Ammonium Cyanide: Its Preparation and Reactions with Transition Metal(0) Cyanides

ELAINE S. DODSWORTH, JANICE P. EATON, MICHAEL P. ELLERBY and DAVID NICHOLLS*

Donnan Laboratories, The University, Liverpool, L69 3BX, U.K.

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A new simplified synthesis of ammonium cyanide is described which avoids the use of hydrogen cyanide. The reactions of ammonium cyanide with the metal(0) cyanide complexes $K_6Cr(CN)_6$, K_8Co-$(CN)_8$, $K_4Ni(CN)_4$, $K_2Pd(CN)_2$ and $K_5Zr(CN)_5$ in liquid ammonia are described. The chromium(0) and cobalt(0) complexes are oxidised to the hexacyano-metallates(III) while the other metals are oxidised to the +2 state. Only in the case of zirconium does a hitherto unknown cyanometallate anion arise.

Introduction

Ammonium cyanide is an extremely useful reagent for preparative work in liquid ammonia [1]. It has a very high solubility in ammonia and any excess of the reagent after a reaction can readily be removed by vacuum sublimation at room temperature. At −63 °C, ammonium cyanide crystallizes from ammonia as a 4-ammoniate; this compound exerts a dissociation pressure of 80 mm Hg becoming the 3-ammoniate which exerts a dissociation pressure of 13 mm Hg at this temperature [2]. It thus resembles the ammonium halides in forming ammoniates bonded by weak ion–dipole forces and it is therefore theoretically possible to quantitatively detect its presence in solid mixtures at low temperatures by means of vapour pressure-composition isotherms. The preparation of ammonium cyanide has hitherto involved the direct combination of ammonia and hydrogen cyanide at low temperatures either in the absence of a solvent, in liquid ammonia [3] or in dichloromethane [2]. We report here direct preparation of ammonium cyanide which avoids the intermediate preparation and use of hydrogen cyanide.

The first metal(0) cyanide complex was prepared in 1945 [4] but transition metal(0) cyanides of the early transition elements have been prepared only in recent years *e.g.* $K_4Ti(CN)_4$ [5], $K_5Zr(CN)_5$ [6] and $K_2V(CN)_2 \cdot 0.5NH_3$ [3]. Very little structural

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information is available concerning these extremely reactive species and very few reactions of them have been studied. We have recently shown [3] the use of ammonium cyanide in the preparation of $K_2V(CN)_4$ and report now on the reactions of other cyanometallates(0) with ammonium cyanide.

Results and Discussion

The reaction between potassium cyanide and ammonium chloride in liquid ammonia proceeds almost quantitatively according to:

$$NH_4Cl + KCN \longrightarrow NH_4CN + KCl$$

the potassium chloride is precipitated and it is this insolubility of potassium chloride which provides the driving force for the reaction. The ammonium cyanide can be recovered by evaporation of the ammonia at −33 °C followed by sublimation of the ammonium cyanide at room temperature; for more quantitative yields however, removal of ammonia at −63 °C is preferable since ammonium cyanide has appreciable volatility above this temperature. For liquid ammonia reactions however, separation of the ammonia and ammonium cyanide is unnecessary so that by taking known weights of potassium cyanide and ammonium chloride we have been able to distill a known excess of ammonium cyanide in liquid ammonia on to our reactants at −78 °C.

