CYANIDE COMPLEXES OF THE TRANSITION METALS

By W. P. GRIFFITH

(DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL., U.S.A.)

THE first known co-ordination complex was Prussian Blue, prepared in 1704 by the German artist Diesbach who heated animal refuse and sodium carbonate together in an iron pot.[1] Subsequent work led to the isolation of potassium ferrocyanide, $K_4[Fe(CN)_6]$.[2] Since then, cyanide complexes of most transition metals have been prepared, as well as simple cyanides of non-transition metals. The CN^- group is capable of stabilising a wide range of stereochemical configurations and metal oxidation states: in unsubstituted cyanide complexes, co-ordination numbers from eight to two and oxidation states from (+5) to (0) are known.

Bonding Properties of the Cyanide Ion.—The CN^- group may be described in molecular-orbital symbolism as $KK(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p)^2(\pi 2p)^4$ and may be represented diagrammatically as in Fig. 1. Overlap of the (σ^*2s) orbitals with the nd_σ, $(n+1)s$, and $(n+1)p_\sigma$ metal orbitals constitutes the normal ligand–metal σ-bond, and there are vacant (π^*2p) orbitals available for receipt of d_π-electrons from the metal atom. Alternatively it may be considered that CN^- has its σ-lone-pairs in *sp*-hybrids, one on the carbon and one on the nitrogen, projecting outwards along the C–N axis; one of these pairs would then overlap with the appropriate metal orbitals to give a σ-bond. Since nitrogen is more electronegative than carbon it is likely that the $(2s_C{}^2)$ pairs will be used for bonding, though there is no evidence that all metal cyanide complexes have metal–carbon rather than metal–nitrogen bonds. In most cases *X*-ray structure determinations do not give the required information because the electron densities around carbon and nitrogen are too similar,[3] but recent spectroscopic and neutron-diffraction measurements indicate that a metal–carbon bond

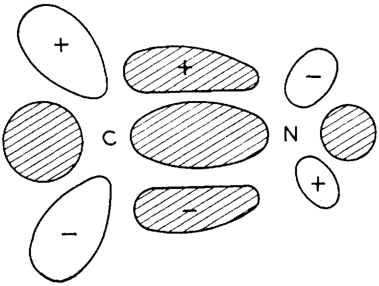

FIG. 1

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[1] Anon., "Miscellanea Berolinensia ad Incrementum scientiarum," Berlin, 1710, p. 277.

[2] Stahl, "Experimentia, Observationes, Animadversiones CCC numero chymicae et physicae," Berlin, 1731, p. 281.

[3] Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, 1950.

is present in all the compounds studied,[4] and the fact that methylation of complex cyanides gives methyl isocyanides supports this conclusion. The limited amount of structural data available indicates that the M–C–N bond is linear in cyanide complexes.[4] However, the possibility of bent or side-on bonding cannot be excluded (cf. Fig. 2). In the case of metal carbonyl complexes the linear M–C–O bond is energetically preferable to the side-on form,[6] and the same is probably true for the cyanide group since CO and CN^- are iso-electronic. Bent M–N–O bonds are known in a few compounds such as $(Me_2N{\cdot}CS_2)_2Co(NO)$ (ref. 7) and may conceivably occur with cyanides, CN^- and NO^+ also being iso-electronic.

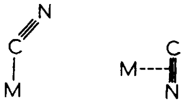

FIG. 2

The bonding characteristics of a ligand are determined largely by its σ-donor and π-accepting properties and, although both are intimately connected and interdependent, it is easier for these qualitative purposes to consider the two effects separately.

The cyanide ion as a σ-bonding ligand.—Since NO^+, CO, and CN^- are isoelectronic, it is interesting to compare their donor strengths. Of the three, CN^- has the best σ-bonding properties, which follows from the fact that it is a stronger base than the other two. It is doubtful whether NO^+ has any basic character at all, but the existence of BH_3,CO suggests that CO has some σ-donor power. It is significant that the cyanide salts of alkali and alkaline-earth metals are well known whereas the "nitroxyls" $M(NO)_x$ and "carbonyls" $M(CO)_x$ have very low chemical stabilities, uncertain compositions and unknown structures. Furthermore, whereas cyanide complexes are commonly formed by transition metals with oxidation states of (+3) and (+2), analogous compounds are unusual with carbonyl or nitrosyl groups unless suitably efficient σ-bonding ligands also participate, although Hieber and Krück[5] recently demonstrated the existence of cationic carbonyl complexes such as $[Fe^{II}(CO)_6]^{2+}$.

The cyanide ion as a π-bonding ligand.—One of the consequences of efficient ligand–metal σ-bonding is that the donor atom becomes more electropositive and therefore more receptive to "back-donation" from the metal d_π-electrons, provided of course that suitable orbitals are available on the ligand, and such π-bonding also relieves the central metal atom of

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[4] Jones, *J. Chem. Phys.*, (*a*) 1957, **26**, 1578; (*b*) **27**, 468; (*c*) Curry and Runciman, *Acta Cryst.*, 1959, **12**, 674.

[5] Hieber and Krück, *Angew Chem.*, 1961, **73**, 580.

[6] Orgel, "Introduction to Transition-metal Chemistry," Methuen, London, 1960, p. 138.

[7] Alderman and Owston, *Nature*, 1956, **178**, 1071.

some of the negative charge which accumulates on it as a result of σ-bonding. Back-donation of metal d_π-electrons to the vacant (π^*2p)-carbon orbitals on CN^- (d_π–p_π-bonding) undoubtedly occurs in many or all transition-metal cyanide complexes, especially those which involve the metal in a low oxidation state. However, one would expect CN^- to be a poorer acceptor than CO since it carries a negative charge which will produce a lower relative electronegativity. It is interesting that the isocyanide group RNC, which is iso-electronic with CO and CN^-, resembles the former rather than the latter in its tendency to stabilise complexes with the metal in a low oxidation state; since there is no formal negative charge on the group the acceptance of metal d_π-electrons is facilitated.

Evidence for π-Bonding in Cyanide Complexes.—(a) *Chemical evidence.* Stabilisation of low oxidation states is typical of good π-accepting ligands (CO, RNC, Ph_3P), and there is some evidence in the case of carbonyls, at least, that their complexes have some metal–ligand multiple-bond character.[8] Efficient σ-bonding ligands do not normally stabilise low oxidation states unless they can readily accept metal d_π-electrons. Thus such groups as OH^- and Cl^- form no complexes of metals in low oxidation states whereas CN^- does so, though the compounds that cyanide does form are chemically less stable than the analogous carbonyls, presumably because CO is a better π-accepting ligand.

(b) *Structural evidence.*—Values of metal–ligand bond distances do not provide impressive evidence for π-bonding owing to lack of information on the length that the bond would have if it were exclusively σ in character. For cyanides the difficulties are increased by the fact that many of the bond distances reported in the literature are of dubious accuracy (*e.g.*, the data of Table 1 show the Co–C bond lengths in $K_3[Co(CN)_6]$ and $Cd_3[Co(CN)_6]_2$ to be 1·89 and 2·05 Å, respectively, but it seems highly unlikely that a change of cation should cause such a change of metal–ligand distance).

Values of k_{M-C} and k_{C-N} (force constants for metal–carbon and carbon–nitrogen bonds) have sometimes been used to assess M–C and C–N bond orders. However, unless accurate values are available for the degree and strength of ligand–metal σ-bonding this method is not valid, and not all force constant values are reliable since in some calculations certain important interactions have been neglected or overlooked.[9] Nevertheless, it is apparent from Table 1 that d^{10} complexes have lower k_{M-C} and higher k_{C-N} values than those with fewer d-electrons, presumably because there is little π-bonding in d^{10} systems.[8] The C–N force constant in simple cyanides is usually higher than in cyanide complexes, which may indicate a certain degree of metal–ligand multiple bonding. Carbon–metal σ-bonding will tend to increase k_{C-N} by drawing negative charge from the carbon

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[8] Nyholm, *Proc. Chem. Soc.*, 1961, 280; Westward and Owen, *J.*, 1959, 1055; Chantry and Plane, *J. Chem. Phys.*, 1961, **35**, 1027.

