TRANSITION METAL CYANIDES AND THEIR COMPLEXES

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I. Introduction

Nearly all transition metals other than the lanthanides and actinides form well-defined cyanides or complex cyanides. Some of these (e.g., the complexes of iron, silver, and gold) have been recognized as stable species for more than a century, and much of the older chemistry of such substances was summarized 20 years ago in a useful book (*530*). Nevertheless, it is only during the past two decades that a systematic investigation of cyanide ion as a ligand in transition metal chemistry has been pursued intensively, and only two reviews (*171*, *189*) summarize the progress made. The aim of this article is to provide a critical review of the preparation, characterization (which is often incomplete), and properties of cyanide complexes of the transition metals. An effort has been made to pay particular attention to structural, thermodynamic, and kinetic data where these exist, but physicochemical information is often scanty, and it is hoped that one effect of this survey will be to draw attention to a field in which much further work is necessary. The literature has been covered to mid-1965.

No useful purpose is served by attempting to draw a clear distinction between simple and complex cyanides of the transition metals. Not only does the cyanide ion often function as a bidentate ligand (e.g., in macromolecular structures such as those of AgCN and AuCN), and even as a tridentate ligand (e.g., in $CuCN{\cdot}NH_3$), but substances which might seem to be simple cyanides sometimes contain nonequivalent metal atoms (e.g., $Co(CN)_2$ and hydrated $Ni(CN)_2$ are best formulated as $Co_2[Co(CN)_6]$ and $Ni(aq)[Ni(CN)_4]$, respectively). In order to conform to a consistent pattern we have, however, under each oxidation state of each metal discussed, begun by describing compounds containing only cyanide and the transition metal concerned; complexes in which cyanide is the only ligand are then considered, followed by compounds in which two or more ligands are present.

Two prominent features of transition metal cyanide chemistry are the wide range of metal:ligand ratios in complexes (accompanied by an unusually wide range in stereochemical configurations) and the existence of many metals in low oxidation states. Configurations for which convincing evidence exists are linear (e.g., in $[Ag(CN)_2]^-$), approximately equilateral triangular (e.g., in $[Cu(CN)_2]_n^{n-}$), regular tetrahedral (e.g., in $[Zn(CN)_4]^{2-}$), square (e.g., in $[Ni(CN)_4]^{2-}$), octahedral (e.g., in $[Co(CN)_6]^{3-}$), and dodecahedral (e.g., in $[Mo(CN)_8]^{4-}$); others, however, may well be found in the many types of complex not yet subjected to detailed structural investigation. Analogous compounds of the metals of a particular triad of transition elements are usually isomorphous (though $K[Cu(CN)_2]$ and $K[Ag(CN)_2]$ constitute an interesting exception), and this is broadly true also for metals in the same series. The hexacyano complexes of Cr(III), Mn(III), Fe(III), and Co(III), for example, have closely similar structures. A further point of interest in the structures of these compounds is that there is a steady decrease in size from Cr to Co; this is readily understood from the fact that all are low-spin complexes, indicating that successive electrons are being accommodated in the t_{2g} orbitals. The erratic variation in size and stereochemistry that occurs among high-spin complexes of these elements in the same oxidation state (e.g., in their fluorides) is therefore absent. A somewhat similar state of affairs persists in the complex nitrites of formula $K_2PbM(NO_2)_6$, where M = Fe – Cu; in this case addition of electrons in antibonding orbitals results in a regular increase in size (*145a*).

The stabilization of low oxidation states at once calls to mind carbon monoxide, with which cyanide ion is isoelectronic. Cyanides, however, show much less tendency than carbonyls to have formulas which conform to the Effective Atomic Number rule: although at present there appears to be no well-characterized species in which a rare gas electronic configuration is exceeded, there are many compounds, including several of metals in low oxidation states, in which such a configuration is not attained. Nevertheless, the relationship with carbon monoxide has been highly influential in chemical thinking, and it is therefore desirable to discuss some general features of cyanide as a ligand, and to compare it briefly with carbon monoxide, before describing individual compounds.

The cyanide ion may be represented as having unshared pairs of electrons on the carbon and nitrogen atoms, and a triple bond (one σ- and two π-bonds) between them. Rigid proof exists in a few instances (*118*, *122*, *254*), and there is now considerable supplementary evidence (*273*, *274*, *275*, *520*) to show that, where a covalent bond to one metal atom is formed, carbon is normally the donor atom. In addition to this σ-bond, a π-bond may be formed by overlap of an occupied *d* orbital of the metal atom and an antibonding π-orbital of the cyanide ion. This "back-donation" avoids the accumulation of a large negative charge on the metal atom, contributes substantially to the metal-carbon bond strength, and weakens the carbon-nitrogen bond. It is noteworthy that cyanide complexes, like carbonyls, appear to be formed readily only by transition metals in oxidation states which have electrons in *d* orbitals available for this d_π–p_π bonding; in octahedral complexes the d_{xy}, d_{xz}, and d_{yz} orbitals, and in tetrahedral complexes the $d_{x^2-y^2}$ and d_{z^2} orbitals, are most suitably orientated for this purpose.

Because of its negative charge, cyanide ion is a poorer acceptor than carbon monoxide. Nevertheless, firm support for the general importance of π-bonding in complex cyanides is provided by studies of the intensities of metal-carbon and carbon-nitrogen stretching absorptions in the infrared spectrum [(*280*) but see (*281a*)]. Accurate values for bond lengths are, unfortunately, so scarce that no supplementary evidence on this point is yet available from diffraction methods.

There are two other important consequences of the fact that cyanide is an ion and not a neutral molecule: metal cyanides and their complexes are nonvolatile salts rather than volatile molecular entities, and much of their chemistry is concerned with processes and measurements in solution in solvents of high complexing power, so that *differences* in complexing by solvent and ligand are involved. We shall return later to the solution chemistry of cyanide complexes; first, however, we shall discuss the bearing of the physical state of metal cyanides on structural investigations.

Although a number of detailed X-ray studies have been made during recent years, and there is considerable further scope for powder photography among compounds of the same formula type, the structural tool most widely used in this field is undoubtedly infrared spectroscopy. Transition metal cyanides show a sharp and intense $C\equiv N$ stretching frequency at about 2100 cm^{-1} [for bridging cyanides at about 2200 cm^{-1} (*135*, *156*, *472*)]. For a given metal and coordination number there is some evidence to indicate that the frequency increases with increase in oxidation state (e.g., it is 1985 cm^{-1} in $[Ni(CN)_4]^{4-}$ and 2135 cm^{-1} in $[Ni(CN)_4]^{2-}$, but it should not be forgotten that these species have different structures). For a given metal in a particular oxidation state $\nu(C\equiv N)$ has often been found to decrease with increase in coordination number for isolated ions in aqueous solution (e.g., 2135 cm^{-1} in $[Ag(CN)_2]^{-}$, 2105 cm^{-1} in $[Ag(CN)_3]^{2-}$, and 2092 cm^{-1} in $[Ag(CN)_4]^{3-}$). Raman and infrared spectroscopic measurements made in solution lead, from consideration of numbers of frequencies, to reliable conclusions concerning molecular or ionic symmetry. For solids, however, great caution has to be exercised in accepting conclusions based on numbers of $C\equiv N$ stretching frequencies observed; not only are the results obtained often determined by the resolving power of the optical system employed, but the site symmetry of the ion being investigated may also exert a great influence. Thus the $[Co(CN)_6]^{3-}$ ion in aqueous solution shows a single $C\equiv N$ stretching frequency; solid $K_3[Co(CN)_6]$ shows two; and its solution in solid NaCl or KCl shows three (see Section VIII,A). In solid $K_3[Cu(CN)_4]$ the anion, which in aqueous media shows a single band at 2076 cm^{-1}, now has $C\equiv N$ stretching frequencies at 2094, 2081, and 2075 cm^{-1} although it is known from X-ray work to be tetrahedral (see Section X,A). Only in a few instances have the vibrational spectra of solid complex cyanides been interpreted in detail; most of this work is by L. H. Jones and his collaborators, whose valuable investigations have covered a very wide field in cyanide chemistry, and whose results or interpretations we have in cases of discrepancy generally preferred to those of other workers.

The two solvents most often employed in the preparation of cyanides are water and ammonia; the potentialities of hydrogen cyanide, which dissolves many salts, have been little investigated, and it has only recently been shown that some elements [e.g., Cu(I), Ag(I)] will form complex cyanides in dimethyl sulfoxide (*133a*). As with all other processes concerned with salts in solution, the solvent plays an essential part in determining what happens. Water, for example, is not only a good complexing agent which competes to some extent even with cyanide ion for the cation present; the hydrogen ions it contains compete for cyanide [K_a for HCN at 25°C is only 6×10^{-10} (*9, 262*)]. Furthermore, because of hydrolysis, aqueous solutions of alkali metal cyanides contain quite high concentrations of hydroxyl ions, and these compete for the metal. A complex acid such as $H_3[Co(CN)_6]$, for example, persists in aqueous solution only if it is thermodynamically stable with respect to abstraction of cyanide from it by hydrogen ions, or if it is kinetically inert with respect to dissociation. It is noteworthy that for most of the acids which can be obtained in aqueous media, the anion does, in fact, exchange CN^- with labeled cyanide solution only extremely slowly, and a survey of available formation constants suggests that $H[Au(CN)_2]$ is probably the only complex cyano acid which is thermodynamically stable with respect to formation of hydrogen cyanide and the metal cyanide or its hydrolysis product. Finally, it should be mentioned that aqueous cyanide is fairly easily oxidized to cyanogen or cyanate; from the standard free energies of the species involved, the following potentials may be calculated:

$$\tfrac{1}{2}C_2N_2 + H^+ + e = HCN(aq) \qquad E^\circ = +0.37\ V$$

$$CNO^- + 2H^+ + 2e = CN^- + H_2O \qquad E^\circ = -0.14\ V$$

Liquid ammonia has two important advantages over water: it is a more basic solvent, in which hydrogen cyanide is a much stronger acid; and it is less easily reduced. The second factor makes it possible to carry out many preparations of complexes of metals in low oxidation states in this medium, using alkali metals as reducing agents (e.g., $K_4[Ni(CN)_4]$, $K_3[Co(CN)_4]$).

Let us consider now the effect of cyanide on the stabilities with respect to oxidation and reduction of metal ions in aqueous media, taking as an example Fe(II) and Fe(III):

$$Fe^{3+}(aq) + e = Fe^{2+}(aq) \qquad E_{aq}^\circ = +0.77\ V$$

$$[Fe(CN)_6]^{3-}(aq) + e = [Fe(CN)_6]^{4-}(aq) \qquad E_{CN^-}^\circ = +0.36\ V$$

The relationship between the standard potentials and the over-all complexing constants K^{III} and K^{II} for Fe(III) and Fe(II) is indicated by the cycle

$$\begin{tikzcd}
Fe^{3+}(aq) + e \arrow[r, "E_{aq}^\circ"] \arrow[d, "K^{III}"', "6CN^-"] & Fe^{2+}(aq) \arrow[d, "K^{II}"', "6CN^-"] \\
{[Fe(CN)_6]^{3-}(aq)} + e \arrow[r, "E_{CN^-}^\circ"] & {[Fe(CN)_6]^{4-}(aq)}
\end{tikzcd}$$

Since for complexing $-\Delta G^\circ = RT \ln K$ and for electron transfer $-\Delta G^\circ = nFE^\circ$, the experimental data imply that the hexacyano complex of Fe(III) is more stable than that of Fe(II), in each case with respect to dissociation into the aquo ion and six hydrated cyanide ions, by a factor of 10^7. This stabilization of the higher oxidation state might seem surprising, since π-bonding ligands, by removing excess of negative charge from the metal, would be expected to favor low oxidation states; here, however, competition with water as ligand is involved, and the change in E° is determined by the difference in the differences between aquo and cyano complexing for Fe(III) and Fe(II). Even though the Fe(III) complex has the higher formation constant, the interaction of ferric salts and cyanides in aqueous solution is not a useful method for the preparation of ferricyanide: when solutions of ferric chloride and potassium cyanide are mixed, most of the iron is precipitated as ferric hydroxide.

It is not possible to cite reliable data for the effect of cyanide complexing on standard potentials for many other metals, since different oxidation states of the same metal may form complexes with different numbers of cyanide ions; complexing constants as well as electron transfer energies are then involved. The quoted value of E° for the Co(III)/Co(II) couple in complex cyanides (*208*), for example, is difficult to interpret since the Co(II) species present is a pentacyanide, while Co(III) is there as $[Co(CN)_6]^{3-}$; further features of this very complicated system are discussed in Section VIII,A. For the systems

$$Mn^{3+} + e = Mn^{2+} \qquad E^\circ = +1.5\ V$$
$$[Mn(CN)_6]^{3-} + e = [Mn(CN)_6]^{4-} \qquad E^\circ = -0.22\ V$$

the data appear to be reliable, however, and clearly cyanide has a much greater effect here than in the Fe(III)/Fe(II) system; a discussion of this in terms of electronic configurations is given in Section VI,A.

Cyanide ion lies at the end of the spectrochemical series

$$I^- < Br^- < Cl^- < F^- < C_2O_4^{2-} < H_2O < NH_3 < en < dipy < NO_2^- < CN^- \sim CO$$

i.e., the quantity $10\,Dq$ or Δ, measuring the difference in energy between the t_{2g} and e_g orbitals, is at a maximum. It is therefore a very powerful ligand for bringing about spin pairing in, for example, the d_{xy}, d_{xz}, and d_{yz} (t_{2g}) orbitals in octahedral complexes. Thus while most six-coordination compounds of Mn(III) (d^4) and Fe(II) (d^6) contain four unpaired electrons, $[Mn(CN)_6]^{3-}$ contains only two and $[Fe(CN)_6]^{4-}$ is diamagnetic. It may be noted that, in accordance with the prediction of the Kotani theory for strong field ligands (*307*), moments higher than the spin-only values are found for d^4 and d^5 complexes in the first transition series; for example, for $K_3[Mn(CN)_6]$ μ is 3.50 B.M. Attempts are now being made by a number of authors (e.g., *185*, *186*, *414*, *473a*) to use simplified molecular orbital theory to interpret the visible and ultraviolet spectra and other electronic properties of complex cyanides, but the results so far obtained do not justify detailed discussion in a general review. Nor do we discuss the origin and consequences of the large "*trans* effect" of cyanide in the chemistry of platinum; this subject has recently been reviewed elsewhere (*27a*).

In view of these features of interest in cyanide as a ligand it is surprising that few thermochemical and formation constant data are available. What is worse, some of these are of doubtful reliability: some electrical measurements do not relate to reversible systems, and in some cases where heats of reactions have been measured the stoichiometry of the process taking place has not been established beyond doubt. Information on many compounds and ions appears in the following sections; other data are given by Latimer (*319*), but it should be pointed out that, for many of these, ΔG° values have been obtained with the aid of estimated entropies and may therefore be in error by a few kilocalories.

Many cyanide-containing species have been classified as labile (e.g., complexes of Cr(II), Ni(II)) or inert (e.g., complexes of Fe(II), Fe(III), Co(III), Mo(IV)) on the basis of their rates of exchange of CN^- with labeled cyanide in aqueous solution; the classification has been interpreted in terms of electronic configuration and the possibility of forming a seven-coordinated intermediate in the case of octahedral complexes (*489*), or of changes in crystal field stabilization energy involved in formation of intermediates (*27*). Lability, however, can arise by several routes: dissociation, association with an extra cyanide, or aquation may all be the decisive stage. The chemistry of Hg(II) cyanide and its complexes (Section XI,C) provides an interesting example of how species containing different numbers of cyanides can differ widely in lability. Most of the limited kinetic and mechanistic data obtained to date relate to the nonlabile complexes of iron and cobalt, and are discussed in Sections VII,A and VIII,A. Recent developments in the study of fast reactions, and the increasing use of nonaqueous solvents to avoid the complications caused by coordination and hydrogen bonding by water should, however, enable much further progress in this field to be made during the next few years.

II. Scandium, Yttrium, Lanthanum, and Actinium; Lanthanides and Actinides

None of these elements has yet been proved to form a cyanide or a complex cyanide, though very few attempts to make such substances have been described. Brief mention has been made (*413*) of cyanides of lanthanum, cerium, and neodymium as being produced when the trichlorides of these metals are heated with potassium cyanide in the presence of iron at 500°–650°C, but no details of identification or analyses were given. A sparingly soluble complex, to which the formula $K_2[UO_2(CN)_4$

was assigned, has been said (*6*) to be obtained by the action of a large excess of potassium cyanide on a solution of uranyl acetate; again, however, no evidence of identification has been published, and the product may well have been a uranate contaminated with cyanide.

It seems very doubtful whether any cyano compounds of these elements would be stable in the presence of water, but the possibility of obtaining them by heating the metals with mercuric cyanide or a mixture of mercuric cyanide and potassium cyanide, or by the interaction of the triiodides and mercuric cyanide in liquid ammonia, might repay investigation.

III. Titanium, Zirconium, and Hafnium

The only cyano compounds of these elements known at the present time are those of Ti(III). The reduction of these has not been studied. Not surprisingly, titanium(IV) chloride and aqueous potassium cyanide give only the hydrated oxide; their interaction in nonaqueous media and the action of HCN on the tetrachloride have not, however, been studied. In this connection it may be noted that the compound $K_2[Ti(SCN)_6]$ has recently been made from the tetrachloride and potassium thiocyanate in acetonitrile (*464*).

The formation of a dark precipitate when titanium(III) chloride and potassium cyanide interact in aqueous solution was noted many years ago by Grossmann (*203*); the precipitate was insoluble in excess of cyanide solution and was slowly converted into titanium dioxide. Later work suggests this may have been a complex cyanide, but no analytical data were reported.

Two better characterized cyanotitanates(III) have been described. Schläfer and Götz (*462*) showed that titanium(III) bromide reacts with potassium cyanide in liquid ammonia to yield a dark green product of composition $K_5[Ti(CN)_8]$, which has a magnetic moment of 1.74 B.M. at 20°C. They suggested the formulation $K_3[Ti(CN)_6]\cdot 2KCN$ on the grounds that eight-coordinated titanium was unlikely, but this argument has since been vitiated by the preparation of a bis(diarsine) complex of titanium tetrachloride in which the titanium atom is coordinated by four chlorine and four arsenic atoms (*103*). The absorption spectrum of $K_5[Ti(CN)_8]$ in liquid ammonia shows peaks at 22,300 and 18,900 cm^{-1}, the latter of slightly lower intensity, with only a slight minimum between them. This led Schläfer and Götz to conclude that the $[Ti(CN)_6]^{3-}$ ion is not present in the solution since, they said, octahedrally coordinated Ti^{3+}, a d^1 system, should show only one peak; they expressed the view that the species present in ammonia was a mixed complex, e.g., of the type $[Ti(CN)_4(NH_3)_2]^-$. Such complexes are, however, very uncommon, and in fact other titanium(III) complexes show a peak and a shoulder separated by about 3000 cm^{-1}; these include Ti^{3+}(aq), $[TiF_6]^{3-}$, and $[Ti(urea)_6]^{3+}$. The origin of the two peaks appears to lie in a Jahn-Teller splitting of the excited ^2E_g state (*37*, *324*).

The situation is further complicated by the existence of the compound $K_3[Ti(CN)_6]$, prepared as a paramagnetic dark blue powder by Heintz (*224*), by slowly adding titanium(III) chloride solution (1 mole) to potassium cyanide solution (6 moles) with rigid exclusion of air; this substance reacts slowly with oxygen-free water, yielding successively $K_3[Ti(CN)_6]{\cdot}K_2[Ti(CN)_6]$ and titanium dioxide. The relationship between Schläfer and Götz's $K_5[Ti(CN)_8]$ and Heintz's $K_3[Ti(CN)_6]$ is not at all clear, and a comparison of the reflectance spectra of the two solids might be revealing; it would also be useful to know whether Heintz's compound is isomorphous with $K_3[Cr(CN)_6]$, $K_3[Mn(CN)_6]$, $K_3[Fe(CN)_6]$, and $K_3[Co(CN)_6]$. Finally, it may be that the spectrum of Schläfer and Götz's compound indicates the presence of an eight-coordinated species; this is suggested by the similarity between the electron spin resonance spectra of $K_5[Ti(CN)_8]$ and $K_3[Mo(CN)_8]$ (*180*). Other preparative methods [e.g., amalgam reduction of Ti(IV) solutions containing cyanide in nonaqueous solvents, fusing Ti(III) compounds with potassium cyanide] might also be worth exploring; precipitation from aqueous solution is a most uncommon way of making a complex cyanide, and an independent route to $K_3[Ti(CN)_6]$ is desirable.

IV. Vanadium, Niobium, and Tantalum

Vanadium forms a wide range of complex cyanides, though no binary compound has yet been obtained. Hexacyano complexes have been reported for V(II), V(III), and V(IV), though the last of these is not confirmed; in addition, there is a nitrosopentacyanide which appears to be a derivative of V(−I) and a substance of doubtful identity alleged to contain V(V) and cyanide. Very little work on niobium and tantalum cyanides has been reported, but the existence of complexes of $[NbCl_4CN]$ has been demonstrated and there is qualitative evidence which may indicate the existence of a complex of Ta(III).

A. VANADIUM

1. Vanadium(−I)

The orange diamagnetic compound $K_5[V(CN)_5NO]{\cdot}H_2O$ is obtained by the interaction of aqueous hydroxylamine, ammonium vanadate, and potassium cyanide, and precipitation with ethanol (*196*). The infrared absorption spectrum shows bands at 2095 and 1575 cm^{-1}. The latter is one of the lowest stretching frequencies yet found for a coordinated NO^+ ion, but since the corresponding frequencies in the isoelectronic nitrosopentacyano complex ions of Cr(0), Mn(I), and Fe(II) are 1515, 1730, and 1925 cm^{-1}, respectively, formulation of the compound as a NO$^+$ complex of V(−I) has been widely accepted and is adopted here. This conclusion has recently been criticized (*175a*) on spectroscopic grounds, and it has been suggested that in the nitrosylpentacyano species usually formulated as NO$^+$ derivatives of V(−I), Cr(0), Cr(I), and Mn(I), NO$^-$ is indeed present and the metals are in oxidation states higher by two units. How the magnetic properties of the ions can be interpreted on this basis has not, however, been discussed.

2. Vanadium(II)

Reduction of vanadium(III) acetate solution with potassium amalgam, followed by addition of potassium cyanide and ethanol, with rigid exclusion of air, yields brown-yellow crystals of $K_4[V(CN)_6]\cdot 3H_2O$, which is very easily oxidized to a blue vanadium(III) complex (*415*, *416*). The magnetic and spectroscopic properties and the stability with respect to precipitation of vanadium(II) hydroxide have not been reported, but the isomorphism of the compound with potassium ferrocyanide is suggested by the growing of a single crystal of both substances for a determination of the nuclear spin of V^{50} (*19*) and an electron spin resonance study: the g-value is isotropic and very nearly equal to 2, just as in the isoelectronic $[Cr(CN)_6]^{3-}$ ion (*20*). A recent determination of the heat of complexing of V^{++}(aq) by excess of cyanide (*210*) gave $\Delta H = -47$ kcal; it was assumed that under the conditions of this experiment $[V(CN)_6]^{4-}$ was formed, but confirmation of the stoichiometry of the reaction is desirable in all instances of complex cyanide formation. Rather surprisingly, the reduction of $K_4[V(CN)_6]$ (e.g., by alkali metals in ammonia) has not been examined.

3. Vanadium(III)

Locke and Edwards (*328*) reported in 1898 that when a solution of vanadium trichloride in very dilute hydrochloric acid is added to excess of potassium cyanide solution, a deep purple precipitate (not identified) is formed; this dissolved to form a deep wine-colored solution, and addition of ethanol to incipient precipitation, followed by cooling in ice-water, gave some large scarlet crystals for which analyses indicated a formula $K_3[V(CN)_6]$. Since that time, it seems, the preparation has not been repeated. The report that $[V(CN)_6]^{3-}$ exchanges rapidly with labeled cyanide ion (*335*) refers only to a solution in which the stoichiometry of the product was not established. The spectrum in solution has been recorded (ν_{max} of 28,600, 22,200, 18,870, and 14,700 cm^{-1} being found), but the authors (*414*) say that no pure preparation was obtained and that the spectrum may be in part spurious.

The present authors (*93*) have also been unable to repeat Locke and Edwards's work, and find that the product has the composition $K_4[V(CN)_7]\cdot 2H_2O$ and has a magnetic moment of 2.8 B.M. (indicating two unpaired electrons). It shows two bands in the infrared at 3500–3600 and one at 1630 cm^{-1} (due to the water), and a $C\equiv N$ stretching frequency under low resolution at 2100 cm^{-1}. The X-ray powder pattern, which shows no lines due to KCN, is quite unlike that of $K_3[Cr(CN)_6]$, etc. In agreement with the data of previous workers (*414*), the reflectance spectrum shows broad bands at 28,600 and 22,200 cm^{-1}. If a $[V(CN)_7]^{4-}$ ion is present this might have a pentagonal bipyramidal structure related to that suggested for $[Mo(CN)_7]^{3-}$ (*400*), but until the coordination number and configuration are determined by an X-ray method there is little point in discussing the structure further. The existence of the $[V(CN)_6]^{3-}$ ion in solution remains an open question.

4. *Vanadium(IV)*

An unconfirmed report (*538*) states that the interaction of vanadyl acetate and KCN gives a green solution which after several weeks deposits $K_2[V(CN)]_6$. Other authors (*25*, *444*, *467a*) report that vanadyl sulfate solution reacts with alkali metal cyanides to give vanadyl cyanide complexes such as $Na_3[VO(CN)_5]\cdot 2C_6H_{12}N_4\cdot 5H_2O$, isolated from $VO(SO_4)$, $NaHCO_3$, NaCN, and hexamethylenetetramine. At the present time it seems that the existence of V(IV), other than vanadyl, cyanide complexes is very doubtful.

5. *Vanadium(V)*

White crystals of composition $K_4V_2O_7\cdot 4KCN\cdot 14H_2O$ are said to have been obtained during the attempted preparation of a vanadium(IV) complex, but they could not be obtained from potassium vanadate and potassium cyanide under any conditions (*416*). Nothing more is known about this substance.

B. NIOBIUM

Niobium pentachloride reacts with hydrogen cyanide in ether to form red-brown $[NbCl_4CN]\cdot Et_2O$; in hydrogen cyanide, pale yellow $NbCl_5\cdot HCN$ is obtained. The latter compound reacts with triethylamine to form red-brown $[Et_3NH]^+[NbCl_5CN]^-$, a poor conductor in ethanol or nitrobenzene. The action of cyanogen on finely divided niobium suspended in ether, or of hydrogen cyanide on the metal, or of potassium cyanide or silver cyanide on niobium chlorides, yields no cyanide-containing product (*75*).

C. TANTALUM

Ruff and Thomas (*451*) reported without analytical data that "tantalum trichloride solution" gives with potassium cyanide a dark green precipitate soluble in excess; there are no other reports of tantalum cyanides.

V. Chromium, Molybdenum, and Tungsten

This group is the first for which well-defined cyano complexes of all three transition metals are known. In keeping with the general character of the elements, chromium is better known in low oxidation states than the others; Cr(0), Cr(I), Cr(II), and Cr(III) all form cyano or cyanonitroso complexes, and there are some peroxycyano complexes of Cr(IV), though these have been little examined. Mo(0) is represented by a carbonylcyano complex and a nitrosopentacyano compound (this may, however, really contain Mo(II)), but the only purely cyano complexes are those of Mo(III), Mo(IV), and Mo(V). (Reduction of the $Mo(CN)_8^{4-}$ ion, however, has not been investigated.) Tungsten forms carbonylcyano complexes of W(0), but only W(IV) and W(V) are known to form complex cyanides. Hexacyano complexes of Mo(II), W(II), and W(III) have recently been reported (*539a*), but are not satisfactorily characterized. For both metals the stabilization of the (IV) state by cyanide is remarkable, but redox potentials show W(IV) to be more easily oxidized than Mo(IV).