Our interest in studying reactions between cyanometallates(0) arose because of possibility of preparing the unknown ammonium cyanometallates(0). It is now clear that ammonium cyanide acts as an acid and consequently an oxidising agent in its reactions with these metal(0) complexes. In all the reactions described here, the metal is oxidised and the ammonium ion reduced to ammonia and hydrogen.

$$NH_4^+ + e^- \longrightarrow NH_3 + \tfrac{1}{2}H_2$$
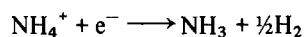
Perhaps the most straightforward example is the oxidation of the palladium compound $K_2Pd(CN)_2$ which dissolves with reaction in ammonium cyanide

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solutions to give the well known salt $K_2Pd(CN)_4$ upon evaporation and removal of all volatiles.

$$K_2Pd(CN)_2 + 2NH_4CN \longrightarrow K_2Pd(CN)_4 + H_2 + 2NH_3$$
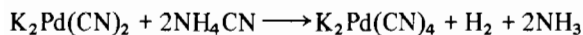
With $K_4Ni(CN)_4$, the nickel is oxidised to the $[Ni(CN)_4]^{2-}$ ion but instead of the salt $K_2[Ni(CN)]_4$ crystallising, the new compound $KNH_4[Ni(CN)_4]$ is obtained in admixture with potassium cyanide:

$$K_4Ni(CN)_4 + 3NH_4CN \longrightarrow$$

$$KNH_4[Ni(CN)_4] + 3KCN + 2NH_3 + H_2$$
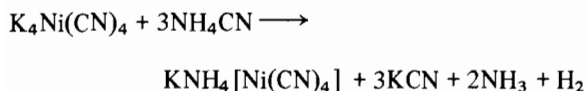
This mixture cannot be formulated as containing $K_2[Ni(CN)]_4 + NH_4CN$ because of the volatility of NH_4CN. A similar double salt is obtained in the oxidation of $K_8[Co_2(CN)_8]$ with ammonium cyanide:

$$K_8[Co_2(CN)_8] + 8NH_4CN \longrightarrow$$

$$2K_2NH_4[Co(CN)_6] + 4KCN + 8NH_3 + 4H_2$$
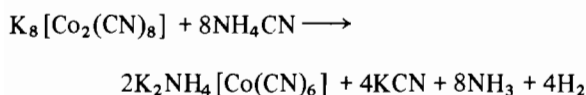
Unlike these last two reactions, the product from the dissolution of $K_6Cr(CN)_6$ in an ammonium cyanide solution does not show any peaks due to NH_4^+ in its i.r. spectrum only those due to KCN and $K_3[Cr(CN)]_6$; the analysis confirms that the over-all reaction is:

$$K_6Cr(CN)_6 + 6NH_4CN \longrightarrow$$

$$2K_3[Cr(CN)]_6 + 6KCN + 6NH_3 + 3H_2$$
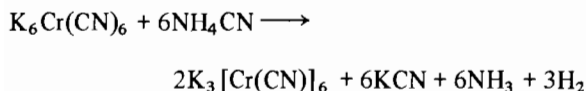
The only new cyanocomplex formed in the reactions studied here is that of zirconium(II). No cyanide complexes of zirconium are known in its usual oxidation states of +2, +3, or +4. When $K_5Zr(CN)_5$ is treated with ammonium cyanide solution followed by filtration and washing, the filtrate contains only potassium cyanide and the mauve residue has the formula $K_2Zr(CN)_4$. The magnetic moment of 2.75 B.M. is in accord with this compound being formulated as containing zirconium(II); the i.r. spectrum differs from that of the starting material in having only three $\nu(CN)$ bands instead of five and in the shift of $\nu(Zr-C)$ to lower wavenumbers in accord with an increase in oxidation state of the zirconium. The electronic spectrum shows three d–d bands rather close together with a much stronger charge transfer band at 28800 cm^{-1}. The oxidation of zirconium(0) to zirconium(II) is similar to that of vanadium, in which $K_2V(CN)_4$ is produced [3]; oxidation to zirconium(III) is impossible in this reaction because of the disproportionation of the latter in cyanide media in liquid ammonia [6].

