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Metal Ion Control of Chemical Reactions

Metal ions control many kinds of chemical reactions by acting as substituents on reactive ligands.

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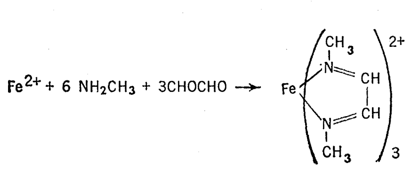
In seeking to elaborate the ways in which metal ions may affect chemical reactions, it seems useful to classify first according to the intimacy of the interaction between metal atom and reactants. Three levels of interaction are evident. In many processes the metal ion serves to alter the character of the medium by changing ionic strength, solvent structuring or destructuring, and possibly other characteristics of the medium, all of which require only long-range interaction between metal ion and reactant. These influences are left for others to treat. In this article attention is focused on metal ion effects at two more intimate levels of interaction. In the second category of interaction the metal ion serves as a reactant. Rather than merely determining the environment within which a given process occurs (the first category), the metal ion in this case is a projectile which produces reaction when it encounters the substrate. The morphological criterion for this category of effect is the initiation of chemical reaction upon contact between substrate and metal. Finally, the third level of interaction involves prior association of the metal ion with a substrate that is to undergo subsequent reaction, either unimolecularly or upon encounter with suitable reagents. Here the metal ion is a substituent, and it is precisely by examination of this category of interaction that the natures of metal ion influences on chemical reactions are most readily evaluated.

Much attention is given today to the subject of homogeneous catalysis, particularly in processes involving metal ions and metal complexes. Reactions of many enzymes that are activated by metal ions may be included under this heading. Clearly, those processes that are truly activated by metal ions must be describable in terms of either or both of the categories of metal ion effects stated here, that is, metal ion derivatives as reagents or metal ion moieties as substituents. By comparison with a single-step process such as might be used to delineate a particular metal ion capability, catalytic processes are, of necessity, multistep processes, since recycling of the catalyst must occur. A catalytic reaction must involve at least two steps. These minimum steps are (i) encounter and alteration of the substrate of interest by the catalyst entity and (ii) restoration of the catalyst to its original condition. Frequently, the complex-forming process is of importance, and homogeneous processes involving metal ion catalysts regularly require at least three clearly definable steps: (i) in a first step the metal atom coordinates to a substrate molecule, either with or without alteration of that substrate; (ii) the complex then encounters a reagent and undergoes chemical change; (iii) thereafter, the complex is disassembled and the metal atom moiety is restored to its original catalyst form. This part of the process may require additional reactions, with or without external reagents, or it may reflect a competition between product and solvent, other ligands, or reactants for coordination sites. Certain minimum criteria must be met in order for these processes to be catalytic. (i) The system is trivial unless there is an appreciable effect on mechanism. The usual reaction path may be greatly accelerated by stabilization of the transition state or destabilization of a reactant, or an unusual reaction path may be followed because of extreme stabilization of its transition state through formation of an unusual intermediate, or by virtue of some polyfunctional or stereochemical consequence of coordination. (ii) Inherent in the requirement that the process must cycle is a further requirement that the metal ion be labile toward at least a certain class of reaction, perhaps substitution or, maybe, oxidative addition and reductive elimination. The hypothetical, but not unreasonable, reductive alkylation of methylamine brought about by the formation and hydrogenation of Schiff base–iron (II) complexes provides a useful illustration. Divalent iron shows a marked affinity toward coordination with α-diimines (*1*) but relatively little affinity for saturated amines. For example, $Fe(NH_3)_6{}^{2+}$ and $Fe(en)_3{}^{2+}$ (where "en" represents ethylenediamine) are best prepared under anhydrous, anaerobic conditions. In consequence of these relative affinities, it is not surprising that the reaction given in Eq. 1 occurs.



$$Fe^{2+} + 6\ NH_2CH_3 + 3CHOCHO \rightarrow \left[Fe(CH_3N{=}CH{-}CH{=}NCH_3)\right]_3^{2+} \tag{1}$$

It must also be realized that the ligand molecule, $CH_3{-}N{=}CH{-}CH{=}N{-}CH_3$, is not particularly stable and generally is not the final product of the pure

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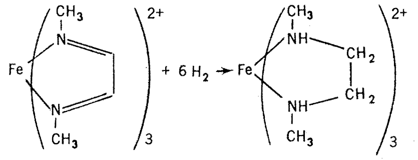
organic system. This system tends, rather, to yield dark insoluble resinous products produced by further condensation. Therefore, at this stage of the reaction, the system does have certain characteristics that are usable in a homogeneous catalytic process. At the least, the system promotes the formation of a fragile molecule. However, the process cannot be used to produce catalytically a Schiff base of this sort because it is not well set up to cycle. The product chelate is stable in the solution since neither methylamine nor solvent will displace the α-diimine from Fe^{2+}. The addition of one more reaction step makes the process cyclic. If the α-diimine complex is hydrogenated (Eq. 2), the ligand is converted to a diamine.



(2)

In view of the ligand preferences of Fe^{2+}, solvent then displaces the product ligand, solvated Fe^{2+} is regenerated, and the catalyst is available for another cycle. There almost certainly would be difficulties in trying to operate continuously the system described here. It is chosen for illustrative purposes only. An additional distinction that should be clear at this stage is that between a "metal ion–promoted process" and a "metal ion–activated catalytic process." Equation 1 taken alone represents a metal ion–promoted process. When viewed overall, homogeneous catalytic processes are indeed multistep *processes* and not single chemical reactions. Each step may be a chemical reaction of importance to those concerned with the broader and more fundamental realm of metal ion effects on chemical reactions.