[9] L. H. Jones, personal communication.

atom, whereas a return of electron density to the carbon by d_π–p_π-bonding will decrease k_{C-N} and the observed C–N stretching frequency will arise from a combination of these two effects. In complexes of high oxidation state, where σ- is more important than π-bonding, a high C–N stretching frequency is to be expected, and the reverse for low oxidation states; other effects such as the number of d_π-electrons on the metal may also influence the frequency. Spectroscopic studies have indicated that, unlike the carbonyls, metal cyanides of the form $[M(CN)_6]^{n-}$ have negligible CN–CN bond interaction since the symmetric and the antisymmetric

TABLE 1. *Structural data on cyanide complexes.*

	Complex	d_{M-C}(Å)	d_{C-N}(Å)	k_{M-C}*	k_{C-N}*	Structure
d^{10}	$K[Au(CN)_2]$	2·12^a	1·17^a	2·75^b	17·17^b	Linear
	$K[Ag(CN)_2]$	2·13^a	1·15^a	1·83^b	17·04^b	Linear
	$K[Cu(CN)_2]$	1·92^a	1·15^a			Spiral
	$K_3[Cu(CN)_4]$			1·30^b	16·31^b	Tetrahed.
d^8	$Na_2[Pd(CN)_4],3H_2O$	1·994^c	1·133^c	3·42^d	16·83^d	Planar
	$Na_2[Ni(CN)_4]$	1·95^c	1·30^c	$\sim$3·42^d	$\sim$16·83^d	Planar
	$K_2[Pt(CN)_4]$			3·12^d	16·82^d	Planar
	$KNa[Pt(CN)_4]$	1·93^e	1·16^e			
	$Na_2[Ni(CN)_4],2H_2O$	1·97^c	1·20^c			Planar
	$Sr[Ni(CN)_4]$	1·86^c	1·18^c			Planar
	$[Ni(CN)_2,NH_3,C_6H_6]$	1·76^f	1·22^f			Clathrate
d^6	$K_3[Co(CN)_6]$	1·89^g	1·15^g	2·31^j	16·5^j	Octahed.
	$Cd_3[Co(CN)_6]_2$	2·05^h	1·18^h			Octahed.
	$[Fe(CNMe)_6]Cl_2,3H_2O$	1·85^c	1·18^c			Octahed.
	$K_4[Os(CN)_6]$			3·34^j	14·9^j	Octahed.
	$K_4[Ru(CN)_6]$			2·79^j	15·3^j	Octahed.
	$K_4[Fe(CN)_6]$			2·43^j	15·1^j	Octahed.
d^5	$K_3[Fe(CN)_6]$			1·73^j	17·0^j	
d^3	$K_3[Cr(CN)_6]$			1·93^k	16·42^k	Octahed.
d^2	$K_4[Mo(CN)_8]$	2·15^l	1·15^l			Dodecahed.
	KCN		1·15^c		17·5±0·5^m	

*k_{M-C} and k_{C-N} are the force constants of the M–C and C–N bonds, in 10^{-5} dyne/cm.

(*a*) Rosenzweig and Cromer, *Acta Cryst.*, 1959, **17**, 709, and refs. therein.
(*b*) McCullough, Jones, and Crosby, *Spectroschim. Acta*, 1960, **16**, 424, and refs. therein.
(*c*) "Interatomic Distances," *Chem. Soc. Special Publ.*, No. 11, and refs. therein.
(*d*) Pistorius, *Z. phys. Chem.* (*Leipzig*), 1960, **23**, 200.
(*e*) Monfort, *Bull. Soc. Sci. Liége*, 1942, **11**, 567. (*f*) Rayner and Powell, *J.*, 1952, 319.
(*g*) Curry and Runciman, *Acta Cryst.*, 1959, **12**, 674.
(*h*) Ferrari, Tani, and Magnano, *Gazzetta*, 1959, **89**, 2512.
(*j*) Nakagawa and Shimanouchi, *Spectrochim. Acta*, 1962, **18**, 101.
(*k*) Caglioto, Sartori, and Furlani, *Atti Accad. Naz. Lincei, Rend. Classe sci. fis. mat. nat.*, 1958, **25**, 260.
(*l*) Hoard and Nordsieck, *J. Amer. Chem. Soc.*, 1939, **61**, 2853.
(*m*) Leroi and Klemperer, *J. Chem. Phys.*, 1961, **35**, 774.

C–N stretching frequencies are fairly close together and there are no significant changes in π-bonding during vibration, although this does not necessarily imply that there is less π-bonding in cyanides than in carbonyls.[9,10]

Crystal field strength of the cyanide ion.—The position of CN^- in the spectrochemical series is (in order of increasing D_q):[11] $I^- < Br^- < Cl^- < F^- <$ Oxalate $< H_2O < NH_3 <$ en $< NO_2^- < CN^- \sim CO \sim NO^+ < P(O{\cdot}CH_2)_3CMe$, and some approximate values of $10D_q$ (in cm.$^{-1}$) are:[12]

$[Co^{III}(CN)_6]^{3-}$	33,500	$[Mn^{III}(CN)_6]^{3-}$	30,000
$[Fe^{II}(CN)_6]^{4-}$	32,500	$[Cr^{III}(CN)_6]^{3-}$	26,700

These values of D_q are comparable with those for CO in carbonyls, but this does not necessarily imply that CN^- is as good a π-acceptor as CO. It has recently been shown that alkyl groups, which cannot easily form π-bonds, also give rise to large D_q values, as apparently do all ligands with carbon as the donor atom.[13] The value of D_q depends not only on the degree of metal–ligand and ligand–metal π-bonding, but also on the effect of ligand lone-pairs and electrostatic repulsions.[14] The CN^- group also shows one of the largest observed *trans*-effects in the substitution reactions of square-planar platinum(II) complexes (although the hydride ion may be even more powerful in this respect).[13]

The Stabilisation of High Oxidation States.—The cyanide group is not noted for its ability to stabilise high oxidation states, since ligands which are capable of this (*e.g.*, F^-, O^{2-}, O_2^{2-}) are usually small and highly electronegative. The only well-established unsubstituted cyanide complexes with high oxidation states are the eight co-ordinated d^1- and d^2-compounds of Re(VI), Re(V), Mo(V), Mo(IV), W(V) and W(IV), and the stability of the compounds is likely to be due to the special stereochemical arrangement of the ligands around the metal atom. Apart from these cases there are two others to be considered, namely, $[Mn^{IV}(CN)_8]^{4-}$ and $[V^{IV}(CN)_6]^{2-}$, neither of which has been satisfactorily characterised.[14] It seems probable that the vanadium complex contains some hydroxyl groups, and it is exceedingly unlikely that manganese(IV) would be eight co-ordinated. There are also a number of substituted cyanides which involve the metal atom in an unusually high oxidation state, but in all cases the other ligands present are good σ-bonding groups. Known oxide cyanides are $[Os^{VI}O_2(CN)_4]^{2-}$,

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[10] Jones, "Advances in Co-ordination Chemistry," Macmillan, New York, 1961, p. 310; Gaufrès, *Compt. rend.*, 1960, **251**, 2001; Nakagawa and Shimanouchi, *Spectrochim. Acta*, 1962, **18**, 101.

[11] Verkade and Piper, ref. 12, p. 634; Tsuchida, *Bull Chem. Soc. Japan*, 1938, **13**, 388, 436, 471; Schäffer and Jörgensen, *J. Inorg. Nuclear Chem.*, 1958, **8**, 143; Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

[12] J. S. Griffith, "Theory of Transition Metal Ions," Cambridge Univ. Press, 1961, p. 310.

[13] Chatt and Hayter, *J.*, 1961, 2605.

[14] Dunn, "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960, p. 267.

and $[Re^{V}O_2(CN)_4]^{3-}$, which may exist in solution as the eight co-ordinated species $[Re^{V}(OH)_4(CN)_4]^{3-}$, and there are peroxide cyanides of cobalt(III) and chromium(IV) (see below). A number of vanadyl cyanides have been reported,[14,15] and have been formulated as $[V^{IV}O(CN)_4]^{2-}$, $[V^{IV}O(CN)_5]^{3-}$, and $[V^{IV}O(CN)_6]^{4-}$; as written, these involve vanadium(IV) in some curious stereochemical arrangements, but they have not been properly characterised and may well be hydroxide complexes of vanadium(IV) or vanadium(III). Platinum(IV) halide cyanides $[Pt^{IV}X_2(CN)_4]^{2-}$ are known, but the only evidence for the existence of $[Pt^{IV}(CN)_6]^{2-}$ is polarographic, based on observations of the reduction of platinum(IV) in cyanide media.[16]

The Stabilisation of Low Oxidation States.—Unsubstituted cyanide complexes which involve the metal atom in an abnormally low oxidation state are listed in Table 2. It has already been mentioned that the reluctance of CN^- to form strong π-bonds is reflected in the comparatively instability of its complexes with metals in low oxidation states. It is noteworthy that cyanide nitrosyls and carbonyls of nickel(I) and nickel(0) are more stable than the corresponding unsubstituted cyanides, presumably because they carry lower external charges and because CO and NO^+ are better π-acceptors than CN^- and drain off negative charge from the nickel atom more efficiently.

