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New Complex Cyanides of Vanadium

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The reaction of VCl_4 with NH_4CN in liquid ammonia leads to a mixture of $V(CN)_3(NH_2)$ and NH_4Cl while VCl_3 and VBr_3 react with NH_4CN to give mixtures of $V(CN)_3(NH_3)$ and ammonium halide. Reduction of a mixture of VBr_3 and KCN with potassium in ammonia yields the pyrophoric vanadium(0) cyanide $K_2V(CN)_2$ $0.5NH_3$ which is oxidised by ammonium cyanide in ammonia to the new vanadium(II) cyanide $K_2V(CN)_4$.

Introduction

The complex cyanides of vanadium have been the subject of considerable interest in recent years [1]. Thus the compounds $K_3[VO(CN)_5]$, $K_4[V(CN)_7]\cdot 2H_2O$ and $K_4[V(CN)_6]$ are well characterised examples of cyanide complexes obtained from aqueous solutions of vanadium(IV), -(III) and -(II) respectively. However, no simple cyanides of vanadium are known and little preparative chemistry has been attempted in solvents other than water. We describe here attempts to prepare simple cyanides of vanadium(IV), and -(III) in liquid ammonia and report new cyanides of vanadium(0) and vanadium(II).

Results and Discussion

Ammonium cyanide is a particularly useful reagent for preparing cyanides in liquid ammonia; it is extremely soluble and its volatility enables any excess to be removed from reaction products by room temperature sublimation. We chose therefore to study the reactions between vanadium halides and ammonium cyanide in ammonia. The fluorides VF_4 and VF_3 are the preferred starting materials in view of the fact that these are likely to be more resistant to ammonolysis; the chlorides of vanadium(IV) and vanadium(III) are known [2, 3] to undergo ammonolysis in liquid ammonia. We find however that no reaction occurs between vanadium(III) fluoride and ammonium cyanide in ammonia over the temperature range −33 to −78 °C nor does any ammonolysis of the fluoride occur. With vanadium(IV) fluoride and ammonium cyanide there is some slight reaction but the fluoride remains largely insoluble and unreacted.

Vanadium(IV) chloride gives a brown solution in liquid ammonia containing an excess of ammonium cyanide. Evaporation of this solution followed by removal of the excess of ammonium cyanide by room temperature sublimation gives a brown solid. The i.r. spectrum of this solid shows the presence of NH_4^+ ions, co-ordinated $-NH_2$ or NH_3 and $-CN$ yet shows no band assignable to $\nu(V-Cl)$ and the magnetic moment confirms that the oxidation state of the vanadium has remained unchanged. A vapour pressure–composition isotherm for the system formed by this brown solid and liquid ammonia at −35 °C shows a univariant step at 84 mm Hg between 14 and 2 mol ratios NH_3:V. This corresponds to the dissociation

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

and thus shows [4] that the brown solid contains four moles of ammonium chloride per mole of vanadium. Further the absence of any other plateau *e.g.* at 115 mm Hg or at 20 mm Hg corresponding to the dissociations [5]

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

$$NH_4CN(s) \rightleftharpoons NH_4CN(g)$$

confirms that no free ammonium cyanide is present in the brown solid. We thus formulate the solid as the mixture $V(CN)_3(NH_2)$ + $4NH_4Cl$, the overall equation for the reaction being

$$VCl_4 + 3NH_4CN + 2NH_3 \rightarrow V(CN)_3(NH_2) + 4NH_4Cl$$

Obviously the reaction is more complex than is indicated by this equation. Vanadium(IV) chloride is ammonolysed in ammonia to $VCl(NH_2)_3$ [2] but this

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is soluble in solutions of ammonium salts because of the formation of soluble complex anions. Thus a likely reaction path is

$$\begin{tikzcd}
 & \mathrm{VCl_4 + 6NH_3 \rightarrow VCl(NH_2)_3 + 3NH_4Cl} \arrow[d, "\mathrm{NH_4CN}"] \\
\mathrm{[NH_4]_2[V(CN)_3(NH_2)_3]} \arrow[d] & \mathrm{V(CN)(NH_2)_3 + NH_4Cl} \arrow[l, "\mathrm{2NH_4CN}"'] \\
\mathrm{V(CN)_3(NH_2) + 4NH_3} &
\end{tikzcd}$$

