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Cobalt(II) Cyanide and its Complexes with Water, Ammonia and Cyanide Ions

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The hydrates and ammoniates of cobalt(II) cyanide have been prepared from aqueous and liquid ammonia solutions respectively. The unsolvated cobalt(II) cyanide has been prepared by four different routes and shown, contrary to previous reports, to be chemically different from $Co_3[Co(CN)_6]_2$. *New complex cyanides of cobalt(II) including* $(NH_4)_6[Co_2(CN)_{10}]$, $KCo(CN)_3$ *and* $K_2Co(CN)_4$ *are described. The magnetic moment of* $Co(CN)_2$ *is interpreted in terms of a structure containing both high and low spin cobalt(II); the i.r. spectra indicate bridging cyanide to be present in all the compounds described.*

Introduction

Treatment of aqueous solutions of cobalt(II) salts with potassium cyanide leads to a light brown precipitate which has been formulated for many years as $Co(CN)_2 \cdot nH_2O$ (n = 2 or 2.5); it has a magnetic moment of 3.27 BM[1]. An anhydrous blue solid is obtained when this hydrate is heated to 250 °C in a stream of nitrogen; this solid is formulated as $Co(CN)_2$ and has a magnetic moment of 3.12 BM [2]. More recent work however [3, 4] has suggested that the aqueous reaction product should be formulated non-stoichiometrically as $Co(CN)_x \cdot yH_2O$ where x = 2.2–2.4 and y = 1.75–2.15. This Co:CN ratio is similar to the 1:2.4 ratio in $Co^{II}_3[Co^{III}(CN)_6]_2$ which can be prepared as a pink dodecahydrate from aqueous solutions of cobalt(II) salts and $K_3[Co(CN)_6]$. One set of authors [4], concludes that $Co(CN)_2$ has no permanent existence; they maintain that the light brown precipitate is a contaminated form of the pink hydrated $Co_3[Co(CN)_6]_2$ (suggesting cobalt metal as a possible contaminant). A pink form of '$Co(CN)_2 \cdot 2H_2O$' has in fact been claimed to be isolated from the reduction of $K_3[Co(CN)_6]$ with hypophosphorous acid [5]; this form has the same X-ray powder pattern and infrared spectrum as the brown form.

Whilst a close structural relationship between $Co(CN)_2 \cdot nH_2O$ and $Co_3[Co(CN)_6]_2 \cdot 12H_2O$ may exist [3] we do not agree that these are one and the same species. Because of the very long reaction times used (by the workers claiming such identity) in the formation of the precipitates, the possibility of oxidation by the solvent water cannot be discounted [6]. Similarly in the reduction of $K_3[Co(CN)_6]$, the pink precipitate may well be $Co_3[Co(CN)_6]_2 \cdot 12H_2O$ and the lack of identity with freshly precipitated $Co(CN)_2 \cdot nH_2O$ is understandable. No attempts to prepare cobalt(II) cyanide in solvents other than water have been made. We describe here our preparations of cobalt(II) cyanide in water and in liquid ammonia and its complexes with water, ammonia and cyanide ion.

Results and Discussion

The aqueous reaction between cobalt(II) chloride and potassium cyanide carried out under nitrogen or *in vacuo* yields brown precipitates in low and medium concentration ranges ($CoCl_2$, 0.1–0.8 *M*; KCN, 0.4–2.0 *M*) and a green precipitate in high concentrations of reactants ($CoCl_2$, 3.2 *M*, KCN, 7.7 *M*). Within the 0–100 °C range we found no dependency of colour on temperature for preparative runs involving the concentration ranges specified above. Stoichiometric concentrations of reagents were used; in an excess of potassium cyanide, the well known green solution of $[Co(CN)_5]^{3-}$ is formed [6]. We confirm that the brown precipitate when filtered off promptly under nitrogen or *in vacuo* and dried *in vacuo* at room temperature (over silica gel) has the formula $Co(CN)_2 \cdot nH_2O$. In our preparations *n* varied between 2.0 and 3.5. The dihydrate $Co(CN)_2 \cdot 2H_2O$ resulted (Table I) when the brown hydrate was dried in a vacuum desiccator over phosphorus pentoxide for 24 hours. Thermal decomposition of this dihydrate at 180 °C *in vacuo* gave a blue monohydrate $Co(CN)_2 \cdot H_2O$ while at 290 °C anhydrous cobalt(II) cyanide was formed (Table I).

