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CYANIDE COMPLEXES OF THE EARLY TRANSITION METALS (GROUPS IVa—VIIa)

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CONTENTS

A. INTRODUCTION

There has recently been a considerable development of interest in the cyano complexes of the early transition metals, particularly those of chromium, molybdenum, tungsten and rhenium. The last full-scale review was that of Chadwick and Sharpe in 1966 [1]. In order to keep the present review to a reasonable length we have concentrated on the twelve elements of Groups IVa—VIIa. The coverage is, it is hoped, comprehensive, but we shall discuss work carried out since Chadwick and Sharpe's review at rather greater length than the material already mentioned in their work.

(i) Scope and arrangement of material

We shall deal with unsubstituted and substituted cyano complexes $[M(CN)_x]^{n-}$ and $[M(CN)_xX_y]^{n-}$, but not with "simple" cyanides $M(CN)_x$. In Section B general preparations and properties, bonding, physical data are considered, concluding with a descriptive group-by-group section (C). Within each periodic group the lighter element is considered first; for each metal, arrangement of material is by decreasing oxidation state, and unsubstituted complexes are discussed before the substituted species.

(ii) Nomenclature

We shall use the term "cyano" to mean a CN^- group coordinated solely by its carbon atom, and isocyano to mean a cyanide group coordinated only via the nitrogen atom. Unless so specified, it will be assumed that a metal—carbon rather than a metal—nitrogen bond is present in the complexes (see p. 179). Bridged complexes (see p. 182) are called μ-cyano complexes.

(iii) Reviews

The best is that by Chadwick and Sharpe (1966) [1]. There are books by Williams (1948) [2] (useful for early material) and a poorly compiled one by Ford-Smith (1964) [3]. The author has written two short general reviews on cyano complexes (1973 [4], 1962 [5]). Shriver has reviewd the ambidentate nature of the cyanide ligand [6], and there is a recent short review on polynuclear cyano complexes [7]. There is a useful but rather out-dated review on the structural chemistry of cyanides [8]. For other more specialised reviews (e.g., photochemistry) see the relevant sections below.

B. GENERAL SURVEY

(i) Preparation and properties

The commonest method of preparation of cyano complexes is to treat another metal compound or complex (usually a halide or ammine) of the same oxidation state with excess of an alkali metal cyanide in aqueous solution. The complex, particularly if it is a potassium salt, may then usually be precipitated by addition of methanol or ethanol, or by means of a heavy cation such as Cs^+ or $(Bu^n_4N)^+$. For hydrolytically unstable species, sodium or potassium cyanide in methanol or liquid ammonia may be used. Fusion of an anhydrous halide with potassium cyanide will often work. For complexes of the early transition metals in particular it is often advantageous to start with a high oxidation state compound (e.g., d^0 species such as $[VO_4]^{3-}$, $[MoO_4]^{2-}$, $NbCl_5$) and to reduce those in the presence of excess cyanide, either chemically (hydrazine, potassium amalgam, hydrogen sulphide) or electrolytically. Cyano complexes of low oxidation state (e.g., $[Cr(CN)_6]^{6-}$, $[Mn(CN)_6]^{5-}$) are usually made by reduction of higher oxidation state species with potassium in liquid ammonia.

Pentacyanonitrosyl complexes may often be made by the action of hydroxylamine in excess cyanide on a d^0 tetra-oxo complex (e.g., $[Cr(NO)(CN)_5]^{3-}$

from $(CrO_4)^{2-}$) or on a hexacyano species (e.g., $[Mn(NO)(CN)_5]^{3-}$ from $[Mn(CN)_6]^{3-}$).

Since the cyanide ligand carries a negative charge its complexes are usually water-soluble electrolytes. Most cyano complexes are fairly stable chemically although those of the early transition elements, particularly octacyano species, are often subject to photolytically-induced hydrolysis or aquation. Reduction to lower oxidation states may often be accomplished in the solid state at high temperatures with gaseous hydrogen, by fusion with potassium cyanide, or in liquid ammonia solution with potassium. One-electron oxidations may sometimes be accomplished with nitrosyl chloride (e.g., $[Mn(CN)_6]^{3-}$ to $[Mn(CN)_6]^{2-}$).

Alkylation of coordinated CN^- may sometimes be effected with methyl fluorosulphonate or alkyl halides, though few such reactions have been investigated for the metals under review here. The formation of isonitrile complexes by such reactions was one of the earliest proofs that cyanide was bonded to metals via the carbon end of the ligand. Protonation of cyanide may occur to give coordinated —CNH ligands (e.g., in $Cr(CNH)(CO)_5$) or in "free acids" to give hydrogen-bonded $M{-}C{\equiv}N\cdots H\cdots N{-}C{\equiv}M$ bridges. The Lewis basicity of coordinated cyanide is shown by the formation of such species as $K_4[Mo(CNBF_3)_8]$ (see p. 220).

(ii) Stereochemistries and oxidation states

In Table 1 we summarise the main types of cyano complex found with these twelve metals. It does not fully represent the extraordinary versatility of CN^- in its ability to stabilise a wide range of stereochemistries. Cyano complexes of all coordination numbers from eight to two inclusive are known [1, 4,5], but only octa-, hepta- and hexa-coordination are established amongst Groups IVa to VIIa, consistent with the tendency of these metals to form few low coordination number complexes. Its versatility in the stabilisation of oxidation states is exemplified, however, by molybdenum and tungsten (V to 0 inclusive) and by rhenium (VI to I). These properties of cyanide arise from the fact that it is always a good σ-donor and a fair π-acceptor (not as effective in this latter respect as the isoelectronic CO ligand since cyanide carries a negative charge, which to some extent deters metal-to-ligand charge delocalisation). Its unique properties derive from its ability to strike a balance between σ-donor and π-acceptor abilities.

(iii) Bonding in cyanide and its complexes

(a) Modes of bonding

(1) Terminal. Cyanide functions as a terminal ligand in the great majority of its complexes with transition metals. In such cases the bond is formed between the carbon atom and the metal rather than from the nitrogen atom, as expected since nitrogen is more electronegative than carbon so that its lone

TABLE 1

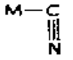
Principal coordination numbers of early transition-metal cyano complexes (unsubstituted)

		IVa	Va	VIa	VIIa
Octacyano	d^1	$[Ti(CN)_8]^{5-}$ (?)	$[Nb(CN)_8]^{4-}$	$[Mo,W(CN)_8]^{3-}$	$[Re(CN)_8]^{2-}$ (?)
	d^2		$[Nb(CN)_8]^{5-}$	$[Mo,W(CN)_8]^{4-}$	$[Re(CN)_8]^{3-}$
Heptacyano	d^2		$[V(CN)_7]^{3-}$		
	d^3			$[Mo(CN)_7]^{3-}$	
Hexacyano	d^2		$[V(CN)_6]^{3-}$ (?)		
	d^3		$[V(CN)_6]^{4-}$	$[M(CN)_6]^{3-}$	
	d^4		$[V(CN)_6]^{5-}$	$[M(CN)_6]^{4-}$	$[M'(CN)_6]^{3-}$
	d^5		$[V(CN)_7]^{7-}$ (?)		$[M''(CN)_6]^{4-}$
	d^6			$[Cr(CN)_6]^{6-}$	$[M'(CN)_6]^{5-}$

M = Cr, Mo. W. M′ = Mn, Tc, Re. M″ = Mn, Tc.

pair is less available for σ-bonding. Since electron densities around carbon and nitrogen are similar it is only recent X-ray studies of high precision which have demonstrated that the bonding is indeed via carbon in all cases studied, and this is also found from EPR and vibrational spectroscopic work.

A few unstable complexes containing the isocyano group, M—N≡C, have been claimed, e.g. $[Cr(NC)(H_2O)_5]^{2+}$ (p. 205), but only as unstable intermediates. There is no intrinsic reason why side-bonded (I) (π-attached) cyano complexes should not exist (such bonding has been proposed for a few complexes of the isoelectronic nitrogeno ligand, N_2), although the tightness of the $(C{\equiv}N)^-$ triple bond might render the necessary π-overlap with metal *d* orbitals rather inefficient. No such complexes have yet been reported, however; nor have species of the type (II) where θ is considerably less than 180°.

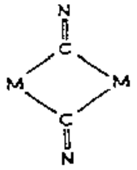


(I)

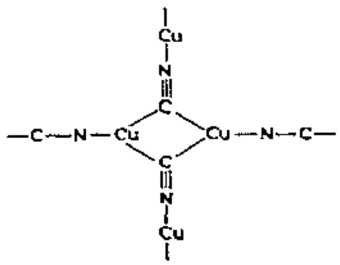
(II)

(2) Bridging. Linear bridges $M^1{-}C{\equiv}N{-}M^2$. These are very common in "simple" polymeric cyanides (a review on these has been published [7] in addition to Chadwick and Sharpe's coverage of the subject [1]) and in "giant" complexes of the Prussian Blue type [7]. The bridges may deviate quite considerably from linearity, however; in the binuclear isomers $[(CN)_5Co^1{-}C{-}N{-}Co^2(NH_3)_5].H_2O$ (I) and $[(CN)_5Co^1{-}N{-}C{-}Co^2(NH_3)_5].H_2O$ (II) the $Co^1{-}C{-}N$ and $C{-}N{-}Co^2$ angles are 172.4 and 159.8° in I, with $Co^1{-}N{-}C$ and $C{-}N{-}Co^2$ angles of 166° in (II). These deviations here have been attributed to intermolecular repulsion effects rather than to electronic or bonding differences [9].

"Bent bridges". Cyanide complexes of the type



are rare (whereas "ketonic" bridges are common with CO). One established example occurs in the giant polymer $[Cu(CN).NH_3]_n$:



The Cu—C distance is 2.18 Å, C—N distance 1.13 Å and the Cu—C—Cu angle is 69.9°. The Cu—Cu distance is 2.418 Å. The cyanide groups are not isolated, however; each nitrogen atom is bonded to another copper atom giving a polymeric structure (Cu—N = 1.98 Å) [10].

(b) Bonding in free CN^-

The cyanide ion is isoelectronic with CO, NO^+ and N_2. The ground state is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$$

and the σ-bond between carbon and nitrogen is found by overlap of sp_σ hybrids on the carbon and nitrogen atoms, leaving a lone-pair on each of the atoms. The π-bonds between carbon and nitrogen are then formed by overlap of the two remaining *p* orbitals on carbon and nitrogen respectively giving a formal triple bond. Free ligand eigenvalues and Mulliken overlap populations per molecular orbital have been computed for CN^-, and the results compared with those obtained for CO [11].

(c) Bonding in metal cyano complexes

Here we shall consider only terminal cyano complexes involving a metal-to-carbon bond. The "nine-orbital" rule provides a semi-empirical rationale for the existance of octa- and hepta-cyano complexes of these early transition metals. This "rule" proposes that transition metals having few *d* electrons will tend to use all five *nd* orbitals as well as $(n + 1)s$ and $(n + 1)p$ orbitals (nine in all) in their complexes [12,13]. Thus, for d^1 species (Ti^{III} possibly, and certainly Nb^{IV}, Mo^{V} and W^{V}) eight electron pairs from the cyanide ligands in $[M(CN)_8]^{n-}$ plus the singly occupied *d* orbital constitute the nine orbitals of the next rare gas. Similarly, second- and third-row d^2 complexes (Nb^{III}, Mo^{IV}, W^{IV}) will give octacyano species with the "metal" electrons paired up in the ninth orbital. For vanadium(III), however, the two *d* electrons for this first-row element (with a lower degree of orbital splitting) occupy unpaired sites in two *d* orbitals leaving room for only seven cyanide lone pairs; similarly for molybdenum(III) (d^3) in $K_4[Mo(CN)_7]$ [14]. Carrying this formalism forward we might predict the possible existence of the as yet unknown species

$$[Ti(CN)_7]^{5-}, \quad [V(CN)_8]^{4-}, \quad [Cr(CN)_7]^{3-} \quad \text{etc.}$$

Octacyano complexes, $[M(CN)_8]^{n-}$. There is still dispute as to which of the two most likely eight coordinate structures (dodecahedral, D_{2d}; or Archimadean antiprism, D_{4d}) octacyano complexes have in solution (see p. 110 and p. 113). In the solid state they may have either structure, depending apparently, on the nature of the cation amongst other factors (Table 2). Indeed, the solute structures may be fluxional [15,16] (one might expect the nature of the solvent to have some effect also) and certainly the energy difference between the D_{2d} and D_{4d} form is very small. This lack of structural information makes theoretical study even more hazardous than usual. The paper by

Hoard et al. [17] discuss some of the problems involved, and tend to dismiss earlier suggestions that [18] dodecahedral coordination would render four of the eight cyanide ligands less susceptible to metal-to-ligand π-acceptance. Nevertheless this proposal of Orgel [18] has recently been revived with the findings of an X-ray crystal structure of $Mo(CN)_4(CNMe)_4$ (see p. 219).

The theory of bonding in dodecahedral octacyano complexes using M.O. theory has been considered by Perumareddi et al. [19] and an electrostatic crystal field approach by Golding and Carrington [20]. The Archimadaean antiprismatic and dodecahedral structures have been considered by molecular orbital methods [21,22]. There are reviews on bonding in octacoordinate complexes [23,24].

Heptacyano complexes $[M(CN)_7]^{n-}$. No theoretical treatment has yet been forthcoming on the subject of heptacyano complexes. The existance of $K_4[V(CN)_7]$ has been rationalised on the grounds of the "nine orbital" rule (see above, p. 182) [14], and there is a review on seven coordination [23].

Hexacyano complexes, $[M(CN)_6]^{n-}$. These are of course all octahedral. Gray et al. have made and applied semi-empirical M.O. calculations to d^6 hexacyano species $[M(CN)_6]^{3-}$ (M = Co, Rh, Ir) and to $[M(CN)_6]^{4-}$ (M = Fe, Ru, Os) [25], calculations later extended to other first-row hexacyano complexes $[M(CN)_6]^{3-}$ (Ti, V, Cr, Mn, Fe) and $[Mn(CN)_6]^{4-}$ [26]. Fenske and co-workers have compared the occupancy of higher energy levels in $[Mn(CN)_6]^{5-}$, $[Mn(CN)_5CO]^{4-}$ and $Mn(CO)_5(CN)$ with those of the isoelectronic $[Mn(CO)_6]^+$. It appears that cyanide is much better able to cope than CO with changes in σ and π donor—acceptor ability to adapt to the demands of environment within the molecule. Thus CN^- is a better π-acceptor but weaker σ-donor in $[Mn(CN)_6]^{5-}$ than in $Mn(CO)_5(CN)$; CO is a much stronger π-acceptor in $[Mn(CN)_5CO]^{4-}$ than in $[Mn(CO)_6]^+$ or $Mn(CO)_5(CN)$, while its σ-donor ability varies little in these three complexes [11].

Five, four, three and two coordinated complexes. None has been established for the early transition metals, but they do occur for some Group VIII and Ib elements [19,27].

Pentacyanonitrosyls, $[M(NO)(CN)_5]^{n-}$. The bonding in these species has aroused much interest, and much of the theoretical treatment of bonding is to be found in papers on the EPR spectra of the paramagnetic species. An M.O. treatment [28] of $[Fe(NO)(CN)_5]^{2-}$, has been extended [29] to cover $[Mn(NO)(CN)_5]^{2-}$, $[M(NO)(CN)_5]^{3-}$ (Mn, Cr) and $[V(NO)(CN)_5]^{3-}$. These studies show clearly that it is the nitrosyl group which dominates the overall bonding rather than cyanide. Orbital energetics and electron distribution in such species have been calculated using M.O. methods [30].

TABLE 2

Structural data for cyano complexes

Complex	d_{CN} (A)	d_{MC} (Å)	∠MCN
$K_4[V(CN)_7].2H_2O$[a]	1.14(1)	2.15(1)	178.0(1)
$K_3[V(NO)(CN)_5].2H_2O$	1.15(2)	2.17(2)	
$K_3[Cr(O_2)_2(CN)_4]$	1.138(20)	2.090(12)	178.0
$Cs_2Li[Cr(CN)_6]$	1.19(2)	2.00(2)	
$Mn_3[Cr(CN)_6].12H_2O$	1.123(17)	2.063(11)	
$Cd_3[Cr(CN)_6].xH_2O$	1.137(17)	2.047(19)	
$K_3[Cr(NO)(CN)_5]$	1.05(12)	1.99(3)	
$[Coen_3][Cr(NO)(CN)_5]$	1.158(7)	2.033(7) eq. 2.075(14) ax.	176.6(6)
$(Bu^n_4N)_3[Mo(CN)_8$	1.16(3)	2.11(3)	176.0(2)
$K_4[Mo(CN)_8].2H_2O$	1.156(6)	2.163(5)	177.4(9)
$Mo(CN)_4(CH_3NC)_4$	1.151(9)	2.172(7)	176.4(6)
$K_4[MoO_2(CN)_4].6H_2O$	1.168(12)	2.175(11)	176.7(5)
$NaK_3[MoO_2(CN)_4].6H_2O$	1.189(13)	2.204(13)	177.6(1.1)
$K_4[Mo(NO)(CN)_5]$	1.17(5)	2.13(5)	175.0(3)
$Na_3[W(CN)_8].4H_2O$	1.164(5)	2.139(5)	176.3(1)
$H_4[W(CN)_8].6H_2O$	1.127(10)	2.180(10)	177.3(5)
$H_4[W(CN)_8].4HCl.12H_2O$	1.150(10)	2.176(10)	175.3(2)
$K_3[Mn(CN)_6]$	1.140(20)	1.990(15)	177.0(1)
$Na_4[Mn(CN)_6].10H_2O$	1.16(3)	1.95(3)	
$K_3[Mn(NO)(CN)_5].2H_2O$	1.16(2)	1.98(2)	177.0(2)
$K_{2n}[ReN(CN)_4]_n.nH_2O$	1.31	2.13	136.0
$K_3[ReO_2(CN)_4]$	1.148(9)	2.115(7)	179.2(6) & 173.7(6)
	1.166(5)	2.135(3)	178.1(5) & 173.4(3)
$[Pt(NH_3)_4][Re_2O_3(CN)_8]$	1.135(9)	2.120(7)	175.1(6)

[a] For $K_3[VO(CN)_5]$ see p. 196.

(iv) Physical measurements on cyano complexes

Here we consider briefly the main physical methods which have been used to study cyanides, summarise information in tabular form where appropriate, and give general references. Specific references will be found in section C. The order of material in this section (structural date, magnetic properties, EPR spectra etc.) follows the same sequence as for each compound considered in section C.

(a) Structural data

These are summarised in Table 2, and individual structures are discussed

Other data	Point group (idealised)	Space group	Z	Ref.
	D_{5h}	$I1$	2	14
V—N 1.66(3); N—O 1.29(5)	C_{4v}	$Pccn$	4	63
Cr—O 1.446(12)	C_{2v}	$P2/a$	4	72
	O_h	$Fm3m$	$1\frac{1}{3}$	76a
Mn—N 2.195(12)	O_h	$Fm3m$	$1\frac{1}{3}$	77
Cd—N 2.265(19)	O_h	$Fm3m$	$1\frac{1}{3}$	78
	C_{4v}	$Pcn2$	4	131
Cr—N 1.71(1); N—O 1.21(1); ∠CrNO 176(1)	C_{4v}	$P2_1/c$	4	132
	D_2	$P4/ncc$	4	174
	D_{2d}	$Pnma$	4	206
Mo—C 2.151(8); C—N 1.132(9) ∠MoCN 175.4(6)	D_{2d}	$C2/c$	4	250
Mo=O 1.828(14)	D_{4h}	$P2_1/c$	2	239
Mo=O 1.834(9)	D_{4h}	$Pmna$	2	238
Mo—N 2.13; ∠MoNO 175.1(2.9)	C_{4v}	$Pbca$	8	268
	D_{4d}	$P2_1/c$	4	180
	D_{4d}	$Pmna$	4	203
	D_{4d}	$C2/c$	4	204
	O_h	$P2_1/n$	2	281
	O_h	$P2_1/n$	4	292
Mn—N 1.66(1); N—O 1.21(2)	C_{4v}	Cc	4	269
Re—N 1.53 and 2.44	C_4	$Imm2$	2	331
Re=O 1.773(8)	D_{4h}	$P\bar{1}$	1	340a
Re=O 1.781(3)				337
Re=O 1.698(7); Re—O 1.949(4)	D_{4h}	$C2/m$	2	341a

under the appropriate compound in section C. Most of the determinations are by X-ray methods, and most of the recent ones show that the cyano ligand is carbon- rather than nitrogen-bonded. The data in Table 2 show that the C—N distance in coordinated cyanides (ca. 1.15 Å) is little different from that in the CN^- ion (ca. 1.16 Å; d_{C-N} in CN is 1.172 Å and 1.156 Å in HCN [8]). The metal—carbon distances fall within the range 2.05—2.2 Å, varying little with oxidation state (compare Mo^{IV} with Mo^{V} for example) or from first to second or third row (e.g., Cr—C in $[Cr(CN)_6]^{3-}$ is only 0.1 Å shorter than Mo—C in $K_4[Mo(CN)_8].2H_2O$). The deviation from linearity of M—C—N groups by about 2° is real in most cases, but is so small that it is difficult to say whether this is due to electronic effects, as has been claimed for some carbonyl complexes with "bent" M—C—O bonds, or due to simple crystal packing effects.

(b) Magnetic susceptibility measurements

Table 3 summarises only information on measurements conducted over a temperature range. Moments measured at room temperature only are given in section C. The 1964 review of Figgis and Lewis is still a valuable source of information [31].

(c) EPR spectra

The use of electron paramagnetic resonance to study structure and bonding in paramagnetic cyano complexes is widespread. Data are collected in Table 4 and additional references given in the appropriate parts of section C. More heat and controversy have been generated by the question of the value of EPR data to, in particular, the structures of $[Mo(CN)_8]^{3-}$ and $[W(CN)_8]^{3-}$ in solution and the bonding in $[Cr(NO)(CN)_5]^{3-}$ than to any other topic in the cyano chemistry of these metals. A useful review of EPR data is that of Goodman and Raynor (1970) [32].

(d) Vibrational spectra

In Tables 5 and 6 we present data on those complexes (respectively $[M(CN)_6]^{n-}$ and $[M(NO)(CN)_5]^{n-}$) for which full or almost complete assignments of fundamental modes have been made, while in Table 7 we give data for infrared and Raman spectra of those complexes for which incomplete assignments have been given. Those compounds not in Tables 5—7 whose spec-

TABLE 3

Magnetic data on cyano complexes

	Temperature range (K)	μ_{eff} (B.M.)	θ	Ref.
"$K_5[Ti(CN)_8]$"	93—294	1.74(294°)	−27°	43
$K_4[V(CN)_7]$	90—296	2.7(295°)	−26°	54
$K_4[V(CN)_6]$	90—295	3.5(295°)	−52°	54
$K_5[V(CN)_6]$	90—295	2.85(295°)	−28°	54
$K_2[Cr(CN)_8]$	81—295	3.87(300°)	1°	79
	76—295	3.85(298°)	0	80
$K_3[Cr(NO)(CN)_5].H_2O$	85—296	1.87(296°)	− 7°	130
$K_4[Mo(CN)_7].2H_2O$	90—295	1.75(295°)		257
	90—298	1.73(298°)		256
	109—293	1.77(293°)	3°	258
$K_3[Mn(CN)_6]$	42—300	3.50(300°)	− 0.09°	284
$K_4[Mn(CN)_6].3H_2O$	80—300	2.18(300°)		293
$K_2[Mn(NO)(CN)_5]$	75—300	0.5(300°)		293
$Ag_2[Mn(NO)(CN)_6]$	73—297	0.55(297°)		301

tra have been measured (normally in the C≡N stretching region only) are given in Section C.