Because of their extreme instability the structures of none of these complexes have been studied by diffraction methods. The degree of metal–ligand multiple bonding would presumably be higher for complexes of low oxidation state, and there is some qualitative evidence for this in the case of $[Ni^{0}(CN)_4]^{4-}$ which has an infrared C–N stretching frequency at 1985 $cm.^{-1}$ as compared with 2127 $cm.^{-1}$ for $[Ni^{II}(CN)_4]^{2-}$, implying a lower C–N bond order and consequently a higher degree of bond multiplicity in the nickel(0) complex.[17] As is the case with the carbonyls, cyanide complexes of metals in a low oxidation state are diamagnetic and most of them obey the inert-gas rule.

Stereochemistry of Cyanide Complexes.—(a) 10-, 9-, *and* 8-*Co-ordination.* Ten-co-ordinate complexes of unknown structure of the form $[Mo^{IV}(OH)_4(CN)_4R_2]^{4-}$ (where R = H_2O, NH_3, or N_2H_4) have been reported,[18] but little evidence in support of this very unusual co-ordination number has been presented; recently it has been suggested that $[Pt^{VIII}(CO)_2F_8]$ is also of this form.[19] Nine-co-ordinated rhenium(VII) has

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[15] Yakimach, *Compt. rend.*, 1930, **190**, 681; **191**, 789; Rivenq, *Bull. Soc. chim. France*, 1947, 971; Barbieri and Parisi, *Ber.*, 1927, **60**, 2415; Brintzinger and Jahn, *Z. anorg. Chem.*, 1938, **235**, 244.

[16] Rius and Molera, *Anales real Soc. españ. Fiz. Quím.*, 1949, **45**, *B*, 1151.

[17] El-Sayed and Sheline, *J. Amer. Chem. Soc.*, 1958, **80**, 2047; Nyholm, *Chem. Rev.*, 1953, **53**, 303.

[18] Jakob and Jakob, *Rocznicki Chem.*, 1952, **26**, 492.

[19] Sharp, *Proc. Chem. Soc.*, 1960, 317.

been suggested[20] for $[Re^{\text{VII}}(OH)(CN)_8]^{2-}$, but since there are no d_π-electrons available in rhenium(VII) this seems unlikely.

TABLE 2. *Cyanide complexes of unusually low oxidation states*

	Complex	Co-ordn. number of metal	Structure	Iso-electronic carbonyl
d^{10}	$[Pt^0(CN)_4]^{4-}$; $[Pd^0(CN)_4]^{4-}$; $[Ni^0(CN)_4]^{4-}$	4	Tetrahedral	$[Ni^0(CO)_4]$
d^9	$[Ni^{\text{I}}(CN)_4]^{3-}$	4	Tetrahedral*	
	$[Ni^{\text{I}}{}_2(CN)_6]^{4-}$	4	Planar with metal–metal bond	
	$[Co^0{}_2(CN)_8]^{8-}$; $[Rh^0{}_2(CN)_8]^{8-}$	5	Square pyrimidal with metal–metal bond	$[Co^0{}_2(CO)_8]$
d^8	$[Co^{\text{I}}(CN)_4]^{3-}$	4	Square planar*	$[Fe^0(CO)_4]$
d^7	$[Co^{\text{II}}{}_2(CN)_{10}]^{6-}$	6	Octahedral with metal–metal bond	$[Mn^0{}_2(CO)_{10}]$
d^6	$[Mn^{\text{I}}(CN)_6]^{5-}$; $[Re^{\text{I}}(CN)_6]^{5-}$; $[Cr^0(CN)_6]^{6-}$	6	Octahedral	$[Cr^0(CO)_6]$
d^5	$[Mn^0(CN)_6]^{6-}$†	6	Octahedral	$[V^0(CO)_6]$

* Structure uncertain. † Existence of complex as formulated uncertain.

Apart from the doubtful case of $[Mn^{\text{IV}}(CN)_8]^{4-}$ mentioned above, all the known eight-co-ordinated complexes involve metal atoms with one or two *d*-electrons, and are usually confined to transition elements of the second and the third row, though recently some eight-co-ordinated titanium complexes have been reported. Two arrangements are favoured for this co-ordination number, the antiprism and the dodecahedron, and in both cases the crystal-field forces would lead to the stabilisation of one *d*-orbital over the other four (the d_{z^2} in the case of the square antiprism and the d_{xy} in the case of dodecahedron).[21] The tendency of d^1- and d^2-complexes to adopt eight-co-ordination is therefore understandable. Only one cyanide complex with this co-ordination number has been studied by *X*-ray diffraction, and from this it appears that $K_4[Mo(CN)_8]$ has a dodecahedral configuration,[23] although it would be expected that the antiprismatic structure might be more stable.* Orgel[21] has explained the favouring of the dodecahedron for $[Mo(CN)_8{}^{4-}$ on the grounds that the d_{xy}-orbital has the correct symmetry for metal–carbon π-bonding, whereas the d_{z^2}-orbital would provide poor back-bonding facilities. On this basis, four of the ligands would be in a better position to form π-bonds by

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* The view that the antiprismatic arrangement is inherently more stable than the dodecahedral has been proposed by Gillespie[21] and challenged by Hoard *et al.*[22]

[20] Colton, Dalziel, Peacock, and Wilkinson, *J.*, 1960, 1374.

[21] Orgel, *J. Inorg. Nuclear Chem.*, 1960, **14**, 136; Gillespie, ref. 10, p. 34; *Canad. J. Chem.*, 1961, **39**, 2336.

[22] Hoard, Glen, and Silverton, *J. Amer. Chem. Soc.*, 1961, **83**, 4293.

[23] Hoard and Nordsieck, *J. Amer. Chem. Soc.*, 1939, **61**, 2853.

receiving d_{xy}-electrons from the metal than the other four, so it would be expected that four of the cyanide groups would be less strongly held to the metal atom and could be replaced by four non-π-bonding ligands (R) to give $[M(CN)_4R_4]^{n-}$. This is observed[24] in the formation of such complexes as $[Mo^{IV}(CN)_4(OH)_4]^{4-}$, although complexes with five cyanide groups also exist,[21,24] such as $[Mo^{IV}(CN)_4(OH)_4]^4$. However, a recent Raman spectroscopic study of the $[Mo^{IV}(CN)_8]^{4-}$ ion indicates that the structure in solution is that of an Archimedean antiprism,[25] in which case the possibilities of metal–ligand π-bonding would seem to be greatly reduced if the d_{z^2} were to be the only metal d_π-orbital available. The very unstable compound $Ti(CN)_3,5KCN$ may be either $K_5[Ti^{III}(CN)_8]$ or $K_3[Ti^{III}(CN)_6],2KCN$;[26] and although the dodecahedral configuration is known for some titanium compounds,[27] the absorption spectra in this case favour a hexaco-ordinated configuration,[26] though it is not clear how the two molecules of potassium cyanide are attached to the complex.

(b) 7-, 6-, *and* 5-*Co-ordination.* No heptaco-ordinated cyanide complexes have been definitely established. The black compound $K_4[Mo(CN)_7],H_2O$ contains molybdenum(III)[28] and has an unpaired electron per molybdenum atom,[29] so that it may be $[Mo^{III}(CN)_7]^{4-}$ or $[Mo^{III}(CN)_7(H_2O)]^{4-}$. On the basis of the "nine-orbital rule", heptaco-ordination may be expected for technetium(IV) or molybdenum(III) (both have three *d*-electrons),[30] and a technetium(IV) cyanide has been shown to exist in the presence of an excess of cyanide ion, perhaps as $[Tc^{IV}(CN)_6]^{2-}$ or as $[Tc^{IV}(CN)_7]^{3-}$;[31] and recently $[Tc^{IV}(CN)_4(OH)_3]^{3-}$ has been isolated.[32] The vanadyl complex $[V^{IV}O(CN)_6]^{4-}$ has already been mentioned. The formation of a heptaco-ordinated intermediate during reaction of CN^- with $[Mn^{III}(CN)_6]^{3-}$ has been proposed, with a water molecule occupying the seventh co-ordination position.[33]

Hexaco-ordination is the commonest stereochemical arrangement in cyanides and will not be considered separately here.

