RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

March 1970

U. D. C. 541.49 + 541.124/128

Types of Reaction Undergone by Coordinated Ligands and the Factors Influencing the Change in Their Reactivity†

Yu.N.Kukushkin

The influence of the following factors on the reactivity of coordinated ligands (chiefly nitrogen-containing ligands) is examined: 1) the nature of the metal ion; 2) displacement of the electrons of the ligand to the central ion; 3) change in the stability of the complexes formed in the reaction relative to that of the original complexes; 4) the charge of the ionic complexes; 5) the influence of π-dative bonding by one ligand to the central atom on the reactivity of another ligand in the same complex; 6) stabilisation of one of the tautomeric forms of a ligand as a result of complex formation with metal ions; and 7) stabilisation of the deprotonated form of a ligand by complex formation. Examples of the masking of individual functional groups by complex formation and the manifestation of new chemical properties of the ligand as a result of coordination are examined. It is shown that in a number of instances the metal ion can be regarded as a matrix on which the synthesis of an organic molecule takes place. Reactions involving "insertion" into a metal-ligand bond are discussed. The bibliography contains 93 references.

CONTENTS

I.	Introduction	169
II.	Change in the acid-base properties of ligands under the influence of the metal ion	170
III.	Change in reactivity as a result of displacement of the electrons of the ligand towards the central ion	170
IV.	Influence of the charge of an ionic complex on the reactivity of a coordinated ligand	172
V.	Influence of π-dative bonding by one of the ligands to the central atom on the reactivity of another ligand in the same complex	172
VI.	Stabilisation of one of the tautomeric forms of a ligand by complex formation with metal ions	173
VII.	Stabilisation of the deprotonated form of a ligand by complex formation	173
VIII.	Elimination of the characteristic properties of ligands as a result of coordination and the use of this phenomenon to mask individual functional groups	174
IX.	Manifestation of new chemical properties by the ligand as a result of coordination	174
X.	Change in the reactivity of coordinated Schiff's bases	174
XI.	The metal ion as a matrix on which an organic molecule is synthesised	175
XII.	Reactions involving "insertion" into a metal-ligand bond	176

I. INTRODUCTION

In recent years, chemists in various countries have been paying increasing attention to the study of the chemical behaviour of molecules or ions in the inner sphere of complex compounds of various metals; a number of reviews[1-5] and a collection of papers[6] have been published. The chief aim of the study of the reactivity of coordinated ligands is the development of a theory of homogeneous catalysis involving metal complexes. A recent review[7] published in the Soviet Union contains material which is also directly related to this question.

† This review is based on a paper presented at a symposium on "The Properties of Organic Ligands in Complexes with Metals", held at Zelenogorsk (Leningrad) in December, 1968.

The aim of the present review was not to present all the factual material available in the literature. The author has tried, on the basis of specific examples, to demonstrate the factors influencing the reactivity of chiefly nitrogen-containing ligands.

II. CHANGE IN THE ACID-BASE PROPERTIES OF LIGANDS UNDER THE INFLUENCE OF A METAL ION

One of the first chemists to raise the question of the change in the properties of ligands when they are introduced into a complex with metal ions was A. A. Grinberg. As early as 1927, he presented a paper entitled "The Change in the Reactivity of Molecules Bound in Complexes".

No one is now surprised by the fact that ammonia, on entering a complex, "loses" its basic properties and exhibits acidic properties. The theory of the acid-base properties of complex compounds was to a considerable extent developed by Grinberg [8]. It is quite familiar, and there is no need to dwell on it.

The influence of the difference in the mobilities of the protons on the nitrogen atom in various reactions of coordinated ammonia can be demonstrated for the example of its reaction with chlorine. It has been established that an ammonia molecule in the inner sphere of Pt^{IV} complexes can be converted into dichloroamine [9]:

$$[PtCl_3(NH_3)_3]^+ \xrightarrow{Cl_2} [PtCl_3(NH_3)_2(NCl_2H)]^+$$
$$[PtCl_3(NH_3)_2(NCl_2H)]^+ \rightarrow [PtCl_3(NH_3)_2(NCl_2)]^0 + H^+$$

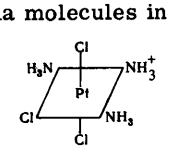
The hydrogen atom in the dichloroamine is so labile that complexes containing the dichloroamido-group NCl_2^- are usually isolated in the solid phase.

Table 1. Acidic dissociation constants of amine complexes of Pt^{IV} and the instability constants of their silver and thallium salts.

Type of complex	K_H^*	K_{Ag^+}	K_{Tl^+}
$[PtCl_2(NH_3)_3(NH_2M)]^{2+}$	6.0×10^{-12}	–	1.5×10^{-4}
$[PtCl(NH_3)_4(NH_2M)]^{3+}$	7.9×10^{-9}	1.3×10^{-8}	(2.0×10^{-6})
$[PtBr(NH_3)_4(NH_2M)]^{3+}$	5.6×10^{-9}	1.2×10^{-8}	–
$[Pt(NH_3)_5(NH_2M)]^{3+}$	1.2×10^{-7}	4.9×10^{-8}	3.6×10^{-4}
$[PtCl(NH_3)_3Py(NH_2M)]^{3+}$	1.2×10^{-7}	5.7×10^{-7}	3.7×10^{-4}
$[PtCl(NH_3)_2Py_2(NH_2M)]^{3+}$	1.6×10^{-6}	2.2×10^{-5}	5.5×10^{-4}
$[PtClPy_4(NH_2M)]^{3+}$	6.0×10^{-5}	3.2×10^{-5}	3.2×10^{-3}

*The acidic dissociation constants are taken from Refs. 19 and 20. The constants for the hexammine is taken from more accurate data [21].

Of the three ammonia molecules in the ion



the greatest lability is shown by the molecule of the Cl–Pt–NH_3 axis. It is this molecule which is converted into dichloroamine. It has been shown [10,11] for a large number of examples that when several coordinated molecules are present, conversion into chloroamines (or bromoamines) is undergone first of all by the molecules in which the protons have the highest lability.

The establishment of the relationship between the acidic properties of complex compounds and the ability of amines to undergo conversion into chloroamines led to the prediction [12,13] of the possibility of preparing chloroamine compounds from amine compounds of palladium(IV), gold(III), and various other metals. A chloroamine compound of palladium was prepared by Babaeva and Khananova [14], and a gold compound by Kukushkin and Zorina [15].