The increase in stability of the high oxidation states is accompanied by an increase in maximum coordination number found in cyano complexes. There is no evidence to indicate that more than six cyanides are ever bonded to chromium, but molybdenum and tungsten in oxidation states (IV) and (V) form octacyano complexes; the Mo(III) compound $K_4[Mo(CN)_7]\cdot 2H_2O$ may contain a seven-coordinated Mo atom, or the anion may contain water as well as cyanide.

A. CHROMIUM

1. *Chromium(0)*

Reduction of $K_3[Cr(CN)_6]$ with potassium in liquid ammonia gives $K_6[Cr(CN)_6]$, a dark green diamagnetic compound which reacts with water to give $K_3[Cr(CN)_6]$, KOH, and H_2, and with carbon monoxide to give $K_3[Cr(CO)_3(CN)_3]$ (*223*). No other properties have been reported.

Three other cyanide-containing compounds of Cr(0) have been described. Electrolytic reduction of $K_3[Cr^{I}(CN)_5NO]$ in a solution of potassium hydroxide and potassium cyanide (*190*) yields blue $K_4[Cr(CN)_5NO]\cdot 2H_2O$, which is very weakly paramagnetic and has a NO^+ stretching frequency at 1515 cm^{-1}. The compounds $Na[Cr(CO)_5CN]$ and $Na_2[Cr(CO)_4(CN)_2]$ are obtained by the action of aqueous sodium cyanide on $Na_2[Cr(CO)_5]$, hydrogen being liberated (*38*); both are diamagnetic.

2. Chromium(I)

The bright green complex $K_3[Cr(CN)_5NO]\cdot H_2O$, obtained from chromium trioxide, potassium cyanide, and hydroxylamine, has a magnetic moment of 1.9 B.M. and a NO^+ stretching frequency at 1645 cm^{-1} (*195*). The optical (*47, 184, 380*) and electron spin resonance (*47, 48, 221, 315, 479*) spectra have been discussed in detail. It has recently been suggested, on the basis of detailed electron spin resonance data, that the ground state is $(d_{xz})^2(d_{z^2})^2(d_{yz})^1$ with the N—O group in the *yz*-plane making an angle of about 45° with the N—M—CN axis (*335a*). Other workers (*171a, 347a, 347b*) have challenged this view and maintain that $(d_{xz})^2(d_{yz})^2(dr_{xy})^1$ is a more satisfactory representation. The kinetics of exchange with labeled cyanide ion at 60°–100°C (*479*) show that substitution in the position axial to the nitroso group is faster than in the equatorial positions, apparently because of greater ease of protonation at the axial position; the participation of $[HCr(CN)_5NO]^{2-}$ in the axial exchange is inferred from the large positive entropy of activation and the effect of acid in increasing the rate.

The formation of a dark brown Cr(I) compound by the action of potassium in ammonia on $K_3[Cr(CN)_6]$ has been mentioned in print (*125*), but no details have been published.

3. Chromium(II)

When chromium(II) acetate is added in small portions to excess of potassium cyanide solution in an inert atmosphere, a red solution is obtained; from this, ethanol precipitates a blue substance which has been generally taken to be $K_4[Cr(CN)_6]\cdot 3H_2O$ (*10, 101, 130*), though the Cr:CN ratio has never been satisfactorily established, and it has never been shown that the compound is isomorphous with $K_4[Fe(CN)_6]\cdot 3H_2O$. Solutions containing the complex are also obtained by addition of potassium cyanide to chromium(II) chloride solution (when a brown precipitate formed at first dissolves in excess of cyanide) or by electrolytic reduction of a solution of $K_3[Cr(CN)_6]$; in the latter case, however, the process does not go to completion and has not yet been used for preparative purposes (*255*).

The solution of the chromium(II) complex is neutral and is stable in the absence of air; acids and platinum bring about reduction of water, and $K_3[Cr(CN)_6]$ results. Both the solution (*258*) and the solid (*10*) have moments of 3.2 B.M. at the ordinary temperature; this suggests that the electronic configuration of the chromium atom is t_{2g}^4 and that the structure of the ion should be very nearly that of a regular octahedron. Exchange with labeled cyanide ion is very fast (*335*).

The standard potential associated with the reduction of the $[Cr(CN)_6]^{3-}$ ion has been determined from polarographic and potentiometric measurements as −1.28 V, or −1.14 V in *M* KCN (*255*); if the Cr(III) and Cr(II) complexes are both hexacyanides, comparison with the value of −0.41 V for the $Cr^{3+}(aq)/Cr^{2+}(aq)$ couple implies that the Cr(III) complex is more stable with respect to dissociation by a factor of 10^{12}. The heat of interaction of chromium(II) sulfate solution and excess of cyanide leads to a value of $\Delta H = -63.2$ kcal for the heat of complexing of $Cr^{2+}(aq)$ (*210*).

Two papers which deal briefly with the oxidation of Cr(II) compounds merit mention here. Chromium(II) perchlorate and ferricyanide give an olive brown precipitate which persists for several days and which is not formed from $[Cr(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$ (*491*); it has been suggested that this is a cyanide-bridged species (*211*) (cf. $[(NC)_5Co(NC)Fe(CN)_5]^{5-}$, Section VIII,A,5). However, oxidation of a solution 0.1 *M* in Cr(II) in 5 *M* CN^- with O_2 or H_2O_2 leads to the formation of $K_3[Cr(CN)_6]$ (isolated in 78% yield) rather than more complex bridged species (*211*). Perhaps rates of competing reactions determine the observed course of events; it is interesting to note that there is a considerable amount of binuclear complex formation in the oxidation of $[Cr(NH_3)_6]^{2+}(aq)$ (*288*).

4. Chromium(III)

The best known complex is the pale yellow $K_3[Cr(CN)_6]$, but several other salts have been described. Chromium trioxide or potassium dichromate is reduced with sulfur dioxide or ethanol, and chromium(III) hydroxide is then precipitated by ammonia and dissolved in acetic acid. The solution is evaporated to remove most of the excess of acid and then added to a boiling solution of potassium cyanide; the anhydrous complex separates on cooling the red solution (*53*, *121*). Potassium hexacyanochromate is very soluble in water, forming a yellow solution.

The $[Cr(CN)_6]^{3-}$ ion is not attacked at an appreciable rate by dilute KOH, ammonia, or sodium carbonate at ordinary temperatures; heating with alkali yields the hydroxide and cyanide ion. Boiling dilute mineral acid, chlorine and bromine water, and carbon monoxide at 130°C also effect decomposition.

Like all other Cr(III) complexes, the hexacyanide has a magnetic moment (3.87 B.M.) which shows the presence of three unpaired electrons (t_{2g}^3), and is a nonlabile complex. Exchange with labeled cyanide ion is very slow, but is accelerated by light, presumably owing to aquation taking place under these conditions (*335*) (see further the discussion of iron complexes in Section VII,A,2). Exchange of radiochromium with the hexaaquo ion is also very slow (*356*).

Solid $K_3[Cr(CN)_6]$ is orthorhombic with lattice constants $a = 13.58$, $b = 10.62$, $c = 8.62$ Å ($N = 4$) [(*183*); see also (*299*)]; it is thus isomorphous with the analogous Mn(III), Fe(III), and Co(III) compounds. Lattice constants for several complexes of formula $M^{II}{}_3[Cr(CN)_6]_2\cdot 6H_2O$, where M^{II} = Mn–Zn, Cd, have been given; all crystallize in the cubic system with $a = 10.1$–10.6 Å and are isostructural with the corresponding complexes of Mn(III), Fe(III), Co(III), Rh(III), and Ir(III) [e.g. (*163–166*)].

Paramagnetic resonance studies of $K_3[Cr(CN)_6]$, diluted with $K_3[Co(CN)_6]$ give a g value closely isotropic at 1.992; the line widths and shapes in different directions suggest there is interaction between neighboring $[Cr(CN)_6]^{3-}$ ions in the lattice of the pure compound (*20*). Bulk magnetic susceptibility measurements, however, provide no evidence of magnetic exchange (*167a*).

The visible and ultraviolet spectrum of the $[Cr(CN)_6]^{3-}$ ion in aqueous solution has been reported (*313*, *458*); Δ is calculated as 26,700 cm^{-1}. The Raman (*123*) and infrared (*85*, *86*, *87*, *231*, *280*) spectra have also been reported. The $[Cr(CN)_6]^{3-}$ ion in aqueous solution exhibits a single C≡N stretching frequency at 2128 cm^{-1} and a M—C stretching frequency at 339 cm^{-1}. It may be noted that although along the series $[Cr(CN)_6]^{3-}$, $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, and $[Co(CN)_6]^{3-}$ the C≡N stretching frequency remains within the range 2110–2130 cm^{-1}, the M—C stretching frequency increases steadily from 339 cm^{-1} to 416 cm^{-1}; it is suggested that the strength of the σ-bond increases owing to the increasing nuclear charge and that of the π-bond increases owing to the increasing number of t_{2g} electrons (*280*). Force constants have been calculated for $[Cr(CN)_6]^{3-}$ (*85*, *87*) but the wrong M—C stretching frequency was employed (*280*).

An aqueous solution of $H_3[Cr(CN)_6]$ is obtained by the action of hydrogen sulfide on a suspension of the silver or lead salt (*289*) or by ion exchange (*422b*). In aqueous solution, even in a stoppered vessel and in the dark, the acid slowly decomposes according to the equation

$$3H^+ + [Cr(CN)_6]^{3-} + 3H_2O = Cr(OH)_3 + 6HCN$$

The equilibrium constant K for this reaction is given by $K_w{}^3/K_f\cdot K_{sp}\cdot K_a{}^6$, where K_w is the dissociation constant of water, K_f the over-all formation constant of the $[Cr(CN)_6]^{3-}$ ion, K_{sp} the solubility product of $Cr(OH)_3$ and K_a the dissociation constant of HCN. If K_{sp} is 10^{-30} (*162*), substitution of the values for K_a and K_w leads to the relationship

$$K_f = 10^{43}/K$$

Since K can hardly be less than 10^{10}, K_f must not be greater than 10^{33} (*422b*).

Evidence for the existence of the ion $Cr(CN)^{2+}(aq)$ (ν_{max} of 19,000 and 25,400 cm^{-1}) has been obtained in a study of the reaction of $[Co(NH_3)_5CN]^{2+}$ and Cr^{2+} ions in acidic perchlorate solution (*154a*).

5. *Chromium(IV)*

Compounds $CrO_4{\cdot}3KCN$ (*525*) and $CrO_4{\cdot}5KCN{\cdot}5H_2O$ (*436*) are obtained by the action of aqueous cyanide on the peroxy compound $CrO_4{\cdot}3NH_3$ and on chromic acid and hydrogen peroxide, respectively; a recent determination of the structure of the former shows the $[Cr(O_2)_2(CN)_3]^{3-}$ ion to be a distorted pentagonal bipyramid with the oxygen atoms of the O_2^{2-} groups and one CN^- roughly in the equatorial plane (*483a*).

B. MOLYBDENUM

1. *Molybdenum(0)*

Colorless diamagnetic complexes $Na_2[Mo(CO)_4(CN)_2]$ and $K_3[Mo(CO)_3(CN)_3]$ have been made by the action of aqueous sodium cyanide on $Na_2[Mo_2(CO)_{10}]$ at 80°C and of potassium cyanide in liquid ammonia on molybdenum hexacarbonyl at 120°C, respectively (*39*).

Nast and Gehring (*385*) obtained a diamagnetic deep violet complex by the action of hydroxylamine on a solution of molybdenum trioxide in alkaline potassium cyanide, and deduced a formula $K_4[Mo^0(CN)_5NO]{\cdot}2H_2O$. Later it was shown that none of the water is lost even at 180°C, and on the basis of a detailed consideration of the infrared absorption spectrum Griffith, Lewis, and Wilkinson revised the formula to $K_4[Mo^{II}(OH)_2(CN)_5NO]$ (*195*). The latest investigation, however, suggests the compound is really anhydrous $K_4[Mo^0(CN)_5NO]$ and that the products investigated previously resulted from partial hydrolysis (*441*).

2. *Molybdenum(III)*

When $K_3[MoCl_6]$ or $K_2[MoCl_5]{\cdot}H_2O$ dissolved in air-free water reacts with cyanide the compound $K_4[Mo(CN)_7]{\cdot}2H_2O$, precipitated by ethanol as black crystals with a greenish tinge, is formed (*540*). The compound is very easily oxidized to $K_4[Mo(CN)_8]$. It has a magnetic moment of 1.75 B.M.; this value, based on a μ/T study, cannot be reconciled with an octahedral configuration, and it seems clear that the anion is $[Mo(CN)_7]^{4-}$ (*323*) or perhaps $[Mo(CN)_7H_2O]^{4-}$ (*189*). It is interesting that attempts to obtain a hexacyano species by the use of less cyanide in the preparation were unsuccessful (*540*).

Another complex of Mo(III), the dark red $K_2[Mo(CN)_5]$, is reported to result from fusion of $K_4[Mo(CN)_8]$ with KCN at 550°; for this μ is 0.6 B.M. in the solid and 0.9 B.M. in solution. The authors (*336*) attribute the low moment to metal-metal bonding, but it is difficult to reconcile this statement with their view, expressed elsewhere in the same paper, that the conductivity of the compound in solution shows three ions to be present.

A deep blue thio complex, $K_3[MoS(CN)_4]\cdot 2H_2O$, is said to be obtained by the prolonged action of hydrogen sulfide on potassium molybdate in aqueous potassium cyanide (*117*).

3. *Molybdenum(IV)*

Several salts containing the $[Mo(CN)_8]^{4-}$ ion are known (*81*), the commonest being $K_4[Mo(CN)_8]\cdot 2H_2O$, for which several preparations from aqueous cyanide and a Mo(III), Mo(IV), or Mo(V) compound have been described (*175, 406, 528*); air acts as an oxidant when Mo(III) compounds are used, and excess of cyanide as a reducing agent when the preparation is from a Mo(V) compound. The best method involves the reduction of molybdenum trioxide to a pyridine-thiocyanate complex of Mo(V) and treatment of this with potassium cyanide; the compound may be purified and obtained as golden yellow diamagnetic orthorhombic crystals by precipitation from aqueous solution by ethanol (*175*). Its aqueous solution is slowly decomposed by light or hot dilute acid, with formation of an aquo complex; the effect of light is reversible (*334*). Strong sulfuric acid effects complete decomposition; concentrated nitric acid gives a brick red product of reported composition $H[MoO_2(CN)_2]\cdot 2H_2O$ (*81*). The acid $H_4[Mo(CN)_8]\cdot 6H_2O$ results from the action of hydrochloric acid on the salt or from ion exchange and crystallization (*222, 447*).

Another series of complexes, red-violet in color, contains the ion $[Mo(CN)_4(OH)_4]^{4-}$, sometimes written as $[MoO_2(CN)_4]^{4-}$ with the remaining water as water of crystallization. The potassium salt, variously reported to contain 8, 6, or 4 H_2O, is obtained if the complex chloride $K_3[MoCl_6]$ or $(NH_4)_2[MoCl_5]$ reacts with 4 gram-moles of potassium cyanide in the presence of air (*81, 447*); the blue solution which is produced is treated with solid potassium hydroxide, when the potassium salt separates out. Excess of cyanide converts it into the octacyanide.

The exchange of labeled cyanide ion with $[Mo(CN)_8]^{4-}$ proceeds slowly at pH 10 in light but is negligible in the dark between pH 4 and 12 (*4*). Exchange of Mo^{99} between $[Mo(CN)_8]^{4-}$ and $[Mo(CN)_8]^{3-}$ is, however, very fast; this is an electron-transfer process between two ions of almost identical size for which the activation energy is negligible (*533*).

The standard electrode potential for the reaction

$$[Mo(CN)_8]^{3-} + e = [Mo(CN)_8]^{4-}$$

has been given as +0.84 V in the presence of potassium chloride of unstated concentration (*106*) or +0.73 V at $\mu = 0$ (25°C) (*303*). Cations affect the value markedly, owing, no doubt, to ion association, but hydrogen ion not more so than lithium, from which it is deduced that $H_4[Mo(CN)_8]$, unlike $H_4[Fe(CN)_6]$, is a strong tetrabasic acid.

Several papers have been published on the structure of the $[Mo(CN)_8]^{4-}$ ion in solid $K_4[Mo(CN)_8]\cdot 2H_2O$ and in aqueous solution. Hoard and Nordsieck (*243*) in an X-ray study found the anion in the solid to be a dodecahedron; although the space group requires the anion to possess only a plane of symmetry and to belong to the point group C_S, the configuration departs little from the symmetry of the point group D_{2d}–$\bar{4}2\,m$, i.e., fourfold axis of rotary inversion with two mutually perpendicular twofold axes and two diagonal planes of symmetry. A wide spread in Mo—C (2.04–2.24 Å) and C—N (1.07–1.27 Å) was found, the average distances being 2.15 and 1.15 Å, respectively. It was pointed out that the repulsive potential energy arising from interactions between ligands would, for the structure described, be smaller than that for a cubic and not much different from that for an antiprismatic structure. Orgel (*403*, *404*) has suggested that for d^1 and d^2 systems the $[Mo(CN)_8]^{4-}$ structure, in which the d_{xy} orbital has much the lowest energy (as shown in Fig. 1), is preferred to the antiprism since it permits the formation of four strong π-bonds. The eight ligands may be divided into two sets of four, one on a flattened and the other on an elongated tetrahedron; the former can form strong π-bonds with the occupied d_{xy} orbital, but the latter can form only weak π-bonds. It is suggested that the latter set bond to hydroxyl ions in $[Mo(CN)_4(OH)_4]^{4-}$. However, a recent redetermination of Mo—C distances in $[Mo(CN)_8]^{4-}$ shows that they

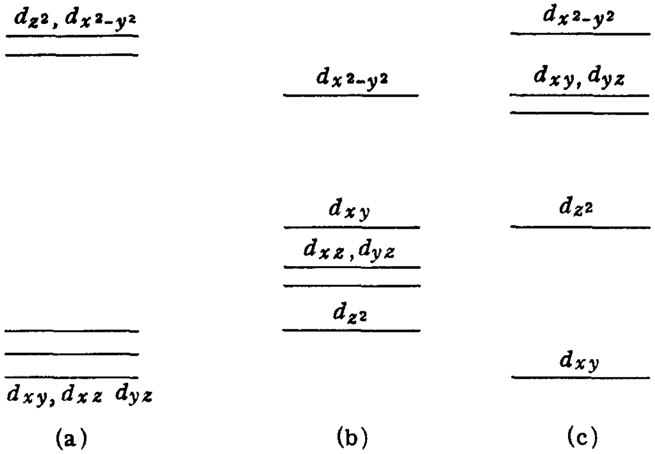


FIG. 1. Energy levels for (a) octahedral coordination, (b) square planar coordination, (c) the $[Mo(CN)_8]^{4-}$ structure (*422c*).

vary very little, so the matter cannot be as simple as Orgel's treatment suggests (*216*, *244*).

The Raman spectrum of $K_4[Mo(CN)_8]$ in aqueous solution (*480*), considered in conjunction with early work on the infrared spectrum of the solid (*65*), has been held to show that in solution the ion is an Archimedean antiprism (symmetry D_{4d}), and it has been stated (*481*) that later results for the infrared spectrum of the solid (*231*), are compatible with such a configuration in the solid state, too. The latest investigation, however, indicates at least six $C{\equiv}N$ stretching frequencies in the infrared spectrum of the solid and confirms that the solution spectrum consists of a single broad band; it is now concluded (*292a*) that neither in the solid state nor in solution is there any evidence to suggest the structure is appreciably different from the dodecahedral arrangement found in the X-ray study of the crystal (*216*, *243*).

It has been reported (*70*) that the infrared spectra of $[Mo(CN)_8]^{4-}$, $[Mo(CN)_8]^{3-}$, $[W(CN)_8]^{4-}$, and $[W(CN)_8]^{3-}$ in the solid state in the $C{\equiv}N$ stretching region are almost identical; it should, however, be noted that the spectrum given for $K_4[Mo(CN)_8]{\cdot}2H_2O$ is significantly different from that in the latest communication (*292a*).

The position concerning the visible and ultraviolet absorption spectrum of the $[Mo(CN)_8]^{4-}$ ion is complicated by the doubts about the configuration. The first results and their interpretation in terms of D_{2d} symmetry (*180*) have been criticized on grounds of lack of spectral resolution, and an interpretation of a redetermined spectrum in terms of the C_S configuration has recently been offered (*414*).

4. Molybdenum(V)

Powerful oxidizing agents (e.g., MnO_4^-, Ce^{IV}) or electrolytic oxidation convert $[Mo(CN)_8]^{4-}$ into $[Mo(CN)_8]^{3-}$; this ion may be separated as the sparingly soluble silver salt and converted into the potassium salt by the action of potassium chloride. The octacyanomolybdates(V) are yellow, very sensitive to light (turning red-brown), and easily reduced (e.g., by iodide or sulfur dioxide); ferrous salts give an intense blue coloration (*81*, *107*, *402*).

The potassium salt has a magnetic moment of 1.66 B.M. (*424*). Electron spin resonance spectra of the ion in solution as normally observed and of the ion enriched in $C^{13}N^-$ indicate that the spin density is 0.96 at the molybdenum nucleus, 0.088 at each carbon, and less than 0.006 at each nitrogen (*520*). The g value in solution is 1.990; in the solid state the spectra of the potassium and silver salts both have a single sharp line at 1.993 (*180*). There is some conflict about the optical spectrum; details are given in reference (*414*).

The acid $H_3[Mo(CN)_8]\cdot 3H_2O$ has been isolated by concentrating the yellow solution obtained from $Ag_3[Mo(CN)_8]$ and HCl *in vacuo* in the dark over KOH and P_2O_5 (*81*).

A blue compound obtained by addition of ethanol to a solution of $K_4[Mo(CN)_4(OH)_4]$, and previously (*81*) formulated as $K_3[Mo^{IV}(CN)_4(OH)_3H_2O]\cdot 2H_2O$, has recently been shown to be paramagnetic ($\mu = 1.9$ B.M.) and to have an infrared absorption spectrum like that of the parent compound; it is therefore suggested that it contains the ion $[Mo^{V}(CN)_4(OH)_4]^{3-}$, though the formula $[Mo^{III}O_2(CN)_4(H_2O)_2]^{3-}$ is also possible (*195*). The redox processes involved in the reaction are very obscure and further investigation is badly needed.

C. TUNGSTEN

1. *Tungsten(0)*

Aqueous sodium cyanide and the carbonyl complex $Na_2[W_2(CO)_{10}]$ yield $Na[W^0(CO)_5CN]\cdot H_2O$ and $Na_2[W^0(CO)_4(CN)_2]$; tungsten hexacarbonyl reacts with potassium cyanide in ammonia yielding $K_3[W(CO)_3(CN)_3]$. All the compounds are diamagnetic and colorless (*39*).

2. *Tungsten(IV)*

Complexes of this oxidation state are obtained by the action of cyanide on, for example, $K_3[W_2Cl_9]$ in the presence of air (*225*) or $(NH_4)_2[WOCl_5]$, which disproportionates, giving $[W(CN)_8]^{4-}$ and tungstate (*541*). The silver and thallous salts are sparingly soluble.

The orange diamagnetic potassium salt, $K_4[W(CN)_8]\cdot 2H_2O$, is isomorphous with the molybdenum compound (*17*); it is very soluble in water, and the solution, which is neutral, is stable to acid and alkali, though in alkaline solution in sunlight aquation takes place (*17*).

The standard potential for the change

$$[W(CN)_8]^{3-} + e = [W(CN)_8]^{4-}$$

is +0.57 V in KCl solution (*106*), or +0.46 V at infinite dilution (*17*); Cl_2, MnO_4^-, and Ce^{IV} effect oxidation of the W(IV) complex. Electron exchange between the W(IV) and W(V) species is very fast (*17*, *182*, *521*), but the exchange of labeled cyanide with $[W(CN)_8^{4-}$ is very slow, the rate being determined by the light intensity (*181*).

The discussion of the structure and of the optical spectrum of the $[W(CN)_8]^{4-}$ ion (*180*, *414*) has followed the same lines as those for the molybdenum-containing species.

The yellow-brown hydroxycyanide complex $K_4[W(CN)_4(OH)_4]\cdot 4H_2O$ is made by the action of aqueous KCN on W_2O_5 in the presence of KOH; ferricyanide oxidizes it to tungstate (*359*).

3. *Tungsten(V)*

Pale yellow $K_3[W(CN)_8]\cdot 2H_2O$ is obtained by oxidation of the tungsten(IV) compound with acid permanganate, precipitation of the silver salt, and treatment with potassium chloride (*181, 402*). Iodide and hydrogen peroxide reduce it to the W(IV) complex, and decomposition to this species also takes place under the influence of light.

The magnetic moment of the potassium salt is 1.61 B.M. (*17*). In the solid state the electron spin resonance spectrum consists of a single resonance with $g = 1.98$; in aqueous solution, three lines with center $g = 1.972$ are observed (*180, 521*). The optical spectrum (*180, 414*) is like that of the Mo(V) complex.

VI. Manganese, Technetium, and Rhenium

As in the preceding group, the stability of cyanide complexes of the elements in higher oxidation states increases with increase in atomic number. Well-defined derivatives of Mn(I), Mn(II), and Mn(III) exist, and there is some evidence for the existence of cyanide complexes of Mn(0) and Mn(IV). No great significance should be attached to the fact that at the present time the only reported cyanide complexes of technetium are those of Tc(I) and Tc(IV), since little work on derivatives of this element has been done. For rhenium, cyano derivatives of everything from Re(I) to Re(VI) have been characterized, and complexes of Re(0) have also been claimed to exist.

The highest coordination number established for manganese is six, but eight-coordinated rhenium is found in the $[Re^{V}(CN)_8]^{3-}$ ion, and probably also in $[Re^{III}(CN)_7NO]^{3-}$ and $[Re^{VI}(CN)_8]^{2-}$.

A. MANGANESE

1. *Manganese(0)*

The reduction of $K_3[Mn(CN)_6]$ with potassium in liquid ammonia gives a yellow product of approximate composition $K_5[Mn(CN)_6]\cdot K_6[Mn(CN)_6]\cdot 2NH_3$, which reduces 1.5 Ag^+ per Mn and has a magnetic moment of 1.25 B.M. (*102*). These results are certainly compatible with the presence of 30–40% of a manganese(0) compound containing a single unpaired electron, but more detailed examination is desirable before the oxidation state is beyond doubt.

2. *Manganese(I)*

Complex cyanides of this oxidation state are obtained by reduction of the manganese(II) compounds with Devarda's alloy (*340*) or, better, electrolytically (*206, 498*) or with metal amalgams (*104, 499*). The only well-defined compounds are the very soluble sodium and sparingly soluble potassium salts of formula $M^{I}_{5}[Mn(CN)_6]$. $K_2[Mn(CN)_3]$ (*340*) and $K_3[Mn(CN)_4]$ (*206*) have also been reported but have not been satisfactorily characterized.

The cyanomanganates(I) are colorless and, when pure, diamagnetic (*498*). They are oxidized on exposure to air, and the soluble sodium salt liberates hydrogen from hot water. In 1.5 *M* NaCN the potential of the system

$$[Mn(CN)_6]^{4-} + e = [Mn(CN)_6]^{5-}$$

is −1.06 V (*498*). Conflicting values for the lattice constants [a = 16.35, c = 13.11 Å (*498*); a = 11.89 Å (*466*)] and densities [2.01 (*236*) and 1.77 (*466*)] of the potassium salt have been reported; it may be that the second set of values refers to a hydrate (see Section VI,C,2). The infrared spectrum of $K_5[Mn(CN)_6]$ is reported to show a single C≡N stretching frequency at 2048 cm^{-1} (*85*); whereas for other triads of transition metals this frequency in analogous compounds varies little, the value is notably higher than those for $[Tc(CN)_6]^{5-}$ and $[Re(CN)_6]^{5-}$. The values for $[Mn(CN)_6]^{4-}$ and $[Mn(CN)_6]^{3-}$ are 2060 and 2125 cm^{-1}, respectively (*85*).

A purple nitrosopentacyanide, $K_3[Mn(CN)_5NO]$, is made from $K_3[Mn(CN)_6]$, KCN, and hydroxylamine (*113*, *238*); the presence of NO^+ (and hence Mn^I) is indicated by the N—O stretching frequency at 1730 cm^{-1} and the diamagnetism of the complex (*113*, *238*, *355*). $E°$ for the system

$$[Mn(CN)_5NO]^{2-} + e = [Mn(CN)_5NO]^{3-}$$

has been given as +0.6 V (*262a*), a value no less than 1.7 V different from that for the hexacyano system.

