553. *The Pentacyanohydride Complexes of Cobalt*(I) *and Rhodium*(I).

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High-resolution nuclear magnetic resonance studies have shown strong proton resonances characteristic of hydrogen atoms bound to the metal atom in reduced aqueous solutions of pentacyano-cobaltate and -rhodate ions; the species present are probably the ions $[HCo^I(CN)_5]^{3-}$ and $[HRh^I(CN)_5]^{3-}$. The cobalt species is found in low concentration in aqueous cobalt(II) cyanide solutions; in the light of this and other information the chemical properties of bivalent cobalt cyano-complex ions are discussed briefly.

The structures of $K_2[Co(CN)_3CO]$, $K_8[Co_2(CN)_8]$, and $K_8[Rh_2(CN)_8]$ are also discussed.

SEVERAL transition-metal complexes absorb molecular hydrogen and function as homogeneous hydrogenation catalysts; [1] it has often been suggested that in such systems species with a hydrogen atom bound to the metal atom are involved. Since it is now known [2] that abnormally large chemical shifts (14—22 p.p.m. on the high-field side relative to water) are characteristic for protons bound to transition-metal atoms, high-resolution nuclear magnetic resonance measurements provide the means for detecting such metal–hydrogen bonds in systems where it would otherwise be difficult to prove their presence.

Preliminary studies on the well-known cobaltous cyanide system showed that in the hydrogenated solutions a species giving a proton resonance signal in the characteristic region was present; however, it was found subsequently that hydrogenation is *not necessary*

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[1] For references see: Halpern, *Quart. Rev.*, 1956, **10**, 463; Winfield, *Austral. J. Sci. Res.*, 1951, *A*, **4**, 385; Baston, Kelso King, and Winfield, " Advances in Catalysis," Academic Press, New York, 1957. Vol. 9, p. 312; Wender and Sternberg, *ibid.*, p. 594.

[2] Green, Pratt, and Wilkinson, *J.*, 1958, 3916, and references given therein.

and that the species is formed on dissolving cobaltous salts in cyanide solutions [3] or dissolving Adamson's salt, $K_6[Co_2(CN)_{10}]$, in water. In order further to elucidate this reaction and the nature of the hydrogen-containing metal species, we have studied reduced solutions of cobalt (and also rhodium) cyano-complexes; we discuss this aspect of the work first.

Reduction of Cobalt Cyano-complexes.—The green solutions of cobalt(II) cyano-species, from either a mixture of cobaltous salts and potassium cyanide or Adamson's salt, are reduced by potassium amalgam or sodium borohydride to yellow solutions. Previously, cobaltic species, *e.g.*, $[Co^{III}(CN)_6]^{3-}$, have been reduced both by potassium amalgam and electrolytically to give yellow solutions,[4] which were held to contain a univalent cobalt complex. Polarographic studies on cobaltous and cobaltic cyano-species have also shown evidence for reduction to a univalent cobalt species.[5,6,7]

The yellow solutions show a proton resonance at 695 ± 3 cycles/sec. (*vs.* the proton resonance of the water at 25° at 40 Mc./sec.), which confirms the diamagnetism of the cobalt species measured independently by the Gouy method. The fraction of the cobalt originally present which appears as the hydride cyano-ion was estimated by comparing the peak area of the proton resonance with a standard chloroform sample. This showed that essentially all of the cobalt was present as the hydride cyano-ion. The hydride species can be formed by reduction of cobalt cyanide solutions only when the CN^-/Co ratio is 5·0 or greater; if the ratio is less than five, metallic cobalt is deposited on treatment with amalgam or borohydride.