There is little evidence for the existence of pentaco-ordinated cyanides in the solid state; most of the complexes alleged to have this structure exist only in solution where they probably take up a solvent molecule as the sixth ligand. $K[Mo^{IV}(CN)_5]$ has been briefly reported but incompletely characterised,[34] and the same is true of $[V^{IV}O(CN)_4]^{2-}$.[15a] The species $[Co^{II}(CN)_5]^{3-}$ and $[Ni^{II}(CN)_5]^{3-}$ have been reported to exist in solution; the former is

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[24] Bertoluzza, Carassiti, and Marinangeli, *Ann. Chim. (Italy)*, 1960, **50**, 806.
[25] Stammreich and Sala, *Z. Elektrochem.*, 1960, **64**, 741.
[26] Schläffer and Götz, *Z. anorg. Chem.*, 1961, **309**, 105.
[27] Clark, Lewis, Nyholm, Pauling, and Robertson, *Nature*, 1961, **192**, 222.
[28] Young, *J. Amer. Chem. Soc.*, 1932, **54**, 1402.
[29] Lewis, Nyholm, and Smith, *J.*, 1961, 4590.
[30] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1806.
[31] Colton, Dalziel, Griffith, and Wilkinson, *J.*, 1960, 71.
[32] Herr and Schwochau, *Angew. Chem.*, 1961, **73**, 492.
[33] Adamson, Welker, and Wright, *J. Amer. Chem. Soc.*, 1951, 73, 4789; Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 114.
[34] Steele, *Austral. J. Chem.*, 1957, **10**, 404.

probably $[Co^{II}(CN)_5(H_2O)]^{3-}$,[35] and the latter may be $[Ni^{II}(CN)_5(H_2O)]^{3-}$,[36] though $[Ni^{II}(CN)_6]^{4-}$ has also been suggested.[37] Recently,[36] the formation constants of $[Ni(CN)_5(H_2O)]^{3-}$ and $[Ni(CN)_6]^{4-}$ have been measured for solutions of $[Ni(CN)_4]^{2-}$ in excess of cyanide ion, and evidence has also been obtained for the existence of $[Ni(CN)_5Cl]^{4-}$. A cupric cyanide complex $[Cu^{II}(CN)_4(HCN)]^{3-}$ has been reported to exist in solution:[38] a more reasonable formulation would be $[Cu^{II}(CN)_5]^{3-}$ or $[Cu^{II}(CN)_5(H_2O)]^{3-}$. It is possible that pentaco-ordinated intermediates are formed during the exchange of CN^- and the tetracyano-complexes of nickel, palladium, and platinum.[39]

(c) 4-, 3-, *and 2-Co-ordination.* Both planar and tetrahedral cyano-complexes are known, confined to metal ions having eight, nine, or ten *d*-electrons. The complexes $[Cu^{I}(CN)_3]^{2-}$ and $[Ag^{I}(CN)_3]^{2-}$ are probably tetrahedral, with a water molecule occupying the fourth co-ordination position.

The only established trico-ordinate cyanide is $[Cu^{I}(CN)_2]^-$, which has a curious polymeric spiral structure with a C–Cu–C angle of 134° and linear C–Cu–N bridging such that each copper atom is linked to three other atoms.[40]

Silver(I) and gold(I), which have filled d^{10} shells, form the linear two co-ordinated complexes $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$. The tendency of these ions to form such complexes is favoured, according to Orgel,[6,41] by the fact that the *d*–*s* separation is small such that the two electrons which, in a d^{10} ion, normally occupy the d_{z^2} orbital, occupy in these cases a *d*–*s* hybrid orbital which leads to the formation of strong bonds along the *z*-axis. A somewhat different interpretation has been given by Nyholm.[8]

Stabilities of Cyanide Complexes.—Very few facts are available on the stabilities of cyanide complexes, and they are certainly insufficient to justify general conclusions. Bjerrum[42] has calculated some free energies of complex formation (relative to the values for the corresponding aquo-complexes) computed from mean complexity constants, and thus demonstrated that most cyanide complexes have a metal–ligand affinity greater than those of aquo-, ammino-, or halogeno-complexes. Chemically, the most stable cyanide complexes are those of Mn(III), Fe(III), Fe(II), Co(III), Ni(II), Cu(I), Mo(IV), Ru(II), Rh(III), Pd(II), Ag(I), W(IV), Re(VI), Re(V),

[35] Adamson, *J. Amer. Chem. Soc.*, 1951, **73**, 5110; Griffith and Wilkinson, *J.*, 1959, 2757.

[36] McCullough, Penneman, and Jones, *J. Inorg. Nuclear Chem.*, 1960, **13**, 286; Penneman and Jones, Abstracts of Papers read at the 141st ACS Meeting, American Chemical Society, Washington, 1962; Penneman, personal communication.

[37] Kisova and Cuprova, *Chem. Listy*, 1958, **52**, 1422; Blackie and Gold, *J.*, 1959, 4033.

[38] Glasner and Asher, *J.*, 1959, 3296.

[39] Grinberg and Nikol'skaya, *Zhur. priklad. Khim.*, 1951, **24**, 893.

[40] Cromer, *J. Phys. Chem.*, 1957, **61**, 1388; Lindquist, *Acta Cryst.*, 1957, **10**, 29.

[41] Orgel, *J.*, 1958, 4186; Orgel and Dunitz, "Advances in Inorganic Nuclear Chemistry," ed. Emeléus and Sharpe, Academic Press, New York, 1960, Vol. II, p. 1.

[42] Bjerrum, *Chem. Rev.*, 1950, **46**, 381.

Os(ii), Ir(iii), Pt(ii), Au(iii), and Au(i); Ta(iii), Ti(iii), V(ii), V(iii), Cr(ii), (Cr(iii), Mn(ii), and Co(ii) have markedly lower chemical stabilities. (There are no known cyanide complexes of zirconium, hafnium, or niobium.) The former group resembles Chatt's "group b" of transition metals, namely, those which are most likely to co-ordinate with carbon, their "class b" character depending on the availability of lower *d*-orbitals for π-bonding with the ligand.

Standard oxidation potentials have been determined for a few cyanide systems (see Table 3). It will be seen that, in general, the most stable complexes are those in which there is the highest degree of spin-pairing, the diamagnetic d^6-state being the most favoured.

Replacement Reactions.—Since cyanide complexes are anionic, the difficulty of outer-sphere association between reacting species in the study of replacements is avoidable, and it becomes possible to distinguish S_N2 and S_N1 mechanisms.[43] Little work has been done on cyanide systems, however, and there is room for much more investigation in this field, especially with the pentacyano-iron(ii) and -iron(iii) systems. It has been shown that the replacement of water in $[Co(CN)_5(H_2O)]^{2-}$ by various ligands such as N_3^-, SCN^-, and Br^- follows a S_N1 mechanism with $[Co^{III}(CN)_5]^{2-}$ as intermediate.[43] A curious reaction between ferrocyanide and nitrite ion has been reported[44] in which nitroprusside is formed:

TABLE 3. *Standard electrode potentials for cyanide systems.*

Couple	E° (v)	Couple	E° (v)
$[Mo(CN)_8]^{4-}/[Mo(CN)_8]^{3-}$	−0·73	$[Ru(CN)_6]^{4-}/[Ru(CN)_6]^{3-}$	−0·89*
$[W(CN)_8]^{4-}/[W(CN)_8]^{3-}$	−0·57	$[Os(CN)_6]^{4-}/[Os(CN)_6]^{3-}$	−0·99*
$[Mn(CN)_6]^{5-}/[Mn(CN)_6]^{4-}$	+0·70	$[Cr(CN)_6]^{4-}/[Cr(CN)_6]^{3-}$	−1·28
$[Mn(CN)_6]^{4-}/[Mn(CN)_6]^{3-}$	+0·22	$[Ni_2(CN)_6]^{4-}/[Ni(CN)_4]^{2-}$	+0·8
$[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$	−0·36	Co(II) to Co(III) (in excess of Co^-)	−0·8

* Estimated from polarographic data. Other values from Latimer's "Oxidation Potentials," Prentice-Hall, New York, 1952.

$$[Fe(CN)_6]^{4-} + NO_2^- + H_2O \rightarrow [Fe(CN)_5NO]^{2-} + CN^- + 2OH^-$$

The rate is increased by the addition of mercuric ion. Studies have also been made on the rate of exchange of CN^- with cyanides $[M(CN)_6]^{n-}$ where M is vanadium, chromium, manganese, iron, and cobalt, and orders of lability have been obtained.[45]

Photochemical Reactions.—It is to be expected that irradiation of solutions of complex ions with light of frequency corresponding to the region of

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[43] Grassi, Haim, and Wilmarth, ref. 10, p. 276.

[44] Schwarzkopf, *Abh. Deutsch. naturmed. Vereins Bohmen, Lotos*, 1911, **3**, 1.

