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Ammoniates of Ammonium Cyanide and Evidence for the Formation of Titanium(III) Cyanide

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Ammonium cyanide is an extremely useful reagent for preparing metal cyanides in liquid ammonia. Unlike the alkali metal cyanides, any excess of this reagent in an ammonia-soluble product can be removed simply by room temperature sublimation.

The reaction of titanium(III) bromide with potassium cyanide in liquid ammonia yields the insoluble complex cyanide of formula $K_5Ti(CN)_8$ [1]; this is believed to be best formulated as containing seven co-ordinated titanium(III), the latter being in a mono-capped trigonal prismatic environment [2]. No simple cyanide of titanium has been reported; reactions of titanium(III) salts with cyanide ion in aqueous solution lead only to the precipitation of titanium(III) hydroxide. We now report the reactions of titanium(III) halides with ammonium cyanide in liquid ammonia and a tensimetric study of the relevant ammonium cyanide-ammonia system.

The vapour pressure of ammonium cyanide requires that tensimetric studies in the NH_4CN–NH_3 system be carried out at –63 °C or lower (at which temperatures the vapour pressure of NH_4CN is less than 1 mm Hg). The vapour pressure–composition isotherm for this system at –63 °C is shown in Fig. 1. This shows (in addition to the saturated solution vapour pressure of 90 mm Hg) the formation of two ammoniates, $NH_4CN \cdot 4NH_3$ and $NH_4CN \cdot 3NH_3$, the univariant portions at pressures 80 and 13 mm Hg corresponding to the equilibria:

$$NH_4CN \cdot 4NH_3(s) \rightleftharpoons NH_4CN \cdot 3NH_3(s) + NH_3(g)$$

$$NH_4CN \cdot 3NH_3(s) \rightleftharpoons NH_4CN(s) + 3NH_3(g)$$

Thermodynamic data for these equilibria were obtained (Table I) by measuring the variation of dissociation pressure of ammonia with temperature in the range –63 to –36 °C and applying the integrated form of the Van't Hoff isochore. Vapour pressures were corrected for the partial pressure of $NH_4CN(s)$ at the higher temperatures. The heats of formation of the two ammoniates can be calculated (using the literature values [7] for $\Delta H_f^\ominus NH_4CN$ and NH_3) to be:

$$NH_4CN \cdot 4NH_3,\ \Delta H_f = -293 \pm 5 \text{ kJ mol}^{-1}$$

$$NH_4CN \cdot 3NH_3,\ \Delta H_f = -225 \pm 5 \text{ kJ mol}^{-1}$$

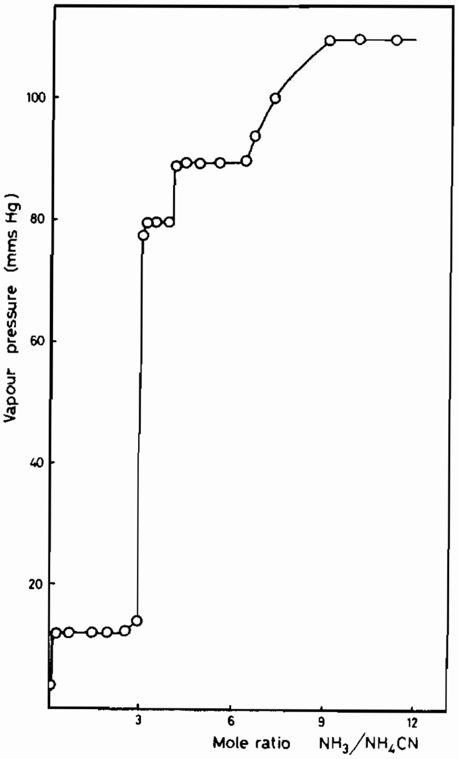

Fig. 1. Vapour pressure–composition isotherm for the system NH_4CN–NH_3 at –63 °C.

The heats of dissociation of these ammoniates per mol of ammonia are similar to those of the ammonium halide ammoniates [8, 9]. The ammonia molecules are almost certainly bonded to the ammonium ion by ion dipole forces; a crystal structure determination has shown [10] this to be the arrangement in $NH_4Cl \cdot 3NH_3$.

Because of the insolubility of potassium chloride in liquid ammonia, transition metal bromides are usually chosen as reactants with potassium cyanide in the preparation of the metal cyanides (potassium

TABLE I. Thermodynamic Data for the NH_4CN–NH_3 Reactions at –63 °C.