The likeliest possibilities for a monomeric, diamagnetic ion are $[HCo(CN)_4]^{2-}$ and $[HCo(CN)_5]^{3-}$. The former does not obey the inert-gas rule and would require a CN^-/Co ratio of 4; the latter obeys the inert-gas rule and its formation by direct reduction of pentacyanocobaltate(III) species as well as of cobaltous–cyanide solutions is understandable. Attempts to isolate the complex hydride ion as a solid salt have failed owing to its instability; *e.g.*, addition of alcohol results in evolution of hydrogen and precipitation of Adamson's salt:

$$2[HCo(CN)_5]^{3-} = [Co_2(CN)_{10}]^{6-} + H_2$$

whilst most precipitating cations are reduced; also ferroin gives a precipitate but this too decomposes rapidly.

Preliminary polarographic data [6] indicate that the number of cyanide groups in the reduced complex is the same as in $[Co(CN)_5H_2O]^{3-}$. These facts thus strongly suggest that the species is $[HCo(CN)_5]^{3-}$; this ion is isoelectronic with $HMn(CO)_5$ and Adamson's ion, $[Co_2(CN)_{10}]^{6-}$, is isostructural with $Mn_2(CO)_{10}$.[6]

TABLE 1. *Absorption spectra of cobalt cyano-complexes.*

Complex	Solvent	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
$[Co(CN)_5H_2O]K_3$ [a]	H_2O	960	3×10^3	640	10	430	50	350	500	278	6×10^3
$[Co_2(CN)_{10}]K_6$	$SOMe_2$	1030	3×10^3	330	20	286	5×10^3	272	6×10^3		
$[Co(CN)_5H]K_3$	H_2O	310	400	283	1300	268	2800				
$H_2 + [Co(CN)_5H_2O]K_3$ [a]	H_2O	960	260	510	80	320	4×10^3	285	3×10^3	268	3×10^3
$[Co(CN)_5H_2O]K_3$ [a] after 10 days' ageing	H_2O	960	40	575	10	350	10^3	285	3×10^3	268	3×10^3

[a] Parts of the spectra have also been described; see Kelso King and Winfield, *J. Amer. Chem. Soc.*, 1958, **80**, 2060; Winfield, personal communication.

In Table 1 is given the absorption spectrum of the yellow solution, and we consider that this represents the spectrum of the pure $[HCo(CN)_5]^{3-}$ ion. Dilute solutions (<0·1M) of the ion in presence of excess of borohydride are stable for at least a week as shown by absorption and nuclear magnetic resonance measurements. In concentrated solutions

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[3] Griffith, Pratt, and Wilkinson, *Nature*, 1958, **182**, 466.

[4] Grübe, *Z. Elektrochem.*, 1926, **32**, 561; Treadwell and Huber, *Helv. Chim. Acta*, 1943, **26**, 10.

[5] Hume and Kolthoff, *J. Amer. Chem. Soc.*, 1949, **71**, 867.

[6] Vlček, personal communication.

[7] Maki, Fujita, and Tsuchida, *Nature*, 1959, **183**, 458.

($>\sim$1M), however, hydrogen is slowly evolved and pentacyanoaquocobaltate(III) is produced.

TABLE 2. *Infrared spectra of some cyano-complexes* (*in Nujol mulls*).

[Absorptions in the C≡N and C=O stretching regions only are reported.]

Complex ...	$K_6[Co_2^{II}(CN)_{10}]$	$K_3[Co(CN)_5H_2O]$	$K_3[Co(CN)_6]$	$K_2[Co(CN)_5H_2O]$
Main bands	2133, 2090, 2079 [a]	2095 [b]	2143 [a]	2140 [b]
Complex ...	$K_3[Co(CN)_5OH],H_2O$ [a]	$Co_3[Co_2(CN)_{10}],5H_2O$	$K_8[Co_2(CN)_8]$	
Main bands	2135 (2114 vw, sh)	2133, 2085, 2063	2120, 2062	
Complex ...	$K_3[Rh(CN)_6]$	$K_3[Ir(CN)_6]$	$K_8[Rh_2(CN)_8]$	[Fe(*o*-phen)$_3$]$_2$[Co(CN)$_3$CO]
Main bands	2163	2185	2130, 2070	2125, 2075, 1995, 1922

[a] Griffith and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 295. [b] In aqueous film between calcium fluoride plates.