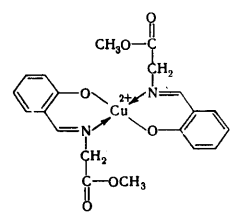
In joint work with Grinberg [16] it was shown that in Pt^{IV} complexes the hydrogen atoms of the ammonia molecules can be replaced by silver, and in work with Rabinovich and Goloseeva [17,18] it was established that this replacement can also be achieved with thallium. It was also shown [17,18] that with increase in the acidic properties of the ammines there is a decrease in the stability of both the silver and the thallium derivatives. For the thallium derivatives, a levelling of the instability constants was observed, but the overall tendency for the stability to change remained.

It can be seen from Table 1 that the silver derivatives are much more stable than the thallium compounds. This corresponds to the stabilities of silver and thallium ammines. The instability constant of $Ag(NH_3)^+$ is 6.3×10^{-4}, and that of $Tl(NH_3)^+$ is 8.3.

The factors determining the acidic properties of amine complexes probably retain their significance in the dissociation of the corresponding silver salts. Two of the main factors influencing the acidic properties of inner-sphere ligands are the charge of the central ion and the charge of the ionic complex. It will be seen from what follows that both of these factors are extremely important for the reactivity of coordinated ligands.

III. CHANGE IN REACTIVITY AS A RESULT OF THE DISPLACEMENT OF THE ELECTRONS OF THE LIGAND TO THE CENTRAL ATOM

Pfeiffer and coworkers [22] carried out the trans-esterification of the ester fragment of the Schiff's base of an aminoacid, coordinated to the bivalent copper ion. These trans-esterifications took place at a much higher rate within the complex

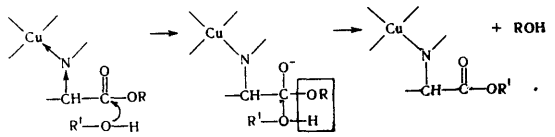


than in the free esters. For example, the replacement of the methoxy group by the butoxy group took place in 10 min in the complex dissolved in butanol.

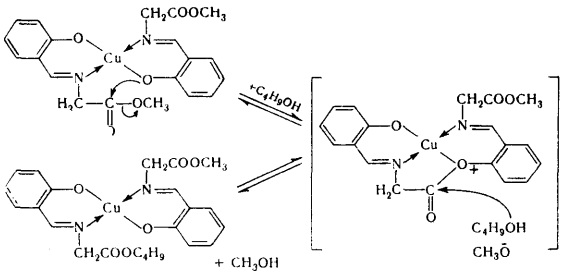
Much later, Verter and Frost [23] continued Pfeiffer's studies with this and similar compounds. In addition to a large number of trans-esterifications within the complexes, Verter and Frost were able to carry out the amidation of coordinated Schiff's bases; in particular, they were able to replace the methoxy group CH_3O by the butylamino group C_4H_9NH.

There are two views regarding the mechanism of these reactions. Martell and Calvin [24] attribute this marked increase in the rate of trans-esterification to the displacement of electrons from the carbonyl carbon towards the copper atom under the influence of the donor–acceptor

bond between the ligand and the central atom. This displacement should facilitate the reaction of the electron-donating oxygen atom of the solvent molecule with the carbon of the carbonyl group. The mechanism of this reaction can be represented schematically as follows:

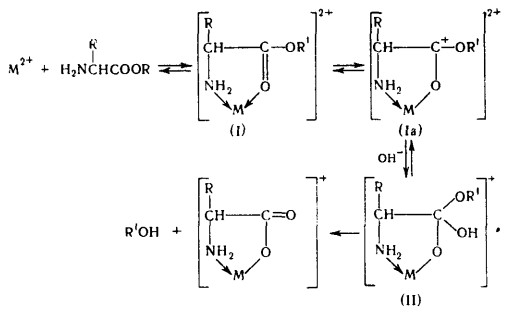


The reaction mechanism proposed by Verter and Frost[23] assumes the mutual influence of the ligands in the complex



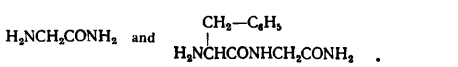
The carbonyl of the ester group is attacked by the oxygen atom of the aldehyde fragment of another ligand with the formation of an intermediate structure of the lactone type. This reaction should be reversible, but with the high active mass of the solvent alcohol it moves preferentially in one direction.

Kroll[25] studied the catalytic action of bivalent heavy metal ions on the hydrolysis of the esters of aminoacids. The rates of these reactions are extremely low in the absence of metal ions, which produce a marked increase in the reaction rates. In Kroll's opinion, the catalytic increase in the rate of hydrolysis of the aminoesters can be explained schematically as follows:

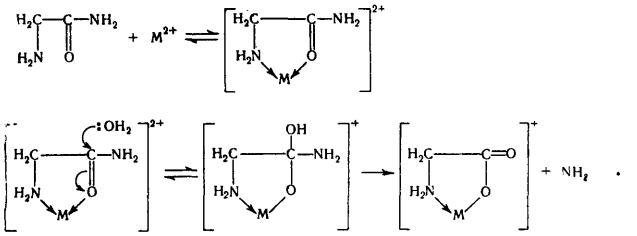


The proposed mechanism is based on the principle that the ligand in the coordinated state (I) and (Ia) exhibits a higher affinity for the hydroxide ion than the free ester. In other words, coordination increases the electrophilic nature of the reaction centre. The intermediate unstable complex (II) decomposes to the alcohol and the complex of the aminoacid, dissociation of which completes the cycle of catalytic reactions. For a series of bivalent ions, Kroll established a correspondence between the tendency to form complexes and the catalytic effect of the ions.

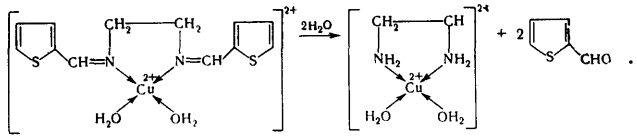
The catalytic influence of Cu^{II} on hydrolysis and isotopic exchange of oxygen in aminoesters was also studied by Bender and Turnquest[26]. Meriwether and Westheimer[27] studied the catalytic influence of bivalent copper, nickel, and cobalt ions on the hydrolysis of the amides



The views of these authors[26,27] regarding the mechanism of the catalysis of these reactions essentially coincide with the mechanism put forward by Kroll[25]. The catalysis of the hydrolysis of aminoacetamide can be represented as follows:

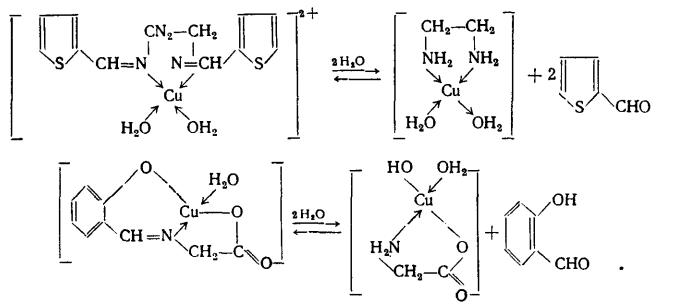


Bailar and Eichhorn[28] established the catalytic action of copper ions on the hydrolysis of the Schiff's base formed from thiophene-2-aldehyde and ethylenediamine:



Under similar conditions but in the absence of Cu^{II}, the hydrolysis of this Schiff's base is very slow. Bailar (like Kroll) considers that the catalytic influence of copper is due to the increase in the electrophilic character of the unsaturated carbon atom as a result of the formation of a donor–acceptor bond. This facilitates attack on the reaction centre by a water molecule.