Reaction	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
$NH_4CN \cdot 4NH_3 \rightleftharpoons NH_4CN \cdot 3NH_3 + NH_3$	3.98	21.5	83.5
$NH_4CN \cdot 3NH_3 \rightleftharpoons NH_4CN + 3NH_3$	21.3	87.3	314.2

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bromide is more soluble and can be extracted with liquid ammonia). The use of ammonium cyanide enables a wider choice of transition metal compounds to be used as starting materials since a large number of ammonium salts are ammonia-soluble. Titanium(III) chloride and bromide form insoluble ammines in liquid ammonia [3] but these dissolve when treated with an excess of ammonium cyanide in ammonia to give red-violet solutions. Evaporation of these solutions at –33 °C and evacuation of the resulting solids at 50 °C, to remove excesses of ammonium cyanide and ammonia yields heterogeneous brown (Cl^-) or pale violet (Br^-) solids of composition $(NH_4)_3TiX_3(CN)_3$ (X = Cl, Br). X-ray powder photographs of these solids show lines due to the respective ammonium halide only. A tensimetric study of the system $(NH_4)_3TiCl_3(CN)_3$–NH_3 at –36 °C shows only one univariant step; this step between 11 and 3 mol ratios NH_3 to $(NH_4)_3TiCl_3(CN)_3$ is at a pressure of 84 mm Hg and thus corresponds [4] to the dissociation

$$NH_4Cl \cdot 3NH_3(s) \rightleftharpoons NH_4Cl(s) + 3NH_3(g)$$

Thus $2\frac{2}{3}$ mol of NH_4Cl are detected in '$(NH_4)_3TiCl_3(CN)_3$' and no univariant step corresponding to the dissociation of ammoniates of ammonium cyanide is observed. Removal of excess ammonia at –36 °C leaves an over-all composition $(NH_4)_3TiCl_3(CN)_3 \cdot 3NH_3$, these three remaining ammonia molecules being evolved upon evacuation of the solid at 50 °C. The electronic spectrum of $(NH_4)_3TiCl_3(CN)_3$ shows in addition to charge transfer bands, a d–d transition at 22,000 cm^{-1} with a shoulder at 18,500 cm^{-1}. This spectrum is very similar to that of $K_3Ti(CN)_6$ [5] in the d–d region and is thus in accord with a formulation of '$(NH_4)_3TiCl_3(CN)_3$' as containing titanium(III) octahedrally co-ordinated with cyanide ion (the $TiCl_6^{3-}$ ion has its d–d absorption at 13,000 cm^{-1} [6] so that any chloride ion contribution to the environment around titanium would reduce the band position significantly from that of $K_3Ti(CN)_6$). We therefore believe that the compositions $(NH_4)_3TiX_3(CN)_3$ are mixtures of $Ti(CN)_3$ and $3NH_4X$. The infrared spectra of these mixtures show the presence of the NH_4^+ ion and have ν(CN) at 2198, 2119, 2098, 2026 cm^{-1} for the chloride product and 2180, 2114 and 2080 cm^{-1} for the bromide product. We interpret the high cyanide stretching frequencies (2198 and 2180 cm^{-1}) to bridging cyanide and the lower ones to terminal cyanide; a possible structure for $Ti(CN)_3$ is thus a polymeric framework of octahedrally co-ordinated titanium(III) ions which are doubly cyanide bridged. The magnetic moment μ_{eff} of 1.31 BM at 20 °C is also in accord with the formulation of a mixture containing non-magnetically dilute titanium(III); titanium(III) chloride also has μ_{eff} = 1.3 BM at 27 °C [11]. Attempts to separate the $Ti(CN)_3$ from ammonium halide using solvents have so far proved unsuccessful. Since sublimation of the ammonium halide seemed possible we studied the thermal decomposition of these mixtures. Unfortunately, at temperatures which the ammonium halides sublime *in vacuo*, reaction occurs so that both ammonium halide and ammonium cyanide sublime to leave non stoichiometric solids *e.g.* in the chloride case, $TiCl_{1.5}(CN)_{1.5}$.

Experimental

Reactions and tensimetric studies in liquid ammonia were carried out *in vacuo* as described elsewhere [4]. Ammonium cyanide was prepared by passing dry ammonia gas through a solution of hydrogen cyanide in dry dichloromethane. The precipitated product was filtered off, washed with cold dichloromethane and purified by vacuum sublimation.

In the reactions of ammonium cyanide with the titanium(III) halides, an excess of liquid ammonia (150 cm^2) was condensed on to a mixture of the halide (1 g) with an excess (4 g; >12 mol ratios) of ammonium cyanide and solution allowed to take place at –50 °C. The solution was filtered and evaporated; final evacuation was carried out at 50 °C to ensure complete removal of excess ammonium cyanide. *Anal.* Found: Ti, 16.6; Cl, 37.0; C, 12.4; N, 29.4. Calcd. for $(NH_4)_3TiCl_3(CN)_3$: Ti, 16.72; Cl, 37.13; C, 12.58; N, 29.34%. Found: Ti, 11.2; Br, 57.0; C, 8.42; N, 20.3. Calcd. for $(NH_4)_3TiBr_3(CN)_3$: Ti, 11.42; Br, 57.13; C, 8.58; N, 20.02%.

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