Cyanide amides are as yet unreported; we have so far been unable to separate this cyanide amide from ammonium chloride using solvents or sublimation techniques. Unfortunately we are unable to detect the d–d transition in the reflectance spectrum of the solid; the spectrum shows only broad absorptions with an intense band centred at 22,000 cm^{-1}. It is likely that like $VCl(NH_2)_3$, $V(CN)_2(NH_2)$ is polymeric; the relatively high ν(CN) is similar to that in $K_3[VO(CN)_5]$ [6] and the presence of a lower ν(CN) at 2046 cm^{-1} may indicate that bridging cyanides are also present.

Vanadium(III) chloride and vanadium(III) bromide give purple solutions when treated with an excess of ammonium cyanide in liquid ammonia, from which purple solids are obtained by removal of ammonia and ammonium cyanide *in vacuo*. I.r. spectra on these clearly show the presence of ammonium ions and the absence of bands attributable to ν(V–X). Tensimetric studies on both solids show the presence of three moles of ammonium halide per mole of vanadium and the absence of ammonium cyanide. It is evident, therefore, from these facts and the analytical data that the reaction products are mixtures of $V(CN)_3 \cdot NH_3$ with NH_4X (X = Cl, Br). Again however we have been unable to separate these mixtures. Upon thermal decomposition, the mixtures evolve one mole ratio of ammonia by 70 °C so that this ammonia is probably only held by weak ion–dipole forces. Above 150 °C, ammonium chloride (Cl^- case) sublimes, but the dark purple residue analyses as $V(CN)_{2.6}Cl_{0.4}$ indicating that some reaction between $V(CN)_3$ and NH_4Cl occurs at temperatures below which NH_4Cl sublimes.

In a further attempt to isolate vanadium(III) cyanide we carried out the reaction between vanadium(III) chloride and ammonium cyanide in methyl cyanide. The purple precipitate was similar to that obtained in ammonia but contained no co-ordinated ammonia, *i.e.* was a mixture of $V(CN)_3$ + $3NH_4Cl$. The electronic and i.r. spectra of these purple mixtures are all very similar (irrespective of solvent or halide used). The visible band ($^3T_{1g} \rightarrow {}^3T_{2g}$ in O_h symmetry) occurs as two peaks at 19,000 and 17,000 cm^{-1}. Clearly these peaks are not compatible with the presence of an octahedral field of six carbon-bonded cyanide ions around vanadium(III) (bearing in mind that the lowest energy band in $[V(H_2O)_6]^{3+}$ occurs [11] at 17,700 cm^{-1}). In a three-dimensional polymeric structure however, with all the cyanide ions bridging, each vanadium(III) ion would be bonded to three carbon atoms and three nitrogen atoms from cyanide ions thus lowering the symmetry from octahedral and the energies of the transitions from that expected for ν_1 in $[V(CN)_6]^{3-}$. The i.r. spectra show ν(CN) at rather lower frequencies than in $Ti(CN)_3$ [5] but at higher frequency than in $K_4[V(CN)_7] \cdot 2H_2O$ [6] which contains vanadium(III) and terminal cyanides.

Two complex cyanides of vanadium(0) have been described. The diamagnetic $K_5V(CN)_5$ is reported to be obtained by the hydrogen reduction of dehydrated $K_3[V(CN)_5(NO)] \cdot 2H_2O$ [7] while both $K_7V(CN)_7$ [6] and $K_5V(CN)_6$ [8] are reported as reduction products of $K_4[V(CN)_7]$ with potassium in liquid ammonia. We now find that reduction of a mixture of vanadium(III) bromide and excess of potassium cyanide with potassium in liquid ammonia gives the dark brown, extremely pyrophoric, $K_2V(CN)_2 0.5NH_3$. This compound has the expected magnetic moment corresponding to one unpaired electron in a low spin d^5 complex and shows a strong ν(CN) at 1905 cm^{-1} in the region expected for lower oxidation state cyanide complexes exhibiting d_π–π^* back bonding. When heated *in vacuo*, $K_2V(CN)_2 \cdot 0.5NH_3$ begins to evolve ammonia at 100 °C and virtually all the ammonia is removed by 212 °C. This is the first metal(0) cyanide complex to have such ammonia of solvation; the stoichiometry $K_2M(CN)_2$ is however known with M = Pd [9] and Pt [10]. We have repeated the earlier work on the reduction of $K_4[V(CN)_7]$ with potassium in ammonia and are unable to confirm either $K_7V(CN)_7$ or $K_5V(CN)_6$ as reduction products. Instead our products show the i.r. spectrum of $K_2V(CN)_2 \cdot 0.5NH_3$ but are of inconsistent analytical results.

