CIS AND TRANS EFFECTS IN COBALT(III) COMPLEXES

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I. Introduction

A. AIMS OF THE REVIEW

The change of one or more ligands in a transition metal complex can have a very marked effect on the properties of both the central metal cation and the other ligands. There is a large amount of quantitative data available on the changes in the spectroscopic and magnetic, i.e., "physical," properties of the metal, and these form the basis of crystal field and ligand field theory. There is by comparison relatively little quantitative information on changes in the properties of the ligands such as bond lengths, force constants, equilibrium constants, and rates of reaction, which can be considered as the more "chemical" properties of the complex and are consequently of more direct interest to the preparative chemist and more relevant to an understanding of problems such

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as catalysis and the role of metals in biological systems. Studies of the physical properties of the metal and of the chemical properties of the ligands are obviously complementary, but with the exception of a brief comparison in Section V, B this review is concerned only with the latter.

The study of the mutual interactions of ligands can be traced back to observations made on the position and relative ease of ligand substitutions in the preparation of square planar platinum(II) complexes. Chernyaev (*56*) was the first to recognize the existence of a certain pattern of reactivity, namely, that one ligand affected the kinetic lability of another ligand in the trans position and that the ligands could be arranged in an order of trans-labilizing power. Since then many additional ligands have been studied and the order of trans activation can now be written (*31*) CO, CN^-, $C_2H_4 > PR_3$, $H^- > CH_3^-$, $SC(NH_2)_2 > C_6H_5^-$, NO_2^-, I^-, $SCN^- > Br^-, Cl^- >$ py, NH_3, HO^-, H_2O. Experimental work has also been extended to include (1) the study of the effect of ligands on other properties of complexes such as equilibrium constants and infrared spectra, (2) a search for cis effects, and (3) other metals and valencies. For a recent survey see the volume by Basolo and Pearson (*31*).

Previous reviews on the trans effect, e.g., (*30*), have concentrated on platinum(II) complexes. The present review is concerned only with cobalt(III) complexes, although a brief comparison with platinum complexes is made in Section V, C. There are two reasons for a review devoted entirely to cobalt(III) complexes. First, there has been a very great increase in our knowledge of cis and trans effects in cobalt(III) complexes over the last 10 years owing to the study of groups of complexes such as the pentacyanides, corrinoids, bisdimethylglyoxime, and related complexes and of ligands such as SO_3^{2-} and alkyl groups. Second, the experimental results present a relatively simple pattern which is much easier to interpret than in the case of platinum(II) complexes.

The theories which have been developed to account for the trans effect can be grouped under the two headings of "polarization" or "σ-donor" and "π-acceptor" theories. The earlier attempts at a theoretical interpretation of the experimental observations were made by Russian workers, in particular Nekrasov (formation of a dipole on the metal ion), Grinberg (mutual polarization of ligands and metal, correlation with the molar refraction and reducing power of the ligands), Gel'man (role of covalency), and Syrkin (*d–s* hybridized orbitals, cis strengthening as opposed to trans weakening); for a good summary of the Russian work up to 1952 see the review by Quagliano and Schubert (*153*). These can all be considered as variants of the "polarization" theory, which was originally developed to explain the ligand order $I^- > Br^- > Cl^- > HO^-$; in modern terminology it relates high trans effect to a strong σ-donor power of the ligand. In order to explain the high trans effect of neutral, unsaturated ligands such as C_2H_4, CO, NO, and thiourea Gel'man (*78*) put forward a rather different mechanism. She suggested that ligands such as C_2H_4 form a multiple bond to the metal, similar to the bonding proposed by Pauling (*142*) for metal carbonyls. This bond was described in valence bond terminology, but corresponds essentially to the formation of a metal-to-ligand π bond, which enhances the ligand-to-metal σ bond. This idea was developed by Chatt (*51, 52, 54*) and Orgel (*141*) and the importance of the π-acceptor capacity of the ligand was emphasized almost to the exclusion of σ-donor effects. More recently, however, it has been found that simple ligands such as H^- and CH_3^- which clearly cannot form π bonds also exert a strong trans effect, and Basolo *et al.* (*28*) and Bersuker (*33*) have all emphasized that a strong trans effect may be due to either a strong σ-donor or a strong π-acceptor capacity of the ligand (or both). As will be shown in Section V, A, the cis and trans effects of cobalt(III) complexes can be explained almost entirely in terms of the σ-donor power of the ligand, and a comparison of the differences between cobalt(III) and platinum(II) complexes underlines the role of π bonding in the latter.

B. CLASSIFICATION OF EFFECTS

The change of one ligand can alter the properties of the rest of the complex by several mechanisms which can be broadly classified under three headings:

(1) Cis and trans effects or "internal" effects, i.e., electronic effects transmitted through the central metal cation.

(2) Steric effects due to direct contact between the atoms of different ligands.

(3) "External" effects due to changes in the outer coordination sphere.

Effect (1) is the main topic of this review; effect (2) will not be discussed. Effect (3) can be extremely important in certain cobalt(III) complexes, examples being the effect of the counterion on bond lengths and ir spectra in the solid state and of ion-pair formation on the kinetics of ligand substitution. These will be discussed, where relevant, together with the "internal" effects.

The experimental approach to the study of cis and trans effects is to compare the relative effect of a series of ligands by following the effect on some property of ligand Y as ligand X is varied. In this review the ligand which is used as the "probe" in ground-state effects is labeled Y. In thermodynamic effects we consider the equilibrium between two ligands

Y and Z, and where a set of equilibria are compared the common ligand, if any, is labeled Y. X is the ligand whose effect we are studying and which we are trying to place in a series relative to other ligands. When four coplanar ligands are changed simultaneously, as when comparing the bisdimethylglyoxime, corrinoid, and other complexes, the four ligands are labeled L_4.

Cis and trans effects can be divided into several categories depending on the observed parameters of the test ligand Y (*150*).

Ground-state effects: Properties of Y in the ground state of the complex e.g., bond lengths and angles, stretching and bending force constants.

Thermodynamic effects: Equilibrium constants for replacing Y by another ligand Z or, in certain cases, for the formation of a complex with lower coordination number, i.e., the difference in free energy between two ground states of known structure.

Kinetic effects: Rates of substitution of Y by Z, i.e., the difference in free energy between a ground state of known structure and a transition state usually of unknown structure.

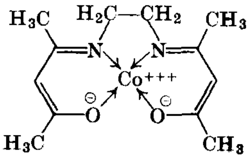
It is obvious that the number of factors involved and hence the difficulty of interpretation increases in the order ground-state < thermodynamic < kinetic effects and that kinetic effects, for example, cannot be understood in isolation from thermodynamic and ground-state effects. In this review relatively more emphasis is placed on ground-state and thermodynamic effects than in previous reviews. Certain authors prefer to restrict the term "trans effects" (and cis effects) to kinetic effects alone. The only justification for making a definition is in order to use it as a tool, in this case for sorting out and interpreting the evidence on the mutual interaction of ligands. We have adopted the above terms and definitions in order to keep a clear distinction between the three categories, while at the same time emphasizing their interdependence, in particular, the dependence of kinetic effects on the other effects.

C. ABBREVIATIONS AND NOMENCLATURE

The following abbreviations for well-known ligands have been used: py, pyridine; tu, thiourea; acac, acetylacetonato-; en, ethylenediamine; dipy, dipyridyl; *o*-phen, 1,10-phenanthroline; DMG, dimethylglyoximato-; and das, *o*-phenylenebis(dimethylarsine). In addition, Bz, 5,6-dimethylbenziminazole (present in certain corrinoids, see below); BAE, bis(acetylacetone)ethylenediamine; and salen, bis(salicylaldehyde)ethylenediamine. R is used to designate an alkyl ligand. Other abbreviations which are used only once are explained in the text.

The tetradentate ligands BAE and salen form a square coplanar ("equatorial") arrangement around the cobalt (**1**, **2**), the coordination sphere being completed by two unidentate "axial" ligands. A similar equatorial arrangement is formed by two DMG ligands which are joined by symmetrical hydrogen bonds (**3**).

The corrinoids are derivatives of vitamin B_{12} with the general structure (**4**). A large number of derivatives are known which differ in the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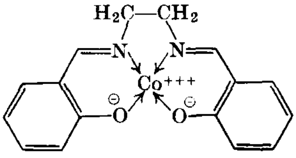
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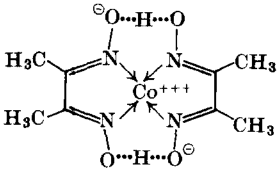
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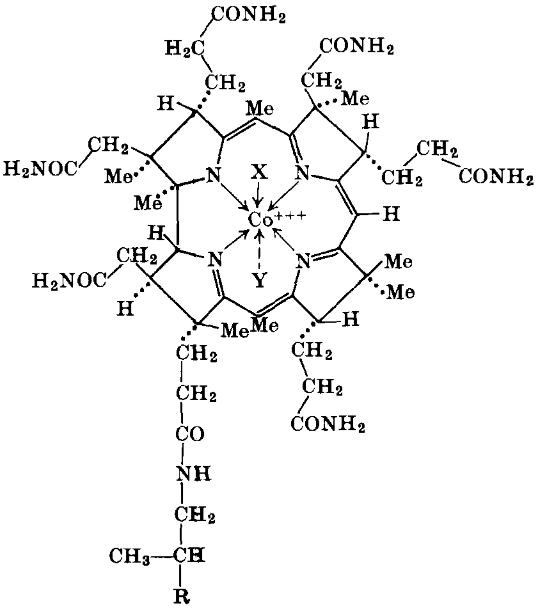
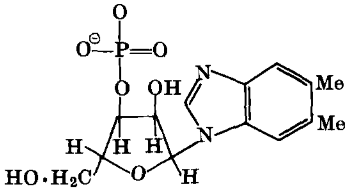
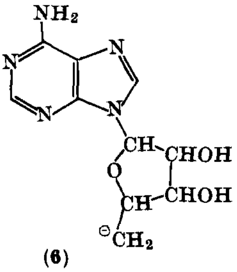

(4)

nature of the axial ligands and side chains. With the exception of certain compounds included in Table III all the corrinoids mentioned in this review have a side chain where R = OH (termed "cobinamides") or R = (**5**) ("cobalamins"). In the latter the side chain terminates in the heterocyclic base, 5,6-dimethylbenziminazole (Bz), which is usually coordinated to the cobalt, although it can be displaced by other ligands such as cyanide or by protonation. Vitamin B_{12} itself is cyanocobalamin [R = (**5**), X = CN^-]. The best known derivative that occurs *in vivo* is Co-5′-deoxyadenosylcobalamin [R = (**5**), X = (**6**)], the first naturally occurring organometallic compound.



(**5**)



(**6**)

II. Ground-State Effects

A. Bond Lengths

Two factors complicate the use of bond lengths for establishing a cis- and trans-effect order of ligands. First, the errors are often rather high [and the estimated standard deviation (e.s.d.) usually not reported] for cobalt complexes because X-ray analyses have been carried out with Cu–K_α radiation, which is strongly absorbed and anomalously dispersed by the cobalt atom. The changes attributable to internal effects may therefore be within experimental error. Second, the ions and molecules in the outer coordination sphere may influence the bond lengths within the complex, and a change of ligand X may alter the other metal–ligand bond lengths by either an internal or external effect or both.

Table I lists compounds chosen in order to test whether a change in the outer coordination sphere can affect bond lengths within the complex. There appear to be two genuine cases. First, salts of the hexammine complex with $TlCl_6^{3-}$ and $TlBr_6^{3-}$ were studied together by Watanabe *et al.* (*177*), who considered the difference in the Co–NH_3 bond lengths to be significant. Second, many chloroammine complexes have been

TABLE I

INFLUENCE OF THE OUTER COORDINATION SPHERE ON BOND LENGTHS WITHIN THE COMPLEX

Compound	Bond lengths (Å)		Ref.
$[Co(NH_3)_6]TlCl_6$	Co–N: 2.07		(*177*)
$[Co(NH_3)_6]TlBr_6$	2.02		(*177*)
$[Co(NH_3)_6]I_3$	1.96 ± 0.02		(*27*)
$K_3[Co(CN)_6]$(1 M)[a]	Co–C: 1.89 ± 0.009	C≡N: 1.15	(*62*)
$K_3[Co(CN)_6]$(2 Or)	2.07	1.16	(*138*)
$Cd_3[Co(CN)_6]_2$	2.05	1.18	(*69*)
trans-$[Co \cdot en_2 \cdot Cl_2]Cl$	Co–Cl: 2.22		(*32a*)
trans-$[Co \cdot en_2 \cdot Cl_2]NO_3$	2.26		(*140*)
$[Co(NH_3)_5Cl]Cl_2$	2.27		(*160*)
trans-$[Co \cdot l\text{-}pn_2Cl_2]Cl \cdot HCl \cdot 2H_2O$[b]	2.29		(*157*)
$[Co(NH_3)_3(NO_2)_2Cl]$	2.30		(*169*)
$[Co(NH_3)_3Cl_2 \cdot H_2O]Cl$	2.33		(*168*)
trans-$[Co \cdot en_2 \cdot Cl_2]Cl \cdot HCl \cdot 2H_2O$	2.33		(*129*)

[a] Determined by neutron diffraction; all others by X-ray diffraction. M, Monoclinic; Or, orthorhombic.

[b] pn, propylenediamine.

studied and the observed Co–Cl bond lengths cover a wide range (see Table I). It is interesting that the extreme values are found for one and the same complex $[Co \cdot en_2 \cdot Cl_2]^+$. Here again the changes in bond length are considered to be significant. In many of these and other ammine complexes the presence of hydrogen bonds, e.g., $Co–NH_3 \ldots ONO_2^-$ and $Co–Cl \ldots H_3N–Co$, is indicated by the short nonbonded contacts and interbond angles.

$K_3[Co(CN)_6]$ occurs in four forms: orthorhombic (2 Or), and one-, three-, and seven-layer monoclinic (1 M, 3 M, 7 M) (*107*). The apparent variation in bond length merely with a change in the lattice is surprising. It is difficult to decide whether these variations are significant and, therefore, whether they can be ascribed to the effects of the lattice and the counterion (K or Cd); but in view of the results mentioned in the previous paragraph, this cannot be excluded. The same applies to the apparent changes in bond lengths in cyanocobalamin observed on simply varying the degree of hydration (see Table III).

Complexes in which apparently genuine internal effects are observed or which contain ligands such as SO_3^{2-} and alkyl groups that are known to show marked thermodynamic and kinetic effects, are listed in Tables II and III (corrinoids).