Much work has been done on the infrared spectra of cyano complexes, since C≡N stretching frequencies (hereafter referred to as ν_{CN}) are strong and sharp, and occur in the relatively clear area of 1900—2200 cm^{-1}. In free cyanide ion ν_{CN} is at 2078 cm^{-1}. The formation of a strong metal—carbon σ bond will tend to tighten the C≡N bond (so ν_{CN} rises), while substantial metal-to-carbon π bonding weakens the C≡N bond by increasing the contribution of (II) (ν_{CN} drops):

$$\underset{\text{(I)}}{\mathrm{M{-}C{\equiv}N}} \qquad \underset{\text{(II)}}{\overset{+}{\mathrm{M}}\mathrm{{=}C{=}}\overset{=}{\mathrm{N}}}$$

Thus ν_{CN} in cyano complexes can be above or below that of free CN$^-$ depending on the relative contributions of metal—ligand σ and π bonding [5,33]. This is illustrated by the frequency of ν_{CN}, which for $[\mathrm{Mn(CN)_6}]^{n-}$ has the values 2150, 2125, 2060 and 1934 cm^{-1} for n = 2 to 5 respectively. Jones has shown that the integrated intensity of ν_6 is a measure of metal—carbon π-bonding in hexacyano complexes [33]. This is borne out by the increase in ν_2 and ν_7 (metal—carbon stretching frequencies) for the series of complexes $\mathrm{Cs_2Li[M(CN)_6]}$ (n = number of d electrons)

	n	ν_1	ν_2	ν_6	ν_7	$I\nu_6$ [a]
$[\mathrm{Cr(CN)_6}]^{3-}$	3	2142	380	2138	362	2100
$[\mathrm{Mn(CN)_6}]^{3-}$	4	2138	395	2125	384	8200
$[\mathrm{Fe(CN)_6}]^{3-}$	5	2140	411	2128	407	12300
$[\mathrm{Co(CN)_6}]^{3-}$	6	2161	432	2140	428	18300

[a] Integrated absorption coefficient, mole^{-1} l cm^{-2} [33]; frequencies (in cm^{-1}) from ref. 34.

The relative invariance of ν_1 and ν_6 arises from an interplay of σ- and π-bonding effects [33], but the increase in ν_2, ν_7 and $I\nu_6$ in the sequence Cr < Mn < Fe < Co arises from an increase in metal—carbon π-bonding with n in t_{2g}^n from 3 to 6. It may be seen from a study of Tables 5 and 7, e.g., for $[\mathrm{Mn(CN)_6}]^{3-}$ — $[\mathrm{Mn(CN)_6}]^{4-}$ — $[\mathrm{Mn(CN)_6}]^{5-}$, that there is a general increase in metal—ligand force constants down a group (e.g., $[\mathrm{M(CN)_6}]^{5-}$, M = Mn, Tc, Re; $[\mathrm{M(CN)_8}]^{4-}$, M = Mo, W).

The ν_{CN} values in bridging cyano complexes lie at some 50 cm^{-1} higher than in corresponding terminal species (e.g. ν_{CN} in $[\mathrm{(CN)_5Co{-}C{\equiv}N{-}Co(NH_3)_5}]\mathrm{.H_2O}$ and in $[\mathrm{(CN)_5Co{-}N{\equiv}C{-}Co(NH_3)_5}]\mathrm{.H_2O}$ lie near 2190 cm^{-1} as against the 2140 cm^{-1} expected for terminal cobalt(III) mono-cyano complexes. This has been useful for detecting such bridges [35].

(e) Electronic spectra

Athough there has been much work on the electronic spectra of cyano

TABLE 4

Electron paramagnetic resonance of cyano complexes

	Sample state;	T (K)	g values		
			g_{iso}	$g_{\parallel}$	$g_{\perp}$
"$K_5[Ti(CN)_8]$"	a;	300	1.990		
$K_3[VO(CN)_5]$	water;	300			
$K_4[V(CN)_6].3H_2O$	$K_4[Fe(CN)_6].3H_2O$;	300	1.992	1.9919	1.9920
$K_4[Nb(CN)_8].2H_2O$	$K_4[Mo(CN)_8].2H_2O$;	100—293		1.976	1.992
	a;	300	1.987		
	glycerol;	100—340	1.980	2.000	1.970
$K_3[Cr(CN)_6]$	$K_3[Co(CN)_6]$;	126—300		1.993	1.991
	$K_3[Co(CN)_6]$;	300	1.998		
	a;	300	1.998		
$K_3[Cr(NO)(CN)_5].2H_2O$	$K_3[Co(CN)_6]$;	77—300	1.9949	1.9745	2.0051
	water;	300	1.9945		
$[Cr(NO)(CN)_4(H_2O)]^{2-}$	water;	300	1.9948		
$[Cr(NO)(CN)_3(H_2O)_2]^{-}$	water;	300	1.9880		
$Cr(NO)(CN)_2(H_2O)_3$	water;	300	1.9832		
$[Cr(NO)(CN)(H_2O)_4]^{+}$	water;	300	1.9748		
$K_3[Mo(CN)_8]$	a;	298	1.993		
	$K_4[Mo(CN)_8].2H_2O$;	298	1.9848	1.9779	1.9882
	glycerine;	77	1.9920	1.9981	1.9889
	water;	298	1.9915		
	ethanol;	77	1.992	1.9987	1.9889
$(Bu^n_4N)_3[Mo(CN)_8]$	a;	100—298	1.991		
	CH_3CN	298	1.991		
$K_3[W(CN)_8]$	a;	298	1.98		
	$K_4[W(CN)_8].2H_2O$;	298	1.963	1.942	1.973
	glycerol;	77	1.9724	1.9819	1.9677
	water;	298	1.9706		
	ethanol;	77	1.9728	1.9855	1.9665
$K_4[Mo(CN)_7].2H_2O$	a;	150		2.103	1.973
$K_3[Mo(NO)(CN)_5]$	$K_3[Co(CN)_6]$;	77	2.0024	1.9736	2.0168
	ethanol;	77	2.004	1.973	2.019
$Na_2[Mn(NO)(CN)_5]$	$Na_2[Fe(NO)(CN)_5]$;	300	2.0146	1.9892	2.0265
			g_x	g_y	g_z
$K_4[Mn(CN)_6].3H_2O$	$K_4[Fe(CN)_6].3H_2O$;	12	2.624	2.182	0.63

[a] Pure solid. [b] value in gauss.

complexes there has also been much disagreement as to their interpretation, so no attempt has been made to list assignments. The two classic and most comprehensive papers are by Perumareddi et al. on octacyano species [19]

A (metal) values (cm^{-1})			A (ligand) values (cm^{-1})			Ref.
A_{iso}	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$A_{\parallel}$	$A_{\perp}$	
						20
79.9			^{13}C: 11.3^{b}			50
−55.5(^{51}V)			(D = −0.0264, E = −0.0072 cm^{-1})			61
−21.1(^{50}V)						
						69
101.0						
97.0	49.0	121.0				
14.7						61
			^{13}C:	−7.9	−9.8	61
						61
17.4	29.9	11.0	^{14}N(NO): ^{13}C(CN)$_{ax}$: ^{13}C(CN)$_{eq}$:	1.8 6.7 9.7	6.6 9.4 12.5	139
17.21			4.9 7.76; 11.7	(^{14}N(NO)) (^{13}C(C$_{ax;eq}$)		139
17.2						156
18.6						156
20.0						156
21.4						156
						20
30.7	14.0	39.1				182
30.3			10.9 (^{13}C)			
29.5	11.2	38.6	0.27 (^{14}N)			181
						231
	18.7	68.5				182
51.9						
			0.63 (^{14}N)			181
						256
	54.4	25.5	^{14}N(NO): 11 ^{14}N(CN)$_{eq}$	1.27 [^{13}C(CN$_{eq}$)] 2.21	3.77 −0.09	264
74.3	149.5	36.6		<1	<4.26	305
A_x	A_y	A_z				61
84.5	46.5	105.0				

and by Alexander and Gray [26] for hexacyano complexes. It is from the latter publication that the list of ligand—field parameters is drawn (Table 8). The value of Δ, the ligand—field splitting energy, increases as expected [26]

TABLE 5

Vibrational spectra of hexacyano complexes

			$Cs_2Li[Cr(CN)_6]$	$Cs_2Li[Mn(CN)_6]$	$K_3[Mn(CN)_6]$
ν_1	(A_{1g})	ν_{CN}	2141	2138	2129
ν_2		ν_{MC}	380	395 [b]	375
ν_3	(E_g)	ν_{CN}	2144		2129
ν_4		ν_{MC}	374	360 [b]	363 [a]
ν_5	(F_{1g})	δ_{MCN}	273	297 [b]	
ν_6	(F_{1u})	ν_{CN}	2138	2125	2112
ν_7		δ_{MCN}	468	490	483
ν_8		ν_{MC}	362	384	361
ν_9		δ_{MCN}	161	166	
ν_{10}	(F_{2g})	δ_{MCN}	384	440 [b]	420 [a]
ν_{11}		δ_{CNC}	175	173	
ν_{12}	(F_{2u})	δ_{MCN}	353 [b]	385 [b]	
ν_{13}		δ_{CMC}	122 [b]	126 [b]	
Reference			34	34	55

All data on solids except for $K_3[Mn(CN)_6]$ (aqueous solution).

[a] Solid state.

[b] Calculated from combination modes.

from "$[Ti(CN)_6]^{3-}$" (see p. 191) to $[Mn(CN)_6]^{3-}$. The lower Δ-value for $[Mn(CN)_6]^{4-}$ compared with $[Mn(CN)_6]^{3-}$ is probably due to the lower σ-bond strength in the former.

There has also been much work on the electronic spectra of pentacyanonitrosyl complexes [28,29].

(f) Miscellaneous data

X-ray photoelectron spectroscopy has been used to study bonding in $[M(CN)_6]^{3-}$ (M = Cr, Mn, Co) and $[M(CN)_6]^{4-}$ (M = Mn, Fe); chemical shifts of core electrons and multiplet splitting in the 3*s* shell were sometimes observed [36,36a]. Thermochemical data on the reaction

$$[M(H_2O)_6]^{2+} + 6CN^- \rightarrow [M(CN)_6]^{4-} + 6H_2O$$

(M = V, Cr, Mn) have been accumulated [37] but the methods used were later criticised [38]. The photolysis of a number of octa- and hexa-cyano complexes has been reviewed [39,40]. Exchange between labelled cyanide ion and octa- or hexa-cyano species has also been studied [41]. Data on electrode potentials are briefly summarised in Table 9 (references in section C).

$K_4[Mn(CN)_6]$	$K_5[Mn(CN)_6]$	$K_5[Tc(CN)_6]$	$K_5[Re(CN)_6]$
2082	1960	1971	1966
423	380	416	436
2066	2030	2041	2046
392	430	470	391
2060	1934	1949	1932
526	605	568	570
386	452	463	
	190	174	182
440	650?	646?	636?
	146	166	166
55	312	312	312

C. DESCRIPTIVE CHEMISTRY

(i) Group IVa (Ti — Zr — Hf)

The only cyanide complexes reported are of titanium, and most of them lack complete or satisfactory characterisation.

Titanium

Titanium(IV) (d^0). $K_2[Ti(CN)_6].K_3[Ti(CN)_6]$ is claimed as an intermediate during reaction of "$K_3[Ti(CN)_6]$" (see below) with air-free water [42], but no real evidence for its existence was given. As indicated above, d^0 cyanide complexes would not be expected to be stable.

Titanium(III) (d^1). $K_5[Ti(CN)_8]$ (or $K_3[Ti(CN)_6].2KCN$) has been made by the prolonged action of potassium cyanide in liquid ammonia on titanium tribromide [43]. The X-ray powder diffraction pattern of the salt was obtained, and the magnetic susceptibility of the dark green compound measured from 93—294 K, the moment at room temperature [43] being 1.74 B.M. The EPR

TABLE 6

Infrared and Raman data (incomplete) for cyano complexes

		ν_{CN}
$Cs_3[VO(CN)_5]$		2095
$K_4[V(CN)_7].3H_2O$		2105, 2087, 2062
$K_4[V(CN)_7]$		2096, 2073
$Na_3[V(CN)_6]$		2077, 2110
$K_{3.5}[V(CN)_{5.5}(OH)_{0.5}]^c$		2105, 2060, 2050
$K_4[V(CN)_6].3H_2O$		2083, 2066
$K_4[V(CN)_6]$		2080, 2065, 2050
$Cr(CN)(CO)_5$ (in CH_2Cl_2)		2112
cis-$K_4[Cr(CN)_4(CO)_2]$		2170, 2050 1991
$Na[Cr(CN)(CO)_5]$ (in CH_2Cl_2)		2112
$[Cr_2(CN)(CO)_{10}]^-$ (in CH_2Cl_2)		2129
$K_4[Mo(CN)_8].2H_2O^c$	IR	2130, 2125, 2097
	R	2135, 2115, 2105
	IR^b	2118, 2108
	R^b	2134^a, 2119^a, 2109
trans-$K_4[MoO_2(CN)_4]$	IR	2065, 2028, 2022
	R	
"$K_2[Mo(CN)_5]$"	IR	2127, 2101
	R	2116
$K_4[Mo(CN)_4(CO)_2]$		2077, 2064, 2007
$K_4[W(CN)_8].2H_2O^c$	IR	2130, 2125, 2097
	R	2138, 2123, 2100
	IR^b	2114, 2104
	R^b	2135^a, 2118^a, 2104
trans-$NaK_3[WO_2(CN)_4]$	IR	2050
$K_4[W(CN)_4(CO)_2]$		2075, 2069, 1998
$(pyH)[W(CN)(CO)_5]$		2106
$W(CNH)(CO)_5$		2095
"$K_2[Mn(CN)_5H_2O].KCN$"^{c}		2075, 2050
$K_{3.62}[Mn(CN)_6].0.13H_2O^c$		2114, 2099, 2088
$K_3[Mn(CN)_4(CO)_2]$		2178, 2092, 2075
$K_2[Mn(CN)_3(CO)_3]$		2116, 2092, 2049
$K_3[Mn(NO)_2(CN)_2]$		2038, 2017
cis-$K_4[Mn(NO)_2(CN)_2]$		2174, 2125
trans-$K_4[Mn(NO)_2(CN)_2]$		2137, 2100
$Mn(CN)(CO)_5$		2145
$K_3[ReN(CN)_5]$	IR	2107
	R	2136, 2122
$K_{2n}[ReN(CN)_4]_n.nH_2O$		2120
trans-$K_3[ReO_2(CN)_4].2H_2O$	IR	2119, 2079
	R	2141, 2130
$Cs[Re(CN)_6]$		2152
$Ph_4As[Re(CN)_6]$		2155
$K_6[Re_2O_3(CN)_8].4H_2O$	IR	2123, 2080
	R	
$[Niphen_3]_2[Re(CN)_4(CO)_2]$		2090, 2077, 2057
$K_2[Re(CN)_3(CO)_3]$		2136, 2109

IR data unless otherwise indicated.
R = Raman.

ν_{MC}	δ_{MCN}	Other assigned bands	Ref.
331	445	947 (ν_{VO})	51
367 340	478		55
363, 340	477, 448		54
338	446		54
328, 304	450	3582 (ν_{OH}), 610 (ν_{VO})	49
349	448		55
328	406		49
420	530	2050, 1983, 1949 (ν_{CO})	163
	680, 660	1738, 1648 (ν_{CO})	166
427	560	2053, 1929, 1894 (ν_{CO})	163
378	537	2052, 1983, 1942, 1879 (ν_{CO})	163
420, 373,361			208
477, 404			209
459, 452, 363			208
420^{a}, 389			209
470	238	705 (ν_{MoO_2} as.)	194
394		779 (ν_{MoO_2} s.)	242
391, 353		820	260
430			260
	675, 626	1743, 1648 (ν_{CO})	164
486, 405			208
405			209
486, 379			208
471^{a}, 404^{a}			209
485		680 (ν_{WO_2} as.)	194
	685, 662	1733, 1640	164
		2040, 1979, 1929 (ν_{CO})	269
		2069, 1964, 1931 (ν_{CO})	269
585 575, 405	390, 315		277
376, 353			278
		1917, 1833 (ν_{CO})	317
		1937 (ν_{CO})	317
		1455, 1425 (ν_{NO})	318
		1737, 1664 (ν_{NO})	318
		1750, 1709 (ν_{NO})	318
		2075, 2055, 1960 (ν_{CO})	319
407, 392		1035 (ν_{ReN})	330
		1037 (ν_{ReN})	330
406,392	482	965,945 (ν_{ReN})	330
477 469	340, 250	768 ($\nu^{as}_{ReO_2}$) 258 (δ_{ReO_2})	329
420	489	871 ($\nu^{s}_{ReO_2}$)	242
442, 424, 406	357		329
421, 409, 394	350		328
476, 467	335	909 (ν_{ReO}), 781 ($\nu^{as}_{ReO_2}$)	242
420		912 (ν_{ReO}), 868 ($\nu^{s}_{ReO_2}$)	242
		1871 1797 (ν_{CO})	356
	470		356

[a] Polarised.

[b] Aqueous solution.

[c] Bands not completely assigned by authors.

TABLE 7

Vibrational spectra of pentacyanonitrosyl complexes, $[M(NO)(CN)_5]^{n-}$

			$K_3[Cr(NO)(CN)_5]$	$K_4[Cr(NO)(CN)_5]$
ν_1	(A_1)	ν_{CN} (ax.)	2120	2095
ν_2		ν_{CN} (eq.)	2120	2077
ν_3		ν_{NO}	1630	1470[a]
ν_4		ν_{MN}	621	645
ν_5		ν_{MC} (ax.)	398	446
ν_6		ν_{MC} (eq.)	346	390
ν_7		δ_{MCN}		464
ν_8		δ_{CMC}		
ν_{10}	(B_1)	ν_{CN} (eq.)	2120	2056
ν_{16}	(E)	ν_{CN} (eq.)	2120	2030[a]
ν_{17}		ν_{MC} (eq.)		
ν_{18}		δ_{MNO}	612	627
ν_{19}		δ_{MCN}		488
ν_{20}		δ_{MCN}	305	350
ν_{21}		δ_{MCN}	290	
ν_{22}		δ_{CMC}		
ν_{23}		δ_{CMN}		
ν_{24}		δ_{CMC}		
Reference			145	145

[a] Multiple splitting of this mode; mean frequency given. All data on solids.

TABLE 8

Ligand—field parameters for hexacyano complexes [26]

	Δ ($cm^{-1} \times 10^{-3}$)	B_{epx} (cm^{-1})	$B_{free\ ion}$ (cm^{-1})	C (cm^{-1})
"$[Ti(CN)_6]^{3-}$"	22.3			
"$[V(CN)_6]^{3-}$"	23.5	375	780	2700
$[Cr(CN)_6]^{3-}$	26.6		845	2670
$[Mn(CN)_6]^{3-}$	34.0	660		3280
$[Mn(CN)_6]^{4-}$	30.0	425	900	1800

$K_4[Mo(NO)(CN)_5]$	$K_2[Mn(NO)(CN)_5]$	$K_3[Mn(NO)(CN)_5].2H_2O$
2120 2106	2150?	2124
2097 2080	2100?	2129
1450^a	1886	1706
604 595	628	660
418	440	370
376 360	380	315
432	285	461
2060	2160	
2028^a	2100	2101
		493
589	550	660
480 474		463
312	330	407
287		270
		174
		130
145	147, 301	315

TABLE 9

Standard electrode potentials

Couple	E_0^{a} (V)	Solute
$[Cr(CN)_6]^{3-}/[Cr(CN)_6]^{4-}$	−1.143	M KCN
$[Cr(NO)(CN)_5]^{3-}/[Cr(NO)(CN)_5]^{4-}$	−1.146^b	M NaCl
$[Mo(CN)_8]^{3-}/[Mo(CN)_8]^{4-}$	+0.84	0.1 M KCN
$[W(CN)_8]^{3-}/[W(CN)_8]^{4-}$	+0.569	0.1 M KCN
$[Mn(CN)_6]^{3-}/[Mn(CN)_6]^{4-}$	−0.24	1.5 M NaCN
$[Mn(CN)_6]^{4-}/[Mn(CN)_6]^{5-}$	−1.06	1.5 M NaCN
$[Mn(NO)(CN)_5]^{2-}/[Mn(NO)(CN)_5]^{3-}$	+0.597	
$[Re(CN)_6]^{3-}/[Re(CN)_6]^{4-}$	−0.72	
$[Re(CN)_5H_2O]^{2-}/[Re(CN)_5H_2O]^{3-}$	−0.636	

[a] Vs. standard hydrogen electrode. [b] E_{12} vs. standard calomel electrode.

spectrum of the powder at room temperature gave a *g*-value [20] of 1.990, and this rather high value for titanium(III) complexes was taken to be indicative of octacoordination in the anion, although this conclusion has been questioned [44]. The electronic spectrum of the solution in liquid ammonia was measured from 300—700 nm. The appearance of a split band near 450 nm led some workers [19,26,43] to suggest that the anion is octahedral (i.e. the salt is $K_3[Ti(CN)_6].2KCN$), but the EPR data and general similarity of the electronic spectrum to other octacyano complexes suggests that $K_5[Ti(CN)_8]$ is indeed the correct formula for the salt [20]. Recently, however, Nicholls et al. [44a] have proposed that the salt is $K_4(Ti(CN)_7).KCN$, and suggested that the heptacyano anion has a mono-capped trigonal prismatic structure (C_{2v}). This is based on the observation of three bands in the electronic spectrum of the substance and on powder pattern data which indicate the presence of potassium cyanide in the lattice. Heintz [42] claimed that $K_3(Ti(CN)_6)$ and $K_4(Ti(CN)_7)$ were formed when potassium cyanide reacts in aqueous solution with titanium trichloride [42,45], but this work could not be repeated [44a], although there is some evidence for the formation of a species containing bridging cyanide ligands from this reaction [46].

Titanium(0) (d^4). $K_4(Ti(CN)_4)$ is a black material made by reduction with potassium of a solution of titanium tribromide and potassium cyanide in liquid ammonia. The magnetic moment at room temperature is 2.17 B.M., and the infrared spectrum shows bands at 2012 and 1943 cm^{-1}, the electronic spectrum having an unresolved broad band in the *d—d* region [44a].

(ii) Group Va (V — Nb — Ta)

Our knowledge of the cyanide chemistry of vanadium has been greatly expanded over the past three years, and more developments in the cyanide chemistry of niobium and tantalum are expected.

(a) Vanadium

Vanadium(V) (d^0). The only cyano "complex" reported was formulated as $K_4V_2O_7.4KCN.14H_2O$; this was made, not from a vanadium(V) species, but during an attempted preparation of a vanadium(IV) cyanide [47].

Vanadium(IV) (d^1). The only fully established cyano complexes of vanadium(IV) are of the "vanadyl" type.

$K_3[VO(CN)_5]$ and other salts of $[VO(CN)_5]^{3-}$ have been made by reaction of cyanide with a deficiency of vanadyl sulphate [48] or acetate [49]*. A preliminary report of the EPR spectrum has been published [50]. The infra-

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* The X-ray crystal structure of $K_3[VO(CN)_5]$ shows that the anion has a C_{4v} structure, with V=O at 1.64 Å, V—C (equatorial) 2.14 and V—C (axial) 2.31 Å [49a].

red spectrum has been studied in some detail over the range 200—4000 cm^{-1} and most of the bands assigned on the basis of C_{4v} symmetry (Table 6) [51]. Assignments have also been proposed for the solid and aqueous solution of the electronic spectrum [49,51].

Although $K_2[V(CN)_6]$ is alleged to be the product of reaction of excess potassium cyanide with vanadyl acetate [52] more recent work shows that $K_3[VO(CN)_5]$ is the only product [49].

Vanadium(III) (d^2). A curious situation is found here: it appears that the coordination number of the anion of the unsubstituted complexes is dependent on the nature of the cation, as with the fluoro complexes of some early transition elements.

$K_4[V(CN)_7].2H_2O$ is the best characterised vanadium(III) cyano complex. It may be prepared from an alkaline solution of ammonium metavanadate with potassium cyanide, hydrogen sulphide being used as the reducing agent [53]. The monohydrate is made by prolonged action of cyanide ion on vanadium(III) chloride in water [49], and the anhydrous complex from methanolic potassium cyanide on vanadium(III) acetate [54]. The hydrates are bright red and the anhydrous compound is brown. They are soluble in water, albeit with some decomposition, but are stable in excess cyanide solution.

The X-ray crystal structure of $K_4[V(CN)_7].2H_2O$ (Table 2) shows the anion to have approximate pentagonal bipyramidal symmetry (D_{5h}), there being no significant difference between equatorial and axial V—C or C—N bond lengths. The C_{axial}—V—C_{axial} angle of 171° and V—C_{axial}—N_{axial} angle of 172.5(3)° are thought to be bent away from 180° by interaction of parts of the anion with the cations. The reasons for the assumption of heptacoordination have been discussed and the "eighteen-electron rule" invoked (see above, p. 182); it has also been pointed out that another stabilizing factor may be that the five equatorial cyanide groups form a stabilizing π-orbital (ring orbital) [14], although of course this does not explain why seven coordinate cyanides are not more common.