[45] MacDiarmid and Hall, *J. Amer. Chem. Soc.*, 1954, **76**, 4222; Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 113.

charge-transfer spectra may cause oxidation–reduction reactions, and that irradiation with light of the same frequency as the *d–d*-transitions of complex ions may induce replacements. It has been observed that photolysis of the hexacyanides of manganese(III), iron(III), chromium(III), and cobalt(III) results in the formation of cyanogen and reduced forms of the complexes, and that this occurs most easily in the sequence Mn > Fe > Cr > Co.[46] Irradiation of ferrocyanide solutions and of solutions of $[Mo(CN)_8]^{4-}$ leads to aquated products.[47,48] The action of light on $[Fe^{II}(CN)_5NO]^{2-}$ (nitroprusside) is reported[48] to result in the formation of the paramagnetic species $[Fe^{II}(CN)_5NO]^{3-}$.

Specific Cyanide Systems.—(a) *Titanium, vanadium, and chromium groups.* In general, there are either no cyanide complexes of transition elements of the left-hand side of the Periodic Table or they are chemically unstable. No cyanide complex has been reported for zirconium, hafnium, or niobium. An unstable titanium(III) complex exists,[26] and there is a report of a tantalum(III) cyanide which was not isolated from solution.[49a] Vanadium(IV) cyanides have been discussed above. The complexes of vanadium(III), vanadium(II), chromium(III) and chromium(II) are not markedly stable, the lower oxidation states being very sensitive to aerial oxidation, while the tervalent compounds are prone to hydrolysis in aqueous solution (they are also light-sensitive). The reason for the instability of the cyanides of this group is presumably that there are insufficient d_π-electrons for back-donation to the ligand and hence for stabilisation of the complex, except in the case of the eight-co-ordinate molybdenum and tungsten compounds. The complex $[Cr^0(CN)_6]^{6-}$, isoelectronic with $[Cr^0(CO)_6]$ and $(Mn^I(CN)_6]^{5-}$, has recently been isolated.[49b]

(b) *Manganese group.* Manganese forms hexaco-ordinated univalent bivalent, and tervalent cyanides. The comparative stability of $[Mn^I(CN)_6]^{5-}$ is accounted for by the fact that it has the maximum stabilisation from metal–ligand back-donation, having an inert-gas configuration. A manganese(0) cyanide has also been reported,[49c] but the existence of such a compound with six cyanide ligands seems unlikely in view of the fact that it would be paramagnetic and require the promotion of a metal electron to an anti-bonding orbital.

Technetium is represented by the complex $[Tc^{IV}(OH)_3(CN)_4]^{3-}$ alone.[32] Rhenium cyanide complexes are unique in that they adopt either hexa- or octa-co-ordination in a wide range of oxidation states. Both

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[46] Schwartz and Weiss, *Ber.*, 1925, **58**, 746; Schwartz and Tede, *Ber.*, 1927, **60**, 69.

[47] Baudisch, *Ber.*, 1929, **62**, *B*, 2706; Ilimori, *Z. anorg. Chem.*, 1927, **167**, 157; Kenney, Flynn, and Gallin, *J. Inorg. Nuclear Chem.*, 1961, **20**, 75; MacDiarmid and Hall, *J. Amer. Chem. Soc.*, 1953, **75**, 5204; Adamson and Sporee, *ibid.*, 1958, **80**, 3865; Asperger, *Trans. Faraday Soc.*, 1952, **48**, 617.

[48] Baudisch, *Science*, 1948, **108**, 443; Jakob, Sanotus-Kosinska, and Stasicka, *Roczniki Chem.*, 1962, **36**, 165.

[49] (*a*) Ruff and Thomas, *Ber.*, 1922, **55**, 1466; (*b*) Heintz, *J. Inorg. Nuclear Chem.*, 1961, **21**, 262; (*c*) Christensen, Kleinberg, and Davidson, *J. Amer. Chem. Soc.* 1953, **75**, 2495.

$[Re^{VI}(CN)_8]^{2-}$ and $[Re^{V}(CN)_8]^{3-}$ have been described, as well as the possible $[Re^{VII}(CN)_8(OH)]^{2-}$ (which may be nine-co-ordinated);[20] and octahedral $[Re^{V}O_2(CN)_4]^{3-}$, $[Re^{IV}O_2(CN)_4]^{4-}$, $[Re(CN)_6]^{3-}$,^{III} $[Re^{II}(CN)_6]^{4-}$, and $[Re^{I}(CN)_6]^{5-}$ have recently been reported.[50] It will be seen that rhenium adopts eight-co-ordination when it has one or two *d*-electrons and hexaco-ordination when it has more than two. Conductometric and E.M.F. measurements have indicated the existence of mono- and bi-nuclear complexes with the oxidation state of the rhenium varying from (+5) to (+1).[51]

(c) *Iron group.* Iron forms the familiar ferri- and ferro-cyanides, $[Fe^{III}(CN)_6]^{3-}$ and $[Fe^{II}(CN)_6]^{4-}$, and there is a report that electrolytic reduction of these in aqueous solution gives a Fe(I) complex.[52] The stability of the d^6- is higher than that of the d^5-configuration in the cases of ruthenium and osmium: $[Ru^{III}(CN)_6]^{3-}$ exists as a very unstable species in solution,[53] and there is polarographic evidence[54] only for the existence of $[Os^{III}(CN)_6]^{3-}$.

(d) *Cobalt group.* The cobalticyanides, rhodicyanides, and iridicyanides $[M(CN)_6]^{3-}$ are all very stable, having six *d*-electrons and inert-gas configurations. The bivalent cyanides would require promotion of an electron to an anti-bonding orbital if they are to have octahedral (spin-pared) co-ordination. The cobaltocyanide ion, formerly formulated as $[Co^{II}(CN)_6]^{4-}$, is now known to be $[Co^{II}(CN)_5]^{3-}$ and is diamagnetic in the solid state, which supports its formulation as $[Co_2^{II}(CN)_{10}]^{6-}$.[35] Measurements of the infrared-active C–N stretching vibrations indicate that the complex may have a structure analagous to that of manganese carbonyl, with which it is formally iso-electronic:[55]

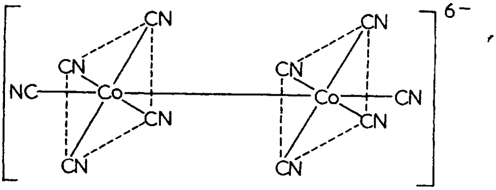

FIG. 3. *The* D_{4h} *structure for* $[Co_2(CN)_{10}]^{6-}$.

A staggered D_{4d}-configuration is probably more likely than a D_{4h} one since repulsions would be minimised in the former. There is a report[56] of

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[50] Sen, *Science and Culture*, 1960, **26**, 139, Clauss and Lissner, *Z. anorg. Chem.*, 1948, **297**, 300; Walter, Kleinberg, and Griswold, *Inorg. Chem.*, 1962, **1**, 10.

[51] Meier and Treadwell, *Helv. Chim. Acta*, 1955, **38**, 1679; Meier, *Diss. Eidg. Techn. Hochschule Zürich*, 1955, No. 2461; Klemm and Frischmuth, *Z. anorg Chem.*, 1937, **230**, 209.

[52] Treadwell and Huber, *Helv. Chim. Acta*, 1943, **26**, 10.

[53] Krauss and Schrader, *Z. anorg. Chem.*, 1928, **173**, 65; De Ford and Davidson, J. *Amer. Chem. Soc.*, 1951, **73**, 1469.

[54] Meites, *J. Amer. Chem. Soc.*, 1957, **79**, 4631.

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

[56] Nartius, *Annalen*, 1961, **117**, 357.

the existence of $[Ir^{II}(CN)_6]^{4-}$, but by analogy with the cobalt case and the rarity of iridium(II) complexes it is unlikely to exist or would at least not have the formulation above. Polarographic evidence for the existence of a rhodium(II) cyanide complex[57] has recently been re-interpreted[58] as indicating the existence of rhodium(I) in the compound. In aqueous solution, $[Co^{II}(CN)_5]^{3-}$ absorbs hydrogen to give a cobalt(I) species which may be $[Co^{I}(CN)_5H]^{3-}$,[59] and takes up acetylene to give a curious binuclear species formulated[60] as $[Co_2^{III}(CN)_{10}(C_2H_2)]^{6-}$. It also absorbs carbon monoxide, nitric oxide, and oxygen. Aqueous solutions of $[Co^{II}(CN)_5]^{3-}$ compounds slowly reduce water to hydrogen in concentrated solution, while in more dilute solutions they disproportionate to cobalt(I) species, possibly $[Co^{I}(CN)_5H)]^{3-}$, and a cobalt(III) complex.[59] There have also been reports[61] of cobalt(II) tetracyanides, either $[Co^{II}(CN)_4]^{2-}$ or $[Co^{II}(CN)_4(H_2O)_x]^{2-}$.