When treated with ammonium cyanide in ammonia, $K_2V(CN)_2 \cdot 0.5NH_3$ dissolves to give a purple solution from which the pale purple vanadium(II) complex cyanide $K_2V(CN)_4$ can be isolated. The ammonium ion has thus acted as an oxidising agent to the very strongly reducing vanadium(0) species:

$$K_2V(CN)_2 \cdot 0.5NH_3 + 2NH_4CN \rightarrow K_2V(CN)_4 + H_2 + 2.5NH_3$$

This vanadium(II) species is quite different from the golden $K_4[V(CN)]_6$ prepared [6] in aqueous solution. Its i.r. spectrum resembles more closely that of $K_4[V(CN)]_7$; the higher ν(CN) bands in $K_2V(CN)_4$ may indicate bridging cyanides in this species with terminal cyanides in $K_4[V(CN)_6]$. The magnetic moment is low for a vanadium(II) complex but is not unexpectedly low for a polymeric cyanide-bridged structure.

Experimental

Manipulations and tensimetric studies and reactions in liquid ammonia were carried out as described elsewhere [4]. All new compounds were handled under atmospheres of de-oxygenated nitrogen or argon when not on the vacuum line. Infrared spectra were measured on a Perkin Elmer model 577 spectrophotometer and reflectance spectra on a Unicam SP 700C instrument. Magnetic moments were measured by the Gouy method at room temperature. Ammonium cyanide was prepared by passing anhydrous hydrogen cyanide in a nitrogen stream into liquid ammonia at −78 °C followed by the removal by distillation of the excess ammonia *in vacuo*; it was stored at −78 °C *in vacuo*. Vanadium halides were prepared as described previously [2, 12].

Preparation of $K_2[V(CN)_2]\cdot 0.5NH_3$

Liquid ammonia (125 cm^3) was condensed on to a mixture of VBr_3 (3 g), K (5 g) and KCN (9 g) at −78 °C. The mixture was warmed to about −40 °C and allowed to react for 30 min with intermittent shaking. Effervescence occurred and a dark precipitate formed in the blue solution; if the reaction mixture was allowed to stand at −78 °C overnight, the blue solution became totally decolourised without detriment to the purity of the product (obviously the product catalyses the decomposition of the potassium in ammonia solution to potassium amide and hydrogen). Filtration of the mixture produced a dark brown solid which was washed ten times with liquid ammonia (100 cm^3) and dried *in vacuo* at room temperature before being removed from the vacuum apparatus under dried and deoxygenated argon. (Found K, 40.8; V, 26.6; C, 12.6; N, 18.3%. $K_2V(CN)_2\cdot 0.5NH_3$ requires K, 41.3; V, 26.9; C, 12.7; N, 18.5%; μ_{eff} = 1.86 B.M.; e.s.r., g = 2.083; i.r. spectrum (cm^{-1}); 3150 (ν_{NH}), 2065, 1943(sh), 1905 (ν_{CN}), 1615 (δ_{NH_3}); u.v. spectrum ($cm^{-1} \times 10^3$) 45.0, 36.0(sh), 28.0(sh), 20.0(br)).

Reaction of $K_2V(CN)_2\cdot 0.5NH_3$ with NH_4CN in Ammonia

An excess of NH_4CN (~10 g) was sublimed on to $K_2V(CN)_2\cdot 0.5NH_3$ (~2 g) at −78 °C and then liquid ammonia (~150 cm^3) condensed on to the mixture. A deep purple solution formed which left almost no residue upon filtration. Evaporation of the solution left a pale purple powder. (Found, K, 33.4; V, 21.5; C, 20.3; N, 23.8%; $K_2V(CN)_4$ requires K, 33.5; V, 21.8; C, 20.6; N, 24.0%; μ_{eff} = 3.2 B.M.; i.r. spectrum (cm^{-1}), 2095, 2073 (ν_{CN}), 475, 445 (ν_{VC}), 365, 335 (δ_{VCN}); u.v. spectrum, ($cm^{-1} \times 10^3$), 46.3, 38.0(sh), 36.5, 27.2, 23.8, 19.3, 17.1(sh)).