Whilst the oxidations of Ni(0), Pd(0) and Zr(0) cyanometallates to the +2 oxidation state of the metal are not unexpected, the oxidations of chromium(0) and cobalt(0) cyano complexes to the +3 state is surprising. Both chromium(II) [7] and cobalt(II) [8] cyanides are stable in liquid ammonia; in an excess of ammonium cyanide however the oxidation

$$[Cr(CN)_6]^{4-} + H^+ \longrightarrow [Cr(CN)_6]^{3-} + \tfrac{1}{2}H_2$$
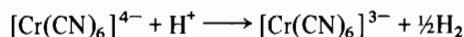
occurs just as it does in water. In the cobalt case the +3 oxidation state is stabilised by the t_{2g}^6 configuration which gives the maximum propensity for π-bonding to the vacant π^* orbitals on CN$^-$.

Experimental

Reactions and manipulations in liquid ammonia were carried out *in vacuo* as described elsewhere [1]. Spectroscopic and magnetic measurements were as previously described [3]. 'Analar' grade ammonium chloride and potassium cyanide were dried by evacuation at 100 °C for several hours; liquid ammonia was dried over sodium. The cyanometallates(0) were prepared as previously described *i.e.* $K_4Ni(CN)_4$ [4], $K_2Pd(CN)_2$ [9], $K_6Cr(CN)_6$ [11], $K_8Co_2(CN)_8$ [10], $K_5Zr(CN)_5$ [6]; they were prepared *in situ* in the apparatus which was used for their reactions with ammonium cyanide.

Preparation of Ammonium Cyanide

Liquid ammonia (~50 cm^3) was condensed on to a mixture on ammonium chloride (5.35 g; 0.001 mol) and potassium cyanide (6.51 g; 0.001 mol) and the mixture warmed to −63 °C (CHCl$_3$ slush bath) at which temperature it was agitated for a few minutes to ensure complete reaction. The ammonia was then removed by distillation at −63 °C and the solid residue then allowed to warm to room temperature. The white sublimate of ammonium cyanide was collected in a clean flask cooled in liquid nitrogen. The material was analysed by condensation of a sample in a weighed evacuated bulb; water was then admitted and the resulting solution made up to standard volume: Found NH$_4^+$ (Kjeldahl) 40.7, CN$^-$ (as AgCN) 58.9%, NH$_4$CN requires NH$_4^+$ 40.91, CN$^-$ 59.09%.

Reaction of Ammonium Cyanide with Cyanometallates(0)

(i) $K_2Pd(CN)_2$

An excess of ammonia (~100 cm^3) and ammonium cyanide (~3 g) was condensed on to $K_2[Pd(CN)_4]$ (~1 g) at −78 °C. On warming to around −60 °C with agitation, hydrogen was evolved and

a colourless solution produced. This solution was filtered *in vacuo* and the filtrate evaporated to yield a white solid; this solid was evacuated at 40 °C for 15 hr. to ensure complete sublimation of excess ammonium cyanide. (*Anal.* Found: C, 16.4; N, 19.7; K, 27.3; $K_2[Pd(CN)_4]$ requires: C, 16.63; N, 19.41; K, 27.09%.) Electronic spectrum and i.r. spectrum of the solid were identical to those of $K_2[Pd(CN)_4]$; the compound was diamagnetic.

(ii) K₄Ni(CN)₄

Reaction similar to that above gave an orange solution which when filtered, evaporated and evacuated at 40 °C gave a yellow solid. (*Anal.* Found: C, 20.3; N, 26.3; H, 0.90; K, 37.0; Ni, 14.2; $K(NH_4)$-$[Ni(CN)_4]$ + 3KCN requires: C, 20.30; N, 27.05; H, 0.96; K, 37.68; Ni, 14.00%). The mixture was diamagnetic, had an electronic spectrum (diffuse reflectance) as for that of $K_2[Ni(CN)_4]$ and in its i.r. spectrum were ν(CN) at 2123 cm^{-1} (as for $K_2[Ni(CN)_4]$) and 2080 cm^{-1} (KCN), ν(NH₄⁺) at 3180 cm^{-1} and δ(NH₄⁺) at 1655 and 1418 cm^{-1}.