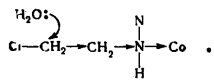
Eichhorn[29] studied the influence of complex formation on the stability, with respect to hydrolysis, of the Schiff's bases formed by thiophene-aldehyde with ethylenediamine and by salicylaldehyde with glycine. He established that copper facilitates the hydrolysis of the former and hinders the hydrolysis of the latter. The hydrolysis of the copper complex of the Schiff's base formed by thiophene-aldehyde with ethylenediamine gives the ethylenediamine complex. Both the initial and the final complexes contain one ring, and the factor determining the relative stability of these complexes is the electron distribution.



As a result of the hydrolysis of the Schiff's base formed by salicylaldehyde and glycine, the complex is converted from a dicyclic to a monocyclic compound. The difference in the stabilities of the dicyclic and monocyclic complexes probably has a greater influence on the reactivity of the original compound than the change in the polarisation of the nitrogen atom. Thus this example shows the need to make allowance for another factor—*the stabilities of the original complexes and reaction products*.

The influence of coordination on the hydrolysis of halogenoalkylamines has been studied[30]. It has been established that in the ionic complex $[Co(H_2O)(Cl{-}CH_2{-}CH_2{-}NH_2)en_2]^{3+}$ the hydrolysis of β-chloroethylamine is 50 times more

rapid than the hydrolysis of the free halogenoalkylamine. The displacement of the electron pair of the nitrogen atom towards the cobalt as a result of the formation of a donor–acceptor bond acts like an inductive effect

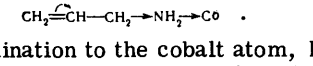


The influence of the coordination of unsaturated aliphatic amines on the addition of hydrogen halides to the amines has been studied[31]. It has been shown that allylamine in the complex *cis*-$[CoCl_2(NH_2CH_2CH{=}CH_2)]Cl_2$ gives a mixture of the γ- and β-isomers. The relative quantities of the isomers obtained from free and coordinated allylamine are given in Table 2.

Table 2. Influence of coordination on the order of attachment of hydrogen halides to allylamine.

Compound	Hydrogen halide	Relative concentration	
		β-isomer, %	γ-isomer, %
$CH_2{=}CHCH_2NH_2$	HCl	55	45
$[CH_2{=}CHCH_2N(C_2H_5)_3]Cl$	HCl	17	83
cis-$[CoCl(CH_2{=}CHCH_2NH_2)en_2]Cl_2$	HCl	42	58
cis-$[CoBr(CH_2{=}CHCH_2NH_2)en_2]Br_2$	HBr	38	62

Thus the displacement of electrons towards the cobalt directs the addition along a path which does not correspond to Markovnikov's rule

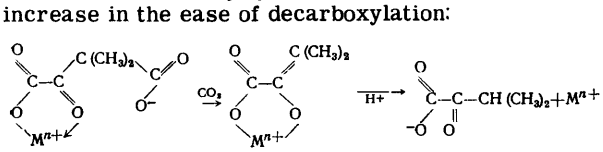


The effect of coordination to the cobalt atom, however, is much weaker than the effect produced by the attachment of a proton to the amino-group.

A large number of published papers have been devoted to the catalytic decomposition of ketoacids under the influence of both enzymes and ions of various metals. Catalysis of the decarboxylation by metal ions is observed for di- and tricarboxylic ketoacids. The rate of the decarboxylation of monocarboxylic ketoacids or nitroacetic acid is not increased by metal ions, and is sometimes even decreased[32,33].

The decomposition of α,α-dimethyloxalacetic acid[34,35] and oxalacetic acid[32,36-42], and the catalytic decarboxylation of acetonedicarboxylic acid[43] and oxalosuccinic acid[37] have been studied.

The mechanism of the decarboxylation is probably the same for these acids. Many authors are of the opinion that an intermediate chelate complex is formed in the decarboxylation. This was first shown in Refs. 34, 35, and 37. A decarboxylation mechanism was proposed by Steinberger and Westheimer[35], who consider that the formation of coordinate bonds by the dicarboxylic acid with the metal ions leads to withdrawal of the electrons from the non-coordinated carboxyl group. This is the reason for the increase in the ease of decarboxylation:

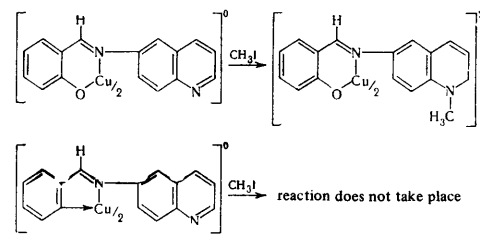


With ketoacids, which can give an enol form, the initial formation of an enol chelate is assumed.

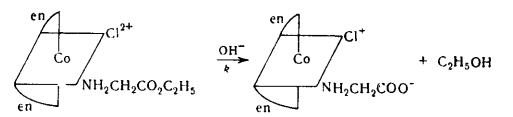
Pedersen[33,38] also considers that a reason for the spontaneous decomposition of nitroacetic acid is the displacement of the electrons from the carboxyl group to the nitro-group. The mechanism of catalysis examined above explains the decrease in the rate of decarboxylation of monocarboxylic acids (or the absence of catalysis) under the influence of metal ions. In this instance the attachment of the metal leads to a displacement of electrons towards the carboxyl group.

IV. INFLUENCE OF THE CHARGE OF THE IONIC COMPLEX ON THE REACTIVITY OF A COORDINATED LIGAND

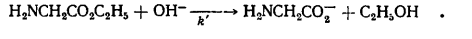
A striking example of the influence of the charge of an ionic complex on the reactivity of a ligand is provided by the alkylation of the nitrogen atom in a quinoline group. Thus it has been shown[44] that the alkylation of this group by methyl iodide in a neutral complex is comparatively rapid, whereas almost no alkylation takes place in a cationic complex



Hay and coworkers[45,46] showed that in a cationic complex with Co^{III}, ethyl glycinate is hydrolysed with a rate constant $k = 3.5 \times 10^3$ litre mole^{-1} min^{-1}:



Under the same conditions, the rate constant for the the hydrolysis of the free ester is $k' = 38$ litre mole^{-1} min^{-1}:

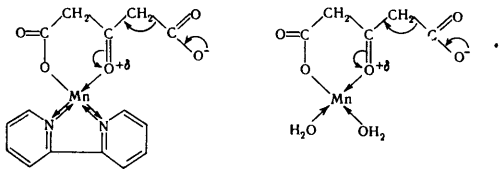


Thus the introduction of the ester into an ionic complex of Co^{III} with a charge of +2 increases the reaction rate by a factor of about 100. This effect can be attributed to electrostatic interaction: the positive charge of the complex facilitates attack by the hydroxide ion.

