The Solid-state Thermal Decompositions of the Decacyano-dicobaltate(II) and Decacyano-μ-superoxo-dicobaltate(III) Ions Studied by Electron Paramagnetic Resonance

By B. M. CHADWICK* and L. SHIELDS
(*School of Chemistry, University of Bradford, Bradford,* 7)

THE principal ion in freshly prepared aqueous solutions of cobalt(II) salts and potassium cyanide is now well established to be a green monomeric pentacyanide with one unpaired electron and a square pyramidal $Co(CN)_5$ moiety.[1,2] However, it is not clear whether the $Co(CN)_5$ moiety has C_{4v} or C_{2v} symmetry,[3] and there is still controversy,[2,4] as to whether there is a water molecule co-ordinated in the vacant axial position; a recent ligand field analysis[5] of the electronic *d*-to-*d* spectrum eliminated substituted octahedral geometry but was unable to distinguish the presence or absence of weak solvation along the four-fold axis. All efforts to obtain this ion in the solid state—as opposed to frozen solution—*viz.*, by precipitation from aqueous solution, have proved unsuccessful[2] owing to the very rapid formation of the violet diamagnetic dimeric anion $Co_2(CN)_{10}{}^{6-}$, which may have a structure[5] analogous to that of $Mn_2(CO)_{10}$. We report, however, that the $Co_2(CN)_{10}{}^{6-}$ ion can undergo thermal decomposition with the formation of solids which contain the green monomeric anion (identified by e.p.r.) at room temperature. In the presence of oxygen some $(NC)_5Co^{III}O{\cdot}OCo^{III}(CN)_5{}^{5-}$ ions are also formed. This latter ion can lose oxygen forming $Co^{II}(CN)_5{}^{3-}$ and $Co^{III}(CN)_5{}^{2-}$ ions.

A sample of $K_6Co_2(CN)_{10}$ on standing at room temperature in an enclosed atmosphere and exposed to natural and artificial light, slowly transformed into a green solid. Room temperature e.p.r. spectra [Figure, (a)] of this material at 9·534 and 34·756 Gc./sec. revealed a broad line (80 G, g 2·021), a resolved eight-line resonance at low field (centre g 2·177, hyperfine splitting 24 G), and an eight-line resonance at high field (centre g 1·996, hyperfine splitting 90 G, fourth and fifth lines obscured by the broad line). These two eight-line resonances are representative of an axially symmetric species with a single unpaired electron interacting with one cobalt nucleus ($I = \frac{7}{2}$) and satisfying the following spin Hamiltonian:

$$\mathcal{H} = g_{\parallel}\beta H_zS_z + g_{\perp}\beta(H_xS_x + H_yS_y) + AI_zS_z + B(I_xS_x + I_yS_y)$$

with the values $g_{\parallel} = 1{\cdot}996 \pm 0{\cdot}005$, $g_{\perp} = 2{\cdot}177 \pm 0{\cdot}005$, $A = 90 \pm 2$ G and $B = 24 \pm 2$ G. This species is clearly the square pyramidal pentacyanocobaltate(II) ion, for which the e.p.r. spectra in frozen ethylene glycol and aqueous ethylene glycol at 77° K, and in frozen methanol solution at 77° K[1] and frozen aqueous solution in isopentane at 165° K,[3] have recently been reported, though our values for $g_{\perp}$ and B are slightly higher and lower, respectively, than those for the frozen solutions. At room temperature in aqueous solution this ion gives only a single broad line e.p.r. spectrum,[1,2,7] in contrast to the 16-line spectrum observed for the green solid at room temperature. Presumably in solution at room temperature the g-value asymmetry and dipolar hyperfine interaction are averaged by rotation of the anion. The paramagnetic species causing the single broad line is most likely to be the dimeric anion $[(NC)_5Co^{III}O{\cdot}OCo^{III}(CN)_5]^{5-}$ for which Bayston *et al.*[7] have reported a distinctive 15-line signal (centre g 2·02) and in which the hyperfine structure can be suppressed by the presence of other materials, leaving a broad line (80 G, g 2·02).