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TABLE I. Analytical Data for Cobalt Cyanide Complexes.

Compound	Found (%)				Theory (%)			
	Co	C	N	NH_3	Co	C	N	NH_3
$Co(CN)_2\cdot 2H_2O$	38.9	16.2	18.8		40.08	16.33	19.06	
$Co(CN)_2\cdot H_2O$	45.9	18.9	22.0		45.69	18.62	21.75	
$Co(CN)_2\cdot NH_3$	46.1	18.7	32.7		46.02	18.76	32.84	
$Co(CN)_2$[a]		21.3	25.0		53.11	21.64	25.25	
$Co(CN)_2$[b]	53.2	21.4	25.1		53.11	21.64	25.25	
$Co(CN)_2$[c]		21.4	25.0		53.11	21.64	25.25	
$Co(CN)_2$[d]	52.8	21.9			53.11	21.64	25.25	
$Co_3[Co(CN)_6]_2$	48.4	23.5	27.5		48.56	23.74	27.70	
$Co_3[Co(CN)_6]_2\cdot 6NH_3$	39.5			13.6	41.57			14.39
$(NH_4)_6[Co_2(CN)_{10}]$	24.3	24.6	45.9	20.9[e]	24.25	24.70	46.11	21.00[e]
$KCo(CN)_3$	34.8	20.3	24.2		33.48	20.47	23.89	
$K_2Co(CN)_4$	23.1	19.9	23.1		24.45	19.98	23.25	

[a] Dehydration of $Co(CN)_2\cdot 2H_2O$. [b] De-ammonation of $Co(CN)_2\cdot NH_3$. [c] From $[Co(H_2O)_6]^{2+} + [Co(CN)_5]^{3-}$. [d] Thermal decomposition of $(NH_4)_6[Co_2(CN)_{10}]$. [e] From the NH_4^+ ion.

TABLE II. Spectroscopic and Magnetic Properties of Cobalt Cyanide Complexes.

Compound	Preparative Medium	Electronic Spectrum (Reflectance) ($cm^{-1} \times 10^{-3}$)	Infrared Spectrum (cm^{-1})		Magnetic Moment μ_{eff} (BM)
			ν(CN)	ν(MC)	
$Co(CN)_2\cdot 2H_2O$	H_2O	46.5 38.0 [a] [a] 7.8	2173, 2123	440	3.4
$Co(CN)_2\cdot H_2O$	H_2O		2173	446	
$Co(CN)_2$	H_2O	45.5 38.0 28.0 br 17.1 8.0	2173	460	3.6
$Co(CN)_2$	NH_3	45.7 38.2 25.7 17.3 8.0	2173	460	3.9
$Co(CN)_2\cdot NH_3$	NH_3	39.8 26.3 17.6 8.0	2165, 2123 2070	458	3.7
$Co_3[Co(CN)_6]_2\cdot 14H_2O$	H_2O	44.2 33.2 23.0 sh 19.8 9.9	2173, 2132	450	3.8
$Co_3[Co(CN)_6]_2$	H_2O	44.6 37.9 28.0 17.5 7.8	2168	455	2.5
$Co_3[Co(CN)_6]_2\cdot 6NH_3$	NH_3	45.0 37.9 31.5 21.0 16.7 8.0	2168, 2130	450	3.75
$(NH_4)_6[Co_2(CN)_{10}]$	NH_3	43.5, 37.3, 35.0, 32.0, 26.4, 20.2, 9.7, 8.0	2175, 2127	412	diamagnetic
$KCo(CN)_3$	NH_3	45.0, 37.8, 26.0, 17.0, 15.0 sh	2165, 2125 2080	423	2.2
$K_2Co(CN)_4$	NH_3	44.8, 37.3, 25.7, 17.5, 14.0	2170, 2122, 2100, 2080	416	2.7