V. INFLUENCE OF π-DATIVE BONDING BY ONE OF THE LIGANDS TO THE CENTRAL ATOM ON THE REACTIVITY OF ANOTHER LIGAND IN THE SAME COMPLEX

It has been established[43,47] that the 1,10-phenanthroline complexes of Mn^{II} have a much higher catalytic activity with respect to the decarboxylation of dicarboxylic acids than the hydrated maganese ion. An analogous phenomenon was observed by Hay and Leong[48], who showed that the decarboxylation of acetonedicarboxylic acid in the

2,2′-bipyridyl complex of Mn^{II} is about 10 times more rapid than that in the corresponding aquo-complex.

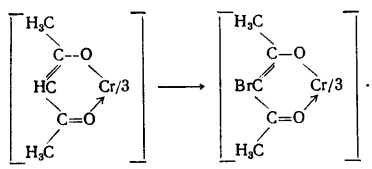


The authors cited consider that the increase in the reaction rate is due to the formation of a π-dative bond by manganese with 1,10-phenanthroline or 2,2′-bipyridyl. The formation of a π-dative bond should increase the positive effective charge of the central ion and hence facilitate decarboxylation.

VI. STABILISATION OF ONE OF THE TAUTOMERIC FORMS OF A LIGAND BY COMPLEX FORMATION WITH METAL IONS

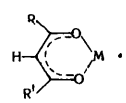
Grinberg and coworkers[49] studied the hydrolysis of dimethyl hydrogen phosphite in the free state and in a platinum(II) complex, and concluded that in dimethyl hydrogen phosphite coordinated to Pt^{II}, the phosphorus atom is in the tervalent state, whereas in the free acid it is in the quinquevalent state. As a result, the coordinated acid has a much stronger acidity than the free acid.

β-Diketones provide the classical example of keto–enol tautomerism. The enol forms have a high tendency to form complexes. The first study of the reactivity of coordinated β-diketones (more accurately, their enol forms) was apparently that of Reihlen[50], who established that the action of bromine on the acetylacetonato-compound of chromium (in alcoholic solution) leads to the replacement of the hydrogen on the central carbon atom by bromine:

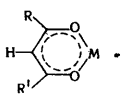


At the time, Reihlen regarded this reaction as confirming Mayer's hypothesis regarding the reactivity of keto–enol forms in tautomeric equilibrium.

In recent years, the complexes of metals with β-diketones have been attracting the attention of chemists from the theoretical viewpoint. Structural data show that the C–C, C–O, and M–O distances in β-dicarbonyl chelates are equivalent[51]. On this basis, the β-dicarbonyl chelates are regarded as forms stabilised by resonance:

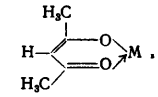


Some authors go further, and regard the β-dicarbonyl complexes of metals as pseudo-aromatic compounds[52]:



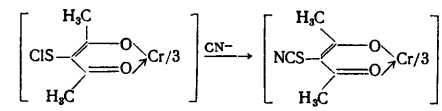
On this basis, many authors are studying the replacement of hydrogen in the pseudo-aromatic ring: halogenation, acetylation, nitration, and the introduction of thiocyanato-groups into the aromatic ring[52–58].

Kluiber[59] studied the action of sulphur dichloride on compounds with the general formula

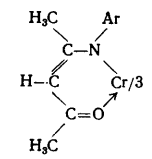


This reaction was studied for the acetylacetonato-compounds of Al^{III}, Cr^{III}, Co^{III}, and Be^{II}. This study showed that the hydrogen on the central carbon atom can be replaced by the –SCl group. An interesting feature is that the usual products of the reaction of sulphur dichloride with enols similar to acetylacetone are sulphides. It is believed that sulphides are formed through an intermediate R–SCl compound. In Kluiber's opinion, the preservation of the –SCl group in this instance is due to the steric protection of this group by the adjoining methyl groups.

The action of cyanide ions on the chromium complex obtained in this way converts the –SCl group into a thiocyanato-group according to the scheme



The same chromium compound was also obtained by the direct reaction of the acetylacetonato-compound of chromium with thiocyanogen. Collman and Kittleman[60] prepared a large number of complexes of Cr^{II} with β-ketoimines with the general formula



The central carbon atom in the β-ketoimines in the chromium complexes, as in the complexes formed by β-diketones, undergoes bromination by N-bromosuccinimide. Nitration and formylation of inner-sphere β-ketoimines does not take place, however, because of the lower stability of the ketoimine complexes compared with the compounds formed by the diketones.

VII. STABILISATION OF THE DEPROTONATED FORM OF A LIGAND BY COMPLEX FORMATION

It is known that the azo-coupling of derivatives of phenol and diazonium ions takes place more readily in alkaline medium, because of the high reactivity of the corresponding phenolato-compounds. Azo-coupling often does not take place at all in acid medium. Kuznetsov[61] gives a number of examples of the influence of complex formation on the ability of various derivatives of phenol to undergo azo-coupling. Thus pyrocatechol in acid solutions is almost unable to couple with diazobenzenesulphonic acid. In the presence of salts of gallium, aluminium, and more particularly zirconium and germanium, azo-coupling takes place even in the presence of mineral acids. Moreover, the production of azo-compounds from, for example, pyrocatechol in alkaline medium is made difficult by its oxidation under the influence of the diazonium ion, and this decreases considerably the yield of the product. In the presence of the ions of the above metals, oxidation of pyrocatechol by diazonium salts does not take place. The influence of metals on this reaction is associated with the

formation of inner-complex salts, in which the proton of the phenol group is replaced by a metal ion.

Like pyrocatechol, 8-quinolinol undergoes almost no coupling with diazobenzenesulphonic acid in mineral acid, but this coupling takes place when the 8-quinolinol is combined in a copper complex.

Azo-coupling is not facilitated by complex formation with all metals, however. The rate of the reaction of 8-quinolinol with diazobenzenedisulphonic acid is decreased by aluminium salts. In the presence of aluminium salts, this reaction takes place very slowly, even in the presence of sodium acetate. Kuznetsov attributes this to the difference in the nature of the O–Cu and O–Al bonds. This sharp difference, however, may be due to the higher charge of the aluminium complex compared with the copper complex. A higher positive charge on the complex should hinder the attack of the diazonium cation on the coordinated 8-quinolinol molecule.