The observation of the proton resonance line indicates that the proton bound to the cobalt atom has a chemical half-life in the solutions of at least 10^{-4} sec. (cf. the case of rhodium below).

Reduction of Rhodium Cyano-complexes.—Manchot [9] reported that hexacyanorhodate-(III) solutions were reduced by hypophosphite to a univalent rhodium complex. We have found that if cyanide is added to the yellow (boiled) aqueous solutions ($\sim$1M) of rhodium trichloride the initial precipitate redissolves and that the solution can be reduced by sodium borohydride. The concentration of the hydride species produced in this case was high enough to enable the proton resonance spectrum to be observed in a 5 mm. o.d. spinning sample tube under conditions of resolution higher than in the cobalt case where dilute solutions in larger-diameter non-spinning tubes had to be employed. The rhodium solution shows a line at $625{\cdot}5 \pm 1$ cycles/sec. on the high-field side relative to water at 40 Mc./sec. The assignment of the line as due to a proton bound directly to the metal atom is strengthened by the fact that the line is a symmetrical doublet with a separation of $13{\cdot}1 \pm 1$ cycles/sec.; the width of each component is $\leqslant 2$ cycles/sec. This doublet splitting could be expected to arise in a covalent rhodium–hydrogen bond from the electron-coupled spin interaction between the proton and the rhodium nucleus (^{103}Rh, abundance 100%) which has spin $\frac{1}{2}$. The observation of the doublet shows that the proton bound to the metal has a chemical lifetime of at least $1/(2\pi \times 13) \sim 0{\cdot}01$ sec. in this solution. In fact, the solutions sealed from air showed no change in the intensity of the proton resonance line, although there was little borohydride ion present during more than seven months.

Attempts to isolate salts of the complex ion failed, but by analogy with cobalt it is probably $[HRh(CN)_5]^{3-}$.

Polarographic reduction of rhodium trichloride in cyanide solutions is reported [10] to show an irreversible one-electron reduction at $-1{\cdot}47$ v (*vs.* S.C.E.), but the value of $n = 1$ has recently been disputed.[11]

A later investigation showed no reduction at the dropping electrode.[12] Using a yellow solution of rhodium trichloride made 1M with respect to potassium cyanide, we find a well-defined irreversible reduction wave at $E_{\frac{1}{2}} = -1{\cdot}54$ v (*vs.* S.C.E.). The diffusion coefficient (D) being assumed to be the same as that for $[Co(CN)_5H_2O]^{3-}$,[5,10] application of the Ilkovič equation leads to a value of $n = 2{\cdot}0$, showing that as in the cobalt case the reduced species contains univalent rhodium.

Formation of $[HCo(CN)_5]^{3-}$ *in Aqueous Cobalt*(II)*-Cyanide Solutions.*—It was noted above that the resonance peak for $[HCo(CN)_5]^{3-}$ was first detected in solutions of cobaltous salts in presence of cyanide ions; the peak is at the same position as in the pure hydride and can be detected even in the freshly mixed solutions which are green and paramagnetic

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[8] Griffith and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 295.

[9] Manchot and Schmid, *Ber.*, 1931, **64**, 2672.

[10] Willis, *J. Amer. Chem. Soc.*, 1944, **66**, 1067.

[11] Cozzi and Pantani, *J. Inorg. Nuclear Chem.*, 1958, **8**, 385.

[12] Rius and Molera, *Anales Fiz. Quim.*, 1948, **44**, 53.