The magnetic susceptibility of the anhydrous potassium salt has been measured over a temperature range (Table 3); the moment of 2.78 B.M. at room temperatures is consistent with the presence of two unpaired electrons [54]. The infrared spectra of the hydrated [49,55] and anhydrous [54] species have been measured and some partial band assignments made (Table 6). The electronic spectra of $K_4[V(CN)_7].2H_2O$ in the solid and aqueous cyanide solution are similar, suggesting retention of the seven coordinate structure in the latter [14,49,56]. Assignment of the bands in the spectra have been made on the basis of D_{5h} symmetry [49] and on the assumption (see below) that the anion has the $[V(CN)_6]^{3-}$ structure [19,26]. In this connection it should perhaps be noted that "$K_3[V(CN)_6]$" has commonly been given the formula [57,58] assigned to the species now known to be $K_4[V(CN)_7]$, although the seven coordinate formulation had been preferred by many workers [1,49,53, 54,59].

$Na_3[V(CN)_6]$ has, however, been isolated and characterised [54]. It is a blue-violet material made from sodium cyanide and vanadium(III) chloride in methanol. The infrared spectrum [54] (200—4000 cm^{-1}) (Table 6) is significantly different from that of $K_4[V(CN)_7]$. Another possibility, however, is that this "$Na_3[V(CN)_6]$" is the sodium analogue of $K_{3.5}[V(CN)_{5.5}]$ (see below). The rate of exchange of labelled cyanide ion with $Na_3[V(CN)_6]$ in solution is immeasurably fast [41].

$K_{3.5}[V(CN)_{5.5}(OH)_{0.5}]$ is the apparent formula of the blue complex obtained by the immediate action of potassium cyanide on vanadium(III) chloride. The apparent oxidation state was measured as about 2.7, and it has been suggested that the deep colour arises from a mixed oxidation state complex involving vanadium(II) and (III). The magnetic moment at room temperature [49] is 3.4 B.M. The blue solid has a similar reflectance spectrum to that of the blue solution formed from vanadium(III) and cyanide. Bennett and Nicholls have shown that, when vanadium(III) chloride is added to excess concentrated cyanide ion, there is a disproportionation reaction, the blue precipitate containing vanadium(II) and (III) and the remaining solution vanadium(III) and (IV) (the latter as $[VO(CN)_5]^{3-}$). In weak cyanide no such disproportionation occurs [49].

Vanadium(II) (d^3). $K_4[V(CN)_6]3H_2O$ can be made by reduction of vanadium(III) acetate with potassium amalgam followed by addition of aqueous potassium cyanide and ethanol [47,60]; by electrolytic reduction of the blue solution formed by interaction of vanadium(III) species with cyanide [49], or by addition of cyanide and HCN to the hydrolysis product of vanadium(II) sulphate [59]. The anhydrous salt has been made by reaction of vanadium(II) acetate with potassium cyanide [49] or by reduction of $K_4[V(CN)_7]$ with potassium in liquid ammonia [54]*. The hydrate is orange and the anhydrous complex gold-coloured. The hydrate is isomorphous [61] with $K_4[Fe(CN)_6].3H_2O$. The magnetic susceptibility has been measured over a temperature range (Table 3) [54], and the moment of 3.5 B.M. at room temperature is a little lower than the value expected for three unpaired electrons. The EPR spectrum of the hydrate in $K_4[Fe(CN)_6].3H_2O$ gave [61] an isotropic g-value of 1.992. The infrared spectra of the hydrated and anhydrous forms have been measured (200—4000 cm^{-1}, Table 6) [49,54,55,59] and some band assignments made. The electronic spectrum is very similar to that of $K_4[V(CN)_7].2H_2O$; spectra of $K_4[V(CN)_6].3H_2O$ in the solid state and in excess aqueous cyanide solution are similar. Some band assignments were made [49]. The heat of complexing of $[V(H_2O)_6]^{2+}$ by excess cyanide has been measured [37,38]; $\Delta H^0 = -197$ kJ mole^{-1}.

Vanadium(I) (d^4). $K_5[V(CN)_6]$ was made as a chocolate-brown material by

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* The X-ray crystal structure of $K_4[V(CN)_6]$ shows the unit cell to be $P2_1/a$ ($Z = 4$) with some disordering. Bond parameters are V—C, 2.161(4) and C—N, 1.153 Å [60a].

the reduction of $K_4[V(CN)_6]$ or of $K_4[V(CN)_7]$ by potassium in liquid ammonia [54]. The magnetic susceptibility was measured over a temperature range (Table 3); the moment at room temperature of 2.85 B.M. is consistent with the two unpaired electrons for an octahedron in a low spin environment. The infrared spectrum [54] has bands at 1910 cm^{-1} (ν_{CN}) and unassigned bands at 800 and 720 cm^{-1}.

$K_4[V(NO)(CN)_6].H_2O$ has been made as yellow crystals by the action of hydroxylamine hydrochloride and hydrogen sulphide on an alkaline solution of ammonium metavanadate in cyanide media [53]. Although unit cell data were obtained from X-ray powder studies the structure of the complex is unknown, beyond the obvious suggestion that the anion may be seven- or eight-coordinate. The infrared spectrum was measured (Table 6) and the very low frequency of 1508 cm^{-1} assigned to the nitrosyl stretching mode [53].

$K_3[V(NO)(CN)_5].2H_2O$. The existence, or at least precise formulation, of this complex is possibly still open to question despite the X-ray data on it. The material was made by the action of cyanide and hydroxylamine hydrochloride on alkaline vanadate [62,63], a preparation previously claimed [64] to give $K_5[V(NO)(CN)_5].2H_2O$ (but see below). The X-ray single crystal study shows the arrangement of ions to be very similar to those in $K_3[Mn(NO)(CN)_5].2H_2O$, but the orientation of the complex anion is disordered with respect to one of the diad axes of its point group *Pccn* so that the nitrosyl and one cyanide groups occupy crystallographic sites statistically. Nevertheless, bond parameters were reported (Table 2) [62,63]. The infrared spectra [62,63] showed bands at 2105 and 2080 cm^{-1} (ν_{CN}) and 1530 cm^{-1} (ν_{N-O}).

Vanadium(0) (d^5). $K_7[V(CN)_7]$ is the product of reduction of $K_4[V(CN)_7].H_2O$ by excess potassium in liquid ammonia, although the sample may have contained potassium hydroxide impurities [49]. The magnetic moment is 3.2 B.M. at room temperature, and an infrared band at 2140 cm^{-1} was observed (very high in frequency for an alleged zerovalent cyano complex) [49]. The absence of any electronic absorption bands below 23000 cm^{-1}, it was claimed [49], might suggest that Δ is less than the 22300 cm^{-1} of $K_4[V(CN)_6]$.

It seems clear that further investigation of this material is called for; neither the high magnetic moment, high $C\equiv N$ stretching frequency or low Δ values are consistent with the presence of vanadium(0). Possibly the compound is a hydrido cyanide.

$K_5[V(CN)_5]$ is an even less satisfactory case. It is said to be the product of the reduction of $K_5[V(NO)(CN)_5].2H_2O$ (see below) with molecular hydrogen at 200°. The yellow complex is quite stable and is diamagnetic, which may suggest the presence of a metal—metal bond, although its molar conductance in water does not suggest this [65]. The infrared spectrum [65] shows bands at 2175, 2078 and 2030 cm^{-1} (ν_{CN}); as with "$K_7[V(CN)_7]$" the $C\equiv N$ frequencies are unusually high for a vanadium(0) complex (the band at 2175 cm^{-1} in particular could arise from a bridging cyanide ligand).

Vanadium(—I) (d^6). $K_5[V(NO)(CN)_5].2H_2O$ was reported to be found by reaction of alkaline vanadate with potassium cyanide and hydroxylamine [64]. Although electronic spectra [29], chemical reactions (e.g., thermal decomposition and reduction by molecular hydrogen to $K_5[V(CN)_5]$) [65] and cyanide exchange data [67] support this formulation, it seems likely that the product may be either a polyvanadate contaminated with cyanide [66] or, possibly [30,62,63], $K_3[V(NO)(CN)_5].2H_2O$.

(b) Niobium

Niobium(V) (d^0). Reaction of niobium pentachloride and an ethanol solution of hydrogen cyanide yields $NbCl_4(CN).Et_2O$ and $HNbCl_5(CN)$; the salts $(Et_3N)[NbX_5(CN)]$ (X = Cl, Br) were also isolated [68].

Niobium(IV) (d^1). $K_4[Nb(CN)_8].2H_2O$ has been isolated as a stable, crystalline yellow material by the action of concentrated potassium cyanide on the electrolytic reduction product of niobium pentachloride in ethanol. The complex is isomorphous with $K_4[Mo(CN)_8].2H_2O$. The magnetic moment at room temperatures [69] is 1.69 B.M. Both the isomorphism and the EPR of the solid (diluted in $K_4[Mo(CN)_8].2H_2O$ as host lattice) are consistent with dodecahedral (D_{2d}) symmetry for the complex anion, but EPR spectra in water and in glycerol suggest that the structure changes to that of an Archimadaean antiprism (D_{4d}) in such solutions (Table 4).

$NbCl_3(CN)(CH_3CN)_2$ has been briefly reported [46].

Niobium(III) (d^2). $K_5[Nb(CN)_8]$ is formed as dark red crystals when a solution of $K_4[Nb(CN)_8]$ is photolysed or reduced with potassium amalgam [69]. The salt is diamagnetic and readily oxidised to $K_4[Nb(CN)_8]$.

(c) Tantalum

The only report of any tantalum cyano complex occurs in a paper by Ruff and Thomas; they found that green tantalum(II) chloride gave a precipitate with aqueous potassium cyanide, redissolving in excess [70].

(iii) Group VIa (Cr—Mo—W)

The cyano chemistry of chromium is quite different from that of molybdenum and tungsten except in the low oxidation states (+I, 0). It is, however, similar in many respects to that of manganese, iron and cobalt, the predominant oxidation states being III and II, and the normal stereochemistry octahedral. With molybdenum and tungsten, however, the V, and particularly the IV, states predominate. Curiously, eight coordination in a sense is rare for these two elements — $[M(CN)_8]^{3-}$ and $[M(CN)_8]^{4-}$ — but the chemistry of these four ions is so interesting that the many octahedral cyano complexes of molybdenum and tungsten have perhaps not received their due attention.

(a) Chromium

The hexacyanochromate(III) ion has been extensively studied but $[Cr(CN)_6]^{4-}$ much less so, mainly on account of its instability. There has also been a large volume of recent work on $[Cr(NO)(CN)_5]^{3-}$.

Chromium(IV) (d^2). The only examples of this rare oxidation state for chromium with cyanide are the highly explosive and unstable peroxocyanides, which two brave chemists in particular have studied with care.

$K_3[Cr(O_2)_2(CN)_3]$ is a deep red crystalline salt, best made by the reaction [71] of potassium cyanide with $Cr(O_2)_2(NH_3)_3$. The magnetic moment at room temperatures is 2.82 B.M., as expected for two unpaired electrons [72]. The X-ray crystal structure shows that the chromium has pentagonal bipyramidal coordination, the pentagonal plane being occupied by two symmetrically "side-bonded" peroxo ligands (Cr—O, 2.090(12), O—O, 1.446(12) Å, ∠OCrO, 45°) and a cyanide ligand making up the fifth partner to a distorted pentagon. The axial ligands are the remaining two cyanide groups [72], there being no significant difference between the equatorial and axial Cr—C distances of 2.090(12) Å.

Reaction of $K_3[Cr(O_2)_2(CN)_3]$ with acid gives a violet colouration which can be extracted into ether, and contains cyanide [71].

$K_2[Cr(O_2)_2(CN)_2NH_3]$ is a deep red material obtained by the action of concentrated aqueous ammonia on "$K_5[Cr_2(O_2)_4(CN)_5].5H_2O$" — this latter substance is obtained from chromium trioxide, potassium cyanide and hydrogen peroxide [71].

Chromium(III) (d^3). $K_3[Cr(CN)_6]$ is best made by the action of excess potassium cyanide on chromic acetate [73] — directions for obtaining the latter from dichromate and sulphur dioxide [73] or, perhaps better, from dichromate and hydrogen peroxide [74] have been given. The salt is pale yellow, dissolving easily in water to give a yellow solution which slowly hydrolyses and is also light-sensitive. A free acid has been prepared in aqueous solution [74].

There is no single crystal X-ray study on $K_3[Cr(CN)_6]$ (it is isomorphous with some other $K_3[M(CN)_6]$ salts (M = Mn, Fe, Co) and its unit cell dimensions are known (a = 10.62, b = 13.66, c = 8.54 Å; space group *Pnca*, Z = 4) [75]. The volumes of the $K_3[M(CN)_6]$ unit cells decrease from Cr > Mn > Fe > Co (volumes in $Å^3$: 1239, 1209, 1174 and 1160) as expected [75]. Unit cell data are also available for $M^{II}_3[Cr(CN)_6]_2.6H_2O$ (M^{II} = Mn, Fe, Co, Ni, Cu, Zn, Cd), and these are isomorphous with the corresponding hexacyanides of iron, cobalt, rhodium and iridium [76]. There is however, a full single crystal X-ray study of $Cs_2Li[Cr(CN)_6]$ (Table 2) [34,76a], and very accurate bond parameters have been produced for the "Prussian Blue" type lattices in $Mn_3[Cr(CN)_6]_2.12H_2O$ [77] and $Cd_3[Cr(CN)_6]_2.nH_2O$ [78]. In the latter the six cyanide ligands are carbon-bonded to the chromium, while the cadmium atom has four cyanide nitrogen atoms and two water molecules coordinated to it (Table 2) [78].

The magnetic behaviour of $K_3[Cr(CN)_6]$ has been measured over a temperature range (Table 3) and the moment at room temperature is the expected 3.87 B.M. [79,80] There have been a number of studies on the EPR spectrum (Table 4). In a dilute solid solution in $K_3[Co(CN)_6]$ or $K_3[Mn(CN)_6]$

two magnetically similar but differently oriented anions are apparent within the unit cell [61,81]. The spectrum of $Cs_2Li[Cr(CN)_6]$ in $Cs_2Li[Co(CN)_6]$ was also studied [82]. At low temperatures (4 K), extra lines were seen in the EPR spectrum of $K_3[Cr(CN)_6]$ in $K_3[Co(CN)_6]$ which may arise from exchange interaction of $[Cr(CN)_6]^{3-}$ anions [83].

A Zeeman effect has been studied in $K_3[Cr(CN)_6]$, the effects of orthorhombic or tetragonal distortions on the g-values being considered [84]. On the basis of the EPR spectrum of normal and ^{13}C-enriched $K_3[Cr(CN)_6]$ in $K_3[Co(CN)_6]$ it was concluded that there is a greater degree of σ-covalent bonding in the hexacyano than in the hexafluoro complex [85]. EPR relaxation times were studied by the broadening of the EPR lines of $[Cr(CN)_6]^{3-}$ brought about by the paramagnetic nitrosyldisulphonate ion, $(ON(SO_3)_2)^{2-}$, and the effect was used to measure the rate of ion-pairing (weak in the case of $[Cr(CN)_6]^{3-}$, much stronger with $[Cr(H_2O)_6]^{3+}$) [86]. The spin—spin relaxation times for $K_3[Cr(CN)_6]$ in 0.06 to 1.5% solid solution in $K_3[Co(CN)_6]$ at 4.2 K indicates a change in the dominant mechanism as the concentration of paramagnetic ion changes [87].

The vibrational spectroscopy of $[Cr(CN)_6]^{3-}$ has received some attention [34,55,88—91], though there are still minor disagreements as to assignments of fundamentals and therefore to the calculation of force constants. Raman and infrared spectra have been measured from 40—4000 cm^{-1} for solid $Cs_2Li[Cr(CN)_6]$ at 90 and 300 K and assignment of all fundamentals proposed (Table 5) [34]; single crystal and solution Raman studies on $K_3[Cr(CN)_6]$ have recently been made [88] over the range 8—4000 cm^{-1}, and also Raman spectra for solid and aqueous solutions of $K_3[Cr(CN)_6]$ (200—4000 cm^{-1}) [55]. The infrared spectra of $K_3[Cr(CN)_6]$ [88a] and $Cs_3[Cr(CN)_6]$ for 10—500 cm^{-1} at 300 K and 90 K were interpreted by factor group analysis, and a full force constant treatment of $[Cr(CN)_6]^{3-}$ made [89]. This supercedes the earlier calculations of Caglioti et al. [90] which were based on rather dubious data for the low frequency modes. Jones [33] measured ν_6, ν_7 and ν_8 in aqueous solution (2128, 458, 379 cm^{-1}) and, from these values and the integrated intensity of ν_6 (which can be related to the degree of chromium—carbon π-bonding), demonstrated a decrease in metal—carbon force constants for $[M(CN)_6]^{3-}$ in the sequence Co—C > Fe—C > Mn—C > Cr—C. Similar conclusions have been reached by other workers [91].

Electronic and luminescence spectra. The electronic spectrum of $[Cr(CN)_6]^{3-}$ has been measured at room temperatures in aqueous solution from 240—500 nm, and also at 143 K over the same range in water—ethylene glycol mixtures; bands were assigned and ligand—field parameters calculated (see p. 194) [26]. The aqueous solution spectrum has also been measured from 250—660 cm^{-1} and band assignments made [92]. The vibrational fine structure associated with the $^4A_2 \rightarrow {}^2T_1$ and $^4A_2 \rightarrow {}^2T_2$ transitions has been measured [93]. Remarkably little variation of the electronic spectrum of $K_3[Cr(CN)_6]$ over the range 2—74°C was found (300—800 nm) [94]. The reflectance spectra of a number of $[Cr(CN)_6]^{3-}$ salts have been measured in connection with luminescence studies (see below). There is only a small magnetic dichroism effect on the spin-allowed transitions of $[Cr(CN)_6]^{3-}$ and other chromic(III) species, whereas it is large for the spin-forbidden transitions [95].

Luminescence spectra on $[Cr(CN)_6]^{3-}$ salts have been made by a number of workers. Electronic (200—1000 nm) and luminescence (700—870 nm) spectra on salts of the type $[CrA_6][Cr(CN)_6]$ were made (A being a nitrogen donor) and the results at first interpreted on the basis that cation-to-cation energy transfer occurred [96], but later the same workers showed that there is no such transfer. It appears that hexacyanochromate has a marked temperature dependence of its overall phosphorescence yield [97]. The lifetime and rate constant for the luminescent decay in $K_3[Cr(CN)_6]$ has been measured and compared with values for other chromium(III) complexes, and luminescent spectra obtained at 77 K; it appears that the metal—carbon separation could be 0.4 Å greater for the $^4T_{2g}$ than the $^4A_{2g}$ state [98]. Luminescence emission from $K_3[Cr(CN)_6]$ has been studied at low temperatures in rigid glasses by other workers and the quantum yields measured at 77 K [99,100]. Emission from crystalline $K_3[Cr(CN)_6]$ also occurs at room temperatures, however, and does not appear to be markedly temperature-dependent as it is for some other chromium(III) species [101]. Phosphorescence of $[Cr(CN)_6]^{3-}$ has been studied in parallel with its photolysis (see below).

The ^{14}N chemical shift in $[Cr(CN)_6]^{3-}$ shows a large Fermi contact interaction between the "metal" unpaired electrons and the nitrogen atoms in the cyanide ligands, but the reason for this is not clear [102]. Studies on the X-ray K_α spectrum of $K_3[Cr(CN)_6]$ have been carried out [103,104]; the $3p$ binding energy for chromium is identical for $K_3[Cr(CN)_6]$ and for $K_3[Cr(NO)(CN)_5]$, which, it is claimed, indicates that the latter is in the (III) rather than the (I) oxidation state [104], but there is other evidence to the contrary (p. 206). The photoelectronic spectrum of $K_3[Cr(CN)_6]$ was measured [36,36a, 105]. Aluminium K_α and magnesium K_α X-rays show no multiplet splitting from the 3*s* shell, perhaps due to extensive delocalisation of the 3*d* electrons (the 3*s* binding energy is 68.7 eV) [36].

The K_β emission spectra of $K_3[Cr(CN)_6]$ were measured and the K shell binding energies tentatively calculated [106]. The width of the ^{14}N resonance line in $K_3[Cr(CN)_6]$ has been measured; although the shift is small [107] it is not as low as reported in early work [108]. The line width is rather large, due perhaps to quadrupole effects [107].

Photolysis of $K_3[Cr(CN)_6]$. Ultra-violet irradiation of $[Cr(CN)_6]^{3-}$ causes release of cyanide ion and also acceleration of the $[Cr(CN)_6]^{3-}/CN^-$ exchange reaction. Irradiation of the ion in the 300—400 nm region causes the pH to rise. Studies at carefully controlled pH showed the quantum yields to be almost wavelength- and temperature-independent. The primary product of photolysis is $[Cr(CN)_5H_2O]^{2-}$ with $[Cr(CN)_4(H_2O)_2]^-$ formed as a secondary photolysis product [109,110]. Studies on the photosensitisation of $[Cr(CN)_6]^{3-}$ aquation reactions suggest that a doublet mechanism is not responsible for the effect [110,111]. The photolysis of $(\text{Bu}^n_4\text{N})_3[\text{Cr(CN)}_6]$ in dimethylformamide yields $[\text{Cr(CN)}_5(\text{DMF})]^{2-}$, and the quantum yield was studied between −60 and 50°C. The phosphorescence behaviour of this system was also studied, and it was demonstrated that the photolysis did not originate from the same excited state as the phosphorescence [112].

The E^0 for the $[\text{Cr(CN)}_6]^{3-}/[\text{Cr(CN)}_6]^{4-}$ couple is −1.143 V [113]. Second harmonic AC polarography has been applied to the $[\text{Cr(CN)}_6]^{3-}/[\text{Cr(CN)}_6]^{4-}$ system [114]. The electrochemical reduction of $[\text{Cr(CN)}_6]^{3-}$ in 2N NaOH has been studied by cyclic voltammetry and chronocoulommetry; $[\text{Cr(CN)}_6]^{4-}$ and $[\text{Cr(H}_2\text{O)}_5\text{OH}]^+$ are formed, and there is then electron exchange between the latter species and $[\text{Cr(CN)}_6]^{3-}$. Rate data were obtained for these processes [115]. The effect of tetra-alkylammonium hydroxides on the electrode kinetics of the $[\text{Cr(CN)}_6]^{3-}/[\text{Cr(CN)}_6]^{4-}$ couple on a mercury electrode has been studied [116].

The chromium(II) catalysed aquation of $[\text{Cr(CN)}_6]^{3-}$ to $[\text{Cr(CN)}_5\text{OH}]^{3-}$ is an outer-sphere electron transfer [117]:

$$[\text{Cr(CN)}_6]^{3-} + [\text{Cr(CN)}_5\text{OH}]^{4-} \rightleftharpoons [\text{Cr(CN)}_6]^{4-} + [\text{Cr(CN)}_5\text{OH}]^{3-}$$

In the electron excitation electron transfer between $[\text{Ru bipy}_3]^{2+}$ and a number of chromium(III) complexes, including $[\text{Cr(CN)}_6]^{3-}$, the rate-determining process is an intermolecular one between counter complex ions [118].

Some chemical reactions of $[\text{Cr(CN)}_6]^{3-}$ are summarised in Fig. 1.

Other $[\text{Cr(CN)}_6]^{3-}$ salts. We have already mentioned the structural studies on the Prussian Blue analogues, $\text{Mn}_3[\text{Cr(CN)}_6]_2.12\text{H}_2\text{O}$ [77] and $\text{Cd}_3[\text{Cr(CN)}_6]_2.n\text{H}_2\text{O}$ [78]. Cyanide linkage isomerism seems to occur in $\text{Fe}_3[\text{Cr(CN)}_6]_2$; as first prepared (by reaction of ferrous sulphate with $\text{K}_3[\text{Cr(CN)}_6]$), Mössbauer and magnetic data show it contains $\text{Fe}^{2+}\text{—N}\equiv\text{C—Cr}^{3+}$ linkages (ν_{CN} 2170 cm^{-1}, ν_{MC} 488 cm^{-1}). On oxidation and subsequent reduction the $\text{Cr}^{3+}\text{—N}\equiv\text{C—Fe}^{2+}$

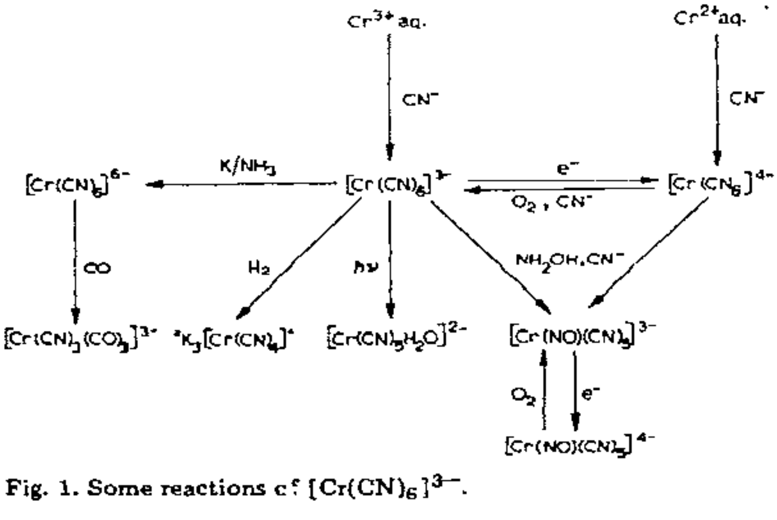

Fig. 1. Some reactions of $[\text{Cr(CN)}_6]^{3-}$.

linkage isomer can be made (ν_{CN} 2100, ν_{MC} 525 cm^{-1}) [119]. Shifts of ν_{CN} have been correlated [7] with lattice constants in $M_3^{II}[Cr(CN)_6]_2.nH_2O$.