An example of the influence of a metal ion on reactivity as a result of stabilisation of the deprotonated form of a ligand is provided by the reaction of 4-dimethylaminophenyldiazonium chloride with chromotropic acid. The dye is obtained in 58% yield, the substitution taking place in the 4-position of chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid). When the calcium complex of this acid is used, the yield can be increased to 90%.[62]

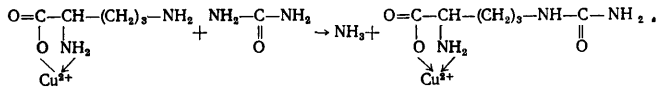
The halogenation (chlorination and bromination) of 8-quinolinol in its complexes with Cr^{III}, Co^{III}, Fe^{III}, and Cu^{II} gives the same products as the halogenation of free 8-quinolinol (for example, 5,7-dichloro-8-quinolinol). Jones[63] reports that in the chlorination of free 8-quinolinol, the yield of the dichloro-derivative does not exceed 30%. In the chlorination of inner-sphere 8-quinolinol, however, the yield of the dichloro-derivative is 80–90%. Jones also attributes this to the presence of the phenolato-form in the complex. Moreover, the metal protects the functional groups from oxidation.

Fernando and coworkers[64] emphasise that the influence of complex formation on the reactivity of aromatic ligands should be estimated not only from the reaction products, but also on the basis of a quantitative comparison of the reaction rates[65,66]. Quantitative studies[64] showed that the rate of the iodination of 8-quinolinol-5-sulphonic acid decreased on formation of complexes. The influence of the complex-forming species was established, and it was also possible to arrange the metal ions in the order of their decreasing influence: $Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Zn^{2+} > Mn^{2+}$.

VIII. ELIMINATION OF THE CHARACTERISTIC PROPERTIES OF LIGANDS AS A RESULT OF COORDINATION AND THE USE OF THIS PHENOMENON TO MASK INDIVIDUAL FUNCTIONAL GROUPS

On coordination, amines may lose the properties associated with the presence of the free pair of electrons. The nitro-group in Pt^{IV} complexes can no longer be oxidised by permanganate. The toxicity of the cyanide ion is reduced or eliminated completely. The fact that complex formation may eliminate completely the ability of various functional groups to react, without altering significantly the reactivity of non-coordinated functional groups, particularly if these are at a distance from the point of coordination, makes it possible to use this phenomenon in preparative work.

For example, it is believed that citrulline $H_2NCONH(CH_2)_3CH(NH_2)COOH$ is present in various proteins, in which it takes part in the formation of urea. Kurtz[67,68] carried out this reaction in the opposite direction by means of complex formation. He prepared the copper complex of ornithine (as a result, the α-amino-group was masked) and carried out the condensation of this complex with urea:

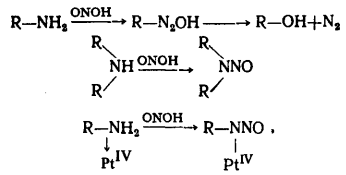


The copper was then removed from the complex by the action of hydrogen sulphide, to give citrulline. Kurtz prepared various aminoacids in this way. The efficiency of the masking action of the metal ions depends to a marked extent on the stability of the complex.

IX. MANIFESTATION OF NEW CHEMICAL PROPERTIES BY THE LIGAND AS A RESULT OF COORDINATION

An example of the manifestation of new chemical properties by a ligand is provided by the azo-coupling of 1,10-phenanthroline and diazosulphanilic acid. 1,10-Phenanthroline cannot couple with diazonium salts, but in its complex with bivalent iron it undergoes vigorous coupling with the diazonium salts of sulphanilic acid and *p*-nitroaniline-*o*-sulphonic acid[69].

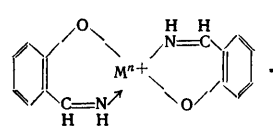
It is well known that the nitrosylation of free primary amines gives unstable diazo-compounds, which decompose with the formation of an alcohol and the liberation of nitrogen, whereas secondary amines form stable nitroso-compounds:



Chernyaev and Andrianova[70] showed that coordinated primary amines may exhibit the properties of secondary amines in nitrosylation. For example, aliphatic amines in a Pt^{IV} complex form stable nitroso-compounds. They exhibit the properties of secondary amines because of the fact that the nitrogen forms a bond with the platinum atom, instead of a second alkyl radical.

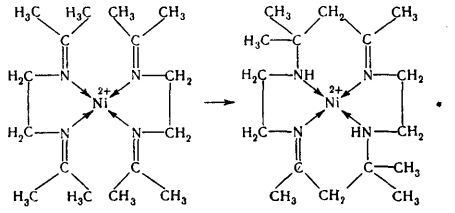
X. CHANGE IN THE REACTIVITY OF COORDINATED SCHIFF'S BASES

Complexes of metals with Schiff's bases are extremely widely encountered. They are obtained both from previously prepared Schiff's bases and by the action of aldehydes and ketones on the amino-complexes of metals. Sometimes, complex formation leads to the stabilisation of aldimines which are unstable in the free state. Thus Pfeiffer[71] prepared salicylideneimine in complexes of zinc, copper, and nickel. The complexes can be represented by the following general formula:



Salicylideneimine is unstable in the free state and cannot be prepared.

An interesting series of studies was carried out by Curtis and coworkers[72-77] on the reaction of cyclic amine-complexes of nickel and copper with acetone and aliphatic aldehydes. They established that the Schiff's bases formed initially undergo inner-complex aldol condensation with the formation of a macrocyclic ligand. This condensation is catalysed by bases:

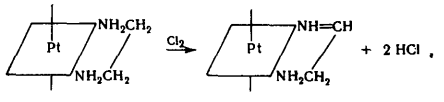


Since the reaction of aldehydes with inner-sphere amines leads to the formation of water, these reactions should most probably be carried out in anhydrous media. The amine-complexes of platinum are generally sparingly soluble in non-aqueous solvents. Various chloroamine-complexes of platinum, however, are soluble in polar organic solvents. In particular, the complex $[PtCl(NO_2)_2(NCl_2)(NH_3)_2]$ is soluble in acetaldehyde.