[a] Broad unresolved absorption between 30.0 and 14.0 $cm^{-1} \times 10^3$.

In order to compare hydrated cobalt(II) cyanide with hydrated cobalt(II) hexacyanocobaltate(III) we prepared the latter by the aqueous reaction between cobalt(II) chloride and potassium hexacyanocobaltate(III). The pink precipitate gave the blue, anhydrous $Co_3[Co(CN)_6]_2$ upon drying *in vacuo* at 100 °C. Analytical data for this compound (Table I) are in good agreement for the empirical formula $Co_5(CN)_{12}$ and differ significantly from our analyses of $Co(CN)_2$. Further we carried out the reaction between cobalt(II) ions and pentacyanocobaltate(II) ions; this produces a brown precipitate resembling cobalt(II) cyanide but unlike the pink precipitate obtained when hexacyanocobaltate(III) is used. In order to achieve the correct stoichiometry we chose to start with Adamson's salt:

The brown precipitate and the anhydrous blue cyanide have very similar spectra (Table II) to $Co(CN)_2\cdot 2H_2O$ and $Co(CN)_2$; the only difference in properties detectable is the greater ease of dehydration of '$Co_3[Co(CN)_5]_2\cdot$*aq*' as compared to $Co(CN)_2\cdot 2H_2O$.

$$\begin{tikzcd} \underset{\text{violet}}{K_6Co_2(CN)_{10}} \arrow[r, "H_2O"] & \underset{\text{green}}{2K_3Co(CN)_5\cdot aq} \arrow[r, "3Co^{2+}"] & \begin{array}{c} Co_3[Co(CN)_5]_2\cdot aq \\ \text{or } Co_3[Co_2(CN)_{10}]aq \\ \\ \text{brown} \end{array} \arrow[d, "100\,^{\circ}\mathrm{C}\ \textit{vacuo}"] \\ & & \underset{\text{blue}}{Co(CN)_2} \end{tikzcd}$$

The stoichiometric reaction between brown cobalt(II) thiocyanate (chosen for solubility reasons and is probably a hemihydrate) and potassium cyanide in liquid ammonia produces a green precipitate which becomes the dark grey mono-ammine $Co(CN)_2\cdot NH_3$ upon evacuation at room temperature. The same product results when cobalt(II) bromide is treated with ammonium cyanide in liquid ammonia. The mono-ammine begins to evolve ammonia above 100 °C *in vacuo* and evacuation at 210 °C produces the blue $Co(CN)_2$ which is indistinguishable from the aqueous preparations.

A major chemical difference between $Co(CN)_2$ and $Co_3[Co(CN)_6]_2$ is in their reactions with ammonia. Vapour pressure–composition isotherms in the $Co(CN)_2$–NH_3 and $Co_3[Co(CN)_6]_2$–NH_3 systems at -36 °C show that both compounds are insoluble but that $Co(CN)_2$ forms a diammoniate while $Co_3[Co(CN)_6]_2$ forms an 18-ammoniate at this temperature (both ammoniates having zero vapour pressure). In the $Co_3[Co(CN)_6]_2$–NH_3 isotherm there is also a univariant portion (p = 48 mm Hg) from 30 to 18 mol ratios $NH_3:Co_3[Co(CN)_6]_2$, indicating dissociation of weakly held ammonia molecules:

$$Co_3[Co(CN)_6]_2\cdot 30NH_3 \rightarrow Co_3[Co(CN)_6]_2\cdot 18NH_3 + 12NH_3$$

Upon warming to room temperature a further 12 mol of ammonia are evolved and the pink $Co_3[Co(CN)_6]_2\cdot 6NH_3$ is formed. This latter compound has been prepared previously [7].

