A New Cobalt(0) Cyanogen Complex

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A study of the reaction between Co^{2+} and CN^- ions in well aerated aqueous solutions has shown that up to a CN/Co molar ratio of 5 and at 0 °C, the solution contains about equal amounts of the cyano and peroxocyano complexes of tervalent cobalt. When the ratio is lowered by the addition of more Co^{2+}, a dark brown precipitate is formed which on drying changes to a black lustrous solid. The latter effervesces with HCl giving cyanogen gas and a $CoCl_2$ solution.

Evidence is provided to indicate that the solid is a cobalt(0) cyanogen complex and the colouration of the mother liquor is attributed to the formation of a mixed cyano–cyanogen complex.

Introduction

In an earlier publication from this laboratory, it has been shown that the controlled addition of cupric salts to cyanide solution leads to the formation of the wine-red mixed species, $[Cu^I(CN)_2NCCN]^-$, which polymerises slowly to a solid [1]. Evidences for the coordination of cyanogen ligand to the central metal ion were inferred from both spectroscopic and preparative methods.

In view of the possibility that other metal ions may form similar complexes, the cobalt cyanide system is being studied in the present investigation.

Experimental

When a cobalt nitrate solution is added to potassium cyanide solution in an inert atmosphere, only the green pentacyanocobalt(II) complex is formed. If, however, the cyanide solution is kept aerated by vigorous stirring, the solution is coloured red due to the formation of the peroxo cobalt(III) complex previously reported by Haim and Wilmarth [2]. The latter is unstable at room temperature and the colour could be discharged by slight warming of the solution. On cooling to 0 °C the colour persists and intensifies greatly. Iodometric titration indicated that the solution contains about equal amounts of the ordinary yellow $[Co(CN)_5]^{2-}$ and the red peroxo complex. The solution remains clear till the CN^-/Co^{2+} ratio reaches 5, but when this ratio is lowered by continuing the addition of the cobalt nitrate solution, a dark brown precipitate starts to appear. The additional amount of the cobalt nitrate which should be added was found to be equivalent to the concentration of the peroxo species, and if exceeded, the brown precipitate will be contaminated with the green pentacyanocobalt(II) complex.

The supernatant liquid in equilibrium with the brown precipitate is also coloured dark red but differs from the red solution produced before precipitation, in that it is stable towards heat, can be left unchanged for weeks and does not liberate iodine from acidified potassium iodide.

The yield of the brown solid was found to depend on the amount of the peroxo complex in solution. If the formation of the latter is prevented, for example by heating the cyanide solution, the green cyanide complex is precipitated exclusively.

The following procedure is recommended for preparation:

Cobalt nitrate solution (1 *M*) is added drop-wise to a 200 ml of vigorously stirred and well aerated potassium cyanide solution (1 *M*) contained in a wide (500 ml) beaker and kept at 0 °C by a cooling mixture. When the CN/Co ratio has reached 5, *i.e.* after adding 40 ml of cobalt solution, an additional 20 ml of this solution is added for complete precipitation. The precipitate is left to settle, filtered, washed with water and dried at 110 °C over night. The final product is a black, coal-like lustrous solid.

Because of the acidity of the cobalt nitrate solution, some HCN is formed during the reaction and polymerises in the alkaline cyanide solution. This contamination could be removed, if necessary by washing with dilute warm NaOH solution.

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TABLE I. Main Bands in the IR Spectra, cm^{-1}.

Assignment[a]	Brown Solid		Cyanogen Polymer		Red Crystals from the supernatant liquid
	100 °C	250 °C	100 °C	250 °C	
ν_{Co-C}					420
ν_{Co-N}	570(b)	570(s,sh)			498
ν_{Co-O}	670(b)	–			
NO_3^-					831
C_2N_2	–	2180 2344	–	2180 2344	2200 2400

[a] b, broad; s, strong; sh, sharp.

Analytical

The cobalt content of the complex was determined by dissolving the solid in warm dilute HCl and titrating the solution against standard Na_2H_2-EDTA solution in the presence of hexamine as a buffer and xylenol orange as indicator. Carbon, hydrogen and nitrogen contents were analysed using the standard micro analytical methods.

The gas evolves upon treating the solid sample with warm acids was identified to be cyanogen, since it reacts with 8-hydroxyquinoline–KCN test paper to give pink colour [3].

Physical Measurements

The magnetic moment of the solid complex and of the supernatant liquid has been measured by the Gouy method, at different temperatures and in helium atmosphere.

The infrared spectra were obtained with a Perkin-Elmer 337 infrared spectrophotometer. The spectra of the complexes were run both in Nujol mulls in NaCl cells and in KBr discs.

The absorption spectra of the solutions were investigated by a Beckman DK 2A recording spectrophotometer.

The X-ray photoelectron spectra were measured on a Vacuum Generators ESCA-3 spectrometer-AlK_α (1486.6 eV). X-ray radiations were used to produce photoionisation. Samples were ground to powder and then dusted onto a double-backed adhesive tape. In these measurements, gold was evaporated on the surface of the sample and the values of the binding energies were referred to the gold $4f_{7/2}$ (84.0 eV) peak.