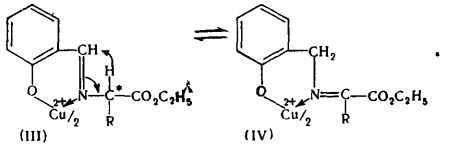
It has been established[78] that an inner-sphere ammonia molecule in $[PtCl(NO_2)_2(NCl_2)(NH_3)_2]$ is converted into acetaldimine on reaction with acetaldehyde. In the presence of active chlorine, however, the inner-sphere acetaldimine is converted into acetonitrile. The reactions can be represented schematically as follows:

$$Cl_2N{-}Pt \leftarrow NH_3 + CH_3CHO \rightleftarrows Cl_2N{-}Pt \leftarrow NH{=}CHCH_3 + H_2O$$
$$Cl_2N{-}Pt \leftarrow NH{=}CHCH_3 + 2H_2O \rightleftarrows H_3N \rightarrow Pt \leftarrow NH{=}CHCH_3 + HClO + ClO^-$$
$$\frac{H_3N \rightarrow Pt \leftarrow NH{=}CHCH_3 + OCl^- \rightarrow H_3N \rightarrow Pt \leftarrow N{\equiv}C{-}CH_3 + H_2O + Cl^-}{Cl_2N{-}Pt \leftarrow NH_3 + CH_3CHO \rightarrow H_3N \rightarrow Pt \leftarrow N{\equiv}C{-}CH_3 + HClO + Cl^-}$$

The dehydrogenation of inner-sphere ligands under the influence of chlorine was observed earlier[79]. It was established that the reaction of chlorine with ethylene-diamine in a Pt^{IV} complex may lead to the formation of aminoacetaldimine:



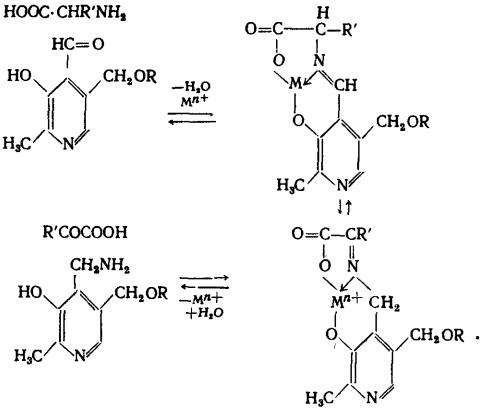
The important role of complex formation in the change in the reactivity of Schiff's bases is shown by the work of Pfeiffer and coworkers[80], who showed that when a chelate Cu^{II} complex is formed with an optically active Schiff's base formed from an aminoester and salicylaldehyde, rapid racemisation takes place. This can be attributed to the existence of an inner-complex tautomeric equilibrium:



(III) (IV)

The loss of the asymmetry of the optically active carbon atom takes place on formation of structure (IV). The reverse conversion of complex (IV) the complex (III) should produce equal quantities of the two optically active antipodes.

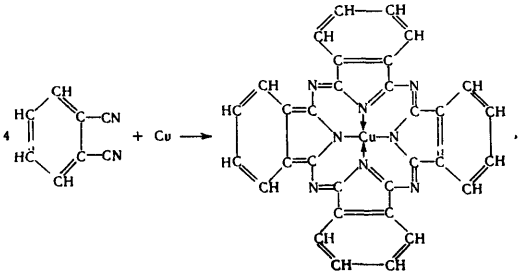
An inner-complex tautomeric equilibrium is the chief stage in the mechanism of catalytic trans-amination between pyridoxal and an aminoacid, proposed by Snell[81]. In his opinion, trans-amination gives a Schiff's base, stabilised by coordination to the metal ion, after which the double bond is displaced to the carbon atom of the aminoacid:



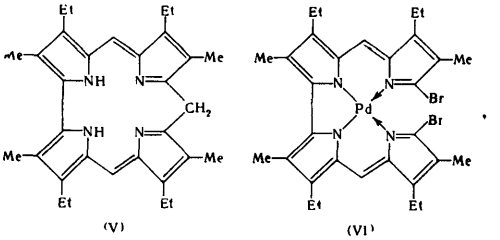
It is considered that trans-amination is extremely important in biology, since it provides an extremely probable means of producing a bond between carbohydrates and proteins.

XI. THE METAL IONS AS A MATRIX ON WHICH AN ORGANIC MOLECULE IS SYNTHESISED

The preparation of metal-containing phthalocyanines from a metal and the dinitrile of phthalic acid takes place much more readily than the direct preparation from the free bases[3]:



A striking example of the matrix effect of a complex-forming metal is provided by the preparation of compound (V). This compound could not be prepared for a long time, but was eventually readily prepared by the reaction of formaldehyde with the palladium(II) complex (structure VI):[82]

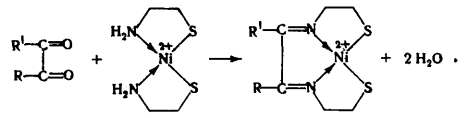


(V) (VI)

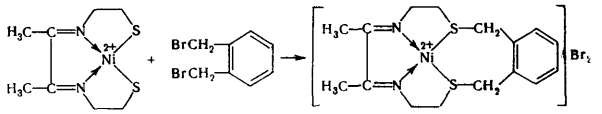
It is assumed that by following the route of ring closure in complex (VI), it is possible to introduce O, NH, or S in place of the methylene group.

The reaction between β-mercaptoethylamine and α-diketones usually gives thiazolidines as chief product, with only small quantities of the α-diimines[83]. Busch[84] showed that if the β-mercaptoethylamine is present in an

Ni^{II} complex, it reacts with α-diketones to form the inner-sphere α-diimine in 70% yield:



Busch then used this complex as a template for the subsequent preparation of a polycyclic chelate[85]. He carried out the following reaction:



which was made possible by the fixation of the sulphur atoms in the cis-position.

XII. REACTIONS INVOLVING "INSERTION" INTO A METAL-LIGAND BOND

Extensive material has now accumulated on reactions involving the "insertion" of various molecules in a metal–ligand bond. The "insertion" of carbon monoxide, alkenes, acetylene derivatives, etc. has been studied[86]. For example, the reaction of carbon monoxide and methanol with cobalt carbonyl hydrides leads to the formation of an ester of formic acid. It is considered[87–89] that the reaction mechanism can be represented as follows:

$$HCo(CO)_4 + CO \rightleftarrows HC(O)Co(CO)_4$$

$$HC(O)Co(CO)_4 + ROH \rightarrow HC(O)OR + HCo(CO)_4 .$$

An interesting reversible carbonylation of an alkyl manganese pentacarbonyl was carried out by Coffield and coworkers[90]:

$$CH_3Mn(CO)_5 + Co \rightleftarrows CH_3COMn(CO)_5 .$$

It was subsequently shown[91] that the "insertion" into the manganese–alkyl bond involves chiefly a carbonyl which is already coordinated to manganese, and not a carbonyl from the outer sphere.