TABLE II

CIS AND TRANS EFFECTS SHOWN BY BOND LENGTHS

Compound	X	Cis group	Bond length (Å)	Trans group	Bond length (Å)	Estimated standard deviation (e.s.d.)	Ref.
$[Co(NH_3)_5NO]Cl_2$ (black monomer)	NO^-	Co–NH_3	1.93	Co–NH_3	2.28	—	(*81*)
$[Co(NH_3)_5NO]Cl_2$ (black monomer)	NO^-	Co–NH_3	1.95, 1.96	Co–NH_3	2.30	—	(*63*)
$[Co(NH_3)_3(NO_2)_2Cl](NO_2^-$ in trans position)	Cl^-	Co–NH_3	1.99	Co–NH_3	1.90	—	(*169*)
$[Co(NH_3)_5Cl]Cl_2$	Cl^-	Co–NH_3	1.97	Co–NH_3	1.91	—	(*160*)
$[Co(NH_3)_4CO_3]Br$ (bidentate CO_3^{2-})	CO_3^{2-}	Co–NH_3	1.95, 1.93	Co–NH_3	2.03	—	(*26*)
trans-$[Co \cdot en_2 \cdot SO_3 \cdot NCS] \cdot 2H_2O$	SO_3^{2-}	Co–N(en)	1.964, 1.925 1.939, 1.948	Co–NCS	1.975	0.015	(*17*)
$K_3[Co(CN)_5R](R = {}^-CF_2 \cdot CF_2H)$	R^-	Co–CN	1.894	Co–CN	1.927	0.014	(*122*)
$[Co(DMG)_2(NH_3)_2]NO_3$	NH_3	Co–N(DMG)	1.97, 1.94	Co–NH_3	1.96	—	(*176*)
$[Co(DMG)_2R \cdot py](R = {}^-CH_2 \cdot COOCH_3)$	R^-	Co–N(DMG)	1.87–1.89	Co–py	2.04	0.006	(*117*)

TABLE III

BOND LENGTHS IN CORRINOID COMPLEXES

	Bond lengths to equatorial ligand atoms (corrin)				
Compound[a]	Co–N_{20}	Co–N_{21}	Co–N_{22}	Co–N_{23}	Average
1	1.90	1.96	1.78	1.87	1.88
2	1.86	1.90	1.91	1.95	1.90_5
3	1.80	1.92	1.86	1.87	1.86
4	1.92	1.91	1.97	1.98	1.94
5	1.88	1.95	1.90	1.88	1.90

	Bond lengths involving axial ligands					
Compound[a]	Co–Cl	Co–CN	C≡N	Co–N(Bz)	Co–C	Co–OH_2
1	2.41	1.96	0.99	—	—	—
2	—	2.02	0.98	2.07	—	—
3	—	1.92	1.11	1.97	—	—
4	—	—	—	2.23	2.05	—
5	—	1.84	1.14	—	—	2.06

[a] (1) Hexacarboxylic acid (*97*), (2) cyanocobalamin (dry) (*96*), (3) cyanocobalamin (wet) (*41*), (4) Co-5′-deoxyadenosylcobalamin (*118*), and (5) cobyric acid (*95*).

Bond lengths have been determined for a large number of ammine complexes, but only a few will be discussed here. The Co–NH_3 and Co–N(en) bond lengths lie within the range 1.97–2.01 Å, when the only other ligands are NH_3, en, NO_2^-, H_2O, and Br^- (*108–110*, *129*, *131*, *132*, *139*, *140*, *167*). A very significant lengthening is, however, found in the position trans to NO^-, whereas shortening is observed trans to Cl^- in two cases (Table II). An interesting distortion is found in the complex $[Co(NH_3)_4CO_3]$ which contains bidentate CO_3^{2-} (Table II). The changes are probably not due to any simple trans effect, since comparable changes are not observed in $[Co(NH_3)_5CO_3]Br\cdot H_2O$ which contains unidentate CO_3^{2-} (*73*), but to distortion of the electron cloud around the cobalt, the O–Co–O bond angle being 70.5° (*26*).

Three alkyl complexes have been studied. The corrinoid, *Co*-5′-deoxyadenosylcobalamin, can be compared directly with cyanocobalamin, which differs only in the nature of one of the axial ligands. Since different bond lengths are apparently found in the wet and dry forms of the latter, Table III also includes bond lengths for the other two corrinoids which have been studied so far. Although the errors are probably rather large, the Co–N bond lengths do appear to be significantly longer in the alkyl complex than in any of the other corrinoids; this indicates that the alkyl group has a greater bond-lengthening effect than CN^-, Bz, H_2O, or Cl^-. It also appears that the alkyl group affects both the cis and trans positions. It should be pointed out that because of the asymmetry of the corrin ring the Co–N(corrin) bonds are not coplanar and their interbond angles are not equal to 90°, so that other effects connected with a distortion of the electron cloud around the cobalt (cf. $[Co(NH_3)_4CO_3]$ above) may be involved.

The fluoroalkyl ligand in the pentacyanide (see Table II) appears to cause a slight lengthening of the Co–CN bond length in the trans position. The alkyl ligand also appears to have a trans-lengthening effect in the DMG complex (see Table II). There is no real reason for expecting the Co–N bond lengths to DMG and pyridine to be the same. The bond lengths of the DMG complex with NH_3 as axial ligands were determined from a two-dimensional X-ray analysis and are probably not accurate enough to provide a good comparison. The Co–py bond length, on the other hand, is longer than would be expected by analogy with Co–NH_3 bond lengths (see above), and provides slight evidence for the trans-lengthening effect of the alkyl ligand.

Very few cobalt(III) complexes containing ligands with the heavier donor atoms S, Se, and I have been studied. The ligands in the complexes $[Co(DMG)_2(SCN)_2]$, $[Co(DMG)_2(SeCN)_2]$ (*2*), and selenocyanatocobalamin (*94*) have been shown to coordinate through S and Se, but no bond lengths were reported. SO_3^{2-} causes no significant bond lengthening in *trans*-$[Co \cdot en_2 \cdot SO_3 \cdot NCS] \cdot 2H_2O$ (Table II).

Evidence from bond lengths can be summarized as follows:

(1) There appear to be genuine examples of changes in the cobalt–ligand (NH_3, Cl^-, and probably CN^-) bond lengths caused by external effects.

(2) Distortion of interligand bond angles can lead to changes in other metal–ligand bond lengths, as shown by $[Co(NH_3)_4CO_3]$.

(3) The bond-lengthening ability of unidentate ligands appears to increase in the order: $Cl^- < H_2O$, NH_3, $NO_2^- \sim CN^- \sim SO_3^{2-} <$ alkyls with electronegative substituents $<$ alkyls $\ll NO^-$.

(4) In the case of Cl^- and NO^- at least the effect is directed to the trans position.

(5) There is no obvious effect of replacing $(NH_3)_4$ by $(DMG)_2$ or by corrin, but the data are meager and too inaccurate for any real comparison.

B. INFRARED SPECTRA

Infrared spectra are potentially a very useful source of information on cis and trans effects. The frequency of a vibration is determined by the kinetic and potential energies of the nuclei involved (theoretically the whole complex, since all vibrations will couple to a certain extent) and the observed frequencies can be analyzed in terms of a generalized valence force field or some more approximate model to eliminate the kinetic energy and yield force constants (for stretching, bending, twisting, etc.) and interaction constants (*130*)

A full coordinate analysis has been carried out only for the fully octahedral complexes $[Co(CN)_6]^{3-}$ (*104, 126*), $[Co(NH_3)_6]^{3+}$ (*127, 161, 170*), and $[Co(NO_2)_6]^{3-}$ (*127, 128*). The following metal–ligand stretching force constants (mdynes/Å) were calculated: Co–CN, 1.83 ± 0.05 (*104*) and 2.308 (*126*); Co–NH_3, 1.47 (*127*); and Co–NO_2, 1.50 (*127*). Nakagawa and Shimanouchi (*127*) also carried out a normal coordinate analysis of the crystal as a whole and showed that low-energy intramolecular vibrations could couple with the lattice vibrations. In studies on the ions *cis*- and *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ and $[CoNO_2(NH_3)_5]^{2+}$ they found good agreement between the observed frequencies and values calculated by using the force constants found in the hexanitro and hexammine complexes (*128*), which suggests that there is no great difference between NH_3 and NO_2^- in their cis and trans effects.

For all the other complexes one is forced to use the frequencies themselves. Since the degree of coupling between modes increases as their difference in frequency decreases, a given mode can be used for studying cis and trans effects only when it is far removed in energy from other modes, and this greatly restricts the types of vibrations which can be used.

A second difficulty is the effect of the counterions and the outer coordination sphere in general. Terrasse *et al.* (*170*) studied the IR spectra of a series of salts $[Co(NH_3)_6]X_3$, and found that the nature of X affects both the intensity and the frequency of the bands. The frequencies of the ν_1 and ν_3 bands decrease in the order PF_6^-, BF_4^-, SiF_6^{2-}, ClO_4^-, F^-, Cl^-, Br^-, I^-, which appears to be the order of increasing polarizability, from $\nu_1 = 3245$ and $3285\ cm^{-1}$ and $\nu_3 = 3342\ cm^{-1}$ to $\nu_1 \sim 3150$ and $\nu_3 \sim 3200\ cm^{-1}$. The symmetry of the lattice, on the other hand, has no effect; no more bands were observed in the monoclinic Cl^- or orthorhombic Br^- salts than in the cubic I^-, ClO_4^-, or BF_4^- salts. Fujita *et al.* (*74*) found a similar variation in the salts $[Co(NH_3)_6]X_3$ where $X = Cl^-$, Br^-, I^-, NO_3^-, or ClO_4^-, and Hill and Rosenberg (*89*) found variations in several pentammine as well as the hexammine salts.

An excellent example of such effects in anionic cyanide complexes is provided by the work of Tanaka *et al.* (*166*) who used the cyanide-stretching frequency to study ion association with $[Fe^{II}(CN)_6]^{4-}$ and $[Fe^{III}(CN)_6]^{3-}$ in the solid state and in solution. Their results are given in Table IV. Calculations showed that in each case 70–90% of the ferricyanide ion was present in solution as the ion-pair; no calculations were made for ferrocyanide, but the greater negative charge would presumably lead to a higher degree of ion-pair formation. From the absence of any effect of ion-pair formation in solution on the infrared spectrum and from certain theoretical calculations they concluded that a molecule of water is held between the cation and the hexacyanide in the ion-pair. Mironov and Rutkovskii (*124*) independently reached the same conclusion from a study of the entropy changes involved in the formation of ion-pairs with ferricyanide. For other examples, e.g., with the complex $[Co(NH_3)_5CN]^{2+}$, see Table V. The nature of the counterion clearly can have a marked effect on the infrared spectrum, at least in the solid state.

TABLE IV

CYANIDE-STRETCHING FREQUENCIES FOR SALTS AND SOLUTIONS OF $[Fe^{II}(CN)_6]$ AND $[Fe^{III}(CN)_6]$[a]

Compound	Stretching frequencies (cm^{-1})	
	Solid	Solution
$[Fe^{II}(CN)_6]K_4$	2047	2020
$[Fe^{II}(CN)_6]Ca_2$	2066	2020
$[Fe^{III}(CN)_6]K_3$	2121 and weaker bands	2121
$[Fe^{III}(CN)_6]Mg_{3/2}$	2165 and weaker bands	2121
$[Fe^{III}(CN)_6]Ca_{3/2}$	2141 and weaker bands	2121
$[Fe^{III}(CN)_6]Ba_{3/2}$	2127 and weaker bands	2121

[a] Data from Tanaka *et al.* (*166*).

A third difficulty is the wide variation found even for the same compound (1) using mulls and pellets, and (2) in different laboratories. A good example is provided by $K_3Co(CN)_6$, for which the following cyanide-stretching frequencies (in cm^{-1}) have been reported: KBr, 2129 and water, 2128 (*38*); fine powder at 77°K, 2129 and 2126 (*67*); Nujol, 2143 (*79*); Nujol, 2130 and KBr, 2131s and 2093w (*65*); Nujol, 2131 and 2128 and water, 2127 (*104*); KBr and/or Nujol, 2118 (*137*); and KBr, 2134 (*85*). This variation makes difficult any comparison of the infrared spectra of different compounds when reported by different workers, and the greatest weight must be given to data concerning a series of compounds all studied by the same workers.

TABLE V

CYANIDE-STRETCHING FREQUENCIES

Ligand (X)	Stretching frequencies $(cm^{-1})^a$	Method	Ref.
A. Pentacyanides $[Co(CN)_5X]$			
CN^-	2134	KBr	(*85*)
H_2O	2128	KBr	
Br^-	2125	KBr	
Cl^-	2124	KBr	
I^-	2117	KBr	
$^-CH_2{\cdot}SO_3^-$	2113	KBr	
$^-CH_2{\cdot}CO_2^-$	2106	KBr	
$^-CH_2{\cdot}COOCH_3$	2105	KBr	
$^-CH_2{\cdot}CO{\cdot}NH_2$	2103	KBr	
H^-	2098	Water	
$^-CH_2{\cdot}CH_2CO_2^-$	2097	KBr	
$^-CH_2{\cdot}CH_2{\cdot}COOCH_3$	2096	KBr	
$^-CH_3$	2094	KBr	
$^-CH_2{\cdot}CH_3$	2094	KBr	
$^-CH_2{\cdot}C_6H_5$	2093	KBr	
$K_3[Co(CN)_6]$	2143	Mull	(*79*)
$K_3[Co(CN)_5OH]{\cdot}H_2O$	2135vs, 2114w sh	Mull	
$K_3[Co(CN)_6]$	2130	Mull	(*65*)
$Na_2[Co(CN)_5H_2O]$	2130s 2202m	Mull	
$K_3[Co(CN)_6]$	2140	KCl	(*23*)
$NaCs_2[Co(CN)_5H]$	2113	KCl	
B. Cyanocorrinoids $[Co{\cdot}corrin{\cdot}X{\cdot}CN]$			
Bz	2132	KCl	(*72*)
HO^-	2130	KCl	
CN^-	2119	KCl	
$^-C{\equiv}CH$	2110	KCl	
$^-CH_2{\cdot}SO_3^-$	2109	KCl	
$^-CH_2{\cdot}CF_3$	2104	KCl	
$^-CH{=}CH_2$	2093	KCl	
$^-$*Co*-5′-deoxyadenosyl	2091	KCl	
$^-CH_2{\cdot}CO_2^-$	2090	KCl	
$^-CH_2{\cdot}CH_2OH$	2089	KCl	
$^-CH_3$	2088	KCl	
$^-CH_2{\cdot}CH_2{\cdot}CH_3$	2083	KCl	
$^-CH_2{\cdot}CH_3$	2082	KCl	

