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The Reactions of Zirconium(IV) Bromide and Zirconium(III) Bromide and Chloride with Ammonia and of Zirconium(IV) Bromide with Ammonium Cyanide

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Abstract

Unlike $ZrCl_4$, $ZrBr_4$ is not ammonolysed in liquid ammonia at temperatures up to −33 °C. The existence of ammoniates $ZrBr_4nH_3$ (n = 17, 12 and 9) at −36 °C has been established; at room temperature, the hexammine $ZrBr_4 \cdot 6NH_3$ is the stable species which becomes $ZrBr_4 \cdot 2NH_3$ at 200 °C. When treated with an excess of NH_4CN in liquid ammonia, complete replacement of bromide ions by cyanide occurs to give an inseparable mixture of $Zr(CN)_4 \cdot 2NH_3$ and NH_4Br. The chloride and bromide of zirconium(III) also undergo no ammonolysis in liquid ammonia; the ammoniates stable at room temperature are $ZrCl_3 \cdot 2.5NH_3$ and $ZrBr_3 \cdot 6NH_3$.

Introduction

It has long been established [1, 2] that while titanium(IV) chloride is ammonolysed to $TiCl(NH_2)_3 \cdot xNH_3$ in liquid ammonia, zirconium(IV) chloride is only ammonolysed as far as the monoazide $ZrCl_3(NH_2) \cdot xNH_3$. Titanium(IV) bromide is more soluble in ammonia than the chloride but undergoes similar ammonolysis followed by complex ion formation [3]. The only report on the reaction of zirconium(IV) bromide with ammonia is the brief statement [4] that it is ammonolysed at 25 °C. In view of the general trend of increasing solubility in ammonia as we go from metal chlorides to the bromides, we considered zirconium(IV) bromide to be the better starting material for preparative reactions of zirconium compounds in this solvent. We have thus studied its reaction with liquid ammonia at near the boiling point of ammonia. Liquid ammonia is the solvent *par excellence* for preparing metal cyanides [5] and we here report on the attempted preparation of zirconium(IV) cyanide using solutions of ammonium cyanide and zirconium(IV) bromide in ammonia.

The reactions of the zirconium(III) halides with ammonia have not been studied previously. Their reactions with alkali metal cyanides in liquid ammonia to give the cyanometallates(0), $M_5{}^1Zr(CN)_5$, by disproportionation has recently been reported [6].

Results and Discussion

The reaction between zirconium(IV) bromide and ammonia was studied by the tensimetric technique [5] and a vapour pressure-composition isotherm constructed at −36 °C. The tensimetric plot (Fig. 1) shows two plateaux (univariant positions) corresponding to the dissociations:

$$ZrBr_4 \cdot 17NH_3 \rightleftharpoons ZrBr_4 \cdot 12NH_3 + 5NH_3$$

$$ZrBr_4 \cdot 12NH_3 \rightleftharpoons ZrBr_4 \cdot 9NH_3 + 3NH_3$$

The sparingly soluble bromide thus forms two ammoniates at −36 °C; the 17- and 12-ammoniates exert dissociation vapour pressures of 210 and 9 mm Hg respectively at this temperature. By measuring the variation of dissociation pressure with temperature for these equilibria (over the range 210–250 K for $ZrBr_4 \cdot 17NH_3$ and 237–293 K for $ZrBr_4 \cdot 12NH_3$) and using the integrated form of the Van't Hoff isochore, we calculate ΔH = 30.4 kJ per mol of ammonia for the dissociation of the 17-ammoniate and 140 kJ per mol of ammonia for dissociation of the 12-ammoniate. These bond dissociation enthalpies are in the region expected for ammonia bonded by weak ion-dipole forces. As no plateau appears in the tensimetric plot at 38 mm Hg corresponding [5] to the dissociation.

$$NH_4Br \cdot 3NH_3 \rightleftharpoons NH_4Br \cdot 1.5NH_3 + 1.5NH_3$$

it is clear that no ammonium bromide has been formed in the reaction *i.e.* that no ammonolysis has occur-