or in similar fresh solutions of Adamson's salt, $K_6[Co_2(CN)_{10}]$, after separation of the paramagnetic precipitate (see below). By comparison with a standard chloroform solution, the proportion of total cobalt in the form of the hydride ion appears to be about 3%. The intensity of the proton signal is unaffected by (*a*) increasing the cyanide concentration from $CN^-/Co = 5$ to 8, (*b*) saturating the freshly prepared green solutions with hydrogen, and (*c*) the ageing process of cobaltous–cyanide solution. Further, if the solutions are prepared in deuterium oxide from anhydrous salts, no proton resonance appears in the high-field region even when hydrogen has been passed through the solution for 1 hr. Since the resonance is found when solutions in water are prepared under nitrogen, these observations can only be interpreted to mean that the $[HCo(CN)_5]^{3-}$ ion must be formed by interaction of cobalt(II) and cyanide ions with water:

$$Co_{aq}^{2+} + 5CN^- + H_2O = [HCo^I(CN)_5]^{3-} + OH$$

We cannot explain why only 3% of the cobalt is transformed to the hydride; since the hydride appears to be formed instantaneously, is always present, and is unaffected by the subsequent changes in the cobalt–cyanide solutions (*e.g.*, ageing or hydrogen uptake), it is possible that the above reaction competes (unfavourably) with the presumably rapid aquation reaction of pentacyanocobaltate(II) ion to give $[Co(CN)_5H_2O]^{3-}$, as for example when the dimeric ion of Adamson's salt is cleaved in water.

The hydroxyl radical formed according to the above equation would undoubtedly oxidise the cobaltous bulk species, perhaps *via* a peroxy-complex.* Several workers have indeed reported the presence of peroxides during oxidation of cobalt(II) cyano-complex solutions.[13] A weak peak at 350 mμ in the absorption spectrum of a fresh solution of $[Co^{II}(CN)_5H_2O]^{3-}$ may well be attributed to a few units % of cobalt(III) species produced by hydroxyl radical reactions.

Nature of freshly prepared Cobaltous Cyanide Complex Solutions.—Apart from the small amounts of $[HCo(CN)_5]^{3-}$ and the corresponding cobaltic species, the components present in solutions of cobaltous ion in cyanide media freshly prepared in an inert atmosphere are probably as follows. (*a*) There is probably a small amount of a tetracyano-complex, most likely $[Co(CN)_4(H_2O)_2]^{2-}$. The existence of a tetracyano-cobalt complex in such solutions has been suggested by amperometric studies;[14] the corresponding tervalent cobalt complex $[Co(CN)_4(H_2O)_2]^-$ is known in solution.[15] Since clear solutions result when the ratio CN^-/Co is as low as 4·6 (precipitation begins at lower ratios), it seems necessary to assume that ions with a ratio CN^-/Co less than 5 are present. (*b*) The bulk of the solution species is undoubtedly a pentacyanocobaltate(II), either $[Co(CN)_5]^{3-}$ or $[Co(CN)_5H_2O]^{3-}$.[16] Although there has been considerable discussion concerning the nature of this ion, the latter formulation is favoured. Thus we find that the infrared spectrum of thin films of a fresh solution show only a single, very strong band in the C–N stretching region (at 2095 cm.$^{-1}$) similar to that in other pentacyanocobaltate species, $[Co(CN)_5X]^{3-}$.[8] † Polarography in non-cyanide media shows a direct reduction from $[Co(CN)_5H_2O]^{2-}$ to the cobalt(II) complex[5,6] and from $[Co(CN)_5X]^{3-}$ complexes to hexaco-ordinate cobalt(II) species.[7] The spin-only magnetic moment of 1·73 B.M. for the aqueous solutions[16,17] may also better support the

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* Potassium cyanide reacts with the ion $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]^{5+}$ in aqueous solution to give $[Co(CN)_5OH]^{3-}$, so that peroxycyano-complexes of cobalt, if they exist at all, must be unstable; we have been unable to find a report of such species in the literature.

† A pentacyano-hexaco-ordinate complex would be expected to show three C≡N stretches in accordance with its C_{4v} configuration; in fact, for all pentacyano-complexes examined only one intense peak is observed, with a small shoulder on this peak, and a very weak peak near 2200 cm.$^{-1}$. It is possible that higher resolution would have shown three distinct peaks.

[13] Peters, *Z. phys. Chem.*, 1898, **26**, 217; Manchot and Herzog, *Z. anorg. Chem.*, 1901, **27**, 404; Adamson, *Rec. Trav. chim.*, 1956, **75**, 809.