TABLE V—*continued*

Ligand (X)	Stretching frequencies (cm^{-1})[a]	Method	Ref.
C. Ammine-monocyanide complexes (all trans)			
$[Co \cdot en_2 \cdot H_2O \cdot CN](NO_3)_2$	2146	Not stated	(*48*)
$[Co \cdot en_2 \cdot Cl \cdot CN]NO_3$	2137	Not stated	
$[Co \cdot en_2 \cdot Cl \cdot CN]Cl \cdot H_2O$	2132	Not stated	
$[Co \cdot en_2 \cdot OH \cdot CN]Cl \cdot H_2O$	2128	Not stated	
$[Co \cdot en_2 \cdot SO_3 \cdot CN]$	2119	Not stated	
$[Co(NH_3)_4 \cdot H_2O \cdot CN]Cl_2$	2140	Mull and KBr	(*162*)
$[Co(NH_3)_5CN](ClO_4)_2 \cdot \frac{1}{2}H_2O$	2145	Mull and KBr	
$[Co(NH_3)_5CN]SO_4$	2140	Mull and KBr	
$[Co(NH_3)_5CN](NO_3)_2$	2135	Mull and KBr	
$[Co(NH_3)_5CN]Cl_2$	2135	Mull and KBr	
$[Co(NH_3)_5CN]Br_2$	2130	Mull and KBr	
$[Co(NH_3)_4SO_3CN] \cdot 2H_2O$	2130	Mull and KBr	
$[Co(NH_3)_4SO_3CN]$anhydr.	2125	Mull and KBr	
$[Co(NH_3)_4OH \cdot CN]Cl \cdot \frac{1}{2}H_2O$	2138	Mull	(*24*)
$[Co(NH_3)_4 \cdot H_2O \cdot CN](NO_3)_2$	2136	Mull	
$[Co(NH_3)_4 \cdot H_2O \cdot CN]Cl_2$	2132	Mull	
$[Co(NH_3)_5CN]Cl_2$	2124	Mull	
$[Co(NH_3)_4SO_3CN] \cdot 2H_2O$	2124	Mull	

[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

The cyanide-stretching frequency has so far provided the only useful IR information on cis and trans effects in cobalt(III) complexes. Two main sets of data are available (Table V). Halpern and Maher (*85*) studied the pentacyanides $[Co(CN)_5X]$ and showed that when X is an alkyl ligand the frequency is significantly lower than for a typical cobalt(III) complex, and they ascribed this to the enhanced donor power of the organic ligand. They observed only a single band instead of the three which might have been expected for C_{4v} symmetry, indicating that the coupling between the different cyanides is small. Table V, part A also lists the frequencies for a few other pentacyanides where direct comparison can be made with the hexacyanide (as "calibration") and only a single band is observed. Cyanide-stretching frequencies have also been reported for pentacyanides with $X = S_2O_3^{2-}$ (*16*, *65*), NCS^- which is bound through S (*43*), and SO_3^{2-} (*55*), but unfortunately the presence of more than one band, due presumably to lattice effects, prevents comparison with the other pentacyanides. Firth *et al.* (*72*) studied cyanocorrinoids with ligands similar to those used by Halpern and Maher and observed a similar variation in the cyanide-stretching frequency (Table V, part B). Finally, Table V, part C lists certain other complexes selected simply to provide a basis for determining the effect of SO_3^{2-}, which is known to have a marked thermodynamic and kinetic trans effect.

Both the pentacyanides and corrinoids show a very similar order of ligands X; CN^- and H_2O occur at the high frequency end, simple alkyls such as CH_3^- at the other, and ligands such as $^-CH_2SO_3^-$ where the alkyl group carries a strongly electronegative substituent in the middle. The large effects and similar order in both series shows that this is a genuine "internal" effect and that it is not unique to a limited class of cobalt(III) complexes. The observation of a large frequency shift without any splitting of the bands in the pentacyanides suggests that the cis and trans positions are equally affected. The dependence of the frequency on external effects has already been pointed out and prevents the establishment of a detailed order of ligands; however, in both the tetrammine and bisethylenediamine complexes SO_3^{2-} does appear to cause a slight but significant lowering of the frequency compared to Cl^-, etc. Table V suggests the following order of ligands in the different groups of complexes: pentacyanides, $CN^- \sim H_2O \sim HO^- \sim Cl^- \sim Br^- > I^- > H^- >$ simple alkyls; corrinoids, $HO^- \sim Bz \sim CN^- > HC{\equiv}C^- > CH_2{=}CH^- >$ simple alkyls; and ammines, $CN^- \sim H_2O \sim Cl^- \sim NH_3 > SO_3^{2-}$. This gives the following approximate order for all the ligands:

$$\left.\begin{array}{l} H_2O,\ HO^-,\ NH_3,\ Bz \\ CN^-,\ Cl^-,\ Br^- \end{array}\right\rangle SO_3^{2-},\ I^- > H^- > \text{simple alkyls, (e.g., } CH_3^-)$$

It is rather unusual for the force constants of a ligand to increase on coordination, as occurs with cyanide in cobalt(III) complexes; this has recently been discussed by Purcell (*152*).

C. NUCLEAR RESONANCE SPECTRA

Proton magnetic resonance (PMR) has been used mainly as a tool for studying rates of racemization, ligand substitution, and exchange between ligand and solvent protons, but some work concerning "ground-state" effects has been reported for ammine, corrinoid, and bisdimethylglyoxime complexes.

Clifton and Pratt (*58*) studied ammine complexes in D_2O and were the first to note that the protons of coordinated NH_3 showed different spectra depending on their position relative to other ligands in the complex. In the pentammines cis protons were shifted to lower field relative to $X = NH_3$, which they ascribed to intramolecular hydrogen bonding and to the effect of the magnetic anisotropy of the ligand X; the trans protons were shifted to higher field, which they attributed to polarization of the metal by the ligand X leading to reduced polarity of the *trans*-NH_3. The shifts of the cis protons to lower field increased in the order: $NH_3(=O) < Br^- \sim CO_3^{2-} < F^- \sim RCO_2^- < Cl^-$, while the shift of the trans protons increased to higher field in the order $NH_3 < Br^- \sim Cl^- < RCO_2^- < CO_3^{2-} < F^-$. Jolly *et al.* (*103*) studied ammines in concentrated sulfuric acid and obtained similar results. In addition they found that the chemical shift of the protons of a given NH_3 could be given by the sum of five terms characteristic of the nature and position of the other ligands (see tabulation). Lantzke and Watts (*116*) have studied bisethylenediamine complexes and found that the shielding depends on the ligands X in the following order:

CONTRIBUTIONS TO CHEMICAL SHIFT (IN PPM)

Position	HSO_4^-	H_2O	Cl^-	Br^-	NO_2^-	NH_3
Cis	−0.65	−0.57	−0.17	−0.06	0	0
Trans	0.84	0.67	0.49	0.42	0	0

trans-$[Co \cdot en_2X_2]$	$NCS^- < Br^- < Cl^- < NO_2^- < N_3^-$
Proximal protons in *cis*-$[Co \cdot en_2X_2]$	$DMF < DMSO < Br^- < Cl^- < NO_2^- < N_3^-$
Distal protons in *cis*-$[Co \cdot en_2X_2]$	$NO_2^- < Br^- \sim Cl^- < N_3^-$
Proximal protons in *cis*-$[Co \cdot en_2XCl]$	$H_2O < DMA < DMSO < DMF < Br^- < Cl^- < NCS^- < N_3^- < NO_2^-$

(DMSO, dimethylsulfoxide; DMA, dimethylacetamide; DMF, dimethylformamide). It seems difficult to obtain any single and simple order of cis and trans effects out of the above results; there are probably several effects in operation.

PMR studies of the corrinoids (*90*, *93*) have shown that the τ value of the proton on the methene bridge C_{10} depends on the nature of the axial ligands, and that there is some correlation between the τ value and the energy of the first electronic transition of the corrin ring. When Y = Bz the resonance moves to higher field in the order $X = H_2O < HO^- < CH_2{=}CH^- < CH_3^-$. Finally Hill *et al.* (*91*) have shown that there is a correlation between the τ value of the methyl protons in $[Co(DMG)_2 \cdot P\phi_3 \cdot X]$ and the Hammett σ_{para} function of X, the τ values increasing in the order $X = \underline{N}O_2^- < CN^- < Cl^- \sim Br^- \sim I^- \sim \underline{O}NO^- <$ alkyls.

The screening constant, which determines the chemical shift (i.e., τ values) can be considered as made up of contributions from four sources (*148*).

(1) Diamagnetic currents on the atom in question. This depends on the absolute electron density on, for example, the proton and gives a measure of the ionic character of the bond; this is therefore of direct relevance to a discussion of cis and trans effects.

(2) Paramagnetic currents on the atom in question. This allows for the fact that the electron cloud does not have spherical symmetry. This term is insignificant for H because the $2p$ and other states lie at such high energies, but is important in cobalt magnetic resonance.

(3) Diamagnetic and paramagnetic currents on neighboring atoms. These effects may be significant (particularly the paramagnetic currents on cobalt) and may upset any simple correlation between the observed chemical shift and the effects mentioned in paragraph (1) above.

(4) Interatomic currents, e.g., in benzene and, among ligands, in aromatic anions, pyridine, and other heterocyclic bases, $P\phi_3$, etc.

The effect of changing one ligand on the PMR of another ligand (H^-, NH_3, pyridine, dimethylglyoxime, etc.) may therefore be the resultant of several factors, and a large number of complexes must be studied before a pattern can be established and the relative importance of the different contributions estimated.

Nuclei with spin $I \geqslant 1$ possess an electric quadrupole which can take up different orientations relative to an electric field gradient. These orientations differ in energy, and transitions between them give rise to the nuclear quadrupole resonance (NQR) spectrum. The NQR of ligand atoms such as Cl, Br, and I could, therefore, provide information on the polarity of the metal–ligand bond and the population of the p orbitals (*111*). The only cobalt(III) complexes that have been studied are *trans*-$[Co \cdot en_2X_2]X \cdot HX \cdot nH_2O$, where $X = Cl$ or Br. Hartmann *et al.* (*87*) calculated 75–80% ionic character for the Co–Cl bond and also reported data for the bromide complex, from which Kubo and Nakamura (*111*) calculated a value of 60% ionic character.

D. Electronic Spectra of Ligands

Electronic spectra have been used to provide information on the cis effects of the axial ligands in the corrinoids (*72, 92, 150*). Even though the transition represents the difference in energy between the ground state and an excited state of the chromophore, it has been argued (*72*) that this may be classified as a "ground-state" effect because the spectra are due to π–π^* transitions localized within the corrin ring, and changes in the spectrum reflect changes in the conformation and/or electron density of the corrin ring as a result of the cis effect of the axial ligands. The spectra of corrinoids show a remarkable diversity, but when one axial ligand is kept constant, as in a series of cobalamins (Y = Bz), the different spectra can be fitted into a series showing gradually changing features (*92*, *150*). Table VI shows the dependence of the wavelength of the main absorption band in the near UV on the nature of the second axial ligand. The data lead (*150*) to the following specific order among the closely related carbanions $N{\equiv}C^- < HC{\equiv}C^- < CH_2{=}CH^- < CH_3CH_2^-$ and the more general order of ligand atoms F, Cl, Br, O, N, C in CN^- < C in CH_3^-, S (except NCS^-), Se, I, i.e., the polarizable ligand atoms are grouped at one end and the electronegative ligand atoms at the other.

TABLE VI

DEPENDENCE OF WAVELENGTH OF THE γ-BAND IN COBALAMINS (CORRIN, Y = Bz) ON THE NATURE OF THE AXIAL LIGAND X[a]

Ligand atom	Axial ligand	Wavelength
C	CH_3NC	360
	$N{\equiv}C^-$	360.5
	$HC{\equiv}C^-$	367
	$CH_2{=}CH^-$	372
	CH_3^-	374
	$CH_3{\cdot}CH_2^-$	~375
N	NO_2^-	356
	NH_3	356
	NCO^-	357
	N_3^-	358
	Imidazole	358
	Pyridine	360
O	H_2O	350
	$CH_3{\cdot}CO_2^-$	352
	HO^-	357
Halides	Cl^-	352
	Br^-	353
	I^-	371
S	NCS^-	357
	SO_3^{2-}	364
	Thiourea	366
	$S_2O_3^{2-}$	367
	Cysteine$^-$	370
Se	$NCSe^-$	371

[a] Ligands grouped according to ligand atom. Wavelength in mμ. Data from Firth *et al.* (*72*).

III. Thermodynamic Effects

Cobalt complexes in which the metal can be considered to have the formal oxidation state (III) may be six-coordinate (octahedral and perhaps trigonal prismatic), five-coordinate (square pyramidal or trigonal bipyramidal), or four-coordinate (square planar or tetrahedral).

The vast majority are, of course, octahedral. Equilibria involving only octahedral complexes are discussed in Section III, A and equilibria involving other configurations in Section III, B.

Formation constants are related to the change in free energy which, in turn, is made up of changes in enthalpy and entropy:

$$-RT \ln K = \Delta G = \Delta H - T\Delta S$$

Only the enthalpy term directly reflects the change in bond energies caused by internal cis and trans effects, but the enthalpy and entropy terms have been separated in very few cases and one must therefore fall back on using formation constants. As will be seen from the discussion in Section III, A, however, the major changes in formation constant do appear to reflect changes caused by cis and trans effects.

A. EQUILIBRIA BETWEEN OCTAHEDRAL COMPLEXES

In this section we wish to examine the effect on the equilibria between various Y/Z pairs when changing one trans or cis ligand (X) or four cis ligands (L_4), and try to answer the questions: (1) Is there a common order of X (and L_4) for all the different Y/Z pairs? (2) Is there a common order of formation constants irrespective of the nature of X and L_4? (3) Does X exert a different effect on the cis and trans positions?

Formation constants can be determined with ease only when the rates of ligand substitution are reasonably fast; since the majority of cobalt(III) complexes are rather inert the range of formation constants is somewhat limited. In the corrinoids, however, substitution of the axial ligands occurs very rapidly (with the exception of the organoligands) and a large number of formation constants have been determined. These will be presented first (Table VII) and used as a basis for the discussion of thermodynamic data relating to other groups of complexes (Table VIII). Although the experimental conditions (temperature, ionic strength, etc.) used in the determination of the formation constants vary considerably, they have not been listed in Tables VII and VIII mainly in order to avoid complicating the tables and obscuring the pattern of constants observed, and because the differences in formation constants which are significant for the study of cis and trans effects are, in most cases, greater than the differences which would be caused by a change in the experimental conditions.