3. Manganese(II)

Manganese cyanide, $Mn(CN)_2$, is not known, though the preparation of a product of approximate composition $Hg(CN)_2 \cdot Mn(CN)_2 \cdot 2\text{–}3NH_3$ from manganese metal and mercuric cyanide in liquid ammonia has been reported (*46*).

When manganese chloride reacts with a limited quantity of potassium cyanide solution, the rose precipitate which is first formed becomes green and is very insoluble; the same green product is also obtained by decomposition of the complex $K_4[Mn(CN)_6]$ in solution (*130*). The composition of the green product corresponds to the formula $KMn(CN)_3$, but the insolubility and the magnetic moment of 4.22 B.M. (*179*), which is intermediate between the values for five unpaired spins (as in most Mn^{2+} compounds) and one unpaired spin (as in $[Mn(CN)_6]^{4-}$), suggest a structural similarity with the white insoluble $K_2Fe[Fe(CN)_6]$ (*522*). A comparison of the X-ray powder diagrams of the two substances would be very instructive.

The action of excess of potassium cyanide solution on manganese acetate or carbonate in an inert atmosphere gives a yellow solution from which blue-violet $K_4[Mn(CN)_6]\cdot 3H_2O$ crystallizes; the more soluble sodium salt can be made similarly. The complex is soluble without decomposition only in potassium cyanide solution of concentration not less than 1.5 *M*; at lower concentrations $KMn(CN)_3$ is deposited. Anhydrous $K_4[Mn(CN)_6]$ can be obtained from the trihydrate by dehydration over sulfuric acid (*101*, *206*, *357*); presumably these compounds are isomorphous with anhydrous and hydrated potassium ferrocyanides, but this has not been established.

The magnetic moment of $K_4[Mn(CN)_6]\cdot 3H_2O$ corresponds to the presence of a single unpaired electron; the latest value, based on a μ/T study, is 2.18 B.M. (*167*); the electron delocalization factor k (where $1 - k$ is the fraction of time the t_{2g} electrons spend on the ligands) is found to be 0.75, in good agreement with the value from electron spin resonance data (*20*).

Few reactions of the $[Mn(CN)_6]^{4-}$ ion have been studied, doubtless owing to its instability with respect to precipitation of $KMn(CN)_3$ and oxidation. Exchange with labeled cyanide takes place at a measurable rate, $t_{1/2}$ at pH 11.8 being about 5 minutes; the rate is not increased on exposure to light (*335*). Although much more labile than the isolectronic ion $[Fe(CN)_6]^{3-}$, therefore, $[Mn(CN)_6]^{4-}$ is nevertheless a nonlabile complex in the Taube sense. Some carbon monoxide is absorbed by the solution, but not enough to correspond to the complete formation of a carbonyl complex (*376*).

Polarographic evidence appears to suggest that an ion other than $[Mn(CN)_6]^{4-}$ can exist in aqueous solution (*292*), but it is not clear what this species is. It has also been reported that a new complex of approximate composition $K_{1.5}[Mn(CN)_{3.7}]$ is obtained by heating $K_3[Mn(CN)_6]$ with a large excess of KCN at 650° (*336*); the X-ray powder photograph of the dark green product, however, is said to be "very like that of $KMn(CN)_3$" and to the present authors it seems highly probable that the product is indeed only the impure tricyano complex.

A yellow nitrosopentacyano complex, $K_2[Mn(CN)_5NO]$, is obtained by oxidation of the corresponding Mn(I) complex with concentrated HNO_3; it has a magnetic moment of 1.73 B.M. and a NO^+ stretching frequency at 1885 cm^{-1} (*113*, *347a*). Contrary to a previous suggestion (*335a*, *335b*), electron spin resonance studies show that the unpaired electron on the Mn does interact with the N^{14} of the NO group (*171a*, *347a*, *347b*).

4. *Manganese(III)*

Potassium hexacyanomanganate(III), the most important salt of this series, may be made by oxidation of the manganese(II) salt (*5*, *357*), but for preparative purposes the standard route is by the action of aqueous potassium cyanide on manganese(III) orthophosphate, prefaced by oxidation of a manganese(II) salt with nitric acid in the presence of phosphoric acid (*330*). Other good methods include the action of potassium cyanide on the complex fluoride $K_2MnF_5{\cdot}H_2O$ (*406*), and the oxidation of freshly precipitated manganese carbonate with hydrogen peroxide in the presence of potassium cyanide (*80*). The dark red compound is best recrystallized from a solution of potassium cyanide, since some hydrolysis takes place in aqueous solution.

Potassium cyanomanganate(III) is isomorphous with the ferricyanide, the lattice constants being $a = 13.59$, $b = 10.62$, $c = 8.52$ Å [(*183*) but see (*299*)]. The magnetic moment, based on a μ/T study, is 3.50 B.M. at room temperature (*110*) (earlier values are slightly lower). $[Mn(CN)_6]^{3-}$ is thus one of the very few spin-paired Mn(III) complexes, the electronic configuration being $t_{2g}{}^4$; in this ion, therefore, the Jahn-Teller distortion, which is so prominent a feature of the structures of six-coordinated Mn(III) fluorides, should at most be very small.

Exchange of cyanide between the complex ion and aqueous cyanide is very fast (*335*); pH and light do not affect the rate, which depends on the first power of the concentration of complex and is independent of the concentration of cyanide. From consideration of the values for the rate constant and activation energy it has been suggested (*5*) that exchange proceeds via formation of the anion $[Mn(CN)_6H_2O]^{3-}$, which then loses cyanide, rather than of $[Mn(CN)_5]^{2-}$.

Bands in the visible and ultraviolet at 21,000, 31,100, and 36,700 cm^{-1} were found in solution (*456*) and have recently been observed in the diffuse reflectance spectrum (*220*); Δ has not yet been evaluated. In $[Mn(CN)_6]^{3-}$ in aqueous solution the C≡N and Mn—C stretching frequencies are at 2112 and 361 cm^{-1}, respectively (*280*); values in solid $K_3[Mn(CN)_6]$ are very similar (*231*).

5. *The Standard Potential of the $[Mn(CN)_6]^{3-}/[Mn(CN)_6]^{4-}$ System and Related Quantities*

The standard potential of the system

$$[Mn(CN)_6]^{3-} + e = [Mn(CN)_6]^{4-}$$

is −0.24 V (*206*, *498*), and the $[Mn(CN)_6]^{4-}$ ion is thus easily oxidized. Comparison with the value of +1.5 V for

$$Mn^{3+}(aq) + e = Mn^{2+}(aq)$$

shows that Mn(III) must be stabilized by complexing to a much greater extent than Mn(II): the ratio of the over-all formation constants is, in fact, 10^{29}:1.

For the reaction

$$[\mathrm{Mn(CN)_6}]^{3-} + 3\mathrm{H_2O} = 3\mathrm{CN^-} + 3\mathrm{HCN} + \mathrm{Mn(OH)_3}$$

K_h, the hydrolysis constant, has been determined [by removal and estimation of the $\mathrm{Mn(OH)_3}$ in equilibrium with a solution of the cyanomanganate] as approximately 10^{-10} at 18°C (*357*); because of the number of particles on the right-hand side of the equation, this corresponds to a degree of hydrolysis of about 1% in 1 *M* solution.

The relationship between K_{diss} for the complex ion, K_h, K_w, K_a for HCN, and K_{sp} for $\mathrm{Mn(OH)_3}$ is expressed by the equation

$$K_{diss} = K_h K_{sp} K_a^3/K_w^3$$

whence $K_{diss}/K_{sp} = 2 \times 10^4$. The $[\mathrm{Mn(CN)_6}]^{3-}$ ion is thus thermodynamically unstable with respect to reaction with the hydroxyl ion and formation of $\mathrm{Mn(OH)_3}$. Despite this, it can be made by interaction of Mn(III) and $\mathrm{CN^-}$ if $[\mathrm{CN^-}]$ is high.

There is, unfortunately, no reliable value for K_{sp} from which K_{diss} can be evaluated. Latimer (*319*), from the National Bureau of Standards (Circular 500) value for the heat of formation of $\mathrm{Mn(OH)_3}$ and his own estimates for the entropy of $\mathrm{Mn(OH)_3}$ and the free energy of formation of $\mathrm{Mn^{3+}(aq)}$, obtains a value $K_{sp} = 10^{-36}$, leading to $K_{diss} = 10^{-31}$. However, this value leads in turn to $K_{diss} = 10^{-2}$ for $[\mathrm{Mn(CN)_6}]^{4-}$; this is clearly absurd, and the most likely source of error lies in K_{sp}. This should probably be very much smaller than 10^{-36}, leading to K_{diss} for $[\mathrm{Mn(CN)_6}]^{3-}$ being far less than 10^{-31}.

When we compare the potentials for the systems

$$\begin{array}{rl}
\mathrm{Mn^{3+}(aq)} + e = \mathrm{Mn^{2+}(aq)} & E^\circ = +1.5\ \mathrm{V} \\
[\mathrm{Mn(CN)_6}]^{3-} + e = [\mathrm{Mn(CN)_6}]^{4-} & E^\circ = -0.24\ \mathrm{V} \\
\mathrm{Fe^{3+}(aq)} + e = \mathrm{Fe^{2+}(aq)} & E^\circ = +0.77\ \mathrm{V} \\
[\mathrm{Fe(CN)_6}]^{3-} + e = [\mathrm{Fe(CN)_6}]^{4-} & E^\circ = +0.36\ \mathrm{V}
\end{array}$$

we see that Mn(III) is stabilized relative to Mn(II) by cyanide complexing much more than Fe(III) is stabilized relative to Fe(II). Stabilizations of the M(III) state also occur for the corresponding Cr and Co systems, though here the situation is complicated because Co(II) does not form a hexacyano species in aqueous solution (see Section VIII,A) and it has not yet been established that Cr(II) does so. Nevertheless, it seems likely that the stabilizations of the M(III) state—in terms of hexacyano species—are in the order

$$\mathrm{Fe} < \mathrm{Cr} < \mathrm{Mn} < \mathrm{Co}$$

and are of such magnitudes that the well-known stability order of M(III) relative to M(II) for water and other weak field ligands

$$\mathrm{Co} < \mathrm{Mn} < \mathrm{Fe} < \mathrm{Cr}$$

—which can be rigorously correlated with the variation in the third ionization potential (*271, 397*)—becomes when cyanide is ligand

$$\mathrm{Fe} < \mathrm{Mn} < \mathrm{Co} < \mathrm{Cr}$$

It is clearly then of considerable interest to try to relate these varying stabilizations of the M(III) state to variations in other energy terms.

When water is replaced by cyanide in a M(III)/M(II) couple many energetic factors are involved, but only variations in ligand field stabilization energies might be expected to lead to such widely differing stabilizations of the M(III) state, variations in other energetic factors involved being expected to be relatively small; the fact that cyanide is an ion and not a molecule, for example, should stabilize the M(III) state to an approximately constant extent.

We have attempted to ascertain whether there is any experimental justification for this hypothesis by computing the appropriate ligand field stabilization energies. These latter can be calculated from values of $10\,Dq$ together with, in the case of the spin-paired complex cyanides, the Racah parameters B and C from which the pairing energy Π can be calculated. Hence the change in ligand field stabilization energy of an aquated ion containing x t_{2g} and y e_g electrons, where for example $x + y \ngtr 6$, on conversion into the corresponding low-spin cyanide ion, is

$$\tfrac{2}{5}(x + y)(10\,Dq^{\mathrm{CN}}) - y\Pi - (\tfrac{2}{5}x - \tfrac{3}{5}y)(10\,Dq^{\mathrm{aq}})$$

We have thus been able to predict the correct order of stabilizations of the M(III) state, though the absolute magnitudes of differences obtained are sometimes in considerable error, e.g., the calculated difference in stabilization of the M(III) states for Mn and Fe is about 25,000 cm^{-1} and the experimental figure about 11,000 cm^{-1}.

It should be realized, however, that any such calculations are highly approximate. For example, in computing the ligand field stabilization energies, the effect of the change in the metal-ligand distance, due to the redistribution of *d* electrons, has been neglected. In addition, the accuracy of the values of $10\,Dq$, B, and C used (Table I) is uncertain. The majority of these have been derived from absorption spectra and the model used (irrespective of any uncertainties in assignments, e.g., for $[\mathrm{Mn(CN)_6}]^{4-}$) is only approximate; moreover, values for $[\mathrm{Cr(CN)_6}]^{3-}$, $[\mathrm{Co(CN)_6}]^{3-}$, and $[\mathrm{Mn(CN)_6}]^{3-}$ have had to be estimated. Nevertheless, these calculations, although tentative and subject to many approximations, give some indica-

TABLE I

LIGAND FIELD PARAMETERS FOR AQUO AND CYANO COMPLEX IONS

		10 Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})	Π[a] (cm^{-1})	Reference	
Cr(II)	H_2O	14,000	—	—	—	(*251, 286*)	[c]
	CN^-	(25,000)	(500)	(3,000)	—	—	[b]
Cr(III)	H_2O	17,400	—	—	—	(*286*)	—
	CN^-	26,700	—	—	—	(*313*)	—
Mn(II)	CN^-	24,400	950	3,300	22,200	(*93*)	—
Mn(III)	H_2O	21,000	—	—	—	(*21, 219*)	[c]
	CN^-	(28,000)	(700)	(3,100)	(20,000)	—	[b]
Fe(II)	H_2O	9,400	—	—	—	—	[d]
	CN^-	34,700	380	3,650	15,600	—	[e]
Fe(III)	CN^-	35,000	720	3,285	21,900	(*379*)	—
Co(II)	H_2O	9,300	—	—	—	(*251, 286*)	—
	CN^-	(30,000)	(800)	(4,000)	—	—	[b]
Co(III)	H_2O	20,800	—	—	—	(*271*)	—
	CN^-	35,500	—	—	—	—	[e]

[a] Π = mean pairing energy per electron transferred from e_g to t_{2g}. $\Pi(d^4) = 6B + 5C$; $\Pi(d^5) = 7\frac{1}{2}B + 5C$; $\Pi(d^6) = 2\frac{1}{2}B + 4C$; $\Pi(d^7) = 4B + 4C$ (*188*).

[b] Estimated values. Because very few absorption spectra of any of these ions have been interpreted these estimates must be regarded as uncertain.

[c] Jahn-Teller distorted ground states.

[d] 10 Dq taken as mean of two observed absorption bands (*112*).

[e] Calculated from the data of Gray and Beach (*186*).

tion of the importance of spin pairing in determining the thermodynamic properties of complex cyanides.

6. *Manganese(IV)*

The sole representative of this oxidation state, the compound $K_4[Mn(CN)_8]$, was reported (*537*) to be formed as red prisms during the interaction of permanganate and cyanide. Goldenberg (*179*) could not repeat the preparation. Since, however, there are many quite stable complexes of Mn(IV), the action of cyanide on the fluoride $K_2[MnF_6]$, which can be made in aqueous media, and electrolytic oxidation of $K_3[Mn(CN)_6]$ in aqueous KCN might be worth examination.

B. TECHNETIUM

1. *Technetium(I)*

Reduction of pertechnate or the Tc(IV) complex described below with potassium amalgam in the presence of cyanide yields the sparingly soluble green compound $K_5[Tc(CN)_6]\cdot 3H_2O$, the formula of which is based on comparison of its X-ray powder diagram (indicating a cubic unit cell with $a = 12.10$ Å) and visible and infrared absorption spectra with those of the analogous rhenium compound (*230*, *466*).

2. Technetium(IV)

The formation of this oxidation state by reduction of pertechnate in aqueous cyanide was first shown polarographically (*108*). A solid compound was later isolated from the solution of technetium dioxide in aqueous cyanide by crystallization as the thallium salt. The infrared spectrum showed the presence of H_2O or OH, and from analytical data the formula was found to be $Tl_3[Tc(OH)_3(CN)_4]$ or perhaps $Tl_3[TcO(OH)(CN)_4]$ (*230*, *465*). The magnetic moment, which would have helped to establish that no change of oxidation state had occurred, was unfortunately not determined; this is the more the pity in that it is known that ReO_2 when treated similarly yields a complex of Re(V).

C. RHENIUM

1. Rhenium(0)

When the complex chloride $K_2[ReCl_6]$ is shaken with cyanide and potassium amalgam for a long period with extreme precautions to exclude air, a yellow precipitate shown by oxidimetry to contain Re(0), and having a K:Re ratio of approximately 6:1, is formed. This may be $K_6[Re(CN)_6]$, but adequate analytical data have not been given to support this formula (*104*).

2. Rhenium(I)

Potassium amalgam reduction of the hexachlororhenate(IV) ion in the presence of cyanide results in the precipitation of the complex $K_5[Re(CN)_6]\cdot 3H_2O$, shown by dichromate oxidation to contain Re(I) [(*104*) see also (*352*)]. Two determinations in agreement show the compound has a cubic unit cell with $a = 12.03$ Å (*104*, *466*), a value between those of the analogous Mn(I) and Tc(I) compounds, for which the cell side is 11.89 and 12.11 Å, respectively. The visible and ultraviolet spectra show maxima at approximately 14,300 and 29,400 cm^{-1}. The infrared spectrum has also been reported (*466*): $\nu(C{\equiv}N)$ is at 1940 cm^{-1}, and the presence of water is indicated.

The same compound (though there is no mention of water of crystallization) is reported to result from borohydride reduction of $K_4[ReO_2(CN)_4]$ plus KCl in the presence of cyanide (*511*). A colorless carbonyl cyanide complex, probably $K[Re(CO)_4(CN)_2]$, is said to be formed from the carbonyl halide $[Re(CO)_5Cl]$ and potassium cyanide in methanol (*240*).

3. Rhenium(II)

When the solution containing Re(I) obtained from sodium perrhenate, sodium amalgam, and cyanide is acidified and oxidized by air, addition of alcohol precipitates brown hygroscopic $Na_3[Re^{II}(CN)_5H_2O]$, which may be converted into the potassium salt via the acid (obtained by ion exchange) (*469*). The potassium salt, to which the formula $K_4[Re(CN)_6]\cdot 3H_2O$ has been assigned (though no analytical data have been given), may be obtained by refluxing the aquo complex with excess of cyanide (*468*). It should be isomorphous with $K_4[Fe(CN)_6]\cdot 3H_2O$, but whether this is so has not been investigated. The electronic absorption spectrum of an aqueous solution has been recorded and interpreted (*22a*). Treatment of the aquo complex with aqueous ammonia and sodium hydroxide is reported to yield $Na_3[Re(CN)_5NH_3]$ and $Na_5[Re(CN)_5O]\cdot 3H_2O$ (*469a*).

4. Rhenium(III)

Rhenium trichloride treated with aqueous potassium cyanide turns successively red, blue, and green, and addition of alkali then precipitates impure $K_3[Re(CN)_6]$. A purer compound of rhenium(III) is obtained by borohydride reduction of $K_3[Re(CN)_8]$ and precipitation of green $[Co(NH_3)_6][Re(CN)_6]$, for which $\mu = 2.6$ B.M. (*109*). A deep blue hydroxycyanide, $K_3[Re(CN)_3(OH)_3]$, is obtained by borohydride reduction of $K_4[Re^{IV}O_2(CN)_4]$ (*511*). The structures of these substances have not been examined, but the moment of the complex cyanide is compatible with a spin-paired ($t_{2g}{}^4$) octahedral complex.

A mauve nitrosocyanide of suggested composition $Ag_3[Re(CN)_7NO]$, obtained by precipitation from the red solution which results when $K_3[Re(CN)_8]$ is warmed with 2 *M* nitric acid, is diamagnetic and has a NO^+ stretching frequency at 1875 cm^{-1}; it has been described (*109*) as a Re(IV) compound, but this is obviously an error.

5. Rhenium(IV)

Two compounds have been reported briefly: $K_3[ReO(CN)_4(OH)]$ from ReO_2 and aqueous KCN (*502*), and gray $K_4[ReO_2(CN)_4]$ from $K_2[ReCl_6]$ and KCN, followed by addition of ethanol (*511*). Their properties have not been described.

6. Rhenium(V)

If potassium iodorhenate, $K_2[ReI_6]$, is heated with cyanide in dry methanol in the presence of air, brown diamagnetic $K_3[Re(CN)_8]$, readily hydrolyzed to $K_3[ReO_2(CN)_4]$, is obtained. The infrared spectrum in solution shows one cyanide stretching frequency at 2100 cm^{-1}; in the solid state, three (at 2140, 2100, and 2050 cm^{-1}) are observed (*109, 327*). The visible and ultraviolet absorption spectra have been discussed (*414*), but later work (*327*, *511*) suggests decomposition occurred.

Orange diamagnetic $K_3[ReO_2(CN)_4]$ is made from potassium hexachlororhenate(IV), potassium cyanide, and hydrogen peroxide, or, together with a pink nitride complex $K_2[ReN(CN)_4(H_2O)]$, by reduction of perrhenate with cyanide and hydrazine hydrate (*297*, *327*, *371*). The formulation of the anion as $[Re(OH)_4(CN)_4]^{3-}$ appears to be excluded for the potassium salt, since analysis showed the presence of only 0.2% H, and the same product may be made in methanolic solution.

In solution, the $[Re^{VI}(CN)_8]^{2-}$ ion (see below) decays rapidly; tetraphenylarsonium chloride then precipitates a diamagnetic purple substance. This was formerly suggested to be $[Ph_4As]_2[Re^{VII}(CN)_8(OH)]$, but re-examination indicates the formula $[Ph_4As]_2[Re^{V}O(OH)(CN)_4]$ (*109*, *327*).

7. *Rhenium(VI)*

When $K_3[Re(CN)_8]$ is treated with acid in the presence of air a purple solution is obtained, and from it $[Co(NH_3)_6]_2[Re(CN)_8]_3$ and $[Ph_4As]_2[Re(CN)_8]$ may be isolated if the cations are introduced at once. Both are purple and paramagnetic ($\mu = 1.9$ B.M.) (*109*, *327*). An unsuccessful attempt to obtain an electronic absorption spectrum has been described (*414*).

VII. Iron, Ruthenium, and Osmium

In this group the dependence of stability of cyanide complexes on atomic number is markedly different from that in the previous ones, and the highest coordination number yet observed is six: in low oxidation states there are too many electrons for high coordination numbers to be possible without the use of antibonding orbitals; high oxidation states oxidize cyanide (even ferric hydroxide suffices for this purpose). Derivatives of Fe(II) and Fe(III) are well known; no solid complex of Ru(III) or Os(III) has yet been isolated, however, and the cyanide chemistry of these elements at the present time is, with the exception of some work on oxycyanide complexes of Os(VI), largely restricted to hexacyano complexes of the metals in the +(II) state and indications of the existence of the +(III) state in solution. This is, no doubt, largely due to incomplete investigation; the $[Ru(CN)_6]^{4-}$ and $[Os(CN)_6]^{4-}$ ions, like $[Fe(CN)_6]^{4-}$, are kinetically inert, and large numbers of substituted derivatives analogous to those for Fe(II) would be expected to exist. There is, in fact, a ruthenium analog of the nitroprusside ion, $[Fe(CN)_5NO]^{2-}$, a NO^+ derivative of Fe(II), but few pentacyanoruthenium(II) species are known, and in the case of osmium no attempt appears to have been made to isolate even the nitrosopentacyanide. Ferro- and ferricyanide are the only pair of complex cyanide ions of the same metal in different oxidation states for which considerable thermodynamic data are available, and this material is dealt with in some detail in Section VII,A,4. This is followed by surveys of compounds containing iron in more than one oxidation state (of which the best known example is Prussian blue) and a limited number of substituted cyanides.

A. Iron

1. *Iron in Oxidation State < (II)*

An ion believed to be $[Fe(CN)_5NO]^{3-}$ (though there is no proof of the coordination number) can be obtained by electrolytic reduction or photoirradiation of nitroprusside in dimethyl formamide or by irradiation with 2 MeV electrons from a linear accelerator. Electron spin resonance studies of the blue solution in dimethyl formamide have been held to show that the odd electron is to some extent delocalized between the metal and the NO^+ group (*49*, *244a*), but is concentrated mainly on the metal in the d_{z^2} orbital, leading to the formulation of the ion as a Fe(I) species (*123a*, *335b*, *433*). However, a recent detailed examination of the optical absorption spectrum of sodium nitroprusside suggests there is a low-lying π^* NO orbital and that this accommodates the extra electron when reduction to $[Fe(CN)_5NO]^{3-}$ takes place (*186a*); moreover, it is argued that the electron spin resonance data support the assignment Fe(II) and NO (*347b*). What may be the same ion (*244a*) can also be made in a brown aqueous solution from the ammine complex $Na_3[Fe(CN)_5NH_3]$ and nitric oxide (*193*, *343*). It reacts with hydroxide (in the absence of air) and cyanide to form $[Fe(CN)_5H_2O]^{3-}$ and $[Fe(CN)_6]^{4-}$, respectively (*193*); it is suggested that these reactions indicate a neutral NO complex of Fe(II), but a change in the oxidation state of the iron on substitution cannot yet be ruled out. No solid salt has yet been isolated, and the N—O stretching frequency is unknown.

Electrolytic reduction of 0.1 *M* $K_4[Fe(CN)_6]$ in 1.2 *M* KCN yields a colorless solution which reduces 1 gram-ion of $[Fe(CN)_6]^{3-}$ (*497*). This observation was interpreted as indicating formation of Fe(I), but formation of a hydride such as $[Fe(CN)_5H]^{3-}$ is another possibility (cf. Section VIII,A); the reduction of $[Fe(CN)_5H_2O]^{3-}$ should be worth examination.

The action of potassium in ammonia on potassium ferricyanide has been stated to involve reduction only to the Fe(II) complex (*83*); other methods which might give a Fe(0) or Fe(I) complex, e.g., the action of cyanide on iron pentacarbonyl or its derivatives, and the reduction of the $[Fe(CN)_5CO]^{3-}$ ion, do not appear to have been examined.

2. *Iron(II)*

Very little is known about the pale green substance of empirical formula $Fe(CN)_2$ which is obtained when ammonium ferrocyanide is heated *in vacuo* at 320°C (*363*). It was suggested several years ago, before the structure of Prussian blue (Section VII,A,5) was known, that it may be $FeFe[Fe(CN)_6]$ (*78*), but a re-examination of the problem is necessary before any conclusion can be reached on this point.

The ferrocyanides are so well known that the following account is largely restricted to the potassium salt and the properties of the ion in solution. Among many routes to the yellow salt $K_4[Fe(CN)_6]\cdot 3H_2O$ are the action of potassium cyanide on ferrous salts, the electrolytic oxidation of iron in cyanide solution, and, on a technical scale, the decomposition of Prussian blue by alkali. The white anhydrous salt may be obtained by heating the trihydrate at $<100°C$.

Potassium ferrocyanide trihydrate, which is diamagnetic, is dimorphic, although the structures of the monoclinic (pseudotetragonal) and tetragonal forms are obviously related, lattice constants being, respectively: $a = c = 9.32$, $b = 16.84$ Å, $\beta = 90° \pm 5'$, $N = 4$; $a = c = 9.35$, $b = 33.63$ Å, $N = 8$ (*419, 544*). The details of the structures, however, are not known.

Ferrocyanide is oxidized to Prussian blue by oxygen in the presence of acid, but in neutral or alkaline solution the reaction does not take place at an appreciable rate (*30*). Among the many reagents which bring about oxidation to ferricyanide are O_3, $S_2O_8^{2-}$, Cl_2, Br_2, H_2O_2, MnO_4^-, ClO_3^-, $Cr_2O_7^{2-}$, and Ce(IV); the energetics of the oxidation are discussed in Section VII,A,4. Dilute sulfuric acid liberates hydrogen cyanide on heating, but sparingly soluble double salts are also formed; the concentrated acid liberates carbon monoxide, though there is some intermediate formation of a carbonyl complex. Prolonged boiling of an aqueous solution of potassium ferrocyanide brings about formation of an aquopentacyano complex and hydrogen cyanide (*529*); ferric hydroxide is also produced, owing, no doubt, to aerial oxidation. When a solution of ferrocyanide is heated under pressure, ferrous hydroxide, ammonia, and formate are formed.