$[Cr(CN)_x(H_2O)_{6-x}]^{3-x}$ species (x = 1 to 6 inclusive) have been isolated by ion-exchange techniques; for the tetra-, tri- and di-cyano species only the *cis* forms were found. Their electronic spectra were measured from 300—600 nm; spectral criteria for distinguishing the isomers were proposed [120].

$[Cr(NC)(H_2O)_5]^{2+}$ is probably an intermediate in the formation of $[Cr(CN)(H_2O)_5]^{2+}$ by reaction of excess chromous ion, $[Cr(H_2O)_6]^{2+}$, with cobalt(III) monocyano complexes, with *cis*-$[Cr(CN)_2(H_2O)_4]^+$ or 1,2,3-$[Cr(CN)_3(H_2O)_3]$ [121]. The kinetics of electron exchange of $[Cr(CN)(H_2O)_5]^{2+}$ with $[Cr(H_2O)_6]^{2+}$ were studied — the isocyano complex is probably also an intermediate in this reaction [122].

$[Cr(CN)_x(SCN)_{6-x}]^{3-}$ species have been made from potassium cyanide and $K_3[Cr(SCN)_6]$ in boiling acetonitrile. All the complexes (x = 1 to 6 inclusive) were obtained and separated by gel ionophoresis; no evidence for *cis* and *trans* isomers of the di-, tri- or tetra-cyano complexes was found. Electronic spectra were measured [123] from 200—700 nm.

$[Cr(CN)_5OH]^{3-}$ has already been mentioned as an intermediate (p. 204) [117].

K[Cr(phthalocyanine)(CN)(OH)] (ν_{CN} 2137 cm^{-1} and K[Cr(phthalocyanine)(CN)$_2$] were obtained by Elvidge and Lever [123a]. The complexes were made by reaction of cyanide with Cr(phthalocyanine)(OH); electronic spectra were measured from 230—1000 nm.

Chromium(II) (d^4). The cyanide chemistry of chromium(II) has been little investigated due to the very easy oxidation of the complexes (unlike the inert d^3 chromium(III) complexes, chromium(II) complexes are labile).

$K_4[Cr(CN)_6].3H_2O$ — as Chadwick and Sharpe point out [1], this formula has never been properly established — can be made from chromous acetate and excess potassium cyanide in solution under nitrogen. The blue salt may be crystallised from the red solution [124]. The magnetic moment is 3.40 B.M. in the solid state and 3.15 B.M. in solution at room temperatures [113].

The rate of exchange of $[Cr(CN)_6]^{4-}$ with labelled CN$^-$ is very fast [41]. The E_0 for the $[Cr(CN)_6]^{3-}/[Cr(CN)_6]^{4-}$ couple is −1.28 V (−1.14 V in molar cyanide) [113]. The kinetics of the oxidation of $[Cr(CN)_6]^{4-}$ by hydroxylamine have been studied polarographically and rate constants measured [125].

It has been suggested that the oxidation of $[Cr(CN)_6]^{4-}$ by oxygen or by hydrogen peroxide proceeds via an outer-sphere mechanism [126,127]. The reaction with hydrogen peroxide was studied by stopped-flow techniques; at high cyanide concentration the reaction sequence is probably

$$[Cr(CN)_6]^{4-} + H_2O_2 \rightarrow [Cr(CN)_6]^{3-} + OH + OH^-$$

$$[Cr(CN)_5H_2O]^{3-} + H_2O_2 \rightarrow [Cr(CN)_5OH]^{3-} + OH + H_2O$$

although chromium(IV) intermediates cannot be ruled out [127]. The rate of reaction of $[Cr(CN)_6]^{4-}$ with hydrated electrons has been measured [128].

The heat of reaction [37,38] of chromous sulphate (hydrated) with excess cyanide ion has a ΔH of -264.3 kJ mole^{-1}.

Chromium(I) (d^5). The cyano chemistry of this oxidation state is dominated by that of $[Cr(NO)(CN)_5]^{3-}$: many studies of this have been carried out, mainly because a wide range of complexes of the form $[Cr^I(NO)L_5]^{n-}$ exist ($L = CN^-$, H_2O, NH_3, DMSO etc.), all of which contain low-spin chromium(I) and are thus susceptible to EPR study.

$K_5[Cr(CN)_6]$ is a dark brown complex [129] formed by the action of potassium in liquid ammonia on $K_3[Cr(CN)_6]$, but further characterisation is required.

$K_3[Cr(CN)_4]$ is the empirical formula assigned to the olive green product formed by the reduction of either $K_3[Cr(CN)_6]$ or $K_3[Cr(NO)(CN)_5]$ with hydrogen at 400°. The compound is extraordinarily inert — it is insoluble in water and is said to be unattacked by concentrated nitric, hydrochloric or sulphuric acids "or by mixtures of these" [65]. The magnetic moment is 2.52 B.M. at room temperatures, and ν_{CN} in the infrared appears at 2178 and 2077 cm^{-1}. Banks and Kleinberg suggest that there are bridging cyanide ligands (certainly the high frequency ν_{CN} bond suggests this) and that perhaps both low-spin and high-spin chromium(I) are involved [65].

$K_3[Cr(NO)(CN)_5].H_2O$ is a bright yellow-green substance, best made by the reaction of hydroxylamine and potassium cyanide on alkaline chromate solutions [130]. The water of crystallisation can be removed in vacuo. The salt is stable and very soluble in water; the solutions slowly deposit a green material, possibly $[Cr(H_2O)_6][Cr(NO)(CN)_5]$.

An X-ray crystal structure study on the potassium salt showed this to have a disordered lattice [131], but a later study on $[Co\ en_3][Cr(NO)(CN)_5].H_2O$ yielded accurate bond parameters (Table 2) [132]. In the complex anion the Cr—N distance is 1.71(1) Å, the Cr—N—O angle is 176(1)°. The Cr—C (equatorial) distance is 2.033(7) Å, while the Cr—C (axial) distance is slightly, but significantly, longer at 2.075(14) Å [132].

Magnetic and EPR data. The susceptibility of $K_3[Cr(NO)(CN)_5].H_2O$ was measured from 85—296 K; it follows the Curie—Weiss law. The moment at room temperature is 1.87 B.M., consistent with low-spin chromium(I) [130].

There have been many studies of the EPR spectra and much controversy over the results or their interpretation. The dust seems now to have settled on most of these arguments, although the apparently large spin density on the nitrogen atom still needs a fuller explanation. The latest data are summarised in Table 4; measurements have been made on the pure substance [133]; its aqueous solution [133—137]; and in solid solution at various temperatures in the following host lattices: $K_3[Mn(NO)(CN)_5]$ [137,138]; $K_3[Co(CN)_6]$ [137,139]; KX (X = Cl, Br, I) and NaCl [135].

Early discussion on these data concentrated on the linearity of the Cr—N—O grouping (before the X-ray data became available). The view that the EPR data were best explained by the assumption of a Cr—N—O angle of ~135° [140] was later modified [139]; a later suggestion was that the deviation from linearity might be of the order of 9° [138], a view borne out by the X-ray data [132] on [Co en$_3$][Cr(NO)(CN)$_5$].H$_2$O. The origin of the apparent large spin density on the nitrogen atom (the cause of the "bent nitrosyl" postulate [139,140]) is still a matter for discussion, as is the ordering of energy levels within the complex [29,139]. It seems possible that spin polarisation effects might be responsible [139], as well as a small deviation from linearity of the Cr—N—O angle [138].

The presence of two magnetically distinct ions within the unit cell has been demonstrated [138]. Nuclear—electron double resonance in solutions of [Cr(NO)(CN)$_5$]$^{3-}$ has been demonstrated [141]. The effect of γ-irradiation on K$_3$[Cr(NO)(CN)$_5$] in a potassium chloride host lattice is to give [Cr(NO)-(CN)$_5$]$^{4-}$, but no evidence was found for the formation of a paramagnetic [Cr(NO)(CN)$_5$]$^{5-}$ (d^7) species [142]. EPR spectroscopy has been used as a probe for determining certain kinetic data (see below).

Vibrational and electronic data. Most of the studies of the vibrational spectra have used infrared spectroscopy: from 400—4000 cm^{-1} [143]; in the NO and Cr—N stretching regions with ^{15}N substituted species to help assignment [144]; 200—4000 cm^{-1} (Table 7) [145,146]; 200—1000 cm^{-1} [147]; Raman spectra from 100—1000 cm^{-1} (solid and aqueous solution) [147].

Electronic spectra have been measured for potassium bromide discs of the solid and the aqueous solution from 300—900 nm [29,133,148], glass in fluorolube at 80 K and 300 K from 320—570 nm [150]. Assignments were proposed in each case, and have also been proposed by others [30,149,151].

Core binding energies of the metal $3p$ electrons in K$_3$[Cr(NO)(CN)$_5$] are identical with those in K$_3$[Cr(CN)$_6$], from which the unjustifiable conclusion was drawn that [104] the nitrosyl complex involved trivalent chromium. The 1s binding energy in K$_3$[Cr(NO)(CN)$_5$] was deduced from photoelectronic spectra [152]. The large ^{14}N chemical shift in the complex is thought to be due to a Fermi contact term (it is the same for the axial and equatorial cyanide groups) [102].

Reduction of [Cr(NO)(CN)$_5$]$^{3-}$ at the dropping electrode gives a single, reversible one-electron wave (E_{1_2} = —1.164 V vs. S.C.E. in potassium chloride solution). The product is [Cr(NO)(CN)$_5$]$^{4-}$ [153]. Polarographic reduction of the ion in buffered solutions in sulphite media leads to a catalytic reduction of SO$_3^{2-}$ to S$_2$O$_4^{2-}$ (the [Cr(NO)(CN)$_5$]$^{3-}$ is regenerated with [Cr(NO)-CN)$_5$]$^{4-}$ as an intermediate). The rate law was deduced [154].

Elegant EPR studies have shown that, whereas in neutral solution the rates of exchange of cyanide ion with the equatorial or axial cyanide ligands in [Cr(NO)(CN)$_5$]$^{3-}$ are roughly equal, in acid solution the axial ligand is more labile to exchange than the equatorial (*cis*) ligands [155]. Acid hydrolysis of [Cr(NO)(CN)$_5$]$^{3-}$ has been followed by EPR methods: [Cr(NO)(CN)$_x$-(H$_2$O)$_{5-x}$]$^{2-x}$ complexes are formed, and [Cr(NO)(H$_2$O)$_5$]$^{2+}$ is the last member of the series [156]. EPR methods were also used to study the aquation to

$[Cr(NO)(CN)_x(H_2O)_{5-x}]^{2-x}$ in the presence of chromic, cupric and ferrous ions [157]. In mildly acid solution, aquation of $[Cr(NO)(CN)_5]^{3-}$ leads to $Cr(NO)(CN)_2(H_2O)_3$ which is inert to further substitution by water, but at pH 2 or less further loss of cyanide occurs and eventually the Cr—(NO) bond breaks. Rate constants for the initial aquation were measured, and a protonated nitrosyl intermediate postulated [158].

$$[Cr(NO)(CN)_5]^{3-} + H^+ \rightleftharpoons [Cr(NO.H)(CN)_5]^{2-}$$

$$[Cr(NO.H)(CN)_5]^{2-} - H_2O \rightarrow [Cr(NO)(CN)_4H_2O]^{2-}$$

Rate constants for electron exchange between $[Cr(NO)(CN)_5]^{3-}$ have been determined by EPR in several solvents [159].

$[Cr(NO)(CN)_4]^{2-}$ is thought to be formed during the reaction of $[Cr(NO)(CN)_5]^{3-}$ in dimethylsulphoxide solution with alkyl halides. The EPR spectra of this and of $[Cr(NO)(CN)(DMSO)_{5-x}]^{2-x}$ formed during this reaction were studied [160].

$[Cr(NO)(CN)_x(H_2O)_{5-x}]^{2-x}$ [156—158] and $[Cr(NO)(CN)_x(DMSO)_{5-x}]^{2-x}$ [160] species have been mentioned above.

$[Cr(CN)_5N_2]^{4-}$ is, it is said, probably formed when $[Cr(CN)_6]^{3-}$, azide and cyanide ions are irradiated in dimethylsulphoxide solution. The evidence seems to be that the EPR spectrum of this melange is similar to that of $[Cr(NO)(CN)_5]^{3-}$ but not identical with it [161]. A band at 2070 cm^{-1} was tentatively assigned to a N—N stretch [161], but ν_{CN} would seem a much more likely possibility.

$[Cr(CN)(CO)_5]$ is a green material, made from $Cr(CO)_5I$ and iodine cyanide. It is paramagnetic ($\mu = 1.7$ B.M. at room temperature) [162]. The infrared spectrum was measured from 200—4000 cm^{-1} (Table 7) [163].

Chromium(0) (d^6). $K_6[Cr(CN)_6]$ — the $[Cr(CN)_6]^{6-}$ ion is totally isoelectronic with $Cr(CO)_6$ — is formed as a dark green complex when $K_3[Cr(CN)_6]$ reacts with a solution of potassium in liquid ammonia. The salt is diamagnetic (as indicated by EPR measurements — not a sure method of establishing this point by any means) and its reducing power is equivalent to that expected for zerovalent chromium. With carbon monoxide, $K_3[Cr(CN)_3(CO)_3]$ is formed (see below, p. 209) [129]. With bipy or phen, $Cr(bipy)_3$ or $Cr(phen)_3$ are formed [164].

$K_4[Cr(NO)(CN)_5].2H_2O$ is a bright blue complex, very unstable to aerial oxidation, made by reduction of $[Cr(NO)(CN)_5]^{3-}$ solution at a mercury cathode [165]. It is diamagnetic. The infrared spectrum has been measured from 200—4000 cm^{-1}, and most of the fundamentals assigned and compared [145] with those for $K_3[Cr(NO)(CN)_5]$ (Table 8).

$K_4[Cr(CN)_4(CO)_2]$ has been prepared by the prolonged action of potassium cyanide in liquid ammonia on *cis*-$Cr(CO)_2(PPh_2CH_2.PPh_2)_2$ at 120°. The *cis* (C_{2v}) configuration of the yellow-green complex was deduced from its infrared spectrum (Table 6), and the CN and CO stretching force constants compared with those of the molybdenum and tungsten analogues [166].

$K_3[Cr(CN)_3(CO)_3]$ can be obtained by reaction of carbon monoxide with $K_6[Cr(CN)_6]$ [129] or, as $K_3[Cr(CN)_3(CO)_3].2NH_3$, from $Cr(CO)_3(NH_3)_3$ and potassium cyanide in liquid ammonia [167]. It is yellow and sensitive to moisture.

$K_2[Cr(CN)_2(CO)_4].\frac{1}{2}H_2O$ has been made by the action of an aqueous solution of potassium cyanide on $Na_2[Cr(CO)_5]$ at 75° (the water can be removed in vacuo [168]). It can also be made from potassium cyanide in liquid ammonia solution with $Cr(CO)_4$bipy [169], or as the $(PPh_3)_2N^+$ salt from $(PPh_3)_2N(CN)$ in dichloromethane with $Cr(CO)_6$ under irradiation [170].

$Na[Cr(CN)(CO)_5].H_2O$ is formed [168] as yellow needles by the action of an aqueous solution of sodium cyanide on $Na_2[Cr(CO)_5]$. The infrared spectrum has been measured from 200—4000 cm^{-1} (Table 6) [163].

$[Cr_2(CN)(CO)_{10}]^-$ has been made by acidification of $[Cr(CO)_5CN]^-$ [168]. The infrared spectrum has been measured from 200—4000 cm^{-1} (Table 6) and a D_{4d} (staggered) symmetry proposed, with a linear Cr—C≡N—Cr bridge [163]. The $(PPh_3)_2N$ salt was made from $(PPh_3)_2N(CN)$ and chromium hexacarbonyl under irradiation (ν_{CN} 2131 cm^{-1}) [170].

(b) Molybdenum and tungsten

The cyano complexes of these two metals have received more attention than any others from Groups IVa to VIIa, mainly on account of the structural problems of the octacyano species $[M(CN)_8]^{3-}$ and $[M(CN)_8]^{4-}$, and also their photochemistry. Because the chemistries of the cyano complexes of the metals are so similar we consider the two metals together in order to avoid undue repetition.

Molybdenum, tungsten(V) (d^1). $K_3[M(CN)_8].H_2O$. These are normally made by oxidation of $[M(CN)_8]^{4-}$ with permanganate (Mo, [171,172]; W [173]), ceric ion (Mo [174]), anodic oxidation (Mo [175]); W [176], nitric acid (W [173]), followed by addition of silver nitrate to give $Ag_3[M(CN)_8]$. This is then treated with potassium chloride. Nitrosyl chloride may be used directly [178] with $K_4[M(CN)_8]$. The sodium salt may be made in similar fashion as a tetrahydrate; evaporation of the solution obtained from $Ag_3[M(CN)_8]$ and hydrochloric acid gives $H_3[Mo(CN)_8].3H_2O$ [171] or $H_3[W(CN)_8].6H_2O$ [179]. The potassium salts are yellow, very sensitive to light and towards reducing agents.

Structural studies have been carried out on $(Bu^n_4N)_3[Mo(CN)_8]$ and on $Na_3[W(CN)_8].4H_2O$ (Table 2). In the former, the anion has a D_2 structure for the anion which however is little distorted from a dodecahedral (D_{2d}) configuration [174]. All the Mo—C distances are equal within the limits of experimental error, although the dodecahedron contains two sets of bonds each which do not have to be equivalent. The authors of the X-ray study on $(Bu^n_4N)_3[Mo(CN)_8]$ suggest that the metal d electron is in an orbital of mixed d_{z^2} and $d_{x^2-y^2}$ character [174]. In $Na_3[W(CN)_8].4H_2O$, which is isomorphous with $Na_3[Mo(CN)_8].4H_2O$, the complex anion is definitely antiprismatic (D_{4d}). It was suggested that the water satisfies the coordination requirement of the sodium cations giving tighter packing and so stabilising an antiprismatic configuration for the anion [180].

Magnetic and EPR data for $[M(CN)_8]^{3-}$. No magnetic data over a temperature range appear to have been obtained, but $K_3[Mo(CN)_8]$ has a moment of 1.66 B.M. and $Ag_3[Mo(CN)_8]$ of 1.77 B.M. at room temperatures [176], while $K_3[W(CN)_8]$ has a moment of 1.61 B.M. [177].

There have been many measurements of the EPR spectra (Table 4). The spectrum of $K_3[Mo(CN)_8]$ in water or ethanol consists of a main line with two overlapping satellites due to ^{95}Mo ($I = {}^5/_2$, abundance 15.78%) and ^{97}Mo ($I = {}^5/_2$, abundance 9.6%), and that of $K_3[W(CN)_8]$ a main line due to the non-magnetic isotope with a doublet due to ^{183}W ($I = ½$, abundance 14.4%) [181]. Data are available [20] for solid $K_3[Mo(CN)_8]$, and $Ag_3[Mo(CN)_8]$.

Solid solutions of $K_3[Mo(CN)_8]$ in $K_4[Mo(CN)_8].2H_2O$ and of $K_3[W(CN)_8]$ in $K_4[W(CN)_8].2H_2O$ differ from the spectra in glycerine [182], or alcohol glasses [181,185]. For the glasses of both salts, $g_\parallel > g_\perp$ and $A_\perp > A_\parallel$ with $g_\parallel$ close to 2.00, a situation expected for antiprismatic (D_{4d}) structures [182, 184]. In the solid solutions in $K_4[M(CN)_8].2H_2O$, however, the g values change and $g_\perp > g_\parallel$, $A_\parallel > A_\perp$ suggesting a change of configuration, probably to the dodecahedral (D_{2d}) form [182]. This evidence is not conclusive, however: the g value for $(Bu_4N)_3[Mo(CN)_8]$ (known to be dodecahedral [174]) is the same as for its solution in acetonitrile [174], (it is possible that the nature of the solvent could have some effect on the $D_{2d} \rightarrow D_{4d}$ transformation). A study of ^{13}C enriched $[Mo(CN)_8]^{3-}$ in aqueous solution shows that all the carbon atoms are equivalent, which could constitute evidence for an antiprismatic structure or for a fluxional structure [15]. This ^{13}C EPR work is of great interest as it shows, from the ligand hyperfine splitting, that the "metal" d electron has a spin density of 0.96 at molybdenum, 0.088 at each carbon atom and less than 0.006 at each nitrogen atom [185].

Although much work has been carried out on the EPR spectra of $[Mo(CN)_8]^{3-}$ and $[W(CN)_8]^{3-}$ it must be concluded that, insofar as they relate to the vexed question of the structures of these species in solution, the results are inconclusive. It would be of interest to compare the EPR spectrum of solid $Na_3[W(CN)_8].4H_2O$* and $(Bu_4N)_3[Mo(CN)_8]$ — the anions are respectively D_{4d} [180] and D_{2d} [174] — in order to check the validity of the EPR results (or of their interpretation) for distinguishing between these two structural forms. It would also be valuable to take the spectra of $[Mo(CN)_8]^{3-}$ and $[W(CN)_8]^{3-}$ in which only one isotope of each metal is present. One may question the validity of using $K_4[M(CN)_8].2H_2O$ as a host lattice for the solid solution studies — perhaps an isomorphous diamagnetic lattice such as could

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* Recent work shows that, whereas the EPR spectrum of $K_3[W(CN)_8]$ and $K_3(Mo(CN)_8]$ [46] changes from solid to solution, there is no such change for the sodium salts [177a].

be provided by the appropriate [Re(CN)$_8$]$^{3-}$ salts would be better. Although the EPR data of Corden et al. [174] are much too limited in scope to draw useful conclusions, one may agree with them that the complexes could be intermediate in structure between the dodecahedral and antiprismatic forms, or that the complexes have fluxional structures in solution [15].

Vibrational and electronic spectra. The sensitivity of [M(CN)$_8$]$^{3-}$ salts to light has made measurement of such spectra difficult. The infrared spectrum of [Co(NH$_3$)$_6$][Mo(CN)$_8$] has ν_{CN} bands at 2150(s) and 2144(m) cm^{-1}, while the Raman spectrum has three such bands [183] at 2156(m), 2151(m) and 2145(w) cm^{-1}. Only the infrared spectrum of [Co(NH$_3$)$_6$][W(CN)$_8$] has been measured in the ν_{CN} region: bands at 2153(s) and 2147(m) were observed [183].

There have been several measurements of electronic spectra; below we give the ranges covered and the configuration assumed, or predicted, from the data. The ease with which either the dodecahedral (D_{2d}) or antiprismatic (D_{4d}) model may be fitted to identical spectra shows that electronic spectroscopy is of little value for solving the problem of the structure of these species in solution. All the spectra were measured in aqueous solution: 200—1000 nm (Mo, W; antiprismatic) [21]; 200—1000 nm (Mo; antiprismatic) [186]; 220—400 nm (Mo, W; distorted dodecahedron (C_s)) [19]; 190—500 nm (Mo, W; dodecahedron, using crystal field theory) [20]; 300—600 nm (Mo; dodecahedral) [187]; W [177a]. A critique of these spectral data has been published [22].

Miscellaneous physical data. Spin relaxation in methanolic solution of K$_3$[Mo(CN)$_8$] was studied by measuring the width of the main line in the EPR spectrum as a function of temperature; more extensive studies using the same method but a variety of solvents for K$_3$[W(CN)$_8$] showed the effect of varying viscosities also (temperature range 150—400 K) [181]. The E^0 potentials for [M(CN)$_8$]$^{3-}$/[M(CN)$_8$]$^{4-}$ couples are +0.73 V (Mo) [175,188] and +0.46 V (W) [175,177].

