

## Spectral and Magnetic Properties of Some Cobalt(II) Cyanide Complexes

DONNATI M.S.MOSHA  
*University of Dar es Salaam*  
*Dar es Salaam, Tanzania.*

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**Summary:** In contrast to aqueous preparative procedures, the liquid ammonia preparations of cobalt(II) cyanide conform to an exact CN/Co stoichiometry of 2:1. The ammonium analogue of Adamson's salt,  $(\text{NH}_4)_6[\text{Co}_2(\text{CN})_{10}]$ , which is readily prepared in this medium also yields  $\text{Co}(\text{CN})_2$  upon thermal decomposition. The preparation and properties of the complexes  $\text{K}[(\text{Co}(\text{CN})_3)]$  and  $\text{K}_2[(\text{Co}(\text{CN})_4)]$  are described and their structures discussed.

### Introduction

The identity of the brown hydrated cobalt (II) cyanide precipitate obtained from aqueous preparations has occasioned considerable dispute. In an early investigation it was formulated as  $\text{Co}(\text{CN})_2 \cdot n\text{H}_2\text{O}$  ( $n = 2$  or  $2.5$ ) with a magnetic susceptibility of 3.27 B.M. per Co [1] which upon dehydration under nitrogen yields  $\text{Co}(\text{CN})_2$  with a moment of 3.12 B.M. per Co [2]. Subsequent investigators have proposed a non-stoichiometric constitution  $\text{Co}(\text{CN})_x \cdot y\text{H}_2\text{O}$  ( $x = 2.2 - 2.4$ ;  $y = 1.75 - 2.15$ ) thereby concluding a similar identity for this solid and  $\text{Co}_3^{\text{II}}[\text{Co}^{\text{III}}(\text{CN})_6]_2$  based on the 2.4:1 CN/Co ratio found in the later [3,4]

$\text{Co}_3^{\text{II}}[\text{Co}^{\text{III}}(\text{CN})_6]_2$  is prepared by  $\text{Co}^{2+}$  (aq) addition to  $\text{K}_3[\text{Co}(\text{CN})_6]$ . In yet another report a pink " $\text{Co}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ " has been obtained via the reduction of  $\text{K}_3[\text{Co}(\text{CN})_6]$  with hypophosphorous acid; the product has the same X-ray powder pattern and infrared spectrum as the brown form [5]. In all these aqueous preparations, solvent water may afford oxi-

dising conditions and therefore in this re-investigation we have resorted to high vacuum preparative techniques using liquid ammonia to exclude this possibility. An excellent description of the routine application of high vacuum techniques in laboratory synthesis with liquid ammonia is to be found elsewhere [6,7]. This work describes the solvated product  $\text{Co}(\text{CN})_2 \cdot \text{NH}_3$  and  $\text{Co}(\text{CN})_2$  with an exact CN/Co stoichiometry of 2:1 from liquid ammonia preparations and investigates the reaction of this product with excess cyanide leading to complexes  $[(\text{Co}_2(\text{CN})_{10})^{6-}]$ ,  $[\text{Co}(\text{CN})_3]^-$  and  $[\text{Co}(\text{CN})_4]^{2-}$  hitherto unreported from this preparative medium.

### Experimental

#### Reagents

**Cobalt(II) thiocyanate:** The brown stock reagent (ex.B.D.H.) is now considered to be  $\text{Co}(\text{CNS})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  and pre-dissolution in EtOH followed by evacuation ( $100^\circ\text{C}$ ) is a recommended dehydration procedure [9] which leaves a blue solid conforming to  $\text{Co}(\text{CNS})_2$ .

*Cobalt(II) bromide:*

This was obtained by a 20-hour evacuation (160°C) of the hydrate  $\text{CoBr}_2 \cdot n\text{H}_2\text{O}$  (ex.B.D.H.).

*Sodium and Potassium cyanide:*

Both reagents (ex.H & W.) were dried by evacuation at 100°C for about 10 hours.

*Ammonium cyanide*

(CAUTION; POISONOUS): A stock of the reagent was prepared by passing a stream of dry gaseous ammonia into a solution of HCN in water-free dichloromethane at 0°C. After filtration and washing with dichloromethane, the product was transferred using a liquid nitrogen bath to safeguard against volatilisation to the high vacuum apparatus where it was further purified by sublimation. There after all handling was by high vacuum methods [6,7].

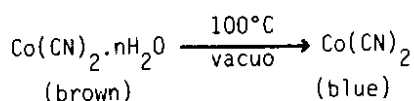
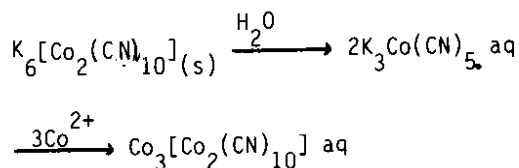
*Liquid ammonia solvent*

The routine preparation and handling of the dry solvent is to be found in the aforementioned reference [6].