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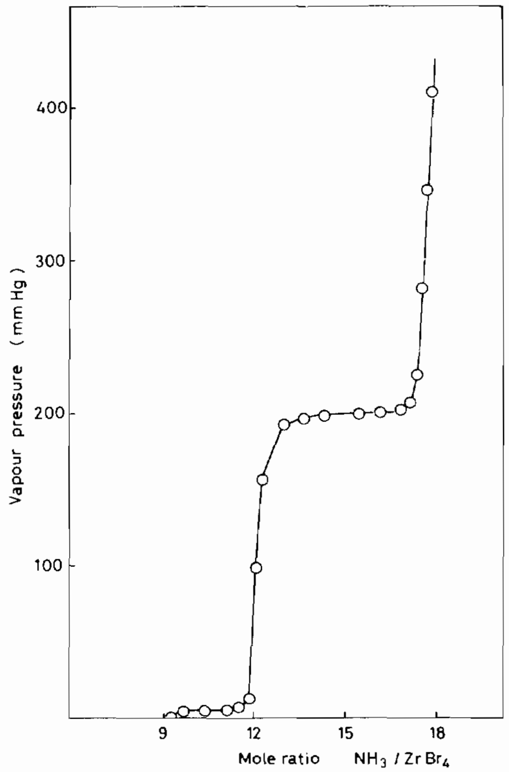

Fig. 1. Vapour pressure-composition isotherm for the system $ZrBr_4-NH_3$ at −36 °C.

red. This finding is in sharp contrast with the reaction between zirconium(IV) chloride and ammonia in which one mole of ammonium chloride per mole of zirconium(IV) chloride is produced [2].

When the composition $ZrBr_4 \cdot 9NH_3$ is warmed *in vacuo* to 20 °C, three more mol of ammonia were evolved to give the hexa-ammoniate, $ZrBr_4 \cdot 6NH_3$, which is thermally stable up to 50 °C. Thereafter, further ammonia is evolved with no other phases appearing to have any stability until the diammoniate is formed at 200 °C. These products were amorphous to X-rays but their IR spectra confirmed that no NH_4Br was present, showing bands due to co-ordinated ammonia only.

Indeed, as no ammonium bromide sublimed during this heating to 200 °C it is evident also that $ZrBr_4 \cdot 6NH_3$ does not undergo ammonolysis upon heating. As we detect no thermal stability associated with $[ZrBr_2(NH_3)_4]Br_2$ (which would be expected if the hexa-ammine was formulated as $[ZrBr_2(NH_3)_4]Br_2 \cdot 2NH_3$), the hexa-ammine may contain $[Zr(NH_3)_6]^{4+}$ cations. The di-ammine is likely to be a halogen-bridged polymer with six co-ordinate zirconium. Both $ZrBr_4 \cdot 2NH_3$ and $ZrBr_4 \cdot 6NH_3$ are diamagnetic and show no bands in their diffuse reflectance spectra over the range, 35000–6000 cm^{-1}.