It is desirable to adopt an overall perspective on species containing metal atoms that may participate in chemical reactions. The terms "ligand reactions" and "homogeneous catalysis by metal ions" should not cause one to conjure up a vision of a positively charged metal ion operating in rather close analogy to a proton. Such an orientation is too limited. It is useful to think of the ways in which metal atoms in their various oxidation states resemble protons, for this causes us to enumerate certain properties of metal ions that lead to the further classification and organization of metal ion effects on chemical reactions. A metal atom, like a proton, may be positively charged—but it could also be negatively charged or electrically neutral. The fact that a metal ion can have several electronic units of charge in contrast to the proton's unit charge is overbalanced by the fact that metal ions are of the order of 10,000 times larger than protons. Of course, a proton is much more effective than a metal ion at polarizing the electron cloud of a substrate, unless the metal ion is itself greatly polarized, in which case the substrate's electrons are exposed to much enhanced polarizing forces. Other contrasts between protons and metal ions are more revealing and useful.

All metal ions are infinitely (almost) *softer* than protons. The fact that metal ions possess electrons must be considered prima facie invalidation of almost all appeals to proton behavior in attempting to rationalize the function of metal ions in various reactions. This conclusion is attested to by the fact that metal atoms are not restricted to functions in which they withdraw electron density; they may also donate electron density or "whole" electrons to reactants or substrates, whereas protons obviously cannot. Further contrast arises from the variety of types of symmetry of the orbitals on metal atoms. Metals may form both σ and π bonds, whereas hydrogen may use its 1*s* orbital to form only σ bonds.

Finally, metal atoms are polyfunctional in numerically and geometrically distinct ways. Although hydrogen can form hydrogen bonds between polar groups or three-center bonds in electron-deficient structures, it simply does not possess the multisite capability for forming several electron-pair bonds in clearly definable geometric juxtaposition.

Metal Atoms as Substituents on Reactants

In considering the various roles metal atoms may play in the reactions of substrates to which they are bound, it is useful to refer back to introductory comments concerning the general characteristics of metal atoms. A metal atom may either donate electron density to or withdraw it from the ligand to which it is bound. It may do so by means of either the σ electron system or the π electron system. Furthermore, metal atoms characteristically form numbers of bonds dictated by their coordination numbers. Consequently, metal atoms are multisite substituents and, since these sites are disposed in accord with the geometry of the metal's coordination sphere, geometric relationships may contribute to the metal ion effect. Effects that can be understood on the basis of interactions between the substrate and a single site on the metal ion will be considered first.

Single-site effects—electron withdrawal. An abundance of examples is available to illustrate the capacity of positive metal ions to withdraw electron density from a substrate by way of σ-bond formation. Most dramatic is the masking of electron pairs of nucleophiles, such as NH_3, through coordination. In $Co(NH_3)_6{}^{3+}$ six ammonia molecules have lost all their basicity and used up all their nucleophilic character. Cyanide is another popular example of a species that undergoes masking through coordination. The work of E. G. J. Hartley *et al.*, F. Hölzl *et al.*, and others has been summarized earlier (*2; 3*, p. 7). The classic synthesis of isonitriles (Eq. 4) requires the use of AgCN, whereas the corresponding reaction of an alkyl halide (RX) with group I A cyanides (Eq. 3) yields nitriles (*4*).

$$NaCN + RX \rightarrow RCN + NaX \quad (3)$$

$$AgCN + RX \rightarrow RNC + AgX \quad (4)$$

The distinction between these two reactions arises from the fact that the cyanide ion coordinates to the silver ion through the electrons of the carbon atom. As a result, the carbon atom is not available for further reaction and the nitrogen terminus of the anion must serve as the nucleophile when the alkyl halide is presented for reaction. This reaction pathway is emphasized by the fact that the isonitrile is usually isolated as the complex RNC–Ag–X. The free cyanide ion (in the case of NaCN) uses the carbon extremity as a nucleophile so that its reaction with an alkyl halide produces a nitrile. The generality of these relationships is shown by the fact that a large number of metal complexes of isonitriles may be produced by the alkylation of appropriate cyanide complexes. Equation 5 outlines the general reaction.

$$M(CN)_m^{q-} + nRX \longrightarrow M(CNR)_n(CN)_{m-n}^{(q-n)-} + nX^- \quad (5)$$

Among the metals participating in this reaction are Hg, Cr, Mo, W, Fe, Ru, and Co (*5*). Many of the reaction conditions that have been employed with such reactants as $Fe(CN)_6{}^{4-}$ yield mixtures that are difficultly characterized, and the earlier literature contains some archaic formulations. However, under certain conditions different extents (*6*) of alkylations can be obtained (Eqs. 6 to 8).

$$Ag_4Fe(CN)_6 + 4C_2H_5I \rightarrow [Fe(CNC_2H_5)_4(CN)_2] + 4AgI \quad (6)$$

$$K_4Fe(CN)_6 + 6(CH_3)_2SO_4 \rightarrow [Fe(CNCH_3)_6]^{2+} + 6CH_3SO_4^- + 4K^+ \quad (7)$$

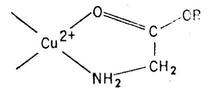
$$K_4Fe(CN)_6 + 5C_6H_5CH_2Br \rightarrow [Fe(CNCH_2C_6H_5)_5CN]Br + 4KBr \quad (8)$$

The consequences of the nonlability (toward substitution) of the iron(II) atom are obvious. The neutral compound $Fe(CNCH_3)_4(CN)_2$ exists in *cis-trans* isomeric forms and can be converted to the isomeric forms of mixed isonitrile complexes (Eq. 9).

$$Fe(CNCH_3)_4(CN)_2 + 2C_2H_5I \rightarrow [Fe(CNCH_3)_4(CNC_2H_5)_2]I_2 \quad (9)$$

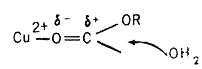
Reactions of either of the two isomers with CH_3I yields the same product, $[Fe(CNCH_3)_6]I_2$.

