*, tin and lead compounds) react with sodium acetylide, giving compounds of the type $\mathrm{Ph_3Pb{\cdot}C{:}C{\cdot}PbPh_3}$ and $\mathrm{Et_3Sn{\cdot}C{:}C{\cdot}SnEt_3}$. Monosubstituted products are not isolated because they readily disproportionate to the disubstituted product and acetylene:

$$\begin{aligned} \mathrm{R_3SnCl + NaC{:}CH} &\rightarrow \mathrm{R_3Sn{\cdot}C{:}CH + NaCl} \\ &\rightarrow \mathrm{R_3Sn{\cdot}C{:}C{\cdot}SnR_3 + C_2H_2} \end{aligned}$$

The $\mathrm{R_3Sn{\cdot}C{:}CH}$ intermediates do, however, react with an excess of the sodium salt and form complex compounds of the type $\mathrm{R_3Sn{\cdot}[C{:}CH]_2{\cdot}Na}$. An alternative route to the disubstituted derivatives is by the reaction:

$$\mathrm{2Ph_3SnNa + C_2I_2 \rightarrow Ph_3Sn{\cdot}C{:}C{\cdot}SnPh_3 + 2NaI}$$

The phenyl compounds are stable to water but the ethyl compounds are more sensitive; the ease of hydrolysis decreases with decreasing polarity of the carbon–metal bond, *i.e.*, $\mathrm{Pb} > \mathrm{Sn} > \mathrm{Si}$.

Transition-metal acetylides have recently been synthesised by Nast and his co-workers.[88] Once again the soluble thiocyanates are used as starting materials:

$$\begin{aligned} &\mathrm{[Ni(NH_3)_6](SCN)_2 + 4K{\cdot}C{:}C{\cdot}Ph \rightarrow} \\ &\quad \mathrm{K_2[Ni(C{:}C{\cdot}Ph)_4],2NH_3 + 2KSCN + 4NH_3} \xrightarrow{Vacuo} \mathrm{K_2[Ni(C{:}C{\cdot}Ph)_4]} \\ &\quad \mathrm{K_2[Ni(C{:}C{\cdot}Ph)_4] + [Ni(NH_3)_6](SCN)_2 \rightarrow Ni(C{:}C{\cdot}Ph)_2,4NH_3} \\ &\quad \xrightarrow{Vacuo} \mathrm{(Ph{\cdot}C{:}C{\cdot}Ni{\cdot}C{:}C{\cdot}Ph)}_x \end{aligned}$$

The ammonia-free complexes are rather unstable, decomposing in several days at room temperature, and derivatives of alkylacetylenes are prone to detonation.

The diamagnetism of $\mathrm{K_2[Ni(C{:}C{\cdot}Ph)_4]}$ suggests that the nickel atom is in a square-planar environment. Like the analogous complex cyanide, the acetylide $\mathrm{K_2[Ni(C{:}CH)_4]}$ can be reduced to the zero-valent compound $\mathrm{K_4[Ni(C{:}CH)_4]}$ by the action of a solution of potassium in ammonia.

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[87] Beerman and Hartmann, *Z. anorg. Chem.*, 1954, **276**, 20.

[88] Nast, Internat. Conference on Co-ordination Chemistry, *Chem. Soc. Special Publ.*, No. 13, 1959, p. 103; Nast, *Z. Naturforsch.*, 1953, **8b**, 381; Nast and Pfab, *Chem. Ber.*, 1956, **89**, 415; Nast and Vester, *Z. anorg. Chem.*, 1955, **279**, 146; Nast and Lewinsky, *ibid.*, 1955, **282**, 210; Nast and Urban, *ibid.*, 1956, **287**, 17; Nast and Pfab, *ibid.*, 1957, **292**, 287.

Analogues of hexacyanoferrate(III) and hexacyanoferrate(II) complexes can be obtained from iron(II) thiocyanate:

$$Fe(SCN)_2,4NH_3 + 6MC{:}CR \rightarrow M_4[Fe(C{:}CR)_6] + 2MSCN + 4NH_3$$
$$2K_4[Fe(C{:}CH)_6] + 2NH_3 + O_2 \rightarrow 2K_3[Fe(C{:}CH)_6] + H_2O + 2KNH_2$$

The iron(III) complex is unstable, exploding above $-30°$. The corresponding cobalt compounds $Na_4[Co(C\vdots CMe)_6]$ (paramagnetic) and $Na_3[Co(C\vdots CMe)_6]$ (diamagnetic) are obtained similarly.