When cobalt(II) cyanide ammoniate is treated with an excess of ammonium cyanide in liquid ammonia a green solution is formed; evaporation of this solution and removal of excess of ammonium cyanide by evacuation at room temperature leaves the light yellow, diamagnetic, ammonium decacyanodicobaltate(II). This, the ammonium analogue of Adamson's salt $K_6[Co_2(CN)_{10}]$ [13] has not been prepared previously; its preparation in ammonia is made possible because of the volatility of ammonium cyanide. A tensimetric study of $(NH_4)_6[Co_2(CN)_{10}]$ in liquid ammonia at -36 °C shows a univariant portion at p = 500 mm Hg corresponding to the saturated solution dissociation pressure, but surprisingly shows that no ammoniates are formed at this temperature. We have not ascertained whether or not dissociation into $[Co(CN)_5]^{3-}$ ions occurs in solution in ammonia, but if it does, it is evident that no strongly bound ammine $[Co(CN)_5(NH_3)]^{3-}$ is formed. Thermal decomposition of $(NH_4)_6[Co_2(CN)_{10}]$ at 210 °C *in vacuo* proceeds quantitatively according to

$$(NH_4)_6[Co_2(CN)_{10}] \rightarrow 2Co(CN)_2 + 6NH_4CN$$

The blue residue is indistinguishable from the other preparations of anhydrous $Co(CN)_2$. This thermal decomposition of the ammonium salt is one further example of the application of this technique as a preparative route to transition metal cyanides; cobalt(III) cyanide is obtained [15] by decomposition of $(NH_4)_3[Co(CN)_6]$. Whilst we prepared $(NH_4)_6[Co_2(CN)_{10}]$ from $Co(CN)_2$ the former could obviously be prepared independently (*e.g.* from $K_6[Co_2(CN)_{10}]$ by ion-exchange) and hence an independent route to $Co(CN)_2$ established. We have not been able to isolate the pure potassium or sodium salts of the decacyanodicobaltate(II) anion from ammonia; instead we obtained green products of approximate empirical formulae $K_3Co(CN)_5$ and $Na_3Co(CN)_5$ which had magnetic moments of 2.21 and 1.90 BM respectively. Their electronic spectra are very similar to those of Adamson's salt and $(NH_4)_6[Co_2(CN)_{10}]$; they may be related to the paramagnetic $K_3Co(CN)_5$ ($\mu \sim 2$ BM) prepared by other workers [8] especially since only two CN stretching bands (2137 and 2086 cm^{-1}) are observed.

The reactions between anhydrous cobalt(II) thiocyanate (green form) and potassium cyanide in ammonia lead to precipitation of the dark green $KCo(CN)_3$ when a $Co(SCN)_2$: KCN ratio of 1:2 is used and dark brown $K_2Co(CN)_4$ when the $Co(SCN)_2$: KCN ratio used is 1:9. These compounds are paramagnetic; the latter compound exhibits catalytic properties in liquid ammonia similar to those shown [9] by the $[Co(CN)_5]^{3-}$ ion in aqueous solution. Thus nitrobenzene can be hydrogenated at -33 °C to a mixture of compounds of which we identify azobenzene as the main component. The differing reactivities of the brown and green forms of cobalt(II) thiocyanate towards potassium cyanide in ammonia is very surprising, especially since we find [16] that both forms give 7- and 8- ammoniates in ammonia at -36 °C.