Electron withdrawal—promotion of electrophiles. Because of their charges, cations are intrinsically electrophilic. It follows that the binding of a functional group to a cation should enhance any electrophilic center that is associated with the group. In the course of extensive studies on the influence of metal ions on the nucleophilic substitutions at the carbonyl groups of amides, peptides, and the esters of amino acids, it has been shown that the carbonyl group coordinates (*7*) as shown in structure **I**.



I

The rate of hydrolysis of ethyl glycinate under this influence of the Cu^{2+} ion is 1.3×10^5 times faster than that of the free ester and 3.1×10^3 times faster than that of the protonated ester (*8*). Clearly, the accelerating influence arises from polarization of the carbonyl linkage by attraction of the electrons toward the oxygen atom. This polarization leaves the carbon atom more positive and facilitates its acceptance of the electrons of a nucleophile (structure **II**).

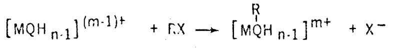


II

Electron withdrawal—promotion of nucleophiles. The suggestion that electron withdrawal can promote a nucleophile seems to represent an anomalous situation when applied literally to the elemental substitution process. Electron withdrawal must certainly decrease the availability of a given electron pair. Certain phenomena do, however, appear to be well described by the title of this section. In general, the phenomenon is manifested in multistep processes wherein the metal ion promotes dissociation of a hydrogen ion from a nucleophile (Eqs. 10 and 11). The product conjugate base then serves as a nucleophile toward some substrate (Eq. 12). Here Q represents the atom that is the basic site in a nucleophilic hydride.

$$M^{m+} + QH_n \rightleftharpoons [MQH_n]^{m+} \quad (10)$$

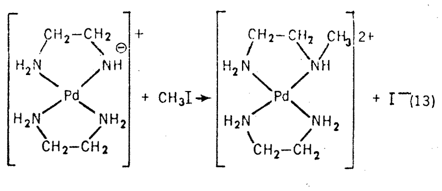
$$[MQH_n]^{m+} \rightleftharpoons [MQH_{n-1}]^{(m-1)+} + H^+ \quad (11)$$



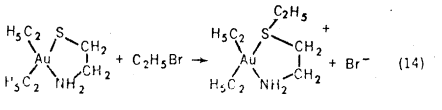
(12)

$$[MQH_{n-1}]^{(m-1)+} + RX \rightarrow [M\overset{R}{Q}H_{n-1}]^{m+} + X^- \quad (12)$$

Coordination of metal ions to such ligands as amines, mercaptans, water, and alcohols generally increases the Bronsted acidity of the hydrogen-containing ligands. The coordinated conjugate bases are known to undergo a variety of nucleophilic reactions (*9*).

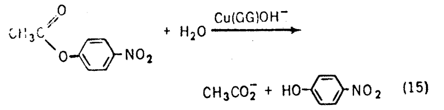


(13)



(14)

It has been pointed out that the acidity of water is increased by about 10^7 upon coordination to Cu^{2+}. The ionization produces a coordinated OH^- ion, and studies (*10*) on the catalyzed hydrolysis of *p*-nitrophenyl acetate have shown that the coordinated hydroxyl group is involved in the case of the glycylglycine (GG) chelate, $Cu(GG)OH^-$.

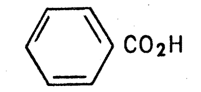
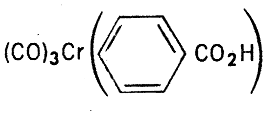
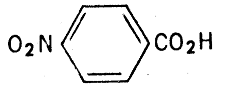


(15)

Thus, although the order of nucleophilic character is $OH^- > Cu^{2+}-OH^- > H-OH$ and the coordinated OH^- is only some 60 times more effective as a nucleophile than H_2O, it is present in much greater concentrations than OH^- at the neutral *p*H of water. It follows that a nucleophilic process has been promoted.

The examples of effects due to electron withdrawal discussed thus far have involved interactions through σ bonds alone. Metal ions may also serve to withdraw charge from a substrate through its π electron system. Perhaps the classic example is dibenzene chromium, the benzene rings of which are not subject to electrophilic attack. On a quantitative basis, the Cr atom has an effect comparable to that of a para-NO_2 group as indicated by the acidities of the compounds listed in Table 1 (*11*).

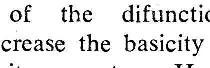
Table 1. Acidities of substituted benzoic acids.

Compound	*pK*
	5.68
	4.77
	4.48

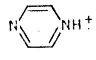
Electron donation. The participation of metal electron pairs of π symmetry in back-donation to appropriate ligands leads to the general expectation that electron-rich metal atoms may donate electron density onto ligands, thereby increasing their reactivities. This is nicely illustrated by the data (*12*) of Table 2. The pK_a values (pK_a is the negative logarithm of the acid constant) refer to the acidities of the various monoprotonated derivatives, for example, Eq. 16.