A cobalt(I) complex formulated as $[Co^{I}(CN)_4]^{3-}$ has been isolated,[62] and other cobalt(I) cyanides have been reported.[63] Reduction of aqueous solutions of cobalt(III) and cobalt(II) cyanides has been shown to give a hydride species, probably $[Co^{I}(CN)_5H]^{3-}$ (see below), and similar hydrides of univalent species are apparently formed by rhodium and iridium cyanides.[58] The chemistry of the cobalt cyanides, especially those with cobalt in the lower oxidation states, is still obscure and needs considerable further investigation.

The cobalt(0) complex $[Co_2(CN)_8]^{8-}$ and its rhodium anolgue[58] have been reported. Infrared studies of the C–N stretching frequency region indicate that the structure is probably that of Fig. 4, with a metal–metal bond. There is no evidence of CN bridging groups and so, though the complex is formally iso-electronic with cobalt carbonyl $[Co_2^0(CO)_8]$, it does not have the same structure.[58]

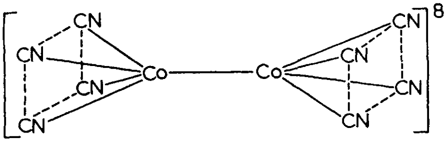

FIG. 4. *Suggested structure for* $[Co_2(CN)_8]^{8-}$.

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

[58] Griffith and Wilkinson, *J.*, 1959, 2757.

[59] Iguchi, *J. Chem. Soc. Japan*, 1952, **63**, 634, 1752; Winfield, *Austral. J. Sci. Res.*, 1951, *A*, **4**, 385; Kelso, King, and Winfield, *J. Amer. Chem. Soc.*, 1961, **83**, 3366.

[60] Griffith and Wilkinson, *J.*, 1959, 1629.

[61] Muller and Schluttig, *Z. anorg. Chem.*, 1924, **134**, 327; Crémoux and Mondain-Monval, *Bull. Soc. chim. France*, 1949, 700.

[62] Watt, Hall, Choppin, and Gentile, *J. Amer. Chem. Soc.*, 1954, **76**, 373; Watt and Thompson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 311.

[63] Grube, *Z. Elektrochem.*, 1926, **32**, 561; Maki and Tsuchida, *Bull. Chem. Soc. Japan*, 1960, **34**, 891.

(e) *Nickel group.* Nickel, palladium, and platinum(II) complexes of the form $[M^{II}(CN)_4]^{2-}$, all planar and diamagnetic, are among the most stable of cyanide complexes. In the presence of an excess of cyanide ion, $[Ni^{II}(CN)_4]^{2-}$ increases its co-ordination number to five or six by formation of the aquo-complex $[Ni^{II}(CN)_x(H_2O)_{6-x}]^{(x-2)-}$ (see above); however, no such complex is formed by platinum or palladium(II) cyanide.[64] No nickel(III) or nickel(IV) cyanide is known, but platinum forms halide cyanides of the form $[Pt^{IV}(CN)_4X_2]^{2-}$. The so-called platinum(III) cyanide $[Pt(CN)_4]^-$ is now believed[65] to have the structure $[Pt^{IV}(CN)_4,Pt^{II}(CN)_4]^{2-}$.

There is no convincing evidence for the existence of a palladium(I) or platinum(I) cyanide; and it appears that the strongly reducing solutions obtained by reduction of the bivalent-metal cyanides obtained by Manchot *et al.*[66] probably contain a hydride cyanide complex (see below). Univalent nickel cyanides are, however, known; $[Ni^I(CN)_4]^{3-}$ has been reported and may have either a tetrahedral or a planar structure[67] (the planar form is the more probable, being favoured by d^9-complexes[8]); and Bellucci's salt, originally formulated as $K_2[Ni^I(CN)_3]$, was recently shown[68] to be dimeric and diamagnetic. Studies of the infrared C–N stretching frequencies indicate that there may be a "half-bridged" structure, presumably involving some sort of three-centre molecular orbitals (III)[69] or a metal-bonded structure (IV) (D_{2d} or D_{2h}) similar to that proposed for the cobalt(II) cyanide complex.[55] A third possibility (V) is that of a bridged structure,[68] but this seems unlikely in view of the spectroscopic evidence.

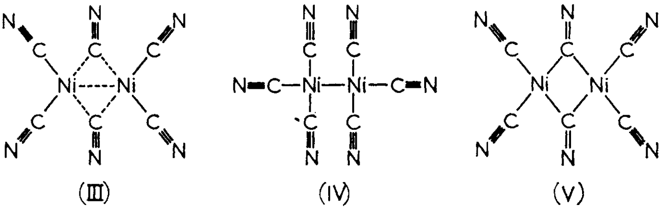

FIG. 5. *Suggested structures for* $[Ni_2(CN)_6]^{4-}$.

In all cases there would be planar co-ordination around the nickel atoms. The complex reacts with nitric oxide to give a compound $[Ni^0(CN)_3NO]$, and with carbon monoxide to give the dimeric complex $[Ni^I_2(CN)_6(CO)_2]^{4-}$, and absorbs acetylene though the composition of this product is unknown.[60]

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[64] Reddy, Thesis, London, 1961.

[65] Terry, *J.*, 1928, 202.

[66] Manchot and Schmid, *Ber.*, 1931, **64**, 2672; Manchot and Lehman, *Ber.*, 1930, **63**, 2775.

[67] Nast and Krakkay, *Z. Naturforsch.*, 1954, **9b**, 798.

[68] Bellucci, *Gazzetta*, 1919, **49**, II, 70; Nast and Krakkay, *Z. Naturforsch.*, 1957, **12b**, 122; Pfab and Nast, *Z. Krist.*, 1959, **111**, 4.

[69] El-Sayed and Sheline, *J. Amer. Chem. Soc.*, 1956, **78**, 702.

Zerovalent complexes of nickel, palladium, and platinum of the form $[M^0(CN)_4]^{4-}$ are known, and they presumably have a tetrahedral structure. However, it has recently been questioned whether any platinum(0) complex at all exists, since certain "zerovalent" phosphine complexes of platinum are in fact dihydrides of platinum(II),[70] though this is apparently not the case for all phosphine complexes of platinum(0).[71] It has been observed that reduced solutions of platinum and palladium(II) cyanides contain hydride atoms bonded to the metal atom, so these solutions may contain the ion $[Pt^{II}(CN)_4H_2]^{4-}$.[58] Whether or not these species are identical with the previously reported ions $[Pt^0(CN)_4]^{4-}$ and $[Pd^0(CN)_4]^{4-}$ is not clear, but there seems no doubt that $[Ni^0(CN)_4]^{4-}$ does not contain hydride atoms.

(f) *Copper group.* The most stable cyanides in this group are the univalent $[M^I(CN)_x]^{x-1}$ series where M is copper, silver, or gold, and x is 2—4. Gold(III) cyanides $[Au^{III}(CN)_4]^-$ are also known, but there is no evidence for the existence of copper(III) or silver(III) analogues.

Although no silver(II) or gold(II) cyanide complexes have been reported, there seems to be no doubt that copper(II) cyanides exist. The reaction in aqueous solution between cupric ion and cyanide ion gives cyanogen and cuprocyanide [E° for the reaction[72] $Cu^{2+} + 3CN^- = [Cu(CN)_2]^- + \frac{1}{2}(CN)_2$ is $+ 1{\cdot}3$ v). Addition of cupric to cyanide ion gives a transient purple colour attributed[38] to a material $[Cu^{II}(CN)_4,HCN]^{2-}$, and addition of cupric ion to a methanolic cyanide solution at $-70°$ gives an intense purple colour without precipitation of cuprocyanide: this colour persists until the temperature is raised.[73] On the basis of viscosity and cryoscopic determinations Molis and Izaguirre[74] claim to have detected the presence of $\{Cu^{II}[Cu^{II}(CN)_4]_2\}^{2-}$ ions in cyanide–cupric ion mixtures, and $[Cu^{II}(CN)_4]^{2-}$ has been suggested as an intermediate in certain reactions.[75] There is an early report of the preparation of a compound $[Cu^{II}(CN)Cl]$,[76] and of mixed copper(II) cyanide ammines.[77] It seems likely that copper(II) cyanide complexes might be stabilised by the participation in the co-ordination sphere of good σ-bonding ligands such as F^-, Cl^-, or OH^-.*

Substituted Cyanide Complexes.—Many substituted cyanides are known, most of them of the form $[M(CN)_5X]^{n-}$ where M is iron(III), iron(II),

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* Recently, evidence has been obtained for the existence of a copper nitrosyl cyanide complex, $[Cu(NO)(CN)_2]$ (possibly associated with solvent molecules) derived from the cupri-cyanide ion (R. T. Frazer and M. Mercer, personal communication).