Results and Discussion

In the following discussion, the nature and composition of the solid complex and the red supernatant liquid will be dealt with separately. More emphasis will be laid upon the solid complex, since the red solution proved to be of a complicated nature and probably contains more than one species.

A) The solid complex

The solid is an amorphous substance as was shown by X-ray examination, and is insoluble in many organic solvents. It dissolves, however, in concentrated KCN solution, and is decomposed by dilute acids. When treated with warm dilute HCl, effervescence and evolution of cyanogen gas takes place, while a cobalt chloride solution is left. This suggests that the solid is a cyanogen compound of cobalt. No gas was obtained when the solid was heated to red heat, and therefore the possibility of a clathrate formation may be ruled out.

Chemical analysis has shown that the average percentages of the different components were: Co, 57.3 ± 0.5; C, 11.4 ± 0.6; N, 13.5 ± 0.1 and H, 1.9 ± 0.1. Neither potassium nor nitrate ions have been detected. These results agree well with the empirical formula: $CoCN \cdot H_2O$.

Infrared spectra of the sample at ordinary temperature, using KBr discs or Nujol mulls showed non of the bands characteristic of the cobalt cyano complexes, gaseous cyanogen [4], or solid paracyanogen polymerised from the gaseous state [5]. The two main bands (see Table I) were observed at 670 cm^{-1} and 570 cm^{-1}. These are assigned respectively to Co–O and Co–N stretching frequencies. The spectrum, however, did not show the band at 2325 cm^{-1} characteristic of coordinated cyanogen as was observed previously in the case of the dicyanomonocyanogencuprate(I) ion [1]. Heating the solid complex to 250 °C, the band at 670 cm^{-1} which was assigned to Co–O bond disappeared, whereas that assigned for the metal–nitrogen bond was intensified markedly and became more sharp. Also, two extra bands appeared at 2180 cm^{-1} and 2344 cm^{-1} which are assigned to the stretching frequencies of the cyanogen molecule.

TABLE II. Magnetic Measurements.

T (K)	63	75	168	194	295	373
$\chi_{M(corr.)}^{a} \times 10^6$	4490	3975	2140	1890	1325	1075

$^a(\chi_{diam.} = -35 \times 10^{-6}$ e.s.u.).

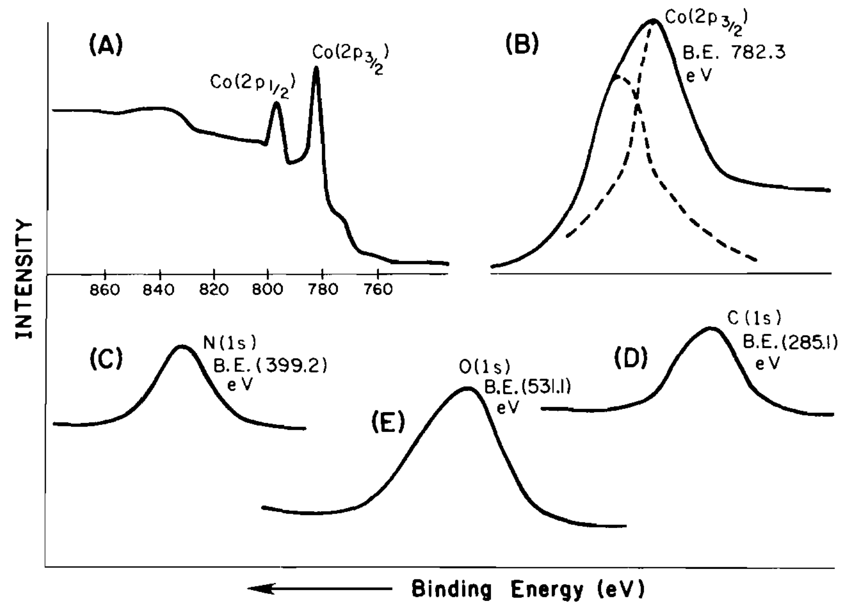
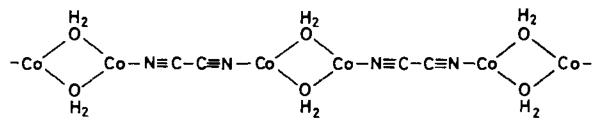


Fig. 1. The photoelectron spectra of cobalt cyanogen complex.

In order to justify this hypothesis, the experimental conditions were simulated and cyanogen gas was passed through a potassium cyanide solution where a brown precipitate of polycyanogen was formed. The latter was washed well with distilled water and dried at 110 °C. The main bands recorded for the spectra of the fresh solid and that heated at 250 °C are shown in Table I. The close agreement between the spectra of the heated samples of both polycyanogen and the cobalt complex suggests that cyanogen ligand in the latter complex is present in polymeric matrix and depolymerisation takes place upon heating, perhaps through the loss of some bridging water molecules.