1. Corrinoids

Table VII presents a selection of formation constants for the corrinoids. Organoligands predominate as X because they are relatively inert

TABLE VII

FORMATION CONSTANTS FOR LIGAND SUBSTITUTION IN CORRINOIDS[a]

	$Y = H_2O$, $Z =$								$Y = Bz$ $Z = CN^-$
X	Bz	CH_3NC	CN^-	HO^-	SO_3^{2-}	N_3^-	Cl^-	I^-	
H_2O	7.1	—	$\geqslant 14$	8.0	~ 11	—	0.5	—	—
Bz	—	4.8	$\geqslant 12$	6.2	7.4	4.9	0.1	1.2	—
CN^-	4.6	2.7	8	3.0	4.6	2.7	+	+	3.8
$HC{\equiv}C^-$	4.0	—	—	—	—	—	—	—	2.7
SO_3^{2-}	2.7	—	4.3	−0.7	< 0	—	—	—	—
$CH_2{=}CH^-$	2.3	0.6	2.7	<0	< 0	0.6	+	~ 0	0.7
CH_3^-	2.2	<0	2.1	<0	< 0	<0	+	+	0.1
$CH_3CH_2^-$	0.8	<0	0.6	<0	< 0	<0	+	+	~ 0

[a] +, Just detectable; <0 not detectable. Constants expressed as $\log_{10} K$ in units of liter/per mole except for Z = Bz (first column) when the constant is a ratio; no corrections made for the presence of any five-coordinate complexes. Data taken from tabulated results in Firth *et al.* (*72*).

toward substitution. The formation constants refer to the equilibrium (only axial ligands given)

$$K = \frac{[\text{X–Co–Z}][\text{Y}]}{[\text{X–Co–Y}][\text{Z}]}$$

When Y is H_2O the concentration of free H_2O is ignored and the constants are expressed in units of liters per mole. In the cobalamins the base (Bz) which is normally coordinated to the cobalt is also attached to a side chain of the corrin. The equilibrium constant for the displacement of Bz by H_2O can therefore be written

$$K = \frac{[\text{X–Co–OH}_2]}{[\text{X–Co–Bz}]}$$

and is expressed as a ratio. As will be mentioned in Section III, B five-coordinate complexes are formed in significant concentrations in aqueous solution at room temperature when X is SO_3^{2-} or an organoligand such as vinyl or ethyl, but not cyanide (*70, 71*); formation constants in Table VII have not been corrected for the presence of five-coordinate complexes. Comparison of these formation constants shows (*72, 88*):

(1) Very large changes in formation constants (e.g., $\geqslant 10^{13}$ for $Y/Z = H_2O/CN^-$) can be caused simply by varying one ligand.

(2) For all Y/Z pairs there appears to be only a single order of ligands X. Among the carbon ligands, where both the ligand atom and the charge are held constant, the observed order (NC^-, $HC{\equiv}C^-$, $CH_2{=}CH^-$, $CH_3CH_2^-$) is a regular one, depending essentially on the effective electronegativity of the carbon atom. SO_3^{2-} occurs in the same position relative to the carbon ligands in three different equilibria and its position in the order of ligands X can be regarded as quantitatively established. Qualitative results for the equilibrium $Y/Z = H_2O/Bz$ extend the order to: Cl^-, H_2O, NH_3, $CH_3NC < CN^- < Br^-$, I^-, HS^-, RS^- (thiols), $S_2O_3^{2-}$, NCS^-, thiourea, SO_3^{2-}, organoligands, though it should be noted that the number of moles of ligand X involved in the equilibrium has not been established in most of these cases (*72*, *88*, *150*).

(3) All formation constants for the substitution of H_2O show the same direction of change as X varies down the list. When $X = CH_3^-$, etc., the formation constants are more characteristic of the ion-pairs formed by alkali and alkaline earth metals than typical transition metals. The rate of change of formation constant with X, which one can consider as the "slope," and the position at which the formation constant falls to zero (the "intercept") varies with the nature of Z (and Y when $Y \neq H_2O$). The "slope" seems to decrease in the very approximate order: $CN^- \sim HO^- \sim SO_3^{2-} > N_3^- \sim CH_3NC > Bz > Cl^- \sim I^-$. There can, therefore, be no single order of pairs Y/Z whose formation constants would always fall in the same order regardless of the nature of X. HO^- is, for example, more strongly bound than N_3^- when $X = Bz$, but the converse is true when $X = CH_2{=}CH^-$.

(4) There is no marked change in the formation constants of the halides as X is varied, i.e., there is no change from strongly class(*a*) to class(*b*) character (*11*) or vice versa.

(5) The very close similarity between CH_3NC and N_3^- and the parallel between CN^- and HO^- is strong evidence that metal-to-ligand π bonding makes no significant contribution to the bond energies of these complexes. This is supported by the failure to detect any complexes with π-bonding ligands such as CO, O_2, Me_2S, and $P\phi_3$, whatever the nature of X (*72*).

2. *Other Complexes*

Formation constants for other cobalt(III) complexes are very sparse. Data relevant to cis and trans effects are listed in Table VIII. Formation constants for $Y/Z = H_2O/HO^-$ are the most common because of the ease of determination. Fortunately, they are very sensitive to the nature of the other ligands in the complex and can be used to study the effect of the trans ligand X (Table VIII, part A) and the cis ligands L_4

TABLE VIII

Formation Constants for Ligand Substitution in other Cobalt(III) Complexes[a]

Cis ligands	X	Y	Z	$\log_{10} K$	Ref.
A. All complexes of *trans* configuration					
$(NH_3)_4$	NH_3	H_2O	HO^-	~ 7.4	(*163*)
	SO_3^{2-}	H_2O	HO^-	4.2	(*82*)
en_2	H_2O	H_2O	HO^-	9.6	(*36*)
	NO_2^-	H_2O	HO^-	7.6	(*32*)
	CN^-	H_2O	HO^-	6.6	(*49*)
	HO^-	H_2O	HO^-	6.1	(*36*)
$(CN)_4$	CN^-	H_2O	HO^-	4.3	(*80*)
	SO_3^{2-}	H_2O	HO^-	2.9	(*55*)
B. All complexes of *trans* configuration					
$(H_2O)_4$	H_2O	H_2O	HO^-	13.3	(*59*)
en_2	H_2O	H_2O	HO^-	9.6	(*36*)
$(DMG)_2$	H_2O	H_2O	HO^-	7–8.2	(*3*)
Corrin	H_2O	H_2O	HO^-	8.0	(*88*)
en_2	CN^-	H_2O	HO^-	6.5	(*49*)
$(CN)_4$	CN^-	H_2O	HO^-	4.3	(*80*)
Corrin	CN^-	H_2O	HO^-	3.0	(*88, 136*)
$(CN)_4$	CN^-	H_2O	N_3^-	3.2	(*80*)
Corrin	CN^-	H_2O	N_3^-	2.7	(*72*)
C. All complexes *cis*- or *trans*-$[Co \cdot en_2 \cdot XY]$					
	H_2O	H_2O	HO^-	9.6, 7.9[b]	(*36*)
	NH_3	H_2O	HO^-	8.2, 7.9[b]	(*173*)
	NCS^-	H_2O	HO^-	7.7, 7.2[b]	(*173*)
	NO_2^-	H_2O	HO^-	7.6, 7.7[b]	(*32*)
	Cl^-	H_2O	HO^-	6.8	(*173*)
	HO^-	H_2O	HO^-	6.1, 5.8[b]	(*36*)
	CN^-	H_2O	HO^-	6.6	(*49*)
D. Complexes $[Co(NH_3)_{6-n} \cdot (H_2O)_n]$ of unknown configuration					
$n = 1$		H_2O	HO^-	8.3	(*42*)
$n = 2$		H_2O	HO^-	8.8	(*42*)
$n = 3$		H_2O	HO^-	9.3	(*42*)
$n = 4$		H_2O	HO^-	10.6	(*42*)
$n = 6$		H_2O	HO^-	13.3	(*59*)
E. All complexes of *trans* configuration					
$(CN)_4$	CN^-	H_2O	Cl^-	+	(*80*)
	CN^-	H_2O	Br^-	0.0	(*80*)
	CN^-	H_2O	I^-	1.6	(*80*)

Table VIII (*continued*)

Cis ligands	X	Y	Z	$\log_{10} K$	Ref.
Corrin	Bz	H_2O	F^-	+	(*150*)
	Bz	H_2O	Cl^-	0.1	(*150*)
	Bz	H_2O	Br^-	0.3	(*150*)
	Bz	H_2O	I^-	1.5	(*150*)
$(DMG)_2$[c]	NO_2^-	H_2O	Cl^-	– 0.2	(*83*)
	NO_2^-	H_2O	Br^-	0.1	(*83*)
	I^-	H_2O	Cl^-	0.6	(*83*)
	I^-	H_2O	Br^-	0.6	(*83*)
$(NH_3)_4$	NH_3	H_2O	Cl^-	0.1	(*179*)
	NH_3	H_2O	Br^-	– 0.3	(*179*)
	NH_3	H_2O	I^-	– 0.7	(*179*)
$(H_2O)_4$	H_2O	H_2O	Cl^-	1.4	(*59*)
F. All complexes of *trans* configuration					
$(NH_3)_4$	NH_3	H_2O	NH_3	4.4	(*35*)
	SO_3^{2-}	H_2O	NH_3	3.0	(*82*)
	NH_3	H_2O	NCS^-	2.7	(*31*)
	SO_3^{2-}	H_2O	NCS^-	2.3	(*82, 86*)

[a] All constants expressed as $\log_{10} K$ in units of liters per mole. +, Just detectable.

[b] First value is the trans value, second value is the cis value.

[c] Calculated from kinetic data at 25°C.

(Table VIII, part B), to compare directly the cis and trans effects of one ligand X (Table VIII, part C), and to see the effect of successive replacement of H_2O by NH_3 (Table VIII, part D). Formation constants involving the halides are given in Table VIII, part E, and some constants involving other ligands in Table VIII, part F.

The following conclusions can be drawn from the data of Table VIII.

(1) There is wide variation in the sensitivity of the formation constants for a given Y/Z pair to the nature of the other ligands. Formation constants for the halides are remarkably insensitive to the nature of the other ligands and to the overall charge of the complex. Although it is true that the cobalt(III) ion does show class(*a*) character in the pentammines, i.e., the chloride is more stable than the iodide (*11*), and class(*b*) character in the pentacyanides and cobalamins, it is much more pertinent to emphasize its apparent lack of "class consciousness." Formation constants for Y/Z = H_2O/HO^-, on the other hand, are very sensitive to the nature of the other ligands. This difference in sensitivity between HO^- and the halides is the same as found for the corrinoids. The few results available suggest that the sensitivity of NH_3 and NCS^-

is intermediate; compare Bz and N_3^-, which also coordinate through nitrogen, among the corrinoids.

(2) No real conclusions can be drawn about the relative effects of ligand X on the cis and trans positions (Table VIII, part C).

(3) Putting together all the data we obtain the following tentative order of trans effect for ligand X, as shown by its effect on the formation constant of the hydroxo complex: $H_2O \sim NH_3 > NO_2^- \sim CN^- \sim HO^- \gg SO_3^{2-}$. In fact, the only significant difference is that between SO_3^{2-} and all the other ligands. Again this is in agreement with the effect of SO_3^{2-} observed in the corrinoids.

(4) The general order of cis effect seems to be: $(H_2O)_4 \gg (NH_3)_4 \sim en_2 \sim (DMG)_2 \sim$ corrin $\sim (CN)_4$. Comparison between $(NH_3)_4$ and $(H_2O)_4$ is important since no complications arise due to any difference in charge, and in addition the regular change observed as H_2O is replaced by NH_3 (Section II, D) indicates that differences in hydrogen bonding probably play no part.

Where comparisons are possible, therefore, there appears to be a general similarity between the corrinoids and other cobalt(III) complexes, and the more detailed information available for the former can probably be taken as representative of cobalt(III) complexes in general.

Finally it should be mentioned that Yatsimirskii (*180*) has calorimetrically determined the enthalpies of formation of various ammine complexes in solution, and from these he has calculated the enthalpies of ligand substitution. His results relating to complexes in which the *cis*-$Co(NH_3)_4$ group remains unchanged are given in Table IX. There is no obvious pattern, either in the order of ligand X or in the sensitivity of ΔH for a given Y/Z pair to the nature of X; but the ligands studied do not include those where large effects might be expected.

TABLE IX

ENTHALPIES OF THE LIGAND SUBSTITUTION REACTIONS
trans-$[Co(NH_3)_4XY] + Z \rightarrow$ *trans*-$[Co(NH_3)_4XZ] + Y$[a]

	Enthalpy of Y/Z					
X	NO_2^-/NH_3	NO_2^-/H_2O	NO_2^-/Cl^-	NH_3/Cl^-	NH_3/H_2O	H_2O/Cl^-
NO_2^-	0.0	−7.5	− 3.8	− 3.8	−7.5	+3.7
Cl^-	−7.6	—	−17.3	− 9.7	—	—
H_2O	−0.6	—	—	—	—	—
NH_3	−1.2	−8.1	−11.4	−10.2	−6.9	−3.3

[a] Data from Yatsimirskii (*180*), given in kcal/mole.

B. EQUILIBRIA BETWEEN FOUR-, FIVE-, AND SIX-COORDINATE COMPLEXES

Although the vast majority of cobalt(III) complexes are six-coordinate, several groups of five and even four-coordinate complexes are known in which the cobalt may be considered as having the formal oxidation state(III). These complexes represent the extreme case where the thermodynamic effects are so great that no ligand, even H_2O, can form a stable bond to the cobalt, i.e., there is a decrease in coordination number.

These complexes usually contain a ligand such as NO or an alkyl group and the change from octahedral coordination, which is characteristic of cobalt(III) complexes, to five- and four-coordination, which is typical of cobalt(II) and (I) complexes, raises the problem of how to designate the oxidation state. This was first discussed in the case of the dithiolate complexes (*114*) and more recently for the alkyl complexes (*70*). The complexes will be treated not in chronological order, but in order of increasing difficulty in designating the oxidation state of the cobalt ion.

1. Trigonal Bipyramidal Complexes

Jensen *et al.* (*101*) found that complexes of the general form $[Co^{II}X_2(PR_3)_2]$, where X = Br or Cl react with NOCl, N_2O_3, and N_2O_4 to give complexes such as $[CoCl_3(PEt_3)_2]$. This particular compound was shown to be monomeric in $CHCl_3$, to have a magnetic susceptibility corresponding to $\mu_{eff} = 3.0$ B.M., and to have zero dipole moment in pentane solution. They concluded that this was a five-coordinate complex with a trigonal bipyramidal configuration, containing two unpaired electrons. This complex therefore presents an example of unusual stereochemistry without any problems of valency. At low temperatures it picks up NO presumably to give the octahedral $[CoCl_3(PEt_3)_2NO]$.

2. Alkyl Complexes

Costa and co-workers found (*61*) that H_2O can be removed from the complexes [Co·BAE·R·H_2O] where R is methyl, ethyl, or phenyl, to give complexes which are monomeric in benzene and which they concluded were five-coordinate. They also found (*60*) that the base Y (H_2O, NH_3, or py) could readily be displaced, e.g., by heating, from the complexes [Co·salen·R·Y], where R is an alkyl ligand such as ethyl, to give the complexes [Co·salen·R], which were also assumed to be five-coordinate. Schrauzer and Windgassen (*158*) observed that the complexes $[Co(DMG)_2R\cdot H_2O]$, where R = Me and Et but not Pr, lose their water in boiling benzene, and suggested that the products might be associated, e.g., by interaction between the cobalt and an oxime oxygen atom of a neighboring molecule; but in the light of the results of Costa it seems likely that their products were also five-coordinate. Similar equilibria have also been reported for the corrinoids [Co•corrin•X•H_2O], where X is an alkyl ligand or SO_3^{2-} (*70, 71*), and interpreted as the reversible removal of H_2O to give the five-coordinate complex. But the final proof of five-coordination in any of these alkylcobalt(III) complexes must await an X-ray structure analysis. In the case of the corrinoids the position of the equilibrium depends on the nature of X, the amount of the five-coordinate complex present in aqueous solution at room temperature increasing in the order: CN^- (only six-coordinate) $\ll CH_2{=}CH^-$ ($\sim 70\%$) $< CH_3^-$ ($\sim 90\%$) $< SO_3^{2-}$ ($\sim 95\%$) $< CH_3CH_2^- \sim (CH_3)_2CH^-$ (both 100%) (*70, 71*).