(16)

All the entries in Table 2, save one, are consistent with the hypothesis that coordination of a positive ion to one nitrogen of the difunctional base should decrease the basicity of the remaining nitrogen atom. However, the Ru(II) complex

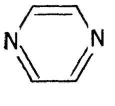
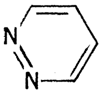
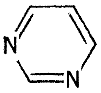


is actually two orders of magnitude less acidic than the conjugate acid of the free base



Clearly, Ru(II) is increasing the basicity of the ligand; that is, it is donating

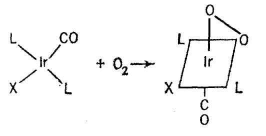
Table 2. Values of pK_a for ruthenium complexes.

Ligand	pK_a		
	Ligand	Ru(II) complex	Ru (III) complex
	0.6	2.5	−0.8
	2.33	0.03	
	1.3	0.00	

electron density to the second nitrogen atom of the base when it coordinates to the first.

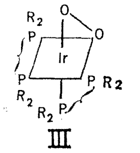
The sensitivity of the trivalent halides of phosphorus to hydrolysis when coordinated to various metal ions also illustrates the effect of electron donation on ligand reactivity. Whereas $PtCl_2(PCl_3)_2$ (*13*) and $AuCl(PCl_3)$ (*14*) hydrolyze rapidly upon exposure to moisture, $IrCl_3(PCl_3)_2$ (*15*) is totally insensitive to water. The fact that $Ni(PF_3)_4$ can be steam-distilled without hydrolysis is probably a reflection of the same phenomenon.

Activation of small molecules. Heavy transition-metal compounds with the electron configurations d^8 and d^{10} often add small molecules with concomitant increases in both their coordination numbers and formal oxidation states. Often the process serves to activate the small molecule toward chemical reaction. The addition of molecular oxygen provides a useful example (Eq. 17).

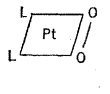


(17)

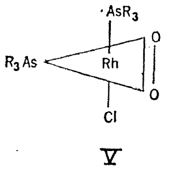
Other products of addition are given in structures **III**, **IV**, and **V**.



III



IV

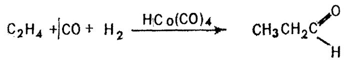


V

A significant threefold correlation exists between the electron-releasing character of the ancillary ligands (L) or the metal ion, or both, the oxygen-to-oxygen bond distance, and the ability of the oxygen complex to oxidize certain substrates under mild conditions. For example, in the oxygenated compound given in Eq. 17, when X = I the O–O bond distance (1.51 angstroms) is greater than when X = Cl ($d_{O\text{-}O}$ = 1.30 angstroms), and the iodide derivative is more effective at oxidizing such nonmetallic oxides as SO_2 and NO_2 (*16*). The effect of coordination on the reactivity of O_2 has an especially interesting aspect. In the heavy transition-metal complexes oxygen exists in a singlet state, and singlet O_2 is expected, on both kinetic and thermodynamic grounds, to be more reactive than the usual triplet form (*17*).

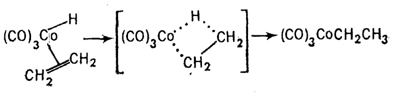
Multisite Effects

Nongeometric processes involving monodentate ligands. There exists a range of important processes in which reactions occur between two (or more) ligands, each of which is (usually) bound to the metal ion through only a single coordination site. Such processes are identified here as nongeometric because the principal need appears to be only that there be two or more coordination sites. In some cases it may not even be necessary for the sites to be adjacent. The overall stereochemistry of the complex is often only of minor importance. The most broadly recognized example is probably hydroformylation. This process involves one of the most basic of all ligand reactions—that union of two ligands within the coordination sphere that has come to be called the insertion reaction. An example of the overall process is given in Eq. 18, where it is shown that, in the presence of $HCo(CO)_4$, ethylene combines with carbon monoxide and hydrogen to form proprionaldehyde.

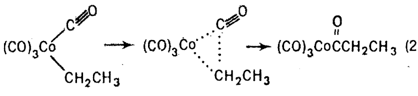


$$C_2H_4 + CO + H_2 \xrightarrow{HCo(CO)_4} CH_3CH_2C\begin{smallmatrix}O\\ H\end{smallmatrix} \qquad (18)$$

The critical insertion reactions are summarized in Eqs. 19 and 20.



(19)



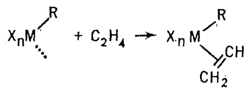
(20)

Table 3. Metal ion promotion of hydrolysis of monoesters of dicarboxylic acids.

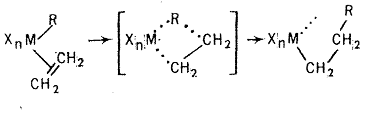
Base	Monoethyl		
	Oxalate	Malonate	Adipate
OH^-	29.2	0.778	2.01
TlOH	1330	5.65	4.37
$BaOH^+$	9200	38.0	
$CaOH^+$		39.8	7.94
$Co(NH_3)_6(OH)_2^+$	1740	16.0	17.1

The reaction of Eq. 19 is preceded by the dissociation of CO from $HCo(CO)_4$ and its replacement by a molecule of ethylene, the latter being coordinated through its π electrons. The first insertion reaction converts "π-bonded" ethylene into the σ-bonded ethyl group by insertion of the C_2H_4 group into the Co–H bond. The immediate product of this insertion is coordinately unsaturated, a condition that is alleviated by coordination of a fourth CO molecule prior to further reaction. The second insertion reaction (Eq. 20) involves an intramolecular process wherein a CO molecule is interposed between the C_2H_5 group and the cobalt atom (*18*).