The cobalt 2p photoelectron lines are shown in Fig. 1A. The separation between the $2P_{1/2}$–$2P_{3/2}$, spin-orbit components was found to be 15.3 eV. This value is slightly higher than that reported for the diamagnetic $[Co(CN)_6]^{3-}$ species [6] and is comparable to that reported for the low spin cobalt species with $S = ½$ [6]. This in fact fits fairly well with our magnetic moment measurements. Table II summarises the magnetic susceptibilities measured at different temperatures. The moment calculated from these results is 1.87 B.M. which may suggest the presence of either a d^9(Co(0)) or a mixed valence species. The possibility of having a low spin-d^7 state is very unlikely because of the relatively low ligand field anticipated from the presence of one water molecule and half a cyanogen molecule surrounding the central ion. Also, a mixed valence species is ruled out because of the absence of photoelectron lines corresponding to the different oxidation states. The assymmetry observed in the high resolution spectra of the $Co(2P_{3/2})$ peak (Fig. 1B) is attributed to the presence of an intense satellite (almost of equal intensity) on the high energy side of the peak. Based on the comparison with the excitation energies from optical spectra of the free ion [7], Rosencwaig *et al.* have suggested that such satellite lines arise from 3d → 4s shake-up processes.

A complex of zero valent cobalt, on the other hand, is expected to exhibit one unpaired electron corresponding to a magnetic moment of 1.73 B.M. The slightly higher value obtained may be due to spin orbit coupling as is the case with Cu^{2+} ion. One of the possible structures which may show how the cobalt is coordinated to cyanogen and water molecules may be represented as follows:



B) The Supernatant Red Solution

This solution is of a complicated composition and probably contains more than one complex species. Spectrophotometric studies indicated that, in addition to the characteristics of the well known cobalt cyanide solutions, the spectrum showed the presence of a strong band at 481 mμ. This band has been observed with some of the μ-superoxo dicobalt complexes [8] such as $[(NC)_5Co^{III}OOCo^{IV}(CN)_5]^{5-}$ (I) and has been assigned to the $Co^{3+} \rightarrow O^{2-}$ charge-transfer transitions [9]. The molal magnetic susceptibility of species (I) was measured to be 1080×10^{-6} e.s.u. [2]. Also, it is reported that this species reacts with acidified iodide ions to liberate iodine and produce $[(NC)_5Co(H_2O)]^{2-}$. On the contrary, the red solution obtained was found to be diamagnetic and inactive toward oxidation-reduction reactions with I^- ions. This suggests that it contains complexes of tervalent cobalt.

Slow evaporation of this solution at 0 °C resulted in the separation of yellow and red crystals. The main bands in the infrared spectrum of the yellow crystals is at 2140 cm^{-1}, which is characteristic of the hydroxopentacyanocobalt (III) complex [10]. That of the red crystals exhibited three main bands at 2125 cm^{-1}, 2200 cm^{-1} and 2400 cm^{-1} (Table I). The first band is assigned to a coordinating CN^- ion while the other two are assigned to a coordinating cyanogen molecule. On heating the crystals at 100 °C, cyanogen is given off, and these two bands disappear. Lower frequency bands were observed at 830, 498 and 420 cm^{-1} which are assigned for NO_3^-, ν_{Co-N} and ν_{Co-C} stretching frequencies respectively [10]. The red solution was found to be retained by an anion exchanger showing that the complex is anionic and the nitrate ion is also coordinated. From the stoichiometry of the different reactions, it is possible to speculate the CN/Co ratio in the red crystals to be 4. To summarise, the following reactions are suggested to account for the different steps involved.

I) *When the CN/Co ratio reaches 5;*

a) Formation of μ-peroxodecacyanocobalt(III) complex;

$$Co^{2+} + 5CN^- + H_2O = Co(CN)_5H_2O^{3-} \qquad (1)$$

$$2Co(CN)_5H_2O^{3-} + O_2 =$$

$$= (NC)_5Co \cdot O_2 \cdot Co(CN)_5^{6-} + 2H_2O \qquad (2)$$

b) Partial decomposition of the peroxo species:

$$(NC)_5Co \cdot O_2 \cdot (CN)_5^{6-} + 2H^+ + 2H_2O =$$

$$= 2Co(CN)_5H_2O^{2-} + H_2O_2 \qquad (3)$$

c) When a limited supply of air is allowed into the solution;

$$2Co(CN)_5^{3-} + (NC)_5Co \cdot O_2 \cdot Co(CN)_5^{6-} + 6H_2O =$$

$$= 4Co(CN)_5H_2O^{2-} + 4OH^- \text{ (Haim and Wilmarth) } (4)$$

II) *When the CN/Co ratio is below 5:*

$$(NC)_5Co \cdot O_2 \cdot Co(CN)_5^{6-} + 2Co(NO_3)_2 + H_2O =$$

$$= Co_2 \cdot C_2N_2 \text{ (brown precipitate) } +$$

$$+ (NC)_3(NO_3)Co^{III}N{\equiv}C{-}C{\equiv}NCo^{III}(NO_3)(CN)_3^{2-}$$

$$\text{(red crystals)}$$

$$+ 2NO_3^- + 2OH^- + \tfrac{1}{2}O_2 \qquad (5)$$

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