These complexes provide a good illustration of the way in which the concept of formal oxidation states breaks down (*70*). By varying only one ligand in the series $CN^- \ldots CH_3CH_2^-$ we can pass from a typical cobalt(III) complex to one which is more characteristic of a low-spin cobalt(II) complex. Cobalt(III) complexes are characterized by an octahedral configuration and high formation constants for the substitution of H_2O by CN^-, NH_3, etc. Low-spin cobalt(II) complexes, on the other hand, show a balance between five- and six-coordination, as exemplified by the cyanide and isocyanide complexes (*149*, *151*), while the formation constant for the substitution of H_2O by CN^- in $[Co^{II}(CN)_5H_2O]$ is $\ll 10^0$ (*44*, *151*). It has also been pointed out (*70*) that the similarity in pK_a for the protonation and displacement of the benziminazole from coordination to the cobalt in the cobalt(II) corrinoid (p$K_a \sim 2.5$) (*92*) and in the methylcobalt(III) corrinoid (p$K_a = 2.5$) (*88*) shows that the $[CH_3^- \rightarrow Co(III)]$ unit is roughly equivalent to [Co(II)] as far as the other ligands are concerned. It is obviously debatable and, in practice, a matter of personal convenience or prejudice, whether these complexes should be considered as Co(III) $+ CH_3^-$, Co(II) $+ CH_3\cdot$ (with antiferromagnetic interaction between the spins of the metal ion and the organic radical), or even Co(I) $+ CH_3^+$. Similar problems of oxidation state arise in the case of hydrides such as $[Co(CN)_5H]^{3-}$ (*23*) and $[CoH_3L_3]^0$ where L = PPh_3 or $PEtPh_2$ (*156*).

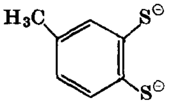
3. *Nitrosyl Complexes*

Many mononitrosyl complexes can be prepared by the reaction of NO with cobalt(II) complexes and the resulting diamagnetic complexes might be considered as Co(III) $+ NO^-$, Co(II) + NO (spins paired), or Co(I) $+ NO^+$. X-Ray analysis has shown that the cobalt ion is six-coordinate in $[Co(NH_3)_5NO]^{2+}$, although the very long Co–NH_3 bond in the trans position suggests that this bond is anomalously weak, and that the Co–NO group is linear, though in fact the N and O atoms cannot be differentiated and it is merely assumed that the ligand atom is N (*63*, *81*). Other complexes such as $K_3[Co(CN)_5NO]\cdot 2H_2O$ (*135*), $[Co(das)_2NO\cdot X]$, and $[Co(en)_2NO\cdot X]$ where X is Cl^-, Br^-, I^-, etc. (*68*), also appear to be six-coordinate. On the other hand, X-ray analysis has shown the cobalt ion to be five-coordinate with an asymmetric Co–N–O group in bis(dimethyldithiocarbamate)nitrosylcobalt (*12*). The following nitrosyl complexes probably also contain five-coordinate cobalt: $[Co(acac)_2NO]^0$ (*133*), bis(8-aminoquinolinato)nitrosylcobalt which has a magnetic susceptibility corresponding to two unpaired electrons per cobalt (*134*), $[CoX_2(PEt_3)_2NO]^0$ where X is F, Cl, or Br (*39*), $[Co(das)_2NO](ClO_4)_2$ (*68*), and $[Co\cdot salen\cdot NO]$ (*66*). Feltham and Nyholm (*68*) made the interesting observation that the NO-stretching frequency is very dependent on the coordination number and changes from ~1550 cm^{-1} in the six-coordinate complexes $[Co(das)_2NO\cdot X]^+X^-$, where X is Cl, Br, or I, to 1852 cm^{-1} in the five-coordinate $[Co(das)_2NO]^{2+}(ClO_4)_2$.

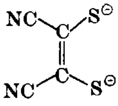
To a first approximation the nitrosyls behave like the alkyl complexes and present the case of a balance between five- and six-coordination in which the metal could be written in the formal oxidation state Co(III). But the situation is complicated by the possibility of π bonding and hence different contributions from the σ and π bonds, together with changes in the configuration of the Co–NO group and in the spin state. For experimental evidence for π bonding in other metal nitrosyls see, e.g., Manoharan and Gray (*121*) and Gans *et al.* (*75*).

4. *Dithiolate Complexes*

Complexes containing dithiolate ligands take us a step further as regards both the range of configurations and the difficulty of using formal oxidation states. Gray and co-workers (*34*) have prepared salts of the square planar complexes $[Co(TDT)_2]^-$ and $[Co(MNT)_2]^-$, where TDT is toluene-3,4-dithiolate (**7**) and MNT is maleonitriledithiolate (**8**). The former is paramagnetic in the solid state and in solution ($\mu_{eff} \sim 3.4$ B.M., corresponding to two unpaired electrons). The latter is diamagnetic in



(7)



(8)

the solid state and in solution in cyclohexanone, but paramagnetic ($\mu_{\text{eff}} = 2.81$ B.M.) in dimethyl sulfoxide (DMSO) and present as a mixture of the two forms in cyclohexanone–DMSO mixtures. Both complexes will pick up one mole of a bidentate ligand such as das or *o*-phen and $[\text{Co(MNT)}_2]^-$ will also pick up unidentate ligands such as $\text{As}\phi_3$ or $\text{P}\phi_3$ (one mole) or py (two moles). The following formation constants are found in acetone at 25°C (*114*).

Complex	Ligand	Log K_1	Log K_2
$[\text{Co(MNT)}_2]^-$	py	3.5	0.7
	$\text{As}\phi_3$	2.8	—
	$\text{P}\phi_3$	6.1	—
$[\text{Co(TDT)}_2]^-$	*o*-phen	1.7	—
	das	2.4	—

The structures of these complexes have not been established, but it was suggested that the five-coordinate complexes are square pyramidal and that the six-coordinate complexes may be trigonal prismatic or at least strongly distorted in that direction.

5. *Ligand Order*

The complexes discussed in this section point to some underlying pattern. If we neglect the possibility that the six-coordinate dithiolate complexes may not be octahedral and strictly comparable with the others, and if all the ligands are considered as anions, then we can tentatively arrange the unidentate ligands in an order of increasing tendency to stabilize the five-coordinate over the six-coordinate complex: CN^-, probably all common ligands with donor atoms N, O, and Cl $< \text{CH}_2{=}\text{CH}^- < \text{CH}_3^- < \text{CH}_2\text{CH}_2^- \sim \text{SO}_3^{2-} < \text{NO}^-$. The cis ligands can also be arranged in the tentative order: $(\text{NH}_3)_4$, $\text{en}_2 \ll (\text{DMG})_2$, BAE, salen $<$ corrin $\ll$ bisdithiolate. It seems that as the amount of negative charge donated by the ligands to the cobalt increases so the coordination number drops from six to five and eventually to four, i.e., the stereochemistry changes from that typical of cobalt(III) to that typical of low-spin cobalt(II) and eventually to that which one would expect for cobalt(I).

6. *Fluoride and Oxide Complexes*

For the sake of completeness it should be mentioned that a few high-spin octahedral cobalt(III) complexes are known. When surrounded by six fluoride anions as in CoF_3 (*178*) or M_3CoF_6, where M = Li, Na, K, Rb, or Cs (*98*), the cobalt ion is paramagnetic. When surrounded by six oxide ions cobalt ion may be high-spin as in Sr_2CoSbO_6 or low-spin as in $LiCoO_2$, Co_3O_4, and $ZnCo_2O_4$, or they may exist as a mixture of the two in La_4LiCoO_8 (see Blasse, *37*, and references therein).

The cobalt(III) ion can apparently also be tetrahedral in the heteropolytungstate ions $[Co^{II}Co^{III}W_{12}O_{42}]^{7-}$ and $[Co^{III}O_4W_{12}O_{36}]^{5-}$ (*18*).

IV. Kinetic Effects

A. MECHANISM OF LIGAND SUBSTITUTION

Ligands, at least those that coordinate to the cobalt(III) cation, are nucleophiles, i.e., anions and bases. By analogy with mechanisms established for substitution reactions in organic chemistry we can distinguish two extreme types of mechanism, called S_N1 and S_N2 (substitution, nucleophilic, unimolecular and bimolecular, respectively); one can also envisage mechanisms intermediate between the two limiting types. In the S_N1 mechanism the initial step is the breaking of one of the metal–ligand bonds to form an intermediate of lower coordination number, five-coordinate in the case of reactions of octahedral cobalt(III) complexes. In the S_N2 mechanism the initial step is the formation of a new bond to give a seven-coordinate intermediate. This is followed by a rapid step involving the gain (in S_N1) or the loss (in S_N2) of one ligand. The S_N1 intermediate may be square pyramidal or trigonal bipyramidal. The incoming ligand in the S_N2 reactions may attack on the same side as the leaving ligand or on the opposite side.

There is still no generally accepted view on the mechanism of ligand substitution in octahedral cobalt(III) complexes as a whole, owing mainly to complications which will be discussed below. In a few cases, however, there is fairly definite evidence for an S_N1 mechanism:

(1) Kinetic studies, i.e., the detection of a limiting first-order reaction at high concentrations of attacking ligand, have established the S_N1 mechanism in reactions of $[Co(CN)_5Y]$ (*80*) and $[Co(NH_3)_4SO_3Y]$ (*86*).

(2) Competition studies have shown the presence of a common S_N1 intermediate in certain aquation reactions of pentammine complexes (e.g., the Hg(II)-catalyzed hydrolysis of the chloro and bromo complexes in water containing ^{16}O and ^{18}O gives the same isotopic ratio in both products), but not in others (*64*). Jordan and Sargeson have pointed out that the ratios of cis and trans isomers produced in the hydroxide-catalyzed hydrolysis of the complexes $[Co{\cdot}en_2{\cdot}XY]$ is virtually independent of the nature of the leaving group Y and have suggested that this again indicates the formation of a common S_N1 intermediate (*105*).

(3) Evidence has been obtained for the occurrence of five-coordinate complexes in the bis-DMG (*158*), BAE (*61*), salen (*60*), and corrin complexes (*70*, *71*) when one of the axial ligands is an alkyl group (see Section III, B). The detection of a five-coordinate complex under certain conditions is, of course, no proof that ligand substitution reactions occur by an S_N1 mechanism under other conditions, but is nevertheless suggestive.

It is much more difficult to get unambiguous evidence for an S_N2 mechanism and none has yet been obtained. Interpretation of the experimental kinetic data is complicated, at least in the case of the ammine complexes, by the formation of ion-pairs and by the occurrence of base-catalyzed hydrolysis. Second-order kinetics could, for example, be observed for the following different mechanisms for the substitution of Y by Z in $[CoX_5Y]$. (1) True S_N2 reaction. (2) Extremely rapid formation of the five-coordinate intermediate, so that one can consider the initial $[CoX_5Y]$ to be in rapid equilibrium with $[CoX_5]$, followed by a much slower reaction with Z. This may be the case in the cobalamins, where no limiting first order reaction could be found (*155*). (3) The formation of an ion-pair $[CoX_5Y]Z$, which then liberates Y by an S_N1 mechanism, followed by the uptake of Z. The formation of ion-pairs is well authenticated and is particularly serious in the ammine complexes. There are several cases where the substitution of Y by Z is catalyzed by a different anion, obviously through the formation of an ion-pair with the latter (*10*, *76*), and it is now generally agreed that many reactions may involve rearrangements of an initially formed ion-pair (*175*). Wilmarth and co-workers have avoided this problem by working with the negatively charged pentacyanide complexes, which do not form ion-pairs with the attacking anions (*80*). (4) The formation of an ion-pair with a base Z which then abstracts a proton from one of the ligands to give the ion-pair $[CoX_4(X{-}H)Y]$ (ZH); this liberates Y in an S_N1 reaction and subsequently picks up the new ligand. The best known case is the base hydrolysis of ammine complexes where $Z = HO^-$. HO^- causes rapid hydrolysis of ammine complexes containing N–H bonds, but not of complexes with ligands such as py, picoline, dipy, phosphines, or das, which strongly suggests that the role of HO^- is to remove a proton from, e.g., NH_3 to give NH_2^-, which then labilizes the complex toward S_N1 substitution. This mechanism is usually termed S_N1CB (S_N1, conjugate base). HO^- does, in fact, form ion-pairs with ammine complexes, and the base-catalyzed rate of exchange between $Co{-}NH_3$ and D_2O is faster that that of ligand substitution, as required by the above theory. For references and further discussion of base hydrolysis see the volume by Basolo and Pearson (*31*).

For the purposes of this review we are interested more in using the kinetic data in order to obtain a rough order of the labilizing power of ligands, and less in the details of the mechanism. But, in the absence of any real evidence to the contrary, it will be assumed in the discussion below that all the complexes react by an S_N1 mechanism and can be compared directly. For a fuller discussion of the kinetic data and possible mechanisms see the reviews by Basolo and Pearson (*29*, *31*), Tobe (*174*, *175*), and Chan and Miller (*46*).

B. KINETICS OF LIGAND SUBSTITUTION

Comprehensive kinetic data, involving both forward and reverse reactions and the overall equilibrium constants, have been obtained for three groups of complexes. Haim, Grassi, and Wilmarth have studied the pentacyanides; their original papers have been summarized in a review article (*80*). Halpern, Palmer, and Blakley (*86*) have studied the reactions

$$[Co(NH_3)_4SO_3Z] + NH_3 = [Co(NH_3)_4SO_3NH_3] + Z$$

in aqueous solution. Randall and Alberty (*154*, *155*) have studied reactions of the cobalamins. All their data are presented in Table X. The occurrence of a limiting S_N1 reaction was shown for both the pentacyanide and sulfitotetrammine complexes, and values were obtained for the rate of the forward reaction k_{-z}, the ratio k_y/k_z, and the overall

$$[CoL_5Z] \underset{k_z}{\overset{k_{-z}}{\rightleftharpoons}} [CoL_5] \underset{k_{-y}}{\overset{k_y}{\rightleftharpoons}} [CoL_5Y]$$

equilibrium constant $K = (k_z/k_{-z})(k_{-y}/k_y)$, where $y = H_2O$ and NH_3 in the former and latter complexes, respectively. No limiting first-order reaction was, however, found for the cobalamins, and simple first- and second-order rate constants are reported.