An alkaline solution of ferrocyanide when heated for 60 hours at 90°C deposits a little ferric hydroxide (*205*), but this arises because although the equilibrium

$$[Fe(CN)_6]^{4-} + 2OH^- \rightleftharpoons Fe(OH)_2 + 6CN^-$$

is well over on the left-hand side, ferric hydroxide is very insoluble, and its formation by the reaction

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 = 2Fe(OH)_3$$

upsets the equilibrium. Foster (*172*) found that potassium hydroxide effects no decomposition even under the influence of ultraviolet light unless oxygen is present; if it is present, a slow decomposition to ferric hydroxide, with some formation of cyanate, occurs.

The aquation of ferrocyanide ion, which occurs in the presence of acids or under the action of light, gives the $[Fe(CN)_5H_2O]^{3-}$ ion (*29*, *267*); for this reason light accelerates the otherwise extremely slow exchange with labeled cyanide ion (*335*). The aquation reaction is reversible so long as hydrogen cyanide does not escape from the solution and further decomposition does not take place (*13*), but the rate of recombination, although much greater than that of aquation, is by no means as fast as the uptake of the first five cyanides in the $Fe^{2+}(aq)$–CN^- reaction (*11*, *93*, *151*). Ferrocyanide is also reported to be decomposed by silver salts (*50*), mercuric oxide, or gold (*530*); in each case, however, ferric hydroxide is formed and hence oxygen appears to be a reactant.

A novel reaction of anhydrous potassium ferrocyanide which has recently been reported (*472*) is that with boron trifluoride. The salt slowly absorbs six molecules of the fluoride; the complex $[Fe(phenan)_2(CN)_2]$, which absorbs $2BF_3$, also absorbs $2BH_3$ when allowed to react with diborane. The products of these reactions are diamagnetic; an increase in the $C{\equiv}N$ stretching frequency leads to the conclusion that in each case a coordinate link from the nitrile nitrogen to boron is formed.

The absorption spectrum of ferrocyanide in solution has been examined (*105*, *186*, *259*), and Δ has been estimated as 33,800 cm^{-1}. In solution, there is a single $C{\equiv}N$ stretching frequency at 2044 cm^{-1} (*280*), but in solid $K_4[Fe(CN)_6]{\cdot}3H_2O$ a large number of bands appear (*66*, *381*, *453*). The Fe—C stretching frequency is at 416 cm^{-1} (*280*). For $[Fe(CN)_6]^{3-}$, it may be noted, $\nu(C{\equiv}N)$ and $\nu(M{-}C)$ are at 2118 and 389 cm^{-1}, respectively (*280*). Quoted M—C force constants (*381*) are too high (*280*).

Ferrocyanic acid can be obtained in aqueous solution by ion exchange; the anhydrous acid may be made by decomposition at 80°C of the "etherate" which is obtained from the potassium salt, sulfuric acid, and ethanol at 0°C, followed by addition of ether (*226*). Its dissociation constants in water have recently been determined (*283*): $K_1 > K_2 > 0.1$; $K_3 = 6 \pm 2 \times 10^{-3}$; $K_4 = 6.7 \pm 0.3 \times 10^{-5}$. The acid is thus weak in its third and fourth ionizations (see further Section VII,A,4). The infrared spectrum of the anhydrous acid shows strong broad absorption in the 3300–2300 cm^{-1} region, shifting on deuteration, and two $C{\equiv}N$ stretching frequencies; this indicates moderately strong hydrogen bonding of NH groups to adjacent $C{\equiv}N$ groups (*156*, *272*). It has been suggested on the basis of a more detailed spectroscopic study that all four hydrogen atoms per $H_4M(CN)_6$ unit are hydrogen-bonded in a *trans*-arrangement (*176a*). The reactions of the acid with alcohols, in which isonitrile esters are formed, have been the subject of a recent review (*227*) and will not be discussed here. Whether ferrocyanic acid can be protonated in a strongly acidic medium (e.g., HF/BF_3) has not been established.

3. Iron(III)

The only compound of empirical formula $Fe(CN)_3$ which has been described is the brown dihydrate of $Fe^{3+}[Fe(CN)_6]^{3-}$ which can be isolated from solutions of ferric nitrate and potassium ferricyanide (*435*). Berlin green (see Section VII,A,5), which is sometimes described as ferric ferricyanide, [e.g., see (*290, 522*)] is, in fact, a product of reduction of the brown compound, and the structure of the latter has not yet been investigated.

Potassium ferricyanide, which forms anhydrous red crystals, is invariably made by oxidation of the ferrocyanide, e.g., with chlorine, permanganate, or electrolytically. It was pointed out in Section I that the reaction of ferric and cyanide ions in aqueous solution resulted in the formation of a substantial amount of ferric hydroxide. In view of this it is surprising to note that the most recent thermodynamic data indicate that the equilibrium constant of the reaction

$$Fe(OH)_3 + 6CN^- = [Fe(CN)_6]^{3-} + 3OH^-$$

is about 10^5 (see the following section).

Ferricyanide ion is rather more reactive than ferrocyanide, even though it is thermodynamically more stable with respect to dissociation into the constituent ions. Thus, unlike the Fe(II) species, it is reported to be poisonous, and aquation takes place more readily than with the Fe(II) compound; in this reaction, the cyanide which is produced reacts with unchanged ferricyanide, forming ferrocyanide and cyanogen or cyanate (*467*). Alkaline ferricyanide is a good oxidizing agent, converting Cr(III) to chromate, for example; E° for the system

$$[Fe(CN)_6]^{3-} + e = [Fe(CN)_6]^{4-}$$

is discussed in the following section. Hot dilute sulfuric acid liberates hydrogen cyanide, the concentrated acid carbon monoxide together with a little carbon dioxide; a carbonyl-substituted ferricyanide is not formed.

The equilibrium constant and the kinetics of the reaction with iodide ion have been the subject of several investigations [e.g., see (*261, 439*)]: in the presence of hydrogen ions there are two reactions, an uncatalyzed one of order one with respect to $[Fe(CN)_6]^{3-}$ and two with respect to I^-, and a catalyzed one of order one with respect to each of $[Fe(CN)_6]^{3-}$, I^-, and H^+. Hydrogen ion appears to act by distorting the coordination sphere of the complex anion; it is interesting to note that La^{3+} has a similar effect (*261*). Although the reaction does not go nearly to completion under normal conditions, it can be made to do so by addition of zinc salts: zinc ferrocyanide is very insoluble, but the ferricyanide dissolves readily.

Anhydrous ferricyanic acid has been obtained from potassium ferricyanide and hydrochloric acid (*77*), but preparation by ion exchange does not seem to have been attempted. In aqueous solution it is a strong tribasic acid (*76, 77, 283*).

Potassium ferricyanide crystallizes in the orthorhombic system with $a = 13.45$, $b = 10.43$, $c = 8.40$ Å, $N = 4$ [(*183*) see also (*299*)], though a monoclinic form is also known (*26*). A detailed study of its paramagnetic susceptibility (*167*) gives a moment of 2.25 B.M. at the ordinary temperature; the electron delocalization factor k has been derived as 0.8, in good agreement with the value of 0.87 from electron spin resonance experiments (*60*). As might be expected, k is larger (1.0) in ferric complexes with *o*-phenanthroline and α,α'-dipyridyl, aromatic ligands which also have strong tendencies to bring about spin pairing.

The absorption spectrum of $[Fe(CN)_6]^{3-}$ in aqueous solution has been reported (*284, 508*) and Δ evaluated as 35,000 cm^{-1} (*379*), a value little different from that for $[Fe(CN)_6]^{4-}$; it should, however, be noted that doubts have been expressed about the assignment of the absorption bands (*21*).

Solid $K_3[Fe(CN)_6]$ has a single strong band in the infrared C≡N stretching region, at 2125 cm^{-1} (*85, 86*); in aqueous solution the band is at 2118 cm^{-1} and the M—C stretching frequency is at 389 cm^{-1} (*280*).

4. The $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$ Standard Potential and Related Quantities

The observed value for the potential of a solution containing equal concentrations of ferricyanide and ferrocyanide varies according to the concentration and the cation present, typical data in the absence of added electrolytes being (*301*):

Concentration	0.1	0.01	0.001	0.0001 *M*
E	+0.459	0.415	0.383	0.366 V

From these and other values $E°$ is derived as +0.356 V at ionic strength zero. Strong acids increase the potential much more than neutral salts at the same ionic strength, owing to the relative weakness of $[H_2Fe(CN)_6]^{2-}$ and, even more, of $[HFe(CN)_6]^{3-}$, as acids (*283, 302*); in 0.1, 0.5, and 1 *M* H_2SO_4, for example, the potentials are +0.57, +0.69, and +0.72 V, respectively (*283, 527*). Hydroxyl ion, conversely, affects the potential relatively little. For alkali metal cations the effect decreases slightly from cesium to lithium (*301*); ion-pair formation between ferrocyanide and cations has been investigated independently by spectrophotometry, and the formation constant for the ion pair $[KFe(CN)_6]^{3-}$ has been determined as 236 (*105*).

As was pointed out in Section I, the difference between the standard potentials for the Fe^{3+}/Fe^{2+} and $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ systems requires that ferricyanide ion be more stable than ferrocyanide with respect to dissociation into constituent ions by a factor of 10^7. Since both ions are kinetically inert, information about their actual dissociation constants must be obtained from thermal data, and it will now be shown in outline how this has been done.

Latimer (*319*) estimated the standard entropy of $[Fe(CN)_6]^{4-}$ in solution as 68 e.u., and from the National Bureau of Standards (Circular 500) value for ΔH_f° he deduced ΔG_f° as 170.4 kcal. This value, combined with data for Fe^{2+} and CN^- (themselves, of course, subject to some uncertainty), gave ΔG° for the reaction

$$[Fe(CN)_6]^{4-} = Fe^{2+} + 6CN^-$$

in aqueous solution as +47 kcal, whence $K_{diss} = 10^{-35}$ for $[Fe(CN)_6]^{4-}$ and 10^{-42} for $[Fe(CN)_6]^{3-}$.

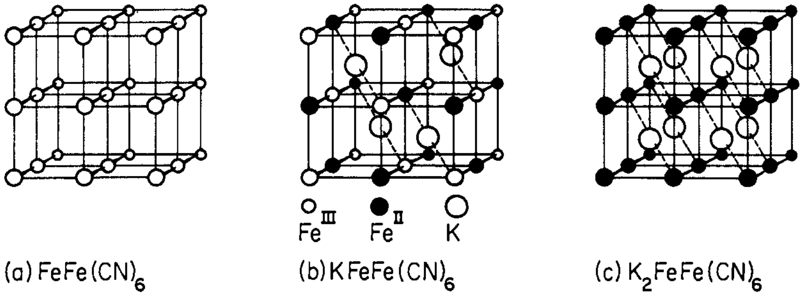
Unfortunately neither Latimer's estimated standard entropy of $[Fe(CN)_6]^{4-}$, nor the very old thermochemical information cited in Circular 500, is correct. The third-law entropy of $K_3Fe(CN)_6$ was determined by Stephenson and Morrow (*483*), who combined their value with the Bureau of Standards data, the standard potential for the $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ system, and solubilities and activity coefficients to obtain values of 64 and 22 eu for the standard entropies and 10^{-31} and 10^{-24} for the dissociation constants of $Fe(CN)_6^{3-}(aq)$ and $Fe(CN)_6^{4-}(aq)$ respectively. A subsequent study (*228*) of the heats of solution of $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and $K_4Fe(CN)_6 \cdot 3H_2O$, and of the heat of oxidation of ferrocyanide by bromine led to standard entropies of 63 and 17 eu for $Fe(CN)_6^{3-}(aq)$ and $Fe(CN)_6^{4-}(aq)$. Recently, the heat of complexing of Fe^{2+} by aqueous cyanide was determined calorimetrically at different ionic strengths and the results were extrapolated to give $\Delta H^\circ = -85.77$ kcal at $\mu = 0$ [since a 50:1 $CN^-:Fe^{2+}$ ratio was used and consistent results were obtained, formation of $Fe(CN)_6^{4-}$ was taken as reasonably certain; the stoichiometry was not, however, rigidly established]. This value, taken in conjunction with those for the standard entropies of the species involved, leads to $K_{diss} = 10^{-35.4}$ (*511a*). In the same study, the heat of oxidation of ferrocyanide by permanganate was also measured, and from this and the other necessary data K_{diss} for ferricyanide was evaluated as $10^{-43.6}$. The agreement between these values and those of Latimer is fortuitous. It is disturbing that the latest values imply that ferric hydroxide, for which $K_{sp} = 10^{-39}$ (*162*), should be readily soluble in a concentrated solution of potassium cyanide to form ferricyanide, for although there is some formation of this ion complete dissolution does not occur except under conditions such that oxidation of cyanide, with formation of ferrocyanide, takes place. It cannot yet said, therefore, that the position is satisfactory.

5. *Complex Cyanides Containing Iron in Two Oxidation States*

It is intended to discuss here only the structures of the Prussian blues and related compounds, which are of interest not only as complex cyanides of iron but also as structure types for other transition metal cyanides. For fuller details of the chemistry of these substances the account by Partington (*407*) should be consulted.

a. Insoluble Prussian Blue. The action of excess of ferrous salt on potassium ferricyanide solution, or of excess of ferric salt on potassium ferrocyanide solution, produces insoluble deep blue substances, formerly known as insoluble Turnbull's blue and insoluble Prussian blue, respectively. These materials, which appear to contain no potassium (though this point is not firmly established), are shown by tracer studies (*494*) to contain two types of iron; they give the same X-ray powder pattern (*517*) and Mössbauer spectrum (*170*), and it has been concluded from the latter that both are ferric ferrocyanide, $Fe^{III}_4[Fe^{II}(CN)_6]_3$, though some water, which may be removed continuously (*516*), is also present (consideration of standard potentials for the Fe^{3+}/Fe^{2+} and $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couples has been held to support formulation as ferrous ferricyanide, but this argument, based on data for ions in solution, ignores the fact that when a highly insoluble substance is precipitated lattice energy considerations become important; the higher charges in ferric ferrocyanide may well play a decisive part in determining the structure). The structure of insoluble Prussian blue is not yet known in detail, though it is undoubtedly closely related to those of the other compounds discussed here.

b. Soluble Prussian Blue. This substance and the so-called soluble Turnbull's blue result from the interaction of 1:1 molar proportions of $FeCl_3$ and $K_4[Fe(CN)_6]$ and $FeCl_2$ and $K_3[Fe(CN)_6]$, respectively; their identity has recently been established by studies of their Mössbauer spectra (*139, 154*). Soluble Prussian blue has the composition $KFe[Fe(CN)_6]\cdot H_2O$, though the water content is variable. The magnetic moment of 5.7 B.M. per formula-weight establishes the presence of two types of iron (*126*). X-Ray powder studies (*290*) show that the unit cell (see Fig. 2) is cubic, but do not distinguish between Fe(II) and Fe(III); studies on related ferricyanides (*51*) confirm that the $C{\equiv}N$ groups lie along the cell edges between the Fe atoms, though they do not distinguish between C and N atoms, which have almost identical scattering powers. The electronic absorption spectrum is consistent with the formulation $KFe^{III}[Fe^{II}(CN)_6]$ (*445*) and this is confirmed by the Mössbauer spectrum (*139*): high-spin Fe(III) is surrounded octahedrally by six nitrogen atoms and low-spin Fe(II) by six carbon atoms. The intense color arises from electron transfer, the low-spin carbon-coordinated Fe(II) being oxidized to low-spin Fe(III) and the high-spin nitrogen-coordinated Fe(III) being reduced to high-spin Fe(II) (*445*).



(a) $FeFe(CN)_6$ (b) $KFeFe(CN)_6$ (c) $K_2FeFe(CN)_6$

FIG. 2. The relationship between the structures of (a) $Fe[Fe(CN)_6]$, (b) $KFe[Fe(CN)_6]$, (c) $K_2Fe[Fe(CN)_6]$.

c. Berlin Green. This material is obtained by oxidation of Prussian blue with nitric acid, by the action of chlorine on a boiling solution of potassium ferrocyanide, or by heating the colloidal solution obtained from 3 moles of $FeCl_3$ and 1 mole of $K_3[Fe(CN)_6]$ at 90°C in the dark. Its unit cell dimensions (*290*) are the same as those of Prussian blue, and it is usually formulated $Fe[Fe(CN)_6]$ with all the iron in the ferric state. The intense color, however, implies the presence of at least a low concentration of Fe(II) species, and indications have recently been obtained that this arises by the reaction $Fe^{3+} + [Fe(CN)_6]^{3-} + 2H_2O = Fe^{2+} + [Fe(CN)_5]^{3-} + NH_4^+ + CO_2$ which takes place even in the solid state (*129a*).

d. The Relationship between the Structures of $K_2Fe[Fe(CN)_6]$, $KFe[Fe(CN)_6]$, and $Fe[Fe(CN)_6]$. The relationship between the structures of Berlin green, soluble Prussian blue, and the white insoluble compound $K_2Fe^{II}[Fe^{II}(CN)_6]$ prepared from ferrous ion and ferrocyanide is shown in Fig. 2. The positions of the iron atoms are the same in all three structures, but in $K_2Fe^{II}[Fe^{II}(CN)_6]$ every small cube, and in $KFe^{III}[Fe^{II}(CN)_6]$ every other small cube, contains a potassium ion at its center. Other compounds with similar structures include $KCu[Fe(CN)_6]$, $KMn[Fe(CN)_6]$, $KCo[Fe(CN)_6]$, and $KFe[Ru(CN)_6]$; cobalt(II) cyanide also belongs to this group, together with many hydrated complex cyanides containing anions $[M^{III}(CN)_6]^{3-}$, (where M^{III} = Cr, Mn, Fe, Co, Rh, or Ir) and dipositive cations such as Mn^{2+}, Fe^{2+}, and Ni^{2+}. The possession of a cubic unit cell of side approximately 10.2 Å (or 5.1 Å if, as in the case of $Fe[Fe(CN)_6]$, all metal atoms are crystallographically equivalent) is, in fact, a very valuable clue to the structures of a large number of compounds.

The nitrogen end of the cyanide ion has been shown to lie below ammonia in the spectrochemical series, and from estimates of Δ in different cyano complexes calculations have been made for different possible structures. In accordance with a prediction made on this basis, $KFe^{II}[Cr^{III}(CN)_6]$ when heated changes into $KCr^{III}[Fe^{II}(CN)_6]$ (*472a*).

6. *Substituted Cyanide Complexes*

Many compounds, mostly monosubstitution products, of this type are known, and we shall mention here only the principal classes, in which a cyanide group has been replaced by H_2O, NO, NO_2, NH_3, CO, or in which *o*-phenanthroline or α,α'-dipyridyl replaces two cyanides. The relationships between some of the Fe(II) species are shown in Fig. 3; the corresponding Fe(III) compounds, where they are known, are generally obtained by similar reactions or by oxidation of the Fe(II) compounds. All of the Fe(II) species are diamagnetic and the Fe(III) species paramagnetic with moments corresponding to the presence of a single unpaired electron, i.e., all are low-spin species (*476*, *523*). The C≡N stretching frequencies of most of the compounds lie in the same region as those of the parent hexacyano complexes (*113*, *229*) and will not be mentioned further.

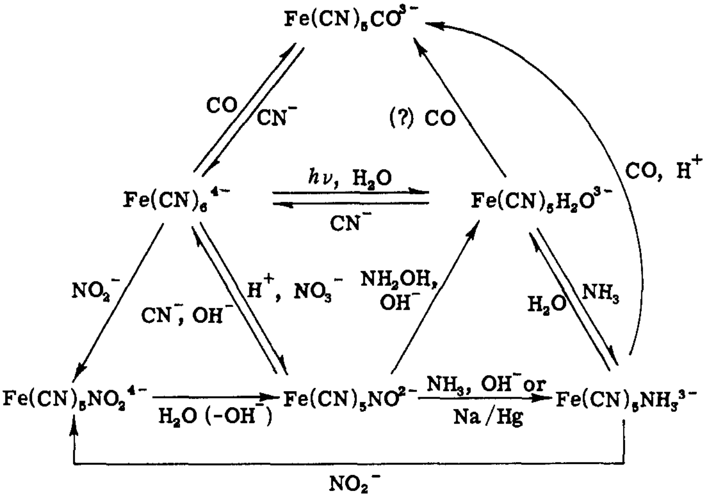


FIG. 3. Monosubstitution products of ferrocyanide.

a. Aquo Complexes. Aquopentacyano complexes of iron(II) are obtained by the action of light on neutral or acidic solutions of ferrocyanide:

$$[Fe(CN)_6]^{4-} + 2H_2O = [Fe(CN)_5H_2O]^{3-} + OH^- + HCN$$

This process, for which the equilibrium constant is 10^{-8} (*152*), is retarded by alkali but promoted by nitrosobenzene (which forms a stable violet complex with the aquopentacyanide), Hg^{2+}, Hg_2^{2+}, Pt(IV), Au(III) and, at elevated temperatures, Ag^+ (*12, 12a, 152, 307a*). A study has been made of the kinetics of the hydrolytic reaction (*320a*). On a preparative scale, however, it is usual to make the sodium salt, $Na_3[Fe(CN)_5H_2O]\cdot H_2O$, from nitroprusside by the reaction

$$[Fe(CN)_5NO]^{2-} + NH_2OH + OH^- = [Fe(CN)_5H_2O]^{3-} + N_2O + H_2O$$

sodium carbonate (not the hydroxide) being used as the source of hydroxyl ion (*250*). Ethanol effects separation of the complex, sometimes as an oil (many aquocyano complexes behave in this way) and sometimes as a deliquescent yellow powder which is extremely soluble in water. There is some evidence to suggest that the brown aqueous solution contains polymeric species (*149, 153, 358*). The combination with cyanide ion to reform ferrocyanide is a second order process with activation energy approximately 25 kcal at 0°–30°C (*11, 151, 320a*).

Iron(III) aquopentacyano complexes are obtained from ferricyanide under the influence of light, heat, or acid, by oxidation of the iron(II) compounds with bromine water, nitrous acid, or permanganate and acetic acid (*250*), or by the action of chlorate on a ferrocyanide or chlorine on a ferricyanide (*89*). In the preparation of the sodium compound from the iron(II) compound and bromine, the hygroscopic violet oily product is dissolved in methanol, precipitated by addition of ether, and dried over sulfuric acid; the water content has been reported as 1 or 2.6 H_2O. The interaction with cyanide does not appear to have been investigated.

Under conditions such that $E°$ for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple was +0.48 V, Davidson (*124*) found that $E°$ for the aquopentacyano ions couple was almost the same. Whether this value is reliable, however, is doubtful: the blue color of the $[Fe(CN)_5H_2O]^{2-}$ ion was not visible until more than 50% of the iron was in the ferric state, and this suggests interaction of the Fe(II) and Fe(III) species, a possibility worthy of further examination.

b. Nitroso Complexes. Sodium nitrosopentacyanoferrate(II) or nitroprusside, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, is usually prepared by the action of nitric acid or sodium nitrite on the ferrocyanide. In the former process (*74*) the over-all reaction is represented by the equation

$$[Fe(CN)_6]^{4-} + 4H^+ + NO_3^- = [Fe(CN)_5NO]^{2-} + CO_2 + NH_4^+$$

In the latter process, the reaction is the sum of the equilibria

$$[Fe(CN)_6]^{4-} + NO_2^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + CN^-$$

$$[Fe(CN)_5NO_2]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5NO]^{2-} + 2OH^-$$

In order to drive it to completion, removal of cyanide (as HCN) and hydroxyl ion is essential; both processes are achieved by adding barium chloride to the reaction mixture and blowing a current of carbon dioxide through the hot solution, the over-all reaction then being (*406*):

$$2[Fe(CN)_6]^{4-} + 2NO_2^- + 3Ba^{2+} + 3CO_2 + H_2O = 2[Fe(CN)_5NO]^{2-} + 2HCN + 3BaCO_3$$

The formulation of the red nitroprusside anion as a NO^+ complex of Fe(II) is established by its diamagnetism (*532*), a N—O stretching frequency of 1939 cm^{-1} (*67, 322*) and a N—O distance of 1.13 ± 0.02 Å in the crystal (*347*). All Fe—C distances are, within experimental error, 1.90 Å; the Fe—N distance is 1.63 Å. A detailed analysis of the optical absorption spectrum of the ion has recently been made (*186a, 347b*). The formation of a nitro complex by the action of OH^- is parallel to the formation of the $[Fe(CN)_5NOS]^{4-}$ ion in the color reaction for SH^-; the compound acts as a source of NO^+ in the conversion of reactive methylenic compounds to oximes.

The reduction of nitroprusside was discussed in Section VII,A,1; its oxidation to a NO^+ complex of Fe(III) has not been described. Alkaline permanganate at 0°C is reported (*250*) to yield red salts containing the $[Fe^{III}(CN)_5NO_2]^{3-}$ ion, but these have been little investigated.

c. Ammino Complexes. Pale yellow sodium amminopentacyanoferrate(II), $Na_3[Fe(CN)_5NH_3]\cdot 6H_2O$, may be made by the action of concentrated aqueous ammonia on the aquo compound, by reduction of sodium nitroprusside with sodium amalgam, or by treating the nitroprusside with ammonia and sodium hydroxide (*248, 249*):

$$[Fe(CN)_5NO]^{2-} + 2NH_3 + OH^- = [Fe(CN)_5NH_3]^{3-} + N_2 + 2H_2O$$

Many amines will displace ammonia to give aminopentacyano-ferrates(II) (*291, 346*). The conductivity of the sodium salt in aqueous solution suggests that, in water, ammonia is largely displaced by the solvent (*247*). With alkaline sodium nitrite, sodium sulfite, or carbon monoxide the ammonia is replaced by NO_2^-, SO_3^{2-}, or CO, respectively (*89, 249, 343*).

Oxidation of the Fe(II) ammine complex with hypobromite or sodium nitrite and acetic acid gives the dark yellow Fe(III) compound (*247, 250*). An aqueous solution of the acids $H_2[Fe(CN)_5NH_3]$ and HN_3 or HSCN, prepared in an ion-exchange column, may be converted into tetrabutylammonium salts containing the mixed anion $[Fe(CN)_5N_3]^{3-}$ or $[Fe(CN)_5SCN]^{3-}$ (*266*). The visible spectra of many of these substituted ferricyanide ions have been reported (*266*).

d. Carbonyl Complexes. Carbon monoxide reacts with potassium ferrocyanide solution at 130°C or above under pressure, forming $K_3[Fe(CN)_5CO]$, ammonia, and formate (*113, 374, 375*); displacement of ammonia from the amminopentacyano complex by carbon monoxide in the presence of acetic acid also occurs (*239, 343*). These reactions suggest that the aquopentacyano complex would react with carbon monoxide; Hieber and his colleagues (*235*) say that this reaction takes place readily, but Cotton and co-workers (*113*) deny this. Potassium cyanide solution decomposes the carbonyl complex to ferrocyanide and carbon monoxide. The free acid, $H_3[Fe(CN)_5CO]\cdot H_2O$, has been isolated (*377*). The $[Fe(CN)_5CO]^{3-}$ anion resists oxidation and attempts to prepare a carbonyl pentacyanoferrate(III) have so far been unsuccessful (*291*).

e. o-Phenanthroline and α,α′-Dipyridyl Complexes. A slow ligand exchange occurs when a solution of an *o*-phenanthroline or α,α′-dipyridyl ferrous salt is treated with cyanide at the boiling point, and products such as $[Fe(phenan)_2(CN)_2]\cdot 2H_2O$ and $K_2[Fe(dipy)(CN)_4]\cdot 3H_2O$ may be isolated (*24, 348, 460, 461*). These preparations may also be carried out starting from ferrocyanide by a photochemical reaction in which aquation of the $[Fe(CN)_6]^{4-}$ ion is the first step (*22*). The nonelectrolytes are easily protonated in concentrated acid (*24*), and the spectra of the ions produced indicate that protonation takes place on the nitrogen rather than on the metal (*215*).