(iii) K₈[Co₂(CN)₈]

The reaction between $K_8[Co_2(CN)_8]$ (2 g) and NH₄CN (6 g) in liquid ammonia (150 cm³) at −50 °C produced a pale yellow solution and a pale yellow solid with evolution of hydrogen. After filtration of the mixture, the insoluble solid was extracted several times with a solution of ammonium cyanide until virtually no insoluble material remained. Evaporation of ammonia from the combined filtrates followed by removal of ammonium cyanide at 40 °C gave a pale yellow solid. (*Anal.* Found: C, 22.4; N, 26.4; H, 0.86; K, 35.9; Co, 13.9; $K_2(NH_4)[Co(CN)_6]$ + 2KCN requires: C, 21.82; N, 28.64; H, 0.91; K, 35.45; Co, 13.18%.) The mixture was diamagnetic, had a diffuse reflectance spectrum as for $K_3[Co(CN)_6]$ and an i.r. spectrum with ν(CN) at 2128 ($[Co(CN)_6]^{3-}$) and 2080 cm^{-1} (KCN), δ(CoCN) at 561 cm^{-1}, ν(CoC) at 415 cm^{-1} ($[Co(CN)_6]^{3-}$) and ν(NH₄⁺) at 3260 and 3020 cm^{-1}, δ(NH₄⁺) at 1420 cm^{-1}.

(iv) K₆Cr(CN)₆

Reaction with NH₄CN was carried out as for cobalt above but gave only a yellow solution with hydrogen evolution. Filtration, evaporation of the ammonia and evacuation at 40 °C gave a yellow solid. (*Anal.* Found: C, 20.1; N, 23.2; K, 43.3; Cr, 9.21; $K_3[Cr(CN)_6]$ + 3KCN requires, C, 20.74; N, 24.20; K, 45.00; Cr, 10.00%). The solid had μ_{eff} = 3.6 B.M.

at 20 °C; its diffuse reflectance spectrum was not identical with that of $K_3[Cr(CN)_6]$ but had bands at 37.500, 29.500 and 26.100 cm^{-1} ($K_3[Cr(CN)_6]$) and a shoulder at 21.000 cm^{-1} (where the strongest band occurs in $K_3[Cr(CN)_6]$). In the i.r. spectrum, ν(CN) occurred at 2132 ($K_3[Cr(CN)_6]$) and 2080 cm^{-1} (KCN); δ(CrCN) at 456 cm^{-1} and ν(CrC) at 338 cm^{-1} ($K_3[Cr(CN)_6]$); there were no bands due to NH₄⁺ or NH₃.

(v) K₅Zr(CN)₅

When ammonia (150 cm³) and NH₄CN (10 g) were condensed on to grey $K_5Zr(CN)_5$ (0.75 g) a mauve solid and colourless solution were formed; reaction was allowed to proceed at −33 °C before filtration and then the residue was extracted four times with a solution of NH₄CN in ammonia prior to evacuation of both the insoluble residue and the combined filtrates. The solid from the filtrate was a cream coloured powder containing only a trace of zirconium (alizarin − S test) and whose i.r. spectrum had only the ν(CN) peak of KCN. The mauve residue had μ_{eff} = 2.75 B.M. at 20 °C. (*Anal.* Found: C, 16.9; N, 19.8; K, 28.2; Zr, 32.9; $K_2Zr(CN)_4$ requires C, 17.55; N, 20.48; K, 28.59; Zr, 33.36%.) The i.r. spectrum showed ν(CN) at 21.85, 2095 and 2073 cm^{-1} δ(ZrCN) at 380 cm^{-1} and ν(ZrC) at 305 cm^{-1}. The diffuse reflectance spectrum showed bands at 44, 500, 28,800, 21,100, 18,100 and 15,900 (sh) cm^{-1}.

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