Zirconium(III) chloride reacts with ammonia at its melting point (−78 °C) to give a swollen green mass. A tensimetric study in this system shows that no ammonolysis occurs and that no intermediate ammoniates are formed greater than $ZrCl_3 \cdot 6NH_3$ which is the composition reached at −36 °C. Upon warming this phase in steps to 215 °C, no phases were found to have any great stability; the final composition approximating to $ZrCl_3 \cdot NH_3$. At room temperature the product has the composition $ZrCl_3 \cdot 2.5NH_3$ and is paramagnetic (μ_{eff} = 1.22 B.M.) so that zirconium has not significantly changed its oxidation state. Zirconium(III) bromide similarly gives the hexa-ammine only at −36° but unlike the chloride analogue, this phase is stable at room temperature. $ZrBr_3 \cdot 6NH_3$ is paramagnetic (μ = 1.42 B.M.) and decomposes to form $ZrBr_3 \cdot NH_3$ (μ_{eff} = 0.85 B.M.) at 100 °C. In the far IR spectra, $ZrBr_3 \cdot 6NH_3$ shows bands attributed to ν(Zr–N) at 446 and 373 cm^{-1} but no lower energy bands down to 200 cm^{-1}; $ZrBr_3 \cdot NH_3$ however shows strong bands at 237 and 220 cm^{-1} which may be attributed to ν(Zr-Br). We therefore believe the hexa-ammine to be best formulated as $[Zr(NH_3)_6]Br_3$. During the course of the reactions of both zirconium(III) halides with liquid ammonia, some hydrogen was slowly evolved. We are not certain whether this arises from traces of zirconium(II) halides in the starting materials or whether slight oxidation of zirconium(III) is occurring. It is apparent however, that no disproportionation of zirconium(III) occurs in the absence of cyanide ions. The magnetic moments of these zirconium(III) ammines are in the region found typically for zirconium(III) complexes and the several peaks found in the diffuse reflectance spectra are reminiscent of the spectra of $ZrCl_3(py)_2$ and $ZrBr_3(py)_2$ [9]. In the absence of solution spectra however, assignment of the spectral bands is not possible.

Ammonium cyanide is an extremely useful synthetic reagent in liquid ammonia; it has a high solubility, its reactions produce soluble ammonium salts as by-products and any excess of the reagent can be sublimed away from reaction products *in vacuo* at room temperature. As there are no known simple cyanides of zirconium we set out to prepare zirconium(IV) cyanide by metathesis between zirconium(IV) bromide and ammonium cyanide in ammonia. Zirconium(IV) bromide dissolves readily in ammonia when an excess of ammonium cyanide is added. The very pale pinkish brown solution yields a similarly pale solid when evaporated; any excess of ammonium cyanide was removed by vacuum sublimation at 50 °C. The diamagnetic solid has the elemental composition $ZrBr_4C_4N_{10}H_{22}$ and an IR spectrum showing the presence of NH_4^+ ions and co-ordinated ammonia with ν(CN) at 2145 cm^{-1} and broad bands attributable to ν(Zr–C) and δ(ZrCN) at 405 and

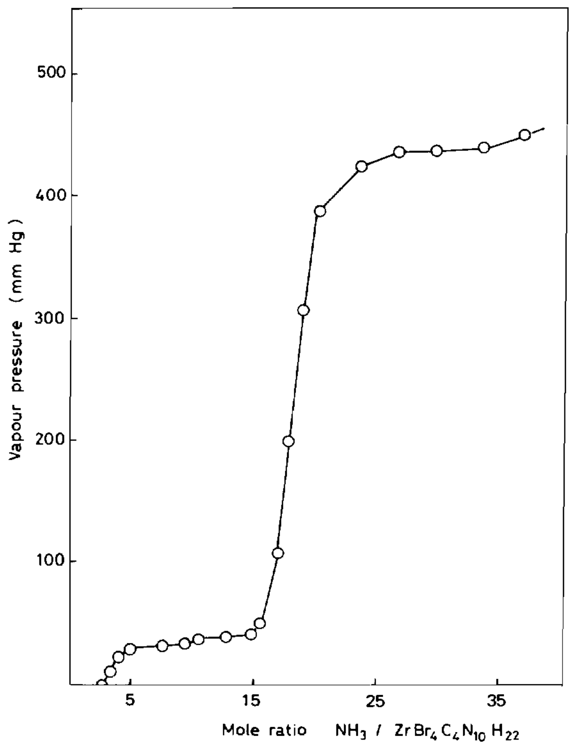

Fig. 2. Vapour pressure-composition isotherm for the mixture $ZrBr_4$–NH_4CN–NH_3 at –36 °C.