We consider that this transformation of violet $K_6Co_2(CN)_{10}$ to the green solid containing the $[Co^{II}(CN)_5]^{3-}$ and $[(NC)_5Co^{III}O{\cdot}OCo^{III}(CN)_5]^{5-}$ ions is a thermal rather than a photolytic process. Thus we have observed that a sample of freshly prepared red-violet $K_6Co_2(CN)_{10},4H_2O$[8] under nitrogen, when exposed to u.v. radiation from a mercury lamp for 10 min., decomposed to a green material which gave a very intense, $Co^{II}(CN)_5{}^{3-}$ e.p.r. signal [Figure, (b)], but that no change took place when the sample was kept cool. There was no broad line due to $[(NC)_5Co^{III}O{\cdot}OCo^{III}(CN)_5]^{5-}$ in this spectrum.

A possible mechanism to explain the formation of square pyramidal $[Co^{II}(CN)_5]^{3-}$ ions (with Co^{II} centres shielded from each other) and also $[(NC)_5Co^{III}O{\cdot}OCo^{III}(CN)_5]^{5-}$ ions from $[Co^{II}{}_2(CN)_{10}]^{6-}$ ions at room temperature is as follows:

$$[(NC)_5Co^{II}Co^{II}(CN)_5]^{6-} \rightarrow [(NC)_5Co^{II}]^{3-} + [Co^{III}(CN)_5]^{2-} + e^-, \qquad (I)$$

$$[(NC)_5Co^{II}Co^{II}(CN)_5]^{6-} + e^- \rightarrow [(NC)_5Co^{I}]^{4-} + [Co^{II}(CN)_5]^{3-} \qquad (II)$$

$$[(NC)_5Co^{I}]^{4-} + O_2 \rightarrow [(NC)_5Co^{III}O_2]^{4-}, \qquad (III)$$

and $$[(NC)_5Co^{II}]^{3-} + [Co^{III}(CN)_5]^{2-} + O_2 \rightarrow [(NC)_5Co^{III}O{\cdot}OCo^{III}(CN)_5]^{5-}. \qquad (IV)$$

If the $Co_2(CN)_{10}^{6-}$ ion does have the $Mn_2(CO)_{10}$ structure then reaction (I) would clearly result in the ready production of square pyramidal $[Co(CN)_5]^{3-}$ ions. The last step may well be a reversible one. Bayston *et al.*[7] observed that when the $[(NC)_5Co^{III}O{\cdot}OCo^{III}(CN)_5]^{5-}$ ion is isolated from oxygenated $[Co^{II}(CN)_5]^{3-}$ solution (heavily contaminated with the diamagnetic $[(NC)_5Co^{III}O{\cdot}OCo^{III}(CN)_5]^{6-}$ ions) the precipitate also gives a 16 line e.p.r. spectrum virtually identical to that obtained by us in the green solid formed from $K_6Co_2(CN)_{10}$ on standing.[7] Bayston *et al.* were unable to deduce the species responsible for this 16-line resonance, but it is clear that it must be the $[Co^{II}(CN)_5]^{3-}$ ion. As it cannot have been precipitated from aqueous solution, it seems likely that it has been formed in the solid by the reverse of reaction (IV). Some support for this conclusion is provided by the further observations of Bayston *et al.*[7] that on exposing the precipitate to air for periods up to several weeks the 16-line signal increases, and that the same effect can be obtained in a few hours *in vacuo*.

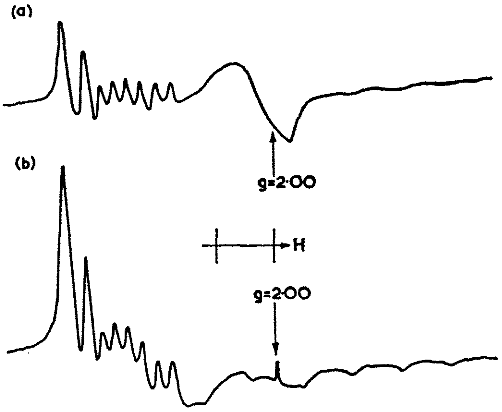

FIGURE. (a) 9·5 *Gc./sec. e.p.r. spectrum of decayed solid polycrystalline* $K_6Co_2(CN)_{10}$; (b) 9·5 *Gc./sec. e.p.r. spectrum of* $K_6Co_2(CN)_{10}{\cdot}4H_2O$ *exposed to u.v. and heat radiation from a high pressure mercury lamp.*

(*Received, April* 18*th*, 1969; *Com.* 536.)

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