The magnetic moments of the various $Co(CN)_2$ preparations (Table II) are in the region of 3.7 BM at room temperature. These are considerably in excess of that for anhydrous $Co_3[Co(CN)_6]_2$ and for low spin Co^{2+} (d^7) but lower than that expected for high spin Co^{2+}. A polymeric three-dimensional structure containing a 1:1 distribution of (i) octahedral carbon co-ordinated CoC_6 units and (ii) octahedral CoN_6 units is consistent with these results. While for (i) low spin magnetic moments are expected, for (ii), high spin magnetic moments are expected in accord with the different ligand fields generated by the opposite ends of the bridged cyanide ion. Such a structure has been proposed previously for $Co(CN)_2$ [10] and for $Co_3[Co(CN)_6]_2$ [7]. Both structures require the presence of 'interstitial' Co^{2+} ions for electroneutrality. It is the presence of these 'interstitial' metal ions and their capability for co-ordination to additional ligand molecules which leads to the possibility of co-ordinated solvent molecules being present. The electronic spectra of the hydrate and ammoniate of $Co_3[Co(CN)_6]_2$ (Table II) are indicative of the presence of $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$ ions [11] and the magnetic moments of these compounds are considerably higher than that of the unsolvated $Co_3[Co(CN)_6]_2$ so that the interstitial Co^{2+} ions may be tetrahedrally rather than octahedrally co-ordinated in the latter. The infrared spectra (Table II) in the cyanide stretching region of $Co(CN)_2$ and the $Co_3[Co(CN)_6]_2 \cdot xL$ compounds show a high ν(CN) around 2170 cm^{-1} indicative of bridging cyanide. In the case of $Co(CN)_2 \cdot NH_3$, $K[Co(CN)_3]$ and $K_2[Co(CN)_4]$ however, cyanide stretches indicative of the presence of both bridging and terminal cyanide, appear. Unfortunately these compounds proved to be amorphous to X-rays but a likely structure for them is a layer structure as found in $Ni(CN)_2 \cdot 1.5H_2O$ [12]. In $K[Co(CN)_3]$ then we would have a 1:1 ratio of octahedral carbon co-ordinated Co^{2+} (low spin) and planar nitrogen co-ordinated Co^{2+}; both of these environments would give rise to a magnetic moment of around 2 BM in accord with the low moment found. In $K_2Co(CN)_4$ the layers would consist of octahedral CoC_6 alternating with high spin octahedral CoN_4C_2 ($\mu_{eff} \sim 5$ BM) both cobalt(II) ions now being bonded to terminal as well as bridging cyanides with a resulting increase in magnetic moment.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer and reflectance spectra on a Unicam SP 700C instrument. Magnetic susceptibilities were by the Gouy method at room temperature.

Adamson's salt [13] and anhydrous cobalt(II) thiocyanate [14] were prepared by literature methods; cobalt(II) halides were prepared by dehydration of the hydrates *in vacuo* at 120 °C. Ammonium cyanide was prepared by passing dry ammonia gas into a methylene chloride solution of hydrogen cyanide at 0 °C; the precipitate was filtered off, washed with ice-cold anhydrous methylene chloride and purified by vacuum sublimation immediately prior to use.

All reactions were carried out under nitrogen using de-aerated distilled water or in high vacuum apparatus. Preparations and tensimetric studies in liquid ammonia were carried out as described elsewhere [17]. All insoluble reaction products were washed many times with liquid ammonia to remove excess of soluble reagents and dried by evacuation for several hours prior to analysis. Hydrogenation of nitrobenzene, benzil and styrene was carried out at −33 °C and atmospheric pressure by adding the organic reagent to a mixture of cobalt(II) thiocyanate and an excess of sodium cyanide in liquid ammonia and passing hydrogen through the mixture. The organic products were extracted with ether after evaporation of the ammonia and identified by mass spectrometry and g.l.c. Only in the case of nitrobenzene however did the hydrogenation produce only one major product (azobenzene); four components arise from benzil and a large number from styrene; these are as yet uncharacterised.

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