The generality of the insertion process is evident from the fact that it may be used to explain the Zeigler-Natta catalysis of the polymerization of olefins.

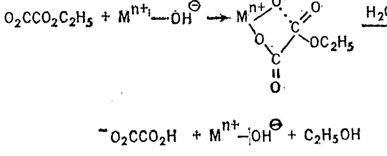


(21)



(22)

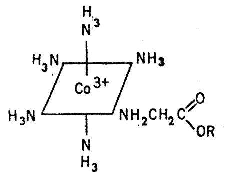
Examples of nongeometric multisite effects dependent on monodentate binding of two or more reactants can also be drawn from the field of nucleophilic substitution reactions. The data of Table 3 for the hydrolysis reactions of the monoethyl esters of oxalic, malonic, and adipic acids are most consistent (*19*) with the mechanism given in Eq. 23.



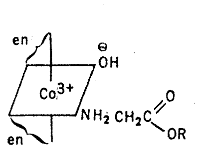
(23)

The multisite effect involves the gathering of the reactive units, OH^- and, for example, $^-O_2CCO_2C_2H_5$, in adjacent coordination sites. For most of the species, a nucleophilic promotion is probably also involved; that is, the metal ion facilitates the dissociation of a proton from H_2O to produce coordinated OH^-. The fact that $Co(NH_3)_6{}^{3+}$ is effective as a catalyst in basic media strongly supports the suggestion that the cation serves mainly to gather the reactants, in this case in an ion cluster that must contain no less than one cation $[Co(NH_3)_6{}^{3+}]$ and two anions (OH^- and $^-O_2CCO_2C_2H_5$).

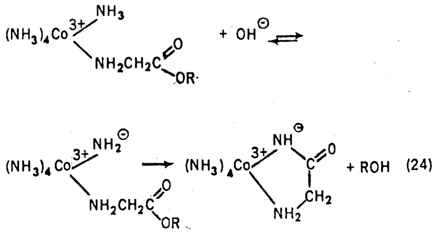
Recent studies (*20*) in which compounds with structures **VI** (*21*) and **VII** (*22*) were used have clearly shown that this class of mechanism operates, as is illustrated in Eq. 24. The inertness of the product makes possible its isolation and characterization.



VI



VII

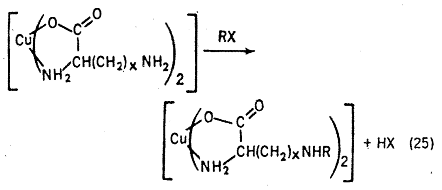


(24)

Nongeometric processes involving chelated ligands. The many roles played by chelation provide one of the most promising areas for rapid progress in the study of metal ion effects on chemical reactions. Even with the restriction that the effects be nongeometric, that is, that they depend only on the availability of a certain number of adjacent sites (usually two), several very general categories of interaction are recognizable. These include masking of normal reactions, activation toward nucleophilic attack (promotion of electrophiles) by polarization by the formation of σ type donor-acceptor bonds, and activation toward electrophilic attack through conjugative π bonding (back-donation).

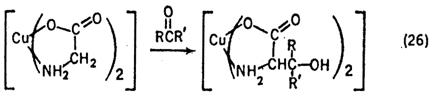
Masking is well illustrated by the classic experiments first performed by Kurtz on α,ω-diaminocarboxylic acids (*3*, p. 120; *23*). Because the α-amino group is well situated to join the carboxyl group in the formation of a five-membered chelate ring, that amino group is perferentially coordinated and prevented from acting as a nucleophile.

The reactivity of the ω-amino group depends on the number of carbon atoms separating it from the α-amino group and the nature of the available metal ion (*24*). In many cases of this type the ω-amino group is still an effective nucleophile (Eq. 25).



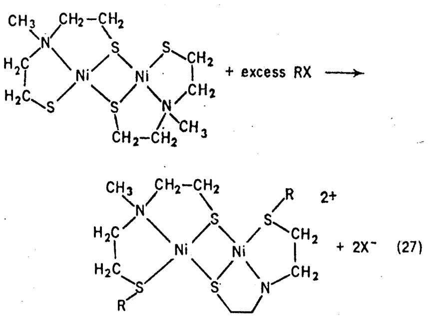
(25)

Application of the Knoevenagel reaction to complexes of α-amino acids illustrates both masking and activation that are concomitant upon chelation through the carboxylate and α-amine functions. The usual condensation of the amino group with the carbonyl group of the aldehyde is prevented by masking. Simultaneously, the electron withdrawal which results from metal ion binding of the two functions adjacent to the CH_2 group greatly enhances the acidity of the CH_2 group (*25*), thereby facilitating reaction at that site (Eq. 26) (*26*).



(26)

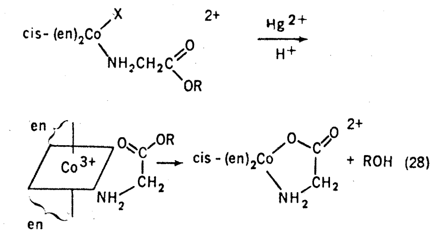
Such a combination of masking and activation is similarly illustrated by the fact that only unbridged coordinated mercaptides act as vigorous nucleophiles. Equation 27 shows the resulting distinction between bridged and terminal groups (*27*) by means of their reactions with alkyl halides.