Reaction of copper(I) iodide with potassium acetylide in ammonia yields the orange cuprous acetylide, which decomposes above $-45°$ to black Cu_2C_2 and acetylene:

$$CuI + K{\cdot}C{:}CH \xrightarrow[-78^\circ]{} Cu{\cdot}C{:}CH \xrightarrow[-45^\circ]{} Cu_2C_2 + C_2H_2$$

Alkynylcuprates(I) of the types $M_2[Cu(C\vdots CR)_3]$ and $M[Cu(C\vdots CR)_2]$ can also be obtained, *e.g.*, when potassium, methyl, or phenyl acetylide is used:

$$CuI + 3K{\cdot}C{:}CMe \xrightarrow{NH_3} K_2[Cu(C{:}CMe)_3],xNH_3 + KI \xrightarrow{Vacuo} K_2[Cu(C{:}CMe)_3]$$

(iv) *Carbonyls.* Reactions of alkali-metal–ammonia solutions with metal carbonyls have recently been studied in some detail by Behrens and his co-workers.[89] With the mononuclear hexacarbonyls of Group VIA metals, reduction occurs with sodium in ammonia, yielding the compounds $Na_2M(CO)_5$ (M = Cr, Mo, or W). These can be recovered from the solution by evaporation of the solvent; they contain ammonia of crystallisation unless warmed to 70° *in vacuo.* A large excess of alkali metal decomposes them.

Sodium reduction of the iron carbonyls $Fe(CO)_5$, $\{Fe(CO)_4\}_3$, $Fe_2(CO)_9$, and $Fe(CO)_4I_2$ leads in each case to $Na_2[Fe(CO)_4]$. At $-75°$ almost no carbon monoxide is liberated when sodium reacts with $\{Co(CO)_4\}_2$, but at higher temperatures ammonia reacts with the carbonyl:

$$3[Co(CO)_4]_2 + 12NH_3 \rightarrow 2[Co(NH_3)_6][Co(CO)_4]_2 + 8CO$$

this ammine is then reduced by sodium to cobalt and $Na[Co(CO)_4]$:

$$2Na + [Co(NH_3)_6][Co(CO)_4]_2 \rightarrow 2Na[Co(CO)_4] + Co + 6NH_3$$

Nickel carbonyl also forms anions of the type $[Ni_2(CO)_6]^{2-}$ and $[Ni_4(CO)_9]^{2-}$ when reduced by solutions of alkali metals in liquid ammonia.[90]

Carbonylcyano-complexes of nickel have been isolated[91] from liquid

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[89] Behrens and Weber, *Z. anorg. Chem.*, 1955, **281**, 190; 1957, **291**, 122; Behrens, *Z. Naturforsch.*, 1952, **7b**, 321.

[90] Behrens and Lohöfer, *Chem. Ber.*, 1961, **94**, 1391, 1497; Hieber, Kroder, and Zahn, *Z. Naturforsch.*, 1960, **15b**, 325.

[91] Nast and Roos, *Z. anorg. Chem.*, 1953, **272**, 242.

ammonia as yellow crystals by passage of oxygen-free carbon monoxide through solutions of complex nickel cyanides at —40°:

$$K_4[Ni_2(CN)_6] + 2CO \rightarrow 2K_2[Ni(CN)_3CO]$$
$$K_4[Ni(CN)_4] + 2CO \rightarrow K_2[Ni(CN)_2(CO)_2] + 2KCN$$

The magnetic properties of $K_2[Ni(CN)_3CO]$ indicate that this compound is dimeric. Reaction with potassium acetylides[92] yields yellow, explosive. octaalkynyldinickelates:

$$K_4[Ni_2(CN)_6(CO)_2] + 8KC{:}CH \rightarrow K_6[Ni_2(C{:}CH)_8] + 6KCN + 2CO$$

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[92] Nast and Kasperl, *Chem. Ber.*, 1959, **92**, 2135.