The ^{99}Mo exchange between [Mo(CN)$_8$]$^{3-}$ and [Mo(CN)$_8$]$^{4-}$ is very fast [189], as is the ^{185}W exchange between [W(CN)$_8$]$^{3-}$ and [W(CN)$_8$]$^{4-}$ [173]. The CN$^-$/[M(CN)$_8$]$^{3-}$ exchange, however, is very slow in the dark but is markedly accelerated by light [173,177]. It seems likely that this effect is due to production of [M(CN)$_8$]$^{4-}$ photolytically [39].

Kinetics if iodide oxidation by [Mo(CN)$_8$]$^{3-}$ have been studied.

$$2[Mo(CN)_8]^{3-} + 3I^- \rightarrow 2[Mo(CN)_8]^{4-} + I_3^-$$

The reaction is second-order and proceeds via an outer-sphere mechanism [176]. The reaction between [Mo(CN)$_8$]$^{3-}$ and hydrazine has also been studied [190].

The many electron-transfer reactions involving [M(CN)$_8$]$^{3-}$ are considered on p. 216. Photolysis of [M(CN)$_8$]$^{3-}$ is considered on p. 214. Magnetic circular dichroism studies have been reported [177a].

K$_3$[M(CN)$_4$(OH)$_4$] salts have been claimed (Mo [130]; W [192]); the electronic spectra were measured for the molybdenum salt for the solid and the aqueous solution from 420—700 nm and a dodecahedral structure proposed [193], while for the tungsten complex the solution spectrum from 300—800 nm was said to indicate a non-dodecahedral structure [187]. However, the molybdenum complex is probably $K_3[Mo^{IV}O(OH)(CN)_4]$ [193] and the tungsten complex is probably analogous. $[W(CN)_7H_2O]^{2-}$ has been claimed [220a, 220b].

Evidence has been presented for the existence of $KFe^{II}[Mo^{V}(CN)_8]$ (from ferric sulphate and $K_4[Mo(CN)_8]$) [195], and also of $[Mo(CN)_4(CNHg(CN)_2)_4]^{3-}$ [196].

Molybdenum, tungsten(IV) (d^2). As with the $[M(CN)_8]^{3-}$ species, much work has been expended on the structural chemistry and the photochemistry of $[M(CN)_8]^{4-}$, and much still needs to be done.

$K_4[M(CN)_8].2H_2O$. The molybdenum salt is probably best made by reduction of molybdate, $[MoO_4]^{2-}$, with a pyridine—thiocyanate mixture to molybdenum(V) followed by treatment with potassium cyanide [197]; a better yield is said to result from the use of hydrazine as reducing agent [198]*. The tungsten salt is best made [199] by the action of potassium cyanide on $K_3[W_2Cl_9]$ or from cyanide and tungsten(V) oxalates [200]*. Another method is to treat "$(pyH)_2[WO_2(CNS)_3]$" with potassium cyanide [201]. The potassium salts are yellow and substantially soluble in water. The "free acids" $H_4[M(CN)_8].6H_2O$ can be made by passing hydrogen chloride gas through a solution obtained by shaking $K_4[Mo(CN)_8]$ in water with cation exchange resin in the hydrogen form [202] (ν_{CN} is at 2160, 2130 and 2090 cm^{-1}; electronic spectra from 400—600 nm are similar to those of $[Mo(CN)_8]^{4-}$ [202]). The tungsten analogue is made by treating $Ag_4[W(CN)_8]$ (ν_{CN} at 2185, 2140 cm^{-1}) with hydrochloric acid [179,203]. Treatment [204] of solutions of $H_4[M(CN)_8]$ in water with hydrochloric acid gas gives $H_4[M(CN)_8].4HCl.12H_2O$. The anhydrous free acids $H_4[M(CN)_8]$ can be prepared from the aquated forms with ether and hydrogen chloride followed by treatment of the etherate in vacuo; infrared data suggest that these contain asymmetric N—H—N bonds [69]. The anhydrous acid $H_4[W(CN)_8]$ has also been made by intensive dehydration of $H_4[W(CN)_8]$aq. (ν_{CN} 2190, 2160 cm^{-1} with ν_{WC} at 485 and δ_{WCN} at 450 cm^{-1}) [179].

There are four X-ray studies on the structures of salts containing $[M(CN)_8]^{4}$ The classic X-ray work of Hoard and Nordsieck [205] on $K_4[Mo(CN)_8].2H_2O$ has been rerefined and reanalysed [206] (Table 2). The anion has dodecahedral coordination, very slightly distorted from the idealised D_{2d} structure; although the dodecahedron has two sets of coordination sites (four A and four B sites) [16,206]) all the Mo—C distances are equal within the limits of experimental error (2.16 Å). It was suggested on the basis of this observation that π-bonding is not an important factor in the stabilisation of the dodecahedral versus the

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* Methods involving the use of $[MO_4]^{2-}$, CN^- and $(BH_4)^-$ have recently been described '00a].

antiprismatic structure [16,206]. A two-dimensional X-ray study on $Cd_2[Mo(CN)_8].2N_2H_4.4H_2O$ (earlier formulated as $Cd_2[Mo(CN)_8(N_2H_4)_2].4H_2O$ — see p. 217) suggests an antiprismatic structure for the anion, but no bond parameters were given. It was stated that the Mo—C—N angle deviated slightly from linearity. It is perhaps not certain that the anion really is D_{4d} rather than D_{2d}; the main interest of the work is its demonstration that the hydrazine molecules are essentially coordinated to the cadmium rather than the molybdenum, there being hydrogen bonding between the hydrazine and the nitrogen atoms of $[Mo(CN)_8]^{4-}$. The water is zeolitically contained in the lattice [207].

Two structural determinations of high quality on free acids have been carries out [203,204] and both show the D_{4d} antiprismatic structure for the anions. In $H_4[W(CN)_8].6H_2O$ the protons were not located, but there were O—H---N bonds (2.58 Å) to all the nitrogen atoms of $[W(CN)_8]^{4-}$, and also extensive O—H---O (2.89 Å) hydrogen bonding. The molybdenum acid $H_4[Mo(CN)_8].6H_2O$ is isomorphous, and its unit cell parameters were determined [203]. In $H_4[W(CN)_8].4HCl.12H_2O$ (again the molybdenum complex is isomorphous) there is also antiprismatic coordination for $[W(CN)_8]^{4-}$: six of the eight nitrogen atoms are hydrogen-bonded as W—C≡N---H---Cl---N≡C—W chains which stabilise the framework (N---Cl 2.38 Å). The two remaining cyanide groups have "direct" N---N contacts of 2.48 Å. It is thought that the four acidic protons form C≡N---$\overset{+}{H}$---Cl linear chains [204].

Although determinations of structures of other $[M(CN)_8]^{4-}$ species would be very interesting, the data already available serve to indicate that the dodecahedral to antiprismatic conversion depends largely on lattice factors, and that the energy difference between the two forms is probably very small [15]. We have already alluded to the suggestion (p. 210) that the coordination difference for the anions in $Na_3[W(CN)_8].4H_2O$ and $K_4[Mo(CN)_8].2H_2O$ may be due to the packing of water molecules around the cations [180]*.

Vibrational and electronic spectra of $[M(CN)_8]^{4-}$. There have been many studies of these; as with $[M(CN)_8]^{3-}$ salts the electronic spectra may, with equal facility, be interpreted as indicating whichever structure the author's whim prefers. Vibrational spectra of solid salts in the C≡N stretching region are normally so complicated that they too yield no useful structural information. Despite numerous attempts at improving resolution, etc., the infrared spectra of $[M(CN)_8]^{4-}$ in solution stubbornly show one broad band only. The Raman spectra of solutions provide the only evidence as to whether the dodecehedral (D_{2d}) or antiprismatic (D_{4d}) structure is present for the anion in solution, and the interpretation of even this is still questionable.

The following studies have been carried out (ranges and deduced structures for the anions indicated). Solid $K_4[M(CN)_8].2H_2O$: 200—400 cm^{-1} (anhydrous

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* Mössbauer (^{182}W) studies suggest D_{2d} configurations for the anions in solid $K_4[W(CN)_8]$-$.2H_2O$, $Li_4[W(CN)_8].nH_2O$, $(EtNC)_4(W(CN)_4)$, and for $K_4[W(CN)_8]$ in frozen solution; the D_{4d} form is found in solid $H_4[W(CN)_8].6H_2O$, $Cd_2[W(CN)_8].8H_2O$, $Na_3[W(CN)_8].4H_2O$ and in $H_4[W(CN)_8]$ in frozen solution [207a].

salts also); IR only, D_{2d} (with C_s for the anhydrous salts), 200—400 [208] IR and Raman, D_{2d}; 33—4000 IR (deuteriated salts also) [183,210], D_{2d}; 1900—2100 IR, D_{2d} [211]; 200—4000, Raman, D_{2d} [212]. $K_4[M(CN)_8]$ in aqueous solution: 100—4000, D_{2d} [209]; 100—4000, Raman, probably D_{4d} [210]; 100—4000, Raman, probably D_{4d} [183]; 1900—2200, IR, probably D_{4d} [211]; 200—4000, Raman, D_{4d} [212]. We see than that there is some disagreement as to the solution structure (the agreed assignment of D_{2d} for the solids is based on the foreknowledge of the X-ray structural information [206] — solid state spectra are too complex to allow any definite conclusions to be drawn). The most careful Raman work is probably that of Long and Vernon, who conclude that the D_{2d} configuration is retained in solution on the basis that the Raman spectra of the solids and solutions are similar, and on the number of polarised C≡N stretches in the Raman solution spectra [209].

Electronic spectra have been measured by several workers: all are for aqueous solution except for that by König [21] who compared the reflexion spectra of $K_4[M(CN)_8].2H_2O$ and $K_4[M(CN)_8]$ with their aqueous solutions from 200—500 nm, the results being interpreted on the basis of D_{4d} symmetry for the solutions [21]. Other data are: 250—600 nm, distorted dodecahedron [19]; 200—500 nm, D_{2d} assignment using crystal field theory [20,177a]; 200—500 nm, D_{2d} symmetry (for the molybdenum complex, vibrational fine structure was observed for one band [187]). In general the electronic spectra of all $[M(CN)_8]^{3-}$ and $[M(CN)_8]^{4-}$ species (M = Mo, W) are similar, although apparently that of $(Bu^n_4N)_3[W(CN)_8]$ differs significantly from that of $K_4[W(CN)_8]$ in solution [15]. The charge transfer spectrum of $K_4[Mo(CN)_8].2H_2O$ has been studied from 250—320 nm in a variety of solvents [213]. For a critique of the spectral data see Golebiewski and Kowalski [22].

The ^{13}C NMR spectrum of $K_4[Mo(CN)_8]$ shows a single line in aqueous solution which may possibly indicate a structure in which all carbon atoms are equivalent (i.e. the D_{4d} antiprismatic) or may simply arise from exchange effects [15], or another possibility is that the $[M(CN)_8]^{4-}$ molecules are fluxional in solution [15]. This is rendered more likely by the observation of only one ^{13}C resonance in $[W(CN)_8]^{4-}$ solution as low as —160°C. As with $[M(CN)_8]^{3-}$ in solution, the suggestion that there is simply no preferred structure [15,16], D_{2d} or D_{4d}, for $[M(CN)_8]^{4-}$ is attractive; certainly none of the vibrational or electronic spectral data really conflict with such a possibility. Magnetic circular dichroism studies have been reported [177a].

The ^{14}N NMR spectrum of $K_4[Mo(CN)_8]$ has been measured in aqueous solution [181]. The bonding in $[M(CN)_8]^{3-}$ and $[M(CN)_8]^{4-}$ has been considered by many [19—21,182,183].

Photochemistry of $[M(CN)_8]^{3-}$ and $[M(CN)_8]^{4-}$. The photochemistry of transition metal cyano complexes has been reviewed, and both give good coverage to the octacyano complexes of molybdenum and tungsten [39,40]. Although there is perhaps less controversy now as to the processes involved than there was three of four years ago, there are still aspects of the photochemistry of these species which need further research.

$[M(CN)_8]^{3-}$. In neutral or acid [220a] solution, irradiation with visible light of $[M(CN)_8]^{3-}$ causes the initial yellow colour to change to red and then to blue; in alkaline solution the colour changes are faster: yellow to darker yellow, to green, finally to blue. The initial photoreduction of $[M(CN)_8]^{3-}$ to $[M(CN)_8]^{4-}$ is pH-dependent [214]. The red and blue products are almost certainly $[Mo(CN)_7H_2O]^{3-}$ and $[MO(OH)(CN)_4]^{3-}$, and for the base reaction $[Mo(CN)_7OH]^{4-}$ and $[MO(OH)(CN)_4]^{3-}$ are probably involved. The initial overall reaction however is a photoreduction to $[M(CN)_8]^{4-}$.

In acid solution, $[W(CN)_8]^{3-}$ or $H_3[W(CN)_8]$ photolyses via an intermolecular redox process involving the hydroxyl radical [220a,220b]:

$$[W(CN)_8]^{3-} + H_2O \xrightarrow{h\nu} [W(CN)_8]^{4-} + OH^{\cdot} + H^+$$

The overall reaction is very complicated, however, due to secondary photolysis of $[W(CN)_8]^{4-}$, and intermediates such as $[W(CN)_7H_2O]^{3-}$, $[W(CN)_7H_2O]^{2-}$, $[W_2(CN)_{15}]^{6-}$ and $[W(CN)_6(H_2O)_2]^{-}$ may be involved (their electronic spectra were recorded [220a,220b]). For acid solutions of $[Mo(CN)_8]^{3-}$ an intramolecular process involving cyanide radical has been proposed [215,216]:

$$\begin{array}{l}[Mo(CN)_8]^{3-} \xrightarrow{h\nu} [Mo(CN)_7CN]^{3-} \xrightarrow{H_2O} [Mo(CN)_7H_2O\,CN]^{3-} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad [Mo(CN)_7H_2O]^{3-} + CN\end{array}$$

While in basis solution $[Mo(CN)_7H_2O]^{3-}$ then undergoes reaction with OH^- to give $[MoO(OH)(CN)_4]^{3-}$ (see below) [216].

Flash photolysis of $[Mo(CN)_8]^{3-}$ has very recently been studied and the sequence proposed [217]:

$$[Mo(CN)_8]^{3-} \xrightarrow[\text{(CTTM)}]{h\nu} [Mo(CN)_7]^{3-} + CN$$

$$[Mo(CN)_7]^{3-} \xrightarrow{H_2O} [Mo(CN)_7H_2O]^{3-}$$

the latter decaying by reaction with CN^- to $[Mo(CN)_8]^{4-}$ either in a dodecahedral (D_{2d}) configuration or an antiprismatic (D_{4d}) form which may be converted thermally to the D_{2d} form [217].

$[M(CN)_8]^{4-}$. For photolysis by light in the visible region the first product is red (this stage can be reversed by putting the solution in the dark or by adding cyanide ion) [218,219]; prolonged photolysis leads irreversibly to a blue product. As soon as irradiation of a neutral solution of $[M(CN)_8]^{4-}$ begins, the pH rises, and in parallel with the formation of a red intermediate [219]. The conductance of $[M(CN)_8]^{4-}$ drops during irradiation [220].

The primary photochemical reaction for neutral aqueous solution with radiation in the ligand field region is [218,219,220a,220b]

$$[M(CN)_8]^{4-} + H_2O \xrightarrow{h\nu} [M(CN)_7H_2O]^{3-} + CN^-$$

and this is also the case for irradiation of the free acids in solution [220,220a]. The red product in this initial photolysis caused much discussion in the earlier literature but it now seems generally agreed that it is $[M(CN)_7H_2O]^{3-}$ (the molybdenum salt has been isolated [202] as $Ag_3[Mo(CN)_7H_2O]$ see p. 217). An earlier theory that ten coordinate "supercomplexes", e.g., $[M(CN)_8(H_2O)_2]^{4-}$ were involved [186,221—223] now seems generally to be discounted. The final blue product of the reaction in neutral or basic solution involves the release of three cyanide ions [39,108,214,219,220].

$$[Mo(CN)_7H_2O]^{3-} + OH^- \rightarrow [Mo(CN)_7OH]^{4-} + H_2O$$

$$[Mo(CN)_7OH]^{4-} + 2OH^- \rightarrow [MoO(OH)(CN)_4]^{3-} + 3CN^- + H_2O$$

The details are however still in dispute; $[M(CN)_6]^{2-}$ has been proposed [224] as a possible intermediate. Thermodynamic data for photolysis of $K_4[W(CN)_8]$ have been given [225].

Flash photolysis of $[M(CN)_8]^{4-}$ is a more recently studied process. Excitation below 300 nm (i.e., in the "charge-transfer" spectral region) produces photoelectrons [226,227]. The main (but apparently not sole) chemical products [228] are $[M(CN)_8]^{3-}$. At 77 K $[Mo(CN)_8]^{3-}$ is produced from $[Mo(CN)_8]^{4-}$ according to the scheme [228]

$$[Mo(CN)_8]^{4-} \xrightarrow{h\nu} [Mo(CN)_8]^{4-*} \rightarrow [Mo(CN)_8]^{3-} + e^-aq.$$

Electron transfer reactions of $[M(CN)_8]^{3-}$ and $[M(CN)_8]^{4-}$. Most of these are very fast, and the Marcus electron-transfer theory for outer-sphere activated complexes applies. Amongst those studied by a variety of techniques are the following: $[Mo(CN)_8]^{4-}/Ce^{IV}$, $/Fe(phen)_3]^{3+}$, $/[Osbipy_3]^{3+}$ [229]; $[Mo(CN)_8]^{4-}/Ce^{IV}$, $/Mo(CN)_8]^{3-}$, $/[IrCl_6]^{2-}$ [230]; $[W(CN)_8]^{4-}/Ce^{IV}$, $/[Fe\text{-}phen_3]^{3+}$, $/[FeMe\text{-}phen_3]^{3+}$ [229]; $[W(CN)_8]^{4-}$, $/[W(CN)_8]^{3-}$ [173,177,231]; $[W(CN)_8]^{4-}/[Mo(CN)_8]^{3-}$, $/[Fe(CN)_6]^{3-}$ [230]; $[Mo(CN)_8]^{3-}/[Fe(CN)_6]^{4-}$ [230].

The E^0 potentials for $[M(CN)_8]^{4-}$ are +0.73 V (Mo) [175,179] and +0.46 V (W) [175,177]. The exchange between CN^- and $[M(CN)_8]^{4-}$ is very slow in the dark but fast in the light (cf. p. 215) [173,232]; exchange of ^{99}Mo between $[Mo(CN)_8]^{4-}$ and $[Mo(CN)_8]^{3-}$ is very fast [189], as is that [173] of ^{185}W between $[W(CN)_8]^{3-}$ and $[W(CN)_8]^{4-}$. The kinetics of the reaction

$$2H_2O + 3[Mo(CN)_8]^{4-} + [CrO_4]^{2-} + 8H^+ \rightarrow 3[Mo(CN)_8]^{3-} + [Cr(H_2O)_6]^{3+}$$

have been studied and a rate-law established [233], and also the kinetics of the reaction [234]

$$2H_2O + 5[Mo(CN)_8]^{4-} + [MnO_4]^- + 8H^+ \rightarrow 5[Mo(CN)_8]^{3-} + [Mn(H_2O)_6]^{2+}$$

Photoelectron spectra of $M[CN_8]^{4-}$ in solution were measured [297].

$[M(CN)_6]^{2-}$ have been suggested [224] as intermediates in the alkaline photolysis of $[M(CN)_8]^{4-}$.

$K[Mo(CN)_5]$ has been reported [235] as a white solid, made from reaction of molybdenum trioxide with potassium cyanide; by heating $K_4[MoO_2(CN)_4]$ to 600°; or by oxidative hydrolysis of $K_4[Mo(CN)_7].2H_2O$. Its existence has not been confirmed.

$M_2^{II}[M(CN)_8R_2]$ (M^{II} = Cd, Mn; R = H_2O, NH_3, N_2H_4) are allegedly ten coordinate "supercomplexes", and their claimed existence at one time was an important step in one of the main theories for the photolytic decomposition of $[M(CN)_8]^{4-}$ [186,221—223]. Salts formulated as $Cd_2[Mo(CN)_8(N_2H_4)_2].4H_2O$, $Mn_2[Mo(CN)_8(NH_3)_2].nH_2O$ and $Cd_2[Mo(CN)_8(H_2O)_2].2H_2O$ and their tungsten analogues were made from $[M(CN)_8]^{4-}$, R and (M^{II}) under irradiation [223]. It was suggested that the anions were ten coordinate, the R ligands being coordinated to the centres of the two square faces of the Archimadaean antiprism (the normal eight coordination positions being occupied by the cyanide ligands). Thus, during photolysis of $[M(CN)_8]^{4-}$, an antiprismatic solute configuration was favoured [223] since it could accommodate two aquo ligands to give "$[M(CN)_8(H_2O)_2]^{4-}$", the celebrated red intermediate now believed to be $[M(CN)_7H_2O]^{3-}$ (cf. below). An X-ray study of "$Cd_2[Mo(CN)_8(N_2H_4)_2].4H_2O$" seemed to suggest that, although the $[Mo(CN)_8]$ residue may have antiprismatic coordination, the hydrazine is coordinated to the cadmium rather than the molybdenum [207]. Thus these species may be $[M(CN)_8]^{4-}$ salts of, for example, $[Cd(H_2O)_6]^{2+}$, $[Cd(N_2H_4)(H_2O)_n]^{2+}$, etc. Recently, however, the suggestion that these "ten coordinate" species exist in solution has been revived [236a,254].

$[M(CN)_7(H_2O)]^{3-}$. The salt $Ag_3[Mo(CN)_7H_2O]$ was isolated by adding silver nitrate to the red solution which results from irradiation of $[Mo(CN)_8]^{4-}$ (see p. 215). Although the analyses fit the given formulation, the report of a band at 898 cm^{-1} in the infrared spectrum — no other bands were listed — is rather alarming since this is where a Mo=O stretch might occur. Deuteriation would show whether the assertion of Mitra et al. that this is a coordinated water mode is true [202]. The species responsible for the blue solution has been variously described as $[Mo(CN)_4(OH)_4]^{4-}$ [18], $[Mo(CN)_4(OH)_2]^{2-}$ [223], $[Mo(CN)_4(OH)_3H_2O]^{3-}$ [236] and $[Mo(CN)_8(H_2O)_2]^{4-}$ [181], but $[M(CN)_7H_2O]^{3-}$ has frequently been invoked as the probable formula of the red intermediate (p. 215).

The tungsten analogue $[W(CN)_6H_2O]^{3-}$ is formed [220a,220b] by photolysis of $[W(CN)_8]^{4-}$.

$[M(CN)_7OH]^{4-}$. The molybdenum salt is probably found during photolysis of $[Mo(CN)_8]^{4-}$ in alkaline solution [216,224].

$K_4[MO_2(CN)_4].6H_2O$. The molybdenum salt can be made by prolonged photolysis of $K_4[Mo(CN)_8]$ until the solution passes beyond the red stage to the blue, followed by addition of potassium hydroxide to give the red complex (the blue colour of the solution is probably due to the protonate, $[MO(OH)(CN)_4]^{3-}$ — see below) [237]. Other methods of preparation of the molybde-

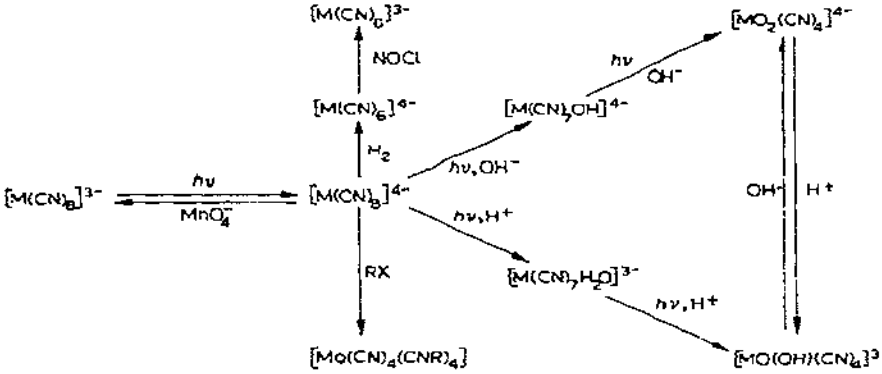

Fig. 2. Some reactions of octacyano-molybdates and -tungstates.

num salt are the treatment of an electrolytically reduced solution of molybdenum trioxide in hydrochloric acid with cyanide and hydroxide [171,237], or reduction of ammonium paramolybdate by hydrazine followed by treatment with a potassium cyanide—hydroxide mixture [194]. The molybdenum salt forms red, diamagnetic crystals, becoming tan-coloured on dehydration [193] at 100°; the aqueous solution is blue. The tungsten analogue can only be obtained as a sodium salt, $Na_4[WO_2(CN)_4].nH_2O$ ($n = 0, 6, 12$) or as mixed salts, $NaK_3[WO_2(CN)_4]$, by photolysis [194] in alkaline solution of $[W(CN)_8]^{4-}$.