There is a large amount of kinetic data available for the substitution, of different ligands by H_2O in ammine complexes; rate constants, activation energies, and preexponential factors have been obtained in many cases. Tobe and co-workers have obtained a fairly comprehensive set of data for the bisethylenediamine complexes, which, together with some results of other workers are given in Tables XI and XII. These data provide information on the trans effect of different ligands X and a comparison of cis and trans effects. For the explanation of base hydrolysis see Section IV, A. For other data on ammine complexes see recent reviews (*31*, *46*, *174*, *175*). Table XIII includes all the kinetic data available for the bisdimethylglyoxime complexes. Certain other quantitative data and some qualitative observations will be mentioned in later sections.

TABLE X

Combined Kinetic and Thermodynamic Data for Ligand Substitution Reactions in Some Cobalt(III) Complexes

Pentacyanides $[Co(CN)_5Y]$[a]

X	Y	Z	K_z/K_{H_2O}[b]	K_{-z}(sec^{-1})[c]	$K(M^{-1})$[d]
CN^-	H_2O	H_2O	1	1.6×10^{-3}	1
		N_3^-	0.53	5.5×10^{-7}	1530
		NCS^-	0.34	3.7×10^{-7}	1460
		Br^-	0.10	1.7×10^{-4}	0.9
		I^-	0.19	7.4×10^{-6}	40

trans-Sulfitotetrammines
$[Co(NH_3)_4SO_3 \cdot Y]$[e]

X	Y	Z	K_z/K_{NH_3}[b]	K_{-z}(sec^{-1})[c]	K[d]
SO_3^{2-}	NH_3	HO^-	$\sim 1 \times 10^4$	~ 10	14
		NCS^-	30	1.7	0.2
		NO_2^-	58	5.4×10^{-1}	1.3
		NH_3	1	1.2×10^{-2}	1
		CN^-	~ 40	—	$> 10^4$
		SO_3^{2-}	$\sim 2 \times 10^2$	1.8×10^{-2}	1.2×10^2

Cobalamins
$[Co \cdot corrin \cdot Bz \cdot Y]$[f]

X	Y	Z	$K_z(M^{-1}sec^{-1})$[b]	K_{-z}(sec^{-1})[c]	$K(M^{-1})$[d]
Bz	H_2O	N_3^-	1.7×10^3	0.03	5.6×10^4
		NCO^-	7.3×10^2	0.95	10^3
		NCS^-	7.1×10^3	1.8	2.3×10^3
		imid°	27	6×10^{-4}	3.8×10^4
		CN^-	1.5×10^3	10^{-9}	10^{12}

---

[a] Data from Haim *et al.* (*80*). Aqueous solutions, 1 M $NaClO_4$, 40°C. They also report the value $k_{-z} = 0.51 \times 10^{-3}$ sec^{-1} for $Y = H_2O$ in 5 M $NaClO_4$ at 20°C.

[b] Forward reaction.

[c] Reverse reaction.

[d] Equilibrium constant.

[e] Preliminary and incomplete values were published in Halpern *et al.* (*86*); data in the table include later and more complete values (*82*). Aqueous solutions, 0.46 M $NaClO_4$ at 25°C.

[f] Data from Randall and Alberty (*155*), which includes a few kinetic and thermodynamic results of other workers. Aqueous solutions, buffers pH 2–9.6, $I = 0.054$, 25°C.

The available information will be arranged to try to answer the questions: (1) Do ligands X exert a different effect on reactions in cis and trans positions? (2) What is the relative cis effect of ligands, in particular chelating ligands such as en, DMG, and corrin? (3) What is the order of the trans effect for single ligands, and is it the same for all groups of complexes?

1. *Cis or Trans Effect*

The kinetic data of Tobe and co-workers on the acid and base hydrolysis of *cis*- and *trans*-[Co•en$_2$•XY] (Tables XI and XII) provide a

TABLE XI

KINETIC DATA FOR ACID HYDROLYSIS[a]

$[\text{Co}\cdot\text{en}_2\cdot\text{X}\cdot\text{Y}] + \text{H}_2\text{O} \rightarrow [\text{Co}\cdot\text{en}_2\cdot\text{X}\cdot\text{H}_2\text{O}] + \text{Y}$

Configuration	X	Y	K_1 (sec^{-1})	E_a (kcal/mole)	Log$_{10}$ B	Ref.
Trans	H_2O	Cl^-	2.5×10^{-6}	—	—	(*45*)
	HO^-	Cl^-	1.6×10^{-3}	26.2	16.4	(*20*)
	N_3^-	Cl^-	2.2×10^{-4}	23.1	13.3	(*164*)
	NCS^-	Cl^-	5×10^{-8}	30.4	14.9	(*21*)
	NO_2^-	Cl^-	1×10^{-3}	21.5	12.8	(*13*)
	NH_3	Cl^-	2.9×10^{-5}***	23.6	10.9	(*172*)
	CN^-	Cl^-	8.3×10^{-5}	22.6	12.4	(*48*)
	Cl^-	Cl^-	3.53×10^{-5}	24.2	13.0	(*20*)
	Br^-	Cl^-	4.5×10^{-5}	25.2	14.1	(*50*)
Cis	H_2O	Cl^-	1.6×10^{-6}	—	—	(*45*)
	HO^-	Cl^-	1.2×10^{-2}	23.1	15.0	(*20*)
	N_3^-	Cl^-	2.0×10^{-4}	21.7	12.3	(*164*)
	NCS^-	Cl^-	1.1×10^{-5}	20.8	10.3	(*21*)
	NO_2^-	Cl^-	1.0×10^{-4}	22.35	12.4	(*13, 32*)
	NH_3	Cl^-	1.4×10^{-6}*	—	—	(*144*)
	Cl^-	Cl^-	2.4×10^{-4}	22.2	12.5	(*20*)
	Br^-	Cl^-	1.4×10^{-4}	23.1	13.1	(*50*)
Trans	HO^-	Br^-	9.5×10^{-3}	25.0	16.3	(*50*)
	NCS^-	Br^-	5×10^{-7}	30.1	15.3	(*21*)
	NO_2^-	Br^-	4.3×10^{-3}	—	—	(*115*)
	NH_3	Br^-	$\sim 9.5 \times 10^{-5}$**	24.6	12.0	(*172*)
	Cl^-	Br^-	1.12×10^{-4}	26.6	15.6	(*50*)
	Br^-	Br^-	1.39×10^{-4}	25.6	14.9	(*50*)
Cis	HO^-	Br^-	6×10^{-2}	23.3	15.8	(*50*)
	NCS^-	Br^-	2.3×10^{-5}	23.1	12.3	(*21*)
	Cl^-	Br^-	5.7×10^{-4}	23.9	14.3	(*50*)
	NH_3	Br^-	1.4×10^{-6}	23.6	11.5	(*173*)

[a] All rate constants refer to 25°C except those marked *, **, and ***, which refer to 35°, 60°, and 63°C, respectively. Ionic strength varies, often pure water.

basis for comparing the effect of X on cis and trans positions. Examination of the data for acid hydrolysis shows that in all cases except when $X = NO_2^-$ and $Y = Cl^-$ both E_a and $\log_{10}B$ are greater in the trans isomer. These two factors in the rate equation tend to balance each other, and the difference in the rate constant may be fairly small; when $X = NCS^-$ and $Y = Cl^-$, the trans isomer reacts slightly faster, but when $X = N_3^-$ and $Y = Cl^-$ the cis isomer reacts about two hundred times faster. The existence of this peculiar compensatory effect in ligand substitution reactions of Pt(II) and Co(III) complexes has been pointed out by Peshchevitskii and Kazakov (*146*, *147*). In the case of base hydrolysis both E_a and $\log_{10}B$, and hence the rate constant, differ far less between isomers (and also vary less with X).

TABLE XII

KINETIC DATA FOR BASE HYDROLYSIS[a]
$[Co{\cdot}en_2{\cdot}XY] + HO^- \rightarrow [Co{\cdot}en_2{\cdot}X{\cdot}OH] + Y$

Configuration	X	Y	$K_2(M^{-1}\ sec^{-1})$	E_a (kcal/mole)	$Log_{10}\ B$
Trans	HO^-	Cl^-	0.017	22.8	16.4
	N_3^-	Cl^-	0.41	—	—
	NCS^-	Cl^-	0.35	23.2	18.7
	NO_2^-	Cl^-	0.080	24.4	18.4
	NH_3	Cl^-	1.25	—	—
	CN^-	Cl^-	0.13	23.2	17.7*
	Cl^-	Cl^-	85.0	23.2	20.5
	Br^-	Cl^-	110.0	24.9	21.9
Cis	HO^-	Cl^-	0.37	22.4	17.4
	N_3^-	Cl^-	0.17	—	—
	NCS^-	Cl^-	1.40	—	—
	NO_2^-	Cl^-	0.032	23.1	17.0
	NH_3	Cl^-	0.50	—	—
	Cl^-	Cl^-	15.1	24.6	20.8
	Br^-	Cl^-	23.0	22.7	19.5
Trans	HO^-	Br^-	0.168	23.7	18.2
	NCS^-	Br^-	1.95	—	—
	Cl^-	Br^-	269.0	24.2	21.8
Cis	HO^-	Br^-	2.7	22.5	18.4
	NH_3	Br^-	3.3	—	—
	Cl^-	Br^-	71.0	23.1	20.3

[a] All data from Chan and Tobe (*47*) except * which is taken from (*48*). Experimental conditions: 0°C, ionic strength varies.

Halpern *et al.* (*86*) report that only one NH_3 in the complex $[Co(NH_3)_5SO_3]$, presumably that in the position trans to SO_3^{2-}, exchanges with labeled NH_3. But they quote no upper limit to the possible rate of exchange of the other NH_3 ligands, so it cannot be seen whether the difference in reactivity of the *cis*- and *trans*-NH_3 ligands is significantly outside the range of random variation observed with the bisethylenediamine complexes.

TABLE XIII

KINETIC DATA FOR THE REACTIONS
$[Co(DMG)_2XY] + Z \rightarrow [Co(DMG)_2XZ] + Y$

X	Y	Z	Rate constant: $10^5 K_1$ (sec^{-1}) at			E_a (kcal/mole)	$Log_{10} B$	Ref.
			18°C	25°C	30°C			
H_2O	Cl^-	H_2O	—	10	—	25.5	14.8	(*9*)
Cl^-	Cl^-	H_2O	10.6	27	—	23.9	14.0	(*1*)
NO_2^-	Cl^-	H_2O	3.84	10.3	19.7	23.5	14.9	(*1*)
H_2O	Br^-	H_2O	—	7	—	27.6	16.0	(*9*)
Br^-	Br^-	H_2O	14.4	—	—	24.5	—	(*1*)
NO_2^-	Br^-	H_2O	4.6	11.5	23.0	23.7	15.1	(*1*)

X	Y	Z	Rate constant: $10^4 K_2$ (M^{-1} sec^{-1}) at		Ref.
			25°C	30°C	
NO_2^-	H_2O	N_3^-	5.7	9.0	(*83*)
		NCS^-	5.8	9.9	
		NO_2^-	—	~3.5	
		Cl^-	0.8	1.5	
		Br^-	1.6	3.3	
		HSO_3^-	85.0	150.0	
I^-	H_2O	NCS^-	12.0	24.0	
		Cl^-	2.3	4.5	
		Br^-	3.0	5.2	
		HSO_3^-	34.0	52.0	

There is certainly no real evidence that ligands X exert a significant and systematic difference on rates of ligand substitution in the cis and trans positions.

2. *Cis Effects*

Since many interesting complexes contain a planar ring system such as $(DMG)_2$ or corrin we now wish to examine the effect of changing all four cis ligands. The following comparisons can be made:

(1) Ideally one would like to compare complexes where X, Y, and Z all remain constant. There are quite a number of rate constants available for the hydrolysis of the dichlorides ($X = Y = Cl^-$, $Z = H_2O$) and these serve to link together many of the simpler chelating ligands with nitrogen donor atoms. There are a few comparable rate constants for monochlorides. These are all listed in Table XIV.

(2) If we assume that the two nitrogenous bases NH_3 and Bz have a similar effect when acting as ligand X, then one comparison is possible between the pentammines and cobalamins (Table XIV)

(3) In the case of the pentacyanides, *trans*-sulfitotetrammines and cobalamins (Table X) and even bisdimethylglyoximates (Table XIII), there are sufficient data available to give a general idea of the cis effect of these ligands even where no direct comparison is possible.

(4) Finally, one can include qualitative observations. Ligand substitution reactions of cobalt(III) porphyrin complexes, for example, appear to be fast or "instantaneous," although many have been studied in nonaqueous solvents and are therefore not really comparable. Cobalt(III) hematoporphyrin is, however, a clear-cut case; the substitution of H_2O by CN^- or py in aqueous solution is instantaneous (*123*).

The effect of charge cannot readily be calculated and, as the discussion will show, probably plays a relatively minor part; it will therefore be neglected. The following generalizations can be made. (1) Merely varying the configuration of the diamine type of chelate (Table XIV) without altering the charge can alter the rate constants by a factor of at least 300 (and probably very much more if we include the qualitative observations). (2) We can compare the relative cis effects of en_2 and $(DMG)_2$ in the presence of different trans ligands X. The en_2 complex appears to react faster than the $(DMG)_2$ complex when $X = NO_2^-$, but slower when $X = Cl^-$ or H_2O, but these are not quantitative comparisons because of the difference in experimental conditions. Nevertheless, it is very likely that there is no single and well-defined order of cis (or trans) effect, only an approximate one. (3) Taking into consideration all the data in Tables X, XIII, and XIV and the qualitative observations on the porphyrins, the approximate order of cis effect appears to be: $py_4 \sim \beta/\gamma\text{-pic}_4 \sim en_2 \sim (DMG)_2 \sim ?(CN)_4 < (NH_3)_4 \sim ?dipy_2 \leqslant ?(H_2O)_4 \ll \text{corrin} \sim$ porphyrin.

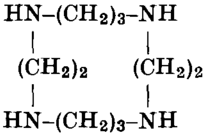
TABLE XIV

KINETIC DATA FOR THE CIS EFFECT[a]

Cis ligands[b]	X	Y	Z	K_1 (sec^{-1})	Ref.
$(NH_3)_4$	Cl^-	Cl^-	H_2O	1.8×10^{-3}	(*144*)
en_2	Cl^-	Cl^-	H_2O	3.2×10^{-5}	(*143*)
pn_2	Cl^-	Cl^-	H_2O	6.2×10^{-5}	(*143*)
dl-bn_2	Cl^-	Cl^-	H_2O	1.5×10^{-4}	(*143*)
m-bn_2	Cl^-	Cl^-	H_2O	4.2×10^{-4}	(*143*)
i-bn_2	Cl^-	Cl^-	H_2O	2.2×10^{-4}	(*143*)
$tetrameen_2$	Cl^-	Cl^-	H_2O	"Instant"	(*143*)
tn_2	Cl^-	Cl^-	H_2O	10^{-2}*	(*143*)
cyclam	Cl^-	Cl^-	H_2O	Very slow**	(*40*)
py_4	Cl^-	Cl^-	H_2O	8.3×10^{-6}	(*145*)
β-$picoline_4$	Cl^-	Cl^-	H_2O	1.5×10^{-5}	(*145*)
γ-$picoline_4$	Cl^-	Cl^-	H_2O	2.5×10^{-5}	(*145*)
$dipy_2$	Cl^-	Cl^-	H_2O	"Instant"	(*145*)
$(DMG)_2$	Cl^-	Cl^-	H_2O	2.7×10^{-4}	(*1*)
en_2	NO_2^-	Cl^-	H_2O	9.8×10^{-4}	(*115*)
$(DMG)_2$	NO_2^-	Cl^-	H_2O	1.03×10^{-4}	(*1*)
en_2	H_2O	Cl^-	H_2O	2.5×10^{-6}	(*45*)
$(DMG)_2$	H_2O	Cl^-	H_2O	1.0×10^{-4}	(*9*)
Corrin	H_2O	Cl^-	H_2O	"Instant"	(*88*)
$(H_2O)_4$	H_2O	Cl^-	H_2O	$\leqslant 5 \times 10^{-2}$	(*59*)
$(NH_3)_4$	NH_3	N_3^-	H_2O	2.1×10^{-9}	(*113*)
Corrin	Bz	N_3^-	H_2O	3×10^{-2}	(*155*)

[a] Rate constants determined at 25°C except * at 10°C. Varied ionic strength and pH. **, equilibrium reached after 24 hours at 80°C.