Booth and Chatt[92] carried out the carbonylation of alkyl and aryl compounds of platinum and palladium. The following are examples of the reactions which they carried out:

$$trans\text{-}[PdCH_3X(PEt_3)_2] \rightarrow trans\text{-}[PdCOCH_3X(PEt_3)_2]$$

$$[Pt(CH_3)_2(PEt_3)_2] \xrightarrow{CO} [Pt(COCH_3)_2(PEt_3)_2] .$$

Chandra and coworkers[93] showed that "insertion" into a metal–nitrogen bond can be carried out. They carried out a number of reactions of two types:

$$M{-}N(CH_3)_2 + RC{\equiv}CR' \rightarrow M{-}C(R){=}C(R'){-}N(CH_3)_2$$

$$M{-}N(CH_3)_2 + \begin{matrix} R & & R^* \\ & C{=}C & \\ R' & & R''' \end{matrix} \rightarrow M{-}C(R,R'){-}C(R^*,R''){-}N(CH_3)_2 .$$

When the hydrocarbons contain groups which show a clearly defined ability to attract electrons, these reactions take place under mild conditions.

---oOo---

In conclusion it should be noted that other factors, in addition to those listed above, influencing the reactivity of ligands may be detected. The detection of additional factors may be made primarily by analysing data on the reactivity of unsaturated organic molecules, since almost no discussion of π-complexes has been given in the present review.

It has already been noted that the change in the reactivity of ligands in complexes sometimes results from several factors. This is apparently the most widely encountered case. The author has encountered considerable difficulty in selecting examples which might illustrate individual factors as far as possible in pure form. Thus the assignment of reactions to various classes may be a subject for discussion.

From the viewpoint of the development of a theory of homogeneous catalysis involving metal complexes, quantitative data characterising the change in reactivity are of considerable importance. Unfortunately, few data of this kind have yet been published. It is to be hoped that with increase in the interest of this problem, the work carried out will be more quantitative in character. One possible approach to this is by the extensive use of correlation equations of the type corresponding to Hammett's equation.

REFERENCES

1. M. L. Tobe, Science prog., **49**, 475 (1961).
2. M. M. Jones and W. A. Connor, Ind. Eng. Chem., **55**, 15 (1963).
3. D. H. Busch, Record Chem. Prog., **25**, 107 (1964).
4. R. W. Hay, J. Chem. Educ., 413 (1965).
5. J. P. Collman, "Transition Metal Chemistry", London–New York. Marcel Dekker Inc., 1966, Vol. 2, p. 1.
6. Reactions of Coordinated Ligands and Homogeneous Catalysis, Adv. in Chemistry Ser. No. 37 (1963).
7. Collected papers "Problemy Kinetiki i Kataliza. XIII. Kompleksoobrazovanie v Katalize" (Collected Papers on Kinetics and Catalysis. XIII. Complex Formation in Catalysis), Izd. Nauka, 1968.
8. A. A. Grinberg, "Vvedenie v Khimiyu Kompleksnykh Soedinenii" (Introduction to the Chemistry of Complex Compounds), Izd. Khimiya, 1966.
9. Yu. N. Kukushkin, Zhur. Neorg. Khim., **2**, 2371 (1957).
10. Yu. N. Kukushkin, Zhur. Neorg. Khim., **4**, 2460 (1959); **5**, 1943 (1960); **6**, 1098, 1762, 2453 (1961); **7**, 769, 1795 (1962); **8**, 823 (1963) [Russ. J. Inorg. Chem., No. 11 (1959); No. 9 (1960); Nos. 5, 8, 11 (1961); Nos. 4, 8 (1962); No. 4 (1963)].
11. Yu. N. Kukushkin and N. N. Zatsepina, Zhur. Neorg. Khim., **6**, 120 (1961) [Russ. J. Inorg. Chem., No. 1 (1961)].
12. Yu. N. Kukushkin, Zhur. Neorg. Khim., **8**, 817 (1963) [Russ. J. Inorg. Chem., No. 4 (1963)].