Oxidation of the Fe(II) compounds with chlorine or concentrated nitric acid gives the corresponding Fe(III) compounds (*461*). These, it may be noted, cannot be made by replacement reactions since free cyanide ion immediately reduces the Fe(III) complexes (*269*).

B. RUTHENIUM

1. *Ruthenium(II)*

The gray-green precipitate formed when potassium cyanide is added to the blue solution of ruthenium dichloride may be the dicyanide, but it has not been analyzed (*438*). Potassium hexacyanoruthenate(II), $K_4[Ru(CN)_6]\cdot 3H_2O$, is obtained by heating almost any ruthenium compound (e.g., K_2RuO_4, $RuCl_3$, RuO_4) with cyanide solution (*127, 253, 308*); it forms very soluble colorless crystals which may be dehydrated at 110°C. The compound is isomorphous with $K_4[Fe(CN)_6]\cdot 3H_2O$, but, very surprisingly, the quoted dimensions of the unit cell are smaller than those of the Fe(II) compound (*419*). The anion undergoes aquation in the same way as ferrocyanide (*150*), but the aquo compound has not been isolated. The free acid is obtained from the potassium salt, acid, and ether (*156, 308*); its infrared spectrum, and that of the analogous osmium acid, closely resemble that of $H_4[Fe(CN)_6]$ (*156*). The similarity to the ferrocyanides is further revealed by the isomorphism and spectral similarities of the insoluble "ruthenium purple," $KRu[Fe(CN)_6]$, and Prussian blue (*290, 445*), and by the formation of nitrosopentacyanoruthenates(II) when the complex cyanides are heated with nitric acid. These salts give red colors with sulfide ion (*337*).

The visible and ultraviolet spectra of the $[Ru(CN)_6]^{4-}$ ion have been reported (*127*, *445*), and Δ has been evaluated as 33,800 cm^{-1} (*186*); this is, surprisingly, the same value given for $[Fe(CN)_6]^{4-}$. For solid $K_4[Ru(CN)_6]\cdot 3H_2O$ there are C≡N stretching bands at 2027 and 2042 cm^{-1}; ν(Ru-C) is at 376 cm^{-1}, the original assignment (*381*) being in error (*280*).

2. Ruthenium(III)

When a solution of $K_4[Ru(CN)_6]$ is treated with chlorine, the color changes to yellow, then red-brown, and warming with sulfuric acid then precipitates green-black $Ru(CN)_3\cdot 5H_2O$; this with concentrated ammonia forms $Ru(CN)_3\cdot 2NH_3\cdot H_2O$, which is also insoluble (*310*). Nothing is known of the constitution of these substances. An intermediate cyanide $Ru_2(CN)_5\cdot H_2O$ is said to be produced from $K_4[Ru(CN)_6]$ and sulfuric acid (*310*).

The yellow solution mentioned above is also obtained when the cyanoruthenate(II) is oxidized with hydrogen peroxide, cerium(IV) or bismuthate in acid, or ozone in neutral solution (*127*). The potassium salt of the Ru(III)-containing species (presumably $[Ru(CN)_6]^{3-}$, since it has an absorption spectrum rather like that of $[Fe(CN)_6]^{3-}$) cannot be isolated, nor is it obtainable by electrolytic oxidation of the Ru(II) compound, but characteristic colored precipitates are formed from the yellow solution and Ag^+, Co^{2+}, Mn^{2+}, and Zn^{2+} salts. None of these has been analyzed, however, and isomorphism with the corresponding ferricyanides, which would also be a good guide to their identity, has not been established. From the potentiometric titration curve for $[Ru(CN)_6]^{4-}$ with Ce(IV) the standard potential for the Ru(III)/Ru(II) couple in cyanide complexes appears to be about +0.9V (*127*).

C. OSMIUM

1. Osmium(II)

Colorless crystals of $K_4[Os(CN)_6]\cdot 3H_2O$, isomorphous with the iron and ruthenium compounds, are obtained by heating potassium osmate(VI) with aqueous cyanide or by fusing potassium hexachloroosmate(IV) with potassium cyanide (*309*). In the infrared spectrum, ν(C≡N) is at 2032 cm^{-1}; ν(Os—C) at 392 cm^{-1} [(*381*) but see also (*280*)] is higher than ν(Ru—C) in $K_4[Ru(CN)_6]\cdot 3H_2O$, suggesting a stronger bond in the osmium complex. The compound $KFe^{III}[Os^{II}(CN)_6]$ is spectroscopically similar to Prussian blue (*445*).

2. Osmium(III)

The oxidation of $[Os(CN)_6]^{4-}$ in the absence of added cyanide has not yet been achieved, but in 0.1 *M* CN^- solution air apparently oxidizes the compound to an intensely blue product containing Os(III) (*353*). Furthermore, polarographic reduction of Os(VI) in aqueous cyanide indicates successive conversion into a blue solution containing Os(III) and a yellow one containing Os(II). No compounds have been isolated, however (*353*).

3. Osmium(VI)

Krauss and Schrader (*311*) obtained an orange-red solution of the compound $K_2[OsO_2(CN)_4]$ by the action of potassium cyanide on osmium tetroxide, and reported that it was stable even toward boiling acid. They could not isolate the compound, but did prepare the sparingly soluble cupric and silver(I) salts and their ammine complexes. The infrared spectrum of the potassium salt (the isolation of which has still not been described) suggests that the anion has the same *trans*-octahedral structure as $[OsO_2Cl_4]^{2-}$ (*191*).

VIII. Cobalt, Rhodium, and Iridium

The cyanide complexes of cobalt have been investigated the most extensively of all during recent years. In some instances the assignment of an oxidation state to the metal is difficult, and in the following account there are three ligands to which we should draw particular attention: we have taken NO to be present as NO^+ or, less commonly, if infrared spectroscopic evidence supports the formulation, as NO^-; hydrogen attached to cobalt has been taken to be H^-; and O_2 has been taken to be O_2^{2-} or, occasionally, O_2^-. The choice of a formulation is sometimes rather arbitrary, and although evidence (or, more often, lack of it) will be mentioned in connection with individual compounds, the reader should be warned that some care is necessary in seeking information on particular substances both in this review and even more, in the chemical literature: $[Co^{III}(CN)_5H]^{3-}$, for example, has often been written as $[Co^{I}(CN)_5H]^{3-}$. We have taken the oxidation states of cobalt in cyanide compounds as 0 (e.g., in $K_8[Co_2(CN)_8]$), I (e.g., in $K_3[Co(CN)_4]$), II (e.g., in $K_6[Co_2(CN)_{10}]$), and III (e.g., in $K_3[Co(CN)_6]$), but not IV. It is interesting to note that cobalt is the first element after vanadium for which a species of formula $[M(CN)_6]^{4-}$ can definitely not be obtained in aqueous solution in measurable concentration.

Very much less is known about cyanide compounds of the other two elements. There is evidence for a derivative of a low oxidation state of rhodium, but nothing has been isolated; in the case of iridium, few serious attempts to prepare compounds other than those of Ir(III) appear to have been made.

Although the C≡N stretching frequencies in the ions $[M(CN)_6]^{3-}$ are almost identical, being 2129, 2133, and 2130 cm^{-1} in aqueous solution for

M = Co, Rh, and Ir, respectively, the M—C infrared stretching frequencies show an interesting variation from 416 cm^{-1} in $[Co(CN)_6]^{3-}$ through 387 cm^{-1} in $[Rh(CN)_6]^{3-}$ to 401 cm^{-1} in $[Ir(CN)_6]^{3-}$. The relative intensities of the C≡N stretching frequencies support the idea that the degree of π-bonding decreases slightly in the order Ir > Co > Rh (*280*), but the metal-carbon force constants, which give an indication of the total bond strength, are 2.7 (Ir), 2.4 (Rh), and 2.1 (Co) × 10^5 dynes/cm; the C≡N force constants are all nearly 16.8 × 10^5 dynes/cm (*281a*).

In this section, in addition to the usual systematic treatment of oxidation states, separate subsections have been included to deal with some special aspects of the chemistry of cobalt-cyanide complexes. These deal with the oxidation, reduction, and "aging" of the $[Co(CN)_5]^{3-}$ ion (the stable Co(II)-cyanide species in solution), substituted cyanide complexes, and the mechanism of substitution of cyanide into Co(III) compounds. These topics are interrelated, however, and no rigid division of subject matter is possible or, indeed, desirable.

A. COBALT

1. *Cobalt(0)*

When $K_3[Co(CN)_6]$ is reduced with excess of potassium in liquid ammonia an air-sensitive brown-violet compound is obtained; this liberates hydrogen from water and reduces 3 moles of ferricyanide. It is weakly paramagnetic (μ = 0.6 B.M.), but this is attributed to the presence of paramagnetic decomposition products, and since the susceptibility is well below that required for a single unpaired electron it is concluded that the formula of the compound is $K_8[Co_2(CN)_8]$, the mononuclear anion $[Co(CN)_4]^{4-}$ being eliminated from consideration since it would necessarily be paramagnetic (*232*, *234*).

It has been briefly reported (*200*) that solid $K_8[Co_2(CN)_8]$ shows only two C≡N stretching frequencies in the infrared (at 2120 and 2062 cm^{-1}), and that this is compatible with a metal-metal bonded D_{4d} (eclipsed) configuration, i.e., a structure quite different from that of the isoelectronic $Co_2(CO)_8$. Some caution should, however, be exercised in accepting a conclusion based on numbers of frequencies found using a sodium chloride prism, as the recent history of attempts to determine the structure of $Co_2(CO)_8$ [summarized in (*382*)] shows.

Indications of the existence of a complex carbonyl cyanide of Co(0) have been obtained: $K_8[Co_2(CN)_8]$ in liquid ammonia absorbs some carbon monoxide, and when the sodium salt of cobalt carbonyl hydride, $Na[Co(CO)_4]$, is treated with sodium cyanide in ammonia some carbon monoxide is liberated. No pure compound has been isolated, however (*234*).

2. Cobalt(I)

The first indication of a low oxidation state of cobalt in aqueous solution came from Treadwell and Huber (*497*), who electrolyzed a solution of cobalt(II) cyanide in excess of potassium cyanide, and obtained an olive-green solution which reduced 2 moles of ferricyanide. Polarographic studies (*256*) also suggested that a cobalt(I) species is formed in the reduction of the cobalt(II) complex cyanide. In view of extensive later work it seems possible that the main product in these reactions was a hydrido complex; it is desirable that this problem should be re-examined.

Reduction of $K_3[Co(CN)_6]$ suspended in liquid ammonia by potassium, using a molar ratio of reactants of about 1:2.3, gives a pale yellow solid of formula $K_3[Co(CN)_4]$ (*512, 514*). When this is warmed to room temperature it turns red-brown, and decomposes rapidly on exposure to air. The anion, being isoelectronic with $[Ni(CN)_4]^{2-}$, would be expected to be a planar monomer, but no structural investigations of any kind have been made.

The interaction of carbon monoxide, potassium hydroxide, and $K_3[Co(CN)_6]$ solution leads to formation of the $[Co(CN)_3CO]^{2-}$ ion, which may be isolated as the tris-*o*-phenanthroline ferrous salt (*233*). This has four bands in the 1900–2150 cm^{-1} region, a number compatible with its expected planar configuration (*200*).

3. Cobalt(II)

Cobalt(II) cyanide is obtained as a light brownish precipitate containing 2 or 2.5 H_2O from cobalt chloride and potassium cyanide solutions; when heated in nitrogen at 250°C it forms the dark blue anhydrous compound. The magnetic moments of both substances, 3.27 (*264*) and 3.12 (*52*) B.M., respectively, are well below the value for three unpaired electrons, and both give the same cubic X-ray powder pattern with $a = 10.12$ Å (*519*).

The X-ray diagrams have been interpreted in terms of a structure which is that of soluble Prussian blue (Section VII,A,5) with Co(II) atoms replacing those of iron and potassium. The material acts as a zeolite by virtue of its open structure, and can include alcohols, acids, nitriles, etc., of van der Waals diameter not greater than 3.6 Å (*519*). It has not yet been shown by tracer experiments that, as in the case of Prussian blue, more than one type of transition metal atom is present. The magnetic data, however, suggest formulation in terms of a framework of composition $CoCo(CN)_6$, Co(II) surrounded by six C having one unpaired electron, and Co(II) surrounded by six N having three unpaired electrons, and

Co^{2+} ions, free or hydrated, having three unpaired electrons (assuming that the usual orbital contributions to the moments of the high spin octahedral ions are absent). It is interesting to note that $Co(CN)_2$ and the pink hydrated and blue anhydrous compounds derived from cobalt(II) salts and potassium cobalticyanide all have about the same cubic lattice constant of 10.2 Å, the same as that for Prussian blue (*165*, *405*, *503*). This suggests that in $Co_3[Co(CN)_6]_2$ the framework is $Co^{II}Co^{III}(CN)_6$ and that only half as many Co^{2+} ions are present at the centers of the small cubes as in $Co(CN)_2$; for the former compound tracer studies (*168*) have shown the presence of nonequivalent cobalt atoms.

When cobalt(II) cyanide is dissolved in excess of aqueous potassium cyanide an olive-green solution, which is rapidly oxidized by air, is obtained. Titration of cyanide with cobalt(II) to the first appearance of a permanent precipitate or potentiometrically, whether in air or under nitrogen or hydrogen, in the light or in the dark, gives an end point at a CN:Co ratio of 5:1 (*1*, *178*, *334*, *373*, *422*, *452*), and the maximum heat evolution also occurs at this ratio (*367*). The solution of the Co(II) compound has a magnetic moment of 1.72 B.M. per Co (*1*, *361*), and exchanges cyanide rapidly with labeled potassium cyanide, but not with $[Co(CN)_6]^{3-}$ (*1*). Furthermore, oxidation of the olive-green solution by ferricyanide (which is discussed in detail later) does not yield the $[Co(CN)_6]^{3-}$ ion (*211*, *256*), and reduction of the latter species to the Co(II) state by potassium amalgam occurs only upon prolonged shaking and with production of free cyanide (*478*).

All this points strongly to $[Co(CN)_5]^{3-}$, or perhaps $[Co(CN)_5H_2O]^{3-}$, as the principal species present in the olive green solution. The rapid exchange with cyanide and the fact that the aquo ion would give cobalt one electron more than krypton have been put forward as arguments in favor of $[Co(CN)_5]^{3-}$ (*1*); the present authors, while not regarding these as strong arguments, favor writing the ion as $[Co(CN)_5]^{3-}$ unless compelling evidence for the six-coordinated structure appears.

The heat evolution for the reaction between $Co^{2+}(aq)$ and aqueous cyanide has been measured as 74.4 kcal (*210*), but the solution which is obtained is extremely reactive, being oxidized very easily and undergoing an aging process even under an inert atmosphere; there is therefore some element of doubt about the interpretation of the thermochemical datum. The two most recent investigations of the visible spectrum of aqueous $[Co(CN)_5]^{2-}$ are in agreement (*295*, *422*), but the spectrum has not yet been interpreted.

The violet solid which is in equilibrium with the olive green solution, and may be precipitated by addition of ethanol, is diamagnetic (*1*, *426*, *486*); although the formula $K_4[Co(CN)_6]$ was reported in the earlier literature (*56, 130, 131, 132, 448*), it now seems quite certain that the compound is really a hydrate of $K_6[Co_2(CN)_{10}]$. The characterization by chemical analysis still leaves something to be desired. Adamson (*1*), to whom the credit for establishing the CN:Co ratio in the solid is due, accounted for a poor analysis by suggesting contamination of the product with potassium cyanide. Griffith and Wilkinson (*198*), who inferred from the diamagnetism and the presence of three strong bands (at 2133, 2090, and 2079 cm^{-1}) in the $C{\equiv}N$ stretching region that the anion had the structure $(NC)_5Co{\cdot}Co(CN)_5$ analogous to $Mn_2(CO)_{10}$, determined only potassium, and erroneously took Adamson's value for his impure compound as the theoretical value for K. Nast and his co-workers (*395*), who used aqueous methanol as solvent, reported that unless potassium hydroxide was added in the preparation $K_4[H_2Co_2(CN)_{10}{\cdot}4H_2O$ was formed; in the presence of alkali, $K_6[Co_2(CN_{10})]{\cdot}6H_2O$ resulted. What is very surprising, however, is that the sodium salt $Na_6[Co_2(CN)_{10}]{\cdot}4H_2O$ was obtained whether alkali was added or not. The present authors find that the potassium salt, when obtained from aqueous solution, is best represented as a tetrahydrate, but can be dehydrated over P_2O_5 *in vacuo* at room temperature.

If, in the preparation of these complexes, a deficiency of cyanide is used, a green precipitate is formed; there has been some discussion of the nature of this substance (*130, 200, 295*), but since no adequate analysis has been reported no conclusion can be reached.

It may be mentioned here that a value attributed to the $[Co(CN)_6]^{3-}/[Co(CN)_6]^{4-}$ standard potential was reported many years ago (*208*). Its magnitude [-0.81 V, compared with $+1.95$ V for $Co^{3+}(aq)/Co^{2+}(aq)$ (*270*)] implies a very high degree of stabilization of Co(III) relative to Co(II) by cyanide complexing. In the light of the evidence against the existence of $[Co(CN)_6]^{4-}$ in solution it is likely that the potential recorded is that for some such process as

$$[Co(CN)_6]^{3-} + e = [Co(CN)_5]^{3-} + CN^-$$

but, in view of its proximity to the potential required for the discharge of hydrogen from alkaline solution and the nonreversibility of the electrode reaction, it is also possible that what was measured was something quite different (*256, 319*). For many years, therefore, the result has been regarded with scepticism. Nevertheless, since it has recently been shown that $E°$ for the $[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}$ system is $+0.09$ V (*271*) and since cyanide modifies standard potentials for aquo ions more than ammonia does, it may well be that -0.8 V for electron transfer and liberation of one cyanide ion is not seriously in error. Certainly $E°$ for the system $[Co(CN)_6]^{3-} + e = [Co(CN)_6]^{4-}$ can hardly be *less* negative than this value.

4. Cobalt(III)

Cobalt(III) cyanide is reported to be obtained as a dark blue powder stable in the absence of moisture, but converted by it into a red-brown dihydrate, when the aquated acids $H[Co(CN)_4]$ and $H_2[Co(CN)_5]$ are heated (the action of heat on $H_3[Co(CN)_6]$ does not seem to have been examined). The anhydrous and hydrated compounds have magnetic moments of 2.8 and 3.1 B.M. (*427*, *428*, *430*). Since fluoride is the only ligand to leave Co(III) in a high-spin state ($[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$ are both diamagnetic) these values, if correct, are very interesting; it seems likely, however, that some decomposition took place. No X-ray powder data are available to show whether the structure is similar to that attributed to Berlin green.

The ion $[Co(CN)_6]^{3-}$ is well known; the pale yellow diamagnetic potassium salt is the ultimate product when a solution of cobalt(II) cyanide in aqueous potassium cyanide is boiled in the presence of air (*43*, *54*). The complex series of reactions involved is discussed in the following section. The $[Co(CN)_6]^{3-}$ ion is very unreactive; chlorine, hydrogen peroxide, alkali, hydrochloric acid, and hydrogen sulfide are without effect on it, but concentrated sulfuric acid liberates carbon monoxide. Exchange with labeled cyanide is extremely slow (*4*, *335*), although the process is accelerated by the action of light, under the influence of which aquation takes place as the rate-determining step:

$$[Co(CN)_6]^{3-} + H_2O = [Co(CN)_5H_2O]^{2-} + CN^-$$

Heavy metal cobalticyanides are generally insoluble, and many have structures related to that of Prussian blue.

Potassium cobalticyanide is very soluble in water, sparingly soluble in liquid ammonia, and insoluble in ethanol. The ordinary product contains no less than four crystalline forms, the dimensions of which are reproduced here to show how closely related they are (*299*):

Unit cell:	*Orthorhombic*	*Monoclinic*	*Monoclinic*	*Monoclinic*
a	13.31	7.00	21.00	49.00
b	10.37	10.38	10.38	10.38
c	8.35	8.37	8.37	8.37
β	—	107°19′	107°19′	107°19′
N	4	2	6	14

A neutron diffraction study of the monoclinic form having the smallest unit cell shows that the Co—C distance is 1.89 and C≡N 1.15 Å (*122*).

The heat of formation of $K_3[Co(CN)_6]$ is unknown, but the standard entropy has been measured as 96 e.u. (*483*). From the heat of solution and activity coefficients the entropy of $[Co(CN)_6]^{3-}(aq)$ is estimated as 56 e.u., rather less than that of $[Fe(CN)_6]^{3-}(aq)$ (*228*). The over-all formation constant of $[Co(CN)_6]^{3-}$ is a quantity of great interest, but unfortunately it is remarkably difficult to get even an estimate of its magnitude. E° for the system Co(III)/Co(II) in cyanide media has been measured (cf. Section VIII,A,3) but the value is subject to some uncertainty; the metal in the two oxidation states is combined with different numbers of cyanide ions, and the formation constant for the Co(II) complex is unknown. It is, however, clear from the great effect of cyanide complexing on E° for the Co(III)/Co(II) system that $[Co(CN)_6]^{3-}$ must be an extremely stable ion. If the formation constant of $[Co(CN)_5]^{3-}$ is 10^x, the first dissociation constant of $[Co(CN)_6]^{4-}$, 10^y, and ΔE° is zV, it is easily shown that the over-all formation constant of $[Co(CN)_6]^{3-}$ is $10^{(x-y+17z)}$. It has been shown earlier that z can hardly be less than about 2.7 V, so that even if the over-all formation constant for $[Co(CN)_6]^{4-}$ were unity, that for $[Co(CN)_6]^{3-}$ would be at least 10^{46}; if x were 20 and y were 6, which seem reasonable values to assume, the figure would be 10^{60}, and this very rough estimate seems the best that can be made at the present time.

The equilibrium constant of the reaction

$$[Co(CN)_6]^{3-} + 3OH^- = Co(OH)_3 + 6CN^-$$

which might throw some light on this matter is, unfortunately, unknown. Freshly precipitated cobalt(III) hydroxide certainly dissolves in hot aqueous cyanide, but it may be that air or water is also a reactant in this process (*93*). The most recent value (obtained indirectly) for the solubility product of $Co(OH)_3$ is 10^{-52} (*271*); the approximate value of 10^{60} for the over-all formation constant of $[Co(CN)_6]^{3-}$ thus implies that, contrary to a previously held view (*378*), the $[Co(CN)_6]^{3-}$ ion is thermodynamically stable to alkali. Nevertheless, the experimental determination of the position of the equilibrium remains of crucial importance.

The visible and ultraviolet spectra of $[Co(CN)_6]^{3-}$ in aqueous solution have been recorded by two sets of workers (*186*, *509*) whose results are in good agreement; Δ is calculated to be 34,800 cm^{-1}. The band at 311 mμ has been widely used for identification of the anion. Raman (*96*, *99*, *123*, *350*, *457*) and infrared (*278*, *279*, *280*) spectra have been investigated in detail; there is some disagreement over assignments, and here as elsewhere we have accepted the interpretation of Jones [see (*280*)]. The conclusion of Chantry and Plane (*96*), based on Raman intensity data, that there is no π-bonding contribution to the Co—C bond is at variance with investigations of Jones (*280*), who has correlated the increase in intensity of ν(CN) along the series $[Cr(CN)_6]^{3-}$, $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, and $[Co(CN)_6]^{3-}$ with an increase in strength of the π-bond. In aqueous solution $[Co(CN)_6]^{3-}$ gives an infrared spectrum with a single C≡N stretching frequency at 2129 cm^{-1} (*280*); in solid $K_3[Co(CN)_6]$ an intense doublet at 2128 and 2131 cm^{-1} is observed; the Co—C stretching frequency is at 416 cm^{-1} (*158, 278*). The C≡N and Co—C force constants are calculated as 16.8 and 2.1×10^5 dynes/cm, respectively (*281a*). For $K_3[Co(CN)_6]$ dissolved in solid NaCl or KCl the C≡N stretching frequency is split into three: when a $[Co(CN)_6]^{3-}$ group replaces a $[MCl_6]^{5-}$ group in the lattice, two neighboring M^+ ions must be removed to achieve electrical neutrality and the site symmetry is lowered (*279*).

A solution of the acid $H_3[Co(CN)_6]$ is readily obtained by ion exchange. It crystallizes with $5H_2O$, but may be dehydrated by heating; the anhydrous acid shows only a single C≡N stretching frequency at 2202 cm^{-1}, rather higher than that in the free ion, together with a NH frequency, and it has been suggested that symmetrical hydrogen bonds are present (*156, 272*). Like $H_3[Fe(CN)_6]$, $H_3[Co(CN)_6]$ is a strong tribasic acid (*76*). With alcohols and hydrochloric acid, it yields oxonium salts (*245*); esters may be obtained from the silver salt and alkyl iodides (*64, 217*), or by heating the acid with alcohols at 100°C in a sealed tube (*246*).

5. *The Action of Oxidizing Agents on the* $[Co(CN)_5]^{3-}$ *Ion*

It was shown many years ago that when the $[Co(CN)_5]^{3-}$ ion in aqueous solution is rapidly oxidized by air at the ordinary temperature, more oxygen than corresponds to the simplest equation,

$$2[Co(CN)_5]^{3-} + 2CN^- + H_2O + \tfrac{1}{2}O_2 = 2[Co(CN)_6]^{3-} + 2OH^-$$

is used, and iodometric determination indicated that the over-all stoichiometry was better expressed by

$$2[Co(CN)_5]^{3-} + 2CN^- + 2H_2O + O_2 = 2[Co(CN)_6]^{3-} + 2OH^- + H_2O_2$$

(*341, 369, 526*). On the other hand, it was found that when the oxidation is carried out slowly, the oxygen absorbed is only slightly in excess of that required by the first equation, and a correspondingly small amount of hydrogen peroxide is formed.

Examination of the product obtained when oxygen is bubbled rapidly into a solution containing Co(II) and CN^- in 1:5 ratio shows that it is the brown peroxy complex $K_6[(NC)_5CoO_2Co(CN)_5]\cdot H_2O$, which may be isolated by addition of ethanol and purified by recrystallization from KOH solution (*33, 34, 211*). It was reported earlier (*478*) that this compound (then obtained by air oxidation of moist $K_6[Co_2(CN)_{10}]$), was $K_3[Co(CN)_5$-

$OH]\cdot H_2O$, but this formula is no longer tenable (*211*).* Detailed instructions for the preparation of the tetrahydrate and anhydrous compound have recently been given (*33*). The binuclear peroxy compound oxidizes the ion $[Co(CN)_5]^{3-}$, with formation of $[Co(CN)_5H_2O]^{2-}$ according to the equation

$$[(NC)_5CoO_2Co(CN)_5]^{6-} + 2[Co(CN)_5]^{3-} + 6H_2O = 4[Co(CN)_5H_2O]^{2-} + 4OH^-$$

When air is passed slowly through a solution containing the $[Co(CN)_5]^{3-}$ ion at 25°C, therefore, the net reaction is (*211*)

$$4[Co(CN)_5]^{3-} + O_2 + 6H_2O = 4[Co(CN)_5H_2O]^{2-} + 4OH^-$$

as may be shown by the absorption spectrum of the resulting solution. If $Co(II){:}CN^-$ is 1:50, some 25% of $[Co(CN)_6]^{3-}$ is formed (*211*), but at room temperature this is always a minor product; uptake of the sixth cyanide by $[Co(CN)_5H_2O]^{2-}$ is a slow process (*295*, *378*). At 95°C, however, conversion into $[Co(CN)_6]^{3-}$ is rapid [(*478*) but see (*33*, *211*)]. It is clear, then, that in the conventional preparation of $K_3[Co(CN)_6]$, which involves boiling in aqueous solution, one possible route involving oxygenation is:

$$[Co(CN)_5]^{3-} \xrightarrow{O_2} [(NC)_5CoO_2Co(CN)_5]^{6-} \xrightarrow{Co(CN)_5^{3-}} [Co(CN)_5H_2O]^{2-} \xrightarrow{CN^-} [Co(CN)_6]^{3-}$$

(For the decomposition of water by the $[Co(CN)_5]^{3-}$ ion see the following section.)