[b] Abbreviations:

pn	$NH_2–CH_2–CH(CH_3)–NH_2$
dl/*m*-bn	$NH_2–CH(CH_3)–CH(CH_3)–NH_2$
i-bn	$NH_2–CH_2–C(CH_3)_2–NH_2$
tetrameen	$NH_2–C(CH_3)_2–C(CH_3)_2–NH_2$
tn	$NH_2–CH_2–CH_2–CH_2–NH_2$
cyclam	 $\begin{array}{c} HN–(CH_2)_3–NH \\ \vert \qquad\quad \vert \\ (CH_2)_2 \quad (CH_2)_2 \\ \vert \qquad\quad \vert \\ HN–(CH_2)_3–NH \end{array}$

3. *Trans Effects*

We can now keep all four cis ligands constant and examine the effects of varying the trans ligand X on the rates of substitution of Y by Z. Each group of complexes is discussed separately.

Quantitative kinetic data can be supplemented by qualitative observations, but with certain reservations, in particular as regards conclusions which can be drawn from the results of competitive reactions. Several workers have tried to construct an order of trans-labilizing ability by allowing a complex, containing the two ligands X_1 and X_2, whose relative position in the order is to be determined, to react with one mole of Z. If Z displaces X_1, it was concluded that X_2 has the greater trans-labilizing effect. The nature of the product is, however, determined by a combination of (*i*) the thermodynamic formation constants for the substitution of X_1 and X_2 separately by Z and (*ii*) the rate constants. If the product comes out of solution as a precipitate, then (*iii*) the solubility products are also involved. Conclusions based on this type of experiment cannot be accepted unless it is shown or can be assumed that the thermodynamically less stable product is formed. Qualitative observations indicating that equilibria are established rapidly at room temperature are, on the other hand, extremely useful additional information, since most cobalt(III) complexes are very inert.

a. Ammine Complexes. The quantitative data of Tobe and co-workers and of others on the acid hydrolysis of bisethylenediamine complexes have been given in Table XI. For the hydrolysis of the chloro complex ($Y = Cl^-$, $Z = H_2O$), we find the following order of effect of the trans ligand X.

Rate constants	$HO^- > NO_2^- > N_3^- > CN^- > Br^- > Cl^- > NCS^- > H_2O$
$\log_{10} B$	$HO^- > NCS^- > Br^- > N_3^- > Cl^- > NO_2^- > CN^- > NH_3$
E_a	$NO_2^- < CN^- < N_3^- < NH_3 < Cl^- < Br^- < HO^- < NCS^-$

A similar order of trans ligands is also found when $Y = Br^-$ (Table XI).

We can also compare the rates of the reactions

$$[Co(NH_3)_5Y] + H_2O \rightarrow [Co(NH_3)_5H_2O] + Y$$
$$[Co(NH_3)_4SO_3Y] + NH_3 \rightarrow [Co(NH_3)_4SO_3NH_3] + Y$$

where $Y = NCS^-$ and NH_3. Gay and Lalor (*77*) studied the hydrolysis of $[Co(NH_3)_5NCS]$ at 80°–100°C and obtained values for E_a from which one can calculate an approximate rate constant at 25°C of $k \sim 10^{-8.5}$ sec^{-1}. Llewellyn *et al.* (*119*) found negligible exchange of $[Co(NH_3)_6]$ after 162 days at 25°C and pH 2.4 or 9.9, which leads to a value of $k \leqslant 10^{-7}$ sec^{-1}. The rate constants (K_1 in sec^{-1}) for the complexes $[Co(NH_3)_4SO_3Y]$ at 25°C have already been given in Table X: $Y = NH_3$, 1.2×10^{-2}; NCS^-, 1.7. The comparison between the two sets of complexes is not exact since Z is different, but the rate appears to vary with Z (see Table X) by only a small factor ($\leqslant 10^3$) compared to the large differences in rate found between the two sets of complexes. SO_3^{2-} clearly has a very marked trans-labilizing effect compared to NH_3, increasing rates by a factor of 10^6–10^8 or more. It appears to exert a similar effect in bisethylenediamine complexes; Baldwin (*19*) noted that [Co·en$_2$·SO$_3$·NCS] is hydrolyzed very rapidly, and Chan and Tobe (*49*) found that both SO$_3^{2-}$ and S$_2$O$_3^{2-}$ acted similarly in labilizing the chloride in [Co·en$_2$·X·Cl] toward substitution by CN$^-$. By contrast, variation of the trans ligand within the series studied by Tobe and co-workers changes the rate constants by a factor of only 2×10^4. NCS$^-$ has a significantly lower trans-labilizing effect than the others, caused by an unusually high activation energy. The order of trans effect in the ammine complexes can therefore be written: $\text{SO}_3^{2-} \gg \text{HO}^- \sim \text{N}_3^- \sim \text{NO}_2^- \sim \text{CN}^- \sim \text{Cl}^- \sim \text{NH}_3 > \text{H}_2\text{O} > \text{NCS}^-$.

Babaeva and Baranovskii have used competitive reactions to obtain the relative positions $\text{SO}_3^{2-} > \text{NO}_2^-$ (*15*), $\text{NO}_2^- > \text{NCS}^-$ (*14*), and $\text{NO}_2^- > \text{CN}^-$ (*24*), but their conclusions are not valid for the reasons given at the beginning of this section.

b. Pentacyanide and Tetracyanide Complexes. There is very little unambiguous evidence on trans effects in this group of complexes which can contain such interesting ligands as SO$_3^{2-}$, H$^-$, and alkyl groups. Wilmarth and co-workers have, however, obtained the following rate constants for $K_{-\text{H}_2\text{O}}$ (i.e., loss of H$_2$O to give the five-coordinate intermediate in an S_N1 reaction): [Co(CN)$_5$H$_2$O], $k = 0.51 \times 10^{-3}$ sec^{-1} in 5 *M* (NaClO)$_4$ at 20°C (*80*) and *trans*-[Co(CN)$_4$SO$_3$H$_2$O], $k = 1.7$ sec^{-1} at unit ionic strength at 25°C (*171*). Assuming that SO$_3^{2-}$ does not act as a bidentate ligand to stabilize the "transition state," this shows the strong trans-labilizing effect of SO$_3^{2-}$ compared to CN$^-$. The pentacyanohydride (*23*) and pentacyanoalkyl complexes (*84, 85, 102, 112*) decompose fairly readily in solution, but these reactions may not be comparable to ligand substitution reactions, e.g., the formation of alkylcyanides through the interaction between neighboring alkyl and cyanide ligands (*102, 112*). In a certain alkyl pentacyanide, however, where the alkyl ligand is 4-pyridiomethyl protonated on the nitrogen, an equilibrium can be observed due to the displacement of one cyanide by H$_2$O which is set up slowly at room temperature, whereas neither [Co(CN)$_6$] nor [Co(CN)$_5$H$_2$O] show any comparable change even in very strong acid (*102*). The alkyl group, therefore, shows a stronger effect than either H$_2$O or CN$^-$ on either or both of the thermodynamic and kinetic properties of the complex, but the two effects cannot be separated. However, in view of the general parallel between thermodynamic and kinetic effects (see Section V, A) it seems very likely that both properties are affected.

c. Bis(dimethylglyoxime) and Related Complexes. The available quantitative kinetic data on the rates of ligand substitution in DMG complexes have been given in Table XIII. For none of the pairs or triads with the same Y and Z does a change of X cause a change in the rate by a factor of more than 3 except for $Y = Br^-$ and $Z = H_2O$ when the rate changes by a factor of about 6. The order of trans-labilizing effect appears to be $I^- \geqslant Br^- \geqslant Cl^- > NO_2^- \geqslant H_2O$, but the differences are very small.

Ablov and co-workers have used the products of competitive reactions to establish a trans effect order; from their results (*2–8*, *159*, *165*) the general order appears to be: $SO_3^{2-} > HO^- > NC\underline{S}e^- \sim NC\underline{S} > SC(NH_2)_2 > I^- > NO_2^- > Br^- > Cl^- > H_2O$. But, for the reasons given at the beginning of this section, these conclusions cannot be regarded as completely valid; this order does not entirely agree with the kinetic data mentioned in the preceding paragraph. Much more interesting, however, are their qualitative observations that certain equilibria involving the substitution of ligands are established rapidly at room temperature in aqueous solution when the trans ligand is I^- (*4*, *5*), $NC\underline{S}^-$, and $NCSe^-$ (*7*), or thiourea (*1*), in contrast to H_2O, HO^-, NO_2^-, Br^-, and Cl^-. NCS^- and $NCSe^-$ are known to coordinate through S and Se, respectively (*2*). It also appears that equilibria are established rapidly when the trans ligand is an alkyl group (*158*). A rough trans-effect order can therefore be written for DMG complexes:

$$\left.\begin{matrix}\text{Alkyls, } SO_3^{2-}\text{, thiourea,}\\ NCS^-\text{, } NCSe^-\text{, } I^-\end{matrix}\right\rangle\ Br^- \geqslant Cl^- \geqslant NO_2^- \geqslant H_2O$$

It seems that the BAE and salen complexes are also labilized when they contain an alkyl ligand (*60*, *61*). There are unfortunately no unambiguous data on the kinetic trans effect in the corrinoids.

4. *Summary*

The above results show that changing the ligands can have very dramatic effects on the rates of ligand substitution in cobalt(III) complexes. By pooling all the results of Section IV, B, 3 we obtain the following general order of labilizing effect for unidentate ligands:

$$\text{Alkyls, } SO_3^{2-} \gg \begin{matrix}CN^-\text{, } N_3^-\text{, } NO_2^-\text{, } NH_3\\ HO^-\text{, } Cl^-\text{, } Br^-\text{, } I^-\end{matrix}\ ?\!> H_2O > \underline{N}CS^-$$

The general validity of this order is indicated by the fact that SO_3^{2-} has a strong labilizing effect in the pentammine, the bisethylenediamine, and bis-DMG complexes, and the alkyls have a similar effect in the bis-DMG, BAE, salen, and possibly pentacyanide complexes, while NO_2^- and Cl^- are virtually indistinguishable in both the bisethylenediamine and bis-DMG complexes. As discussed in section IV, A, HO^- catalyzes the aquation of ammine complexes by a mechanism which probably involves the abstraction of a proton to give the ligand NH_2^-, which labilizes the complex. If this mechanism is accepted, then NH_2^- can be classed together with CH_3^- and SO_3^{2-}. There is no real evidence as to whether these unidentate ligands exert a different effect on the cis and trans positions.

A second order of ligands has been built up in order to compare the cis effect of ligands such as corrin (Section IV, B, 2). The following very rough order of labilizing effect of four cis ligands was obtained:

$$\begin{array}{l} \mathrm{py}_4 \sim \beta/\gamma\text{-}\mathrm{pic}_4 \\ \mathrm{en}_2 \sim (\mathrm{DMG})_2 \\ ?\ (\mathrm{CN})_4 \end{array} < \begin{array}{l} (\mathrm{NH}_3)_4 \\ ?\ \mathrm{dipy}_2 \end{array} \leqslant (\mathrm{H_2O})_4 \ll \begin{array}{l} \text{corrin} \\ \text{porphyrin} \end{array}$$

The corrin and porphyrin rings exert a very strong labilizing effect and occur at one end of the series, while all the remaining ligands, with the exception of $(H_2O)_4$, cluster at the other end. It is to be hoped that more work can be done on the aquo complexes and that other ligands of intermediate labilizing power will be discovered which can close the gap.

Until fairly recently it was assumed that large kinetic effects of the type found in platinum(II) complexes did not occur in cobalt(III) complexes. The situation has now been reversed. The rate constants for the reaction

$$trans\text{-}[\mathrm{Pt(PEt_3)_2L \cdot Cl}] + \mathrm{py} \rightarrow trans\text{-}[\mathrm{Pt(PEt_3)_2 \cdot py \cdot Cl}] + \mathrm{L}$$

change by a factor of only 10^5 as L is varied (*28*); and this appears to be the largest variation yet found for the change of only one ligand in any platinum(II) complex (*31*). By contrast the order of unidentate ligands in cobalt(III) complexes corresponds to a variation in rate constants of at least 10^6–10^8 (Section IV, B, 3, a). No quantitative data are yet available for the effect of alkyl ligands which from their effect on ground-state and thermodynamic properties one might expect to show a labilizing effect several orders of magnitude larger again. The extremes of cis effect (corrin and cyclam) also correspond to a variation in rates of $\geqslant 10^{10}$. It is interesting to note that in the naturally occurring corrinoid (*Co*-5′-deoxyadenosylcobalamin) nature has hit upon the best possible combination of cis and trans ligands (corrin and alkyl) to labilize the remaining coordination position toward ligand substitution.

V. Summary

A. CIS AND TRANS EFFECTS IN COBALT(III) COMPLEXES

The key role in the experimental study of cis and trans effects in cobalt(III) complexes has been played by the corrinoid group of complexes and by SO_3^{2-} and the alkyl ligands. The data relating to the corrinoids will be summarized and used as a basis for a discussion of the other complexes, with particular emphasis on SO_3^{2-} and the alkyl ligands. But it is useful first to attempt to answer the questions: (1) Are the corrinoids representative of cobalt(III) complexes? (2) Does metal–ligand π bonding play any significant part in cobalt(III) complexes? (3) Are the effects of a given ligand transmitted differently to the cis and trans positions?