The formulation and *trans*-configuration of the anion has been proved by X-ray studies of $NaK_3[MoO_2(CN)_4].6H_2O$ [238] and $K_4[MoO_2(CN)_4].6H_2O$ [239]. The two anions are very similar in their dimensions (Table 2): the $Mo{=}O$ length is longer than that for $Re{=}O$ in $K_3[ReO_2(CN)_4]$ although rhenium is a third-row element [240]; a possible explanation is suggested later (p. 234). A preliminary X-ray study of "$K_4[Mo(CN)_4(OH)_4].2H_2O$", while this formulation was retained by the authors [241], is described as being isomorphous with $NaK_3[MoO_2(CN)_4].6H_2O$, so presumably this also contains the *trans*-$[MoO_2(CN)_4]^{4-}$ ion.

Infrared (200—4000 cm^{-1}) and Raman (200—1000 cm^{-1}) spectra of $K_4[MoO_2(CN)_4]$ have been measured (Table 6), and comparison of the approximate $Mo{=}O$ force constant with that for $Re{=}O$ in $K_3[ReO_2(CN)_4]$ bears out the greater metal—oxo strength in the latter [242]. The infrared spectra of several of these salts have also been recorded (Table 6) [194,243a]. Electronic spectra of the solid molybdenum and tungsten salts were measured from 330—700 nm [194,237], and of the molybdenum salt in solution of varying pH from 200—700 nm [243].

It seems likely that "$K_2[Mo(CN)_4(OH)_2]$" in the form reported by Jakob [247] is in fact $K_4[MoO_2(CN)_4]$, as are "$K_4[Mo(CN)_4(OH)_4].4H_2O$" [214, 223, 241] and "$K_3[Mo(CN)_4(OH)_3H_2O]$" [243], while "$K_4[W(CN)_4(OH)_4].4H_2O$" [236] is $K_4[WO_2(CN)_4].6H_2O$ [237]. Protonation of $[WO_2(CN)_4]^{3-}$ has been studied [237a].

$K_4[MoS_2(CN)_4]$ has been reported as a black solid being formed from potassium cyanide and molybdenum disulphide [244]; it is unlikely however, to contain a S=Mo=S group.

$K_3[MoO(OH)(CN)_4]$. The molybdenum salt can be obtained as a dihydrate by the action of methanol on the blue solution formed by the prolonged irradiation of $K_4[Mo(CN)_8]$; it is blue [237]. The anhydrous tungsten salt can be obtained in an analogous fashion, and is purple [237]. Both salts are diamagnetic. The anhydrous molybdenum salt has been obtained [194] from a procedure involving the use of a cation exchange resin in the hydrogen form on $K_4[MoO_2(CN)_4]$. The infrared spectrum of the molybdenum salt has bands at 2095 and 2060 cm^{-1} (ν_{CN}); 1057 shifting to 822 cm^{-1} on deuteriation (Mo—OH bend); and 921 cm^{-1} ($\nu_{Mo=O}$); the corresponding modes in the tungsten salt are at 2075, 1072 and 875 cm^{-1} [237]. The electronic spectra of the solids were measured over the 330—700 nm range [237], and from 200—500 nm for the aqueous solution [216]. The X-ray crystal structure of $Na_3[MoO(OH)(CN)_4].4H_2O$ (z/m, z = 2) shows a *trans* configuration, Mo=O 1.72 Å; Mo—O (OH) 2.15 Å; Mo—C 2.15 Å; C—N 1.15 Å; and a Mo—C—N angle of 175° [245a].

$K_2[Mo(CN)_4(OH)_2]$. This green diamagnetic complex has been prepared by treatment of $K_4[MoO_2(CN)_4]$ in solution with cation exchange resin in the hydrogen form followed by alcohol precipitation. It has an alarmingly complicated infrared spectrum between 400—1000 cm^{-1} [194]. The $[Cd(H_2O)_6]^{2+}$ salt has also been made as a brown-green material [194], and there is a brief report of $(Ph_4As)_2[Mo(CN)_4(OH)_2]$ [237]. The blue material reported as $K_2[Mo(CN)_4(OH)_2]$ obtained from disproportionation of $[Mo(CN)_8]^{3-}$ solutions [247] is probably a mixture of $K_2[MoO_4]$ and $K_3[MoO(OH)(CN)_4]$ [194].

$K_4[M(CN)_4(OH)_4].4H_2O$ salts have been claimed (e.g., for molybdenum [201,214,223,241,244,247], and for tungsten [236]) but these [237a] are almost certainly $K_4[MO_2(CN)_4].6H_2O$. On the basis of electronic spectral measurements it has been claimed that $[Mo(CN)_4(OH)_4]^{4-}$ has a dodecahedral [193] and $[W(CN)_4(OH)_4]^{4-}$ a non-dodecahedral structure [187] in solution, and thermochemical data have been given for photolysis of the latter "salt" [225].

$K_4[M(CN)_5(OH)_3].nH_2O$ is said to be found by reaction of $K_4[M(CN)_8]$ with potassium hydroxide [248], and a non-dodecahedral structure proposed for the Mo complex on the basis of its electronic spectrum in the solid state and in aqueous solution [193]. It is possible however that these are mixtures of $K_4[M(CN)_8]$ and $K_4[MO_2(CN)_4].4H_2O$.

$K_3[Mo(CN)_4(OH)_3H_2O]$ [171,218,236,243] is probably $K_3[MoO(OH)(CN)_4]$ [194].

$M(CN)_4(CNR)_4$. A number of these have been made by alkylation or arylation of $Ag_4[M(CN)_8]$ with the appropriate organic halide (Mo : R = CH_3 [249, 250], C_2H_5 [249]; Pr^n, Bu^t, allyl, Ph_2CH [250], W : R = CH_3 [251,252], C_2H_3, Pr^n, Pr^i, Bu^t, $PhCH_2$ [251]). The complexes are diamagnetic; the best general methods for their preparation are given by Novotny et al. [250] for molybdenum and by Latka [251] for tungsten. Prolonged reaction times may lead to heptacoordinated fully alkylated species, e.g. [250], $[Mo(CNCH_3)_6I]I$.

An X-ray crystal structure study of $Mo(CN)_4(CNCH_3)_4$ (Table 2) shows that the structure is dodecahedral. The four cyanide carbon atoms occupy the four "A" sites of the dodecahedron (i.e. those sites which are best adapted for metal-to-ligand π-bonding), the methyl carbon atoms occupying the remaining four "B" sites. The Mo—C (cyanide) bond distance is slightly longer, however (2.175(7) Å) than the Mo—C (methyl) (2.148(7) Å). This interesting result suggests that Orgel's prediction [18] that four ligands will π-bond preferentially to the "A" sites, using principally the $d_{x^2-y^2}$ orbital, may be correct [250]*.

Infrared spectra of the complexes were measured; we list here the ν_{CN} values before the $\nu_{C-N(methyl)}$ for each. For $[Mo(CN)_4(CNR)_4]$ R = Me 2196 and 2145, 2251 and 2234; R = Pr^n, 2145, 2227 and 2189; R = Bu^t, 2181 and 2144, 2212; R = allyl, 2195 and 2145, 2233; R = Ph_2CH, R = 2144, and 2135, 2218 and 2183 cm^{-1} [250]. For $W(CN)_4(CNR)_4$, R = Me (this complex only is a monohydrate) 2137, 2219; R = C_2H_5, 2137, 2219; R = Pr^n, 2141, 2211; R = Pr^i, 2141, 2211; R = Bu^t, 2137, 2188; R = $PhCH_2$, 2137, 2219 cm^{-1} [251].

Elelctronic spectra were measured from 200—400 nm for $Mo(CN)_4(CNR)_4$ (R = Et, Pr, Bu). Only one ^{13}C resonance was seen over a temperature range of 90°, but this could arise from rapid interconversion effects [250].

"$K_6[Mo_2^{VI},Mo^{IV}(CN)_8O_6].2H_2O$" is a blue material obtained by repeated precipitation of $K_4[MoO_2(CN)_4]$ solutions with methanol [193]. The formula sounds highly improbable.

"$Mo(CN)_2(OH)_2$" is a black, insoluble material, formed [193] by acidification of $K_4[MoO_2(CN)_4].4H_2O$.

$K_4[MoO_2(NO)(CN)_5].3H_2O$ is a yellow complex said to be formed by oxidation of $K_4[Mo(NO)(CN)_5]$. The infrared spectrum has bands at 2125(ν_{CN}), 1580(ν_{NO}), 890($\nu_{Mo=O}$) cm^{-1} [165].

Interaction of $[M(CN)_8]^{4-}$ with other molecules. Alkylation of the cyanide ligands in $[M(CN)_8]^{4-}$ is dealt with above (p. 219). The Lewis base-like function of the nitrogen atoms in $[M(CN)_8]^{4-}$ is illustrated by the formation of $K_4[Mo(CNBF_3)_8]$ from the reaction of $K_4[Mo(CN)_8]$ with boron trifluoride. The CN stretching frequency in the infrared increases to 2235 cm^{-1}, but the reflectance spectrum of the solid is very similar to that of $K_4[Mo(CN)_8]$ itself [253]. The interaction of uranyl ion with $[Mo(CN)_8]^{4-}$ was studied to see whether ten coordinate "supercomplexes" were formed (see p. 216 above). Uranyl nitrate and $[Mo(CN)_8]^{4-}$ gave $(UO_2)_2[Mo(CN)_8].6H_2O$, but the infrared spectrum indicated that the nitrogen atoms of the CN ligands interacted with the uranyl oxo ligands (ν_{CN} at 2140 cm^{-1}), the molybdenum retaining its eight coordination [254]. The interaction of mercuric cyanide with $[Mo(CN)_8]^{4-}$ has been studied and thermodynamic data derived [196].

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* *Mössbauer studies on $W(CN)_4(CNEt)_4$ indicate a D_{2d} configuration for the solid [207a].*

$KFe^{III}[Mo(CN)_8]$ has been claimed [195], made by interaction of ferric chloride with $K_4[Mo(CN)_8]$.

Molybdenum, tungsten(III) (d^3). $K_4[Mo(CN)_7].2H_2O$ has long been known. It can be made as shiny black flakes by the action [255] of potassium cyanide in $K_3[MoCl_6]$, or from cyanide and molybdenum trichloride [235]. The salt can be dehydrated by heating to 95° [256]. There have been a number of measurements of the magnetic moment over a temeprature range (Table 3) [256—258]; at room temperature the moment is 1.6 B.M. (1.80 for the aqueous solution). The EPR spectrum could not be obtained for the solid or its aqueous solution, but the dihydrate gave a signal below 150 K (Table 4). The g-values ($g_\parallel > 2.00$ and $g_\perp < 2.00$) have been interpreted in favour of a monocapped trigonal prismatic structure (it should be noted that no hyperfine structure due to ^{95}Mo or ^{97}Mo was seen) [256]. The infrared spectra of the solid and solution are similar (ν_{CN} at 2078 and 2046 cm^{-1}, and the solid also has bands at 358 and 432 cm^{-1}; in solid $Cs_3[Mo(CN)_7].nH_2O$ ν_{CN} is at 2077 and 2034 cm^{-1} with a band at 353 cm^{-1}). The Raman spectrum of the aqueous solution has ν_{CN} bands at 2106 and 2063 cm^{-1}. The similarity of solid and solution spectra (also true of the electronic spectra from 200—900 nm) suggests retention of heptacoordination in solution [256]. The electronic spectrum has also been measured from 460—700 nm [213].

$K_2[Mo(CN)_5]$ is said to be formed when $K_4[Mo(CN)_8]$ is heated with potassium cyanide to 550°; the complex is red and has a magnetic moment of 0.59 B.M. at room temperatures (0.87 B.M. in aqueous solution) [259]. A metal—metal bonded structure has been proposed [259], but no evidence for this could be found from the Raman and infrared spectra (200—400 cm^{-1}, Table 6) [260].

$K_3[M(CN)_6]$. The molybdenum complex can be made by treatment of $K_4[Mo(CN)_6]$ with methanol [261] or by the action of nitrosyl chloride on that complex [178]. The brown salt has ν_{CN} bands in the infrared at 2104 and 2045 cm^{-1}, and the magnetic moment is 1.24 B.M. at room temperatures [178]. The tungsten salt is made from $K_4[W(CN)_6]$ and methanol; it is brown, has a magnetic moment of 1.76 B.M., and infrared ν_{CN} bands at 2099, 2041 and 2023 cm^{-1} [178].

$K_3[Mo_2(CN)_{10}]$ is said to be formed when $K_2[Mo(CN)_5]$ is treated with nitrosyl chloride; it is olive-coloured. The magnetic moment is 1.41 B.M. per two metal atoms and a mixed III/IV oxidation state was proposed [178].

$K_2[W(CN)_5H_2O]$ is a brown complex made by the action of nitrosyl chloride on $K_4[W(CN)_6]$; the magnetic moment is 1.18 B.M. at room temperatures, and ν_{CN} in the infrared are at 2150 and 2104 cm^{-1} [178].

A number of rather ill-defined molybdenum(III) species have been reported: $K_6[Mo_2O_2(NO)_2(CN)_{10}]$ as a green, diamagnetic material made [262] by oxygenation of $K_3[Mo(NO)(CN)_5]$; $K_3[MoS(CN)_4].2H_2O$, a blue species obtained from molybdenum trioxide, hydrogen sulphide, potassium hydroxide and potassium cyanide [260], and these reactants can be persuaded [245] to give $K_6[Mo_2S_3(CN)_6]$, $K_4[Mo_2OS(CN)_6].4H_2O$ and $K_5[Mo_2S_4(CN)_8].7H_2O$.

Molybdenum, tungsten(II) (d^4). $K_4[M(CN)_6]$ salts are obtained by reduction of $K_4[M(CN)_8]$ with hydrogen at 110–300°C. The green molybdenum salt has a magnetic moment of 1.13 B.M. at room temperatures, and the infrared spectrum has ν_{CN} bands at 2055, 2035, 2010 and 1960 cm^{-1}; the green tungsten salt has an even lower moment of 0.94 B.M., with the infrared ν_{CN} bands at 2080, 2010 and 1950 cm^{-1} [261].

$K_2[Mo(NO)(CN)_5]$ is said to be formed [262] as a yellow, diamagnetic species by hypobromite oxidation of $[Mo(NO)(CN)_5]^{4-}$. It was not isolated.

$K_3[Mo(NO)O(CN)_4]$ is another yellow, diamagnetic species, obtained by oxidation of $[Mo(NO)(CN)_5]^{3-}$ with ferricyanide in alkali. The salt was apparently not isolated [262]. $K_4[Mo(NO)(OH)_2(CN)_4]$ is in fact $K_4[Mo(NO)(CN)_5]$ (see below).

Molybdenum, tungsten(I) (d^5). $K_3[Mo(NO)(CN)_5]$ can be made in solution by oxidation of $K_4[Mo(NO)(CN)_5]$ by ferricyanide or by aerial oxidation; it is yellow, and the moment is 1.24 B.M. at room temperatures [259]. Although the salt seems not to have been isolated the existence of the $[Mo(NO)(CN)_5]^{3-}$ anion seems to be fairly well established [264] by the EPR spectrum of an aerially oxidised solid sample of $K_4[Mo(NO)(CN)_5]$. The spectrum was measured in potassium bromide and in $K_3[Co(CN)_6]$ as host lattices, in an ethanol–dimethylformamide glass and in aqueous solution (Table 4). It was shown that the fraction of electron density at each nitrogen atom is 0.053 [264].

Molybdenum, tungsten(0) (d^6). Here chromium, molybdenum and tungsten display the greatest similarity in their cyanide chemistries, due, no doubt, to the presence of the t_{2g}^6 shell which allows of maximum metal-to-ligand π bonding to acceptors like CO and CN^-.

$K_4[Mo(NO)(CN)_5].2H_2O$ is made as a purple material by the reaction of hydroxylamine with molybdate ion in the presence of excess potassium cyanide and hydroxide [245,262,265,266]. The formulation as $K_4[Mo(NO)(OH)_2(CN)_6]$ is no longer accepted [130]. The salt is diamagnetic.

An X-ray crystal structure determination indicates a disordered lattice, but molybdenum—nitrogen distance of 1.95 Å was reported for the Mo—NO moiety [268] (this seems very strange — the corresponding Mn—N distance in $K_3[Mn(NO)(CN)_5]$ is alleged to be 1.66 Å [269], but the much lower ν_{NO} frequency for the molybdenum complexes (1455 cm^{-1} as against 1706 cm^{-1} for $[Mn(NO)(CN)_5]^{3-}$) argues for a much lower Mo—N distance). Details of the structure are given in Table 2 [268]. The infrared spectrum has been measured from 80–4000 cm^{-1} [145,146] (see Table 6). The electronic spectrum was taken from 200–600 nm [262].

cis-$K_4[M(CN)_4(CO)_2]$ salts can be made [164] as white solids from the reaction of potassium cyanide with $Na_2[M(CO)_{10}]$. The *cis* configuration is indicated [164] by the infrared spectrum (Table 7); CO and CN force constants were calculated.

$K_4[M(CN)_3(CO)_3]$ can be made as white solids by reaction of $M(CO)_4$—bipy [169] or $M(CO)_6$ [270] with a solution of potassium cyanide in liquid ammonia. The molybdenum salt can also be made from $[Mo(CO)_3bipy]_2$ and potassium cyanide (ν_{CN} 2095; ν_{CO} 1900, 1745 cm^{-1}).

$Na_2[M(CN)_2(CO)_4]$ can be made as white crystalline solids from $Na_2[M_2(CO)_{10}]$ and aqueous sodium cyanide. The molybdenum complex is dehydrated, the tungsten anhydrous [270]. Salts of $[W(CN)_2(CO)_4]$ have also been obtained from $W(CO)_6$ and $(PPh_3)_2N(CN)$ in dichloroethane (ν_{CN} at 2088 cm^{-1}) [170].

$Na[W(CN)(CO)_5].H_2O$ can be made from $Na_2[W_2(CO)_{10}]$ and aqueous sodium cyanide in a sealed tube at 60° [267]; the $(PPh_3)_2N^+$ salt has been made from irradiated $W(CO)_6$ and $(PPh_3)_2N(CN)$ (ν_{CN} at 2098 cm^{-1}) [170]. The piperidinium salt $(pipH)[W(CN)(CO)_5]$ has been made from addition of piperidine to a solution of $W(CO)_6$ in hydrocyanic acid and tetrahydrofuran (a mixture [272] which itself yields $W(CNH)(CO)_5$). The infrared spectrum (Table 7) has been measured [272]. The nucleophilicities of $[Mn(CN)(CO)_5]^-$ (M = Cr, Mo, W) have been compared from their rates of reaction with alkyl halides [273].

$K[M(CN)(CO)_3L]$ (L = bipy, phen, en) have been made from $C_7H_8Mo(CO)_3$ with L in the presence of cyanide. The infrared spectra suggest a C_{3v} symmetry (ν_{CN} for Mo and W, 2100 and 2096 cm^{-1} (L = bipy); 2080 cm^{-1} (Mo, L = phen); 2100 cm^{-1} (Mo, L = en) [271].

$Na[M(CN)(CO)(NO)(\pi\text{-}C_5H_5)].H_2O$ are red-brown complexes obtainable from the reaction between $NaN(SiMe_3)_2$ with $M(CO)_2(NO)(\pi\text{-}C_5H_5)$. The infrared ν_{CN}, ν_{CO} and ν_{NO} frequencies respectively are 2094, 1884, 1597 cm^{-1} (Mo) 2074, 1867, 1578 cm^{-1} (W) [274].

$[W_2(CN)(CO)_{10}]^-$ has been made from an irradiated solution in tetrahydrofuran of $(PPh_3)_2N(CN)$ and $W(CO)_6$ (ν_{CN} at 2121 cm^{-1}) [170].

(iv) Group VIIa (Mn—Tc—Re)

The cyano complexes of manganese in particular have been extensively investigated although some lacunae still remain; rhenium has received a fair amount of attention and technetium understandably little. On the whole, manganese represents faithfully in its cyano chemistry the "middle block" of transition elements: the predominant coordination number is six and the predominant oxidation states (III) and (II). Rhenium however, retains some of the characteristics of the other early transition elements, e.g., in its formation of $[Re(CN)_8]^{3-}$ and in the extensive cyano chemistry of its pentavalent state.

Manganese

Manganese(IV) (d^3). Only one complex is fully established.

$K_2[Mn(CN)_6]$ is a yellow species prepared by the oxidation of $K_3[Mn(CN)_6]$ by nitrosyl chloride. The magnetic moment of 3.94 B.M. at room temperature is close to the "spin only" value for three unpaired electrons. The infrared spectrum shows bands at 2240 and 2150 cm^{-1} (ν_{CN}) [176].

"$K_4[Mn(CN)_8]$" was claimed as the product of reaction of potassium cyanide and potassium permanganate [275]. Later workers obtained the pink solid originally reported, but have variously identified it as $K_3[Mn_2(CN)_9].4KOH$ [276], $K_2[Mn(CN)_5H_2O]KCN$ [277] or the mixed oxidation state species "$K_{3.62}[Mn(CN)_6].0.13H_2O$" [278]*.

$Mn(CN)_2$(phthalocyanine) is said to be formed when an ethanolic solution of cyanide reacts with manganese(IV) phthalocyanine [279].

Manganese(III) (d^4). $K_3[Mn(CN)_6]$ is one of the few examples of a low-spin manganese(III) complex. Although the reaction of manganese(III) orthophosphate with potassium cyanide is the standard procedure for the preparation of the complex [280], an easier method is to oxidise manganous salts such as the carbonate with hydrogen peroxide followed by reaction with excess cyanide [198]. The potassium salt forms deep red crystals.

An X-ray study of $K_3[Mn(CN)_6]$ revealed a disordered lattice isomorphous with that of potassium ferricyanide [281]. There are also structural data [34, 282] for the salt $Cs_2Li[Mn(CN)_6]$ (Table 2). Unit cell parameters for a number of hexacyanomanganates of bivalent cations (M^{II} = Mn, Fe, Co, Ni, Cu, Zn, Cd) have been determined for $M_3^{II}[Mn(CN)_6].3H_2O$, these belonging to the $F\bar{4}3m$ space group [283]. Unit cell data for $K_3[Mn(CN)_6]$ and $K_3[Cr(CN)_6]$ were compared [75].

Careful magnetic measurements on $K_3[Mn(CN)_6]$ over the range 4.2—300 K show that the susceptibility follows a Curie law near room temperatures (μ_{eff} 3.50 B.M. at room temperature, as expected for a low-spin octahedral d^4 complex) but approaches a temperature-independent value at lower temperatures. The general features are in agreement with the prediction of Kotani's theory (Table 3) [284]. No EPR spectrum is observed [61] for $K_3[Mn(CN)_6]$.

The Raman and infrared spectra of $Cs_2Li[Mn(CN)_6]$ have been measured and a full assignment of bands given (Table 5) [34,282]; partial assignments have been given for $K_3[Mn(CN)_6]$ in the solid state and in solution [55,88a]. The infrared spectrum of $K_3[Mn(CN)_6]$ has been measured from 200—4000 cm^{-1} over a pressure range [88a]. Electronic absorption spectra of $[Mn(CN)_6]^{3-}$ over the range 190—4000 nm in solution and at 143 K in water—glycerol mixtures, have been measured and assignments proposed; ligand field parameters were derived (see Table 8) [26]. Similar correlations between the results of electronic spectra [91]; infrared spectra [33,34,91] and unit cell constants [34] have been drawn, viz. that the M—C bond strength falls in the series $Fe > Co > Mn > Cr$ (see also p. 201).

The X-ray photoelectron spectra of $K_3[Mn(CN)_6]$, $K_4[Mn(CN)_6]$ and $K_3[Cr(CN)_6]$ have been measured and calculated charges on the metal atoms

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* A recent X-ray crystal structure determination showed that the main product of this reaction is $K_7[Mn_2O(CN)_{10}]CN$ [278a].

compared (see p. 203) [36a]; the charge on the metal and $2p_{\frac{1}{2}}$ binding energies for the two manganese salts were virtually identical [36]. Fine structure of the K_α absorption edge was measured for $K_3[Mn(CN)_6]$, $K_4[Mn(CN)_6]$ and $K_5[Mn(CN)_6]$, and the K_β X-ray emission spectra of $K_3[M(CN)_6]$ (M = Cr, Mn, Fe) were measured and correlated with the degree of covalency in the metal—carbon bond [106]. The ^{14}N magnetic resonance has been measured for $K_3[Mn(CN)_6]$ in solution (see p. 203) [107], and paramagnetic ^{13}C magnetic resonance shifts observed (using naturally abundant ^{13}C) for $K_3[M(CN)_6]$ (M = Mn, Fe) and $K_4[Mn(CN)_6]$ in polycrystalline samples and in aqueous solution [286].