The peroxy complex, which has an absorption maximum at 327 mμ, is rapidly decomposed by acid, first with formation of the species $[(NC)_5Co^{III}\cdot OOH\cdot Co^{III}(CN)_5]^{5-}$ (maximum at 300 mμ), then of $[Co(CN)_5H_2O]^{2-}$ (maximum at 380 mμ) and $[Co(CN)_5OOH]^{3-}$ (maximum at 272 mμ), and finally of $2[Co(CN)_5H_2O]^{2-}$ and hydrogen peroxide (*33*, *35*). The mononuclear peroxy ion, which is also formed from the hydride complex $[Co(CN)_5H]^{3-}$ and oxygen (*33*), may be isolated as the potassium salt $K_3[Co(CN)_5OOH]$ (contaminated with a small amount of $K_2[Co(CN)_5H_2O]$) by precipitation with methanol and acetone (*35*).

Three other species are also formed in small amounts by the action of

* The ion $[Co(CN)_5OH]^{3-}$ has often been mentioned in connection with the oxidation or aging of $[Co(CN)_5]^{3-}$(aq). The absorption spectrum of $[Co(CN)_5H_2O]^{2-}$ is constant from pH 1 to 10 but in 1 *M* KOH the 380-mμ band moves slowly to about 371 mμ (*33*). A spectrophotometric determination, however, gives K_a for $[Co(CN)_5H_2O]^{2-}$ as 2×10^{-10} (*212*). When $K_2[Co(CN)_5]\cdot H_2O$ solution is allowed to stand, species having absorption maxima at 368 and 353 mμ are produced; these bands may be due to the hydroxypentacyano complex and a polymer of the aquopentacyano compound, respectively (*33*), but this point has not been firmly established. For the present it seems best to represent any species having a maximum at 380 mμ as $[Co(CN)_5H_2O]^{2-} + OH^-$ rather than as $[Co(CN)_5OH]^{3-} + H_2O$. The fact that claims to have isolated a solid derivative of the hydroxy complex (*478*) are untenable (*211*) is, of course, no proof that the ion is not a well-defined species in alkaline solution.

oxygen on aqueous $[Co(CN)_5]^{3-}$, but only one of these has been isolated and analyzed. This is the complex $K_5[(NC)_5CoO_2Co(CN)_5]\cdot 5H_2O$, which has an intense absorption band at 310 mμ and is formed to the extent of 2–3%. It may be prepared by the action of bromine on a solution of $K_6[(NC)_5CoO_2Co(CN)_5]$ in aqueous potassium hydroxide at 0°C; on addition of ethanol a red oil separates and later solidifies. Oxidation may also be effected by the use of hypochlorite, persulfate, iodine, hydrogen peroxide, or ferricyanide in alkaline solution (*33, 211*). This compound is paramagnetic (μ = 1.6 B.M.) (*211*) and gives a 15-line e.s.r. spectrum, with a mean g value of 2.02 (*34*), almost identical with that of $[(H_3N)_5CoO_2Co(NH_3)_5]^{5+}$ (*145*), in which it was shown that the unpaired electron interacts equally with both cobalt nuclei; on this basis the formulation as a superoxide derivative of two Co(III) atoms is preferable to the formulation (*33, 34, 211*) as a peroxy complex of Co(III) and Co(IV). The other species, not yet identified, are characterized by their 16-line (center g = 2.18) and 8-line (center g = 2.00) e.s.r. spectra (*34*).

We may now review briefly the action of other oxidizing agents on the $[Co(CN)_5]^{3-}$ ion. When ferricyanide is used, the main product is the reddish yellow ion $[(NC)_5CoNCFe(CN)_5]^{6-}$, characterized as the barium salt and oxidized to $[(NC)_5CoNCFe(CN)_5]^{5-}$ ion by iodine (this change is reversed by sulfite). The first binuclear anion is hydrolyzed to $[Fe(CN)_6]^{4-}$ and $[Co(CN)_5H_2O]^{2-}$ by heating for 8 hours at 80°C (*211*). [Earlier polarographic work (*256*) which indicated that these products were rapidly formed on addition of $[Fe(CN)_6]^{3-}$ to $[Co(CN)_5]^{3-}$ could not be repeated (*211*).] Bridged species of this kind are now well established as intermediates in many redox processes (*490*), but this one is of unusual stability.

Hydrogen peroxide and persulfate with $[Co(CN)_5]^{3-}$ give only $[Co(CN)_5H_2O]^{2-}$; if any sulfato complex is formed it must be very rapidly hydrolyzed. In this case an outer-sphere, rather than a bridged, activated complex seems likely (*211*).

6. *The Action of Hydrogen and Reducing Agents on $[Co(CN)_5]^{3-}$ and the Aging of the Ion in Solution:*

Freshly prepared solutions of $K_3[Co(CN)_5]$ absorb up to half a mole of hydrogen per mole of complex (*260, 295, 361*), with substantial reduction in paramagnetic susceptibility (*361*). Complete conversion to hydrido species is obtained by reduction with borohydride (*200, 295*); electrolytic reduction is said to produce a similar result (*295*). The colorless solution from borohydride reduction shows a maximum at 305 mμ and a proton resonance characteristic of hydrogen bonded to a metal (*200, 295*). Preliminary polarographic data (*506*) were said to indicate no change in the number of cyanides per cobalt; but the same author in a recent review (*507*) discussing the oxidation state of the ion gives no details of this evidence and merely states that $[Co(CN)_5H]^{3-}$ is assumed to be formed. Furthermore, titration of $Co^{2+}(aq)$ with CN^- in dilute solution in an atmosphere of hydrogen with vigorous stirring gave an end point at 1:4.5; species other than a pentacyanide must therefore be formed under these conditions (*33a*). No solid compound has yet been isolated; addition of ethanol, for example, results in liberation of hydrogen and separation of $K_6[Co_2(CN)_{10}]$ (*200, 295*). Decomposition also takes place when the solution is warmed, H_2 and $[Co(CN)_5]^{3-}$ (identified by its band at 967 mμ) being produced (*295*).

When solutions of $[Co(CN)_5]^{3-}$ are allowed to "age," their paramagnetism disappears, very slowly in the case of dilute solutions but much more rapidly at 0.1 *M* or higher concentrations (*361*). In the case of a dilute solution containing Cs^+ (which promotes aging) the 305-mμ hydride species and a species having a maximum at 380 mμ, apparently $[Co(CN)_5H_2O]^{2-}$, are formed (*295*):

$$2[Co(CN)_5]^{3-} + 2H_2O = [Co(CN)_5H]^{3-} + [Co(CN)_5H_2O]^{2-} + OH^-$$

(The aquopentacyano ion may also undergo polymerization.)

Since the hydride decomposes when its solution is heated, this reaction may be an intermediate stage in the over-all change which takes place on heating a solution of $K_3[Co(CN)_5]$ in the absence of air and in the presence of excess of cyanide (which substitutes in $[Co(CN)_5H_2O]^{2-}$ quite rapidly at higher temperatures):

$$2[Co(CN)_5]^{3-} + 2CN^- + 2H_2O = 2[Co(CN)_6]^{3-} + H_2 + 2OH^-$$

Manchot and Herzog (*341*) showed many years ago that when a deaerated solution of $K_3[Co(CN)_5]$ in the presence of excess of cyanide is boiled, a volume of hydrogen indicated by the above equation is evolved.

It may be noted that the orange species (with absorption maxima at 267 and 285 mμ) which is formed in considerable amount during the conventional preparation of potassium cobalticyanide (*33*) has been detected, together with $[Co(CN)_6]^{3-}$, after prolonged aging (*294*) but not in the reaction of $[Co(CN)_5]^{3-}$ and O_2 (*33*).

The kinetics of hydrogenation of $[Co(CN)_5]^{3-}$ have recently been investigated (*129, 295, 361*). In the most recent work it has been found that in solutions of high ionic strength in which $([Co(CN)_5]^{3-})$ is low and $[CN^-]$ is high this process, like that of decay, is second order with respect to $[Co(CN)_5]^{3-}$, and the scheme

$$\begin{tikzcd}
 & {[Co(CN)_5H]^{3-} + [Co(CN)_5H_2O]^{2-} + OH^-} \\
{2[Co(CN)_5]^{3-}} \arrow[r, shift left] & {[Co_2(CN)_{10}]^{6-}} \arrow[l, shift left] \arrow[u, "H_2O"] \arrow[d, "H_2"'] \\
 & {2[Co(CN)_5H]^{3-}}
\end{tikzcd}$$

is suggested to illustrate the relationship between the processes (*129*). It is interesting to note that the activation of hydrogen by Ag^+(aq) and Cu^+ (in quinoline) also shows third-order kinetics (*88, 515, 532*), and is believed to proceed by homolytic fission of the hydrogen molecule. For the equilibrium

$$2[Co(CN)_5]^{3-} + H_2 \rightleftharpoons 2[Co(CN)_5H]^{3-}$$

K_c decreases from 930 at 0°C to 82 at 35°C in a solution 0.86 M with respect to KCN and 0.004 M with respect to $CoCl_2$, and from 590 at 0°C to 60 at 35°C for one 1.0 M in NaOH, 0.065 M in KCN, and 0.002 M in $CoCl_2$. For both media ΔH is -11.2 kcal per mole of H_2 absorbed (*129*).

Some interest has recently been shown in solutions of $[Co(CN)_5]^{3-}$ as hydrogenation catalysts for organic compounds (e.g., *128, 316*), but it is not intended to review this topic here.

7. *Substituted Cyanide Complexes*

Reference has already been made to many substituted cyanide complexes, but for the sake of comparisons such species are mentioned again here with cross-references, the ligands dealt with being H_2O, NH_3, Cl, Br, I, CO, NO, SCN, NCSe, benzyl, C_2F_4, and C_2H_3. Vitamin B_{12} is a monocyano complex of Co(III), but we have had to exclude its chemistry from discussion here; reference may be made to those recent papers (*240a, 240b, 422a*) in which its properties and reactions are described.

a. Aquo Complexes. There is no convincing evidence for the existence of aquo-substituted cyanide complexes of Co(II); the preparation and properties of the ion $[Co(CN)_5]^{3-}$ and the solid compound $K_6[Co_2(CN)_{10}]$ have been described in Section VIII,A,3.

The ion $[Co(CN)_5H_2O]^{2-}$ is, on the other hand, well known. It was first characterized (*427*) in the silver salt, obtained as a yellow precipitate on addition of silver nitrate to the solution prepared by the action of hydrogen peroxide on the complex $K_4[Co(CN)_5S_2O_3]$, which is made (*425*) from aqueous cyanide and $[Co(NH_3)_5S_2O_3]Cl$; from this the hygroscopic potassium salt and the free acid were made by the action of potassium iodide and hydriodic acid, respectively. The deep blue product obtained by dehydration of $Ag_2[Co(CN)_5]\cdot H_2O$ was originally believed to be $Ag_2[Co(CN)_5]$, but later work (*211*) showed some decomposition to have taken place; the pure anhydrous compound is yellow-green.

As described earlier, the aquopentacyano ion is also obtained by peroxide or persulfate oxidation of $[Co(CN)_5]^{3-}$. It has an absorption maximum at 380 mμ. Both the ion in aqueous solution on standing and the solid silver salt on dehydration are believed to polymerize, the 380-mμ band moving to 350 mμ; the pH of the solution is unchanged (*211*). Other workers report that a band near 368 or 353 mμ is formed when the ion is allowed to stand in aqueous solution (*33*).

Recently it has been shown that the potassium salt can conveniently be made by irradiation of $K_3[Co(CN)_6]$ solution with a mercury lamp, filtering out the 254-mμ band. The resulting liquid is poured into acetone, when $K_2[Co(CN)_5H_2O]$ separates as a yellow oil which is purified by dissolution in water and precipitation with methanol at 0°C (*33*). The action of sodium borohydride in solution slowly gives the $[Co(CN)_5H]^{3-}$ ion at pH 9; CO, H_2S, and chloride ion have no effect at room temperature. The absorption of the freshly dissolved salt at 380 mμ is independent of pH between pH 1 and 10. The stability of the compound depends very markedly on its purity.

The diaquotetracyano complex $K[Co(CN)_4(H_2O)_2]$, the corresponding sodium and silver salts, and the free acid were also described briefly several years ago (*428*); the sulfito complex $Na_5[Co(CN)_4(SO_3)_2]$ is oxidized to the sulfato complex by nitric acid and converted into the diaquo complex by the action of water. Very little is known about the properties of these substances.

b. Ammine Complexes. Cyanide usually replaces coordinated ammonia more readily than other groups, and only a few substances containing both groups are known at the present time. Salts of the ion $[Co(NH_3)_5CN]^{2+}$ are obtained via the complex $[Co(NH_3)_4(CN)(SO_3)]$ from cobalt(II) sulfate, ammonia, cyanide, and bisulfite (*475*), and the action of ammonia and hydrogen peroxide on the complex $K_6[Co_2SO_2(CN)_{10}]$, made from cobalt(II) acetate, hydrocyanic acid, and potassium sulfite, is reported to give $K_2[Co(CN)_5NH_3]\cdot 3H_2O$ (*91*).

Recently, the action of potassium cyanide, ammonia, and ammonium chloride on the complex carbonate $K_3Co(CO)_3$ in the presence of charcoal has been used to obtain the compounds $[Co(NH_3)_5CN]Cl_2$ and $[Co(CN)_3(NH_3)_3]$ (*471a*). That the latter compound is not $[Co(NH_3)_6][Co(CN)_6]$ has not yet, however, been established with certainty.

c. Halogen Complexes. Potassium bromopentacyanocobaltate(III), $K_3[Co(CN)_5Br]$, may be obtained by the action of cyanide on the compound $[Co(NH_3)_5Br]Br_2$ or by adding $K_3[Co(CN)_5]$ solution to bromine water; addition of ethanol then precipitates a light brown powder, although by neither method is an analytically pure product obtained. Iodine may replace bromine in the second method, giving red-brown $K_3[Co(CN)_5I]$; chlorine appears to give some yellow $K_3[Co(CN)_5Cl]$, but the main product is $K_3[Co(CN)_6]$ (*2*). The iodo complex has also been obtained from $K_6[Co_2SO_2(CN)_{10}]$ and iodine (*91*). Mechanistic features of these substitutions are mentioned in the following section.

The photochemical aquation of the four ions $[Co(CN)_5X]^{3-}$ where

X = I, CN, Br, Cl, has been studied; the quantum yield decreases significantly along this series; it is suggested that the first step in these reactions is homolytic fission (*3*).

d. Carbonyl Complexes. Mention was made earlier of the possible existence of a carbonyl cyanide complex of Co(0) and of the ion $[Co(CN)_3(CO)]^{2-}$, a derivative of Co(I). No carbonylpentacyano complex of Co(II) or Co(III) has been satisfactorily characterized. The action of carbon monoxide on a mixture of cobalt(II) and potassium acetates in potassium cyanide solution was reported (*338*) to yield $K_3[Co(CN)_5CO]$, but later workers (*235*) believed the product, which was diamagnetic (*298*), was really a mixture of $K_3[Co(CN)_6]$ and $K[Co(CO)_4]$. No carbonyl compound was obtained from CO and $K_2[Co(CN)_5H_2O]$, and all other attempts to obtain the ion $[Co(CN)_5CO]^{2-}$ have been unsuccessful (*235*).

e. Nitrosyl Complexes. The chemistry of nitrosocyano complexes of cobalt is in a confused state. The carbonyl nitrosyl $[Co(CO)_3NO]$ has been said (*393*) to react with methanolic KCN to give impure $K[Co(CN)(CO)_2NO]$, a diamagnetic red-brown solid, which when heated with aqueous cyanide gives a solution containing the $[Co(CN)_3NO]^{3-}$ ion; nothing more has been heard of these species, however. In the same paper (*393*) the black nitrosopentammine $[Co(NH_3)_5NO]Cl_2$ was described as giving yellow diamagnetic $K_3[Co(CN)_5NO]\cdot 2H_2O$ by reaction with aqueous cyanide; formulation of the complex as a NO^- derivative of Co(III) was supported by detailed spectroscopic studies (*194*, *197*), and it was shown that the same substance is obtained from the red nitrosopentammine complex (which also contains the NO^- group). Soon afterwards, however, a further communication (*396*) stated that the original analytical results were erroneous, and that new analyses and cryoscopic measurements indicated that the compound was really $K_2[HCo(CN)_5NO]$, but that this is converted by 50% KOH into $K_3[Co(CN)_5NO]$. Finally, it has been reported briefly (*395*) that nitric oxide reacts with $K_2[HCo(CN)_5]$ solution to yield $K_2[HCo(CN)_5NO]\cdot 2H_2O$ and that in the presence of strong alkali $K_3[Co(CN)_5NO]\cdot 2H_2O$ is obtained. No nuclear magnetic resonance study, which might show the proton to be bonded to cobalt, has been made; further work is clearly needed.

f. Thiocyanate and Isoselenocyanate Complexes. The compound $K_3[Co(CN)_5SCN]$ has been obtained as a pale yellow solid by the Co(II)-catalyzed displacement of ammonia from $[Co(NH_3)_5NCS]SO_4$ by cyanide in aqueous solution at room temperature; infrared evidence shows that the cobalt in the product is bonded to sulfur, and a bridged intermediate $[(NH_3)_5Co^{III}\text{-}NCSCo^{II}(CN)_5]^-$ therefore seems highly probable [(*84*); see also (*92*)]. A brown compound formulated as $K_4[Co_2(CN)_8(SCN)_2]\cdot 5H_2O$ has been isolated from the interaction of $[Co(CN)_5]^{3-}$ and $K_2[Hg(SCN)_4]$; on the basis of its infrared spectrum in the C≡N stretching region it has been suggested that the bridging groups are thiocyanates. Substitution of selenocyanate in the above reactions results in the formation of $K_2[Co(CN)_5H_2O]$ and $K_3[Co(CN)_5NCSe]$ respectively. The infrared spectrum of the latter indicates that cobalt is bonded to nitrogen rather than to selenium (*84a*).

g. Alkyl and Benzyl Complexes. The $[Co(CN)_5]^{3-}$ ion has recently been shown to react with alkyl or benzyl halides in aqueous media. When benzyl bromide is used, fractional precipitation and recrystallization from alcoholic solution lead to the isolation of the yellow, somewhat deliquescent water-soluble $Na_3[C_6H_5CH_2Co(CN)_5]\cdot 2H_2O$, stable in alkaline solution and undergoing no reaction with $NaBH_4$ or CO. The ultraviolet spectrum of the methyl compound resembles that of other pentacyanocobaltates, and a band at 318 mμ suggests that the ligand field strength of CH_3 approaches that of CN^-, at least in this compound (λ_{max} for $[Co(CN)_6]^{3-}$ is at 311 mμ) (*214*). Other alkyl derivatives have been made by adding activated olefins to the $[Co(CN)_5H]^{3-}$ ion and by its reaction with alkyl halides, and the protonation of the resulting complexes has been studied (*315a*).

Stable complexes $K_3[(NC)_5CoCF_2CF_2H]$ and $K_6[(NC)_5CoCF_2CF_2Co(CN)_5]\cdot 2H_2O$ have recently been made by the action of C_2F_4 on $K_3[Co(CN)_5H]$ and $K_3[Co(CN)_5]$ in aqueous solution (*351a*). In the former compound the axial Co—C (cyanide) bond length (1.93 Å) appears to be significantly longer than the average equatorial Co—C (cyanide) distance (1.89 Å) (*349a*).

h. Acetylene Complexes. The compound $K_6[Co_2(CN)_{10}C_2H_2]\cdot 4H_2O$ is obtained by the action of acetylene on $K_3[Co(CN)_5]$ solution. It is diamagnetic. Infrared and proton magnetic resonance studies show that the carbon-carbon bond is olefinic, and a *trans* structure is suggested (*199*).

8. *The Mechanism of Reactions of Cobalt(III) Complexes with Cyanide*

The preparation of $[Co(CN)_5Br]^{3-}$ by interaction of $[Co(NH_3)_5Br]^{2+}$ and CN^- cannot involve displacement and replacement of bromine since the aquo complex is stable with respect to substitution by bromide (*2*). The reaction is very fast in alkaline solution but quite slow at pH 5, and is catalyzed by $Co^{2+}(aq)$ so long as this is added to the solution of the bromo complex and not to that of the cyanide (in the latter case oxidation presumably intervenes). Catalyzed substitution is suggested to take the path

$$[Co(CN)_5]^{3-} + [Co(NH_3)_5X]^{2+} = [Co(CN)_5X]^{3-} + [Co(NH_3)_5]^{2+}$$

$$[Co(NH_3)_5]^{2+} + 5CN^- = [Co(CN)_5]^{3-} + 5NH_3$$

a reasonable route since Co(II) complexes are substitution-labile, whereas those of Co(III) generally substitute much more slowly. It was suggested that substitution in the absence of added catalyst involved Co(II) impurity.

Later work (*93*, *378*) showed that $[Co(NH_3)_6]^{3+}$ in dilute solution is inert toward cyanide at room temperature except when $[CN^-]$ is very high; the fact that the chloro- and aquo-pentammine complexes react much faster, forming pentacyano species, suggests that aquation of the hexammine is the slowest step. Addition of potassium hydroxide to the cyanide solution slows down substitution (*378*); it has been argued that since even in a solution 0.05 *M* with respect to both OH^- and CN^- a pentacyano complex is still formed, CN^- may, in certain circumstances, be a better nucleophilic reagent than OH^- for substitution at a Co(III) atom. This suggestion has received support from kinetic studies (*252*) of the rates of attack of these two ions on a sexadentate Co(III) complex. In these experiments on ammine complexes in dilute aqueous solution, substitution was very slow after five cyanides had been taken up; in more concentrated solutions, however, hexamminecobaltic chloride, even at room temperature, yields a precipitate of $[Co(NH_3)_6][Co(CN)_6]$ (*61*). Under these conditions, the reaction has been suggested to involve slow formation of $[Co(NH_3)_5CN]^{2+}$, followed by cyanide transfer to $[Co(CN)_5]^{3-}$ (*61*), although how the latter ion comes to be present in an aqueous solution of $[Co(NH_3)_6]Cl_3$ and NaCN exposed to the atmosphere is not clear. One possible explanation would involve reduction of the Co(III) complex to Co(II) by cyanide, and catalytic action of this.

Although the kinetics of the reaction between $[Co(CN)_5H_2O]^{2-}$ and CN^- have not been investigated, information is available on those of the complex and N_3^-, SCN^-, and H_2O^{18}, and of the replacement of N_3^- in $[Co(CN)_5N_3]^{3-}$ by H_2O or SCN^-. In each case the mechanism appears to involve a dissociative pre-equilibrium to give $[Co(CN)_5]^{2-}$, followed by competition for this by the anions present (*212*, *213*). It seems likely, therefore, that the formation of $[Co(CN)_6]^{3-}$ from $[Co(CN)_5H_2O]^{2-}$ also involves loss of coordinated water as an intermediate step.

An important preliminary communication on the kinetics of $[Co(CN)_5]^{3-}$ ion-catalyzed reactions of cyanide with species $[Co(NH_3)_5X]$ (where X may be one of a large number of ligands) has recently appeared (*92*). For $X = Cl^-$, N_3^-, SCN^-, or OH^-, the stoichiometry of the reaction is

$$[Co^{III}(NH_3)_5X] + 5CN^- = [Co^{III}(CN)_5X] + 5NH_3$$

and the rate is proportional to $[Co(NH_3)_5X][Co(CN)_5{}^{3-}]$, suggesting a bridged intermediate $[(NC)_5Co^{II}—X—Co^{III}(NH_3)_5]$. Rate constants decrease from 5×10^7 (Cl^-) to 9×10^4 (OH^-) $mole^{-1}sec^{-1}$. For $X = PO_4{}^{3-}$, $CO_3{}^{2-}$, OAc^-, $SO_4{}^{2-}$, or NH_3, the reaction follows the course

$$[Co^{III}(NH_3)_5X] + 6CN^- = [Co^{III}(CN)_6]^{3-} + 5NH_3 + X$$

and the rate is proportional to $[Co(NH_3)_5X][Co(CN)_5{}^{3-}][CN^-]$. In this case outer-sphere electron transfer between $[Co(CN)_6]^{4-}$ (formed in the solution) and $[Co^{III}(NH_3)_5X]$ is postulated:

$$\begin{array}{c}
[Co^{II}(CN)_5]^{3-} + CN^- \rightleftharpoons [Co^{II}(CN)_6]^{4-} \\
[Co^{II}(CN)_6]^{4-} + [Co^{III}(NH_3)_5X] = [(NC)_5Co^{II}(CN){-}X{-}Co^{III}(NH_3)_5] \\
\downarrow \\
[Co^{III}(CN)_6]^{3-} + [Co^{II}(NH_3)_5X]
\end{array}$$

Rate constants increase from 5×10^2 ($PO_4{}^{3-}$) to 8×10^4 mole^{-2} sec^{-1} (NH_3). For $X = F^-$, $NO_2{}^-$ (N-bonded), and CN^-, rate constants are about the same for both routes [(*92, 214a*); see also (*84*)]; thus for $[Co(NH_3)_5CN]^{2+}$ at 0.03 M CN^-, the inner-sphere path accounts for about 70% of the reaction. Evidence for the transient intermediates $[Co(CN)_5ONO]^{3-}$ and $[Co(CN)_5NC]^{3-}$ has been obtained (*214a*).

Since replacement of, for example, the six molecules of ammonia in $[Co(NH_3)_6]^{3+}$ obviously involves many stages, the interaction of cyanide and a species such as *trans*-$[Co(en)_2Cl_2]^+$ might seem to offer a simpler system for investigation. Recent work (*95*), however, shows that this is not so. In concentrated solution, $[Co(en)_3Cl_3]$ and an unidentified orange compound are observed at 0°C, though in the presence of cobalt(II) chloride the $[Co(CN)_5Cl]^{3-}$ ion is formed, just as in the preparative reaction between $[Co(NH_3)_5Cl]^{2+}$ and cyanide (*2*).

Charcoal catalysis of the otherwise extremely slow reaction between $[Co(NH_3)_6]^{3+}$ and cyanide in dilute solution has been observed (*378*). Such catalysis is, of course, a common feature of the preparative chemistry of cobalt(III) complexes. In the light of the part played by Co(II) catalysis in cyanide substitutions, it is tempting to attribute its action to the formation of labile Co(II) complexes which then serve as intermediates. No conclusion can be reached on this point: evidence is available both for (*141*) and against (*485*) this view.

This section has been concerned with reactions which may be represented formally as substitution of cyanide into cobalt(III) complexes. That catalysis by Co(II) cyanide complexes plays an important part in many of these processes is established beyond doubt, but the present writers are not convinced that *all* such substitutions involve intermediates of this kind. The study of substitutions in the presence of oxidizing agents might provide useful evidence on this matter.

B. RHODIUM

A number of workers have found evidence for the formation of complex cyanides of low oxidation states of rhodium by reduction of $K_3[Rh(CN)_6]$ with potassium in liquid ammonia (*200*), hypophosphite (*345*), or electrolytically (*531*) [though see also (*116*)]; in no case, however, has a definite species been isolated or adequately characterized. It is worth remembering that the final product of reduction of $[Co(CN)_6]^{3-}$ in aqueous solution is a hydride of Co(III).

Rhodium(III)

The colorless very soluble $K_3[Rh(CN)_6]$ may be made by fusing the ammine $[Rh(NH_3)_5Cl]Cl_2$ with KCN (*312*, *463*). Addition of cyanide to a solution of rhodium trichloride gives a precipitate which dissolves in excess, but whether the hexacyano anion or a pentacyano species results has not been established. The $[Rh(CN)_6]^{3-}$ ion is unreactive, but warm sulfuric acid effects decomposition to a yellow-brown hydrate of $Rh(CN)_3$; this, however, is insoluble in cyanide solution, and is therefore presumably a polymer. Borohydride reduction of the solution obtained from $RhCl_3$ and excess of KCN gives a hydride complex, but no solid has been isolated (*200*); by the action of cyanide on the compound $Rh(CO)_2Cl$, however, $K_2[Rh(CN)_4H(H_2O)]$ may be obtained (*319a*).