1. *Comparison of Corrinoids with Other Cobalt(III) Complexes*

The limited amount of data on bond lengths and their relatively low accuracy prevents any detailed comparison of corrinoids with other complexes; there are, however, no obvious differences (Section II, A). There is, on the other hand, a fairly close similarity in the effect of ligands X on the cyanide-stretching frequency of pentacyanides and cyanocorrinoids, although the range of frequencies observed is slightly greater in the latter (Section II, B). The corrinoids show a pattern of equilibria very similar to that of all other groups of cobalt(III) complexes, where only six-coordinate complexes are involved (Section III, A). BAE, salen, and bis-DMG complexes containing an ethyl or methyl ligand form five-coordinate complexes almost as easily as the analogous corrinoids; no quantitative data are available for comparison, but the relevant equilibrium constants probably differ by less than 10^2 (Section III, B). No direct comparison is possible with the alkylpentacyanides, since they decompose readily in solution (*84*, *85*, *102*, *112*), and no alkylammine complexes are available for comparison. There is, therefore, no obvious difference between corrinoids and other groups as regards ground-state and thermodynamic properties. The corrinoids do, however, behave differently from all other cobalt(III) complexes except the porphyrins in being kinetically much more labile (Section IV, B); the reason for these differences is not known, but they are not relevant to the discussion below.

2. *Metal–Ligand π Bonding*

There can be no question that π bonds are formed when the metal and ligand orbitals have the correct symmetry for overlap; the only realistic question is whether they make any significant contribution to the properties of the complex. One would expect metal-to-ligand π bonding to increase with ligands in the following order: $CN^- < CNR < CO < NO^+$. The very close parallel between the effects of ligands X on the formation constants toward CH_3NC and N_3^- is evidence that significant π bonding does not occur with isocyanides (Section III, A). The π-acceptor capacity will be even less pronounced in the negatively charged cyanide anion; again the pattern of formation constants toward CN^- is not significantly different from those toward, for example, HO^-, where metal-to-ligand π bonds cannot occur (Section III, A). The nonexistence of any cobalt(III) complexes containing CO or phosphines which are stable to water is additional evidence for the absence of π bonds; contrast the low-spin Fe(II) ion, which has the same electronic configuration but lower charge and which forms complexes with CO such as $[Fe(CN)_5CO]^{3-}$ and carboxyhemoglobin. The nitrosyl complexes, on the other hand, which are formed by the reaction of nitric oxide with cobalt(II) complexes and which may be written as $Co(III) + NO^-$ or $Co(I) + NO^+$, may possibly involve strong π bonds (Section III, B, 3). It is also possible that significant π bonding may occur between the cobalt(III) ion and corrin, DMG, etc., but the similarity of the equilibrium constants for all groups of complexes (Section III, A) argues against this. With the possible exception of the nitrosyl ligand, it will be assumed that metal–ligand π bonding does not play any significant role in the properties of six-coordinate cobalt(III) complexes. The situation is clearly different in, for example, the cobalticenium cation $Co(C_5H_5)_2^+$ and the square planar bisdithiolate complexes.

3. *Directional Nature of Effects*

Bond lengths provide definite evidence for a trans-directional effect in the case of NO^-, Cl^-, and possibly alkyl ligands, at least in the simpler complexes (Section II, A). In the corrinoids both cis and trans positions appear to be affected almost equally; but other factors may be involved since the ring is not planar and the geometry around the cobalt far from symmetrical. Infrared data, on the other hand, suggest that the influence of the ligand is not directional (Section II, B); the cyanide-stretching frequency in the pentacyanides can vary over a wide range depending on the nature of the sixth ligand, but only one band is observed, indicating identical bond strengths for both *cis-* and *trans*-cyanide ligands. The limited thermodynamic (Section III, A, 2) and kinetic data (Section IV, B, 1) also fail to reveal any significant differences between the cis and trans positions. There appears, therefore, to be a difference between the bond lengths and the remaining evidence. NMR spectra also show clear differences between cis and trans ligands, but several interpretations are possible (Section II, C). It should be pointed out that although a correlation exists between bond lengths, bond dissociation energies, and bond-stretching force constants in simple molecules (e.g., organic compounds), there is no reason why the same correlation should still hold in transition metals such as cobalt, which possess low-lying excited states and numerous "lone pairs" of electrons. The discrepancy between the bond lengths and other data may be a genuine result, reflecting the breakdown of such a correlation. Clearly much more work remains to be done before any conclusions can be made about the directional character of these effects in cobalt(III) complexes, and the differences between cis and trans positions will be neglected in the remainder of the discussion.

4. *Comparison of All Data*

There is a greater range of quantitative data available for the corrinoids than for any other group of cobalt(III) complexes, and they will be discussed first. Table XV summarizes the effect of changing one axial ligand on (1) the bond lengths (ground-state cis and trans effects), (2) the stretching frequency of coordinated CN^- (ground-state trans effect), (3) the energy of the electronic transitions within the corrin ring (ground state cis effect; see Section II, D), (4) formation constants between six-coordinate complexes, and (5) equilibria between five- and six-coordinate complexes (both thermodynamic trans effects). With the exception of SO_3^{2-}, i.e., considering only ligands with the light donor atoms, C, N, and O, there is very good correlation between all the listed properties. SO_3^{2-}, on the other hand, shows some variation in its position in the ligand order depending on the properties being studied (Table XV) and qualitative results suggest similar discrepancies in the case of other ligands such as Br^-, I^-, and thiourea (*72*). It appears that additional factors are involved in the bond between the cobalt and heavier donor atoms such as S, Br, and I.

Table XVI summarizes all the ligand sequences observed for cobalt(III) complexes as a whole using the different experimental techniques. The direction of a sequence, as written in Table XVI, is determined by reference to the corrinoids in ground-state and thermodynamic properties and by obvious parallels in the case of kinetic properties. Examination of the results shows that a similar order of ligands is observed for all groups of complexes and at all levels. As a broad generalization, we can say that the ligands which contain the more electronegative donor atoms such as Cl, O, N (except in NO^-), and C in CN^- occur at one end, those with S, Se, I, H, and C toward the other, with the simple alkyls such as CH_3^- together with NO^- at the extreme end.

Both this general order of ligand atoms Cl, O, N, C(in CN^-) < H, S, Se, I, C(in CH_3^-, etc.), N (in NO^-) and the specific order of carbon ligands $CN^- < HC{\equiv}C^- < CH_2{=}CH^- < CH_3CH_2^-$ indicate (*72*, *150*) that the most important property of the ligand which determines its influence on the rest of the complex is the amount of negative charge donated via the σ bond to the cobalt ion.

TABLE XV

COMPARISON OF GROUND STATE AND THERMODYNAMIC EFFECTS IN CORRINOIDS[a]

Axial ligand (X)	Bond lengths (Å) in cobalamins (Y = Bz)		CN-stretching frequency (cm^{-1}) Y = CN$^-$	Wavelength (mμ) of γ-band where Y =			Formation constants[b] ($\log_{10} K$) where Y/Z =				Equilibrium[d] (%) Y = H_2O
	Co-Bz	Co-corrin (average)		CN$^-$	Bz	H_2O	H_2O/CN^-	H_2O/Bz	Bz/CN$^-$	H_2O/HO^-	
H_2O	—	—	—	354	350	348	⩾14	7.1	—	8.0	—
BZ	—	—	2132	360.5	354	350	⩾12	—	—	6.2	—
HO^-	—	—	2130	361	357	—	—	—	—	—	—
CN^-	2.07, 1.97[c]	1.90_5, 1.86[c]	2119	367	360.5	354	8	4.6	3.8	3.0	~0
$HC{\equiv}C^-$	—	—	2110	377	367	355	—	4.0	2.7	—	—
SO_3^{2-}	—	—	—	372	364	—	4.3	2.7	—	−0.7	~95
$CH_2{=}CH^-$	—	—	2093	393	372	367	2.7	2.3	0.7	<0	~70
CH_3^-	—	—	2088	398	374	372	2.1	2.2	0.1	<0	~90
Co-5′-deoxyadenosyl	2.23	1.94	2091	396	375	—	—	1.3	—	—	—
$CH_3{-}CH_2^-$	—	—	2082	399	~375	—	0.6	0.8	—	<0	~100

[a] Data taken from tabulated lists in Firth *et al.* (*71*, *72*).

[b] Formation constants have not been corrected for the presence of five-coordinate complexes.

[c] First figure refers to the dry, the second to the wet form of cyanocobalamin.

[d] Five coordinate complex in equilibrium with the six-coordinate aquo complex in aqueous solution at room temperature, given as percent.

TABLE XVI

SUMMARY OF EXPERIMENTALLY DETERMINED LIGAND ORDERS

Experimental parameter	Complexes included	Section of chapter	Ligand order[a]	
			Weak donor	Strong donor
Ground-state effects				
Bond lengths	All	II, A	$Cl^- < H_2O, NH_3, NO_2^-, CN^-, SO_3^{2-} < R^* < R^- \ll NO^-$	
IR spectra ($C\equiv N$ stretch)	Pentacyanides and corrinoids	II, B	H_2O, HO^-, NH_3, Bz, $CN^-, Cl^-, Br^- < SO_3^{2-}, I^-, R^* < H^- < R^-$	
Electronic spectra of ligands	Corrinoids	II, D	Donor atoms F, Cl, Br, O, N, C in CN^-, S in NCS^- $<$ C in CH_3^-, etc., $NCSe^-$, I^-, S in SO_3^{2-}, $S_2O_3^{2-}$, RS^- (thiols), tu	
Thermodynamic effects				
Formation constants in octahedral complexes				
trans-X	Corrinoids	III, A, 1	$Cl^-, H_2O, NH_3, CH_3NC < CN^- < Br^-, I^-, R^-, HS^-$, RS^- (thiols), $S_2O_3^{2-}, SO_3^{2-}$, tu, NCS^-	
trans-X	Others	III, A, 2	$H_2O, NH_3 < NO_2^-, CN^-, HO^- \ll SO_3^{2-}$	
cis-L_4	All	III, A, 2	$(H_2O)_4 \ll (NH_3)_4, (CN)_4$, en$_2$, $(DMG)_2$, corrin	
Equilibria between six- and five-coordinate complexes				
trans-X	All	III, B, 5	CN^-, Cl^-, donor atoms N and O $< R^-, SO_3^{2-} < NO^-$	
cis-L_4	All	III, B, 5	$(NH_3)_4$, en$_2 \ll (DMG)_2$, BAE, salen $\leqslant$ corrin $\ll$ dithiolates	
Kinetic effects				
Unidentate X	All	IV, B, 4	$\underline{N}CS^- < H_2O$? $< CN^-, N_3^-, NO_2^-, NH_3, HO^-, Cl^-, Br^-, I^- \ll R^-, SO_3^{2-}$	
cis-L_4	All	IV, B, 4	py$_4$, β/γ-pic$_4$, en$_2$, $(DMG)_2$, ?$(CN)_4 < (NH_3)_4$, ? dipy$_2 \leqslant (H_2O)_4 \ll$ corrin, porphyrin	

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[a] R^- indicates an alkyl ligand; R^* an alkyl ligand with electronegative substituents.

B. COMPARISON WITH THE SPECTROCHEMICAL AND NEPHELAUXETIC SERIES

Ligands affect the energy levels of the *d* orbitals of the transition metal. For octahedral complexes the changes in energy can be represented by ascribing to each ligand two parameters which place it in the order of the spectrochemical and nephelauxetic series. For the case of low-spin, octahedral cobalt(III) cation, the configuration of lowest energy $(t_{2g})^6(e_g)^0$, gives rise to only one term $^1A_1$, while the configuration of next higher energy $(t_{2g})^5(e_g)^1$ gives rise to two singlet terms $^1T_1$ and $^1T_2$ in order of increasing energy (together with the corresponding triplet terms at lower energy, $^3T_1$ and $^3T_2$). The splitting between the $^1A_1$ and $^1T_1$ levels determines the position of the ligand in the spectrochemical series. that between $^1T_1$ and $^1T_2$ its position in the nephelauxetic series. To a first approximation the position of a ligand in the spectrochemical series depends on the nature of the ligand atom and can be written (*106*) $I < Br < Cl < S < F < O < C$ and $Se < S$; CH_3^- as well as CN^- is known to come high in the spectrochemical series (*53*, *84*). There is less information about the nephelauxetic series, but the order appears to be (*106*) $F < O \sim N < Cl < C \sim Br < S \sim Se \sim I$. It has been pointed out (*70*, *72*, *150*) that the order of ligands observed for cis and trans effects in cobalt(III) complexes shows a general similarity to the nephelauxetic series, but none with the spectrochemical series. This is consistent with the conclusions (previous paragraph) regarding the property of the ligand which determines its position in the cis and trans effect order, since the nephelauxetic series is probably also determined by the amount of negative charge donated by the ligand to the metal (*106*).

C. COMPARISON WITH PLATINUM(II) COMPLEXES

By far the greatest amount of information on cis and trans effects in other complexes refers to square planar complexes of platinum(II), in which the phenomenon of the trans effect was first noticed. Platinum(II) complexes show interesting differences from cobalt(III) complexes. First, the effects *appear* to be more strongly trans directed in the platinum(II) complexes, but there is insufficient evidence on the directional nature of strongly activating ligands such as CH_3^- in the cobalt(III) complexes to allow one to draw any final conclusions. Second, the generalized trans effect order of ligands in platinum(II) complexes is CO, CN^-, $C_2H_4 > PR_3$, $H^- > CH_3^-$, $SC(NH_2)_2 > C_6H_5^-$, NO_2^-, I^-, $SCN^- > Br^-$, $Cl^- >$ py, NH_3, HO^-, H_2O (*31*), which is slightly different from the order found for cobalt(III) complexes. Neglecting CO, C_2H_4, and PR_3, which have not yet been placed in the order for cobalt(III) complexes, the most interesting difference is the high position of CN^- and NO_2^-; the two orders are otherwise fairly similar. In octahedral Pt(IV) complexes, on the other hand, both CN^- (*25*) and NO_2^- (*57*, *181*) show a much smaller trans-labilizing, i.e., kinetic, effect. It is interesting that CO (but not PR_3) also exerts a much smaller trans effect in octahedral Ir(III) complexes (ground-state effect, as shown by IR spectra) and Ru(II) complexes (ground-state effect, as shown by IR; also kinetic) (*99*, *100*, *120*). In this respect all the octahedral d^6 metal ions, Co(III), Ru(II), Ir(III), and Pt(IV), show common features which distinguish them from the square planar d^8 Pt(II). All three ligands have the ability to form metal-to-ligand π bonds, and the obvious explanation is that in the octahedral complexes the trans effect of CN^-, NO_2^-, and CO is due mainly to their σ-donor strength and is therefore small, whereas in the d^8 Pt(II) complexes, where the increased electron density on the metal would favor metal-to-ligand π bonding, both σ-donor and π-acceptor capacities play their part and result in a high trans effect.

Comparison of cobalt(III) and platinum(II) complexes, therefore, provides further evidence for the duality of mechanism (σ and π) for the trans effect in the latter and shows that there is no single order of ligands which can be transferred from one metal cation to another. A comparison of the ligand orders observed for different metal cations should lead to a much better understanding of the importance of different types of bonds between the metal and ligand, and hence of the chemical properties of complexes. It is hoped that this review will stimulate interest in obtaining more experimental data on cis and trans effects in complexes of other metal cations.

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