[70] Chapoorian, Lewis, and Nyholm, *Nature*, 1961, **190**, 528.

[71] Chatt and Rowe, *Nature*, 1961, **191**, 1191.

[72] Latimer, "Oxidation Potentials," 2nd edn., Prentice -Hall, New York, 1952, p. 186.

[73] D. F. Evans, personal communication.

[74] Molis and Izaguirre, *Anales real Soc. españ. Fiz. Quím.*, 1921, **19**, 33.

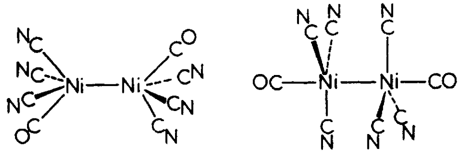
[75] Tanaka, Kamada, and Murayama, *Bull. Chem. Soc. Japan*, 1958, **31**, 895.

[76] Rabaut, *Bull. Soc. chim. France*, 1898, **19**, 786.

[77] Treadwell and Girsewald, *Z. anorg. Chem.*, 1904, **39**, 87.

cobalt(III), or cobalt(II), and where X may be one of a wide range of neutral or charged ligands.

The known carbonyl cyanides and nitrosyl cyanides are summarised in Table 4. Carbonyl cyanides involving the central metal atom in a (+3) or (+2) state are uncommon: an ion $[Fe^{II}(CN)_5CO]^{3-}$ is known, but not the iso-electronic $[Co^{III}(CN)_5CO]^{2-}$ or $[Mn^{I}(CN)_5CO]^{4-}$ {the cobalt carbonyl cyanide $[Co^{III}(CN)_5CO]^{2-}$ recorded in the literature[78] has been shown to consist of a mixture of $[Co^{-I}(CO)_4]^-$ and $[Co^{III}(CN)_6]^{3-}$}.[79] A rhenium complex $[Re^{II}(CN)_5CO]^{3-}$ has been reported[80] and would be of particular interest if this formulation were correct since it would be the only known paramagnetic carbonyl cyanide. A number of carbonyl cyanides of metals in a low oxidation state are known, including $[Ni^{I}_2(CN)_6(CO)_2]^{4-}$ which, though it is iso-electronic with cobalt carbonyl $[Co^{0}_2(CO)_8]$, has apparently no bridging carbonyl group[81] (this view has been disputed[82]). The structure (VI) in Fig. 6 (C_{2h}) is favoured for this complex, and is analogous to that of $[Co_2(CN)_8]^{8-}$ (Fig. 4). Structure (VII) is also a possibility. The complex $[Co^{I}(CN)_3CO]^{2-}$ is apparently planar[58] and may be an analogue of the postulated but unknown planar $[Fe^{0}(CO)_4]$.[83]



(VI) (VII)

FIG. 6. *Suggested structures for* $[Ni_2(CN)_6(CO)_2]^{4-}$.

Octahedrally co-ordinated nitrosyl cyanides are particularly stable, and most of them have inert-gas configurations although the formal oxidation state may be very low since normally the nitric oxide donates three electrons to the metal atom.[84]

That in most cases nitric oxide does co-ordinate as the nitrosonium (NO^+) ion has been shown by magnetochemical, spectroscopic, and—in one case[85]—paramagnetic resonance measurements. However, in the ion $[Co^{III}CN)_5NO]^{3-}$ the ligand may be bonded as an NO^- group or attached

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[78] Manchot and Gall, *Ber.*, 1926, **59**, 1056.
[79] Hieber and Bartenstein, *Z. anorg. Chem.*, 1954, **276**, 12.
[80] Bandopadhyay, *Science and Culture*, 1959, **25**, 278.
[81] Griffith, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **10**, 23.
[82] Nast and Kasperl, *Chem. Ber.*, 1959, **92**, 2135.
[83] Orgel, *Chem. Soc. Special Publ.*, 1959, No. 13, p. 93.
[84] Irving, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.
[85] Bernal and Harrison, *J. Chem. Phys.*, 1961, **34**, 102; Naiman, *ibid.*, 1961, **35**, 1503.

TABLE 4. *Nitrosyl and carbonyl cyanide complexes.*

	Complex	Structure	Iso-electronic carbonyl
d^{10}	$[Ni^{0}(CN)_{3}NO]^{2-}$; $[Ni^{0}(CN)^{I}(CO)_{2}]^{2-}$	Tetrahedral	$[Ni^{0}(CO)_{4}]$
	$[Co^{-I}(CN)(CO)_{2}(NO)]^{-}$; $[Co^{-I}(CN)(CO)_{3}]^{2-}$	Tetrahedral	$[Ni^{0}(CO)_{4}]$
d^{9}	$[Co^{0}_{2}(CN)_{3}(CO)_{5}]^{3-}$; $[Co^{0}_{2}(CN)_{7}(CO)]^{7-}$; $[Ni^{I}_{2}(CN)_{6}(CO)_{2}]^{4-}$	Square-based pyramidal*	$[Co^{0}_{2}(CO)_{8}]$
d^{8}	$[Co^{I}(CN)_{3}(CO)]^{2-}$; $[Co^{I}(CN)_{2}(CO)_{2}]^{-}$	Planar	$[Fe^{0}(CO)_{4}]$
d^{6}	$[V^{-I}(CN)_{5}NO]^{5-}$; $[Cr^{0}(CN)_{5}NO]^{4-}$	Octahedral	$[Cr^{0}(CO)_{6}]$
	$[Mn^{I}(CN)_{5}NO]^{3-}$; $[Fe^{II}(CN)_{5}NO]^{2-}$; $[Fe^{II}(CN)_{5}CO]^{3-}$	Octahedral	$[Cr^{0}(CO)_{6}]$
	$[Co^{III}(CN)_{5}NO]^{3-}$; $[Fe^{II}(CN)_{5}NO]^{4-}$;	Octahedral†	$[Cr^{0}(CO)_{6}]$
	$[Fe^{II}(CN)_{5}NO]^{3-}$	Octahedral‡	
d^{5}	$[Mn^{II}(CN)_{5}NO]^{2-}$; $[Re^{II}(CN)_{5}NO]^{2-}$;		$[V^{0}(CO)_{6}]$
	$[Cr^{I}(CN)_{5}NO]^{3-}$; $[Re^{II}(CN)_{5}CO]^{3-}$	Octahedral	
d^{4}	$[Re^{III}(CN)_{7}NO]^{3-}$; $[Mo^{II}(CN)_{5}(NO)(OH)_{2}]^{4-}$	Dodecahedral	—
	$[Cr^{II}(CN)_{5}NO]^{2-}$	Octahedral	—

* Structure uncertain. † NO bonded as NO^{-} or through oxygen. ‡ NO bonded as a neutral ligand.

through the oxygen atom,[86] and the same may be true of the incompletely characterised material $[Fe(CN)_{5}NO]^{4-}$.[87] In the case of the curious paramagnetic complex $[Fe^{II}(CN)_{5}NO]^{3-}$, magnetic measurements and chemical reactions indicate that the single unpaired electron may be localised on the nitrogen rather than on the iron atom,[88] Baudisch[48] reports that photolysis of nitroprusside $[Fe^{II}(CN)_{5}NO]^{2-}$ gives this complex; if this is so, the series of complexes $[Fe^{II}(CN)_{5}NO]^{2-}$, $[Fe^{II}(CN)_{5}NO]^{3-}$, and $[Fe^{II}(CN)_{5}NO]^{4-}$ may be considered to differ in external charge simply because the nitric oxide co-ordinates respectively as NO^{+}, $NO\cdot$ (radical), and NO^{-} (or ON). It is interesting that in the similar series $[Cr^{0}(CN)_{5}NO]^{4-}$, $[Cr^{I}(CN)_{5}NO]^{3-}$, and $[Cr^{II}(CN)_{5}NO]^{2-}$ magnetic and spectrochemical measurements indicate that the nitric oxide co-ordinates as NO^{+} in all three cases, while the oxidation state of the chromium atom changes.[90] There are two eight-co-ordinated nitrosyl cyanide complexes known, namely, $[Mo^{II}(CN)_{5}NO(OH)_{2}]^{4-}$ and $[Re^{III}(CN)_{7}NO]^{3-}$, which have d^{4}-configurations and are diamagnetic.[20,89]

It seems likely that there should exist a series of nitrosyl cyanides analagous to the carbonyl nitrosyl complexes, $[Co(CO)_{3}NO]$, $[Fe(CO)_{2}(NO)_{2}]$, $[Mn(CO)(NO)_{3}]$, but only one compound of this type is known,

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[86] Nast and Rohmer, *Z. anorg. Chem.*, 1956, **285**, 271; Griffith, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38; Nast and Thorne, *Z. anorg. Chem.*, 1961, **309**, 283; Griffith, Lewis, and Wilkinson, *J.* 1961, 775.