The salt $K_3[Rh(CN)_6]$ is isomorphous with $K_3[Fe(CN)_6]$ (*137*). The visible and ultraviolet spectra in solution have recently been measured and Δ estimated as 45,500 cm^{-1} (*463*). The results of infrared studies (*280*, *281a*) were mentioned at the beginning of Section VIII; the Raman spectrum has also been reported (*350*). The acid $H_3[Rh(CN)_6]$ (and $H_3[Ir(CN)_6]$) may be prepared from the potassium salt by the hydrochloric acid-ether method; both compounds give infrared spectra almost identical with that of $H_3[Co(CN)_6]$, and identical interpretations have been suggested (*156*).

C. IRIDIUM

The only known complex cyanides of this element are those of iridium(III).

Iridium(III)

Fusion of $(NH_4)_3[IrCl_6]$ with KCN, followed by crystallization from water, gives very pale yellow $K_3[Ir(CN)_6]$ (*349*, *442*). Recently, detailed preparative instructions using $K_3[IrCl_6]$, said to be by far the best starting material, have been given (*513*); use of other compounds apparently often leads to extensive deposition of elemental iridium. $K_3[Ir(CN)_6]$ is isomorphous with $K_3[Fe(CN)_6]$: for the orthorhombic unit cell, $a = 13.73$, $b = 10.55$, $c = 8.36$ Å [(*183*) see also (*299*)]. The complex is decomposed by hot sulfuric acid with formation of a brown product, probably $Ir(CN)_3$ or a hydrate; halogens and acids are without action on the ion $[Ir(CN)_6]^{3-}$ in aqueous solution. Raman (*350*) and infrared (*280*, *281a*) spectra of

$K_3[Ir(CN)_6]$ have been reported; C≡N and Ir—C stretching frequencies in the infrared spectrum and force constants have been discussed earlier. The visible and ultraviolet spectra of $[Ir(CN)_6]^{3-}$ have been reported (*456*). $K_3[Ir(CN)_6]$ is not reduced by potassium in ammonia at −33°C (*513*), in contrast to $K_3[Co(CN)_6]$ and, apparently, $K_3[Rh(CN)_6]$.

Mention has been made (*187*) of unpublished work on the interaction of $K_3[Ir(CN)_6]$ and borohydride in aqueous solution, which are said to yield a hydride complex, but no details have been reported.

IX. Nickel, Palladium, and Platinum

The oxidation states attained by these elements in cyano compounds present an interesting picture. Nickel forms one definite cyanide, $Ni(CN)_2$, and probably another, NiCN; among complex ions, $[Ni^0(CN)_4]^{4-}$, $[Ni_2^I(CN)_6]^{4-}$, and $[Ni^{II}(CN)_4]^{2-}$ may be obtained in stable salts. In aqueous solution $[Ni(CN)_4]^{2-}$ reacts with cyanide to form $[Ni(CN)_5]^{3-}$ (or $[Ni(CN)_5H_2O]^{3-}$). Palladium forms $[Pd(CN)_4]^{4-}$ and $[Pd(CN)_4]^{2-}$; reduction of the latter species yields a product which may be a derivative of Pd(I) or a hydride complex. Only one incomplete attempt seems to have been made to prepare derivatives of Pt(0) or Pt(I), but many compounds of Pt(II) are well known, and several cyanide complexes of Pt(IV) have recently been obtained.

Unlike $[Ni(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$ do not interact with cyanide in aqueous solution to an extent sufficient to permit the detection of five-coordinated species by the infrared technique, though the possible formation of such species as reaction intermediates (e.g., in the rapid exchange of the four-coordinated ions with labeled cyanide) cannot be excluded.

Little is known of the structures of the binary cyanides. The diamagnetic $[Ni(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$, and $[Pt(CN)_4]^{2-}$ ions, however, are known to be planar in their salts, and corresponding compounds are generally isomorphous (*71, 72, 73, 317, 368, 504a*). In view of the large uncertainty in atomic positions nothing can be said about bond lengths, but it does seem clear that the unit cells of platinum compounds are smaller than those of the isomorphous palladium compounds. It is interesting to note in this connection that Raman data apparently indicate (*418*) that here, as in other groups, the heavier element forms a stronger bond than the middle one.

The planar structure and diamagnetism of the $[M(CN)_4]^{2-}$ ions are simply interpreted on crystal field theory as the limit of tetragonal distortion of an octahedral complex, the $d_{x^2-y^2}$ orbital being empty; it must, however, be noted that no square-planar complex can be treated adequately on a purely electrostatic basis, and it is noteworthy that in the case of Ni(II), planar complexes are formed only with ligands that have the ability to form strong π-bonds. Furthermore, whereas considerable success has been obtained in the analysis of the visible and ultraviolet absorption spectra of octahedral Ni(II) complexes and such measurements have become of great importance, the interpretation of planar M(II) spectra is difficult and subject to much disagreement (see for example (*21a, 185, 287, 414*) and references therein).

Further discussion of cyanide complexes of these elements in relation to theoretical considerations and stereochemistry is considered in a recent review by Miller (*360*), who describes in detail some of the structures only briefly mentioned here.

A. NICKEL

1. *Nickel(0)*

The compound $K_4[Ni(CN)_4]$ is obtained when $K_2[Ni(CN)_4]$ is reduced by excess of potassium in liquid ammonia (*142*). It is also formed, in poor yield, by heating $K_2[Ni(CN)_4]$ with KCN at 480°C, when cyanogen is evolved, or by heating a mixture of nickel powder, mercuric cyanide, and potassium cyanide *in vacuo* at 500°C (*510*). When dry, $K_4[Ni(CN)_4]$ is copper-colored; it blackens in air, and decomposes water. Treated with carbon monoxide in liquid ammonia, it gives the yellow salt $K_2[Ni(CN)_2(CO)_2]$ (*394*).

The structure of the $[Ni(CN)_4]^{4-}$ ion is generally believed to be tetrahedral, like that of the isoelectronic species $Ni(CO)_4$, though no detailed structural investigation has been reported. The C≡N stretching frequency region in the infrared, at least if rock salt optics are used, shows only one band at 1985 cm^{-1}, well below that in $[Ni(CN)_4]^{2-}$, and it has been suggested that this indicates a lower C≡N and a higher Ni—C bond order, the latter being required to remove the high formal negative charge from the metal atom (*147*).

The nitrosyl complex $K_2[Ni(CN)_3NO]$, a NO^+ derivative of Ni(0), as is shown by a band at 1780 cm^{-1} indicative of NO^+ in the infrared spectrum (*198*), is obtained by the action of nitric oxide on $K_4[Ni_2(CN)_6]$ in liquid ammonia (*237*); this substance is diamagnetic and the presence of a mononuclear anion has been shown by cryoscopy (*384*).

2. *Nickel(I)*

What is said to be nickel(I) cyanide, though adequate analytical data are lacking, is obtained as an orange precipitate by the action of acids on aqueous solutions of $K_4[Ni_2(CN)_6]$. Air oxidizes it to nickel(II) cyanide and oxide; carbon monoxide forms a yellow adduct; aqueous cyanide regenerates the complex anion (*40, 41*).

The complex $K_4[Ni_2(CN)_6]$, often known as "Bellucci's salt," is made by reduction of an aqueous solution of $K_2[Ni(CN)_4]$ with sodium or potassium amalgam, or electrolytically, under an atmosphere of hydrogen; the dark red nickel(I) derivative is precipitated by addition of ethanol (*40, 41, 142, 207*). Potassium in liquid ammonia may also be used as the reducing agent; in this case excess of the nickel(II) complex must be taken in order to avoid formation of $K_4[Ni(CN)_4]$ (*142, 144, 512*).

The diamagnetism of the complex in aqueous solution (*354, 486*), and also cryoscopic measurements (*392*), indicate a dimeric anion. X-ray investigations have been said to indicate the presence of bridging cyanide groups (*417*), and the infrared absorption spectrum (in which three bands in the C≡N stretching region were observed) was first interpreted on the assumption that this was indeed the case (*146*). Later workers, however, pointed out that the X-ray evidence for bridging cyanides was not unequivocal and considered that the infrared evidence actually excluded this possibility; a re-examination of the spectrum led to the conclusion that the anion is planar and contains a Ni—Ni bond (*198*). Both examinations were made on nujol mulls using rock salt optics, however, so the possibility of further complications cannot be excluded.

Aqueous solutions of $K_4[Ni_2(CN)_6]$ slowly decompose in the presence of cyanide according to the equation (*443*)

$$[Ni_2(CN)_6]^{4-} + 2H_2O + 2CN^- = 2[Ni(CN)_4]^{2-} + H_2 + 2OH^-$$

In the presence of air, the Ni(II) complex and some hydrogen peroxide are formed, suggesting that a peroxy species may well be an intermediate product.

Carbon monoxide reacts with aqueous $K_4[Ni_2(CN)_6]$, forming an orange solution containing the $[Ni_2(CN)_6(CO)_2]^{4-}$ ion (*268, 339, 390*); the solid potassium salt may be isolated if the reaction is carried out in ammonia (*394*). The structure of this anion, which is isoelectronic with $[Co_2(CN)_8]^{8-}$ and $Co_2(CO)_8$, is uncertain; cryoscopy (*384*) and the diamagnetism of the compound (*394*) establish the dimeric formula in both solution and the solid, but the infrared spectrum of the solid has been interpreted on the basis of both bridged (*389*) and nonbridged (*192*) structures. Until the structure of $K_4[Ni_2(CN)_6]$ is firmly established it will be difficult to reach a decision. Potassium derivatives of alkynes react with the carbon monoxide adduct to give complex alkynes of formula $K_6[Ni_2(C_2R)_8]$ (*389*); in aqueous solution $K_4[Ni_2(CN)_6]$ and acetylene give a compound formulated as $K_4[Ni_2(CN)_6C_2H_2]$ on the basis of its diamagnetism and infrared spectrum (*199*).

Another red nickel(I) complex, $K_3[Ni(CN)_4]$, for which $\mu = 1.73$ B.M., is said to be formed by reduction of $Ni(CN)_2$ in an alkaline solution of $K_2[Ni(CN)_4]$ with hydrazine (*391*), but nothing more is known about it.

3. Nickel(II)

A gray-green or gray-blue precipitate of hydrated nickel(II) cyanide, variously reported to contain 7, 4, 3, or 2 H_2O, is obtained by mixing aqueous solutions of nickel salts and potassium cyanide; it is paramagnetic, with a moment of 2.3 B.M. per nickel atom (*90*). The brownish yellow anhydrous compound may be obtained by heating the hydrate at 140°–200°C (*15*, *56*, *429*); it has never been proved to be diamagnetic, but the moment decreases steadily on dehydration (*68*) and it is likely that a modern determination with precautions to exclude moisture would give a moment of zero.

The constancy of the solubility product of the hydrate (1.7×10^{-9} mole^2 liter^{-2}) whether made from $Ni^{2+}(aq)$ and CN^- or $Ni^{2+}(aq)$ and $[Ni(CN)_4]^{2-}$ led Hume and Kolthoff (*257*) to suggest that the structure is $Ni[Ni(CN)_4]$, and the presence of two types of nickel atom in precipitated nickel cyanide is confirmed by tracer work (*329*). Both of these arguments really apply only to the hydrate, however, which is thus shown to be $[Ni(H_2O)_x]^{2+}[Ni(CN)_4]^{2-}$. The most likely structure for the anhydrous compound would have each nickel coordinated only by either carbon or nitrogen; if this is so, it is unlikely that exchange would take place when hydrated nickel cyanide is heated and then rehydrated, but it would be interesting to have this question settled. A $C{\equiv}N$ stretching frequency of 2176 cm^{-1} in the compound (*148*) has been held (*135*) to suggest the presence of bridging cyanide groups, but this argument in isolation is not a compelling one. (It is also not clear whether the infrared stretching frequency refers to the hydrate or the anhydrous compound.)

Many clathrates of formula $Ni(CN)_2{\cdot}NH_3{\cdot}X$, where X = benzene, thiophene, aniline, etc., have been prepared, and the structure of the benzene complex has been examined by X-ray and spectroscopic methods (*69*, *431*). Half of the nickel atoms are planar four-coordinated by carbon, and half have, in addition to the nitrogen atoms of four cyanides distributed around the metal atom in a plane, two molecules of ammonia completing an octahedral environment. Only nickel atoms of the latter type are in the spin-free state, as is shown by the average magnetic moment of 2.2 B.M. per nickel atom (*90*, *136*, *264*, *304*). The size of the gaps in the structure, which serve to accommodate the organic molecule, is the basis of a novel method for the separation of benzene from its homologs, the molecules of which are too large to be included (*157*). Recently it has been found that metal-ammine cyanonickelates, e.g., $[Cd(NH_3)_6][Ni(CN)_4]$, $[Cu(NH_3)_4][Ni(CN)_4]$ form similar clathrates (*31*). Both ammines (*14*) and ammine hydrates (*16*, *432*) of nickel cyanide have also been reported, and nickel cyanide suspended in liquid ammonia has been shown to react with potassium phenylacetylide to yield the compound $K_2[Ni(C_2Ph)_4]$ (*388*).

Nickel(II) cyanide dissolves readily in aqueous potassium cyanide, and from the solution apricot yellow crystals of $K_2[Ni(CN)_4]\cdot H_2O$, which are monoclinic (*446*), may be obtained; this was the only solid complex found in the system $KCN–Ni(CN)_2–H_2O$ (*111*), though reference to a triclinic trihydrate appears in a structure determination (*73*). The $[Ni(CN)_4]^{2-}$ ion is one of the most stable complexes of nickel (nickel dimethylglyoximate, for instance, is soluble in aqueous cyanide), but hypobromite gives a precipitate of hydrated NiO_2, and *o*-phenanthroline replaces two cyanides (*372*). An aqueous solution of the acid $H_2Ni(CN)_4$ may be obtained by the ion-exchange method, but it quickly decomposes into hydrated nickel cyanide and hydrocyanic acid (*422b*). The $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ ions exchange radioactive nickel with $[Ni(CN)_4]^{2-}$ very rapidly, while exchange with the complex oxalate and tartrate is slow; the effects of neutral salts show that the exchange processes are typical bimolecular reactions between ions (*329*). Exchange of labeled cyanide between $[Ni(CN)_4]^{2-}$ and aqueous cyanide is very fast (*4*, *329*); in view of the formation of higher complexes this is not surprising. The visible and ultraviolet (*21a*, *185*, *286*, *414*), Raman (*350*, *351*, *457*), and infrared (*231*, *332*) spectra of the anion have been reported; the infrared spectra of solid triclinic $Na_2[Ni(CN)_4]\cdot 3H_2O$ and monoclinic $Ba[Ni(CN)_4]\cdot 4H_2O$ have been analyzed in detail, and force constants have been calculated (*332*).

The over-all formation constant of the $[Ni(CN)_4]^{2-}$ ion has only recently been determined accurately as $10^{30.3\pm0.1}$ [(*174*) see also (*100*)] or $10^{30.1\pm0.2}$ (*100*) at 25°C. Older values (*57*) are much lower, and the fact that some of them are quite incompatible with the value for $[Ag(CN)_2]^-$ and the widely used silver ion–cyanide method for the determination of nickel appears to have gone unnoticed for many years. It is interesting to note in retrospect that until 1959 what was in fact the most accurate determination was made by studying the toxicity toward fish of solutions containing Ni^{2+} and CN^- in various ratios (*140*).

It was noticed some 20 years ago that when aqueous solutions of $K_2[Ni(CN)_4]$ and KCN are mixed, heat is evolved and the color changes to a deep red (*454*). No solid compound was isolated, but from spectrophotometric data it was suggested that $[Ni(CN)_6]^{4-}$ was being formed [(*454*); see also (*296*)].

More recently, a detailed study of the $[Ni(CN)_4]^{2-}–CN^-–H_2O$ system has been made by means of infrared spectroscopy (*333*, *409*), and it has been shown that the principal species formed is actually $[Ni(CN)_5]^{3-}$. This has an absorption band at 2103 cm^{-1}, whereas $[Ni(CN)_4]^{2-}$ in aqueous solution absorbs at 2124 cm^{-1}; K_5 is 0.28 ± 0.008 at 25°C and $\mu = 4$; ΔH for the reaction

$$[Ni(CN)_4]^{2-}(aq) + CN^-(aq) = [Ni(CN)_5]^{3-}(aq)$$

is about -3 kcal over the temperature range 15°–35°C. Contrary to an earlier report (*59*), all the solutions are diamagnetic (*409*), and the proton relaxation times of aqueous solutions containing $[Ni(CN)_4]^{2-}$ and CN^- give no indication of the presence of paramagnetic species (*504*). The latest studies (*36*, *105a*) of the $[Ni(CN)_4]^{2-}$–CN^- system in the presence of added salts provide no evidence for the formation of $[Ni(CN)_6]^{4-}$ or $[Ni(CN)_5F]^{4-}$ in solutions containing KF, KCN, and $K_2[Ni(CN)_4]$; iodide and thiocyanate, however, form complexes of the type $[Ni(CN)_4X]^{3-}$. Three C≡N stretching frequencies have been found for the $[Ni(CN)_5]^{3-}$ ion in solution, at 2123, 2103, and 2083 cm^{-1}, and their presence suggests the ion is a square bipyramid (*105a*); whether water occupies a sixth position is unknown.

Like several other complex cyanides, $K_2[Ni(CN)_4]$ forms an adduct with boron trifluoride, four molecules of the latter being taken up; the effect of donation to the halide on the carbon-nitrogen bond is shown by the increase in the C≡N stretching frequency from 2130 to 2245 cm^{-1} (*472*). Potassium acetylides in liquid ammonia give complex acetylides of formula $K_2[Ni(C{\equiv}C{\cdot}R)_4]$ (*388*); this reaction is reversed by the action of aqueous potassium cyanide (*383*). Sulfide ion in aqueous solution is reported to bring about a curious cyanide elimination reaction, resulting in the formation of the yellow salt $K_3[NiS(CN)_3]{\cdot}H_2O$ (*470*).

B. PALLADIUM

1. *Palladium(0)*

Reduction of $K_2[Pd(CN)_4]$ by potassium in liquid ammonia gives yellowish white $K_4[Pd(CN)_4]$, a powerful reducing agent which liberates hydrogen from water (*82*). Very little appears to be known about this compound.

2. *Palladium(II)*

Palladium(II) cyanide is obtained as a yellowish white solid by the interaction of solutions of a Pd(II) compound and mercuric cyanide, or by warming a solution of $K_2[Pd(CN)_4]$ with hydrochloric acid (*18*, *173*). It is diamagnetic and forms adducts with ammonia and many organic bases

(*159*, *161*, *265*). A high $C{\equiv}N$ stretching frequency (2220 cm^{-1}) (*148*) suggests cyanide bridging (*135*).

The complex cyanide $K_2[Pd(CN)_4]$, a diamagnetic colorless solid, may be crystallized as a trihydrate from a solution of palladium(II) cyanide in aqueous potassium cyanide (*55*); it loses water readily in air, and when heated at 100°C forms a monohydrate. $Na_2[Pd(CN)_4]\cdot 3H_2O$ (like the corresponding platinum compound) is isomorphous with $Na_2[Ni(CN)_4]\cdot 3H_2O$ (*73*), but, surprisingly, $K_2[Pd(CN)_4]\cdot H_2O$ (monoclinic form) is not isomorphous with $K_2[Ni(CN)_4]\cdot H_2O$ (*318*). The ion $[Pd(CN)_4]^{2-}$, like $[Ni(CN)_4]^{2-}$, shows a very rapid exchange with labeled cyanide ion (*4*); on treatment with excess of cyanide, however, a 5:1 complex cannot be detected (*434*). It reacts with potassium acetylides in liquid ammonia forming complexes of formula $K_2[Pd(CN)_2(C{\equiv}C{\cdot}R)_2]$ (*387*). The visible and ultraviolet (*285*, *455*), Raman (*350*), and infrared (*148*, *231*, *351*) spectra have been reported; the $C{\equiv}N$ stretching frequency in the infrared is about 2140 cm^{-1}.

The acids $H_2[Pd(CN)_4]$ and $H_2[Pt(CN)_4]$ may be prepared by the hydrochloric acid–ether method; interpretation of the almost identical infrared spectra of these compounds leads to the conclusion, as with other anhydrous acids in which the H:CN ratio is 1:2, that symmetrical hydrogen bonds are present (*156*). Whether these acids are thermodynamically stable with respect to formation of HCN and $M(CN)_2$ is unfortunately not clear—neither solubility products of the binary cyanides, nor formation constants of the anions, are known. (The rapid exchange of CN^- by the anions does not clarify this point because exchange via a 5:1 complex cannot be excluded.)

In the absence of any measured value for the formation constant of $[Pd(CN)_4]^{2-}$ it is, however, interesting to note that since palladium can be determined by addition of a Pd(II)-containing solution to one containing excess of $[Ni(CN)_4]^{2-}$ and titration of the Ni^{2+} liberated with EDTA (*507a*) the over-all constant must be at least about 10^{35}.

Another Pd(II) complex cyanide appears to be formed when palladium metal is heated with $Hg(CN)_2$ and KCN at 550°C or when $K_2[Pd(CN)_4]$ is heated with KCN. This shows an infrared absorption at 2180 cm^{-1}, but nothing more is known about it (*336*).

When a 2% aqueous solution of $Na_2[Pd(CN)_4]$ is reduced with sodium amalgam a yellow solution, which contains free cyanide, is obtained (*344*); this has powerful reducing properties and slowly liberates hydrogen, giving palladium metal and a solution containing Pd(II). It may contain a Pd(I) compound, or it may contain a hydride; brief reference has been made (*187*) to unpublished work on the formation of hydride species by the action of borohydride on $Na_2[Pd(CN)_4]$ solution.

C. PLATINUM

1. *Platinum(II)*

There is very little information on platinum(II) cyanide in the recent literature; it is reported as a yellow compound, insoluble in water but soluble in aqueous cyanide, obtainable by the action of acids on $K_2[Pt(CN)_4]$, by heating $(NH_4)_2[Pt(CN)_4]$ at 300°C, or by interaction of $K_2[PtCl_4]$ and $K_2[Pt(CN)_4]$ in aqueous solution (*209*). The compounds *trans*-$[Pt(CN)_2(NH_3)_2]$ and $[Pt(CN)_2(en)]$ have been reported (*97*, *98*).

The complex $K_2[Pt(CN)_4]$ is made from platinum(II) chloride and aqueous potassium cyanide; it is also produced by the action of cyanide on many other Pt(II) compounds [including glyoximates (*501*) and Zeise's salt (*8*)], and even by heating platinum sponge with concentrated aqueous potassium cyanide. Yellow crystals of the trihydrate show a blue fluorescence; hydrates with 5, 3, 2, and 1 H_2O are stable at increasing temperatures (*493*). Many other colored salts with colorless cations are known. These are often fluorescent and sometimes dichroic. The colors usually vary with the amount of water of crystallization [see (*45*)]. The barium salt, obtained by electrolytic oxidation of platinum in barium cyanide solution, is a sparingly soluble yellow salt widely used in X-ray fluorescence detectors.

The $[Pt(CN)_4]^{2-}$ ion exchanges rapidly with labeled cyanide (*201*), though there is no evidence for the formation of appreciable concentrations of $[Pt(CN)_5]^{3-}$ from $[Pt(CN)_4]^{2-}$ and CN^- in aqueous solution (*434*). Visible and ultraviolet (*285*, *287*, *293*, *366*, *539*), Raman (*350*), and infrared absorption spectra (*231*, *351*, *484*) have been reported and discussed; the infrared C≡N stretching frequency in solution is at 2137 cm^{-1}, almost the same value as for the corresponding palladium compound (*351*); Pt—C and C≡N force constants have been calculated (*484*). Similar values have been obtained (*418*), apparently using only Raman data; a comparison of the Pt—C force constant with the similarly obtained Pd—C force constant (3.42 and 3.12×10^5 dynes/cm, respectively) (*418*) indicates that the Pt—C bond is stronger than the Pd—C bond.

The formation constant of the $[Pt(CN)_4]^{2-}$ ion has been estimated as 10^{40} (*200a*); this value, however, depends on that for the Pt(II)/Pt standard potential, which is not reliably known, and may well be in error by several powers of ten. It is clear, nevertheless, that the ion is much more stable than the corresponding complex halide ions.

Indications of the formation of a complex of platinum in a low oxidation were obtained in a fragmentary study of the action of potassium on $K_2[Pt(CN)_4]$ in ammonia, but no pure compound was isolated (*82*).

When $K_2[Pt(CN)_4]$ is treated with potassium acetylides and potassium in liquid ammonia, complex acetylides of formula $K_2[Pt^0(C{\equiv}C{\cdot}R)_2]$ are precipitated (*386*). As with $K_2[Pd(CN)_4]$, the action of sodium amalgam on an aqueous solution of the compound yields a reducing solution formerly thought to contain Pt(I) (*342*); more recently, however, it has been reported that the action of borohydride yields a hydride (*187*), and the same product may result from sodium amalgam reduction.

2. Platinum(IV)

When a solution of $H_2[Pt(CN)_4]$ is treated with hydrogen peroxide and evaporated, a green mass results. Evaporation over sulfuric acid *in vacuo* gives a transparent jelly which gradually turns pink, then brown. These products all appear to be hydrates of $H[Pt(CN)_4]$; when heated, they yield a yellow mass of approximate composition $Pt(CN)_3$, insoluble in water but soluble in boiling aqueous potassium cyanide (*321*). Oxidation of $K_2[Pt(CN)_4]$ by hydrogen peroxide and sulfuric acid yields a potassium salt of probable composition $K[Pt(CN)_4]$; by analogy with other compounds which from their empirical formulas might seem to contain Pt(III), however, it has been suggested that Pt(II) and Pt(IV) are present (*492*). There is no recent work on these compounds, and not even the magnetic properties have been investigated.

Although there is no evidence for the formation of mixed complexes in solution (*293*), oxidation of $K_2[Pt(CN)_4]$ or $Ag_2[Pt(CN)_4]$ by chlorine, bromine, or iodine is reported to give salts containing the ion $[Pt(CN)_4X_2]^{2-}$ (*63*, *97*, *362*). A re-examination of these substances, using modern techniques, seems desirable.

Potassium cyanide solution reduces chloroplatinate; but, if potassium hexaiodoplatinate is ground with potassium cyanide and the product crystallized from water, potassium hexacyanoplatinate, $K_2[Pt(CN)_6]$, is obtained as almost colorless hexagonal prisms, sparingly soluble in ethanol (*96a*). Its visible and ultraviolet absorption spectra have been described, but little information concerning its chemical properties is available. The acid $H_2Pt(CN)_6$ has been obtained by crystallization of the solution resulting from the action of hydriodic acid on the silver salt. It is a strong acid that dissolves zinc without reduction of the Pt(IV) (*96b*).

X. Copper, Silver, and Gold

For each of these elements the stable oxidation state in cyanide compounds is I, and for silver it is the only oxidation state. It has recently been shown that Cu(II) forms the complex $[Cu(CN)_4]^{2-}$ at low temperatures, and some work on compounds of Au(III) has been reported. Neither $K_3[Cu(CN)_4]$ nor $K[Ag(CN)_2]$ yields a derivative of the transition metal in zero oxidation state on treatment with potassium in liquid ammonia;

copper and silver are deposited (*143*). In common with the rest of the chemistry of these elements, Cu(I) shows a tendency to higher coordination numbers than Ag(I) or Au(I), and the stable species in solution are $[Cu(CN)_4]^{3-}$, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$, respectively; the ion $[M(CN)_3]^{2-}$ (or $[M(CN)_3H_2O]^{2-}$) is an important solution species, however, for Cu and Ag. Solid $K[Cu(CN)_2]$, unlike the formally analogous complexes of silver and gold, contains a helical chain anion in which the coordination number of the metal is three. The over-all formation constants of $[Cu(CN)_2]^-$, $[Ag(CN)_2]^-$, and $[Au(CN)_2]^-$ are 10^{24}, 10^{20}, and 10^{38}, respectively. (That of $[Cu(CN)_4]^{3-}$ is 10^{31}). The difference in stabilities between the silver and gold complexes is paralleled by a substantial difference in the M—C stretching frequencies (Raman: 360 and 452 cm^{-1}; infrared: 390 and 427 cm^{-1}) and force constants (1.8 and 2.8×10^5 dynes/cm, respectively) (*273*, *274*, *281c*), and the conclusion that metal-carbon π-bonding is stronger in $[Au(CN)_2]^-$ (*280*) is reinforced by a study of Raman spectra (*281*).

