CYANIDE LINKAGE ISOMERS IN THE ESR SPECTRUM OF ELECTRON IRRADIATED $K_3Co(CN)_6$

by

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The reduction of $K_3Co^{III}(CN)_6$ has been object of numerous investigations [1] and so far a few doubts persist as to the nature of the complex formed. Adamson [2] has shown that contrary to what was formely supposed it is not $K_4Co^{II}(CN)_6$ that is produced but $K_3Co^{II}(CN)_5$, with elimination of one cyanide ligand.

The complex cyanides of Co^{II} with octahedral or related symmetry must be paramagnetic for the central ion configuration is $d^6 d^1$, with an unpaired electron in an antibonding orbital. The relative instability of these complexes may be related to the presence of an extra electron in an antibonding position.

In a recent study [3] it has been shown that complexes with transition ion configuration $d^6 d^1$ which are unstable in solution or in the

presence of ox..gen of the air, can be obtained by direct electron irradiation of the diamagnetic solid containing the corresponding transition ion in the stable d_ϵ^6 configuration. The reduced paramagnetic species is formed inside the diamagnetic matrix which confers to it a relatively high stability.
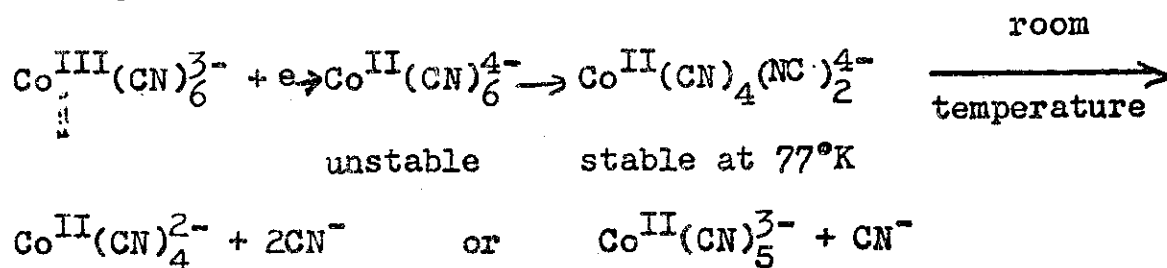
In the present work we investigated the reduction of $K_3Co(CN)_6$ by electron irradiation from a 2 MeV linear accelerator [4]. Single crystals of the complex have been irradiated at liquid nitrogen and the esr spectrum was examined in a Varian 3 cm spectrometer, the crystals kept in liquid nitrogen all the time.

At low temperature the irradiated crystals exibit a violet colour and are strongly paramagnetic. The spectrum reproduced in fig. 1 consists of two groups of eight quintets (signal A): one group shows a well resolved structure with intensities 1:2:3:2:1 and in the other group the same quintets are poorly resolved. Leav ing the crystal for a few minutes at room temperature the two groups of resolved quintets disappear remaing octacts (signal B) without any extra hyperfine structure. Table 1 lists the values of the gyro- magnetic and hyperfine parameters for both species.

The presence of the quintets in signal A with the indicated intensity radio can be attributed to an hyperfine interaction of a single electron with two equivalent nuclei of N^{14}(spin 1). The hyperfine interaction with the nucleus of Co^{59}(spin 7/2) gives rises to the octets. The fact that there are more than one group is due to non-equivalent position of the complex in the unit

cell of the crystal [5].

The esr spectrum of species A arises from the interaction of an unpaired electron in a molecular species with two equivalent nitrogens and the central Co^{II} ion. The value g and A are consistent with the assignement of this electron to a d_{z^2} orbital [6] with some delocalization between the two nitrogens [5]. This suggests the following mechanism for the reduction:

$$Co^{III}(CN)_6^{3-} + e \rightarrow Co^{II}(CN)_6^{4-} \rightarrow Co^{II}(CN)_4(NC)_2^{4-} \xrightarrow[\text{temperature}]{\text{room}}$$

$$\text{unstable} \qquad \text{stable at } 77°K$$

$$Co^{II}(CN)_4^{2-} + 2CN^- \qquad \text{or} \qquad Co^{II}(CN)_5^{3-} + CN^-$$

The absence of hyperfine interaction with the nitrogen of the cyanide ligands in transition metal cyanides has been taked as an evidence for metal-carbon bonding in these complexes [7]. Direct evidence for this type of coordination is given by neutron diffraction of $K_3Co^{III}(CN)_6$ which shows that the Co ion is linked to the carbon of the CN ligands [8]. The presence of hyperfine interaction with the equivalent nitrogens in species A strongly suggests that the cobalt ion is bonded to two of the cyanide ligands by their nitrogen ends. In this respect it is important to observe that the value for A_{14_N} = 3.4 to 4.4 G is close to that obtained with the free CN radical (A_{14_N} = 4.6 G) in which the unpaired electron is delocalized at the nitrogen [9].

Investigations on cubic cyanide polymers have shown that the nitrogen end of the cyanide has a ligand field strength much lower

than that of the carbon end [10]. Thus, the unstable $Co^{II}(CN)_6^{4-}$ ion could be stabilized as $Co^{II}(CN)_4(NC)_2^{4-}$ by making the electron at the d_z2 less antibonding by flipping the axial cyanides to the lower strength ligand field end of the CN. Evidence for such CN flips were first derived from the investigations with the cyanide polymers. It has also been suggested that the $Co^{II}(CN)_5NC^{4-}$ ion is formed as a transient intermediate (1.6 sec period) during the oxidation of $Co^{II}(CN)_5^{3-}$ to $Co^{III}(CN)_6^{3-}$ at room temperature [11,12]. It is interesting to observe that the period of decay of species A at room temperature is also of a few seconds. However, it has not been possible to decide on the basis of the esr parameters if species A decays to species B by elimination of one or two of the cyanides, forming $Co^{II}(CN)_5^{3-}$ or $Co^{II}(CN)_4^{2-}$, which are known to be relatively stable [13].

* * *

Table 1

g – values and hyperfine splittings of the observed esr spectra

	SPECTRUM A	SPECTRUM B
$g_{\shortparallel}$	2.006 ± 0.005	2.004 ± 0.002
$g_{\perp}$	2.095 ± 0.005	2.174 ± 0.002
$A_{\shortparallel}{}^{59}Co$	54.0 G	89.0 G
$A_{\perp}{}^{59}Co$	70.0 G	25.0 G
A_{14N}	3.4 — 4.4 G	

Parallel and perpendicular values of the esr parameters refer to directions, respectively along and perpendicular to the quaternary axis of the complex.

164

100 G

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