(27)

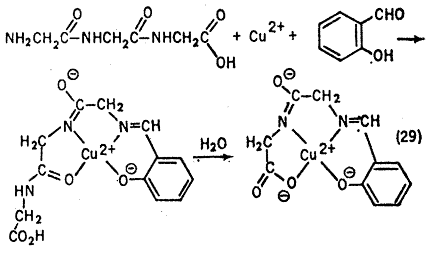
The binding of two Ni^{2+} ions to a single mercaptide apparently decreases the electron density on that function so greatly that it fails to act as a nucleophile.

The combination of chelation and promotion of an electrophile is very well illustrated in the detailed studies on the substitution reactions of amides, simple peptides, and the esters of amino acids (see below). The formation of the critical intermediate shown in Eq. 28 is well established (*7*, *28*).

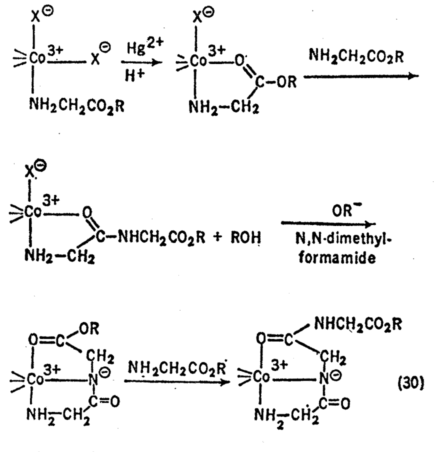


(28)

The way in which the specific number of sites comes into play in determining the characteristics of the reaction and the nature of the product is well illustrated by the absolute requirement for chelation in order to observe the accelerating effect of a metal ion on ester hydrolysis (*29*). For example, Cu^{2+} does not accelerate the rate of hydrolysis of ethyl acetate in acidic aqueous solution, whereas it has a very large effect on the rate of hydrolysis of the ethyl ester of glycine (*29*). As indicated above, two sites on the metal ion must be occupied by the substrate. The availability of three coordination sites has been put to use in the specific production of chelated dipeptides by hydrolysis of higher peptides (Eq. 29) (*30*) and in the stepwise addition of two peptide moieties to the N-terminus of a peptide (Eq. 30) (*31*). In the latter case, the three sites not involved are blocked by the tridentate ligand, diethylenetriamine.

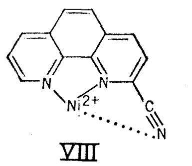


(29)

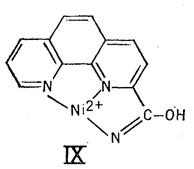


(30)

The hydrolysis of 2-cyano-1,10-phenanthroline provides an example of what is probably a rather different class of activation connected with the demands of chelation (*32*). It is a familiar fact of coordination chemistry that substitution of bulky groups in the 2-position or 9-position, or both, of 1,10-phenanthroline prevents the formation of six-coordinate tris(substituted-phenanthroline) complexes of the usual great stability and limited lability. The presence of the CN group in the 2-position may prevent coordination of one water molecule or, through repulsion, may generate a very long metal–oxygen bond. An appealing model suggests that a water molecule is displaced and that the CN group, although poorly placed for coordination, is still strongly attracted to the metal ion (structure **VIII**). The strain inherent in this interaction is greatly relieved upon the addition of OH$^-$ to the carbon atom to produce a trigonal amide carbon (tautomer) well suited to the coordination of its nitrogen atom to the metal (structure **IX**). Such a process has been related to the so-called "rack-mechanism" for some enzymatic processes wherein the binding of the substrate to an enzyme is presumed to induce a distortion toward the geometry of the transition state.

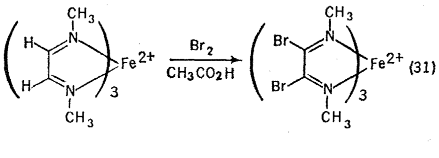


VIII

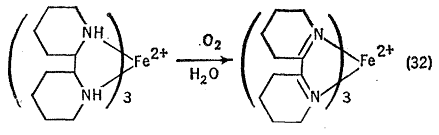


IX

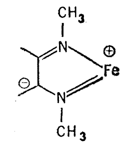
In addition to nucleophilic processes such as those described above, chelation very clearly promotes certain electrophilic substitution reactions. Bayer's example (*33*) is outstanding. He has shown that electrophilic substitution occurs when tris(glyoxal-bis-methylimine)iron(II) reacts with bromine (Eq. 31). This reaction stands in strong contrast to the usual oxidation of Fe^{2+} to Fe^{3+} by Br$_2$ and clearly indicates the high electron density on the chelate ring. This high electron density arises from π back-bonding by means of the *d* electron pairs of the low-spin d^6 Fe^{2+} ion (*34*).



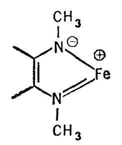
The very existence of these diimine complexes is a reflection of the stabilization of an organic molecule through chelation (*34*). This stabilization is shown emphatically by the ready oxidation of α,α'-dipiperidyl in the presence of Fe^{2+} to form a new chelated ligand having the α-diimine function (Eq. 32).



Here again, the metal ion is not subject to oxidation in such processes (*1*). Both the ligand and metal ion are stabilized by the cyclic resonance of the chelate ring, for example, canonical forms of structures **X** and **XI**.