[14] Crémoux and Mondain-Merval, *Bull. Soc. chim. France*, 1949, 700.

[15] Smith, Kleinberg, and Griswold, *J. Amer. Chem. Soc.*, 1953, **75**, 149.

[16] Adamson, *J. Amer. Chem. Soc.*, 1951, **73**, 5710.

[17] Mills, Weller, and Wheeler, *J. Phys. Chem.*, 1959, **63**, 403.

aquated ion, since the odd electron is likely to occupy an *S*-state with no orbital contribution as in other inner orbital cobalt(II) ions, *e.g.*, $[Co(NO_2)_6]^{4-}$.[18] Finally, the absorption spectrum of $K_6[Co_2(CN)_{10}]$ is radically different in dimethyl sulphoxide from that in water (Table 1), as might be expected if a solvent molecule of such a different nature entered the co-ordination sphere.

Since the exchange of radio-CN^- with Adamson's salt [16] is unusually rapid, it seems likely that the water molecule in the aquated mononuclear ion is very weakly bound.

Precipitated Species, Ageing, and Hydrogen Absorption by Cobalt–Cyanide Solutions.—When the ratio CN^-/Co in Co^{II}–cyanide solutions is below 4·6, a green solid is deposited,[19] and when pure $K_6[Co_2(CN)_{10}]$ is dissolved in water a green solid is also deposited rather quickly (20 min.). This solid has been considered to be $K_2Co[Co(CN)_6]$,[20] but analyses and infrared measurements (Table 2) show that it is $Co^{II}_3[Co^{II}_2(CN)_{10}]$. There have been several reports [21] of cobaltous salts of cyano-complexes of Co^{II} and Co^{III}; some of these, which are red, are almost certainly cobaltous salts of the ion $[Co(CN)_5OH]^{3-}$.

It seems fairly clear from the results discussed above that the $[Co(CN)_5H]^{3-}$ ion is not a predominating factor in the ageing or the hydrogen-uptake process [17, 19] of cobaltous cyanide solutions, and if complexes with metal–hydrogen bonds are involved in these cases the bonds must have an existence shorter than the nuclear magnetic resonance time scale. When the cobaltous–cyanide solution in deuterium oxide was saturated with hydrogen as noted above, a transformation of even 1% of the cobalt to $[HCo(CN)_5]^{3-}$ would have been detected; the only observable change was a slight increase in the intensity of the signal from the water contaminant in the deuterium oxide; this was of the right order of magnitude for the amounts of cobalt and hydrogen involved. The similarity of the absorption spectra (Table 1) for aged and hydrogenated fresh solutions of $[Co(CN)_5H_2O]^{3-}$ suggests that the final complexes may be the same in both cases and that a cobalt(I) species is produced. This was suggested for the hydrogenated solution by Mills *et al.*[17] In the case of the aged complex in dilute solution * the production of a cobalt(I) species from cobalt(II) must also produce an equivalent amount of cobalt(III), so that the process may be of the overall form:

$$2[Co^{II}(CN)_5H_2O]^{3-} = [Co^{I}(CN)_5H_2O]^{4-} + [Co^{III}(CN)_5H_2O]^{2-}$$

It may be noted that on addition of alcohol to either the yellow aged or the hydrogenated solutions a precipitate is obtained which appears to be a mixture of $K_6[Co_2(CN)_{10}]$ (purple-red) and $K_2[Co(CN)_5H_2O]$ (yellow) and whose infrared spectrum shows bands which would agree with those expected for a mixture; the former is presumably obtained by oxidation of a cobalt(I) species. The presence of $K_6[Co_2(CN)_{10}]$ is confirmed by the fact that dissolution of the mixed solid gives a green solution showing the appropriate absorption bands for $[Co(CN)_5H_2O]^{3-}$.