655 cm^{-1}. An X-ray powder photograph on this solid shows lines due to NH_4Br only. In order to determine how much ammonium bromide was present in this mixture, a tensimetric study with liquid ammonia was carried out at –36 °C. The plot (Fig. 2) shows univariant positions only at 39 mm Hg between 15 and 9 mol ratios NH_3/mixture corresponding to the dissociation [5] and at 31 mm Hg between 9 and

$$NH_4Br \cdot 3NH_3 \rightleftharpoons NH_4Br \cdot 1.5NH_3 + 1.5NH_3$$

3 mole ratios NH_3/mixture corresponding to the dissociation [5].

$$NH_4Br \cdot 1.5NH_3 \rightleftharpoons NH_4Br + 1.5NH_3$$

It is thus evident that 4 mol of NH_4Br are present per mole of zirconium in the mixture. We therefore formulate the mixture as $4NH_4Br + Zr(CN)_4 \cdot 2NH_3$. Three further moles of ammonia are evidently held by the $Zr(CN)_4 \cdot 2NH_3$ at –36 °C; these are evolved when the mixture is warmed to room temperature. Confirmation of our belief that the mixture contains no ammonium cyanide is found in the absence of plateau in the tensimetric study at 300 and 115 mm Hg corresponding [7] to the dissociation pressures of $NH_4CN \cdot 4NH_3$ and $NH_4CN \cdot 3NH_3$ at –36 °C.

In an attempt to isolate zirconium(IV) cyanide we studied the thermal decomposition of the mixture with ammonium bromide hoping to achieve fractional vacuum sublimation. Up to 100 °C only the two coordinated ammonia molecules were evolved. At 132 °C, ammonium cyanide was evolved (collected in a liquid nitrogen trap) and at 155 °C a white sublimate of ammonium bromide collected above the hot zone and the residue became brown. Sublimation of ammonium bromide was completed at 250 °C *in vacuo* and the brown residue was then found to have the composition $Zr(CN)_2Br_2$. The reactions occurring are thus:

$$Zr(CN)_4 \cdot 2NH_3 + 4NH_4Br \xrightarrow{100\,°C} Zr(CN)_4 + 4NH_4Br + 2NH_3$$

$$Zr(CN)_4 + 4NH_4Br \xrightarrow{155-250\,°C} Zr(CN)_2Br_2 + 2NH_4CN + 2NH_4Br$$

Our further attempts to separate zirconium(IV) cyanide have included soxholet extractions with petrol, methyl cyanide, nitromethane, and using 18-crown-6 in chloroform but have all proved unsuccessful.

Experimental

All the zirconium compounds mentioned in this work were sensitive to moist air and all manipulations with them were carried out either *in vacuo* or under dry, oxygen-free argon. Reactions and manipulations in liquid ammonia were carried out as described elsewhere [5]. Spectroscopic and magnetic measurements were performed as previously described [8] Zirconium(IV) bromide was prepared by direct bromination of zirconium metal at 400 °C; zirconium(III) chloride and bromide were obtained by aluminium reduction of the corresponding tetrahalides at 250–300 °C [9]. Ammonium cyanide was prepared from ammonium chloride and potassium cyanide in liquid ammonia [10].

Reaction of $ZrBr_4$ with Ammonia

A known excess of ammonia condensed on to $ZrBr_4$ at –78 °C; the reaction was then thermostatted at –36 °C and the vapour pressure-composition isotherm was constructed as described elsewhere [5]. Removal of liquid ammonia and evacuation of the product at room temperature gave the pale pink-brown hexammine (Found: Zr, 17.9; Br, 61.9; NH_3 20.1; $ZrBr_4(NH_3)_6$ requires, Zr, 17.79; Br, 62.32; NH_3, 19.89%). Upon heating this material to 200 °C *in vacuo* for 12 h, 4.1 mol of NH_3 were evolved and the diammoniate left as a grey residue

(Found: Zr, 20.8; Br, 71.1; NH_3, 7.38; $ZrBr_4(NH_3)_2$ requires, Zr, 20.51; Br, 71.85; NH_3, 7.64%).