13. Yu. N. Kukushkin, "Reaktsionnaya Sposobnost' Aminov, Koordinirovannykh vo Vnutrennei Sfere Kompleksnykh Soedinenii" (The Reactivity of Amines, Coordinated in the Inner Sphere of Complex Compounds), Summary of Doctoral Thesis, Lensovet Leningrad Technological Institute, Leningrad, 1964.
14. A. V. Babaeva and E. Ya. Khananova, Zhur. Neorg. Khim., **10**, 2653 (1965) [Russ. J. Inorg. Chem., No. 12 (1965)].
15. Yu. N. Kukushkin and L. I. Zorina, Zhur. Neorg. Khim., **12**, 568 (1967) [Russ. J. Inorg. Chem., No. 2 (1967)].
16. A. A. Grinberg and Yu. N. Kukushkin, Dokl. Akad. Nauk SSSR, **145**, 97 (1962).
17. Yu. N. Kukushkin, V. A. Rabinovich, and R. A. Goloseeva, Zhur. Neorg. Khim., **14**, 1863 (1969) [Russ. J. Inorg. Chem., No. 7 (1969)].
18. Yu. N. Kukushkin, V. A. Rabinovich, and R. A. Goloseeva, Zhur. Neorg. Khim., **14**, 2820 (1969) [Russ. J. Inorg. Chem., No. 10 (1969)].
19. A. A. Grinberg, see Ref. 3, p. 371.
20. A. A. Grinberg, Kh. I. Gil'dengershel', and V. F. Budanova, Zhur. Neorg. Khim., **13**, 1365, 3040 (1968) [Russ. J. Inorg. Chem., Nos. 5, 11 (1968)].
21. Yu. N. Kukushkin and V. V. Sibirskaya, Zhur. Neorg. Khim., **14**, 783 (1969) [Russ. J. Inorg. Chem., No. 3 (1969)].
22. P. Pfeiffer, W. Offermann, and H. Werner, J. prakt. Chem., **159**, 313 (1942).
23. H. S. Verter and A. E. Frost, J. Am. Chem. Soc., **82**, 85 (1960).
24. A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, Inc. N. Y., 1952, p. 400.
25. H. Kroll, J. Am. Chem. Soc., **74**, 2036 (1952).
26. M. L. Bender and B. W. Turnquest, J. Am. Chem. Soc., **79**, 1889 (1957).
27. L. Meriwether and F. H. Westheimer, J. Am. Chem. Soc., **78**, 5119 (1956).
28. G. L. Eichhorn and J. C. Bailar, J. Am. Chem. Soc., **75**, 2905 (1953).
29. G. L. Eichhorn and N. D. Marchand, J. Am. Chem. Soc., **78**, 2688 (1956).
30. S. C. Chan and F. Leh, J. Chem. Soc., (A) 908 (1967).
31. S. C. Chan and F. Leh, J. Chem. Soc., (A) **136** (1968).
32. J. F. Speck, J. Biol. Chem., **178**, 315 (1949).
33. K. J. Pedersen, Acta chem. scand., 3, 676 (1949).
34. R. Steinberger and F. H. Westheimer, J. Am. Chem. Soc., **71**, 4158 (1949).
35. R. Steinberger and F. H. Westheimer, J. Am. Chem. Soc., **73**, 429 (1951).
36. H. A. Krebs, Biochim. J., **36**, 303 (1942).
37. A. Kornberg, S. Ochoa, and A. H. Mehler, J. Biol. Chem., **174**, 159 (1948).
38. K. J. Pedersen, Acta chem. scand., **6**, 285 (1952).
39. E. Gelles and J. P. Clayton, Trans. Faraday Soc., **52**, 553 (1956).
40. E. Gelles, J. Inorg. Nucl. Chem., **8**, 625 (1956).
41. E. Gelles and R. W. Hay, J. Chem. Soc., 3673 (1958).
42. E. Gelles and A. Salama, J. Chem. Soc., 3683 (1958).
43. J. E. Prue, J. Chem. Soc., 2331 (1952).
44. F. P. Dwyer and D. P. Mellor, "Chelating Agents and Metals Chelates", Academic Press, N. Y.,
45. R. W. Hay, L. J. Porter, and P. J. Morris, Austr. J. Chem., **19**, 1197 (1966).
46. R. W. Hay, M. L. Jansen, and P. L. Cropp, Chem. Commun., 621 (1967).
47. J. V. Rund and R. A. Plane, J. Am. Chem. Soc., **86**, 367 (1964).
48. R. W. Hay and K. N. Leong, Chem. Commun., 800 (1967).
49. A. A. Grinberg, T. B. Itskovich, and A. D. Troitskaya, Zhur. Neorg. Khim., **4**, 79 (1959) [Russ. J. Inorg. Chem., No. 1 (1959)].
50. H. Reihlen, R. Illig, and R. Wittig, Ber., **58**, 12 (1925).
51. R. H. Holm and F. A. Cotton, J. Am. Chem. Soc., **80**, 5658 (1958).
52. R. W. Kluiber, J. Am. Chem. Soc., **82**, 4839 (1960).
53. J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, J. Am. Chem. Soc., **83**, 531 (1960).
54. J. P. Collman, R. A. Moss, S. D. Goldby, and W. S. Trahanovsky, Chem. a. Ind., 1213 (1960).
55. J. P. Collman and E. T. Kittleman, J. Am. Chem. Soc., **83**, 3529 (1961).
56. C. Djordjevic, J. Lewis, and R. S. Nyholm, J. Chem. Soc., 4778 (1962).
57. K. J. Pedersen, Acta chem. scand., **2**, 252 (1948).
58. K. J. Pedersen, Acta chem. scand., **2**, 385 (1948).
59. R. W. Kluiber, J. Am. Chem. Soc., **83**, 3030 (1961).
60. J. P. Collman and E. T. Kittleman, Inorg. Chem., **1**, 499 (1962).
61. V. I. Kuznetsov, Zhur. Obshch. Khim., **20**, 802 (1950).
62. V. I. Kuznetsov, Zhur. Obshch. Khim., **26**, 3657 (1956).
63. K. D. Maguire and M. M. Jones, J. Am. Chem. Soc., **84**, 2316 (1962).
64. C. Bostic, Q. Fernando, and H. Freiser, Inorg. Chem., **2**, 232 (1963).
65. J. C. Taft and M. M. Jones, J. Am. Chem. Soc., **82**, 4196 (1960).
66. R. L. Jetton and M. M. Jones, Inorg. Chem., **1**, 309 (1962).
67. A. C. Kurtz, J. Biol. Chem., **122**, 477 (1937–1938).
68. A. C. Kurtz, J. Biol. Chem., **180**, 1253 (1949).
69. V. I. Kuznetsov, Zhur. Obshch. Khim., **20**, 809 (1950).
70. I. I. Chernyaev, O. N. Andrianova, and A. Sh. Leites, Zhur. Neorg. Khim., **6**, 497 (1961) [Russ. J. Inorg. Chem., No. 2 (1961)].
71. P. Pfeiffer, E. Buchholz, and O. Bauer, J. prakt. Chem., **129**, 163 (1931).
72. N. F. Curtis, J. Chem. Soc., 4409 (1960).
73. M. M. Blight and N. F. Curtis, J. Chem. Soc., 1204 (1962).
74. N. F. Curtis and D. A. House, Chem. a. Ind., **42**, 1708 (1961).
75. D. A. House and N. F. Curtis, J. Am. Chem. Soc., **84**, 3248 (1962).
76. N. F. Curtis and D. A. House, J. Am. Chem. Soc., **86**, 1331 (1964).
77. N. F. Curtis and D. A. House, J. Chem. Soc., 5502 (1965).
78. Yu. N. Kukushkin, Z. V. Drokina, Yu. S. Varshavskii, and N. V. Ivannikova, Zhur. Neorg. Khim., **13**, 3285 (1968) [Russ. J. Inorg. Chem., No. 12 (1968)].
79. Yu. N. Kukushkin and Yu. S. Varshavskii, Zhur. Neorg. Khim., **11**, 356 (1966) [Russ. J. Inorg. Chem., No. 2 (1966)].
80. P. Pfeiffer, W. Offermann, and H. Werner, J. prakt. Chem., **159**, 313 (1942).
81. E. E. Snell, Physiol. Revs., **33**, 509 (1953).
82. A. W. Johnson, I. T. Kay, and R. Rodrigo, J. Chem. Soc., 2374 (1963).
83. A. H. Cook and I. M. Heilbron, "The Chemistry of Penicillin", Princeton Univ. Press, 1949, p. 921.
84. D. H. Busch and M. C. Thompson, J. Am. Chem. Soc., **84**, 1762 (1962).

85. D. H. Busch, Record Chem. Progress, Kresge-Hooker Sci. Lib., 25, 107 (1969).
86. R. F. Heck, "Mechanisms of Inorganic Reactions Advances in Chemistry series", 49, 181 (1965).
87. H. W. Sternberg and I. Wender, Chem. Soc. (London) Spec. Publ., No. 3, 35 (1959).
88. L. Marko, Chem. a. Ind., 260 (1962).
89. L. Marko, Proc. Chem., 67 (1962).
90. T. H. Coffield, J. Kozikowski, and R. D. Closson, J. Org. Chem., 22, 598 (1957).
91. Y. H. Coffield, J. Kozikowski, and R. D. Closson, Chem. Soc. (London), Spec. Publ., No. 13, 126 (1959).
92. G. Booth and J. Chatt, J. Chem. Soc., (A) 634 (1966).
93. G. Chandra, T. A. George, and M. F. Lappert, Chem. Commun., 116 (1967).

Lensovet Leningrad
Technological Institute