Reactions of Vanadium(III) Halides with NH_4CN in Ammonia

VCl_3

NH_4CN (~8 g) was sublimed on to VCl_3 (~2 g) and then liquid ammonia (~150 cm^3) condensed on to the mixture. A deep purple solution formed which when filtered (no residue) and evaporated *in vacuo* followed by evacuation at room temperature, left a purple solid. (Found, V, 16.8; C, 11.7; H, 5.5; N, 34.5%. $V(CN)_3\cdot NH_3$ + $3NH_4Cl$ requires V, 16.6; C, 11.8; H, 4.9, N, 32.0%; μ_{eff} = 2.4 B.M.; i.r. spectrum (cm^{-1}) 3150, 3055 (ν_{NH_3}), 2120, 2095 (ν_{CN}), 1719 ($\nu_{NH_4^+}$), 1604 (δ_{NH_3}), 1408 ($\nu_{NH_4^+}$), 1261(δ_{NH_3}), 971 (δ_{NH_3}), 449 (ν_{VC}); u.v. spectrum ($cm^{-1} \times 10^3$), 43.6, 36.6, 28.3(sh), 18.8, 16.9.)

VBr_3

This was treated as for VCl_3 and similarly gave a purple solution which yielded a purple solid upon evacuation. (Found, V, 11.6; C, 8.08; H, 3.44; N, 22.2. $V(CN)_3\cdot NH_3$ + $3NH_4Br$ requires V, 11.6; C, 8.19; H, 3.44; N, 22.3%: μ_{eff} = 2.2 B.M.; i.r. spectrum (cm^{-1}) 3120, 3020 (ν_{NH_3}), 2120, 2090 (ν_{CN}), 1719 ($\nu_{NH_4^+}$), 1602 (δ_{NH_3}), 1399 ($\nu_{NH_4^+}$), 1260 (δ_{NH_3}), 968 (δ_{NH_3}), 470 (ν_{VC}); u.v. spectrum ($cm^{-1} \times 10^3$), 38.0, 28.4, 19.0, 17.1).

Reaction of Vanadium(III) Chloride with Ammonium Cyanide in Methyl Cyanide

A green solution of VCl_3 (~1 g) in dried CH_3CN (~150 cm^3) was treated with solid NH_4CN (~5 g) at room temperature under a nitrogen atmosphere. The purple precipitate which formed was filtered off and dried *in vacuo* at 40 °C for 6 hr. (Found, V, 17.8; C, 10.1; N, 28.7: $V(CN)_3$ + $3NH_4Cl$ requires V, 17.6; C, 12.4; N, 29.0%; μ_{eff} = 2.84 B.M., i.r. and u.v. spectra as for ammonia preparations).

Reaction of Vanadium(IV) Chloride with NH_4CN in Ammonia

Ammonia (150 cm^3) was condensed on to a mixture of VCl_4 (~2 g) and NH_4CN (~8 g) at −78 °C and the mixture allowed to warm to −50 °C to give a brown solution. This was filtered (no residue) and evaporated; evacuation at room temperature gave a brown solid. (Found, V, 14.4; C, 10.1; H, 5.61; N, 31.4; $V(CN)_3(NH_3)$ + $4NH_4Cl$ requires, V, 14.2; C, 10.0; H, 5.06; N, 31.2%: μ_{eff} = 1.79 B.M.; i.r. spectrum (cm^{-1}) 3138 (ν_{NH}), 3020 (ν_{NH}), 2138 (ν_{CN}), 2046 (ν_{CN}), 1720 ($\nu_{NH_4^+}$); 1600 (δ_{NH_2}), 1400 ($\nu_{NH_4^+}$), 1260 (δ_{NH_2}), 968 (δ_{NH_2}), 460(br) (ν_{VC} or δ_{MCN}): u.v. spectrum ($cm^{-1} \times 10^3$), 45.3, 22.0 (v.br.)).

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