Other Cobalt and Rhodium Cyano-complexes.—The infrared spectrum (Table 2) of the ferroin salts of the tricyanocarbonyl cobaltate(I) ion,[22] $[Co^{I}(CN)_3CO]^{2-}$, shows three C–N and one C–O stretching frequency in agreement with its expected planar (C_{2v}) configuration. The octacyanodicobaltate(0) ion,[23] $[Co_2(CN)_8]^{8-}$, which is necessarily dimeric because of its diamagnetism, shows two C–N stretching modes in accordance with a D_{4h} configuration similar to that preferred [24] for the ion $[Ni_2(CN)_6(CO)_2]^{4-}$. A rhodium

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* In concentrated (> ~ 0·5M) solution $[Co^{II}(CN)_5H_2O]^{3-}$ evolves hydrogen [18] and the final product appears to be $[Co^{III}(CN)_5H_2O]^{2-}$.

[18] Figgis and Nyholm, *J.*, 1959, 338.

[19] Kelso King and Winfield, *J. Amer. Chem. Soc.*, 1958, **80**, 2060.

[20] Descampes, *Ann. Chim. Phys.*, 1878, **15**, 431.

[21] Alvarez, *Ann. Chim. Anal.*, 1910, **15**, 130; Benedetti-Pichler, *Z. anal. Chem.*, 1927, **70**, 258; Gmelin, "Handbuch der Anorganischen Chemie," Kobalt, Teil A, **58**, 1932 (Berlin, Verlag Chemie G.M.B.H.), pp. 377—379.

[22] Hieber and Bartenstein, *Z. anorg. Chem.*, 1954, **276**, 1.

[23] Watt, Hall, Choppin, and Gentile, *J. Amer. Chem. Soc.*, 1954, **76**, 373; Hieber and Bartenstein, *Naturwiss.*, 1952, **39**, 300; *Z. anorg. Chem.*, 1954, **276**, 12.

[24] Griffith, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **10**, 23.

analogue prepared by reduction of $K_3[Rh(CN)_6]$ with potassium in liquid ammonia is unstable and gave variable analyses; its infrared spectrum, however, is similar to that of the cobalt compound and it is probably $K_8[Rh_2(CN)_8]$.

EXPERIMENTAL

The salt $K_6[Co_2(CN)_{10}]$ was prepared by Adamson's method.[16] Cobaltous cyanide solutions were made from " AnalaR " salts under oxygen-free nitrogen. Rhodium and iridium hexacyanide complexes were prepared by published methods.[25,26]

Polarograms were obtained by using a Tinsley Mark 19 recording instrument with a dropping-mercury electrode [$C = 0{\cdot}56$ mole/l.; $m^{\frac{2}{3}}t^{\frac{1}{6}} = 1{\cdot}93$].

Absorption spectra were measured on a Perkin-Elmer Model 4000 recording spectrophotometer with 1-cm. stoppered silica cells; infrared spectra were taken on a Perkin-Elmer Model 21 recording spectrophotometer with sodium chloride optics.

High-resolution nuclear magnetic resonance measurements were made with a Varian Associates spectrometer at 40 Mc./sec., 5-mm. o.d. spinning tubes being used, or 15-mm. non-spinning tubes when necessary. The approximate measurements of $[HCo(CN)_5]^{3-}$ and $[HRh(CN)_5]^{3-}$ concentrations were made by comparing the peak area with that produced by a standard solution of chloroform in carbon tetrachloride under the same conditions of measurement.

Cobalt(II) *Decacyanodicobaltate*(II).—The green precipitate obtained on dissolving Adamson's salt in water was removed by centrifugation, washed with air-free water, and dried by alcohol and ether washes (Found: Co, 45·3. $Co_3[Co_2(CN)_{10}],5H_2O$ requires Co, 45·7%). No potassium could be detected in the solid *salt.* Its infrared spectrum shows the same bands as Adamson's salt.[8]

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[25] Krauss and Umbach, *Z. anorg. Chem.*, 1929, **179**, 359.
[26] Martius, *Annalen*, 1861, **117**, 357.