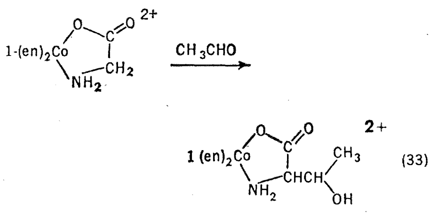


X



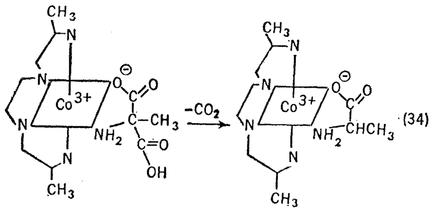
XI

Geometric effects controlled by interactions between nonbonded atoms. Geometric relationships enter into these reactions of coordinated ligands having polyfunctional requirements in two clearly discernible ways. The first to be discussed relates to the influence of the particular atoms bonding the coordination sites utilized in chelation. In the simplest view, these relationships are determined by nonbonded repulsions between the substrate and the atoms of other ligands. Enantiomorphic stereospecificity best illustrates this phenomenon. When an optically active complex is used in the Knoevenagel reaction (see also Eq. 26), evidence (*35*) suggests that the new hydroxyamino acid (usually serine or threonine) is produced with at least partial stereospecific preference of one antipode. Murakami and Takahashi were the first to claim success in such processes as that given in Eq. 33.

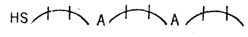


In view of the well-known stereoselectivity of optically active complex ions toward optically active ligands, this effect is to be expected.

An outstanding example of this phenomenon is found in the formation of alanine within a cobalt(III) complex from 2-methyl-2-amino malonic acid by decarboxylation (Eq. 34) (*36*).

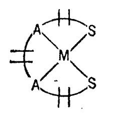


Geometric effects controlled by sites of coordination—template effects. In certain chemical processes a reagent serves to transmit information to a substrate in such a way that the structure of the reaction product is determined. Metal ions are among the simplest reagents of this class. The regular geometries of the coordination spheres of metal ions may be viewed as the sources of geometric information. Ligands bound to these sites have definable mutual geometric relationships. If the ligands undergo reaction while coordinated, these relationships may determine the structure of the final product. As a simple example, let us consider a linear tetrafunctional molecule with good nucleophiles at its extremities (structure **XII**).

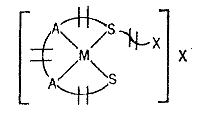


XII

Reaction of such a molecule with a dihalide such as ethylene dibromide under ordinary conditions is expected to yield polymers as the primary products. If this same molecule is bound to four coordination sites about a metal ion, its sulfur atoms are brought into juxtaposition (structure **XIII**). Now the expectations upon reaction with an organic dihalide are quite different. Consider the intermediate formed as a result of displacement of the first halide ion (structure **XIV**).

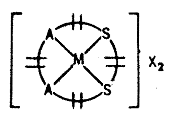


XIII



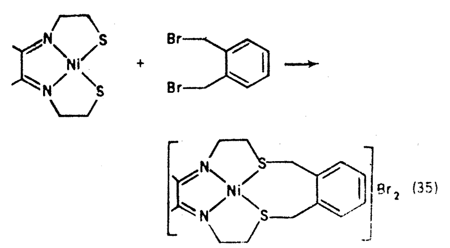
XIV

What is the probability that the second halide will be displaced by the remaining mercaptide within the same complex rather than by a function from a second molecule of the complex? A simple model is useful to illustrate the expectation. One can assume normal bond distances and angles and estimate the average distance of the second halogen-substituted carbon atom from the remaining intramolecular nucleophile. Then, using this crude measure of distance and assuming that the solute molecules occupy cubic close-packed orientations with respect to each other, one may make the simplest possible estimate of the concentration of complex at which the sulfur atom of a second molecule might be as close to the reactive center as is the intramolecular nucleophile. Such estimates yield concentrations of some 1*M* to 10*M*. On this basis, ring closure (structure **XV**) is greatly favored in solutions of even moderate dilution, that is $10^{-1}M$ to $10^{-2}M$.

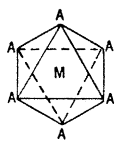


XV

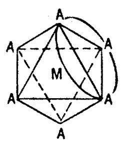
This particular example of the "mechanistic coordination template effect" is well illustrated by Thompson and Busch's synthesis (*37*) of a macrocyclic ligand, with the use of a complex of nickel(II) (Eq. 35).



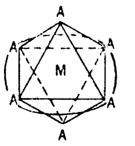
A variety of schemes can be devised to attempt applications of this principle. One of the most intriguing notions is that of polymerization within the coordination sphere. Structure **XVI** illustrates an ordinary octahedral complex having six monodentate ligands bound to the central metal ion. If these ligands can condense with each other, arguments based on probability suggest that they would do so within the coordination sphere of the metal ion to which they are coordinated. If a reagent (ligand) could be chosen such that reaction with itself also served the chain-stopping function, a series of rings should be produced (structures **XVII, XVIII, XIX,** and **XX**), varying in their polydentate character from tridentate through sexadentate. Conceivably, at some point in the polymerization it might become favorable to branch onto a second metal ion so that structures encompassing more than one metal ion might occur.