[87] Ungarelli, *Atti Istit. Veneto*, 1924, **83**, 11, 81; Giral, *Anales real Soc. españ. Fiz. Quim.*, 1923, **21**, 236.

[88] Sidgwick, "Chemical Elements and their Compounds," Oxford Univ. Press, 1950, p. 1360; Krauss and Rittenberg, *J. Amer. Chem. Soc.*, 1955, **77**, 5296; Morgan, *Talanta*, 1959, **3**, 113; Griffith, Lewis, and Wilkinson, *J.*, 1958, 3993.

[89] Griffith, Lewis, and Wilkinson, *J.*, 1959, 872.

[90] Griffith, unpublished work.

namely, $[Co^{-I}(CO)_2(CN)NO]^-$,[86] though reaction of CN^- in methanol with $[Fe(CO)_2(NO)_2]$ gives a very unstable product which may have the structure $[Fe^{-II}(CO)(CN)(NO)_2]^-$.[90]

Peroxide cyanides.—An interesting complex of cobalt(III), analogous to the cobalt peroxide ammines, has been prepared by direct oxidation of the cyanide $[Co^{II}(CN)_5]^{3-}$.[91] The product is diamagnetic and probably identical with the reported substance "$[Co^{III}(CN)_5OH]^{3-}$",[92] and it has the composition $[(NC)_5Co^{III}{-}O_2{-}Co^{III}(CN)_5]^{6-}$. This may be further oxidised to the paramagnetic material $[(NC)_5Co{-}O_2{-}Co(CN)_5]^{5-}$ which has a single unpaired spin, as has $[(H_3N)_5Co{-}O_2{-}Co(NH_3)_5]^{5+}$, and presumably, as with the latter complex, the electron is not predominantly localised on the oxygen atom.[93] Slightly acidic solutions of the ion $[Fe^{II}(CN)_5NH_3]^{3-}$ absorb oxygen to give a dark product which may be a peroxide cyanide complex;[90,94] Baudisch[47] reports that irradiation of ferrocyanides in the presence of oxygen also gives peroxides, of unspecified nature, but recent work by Kenney *et al.*[47] indicates that there is oxidation to iron(III) cyanides rather than oxygenation.

In view of the similarity between the co-ordination chemistry of cobalt and chromium it might be expected that oxidation of chromium(II) cyanides would give binuclear oxide or peroxide species, especially since oxidation of $[Cr^{II}(H_2O)_6]^{2+}$ and $[Cr^{II}(NH_3)_6]^{2+}$ gives dihydroxide or oxide complexes.[95] However, the cyanide $[Cr^{II}(CN)_6]^{4-}$ with air or with hydrogen peroxide simply gives an ion $[Cr^{III}(CN)_6]^{3-}$, and this difference in behaviour between cyanide and ammine complexes of chromium(II) has been attributed to the fact that electrons can travel more easily through CN^- groups than H_2O or NH_3, or that there is spin-pairing in the cyanide.[91] This does not, however, explain the formation of peroxide complexes or oxidation of cobalt(II) ammines and cyanides.

The complexes $[CrO_4(CN)_3]^{3-}$ and $[CrO_4(CN)_2NH_3]^{2-}$ have been reported and appear to contain the two peroxide groups co-ordinated to a chromium(IV) atom.[90,95]

Systems Involving Bridging Cyanide Groups.—From the well-known tendency of carbon monoxide to participate as a bridging >CO group and not merely as –C–O, it might be expected that the iso-electronic CN^- group should behave similarly, but there is no convincing evidence of this. However, linear –C–N– bridges are quite common, especially in the simple cyanides such as AgCN, AuCN, $Zn(CN)_2$, and $Cd(CN)_2$, which are polymeric with infinite chains, and also in $KFe_2(CN)_6$[96] and in

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[91] Haim and Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.
[92] Smith, Kleinberg, and Griswold, *J. Amer. Chem. Soc.*, 1953, **75**, 449.
[93] Ebsworth and Weil, *J. Phys. Chem.*, 1959, **63**, 1890.
[94] Manchot, Merry, and Worringer, *Ber.*, 1912, **45**, 2869.
[95] Wiede, *Ber.*, 1899, **32**, 378; Reisenfeld, *Ber.*, 1908, **41**, 3536.
[96] Zhdanov, *Doklady Akad. Nauk S.S.S.R.*, 1941, **31**, 352.

$[R_2Au^{III}(CN)]_4$.[97] It has recently been observed that the infrared C–N stretching frequency is about 50 cm.$^{-1}$ higher for bridging CN groups than for terminal CN^-.[98] The complex $[NC_5Co^{III}–C–N–Fe^{II}(CN)_5]^{6-}$ has been prepared by the reaction of the two ions $[Fe^{III}(CN)_6]^{3-}$ with $[Co^{II}(CN)_5]^{3-}$;[91] this presumably has the same geometry as the activated complex proposed for the electron-transfer reaction in this process.[99] The curious compound $Ag_2[Co(CN)_5]$ reported by Ray and Dutt[100] as feebly paramagnetic and pentaco-ordinate has been shown[99] to be polymeric with linear –C–N– bridging groups.

Cyanide Hydrides.—Ligands such as cyclopentadienyl, carbon monoxide, and phosphines which are assumed to have good π-bonding properties form hydrides with a number of transition metals in low oxidation states. In these compounds it appears that the proton is directly bonded to the metal atom, and a convenient way of detecting these shielded protons is by the observation of their nuclear magnetic resonance chemical shifts.[101] It is to be expected that CN^-, which is a moderately good π-bonding ligand, should be capable of participating in hydride complexes, and recent studies on solutions of the complex ions $[Pt^{II}(CN)_4]^{2-}$, $[Pd^{II}(CN)_4]^{2-}$, $[Co^{III}(CN)_6]^{3-}$, $[Rh^{III}(CN)_6]^{3-}$, and $[Ir^{III}(CN)_6]^{3-}$ after reduction with aqueous borohydride or with potassium in liquid ammonia do show such shifts.[58,101] In none of these cases has a product been isolated or the composition determined. It is curious that, since a hydride complex of rhenium in a low oxidation state is known involving no ligand other than OH^-, H_2O, and (presumably) H^-, none of which can form π-bonds, no cyanide hydride of rhenium has been detected:[32] it may be that the external charge required would be too great for stability of the complex. Recently, Schilt[102] has found that acidification of iron(II) bipyridyl and *o*-phenanthroline dicyanide complexes causes marked shifts in the spectra of the compounds, and suggests that a metal–hydrogen bond may be present. However, there are no proton resonances in the nuclear magnetic resonance spectrum of the compounds,[103] and recent work by Orgel and Hamer[104] suggests that it is the CN groups that have been protonated.

Cyanide Systems of Biological Interest.—Various porphyrin-type iron complexes contain cyanide groups as part of the co-ordination sphere. It is interesting that, whereas such compounds as the hæmoglobins, catalase, and peroxidase may be "poisoned" by cyanide (presumably by the blocking of reactive positions around the metal atom and formation of mono- and di-cyanide complexes), one form of vitamin B_{12} contains a cyanide

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[97] Kharasch and Isbell, *J. Amer. Chem. Soc.*, 1931, **53**, 2701.
[98] Dows, Haim, and Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, **21**, 83.
[99] Taube, *Chem. Rev.*, 1952, **50**, 69.
[100] Ray and Dutt, *Z. anorg. Chem.*, 1937, **234**, 65; *Current Sci.*, 1937, **5**, 476.
[101] Green, *Angew. Chem.*, 1960, **72**, 719.
[102] Schilt, *J. Amer. Chem. Soc.*, 1960, **82**, 5779.
[103] G. Wilkinson, personal communication.
[104] Orgel and Hamer, *Nature*, 1961, **190**, 439.

group in the sixth co-ordination position of cobalt(III), though it is very liable to replacement by other groups. Dicyanide complexes of certain transition-metal phthalocyanines are also known.[105] Poisoning by cyanide has been attributed to inhibition of a number of enzymes, including the cytochrome oxidase system for oxygen stabilisation in cells;[106] in general, complex cyanides do not appear to have markedly poisonous properties unless one or more cyanide groups are easily removable from the co-ordination sphere.

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[105] A. B. P. Lever, personal communication.

[106] Dreisbach, "Handbook of Poisons, Diagnoses and Treatment," 2nd edn., Lange Medical Publ., Los Altos, p. 179.