The standard potential E^0 for

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

is −0.24 V [287] (for a discussion of this and other potentials involving cyano systems, see ref. 1). The hydrolysis constant K_h for the process

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

is approximately 10^{-10} at 18°C, corresponding to a degree of hydrolysis of some 1% for a molar solution [288].

The exchange of $[Mn(CN)_6]^{3-}$ with labelled cyanide ion in aqueous solution has been studied [41,289]: the rate is fast and the exchange is first-order [289] in $[Mn(CN)_6]^{3-}$. It has been suggested that a heptacoordinate species, $[Mn(CN)_6H_2O]^{3-}$, is involved as an intermediate [289].

The principal chemical reactions of $[Mn(CN)_6]^{3-}$ are summarized in the reaction scheme, Fig. 2.

$K_3[Mn(CN)_6H_2O]$ has already been mentioned [289] as a possible intermediate during exchange of $[Mn(CN)_6]^{3-}$ with CN^-. It has been claimed that this (or $K_2[Mn(CN)_5H_2O].KCN$) is one of the products of the reaction between potassium cyanide and potassium permanganate, another being $K_3[Mn(CN)_6]$. The complex is pinkish-brown and diamagnetic [277], (the latter seems unlikely for a salt containing $[Mn(CN)_5H_2O]^{2-}$). The infrared spectrum differs

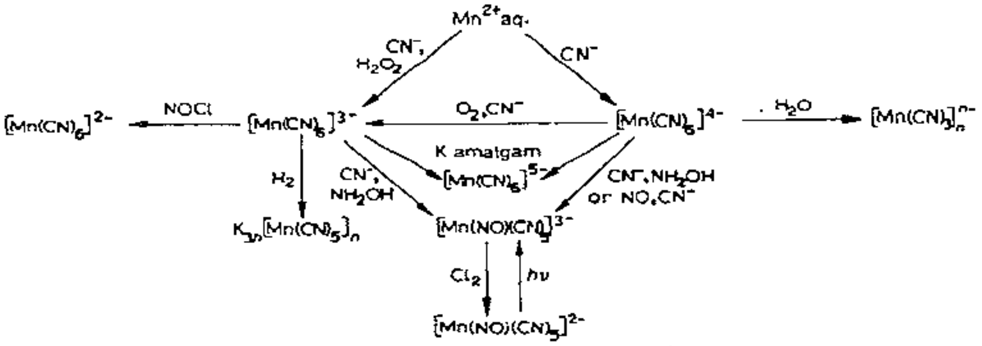


Fig. 3. Some reactions of $[Mn(CN)_6]^{3-}$ and $[Mn(CN)_6]^{4-}$.

from that of $K_3[Mn(CN)_6]$ (Table 7). The electronic absorption spectrum was also measured [277]. See also p. 224 [278a].

$K_3[Mn(CN)_5NO_2]$ is obtained by ultraviolet irradiation of a solution of K_3-$[Mn(CN)_5NO]$ in cyanide media in the presence of oxygen [290].

$K_3[Mn_2(CN)_9].4KOH$ was claimed by Goldenberg to be the product of reaction of potassium cyanide with potassium permanganate [276], but later work indicates that this species does not exist [277,278].

$[Mn(CN)_2$ phthalocyanine$)]^-$ has been made by the action of cyanide ion on manganese phthalocyanine [279]. For mixed oxidation state complexes of Mn^{III} and Mn^{II} see below, p. 231.

$Mn(CN)_2(OH)(H_2O)_3$ is formed when aqueous solutions of $K_3[Mn(CN)_6]$ are allowed to stand [279a].

Manganese(II), (d^5). The special stability associated with a half-filled *d* shell means that there are few low-spin complexes of manganese(II); almost all manganese(II) cyano complexes are of this type however due to the strong ligand field exerted by the cyanide ion.

$K_4[Mn(CN)_6].3H_2O$ is a blue-violet material which gives a yellow solution (if the free cyanide concentration falls to 1.5 M "$K[Mn(CN)_3]$" is precipitated). The complex is usually made by the action of excess cyanide on a manganese(II) salt, usually the acetate or carbonate; it is very easily oxidised so that air must be rigorously excluded during its preparation [26,289]. The anhydrous potassium salt can be obtained by dehydration of $K_4[Mn(CN)_6]$.-$3H_2O$ over concentrated sulphuric acid. The free acid, $H_4[Mn(CN)_6]$, has been made from $Pb_2[Mn(CN)_6]$ and hydrogen sulphide [291].

The X-ray crystal structure of $Na_4[Mn(CN)_6].10H_2O$ has been reported (Table 2) [292].

The magnetic moment of $K_4[Mn(CN)_6].3H_2O$ has been measured (Table 3) over the range 80—300 K; at the latter temperature it is 2.18 B.M. [293]. Theoretical interpretations of the magnetic behaviour have been given [293, 294]. The EPR spectrum of the solid dispersed in the isomorphous diamagnetic host lattice $K_4[Fe(CN)_6].3H_2O$ was measured (Table 4) [61]. Owing to the short relaxation time no hyperfine structure at temperatures higher than 12 K could be detected, but at 12 K there is substantial anisotropy [61]. The theoretical implications of these EPR spectra have been discussed [61,294]. In an ice glass at 77 K, $K_4[Mn(CN)_6]$ shows an EPR spectrum which is thought to derive [295], not from $[Mn(CN)_6]^{4-}$, but from cyano-bridged polymeric species such as $[(CN)_5Mn{-}C{\equiv}N{-}Mn(CN)_5]^{7-}$. There have also been studies [296] on the EPR spectra of $K_4[Mn_xFe_{1-x}(CN)_6].3H_2O$.

Partial assignments of the Raman and infrared spectra of solid $K_4[Mn(CN)_6]$.-$3H_2O$ have been given from studies over the range 200—4000 cm^{-1} (Table 6) [55] and the infrared spectrum has been studied from 200—4000 cm^{-1} over a pressure range [88a]. The electronic absorption spectrum of the aqueous solution has also been measured over the range 190—4000 nm in aqueous solution and in water—ethanol at 143 K, and ligand field parameters and bond assignments given [26] (see p. 186).

Photoelectron emission (PEE) spectra of aqueous solutions of $K_4[Mn(CN)_6]$ in excess cyanide have been measured; the quantum yields for a given photon energy were somewhat different from those of other hexacyano complexes [297]. As with $K_3[Mn(CN)_6]$, data have been collected on binding energies of $2p_{\frac{3}{2}}$ electrons [36]; on fine structure of the K absorption edge [285], and on the ^{13}C paramagnetic nuclear resonance [286] for the aqueous solution and for polycrystalline $K_4[Mn(CN)_6].3H_2O$.

Polarographic reduction of $K_4[Mn(CN)_6]$ at the dropping mercury electrode shows two waves ($E_{\frac{1}{2}}$ — 1.33 and −1.61 V vs. S.C.E.) [297]. The standard potential of the $[Mn(CN)_6]^{3-}/[Mn(CN)_6]^{4-}$ couple is −0.24 V [1,287]. The heat of complexation of $Mn^{2+}(aq)$ with cyanide to give $[Mn(CN)_6]^{4-}$ has been determined as −144.3 kJ mole^{-1} [37,38]. Exchange of $[Mn(CN)_6]^{4-}$ with labelled cyanide ion is measurably slow and is not affected by light [41]. The rate of hydrated electron reaction with $K_4[Mn(CN)_6]$ has been measured [118].

The important chemical properties of $[Mn(CN)_6]^{4-}$ are summarised in Fig. 3.

Prussian Blue analogues. Amperometric evidence for the existence of such species as $[Mn^{II}Fe^{II}(CN)_6]^{2-}$ and $[Mn^{II}Fe^{III}(CN)_6]^{-}$ has been presented [298], and the EPR spectra of mixed $[Mn_xFe_{1-x}(CN)_6]^{4-}$ species have been studied [296].

"$K[Mn(CN)_3]$" the dark green product obtained upon mixing manganese(II) salts with a deficiency of potassium cyanide, is probably best formulated as $K_2Mn^{II}[Mn^{II}(CN)_6]$. The moment is 4.53 B.M. at room temperature, close to the value of 4.4 B.M. to be expected for equal numbers of low-spin (C-bonded) and high-spin (N-bonded) manganese(II) centres. The X-ray powder pattern has been indexed on the basis of a simple unit cell. The infrared spectrum has a simple band at 2062 cm^{-1} in the C≡N stretching region [299]. It is probable that "$K_{1.52}[Mn(CN)_{3.72}]$" (or $K_{3.22}[Mn(CN)_6]$), made by fusion of $K_3[Mn(CN)_6]$ and potassium cyanide at 650° [259], is an impure form of $K[Mn(CN)_3]$. It too has a single C≡N stretch at 2057 cm^{-1} [259]. Species of the form $Mn^{II}[M(CN)_6].8H_2O$ (M = Fe, Ru, Os) and $Mn_3^{II}[M(CN)_6].nH_2O$ (M = Cr, Co) have been reviewed by Ludi and Gudel [7] (see also p. 201). The single crystal X-ray determination of $Mn_2[Ru(CN)_6].8H_2O$ shows that the ruthenium is coordinated by the six carbon atoms of six cyanide ligands (Ru—C 2.03(5) Å), and the manganese by three nitrogen ends of three cyanide groups (Mn—N 2.14(6) Å) and three oxygen atoms of water molecules, one being a terminal aquo ligand (Mn—O 2.21(6) Å) and two bridging (Mn—O 2.35(1) Å). The manganese atoms are in binuclear $Mn_2(NC—)_3(H_2O)_4$ units, the three N atoms taking up facial positions about the MnN_3O_3 octahedra which are linked by two bridging aquo groups [300].

$K_3[Mn(CN)_5]$ has been made by reduction of $K_3[Mn(CN)_6]$ in hydrogen at 420°. The brown product is completely insoluble in water and the presence of a band at 2178 cm^{-1} in its infrared spectrum (in addition to bands at 2090, 2060 and 2040 cm^{-1}) suggests the presence of bridging cyanide groups as well as terminal ones. The magnetic moment at room temperatures is 4.4 B.M.

This species too may have a "Prussian Blue" type of structure [261].

$K_2[Mn(NO)(CN)_5]$ is to be considered as a manganese(II) (d^5) complex on the assumption that the nitric oxide ligand coordinates as NO^+, a view broadly confirmed by the magnetic and EPR properties of the complex. It is a canary yellow substance, first prepared by oxidation of $K_3[Mn(NO)(CN)_5]$ (q.v.) with nitric acid [301], but a simple procedure [302] is to pass chlorine gas through an aqueous solution of $K_3[Mn(NO)(CN)_5]$. Although Cotton et al. studied the magnetic properties of the potassium and similar salts over a temperature range (Table 3) they reported a moment of 0.50 B.M. for the potassium salt at room temperature and a moment of 1.73 B.M. in acetone solution [301], whereas later workers found 1.73 B.M. for the solid at room temperatures [303].

There have been a number of studies of the EPR spectrum of the complex (Table 4). The earliest of these, carried out on solutions and glasses of $K_3[Mn(NO)(CN)_5]$, showed no ^{14}N hyperfine splitting [304]. Measurements on a single crystal diluted in $Na_2[Fe(NO)(CN)_5].2H_2O$ did show such splitting however [29,303] and this was confirmed by other workers [29]. The spin-density observed on the nitrogen has been attributed to mixing in of an excited E state (with considerable $\pi^*(NO)$ character) with the B_2 ground state [29,303], while Fortman and Hayes prefer an explanation based on spin—polarisation effects [137]. The EPR spectrum of $[Mn(NO)(CN)_5]^{2-}$ has also been observed in crystals of $[Mn(NO)(CN)_5]^{3-}$ in alkali metal halides after γ-irradiation [142]. The g and A values for $[Mn(NO)(CN)_5]^{2-}$ are given in Table 4.

The infrared spectrum of normal and ^{15}N-enriched [142] $K_2[Mn(NO)(CN)_5]$ has been measured over the range 200—4000 cm^{-1} [29,143,306], and the Raman spectrum of the solid from 100—1000 cm^{-1} [147]. Provisional assignments of the bands were made (Table 7); the metal—nitrogen stretching and metal—nitrosyl deformation modes are very close to each other (ca. 623 cm^{-1}). The electronic absorption spectrum of the solution was measured over the range 190—600 nm and also from 200—900 nm [148] and band assignments proposed on the basis of Manoharan and Gray's model [29]. The bonding in $[Mn(NO)(CN)_5]^{2-}$ has been discussed by a number of workers [29,30,137,142,303,304]. The 1s nitrogen bonding energy in the complex has been studied by measuring the photo-electronic spectrum [152].

The standard potential for

$$[Mn(NO)(CN)_5]^{2-} + e^- \rightarrow [Mn(NO)(CN)_5]^{3-}$$

is +0.597 V [302] (compared with −0.27 V for the $[Mn(CN)_6]^{3-}/[Mn(CN)_6]^{4-}$ couple [287]).

$[Mn(CN)Cl_5]^{4-}$ has been postulated as an intermediate formed during γ-irradiation of $[Mn(NO)(CN)_5]^{3-}$ in a KCl host lattice [304].

$[Mn(CN)(phthalocyanine)(EtOH)]^-$ is said to be formed when a solution of $[Mn(CN)_2(phthalocyanine)]^-$ is irradiated [279].

Manganese(I) (d^6). This is an unusually low oxidation state for manganese, but the cyanide ligands in such species exert their π-acceptor properties to take advantage of the filled t_{2g} shell which is of course a particularly advantageous configuration (rare gas configuration) for π-acceptor ligands.

$K_5[Mn(CN)_6]$ can be made by reduction of $K_3[Mn(CN)_6]$ or $K_4[Mn(CN)_6]$ by Devarda's alloy [198], electrolytic methods [287,308] or, probably the best procedure, by the use of potassium amalgam [309]. The colourless, sparingly soluble potassium salt is diamagnetic, as is the much more soluble sodium salt. Reduction of $K_3[Mn(CN)_6]$ with potassium in liquid ammonia is said [310] to give $K_5[Mn(CN)_6].NH_3$ (but see p. 231).

Two quite different sets of unit-cell dimensions have been given for $K_5[Mn(CN)_6]$. Treadwell and Raths [308] measured a tetragonal lattice ($a = 16.35$, $c = 13.11$ Å) while Schwochau and Herr [311] claimed that $K_5[M(CN)_6]$ (M = Mn, Tc, Re) were isomorphous (cubic; $a = 11.890$ Å for $K_5[Mn(CN)_6]$). It is quite possible, as suggested by Chadwick and Sharpe [1] that one "form" is a hydrate.

The Raman and infrared spectra of solid $K_5[Mn(CN)_6]$ were measured [55, 312] and compared with those of the corresponding technetium and rhenium complexes [312]. The C≡N stretches are higher and M—C stretches lower (as are the corresponding force constants) for rhenium than for manganese, as is to be expected from the more efficient overlap of orbitals in the third row. The fine structure of the K_α absorption edge has been measured [285] and compared with those for $K_3[Mn(CN)_6]$ and $K_4[Mn(CN)_6]$.

The standard potential for

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

in 1.5 M sodium cyanide is −1.06 V [308].

$K_3[Mn(CN)_4]$ and $K_2[Mn(CN)_3]$ are said to be formed with $K_3[Mn(CN)_6]$ when $K_4[Mn(CN)_6]$ is electrolytically reduced [313,314], but no clear evidence for their existence as pure species has been given.

$K_3[Mn(NO)(CN)_5].2H_2O$ is formally a manganese(I) complex if the nitric oxide group is taken to function as the NO^+ ligand; this is borne out by the observed diamagnetism of the complex. It may be obtained in poor yield by the action of nitric oxide on a solution of $[Mn(CN)_6]^{4-}$ in cyanide, but the best preparation [301] is to react hydroxylamine in excess potassium cyanide with a manganese salt [302], or with a solution of $K_3[Mn(CN)_6]$ or $K_4[Mn(CN)_6]$. It forms purple crystals.

The X-ray crystal structure of $K_3[Mn(NO)(CN)_5].2H_2O$ shows the expected C_{4v} symmetry for the complex anion with a linear Mn—N—O linkage; the Mn—N distance is only 1.66 Å (Table 2) [269]. The infrared spectrum has been measured from 200—5000 cm^{-1} [143,146,147,315,316] and msot of the normal modes assigned (Table 6) [315]; ^{15}N substitution shows the Mn—N stretch to lie in the 660 cm^{-1} region close to the Mn—N—O bonding mode [306,315]. Raman spectra of the solid and aqueous solution were measured from 200—1000 cm^{-1} [147]. The electronic absorption spectrum has been recorded over the range 190—700 nm [29,307] and assigned according to the model of Manoharan and Gray [2]. The bonding in $[Mn(NO)(CN)_5]^{3-}$ has been discussed by a number of workers [29,30,143].

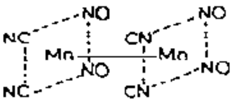
The standard potential of $[Mn(NO)(CN)_5]^{2-}/[Mn(NO)(CN)_5]^{3-}$ is +0.597 V [302]. Unlike $[Mn(NO)(CN)_5]^{2-}$, $[Cr(NO)(CN)_5]^{3-}$ and $[Fe(NO)(CN)_5]^{2-}$, $[Mn(NO)(CN)_5]^{3-}$ is not reduced at the dropping mercury electrode within the potential range studied [302,307]. Studies on photolysis of the ion by ultraviolet radiation show that in the presence of cyanide, but absence of air, nitric oxide and $[Mn(CN)_6]^{4-}$ are the main products [307], whereas if oxygen is present $[Mn(NO_2)(CN)_5]^{3-}$ is formed [290]. Irradiation [304] of a solid solution of $K_3[Mn(NO)(CN)_5]$ in KCl gives $[Mn(NO)(CN)_5]^{2-}$. Methylation of the complex to $[Mn(NO)(CNCH_3)_5](SO_3F)_2$ may be accomplished with methyl fluorosulphonate [316]. The fast reaction between $[Mn(NO)(CN)_5]^{3-}$ and $(Osbipy_3)^{3+}$ has been studied by flow techniques [229].

cis-$K_3[Mn(CN)_4(CO)_2]$ can be made from $Mn_2(CO)_{10}$ [317] or from $Mn(NO)(CO)_4$ [318] with a solution of potassium cyanide in liquid ammonia. It forms colourless crystals, and the infrared spectrum (Table 7) supports the C_{2v} (*cis*) configuration. Force constants for the cyanide ligands were contrasted with those for the isoelectronic $[Cr(CN)_4(CO)_2]^{4-}$ ion [317].

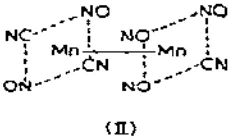
fac-$K_2[Mn(CN)_3(CO)_3]$ is made from $Mn(NO)(CO)_4$ and potassium cyanide in liquid ammonia [318], or, more easily, from $Mn(CO)_5Cl$ and an ethanolic solution of potassium cyanide at 120° under pressure [317]. The infrared spectra (Table 5) support the C_{3v} structure [317].

$Mn(CN)(CO)_5$ can be made as a pale yellow crystalline solid by reaction of $Na[Mn(CO)_5]$ with iodocyanogen. The infrared (Table 6) and mass spectra were measured. With tris-*o*-diphenylphosphinophenylphosphine (QP), Mn(CN)(CO)QP is formed (ν_{C-N} 2132 cm^{-1}, ν_{C-O} 1833 cm^{-1}) [319]. Fenske et al. [11] have compared the bonding characteristics of CN^- and CO in $[Mn(CN)(CO)_5]$.

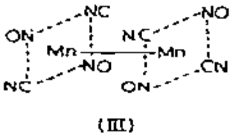
$[Mn(CN)(CO)_2(\pi\text{-}C_5H_5)]^-$ salts have been made from $(\pi\text{-}C_5H_5)Mn(CO)_3$ and sodium cyanide (for the sodium salt ν_{CN} 2058 cm^{-1}, ν_{C-O} 1905 and 1828 cm^{-1}). Acidification of this with orthophosphoric acid yields $Mn(CNH)(CO)_2(\pi\text{-}C_5H_5)$; the presence of an N—H bond is shown by the infrared spectra of



(I)



(II)



(III)

the normal and deuterated species (ν_{C-N} 2016, ν_{C-O} 1919 and 1859 cm^{-1}, ν_{N-H} 3413 cm^{-1} for the hydrogen complex; for the deuterate the frequencies are respectively 1968, 1919 and 1859, 2618 cm^{-1}) [320].

Complexes of manganese(0) or lower oxidation states. For "$K_6[Mn(CN)_6]$", see below. Attempts to obtain $K_4[Mn(NO)(CN)_5]$ (isoelectronic with the known $K_3[Fe(NO)(CN)_5]$) have so far been unsuccessful [304].

cis- and *trans*-$K_4[Mn(NO)_2(CN)_2]_2$ have been made by reaction of $Mn(NO)_3$-CO with potassium cyanide in liquid ammonia (*cis* form); the *trans* complex was made by heating the *cis* species in a sealed tube in ethanol. On the basis of the infrared spectra (Table 6) the C_{2v} (I) structure was proposed for the *cis* form and either the D_{2h} (II) or D_{2d} (III) for the *trans* [318]:

$K_3[Mn(CN)_2(NO)_2]$ is made by reduction of $K_4[Mn(CN)_2(NO)_2]_2$ with potassium in liquid ammonia. Infrared spectra [318] (Table 6) of the green complex suggest a tetrahedral structure similar to the isoelectronic $[Fe(CN)_2(NO)_2]^{2-}$.

Mixed oxidation state species. Mn^{III}—Mn^{II}. We have already mentioned "$K_{1.52}[Mn(CN)_{3.72}]$" which is probably impure $K_2Mn^{II}[Mn^{II}(CN)_6]$ rather than a Mn^{III}—Mn^{II} species. A better example of the latter, however, is probably "$K_{3.62}[Mn(CN)_6].0.13H_2O$", formulated by McCarthy [278] as $0.7K_3[Mn(CN)_6].1.2K_4[Mn(CN)_6].0.25H_2O$. This red-brown crystalline material may be obtained by interaction of potassium cyanide and potassium permanganate in aqueous solution, or by mixing $K_3[Mn(CN)_6]$ and $K_4[Mn(CN)_6].3H_2O$ in saturated potassium cyanide solution. The electronic spectrum of the substance measured by diffuse reflectance suggests that it is a class (II) mixed oxidation state complex (using Robin and Day's classification). The magnetic moment is 1.04 B.M. at room temperature per two manganese atoms, but the complex may be antiferromagnetic, again consistent with a class (II) species. The infrared spectrum was measured (Table 7) and X-ray powder data gathered [278]*.

Mn^{II}—Mn^{I}. Electrolytic reduction [308] of $K_4[Mn(CN)_6]$ in cyanide solution leads to "$K_2[Mn^{I}(CN)_3].K_4[Mn^{II}(CN)_6]$".

Mn^{I}—Mn^{0}. Reduction of $K_3[Mn(CN)_6]$ by potassium in liquid ammonia gives a yellow complex formulated as $K_5[Mn(CN)_6].K_6[Mn(CN)_6].2NH_3$. It has a magnetic moment at room temperature [310] of 1.25 B.M. per two manganese atoms and a reducing power corresponding to $Mn^{0.5}$.

(b) Technetium

Perhaps because the element is so rare we know little of the cyanide chemistry of technetium. It is however puzzling that no technetium(V) cyano complexes are known since rhenium(V) has so extensive a cyanide chemistry: normally second and third row homologous elements are very similar, and this is largely true of the lower members of the triads flanking technetium and rhe-

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* See, however, footnote on p. 224 and ref. 278a.

nium in the Periodic Table (molybdenum and tungsten; ruthenium and osmium).

Technetium(V) (d^2). No complexes with cyanide are known for this oxidation state, though some of the properties of $[Tc(OH)_3(CN)_4]^{3-}$ (see below) suggest that this might possibly be such a complex. However, polarographic studies of the reduction of pertechnetate ion in excess cyanide give no indication of the existence of a technetium(V) cyano complex [321], and attempts to prepare $Na_3[TcO_2(CN)_4]$ failed [323].