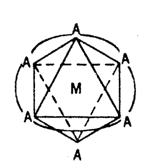
XVI



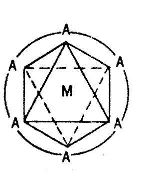
XVII



XVIII

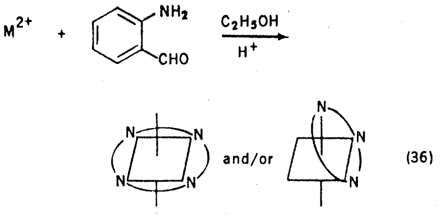


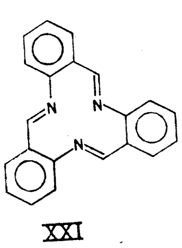
XIX



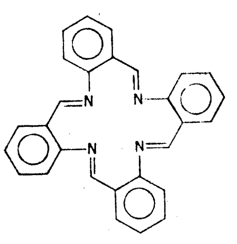
XX

The polymerization of *o*-aminobenzaldehyde in the presence of metal ions constitutes a system that can be rationalized on the basis of the model presented immediately above (*38*). The process is summarized in Eq. 36, and the structures of the cyclic tridentate and tetradentate ligands are presented in **XXI** and **XXII**.



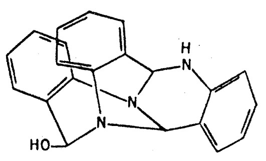


XXI



XXII

In the absence of the metal ion, *o*-aminobenzaldehyde forms very different structures (**XXIII**) which contain no C=N functions but are polycyclic.



XXIII

As predicted (*39*), the application of the hypothesis of a coordination template effect has led to the formation of more complicated polycyclic ligands that completely (*40*) or partially enclose the metal ion (*41*). These clathrochelates illustrate the power of the concept. Although the task would be formidable, metal ion clusters might be used as templates to apply the principles of topology to the construction of large organic molecules of truly exceptional structures.

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Pacific Geomagnetic Secular Variation

A smooth field over the central Pacific for a million years indicates a nonuniform lower mantle of the earth.

Richard R. Doell and Allan Cox

Among the more important recent advances in geophysics has been the discovery that the earth's upper mantle is heterogeneous. There have been several attempts to determine whether the lower part of the mantle is also heterogeneous and to discover something about the shape of the interface between the earth's core and mantle. Geophysical information of two types has been used in this search: seismic signals from earthquakes that penetrate to the core-mantle boundary and changes in the earth's magnetic field (geomagnetic secular variation) as recorded at magnetic observatories and as recorded by remanent magnetism in rocks and archeological objects.

The main difficulty in the seismic approach is that seismic waves passing through the lower mantle must also pass through two different parts of the upper mantle—the first near the source of the signals and the second near the seismic observatory. Therefore, it is difficult to ascribe differences in the time of travel of these waves from source to receiver to heterogeneity along any particular part of the ray path. One may assume (*1*) that the upper mantle is homogeneous and that observed differences in travel time of waves reflected from the core are due to variations of about 100 kilometers in the radius of the boundary between the core and mantle. However, these seismic data fit equally well an earth model in which the core-mantle boundary is smooth and the mantle is laterally inhomogeneous.

In an attempt to reduce this inherent ambiguity of analyzing seismic travel times, Alexander and Phinney (*2*) studied waves that had been diffracted by the core (waves that travel along the core-mantle boundary during part of their propagation); they restricted their attention to a parameter that depends mainly on the diffraction process itself. This parameter is the seismic attenuation coefficient along paths of constant azimuth from an epicenter. Along ray paths diffracted by patches of the core beneath the Pacific Ocean, they found that the attenuation coefficient has certain properties that are missing for rays diffracted by the core beneath the Atlantic Ocean. Various theoretical reasons have been proposed for these differences. For present purposes, however, the importance of this line of research lies less in the details of the models than in the observational evidence that seismic parameters sensitive to physical properties in the lower 200 kilometers of the mantle are different beneath the Pacific and Atlantic regions.

The use of geomagnetic secular variation to determine mantle properties began with the classic determination of Lahiri and Price (*3*) of the electrical conductivity of the upper mantle by use of short-period magnetic waves that originate in the ionosphere. Because electrical induction in the mantle suppresses the propagation of these short-period waves into the mantle, information about the conductivity of the lower mantle has had to come from analyzing magnetic waves generated in the earth's core. In these studies, the electrical induction in the lower portion of the mantle suppresses the shorter-period waves originating in the core and allows the longer-period ones to propagate to the surface (*4*). From spectrum analysis of observatory records over the period range of 40 days to 22 years, Currie (*5*) determined that waves with periods less than about 4 years did not reach the surface, and he used this determination to place constraints on the conductivity structure of the lower mantle. He did not find a significant difference between the spectra of records from different parts of the world; however, he noted that models of lower-mantle conductivity are not unique, owing to uncertainty about the frequency characteristics of the geomagnetic waves originating in the core.

A different approach to interpreting the longer-period part of the geomagnetic spectrum is based on the concept that it is not attenuation in the mantle that might vary laterally but, rather, the frequency characteristics of the sources that produce the geomagnetic waves (*6, 7*). The nature of the magnetic waves originating in the core may be controlled by lateral variations in mantle properties or by undulations of the core-mantle boundary in the following way. An essential feature of theories of the geomagnetic dynamo is partial control by Coriolis forces of the fluid motion of the earth's core; this motion is therefore similar to the planetary movement of the earth's atmosphere, with both motions having approximate symmetry about the earth's rotation axis. Fluid motions in both the earth's core and atmosphere undergo transient departures from axial symmetry because of turbulence and other random processes. These short-term departures

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