**Preparative Work***Amminecobalt(II) cyanide and cobalt (II) cyanide:*

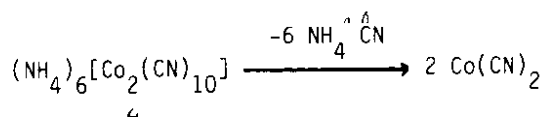
To a liquid ammonia solution of either  $\text{Co(NCS)}_2$  or  $\text{CoBr}_2$  was added a stoichiometric amount of KCN or NaCN [6-10]. The green precipitate after a threefold solvent wash and a six-hour evacuation (R.T) gave the solid  $\text{Co(CN)}_2 \cdot \text{NH}_3$ . The evacuation of this solid at 210°C (boiling ethylbenzoate bath) for 10 hours leaves a blue solid,  $\text{Co(CN)}_2$ . The alternative aqueous preparation under a nitrogen atmos-

phere involves addition of  $\text{Co(NCS)}_2$  aq. to a solution of Adamson's salt [7,11] giving  $\text{Co(CN)}_2$  according to Scheme (I)

*Ammonium decacyanodicobaltate(II):*

An excess of  $\text{NH}_4\text{CN}$  was sublimed into a suspension of  $\text{Co(CN)}_2 \cdot \text{NH}_3$  yielding a green solution of  $(\text{NH}_4)_3[\text{Co(CN)}_5]$ . The pentacyanocobaltate (II) species dimerises upon solvent removal, and unreacted excess  $\text{NH}_4\text{CN}$  is removed by sublimation leaving a yellow diamagnetic analogue of Adamson's salt,  $(\text{NH}_4)_6[\text{Co}_2(\text{CN})_{10}]$ .

Thermal decomposition of  $(\text{NH}_4)_6[\text{Co}_2(\text{CN})_{10}]$  at 210°C leaves  $\text{Co(CN)}_2$  according to

*Potassium tri- and tetra- cyanocobaltate(II):*

The compounds  $\text{K}[\text{Co(CN)}_3]$  and  $\text{K}_2[\text{Co(CN)}_4]$  were isolated in liquid ammonia preparations involving  $\text{Co(NCS)}_2$  and KCN starting with CN/Co reactant stiochiometries of 3:1 and 9:1 respectively.

## Results and Discussion

The analytical, magnetic susceptibility and infrared spectral data for the compounds studied are presented in table below:

The mode of attachment of cyanide in a complex can be correlated to the CN stretching frequency [10,11]. The lower value is obtained in "free" CN ( $2070 \text{ cm}^{-1}$  in KCN) and highest in bridging -M-C-N-M ( $2165 \text{ cm}^{-1}$  in AgCN). Terminally attached CN lies in the intermediate range ( $2100 \text{ cm}^{-1}$  in  $\text{Ag}(\text{CN})_2$ ). The diamagnetism and the terminal CN attachment (i.r. evidence) in  $(\text{NH}_4)_6 [\text{Co}_2(\text{CN})_{10}]$  confirm this to be the ammonium

analogue of Adamson's salt whose structure is now fully characterised [13]. The dinuclear complex  $[\text{Co}_2(\text{CN})_{10}]^{6-}$  is derived from the paramagnetic square pyramidal monomer  $[\text{Co}(\text{CN})_5]^{3-}$  ( $\mu = 1.73 \text{ B.M.}$ ) through pairing of the odd electron by formation of a Co-Co metal bond. The infrared stretch is supportive of a bridging cyanide linkage in  $\text{Co}(\text{CN})_2 \cdot \text{NH}_3$  and the magnetic data is interpreted in terms of a similar structure to the cage-like complex  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3$  [14] as shown in the figure. The 1:1 ratio of  $\text{CoN}_4\text{N}_2$  (high spin octahedral) and  $\text{CoC}_4$  (planar) environments would separately lead to

Analytical, magnetic susceptibility and infrared spectral data for some cobalt(II) cyanide complexes

| Compound  | effect<br>(B.M./Co) | CN( $\text{cm}^{-1}$ ) | Found (%) |      |       | Theory (%)        |       |       |       |                    |
|---|---------------------|------------------------|-----------|------|-------|-------------------|-------|-------|-------|--------------------|
|   |                     |                        | Co        | C    | N     | $\text{NH}_3$     | Co    | C     | N     | $\text{NH}_3$      |
| $\text{Co}(\text{NH})_2 \cdot \text{NH}_3$      | 3.7                 | 2165                   | 46.1      | 18.7 | 32.7  | 13.7              | 46.05 | 18.76 | 32.84 | 13.30              |
| $\text{Co}(\text{CN})_2^a$                      | 3.6                 | 2180                   |           | 21.3 | 25.0  |                   | 53.11 | 21.64 | 25.25 |                    |
| $\text{Co}(\text{CN})_2^b$                      | 3.8                 | 2175                   | 53.2      | 21.4 | 25.10 |                   | 53.11 | 21.64 | 25.25 |                    |
| $\text{Co}(\text{CN})_2^c$                      | 3.4                 | 2165                   |           | 21.4 | 25.0  |                   | 53.11 | 21.64 | 25.25 |                    |
| $(\text{NH}_4)_6 [\text{Co}_2(\text{CN})_{10}]$ | diamagnetic         | 2095                   | 24.3      | 24.6 | 45.9  | 20.9 <sup>d</sup> | 24.25 | 24.70 | 46.11 | 21.00 <sup>d</sup> |
| $\text{K}[\text{Co}(\text{CN})_3]$              | 2.2                 | 2080                   | 34.8      | 20.3 | 24.2  |                   | 33.48 | 20.47 | 23.89 |                    |
| $\text{K}_2[\text{Co}(\text{CN})_4]$            | 2.7                 | 2075                   | 23.4      | 19.9 | 23.1  |                   | 24.45 | 19.98 | 23.25 |                    |