Technetium(IV) (d^3). The existence of $[Tc(CN)_6]^{2-}$ has been postulated from the polarographic reduction of $[TcO_4]^-$ in excess cyanide; a three-electron wave ($E_{1_2} = -0.81$ V vs. S.C.E.) was seen [321]. Such a complex has not yet been isolated, but reaction of hydrated technetium dioxide with cyanide followed by addition of thallous ion gave $Tl_3[TcO(OH)(CN)_4]$ as a brown material. The infrared spectrum showed a C—N stretch at 2060 cm^{-1} and a band at 970 cm^{-1} presumably due to a Tc=O stretch [322,323]; few mono-oxo complexes with the d^3 configuration are known however, and intuitively one feels that a d^2 complex is more likely with an oxo ligand. As Chadwick and Sharpe [1] observe a magnetic susceptibility measurement would have been of interest. It was suggested that the complex could be seven coordinate in solution, $Tl_3[Tc(CN)_4(OH)_4]$, although no evidence was offered for this. The existence of $[Tc(CN)_3(OH)_4]^{3-}$ and $[Tc(CN)_7]^{3-}$ in solution was tentatively proposed [322,323]. The electronic spectrum was recorded from 200—1000 nm and an X-ray powder diagram obtained [322,323].

Technetium(I) (d^6). Here technetium does show a marked similarity both to manganese and rhenium in forming $[Tc(CN)_6]^{5-}$; vertical triads often show considerable similarity in their lowest oxidation states.

$K_5[Tc(CN)_6]$ is obtained by reduction of $(NH_4)[TcO_4]$ with potassium cyanide solution by potassium amalgam. The salt is green, and its X-ray powder diagram [311] shows it to belong to the face-centred cubic system (a = 12.106 Å) as do $K_5[Mn(CN)_6]$ and $K_5[Re(CN)_6]$. The infrared and Raman spectra of the solid were measured over the 40—4000 cm^{-1} range, fundamental modes assigned (Table 5) and force constants evaluated using a generalised valence force field. It was deduced from these studies [312] and calculations that the degree of carbon—nitrogen π-bonding was greater in $[Tc(CN)_6]^{5-}$ than in $[Mn(CN)_6]^{5-}$ or in $[Re(CN)_6]^{5-}$.

(c) Rhenium

There is an extensive cyanide chemistry of rhenium, particularly of the pentavalent state, and on the face of it, it seems that the subject has been well investigated. However, there is still some mystery surrounding the unsubstituted cyano complexes of the hexavalent, pentavalent, tri- and di-valent states. The only such species fully established are $[Re(CN)_8]^{3-}$ and $[Re(CN)_6]^{5-}$.

There is much chemistry of substituted rhenium cyanides, but again those of rhenium(IV), (III) and (II) are poorly characterised.

Rhenium(VII) (d^0). Reports of some rhenium(VII) cyano complexes [324] have been disproved [325].

Rhenium(VI) (d^1). $[Re(CN)_8]^{2-}$ salts (of $[Co(NH_3)_6]^{3+}$ and of Ph_4As^+) have been made by the oxidation of acid solutions of $[Re(CN)_8]^{3-}$. The purple tetraphenylarsonium salt has a magnetic moment of 2.0 B.M. at room temperatures, and $[Co(NH_3)_6]_2[Re(CN)_8]_3$ has a C≡N stretch at 2090 cm^{-1} in the infrared [325]. Attempts to measure the electronic spectra failed but the positions of spin-forbidden bands in $[Re(CN)_8]^{2-}$ have been predicted [19].

Rhenium(V) (d^2). $K_3[Re(CN)_8]$ was first claimed by Colton et al. [324] to be be the product of reaction of $K_2[ReI_6]$ with potassium cyanide in methanol. Later work showed that the product was extensively hydrolysed but that this method of preparation gives the brown diamagnetic anhydrous salt if water is rigorously excluded [325]. Another method is to treat $K_2[ReCl_6]$ with excess cyanide in aqueous solution: it is claimed that this gives a higher yield of product [326]. The infrared spectrum shows three strong bands in the C≡N stretching region (2140, 2100 and 2050 cm^{-1}) [325]. The electronic spectrum has been reported of the aqueous solution from 250—900 nm and assignments proposed [19]. Basu and Basu have also reported the spectrum in solution for 340—700 nm and from the fine structure of one of the bands claim that an Re—C stretch lies at 581 and 362 cm^{-1} [327]. It has been suggested that the structure in solution is fluxional [15]. The potassium salt can be oxidised by water and air to $[Re(CN)_8]^{2-}$, hydrolysed to $[ReO(CH)(CN)_4]^{2-}$ or $[ReO_2(CN)_4]^{3-}$, or reduced to $[Re(CN)_6]^{5-}$.

$Ph_4As[Re(CN)_6]$ has been made as a brown material by fusion of $K_2[ReCl_6]$ with potassium cyanide and potassium thiocyanate and subsequent treatment of the reaction mixture with tetraphenylarsonium chloride. The moment is 1.50 B.M. at room temperatures [328]. The infrared spectrum of the salt was measured (ν_{CN} 2155 cm^{-1} (Table 6)) [328] and also that of $Cs[Re(CN)_6]$ from 200—4000 cm^{-1} (Table 6) [329]. The electronic spectrum of the $(Ph_4As)^+$ salt was also recorded [328]. The preparation of a rhenium(V) complex by fusion of a rhenium(IV) complex with the reducing mixture of cyanide and thiocyanate is certainly remarkable.

$K_3[ReN(CN)_5]$ can be made as a yellow, crystalline material from $K_{2n}[ReN(CN)_4]_n \cdot nH_2O$ and potassium cyanide in methanol. The infrared spectrum of the complex was taken over the range 200—4000 cm^{-1} as well as the Raman spectrum (Table 7) [330]. The electronic absorption spectrum was also measured for the solid and the aqueous solution in excess cyanide, and was similar for both [330].

$K_{2n}[ReN(CN)_4]_n \cdot nH_2O$ can be made as pink material by reduction of potassium perrhenate in potassium cyanide solution with hydrazine [325] or, more simply, by treatment of $ReNBr_2(PPh_3)_2$ with potassium cyanide in methanol [330]. The X-ray crystal structure of the solid shows (Table 2) that $Re(CN)_4$ groups are joined by asymmetric, linear nitride bridges [331]:

$$\mathrm{Re} \overset{1.53}{\text{——}} \mathrm{N} \overset{2.44}{\text{- - -}} \mathrm{Re} \text{ —— } \mathrm{N} \text{ - - - } \mathrm{Re} \text{ —}$$

In aqueous solution, however, the complex anion is probably *trans*-$[ReN(CN)_4H_2O]^{2-}$; the infrared spectrum of the solid (200—4000 cm^{-1}, Table 6) is quite different from that of the aqueous solution, and the electronic spectra of solid and aqueous solute differ also [330]. The Re≡N stretch is seen [330] as a single sharp band at 1035 cm^{-1} in $K_3[ReN(CN)_5]$ but as a broader doublet (965 and 945 cm^{-1}) in $K_{2n}[ReN(CN)_4]_n . nH_2O$.

$[ReN(CN)_4(OH)]^{3-}$ may be present [330] in hydroxide solutions of $[ReN(CN)_4H_2O]^{2-}$.

trans-$K_3[ReO_2(CN)_4]$ is one of the oldest established rhenium complexes and has received much structural study. It is a yellow, diamagnetic solid, made by reaction of cyanide ion with almost any *trans*-rhenium(V)-dioxo complex (e.g., with $[ReO_2en_2]Cl$ [332] or with $[ReO_2py_4]Cl$ [333]. Other recommended methods are the treatment of $K_2[ReCl_6]$ with cyanide in the presence of hydrogen peroxide [334] or treatment of $ReOCl_2(OEt)(PPh_3)_2$ with potassium cyanide in methanol [325]. The old method of reacting perrhenate and cyanide with hydrazine [335] gives [325] mainly $K_{2n}[ReN(CN)_4]_n . nH_2O$.

The old X-ray study [336] of the complex used limited data and has been superceded by two recent studies of high accuracy, one by neutron diffraction [340] and the other by X-ray diffraction [337]. The bond parameters (Table 2) show that the Re—O bond length of 1.773(8) Å is significantly longer than the Re—O bond length in rhenium(V) complexes where only one oxo ligand is present (e.g., in $[ReOBr_4(H_2O)]^-$); this is to be expected since the two oxo ligands in *trans*-$[ReO_2(CN)_4]^{3-}$ compete for the two metal t_{2g} orbitals of which the one oxo ligand in $[ReOBr_4H_2O]^-$ has virtually exclusive use [242,338]. The distance is shorter however than that in *trans*-$[Mo^{IV}O_2(CN)_4]^{4-}$ (p. 218) due perhaps to π-bonding effects within the molybdenum complex or the higher external charge on the latter. It is interesting to note that, whereas one oxo ligand can be protonated in $[ReO_2(CN)_4]^{3-}$ to give $[ReO(OH)(CN)_4]^{2-}$, no such protonation occurs in the isoelectronic $[OsO_2(CN)_4]^{2-}$, due perhaps to the tighter Os=O bonding in the osmium(VI) complex.

Infrared spectra (200—4000 cm^{-1}) have been measured for the complex by a number of workers [51,242] (Table 6) [329] and interpreted on the basis of D_{4h} symmetry; the Raman spectra of the solid and aqueous solution were also recorded (200—1000 cm^{-1}) [242] and show that the solute species has the same structure as the solid. Force constant calculations have been made on the complex [329]. Electronic spectra of the aqueous solution (340—700 nm) have been measured [327,339], Basu and Basu have suggested that the structure in solution is eight coordinate, $[Re(CN)_4(OH)_4]^{3-}$ [327], but Johnson has pointed out that it is in fact $[ReO_2(CN)_4]^{3-}$ both in the solid and in solution [340].

The exchange of labelled free cyanide with $[ReO_2(CN)_4]^{3-}$ is very fast, and a seven coordinate intermediate was suggested [332]. Hydrolysis constants for the complex anion have been measured [333] but the validity of the data questioned [341]. Polarographic reduction of $[ReO_2(CN)_4]^{3-}$ in cyanide media suggests that rhenium(I) and rhenium(—I) species may be formed [342]. The kinetics of the ^{18}O-$[ReO_2(CN)_4]^{3-}$ reaction have been studied [341].

$K_2[ReO(OH)(CN)_4]$ is the purple product of protonation of $[ReO_2(CN)_4]^{3-}$. The easiest preparation is to treat $K_3[ReO_2(CN)_4]$ with acid ion-exchange resin and freeze-dry the product [341]:

$$[ReO_2(CN)_4]^{3-} + H^+ \overset{fast}{\rightarrow} [ReO(OH)(CN)_4]^{2-}$$

$$2[ReO(OH)(CN)_4]^{2-} \overset{slow}{\rightarrow} [Re_2O_3(CN)_8]^{4-} + H_2O$$

Another method is treatment of $K_3[ReO_2(CN)_4]$ with hydrochloric acid followed by precipitation with a suitable large cation [325]. The infrared spectrum of $(Ph_4As)_2[ReO(OH)(CN)_4]$ has C≡N stretches at 2190 and 2150 cm^{-1} with the Re=O stretch at 956 cm^{-1} [325].

$K_4[Re_2O_3(CN)_8]$ is a purple, diamagnetic product obtained by reaction of $K_3[ReO_2(CN)_4]$ with hydrochloric acid [341,343]. The X-ray crystal structure of $[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$ has been determined (Table 2). There is a linear O=Re—O—Re=O unit (Re=O 1.698(7) Å, Re—O (bridge 1.915(1) Å)); the eclipsed (D_{4h}) configuration and Re—O bridge bond length suggest that the bridging oxo ligand is partly π-bonded to the rhenium atoms [343]. The infrared spectrum has bands at 725 cm^{-1} assigned to the asymmetric Re—O—Re stretch and at 995 cm^{-1} for the terminal Re=O stretch [342]. The electronic spectrum was also measured [341]. In $H_2^{16}O$ the terminal oxo ligands of the ^{18}O-labelled complex exchange much faster than does the bridging oxygen atom [341].

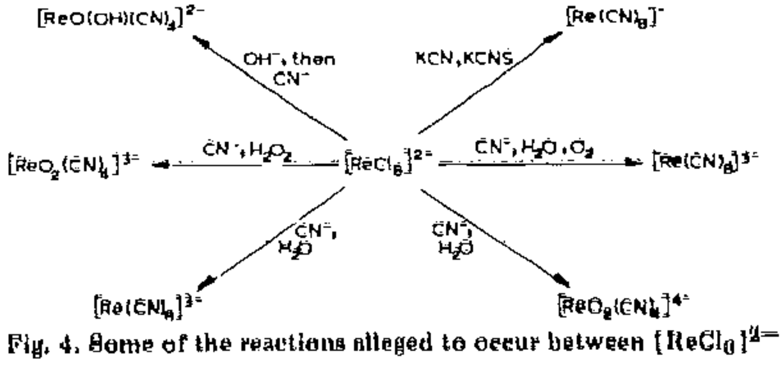
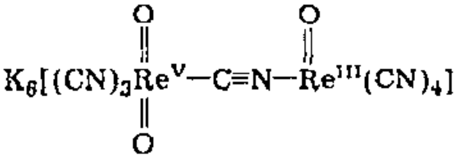


Fig. 4. Some of the reactions alleged to occur between $[ReCl_6]^{2-}$ and CN^-.

There are a few other rather ill-defined rhenium(V) oxo cyano complexes: $[ReO_2(CN)_6Fe]^{3-}$ (from the perrhenate—ferricyanide—stannous chloride system); $K[FeO(OH)(H_2O)(CN)_3]$ (ν_{CN} at 2140 cm^{-1}) and $K_2[ReO(OH)_2(CN)_3]$ (ν_{CN} at 2125 cm^{-1}), from acidification of $K_3[ReO_2(CN)_4]$ followed by alkali treatment; the polymers $Re_2O_3(CN)_4$ and $H_2[(H_2O)O(NC)_3Re—O—Re(CN)_3O(H_2O)]$ (ν_{CN} 2170 cm^{-1}) were similarly made from $K_3[ReO_2(CN)_4]$ and hydrofluoric acid, $K[ReOF(H_2O)(CN)_3]$ (ν_{CN} 2130 cm^{-1}) and a polymer, $K[Re_2C_2F(H_2O)_2(CN)_6]$ were obtained [333].

Rhenium(IV) (d^3). It is a curious circumstance that $[Re^{IV}Cl_6]^{2-}$ is often used as a starting material for the preparation of rhenium cyano complexes (Fig. 4) but that no rhenium(IV) cyano species are fully established. The reactions claimed by various workers in Fig. 4 would undoubtedly repay investigation.

"$K_4[ReO_2(CN)_4]$" is formed as a greyish solid when $K_2[ReCl_6]$ and potassium cyanide react in aqueous solution with exclusion of air. On treatment with potassium borohydride reduction to $K_3[Re(CN)_3(OH)_3]$ and finally to $K_5[Re(CN)_6]$ occurs [345]. The author very tentatively suggested a mixed valence state formulation for this [242]:



$$K_6[(CN)_3\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Re^{V}}}—C{\equiv}N—\overset{\overset{O}{\|}}{Re^{III}}(CN)_4]$$

(i.e., $K_6[Re_2O_3(CN)_8].4H_2O$ — the observed magnetic moment of 1.25 B.M. per rhenium atom is consistent with this, and the infrared spectra supported it to some extent [242]). However the idea of an oxo ligand coordinated to rhenium(III) is unlikely. The infrared (200—4000 cm^{-1}) [242,329] and Raman spectra [242] (200—1000 cm^{-1}) of the substance have been measured.

Rhenium(III) (d^3). The chemistry of the cyanide complexes of rhenium(III) is badly in need of further investigation.

$K_3[Re(CN)_6]$. Two preparations have been reported, neither fully satisfactory. Reaction of rhenium trichloride with potassium cyanide leads, after a bewildering variety of colour changes, to an impure form of the complex. A purer form may be made by borohydride reduction of $K_3[Re(CN)_8]$ followed by precipitation of the salt as $[Co(NH_3)_6][Re(CN)_6]$. The magnetic moment of the green complex is 2.6 B.M. at room temperatures [324]. Skolozdra et al. claim to have made $K_3[Re(CN)_6].3H_2O$ by addition of $K_2[ReCl_6]$ to concentrated potassium cyanide solution under nitrogen [348]; the salt is green and belongs to the face-centered cubic system (a = 12.19 Å). The infrared spectrum (700—2400 cm^{-1}) has strong bands at 1913 (ν_{CN}) and one at 907 cm^{-1} assigned to a rhenium—carbon stretch [348]. They claim that the $K_5[Re(CN)_6]$ made by Clauss and Lissner [309] is identical with their "$K_3[Re-$

$(CN)_6].3H_2O$". Certainly the X-ray powder patterns of the two products are similar, and it appears that the infrared spectrum of their salt is the same as that of a product made by them using Clauss and Lissner's method (reduction of $K_2[ReCl_6]$ with potassium amalgam in potassium cyanide) [324]. However, the spectrum of $K_5[Re(CN)_6]$ as reported by Schwochau et al. [312] has ν_{CN} at 1932 cm^{-1} and no band at 907 cm^{-1}.

The potential of the $[Re(CN)_6]^{3-}/[Re(CN)_6]^{4-}$ couple is reported to be −0.72 V [344].

$Na_2[Re(H_2O)(CN)_5]$ is said to be formed when $Na_2[Re(H_2O)(CN)_5]$ is oxidised by bromine. It is green, and gives $Na_2[Re(NO)(CN)_5]$ when treated with nitric oxide [345]. The $[Re(H_2O)(CN)_5]^{2-}/[Re(H_2O)(CN)_5]^{3-}$ couple is −0.636 V [344]. The $[Re(CN)_2(MeCN)_4]^-$ ion has been reported [345a].

"$Ag_3[Re(NO)(CN)_7]$" was made as a mauve diamagnetic material by treating $K_3[Re(CN)_8]$ with 2 N nitric acid. The NO stretching frequency was assigned to a band at 1875 cm^{-1}. The analyses [324] however did not discriminate between this formula and $Ag_3[Re(NO)(CN)_5]$.

$K_3[Re(CN)_3(OH)_3]$ was made as a dark blue crystalline material by reduction of "$K_4[ReO_2(CN)_4]$" (p. 000) with potassium borohydride [345].

$(Et_4N)_3[Re_3Cl_3(CN)_9]$ and $(Et_4N)_3[Re_3Cl_8(CN)_3]$ were obtained as violet materials by reaction of rhenium trichloride and tetraethylammonium cyanide in dimethylsulphoxide. The electronic spectra were measured [346].

Rhenium(II) (d^5). Again, the complexes under this oxidation state are for the most part poorly characterised, and further investigation would be highly desirable.

$K_4[Re(CN)_6].3H_2O$ has been made [347] as a dark brown crystalline solid, fairly soluble in water, by refluxing solutions of potassium cyanide and $K_2[Re(H_2O)(CN)_5]$. The crystals are triclinic [349] and belong to either the *P* or *P*$\bar{1}$ space group with $Z = 2$ [349]. The salt may be dehydrated over phosphorous pentoxide [347]. The infrared spectrum of the silver salt has two bands in the C≡N stretching region at 2082 and 2030 cm^{-1}; the magnetic moment at 301 K is only 0.55 B.M. for the potassium salt, and this low value has been ascribed to a large spin—orbit coupling constant [349]. The $[Re(CN)_6]^{3-}/[Re(CN)_6]^{4-}$ potential is said to be −0.72 V [344]. The silver salt $Ag_4[Re(CN)_6]$ can be methylated [350] to $[Re(CNCH_3)_6]^{2+}$.

$[Re_2(CN)_8]^{2-}$ (as a mixed rhenium(IV)—rhenium(II) species) is, it is claimed, found when rhenium trichloride reacts with potassium cyanide [351].

$K_3[Re(CN)_5]$ is a hygroscopic brown solid [352], made by dehydration of $K_3[Re(H_2O)(CN)_5]$.

$Na_3[Re(H_2O)(CN)_5]$ has been made as a brown hygroscopic material by reduction of sodium perrhenate by sodium amalgam in the presence of sodium cyanide, acetic acid added and air passed through the solution. A "free acid" was also made [352]. The compound is a useful source for the following sodium salts, made by reaction with ligand X under appropriate conditions as noted.

$Na_n[Re^{II}X(CN)_5]$ (X = NH_3 [355]; CNS (for the potassium salt the magnetic moment is 0.55 B.M. at room temperatures; ν_{CN} is at 2100 and 2085 cm^{-1}) [349]; SO_3 [353]; CO (blue; from CO at 140° on the aquo complex [354]). The $[Re(H_2O)(CN)_5]^{2-}/[Re(H_2O)(CN)_5]^{3-}$ potential is −0.636 V [344].

$Na_2[Re(NO)(CN)_5]$ is obtained by the action of nitric acid on $Na_3[Re(H_2O)(CN)_5]$; it is red, and undergoes reversible polarographic reduction to $[Re(NO)(CN)_5]^{3-}$ (E_{1_2} = −0.75 V vs. SCE) [354]. With alkali [353,354] it gives salts of $[Re(NO_2)(CN)_5]^{4-}$.

$Na_5[ReO(CN)_5]$ is the improbable formula claimed for the reaction product of $Na_3[Re(H_2O)(CN)_5]$ and sodium hydroxide. The salt is yellow [355].

$Na_2[Re(CN)_4L]$ (L = phen, bipy, en) can be obtained from $Na_3[Re(H_2O)(CN)_5]$ and the ligand L. The electronic spectra were recorded from 200—600 nm [355].

Rhenium(I) (d^6). $K_5[Re(CN)_6]$ can be made by reduction of $K_2[ReCl_6]$ with potassium cyanide by potassium amalgam [309]; it is variously claimed as a trihydrate [309] and as an anhydrous species [323,347]. The latter is the more likely since it is isomorphous with $K_5[Mn(CN)_6]$ and $K_5[Tc(CN)_6]$; it has a face-centered cubic lattice (a = 12.05 Å) [309,323]. It may also be made by reduction of "$K_4[ReO_2(CN)_4]$" with potassium borohydride [345]. The salt is colourless and quite soluble in water, and is diamagnetic. The infrared and Raman spectra of the solid have been measured (Table 5) (40—4000 cm^{-1}) and fundamental modes assigned; force constants were calculated on the basis of a generalised valence force field and compared with those for the corresponding manganese and technetium salts (see p. 189) [312]. The electronic spectrum was measured over the range 300—1000 nm [323].

$Na_3[Re(NO)(CN)_5]$ has been claimed. It was made by passing nitric oxide over $Na_3[Re(H_2O)(CN)_5]$ at 130° [354]. The possibility that "$Ag_3[Re(NO)(CN)_7]$" should be formulated as $Ag_3[Re(NO)(CN)_5]$ has already been mentioned (see p. 237) [324].

cis-$K_3[Re(CN)_4(CO)_2]$ can be obtained from potassium cyanide and $Re(CO)_2(PPh_2(CH_2)_2PPh_2)_2$. It is colourless. The infrared spectrum (Table 7) was compared with that for the isoelectronic $[W(CN)_4(CO)_2]^{4-}$ and force constants calculated; the *cis* (C_{2v}) structure was deduced from the spectrum [356].

$Na_3[Re(CN)_4phen).H_2O$ and $H[Re(CN)_2bipy_2]$ were made by reduction of $[ReO_2(CN)_4]^{3-}$ with sodium amalgam in the presence of phen or bipy [342].

fac-$K_3[Re(CN)_3(CO)_3]$ is obtained by the action of ethanolic potassium cyanide on $Re(CO)_5Cl$ at high pressure. The C_{3v} structure was indicated by the infrared spectrum (200—4000 cm^{-1}) (Table 7) [356].

$K[Re(CN)_2(CO)_4]$. This colourless complex [358] has been obtained by the action of methanolic potassium cyanide on $Re(CO)_5Cl$.

$K[Re(CN)_2(CO)_3(NH_3)]$ and $Re(CN)(CO)_3(NH_3)_2$ can be made from potassium cyanide in liquid ammonia on $Re(CO)_5Cl$ at high pressures at 120°. Infrared spectra of the former complex showed ν_{CN} at 2011 cm^{-1} with δ_{Re-O-N} at 480 and 469 cm^{-1}; for the latter at 2120 and 465 cm^{-1} [356].

Rhenium(0) (d^7). Colton [359] has pointed out that the analyses of the "$K_5[Re(CN)_6]$" obtained by borohydride reduction of "$K_4[ReO_2(CN)_4]$" [345] are closer to $K_6[Re(CN)_6]$ than to $K_5[Re(CN)_6]$. He suggests [359] that the compound could be a hydride, $K_6[ReH(CN)_6]$.

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