Reaction of $ZrBr_4$ with NH_4CN

Liquid ammonia (~100 cm^3) was condensed on to $ZrBr_4$ (~2.5 g) and then an excess (~5 g) of NH_4CN sublimed into this mixture at −78 °C. After agitation, the pale coloured solution was filtered and the ammonia removed by distillation to leave a pale buff solid which was evacuated for 6 h at 50 °C to remove excess of ammonium cyanide. (Found, Zr, 14.6; Br, 51.5; C, 8.00; N, 22.0; H, 3.80; $ZrBr_4$-$C_4N_{10}H_{22}$ requires, Zr, 14.69; Br, 51.48; C, 7.73; N, 22.55; H, 3.54%). When this mixture was heated to 132 °C, NH_4CN sublimed out (identified by gas phase IR) and at 155 °C, NH_4Br collected as a white sublimate (Found Br, 80.9; NH_4Br requires, Br, 81.61%; IR as for NH_4^+ only). The residue after evacuation for 12 hours at 250 °C was brown and diamagnetic (Found, Zr, 30.2; Br, 53.0; C, 7.75; N, 9.08; $ZrBr_2(CN)_2$ requires, Zr, 30.10; Br, 52.73; C, 7.92; N, 9.25%: IR spectrum ν(CN) 2100 cm^{-1} v.br., ν(ZrC) 470 cm^{-1}, br).

Reaction of $ZrCl_3$ with Ammonia

A known excess of liquid ammonia was condensed on to a weighed quantity of $ZrCl_3$ and after reaction at −36 °C the excess of ammonia was removed and measured to leave the green mass of composition $ZrCl_3(NH_3)_6$. When this was warmed to 20 °C *in vacuo,* the composition became $ZrCl_3(NH_3)_{2.5}$ (Found, Zr, 36.6; Cl, 42.8; NH_3, 17.8; $ZrCl_3(NH_3)_{2.5}$ requires Zr, 37.98; Cl, 44.29; NH_3, 17.73%; diffuse reflectance spectrum, 45.9, 29.8, 21.6, 15.0, 9.3 $cm^{-1} \times 10^3$: IR spectrum; $\nu(NH_3)$ 3325, 3251, 3155; $\delta_d(NH_3)$, 1599, $\delta_s(NH_3)$, 1258, $\rho(NH_2)$, 776, 625, ν(ZrN)/(ZrCl), 303, 246 cm^{-1}.

Reaction of $ZrBr_3$ with Ammonia

This reaction carried out as for $ZrCl_3$ gave a dark brown solid and a pale brown solution. After removal of excess ammonia both −36 °C and 20 °C the composition of the brown solid was that of a hexammine (Found, Zr, 21.4; Br, 55.1; NH_3, 23.4; $ZrBr_3$-$(NH_3)_6$ requires Zr, 21.06; Br, 55.35; NH_3, 23.59%). Thermal decomposition of this solid for 15 h at 100 °C *in vacuo* gave the dark grey monoammine (Found, Zr, 26.4; Br, 68.7; NH_3, 5.20; $ZrBr_3(NH_3)$ requires, Zr, 26.21; Br, 68.89; NH_3, 4.89%). Diffuse reflectance spectra: $ZrBr_3\cdot 6NH_3$, 46.2; 42.1, 37.2, 27.1, 17.0, 9.4; $ZrBr_3\cdot NH_3$, 45.1, 37.9, 31.3, 27.2, 19.6, 11.6 $cm^{-1} \times 10^3$. IR spectra: $ZrBr_3\cdot 6NH_3$; $\nu(NH_3)$, 3100, $\delta_d(NH_3)$, 1573; $\delta(NH_3)$, 1290; ρ-(NH_3), 654; ν(ZrN) 446, 373 cm^{-1}; $ZrBr_3\cdot NH_3$; $\nu(NH_3)$, 3130; $\delta_d(NH_3)$, 1584; $\delta_s(NH_3)$, 1256; ρ-(NH_3), 749, 628; ν(ZrN), 237; ν(ZrBr), 220 cm^{-1}.

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