A. Copper

1. *Copper(I)*

Copper(I) cyanide may be obtained by the action of aqueous cyanide on a copper(II) salt if the solution is heated to decompose an intermediate light green product of probable composition $Cu^{2+}(aq)[Cu(CN)_2]_2$, many ammine and amine complexes of which are known (*44*, *370*, *496*). A better preparation, however, which avoids the liberation of cyanogen, is by the action of sodium bisulfite and potassium cyanide on an aqueous solution of copper sulfate at 60°C (*23*).

Copper(I) cyanide forms colorless diamagnetic crystals which melt at 473°C; a partial determination of the structure shows it to be very complicated, with 36 CuCN in the orthorhombic unit cell (*119*); the $C{\equiv}N$ stretching frequency is at 2172 cm^{-1} (*410*).

The solubility product expressed in terms of Cu^+ and CN^- is estimated as 3×10^{-20} gram-ion^2/liter^2 at 25°C (*505*). Copper(I) cyanide is soluble in aqueous ammonia, presumably forming $[Cu(NH_3)_2]^+[Cu(CN)_2]^-$ or a similar complex (*364*). In solid $CuCN{\cdot}NH_3$, however, there are sheets of composition CuCN and ammonia molecules are bonded to copper so as to give a five-coordinated metal atom (*120a*). Stable adducts are formed between the solid cyanide and ammonia, methyl iodide, and many organic bases.

Several types of complex between copper(I) cyanide and alkali metal cyanides exist; all that have been investigated are diamagnetic, as expected. In the fused system CuCN–KCN, $K[Cu_2(CN)_3]$, $K[Cu(CN)_2]$, and $K_3[Cu(CN)_4]$ exist (*500*); in the presence of water, complex phases are

$K[Cu_2(CN)]_3 \cdot H_2O$, $K[Cu(CN)_2]$, and $K_3[Cu(CN)_4]$ (*28, 482, 495*). A report (*28*) of a monohydrate of the last compound has not been confirmed (*482*), but since no analyses were presented in reference (*482*) and the infrared spectrum of the "anhydrous" $K_3[Cu(CN)_4]$ indicates the presence of some water (*276*), and since another author has reported analytical data for the monohydrate (*77*), further investigation is clearly required. In addition, rubidium and cesium, but not potassium, have been reported to form $M^I_2[Cu_3(CN)_5]$, and sodium, but not potassium, $M^I_2[Cu(CN)_3] \cdot 3H_2O$ from aqueous solutions (*202, 204*); whether the ions $[Cu_3(CN)_5]^{2-}$ and $[Cu(CN)_3]^{2-}$ are present in these compounds, however, is not clear.

A partial structure determination shows that $K_3[Cu(CN)_4]$ contains a tetrahedral anion (*115*). In $K[Cu(CN)_2]$, each copper atom forms three approximately coplanar bonds, one to the C of an unshared CN, and one to the C, and one to the N, of shared CN's; the anion as a whole is a helical chain (*118*). The coordination number of copper is also three in $K[Cu_2(CN)_3] \cdot H_2O$, but in this instance the anion is a sheet polymer $[Cu_2(CN)_3]_\infty$; water molecules are accommodated in the gaps in the sheet, which consists of linked hexagons rather as in graphite, and K^+ ions hold the sheets together. Copper atoms are located at the corners of the hexagons, cyanide ions along the edges; all C≡N distances are 1.15 ± 0.025 Å (*120*).

The infrared spectrum of solid $K_3[Cu(CN)_4]$ shows three C≡N stretching frequencies, at 2094, 2081, and 2075 cm^{-1} (*276, 420*), though in solution, as expected, there is only a single band, at 2076 cm^{-1} (*410*). The spectra of $K[Cu(CN)_2]$ and $K[Cu_2(CN)_3] \cdot H_2O$, which would be of interest since the compounds contain bridging cyanides, have not been investigated. Raman and infrared spectra for the species $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, and $[Cu(CN)_4]^{3-}$ in aqueous solution have been investigated in detail (*95, 96, 410*), and the different infrared absorption maxima of the last two ions (2094 and 2976 cm^{-1}, respectively) have been utilized in the determination of stability constants (*410*). For the reaction

$$[Cu(CN)_4]^{3-}(aq) = [Cu(CN)_3]^{2-}(aq) + CN^-(aq)$$

K is 0.0076 mole $liter^{-1}$ (in terms of concentrations) or 0.026 mole $liter^{-1}$ (in terms of activities) at 29°C.

For

$$[Cu(CN)_3]^{2-}(aq) = [Cu(CN)_2]^-(aq) + CN^-(aq)$$

K is 2.4×10^{-5} mole $liter^{-1}$ (concentrations) or 4.2×10^{-5} mole $liter^{-1}$ (activities) at 29°C. Combination of these values with the value of K for the reaction

$$[Cu(CN)_2]^-(aq) = Cu^+(aq) + 2CN^-(aq)$$

of 1 × 10^{-24} (calculated from the results of Vladimirova and Kokavskii) (*505*) leads to a value for the over-all dissociation constant of the ion $[Cu(CN)_4]^{3-}$ at 29° of 5 × 10^{-31} (*410*). Over the temperature range 0–60° the values of ΔH for the loss of one CN^- from $[Cu(CN)_4]^{3-}$ and $[Cu(CN)_3]^{2-}$ in aqueous solution are, respectively, about +12 and +20 kcal/gram-ion (*410*). Values for equilibrium constants given above are in good agreement with those derived from studies of the ultraviolet absorption spectra of solutions of copper(I) cyanide in aqueous alkali metal cyanides (*32*, *477*) and from calorimetric work (*75a*). A solution in which, according to the data given above, the principal species present would be $[Cu(CN)_2]^-$ and $[Cu(CN)_3]^{2-}$, undergoes rapid exchange of labeled cyanide with aqueous cyanide (*335*); $[Cu(CN)_4]^{3-}$ undergoes rapid exchange in methanol (*42*).

2. Copper(II)

When Cu^{2+}(aq) solutions react with cyanide below 0° a violet solution, which is suggested to contain $[Cu(CN)_4]^{2-}$, is formed, but rapidly decomposes (*365*); cyanide complexes of Cu(II) have also been postulated as reaction intermediates (*32, 138, 487*). Even at room temperature an intense transient violet color may be noted in neutral or slightly alkaline media (*177*, *189*). A similar reaction has also been observed in methanol at low temperatures (*155*, *407a*); the over-all formation constant of $[Cu(CN)_4]^{2-}$ has recently been estimated as 10^{27} at −45° in 60% methanol; the rate of decomposition is proportional to $([Cu(CN)_4]^{2-})^2$ (*407a*).

B. Silver

1. Silver(I)

Silver cyanide is best prepared in the form of colorless crystals from aqueous silver nitrate and potassium cyanide in the presence of a slight excess of ammonia, the ammonia being removed gradually from solution by means of a current of air (*406*, *524*). It is soluble in aqueous ammonia owing to formation of $[Ag(NH_3)_2]^+[Ag(CN)_2]^-$; crystallization gives a solid of composition $AgCN{\cdot}NH_3$ of unknown structure (*331*). The solubility in water is about 2 × 10^{-6} *M* AgCN but, as in aqueous ammonia, the situation is complicated by formation of the $[Ag(CN)_2]^-$ ion, and the best solubility product expressed as $[Ag^+][CN^-]$ is 1.2 × 10^{-16} at 25°C (*440*).

In the solid state silver cyanide consists of linear chains —Ag—C≡N—Ag—C≡N—, the Ag-Ag distance being 5.26 Å (*524*). The C≡N stretching frequency is at 2164 cm^{-1} (*282*). The formation of alkyl isocyanides as the main products of the reaction of silver cyanide with alkyl halides has long been known; among the factors which influence the course of the reaction appear to be the difference in crystal structure between AgCN and the alkali metal cyanides (which normally give alkyl cyanides), and the effect of silver ion on the C—X bond before reaction (*305*). It is interesting to note that silver cyanide forms addition products with methyl iodide (*218*); compounds of this type may be intermediates in the formation of isocyanides, but their structures have not been determined.

A phase study of the system KCN–AgCN–H_2O shows the existence of the compounds $K[Ag_2(CN)_3]\cdot H_2O$, $K[Ag(CN)_2]$, and $K_3[Ag(CN)_4]\cdot H_2O$ (*28*), though it has been later reported (*482*) that the last compound is not hydrated. Only the structure of $K[Ag(CN)_2]$ is known: this contains linear anions with Ag—C = 2.13 and C—N = 1.15 Å (*242*). The ion $[Ag(CN)_3]^{2-}$ may be present in sodium, calcium, and magnesium salts (*25*), but a polymeric ion or a 1:1 mixture of $[Ag(CN)_2]^-$ and $[Ag(CN)_4]^{3-}$ is equally likely. In aqueous solution, the species $[Ag(CN)_2]^-$, $[Ag(CN)_3]^{2-}$, and $[Ag(CN)_4]^{3-}$ are formed and may be characterized by their infrared absorptions at 2135, 2105, and 2092 cm^{-1}, respectively (*282*); first dissociation constants of $[Ag(CN)_3]^{2-}$ and $[Ag(CN)_4]^{3-}$ in water, determined by infrared spectroscopy, are 0.2 and 13.4 mole $liter^{-1}$ (in terms of activities) at 21°C (*282*). For solid $K[Ag(CN)_2]$, the C≡N stretching frequency is at 2140 cm^{-1}; for solid $K_3[Ag(CN)_4]$, there are two bands, at 2097 and 2091 cm^{-1} (*273*, *282*). Raman (*95*, *96*, *281*) and visible and ultraviolet spectra (*77*) of these compounds have also been reported.

For the species formed at low cyanide ion concentration, $[Ag(CN)_2]^-$, many determinations of the over-all formation constant have been made; the latest critical survey of published data indicates that the best value is probably 10^{20} (*440*). ($K_{HCN} = 6.2 \times 10^{-10}$ (*9*, *262*) alters this to 3×10^{19}.) Not surprisingly, $[Ag(CN)_2]^-$ exchanges labeled cyanide with KCN solution very rapidly (*335*).

Silver hydroxide is much more soluble in $K[Ag(CN)_2]$ solution than in water, the mixed anion $[Ag(CN)(OH)]^-$ being formed; *K* for the reaction

$$Ag^+ + 2OH^- + [Ag(CN)_2]^- = 2[Ag(CN)(OH)]^-$$

is about 3×10^6 (*300*).

C. Gold

1. *Gold(I)*

Gold(I) cyanide is obtained by heating the acid $H[Au(CN)_2]$ at 110°C as a yellow powder sparingly soluble in water but readily soluble in aqueous cyanide solutions. It has a structure which is related to that of AgCN, but the two compounds are not isomorphous (*543*); the C≡N stretching frequency is at 2261 cm^{-1} (*282*), substantially higher than in AgCN.

The only complex cyanide anion of gold(I) appears to be $[Au(CN)_2]^-$, the stability of which forms the basis for the cyanide process for the extraction of gold, which depends on the reaction

$$4Au + 8CN^- + 2H_2O + O_2 = 4[Au(CN)_2]^- + 4OH^-$$

The complex $K[Au(CN)_2]$ is conveniently prepared by treating a solution of gold(III) chloride with ammonia, and dissolving the precipitate of "fulminating gold" in potassium cyanide solution (*74*); this compound is the only one isolable in the system KCN–$AuCN$–H_2O (*28*), and infrared studies similar to those carried out on the Ag^+–CN^- system reveal no evidence for other complexes (*282*). Like $[Ag(CN)_2]^-$, the anion is diamagnetic and linear; the structure of $K[Au(CN)_2]$ is generally like that of $K[Ag(CN)_2]$, but the stacking of layers of anions and cations is slightly different (*449*).

Visible and ultraviolet (*77*), Raman (*281*, *281c*), and infrared (*281c*, *282*) spectra of $[Au(CN)_2]^-$ in aqueous solution have been reported. The infrared $C{\equiv}N$ stretching frequency (2146 cm^{-1}) is almost the same as that in $[Ag(CN)_2]^-$ (2135 cm^{-1}), but, as pointed out earlier, the metal-carbon vibration frequencies and force constants are appreciably different. Force constants calculations indicate that there is significant Au—C, C—N interaction (*281c*). The infrared spectrum of solid $K[Au(CN)_2]$ has been analyzed in detail (*273*).

The exchange of $[Au(CN)_2]^-$ with labeled cyanide, which might be slow like that of $Hg(CN)_2$ (see Section XI,C), has not been studied.

The formation constant of the $[Au(CN)_2]^-$ ion, estimated as 10^{38} from E° for the reaction

$$[Au(CN)_2]^- + e = Au + 2CN^-$$

(*319*) is very high, especially when one considers that only two successive formation constants are involved. Hot concentrated sulfuric acid will decompose the salts, but hydrogen sulfide is without action. The free acid $H[Au(CN)_2]$ is obtained by ion exchange and evaporation of the resulting solution at room temperature; there is disagreement about its infrared spectrum (*272*, *412*) but one suggestion (*156*, *272*) is that it contains a symmetrical N—H—N hydrogen bond. With α,α'-dipyridyl and *o*-phenanthraneline, derivatives of 4-covalent gold(I) e.g., $K[Au(CN)_2(dipy)]$, are formed (*134*); these have been reported on the basis of a preliminary X-ray study to contain planar anions, but this surprising conclusion requires confirmation.

2. Gold(III)

There are now several cyanide complexes of gold(III). The action of cyanide on gold(III) chloride solution which has been nearly neutralized, followed by crystallization, gives colorless $K[Au(CN)_4]\cdot H_2O$, which loses its water upon being allowed to stand in dry air. When a solution of this salt is treated with fluorosilicic acid (to precipitate $K_2[SiF_6]$) and the solution is evaporated, a gold(III) cyanide, $Au(CN)_3\cdot 3H_2O$, is said to be obtained (*241, 326, 459*).

An estimate of the standard potential for the system $[Au(CN)_4]^-/[Au(CN)_2]^-$ as +0.5 V in dilute H_2SO_4 has been made by comparative studies (*437*); the fact that cyanide transfer as well as electron transfer occurs makes it difficult, however, to deduce anything quantitative about the stability of the $[Au(CN)_4]^-$ ion. The Raman and infrared spectra of aqueous and solid $K[Au(CN)_4]$ have been studied in detail, and the vibrations of the planar anion have been assigned and the stretching and some bending force constants calculated; the high C≡N and M—C stretching force constants (17.4 and 3.0 $\times 10^5$ dynes/cm respectively) indicate strong M—C σ-bonding and weak π-bonding, as in mercuric cyanide (*282a*). The infrared C≡N stretching frequency is at 2189 cm^{-1} (*477a*). Evaporation of a solution of the acid obtained by ion-exchange yields the stable solid $H[Au(CN)_4\cdot 2H_2O$, which contains a H_3O^+ ion (*477a*). It is not yet known whether $[Au(CN)_4]^-$ exchanges rapidly with labeled cyanide like the $[Pt(CN)_4]^{2-}$ ion.

The action of chlorine, bromine, or iodine on $K[Au(CN)_2]$ gives complexes of formula $K[Au(CN)_2X_2]$ which are converted by aqueous cyanide into $K[Au(CN)_4]$ (*62, 325, 477a*). Raman and infrared spectra of these substances have been obtained, and some force constants have been calculated: when two X replace two CN in $[Au(CN)_4]^-$ the drop in the C≡N stretching force constant is greatest for X = I and least for X = Cl (*281b*).

XI. Zinc, Cadmium, and Mercury

All three metals, in both simple and complex cyanides, are restricted to oxidation state II; mercurous salts decompose on treatment with aqueous cyanide to give mercury(II) cyanide or its complexes and mercury. The possibility of preparing $Hg_2(CN)_2$ in nonaqueous media at low temperatures has not, however, been examined. For zinc and cadmium, reduction of $[M(CN)_4]^{2-}$ by alkali metals in liquid ammonia yields only the metal and no M(I) or M(0) derivative (*143*).

The cyanides and their complexes are all colorless and diamagnetic. Stepwise complex formation is well established for all three metals, successive formation constants decreasing in magnitude; $ZnCN^+$, however, has not been detected. For the tetrahedral $[M(CN)_4]^{2-}$ ions, the C≡N bonds appear to be almost identical, but the lengths and force constants of the M—C bonds vary in an irregular manner (*277*): lattice constants of the cubic unit cells of the potassium salts are 12.57, 12.87, and 12.79 Å for

M = Zn, Cd, Hg, respectively, and M—C stretching force constants are 1.30, 1.28, and 1.53 × 10^5 dynes/cm. These variations may be compared with the variation in formation constants (the over-all values for which are approximately 10^{20}, 10^{19}, and 10^{41}). Although these constants measure differences between aquo and cyano species, the greater interaction of cyanide with mercury than with cadmium is unmistakable, and suggests that, as in previous groups, the heavier element forms a stronger bond. [However, it seems the π-bonding contribution is least for Hg—C (*277*).] The very high formation constants of $[Au(CN)_2]^-$ (10^{38}) and $Hg(CN)_2$ (10^{35}) lend further support to this conclusion, and the failure of gold to form $[Au(CN)_3]^{2-}$ and the low values for the third and fourth formation constants for mercury are in line with the general tendency of these elements to be restricted to lower coordination numbers than lighter metals in the same groups.

The acids $H_2[M(CN)_4]$ cannot be obtained in aqueous solution; the anions are not very stable, either thermodynamically or kinetically, with respect to loss of cyanide and formation of the $M(CN)_2$ species.

A. ZINC

Zinc cyanide, which is very sparingly soluble in water, is readily made by precipitation from a soluble zinc salt. It has the anticuprite structure, each zinc atom being bonded to four cyanide groups distributed tetrahedrally; as in cuprite, the structure contains two interpenetrating lattices (*542*).

The only well-defined complexes of zinc cyanide are those containing the anion $[Zn(CN)_4]^{2-}$, which, as expected, is tetrahedral (*133*). The Raman spectrum of the solid potassium salt has been analyzed (*114*). The ion $[Zn(CN)_3]^-$ appears to be present in low concentrations in solutions of $K_2[Zn(CN)_4]$: *K* for the reaction

$$[Zn(CN)_4]^{2-} = [Zn(CN)_3]^- + CN^-$$

is about 10^{-4} (*261a*, *411*), but the resulting low concentration of the 1:3 species has not been detected by infrared spectroscopy, in contrast to the corresponding cadmium and mercury species.

The infrared C≡N stretching frequency of the $[Zn(CN)_4]^{2-}$ ion in aqueous solution is at 2149 cm^{-1} (*411*); the Raman spectrum (*95*, *351*) similarly shows a single band at 2152 cm^{-1}. There is nothing in the spectroscopic evidence to confirm the existence in $[Zn(CN)_4]^{2-}$–CN^- solutions of $[Zn(CN)_5]^{3-}$ and $[Zn(CN)_6]^{4-}$, the presence of which has been proposed in polarographic studies (*401*).

The most recent value for the over-all dissociation constant of the $[Zn(CN)_4]^{2-}$ ion is 4 × 10^{19} (*261a*), which is in satisfactory agreement with earlier studies (*57*, *58*). Calorimetric and polarographic studies of the Zn^{2+}–CN^- system have also been made. Only $Zn(CN)_2$, $[Zn(CN)_3]^-$, and $[Zn(CN)_4]^{2-}$ are formed, there being no evidence for $ZnCN^+$ (*261a*). The over-all formation constant, taken in conjunction with that of 10^{30} for $[Ni(CN)_4]^{2-}$, accounts satisfactorily for the interesting observation (*160*) that green nickel cyanozincate rearranges spontaneously to yellow zinc cyanonickelate. Exchange of labeled CN^- between $[Zn(CN)_4]^{2-}$ and cyanide solutions is complete in 2 minutes at pH 10.3 (*335*).

B. CADMIUM

Cadmium cyanide is isostructural with zinc cyanide (*473*), and except for being considerably more soluble in water it resembles the latter compound very closely.

Although $K_2[Cd(CN)_4]$, which is isomorphous with $K_2[Zn(CN)_4]$ (*133*) is the only solid complex isolable in the system KCN–$Cd(CN)_2$–H_2O (*111*), the existence of the $[Cd(CN)_3]^-$ ion as well as $[Cd(CN)_4]^{2-}$ is indicated by the solubility of cadmium cyanide in potassium cyanide solution provided CN^-:Cd is above 3.5:1, and is confirmed by infrared spectroscopy; the $C\equiv N$ stretching frequencies in the two ions are at 2148 and 2140 cm^{-1}, respectively (*411*). There is no indication of $[Cd(CN)_5]^{3-}$ or $[Cd(CN)_6]^{4-}$ (*411*). The Raman spectrum, a single line at 2141 cm^{-1}, has been observed only for $[Cd(CN)_4]^{2-}$ (*95*), and this is also the case for the visible and ultraviolet absorption spectra (*77*).

Successive complexing constants for $Cd^{2+}(aq)$ by cyanide are $10^{5.48}$, $10^{5.15}$, $10^{4.55}$, and $10^{3.58}$ (*450*) giving an over-all formation constant for $[Cd(CN)_4]^{2-}$ of $10^{18.8}$, values in good agreement with earlier determinations (*320*). Rates of successive rapid dissociations of $[Cd(CN)_4]^{2-}$ have been determined (*169*, *176*, *306*); in conformity with the results of these experiments, it is found that $[Cd(CN)_4]^{2-}$ exchanges cyanide with free cyanide ion very rapidly in methanol (*42*).

There is some evidence for mixed cyanide-chloride complexes of cadmium: $Cd(CN)_2$ is appreciably soluble in sodium chloride solution without the formation of free cyanide, and an infrared peak at 2147 cm^{-1} has been attributed to the ion $[Cd(CN)_2Cl]^-$ (*411*).

C. MERCURY

Mercury(II) cyanide is readily soluble in water; since it is little ionized [the dissociation constant into $Hg^{2+}(aq)$ and $2CN^-(aq)$ is 10^{-35}] it is formed when most mercury(II) compounds react with cyanides, but for preparative purposes hydrocyanic acid should be used and the product crystallized from water. The aqueous solution is practically a nonelectrolyte, and neither silver ion nor alkali affects it, but hydrogen sulfide precipitates mercury(II) sulfide. Mercury(II) cyanide is also readily soluble in ethanol, methanol, liquid ammonia [with which it forms ammines (*79*)], and liquid ethylenediamine (*408*).

In the solid state mercury(II) cyanide forms a lattice of nearly linear $Hg(CN)_2$ molecules; Hg—C = 1.986 ± 0.016; C—N = 1.186 ± 0.024 Å; ∠CHgC = 171 ± 2° and ∠Hg—C—N = 173 ± 2°. However, each mercury atom also has two nitrogen atoms belonging to other molecules at 2.70 Å, completing a very much distorted tetrahedron (*254*). In aqueous and methanolic solution the molecular is linear, according to Raman spectroscopy (*281*, *421*, *536*). A detailed study of the infrared spectrum of the solid has been reported (*275*). The assignment of 415 ± 5 cm^{-1} as the symmetrical Hg—C stretching frequency vitiates a former argument (*474*) (based on the assignment of a bond at 276 cm^{-1} to this vibration) that the force constant is very low and hence the metal-carbon bonding in $Hg(CN)_2$ is remarkably weak; it is in fact a strong bond (*275*), a conclusion more easily reconciled with the very high formation constant. It is interesting to note that intensity data and MC-MC interaction constants indicate that there is very little metal-carbon π-bonding (*280*).

In the systems KCN–$Hg(CN)_2$–H_2O, KCN–$Hg(CN)_2$–CH_3OH, and KCN–$Hg(CN)_2$–HCN, $K_2[Hg(CN)_4]$, the anion of which is tetrahedral (*133*), is the only solid complex (*111*, *411*). In aqueous solution, however, several other species have been identified at low $[CN^-]$: Hg ratios, among them not only $[Hg(CN)_3]^-$ (which has in addition been established in liquid HCN and methanol) but also $[Hg_2CN]^{3+}$, $[Hg_3(CN)_2]^{4+}$, and $[Hg(OH)CN]$ (*411*). The presence of such species no doubt explains the markedly alkaline reaction of aqueous solutions of $K_2[Hg(CN)_4]$, and the fact that they do not obey Beer's law (*77*). Contrary to a suggestion based on Raman spectra (*421*), there is no evidence for $[Hg_2(CN)_6]^{2-}$ (*95*, *191a*, *411*). The infrared C≡N stretching frequency decreases as usual with increase in coordination number of the metal atom in the series $Hg(CN)_2(s)$, $[Hg(CN)_3]^-(aq)$, and $[Hg(CN)_4]^{2-}(aq)$, the values being 2193, 2162, and 2143 cm^{-1}, respectively (*411*); the Raman spectra of the two aquated species have also been reported (*95*, *421*, *536*). While the formation of $[Hg(CN)_5]^{3-}$ and higher species seems unlikely, there is no infrared study of the system Hg^{2+}–CN^- beyond a 1:4 ratio. The ion $[Hg(CN)_3]^-$ does not appear to exist in the solid state; the "$KHg(CN)_3$" [prepared in liquid HCN (*263*)] has been shown to be a 1:1 mixture of $Hg(CN)_2$ and $K_2[Hg(CN)_4]$ (*411*), and it seems likely that $Na_2[Hg_2(CN)_6]\cdot 3H_2O$ (*202*) is a similar mixture.

The metal-carbon stretching frequencies (Raman) and force constants in $Hg(CN)_2$ and $[Hg(CN)_4]^{2-}$ (ca. 415 and 335 cm^{-1}; 2.61 and 1.53 × 10^5 dynes/cm, respectively (*275*, *277*)), are significantly different. A similar, variation occurs between mercury(II) halides and their complexes (*536*) and an interesting correlation can be made with stability constants in aqueous solution.

Typical values for successive complexing constants for $Hg^{2+}(aq)$ are $10^{18.0}$, $10^{16.7}$, $10^{3.8}$, and $10^{3.0}$, the over-all formation constant for $[Hg(CN)_4]^{2-}$ being $10^{41.5}$ (*7*); several other results confirm these values (*99a, 398, 471, 488*). The ΔH° values for successive complexing, determined by studying the temperature dependence of the formation constant or calorimetrically, are −23.0, −25.5, −7.6, and −7.2 kcal (*99a*). Exchange with labeled cyanide is very fast according to a radiochemical study involving separation of AgCN or $Zn(CN)_2$ (*4*), but it has also been reported that the uptake of cyanide is too slow to form the basis of a thermometric titration (*423*). These observations are reconciled by the detailed studies of Wolfgang and Dodson (*534, 535*), who showed that $[HgCN]^+$ is not in rapid equilibrium with $Hg^{2+}(aq)$ and CN^-, and that $Hg(CN)_2$ dissociates slowly; the equilibrium between $Hg(CN)_2$, $2CN^-$, and $[Hg(CN)_4]^{2-}$ is, however, rapidly set up. Thus the low values for the third and fourth constants explain the formation of $Hg(CN)_2$ when solutions of $K_2[Hg(CN)_4]$ are acidified. An interesting corollary to these results is that $Hg(CN)_2$ should exchange cyanide with labeled cyanide solution much more slowly than $[Hg(CN)_4]^{2-}$.

Mercury(II) oxide is soluble in aqueous mercury(II) cyanide, and from the solution the compound $(NCHg)_2O$ can be obtained; this has a molecular oxide structure in the solid state (*518*) but in solution it forms Hg(OH)CN, for which an infrared stretching frequency (*411*) and formation constants (*399*) have been given.

Many compounds of formula $M^I[Hg(CN)_2X]$, where X = Cl, Br, or I, are also known and may be made from mercury(II) cyanide and an alkali metal halide. Typical of these is $K[Hg(CN)_2I]$, which in the solid state has a lattice composed of linear $Hg(CN)_2$ molecules incorporated in sheets of I^- ions, the C—Hg—C axis being perpendicular to the layer; these layers are held together by K^+ ions. Each Hg has four I at 3.38 Å, and two C atoms of the CN groups at 2.08 Å [compared with 1.99 Å in $Hg(CN)_2$] (*314*). In aqueous solution the $[Hg(CN)_2I]^-$ ion shows a characteristic infrared absorption at 2181 cm^{-1}, and the 2193 cm^{-1} peak of $Hg(CN)_2$ is not detectable (*411*).

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