a----- from dehydration of  $\text{Co}_3[\text{Co}_2(\text{CN})_{10}]_{\text{aq}}$ .

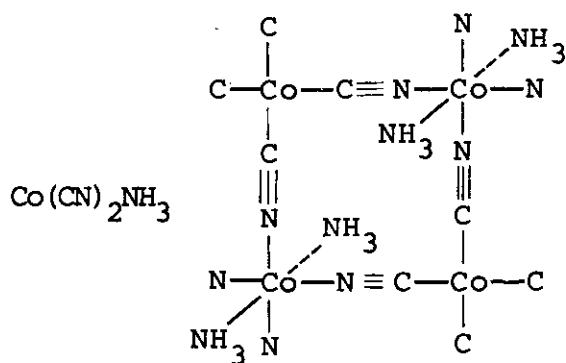
b-----from deammonation of  $\text{Co}(\text{CN})_2 \cdot \text{NH}_3$

c-----from thermal decomposition of  $(\text{NH}_4)_6 [\text{Co}_2(\text{CN})_{10}]$

d-----from the  $\text{NH}_4^+$  ion

Expected  $\mu_{\text{eff}}$  (B.M.)

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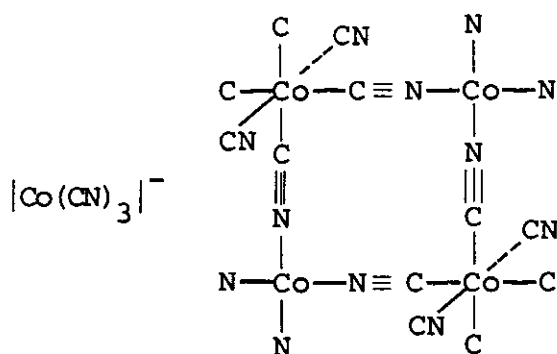


$$\text{CoN}_4\text{N}_2 - 5.0$$

$$\text{CoC}_4 - 2.2$$

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$$3.6$$

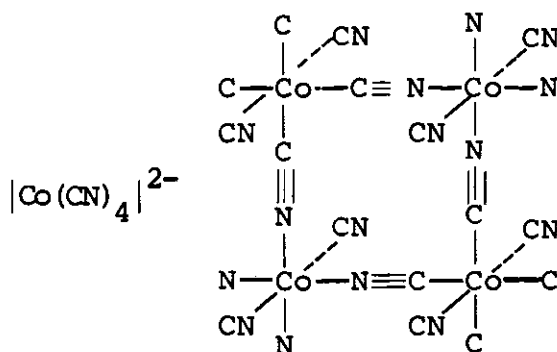


$$\text{CoC}_6 - 2.0$$

$$\text{CoN}_4 - 2.2$$

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$$2.1$$



$$\text{CoC}_6 - 2.0$$

$$\text{CoN}_6 - 5.0$$

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$$3.5$$

about 2.2 and 5 B.M./Co respectively thereby averaging to the observed value of about 3.6 B.M. per Co. Upon de-ammonation both environments become planar ( $\text{CoN}_4$  and  $\text{CoC}_4$ ) implying a drop in the magnetic moment and retention of the bridging cyanide mode.

The structures illustrated for the tri- and tetra-cyano complex are based on similar arguments.

In  $[(\text{Co}(\text{CN})_3)]$  there exists a 1:1 ratio of  $\text{CoC}_6$  (low spin octahedral) and  $\text{CoN}_4$  (planar) environments with about

2 and 2.2 B.M./Co for the respective cases leading to the observed mean value of 2 B.M./Co. In accord to infrared evidence, both terminal and bridging cyanide modes occur in the structure. The carbon atom in bridged cyanide exerts a stronger field than the nitrogen end; the latter has a ligand strength below that of ammonia [11].

The considerations correspondingly affect the spin state. In the  $[\text{Co}(\text{CN})_4]^{2-}$  case all environments are octahedral being either  $\text{CoC}_6$  (low spin) or  $\text{CoN}_4\text{C}_2$  (or  $\text{CoN}_4\text{N}_2$ ?). This last environment gives rise to a high spin configuration.

The two environments would give respective susceptibilities of 2 and 5 B.M./Co thus approximating to the 2.7 B.M./Co experimental value. Bridging and terminal  $\text{CN}^-$  linkage modes are manifested in the infrared spectrum.

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